Supplementary Information

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

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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 CH_2Cl_2 (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 CH_2Cl_2 (15 mL), the mixture was stirred for a further 30 min. Then, Et_3N (3 mL, 21 mmol) and $BF_3{\cdot}Et_2O$ (3 mL, 24 mmol) were added and the mixture was stirred for a further 30 min, washed with H_2O (3 × 100 mL) and dried over Na_2SO_4. 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 yield **1a** (187 mg, 22%) as an orange powder. ESIMS: *m*/*z* = 628.3351 $[M]^+$ (*m*/*z* calcd. for $C_{40}H_{42}BF_2N_3O$ = 628.3312); ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 CH_2Cl_2 (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 CH_2Cl_2 (15 mL), the mixture was stirred for a further 30 min. Then, Et_3N (2 mL, 14 mmol) and $BF_3{\cdot}Et_2O$ (2 mL, 16 mmol) were added and the mixture was stirred for a further 30 min, washed with H_2O (3 × 100 mL) and dried over Na_2SO_4. 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 yield **2a** (81 mg, 57%) as an orange powder. ESIMS: *m*/*z* = 697.3182 $[M + Na]^+$ (*m*/*z* calcd. for $C_{40}H_{41}BF_2N_4NaO_3$ = 697.3139); ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 [SiO_2: 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* calcd. for $C_{47}H_{45}BF_2N_4NaO_3$ = 785.3453); ^{1}H NMR ($CDCl_3$): δ = 0.90 (3H, s), 1.00 (3H, t, 7 Hz), 1.14 (3H, t, 7 Hz), 1.31 (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); ^{13}C NMR ($CDCl_3$): 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.

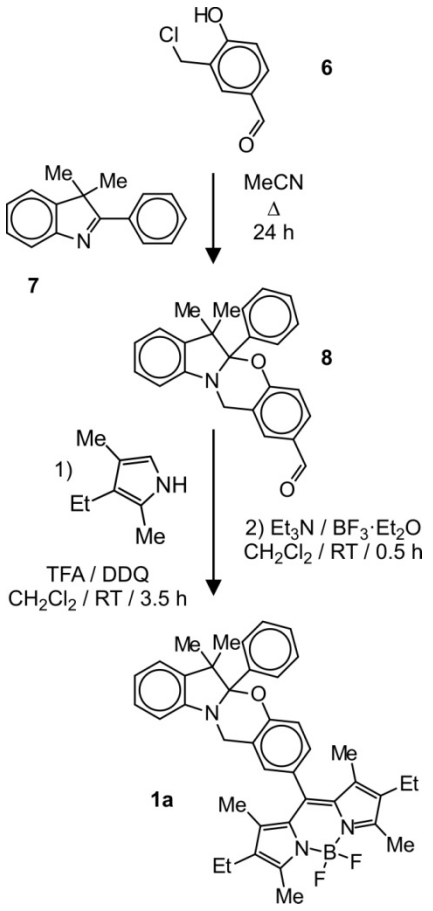

Fig. S1 Synthesis of the dyad **1a**.

***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 [SiO_2: 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 $C_{38}H_{36}BF_2N_4O_3$ = 645.2850); ^{1}H NMR ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 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 CH_2Cl_2 (3 mL). The addition of Et_2O (20 mL) caused the precipitation of a purple solid. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with H_2O (20 mL). The organic phase was dried over Na_2SO_4 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 $C_{48}H_{47}BN_4O_5$ = 771.3720); ^{1}H NMR ($CDCl_3$): δ = 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,

