Electronic Supplementary Information

A Boron Dipyrromethene-Phthalocyanine Pentad as an Artificial Photosynthetic Model

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^{1}H NMR spectra of the new compounds.

Experimental Section

General. All the reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF), toluene and pyridine were distilled from sodium benzophenone ketyl, sodium and potassium hydroxide respectively. Toluene used for photophysical measurements was of spectroscopic grade (Aldrich) and used without prior purification. Chromatographic purifications were performed on silica gel (Macherey-Nagel, 70-230 mesh) columns with the indicated eluents. Size exclusion chromatography was carried out on Bio-Rad Bio-Beads S-X1 beads (200-400 mesh). All other solvents and reagents were of reagent grade and used as received. Pc **5**[1] and BDP **6**[2] were prepared as described.

^{1}H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) or AVANCE II 400 (400 MHz) spectrometer in $CDCl_3$ or acetone-d_6. Spectra were referenced internally using the residual solvent (δ 7.26 for $CDCl_3$ and δ 2.05 for acetone-d_6) relative to $SiMe_4$. Electrospray ionisation (ESI) mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer. Matrix assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectra were taken on a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer.

Photophysical Studies. UV-Vis and steady-state fluorescence spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer and a Hitachi F-4500 spectrofluorometer respectively. Fluorescence quantum yields were determined by the equation: $\Phi_{F(\text{sample})} = (F_{\text{sample}}/F_{\text{ref}})(A_{\text{ref}}/A_{\text{sample}})(n_{\text{sample}}^2/n_{\text{ref}}^2)\Phi_{F(\text{ref})}$,[3] where F, A and n are the integrated fluorescence intensity, the absorbance at the excitation position and the refractive index of the solvent respectively. Rhodamine 110 in ethanol [$\Phi_{\mathrm{F(ref)}} = 0.94$],[4] rhodamine 6G in ethanol [$\Phi_{\mathrm{F(ref)}} = 0.95$][5] and *meso*-tetraphenylporphyrin in *N*,*N*-dimethylformamide (DMF) [$\Phi_{\mathrm{F(ref)}} = 0.11$][6] were used as the references for BDP-, MSBDP- and Pc-part emission respectively. Time-resolved fluorescence and transient absorption spectroscopic studies were carried out using the set-ups described previously.[7]

Electrochemical Studies. Electrochemical measurements were carried out with a Princeton Applied Research Potentiostat/Galvanostat Model 263A analyser. The cell comprised inlets for a platinum-sphere working electrode, a platinum-plate counter electrode and a silver-wire pseudo-reference electrode. Typically, a 0.1 M solution of $[\mathrm{Bu_4N}][\mathrm{PF_6}]$ in DMF containing the sample was purged with nitrogen for 20 min, and then the voltammograms were recorded at ambient temperature. Potentials were referenced to the saturated calomel electrode (SCE) using ferrocene as an internal standard ($E_{1/2} = +\,0.38$ V *vs*. SCE).[8]

Estimation of Free-Energy Change of Charge Separation in 4. The following Rehm-Weller equation[9] was used to estimate the free-energy change (ΔG_0) of charge separation in **4**:

$$\Delta G_0^{D/A} = e(E_{1/2}^{oxd}(D/D^{\bullet+}) - E_{1/2}^{red}(A/A^{\bullet-})) - E_{0,0}^{D/A} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_S R} - \frac{e^2}{8\pi\varepsilon_0}\left[\frac{1}{r_{D^{\bullet+}}} + \frac{1}{r_{A^{\bullet-}}}\right]\left[\frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_S}\right]$$

where $\Delta G_0^{D/A}$ is the change in free energy of charge separation with selective excitation of the electron donor D (i.e. MSBDP) or the electron acceptor A (i.e. Pc), $E_{1/2}^{oxd} = 0.82$ V and $E_{1/2}^{red} = -0.57$ V are the half-wave oxidation and reduction potentials of the donor

$D/D^{\bullet+}$ and acceptor $A/A^{\bullet-}$ couples in volt, $E_{0,0}^{D/A}$ is the energy of the $S_0 \rightarrow S_1$ transition of the donor or acceptor (2.15 eV for MSBDP and 1.81 eV for Pc), R is the separation distance between the donor and acceptor moieties (6 Å estimated by using the HyperChem programme package), ε_s is the dielectric constant of the solvent in which the spectroscopic measurements were performed (2.4 for toluene), ε_{ref} is added to account for the different dielectric constant for the solvent used for electrochemical studies (38.3 for DMF), $r_{D^{\bullet+}}$ (= 4 Å) and $r_{A^{\bullet-}}$ (= 4.6 Å) are the effective radii of the radical cation and anion respectively, ε_0 is the vacuum permittivity and e is the charge of the transferred electron. It followed that upon MSBDP-part excitation, ΔG_0 = -0.45 eV whereas the value was calculated to be -0.11 eV when Pc was excited.

