

Supporting Information

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Electron Transfer in Self-Assembled Micelles Built by
Conductive Polyoxometalate-Surfactants Showing Battery-
Like Behavior

*Alexander Klaiber, Tom Kollek, Simon Cardinal, Nicolas Hug,
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Analytical Methods.

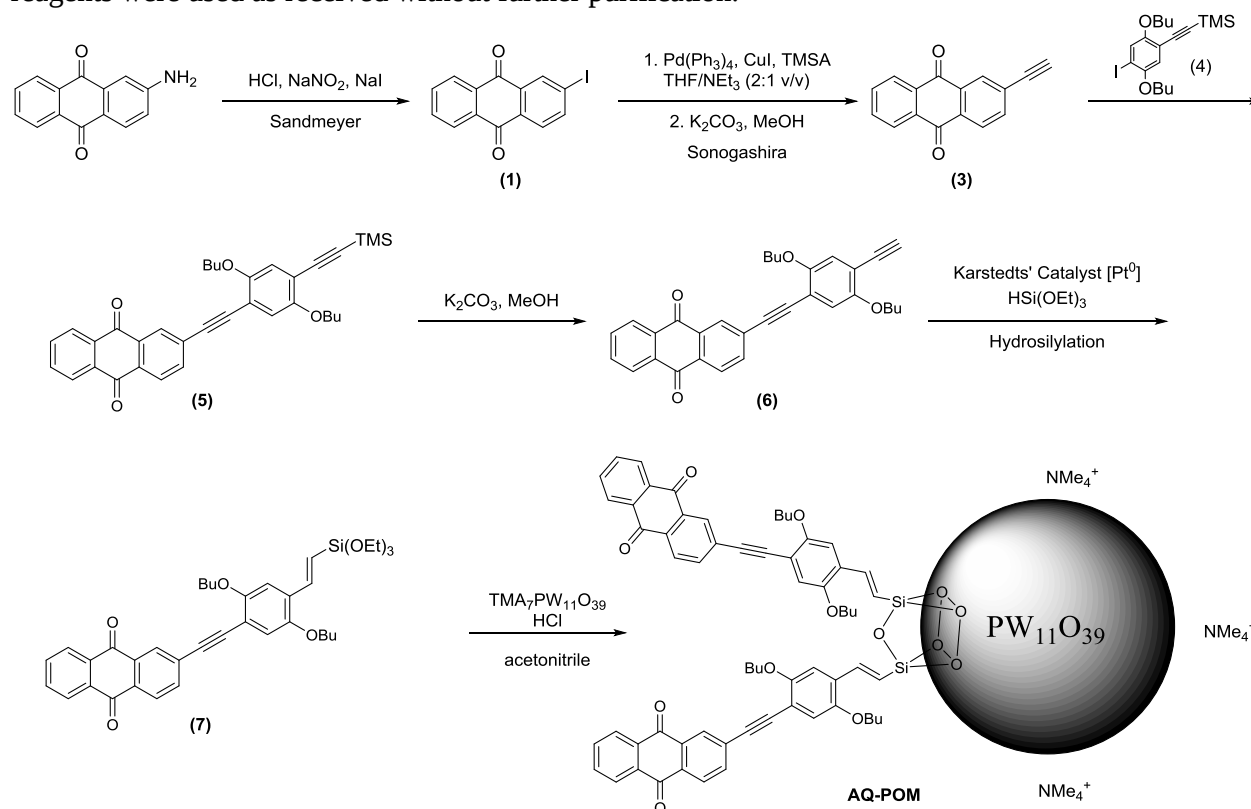
NMR measurements (^1H , ^{13}C , ^{31}P) were performed on a Varian Unity INOVA 400 spectrometer. The ^{183}W NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer with 10 mm NMR tubes. **ESIMS** data were acquired on a Bruker microtof II system. The solutions were injected directly into the evaporation chamber. For **cryo transmission electron microscopy** studies, a sample droplet of 2 μl was put on a lacey carbon filmed copper grid (Science Services, Muenchen), which was hydrophilized by air plasma glow discharge unit (30s with 50W, Solarus 950, Gatan, Muenchen, Germany). Subsequently, most of the liquid was removed with blotting paper in a Leica EM GP (Wetzlar, Germany) grid plunge device, leaving a thin film stretched over the lace holes in the saturated water atmosphere of the environmental chamber. The specimens were instantly shock frozen by rapid immersion into liquid ethane cooled to approximately 97K by liquid nitrogen in the temperature-controlled freezing unit of the Leica EM GP. The temperature was monitored and kept constant in the chamber during all the sample preparation steps. The specimen was inserted into a cryotransfer holder (CT3500, Gatan, Muenchen, Germany) and transferred to a Zeiss/LEO EM922 Omega EFTEM (Zeiss Microscopy GmbH, Jena, Germany). Examinations were carried out at temperatures around 95K. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ($\Delta E = 0 \text{ eV}$) were taken under reduced dose conditions (100 – 1000 e/nm^2). All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 1000, Gatan, Muenchen, Germany) combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.9, Gatan, Muenchen, Germany). Collected images were processed with a background-subtraction routine, and where appropriate, a smoothing filter (Butterworth Filter) was applied to reduce noise. **IR spectroscopy** was performed on a PerkinElmer 100 system. **UV/vis spectroscopy** was performed on a Varian Cary 100. **Dynamic light scattering** was measured on a Malvern Zetasizer Nano ZSP machine. Reduced species were generated in a bulk electrolysis cell, equipped with a Pt working electrode and an Ag reference electrode. The counter electrode contained potassium hexacyanidoferrate(II) as sacrificial reductant.

