Electronic supplementary information

Synthesis, electrochemical and photophysical properties of covalently linked porphyrin-polyoxometalates

Clémence Allain, ‡ [a,b] Delphine Schaming,§ [b] Nikolaos Karakostas,[b] Marie Erard,[b] Jean-Paul Gisselbrecht,[c] Sébastien Sorgues, [b] Isabelle Lampre [b]*, Laurent Ruhlmann [b,c]* and Bernold Hasenknopf [a]*

[a] *UPMC Univ. Paris 06, Institut de Chimie Moléculaire, UMR CNRS 7071, 4 place Jussieu, 75005 Paris, France. E-mail: bernold.hasenknopf@upmc.fr*
[b] *Université Paris-Sud 11, Laboratoire de Chimie Physique, UMR CNRS 8000, Bâtiment 349, 91405 Orsay cedex, France.*
[c] *Université de Strasbourg, Institut de Chimie, Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, UMR CNRS 7177, 4 rue Blaise Pascal, CS 90032, 67081 Strasbourg cedex, France. E-mail: lruhlmann@unistra.fr*
‡ Present address: ENS Cachan, PPSM, UMR CNRS 8531, 61, avenue du Président Wilson, 94235 Cachan cedex, France.
§ Present address: Université Paris Diderot - Sorbonne Paris Cité, ITODYS, UMR CNRS 7086, Bât. Lavoisier, 15 rue Jean-Antoine de Baïf, Case 7107, 75205 Paris Cedex 13, France.

Summary

General procedures

$[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$[1] and $[N(C_4H_9)_4]_5H_4[P_2W_{15}V_3O_{62}]$[2] were prepared by literature methods. Acetonitrile for polyoxometalates synthesis was freshly distilled from CaH_2, pyrrole and benzaldehyde for porphyrin synthesis were freshly distilled prior to use. All other chemicals, including solvents, were commercially available as reagent grade and used as received. Elemental analyses were performed by the ''Service de microanalyse'', ICSN, Gif-sur-Yvette, France and by the ''Service central d'analyse'', CNRS, Vernaison, France.

NMR

NMR spectra (^1H, ^{13}C, ^{31}P, ^{51}V, ^{183}W) were recorded with a Bruker AC300 spectrometer at 300, 75.5, 121.5, 79.0 and 12.5 MHz, respectively, at 25 °C unless otherwise stated. Chemical shifts (δ) are expressed in ppm relative to Me_4Si for ^1H and ^{13}C, with the residual solvent peak as standard, relative to 100 % $VOCl_3$ for ^{51}V, relative to 85% H_3PO_4 for ^{31}P and relative to WO_4^{2-} for ^{183}W using $[SiW_{12}O_{40}]^{4-}$ as standard ($\delta = -103.8$ ppm).
IR spectra were recorded using KBr pellets with a Bio-Rad FTS 165 spectrometer at 4 cm^{-1} resolution. Relative intensities are given after the wavenumber as vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br. = broad.

IR spectroscopy

IR spectra were recorded on a Bio-Rad FTS 165 FTIR spectrophotometer on KBr pellets.

Mass spectrometry

Mass spectrometry experiments have been carried out on an electrospray-ion trap instrument (Bruker, Esquire 3000). The 50 $\mu mol \cdot L^{-1}$ solutions of POMs were infused using a syringe pump (160 $\mu L \cdot h^{-1}$). The negative ion mode was used with capillary high voltage 3500 V. The orifice/skimmer voltage difference was set to 45 V to avoid decomposition of the POMs. The low-mass-cutoff (LMCO) of the ion trap was set to 80 Th.

Absorption and fluorescence spectroscopy

Steady-state optical absorption spectra were recorded with a Perkin Elmer Lambda 9 spectrophotometer. Steady-state luminescence emission spectra were obtained using a Spex fluorolog 1681 spectrofluorimeter equipped with a Hamamatsu R3896 photomultiplier which was cooled to the temperature of -20°C. The fluorescence spectra were not corrected for the response of the detection system. All measurements were carried out at room temperature.

Time resolved measurements

Fluorescence decays were recorded using a time-correlated single-photon counting set-up. The source was a titane:sapphire laser (MIRA 900F) pumped by a $Nd:YVO_4$ laser (VERDI) producing 100 fs pulses at 840 nm with 76 MHz a repetition rate. The repetition rate was reduced down to 3.8 MHz by a pulse-picker. The second harmonic (420 nm, vertically polarized, 4.5 μJ/pulse) was generated in a BBO crystal and used to excited the samples. The emission was detected at 90° with respect to the excitation beam via a polarizer set at the

---

[1] N. Hur, W. G. Klemperer, R.-C. Wang, in *Inorg. Synth.*, vol. 27 (Ed.: A. P. Ginsberg), John Wiley & Sons, New York, **1990**, p. 78.

[2] R. G. Finke, B. Rapko, R. J. Saxton, P. J. Domaille, *J. Am. Chem. Soc.*, 1986, **108**, 2947-2960.

magic angle (54.7°) with respect to the excitation polarization. A monochromator was used for wavelength selection of emission and the detector was a microchannel plate. The instrument response function was 50 ps fwhm. The analysis of the profiles was performed with standard iterative procedure based on maximum entropy principle..

Laser flash photolysis studies were achieved with the third harmonic of a Nd:YAG laser (BMI) (355 nm pulses, 3 ns FWHM, 10 mJ/pulse, 2 Hz). Detection of the transient species was carried out by an optical absorption set-up, consisting of a pulsed Xe arc lamp, monochromator and photomultiplier (Hamamatsu R955S). The cell length was 1 cm. The samples were deaerated by bubbling nitrogen for around 30 minutes and kept under nitrogen during measurements.

Femtosecond transient absorption experiments were performed with a pump–probe set-up using a amplified titane:sapphire laser system (Spectra Physics) delivering 100 fs pulses at 790 nm with a pulse energy of 1 mJ and a 1 kHz repetition rate. The pump (395 nm) was generated by frequency doubling in a BBO crystal of 90% of the fundamental beam, then attenuated to 10 µJ and focused to a 0.5 mm beam on the sample. After traveling along the optical delay line 10% of the Ti:sapphire output was used for white light continuum generation in a 3 mm sapphire plate. The continuum beam was divided into a probe and a reference beam by a broad band beam-splitter. Pump and probe beams overlapped into a fused silica sample cell with 1 mm path. The detection system consisted of an imaging polychromator and a CCD camera (1340×400 Princeton Instruments). The polarization between the pump and the probe beams was kept at magic angle (54.7°). Transient absorption spectra were recorded from 400 to 690 nm and corrected for the group velocity dispersion. Measurements were performed in aerated solutions at room temperature (23 ºC).

Electrochemical Experiments

The solutions were deaerated thoroughly for at least 30 minutes by bubbling argon (Ar-U from Air Liquide) and kept under argon atmosphere during the whole experiment. The working glassy carbon (GC, Tokai, Japan) had a diameter of 3 mm. The electrochemical set-up was an EG&G 273A or PARSTAT 2273 (Princeton Applied Research). Potentials are measured first against a saturated calomel electrode (SCE), then potential are referred against Fc^+/Fc that was measured with the identical set-up.

The counter electrode was platinum. All voltammetric experiments were carried out at room temperature.

Bulk electrolysis were performed in using a large glassy carbon tube as the working electrode. A fritted glass disk to prevent diffusion of the electrogenerated species separated the anodic and cathodic compartments. We have made a pre-electrolysis at the same potentials, which have always shown a small current measured before the compound to be electrolyzed was added to the solution. This current was not considered for the electron count.

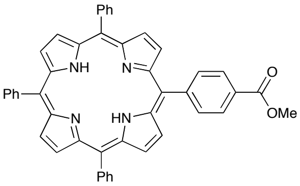
The spectrophotometric analyses were performed with a Hewlett- Packard 8452 A diode array spectrometer. The used OTTLE cell (Optically Transparent Thin Electrode) was a Pyrex glass made cell described previously by Bernard et al.[3] The working electrode was a Pt grid (100 mesh).

---

[3] C. Bernard, J.-P. Gisselbrecht, M. Gross, E. Vogel, M. Lausmann, *Inorg. Chem*. 1994, **33**, 2393.

Synthesis

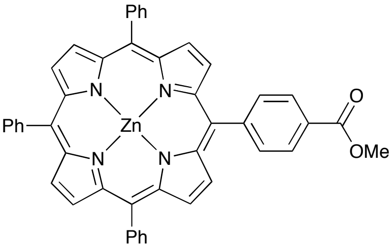
Porphyrin H_2TPP-1E:[4]



Dichloromethane (1 L) is introduced in a dried 2L two-necked flask under argon. Methyl-4-formylbenzoate (0.74 g, 4.5 mmol, 1.2 eq.), benzaldehyde (1.14 mL, 1.19 g, 11.25 mmol, 3 eq.) and pyrrole (1.05 mL, 1.01 g, 15 mmol, 4 eq.) are successively added and the colorless solution is stirred at room temperature for 15 min. $BF_3(OEt_2)$ (0.19 mL, 0.213 g, 1.5 mmol, 0.4 eq.) is then added, and the solution goes gradually from yellow to dark red. After 1h10 of stirring at room temperature under argon, *p*-chloranil (2.78 g, 11.3 mmol, 3 eq.) is added and the black solution is refluxed for 1h30 using a pre-heated water bath. A few drops of triethylamine are added to quench the reaction. The crude mixture is adsorbed on silica gel (10 g) and purified by flash chromatography (elution with a gradient from cyclohexane/CH_2Cl_2 4/1 to CH_2Cl_2) to give, by order of elution, *meso*-tetraphenylporphyrin (0.163 g, 7 % yield), **H_2TPP-1E**, and a mixture of cis- and trans- disubstituted porphyrins after which the elution is stopped. Fractions containing **H_2TPP-1E** are recrystallised from a CH_2Cl_2 solution exposed to methanol vapors to yield the title compound as violet crystals (0.35 g, 14 % yield).

$C_{46}H_{32}N_4O_2$ (672.8 g·mol^{-1}): calcd. C 82.12, H 4.79, N 8.33; found C 81.66, H 4.92, N 8.73. IR: ν_{max} = 3420 (ν O-H, m, br), 3319 (w), 3057-3025-2952 (ν C-H, w), 1812 (w), 1724 (ν C=O, s), 1607 (m), 1598 (m), 1559 (w), 1492 (δ C-H, w), 1473 (m), 1440 (m), 1401 (w), 1350 (w), 1311 (w), 1276 (s), 1222 (w), 1213 (w), 1187 (w), 1178 (w), 1155 (w), 1112 (m), 1100 (m), 1073 (ν C-O, w), 1022 (w), 1002 (w), 980 (w), 965 (s), 877 (w), 868 (w), 848 (w), 819 (w), 799 (s), 750 (w), 728 (m), 701 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.89-8.87 (m, 6H, β-H), 8.81 (d, *J* = 4.8 Hz, 2H, β-H), 8.46 (d, *J* = 8.4 Hz, 2H, 5-Ar *m*-H), 8.33 (d, *J* = 8.4 Hz, 2H, 5-Ar *o*-H), 8.24 (dd, *J* = 7.2 Hz, *J* = 1.5 Hz, 6H, 10,15,20-Ar *o*-H), 7.80-7.75 (m, 9 H, 10,15,20-Ar *m*- and *p*-H), 4.14 (s, 3H, COOMe), -2.74 (s, 2H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 168.4 (C=O), 148.1, 143.1, 140.0, 135.6, 132.4, 130.7, 129.4, 129.0, 128.9, 127.8, 121.6, 121.4, 119.6, 53.5 ppm.