Bis-BDP 1. Three drops of trifluoroacetic acid (TFA) were added to a solution of terephthalaldehyde (0.21 g, 1.57 mmol) and 2,4-dimethylpyrrole (0.60 g, 6.31 mmol) in THF (90 mL). The resulting mixture was stirred at room temperature overnight. A solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.72 g, 3.17 mmol) in THF (120 mL) was added, and then the mixture was stirred for a further 4 h. After the addition of triethylamine (16 mL), $BF_3 \bullet OEt_2$ (16 mL) was added dropwise while keeping the mixture at 0°C. It was followed by continuous stirring at room temperature overnight. The mixture was filtered through a pad of celite to remove the black solid, which was washed with CH_2Cl_2. The filtrate was rotary evaporated to dryness. The residue was dissolved in CH_2Cl_2 (180 mL). The solution was washed with 5% $NaHCO_3$ solution (200 mL), followed with H_2O (200 mL × 2), and then dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography using CH_2Cl_2/hexane (1:1 *v*/*v*) as the eluent. Compound **1** was obtained as an orange solid (0.22 g, 25%). R_f (CH_2Cl_2) = 0.66. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (s, 4 H, ArH), 6.01 (s, 4 H, pyrrole-H), 2.58 (s, 12 H, CH_3), 1.53 (s, 12 H, CH_3); MS (ESI): isotopic clusters peaking at *m*/z 551 {100%, $[M - F]^-$} and 571 {23%, $[M + H]^+$}; HRMS (ESI): *m/z* calcd for $C_{32}H_{33}B_2F_4N_4$ $[M + H]^+$: 571.2833, found 571.2843.

Dyad 2. A mixture of compound **1** (0.13 g, 0.23 mmol), 4-hydroxybenzaldehyde (26 mg, 0.21 mmol), glacial acetic acid (1.5 ml), piperidine (1.8 ml) and a small amount of $Mg(ClO_4)_2$ in toluene (130 ml) was refluxed for 5 h. The water formed during the reaction was removed azeotropically using a Dean-Stark apparatus. The crude product was concentrated *in vacuo*. The residue was subject to silica gel column chromatography using CH_2Cl_2 as the eluent. The orange fraction containing unreacted compound **1** was discarded. The pink coloured fraction was collected and the solvent was removed under reduced pressure. The crude product was further purified by recrystallisation from a mixture of CH_2Cl_2 and hexane to give the desired product as a purple solid (54 mg, 38%). R_f (CH_2Cl_2) = 0.11. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.88 (s, 1 H, OH), 7.73-7.78 (m, 4 H, ArH), 7.47-7.59 (m, 4 H, ArH and CH=CH), 6.95 (d, *J* = 8.0 Hz, 2 H, ArH), 6.88 (s, 1 H, pyrrole-H), 6.18 (s, 3 H, pyrrole-H), 2.57 (s, 3 H, CH_3), 2.54 (s, 6 H, CH_3), 1.67 (s, 3 H, CH_3), 1.63 (s, 9 H, CH_3); MS (ESI): an isotopic cluster peaking at *m*/z 674 {100%, $[M]^+$}; HRMS (ESI): *m/z* calcd for $C_{39}H_{36}B_2F_4N_4O$ $[M]^+$: 674.3019, found 674.3019.

Pentad 4. A mixture of compound **2** (80 mg, 0.12 mmol), silicon(IV) phthalocyanine dichloride (**3**) (16 mg, 26 μmol) and a small amount of pyridine (0.5 mL) in toluene (15 mL) was refluxed for 8 h. It was then rotary evaporated to dryness. The residue was subject to silica gel column chromatography using $CHCl_3$ as the eluent. The purple fraction was collected and the solvent was removed under reduced pressure. The crude product was further purified by size exclusion chromatography and recrystallisation from a mixture of $CHCl_3$ and hexane to give **4** as a purple solid (40 mg, 82%). R_f ($CHCl_3$) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67-9.69 (m, 8 H, Pc-H_α), 8.38-8.41 (m, 8 H, Pc-H_β), 7.44 (s, 8 H, ArH), 6.76 (d, *J* = 16.4 Hz, 2 H, CH=CH), 6.37 (d, *J* = 16.4 Hz, 2 H, CH=CH), 6.20 (s, 2 H, pyrrole-H), 5.98 (s, 2 H, pyrrole-H), 5.97 (s, 2 H, pyrrole-H), 5.94 (s, 2 H, pyrrole-H), 5.87 (d, *J* = 8.4 Hz, 4 H, ArH), 2.55 (s, 12 H, CH_3), 2.48 (s, 6 H, CH_3), 2.46 (d, *J* = 8.8 Hz, 4 H, ArH), 1.48 (s, 6 H, CH_3), 1.46 (s, 12 H, CH_3), 1.40 (s, 6 H, CH_3); MS (MALDI-TOF): an isotopic cluster peaking at *m*/z 1213 {100%, $[M - C_{39}H_{35}B_2F_4N_4O]^+$}; HRMS (MALDI-TOF): *m*/*z* calcd for $C_{71}H_{51}B_2F_4N_{12}OSi$ $[M - C_{39}H_{35}B_2F_4N_4O]^+$: 1213.4216, found 1213.4255.

MSBDP 7. A mixture of compound **6** (0.49 g, 1.51 mmol), 4-hydroxybenzaldehyde (0.25 g, 2.05 mmol), glacial acetic acid (0.5 ml), piperidine (0.6 ml) and a small amount of $Mg(ClO_4)_2$ in toluene (40 ml) was refluxed for 2 h. The water formed during the reaction was removed azeotropically using a Dean-Stark apparatus. The mixture was concentrated *in vacuo*. The residue was then subject to silica gel column chromatography using CH_2Cl_2 as the eluent. The pink coloured fraction was collected and concentrated under reduced pressure. The crude product was further purified by recrystallisation from a mixture of CH_2Cl_2 and hexane to give the desired product **7** as a golden-green solid (0.05 g, 8%). R_f (CH_2Cl_2) = 0.17. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.57 (m, 6 H, ArH and

CH=CH), 7.29-7.32 (m, 2 H, ArH), 7.18 (d, *J* = 15.9 Hz, 1 H, CH=CH), 6.84 (d, *J* = 8.7 Hz, 2 H, ArH), 6.59 (s, 1 H, pyrrole-H), 6.00 (s, 1 H, pyrrole-H), 5.05 (s, 1 H, OH), 2.60 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3); MS (ESI): isotopic clusters peaking at *m*/z 428 {100%, $[M]^+$} and 409 {67%, [M – F]}$^-$; HRMS (ESI): *m/z* calcd for $C_{26}H_{23}BF_2N_2O$ $[M]^+$: 428.1871, found 428.1867.

