Naphthalimide-Fused Dipyrrins: Tunable Halochromic Switches and Photothermal NIR-II Dyes

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Supporting Information

for Adv. Sci., DOI: 10.1002/advs.202105886

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Experimental
General. Tetrahydrofuran was dried using a commercial solvent purification system. Dichloromethane was distilled from calcium hydride when used as reaction solvents. NBS was purified as described previously.\cite{1} All other solvents and reagents were used as received. Compound S1 was synthesized as previously described.\cite{2} Microwave reactions were performed in a CEM Discover unit using external infrared temperature control system monitoring. $^1$H NMR spectra were recorded on high-field spectrometers ($^1$H frequency 500.13 or 600.13 MHz), equipped with broadband inverse or conventional gradient probeheads. Spectra were referenced to the residual solvent signals (chloroform-$d$, 7.24 ppm). $^{13}$C NMR spectra were recorded with $^1$H broadband decoupling and referenced to solvent signals ($^{13}$CDCl$_3$, 77.0 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the $t_2$ domain and up to 2048 points in the $t_1$ domain, with a 1 s recovery delay. All 2D spectra were recorded with gradient selection. High resolution mass spectra were recorded using electrospray or MALDI ionization in the positive or negative mode on Bruker Daltonics micrOTOF-Q II™ – ESI-Q-TOF, Apex ultra FT-ICR 7T and Ultraflextreme MALDI TOF/TOF instruments. Absorption spectrometry was performed using Agilent Cary 60 UV-Vis and Cary 5000 UV-Vis-NIR spectrophotometers. Electrochemical measurements (DCM, 0.1 M [NBu$_4$][PF$_6$], 293 K) were performed on an Autolab (Metrohm) potentiostat/galvanostat system using a glassy-carbon working electrode, platinum wire as the auxiliary electrode, and silver/silver chloride as a reference electrode. The voltammograms were referenced against the half-wave potential of ferrocenium/ferrocene couple.

Fluorescence Spectrometer from Edinburgh Instruments Ltd. A 450 W Xenon arc lamp (PL and PLE) was used as excitation sources. Emission spectra were corrected for the recording system efficiency and excitation spectra were corrected for the incident light intensity. PLE and PL spectra and QY were measured using a cooled extended-red Hamamatsu photomultiplier operating in a 200 – 1050 nm range. Quantum yield measurements were performed by using an Edinburgh Instruments integrating sphere equipped with a small elliptical mirror and a baffle plate for beam steering and shielding against directly detected light. For the measurement, the integrating sphere replaced the standard sample holder inside the sample chamber. Calculations of quantum yields were made using the software provided by Edinburgh Instruments.

A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (center wavelength of 800 nm with 80 fs at FWHM) with high repetition rate (80 MHz). This high repetition rate was reduced to 800 kHz by using homemade pulse-picker. The pulse-picked output was frequency doubled by a 1-mm-thick BBO crystal (typeI, $\theta = 29.2^\circ$, EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickel SPC-130). The overall instrumental response function was about 25 ps (FWHM). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer set at an angle complementary to the magic angle (54.7$^\circ$), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Femtosecond Transient Absorption Spectroscopy: A femtosecond time-resolved transient absorption (TA) spectrometer used for this study consisted of a femtosecond optical parametric amplifier (OPA, Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical detection system. The generated OPA pulses had a pulse width of ~100 fs and an average power of 1 mW in the range 550 to 690 nm, which
were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm thick) by focusing of small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by high speed spectrometer (Ultrafast Systems). To obtain the timeresolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses were used to excite samples and to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation FWHM in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 450-850 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photooxidation of the samples in question.

**Chemical Oxidation of 2a and 2d:** The chemical oxidation experiments were performed in dichloromethane solution using various commercially available oxidants such as tris(4-bromophenyl)ammoniumyl hexachloroantimonate, and silver hexafluorophosphate. The stock or saturated solutions of oxidants were prepared in dichloromethane and was titrated in UV cuvette into the solution of desired dipyrrin (keeping the absorbance value around 1.0 (A = 1.0), V = 2.5 mL). The progress of the oxidation events was monitored spectrophotometrically upon gradually increasing the concentration of oxidant. The reduction of the oxidized species of dipyrrin was attempted using hydrazine hydrate or KO$_2$ solution dissolved in dichloromethane. The bulk oxidation experiment was monitored via NMR spectroscopy and the samples of dipyrrin (2d) and BAHA were prepared in deuterated dichloromethane solution. The desired 1D and 2D NMR spectra were recorded at 240 K for the oxidized and subsequent reduced form of dipyrrins. NMR measurements were carried out in deuterated chloroform when the oxidant was AgPF$_6$.

**Protonation of Dipyrrins:** The protonation forms of several dipyrrins were achieved from the stepwise titration using TFA as acid. To achieve the fully last stage protonation form of 1b and 2b, the stronger acid H$_2$SO$_4$ was used. The dipyrrins were titrated from the stock solutions of TFA (and H$_2$SO$_4$ whereever needed). The increasing concentrations of added TFA was used from the stock solutions of 6.47 x 10$^{-3}$ M, 5.16 x 10$^{-2}$ M, 1.03 x 10$^{-1}$ M, 2.04 x 10$^{-1}$ M and neat TFA. The increasing concentrations of added H$_2$SO$_4$ was used from the stock solution of 4.36 x 10$^{-1}$ M. The high concentrations of acid solution were made in order to avoid the solvent volume increase in the UV cuvette cells.

**Photothermal experiments:** Similar as in titration experiments, TFA acid was used to protonate the dipyrrin 2d and 2e. Triethylamine was used as a base to deprotonate 2d–H$^+$ and 2e–H$^+$. After checking the photostability test, a toluene solution (volume 4 mL) of 2d–H$^+$ and 2e–H$^+$ were irradiated with 1064 nm laser (3 W) at a power density of 25 W/cm$^2$. In the experiment, a pulsed fiber laser was used (SPI G4). The laser emitted at the wavelength of 1064 nm with the repetition of 33 kHz and a pulse duration of 250 ns. During the experiment, the laser power of 3 W was used. The collimated laser beam of the diameter around 4mm was directed at the cuvette with the solution and passed vertically through the
sample. On the top of the container, a temperature detector (thermocouple) was installed. During the experiment, solvents were stirred. The thermocouple was dipped into the UV cuvette solution to record the change in temperature over time. The photothermal conversion efficiency (PCE) was calculated according to the equation (1) [3]

\[ \eta = \frac{hS(T_{\text{max}} - T_{\text{surr}}) - Q_{\text{dis}}}{I(1 - 10^{-A_{1064}})} \]  

where \( h \) is the heat transfer coefficient, \( S \) is the surface area of the container, \( T_{\text{max}} \) represents the maximum steady-state temperature, \( T_{\text{surr}} \) is the ambient temperature of the environment, \( Q_{\text{dis}} \) represents the heat dissipation from the light absorbed by the solvent and the quartz sample cell, \( I \) is the incident laser power (3.2 W/cm²), and \( A_{1064} \) is the absorbance of the sample at 1064 nm. For \( 2d-H^+ \), \( T_{\text{max}} \) is 58 °C, \( T_{\text{surr}} \) is 25 °C, \( A_{1064} \) is 1.15 and for \( 2e-H^+ \), \( T_{\text{max}} \) is 75 °C, \( T_{\text{surr}} \) is 24 °C, \( A_{1064} \) is 1.28. \( Q_{\text{dis}} \) was assumed nearly zero here as the change in temperature in case of pure toluene was found to be only 1 °C (in 7 minutes).

\( hS \) was calculated referring to the following equation (2)

\[ \tau_s = \frac{m_D C_D}{hS} \]  

where \( m_D \) and \( C_D \) index the solution mass and heat capacity (1.7 J g⁻¹) of pure toluene used as the solvent, respectively.

\( \tau_s \) was calculated from a linear graph from equation (3)

\[ t = -\tau_s \ln \left( \frac{T_{\text{rt}} - T_{\text{surr}}}{T_{\text{max}} - T_{\text{surr}}} \right) \]  

where \( T_{\text{rt}} \) denotes as the real-time temperature in the cooling period. For \( 2d-H^+ \), \( \tau_s \) is calculated to be 207.5 s and for \( 2e-H^+ \), \( \tau_s \) is calculated to be 206.5 s.

According to the obtained data and substituting the values in equation (1), the photothermal conversion efficiency of \( 2d-H^+ \) and \( 2e-H^+ \) was determined to be 4.1 % and 6.1 %, respectively.

**Computational methods.** Density functional theory (DFT) calculations were performed using Gaussian 16 [4]. DFT geometry optimizations were carried out in unconstrained C1 symmetry, using extended tight binding (xTB) [5,6] or semiempirical models as starting geometries. DFT geometries were refined to meet standard convergence criteria, and the existence of a stationary point was verified by a normal mode frequency calculation. Geometry optimizations, frequency calculations, and thermochemistry calculations were performed using the hybrid functional B3LYP [7-9] combined with the 6-31G(d,p) basis set and the GD3BJ dispersion correction [10]. In the calculations of absorption spectra, up to 25-50 electronic transitions were calculated by means of time-dependent DFT (TD-DFT), using the above level of theory, PCM solvation (standard dichloromethane parameters) [11]. Open-shell singlets were optimized using the broken-symmetry formalism, with mixed initial guesses. The dication of dipyrrins were optimized using the 6-31G(d,p) basis set and the PCM solvent model using standard dichloromethane parameterization. The percent (%) contribution of fragments (NMI-dipyrrin, alpha-aryl and meso-aryl) to each molecular orbital (PDOS) were obtained using GaussSum version 3.0. In structure 1f', the mesityl groups were replaced with methyl.
**X-ray crystallography.** X-ray quality crystals for dipyrrins, 1a were grown using chloroform/methanol/n-hexane solution, 1b were grown using chloroform/n-hexane solution, 1e were grown using chloroform/n-hexane solution, 2e were grown in CDCl₃, 3d were obtained in CDCl₃. X-ray crystals of protonated dipyrrins, 1a–H⁺ were obtained in CDCl₃ solution using HBr as acid source, 1b–H⁺ were obtained in CDCl₃ solution using HCl as acid source. Diffraction measurements were performed on a κ geometry XCALIBUR diffractometer (ω scans), equipped with an ONYX CCD camera, with graphitemonochromatized Cu Kα radiation. The data were collected at 110 K, corrected for Lorenz and polarization effects. Data collection, cell refinement, data reduction and analysis were carried out with the Xcalibur PX software, CRYSTALS CCD and CRYSTALS RED, respectively (Oxford Diffraction Ltd., Abignon, England, 2009). An analytical absorption correction was applied with the use of CRYSTALS RED. All structures were solved by direct methods with the SHELXS-97 program and refined using SHELXL-97 with anisotropic thermal parameters for non-H atoms. In the final refinement cycles, all H atoms were treated as riding atoms in geometrically optimized positions. CCDC 2108054, 2110050, 2110061, 2110067, 2110070 and 2110072 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Statistical analysis.** The majority of work presented herein did not require statistical analyses. Statistical treatment of X-ray diffraction data was performed using standard approaches.
Scheme S1. Synthesis of monopyrroles. Reagents and conditions: (a) NBS, CH$_2$Cl$_2$, RT; (b) pressure tube, PhB(OH)$_2$, K$_2$CO$_3$, Pd(dba)$_2$, XPhos, THF/water (1/0.1, v/v), 100 °C; (c) KOH, (CH$_2$OH)$_2$, MW (100W, 190 °C, PowerMax); (d) pressure tube, p-$C_6H_4N(CH$_3$_)$_2$Bpin, K$_2$CO$_3$, Pd(dba)$_2$, XPhos, THF/water (1/0.1, v/v), 100 °C, (e) KOH, (CH$_2$OH)$_2$, MW (100W, 190 °C, PowerMax); (f) pressure tube, p-$C_6H_4NO$_2Bpin, K$_2$CO$_3$, Pd(dba)$_2$, THF/water (1/0.1, v/v), 100 °C, (g) KOH, (CH$_2$OH)$_2$, MW (100W, 190 °C, PowerMax).
Scheme S2. Synthesis of dipyrrins 1a–1e. Reagents and conditions: (a) R^1CHO, CF₃COOH, CH₂Cl₂, RT, 2 days; (ii) DDQ, RT, 30 min–4 h.

Scheme S3. Synthesis of dipyrrins 2a–2e. Reagents and conditions: (a) R^1CHO, CF₃COOH, CHCl₃, RT, 4 days; (ii) DDQ, RT, 20 min.
Ethyl 8-bromo-2-(2,6-diisopropylphenyl)-1,3-dioxo-1,2,3,7-tetrahydropyrrolo[3′,4′:2,3]indeno[6,7,1-def] isoquinoline-6-carboxylate (3). Compound S1 (0.40 g, 0.81 mmol) was dissolved in dichloromethane and freshly crystallized NBS (0.15 g, 0.84 mmol) was added to the reaction flask and the reaction mixture was stirred at room temperature for overnight. The reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on alumina (Grade V) using 50-60% dichloromethane in n-hexane. The solvent was evaporated on vaccuo to give yellow color solid powder as the desired product (0.45 g, 98%). \(^1\)H NMR (500 MHz, chloroform-\(d\), 300 K): \(\delta\) 9.22 (s, 1H), 8.53 (d, \(J = 7.4\) Hz, 1H), 8.49 (d, \(J = 7.3\) Hz, 1H), 8.14 (d, \(J = 7.3\) Hz, 1H), 7.84 (d, \(J = 7.8\) Hz, 1H), 7.30 (d, \(J = 7.8\) Hz, 2H), 4.51 (q, \(J = 7.1\) Hz, 2H), 2.77 (sept, \(J = 6.8\) Hz, 2H), 1.53 (t, \(J = 7.1\) Hz, 3H), 1.14 (d, \(J = 6.8\), 12H). \(^{13}\)C NMR (125 MHz, chloroform-\(d\), 300 K): \(\delta\) 163.97, 163.95, 159.67, 145.86, 137.15, 136.84, 135.93, 132.88, 132.81, 131.13, 129.65, 129.41, 126.38, 123.95, 123.60, 121.81, 120.94, 119.95, 119.78, 100.93, 77.28, 77.03, 76.77, 61.78, 29.09, 24.03, 14.65. HRMS (ESI-TOF): \(m/z\) [M - H]⁺ Calcd for C\(_{31}\)H\(_{26}\)BrN\(_{2}\)O\(_{2}\): 569.1070; Found 569.1026. UV-vis (dichloromethane, 300 K) \(\lambda\) [nm] (\(e\) in M\(^{-1}\) cm\(^{-1}\)): 303 (15300), 339 (5000), 356 (8500), 418 (21900), 438 (22800).

Ethyl 2-(2,6-diisopropylphenyl)-1,3-dioxo-8-phenyl-1,2,3,7-tetrahydropyrrolo[3′,4′:2,3]indeno[6,7,1-def]isoquinoline-6-carboxylate (4). A solution of compound 3 (100 mg, 0.175 mmol), phenylboronic acid (33.7 mg, 0.262 mmol), and K₂CO₃ (60.5 mg, 0.437 mmol), in aq-THF (water/THF: 0.5/5 mL) was mixed in pressure tube and then filled with Argon. After Pd(dba)\(_{2}\) (3 mg, 3 mol%) and XPhos (5 mg, 6 mol%) was added, the mixture was heated at 100 °C for 20 h. The reaction mixture was cooled to room temperature and quenched with water. The organic phase was washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo. The crude was purified by column chromatography on alumina (Grade V) using 20-30% dichloromethane in n-hexane as eluent. The solvent was evaporated on vaccuo to give orange-red color powder as the desired product. (Yield: 93 mg, 93 %). \(^1\)H NMR (500 MHz, chloroform-\(d\), 300 K): \(\delta\) 9.06 (s, 1H), 8.53 (d, \(J = 7.3\) Hz, 1H), 8.44 (d, \(J = 7.4\) Hz, 1H), 8.18 (d, \(J = 7.3\) Hz, 1H), 7.90 (d, \(J = 7.4\) Hz, 1H), 7.81 (d, \(J = 7.2\) Hz, 2H), 7.60 (t, \(J = 7.7\) Hz, 2H), 7.50 (t, \(J = 7.5\) Hz, 1H), 7.44 (t, \(J = 7.8\) Hz, 1H), 7.30 (d, \(J = 7.8\) Hz, 2H), 4.55 (q, \(J = 7.1\) Hz, 2H), 2.79 (sept, \(J = 6.9\) Hz, 2H), 1.56 (t, \(J = 7.1\) Hz, 3H), 1.15 (d, \(J = 6.9\) Hz, 12H). \(^{13}\)C NMR (151 MHz, chloroform-\(d\), 300 K): \(\delta\) 164.09, 164.00, 160.61, 145.89, 138.83, 137.70, 136.43, 133.82, 133.00,
concentrated in vacuo. The crude was purified by column chromatography on alumina (Grade V) using 30-40% dichloromethane in n-hexane as eluent. The solvent was evaporated on vacuum to give 2-(6-diisopropylphenyl)-6-phenylpyrrolo[3',4':2,3]indeno[6,7,1-def] isoquinoline-1,3(2H,7H)-dione (6). The mixture of compound 4 (50 mg, 0.088 mmol) and potassium hydroxide, KOH (19.7 g, 0.532 mmol) was dissolved in ethylene glycol in microwave vial. The solution was purged with nitrogen for 10 min, and the reaction mixture was irradiated at 190 °C for 1.5 hour. The mixture was cooled to room temperature, poured into water and extracted with dichloromethane. The organic phase was washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The desired compound was obtained as orange-red powder (34 mg, 78 %). \textsuperscript{1}H NMR (600 MHz, chloroform-d, 300 K): \(\delta\) 8.52 (s, 1H), 8.42 (d, \(J = 7.4\) Hz, 2H), 7.84 (d, \(J = 7.4\) Hz, 1H), 7.73 (d, \(J = 7.3\) Hz, 2H), 7.66 (d, \(J = 7.3\) Hz, 1H), 7.55 (t, \(J = 7.8\) Hz, 2H), 7.43 (m, 2H), 7.30 (d, \(J = 7.8\) Hz, 2H), 7.06 (d, \(J = 2.4\) Hz, 1H), 2.79 (sept, \(J = 6.9\) Hz, 2H), 1.15 (d, \(J = 6.8\) Hz, 12H). \textsuperscript{13}C NMR (151 MHz, chloroform-d, 300 K): \(\delta\) 164.36, 164.28, 145.94, 140.15, 139.67, 136.96, 133.11, 132.91, 131.61, 131.48, 130.42, 130.10, 129.41, 129.24, 128.45, 126.93, 125.69, 125.07, 123.87, 119.80, 119.74, 119.28, 118.84, 115.44, 77.23, 77.02, 76.81, 29.06, 24.03. HRMS (ESI–TOF): \(m/z: [M – H]^–\) Calcd for C_{24}H_{23}N_2O_5: 495.2067; Found 495.2051. UV-vis (dichloromethane, 300 K) \(\lambda\) [nm] (\(\varepsilon\) in M\(^{-1}\) cm\(^{-1}\)): 313 (11700), 339 (5700), 356 (7400), 459 (23800), 483 (25400).

**Ethyl 2-(6-diisopropylphenyl)-8-(4-(dimethylamino)phenyl)-1,3-dioxo-1,2,3,7-tetrahydropyrrolo[3',4':2,3]indeno[6,7,1-def] isoquinoline-6-carboxylate (5).** A solution of compound 3 (74 mg, 0.13 mmol), 4-(dimethylamino)phenylboronic acid pinacol ester (49.5 mg, 0.19 mmol), and K_2CO_3 (43.8 mg, 0.317 mmol), in aq-THF (water/THF: 0.4/4 mL) was mixed in pressure tube and then filled with Argon. After Pd(dbq)_2 (2.2 mg, 3 mol%) and XPhos (3.6 mg, 6 mol%) was added, the mixture was heated at 100 °C for 20 h. The reaction mixture was cooled to room temperature and quenched with water. The organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude was purified by column chromatography on alumina (Grade V) using 30-40% dichloromethane in n-hexane as eluent. The solvent was evaporated on vacuum to give dark
blue-voilet color powder as the desired product (Yield: 74 mg, 94 %). 1H NMR (500 MHz, chloroform-
d, 300 K): δ 8.85 (s, 1H), 8.50 (d, J = 7.4 Hz, 1H), 8.42 (d, J = 7.4 Hz, 1H), 8.15 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 7.4 Hz, 1H), 7.68 (d, J = 8.9 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.53 (q, J = 7.1 Hz, 2H), 2.80 (sept, J = 6.9 Hz, 2H), 1.55 (t, J = 7.2 Hz, 3H, overlapping with water peak), 1.15 (d, J = 6.8 Hz, 12H). 13C NMR (151 MHz, chloroform-d, 300 K): δ 164.20, 164.12, 151.03, 145.91, 139.51, 137.95, 134.48, 132.97, 129.27, 127.40, 123.86, 123.16, 121.33, 119.39, 117.79, 117.72, 112.41, 77.01, 76.80, 61.34, 40.28, 29.05, 24.02, 14.73. HRMS (ESI–TOF): m/z: [M – H]+ Calcd for C39H36N2O4: 610.2700; Found 610.2642. UV-vis (dichloromethane, 300 K) λ [nm] (ε in M⁻¹ cm⁻¹): 364 (42300), 529 (17600).

2-(2,6-diisopropylphenyl)-6-[4-(dimethylamino)phenyl]pyrrolo[3',4':2,3]indeno[6,7,1-def]
isoquinoline-1,3(2H,7H)-dione (7). The mixture of compound 5 (40 mg, 0.066 mmol) and potassium hydroxide, KOH (14.5 mg, 0.262 mmol) was dissolved in ethylene glycol in microwave vial. The solution was purged with nitrogen for 10 min, and the reaction mixture was irradiated at 190 °C for 1.5 hour. The mixture was cooled to room temperature, poured into water and extracted with dichloromethane. The organic phase was washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The desired compound was obtained as orange powder (26 mg, 73 %). 1H NMR (600 MHz, chloroform-d, 300 K): δ 8.41 (d, J = 7.4 Hz, 1H), 8.38 (d, J = 7.5 Hz, 1H), 8.21 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.62 (m, 3H), 7.43 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 2.4 Hz, 1H), 6.86 (d, J = 8.9 Hz, 2H), 2.80 (sept, J = 6.8 Hz, 2H), 1.14 (d, J = 6.9 Hz, 12H). 13C NMR (151 MHz, chloroform-d, 300 K): δ 164.40, 164.33, 150.46, 145.94, 140.65, 139.80, 137.06, 137.06, 133.21, 132.73, 131.74, 131.61, 129.86, 129.14, 127.04, 126.77, 123.81, 123.22, 119.50, 119.17, 119.10, 118.94, 118.20, 114.73, 112.55, 77.22, 77.01, 76.80, 40.35, 24.02. HRMS (ESI–TOF): m/z: [M – H]+ Calcd for C39H36N2O4: 538.2489; Found 538.2459. UV-vis (dichloromethane, 300 K) λ [nm] (ε in M⁻¹ cm⁻¹): 336 (14000), 359 (11500), 536 (18300).

4’-(dimethylamino)-[1,1’-biphenyl]-4-carbaldehyde (S2). Compound S2 was prepared by using modified procedure to that of reported compound. A solution of 4-bromobenzaldehyde (50 mg, 0.268 mmol), 4-(dimethylamino)phenylboronic acid pinacol ester (67.5 mg, 0.268 mmol), and K2CO3 (73.9 mg, 0.54 mmol), in aq-THF (water/ THF: 0.2/2 mL) was mixed in pressure tube and then filled with Argon. After PdCl2(dppf) (2.2 mg, 3 mol%) was added, the mixture was heated for overnight at 100 °C. The reaction mixture was cooled to room temperature and quenched with water. The organic
phase was washed with water and brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude was recrystallized using n-hexane/dcm and the product was collected as brown-orange solid (Yield: 59 mg, 98%) Spectroscopic data matches well with that of the reported compound.

4-(4,5-bis(mesityloxy)anthracen-9-yl)benzaldehyde (S3). 10-bromo-1,8-bis(mesityloxy)anthracene[12] (50 mg, 0.095 mmol) and 4-formylphenylboronic acid (19.12 mg, 0.12 mmol) was dissolved in 4 mL of 5:2:1 of toluene/water/ethanol mixture and the solution was purged with nitrogen for 15 minutes. Potassium carbonate (52.60 mg, 0.38 mmol) was added to the mixture followed by the addition of tetrakis(triphenylphosphine)palladium(0) (5.57 mg, 0.005 mmol) The mixture was purged with nitrogen for few minutes and heated at 110 °C for overnight. After cooling to room temperature, water was added and extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous sodium sulfate and the solvent was removed on rotary evaporator. The crude mixture was purified via silica column chromatography using 30% dichloromethane in n-hexane as an eluent to give compound S3 (47 mg, 89%) as a yellow solid. $^1$H NMR (500 MHz, chloroform-d, 300 K): δ 10.17 (1H, s), 9.92 (1H, s), 8.09 (2H, d, $^3$J = 8.2 Hz), 7.65 (2H, d, $^3$J = 8.2 Hz), 7.12 (4H, d, $^3$J = 4.5 Hz), 6.95 (4H, s), 6.32 (2H, t, $^3$J = 4.1 Hz), 2.33 (6H, s), 2.17 (12H, s). $^{13}$C NMR (125 MHz, chloroform-$d_6$, 300 K): δ 192.05, 154.07, 149.10, 146.37, 135.58, 134.59, 132.09, 131.35, 130.95, 129.64, 126.12, 123.70, 118.96, 116.62, 104.12, 20.84, 16.12. MS (ESI–TOF): m/z: [M + H]$^+$ Calcd for C$_{39}$H$_{34}$O$_3$: 550.2502; Found 550.2607.

Dipyrrin (1a). A solution of compound 6 (7 mg, 0.14 mmol) and benzaldehyde (1.5 µL, 0.14 mmol, excess) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (15 µL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2 mg) was added and the mixture was stirred for additional 4 h. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH$_2$Cl$_2$/n-hexane (1/2, v/v to 2/1, v/v) as eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH$_2$Cl$_2$/n-hexane to give a product as a black solid (6.4 mg, 79%). $^1$H NMR (600 MHz, chloroform-$d$, 300 K): δ 14.60 (s, 1H), 8.40 (d, J = 7.4 Hz, 2H), 8.12 (d, J = 7.8 Hz, 4H), 8.02 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 7.93 (d, J = 7.5 Hz, 1H), 7.85 (t, J = 7.6 Hz, 2H), 7.73 (d, J = 6.9 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.4 Hz, 2H)
Hz, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.28 (d, J = 7.9 Hz, 4H), 4.94 (d, J = 7.5 Hz, 2H), 2.73 (sept, J = 6.8 Hz, 2H), 1.12 (d, J = 7.1 Hz, 24H). $^{13}$C NMR (151 MHz, chloroform-$d$, 300 K): δ 163.77, 150.76, 146.66, 145.83, 139.91, 138.70, 138.19, 137.55, 135.87, 134.65, 132.63, 132.36, 132.21, 131.77, 130.99, 130.51, 130.48, 129.43, 129.40, 129.13, 127.58, 124.67, 123.91, 121.94, 121.69, 121.31, 77.23, 77.02, 76.81, 29.12, 23.99. HRMS (ESI–TOF): $m/z$: [M + H]$^+$ Calcd for $C_{75}H_{59}N_4O_4$: 1079.4536; Found 1079.4531. UV-vis (dichloromethane, 300 K) λ [nm] (ε in M$^{-1}$ cm$^{-1}$): 376 (23 500), 396 (19 500), 484 (14 800), 519 (14 000), 668 (58 000), 723 (80 000).

Dipyrrin (1b). A solution of compound 6 (30 mg, 0.061 mmol) and 4-(dimethylamino)benzaldehyde (4.5 mg, 0.031 mmol) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (2 µL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 8.3 mg, 0.037 mmol) was added and the mixture was stirred for additional 30 min. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH$_2$Cl$_2$/n-hexane (1/2, v/v to 2/1, v/v) as the eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH$_2$Cl$_2$/n-hexane to give a product as a black solid (24 mg, 70%). $^1$H NMR (600 MHz, chloroform-$d$, 300 K): δ 13.70 (s, 1H), 8.40 (d, J = 7.4 Hz, 2H), 8.12 (d, J = 7.1 Hz, 4H), 8.07 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 7.6 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 2H), 5.43 (d, J = 7.5 Hz, 2H), 3.23 (s, 6H), 2.75 (sept, J = 6.8 Hz, 4H), 1.13 (d, J = 6.8, 24H). $^{13}$C NMR (151 MHz, chloroform-$d$, 300 K): δ 164.03, 163.90, 152.81, 150.15, 146.61, 145.88, 142.48, 138.47, 138.09, 135.50, 134.87, 132.95, 132.45, 132.29, 131.10, 130.22, 129.38, 127.48, 125.89, 125.55, 125.01, 123.88, 121.67, 121.35, 121.06, 113.99, 77.22, 77.01, 76.80, 40.70, 29.08, 24.00, 23.97. HRMS (ESI–TOF): $m/z$: [M + H]$^+$ Calcd for $C_{77}H_{64}N_5O_4$: 1122.4958; Found 1122.5016. UV-vis (dichloromethane, 300 K) λ [nm] (ε in M$^{-1}$ cm$^{-1}$): 377 (26 800), 395 (25 500), 486 (15 500), 523 (16 500), 668 (58 500), 728 (87 000).