Cyclic voltammetry was measured with an Epsilon-potentiostat (BASi) (working electrode: glassy carbon, reference electrode: Ag/AgCl electrode (3M KCl); counter electrode: Pt wire). **SAXS** was acquired on a Bruker Nanostar system equipped with pinhole collimation and Cu K α radiation. The liquid sample was sealed in a 1 mm Mark tube made of soda lime glass. **Geometry optimization and orbital calculation** was performed using Density-Functional Theory (DFT) with the TURBOMOLE Program Package for ab initio Electronic Structure Calculations using BP86/def2-TZVP level of theory. TURBOMOLE V7.1 2016, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>. The authors acknowledge support by the state of Baden-Württemberg through bwHPC.

Experimental Section

General Information.

All experiments involving Pd complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Unless otherwise specified, reagents were used as received without further purification.



2-Iodo-anthraquinone (1)

2-Iodo-anthraquinone has been synthesized according to standard Sandmeyer-procedure, for example described by Yamada *et al.*¹

2-(Trimethylsilyl)ethynyl-anthraquinone (2)

A solution of 5.9 g (17.6 mmol) of 2-iodo-anthraquinone, 50 mg (0.7 mol %) CuI, 150 mg Pd(PPh₃)₄ (1.5 mol %) and 2.6 mL of trimethylmethylsilylacetylene (TMSA) (19.4 mmol, 1.1 eq) in 60 mL tetrahydrofuran (THF) and trimethylamine (NEt₃) (2/1, v/v) was prepared. After stirring for 48 h at 50°C the solvent was evaporated and the residue was extracted with pentane. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel and pentane as eluent. The product was obtained as colorless powder (5.3 g, 17.4 mmol, 98 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 1.7 Hz, 1H), 8.34 – 8.30 (m, 2H), 8.26 (d, *J* = 8.0 Hz, 3H), 0.29 (s, 9H, TMS).

2-Ethynyl-anthraquinone (3)

3.0 g (10 mmol) of TMS-protected alkyne (2) was dissolved in 150 mL of CH₂Cl₂/MeOH (1:2, v/v), and 15 equiv. of K₂CO₃ was added. After stirring the resulting dispersion for 2 h, 200 mL of water was added. After separation of the phases, the organic solvent was dried using MgSO₄ and removed

under reduces pressure. The obtained product was used without further purification (2.2 g, 9.3 mmol, 95 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.43 (dd, J = 1.7, 0.5 Hz, 1H), 8.36 – 8.33 (m, 2H), 8.30 (dd, J = 8.0, 0.5 Hz, 1H), 7.89 (dd, J = 8.0, 1.7 Hz, 1H), 7.86 – 7.82 (m, 2H), 3.39 (s, 1H, Alkyne).

