

**Supporting Information for**  
**Electronically coupled zinc phthalocyanine-tin porphyrin dyad**  
**performing ultra-fast single step charge separation over a 34 Å**  
**distance**

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**-1- Materials and methods:**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX 300 MHz or a Bruker AMX 400 MHz spectrometer. Chemical shifts for <sup>1</sup>H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl<sub>3</sub> δ = 7.26 ppm). High resolution electro-spray mass spectra (HR- ESMS) were collected in positive mode on a MS/MS ZABSpec TOF of Micromass equipped with a geometry EBE TOF. The samples were injected in mixture of CHCl<sub>3</sub>/MeOH : 9/1. Electron-impact mass spectrometry (EI-MS) were recorded on a HP 5989A spectrometer. Matrix assisted laser desorption mass spectrometry analyses were performed on Bruker biflex III MALDI-TOF spectrometer using cyano 4-hydroxycinnamic acid (CHCA) or dithranol as matrix. The instrument is equipped with a nitrogen laser emitting at 337 nm, a 2-GHz sampling rate digitizer, a pulsed ion extraction source and a reflectron.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh) or with SDS neutral alumina (0.05-0.2 mm mesh). Air sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals

were purchased from Aldrich or Acros and used as received. The solvents for the reactions were distilled prior to use following the standard purification procedures.

Zinc(II)-iodophthalocyanine **1**<sup>1</sup>, zinc(II)-5,15-bis-(3,5-diterbutylphenyl)-10-phenyl-20-iodoporphyrin **5**<sup>2,3</sup>, tin(IV)-5,10,15,20-tetrakis(3,5-diterbutylphenyl)-porphyrin **14**<sup>4</sup>, the spacers **2**<sup>3,5</sup> **15**<sup>3,5</sup> and **9**<sup>3,5</sup> were prepared according to literature methods.

### Electrochemistry and spectroelectrochemistry

The electrochemical measurements were performed with a potentiostat-galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows) using a conventional single-compartment three-electrode cell. The working electrode was a platinum disk of 4 mm<sup>2</sup> area, the auxiliary was a Pt wire and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.15 N Bu<sub>4</sub>NPF<sub>6</sub> in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s for the cyclic voltammetry and 15 Hz for pulse voltammetry. Spectroelectrochemical spectra were recorded in a thin quartz UV-Visible cell (0.5 mm) surmounted with a reference electrode (SCE) and a platinum wire as counter electrode. The working electrode was a platinum grid inserted within the quartz cell and the other conditions are the same as those for the cyclic voltammetry.

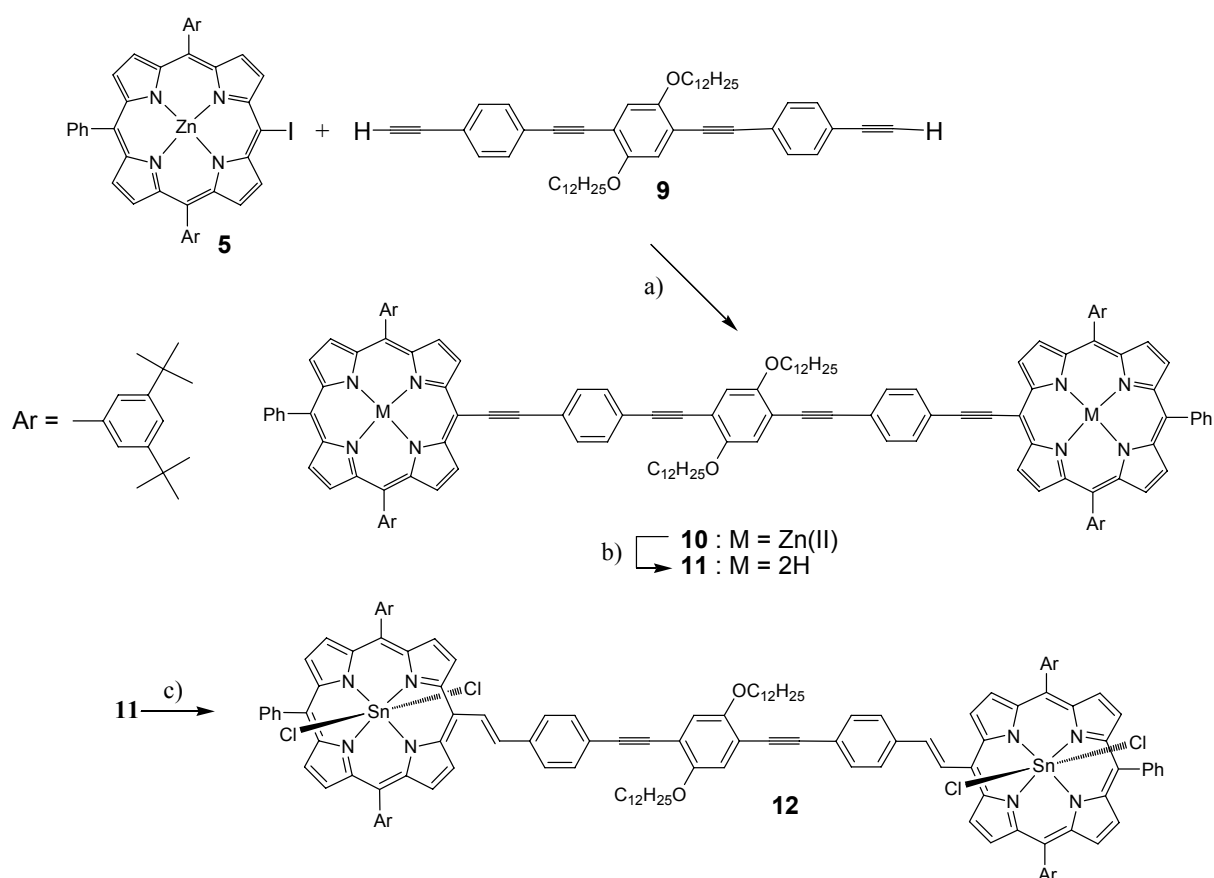
### Spectroscopy

UV-Visible absorption spectra were recorded on a CARY 50 spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog 2 fluorimeter and were corrected for the wavelength dependent response of the detector system (Hamamatsu R928). Time-resolved correlated single photon counting (TCSPC) measurements were performed on a system previously described.<sup>6</sup> The emission was collected at magic angle polarization (55.4°) relative to the excitation light and the instrument had a response function with a FWHM of ~60 ps. Samples for steady-state spectroscopy and TCSPC were contained in a 10x10 mm quartz cuvette. The concentration of the samples in the emission experiments was controlled so the absorption at the excitation wavelength was held around 0.1.