Porphyrin ZnTPP-1E:



A solution of $Zn(OAc)_2$ (2.41 g, 11 mmol, 20 eq.) in methanol (75 mL) is added to a solution of free base porphyrin **H2TPP-1E** (0.35 g, 0.52 mmol, 1 eq.) in CH_2Cl_2 (85 mL). The mixture is stirred are room temperature for 3h30, then the solvents are removed under vacuum, the residue is dissolved in CH_2Cl_2 (140 mL) and washed with water (100 mL), saturated aqueous

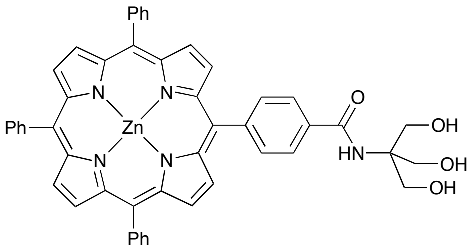
---

[4] J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827-836.

$KHCO_3$ (100 mL), water (100 mL), brine (100 mL) and water (100 mL). The organic phase is dried on sodium sulfate and concentrated to give **ZnTPP-1E** as a pink violet powder (0.330 g, 86 % yield).

$C_{46}H_{30}N_4O_2Zn$ (736.2 g·mol^{-1}): TLC: $R_f = 0.43$ (CH_2Cl_2). IR: ν_{max} 3420 (ν O-H, m, br), 3105, 3059, 2960 (ν C-H, w), 1812 (w), 1724 (ν C=O, m), 1695 (s), 1606 (m), 1598 (m), 1561 (w), 1523 (w), 1488 (δ C-H, w), 1458 (w), 1440 (s), 1401 (w), 1386 (w), 1340 (m), 1311 (w), 1274 (s), 1206 (m), 1178 (w), 1114 (m), 1102 (m), 1070 (ν C-O, w), 1004 (vs), 995 (vs), 871 (w), 822 (w), 797 (s), 761 (m), 751 (m), 742 (m), 730 (w), 718 (m), 703 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 9.00-8.99 (m, 6H, β-H), 8.94 (d, J = 4.8 Hz, 2H, β-H), 8.44 (d, J = 8.4 Hz, 2H, 5-Ar *m*-H), 8.35 (d, J = 8.4 Hz, 2H, 5-Ar *o*-H), 8.26 (dd, J = 7.2 Hz, J = 1.8 Hz, 6H, 10,15,20-Ar *o*-H), 7.82-7.78 (m, 9 H, 10,15,20-Ar *m*- and *p*-H), 4.10 (s, 3H, COO$\underline{Me}$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 207.7 (C=O), 151.4, 151.3, 143.8, 135.5, 133.2, 133.1, 133.0, 132.5, 128.7, 128.6, 127.6, COO$\underline{Me}$ masqued by CD_2Cl_2 around 54 ppm.

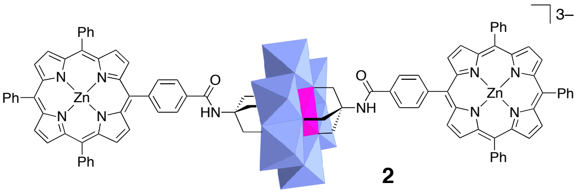
Porphyrin ZnTPP-Tris 1:



Porphyrin **ZnTPP-1E** (0.370 g, 0.503 mmol, 1 eq.), K_2CO_3 (0.083 g, 0.603 mmol, 1.2 eq.) and Tris-hydroxylaminomethane (0.073 g, 0.603 mmol, 1.2 eq.) are introduced in a 2 mL flask. DMSO (1 mL, dried on molecular sieves) is added and the mixture is protected from light and stirred for 17h under argon. The mixture is poured in water (30 mL), the resulting precipitate is collected by centrifugation, adsorbed on silica gel and purified by flash chromatography (SiO_2 15 g, elution with a gradient from ethyl acetate to ethyl acetate / methanol 96/4) to yield the expected product as a violet powder (0.295 g, 71 % yield).

$C_{49}H_{37}N_5O_4Zn$, 1 MeOH, 2 H_2O (893.3): calcd. C 67.23, H 5.08, N 7.84; found C 67.53, H 4.73, N 7.76. IR: ν_{max} = 3430 (ν O-H, m, br), 3020-2961-2925 (ν C-H, w), 2362 (w), 2335 (w), 1724 (m), 1642 (ν C=O, s), 1607 (m), 1596 (m), 1560 (w), 1541 (w), 1522 (m), 1487 (δ C-H, m), 1459 (w), 1440 (w), 1372 (w), 1339 (m), 1319 (w), 1263 (w), 1204 (m), 1176 (w), 1157 (w), 1104 (w), 1066 (m), 1047 (ν C-O, s), 1001 (s), 994 (s), 953 (w), 882 (w), 867 (w), 820 (w), 797 (s), 755 (m), 749 (m), 719 (m), 701 (s), 669 (s), 660 (w), 572 (w) cm^{-1}. ^{1}H NMR (DMSO-*d6*): δ = 8.77-8.78 (m, 8H, β-H), 8.25 (d, J = 6.6 Hz, 2H, 5-Ar *m*-H), 8.17-8.20 (m, 8H, *o*-H), 7.81-7.82 (m, 9H, 10,15,20-Ar *o*-H), 7.80 (s, 1 H, NH), 4.90 (t, 3H, OH, J = 6.0 Hz), 3.85 (d, 6H, CH_2, J = 6.0 Hz). ^{13}C NMR (CD_2Cl_2): δ = 150.9, 150.5, 144.2, 135.7, 133.3, 133.2, 132.9, 129.0, 128.2, 127.2, 122.0, 121.9 (C_{arom}), 64.4 (CH_2O), 62.1 (CNH) ppm. MS (ESI$^+$MS): m/z 848.4 (100%) [M+Na]$^+$, 825.4 (25%) [M+H]$^+$.

Anderson-ZnTPP 2:

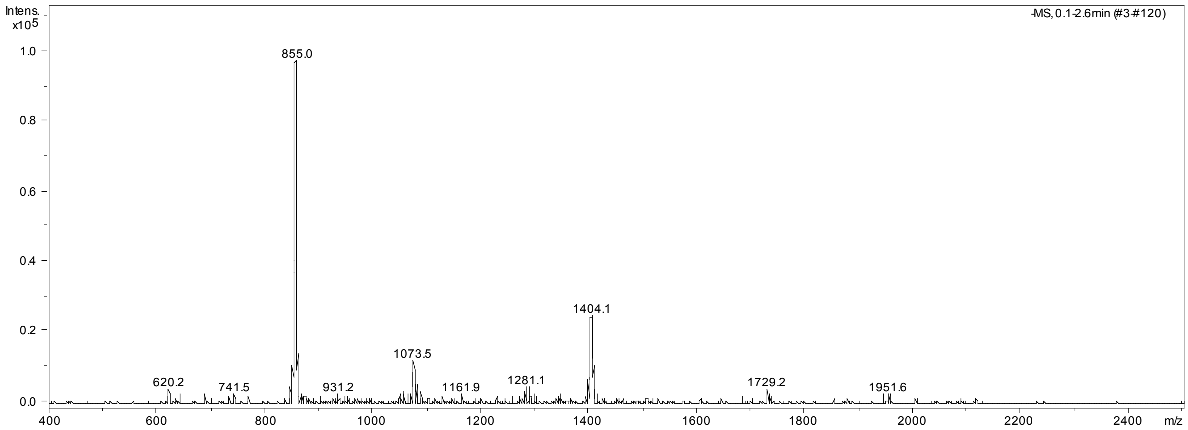


2

$[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ (60 mg, 0.028 mmol, 1 eq.), $Mn(OAc)_3$ (0.011 g, 0.042 mmol, 1.5 eq.) and ZnTPP-Tris (0.080 g, 0.097 mmol, 3.5 eq.) are introduced in a Schlenk under argon atmosphere. N,N-dimethylacetamide (2 mL, dried on molecular sieve) is added and the resulting suspension is heated at 80-90°C under argon for 60h. The mixture is then cooled to rt, filtered and added dropwise to diethyl ether (40 mL). The precipitate is collected by centrifugation and washed thoroughly with ether to remove unreacted porphyrin. The product is then dissolved in ca. 8 mL DMF and the solution is exposed to ether vapor. After one day, small violet crystals have formed (0.097 g, 80 % yield based on Mo).

$[N(C_4H_9)_4]_3[C_{98}H_{68}N_{10}O_{26}MnMo_6Zn_2]\cdot 5H_2O$ (2645.1): calcd. C 51.87, H 5.55, N 5.39; found C 51.87, H 5.27, N 5.33; IR: ν_{max} = 3430 (νO-H, s, br), 2961-2872 (ν C-H, s), 1656 (ν C=O, s), 1519 (w), 1484 (δ C-H, m), 1441 (w), 1384 (w), 1339 (w), 1321 (w), 1263 (w), 1204 (w), 1100 (s, ν C-O), 1069 (w), 1031 (m), 1002 (s), 994 (s), 941-921-903 (s, ν Mo=O), 796 (m), 757 (w), 718 (w), 702 (w), 669 (vs, br, ν Mo-O-Mo), 564 (m), 398 (w), 365 (w) cm^{-1}.

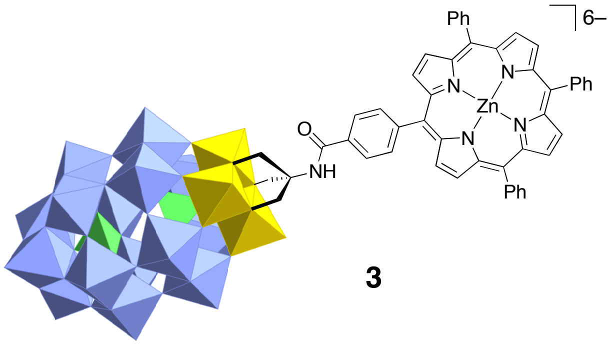
^{1}H NMR (CD_3CN/DMSO-*d6* 0.5/0.05): δ = 64.0, 8.84-8.81 (2 s, 16H, β-H), 8.22-8.20 (2 s, 20H, 16 *o*-H + 4 5-Ar *m*-H), 7.91 (s, 2H, NH), 7.79-7.77 (2 s, 18H, 10,15,20-Ar *m*- and *p*-H) 3.08 (m, 24H, TBA), 1.57 (m, 24H, TBA), 1.34 (m, 24H, TBA), 0.95 (t, 36H, TBA) ppm. ^{13}C NMR (CD_3CN/DMSO-*d6* 0.5/0.05): δ = 162.8, 150.4, 143.7, 135.0, 134.2, 132.3, 128.1, 121.4, 120.4, 58.9 (TBA), 24.0 (TBA), 20.1 (TBA), 13.6 (TBA) ppm.



Entry	Charge	Calculated m/z	Observed m/z	Rel. Int. (%)	Composition
1	2–	1403.0	1404.1	26	TBA {Anderson-ZnTPP}
2	2–	1281.8	1281.1	5	H {Anderson-ZnTPP}
3	3–	854.2	855.0	100	{Anderson-ZnTPP}

{Anderson-ZnTPP} = $C_{98}H_{68}N_{10}O_{26}MnMo_6Zn$, TBA = $NC_{16}H_{36}$.

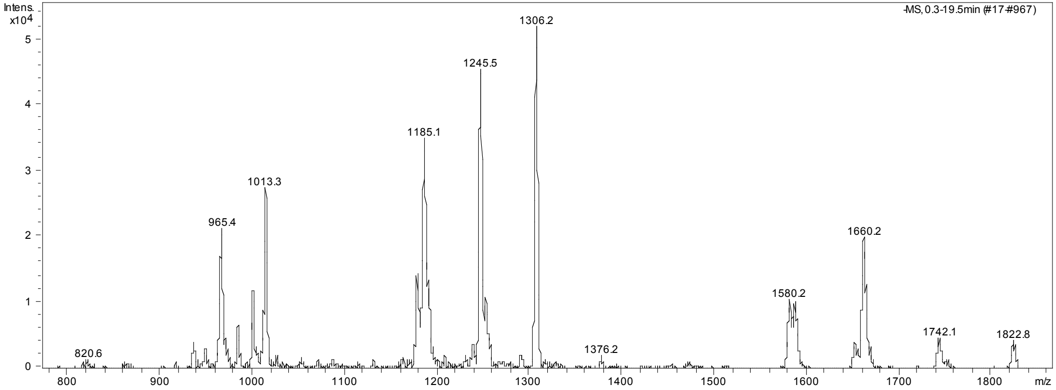
Dawson-ZnTPP 3:



3

$[N(C_4H_9)_4]_5[P_2W_{15}V_3O_{62}H_4]$ (250 mg, 0.048 mmol, 1 eq.), and ZnTPP-Tris (0.060 g, 0.072 mmol, 1.5 eq.) are introduced in a Schlenk under argon atmosphere. N,N-dimethylacetamide (2 mL, dried on molecular sieve) is added, the resulting suspension is protected from light and heated at 80-90°C under argon for 7 days. The mixture is then cooled to rt and added dropwise to diethyl ether (50 mL). The precipitate is collected by centrifugation and washed thoroughly with ether to remove unreacted porphyrin. Dawson-ZnTPP is obtained as a violet powder (0.23 g, 80 % yield).

