

Molecular photovoltaic system based on Dawson type polyoxometalate and porphyrin formed by layer-by-layer self assembly†

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1. Experimental

Materials. Most common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Water was obtained by passing through a Milli-RO₄ unit and subsequently through a Millipore Q water purification set.

The Dawson-type POM K₇[α_2 -Fe^{III}P₂W₁₇O₆₁] were prepared in acidic medium as described previously.¹ H₂TPhN(Me)₃P⁴⁺4TsO⁻ was purchased from Sigma Aldrich.

Poly(-ethylenimine) (PEI; MW = 50,000), poly(styrenesulfonate) (PSS; MW = 70,000) and poly(allylamine hydrochloride) (PAH; MW = 70,000) were purchased from Aldrich and were used without further treatment.

Electrochemistry. Voltammetric data were obtained with a standard three-electrode system using a PARSTAT 2273 potentiostat. A one side indium-tin-oxide (ITO, Aldrich, 8-12 Ω /square) electrode with a surface of about 1 cm² was used to record the electrochemical behavior of the deposited films. A platinum wire was used as an auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). It was electrically connected to the solution by a junction bridge filled with the electrolyte.

UV-visible Spectroscopic Measurements. UV-visible absorption spectra were recorded either with a single beam Hewlett-Packard HP 8453 diode array spectrophotometer operated at a resolution of 2 nm or with a double beam Perkin-Elmer Lambda 9 spectrophotometer operated at a resolution of 1 nm.

Fluorescence Measurements. Fluorescence emission spectra were obtained with a Spex fluorolog 1681 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier cooled to -20 °C.

Atomic Force Microscopy (AFM). 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). XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with MgKR radiation ($h\nu=1253.6$ 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

¹ S. Vanhaecht, G. Absillis, T .N. Parac-Vogt, *Dalton Trans.* 2012, 10028-10034.

B) A. P. Ginsberg, *Inorg. Synth.*, Wiley-Interscience, 1990. c) D. K. Lyon, W .K. Miller, T. Novet, P. J. Domaille, E. Evitt, D. C. Johnson, R. G. Finke, *J. Am. Chem. Soc.* 1991, **113**, 7209-7221.

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).

Fabrication of Films. Films were prepared at room temperature by soaking the solid substrate (quartz or ITO) in a 0.5 mM aqueous solution of porphyrin for 1 min, followed by dipping the substrate in unbuffered Millipore Q water to remove the excess (nonbound porphyrin solution) from the substrate. After drying, POMs were added by soaking the substrate for 1 min in a 0.5 mM aqueous solution of POMs and rinsed by dipping in Millipore Q water. The procedure was repeated until the desired number of deposition cycles was carried out.

Films can also be prepared using smaller (or even higher) concentration of aqueous solution of porphyrin and POM. The use of more diluted solution need to soak the substrate for a longer time. If the POM and porphyrins are at different concentrations, the film growing is still efficient.

In addition, the mother solutions concentrations have no effects on the photocurrent generation of the films.

Preparation of PEI/PSS/PAH/[α_2 -Fe^{III}P₂W₁₇O₆₁⁷⁻] self-assembly film.

The substrates (quartz and ITO) were cleaned by immersion in the “piranha solution” containing three parts H₂O₂ (30% aqueous solution) and seven parts oil of vitriol (H₂SO₄) at 80 °C for 40 min and rinsed with copious deionized water. Then, the substrate was immersed in a solution of NH₄OH (29% aqueous solution), H₂O₂ (30% aqueous solution) and pure water with a volume ratio 1:1:5 at 70 °C for 20 min, followed by extensively washing with water.

The cleaned substrates (quartz and ITO) were immersed in 10⁻² M Poly(-ethylenimine) (PEI) solution (based on the molecular weight of the monomer unit, pH = 9.0) for 20 min, 10⁻² M poly(styrenesulfonate) (PSS) solution for 20 min and 10⁻² M poly(allylamine hydrochloride) (PAH) solution (pH = 4.0, containing 1 M NaCl) for 20 min, and then one immersion in POM (10⁻³ M, pH = 4–5) solution. Water rinsing and N₂ drying steps were performed after each adsorption cycle. This procedure resulted in the buildup of film containing the [α_2 -Fe^{III}P₂W₁₇O₆₁⁷⁻].