The laser pulses generated for the transient absorption pump-probe experiments have been previously described.<sup>7</sup> The 800 nm output was converted to 450 or 550 nm, with a temporal width of ~150 fs, in an optical parametric amplifier (TOPAS). A mechanical chopper blocked every second pump beam. The probe light was passed through a movable

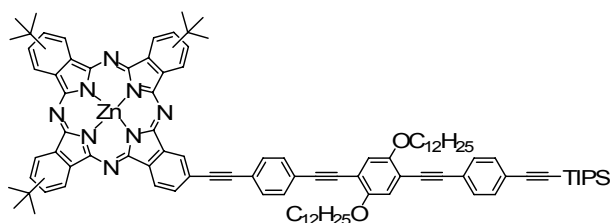
delay line allowing the delay between pump and probe to vary with as much as 10 ns. A vertically moving CaF<sub>2</sub> crystal in the probe beam produced a continuous white light and a  $\lambda/2$ -plate adjusted the polarization of the light so that the difference in polarization between pump and probe was fixed at magic angle conditions. The pump and probe beam was then focused in a vertically moving 1×10 mm optical quartz cell. The pump energy at the sample was c.a. 0.2  $\mu\text{J}/\text{pulse}$ . The transmitted probe light was divided spatially on an optical diffraction grating and further detected on a diode array. To adjust for differences in laser intensity parts of the probe light was passed to the detector without passing the sample and the transient absorption was calculated as  $\Delta\text{abs} = -\log[(I_{\text{probe}, \tau=t} / I_{\text{reference}, \tau=t}) / (I_{\text{probe}, \tau=0} / I_{\text{reference}, \tau=0})]$ . The reported values are averages of 5000-10000 individual measurements.

## -2- Synthesis of the compounds



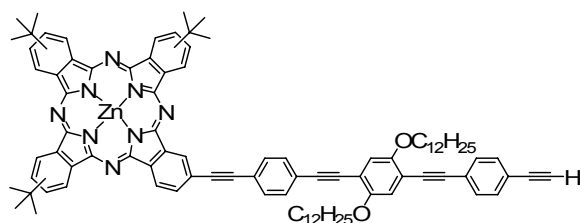
Scheme S1 : Synthetic route to the preparation of the reference bis(tin porphyrin) **12**. Reagents and conditions : a) Toluene, Et<sub>3</sub>N, Pd<sub>2</sub>dba<sub>3</sub>-CHCl<sub>3</sub>, (OTol)<sub>3</sub>P, 50°C, 15h (14%); b) HCl, CH<sub>2</sub>Cl<sub>2</sub> (27%); c) pyridine, SnCl<sub>2</sub>-2H<sub>2</sub>O, 185°C, 40 min. (39%).

### Compound 3



In a schlenk, zinc tri-*tert*-butyl-iodophthalocyanine **1** (74 mg, 84.9  $\mu\text{mol}$ ) and the spacer **2** (72 mg, 84.9  $\mu\text{mol}$ ) were dissolved in dry piperidine (5 mL) and the mixture purged with argon. Triphenylarsine (61 mg, 0.20 mmol) and  $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$  (27 mg, 26.3  $\mu\text{mol}$ ) were added and the solution was degassed again with argon. The reaction mixture was stirred and heated at 40°C overnight under argon atmosphere. The solvent was removed and the crude solid was dissolved in dichloromethane. The organic phase was washed successively with water (2x), dried over  $\text{MgSO}_4$  and evaporated to dryness. The crude was purified by column chromatography over silica gel (eluent : petroleum ether/dioxane : 9/1), to yield **3** as a green-blue solid (58 mg, 43%).  $^1\text{H NMR}$   $\delta$  (300MHz,  $\text{CDCl}_3$ , 25°C): 0.89 (m, 6H,  $\text{CH}_3$ ), 1.16 (m, 21H, TIPS), 1.29 (m, 36H,  $\text{CH}_2$ ), 1.62 (s, 27H, tBu), 1.84-1.94 (m, 4H,  $\text{CH}_2$ ), 4.06 (m, 4H,  $\text{CH}_2$ ), 6.98-7.02 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.47 (m, 4H,  $\text{H}_{\text{aro}}$ ), 7.64 (m, 4H,  $\text{H}_{\text{aro}}$ ), 7.75-8.05 (m, 3H,  $\text{H}_{\text{Phtha}}$ ), 8.10-8.80 (m, 9H,  $\text{H}_{\text{Phtha}}$ ); UV-vis (PhCN):  $\lambda/\epsilon$  ( $\text{nm}/\times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ): 367 (6.83), 616 (3.06), 640 (3.06), 679 (14.2), 695 (16.2); HR-MS (ESI): m/z: calcd for  $\text{C}_{103}\text{H}_{120}\text{N}_8\text{O}_2\text{SiZn}$ , 1593.8673  $[\text{M}+\text{H}]^+$ ; found 1593.8668  $[\text{M}+\text{H}]^+$ .

