SUPPORTING INFORMATION

Diketopyrrolopyrrole-zinc porphyrin, a tuned panchromatic association for dye-sensitized solar cells

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GENERAL:

^{1}H and ^{13}C NMR spectra were recorded on an *AVANCE 300 UltraShield BRUKER, AVANCE 400 BRUKER* or *AVANCE III 500 BRUKER.* Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent (**$CDCl_3$** δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C; **THF-d8** δ = 3.57, 1.72 ppm for ^{1}H and δ = 25.4, 67.6 ppm for ^{13}C). Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. MALDI-TOF analyses were performed on a *Bruker Ultraflex III*, microTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix. Electrochemical measurements were performed with a potentiostat-galvanostat *AutoLab PGSTAT 302N* controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a glassy carbon, a platinum electrode or a FTO coated glass plate, with a layer of mesoporous TiO_2 (18NR-T), dyed with the studied sensitizer. The auxiliary electrode was a Pt plate of 1 cm² and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N *n*-Bu_4NPF_6 (TBAP) in adapted dry solvent and 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.
UV-Visible absorption spectra were recorded on a *UV-2401PC Shimadzu* spectrophotometer. Fluorescence spectra were recorded on a *SPEX Fluoromax* fluorimeter.
Infrared spectra (IR) were recorded on a *BRUKER Vector 22* spectrometer; frequencies are reported in cm^{-1}. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F$_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh), or with CombiFlash®Rf. apparatus. Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Chenodeoxycholic acid, **N719** and titanium dioxide screen printing pastes were purchased from Solaronix SA (Switzerland) and Dyesol SA (Australia). The thickness of the TiO_2 films was measured by a Sloan Dektak 3 profilometer. Compounds **1**[1], **DPP1**[2] and **5**[3] were prepared according to literature methods.

PREPARATION OF DYE-SENSITIZED NANOCRYSTALLINE TIO_2 ELECTRODES:

Conductive glass substrates (F-doped SnO_2) were purchased from Pilkington (TEC8, sheet resistance 8 Ω/square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. TiO_2 films were then prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous $TiCl_4$ solution at 80 °C. Layers of TiO_2 were then screen printed with transparent colloidal paste Ti-Nanoxide T20/SP and light scattering Ti-Nanoxide 300 as final layer, with drying steps at 150 °C for 20 min between each layer. The obtained substrates were then sintered at 450 °C, following a progressive heating ramp (325 °C for 5 min, 375 °C for 5 min, 450 °C for 30 min). A second $TiCl_4$ treatment was applied while cells are still hot. Thicknesses were measured by a Sloan Dektak 3 profilometer. The prepared TiO_2 electrodes were soaked while still hot (80 °C) in a solution (0.16 mM) of each dye during one night. A mixture of distilled dichloromethane and tetrahydrofuran was used (3/1, v/v) for all new dyes bath preparation. In case of co-adsorption, the required quantity of chenodeoxycholic acid, (0.6 mM) was added to the bath before soaking

DYE-SENSITIZED SOLAR CELL FABRICATION:

Solar cell devices were prepared using the dye-sensitized electrodes as the working electrodes and platinum-coated conducting glass electrodes as counter electrodes. Counter electrodes were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (2 mg per mL). The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (DuPont, 25 µm) as a spacer to form the electrolyte space. The empty cell was tightly held, and the edges were heated to 110°C to seal the two electrodes together. A drop of electrolyte was introduced by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with Surlyn and a cover glass. The cell had an active area of 0.25 cm^2.

PHOTOELECTROCHEMICAL MEASUREMENTS:

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (I_{Ph}). The photovoltaic cell was illuminated with an Oriel lamp calibrated to AM 1.5 (air mass) intensity (1000 $W.m^{-2}$).

THEORETICAL CALCULATIONS:

All simulations have been achieved with the Gaussian09 program, using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT), for the ground and excited state properties, respectively. The computational protocol proceeds through a four step strategy that is efficient to determine the charge transfer features of rod-like organic dyes: 1) the ground-state geometrical parameters have been determined at the PBE0/6-31G(d) level [LanL2DZ pseudo-potential and basis set for Zn], via a force-minimization process using a SCF convergence threshold of 10^{-10} a.u.; 2) the vibrational spectrum of each derivative has been determined analytically at the same level of theory, that is PBE0/6-31G(d), and it has been checked that all structures correspond to true minima of the potential energy surface; 3) the first fifteen low-lying excited-states have been determined within the vertical TD-DFT approximation using the CAM- B3LYP/6-31+G(d) [LanL2DZ pseudo-potential and basis set for Zn] level of approximation with a tight SCF convergence threshold (at least 10^{-7} a.u.) ; 4) the charge-transfer parameters have been estimated with the procedure defined by Ciofini, Le Bahers and coworkers[4] using the CAM-B3LYP electronic densities. It proposes to evaluate the distance separating the barycenters of the electron density gain/depletion upon electron transition. All calculations systematically include a modelling of bulk solvent effects (here CH_2Cl_2) through the Polarizable Continuum Model (PCM). During the simulations, the long alkyl chains such as alkyl moiety have been replaced by methyl groups in order to lighten the computational burden.

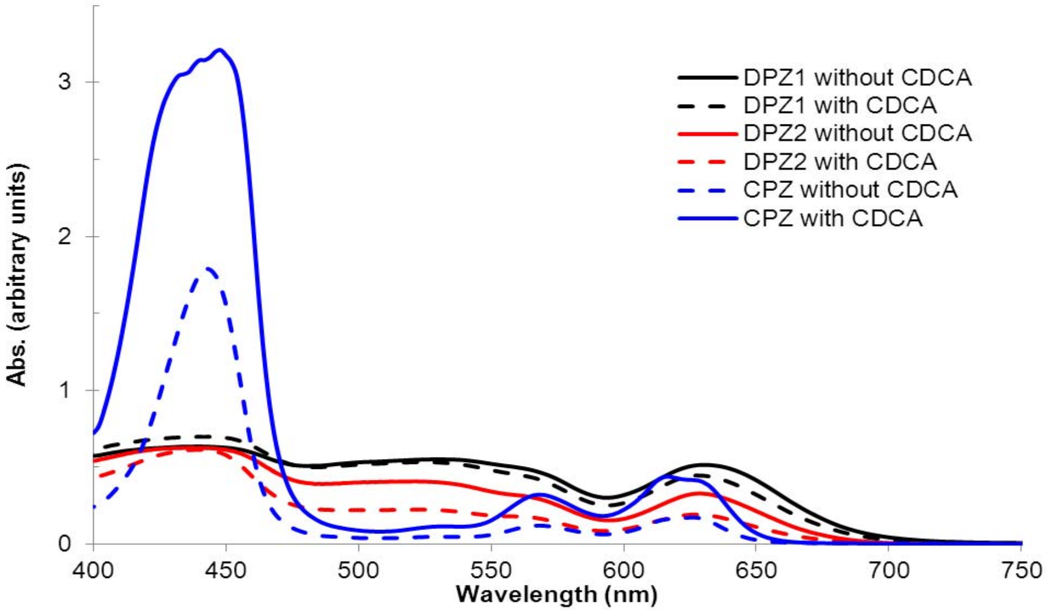


Figure S1. Absorption spectra of dyes **DPZ1**, **DPZ2** and **CPZ** with or without CDCA recorded on 4 µm thick TiO_2

