Rigid-Rod Push-Pull Naphthalenediimide Photosystems

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Supporting Information

Table of Content

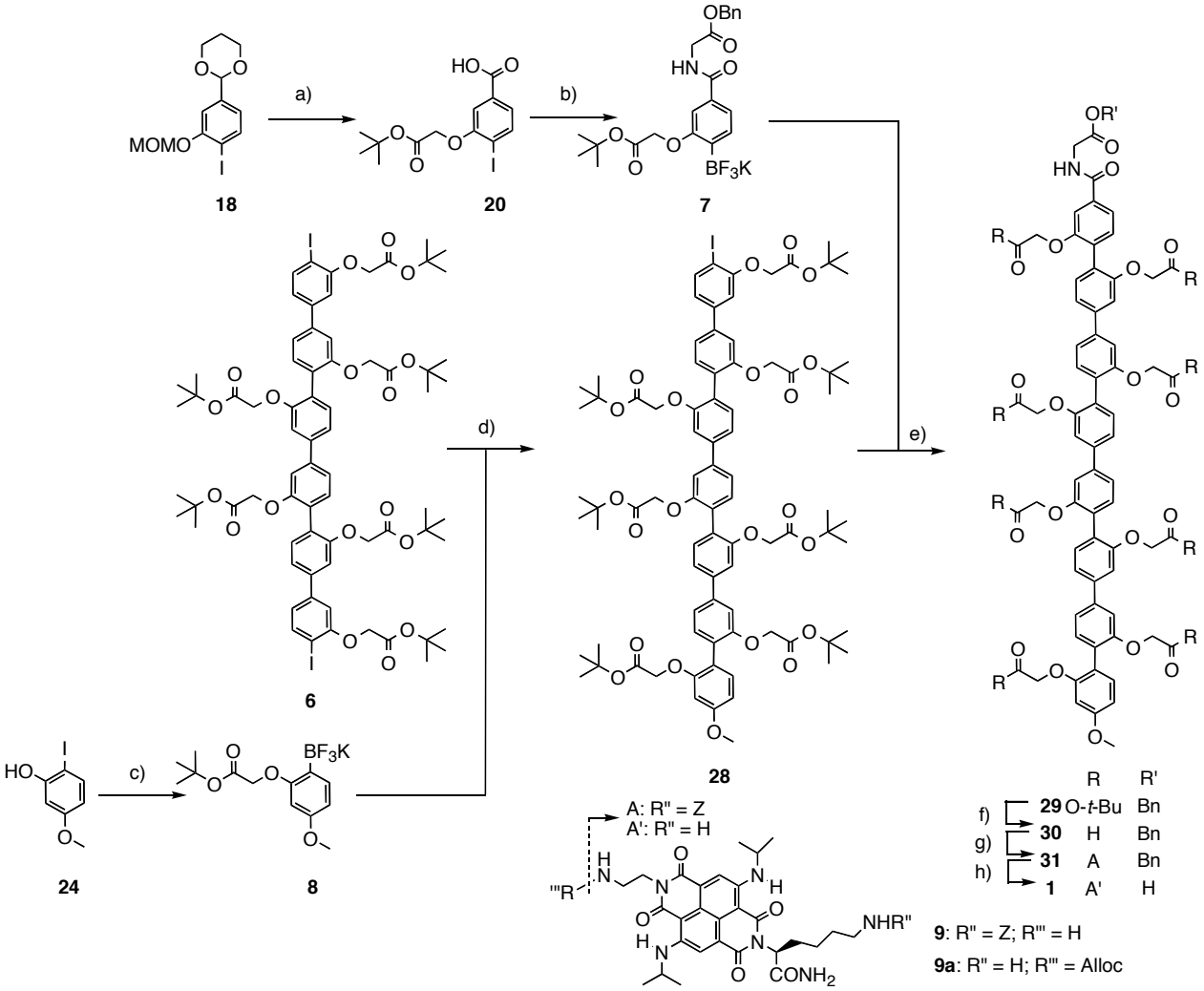
1. Materials and methods

As in ref. S1, Supporting Information. In brief, reagents for synthesis, solvents, buffers, salts and egg yolk phosphatidylcholine were from Fluka, Aldrich, Sigma and Avanti Polar Lipids. *N*-(7-Nitrobenz-2-oxa-1,3-diazol-4-yl)-1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine, triethylammonium salt (NBD-PE) was from Molecular Probes. $Co(bpy)_3(ClO_4)_3$ was prepared following reported procedures.[S2] Photosystem **1** was newly synthesized (below, Scheme S1). Control molecules **2**,[S1] **3**[S3] and **9a** [S1] were synthesized as reported. Large unilamellar egg yolk phosphatidylcholine vesicles loaded with $Co(bpy)_3(ClO_4)_3$ (EYPC-LUVs⊃$Co(bpy)_3^{3+}$) were prepared with a Mini-Extruder (polycarbonate membrane, 50 nm, Avanti). HPLC was performed using either Jasco HPLC system (PU-980, UV-970, FP-920) or an Agilent 1100 series apparatus with a photo diode array detector. $[\alpha]^{20}_D$ values were recorded on a Jasco P-1030 Polarimeter, melting points (m.p.) on a heating table from Reichert (Austria), ESI-MS on a Finnigan MAT SSQ 7000 instrument, or an ESI API 150EX mass spectrometer, ^1H and ^{13}C spectra on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer, and UV-Vis spectra on a Varian Cary 1 Bio spectrophotometer equipped with a stirrer and a temperature controller (25 ºC). Fluorescence measurements were preformed either on a FluoroMax-2 or a FluoroMax-3, Horiba Jobin Yvon, both equipped with an injector port, a stirrer and a temperature controller (25 ºC).

2. Abbreviations

Alloc: Allyloxycarbonyl; Bn: Benzyl; bpy: Bipyridine; br: Broad; DMF: N,N-Dimethylformamide; *en*: Ethylenediamine; EDTA: Ethylenediaminetetraacetic acid; EYPC LUVs: Egg yolk phosphatidylcholine large unilamellar vesicles; FRET: Fluorescence resonance energy transfer; *Gla*: Glycolic acid; HATU: N-[(Dimethylamino)-1*H*-1,2,3-triazolo[4,5-b]pyridin-1-ylmethylene]-N-methylmethanaminium hexafluorophosphate N-oxide; Lys: L-Lysine; NBD-PE: *N*-(7-Nitrobenz-2-oxa-1,3-diazol-4-yl)-1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine, triethylammonium salt; NDI: Naphthalene diimide; rt: Room temperature; TEA: Triethylamine; TFA: Trifluoroacetic acid; TFE: 2,2,2-Trifluoroethanol; Tris: Tris(hydroxymethyl)aminomethane; Z: Benzyloxycarbonyl.

