Supplementary Information

Insights on the isomerization of photochromic oxazines from the excitation dynamics of BODIPY–oxazine dyads

Erhan Deniz, a Mutlu Battal, a Janet Cusido, a Salvatore Sortino*b and Francisco M. Raymo* a

a Laboratory for Molecular Photonics, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, Florida, 33146-0431, USA. E-mail: fraymo@miami.edu

b Laboratory of Photochemistry, Department of Drug Sciences, University of Catania, Viale Andrea Doria 6, I-95125 Catania, Italy. E-mail: ssortino@unict.it

- Synthetic procedures for the preparation of 1a–5a and 22–25 ...............................................................S2
- Steady-state absorption and emission spectra of 3a ..................................................................................S9
- Time-resolved absorption spectra of 2a, 4a, 5a and 12 .....................................................................S10
- Temporal absorbance profiles recorded upon excitation of 2a, 4a and 5a ........................................S11
- Dependence of the transient absorbance of 2a and 12 on the laser energy .....................................S12
- Excitation spectrum of 3a ..................................................................................................................S13
Synthetic procedures for the preparation of 1a–5a and 22–25

**Synthesis of 1a:** A solution of 8 (480 mg, 1.4 mmol) and 3-ethyl-2,4-dimethylpyrrole (330 mg, 2.7 mmol) and TFA (10 μL, 0.1 mmol) in CH₂Cl₂ (100 mL) was stirred for 3 h at ambient temperature under Ar. After the addition of a solution of DDQ (310 mg, 1.4 mmol) in CH₂Cl₂ (15 mL), the mixture was stirred for a further 30 min. Then, Et₃N (3 mL, 21 mmol) and BF₃·Et₂O (3 mL, 24 mmol) were added and the mixture was stirred for a further 30 min, washed with H₂O (3 × 100 mL) and dried over Na₂SO₄. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO₂: hexanes/EtOAc (1:1, v/v)] to yield 1a (187 mg, 22%) as an orange powder. ESIMS: m/z = 628.3351 [M]+ (m/z calcld. for C₄₀H₄₂BF₂N₃O = 628.3312); ¹H NMR (CDCl₃): δ = 1.72 (1H, s), 4.73 (2H, s), 6.46 (1H, s), 7.02 (1H, d, 6 Hz), 7.82 (1H, dd, 3 and 6 Hz), 7.90 (1H, d, 3 Hz), 7.90 (1H, d, 3 Hz), 9.90 (1H, s); ¹³C NMR (CDCl₃): δ = 11.4, 12.6, 12.9, 15.0, 15.1, 17.4, 17.5, 19.1, 28.3, 41.9, 49.7, 104.4, 109.2, 119.2, 120.5, 121.9, 122.7, 126.5, 127.7, 128.0, 128.1, 128.7, 131.3, 131.5, 133.0, 136.8, 138.2, 138.8, 140.4, 148.2, 153.8, 153.9, 154.7.

**Synthesis of 2a:** A solution of 3-ethyl-2,4-dimethylpyrrole (54 mg, 0.4 mmol), 11 (85 mg, 0.2 mmol) and TFA (10 μL, 0.1 mmol) in CH₂Cl₂ (100 mL) was stirred for 12 h at ambient temperature under Ar. After the addition of a solution of TCBQ (52 mg, 0.2 mmol) in CH₂Cl₂ (15 mL), the mixture was stirred for a further 30 min. Then, Et₃N (2 mL, 14 mmol) and BF₃·Et₂O (2 mL, 16 mmol) were added and the mixture was stirred for a further 30 min, washed with H₂O (3 × 100 mL) and dried over Na₂SO₄. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO₂: hexanes/EtOAc (1:1, v/v)] to yield 2a (81 mg, 57%) as an orange powder. ESIMS: m/z = 697.3182 [M + Na]+ (m/z calcld. for C₄₀H₄₁BF₂N₄NaO₃ = 697.3139); ¹H NMR (CDCl₃): δ = 0.90 (3H, s), 0.94–0.97 (9H, m), 1.34 (3H, s), 1.64 (3H, s), 2.18–2.37 (4H, m), 2.54 (6H, s), 4.54 (1H, d, 18 Hz), 4.69 (1H, d, 18 Hz), 6.76 (1H, d, 8 Hz), 6.94 (2H, t, 7 Hz), 7.20 (2H, t, 7 Hz), 7.36 (2H, d, 7 Hz), 7.71–7.79 (2H, m), 7.96–7.99 (2H, m); ¹³C NMR (CDCl₃): δ = 12.9, 15.0, 17.4, 19.0, 28.2, 39.1, 41.3, 49.9, 105.5, 109.5, 118.7, 120.5, 121.5, 123.0, 123.2, 124.3, 128.3, 129.1, 131.0, 133.4, 137.0, 137.1, 137.6, 138.3, 139.5, 141.4, 147.0, 159.3.

