Electronic Supplementary Information

Synthesis and Characterization of Conjugated Polyoxometalate-Porphyrin Copolymers Obtained from a Dawson-Type Polyoxophosphovanadotungstate †

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General Remarks

Reagents and chemicals were purchased from commercial sources and used as received. The starting TBA₅H₄[P₂V₃W₁₅O₆₂] was prepared as described in the literature.¹

¹H NMR [¹³C NMR] spectra were recorded at room temperature with a 300 MHz [75 MHz] Bruker 300 UltraShield Spectrometer equipped with a QNP probe, a 400 MHz [100MHz] Bruker Avance 400 spectrometer equipped with a QNP probe, or with a 500 MHz Bruker Avance 500 UltraShield equipped with a BBI ATM probe. Chemical shifts are given in ppm, referenced to TMS (δ = 0 ppm) using the solvent signals (δ = 1.94 ppm for CHD₂CN [δ = 1.32 ppm for CD₃CN] and δ = 7.26 ppm for CHCl₃ [δ = 77.16 ppm for CDCl₃] for calibration. Coupling constants (J) are given in Hertz (Hz).

Mass spectrometry experiments have been carried out on an electrospray-time of flight instrument (Waters, LCT Premier XE) for organic compounds and on an electrospray-ion trap instrument (Bruker, Esquire 3000) for polyoxometalate hybrids. The 50 µmol·L⁻¹ solutions of POMs were infused using a syringe pump (160 µL·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.

Elemental analyses were carried out by ICSN (CNRS, Gif, France).

IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer for organic compounds, and Bio-Rad FTS 165 (KBr) for polyoxometalates hybrids.

Cyclovoltammograms [and electropolymerisation experiments] were recorded at room temperature with a potentiostat model 273A from EG&G Princeton Applied Research using a conventional three electrode set-up. The working electrode was glassy carbon [ITO plates, Aldrich, 8-12 Ω/square, surface of about 1 cm²], the counter electrode was platinum wire, and the reference electrode was a saturated calomel electrode (SCE) connected through a salt bridge. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M, and analyte concentration was 0.5 mM. The solutions were deaerated thoroughly by bubbling argon through the solution and kept under argon atmosphere during the whole experiment. The POM(py)₂ hybrids reported here have a high tendency to stick to the electrode, consequently the electrode necessitate to be washed after each scan.

UV-visible absorption spectra in solution were recorded either with a double beam Perkin-Elmer Lambda 9 spectrophotometer operated at a resolution of 1 nm while those on ITO electrode were recorded in transmission mode.

Atomic Force Microscopy (AFM) was performed directly on the surface of the ITO using a Dimension 3100 (Veeco) in the tapping mode under ambient conditions. Silicon cantilevers (Veeco probes) with a spring constant of 300 N/m and a resonance frequency in the range of 120-139 kHz were used. The scanning rate was 1.0 Hz.

X-ray Photoelectron Spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with MgKR radiation (hν = 1253.6 eV) or Al KR radiation (hν = 1486.6 eV). In general, the X-ray anode was run at 250W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.5, 46.95, or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5.10⁻⁸ Pa. The sample was directly pressed to a self-supported disk (10 x 10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra (0-1100 eV) and the narrow spectra of all the elements with higher resolution were both recorded by using RBD 147 interface (RBD Enterprises, U.S.A.) through the Auger Scan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). The data analysis was carried out by using the RBD Auger Scan 3.21 software provided by RBD Enterprises or XPS Peak4.1 provided by Raymund W.M. Kwok (The Chinese University of Hongkong, China)

Ligand Synthesis

2-propenoic acid, 3-(3,5-dibromophenyl)-methyl ester: To a solution of 3,5-dibromobenzaldehyde (1.5 g, 5.68 mmol) in CH$_2$Cl$_2$ (45 mL), methyl(triphenylphosphoranylidene)acetate (2.58 g, 7.57 mmol) was added. The solution was stirred under argon for 7 h. The reaction was monitored by TLC. The solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$:Hept = 1:1) to give the product as white solid (82.3 mg, 0.218 mmol) in 95% yield. mp: 142°C.

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.66 (s, 1H), 7.57 (s, 2H), 7.52 (d, J = 16 Hz, 1H), 6.42 (d, J = 16 Hz, 1H), 3.81 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ: 166.6 (C=O), 141.6 (CH=C), 137.9 (C$_{q}$Ar), 135.4 (CH$_3$Ar), 129.6 (CH$_3$Ar), 123.5 (C$_{q}$Ar), 120.7 (CH=C), 52.0 (CH$_3$).

IR (ATR, cm$^{-1}$): 3073, 2950, 1721, 1639, 1582, 1547, 1432, 1412, 1368, 1316, 1308, 1291, 1261, 1207, 1190, 1176, 1012, 984, 889, 849, 800, 742, 682, 656.

Elemental Analysis: Calc C 37.54%, H 2.52%, N 0%. Found C 37.78%, H 2.57%, N 0%.

evba3,3: In a dry Schlenk tube, Pd(PPh$_3$)$_4$ (101.1 mg, 0.088 mmol) was solubilised in freshly distilled and degassed triethylamine (15 mL) at 80°C. 2-propenoic acid, 3-(3,5-dibromophenyl)-methyl ester (280 mg, 0.875 mmol), 3-ethynylpyridine (255 mg, 2.48 mmol) and CuI (33 mg, 0.17 mmol) were successively added, and the resulting mixture was heated to 80°C under argon overnight. The solvent was removed in vacuo and the crude brown powder was purified by column chromatography on silica gel (CH$_2$Cl$_2$:MeOH = 97:3) to give evb3,3 as a pale yellow solid (315 mg, 0.86 mmol) in 99% yield. mp: 142°C.