^{13}C NMR (101 MHz, CDCl_3) δ 182.59, 182.55, 137.25, 134.50, 134.44, 133.61, 133.57, 133.52, 133.06, 131.02, 128.47, 127.51, 127.49, 127.48, 82.20, 82.02.

((2,5-Dibutoxy-4-iodophenyl)ethynyl)trimethylsilane (4)

(4) was prepared *via* standard etherification, iodination and Sonogashira reaction, for example described by Shinomiya *et al.*¹¹

2-((2,5-Dibutoxy-4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-anthraquinone (5)

A solution of 1.3 g (6.5 mmol) of alkyne **(3)**, 50 mg (4 mol %) CuI, 150 mg $\text{Pd}(\text{PPh}_3)_4$ (2 mol %) and 2.5 g of compound **(4)** (6.5 mmol, 1.0 eq) in 60 ml THF/ NEt_3 (2/1, v/v) was prepared. After stirring for 48 h at 50°C the solvent was evaporated and the residue was extracted with pentane. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel and CH_2Cl_2 /pentane (1:1, v/v) as eluent. The product was obtained as orange powder (1.8 g, 3.3 mmol, 50 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, J = 1.6 Hz, 1H), 8.32 (ddd, J = 5.2, 4.1, 1.2 Hz, 2H), 8.29 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 8.0, 1.7 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.00 (s, 1H), 6.97 (s, 1H), 4.03 (dt, J = 7.6, 6.4 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.90 – 1.76 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.66 – 1.51 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (dt, J = 12.3, 7.4 Hz, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.27 (s, 9H, TMS).

^{13}C NMR (101 MHz, CDCl_3) δ 182.62, 182.48, 154.17, 153.87, 136.35, 134.28, 134.16, 133.60, 133.50, 133.45, 132.25, 130.12, 129.82, 127.39, 127.31, 127.30, 117.17, 117.06, 114.96, 113.03, 100.96, 100.82, 93.38, 91.12, 69.35, 69.32, 31.38, 31.33, 19.31, 19.27, 13.90, -0.07.

2-((2,5-Dibutoxy-4-ethynylphenyl)ethynyl)-anthraquinone (6)

1.8 g (3.3 mmol) of TMS-protected alkyne **(5)** was dissolved in 150 mL of CH_2Cl_2 /MeOH (1:2, v/v), and 15 equiv. of K_2CO_3 was added. After stirring the resulting dispersion for 2 h, 200 mL of water was added. After separation of the phases, the organic solvent was dried using MgSO_4 and removed under reduces pressure. The obtained product was used without further purification (1.6 g, 3.3 mmol, 99 %).

^1H NMR (400 MHz, CDCl_3) 8.44 (d, J = 1.7 Hz, 1H), 8.35 – 8.29 (m, 3H), 7.88 (dd, J = 8.1, 1.7 Hz, 1H), 7.81 (ddd, J = 6.4, 2.6, 1.2 Hz, 2H), 7.04 (s, 1H), 7.01 (s, 1H), 4.04 (td, J = 6.5, 1.9 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.37 (s, 1H, alkyne) 1.93 – 1.76 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 – 1.48 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (dt, J = 14.6, 7.4 Hz, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ 182.72, 182.59, 154.26, 153.94, 136.50, 134.42, 134.30, 133.71, 133.63, 133.56, 132.42, 130.28, 129.86, 127.51, 127.43, 117.85, 117.11, 113.89, 113.58, 93.54, 91.01, 82.97, 79.98, 77.48, 77.36, 77.16, 76.84, 69.54, 69.48, 31.45, 31.39, 19.45, 19.35, 14.04, 14.03.