2. Study of the complex $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2$ in aqueous solution

Previously to the study of the films presented in this work, we have studied the interactions between these same entities, POM and porphyrin, in aqueous solution. Thus, the formation of an electrostatic complex between this Dawson-type POM and a tetracationic porphyrin has been evidenced by a titration of a diluted aqueous solution of porphyrin by a more concentrated aqueous solution of POM. This titration was followed by UV-vis absorption and luminescence spectroscopies (Fig S1 and S2, respectively).

During titration, absorption bands of the porphyrin are decreased and red-shifted, and the luminescence of the porphyrin is quenched totally.

In order to determine the stoichiometry of the complex formed and to estimate its global association constant, we have used a variant of the well-known Job's method, applied to the absorption spectra. For a given wavelength λ , the difference $\Delta \epsilon(\lambda)$ between the measured absorption and the expected absorption in the case of absence of complexation is calculated according to the relation:

$$\Delta \epsilon(\lambda) = \frac{A}{l C_t} - (1 - X_{\text{POM}}) \epsilon_{\text{porph}}(\lambda) - X_{\text{POM}} \epsilon_{\text{POM}}(\lambda)$$

where A is the measured absorbance, λ is the optical length, C_t corresponds to the total concentration of compounds in solution ($C_t = \text{sum of the concentrations of porphyrin and POM}$), $\epsilon_{\text{porph}}(\lambda)$ and $\epsilon_{\text{POM}}(\lambda)$ are the molar extinction coefficients of the porphyrin and the POM, respectively, at the chosen wavelength λ and X_{POM} is the mole fraction of the POM. $\Delta \epsilon(\lambda)$ is plotted as a function of X_{POM} at the chosen wavelength. For each titration, the curve of $\Delta \epsilon$ shows two parts which can be fitted with straight lines, the line intersection occurring at the stoichiometry of the complex.

Global association constant β of this complex can be estimated from relation:

$$\beta = \frac{\frac{1}{N+1} - \frac{\overline{\text{EI}}}{P}}{N^N \cdot C_t^{\text{eq}N} \cdot \left(\frac{\overline{\text{EI}}}{P} \right)^{N+1}}$$

where $\overline{\text{EI}}$ is the distance between the intersection point I of the two straight lines of the Job's function and the experimental point E of $\Delta \epsilon$ at the complex stoichiometry, P is the slope of the Job's function before the stoichiometry, C_t^{eq} is the total concentration of porphyrin and POM at the stoichiometry, and N is the number of porphyrins in one complex.

Result obtained shows the formation of the complex $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2$ with association constant estimated to be ca. 10^{17}M^{-2} (stoichiometry 1/2, one POM for 2 porphyrin units).

Note that the titration has been conducted at natural pH (near pH = 6.5). Consequently, H^+ or OH^- cannot be considered, at least conceivable, cations and anions leading to non 1/2 complex.

If the solution is concentrated, the complex $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2$ precipitate with the time and can be collected. Elemental analysis of the powder obtained

from solution show the presence of one additional TsO^- for the 1:2 stoichiometry of POM/porphyrin complex in solution state. The additional tosylate anion render the system neutral as expected.

Anal. Calcd for $[\text{TsO}^-]_1[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2 \cdot 15\text{H}_2\text{O}$, $\text{C}_{119}\text{Fe}_2\text{H}_{161}\text{O}_{140}\text{P}_4\text{SW}_{34}$: Fe, 1.06; P, 1.17; W, 59.11; C, 13.52; N, 2.12; H_2O , 2.56. Found: Fe, 1.02; P, 1.16; W, 59.02; C, 13.49; N, 2.10; H_2O , 2.50.