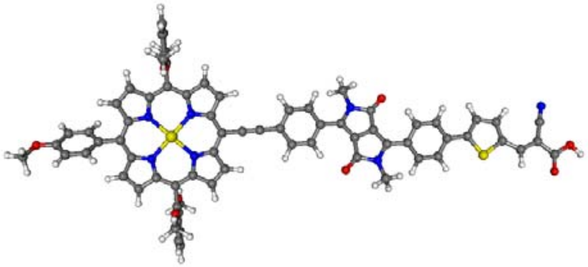
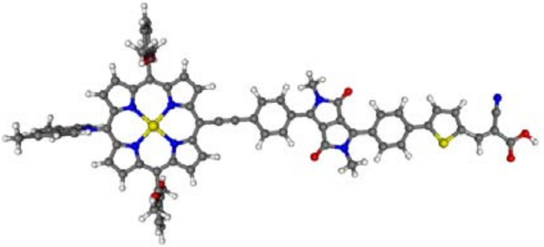
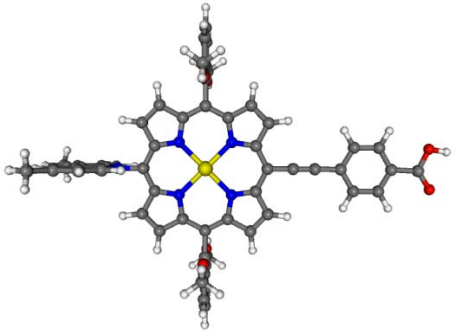
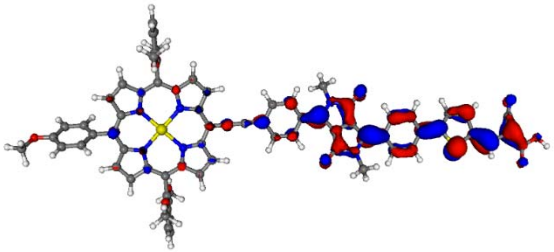
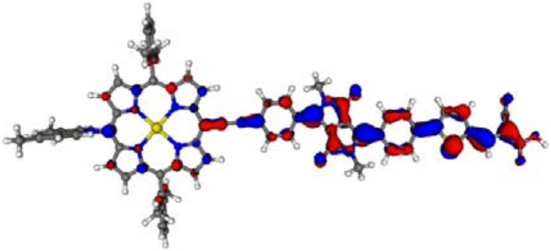
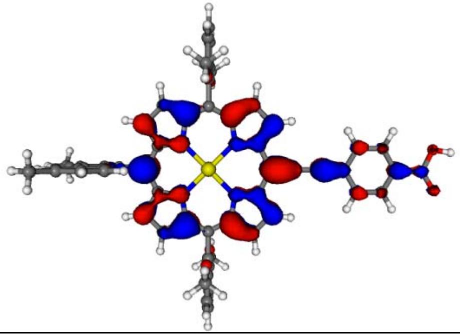
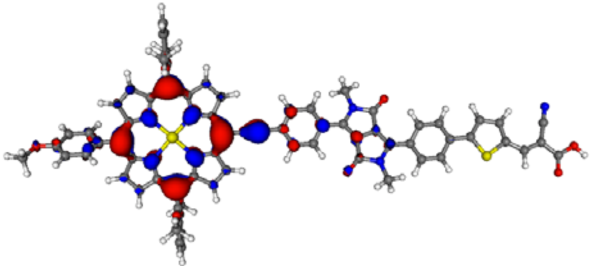
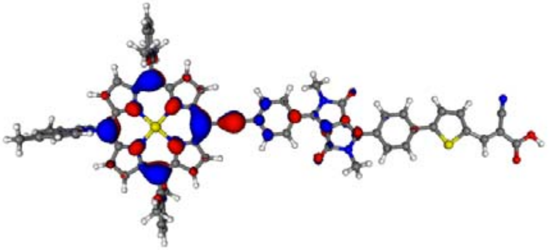
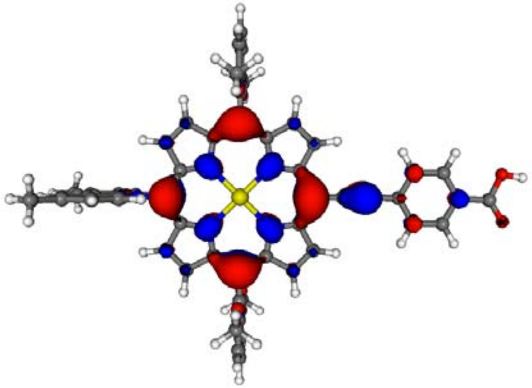
	DPZ1	**DPZ2**	**CPZ**
			
LUMO			
HOMO			

Figure S2. Frontier molecular orbitals of compounds **DPZ1**, **DPZ2** and **CPZ**

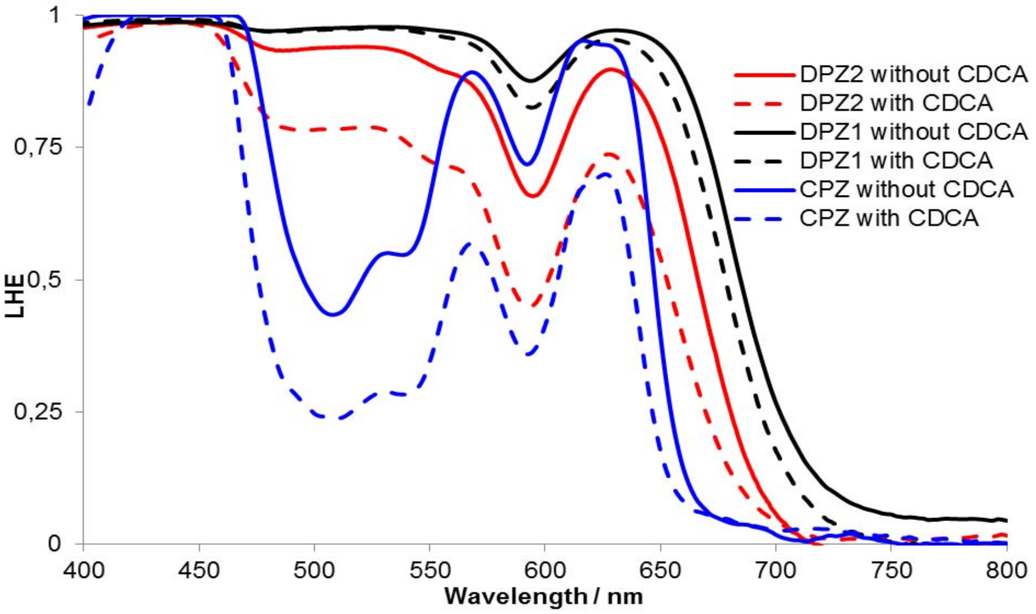


Figure S3. LHE spectra of cells dyed with **DPZ1**, **DPZ2** and **CPZ**, with or without CDCA, corresponding to 12 μm thick TiO_2 electrodes

