Supporting Information

Large-Size Star-Shaped Conjugated (Fused) Triphthalocyaninehexaazatriphenylene

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General methods

All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. 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 (40–63 μm) 60F254, and they were visualized by UV light. NMR spectra were measured with a Bruker AC 300. UV-vis spectra were recorded with a Helios Gamma spectrophotometer. Fluorescence spectra were recorded with a Perkin Elmer LS 55 Luminiscence Spectrometer and IR spectra with a Nicolet Impact 400D spectrophotometer. Mass spectra were obtained from a Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF).

Electrochemical measurements

CV measurements were performed in a conventional three-electrode cell using a μ-AUTOLAB type III potentiostat/galvanostat at 298K, over PhCN and deaerated sample solutions (~0.5 mM), containing 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. A platinum working electrode, $Ag/AgNO_3$ reference electrode and a platinum wire counter electrode were employed. Ferrocene/ferrocenium couple was used as an internal standard for all measurements.

AFM measurements

AFM measurements were performed with an Agilent 5100 in tapping mode. FORT tips (AppNano) with 6 nm radius were used. The data analysis was carried out using the Gwyddion software.

Synthesis of 2,9,16,-tri-(*tert*-butyl)-22,23-(thiadiazole)-phthalocyaninate zinc (II) (ZnPc 2)

A mixture of 150 mg (0.805 mmol) of 1,2-(thiadiazole)phthalonitrile[1], 457 mg (2.415 mmol) of 4-(*tert*-butyl)phthalonitrile, 350 mg (1.611mmol) of zinc acetate and two drops of DBN were dissolved in 2 mL of DMAE in argon atmosphere. The reaction mixture was refluxed for 10 h, then was cooled to room temperature and diluted with toluene. The crude was concentrate in vacuum and purified by column chromatography ($CHCl_3$:THF /95:5), yielding 78 mg (12%) of **ZnPc 2** as a dark blue solid.

- ^{1}H NMR (THF-d_8) δ 1.87-1.95 (m, 27H, *tert*-butyl), 8.13-8.37 (m, 3H, Pc), 8.93-9.50 (m, 8H, Pc).
- IR (KBr): 3384, 2954, 2901, 2865, 1719, 1613, 1487, 1392, 1331, 1256, 1099, 1042, 920, 744 cm^{-1}.
- UV-Vis (THF), λ_{max}/nm (log ε): 354 (4.88), 619 (4.40), 682 (4.92), 716 (4.86).
- MS (MALDI-TOF): *m/z* for $C_{44}H_{38}N_{10}SZn$ calcd, 802.2287; found 802.2425 (M^+).

Synthesis of 2,9,16,-tri-(*tert*-butyl)-22,23-(amino)-phthalocyaninate zinc (II) (ZnPc 3)

75 mg (0.093 mmol) of **ZnPc 2** and 93 mg (0.372 mmol) of nickel acetate tetrahydrate were dissolved in 7.5 mL of dry THF:EtOH/1:2 at 0°C under argon. After 10 min, 43 mg (1.116 mmol) of sodium borohydride was added. The reaction mixture was filtered over celite and the organic layer was washed with NH_4Cl (2M) and H_2O two times. The organic layer was dried with $MgSO_4$ and concentrate in vacuum. The crude was purified by column chromatography ($CHCl_3$:THF /9:1), yielding 53 mg (74%) of **ZnPc 3** as a green solid.

- ^{1}H NMR (THF-d_8) δ 1.73-1.78 (m, 27H, *tert*-butyl), 4.95 (m, 4H, NH_2), 8.27 (m, 3H, Pc), 8.66 (d, ,2H, Pc), 9.38-9.62 (m, 6H, Pc).
- IR (KBr): 3369, 2956, 2921, 2851, 1713, 1617, 1487, 1399, 1363, 1325, 1144, 1088, 1045, 747 cm^{-1}.
- UV-Vis (THF), λ_{max}/nm (log ε): 346 (4.73), 615 (4.31), 680 (4.99).
- MS (MALDI-TOF): *m/z* for $C_{44}H_{42}N_{10}Zn$ calcd, 773.2801; found 773.2948 (M-H).

[1] C. Burmester and R. Faust, *Synthesis*, **2008**, 8, 1179.

