Supporting Information

β-Octakis(methylthio)porphycenes: Synthesis, Characterisation and Third Order Nonlinear Optical Studies

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Instrumentation and reagents:

NMR spectra were recorded on Bruker Avance-400 MHz and 500 MHz FT NMR spectrometer tetramethylsilane (TMS, $\delta = 0$ for proton) and solvent peak for ^{13}C is used as an internal standard at room temperature. Mass spectral determinations were carried out by Bruker Maxis HRMS by ESI techniques. Melting points were determined by a Lab India MR-VIS$^+$ visual melting point apparatus and uncorrected. IR spectra were recorded on NICOLET 5700 FT-IR spectrometer. All UV-VIS spectra were recorded using Perkin Elmer Lambda-750 UV-VIS-NIR spectrometer. All fluorescence spectra were recorded in Fluorolog-3-221 spectrofluorometer.

The steady-state luminescence of singlet oxygen of porphycene **1** and their M(II) complex was measured by using a Fluorolog-3-221 spectrofluorometer equipped with Hamamatsu H10330-75 TE cooled NIR detector. Tetraphenylporphyrin (**H_2TPP**) in toluene was taken as standard (ϕ_Δ 0.7). All samples exhibit the emission bands ranging from 1240 to 1320 nm with the peak maxima at about 1278 nm. The singlet oxygen quantum yields ϕ_Δ for all samples can be determined by using eq 1 (comparative actinometry method):[S1]

$$\phi_\Delta = \phi^{std}_\Delta \frac{I \ \ 1 - 10^{-A^{std}}}{I_{std} \ \ 1 - 10^{-A}} \qquad (1)$$

where ϕ^{std}_Δ (0.7) is the singlet oxygen quantum yield of **H_2TPP** as the standard sample in aerated toluene, I and I_{std} refer to the singlet oxygen emission intensities at the peaks for the tested sample and **H_2TPP**, respectively, and A and A^{std} stand for the ground-state absorbance of the tested sample and **H_2TPP** at the excited wavelength. Each sample was recorded for three times under identical condition and average value was taken to determine peak intensity.

The femtosecond time-resolved transient absorption (fs-TA) spectrometer consists of an optical parametric amplifier (OPA; Palitra, Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C, Quantronix) operating at 1 kHz repetition rate and an optical detection system. The generated OPA pulses have a pulsewidth of ~ 100 fs and an average power of 100 mW in the range 280-2700 nm, which are used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3 mm thick) by focusing a small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by a High Speed spectrometer (Ultrafast Systems) for both visible and near-infrared measurements. To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses excite the samples to obtain the fs-TA spectra at each delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization-dependent signals. Cross-correlation *fwhm* in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in the probe beam path and a quartz cell of 2 mm path length were used. After fs-TA experiments, the absorption spectra of all compounds were carefully examined to detect if there were artifacts due to degradation and photo-oxidation of samples. The three-dimensional data sets of ΔA versus time and wavelength were subjected to singular value decomposition and global fitting to obtain the kinetic time constants and their associated spectra using Surface Xplorer software (Ultrafast Systems).

The two-photon absorption spectrum was measured in the NIR region using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a repetition rate of 1 kHz generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). After passing through a 10 cm focal length lens, the laser beam was focused and passed through a 1 mm quartz cell. Since the position of the sample cell could be controlled along the laser beam direction (z axis) using the motor controlled delay stage, the local power density within the sample cell could be simply controlled under constant laser intensity. The transmitted laser beam from the sample cell was then detected by the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 60 GW cm^{-2}. For a Gaussian beam profile, the nonlinear absorption coefficient can be obtained by curve fitting of the observed open-aperture traces *T(z)* with the following equation:

$$T(z) = 1 - \frac{\beta I_0(1 - e^{-\alpha_0 l})}{2\alpha_0[1 + \left(\frac{z}{z_0}\right)^2]}$$

where α_0 is the linear absorption coefficient, l is the sample length, and z_0 is the diffraction length of the incident beam. After the nonlinear absorption coefficient has been obtained, the TPA cross section $\sigma^{(2)}$ of one solute molecule (in units of GM, where 1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}) can be determined by using the following relationship:

$$\beta = \frac{10^{-3}\sigma^{(2)}N_A d}{h\nu}$$

where N_A is the Avogadro constant, d is the concentration of the compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.

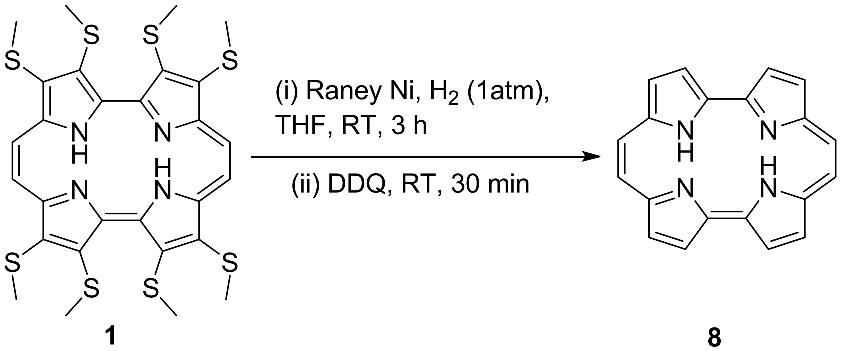
Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using Zahner Zennium Electrochemical Workstation and electrodes were purchased from CH Instruments

Inc. The solution was deaerated by purging with oxygen free ultra-high pure nitrogen for 15 min prior each measurement. All measurements were done in dichloromethane with constant flow of nitrogen over solution and 0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) used as a supporting electrolyte. Platinum disc as working electrode, platinum wire as counter electrode and Ag/AgCl in 1(M) KCl as reference electrode were used. Ferrocenium/Ferrocene, Fc^+/Fc couple (0.48 V *vs* SCE) was used as external reference for calibration. The redox potentials were referenced *vs.* saturated calomel electrode (SCE). All cyclic voltammetric data were recorded at 50 mV/s scan rate.

Crystallographic data for **1** and **7** were collected on Oxford Gemini A Ultra diffractometer with dual source. Mo-Kα (λ = 0.71073 Å) radiation was used for **1** and Cu-Kα (λ = 1.54184 Å) radiation was used for **7** to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlisPro 171.33.55 software.[S2] Structures were solved and refined using Olex2-1.0 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON[S3] did not show any missed symmetry.

Porphycene **1** and bipyrrole dialdehyde **7** were crystallized by slow evaporation of benzene and chloroform solution respectively. Crystallographic data (excluding the structure factor) for structures **1** and **7** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1052052 and 1052053 respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Scheme:



Scheme S1: Synthesis of porphycene **8**.

Detailed Synthetic Procedure:

Synthesis of 3,3',4,4'-tetrakis(methylthio)-2,2'-bipyrrole (6):

To a stirred solution of 3,4-dimethylthiopyrrole (**5**) (800 mg, 5.02 mmol) in dry CH_2Cl_2 (80 mL), PIFA (1.08 g, 2.51 mmol) and $BF_3.OEt_2$ (620 µL, 5.02 mmol) were quickly added at –78 °C under nitrogen. The reaction mixture was then stirred for 3 hour, while the reaction temperature was maintained below –40 °C. After the reaction completion, saturated aqueous $NaHCO_3$ (ca. 100 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 .The combined extract was dried with anhydrous Na_2SO_4 and evaporated to dryness under reduce pressure. The crude reaction mixture was purified by silica gel column using EtOAc/hexane (1:9) as eluent gives desired **6** (272 mg) as white crystalline solid. Yield: 34%; m.p: 170.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 10.99 (br s, 2H), 6.84 (d, 2H, *J* = 2.8 Hz), 2.41 (s, 6H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):127.74, 121.10, 119.51, 110.79, 20.67, 19.94; HRMS (ESI+): m/z: calculated for $C_{12}H_{17}N_2S_4$ ($M+H^+$): 317.0269; found: 317.0273.

Synthesis of 3,3',4,4'-tetrakis(methylthio)-[2,2'-bipyrrole]-5,5'-dialdehyde (7):

3,3',4,4'-tetrakis(methylthio)-2,2'-bipyrrole (**6**) (500 mg, 1.58 mmol) in dry DCE (15 mL) was rapidly added to ice cooled stirred Vilsmeier-Haack formylating mixture prepared from freshly distilled $POCl_3$ (737 µL, 7.91 mmol) and dry DMF (700 µL, 8.69 mmol) in dry DCE (10 mL) under nitrogen. After addition was over ice-bath was replaced with oil bath and the reaction mixture was refluxed for 4 h. Then reaction mixture was cooled on ice bath and sat. NaOAc (3.24 g, 39.5 mmol) in water (20mL) added carefully and refluxed the reaction mixture for additional 2 h resulting precipitation of the product **7** as yellow fibrous crystalline solid. After cooling to room temperature, the reaction mixture was filtered, washed with water to leave the desired compound as yellow crystalline solid and some additional compound was also obtained from the evaporation of DCE layer under reduce pressure. Yield: 552 mg (93%); m.p: 264 °C; IR (neat): ν (cm^{-1}) 3266, 1644; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 11.81 (br s, 2H), 9.91 (s, 2H), 2.53 (s, 6H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 179.00, 132.95, 132.79, 130.45, 119.15, 20.81, 20.28; UV-Vis data in $CHCl_3$, λ_{max} nm (log ε): 370 (4.32), 388 (4.38); Fluorescence in $CHCl_3$ λ_{max} nm : 450; Fluorescence quantum yield in $CHCl_3$ (ϕ_f): 0.08; HRMS (ESI+): m/z: calculated for $C_{14}H_{17}N_2O_2S_4$ ($M+H^+$): 373.0167; found: 373.0177. Elemental analysis Calcd for $C_{14}H_{17}N_2O_2S_4$: C, 45.13; H, 4.33; N, 7.52. Found: C, 45.26; H, 4.26; N, 7.58.

Synthesis of 2,3,6,7,12,13,16,17-octa(methylthio)porphycene (1):

To a slurry of low-valent titanium reagent, generated by reduction of titanium tetrachloride (1.48 mL, 13.5 mmol) in dry THF (180 mL) with activated zinc (1.77 g) and CuCl (268 mg, 1.35 mmol) by refluxing 3 h, a solution of **8** (200 mg, 0.54 mmol) in dry THF (120 mL) was added dropwise slowly over 2 h under reflux condition with vigorous stirring. The reaction mixture was heated under reflux for an additional 1 h and then hydrolyzed by slow addition of 10% aqueous sodium carbonate (ca. 100 mL) to the ice cooled reaction mixture. Filtered through celite to remove the excess metal, washed with chloroform and organic layer was separated. Organic layer was evaporated to dryness under reduced pressure. Resulting crude reaction mixture was dissolved in DCM (50 mL), washed with water, organic layer was passed through anhydrous sodium sulphate and evaporated to dryness under reduced pressure. Unoxidised crude reaction mixture was dissolved in $CHCl_3$ (100 mL) and DDQ (62 mg, 0.27 mmol) was added, stirred at room temperature for 1 h. Then, chloroform was evaporated under reduce pressure. The crude reaction mixture was purified by silica gel column chromatography using $CHCl_3$ as eluent thus resulted greenish-blue fraction was collected, yields compound **1** (31 mg) as blue purple crystalline solid. Yield: 17%. m.p: > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.68 (s, 4H), 3.08 (s, 12H), 2.98 (s, 2H), 2.65 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 144.94, 141.70, 138.63, 135.46, 114.07, 20.08, 20.01; UV-Vis data in $CHCl_3$, λ_{max} nm (log ε): 411 (4.86), 699 (4.70); HRMS (ESI+): m/z: calculated for $C_{28}H_{31}N_4S_8$ ($M+H^+$): 679.0309; found: 679.0313. Elemental analysis Calcd for $C_{28}H_{30}N_4S_8$: C, 49.52; H, 4.45; N, 8.25. Found: C, 49.63; H, 4.51; N, 8.16.

