

Supporting Information

Small Molecule Solar Cells Based on a Series of Water Soluble Zinc Phthalocyanine Donors

James Ryan¹, Eduardo Anaya-Plaza², Andrés de la Escosura², Tomas Torres², Emilio
Palomares^{1,3}

¹Institute of Chemical Research of Catalonia, Avda. Paisos Catalans 16, Tarragona 43007,
Spain

²Universidad Autónoma de Madrid, Organic Chemistry Department, Cantoblanco 28049,
Spain

³ICREA, Avda. Lluís Companys 23, Barcelona E-08010, Spain

Corresponding-author email address: epalomares@iciq.es

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1. Experimental Details

1.1. Reagents

Reagents were purchased from Sigma-Aldrich and Alfa-Aesar, and used without further purification except potassium 4-sulfonatophthalate, which was obtained from 4-sulfophthalic acid by basic treatment with aqueous KOH. Silica gel (Merck 60, 230-400 mesh, 60 Å) and TLC plates (Silica gel 60 F254) were purchased from Merck. Solvents were purchased from Carlo Erba Reagents. The ionic exchange resin Amberlite IR-120 (plus) was purchased from SUPELCO.

1.2. General characterization of compounds

¹H-NMR spectra were recorded with a Bruker AV-300. Mass spectra were recorded with a Bruker Ultraflex III spectrometer.

HPLC chromatograms were recorded with an Agilent 1290 Infinity LC System (Vacuum degasser, quaternary pump, standard autosampler, thermostated column compartment and diode array detector) equipped with an Agilent Eclipse XDB C18 column (4.6 mm ID x 250 mm, 80 Å pore and 5 μm of particle size).

1.3. Absorption and Photoluminescence Spectra

UV-Vis measurements were carried out using a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D2 and W light sources. Photoluminescence measurements were obtained using on an Aminco-Bowman Series 2 Luminescence spectrofluorimeter equipped with a high voltage PMT detector and continuum Xe Light source.

1.4. Differential Pulse Voltammetry

Differential pulse voltammetry (DPV) experiments were carried out using a CH Instruments 660c Electrochemical Workstation, with a standard three-electrode setup employed that utilized a Pt disc working electrode, Pt wire working electrode and SCE reference electrode. A 0.1 M solution of tetrabutylammonium phosphate in DMSO was used as the background electrolyte. To determine the HOMO of the respective molecules, the following formula:^{S1}

$$E_{\text{HOMO}} = -(1.4 \pm 0.1) \times (qV_{\text{CV}}) - (4.6 \pm 0.08) \text{ eV}$$

where V_{CV} corresponds to E^{OX} of the substrate vs. ferrocene/ferrocenyl couple (Fc/Fc⁺). Peak potential (E_p).

1.5. Device Fabrication and Characterization

Devices were prepared on ITO substrates (5 ohm/square, Psitech Ltd. U.K.). The substrates were cleaned by sonicating in acetone and 2-propanol, followed by 20 min exposure to UV/O₃. Thin films of the sulfonated ZnPc donors were prepared by spin-coating a 10 mg/ml solution (Mill-Q ultrapure water) of the respective donor, which had been left overnight stirring

at 50 °C, and filtered using a 0.2 mm cellulose acetate membrane. The spin-coating conditions employed were 2000 rpm for 1 minute. Subsequently, the films were allowed to dry for 30 min in ambient conditions before transferring to a nitrogen rich glove box, where they were annealed at a temperature of 100 °C for 15 min in an attempt to remove any residual water. Finally the substrates were placed in the evaporator where the C₆₀ (40 nm, MER Corp., 99.9+%), BCP (8 nm, Sigma Aldrich), and Al (100 nm, Sigma Aldrich) were deposited at a base pressure of 1 x 10⁻⁶ mbar. Device *J-V* curves were recorded using a 150 W solar simulator (Abet Technologies) at 1 sun conditions (AM 1.5, 100 mW/cm²). Incident to photon current efficiency (IPCE) studies were carried out using a home-built system utilising a 150 W Oriel Xenon lamp as the light source.