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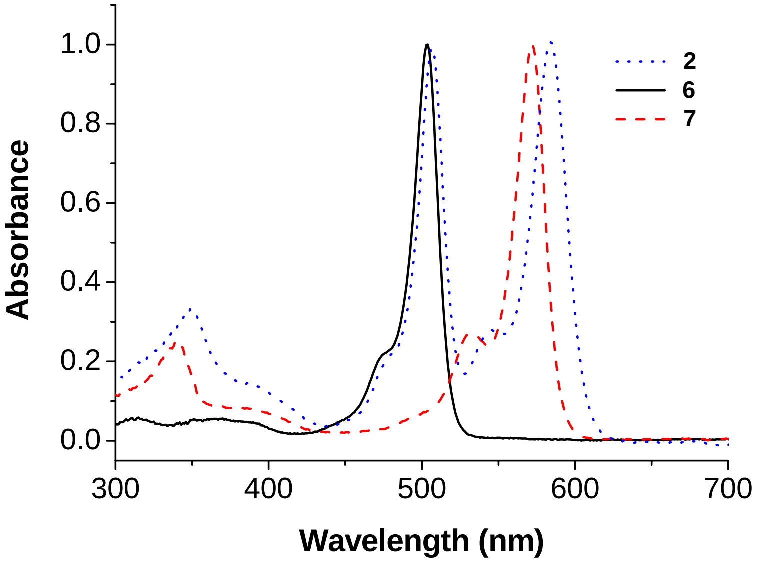


Fig. S1 Normalised electronic absorption spectra of dyad **2** and the reference compounds **6** and **7** in toluene.

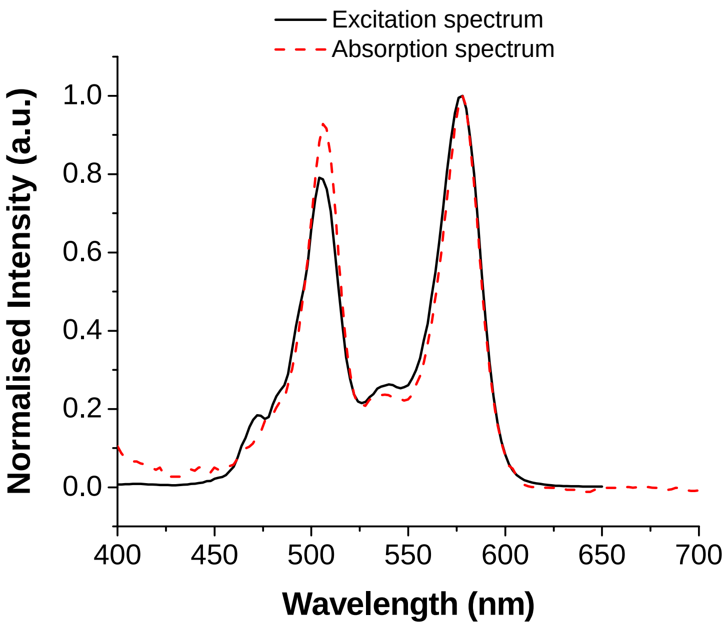


Fig. S2 The normalised (at 584 nm) absorption and excitation (monitored at 590 nm) spectra of dyad **2** in toluene.

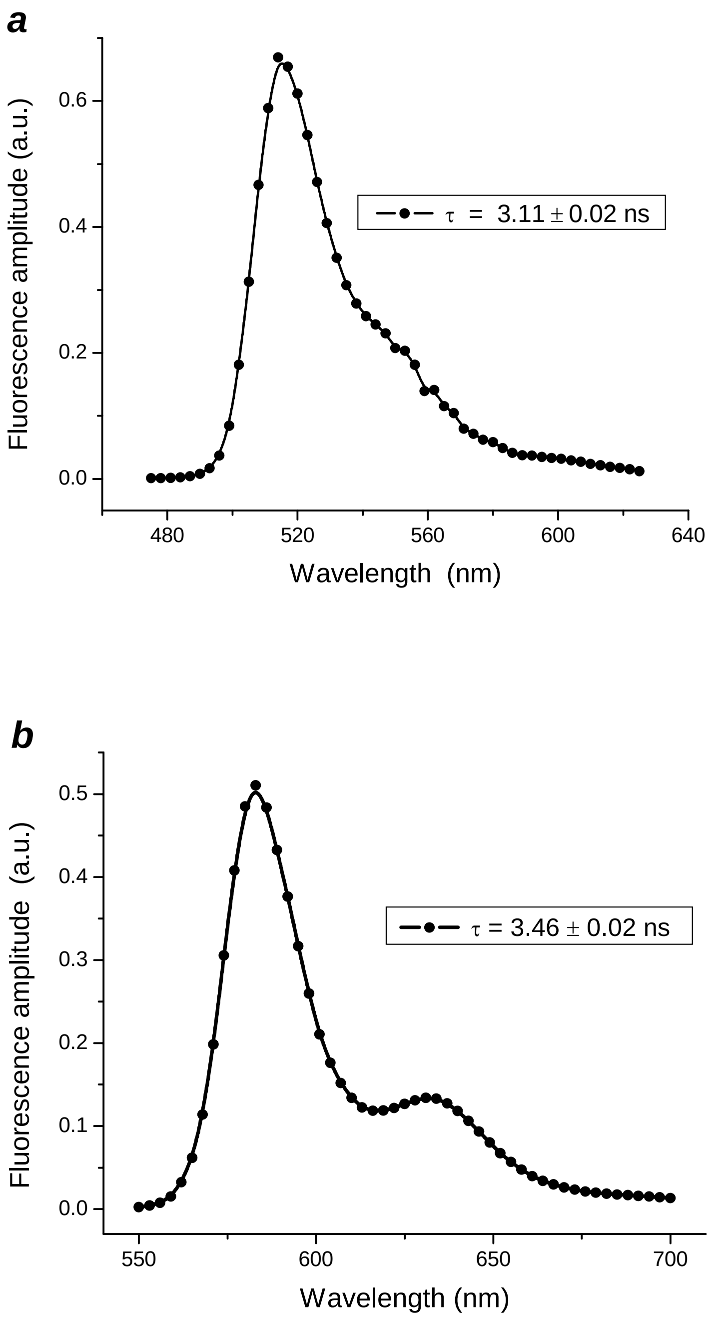
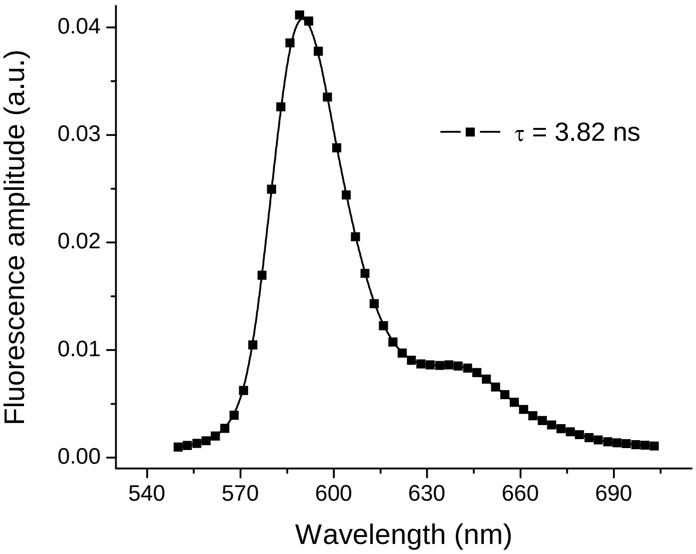