$^1$H NMR (500 MHz, CDCl$_3$) δ: 8.79 (d, J = 1.3 Hz, 2H), 8.59 (dd, J = 1.5 Hz, J = 4.9 Hz, 2H), 7.83 (dt, J = 1.5 Hz, J = 7.7 Hz, 2H), 7.74 (s, 1H), 7.66 (m, 3H), 7.32 (dd, J = 4.9 Hz, J = 7.7 Hz, 2H), 6.52 (d, J = 15.9 Hz, 1H), 3.83 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ: 166.9 (C=O), 152.3 (CH$_3$py), 149.0 (CH$_3$py), 142.7 (CH=C), 138.6 (CH$_3$py), 135.8 (C$_q$), 131.0 (CH$_3$Ar), 123.9 (CH$_3$), 123.2 (CH$_3$py), 120.0 (CH=C), 119.9 (C$_q$), 90.8 (C=O), 87.4 (C=C), 51.9 (CH$_3$).

IR (ATR, cm$^{-1}$): 3050, 2923, 2853, 2213, 1718, 1640, 1592, 1561, 1478, 1437, 1408, 1377, 1300, 1266, 1208, 1190, 1173, 1120, 1093, 1040, 1021, 979, 922, 856, 800, 722, 695, 670.

TOF MS (ES+) calc for C$_{24}$H$_{16}$N$_2$O$_2$-H$: 365.1285$, found: 365.1285.

evba4,4 and evba4,Br: In a dry Schlenk tube, 4-ethynlypyridine hydrochloride (295 mg, 2.1 mmol) was solubilized in dry and degassed DMF (30 mL). To this dark blue suspension was added compound 2-propenoic acid, 3-(3,5-dibromophenyl)-methyl ester (225 mg, 0.70 mmol) and freshly distilled and deaerated triethylamine (15 mL), followed by PdCl$_2$(PPh$_3$)$_2$ (49.4 mg, 0.07 mmol) and CuI (26.8 mg, 0.14 mmol). The mixture was heated under argon at 75°C for 4 days. Solvents were removed in vacuo and the crude product was purified by column chromatography on silica gel (gradient elution from...
Hept:EA = 6:4 to 3:7) to give evb4,4 as a pale yellow solid (143.9 mg, 0.86 mmol) in 56% yield and evb4,Br (50.4 mg, 0.15 mmol) in 21% yield.

**evb4,4:**

mp : 197°C.

1H NMR (300 MHz, CDCl₃) δ: 8.64 (d, J = 5.1 Hz, 4H), 7.74 (t, J = 1.4 Hz, 1H), 7.69 (d, J = 1.3 Hz, 2H), 7.65 (d, J = 16 Hz, 1H), 7.39 (d, J = 4.5 Hz, 4H), 6.52 (d, J = 16 Hz, 1H), 3.83 (s, 3H).

13C NMR (75 MHz, CDCl₃) δ: 166.8 (C=O), 149.9 (CHpy), 142.4 (CH=C), 136.1 (CHAr), 135.4 (Cq), 131.5 (CHAr), 130.7 (Cq), 125.6 (CHpy), 123.6 (Cq), 120.2 (CH=)C, 91.8 (C=C), 88.1 (C=C), 52.0 (CH₃).

IR (ATR, cm⁻¹): 3053, 2923, 2853, 2217, 1711, 1594, 1538, 1488, 1459, 1439, 1377, 1328, 1304, 1260, 1221, 1189, 1172, 1091, 1012, 922, 867, 814, 801, 742, 696, 672.

TOF MS (ES+) calc for C₂₄H₁₆N₂O₂ : 365.1285, found: 365.1288.

**evb4,Br**

mp : 157°C.

1H NMR (300 MHz, CDCl₃) δ: 8.62 (d, J = 5.8 Hz, 2H), 7.67 (t, J = 1.5 Hz, 1H), 1.64 (t, J = 1.5 Hz, 1H), 7.57 (m, 2H), 7.36 (d, J = 6Hz, 2H), 6.46 (d, J = 16 Hz, 1H), 3.81 (s, 3H).

13C NMR (75 MHz, CDCl₃) δ: 166.7 (C=O), 149.9 (CHpy), 142.0 (CH=C), 136.6 (Cq), 135.6 (CHAr), 131.3 (CHAr), 130.6 (Cq), 129.9 (CHAr), 125.6 (CHpy), 124.7 (Cq), 122.9 (Cq), 120.4 (CH=), 91.3 (C=C), 88.4 (C=C), 52.0 (CH₃).

IR (ATR, cm⁻¹): 3037, 2950, 2219, 1718, 1641, 1594, 1537, 1540, 1489, 1436, 1413, 1329, 1286, 1218, 1203, 1155, 1112, 1037, 990, 925, 854, 819, 743, 670.

TOF MS (ES+) calc for C₁₇H₁₂BrNO₂ : 342.0125, found: 342.0145.