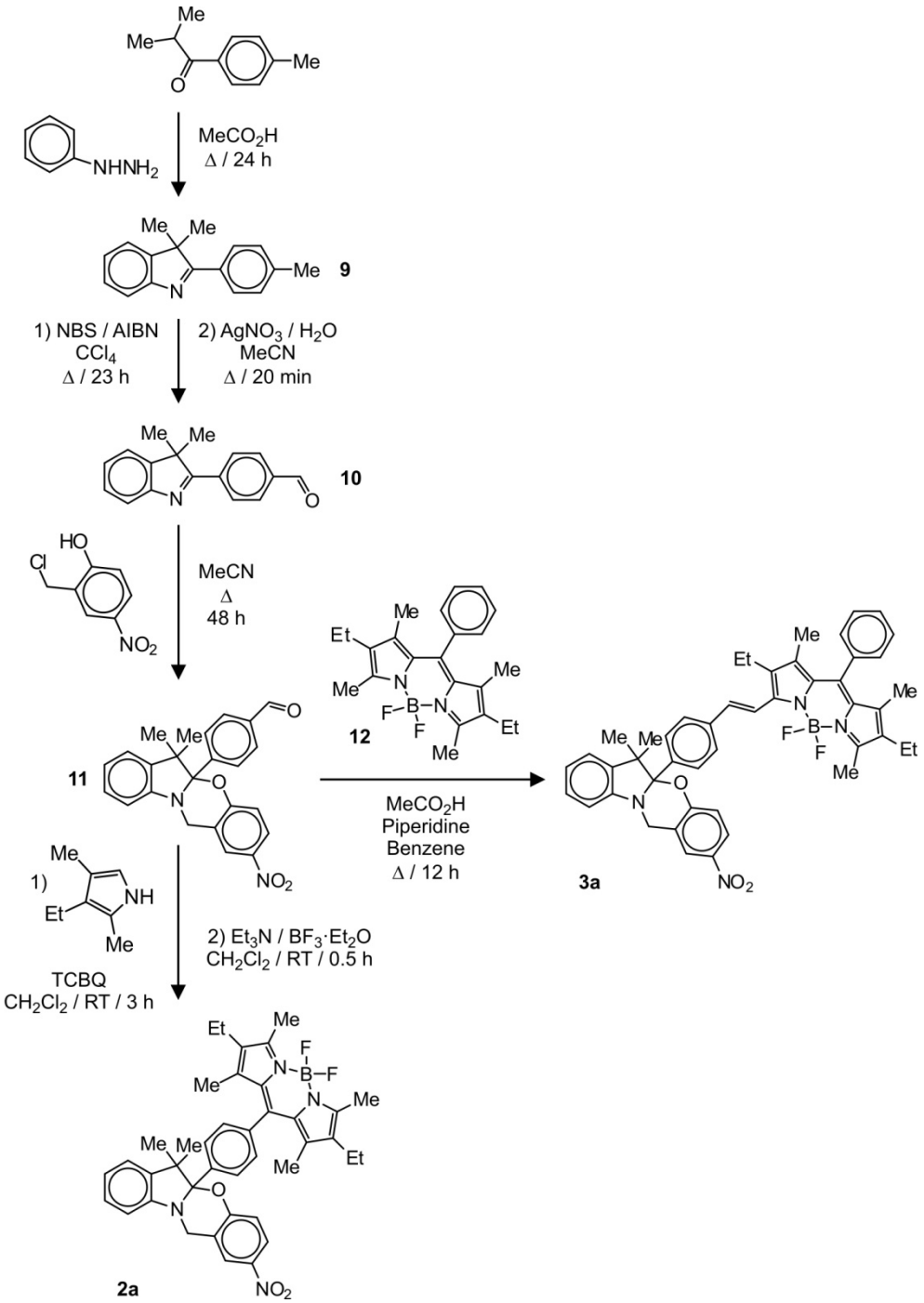

Fig. S2 Synthesis of the dyads **2a** and **3a**.

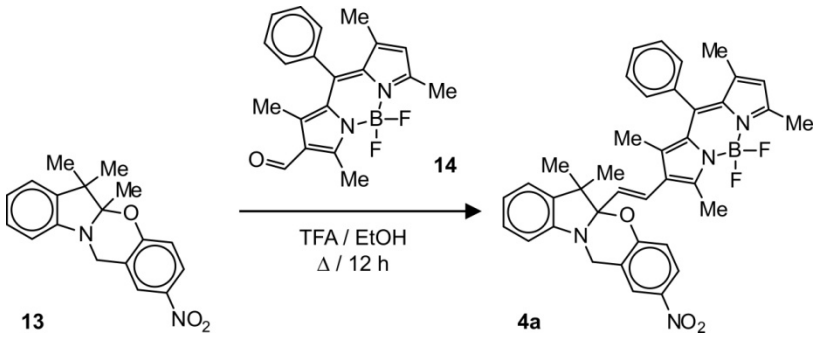

Fig. S3 Synthesis of the dyad **4a**.