Dipyrrin (1c). A solution of compound 6 (14 mg, 0.027 mmol) and S2 (3.2 mg, 0.013 mmol) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (2 µL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3.7 mg, 0.016 mmol) was added and the mixture was stirred for additional 30 min. The
solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH$_2$Cl$_2$/n-hexane (1/2, v/v to 2/1, v/v) as eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH$_2$Cl$_2$/n-hexane to give a product as a black solid (9.5 mg, 58%). $^1$H NMR (600 MHz, chloroform-$d$, 300 K): δ 14.51 (s, 1H), 8.40 (d, $J$ = 7.4 Hz, 2H), 8.14 (d, $J$ = 7.1 Hz, 4H), 8.02 (d, $J$ = 8.3 Hz, 2H), 7.98 (d, $J$ = 7.6 Hz, 2H), 7.96 (d, $J$ = 7.6 Hz, 2H), 7.74 (d, $J$ = 8.7 Hz, 2H), 7.70 (d, $J$ = 7.9 Hz, 6H), 7.62 (t, $J$ = 7.4 Hz, 2H), 7.42 (t, $J$ = 7.8 Hz, 2H), 7.27 (d, $J$ = 7.9 Hz, 4H), 6.90 (d, $J$ = 8.8 Hz, 2H), 5.25 (d, $J$ = 7.5 Hz, 2H), 2.71 (sept, $J$ = 6.9 Hz, 2H), 1.10 (d, $J$ = 6.9 Hz, 24H). $^{13}$C NMR (151 MHz, chloroform-$d$, 300 K): δ 163.83, 163.77, 150.96, 150.65, 146.72, 145.85, 144.48, 140.59, 138.33, 137.83, 137.69, 135.81, 135.54, 134.72, 132.77, 132.35, 131.04, 130.44, 129.41, 129.36, 129.08, 127.94, 127.59, 126.93, 125.85, 125.02, 123.85, 121.89, 121.59, 121.26, 113.08, 77.23, 77.02, 76.80, 40.50, 31.93, 29.71, 29.08, 23.99, 23.96, 22.70, 14.12. HRMS (ESI–TOF): $m/z$: [M + H]$^+$ Calcd for C$_{63}$H$_{66}$N$_{10}$O$_{6}$: 1198.5271; Found 1198.5147. UV–vis (dichloromethane, 300 K) λ [nm] (ε in M$^{-1}$ cm$^{-1}$): 376 (26 700), 396 (21 500), 483 (14 200), 521 (13 800), 665 (53 400), 725 (74 600).

**Dipyrnin (1d).** A solution of compound 6 (7.5 mg, 0.015 mmol) and 2,3,4,5,6-pentafluorobenzaldehyde (1.5 µL, 0.015 mmol) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (15 µL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2 mg) was added and the mixture was stirred for additional 4 h. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH$_2$Cl$_2$/n-hexane (1/2, v/v to 2/1, v/v) as the eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH$_2$Cl$_2$/n-hexane to give a product as a black solid (5.6 mg, 65%). $^1$H NMR (500 MHz, chloroform-$d$, 300 K): δ 14.75 (s, 1H), 8.46 (d, $J$ = 7.4 Hz, 2H), 8.27 (d, $J$ = 7.5 Hz, 2H), 8.12 (d, $J$ = 7.0 Hz, 4H), 8.04 (d, $J$ = 7.4 Hz, 2H), 7.70 (t, $J$ = 7.3 Hz, 4H), 7.65 (t, $J$ = 7.3 Hz, 2H), 7.46 (t, $J$ = 7.8 Hz, 2H), 7.30 (d, $J$ = 7.9 Hz, 4H), 5.45 (d, $J$ = 7.5 Hz, 2H), 2.74 (sept, $J$ = 6.7 Hz, 4H), 1.14 (d, $J$ = 6.8, 24H). $^{13}$C NMR (125 MHz, chloroform-$d$, 300 K): δ 163.59, 163.50, 152.15, 145.84, 145.08, 137.82, 137.89, 137.01, 134.68, 132.88, 132.23, 131.09, 130.78, 129.56, 127.79, 126.21, 123.98, 122.74, 122.62, 121.87, 121.83, 121.10, 77.27, 77.02, 76.76, 29.71, 29.14, 23.99, 23.97. HRMS (ESI–TOF): $m/z$: [M + H]$^+$ Calcd for C$_{63}$H$_{66}$F$_{13}$N$_{10}$O$_{6}$: 1169.4065; Found 1169.4045. UV–vis (dichloromethane, 300 K) λ [nm] (ε in M$^{-1}$ cm$^{-1}$): 381 (25 100), 485 (17 400), 521 (14 700), 681 (60 200), 733 (76 400).
Dipyrrin (1e). A solution of compound 6 (7 mg, 0.014 mmol) and 2,4-dinitrobenzaldehyde (1.5 mg, 0.008 mmol) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (15 μL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2 mg) was added and the mixture was stirred for additional 4 h. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH₂Cl₂/n-hexane (1/2, v/v to 2/1, v/v) as eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH₂Cl₂/n-hexane to give a product as a black solid (5.0 mg, 63%).

\[ ^1H \text{NMR (500 MHz, chloroform-d, 300 K): } \delta \text{ ppm} \]

\[ 14.79 (s, 1H), 9.38 (d, J = 2.3 Hz, 1H), 8.93 (dd, J = 8.3, 2.3 Hz, 1H), 8.44 (d, J = 7.4 Hz, 2H), 8.24 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 7.0 Hz, 4H), 8.02 (dd, J = 7.5, 2.7 Hz, 4H), 7.71 (t, J = 7.3 Hz, 4H), 7.65 (t, J = 7.3 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.9 Hz, 4H), 4.90 (d, J = 7.5 Hz, 2H), 2.70 (m, 4H), 1.14 (m, 24H). \]

\[ ^{13}C \text{NMR (151 MHz, chloroform-d, 300 K): } \delta \text{ ppm} \]

\[ 163.52, 163.40, 151.82, 149.82, 149.47, 145.77, 145.83, 144.76, 139.03, 137.14, 137.06, 136.96, 136.72, 134.63, 132.86, 132.18, 131.91, 131.44, 131.06, 130.72, 129.74, 129.56, 127.77, 126.10, 124.00, 123.91, 122.58, 122.11, 121.77, 77.22, 77.01, 76.80, 29.70, 29.12, 23.98, 23.95, 23.92. \]

HRMS (ESI–TOF): m/z: [M + H]^+ Calcd for C₇₅H₅₇N₆O₈: 1169.4238; Found 1169.4246. UV-vis (dichloromethane, 300 K) \( \lambda \text{ [nm]} \) (\( \varepsilon \) in M⁻¹ cm⁻¹): 379 (25 800), 483 (17 600), 521 (14 500), 682 (62 000), 734 (78 300).

Dipyrrin (1f). A solution of compound 6 (13 mg, 0.026 mmol) and S3 (7.9 mg, 0.014 mmol) in dichloromethane was purged with nitrogen for 10 min and trifluoroacetic acid (25 μL) was added to the solution and the resulting mixture was stirred for 2 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 4 mg) was added and the mixture was stirred for additional 4 h. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH₂Cl₂/n-hexane (1/2, v/v to 2/1, v/v) as eluent. The green color fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH₂Cl₂/n-hexane to give a product as a black solid (14 mg, 71%).

\[ ^1H \text{NMR (500 MHz, chloroform-d, 300 K): } \delta \text{ ppm} \]

\[ 14.66 (s, 1H), 10.03 (s, 1H), 8.44 (d, J = 7.4 Hz, 2H), 8.38 (d, J = 7.4 Hz, 2H), 8.17 (d, J = 7.1 Hz, 4H), 8.06 (d, J = 8.1 Hz, 2H), 8.02 (m, 4H), 7.91 (d, J = 8.8 Hz, 2H), 7.71 (t, J = 7.5 Hz, 4H), 7.64 (t, J = 7.4 Hz, 2H), 7.42 (m, 4H), 7.28 (d, J = 7.9 Hz, 4H), 6.96 (s, 4H), 6.37 (d, J = 7.3 Hz, 2H), 5.85 (d, J = 7.4 Hz, 2H), 2.74 (m, 4H), \]

S16
2.33 (s, 6H), 2.17 (s, 10H), 1.11 (m, 24H). 13C NMR (151 MHz, chloroform-\(d\), 300 K): \(\delta\) 163.77, 163.68, 154.52, 150.92, 149.12, 146.62, 145.79, 142.32, 140.33, 138.56, 138.01, 137.67, 137.42, 136.16, 135.11, 134.83, 134.64, 133.70, 132.68, 132.57, 132.48, 131.47, 130.98, 130.85, 130.57, 129.80, 129.73, 129.46, 127.66, 127.19, 125.96, 124.67, 124.00, 123.94, 122.29, 121.87, 121.44, 118.59, 117.33, 104.79, 29.11, 24.00, 23.97, 20.86, 16.19. HRMS (ESI–TOF): \(m/z\) [M + H]+: 484 (14 \(\mu\)L, 300 K) \(\lambda\) [nm] (\(\varepsilon\) in M\(^{-1}\) cm\(^{-1}\)): 376 (34 100), 393 (33 500), 484 (14 000), 521 (12 800), 673 (51 400), 726 (70 600).

Dipyrrin (2a). A solution of compound 7 (7.5 mg, 0.0138 mmol) and benzaldehyde (1.0 \(\mu\)L, 0.010 mmol) in chloroform was purged with nitrogen for 10 min and trifluoroacetic acid (6 \(\mu\)L) was added to the solution and the resulting mixture was stirred for 4 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.9 mg, 0.008 mmol) was added and the mixture was stirred for additional 20 min. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH\(_2\)Cl\(_2\)/n-hexane (1/2, v/v) to pure CH\(_2\)Cl\(_2\) as the eluent. The red-black fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH\(_2\)Cl\(_2\)/n-hexane to give a product as a grey-black solid (5.6 mg, 70%). \(^1\)H NMR (500 MHz, chloroform-\(d\), 300 K): \(\delta\) 14.62 (s, 1H), 8.37 (d, \(J = 7.4\) Hz, 2H), 8.05 (d, \(J = 8.8\) Hz, 4H), 7.97 (d, \(J = 7.5\) Hz, 4H), 7.89 (t, \(J = 7.4\) Hz, 1H), 7.80 (t, \(J = 7.7\) Hz, 2H), 7.70 (d, \(J = 7.0\) Hz, 2H), 7.43 (t, \(J = 7.9\) Hz, 2H), 7.28 (d, \(J = 7.9\) Hz, 4H), 6.96 (d, \(J = 8.8\) Hz, 4H), 4.88 (d, \(J = 7.6\) Hz, 2H), 3.16 (s, 12H), 2.73 (m, 4H), 1.12 (d, \(J = 7.0\) Hz, 24H). 13C NMR (151 MHz, chloroform-\(d\), 300 K): \(\delta\) 163.97, 163.92, 151.66, 150.90, 146.05, 145.88, 139.26, 138.46, 138.37, 138.12, 136.58, 135.17, 134.73, 132.40, 132.16, 131.56, 131.15, 130.10, 129.52, 129.33, 129.15, 125.83, 124.28, 123.85, 121.45, 121.28, 120.68, 120.12, 112.18, 77.22, 77.01, 76.79, 40.31, 29.70, 29.32, 29.06, 27.22, 23.97, 22.69, 14.11. HRMS (ESI–TOF): \(m/z\) [M + H]+: [M + H]+ Calcld for C\(_{102}\)H\(_{89}\)N\(_2\)O\(_6\): 1165.5375; Found 1165.5447. UV-vis (dichloromethane, 300 K) \(\lambda\) [nm] (\(\varepsilon\) in M\(^{-1}\) cm\(^{-1}\)): 376 (34 800), 464 (33 500), 580 (26 300), 843 (70 000).

Dipyrrin (2b). A solution of compound 7 (8.0 mg, 0.015 mmol) and 4-(dimethylamino)benzaldehyde (1.1 mg, 0.007 mmol) in chloroform was purged with nitrogen for 10 min and trifluoroacetic acid (6 \(\mu\)L)
was added to the solution and the resulting mixture was stirred for 4 days. Then 2,3- dichloro-5,6-
dicyano-1,4-benzoquinone (DDQ, 2.0 mg, 0.009 mmol) was added and the mixture was stirred for
additional 20 min. The solvent was evaporated and the residue was passed through alumina (grade V) 
column chromatography with CH\textsubscript{2}Cl\textsubscript{2}/n-hexane (1/2, v/v to pure CH\textsubscript{2}Cl\textsubscript{2}) as the eluent. The red-black
fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product
was recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/n-hexane to give a product as a grey-black solid (6.2 mg, 70%).

\textbf{\textsuperscript{1}H NMR} (500 MHz, chloroform-\textit{d}, 300 K): \(\delta\) 13.98 (s, 1H), 8.36 (d, \(J = 7.4\) Hz, 2H), 8.03 (d, \(J = 7.7\) Hz, 6H), 7.92 (d, \(J = 7.5\) Hz, 2H), 7.44 (dd, \(J = 15.7, 8.2\) Hz, 4H), 7.29 (d, \(J = 7.9\) Hz, 4H), 6.99 (d, \(J = 8.8\) Hz, 2H), 6.94 (d, \(J = 8.9\) Hz, 4H), 5.33 (d, \(J = 7.6\) Hz, 2H), 3.20 (s, 6H), 3.15 (s, 12H), 2.76 (sept, \(J = 6.8\) Hz, 4H), 1.13 (t, \(J = 6.5\) Hz, 24H). \textbf{\textsuperscript{13}C NMR} (151 MHz, chloroform-\textit{d}, 300 K): \(\delta\) 164.16, 164.06, 151.51, 150.45, 146.15, 145.92, 138.82, 138.76, 138.40, 134.88, 134.76, 132.44, 132.25, 131.25, 130.93, 129.29, 128.99, 125.90, 124.73, 123.83, 120.95, 120.43, 120.37, 114.05, 112.20, 77.22, 77.01, 76.80, 40.73, 40.32, 29.70, 29.06. \textbf{HRMS} (ESI-TOF): \(m/z\): [M + H]\textsuperscript{+} Calcd for C\textsubscript{61}H\textsubscript{33}N\textsubscript{2}O\textsubscript{4}: 1208.5797; Found 1208.5792. \textbf{UV-vis} (dichloromethane, 300 K) \(\lambda\) [nm] (\(\varepsilon\) in M\textsuperscript{-1} cm\textsuperscript{-1}): 380 (45 200), 392 (44 400), 458 (42 800), 582 (32 000), 839 (81 000).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{dipyrrin.png}
\caption{Dipyrrin (2c). A solution of compound 7 (17 mg, 0.03 mmol) and S2 (3.5 mg, 0.015 mmol) in chloroform
was purged with nitrogen for 10 min and trifluoroacetic acid (8 \(\mu\)L) was added to the solution and the
resulting mixture was stirred for 4 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 4.3
mg, 0.019 mmol) was added and the mixture was stirred for additional 30 min. The solvent was
 evaporated and the residue was passed through alumina (grade V) column chromatography with
CH\textsubscript{2}Cl\textsubscript{2}/n-hexane (1/2, v/v to pure CH\textsubscript{2}Cl\textsubscript{2}) as the eluent. The red-black fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/n-hexane to give a product as a grey-black solid (13.2 mg, 66%). \textbf{\textsuperscript{1}H NMR} (500 MHz, chloroform-\textit{d}, 300 K): \(\delta\) 14.63 (s, 1H), 8.31 (d, \(J = 7.4\) Hz, 2H), 7.97 (d, \(J = 8.8\) Hz, 4H), 7.92 (d, \(J = 8.2\) Hz, 2H), 7.86 (d, \(J = 7.6\) Hz, 2H), 7.81 (d, \(J = 7.5\) Hz, 2H), 7.69 (d, \(J = 7.3\) Hz, 4H), 7.42 (t, \(J = 7.9\) Hz, 2H), 7.27 (d, \(J = 7.9\) Hz, 4H), 6.92 (d, \(J = 8.9\) Hz, 4H), 6.89 (d, \(J = 8.8\) Hz, 2H), 5.11 (d, \(J = 7.6\) Hz, 2H), 3.15 (s, 12H), 3.05 (s, 6H), 2.74 (sept, \(J = 6.8\) Hz, 4H), 1.12 (d, \(J = 6.9\) Hz, 24H). The compound produced broadened \textbf{\textsuperscript{13}C NMR} spectrum, which were not analytically useful. \textbf{HRMS} (ESI-TOF): \(m/z\): [M + H]\textsuperscript{+} Calcd for C\textsubscript{61}H\textsubscript{33}N\textsubscript{2}O\textsubscript{4}: 1284.6110; Found 1284.6245. \textbf{UV-vis} (dichloromethane, 300 K) \(\lambda\) [nm] (\(\varepsilon\) in M\textsuperscript{-1} cm\textsuperscript{-1}): 376 (43 900), 463 (36 500), 580 (28 600), 846 (68 800).}
Dipyrrin (2d). A solution of compound 7 (18 mg, 0.033 mmol) and 2,3,4,5,6-pentafluorobenzaldehyde (3.2 μL, 0.017 mmol) in chloroform was purged with nitrogen for 10 min and trifluoroacetic acid (5 μL) was added to the solution and the resulting mixture was stirred for 4 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 6.5 mg, 0.029 mmol) was added and the mixture was stirred for additional 20 min. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH₂Cl₂/n-hexane (1/2, v/v to pure CH₂Cl₂) as the eluent. The red-black fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH₂Cl₂/n-hexane to give a product as a grey-black solid (15.5 mg, 75%).

1H NMR (500 MHz, chloroform-d, 300 K): δ 14.84 (s, 1H), 8.43 (d, J = 7.4 Hz, 2H), 8.22 (d, J = 7.5 Hz, 2H), 8.03 (m, 6H), 7.45 (t, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 5.38 (d, J = 7.5 Hz, 2H), 3.18 (s, 11H), 2.75 (sept, J = 13.6, 6.8 Hz, 4H), 1.13 (d, J = 6.8, 23H).

13C NMR (151 MHz, chloroform-d, 300 K): δ 163.76, 163.66, 151.92, 151.83, 145.88, 144.30, 138.18, 138.00, 137.69, 136.24, 134.75, 132.85, 132.14, 130.95, 129.60, 129.46, 126.21, 123.93, 122.15, 122.12, 121.38, 121.16, 119.54, 112.52, 112.14, 40.24, 29.12, 24.00, 23.97. HRMS (ESI–TOF): m/z: [M + H]+ Calcd for C₇₉H₆₄F₅N₆O₄: 1255.4909; Found 1255.4902.

UV-vis (dichloromethane, 300 K) λ [nm] (ε in M⁻¹ cm⁻¹): 377 (37 800), 474 (38 400), 582 (30 300), 886 (66 000).

Dipyrrin (2e). A solution of compound 7 (26 mg, 0.048 mmol) and 2,4-dinitrobenzaldehyde (4.7 mg, 0.023 mmol) in chloroform was purged with nitrogen for 10 min and trifluoroacetic acid (10 μL) was added to the solution and the resulting mixture was stirred for 4 days. Then 2,3- dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 6.4 mg, 0.028 mmol) was added and the mixture was stirred for additional 20 min. The solvent was evaporated and the residue was passed through alumina (grade V) column chromatography with CH₂Cl₂/n-hexane (1/2, v/v to pure CH₂Cl₂) as the eluent. The red-black fraction was collected and solvent was evaporated on rotary evaporator. Subsequently, the product was recrystallized from CH₂Cl₂/n-hexane to give a product as a grey-black solid (20 mg, 68%).

1H NMR (500 MHz, chloroform-d, 300 K): δ 14.96 (s, 1H), 9.22 (s, 1H), 8.61 (broad, 1H), 8.35 (broad, 1H), 8.25 (broad, 2H), 7.71 (broad, 8H), 7.45 (m, 2H), 7.30 (m, 4H), 6.89 (d, J = 8.7 Hz, 4H), 4.65 (broad, 2H), 3.18 (s, 12H), 2.82 (broad, 2H), 2.71 (m, 2H), 1.21 (m, 12H), 1.11 (m, 12H). The compound produced broadened 13C NMR spectrum, which were not analytically useful. HRMS (ESI–TOF): m/z: [M + H]+ Calcd for
C$_{78}$H$_{79}$N$_8$O$_8$: 1255.5076; Found 1255.5578. **UV-vis** (dichloromethane, 300 K) $\lambda$ [nm] ($\varepsilon$ in M$^{-1}$ cm$^{-1}$): 381 (35 800), 485 (40 200), 595 (30 200), 878 (73 900).
Additional Figures
Figure S1. X-ray crystal structure (a) top view and (b) side view of 1a. For clarity, all solvent molecules are omitted (ellipsoids are scaled to 10% probability level).
Figure S2. X-ray crystal structure (a) top view and (b) side view of 1b. For clarity, all solvent molecules are omitted.
**Figure S3.** Short intermolecular (a) plane contacts and (b) hydrogen bonding (H--N) meso-aryl (H) - pyrrolic(N) interactions in the crystal structure of 1b.
Figure S4. X-ray crystal structure (a) top view and (b) side view of 1e. For clarity, all solvent molecules are omitted.
Figure S5. Short intermolecular (a) plane contacts and (b) hydrogen bonding (H--N) meso-aryl (H) - pyrrolic(N) interactions in the crystal structure of 1e.
Figure S6. X-ray crystal structure of (a) top view and (b) side view of 2e. For clarity, all solvent molecules are omitted.
Figure S7. Short intermolecular (a) plane contacts and (b) hydrogen bonding (H--N) meso-aryl (H) - pyrrolic(N) interactions in the crystal structure of 2e.

Figure S8. Atoms marked with red asterisk (*) are used to define the mean plane of dipyrrins.
Figure S9. X-ray crystal structure of 1a–H⁺. For clarity, all solvent molecules are omitted. Brown sphere show bromine atom as a counter anion.
Figure S10. Cyclic dimer structure a) side view and b) top view of 1a–H⁺. For clarity, all solvent molecules are omitted. Brown sphere show bromine atom as a counter anion.
Figure S11. X-ray crystal structure of 1b–H+. For clarity, all solvent molecules are omitted. Green sphere show chlorine atom as a counter anion.
Figure S12. Cyclic dimer structure a) side view and b) top view of 1b–H⁺ For clarity, all solvent molecules are omitted. Green sphere show chlorine atom as a counter anion.
**Figure S13.** Preliminary X-ray crystal structure (stick views) of (a) top view and (b) side view of 3d. For clarity, all solvent molecules are omitted. In this structure, chlorine element occupancy was found to be 10.8% and 31.2%.
Figure S14. Absorption spectra of 3–7 in dichloromethane at 293K.

Figure S15. Absorption spectra of 3 in different solvents (blue line - toluene solution, black line - dichloromethane solution, red line - methanol solution). (Insets shows the solution in different solvents at ≈ 60 μM concentrations).
Figure S16. Absorption spectra of 4 in different solvents (blue line - toluene solution, black line - dichloromethane solution, red line - methanol solution). (Insets shows the solution in different solvents at ≈ 60 μM concentrations).

Figure S17. Absorption spectra of 6 in different solvents (blue line - toluene solution, black line - dichloromethane solution, red line - methanol solution). (Insets shows the solution in different solvents at ≈ 60 μM concentrations).
Figure S18. Absorption spectra of 5 in different solvents (blue line - toluene solution, black line - dichloromethane solution, red line - methanol solution). (Insets shows the solution in different solvents at ≈ 60 μM concentrations).

Figure S19. Absorption spectra of 7 in different solvents (blue line - toluene solution, black line - dichloromethane solution, red line - methanol solution). (Insets shows the solution in different solvents at ≈ 60 μM concentrations).
**Figure S20.** Absorption spectral change of 1d in CH$_2$Cl$_2$ seen upon the addition of TFA with increasing concentrations from stock solution. The black spectral line represents the neutral form and the red spectral line represents the protonated form upon addition of acid.

**Figure S21.** Absorption spectral change of 1f in CH$_2$Cl$_2$ seen upon the addition of TFA. The black spectral line represents the neutral form and the red spectral line represents the protonated form.
Figure S22. Absorption spectra showing the neutral and the first protonation state of 2a in CH$_2$Cl$_2$ at 293K using various acid source, CSA, HCl, and TFA.
Figure S23. Comparison of $^1$H NMR spectra upon stepwise addition of camphorsulphonic acid (CSA) to dipyrrin 1b recorded in CDCl$_3$ at room temperature. The complete protonation was achieved by using a drop of 98% H$_2$SO$_4$ solution dissolved in CDCl$_3$. 
**Figure S24.** Comparison of $^1$H NMR spectra upon addition of 0-5.0 equiv. of BAHA (dissolved in CD$_2$Cl$_2$) to dipyrrin 2d recorded in CD$_2$Cl$_2$ at 240 K.
Figure S25. A) Overlay of partial COSY (red) and ROESY (green/blue) of chemically oxidized 2d using 2.5 equivalent of BAHA recorded in CD$_2$Cl$_2$ at 240 K. B) Partial ROESY spectrum showing the iPr group peak signals corresponding to the presence of both radical monocation and dication species. c) Partial $^1$H NMR showing the integral peaks of selected region which are assigned to the peaks in ROESY spectrum suggesting the radical monocation is in exchange with dication species.
Figure S26. Reversibility of chemical oxidation. Comparison of $^1$H NMR spectra of 2d and reduced form of oxidized dipyrrin recorded in CDCl$_3$ at room temperature. In this experiment, AgPF$_6$ was used as an oxidant and the solid was added to the NMR tube containing dipyrrin solution; KO$_2$ was used as reductant and the solid was added to the NMR tube containing oxidized dipyrrin.
Figure S27. Chemical oxidation investigated for 1a in CH$_2$Cl$_2$ at 293K using BAHA as chemical oxidant; black line represents the neutral dipyrrin; inset in the bottom figure shows the formation of radical dipyrrin.
Figure S28. Chemical oxidation investigated for 2a in CH$_2$Cl$_2$ at 293K using BAHA as chemical oxidant. In the top figure, black line corresponds to the neutral dipyrrin; blue line corresponds to the dicationic solution; red line corresponds to the protonated dicationic solution. In the bottom figure, dashed black line corresponds to the reduction with excess hydrazine hydrate solution; dashed blue line corresponds to the protonated form of the partially chlorinated dipyrrin.
Figure S29. Reversibility of chemical oxidation investigated for 2d in CH₂Cl₂ at 293K using AgPF₆ as chemical oxidant. The blue curve was obtained upon adding hydrazine hydrate dissolved in dichloromethane to the oxidized 2d dipyrrin.
Figure S30. Differential pulse voltammogram (top curve) and cyclic voltammogram (bottom curves) for dipyrrin 1a–e in different potential setup (dichloromethane solvent, [Bu₄N]PF₆ as supporting electrolyte; glassy carbon as working electrode, Au wire as pseudoreference electrode, and Pt rod as counter electrode, scan rate: 100 mV/s.
Figure S31. Differential pulse voltammogram (top curve) and cyclic voltammogram (bottom curves) for dipyrrin 2a–e in different potential setup (dichloromethane solvent, [Bu4N]PF6 as supporting electrolyte; glassy carbon as working electrode, Au wire as pseudoreference electrode, and Pt rod as counter electrode, scan rate: 100 mV/s.
Figure S32. UV-vis-NIR spectroelectrochemistry of 2a in different potential setup (dichloromethane solvent, [Bu4N]PF6 as supporting electrolyte, Pt, Ag, Pt, with an increasing applied oxidation potential up to 1.7 V vs Ag/Ag⁺.)
Figure S33. Emission spectra of 3-7 monopyrroles recorded in toluene.
**Figure S34.** Absorption and emission spectra of 1a–1e in different solvents (toluene, dichloromethane and benzonitrile solvent).
Figure S35. TCSPC data of 1a and 1b in toluene, dichloromethane and benzonitrile solvent.
Figure S36. Transient absorption spectra of 1a and 1b in toluene and benzonitrile.

Figure S37. (A) Photothermal response of 2d and [2d-H]+ to irradiation with a 1064 nm laser source (16 μM, toluene in air, 25 W/cm²). (B) Temperature variation observed for [2d-H]+ during 5 on–off irradiation cycles.
Figure S38. Kohn-Sham frontier molecular orbitals of dipyrrin 1a calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S39. Kohn-Sham frontier molecular orbitals of dipyrrin 1b calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S40. Kohn-Sham frontier molecular orbitals of dipyrrin 1c calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S41. Kohn-Sham frontier molecular orbitals of dipyrrin 1d calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S42. Kohn-Sham frontier molecular orbitals of dipyrrin 1e calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S43. Kohn-Sham frontier molecular orbitals of dipyrrin 1f' calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S44. Kohn-Sham frontier molecular orbitals of dipyrrin 2a calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S45. Kohn-Sham frontier molecular orbitals of dipyrrin 2b calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S46. Kohn-Sham frontier molecular orbitals of dipyrrin 2c calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S47. Kohn-Sham frontier molecular orbitals of dipyrrin 2d calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S48. Kohn-Sham frontier molecular orbitals of dipyrrin 2e calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S49. Kohn-Sham frontier molecular orbitals of dipyrrin 1a–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S50. Kohn-Sham frontier molecular orbitals of dipyrrin 1b–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S51. Kohn-Sham frontier molecular orbitals of dipyrrin 1c–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S52. Kohn-Sham frontier molecular orbitals of dipyrrin 1d–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S53. Kohn-Sham frontier molecular orbitals of dipyrrin 1e–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S54. Kohn-Sham frontier molecular orbitals of dipyrrin 1f'–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S55. Kohn-Sham frontier molecular orbitals of dipyrrin 2a–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S56. Kohn-Sham frontier molecular orbitals of dipyrrin 2b–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S57. Kohn-Sham frontier molecular orbitals of dipyrrin 2c–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).