**evb3,4:**

In a dry Schlenk tube under argon compound evb4,Br (63.5 mg, 0.19 mmol) and Pd(PPh₃)₄ (55 mg, 0.048 mmol) were solubilised in distilled and deaerated triethylamine (4 mL) and dry DMSO (0.5 mL) at 80°C. 3-ethynylypyridine (57.4 mg, 0.056 mmol), CuI (7.1 mg, 0.037 mmol) and triethylamine (3 mL) were added and the mixture was heated at 80°C for 24h. The clear orange solution was evaporated in vacuo and the crude product was purified by column chromatography on silica gel (CH₂Cl₂:MeOH = 98:2) to give evb3,4 in presence of an impurity.

1H NMR (500 MHz, CDCl₃) δ: 8.79 (m, 1H), 8.64 (m, 2H), 8.59 (m, 1H), 7.82 (d, J= 7.6Hz, 1H), 7.74 (s, 1H), 7.68 (m, 3H), 7.4 (d, J = 5.5 Hz, 2H), 7.32 (m, 1H), 6.52 (d, J = 16 Hz, 1H), 3.83 (s, 3H).

**dvb3,3:**

In a 25mL round bottom flask is added evb3,3 (150 mg, 0.41 mmol), 2-Amino-2-ethyl-1,3-propanediol (73.48 mg, 0.62 mmol) solution in CH₂Cl₂/DMSO (4.5/0.2 mL) and K₂CO₃ (56.8 mg, 0.41 mmol). The resulting mixture was heated to reflux overnight. The mixture was diluted with CH₂Cl₂ and MeOH and K₂CO₃ was removed by centrifugation. The clear supernatant was evaporated in vacuo and the residue was purified by column chromatography on silica gel (gradient electronic supplementary material (ESI) for Dalton Transactions, 2013).
elution from CH2Cl2:MeOH = 100:0 to 95:5) to give dbv3, as a waxy solid (149 mg, 0.33 mmol) in 80% yield.

1H NMR (300 MHz, CDCl3) δ: 8.73 (d, J = 1.3 Hz, 2H), 8.54 (dd, J = 1.5 Hz, J = 4.9 Hz, 2H), 7.78 (dt, J = 1.9 Hz, J = 7.9 Hz, 2H), 7.64 (m, 1H), 7.58 (m, 2H), 7.51 (d, J = 15.5 Hz), 7.29 (m, 2H), 6.53 (d, J = 15.5 Hz, 1H), 3.90 (d, J = 11.6 Hz, 2H), 3.69 (d, J = 11.6 Hz, 2H), 1.77 (q, J = 7.6 Hz, 2H), 0.92 (t, J = 7.6 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ: 166.6 (C=O), 152.3 (CH3p), 149.0 (CH3p), 139.4 (CH=C), 138.8 (CH3p), 135.6 (Cq), 135.5 (CH2a), 131.0 (Cq), 123.8 (Cq), 123.3 (CH3p), 123.0 (CH=C), 120.1 (Cq), 91.2 (C=C), 87.3 (C=C), 65.9 (CH2OH), 61.8 (Cq), 25.5 (CH2), 7.8 (CH3).

IR (ATR, cm⁻¹): 3277, 2930, 2399, 2216, 1660, 1618, 1477, 1407, 1337, 1230, 1187, 1044, 1024, 976, 856, 804, 731.


dbv4,4: In 25mL round bottom flask is added evb4,4 (112 mg, 0.31 mmol), 2-Amino-2-ethyl-1,3-propanediol (54.9 mg, 0.46 mmol) solution in CH2Cl2/DMSO (5.5/0.2 mL) and K2CO3 (42.4 mg, 0.31 mmol). The resulting mixture was heated to reflux 4 days. The mixture was diluted with CH2Cl2 and MeOH and K2CO3 was removed by centrifugation. The clear supernatant was evaporated in vacuo and the residue was purified by column chromatography on silica gel (gradient elution from CH2Cl2:MeOH = 100:0 to 95:5) to give dbv4,4 as a waxy solid (94.6 mg, 0.21 mmol) in 68% yield.

1H NMR (300 MHz, CDCl3) δ: 8.52 (s, 4H), 7.74 (t, J = 1.4 Hz, 1H), 7.62 (m, 3H), 7.46 (d, J = 15.6 Hz, 1H), 7.34 (d, J = 5.6 Hz, 4H), 6.55 (d, J = 15.6 Hz, 1H), 3.77 (d, J = 11.6 Hz, 2H), 3.60 (d, J = 11.6 Hz, 2H), 1.73 (q, J = 7.5 Hz, 2H), 0.86 (t, J = 7.5 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ: 166.4 (C=O), 149.5 (CH3p), 138.7 (CH=C), 135.8 (Cq), 135.6 (CH2a), 131.4 (Cq), 125.8 (CH3p), 123.4 (Cq), 123.3 (CH=C), 92.4 (C=C), 87.7 (C=C), 65.0 (CH2OH), 61.7 (Cq), 25.0 (CH2), 7.7 (CH3).

IR (ATR, cm⁻¹): 3273, 2927, 2217, 1663, 1623, 1595, 1539, 1411, 1338, 1222, 1026, 999, 858, 821.


dbv3,4: In 25mL round bottom flask is added evb3,4 (43.1 mg, 0.12 mmol), 2-Amino-2-ethyl-1,3-propanediol (21.1 mg, 0.18 mmol) solution in CH2Cl2/DMSO (5.5/0.2 mL) and K2CO3 (16.3 mg, 0.12 mmol). The resulting mixture was heated to reflux 4 days. The mixture was diluted with CH2Cl2 and MeOH and K2CO3 was removed by centrifugation. The clear supernatant was evaporated in vacuo and the residue was purified by column chromatography on silica gel (gradient elution from CH2Cl2:MeOH = 100:0 to 95:5) to give dbv3,4 as a waxy solid (39.7 mg, 0.088 mmol) in 73% yield.