Fig. S3 DAF spectra of the reference compounds (a) BDP **6** and (b) MSBDP **7** in toluene.

(a)



(b)

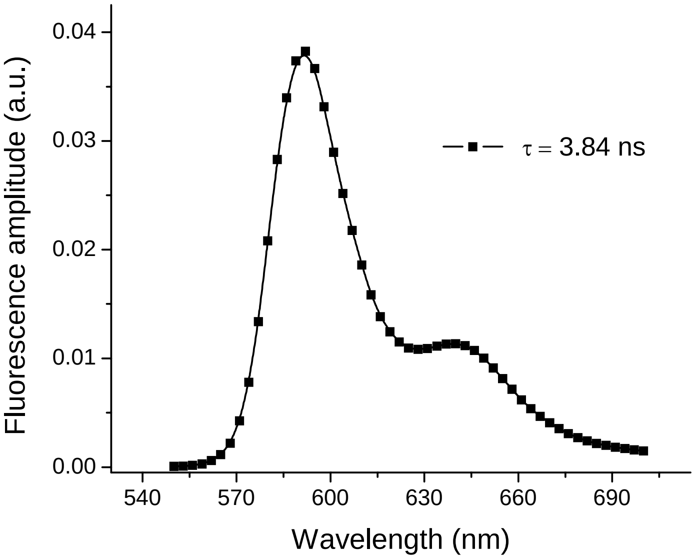


Fig. S4 DAF spectra of dyad **2** in toluene upon (a) BDP- or (b) MSBDP-part excitation.