$TBA_5H[P_2V_3W_{15}O_{62}\{C_{49}H_{34}N_5OZn\}]\cdot 3CH_3CN$: $C_{135}H_{224}N_{13}P_2W_{15}V_3O_{63}Zn$ (6075.0 g·mol^{-1}): calcd. C 26.69, H 3.72, N 2.99; found C 27.18, H 3.68, N 2.69; IR: ν_{max} = 3424 (νO-H, s, br), 2960-2929-2873 (ν C-H, s), 1636 (ν C=O, s), 1519 (w), 1483 (δ C-H, m), 1442 (w), 1384 (w), 1340 (w), 1321 (w), 1264 (w), 1204 (w), 1154 (w), 1087 (s), 1066 (m), 1003 (m), 994 (m), 951 (s), 911 (s), 817 (vs, ν W-O-W), 732 (s, ν W-O-W), 757 (w), 526 (m), 395 (m), 381 (m) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 8.84 (m, 8H, β-H), 8.22-8.16 (m, 10H, *o*-H and 5-*m*-H), 7.79-7.77 (m, 9 H, 10,15,20-*m*- and *p*-H), 6.92 (s, 1 H, NH), 5.98 (s, 6H, OCH_2), 3.14 (m, 40H, TBA), 1.64 (m, 40H, TBA), 1.44 (m, 40H, TBA), 1.01 (t, 60H, TBA) ppm. ^{31}P NMR (CD_3CN): δ = -12.16, -6.13 ppm. ^{51}V NMR (CD_3CN): δ = -538.3 ppm. ^{183}W NMR (CD_3CN): δ = –121.4, –150.1, –163.3 ppm.

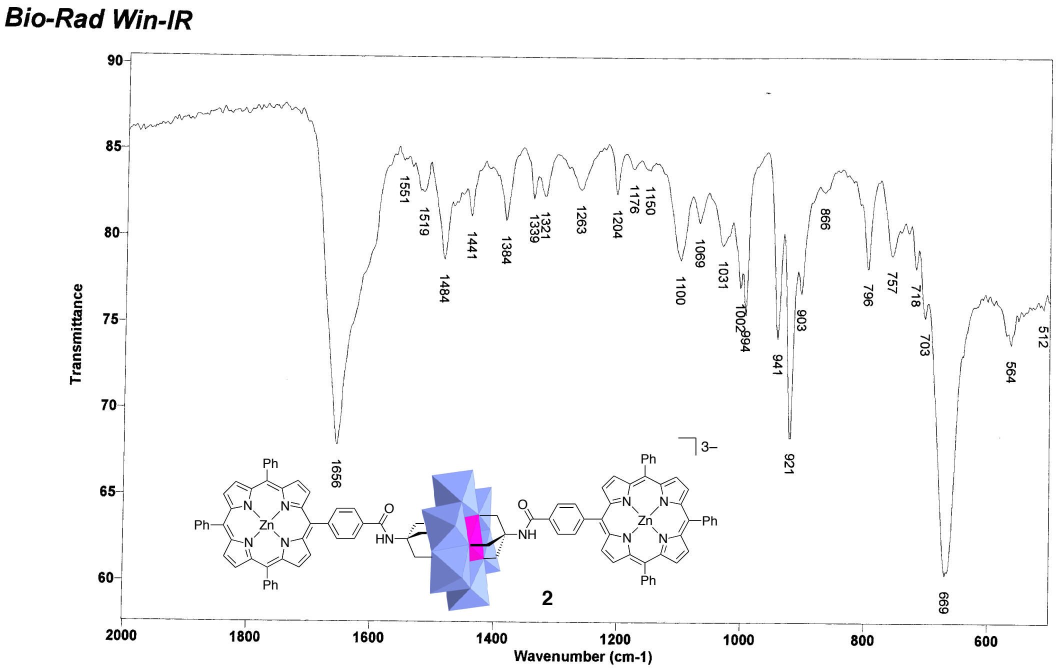


Entry	Charge	Calculated m/z	Observed m/z	Rel. Int. (%)	Composition
1	3–	1821.9	1822.7	8	TBA_3 {Dawson-ZnTPP}
2	3–	1741.5	1742.1	9	TBA_2H {Dawson-ZnTPP}
3	3–	1661.1	1660.5	38	$TBAH_2$ {Dawson-ZnTPP}
4	3–	1580.3	1580.2	20	H_3 {Dawson-ZnTPP}
5	4–	1305.9	1306.1	100	TBA_2 {Dawson-ZnTPP}
6	4–	1245.6	1245.5	87	TBAH {Dawson-ZnTPP}
7	4–	1185.0	1185.1	67	H_2 {Dawson-ZnTPP}
8	5–	947.8	948.2	5	H {Dawson-ZnTPP}

{Dawson-ZnTPP} = $C_{49}H_{34}N_5P_2V_3W_{15}O_{63}Zn$, TBA = $C_{16}H_{36}N$.

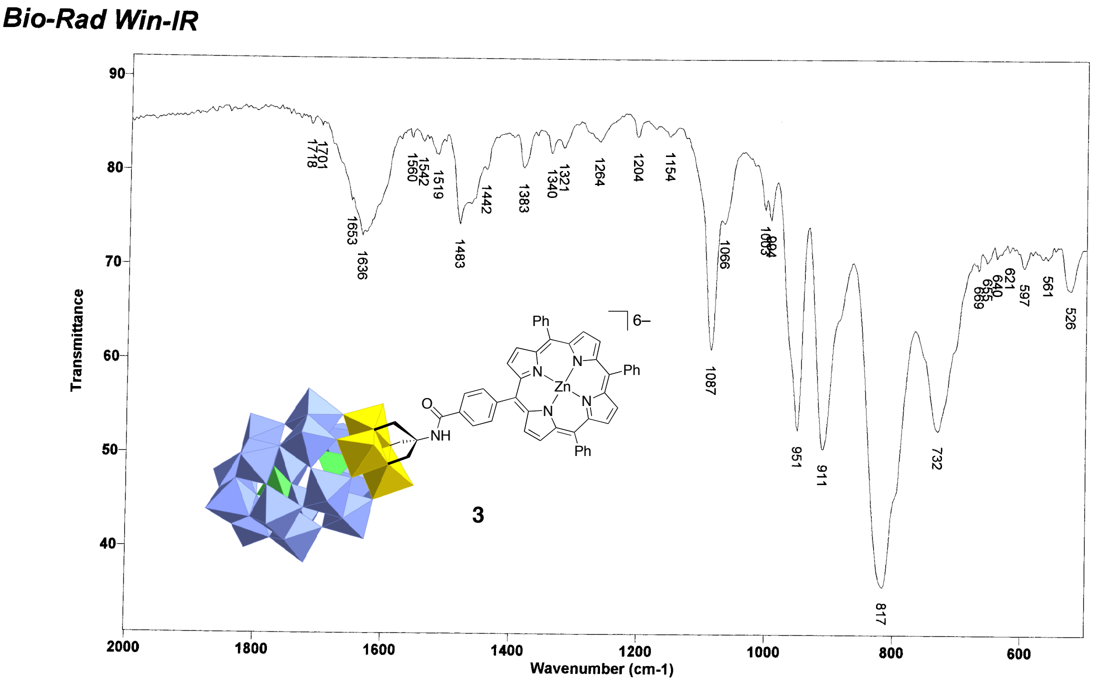
Figures

Figure S1: IR spectra of porphyrin-polyoxometalates **2** and **3**.



File # 1 = CA-I-163
Number of Scans: 96
Comment: AndersonMnTPP

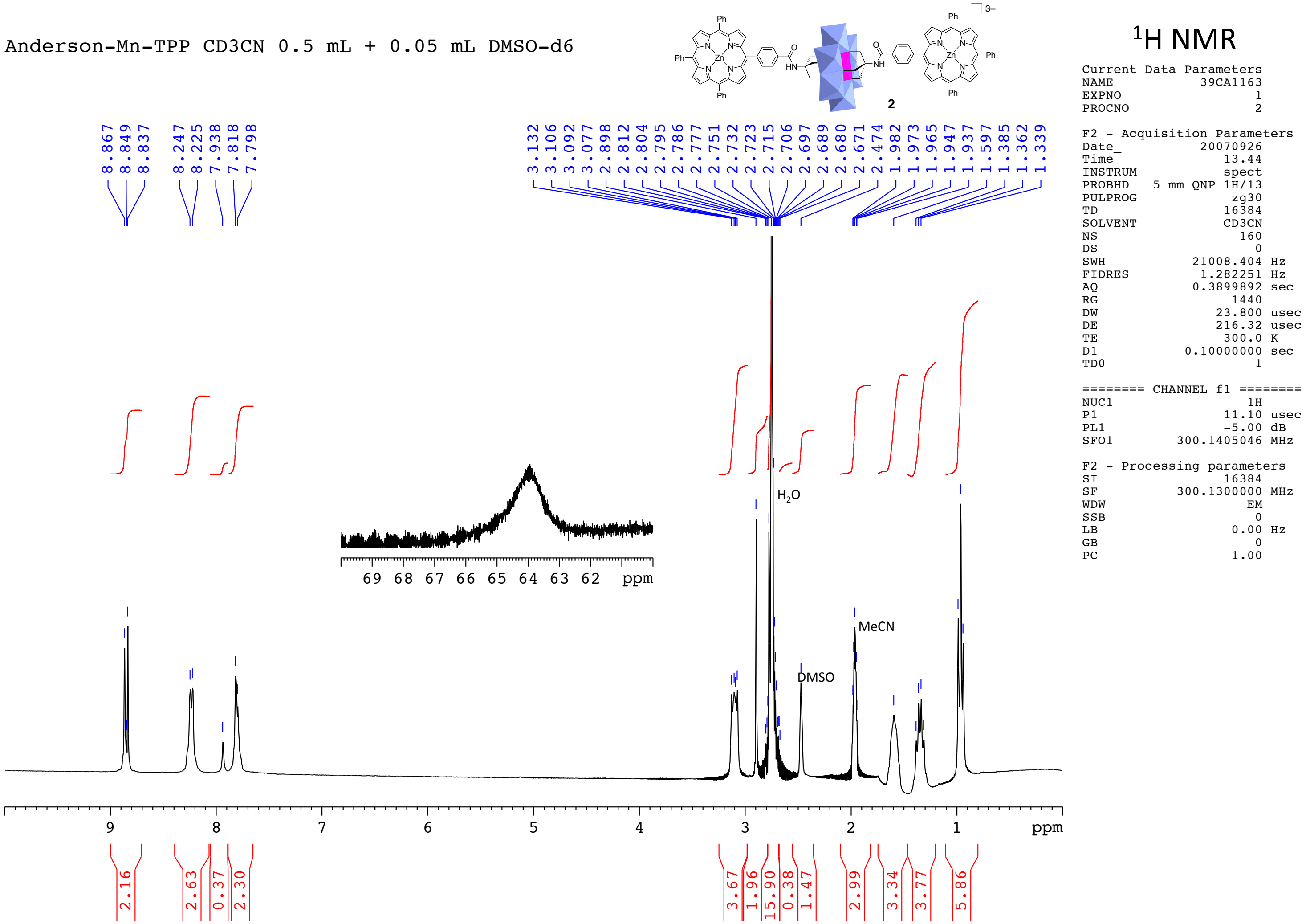
View Mode: Peaks
07/09/2007 09:26 Res=4cm-1