1H NMR (300 MHz, CDCl3) δ: 8.66 (s, 1H, 3py), 8.49 (m, 3H, 3py(1H) + 4py(2H)), 7.79 (d, J = 7.9 Hz, 1H, 3py), 7.62 (m, 3H, CH2a), 7.46 (d, J = 15.6 Hz, 1H, CH=C), 7.36 (d, J = 4.71, 2H, 4py), 7.29 (m, 1H, 3py), 6.57 (d, J = 15.6 Hz, 1H), 3.74 (d, J = 11.7 Hz, 2H, CH2OH), 3.58 (d, J = 11.7 Hz, 2H, CH2OH), 1.72 (q, J = 7.4 Hz, 2H, CH3), 0.85 (t, J = 7.4 Hz, 3H, CH3).

13C NMR (75 MHz, CDCl3) δ: 166.6 (C=O), 151.8 (CH3p), 149.4 (CH4p), 148.6 (CH4p), 138.9 (CH=C), 135.8 (Cq), 135.5 (CH2a), 131.5 (Cq), 131.2 (CH2a), 131.2 (CH2a), 125.9 (CH3p), 123.8 (Cq), 123.5 (CH3p), 123.2 (CH=C), 120.2 (Cq), 92.6 (C=C), 91.1 (C=C), 87.6 (C=C), 87.1 (C=C), 64.9 (CH2OH), 61.7 (Cq), 24.9 (CH2), 7.6 (CH3).

IR (ATR, cm⁻¹): 3301, 2949, 2216, 1660, 1625, 1599, 1413, 1339, 1232, 1017.

**tvb3,3:** To a solution of **evb3,3** (77.8 mg, 0.21 mmol) in DCM (2mL), is added 2-Amino-2-hydroxyméthyl-1,3-propanediol (38.8 mg, 0.32 mmol), DMSO (0.1 mL) and K$_2$CO$_3$ (29.5 mg, 0.21 mmol). The resulting mixture was heated to reflux overnight. The mixture was diluted with CH$_2$Cl$_2$ and MeOH and K$_2$CO$_3$ was removed by centrifugation. The clear supernatant was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (gradient elution from CH$_2$Cl$_2$:MeOH = 100:0 to 95:5) to give **tvb3,3** as a waxy solid (66.6 mg, 0.088 mmol) in 69% yield.

$^1$H NMR (300 MHz, CDCl$_3$) δ: 8.71 (s, 2H), 8.51 (dd, J = 1Hz, J = 4.8 Hz, 2H), 7.84 (dt, J = 1.8 Hz, J = 7.9 Hz, 2H), 7.67 (m, 1H), 7.64 (m, 2H), 7.52 (d, J = 15.6 Hz, 1H), 7.33 (m, 2H), 6.62 (d, J = 15.6Hz, 1H), 3.71 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ: 166.9 (C=O), 151.8 (CH$_{py}$), 148.5 (CH$_{py}$), 139.5 (CH=C), 139.0 (CH$_{py}$), 135.5 (C$_q$), 135.4 (CH$_{Ar}$), 130.9 (CH$_{Ar}$), 131.0 (CH$_{Ar}$), 123.6 (C$_q$), 123.4 (CH$_{3py}$), 122.6 (CH=C),120.4 (C$_q$), 91.1 (C≡C), 86.9 (C≡C), 62.6 (C$_q$), 62.0 (CH$_2$OH).

IR (ATR, cm$^{-1}$): 3287, 2961, 1662, 1622, 1560, 1478, 1410, 1258, 1016, 860, 794

TOF MS (ES+) calc for C$_{28}$H$_{25}$N$_3$O$_3$H$^+$: 454.1762 , found: 454.1765.
Hybrids synthesis:

General Procedure:
A solution of TBA$_2$H$_4$[P$_2$V$_3$W$_{15}$O$_{62}$] (300 mg, 0.056 mmol, 1 eq.), the diol-amide ligand (1.4 eq.), and APTS (5.82 mg, 0.034 mmol, 0.6 eq.) in DMAC (0.6 mL) is heated at 80°C for 1h by microwave irradiation. The light orange solution turned brown. After removal in vacuo of the solvent, the brownish oil is solubilized in acetonitrile, precipitated by addition of diethyl ether and centrifuged for 10 min. The recovered yellow solid is solubilized in acetonitrile, and TBA resin is added to the solution for 30 min. The resin is then filtered off, and the orange solution is reduced in vacuo, precipitated by diethyl ether, and centrifuged for 10 min. The recovered solid is solubilized in a minimum amount of acetonitrile, precipitated by addition of EtOH and centrifuged for 30 min. The recovered solid is solubilized in acetonitrile, precipitated by diethyl ether, centrifuged, then triturated with diethyl ether, centrifuged and dried under vacuum. The ethanol supernatant is evaporated, and the oil is precipitated by addition of small amount of ethanol, followed by centrifugation, and two diethyl ether precipitation/centrifugation steps.

POM-dvb3,3: prepared with 72% yield.

IR (KBr, cm$^{-1}$): 3457, 2962, 2873, 1637, 1594, 1483, 1087, 953, 902, 817, 738.

$^{31}$P NMR (162 MHz, CD$_3$CN) δ: -6.99, -13.06.