8 Hz), 4.81 (2H, bs), 6.74–6.77 (1H, m), 7.02 (4H, bs), 7.21–7.28 (5H, m), 7.50–7.52 (4H, m), 7.98–8.01 (3H, m).

***Synthesis of* 8:** A solution of **6** (511 mg, 3 mmol) and **7** (700 mg, 3 mmol) in MeCN (20 mL) was heated for 24 h under reflux. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure and the residue was dissolved in CH_2Cl_2 (20 mL). The resulting solution was washed with H_2O (2 × 20 mL). The solvent of the organic phase was distilled off under reduced pressure and the residue was purified by column chromatography (SiO_2: CH_2Cl_2) to afford **8** (480 mg, 45%) as a white solid. ESIMS: *m/z* = 356.1641 $[M + H]^+$ (*m/z* calcd. for $C_{24}H_{22}NO_2$ = 356.1645); ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 H_2O (20 mL) and the pH was adjusted to *ca.* 8 with aqueous KOH (0.3 M). Then, the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: hexanes/CH_2Cl_2 (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 $C_{17}H_{18}N$ = 236.1434); ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 CCl_4 (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 Na_2SO_4. 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 $AgNO_3$ (340 mg, 2 mmol) in H_2O (0.3 mL). The mixture was heated for 20 min under reflux, allowed to cool down to ambient temperature, filtered and washed with CH_2Cl_2 (3 × 5 mL). The

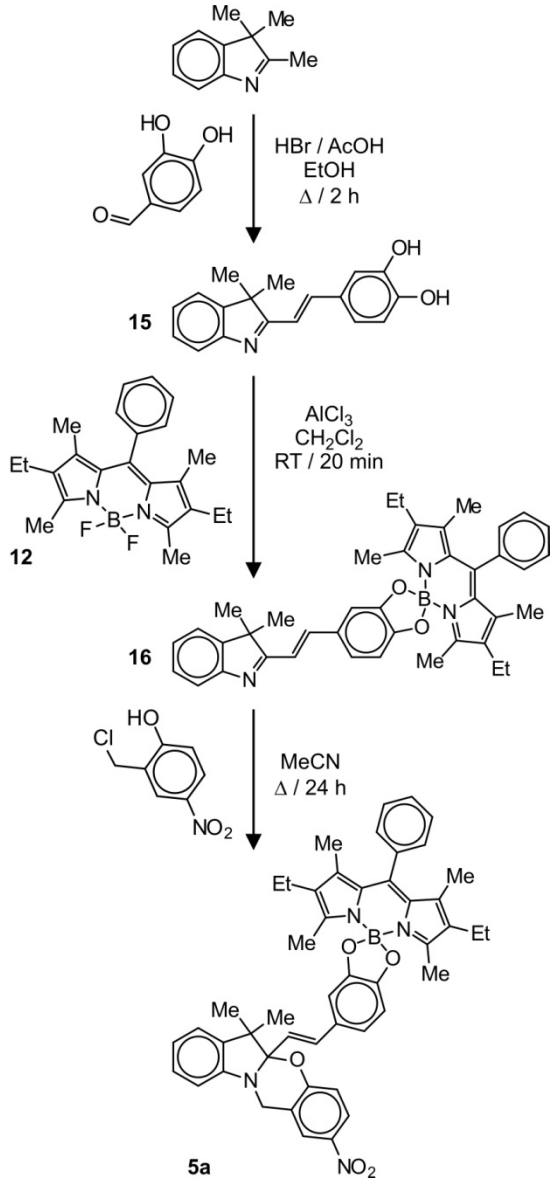

Fig. S4 Synthesis of the dyad **5a**.

