Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Photodynamics of excitation energy transfer in self-assembled dyads. Evidence for back transfer

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Experimental

General. Compounds **1**, **3,** and **5** were prepared according to references 6, 7, and 9, respectively. Reagents and solvents of reagent-grade were purchased and used without further purification. NEt_3 was distilled under argon over KOH prior to use. Anhydrous Na_2SO_4 was used as drying agent after aqueous workup. Evaporation and concentration in vacuo were carried out at H_2O-aspirator pressure. Column chromatography was performed with silica gel (0.063-0.200 mm) from Merck. Melting points are uncorrected. Mass spectra were recorded using a nitrobenzyl alcohol matrix. Elemental analyses were performed by le Service de Microanalyse de l'Institut de Chimie, Université Louis Pasteur and by le Service d'Analyse Elementaire de l'Institut Universitaire de Technologie, Strasbourg, Sud.

1-{[2-(Trimethylsilyl)ethoxy]methyl}-2-[2-(4-bromophenyl)ethynyl]imidazole (2). To a degassed solution of 1-{[2-(trimethylsilyl)ethoxy]methyl}2-(ethynyl)imidazole (**1**) (1.50 g, 6.76 mmol) and *p*-bromoiodobenzene (1.90 g, 6.76 mmol) in 20 mL of dry NEt_3, $PdCl_2(PPh_3)_4$ (94 mg, 0.14 mmol) and CuI (13 mg, 0.07 mmol) were added. The mixture was degassed then heated at 55° for 6 h under argon. Solvent was removed in vacuo. The crude product was dissolved in CH_2Cl_2 and washed with sat. NH_4Cl(aq). The organic phase was dried, filtered and evaporated to dryness. Column chromatography over silica gel (EtOAc/hex : 1/1) afforded compound **2** (2.16 g, 5.73 mmol, 85%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.51 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.26 (d, J=1.1 Hz, 2H), 7.19 (br s, 1H), 5.44 (s, 2H), 3.57 (t, J = 8.1 Hz, 2H), 0.92 (t, J = 8.1 Hz, 2H), -0.04 (s, 9H).

Porphyrin boronic ester 3. Pyrrole (1.34 g, 20 mmol) was added to a degassed solution of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzaldehyde[i] (1.09 g, 5 mmol) and benzaldehyde (1.56 g, 15 mmol) in 0.8 L of $CHCl_3$. Boron trifluoride etherate (0.75 ml, 6 mmol) was added via syringe. the resulting yellow solution was stirred under argon, in the absence of light, for 2 h. DDQ (3.4 g, 15 mmol) was added and the mixture was stirred for 2 h. After the addition of triethylamine (2 eq.), solvent was removed in vacuo. Two successive column chromatographies over SiO_2 (CH_2Cl_2, up to 5% MeOH) afforded the desired porphyrin boronic ester (182 mg, 0.25 mmol, 5%). This compound was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.85 (br s, 8H), 8.22 (m, 10H), 7.76 (m, 9H), 3.95 (s, 4H), 1.18 (s, 6H), -2.77 (s, 2H). FAB MS: calc for $C_{49}H_{39}BN_4O_2$ m/z = 726.7; found 727.1 (100%).

BH_2P. To a degassed solution of **2** (40 mg, 0.11 mmol) in 20 mL of toluene, the following reagents were added successively, degassing after each addition: $Pd(PPh_3)_4$ (5 mg, 4.3 umol), degassed 2M Na_2CO_3(aq) (1 mL), and a degassed solution of porphyrin boronic ester **3** (50 mg, 69 μmol) in MeOH (5mL). The reaction mixture was heated at 80° for 24 h. After cooling, the mixture was washed with 50 mL of 2M Na_2CO_3(aq) containing 5 mL of conc. NH_3 (aq). The organic layer was dried, filtered, and solvents were removed in vacuo. Purification by column chromatography over SiO_2 (CH_2Cl_2 with 0-10% gradient of EtOAc) afforded an enriched fraction of the coupled product **4**. This product, which was contaminated with unreacted compound **2**, was used without further purification for the next step.

