

Supporting Information

New porphyrin–polyoxometalate hybrid materials: Synthesis, characterization and investigation of catalytic activity in the acetylation reactions

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Experimental Details

Instruments. The ^1H NMR spectra were recorded on a Bruker-Avance AQS 400 (MHz) NMR spectrometer using DMSO as solvent and TMS as internal standard. Elemental analyses were measured by a Perkin Elmer 2400 instrument. The amount of Mo was measured by a Leaman inductively coupled plasma (ICP) spectrometer. Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. The electronic spectra of the compounds in the UV–Vis region were recorded in DMF solution using a Shimadzu 160 UV–Vis or a Varian Cary NIR spectrophotometer. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Nicolet-Impact 400D instrument. Gas chromatography experiments (GC) were performed on a Shimadzu GC 16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20m. Redox potentials of the compounds (10^{-3} mol/L) in dried DMF containing 0.1 mol/L tetrabutylammonium bromide (TBAB) as a supporting electrolyte were determined at room temperature by cyclic voltammetry with a PGSTAT30 (Eco Chemie, Utrecht, The Netherlands) electrochemical analyzer. A three-electrode cell was used, including glassy carbon electrode as working electrode, together with an Ag/AgCl (saturated KCl) and a platinum wire as reference and counter electrode, respectively. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.

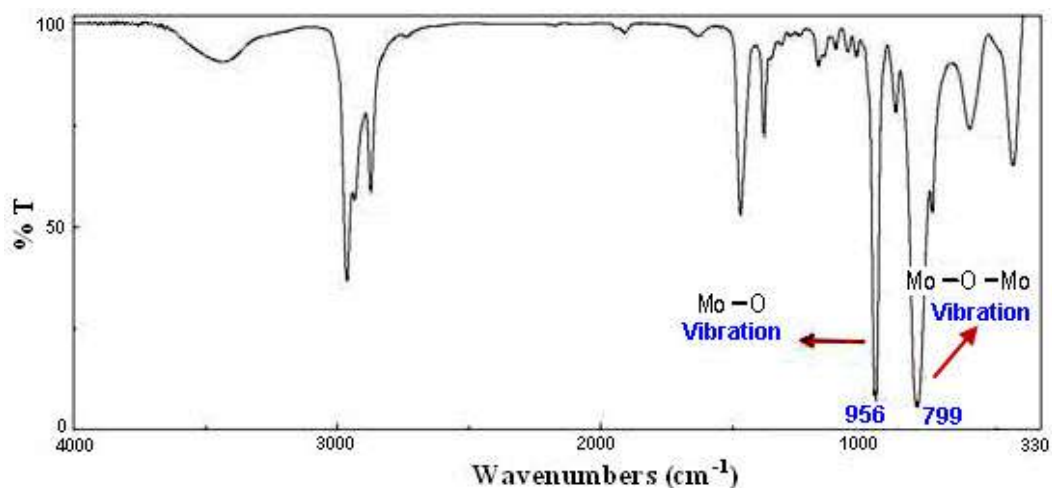
Materials. All chemicals were used as received from the suppliers. Solvents were used as received or distilled and dried using the standard procedures. Tetrabutylammonium hexamolybdate, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ was prepared according to the literature method. (N. H. Hur, W. G. Klemperer, R. C. Wang, *Inorg. Syn.* 27, 77.) 5,10,15,20-*Tetrakis*(4-nitrophenyl)porphyrin, 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrin (**1**), 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatozinc(II) (**2**) and 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatotin(IV) chloride (**3**) were prepared according to known procedures. (A. Bettelheim, B. A. White, S. A. Raybuck, R. W. Murray, *Inorg. Chem.* **1987**, 26, 1009-1017.) All the synthetic procedures were performed protected from light.

Synthesis of hybrid compound (1a).

