Electronic Supplementary Information

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

Iban Azcarate,[a,b,c] Iftikhar Ahmed, [d] Rana Farha,[e,f] Michel Goldmann, [e,g] Xiaoxia Wang, [h] Hualong Xu, [h] Bernold Hasenknopf,*[a] Emmanuel Lacôte,*[b,i] Laurent Ruhlmann*[c,d]

a) Institut Parisien de Chimie Moléculaire, UPMC Sorbonne Universités & CNRS, UMR 7201, 4 Place Jussieu, 75005 Paris, France.

b) ICSN CNRS, Av. de la Terrasse, 91198 Gif-sur-Yvette Cedex, France.

c) Université de Strasbourg, Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie, 4 rue Blaise Pascal CS 90032 F-67081 Strasbourg Cedex, France.

d) Université Paris-Sud 11, Laboratoire de Chimie Physique, U.M.R. 8000 CNRS, Bâtiment 349, 91405 Orsay cedex, France.

e) Institut des NanoSciences de Paris, UMR 7588 au CNRS, Université Paris 6, 4 place Jussieu, boîte courrier 840, F - 75252 Paris, France.

f) Laboratoire d'Analyse et Contrôle des Systèmes Complexes - LACSC-ECE Paris Ecole d'Ingénieurs, 37 Quai de Grenelle, F - 75015 Paris, France,

g) Université Paris Descartes, 45 rue des Saints Pères, F - 75006 Paris, France,

h) Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China.

i) Université de Lyon, Institut de chimie de Lyon, UMR 5265 CNRS-Université Lyon I-ESCPE Lyon, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.

Summary

General Remarks

Reagents and chemicals were purchased from commercial sources and used as received.
The starting $TBA_5H_4[P_2V_3W_{15}O_{62}]$ was prepared as described in the literature.[1]

^{1}H NMR [^{13}C 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 CHD_2CN [δ = 1.32 ppm for CD_3CN] and δ = 7.26 ppm for $CHCl_3$ [δ = 77.16 ppm for $CDCl_3$] 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 $\mu mol \cdot L^{-1}$ 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.

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 Resarch using a conventional three electrode set-up. The working electrode was glassy carbon [ITO plates, Aldrich, 8-12 Ω/square, surface of about 1 cm^2], 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 ($TBAPF_6$) 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.

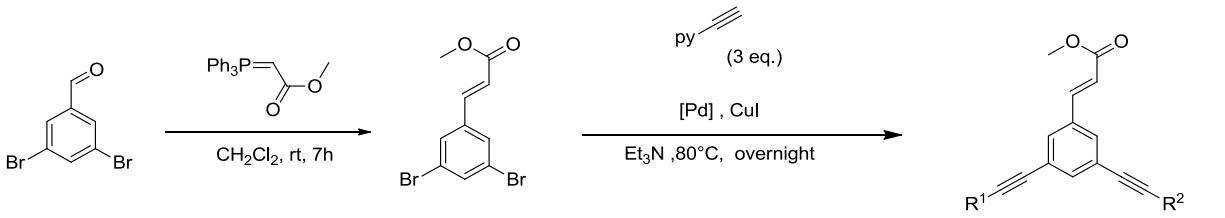
UV-visible absorption spectra in solution were recorded either with a double beam Perkin-Elmer Lambda 9 spectrophotometer operated at a resolution of 1 nm while those on ITO electrode were recorded in transmission mode.

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 (h□=1253.6 eV) or Al KR radiation ($h\nu$ = 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)

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

Ligand Synthesis



evb3,3 : R1 = R2 = 3-py
evb4,4 : R1 = R2 = 4-py
evb3,4 : R1 = 3-py, R2 = 4-py

2-propenoic acid, 3-(3,5-dibromophenyl)-methyl ester : To a solution of 3,5-dibromobenzadehyde (1.5 g, 5.68 mmol) in CH_2Cl_2 (45 mL), methyl(triphenylphosphoranylidene)acetate (2.58 g, 7.57 mmol) was added. The solution was stirred under argon for 7h. 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_2Cl_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 = 16Hz, 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 ($C_{q\text{-}Ar}$), 135.4 (CH_{Ar}), 129.6 (CH_{Ar}), 123.5 ($C_{q\text{-}Ar}$), 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, 1102, 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%.

evb3,3 : In a dry Schlenk tube, $Pd(PPh_3)_4$ (101.1 mg, 0.088 mmol) was solubilised in freshly distilled and degassed triethylamine (15mL) 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_2Cl_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 = 1.3Hz, 2H), 8.59 (dd, J = 1.5 Hz, J = 4.9 Hz, 2H), 7.83 (dt, J = 1.5Hz, 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_{py}), 149.0 (CH_{py}), 142.7 (CH=C), 138.6 (CH_{py}), 135.8 (CH_{Ar}), 135.3 (C_q), 131.0 (CH_{Ar}), 123.9 (C_q), 123.2 (CH_{py}), 120.0 (CH=C), 119.9 (C_q), 90.8 (C≡C), 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 $C_{24}H_{16}N_2O_2$-H$^+$: 365.1285 , found : 365.1285.

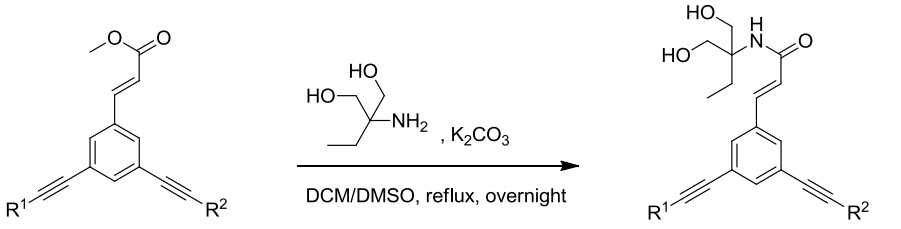
evb4,4 and evb4,Br: In a dry Schlenk tube, 4-ethynylpyridine hydrochloride (295 mg, 2.1 mmol) was solubilized in dry and degassed DMF (30 mL). To this dark blue suspension was added compound 2-propenoic acid, 3-(3,5-dibromophenyl)-methyl ester (225 mg, 0.70 mmol) and freshly distilled and deaerated triethylamine (15mL), 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.
^{1}H NMR (300 MHz, $CDCl_3$) 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).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.8 (C=O), 149.9 (CH_{py}), 142.4 (CH=C), 136.1 (CH_{Ar}), 135.4 (C_q), 131.5 (CH_{Ar}), 130.7 (C_q), 125.6 (CH_{py}), 123.6 (C_q), 120.2 (CH=C), 91.8 (C≡C), 88.1 (C≡C), 52.0 (CH_3).
IR (ATR, cm^{-1}):.3053, 2923, 2853, 2217, 1711, 1635, 1594, 1538, 1488, 1459, 1439, 1413, 1377, 1328, 1304, 1260, 1221, 1189, 1172, 1091, 1012, 922, 867, 814, 801, 742, 696, 672.
TOF MS (ES+) calc for $C_{24}H_{16}N_2O_2$-H^+: 365.1285 , found: 365.1288.

evb4,Br
mp : 157°C.
^{1}H NMR (300 MHz, $CDCl_3$) 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).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.7 (C=O), 149.9 (CH_{py}), 142.0 (CH=C), 136.6 (C_q), 135.6 (CH_{Ar}), 131.3 (CH_{Ar}), 130.6 (C_q), 129.9 (CH_{Ar}), 125.6 (CH_{py}), 124.7 (C_q), 122.9 (C_q), 120.4 (CH=C), 91.3 (C≡C), 88.4 (C≡C), 52.0 (CH_3).
IR (ATR, cm^{-1}):3037, 2950, 2219, 1718, 1641, 1594, 1537, 1540, 1489, 1436, 1413, 1329, 1286, 1218, 1203, 1175, 1112, 1037, 990, 925, 854, 819, 743, 670.
TOF MS (ES+) calc for $C_{17}H_{12}BrNO_2$-H^+: 342.0125 , found: 342.0145.

evb3,4:
In a dry Schlenk tube under argon compound **evb4,Br** (63.5 mg, 0.19 mmol) and $Pd(PPh_3)_4$ (55 mg, 0.048 mmol) were solubilised in distilled and deaerated triethylamine (4 mL) and dry DMSO(0.5 mL) at 80°C. 3-ethynylylpyridine (57.4 mg, 0.056 mmol), CuI (7.1 mg, 0.037 mmol) and triethylamine (3mL) 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 (CH_2Cl_2:MeOH = 98:2) to give evb3,4 in presence of an impurity.
^{1}H NMR (500 MHz, $CDCl_3$) 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 = 16.1 Hz, 1H), 3.83 (s, 3H).



dvb3,3 : R1 = R2 = 3-py
dvb4,4 : R1 = R2 = 4-py
dvb3,4 : R1 = 3-py, R2 = 4-py

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

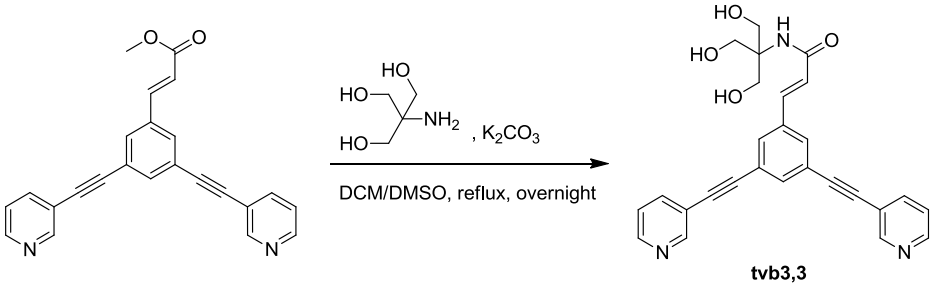
elution from CH2Cl2:MeOH = 100:0 to 95:5) to give dvb3,3 as a waxy solid (149 mg, 0.33 mmol) in 80% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.73 (d, J = 1.3Hz, 2H), 8.54 (dd, J = 1.5 Hz, J = 4.9 Hz, 2H), 7.78 (dt, J = 1.9Hz, 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).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3 (C=O), 152.3 (CH_{py}), 149.0 (CH_{py}), 139.4 (CH=C), 138.8 (CH_{py}), 135.6 (C_q), 135.5 (CH_{Ar}), 131.0 (CH_{Ar}), 123.8 (C_q), 123.3 (CH_{py}), 123.0 (CH=C), 120.1 (C_q), 91.2 (C≡C), 87.3 (C≡C), 65.9 (CH_2OH), 61.8 (C_q), 25.5 (CH_2), 7.8 (CH_3).
IR (ATR, cm^{-1}): 3277, 2930, 2399, 2216, 1726, 1660, 1618, 1477, 1421, 1407, 1337, 1230, 1187, 1044, 1024, 976, 856, 804, 731.
TOF MS (ES+) calc for $C_{28}H_{25}N_3O_3$-H^+: 452.1969, found: 452.1970.

dvb4,4: 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 CH_2Cl_2/DMSO (5.5/0.2 mL) and K_2CO_3 (42.4 mg, 0.31 mmol). The resulting mixture was heated to reflux 4 days. The mixture was diluted with CH_2Cl_2 and MeOH and K_2CO_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_2Cl_2:MeOH = 100:0 to 95:5) to give **dvb4,4** as a waxy solid (94.6 mg, 0.21 mmol) in 68% yield.
^{1}H NMR (300 MHz, $CDCl_3$) 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, 2 H), 1.73 (q, J = 7.5 Hz, 2H), 0.86 (t, J = 7.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.4 (C=O), 149.5 (CH_{py}), 138.7 (CH=C), 135.8 (C_q), 135.6 (CH_{Ar}), 131.4 (CH_{Ar}), 131.3 (C_q), 125.8 (CH_{py}), 123.4 (C_q), 123.3 (CH=C), 92.4 (C≡C), 87.7 (C≡C), 65.0 (CH_2OH), 61.7 (C_q), 25.0 (CH_2), 7.7 (CH_3).
IR (ATR, cm^{-1}): 3273, 2927, 2217, 1663, 1623, 1595, 1539, 1411, 1338, 1222, 1026, 999, 858, 821
TOF MS (ES+) calc for $C_{28}H_{25}N_3O_3$-H^+: 452.1969 , found: 452.2006.

dvb3,4: 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 CH_2Cl_2/DMSO (5.5/0.2 mL) and K_2CO_3 (16.3 mg, 0.12 mmol). The resulting mixture was heated to reflux 4 days. The mixture was diluted with CH_2Cl_2 and MeOH and K_2CO_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_2Cl_2:MeOH = 100:0 to 95:5) to give **dvb3,4** as a waxy solid (39.7 mg, 0.088 mmol) in 73% yield.
^{1}H NMR (300 MHz, $CDCl_3$) 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, CH_{Ar}), 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, CH_2OH), 3.58 (d, J = 11.7 Hz, 2H, CH_2OH), 1.72 (q, J = 7.4 Hz, 2H, CH_2), 0.85 (t, J = 7.4 Hz, 3H, CH_3).
^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6 (C=O), 151.8 (CH_{3py}), 149.4 (CH_{4py}), 148.6 (CH_{3py}), 139.0 (CH_{3py}), 138.9 (CH=C), 135.8 (C_q), 135.5 (CH_{Ar}), 131.5 (C_q), 131.2 (CH_{Ar}), 131.2 (CH_{Ar}), 125.9 (CH_{4py}), 123.8 (C_q), 123.5 (CH_{3py}), 123.2 (CH=C),120.2 (C_q), 92.6 (C≡C), 91.1 (C≡C), 87.6 (C≡C), 87.1 (C≡C), 64.9 (CH_2OH), 61.7 (C_q), 24.9 (CH_2), 7.6 (CH_3).
IR (ATR, cm^{-1}): 3301, 2949, 2216, 1660, 1625,1599, 1413,1339, 1232, 1017.
TOF MS (ES+) calc for $C_{28}H_{25}N_3O_3$-H^+: 452.1969, found: 452.1986.



tvb3,3

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_2CO_3 (29.5 mg, 0.21 mmol). The resulting mixture was heated to reflux overnight. The mixture was diluted with CH_2Cl_2 and MeOH and K_2CO_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_2Cl_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_2OH).

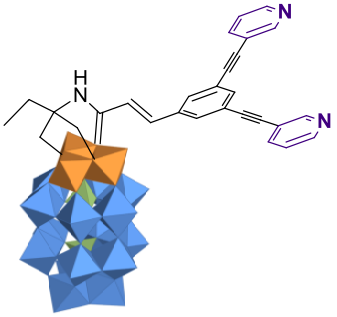
IR (ATR, cm^{-1}): 3287, 2961, 1662, 1622, 1560, 1478, 1410, 1258, 1016, 860, 794

TOF MS (ES+) calc for $C_{28}H_{25}N_3O_3$-H^+: 454.1762 , found: 454.1765.

Hybrids synthesis:

General Procedure :

A solution of $TBA_5H_4[P_2V_3W_{15}O_{62}]$ (300 mg, 0.056 mmol, 1eq.), 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_3CN) δ: - 6.99, -13.06.

^{1}H NMR (400 MHz, CD_3CN) δ: 9.6 (br, 1H, N**H**), 8.79 (s, 2H, H_{py}), 8.73 (d, 1H, J=15.2 Hz, C<u>H</u>=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=C<u>H</u>), 5.61 (d, 2H, J=12.7 Hz, C**H**$_2$OV), 5.48 (d, 2H, J=12.7Hz, C**H**$_2$OV), 3.17 (m, 43,1H, $^{+}N(C\mathbf{H}_2CH_2CH_2CH_3)_4$), 1.86 (q, 2H, J=7.2Hz, C**H**$_2$-CH_3), 1.65 (m, 43.3H, $^{+}N(CH_2C\mathbf{H}_2CH_2CH_3)_4$), 1.43 (q, 43.4H, J = 7.24Hz, $^{+}N(CH_2CH_2C\mathbf{H}_2CH_3)_4$), 1.13 (t, 3H, J= 7.2Hz, CH_2-C**H**$_3$), 1.00 (t, 64.8H, J=7.24Hz, $^{+}N(CH_2CH_2CH_2C\mathbf{H}_3)_4$).

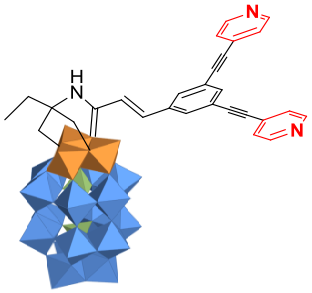
^{13}C NMR (100 MHz, CD_3CN) δ: 181.7 (C=O), 154.2 (**C**H=CH), 152.7 (C_{py}), 150.3 (C_{py}), 140.3 (C_{py}), 136.9 (**C**H$_{Ar}$), 136.5 (C_q), 134.3 (**C**H$_{Ar}$), 125.2 (C_q), 124.9 (C_{py}), 120.6 (C_q), 117.4 (CH=**C**H), 91.7 (**C**≡C), 89.8 (**C**H$_2$OV), 88.9 (C≡**C**), 64.8 (C_q), 59.3 ($^{+}N(\mathbf{C}H_2CH_2CH_2CH_3)_4$), 29.5 (**C**H$_2$-$CH_3$), 24,5 ($^{+}N(CH_2\mathbf{C}H_2CH_2CH_3)_4$), 20.4 ($^{+}N(CH_2CH_2\mathbf{C}H_2CH_3)_4$), 14.0 ($^{+}N(CH_2CH_2CH_2\mathbf{C}H_3)_4$), 7.52 ($CH_2$-**C**H$_3$)

Anal. calc. for $TBA_5(C_{28}H_{23}N_3O_{62}P_2V_3W_{15}).(Et_2O)_{0.7}$ (5630,04 $g.mol^{-1}$): C 23.64, H 3.76, N 1,99 ; found : C 23.64, H 3.76, N 2.00.