2-((2,5-Dibutoxy-4-(2-(triethoxysilyl)vinyl)phenyl)ethynyl)-anthraquinone (7)

To a degassed solution of 640 mg (0.9 mmol, 1.0 equiv) of **(6)** in 30 mL of CH_2Cl_2 were added 160 mg of triethoxysilane (0.9 mmol, 1.0 equiv) and 3 drops of Karstedt 's catalyst in xylene. After stirring for 48 h the solvent was removed after reaction control. Here, the alkyne-signal in ^1H -NMR

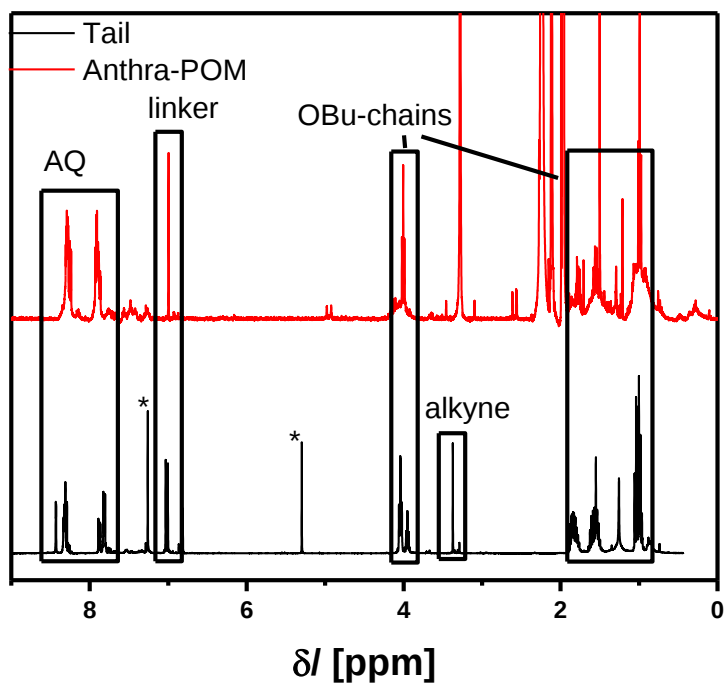
vanished and characteristic vinyl-signals arose. The resulting orange residue was used without further purification.

Synthesis of AQ-POM

Synthesis of AQ-POM as well as ion exchange was performed analogous to previously described procedure.³

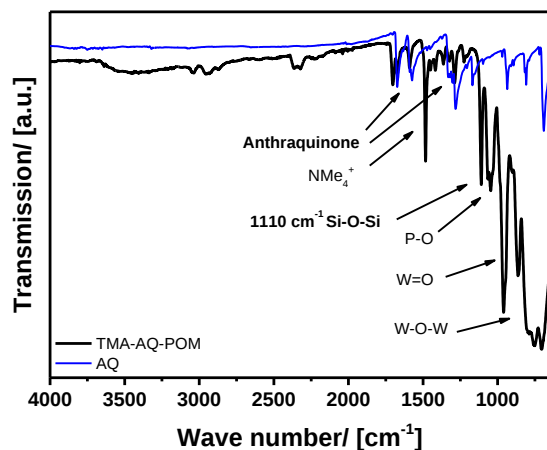
¹H NMR (400 MHz, CD₃CN): as the signals are very broad, integration was not possible.

Comparison with the spectrum of the pure chain (**6**) reveals that the reaction was successful.



S-1: IR-spectroscopy

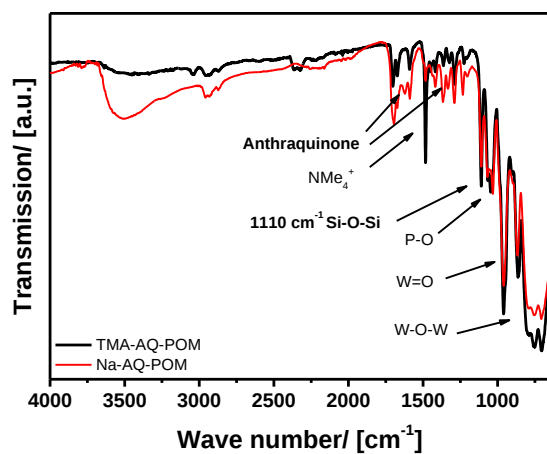
Comparison of Anthraquinone and AQ π POM (TMA counter ion)



In the IR spectra, one can clearly see the Si-O-Si vibration, the characteristic motif of the linkage of organic chain and cluster. Furthermore the presence of vibrations of both, cluster and anthraquinone, confirm the correct structure of AQ-POM.