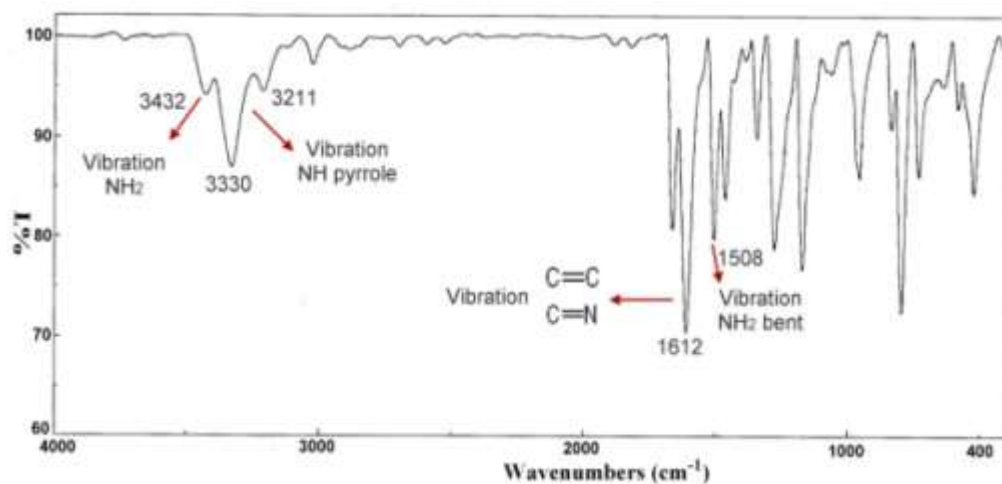
The 0.1 g (0.14 mmol) dry **1**, 0.81 g (0.59 mmol, 4.2 eq) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ and 0.17 g (0.84 mmol, 6 eq) *N,N'*-dicyclohexylcarbodiimide (DCC) were dissolved in 10 mL anhydrous DMSO and heated to 100 °C under a dry atmosphere. The reaction was cooled to room temperature and filtered under vacuum (to remove the dicyclohexylcarbodiurea) into a flask containing 100 mL dry ether and 20 mL dry methanol. A precipitate was formed and washed several times with acetone and ether. The dried product (0.63 g, 73% yield) was stored in a desiccator. IR (cm^{-1}): 433 (m), 599 (m), 781 (s), 944 (s), 975 (sh), 1030 (m), 1180 (m), 1381 (m), 1459 (s), 1608 (s), 1664 (s), 2873 (s), 2963 (s). ^1H NMR at 400 MHz (DMSO- d_6): δ = 0.94 [t (J = 7.2 Hz), 96H, ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$)], 1.31 [q (J = 7.2 Hz), 64H, ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$)], 1.57 [m, 64H, ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$)], 3.17 [t (J = 8.4 Hz), 64H, ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$)], 7.67 [d (J = 8.4 Hz), 8H, protons 2,6-AminoPh], 8.14 [d (J = 8.4 Hz), 8H, protons 3,5-AminoPh], 8.93 [s, 8H, protons β -pyrrole]. UV- Vis spectra (in DMF): (λ_{max} = 377 nm). Anal. Calcd for $\text{C}_{172}\text{H}_{312}\text{N}_{16}\text{O}_{72}\text{Mo}_{24}\text{Zn}$: C, 33.73; H, 5.13; N, 3.66; Mo%, 37.60. Found: C, 33.85; H, 5.04; N, 3.50. Mo%, 37.41.

Synthesis of hybrid compound (2a). A 0.1 g (0.12 mmol) dry **2**, 0.69 g (0.50 mmol, 4.2 eq) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ and 0.15 g (0.72 mmol, 6 eq) *N,N'*-dicyclohexylcarbodiimide (DCC) were dissolved in 10 mL anhydrous DMSO and heated to 100 °C under a dry atmosphere. The reaction was cooled to room temperature and filtered under vacuum (to remove the dicyclohexylcarbodiurea) into a flask containing 100 mL dry ether and 20 mL dry methanol. A precipitate was formed and washed several times with acetone and ether. The dried product (0.52 g, 70% yield) was stored in a desiccator. IR (cm^{-1}): 432 (m), 599 (w), 739 (sh), 780 (s), 943 (s), 975 (sh), 1034 (w), 1181 (m), 1381 (m), 1469 (s), 1604 (s), 1624 (s), 2872 (s) 2963 (s). Anal. Calcd for $\text{C}_{172}\text{H}_{312}\text{N}_{16}\text{O}_{72}\text{Mo}_{24}\text{SnCl}_2$: C, 33.06; H, 5.03; N, 3.59; Mo%, 36.85. Found: C, 33.15; H, 4.92; N, 3.48. Mo%, 36.67.