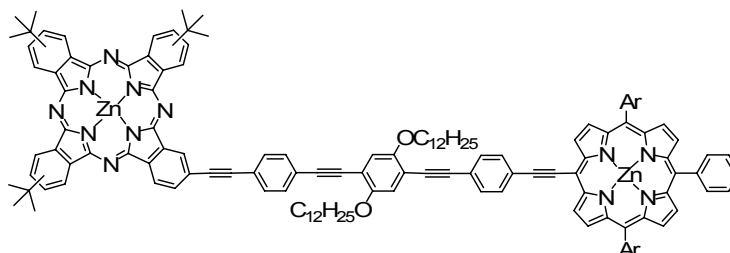
### Compound 4



The compound **3** (38 mg, 23.9  $\mu\text{mol}$ ) was dissolved in THF (2.5 mL) and  $\text{Bu}_4\text{NF}$  (57.3  $\mu\text{L}$ , 1M in THF) was added. The solution was stirred at room temperature for 2 h. The THF was removed and  $\text{CH}_2\text{Cl}_2$  was added. The organic phase was washed with water, dried over  $\text{MgSO}_4$  and the solvent evaporated to afford **4** as a green solid (34 mg, 100 %).  $^1\text{H NMR}$   $\delta$

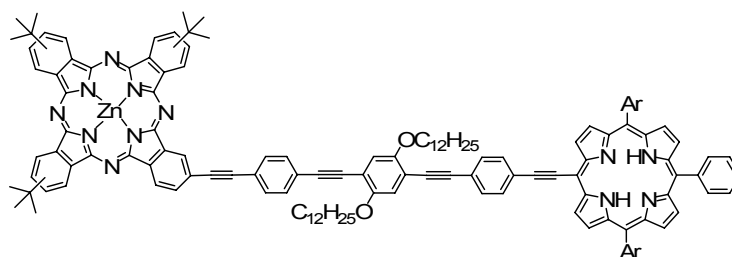
(300MHz, CDCl<sub>3</sub>, 25°C): 0.84 (m, 6H, CH<sub>3</sub>), 1.24 (m, 36H, CH<sub>2</sub>), 1.67 (s, 27H, tBu), 1.78-1.82 (m, 4H, CH<sub>2</sub>), 3.12 (s, 1H, H ethynyl), 3.96 (m, 4H, CH<sub>2</sub>), 6.90-6.95 (m, 2H, H<sub>aro</sub>), 7.40 (m, 4H, H<sub>aro</sub>), 7.58 (m, 4H, H<sub>aro</sub>), 7.60-7.69 (m, 3H, H<sub>Phtha</sub>), 7.80-8.10 (m, 9H, H<sub>Phtha</sub>); MALDI-TOF: m/z: calcd for C<sub>94</sub>H<sub>100</sub>N<sub>8</sub>O<sub>2</sub>Zn, 1437.7 [M+H]<sup>+</sup>; found 1437.6 [M+H]<sup>+</sup>.

## Compound 6



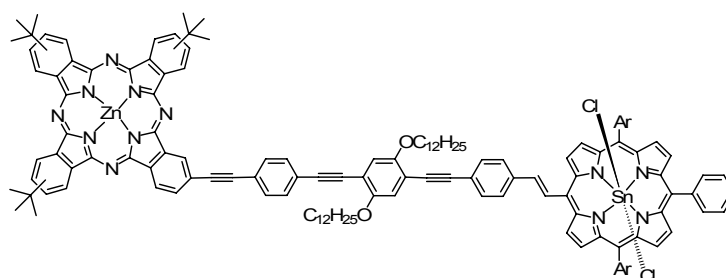
The zinc iodo porphyrin **5** (27 mg, 28.5 μmol), the compound **4** (45 mg, 31.3 μmol), Pd<sub>2</sub>dba<sub>3</sub>-CHCl<sub>3</sub> (8 mg, 7.8 μmol) and AsPh<sub>3</sub> (9 mg, 28.5 μmol) were dissolved in dry Et<sub>3</sub>N (1.5 mL) and dry THF (4 mL). The solution was purged with argon through 3 freeze-pump-thaw cycles and was heated at 60°C for 15 h. The solvents were removed and CH<sub>2</sub>Cl<sub>2</sub> was added. The organic phase was washed with water, dried over MgSO<sub>4</sub> and rotary evaporated. The product was purified by column chromatography over silica (eluent, petroleum ether/ dioxane : 9/1) to afford **6** as a green solid (21 mg, 33%). <sup>1</sup>H NMR δ (400MHz, C<sub>4</sub>D<sub>8</sub>O, 25°C): 0.81 (m, 6H, CH<sub>3</sub>), 1.25 (m, 36H, CH<sub>2</sub>), 1.54 (s, 36H, tBu), 1.67 (s, 27H, tBu), 1.80-1.88 (m, 4H, CH<sub>2</sub>), 4.15 (m, 4H, CH<sub>2</sub>), 7.18 (m, 2H, H<sub>aro</sub>), 7.50 (m, 4H, H<sub>aro</sub>), 7.71 (m, 2H, H<sub>aro</sub>), 7.74 (m, 3H, H phenyl), 7.88 (m, 2H, 2H para), 8.08 (m, 2H, H<sub>aro</sub>), 8.11 (m, 4H, H ortho), 8.16 (m, 2H, H phenyl), 8.32 (m, 3H, H<sub>Phtha</sub>), 8.74 (d, <sup>3</sup>J = 4.5 Hz, 2H, H β), 8.88 (d, <sup>3</sup>J = 4.5 Hz, 2H, H β), 8.97 (d, <sup>3</sup>J = 4.5 Hz, 2H, H β), 9.41 (m, 5H, H<sub>Phtha</sub>), 9.57 (m, 4H, H<sub>Phtha</sub>), 9.82 (d, <sup>3</sup>J = 4.5 Hz, 2H, H β); UV-vis (PhCN): λ/ ε (nm/x10<sup>4</sup> M<sup>-1</sup>.cm<sup>-1</sup>): 351 (5.02), 454 (16.2), 583 (1.1), 637 (3.45), 679 (7.30), 696 (8.63); MALDI-TOF: m/z: calcd for C<sub>148</sub>H<sub>154</sub>N<sub>12</sub>O<sub>2</sub>Zn<sub>2</sub>, 2263.1 [M]<sup>+</sup>; found 2263.5 [M]<sup>+</sup>.

