Backbone-controlled LUMO energy induces intramolecular C–H activation in \textit{ortho}-bis-9-borafluorene-substituted phenyl and \textit{o}-carboranyl compounds leading to novel 9,10-diboraanthracene derivatives

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## Table of Contents

General experimental details ........................................................................................................... S3
Synthetic procedures .................................................................................................................... S7
Single-crystal X-ray diffraction ..................................................................................................... S27
Geometry tables .......................................................................................................................... S32
Photophysical data ...................................................................................................................... S36
Cyclic voltammetry ...................................................................................................................... S39
DFT and TD-DFT results ............................................................................................................. S41
References ..................................................................................................................................... S69
General experimental details

Unless otherwise noted, the following conditions apply.
All syntheses were carried out using standard Schlenk and glovebox techniques under an argon atmosphere. The solvents used were dried using either a solvent purification system (SPS) from Innovative Technology or were distilled and degassed from appropriate drying agents and stored under argon. Deuterated solvents (CD$_2$Cl$_2$ and C$_6$D$_6$) used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories. C$_6$D$_6$ and CD$_2$Cl$_2$ were dried over molecular sieves, degassed by three freeze-pump-thaw cycles and stored under an argon atmosphere prior to use. n-Butyllithium (2.5 M solution in hexane) was purchased from Acros Organics and used as received. The compounds 9-bromo-9-borafluorene$^1$ and 1,2-bis(dichloroboryl)benzene$^2$ were prepared according to literature procedures. The dilithiated carborane 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ was prepared in situ according to a published procedure.$^3$ Isolation of 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ from lithiation in toluene at 80 °C overnight does not result in a fully dilithiated product, as a significant portion of monolithiated product remains. To lower the amount of side product formation and problems of identification in NMR experiments, we synthesized 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ in Et$_2$O following a known route.$^4$ This results in the formation of 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$. All other starting materials were purchased from commercial sources and were used without further purification.

**NMR** Spectra were recorded on a Bruker Avance 500 FT NMR spectrometer (operating at $^1$H: 500 MHz, $^{11}$B: 160 MHz, $^{13}$C{$^1$H}: 126 MHz) or Bruker Avance III HD 300 spectrometer (operating at $^1$H: 300 MHz, $^{11}$B: 96 MHz, $^{13}$C{$^1$H}: 75 MHz). Chemical shifts (δ) are given in ppm and $^{11}$B{$^1$H} NMR spectra are referenced to external BF$_3$·Et$_2$O. $^1$H NMR spectra were referenced via residual proton resonances of CD$_2$Cl$_2$ (5.32 ppm), C$_6$D$_6$ (7.16 ppm), and THF-d$_8$ (1.72 ppm). $^{13}$C{$^1$H} spectra were referenced to CD$_2$Cl$_2$ (53.84 ppm), C$_6$D$_6$ (128.06 ppm), and THF-d$_8$ (25.31 ppm).

**HRMS** were recorded using a Thermo Scientific Exactive Plus Orbitrap MS system by Liquid Injection Field Desorption Ionization (LIFDI) or an Atmospheric Sample Analysis Probe (ASAP).

**Single-crystal X-ray diffraction:** Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil or polybutyl oil, mounted on a polyimide microloop.
(MicroMounts from MiTeGen) and transferred to a stream of cold nitrogen (Oxford Cryostream 700 or 800, respectively). Diffraction data were collected on a Bruker X8 Apex II 4-circle diffractometer with a CCD area detector, using Mo-Kα radiation generated by a Nonius FR591 rotating anode and monochromated by graphite (3a) or by multi-layer focusing mirrors (2b). Diffraction data were collected on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer with a semiconductor HPA-detector (HyPix-6000 or HyPix-Arc-150) and multi-layer mirror monochromated Cu-Kα radiation generated by a PhotonJet (3a·THF) or a PhotonJet-R (3b, 5, 9-(4-bromobutoxy)-9-borafluorene, 9-(Me₂S)-9-Br-9-borafluorene, and 1-MeS-2-(Me₂S-9-borafluorene)-1,2-C₂B₁₀H₁₀) source. Data were collected at 100 K or 173 K (5). The images were processed and corrected for Lorentz-polarization effects and absorption (empirical scaling) as implemented in the Bruker software packages (2b and 3a) or using the CrysAlis pro software from Rigaku Oxford Diffraction (3b, 3a·THF, 5, 9-(4-bromobutoxy)-9-borafluorene, 9-(Me₂S)-9-Br-9-borafluorene, and 1-MeS-2-(Me₂S-9-borafluorene)-1,2-C₂B₁₀H₁₀). The structures were solved using the intrinsic phasing method (SHELXT)⁵ and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with all hydrogen atoms ‘riding’ in idealized positions, by full-matrix least squares against F² of all data, using SHELXL⁶ software and the SHELXLE⁷ graphical user interface. In the case of 3a disordered solvent was masked using SQUEEZE/PLATON.⁸ 3b and 3a·THF were refined as two-component twins, both with twin fractions of 48%. 1-MeS-2-(Me₂S-9-borafluorene)-1,2-C₂B₁₀H₁₀ was refined as two-component twin with a twin fraction of 43%. Diamond software was used for graphical representation.⁹ Crystal data and experimental details are listed in Table S1. Full structural information has been deposited with the Cambridge Crystallographic Data Centre. CCDC-2174245 (2b), 2174247 (3a), 2174246 (3b), 2174248 (3a·THF), 2174249 (5), 2216649 (9-(4-bromobutoxy)-9-borafluorene), 2216647 (9-(Me₂S)-9-Br-9-borafluorene), and 2216648 (1-MeS-2-(Me₂S-9-borafluorene)-1,2-C₂B₁₀H₁₀).

**Photophysical measurements:** All measurements were performed in standard quartz cuvettes (1 cm x 1 cm cross-section). UV–visible absorption spectra were recorded using a Perkin Elmer Lambda 465 UV-visible spectrophotometer. **Emission spectra** were recorded using an Edinburgh Instruments FLSP920 spectrophotometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument. **Fluorescence quantum yields** were measured using a calibrated integrating sphere (inner diameter: 150 mm) from Edinburgh Instruments combined with the FLSP920 spectrophotometer described above. For solution-state and solid-state measurements, the longest-wavelength absorption maximum of the
compound in the respective solvent was chosen as the excitation wavelength. **Fluorescence lifetimes** were recorded using the time-correlated single-photon counting (TCSPC) method using the same FLSP920 spectrometer described above. Solutions were excited with a picosecond pulsed diode laser at 376.6 nm. The full width at half maximum (FWHM) of the laser pulses were ca. 70–200 ps, while the instrument response function (IRF) had a FWHM of ca. 1.0 ns, measured from the scatter of a Ludox solution at the excitation wavelength. Decays were recorded to at least 10000 counts in the peak channel with a record length of at least 1000 channels. The band pass of the monochromator was adjusted to give a signal count rate of <10 kHz. Iterative reconvolution of the IRF with one decay function and non-linear least-squares analysis were used to analyze the data. The quality of the fit was judged by the calculated value of the reduced $\chi^2$ and visual inspection of the weighted residuals.

**Computational methods**

All molecular geometries were fully optimized via DFT calculations at the B3LYP-D(BJ), wB97X-D\(^1\) and M062X\(^{11-13}/6-31G(d,p)\)\(^{14,15}\) level of theory. Frequency calculations at the same level of theory were performed to confirm that all stationary points are local minima (no imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K. Transition states were located using the Berny algorithm and further confirmed by calculations of intrinsic reaction coordinates (IRC)\(^{16}\) showing that the transition states indeed connect the two relevant minima. All DFT calculations were performed with the Gaussian 09 (D.01) program.\(^{17}\)

All calculations regarding the photophysical experiments of 2a, 2b, 3a, and 3b (DFT and TD-DFT) were carried out with the Gaussian 09 (9.E.01)\(^{18}\) program package and were performed on a parallel cluster system. GaussView (6.0.16) and multiwfn\(^{19}\) were used to visualize the results, to measure calculated structural parameters, and to plot orbital surfaces (isovalue: ± 0.030 \[a_0^{-3}\])\(^{1/2}\). The ground-state geometries were optimized using the B3LYP functional\(^{20}\) in combination with the 6-31+G(d,p) basis set.\(^{21,22}\)

The orbital overlap parameter was calculated with $\Lambda = \frac{\sum_i c_i^2 \langle \varphi_i | \varphi_a \rangle}{\sum_i c_i^2}$, resulting in $0 \leq \Lambda \leq 1$, where $\Lambda = 0$ corresponds to no overlap and $\Lambda = 1$ corresponds to complete overlap.\(^{23}\)

The ultrafine integration grid and symmetry constraints were used for all molecules. Frequency calculations were performed on the optimized structures to confirm them to be local minima showing no negative (imaginary) frequencies. Based on these optimized structures, the lowest-energy vertical transitions (using the polarizable continuum model) were calculated (singlets, 25 states) by TD-DFT, using the Coulomb attenuated functional CAM-B3LYP\(^{24}\) as well as
B3LYP. The CAM-B3LYP functional has been shown to more accurately describe CT systems in comparison to B3LYP.\textsuperscript{23} The optimized ground-state geometries were used as starting coordinates for TD-DFT geometry optimizations.
Synthetic procedures

Bis(bis-9-borafluorenyl)benzene (2b)

Via syringe, a solution of 1,2-bis(dichloroboryl)benzene 4 (119 mg, 495 µmol, 1.0 eq.) in 10 mL toluene was slowly added to a solution of dimethyldibenzostannole (300 mg, 990 µmol, 2.0 eq.) in 10 mL toluene at −78 °C in a Schlenk tube. The solution was stirred and allowed to warm to room temperature overnight. After removal of all volatiles including Me₂SnCl₂ in vacuo, the residue was washed with hexane (3 x 20 mL) to yield a yellow solid 2b (158 mg, 393 µmol, 79%).

\[ ^1\text{H NMR} \ (500.1 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 8.03 (\text{m, 2H, CH}\_\text{Ar}), 7.70 (\text{m, 2H, CH}\_\text{Ar}), 7.47 (\text{m, 4H, CH}), 7.29 (\text{m, 4H, CH}), 7.23 (\text{m, 4H, CH}), 6.95 (\text{m, 4H, CH}) \text{ ppm.} \]

\[ ^{11}\text{B NMR} \ (160.5 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 67.0 \text{ (br) ppm.} \]

\[ ^{13}\text{C}[^{1}\text{H}] \text{NMR} \ (125.8 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 154.03 (C_{q,\text{Ar}}), 145.03 (C_{q,\text{Ar}}), 143.78 (C_{q,\text{Ar}}), 134.81 (CH\_\text{Ar}), 134.43 (CH\_\text{Ar}), 134.16 (CH\_\text{Ar}), 130.70 (C_{q,\text{Ar}}), 128.42 (CH\_\text{Ar}), 120.06 (CH\_\text{Ar}) \text{ ppm.} \]

\text{HRMS LIFDI calc. for } [C\_30H\_20B\_2]^+ = [M]^+: 402.1746, \text{ found } 402.1744.
3-([1,1′-biphenyl]-2-yl)-3H-1,2-(1,2-ortho-carboranyl)-3,10b-diborafluoranthene (3a)

Ortho-carborane (200 mg, 1.39 mmol, 1.0 eq.) was dissolved in toluene (5 mL) and a 2.5 M nBuLi solution in hexane (1.16 mL, 2.91 mmol, 2.1 eq.) was added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred at 80 °C overnight to obtain the dilithiated species 1 in situ. Then 9-bromo-9-borafluorene (707 mg, 2.91 mmol, 2.1 eq.) in toluene (5 mL) was added dropwise at −78 °C after which the reaction was slowly warmed to room temperature and stirred for 4 d. The suspension was filtered, the solid was washed with toluene (5 mL) and all volatiles were removed from the filtrate in vacuo. The crude product was recrystallized from toluene by hexane diffusion at −30 °C to give 3b as orange crystals (85.0 mg, 182 μmol, 13%).

1H NMR (500.1 MHz, CD2Cl2): \( \delta = 7.65 \) (m, 1H, \( CH_A \)), 7.59 (m, 1H, \( CH_A \)), 7.56 (m, 1H, \( CH_A \)), 7.42 (m, 3H, \( CH_A \)), 7.36 (m, 1H, \( CH_A \)), 7.31 (m, 6H, \( CH_A \)), 7.25 (m, 1H, \( CH_A \)), 7.18 (m, 1H, \( CH_A \)), 7.16 (m, 1H, \( CH_A \)), 3.18–1.53 (br, 10H, \( BH \)) ppm.

1H{11B} NMR (500.1 MHz, CD2Cl2): \( \delta = 7.65 \) (m, 1H, \( CH_A \)), 7.59 (m, 1H, \( CH_A \)), 7.56 (m, 1H, \( CH_A \)), 7.42 (m, 3H, \( CH_A \)), 7.36 (m, 1H, \( CH_A \)), 7.31 (m, 6H, \( CH_A \)), 7.25 (m, 1H, \( CH_A \)), 7.18 (m, 1H, \( CH_A \)), 7.16 (m, 1H, \( CH_A \)), 2.61(s, 1H, \( BH \)), 2.45–2.34 (m, 5H, \( BH \)), 2.27 (s, 1H, \( BH \)), 2.21(s, 1H, \( BH \)), 2.05(s, 1H, \( BH \)), 1.55(s, 1H, \( BH \)) ppm.

11B NMR (160.5 MHz, CD2Cl2): \( \delta = 66.1, 3.2, –4.4, –8.8 \) ppm.

11B{1H} NMR (160.5 MHz, CD2Cl2): \( \delta = 66.1, 2.6, 2.2, –5.0, –5.7, –9.6 \) ppm.