**Synthesis of 3a:** A mixture of 11a (68 mg, 0.2 mmol), 12 (65 mg, 0.2 mmol), piperidine (0.3 mL, 3 mmol) and acetic acid (0.2 mL, 3 mmol) in benzene (20 mL) was heated for 12 h under reflux in a Dean-Stark apparatus. After cooling down to ambient temperature, the solvent distilled off under reduced pressure and the residue was purified by column chromatography [SiO₂: hexanes/EtOAc (1:1, v/v)] to afford 3a (25 mg, 19%) as a purple solid. ESIMS: m/z = 785.3487 [M + Na]⁺ (m/z calcld. for C₄₇H₄₅BF₂N₄NaO₃ = 785.3453); ¹H NMR (CDCl₃): δ = 0.90 (3H, s), 0.94–0.97 (9H, m), 1.34 (3H, s), 1.32 (3H, s), 1.61 (3H, s), 2.33 (2H, q, 7 Hz), 2.56–2.58 (5H, m), 4.56 (1H, d, 18 Hz), 4.66 (1H, d, 18 Hz), 6.74 (1H, d, 8 Hz), 6.92 (2H, t, 7 Hz), 7.14–7.19 (3H, m), 7.30–7.31 (2H, m), 7.49–7.51 (3H, m), 7.63 (4H, bs), 7.74 (1H, d, 17 Hz), 7.94–7.97 (2H, m); ¹³C NMR (CDCl₃): δ = 13.3, 17.5, 18.7, 18.9, 50.2, 75.4, 105.6, 120.5, 121.5, 123.6, 124.1, 128.1, 128.8, 129.4, 132.2, 132.7, 133.3, 134.5, 136.1, 138.0, 138.7, 140.0, 140.2, 141.3, 147.2, 157.0, 159.5.

Fig. S1 Synthesis of the dyad 1a.
Synthesis of 4a: A mixture of 13 (183 mg, 0.6 mmol), 14 (104 mg, 0.3 mmol) and TFA (0.3 mmol, 20 μL) in EtOH (20 mL) was heated for 12 h under reflux. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO2: hexanes/EtOAc (4:1, v/v)] to afford 4a (20 mg, 10%) as a purple solid. ESIMS: \( m/z = 645.2894 \) [M + H]+ (\( m/z \) calcd. for C38H36BF2N4O3 = 645.2850); \(^1\)H NMR (CDCl3): \( \delta = 1.26 \) (6H, s), 1.31 (3H, s), 1.38 (3H, s), 2.57 (3H, s), 2.59 (3H, s), 4.59 (2H, s), 5.89 (1H, d, 16 Hz), 6.03 (1H, s), 6.65 (2H, d, 8 Hz), 6.82−6.93 (2H, m), 7.10−7.15 (2H, m), 7.24−7.26 (1H, m), 7.48−7.50 (3H, m), 7.96−8.06 (2H, m); \(^{13}\)C NMR (CDCl3): \( \delta = 13.1, 14.2, 15.0, 15.2, 30.1, 41.3, 50.1, 76.5, 76.8, 77.6, 109.3, 118.1, 120.4, 121.4, 122.6, 122.8, 123.6, 124.1, 124.5, 125.3, 125.8, 126.9, 128.1, 128.3, 129.6, 129.7, 131.1, 132.6, 135.2, 138.5, 138.9, 140.9, 142.4, 145.0, 146.6, 153.7.