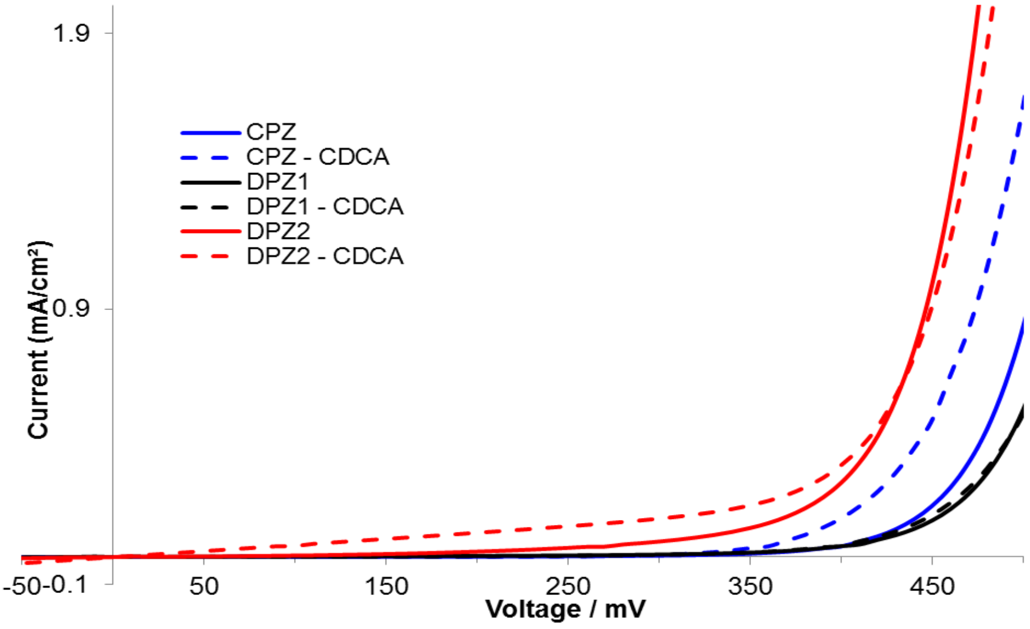


Figure S4. J-V curves of cells dyed with **DPZ1**, **DPZ2** and **CPZ**, with or without CDCA, in absence of light

Table S1: Photovoltaic performances of dyes **DPZ1**, **DPZ2** and **CPZ** tested with chenodeoxycholic acid (CDCA) and 4-*tert*-butylpyridine (TBP)

Dye	cDCA (mmol/L)	TBP (mol/L)	V_{OC} (mV)	J_{SC} (mA/cm²)	ff (%)	η (%)
DPZ1	/	/	595	10.66	73.2	4.64
		0.5	645	8.10	76.4	3.99
	0.8	/	625	17.70	69.8	7.70
		0.5	635	12.90	74.6	6.10
DPZ2	/	/	495	6.91	72.6	2.48
		0.5	605	5.23	74.8	2.37
	0.8	/	525	9.11	69.8	3.40
		0.5	615	5.22	74.3	2.39
CPZ	/	/	535	6.54	74.0	2.58
		0.5	655	4.47	76.5	2.24
	0.8	/	565	7.34	71	2.93
		0.5	675	5.90	76.3	3.04
N719	/	/	645	21.31	63.6	8.75

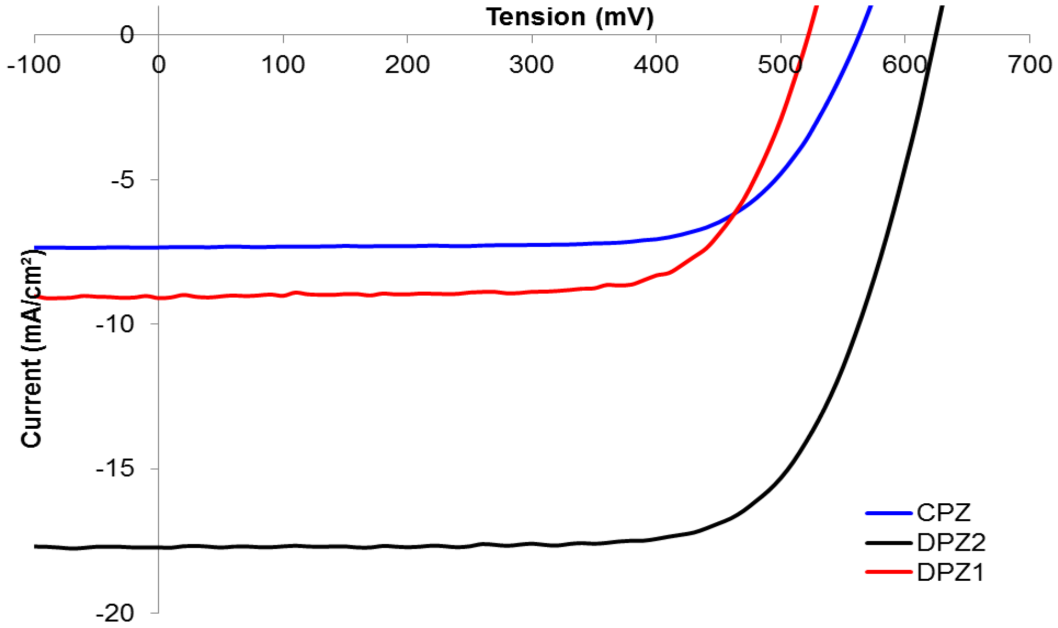
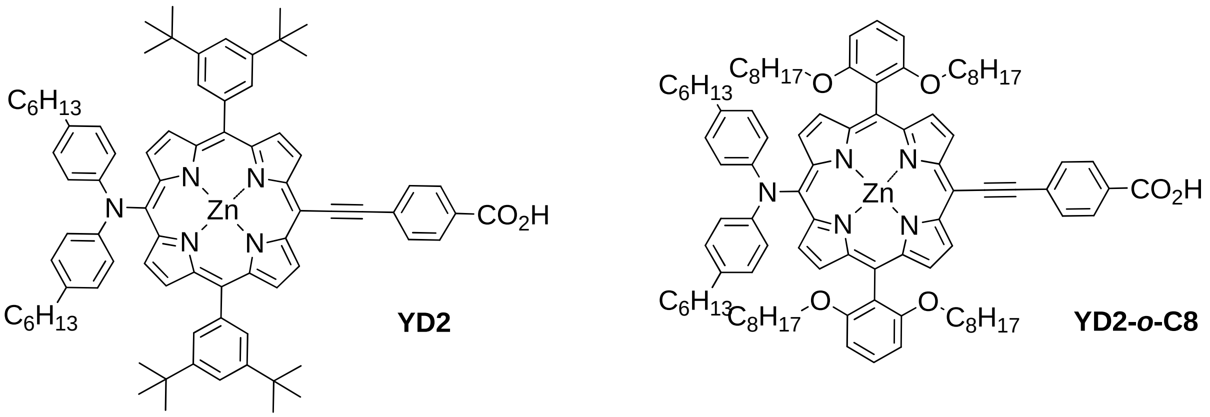


