SUPPORTING INFORMATION

Controlling Two-Photon Action Cross Section by Changing a Single Heteroatom Position in Fluorescent Dyes

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Synthesis

The synthesis of the precursors of 1-5 was performed by the reaction of the aminoheterocycle available from commercial sources with ethyl (N,N-dimethylamino)cinnamate according to the procedure described elsewhere. [1] The ethyl (N,N-dimethylamino)cinnamate was obtained as described before. [2] The resulting amides were converted to BF₂-carrying dyes using known procedure. [1, 3]

Characterization of obtained fluorescent dyes

Compound 2.

Diffuoroboranyl (Z,2E)-3-[4-(dimethylamino)phenyl]-N-(pyrimidin-2-yl)prop-2-enimidate. Orange-red powder. Mp >360 °C (dec). ¹H NMR (400 MHz, CDCl₃) δ 9.06 (dd, J = 4.5, 2.5 Hz, 1H), 8.50 (dd, J = 6.1, 2.5 Hz, 1H), 8.08 (d, J = 15.6 Hz, 1H), 7.53 (d, J = 8.9 Hz, 2H), 7.25 (dd, J = 6.0, 4.5 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 15.6 Hz, 1H), 3.07 (s, 6H). ¹¹B NMR (128 MHz, CDCl₃) δ 0.62 (t). ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 165.8, 158.1, 152.2, 148.6, 147.5, 131.1, 123.0, 115.4, 115.2, 112.4, 40.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.52 (m). Elemental for C₁₅H₁₅BF₂N₄O calcd.: C (56.99), H (4.78), B (3.42), F (12.02), N (17.72), O (5.06), found C (56.85), H (4.83), N (17.58).

Compound 3.

Diffuoroboranyl (Z,2E)-3-[4-(dimethylamino)phenyl]-N-(pyrazin-2-yl)prop-2-enimidate. Red solid. Mp >360 °C (dec). ¹H NMR (400 MHz, CDCl₃) δ 8.81 (d, J = 1.3 Hz, 1H), 8.47 (d, J = 3.6 Hz, 1H), 8.03 (s, 1H), 8.01 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 9.0 Hz, 1H), 6.55 (d, J = 15.5 Hz, 1H), 3.07 (s, 6H). ¹¹B NMR (128 MHz, CDCl₃) δ 0.07 (t). ¹³C NMR (101 MHz, CDCl₃) δ 169.9, 148.6, 148.2, 138.8, 131.0, 128.9, 115.1, 112.6, 40.6. ¹⁵N NMR (41 MHz, CDCl₃) δ 57.7, 205.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -138.25 – -138.51 (m). Elemental for C₁₅H₁₅BF₂N₂O calcd.: C (56.99), H (4.78), B (3.42), F (12.02), N (17.72), O (5.06), found C (56.93), H (4.89), N (17.56).

Compound 4.
Difluoroboranyl (Z,2E)-3-[4-(dimethylamino)phenyl]-N-(pyrimidin-4-yl)prop-2-enimidate. Deep-red crystals. Mp >360 °C (dec) 1H NMR (400 MHz, CDCl3) δ 8.90 (d, J = 1.1 Hz, 1H), 8.66 (d, J = 5.9 Hz, 1H), 8.05 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 5.5 Hz, 1H), 6.70 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 15.5 Hz, 1H), 3.08 (s, 6H). 13B NMR (128 MHz, CDCl3) δ 0.05 (t). 13C NMR (101 MHz, CDCl3) δ 170.90, 159.61, 158.34, 152.71, 150.35, 149.80, 131.34, 122.12, 117.30, 114.22, 111.92, 40.15. 15N NMR (41 MHz, CDCl3) δ 59.3, 202.4, 275.1. 19F NMR (376 MHz, CDCl3) δ -137.60 (m). Elemental for C15H15BF2N4O calcd.: C (56.99), H (4.78), N (17.72), found C (56.77), H (4.90), N (17.66).

Compound 5.