Electrospray mass spectrometry:

Entry	Charge	Simulated m/z	Observed m/z	Relative Intensity (%)	Composition
1	3-	1617.2	1617.4	18	$TBA_2(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
2	4-	1152.3	1152.4	93	$TBA(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
3	4-	1212.9	1212.9	11	TBA_2 $(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$ R.
4	5-	873.4	873.2	100	$(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$

(**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.

^{31}P NMR (162MHz, CD_3CN) δ: -7.54, -13.51.

^{1}H NMR (400 MHz, CD_3CN) δ: 8.66 (d, 4H, J=4.9 Hz, H_{py}), 8.29 (m, 3H, H_{Ar} + C**H**=CH), 7.73 (s, 1H, H_{Ar}), 7.58 (d, 4H, J = 4.9 Hz, H_{py}), 6.96 (d, 1H, J = 15,7Hz, CH=C**H**), 5.55 (d, 2H, J = 11.9 Hz, C**H**$_2$OV), 5.41 (d, 2H, J=11.9 Hz, C**H**$_2$OV), 3.19 (m, 51H, $^{+}N(C\mathbf{H}_2CH_2CH_2CH_3)_4$), 1.66 (m, 53H, $^{+}N(CH_2C\mathbf{H}_2CH_2CH_3)_4$ + C**H**$_2$-CH_3), 1.43 (q, 51H, J = 7.0Hz, $^{+}N(CH_2CH_2C\mathbf{H}_2CH_3)_4$), 1.13 (t, 3H, J= 7.1Hz, CH_2-C**H**$_3$), 1.00 (t, 75H, J=7.0Hz, $^{+}N(CH_2CH_2CH_2C\mathbf{H}_3)_4$).

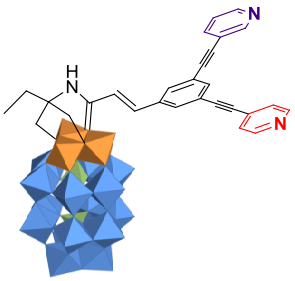
^{13}C NMR (100 MHz, CD_3CN) δ: 151,1 (C_{py}), 151.0 (**C**H=CH), 138.5 (C_q), 135.2 (CH_{Ar}), 134,1 (CH_{Ar}), 131.5 (C_q), 126.6 (CH_{Py}), 124.4 (C_q), 116.8 (CH=**C**H), 93.2 (**C**≡C), 90.3 (**C**H$_2$OV), 88.9 (C≡**C**), 63.1 (C_q), 59.3 ($^{+}N(\mathbf{C}H_2CH_2CH_2CH_3)_4$), 32.6 (**C**H$_2$-$CH_3$), 24,4 ($^{+}N(CH_2\mathbf{C}H_2CH_2CH_3)_4$), 20.4 ($^{+}N(CH_2CH_2\mathbf{C}H_2CH_3)_4$), 14.0 ($^{+}N(CH_2CH_2CH_2\mathbf{C}H_3)_4$), 8.02 ($CH_2$-**C**$H_3$).

Anal. calc. for $TBA_5(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$: C 23.25, H 3.67, N 2.01 ; found: C 23.35, H 3.58, N 2.05

Electrospray mass spectrometry:

Entry	Charge	Simulated m/z	Observed m/z	Relative Intensity (%)	Composition
1	3-	1697.9	1697.9	12	$TBA_3(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$ **R**
2	3-	1617.2	1617.0	20	$TBA_2(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
3	4-	1212.9	1212.9	54	TBA_2 $(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$ **R**
4	4-	1152.3	1152.1	100	$TBA(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
5	4-	1092.0	1088.3	27	$H(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
6	5-	873.4	873.4	74	$(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$

(**R** = 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.

^{31}P NMR (162 MHz, CD_3CN) δ: -7.26; -13.3.

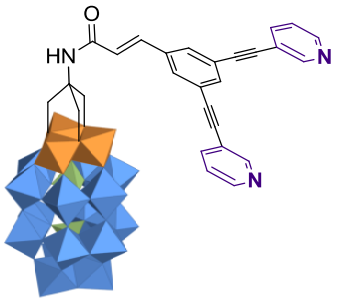
^{1}H NMR (500 MHz, CD_3CN) δ: 8.78 (s, 1H, H_{3py}), 8.67 (m, 3H, J = 4.5 Hz, C**H**=CH + H_{4py}), 8.59 (d, 1H, J = 3.65 Hz, H_{3py}), 8.54 (s, 1H, H_{Ar}), 8.28 (s, 1H, H_{Ar}), 8.10 (d, 1H, J = 7.65, H_{3py}), 7.82 (s, 1H, H_{Ar}), 7.59 (d, 2H, J = 4.25 Hz, H_{4py}), 7.52 (m, 1H, H_{3py}), 5.60 (d, 2H, J = 12.8 Hz, C$\mathbf{H_2}$OV), 5.46 (d, 2H, J = 12.2 Hz, , C$\mathbf{H_2}$OV), 3.18 (m, 42H, $^{+}N(C\mathbf{H_2}CH_2CH_2CH_3)_4$),), 1.86 (m, 2H, C$\mathbf{H_2}$-$CH_3$), 1.65 (m, 42H, $^{+}N(CH_2C\mathbf{H_2}CH_2CH_3)_4$), 1.43 (m, 42H, $^{+}N(CH_2CH_2C\mathbf{H_2}CH_3)_4$), 1.13 (m, 3H, CH_2-C$\mathbf{H_3}$), 1.00 (t, 62H, J=7.0Hz, $^{+}N(CH_2CH_2CH_2C\mathbf{H_3})_4$).

^{13}C NMR (100 MHz, CD_3CN) δ: 181.6 (CO), 154.1 (**C**H=CH), 152.7 (C_{3py}), 151.2 (C_{4py}), 150.2 (C_{3py}), 140.2 (C_{3py}), 136.9 (CH_{Ar}), 136.5 ($\mathbf{C}_{qAr}$-CH=CH), 135.3 (CH_{Ar}), 134.1 (CH_{Ar}), 131.4 (C_{q4py}), 126.6 (C_{4py}), 125.2 ($C_{qAr-≡-3py}$), 124.9 (C_{3py}), 124.8 ($C_{qAr-≡-4py}$), 120.6 (C_{q3py}), 118.3 (CH=**C**H, masked), 92.8 (**C**≡C), 91.6 (**C**≡C), 89.8 (**C**H_2OV), 89.4 (C≡**C**), 88.9 (C≡**C**), 64.8 (Cq), 29.5 (**C**H_2-CH_3), 7.56 (CH_2-**C**H_3).

Anal. calc. for $TBA_5(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$: C 23.25, H 3.67, N 2.01 ; found: C 23.26, H 3.65, N 1.87.

Electrospray mass spectrometry:

Entry	Charge	Simulated m/z	Observed m/z	Relative Intensity (%)	Composition
1	3-	1617.2	1617.9	25	$TBA_2(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
2	4-	1152.3	1152.6	100	$TBA(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
3	4-	1092.0	1091.3	7.6	$H(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$
3	5-	873.4	872.9	98	$(C_{28}H_{23}N_3O_{62}P_2V_3W_{15})$



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_3CN) δ: -7.45; -13.54.

^{1}H NMR (400 MHz, CD_3CN) δ: 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, C**H**=CH), 7.40 (dd, 2H, J=4.9Hz, J= 7.7 Hz, H_{py}), 6.66 (d, 1H, J=15.6 Hz, CH=C**H**), 6.42 (s, 1H, N**H**), 5.73 (s, 6H, C**H**$_2$OV), 3.8 (m, 59H, $^{+}N(C\mathbf{H}_2CH_2CH_2CH_3)_4$), 1.65 (quint, 59H, J= 7.7 Hz, $^{+}N(CH_2C\mathbf{H}_2CH_2CH_3)_4$), 1.43 (sext, 59H, J = 7.3Hz, $^{+}N(CH_2CH_2C\mathbf{H}_2CH_3)_4$), 0.99 (t, 89H, J=7.3Hz, $^{+}N(CH_2CH_2CH_2C\mathbf{H}_3)_4$).

^{13}C NMR (100 MHz, CD_3CN) δ: 166.0 (C=O), 152.9 (C_{py}), 150.2 (C_{py}), 139.6 (C_{py}), 138.7 (**C**H=CH), 137.5 ($\mathbf{C}_{qAr}$-CH=CH), 135.6 ($\mathbf{C}H_{Ar(1H)}$), 131.7 ($\mathbf{C}H_{Ar(2H)}$), 125.3 (CH=**C**H), 124.7 ($C_{qAr-\equiv-3py}$), 124.5 (C_{py}), 120.5 (C_{q3py}), 91.4 (**C**≡C), 88.1 (C≡**C**), 86.9 (**C**H$_2$OV), 59.3 ($^{+}N(\mathbf{C}H_2CH_2CH_2CH_3)_4$), 55.6 ($C_q$), 29.5 (**C**H$_2$-CH$_3$), 24,5 ($^{+}N(CH_2\mathbf{C}H_2CH_2CH_3)_4$), 20.5 ($^{+}N(CH_2CH_2\mathbf{C}H_2CH_3)_4$), 14.0 ($^{+}N(CH_2CH_2CH_2\mathbf{C}H_3)_4$).

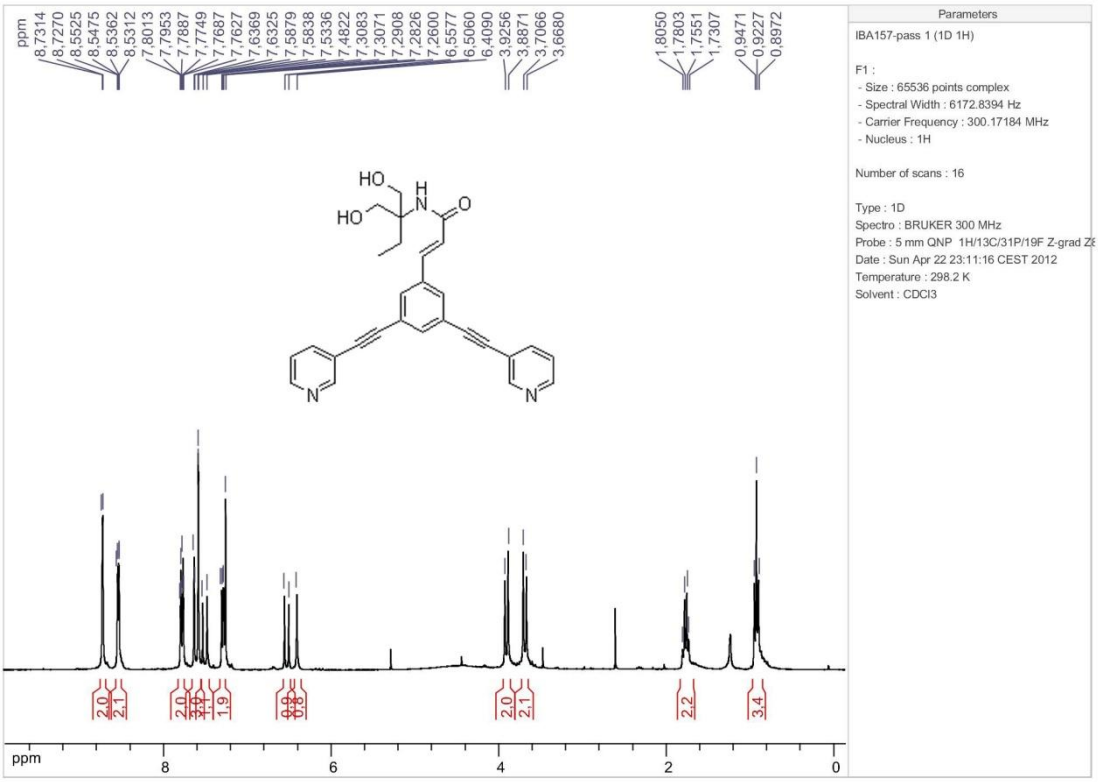
Anal. calc. for $TBA_{5.7}H_{0.3}(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$ (5749.2 $g.mol^{-1}$): C 24.69, H 3.95, N 2.12 ; found: C 24.36, H 4.01, N 2.07.

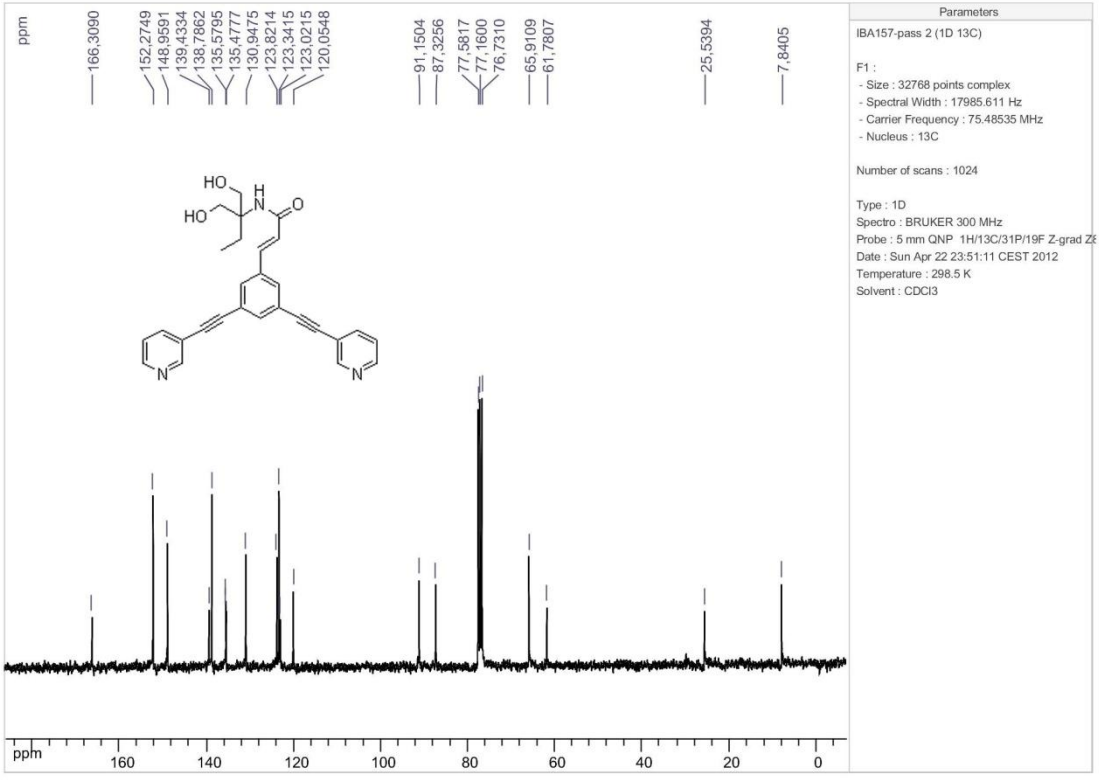
Electrospray mass spectrometry:

Entry	Charge	Simulated m/z	Observed m/z	Relative Intensity (%)	Composition
1	3-	1698.2	1698.0	11	$TBA_3(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$
2	4-	1213.1	1212.9	68	$TBA_2(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$
3	4-	1152.8	1152.3	5	$TBAH(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$
4	4-	1092.5	1091.3	18	$H_2(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$
5	5-	922.0	921.7	100	$TBA(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$
6	5-	873.8	874.2	5	$H(C_{27}H_{20}N_3O_{63}P_2V_3W_{15})$

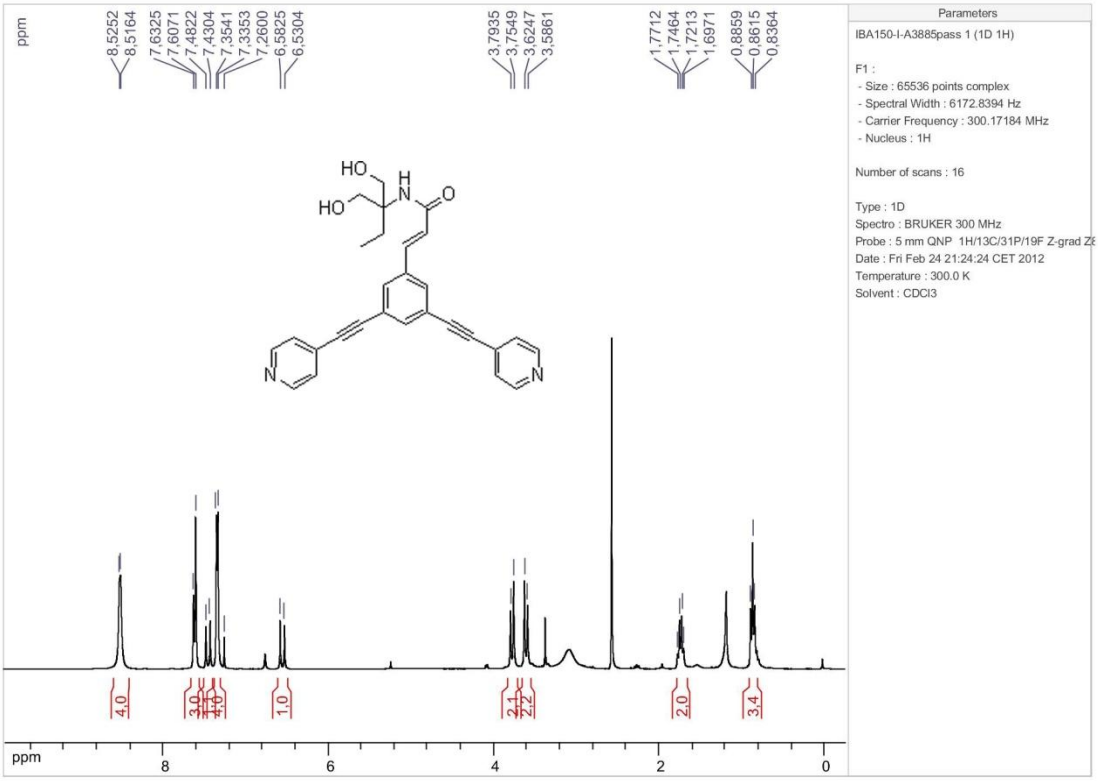
NMR Spectra

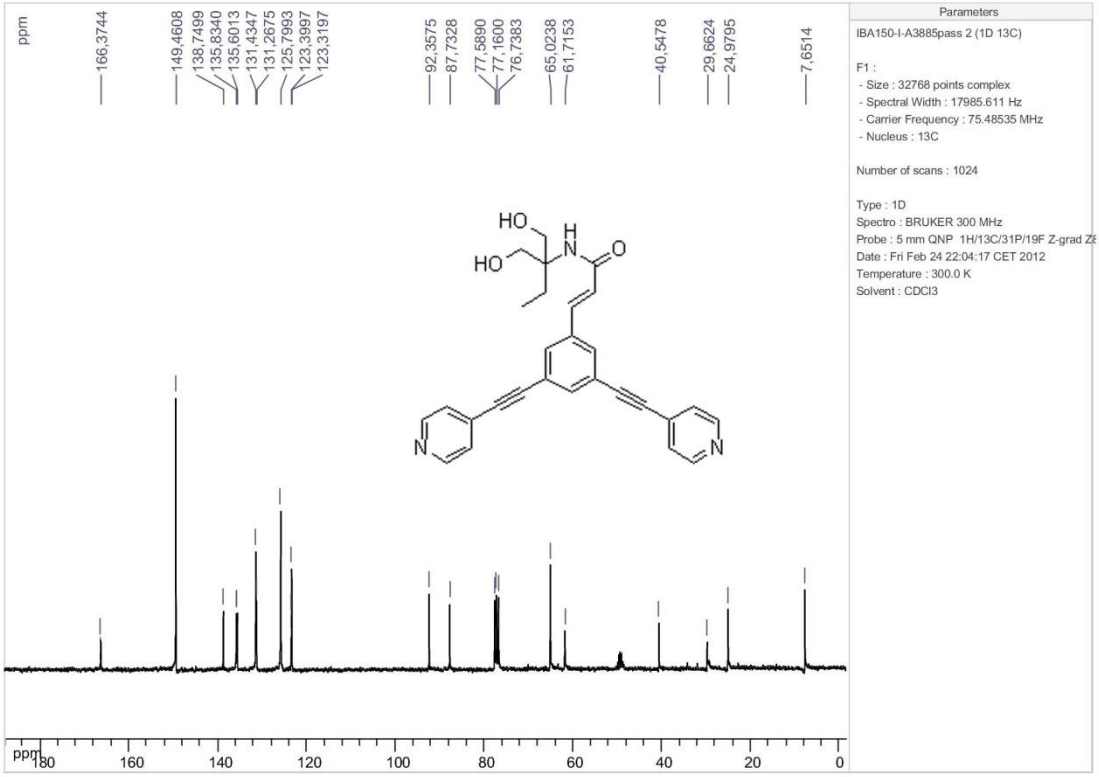
dvb3,3:



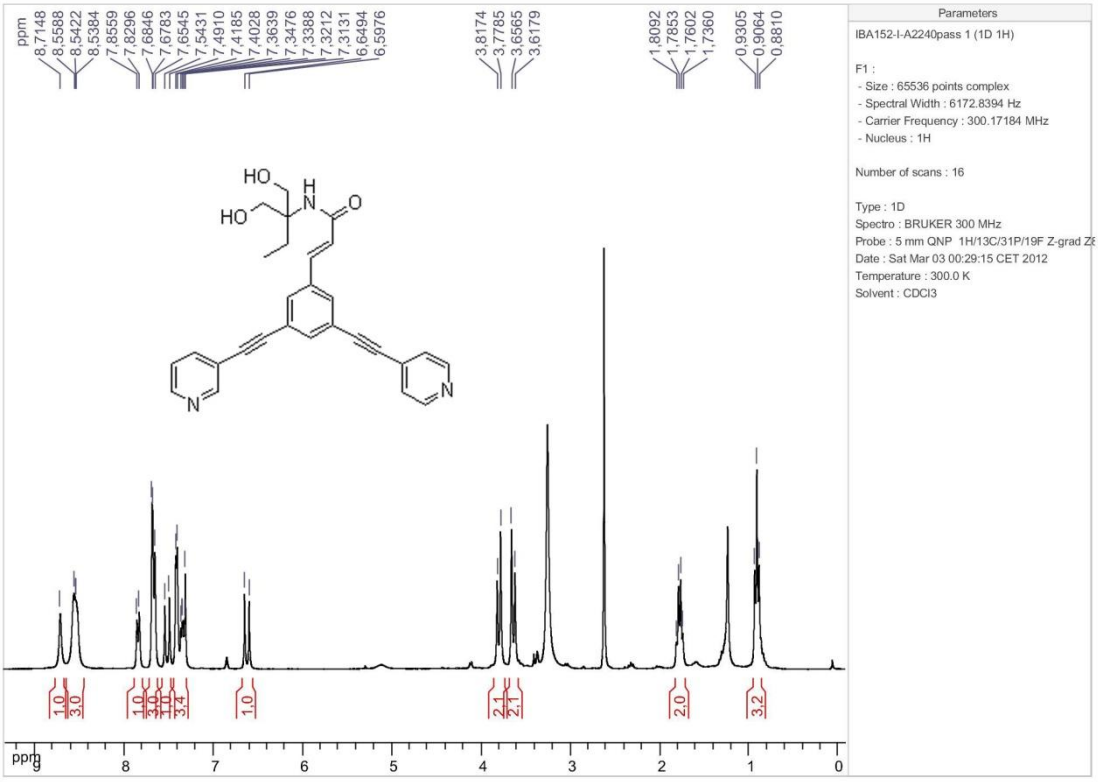


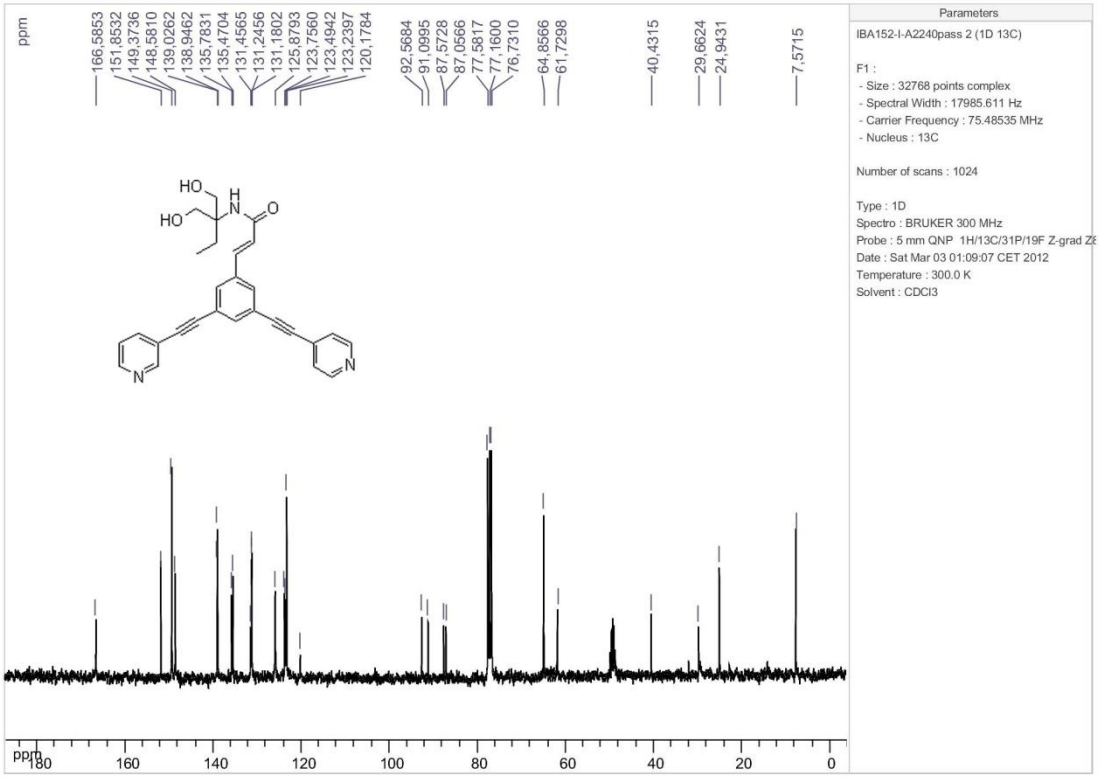
dvb4,4:


ppm
8,5252
8,5164
7,6325
7,6071
7,4822
7,4304
7,3541
7,3353
7,2600
6,5825
6,5304
3,7935
3,7549
3,6247
3,5861
1,7712
1,7464
1,7213
1,6971
0,8859
0,8615
0,8364
HO
HO
H
N
O
N
N
4,0
3,0
4,0
1,0
2,1
2,2
2,0
3,4
ppm
8
6
4
2
0
Parameters
IBA150-I-A3885pass 1 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 6172.8394 Hz
- Carrier Frequency : 300.17184 MHz
- Nucleus : 1H
Number of scans : 16
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Fri Feb 24 21:24:24 CET 2012
Temperature : 300.0 K
Solvent : CDCl3

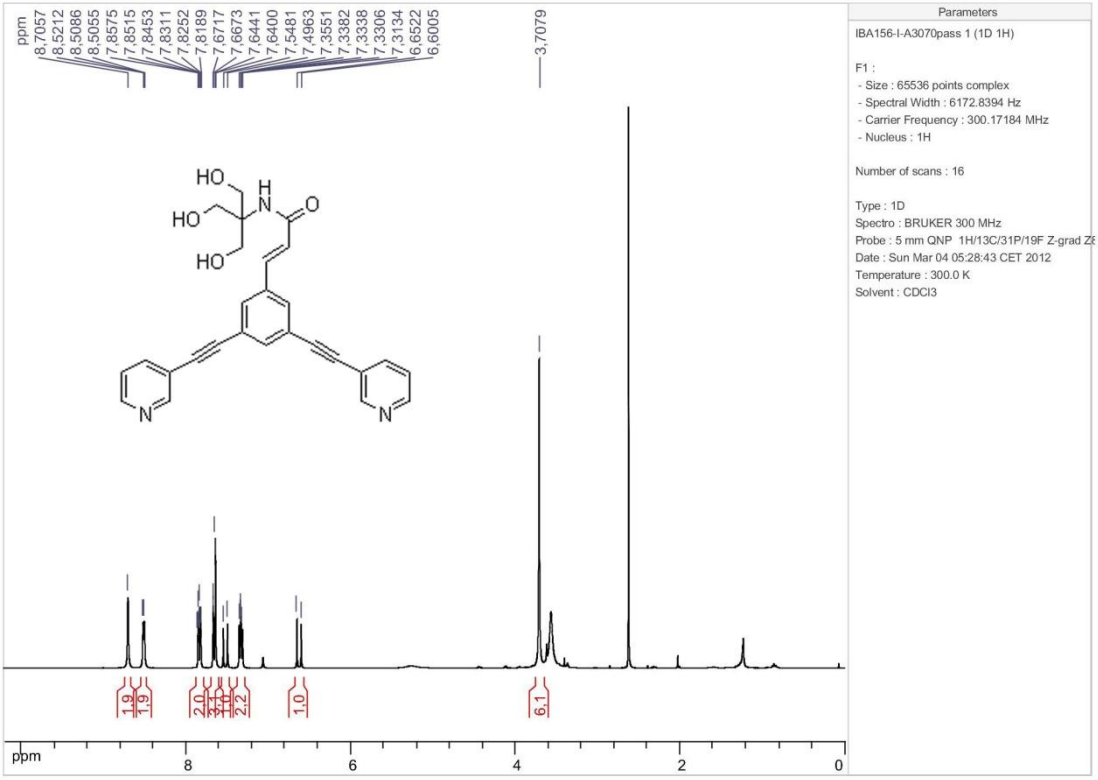

ppm
166,3744
149,4608
138,7499
135,8340
135,6013
131,4347
131,2675
125,7993
123,3997
123,3197
92,3575
87,7328
77,5890
77,1600
76,7383
65,0238
61,7153
40,5478
29,6624
24,9795
7,6514
HO
HO
H
N
O
N
N
ppm
180
160
140
120
100
80
60
40
20
0
Parameters
IBA150-I-A3885pass 2 (1D 13C)
F1 :
- Size : 32768 points complex
- Spectral Width : 17985.611 Hz
- Carrier Frequency : 75.48535 MHz
- Nucleus : 13C
Number of scans : 1024
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Fri Feb 24 22:04:17 CET 2012
Temperature : 300.0 K
Solvent : CDCl3

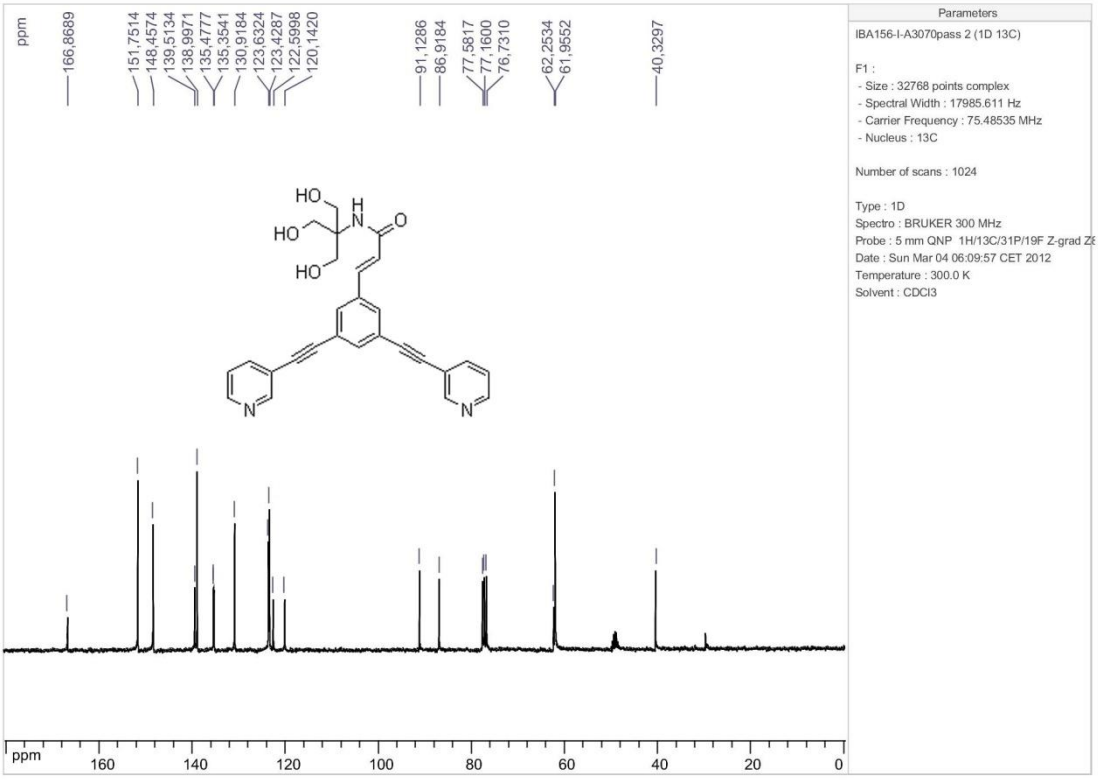
dvb3,4:


ppm
8,7148
8,5588
8,5422
8,5384
7,8559
7,8296
7,6846
7,6783
7,6545
7,5431
7,4910
7,4185
7,4028
7,3639
7,3476
7,3388
7,3212
7,3131
6,6494
6,5976
3,8174
3,7785
3,6565
3,6179
1,8092
1,7853
1,7602
1,7360
0,9305
0,9064
0,8810
HO
HO
H
N
O
N
N
1,0
3,0
1,0
3,0
1,0
3,4
1,0
2,1
2,1
2,0
3,2
ppm
9
8
7
6
5
4
3
2
1
0
Parameters
IBA152-I-A2240pass 1 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 6172.8394 Hz
- Carrier Frequency : 300.17184 MHz
- Nucleus : 1H
Number of scans : 16
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Sat Mar 03 00:29:15 CET 2012
Temperature : 300.0 K
Solvent : CDCl3

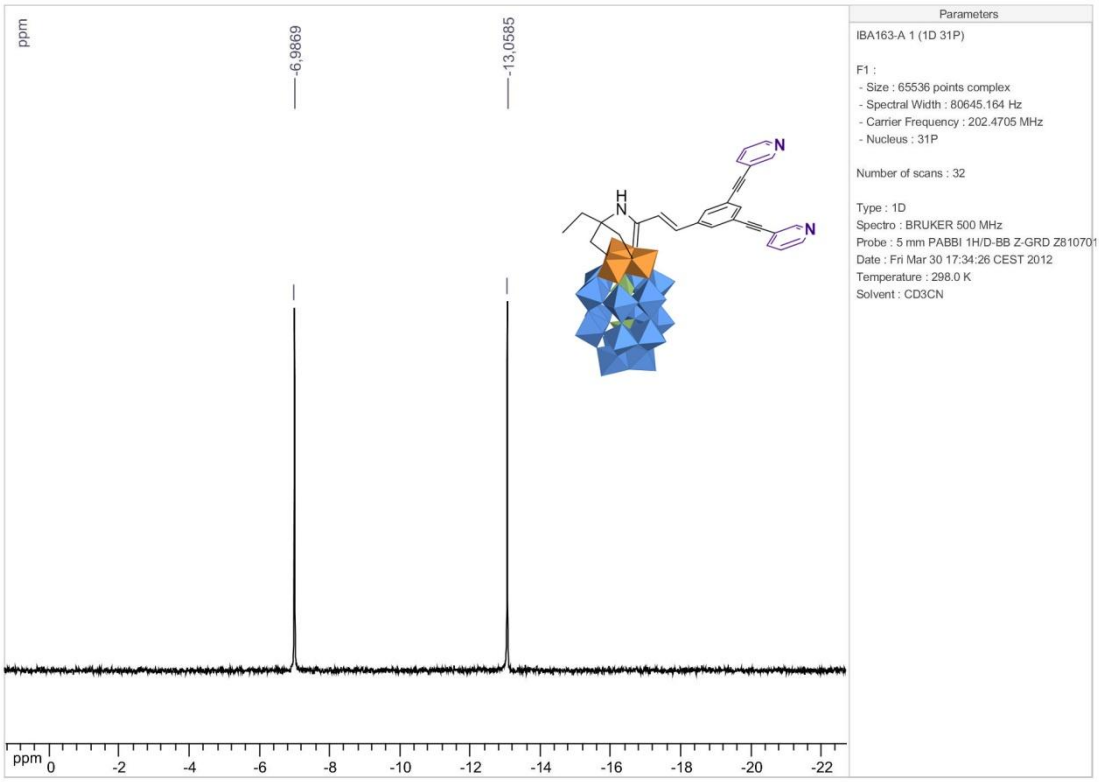

ppm
166,5853
151,8532
149,3736
148,5810
139,0262
138,9462
135,7831
135,4704
131,4565
131,2456
131,1802
125,8793
123,7560
123,4942
123,2397
120,1784
92,5684
91,0995
87,5728
87,0566
77,5817
77,1600
76,7310
64,8566
61,7298
40,4315
29,6624
24,9431
7,5715
HO
HO
H
N
O
N
N
ppm
180
160
140
120
100
80
60
40
20
0
Parameters
IBA152-I-A2240pass 2 (1D 13C)
F1 :
- Size : 32768 points complex
- Spectral Width : 17985.611 Hz
- Carrier Frequency : 75.48535 MHz
- Nucleus : 13C
Number of scans : 1024
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Sat Mar 03 01:09:07 CET 2012
Temperature : 300.0 K
Solvent : CDCl3