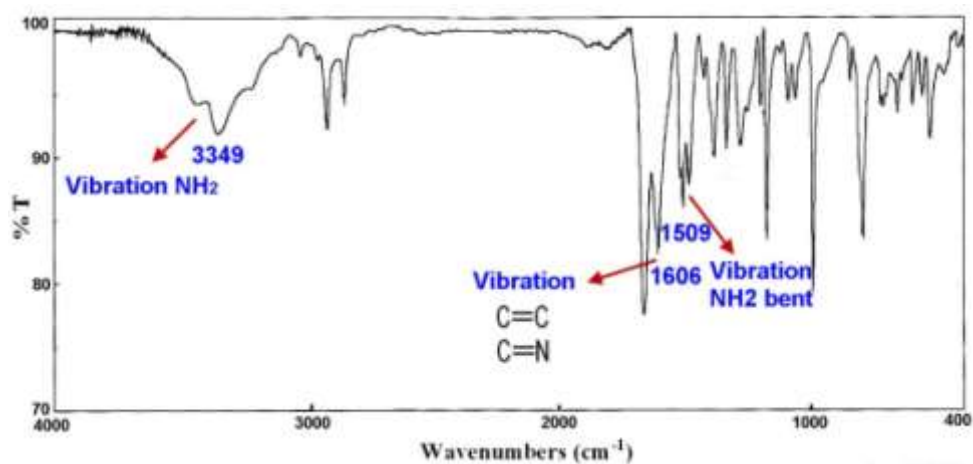
Fig S1. FT IR spectra of: (A) Tetrabutylammonium hexamolybdate, $[(C_4H_9)_4N]_2[Mo_6O_{19}]$; (B) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrin; (C) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatozinc(II) (**1**); (D) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatotin(IV) chloride (**2**); (E) hybrid compound (**2a**); (F) hybrid compound (**2a**); (G) Recovered hybrid compound (**2a**) after nine consecutive runs.



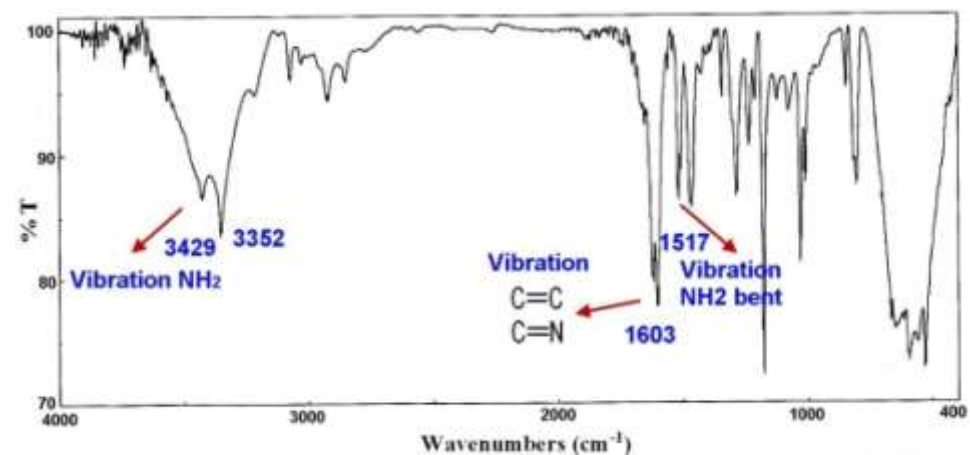
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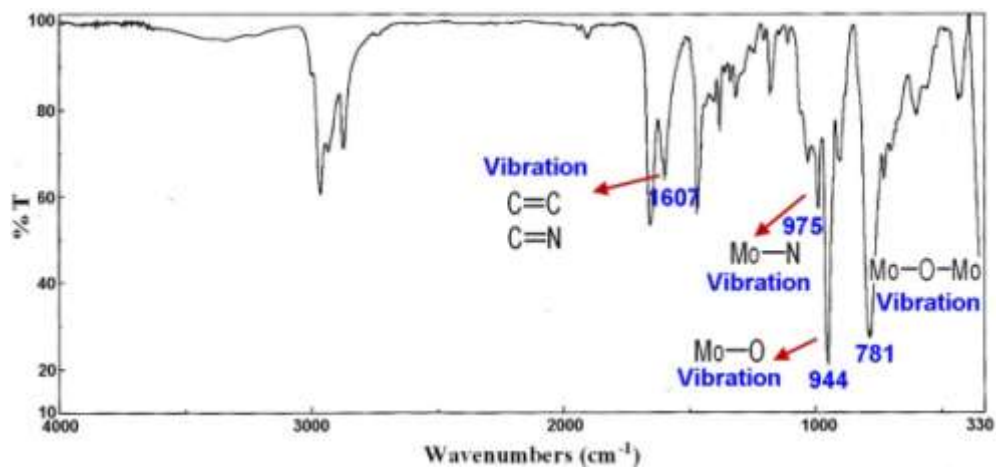
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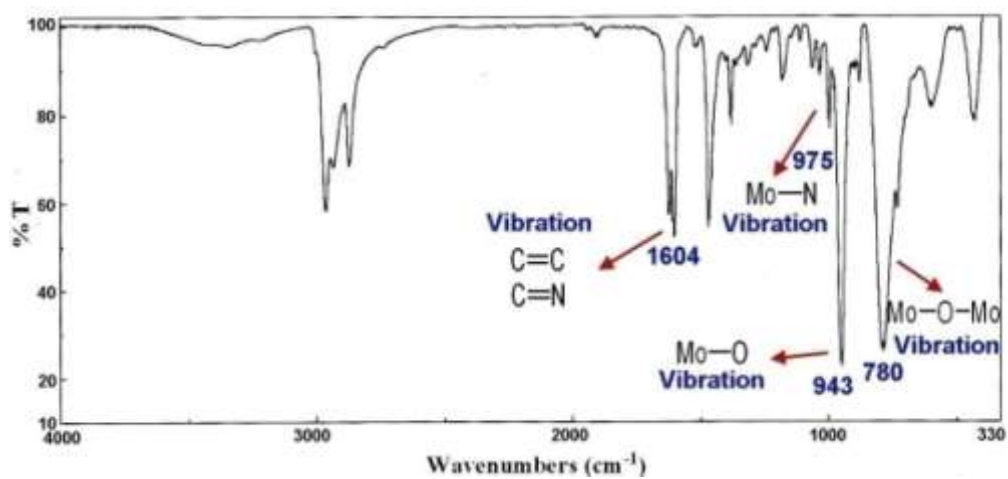
(C)