Figure S58. Kohn-Sham frontier molecular orbitals of dipyrrin 2d–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S59. Kohn-Sham frontier molecular orbitals of dipyrrin 2e–H⁺ calculated at the level of GD3BJ-B3LYP/6-31G(d,p) with PCM solvation (dichloromethane).
Figure S60. Simulated electronic absorption spectrum of 1a (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S61. Simulated electronic absorption spectrum of 1a–H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S62. Simulated electronic absorption spectrum of 1a−H⁺ (E-anti) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S63. Simulated electronic absorption spectrum of 1a−H⁺ (Z-syn) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
**Figure S64.** Simulated electronic absorption spectrum of 1b (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

**Figure S65.** Simulated electronic absorption spectrum of 1b−H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S66. Simulated electronic absorption spectrum of 1b-H⁺ (E-anti) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S67. Simulated electronic absorption spectrum of 1b-H⁺ (Z-syn) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
**Figure S68.** Simulated electronic absorption spectrum of $1b-2H^{2+}$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

**Figure S69.** Simulated electronic absorption spectrum of $1c$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S70. Simulated electronic absorption spectrum of 1c−H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S71. Simulated electronic absorption spectrum of 1c−2H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S72. Simulated electronic absorption spectrum of 1d (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S73. Simulated electronic absorption spectrum of 1d−H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S74. Simulated electronic absorption spectrum of 1e (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S75. Simulated electronic absorption spectrum of 1e--H+ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S76. Simulated electronic absorption spectrum of $1^f$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S77. Simulated electronic absorption spectrum of $1f^-\text{H}^+$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S78. Simulated electronic absorption spectrum of 2a (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S79. Simulated electronic absorption spectrum of 2a–H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S80. Simulated electronic absorption spectrum of 2a−H⁺ (E-anti) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S81. Simulated electronic absorption spectrum of 2a−H⁺ (Z-syn) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S82. Simulated electronic absorption spectrum of 2a−3H3+ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S83. Simulated electronic absorption spectrum of 2b (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
**Figure S84.** Simulated electronic absorption spectrum of $\text{2b-H}^+$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

**Figure S85.** Simulated electronic absorption spectrum of $\text{2b-4H}^+$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S86. Simulated electronic absorption spectrum of 2c (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S87. Simulated electronic absorption spectrum of 2c−1H+ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S88. Simulated electronic absorption spectrum of $2c-4H^+$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S89. Simulated electronic absorption spectrum of $2d$ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
**Figure S90.** Simulated electronic absorption spectrum of 2d–1H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

**Figure S91.** Simulated electronic absorption spectrum of 2d–3H³⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S92. Simulated electronic absorption spectrum of 2e (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).

Figure S93. Simulated electronic absorption spectrum of 2e−1H⁺ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S94. Simulated electronic absorption spectrum of 2e−·3H3+ (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S95. Simulated electronic absorption spectrum of $2a^{2+}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).

Figure S96. Simulated electronic absorption spectrum of $2d^{2+}$ (closed-shell configuration) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S97. Simulated electronic absorption spectrum of 2a$^{3+}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).

Figure S98. Simulated electronic absorption spectrum of protonated radical, 2a−H$^{3+}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).
Figure S99. Simulated electronic absorption spectrum of $2d^{10}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).

Figure S100. Simulated electronic absorption spectrum of $2d^{10}$ (closed-shell configuration) (TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p)).
Figure S101. Simulated electronic absorption spectrum of $2d^{1+}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).

Figure S102. Simulated electronic absorption spectrum of protonated radical, $2d^-\text{H}^{++}$ (TD/PCM(dichloromethane)GD3BJ-UB3LYP/6-31G(d,p)).
Additional Tables
Table S1. Crystal data and structure refinement for 1a·0.5C₆H₁₄·CH₃OH

| Property                                              | Value                        |
|-------------------------------------------------------|------------------------------|
| Identification code                                   | ym115-2                      |
| Empirical formula                                     | C₇₉H₆₉N₄O₅                  |
| Formula weight                                        | 1154.38                      |
| Temperature                                           | 80(2) K                      |
| Wavelength                                            | 1.54184 Å                    |
| Crystal system                                        | Triclinic                    |
| Space group                                           | P-1                          |
| Unit cell dimensions                                  |                              |
| a = 17.336(10) Å                                      | α = 92.02(5)°.               |
| b = 17.795(10) Å                                      | β = 97.60(5)°.               |
| c = 21.42(2) Å                                       | γ = 104.28(5)°.              |
| Volume                                                | 6331(8) Å³                   |
| Z                                                     | 4                            |
| Density (calculated)                                  | 1.211 Mg/m³                  |
| Absorption coefficient                                | 0.591 mm⁻¹                   |
| F(000)                                                | 2444                         |
| Crystal size                                          | 0.570 x 0.250 x 0.030 mm³    |
| Theta range for data collection                       | 3.702 to 66.997°.            |
| Index ranges                                          | -20<=h<=20, -21<=k<=19, -20<=l<=25 |
| Reflections collected                                 | 47155                        |
| Independent reflections                               | 22202 [R(int) = 0.1942]      |
| Completeness to theta = 67.000°                      | 98.3 %                       |
| Absorption correction                                 | None                         |
| Refinement method                                     | Full-matrix least-squares on F² |
| Data / restraints / parameters                        | 22202 / 28 / 1420            |
| Goodness-of-fit on F²                                  | 0.980                        |
| Final R indices [I>2sigma(I)]                         | R1 = 0.1568, wR2 = 0.2860    |
| R indices (all data)                                  | R1 = 0.3768, wR2 = 0.4110    |
| Extinction coefficient                                | n/a                          |
| Largest diff. peak and hole                           | 0.295 and -0.306 e.Å⁻³       |
**Table S2.** Crystal data and structure refinement for 1b·3CHCl₃.

| Property                                      | Value                                |
|-----------------------------------------------|--------------------------------------|
| Identification code                           | ymo67a                               |
| Empirical formula                            | C₈₀H₆₆Cl₉N₅O₄                       |
| Formula weight                                | 1480.42                              |
| Temperature                                   | 100(2) K                             |
| Wavelength                                    | 1.54184 Å                            |
| Crystal system                                | Monoclinic                           |
| Space group                                   | P2₁/c                                |
| Unit cell dimensions                          |                                       |
| a                                             | 9.765(3) Å                           |
| b                                             | 24.206(8) Å                          |
| c                                             | 30.365(8) Å                          |
| Volume                                        | 7166(4) Å                            |
| Z                                             | 4                                    |
| Density (calculated)                          | 1.372 Mg/m³                          |
| Absorption coefficient                        | 3.655 mm⁻¹                           |
| F(000)                                        | 3064                                 |
| Crystal size                                  | 0.370 x 0.040 x 0.040 mm³            |
| Theta range for data collection               | 2.336 to 75.751°                     |
| Index ranges                                  | -11<≤h≤10, -29<≤k≤29, -37<≤l≤31      |
| Reflections collected                         | 30591                                |
| Independent reflections                       | 14384 [R(int) = 0.0870]              |
| Completeness to theta = 68.000°               | 99.9 %                               |
| Absorption correction                         | Analytical                           |
| Max. and min. transmission                    | 0.880 and 0.513                      |
| Refinement method                             | Full-matrix least-squares on F²      |
| Data / restraints / parameters                | 14384 / 0 / 894                      |
| Goodness-of-fit on F²                          | 0.835                                |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0574, wR2 = 0.0818            |
| R indices (all data)                          | R1 = 0.1442, wR2 = 0.0904            |
| Extinction coefficient                        | n/a                                  |
| Largest diff. peak and hole                   | 0.492 and -0.447 e.Å⁻³              |
| **Table S3. Crystal data and structure refinement for 1e·0.5C₆H₁₄·CHCl₃.** |
| --- |
| **Identification code** | ym204a |
| **Empirical formula** | C₇₉H₆₄Cl₃N₆O₈ |
| **Formula weight** | 1331.71 |
| **Temperature** | 100(2) K |
| **Wavelength** | 1.54184 Å |
| **Crystal system** | Monoclinic |
| **Space group** | P2₁/c |
| **Unit cell dimensions** | |
| a | 24.954(4) Å | α = 90°. |
| b | 9.5250(11) Å | β = 107.66(3)°. |
| c | 29.697(4) Å | γ = 90°. |
| **Volume** | 6725.9(19) Å³ |
| **Z** | 4 |
| **Density (calculated)** | 1.315 Mg/m³ |
| **Absorption coefficient** | 1.745 mm⁻¹ |
| **F(000)** | 2780 |
| **Crystal size** | 0.470 x 0.056 x 0.013 mm³ |
| **Theta range for data collection** | 3.113 to 71.262°. |
| **Index ranges** | -30≤h≤29, -11≤k≤11, -30≤l≤36 |
| **Reflections collected** | 54813 |
| **Independent reflections** | 12742 [R(int) = 0.0458] |
| **Completeness to theta = 67.000°** | 99.9 % |
| **Absorption correction** | Gaussian |
| **Max. and min. transmission** | 1.000 and 0.491 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 12742 / 27 / 928 |
| **Goodness-of-fit on F²** | 1.221 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0857, wR2 = 0.2101 |
| **R indices (all data)** | R1 = 0.1017, wR2 = 0.2177 |
| **Extinction coefficient** | n/a |
| **Largest diff. peak and hole** | 0.675 and -0.658 e.Å⁻³ |
Table S4. Crystal data and structure refinement for $2e \cdot 4\text{CHCl}_3$

| Identification code | ym244a |
|---------------------|-------|
| Empirical formula   | C$_8$H$_{66}$D$_4$Cl$_{12}$N$_8$O$_8$ |
| Formula weight      | 1736.89 |
| Temperature         | 120(2) K |
| Wavelength          | 1.5418 Å |
| Crystal system      | Monoclinic |
| Space group         | P2$_1$/n |
| Unit cell dimensions| $a = 21.760(7)$ Å, $\alpha = 90^\circ$.
|                     | $b = 14.957(5)$ Å, $\beta = 94.58(5)^\circ$.
|                     | $c = 24.800(7)$ Å, $\gamma = 90^\circ$. |
| Volume              | 8046(4) Å$^3$ |
| Z                   | 4 |
| Density (calculated)| 1.434 Mg/m$^3$ |
| Absorption coefficient | 4.286 mm$^{-1}$ |
| F(000)              | 3568 |
| Crystal size        | 0.600 x 0.110 x 0.100 mm$^3$ |
| Theta range for data collection | 2.601 to 67.000°. |
| Index ranges        | -20<=h<=25, -17<=k<=17, -29<=l<=29 |
| Reflections collected | 40841 |
| Independent reflections | 14342 [R(int) = 0.1737] |
| Completeness to theta = 67.000° | 99.9 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.725 and 0.327 |
| Refinement method   | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 14342 / 0 / 1009 |
| Goodness-of-fit on F$^2$ | 1.007 |
| Final R indices [I>2sigma(I)] | R1 = 0.0978, wR2 = 0.2165 |
| R indices (all data) | R1 = 0.1953, wR2 = 0.2984 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.500 and -0.614 e.Å$^{-3}$ |
| Identification code       | ym178          |
|--------------------------|----------------|
| Empirical formula        | C_{79}H_{59}D_{4}BrCl_{12}N_{4}O_{4} |
| Formula weight           | 1641.66        |
| Temperature              | 100(2) K       |
| Wavelength               | 0.71073 Å      |
| Crystal system           | Triclinic      |
| Space group              | P-1            |
| Unit cell dimensions     | a = 10.492(3) Å, α = 93.69(3)°. |
|                         | b = 17.053(4) Å, β = 98.39(3)°. |
|                         | c = 22.142(5) Å, γ = 105.31(3)°. |
| Volume                   | 3758.1(17) Å³ |
| Z                        | 2              |
| Density (calculated)     | 1.451 Mg/m³    |
| Absorption coefficient   | 1.027 mm⁻¹     |
| F(000)                   | 1672           |
| Crystal size             | 0.500 x 0.300 x 0.300 mm³ |
| Theta range for data collection | 2.879 to 25.500°. |
| Index ranges             | -10≤h≤12, -20≤k≤20, -26≤l≤26 |
| Reflections collected    | 38738          |
| Independent reflections  | 13962 [R(int) = 0.1104] |
| Completeness to theta = 25.500° | 99.8 % |
| Absorption correction    | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000000 and 0.93164 |
| Refinement method        | Full-matrix least-squares on F² |
| Data / restraints / parameters | 13962 / 0 / 909 |
| Goodness-of-fit on F²    | 1.039          |
| Final R indices [I>2σ(I)] | R1 = 0.0845, wR2 = 0.2001 |
| R indices (all data)     | R1 = 0.1526, wR2 = 0.2461 |
| Extinction coefficient   | n/a            |
| Largest diff. peak and hole | 1.055 and -1.082 e.Å⁻³ |

Table S5. Crystal data and structure refinement for 1a–H⁺·4CDCl₃Br.
### Table S6. Crystal data and structure refinement for 1b−H\(^+\)-3.15CDCl\(_3\)-Cl-0.6H\(_2\)O

| Property | Value |
|----------|-------|
| Identification code | ym179a |
| Empirical formula | C\(_{80.15}\) H\(_{64.60}\) Cl\(_{10.45}\) D\(_{3.15}\) N\(_{5}\) O\(_{4.60}\) |
| Formula weight | 1548.16 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | 
| \(a = 20.023(5)\) Å | \(\alpha = 90^\circ\) |
| \(b = 23.518(7)\) Å | \(\beta = 97.91(2)^\circ\) |
| \(c = 33.749(9)\) Å | \(\gamma = 90^\circ\) |
| Volume | 15741(7) Å\(^3\) |
| Z | 8 |
| Density (calculated) | 1.307 Mg/m\(^3\) |
| Absorption coefficient | 3.797 mm\(^-1\) |
| F(000) | 6385 |
| Crystal size | 0.320 x 0.100 x 0.060 mm\(^3\) |
| Theta range for data collection | 3.724 to 66.996° |
| Index ranges | -23<=h<=11, -28<=k<=27, -39<=l<=40 |
| Reflections collected | 33630 |
| Independent reflections | 13792 [R(int) = 0.0749] |
| Completeness to theta = 67.000° | 98.2 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.842 and 0.577 |
| Refinement method | Full-matrix least-squares on F\(^2\) |
| Data / restraints / parameters | 13792 / 150 / 1005 |
| Goodness-of-fit on F\(^2\) | 1.020 |
| Final R indices [I>2sigma(I)] | R1 = 0.0786, wR2 = 0.1955 |
| R indices (all data) | R1 = 0.1334, wR2 = 0.2301 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.570 and -0.443 e.Å\(^{-3}\) |
**Table S7.** Crystal data and structure refinement for disordered co-crystal of 2d and 3d. The data were not deposited because of their low quality.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | ym294                                      |
| Empirical formula                             | C_{100}H_{100}N_{4}O_{4}F_{5}ClSb          |
| Formula weight                                 | 1674.03                                    |
| Temperature                                    | 100(2) K                                   |
| Wavelength                                    | 1.54184 Å                                  |
| Crystal system                                 | Monoclinic                                 |
| Space group                                    | P2_1/n                                     |
| Unit cell dimensions                          | a = 8.6176(5) Å, b = 22.4452(19) Å, c = 42.943(3) Å |
| Volume                                        | 8306.1(10) Å³                            |
| Z                                             | 4                                          |
| Density (calculated)                          | 1.339 Mg/m³                                |
| Absorption coefficient                        | 3.477 mm⁻¹                                 |
| F(000)                                        | 3492.0                                     |
| Crystal size                                  | n/a                                        |
| Theta range for data collection               | 4.116 to 178.592°                         |
| Index ranges                                  | -10 ≤ h ≤ 11, -25 ≤ k ≤ 24, -25 ≤ l ≤ 24  |
| Reflections collected                         | 40808                                      |
| Independent reflections                       | 8430 [R_int = 0.5266, R_sigma = 0.2883]     |
| Completeness to theta = 68.000°               | n/a                                        |
| Absorption correction                         | n/a                                        |
| Max. and min. transmission                    | n/a                                        |
| Refinement method                             | n/a                                        |
| Data / restraints / parameters                 | 8430/13/979                                |
| Goodness-of-fit on F²                          | 5.322                                      |
| Final R indices [I>2sigma(I)]                 | R1 = 0.8317, wR2 = 0.9585                  |
| R indices (all data)                          | R1 = 0.8592, wR2 = 0.9741                  |
| Extinction coefficient                        | n/a                                        |
| Largest diff. peak and hole                   | 3.29 and -1.96 e.Å⁻³                      |
Table S8. Quantum yields of dipyrrin 1a–1e in different solvents.

|       | toluene | dichloromethane | benzonitrile |
|-------|---------|-----------------|--------------|
| 1a    | 0.7     | 1.1             | 2.1          |
| 1b    | 0.8     | 0.5             | < 0.1        |
| 1c    | < 0.1   | < 0.1           | < 0.1        |
| 1d    | < 0.1   | < 0.1           | < 0.1        |
| 1e    | 0.1     | < 0.1           | < 0.1        |

Table S9. Photophysical Properties.

|       | 1a in tol | 1b in tol | 1a in BCN | 1a in DCM | 1b in DCM |
|-------|-----------|-----------|-----------|-----------|-----------|
| QY (%)| 0.7       | 0.8       | 2.1       | 1.1       | 0.5       |
| $k_r \text{ (s}^{-1}\text{)}$| 3.43E+06 | 3.40E+06 | 6.38E+06 | 4.68E+07 | 1.73E+07 |
| $k_{nr} \text{ (s}^{-1}\text{)}$| 4.87E+08 | 4.22E+08 | 2.97E+08 | 4.21E+08 | 3.66E+08 |
| Singlet lifetime (ns) | 2.04 | 2.35 | 3.29 | 2.35 | 2.72 |
Table S10. Redox potentials (in volts vs. ferrocene internal standard) from differential pulse voltammetry of dichloromethane solutions with tetrabutylammonium hexafluorophosphate as a supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode, and silver chloride reference electrode.

| code | \(E_{\text{Ox}1}\) | \(E_{\text{Ox}2}\) | \(E_{\text{Ox}3}\) | \(E_{\text{Ox}4}\) | \(E_{\text{Ox}5}\) | \(E_{\text{Red}1}\) | \(E_{\text{Red}2}\) | \(E_{\text{Red}3}\) | \(E_{\text{Red}4}\) | \(E_{\text{Red}5}\) | \(\Delta E\) |
|------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------|
| 1a   | 0.82             | 1.15            | —               | —               | —               | -0.94           | -1.28           | -1.83           | -2.22           | —               | 1.76        |
| 1b   | 0.62\(^a\)      | 0.89            | 1.00\(^a\)     | 1.16            | —               | -1.02           | -1.33           | -1.88           | -2.27           | —               | 1.62        |
| 1c   | 0.43             | 0.80            | 1.17            | —               | —               | -0.96           | -1.29           | -1.85           | -2.31\(^a\)    | —               | 1.39        |
| 1d   | 0.89             | 1.23\(^a\)     | —               | —               | —               | -0.77           | -1.13           | -1.80           | -2.21\(^a\)    | —               | 1.66        |
| 1e   | 0.88             | 1.25\(^a\)     | 1.48\(^a\)     | —               | —               | -0.78           | -1.03           | -1.59           | -1.87           | -2.12\(^a\)    | 1.66        |
| 2a   | 0.19             | 0.30            | 1.03            | 1.42\(^a\)     | —               | -1.04           | -1.31           | -1.88           | -2.25           | —               | 1.23        |
| 2b   | 0.19             | 0.30            | 0.58            | 0.89\(^a\)     | 1.04\(^a\)     | -1.06           | -1.34           | -1.94           | —               | —               | 1.25        |
| 2c   | 0.21             | 0.33            | 0.49            | 1.02\(^a\)     | 1.34\(^a\)     | -1.05           | -1.34           | -1.95           | —               | —               | 1.26        |
| 2d   | 0.24             | 0.33            | 1.14\(^a\)     | —               | —               | -0.90           | -1.20           | -1.89           | —               | —               | 1.14        |
| 2e   | 0.26             | 0.36            | 1.13            | —               | —               | -0.92           | -1.13           | -1.62           | -1.97           | -2.20\(^a\)    | 1.18        |

\(^a\)Irreversible couple
Table S11. Computational details obtained at B3LYP-GD3BJ/6-31G(d,p)/PCM(dichloromethane) level of theory.

| Code\(^{[a]}\) | Formula | Charge | SCF E\(^{[b]}\) a.u. | ZPV\(^{[c]}\) a.u. | lowest freq. \(^{[d]}\) cm\(^{-1}\) | H\(^{[e]}\) a.u. | G\(^{[f]}\) a.u. |
|-------------|---------|--------|-----------------|----------------|----------------|--------|--------|
| 1a–H\(^{+}\) | C75H58N4O4 | 0 | -3413.473263 | 1.138495 | 7.91 | -3412.264795 | -3412.454537 |
| 1b | C77H63N5O4 | 0 | -3547.468485 | 1.211591 | 6.70 | -3546.182335 | -3546.374143 |
| 1b–H\(^{+}\) | C77H64N5O4 | 1 | -3547.933362 | 1.226208 | 7.53 | -3546.632555 | -3546.823428 |
| 1b–H\(^{+}\) | C77H65N5O4 | 2 | -3548.348604 | 1.242211 | 5.61 | -3547.03235 | -3547.221115 |
| 1c | C83H67N5O4 | 0 | -3778.558138 | 1.292516 | 6.79 | -3777.18633 | -3777.389375 |
| 1c–H\(^{+}\) | C83H68N5O4 | 1 | -3779.017316 | 1.306244 | 4.20 | -3777.631429 | -3777.836698 |
| 1c–H\(^{+}\) | C83H69N5O4 | 2 | -3779.486484 | 1.322478 | 6.54 | -3778.047123 | -3778.24782 |
| 1d | C75H53F5N4O4 | 0 | -3909.592197 | 1.097446 | 7.60 | -3908.420007 | -3908.611356 |
| 1d–H\(^{+}\) | C75H54F5N4O4 | 1 | -3910.041588 | 1.110632 | 5.32 | -3909.855748 | -3909.050355 |
| 1e | C75H56N6O8 | 0 | -3822.474715 | 1.142817 | 7.13 | -3821.25651 | -3821.451047 |
| 1e–H | C75H57N6O8 | 1 | -3822.922289 | 1.156443 | 5.36 | -3821.69013 | -3821.886197 |
| 1f | C91H70N4O6 | 0 | -4180.964823 | 1.379421 | 5.32 | -4179.500144 | -4179.715359 |
| 1f–H\(^{+}\) | C91H71N4O6 | 1 | -4181.413750 | 1.392694 | 5.54 | -4179.935416 | -4180.151698 |
| 2a | C79H68N6O4 | 0 | -3681.463250 | 1.284142 | 5.08 | -3680.099924 | -3680.302986 |
| 2a–H\(^{+}\) | C79H69N6O4 | 1 | -3681.926203 | 1.298655 | 6.42 | -3680.548153 | -3680.750973 |
| 2a–H\(^{+}\) | C79H71N6O4 | 3 | -3682.770858 | 1.331048 | 7.01 | -3681.361623 | -3681.558868 |
| 2b | C81H73N7O4 | 0 | -3815.457047 | 1.357099 | 6.14 | -3814.016031 | -3814.21117 |
| 2b–H\(^{+}\) | C81H74N7O4 | 1 | -3815.927672 | 1.37175 | 5.22 | -3814.472033 | -3814.685424 |
| 2b–H\(^{+}\) | C81H77N7O4 | 4 | -3817.182534 | 1.422200 | 10.63 | -3815.79168 | -3815.877396 |
| 2c | C87H77N7O4 | 0 | -4046.547905 | 1.438233 | 6.74 | -4045.021262 | -4045.245386 |
| 2c–H\(^{+}\) | C87H78N7O4 | 1 | -4047.013336 | 1.452513 | 4.96 | -4045.472028 | -4045.698496 |
| 2c–H\(^{+}\) | C87H81N7O4 | 4 | -4048.285218 | 1.502439 | 5.12 | -4046.696404 | -4046.909179 |
| 2d | C79H63F5N6O4 | 0 | -4177.583583 | 1.243168 | 6.20 | -4176.256507 | -4176.469654 |
| 2d–H\(^{+}\) | C79H64F5N6O4 | 1 | -4178.043250 | 1.257258 | 5.56 | -4176.701264 | -4176.91405 |
| 2d–H\(^{+}\) | C79H66F5N6O4 | 3 | -4178.883414 | 1.291116 | 8.01 | -4177.51008 | -4177.729424 |
| 2e | C79H66N8O8 | 0 | -4090.465704 | 1.288466 | 5.38 | -4089.092588 | -4089.307889 |
| 2e–H\(^{+}\) | C79H67N8O8 | 1 | -4090.924162 | 1.303232 | 6.16 | -4089.536322 | -4089.750998 |
| 2e–H\(^{+}\) | C79H69N8O8 | 3 | -4091.764458 | 1.337289 | 9.75 | -4090.344439 | -4090.549931 |

\(^{[a]}\) Structure code (see the zip file for Cartesian coordinates). \(^{[b]}\) SCF electronic energy. \(^{[c]}\) Zero-point vibrational energy. \(^{[d]}\) Lowest vibrational frequency. \(^{[e]}\) Enthalpy. \(^{[f]}\) Gibbs free energy.
Table S12. Energy comparison of protonated dipyrrins.

| code     | SCF E[a]  | ZPV[b] | lowest freq. [c] | H[d]  | G[e]  | ΔSCFrel | kcal/mol |
|----------|-----------|--------|------------------|-------|-------|---------|----------|
| 1a–H⁺ (E-anti) | -3413.92816 | 1.152328 | 0.95             | -3412.70549 | -3412.88863 | 0.00     |
| 1a–H⁺ (Z-anti) | -3413.92772 | 1.152713 | 6.14             | -3412.70486 | -3412.88608 | 0.28     |
| 1a–H⁺ (Z-syn)  | -3413.92647 | 1.153524 | 8.81             | -3412.70286 | -3412.88449 | 1.06     |
| 2a–H⁺ (E-anti) | -3681.9262  | 1.298484 | 6.42             | -3680.54815 | -3680.75097 | 0.00     |
| 2a–H⁺ (E-anti) | -3681.92544 | 1.298653 | 7.86             | -3680.54756 | -3680.74938 | 0.28     |
| 2b–H⁺ (Z-anti) | -3547.93306 | 1.225909 | 8.74             | -3546.63248 | -3546.82327 | 0.19     |
| 2b–H⁺ (Z-syn)  | -3547.93336 | 1.226208 | 7.53             | -3546.63255 | -3546.82343 | 0.00     |

[a] SCF electronic energy. [b] Zero-point vibrational energy. [c] Lowest vibrational frequency. [d] Enthalpy. [e] Gibbs free energy.