Difluoroboranyl (Z,2E)-3-[4-(dimethylamino)phenyl]-N-(pyridazin-3-yl)prop-2-enimidate. Red solid. Mp 245-246 °C. 1H NMR (400 MHz, CDCl3) δ 8.81 (dd, J = 4.4, 1.6 Hz, 1H), 8.03 (d, J = 15.5 Hz, 1H), 7.73 (dd, J = 9.0, 4.4 Hz, 1H), 7.59 (dd, J = 9.0, 1.6 Hz, 1H), 7.52 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 15.5 Hz, 1H), 3.07 (s, 6H). 13B NMR (128 MHz, CDCl3) δ 0.20 (t). 13C NMR (101 MHz, CDCl3) δ 169.3, 156.9, 152.3, 148.9, 147.0, 133.3, 131.1, 130.3, 114.3, 112.2, 40.3. 15N NMR (41 MHz, CDCl3) δ 57.7. 19F NMR (376 MHz, CDCl3) δ -138.81. Elemental for C15H15BF2N4O calcd.: C (56.99), H (4.78), N (17.59), found C (56.71), H (4.99), N (17.59).
NMR spectra

Fig. S1. The $^1$H NMR spectrum for 2

Fig. S2. The $^{11}$B NMR spectrum for 2
Fig. S3. The $^{13}$C NMR spectrum for 2

Fig. S4. The $^1$H,$^{15}$N HMBC NMR spectrum for 2
Fig. S5. The $^{19}$F NMR spectrum for 2
Fig. S6. The $^1$H NMR spectrum for 3

Fig. S7. The $^{11}$B NMR spectrum for 3
Fig. S8. The $^{13}$C NMR spectrum for 3

Fig. S9. The $^1$H,$^{15}$N HMBC NMR spectrum for 3
Fig. S10. The $^{19}$F NMR spectrum for 3
Fig. S11. The $^1$H NMR spectrum for 4

Fig. S12. The $^{11}$B NMR spectrum for 4
Fig. S13. The $^{13}$C NMR spectrum for 4

Fig. S14. The $^1$H,$^{15}$N HMBC NMR spectrum for 4
Fig. S15. The $^{19}$F NMR spectrum for 4

Fig. S16. The $^1$H NMR spectrum for 5
Fig. S17. The $^{11}$B NMR spectrum for 5

Fig. S18. The $^{13}$C NMR spectrum for 5
Fig. S19. The $^1$H,$^{15}$N HMBC NMR spectrum for 5

Fig. S20. The $^{19}$F NMR spectrum for 5
Absorption and fluorescence measurements (experimental setup)

Absorption spectra were recorded at room temperature with a Shimadzu UV-vis Multispec-1501 spectrophotometer (Japan), using quartz cells with a path length of 1.0 cm. The concentration of the compounds was ca. 1.0 x 10^{-5} M.

Emission spectra were taken on a Hitachi F-7100 spectrometer (Japan) in ca. 1.0 x 10^{-6} M solutions. Fluorescence quantum yields were determined based on the equation below following a literature protocol.[4]

\[ \Phi_{dye} = \frac{\Phi_{ref}}{\frac{l_{dye}A_{dye}}{l_{ref}A_{ref}} \cdot n_s^2} \]  

(eq. 1)

where \( \Phi \) is the fluorescence quantum yield, \( A \) is the absorbance at the excitation wavelengths, \( I \) is the integrated emission intensity and \( n \) is the refractive indices of the solvents used. The “dye” and “ref” index refer to the dye and standard samples, respectively. As a standard[5] we used Coumarin 153 in anhydrous ethanol, Ex=450 nm or 420 nm, \( \Phi_{ref} = 0.38 \) and Fluorescein in 0.1N NaOH, Ex=470 nm, \( \Phi_{ref} = 0.91 \).