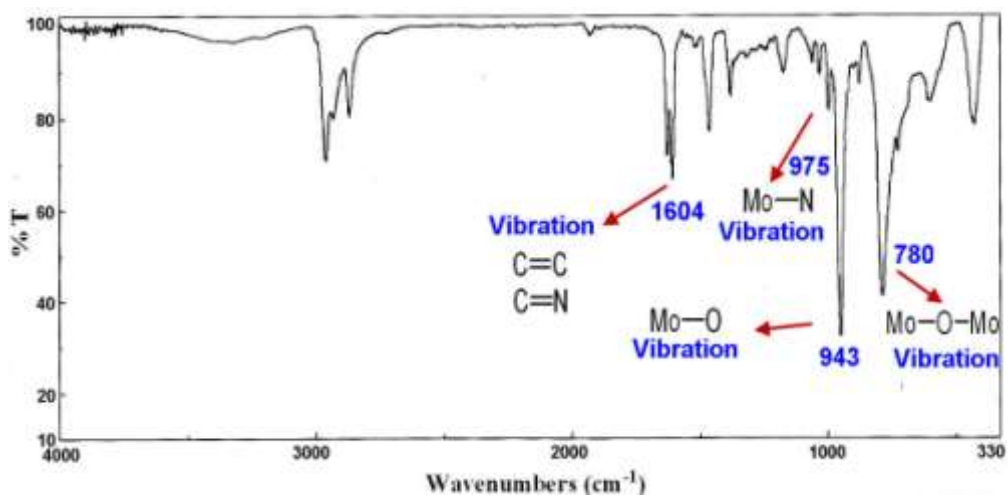
(D)



(E)

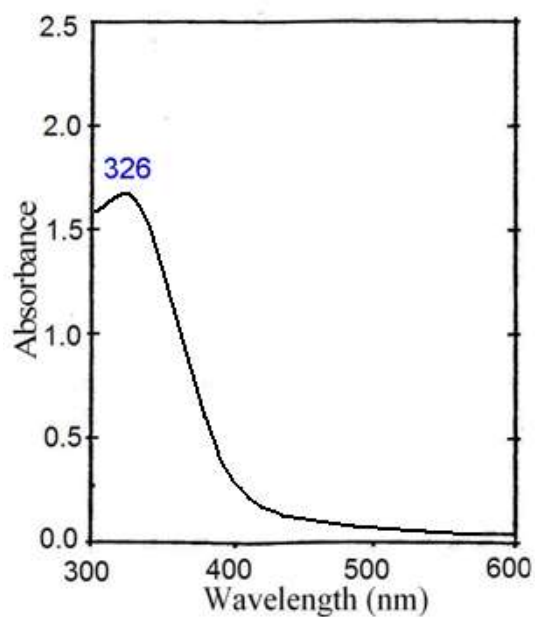


(F)

