Supplementary Material for Energy & Environmental Science

Supplementary Information

Energetic factors governing injection, regeneration and recombination in dye sensitized solar cells

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Materials, characterization techniques, and experimental protocols.

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Reactions under anhydrous conditions were performed in dried solvents under argon atmosphere. Column chromatography was performed on silica gel 60 ACC 40-63 μm. Thin layer chromatography was carried out on TLC plates coated with SiO_2 60F254. Melting points (mp) were determined using a Stuart Scientific melting point apparatus SMP3. Infrared spectra (IR) were recorded on a Nicolet Impact 400D spectrophotometer using KBr pellets. Nuclear magnetic resonance (NMR) spectra for proton and carbon were recorded with an AC 300 and a Bruker AVANCE DRX-500. TMS was used as the internal standard. The ultraviolet-visible spectra (UV-Vis) were recorded on a Helios Gamma spectrophotometer. Mass spectra (MS) were obtained using a Bruker Ultraflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer and a VG AutoSpec spectrometer. Electrochemical measurements were performed on a microAutolab III apparatus with a three-electrode configuration system. The measurements were carried out in benzonitrile solutions containing tetrabutylammoniun hexafluorophosphate ($TBAPF_6$, 0.1M). A single-crytal platinum electrode (1 mm diameter) was used as the working electrode and a platinum wire and an $Ag/AgNO_3$ (0.01M) electrode were employed as the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly inmersed in the electrolyte solution. Solutions were deaerated by bubbling argon for a few minutes prior to each voltammetric measurements. The scan rate was 100 mV s^{-1}.

4,5-Bis[4-(1,1,3,3-tetramethylbutyl)phenoxy]-1,3-diiminoisoindoline (4). A solution of 4,5-Bis[4-(1,1,3,3-tetramethylbutyl)phenoxy]phthalonitrile (3.0 g, 5.59 mmol) and sodium methoxide (100.0 mg, 1.86 mmol) in methanol (240 mL) under argon, anhydrous ammonia gas was bubbled through the mixture for 15 h at reflux. The volume of the solution was reduced in vacuo and neutralized with ammonium chloride. The precipitate was filtered off, washed several times with cold water and dried a reduced pressure to give 2.80 g (61%) of the product **4** as a light green solid; m.p. 157.0-157.8 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ0.66 [s, 18H, [2xC$(CH_3)_3$]], 1.31 [s, 12H, [2xC$(CH_3)_2$]], 1.68 (s, 4H, 2xCH_2), 6.90 (d, J = 8.8 Hz, 4H, ArH), 7.35 (d, J = 8.8 Hz, 4H, ArH) and 7.56 (s, 2H, H3, H6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.7

[2xC(CH_3)$_2$], 31.9 [2xC(CH_3)$_3$], 32.5 [2xC(CH_3)$_3$], 38.4 [2xC(CH_3)$_2$], 57.2 (2xCH_2), 111.7 (2xCH, C7, C4), 118.6 (4xCH, C2'), 127.8 (4xCH, C3'), 129.0 (2xC, C7a, C3a), 146.4 (2xC), 151.7, 153.5 (4xCO) and 164.4 (2xC, C1, C3); FT-IR (KBr) 3600-2400br, 1723, 1659, 1507, 1291, 1216 (CO), 1015, 877 and 828 cm^{-1}; MS-FAB (*m*-NBA) m/z 554 amu (100%)