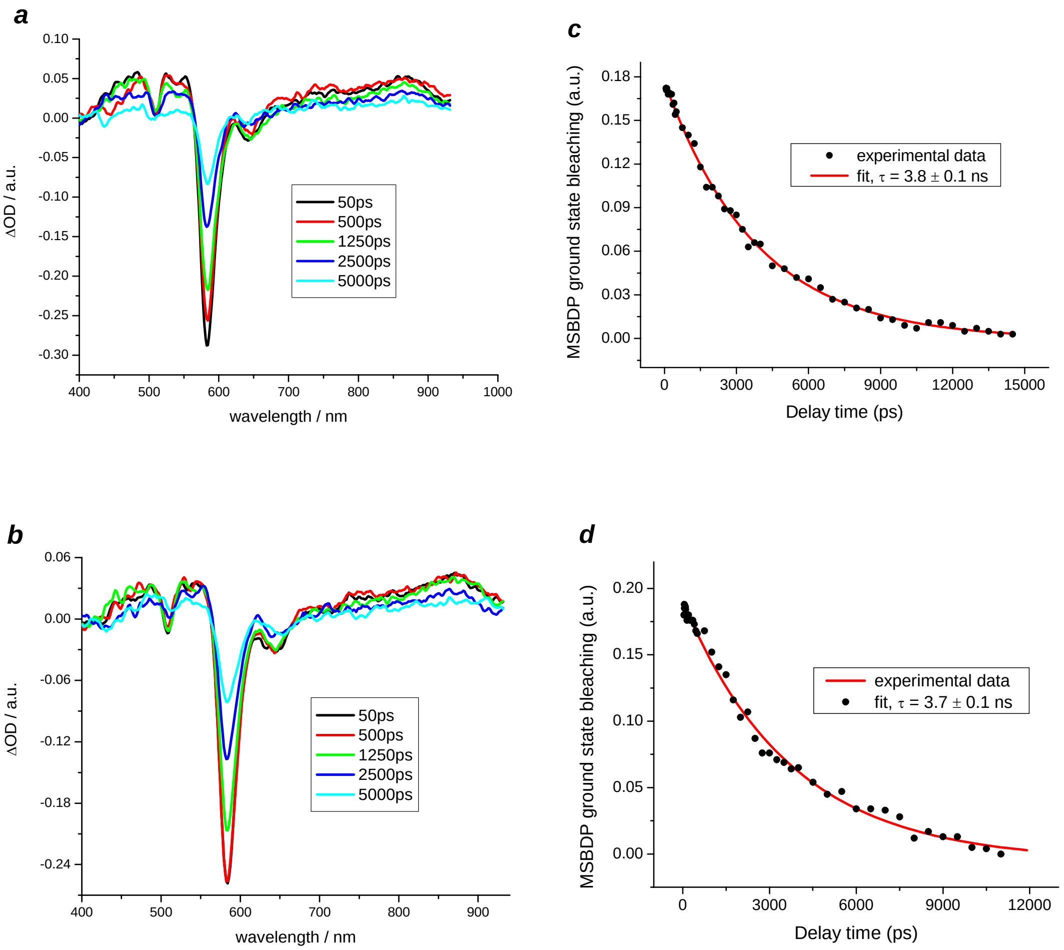


Fig. S5 Transient absorption spectra of dyad **2** in toluene at different delay times after (a) BDP- or (b) MSBDP-part excitation. The corresponding ground-state recovery profiles of the MSBDP moiety are given in (c) and (d) respectively.

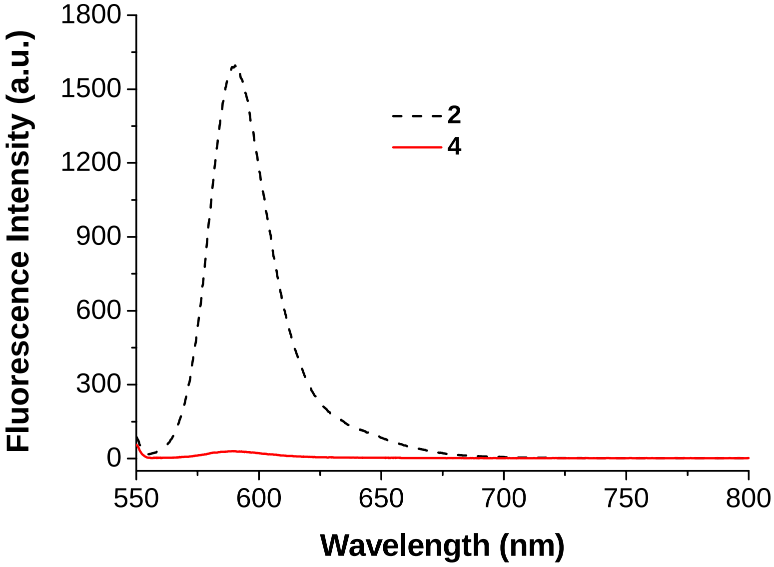


Fig. S6 Fluorescence spectra of dyad **2** and pentad **4** with equal absorbance at the excitation position at 544 nm in toluene.

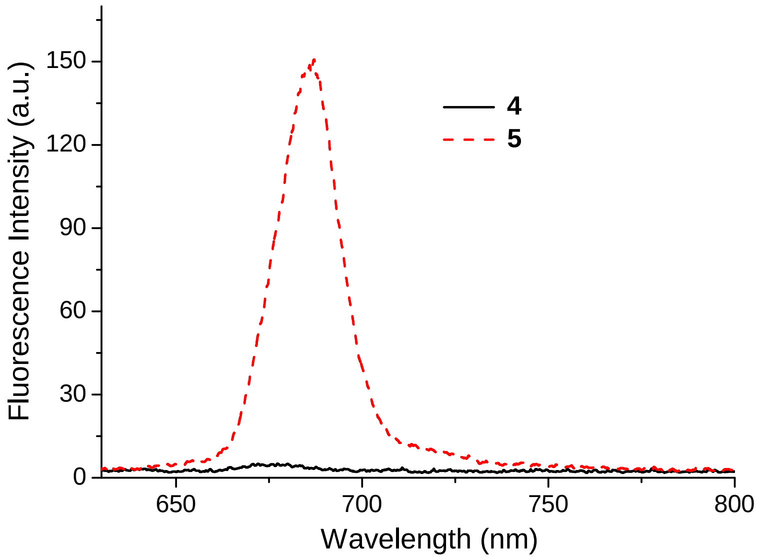


Fig. S7 Fluorescence spectra of pentad **4** and the reference compound **5** with equal absorbance at the excitation position at 613 nm in toluene.