A solution of 4 in THF (10 mL) and NBu_4F (1 M in THF, 0.5 ml, 0.5 mmol) was heated at 55° under argon for 3 h. Solvent was removed in vacuo, then the residue was taken

[i] I. M. Dixon, J.-P. Collin, J.-P. Sauvage, L. Flamigni, *Inorg. Chem*. 2001, 40, 5507-5517.

in CH_2Cl_2, washed with Na_2CO_3(aq) and then with brine. To remove the 2-[2-(4-bromophenyl)ethynyl]imidazole contaminate, the organic layer was acidified with 5N HCl(aq). The organic phase was then basified (pH 8) with 2M Na_2CO_3(aq) dried, filtered and evaporated to dryness. Column chromatography over silica gel (CH_2Cl_2/EtOAc: 1/4) and recrystallization from MeOH gave porphyrin **BH_2P** in 37% overall yield (20 mg, 26 μmol) based on starting material **3**. Mp. decomposes >250°. ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.38 (br s, 1H), 8.91 (d, J = 4.4 Hz, 2H), 8.86 (m, 6H), 8.31 (d, J = 7.7 Hz, 2H), 8.22 (m, 6H), 8.00 (d, J = 7.7 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.77 (m, 11H), 7.23 (s, 1H), 7.07 (s, 1H), -2.75 (s, 2H). UV-vis (CH_2Cl_2) : 307 (32200), 373 (20000), sh 402 (73200), 419 (387400), 516 (14500), 551 (7500), 592 (4300), 646 (3600). FAB MS: calc for $C_{55}H_{36}N_6$ m/z = 780.9; found 781.5 (100%). E.A.: found (calc) for $C_{55}H_{36}N_6$ + CH_2Cl_2 + H_2O: C 75.98 (76.10), H 4.75 (4.65), N 9.46 (9.51).

5,15-Bis[3,5-(di-t-butyl)phenyl]-10-(*m*-xylyl)porphyrin (6). To a degassed solution of the 10-bromo-5,15-bis[3,5-(di-t-butyl)phenyl]porphyrin (**5**) (172 mg, 0.22 mmol) in 30 mL of toluene, the following reagents were successively added : $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), a degassed solution of 2M Na_2CO_3(aq) (0.35 mL), and a degassed methanolic solution (0.5 mL) of the xylyl boronic ester (43 mg, 0.29 mmol). The reaction mixture was refluxed under argon for 36 h. After cooling, the mixture was partitioned between toluene (100 mL) and a 2M aqueous solution of Na_2CO_3 (50 mL) containing 5 mL of conc. NH_4OH. The organic layer was dried, filtered, and solvents were removed in vacuo. Purification by column chromatography over SiO_2 (CH_2Cl_2: hex:1/5, then 1/4) afforded an enriched fraction of porphyrin (**6**) (160 mg, 0.20 mmol, 92%). This product was used without further purification for the next step. ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.21 (s, 1H), 9.34 (d, J=4.7 Hz, 2H), 9.06

(d, J=4.7 Hz, 2H), 8.93 (d, J=4.7 Hz, 2H), 8.90 (d, J=4.7 Hz, 2H), 8.11 (d, J=1.8 Hz, 4H), 7.84 (s, 2H), 7.81 (t, J=1.8 Hz, 2H), 7.40 (s, 1H), 2.60 (s, 6H), 1.55 (s, 36H), -2.92 (s, 2H).

5-Iodo-10,20-bis[3',5'-(di-t-butyl)phenyl]-15-(*m*-xylyl)porphyrin (7). A solution of iodine (61 mg, 0.24 mmol) in 8 mL $CHCl_3$ was added to a light-protected solution of [bis(trifluoroacetoxy)iodo]benzene (129 mg, 0.30 mmol) in 15 ml of $CHCl_3$. Pyridine (6 pipette drops) was added to this solution, causing decoloration to light yellow. This solution was added dropwise over 25 min to a light-protected solution of porphyrin **6** (160 mg, 0.20 mmol) in 150 ml of $CHCl_3$. After stirring for 2 h at r.t., the solution was washed with sat. $Na_2S_2O_3$(aq) (2 x 80 mL), dried, filtered, and evaporated in vacuo. The crude product was purified by column chromatography (SiO_2, hex/CH_2Cl_2: 1/3) to afford the iodoporphyrin **7** (144 mg, 0.16 mmol) in 79% yield. Mp: >300°. ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.67 (d, J=4.7 Hz, 2H), 8.89 (d, J=4.6 Hz, 2H), 8.81 (d, J=4.6 Hz, 2H), 8.80 (d, J=4.6 Hz, 2H), 8.04 (d, J=1.8 Hz, 4H), 7.81 (t, J=1.8 Hz, 2H), 7.79 (s, 2H), 7.38 (s, 1H), 2.58 (s, 6H), 1.54 (s, 36H), -2.67 (s, 2H). UV-visible (CH_2Cl_2): 304 (23100), 327 (20300), sh 379 (33300), 490 (5900), 522 (24000), 558 (16500), 598 (7600), 655 (8900). E.A.: found (calc) for $C_{56}H_{61}N_4I$: C 73.05 (73.35), H 6.53 (6.71), N 6.28 (6.11).