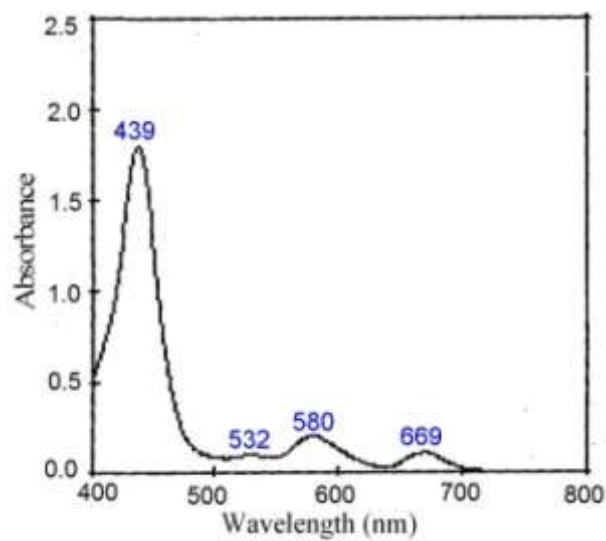


(G)

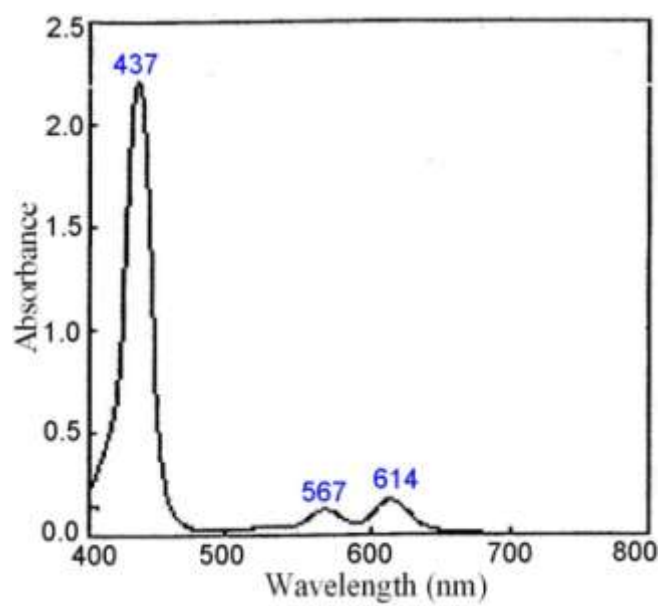
Fig S2. UV-Vis spectra of : (A) Tetrabutylammonium hexamolybdate, $[(C_4H_9)_4N]_2[Mo_6O_{19}]$; (B) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrin; (C) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatozinc(II) (**1**); (D) hybrid compound (**1a**)



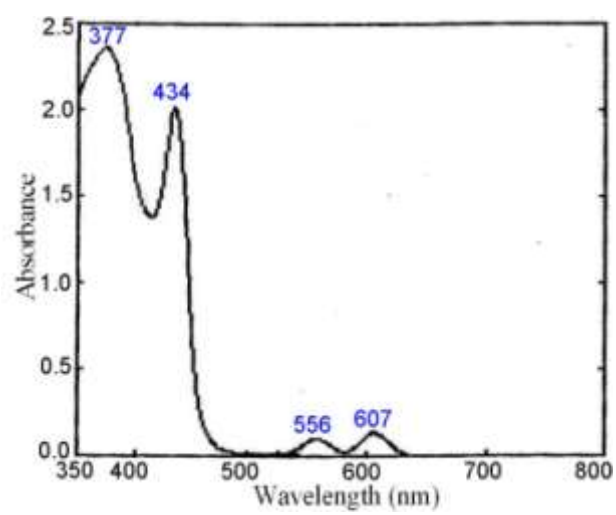
(A)



(B)

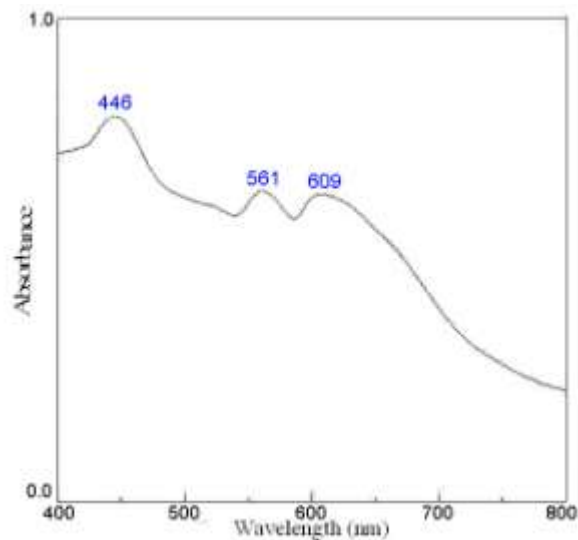


(C)