13C{1H} NMR (125.8 MHz, CD2Cl2): \( \delta = 155.8 \) (\( C_{q,A} \)), 152.9 (\( C_{q,A} \)), 143.9 (\( C_{q,A} \)), 143.8 (\( C_{q,A} \)), 138.6 (\( CH_A \)), 137.1 (\( CH_A \)), 136.4 (\( CH_A \)), 136.2 (\( CH_A \)), 129.9 (\( CH_A \)), 129.7 (\( CH_A \)), 129.6 (\( CH_A \)), 126.5 (\( CH_A \)), 129.1 (\( CH_A \)), 129.0 (\( CH_A \)), 128.1 (\( CH_A \)), 126.1 (\( CH_A \)), 125.7 (\( CH_A \)), 121.7 (\( CH_A \)) ppm.

HRMS LIFDI calc. for [C26H26B12]+ = [M]+: 468.3219, found 468.3218.
5-([1,1'-biphenyl]-2-yl)-5H-benzo[4,5]borolo[3,2,1-de]boranthrene (3b)

Compound 2b (37.0 mg, 92.0 µmol) was heated for 3 d at 120 °C in toluene. Removal of all volatiles in vacuo led to the isolation of 3b as an orange solid (34.0 mg, 84.5 µmol, 92%).

$^1$H NMR (500.1 MHz, CD$_2$Cl$_2$): δ = 8.33 (m, 1H, CH$_{Ar}$), 8.02 (m, 1H, CH$_{Ar}$), 7.73 (m, 1H, CH$_{Ar}$), 7.67 (m, 1H, CH$_{Ar}$), 7.58 (m, 1H, CH$_{Ar}$), 7.55 (m, 1H, CH$_{Ar}$), 7.48 (m, 3H, CH$_{Ar}$), 7.42 (m, 1H, CH$_{Ar}$), 7.39 (m, 1H, CH$_{Ar}$), 7.35 (m, 3H, CH$_{Ar}$), 7.20 (m, 1H, CH$_{Ar}$), 7.13 (m, 4H, CH$_{Ar}$), 6.98 (m, 1H, CH$_{Ar}$) ppm.

$^{11}$B NMR (160.5 MHz, CD$_2$Cl$_2$): δ = 63.9 (br) ppm.

$^{13}$C($^1$H) NMR (125.8 MHz, CD$_2$Cl$_2$): δ = 156.80 (C$_q$Ar), 153.26 (C$_q$Ar), 150.80 (C$_q$Ar), 149.68 (C$_q$Ar), 145.62 (C$_q$Ar), 144.32 (C$_q$Ar), 144.11 (C$_q$Ar), 143.36 (C$_q$Ar), 141.99 (C$_q$Ar), 141.12 (CH$_{Ar}$), 137.49 (CH$_{Ar}$), 135.79 (CH$_{Ar}$), 135.60 (CH$_{Ar}$), 134.72 (CH$_{Ar}$), 133.97 (CH$_{Ar}$), 133.95 (CH$_{Ar}$), 132.18 (CH$_{Ar}$), 131.51 (CH$_{Ar}$), 129.08 (CH$_{Ar}$), 128.96 (CH$_{Ar}$), 128.93 (CH$_{Ar}$), 128.50 (CH$_{Ar}$), 128.44 (CH$_{Ar}$), 127.52 (CH$_{Ar}$), 126.46 (CH$_{Ar}$), 123.40 (CH$_{Ar}$), 121.14 (CH$_{Ar}$), ppm.

HRMS LIFDI calc. for [C$_{30}$H$_{20}$B$_2$]$^+$ = [M]$^+$: 402.1746, found 402.1743.
Synthesis of 5

The compound 9-Br-9-borafluorene (10 mg, 41.2 µmol, 2.5 eq) was suspended in THF-d₈ (1 mL) and the mixture was stirred at 60 °C for 1 h. The reaction was monitored by ¹¹B NMR spectroscopy. Then, 1,2-Li₂·1,2-C₂B₁₀H₁₀·(Et₂O)₂ (5 mg, 16.4 µmol, 1.0 eq) was added at −30 °C and the reaction was allowed to warm to room temperature. The reaction was monitored by ¹H and ¹¹B NMR spectroscopy. Crystals of 5 were obtained from the reaction solution by pentane diffusion at −30 °C.

¹H NMR (300.2 MHz, THF-d₈): δ = 7.82 (m, 2H, C₆H₄Ar), 7.39 (m, 2H, C₆H₄Ar), 6.96 (m, 4H, C₆H₄Ar) ppm.

¹¹B{¹H} NMR (96.3 MHz, THF-d₈): δ = 4.1, −3.2, −6.7, −8.4 ppm.

¹³C{¹H} NMR (75.5 MHz, THF-d₈): δ = 149.9 (C₆q,Ar), 133.5 (CH₆Ar), 125.6 (CH₆Ar), 124.9 (CH₆Ar), 117.9 (CH₆Ar) ppm.

Synthesis of 9-(4-bromobutoxy)-9-borafluorene

The compound 9-Br-9-borafluorene (10 mg, 41.2 µmol) was suspended in THF (1 mL). The reaction mixture was stirred at 60 °C for 1 h and was monitored by ¹¹B NMR spectroscopy. Removal of all volatiles in vacuo led to the isolation of 9-(4-bromobutoxy)-9-borafluorene. Crystals of the product were obtained from a CD₂Cl₂ solution by pentane diffusion at −30 °C.

¹H NMR (500.1 MHz, CD₂Cl₂): δ = 7.55 (m, 2H, C₆H₄Ar), 7.49 (m, 2H, C₆H₄Ar), 7.35 (m, 2H, C₆H₄Ar), 7.19 (m, 2H, C₆H₄Ar), 4.61 (t, 3JHH = 6.24 Hz, 2H, CH₂), 3.54 (t, 3JHH = 6.59 Hz, 2H, CH₂), 2.11 (m, 2H, CH₂), 2.00 (m, 2H, CH₂) ppm.

¹¹B NMR (160.5 MHz, CD₂Cl₂): δ = 45.0 ppm.

¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ = 152.8 (C₆q,Ar), 132.9 (CH₆Ar), 132.3 (CH₆Ar), 128.2 (CH₆Ar), 120.0 (CH₆Ar), 68.0 (CH₂), 34.2 (CH₂), 30.7 (CH₂), 29.8 (CH₂) ppm.

HRMS LIFDI calc. for [C₁₆H₁₆B₁O₁]⁺ = [M]⁺: 314.0472, found 314.0463.
Synthesis of 9-(Me₂S)-9-Br-9-borafluorene

The compound 9-Br-9-borafluorene (10 mg, 41.2 µmol) was dissolved in toluene (1 mL), one drop of Me₂S was added, and a colorless solid precipitated from the solution. The reaction mixture was stirred at room temperature overnight. Removal of all volatiles \textit{in vacuo} led to the formation of the Me₂S adduct in quantitative yield according to \(^1\text{H}\) and \(^{11}\text{B}\) NMR spectroscopy. Crystals of the product were obtained from a Me₂S solution by pentane diffusion at –30 °C.

\(^1\text{H}\) NMR (500.1 MHz, CD₂Cl₂): \(\delta = 7.64\) (m, 2H, \(CH_{Ar}\)), 7.54 (m, 2H, \(CH_{Ar}\)), 7.33 (m, 2H, \(CH_{Ar}\)), 7.23 (m, 2H, \(CH_{Ar}\)), 2.18 (s, 6H, \(CH_3\)) ppm.

\(^{11}\text{B}\) NMR (160.5 MHz, CD₂Cl₂): \(\delta = 0.3\) ppm.

\(^{13}\text{C}\{^1\text{H}\}\) NMR (125.8 MHz, CD₂Cl₂): \(\delta = 148.5\) (\(C_{q,Ar}\)), 131.2 (\(CH_{Ar}\)), 129.4 (\(CH_{Ar}\)), 127.6 (\(CH_{Ar}\)), 120.1 (\(CH_{Ar}\)), 20.7 (\(CH_3\)) ppm.
$^1$H NMR spectrum of 2b in CD$_2$Cl$_2$

$^{11}$B NMR spectrum of 2b in CD$_2$Cl$_2$
$^{13}$C$^{1}$H NMR spectrum of 2b in CD$_2$Cl$_2$

$^1$H NMR spectrum of 3a in CD$_2$Cl$_2$
$^{1}$H {^{11}B} NMR spectrum of 3a in CD$_2$Cl$_2$
\( ^{11}\text{B} \) NMR spectrum of 3a in CD\(_2\)Cl\(_2\)

\( ^{11}\text{B}\{^1\text{H}\} \) NMR spectrum of 3a in CD\(_2\)Cl\(_2\)

\( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum of 3a in CD\(_2\)Cl\(_2\)
$^1$H NMR spectrum of 3b in CD$_2$Cl$_2$

$^{11}$B NMR spectrum of 3b in CD$_2$Cl$_2$
$^{13}\text{C}[^1\text{H}]$ NMR spectrum of 3b in CD$_2$Cl$_2$

$^1\text{H}$ NMR spectrum of 9-(4-bromobutoxy)-9-borafluorene in CD$_2$Cl$_2$
$^{11}$B NMR spectrum of 9-(4-bromobutoxy)-9-borafluorene in CD$_2$Cl$_2$

$^{13}$C($^1$H) NMR spectrum of 9-(4-bromobutoxy)-9-borafluorene in CD$_2$Cl$_2$
$^1$H NMR spectrum of the 9-(Me$_2$S)-9-Br-9-borafluorene in CD$_2$Cl$_2$

$^{11}$B NMR spectrum of the 9-(Me$_2$S)-9-Br-9-borafluorene in CD$_2$Cl$_2$
$^{13}$C\text{${}^{1}$H} NMR spectrum of the 9-(Me$_2$S)-9-Br-9-borafluorene in CD$_2$Cl$_2$
Additional reactions

A clean reaction was observed for the synthesis of 5 when the reaction was carried out in THF-d₈ as a one pot synthesis with an excess of 9-Br-9-borafluorene, with the formation of a single new species by NMR spectroscopy (see below). As the ring-opened species arises from the deuterated THF solvent, the alkyl chain was not observed in the ¹H and ¹³C NMR spectrum. Compound 5 was not detected by HRMS (LIFDI) as it is an anion.

When this reaction was repeated in non-deuterated THF, removal of all volatiles in vacuo after the formation of 9-(4-bromobutoxy)-9-borafluorene led to the formation of some impurities. Continuing the reaction in THF-d₈ resulted in a mixture of compounds in the ¹H and ¹¹B NMR spectra.

The following NMR spectra show a comparison of the deuterated and non-deuterated 9-(4-bromobutoxy)-9-borafluorene and the reaction of the deuterated 9-(4-bromobutoxy)-9-borafluorene monitored by ¹H and ¹¹B NMR spectra.
$^1$H NMR spectrum (300.2 MHz, THF-d$_8$): Comparison of the deuterated (blue) and non-deuterated (red) 9-(4-bromobutoxy)-9-borafluorene.

$^1$H NMR spectrum (300.2 MHz, THF-d$_8$): Reaction before (blue) and after (red) the addition of 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$. 
\(^{13}\text{C}\,^{1\text{H}}\) NMR spectrum (75.5 MHz, THF-\text{d}_8): Reaction before (blue) and after (red) the addition of 1,2-Li_2-1,2-C_2B_{10}H_{10^-}(Et_2O)_2.

\(^{11}\text{B}\,^{1\text{H}}\) NMR spectrum (96.3 MHz, THF-\text{d}_8): Reaction before (blue) and after (red) the addition of 1,2-Li_2-1,2-C_2B_{10}H_{10^-}(Et_2O)_2.
$^1$H NMR spectrum (300.2 MHz, THF-d$_8$): Difference between the reaction of (impure) non-deuterated 9-(4-bromobutoxy)-9-borafluorene (red) and deuterated 9-(4-bromobutoxy)-9-borafluorene (blue) after the addition of 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$. 

![NMR spectrum image]
When 9-(Me$_2$S)-9-Br-9-borafluorene was reacted with 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$ in C$_6$D$_6$, solubility was low and the reaction led to a complex mixture, as observed by NMR spectroscopy and HRMS. When the same reaction was carried out in Me$_2$S, reaction between the solvent and 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$ formed a complex mixture from which a crystal of 1-MeS-2-(Me$_2$S-9-borafluorene)-1,2-C$_2$B$_{10}$H$_{10}$ was isolated and characterized by single-crystal X-ray diffraction. To confirm the reaction between the solvent and dilithium salt, as similar reactions are known for n-butyllithium, 25 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$·(Et$_2$O)$_2$ was dissolved in Me$_2$S. In this experiment 1-MeS-1,2-C$_2$B$_{10}$H$_{11}$ (calc. for [C$_3$H$_4$B$_{10}$S] = [M]: 190.2, found 190.1), 1,2-(MeS)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (calc. for [C$_4$H$_{16}$B$_{10}$S$_2$] = [M]: 236.2, found 236.1) were visible in GCMS, and $\mu$-1,2-CH$_2$-(1,2-C$_2$B$_{10}$H$_{11}$) (calc. for [C$_5$H$_{24}$B$_{20}$] $^-$ = [M]$^-$: 300.3884, found 300.3889), as well as compounds of higher mass were visible in the HRMS.