Synthesis of 5a: A solution of 16 (100 mg, 0.2 mmol) and 2-chloromethyl-4-nitrophenol (37 mg, 0.2 mmol) in MeCN (10 mL) was heated under reflux for 24 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH2Cl2 (3 mL). The addition of Et2O (20 mL) caused the precipitation of a purple solid. The solid was dissolved in CH2Cl2 (30 mL) and washed with H2O (20 mL). The organic phase was dried over Na2SO4 and the solvent was distilled off under reduced pressure to give 5a (87 mg, 70%) as a red solid. ESIMS: \( m/z = 771.3734 \) [M + H]+ (\( m/z \) calcd. for C48H47BN4O5 = 771.3720); \(^1\)H NMR (CDCl3): \( \delta = 0.93 \) (6H, t, 7 Hz), 1.29 (6H, s), 1.51 (6H, bs), 2.02 (3H, s), 2.03 (3H, s), 2.22 (4H, q.

Fig. S2  Synthesis of the dyads 2a and 3a.
CH₂Cl₂ (20 mL). The resulting solution was washed with H₂O (2 × 20 mL). The solvent of the organic phase was distilled off under reduced pressure and the residue was purified by column chromatography (SiO₂; CH₂Cl₂) to afford 8 (480 mg, 45%) as a white solid. ESIMS: m/z = 356.1641 [M + H]+ (m/z calcd. for C₂₄H₂₂NO₂ = 356.1645); ¹H NMR (CDCl₃): δ = 0.84 (3H, s), 1.60 (3H, s), 4.54 (1H, d, 8 Hz), 4.64 (1H, d, 8 Hz), 6.73 (1H, 8 Hz), 6.91 (2H, q, 8 Hz), 7.11–7.18 (2 H, m), 7.83 (3H, m), 7.53 (1H, s), 7.56 (1H, dd, 2 and 8 Hz), 7.66 (2H, d, 8 Hz), 9.72 (1H, s); ¹³C NMR (CDCl₃): δ = 18.2, 19.9, 41.2, 50.2, 105.2, 108.5, 110.8, 117.6, 119.7, 120.1, 120.7, 122.2, 127.5, 128.4, 129.7, 130.0, 130.5, 136.7, 138.3, 147.8, 159.4, 192.3.

**Synthesis of 9:** A solution of i-propyltolylketone (2.88 g, 18 mmol) and phenylhydrazine (1.78 mL, 18 mmol) in acetic acid (12 mL) was heated for 24 h under reflux. After cooling down to ambient temperature, the solution was diluted with H₂O (20 mL) and the pH was adjusted to ca. 8 with aqueous KOH (0.3 M). Then, the mixture was extracted with CH₂Cl₂ (3 × 20 mL). The organic phase was dried over Na₂SO₄, filtered and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO₂; hexanes/CH₂Cl₂ (1:2, v/v)] to afford 9 (2.8 g, 68%) as a white solid. ESIMS: m/z = 236.1442 [M + H]+ (m/z calcd. for C₁₇H₁₈N = 236.1434); ¹H NMR (CDCl₃): δ = 1.58 (6H, s), 2.40 (3H, s), 7.26–7.36 (4H, m), 7.38 (2H, dt, 1 and 8 Hz), 7.39 (1H, d, 8 Hz), 8.14 (2H, d, 8 Hz); ¹³C NMR (CDCl₃): δ = 21.9, 24.6, 121.4, 128.2, 129.9, 131.9, 141.3, 148.1, 153.7, 183.5.