3. Synthesis of push-pull octakis([N,N]-NDI)-*p*-octiphenyl 1



Scheme S1. *a) 1. HCl, THF (88 %); 2. tert-Butyl bromoacetate, Cs_2CO_3 (91 %); 3. $NaClO_2$, H_2O_2, NaH_2PO_4 (91 %); b) 1. H-Gly-OBn, HATU, iPr_2NEt (quant); 2. pinacolborane, $PdCl_2$(dppf), TEA; 3. KHF_2 (2 steps 47 %); c) 1. tert-Butyl bromoacetate, Cs_2CO_3 (92 %); 2. pinacolborane, $PdCl_2$(dppf), TEA (88 %); 3. KHF_2 (quant); d) $PdCl_2$(dppf), TEA (25 %, conversion yield 42 %); e) $PdCl_2$(dppf), TEA (49 %, conversion yield 66 %); f) TFA (quant); g)* ***9****, HATU, TEA, 2,6-di-tert-butylpyridine (75 %); h) HBr, AcOH, thioanisole, pentamethylbenzene, TFA (quant).*

2-[4-Iodo-3-(methoxymethoxy)phenyl]-1,3-dioxane (18). This compound was prepared from 3-hydroxybenzaldehyde (**17**) following the reported procedure.[S4]

3-Hydroxy-4-iodobenzaldehyde (19). A solution of **18** (0.73 g, 2.1 mmol) in THF (4 ml) and 10 % HCl aqueous solution (4 ml) was stirred for 40 h at rt. After dilution with brine, the mixture was extracted by EtOAc (x 3), dried over Na_2SO_4 and concentrated *in vacuo*. Silica gel column chromatography (CH_2Cl_2, R_f = 0.17) of the residue afforded pure title compound as a colorless solid (0.46 g, 88 %). MP: 128-129 °C (lit: 126-128 °C)[S5]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1 H), 7.92 (d, ^3J (H,H) = 8.0 Hz, 1 H), 7.49 (d, ^4J (H,H) = 1.4 Hz, 1 H), 7.23 (dd, ^3J (H,H) = 8.0 Hz, ^4J (H,H) = 1.4 Hz, 1 H), 5.87 (s, 1 H); MS (ESI, MeOH): *m/z* (%) 249.3 (100 $[M + H]^+$).

3-*tert*-Butoxycarbonylmethoxy-4-iodo-benzoic acid (20). A suspension of 3-hydroxy-4-iodobenzaldehyde (**19**, 0.12 g, 0.48 mmol), *tert*-bromoacetate (**11**, 0.14 ml, 0.95 mmol) and cesium carbonate (0.31 g, 0.95 mmol) in DMF (1 ml) was stirred at 90 °C for 15 min. The mixture was allowed to cool down to rt, and water was added to it. The product was extracted by EtOAc (x 3), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum-ether / CH_2Cl_2 1 / 1 to 0 / 1) to give pure *tert*-butyl (5-formyl-2-iodo-phenoxy)-acetate as a colorless solid (158 mg, 91 %). MP: 111 - 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1 H), 8.06 (d, ^3J (H,H) = 7.8 Hz, 1 H), 7.25 (dd, ^3J (H,H) = 7.8 Hz, ^4J (H,H) = 1.5 Hz, 1 H), 7.20 (d, ^4J (H,H) = 1.5 Hz, 1 H), 4.71 (s, 2 H), 1.53 (s, 9 H). To a solution of obtained aldehyde (0.56 g, 1.6 mmol) in a mixture of acetonitrile (8.4 ml) and water (1.4 ml) at 0 °C, NaH_2PO_4 (65 mg, 0.54 mmol), H_2O_2 (35 %, 215 μl, 2.22 mmol) and $NaClO_2$ (0.26 g, 2.9 mmol) were successively added. A mixture was allowed to warm up to rt, and stirred for 2 h. After the addition of brine, the mixture was extracted by EtOAc, dried over Na_2SO_4, and concentrated *in vacuo* to give **20** (0.53 g, 91 %). According to ^{1}H and ^{13}C NMR

spectra, the obtained product appeared pure and thus, used for the next reaction without further purification. MP: 182 - 184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.30 (br.s, 1 H), 7.92 (d, ^{3}J (H,H) = 8.1 Hz, 1 H), 7.31 (dd, ^{3}J (H,H) = 8.1 Hz, ^{4}J (H,H) = 1.8 Hz, 1 H), 7.26 (d, ^{4}J (H,H) = 1.8 Hz, 1 H), 4.84 (s, 2 H), 1.42 (s, 9 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.3 (s), 166.6 (s), 156.5 (s), 139.5 (d), 132.2 (s), 123.6 (d), 112.2 (d), 92.7 (s), 81.8 (s), 66.0 (t), 27.6 (3 x q); MS (ESI, MeOH): *m/z* (%) 377.0 (100 [M - H]$^-$).

***tert*-Butyl [5-(benzyloxycarbonylmethyl-carbamoyl)-2-iodo-phenoxy]-acetate (22).** A solution of **20** (0.25 g, 0.66 mmol), glycin benzylester, *p*-toluenesulfonate salt (**21**, 0.24 g, 0.71 mmol), *i*Pr_2NEt (0.34 ml, 1.95 mmol) and HATU (0.30 g, 0.79 mmol) in DMF (3 ml) was stirred for 1 h at rt before addition of brine. The product was extracted by EtOAc, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (petroleum ether / EtOAc 2 / 1) afforded the pure desired product as a colorless solid (0.35 g, quant). M.p. 117 - 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, ^{3}J (H,H) = 8.1 Hz, 1 H), 7.38 (br.s, 5 H), 7.21 (d, ^{4}J (H,H) = 1.8 Hz, 1 H), 7.07 (dd, ^{3}J (H,H) = 8.1 Hz, ^{4}J (H,H) = 1.8 Hz, 1 H), 6.74 (br.t, ^{3}J (H,H) = 5.0 Hz, 1H), 5.23 (s, 2 H), 4.64 (s, 2 H), 4.25 (d, ^{3}J (H,H) = 5.0 Hz, 2 H), 1.50 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (s), 167.1 (s), 166.6 (s), 157.3 (s) 140.0 (d), 135.3 (s), 135.2 (s), 128.9 (2 x d), 128.7 (3 x d), 120.8 (d), 111.2 (d), 91.4 (s), 83.1 (s), 67.7 (t), 66.7 (t), 42.2 (t), 28.3 (3 x q); MS (ESI, MeOH): *m/z* (%) 548.3 (29 [M + Na]$^+$), 526.3 (26 [M + H]$^+$), 492.3 (24 [M + Na + H - *t*-Bu]$^+$), 470.3 (100 [M + 2 H - *t*-Bu]$^+$).

***tert*-Butyl [5-(benzyloxycarbonylmethyl-carbamoyl)-2-BF_3K-phenoxy]-acetate (7).** To a solution of **22** (0.35 g, 0.67 mmol) in acetonitrile (3 ml) was added Pd(dppf)Cl_2 (14 mg, 0.02 mmol), TEA (0.30 ml, 2.15 mmol) and pinacolborane (0.15 ml, 1.04 mmol) under N_2 atmosphere.[S6] The resulting mixture was refluxed for 1 h, and concentrated *in vacuo*. The residue was dissolved in MeOH (2.5 ml) and transferred into a plastic centrifuge tube. A

solution of KHF_2 (235 mg, 3.0 mmol) in water (5 ml) was added to it, and the resulting mixture was vigorously stirred for 2 h at rt.[S7] The solvent was evaporated *in vacuo*, and the resulting solid was taken up in warm acetone. After evaporation of acetone *in vacuo*, CH_2Cl_2 was added to the residue, and supernatant was discarded after centrifugation. The precipitate was again taken up in acetone, centrifuged, and the supernatant was concentrated *in vacuo* to give pure trifluoroborate **7** (0.16 g, 2 steps 47 %). M.p. 180.0 - 180.5 °C; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.04 (brt, ^3J (H,H) = 6.1 Hz, 1 H), 7.61 (d, ^3J (H,H) = 7.5 Hz, 1 H), 7.40 ~ 7.31 (m, 7 H), 4.56 (s, 2 H), 4.18 (d, ^3J (H,H) = 6.1 Hz, 2 H), 1.52 (s, 9 H); MS (ESI, MeOH): *m/z* (%) 466.5 (100 $[M - K]^-$).