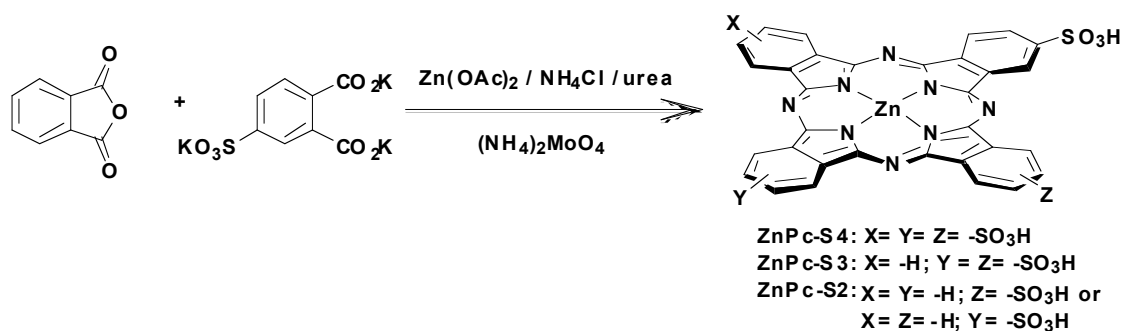
2. Synthetic procedure and characterization

2.1. Synthesis of sulfonated ZnPcs

In order to synthesize the asymmetrically substituted phthalocyanines (Pcs) ZnPc-S2 and ZnPc-S3, a statistical condensation of potassium 4-sulfonatophthalate and phthalic anhydride in a 1:1 ratio was carried out in melted urea as solvent (adapting a method reported by van Lier et al.),^{S2} in the presence of Zn(OAc)₂, ammonium chloride and ammonium molybdate (Scheme S1). ZnPc-S2 and ZnPc-S3 were separated from the crude mixture by column chromatography, using chromatographic conditions described by Siejak et al. (i.e., in silica gel, with ethyl acetate/ethanol/aqueous ammonia 25% (7:4:4) as the eluent).^{S3} Although in this reaction ZnPc-S4 is also generated, it was not produced in high amount (because of the employed ratio of potassium 4-sulfonatophthalate and phthalic anhydride, i.e., 1:1), and it was

impossible to elute it from the column due to its extreme polarity. For the synthesis of ZnPc-S4 in higher yield, a procedure previously reported in the literature was adapted.^{S4}

The UV-Vis spectra reported by Siejak et al. for ZnPc-S2, ZnPc-S3 and ZnPc-S4, purified under the aforementioned chromatographic conditions, show an unexpected splitting of the zinc phthalocyanine (ZnPc) Q-band.^{S3} They argue the splitting may be due to aggregation, which is quite unlikely in a coordinating solvent as DMSO, or to 'the additional energy transition owing to the presence of the sulfo substituents', although such effect has never been described for sulfonated Pcs. In contrast, it is well known that under acidic conditions, the protonation of Pc nitrogen atoms in *meso* positions results in a splitting of the Q-band, with significant bathochromic shifts of the Pc absorption.^{S5,S6,S7} On these bases, we have reasons to think that during the eluent evaporation (under vacuum) after the column (i.e., ethyl acetate/ethanol/aqueous ammonia 25% (7:4:4)), the occurrence of basic hydrolysis of ethyl acetate (due to heating in the rotavap) and the removal of ammonia when drying under vacuum (which lowers the pH) might result in the production of acetic acid to some extent, leading to protonation of the *meso* positions of the ZnPc macrocycle. We are not sure whether this might be the reason for Siejak et al.'s observations, or if it influenced their results of photocurrent generation in sulfonated ZnPc thin films. In any case, we did an additional purification step consisting on the re-precipitation of each compound from water/acetone or DMSO/acetone. In this way, the UV-Vis spectra of ZnPc-S2, ZnPc-S3 and ZnPc-S4 in DMSO showed in the three cases the non-split Q-band characteristic of neutral metallated Pcs (Fig. S1).