2,3-Dicyano-9,10,16,17,23,24-hexakis-[4'-(1'',1'',3'',3''-tetramethylbutyl)phenoxy] phthalocyanine (3). A solution of diiminoisoindoline **4** (851 mg, 1.536 mmol) and 5,6-dicyano-1,3-diiminoisoindoline [2] (100 mg, 0.512 mmol) in DMAE was heated at reflux under argon atmosphere for 12 h. The green solution obtained was cooled, methanol was added and the residue was centrifuged. The green solid obtained was purified by flash chromatography (SiO_2, Hx:EtOAc/97:3) to give 155 mg (17%) of product **3** as a green solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ -3.00 (br s, 2H, 2xNH), 0.75, 0.78, 0.95 [3xbr s, 54H, [6xC(CH_3)$_3$]], 1.40, 1.50 [2xbr s, 36H, 6xC(CH_3)$_2$], 1.77, 1.89 (2s, 8H, 4H, 6xCH_2), 7.18-7.43 (m, 20H, ArH), 7.53-7.58 (m, 4H, ArH), 8.20, 8.26, 8.44 and 8.70 (4xbr s, 4x2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ31.8, 31.85, 31.9 [6xC(CH$_3$)$_3$, 6xC(CH$_3$)$_2$] δ32.4, 32.4, 32.6δ[6xC(CH_3)$_3$], 38.3, 38.5 [6xC(CH_3)$_2$]δ57.1 (4xCH_2) δ57.3 (2xCH_2), 110.8 (CH), 113.3, 114.6 (CH), 114.8 (CH), 116.4 (2xCN), 117.3 (CH), 117.6 (CH), 119.5 (CH), 126.9 (CH), 127.5 (CH), 127.6, 127.7 (CH), 128.0 (CH), 129.7, 134.7, 138.3, 139.9, 143.2, 145.2, 145.3, 146.8, 150.0, 150.4, 151.0, 153.2, 153.9, 154.8, 155.1 and 159.7; FT-IR (KBr) 3298, 2954, 2229 (CN), 1602, 1504, 1271, 1213, 1170, 1087, 880, 828 and 750 cm^{-1}; Anal. Calcd for $C_{118}H_{136}N_{10}O_6$: C, 79.16; H, 7.66; N, 7.82. Found: C, 79.29; H, 7.70; N, 7.80. UV/Vis ($CHCl_3$), λ_{max}/nm (log ε) ($CHCl_3$) 337 (4.94), 445 (4.60), 622 (4.60), 651 (4.74), 686 (5.37) and 705 (5.31)**;** MALDI-TOF (Dithranol) m/z 1789 amu (M^+).

2,3-Dicarboxyanhydride-9,10,16,17,23,24-[4-(1,1,3,3-tetramethylbutyl)phenoxy] phthalocyanine (2). To a solution of 272 mg of sodium hydroxide in 160 µl of distilled water dicyanophthalocyanine **3** (115 mg, 0.064 mmol) solved in 360 µl of diethyleneglycol was added and the reaction mixture was heated at 160 ^{o}C for 6h. The green suspension obtained was cooled, added to water (20 ml) and the pH was adjusted to 3 with HCl 2M. The suspension was centrifugated, the solid washed with methanol and dried under vacuum. The crude product was refluxed in acetyl chloride (2 ml) for 1.5 h and the solvent was removed by distillation. The residue was purified by flash

chromatography (SiO_2, $CHCl_3$) to give 30 mg (26%) of product **2** as a bright green. ^{1}H NMR (300 MHz, $CDCl_3$) δ-3.25 (br s, 2H, 2xNH), 0.75, 0.80, 0.90 [3xbr s, 54H, [6x$C(CH_3)_3$]], 1.40, 1.48 [2xbr s, 36H, 6x$C(CH_3)_2$], 1.77, 1.78, 1.85 (3xbr s, 12H, 6xCH_2), 7.16-7.53 (m, 24H, ArH), 8.08, 8.31, 8.39 and 8.60 (4xbr s, 4x2H, ArH); FT-IR (KBr) 3296, 1840, 1780, 1600, 1506, 1469, 1272, 1254, 1214, 1173 and 1014 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max}/nm (log ε) ($CHCl_3$) 340 (4.84), 438 (4.53), 623 (4.53), 653 (4.67), 688 (5.27) and 707 (5.18); HR-MS (MALDI-TOF, Dithranol): *m/z*= 1809.0395 amu. [M^+]; calculated for $C_{118}H_{136}N_8O_9$: 1809.0396 amu.

2,3-Dicarboxyanhydride-9,10,16,17,23,24-[4'-(1'',1'',3'',3''-tetramethylbutyl)phenoxy] phthalocyaninate Zn (II) (1)

To a solution of 63 mg (0.034 mmol) of phthalocyanine **2** in 715 μl of DMF and 300 μl of dichlorobenzene, $Zn(OAc)_2$ (19 mg, 0.103 mmol) was added and the mixture was heated at 100^{o}C for 24 h. After cooling, methanol was added and the green solid obtained was centrifuged and washed extensively with methanol. The precipitate was dried a reduced pressure and purified by flash chromatography (SiO_2, $CHCl_3$:AcOEt/97:3) to give 16 mg (26%) of **1** as a green solid; ^{1}H NMR (300 MHz, THF-d_8) δ 0.81, 0.85, 0.98 [3xbr s, 54H, [6x$C(CH_3)_3$]], 1.43, 1.50 [2xbr s, 36H, 6x$C(CH_3)_2$], 1.82, 1.85, 1.92 (3xbr s, 12H, 6xCH_2), 7.20-7.33 (m, 12H, ArH), 7.44-7.60 (m, 12H, ArH), 8.54, 8.70, 8.76 and 9.39 (4xbr s, 8H, ArH); FT-IR (KBr) 2955, 1841, 1782, 1600, 1506, 1473, 1453, 1403, 1273, 1217, 1172, 1092, 1027, 890 cm^{-1}; λ_{max}/nm (log ε) (DMF) 365 (4.99), 613 (4.67) and 681 (5.40); HR-MS (MALDI-TOF, DCTB): *m/z*= 1870.9517 amu. [M^+]; calculated for $C_{118}H_{134}N_8O_9Zn$: 1870.9560 amu.