Table S13. Computational details for the oxidation levels of 2a and 2d.

| Code  | Formula           | SCF E[a]  | ZPV[b] | lowest freq. [c] | H[d]  | G[e]  | ΔSCFrel | kcal/mol |
|-------|-------------------|-----------|--------|------------------|-------|-------|---------|----------|
| 2a**  | C79H68N6O4        | -3681.28846 | 1.25381 | 7.18             | -3679.924028 | -3680.12747 | 0.00     |
| 2a⁻   | C79H68N6O4        | -3681.08878 | 1.28760 | 8.59             | -3679.722405 | -3679.92221 | 0.19     |
| 2a⁻⁻  | C79H68N6O4        | -3680.85360 | 1.288692 | 9.69             | -3679.48699 | -3679.68307 | 0.28     |
| 2a⁻⁻⁻ | C79H69N6O4        | -3681.731113 | 1.299781 | 6.68             | -3680.352185 | -3680.5542  | 0.00     |
| 2d**  | C79H63F5N6O4      | -4177.40676 | 1.244716 | 7.85             | -4176.078504 | -4176.28926 | 0.00     |
| 2d⁻   | C79H63F5N6O4      | -4177.20467 | 1.246611 | 8.59             | -4175.874629 | -4176.08576 | 0.19     |
| 2d⁻⁻  | C79H63F5N6O4      | -4176.966229 | 1.248026 | 9.12             | -4175.635751 | -4175.84084 | 0.28     |
| 2d⁻⁻⁻ | C79H64F5N6O4      | -4177.846533 | 1.25897  | 8.56             | -4176.503957 | -4176.71381 | 0.00     |

[a] SCF electronic energy. [b] Zero-point vibrational energy. [c] Lowest vibrational frequency. [d] Enthalpy. [e] Gibbs free energy.
Table S14. MO composition analysis of the selected molecular orbitals of 1a–1e obtained at B3LYP-GD3BJ/6-31G(d,p)/PCM(dichloromethane) level of theory.

|   | 1a  | 1b  | 1c  | 1d  | 1e  |
|---|-----|-----|-----|-----|-----|
| MO | Energy | D | M | A | Energy | D | M | A | Energy | D | M | A | Energy | D | M | A | Energy | D | M | A |
| L+4 | -0.78 | 87 | 12 | 1 | -0.75 | 91 | 6 | 3 | -0.89 | 15 | 82 | 3 | -1.11 | 50 | 22 | 28 | -2.38 | 82 | 2 | 16 |
| L+3 | -1.04 | 63 | 2 | 35 | -1.01 | 65 | 2 | 33 | -1.03 | 61 | 6 | 33 | -1.18 | 20 | 73 | 7 | -2.85 | 92 | 5 | 3 |
| L+2 | -2.29 | 82 | 1 | 17 | -2.23 | 80 | 3 | 17 | -2.26 | 81 | 2 | 17 | -2.41 | 83 | 2 | 16 | -2.98 | 6 | 94 | 0 |
| L+1 | -2.77 | 96 | 0 | 4 | -2.73 | 96 | 0 | 4 | -2.75 | 96 | 0 | 4 | -2.85 | 96 | 0 | 3 | -3.27 | 2 | 97 | 0 |
| LUMO | -3.47 | 96 | 1 | 3 | -3.37 | 92 | 5 | 2 | -3.44 | 96 | 1 | 3 | -3.62 | 95 | 2 | 4 | -3.61 | 94 | 3 | 3 |
| HOMO | -5.49 | 82 | 0 | 18 | -5.4 | 59 | 29 | 12 | -5.12 | 1 | 99 | 0 | -5.58 | 81 | 0 | 19 | -5.59 | 81 | 0 | 19 |
| H-1 | -6.08 | 97 | 0 | 3 | -5.54 | 32 | 61 | 7 | -5.47 | 81 | 0 | 18 | -6.2 | 97 | 0 | 3 | -6.21 | 96 | 0 | 3 |
| H-2 | -6.41 | 96 | 0 | 4 | -5.98 | 97 | 0 | 2 | -6.05 | 97 | 0 | 3 | -6.47 | 100 | 0 | 0 | -6.47 | 100 | 0 | 0 |
| H-3 | -6.46 | 100 | 0 | 0 | -6.37 | 96 | 1 | 3 | -6.39 | 95 | 0 | 4 | -6.47 | 100 | 0 | 0 | -6.47 | 100 | 0 | 0 |
| H-4 | -6.46 | 100 | 0 | 0 | -6.45 | 100 | 0 | 0 | -6.45 | 100 | 0 | 0 | -6.5 | 97 | 0 | 3 | -6.51 | 96 | 0 | 4 |

In the table, D stands for NMI-dipyrrin, M stands for meso-aryl, A stands for alpha substituent and their composition values are given in percent.

Table S15. MO composition analysis of the selected molecular orbitals of 1a–1e–H⁺ obtained at B3LYP-GD3BJ/6-31G(d,p)/PCM(dichloromethane) level of theory.

|   | 1a–H⁺ | 1b–H⁺ | 1c–H⁺ | 1d–H⁺ | 1e–H⁺ |
|---|-------|-------|-------|-------|-------|
| MO | Energy | D | M | A | Energy | D | M | A | Energy | D | M | A | Energy | D | M | A |
| L+4 | -1.57 | 49 | 32 | 19 | -1.41 | 58 | 20 | 22 | -1.66 | 38 | 45 | 17 | -1.82 | 33 | 54 | 13 | -3.01 | 66 | 22 | 12 |
| L+3 | -1.86 | 69 | 1 | 30 | -1.73 | 71 | 1 | 28 | -1.77 | 66 | 7 | 27 | -1.92 | 69 | 1 | 30 | -3.24 | 12 | 87 | 1 |
| L+2 | -3.03 | 85 | 4 | 11 | -2.92 | 83 | 6 | 11 | -2.96 | 84 | 6 | 10 | -3.1 | 86 | 4 | 11 | -3.33 | 96 | 1 | 3 |
| L+1 | -3.25 | 97 | 0 | 3 | -3.15 | 97 | 0 | 3 | -3.17 | 96 | 0 | 3 | -3.31 | 97 | 0 | 3 | -3.51 | 25 | 75 | 0 |
| LUMO | -4.22 | 84 | 10 | 6 | -3.93 | 76 | 21 | 3 | -4.06 | 75 | 21 | 4 | -4.42 | 86 | 7 | 7 | -4.52 | 76 | 17 | 7 |
| HOMO | -6.28 | 76 | 1 | 23 | -6.11 | 31 | 62 | 8 | -5.54 | 10 | 88 | 2 | -6.32 | 75 | 1 | 23 | -6.36 | 76 | 1 | 23 |
| H-1 | -6.61 | 100 | 0 | 0 | -6.19 | 76 | 1 | 22 | -6.2 | 76 | 1 | 23 | -6.62 | 99 | 0 | 0 | -6.63 | 99 | 0 | 0 |
| H-2 | -6.64 | 100 | 0 | 0 | -6.6 | 99 | 0 | 0 | -6.59 | 100 | 0 | 0 | -6.65 | 99 | 0 | 0 | -6.64 | 99 | 0 | 0 |
| H-3 | -6.87 | 100 | 0 | 0 | -6.61 | 100 | 0 | 0 | -6.61 | 100 | 0 | 0 | -6.89 | 100 | 0 | 0 | -6.89 | 100 | 0 | 0 |
| H-4 | -6.89 | 98 | 1 | 1 | -6.84 | 100 | 0 | 0 | -6.79 | 65 | 22 | 13 | -6.91 | 100 | 0 | 0 | -6.91 | 100 | 0 | 0 |

In the table, D stands for NMI-dipyrrin, M stands for meso-aryl, A stands for alpha substituent and their composition values are given in percent.

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Table S16. MO composition analysis of the selected molecular orbitals of 2a–2e obtained at B3LYP-GD3BJ/6-31G(d,p)/PCM(dichloromethane) level of theory.

|     | 2a       | 2b       | 2c       | 2d       | 2e       |
|-----|----------|----------|----------|----------|----------|
|     | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    |
| L+4 | -0.69    | 85 14 1  | -0.65    | 97 2 1   | -0.78    | 41 50 9 | -0.89    | 73 9 18  | -2.16    | 81 2 17  |
| L+3 | -0.83    | 79 2 19  | -0.79    | 84 1 15  | -0.84    | 47 42 11| -1.06    | 7 92 1   | -2.73    | 94 2 4   |
| L+2 | -2.06    | 81 1 18  | -2.02    | 80 3 17  | -2.05    | 81 2 18 | -2.18    | 81 2 17  | -2.9     | 3 97 0   |
| L+1 | -2.65    | 95 0 4   | -2.62    | 95 0 4   | -2.64    | 95 0 4  | -2.72    | 95 0 4   | -3.19    | 1 98 0   |
| LUMO| -3.35    | 96 1 3   | -3.27    | 94 3 3   | -3.33    | 96 1 3  | -3.48    | 94 1 5   | -3.47    | 94 2 4   |
| HOMO| -4.87    | 46 0 54  | -4.84    | 45 1 54  | -4.85    | 46 0 54 | -4.92    | 45 0 55  | -4.94    | 44 0 56  |
| M   | -5.39    | 18 0 82  | -5.26    | 12 35 53 | -5.09    | 1 99 0  | -5.46    | 18 0 82  | -5.44    | 16 1 83  |
| H-2 | -5.89    | 84 0 16  | -5.5     | 13 56 31 | -5.37    | 18 1 82 | -5.98    | 82 0 19  | -5.98    | 80 0 20  |
| H-3 | -6.08    | 67 0 15  | -5.83    | 83 2 15  | -5.87    | 85 0 15 | -6.17    | 71 0 29  | -6.17    | 74 0 26  |
| H-4 | -6.27    | 98 0 2   | -6.01    | 64 0 34  | -6.07    | 65 0 35 | -6.35    | 99 0 1   | -6.36    | 99 0 1   |

In the table, D stands for NMI-dipyrin, M stands for meso-aryl, A stands for alpha substituent and their composition values are given in percent.

Table S17. MO composition analysis of the selected molecular orbitals of 2a–2e–H* obtained at B3LYP-GD3BJ/6-31G(d,p)/PCM(dichloromethane) level of theory.

|     | 2a–H*   | 2b–H*   | 2c–H*   | 2d–H*   | 2e–H*   |
|-----|----------|----------|----------|----------|----------|
|     | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    | Energy   | D M A    |
| L+4 | -1.34    | 59 31 10 | -1.21    | 71 18 11 | -1.44    | 45 43 12 | -1.59    | 37 53 10 | -2.78    | 70 15 15 |
| L+3 | -1.58    | 77 1 22  | -1.48    | 79 2 19  | -1.53    | 69 13 18 | -1.64    | 74 4 22  | -3.09    | 4 95 1   |
| L+2 | -2.78    | 82 5 14  | -2.7     | 80 6 14  | -2.74    | 81 7 13  | -2.86    | 82 5 13  | -3.18    | 95 1 4   |
| L+1 | -3.11    | 96 0 4   | -3.04    | 97 0 3   | -3.06    | 96 0 4   | -3.16    | 96 0 4   | -3.38    | 28 72 0  |
| LUMO| -3.98    | 84 7 9   | -3.79    | 80 15 5  | -3.89    | 81 12 7  | -4.13    | 84 5 12  | -4.25    | 70 17 13 |
| HOMO| -5.4     | 33 0 66  | -5.35    | 32 0 67  | -5.35    | 7 81 12  | -5.44    | 34 0 65  | -5.47    | 33 0 66  |
| M   | -5.88    | 17 4 79  | -5.59    | 14 28 58 | -5.36    | 31 5 64  | -5.99    | 18 3 79  | -6.02    | 18 3 79  |
| H-2 | -6.57    | 92 0 8   | -6.2     | 22 49 30 | -5.85    | 15 13 72 | -6.59    | 98 0 2   | -6.59    | 99 0 1   |
| H-3 | -6.61    | 85 0 14  | -6.52    | 72 0 28  | -6.54    | 76 0 24  | -6.63    | 97 0 3   | -6.63    | 98 0 2   |
| H-4 | -6.63    | 90 0 10  | -6.58    | 97 0 3   | -6.58    | 94 0 6   | -6.67    | 72 0 28  | -6.7     | 70 0 30  |

In the table, D stands for NMI-dipyrin, M stands for meso-aryl, A stands for alpha substituent and their composition values are given in percent.
Table S18. Electronic transitions calculated for 1a using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | $\lambda$ (nm) | $f$[a] | Major excitations[b] |
|-----|---------------------|----------------|--------|----------------------|
| 1   | 14168               | 705.8          | 1.221  | HOMO$\rightarrow$LUMO (98%) |
| 2   | 16311               | 613.1          | 0.099  | H$\rightarrow$1$LUMO$ (95%) |
| 3   | 18896               | 529.2          | 0.085  | H$\rightarrow$2$LUMO$ (41%) HOMO$\rightarrow$L+1 (50%) |
| 4   | 19780               | 505.6          | 0.256  | H$\rightarrow$2$LUMO$ (49%) HOMO$\rightarrow$L+1 (46%) |
| 5   | 21394               | 467.4          | 0.004  | H$\rightarrow$4$LUMO$ (43%) H$\rightarrow$3$LUMO$ (54%) |
| 6   | 21699               | 460.9          | 0.003  | H$\rightarrow$4$LUMO$ (54%) H$\rightarrow$3$LUMO$ (42%) |
| 7   | 22088               | 452.7          | 0.013  | H$\rightarrow$1$L+1$ (72%) H$\rightarrow$1$L+2$ (12%) |
| 8   | 22737               | 439.8          | 0.001  | H$\rightarrow$7$LUMO$ (91%) |
| 9   | 22810               | 438.4          | 0.046  | H$\rightarrow$8$LUMO$ (12%) H$\rightarrow$1$L+1$ (10%) HOMO$\rightarrow$L+2 (70%) |
| 10  | 23105               | 432.8          | 0.010  | H$\rightarrow$5$LUMO$ (81%) |
| 11  | 23113               | 432.7          | 0.003  | H$\rightarrow$6$LUMO$ (87%) |
| 12  | 24151               | 414.1          | 0.098  | H$\rightarrow$8$LUMO$ (83%) HOMO$\rightarrow$L+2 (11%) |
| 13  | 24180               | 413.6          | 0.042  | H$\rightarrow$2$L+1$ (77%) |
| 14  | 24998               | 400.0          | 0.109  | H$\rightarrow$11$LUMO$ (13%) H$\rightarrow$9$LUMO$ (80%) |
| 15  | 25546               | 391.5          | 0.011  | H$\rightarrow$10$LUMO$ (91%) |
| 16  | 25658               | 389.7          | 0.075  | H$\rightarrow$14$LUMO$ (26%) H$\rightarrow$11$LUMO$ (55%) |
| 17  | 26036               | 384.1          | 0.024  | H$\rightarrow$14$LUMO$ (60%) H$\rightarrow$11$LUMO$ (21%) |
| 18  | 26220               | 381.4          | 0.021  | H$\rightarrow$1$L+1$ (12%) H$\rightarrow$1$L+2$ (74%) |
| 19  | 26587               | 376.1          | 0.000  | H$\rightarrow$16$LUMO$ (80%) |
| 20  | 26749               | 373.9          | 0.051  | H$\rightarrow$12$LUMO$ (83%) |
| 21  | 26869               | 372.2          | 0.001  | H$\rightarrow$4$L+1$ (48%) H$\rightarrow$3$L+1$ (44%) |
| 22  | 26951               | 371.0          | 0.000  | H$\rightarrow$15$LUMO$ (63%) H$\rightarrow$15$L+1$ (14%) |
| 23  | 27158               | 368.2          | 0.002  | H$\rightarrow$13$LUMO$ (92%) |
| 24  | 27394               | 365.0          | 0.001  | H$\rightarrow$4$L+1$ (45%) H$\rightarrow$3$L+1$ (47%) |
| 25  | 27739               | 360.5          | 0.002  | H$\rightarrow$17$LUMO$ (82%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S19. Electronic transitions calculated for 1a–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a] | Major excitations[^b] |
|-----|---------------|--------|-------|-----------------------|
| 1   | 13960         | 716.3  | 0.685 | HOMO→LUMO (99%)       |
| 2   | 16964         | 589.5  | 0.001 | H→1=LUMO (99%)        |
| 3   | 17061         | 586.1  | 0.004 | H→2=LUMO (99%)        |
| 4   | 18175         | 550.2  | 0.084 | H→6=LUMO (31%)        |
|     |               |        |       | H→5=LUMO (50%)        |
| 5   | 18731         | 533.9  | 0.030 | H→7=LUMO (19%)        |
|     |               |        |       | H→6=LUMO (37%)        |
|     |               |        |       | H→4=LUMO (33%)        |
| 6   | 18782         | 532.4  | 0.002 | H→3=LUMO (89%)        |
| 7   | 18880         | 529.7  | 0.006 | H→7=LUMO (14%)        |
|     |               |        |       | H→6=LUMO (14%)        |
|     |               |        |       | H→5=LUMO (17%)        |
|     |               |        |       | H→4=LUMO (53%)        |
| 8   | 19652         | 508.9  | 0.133 | H→7=LUMO (49%)        |
|     |               |        |       | H→6=LUMO (10%)        |
|     |               |        |       | H→5=LUMO (27%)        |
|     |               |        |       | HOMO→L+1 (12%)        |
| 9   | 21463         | 465.9  | 0.357 | HOMO→L+1 (81%)        |
| 10  | 21952         | 455.5  | 0.050 | H→8=LUMO (78%)        |
|     |               |        |       | HOMO→L+2 (16%)        |
| 11  | 23088         | 433.1  | 0.041 | H→9=LUMO (88%)        |
| 12  | 23142         | 432.1  | 0.103 | H→10=LUMO (82%)       |
| 13  | 23592         | 423.9  | 0.172 | H→11=LUMO (43%)       |
|     |               |        |       | HOMO→L+2 (36%)        |
| 14  | 23664         | 422.6  | 0.265 | H→11=LUMO (41%)       |
|     |               |        |       | HOMO→L+2 (35%)        |
| 15  | 23969         | 417.2  | 0.003 | H→12=LUMO (81%)       |
| 16  | 24000         | 416.7  | 0.000 | H→13=LUMO (87%)       |
| 17  | 24070         | 415.5  | 0.001 | H→14=LUMO (21%)       |
|     |               |        |       | H→2=L+1 (60%)         |
| 18  | 24131         | 414.4  | 0.002 | H→14=LUMO (53%)       |
|     |               |        |       | H→2=L+1 (29%)         |
| 19  | 24178         | 413.6  | 0.000 | H→1=L+1 (79%)         |
|     |               |        |       | H→1=L+2 (17%)         |
| 20  | 24504         | 408.1  | 0.014 | H→16=LUMO (10%)       |
|     |               |        |       | H→15=LUMO (78%)       |
| 21  | 24810         | 403.1  | 0.022 | H→16=LUMO (69%)       |
|     |               |        |       | H→15=LUMO (10%)       |
| 22  | 25169         | 397.3  | 0.049 | H→7=L+1 (10%)         |
|     |               |        |       | H→6=L+2 (10%)         |
|     |               |        |       | H→5=L+1 (51%)         |
| 23  | 25582         | 390.9  | 0.005 | H→7=L+1 (15%)         |
|     |               |        |       | H→6=L+1 (29%)         |
|     |               |        |       | H→4=L+1 (26%)         |
| 24  | 25726         | 388.7  | 0.002 | H→7=L+1 (11%)         |
|     |               |        |       | H→5=L+1 (10%)         |
|     |               |        |       | H→4=L+1 (48%)         |
| 25  | 25774         | 388.0  | 0.000 | H→3=L+1 (70%)         |
|     |               |        |       | H→3=L+2 (21%)         |

[^a]: Oscillator strength. [^b]: Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S20. Electronic transitions calculated for 1a–H⁺ (Z-anti) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|----------------------|
| 1   | 13460         | 743.0  | 0.492| HOMO–LUMO (100%)     |
| 2   | 16707         | 598.6  | 0.002| H–1→LUMO (99%)       |
| 3   | 16785         | 595.8  | 0.008| H–2→LUMO (99%)       |
| 4   | 17777         | 562.5  | 0.018| H–7→LUMO (32%)       |
| 5   | 18210         | 549.1  | 0.015| H–6→LUMO (98%)       |
| 6   | 18535         | 539.5  | 0.000| H–3→LUMO (98%)       |
| 7   | 18547         | 539.2  | 0.003| H–4→LUMO (95%)       |
| 8   | 19047         | 525.0  | 0.172| H–7→LUMO (57%)       |
| 9   | 21457         | 466.1  | 0.647| H–7→LUMO (10%)       |
| 10  | 22163         | 451.2  | 0.017| H–8→LUMO (92%)       |
| 11  | 22358         | 447.3  | 0.010| H–9→LUMO (86%)       |
| 12  | 23310         | 429.0  | 0.059| H–12→LUMO (51%)      |
|     |               |        |      | HOMO→L+2 (37%)       |
| 13  | 23638         | 423.0  | 0.009| H–10→LUMO (77%)      |
| 14  | 23640         | 423.0  | 0.006| H–11→LUMO (81%)      |
| 15  | 23779         | 420.5  | 0.000| H–15→LUMO (45%)      |
| 16  | 23793         | 420.3  | 0.020| H–14→LUMO (74%)      |
| 17  | 23846         | 419.4  | 0.469| H–12→LUMO (41%)      |
| 18  | 23850         | 419.3  | 0.009| H–15→LUMO (31%)      |
| 19  | 24055         | 415.7  | 0.000| H–1→L+1 (94%)        |
| 20  | 24126         | 414.5  | 0.011| H–2→L+1 (92%)        |
| 21  | 24412         | 409.6  | 0.011| H–16→LUMO (96%)      |
| 22  | 25038         | 399.4  | 0.082| H–7→L+1 (26%)        |
| 23  | 25566         | 391.1  | 0.003| H–6→L+1 (75%)        |
| 24  | 25670         | 389.6  | 0.000| H–3→L+1 (85%)        |
| 25  | 25682         | 389.4  | 0.001| H–4→L+1 (85%)        |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S21. Electronic transitions calculated for 1a–H⁺ (Z-syn) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b]          |
|-----|---------------|--------|------|------------------------------|
| 1   | 14278         | 700.4  | 1.181| HOMO→LUMO (100%)             |
| 2   | 17182         | 582.0  | 0.000| H–1→LUMO (99%)               |
| 3   | 17202         | 581.3  | 0.001| H–2→LUMO (99%)               |
| 4   | 18456         | 541.8  | 0.040| H–7→LUMO (15%)               |
| 5   | 18992         | 526.5  | 0.002| H–4→LUMO (97%)               |
| 6   | 18996         | 526.4  | 0.000| H–3→LUMO (97%)               |
| 7   | 19344         | 517.0  | 0.165| H–6→LUMO (95%)               |
| 8   | 20307         | 492.4  | 0.015| H–7→LUMO (67%)               |
| 9   | 21726         | 460.3  | 0.134| H–5→LUMO (17%)               |
| 10  | 22028         | 454.0  | 0.027| H–8→LUMO (86%)               |
| 11  | 23324         | 428.7  | 0.054| H–10→LUMO (35%)              |
| 12  | 23432         | 426.8  | 0.354| H–9→LUMO (90%)               |
| 13  | 23806         | 420.1  | 0.104| H–10→LUMO (36%)              |
| 14  | 24150         | 414.1  | 0.001| H–14→LUMO (54%)              |
| 15  | 24151         | 414.1  | 0.000| H–15→LUMO (52%)              |
| 16  | 24221         | 412.9  | 0.044| H–11→LUMO (82%)              |
| 17  | 24299         | 411.5  | 0.003| H–14→LUMO (33%)              |
| 18  | 24331         | 411.0  | 0.004| H–15→LUMO (28%)              |
| 19  | 24359         | 410.5  | 0.001| H–2→L+1 (13%)                |
| 20  | 24372         | 410.3  | 0.000| H–2→L+1 (85%)                |
| 21  | 25202         | 396.8  | 0.007| H–1→L+1 (13%)                |
| 22  | 25536         | 391.6  | 0.023| H–7→LUMO (17%)               |
| 23  | 25961         | 385.2  | 0.001| H–4→L+1 (76%)                |
| 24  | 25966         | 385.1  | 0.000| H–4→L+2 (16%)                |
| 25  | 26153         | 382.4  | 0.057| H–6→L+1 (57%)                |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S22. Electronic transitions calculated for 1b using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f^{\text{[a]}}\) | Major excitations\(^{[b]}\) |
|-----|-----------------------|-------------------|-----------------|-----------------------------|
| 1   | 13583                 | 736.2             | 0.299           | H–1\text{=}LUMO (27%) H\text{=}O\text{=}LUMO (73%) |
| 2   | 14570                 | 686.3             | 0.940           | H–1\text{=}LUMO (72%) H\text{=}O\text{=}LUMO (26%) |
| 3   | 16288                 | 614.0             | 0.077           | H–2\text{=}LUMO (94%)      |
| 4   | 18370                 | 544.4             | 0.060           | H–1\text{=}L\text{=}1 (14%) H\text{=}O\text{=}L\text{=}1 (83%) |
| 5   | 19290                 | 518.4             | 0.055           | H–3\text{=}LUMO (33%) H–1\text{=}L\text{=}1 (55%) |
| 6   | 20040                 | 499.0             | 0.193           | H–3\text{=}LUMO (55%) H–1\text{=}L\text{=}1 (29%) |
| 7   | 21628                 | 462.4             | 0.008           | H–2\text{=}L\text{=}1 (75%) H–2\text{=}L\text{=}2 (13%) |
| 8   | 22127                 | 451.9             | 0.004           | H–4\text{=}LUMO (85%)      |
| 9   | 22345                 | 447.5             | 0.086           | H\text{=}O\text{=}L\text{=}2 (69%) |
| 10  | 22442                 | 445.6             | 0.011           | H–5\text{=}LUMO (88%)      |
| 11  | 23110                 | 432.7             | 0.041           | H–6\text{=}LUMO (26%) H–1\text{=}L\text{=}2 (55%) |
| 12  | 23404                 | 427.3             | 0.000           | H–7\text{=}LUMO (91%)      |
| 13  | 23640                 | 423.0             | 0.128           | H–6\text{=}LUMO (58%) H–1\text{=}L\text{=}2 (32%) |
| 14  | 23774                 | 420.6             | 0.000           | H–8\text{=}LUMO (90%)      |
| 15  | 24212                 | 413.0             | 0.044           | H–3\text{=}L\text{=}1 (67%) |
| 16  | 24277                 | 411.9             | 0.069           | H–9\text{=}LUMO (75%)      |
| 17  | 25258                 | 395.9             | 0.128           | H–12\text{=}LUMO (15%) H–10\text{=}LUMO (75%) |
| 18  | 25638                 | 390.0             | 0.017           | H–2\text{=}L\text{=}1 (13%) H–2\text{=}L\text{=}2 (76%) |
| 19  | 26023                 | 384.3             | 0.022           | H–11\text{=}LUMO (85%)     |
| 20  | 26298                 | 380.3             | 0.061           | H–12\text{=}LUMO (70%) H–10\text{=}LUMO (15%) |
| 21  | 27059                 | 369.6             | 0.004           | H–15\text{=}LUMO (73%) H–15\text{=}L\text{=}1 (10%) |
| 22  | 27120                 | 368.7             | 0.044           | H–13\text{=}LUMO (80%)     |
| 23  | 27193                 | 367.7             | 0.002           | H–5\text{=}L\text{=}1 (85%) |
| 24  | 27425                 | 364.6             | 0.000           | H–16\text{=}LUMO (57%) H–16\text{=}L\text{=}1 (16%) |
| 25  | 27649                 | 361.7             | 0.002           | H–4\text{=}L\text{=}1 (86%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S23. Electronic transitions calculated for 1b•+ using the TD/PCM(dichloromethane)GD3BJ/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f^{[a]}\) | Major excitations\(^{[b]}\) |
|-----|----------------------|----------------|------------|--------------------------|
| 1   | 14977                | 667.7          | 0.503      | H→1\(\rightarrow\)LUMO (99%) |
| 2   | 15899                | 629.0          | 0.681      | HOMO→LUMO (99%)          |
| 3   | 19088                | 523.9          | 0.003      | H→2\(\rightarrow\)LUMO (92%) |
| 4   | 19128                | 522.8          | 0.002      | H→3\(\rightarrow\)LUMO (94%) |
| 5   | 19344                | 517.0          | 0.026      | H→6\(\rightarrow\)LUMO (87%) |
| 6   | 19949                | 501.3          | 0.020      | H→7\(\rightarrow\)LUMO (75%) |
| 7   | 20683                | 483.5          | 0.083      | H→1\(\rightarrow\)L+1 (11%)  |
|     |                      |                |            | HOMO→L+1 (82%)          |
| 8   | 20796                | 480.9          | 0.000      | H→4\(\rightarrow\)LUMO (93%) |
| 9   | 20802                | 480.7          | 0.002      | H→5\(\rightarrow\)LUMO (87%) |
| 10  | 21315                | 469.2          | 0.257      | H→1\(\rightarrow\)L+1 (72%)  |
|     |                      |                |            | HOMO→L+1 (10%)          |
| 11  | 22372                | 447.0          | 0.088      | H→8\(\rightarrow\)LUMO (28%) |
|     |                      |                |            | HOMO→L+2 (64%)          |
| 12  | 23026                | 434.3          | 0.038      | H→9\(\rightarrow\)LUMO (36%) |
|     |                      |                |            | H→1\(\rightarrow\)L+2 (60%) |
| 13  | 23613                | 423.5          | 0.409      | H→8\(\rightarrow\)LUMO (51%) |
|     |                      |                |            | HOMO→L+2 (31%)          |
| 14  | 24047                | 415.9          | 0.306      | H→9\(\rightarrow\)LUMO (60%) |
|     |                      |                |            | H→1\(\rightarrow\)L+2 (33%) |
| 15  | 24699                | 404.9          | 0.000      | H→3\(\rightarrow\)L+1 (89%)  |
| 16  | 24790                | 403.4          | 0.023      | H→10\(\rightarrow\)LUMO (95%) |
| 17  | 24935                | 401.0          | 0.001      | H→2\(\rightarrow\)L+1 (80%) |
|     |                      |                |            | H→2\(\rightarrow\)L+2 (16%) |
| 18  | 25109                | 398.3          | 0.016      | H→6\(\rightarrow\)L+1 (68%) |
| 19  | 25306                | 395.2          | 0.032      | H→13\(\rightarrow\)LUMO (28%) |
|     |                      |                |            | H→12\(\rightarrow\)LUMO (39%) |
|     |                      |                |            | H→7\(\rightarrow\)L+1 (20%)  |
| 20  | 25383                | 394.0          | 0.010      | H→13\(\rightarrow\)LUMO (23%) |
|     |                      |                |            | H→7\(\rightarrow\)L+1 (46%)  |
| 21  | 25489                | 392.3          | 0.001      | H→16\(\rightarrow\)LUMO (13%) |
|     |                      |                |            | H→14\(\rightarrow\)LUMO (45%) |
| 22  | 25498                | 392.2          | 0.000      | H→16\(\rightarrow\)LUMO (12%) |
|     |                      |                |            | H→15\(\rightarrow\)LUMO (26%) |
|     |                      |                |            | H→14\(\rightarrow\)LUMO (26%) |
| 23  | 25672                | 389.5          | 0.000      | H→11\(\rightarrow\)LUMO (90%) |
| 24  | 25768                | 388.1          | 0.035      | H→13\(\rightarrow\)LUMO (43%) |
|     |                      |                |            | H→12\(\rightarrow\)LUMO (44%) |
| 25  | 26111                | 383.0          | 0.009      | H→16\(\rightarrow\)LUMO (44%) |
|     |                      |                |            | H→15\(\rightarrow\)LUMO (47%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S24. Electronic transitions calculated for 1b–H\(^+\) (Z-anti) using the TD/PCM(dichloromethane) GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f^{[a]}\) | Major excitations\(^{[b]}\) |
|-----|-----------------|-----------------|-----------|------------------------|
| 1   | 14388           | 695.0           | 0.337     | H–1\(\rightarrow\)LUMO (99%) |
| 2   | 15859           | 630.5           | 0.880     | HOMO\(\rightarrow\)LUMO (99%) |
| 3   | 18898           | 529.1           | 0.002     | H–2\(\rightarrow\)LUMO (96%) |
| 4   | 18978           | 526.9           | 0.000     | H–3\(\rightarrow\)LUMO (98%) |
| 5   | 19193           | 521.0           | 0.005     | H–7\(\rightarrow\)LUMO (92%) |
| 6   | 19218           | 520.4           | 0.041     | H–6\(\rightarrow\)LUMO (81%) |
| 7   | 20633           | 484.7           | 0.000     | H–4\(\rightarrow\)LUMO (97%) |
| 8   | 20640           | 484.5           | 0.030     | H–5\(\rightarrow\)LUMO (84%) |
| 9   | 20682           | 483.5           | 0.298     | H–8\(\rightarrow\)LUMO (12%) |
|     |                 |                 |           | H–5\(\rightarrow\)LUMO (11%) |
|     |                 |                 |           | H–4\(\rightarrow\)LUMO (70%) |
| 10  | 20702           | 483.0           | 0.057     | HOMO\(\rightarrow\)L+1 (96%) |
| 11  | 22274           | 449.0           | 0.154     | H–8\(\rightarrow\)LUMO (65%) |
|     |                 |                 |           | H–5\(\rightarrow\)LUMO (11%) |
|     |                 |                 |           | H–4\(\rightarrow\)L+1 (70%) |
| 12  | 23439           | 426.6           | 0.179     | H–9\(\rightarrow\)LUMO (17%) |
|     |                 |                 |           | H–1\(\rightarrow\)L+1 (81%) |
| 13  | 23529           | 425.0           | 0.004     | HOMO\(\rightarrow\)L+2 (84%) |
| 14  | 24358           | 410.5           | 0.206     | H–11\(\rightarrow\)LUMO (10%) |
|     |                 |                 |           | H–9\(\rightarrow\)LUMO (71%) |
|     |                 |                 |           | H–1\(\rightarrow\)L+2 (13%) |
| 15  | 24460           | 408.8           | 0.000     | H–2\(\rightarrow\)L+1 (94%) |
| 16  | 24534           | 407.6           | 0.006     | H–3\(\rightarrow\)L+1 (92%) |
| 17  | 24690           | 405.0           | 0.077     | H–6\(\rightarrow\)L+1 (77%) |
| 18  | 24867           | 402.1           | 0.004     | H–7\(\rightarrow\)L+1 (78%) |
| 19  | 24931           | 401.1           | 0.149     | H–11\(\rightarrow\)LUMO (84%) |
| 20  | 25298           | 395.3           | 0.000     | H–16\(\rightarrow\)LUMO (22%) |
|     |                 |                 |           | H–12\(\rightarrow\)LUMO (56%) |
| 21  | 25298           | 395.3           | 0.001     | H–15\(\rightarrow\)LUMO (26%) |
|     |                 |                 |           | H–13\(\rightarrow\)LUMO (58%) |
| 22  | 25319           | 395.0           | 0.029     | H–14\(\rightarrow\)LUMO (17%) |
|     |                 |                 |           | H–10\(\rightarrow\)LUMO (69%) |
| 23  | 25387           | 393.9           | 0.003     | H–16\(\rightarrow\)LUMO (35%) |
|     |                 |                 |           | H–12\(\rightarrow\)LUMO (42%) |
|     |                 |                 |           | H–4\(\rightarrow\)L+1 (10%) |
| 24  | 25393           | 393.8           | 0.000     | H–15\(\rightarrow\)LUMO (39%) |
|     |                 |                 |           | H–13\(\rightarrow\)LUMO (41%) |
|     |                 |                 |           | H–5\(\rightarrow\)L+1 (11%) |
| 25  | 25573           | 391.0           | 0.000     | H–14\(\rightarrow\)LUMO (72%) |
|     |                 |                 |           | H–10\(\rightarrow\)LUMO (10%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S25. Electronic transitions calculated for 1b–H⁺ (Z-syn) using the TD/PCM(dichloromethane) GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f(0) | Major excitations ²(b) |
|-----|---------------|-------|------|-------------------------|
| 1   | 14945         | 669.1 | 0.993 | H–1→LUMO (100%)         |
| 2   | 15396         | 649.5 | 0.289 | HOMO→HOMO (100%)        |
| 3   | 19097         | 523.6 | 0.002 | H–2→LUMO (97%)          |
| 4   | 19106         | 523.4 | 0.001 | H–3→LUMO (97%)          |
| 5   | 19411         | 515.2 | 0.002 | H–6→LUMO (86%)          |
| 6   | 20084         | 497.9 | 0.002 | H–7→LUMO (58%)          |
|     |               |       |      | HOMO→L+1 (38%)          |
| 7   | 20624         | 484.9 | 0.260 | H–7→LUMO (35%)          |
|     |               |       |      | HOMO→L+1 (60%)          |
| 8   | 20799         | 480.8 | 0.003 | H–4→LUMO (92%)          |
| 9   | 20808         | 480.6 | 0.001 | H–5→LUMO (93%)          |
| 10  | 21250         | 470.6 | 0.095 | H–8→LUMO (10%)          |
|     |               |       |      | H–1→L+1 (82%)           |
| 11  | 22271         | 449.0 | 0.009 | H–8→LUMO (33%)          |
|     |               |       |      | HOMO→L+2 (57%)          |
| 12  | 23106         | 432.8 | 0.062 | H–9→LUMO (27%)          |
|     |               |       |      | H–1→L+2 (71%)           |
| 13  | 23675         | 422.4 | 0.683 | H–8→LUMO (47%)          |
|     |               |       |      | HOMO→L+2 (41%)          |
| 14  | 23992         | 416.8 | 0.131 | H–9→LUMO (67%)          |
|     |               |       |      | H–1→L+2 (25%)           |