Vibrations of AQ-POM (cm^{-1}): 1672 (AQ), 1483 (N-Me), 1282 (AQ), 1111 (Si-O-Si), 1063, 1046, 1032 (all P-O), 996, 985, 961, 945 (all W=O), 861, 800, 756 (W-O-W)

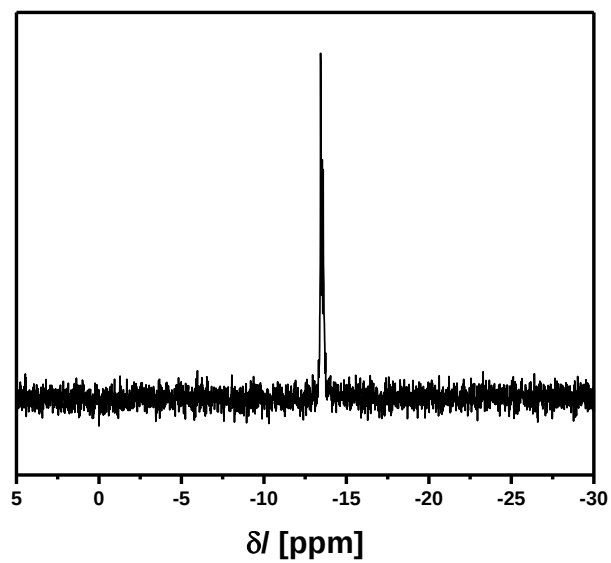
Comparison of TMA and Na-form of AQ π POM



In the lower spectrum the complete ion exchange is confirmed as the TMA signal at 1483 cm^{-1} vanished, whereas the other signals are unaffected.

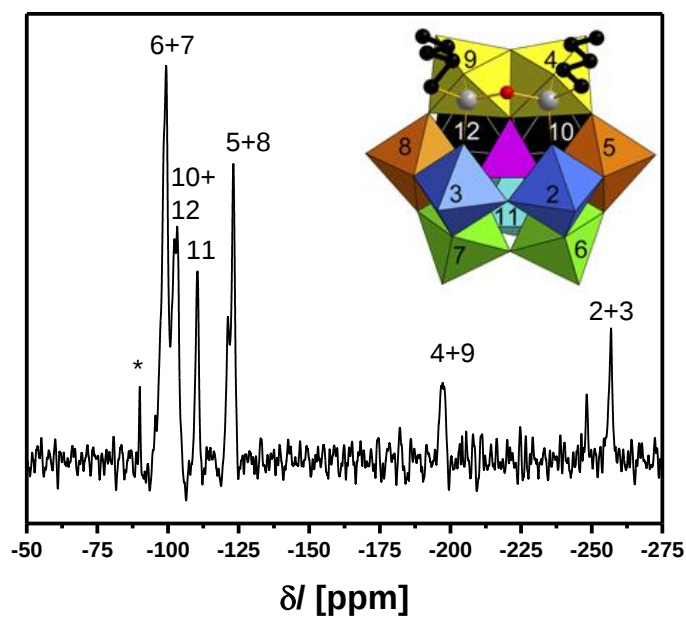
S-2: Multicore NMR spectra

^{31}P -NMR



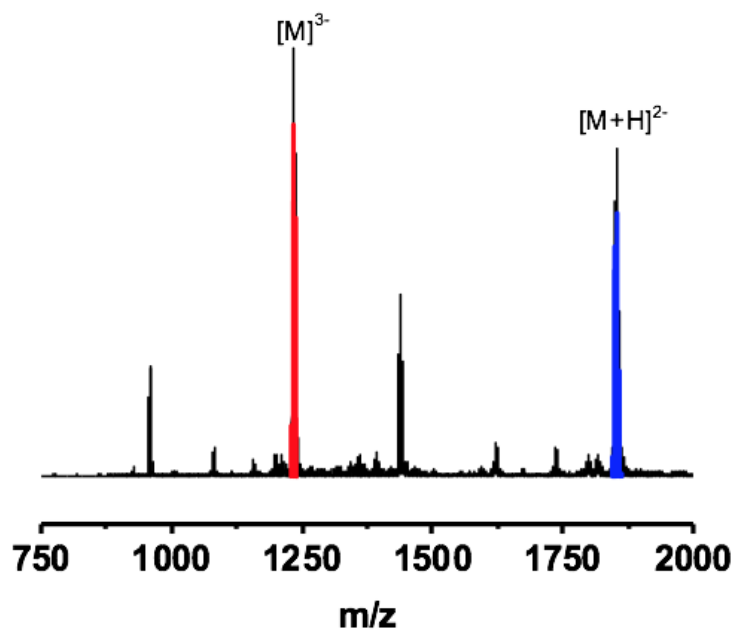
^{31}P NMR (162 MHz, CD_3CN) δ -13.35.
Chemical shift fits to organically substituted Keggin-Cluster.³⁻⁴