Table S1: Electronic absorption, electrochemical data, HOMO –LUMO levels and the energy gap, E_{gap}, of the dye of the Phthalocyanines used in this study.

Compound	$E_{1/2}$ [a] (eV)	HOMO (eV)	LUMO (eV)	E_{gap} (eV)
ZnPc-1	-0.48	-5.48	-3.94	1.54
H_2Pc-2	-0.65	-5.65	-4.13	1.52
N719		-5.50 [b]	-3.80	1.70

[a] The electrochemical data were measured in benzonitrile with 0.1 M $TBAPF_6$ as supporting electrolyte using a platinum electrode and a $Ag^+/AgNO_3$ 0.01 M as reference electrode.

[b] Data obtained from literature [2]

To calculate the energy level of the HOMO with respect to Vaccum, Fc^+/Fc redox was measured in the same condition of the dye, obtaining a potential $E_{Fc^+/Fc\,vs\,Ag^+/AgNO_3}$ = -0.07 eV. Taking the energies $E_{Fc^+/Fc\,vs\,NHE}$ = -0.63 eV[3] and $E_{NHE\,vs\,vacuum}$ = -4.44 eV, the HOMO position was determined by using the equation:

$$E_{HOMO\,vs\,vacuum} = E_{1/2} - E_{Fc^+/Fc\,vs\,Ag^+/AgNO_3} + E_{Fc^+/Fc\,vs\,NHE} + E_{NHE\,vs\,vacuum} \qquad \text{(S1)}$$

Data from the E_{gap} has been obtained by two different methods:

(i) Measuring the difference of the HOMO and LUMO levels in the voltammetric measurement used to determine the HOMO level.

(ii) Considering the energy at which the dye sensitized TiO_2 starts to absorb light in Fig. 5.

Both methods provided the same value as indicated in Table S1

Optimized N719 cell

In Fig. S6 the performance of the N719 cell with the same configuration of the Pc samples is compared with an optimized cell. For the cell with lower photocurrent (N719) the electrolyte composition is 0.7 M LiI (99,9%) and 0.05M I_2 (99,9%) in 3-methoxypropionitrile, the photoelectrode used consist in one transparent layer of TiO_2 of 8 μm thick which was deep in dye solution four hours, as mentioned int the text. For the high performance cell (N719-op), the electrolyte composition is 0.03M I_2, 0.6M 1-butyl-3-methylimidazolium iodide, 0.10M guanidinium thiocyanate, 0.5M 4-*tert*-butylpyridine in acetonitrile:valeronitrile (85:15 v/v) and the photoelectrode consisted in a 8 μm thick transparent layer of TiO_2 and a 4μm thick scatter layer, which was immersed in the dye solution during 14 hours. The combined effect of higher amount dye absorbed and scatter layer improved the photocurrent to 14.55 mA/cm^2 what, together with the optimized electrolyte composition, enhanced V_{OC} to 0.81 V. *FF* is also improved to 0.61 that with the enhancement of the other parameters provided an increase of the overall efficiency to a 7.20 %.

Recombination and series resistance

Recombination resistance includes the different interfacial charge transfer mechanisms responsible for the losses in the cell. In DSCs there have been described two contributions: the recombination at the nanocolloidal TiO_2/electrolyte interface, R_r, and the recombination at the compact TiO_2 back layer in contact with the electrolyte, R_{BL}. The total recombination resistance is the parallel contribution of these two contributions. $R_{rec} = R_r \,||\, R_{BL}$. In good cells, the recombination at intermediate and high potentials is dominated by the recombination at the TiO_2/electrolyte interface ($R_{rec} \approx R_r$), as described in the following expression:[4,5]

$$R_r = R_0^{'} \exp\left[-\beta \frac{E_{Fn} - E_{redox}}{k_B T} \right] \quad \text{(S2)}$$

being E_{redox} the redox potential of the I_3^- / I^- couple. E_{Fn} and E_{redox} are related to the applied potential through $V = (E_{Fn} - E_{redox})/q$. The parameters β and $R_0^{'}$ depend on a number of microscopic factors as described in previous publications. [4,5] R_{rec}, together with j_{sc}, provides the maximum power that may be generated through the *j-V* curve. The presence of the series resistance, R_{series}, modulates this *j-V* curve by reducing the FF and thus, the real performance of the solar cell.