$^1$H NMR (400 MHz, CD$_3$CN) δ: 9.6 (br, 1H, NH), 8.79 (s, 2H, H$_{py}$), 8.73 (d, 1H, J=15.2 Hz, CH=CH), 8.60 (d, 2H, J=4.0 Hz, H$_{py}$), 8.29 (s, 2H, H$_{ar}$), 8.11 (d, 2H, J= 7.64 Hz, H$_{py}$), 7.83 (s, 1H, H$_{ar}$). 7.53 (dd, 2H, J=4.9Hz, J= 7.6 Hz, H$_{py}$), 7.16 (d, 1H, J= 15.2Hz, CH=CH), 5.61 (d, 2H, J=12.7 Hz, CH$_2$OV), 5.48 (d, 2H, J=12.7Hz, CH$_2$OV), 3.17 (m, 43,1H, J=7.24Hz, J=6.99, 88.9 (C=O), 134.3 (CH$_2$), 134.3 (CH$_2$), 125.6 (C$_6$), 124.9 (C$_6$), 120.6 (C$_6$), 117.4 (CH=CH), 91.7 (C=C), 89.8 (CH$_2$OV), 88.9 (C=C), 64.8 (C$_6$), 59.3 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 29.5 (CH$_2$-CH$_2$), 24.5 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 20.4 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 14.0 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 7.52 (CH$_2$-CH$_2$)

$^{13}$C NMR (100 MHz, CD$_3$CN) δ: 181.7 (C=O), 154.2 (CH=CH), 152.7 (C$_6$), 150.3 (C$_6$), 140.3 (C$_6$), 136.9 (CH$_2$), 136.5 (C$_6$), 134.3 (CH$_2$), 125.6 (C$_6$), 124.9 (C$_6$), 120.6 (C$_6$), 117.4 (CH=CH), 91.7 (C=C), 89.8 (CH$_2$OV), 88.9 (C=C), 64.8 (C$_6$), 59.3 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 29.5 (CH$_2$-CH$_2$), 24.5 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 20.4 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 14.0 (Ni(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 7.52 (CH$_2$-CH$_2$)

Anal. calc. for TBA$_3$(C$_2$H$_2$N$_3$O$_{62}$P$_2$V$_3$W$_{15}$): C 23.64, H 3.76, N 1.99; found: C 23.64, H 3.76, N 2.00.

Electrospray mass spectrometry:

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<th>Simulated m/z</th>
<th>Observed m/z</th>
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<td>18</td>
<td>TBA$<em>2$(C$</em>{28}$H$_{22}$N$<em>3$O$</em>{62}$P$_2$V$<em>3$W$</em>{15}$)</td>
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<td>1212.9</td>
<td>11</td>
<td>TBA$<em>2$(C$</em>{28}$H$_{22}$N$<em>3$O$</em>{62}$P$_2$V$<em>3$W$</em>{15}$) R.</td>
</tr>
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<td>873.2</td>
<td>100</td>
<td>(C$<em>{28}$H$</em>{22}$N$<em>3$O$</em>{62}$P$_2$V$<em>3$W$</em>{15}$)</td>
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(R = reduced form of the POM)
POM-dvb4,4: prepared with 70% yield.

IR (KBr, cm\(^{-1}\)) : 2962, 2874, 2216, 1632, 1595, 1484, 1087, 953, 903, 816, 737.

\(^3\)P NMR (162MHz, CD\(_3\)CN) \(\delta\): -7.54, -13.51.

\(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\): 8.66 (d, 4H, J=4.9 Hz, \(H_{py}\)), 8.29 (m, 3H, \(H_{ax} + CH=CH\)), 7.73 (s, 1H, \(H_{ax}\)), 7.58 (d, 4H, J = 4.9 Hz, \(H_{py}\)), 6.96 (d, 1H, J = 15.7Hz, \(CH=CH\)), 5.55 (d, 2H, J = 11.9 Hz, \(CH_{2}OV\)), 5.41 (d, 2H, J=11.9 Hz, \(CH_{2}OV\)), 3.19 (m, 51H, \(N(CH_{2}CH_{2}CH_{3})_{4}\)), 1.66 (m, 53H, \(N(CH_{2}CH_{2}CH_{3})_{4}\)), 1.43 (q, 51H, J = 7.0Hz, \(N(CH_{2}CH_{2}CH_{3})_{4}\)), 1.13 (t, 3H, J=7.1Hz, \(CH_{2}-C_{H}3\)), 1.00 (t, 75H, J=7.0Hz, \(N(CH_{2}CH_{2}CH_{3})_{4}\)).

\(^13\)C NMR (100 MHz, CD\(_3\)CN) \(\delta\): 151.1 (\(C_{py}\)), 151.0 (\(CH=CH\)), 138.5 (\(C_{q}\)), 135.2 (\(CH_{ax}\)), 131.5 (\(C_{q}\)), 126.6 (\(CH_{ax}\)), 124.4 (\(C_{q}\)), 116.8 (\(CH=CH\)), 93.2 (\(C=C\)), 90.3 (\(CH_{2}OV\)), 88.9 (\(C=C\)), 63.1 (\(C_{q}\)), 59.3 (\('N(CH_{2}CH_{2}CH_{2}CH_{3})_{4}\)), 32.6 (\(CH_{2}-CH_{3}\)), 24.4 (\('N(CH_{2}CH_{2}CH_{2}CH_{3})_{4}\)), 20.4 (\('N(CH_{2}CH_{2}CH_{2}CH_{3})_{4}\)), 14.0 (\('N(CH_{2}CH_{2}CH_{2}CH_{3})_{4}\)), 8.02 (\(CH_{2}-CH_{3}\)).