Synthesis of $(ZnPc)_3$HAT 1

33 mg (0.042 mmol) of **ZnPc 3** and 1.84 mg (0.011 mmol) of cyclohexane-1,2,3,4,5,6-hexaone were dissolved in 4 mL of a mixture degassed ($CHCl_3$:AcOH /1:2) at 60 °C under argon after 24 h, 20 mg (0.025 mmol) of **ZnPc 3** were added in 2 mL of $CHCl_3$ and continue with the reaction during 72 h. The organic layer was washed with H_2O two times, dried with $MgSO_4$ and concentrate in vacuum. The crude was purified by column chromatography ($CHCl_3$:THF /95:5), yielding 12 mg (45%) of **$(ZnPc)_3$HAT 1** as a green solid.

- ^{1}H NMR (THF-d_8) δ 1.96-2.03 (m, 81H, *tert*-butyl), 8.11-8.45 (m, 9H, Pc), 9.39-9.59 (m, 24H, Pc).
- IR (KBr): 3400, 2956, 2924, 2854, 1716, 1614, 1533, 1485, 1463, 1393, 1363, 1326, 1257, 1091, 1044, 750 cm^{-1}.
- UV-Vis (THF), λ_{max}/nm (log ε): 347 (4.66), 698 (4.64).
- MS (MALDI-TOF): *m/z* for $C_{138}H_{114}N_{30}Zn_3$calcd, 2383.7789; found 2383.7760 (M+H).

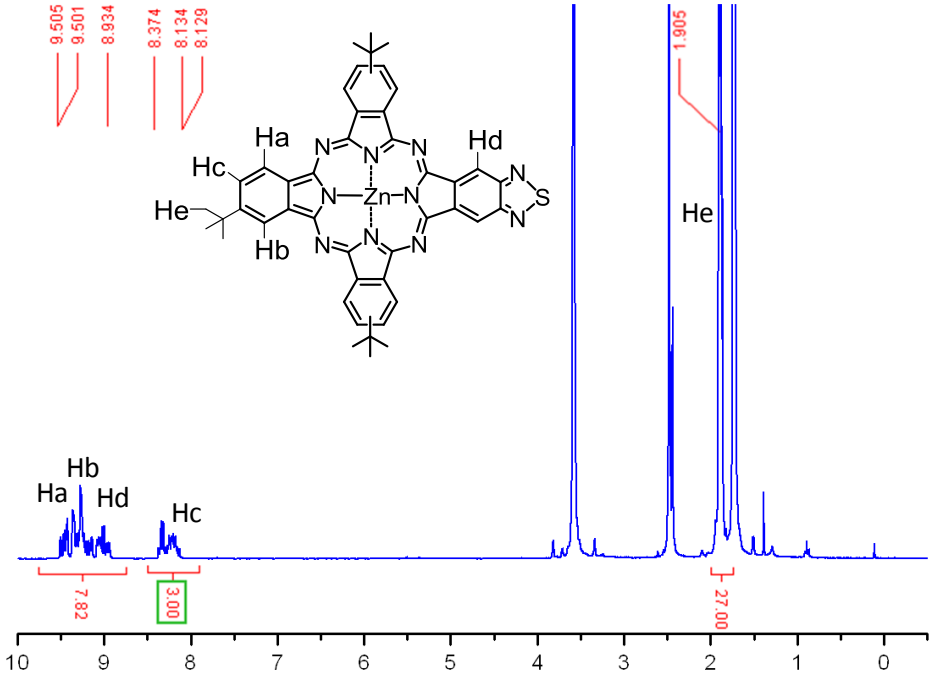

Figure S1. ^{1}H NMR spectrum of **ZnPc 2** in THF-d_8, 300 MHz, 298 K.