Scheme S1 Synthesis of sulfonated ZnPcs.

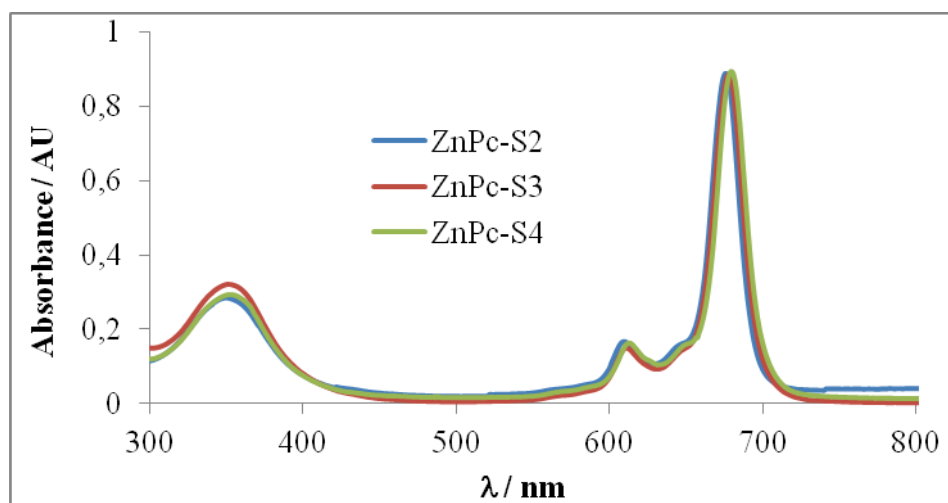


Fig. S1 Normalized UV-Vis spectra of ZnPc-S2, ZnPc-S3 and ZnPc-S4 in DMSO.

Procedure for the synthesis of ZnPc-S4 (adapted from reference S4)

Potassium 4-sulfonatophthalate (10 g, 28 mmol), ammonium chloride (1.94 g, 36.3 mmol), urea (25.4 g, 423 mmol), ammonium molybdate (0.18 g, 0.90 mmol) and anhydrous zinc acetate (1.8 g, 98 mmol) were placed in a round-bottom flask and heated at 170 °C for 30 min. At this point, the solution became light green. The temperature was then raised to 210 °C, and gradually over 6 hours up to 230 °C. After cooling down, the crude black solid was suspended in 10% aqueous HCl saturated with NaCl (200 mL). The precipitate was filtered

and subsequently washed with acetone and a mixture of acetone/ethanol/water (10:10:1). A green-black solid was obtained (6.95 g) and further purified by ionic exchange with 55 g of appropriately conditioned ionic exchange resin (Amberlite IR-120 (plus)). A dark-blue solid was collected from the column and subsequently re-precipitated from water/acetone, yielding 0.96 g (15%) of the desired blue solid. The re-precipitation process can also be performed from DMSO/acetone, yielding 2.97 g of product (48%), although less crystalline than from the former re-precipitation process.

$^1\text{H NMR}$ (300 MHz, d_6 -DMSO) δ ppm = 9.65 (Ar-H, 4H, d, $J=3.0$ Hz), 9.38 (Ar-H, 4H, m), 8.48 (3.0 Hz, Ar-H, 4H, dd, $J = 7.89$).

m/z (MALDI-TOF, α -cyano-4-hydroxycinnamic acid): 896.9 [$\text{ZnPc}(\text{SO}_3\text{H})_3(\text{SO}_3^-)$], 918.9 [$\text{ZnPc}(\text{SO}_3\text{H})_2(\text{SO}_3\text{Na})(\text{SO}_3^-)$], 940.9 [$\text{ZnPc}(\text{SO}_3\text{H})(\text{SO}_3\text{Na})_2(\text{SO}_3^-)$].

UV/Vis (DMSO, λ_{max} (nm) ($\log \epsilon$): 679 (4.93), 612 (4.2), 351 (4.45).