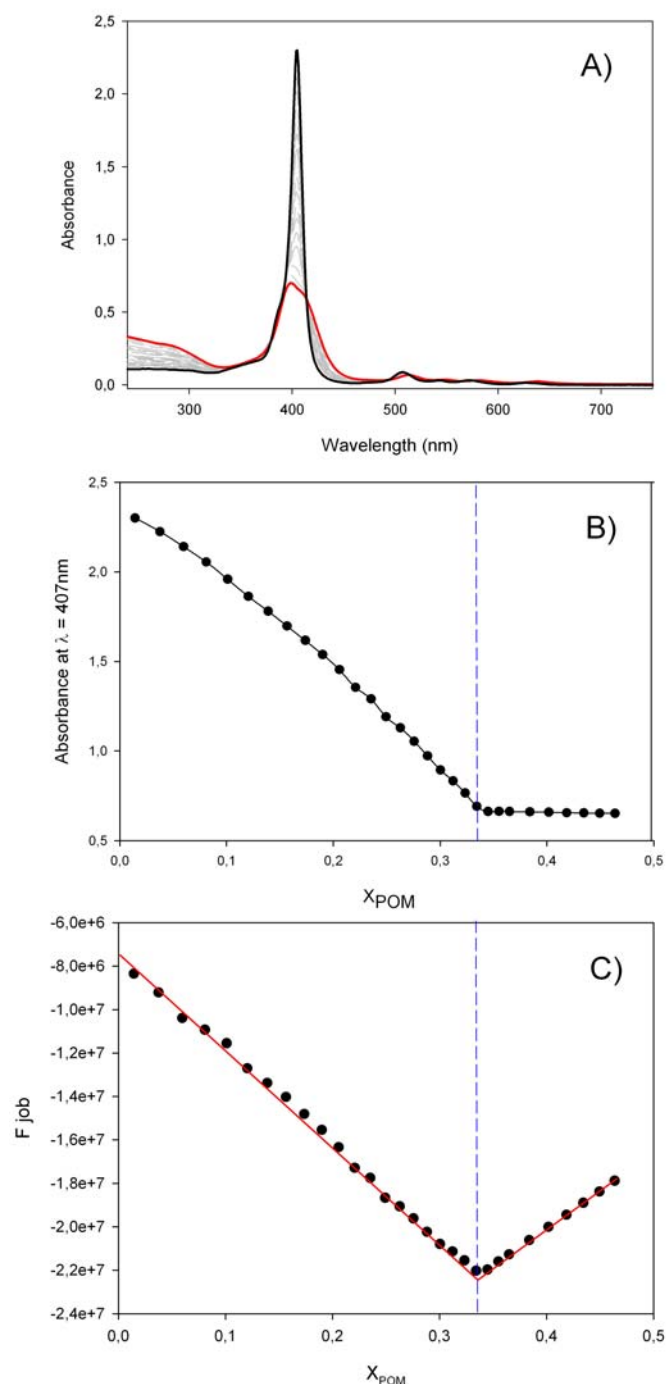


Figure S1. A) UV-visible absorption measurement. B) Absorbance at $\lambda = 407 \text{ nm}$ versus X_{POM} and C) Job's plot during titration corresponding to the formation of the electrostatic complex $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2$ in aqueous solution.