HRMS (APCI neg) of the reaction of Me$_2$S with 1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$(Et$_2$O)$_2$
GCMS of the reaction of Me₂S with 1,2-Li₂-1,2-C₂B₁₀H₁₀(Et₂O)₂

![GCMS Graph]

- C₂B₁₀H₁₂
- m/z = 190.1
- m/z = 236.1
Single-crystal X-ray diffraction

Table S1. Single-crystal X-ray diffraction data and structure refinements of 2b, 3a, 3b, 3a·THF, 5, 9-(Me2S)-9-Br-9-borafluorene, 1-MeS-2-(Me2S-9-borafluorene)-1,2-C2B10H10, and 9-(4-bromobutoxy)-9-borafluorene.

|          | 2b                  | 3a                  | 3b                  | 3a·THF            |
|----------|---------------------|---------------------|---------------------|-------------------|
| CCDC     | 2174245             | 2174247             | 2174246             | 2174248           |
| Empirical formula | C30H20B2 | C30H20B2 | C30H20B2 [+]solvent | 2(C30 H34 B12 O), |
| ρ calc/g cm⁻³ | 1.260 | 1.213 | 1.065 | 1.207 |
| F(000)   | 840 | 968 | 1680 | 614 |
| Crystal size/mm³ | 0.22×0.20×0.16 | 0.68×0.32×0.27 | 0.15×0.04×0.02 | 0.31×0.18×0.13 |
| Crystal colour, habit | yellow block | orange block | orange block | colourless block |
| μ/mm⁻¹ | 0.070 | 0.062 | 0.445 | 0.476 |
| Mr/g mol⁻¹ | 402.08 | 468.19 | 402.08 | 1172.71 |
| Temperature/K | 100(2) | 100(2) | 100(2) | 100(2) |
| Radiation, λ/Å | MoKα, 0.71073 | MoKα, 0.71073 | CuKα, 1.54184 | CuKα, 1.54184 |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | P2₁/n | P2₁/c | P2₁ | P̅ |
| a/Å     | 10.040(3) | 11.6705(5) | 9.81472(6) | 10.0646(3) |
| b/Å     | 14.612(6) | 11.4351(5) | 30.3107(2) | 11.5240(4) |
| c/Å     | 14.451(4) | 19.4944(8) | 16.86116(12) | 15.6916(5) |
| α°      | 90 | 90 | 90 | 105.086(3) |
| β°      | 90.177(9) | 99.7240(10) | 90.0056(6) | 98.763(3) |
| γ°      | 90 | 90 | 90 | 108.320(3) |
| Volume/Å³ | 2120.0(12) | 2564.21(19) | 5016.04(6) | 1612.85(9) |
| Z       | 4 | 4 | 8 | 4 |
| 2Θ/°    | 3.96–53.46 | 3.54–52.08 | 5.24–150.63 | 6.03–153.86 |
| Reflections collected | 40200 | 32404 | 255080 | 32353 |
| Unique reflections | 4510 | 5057 | 20250 | 12402 |
| Parameters / restraints | 289/0 | 383/0 | 1154/1 | 463/122 |
| Goof on F² | 1.076 | 1.032 | 1.039 | 1.046 |
| R₁ [I>2σ (I)] | 0.0443 | 0.0432 | 0.0575 | 0.0654 |
| wR₂ [all data] | 0.1072 | 0.1134 | 0.1629 | 0.1955 |
| Max./min. res. electron density/ e Å⁻³ | 0.33 / –0.26 | 0.30 / –0.26 | 0.39 / –0.28 | 0.30 / –0.35 |
| 5               | 9-(Me₂S)-9-Br-9-borafluorene | 1-Br-2-(Me₂S-9-borafluorene)-1,2-C₆B₁₀H₁₀ | 9-(4-bromobutoxy)-9-borafluorene |
|-----------------|------------------------------|-------------------------------------------|----------------------------------|
| CCDC            | 2174249                      | 2216647                                   | 2216648                          | 2216649                          |
| Empirical formula| C₃₀H₂₂Br₂Li₂O₁₃,             | C₁₆H₁₁BB₉S                               | C₁₇H₁₂B₁₁S₂                     | C₁₆H₁₂BBR₀                     |
| \(\rho_{calc}/g\cdot cm^{-3}\) | 1.132                        | 1.525                                     | 1.256                           | 1.513                           |
| \(F(000)\)      | 2392                         | 616                                       | 864                             | 640                             |
| Crystal size/mm³ | 0.24×0.13×0.12               | 0.28×0.20×0.03                           | 0.34×0.04×0.02                  | 0.21×0.03×0.03                  |
| Crystal colour, habit | yellow block                | colourless block                         | colourless needle               | colourless needle               |
| \(\mu/mm²\)    | 2.082                        | 5.445                                     | 2.180                           | 3.933                           |
| \(M_r/g\cdot mol^{-1}\) | 1146.60                     | 305.03                                    | 414.41                          | 315.01                          |
| Temperature/K    | 173.01(10)                   | 100(2)                                    | 100(2)                          | 100(2)                          |
| Radiation, \(\lambda/\AA\) | CuKα, 1.54184               | CuKα, 1.54184                             | CuKα, 1.54184                   | CuKα, 1.54184                   |
| Crystal system   | orthorhombic                 | monoclinic                                | monoclinic                      | monoclinic                      |
| Space group      | \(P2₁₂₂₁\)                   | \(P2₁/n\)                                 | \(P2₁/c\)                       | \(P2₁/c\)                       |
| \(a/\AA\)       | 10.14540(10)                | 11.8821(4)                                | 13.0013(3)                      | 16.3598(3)                      |
| \(b/\AA\)       | 15.55010(10)                | 6.7210(2)                                 | 19.0378(4)                      | 5.11900(10)                     |
| \(c/\AA\)       | 37.9243(2)                  | 17.0968(5)                                | 8.8640(2)                       | 16.5080(3)                      |
| \(\alpha/°\)    | 90                           | 90                                        | 90                              | 90                              |
| \(\beta/°\)     | 90                           | 103.399(3)                                | 93.062(2)                       | 90.050(2)                       |
| \(\gamma/°\)    | 90                           | 90                                        | 90                              | 90                              |
| Volume/\(\AA³\) | 5983.02(8)                  | 1328.18(7)                                | 2190.85(9)                      | 1382.48(4)                      |
| \(Z\)           | 4                            | 4                                         | 4                               | 4                               |
| \(2\Theta/°\)   | 4.66–151.03                 | 4.12–75.19                                | 3.40–74.50                      | 2.70–74.94                      |
| Reflections     | 131709                      | 11292                                    | 35742                           | 8247                            |
| collected       |                              |                                           |                                 |                                 |
| Unique reflections | 12305                        | 2694                                     | 8080                            | 2619                            |
| Parameters / restraints | 919 / 624                  | 156 / 0                                  | 275 / 0                         | 172 / 0                         |
| GooF on \(F^2\) | 1.020                        | 1.083                                     | 1.089                           | 1.084                           |
| \(R_I\) \([I>=2\sigma(I)]\) | 0.0519                      | 0.0268                                    | 0.0574                          | 0.0633                          |
| \(wR_2\) [all data] | 0.1512                      | 0.0718                                    | 0.1634                          | 0.0643                          |
| Max./min. res. electron density/ e \(\AA⁻³\) | 0.65 / −0.60                 | 0.75 / −0.66                              | 0.93 / −0.60                    | 0.36 / −0.28                    |
Figure S1. Solid state molecular structure of 2b from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Figure S2. Solid state molecular structure of 3a from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Figure S3. Solid state molecular structure of 3b from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms and solvent molecules are omitted for clarity. Only one of four symmetry-independent molecules is shown.
Figure S4. Solid state molecular structure of $3a\cdot$THF from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and solvent molecules and hydrogen atoms are omitted for clarity.

Figure S5. Solid state molecular structure of $5$ from single-crystal X-ray diffraction at 100 K, on the left with the lithium counterion and on the right from a different angle. Atomic displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms and the minor occupied components of disordered THF and alkyl groups are omitted for clarity. Only one of two symmetry-independent anions and cations are shown.

Figure S6. Solid state molecular structure of the dimethyl sulfide adduct of 9-Br-9-borafluorene, $9$-(Me$_2$S)-9-Br-9-borafluorene, from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.
Figure S7. Solid state molecular structure of an isolated product \textbf{1-MeS-2-(Me$_2$S-9-borafluorene)-1,2-C$_2$B$_{10}$H$_{10}$} from the reaction in SMe$_2$ described above from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Figure S8. Solid state molecular structure of \textbf{9-(4-bromobutoxy)-9-borafluorene} from single-crystal X-ray diffraction at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.
Geometry tables

Scheme S1. Atom labeling in compound 2b.

Table S2. Selected bond lengths [Å], distances [Å], and angles [°] in the crystal and calculated at the B3LYP-d3bj and ωB97X-D level of theory (starting molecule).

|                  | 2a calc. B3LYP-d3bj | 2a calc. ωB97X-D | 2b crystal | 2b calc. B3LYP-d3bj | 2b calc. ωB97X-D |
|------------------|----------------------|-------------------|------------|----------------------|-------------------|
| C1–C2            | 1.674                | 1.674             | 1.426(2)   | 1.420                |
| C1–C6 / C2–C3    | –                    | –                 | 1.402(2) / 1.405(2) | 1.402 |
| C3–C8 / C3–C4    | –                    | –                 | 1.388(2) / 1.389(2) | 1.393 |
| C5–C8            | –                    | –                 | 1.396       | 1.393                |
| B1–C2a           | 1.591                | 1.600             | 1.554(2) / 1.551(2) | 1.556 |
| B1–C14a          | 1.566                | 1.570             | 1.571(2) / 1.571(2) | 1.564 |
| B1–C7a           | 1.562                | 1.566             | 1.568(2) / 1.571(2) | 1.565 |
| B2–B2            | 3.025                | 3.054             | 3.186(2)   | 3.083                |
| B2–C15a          | 3.428                | 3.487             | 3.252(2) / 3.354(2) | 3.231 |
| C10–C13a         | 1.426                | 1.418             | 1.417(2) / 1.415(2) | 1.414 |
| C7–C8a           | 1.421                | 1.413             | 1.416(2) / 1.419(2) | 1.413 |
| C8–C11a          | 1.480                | 1.483             | 1.487(2) / 1.489(2) | 1.489 |
| C1–B1–C14a       | 129.0                | 128.8             | 128.1(1) / 128.5(1) | 126.7 |
| C14–B1–C7a       | 105.1                | 105.0             | 103.9(1) / 103.7(1) | 104.2 |
| C7–B1–C1a        | 125.1                | 125.1             | 127.5(1) / 127.5(1) | 128.9 |
| ΣC–B1–C8         | 359.2                | 358.9             | 359.5(3) / 359.8(3) | 359.8 |
| C2–C1–B7, C1–C7–B2 | 115.0              | 115.6             | 124.9(1) / 123.6(1) | 120.4 |
| B1–C1–C2–B2      | 5.8                  | 6.3               | 13.2(2)    | 8.5                  | 9.4               |
Values are given for both borafluorene moieties of B1 and B2, respectively, for the crystal of 2b.

Scheme S2. Atom labeling in compounds 3a and 3b.

Table S3. Selected bond lengths [Å], distances [Å], and angles [°] in the crystals and calculated structures of 3a and 3b at the B3LYP-d3bj and oB97X-D level of theory.

|                  | 3a crystal | 3a B3LYP-d3bj | 3a oB97X-D | 3b crystal | 3b B3LYP-d3bj | 3b oB97X-D | 3a-THF crystal |
|------------------|------------|---------------|------------|------------|---------------|------------|---------------|
|                  |            |               |            |            |               |            |               |
| C1–C2            | 1.718(2)   | 1.712         | 1.693      | 1.460(8),  | 1.459(7),     | 1.429      | 1.717(2)      |
|                  |            |               |            | 1.425(7),  |               |            |               |
|                  |            |               |            | 1.425(7)   |               |            |               |
| C2–C27           | –          | –             | –          | 1.399(7),  | 1.401(7),     | 1.399      | –             |
|                  |            |               |            | 1.423(7),  |               |            |               |
|                  |            |               |            | 1.402(7)   |               |            |               |
| C27–C28          | –          | –             | –          | 1.393(7),  | 1.389(8),     | 1.394      | –             |
|                  |            |               |            | 1.380(8),  |               |            |               |
|                  |            |               |            | 1.396(7)   |               |            |               |
| C28–C29          | –          | –             | –          | 1.403(7),  | 1.360(9),     | 1.390      | –             |
|                  |            |               |            | 1.403(9),  |               |            |               |
|                  |            |               |            | 1.390(8)   |               |            |               |
| C29–C30          | –          | –             | –          | 1.364(8),  | 1.402(9),     | 1.393      | –             |
|                  |            |               |            | 1.417(8),  |               |            |               |
|                  |            |               |            | 1.376(8)   |               |            |               |
| C30–C1           | –          | –             | –          | 1.379(7),  | 1.407(8),     | 1.398      | –             |
|                  |            |               |            | 1.384(8),  |               |            |               |
|                  |            |               |            | 1.391(8)   |               |            |               |
| B1–C1            | 1.551(2)   | 1.549         | 1.555      | 1.555(8),  | 1.548(8),     | 1.541      | 1.624(3)      |
|                  |            |               |            | 1.565(8),  |               |            |               |
|                  |            |               |            | 1.554(8)   |               |            |               |
| B1–C3            | 1.546(2)   | 1.549         | 1.551      | 1.545(9),  | 1.591(9),     | 1.570      | 1.622(2)      |
|                  | B1–C10 | B2–C2  | B2–C11 | B2–C15 | C3–C4  | C9–C10 | C4–C9  | B1–C1–C2 | B2–C2–C1 | C1–B1–C10 / C10–B1–C3 / C3–B1–C1 | ΣC–B1–C |
|------------------|--------|--------|--------|--------|--------|--------|--------|----------|----------|----------------------------------|----------|
|                  | 1.538(2) | 1.541  | 1.544  | 1.567(9), 1.554(9), 1.561(9), 1.533(9) | 1.563  | 1.567  | 1.541(2) | 1.572(2) | 1.568  | 1.538(2) / 1.597(8), 1.570(8), 1.573(8) | 1.553(9), 1.604(9) |
|                  | 1.607(2) | 1.599  | 1.604  | 1.578(9), 1.577(8), 1.557(8), 1.564(8) | 1.563  | 1.567  | 1.541(2) | 1.572(2) | 1.568  | 1.538(2) / 1.597(8), 1.570(8), 1.573(8) | 1.553(9), 1.604(9) |
|                  | 1.557(2) | 1.557  | 1.562  | 1.558(8), 1.557(8), 1.564(8) | 1.563  | 1.567  | 1.541(2) | 1.572(2) | 1.568  | 1.538(2) / 1.597(8), 1.570(8), 1.573(8) | 1.553(9), 1.604(9) |
|                  | 1.424(2) | 1.430  | 1.422  | 1.401(9), 1.431(9), 1.457(9), 1.423(8) | 1.432  | 1.424  | 1.419(3) | 1.492(2) | 1.495  | 1.470(10), 1.450(10), 1.440(10), 1.545(8) | 1.491(9), 1.577(8), 1.556(9), 1.604(8) |
|                  | 1.406(2) | 1.410  | 1.403  | 1.415(9), 1.421(9), 1.414(8), 1.396(8) | 1.405  | 1.399  | 1.399(2) | 1.492(2) | 1.495  | 1.470(10), 1.450(10), 1.440(10), 1.545(8) | 1.491(9), 1.577(8), 1.556(9), 1.604(8) |
|                  | 1.114(1) | 114.2  | 114.3  | 116.6(5), 117.9(5), 117.5(4), 116.9(5) | 117.3  | 117.2  | 114.0(1) | 118.5(1) | 118.8  | 122.3(5), 122.9(4), 124.0(5), 122.3(5) | 118.5(5), 117.9(5), 117.5(4), 116.9(5) |
|                  | 119.5(1) | 105.5(1) | 135.0(1) | 122.3(5), 122.9(4), 124.0(5), 122.3(5) | 122.7  | 122.7  | 119.6(1) | 120.0 / 105.2 / 134.8 | 119.9 / 105.1 / 134.9 | 118.4(5) / 104.0(5) / 137.6(5), 117.5(5) / 103.8(5) / 138.7(5), 116.9(5) / 102.4(5) / 140.6(5), 118.8(5) / 103.7(5) / 137.5(5) | 118.5 / 103.5 / 138.0 | 118.5 / 103.3 / 138.2 | 112.1(1) / 100.0(1) / 123.9(1) |
|                  | 360.0 | 360.0 | 359.9 | 360.0 | 360.0 | 360.0 | 336.0 | 120.1 / 119.6 / 119.7 | 119.9 / 119.9 / 119.6 | 120.6(5) / 119.3(5) / 120.1(5), 117.8(5) / 120.9(5) / 121.3(5), 119.1(5) / 119.2(5) / 121.7(5), 120.9 / 119.9 / 119.8 / 119.2 | 118.3(1) / 122.2(2) / 118.1(1) |
|                  | 2a-3a | 2b-3b |
|------------------|-------|-------|
| C1–C1*           | 1.689 | 1.422 |
| B1–B1            | 3.229 | 3.101 |
| B1–C1            | 1.551 | 1.534 |
| B1–C3            | 1.551 | 1.577 |
| B1–C10           | 1.548 | 1.554 |
| B1–C2            | 1.638 | 1.610 |
| B1–C15           | 1.596 | 1.597 |
| B1–C22           | 1.723 | 1.733 |
| B1–C11           | 1.771 | 1.750 |
| B1–C1–C2         | 114.6 | 118.1 |
| B2–C2–C1         | 123.0 | 126.4 |
| B1–C1–C2–B2     | 2.6   | 4.7   |
| C2–C1–B1–C3     | 175.0 | 172.6 |
| C15–C16–C21–C22 | 176.2 | 176.6 |