File # 1 = CA-1-164
Number of Scans: 16
Comment: P2W15V3-TPP

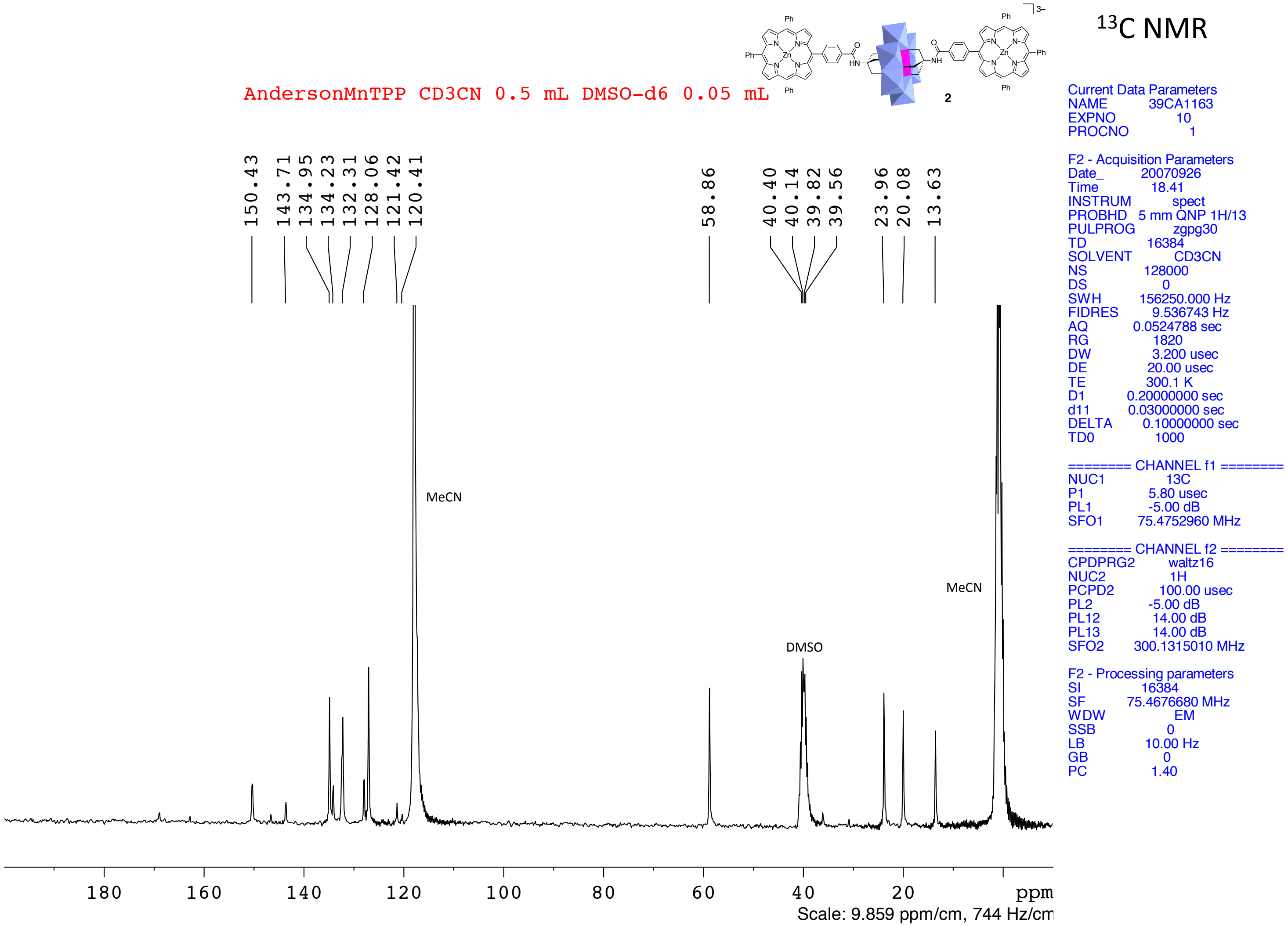
View Mode: Peaks
20/09/2007 01:40 Res=4cm-1

Figure S2: ^{1}H NMR spectrum of Anderson POM **2**.



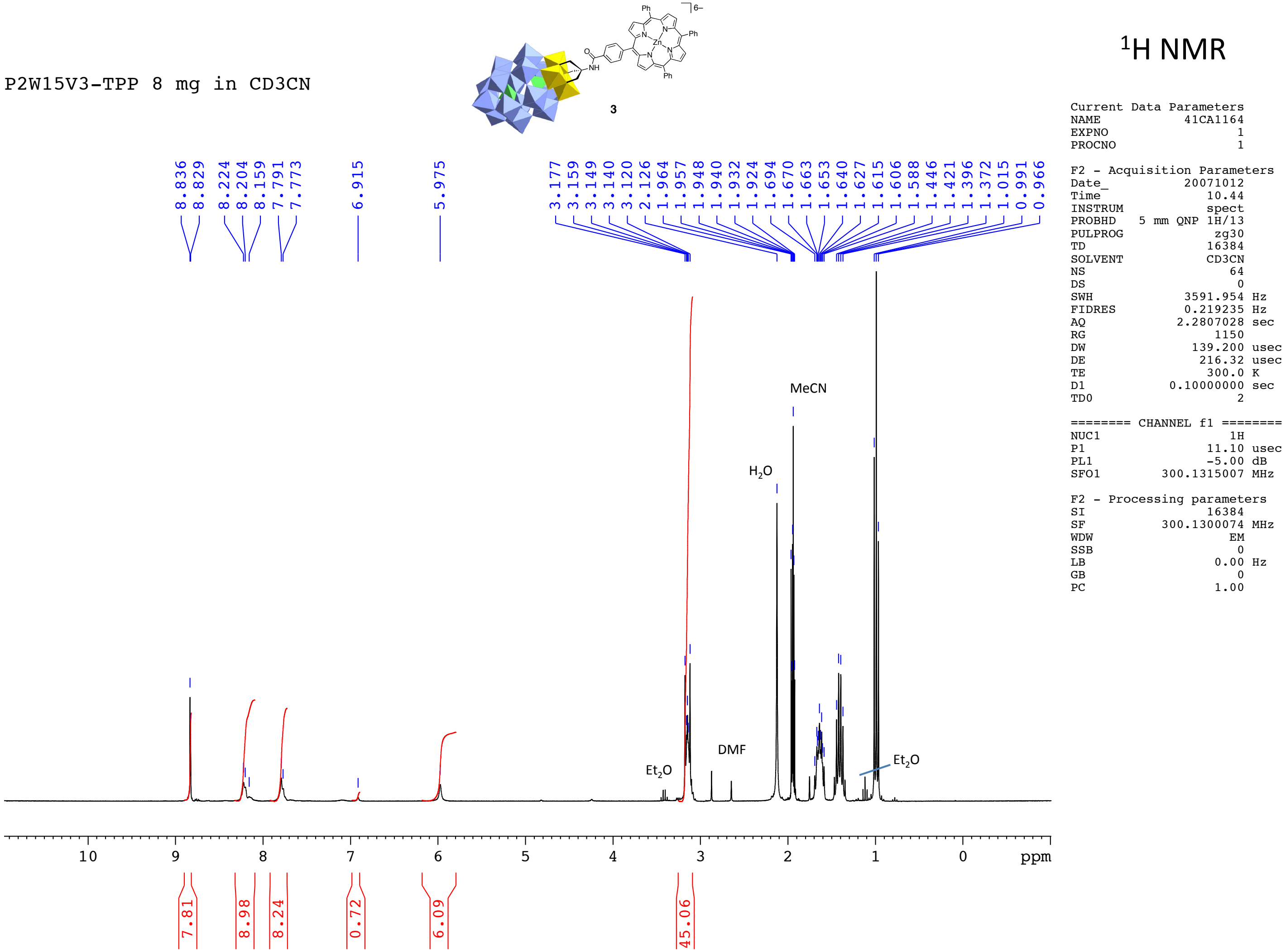
```
Current Data Parameters
NAME              39CA1163
EXPNO                    1
PROCNO                   2

F2 - Acquisition Parameters
Date_             20070926
Time                 13.44
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   16384
SOLVENT              CD3CN
NS                     160
DS                       0
SWH              21008.404 Hz
FIDRES            1.282251 Hz
AQ               0.3899892 sec
RG                    1440
DW                  23.800 usec
DE                  216.32 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.10 usec
PL1                  -5.00 dB
SFO1           300.1405046 MHz

F2 - Processing parameters
SI                   16384
SF             300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

Figure S3: ^{13}C NMR spectrum of Anderson POM **2**.



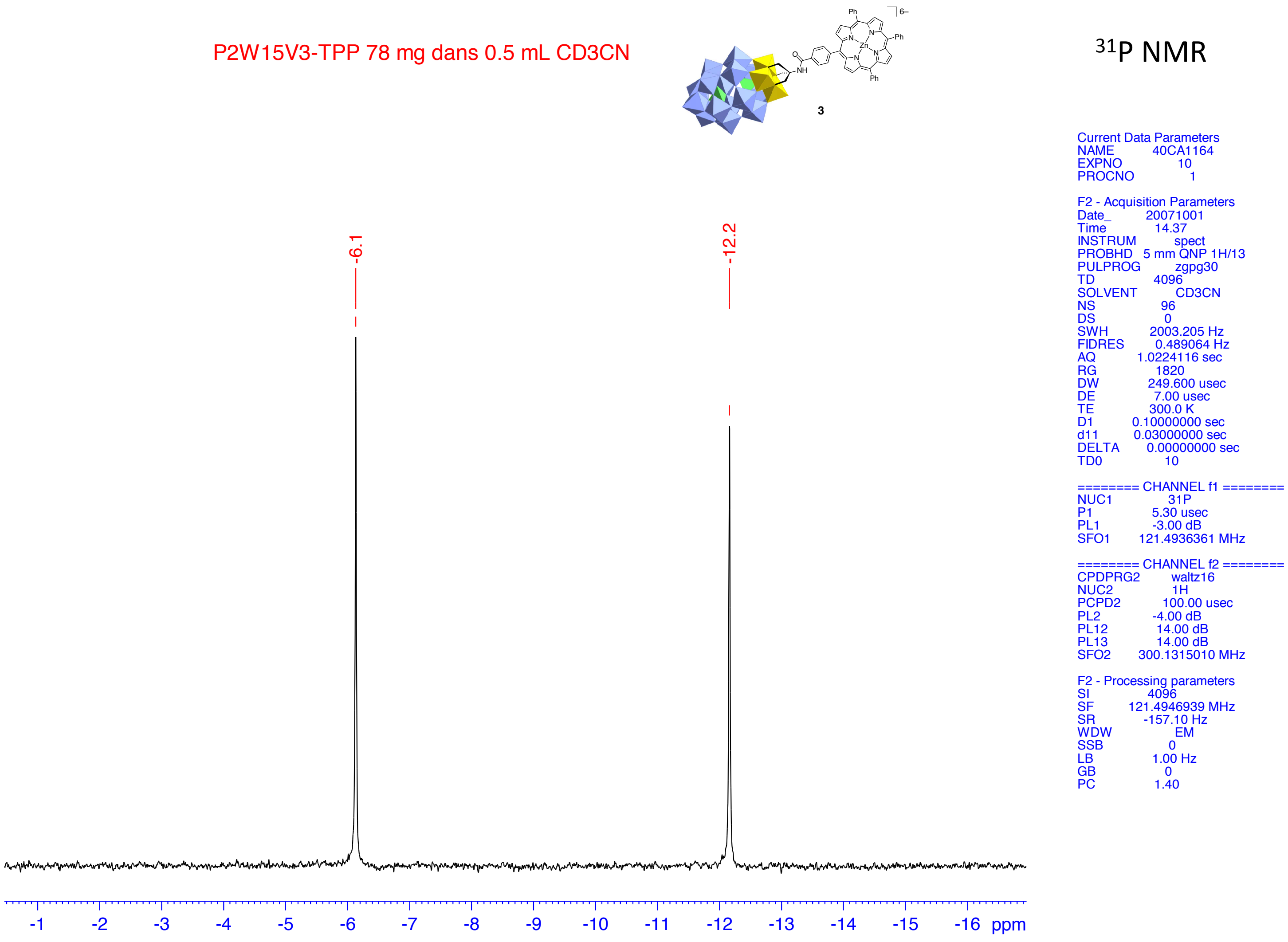
```
Current Data Parameters
NAME          39CA1163
EXPNO               10
PROCNO               1