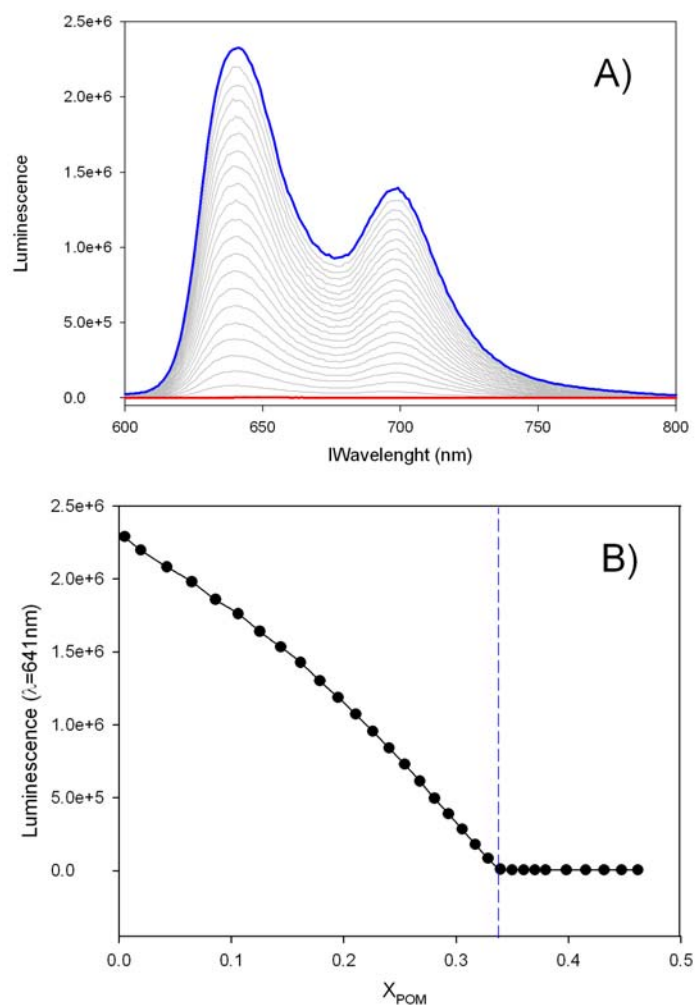


Figure S2. A) Luminescence measurements ($\lambda_{\text{exc}} = 515 \text{ nm}$). B) Luminescence measured at $\lambda = 641 \text{ nm}$ versus X_{POM} during titrations corresponding to the formation of the electrostatic complex $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]_1[\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_2$ in aqueous solution.

3. UV-visible absorption spectroscopy. UV-visible absorption spectroscopy has been employed to follow the deposition process of the films. In Fig. S3, we can see that the absorption intensity increases progressively for each deposition cycle using ITO substrate. Moreover, as shown in the inset of Fig. S3, the plot of the absorbance at $\lambda = 421$ nm (maximum of the Soret band of the porphyrin) versus the number n of deposition cycles of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}/\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_n$ results in a nearly straight line, showing a linear growth of the film up to at least a n value of 25. The same behavior is observed in the case of the plot of the absorbance at 260 nm (O to W transfer band of $\alpha_2\text{-}[\text{Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$) versus the number n of deposition cycles of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}/\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_m$ when using quartz substrate. It indicates that an approximately equal amount of porphyrin or POM is deposited upon each dipping cycle and that the $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}/\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_n$ film grows uniformly and homogeneously. The Soret absorption band of the porphyrin in the films shows a slight red shift by ca. 14 nm accompanied by a broadening of the absorption bands compared to that in solution. The red shift and the broadening of the UV-visible spectra are likely ascribed to interactions of porphyrins either with other porphyrins or with POMs.