HPLC (retention time): 21.8 min.

Procedure for the synthesis of ZnPc-S2 and ZnPc-S3 (Adapted from reference S2)

Potassium 4-sulfonatophthalate (2.5 g, 6.9 mmol), phthalic anhydride (1 g, 7.0 mmol), ammonium chloride (1.0 g, 19 mmol), urea (12.7 g, 211 mmol), ammonium molybdate (0.08 g, 0.4 mmol) and anhydrous zinc acetate (0.9 g, 4.9 mmol) were placed in a 100 mL round-bottomed flask and heated to 170 °C, at which point urea melted and started to decompose into ammonia. The solution gets light green and, after 30 min, the mixture was heated up to 210 °C and the reaction mixture turned dark blue. The temperature was raised gradually over 6 hours up to 230 °C and finally became solid. After cooling down, the crude black solid was suspended in 10% aqueous HCl saturated with NaCl (200 mL). The precipitate was filtered

and subsequently washed with acetone and a mixture of acetone/ethanol/water (10:10:1). The solid was purified by column chromatography, using ethyl acetate/ethanol/aqueous ammonia 25% (7:4:4) as the eluent (chromatographic conditions from reference S3). The second and third fractions eluted from the column corresponded to ZnPc-S2 and ZnPc-S3, respectively. Unfortunately, HPLC analysis (see below) revealed that the third fraction also contained 8.8% of ZnPc-S4 as impurity, due to the extremely polar solvent needed to elute these compounds and the similar R_f values of ZnPc-S3 and ZnPc-S4 under the employed chromatographic conditions. Finally, each of the samples was re-precipitated from DMSO/acetone.

ZnPc-S3 (5% yield):

¹H NMR (300 MHz, d₆-DMSO) δ (ppm): 8.7-8.3 (Ar-H, 2H, m), 8.3-7.5 (Ar-H, 4H, m), 7.5-7.2 (Ar-H, 2 H, m), 7.0-5.9 (Ar-H, 7H, m).

m/z (MALDI, ACC): 816.9 [ZnPc(SO₃H)₃]⁻, 838.9 [ZnPc(SO₃Na)(SO₃H)₂]⁻, 897.9 [ZnPc(SO₃H)₄]⁺, 919.9 [ZnPc(SO₃Na)(SO₃H)₃]⁻, 1630.0-1806.9 [ZnPc(SO₃Na)_x(SO₃H)_(3-x)]₂⁻, 2475.9-2671.9 [ZnPc(SO₃Na)_(x>1)(SO₃H)_(3-x)]₃⁻.

UV/Vis (DMSO, λ_{max} (nm) (log ε)): 677 (5.02), 610 (4.26), 350 (4.60).

HPLC (retention time): 21.8 min (ZnPc-S4, 8.8%), and 27.5, 28.7 and 31.7 min for the different regioisomers of ZnPc-S3 (91.2%).

ZnPc-S2 (16% yield):

UV/Vis (DMSO, λ_{max} (nm) (log ε)): 675 (4.99), 609 (4.23), 349 (4.57).

¹H NMR (300 MHz, d₆-DMSO) δ (ppm): 8.5-8.2 (Ar-H, 1H, m), 8.1-7.2 (Ar-H, 5H, m), 7.2-6.1 (Ar-H, 8 H, m).

m/z (MALDI, ACC): 735.1 [ZnPc(SO₃H)(SO₃⁻)], 757.1 [ZnPc(SO₃Na)(SO₃H)]⁻, 779.2 [ZnPc(SO₃Na)₂]⁻, 1469.9-1563.8 [ZnPc(SO₃Na)_x(SO₃H)_(2-x)]₂⁻, 2226.9-2363.8 [ZnPc(SO₃Na)_(x>1)(SO₃H)_(2-x)]₃⁻.

HPLC (retention time): 35.8, 36.5, 38.7, 40.6 and 42.7 min (for the different regioisomers of ZnPc-S2).