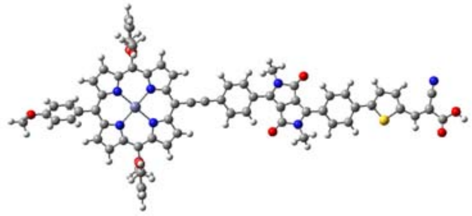
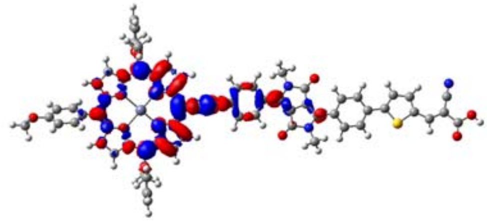
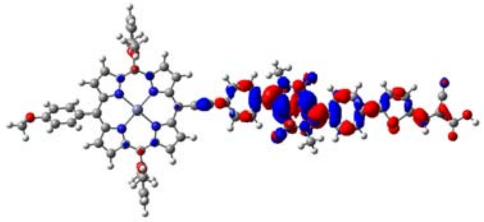
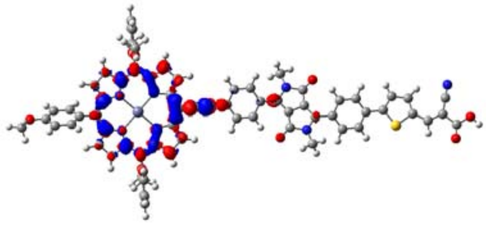
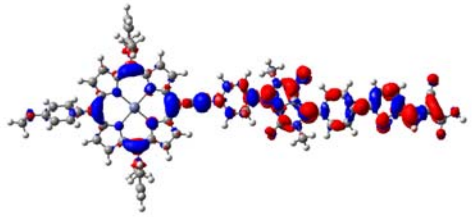
Figure S5. J-V curves of cells dyed with **DPZ1**, **DPZ2** and **CPZ**, with CDCA, under illumination AM1.5 (100 mW/cm²)

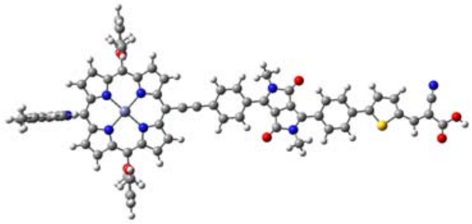
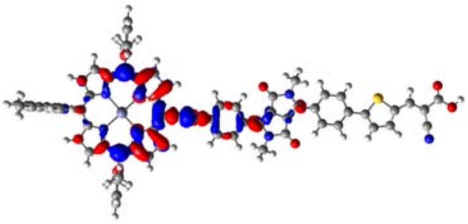
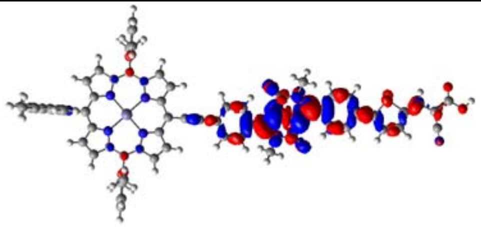
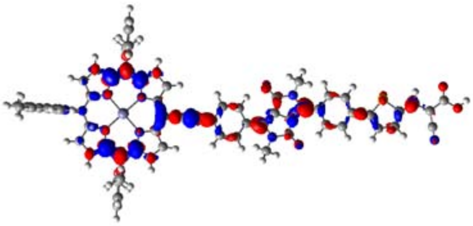
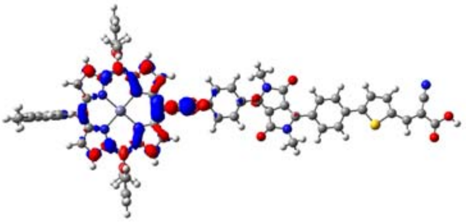
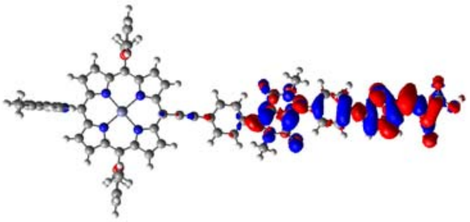
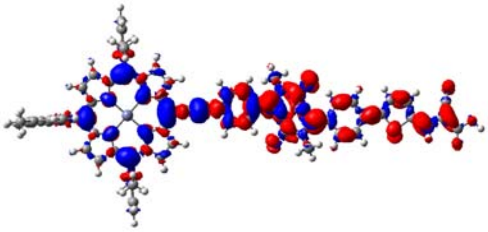


YD2

YD2-*o*-C8

Figure S6. Structures of dyes **YD2** and **YD2-o-C8**[5]

Compound	S_n	Representation	Computed data				
			λ (nm)	f	D_{CT} (Å)	q_{CT} (e)	μ_{CT} (D)
DPZ1		 HOMO=-6.96 eV LUMO=-2.33 eV μ_{s0}=10.2 D					
	1		609	1.03	1.40	0.39	2.58
	3		510	1.51	3.70	0.38	6.81
	5		405	1.38	2.83	0.26	3.57
	7		348	1.35	8.60	0.54	22.19

DPZ2		 HOMO=-6.23 eV LUMO=-2.36 eV μ_{s0}=5.37 D					
	1		606	0.89	1.05	0.32	1.62
	3		508	1.60	2.85	0.39	5.27
	4		414	0.84	4.88	0.37	8.56
	6		402	1.37	1.30	0.26	1.61
	7		388	1.22	3.67	0.46	8.02
	8		375	0.34	8.67	0.83	34.40

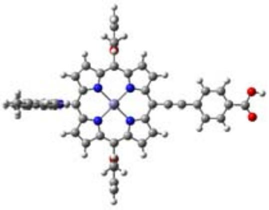
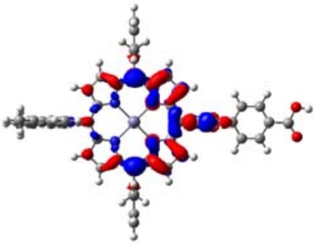
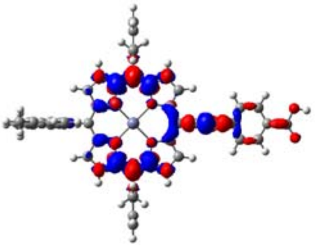
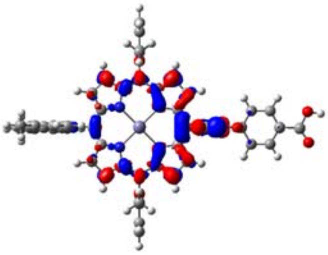
CPZ		 HOMO=-6.30 eV LUMO=-2.12 eV μ_{s0}=2.40 D					
	1		591	0.29	0.14	0.24	0.17
	3		410	2.38	1.14	0.32	1.75
	5		398	1.50	0.26	0.24	0.29

Figure S7: Representation of the modeled dyes together with density difference plots for the main excited-states (red/blue regions indicate increase/decrease of electronic density upon absorption). Only states with significant oscillator strength are shown. For each state, the computed wavelength, oscillator strength as well as CT analysis in terms of transferred distance, charge and dipole are given.