* Four symmetry-independent molecules are present in the crystal structure of 3b. Values are given for all four molecules.

Table S4. Selected bond lengths [Å], distances (B–B, B–C15 [Å]), and angles [°] of the calculated transition state structures at the oB97X-D level of theory.
Photophysical data

2b

Figure S9. Excitation (solid) and emission (dashed) spectra of 2b in the solid state.

Figure S10. Absorption spectra of compound 2b in toluene.

Figure S11. Normalized emission spectra of compound 2b in toluene.
**3a**

Figure S12. Absorption spectra of 3a in hexane (black), toluene (blue) and CH\textsubscript{2}Cl\textsubscript{2} (red).

Figure S13. Emission spectra of 3a in hexane (black), toluene (blue), CH\textsubscript{2}Cl\textsubscript{2} (turquoise) and in the solid state (green).

Figure S14. Excitation spectra of 3a in hexane (black), toluene (blue), CH\textsubscript{2}Cl\textsubscript{2} (turquoise) and in the solid state (green).
3b

Figure S15. Excitation (solid) and emission (dashed) spectra of 3b in the solid state.

Figure S16. Absorption (black, solid), emission (black, dashed) and excitation (red, dashed) spectra of 3b in hexane initially and after 3 h (green, dashed).
Cyclic voltammetry

Figure S17. Cyclic voltammograms of 2b measured in CH$_2$Cl$_2$ with [nBu$_4$N][PF$_6$] as the electrolyte with a scan rate of 250 mVs$^{-1}$. All measurements are referenced to the Fc/Fc$^+$ ion couple.

Figure S18. Cyclic voltammograms of 3a measured in CH$_2$Cl$_2$ with [nBu$_4$N][PF$_6$] as the electrolyte with a scan rate of 250 mVs$^{-1}$. All measurements are referenced to the Fc/Fc$^+$ ion couple.
Figure S19. Cyclic voltammograms of 3b measured in CH₂Cl₂ with [nBu₄N][PF₆] as the electrolyte with a scan rate of 250 mVs⁻¹. All measurements are referenced to the Fc/Fc⁺ ion couple.

Table S5. Reduction and oxidation potentials of 2b, 3a and 3b.

| compound | 1ˢᵗ reduction | 2ⁿᵈ reduction | 1ˢᵗ oxidation |
|----------|----------------|----------------|----------------|
| 2a       | E_{pc} = -1.50 V | E_{pc} = -1.96 V | E_{pa} = 0.98 V |
| 3a       | E_{1/2} = -1.03 V | E_{pc} = -2.14 V | E_{pa} = 0.84 V |
| 3b       | E_{1/2} = -1.17 V | E_{pc} = -1.85 V |                |

[a] partially reversible.
### DFT and TD-DFT results

Cartesian coordinates of the optimized structures of 2a, 2b, 3a and 3b in the transition state calculations

| 64 | M062X 2a (E = −1304.38314 a.u.) | 64 | M062X 751 2a/3a (E = −1304.336144 a.u.) |
|----|----------------------------------|----|------------------------------------------|
| H  | −1.674587000                    | H  | −0.407583000                             |
| B  | −2.396944000                    | B  | −0.519596000                             |
| C  | 1.869236000                     | C  | −3.686268000                             |
| C  | −0.488890000                    | C  | 0.004446000                              |
| C  | −1.674526000                    | B  | 1.125593000                              |
| C  | −3.097740000                    | H  | −0.662770000                             |
| C  | −0.488843000                    | H  | −2.894686000                             |
| C  | −0.471956000                    | C  | −2.083154000                             |
| C  | −1.532345000                    | B  | −0.121377000                             |
| H  | −1.930180000                    | B  | 1.081675000                              |
| H  | −2.379357000                    | C  | 3.142505000                              |
| C  | −4.727725000                    | C  | −1.706638000                             |
| C  | 0.076294000                     | C  | 1.324505000                              |
| B  | −2.374104000                    | H  | 4.040090000                              |
| C  | −3.581590000                    | B  | 1.342505000                              |
| B  | −5.689301000                    | H  | −0.398674000                             |
| B  | −1.930200000                    | H  | 1.321710000                              |
| C  | −2.397140400                    | B  | −1.138165000                             |
| C  | 0.353988000                     | C  | −0.553850000                             |
| C  | −0.70745000                     | H  | −0.257261000                             |
| C  | 2.295324000                     | C  | −1.449590000                             |
| B  | 3.367848000                     | H  | −0.135419000                             |
| C  | −4.699862000                    | H  | −0.386647000                             |
| H  | −1.723287000                    | B  | −1.846269000                             |
| H  | 2.355234000                     | C  | −1.941430000                             |
| B  | −3.255077000                    | H  | −2.674379000                             |
| C  | 2.295324000                     | C  | −0.220940000                             |
| H  | 3.367848000                     | C  | 3.7669670000                             |
| H  | −3.143274000                    | B  | 1.959389000                              |
| B  | 1.470733000                     | B  | 2.052741000                              |
| B  | −2.355139000                    | H  | −2.234852000                             |
| C  | −3.143175000                    | B  | 2.113624000                              |
| H  | 0.378957000                     | H  | −2.726184000                             |
| H  | −4.699859000                    | H  | −3.597266000                             |
| H  | 3.255077000                     | H  | 0.620490000                              |
| H  | 0.340647000                     | H  | −0.152270000                             |
| H  | 3.136784000                     | H  | −0.406800000                             |
| H  | 3.367848000                     | H  | −0.914630000                             |
| H  | 3.367848000                     | H  | −0.948351000                             |
| H  | 3.367848000                     | H  | −6.075425000                             |
| H  | 2.326141000                     | H  | −7.046154000                             |
| H  | 2.381679000                     | H  | −6.003880000                             |
| C  | 0.942537000                     | H  | −6.916415000                             |
| B  | 2.381679000                     | B  | −0.092312000                             |
| C  | 0.942537000                     | C  | 0.493106000                              |
| H  | 0.711040000                     | B  | 1.415280000                              |
| H  | −0.701317000                    | H  | −0.701317000                             |
| H  | 1.470733000                     | H  | −0.701317000                             |
| B  | −3.231830000                    | H  | −0.701317000                             |
| B  | 0.353610000                     | H  | −0.701317000                             |
| H  | −0.705288000                    | H  | −0.701317000                             |
| H  | 1.722891000                     | H  | −0.701317000                             |
| H  | 2.354737000                     | H  | −0.701317000                             |
| H  | 2.295083000                     | H  | −0.701317000                             |
| H  | 1.470634000                     | H  | −0.701317000                             |
| H  | 1.869285000                     | H  | −0.701317000                             |
| H  | 3.150758000                     | H  | −0.701317000                             |
| H  | 4.009827000                     | H  | −0.701317000                             |
| H  | 3.329263000                     | H  | −0.701317000                             |
| H  | 4.330770000                     | H  | −0.701317000                             |
| B  | 4.330770000                     | B  | −0.701317000                             |
| C  | 2.381991000                     | B  | −0.701317000                             |
| C  | 0.942748000                     | H  | −0.701317000                             |
| H  | 0.114756000                     | H  | −0.701317000                             |
| C  | 0.739044000                     | H  | −0.701317000                             |