2.2. HPLC analysis

General procedure:

The sample was dissolved in sodium phosphate buffer (10 mM, pH5, concentration: 10⁻⁴ M), filtered (0.45 μm pore size, Millipore nylon filters), injected, and eluted from 0% to 95% methanol in sodium phosphate buffer, with a 50 min linear gradient and a flow rate of 1.0 mL/min, at 25 °C. The detection was performed at 680nm (16 nm band width) and 850nm (100 nm band width) as reference wavelength.

In order to assign the observed HPLC peaks (from chromatograms shown in the next page) to the different regioisomers of ZnPc-S2 and ZnPc-S3, the dipolar moment of each regioisomer (Fig. S2) was calculated through a semi-empirical procedure at AM1 level, using *Spartan '02* software for this purpose.

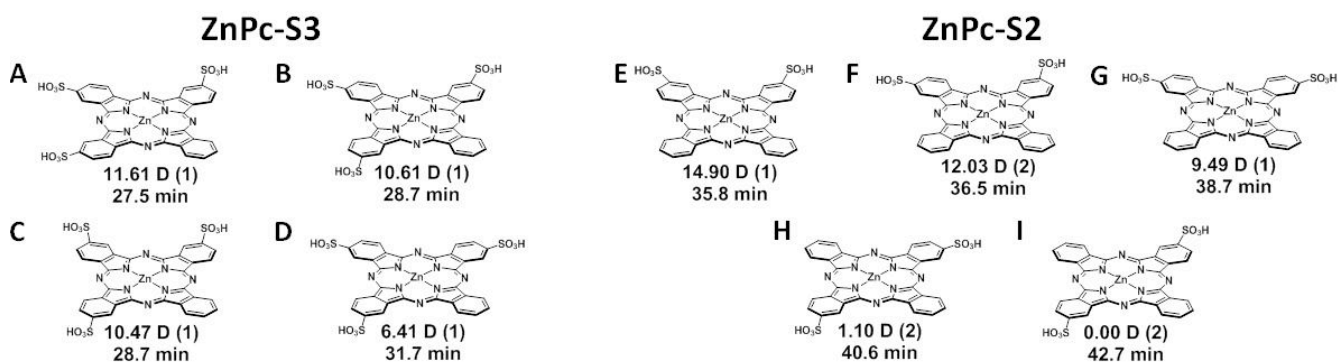
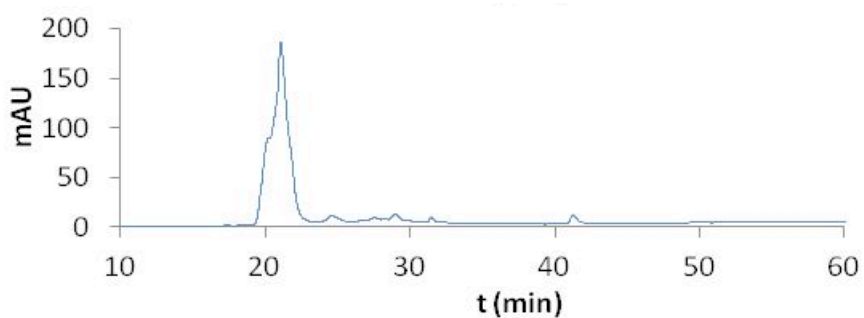
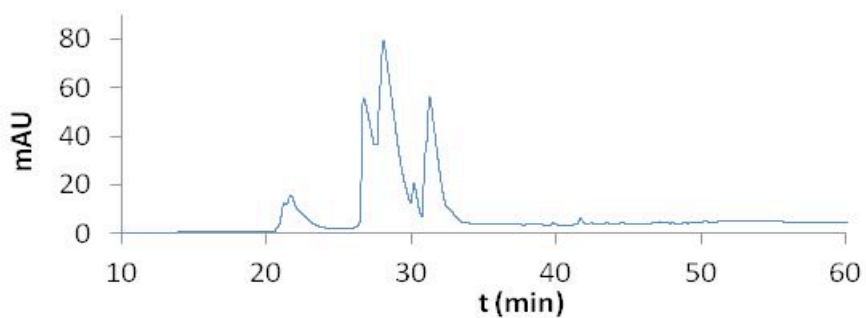


Fig. S2 Regioisomers of ZnPc-S3 and ZnPc-S2, with their calculated dipolar moments indicated below each structure. Their retention times and relative abundances (in brackets) are also indicated.