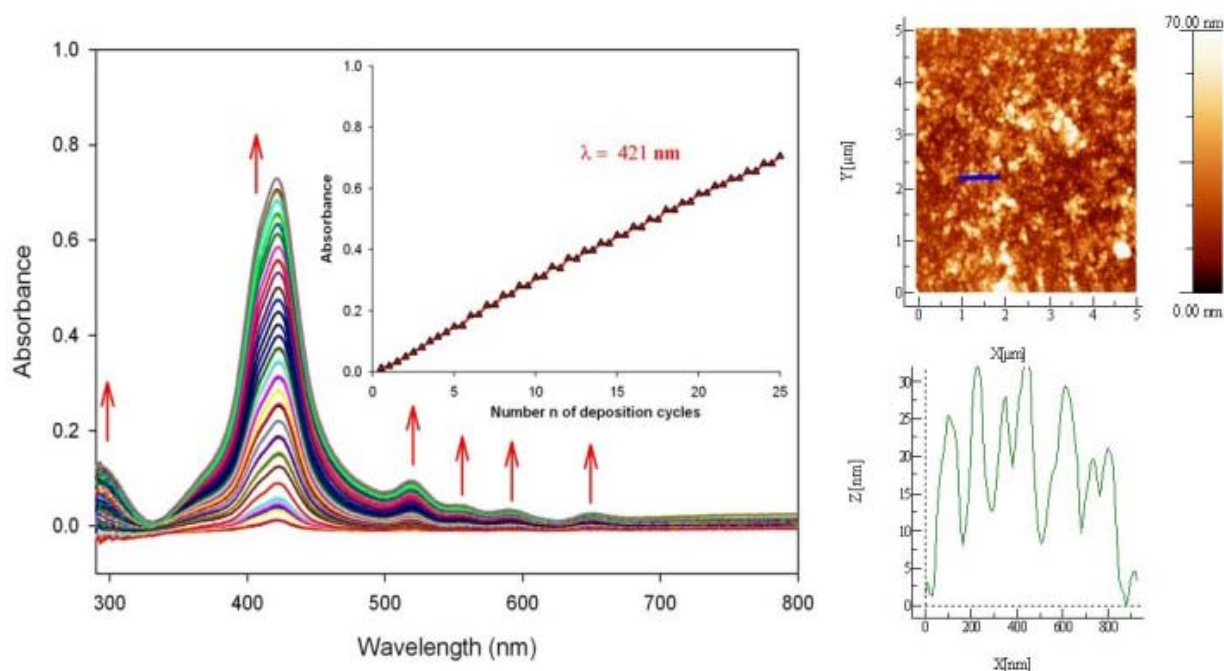


Fig. S3 Left: UV-visible absorption spectra of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}/\text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_n$ films onto ITO, with different numbers n of deposition cycles. Inset: Plots of the absorbance at 421 nm as a function of n of deposition. Right: typical tapping mode AFM topography and section analysis.

4. Cyclic Voltammetry

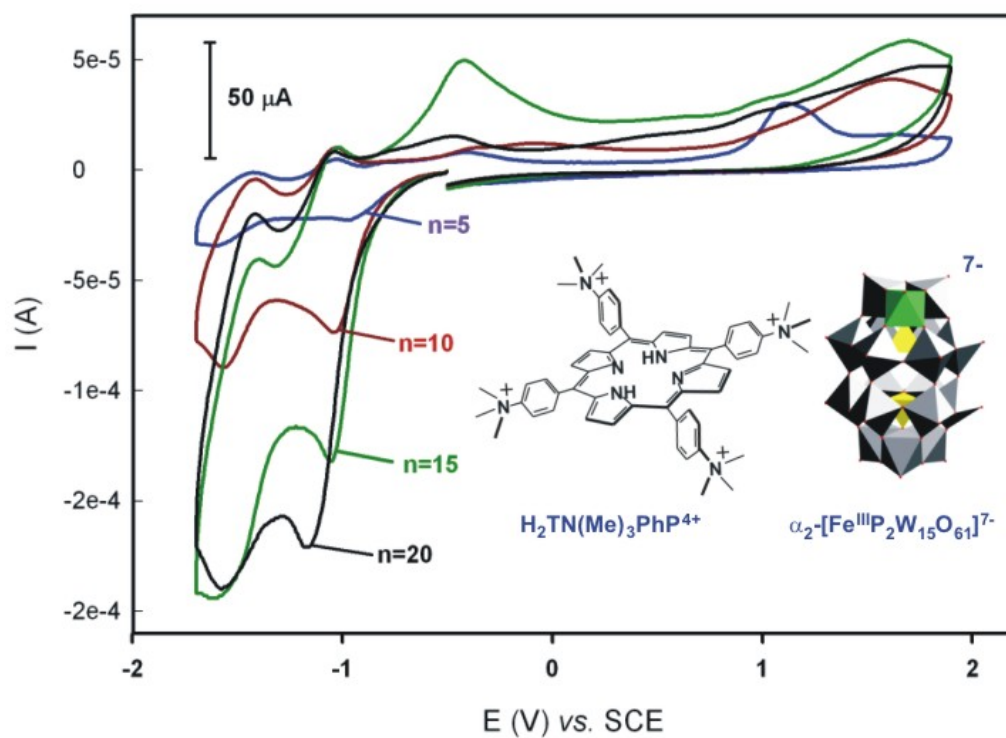


Fig. S4. Cyclic voltammograms of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-} / \text{H}_2\text{TPHN}(\text{Me})_3\text{P}^{4+}$ films for different values n of deposition cycles ($n=5, 10, 15$, and 20 from inner to outer) on ITO in CH_3CN and 0.1M TBAPF_6 at 100mVs^{-1} (only one side is recovered by ITO in this case).