**Synthesis of 10:** A suspension of 9 (80 mg, 0.3 mmol), NBS (121 mg, 0.7 mmol) and AIBN (16 mg, 0.1 mmol) in CCl₄ (10 mL) was heated for 23 h under reflux and Ar. The mixture was diluted with EtOAc (25 mL), extracted with aqueous HCl (3%, 3 × 20 mL), washed with brine and dried over Na₂SO₄. The organic phase was filtered and the solvent was distilled off under reduced pressure. The residue was dissolved in MeCN (0.6 mL) and diluted with a solution of AgNO₃ (340 mg, 2 mmol) in H₂O (0.3 mL). The mixture was heated for 20 min under reflux, allowed to cool down to ambient temperature, filtered and washed with CH₂Cl₂ (3 × 5 mL). The

**Fig. S3** Synthesis of the dyad 4a.

**Fig. S4** Synthesis of the dyad 5a.
organic phase was washed with H2O (25 mL) and dried over Na2SO4. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO2: hexanes/CH2Cl2 (1:3, v/v)] to afford 10 (60 mg, 80%) as a yellow gel. FABMS: m/z = 250 [M + H]+; 1H NMR (CDCl3): δ = 1.58 (6H, s), 7.22–7.38 (3H, m), 7.72 (1H, d, 8 Hz), 7.97 (4H, d, 8 Hz), 8.41 (4H, d, 8 Hz), 10.06 (1H, s); 13C NMR (CDCl3): δ = 24.8, 54.0, 121.5, 121.8, 127.1, 127.1, 128.4, 128.9, 129.1, 130.2, 137.6, 148.1, 153.2, 182.2, 192.1.

**Synthesis of 11:** A solution of 10 (130 mg, 0.5 mmol) and 2-chloromethyl-4-nitrophenol (107 mg, 0.6 mmol) in MeCN (30 mL) was heated for 48 h under reflux and Ar. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH2Cl2 (15 mL) and washed with H2O (20 mL). The solvent of the organic phase was distilled off under reduced pressure and the residue was purified by column chromatography (SiO2: CH2Cl2) to afford 11 (116 mg, 56%) as a white solid. ESIMS: m/z = 401 [M + H]+; 1H NMR (CDCl3): δ = 0.85 (3H, s), 1.61 (3H, s), 4.50 (1H, d, 18 Hz), 4.68 (1H, d, 18 Hz), 6.75 (1H, d, 8 Hz), 6.94 (2H, t, 8 Hz), 7.17–7.21 (2H, m), 7.85 (2H, bs), 7.94–7.97 (4H, m); 13C NMR (CDCl3): δ = 41.1, 50.8, 105.2, 117.4, 119.6, 120.4, 121.9, 122.6, 123.1, 124.0, 125.3, 127.2, 128.1, 129.5, 130.3, 131.4, 137.0, 137.6, 141.4, 143.2, 147.0, 159.0.

**Synthesis of 14:** A solution of 19 (200 mg, 0.6 mmol) in 1,2-dichloroethane (50 mL) was added to a solution of POCl3 (2 mL, 22 mmol) in dry N,N'-dimethylformamide (2 mL) maintained at ambient temperature under Ar. The mixture was heated at 50 °C for 2 hours and, after cooling down to ambient temperature, was slowly poured into a saturated aqueous solution of NaHCO3 (200 mL) maintained in an ice bath. The resulting mixture was stirred for a further 30 min and washed with H2O (50 mL). The organic layer was dried over Na2SO4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO2: hexanes/EtOAc (9:1, v/v)] to afford 14 (100 mg, 33%) as an orange solid. ESIMS: m/z = 375 [M + Na]+; 1H NMR (CDCl3): δ = 1.44 (3H, s), 1.67 (3H, s), 2.63 (3H, s), 2.84 (3H, s), 6.17 (1H, s), 7.21–7.31 (2H, m), 7.53–7.57 (3H, m), 9.96 (1H, s); 13C NMR (CDCl3): δ = 11.6, 13.0, 14.8, 15.1, 97.6, 99.9, 101.4, 102.4, 124.1, 127.7, 129.5, 134.1, 143.6, 147.4, 156.5, 161.7, 186.0.