15 24959 400.7 0.000 H–3→L+2 (11%) H–2→L+1 (82%)
16 24969 400.5 0.000 H–3→L+1 (83%) H–2→L+2 (11%)
17 25106 398.3 0.038 H–11→LUMO (76%) H–6→L+1 (12%)
18 25259 395.9 0.002 H–14→LUMO (13%) H–10→LUMO (78%)
19 25261 395.9 0.001 H–11→LUMO (13%) H–7→L+2 (11%) H–6→L+1 (65%)
20 25491 392.3 0.000 H–15→LUMO (63%)
21 25497 392.2 0.000 H–16→LUMO (62%)
22 25717 388.8 0.006 H–14→LUMO (50%) H–7→L+1 (26%) H–6→L+2 (15%)
23 25755 388.3 0.003 H–12→LUMO (91%)
24 25770 388.0 0.000 H–13→LUMO (90%)
25 25902 386.1 0.024 H–14→LUMO (32%) H–7→L+1 (35%) H–6→L+2 (16%)

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S26. Electronic transitions calculated for 1b–2H²⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f⁰ | Major excitations¹ [b] |
|-----|---------------|--------|----|------------------------|
| 1   | 13343         | 749.5  | 0.729 | HOMO→LUMO (99%)         |
| 2   | 15275         | 654.7  | 0.005 | H-1→LUMO (99%)          |
| 3   | 15520         | 644.3  | 0.001 | H-2→LUMO (99%)          |
| 4   | 17142         | 583.4  | 0.000 | H-3→LUMO (98%)          |
| 5   | 17436         | 573.5  | 0.001 | H-4→LUMO (98%)          |
| 6   | 17681         | 565.6  | 0.062 | H-7→LUMO (13%)          |
|     |               |        |      | H-5→LUMO (74%)          |
| 7   | 18189         | 549.8  | 0.076 | H-7→LUMO (13%)          |
|     |               |        |      | H-6→LUMO (82%)          |
| 8   | 19616         | 509.8  | 0.091 | H-7→LUMO (61%)          |
|     |               |        |      | H-5→LUMO (19%)          |
|     |               |        |      | HOMO→L+1 (12%)          |
| 9   | 21167         | 472.4  | 0.036 | H-8→LUMO (88%)          |
|     |               |        |      | HOMO→L+2 (10%)          |
| 10  | 21556         | 463.9  | 0.369 | H-7→LUMO (10%)          |
|     |               |        |      | HOMO→L+1 (84%)          |
| 11  | 22050         | 453.5  | 0.012 | H-9→LUMO (98%)          |
| 12  | 22833         | 438.0  | 0.058 | H-12→LUMO (31%)         |
|     |               |        |      | H-11→LUMO (11%)         |
|     |               |        |      | H-10→LUMO (52%)         |
| 13  | 22846         | 437.7  | 0.039 | H-12→LUMO (28%)         |
|     |               |        |      | H-11→LUMO (19%)         |
|     |               |        |      | H-10→LUMO (39%)         |
| 14  | 22984         | 435.1  | 0.000 | H-12→LUMO (26%)         |
|     |               |        |      | H-11→LUMO (69%)         |
| 15  | 23117         | 432.6  | 0.038 | H-14→LUMO (81%)         |
| 16  | 23137         | 432.2  | 0.032 | H-13→LUMO (69%)         |
|     |               |        |      | HOMO→L+2 (17%)          |
| 17  | 23166         | 431.7  | 0.227 | H-15→LUMO (29%)         |
|     |               |        |      | H-13→LUMO (14%)         |
|     |               |        |      | HOMO→L+2 (30%)          |
| 18  | 23234         | 430.4  | 0.008 | H-1→L+1 (80%)           |
|     |               |        |      | H-1→L+2 (12%)           |
| 19  | 23427         | 426.9  | 0.073 | H-15→LUMO (31%)         |
|     |               |        |      | H-2→L+1 (43%)           |
|     |               |        |      | HOMO→L+2 (11%)          |
| 20  | 23467         | 426.1  | 0.103 | H-15→LUMO (27%)         |
|     |               |        |      | H-2→L+1 (39%)           |
|     |               |        |      | HOMO→L+2 (19%)          |
| 21  | 24851         | 402.4  | 0.000 | H-3→L+1 (79%)           |
|     |               |        |      | H-3→L+2 (16%)           |
| 22  | 25097         | 398.5  | 0.000 | H-4→L+1 (75%)           |
|     |               |        |      | H-4→L+2 (20%)           |
| 23  | 25328         | 394.8  | 0.037 | H-17→LUMO (19%)         |
|     |               |        |      | H-6→L+2 (12%)           |
|     |               |        |      | H-5→L+1 (54%)           |
| 24  | 25481         | 392.4  | 0.021 | H-16→LUMO (68%)         |
|     |               |        |      | H-6→L+1 (14%)           |
| 25  | 25691         | 389.2  | 0.000 | H-1→L+1 (13%)           |
|     |               |        |      | H-1→L+2 (85%)           |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
**Table S27.** Electronic transitions calculated for 1c using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f^{[a]}\) | Major excitations\(^{[b]}\) |
|-----|------------------------|-------------------|-------------|--------------------------|
| 1   | 10726                  | 932.4             | 0.022       | HOMO\(\rightarrow\)LUMO (100%) |
| 2   | 14211                  | 703.7             | 1.200       | H\(-1\)\(\rightarrow\)LUMO (98%) |
| 3   | 16317                  | 612.9             | 0.082       | H\(-2\)\(\rightarrow\)LUMO (89%) |
| 4   | 16438                  | 608.4             | 0.014       | HOMO\(\rightarrow\)L+1 (94%)    |
| 5   | 18929                  | 528.3             | 0.066       | H\(-3\)\(\rightarrow\)LUMO (37%) |
|     |                        |                   |            | H\(-1\)\(\rightarrow\)L+1 (55%) |
| 6   | 19805                  | 504.9             | 0.231       | H\(-3\)\(\rightarrow\)LUMO (53%) |
|     |                        |                   |            | H\(-1\)\(\rightarrow\)L+1 (41%) |
| 7   | 20472                  | 488.5             | 0.039       | HOMO\(\rightarrow\)L+2 (98%)    |
| 8   | 21566                  | 463.7             | 0.004       | H\(-5\)\(\rightarrow\)LUMO (12%) |
|     |                        |                   |            | H\(-4\)\(\rightarrow\)LUMO (85%) |
| 9   | 21879                  | 457.1             | 0.003       | H\(-5\)\(\rightarrow\)LUMO (82%) |
|     |                        |                   |            | H\(-4\)\(\rightarrow\)LUMO (11%) |
| 10  | 22046                  | 453.6             | 0.012       | H\(-2\)\(\rightarrow\)L+1 (71%)  |
|     |                        |                   |            | H\(-2\)\(\rightarrow\)L+2 (12%)  |
| 11  | 22775                  | 439.1             | 0.041       | H\(-9\)\(\rightarrow\)LUMO (10%) |
|     |                        |                   |            | H\(-8\)\(\rightarrow\)LUMO (19%) |
|     |                        |                   |            | H\(-1\)\(\rightarrow\)L+2 (55%)  |
| 12  | 22885                  | 437.0             | 0.000       | H\(-7\)\(\rightarrow\)LUMO (90%) |
| 13  | 22955                  | 435.6             | 0.010       | H\(-6\)\(\rightarrow\)LUMO (64%) |
|     |                        |                   |            | H\(-1\)\(\rightarrow\)L+2 (24%)  |
| 14  | 23271                  | 429.7             | 0.000       | H\(-8\)\(\rightarrow\)LUMO (90%) |
| 15  | 24128                  | 414.5             | 0.061       | H\(-9\)\(\rightarrow\)LUMO (77%) |
|     |                        |                   |            | H\(-1\)\(\rightarrow\)L+2 (11%)  |
| 16  | 24190                  | 413.4             | 0.038       | H\(-3\)\(\rightarrow\)L+1 (77%)  |
| 17  | 24594                  | 406.6             | 0.048       | H\(-12\)\(\rightarrow\)LUMO (12%) |
|     |                        |                   |            | H\(-11\)\(\rightarrow\)LUMO (44%) |
|     |                        |                   |            | H\(-10\)\(\rightarrow\)LUMO (36%) |
| 18  | 24644                  | 405.8             | 0.009       | H\(-12\)\(\rightarrow\)LUMO (15%) |
|     |                        |                   |            | H\(-11\)\(\rightarrow\)LUMO (20%) |
|     |                        |                   |            | H\(-10\)\(\rightarrow\)LUMO (58%) |
| 19  | 25012                  | 399.8             | 0.095       | H\(-14\)\(\rightarrow\)LUMO (14%) |
|     |                        |                   |            | H\(-12\)\(\rightarrow\)LUMO (58%) |
|     |                        |                   |            | H\(-11\)\(\rightarrow\)LUMO (19%) |
| 20  | 25686                  | 389.3             | 0.002       | H\(-13\)\(\rightarrow\)LUMO (95%) |
| 21  | 25898                  | 386.1             | 0.095       | H\(-14\)\(\rightarrow\)LUMO (74%) |
| 22  | 26146                  | 382.5             | 0.019       | H\(-2\)\(\rightarrow\)L+1 (12%)  |
|     |                        |                   |            | H\(-2\)\(\rightarrow\)L+2 (73%)  |
| 23  | 26670                  | 375.0             | 0.000       | H\(-18\)\(\rightarrow\)LUMO (81%) |
| 24  | 26786                  | 373.3             | 0.069       | H\(-15\)\(\rightarrow\)LUMO (89%) |
| 25  | 26980                  | 370.6             | 0.002       | H\(-5\)\(\rightarrow\)L+1 (77%)  |
|     |                        |                   |            | H\(-4\)\(\rightarrow\)L+1 (14%)  |

\(^{[a]}\) Oscillator strength. \(^{[b]}\) Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S28. Electronic transitions calculated for 1c–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a] | Major excitations[^b]                      |
|-----|---------------|--------|-------|------------------------------------------|
| 1   | 10856         | 921.1  | 0.824 | HOMO–LUMO (101%)                         |
| 2   | 14324         | 698.1  | 0.568 | H–1→LUMO (99%)                           |
| 3   | 16759         | 596.7  | 0.038 | HOMO+1→LUMO (98%)                        |
| 4   | 18062         | 553.6  | 0.005 | H–2→LUMO (95%)                           |
| 5   | 18177         | 550.1  | 0.011 | H–3→LUMO (95%)                           |
| 6   | 18357         | 544.7  | 0.194 | HOMO→LUMO+2 (82%)                        |
| 7   | 18543         | 539.3  | 0.039 | H–7→LUMO (49%) H–4→LUMO (42%)           |
| 8   | 19208         | 520.6  | 0.054 | H–8→LUMO (41%) H–7→LUMO (35%)           |
|     |               |        |       | H–4→LUMO (16%)                           |
| 9   | 19827         | 504.4  | 0.000 | H–5→LUMO (97%)                           |
| 10  | 19916         | 502.1  | 0.000 | H–6→LUMO (95%)                           |
| 11  | 19980         | 500.5  | 0.017 | H–8→LUMO (40%) H–4→LUMO (26%)           |
|     |               |        |       | H–1→LUMO (18%)                           |
| 12  | 21516         | 464.8  | 0.367 | H–8→LUMO (10%) H–1→LUMO (77%)           |
| 13  | 22424         | 446.0  | 0.001 | H–9→LUMO (66%) H–1→LUMO (32%)           |
| 14  | 23224         | 430.6  | 0.013 | H–10→LUMO (93%)                          |

[^a]: Oscillator strength.[^b]: Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S29. Electronic transitions calculated for 1c–2H$^{2+}$ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | λ (nm) | $f$ | Major excitations$^{[a]}$, $^{[b]}$ |
|-----|-------------------|--------|-----|-----------------------------------|
| 1   | 13709             | 729.4  | 0.687 | HOMO$\rightarrow$LUMO (99%) |
| 2   | 16346             | 611.8  | 0.005 | H-1$\rightarrow$LUMO (99%) |
| 3   | 16595             | 602.6  | 0.001 | H-2$\rightarrow$LUMO (99%) |
| 4   | 17860             | 559.9  | 0.157 | H-5$\rightarrow$LUMO (62%) |
| 5   | 18183             | 550.0  | 0.009 | H-3$\rightarrow$LUMO (88%) |
| 6   | 18435             | 542.4  | 0.003 | H-4$\rightarrow$LUMO (93%) |
| 7   | 18505             | 540.4  | 0.055 | H-7$\rightarrow$LUMO (19%), H-6$\rightarrow$LUMO (62%), H-5$\rightarrow$LUMO (11%) |
| 8   | 19033             | 525.4  | 0.275 | H-7$\rightarrow$LUMO (68%), H-5$\rightarrow$LUMO (17%) |
| 9   | 21204             | 471.6  | 0.270 | H-9$\rightarrow$LUMO (13%), HOMO$\rightarrow$L+1 (81%) |
| 10  | 21656             | 461.8  | 0.039 | H-8$\rightarrow$LUMO (84%), HOMO$\rightarrow$L+2 (14%) |
| 11  | 22450             | 445.4  | 0.202 | H-9$\rightarrow$LUMO (83%), HOMO$\rightarrow$L+1 (10%) |
| 12  | 22726             | 440.0  | 0.040 | H-10$\rightarrow$LUMO (95%) |
| 13  | 23370             | 427.9  | 0.353 | H-8$\rightarrow$LUMO (12%), HOMO$\rightarrow$L+2 (72%) |
| 14  | 23554             | 424.6  | 0.079 | H-12$\rightarrow$LUMO (90%) |
| 15  | 23588             | 424.0  | 0.000 | H-14$\rightarrow$LUMO (36%), H-13$\rightarrow$LUMO (14%), H-11$\rightarrow$LUMO (36%) |

$^{[a]}$ Oscillator strength. $^{[b]}$ Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S30. Electronic transitions calculated for 1d using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a]  | Major excitations[b] |
|-----|---------------|--------|-------|----------------------|
| 1   | 13841         | 722.5  | 1.211 | HOMO→LUMO (98%)      |
| 2   | 16015         | 624.4  | 0.091 | H-1→LUMO (96%)       |
| 3   | 18665         | 535.8  | 0.033 | H-4→LUMO (63%)       |
| 4   | 19669         | 508.4  | 0.294 | H-4→LUMO (26%)       |
| 5   | 20313         | 492.3  | 0.006 | H-3→LUMO (84%)       |
| 6   | 20619         | 485.0  | 0.002 | H-3→LUMO (11%)       |
| 7   | 21779         | 459.2  | 0.000 | H-6→LUMO (95%)       |
| 8   | 22143         | 451.6  | 0.002 | H-5→LUMO (89%)       |
| 9   | 22158         | 451.3  | 0.025 | H-1→L+1 (46%)        |
| 10  | 22659         | 441.3  | 0.028 | H-8→LUMO (15%)       |
| 11  | 23019         | 434.4  | 0.014 | H-7→LUMO (84%)       |
| 12  | 23713         | 421.7  | 0.148 | H-8→LUMO (77%)       |
| 13  | 24113         | 414.7  | 0.033 | H-4→L+1 (73%)        |
| 14  | 24490         | 408.3  | 0.073 | H-11→LUMO (20%)      |
| 15  | 24678         | 405.2  | 0.002 | H-10→LUMO (97%)      |
| 16  | 25048         | 399.2  | 0.097 | H-11→LUMO (69%)      |
| 17  | 25904         | 386.0  | 0.000 | H-15→LUMO (84%)      |
| 18  | 26115         | 382.9  | 0.003 | H-12→LUMO (94%)      |
| 19  | 26179         | 382.0  | 0.040 | H-13→LUMO (74%)      |
| 20  | 26261         | 380.8  | 0.001 | H-2→L+1 (82%)        |
| 21  | 26312         | 380.1  | 0.000 | H-14→LUMO (70%)      |
| 22  | 26357         | 379.4  | 0.038 | H-13→LUMO (13%)      |
| 23  | 26822         | 372.8  | 0.001 | H-3→L+1 (81%)        |
| 24  | 26846         | 372.5  | 0.002 | H-16→LUMO (80%)      |
| 25  | 27476         | 364.0  | 0.001 | H-23→LUMO (11%)      |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S31. Electronic transitions calculated for 1d–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f⁽ᵃ⁾ | Major excitations⁽ᵇ⁾ |
|-----|---------------|--------|------|----------------------|
| 1   | 13142         | 760.9  | 0.784| HOMO→LUMO (100%)     |
| 2   | 15494         | 645.4  | 0.001| H→1→LUMO (99%)       |
| 3   | 15600         | 641.0  | 0.004| H→2→LUMO (99%)       |
| 4   | 17366         | 575.8  | 0.012| H→3→LUMO (11%)       |
| 5   | 17416         | 574.2  | 0.027| H→4→LUMO (14%)       |
| 6   | 17473         | 572.3  | 0.025| H→5→LUMO (26%)       |
| 7   | 17931         | 557.7  | 0.068| H→6→LUMO (54%)       |
| 8   | 19540         | 511.8  | 0.080| H→7→LUMO (64%)       |
| 9   | 21054         | 475.0  | 0.044| H→8→LUMO (85%)       |
| 10  | 21400         | 467.3  | 0.337| H→9→LUMO (10%)       |
| 11  | 21973         | 455.1  | 0.045| H→10→LUMO (10%)      |
| 12  | 22167         | 451.1  | 0.013| H→11→LUMO (16%)      |
| 13  | 22524         | 444.0  | 0.127| H→12→LUMO (38%)      |
| 14  | 22753         | 439.5  | 0.001| H→13→LUMO (93%)      |
| 15  | 22915         | 436.4  | 0.000| H→14→LUMO (92%)      |
| 16  | 23000         | 434.8  | 0.002| H→15→LUMO (89%)      |
| 17  | 23152         | 431.9  | 0.226| H→16→LUMO (57%)      |
| 18  | 23200         | 431.0  | 0.049| H→17→LUMO (57%)      |
| 19  | 23465         | 426.2  | 0.213| H→18→LUMO (46%)      |
| 20  | 23695         | 422.0  | 0.001| H→19→LUMO (32%)      |
| 21  | 23715         | 421.7  | 0.001| H→20→LUMO (21%)      |
| 22  | 25254         | 396.0  | 0.014| H→21→LUMO (18%)      |
| 23  | 25306         | 395.2  | 0.014| H→22→LUMO (18%)      |
| 24  | 25335         | 394.7  | 0.007| H→23→LUMO (18%)      |
| 25  | 25459         | 392.8  | 0.019| H→24→LUMO (14%)      |

⁽ᵃ⁾ Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S32. Electronic transitions calculated for 1e using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | λ (nm) | $f$ | Major excitations[a] |
|-----|-------------------|--------|----|---------------------|
| 1   | 13908             | 719.0  | 1.158 | HOMO$ightarrow$LUMO (98%) |
| 2   | 14702             | 680.2  | 0.027 | HOMO$ightarrow$L+1 (95%) |
| 3   | 16181             | 618.0  | 0.086 | H-1$ightarrow$LUMO (95%) |
| 4   | 17379             | 575.4  | 0.027 | HOMO$ightarrow$L+2 (95%) |
| 5   | 18776             | 532.6  | 0.035 | H-4$ightarrow$LUMO (58%) |
|     |                   |        |      | HOMO$ightarrow$L+3 (32%) |
| 6   | 19392             | 515.7  | 0.001 | H-1$ightarrow$L+1 (94%) |
| 7   | 19732             | 506.8  | 0.279 | H-4$ightarrow$LUMO (30%) |
|     |                   |        |      | HOMO$ightarrow$L+3 (62%) |
| 8   | 20407             | 490.0  | 0.005 | H-3$ightarrow$LUMO (59%) |
|     |                   |        |      | H-2$ightarrow$LUMO (35%) |
| 9   | 20731             | 482.4  | 0.002 | H-3$ightarrow$LUMO (38%) |
|     |                   |        |      | H-2$ightarrow$LUMO (58%) |
| 10  | 21871             | 457.2  | 0.000 | H-6$ightarrow$LUMO (94%) |
| 11  | 22033             | 453.9  | 0.001 | H-4$ightarrow$L+1 (21%) |
|     |                   |        |      | H-1$ightarrow$L+2 (73%) |
| 12  | 22081             | 452.9  | 0.001 | H-4$ightarrow$L+1 (68%) |
|     |                   |        |      | H-1$ightarrow$L+2 (20%) |
| 13  | 22257             | 449.3  | 0.002 | H-5$ightarrow$LUMO (87%) |
| 14  | 22268             | 449.1  | 0.023 | H-7$ightarrow$LUMO (10%) |
|     |                   |        |      | H-1$ightarrow$L+3 (46%) |
|     |                   |        |      | HOMO$ightarrow$L+4 (16%) |