5. X-ray Photoelectron Spectroscopy (XPS).

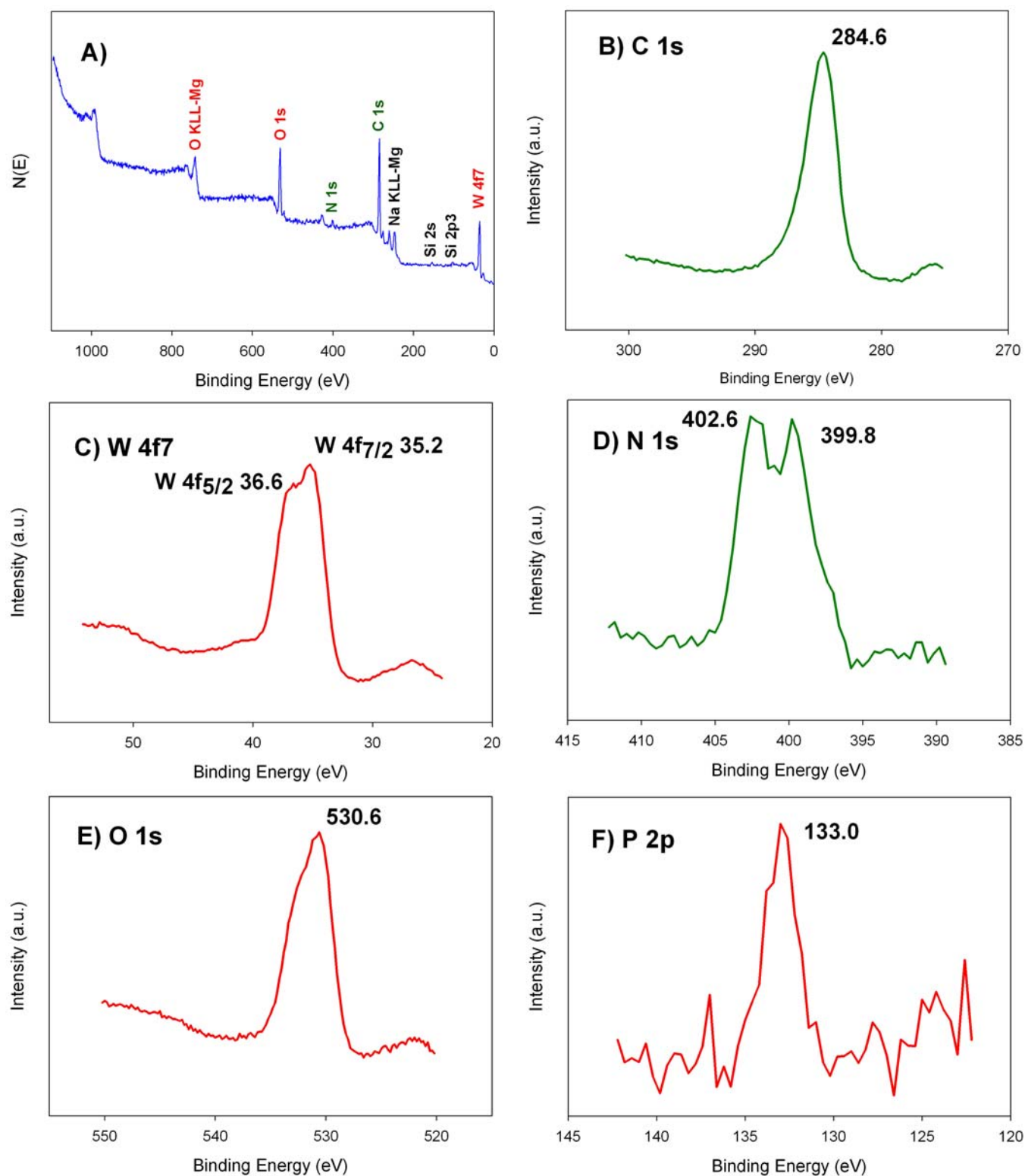


Fig. S5. XPS spectra of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-} / \text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_{15}$ films on quartz. (A) Global XPS spectra, (B) C 1s, (C) W 4f7, (D) N 1s, (E) O 1s, and (F) P 2p. The green color corresponds to the porphyrin subunits, the red color to the POM subunits. Excepted iron signal is not detectable.

6. Effect of the absence of the photosensitizer (porphyrin) onto the photocurrent measured