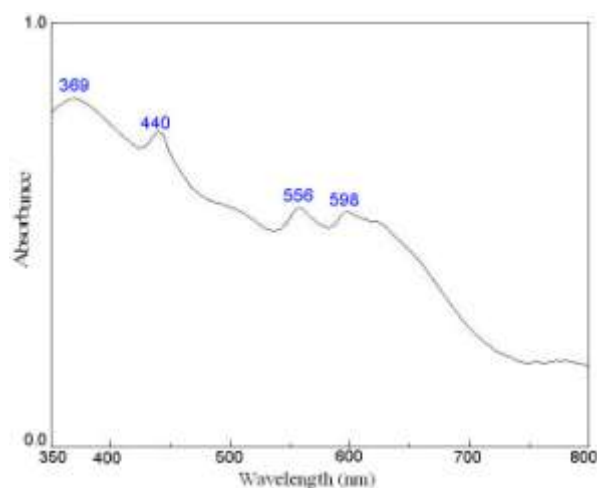


(D)

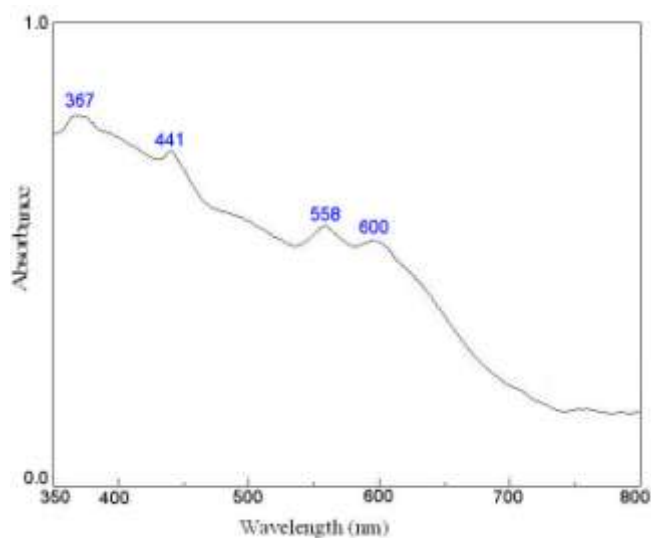
Figure S3. The Diffuse Reflectance UV-Vis Spectrum of: (A) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatotitan(IV) (**2**), (B) hybrid compound (**2a**); (C) Recovered hybrid compound (**2a**) after nine consecutive runs



(A)

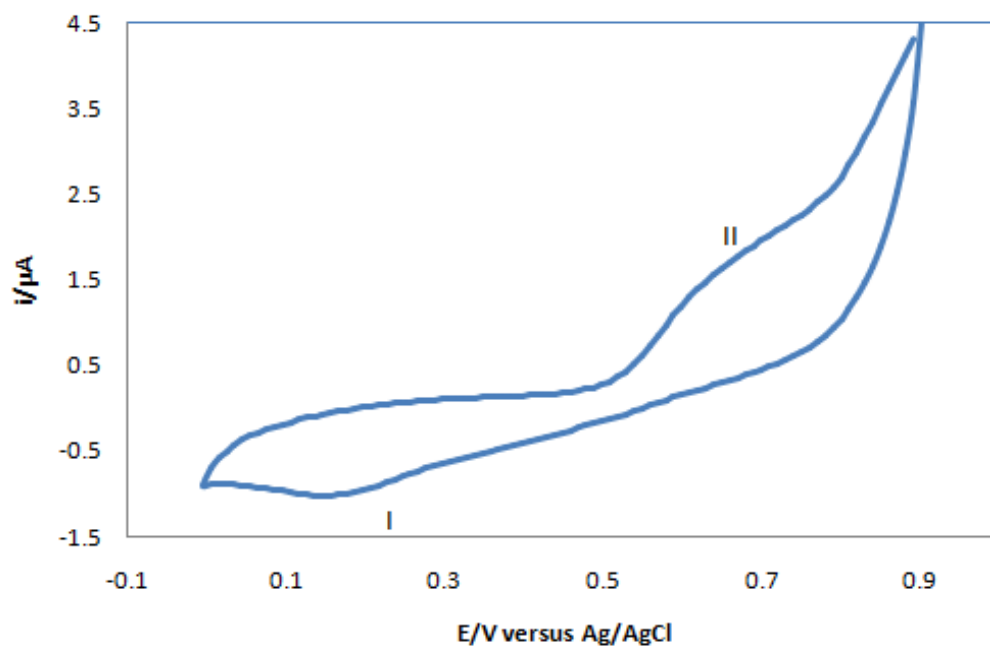
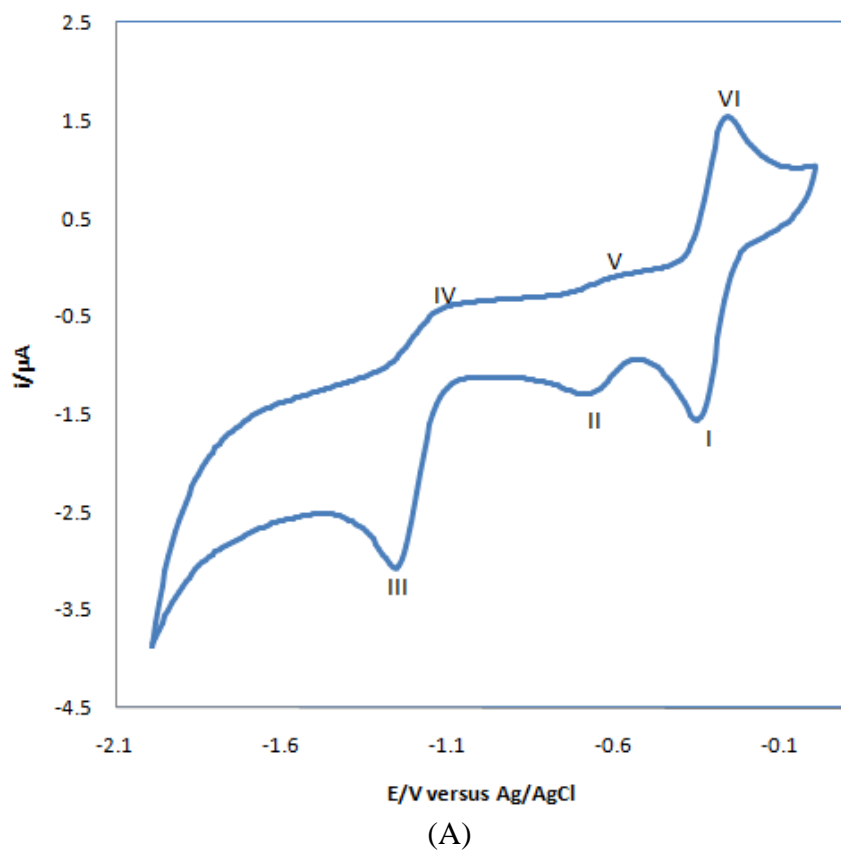