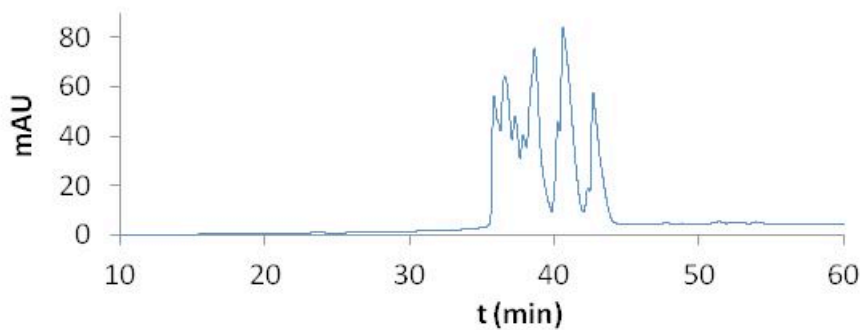
ZnPc-S4



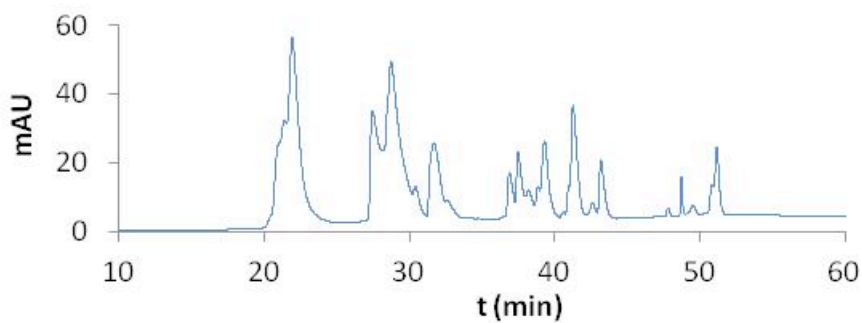
ZnPc-S3



ZnPc-S2

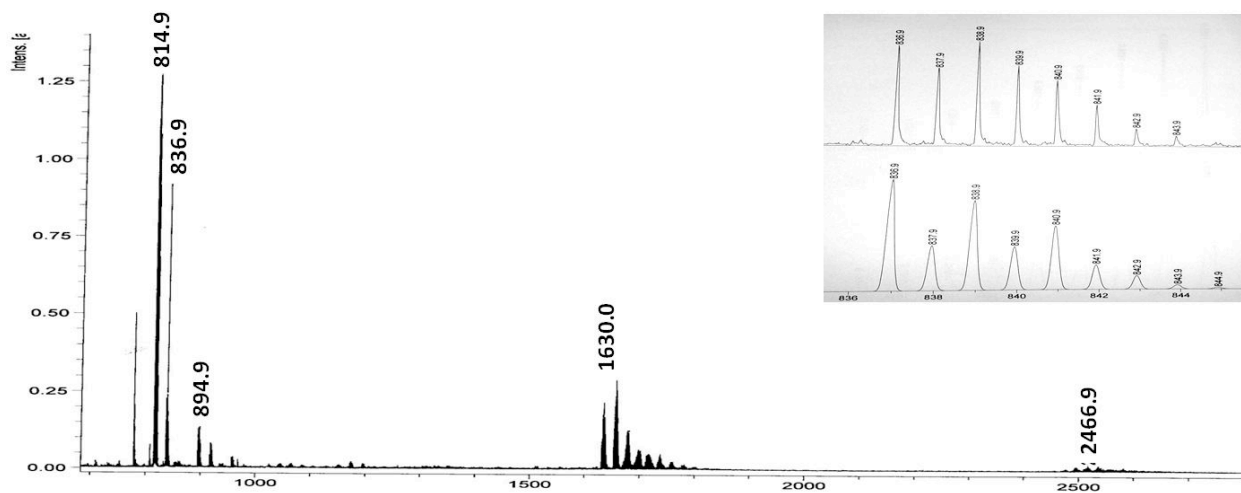


Crude mixture obtained from the procedure to synthesize ZnPc-S2 and ZnPc-S3



2.3. Mass spectra

ZnPc-S3



ZnPc-S2

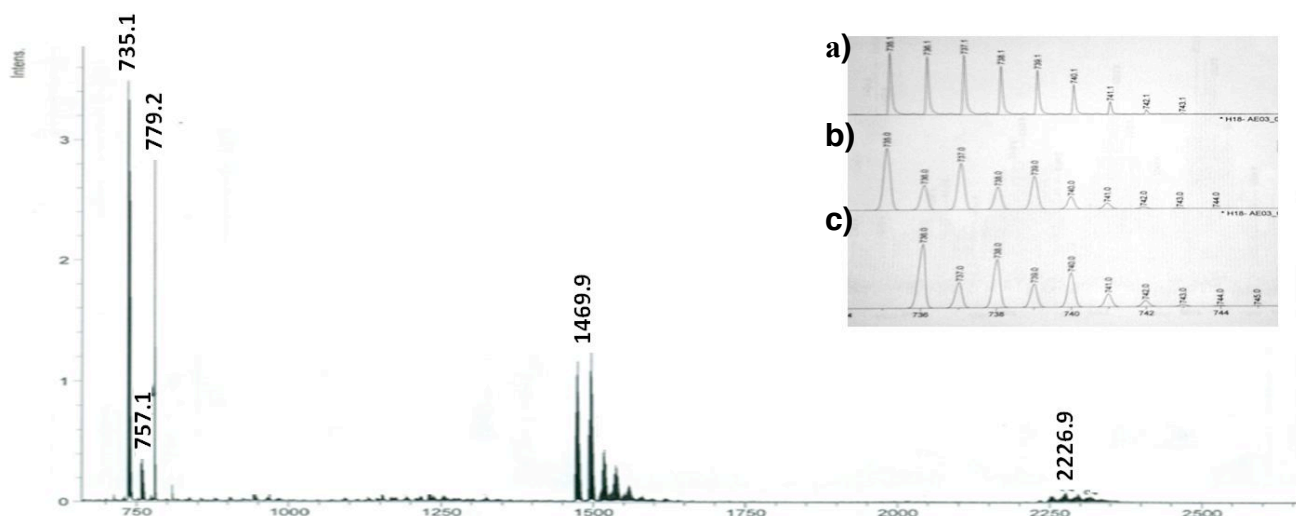


Fig. S3 The monomer set of peaks (**a**, experimental isotopic distribution) consists of a mixture of the molecular anions $[M-H]^-$ (**b**, theoretical isotopic distribution) and $[M]^-$ (**c**, theoretical isotopic distribution). The sets of peaks around doubled and tripled mass of the molecular ion, for both ZnPc-S2 and ZnPc-S3, correspond to supramolecular dimers and trimers.