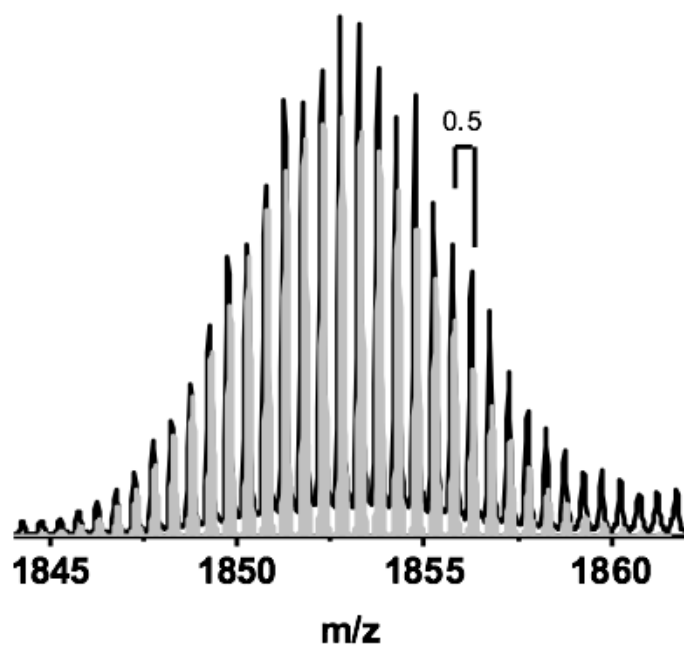
^{183}W -NMR



^{183}W NMR (25 MHz, CDCl_3) δ -99.35, -110.41, -121.18, -123.15, -197.23, -256.84. Comparison with previously described hybrid POM-SURF shows similar chemical shifts. Assignment of peaks has been done accordingly.³

S-3: ESI-MS





black = experimental pattern

grey = simulated pattern for $[M+H]^{2-}$

S-4: Optical properties.

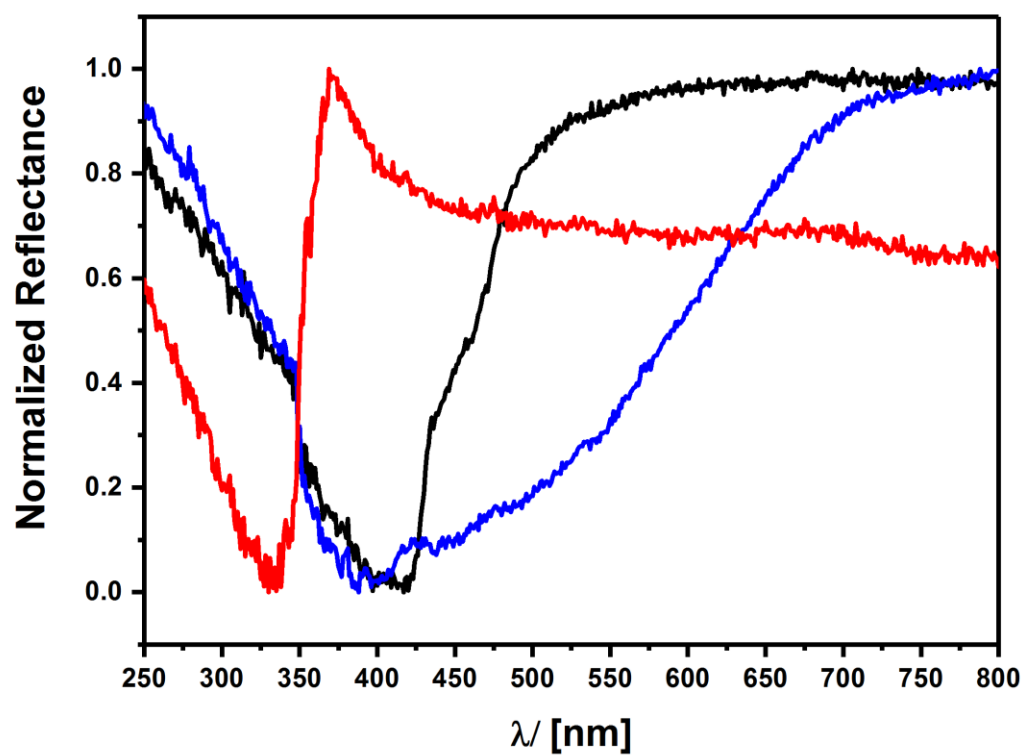
AQ π :