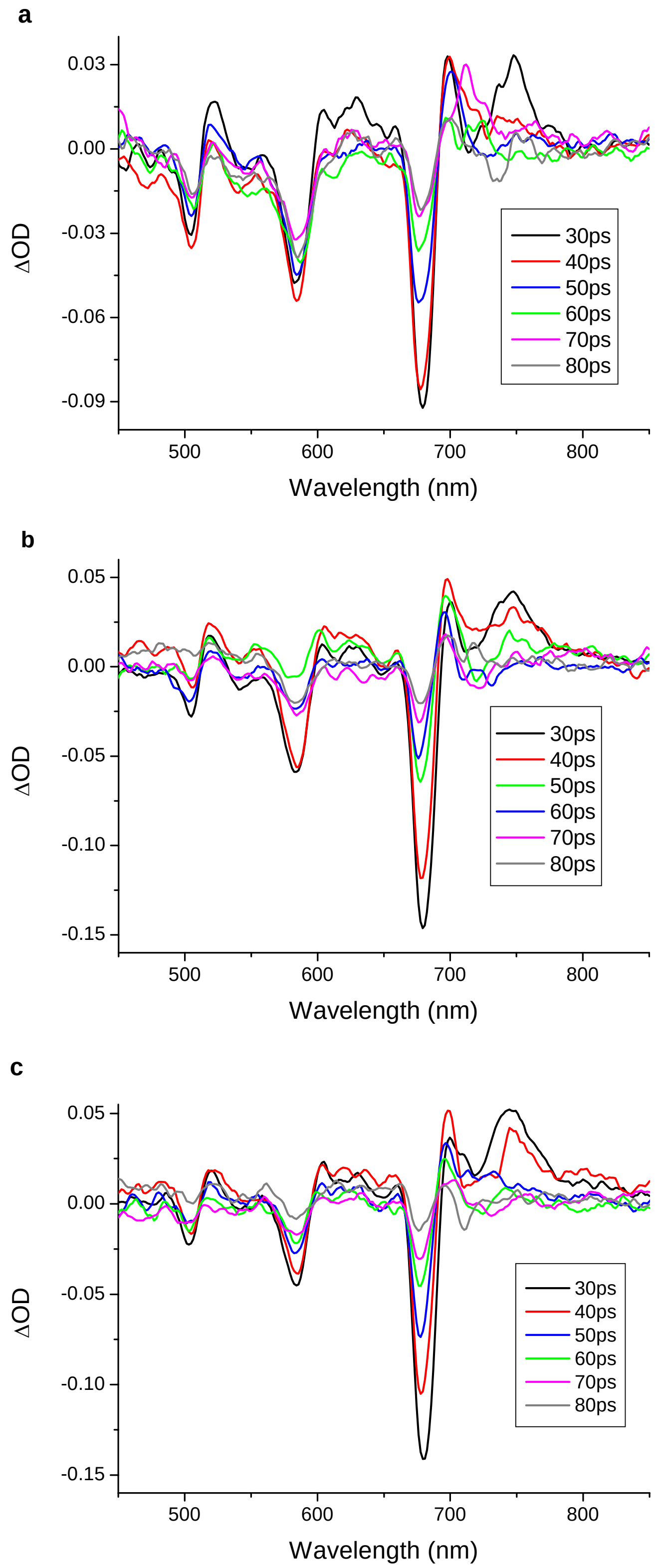


Fig. S8 Transient absorption spectra of pentad **4** in chloroform upon selective excitation at the (a) BDP-, (b) MSBDP- or (c) Pc-part.