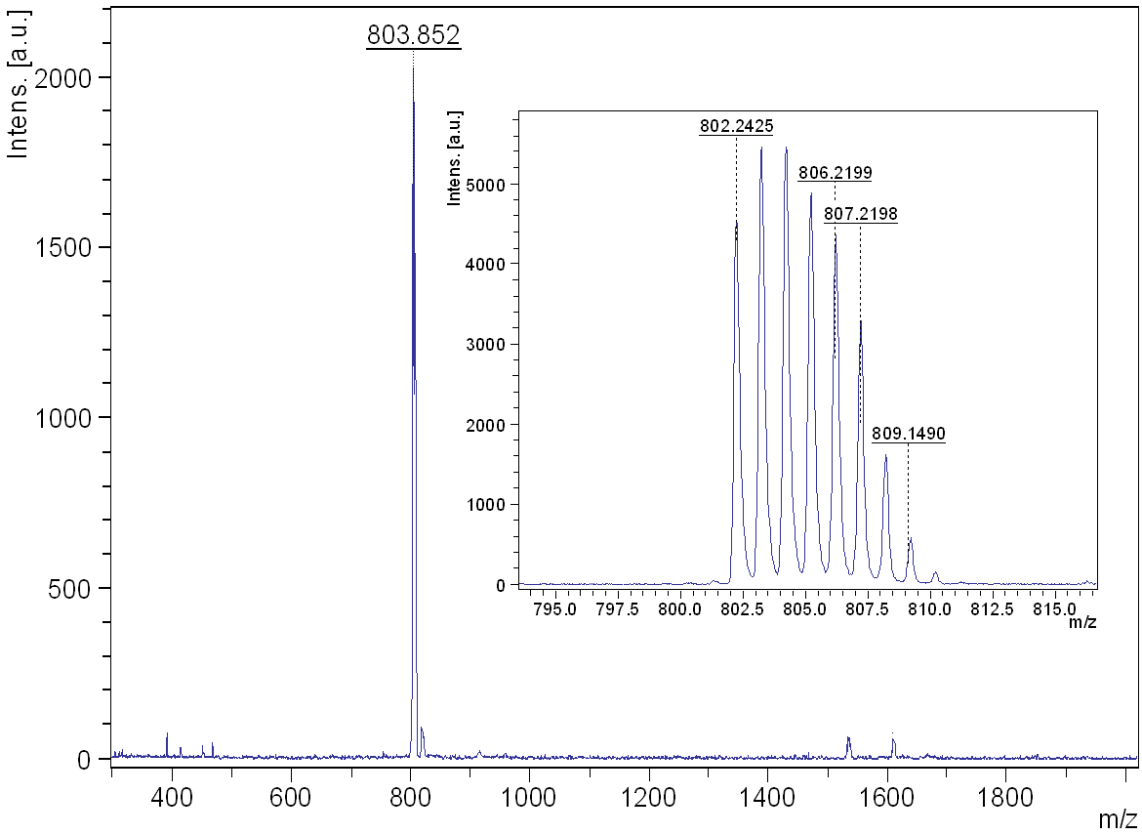

Figure S2. MS of **ZnPc 2**.

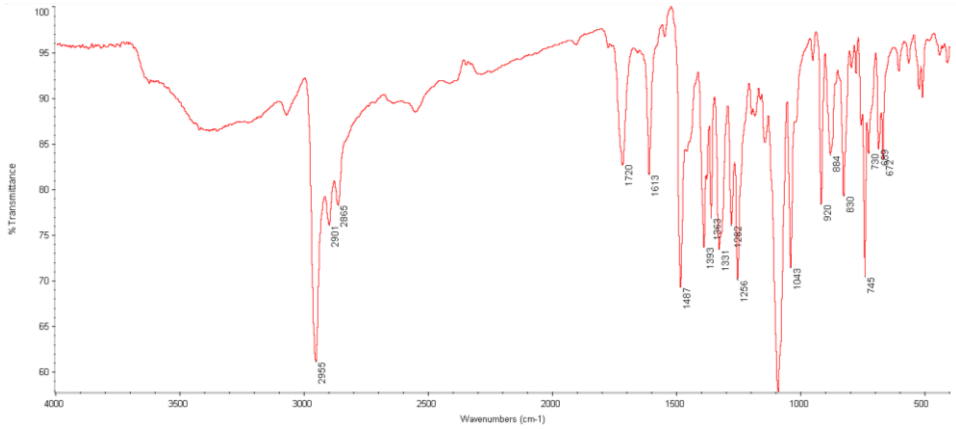

Figure S3.IR Spectrum (KBr) of **ZnPc 2**.