3. Absorption and Photoluminescence Spectra

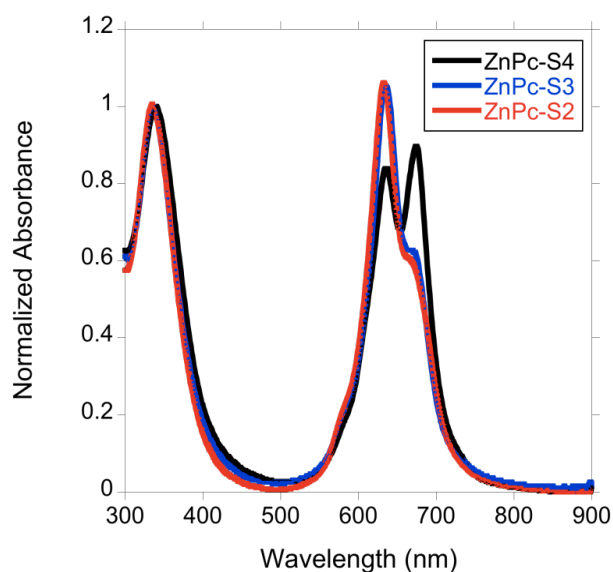


Fig. S4 Absorption spectra for wsZnPc in water

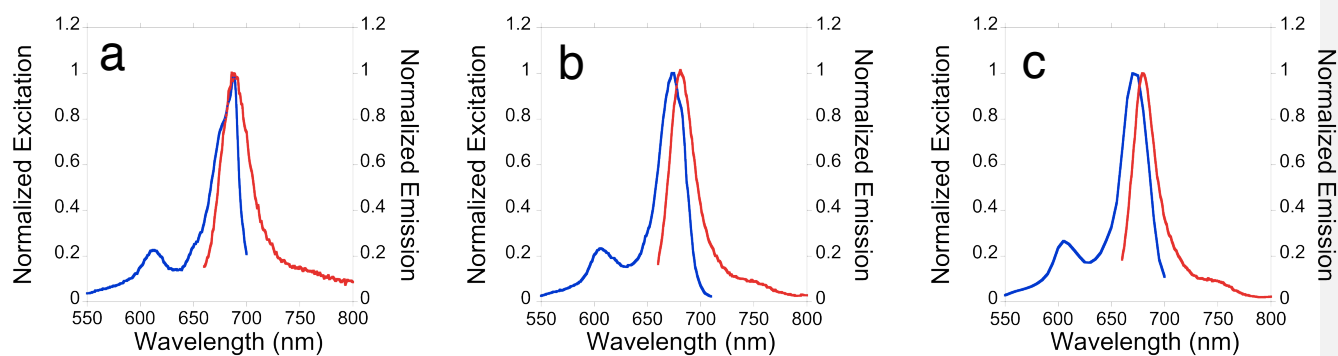


Fig. S5 Photoluminescence emission (red) and excitation (blue) for (a) ZnPc-S2, (b) ZnPc-S3, and (c) ZnPc-S4

4. Differential Pulse Voltammetry

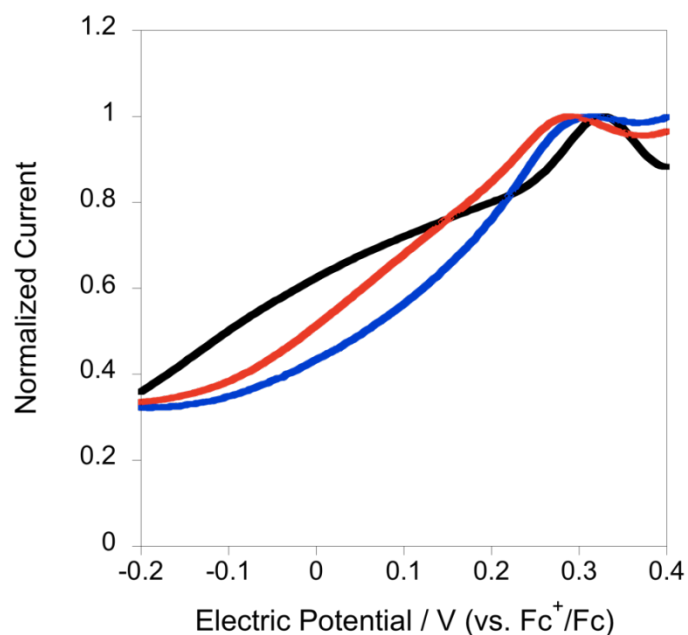


Fig. S6 Differential pulse voltammetry for ZnPc-S2 (red), ZnPc-S3 (blue) and ZnPc-S4, recorded vs. a Fc^+/Fc internal reference.

5. References

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