**Synthesis of 15:** A solution of 2,3,3-trimethyl-3H-indole (480 mg, 2 mmol), 3,4-dihydroxybenzaldehyde (330 mg, 2.4 mmol) and HBr (0.5 mL, 33 % in AcOH) in EtOH (10 mL) was heated under reflux for 2 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH2Cl2 (30 mL) and washed with a saturated aqueous solution of NaHCO3 (2 × 20 mL). The organic phase was dried over Na2SO4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO2: hexane/EtOAc (1:1, v/v)] to afford 15 (120 mg, 21%) as a red solid. ESIMS: m/z = 280 [M + H]+; 1H NMR (CDCl3): δ = 1.45 (6H, s), 6.8 (1H, s), 6.84–6.87 (2H, m), 7.18 (1H, s), 7.23–7.27 (1H, m), 7.32 (2H, t, 8 Hz), 7.52–7.59 (2H, m).

**Synthesis of 16:** AlCl3 (58 mg, 0.4 mmol) was added to a solution of 12 (110 mg, 0.3 mmol) in dry CH2Cl2 (10 mL) maintained under argon. The suspension was stirred for 15 min and then 15 (120 mg, 0.43 mmol) was added. The mixture was stirred for a further 20 min and then washed with a saturated aqueous solution of NaHCO3 (2 × 20 mL). The organic phase was dried over Na2SO4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO2: CH2Cl2] to give 16 (155 mg, 86%) as a red solid. ESIMS: m/z = 620.3430 [M + H]+ (m/z calcd. for C41H43BN3O2 = 620.3450); 1H NMR (CDCl3): δ = 0.95 (6H, t, 7 Hz), 1.30 (6H, s), 1.50 (3H, s), 1.60 (3H, s), 2.08 (6H, s), 2.24 (4H, q, 7 Hz), 6.79–6.82 (1H, m), 6.95 (1H, d, 18 Hz), 7.09 (1H, d, 9 Hz), 7.16 (1H, s), 7.22–7.33 (6H, m), 7.46–7.52 (2H, m), 7.63 (1H, d, 9 Hz), 7.73 (1H, d, 18 Hz).

**Synthesis of 18:** A mixture of benzaldehyde (16 mg, 0.16 mmol), 12 (61 mg, 0.16 mmol), piperidine (0.3 mL, 3 mmol) and acetic acid (0.2 mL, 3 mmol) in benzene (20 mL) was heated for 12 h under reflux in a Dean-Stark apparatus. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was purified by column
chromatography [SiO$_2$: hexanes/EtOAc (1:1, v/v)] to afford 18 (15 mg, 20%) as a purple solid. ESIMS: $m/z = 491$ [M + Na]$^+$; $^1$H NMR (CDCl$_3$): $\delta = 0.99$ (3H, t, 8 Hz), 1.15 (3H, t, 8 Hz), 1.29 (3H, s), 1.31 (3H, s), 1.57 (3H, s), 2.60 (4H, q, 8 Hz), 7.19 (1H, d, 16 Hz), 7.28–7.40 (5H, m), 7.48–7.50 (3H, m), 7.60 (2H, d, 8 Hz), 7.73 (1H, d, 16 Hz).