Synthesis of Zn(II) 2,3,6,7,12,13,16,17-Octa(methylthio)porphycene (Zn1):

To a stirred solution of **1** (10 mg, 0.015 mmol) in chloroform (10 mL) under nitrogen, $Zn(OAc)_2.2H_2O$ (65 mg, 0.30 mmol) in methanol (10 mL) was added and reaction mixture was refluxed for 4 h. Then reaction mixture was evaporated to dryness, re-dissolved in chloroform, washed with water, $CHCl_3$ layer was passed through anhydrous Na_2SO_4 and evaporated under reduce pressure. Crude product was finally purified by activated neutral alumina flash column using chloroform/ methanol (99:1) as eluent to obtain **Zn1** (7.6 mg) as purple solid. Yield: 68%. m.p: 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.94 (s, 4H), 3.01 (s, 12H), 2.81 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm):145.65, 145.58, 143.02, 113.78, 20.88, 20.74; UV-Vis data, λ_{max} nm (log ε): 409 (4.75), 664 (4.30), 719 (4.68); HRMS (ESI+): m/z:

calculated for $C_{28}H_{28}N_4S_8ZnNa$ ($M+Na^+$): 762.9263; found: 762.9268. Elemental analysis Calcd for $C_{28}H_{28}N_4S_8Zn$: C, 45.30; H, 3.80; N, 7.55. Found: C, 45.26; H, 3.72; N, 7.65.

Synthesis of Ni(II) 2,3,6,7,12,13,16,17-octa(methylthio)porphycene (Ni1):

To a stirred solution of **1** (10 mg, 0.015 mmol), Ni(acac)$_2$ (77 mg, 0.30 mmol) in *o*-xylene (10 mL) was added and refluxed for 4 h. After reaction mixture was cooled to room temperature, *o*-xylene was evaporated under reduced pressure and crude compound was purified by silica gel column chromatography using chloroform/hexane (1:1) as eluent to obtain **Ni1** (7.3 mg) as purple crystalline solid. Yield: 67%. m.p: 205.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.76 (s, 4H), 2.95 (s, 12H), 2.79 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 147.37, 146.58, 145.24, 135.26, 111.61, 21.19, 21.11; UV-Vis data, λ_{max} nm (log ε): 408 (4.91), 691 (4.83); HRMS (ESI+): m/z: calculated for $C_{28}H_{28}N_4S_8NiNa$ ($M+Na^+$): 756.9325; found: 756.9339. Elemental analysis Calcd for $C_{28}H_{28}N_4S_8Ni$: C, 45.71; H, 3.84; N, 7.61. Found: C, 45.86; H, 3.81; N, 7.73.

Synthesis of porphycene (8):

Porphycene **1** (5 mg, 0.0073 mmol) and Raney Ni (~500 mg, slurry in water) were taken in THF (10 mL) under hydrogen (1 atm, hydrogen balloon). The reaction mixture was stirred for 3 h at room temperature. After completion, reaction mixture was passed through celite and washer with chloroform (3 × 10 mL). Combined organic layer was passed through anhydrous Na_2SO_4 and taken in a conical flask; DDQ (5 mg, 0.0219 mmol) was added and stirred for additional 30 min. Then reaction mixture was evaporated under reduce pressure and purified by silica gel column chromatography by using EtOAc/hexane (1:9) as eluent gives desired product porphycene **8** (1.4 mg) as blue purple crystalline solid. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.84 (s, 4H), 9.68 (d, 4H, $J = 3.2$ Hz), 9.25 (d, 4H, $J = 3.2$ Hz), 3.17 (br s, 2H).

^{1}H and ^{13}C NMR Spectra for compounds:

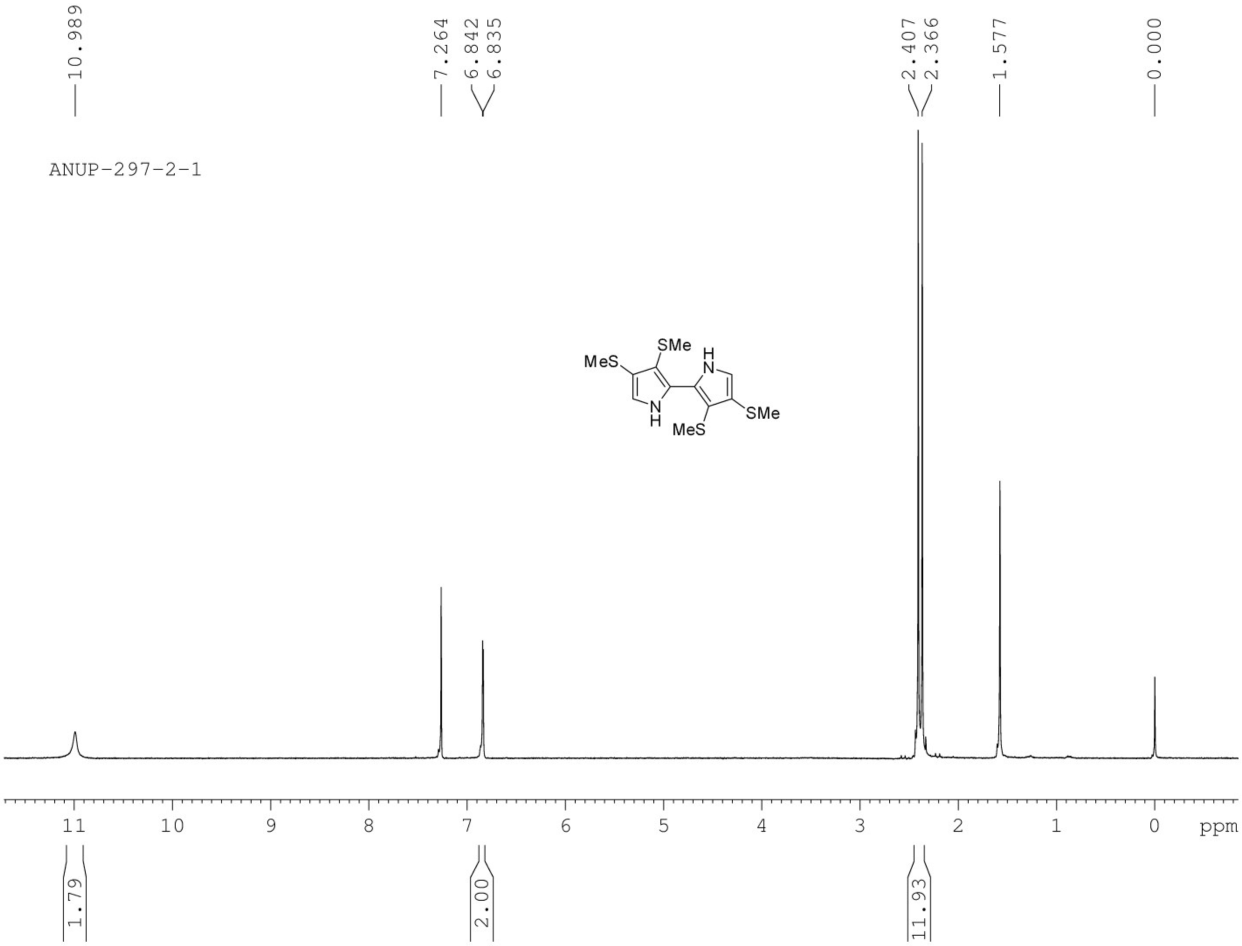


Figure S1: ^{1}H NMR spectrum of **6** in $CDCl_3$.

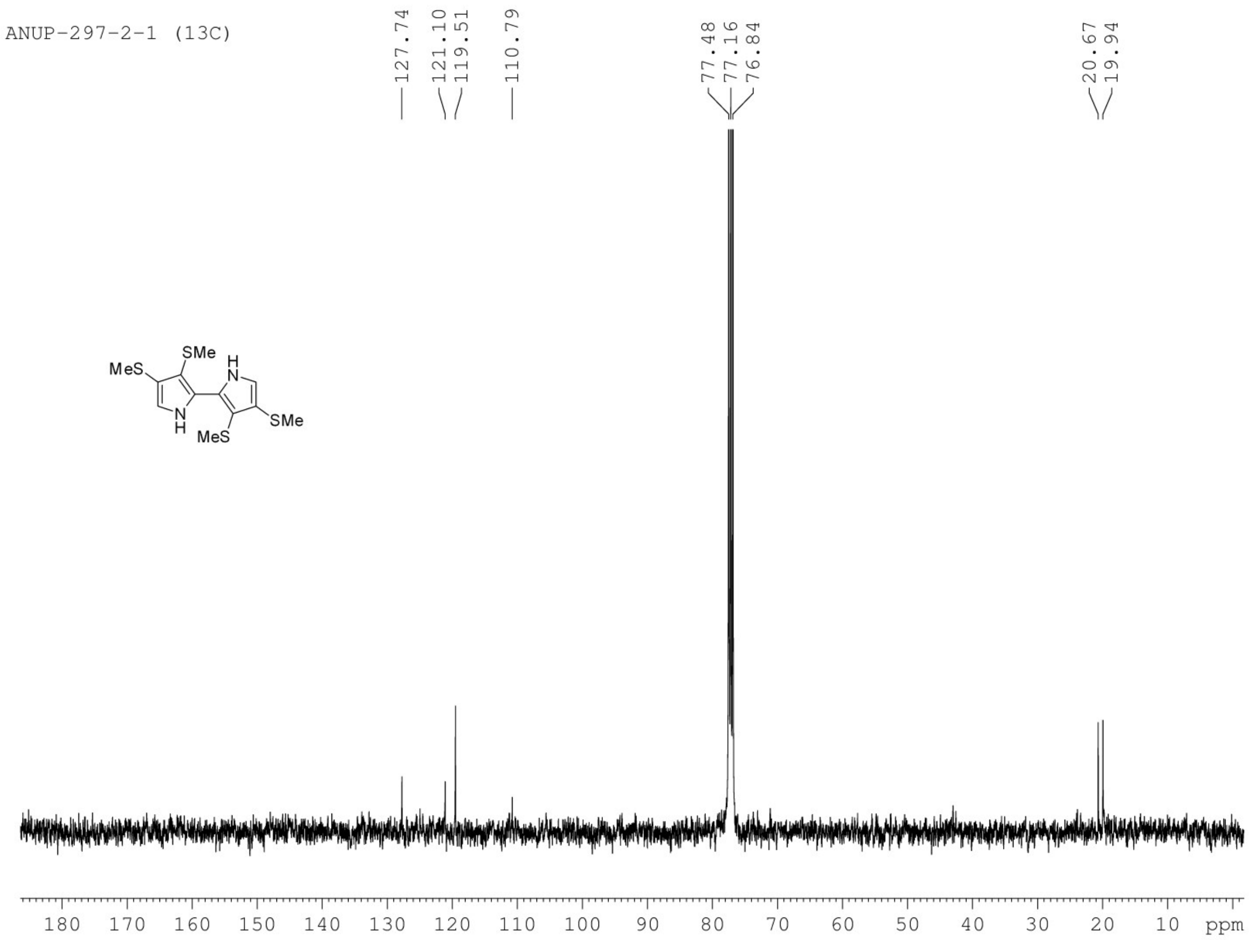


Figure S2: ^{13}C NMR spectrum of **6** in $CDCl_3$.