For a systematic treatment of parameters of IS of DSC see: www.istest.eu

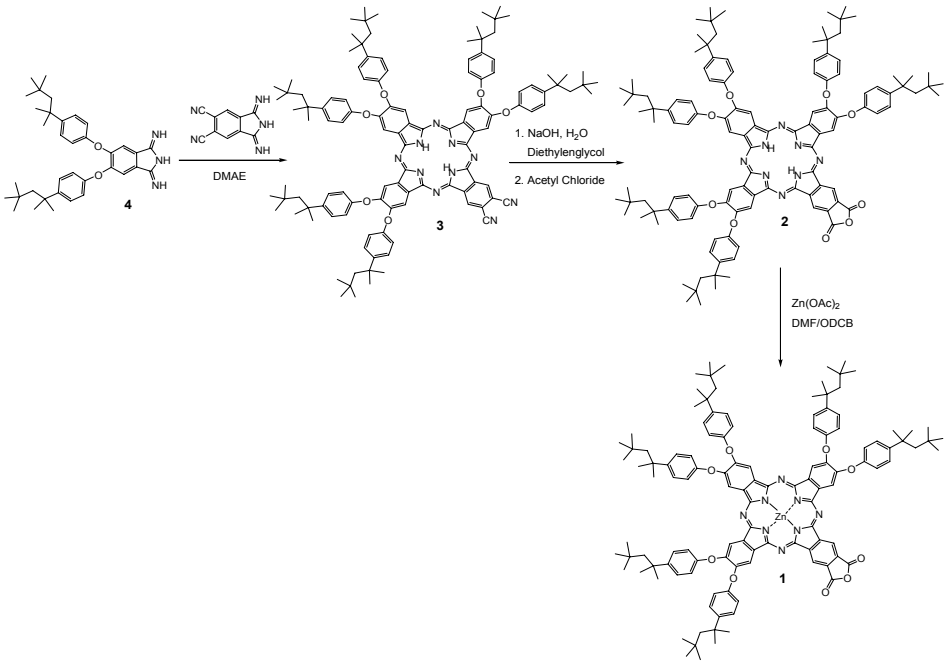

Figure S1. Synthesis route of the phthalocyanines: the dicyanosubstituted Pc (**3)** was obtained by statistical condensation of the 5,6-bis[4'-(1'',1'',3'',3''-tetramethylbutyl)phenoxy]-1,3-diiminoisoindoline (**4)** with the 5,6-dicyano-1,3-diiminoisoindoline in 17 % yield. Hydrolysis of the corresponding dicyanosubstituted Pc (**3**) followed by dehydration of the biscarboxylic acid using acetyl chloride afforded the desired H_2Pc-2 (**2**). Finally, ZnPc-1 (**1**) was prepared by metalation ($ZnCl_2$, DMAE/ODCB) of the free base H_2Pc-2