## Compound 7



The compound **6** (17 mg, 7.52  $\mu\text{mol}$ ) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL) then concentrated HCl (4 mL, 37% in water) was added. The solution was stirred at room temperature for 30 min. The organic phase was washed with water (2x), dried over  $\text{MgSO}_4$  and evaporated to dryness to afford **7** as a green solid (15 mg, 91 %).  $^1\text{H NMR}$   $\delta$  (400MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C): -2.21 (m, 2H, NH), 0.83 (m, 6H,  $\text{CH}_3$ ), 1.26 (m, 36H,  $\text{CH}_2$ ), 1.54 (s, 36H, tBu), 1.67 (s, 27H, tBu), 1.96 (m, 4H,  $\text{CH}_2$ ), 4.15 (m, 4H,  $\text{CH}_2$ ), 7.19 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.50-7.55 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.69-7.71 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.78 (m, 5H,  $2\text{H}_{\text{aro}} + 3\text{H phenyl}$ ), 7.93 (m, 2H, 2H para), 8.10-8.16 (m, 8H,  $2\text{H}_{\text{aro}} + 4\text{H ortho} + 2\text{H phenyl}$ ), 8.33 (m, 3H,  $\text{H}_{\text{Phtha}}$ ), 8.69-8.82 (m, 4H, H  $\beta$ ), 8.94 (m, 2H, H  $\beta$ ), 9.35-9.45 (m, 5H,  $\text{H}_{\text{Phtha}}$ ), 9.56 (m, 4H,  $\text{H}_{\text{Phtha}}$ ), 9.78 (m, 2H, H  $\beta$ ); UV-vis (PhCN):  $\lambda/\epsilon$  (nm/ $\times 10^4\text{ M}^{-1}\cdot\text{cm}^{-1}$ ): 355 (2.82), 446 (7.36), 586 (1.09), 616 (0.93), 641 (0.84), 678 (3.51), 696 (3.84); HR-MS (ESI): m/z: calcd for  $\text{C}_{148}\text{H}_{156}\text{N}_{12}\text{O}_2\text{Zn}$ , 2198.1844  $[\text{M}+\text{H}]^+$ ; found 2198.1905  $[\text{M}+\text{H}]^+$ .

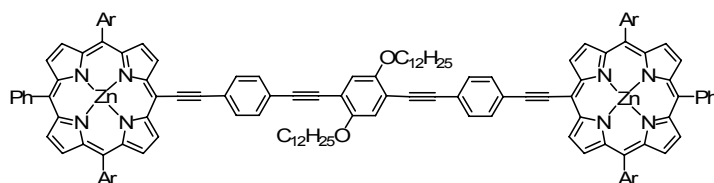
## Compound 8



The compound **7** (11 mg, 5  $\mu\text{mol}$ ) and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  (22 mg, 97  $\mu\text{mol}$ ) were dissolved in pyridine (3 mL). The solution was stirred for 3 h at 185°C under argon. Water was added and the precipitate was filtered and then dissolved in  $\text{CH}_2\text{Cl}_2$ . This solution was washed with water (2x), then with an aqueous solution of HCl (1M) and finally with water. The organic

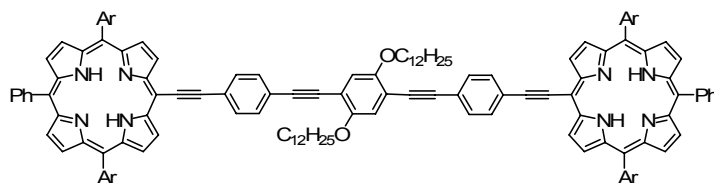
phase was dried over  $\text{MgSO}_4$  and the solvent evaporated. The crude product was purified by column chromatography over neutral alumina (eluent,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  : 98/2), to afford **8** as a green solid (10 mg, 83%).  $^1\text{H NMR}$   $\delta$  (400MHz,  $\text{C}_4\text{D}_8\text{O}$ ,  $25^\circ\text{C}$ ): 0.83 (m, 6H,  $\text{CH}_3$ ), 1.26 (m, 36H,  $\text{CH}_2$ ), 1.55 (s, 36H, tBu), 1.67 (s, 27H, tBu), 2.01 (m, 4H,  $\text{CH}_2$ ), 4.16 (m, 4H,  $\text{CH}_2$ ), 6.96 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.65-7.67 (m, 4H,  $\text{H}_{\text{aro}}$ ), 7.72-7.75 (br, 1H, H ethylene), 7.77-7.84 (m, 7H,  $4\text{H}_{\text{aro}}$  + 3H phenyl), 7.98 (m, 2H, H para), 8.26-8.33 (m, 9H, 4H ortho + 2H phenyl + 3  $\text{H}_{\text{Phtha}}$ ), 9.09-9.15 (m, 4H, H  $\beta$ ), 9.38-9.42 (m, 5H,  $\text{H}_{\text{Phtha}}$ ), 9.57-9.61 (m, 4H,  $\text{H}_{\text{Phtha}}$ ), 9.67 (m, 2H, H  $\beta$ ), 9.98 (m, 2H, H  $\beta$ ), 10.01-10.07 (br, 1H, H ethylene); UV-vis (PhCN):  $\lambda/\epsilon$  ( $\text{nm}/\times 10^4 \text{M}^{-1}\cdot\text{cm}^{-1}$ ): 357 (2.21), 435 (4.03), 575 (0.33), 618 (0.89), 641 (1.17), 679 (7.30), 696 (8.63); MALDI-TOF: m/z: calcd for  $\text{C}_{148}\text{H}_{156}\text{ClN}_{12}\text{O}_2\text{SnZn}$ , 2354.4  $[\text{M}]^+$ ; found 2354.3  $[\text{M}]^+$ .