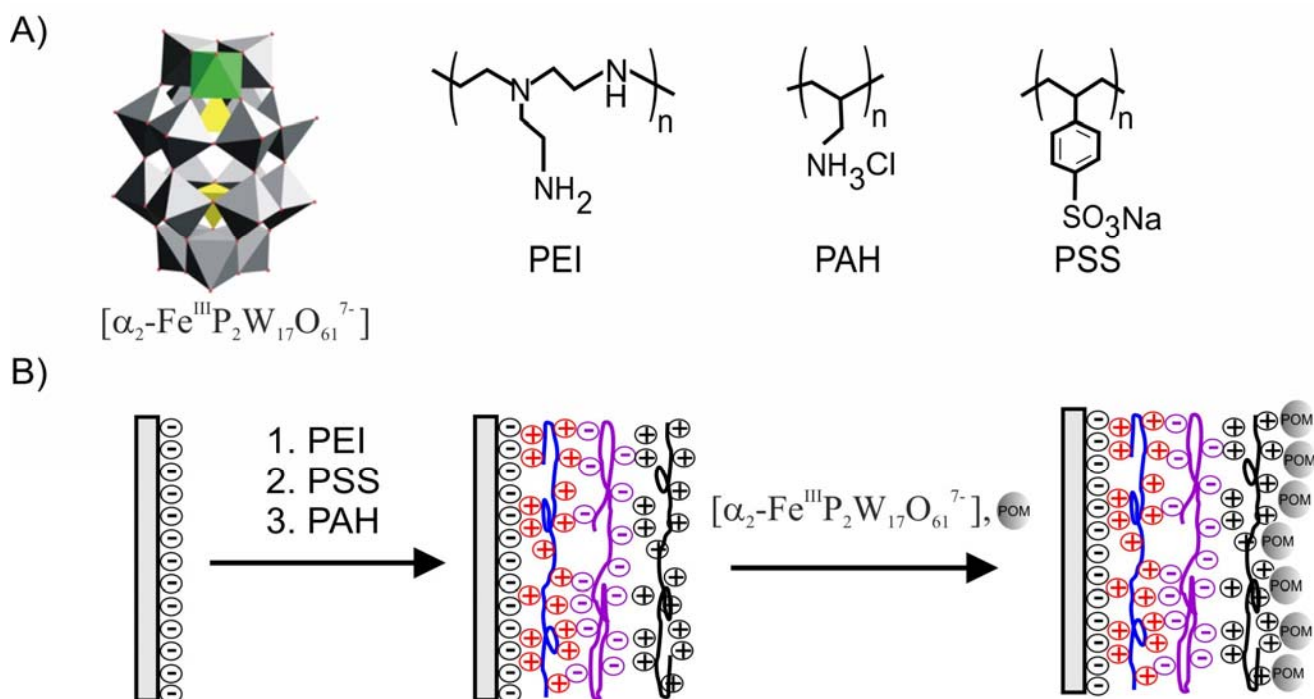


Fig. S6. A) Chemical structures of the polyelectrolytes and the $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]$ clusters used in the work. (B) Schematic diagram of the buildup of PEI/PSS/PAH/ $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]$ self-assembly film via alternate adsorption of cationic polyelectrolytes and anionic $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-}]$ cluster on substrates.