organic phase was washed with H_2O (25 mL) and dried over Na_2SO_4. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2: hexanes/CH_2Cl_2 (1:3, v/v)] to afford **10** (60 mg, 80%) as a yellow gel. FABMS: *m/z* = 250 $[M + H]^+$; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): δ = 24.8, 54.0, 121.5, 121.8, 127.1, 128.4, 128.9, 129.1, 130.2, 137.6, 138.9, 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 CH_2Cl_2 (15 mL) and washed with H_2O (20 mL). The solvent of the organic phase was distilled off under reduced pressure and the residue was purified by column chromatography (SiO_2: CH_2Cl_2) to afford **11** (116 mg, 56%) as a white solid. ESIMS: *m/z* = 401 $[M + H]^+$; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 $POCl_3$ (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 $NaHCO_3$ (200 mL) maintained in an ice bath. The resulting mixture was stirred for a further 30 min and washed with H_2O (50 mL). The organic layer was dried over Na_2SO_4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: hexanes/EtOAc (9:1, v/v)] to afford **14** (100 mg, 33%) as an orange solid. ESIMS: *m/z* = 375 $[M + Na]^+$; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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-3*H*-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 CH_2Cl_2 (30 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (2 × 20 mL). The organic phase was dried over Na_2SO_4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: hexane/EtOAc (1:1, v/v) to afford **15** (120 mg, 21%) as a red solid. ESIMS: *m/z* = 280 $[M + H]^+$; ^{1}H NMR ($CDCl_3$): 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:** $AlCl_3$ (58 mg, 0.4 mmol) was added to a solution of **12** (110 mg, 0.3 mmol) in dry CH_2Cl_2 (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 $NaHCO_3$ (2 × 20 mL). The organic phase was dried over Na_2SO_4 and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: CH_2Cl_2] to give **16** (155 mg, 86%) as a red solid. ESIMS: *m/z* = 620.3430 $[M + H]^+$ (*m/z* calcd. for $C_{41}H_{43}BN_3O_2$ = 620.3450) ; ^{1}H NMR ($CDCl_3$): 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 ($CDCl_3$): δ = 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_2Cl_2 (6 mL) was stirred for 30 min under Ar at ambient temperature. After washing with H_2O (50 mL), the solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2: CH_2Cl_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 ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 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_2Cl_2 (3 mL). The addition of Et_2O (20 mL) caused the precipitation of a purple solid, which was filtered off and dissolved in Me_2CO (5 mL). After the addition of a saturated aqueous solution of NH_4PF_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 $C_{34}H_{39}BF_2N_3$ = 538.3206); ^{1}H NMR ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 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_2Cl_2 (3 mL). The addition of Et_2O (20 mL) caused the precipitation of a purple solid, which was filtered off and dissolved in Me_2CO (5 mL). After the addition of a saturated aqueous solution of NH_4PF_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