### Compound 10



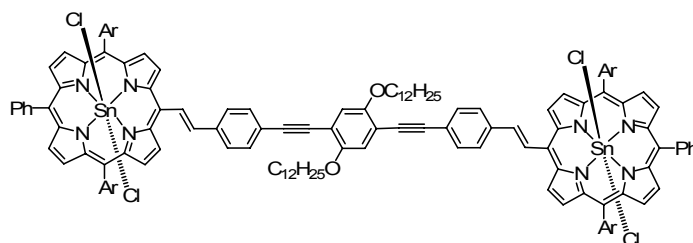
The zinc iodo porphyrin **5** (84 mg, 88.3  $\mu\text{mol}$ ), the compound **9** (34 mg, 45.1  $\mu\text{mol}$ ),  $\text{Pd}_2\text{dba}_3\text{-CHCl}_3$  (14 mg, 13.5  $\mu\text{mol}$ ) and  $\text{P}(\text{o-tol})_3$  (33 mg, 0.11 mmol) were dissolved in dry  $\text{Et}_3\text{N}$  (6 mL) and dry toluene (32 mL). The solution was purged with argon through 3 freeze-pump-thaw cycles and was heated at  $50^\circ\text{C}$  for 18 h. The solvents were removed and the crude solid was dissolved in  $\text{CH}_2\text{Cl}_2$ . This latter solution was washed with water, dried over  $\text{MgSO}_4$  and the solvent evaporated. The crude solid was purified by column chromatography over flash silica gel (eluent, petroleum ether/ $\text{CH}_2\text{Cl}_2$  : 6/4) to afford **10** as a green solid. This solid was then purified by size exclusion chromatography over Sephadex LH20 (eluent : THF) and finally over preparative TLC (eluent : petroleum ether/ $\text{CH}_2\text{Cl}_2$  : 1/1) to yield a green solid (15 mg, 14%).  $^1\text{H NMR}$   $\delta$  (300MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ): 0.85 (m, 6H,  $\text{CH}_3$ ), 1.26 (m, 32H,  $\text{CH}_2$ ), 1.56 (s, 72H, tBu), 1.74 (m, 4H,  $\text{CH}_2$ ), 2.04 (m, 4H,  $\text{CH}_2$ ), 4.05 (m, 4H,  $\text{CH}_2$ ), 6.59 (d,  $^3\text{J} = 8.1$  Hz, 4H, H aro), 7.05-7.09 (m, 2H,  $\text{H}_{\text{aro}}$ ), 7.72-7.74 (m, 6H, H phenyl), 7.82 (s, 4H, H para), 8.03 (d,  $^3\text{J} = 8.1$  Hz, 4H,  $\text{H}_{\text{aro}}$ ), 8.09 (s, 8H, H ortho), 8.19 (m, 4H, H phenyl), 8.86 (d,  $^3\text{J} = 4.2$  Hz, 4H, H  $\beta$ ), 8.91 (d,  $^3\text{J} = 4.2$  Hz, 4H, H  $\beta$ ), 9.06 (d,  $^3\text{J} = 5.1$  Hz, 4H, H  $\beta$ ), 9.84 (d,  $^3\text{J} = 4.2$  Hz, 4H, H  $\beta$ ); MALDI-TOF: m/z: calcd for  $\text{C}_{158}\text{H}_{170}\text{N}_8\text{O}_2\text{Zn}_2$ , 2243.9  $[\text{M}]^+$ ; found 2244.5  $[\text{M}]^+$ .

## Compound 11



The compound **10** (39 mg, 16.2  $\mu\text{mol}$ ) was dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  (33 mL) and concentrated HCl (8 mL, 37% in water) was added. The solution was stirred for 30 min at room temperature. The organic phase was washed with water (2x), dried over  $\text{MgSO}_4$  and the solvent evaporated. The resulting crude solid was purified over preparative TLC (petroleum ether/  $\text{CH}_2\text{Cl}_2$  : 1/1) to afford **11** as a green solid (10 mg, 27 %).  $^1\text{H}$  NMR  $\delta$  (300MHz,  $\text{CDCl}_3$ , 25°C): -2.21 (s, 4H, NH), 0.83 (m, 6H,  $\text{CH}_3$ ), 1.26 (m, 36H,  $\text{CH}_2$ ), 1.56 (s, 72H, tBu), 1.96 (m, 4H,  $\text{CH}_2$ ), 4.14 (m, 4H,  $\text{CH}_2$ ), 7.14 (s, 2H,  $\text{H}_{\text{aro}}$ ), 7.74 (d,  $^3J = 8.1$  Hz, 4H,  $\text{H}_{\text{aro}}$ ), 7.76 (m, 6H, H phenyl), 7.83 (m, 4H, H para), 8.03 (d,  $^3J = 8.1$  Hz, 4H,  $\text{H}_{\text{aro}}$ ), 8.09 (m, 8H, H ortho), 8.18-8.20 (4H, H phenyl), 8.77 (d,  $^3J = 4.5$  Hz, 4H, H  $\beta$ ), 8.82 (d,  $^3J = 4.5$  Hz, 4H, H  $\beta$ ), 8.98 (d,  $^3J = 4.8$  Hz, 4H, H  $\beta$ ), 9.76 (d,  $^3J = 4.8$  Hz, 4H, H  $\beta$ ); UV-vis (PhCN):  $\lambda/\epsilon$  ( $\text{nm}/\times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ): 380 (2.16), 446 (12.6), 587 (2.27), 675 (1.12); MALDI-TOF: m/z: calcd for  $\text{C}_{158}\text{H}_{174}\text{N}_8\text{O}_2$ , 2217.1  $[\text{M}]^+$ ; found 2217.4  $[\text{M}]^+$ .