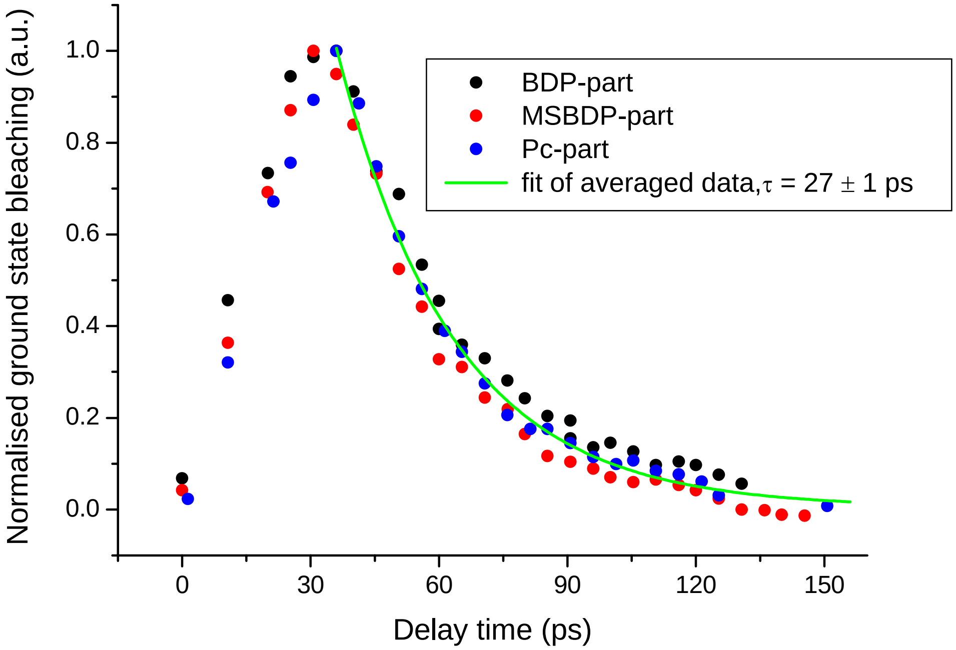


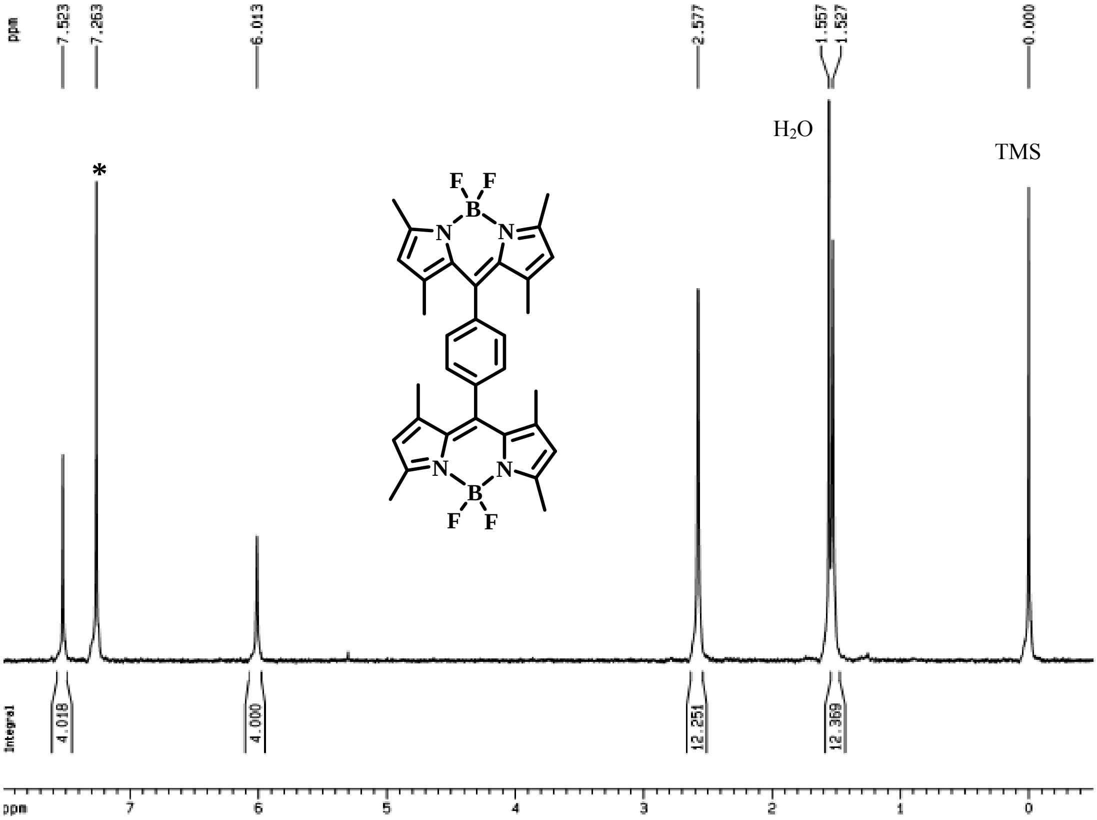
Fig. S9 Ground-state bleaching of BDP-, MSBDP- and Pc-part of pentad **4** in chloroform. Since the time behaviour of all the three ground-state bleaching signals was the same, the data were averaged and fitted with a mono-exponential function as shown by the green curve.

Table S1. Electrochemical data for **2** and **5**.[a]

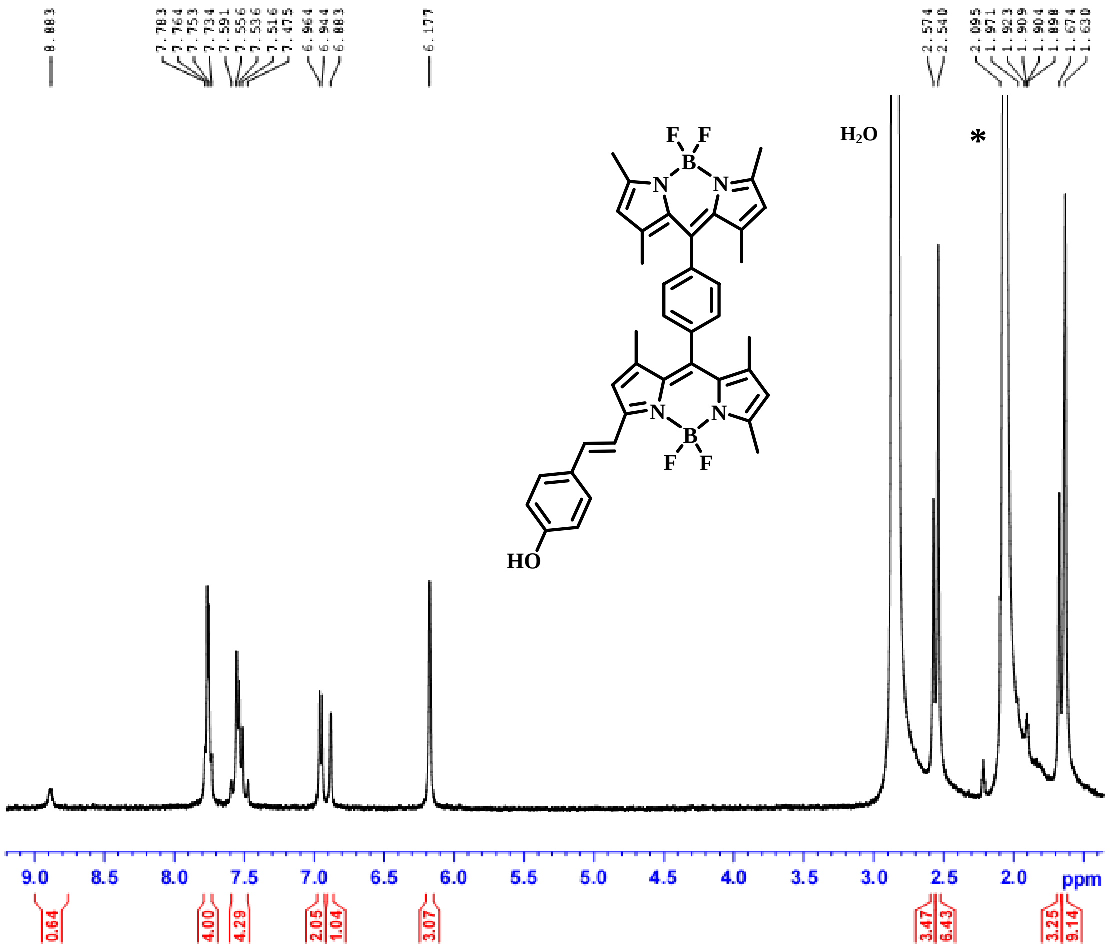
Compound	**E_{red} / V**	**E_{ox} / V**
2	-1.10	0.82
5	-0.57, -1.11	1.13