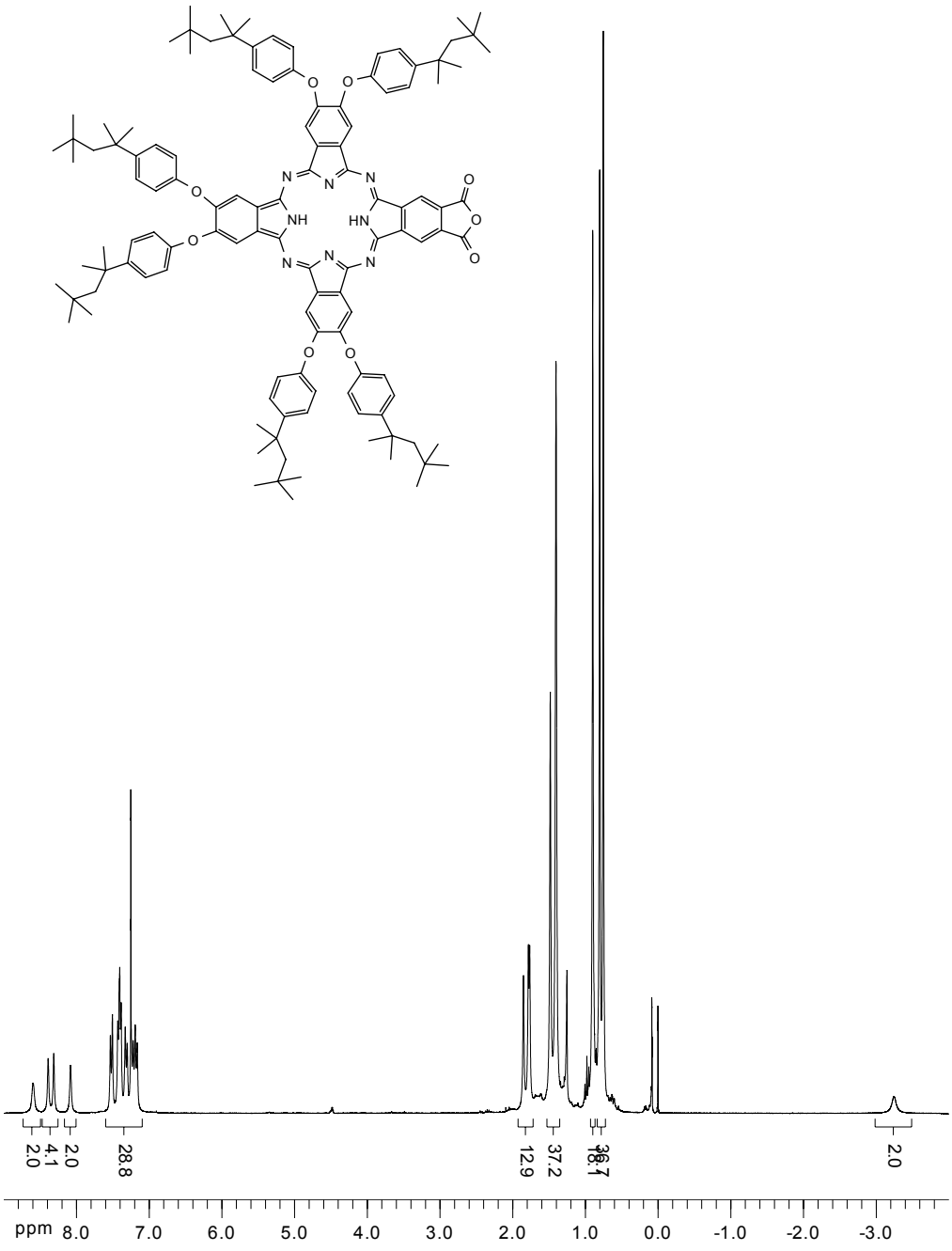

Figure S2. ^{1}H-NMR spectrum of H_2Pc-2 in $CDCl_3$ as solvent.