Anal. calc. for \(C_{28}H_{23}N_{3}O_{62}P_{2}V_{3}W_{15}\): C 23.25, H 3.67, N 2.01; found: C 23.35, H 3.58, N 2.05.

Electrospray mass spectrometry:

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<th>Relative Intensity (%)</th>
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<td>20</td>
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<td>1212.9</td>
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<td>TBA(<em>2)(C(</em>{28})H(<em>{23})N(</em>{3})O(<em>{62})P(</em>{2})V(<em>{3})W(</em>{15})) (R)</td>
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<tr>
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<td>100</td>
<td>TBA(<em>2)(C(</em>{28})H(<em>{23})N(</em>{3})O(<em>{62})P(</em>{2})V(<em>{3})W(</em>{15}))</td>
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<tr>
<td>5</td>
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<td>1092.0</td>
<td>1088.3</td>
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<td>H(C(<em>{28})H(</em>{23})N(<em>{3})O(</em>{62})P(<em>{2})V(</em>{3})W(_{15}))</td>
</tr>
<tr>
<td>6</td>
<td>5-</td>
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<td>873.4</td>
<td>74</td>
<td>(C(<em>{28})H(</em>{23})N(<em>{3})O(</em>{62})P(<em>{2})V(</em>{3})W(_{15}))</td>
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\((R = \text{reduced form of the POM})\)
POM-dvb3,4 prepared with 46% yield.

IR (KBr, cm⁻¹): 3449, 2962, 2874, 1634, 1595, 1483, 1087, 953, 902, 816, 737.

³¹P NMR (162 MHz, CD₃CN) δ: -7.26, -13.3.

¹H NMR (500 MHz, CD₃CN) δ: 8.78 (s, 1H, H₃py), 8.67 (m, 3H, J = 4.5 Hz, CH=CH + H₄py), 8.59 (d, 1H, J = 3.65 Hz, H₃py), 8.54 (s, 1H, H₄py), 8.28 (s, 1H, H₄py), 8.10 (d, 1H, J = 7.65 Hz, H₃py), 7.82 (s, 1H, H₃py), 7.59 (d, 2H, J = 4.25 Hz, H₄py), 7.52 (m, 1H, H₃py), 7.26 (d, 2H, J = 12.2 Hz, CH₂OV), 1.86 (m, 2H, CH₂-, 1.65 (m, 42H, ᵅ(CH₂CH₂CH₃)₄), 1.43 (m, 42H, ᵅ(CH₂CH₂CH₂CH₃)₄), 1.13 (m, 3H, CH₂-, 1.00 (t, 62H, J = 7.0 Hz, ᵅ(CH₂CH₂CH₂CH₃)₄).

¹³C NMR (100 MHz, CD₃CN) δ: 181.6 (CO), 154.1 (CH=CH), 152.7 (C₃py), 151.2 (C₄py), 150.2 (C₃py), 140.2 (C₃py), 136.9 (CH₄), 136.5 (C₃Ar=CH=CH), 135.3 (CH₃), 134.1 (CH₃), 131.4 (C₃Ar=CH=CH), 126.6 (C₄py), 125.2 (C₃Ar=CH=CH), 124.9 (C₃py), 124.8 (C₃Ar=CH=CH), 120.6 (C₄py), 118.3 (CH=CH, masked), 92.8 (C=C), 91.6 (C=C), 89.8 (CH₂OV), 89.4 (C=C), 88.9 (C=C), 64.8 (Cq), 29.5 (CH₂-CH₃), 7.56 (CH₂-CH₃).

Anal. calc. for TBA₅(C₂₈H₂₃N₃O₆₂P₂V₃W₁₅) : C 23.25, H 3.67, N 2.01; found: C 23.26, H 3.65, N 1.87.

Electrospray mass spectrometry:

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<th>Entry</th>
<th>Charge</th>
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<td>TBA(C₂₈H₂₃N₃O₆₂P₂V₃W₁₅)</td>
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<tr>
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<td>1091.3</td>
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<td>H(C₂₈H₂₃N₃O₆₂P₂V₃W₁₅)</td>
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<td>872.9</td>
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<td>(C₂₈H₂₃N₃O₆₂P₂V₃W₁₅)</td>
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</table>
POM-tvb3,3 prepared in 40% yield.

IR (KBr, cm\(^{-1}\)) : 3455, 2962, 2873, 1632, 1483, 1086, 950, 911, 818, 734.

\(^{31}\)P NMR (162 MHz, CD\(_3\)CN) \(\delta\): -7.45; -13.54.

\(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\): 8.75 (s, 2H, H\(_{py}\)), 8.58 (d, 2H, J=3.8 Hz, H\(_{py}\)), 7.91 (m, 2H, H\(_{py}\)), 7.71 (m, 3H, H\(_{Ar}\)), 7.50 (d, 1H, J= 15.7 Hz, CH=CH), 7.40 (dd, 2H, J=4.9Hz, J= 7.7 Hz, H\(_{py}\)), 6.66 (d, 1H, J=15.6 Hz, CH=CH), 6.42 (s, 1H, NH), 5.73 (s, 6H, CH\(_2\)OV), 3.8 (m, 59H, \(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 1.65 (quint, 59H, J= 7.7 Hz, \(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 1.43 (sext, 59H, J = 7.3Hz, \(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 0.99 (t, 89H, J=7.3Hz, \(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)).