5-Iodo-10,20-bis[3',5'-(di-t-butyl)phenyl]-15-(*m*-xylyl)porphyrinato zinc(II) (Zn-7). A solution of iodoporphyrin **7** (166 mg, 0.18 mmol) and zinc(II) acetate (397 mg, 1.8 mmol) in $CHCl_3$/MeOH (45mL/10 mL) was refluxed for 1.5 h. After cooling, the solution was washed with water (3 x 50 mL), dried, filtered, and solvent removed in vacuo. Recrystallization from CH_2Cl_2/MeOH gave violet needles of the zinc porphyrin **Zn-7** (159 mg, 0.17 mmol, 95%). If necessary, the crude product could be purified over a column of Al_2O_3 (hex/CH_2Cl_2: gradient from 1/1 to 1/2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.81 (d, J=4.7 Hz, 2H), 9.01 (d, J=4.7 Hz,

2H), 8.95 (d, J=4.7 Hz, 2H), 8.93 (d, J=4.7 Hz, 2H), 8.06 (d, J=1.8 Hz, 4H), 7.81 (t, J=1.8 Hz, 2H), 7.80 (s, 2H), 7.39 (s, 1H), 2.59 (s, 6H), 1.54 (s, 36H).

EH_2P. The catalyst $PdCl_2(PPh_3)_2$ (1 mg, 1 mmol) was added to a degassed solution of zinc iodoporphyrin **Zn-7** (75 mg, 0.08 mmol) in 10 mL of distilled triethylamine. SEM-2-(2-ethynyl)imidazole (20 mg, 0.09 mmol) in 2 mL of toluene, and then CuI (0.3 mg, 1.5 μmol) were successively added, degassing between each addition. The reaction mixture was heated at 50° under argon for 42 h. Solvent was removed in vacuo. The residue was dissolved in dichloromethane and washed with sat NH_4Cl(aq). The organic layer was dried and filtered. Several drops of trifluoroacetic acid was added to the blue-violet solution of **Zn-8**. After stirring for 30 min, the solution was washed twice with 1M Na_2CO_3 (aq). The aqueous layer was extracted with dichloromethane and the combined organic phases were dried, filtered, and evaporated in vacuo. The deep pink solid was enriched by column chromatography over SiO_2 (CH_2Cl_2) to afford **8** (45 mg, 0.05 mmol, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.53 (d, J=4.9 Hz, 2H), 8.81 (d, J=4.9 Hz, 2H), 8.81 (d, J=4.8 Hz, 2H), 8.75 (d, J=4.8 Hz, 2H), 8.01 (d, J=1.8 Hz, 4H), 7.78 (m, 4H), 7.54 (d, J=1 Hz, 1H), 7. (d, J=1 Hz, 1H), 7.38 (s, 1H), 5.89 (s, 2H), 3.63 (t, J=8.3 Hz, 2H), 2.57 (s, 6H), 1.50 (s, 36H), 0.86 (m, 2H), -2.32 (s, 2H). This compound was dissolved in THF (15 mL) and treated with Bu_4NF (1 M in THF, 4 ml, 4 mmol). This degassed solution was heated at 55° for 2.5 h under argon. Solvent was removed in vacuo, then the residue was taken in CH_2Cl_2, washed with Na_2CO_3(aq) and then with brine. The organic layer was dried, filtered and evaporated to dryness. Column chromatography over silica gel (CH_2Cl_2/hex, 4/1) gave the desired compound (**EH_2P**) in 56% yield (24 mg, 25 umol). Mp. >300°. ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.80 (br s, 1H), 9.71 (d, J=4.7 Hz, 2H), 8.95 (d, J=4.7 Hz, 2H), 8.80 (m, 4H), 8.07 (d, J=1.8 Hz, 4H), 7.82 (t, J=1.8 Hz, 2H), 7.80 (s, 2H), 7.39 (s, 2H), 7.18 (s, 1H), 2.59 (s, 6H), 1.55 (s, 36H), -2.28 (s, 2H).