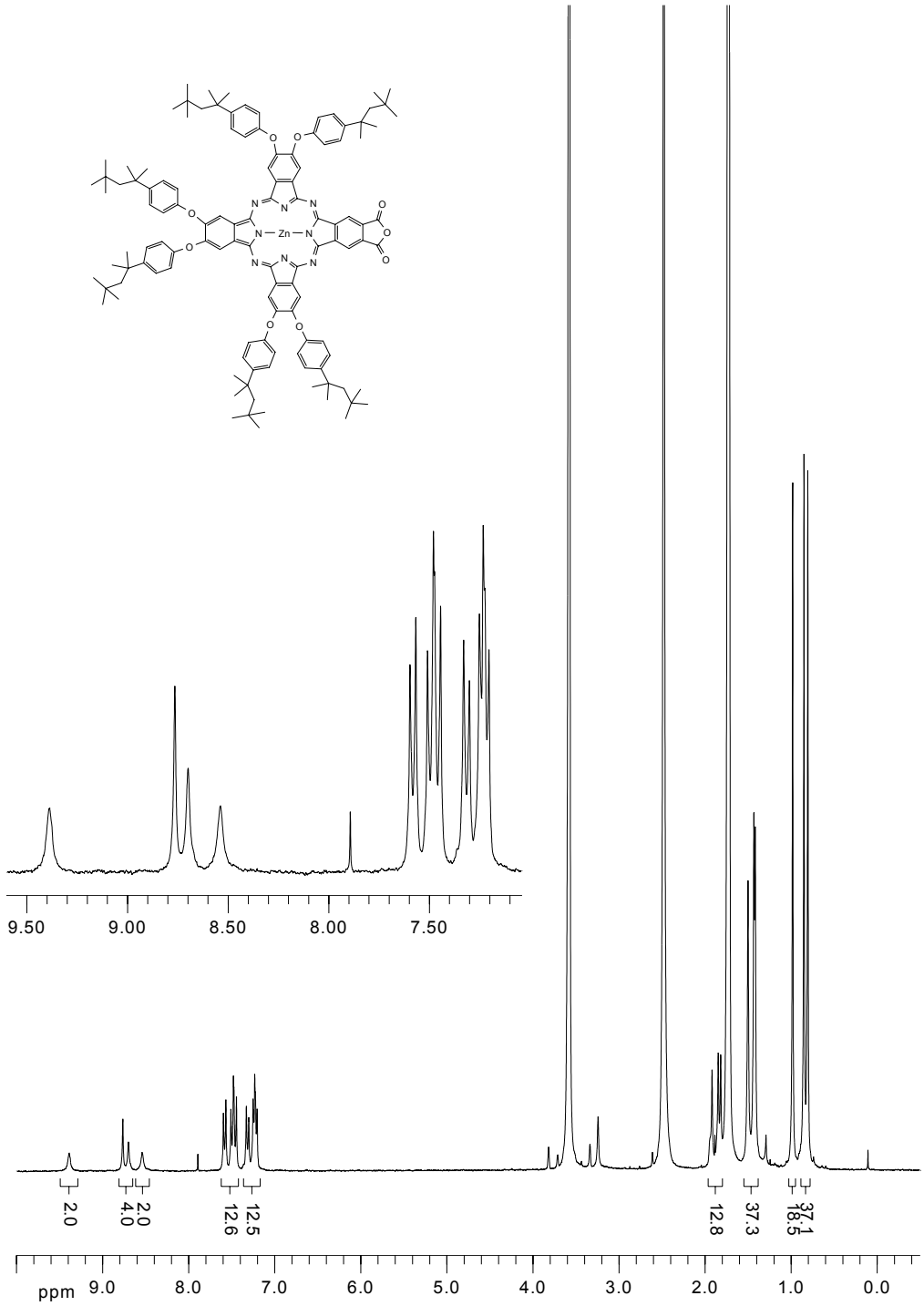

Figure S3. ^{1}H-NMR spectrum of ZnPc-1 in THF-d_8 as solvent.