Time-correlated single-photon counting measurements were performed with an Edinburgh Analytical Instruments F920P spectrometer. Samples were excited at 466.6 nm using a laser diode with a pulse width of about 81.5 ps, and maximal average power 5 mW. The emission intensity was recorded at fluorescence maximum wavelength. A solution of colloidal silica was used to obtain the instrument response function (IRF). Fluorescence lifetimes were calculated using the FAST software package by fitting an exponential decay curve to the obtained data. The average lifetime, \( \tau_{av} \), was calculated as

\[ \tau_{av} = \frac{\Sigma \tau_i \alpha_i}{\Sigma \alpha_i} \]  

(eq. 2)

were \( \alpha_i \) and \( \tau_i \) are the amplitudes and lifetimes.

The radiative (\( k_r \)) and nonradiative (\( k_{nr} \)) rate constants were calculated based on the average lifetime of the \( S_1 \) excited state (\( \tau_{av} \)) and the fluorescence quantum yield (\( \Phi \)), using following equations:

\[ k_r = \frac{\Phi_{dye}}{\tau_{av}} \]  

(eq. 3)

\[ k_{nr} = \frac{1-\Phi_{dye}}{\tau_{av}} \]  

(eq. 4)

The measurements of bleaching process studied by UV-Vis spectroscopy were performed in a quartz cuvette with dimensions 4x1x1 cm. In order to ensure complete absorption of light, the cuvette was placed in a horizontal position and irradiated with diode-pumped solid state (DPSS) laser light (\( \lambda_{EM}=457 \) nm; intensity 50 mW) through the bottom wall (the optical path length = 4 cm). The solution was stirred during irradiation.
Table S1. The spectral properties of 1-5 in chosen solvents

| Solvent | λ\_abs | λ\_flu | FQY | λ\_abs | λ\_flu | FQY | λ\_abs | λ\_flu | FQY | λ\_abs | λ\_flu | FQY |
|---------|---------|---------|-----|---------|---------|-----|---------|---------|-----|---------|---------|-----|
| MCH     |        |         |     |        |         |     |        |         |     |        |         |     |
| Dioxane | 429.5   | 441     | 465.5 | 462    | 449.5   | 605  | 4060    | 3970    | 4211 | 3343    | 4196    |     |
| Et\_2O  | 425.5   | 437     | 462.5 | 460    | 443     | 605  | 4024    | 3980    | 4200 | 3289    | 4258    |     |
| CHCl\_3 | 441.5   | 468     | 486.5 | 481.5  | 471.5   | 605  | 3675    | 3059    | 4220 | 3044    | 3818    |     |
| EA      | 428.5   | 442     | 465.5 | 464    | 447     | 605  | 4887    | 4574    | 5679 | 4130    | 5010    |     |
| THF     | 432     | 444     | 471   | 466    | 450     | 605  | 4766    | 4601    | 5708 | 4116    | 5415    |     |
| AcMe    | 434     | 444     | 470   | 466    | 453     | 605  | 5374    | 4684    | 7232 | 4869    | 4025    |     |
| ACN     | 431.5   | 447     | 467.5 | 468    | 453.5   | 605  | 5814    | 4660    | 7424 | 5033    | 3809    |     |
| DMF     | 443     | 454     | 478   | 475.5  | 461.5   | 605  | 5421    | 4528    | 6149 | 4854    | 3811    |     |
| MeOH    | 437.5   | 453     | 473   | 472    | 456.5   | 605  | 5436    | 4025    | 5565 | 4641    | 4207    |     |

\(a\) – Absorption maximum (λ\_max), extinction coefficient (ε), emission maximum (λ\_flu), Stokes shift (ΔS) and fluorescence quantum yield (FQY), \(b\) – vibrational features, \(c\) – values very close to the benzoate derivative [6]
Table S2. The time-resolved fluorescence data of 1-5 in chosen solvents:

| Solvent | t1 (%) | t2 (%) | t1 (%) | t2 (%) | t1 (%) | t2 (%) |
|---------|--------|--------|--------|--------|--------|--------|
| MCH     | 1.793  | 1.434  | 1.488  | 1.727  | 1.551  |
| Dioxane | 1.294  | 1.192  | 1.530  | 1.014  | 1.476  |
| EtO     | 1.111  | 1.184  | 1.390  | 1.487  | 1.326  |
| CHCl3   | 1.054  | 1.657  | 1.453  | 1.437  | 1.176  |
| EA      | 1.073  | 1.896  | 1.628  | 1.233  | 2.744  |
| THF     | 1.054  | 1.155  | 1.337  | 1.240  | 0.844  |
| AcMe    | 1.073  | 1.896  | 1.628  | 1.233  | 2.744  |
| ACN     | 1.040  | 2.034  | 1.386  | 1.700  | 1.640  |
| DMSO    | 1.212  | 1.729  | 1.536  | 1.566  | 1.581  |
| MeOH    | 1.155  | 1.753  | 1.505  | 1.214  | 1.092  |

* - t1/2 (%) fluorescence lifetimes and their amplitudes, radiative (k_r) and non-radiative (k_n) rate constants [*10^9 s^-1].

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Time-correlated single-photon counting measurements

Fig. S21. The time-resolved measurements for fluorescence of 1 in methylcyclohexane

Fig. S22. The time-resolved measurements for fluorescence of 1 in 1,4-dioxane
Fig. S23. The time-resolved measurements for fluorescence of 1 in diethyl ether

Fig. S24. The time-resolved measurements for fluorescence of 1 in chloroform
Fig. S25. The time-resolved measurements for fluorescence of 1 in ethyl acetate

Fig. S26. The time-resolved measurements for fluorescence of 1 in tetrahydrofuran
Fig. S27. The time-resolved measurements for fluorescence of 1 in acetone

Fig. S28. The time-resolved measurements for fluorescence of 1 in acetonitrile
Fig. S29. The time-resolved measurements for fluorescence of 1 in dimethylformamide

Fig. S30. The time-resolved measurements for fluorescence of 1 in methanol
Fig. S31. The time-resolved measurements for fluorescence of 2 in methylcyclohexane

Fig. S32. The time-resolved measurements for fluorescence of 2 in 1,4-dioxane
Fig. S33. The time-resolved measurements for fluorescence of 2 in diethyl ether

Fig. S34. The time-resolved measurements for fluorescence of 2 in chloroform
Fig. S35. The time-resolved measurements for fluorescence of 2 in ethyl acetate

Fig. S36. The time-resolved measurements for fluorescence of 2 in tetrahydrofuran
Fig. S37. The time-resolved measurements for fluorescence of 2 in acetone

Fig. S38. The time-resolved measurements for fluorescence of 2 in acetonitrile
Fig. S39. The time-resolved measurements for fluorescence of 2 in dimethylformamide

Fig. S40. The time-resolved measurements for fluorescence of 2 in methanol
Fig. S41. The time-resolved measurements for fluorescence of 3 in methylcyclohexane

Fig. S42. The time-resolved measurements for fluorescence of 3 in 1,4-dioxane
Fig. S43. The time-resolved measurements for fluorescence of 3 in diethyl ether

Fig. S44. The time-resolved measurements for fluorescence of 3 in chloroform
Fig. S45. The time-resolved measurements for fluorescence of 3 in ethyl acetate

Fig. S46. The time-resolved measurements for fluorescence of 3 in tetrahydrofuran
Fig. S47. The time-resolved measurements for fluorescence of 3 in acetone

Fig. S48. The time-resolved measurements for fluorescence of 3 in acetonitrile
Fig. S49. The time-resolved measurements for fluorescence of 3 in dimethylformamide

Fig. S50. The time-resolved measurements for fluorescence of 3 in methanol
Fig. S51. The time-resolved measurements for fluorescence of 4 in methylcyclohexane

Fig. S52. The time-resolved measurements for fluorescence of 4 in 1,4-dioxane
Fig. S53. The time-resolved measurements for fluorescence of 4 in diethyl ether.

Fig. S54. The time-resolved measurements for fluorescence of 4 in chloroform.
Fig. S55. The time-resolved measurements for fluorescence of 4 in ethyl acetate

Fig. S56. The time-resolved measurements for fluorescence of 4 in tetrahydrofuran
Fig. S57. The time-resolved measurements for fluorescence of 4 in acetone

Fig. S58. The time-resolved measurements for fluorescence of 4 in acetonitrile
Fig. S59. The time-resolved measurements for fluorescence of 4 in dimethylformamide.