## Compound 12

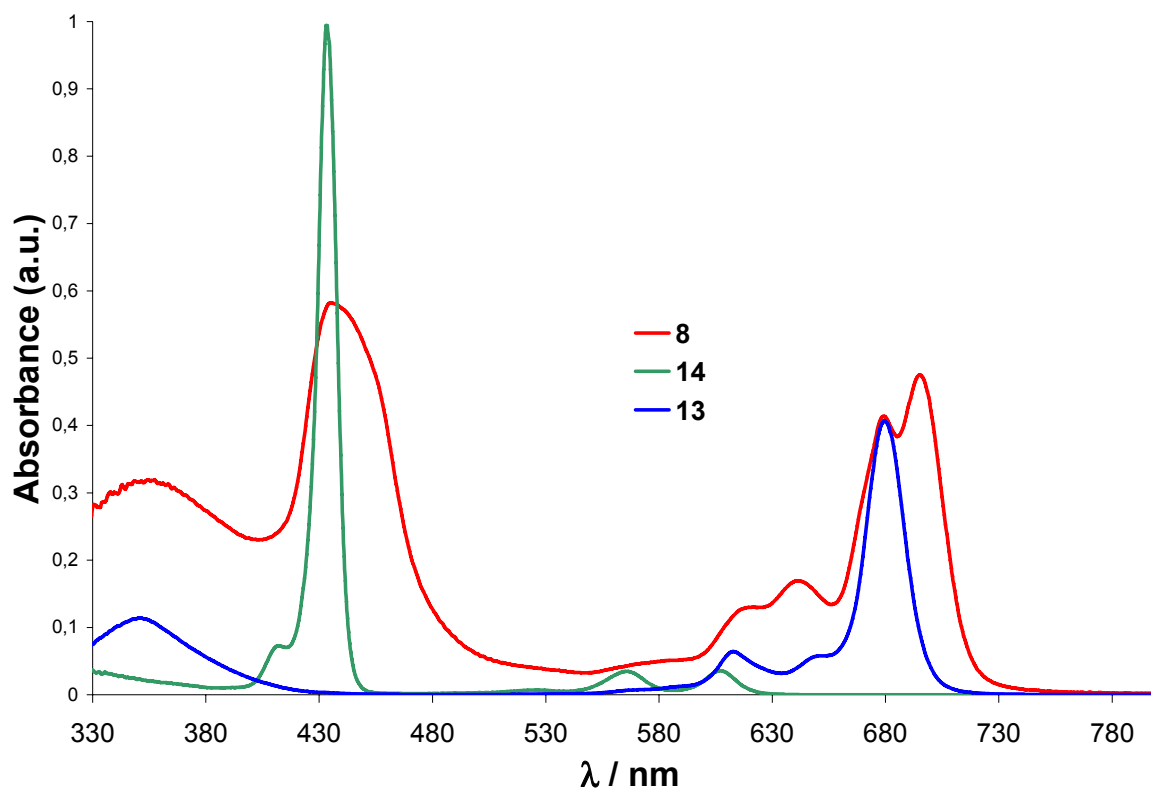


The compound **11** (20 mg, 8.8  $\mu\text{mol}$ ) and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  (38 mg, 0.17  $\mu\text{mol}$ ) were dissolved in pyridine (6 mL). The solution was stirred for 40 min at 185°C under argon. Water was added, the precipitate was filtered and dissolved in  $\text{CH}_2\text{Cl}_2$ . The solution was washed with water (2x), then with an aqueous solution of HCl (1 M) and finally with water. This solution was dried over  $\text{MgSO}_4$  and the solvent was evaporated. The crude product was purified by column chromatography over neutral alumina (eluent :  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , starting with 10/0 until 9/1) to afford **11** as a green solid (9 mg, 39 %).  $^1\text{H}$  NMR  $\delta$  (300MHz,  $\text{CDCl}_3$ , 25°C): 0.86 (m, 6H,  $\text{CH}_3$ ), 1.26 (m, 36H,  $\text{CH}_2$ ), 1.57 (s, 72H, tBu), 1.98-2.02 (m, 4H,  $\text{CH}_2$ ), 4.14 (m, 4H,  $\text{CH}_2$ ),



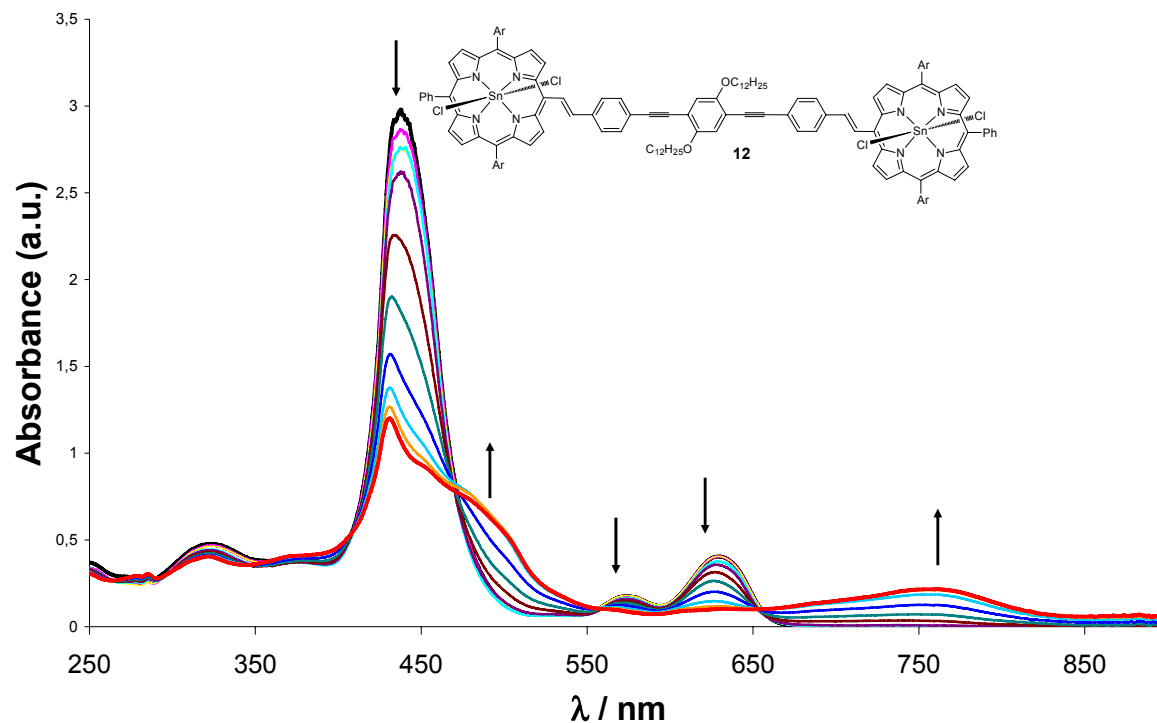
7.17 (m, 2H, H<sub>aro</sub>), 7.50-7.55 (m, 4H, H<sub>aro</sub>), 7.65 (d, <sup>3</sup>J = 16.2 Hz, 2H, H ethylene), 7.80-7.83 (m, 6H, H phenyl), 7.90 (m, 4H, H para), 7.98-8.00 (m, 4H, H<sub>aro</sub>), 8.19 (m, 8H, H ortho), 8.31 (m, 4H, H phenyl), 9.17 (d, <sup>3</sup>J = 5.1 Hz, 4H, H β), 9.22 (d, <sup>3</sup>J = 5.1 Hz, 4H, H β), 9.33 (d, <sup>3</sup>J = 4.5 Hz, 4H, H β), 9.77 (d, <sup>3</sup>J = 16.2 Hz, 2H, H ethylene), 9.76 (d, <sup>3</sup>J = 4.5 Hz, 4H, H β); UV-vis (PhCN): λ/ ε (nm/×10<sup>4</sup> M<sup>-1</sup>.cm<sup>-1</sup>): 375 (0.75), 441 (5.48), 577 (0.35), 634 (0.90); MALDI-TOF: m/z: calcd for C<sub>158</sub>H<sub>174</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>2</sub>Sn<sub>2</sub>, 2560.0 [M-Cl]<sup>+</sup>; found 2560.4 [M-Cl]<sup>+</sup>.