[a] Recorded with $[Bu_4N][PF_6]$ as electrolyte in DMF (0.1 M) at ambient temperature with a scan rate of 100 mV s^{-1}. Potentials were referenced to a saturated calomel electrode (SCE) using ferrocene as an internal standard ($E_{1/2}$ = + 0.38 V *vs*. SCE).[8]

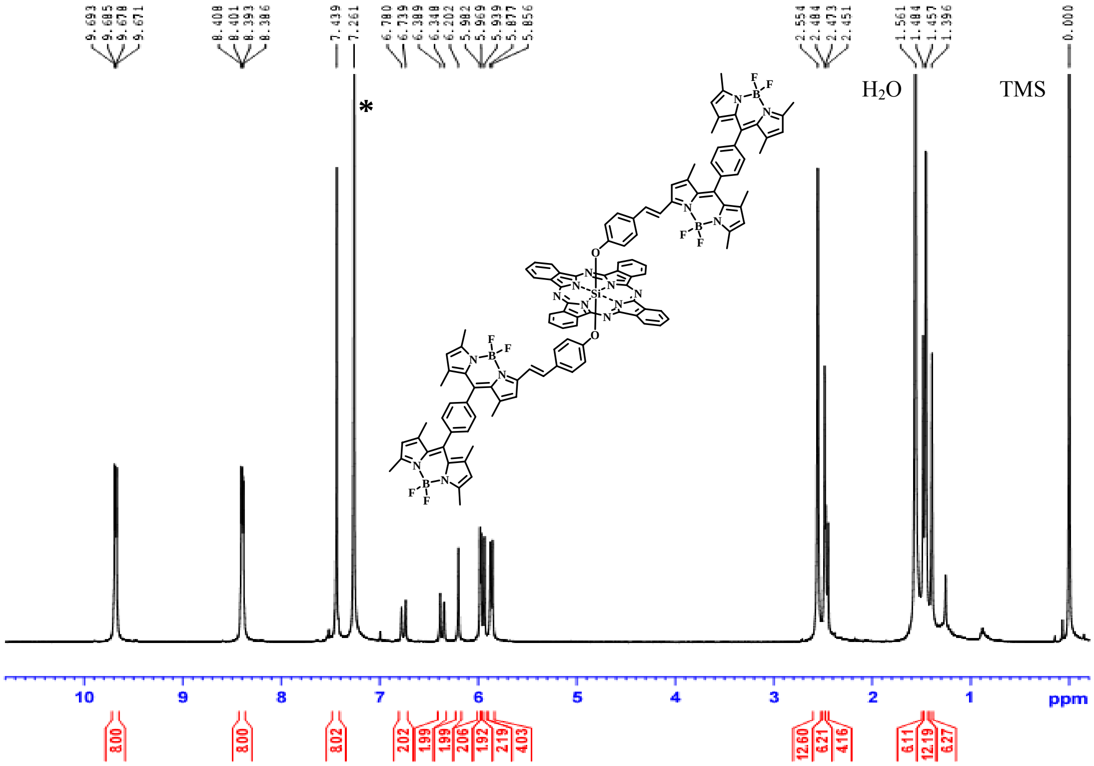
In all of the following spectra, the residual solvent signals are marked with asterisks



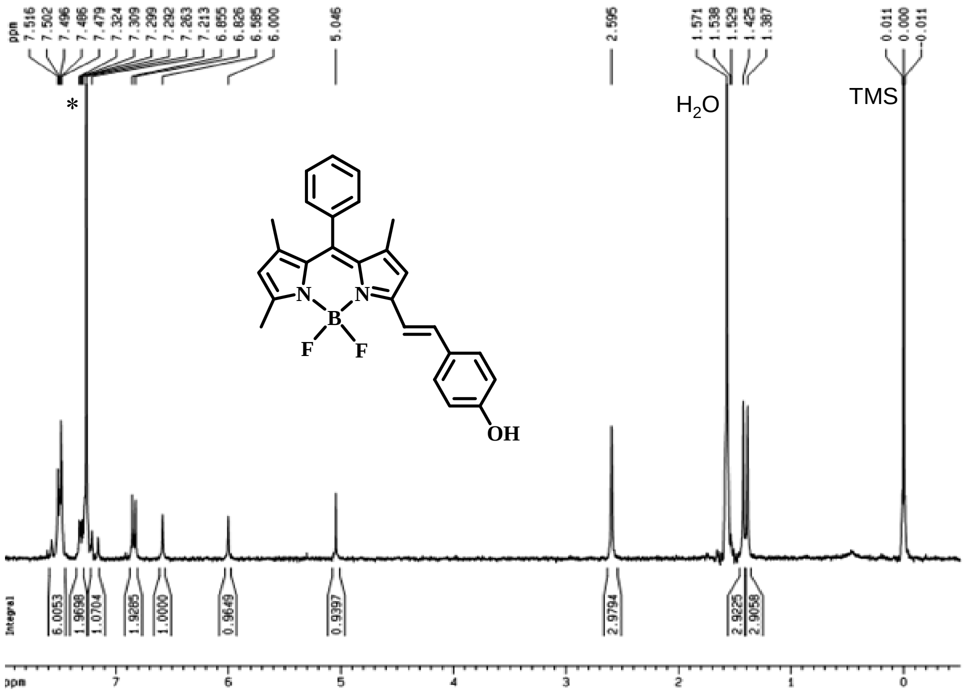
^{1}H NMR spectrum of bis-BDP **1** in $CDCl_3$.



^{1}H NMR spectrum of dyad **2** in acetone-d$_6$.



^{1}H NMR spectrum of pentad **4** in $CDCl_3$.



^{1}H NMR spectrum of MSBDP **7** in $CDCl_3$.