S41
|      |         |         |         |
|------|---------|---------|---------|
| H    | 5.342206| 1.759171| 2.829741|
| C    | 3.475352| 0.932181| 3.512285|
| H    | 3.487539| 1.470954| 4.453890|
| C    | 2.421768| 0.075346| 3.209774|
| H    | 1.615097| -0.069181| 3.921353|
| C    | 2.402963| -0.606815| 1.996016|
| H    | 1.595766| -1.306740| 1.788480|
|      | x  | y  | z    |     |      |      |
|------|----|----|------|-----|------|------|
| C    | -3.784105000 | -1.019414000 | 0.227679000 |
| C    | -0.107061000 | -1.211044000 | 0.178587000 |
| B    | 1.028634000  | 0.062209000  | -0.210380000 |
| B    | -2.021785000 | 0.599729000  | -0.088230000 |
| C    | 2.209790000  | -1.118985000 | -2.328961000 |
| H    | 1.287694000  | -1.115080000 | -2.940152000 |
| C    | -1.435475000 | -0.831611000 | 0.182665000 |
| C    | 0.185328000  | -2.581193000 | 0.307235000 |
| C    | 1.217894000  | -2.918498000 | 0.320805000 |
| C    | -0.852061000 | -3.000755000 | 0.410120000 |
| H    | -0.619454000 | -4.557429000 | 0.501129000 |
| C    | -2.196155000 | -3.094836000 | 0.399685000 |
| H    | 2.980476000  | -3.838847000 | 0.477606000 |
| H    | -2.480242000 | -1.743559000 | 0.283094000 |
| H    | -3.578105000 | 0.373525000  | 0.037343000 |
| C    | -5.057959000 | -1.550090000 | 0.340985000 |
| H    | -5.209821000 | -2.617297000 | 0.482203000 |
| C    | -6.157835000 | -0.689991000 | 0.277585000 |
| H    | -7.161235000 | -1.093693000 | 0.370794000 |
| H    | -5.978042000 | 0.678148000  | 0.103696000 |
| H    | -6.841048000 | 1.335338000  | 0.057176000 |
| C    | -4.689239000 | 1.207553000  | -0.022978000 |
| H    | -4.566736000 | 2.278140000  | -0.160830000 |
| C    | 2.227950000  | -0.584305000 | -1.042980000 |
| C    | 3.372166000  | -1.654920000 | -2.878883000 |
| H    | 3.358718000  | -2.063166000 | -3.885992000 |
| C    | 4.557660000  | -1.674406000 | -2.141275000 |
| H    | 5.456828000  | -2.099362000 | -2.576891000 |
| C    | 4.592892000  | -1.156272000 | -0.850861000 |
| C    | 5.516425000  | -1.180630000 | -0.278838000 |
| C    | 3.428630000  | -0.611976000 | -0.396370000 |
| C    | 3.250223000  | 0.008576000  | 1.021234000 |
| C    | 4.218396000  | 0.271202000  | 1.982833000 |
| C    | 5.257914000  | 0.005412000  | 1.814227000 |
| H    | 3.846816000  | 0.916532000  | 3.160745000 |
| H    | 5.600646000  | 1.136157000  | 3.910540000 |
| C    | 2.522385000  | 1.292102000  | 3.385037000 |
| H    | 2.251667000  | 1.800282000  | 4.304943000 |
| C    | 1.550466000  | 1.016333000  | 2.426081000 |
| H    | 0.514680000  | 1.302514000  | 2.591310000 |
| C    | 1.912530000  | 0.366212000  | 1.249624000 |
| H    | 0.808190100  | -0.531815000 | 0.902210000 |
| C    | -1.552132000 | 2.989171000  | -0.946336000 |
| C    | -1.082986000 | 1.721212000  | -0.550663000 |
| C    | 0.306215000  | 1.433886000  | -0.644068000 |
| C    | 1.157897000  | 2.439551000  | -1.126350000 |
| C    | 0.671944000  | 3.681975000  | -1.509144000 |
| C    | -0.692003000 | 3.965828000  | -1.419423000 |
| H    | -2.616006000 | 3.020103000  | -0.884694000 |
| H    | 2.223910000  | 2.241118000  | -1.203237000 |
| H    | 1.358722000  | 4.435437000  | -1.884793000 |
| H    | -1.071532000 | 4.937065000  | -1.721701000 |
| Column 1 | Column 2 | Column 3 |
|----------|----------|----------|
| H        | -0.20637100 | 1.16552300 | 1.82897800 |
| B        | -0.48475400 | 1.38892200 | -1.98268500 |
| C        | -3.98708100 | -1.27456900 | 0.34583400 |
| C        | -0.35180100 | -1.65938500 | -0.27097000 |
| B        | 0.77076200  | -0.61695800 | -0.54688000 |
| H        | -0.79318300 | 0.54111300  | -2.74599500 |
| H        | -2.67401000 | 2.71432300  | -1.94651600 |
| B        | -2.19521200 | 0.23217800  | -0.13705400 |
| C        | 2.25135800  | -1.68749300 | -2.27054050 |
| C        | 1.34062300  | -1.79858300 | -2.85779600 |
| C        | -1.22824600 | 1.40511800  | -0.43619500 |
| B        | -1.36644400 | 2.93503900  | 0.266409000 |
| H        | -0.06443500 | 3.49644200  | -3.30156700 |
| C        | -1.65902800 | -1.21069900 | -0.07568600 |
| B        | 1.18018800  | 1.95864500  | -1.72504900 |
| B        | 1.95617600  | 4.37765200  | 0.25614100  |
| H        | -0.98176500 | 5.15654600  | -0.98626000 |
| C        | 0.41215600  | 0.94059200  | -0.58733200 |
| B        | -0.12804800 | 1.76928900  | 0.81922000  |
| H        | -0.13320300 | -3.05449000 | -0.18025100 |
| H        | 0.86567800  | -3.45427200 | -0.32500100 |
| H        | 0.57112200  | 4.16002600  | 1.47392800  |
| B        | -0.07167400 | 3.08079100  | 2.29214400  |
| H        | 2.40883300  | 1.89965600  | 0.53730000  |
| B        | -0.60503100 | 4.04703900  | -0.88191300 |
| C        | -1.19179500 | -3.01857700 | 0.97383000  |
| H        | -1.00423300 | -4.98626000 | 0.16567300  |
| B        | -1.59223400 | 2.69685900  | -1.46739900 |
| C        | -2.50395600 | -3.44312100 | 0.29179700  |
| H        | -3.30585500 | -4.44500500 | 0.50542500  |
| B        | 0.29649100  | 3.46050900  | 0.55379000  |
| H        | 2.03195100  | 1.47907500  | -2.38697400 |
| H        | -2.73671100 | -2.07639300 | 0.20173800  |
| B        | 1.40234500  | 2.19163500  | 0.00709500  |
| B        | -2.29308800 | 3.11919700  | 0.97854500  |
| C        | -3.71393600 | 0.11462200  | -0.18047040 |
| B        | 1.09782400  | 3.58956500  | -0.03919800 |
| C        | -5.27127600 | -1.71074500 | 0.62880200  |
| C        | -5.48683800 | -2.76442200 | 0.78127400  |
| C        | -6.30456600 | -0.76154600 | 0.71966000  |
| H        | -7.31493300 | -1.09410300 | 0.40919200  |
| C        | -6.05377200 | 0.59600000  | 0.52589980  |
| H        | -6.86709000 | 1.31098100  | 0.59913500  |
| C        | -4.75313400 | 1.07313400  | 0.23937200  |
| H        | -4.55570500 | 2.09472100  | -0.09067200 |
| C        | 2.18457900  | -1.10719100 | -0.99533500 |
| C        | 3.46437000  | -0.69597600 | -0.27043400 |
| C        | 3.94319500  | -2.51966800 | -3.82619900 |
| C        | 4.63776500  | -1.90687000 | -2.08480100 |
| H        | 5.58698200  | -2.28912800 | -2.49723700 |
| C        | 4.58716600  | -1.42729200 | -0.79999700 |
| C        | 5.49363100  | -1.36643000 | -0.20573800 |
| C        | 3.37481800  | -0.99601200 | -0.24139300 |
| C        | 3.34047500  | -0.64120000 | -0.51238000 |
| C        | 4.36164100  | 0.37821000  | 1.61280100  |
| H        | 5.18689600  | 0.63397400  | 0.95613300  |
| C        | 4.28993000  | 0.93613600  | 2.88569500  |
| H        | 5.07728700  | 1.60214900  | 3.22588100  |
| C        | 3.19826600  | 0.66424300  | 3.71470600  |
| C        | 3.13826400  | 1.11028000  | 4.70248400  |
| C        | 2.18981200  | -0.18605600 | 3.26577500  |
| C        | 1.34563800  | -0.42010700 | 3.90746200  |
| C        | 2.26683100  | -0.75339800 | 1.99362400  |
| C        | 1.50106400  | -1.45388300 | 1.67662500  |
Cartesian coordinates of optimized structures of 2a, 2b, 3a and 3b for the TD-DFT calculations, orbital energies, and transitions

**TD-DFT calculations 2a:**

![Calculated absorption spectrum](image)

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Orbital | Energy [eV] | Symmetry |
|-------|----------|----------------|----|----------|---------|-------------|----------|
| 1     | 2.77     | 448.08         | 0.0026 | Singlet-A | L+4     | -0.41       | A        |
| 2     | 2.88     | 430.84         | 0.0002 | Singlet-A | L+3     | -0.09       | A        |
| 3     | 3.77     | 329.00         | 0.0019 | Singlet-A | L+2     | -0.29       | A        |
| 4     | 3.93     | 315.36         | 0.1006 | Singlet-A | L+1     | -1.72       | A        |
| 5     | 3.97     | 312.18         | 0.0363 | Singlet-A | HOMO    | -2.04       | A        |
| 6     | 4.02     | 308.27         | 0.0042 | Singlet-A | HOMO+1  | -7.53       | A        |
| 7     | 4.31     | 287.89         | 0.0582 | Singlet-A | HOMO+2  | -7.86       | A        |
| 8     | 4.53     | 273.71         | 0.0468 | Singlet-A | HOMO+3  | -8.57       | A        |
| 9     | 4.65     | 266.87         | 0.0024 | Singlet-A | HOMO+4  | -8.58       | A        |
| 10    | 4.78     | 259.22         | 0.0104 | Singlet-A | HOMO+5  | -8.94       | A        |

**TD-DFT CAMB3LYP/6-31+G(d,p), gas phase**

Table S6: Lowest energy singlet electronic transition of 2a (TD-DFT CAM-B3LYP/6-31+G(d,p), gas phase).

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|----------|----------------|----|----------|---------------------|-----------|
| 1     | 2.77     | 448.08         | 0.0026 | Singlet-A | H-1→L+1 (22%), HOMO→LUMO (75%) | 0.60 |
| 2     | 2.88     | 430.84         | 0.0002 | Singlet-A | H-1→LUMO (51%), HOMO→L+1 (46%) | 0.60 |
| 3     | 3.77     | 329.00         | 0.0019 | Singlet-A | H-2→LUMO (12%), H-1→LUMO (35%), HOMO→L+1 (45%) | 0.60 |
| 4     | 3.93     | 315.36         | 0.1006 | Singlet-A | H-3→LUMO (14%), H-1→L+1 (54%), HOMO→LUMO (20%) | 0.60 |
| 5     | 3.97     | 312.18         | 0.0363 | Singlet-A | H-3→LUMO (54%), H-1→L+1 (21%) | 0.61 |
| 6     | 4.02     | 308.27         | 0.0042 | Singlet-A | H-3→L+1 (17%), H-2→LUMO (50%), H-1→LUMO (11%) | 0.62 |
| 7     | 4.31     | 287.89         | 0.0582 | Singlet-A | H-4→LUMO (50%), H-3→LUMO (11%), H-2→L+1 (22%) | 0.63 |
| 8     | 4.53     | 273.71         | 0.0468 | Singlet-A | H-5→LUMO (13%), H-4→L+1 (21%), H-3→L+1 (44%), H-2→LUMO (10%) | 0.62 |
| 9     | 4.65     | 266.87         | 0.0024 | Singlet-A | H-5→LUMO (44%), H-3→L+1 (25%), H-2→LUMO (10%) | 0.65 |
| 10    | 4.78     | 259.22         | 0.0104 | Singlet-A | H-5→L+1 (20%), H-4→LUMO (14%), H-3→LUMO (13%), H-2→L+1 (32%) | 0.63 |
| 11    | 4.85     | 255.67         | 0.0016 | Singlet-A | H-5→LUMO (17%), H-4→L+1 (17%), H-12→LUMO (22%), H-7→LUMO (11%) | 0.44 |
| 12    | 4.85     | 255.67         | 0.0016 | Singlet-A | H-14→LUMO (22%), H-12→L+1 (11%), H-9→LUMO (10%), HOMO→L+2 (14%) | 0.50 |
| 13    | 4.90     | 253.02         | 0.0026 | Singlet-A | H-1→L+3 (10%), HOMO→L+2 (52%) | 0.68 |
| 14    | 5.15     | 240.97         | 1.0913 | Singlet-A | H-2→L+1 (18%), H-1→L+2 (26%), HOMO→L+2 (46%) | 0.71 |
| 15    | 5.21     | 237.82         | 0.1028 | Singlet-A | H-2→L+1 (18%), H-1→L+2 (26%), HOMO→L+3 (46%) | 0.71 |
| 16    | 5.24     | 236.69         | 0.0552 | Singlet-A | H-2→L+1 (18%), H-1→L+2 (26%), HOMO→L+3 (46%) | 0.71 |
| 17    | 5.29     | 234.50         | 0.0072 | Singlet-A | H-6→LUMO (12%), LUMO→L+1 (50%) | 0.68 |
| 18    | 5.30     | 233.89         | 0.0003 | Singlet-A | H-6→LUMO (10%), H-11→LUMO (14%), H-10→L+1 (17%), H-9→LUMO (20%) | 0.44 |
| 19    | 5.49     | 225.84         | 0.1545 | Singlet-A | H-6→LUMO (59%) | 0.71 |
| 20    | 5.52     | 224.63         | 0.0341 | Singlet-A | H-8→LUMO (20%), H-6→L+1 (24%), H-5→L+1 (36%) | 0.68 |
| 21    | 5.53     | 224.13         | 0.0296 | Singlet-A | H-3→L+2 (44%), HOMO→L+3 (33%) | 0.71 |
| 22    | 5.59     | 221.98         | 0.0722 | Singlet-A | H-3→L+2 (44%), HOMO→L+3 (33%) | 0.71 |
| 23    | 5.71     | 216.98         | 0.0023 | Singlet-A | H-4→L+2 (12%), H-1→L+3 (13%), HOMO→L+9 (10%) | 0.64 |
| 24    | 5.78     | 214.34         | 0.0021 | Singlet-A | H-3→L+3 (17%), H-2→L+2 (16%), HOMO→L+6 (11%) | 0.59 |
| 25    | 5.79     | 214.05         | 0.0034 | Singlet-A | H-7→LUMO (71%) | 0.34 |
Orbitals relevant to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions

- LUMO: $-2.04 \text{ eV}$
- LUMO+1: $-1.72 \text{ eV}$
- HOMO: $-7.53 \text{ eV}$
- HOMO-1: $-7.86 \text{ eV}$

Isovalue = 0.03
TD-DFT CAMB3LYP/6-31+G(d,p), gas phase

Table S7: Lowest energy singlet electronic transition of 3a (TD-DFT CAM-B3LYP/6-31+G(d,p), gas phase).

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|---------|----------------|-----|----------|---------------------|---------|
| 1     | 2.93    | 422.45         | 0.0014 | Singlet-A | H-1→LUMO (85%) | 0.55    |
| 2     | 3.74    | 331.07         | 0.0403 | Singlet-A | HOMO→LUMO (64%), HOMO→L+1 (13%) | 0.29    |
| 3     | 3.99    | 310.81         | 0.0153 | Singlet-A | H-4→LUMO (39%), H-1→L+1 (39%) | 0.65    |
| 4     | 4.25    | 291.41         | 0.004  | Singlet-A | H-2→LUMO (59%), H-2→L+1 (13%), HOMO→LUMO (12%) | 0.23    |
| 5     | 4.39    | 282.10         | 0.3311 | Singlet-A | H-4→LUMO (39%), H-1→L+1 (33%) | 0.65    |
| 6     | 4.61    | 269.21         | 0.1259 | Singlet-A | H-6→LUMO (63%), H-3→LUMO (11%) | 0.65    |
| 7     | 4.67    | 265.75         | 0.0038 | Singlet-A | H-5→LUMO (12%), H-11→LUMO (25%), H-7→LUMO (14%), HOMO→L+1 (17%) | 0.38    |
| 8     | 4.76    | 260.51         | 0.0084 | Singlet-A | H-3→LUMO (62%) | 0.28    |
| 9     | 4.81    | 257.75         | 0.0091 | Singlet-A | HOMO→L+1 (46%) | 0.36    |
| 10    | 5.09    | 243.52         | 0.0208 | Singlet-A | H-5→LUMO (16%), H-2→L+2 (11%), HOMO→L+5 (18%) | 0.47    |
| 11    | 5.12    | 242.11         | 0.0008 | Singlet-A | H-14→LUMO (21%), H-13→LUMO (29%) | 0.42    |
| 12    | 5.15    | 240.63         | 0.0688 | Singlet-A | H-5→LUMO (13%), H-2→L+2 (10%) | 0.46    |
| 13    | 5.17    | 239.65         | 0.0991 | Singlet-A | H-6→L+1 (14%), H-4→L+1 (13%) | 0.56    |
| 14    | 5.20    | 238.29         | 0.2662 | Singlet-A | H-5→LUMO (10%), HOMO→L+2 (57%) | 0.68    |
| 15    | 5.28    | 235.03         | 0.0206 | Singlet-A | H-9→LUMO (15%), H-8→LUMO (22%) | 0.50    |
| 16    | 5.28    | 234.80         | 0.3035 | Singlet-A | H-6→LUMO (12%), H-4→L+1 (38%) | 0.61    |
| 17    | 5.37    | 230.98         | 0.0188 | Singlet-A | H-9→LUMO (13%), H-5→LUMO (28%), H-3→L+2 (11%) | 0.39    |
| 18    | 5.39    | 230.19         | 0.0023 | Singlet-A | H-2→LUMO (13%), H-2→L+1 (44%) | 0.29    |
| 19    | 5.46    | 227.26         | 0.0021 | Singlet-A | H-11→LUMO (24%), H-7→LUMO (50%) | 0.35    |
| 20    | 5.62    | 220.79         | 0.1826 | Singlet-A | H-10→LUMO (16%), H-9→LUMO (15%), H-1→L+3 (26%) | 0.56    |
| 21    | 5.67    | 218.63         | 0.0146 | Singlet-A | H-15→LUMO (37%), H-9→LUMO (13%) | 0.48    |
| 22    | 5.69    | 217.86         | 0.011  | Singlet-A | H-10→LUMO (46%), H-8→LUMO (15%), H-3→L+1 (14%) | 0.50    |
| 23    | 5.70    | 217.35         | 0.0744 | Singlet-A | H-10→LUMO (20%), H-3→L+1 (49%) | 0.36    |
| 24    | 5.75    | 215.55         | 0.0142 | Singlet-A | H-12→LUMO (79%) | 0.42    |
| 25    | 5.81    | 213.56         | 0.0047 | Singlet-A | H-14→LUMO (23%), H-13→LUMO (38%) | 0.38    |
Orbitals relevant to the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ transitions