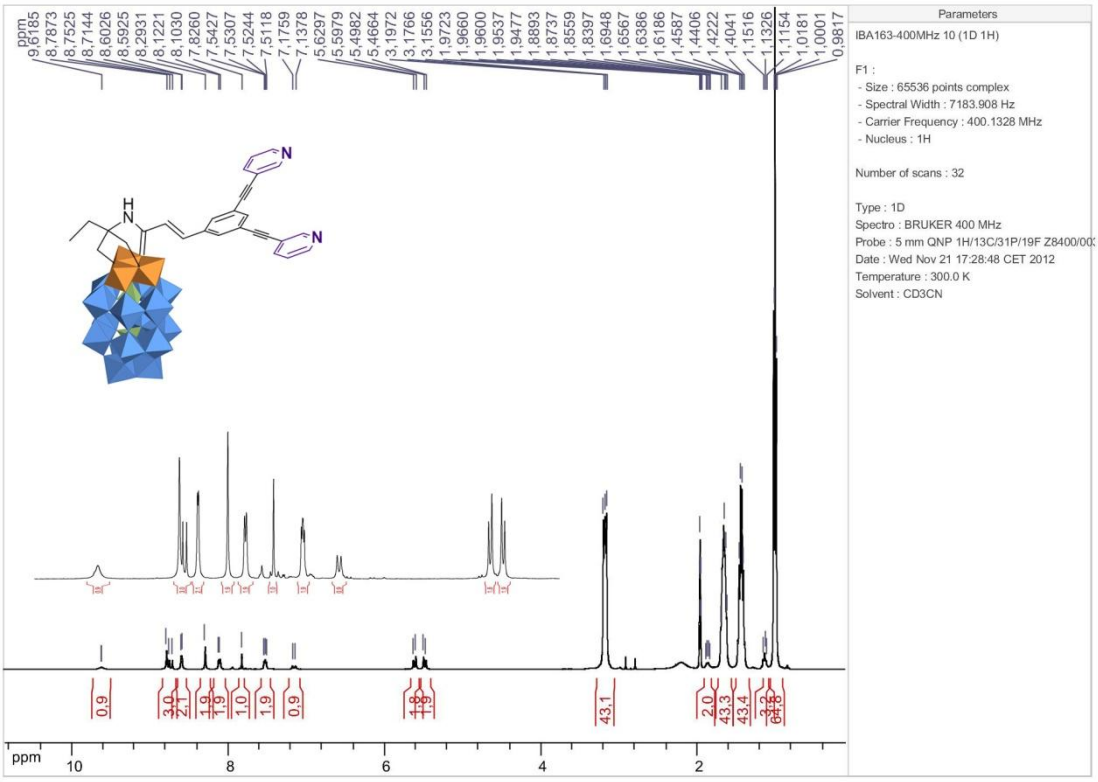
tvb3,3:

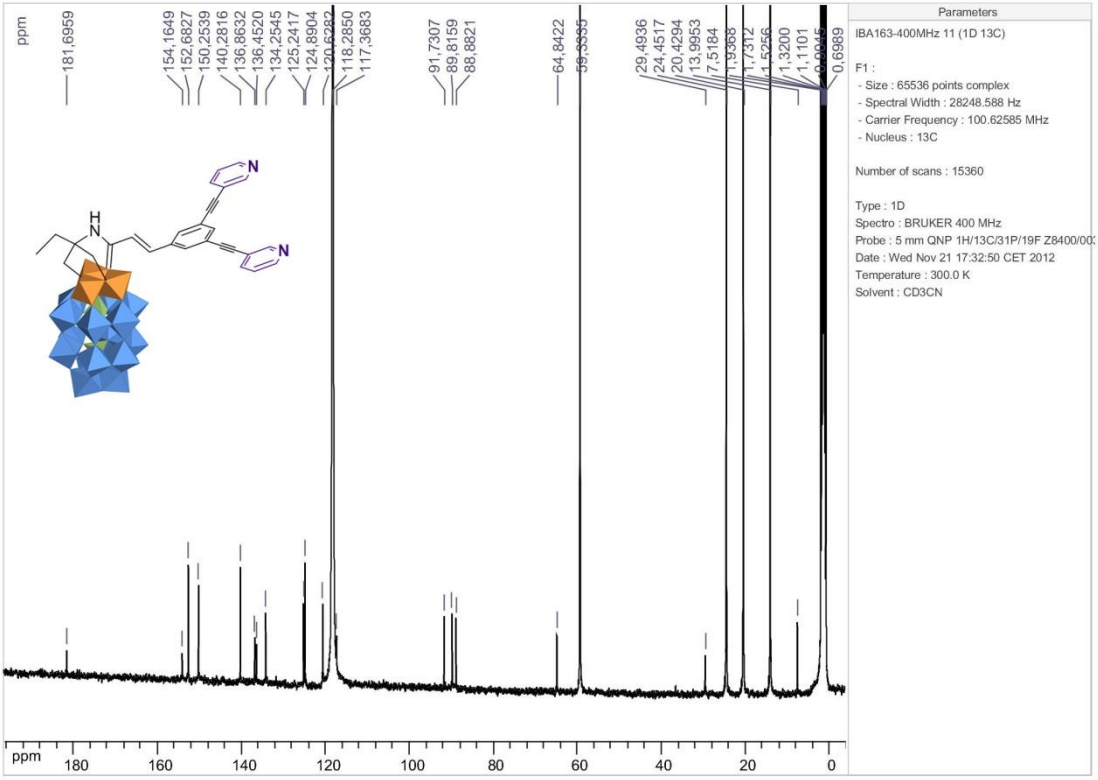

ppm
8,7057
8,5212
8,5086
8,5055
7,8575
7,8515
7,8453
7,8311
7,8252
7,8189
7,6717
7,6673
7,6441
7,6400
7,5481
7,4963
7,3551
7,3382
7,3338
7,3306
7,3134
6,6522
6,6005
3,7079
HO
HO
HO
H
N
O
N
N
1,9
1,9
2,0
2,2
1,0
6,1
ppm
8
6
4
2
0
Parameters
IBA156-I-A3070pass 1 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 6172,8394 Hz
- Carrier Frequency : 300,17184 MHz
- Nucleus : 1H
Number of scans : 16
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Sun Mar 04 05:28:43 CET 2012
Temperature : 300.0 K
Solvent : CDCl3


ppm
166,8689
151,7514
148,4574
139,5134
138,9971
135,4777
135,3541
130,9184
123,6324
123,4287
122,5998
120,1420
91,1286
86,9184
77,5817
77,1600
76,7310
62,2534
61,9552
40,3297
HO
HO
HO
H
N
O
N
N
ppm
160
140
120
100
80
60
40
20
0
Parameters
IBA156-I-A3070pass 2 (1D 13C)
F1 :
- Size : 32768 points complex
- Spectral Width : 17985,611 Hz
- Carrier Frequency : 75,48535 MHz
- Nucleus : 13C
Number of scans : 1024
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-grad Z
Date : Sun Mar 04 06:09:57 CET 2012
Temperature : 300.0 K
Solvent : CDCl3

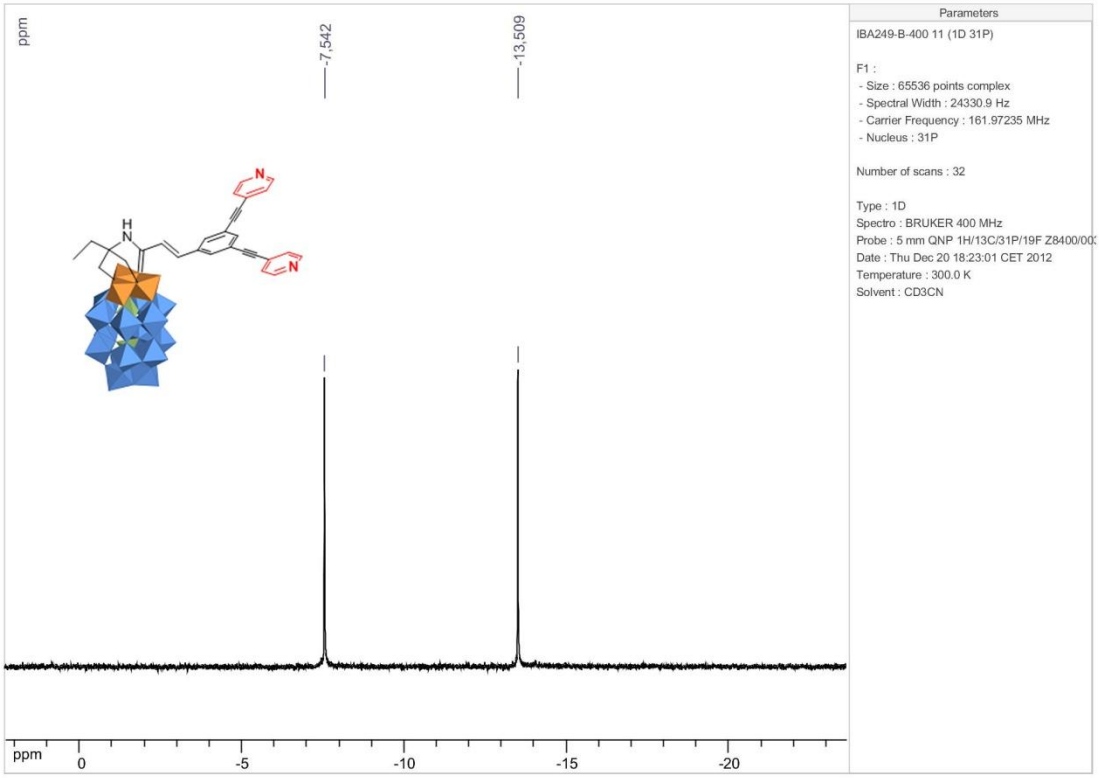
POM-dvb3,3:

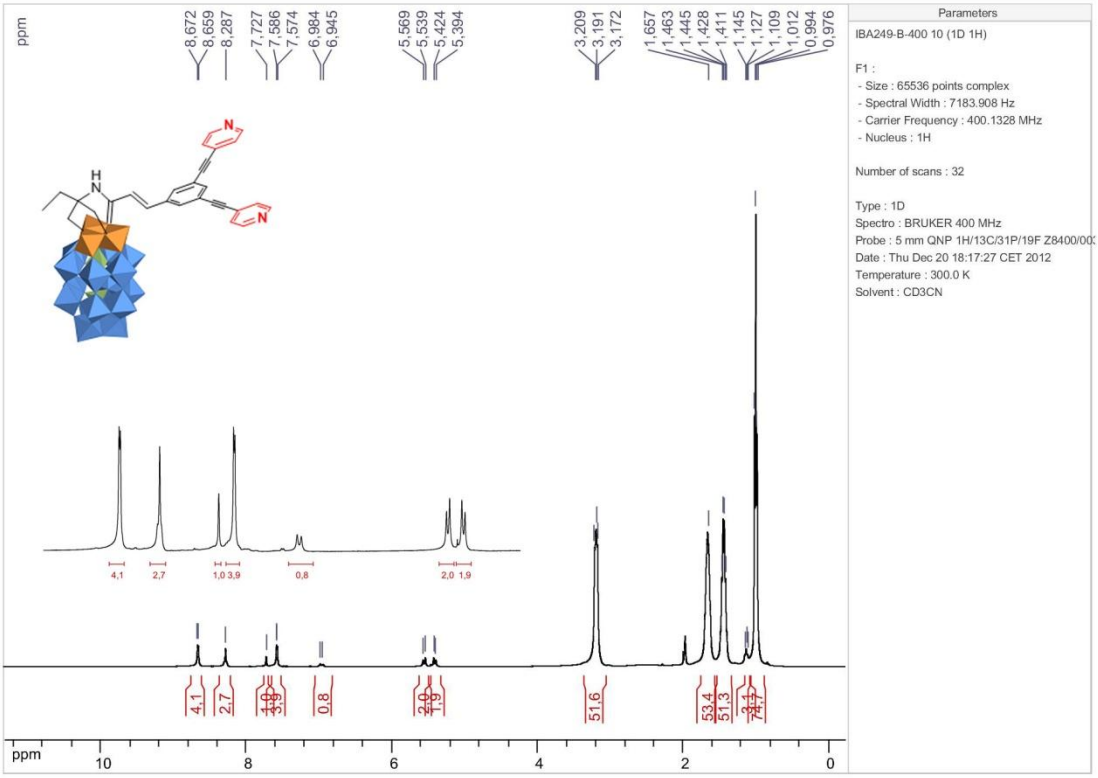

ppm
-6,9869
-13,0585
Parameters
IBA163-A 1 (1D 31P)
F1 :
- Size : 65536 points complex
- Spectral Width : 80645.164 Hz
- Carrier Frequency : 202.4705 MHz
- Nucleus : 31P
Number of scans : 32
Type : 1D
Spectro : BRUKER 500 MHz
Probe : 5 mm PABBI 1H/D-BB Z-GRD Z810701
Date : Fri Mar 30 17:34:26 CEST 2012
Temperature : 298.0 K
Solvent : CD3CN
ppm 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22

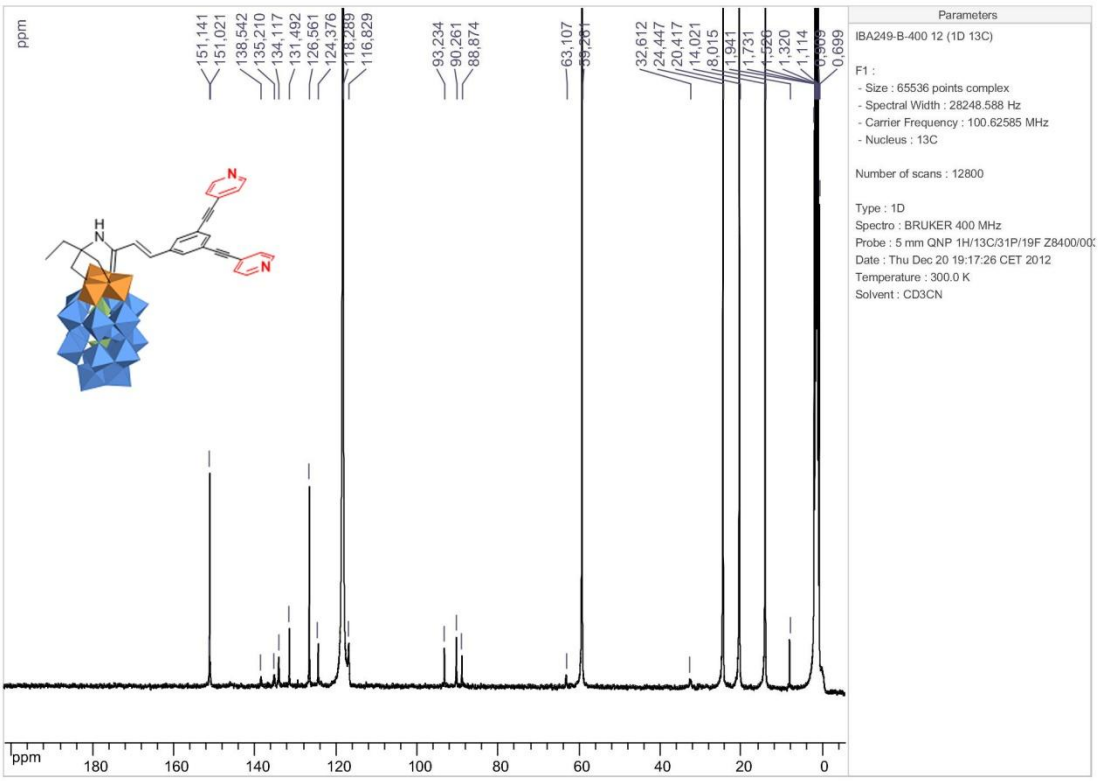

ppm
9,6185 8,7873 8,7525 8,7144 8,6026 8,5925 8,2931 8,1221 8,1030 7,8260 7,5427 7,5307 7,5244 7,5118 7,1759 7,1378 5,6297 5,5979 5,4982 5,4664 3,1972 3,1766 3,1556 1,9723 1,9660 1,9600 1,9537 1,9477 1,8893 1,8737 1,8559 1,8397 1,6948 1,6567 1,6386 1,6186 1,4587 1,4406 1,4222 1,4041 1,1516 1,1326 1,1154 1,0181 1,0001 0,9817
Parameters
IBA163-400MHz 10 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 7183.908 Hz
- Carrier Frequency : 400.1328 MHz
- Nucleus : 1H
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Wed Nov 21 17:28:48 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
0,9 3,0 2,4 1,9 1,9 1,0 1,9 0,9 1,8 1,9 43,1 2,0 43,3 43,4 3,2 64,8
ppm 10 8 6 4 2


ppm
181,6959
154,1649
152,6827
150,2539
140,2816
136,8632
136,4520
134,2545
125,2417
124,8904
120,6282
118,2850
117,3683
91,7307
89,8159
88,8821
64,8422
59,3335
29,4936
24,4517
20,4294
13,9953
7,5184
1,9368
1,7312
1,5256
1,3200
1,1101
0,6989
N
H
N
N
ppm
180
160
140
120
100
80
60
40
20
0
Parameters
IBA163-400MHz 11 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 28248.588 Hz
- Carrier Frequency : 100.62585 MHz
- Nucleus : 13C
Number of scans : 15360
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Wed Nov 21 17:32:50 CET 2012
Temperature : 300.0 K
Solvent : CD3CN