**Synthesis of 20:** A mixture of catechol (25 mg, 0.23 mmol), 12 (57 mg, 0.15 mmol) and AlCl$_3$ (30 mg, 0.23 mmol) in dry CH$_2$Cl$_2$ (6 mL) was stirred for 30 min under Ar at ambient temperature. After washing with H$_2$O (50 mL), the solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO$_2$: CH$_2$Cl$_2$/hexanes (1:1, v/v)] to afford 20 (61 mg, 95%) as a dark red solid. ESIMS: $m/z = 451$ [M + H]$^+$; $^1$H NMR (CDCl$_3$): $\delta = 0.93$ (6H, t, 8 Hz), 1.29 (6H, s), 2.06 (6H, s), 2.25 (4H, q, 8 Hz), 6.80 (4H, s), 7.30–7.32 (2H, m), 7.48–7.50 (3H, m); $^{13}$C NMR (CDCl$_3$): $\delta = 12.2, 13.1, 15.0, 17.5, 109.5, 119.8, 128.7, 129.1, 129.5, 131.9, 133.8, 136.4, 139.6, 152.4, 155.8.$

**Synthesis of the Hexafluorophosphate Salt of 22:** A solution of 26 (340 mg, 0.7 mmol) and methyl iodide (1.0 mL, 16 mmol) in MeCN (20 mL) was heated under reflux for 24 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ (3 mL). The addition of Et$_2$O (20 mL) caused the precipitation of a purple solid, which was filtered off and dissolved in Me$_2$CO (5 mL). After the addition of a saturated aqueous solution of NH$_4$PF$_6$ (5 mL), the solution was concentrated under reduced pressure to half of its original volume and the resulting precipitate was filtered off to give the hexafluorophosphate salt of 22 (324 mg, 73%) as dark red solid. ESIMS: $m/z = 538.3217$ [M – PF$_6$]$^+$ ($m/z$ calcd. for C$_{34}$H$_{39}$BF$_2$N$_3$ = 538.3206); $^1$H NMR (CDCl$_3$): $\delta = 0.98$ (6H, t, 8 Hz), 1.30 (6H, s), 1.70 (6H, s), 2.30 (4H, q, 8 Hz), 2.52 (6H, s), 4.20 (3H, s), 7.56–7.63 (4H, m), 7.80 (2H, d, 8 Hz), 8.13 (2H, d, 8 Hz); $^{13}$C NMR (CDCl$_3$): $\delta = 12.3, 13.0, 15.0, 17.5, 23.2, 39.1, 56.1, 117.4, 123.5, 126.0, 130.0, 130.2, 130.3, 130.6, 131.4, 134.0, 137.6, 138.0, 141.4, 142.0, 142.3, 155.2, 190.7.$

**Synthesis of the Hexafluorophosphate Salt of 23:** A solution of 27 (34 mg, 0.06 mmol) and methyl iodide (1.0 mL, 16 mmol) in MeCN (20 mL) was heated under reflux for 24 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ (3 mL). The addition of Et$_2$O (20 mL) caused the precipitation of a purple solid, which was filtered off and dissolved in Me$_2$CO (5 mL). After the addition of a saturated aqueous solution of NH$_4$PF$_6$ (5 mL), the solution was concentrated under reduced pressure to half of its original volume and the resulting precipitate was filtered off to give the hexafluorophosphate salt of 23 (28 mg, 65%) as purple.

![Fig. S5 Synthesis of 22 and 23.](image-url)
solid. ESIMS: m/z = 626 [M – PF₆]+; ¹H NMR (CD₃CN): δ = 1.01 (3H, t, 8 Hz), 1.17 (3H, t, 8 Hz), 1.36 (3H, s), 1.37 (3H, s), 1.66 (6H, s), 2.37 (2H, q, 8 Hz), 2.56 (3H, s), 2.68 (2H, q, 8 Hz), 3.96 (3H, s), 7.28–7.30 (3H, m), 7.58–7.60 (3H, m), 7.64–7.76 (4H, m), 7.81 (1H, d, 8 Hz), 7.82–7.85 (2H, m), 7.94 (2H, d, 8 Hz).