LUMO: $-2.13 \text{ eV}$

HOMO: $-7.83 \text{ eV}$

LUMO+1: $-1.19 \text{ eV}$

HOMO-1: $-7.92 \text{ eV}$

Isovalue = 0.03
|        |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|        |        |        |        |        |        |        |        |        |        |
| H      | -0.11437800 | 1.00249100 | 1.90953000 |
| B      | -0.66272300 | 1.70243700 | -1.83068800 |
| C      | -3.94761000 | -1.40795800 | 0.21882800 |
| C      | -0.31763500 | -1.55962400 | -0.55747600 |
| B      | 0.77129200  | -0.44580200 | -0.69711300 |
| H      | -0.99693100 | 0.95728500  | -2.68533400 |
| H      | -2.87763800 | 2.94547900  | -1.48300900 |
| B      | -2.22158200 | 0.23059900  | -0.07412900 |
| C      | 2.36030800  | -1.11549000 | 2.52665200 |
| H      | 1.47682400  | -1.10399400 | 3.16134200 |
| C      | -1.30477100 | 1.48123600  | -0.24723600 |
| B      | -1.43151900 | 2.91268700  | 0.66071900 |
| H      | -0.38941200 | 3.99032900  | -2.98385800 |
| C      | -1.63424000 | -1.19017600 | -0.25562200 |
| B      | 1.00646300  | 2.29015700  | -1.60384400 |
| H      | 1.75081900  | 4.65951800  | -0.87036500 |
| H      | -1.18719000 | 5.30375200  | -0.31109700 |
| C      | 0.34311000  | 1.09949000  | 0.55994900 |
| B      | 0.12464600  | 1.72832300  | 0.97855400 |
| C      | -0.05962400 | 2.94633100  | 0.69279900 |
| H      | 0.94301300  | -3.29059800 | -0.93364200 |
| H      | 0.55371400  | 4.04042900  | 1.89621900 |
| B      | -0.31197800 | 3.43530900  | 1.93861800 |
| H      | 2.38989500  | 1.97318700  | 0.55092900 |
| B      | 0.77361700  | 4.93825200  | -0.37950100 |
| H      | -1.08415600 | -3.88041500 | -0.53543800 |
| H      | -0.86341700 | -4.93813500 | -0.64812700 |
| B      | -1.76706600 | 2.89584600  | -1.07576900 |
| C      | 2.40167900  | -3.48515800 | -0.22775500 |
| H      | -3.17552210 | -4.23910700 | -0.10877100 |
| B      | 0.23788500  | 3.46281900  | 0.90991500 |
| H      | 1.82589900  | 1.93845900  | -2.37892000 |
| C      | -2.67523700 | -2.12821700 | -0.08796600 |
| B      | 1.33994100  | 2.30494500  | 0.12986400 |
| H      | -2.31116500 | 2.79699800  | 1.45061100 |
| C      | 1.73055000  | 0.00507400  | 0.23887600 |
| B      | 0.92918500  | 3.81988200  | -0.70463000 |
| C      | -5.20787700 | 1.93710000  | 0.46170900 |
| H      | -5.38151100 | -3.00971200 | 0.44737900 |
| C      | -6.27409500 | -1.05939500 | 0.73076200 |
| H      | -7.26338500 | -1.46553000 | 0.92242500 |
| C      | -6.07860400 | 0.32204200  | 0.75395400 |
| H      | -6.91402000 | 0.98355100  | 0.96296500 |
| C      | -4.80371200 | 0.85664600  | 0.50677800 |
| H      | -4.65702700 | 1.93255400  | 0.52511100 |
| C      | 2.23206500  | -0.81651300 | -1.15402000 |
| C      | 3.59598900  | -1.40005300 | -3.10850100 |
| H      | 3.65963900  | -1.60967600 | -4.17223600 |
| C      | 4.74161600  | -1.41624500 | -2.31134800 |
| H      | 5.71043700  | -1.64713600 | -2.74476700 |
| C      | 4.63442400  | -1.15611500 | -0.94639400 |
| H      | 5.52058800  | -1.21100600 | -0.32090200 |
| C      | 3.39702800  | -0.85609300 | -0.34784400 |
| C      | 3.35372900  | -0.63108600 | 1.12467200 |
| C      | 4.32654900  | 0.16512400  | 1.75712700 |
| H      | 5.08720700  | 0.65507300  | 1.15651200 |
| C      | 4.30370600  | 0.36637000  | 3.13688100 |
| H      | 5.05664700  | 0.99776400  | 3.59997700 |
| C      | 3.30876000  | -0.22738700 | 3.92031500 |
| H      | 3.28978100  | -0.06838400 | 4.99443600 |
| C      | 2.34118300  | -1.02648500 | 3.30907500 |
| H      | 1.57023400  | -1.50417700 | 3.90707100 |
| C      | 2.36604100  | -1.22850400 | 1.92636000 |
| H      | 1.63072900  | -1.88633000 | 1.47437100 |
TD-DFT calculations 2b:

Calculated absorption spectrum

TD-DFT CAMB3LYP/6-31+G(d, p), gas phase

Table S8: Lowest energy singlet electronic transition of 2b (TD-DFT CAM-B3LYP/6-31+G(d,p), gas phase).

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|---------|----------------|-----|----------|--------------------|---------|
| 1     | 3.07    | 403.46         | 0.0016 | Single-A | H-1$\rightarrow$L+1 (30%), HOMO$\rightarrow$LUMO (66%) | 0.61    |
| 2     | 3.10    | 400.57         | 0.0001 | Single-A | H-1$\rightarrow$LUMO (62%), HOMO$\rightarrow$L+1 (35%) | 0.61    |
| 3     | 3.97    | 312.68         | 0.1529 | Single-A | H-2$\rightarrow$LUMO (83%) | 0.61    |
| 4     | 4.11    | 301.61         | 0.0315 | Single-A | H-4$\rightarrow$L+1 (10%), H-3$\rightarrow$LUMO (46%), H-1$\rightarrow$L+1 (14%) | 0.66    |
| 5     | 4.15    | 298.63         | 0.0173 | Single-A | H-4$\rightarrow$LUMO (45%), H-3$\rightarrow$L+1 (17%), HOMO$\rightarrow$L+2 (11%) | 0.68    |
| 6     | 4.31    | 287.37         | 0.1489 | Single-A | H-5$\rightarrow$LUMO (67%) | 0.56    |
| 7     | 4.34    | 285.63         | 0.0197 | Single-A | H-1$\rightarrow$LUMO (34%), HOMO$\rightarrow$L+1 (52%) | 0.62    |
| 8     | 4.39    | 282.70         | 0.0481 | Single-A | H-1$\rightarrow$L+1 (51%), HOMO$\rightarrow$LUMO (29%) | 0.63    |
| 9     | 4.53    | 273.78         | 0.0319 | Single-A | H-2$\rightarrow$L+1 (70%) | 0.56    |
| 10    | 4.68    | 265.18         | 0.0236 | Single-A | H-7$\rightarrow$L+1 (12%), H-6$\rightarrow$LUMO (50%) | 0.72    |
| 11    | 4.79    | 258.88         | 0.0038 | Single-A | H-7$\rightarrow$LUMO (41%), H-6$\rightarrow$L+1 (25%) | 0.75    |
| 12    | 4.95    | 250.37         | 0.0103 | Single-A | H-10$\rightarrow$LUMO (19%), H-5$\rightarrow$L+1 (42%), H-4$\rightarrow$L+1 (17%) | 0.56    |
| 13    | 5.03    | 246.43         | 0.0616 | Single-A | H-4$\rightarrow$LUMO (28%), H-1$\rightarrow$L+3 (21%), HOMO$\rightarrow$L+2 (28%) | 0.69    |
| 14    | 5.08    | 243.91         | 0.3361 | Single-A | H-10$\rightarrow$LUMO (39%), H-3$\rightarrow$LUMO (12%), H-1$\rightarrow$L+2 (12%), HOMO$\rightarrow$L+3 (11%) | 0.60    |
| 15    | 5.10    | 242.93         | 0.5115 | Single-A | H-10$\rightarrow$LUMO (17%), H-5$\rightarrow$L+1 (15%), H-3$\rightarrow$LUMO (17%), H-1$\rightarrow$L+2 (17%), HOMO$\rightarrow$L+3 (15%) | 0.64    |
| 16    | 5.14    | 241.28         | 0.1113 | Single-A | H-3$\rightarrow$L+1 (46%), HOMO$\rightarrow$L+2 (15%) | 0.69    |
| 17    | 5.29    | 234.49         | 0.0401 | Single-A | H-12$\rightarrow$LUMO (36%), H-11$\rightarrow$L+1 (24%), H-4$\rightarrow$L+1 (11%) | 0.60    |
| 18    | 5.30    | 233.92         | 0.0296 | Single-A | H-13$\rightarrow$LUMO (20%), H-12$\rightarrow$L+1 (13%), H-11$\rightarrow$LUMO (29%), H-10$\rightarrow$L+1 (23%) | 0.53    |
| 19    | 5.30    | 233.91         | 0.7495 | Single-A | H-5$\rightarrow$L+1 (20%), H-4$\rightarrow$L+1 (31%) | 0.66    |
| 20    | 5.36    | 231.29         | 0.0998 | Single-A | H-13$\rightarrow$LUMO (19%), H-11$\rightarrow$LUMO (14%), H-10$\rightarrow$L+1 (20%), H-3$\rightarrow$L+1 (13%) | 0.58    |
| 21    | 5.62    | 220.63         | 0.0395 | Single-A | H-12$\rightarrow$LUMO (11%), H-9$\rightarrow$LUMO (26%), H-8$\rightarrow$L+1 (11%), H-6$\rightarrow$LUMO (19%) | 0.69    |
| 22    | 5.64    | 219.69         | 0.0496 | Single-A | H-11$\rightarrow$LUMO (11%), H-9$\rightarrow$L+1 (10%), H-8$\rightarrow$LUMO (35%) | 0.70    |
| 23    | 5.78    | 214.32         | 0.0665 | Single-A | H-6$\rightarrow$L+1 (13%), H-5$\rightarrow$LUMO (11%), H-2$\rightarrow$L+5 (22%) | 0.64    |
| 24    | 5.80    | 213.68         | 0.0049 | Single-A | H-7$\rightarrow$LUMO (13%), H-4$\rightarrow$L+3 (13%), H-3$\rightarrow$L+2 (21%) | 0.69    |
| 25    | 5.82    | 212.99         | 0.0029 | Single-A | H-9$\rightarrow$LUMO (23%), H-7$\rightarrow$L+1 (11%), H-6$\rightarrow$LUMO (17%) | 0.73    |
Orbitals relevant to the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ transitions