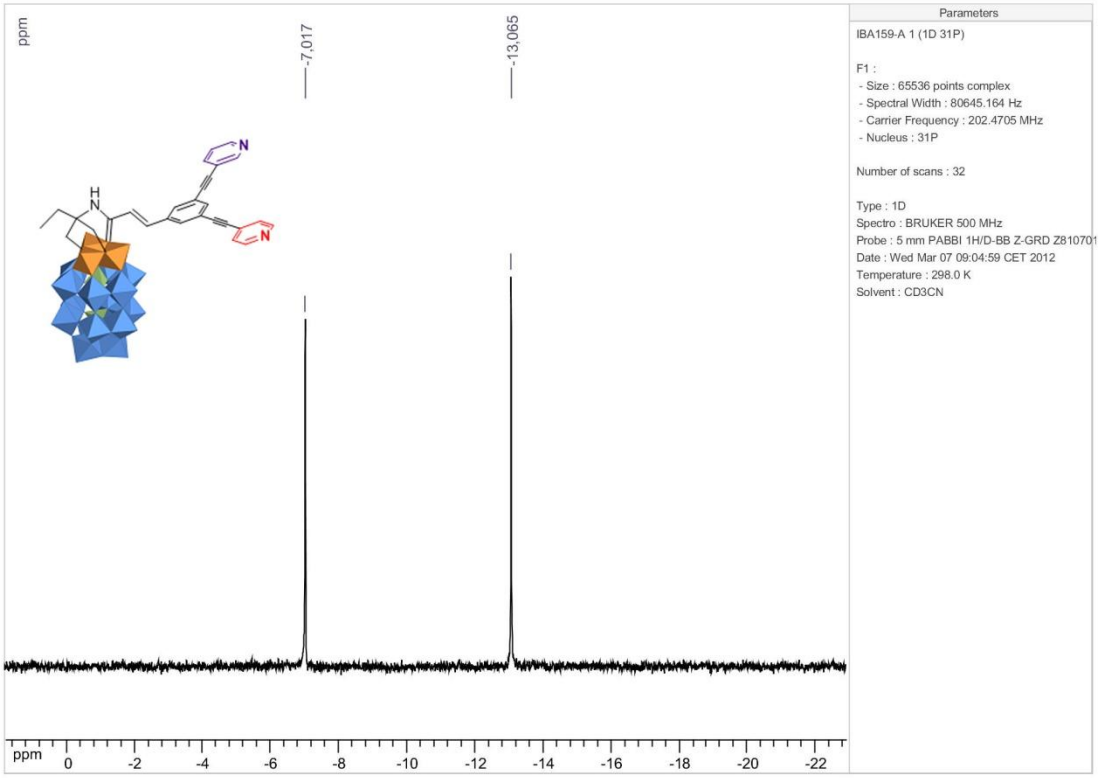
POM-dvb4,4:

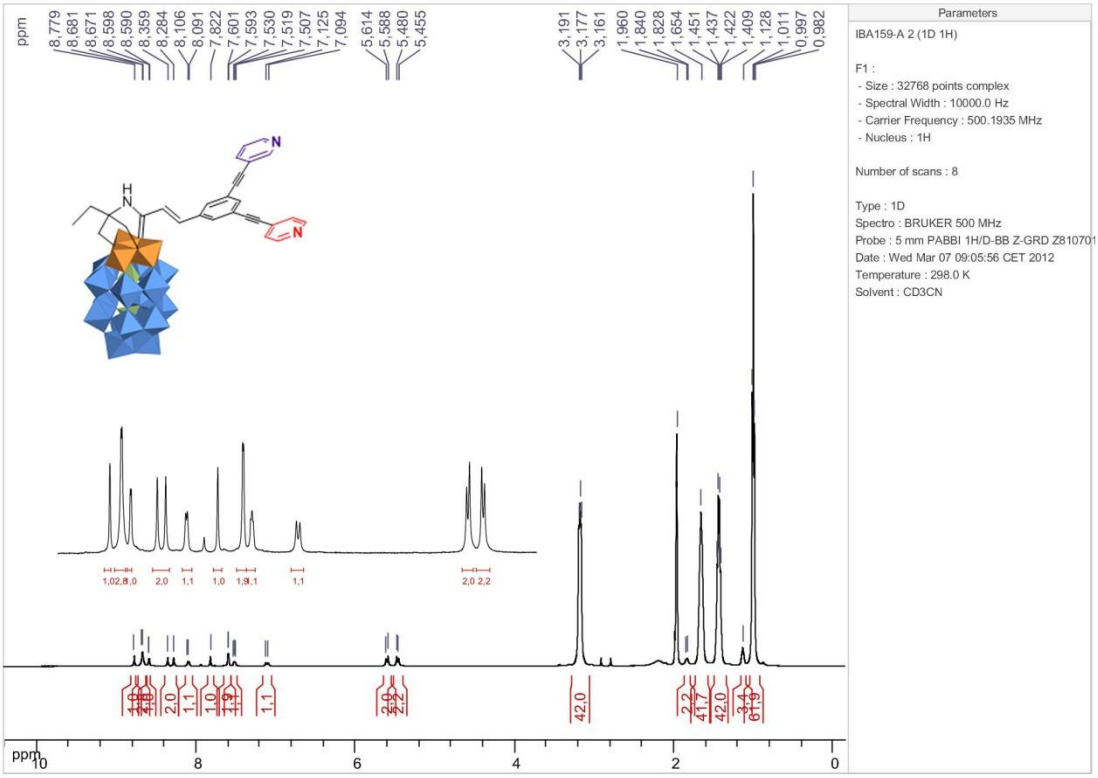

ppm
-7,542
-13,509
Parameters
IBA249-B-400 11 (1D 31P)
F1 :
- Size : 65536 points complex
- Spectral Width : 24330.9 Hz
- Carrier Frequency : 161.97235 MHz
- Nucleus : 31P
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Thu Dec 20 18:23:01 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
ppm
0
-5
-10
-15
-20

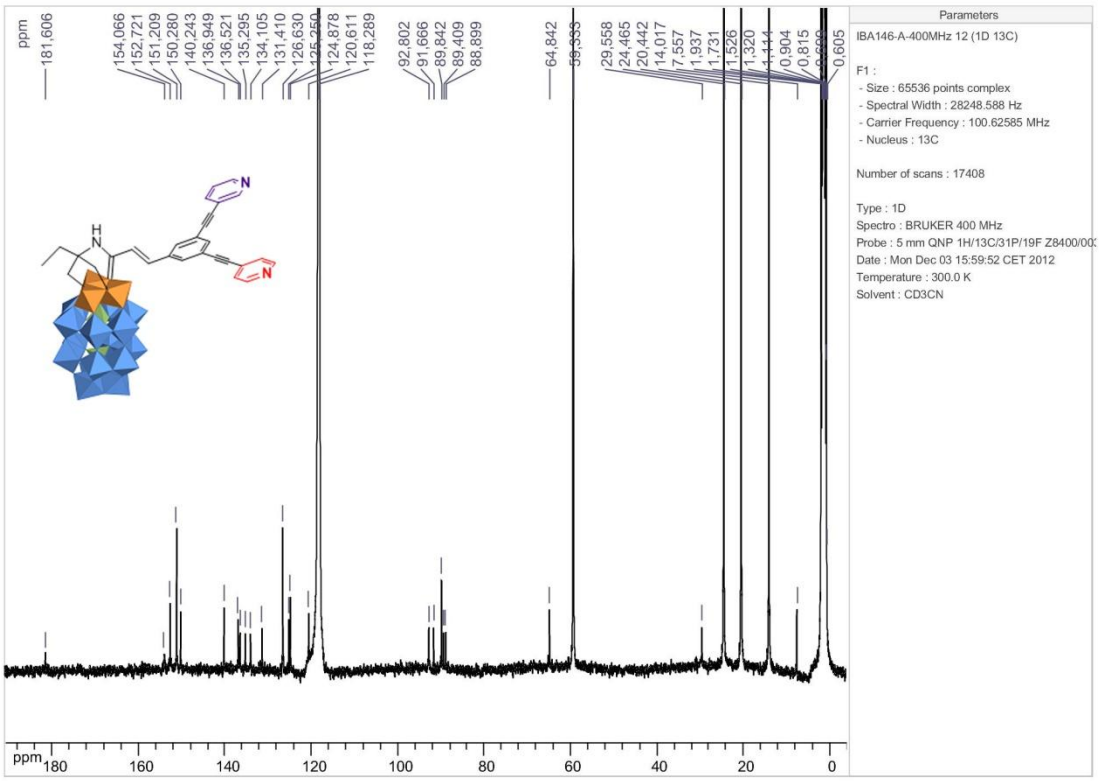

ppm
8,672
8,659
8,287
7,727
7,586
7,574
6,984
6,945
5,569
5,539
5,424
5,394
3,209
3,191
3,172
1,657
1,463
1,445
1,428
1,411
1,145
1,127
1,109
1,012
0,994
0,976
Parameters
IBA249-B-400 10 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 7183.908 Hz
- Carrier Frequency : 400.1328 MHz
- Nucleus : 1H
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Thu Dec 20 18:17:27 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
4,1
2,7
1,0 3,9
0,8
2,0 1,9
51,6
53,4
51,3
ppm
10
8
6
4
2
0


ppm
151,141
151,021
138,542
135,210
134,117
131,492
126,561
124,376
118,289
116,829
93,234
90,261
88,874
63,107
59,261
32,612
24,447
20,417
14,021
8,015
1,941
1,731
1,526
1,320
1,114
0,909
0,699
H
N
N
N
ppm
180
160
140
120
100
80
60
40
20
0
Parameters
IBA249-B-400 12 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 28248.588 Hz
- Carrier Frequency : 100.62585 MHz
- Nucleus : 13C
Number of scans : 12800
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Thu Dec 20 19:17:26 CET 2012
Temperature : 300.0 K
Solvent : CD3CN

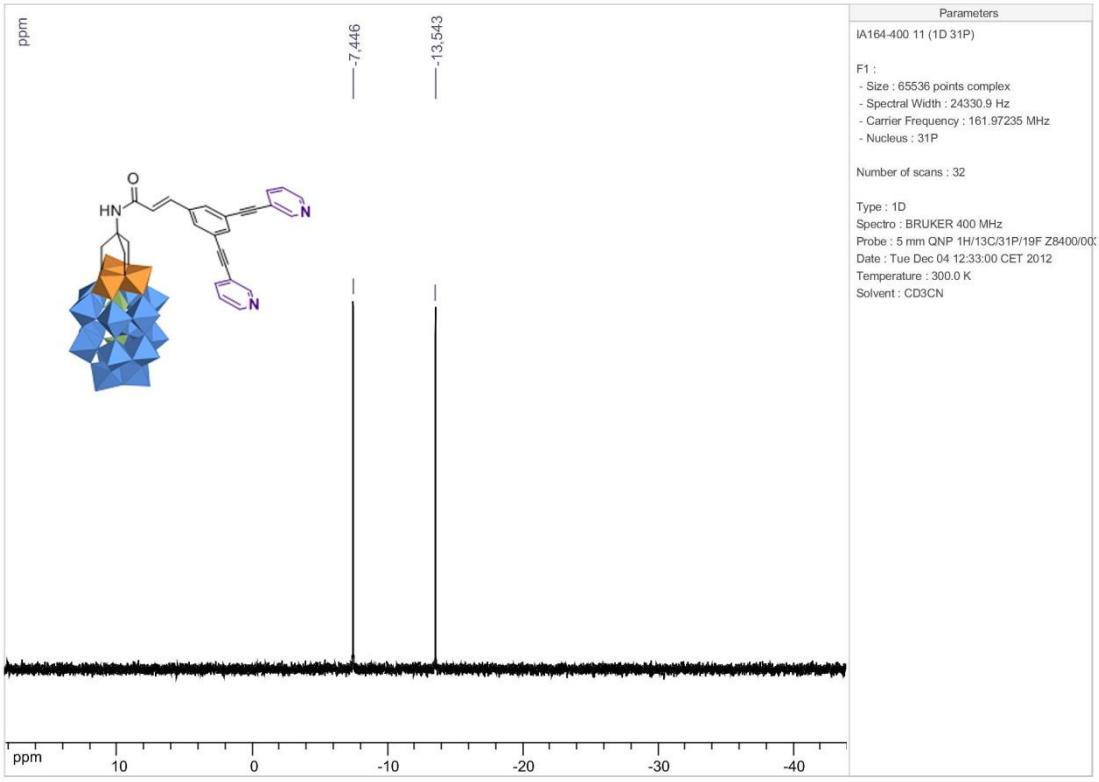
POM-dvb3,4:

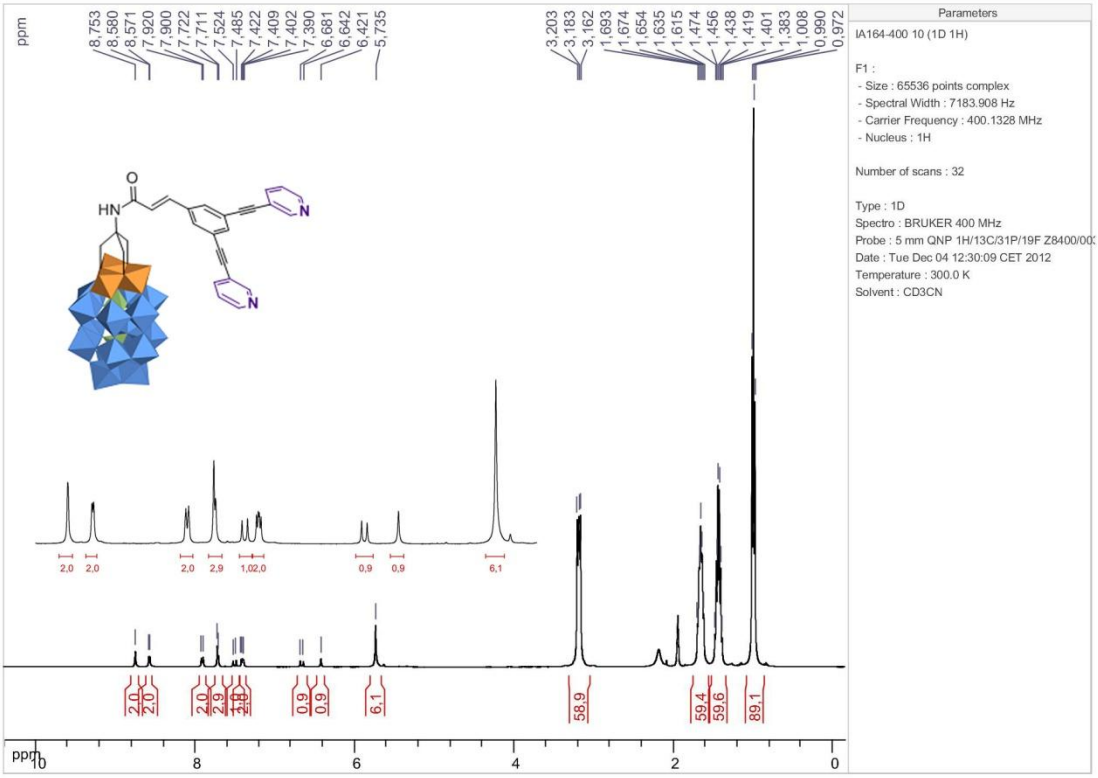

ppm
-7,017
-13,065
Parameters
IBA159-A 1 (1D 31P)
F1 :
- Size : 65536 points complex
- Spectral Width : 80645.164 Hz
- Carrier Frequency : 202.4705 MHz
- Nucleus : 31P
Number of scans : 32
Type : 1D
Spectro : BRUKER 500 MHz
Probe : 5 mm PABBI 1H/D-BB Z-GRD Z810701
Date : Wed Mar 07 09:04:59 CET 2012
Temperature : 298.0 K
Solvent : CD3CN
0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22