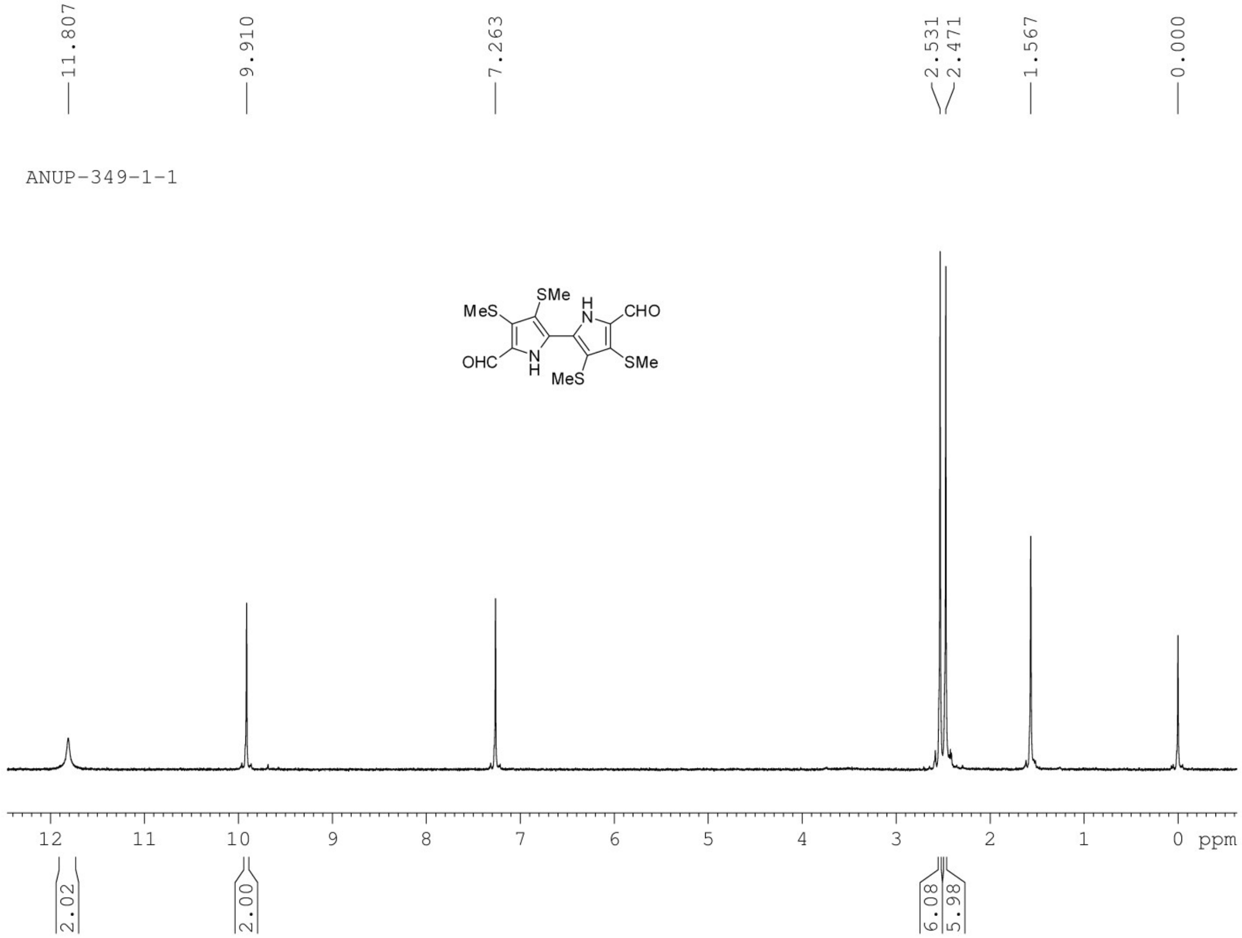


Figure S3: ^{1}H NMR spectrum of **7** in $CDCl_3$.

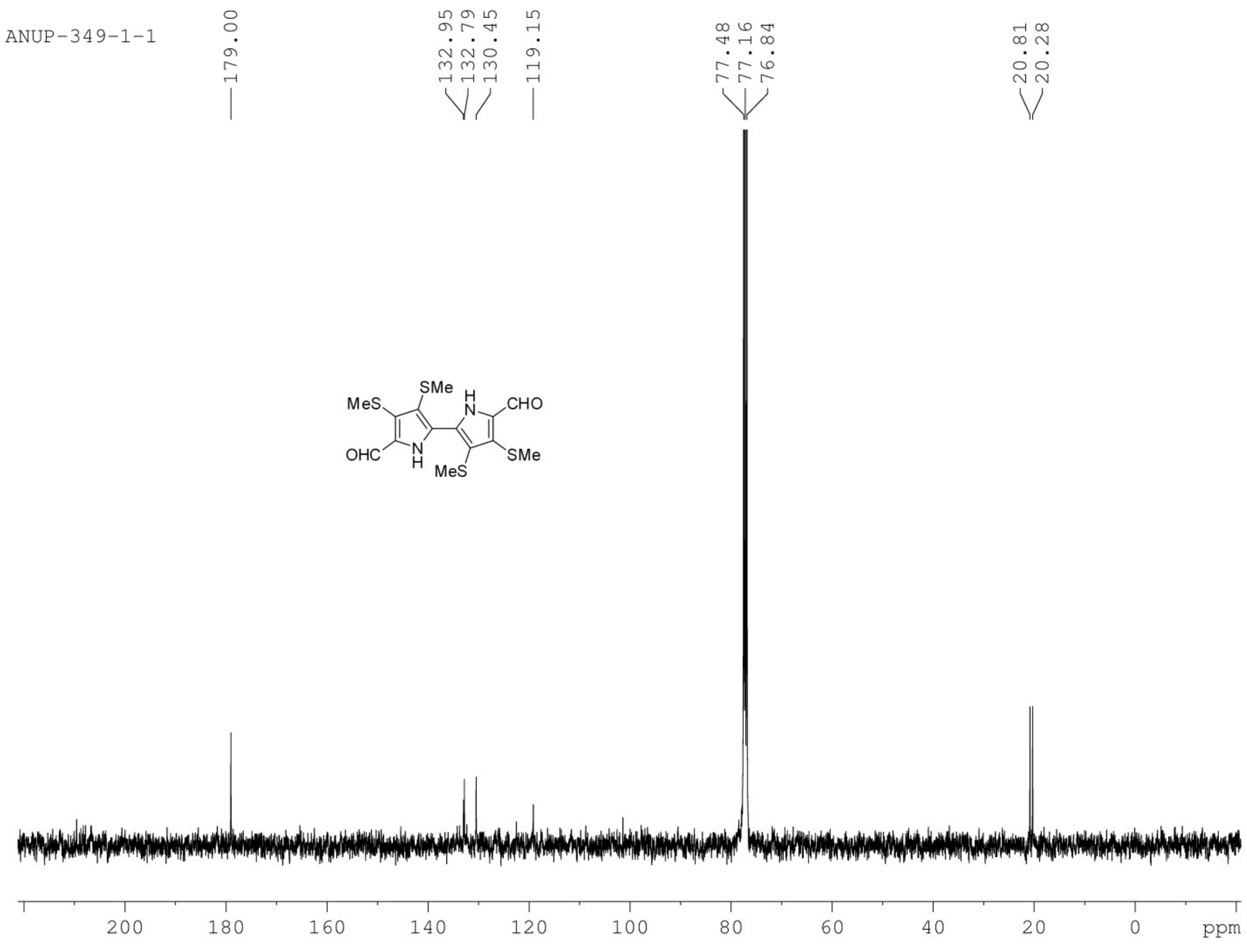


Figure S4: ^{13}C NMR spectrum of **7** in $CDCl_3$.