F2 - Acquisition Parameters
Date_         20070926
Time             18.41
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD               16384
SOLVENT          CD3CN
NS              128000
DS                   0
SWH        156250.000 Hz
FIDRES        9.536743 Hz
AQ           0.0524788 sec
RG                1820
DW               3.200 usec
DE               20.00 usec
TE               300.1 K
D1          0.20000000 sec
d11         0.03000000 sec
DELTA       0.10000000 sec
TD0               1000

======== CHANNEL f1 ========
NUC1               13C
P1                5.80 usec
PL1              -5.00 dB
SFO1        75.4752960 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2              -5.00 dB
PL12             14.00 dB
PL13             14.00 dB
SFO2       300.1315010 MHz

F2 - Processing parameters
SI               16384
SF          75.4676680 MHz
WDW                 EM
SSB                  0
LB               10.00 Hz
GB                   0
PC                1.40
```

Figure S4: ^{1}H NMR spectrum of Dawson POM **3**.



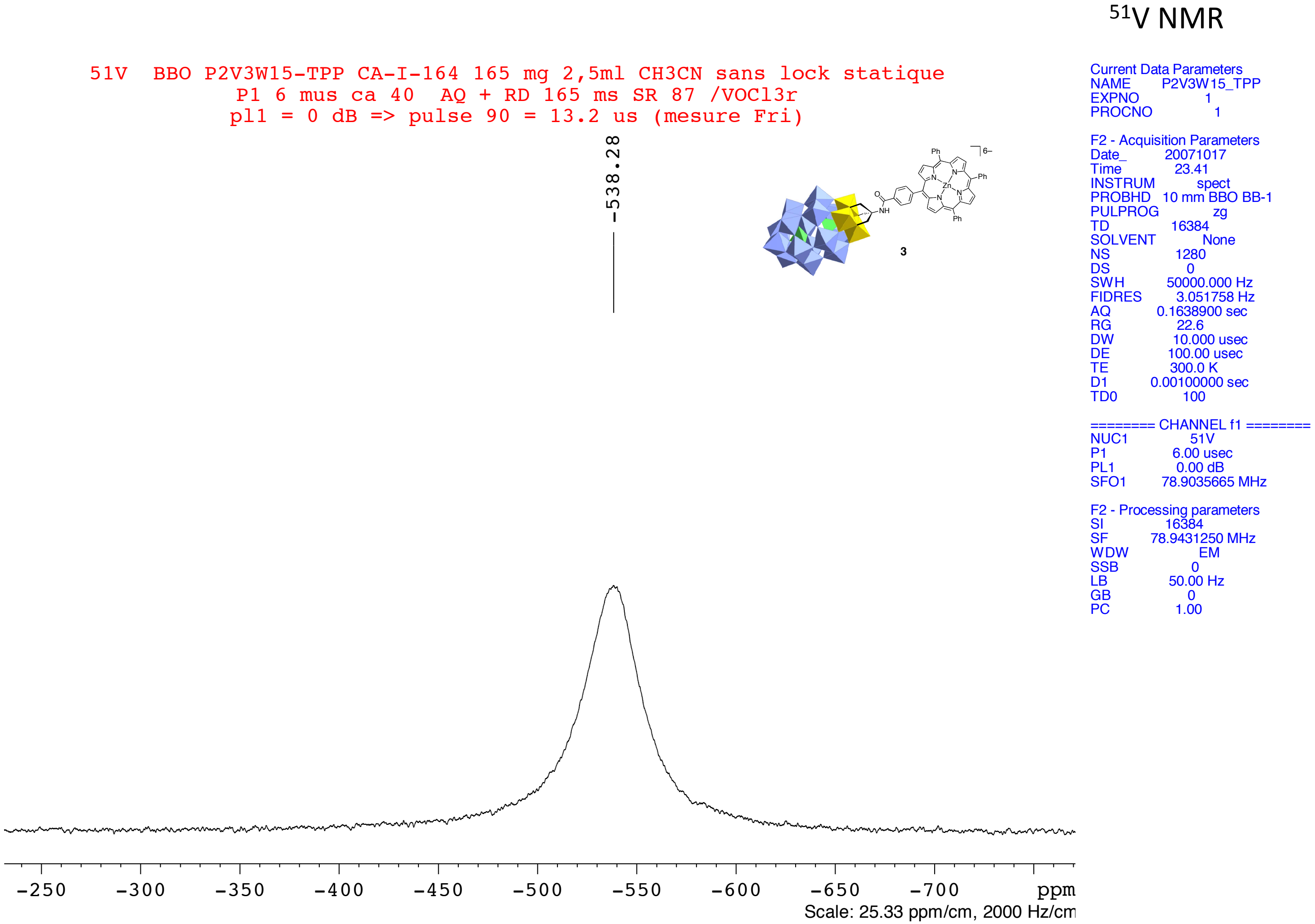
```
Current Data Parameters
NAME             41CA1164
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071012
Time                10.44
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  16384
SOLVENT             CD3CN
NS                     64
DS                      0
SWH              3591.954 Hz
FIDRES           0.219235 Hz
AQ              2.2807028 sec
RG                   1150
DW                139.200 usec
DE                 216.32 usec
TE                  300.0 K
D1             0.10000000 sec
TD0                     2

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.10 usec
PL1                 -5.00 dB
SFO1          300.1315007 MHz

F2 - Processing parameters
SI                  16384
SF            300.1300074 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

Figure S5: ^{31}P NMR spectrum of Dawson POM **3**.



```
Current Data Parameters
NAME          40CA1164
EXPNO               10
PROCNO               1

F2 - Acquisition Parameters
Date_         20071001
Time             14.37
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG        zgpg30
TD                4096
SOLVENT          CD3CN
NS                  96
DS                   0
SWH           2003.205 Hz
FIDRES        0.489064 Hz
AQ           1.0224116 sec
RG                1820
DW             249.600 usec
DE                7.00 usec
TE               300.0 K
D1          0.10000000 sec
d11         0.03000000 sec
DELTA       0.00000000 sec
TD0                 10

======== CHANNEL f1 ========
NUC1               31P
P1                5.30 usec
PL1              -3.00 dB
SFO1       121.4936361 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              -4.00 dB
PL12             14.00 dB
PL13             14.00 dB
SFO2       300.1315010 MHz

F2 - Processing parameters
SI                4096
SF         121.4946939 MHz
SR             -157.10 Hz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

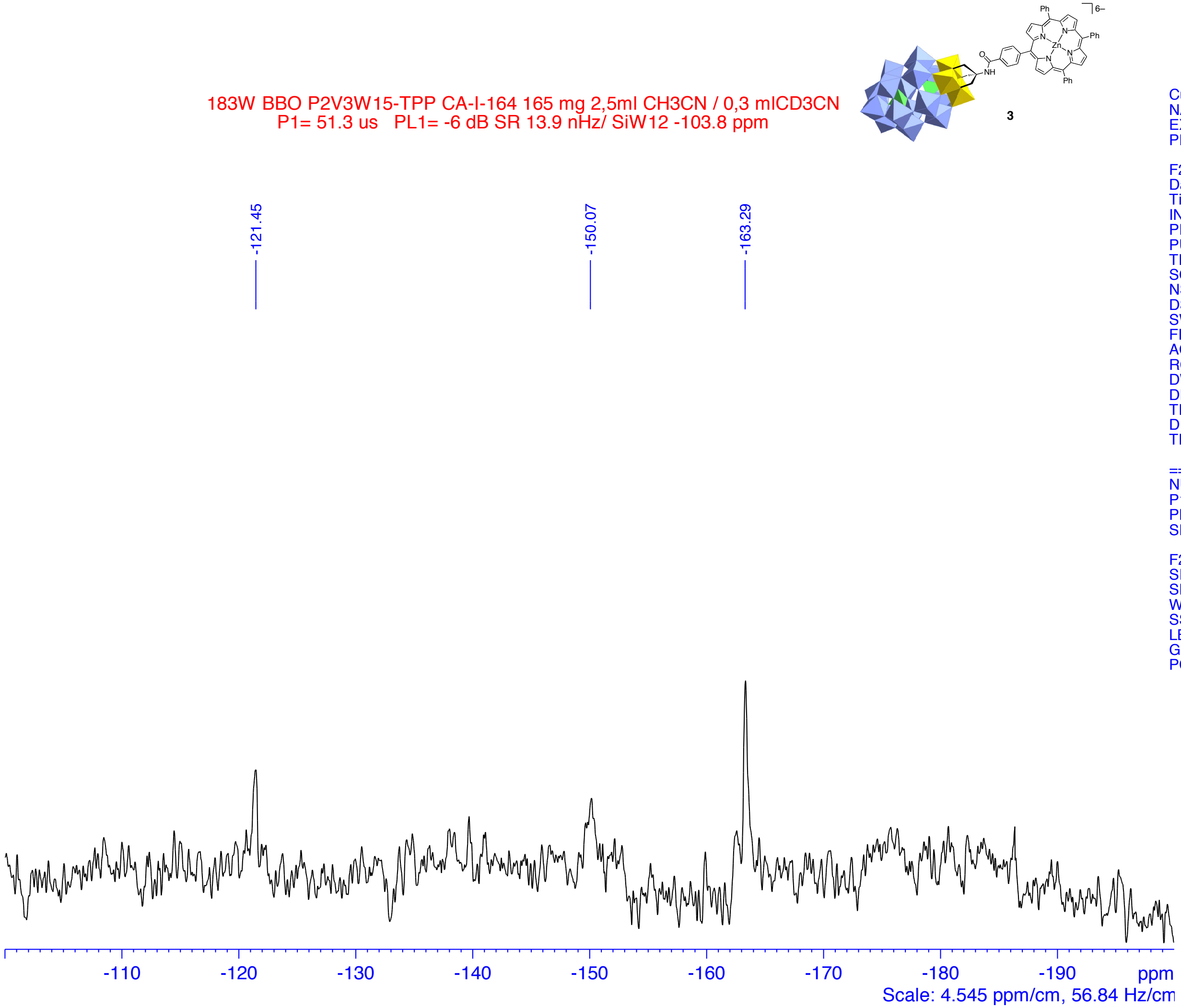
Figure S6: ^{51}V NMR spectrum of Dawson POM **3**.