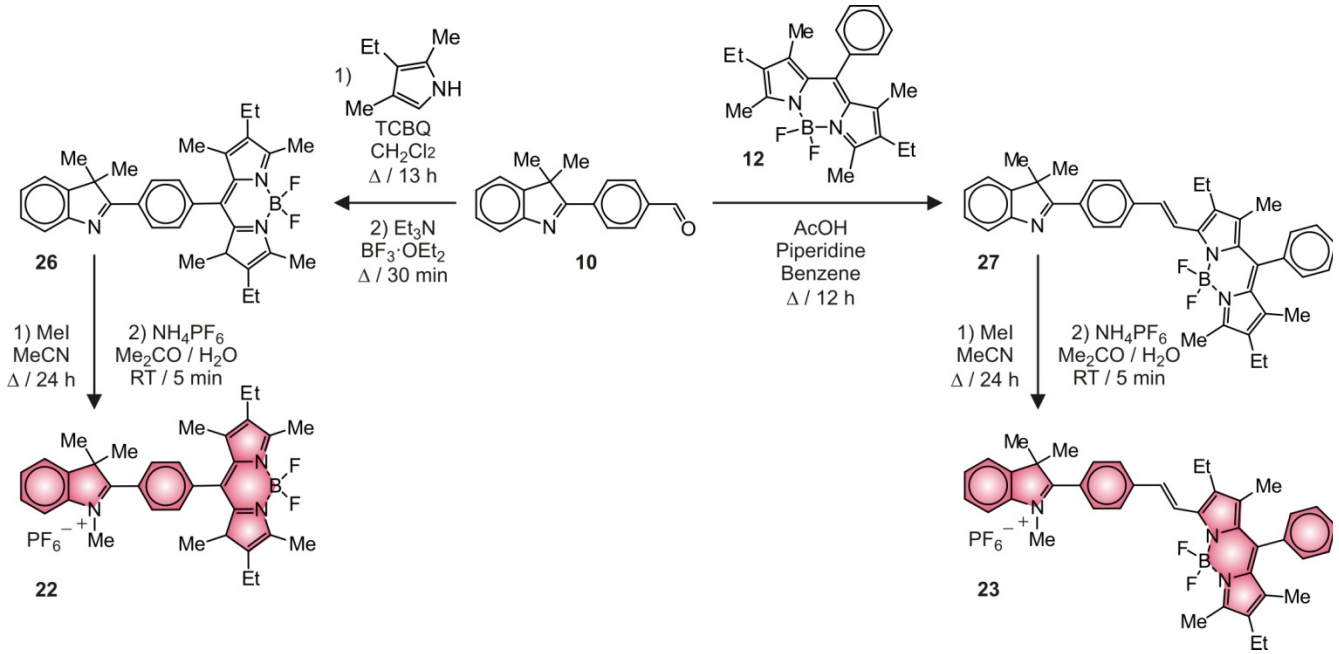

Fig. S5 Synthesis of **22** and **23**.

solid. ESIMS: *m/z* = 626 $[M - PF_6]^+$;^{1}H NMR (CD_3CN): 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).

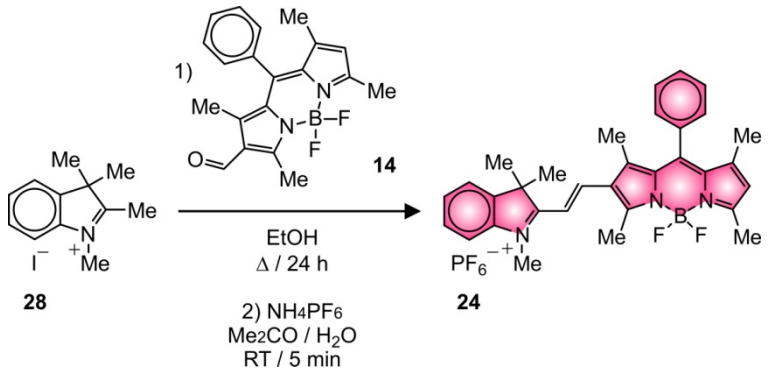

Fig. S6 Synthesis of **24**.

***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 CH_2Cl_2 (5 mL). The addition of Et_2O (30 mL) caused the precipitation of a solid, which was filtered off and dissolved in Me_2CO (5 mL). After the addition of a saturated aqueous solution of NH_4PF_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 **24** (25 mg, 36%) as a purple solid. ESIMS: *m/z* = 508.2751 $[M - PF_6]^+$ (*m/z* calcd. for $C_{32}H_{33}BF_2N_3$ = 508.2736); ^{1}H NMR [$(CD_3)_2CO$]: 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); ^{13}C NMR [$(CD_3)_2CO$]: 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, 129.2, 129.7, 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 CH_2Cl_2 (3 mL). The addition of Et_2O (20 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* calcd. for $C_{42}H_{45}BN_3O_2$ = 634.3607); ^{1}H NMR (CD_3CN): 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); ^{13}C NMR ($CDCl_3$): 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.

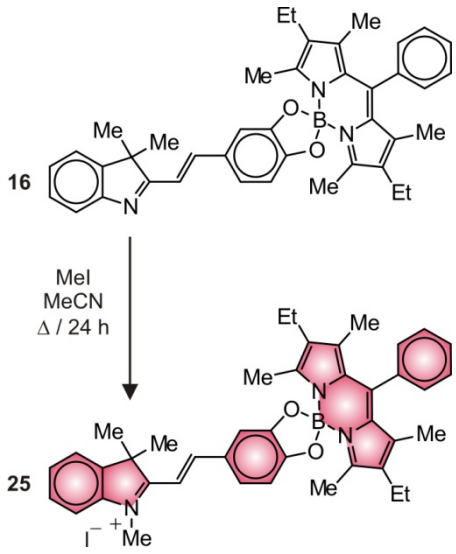

Fig. S7 Synthesis of **25**.