2-Iodo-5-methoxyphenol (25). This compound was prepared from 3-methoxyphenol (**24**) following the reported procedures.[S7]

***tert*-Butyl (2-iodo-5-methoxy-phenoxy)-acetate (26).** To a solution of **25** (0.54 g, 2.2 mmol) in DMF (2 ml) was added cesium carbonate (1.4 g, 4.3 mmol). The mixture was stirred for 1 h at 90 °C under N_2 atmosphere before the addition of *tert*-butyl bromoacetate (**11**, 0.65 ml, 4.4 mmol). The mixture was stirred for 30 more minutes at the same temperature before the addition of water, and the product was extracted in EtOAc. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2 / petroleum ether 2 / 1) to give pure desired compound as pale yellow oil (0.73 g, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, ^3J (H,H) = 11.4 Hz, 1 H), 6.39 (dd, ^3J (H,H) = 11.4 Hz, ^4J (H,H) = 3.2 Hz, 1 H), 6.35 (d, ^4J (H,H) = 3.2 Hz, 1 H), 4.59 (s, 2 H), 3.81 (s, 3 H), 1.53 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4 (s), 161.3

(s), 157.6 (s), 139.7 (d), 108.3 (d), 100.4 (d), 82.8 (s), 75.3 (s), 66.8 (t), 55.7 (q), 28.3 (3 x q); MS (ESI, MeOH): *m/z* (%) 365.3 (21 $[M + H]^+$), 309.3 (79 $[M + 2H- t\text{-Bu}]^+$), 182.4 (100 $[M + 2H]^{2+}$).

***tert*-Butyl (2-BF_3K-5-methoxy-phenoxy)-acetate (8).** To a solution of **26** (0.73 g, 2.0 mmol) in acetonitrile (6 ml) was added Pd(dppf)Cl_2 (60 mg, 0.085 mmol), TEA (0.86 ml, 6.1 mmol) and pinacolborane (0.43 ml, 3.0 mmol) under N_2 atmosphere. The resulting mixture was refluxed for 1 h, and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether / EtOAc 4 / 1) to give pure *tert*-butyl [5-methoxy-2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenoxy]-acetate (**27**) as a pale yellow oil (0.64 g, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, ^3J (H,H) = 8.3 Hz, 1 H), 6.56 (dd, ^3J (H,H) = 8.3 Hz, ^4J (H,H) = 1.9 Hz, 1 H), 6.38 (d, ^4J (H,H) = 1.9 Hz, 1 H), 4.56 (s, 2 H), 3.83 (s, 3 H), 1.52 (s, 9 H), 1.38 (s, 12 H). Obtained boronate **27** (0.2 g, 0.55 mmol) and KHF_2 (0.13 g, 1.7 mmol) were dissolved in a mixture of MeOH (1.5 ml) and water (3 ml) in a plastic tube. The resulting solution was vigorously stirred for 2 h at rt, and concentrated *in vacuo*. The residue was taken up in acetone. After evaporation of acetone, impurities were removed by solid-liquid extraction with diethylether to give pure trifluoroborate **8** as colorless solid (0.20 g, quant). M. p. 186 - 187 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.43 (d, ^3J (H,H) = 8.0 Hz, 1 H), 6.42 (br.d, ^3J (H,H) = 8.0 Hz, 1 H), 6.35 (br.s, 1 H), 4.50 (s, 2 H), 3.73 (s, 3 H), 1.52 (s, 9 H); MS (ESI, MeOH): *m/z* (%) 305.0 (100 $[M - K]^-$).

1^4,6^4-Diiodo-1^3,2^3,3^2,4^3,5^2,6^3-hexakis(*Gla*-O*t*-Bu)-*p*-sexiphenyl (6). This compound was prepared from Fast Blue B salt (**10**) following the previously reported procedure.[S9]

1^4-Iodo-1^3,2^3,3^2,4^3,5^2,6^3,7^2-heptakis(*Gla*-O*t*-Bu)-7^4-methoxy-*p*-septiphenyl (28). A solution of trifluoroborate **8** (31 mg, 90 μmol), bis-iodo-*p*-sexiphenyl **6** (136 mg, 91 μmol), $PdCl_2$(dppf) (3.0 mg, 3.7 μmol) and TEA (40 μl, 0.29 mmol) in THF (0.7 ml) and MeOH

(3.5 ml) was refluxed for 30 min. The mixture was concentrated and purified with PTLC (CH_2Cl_2 / acetone 49 / 1) to give mono-iodo-*p*-septiphenyl **28** (36 mg, 25 %, conversion yield 42 %), together with recovered **6** (57 mg) and symmetric bis-methoxy-octiphenyl (28 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, ^3J (H,H) = 7.9 Hz, 1 H), 7.57 (d, ^3J (H,H) = 8.3 Hz, 1 H), 7.56 (br.d, ^3J (H,H) = 8.0 Hz, 2 H), 7.54 (m, 1 H), 7.50 (d, ^3J (H,H) = 7.9 Hz, 1 H), 7.42 (d, ^3J (H,H) = 8.2 Hz, 1 H), 7.35 ~ 7.30 (m, 6 H), 7.27 (br.d, ^3J (H,H) = 8.0 Hz, 1 H), 7.15 (m, 4 H), 7.06 (d, ^4J (H,H) = 1.9 Hz, 1 H), 7.04 (dd, ^3J (H,H) = 7.9 Hz, ^4J (H,H) = 1.9 Hz, 1 H), 6.99 (d, ^4J (H,H) = 1.9 Hz, 1 H), 6.67 (dd, ^3J (H,H) = 8.2 Hz, ^4J (H,H) = 2.3 Hz, 1 H), 6.50 (d, ^4J (H,H) = 2.3 Hz, 1 H), 4.70 (s, 2 H), 4.63 (s, 6 H), 4.61 (s, 2 H), 4.58 (s, 2 H), 4.55 (s, 2 H), 3.88 (s, 3 H), 1.56 (s, 9 H), 1.52 (s, 54 H).