LUMO: -1.54 eV

HOMO: -7.32 eV

LUMO+1: -1.10 eV

HOMO-1: -7.37 eV

Isovalue = 0.03
|     |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|
| B   | -1.54656300 | 0.77025200 | -0.41969800 |
| B   | -1.54649400 | 0.77027300 | 0.41962900 |
| C   | -1.22882400 | -0.41793300 | 1.39776300 |
| C   | -0.15304600 | -0.69248400 | 2.24415100 |
| H   | 0.69777000  | -0.01752600 | 2.28951800 |
| C   | -0.16236500 | -1.84501700 | 3.04618100 |
| H   | 0.67868800  | -2.06119900 | 3.69850700 |
| C   | -1.25508500 | -2.71284300 | 3.00801500 |
| H   | -1.25856500 | -3.60242600 | 3.63212200 |
| C   | -2.35713800 | -2.44647100 | 2.17376100 |
| H   | -3.20419500 | -3.12743600 | 2.69106000 |
| C   | -2.34039000 | -1.30543500 | 1.38302600 |
| C   | -3.87498000 | -0.80584900 | 0.45080200 |
| H   | -4.61142600 | -1.38151300 | 0.12620200 |
| H   | -4.92710300 | -2.32250700 | 0.56901800 |
| C   | -5.44732500 | -0.72855500 | -0.79564200 |
| H   | -6.40550100 | -1.70667000 | -1.05515500 |
| C   | -5.05932000 | 0.47661400  | -1.38447400 |
| H   | -5.71512600 | 0.96594600  | -2.09892000 |
| C   | -3.82090500 | 1.05130700  | -1.05464000 |
| H   | -3.52004100 | 1.98444400  | -1.52519700 |
| C   | -2.97966100 | 0.42513200  | -0.13307000 |
| C   | -0.70297100 | 2.04896900  | 0.13047400  |
| C   | -1.36575600 | 3.28918200  | 0.24157500  |
| H   | -2.43360800 | 3.30368800  | 0.44478800  |
| C   | -0.68642300 | 4.50447900  | 0.12372100  |
| H   | -1.22717400 | 5.44185300  | 0.22205500  |
| C   | 0.68647100  | 4.50451100  | -0.12366600 |
| H   | 1.22719200  | 5.44191100  | -0.22192300 |
| C   | 1.36584400  | 3.28924800  | -0.24161700 |
| H   | 2.43369300  | 3.30380400  | -0.44485100 |
| C   | 0.70311400  | 2.04900900  | -0.13060800 |
| C   | 1.22879800  | -0.41793300 | -1.39772400 |
| C   | 0.15298000  | -0.69248400 | -2.24405800 |
| H   | -0.69779500 | -0.01750000 | -2.28946400 |
| C   | 0.16219900  | -1.84518900 | -3.04597500 |
| H   | -0.67888700 | -2.06138000 | -3.69825500 |
| C   | 1.25486400  | -2.71308100 | -3.00775600 |
| H   | 1.25826700  | -3.60272700 | -3.63177500 |
| C   | 2.35696100  | -2.44669800 | -2.17716500 |
| H   | 3.20397400  | -3.12771800 | -2.16886300 |
| C   | 2.34030800  | -1.30558700 | -1.38293700 |
| C   | 3.38748500  | -0.80597000 | -0.45080500 |
| C   | 4.61140900  | -1.38165300 | -0.12623000 |
| H   | 4.92701900  | -2.32270400 | -0.56897200 |
| C   | 5.44739400  | -0.72863800 | 0.79549700 |
| H   | 6.40556600  | -1.17076700 | 1.05499700 |
| C   | 5.05947800  | 0.47660600  | 1.38423300 |
| H   | 5.71534900  | 0.96598300  | 2.09858900 |
| C   | 3.82106600  | 1.05132000  | 1.05442100 |
| H   | 3.52026600  | 1.98450800  | 1.52491500 |
| C   | 2.97973900  | 0.42509200  | 0.13296200 |
### TD-DFT calculations 3b:

#### Calculated absorption spectrum

![Calculated absorption spectrum](image)

### TD-DFT CAMB3LYP/6-31+G(d,p), gas phase

Table S9: Lowest energy singlet electronic transition of 3b (TD-DFT CAM-B3LYP/6-31+G(d,p), gas phase).

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|---------|---------------|-----|----------|---------------------|---------|
| 1     | 2.89    | 429.67        | 0.0022 | Singlet-A | HOMO→LUMO (91%) | 0.51    |
| 2     | 3.54    | 350.44        | 0.0066 | Singlet-A | H-2→LUMO (89%) | 0.60    |
| 3     | 3.70    | 335.18        | 0.0571 | Singlet-A | H-3→LUMO (16%), H-1→LUMO (62%) | 0.34    |
| 4     | 3.98    | 311.74        | 0.0791 | Singlet-A | H-4→LUMO (56%), HOMO→L+1 (23%) | 0.60    |
| 5     | 4.11    | 301.52        | 0.008 | Singlet-A | H-9→LUMO (28%), H-3→LUMO (26%), H-1→LUMO (14%) | 0.50    |
| 6     | 4.23    | 293.04        | 0.0753 | Singlet-A | H-6→LUMO (24%), H-3→LUMO (13%), HOMO→L+1 (23%) | 0.54    |
| 7     | 4.41    | 281.31        | 0.3153 | Singlet-A | H-6→LUMO (25%), H-4→LUMO (17%), HOMO→L+1 (24%) | 0.62    |
| 8     | 4.49    | 276.13        | 0.0047 | Singlet-A | H-9→LUMO (29%), H-3→LUMO (22%) | 0.53    |
| 9     | 4.74    | 261.55        | 0.0231 | Singlet-A | H-11→LUMO (46%), H-5→LUMO (27%) | 0.47    |
| 10    | 4.77    | 260.19        | 0.0716 | Singlet-A | H-11→LUMO (30%), H-5→LUMO (41%) | 0.43    |
| 11    | 4.96    | 249.72        | 0.1841 | Singlet-A | H-8→LUMO (16%), H-2→L+1 (10%), H-1→L+1 (18%), HOMO→L+1 (11%) | 0.55    |
| 12    | 5.03    | 246.61        | 0.2885 | Singlet-A | H-2→L+1 (45%), H-1→L+1 (23%) | 0.50    |
| 13    | 5.05    | 245.74        | 0.2508 | Singlet-A | H-12→LUMO (10%), H-8→LUMO (14%), H-1→L+1 (17%) | 0.55    |
| 14    | 5.10    | 243.01        | 0.0764 | Singlet-A | H-12→LUMO (20%), H-7→LUMO (12%), H-3→L+2 (10%), H-1→L+5 (12%) | 0.53    |
| 15    | 5.16    | 240.19        | 0.019 | Singlet-A | H-12→LUMO (37%), H-1→L+5 (10%) | 0.51    |
| 16    | 5.21    | 238.12        | 0.2103 | Singlet-A | H-1→L+2 (48%) | 0.67    |
| 17    | 5.26    | 235.51        | 0.1306 | Singlet-A | H-3→L+2 (12%), H-1→L+2 (26%) | 0.760   |
| 18    | 5.31    | 233.29        | 0.0288 | Singlet-A | H-10→LUMO (23%), H-9→LUMO (14%), H-8→LUMO (29%) | 0.67    |
| 19    | 5.38    | 230.27        | 0.1095 | Singlet-A | H-7→LUMO (16%), H-6→LUMO (13%), H-4→L+1 (17%) | 0.56    |
| 20    | 5.43    | 228.32        | 0.1167 | Singlet-A | H-9→L+1 (12%), H-7→LUMO (27%), H-3→L+1 (12%) | 0.47    |
| 21    | 5.46    | 227.00        | 0.0253 | Singlet-A | H-13→LUMO (16%), H-9→L+1 (12%), H-1→L+1 (11%) | 0.51    |
| 22    | 5.55    | 223.40        | 0.056 | Singlet-A | H-4→L+1 (36%), HOMO→L+3 (23%) | 0.58    |
| 23    | 5.66    | 219.15        | 0.0198 | Singlet-A | H-13→LUMO (36%), H-3→L+1 (36%) | 0.42    |
| 24    | 5.73    | 216.23        | 0.1017 | Singlet-A | H-6→L+1 (40%), H-5→L+1 (12%) | 0.59    |
| 25    | 5.77    | 214.90        | 0.0996 | Singlet-A | H-10→LUMO (11%), H-8→L+1 (10%), HOMO→L+3 (11%), HOMO→L+12 (14%) | 0.64    |
Orbitals relevant to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions

LUMO: -1.81 eV

LUMO+1: -0.67 eV

HOMO: -7.38 eV

HOMO-1: -7.62 eV

Isovalue = 0.03
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C | 4.01006900 | 0.68943100 | 0.36383000 |   |   |   |
| C | 0.43005200 | 1.52432700 | -0.11335700 |   |   |   |
| B | -0.72385700 | 0.59121100 | -0.62791500 |   |   |   |
| B | 2.07660800 | -0.50699000 | -0.46751900 |   |   |   |
| C | -2.42304500 | 2.16556000 | -1.68631600 |   |   |   |
| H | -1.58168500 | 2.55512800 | -2.25524300 |   |   |   |
| C | 1.69948800 | 0.94017200 | -0.05059200 |   |   |   |
| C | 0.32325100 | 2.86154600 | 0.33657100 |   |   |   |
| H | -0.63747700 | 3.36955700 | 0.32423400 |   |   |   |
| C | 1.45075300 | 3.54495100 | -0.80503200 |   |   |   |
| H | 1.34787400 | 2.55512800 | -2.25524300 |   |   |   |
| C | 2.71901500 | 2.93337800 | 0.85787100 |   |   |   |
| H | 3.57148600 | 3.49494100 | 1.23237100 |   |   |   |
| C | 3.61951900 | -0.58611600 | -0.15761500 |   |   |   |
| C | 5.32570300 | 0.94015000 | 0.73557400 |   |   |   |
| H | 5.62167500 | 1.90858600 | 1.13050600 |   |   |   |
| C | 6.28265100 | -0.07982200 | 0.59657600 |   |   |   |
| H | 7.31294900 | 0.10909800 | 0.88568100 |   |   |   |
| C | 5.92283400 | -1.33020600 | 0.92836000 |   |   |   |
| H | 6.67255900 | -2.10962700 | -0.08316000 |   |   |   |
| C | 4.59264400 | -1.58016200 | -0.28289800 |   |   |   |
| H | 4.33068700 | -2.56049800 | -0.67231200 |   |   |   |
| C | -2.19730000 | 1.14785000 | -0.73612400 |   |   |   |
| H | -3.69872200 | 2.67110800 | -1.94304400 |   |   |   |
| C | -3.83693100 | 3.44418000 | -2.69375600 |   |   |   |
| C | -4.78977800 | 2.18316900 | -1.22083000 |   |   |   |
| H | -5.78660100 | 2.57807500 | -1.39582500 |   |   |   |
| C | -4.59084600 | 1.19922100 | -0.25991100 |   |   |   |
| H | -5.43966400 | 0.85026700 | 0.33672200 |   |   |   |
| C | -3.1256700 | 0.67071000 | 0.00095000 |   |   |   |
| C | -3.1544400 | -0.35827900 | 1.06633300 |   |   |   |
| C | -4.06195200 | -1.42723200 | 1.17941700 |   |   |   |
| H | -4.87238300 | -1.51724400 | 0.46154200 |   |   |   |
| C | -3.91702800 | -2.39027000 | 2.17887500 |   |   |   |
| H | -4.62354200 | -3.21351900 | 2.23877300 |   |   |   |
| C | -2.86164800 | -2.30496500 | 3.09225100 |   |   |   |
| H | -2.74799700 | -3.05520400 | 3.86932900 |   |   |   |
| C | -1.95637400 | -1.24578000 | 2.99744000 |   |   |   |
| H | -1.13822800 | -1.16167600 | 3.70713800 |   |   |   |
| C | -2.10379200 | -0.28178900 | 1.99735400 |   |   |   |
| H | -1.41305600 | 0.55524000 | 1.95850200 |   |   |   |
| C | 1.20746100 | -2.71651800 | -1.52831800 |   |   |   |
| C | 0.96756400 | -1.41801900 | -1.04798300 |   |   |   |
| C | -0.36214800 | -0.87388400 | -1.12798300 |   |   |   |
| C | -1.36286800 | -1.67178400 | -1.70884200 |   |   |   |
| C | -1.09920700 | -2.96147600 | -2.8536800 |   |   |   |
| C | 0.18806400 | -3.48987800 | -2.09209700 |   |   |   |
| H | 2.21008000 | -3.13093600 | -1.46776500 |   |   |   |
| H | -2.37211100 | -1.28068800 | -1.79502800 |   |   |   |
| H | -1.89946500 | -3.54926900 | -2.62715700 |   |   |   |
| H | 0.39830400 | -4.49103400 | -2.45857400 |   |   |   |
CAM-B3LYP-Hexane

**TD-DFT calculations 3a:**

**Calculated absorption spectrum**

![Calculated absorption spectrum](image)

| State | $E$ [eV] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|---------|-----|----------|---------------------|----------|
| 1     | 2.90    | 0.0021 | Singlet-A | H-1→LUMO (68%), HOMO→LUMO (25%) | 0.51     |
| 2     | 3.75    | 0.059  | Singlet-A | H-1→LUMO (16%), HOMO→LUMO (52%), HOMO→L+1 (12%) | 0.41     |
| 3     | 3.97    | 0.0231 | Singlet-A | H-4→LUMO (40%), H-1→L+1 (33%) | 0.62     |
| 4     | 4.26    | 0.0106 | Singlet-A | H-2→LUMO (59%), H-2→L+1 (13%), HOMO→LUMO (10%) | 0.25     |
| 5     | 4.32    | 0.4836 | Singlet-A | H-4→LUMO (39%), H-1→L+1 (30%), HOMO→L+1 (10%) | 0.63     |
| 6     | 4.57    | 0.1269 | Singlet-A | H-6→LUMO (69%) | 0.68     |
| 7     | 4.67    | 0.0036 | Singlet-A | H-15→LUMO (10%), H-11→LUMO (24%), H-8→LUMO (24%), HOMO→L+1 (12%) | 0.42     |
| 8     | 4.77    | 0.0097 | Singlet-A | H-3→LUMO (66%) | 0.29     |
| 9     | 4.83    | 0.02   | Singlet-A | H-1→L+1 (10%), HOMO→L+1 (41%) | 0.47     |
| 10    | 5.09    | 0.0928 | Singlet-A | H-5→LUMO (11%), H-2→L+2 (10%), HOMO→L+2 (19%), HOMO→L+5 (12%) | 0.53     |
| 11    | 5.12    | 0.1836 | Singlet-A | H-7→LUMO (29%), H-6→L+1 (21%), H-4→L+1 (14%) | 0.65     |
| 12    | 5.13    | 0.0104 | Singlet-A | H-14→LUMO (17%), H-13→LUMO (34%) | 0.42     |
| 13    | 5.16    | 0.1856 | Singlet-A | H-2→L+2 (11%), HOMO→L+2 (20%) | 0.61     |
| 14    | 5.17    | 0.1557 | Singlet-A | H-5→LUMO (28%), HOMO→L+2 (21%) | 0.47     |
| 15    | 5.23    | 0.4388 | Singlet-A | H-7→LUMO (13%), H-6→LUMO (11%), H-4→L+1 (35%) | 0.62     |
| 16    | 5.31    | 0.0083 | Singlet-A | H-9→LUMO (24%), H-5→LUMO (19%) | 0.34     |
| 17    | 5.39    | 0.0096 | Singlet-A | H-9→LUMO (16%), H-5→LUMO (22%), H-3→L+2 (11%) | 0.37     |
| 18    | 5.41    | 0.0015 | Singlet-A | H-9→LUMO (19%), H-2→LUMO (10%), H-2→L+1 (35%) | 0.30     |
| 19    | 5.54    | 0.0005 | Singlet-A | H-11→LUMO (33%), H-8→LUMO (34%) | 0.41     |
| 20    | 5.56    | 0.2281 | Singlet-A | H-7→LUMO (39%), H-1→L+3 (22%) | 0.65     |
| 21    | 5.71    | 0.0881 | Singlet-A | H-3→L+1 (58%) | 0.31     |
| 22    | 5.74    | 0.0345 | Singlet-A | H-15→LUMO (34%), H-9→LUMO (24%) | 0.43     |
| 23    | 5.80    | 0.0415 | Singlet-A | H-10→LUMO (85%) | 0.40     |
| 24    | 5.80    | 0.5111 | Singlet-A | H-6→L+1 (36%), H-4→L+1 (10%) | 0.60     |
| 25    | 5.85    | 0.019  | Singlet-A | H-12→LUMO (82%) | 0.33     |
Orbitals relevant to the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ transitions