```
Current Data Parameters
NAME        P2V3W15_TPP
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20071017
Time              23.41
INSTRUM           spect
PROBHD   10 mm BBO BB-1
PULPROG              zg
TD                16384
SOLVENT            None
NS                 1280
DS                    0
SWH        50000.000 Hz
FIDRES      3.051758 Hz
AQ        0.1638900 sec
RG                 22.6
DW           10.000 usec
DE           100.00 usec
TE              300.0 K
D1       0.00100000 sec
TD0                 100

======== CHANNEL f1 ========
NUC1                51V
P1            6.00 usec
PL1             0.00 dB
SFO1      78.9035665 MHz

F2 - Processing parameters
SI                16384
SF        78.9431250 MHz
WDW                  EM
SSB                   0
LB             50.00 Hz
GB                    0
PC                 1.00
```

Figure S7: ^{183}W NMR spectrum of Dawson POM **3**.

Note : The low resonance frequency and natural abundance of 14.3% of ^{183}W result in low receptivity.



^{183}W NMR

Current Data Parameters
NAME P2V3W15_TPP
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071018
Time 0.48
INSTRUM spect
PROBHD 10 mm BBO BB-1
PULPROG zg
TD 8192
SOLVENT CD3CN
NS 15360
DS 0
SWH 2500.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384500 sec
RG 2050
DW 200.000 usec
DE 200.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1000

======== CHANNEL f1 ========
NUC1 183W
P1 51.30 usec
PL1 -6.00 dB
SFO1 12.5027013 MHz

F2 - Processing parameters
SI 8192
SF 12.5045909 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure S8: UV-vis absorption spectra

of ZnTPP-tris (compound **1**, black), Anderson-ZnTPP (compound **2**, blue) and Dawson-ZnTPP (compound **3**, red) in DMF solution

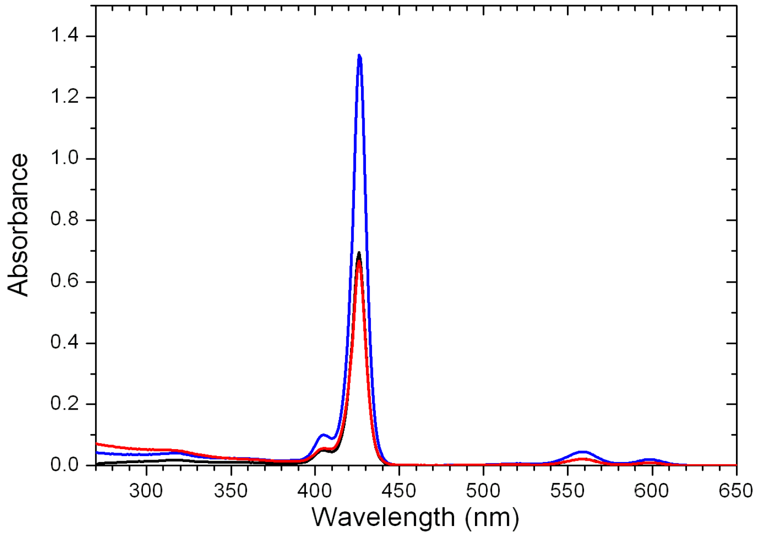


Figure S9: Excitation spectrum