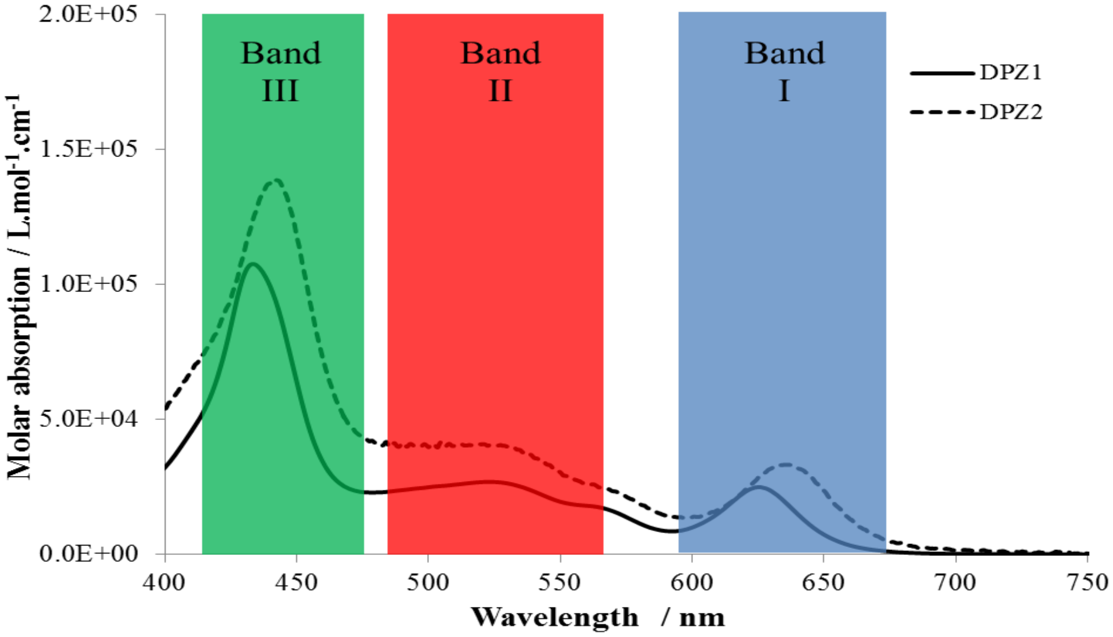


Figure S8. UV-visible absorption of **DPZ1** and **DPZ2** recorded in dichloromethane

SYNTHESIS OF THE SENSITIZERS:

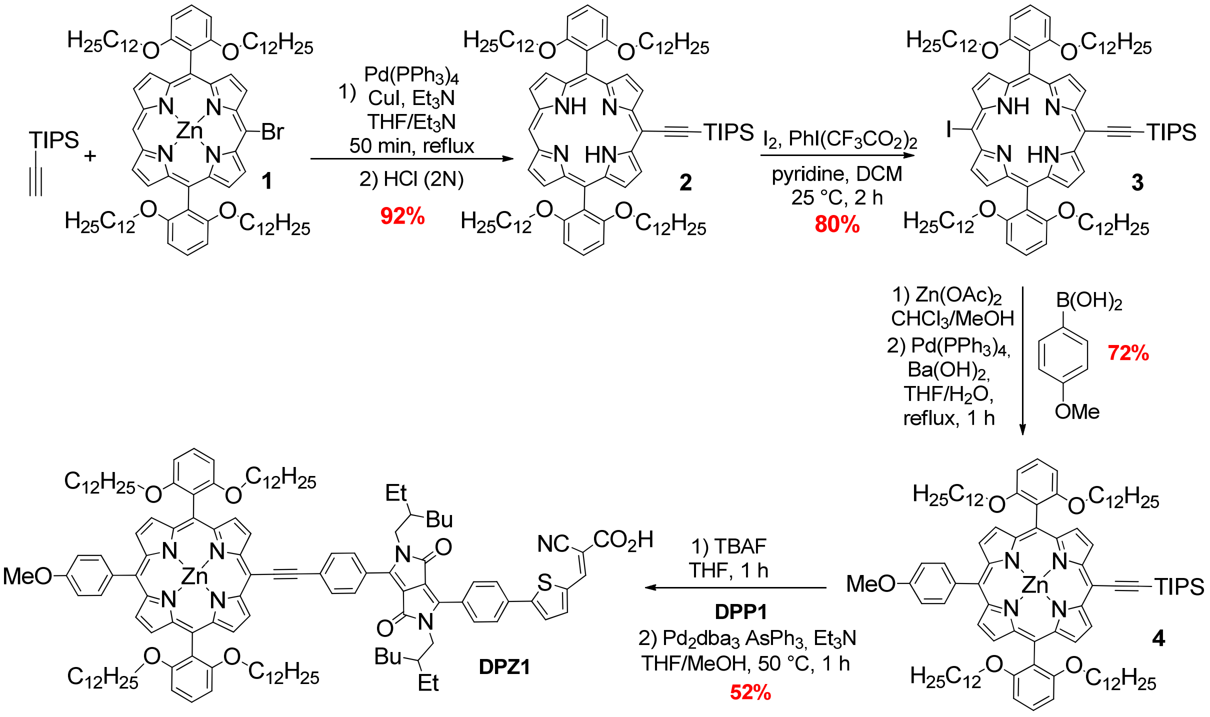


Figure S9. Synthesis of compound **DPZ1**

Compound **2**:

Porphyrin **1** (441 mg, 0.329 mmol) was placed in an oven-dried 250 mL flask under argon, followed by 68 mL of dry THF and 23 mL of dry triethylamine. The resulting mixture was freed from oxygen by nitrogen bubbling while sonicating (15 min). Then $Pd(PPh_3)_4$ (38 mg, 0.033 mmol), copper iodide (6.3 mg, 0.033 mmol) and ethynyltriisopropylsilyl (3.29 mmol) were added in the flask. The reaction mixture was shielded from light and stirred for 50 min at 68 °C. After cooling to room temperature, the mixture was concentrated under reduced pressure. The crude product was placed in 60 mL of a mixture of dichloromethane and methanol (1/1) and 12 mL of a solution of hydrochloric acid (2N) were added. The resulting mixture was stirred for one hour and the organic layer was washed with water twice and concentrated under reduced pressure. Purification was realized by flash column chromatography (silica gel, petroleum spirit/dichloromethane, 8/2) affording a red solid (410 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.66 (2H, d, ^3J = 4.7 Hz), 9.13 (2H, d, ^3J = 4.5 Hz), 8.86 (2H, d, ^3J = 4.6 Hz), 8.84 (2H, d, ^3J = 4.6 Hz), 7.68 (2H, t, ^3J = 8.5 Hz), 6.99 (4H, d, ^3J = 8.5 Hz), 3.81 (8H, bt), 1.44 (21H, m), 1.23-1.05 (24H, m), 0.93 (16H, m), 0.82 (20H, bt), 0.66 (8H, m), 0.57-0.41 (24H, m), -2.54 (2H, s)
^{13}C NMR (125 MHz, $CDCl_3$): δ_c = 160.2, 130.2, 120.3, 113.2, 110.0, 105.2, 98.6, 96.8, 68.9, 66.0, 53.6, 32.0, 29.6, 29.5, 29.4, 29.3, 29.1, 28.8, 28.7, 25.4, 22.8, 19.3, 14.2, 12.1
MALDI-TOF: m/z calculated for 1380.0560 $[M+H]^+$, Found 1380.0529 $[M+H]^+$, Δ= 2.2 ppm.

Compound **3**:

Porphyrin **2** (421 mg, 0.305 mmol) was dissolved in 200 mL of dry dichloromethane under an argon atmosphere and freed from oxygen by nitrogen bubbling while sonicating (15 min). Then iodine (104 mg, 0.408 mmol), 20 drops of dry pyridine and [bis(trifluoroacetoxy)iodo]benzene (126 mg, 0.292 mmol) were added to the mixture. The reaction flask was shielded from light and the reaction mixture was stirred for 4 h at 30 °C. The solvent was removed under reduced pressure and the purification was realized by flash column chromatography (silica gel, petroleum spirit/dichloromethane, 8/2) affording a red solid (370 mg, 80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 9.56 (2H, d, J = 4.7 Hz), 9.52 (2H, d, ^3J = 4.7 Hz), 8.80 (2H, d, ^3J = 4.7 Hz), 8.75 (2H, d, ^3J = 4.7 Hz), 7.70 (2H, t, ^3J = 8.3 Hz), 6.98 (4H, d, ^3J = 8.3 Hz), 3.84 (8H, t, ^3J = 6.5 Hz), 1.44 (21H, m), 1.23-1.05 (24H, m), 0.99-0.90 (16H, m), 0.84 (20H, bt), 0.70-0.41 (32H, m), -2.25 (2H, s)
^{13}C NMR (75 MHz, $CDCl_3$): δ_c = 160.0, 130.2, 120.1, 114.4, 109.5, 105.2, 99.2, 97.5, 79.5, 68.7, 31.9, 29.5, 29.4, 29.3, 29.2, 29.0, 28.7, 28.6, 25.3, 22.7, 19.1, 14.1, 11.8
MALDI-TOF: m/z calculated for 1505.9526 $[M+H]^+$, Found 1505.9537 $[M+H]^+$, Δ= 0.7 ppm.

Compound **4**:

Zinc insertion in compound **3** (220 mg, 0.15 mmol) was carried out as usual with $Zn(OAc)_2$, $2H_2O$ (160 mg, 0.87 mmol) in 30 mL of a mixture of methanol/dichloromethane (1/1) at reflux for 2 h. The reaction mixture was washed with H_2O twice and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure to give the corresponding zinc porphyrin as a purple solid (0.14 mmol, 90%).

The porphyrin (65 mg, 0.041 mmol) was then placed in an oven-dried flask of 50 mL under argon followed by methoxyphenyl boronic acid (6.2 mg, 0.037 mmol), barium hydroxide (23 mg, 0.075 mmol), $Pd(PPh_3)_4$ (2 mg, 1.7 µmol) and a mixture of THF and water (5 mL, 3/1). The resulting mixture was freed from oxygen by nitrogen bubbling while sonicating (25 min). The reaction mixture was shielded from light and refluxed for 1 h. After cooling to room temperature, ethyl acetate and water were added and the organic phase was washed with water, dried with Na_2SO_4, filtered and concentrated under vacuum.

The product was then purified by flash column chromatography (silica gel, petroleum spirit/dichloromethane, 75/25) to give the title compound as a red solid (0.057 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 9.71 (2H, d, ^3J = 4.6 Hz), 8.91 (2H, d, ^3J = 4.6 Hz), 8.80 (4H, s), 8.08 (2H, d, ^3J = 8.4 Hz), 7.67 (2H, m), 7.23 (2H, d, ^3J = 8.5 Hz), 6.98 (4H, d, ^3J = 8.4 Hz), 4.08 (3H, s), 3.81 (8H, t, ^3J = 6.5 Hz), 1.46 (21H, s), 1.21-1.05 (24H, m), 1.00-0.91 (16H, m), 0.86 (20H, bt), 0.69 (8H, m), 0.62-0.40 (24H, m)
^{13}C NMR (100 MHz, $CDCl_3$): δ_c = 160.0, 159.0, 152.5, 150.9, 150.3, 149.7, 135.7, 135.3, 132.0, 131.7, 130.8, 130.5, 129.6, 121.5, 121.1, 98.1, 95.8, 68.7, 66.5, 55.5, 31.8, 29.4, 29.3, 29.2, 29.2, 29.0, 28.7, 28.6, 25.2, 24.5, 22.6, 19.1, 14.0, 12.0
MALDI-TOF: m/z calculated for 1547.0035 $[M]^+$, Found 1547.0007 $[M]^+$, Δ= 1.8 ppm.

Dyad **DPZ1**:

TBAF (0.11 mL, 1M in THF) was added to a solution of **4** (29 mg, 0.019 mmol) in 4 mL of dry THF. The mixture was stirred at 20 °C for 45 min under argon, shielded from light. Water and dichloromethane were poured and the organic layer was dried over anhydrous Na_2SO_4. The concentrated crude and the compound **DPP1** (25 mg, 0.033 mmol) were dissolved in 6 mL of a mixture of dry THF and dry methanol (2/1) and 0.38 mL of dry triethylamine (275 mg, 2.71 mmol) was added. The mixture was freed from oxygen by nitrogen bubbling while sonicating (15 min). Then, $Pd_2(dba)_3$ (4.2 mg, 0.0041 mmol) and $AsPh_3$ (25 mg, 0.081 mmol) were added to the mixture. The solution was heated at 50 °C for 1 h under argon, shielded from light. The solvent was removed under reduced pressure and the purification was realized by flash column chromatography (silica gel, methanol/dichloromethane, 5/95) to afford a brown solid (20 mg, 52%).