***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 CH_2Cl_2 (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 CH_2Cl_2 (30 mL), the mixture was stirred for a further 30 min. Then, Et_3N (5 mL, 35 mmol) and $BF_3{\cdot}Et_2O$ (5 mL, 40 mmol) were added and the mixture was stirred for a further 30 min, washed with H_2O (3 × 100 mL) and dried over Na_2SO_4. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2: 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* calcd. for $C_{33}H_{37}BF_2N_3$ = 524.3049); ^{1}H NMR (CD_3CN): 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); ^{13}C NMR ($CDCl_3$): 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 [SiO_2: 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 $C_{40}H_{41}BF_2N_3$ = 612.3363); ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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

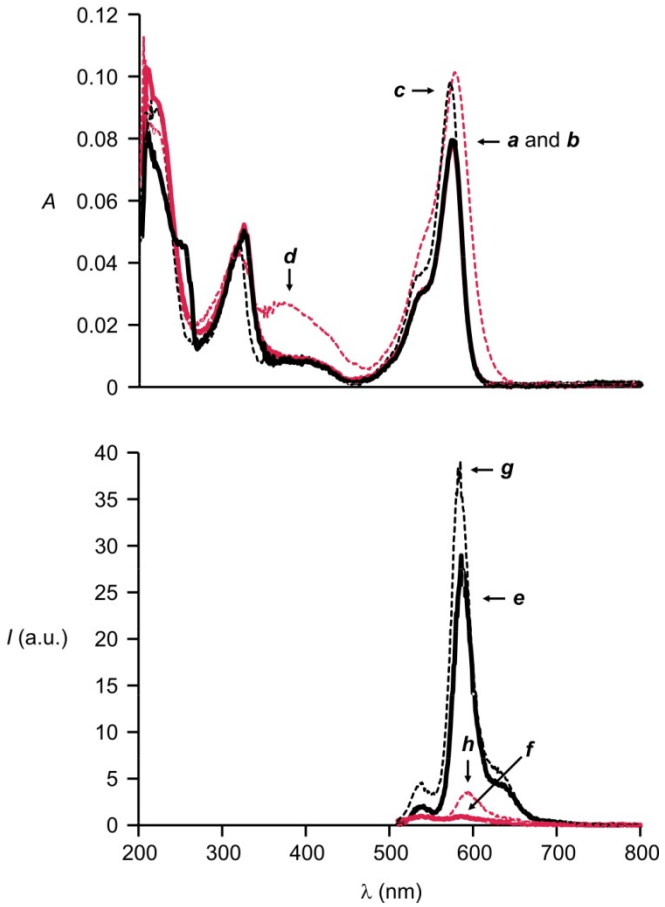

Fig. S8 Steady-state absorption spectra (5 μM, MeCN, 20 °C) of **3a** before (***a***) and after (***b***) the addition of TFA (2000 eq.), of **18** (***c***) and of **23** (***d***). Steady-state emission spectra (5 μM, MeCN, 20 °C, λ_{Ex} = 500 nm) of **3a** before (***e***) and after (***f***) the addition of TFA (2000 eq.), of **18** (***g***) and of **23** (***h***).