of Dawson-ZnTPP (compound **3**) in DMF solution recorded at λ_{em} = 720 nm and revealing the presence of traces of free-base porphyrin H_2TPP.

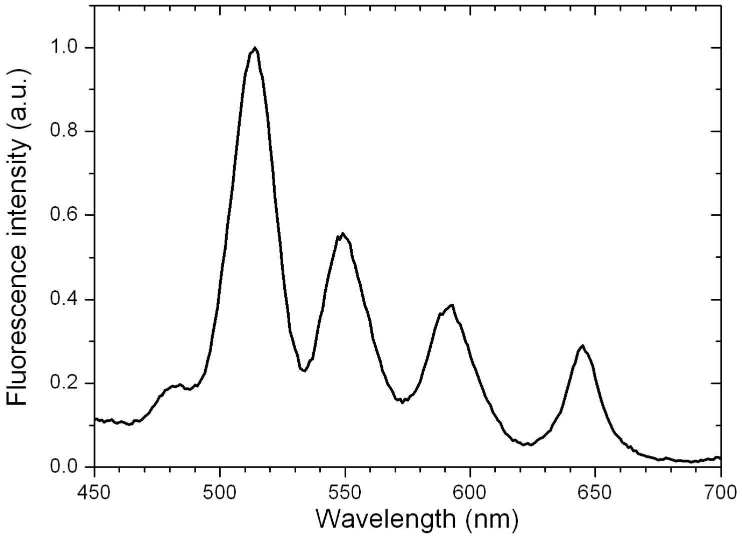


Figure S10: Purification of POM-porphyrin compounds

(a) Steady-state emission spectra (λ_{exc} = 725 nm) and **(b)** fluorescence decays (λ_{em} = 610 nm, λ_{exc} = 420 nm) of ZnTPP-tris (**1**, black) and Dawson-ZnTPP (compound **3**) before (green) and after additional purification by repeated precipitation in ethylacetate (red).

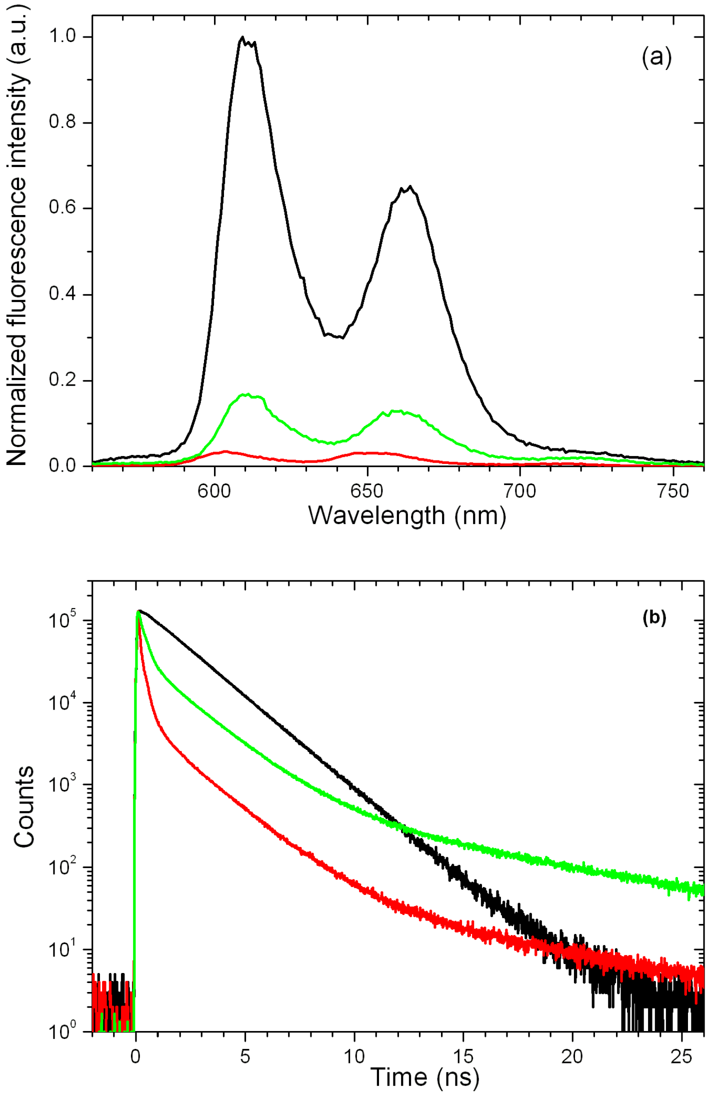
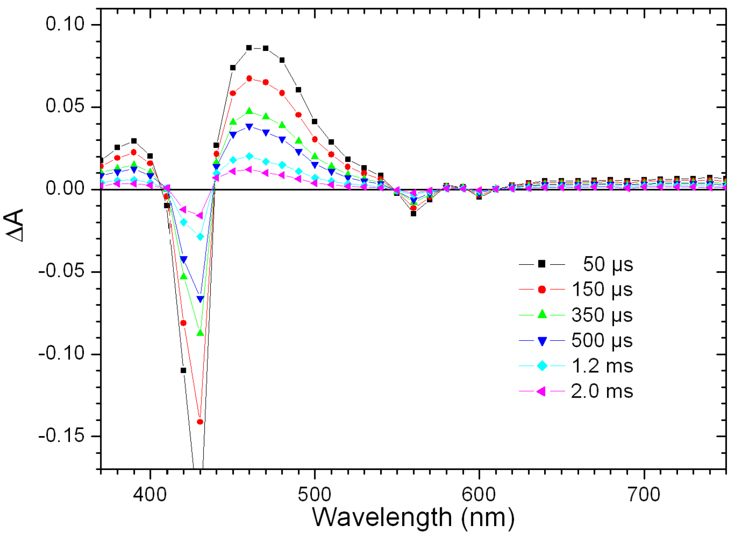
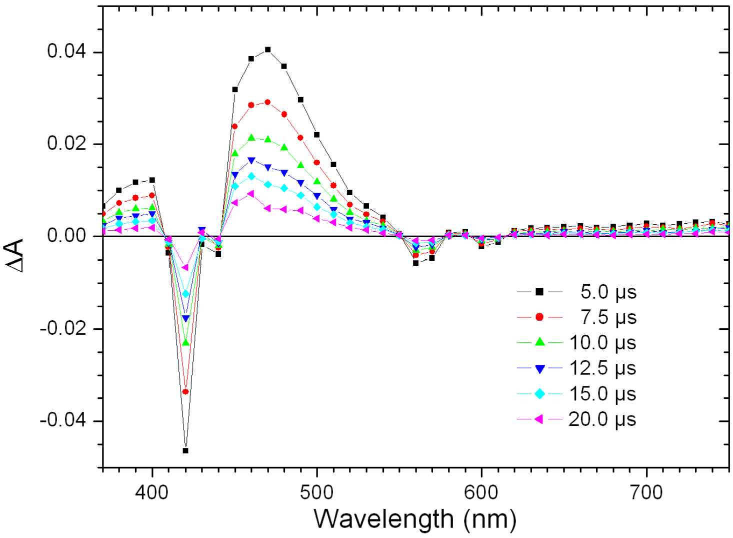


Figure S11: Transient absorption spectra recorded in deaerated DMF solutions for the three compounds after 532 nm laser excitation (3 ns pulses).

a) ZnTPP-Tris, compound **1**



b) Anderson-ZnTPP, compound **2**



c) Dawson-ZnTPP, compound **3**

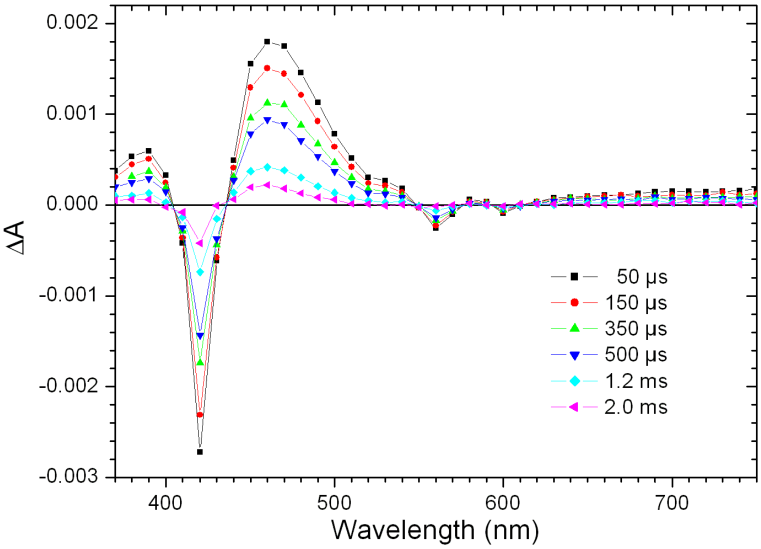

0.002
0.001
0.000
-0.001
-0.002
-0.003
ΔA
400
500
600
700
Wavelength (nm)
50 µs
150 µs
350 µs
500 µs
1.2 ms
2.0 ms

Figure S12: Picosecond transient absorption spectra and time profiles of ZnTPP-Tris in DMF solution obtained after 395 nm laser excitation (100 fs pulses).

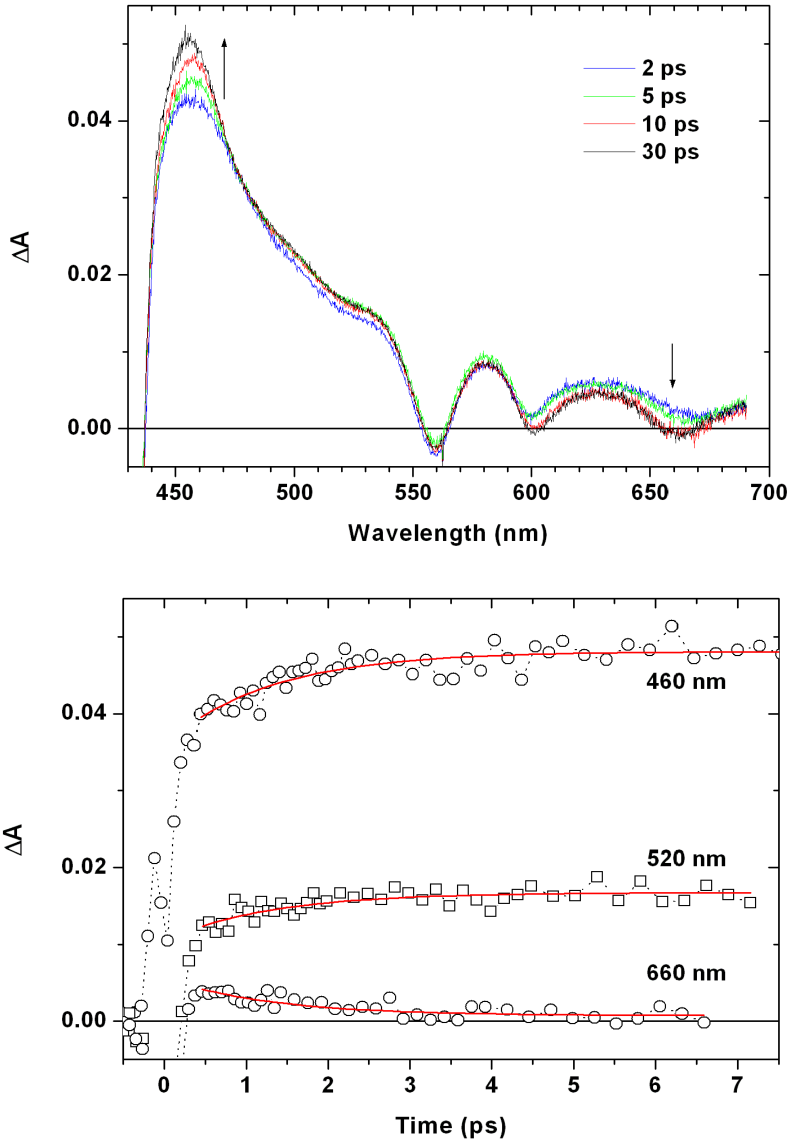


Figure S13: Comparison of the differential absorption spectrum obtained by substracting the spectrum recorded at 500 ps from the spectrum measured at 30 ps for Dawson-ZnTPP with the spectrum measured at 30 ps for ZnTPP-Tris in DMF solutions.

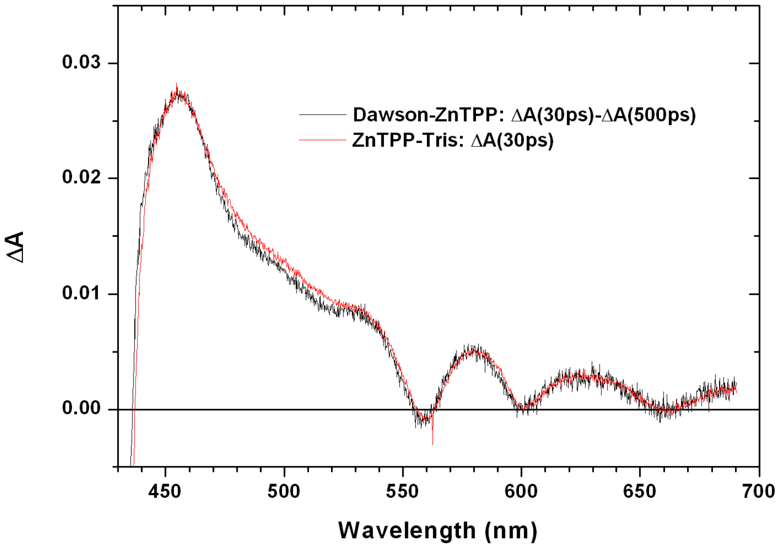


Figure S14: Cyclic voltammograms of Anderson POM **2** with different scan limits in DMF using 0.1 M TBAPF$_6$ as electrolyte. c = 0.5 mmol·L^{-1}. A) Full voltammogram, B) Cathodic part with different negative limits.

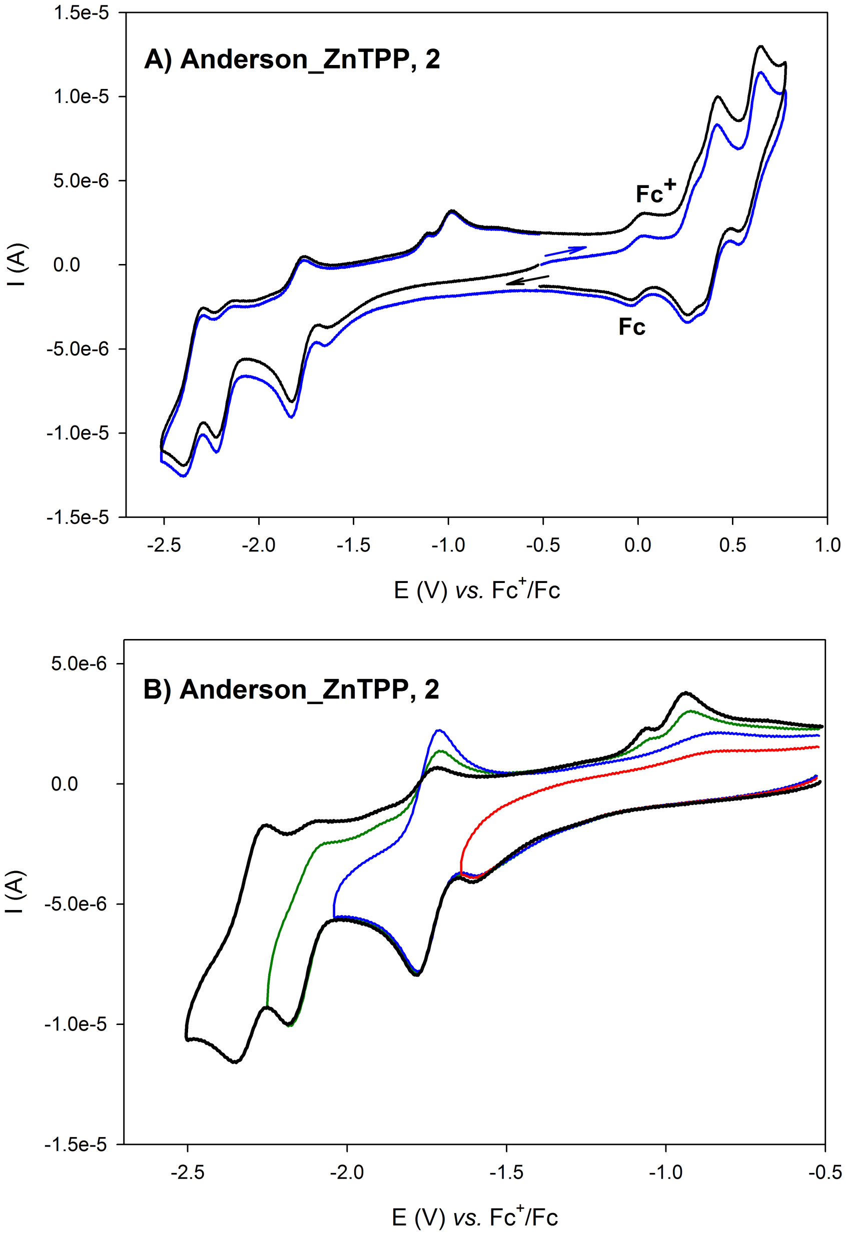