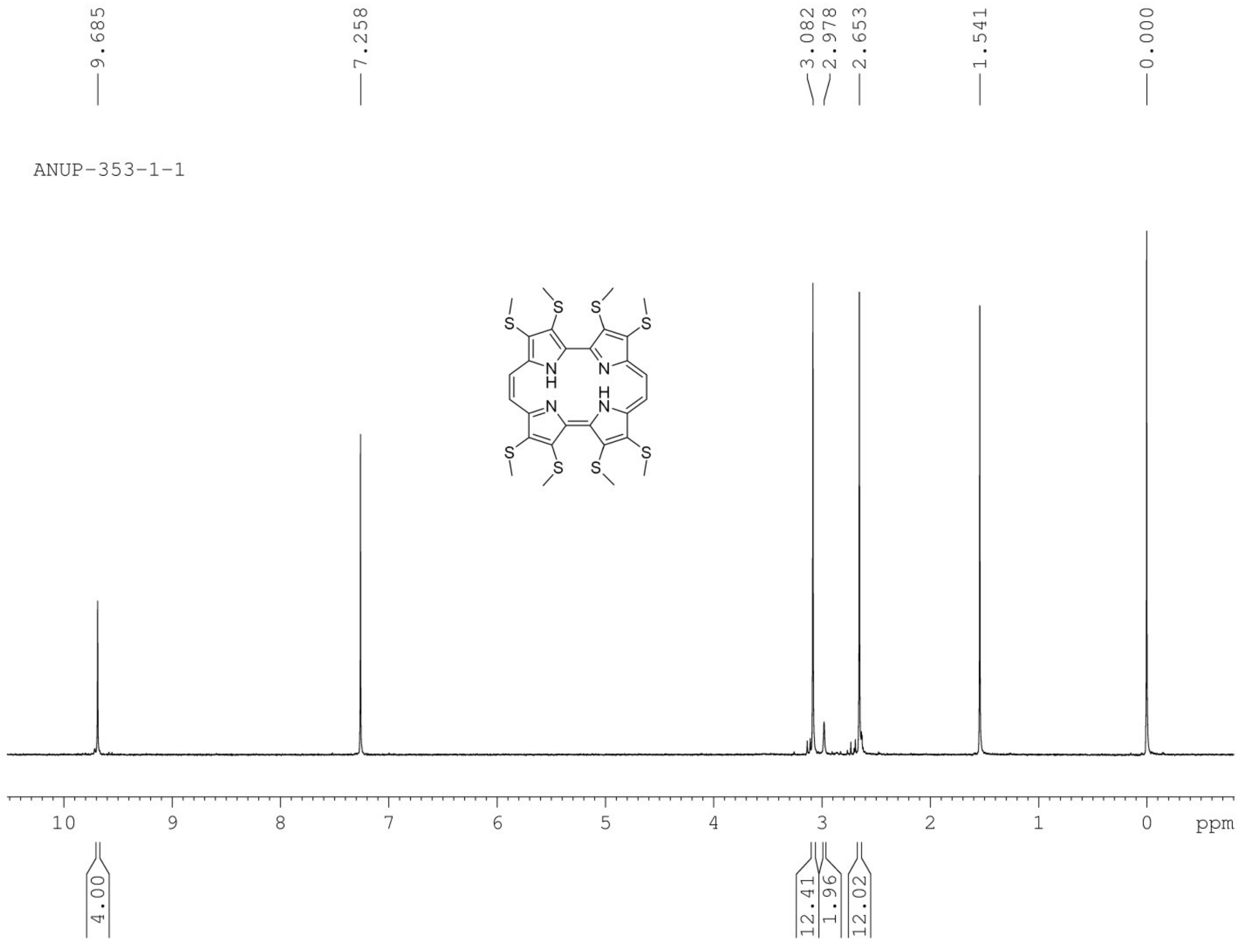


Figure S5: ^{1}H NMR spectrum of **1** in $CDCl_3$.

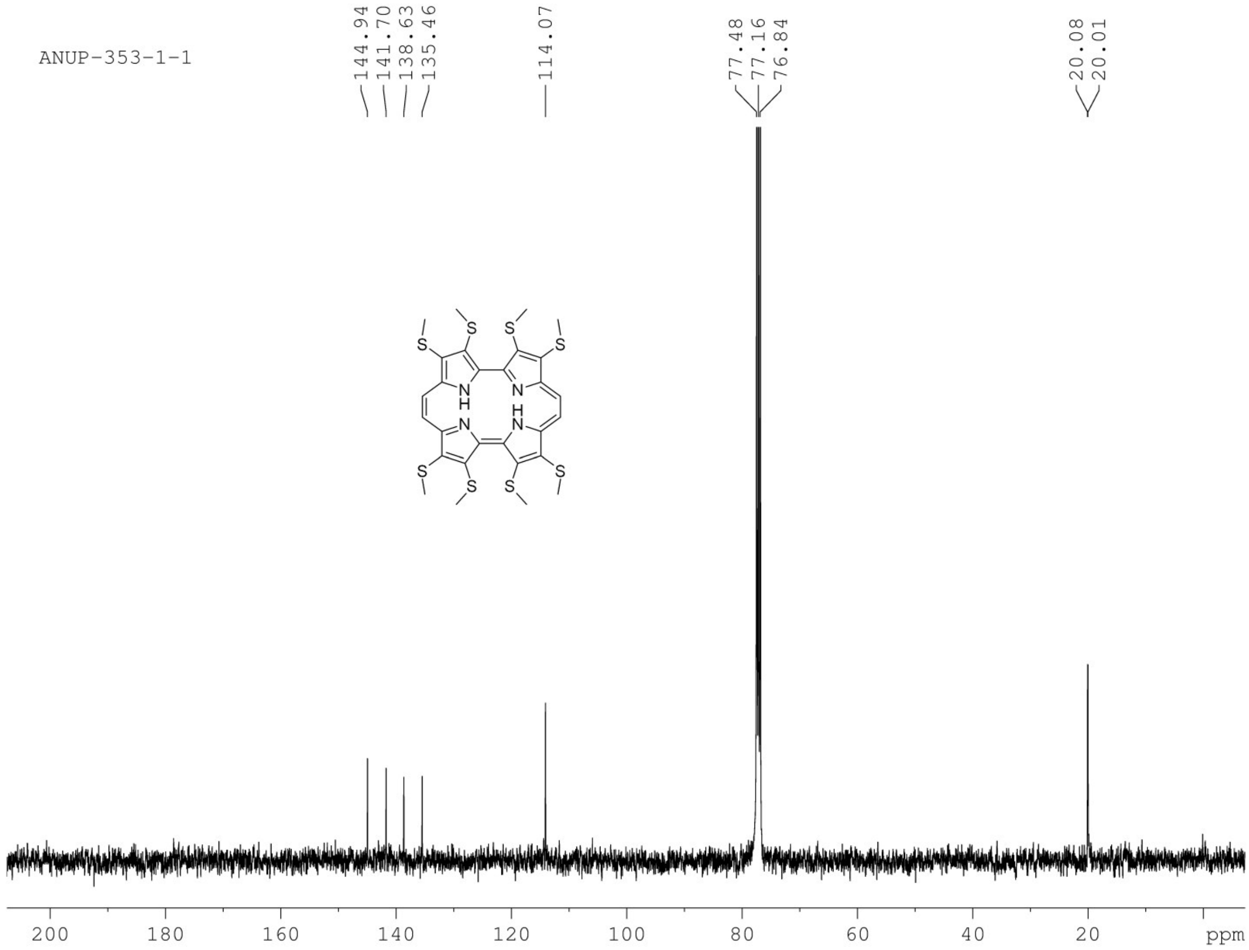


Figure S6: ^{13}C NMR spectrum of **1** in $CDCl_3$.

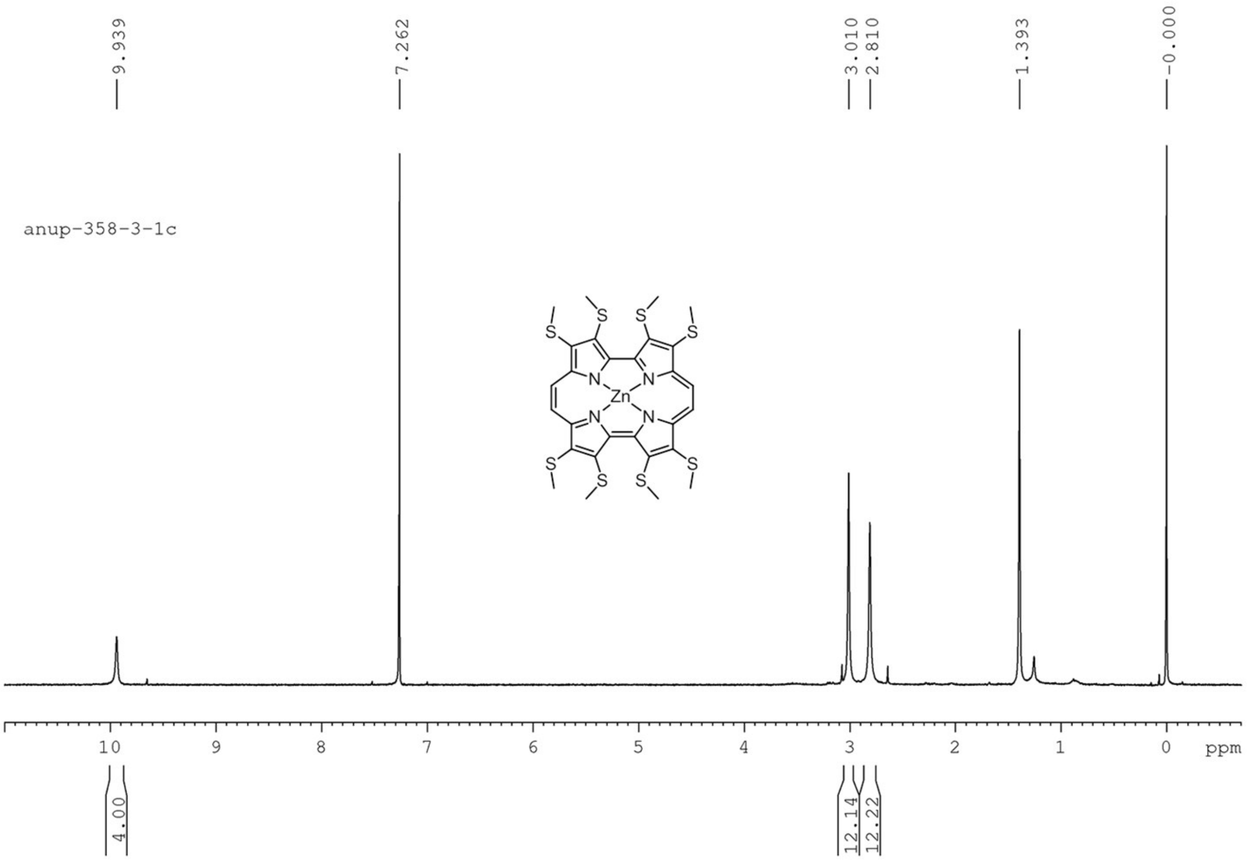


Figure S7: ^{1}H NMR spectrum of **Zn1** in $CDCl_3$.