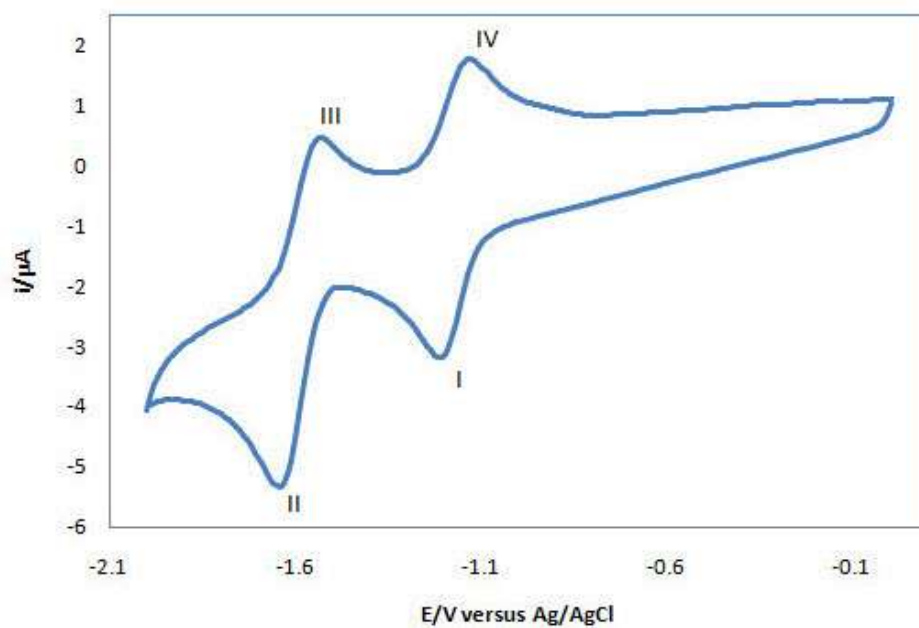
(B)