Figure S15: Cyclic voltammograms of Anderson POM **2** at different scan rates: reduction. A) and B) Cyclic voltammograms of compound **2** in DMF using 0.1 M $TBAPF_6$ as electrolyte at various scan rates. $c = 0.5\ mmol \cdot L^{-1}$. C) First and second cathodic peak current dependence with the square root of the scan rate. D) First and second cathodic peak current dependence with the scan rate.

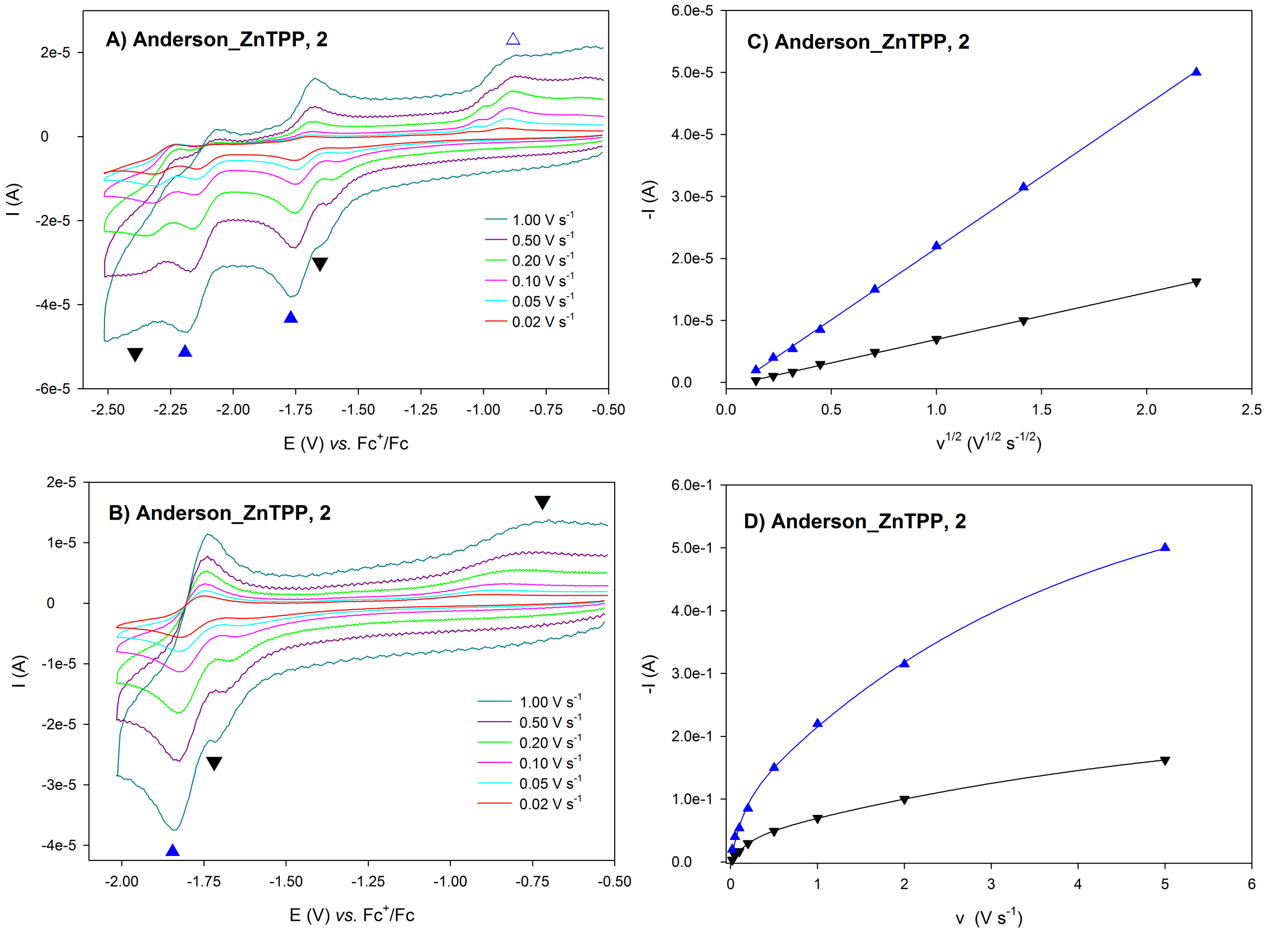


Figure S16: Cyclic voltammograms of Anderson POM **2** at different scan rates: oxidation.

A) Cyclic voltammograms of compound **2** in DMF using 0.1 M $TBAPF_6$ as electrolyte at various scan rates. c = 0.5 mmol·L^{-1}. B) First anodic peak current dependence with the square root of the scan rate.

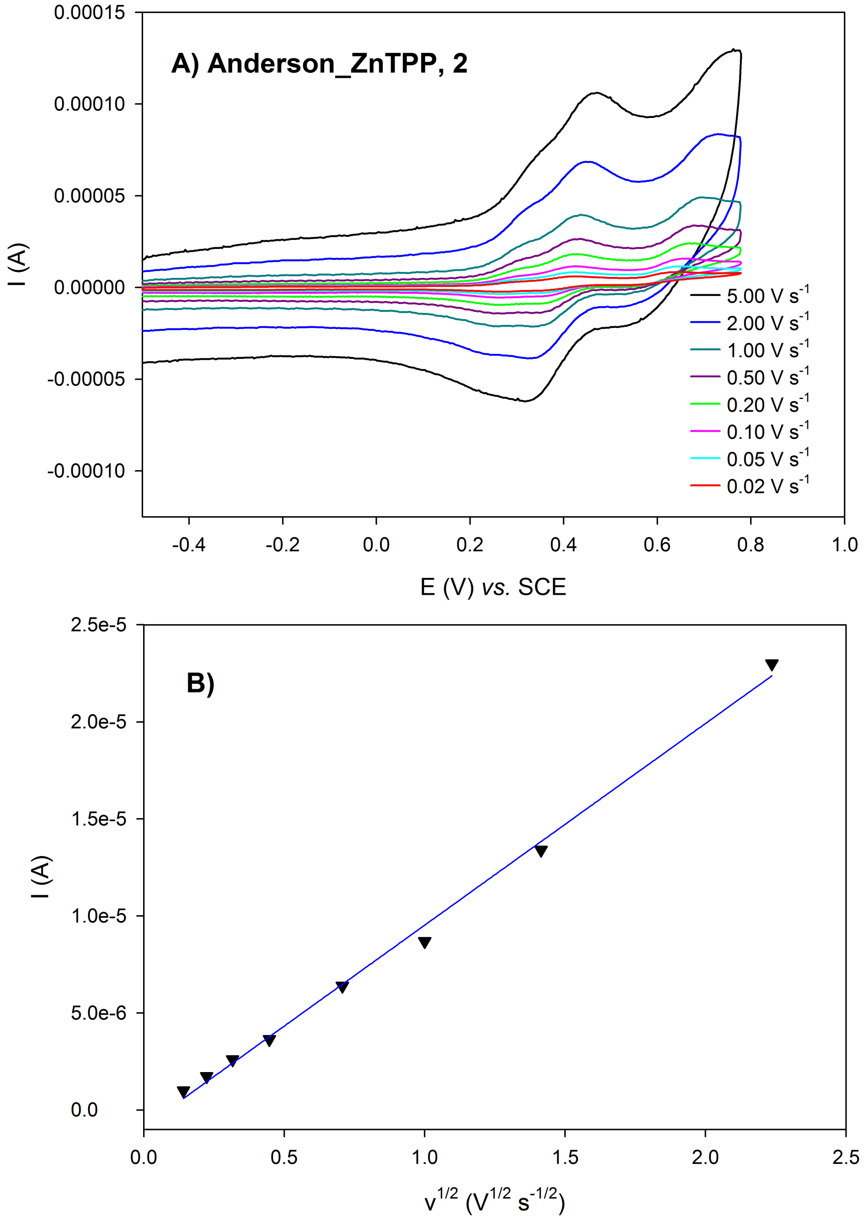


Figure S17: Normal pulse, Linear sweep and Differential pulse voltammetry of Anderson POM **2**

Normal pulse voltammogram (pulse time: 70 ms, potential step: 1 mV), linear sweep voltammogram (scan rate: 10 mV s^{-1}, N = 1000 rpm), and differential pulse voltammogram (pulse time: 50 ms, potential step: 1 mV) of Anderson POM **2** in DMF, using 0.1 M $TBAPF_6$ as electrolyte. c = 0.5 mmol·L^{-1}.

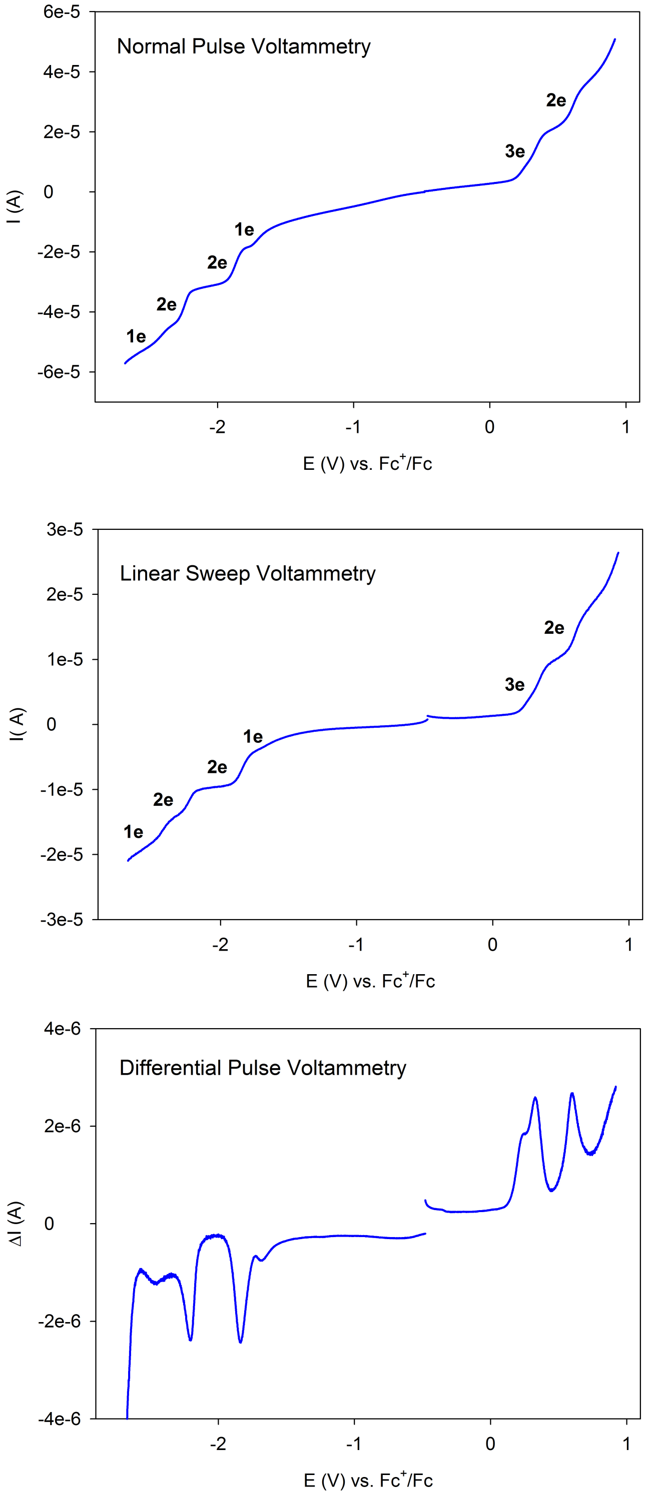
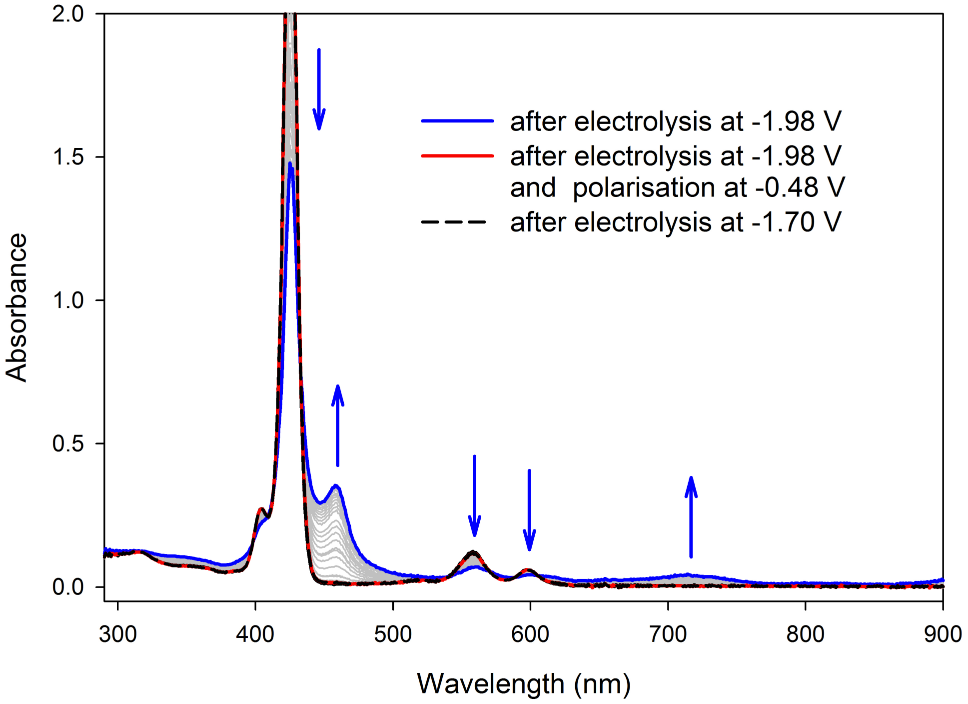


Figure S18: Spectroelectrochemistry of Anderson POM **2**.
Thin-layer visible spectroscopy obtained during (top) the reduction of the compound **2** at -1.98 V and -1.70 V *vs.* Fc^+/Fc and (bellow) its oxidation at +0.42 V *vs.* Fc^+/Fc using an OTTLE (optically transparent thin layer electrode).



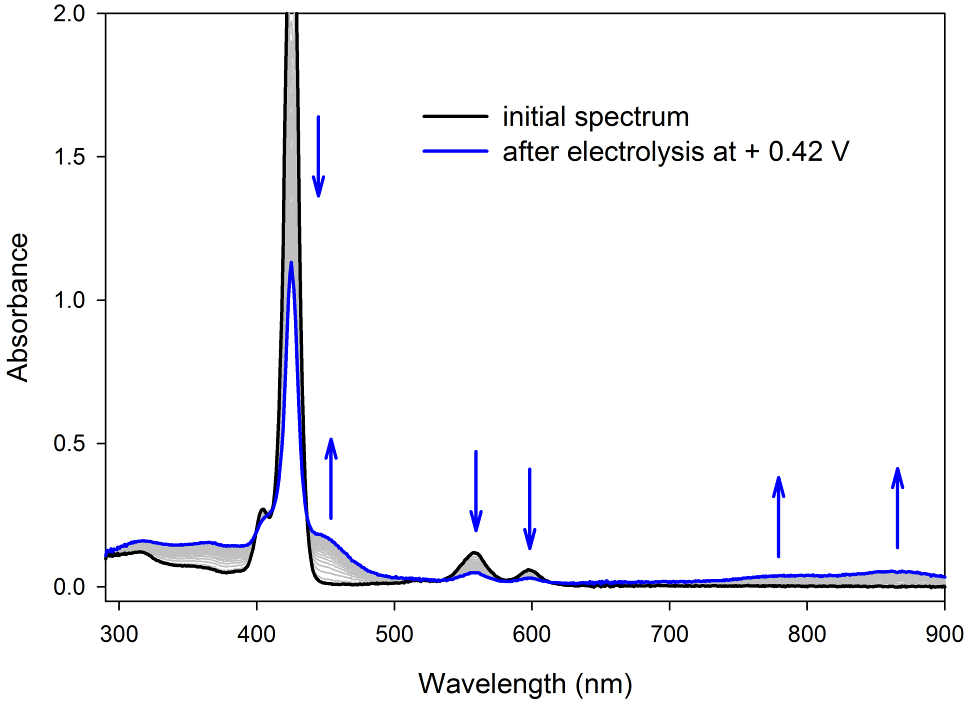


Figure S19: Spectroelectrochemistry of Dawson POM **3**.

Thin-layer visible spectroscopy obtained during the reduction of the compound **3** at -1.08 V, -1.58 V and -1.83 V *vs.* Fc^+/Fc using an OTTLE (optically transparent thin layer electrode).