^{1}H NMR (500 MHz, THF-d8): δ_H = 10.81 (1H, bs), 9.68 (2H, d, ^3J = 4.5 Hz), 8.83 (2H, d, ^3J = 4.4 Hz), 8.66 (4H, m), 8.18 (4H, m), 8.04 (4H, d, ^3J = 8.4 Hz), 7.93 (2H, m), 7.84 (1H, bs), 7.67-7.63 (4H, m), 7.24 (2H, d, ^3J = 8.4 Hz), 7.02 (4H, d, ^3J = 8.4 Hz), 4.04(3H, s), 4.00 (2H, bm), 3.93 (2H, bm), 3.84 (8H, t, ^3J = 6.1 Hz), 1.49 (2H, m), 1.28-1.07 (40H, m), 1.02 (8H, m), 0.98-0.86 (24H, m), 0.82 (32H, m), 0.68 (16H,m), 0.57 (8H, m)
^{13}C NMR (125 MHz, THF-d8): δ_c = 163.0, 162.8, 160.9, 160.1, 152.7, 151.8, 150.9, 150.2, 148.2, 147.8, 144.1, 138.2, 137.9, 137.8, 136.7, 136.2, 136.0, 135.9, 132.4, 131.9, 131.7, 131.5, 131.0, 130.4, 130.3, 129.9, 129.7, 128.5, 128.4, 126.8, 126.0, 122.1, 118.3, 115.1, 112.3, 111.2, 111.1, 105.4, 98.5, 97.2, 95.3, 68.9, 59.4, 55.5, 45.4, 39.5, 32.6, 31.2, 31.1, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.6, 29.5, 29.1, 29.0, 26.1, 24.7, 24.5, 23.7, 23.6, 23.3, 14.2, 10.7
FT-IR (KBr, cm^{-1}): 2958, 2923, 2853, 2212, 2185, 1730, 1673, 1605, 1507, 1457, 1383, 1262
MALDI-TOF: m/z calculated for 2078.1832 $[M]^+$, Found 2078.1773 $[M]^+$, Δ= 2.8 ppm.

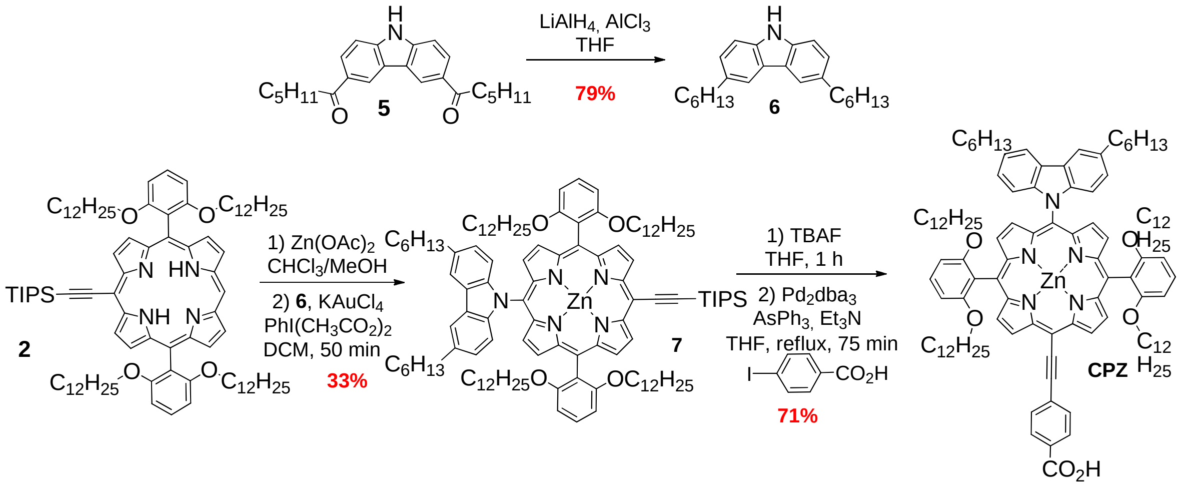


Figure S10. Synthesis of compound **CPZ**

Compound **6**:

Prepared as previously described[6] starting from compound **5**.
Yield: 79%

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.87 (2H, d, ^{4}J = 1.6 Hz), 7.30 (2H, d, ^{3}J = 8.2Hz), 7.23 (2H, dd, ^{3}J = 8.2 Hz, ^{4}J = 1.6 Hz), 2.78 (4H, t, ^{3}J = 7.8 Hz), 1.74 (4H, m), 1.44-1.34 (12H, m), 0.91 (6H, t, ^{3}J = 7.2 Hz)
^{13}C NMR (100 MHz, CDCl$_3$): δ_c = 138.4, 134.0, 126.6, 123.6, 119.7, 110.4, 36.2, 32.5, 32.0, 29.2, 22.8, 14.3
MALDI-TOF: m/z calculated for 335.2608 [M]$^+$, Found 335.2614 [M]$^+$, Δ= 1.8 ppm.

Compound **7** (adapted from previously reported procedure)[7]:

Zinc insertion in compound **2** was carried out as usual with Zn(OAc)$_2$, 2H$_2$O in of a mixture of methanol/dichloromethane (1/1) at reflux for 2 h. The reaction mixture was washed with H$_2$O twice and the organic layer was dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to give the corresponding zinc porphyrin as a purple solid.
A solution of the latter porphyrin (50 mg, 0.035 mmol) in dichloromethane (10 mL) was then added drop by drop into a solution of carbazole **6** (58 mg, 0.17 mmol), iodobenzene diacetate (11 mg, 0.035 mmol) and KAuCl$_4$-nH$_2$O (22 mg, ≈0.052 mmol) in 10 mL of dichloromethane. The resulting mixture was agitated at room temperature under normal atmosphere for 2 h. The solution turned green and a saturated solution of Na$_2$S$_2$O$_3$ was added. The organic layer was washed three times with water, dried with Na$_2$SO$_4$, filtered and concentrated under vacuum. The purification was realized by column chromatography with a solvent mixture of petroleum spirit/toluene (75/25) to afford a green solid (0.012 mmol, 33%).

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 9.75 (2H, d, ^{3}J = 4.5 Hz), 8.93 (2H, d, ^{3}J = 4.6 Hz), 8.67 (2H, d, ^{3}J = 4.6 Hz), 8.41 (2H, d, ^{3}J = 4.6 Hz), 8.19 (2H, s), 7.64 (2H, t, ^{3}J = 8.4 Hz), 7.03 (2H, d, ^{3}J = 8.4 Hz), 6.93 (4H, d, ^{3}J = 8.5 Hz), 6.74 (2H, d, ^{3}J = 8.3 Hz), 3.81 (8H, t, ^{3}J = 6.4 Hz), 2,85 (4H, t, J = ^{3}7.5 Hz), 1.80 (4H, m), 1.46 (21H, s), 1.36 (12H, m), 1.17 (8H, m), 1.13-0.95 (22H, m), 0.91 (16H, m), 0.81 (20H, s), 0.69-0.42 (32H, m)

^{13}C NMR (100 MHz, $CDCl_3$): δ_c = 159.9, 152.3, 151.2, 150.9, 150.0, 147.4, 134.0, 132.2, 131.0, 129.9, 129.2, 126.6, 122.6, 120.7, 119.3, 114.8, 113.3, 110.9, 109.9, 105.2, 100.3, 96.8, 68.6, 53.4, 36.3, 32.3, 31.9, 29.7, 29.4, 29.3, 29.2, 28,9, 28.5, 25.1, 22.7, 22.6, 19.1, 14.1, 14.0, 12.0
MALDI-TOF: m/z calculated for 1774.2073 $[M]^+$, Found 1774.2041 $[M]^+$, Δ= 1.8 ppm.