### -3- UV-Vis. Absorption spectra

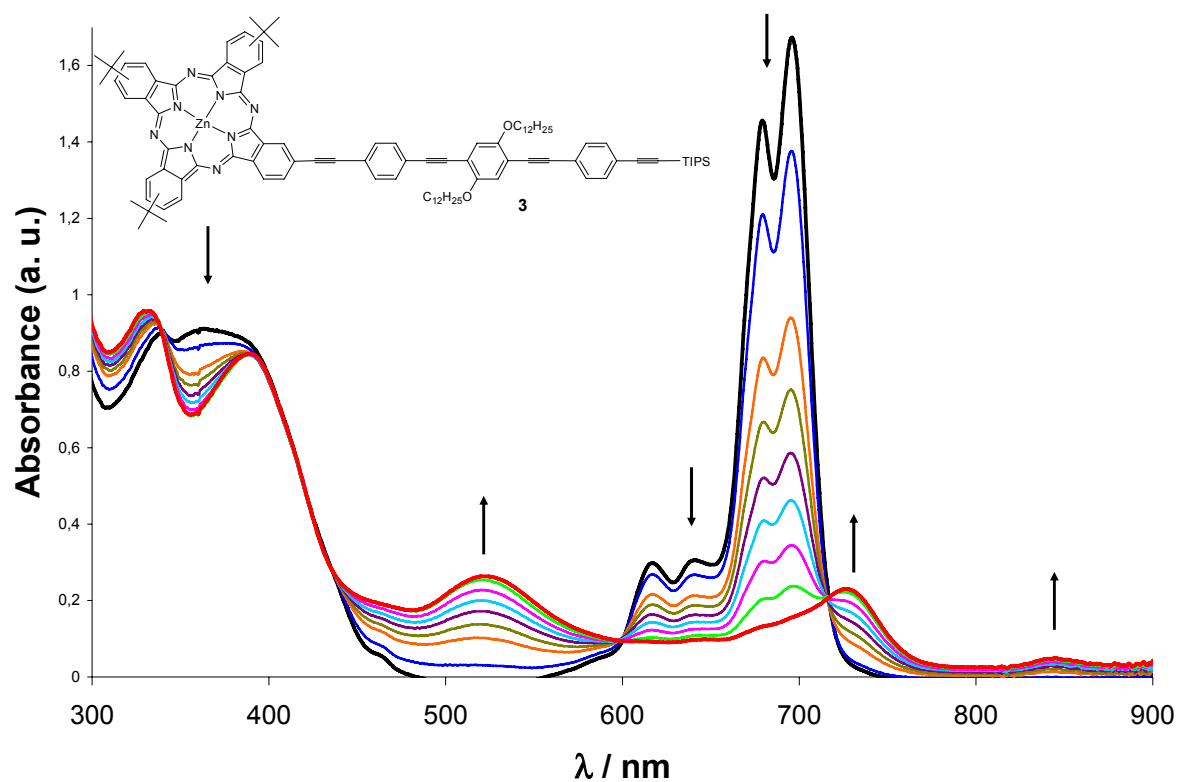


**Figure S1.** Overlay of the absorption spectra of ZnPc **13** (blue), tin(IV) tetraaryl porphyrin **14** (green) and the dyad **8** (red) recorded in benzonitrile.

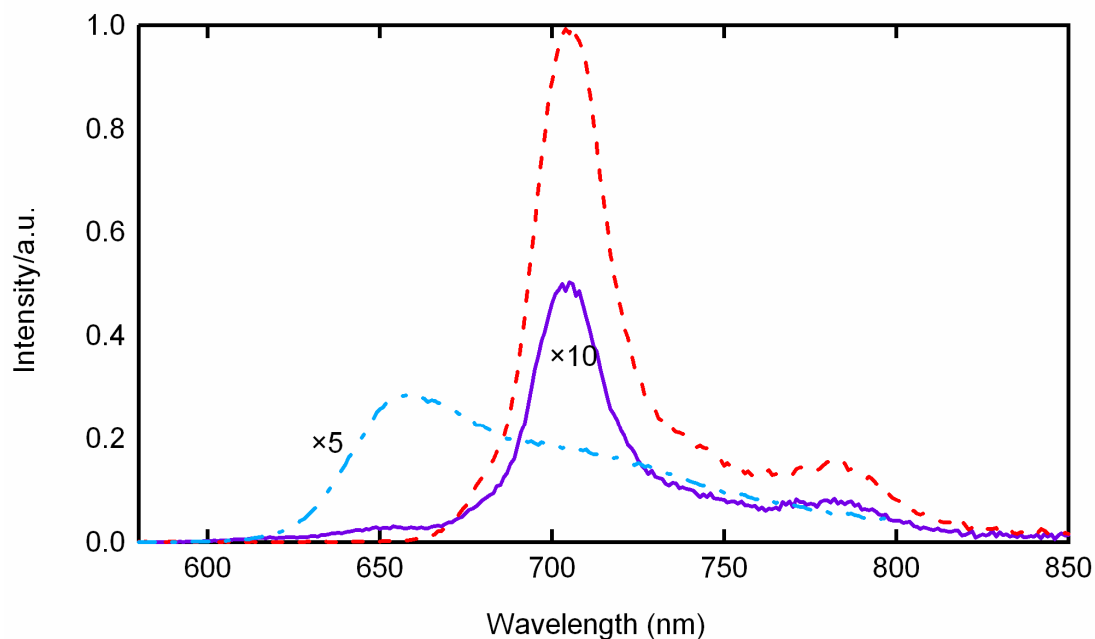
#### -4- Spectroelectrochemistry



**Figure S2.** Thin-layer UV-Vis spectral changes recorded during the reductive electrolysis of **12** in dichloromethane containing 0.15 M of Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. The arrows indicate the changes upon reduction. The black bold trace is the initial spectrum and the red bold trace is the final spectrum.