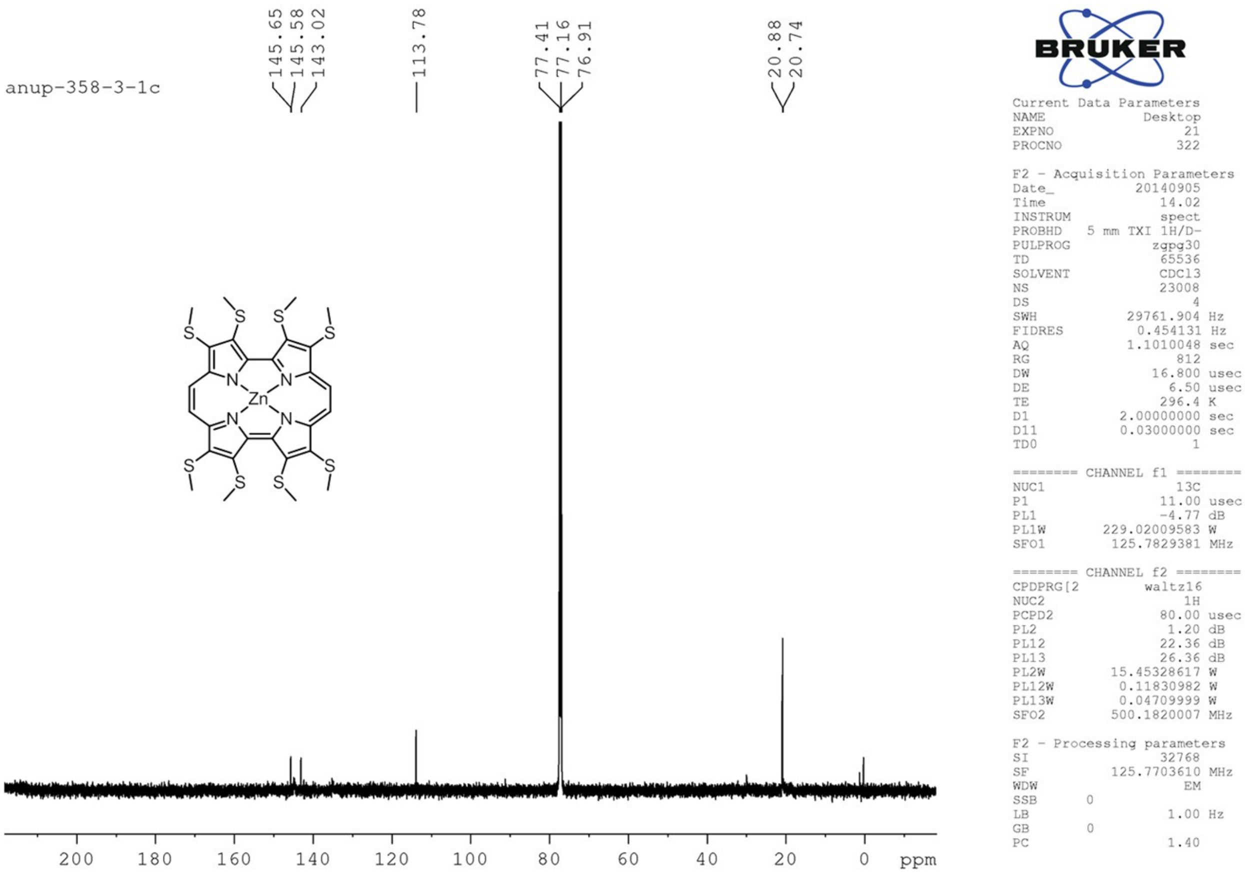


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Figure S7: ^{13}C NMR spectrum of **Zn1** in $CDCl_3$.

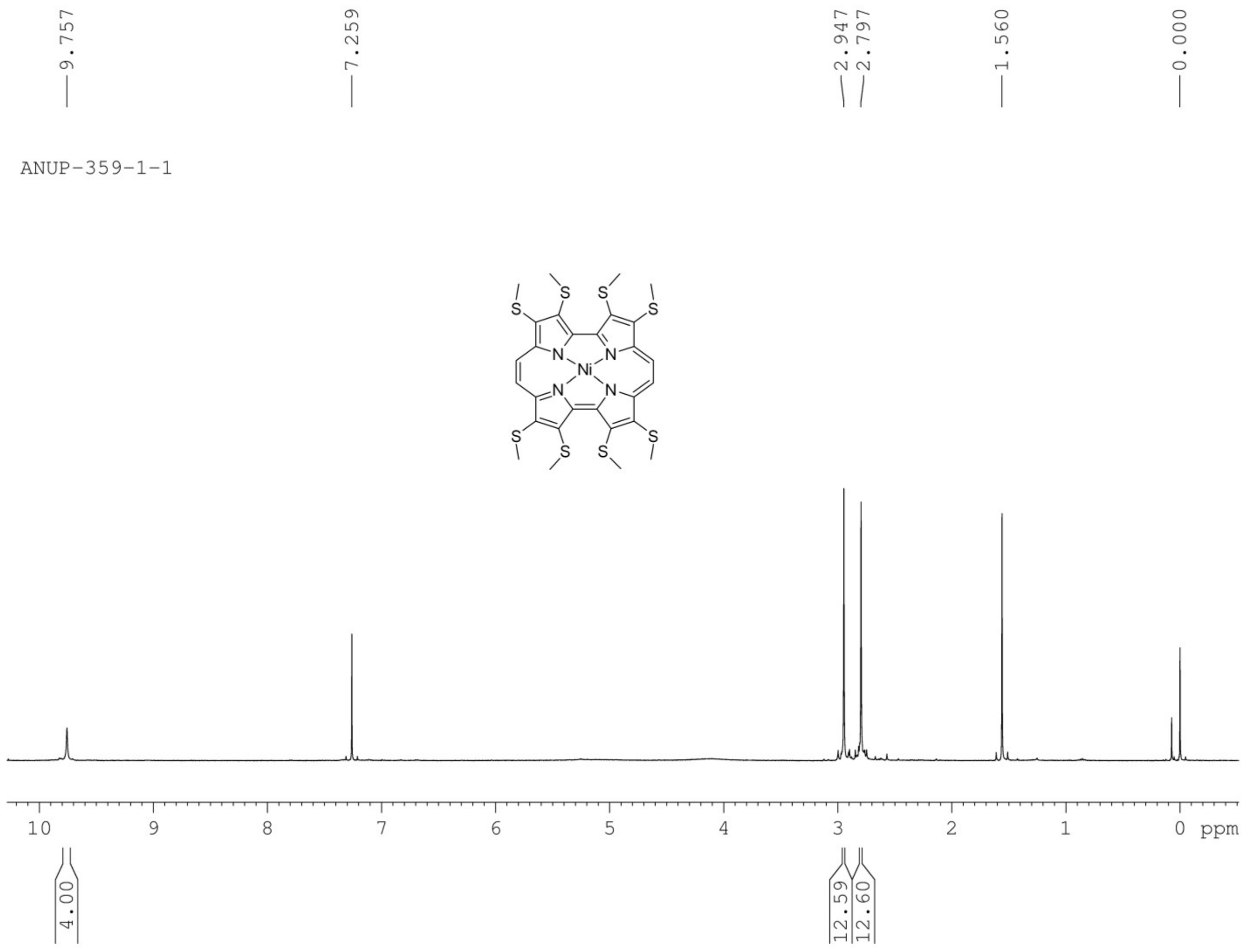

Figure S8: ^{1}H NMR spectrum of **Ni1** in $CDCl_3$.

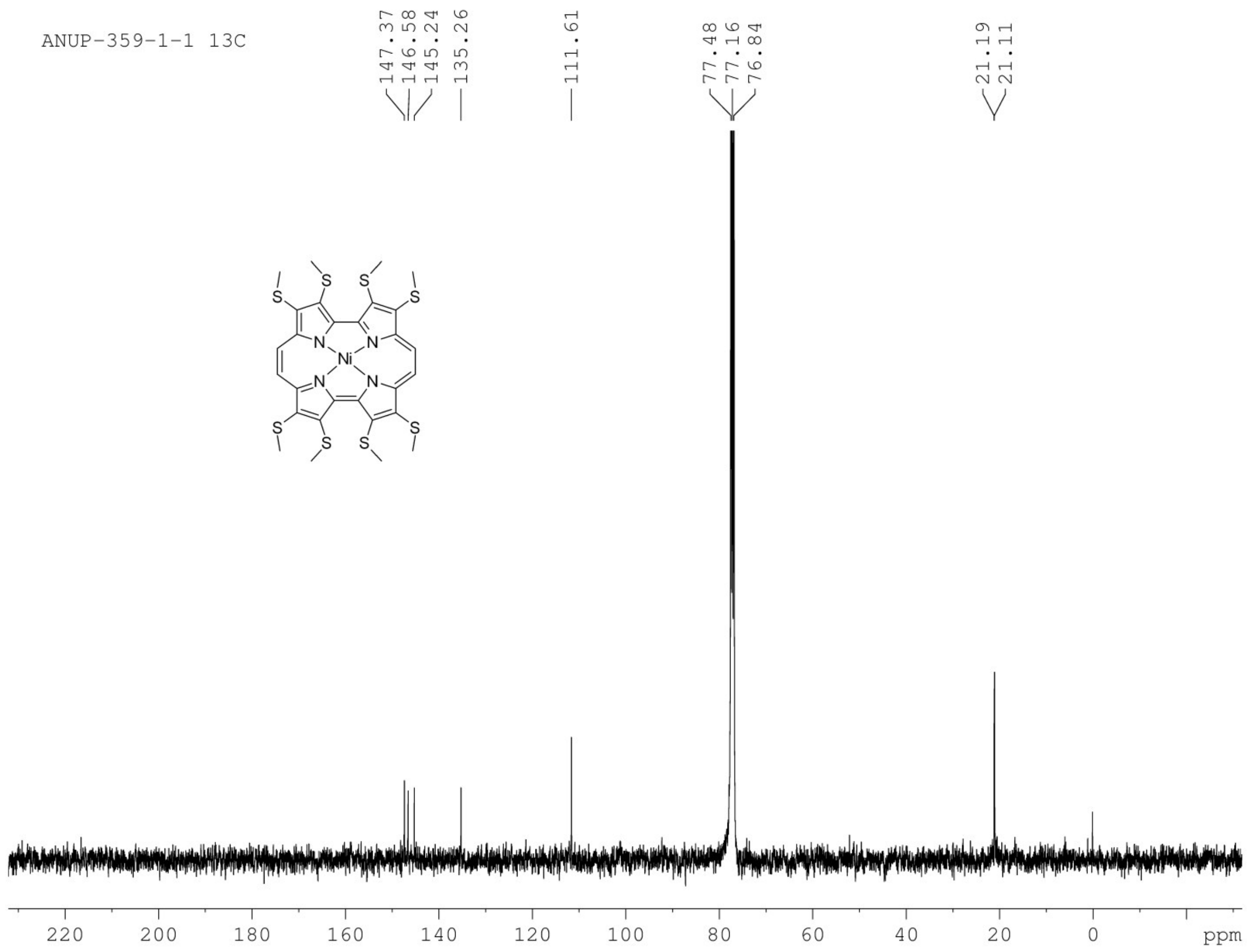

Figure S9: ^{13}C NMR spectrum of **Ni1** in $CDCl_3$.