1^4-Methoxy-1^2,2^2,3^3,4^2,5^3,6^2,7^3,8^2-octakis(*Gla*-O*t*-Bu)-8^4-benzyloxycarbonylmethyl-carbamoyl-*p*-octiphenyl (29) A solution of pull-boronate (**7**, 34 mg, 67 μmol), mono-iodo-septiphenyl (**28**, 36 mg, 22 μmol), $PdCl_2$(dppf) (1.8 mg, 2.2 μmol) and TEA (28 μl, 0.20 mmol) in THF (0.2 ml) and MeOH (1 ml) was refluxed for 30 min. The mixture was concentrated and purified with column chromatography (CH_2Cl_2 / acetone 100 / 3) followed by PTLC (CH_2Cl_2 / acetone 100 / 3) to give pure push-pull octiphenyl **29** (20 mg, 49 %, conversion yield 66 %), together with recovered **28** (10 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (br.d, ^3J (H,H) = 7.9 Hz, 5 H), 7.57 (d, ^3J (H,H) = 8.0 Hz, 1 H), 7.53 (d, ^3J (H,H) = 8.0 Hz, 1 H), 7.50 ~ 7.39 (m, 8 H), 7.38 ~ 7.27 (m, 6 H), 7.17 ~ 7.13 (m, 6 H), 6.72 (br.t, ^3J (H,H) = 5.0 Hz, 1 H), 6.67 (dd, ^3J (H,H) = 8.3 Hz, ^4J (H,H) = 2.2 Hz, 1 H), 6.50 (d, ^4J (H,H) = 2.2 Hz, 1 H), 5.30 (s, 2 H), 4.63 (s, 10 H), 4.60 (s, 2 H), 4.59 (s, 2 H). 4.55 (s, 2 H), 4.36 (d, ^3J (H,H) = 5.0 Hz, 2 H), 3.88 (s, 3 H), 1.53 (s, 72 H); MS (ESI, MeOH / acetone / CH_2Cl_2 1 : 1 : 2): *m*/*z* (%) 2832.2 (4 $[3M + 2Na]^{2+}$), 1895.8 (100 $[M + Na]^+$).

H-*en*-[N,N]-NDI-Lys(Z)-NH$_2$ (9). This compound was prepared from pyrene (**12**) following the previously reported procedure.[S1]

1^4-Methoxy-1^2,2^2,3^3,4^2,5^3,6^2,7^3,8^2-octakis(*Gla-en*-[N,N]-NDI-Lys(Z)-NH_2)-8^4-benzyloxycarbonylmethyl-carbamoyl-*p*-octiphenyl (31). A solution of push-pull octamer (**29**, 10 mg, 5.3 μmol) in CH_2Cl_2 and TFA (1 : 1, 1 ml) was stirred for 30 min at rt, and concentrated *in vacuo*. The residue was further treated with TFA (1 ml) for 30 min, and the solvent was evaporated *in vacuo* to give octa-acid (**30**, 8 mg, quant). To a solution of **30** in DMF (0.5 ml) was added HATU (32 mg, 84 μmol) and 2,6-di-*tert*-butylpyridine (60 μl, 0.27 mmol) at rt. A mixture was stirred for 15 min, before the addition of a solution of **9** (50 mg, 73 μmol), 2,6-di-*tert*-butylpyridine (60 μl, 0.27 mmol), and TEA (50 μl, 0.36 mmol) in DMF (2 ml). The resulting mixture was stirred for 19 h at rt under N_2 atmosphere, and then concentrated *in vacuo*. The product was purified by column chromatography (CH_2Cl_2 / MeOH 19 / 1 to 9 / 1), PTLC (CH_2Cl_2 / MeOH 9 / 1), and HPLC (YMC-SIL 10 x 250 mm, $CHCl_3$ / MeOH 9 / 1, 2 ml / min, R_t = 5.9 min) to give pure desired compound as a dark blue solid (27 mg, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$: CD_3OD 1 : 1): δ 7.93 - 7.60 (m, 16 H), 7.55 - 7.12 (m, 67 H), 6.52 (br.d, ^3J (H,H) = 9.9 Hz, 1 H) 6.33 (br.s, 1 H), 5.64 - 5.45 (m, 8 H), 5.07 (s, 2 H), 4.96 (s, 2 H), 4.90 (s, 14 H), 4.50 - 4.30 (m, 14 H), 4.25 - 3.95 (m, 20 H), 3.90 - 3.63 (m, 19 H), 3.50 - 3.30 (m, 13 H), 3.06 (br.s, 16 H), 2.28 (br.s, 8 H), 2.06 (br.s, 8 H), 1.55 - 1.15 (m, 128 H).

[1^4-Methoxy-1^2,2^2,3^3,4^2,5^3,6^2,7^3,8^2-octakis (*Gla-en*-[N,N]-NDI-Lys-NH_2)-*p*-octiphenyl-8^4-carbonyl)-amino] acetic acid (1) A mixture of octa-NDI **31** (4.5 mg, 0.67 μmol), 30 % HBr in acetic acid (20 μl), thioanisole (30 μl), pentamethylbenzene (25 μl) and TFA (0.5 ml) was stirred for 1.5 h at rt and concentrated *in vacuo*. The impurities were taken up in ethylether (5 times) from the residue to give HPLC pure (YMC ODS-A, 10 x 250 mm, 2 ml / min, 1% TFA in MeOH : H_2O, linear gradient 4 : 1 to 1 : 0 over 10 min, R_t = 5.3 min) product as a dark blue solid (3.7 mg, quant). ^{1}H NMR (300 MHz, CD_3OD): δ 7.94 - 7.10 (m, 38 H), 6.58 (br.s, 1 H), 6.42 (br.s, 1 H), 5.65 - 5.40 (m, 8 H), 4.60 - 3.55 (m, 66 H), 3.10 - 2.90 (m, 16 H), 2.42 (m, 8 H), 2.05 (m, 8 H), 1.90 - 1.10 (m, 128 H); MS (ESI, MeOH): *m/z* (%) 1869 (19 [M + 3H]$^{3+}$), 1402 ([M + 4H]$^{4+}$), 1122 (41 [M + 5H]$^{5+}$), 935.5 (54 [M + 6H]$^{6+}$), 802 (49 [M +

$7H]^{7+}$).

4. Solvent dependence

NBD-PE + EYPC-LUVs. A solution of EYPC (25 mg) and NBD-PE (0.25 mol%) in $CHCl_3$/MeOH 1:1 was dried using a rotary evaporator and then under vacuum (overnight) to form a thin film. Hydration for >30 min (1 ml, 40 mM Tris, at pH 7.9), freeze-thaw cycles (5x), and extrusion (15x, 100 nm polycarbonate membranes) gave NBD-PE + EYPC-LUVs: ~33 mM EYPC, inside and outside: 40 mM Tris, pH 7.9.

FRET experiments (Figures 4A and S1). NBD-PE + EYPC-LUVs (67 μl) and EDTA (0.2 ml, 0.1 M) were added to gently stirred, thermostated buffer (1.74 ml, 40 mM Tris, pH 7.9) in a fluorescence cuvette. Fluorescence emission spectra (λ_{ex} = 463 nm) were recorded after the addition of aliquots of monomeric NDI **9a**[S1] (0 to 20 μl of 0.1 mM in MeOH) or push-pull NDI **1** (0 to 30 μl of 10 μM in MeOH, DMSO, TFE, or THF).