UV-vis (CH_2Cl_2) : 304 (124000), sh 413 (56600), 435 (242600), sh 497 (3700), 534 (8700), 578 (18800), 608 (4800), 667 (8200).FAB MS: calc for $C_{61}H_{64}N_6$ m/z = 881.2; found 881.6 (100%). E.A. found (calc) for $C_{61}H_{64}N_6 + H_2O + 0.5CH_2Cl_2$: C78.88 (78.44), H 6.80 (7.17), N 9.44 (8.92).

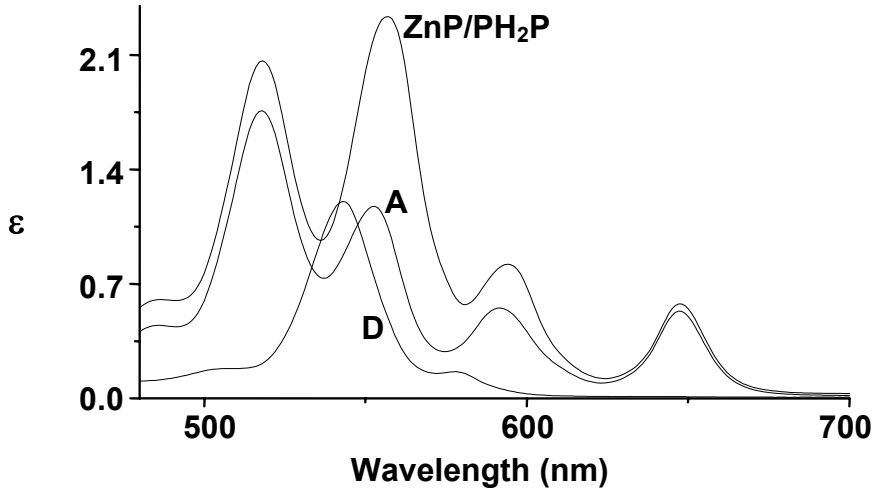

Figure S1. Q band region of the UV-Visible spectra of the donor (**D**) **ZnP**, acceptor (**A**) **PH_2P**, and dyad **ZnP/PH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. ε in ($M^{-1}cm^{-1}$)x 10^4