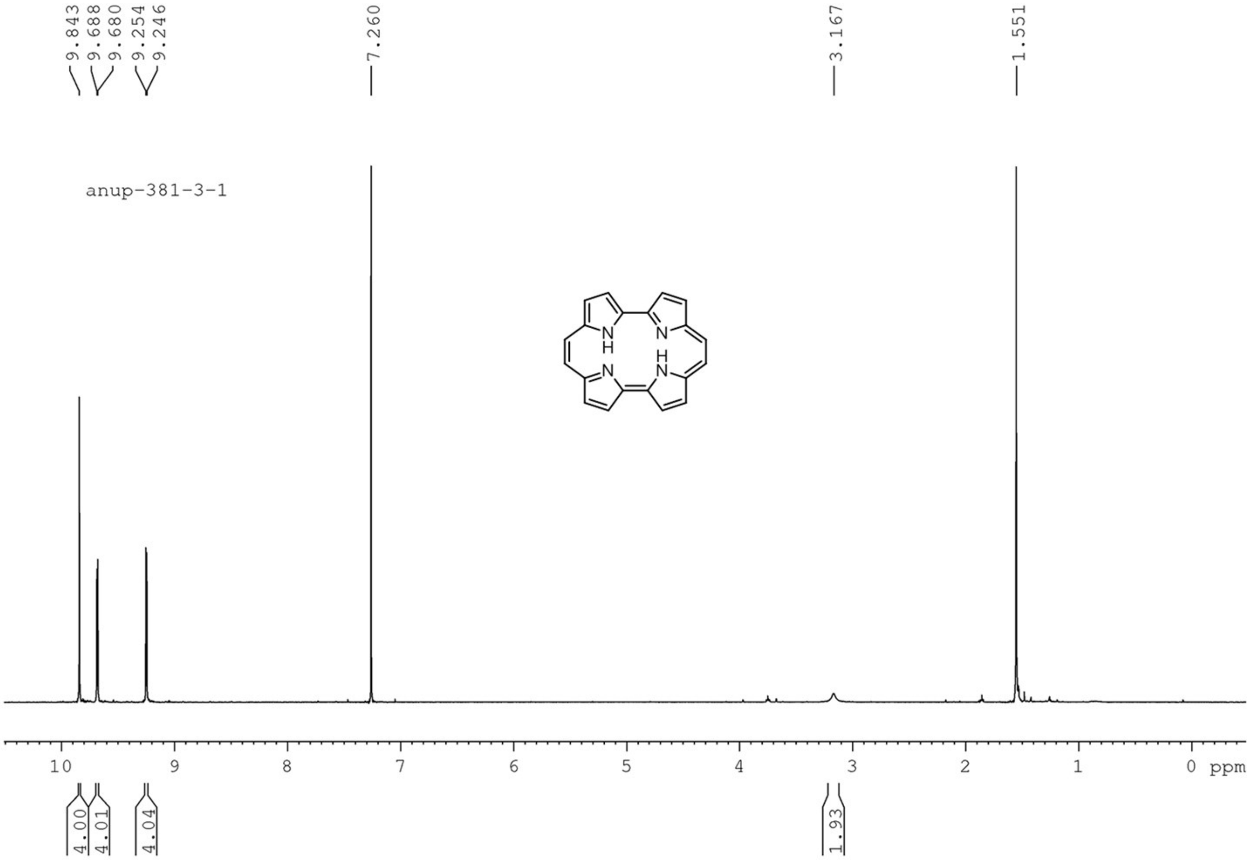

Figure S10: ^{1}H NMR spectrum of **8** in CDCl$_3$.

Crystallographic Data:

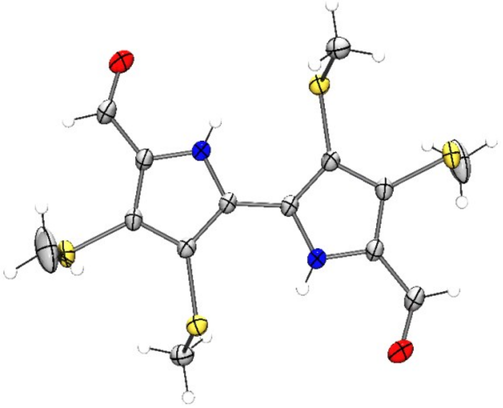

Figure S11: Molecular structure of **7** drawn at 35% probability level. Colour code: grey: C, blue: N, red: O, yellow: S, white: H).

Author's comment on IUCR check.cif alert:

For 1:

PLAT430_ALERT_2_A Short Inter D...A Contact O1 .. N4 .. 1.91 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact O1 .. N1 .. 1.93 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact O1 .. N3 .. 1.94 Ang.

PLAT430_ALERT_2_A Short Inter D...A Contact O1 .. N2 .. 1.95 Ang.

Author Response:

Crystal quality was not good. After several attempts of data collection, reported one is found to be best one. Due to poor data we are not able to model embedded solvent molecule.

Photophysical Data:

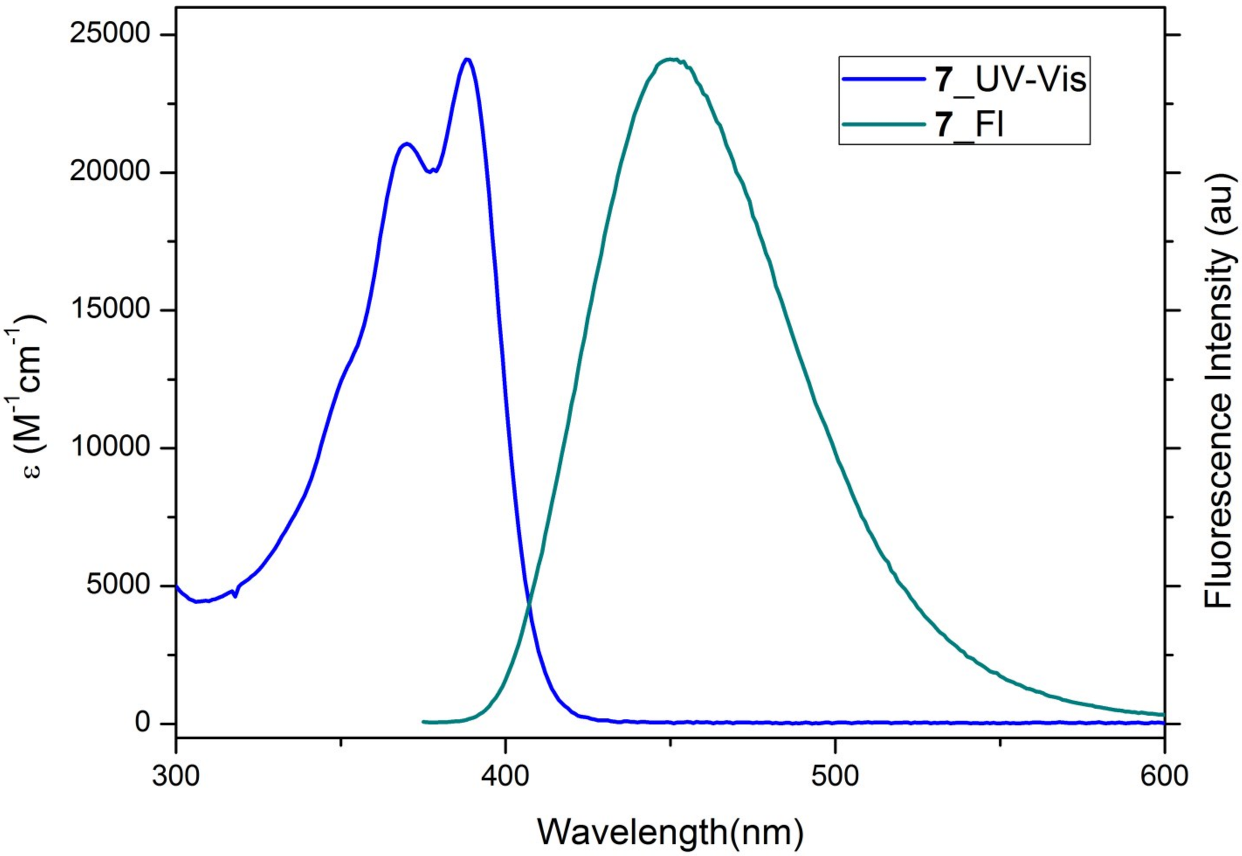

Figure S12: UV-Vis and fluorescence spectra of **7** in $CHCl_3$.

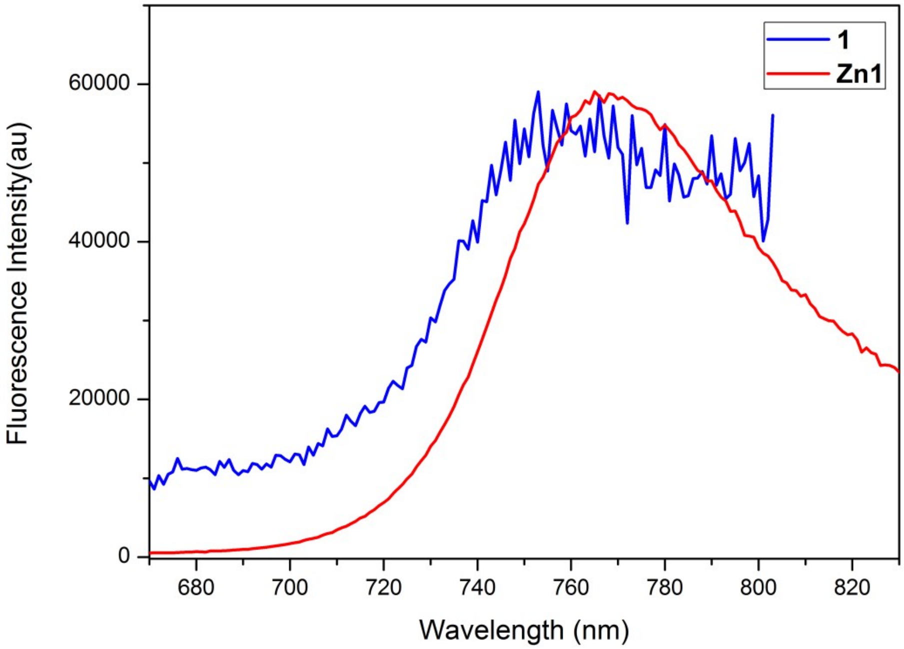

Figure 13: Fluorescence spectra of **1** and **Zn1** in $CHCl_3$ (λ_{exc} 420 nm).

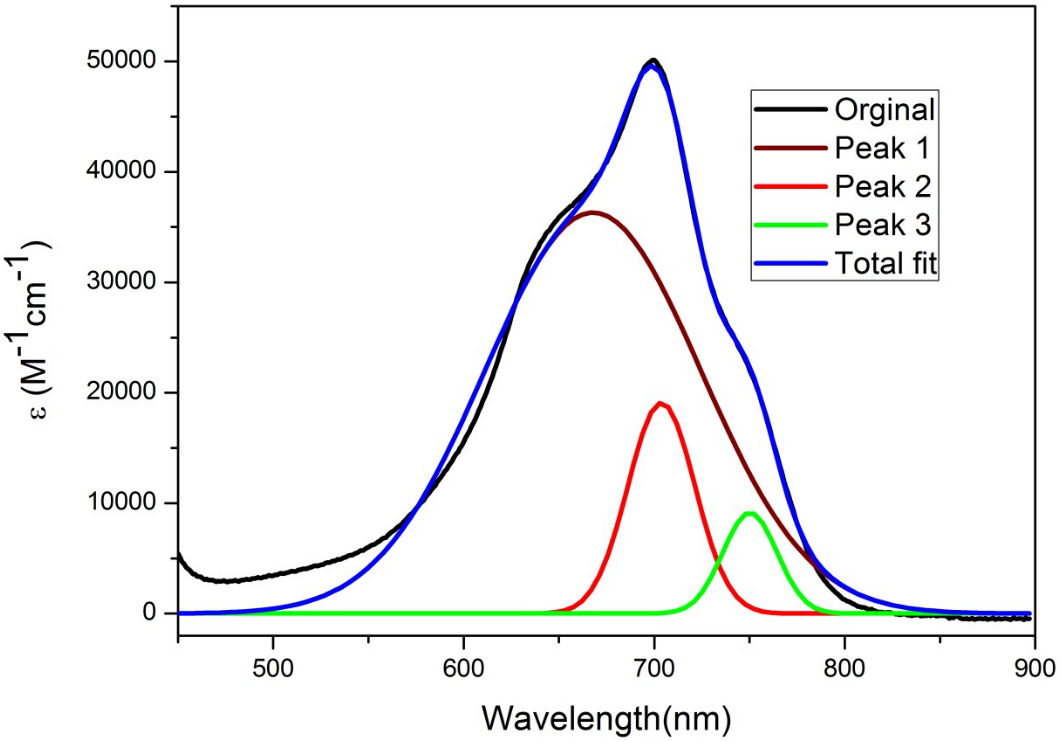

Figure 14: Deconvolution of Q-band of porphycene **1**.