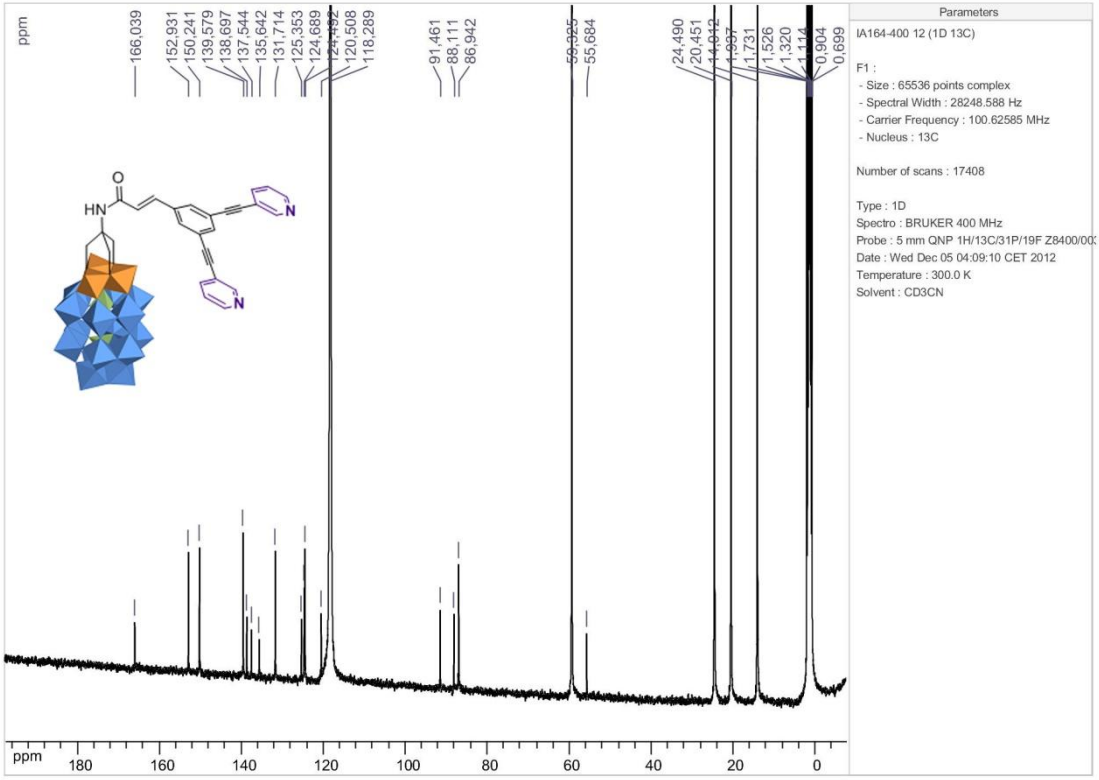

ppm
8,779 8,681 8,671 8,598 8,590 8,359 8,284 8,106 8,091 7,822 7,601 7,593 7,530 7,519 7,507 7,125 7,094 5,614 5,588 5,480 5,455
3,191 3,177 3,161 1,960 1,840 1,828 1,654 1,451 1,437 1,422 1,409 1,128 1,011 0,997 0,982
Parameters
IBA159-A 2 (1D 1H)
F1 :
- Size : 32768 points complex
- Spectral Width : 10000.0 Hz
- Carrier Frequency : 500.1935 MHz
- Nucleus : 1H
Number of scans : 8
Type : 1D
Spectro : BRUKER 500 MHz
Probe : 5 mm PABBI 1H/D-BB Z-GRD Z810701
Date : Wed Mar 07 09:05:56 CET 2012
Temperature : 298.0 K
Solvent : CD3CN
2,0 1,1 1,0 1,1 1,1 2,0 2,2 42,0 2,2 4,1 7 42,0 3,1 6,1 9
10 8 6 4 2 0


ppm
181,606
154,066
152,721
151,209
150,280
140,243
136,949
136,521
135,295
134,105
131,410
126,630
125,260
124,878
120,611
118,289
92,802
91,666
89,842
89,409
88,899
64,842
59,333
29,558
24,465
20,442
14,017
7,557
1,937
1,731
1,526
1,320
1,114
0,904
0,815
0,605
H
N
N
N
ppm
180
160
140
120
100
80
60
40
20
0
Parameters
IBA146-A-400MHz 12 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 28248.588 Hz
- Carrier Frequency : 100.62585 MHz
- Nucleus : 13C
Number of scans : 17408
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Mon Dec 03 15:59:52 CET 2012
Temperature : 300.0 K
Solvent : CD3CN

POM-tvb3,3:

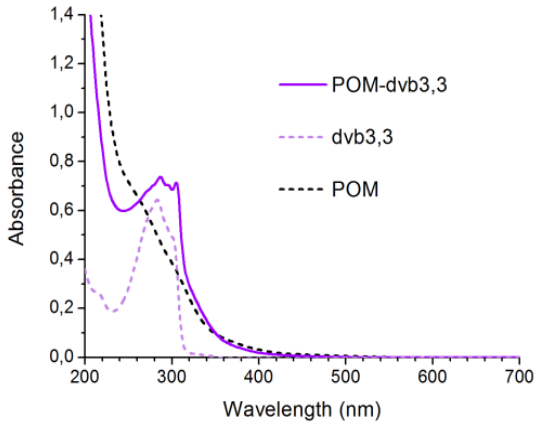

ppm
-7,446
-13,543
Parameters
IA164-400 11 (1D 31P)
F1 :
- Size : 65536 points complex
- Spectral Width : 24330.9 Hz
- Carrier Frequency : 161.97235 MHz
- Nucleus : 31P
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Tue Dec 04 12:33:00 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
10
0
-10
-20
-30
-40


ppm
8,753
8,580
8,571
7,920
7,900
7,722
7,711
7,524
7,485
7,422
7,409
7,402
7,390
6,681
6,642
6,421
5,735
3,203
3,183
3,162
1,693
1,674
1,654
1,635
1,615
1,474
1,456
1,438
1,419
1,401
1,383
1,008
0,990
0,972
Parameters
IA164-400 10 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 7183.908 Hz
- Carrier Frequency : 400.1328 MHz
- Nucleus : 1H
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Tue Dec 04 12:30:09 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
2,0 2,0
2,0 2,9 1,02,0
0,9 0,9
6,1
2,0
2,0
2,0
2,9
1,0
0,9
0,9
6,1
58,9
59,4
59,6
89,1
10
8
6
4
2
0

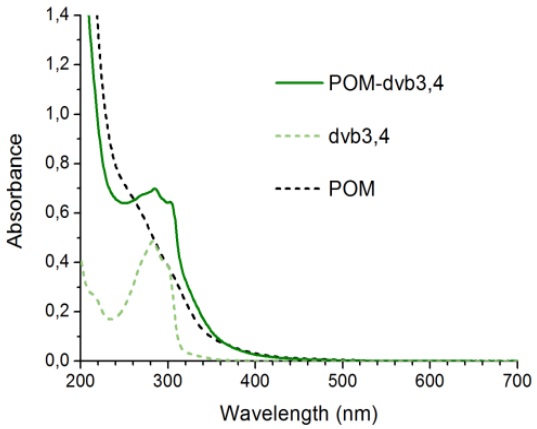

ppm
166,039
152,931
150,241
139,579
138,697
137,544
135,642
131,714
125,353
124,689
124,482
120,508
118,289
91,461
88,111
86,942
59,325
55,684
24,490
20,451
14,642
1,997
1,731
1,526
1,320
1,114
0,904
0,699
HN
O
N
N
Parameters
IA164-400 12 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 28248.588 Hz
- Carrier Frequency : 100.62585 MHz
- Nucleus : 13C
Number of scans : 17408
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z8400/00
Date : Wed Dec 05 04:09:10 CET 2012
Temperature : 300.0 K
Solvent : CD3CN
ppm
180
160
140
120
100
80
60
40
20
0

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

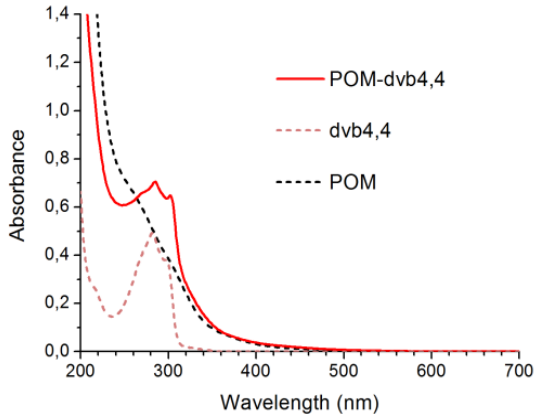
a)



b)



c)



d)

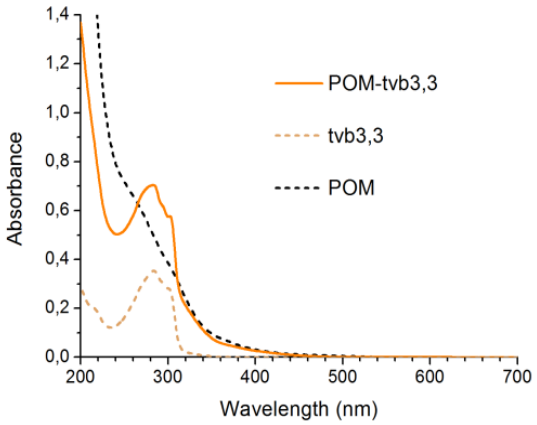


Fig S1 UV-Vis absorption spectra of a) **POM-dvb3,3** , b) **POM-dvb3,4** , c) **POM-dvb3,4**, d) **POM-tvb3,3** compared to $TBA_5H_4[P_2V_3W_{15}O_{62}]$ and their corresponding non-grafted ligand. Concentration is 6.25 10^{-6} M in CH_3CN.

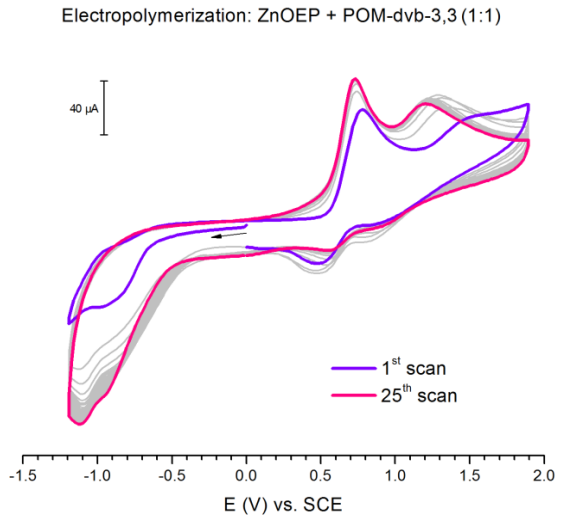
Fabrication of Films

Copolymer Poly-ZnOEP-POM

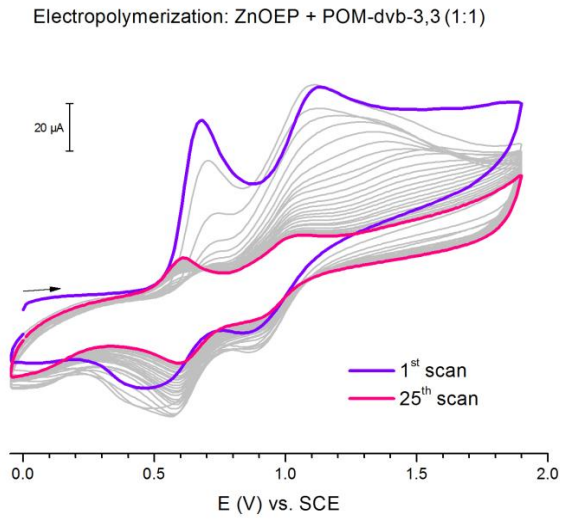
Electropolymerization was performed under an argon atmosphere in a 0.1 mol L^{-1} solution of tetrabutylammonium hexafluorophosphate in 1,2-$C_2H_4Cl_2$/CH_3CN (7:3) containing 0.25 mmol L^{-1} ZnOEP and 0.25 mmol L^{-1} $POM(py)_2$ using iterative scans. Cyclic scanning (0.2 V s^{-1}) was applied at 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 CH_3CN to remove traces of the conducting salt present on the deposited films.

CV evolution during electropolymerization

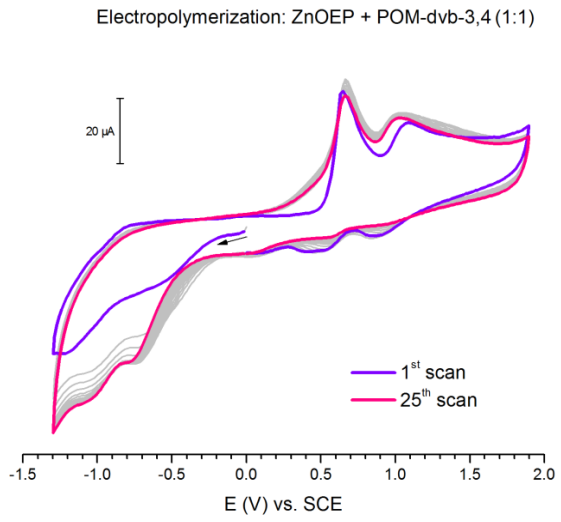
a)



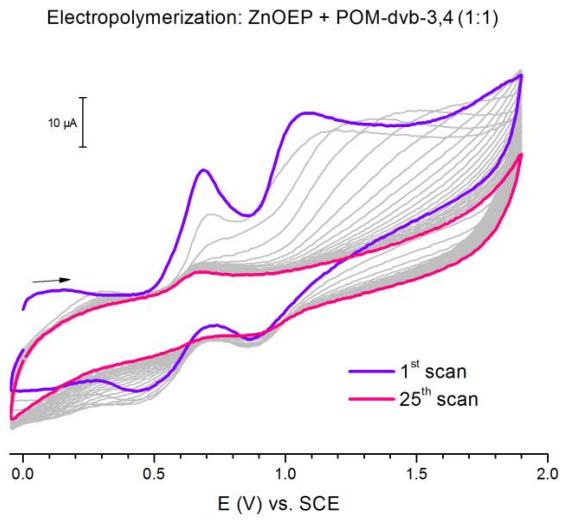
b)



c)



d)



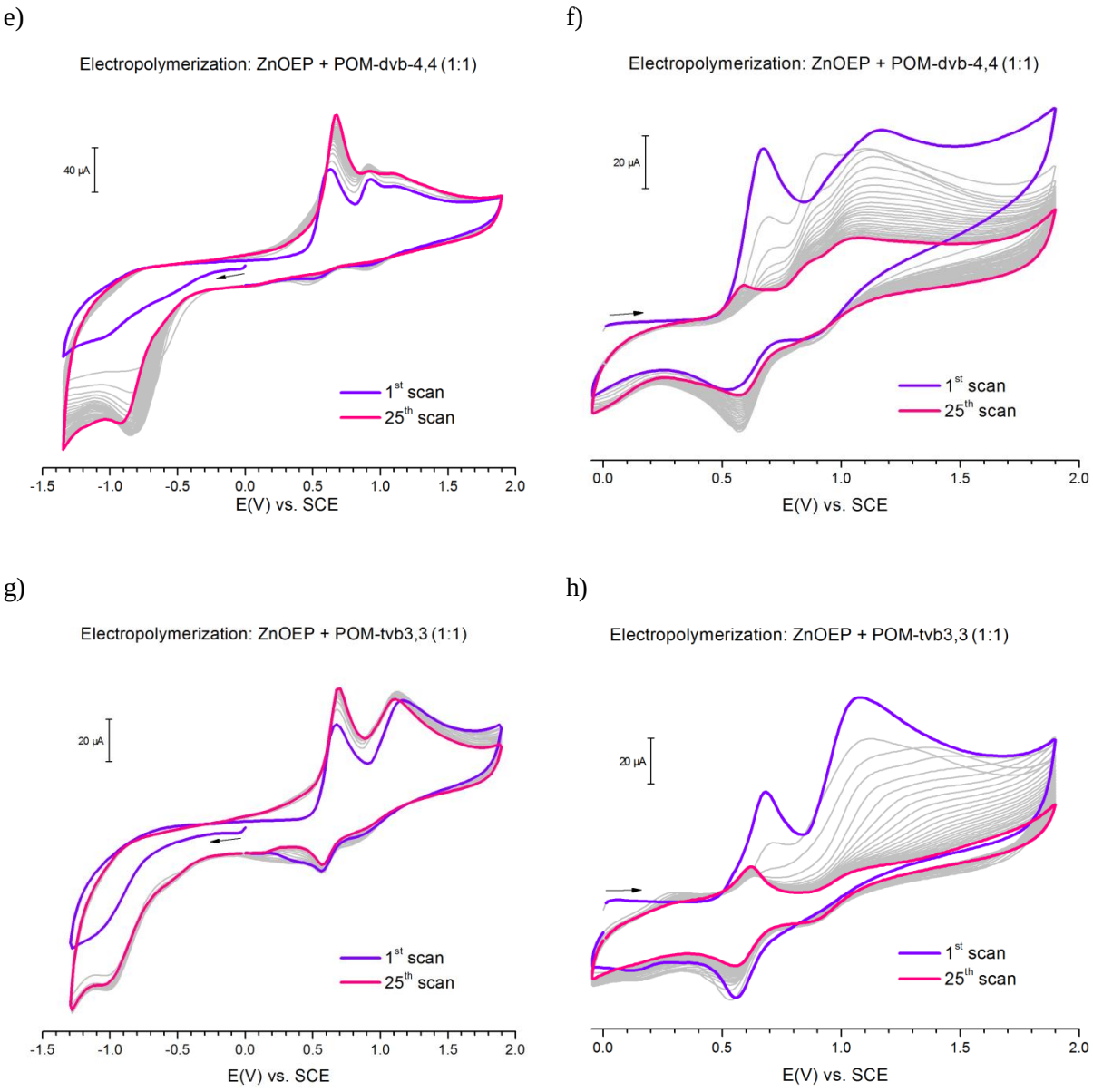


Fig S2 Cyclic voltammograms recorded during the electropolymerization of ZnOEP in the presence of a), b) **POM-dvb3,3** , c) and d) **POM-dvb3,4**, e) and f) **POM-dvb4,4**, g and h) **POM-tvb3,3** in 1,2-C2H4Cl2/CH3CN (7:3) (NBu4)PF6 0.1mol L^{-1}. Working electrode: ITO. S = 1 cm2. Scan rate: 0.1 $V.s^{-1}$. (←) 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