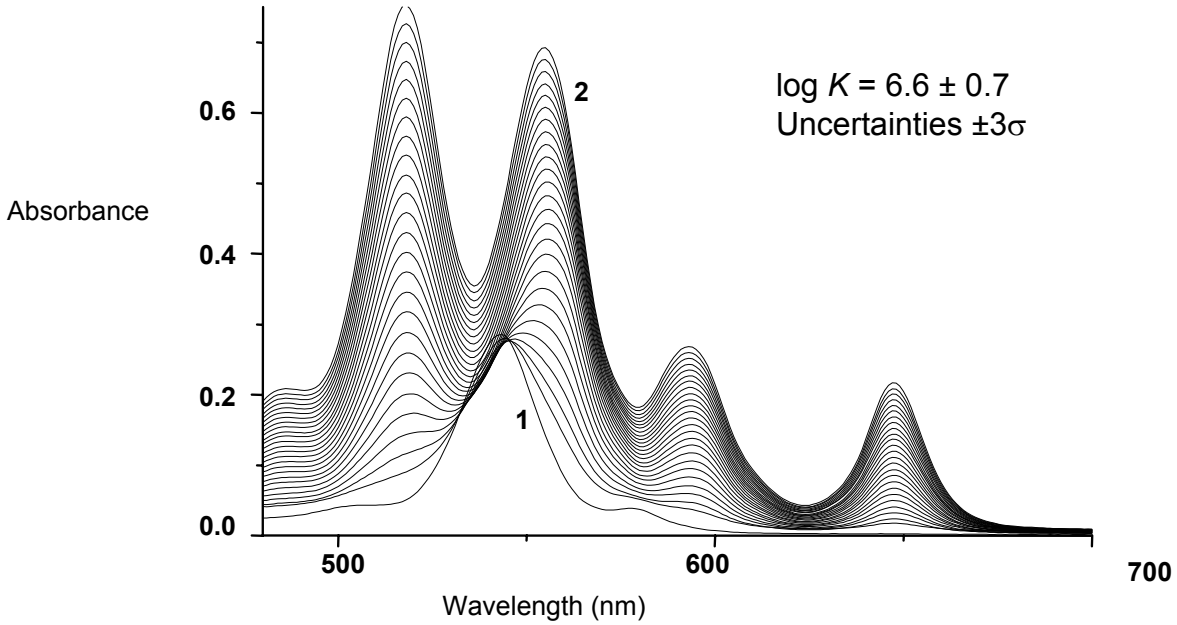

Figure S2. UV-visible titration (Q band region) of **ZnP** with **PH_2P**, to form dyad **ZnP/PH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. $[\mathbf{ZnP}]_{tot}$ = 1.18 x 10^{-5} M; $[\mathbf{PH_2P}]_{tot}$ =1.18 x 10^{-5} M; (**1**): $[\mathbf{PH_2P}]_{tot}/[\mathbf{ZnP}]_{tot}$ = 0, (**2**) $[\mathbf{PH_2P}]_{tot}/[\mathbf{ZnP}]_{tot}$ = 1.64.

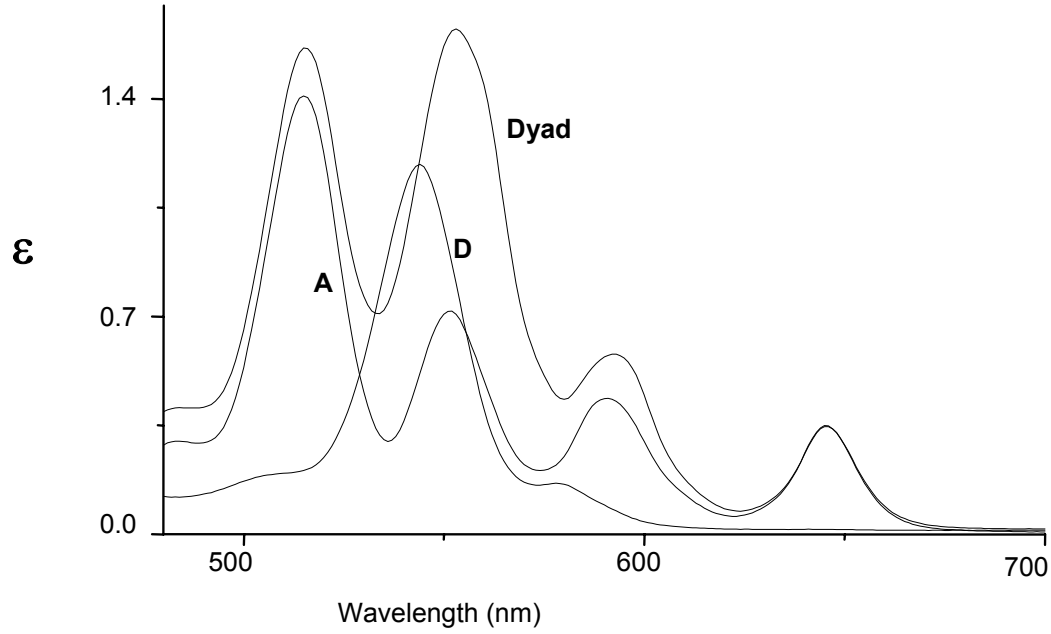

Figure S3. Q band region of the UV-Visible spectra of donor (**D**) **ZnP**, acceptor (**A**) **BH_2P**, and dyad **ZnP/BH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. ε in ($M^{-1}cm^{-1}$)x 10^4.