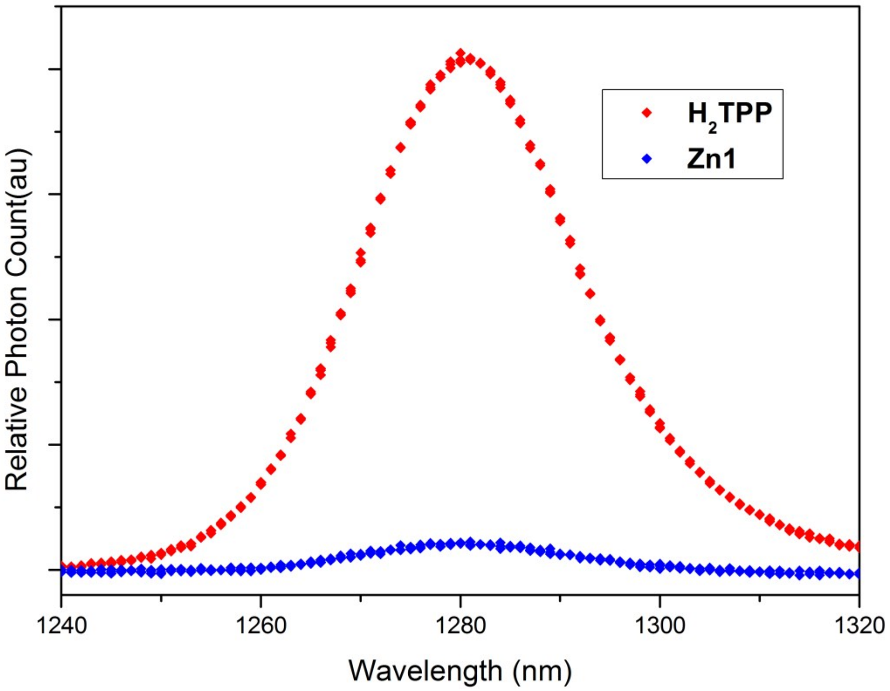

Figure 15: Singlet oxygen luminescence of optically matched **H$_2$TPP** and **Zn1** in air saturated toluene at 25 °C.

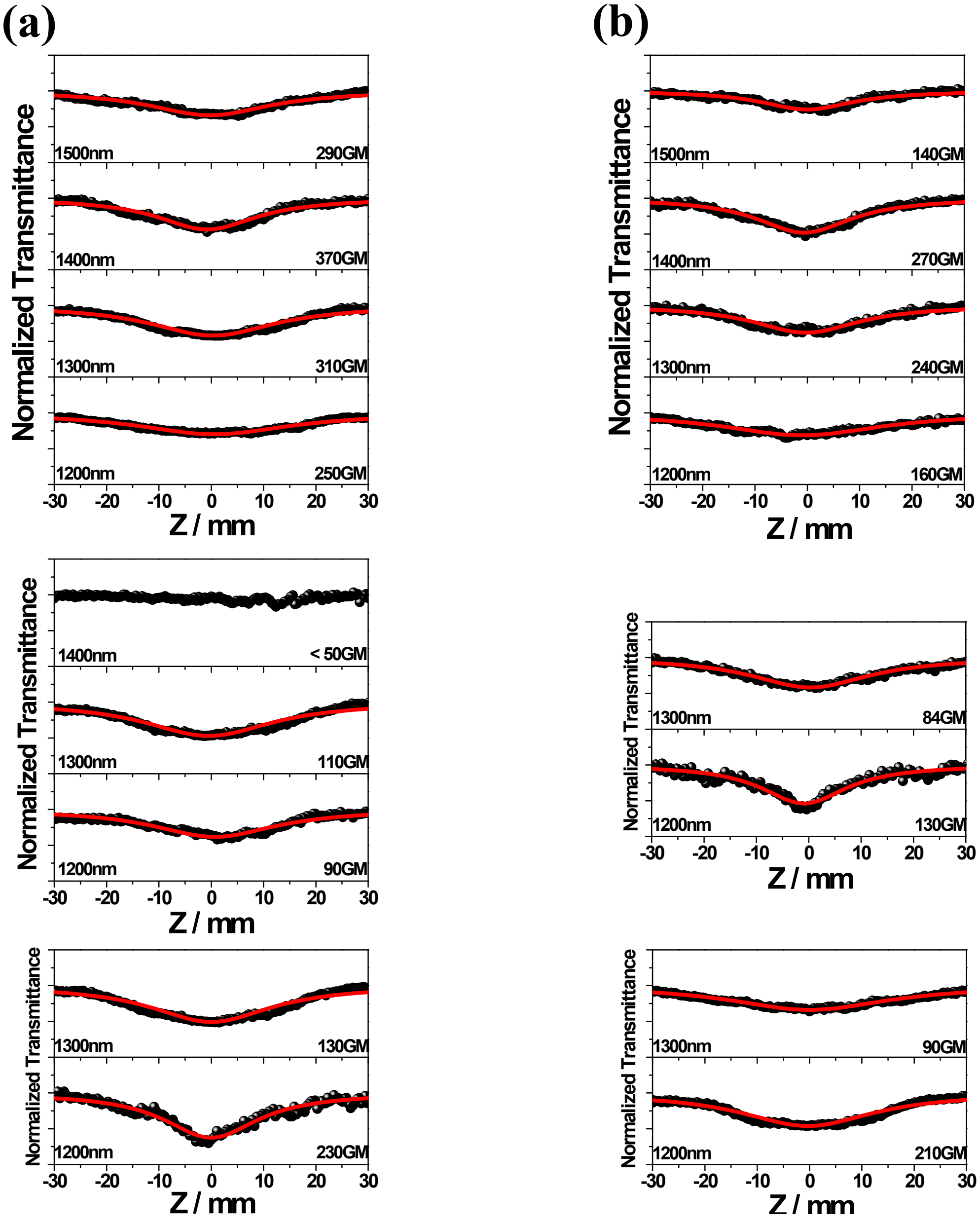

Figure S16: (a) Z-scan curve of **1** (top), **2** (middle) and **3** (bottom). (b) Z-scan curve of **Ni1** (top), **Ni2** (middle) and **Ni3** (bottom).

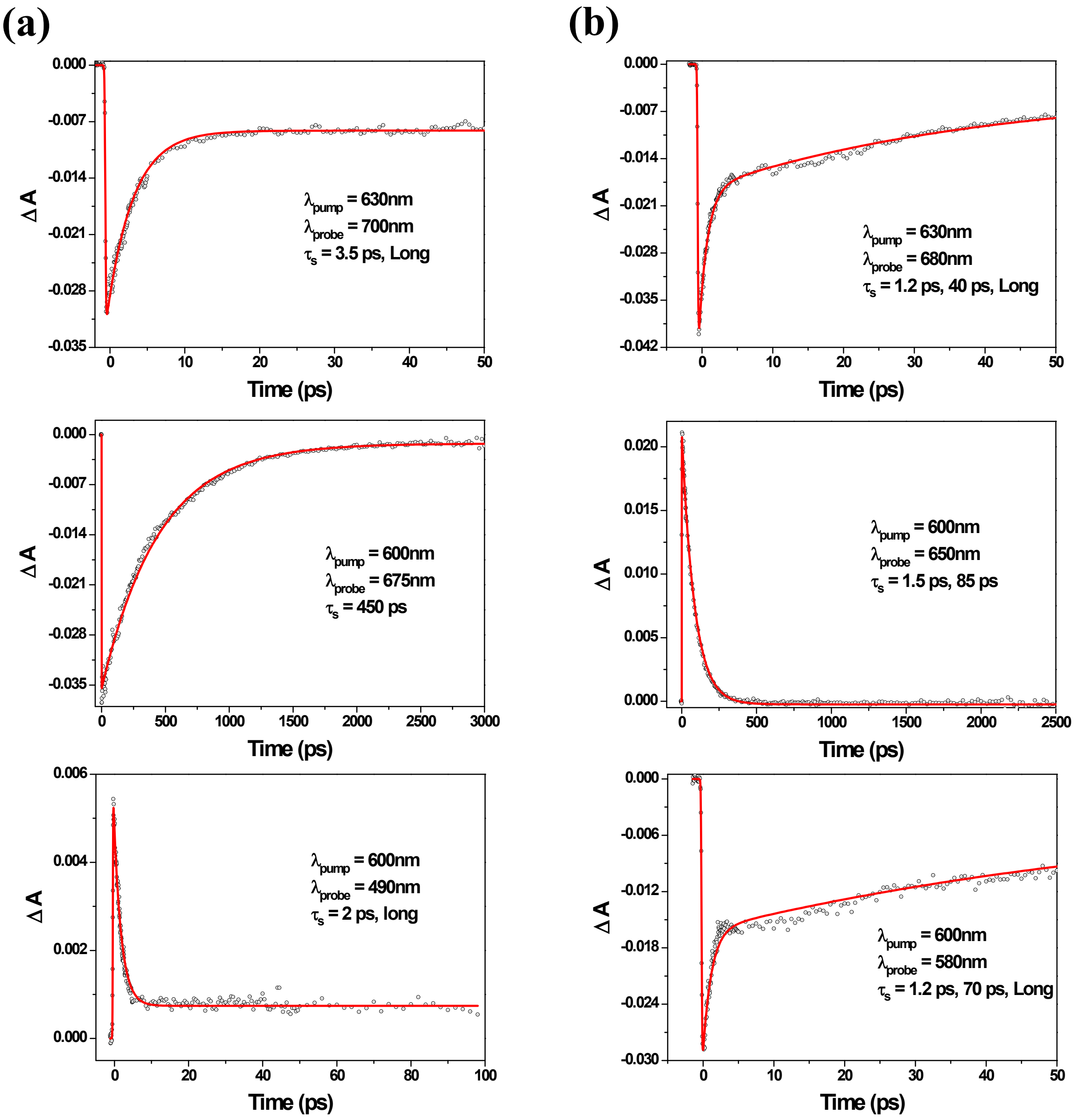

Figure S17: (a) The decay profiles of **1** (top), **2** (middle) and **3** (bottom). (b) The decay profiles of **Ni1** (top), **Ni2** (middle) and **Ni3** (bottom).