Time-resolved absorption spectra of 2a, 4a, 5a and 12

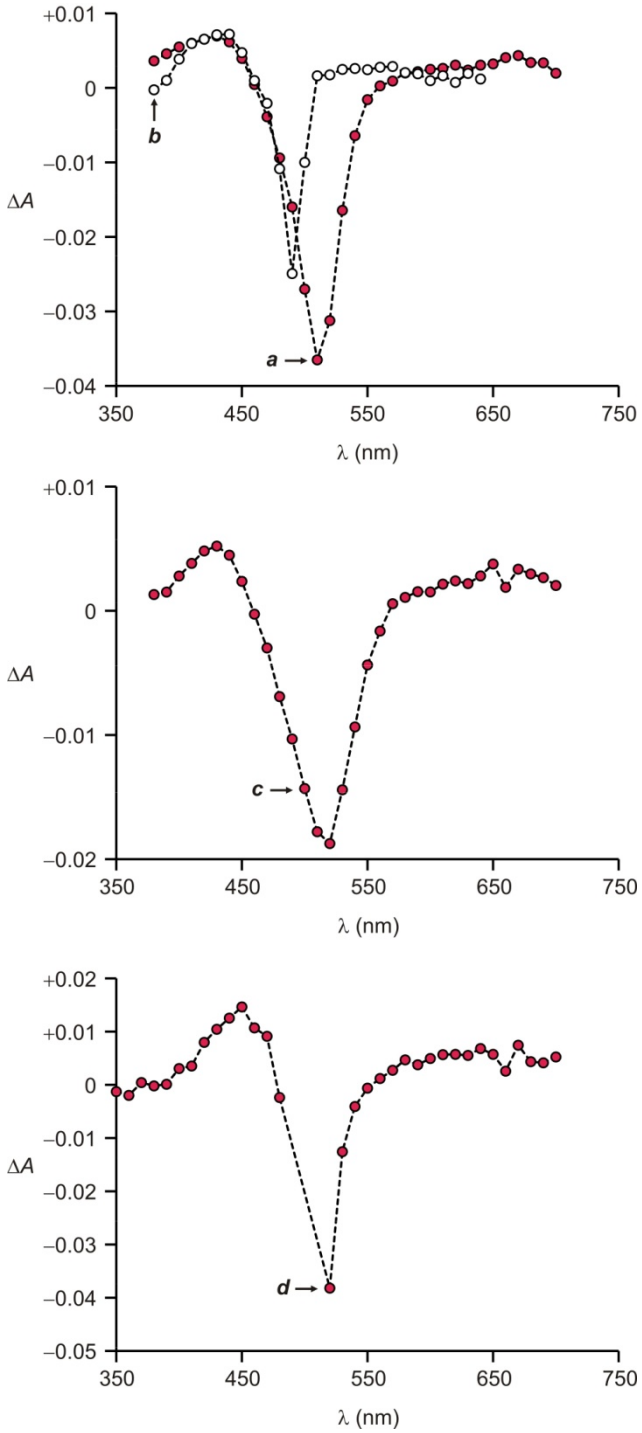

Fig. S9 Time-resolved absorption spectra (MeCN, 20 °C) of optically-matched (A_{355} = 0.3) solutions of **2a** (***a***), **12** (***b***), **4a** (***c***) and **5a** (***d***) recorded after 0.1 μs from pulsed laser irradiation (355 nm, 6 ns, 12 mJ).