15 | 22781 | 439.0 | 0.020 | H-7$ightarrow$LUMO (44%) |
|   |       |       |      | H-1$ightarrow$L+3 (24%) |
|   |       |       |      | HOMO$ightarrow$L+4 (14%) |
16 | 22917 | 436.3 | 0.030 | H-7$ightarrow$LUMO (36%) |
|   |       |       |      | HOMO$ightarrow$L+4 (52%) |
17 | 23615 | 423.5 | 0.000 | H-7$ightarrow$L+1 (14%) |
|   |       |       |      | H-2$ightarrow$L+1 (79%) |
18 | 23715 | 421.7 | 0.000 | H-3$ightarrow$L+1 (98%) |
19 | 23907 | 418.3 | 0.155 | H-8$ightarrow$LUMO (75%) |
|   |       |       |      | HOMO$ightarrow$L+4 (12%) |
20 | 24000 | 416.7 | 0.019 | H-4$ightarrow$L+2 (34%) |
|   |       |       |      | H-4$ightarrow$L+3 (42%) |
21 | 24123 | 414.5 | 0.015 | H-7$ightarrow$L+1 (71%) |
|   |       |       |      | H-2$ightarrow$L+1 (12%) |
22 | 24750 | 404.0 | 0.002 | H-10$ightarrow$LUMO (87%) |
|   |       |       |      | H-9$ightarrow$LUMO (10%) |
23 | 24864 | 402.2 | 0.092 | H-10$ightarrow$LUMO (11%) |
|   |       |       |      | H-9$ightarrow$LUMO (78%) |
24 | 24898 | 401.6 | 0.004 | H-4$ightarrow$L+2 (52%) |
|   |       |       |      | H-4$ightarrow$L+3 (31%) |
25 | 25506 | 392.1 | 0.000 | H-5$ightarrow$L+1 (99%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S33. Electronic transitions calculated for 1e−H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f⁻⁴ | Major excitations[a] |
|-----|---------------|--------|-----|----------------------|
| 1   | 12615         | 792.7  | 0.689 | HOMO»LUMO (100%)     |
| 2   | 14691         | 680.7  | 0.001 | H-1»LUMO (99%)       |
| 3   | 14783         | 676.5  | 0.004 | H-2»LUMO (99%)       |
| 4   | 16620         | 601.7  | 0.001 | H-3»LUMO (99%)       |
| 5   | 16699         | 598.8  | 0.000 | H-4»LUMO (98%)       |
| 6   | 17001         | 588.2  | 0.044 | H-7»LUMO (10%)       |
| 7   | 17451         | 573.0  | 0.052 | H-6»LUMO (90%)       |
| 8   | 19008         | 526.1  | 0.110 | H-7»LUMO (10%)       |
| 9   | 19118         | 523.1  | 0.115 | H-7»LUMO (67%)       |
| 10  | 20532         | 487.0  | 0.060 | H-8»LUMO (89%)       |
| 11  | 21437         | 466.5  | 0.223 | HOMO»L+2 (49%)       |
| 12  | 21634         | 462.2  | 0.125 | H-10»LUMO (39%)      |
| 13  | 21708         | 460.7  | 0.062 | H-10»LUMO (57%)      |
| 14  | 21834         | 458.0  | 0.002 | H-9»LUMO (99%)       |
| 15  | 22187         | 450.7  | 0.048 | H-12»LUMO (71%)      |
| 16  | 22282         | 448.8  | 0.052 | H-13»LUMO (12%)      |
| 17  | 22331         | 447.8  | 0.010 | H-13»LUMO (80%)      |
| 18  | 22379         | 446.9  | 0.001 | H-14»LUMO (92%)      |
| 19  | 22558         | 443.3  | 0.000 | H-1»L+1 (79%)        |
| 20  | 22580         | 442.9  | 0.016 | H-15»LUMO (93%)      |
| 21  | 22841         | 437.8  | 0.000 | H-2»L+1 (70%)        |
| 22  | 23910         | 418.2  | 0.006 | H-1»L+1 (19%)        |
| 23  | 24037         | 416.0  | 0.007 | H-2»L+1 (28%)        |
| 24  | 24147         | 414.1  | 0.391 | HOMO»L+4 (87%)       |
| 25  | 24342         | 410.8  | 0.000 | H-3»L+1 (65%)        |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S34. Electronic transitions calculated for 1f using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | λ (nm) | \(f^\text{[a]}\) | Major excitations\(^{[b]}\) |
|-----|----------------------|--------|-----------------|----------------------|
| 1   | 10013                | 998.7  | 0.010           | HOMO=\text{LUMO} (100%) |
| 2   | 14029                | 712.8  | 1.086           | H=1=\text{LUMO} (98%) |
| 3   | 15564                | 642.5  | 0.009           | HOMO=\text{L}+1 (98%) |
| 4   | 16193                | 617.5  | 0.055           | H=2=\text{LUMO} (95%) |
| 5   | 18694                | 534.9  | 0.000           | H=3=\text{LUMO} (98%) |
| 6   | 18812                | 531.6  | 0.088           | H=4=\text{LUMO} (27%) |
| 7   | 19680                | 508.1  | 0.122           | H=4=\text{LUMO} (43%) |
| 8   | 19698                | 507.7  | 0.115           | H=4=\text{LUMO} (18%) |
| 9   | 21340                | 468.6  | 0.003           | H=6=\text{LUMO} (23%) |
| 10  | 21637                | 462.2  | 0.003           | H=6=\text{LUMO} (69%) |
| 11  | 21886                | 456.9  | 0.017           | H=7=\text{LUMO} (10%) |
| 12  | 22214                | 450.2  | 0.004           | H=7=\text{LUMO} (70%) |

\(\text{[a]}\) Oscillator strength. \(\text{[b]}\) Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S35. Electronic transitions calculated for 1f–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[α] | Major excitations[b] |
|-----|---------------|--------|------|----------------------|
| 1   | 6768          | 1477.6 | 0.095| HOMO→LUMO (100%)     |
| 2   | 13993         | 714.6  | 0.658| H–1→LUMO (99%)       |
| 3   | 14637         | 683.2  | 0.023| HOMO→L+1 (89%)       |
| 4   | 14986         | 667.3  | 0.004| H–2→LUMO (94%)       |
| 5   | 16361         | 611.2  | 0.016| HOMO→L+2 (95%)       |
| 6   | 17129         | 583.8  | 0.001| H–3→LUMO (99%)       |
| 7   | 17262         | 579.3  | 0.004| H–4→LUMO (99%)       |
| 8   | 18191         | 549.7  | 0.119| H–9→LUMO (26%)       |
| 9   | 18826         | 531.2  | 0.038| H–10→LUMO (24%)      |
| 10  | 18933         | 528.2  | 0.000| H–5→LUMO (97%)       |
| 11  | 19045         | 525.1  | 0.001| H–7→LUMO (59%)       |
| 12  | 19244         | 519.7  | 0.008| H–8→LUMO (96%)       |
| 13  | 19525         | 512.2  | 0.194| H–10→LUMO (57%)      |
| 14  | 21329         | 468.9  | 0.318| H–1→L+1 (83%)        |
| 15  | 21976         | 455.0  | 0.037| H–11→LUMO (80%)      |

(a) Oscillator strength, (b) Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S36. Electronic transitions calculated for 2a–2H2⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f [a] | Major excitations [b] |
|-----|---------------|--------|-------|-----------------------|
| 1   | 10513         | 951.2  | 0.753 | HOMO→LUMO (100%)      |
| 2   | 13749         | 727.4  | 0.086 | H→1→LUMO (96%)        |
| 3   | 15493         | 645.4  | 0.258 | H→2→LUMO (14%), HOMO→L+1 (83%) |
| 4   | 16138         | 619.7  | 0.187 | H→2→LUMO (72%), HOMO→L+1 (15%) |
| 5   | 18795         | 532.1  | 0.620 | H→3→LUMO (59%), H→1→L+1 (27%) |
| 6   | 18898         | 529.1  | 0.038 | H→4→LUMO (51%), H→3→LUMO (19%), H→1→L+1 (19%) |
| 7   | 19492         | 513.0  | 0.066 | H→4→LUMO (33%), H→1→L+1 (30%) |
| 8   | 19706         | 507.5  | 0.000 | HOMO→L+2 (87%)        |
| 9   | 21829         | 458.1  | 0.006 | H→2→L+1 (77%)        |
| 10  | 22166         | 451.1  | 0.008 | H→6→LUMO (69%), H→5→LUMO (28%) |
| 11  | 22425         | 445.9  | 0.008 | H→6→LUMO (28%), H→5→LUMO (69%) |
| 12  | 23374         | 427.8  | 0.001 | H→9→LUMO (86%)       |
| 13  | 23556         | 424.5  | 0.474 | H→8→LUMO (18%), H→7→LUMO (40%), H→1→L+2 (33%) |
| 14  | 23672         | 422.4  | 0.004 | H→8→LUMO (57%), H→7→LUMO (33%) |
| 15  | 23930         | 417.9  | 0.055 | H→8→LUMO (11%), H→7→LUMO (13%), H→4→L+1 (29%), H→1→L+2 (25%) |
| 16  | 24266         | 412.1  | 0.072 | H→4→L+1 (51%), H→3→L+1 (18%), H→1→L+2 (21%) |
| 17  | 25131         | 397.9  | 0.013 | H→3→L+1 (54%), H→1→L+2 (16%) |
| 18  | 25323         | 394.9  | 0.013 | H→10→LUMO (83%)      |
| 19  | 25711         | 388.9  | 0.000 | H→11→LUMO (92%)      |
| 20  | 25993         | 384.7  | 0.011 | H→15→LUMO (91%)      |
| 21  | 26644         | 375.3  | 0.038 | H→13→LUMO (11%), H→12→LUMO (25%), H→2→L+2 (40%) |
| 22  | 26708         | 374.4  | 0.037 | H→12→LUMO (55%), H→2→L+2 (32%) |
| 23  | 27003         | 370.3  | 0.000 | H→17→LUMO (81%)      |
| 24  | 27116         | 368.8  | 0.090 | H→13→LUMO (76%)      |
| 25  | 27273         | 366.7  | 0.001 | H→16→LUMO (60%), H→16→L+1 (12%), H→14→LUMO (12%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
| No. | Energy (cm⁻¹) | λ (nm) | f [a] | Major excitations[b] |
|-----|---------------|--------|-------|---------------------|
| 1   | 9591          | 1042.7 | 0.527 | HOMO→LUMO (100%)    |
| 2   | 13092         | 763.8  | 0.118 | H-1→LUMO (98%)      |
| 3   | 15683         | 637.6  | 0.214 | HOMO→L+1 (97%)      |
| 4   | 17805         | 561.6  | 0.261 | H-4→LUMO (13%)      |
| 5   | 18602         | 537.6  | 0.219 | H-2→LUMO (50%)      |
| 6   | 18681         | 535.3  | 0.216 | H-8→LUMO (14%)      |
| 7   | 18798         | 532.0  | 0.001 | H-3→LUMO (20%)      |
| 8   | 19142         | 522.4  | 0.136 | H-1→L+1 (79%)       |
| 9   | 19314         | 517.8  | 0.080 | H-9→LUMO (15%)      |
| 10  | 19607         | 510.0  | 0.198 | H-8→LUMO (14%)      |
| 11  | 20317         | 492.2  | 0.000 | H-5→LUMO (97%)      |
| 12  | 20440         | 489.2  | 0.001 | H-6→LUMO (96%)      |
| 13  | 20945         | 477.4  | 0.306 | H-9→LUMO (61%)      |
| 14  | 22388         | 446.7  | 0.217 | H-1→L+2 (92%)       |
| 15  | 24338         | 410.9  | 0.056 | H-10→LUMO (86%)     |
| 16  | 24414         | 409.6  | 0.033 | H-11→LUMO (92%)     |
| 17  | 25021         | 399.7  | 0.021 | H-14→LUMO (46%)     |
| 18  | 25060         | 399.0  | 0.031 | H-14→LUMO (26%)     |
| 19  | 25106         | 398.3  | 0.003 | H-15→LUMO (61%)     |
| 20  | 25217         | 396.6  | 0.020 | H-13→LUMO (16%)     |
| 21  | 25280         | 395.6  | 0.020 | H-12→LUMO (28%)     |
| 22  | 25328         | 394.8  | 0.007 | H-13→LUMO (33%)     |
| 23  | 25410         | 393.6  | 0.003 | H-13→LUMO (19%)     |
| 24  | 25630         | 390.2  | 0.016 | H-17→LUMO (14%)     |
| 25  | 25780         | 387.9  | 0.006 | H-16→LUMO (55%)     |

(a) Oscillator strength. (b) Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S38. Electronic transitions calculated for 2a–H⁺ (Z-anti) using the TD/PCM(dichloromethane) GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|--------------|--------|------|---------------------|
| 1   | 9519         | 1050.5 | 0.568| HOMO-LUMO (100%)    |
| 2   | 12998        | 769.4  | 0.000| H-1→LUMO (98%)      |
| 3   | 15858        | 630.6  | 0.149| HOMO→L+1 (96%)      |
| 4   | 17689        | 565.3  | 0.123| H-4→LUMO (41%)      |
|      |              |        |      | H-2→LUMO (45%)      |
| 5   | 18456        | 541.8  | 0.048| H-4→LUMO (35%)      |
|      |              |        |      | H-2→LUMO (54%)      |
| 6   | 18476        | 541.3  | 0.020| H-3→LUMO (96%)      |
| 7   | 18630        | 536.8  | 0.241| H-8→LUMO (50%)      |
|      |              |        |      | H-4→LUMO (21%)      |
|      |              |        |      | HOMO→L+2 (27%)      |
| 8   | 18745        | 533.5  | 0.001| H-9→LUMO (38%)      |
|      |              |        |      | H-5→LUMO (56%)      |
| 9   | 19107        | 523.4  | 0.421| H-8→LUMO (36%)      |
|      |              |        |      | HOMO→L+2 (57%)      |
| 10  | 19410        | 515.2  | 0.298| H-1→L+1 (93%)       |
| 11  | 20128        | 496.8  | 0.000| H-6→LUMO (87%)      |
| 12  | 20129        | 496.8  | 0.062| H-7→LUMO (94%)      |
| 13  | 20255        | 493.7  | 0.442| H-9→LUMO (54%)      |
|      |              |        |      | H-5→LUMO (39%)      |
| 14  | 22619        | 442.1  | 0.000| H-1→L+2 (96%)       |
| 15  | 24390        | 410.0  | 0.055| H-10→LUMO (96%)     |

16  24831  402.7  0.034 | H-14→LUMO (25%) |
|    |          |        |      | H-13→LUMO (24%)     |
|    |          |        |      | H-11→LUMO (43%)     |
| 17  24841  402.6  0.002 | H-15→LUMO (73%) |
|    |          |        |      | H-12→LUMO (14%)     |
| 18  24851  402.4  0.037 | H-16→LUMO (17%) |
|    |          |        |      | H-14→LUMO (39%)     |
|    |          |        |      | H-13→LUMO (23%)     |
| 19  24941  400.9  0.076 | H-2→L+1 (76%)  |
| 20  25064  399.0  0.001 | H-13→LUMO (38%) |
|    |          |        |      | H-11→LUMO (45%)     |
| 21  25064  399.0  0.044 | H-15→LUMO (13%) |
|    |          |        |      | H-12→LUMO (78%)     |
| 22  25110  398.3  0.004 | H-3→L+1 (89%)  |
| 23  25273  395.7  0.138 | H-16→LUMO (28%) |
|    |          |        |      | H-4→L+1 (57%)       |
| 24  25302  395.2  0.000 | H-18→LUMO (22%) |
|    |          |        |      | H-17→LUMO (30%)     |
|    |          |        |      | H-9→L+1 (19%)       |
|    |          |        |      | H-5→L+1 (20%)       |
| 25  25424  393.3  0.010 | H-17→LUMO (48%) |
|    |          |        |      | H-9→L+1 (15%)       |
|    |          |        |      | H-5→L+1 (27%)       |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S39. Electronic transitions calculated for 2a–H⁺ (Z-syn) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f [a] | Major excitations [b] |
|-----|---------------|--------|------|----------------------|
| 1   | 10288         | 972.0  | 0.737| HOMO+LUMO (101%)     |
| 2   | 13711         | 729.3  | 0.214| H-1»LUMO (96%)       |
| 3   | 16444         | 608.1  | 0.339| HOMO+L+1 (96%)       |
| 4   | 18131         | 551.5  | 0.477| H-4»LUMO (19%)       |
|     |               |        |      | H-2»LUMO (56%)       |
|     |               |        |      | HOMO+L+2 (23%)       |
| 5   | 18870         | 529.9  | 0.072| H-4»LUMO (15%)       |
|     |               |        |      | H-2»LUMO (42%)       |
|     |               |        |      | HOMO+L+2 (39%)       |
| 6   | 18885         | 529.5  | 0.003| H-3»LUMO (98%)       |
| 7   | 19073         | 524.3  | 0.163| H-4»LUMO (64%)       |
|     |               |        |      | HOMO+L+1 (31%)       |
| 8   | 19635         | 509.3  | 0.002| H-9»LUMO (13%)       |
|     |               |        |      | H-7»LUMO (83%)       |
| 9   | 19865         | 503.4  | 0.090| H-8»LUMO (21%)       |
|     |               |        |      | H-1»L+1 (71%)        |
| 10  | 20193         | 495.2  | 0.054| H-8»LUMO (70%)       |
|     |               |        |      | H-1»L+1 (25%)        |
| 11  | 20569         | 486.2  | 0.000| H-5»LUMO (95%)       |
| 12  | 20570         | 486.2  | 0.000| H-6»LUMO (95%)       |
| 13  | 21511         | 464.9  | 0.126| H-9»LUMO (81%)       |
|     |               |        |      | H-7»LUMO (13%)       |
| 14  | 22883         | 437.0  | 0.358| H-1»L+2 (93%)        |
| 15  | 23786         | 420.4  | 0.048| H-10»LUMO (92%)      |
| 16  | 25190         | 397.0  | 0.001| H-15»LUMO (45%)      |
|     |               |        |      | H-13»LUMO (25%)      |
|     |               |        |      | H-2»L+1 (14%)        |
| 17  | 25231         | 396.3  | 0.000| H-16»LUMO (54%)      |
|     |               |        |      | H-14»LUMO (25%)      |
| 18  | 25320         | 394.9  | 0.000| H-17»LUMO (12%)      |
|     |               |        |      | H-15»LUMO (10%)      |
|     |               |        |      | H-2»L+1 (66%)        |
| 19  | 25394         | 393.8  | 0.075| H-11»LUMO (95%)      |
| 20  | 25448         | 393.0  | 0.003| H-3»L+1 (88%)        |
| 21  | 25609         | 390.5  | 0.005| H-17»LUMO (22%)      |
|     |               |        |      | H-4»L+1 (66%)        |
| 22  | 25690         | 389.3  | 0.002| H-12»LUMO (86%)      |
| 23  | 25761         | 388.2  | 0.000| H-15»LUMO (29%)      |
|     |               |        |      | H-13»LUMO (67%)      |
| 24  | 25814         | 387.4  | 0.000| H-16»LUMO (23%)      |
|     |               |        |      | H-14»LUMO (64%)      |
| 25  | 26128         | 382.7  | 0.020| H-9»L+1 (13%)        |
|     |               |        |      | H-8»L+2 (13%)        |
|     |               |        |      | H-7»L+1 (67%)        |

[a] Oscillator strength.  [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S40. Electronic transitions calculated for 2a–3H\textsuperscript{3+} using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\textsuperscript{-1}) | λ (nm) | \( f^{(a)} \) | Major excitations\([b]\) |
|-----|-------------------------------|--------|-------------|-------------------|
| 1   | 14401                         | 694.4  | 0.471       | H–1\textarrow{a}\LUMO (40%) HOMO\textarrow{a}\LUMO (58%) |
| 2   | 14741                         | 678.4  | 0.192       | H–1\textarrow{a}\LUMO (58%) HOMO\textarrow{a}\LUMO (41%) |
| 3   | 15580                         | 641.8  | 0.012       | H–2\textarrow{a}\LUMO (98%) |
| 4   | 16616                         | 601.8  | 0.000       | H–3\textarrow{a}\LUMO (99%) |
| 5   | 17435                         | 573.5  | 0.000       | H–4\textarrow{a}\LUMO (98%) |
| 6   | 17914                         | 558.2  | 0.131       | H–6\textarrow{a}\LUMO (72%) H–5\textarrow{a}\LUMO (24%) |
| 7   | 18456                         | 541.8  | 0.015       | H–7\textarrow{a}\LUMO (35%) H–6\textarrow{a}\LUMO (21%) H–5\textarrow{a}\LUMO (42%) |
| 8   | 19261                         | 519.2  | 0.165       | H–7\textarrow{a}\LUMO (59%) H–5\textarrow{a}\LUMO (32%) |
| 9   | 22150                         | 451.5  | 0.020       | H–8\textarrow{a}\LUMO (73%) |
| 10  | 22372                         | 447.0  | 0.130       | H–1\textarrow{a}\L+1 (16%) HOMO\textarrow{a}\L+1 (47%) HOMO\textarrow{a}\L+2 (16%) |
| 11  | 22478                         | 444.9  | 0.035       | H–10\textarrow{a}\LUMO (23%) H–1\textarrow{a}\L+1 (27%) HOMO\textarrow{a}\L+1 (13%) HOMO\textarrow{a}\L+2 (24%) |
| 12  | 22545                         | 443.6  | 0.003       | H–9\textarrow{a}\LUMO (86%) |
| 13  | 22835                         | 437.9  | 0.118       | H–10\textarrow{a}\LUMO (31%) H–2\textarrow{a}\L+1 (33%) H–1\textarrow{a}\L+1 (19%) |

14  22921  436.3  0.159  H–10\textarrow{a}\LUMO (12%) H–2\textarrow{a}\L+1 (60%) H–1\textarrow{a}\L+1 (13%) 
15  23265  429.8  0.000  H–11\textarrow{a}\LUMO (85%) 
16  23507  425.4  0.014  H–12\textarrow{a}\LUMO (78%) 
17  23664  422.6  0.039  H–15\textarrow{a}\LUMO (36%) H–13\textarrow{a}\LUMO (20%) H–12\textarrow{a}\LUMO (13%) H–1\textarrow{a}\L+2 (11%) 
18  24021  416.3  0.013  HOMO\textarrow{a}\L+1 (34%) HOMO\textarrow{a}\L+2 (53%) 
19  24165  413.8  0.002  H–3\textarrow{a}\L+1 (47%) H–3\textarrow{a}\L+2 (47%) 
20  24253  412.3  0.107  H–14\textarrow{a}\LUMO (35%) H–13\textarrow{a}\LUMO (39%) 
21  24498  408.2  0.005  H–4\textarrow{a}\L+1 (87%) 
22  24543  407.4  0.503  H–14\textarrow{a}\LUMO (15%) H–10\textarrow{a}\LUMO (13%) H–1\textarrow{a}\L+2 (58%) 
23  25059  399.1  0.031  H–15\textarrow{a}\LUMO (42%) H–14\textarrow{a}\LUMO (27%) H–13\textarrow{a}\LUMO (17%) 
24  25486  392.4  0.058  H–7\textarrow{a}\L+1 (45%) H–5\textarrow{a}\L+1 (33%) 
25  25585  390.9  0.008  H–2\textarrow{a}\L+2 (89%) 

\[a\] Oscillator strength. \[b\] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S41. Electronic transitions calculated for 2b using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|----------------------|
| 1   | 10769         | 928.6  | 0.737| HOMO»LUMO (100%)     |
| 2   | 12920         | 774.0  | 0.103| H-1»LUMO (93%)       |
| 3   | 14655         | 682.4  | 0.028| H-2»LUMO (90%)       |
| 4   | 15525         | 644.1  | 0.258| HOMO=L+1 (88%)       |
| 5   | 16277         | 614.4  | 0.116| H-3»LUMO (75%)       |
|    |               |        |      | HOMO=L+1 (10%)       |
| 6   | 18109         | 552.2  | 0.044| H-1=1+L (92%)        |
| 7   | 18940         | 528.0  | 0.589| H-4=1+LUMO (83%)     |
| 8   | 19390         | 515.7  | 0.084| H-5=1+LUMO (72%)     |
|    |               |        |      | H-2=1+L (16%)        |
| 9   | 19815         | 504.7  | 0.027| HOMO=1+L (95%)       |
| 10  | 20087         | 497.8  | 0.012| H-5=1+LUMO (15%)     |
|    |               |        |      | H-2=1+L (17%)        |
| 11  | 21681         | 461.2  | 0.012| H-3=1+L (77%)        |
| 12  | 22690         | 440.7  | 0.011| H-7=1+LUMO (34%)     |
|    |               |        |      | H-6=1+LUMO (62%)     |
| 13  | 22919         | 436.3  | 0.472| H-1=1+L (91%)        |
| 14  | 22957         | 435.6  | 0.001| H-7=1+LUMO (60%)     |
|    |               |        |      | H-6=1+LUMO (33%)     |
| 15  | 23776         | 420.6  | 0.167| H-8=1+LUMO (78%)     |
| 16  | 23847         | 419.3  | 0.016| H-10=1+LUMO (85%)    |
| 17  | 24152         | 414.0  | 0.001| H-9=1+LUMO (87%)     |
| 18  | 24186         | 413.5  | 0.021| H-5=1+L (74%)        |
| 19  | 24370         | 410.3  | 0.051| H-4=1+L (54%)        |
|    |               |        |      | H-3=1+L (10%)        |
|    |               |        |      | H-2=1+L (27%)        |
| 20  | 24985         | 400.2  | 0.024| H-11=1+LUMO (87%)    |
| 21  | 25405         | 393.6  | 0.004| H-8=1+LUMO (10%)     |
|    |               |        |      | H-4=1+L (26%)        |
|    |               |        |      | H-2=1+L (50%)        |
| 22  | 26082         | 383.4  | 0.000| H-12=1+LUMO (91%)    |
| 23  | 26486         | 377.6  | 0.048| H-3=1+L (73%)        |
| 24  | 26871         | 372.1  | 0.039| H-13=1+LUMO (83%)    |
| 25  | 27328         | 365.9  | 0.027| H-18=1+LUMO (41%)    |
|    |               |        |      | H-14=1+LUMO (29%)    |

[a] Oscillator strength, [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S42. Electronic transitions calculated for 2b–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a]  | Major excitations[^b]               |
|-----|---------------|--------|--------|-------------------------------------|
| 1   | 10166         | 983.7  | 0.401  | HOMO→LUMO (99%)                     |
| 2   | 12474         | 801.7  | 0.252  | H-1→LUMO (98%)                      |
| 3   | 15755         | 634.7  | 0.179  | HOMO→L+1 (95%)                      |
| 4   | 16951         | 590.0  | 0.205  | H-2→LUMO (86%) H-1→L+1 (13%)       |
| 5   | 17671         | 565.9  | 0.224  | H-2→LUMO (12%) H-1→L+1 (83%)       |
| 6   | 18399         | 543.5  | 0.281  | H-3→LUMO (43%) HOMO→L+2 (52%)      |
| 7   | 18999         | 526.3  | 0.432  | H-3→LUMO (46%) HOMO→L+2 (39%)      |
| 8   | 19879         | 503.0  | 0.068  | H-7→LUMO (75%)                      |
| 9   | 20053         | 498.7  | 0.002  | H-4→LUMO (85%)                      |
| 10  | 20146         | 496.4  | 0.002  | H-5→LUMO (90%)                      |
| 11  | 20233         | 494.2  | 0.129  | H-9→LUMO (69%)                      |
| 12  | 20620         | 485.0  | 0.486  | H-1→L+2 (92%)                       |
| 13  | 21630         | 462.3  | 0.000  | H-6→LUMO (92%)                      |
| 14  | 21684         | 461.2  | 0.000  | H-9→LUMO (11%) H-8→LUMO (84%)      |
| 15  | 22320         | 448.0  | 0.047  | H-2→L+1 (94%)                       |
| 16  | 22960         | 435.5  | 0.105  | H-10→LUMO (84%)                     |
| 17  | 24803         | 403.2  | 0.066  | H-7→L+1 (23%) H-3→L+1 (49%) H-2→L+2 (17%) |
| 18  | 25275         | 395.6  | 0.021  | H-11→LUMO (94%)                     |
| 19  | 25464         | 392.7  | 0.017  | H-12→LUMO (10%) H-7→L+1 (46%) H-3→L+1 (19%) |
| 20  | 25560         | 391.2  | 0.037  | H-12→LUMO (30%) H-9→L+1 (16%) H-2→L+2 (22%) |
| 21  | 25671         | 389.5  | 0.017  | H-12→LUMO (25%) H-4→L+1 (58%)      |
| 22  | 25769         | 388.1  | 0.001  | H-9→L+1 (42%) H-5→L+1 (16%)        |
| 23  | 25793         | 387.7  | 0.016  | H-12→LUMO (11%) H-5→L+1 (56%) H-4→L+1 (11%) |
| 24  | 25963         | 385.2  | 0.073  | H-5→L+1 (20%) H-3→L+1 (13%) H-2→L+2 (27%) |
| 25  | 25994         | 384.7  | 0.003  | H-15→LUMO (67%)                     |

[^a]: Oscillator strength.  
[^b]: Contributions smaller than 10% are not included.  
H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S43. Electronic transitions calculated for 2b–4H⁺⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a^] | Major excitations[^b^] |
|-----|---------------|--------|--------|------------------------|
| 1   | 12992         | 769.7  | 0.032  | HOMO→LUMO (99%)         |
| 2   | 13729         | 728.4  | 0.309  | H₂→LUMO (16%)          |
|     |               |        |        | H₁→LUMO (83%)          |
| 3   | 14006         | 714.0  | 0.321  | H₂→LUMO (83%)          |
|     |               |        |        | H₁→LUMO (16%)          |
| 4   | 15086         | 662.9  | 0.000  | H₃→LUMO (99%)          |
| 5   | 15840         | 631.3  | 0.000  | H₄→LUMO (99%)          |
| 6   | 17190         | 581.7  | 0.147  | H₆→LUMO (52%)          |
|     |               |        |        | H₅→LUMO (44%)          |
| 7   | 17803         | 561.7  | 0.016  | H₇→LUMO (41%)          |
|     |               |        |        | H₆→LUMO (32%)          |
|     |               |        |        | H₅→LUMO (26%)          |
| 8   | 18916         | 528.6  | 0.122  | H₇→LUMO (55%)          |
|     |               |        |        | H₆→LUMO (14%)          |
|     |               |        |        | H₅→LUMO (28%)          |
| 9   | 21489         | 465.4  | 0.000  | H₈→LUMO (93%)          |
| 10  | 21670         | 461.5  | 0.012  | H₉→LUMO (87%)          |
| 11  | 21707         | 460.7  | 0.012  | HOMO→L₁ (48%)          |
|     |               |        |        | HOMO→L₂ (43%)          |
| 12  | 21818         | 458.3  | 0.028  | H→10→LUMO (70%)        |
| 13  | 22004         | 454.5  | 0.001  | H→11→LUMO (81%)        |
| 14  | 22132         | 451.8  | 0.021  | H→1→L₁ (71%)           |
| 15  | 22280         | 448.8  | 0.017  | H→12→LUMO (88%)        |
| 16  | 22862         | 437.4  | 0.413  | H→2→L₁ (75%)           |
| 17  | 23363         | 428.0  | 0.009  | HOMO→L₁ (43%)          |
|     |               |        |        | HOMO→L₂ (52%)          |
| 18  | 23484         | 425.8  | 0.000  | H→3→L₁ (45%)           |
|     |               |        |        | H→3→L₂ (51%)           |
| 19  | 23809         | 420.0  | 0.000  | H→4→L₁ (89%)           |
| 20  | 23929         | 417.9  | 0.033  | H→13→LUMO (92%)        |
| 21  | 24161         | 413.9  | 0.343  | H→10→LUMO (10%)        |
|     |               |        |        | H→2→L₂ (54%)           |
|     |               |        |        | H→1→L₂ (24%)           |
| 22  | 24556         | 407.2  | 0.048  | H→14→LUMO (84%)        |
| 23  | 24689         | 405.0  | 0.018  | H→2→L₂ (28%)           |
|     |               |        |        | H→1→L₂ (62%)           |
| 24  | 25129         | 397.9  | 0.014  | H→15→LUMO (94%)        |
| 25  | 25329         | 394.8  | 0.246  | H→16→LUMO (92%)        |