Fig. S60. The time-resolved measurements for fluorescence of 4 in methanol.
Fig. S61. The time-resolved measurements for fluorescence of 5 in methylcyclohexane

Fig. S62. The time-resolved measurements for fluorescence of 5 in 1,4-dioxane
Fig. S63. The time-resolved measurements for fluorescence of 5 in diethyl ether

Fig. S64. The time-resolved measurements for fluorescence of 5 in chloroform
Fig. S65. The time-resolved measurements for fluorescence of 5 in ethyl acetate

Fig. S66. The time-resolved measurements for fluorescence of 5 in tetrahydrofuran
Fig. S67. The time-resolved measurements for fluorescence of 5 in acetone

Fig. S68. The time-resolved measurements for fluorescence of 5 in acetonitrile
Fig. S69. The time-resolved measurements for fluorescence of 5 in dimethylformamide

Fig. S70. Fluorescence quantum yields for the set of studied compounds
Fig. S71. The phosphorescence and fluorescence for 2-5 recorded in MeTHF at 77K
Photoisomerisation experiments

**Fig. S72.** The absorption spectrum of 1 during irradiation (time given in [s])

**Fig. S73.** The absorption spectrum of 2 during irradiation (time given in [s])
Fig. S74. The absorption spectrum of 3 during irradiation (time given in [s])

Fig. S75. The absorption spectrum of 4 during irradiation (time given in [s])
Fig. S76. The absorption spectrum of 5 during irradiation (time given in [s]).
Table S3. The values of the $\Delta f_{LM}$ solvent parameter (Lippert-Mataga model)

| Solvent            | $\Delta f$ |
|--------------------|------------|
| methylcyclohexane  | -0.00062  |
| diethyl ether      | 0.166898  |
| chloroform         | 0.148156  |
| ethyl acetate      | 0.200218  |
| THF                | 0.209585  |
| acetone            | 0.284314  |
| acetonitrile       | 0.304568  |
| N,N-dimethylformamide | 0.274396 |

Table S4. Ground- ($\mu$, $S_0$) and excited-state ($\mu$, $S_1$) dipole moments predicted by CC2 method for 1-5 in CHCl$_3$ and dipole moment difference ($\Delta \mu$) estimated from Lippert-Mataga plots (shown i salso the corresponding coefficient $\chi^2$)

| compound | Lippert-Mataga | CC2/aug-cc-pVDZ |
|----------|----------------|-----------------|
|          | $\Delta \mu$ [D] | $\chi^2$ | $\mu$ ($S_0$) [D] | $\mu$ ($S_1$) [D] | $\Delta \mu$ [D] |
| 1        | 13.84           | 0.978           | 5.93 | 18.38 | 12.45 |
| 2        | 13.98           | 0.832           | 4.92 | 18.78 | 13.86 |
| 3        | 17.77           | 0.972           | 7.43 | 21.73 | 14.30 |
| 4        | 14.93           | 0.981           | 9.65 | 23.09 | 13.44 |
| 5        | 11.33           | 0.423           | 8.89 | 20.98 | 12.09 |

Fig. S7. The relation of the Stokes shift with the $f(e,n)$ function in the Lippert-Mataga model of solvation for 1
**Fig. S78.** The relation of the Stokes shift with the $f(e, n)$ function in the Lippert-Mataga model of solvation for 2

**Fig. S79.** The relation of the Stokes shift with the $f(e, n)$ function in the Lippert-Mataga model of solvation for 3

**Fig. S80.** The relation of the Stokes shift with the $f(e, n)$ function in the Lippert-Mataga model of solvation for 4
Fig. S81. The relation of the Stokes shift with the $\Delta f_{LM}$ function in the Lippert-Mataga model of solvation for 5.
Z-scan setup and experiment (experimental setup)