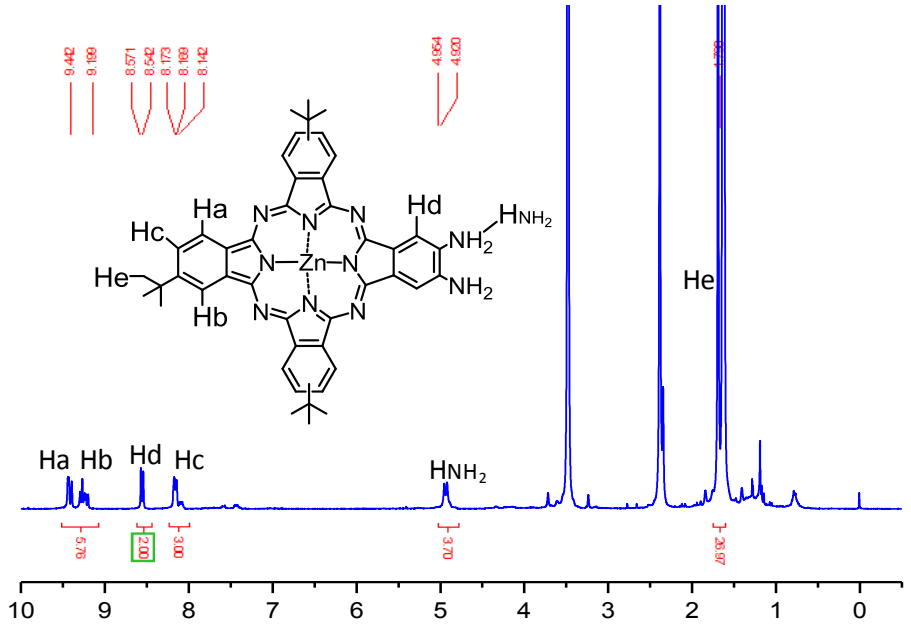

Figure S4.[1]H NMR spectrum of **ZnPc 3** in THF-d_8, 300 MHz, 298 K.

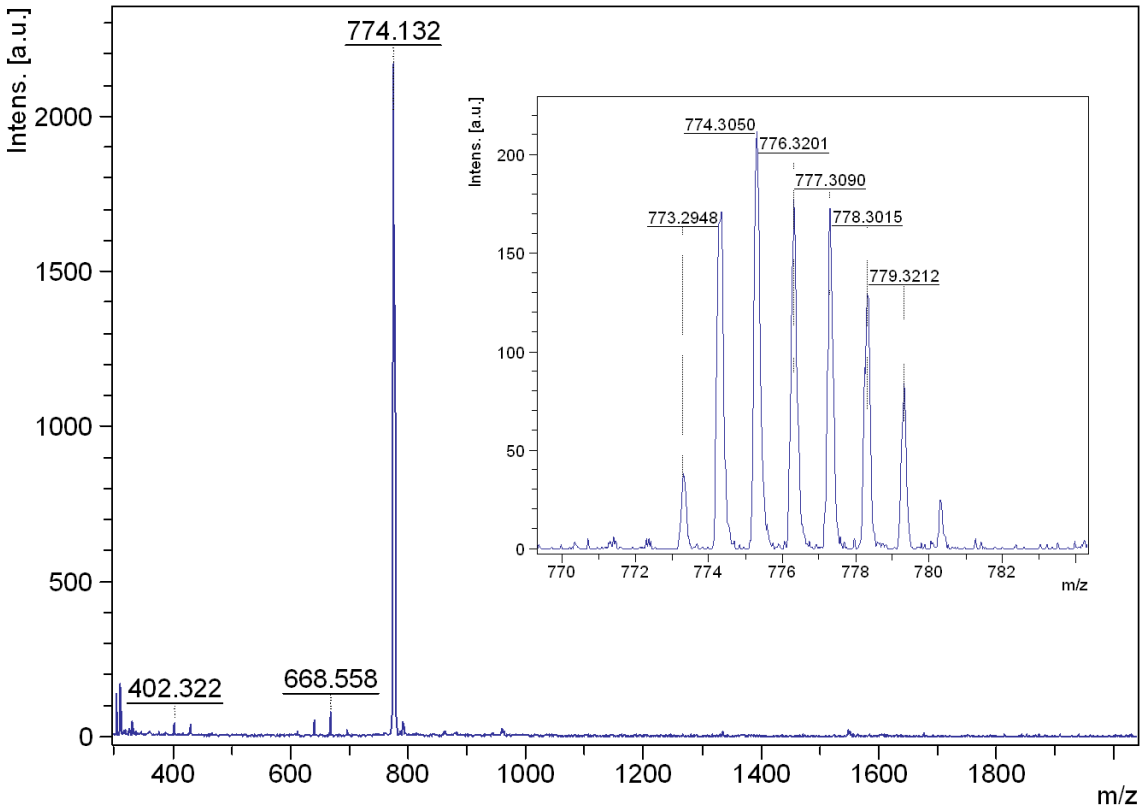

Figure S5. MS of **ZnPc 3**.