LUMO: $-2.10 \text{ eV}$

LUMO+1: $-1.15 \text{ eV}$

HOMO: $-7.81 \text{ eV}$

HOMO-1: $-7.87 \text{ eV}$

Isovalue = 0.03
|   | H     | B     | C     | B     | H     | B     | C     | B     | H     | B     | C     | B     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 | -0.11437800 | 1.00249100 | 1.90953000 | -0.66272300 | 1.70243700 | -1.83068800 | -3.94761000 | -1.40795800 | 0.21882800 | -0.31763500 | -1.55962400 | -0.55747600 | 0.77129200 | -0.44580200 | -0.69711300 | -0.99693100 | 0.95728500 | -2.68533400 | -2.87763800 | 2.95457900 | -1.48300900 | -2.22158200 | 0.23059900 | -0.07412900 | 2.36030800 | -1.11549000 | 2.52665200 | 1.47682400 | -1.10399400 | 3.16134200 | -1.30477100 | 1.48123600 | -0.24723600 | -1.43151900 | 2.91268700 | 0.66071900 | -0.38941200 | 3.99032900 | -2.98385800 | -1.63424000 | -1.19017600 | -0.25562200 | 1.00646300 | 2.29015700 | -1.60384400 | 1.75081900 | 4.65951800 | -0.87036500 | -1.18719000 | 5.30375200 | -0.31109700 | 0.34311000 | 1.09949000 | 0.55994900 | -0.12464600 | 1.72832300 | 0.97855400 | -0.05962400 | 2.94633100 | -0.69729900 | 0.94301300 | -3.29059800 | -0.33364200 | 0.55371400 | 4.04042900 | 1.89621900 | -0.31197800 | 3.45530900 | 1.93861800 | 2.38989500 | 1.97381700 | 0.55092900 | -0.77361700 | 4.19382500 | -0.37950100 | -1.08415600 | -3.88041500 | -0.53543800 | -0.86341700 | -4.93831500 | -0.64812700 | -1.76706600 | 2.89584600 | -1.07576900 | -2.40167900 | -3.48515800 | -0.22775500 | -3.17552210 | -4.23910700 | -0.10877100 | 0.23788500 | 3.46281900 | 0.90991500 | 1.82589900 | 1.93845900 | -2.37892000 | -2.67523700 | -2.12821700 | -0.08796600 | 1.33994100 | 2.30494500 | 0.12986400 | -2.31116500 | 2.97699800 | 1.45061100 | -3.73055000 | 0.00507400 | 0.23887600 | 0.92918500 | 3.81988200 | -0.70463000 | -5.20787700 | -1.93710000 | 0.46170900 | -5.38151100 | -3.00971200 | 0.44737900 | -6.27409500 | -1.05939500 | 0.73076200 | -7.26338500 | -1.46553000 | 0.92242500 | -6.07860400 | 0.32204200 | 0.75395400 | -6.91402000 | 0.98335100 | 0.96296500 | -4.80371200 | 0.85646300 | 0.50677800 | -4.65702700 | 1.93255400 | 0.52511100 | 2.23206500 | -0.81651300 | -1.15402000 | 3.59598900 | -1.40005300 | -3.10850100 | 3.65963900 | -1.60986700 | -4.17223600 | 4.74161600 | -1.41624500 | -2.31134800 | 5.71043700 | -1.64713600 | -2.74476700 | 4.63442400 | -1.15611500 | -0.96439400 | 5.52058800 | -1.21100500 | -0.32090200 | 3.39702800 | -0.85659300 | -0.34784400 | 3.35372900 | -0.63108600 | 1.12467200 | 4.32654900 | 0.16512400 | 1.75712700 | 5.08720700 | 0.65507300 | 1.15651200 | 4.30370600 | 0.36637000 | 3.13688100 | 5.05664700 | 0.99776400 | 3.59997700 | 3.30870600 | -0.22738700 | 3.92031500 | 3.28978100 | -0.06838400 | 4.99443600 | 2.34118300 | -1.02648500 | 3.30907500 | 1.57023400 | -1.50417700 | 3.90707100 | 2.36604100 | -1.22850400 | 1.92636000 | 1.63072900 | -1.88633000 | 1.47437100 | S65
TD-DFT calculations 3b:
Calculated absorption spectrum

| State | $E$ [eV] | $\lambda$ [nm] | $f$ | Symmetry | Major contributions | $\Lambda$ |
|-------|---------|-------------|-----|-----------|---------------------|---------|
| 1     | 2.88    | 430.44      | 0.0031 | Singlet-A | HOMO→LUMO (91%) | 0.51 |
| 2     | 3.53    | 350.79      | 0.0091 | Singlet-A | H-2→LUMO (89%) | 0.60 |
| 3     | 3.69    | 335.95      | 0.0738 | Singlet-A | H-3→LUMO (16%), H-1→LUMO (62%) | 0.34 |
| 4     | 3.96    | 313.04      | 0.1311 | Singlet-A | H-4→LUMO (61%), HOMO→L+1 (19%) | 0.60 |
| 5     | 4.11    | 301.89      | 0.0114 | Singlet-A | H-9→LUMO (30%), H-3→LUMO (25%), H-1→LUMO (13%) | 0.50 |
| 6     | 4.21    | 294.42      | 0.1364 | Singlet-A | H-6→LUMO (17%), H-3→LUMO (12%), HOMO→L+1 (31%) | 0.54 |
| 7     | 4.37    | 283.97      | 0.4162 | Singlet-A | H-6→LUMO (32%), H-4→LUMO (14%), HOMO→L+1 (21%) | 0.62 |
| 8     | 4.48    | 276.50      | 0.0099 | Singlet-A | H-9→LUMO (30%), H-3→LUMO (22%) | 0.53 |
| 9     | 4.73    | 261.88      | 0.0332 | Singlet-A | H-11→LUMO (43%), H-5→LUMO (28%) | 0.47 |
| 10    | 4.76    | 260.65      | 0.1    | Singlet-A | H-11→LUMO (33%), H-5→LUMO (38%) | 0.45 |
| 11    | 4.93    | 251.34      | 0.3167 | Singlet-A | H-8→LUMO (13%), H-2→L+1 (31%), HOMO→L+1 (11%) | 0.59 |
| 12    | 4.98    | 249.08      | 0.5429 | Singlet-A | H-8→LUMO (10%), H-2→L+1 (39%), H-1→L+1 (12%) | 0.55 |
| 13    | 5.03    | 246.34      | 0.1075 | Singlet-A | H-1→L+1 (39%) | 0.46 |
| 14    | 5.09    | 243.47      | 0.1119 | Singlet-A | H-12→LUMO (24%), H-7→LUMO (10%), H-1→L+5 (10%) | 0.54 |
| 15    | 5.16    | 240.42      | 0.0123 | Singlet-A | H-12→LUMO (34%), H-1→L+5 (11%) | 0.51 |
| 16    | 5.16    | 240.04      | 0.3739 | Singlet-A | H-1→L+2 (62%) | 0.72 |
| 17    | 5.25    | 236.02      | 0.0694 | Singlet-A | H-5→L+2 (10%), H-3→L+2 (15%) | 0.53 |
| 18    | 5.29    | 234.53      | 0.0334 | Singlet-A | H-10→LUMO (25%), H-9→LUMO (12%), H-8→LUMO (31%) | 0.70 |
| 19    | 5.37    | 231.05      | 0.1904 | Singlet-A | H-6→LUMO (12%), H-4→L+1 (22%), HOMO→L+3 (11%) | 0.60 |
| 20    | 5.42    | 228.71      | 0.0785 | Singlet-A | H-9→L+1 (12%), H-7→LUMO (40%), H-3→L+1 (11%) | 0.43 |
| 21    | 5.46    | 227.27      | 0.0174 | Singlet-A | H-13→LUMO (18%), H-9→L+1 (14%), H-1→L+1 (11%) | 0.51 |
| 22    | 5.52    | 224.48      | 0.0452 | Singlet-A | H-10→LUMO (11%), H-4→L+1 (39%), HOMO→L+3 (24%) | 0.58 |
| 23    | 5.65    | 219.41      | 0.0255 | Singlet-A | H-13→LUMO (32%), H-3→L+1 (37%) | 0.41 |
| 24    | 5.71    | 217.24      | 0.1148 | Singlet-A | H-13→LUMO (12%), H-6→L+1 (43%), H-5→L+1 (12%) | 0.60 |
| 25    | 5.76    | 215.40      | 0.1041 | Singlet-A | H-10→LUMO (13%), H-8→L+1 (11%), HOMO→L+11 (16%) | 64 |

TD-DFT CAMB3LYP/6-31+G(d,p), n-Hexane

Table S11: Lowest energy singlet electronic transition of 3b (TD-DFT CAM-B3LYP/6-31+G(d,p), n-Hexane).
Orbitals relevant to the $S_1 \leftrightarrow S_0$ and $S_2 \leftrightarrow S_0$ transitions

LUMO: -1.84 eV

HOMO: -7.41 eV

LUMO+1: -0.70 eV

HOMO-1: -7.65 eV

Isovalue = 0.03
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C | 4.0106900 | 0.68943100 | 0.36383000 |
| C | 0.49005200 | 1.52432700 | -0.11335700 |
| B | -0.72385700 | 0.59121100 | -0.62791500 |
| B | 2.07660800 | -0.50699000 | -0.46751900 |
| C | -2.42304500 | 2.16556000 | -1.68631600 |
| H | -1.58168500 | 2.55512800 | -2.25524300 |
| C | 1.69948800 | 0.94017200 | -0.05059200 |
| C | 0.32325100 | 2.86154600 | 0.33657100 |
| H | -0.63747700 | 3.36955700 | 0.32423400 |
| C | 1.45075300 | 3.54495100 | -1.68631600 |
| H | 1.34787400 | 4.57312300 | 1.14219000 |
| C | 2.71901500 | 2.93337800 | 0.85787100 |
| H | 3.57148600 | 3.49494100 | 1.23237100 |
| C | 2.83832900 | 1.61316500 | 0.42747400 |
| H | 3.61951900 | 0.94015000 | 0.73557400 |
| H | 5.32570300 | 0.94015000 | 0.73557400 |
| H | 6.28265100 | -0.07982200 | 0.59657600 |
| C | 6.21675000 | 1.90858600 | 0.32234000 |
| C | 7.31294900 | 0.10909800 | 0.88568100 |
| C | 5.92283400 | -1.30206000 | 0.92836000 |
| H | 6.67255900 | -2.10962700 | -0.00831600 |
| C | 4.59264400 | -1.58016200 | -0.28289800 |
| H | 4.33068700 | -2.56049800 | -0.67231200 |
| C | -2.19730000 | 1.14785000 | -0.73612400 |
| C | -3.69872200 | 2.67110800 | -1.94304400 |
| H | -3.83693100 | 3.44418000 | -2.69375600 |
| C | -4.78977800 | 2.18316900 | -1.22083000 |
| H | -5.78660100 | 2.57807500 | -1.39582500 |
| C | -4.59084600 | 1.19922100 | -0.25991100 |
| H | -5.43396400 | 0.85026700 | 0.33672200 |
| C | -3.31256700 | 0.67067100 | 0.00095000 |
| C | -3.15444000 | -0.35827900 | 1.06633300 |
| C | -4.06195200 | -1.42732300 | 1.17941700 |
| H | -4.87238300 | -1.51724400 | 0.46514200 |
| C | -3.91702800 | -2.39027000 | 2.17887500 |
| H | -4.62354200 | -3.21351900 | 2.23877300 |
| C | -2.86164800 | -2.30496500 | 3.09225100 |
| H | -2.74799700 | -3.05520400 | 3.86932900 |
| C | -1.95637400 | -1.24578000 | 2.99744000 |
| H | -1.13822800 | -1.16167600 | 3.70738000 |
| C | -2.10379200 | -0.28187900 | 1.99735400 |
| C | -1.41305600 | 0.55524000 | 1.95850200 |
| C | 1.20746100 | -2.71651800 | -1.52831800 |
| C | 0.96756400 | -1.41801900 | -1.04798300 |
| C | -0.36214800 | -0.87388400 | -1.12798300 |
| C | -1.36286800 | -1.67178400 | -1.70884200 |
| C | -1.09920700 | -2.96147600 | -2.18536800 |
| C | 0.18806400 | -3.48987800 | -2.09209700 |
| H | 2.21008000 | -3.13093600 | -1.46776500 |
| H | -2.37211100 | -1.28068800 | -1.79502800 |
| H | -1.89946500 | -3.54926900 | -2.62715700 |
| H | 0.39830400 | -4.49103400 | -2.45874000 |
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