[^a^] Oscillator strength.[^b^] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
**Table S44.** Electronic transitions calculated for 2c using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | $\lambda$ (nm) | $f^{[a]}$ | Major excitations$^{[b]}$ |
|-----|-----------------|----------------|----------|-------------------------|
| 1   | 10548           | 948.0          | 0.743    | HOMO$\rightarrow$LUMO (100%) |
| 2   | 11368           | 879.6          | 0.009    | H$\rightarrow$1LUMO (100%) |
| 3   | 13805           | 724.4          | 0.090    | H$\rightarrow$2LUMO (96%) |
| 4   | 15491           | 645.5          | 0.258    | HOMO$\rightarrow$L+1 (13%) |
| 5   | 16155           | 519.0          | 0.187    | H$\rightarrow$3LUMO (73%) |
| 6   | 17106           | 584.6          | 0.001    | H$\rightarrow$1L+1 (100%) |
| 7   | 18830           | 531.1          | 0.549    | H$\rightarrow$4LUMO (50%) |
| 8   | 18950           | 527.7          | 0.085    | H$\rightarrow$5LUMO (46%) |
| 9   | 19518           | 512.4          | 0.064    | HOMO$\rightarrow$L+2 (15%) |
| 10  | 19697           | 507.7          | 0.001    | HOMO$\rightarrow$L+2 (81%) |
| 11  | 21805           | 458.6          | 0.006    | H$\rightarrow$3L+1 (77%) |
| 12  | 21926           | 456.1          | 0.016    | H$\rightarrow$1L+2 (97%) |
| 13  | 22293           | 448.6          | 0.010    | H$\rightarrow$7LUMO (69%) |
| 14  | 22544           | 443.6          | 0.009    | H$\rightarrow$7LUMO (28%) |
| 15  | 23463           | 426.2          | 0.335    | H$\rightarrow$8LUMO (71%) |
| 16  | 23485           | 425.8          | 0.018    | H$\rightarrow$10LUMO (88%) |
| 17  | 23776           | 420.6          | 0.000    | H$\rightarrow$9LUMO (90%) |
| 18  | 23893           | 418.5          | 0.151    | H$\rightarrow$B+LUMO (13%) |
| 19  | 24264           | 412.1          | 0.082    | H$\rightarrow$5L+1 (53%) |
| 20  | 24712           | 404.7          | 0.061    | H$\rightarrow$12LUMO (69%) |
| 21  | 25052           | 399.2          | 0.022    | H$\rightarrow$13LUMO (48%) |
| 22  | 25221           | 396.5          | 0.004    | H$\rightarrow$12LUMO (13%) |
| 23  | 25318           | 395.0          | 0.005    | H$\rightarrow$13LUMO (27%) |
| 24  | 25798           | 387.6          | 0.000    | H$\rightarrow$14LUMO (93%) |
| 25  | 26609           | 375.8          | 0.042    | H$\rightarrow$3L+2 (64%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S45. Electronic transitions calculated for 2c–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a]  | Major excitations[b]                  |
|-----|---------------|--------|-------|--------------------------------------|
| 1   | 9759          | 1024.7 | 0.457 | H–1»LUMO (99%)                       |
| 2   | 10077         | 992.3  | 0.532 | HOMO»LUMO (100%)                     |
| 3   | 13591         | 735.8  | 0.052 | H–2»LUMO (97%)                       |
| 4   | 15711         | 636.5  | 0.182 | H–1»L+1 (97%)                        |
| 5   | 16113         | 620.6  | 0.052 | HOMO»L–1 (98%)                       |
| 6   | 17991         | 555.8  | 0.235 | H–3»LUMO (58%)                       |
|     |               |        |       | H–1»L+2 (31%)                        |
| 7   | 18572         | 538.5  | 0.154 | HOMO»L+2 (93%)                       |
| 8   | 18683         | 535.2  | 0.540 | H–9»LUMO (15%)                       |
|     |               |        |       | H–3»LUMO (23%)                       |
|     |               |        |       | H–1»L+2 (55%)                        |
| 9   | 19223         | 520.2  | 0.019 | H–4»LUMO (74%)                       |
|     |               |        |       | H–3»LUMO (15%)                       |
| 10  | 19340         | 517.1  | 0.036 | H–5»LUMO (68%)                       |
| 11  | 19446         | 514.2  | 0.158 | H–9»LUMO (19%)                       |
|     |               |        |       | H–5»LUMO (24%)                       |
|     |               |        |       | H–2»L+1 (41%)                        |
| 12  | 19552         | 511.4  | 0.052 | H–10»LUMO (19%)                      |
|     |               |        |       | H–9»LUMO (10%)                       |
|     |               |        |       | H–7»LUMO (35%)                       |
|     |               |        |       | H–2»L+1 (24%)                        |
| 13  | 19805         | 504.9  | 0.157 | H–10»LUMO (26%)                      |
|     |               |        |       | H–9»LUMO (29%)                       |
|     |               |        |       | H–7»LUMO (13%)                       |
|     |               |        |       | H–2»L+1 (23%)                        |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S46. Electronic transitions calculated for 2c–4H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f(α)  | Major excitations[^b] |
|-----|----------------|--------|--------|-----------------------|
| 1   | 14181          | 705.2  | 0.337  | H−1→LUMO (17%)        |
|     |                |        |        | HOMO→LUMO (74%)       |
| 2   | 14482          | 690.5  | 0.280  | H−2→LUMO (16%)        |
|     |                |        |        | H−1→LUMO (59%)        |
|     |                |        |        | HOMO→LUMO (25%)       |
| 3   | 14873          | 672.4  | 0.057  | H−2→LUMO (75%)        |
|     |                |        |        | H−1→LUMO (24%)        |
| 4   | 16338          | 612.1  | 0.000  | H−3→LUMO (99%)        |
| 5   | 16759          | 596.7  | 0.000  | H−4→LUMO (98%)        |
| 6   | 17733          | 563.9  | 0.210  | H−6→LUMO (47%)        |
|     |                |        |        | H−5→LUMO (48%)        |
| 7   | 17997          | 555.7  | 0.124  | H−6→LUMO (50%)        |
|     |                |        |        | H−5→LUMO (42%)        |
| 8   | 18644          | 536.4  | 0.215  | H−7→LUMO (87%)        |
| 9   | 21563          | 463.8  | 0.211  | H−8→LUMO (82%)        |
| 10  | 22228          | 449.9  | 0.027  | H−11→LUMO (12%)       |
|     |                |        |        | H−10→LUMO (35%)       |
|     |                |        |        | H−1→L+1 (27%)         |
| 11  | 22353          | 447.4  | 0.015  | H−1→L+1 (11%)         |
|     |                |        |        | HOMO→L+1 (37%)        |
|     |                |        |        | HOMO→L+2 (37%)        |
| 12  | 22389          | 446.6  | 0.001  | H−9→LUMO (81%)        |
| 13  | 22417          | 446.1  | 0.004  | H−10→LUMO (35%)       |
|     |                |        |        | H−2→L+1 (19%)         |
|     |                |        |        | H−1→L+1 (17%)         |
|     |                |        |        | HOMO→L+1 (11%)        |
| 14  | 22504          | 444.4  | 0.010  | H−11→LUMO (39%)       |
|     |                |        |        | H−2→L+1 (29%)         |

[^a]: Oscillator strength. [^b]: Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S47. Electronic transitions calculated for 2d using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|---------------------|
| 1   | 10055         | 994.6  | 0.726| HOMO→LUMO (100%)    |
| 2   | 13361         | 748.5  | 0.112| H-1→LUMO (96%)      |
| 3   | 15357         | 651.2  | 0.232| H-2→LUMO (18%)      |
|     |               |        |      | HOMO→L-1 (78%)      |
| 4   | 15942         | 627.3  | 0.236| H-3→LUMO (11%)      |
|     |               |        |      | H-2→LUMO (65%)      |
|     |               |        |      | HOMO→L-1 (19%)      |
| 5   | 18440         | 542.3  | 0.582| H-3→LUMO (75%)      |
|     |               |        |      | H-2→LUMO (13%)      |
| 6   | 18682         | 535.3  | 0.116| H-4→LUMO (68%)      |
|     |               |        |      | H-1→L-1 (22%)       |
| 7   | 19249         | 519.5  | 0.004| H-1→L-1 (18%)       |
|     |               |        |      | HOMO→L-2 (80%)      |
| 8   | 19379         | 516.0  | 0.020| H-4→LUMO (20%)      |
|     |               |        |      | H-1→L-1 (56%)       |
|     |               |        |      | HOMO→L-2 (14%)      |
| 9   | 21261         | 470.3  | 0.004| H-6→LUMO (89%)      |
| 10  | 21518         | 464.7  | 0.004| H-5→LUMO (89%)      |
| 11  | 21955         | 455.5  | 0.009| H-3→L-1 (12%)       |
|     |               |        |      | H-2→L-1 (72%)       |
| 12  | 22588         | 442.7  | 0.000| H-8→LUMO (93%)      |
| 13  | 22880         | 437.1  | 0.000| H-7→LUMO (93%)      |
| 14  | 23272         | 420.7  | 0.506| H-9→LUMO (53%)      |
|     |               |        |      | H-1→L-2 (42%)       |
| 15  | 23722         | 421.5  | 0.052| H-9→LUMO (34%)      |
|     |               |        |      | H-4→L-1 (16%)       |
|     |               |        |      | H-1→L-2 (29%)       |
| 16  | 24212         | 413.0  | 0.050| H-4→L-1 (66%)       |
|     |               |        |      | H-1→L-2 (15%)       |
| 17  | 25061         | 399.0  | 0.005| H-10→LUMO (51%)     |
|     |               |        |      | H-3→L-1 (28%)       |
| 18  | 25139         | 397.8  | 0.015| H-12→LUMO (16%)     |
|     |               |        |      | H-11→LUMO (65%)     |
| 19  | 25167         | 397.3  | 0.002| H-10→LUMO (35%)     |
|     |               |        |      | H-3→L-1 (30%)       |
| 20  | 26222         | 381.4  | 0.025| H-12→LUMO (72%)     |
|     |               |        |      | H-11→LUMO (18%)     |
| 21  | 26436         | 378.3  | 0.000| H-17→LUMO (81%)     |
| 22  | 26534         | 376.9  | 0.011| H-14→LUMO (41%)     |
|     |               |        |      | H-2→L-2 (37%)       |
| 23  | 26618         | 375.7  | 0.007| H-13→LUMO (84%)     |
| 24  | 26739         | 374.0  | 0.000| H-15→LUMO (72%)     |
|     |               |        |      | H-15→L-1 (12%)      |
| 25  | 26799         | 373.2  | 0.099| H-14→LUMO (47%)     |
|     |               |        |      | H-2→L-2 (27%)       |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S48. Electronic transitions calculated for 2d–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a]  | Major excitations[b] |
|-----|---------------|--------|-------|----------------------|
| 1   | 9120          | 1096.5 | 0.616 | HOMO=LUMO (101%)     |
| 2   | 13008         | 768.8  | 0.130 | H-1=LUMO (98%)       |
| 3   | 15617         | 640.3  | 0.210 | HOMO+1 (96%)         |
| 4   | 17163         | 582.6  | 0.218 | H-4=LUMO (40%)      |
|     |               |        |       | H-3=LUMO (13%)      |
|     |               |        |       | H-2=LUMO (30%)      |
|     |               |        |       | HOMO+2 (14%)        |
| 5   | 17547         | 569.9  | 0.015 | H-4=LUMO (14%)      |
|     |               |        |       | H-3=LUMO (15%)      |
|     |               |        |       | H-2=LUMO (67%)      |
| 6   | 17743         | 563.6  | 0.014 | H-4=LUMO (25%)      |
|     |               |        |       | H-3=LUMO (70%)      |
| 7   | 18237         | 548.3  | 0.342 | H-8=LUMO (31%)      |
|     |               |        |       | H-7=LUMO (10%)      |
|     |               |        |       | HOMO+2 (48%)        |
| 8   | 18674         | 535.5  | 0.071 | H-8=LUMO (59%)      |
|     |               |        |       | HOMO+2 (28%)        |
| 9   | 18953         | 527.6  | 0.364 | H-8=LUMO (59%)      |
|     |               |        |       | HOMO+2 (28%)        |
| 10  | 19265         | 519.1  | 0.000 | H-5=LUMO (97%)      |
| 11  | 19424         | 514.8  | 0.000 | H-6=LUMO (97%)      |
| 12  | 19726         | 506.9  | 0.146 | H-1=L+1 (95%)       |
| 13  | 20915         | 478.1  | 0.230 | H-9=LUMO (85%)      |
| 14  | 22646         | 441.6  | 0.152 | H-1=L+2 (90%)       |
| 15  | 23272         | 429.7  | 0.032 | H-10=LUMO (89%)     |
| 16  | 23774         | 420.6  | 0.031 | H-11=LUMO (94%)     |
| 17  | 24258         | 412.2  | 0.001 | H-14=LUMO (31%)     |
| 18  | 24330         | 411.0  | 0.000 | H-16=LUMO (11%)     |
| 19  | 24504         | 408.1  | 0.001 | H-12=LUMO (11%)     |
| 20  | 24647         | 405.7  | 0.015 | H-16=LUMO (13%)     |
|     |               |        |       | H-15=LUMO (15%)     |
|     |               |        |       | H-14=LUMO (36%)     |
|     |               |        |       | H-13=LUMO (20%)     |
| 21  | 24816         | 403.0  | 0.015 | H-2=L+1 (80%)       |
| 22  | 24858         | 402.3  | 0.009 | H-17=LUMO (81%)     |
| 23  | 24949         | 400.8  | 0.008 | H-16=LUMO (29%)     |
|     |               |        |       | H-3=L+1 (42%)       |
| 24  | 25055         | 399.1  | 0.025 | H-16=LUMO (21%)     |
|     |               |        |       | H-3=L+1 (46%)       |
| 25  | 25349         | 394.5  | 0.080 | H-3=L+1 (11%)       |
|     |               |        |       | H-4=L+1 (66%)       |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S49. Electronic transitions calculated for 2d–3H\(^{1+}\) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f^{[a]}\) | Major excitations\(^{[b]}\) |
|-----|----------------------|-----------------|---------|-----------------|
| 1   | 12985               | 770.1           | 0.049   | HOMO→LUMO (99%) |
| 2   | 13641               | 733.1           | 0.559   | H-1→LUMO (97%)  |
| 3   | 14013               | 713.6           | 0.116   | H-2→LUMO (98%)  |
| 4   | 15064               | 663.8           | 0.000   | H-3→LUMO (99%)  |
| 5   | 15897               | 629.0           | 0.000   | H-4→LUMO (99%)  |
| 6   | 16945               | 590.1           | 0.130   | H-6→LUMO (49%)  |
| 7   | 17533               | 570.4           | 0.015   | H-7→LUMO (37%)  |
| 8   | 18806               | 531.7           | 0.121   | H-7→LUMO (35%)  |
| 9   | 20663               | 484.0           | 0.020   | H-12→LUMO (26%) |
| 10  | 21292               | 469.7           | 0.000   | H-9→LUMO (84%)  |
| 11  | 21647               | 462.0           | 0.032   | H-10→LUMO (75%) |
| 12  | 21867               | 457.3           | 0.014   | H-13→LUMO (10%) |
| 13  | 21950               | 455.6           | 0.015   | HOMO→L+1 (55%)  |
| 14  | 22022               | 454.1           | 0.000   | H-11→LUMO (86%) |
| 15  | 22224               | 450.0           | 0.018   | H-13→LUMO (79%) |
| 16  | 22359               | 447.2           | 0.046   | H-2→L+1 (45%)   |
| 17  | 22705               | 440.4           | 0.359   | H-2→L+1 (45%)   |
| 18  | 23563               | 424.4           | 0.005   | HOMO→L+1 (42%)  |
| 19  | 23709               | 421.8           | 0.033   | H-3→L+1 (44%)   |
| 20  | 23736               | 421.3           | 0.082   | H-15→LUMO (14%) |
| 21  | 23902               | 418.4           | 0.081   | H-15→LUMO (70%) |
| 22  | 24019               | 416.3           | 0.005   | H-4→L+1 (89%)   |
| 23  | 24141               | 414.2           | 0.513   | H-2→L+2 (12%)   |
| 24  | 24554               | 407.3           | 0.046   | H-16→LUMO (87%) |
| 25  | 24949               | 400.8           | 0.001   | H-17→LUMO (95%) |

\(^{[a]}\) Oscillator strength. \(^{[b]}\) Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S50. Electronic transitions calculated for 2e using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a] | Major excitations[^b] |
|-----|---------------|--------|-------|-----------------------|
| 1   | 10109         | 989.2  | 0.693 | HOMO→LUMO (100%)      |
| 2   | 10811         | 925.0  | 0.003 | HOMO→L+1 (96%)        |
| 3   | 13256         | 754.4  | 0.088 | H→1→LUMO (72%)        |
|     |               |        |       | HOMO→L+2 (25%)        |
| 4   | 13303         | 751.7  | 0.037 | H→1→LUMO (25%)        |
|     |               |        |       | HOMO→L+2 (71%)        |
| 5   | 15311         | 653.1  | 0.003 | H→1→L+1 (94%)         |
| 6   | 15416         | 648.7  | 0.237 | H→2→LUMO (14%)        |
|     |               |        |       | HOMO→L+3 (79%)        |
| 7   | 16027         | 623.9  | 0.204 | H→3→LUMO (12%)        |
|     |               |        |       | H→2→LUMO (67%)        |
|     |               |        |       | HOMO→L+3 (15%)        |
| 8   | 17735         | 563.9  | 0.003 | H→1→L+2 (96%)         |
| 9   | 18467         | 541.5  | 0.616 | H→3→LUMO (74%)        |
|     |               |        |       | H→2→LUMO (15%)        |
| 10  | 18712         | 534.4  | 0.064 | H→4→LUMO (32%)        |
|     |               |        |       | H→2→L+1 (34%)         |
|     |               |        |       | H→1→L+3 (24%)         |
| 11  | 18719         | 534.2  | 0.010 | H→4→LUMO (23%)        |
|     |               |        |       | H→2→L+1 (32%)         |
|     |               |        |       | H→1→L+3 (14%)         |
| 12  | 19264         | 519.1  | 0.043 | H→4→LUMO (32%)        |
|     |               |        |       | H→1→L+3 (55%)         |
| 13  | 19511         | 512.5  | 0.003 | HOMO→L+4 (90%)        |
| 14  | 20434         | 489.4  | 0.000 | H→3→L+1 (86%)         |
| 15  | 21212         | 471.4  | 0.000 | H→2→L+2 (87%)         |
| 16  | 21294         | 469.6  | 0.004 | H→6→LUMO (85%)        |
|     |               |        |       | H→5→LUMO (12%)        |
| 17  | 21508         | 464.9  | 0.000 | H→4→L+1 (94%)         |
| 18  | 21586         | 463.3  | 0.004 | H→6→LUMO (12%)        |
|     |               |        |       | H→5→LUMO (85%)        |
| 19  | 22014         | 454.3  | 0.011 | H→3→L+3 (14%)         |
|     |               |        |       | H→2→L+3 (71%)         |
| 20  | 22621         | 442.1  | 0.000 | H→8→LUMO (93%)        |
| 21  | 22874         | 437.2  | 0.007 | H→3→L+2 (87%)         |
| 22  | 22953         | 435.7  | 0.001 | H→7→LUMO (93%)        |
| 23  | 23265         | 429.8  | 0.459 | H→9→LUMO (57%)        |
|     |               |        |       | H→1→L+4 (37%)         |
| 24  | 23658         | 422.7  | 0.028 | H→9→LUMO (23%)        |
|     |               |        |       | H→4→L+2 (26%)         |
|     |               |        |       | H→4→L+3 (20%)         |
|     |               |        |       | H→1→L+4 (14%)         |
| 25  | 23906         | 418.3  | 0.095 | H→4→L+2 (42%)         |
|     |               |        |       | H→1→L+4 (31%)         |

[^a]: Oscillator strength.  
[^b]: Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S51. Electronic transitions calculated for 2e–H⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|----------------------|
| 1   | 8474          | 1180.1 | 0.555| HOMO→LUMO (101%)     |
| 2   | 12383         | 807.6  | 0.112| H→1→LUMO (96%)       |
| 3   | 13640         | 733.2  | 0.061| HOMO→L+1 (93%)       |
| 4   | 15683         | 637.6  | 0.189| HOMO→L+2 (84%)       |
|     |               |        |      | HOMO→L+3 (12%)       |
| 5   | 15917         | 628.3  | 0.014| HOMO→L+2 (12%)       |
|     |               |        |      | HOMO→L+3 (82%)       |
| 6   | 16526         | 605.1  | 0.146| H→4→LUMO (19%)       |
|     |               |        |      | H→2→LUMO (71%)       |
| 7   | 16775         | 596.1  | 0.093| H→4→LUMO (29%)       |
|     |               |        |      | H→3→LUMO (42%)       |
|     |               |        |      | H→2→LUMO (25%)       |
| 8   | 16965         | 589.4  | 0.052| H→4→LUMO (43%)       |
|     |               |        |      | H→3→LUMO (51%)       |
| 9   | 18066         | 553.5  | 0.067| H→8→LUMO (41%)       |
|     |               |        |      | H→7→LUMO (42%)       |
|     |               |        |      | H→1→L+1 (11%)        |
| 10  | 18185         | 549.9  | 0.056| H→8→LUMO (37%)       |
|     |               |        |      | H→1→L+1 (46%)        |
| 11  | 18283         | 547.0  | 0.041| H→8→LUMO (12%)       |
|     |               |        |      | H→7→LUMO (40%)       |
|     |               |        |      | H→1→L+1 (38%)        |
| 12  | 18465         | 541.6  | 0.000| H→5→LUMO (98%)       |
| 13  | 18646         | 536.3  | 0.000| H→6→LUMO (97%)       |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S52. Electronic transitions calculated for 2e–3H\(^{3+}\) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f[^{a}]\) Major excitations[^b] |
|-----|----------------------|------------------|---------------------------------|
| 1   | 12149                | 823.1            | 0.026 HOMO\(\rightarrow\)LUMO (100%) |
| 2   | 12964                | 771.4            | 0.303 H\(1\rightarrow\)LUMO (91%) |
| 3   | 13251                | 754.7            | 0.315 H\(2\rightarrow\)LUMO (91%) |
| 4   | 14241                | 702.2            | 0.000 H\(3\rightarrow\)LUMO (99%) |
| 5   | 15089                | 662.7            | 0.000 H\(4\rightarrow\)LUMO (99%) |
| 6   | 16524                | 605.2            | 0.119 H\(6\rightarrow\)LUMO (38%) H\(5\rightarrow\)LUMO (58%) |
| 7   | 17033                | 587.1            | 0.200 H\(7\rightarrow\)LUMO (33%) H\(6\rightarrow\)LUMO (46%) H\(5\rightarrow\)LUMO (20%) |
| 8   | 18319                | 545.9            | 0.111 H\(7\rightarrow\)LUMO (62%) H\(6\rightarrow\)LUMO (14%) H\(5\rightarrow\)LUMO (21%) |
| 9   | 20631                | 484.7            | 0.000 H\(8\rightarrow\)LUMO (95%) |
| 10  | 20774                | 481.4            | 0.013 H\(9\rightarrow\)LUMO (76%) H\(2\rightarrow\)L+1 (11%) |
| 11  | 20870                | 479.2            | 0.085 H\(9\rightarrow\)LUMO (15%) H\(2\rightarrow\)L+1 (43%) H\(1\rightarrow\)L+1 (18%) HOMO\(\rightarrow\)L+1 (11%) |
| 12  | 21252                | 470.5            | 0.059 H\(10\rightarrow\)LUMO (10%) H\(1\rightarrow\)LUMO (71%) |
| 13  | 21281                | 469.9            | 0.007 HOMO\(\rightarrow\)L+1 (38%) HOMO\(\rightarrow\)L+2 (30%) HOMO\(\rightarrow\)L+3 (11%) |
| 14  | 21369                | 468.0            | 0.016 H\(11\rightarrow\)LUMO (91%) |
| 15  | 21458                | 466.0            | 0.010 H\(12\rightarrow\)LUMO (81%) H\(10\rightarrow\)LUMO (11%) |
| 16  | 21906                | 456.5            | 0.010 H\(2\rightarrow\)L+1 (16%) H\(1\rightarrow\)L+1 (37%) H\(1\rightarrow\)L+2 (36%) |
| 17  | 22112                | 452.2            | 0.010 HOMO\(\rightarrow\)L+1 (45%) HOMO\(\rightarrow\)L+2 (38%) HOMO\(\rightarrow\)L+3 (12%) |
| 18  | 22806                | 438.5            | 0.334 H\(2\rightarrow\)L+2 (58%) H\(1\rightarrow\)L+2 (21%) |
| 19  | 23041                | 434.0            | 0.058 H\(13\rightarrow\)LUMO (89%) |
| 20  | 23084                | 433.2            | 0.000 H\(3\rightarrow\)L+1 (36%) H\(3\rightarrow\)L+2 (42%) H\(3\rightarrow\)L+3 (17%) |
| 21  | 23357                | 428.1            | 0.008 H\(2\rightarrow\)L+2 (16%) H\(1\rightarrow\)L+1 (32%) H\(1\rightarrow\)L+2 (35%) |
| 22  | 23437                | 426.7            | 0.088 H\(2\rightarrow\)L+3 (20%) H\(1\rightarrow\)L+3 (11%) HOMO\(\rightarrow\)L+2 (10%) HOMO\(\rightarrow\)L+3 (37%) |
| 23  | 23593                | 423.9            | 0.001 H\(4\rightarrow\)L+1 (45%) H\(4\rightarrow\)L+2 (45%) |
| 24  | 23634                | 423.1            | 0.061 H\(2\rightarrow\)L+3 (29%) H\(1\rightarrow\)L+3 (13%) HOMO\(\rightarrow\)L+2 (13%) HOMO\(\rightarrow\)L+3 (31%) |
| 25  | 23756                | 420.9            | 0.014 H\(14\rightarrow\)LUMO (86%) |

[^a]: Oscillator strength.[^b]: Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table 553. Electronic transitions calculated for 2a** using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f [a] | Major excitations [b] |
|-----|--------------|--------|-------|---------------------|
| 1   | 6121         | 1633.7 | 0.079 | HOMO(B)→LUMO(B) (93%) |
| 2   | 8876         | 1126.6 | 0.016 | H-2(B)→LUMO(B) (18%) |
|     |              |        |       | H-1(B)→LUMO(B) (70%)  |
| 3   | 10448        | 957.1  | 0.439 | HOMO(A)→LUMO(A) (83%) |
| 4   | 10888        | 918.5  | 0.322 | H-2(B)→LUMO(B) (58%) |
|     |              |        |       | H-1(B)→LUMO(B) (19%)  |
| 5   | 12029        | 831.3  | 0.012 | H-7(B)→LUMO(B) (28%) |
|     |              |        |       | H-6(B)→LUMO(B) (36%) |
|     |              |        |       | HOMO(B)→L+1(B) (16%) |
| 6   | 12937        | 773.0  | 0.022 | H-1(A)→LUMO(A) (10%) |
|     |              |        |       | H-7(B)→LUMO(B) (10%) |
|     |              |        |       | H-6(B)→LUMO(B) (13%) |
|     |              |        |       | HOMO(B)→L+1(B) (59%) |
| 7   | 13765        | 726.5  | 0.017 | H-4(B)→LUMO(B) (18%) |
|     |              |        |       | H-3(B)→LUMO(B) (72%) |
| 8   | 13817        | 723.7  | 0.000 | H-4(B)→LUMO(B) (77%) |
|     |              |        |       | H-3(B)→LUMO(B) (20%) |
| 9   | 13892        | 719.8  | 0.003 | H-2(A)→LUMO(A) (43%) |
|     |              |        |       | H-1(B)→L+1(B) (16%) |
| 10  | 15011        | 666.2  | 0.144 | HOMO(A)→L+1(A) (20%) |
|     |              |        |       | H-8(B)→LUMO(B) (36%) |
| 11  | 15151        | 660.0  | 0.171 | H-1(A)→LUMO(A) (11%) |
|     |              |        |       | HOMO(A)→L+1(A) (19%) |
|     |              |        |       | H-8(B)→LUMO(B) (28%) |
| 12  | 15635        | 639.6  | 0.000 | H-5(B)→LUMO(B) (98%) |
| 13  | 15658        | 638.6  | 0.000 | H-7(B)→LUMO(B) (55%) |
|     |              |        |       | H-6(B)→LUMO(B) (43%) |
| 14  | 16191        | 617.6  | 0.295 | H-1(A)→LUMO(A) (44%) |
|     |              |        |       | HOMO(A)→L+1(A) (20%) |
|     |              |        |       | H-1(B)→L+1(B) (12%) |
|     |              |        |       | HOMO(B)→L+1(B) (11%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S54. Electronic transitions calculated for $2a^{2+}$ (closed shell) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | $\lambda$ (nm) | $f$ | Major excitations$^{[b]}$ |
|-----|--------------------|----------------|-----|--------------------------|
| 1   | 9358               | 1068.6         | 0.054 | H–S=1LUMO (81%) HOMO=1LUMO (18%) |
| 2   | 9577               | 1044.2         | 0.005 | H–1=1LUMO (99%)           |
| 3   | 9715               | 1029.3         | 0.004 | H–2=1LUMO (99%)           |
| 4   | 10547              | 948.1          | 0.474 | H–5=1LUMO (17%) HOMO=1LUMO (85%) |
| 5   | 11668              | 857.0          | 0.000 | H–3=1LUMO (99%)           |
| 6   | 11847              | 844.1          | 0.000 | H–4=1LUMO (99%)           |
| 7   | 13038              | 767.0          | 0.009 | H–8=1LUMO (15%) H–7=1LUMO (82%) |
| 8   | 13400              | 746.3          | 0.444 | H–6=1LUMO (89%)           |
| 9   | 14783              | 676.5          | 0.307 | H–8=1LUMO (83%) H–7=1LUMO (15%) |
| 10  | 15812              | 632.4          | 0.000 | H–9=1LUMO (89%)           |
| 11  | 16707              | 598.6          | 0.308 | HOMO=1L+1 (65%)           |
| 12  | 16913              | 591.3          | 0.027 | H–12=1LUMO (14%) H–11=1LUMO (10%) H–10=1LUMO (71%) |
| 13  | 17601              | 568.2          | 0.034 | H–11=1LUMO (68%) H–10=1LUMO (13%) |
| 14  | 17826              | 561.0          | 0.004 | H–1=1=1 (97%)             |
| 15  | 17889              | 559.0          | 0.004 | H–2=1LUMO (97%)           |
| 16  | 18114              | 552.1          | 0.000 | H–12=1LUMO (82%) H–10=1LUMO (12%) |
| 17  | 18252              | 547.9          | 0.024 | H–5=1L+1 (79%)            |
| 18  | 18474              | 541.3          | 0.000 | H–13=1LUMO (92%)          |
| 19  | 18678              | 535.4          | 0.116 | H–15=1LUMO (21%) H–14=1LUMO (56%) |
| 20  | 19783              | 505.5          | 0.000 | H–3=1L+1 (95%)            |
| 21  | 19840              | 504.0          | 0.196 | H–15=1LUMO (51%) H–14=1LUMO (13%) |
| 22  | 19886              | 502.9          | 0.004 | H–4=1L+1 (93%)            |
| 23  | 20047              | 498.8          | 0.006 | H–16=1LUMO (83%)          |
| 24  | 20512              | 487.5          | 0.118 | H–17=1LUMO (66%)          |
| 25  | 20676              | 483.7          | 0.264 | H–17=1LUMO (12%) H–6=1L+1 (80%)|