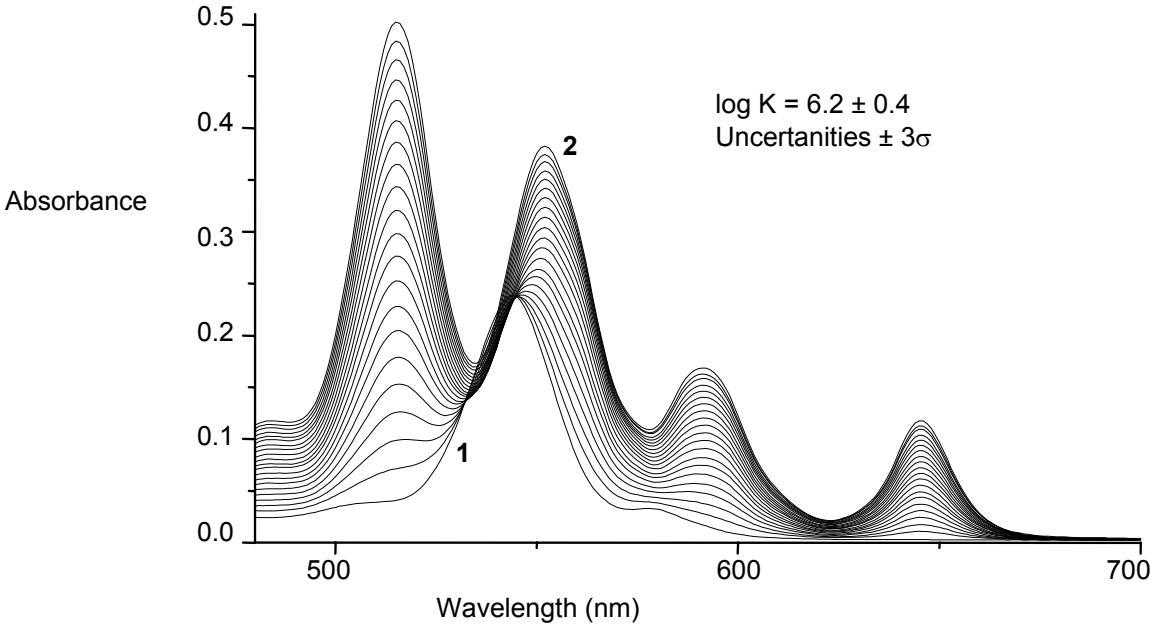

Figure S4. UV-visible titration (Q band region) of **ZnP** with **BH_2P**, to form dyad **ZnP/BH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. [**ZnP**]$_{tot}$ = 1.01 x 10^{-5} M; [**BH_2P**]$_{tot}$ =7.35 x 10^{-5} M; (**1**): [**BH_2P**]$_{tot}$/[**ZnP**]$_{tot}$ = 0, (**2**) [**BH_2P**]$_{tot}$/[**ZnP**]$_{tot}$ = 1.68.