The multiphoton absorption properties of 2-5 were investigated in broad range (650 - 1700 nm) using the Z-scan technique with a laser system consisting of a Quantronix Integra-C Ti:sapphire regenerative amplifier operating as an 800 nm pump and a Quantronix-Palitra-FS BIBO crystal-based optical parametric amplifier. This system allows for wavelength tuning between 530 and 2000 nm pulses of ~130 fs length and operates at the repetition rate of 1 kHz. The solutions of 2-5 in chloroform (with concentration of ca. 0.3% w/w) were placed in 1 mm path length Starna glass cuvettes, which were moved along focused femtosecond laser beam in the Z axis typically from -20 to 20 mm. To determine the value of the laser intensity, scans of a 4.6 mm thick silica glass plate (used as a reference) and a cuvette filled with chloroform were investigated together with scans of the samples. The solvent measurement was conducted to eliminate the influence of the cuvette walls and the solvent itself to the closed aperture (CA) Z-scan traces. The open aperture (OA) scans for the solvent revealed absence of 2PA. To monitor the laser input, the CA signal and OA signal, the data were collected using three Si and InGaAs photodiodes (Thor Laboratories Inc.) for VIS and NIR range, respectively. Studying wavelength dependences by Z-scan requires aligning the system and determining the properties of the laser beam at each wavelength separately. Employment of appropriate expressions, introduced by Sheik-Bahae et al. [7], allows us to fit the transmittance traces corresponding to closed-aperture (CA) and open-aperture (OA) Z-scan signals, which were analyzed with the help of a custom fitting program. The detailed description of experimental setup can be found in our previous paper. The real and imaginary parts of the second hyperpolarizability $\gamma$ of the solutes were computed assuming additivity of the nonlinear contributions of the solvent and the solute and the applicability of the Lorentz local field approximation [8].
Fig. S82. Representative CA (left side) and OA (right side) experimental Z-scan traces (circles), and the theoretical fits (lines) for 2, 3, 4 at 800 nm and 5 at 825 nm. The theoretical OA curves assume 2PA.
Fig. S83. Wide-range wavelength dependence of the two-photon absorption cross-section $\sigma_2$, measured by Z-scan technique (black squares) for 2-5.
Quantum-chemical calculations

The ground state geometries of 5 molecules (both trans and cis isomers were optimized using the density functional theoretical method with the M06-2X functional [9] and the 6-31G* basis set [10, 11]. In doing so, we employed IEF-PCM method. The minima on potential energy hypersurface were confirmed by evaluation of hessian. Subsequently, the minimum-energy geometries were used for electronic-structure calculations.

Molecular dynamics simulations

All structures were solvated by adding about 470 chloroform molecules to form 40x40x40 Å box (density of such system is close to chloroform density at room temperature (1.49 g/cm³)). Total charge for each system was zero. Molecular dynamics simulations program NAMD was used to perform simulations [12]. The partial charges were obtained from M06-2X/6-31G* calculations employing IEF-PCM model at the equilibrium geometry using the CHelpG method. The CHARMM force field and chloroform force field of Dietz and Heinzinger were used to describe the system [13-15]. The system was minimized during 10000 steps followed by constant temperature NVT dynamics for 2 ns (1 step = 2 fs) at 300 K using a Langevin thermostat. MD simulations were performed for the rigid geometry of solute. Periodic boundary conditions were applied. After hydrogen bonds balance and energy equilibrium had been achieved, 50 snapshots were taking from the resulting trajectory for subsequent electronic-structure calculations.