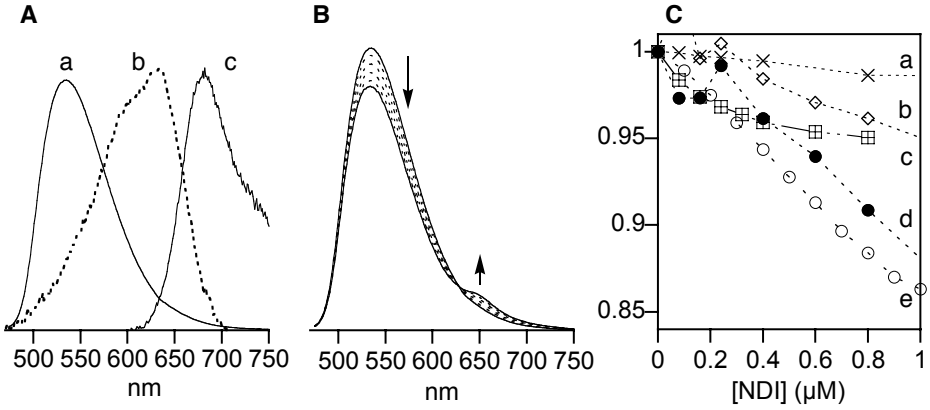


***Figure S1: A**, Normalized fluorescence emission (a and c) and absorption (b) spectra of NBD-PE (a) and monomeric NDI **9a** (b and c). **B**, Change in emission spectra of NBD-PE-LUVs upon addition of **9a**. Note, fluorescence of push-pull octa-NDI **1** is nearly completely quenched,*

*and thus the FRET emission band at about 650 nm observed with monomeric NDI (**9a**) could not be found with **1**. Therefore, FRET was detected as the quenching of NBD emission at 535 nm (see **C**). **C**, Change in emission intensity of NBD at 535 nm as a function of added NDI concentration ([NDI] = 8 x [**1**]): a, **1** in MeOH; b, **1** in THF; c, **1** in DMSO; d, **1** in TFE; e, **9a** in MeOH.*

CD and UV studies: Solvent dependence (Figures 2 and S2). CD and UV spectra of push-pull octa-NDI **1** in various solvents (74 μM in MeOH; 47 μM in acetonitrile, *i*-PrOH, or THF; 91 μM in TFE) were recorded at 25 °C. Path length of the cuvette was 1 mm.

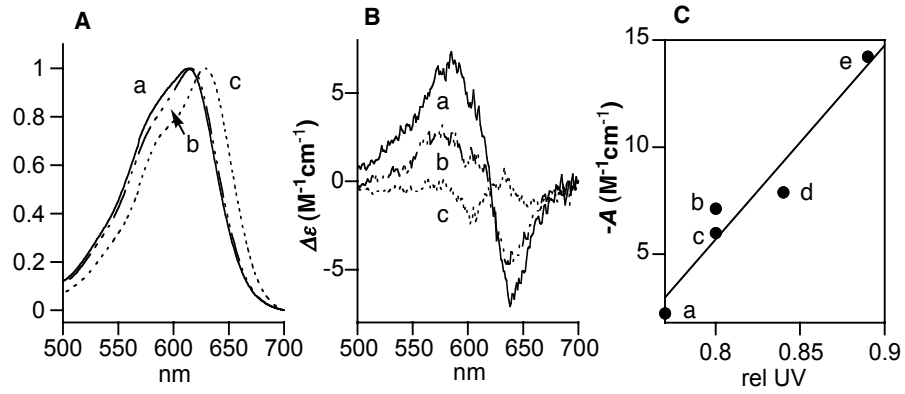


***Figure S2:** **A**, **B**, Absorption (**A**) and CD (**B**) spectra of push-pull octa-NDI (**1**) in i-PrOH (a), MeOH (b) or TFE (c). **C**, Correlation of CD amplitude (A = Δε (638 nm) - Δε (585 nm)) vs absorption intensity of high energy band (~ 570 nm) relative to the absorption maximum in TFE (a), acetonitrile (b), THF (c), MeOH (d), or i-PrOH (e).*

5. Photosynthetic activity

EYPC-LUVs⊃Co(bpy)$_3^{3+}$. Vesicles were prepared as described in the ref S3. Namely, a solution of EYPC (25 mg) in $CHCl_3$ was dried using a rotary evaporator and then under vacuum (> 2h) to form a thin film. Hydration for > 30 min. (1 ml, 10 mM $Co(bpy)_3(ClO_4)_3$,[S2] 10 mM $K_XH_YPO_4$, 90 mM KCl, pH 7.1), freeze-thaw cycles (> 10×), extrusion (> 15×, 50 nm polycarbonate membranes), external buffer exchange (Sephadex G-50 column, 10 mM $K_XH_YPO_4$, 100 mM KCl, pH 7.1) and dilution to 6 ml gave EYPC-LUVs⊃$Co(bpy)_3^{3+}$: ~ 2 mM EYPC; inside: 10 mM $Co(bpy)_3(ClO_4)_3$, 10 mM $K_XH_YPO_4$, 90 mM KCl, pH 7.1, outside: 10 mM $K_XH_YPO_4$, 100 mM KCl, pH 7.1.

Photosynthetic activity measurements (Fig. 4B). EYPC-LUVs⊃$Co(bpy)_3^{3+}$ (400 μl), EDTA (200 μl, 0.1 M, pH 7.1) and buffer (1400 μl, 10 mM $K_XH_YPO_4$, 100 mM KCl, pH 7.1) were added to a fluorescence cuvette giving vesicles suspended in a stirred solution (10 mM EDTA, 9 mM $K_XH_YPO_4$, 90 mM KCl, pH 7.1). To this solution was added push-pull NDI **1**, symmetrical octa-NDIs **2** and **3** as a solution in TFE (< 25 μl) at varying concentrations and the resultant solutions were degassed by bubbling nitrogen through (> 1 min.) before the vessel was sealed by parafilm. Immediately the cuvettes were placed in a waterbath (20 ± 2 °C) which was shielded from outside light except through a 1 cm × 1.5 cm aperture and, with stirring, irradiated (200 W Xe lamp, cut off filter at 540 nm) for 5 min. Then, Triton X (40 μl, 1.2 % w/w solution in water) was added to the cuvette and it was further irradiated for 10 min. Absorption at 320 nm of the mixture before irradiation (I_0), after 5 min irradiation (I_t), and after 10 more min irradiation with Triton X (I_∞) were used to calculate fractional photoactivity (Y) using the eq. *S1*.

$$Y = (I_t - I_0) / (I_\infty - I_0) \qquad [S1]$$

Fractional photoactivity Y was further normalized against the value obtained with 1.6 μM of **3** (Y_∞) using the eq. S2 to give fractional reduction of $[Co(bpy)_3]^{3+}$.

$$[Co^{2+}]\ (rel) = Y / Y_\infty \qquad [S2]$$

6. Steady-state photophysics

The photophysics of push-pull *p*-octiphenyl **1** was investigated in solution in methanol (MeOH) and 2,2,2-trifluoroethanol (TFE) using steady-state absorption and steady-state and time-resolved fluorescence techniques. Absorption spectra were recorded on a Cary 50 spectrophotometer and fluorescence spectra on a Cary Eclipse fluorimeter in a 1 cm quartz cell. Results are compared to those previously obtained with the symmetric *p*-octiphenyl **2**.[S1]

1 and **2** display a single absorption band above 400 nm which is centered around 610 nm in MeOH and 620 nm in TFE (Figure S3). The fluorescence spectra (excitation at 560 nm) of **1** and **2** are very similar both in MeOH and TFE and peak around 650 nm in MeOH and 665 nm in TFE (Figure S4). The fluorescence quantum yield was determined against cresyl violet.[S1] It is lower with **1** than with **2** in MeOH and similar with **1** and **2** in TFE (Table S1).