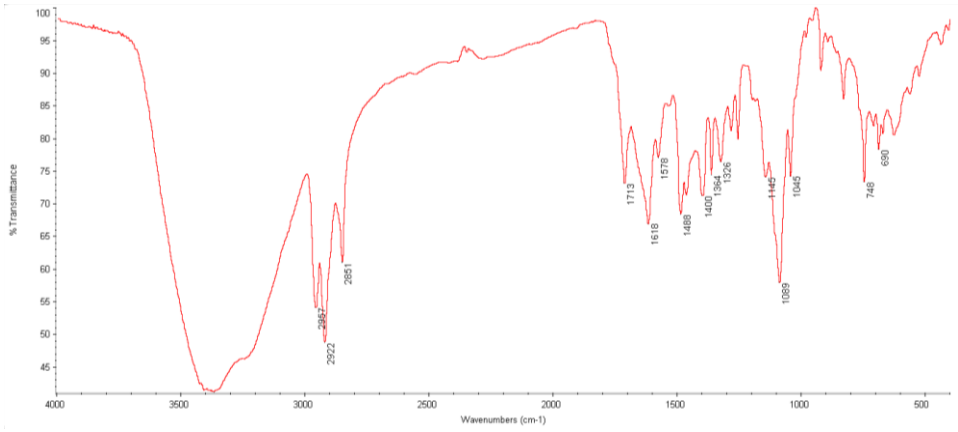

Figure S6.IR Spectrum (KBr) of **ZnPc 3**.