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S55. Electronic transitions calculated for 2a** using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|---------------------|
| 1   | 3500          | 2856.8 | 0.000| HOMO(B)→LUMO(B) (100%) |
| 2   | 3588          | 2786.8 | 0.000| H−1(B)→LUMO(B) (100%) |
| 3   | 5172          | 1933.3 | 0.004| HOMO(A)→LUMO(A) (100%) |
| 4   | 5264          | 1899.8 | 0.002| H−4(B)→LUMO(B) (99%) |
| 5   | 5342          | 1872.0 | 0.004| H−1(A)→LUMO(A) (99%) |
| 6   | 5793          | 1726.3 | 0.000| H−2(B)→LUMO(B) (99%) |
| 7   | 5935          | 1685.0 | 0.000| H−3(B)→LUMO(B) (100%) |
| 8   | 5988          | 1670.0 | 0.001| H−4(A)→LUMO(A) (76%) |
| 9   | 6306          | 1585.9 | 0.017| H−5(A)→LUMO(A) (13%) |
| 10  | 7364          | 1358.0 | 0.000| H−2(A)→LUMO(A) (99%) |
| 11  | 7587          | 1318.0 | 0.000| H−3(A)→LUMO(A) (99%) |
| 12  | 7690          | 1300.3 | 0.002| HOMO(B)→L+1(B) (99%) |
| 13  | 8004          | 1249.3 | 0.002| H−1(B)→L+1(B) (99%) |
| 14  | 8606          | 1162.0 | 0.044| H−7(B)→LUMO(B) (30%) |
|     |               |        |      | H−6(B)→LUMO(B) (37%) |
| 15  | 8870          | 1127.3 | 0.076| H−5(A)→LUMO(A) (33%) |
|     |               |        |      | H−7(B)→LUMO(B) (19%) |
| 16  | 9218          | 1084.8 | 0.004| H−5(B)→L+1(B) (10%) |
|     |               |        |      | H−4(B)→L+1(B) (57%) |
| 17  | 9426          | 1060.9 | 0.187| H−5(A)→LUMO(A) (30%) |
|     |               |        |      | H−7(B)→LUMO(B) (31%) |
|     |               |        |      | H−4(B)→L+1(B) (17%) |
| 18  | 9508          | 1051.7 | 0.008| H−6(A)→LUMO(A) (19%) |
|     |               |        |      | H−6(B)→LUMO(B) (46%) |
|     |               |        |      | H−5(B)→L+1(B) (13%) |
| 19  | 9948          | 1005.2 | 0.000| H−2(B)→L+1(B) (99%) |
| 20  | 10196         | 980.8  | 0.122| H−7(A)→LUMO(A) (55%) |
|     |               |        |      | H−6(A)→LUMO(A) (13%) |
| 21  | 10332         | 967.9  | 0.000| H−3(B)→L+1(B) (99%) |
| 22  | 11151         | 896.7  | 0.010| H−8(B)→LUMO(B) (63%) |
| 23  | 11777         | 849.1  | 0.214| H−6(A)→LUMO(A) (32%) |
|     |               |        |      | H−8(B)→LUMO(B) (10%) |
|     |               |        |      | H−5(B)→L+1(B) (28%) |
| 24  | 12076         | 828.1  | 0.072| H−8(A)→LUMO(A) (50%) |
|     |               |        |      | H−8(B)→LUMO(B) (17%) |
| 25  | 12836         | 779.1  | 0.037| H−9(A)→LUMO(A) (26%) |
|     |               |        |      | H−8(A)→LUMO(A) (11%) |
|     |               |        |      | H−10(B)→LUMO(B) (15%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S56. Electronic transitions calculated for protonated dipyrrin radical 2a–H⁺⁺ using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[^a] | Major excitations[^b] |
|-----|---------------|--------|-------|----------------------|
| 1   | 15546         | 1803.1 | 0.329 | HOMO(B)→LUMO(B) (91%) |
| 2   | 10307         | 970.2  | 0.015 | H⁻¹(B)→LUMO(B) (90%)  |
| 3   | 10384         | 963.0  | 0.069 | H⁻²(A)→LUMO(A) (12%)  |
|     |               |        |       | HOMO(B)→L+1(B) (75%)  |
| 4   | 10491         | 953.2  | 0.007 | H⁻¹(B)→LUMO(B) (90%)  |
| 5   | 10707         | 934.0  | 0.234 | HOMO(A)→LUMO(A) (59%) |
|     |               |        |       | H⁻⁴(B)→LUMO(B) (21%)  |
|     |               |        |       | H⁻⁴(B)→LUMO(B) (20%)  |
|     |               |        |       | H⁻⁴(B)→LUMO(B) (19%)  |
| 6   | 10853         | 921.4  | 0.318 | H⁻³(B)→LUMO(B) (99%)  |
| 7   | 12416         | 805.4  | 0.000 | H⁻⁵(B)→LUMO(B) (99%)  |
| 8   | 12546         | 797.1  | 0.000 | H⁻⁵(B)→LUMO(B) (99%)  |
| 9   | 12831         | 779.3  | 0.029 | H⁻⁷(B)→LUMO(B) (13%)  |
|     |               |        |       | H⁻⁷(B)→LUMO(B) (57%)  |
|     |               |        |       | H⁻⁶(B)→LUMO(B) (29%)  |
| 10  | 12952         | 772.1  | 0.019 | H⁻⁸(B)→LUMO(B) (28%)  |
|     |               |        |       | H⁻⁷(B)→LUMO(B) (33%)  |
|     |               |        |       | H⁻⁶(B)→LUMO(B) (29%)  |
| 11  | 13373         | 747.8  | 0.079 | H⁻⁸(B)→LUMO(B) (50%)  |
|     |               |        |       | H⁻⁶(B)→LUMO(B) (37%)  |
| 12  | 14904         | 670.9  | 0.034 | H⁻²(A)→LUMO(A) (43%)  |
|     |               |        |       | HOMO(B)→L⁺⁺(B) (10%)  |
| 13  | 16033         | 623.7  | 0.022 | H⁻⁶(A)→LUMO(A) (12%)  |
|     |               |        |       | H⁻⁴(B)→L+1(B) (43%)   |
|     |               |        |       | f[^a] Oscillator strength.[^b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S57. Electronic transitions calculated for 2d** using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm⁻¹) | λ (nm) | f[a] | Major excitations[b] |
|-----|---------------|--------|------|----------------------|
| 1   | 6076          | 1645.9 | 0.052| HOMO(B) → LUMO(B) (91%) |
| 2   | 9118          | 1096.7 | 0.026| H–2(B) → LUMO(B) (14%) H–1(B) → LUMO(B) (63%) |
| 3   | 9987          | 1001.3 | 0.450| HOMO(A) → LUMO(A) (79%) |
| 4   | 10980         | 910.8  | 0.295| H–4(B) → LUMO(B) (18%) H–2(B) → LUMO(B) (38%) H–1(B) → LUMO(B) (21%) |
| 5   | 11805         | 847.1  | 0.016| H–1(A) → LUMO(A) (13%) H–7(B) → LUMO(B) (36%) HOMO(B) → L+1(B) (38%) |
| 6   | 12636         | 791.4  | 0.009| H–7(B) → LUMO(B) (46%) HOMO(B) → L+1(B) (38%) |
| 7   | 13365         | 748.2  | 0.009| H–4(B) → LUMO(B) (24%) H–3(B) → LUMO(B) (71%) |
| 8   | 13405         | 746.0  | 0.901| H–4(B) → LUMO(B) (50%) H–3(B) → LUMO(B) (10%) H–2(B) → LUMO(B) (39%) |
| 9   | 13590         | 735.9  | 0.003| H–2(A) → LUMO(A) (45%) H–1(B) → L+1(B) (15%) |
| 10  | 14927         | 669.9  | 0.039| H–1(A) → LUMO(A) (17%) HOMO(A) → L+1(A) (28%) H–8(B) → LUMO(B) (15%) |
| 11  | 15133         | 660.8  | 0.232| H–8(B) → LUMO(B) (41%) |
| 12  | 15270         | 654.9  | 0.000| H–6(B) → LUMO(B) (98%) |
| 13  | 15300         | 653.6  | 0.000| H–5(B) → LUMO(B) (99%) |
| 14  | 15979         | 625.8  | 0.352| H–1(A) → LUMO(A) (33%) HOMO(A) → L+1(A) (26%) H–1(B) → L+1(B) (11%) |
| 15  | 16978         | 589.0  | 0.179| H–2(A) → LUMO(A) (33%) H–1(B) → L+1(B) (35%) |
| 16  | 17107         | 584.6  | 0.003| H–8(B) → LUMO(B) (31%) H–2(B) → L+1(B) (21%) |
| 17  | 17297         | 578.1  | 0.003| H–9(A) → LUMO(A) (10%) H–8(A) → LUMO(A) (23%) HOMO(A) → L+1(A) (10%) H–9(B) → LUMO(B) (10%) |
| 18  | 17782         | 562.4  | 0.023| H–8(A) → LUMO(A) (18%) HOMO(A) → L+1(A) (19%) H–9(B) → LUMO(B) (14%) H–7(B) → L+1(B) (12%) |
| 19  | 18377         | 544.2  | 0.004| H–10(B) → LUMO(B) (18%) H–9(B) → LUMO(B) (61%) |
| 20  | 18514         | 540.1  | 0.111| HOMO(A) → L+2(A) (60%) |
| 21  | 18735         | 533.7  | 0.003| H–15(B) → LUMO(B) (84%) |
| 22  | 18896         | 529.2  | 0.028| H–3(A) → LUMO(A) (87%) |
| 23  | 19081         | 524.1  | 0.013| H–4(A) → LUMO(A) (88%) |
| 24  | 19184         | 521.3  | 0.034| H–11(B) → LUMO(B) (51%) H–10(B) → LUMO(B) (17%) |
| 25  | 19301         | 518.1  | 0.023| H–10(B) → LUMO(B) (14%) HOMO(B) → L+2(B) (48%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S58. Electronic transitions calculated for $2d^{2+}$ (closed shell) using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm$^{-1}$) | $\lambda$ (nm) | $f$[a] | Major excitations[b] |
|-----|-------------------|----------------|--------|---------------------|
| 1   | 9196              | 1087.4         | 0.005  | H–1+LUMO (100%)     |
| 2   | 9311              | 1074.0         | 0.007  | H–2+LUMO (99%)      |
| 3   | 9600              | 1041.7         | 0.051  | H–5+LUMO (80%)      |
|     |                   |                |        | HOMO=LUMO (8%)      |
|     |                   |                |        | H–2+LUMO (99%)      |
| 4   | 10759             | 929.4          | 0.467  | H–5+LUMO (18%)      |
|     |                   |                |        | HOMO=LUMO (94%)     |
| 5   | 11338             | 882.0          | 0.000  | H–3+LUMO (99%)      |
| 6   | 11493             | 870.1          | 0.000  | H–4+LUMO (99%)      |
| 7   | 13281             | 753.0          | 0.010  | H–8+LUMO (22%)      |
|     |                   |                |        | H–7+LUMO (73%)      |
| 8   | 13455             | 743.2          | 0.361  | H–6+LUMO (84%)      |
|     |                   |                |        | HOMO=L+1 (12%)      |
| 9   | 14948             | 669.0          | 0.302  | H–8+LUMO (75%)      |
|     |                   |                |        | H–7+LUMO (23%)      |
| 10  | 15864             | 630.4          | 0.007  | H–9+LUMO (90%)      |
| 11  | 16463             | 607.4          | 0.442  | H–14+LUMO (10%)     |
|     |                   |                |        | HOMO=L+1 (65%)      |
| 12  | 16746             | 597.2          | 0.002  | H–1+L+1 (98%)       |
| 13  | 16853             | 593.4          | 0.003  | H–2+L+1 (98%)       |
| 14  | 17546             | 569.9          | 0.011  | H–11+LUMO (44%)     |
|     |                   |                |        | H–5+L+1 (47%)       |

| 15  | 17889             | 555.0          | 0.057  | H–11+LUMO (36%)     |
|     |                   |                |        | H–10+LUMO (14%)     |
|     |                   |                |        | H–5+L+1 (41%)       |
| 16  | 17946             | 557.2          | 0.007  | H–11+LUMO (13%)     |
|     |                   |                |        | H–10+LUMO (79%)     |
| 17  | 18277             | 547.2          | 0.002  | H–12+LUMO (92%)     |
| 18  | 18566             | 538.6          | 0.025  | H–14+LUMO (13%)     |
|     |                   |                |        | H–13+LUMO (78%)     |
| 19  | 18785             | 532.3          | 0.000  | H–3+L+1 (94%)       |
| 20  | 18948             | 527.8          | 0.002  | H–4+L+1 (91%)       |
| 21  | 19144             | 522.3          | 0.102  | H–16+LUMO (64%)     |
|     |                   |                |        | H–14+LUMO (16%)     |
| 22  | 19819             | 504.6          | 0.183  | H–16+LUMO (14%)     |
|     |                   |                |        | H–15+LUMO (16%)     |
|     |                   |                |        | H–14+LUMO (31%)     |
|     |                   |                |        | H–6+L+1 (15%)       |
| 23  | 19887             | 502.8          | 0.016  | H–16+LUMO (18%)     |
|     |                   |                |        | H–15+LUMO (65%)     |
| 24  | 20238             | 494.1          | 0.315  | H–14+LUMO (13%)     |
|     |                   |                |        | H–6+L+1 (77%)       |
| 25  | 20456             | 488.9          | 0.048  | H–17+LUMO (81%)     |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S59. Electronic transitions calculated for 2d^{10} using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory

| No. | Energy (cm^{-1}) | \(\lambda\) (nm) | \(f^{[a]}\) | Major excitations^{[b]} |
|-----|------------------|------------------|-----------|-------------------------|
| 1   | 2822             | 3543.4           | 0.001     | HOMO(B)\(\Rightarrow\)LUMO(B) (100%) |
| 2   | 2970             | 3367.3           | 0.000     | H\(\rightarrow\)1(B)\(\Rightarrow\)LUMO(B) (100%) |
| 3   | 4580             | 2183.2           | 0.004     | HOMO(A)\(\Rightarrow\)LUMO(A) (100%) |
| 4   | 4680             | 2136.9           | 0.004     | H\(\rightarrow\)1(A)\(\Rightarrow\)LUMO(A) (99%) |
| 5   | 5118             | 1954.0           | 0.003     | H\(\rightarrow\)2(B)\(\Rightarrow\)LUMO(B) (72%) |
| 6   | 5148             | 1942.4           | 0.001     | H\(\rightarrow\)4(B)\(\Rightarrow\)LUMO(B) (23%) |
| 7   | 5364             | 1864.1           | 0.000     | H\(\rightarrow\)3(B)\(\Rightarrow\)LUMO(B) (100%) |
| 8   | 6115             | 1635.2           | 0.005     | H\(\rightarrow\)4(A)\(\Rightarrow\)LUMO(A) (59%) |
| 9   | 6305             | 1586.1           | 0.028     | H\(\rightarrow\)5(A)\(\Rightarrow\)LUMO(A) (11%) |
| 10  | 6812             | 1468.0           | 0.000     | H\(\rightarrow\)2(A)\(\Rightarrow\)LUMO(A) (99%) |
| 11  | 6964             | 1436.0           | 0.000     | H\(\rightarrow\)3(A)\(\Rightarrow\)LUMO(A) (99%) |
| 12  | 7203             | 1388.4           | 0.001     | HOMO(B)\(\Rightarrow\)L\(\rightarrow\)1(B) (100%) |
| 13  | 7486             | 1335.9           | 0.002     | H\(\rightarrow\)1(B)\(\Rightarrow\)L\(\rightarrow\)1(B) (99%) |
| 14  | 8643             | 1157.0           | 0.032     | H\(\rightarrow\)7(B)\(\Rightarrow\)LUMO(B) (28%) |
| 15  | 8959             | 1116.2           | 0.075     | H\(\rightarrow\)7(A)\(\Rightarrow\)LUMO(A) (10%) |

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
Table S60. Electronic transitions calculated for protonated dipyrrin radical 2d–H\textsuperscript{**} using the TD/PCM(dichloromethane)GD3BJ-B3LYP/6-31G(d,p) level of theory.

| No. | Energy (cm\textsuperscript{-1}) | λ (nm) | f\textsuperscript{[a]} | Major excitations\textsuperscript{[b]} |
|-----|--------------------------------|--------|----------------|----------------------------------|
|     |                                |        |                | HOMO(A)\textsuperscript{+}→LUMO(A) (15%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (84%) |
| 1   | 5960                           | 1677.7 | 0.258          | HOMO(A)\textsuperscript{+}→LUMO(A) (15%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (10%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (21%) |
| 2   | 10063                          | 993.7  | 0.531          | HOMO(A)\textsuperscript{+}→LUMO(A) (54%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (10%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (21%) |
| 3   | 10168                          | 983.5  | 0.044          | H−1(B)\textsuperscript{+}→LUMO(B) (62%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (14%) |
| 4   | 10285                          | 972.3  | 0.084          | HOMO(A)\textsuperscript{+}→LUMO(A) (15%) |
|     |                                |        |                | H−1(B)\textsuperscript{+}→LUMO(B) (36%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (32%) |
| 5   | 10416                          | 960.1  | 0.007          | H−2(B)\textsuperscript{+}→LUMO(B) (96%) |
| 6   | 11013                          | 908.0  | 0.094          | H−5(B)\textsuperscript{+}→LUMO(B) (81%) |
| 7   | 12331                          | 811.0  | 0.000          | H−3(B)\textsuperscript{+}→LUMO(B) (99%) |
| 8   | 12437                          | 804.0  | 0.000          | H−4(B)\textsuperscript{+}→LUMO(B) (99%) |
| 9   | 13015                          | 768.3  | 0.023          | H−8(B)\textsuperscript{+}→LUMO(B) (10%) |
|     |                                |        |                | H−6(B)\textsuperscript{+}→LUMO(B) (74%) |
| 10  | 13189                          | 758.2  | 0.005          | H−8(B)\textsuperscript{+}→LUMO(B) (20%) |
|     |                                |        |                | H−7(B)\textsuperscript{+}→LUMO(B) (60%) |
| 11  | 13986                          | 715.0  | 0.135          | H−8(B)\textsuperscript{+}→LUMO(B) (48%) |
|     |                                |        |                | H−7(B)\textsuperscript{+}→LUMO(B) (19%) |
|     |                                |        |                | H−5(B)\textsuperscript{+}→LUMO(B) (10%) |
| 12  | 14875                          | 672.3  | 0.041          | H−3(A)\textsuperscript{+}→LUMO(A) (41%) |
|     |                                |        |                | HOMO(B)\textsuperscript{+}→LUMO(B) (11%) |
| 13  | 15291                          | 654.0  | 0.012          | H−1(A)\textsuperscript{+}→LUMO(A) (94%) |
| 14  | 15620                          | 640.2  | 0.001          | H−1(B)\textsuperscript{+}→LUMO(B) (75%) |
| 15  | 15769                          | 634.2  | 0.013          | H−2(A)\textsuperscript{+}→LUMO(A) (94%) |
| 16  | 15888                          | 629.4  | 0.003          | H−5(B)\textsuperscript{+}→LUMO(B) (31%) |
|     |                                |        |                | H−2(B)\textsuperscript{+}→LUMO(B) (14%) |
|     |                                |        |                | H−1(B)\textsuperscript{+}→LUMO(B) (21%) |
| 17  | 16066                          | 622.4  | 0.027          | H−2(B)\textsuperscript{+}→LUMO(B) (68%) |
| 18  | 16209                          | 616.9  | 0.110          | H−7(A)\textsuperscript{+}→LUMO(A) (14%) |
|     |                                |        |                | H−3(A)\textsuperscript{+}→LUMO(A) (12%) |
|     |                                |        |                | H−2(B)\textsuperscript{+}→LUMO(B) (15%) |
| 19  | 16846                          | 593.6  | 0.073          | H−8(A)\textsuperscript{+}→LUMO(A) (11%) |
|     |                                |        |                | HOMO(A)\textsuperscript{+}→LUMO(A) (20%) |
|     |                                |        |                | HOMO(A)\textsuperscript{+}→LUMO(A) (15%) |
| 20  | 17184                          | 581.9  | 0.069          | H−9(A)\textsuperscript{+}→LUMO(A) (29%) |
|     |                                |        |                | HOMO(A)\textsuperscript{+}→LUMO(A) (11%) |
|     |                                |        |                | H−8(B)\textsuperscript{+}→LUMO(B) (10%) |
| 21  | 17256                          | 579.5  | 0.000          | H−4(A)\textsuperscript{+}→LUMO(A) (96%) |
| 22  | 17313                          | 577.6  | 0.001          | H−9(A)\textsuperscript{+}→LUMO(B) (91%) |
| 23  | 17650                          | 566.6  | 0.000          | H−3(A)\textsuperscript{+}→LUMO(B) (93%) |
| 24  | 17662                          | 566.2  | 0.000          | H−5(A)\textsuperscript{+}→LUMO(A) (94%) |
| 25  | 17900                          | 558.7  | 0.001          | H−12(B)\textsuperscript{+}→LUMO(B) (53%) |
|     |                                |        |                | H−11(B)\textsuperscript{+}→LUMO(B) (10%) |

\[a\] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.
NMR Spectra
Figure S103. $^1$H NMR spectrum of 3 (500 MHz, chloroform-$d$, 300 K).

Figure S104. $^{13}$C NMR spectrum of 3 (125 MHz, chloroform-$d$, 300 K).
Figure S105. $^1$H NMR spectrum of 4 (500 MHz, chloroform-$d$, 300 K).

Figure S106. $^{13}$C NMR spectrum of 4 (151 MHz, chloroform-$d$, 300 K).
Figure S107. $^1$H NMR spectrum of 6 (600 MHz, chloroform-$d$, 300 K).

Figure S108. $^{13}$C NMR spectrum of 6 (151 MHz, chloroform-$d$, 300 K).
Figure S109. $^1$H NMR spectrum of 5 (500 MHz, chloroform-$d$, 300 K).

Figure S110. $^{13}$C NMR spectrum of 5 (151 MHz, chloroform-$d$, 300 K).
Figure S111. $^1$H NMR spectrum of 7 (600 MHz, chloroform-$d$, 300 K).

Figure S112. $^{13}$C NMR spectrum of 7 (151 MHz, chloroform-$d$, 300 K).
Figure S113. $^1$H NMR spectrum of S3 (600 MHz, chloroform-$d$, 300 K).

Figure S114. $^{13}$C NMR spectrum of S3 (151 MHz, chloroform-$d$, 300 K).
Figure S115. $^1$H NMR spectrum of 1a (600 MHz, chloroform-$d$, 300 K).

Figure S116. $^{13}$C NMR spectrum of 1a (151 MHz, chloroform-$d$, 300 K).
Figure S117. $^1$H NMR spectrum of 1b (600 MHz, chloroform-$d$, 300 K).

Figure S118. $^{13}$C NMR spectrum of 1b (151 MHz, chloroform-$d$, 300 K).
Figure S119. $^1$H NMR spectrum of $1c$ (600 MHz, chloroform-$d$, 300 K).

Figure S120. $^{13}$C NMR spectrum of $1c$ (151 MHz, chloroform-$d$, 300 K).
Figure S121. $^1$H NMR spectrum of 1d (500 MHz, chloroform-$d$, 300 K).

Figure S122. $^{13}$C NMR spectrum of 1d (125 MHz, chloroform-$d$, 300 K).
Figure S123. $^1$H NMR spectrum of 1e (500 MHz, chloroform-$d$, 300 K).

Figure S124. $^{13}$C NMR spectrum of 1e (151 MHz, chloroform-$d$, 300 K).
Figure S125. $^1$H NMR spectrum of 1f (500 MHz, chloroform-$d$, 300 K).

Figure S126. $^{13}$C NMR spectrum of 1f (151 MHz, chloroform-$d$, 300 K).
**Figure S127.** $^1$H NMR spectrum of 2a (500 MHz, chloroform-$d$, 300 K).

**Figure S128.** $^{13}$C NMR spectrum of 2a (151 MHz, chloroform-$d$, 300 K).
Figure S129. $^1$H NMR spectrum of 2b (500 MHz, chloroform-$d$, 300 K).

Figure S130. $^{13}$C NMR spectrum of 2b (151 MHz, chloroform-$d$, 300 K).
Figure S131. $^1$H NMR spectrum of 2c (500 MHz, chloroform-$d$, 300 K).

Figure S132. $^1$H NMR spectrum of 2d (500 MHz, chloroform-$d$, 300 K).
**Figure S133.** $^{13}$C NMR spectrum of 2d (151 MHz, chloroform-$d$, 300 K).

**Figure S134.** $^1$H NMR spectrum of 2e (500 MHz, chloroform-$d$, 300 K).
Mass Spectra
Figure S135. High resolution mass spectrum of 3 (ESI–TOF, top: experimental, bottom: simulated).

Figure S136. High resolution mass spectrum of 4 (ESI–TOF, top: experimental, bottom: simulated).
Figure S137. High resolution mass spectrum of 6 (ESI–TOF, top: experimental, bottom: simulated).

Figure S138. High resolution mass spectrum of 5 (ESI–TOF, top: experimental, bottom: simulated).
Figure S139. High resolution mass spectrum of 7 (ESI–TOF, top: experimental, bottom: simulated).

Figure S140. High resolution mass spectrum of S3 (LC-MS, top: experimental, bottom: simulated).
Figure S141. High resolution mass spectrum of 1a (ESI–TOF, top: experimental, bottom: simulated).

Figure S142. High resolution mass spectrum of 1b (ESI–TOF, top: experimental, bottom: simulated).
Figure S143. High resolution mass spectrum of 1c (ESI–TOF, top: experimental, bottom: simulated).

Figure S144. High resolution mass spectrum of 1d (ESI–TOF, top: experimental, bottom: simulated).
Figure S145. High resolution mass spectrum of 1e (ESI–TOF, top: experimental, bottom: simulated).

Figure S146. High resolution mass spectrum of 1f (LC-MS, top: experimental, bottom: simulated).
Figure S147. High resolution mass spectrum of 2a (ESI–TOF, top: experimental, bottom: simulated).

Figure S148. High resolution mass spectrum of 2b (ESI–TOF, top: experimental, bottom: simulated).
Figure S149. High resolution mass spectrum of 2c (LC-MS, top: experimental, bottom: simulated).

Figure S150. High resolution mass spectrum of 2d (ESI–TOF, top: experimental, bottom: simulated).
Figure S151. High resolution mass spectrum of 2e (LC-MS, top: experimental, bottom: simulated).

Figure S152. High resolution mass spectrum of 3d (ESI-TOF, top: experimental, bottom: simulated).
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