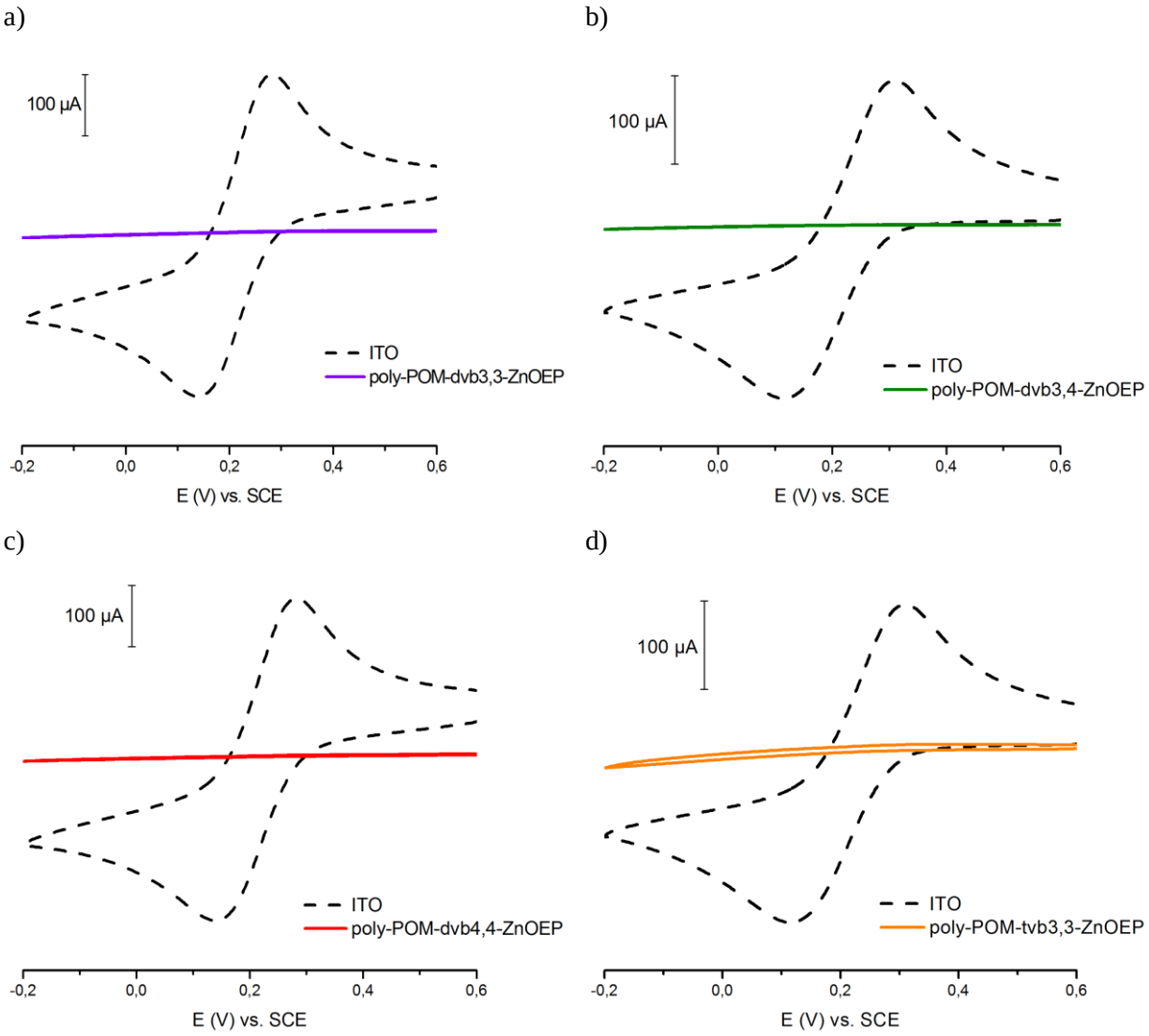


Fig. S3 Cyclic voltammograms of 1 mM of $K_3Fe(CN)_6$, in 0.5 M Na_2SO_4 of modified ITO electrode with a) **poly-POM-dvb3,3-ZnOEP** b) **poly-POM-dvb3,4-ZnOEP , c) poly-POM-dvb4,4-ZnOEP**, d) **poly-POM-tvb3,3-ZnOEP** film (full line) and of noncoated ITO electrode (dotted black line). v=100 mV s^{-1}.

Reduction potentials explanation

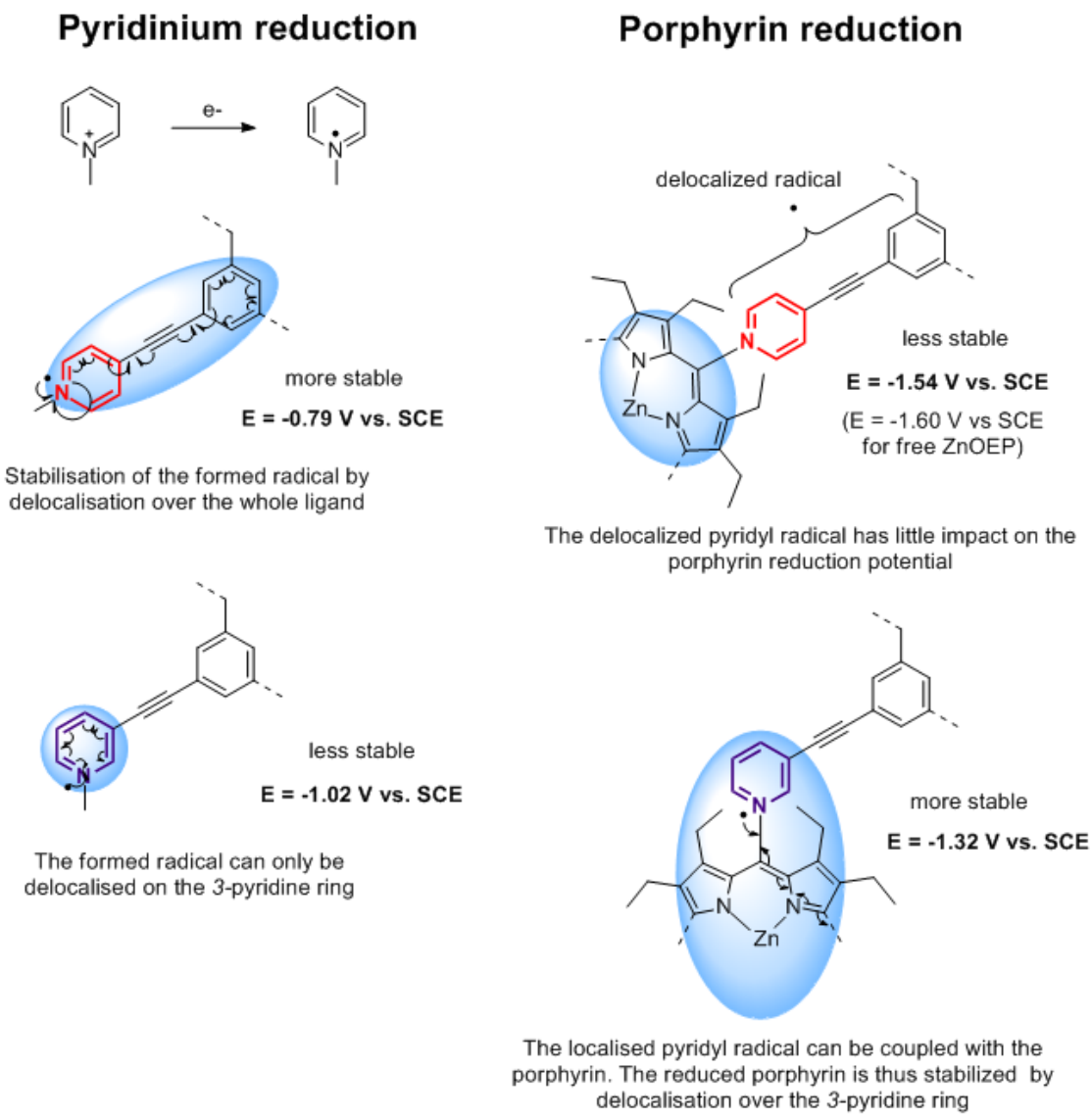


Fig. S4 Tentative explanation of the poly-POM-ZnOEP reduction potential in term of π-conjugation and ligand geometry.

UV-vis spectra of poly-POM-ZnOEP

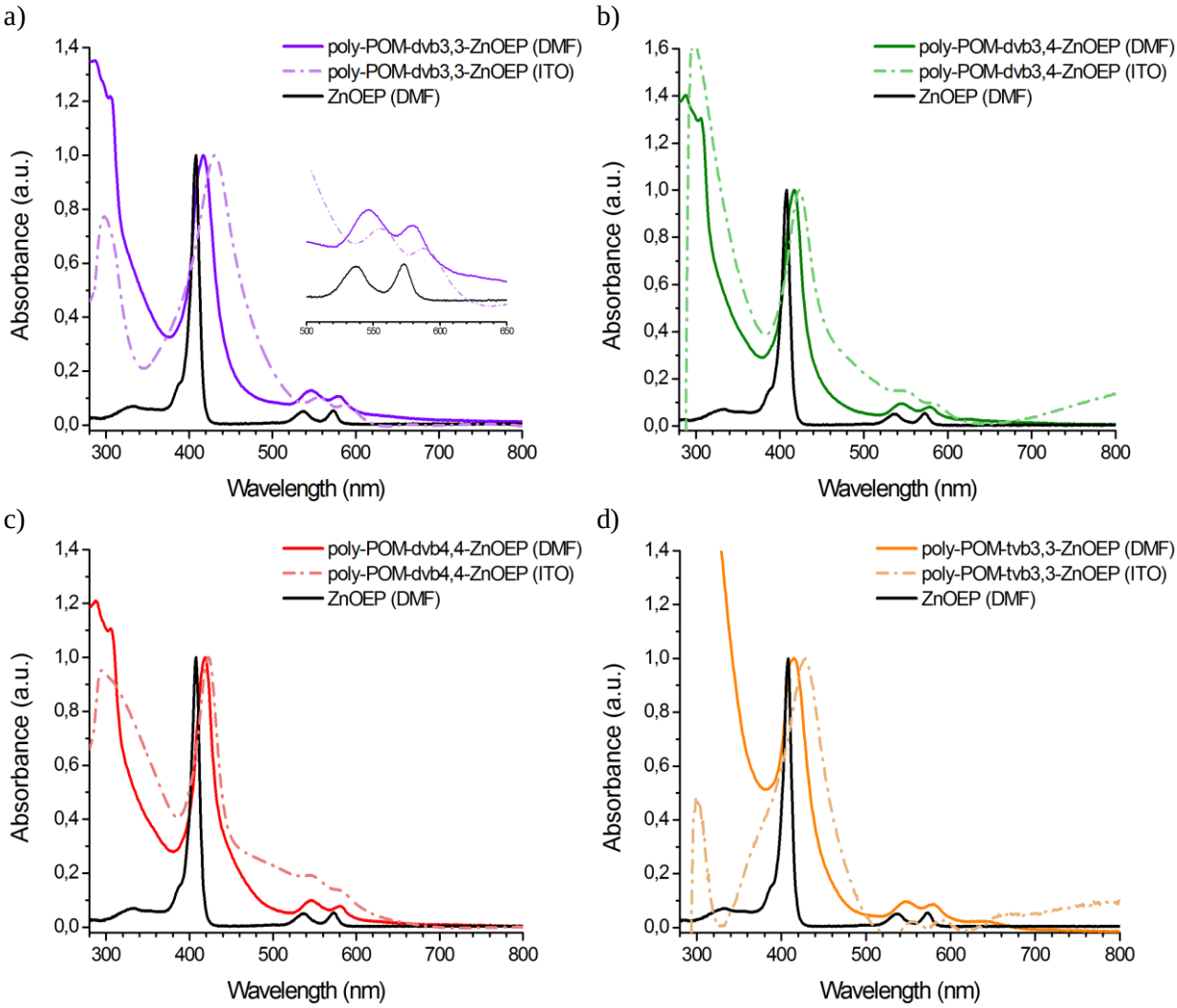


Fig S5 Normalized UV-vis spectra of a) **poly-POM-dvb3,3-ZnOEP**, b) **poly-POM-dvb3,4-ZnOEP**, c) **poly-POM-dvb4,4-ZnOEP**, and d) **poly-POM-tvb3,3-ZnOEP** copolymers deposited on ITO electrode after 25 iterative scans between -0.05 V and 1.90 V *vs.* SCE (plain line), and in DMF solution (dotted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

UV-vis evolution during electropolymerization

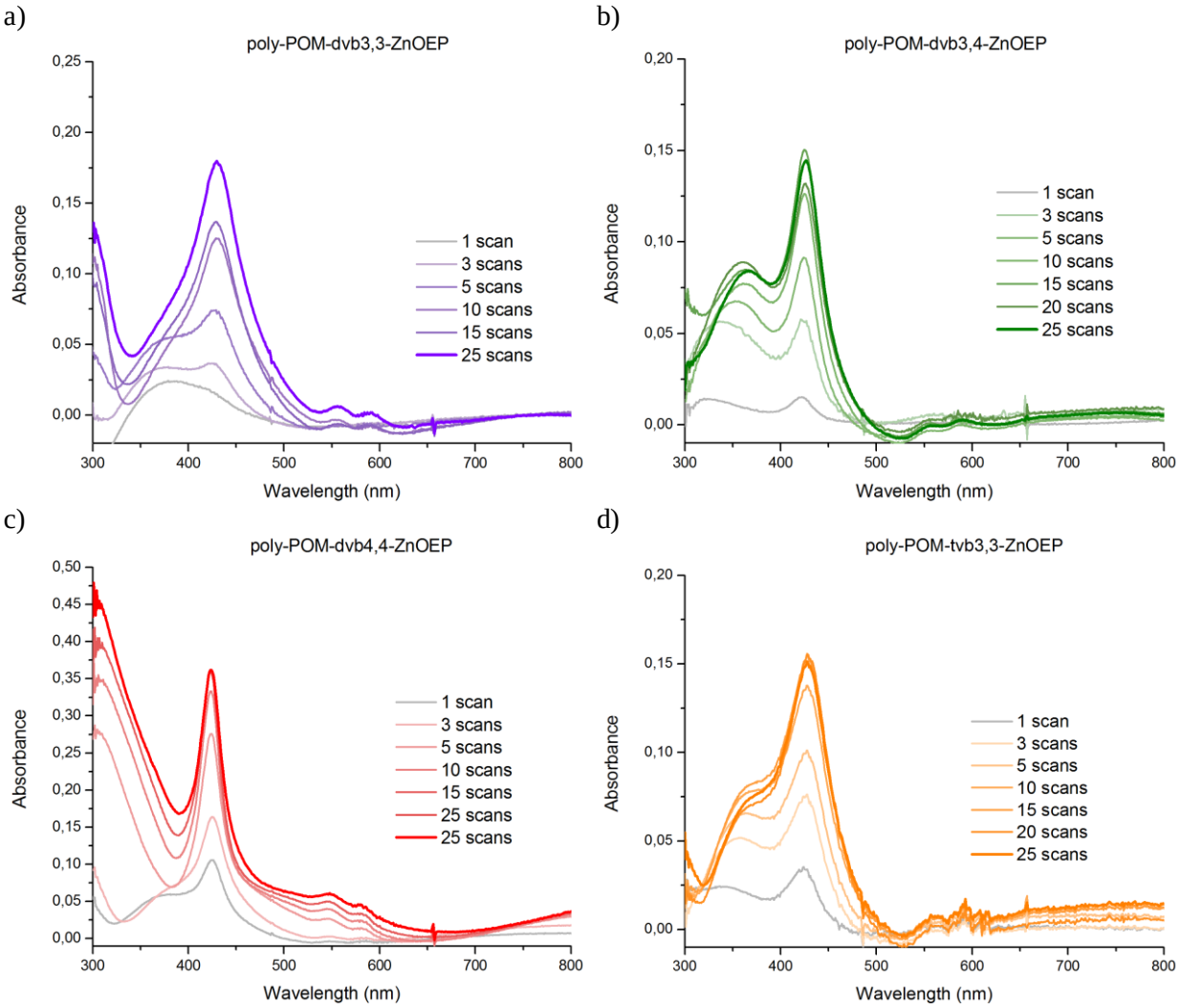


Fig. S6 UV-visible absorption spectra of a) **poly-POM-dvb3,3-ZnOEP** , b) **poly-POM-dvb3,4-ZnOEP**, c) **poly-POM-dvb4,4-ZnOEP** and d) **poly-POM-tvb3,3-ZnOEP** (onto ITO) with different numbers of iterative scans (between -0.05 V and 1.90 V *vs.* SCE). Only one side is recovered by ITO.

XPS

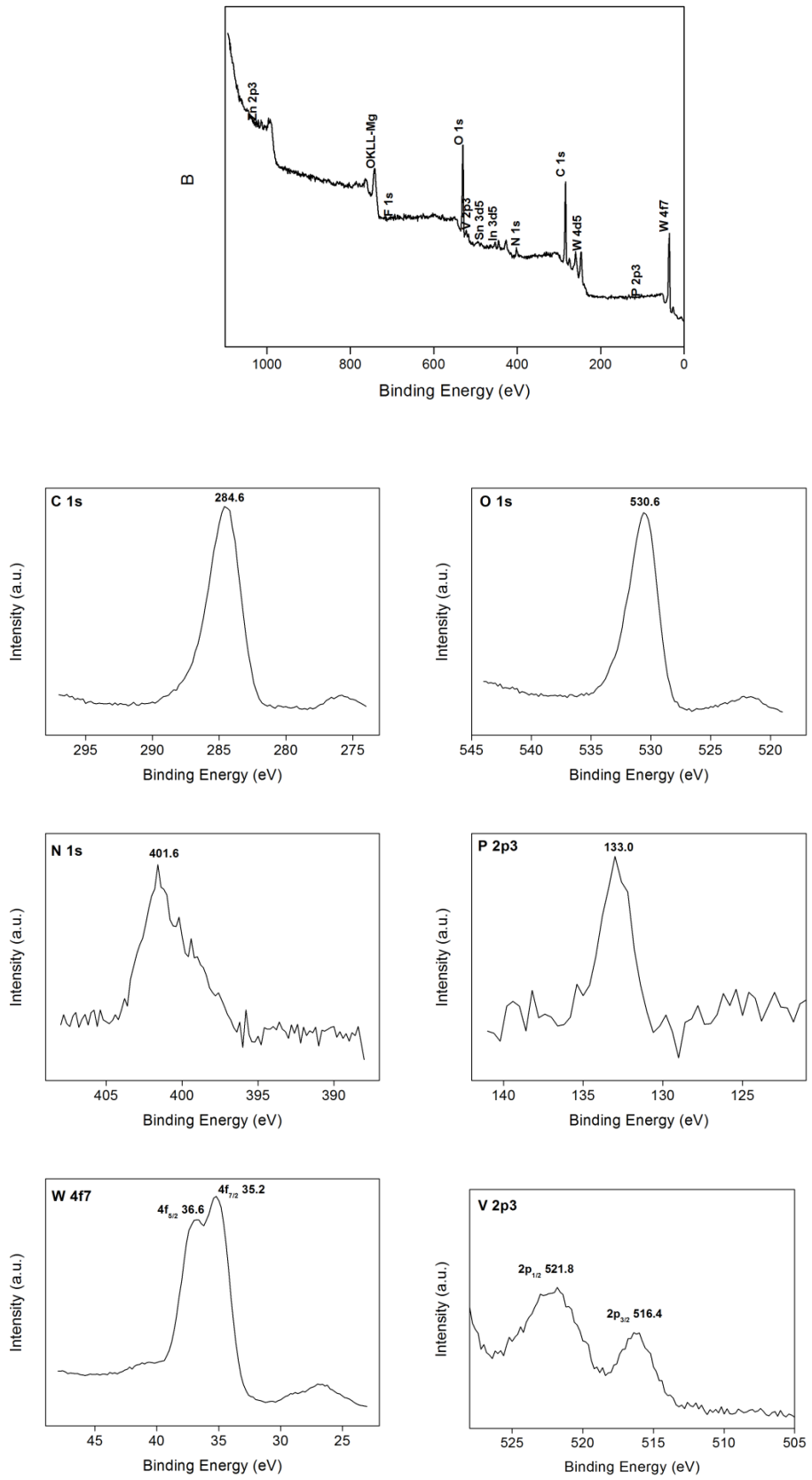


Fig. S7-A XPS spectra of the modified ITO electrodes with **poly-POM-dvb3,4-ZnOEP** obtained after 25 iterative scans between -0.05 V and 1.90 V *vs.* SCE.) Global XPS spectra, and C1s, O1s, N1s, P 2p3, W 4f7, V 2p3 region.