**Synthesis of the Hexafluorophosphate Salt of 24:** A mixture of 14 (50 mg, 0.14 mmol) and the iodide salt of 28 (43 mg, 0.14 mmol) in EtOH (20 mL) was heated for 24 hours under reflux. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH₂Cl₂ (5 mL). The addition of Et₂O (30 mL) caused the precipitation of a solid, which was filtered off and dissolved in Me₂CO (5 mL). After the addition of a saturated aqueous solution of NH₄PF₆ (5 mL), the solution was concentrated under reduced pressure to half of its original volume and the resulting precipitate was filtered off to give the hexafluorophosphate salt of 24 (25 mg, 36%) as a purple solid. ESIMS: m/z = 508.2751 [M – PF₆]+ (m/z calc. for C₃₂H₃₃BF₂N₃ = 508.2736); ¹H NMR [(CD₃)₂CO]: δ = 1.51 (3H, s), 1.73 (3H, s), 1.88 (6H, s), 2.65 (3H, s), 4.20 (3H, s), 6.48 (1H, s), 7.09 (1H, d, 8 Hz), 7.53–7.56 (2H, m), 7.62–7.69 (5H, m), 7.76–7.85 (2H, m), 8.32 (1H, d, 8 Hz); ¹³C NMR [(CD₃)₂CO]: δ = 12.5, 13.5, 14.3, 25.9, 33.6, 51.9, 97.6, 98.6, 99.9, 101.4, 110.3, 114.4, 122.8, 128.8, 129.0, 129.9, 134.0, 143.1, 145.9, 148.4.

**Synthesis of the Iodide Salt of 25:** A solution of 16 (55 mg, 0.1 mmol) and methyl iodide (0.5 mL, 8 mmol) in MeCN (10 mL) was heated under reflux for 24 hours. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH₂Cl₂ (3 mL). The addition of Et₂O (30 mL) caused the precipitation of a purple solid, which was filtered off to give the iodide salt of 25 (45 mg, 66%) as red solid. ESIMS: m/z = 634.3624 [M – I]+ (m/z calc. for C₄₂H₄₅BN₃O₂ = 634.3607); ¹H NMR (CD₃CN): δ = 0.93 (6H, t, 8 Hz), 1.26 (6H, s), 1.83 (6H, s), 1.98 (6H, s), 2.25 (4H, q, 8 Hz), 4.26 (3H, s), 6.91 (1H, d, 8 Hz), 6.98 (1H, d, 8 Hz), 7.41–7.66 (11H, m), 8.16 (1H, d, 16 Hz); ¹³C NMR (CDCl₃): δ = 11.9, 12.7, 14.7, 17.0, 27.4, 29.7, 35.7, 51.7, 107.9, 108.5, 109.8, 114.0, 119.3, 122.7, 127.2, 127.9, 128.0, 128.9, 129.1, 129.2, 129.30, 131.4, 131.5, 134.0, 140.2, 140.5, 141.7, 153.4, 155.4, 156.3, 160.7, 180.9.

**Synthesis of 26:** A solution of 3-ethyl-2,4-dimethylpyrrole (370 mg, 3 mmol), 10 (370 mg, 1.5 mmol) and TFA (10 μL, 0.1 mmol) in CH₂Cl₂ (300 mL) was stirred for 12 hours at ambient temperature under Ar. After the addition of a solution of TCBQ (370 mg, 1.5 mmol) in CH₂Cl₂ (30 mL), the mixture was stirred for a further 30 min. Then, Et₃N (5 mL, 35 mmol) and BF₃·Et₂O (5 mL, 40 mmol) were added and the mixture was stirred for a further 30 min, washed with H₂O (3 × 100 mL) and dried over Na₂SO₄. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO₂: hexanes/EtOAc (2:1, v/v)] to yield 26 (370 mg, 48%) as an orange powder. ESIMS: m/z = 524.3066 [M + H]+ (m/z calc. for C₃₃H₃₇BF₂N₃ = 524.3049); ¹H NMR (CD₃CN): δ = 1.00 (6H, t, 8 Hz), 1.36 (6H, s), 1.64 (6H, s), 2.31 (4H, q, 8 Hz), 2.56 (6H, s), 7.32 (1H, d, 8 Hz), 7.39 (2H, d, 8 Hz), 7.44 (2H, d, 8 Hz), 7.23 (1H, d, 8 Hz), 7.26 (2H, d, 8 Hz); ¹³C NMR (CDCl₃): δ = 11.2, 12.7, 14.7, 17.2, 24.7,
24.8, 53.8, 121.1, 121.2, 126.4, 128.0, 128.9, 129.0, 130.6, 133.1, 134.0, 138.2, 138.4, 139.3, 147.6, 153.0, 154.2, 182.9.