Dye **CPZ**:

TBAF (0.09 mL, 1M in THF) was added to a solution of **7** (40 mg, 0.023 mmol) in 4 mL of dry THF. The mixture was stirred at 20 °C for 45 min under argon, shielded from light. Water and dichloromethane were poured and the organic layer was dried over anhydrous Na_2SO_4. The concentrated crude and 4-iodobenzoic acid (28 mg, 0.113 mmol) were dissolved in 3 mL of dry THF and 0.7 mL of dry triethylamine was added. The mixture was freed from oxygen by nitrogen bubbling while sonicating (15 min). Then, $Pd_2(dba)_3$ (7 mg, 0.0068 mmol) and $AsPh_3$ (21 mg, 0.068 mmol) were added to the mixture. The solution was heated at 50 °C for 1 h under argon, shielded from light. The solvent was removed under reduced pressure and the purification was realized by flash column chromatography (silica gel, methanol/dichloromethane, 5/95) to afford a green solid (28.4 mg, 71%).

^{1}H NMR (400 MHz, THF-d8): δ_H = 9.70 (2H, d, ^3J = 4.5 Hz), 8.85 (2H, d, ^3J = 4.6 Hz), 8.57 (2H, d, ^3J = 4.6 Hz), 8.25 (2H, d, ^3J = 4.6 Hz), 8.24 (2H, d, ^3J = 8.5 Hz), 8.21 (2H, bs), 8.12 (2H, d, ^3J = 8.5 Hz), 7.66 (2H, t, ^3J = 8.4 Hz), 7.03 (4H, d, ^3J = 8.5 Hz), 7.02 (2H, d, ^3J = 5.6 Hz), 6.67 (2H, d, ^3J = 8.3 Hz), 3.81 (8H, m), 2,86 (4H, t, ^3J = 7.7 Hz), 1.80 (4H, m), 1.49 (4H, m), 1.38 (8H, m), 1.21 (8H, m), 1.15-1.10 (16H, m), 1.08-1.00 (8H, m), 1.00-0.82 (28H, m),0.82 (16H, m), 0.80-0.72 (12H, m), 0.70-0.59 (10H, m)
^{13}C NMR (100 MHz, THF-d8): δ_c = 164.1, 157.8, 149.4, 149.0, 148.5, 147.3, 145.5, 131.3, 129.5, 129.4, 128.7, 127.9, 127.7, 127.5, 126.9, 126.0, 124.1, 120.4, 118.4, 117.0, 112.5, 110.7, 108.3, 102.3, 95.8, 94.8, 92.1, 65.8, 34.0, 30.2, 29.7, 29.6, 27.3, 27.2, 27.1, 27.0, 26.9, 26.6, 26.5, 23.0, 22.7, 20.4, 20.3, 11.3, 11.2
MALDI-TOF: m/z calculated for 1738.0950 $[M]^+$, Found 1738.0894 $[M]^+$, Δ= 3.2 ppm.

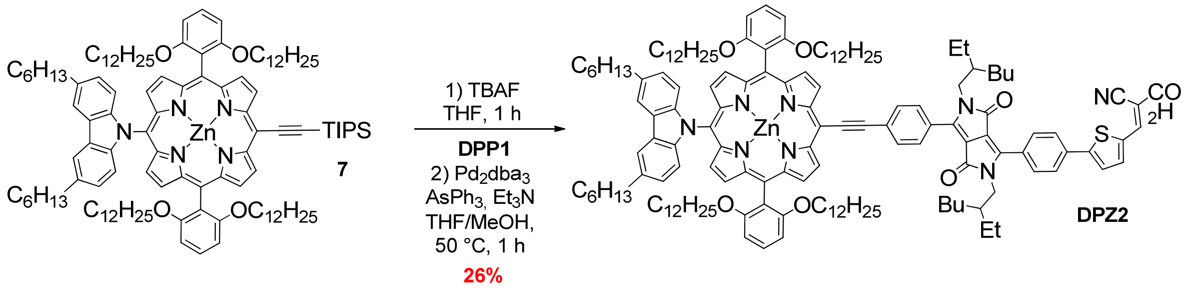


Figure S11. Synthesis of compound **DPZ2**

Dye **DPZ**2:

The reaction was carried out using the same procedure as for the porphyrin **DPZ1** starting from compounds **7** and **DPP1** with a reaction time of 2 h at 50 °C.
Purification was realized by flash column chromatography (silica gel, methanol/dichloromethane, 5/95) to afford a brown solid (26%).

^{1}H NMR (300 MHz, THF-d8): δ_H = 10.81 (1H, bs), 9.71 (2H, d, ^3J = 4.6 Hz), 8.85 (2H, d, ^3J = 4.6 Hz), 8.56 (2H, d, ^3J = 4.6 Hz), 8.23 (2H, d, ^3J = 4.6 Hz) 8.20 (4H, s), 8.08 (2H, d, ^3J = 8.2 Hz), 7.97 (2H, d, ^3J = 8.2 Hz), 7.84 (1H, bs), 7.77 (1H, bs), 7.70 (1H, s), 7.66 (2H, t, ^3J = 8.4 Hz), 7.65 (2H, t, ^3J = 8.5 Hz), 7.01 (6H, m), 6.65 (2H, d, ^3J = 8.4 Hz), 3.98 (2H, bm), 3.93 (2H, bm), 3.87 (8H, m), 2.85 (4H, t, J = 4.6 Hz), 1.24-1.07 (40H, m) ,1.07-0.69 (92H, bm), 0.65 (8H, m)
^{13}C NMR (75 MHz, THF-d8): δ_c = 162.9, 162.8, 160.8, 152.4, 152.1, 151.5, 150.3, 148.4, 148.1, 147.7, 134.3, 132.5, 132.4, 132.3, 132.1, 132.0, 130.6, 130.5, 130.4, 129.9, 129.8, 129.7, 129.2, 129.0, 128.8, 128.2, 127.1, 126.8, 126.0, 125.8, 123.4, 121.4, 120.0, 115.5, 113.7, 111.3, 111.2, 111.1, 105.3, 99.0, 98.9, 98.1, 95.6, 69.8, 69.1, 68.8, 59.3, 46.7, 45.5, 39.6, 39.5, 38.4, 37.0, 36.4, 33.3, 32.7, 32.6, 31.1, 30.4, 30.3, 30.1, 30.0, 29.9, 29.5, 29.4, 29.1, 26.0, 23.6, 23.5, 23.4, 23.3, 20.5, 14.2, 13.9, 10.6
FT-IR (KBr, cm^{-1}): 2958, 2924, 2851, 2214, 2187, 1635, 1530, 1457, 1384, 1261
MALDI-TOF: m/z calculated for 2306.3947 $[MH]^+$, Found 2306.3908 $[MH]^+$, Δ= 1.7 ppm.

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