\(^{13}\)C NMR (100 MHz, CD\(_3\)CN) \(\delta\): 166.0 (C=O), 152.9 (C\(_{py}\)), 150.2 (C\(_{py}\)), 139.6 (C\(_{py}\)), 138.7 (C\(_{H=CH}\)), 137.5 (C\(_{Ar}-\text{CH}=\text{CH}\)), 135.6 (CH\(_{Ar(1H)}\)), 131.7 (CH\(_{Ar(2H)}\)), 125.3 (CH=CH), 124.7 (C\(_{Ar(3-3py)}\)), 124.5 (C\(_{py}\)), 120.5 (C\(_{Ar(4-3py)}\)), 91.4 (C=C), 88.1 (C=C), 86.9 (CH\(_2\)OV), 59.3 (\(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 55.6 (C\(_3\)), 29.5 (CH\(_2\)CH\(_3\)), 24.5 (\(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 20.5 (\(^6\)N(CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))\(_4\)), 14.0 (\(^6\)N(CH\(_3\)CH\(_2\)CH\(_3\))\(_4\)).

Anal. calc. for TBA\(_3\)H\(_0.5\)(C\(_{27}\)H\(_{20}\)N\(_3\)O\(_6\)P\(_2\)V\(_3\)W\(_15\)) (5749.2 g.mol\(^{-1}\)) : C 24.69, H 3.95, N 2.12 ; found: C 24.36, H 4.01, N 2.07.

Electrospray mass spectrometry:

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<td>5</td>
<td>H(C(<em>{27})H(</em>{20})N(_3)O(_6)P(_2)V(_3)W(_15))</td>
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NMR Spectra

dvb3,3:
POM-dvb3.3:
Parameters

BA/160-240MHz 11 (1D 13C)

- FID:
  - Size: 60536 points complex
  - Spectral Width: 20048.568 Hz
  - Carrier Frequency: 108.626561MHz
  - Nucleus: 13C

- Number of scans: 15360

- Type: 1D

- Spectro: Bruker 403-MHz
- Puls: 3.0 mm QNP 6H132.06919F 2300802
- Date: Wed Nov 01 17:32:39 CET 2012
- Temperature: 300.0 K
- Software: CECCH
POM-dvb3,4:

Parameters

BA159A-1 (1D 31P)

P1:
- Site: 02008 points complex
- Spectral Width: 5064.154 Hz
- Carrier Frequency: 202.41595 MHz
- Nucleus: 31P

Number of scans: 32

Type: 1D

Spectra: BRUKER 503 MHz

Probe: 5 mm PA91 H40-80 Z-CRZ 2010/2011

Date: Wed Mar 07 09:24:51 CET 2012

Temperature: 296 (K)

Solvent: CDCl3

Parameters

BA159A-2 (1D 1H)

P1:
- Site: 32786 points complex
- Spectral Width: 1503.30 Hz
- Carrier Frequency: 500.19351 MHz
- Nucleus: 1H

Number of scans: 8

Type: 1D

Spectra: BRUKER 503 MHz

Probe: 5 mm PA91 H45-80-Z-CRZ 2013/2011

Date: Wed Mar 07 09:25:56 CET 2012

Temperature: 298 (K)

Solvent: CDCl3
POM-tvb3,3:

Parameters

(A184-000 11 (1D 3P)

F1:
- Size: 450000 points complex
- Spectral Width: 24236.9 Hz
- Carrier Frequency: 46.672156 MHz
- Nucleus: 1H

Number of scans: 32

Type: 1D

Spectra: Bruker 400 MHz

Probe: 5 mm QNP H4/IQ3/IQ1/IF 25H90D

Date: Tue Dec 04 12:30:39 CET 2012

Temperature: 296.0 K

Solvent: CD3OD

Parameters

(A184-000 10 (1D 1H)

F1:
- Size: 65000 points complex
- Spectral Width: 7183.00 Hz
- Carrier Frequency: 400.1321 MHz
- Nucleus: 1H

Number of scans: 32

Type: 1D

Spectra: Bruker 400 MHz

Probe: 5 mm QNP H4/IQ3/IQ1/IF 25H90D

Date: Tue Dec 04 12:30:39 CET 2012

Temperature: 296.0 K

Solvent: CD3OD
UV-vis spectra of POM(py)$_2$ hybrids

Fig S1 UV-Vis absorption spectra of a) POM-dvb3,3, b) POM-dvb3,4, c) POM-dvb4,4, d) POM-tvb3,3 compared to TBA$_3$H$_4$$[P_2V_3W_{15}O_{62}]$ and their corresponding non-grafted ligand. Concentration is $6.25 \times 10^{-6}$ M in CH$_3$CN.
Fabrication of Films

Copolymer Poly-ZnOEP-POM

Electropolymerization was performed under an argon atmosphere in a 0.1 mol L⁻¹ solution of tetrabutylammonium hexafluorophosphate in 1,2-C₂H₄Cl₂/CH₃CN (7:3) containing 0.25 mmol L⁻¹ ZnOEP and 0.25 mmol L⁻¹ POM(py)₂ using iterative scans. Cyclic scanning (0.2 V s⁻¹) was applied at potentials between −1.30 and 1.90 V versus SCE or between 0 and 1.90 V versus SCE. The starting potential of the first scan and the ending potential value of the final scan were 0.0 and 0.5 V, respectively. Thus, at the end of the electropolymerization, the porphyrin subunits (ZnOEP) of the polymers were not oxidized (neutral form). The direction of the first scan was cathodic in order to record the eventual presence of reduction signals attributed to the pyridinium unit(s) before polymer formation. Polymers were obtained during the reverse anodic scan when the potential reached the oxidation potential value of the porphyrin ligand corresponding to the dications formation. After electrolysis, the working electrodes were washed five times with 10 mL of CH₃CN to remove traces of the conducting salt present on the deposited films.