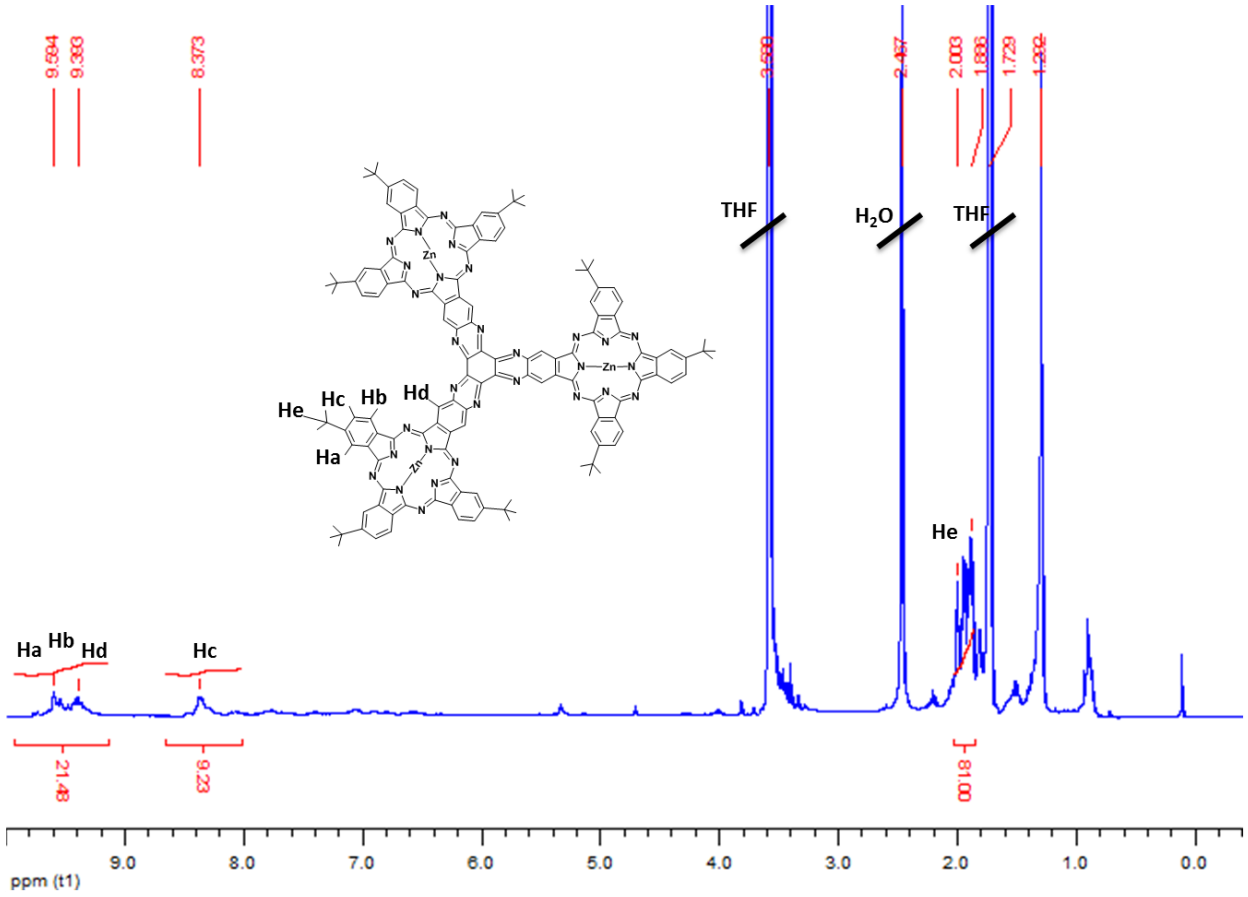

Figure S7. ^{1}H NMR spectrum of Triad **HAT(ZnPc)$_3$ 1** in THF-d_8, 300 MHz, 300 K.