**Synthesis of 27:** A solution of 10 (250 mg, 1 mmol), 12 (430 mg, 1 mmol), piperidine (1 mL, 10 mmol) and acetic acid (0.8 mL, 10 mmol) in benzene (30 mL) was heated under reflux for 12 hours in a Dean-Stark apparatus. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO2: hexanes/EtOAc (9:1, v/v)] to afford 27 (118 mg, 24%) as an orange solid. ESIMS: m/z = 612.3379 [M + H]+ (m/z calcd. for C40H41BF2N3 = 612.3363); 1H NMR (CDCl3): δ = 1.01 (3H, t, 8 Hz), 1.86 (3H, t, 8 Hz), 1.32 (3H, s), 1.34 (3H, s), 1.63 (6H, s), 2.34 (4H, q, 8 Hz), 2.61 (3H, s), 7.23–7.40 (5H, m), 7.50 (3H, bs), 7.72 (4H, d, 8 Hz), 7.85 (1H, d, 16 Hz), 8.20 (2H, d, 8 Hz); 13C NMR (CDCl3): δ = 11.7, 12.2, 13.3, 14.6, 14.9, 17.5, 18.7, 25.3, 53.8, 121.3, 122.0, 126.2, 127.6, 128.2, 128.8, 129.1, 129.3, 129.5, 132.4, 132.8, 133.1, 133.6, 133.9, 134.6, 136.1, 138.6, 140.0, 140.1, 148.1, 148.3, 153.6, 157.1, 183.1.
Steady-state absorption and emission spectra of 3a

Fig. S8  Steady-state absorption spectra (5 μM, MeCN, 20 °C) of 3a before (a) and after (b) the addition of TFA (2000 eq.), of 18 (c) and of 23 (d). Steady-state emission spectra (5 μM, MeCN, 20 °C, λ_ex = 500 nm) of 3a before (e) and after (f) the addition of TFA (2000 eq.), of 18 (g) and of 23 (h).
Time-resolved absorption spectra of 2a, 4a, 5a and 12

Fig. S9 Time-resolved absorption spectra (MeCN, 20 °C) of optically-matched \( A_{355} = 0.3 \) solutions of 2a (a), 12 (b), 4a (c) and 5a (d) recorded after 0.1 \( \mu s \) from pulsed laser irradiation (355 nm, 6 ns, 12 mJ).
Temporal absorbance profiles recorded upon excitation of 2a, 4a and 5a

**Fig. S10** Temporal absorbance profiles (MeCN, 20 °C) of optically-matched \((A_{355} = 0.3)\) solutions of 2a at 430 (a) and 670 nm (b), 4a at 430 (c) and 650 nm (d) and 5a at 450 (e) and 640 nm (f) recorded upon pulsed laser irradiation (355 nm, 6 ns, 12 mJ).
Dependence of the transient absorbance of 2a and 12 on the laser energy

Fig. S11  Absorbance measured at 430 nm upon pulsed laser irradiation (355 nm, 6 ns) of optically-matched ($A_{355} = 0.3$) solutions of 2a (a) and 12 (b) against the laser energy.
Excitation spectrum of 3a

**Fig. S12** Excitation (a, $\lambda_{\text{Em}} = 585$ nm) and absorption (b) spectra of 3a and absorption spectrum (c) of 18 (23 µM, MeCN, 20 °C).