AQ π POM:



UV-Vis spectroscopy (solid state; diffuse reflectance modus):



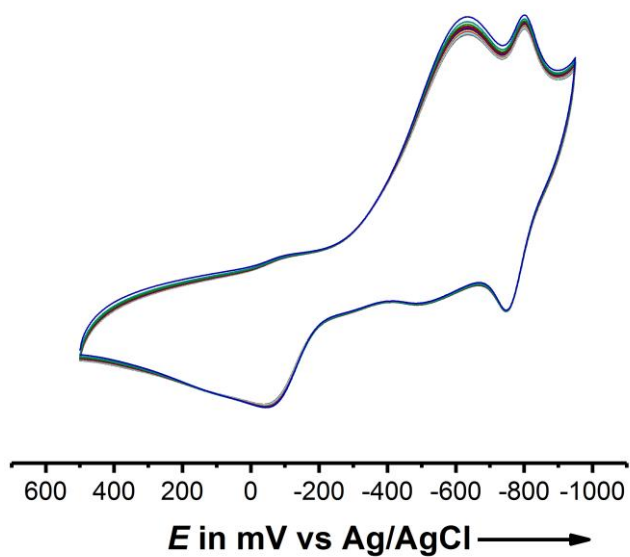
blue curve = AQ π POM

red curve = PW₁₁O₃₉

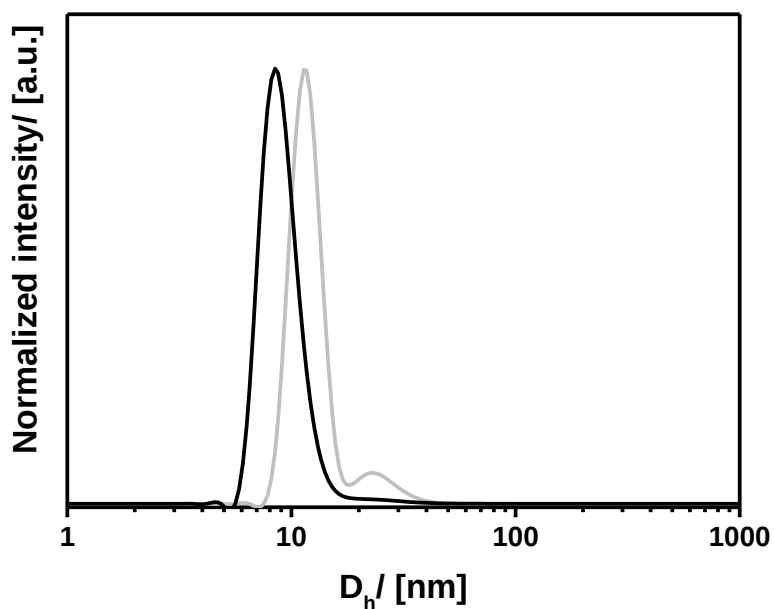
black curve = AQ π

S-5: Electronic properties.

Multi-cyclic voltammetry (20 cycles) measurement of AQ π POM ($c=5$ mg/mL, $v = 1000$ mV/s, in water at $T = 293(\pm 3)$ K with 0.1 M NaClO₄ electrolyte.) showing the reversible redox properties.



S-6: DLS of reduced system



DLS of unreduced (black) and reduced (grey) micellar solution ($c=0.01$ g/L), $V = -1000$ mV

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