CV evolution during electropolymerization

![Graph a)](Evolution_of_BF-MeH.png)

Electropolymerization: ZnOEP + POM-dvb-3,3 (1:1)

![Graph b)](Evolution_of_BF-MeH.png)

Electropolymerization: ZnOEP + POM-dvb-3,3 (1:1)

![Graph c)](Evolution_of_BF-MeH.png)

Electropolymerization: ZnOEP + POM-dvb-3,4 (1:1)

![Graph d)](Evolution_of_BF-MeH.png)

Electropolymerization: ZnOEP + POM-dvb-3,4 (1:1)
Fig S2 Cyclic voltammograms recorded during the electropolymerization of ZnOEP in the presence of a), b) POM-dvb3,3, c) and d) POM-dvb3,4, e) and f) POM-dvb4,4, g and h) POM-tvb3,3 in 1,2-C2H4Cl2/CH3CN (7:3) (NBu4)PF6 0.1mol L⁻¹. Working electrode: ITO. S = 1 cm². Scan rate: 0.1 V.s⁻¹. (←) Start of the scan. Cyclic scanning was applied at potentials between -1.30 (-1.35 V for POM-dvb4,4) and 1.90 V vs. SCE (left) or between -0.05 V and 1.90 V vs. SCE (right).
Permeability

**Fig. S3** Cyclic voltammograms of 1 mM of K₃Fe(CN)₆ in 0.5 M Na₂SO₄ of modified ITO electrode with a) poly-POM-dvb3,3-ZnOEP b) poly-POM-dvb3,4-ZnOEP , c) poly-POM-dvb4,4-ZnOEP, d) poly-POM-tvb3,3-ZnOEP film (full line) and of noncoated ITO electrode (dotted black line). v=100 mV s⁻¹.
Reduction potentials explanation

**Pyridinium reduction**

More stable

\[ E = -0.79 \text{ V vs. SCE} \]

Stabilization of the formed radical by delocalization over the whole ligand

Less stable

\[ E = -1.02 \text{ V vs. SCE} \]

The formed radical can only be delocalized on the 3-pyridine ring

**Porphyrin reduction**

More stable

\[ E = -1.32 \text{ V vs. SCE} \]

The localized pyridyl radical can be coupled with the porphyrin. The reduced porphyrin is thus stabilized by delocalization over the 3-pyridine ring

Less stable

\[ E = -1.54 \text{ V vs. SCE} \]

(E = -1.60 V vs SCE for free ZnOEP)

The delocalized pyridyl radical has little impact on the porphyrin reduction potential

---

**Fig. S4** Tentative explanation of the poly-POM-ZnOEP reduction potential in term of \( \pi \)-conjugation and ligand geometry.
UV-vis spectra of poly-POM-ZnOEP

Fig S5 Normalized UV-vis spectra of a) poly-POM-dvb3,3-ZnOEP, b) poly-POM-dvb3,4-ZnOEP, c) poly-POM-dvb4,4-ZnOEP, and d) poly-POM-tvb3,3-ZnOEP copolymers deposited on ITO electrode after 25 iterative scans between -0.05 V and 1.90 V vs. SCE (plain line), and in DMF solution (dotted line). For comparison, normalized UV-Vis spectrum of ZnOEP in DMF is plotted on each graph.
UV-vis evolution during electropolymerization

Fig. S6 UV-visible absorption spectra of a) poly-POM-dvb3,3-ZnOEP, b) poly-POM-dvb3,4-ZnOEP, c) poly-POM-dvb4,4-ZnOEP and d) poly-POM-tvb3,3-ZnOEP (onto ITO) with different numbers of iterative scans (between -0.05 V and 1.90 V vs. SCE). Only one side is recovered by ITO.
Fig. S7-A XPS spectra of the modified ITO electrodes with poly-POM-dvb3,4-ZnOEP obtained after 25 iterative scans between -0.05 V and 1.90 V vs. SCE. Global XPS spectra, and C 1s, O 1s, N 1s, P 2p 3, W 4f 7, V 2p 3 region.
Fig. S7-B XPS spectra of the modified ITO electrodes with poly-POM-dvb4,4-ZnOEP obtained after 25 iterative scans between -0.05 V and 1.90 V vs. SCE. Global XPS spectra, and C1s, O1s, N1s, P 2p3, W 4f7, V 2p3 region.
AFM

poly-POM-dvb3,3-ZnOEP

(b)

poly-POM-dvb3,4-ZnOEP

d)
**poly-POM-dvb4,4-ZnOEP**

![Image of poly-POM-dvb4,4-ZnOEP](image1)

**poly-POM-tvb3,3-ZnOEP**

![Image of poly-POM-tvb3,3-ZnOEP](image2)

**Fig S8** Tapping mode AFM topography of a) and b) poly-POM-dvb3,3-ZnOEP, c) and d) poly-POM-dvb3,4-ZnOEP, e) and f) poly-POM-dvb4,4-ZnOEP, g) and h) poly-POM-tvb3,3-ZnOEP copolymer films deposited on ITO electrode after 25 iterative scans between -0.05 V and 1.90 V vs. SCE. Section analyses of the marked white line on the images are reported under each image.