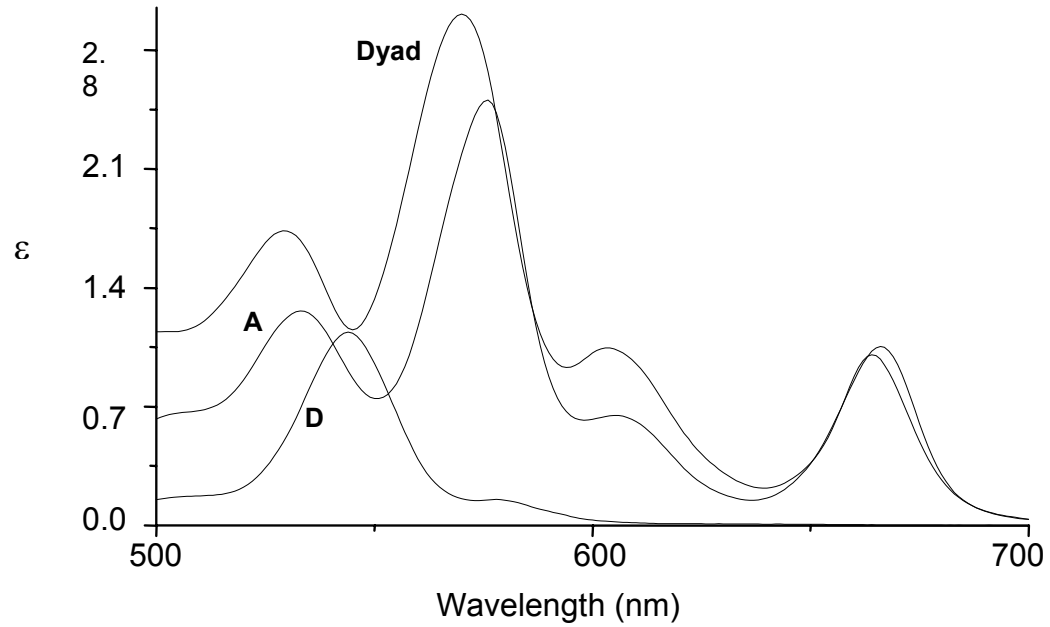

Figure S5. Q band region of the UV-Visible spectra of donor (**D**) **ZnP**, acceptor (**A**) **EH_2P**, and dyad **ZnP/EH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. ε in $(M^{-1}cm^{-1})x\ 10^4$.

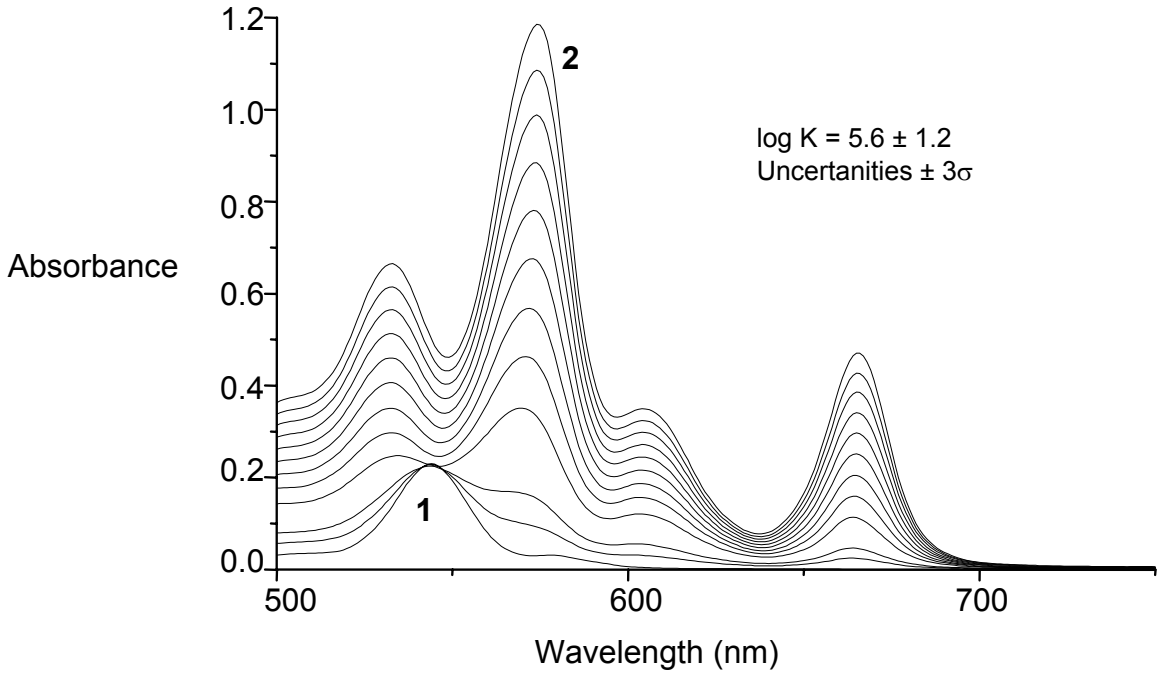

Figure S6. UV-visible titration (Q band region) of **ZnP** with **EH_2P**, to form dyad **ZnP/EH_2P** in CH_2Cl_2 + 0.01% 2,6-lutidine. $[\mathbf{ZnP}]_{tot} = 1.01 \times 10^{-5}$ M; $[\mathbf{EH_2P}]_{tot} = 2.55 \times 10^{-4}$ M; (**1**): $[\mathbf{EH_2P}]_{tot}/[\mathbf{ZnP}]_{tot} = 0$, (**2**) $[\mathbf{EH_2P}]_{tot}/[\mathbf{ZnP}]_{tot} = 2.29$.