Temporal absorbance profiles recorded upon excitation of 2a, 4a and 5a

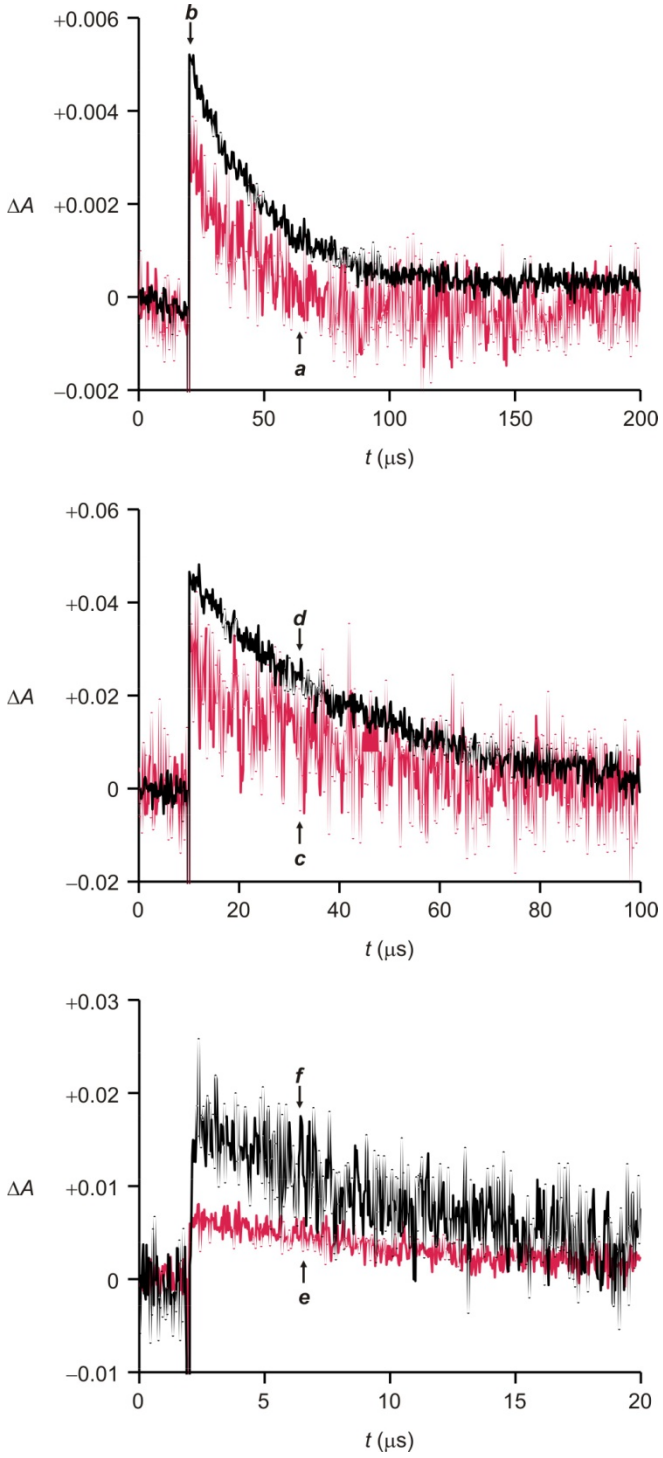

Fig. S10 Temporal absorbance profiles (MeCN, 20 °C) of optically-matched (A_{355} = 0.3) solutions of **2a** at 430 (***a***) and 670 nm (***b***), **4a** at 430 (***c***) and 650 nm (***d***) and **5a** at 450 (***e***) and 640 nm (***f***) recorded upon pulsed laser irradiation (355 nm, 6 ns, 12 mJ).

Dependence of the transient absorbance of 2a and 12 on the laser energy

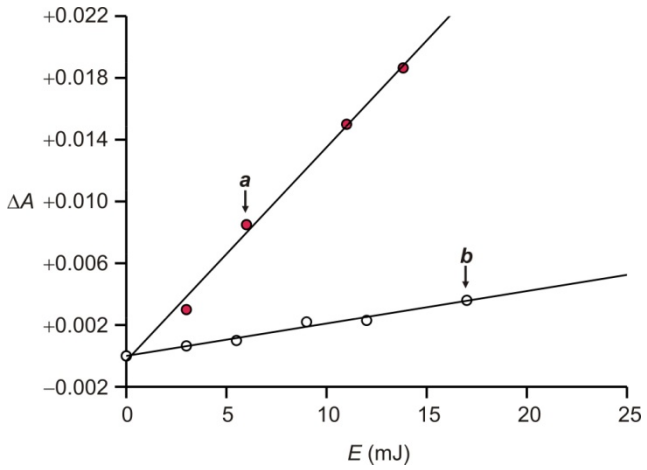

Fig. S11 Absorbance measured at 430 nm upon pulsed laser irradiation (355 nm, 6 ns) of optically-matched (A_{355} = 0.3) solutions of **2a** (***a***) and **12** (***b***) against the laser energy.

Excitation spectrum of 3a

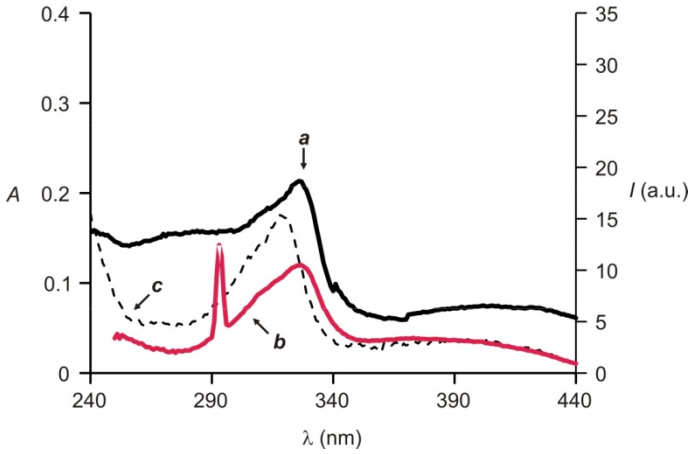

Fig. S12 Excitation (***a***, λ_{Em} = 585 nm) and absorption (***b***) spectra of **3a** and absorption spectrum (***c***) of **18** (23 μM, MeCN, 20 °C).