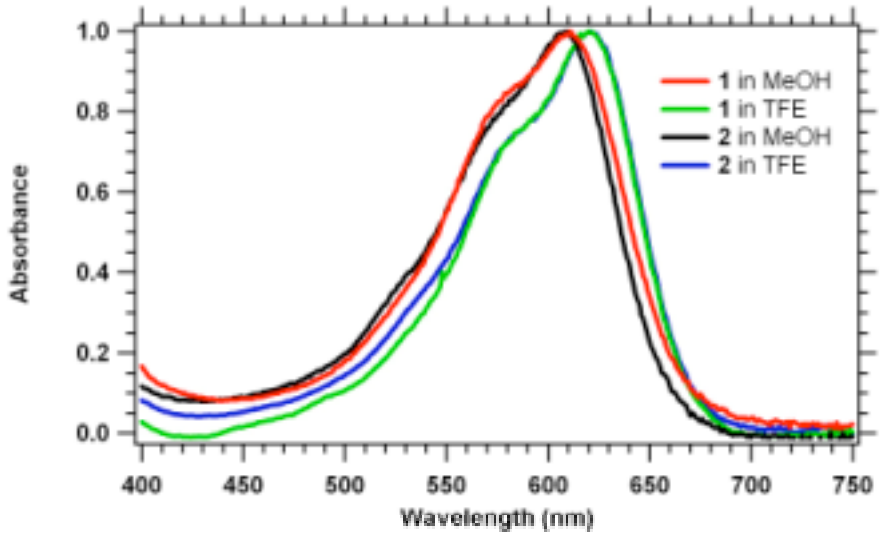


Figure S3. *Normalized absorption spectra of the investigated dyes in MeOH and TFE.*

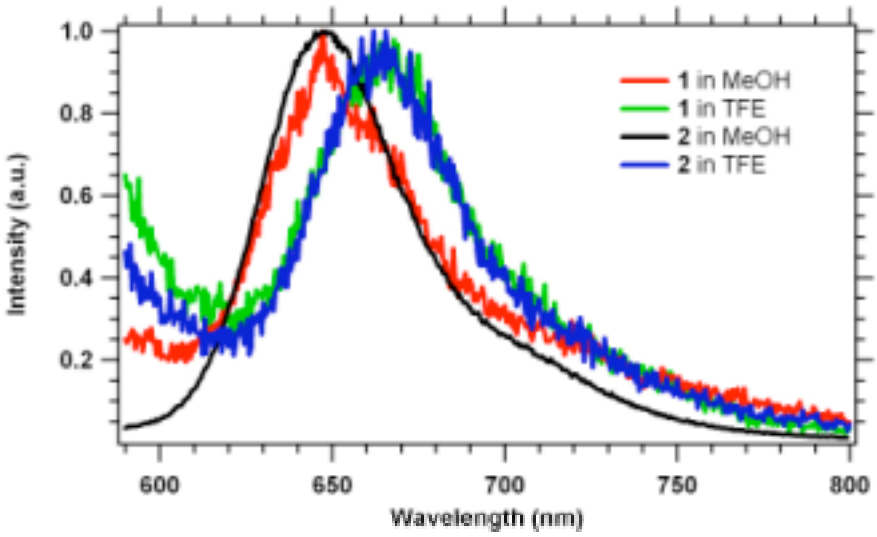


Figure S4. *Intensity-normalized fluorescence spectra of the investigated dyes in MeOH and TFE. The spectrum of the neat solvent was subtracted.*

Table S1. *Fluorescence quantum yields of the investigated dyes.*

Dye	Solvent	Φ_{fl}
1	MeOH	$4 \cdot 10^{-4}$
1	TFE	$3 \cdot 10^{-4}$
2[a]	MeOH	$9 \cdot 10^{-3}$
2	TFE	$3 \cdot 10^{-4}$

[a]from S1.

7. Fluorescence dynamics

The fluorescence dynamics was recorded using the time-correlated single photon counting (TCSPC, Figure S5) and the fluorescence up-conversion (Figure S6, 400 nm excitation, 650 nm detection in MeOH, 665 nm detection in TFE) techniques.

For TCSPC measurements, excitation was performed at 395 nm with a pulsed laser diode (Picoquant model LDH-P-C-400B). The pulses had duration of about 65 ps and the average power was about 0.5 mW at 20 MHz. Fluorescence was collected at 90°, and passed through an

analyzer set at the magic angle with respect to the excitation polarization, and a 450 nm-cutoff filter located in front of a photomultiplier tube (Hamamatsu, H5783-P-01). The detector output was connected to the input of a TCSPC computer board module (Becker and Hickl, SPC-300-12). The full width at half maximum (FWHM) of the instrument response was around 200 ps. Measurements were performed in a 1 cm quartz cell. Data were reproduced by iterative reconvolution of a sum of exponentials to the measured instrument response function. The accuracy on the lifetimes is estimated to ± 10%.

The fluorescence up-conversion set-up uses the frequency-doubled output of a Kerr lens mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) for excitation of the sample at 400 nm.[S10] The output pulses centered at 800 nm had duration of 100 fs and repetition rate of 82 MHz.

Experiments were carried out in a 1 mm rotating cell. Fluorescence decays were analyzed by iterative reconvolution of a sum of exponential functions with a Gaussian response function of 280 fs FWHM.

The fluorescence decay was highly non-exponential with both **1** and **2** in MeOH and in TFE. In addition to an ultrafast rise (<1 ps), at least 5 exponential terms were needed to accurately reproduce the dynamics (Table S2). Between 94 and 99% of the decay occurred on a timescale shorter than 200 ps.

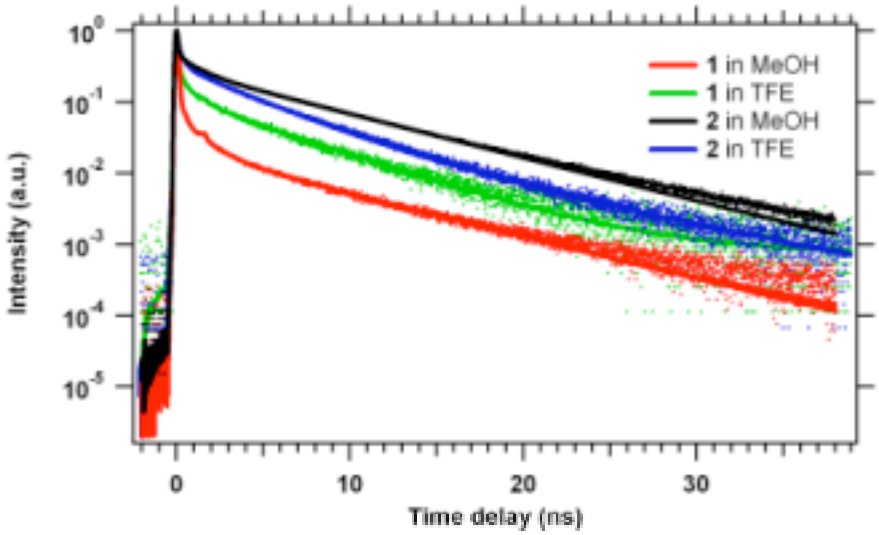


Figure S5. *Intensity-normalized time profiles of the fluorescence decay of the investigated dyes measured by TCSPC. The solid traces represent best fits to the data points.*