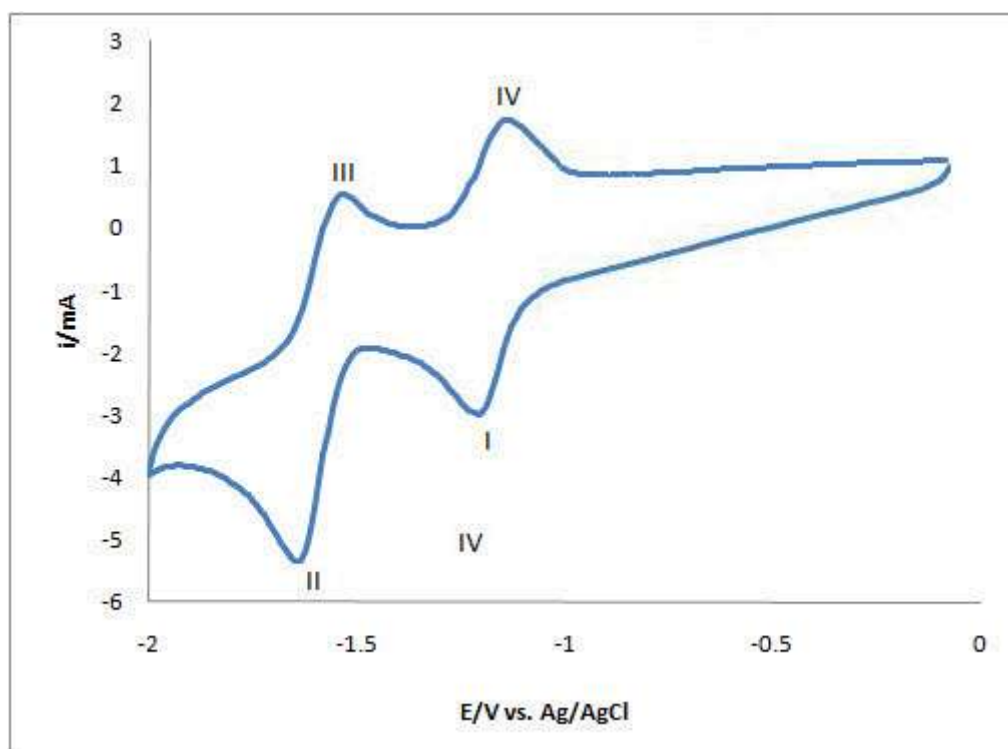
(C)

Fig S4. Cyclic voltammetry of: (A) Tetrabutylammonium hexamolybdate, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$; (B) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrin; (C) 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrinatozinc(II) (**1**); (D) hybrid compound (**1a**).

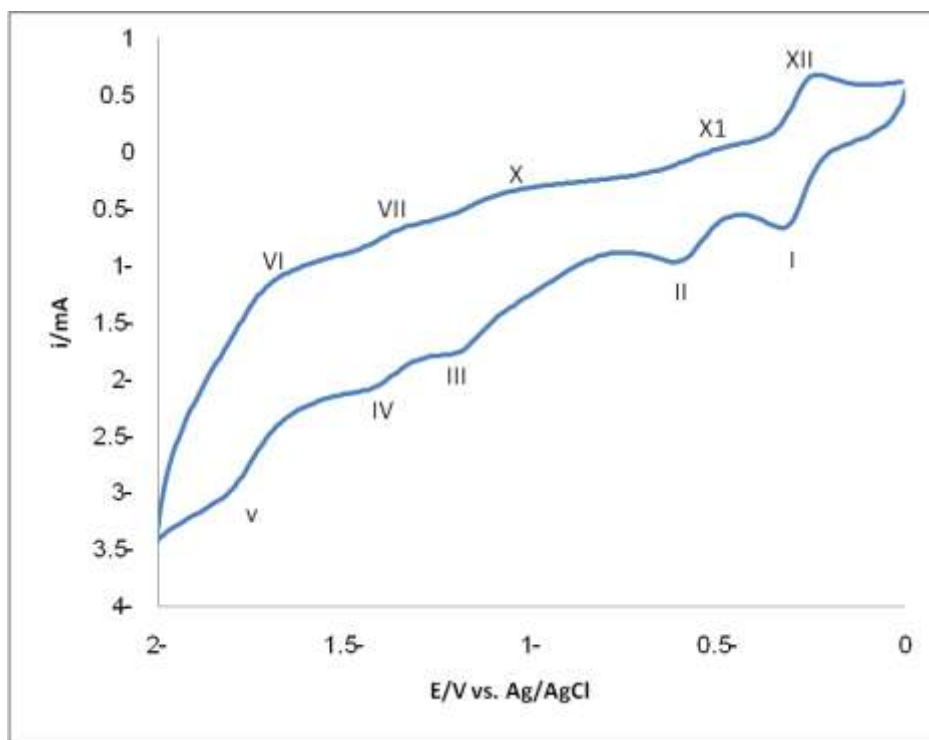




(B)



(C)



(E)