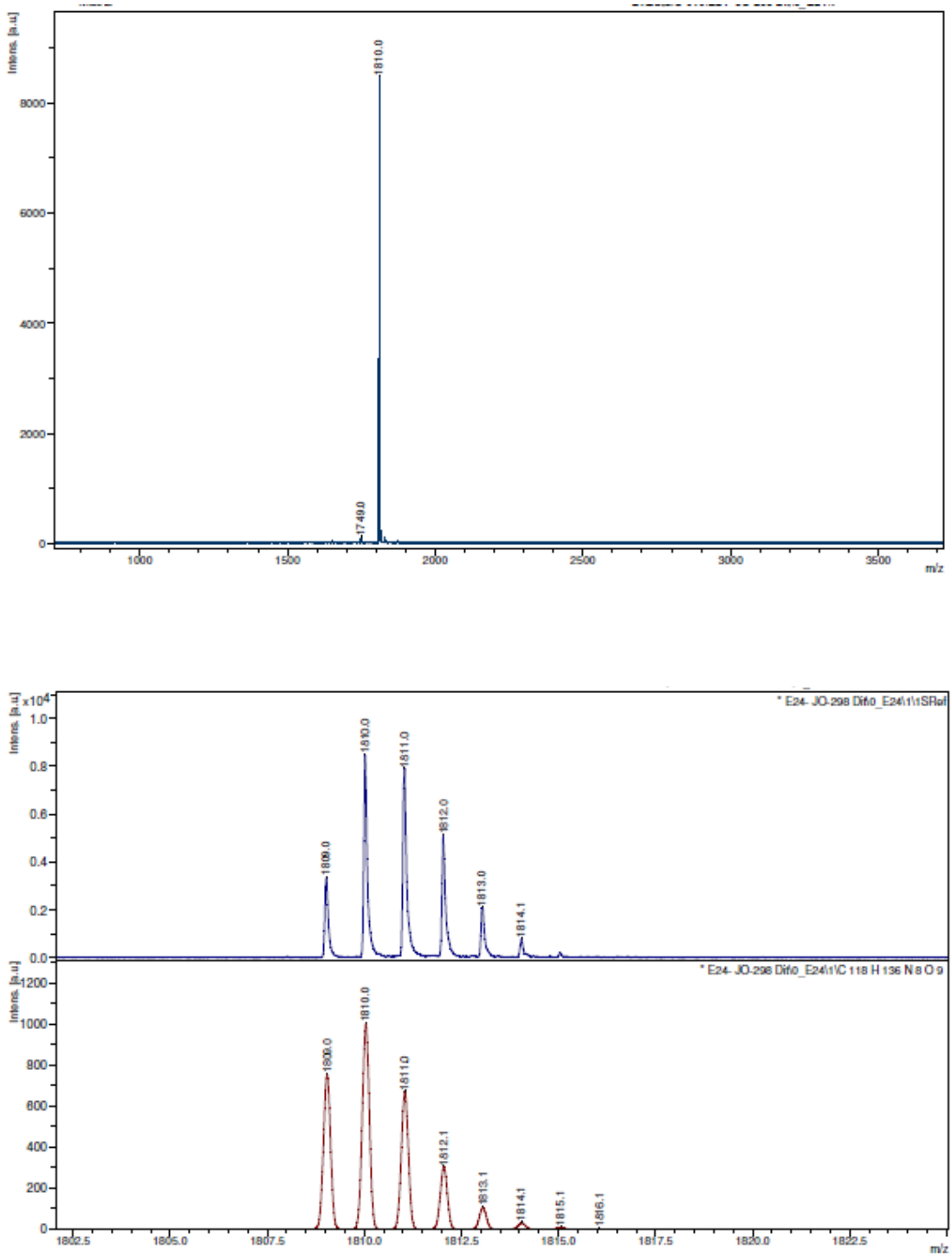

Figure S4. MALDI-TOF spectrum of H_2Pc-2 using dithranol as matrix.

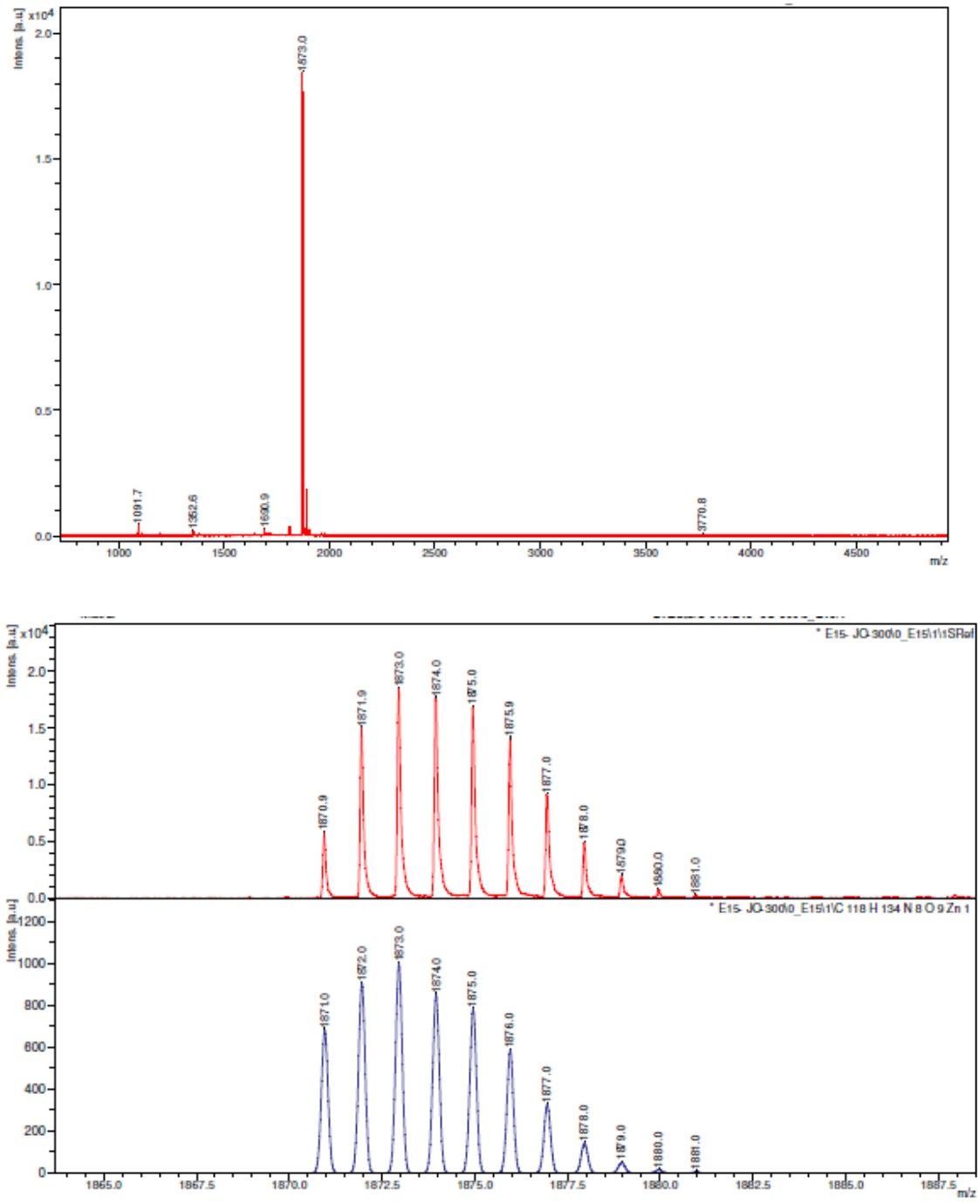

Figure S5. MALDI-TOF spectrum of ZnPc **2** using dithranol as matrix.