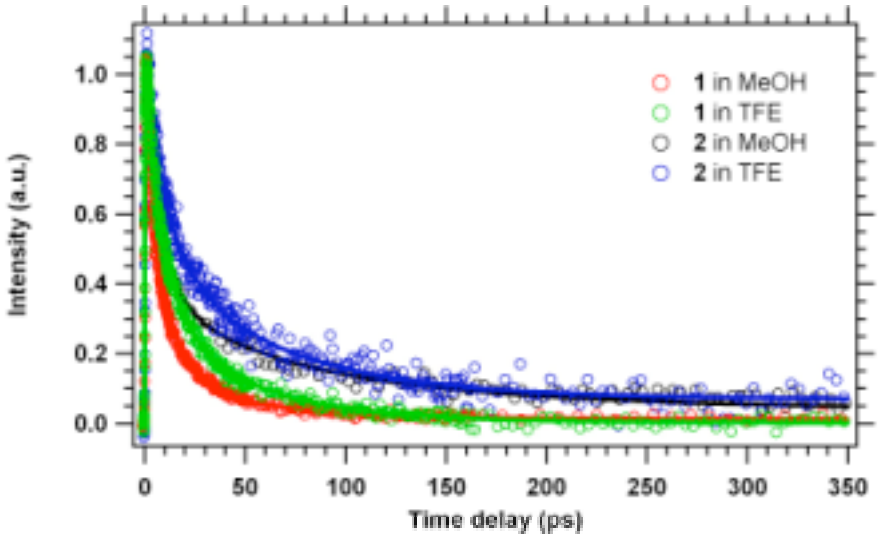


Figure S6. *Early fluorescence dynamics of the investigated dyes monitored by fluorescence up-conversion.*

Table S2. *Time constants and relative amplitudes (in brackets) used to reproduce the fluorescence decay of the investigated systems.*

Dye	Solvent	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)
1	MeOH	3.3 (0.58)	14 (0.31)	52 (0.10)	1.4 (0.01)	7.2 (<0.01)
1	TFE	3.3 (0.32)	12 (0.44)	52 (0.24)	1.0 (<0.01)	5.4 (<0.01)
2[a]	MeOH	7.1 (0.66)	51 (0.19)	160 (0.12)	1.8 (0.01)	7.3 (0.02)
2	TFE	2.7 (0.25)	13 (0.36)	64 (0.33)	3.8 (0.05)	8.5 (0.01)

[a]from S1.

8. Transient absorption spectroscopy

For transient absorption measurements, samples were prepared in MeOH and TFE so that the steady-state absorbance of the sample in a 1 mm cell was 0.3-0.4 at the excitation wavelength. This amounted to an effective concentration of $2 \cdot 10^{-4}$ M of blue chromophore. Excitation at 610 nm was performed with a two-stage noncollinear optical parametric amplifier (NOPA, Clark-MXR), fed by the 800 nm output of a standard 1 kHz amplified Ti:Sapphire system (Spectra-Physics). After recompression with a pair of prisms, the pulse duration was of the order of 50 fs. The energy per pulse at the sample was around 1 μJ. Probing was achieved with a white light continuum obtained by focussing 800 nm pulses in a H_2O/D_2O mixture. The probe beam was split into a pumped signal beam and an un-pumped reference beam before the sample. The transmitted signal and reference beams were detected by ORIEL Multispec™ 125 spectrographs coupled to CCD detectors (Entwicklungsbüro G. Stresing, Berlin). To improve the sensitivity, the pump light was chopped at half the amplifier frequency, and the transmitted signal intensity was recorded shot by shot. It was corrected for intensity fluctuations using the reference beam. The transient spectra were averaged until the desired signal-to-noise ratio was achieved. Artefacts due to parasite light (pump light reaching the detectors, dispersed spontaneous fluorescence of the sample) were subtracted. Kinetics at a single wavelength were extracted from the transient spectra.

Some transient absorption spectra of **1** in MeOH and TFE are shown in Figures S7 and S8. They have essentially the same features as the spectra of **2** [S1], *i.e.* anion bands around 510 nm and 700 nm and a combined negative bleach/stimulated emission band around 630 nm. The anion band at 510 nm is a little bit broader for **1** than for **2**, especially in TFE. It seems much more intense compared to the bleach/emission peak, because the stimulated emission has smaller quantum yield. The quenching of the stimulated emission is very clearly observable at 650 nm, and there is also a rise in the anion absorption at 700 nm. There are some pronounced spectral dynamics in the anion and bleach signals at 550 nm. The band at 510 nm (Figure S9) decays with 50 ± 5 ps in MeOH and with 40 ± 5 ps in TFE, mainly due to charge recombination. This is slightly faster than for **2** in either solvent, but because of experimental error and distinct charge separation rates this difference should not be considered as significant. The bleach at 600 nm decays monoexponentially with 30 ± 5 ps in MeOH and with 30 ± 5 ps in TFE (Figure S10), indicating almost no solvent effect. It is obvious that the lifetime of the charge-separated state in MeOH is not increased with **1** compared to **2**: it is of the same order of magnitude for **1** and **2** in both solvents.

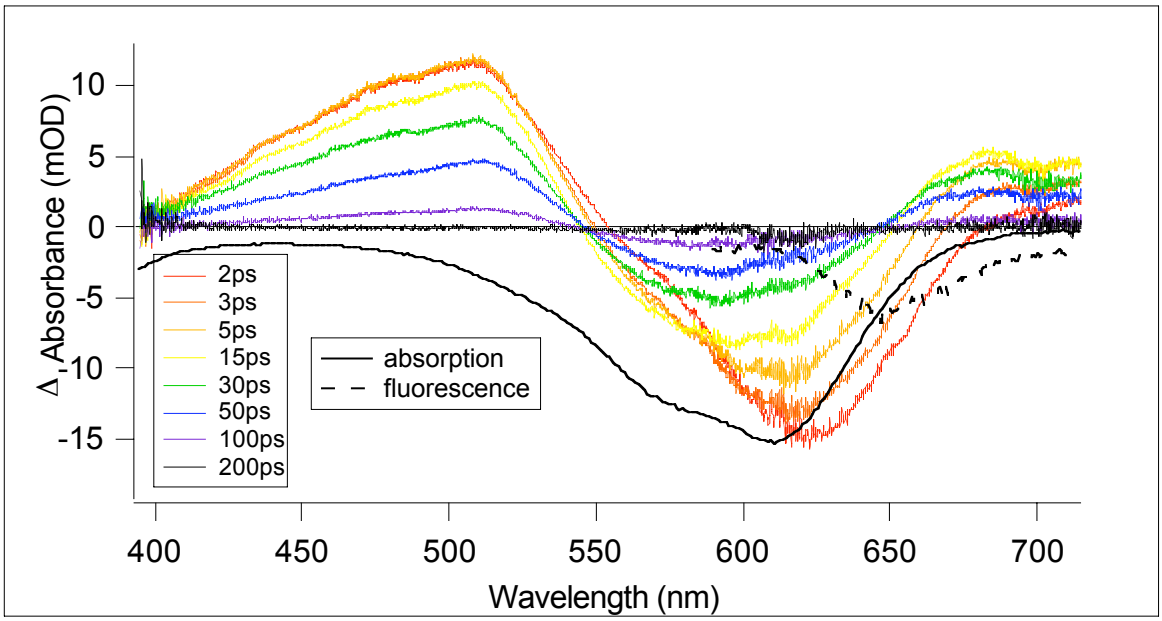


Figure S7. *Transient absorption spectra of* ***1*** *in MeOH after excitation at 610 nm.*