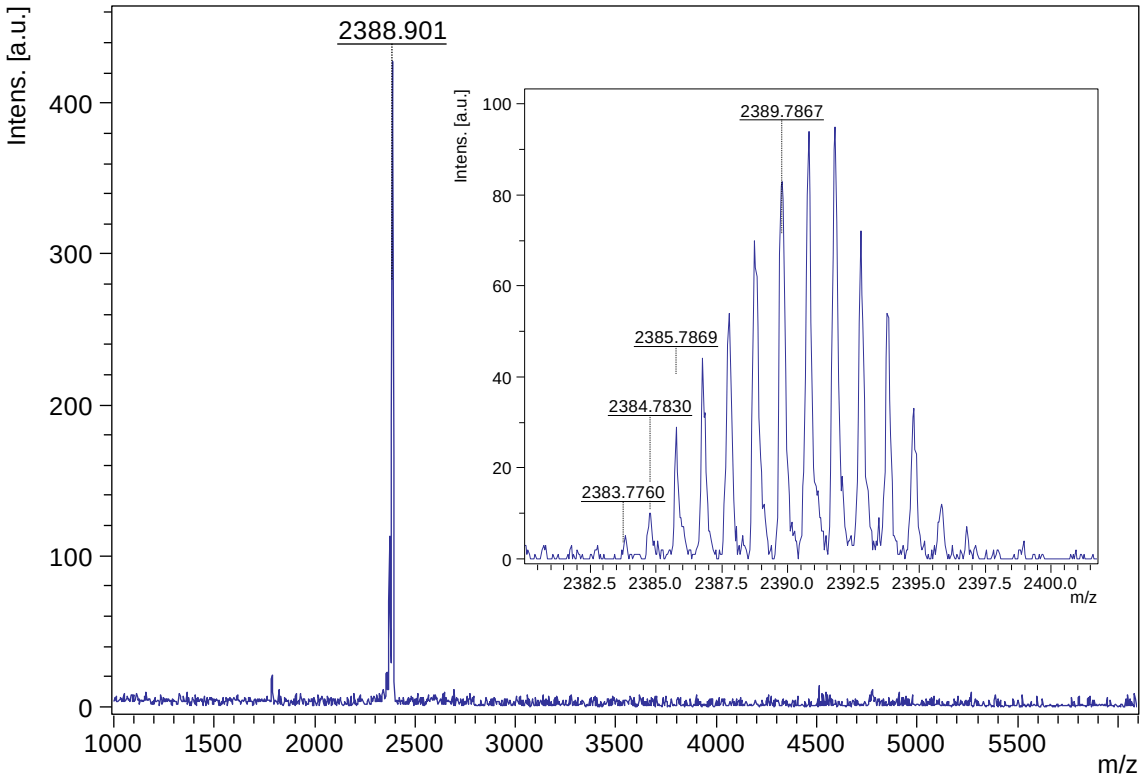

Figure S8. MS of Triad **HAT(ZnPc)$_3$ 1.**

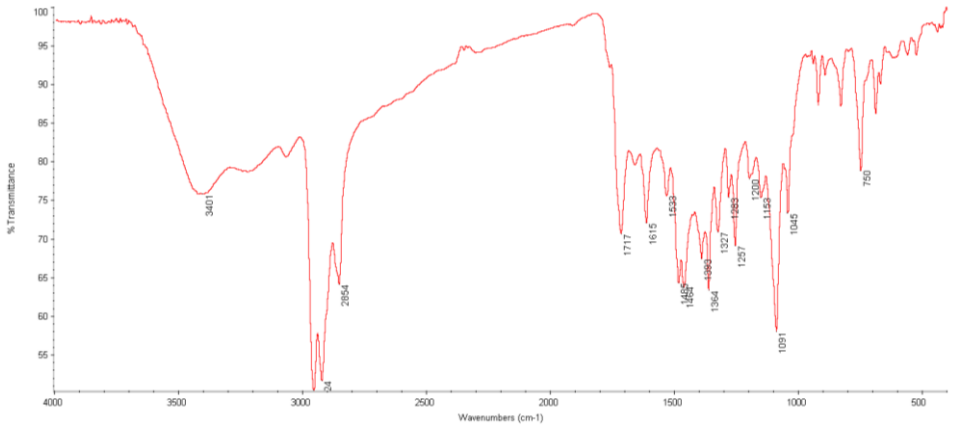

Figure S9.IR Spectrum (KBr) of Triad **HAT(ZnPc)$_3$ 1**.

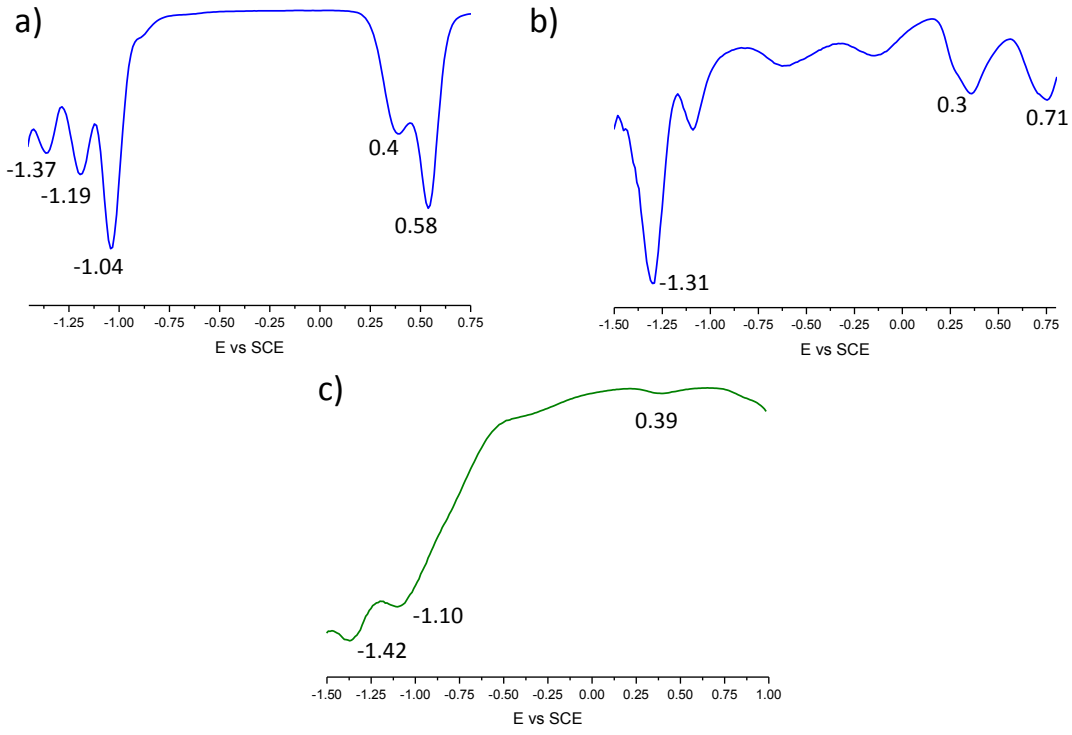

FIGURE S10: DPV of a) **ZnPc 2**, b) **ZnPc 3** and c) **HAT(ZnPc)$_3$ 1** *vs* SCE.