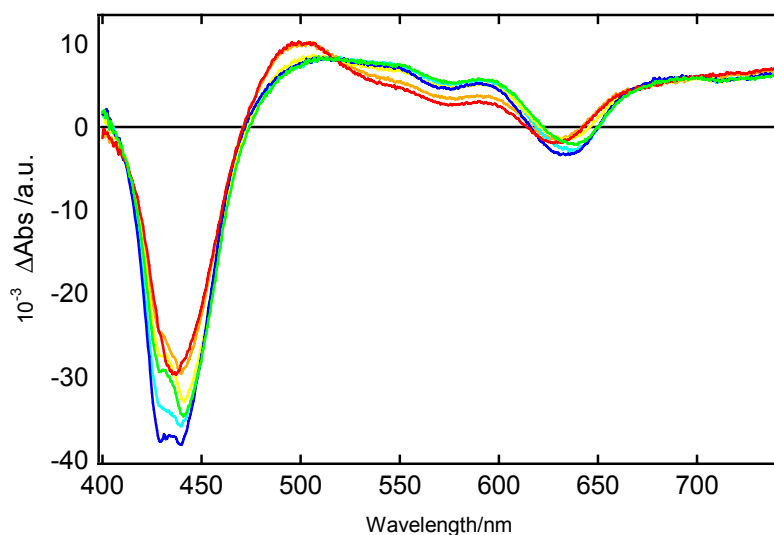


**Figure S3.** Thin-layer UV-Vis spectral changes recorded during the oxidative electrolysis of **3** in dichloromethane containing 0.15 M of Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. The arrows indicate the changes upon oxidation. The black bold trace is the initial spectrum and the red bold trace is the final spectrum.

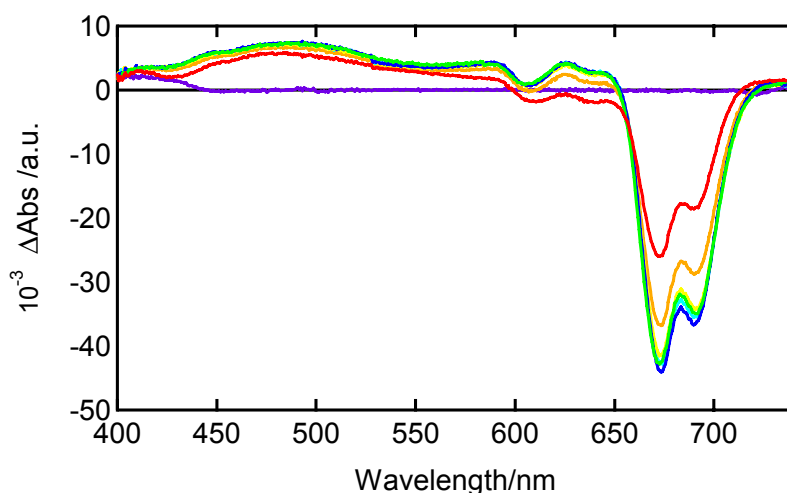


**Figure S4.** Corrected fluorescence spectra of the dyad **8** (blue, solid line) and the reference compounds **3** (red, dashed) and **12** (light blue, dot-dashed) in benzonitrile. All samples had the same absorption at the wavelength of excitation (440 nm). For clarity, the intensity of sample **8** was multiplied ten times, and that of **12** five times.

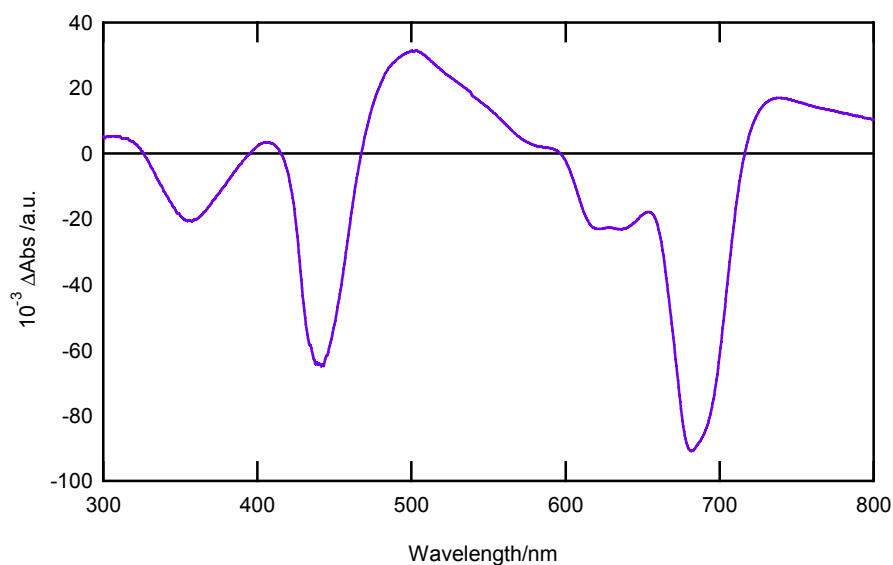
Time-resolved fluorescence measurements on **8** indicated that there was a fraction (<15 %) that was not quenched, but rather decayed with a time constant similar to the reference's. This fraction can be assumed to be responsible for most of the steady-state fluorescence. Since the steady-state measurements have the mildest conditions it is reasonable to assume that the fraction of unquenched compounds is 5 % and that this unquenched fraction grows due to photodecomposition of **8** under the harsher conditions of laser light.



**Figure S5.** Transient absorption spectra for **12** after 440 nm excitation. The delay times are 2 ps (purple), 10 ps (blue), 50 ps (green), 200 ps (yellow), 1000 ps (orange) and 6000 ps (red).



**Figure S6.** Transient absorption spectra for **3** after 680 nm excitation. The delay times are 2 ps (purple), 10 ps (blue), 50 ps (green), 200 ps (yellow), 1000 ps (orange) and 6000 ps (red). The reversed relative intensity of the strongest Q-band bleaches compared to the ground state spectrum indicates that some decomposition occurred during measurements (estimated to c.a. 15%).



**Figure S7.** Simulated difference spectrum for the charge separated state minus the ground state, obtained from the spectroelectrochemical data in Figures S2 and S3.

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