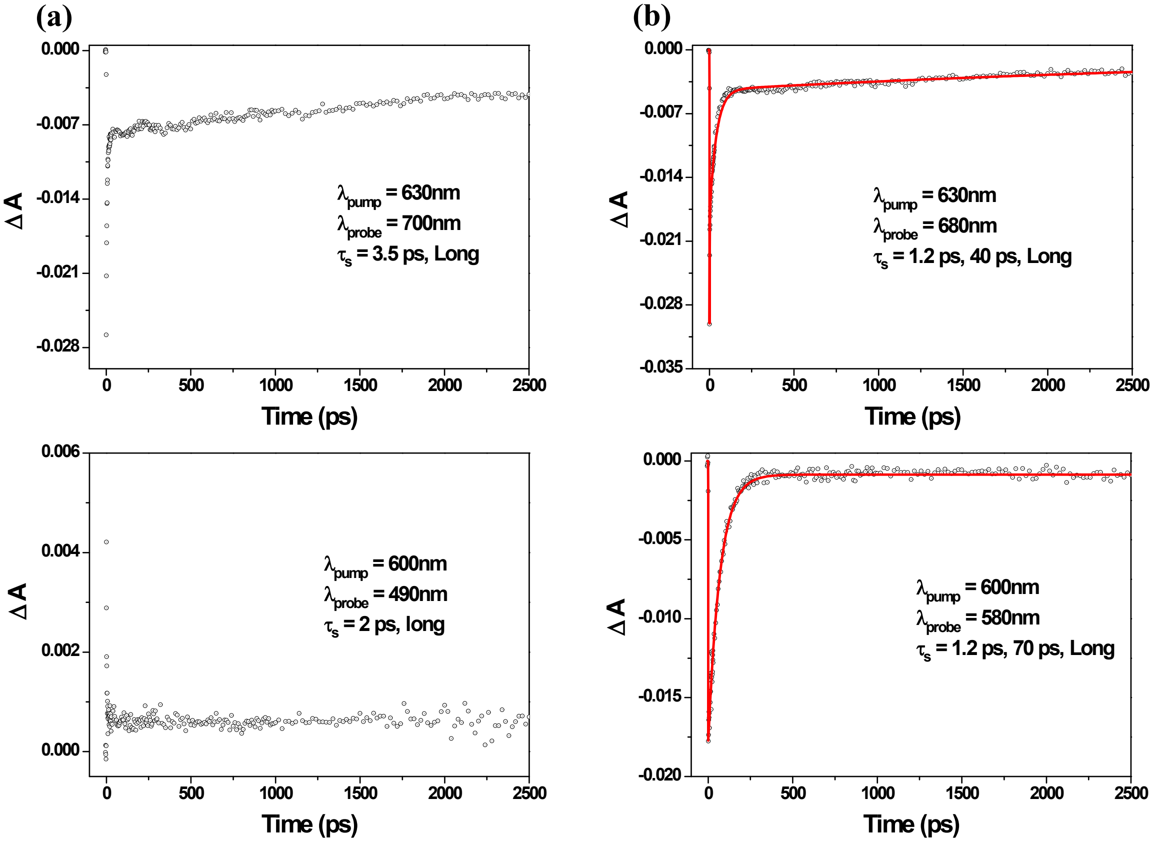

Figure S18: (a) The decay profiles of **1** (top) and **3** (bottom) on long delay. (b) The decay profiles of **Ni1** (top) and **Ni3** (bottom) on long delay.

Electrochemical Data:

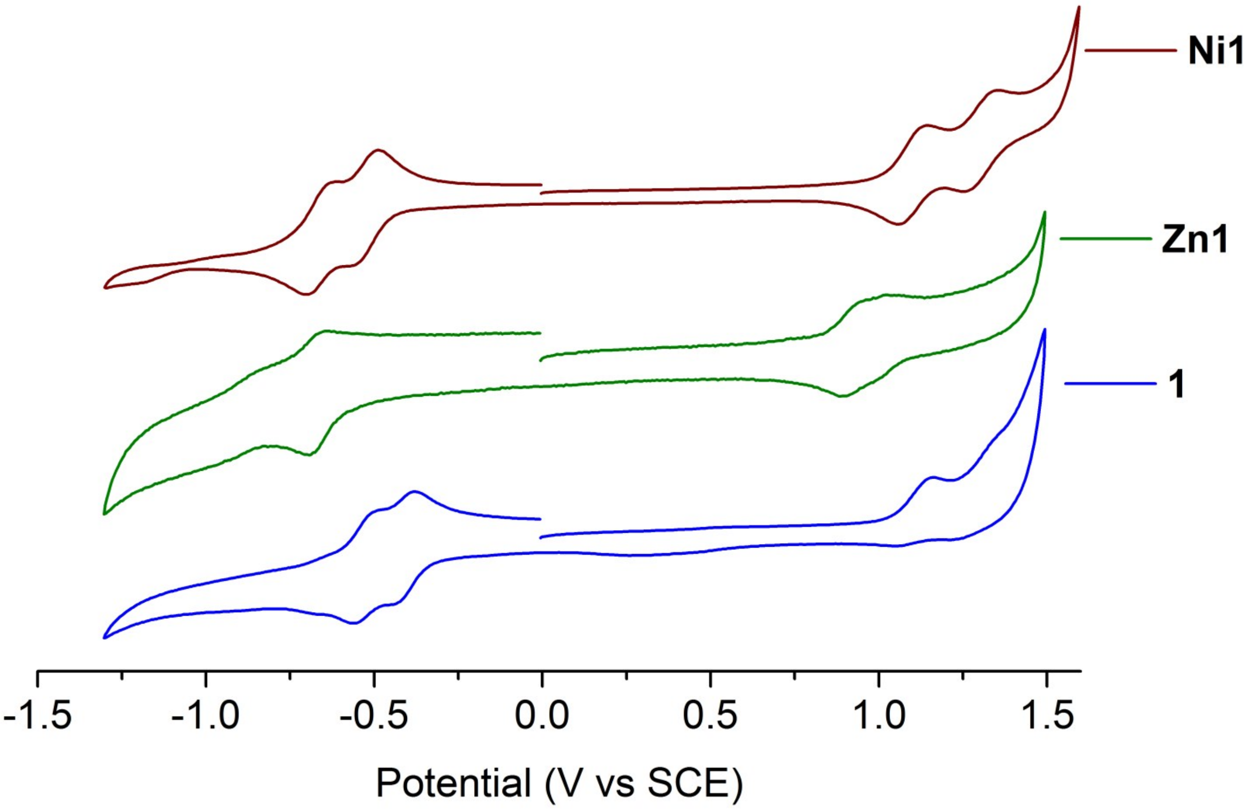

Figure S19: Cyclic voltammograms of **1**, **Zn1**, and **Ni1** in dichloromethane at 25 °C (scan rate 50 mV/s).

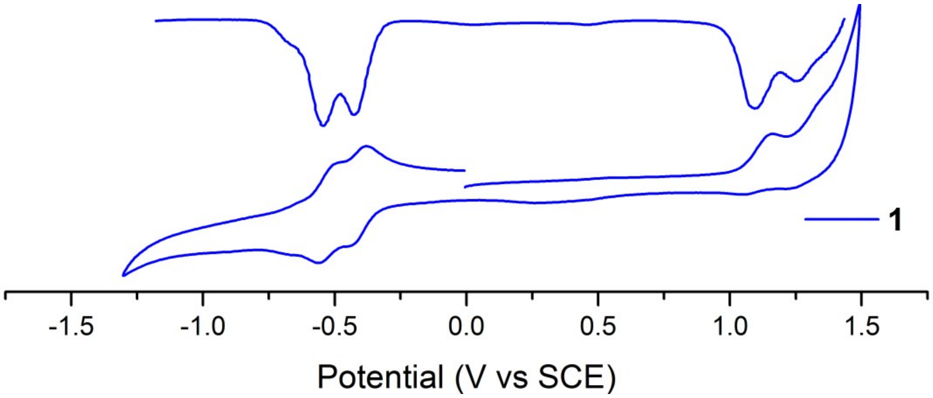

Figure 20: Combined CV (below) and DPV (above) of **1** in dichloromethane measured at 25 °C.

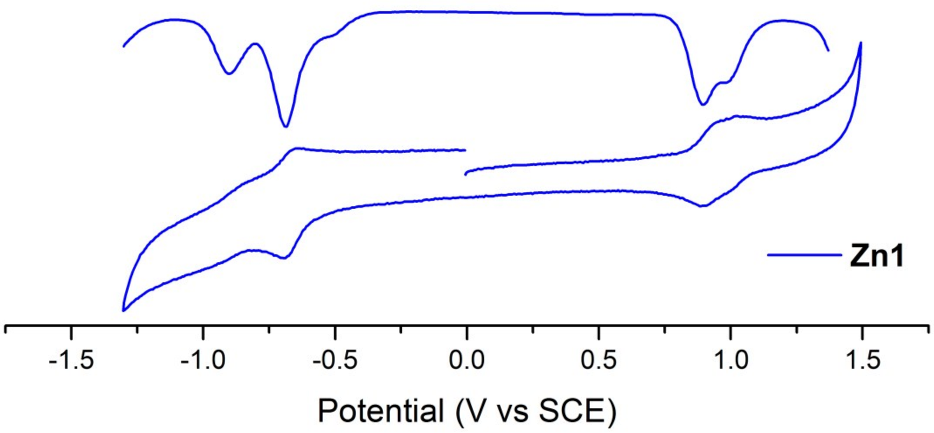

Figure 21: Combined CV (below) and DPV (above) of **Zn1** in dichloromethane measured at 25 °C.

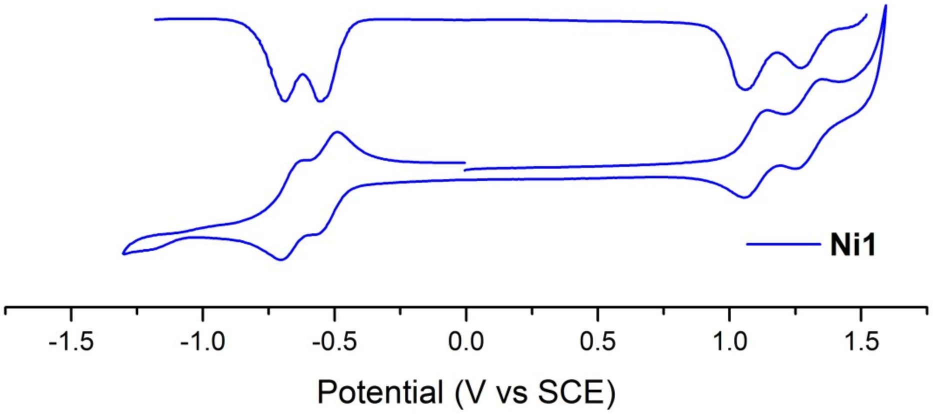

Figure 22: Combined CV (below) and DPV (above) of **Ni1** in dichloromethane measured at 25 °C.

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