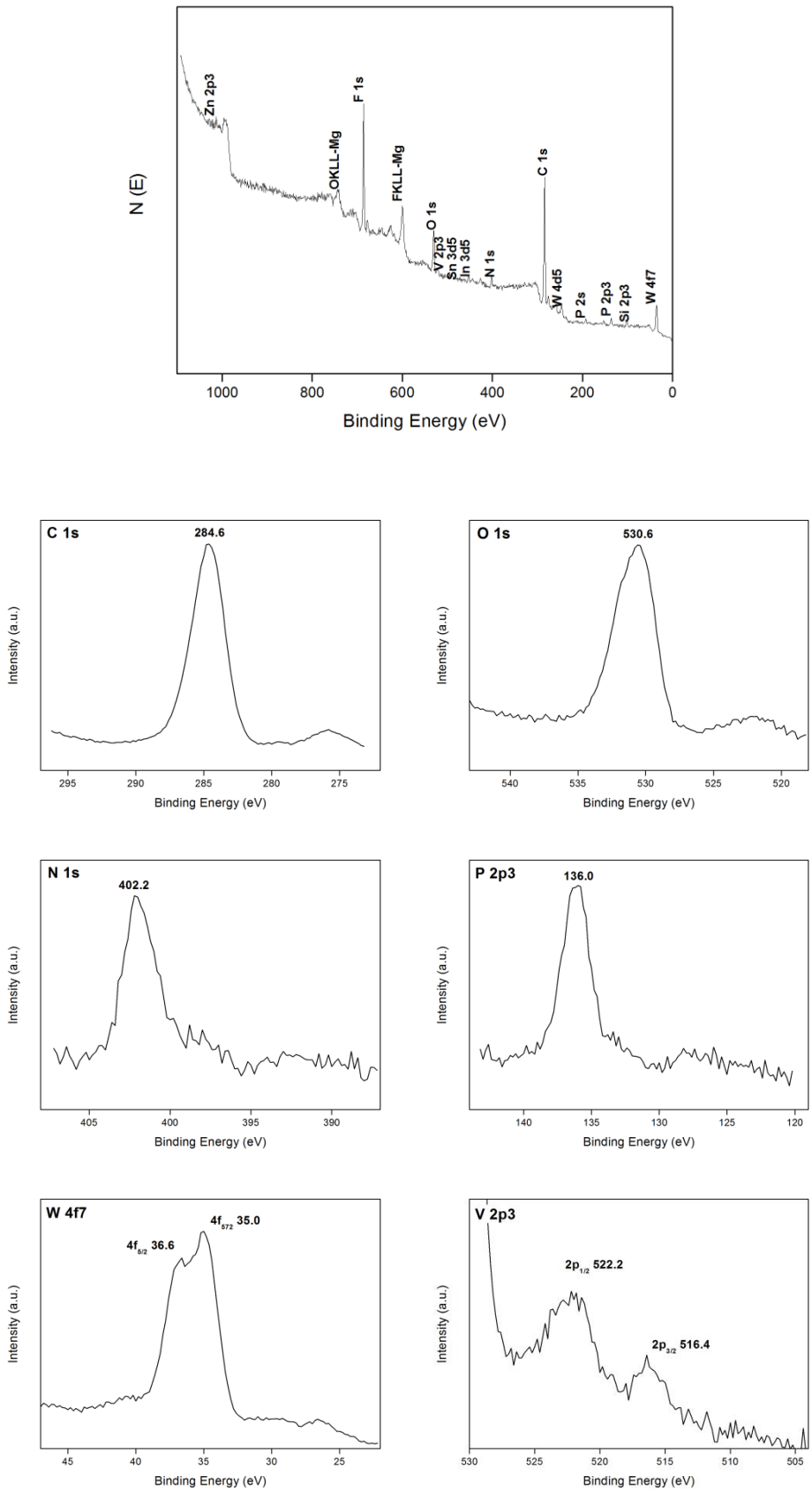
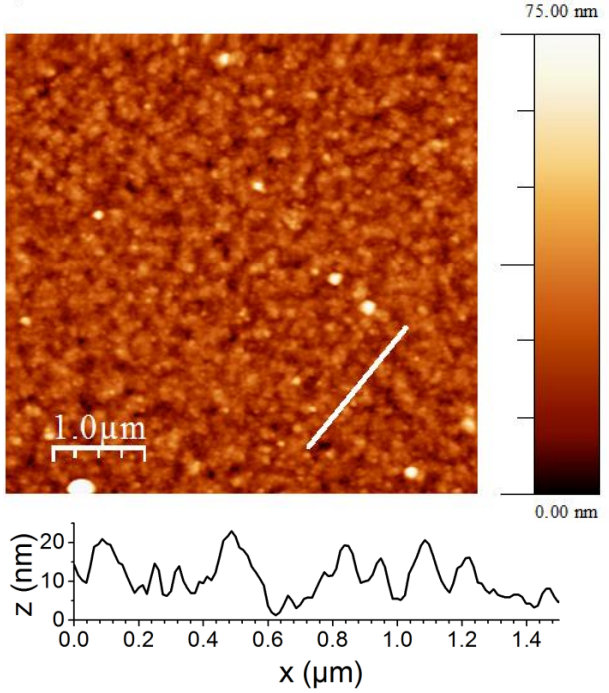


Fig. S7-B XPS spectra of the modified ITO electrodes with **poly-POM-dvb4,4-ZnOEP** obtained after 25 iterative scans between -0.05 V and 1.90 V *vs.* SCE.) Global XPS spectra, and C1s, O1s, N1s, P 2p3, W 4f7, V 2p3 region.

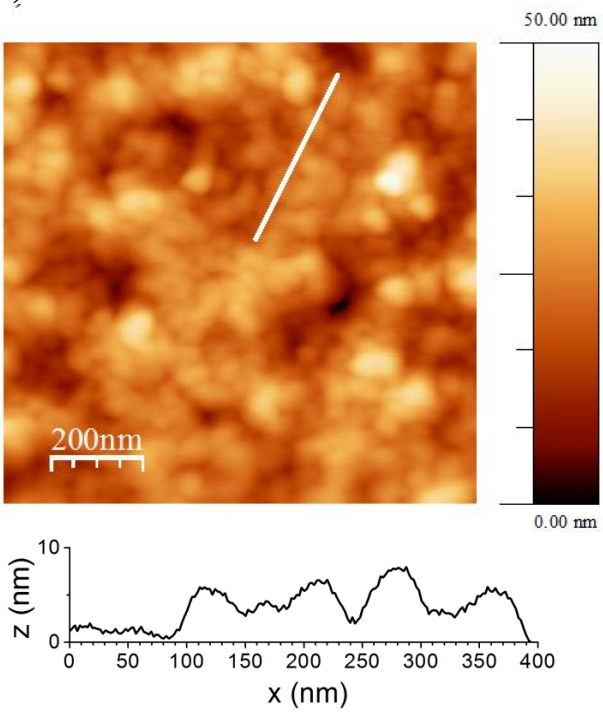
AFM

poly-POM-dvb3,3-ZnOEP

a)

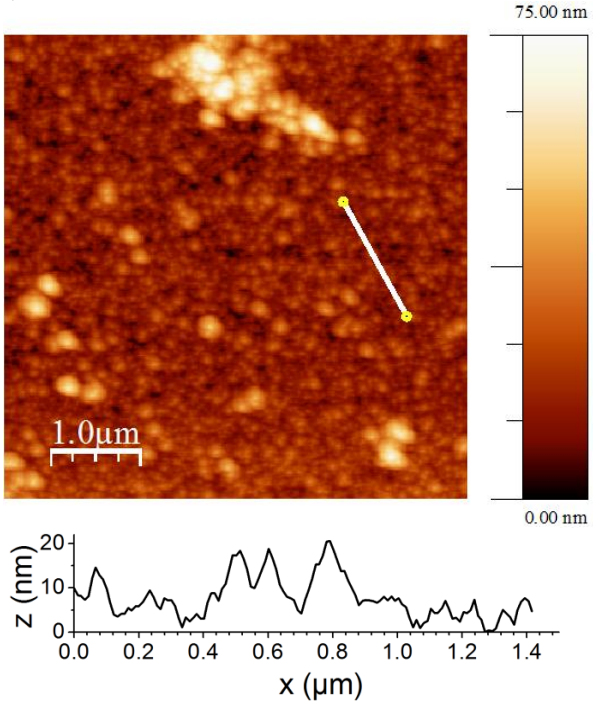


b)

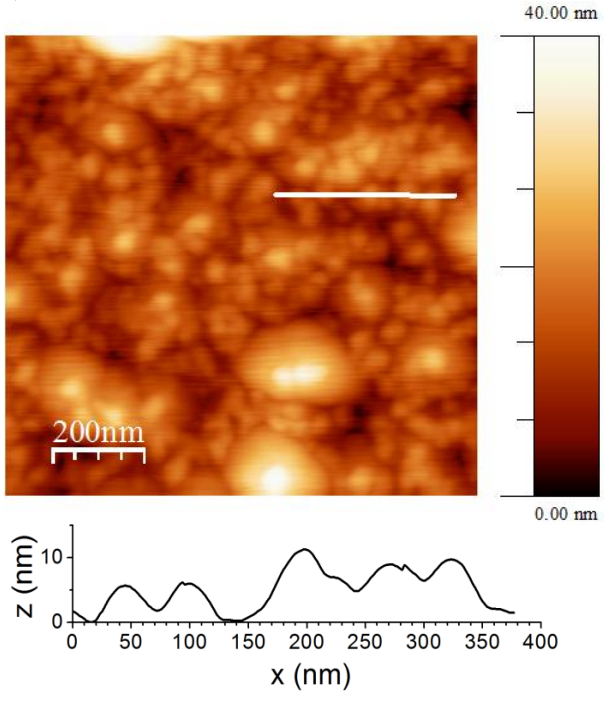


poly-POM-dvb3,4-ZnOEP

c)

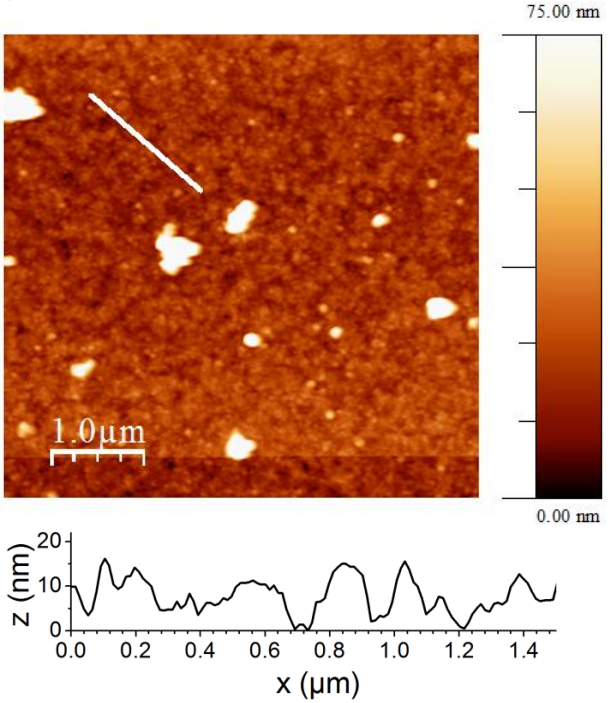


d)

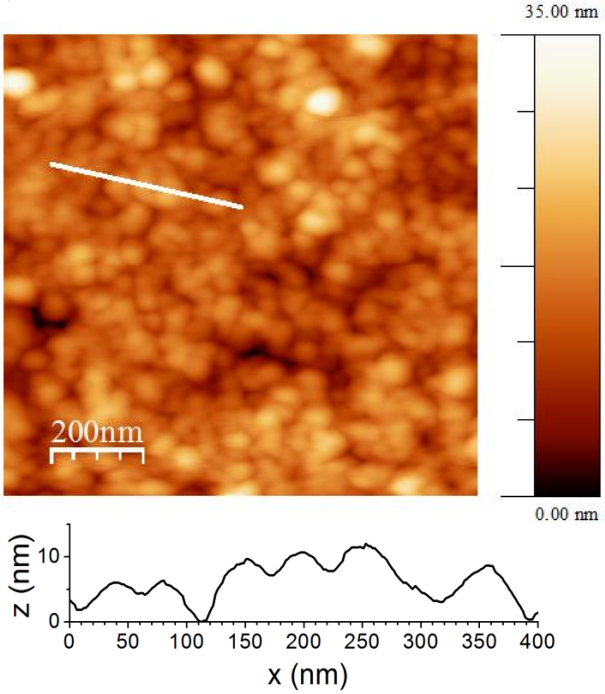


poly-POM-dvb4,4-ZnOEP

e)

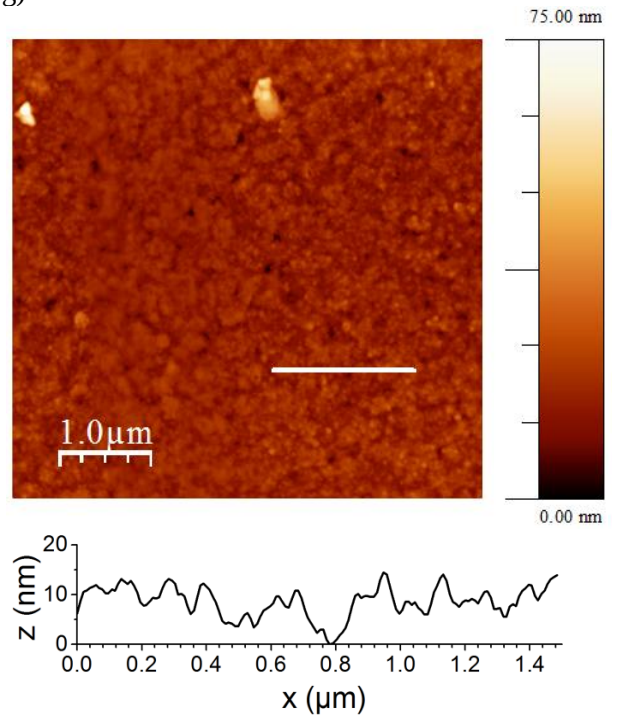


f)



poly-POM-tvb3,3-ZnOEP

g)



h)

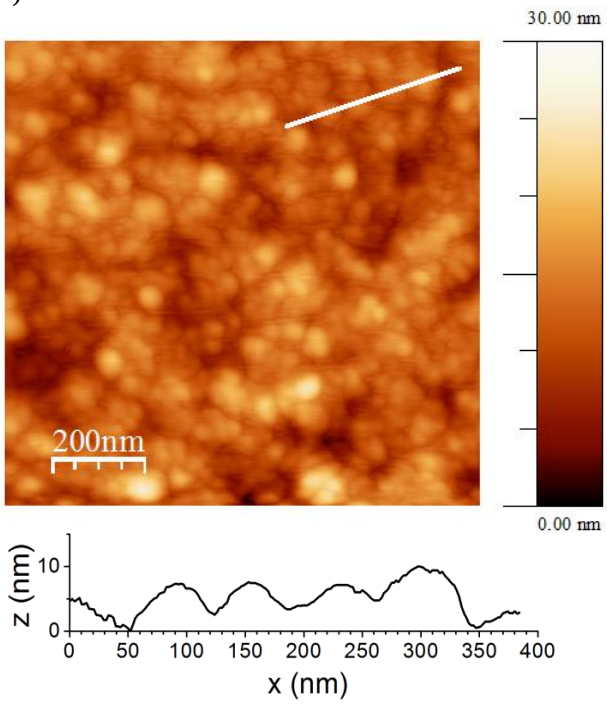


Fig S8 Tapping mode AFM topography of a) and b) **poly-POM-dvb3,3-ZnOEP**, c) and d) **poly-POM-dvb3,4-ZnOEP**, e) and f) **poly-POM-dvb4,4-ZnOEP** , g) and h) **poly-POM-tvb3,3-ZnOEP** copolymer films deposited on ITO electrode after 25 iterative scans between -0.05 V and 1.90 V *vs.* SCE. Section analyses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