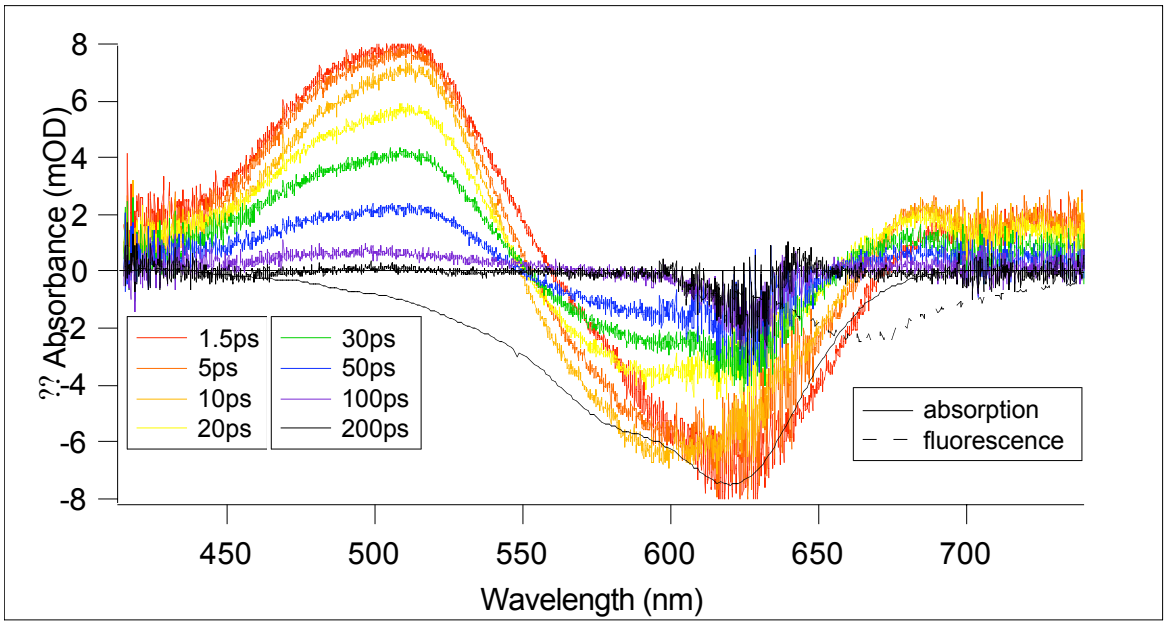


Figure S8. *Transient absorption spectra of* ***1*** *in TFE after excitation at 610 nm.*

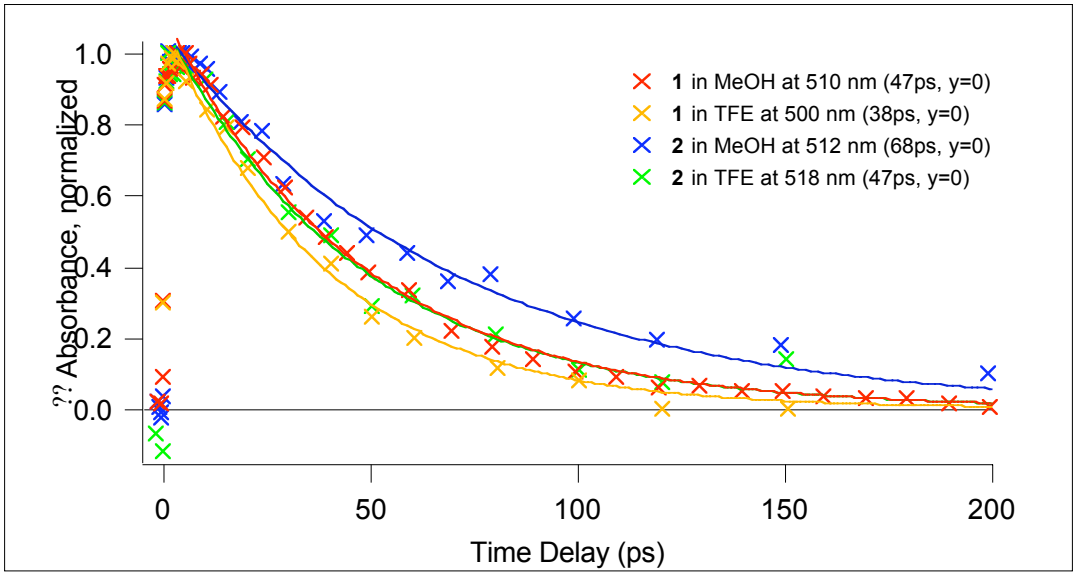


Figure S9. *Kinetics extracted at selected wavelengths in the anion band from the transient absorption spectra of* ***1*** *and* ***2*** *in MeOH and TFE (excitation at 610 nm). The solid lines represent best monoexponential fits to the data, fitting parameters are given in the figure.*

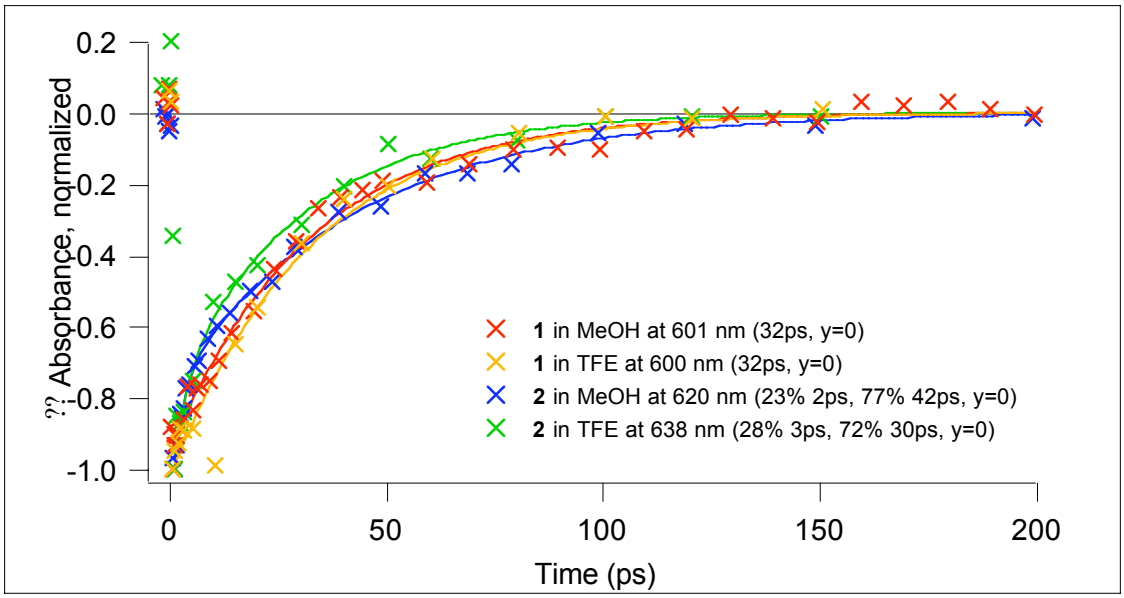


Figure S10. *Kinetics extracted at selected wavelengths in the bleach/stimulated emission band from the transient absorption spectra of* ***1*** *and* ***2*** *in MeOH and TFE (excitation at 610 nm). The solid lines represent best mono- or biexponential fits to the data, fitting parameters are given in the figure.*

9. References

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