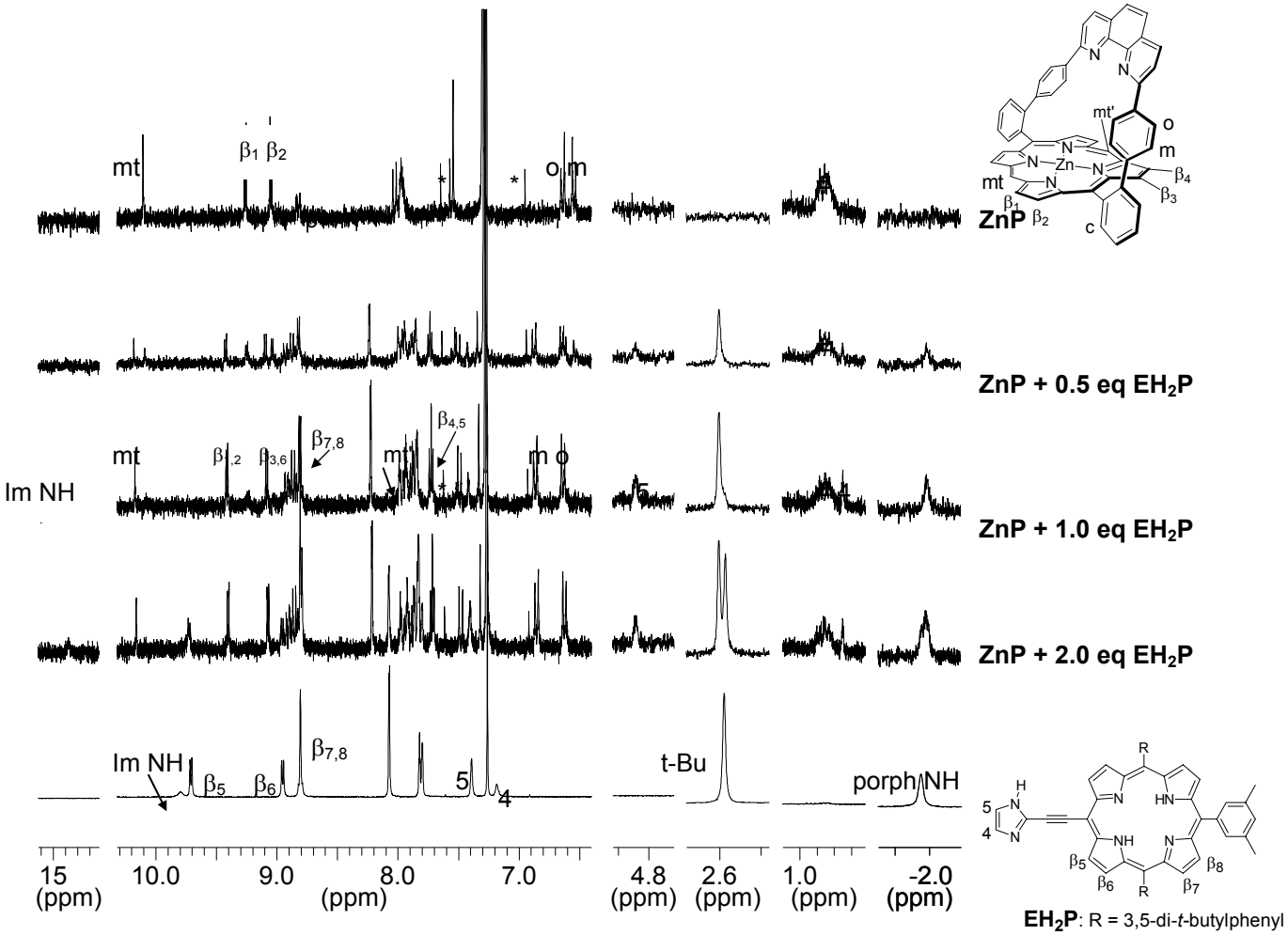

Figure S7. 300 MHz ^{1}H NMR titration of **ZnP** (4.6 x 10^{-4} M) with **EH_2P** in $CDCl_3$, 298 K. * = rotation band; # = grease.

Figure S8. Typical voltammograms of dyad **ZnP-PH_2P** and its components. Conditions: CH_2Cl_2, $(t\text{-Bu})_4NPF_6$ 0.1M, 298K, 0.1 V/s, Glassy Carbon Working Electrode, Fc+/Fc as reference (*).