Electronic-structure calculations

Based on rigid-body MD simulations, for each molecule (1-5) we performed we performed ab initio quantum-chemistry calculations using resolution-of-identity coupled-cluster CC2 model [16] and the aug-cc-pVDZ basis set [17]. In particular we calculated one- and two-photon transition strengths using electrostatic embedding to account for discrete solvent representation. The choice of RI-CC2 method is dictated by recent reports that all studied density functional theory approximations show serious limitations as far as predictions of two-photon absorption strengths are concerned, i.e. hybrid functionals with fixed amount of HF exchange are burdened by cancellations of significant errors, while range-separated functionals systematically underestimate two-photon transition strengths due to their inability to correctly reproduce excited-state density distributions [18, 19]. RI-CC2 calculations were performed with the TURBOMOLE--7.3 program [20]. Moreover, to shed light on ground- and excited-state density distribution we have determined the electron density difference plots at the M06-2X/6-31G* level of theory. The calculations in question were performed using GAUSSIAN 16 program.
Fig. S84. Electron density difference maps showing changes upon $S_0 \rightarrow S_1$ electronic excitations. Calculations were done at the M06-2X/6-31G* level of theory. Solvents effects were taken into account employing IEF-PCM model.
Fig. S85. The charge transfer in 1 and the associated mesomerism
Fig. S86. Excited-state geometries (in the first singlet \( S_1 \) state) of compounds 2, 3, 4 with explicit CHCl\(_3\) molecules. Calculations were performed at the M06-2X/6-31G* level of theory using IEF-PCM model.
Fig. S87. Comparison of excited-state geometries (in the first singlet $S_1$ state) of compounds 2,3,4 optimized with explicit CHCl$_3$ molecules. Shown are only cores of the molecules (without hydrogen atoms). Calculations were performed at the M06-2X/6-31G* level of theory using IEF-PCM model.
Fig. S8. Simulated one-photon absorption spectra corresponding to *cis* isomers. Shown are the results of calculations for 50 solute-solvent snapshots performed at the RI-CC2/aug-cc-pVDZ level of theory.
Fig. S89. Simulated one-photon absorption spectra corresponding to trans isomers. Shown are the results of calculations for 50 solute-solvent snapshots performed at the RI-CC2/aug-cc-pVDZ level of theory.
Fig. S90. Simulated two-photon absorption spectra corresponding to cis isomers. Shown are the results of calculations for 50 solute-solvent snapshots performed at the RI-CC2/aug-cc-pVDZ level of theory.
Fig. S91. Simulated two-photon absorption spectra corresponding to trans isomers. Shown are the results of calculations for 50 solute-solvent snapshots performed at the RI-CC2/aug-cc-pVDZ level of theory.

| Molecule | Spin symmetry | Excitation energy, eV |
|----------|---------------|-----------------------|
| 2        | T1            | 2.53306               |
|          | S1            | 3.04774               |
|          | T2            | 3.74842               |
|          | S2            | 4.08453               |
| 3        | T1            | 2.49019               |
|          | S1            | 2.96363               |
|          | T2            | 3.36541               |
|          | S2            | 3.97018               |
| 4        | T1            | 2.48339               |
|          | S1            | 2.95842               |
|          | T2            | 3.74003               |
|          | S2            | 4.16710               |
| 5        | T1            | 2.55697               |
|          | S1            | 3.08035               |
|          | T2            | 3.54001               |
|          | S2            | 4.05267               |
Table S6. Summary of statistical analysis of one-photon absorption spectra. Shown are average values of excitation energies and corresponding excitation wavelengths.

|   | trans $\overline{E}$ [eV] | $\overline{\lambda}$ [nm] | cis $\overline{E}$ [eV] | $\overline{\lambda}$ [nm] |
|---|-----------------|-----------------|-----------------|-----------------|
| 1 | 3.1519          | 393             | 2.9719          | 417             |
| 2 | 3.0781          | 403             | 2.8314          | 438             |
| 3 | 2.9573          | 419             | 2.7635          | 449             |
| 4 | 2.9709          | 417             | 2.7893          | 444             |
| 5 | 3.0450          | 407             | 2.8351          | 437             |

Table S7. Comparison of two-photon transition strengths (in au) based on the generalized two- and three-state model.

| molecule | response theory | two-state model | three-state model |
|----------|-----------------|-----------------|-----------------|
| 2        | 129             | 156             | 156             |
| 3        | 138             | 174             | 174             |
| 4        | 142             | 208             | 210             |
| 5        | 119             | 148             | 147             |

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