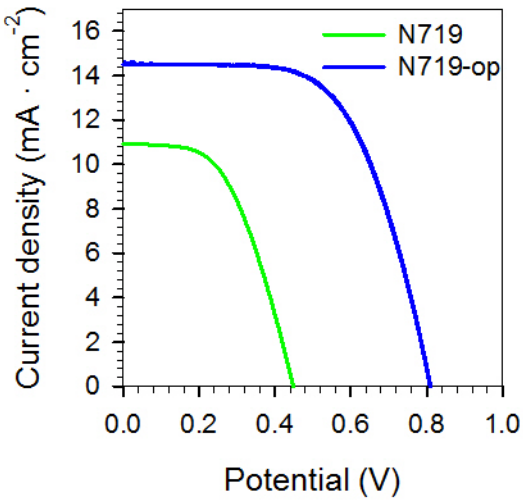

Fig S6. Current density-potential curves for DSCs with a commercial N719 dye as sensitizer, at 1 sun light intensity, with different configuration: **N719** electrolyte without additives, TiO_2 film thickness 8 μm transparent, dye absorption time 4 h; **N719-op** electrolyte with additives, TiO_2 film thickness 8 μm transparent plus 4 μm scatter, dye absorption time 14 h.

Cell parameters

Sample	V_{oc} **(V)**	j_{sc} **(mA/cm^2)**	***FF***	η**(%)**
N719-op	0.81	14.55	0.61	7.20

Gap calculations:

The HOMO-LUMO distance in a dye (its Energy gap) is generally estimated using the intersection between the absorption and the emission spectra after normalizing their respective maximums to unity, dashed line in Fig. S7.[6] However this approximation is not always good enough as due to several experimental limitation, in most of the cases the dyes are not surrounded by the same environment as in the real operating devices. Therefore, in general:

- Different solvents are used to improve solubility of the dye for spectroscopic measurements
- Dyes are not absorbed over TiO_2 to avoid quenching of the radiative emission.
- Etc.

However when measuring IPCE, we may obtain a reasonable amount of current for wavelengths below this estimated potential, Fig. S7, what by definition is not possible. This effect is even more pronounced if as in the case, absorption and emission spectra have large overlapping.[6] This approach in general overestimates the gap. In DSC, it is more accurate to take the value for the gap from the onset of the absorbance of the dye absorbed on the TiO_2 and measured in the same (or at least similar electrolyte) as in operating conditions.

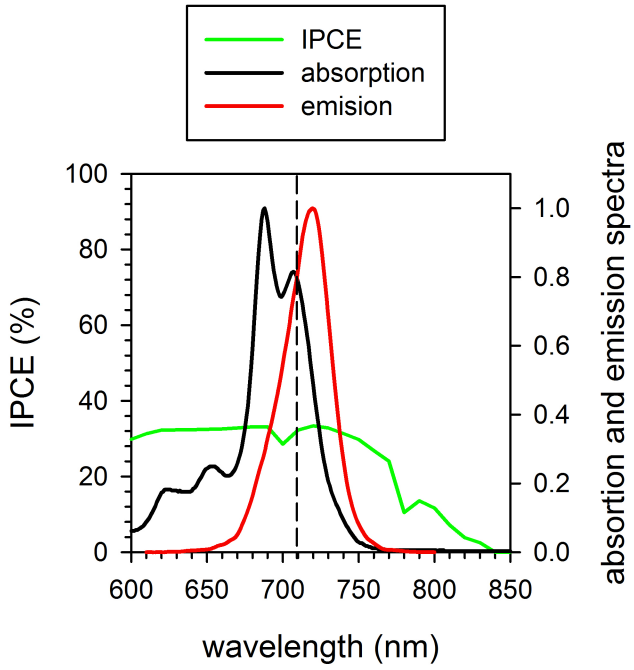

Fig. S7: IPCE spectrum of a DSC sensitized with the H_2Pc-2 dye compared to absorption and emission spectra of the same dye solved in chloroform. Dashed line represents the estimated gap using standard methods.

References:

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