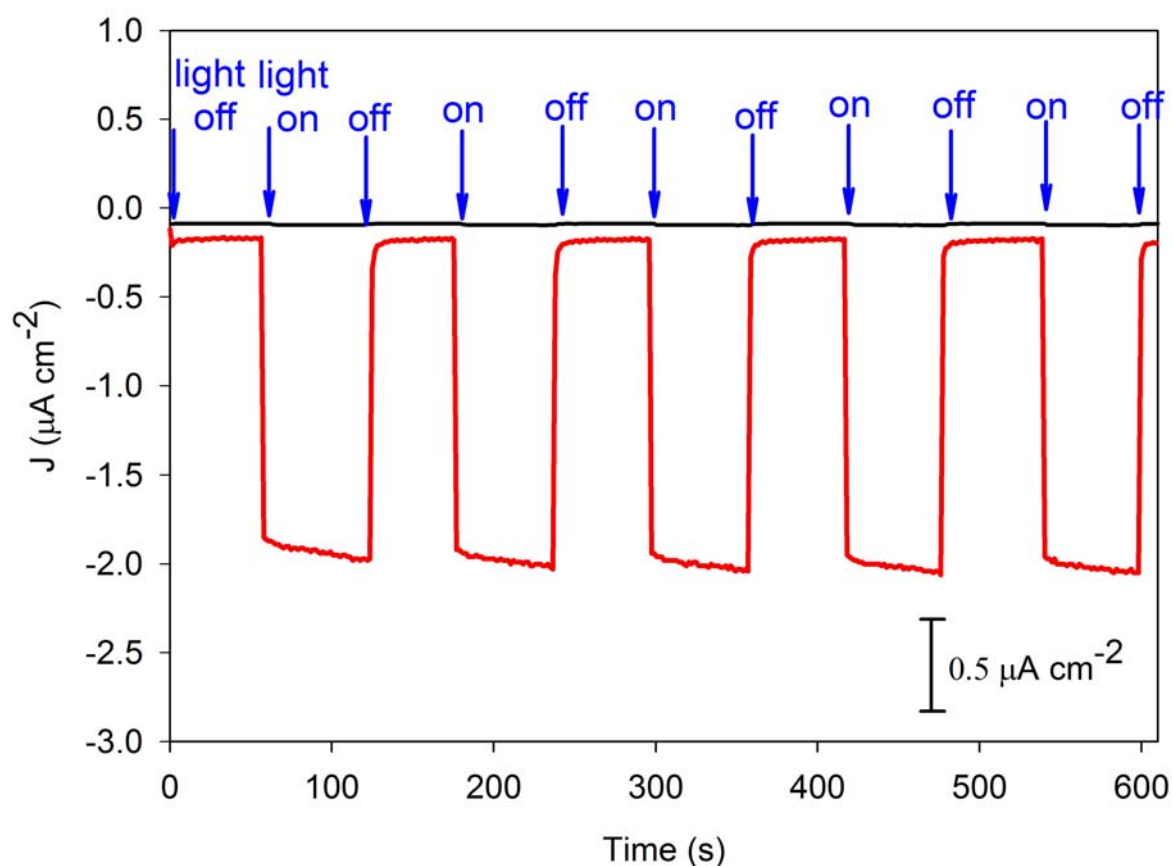


Fig. S7. Photocurrent density under visible light illumination from 300 W Xe arc lamp (with $\lambda > 385$ nm long pass filter) in acetonitrile containing I_3^- 0.1 mol L^{-1} and I^- 0.5 mol L^{-1} for the PEI/PSS/PAH/ $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ self-assembly film (black curve) compared with $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-} / \text{H}_2\text{TN}(\text{Me})_3\text{PhP}^{4+}]_{25}$ film (red curve). Applied potential -0.1 V .

7. Effect of the thickness of the film onto the photocurrent measured

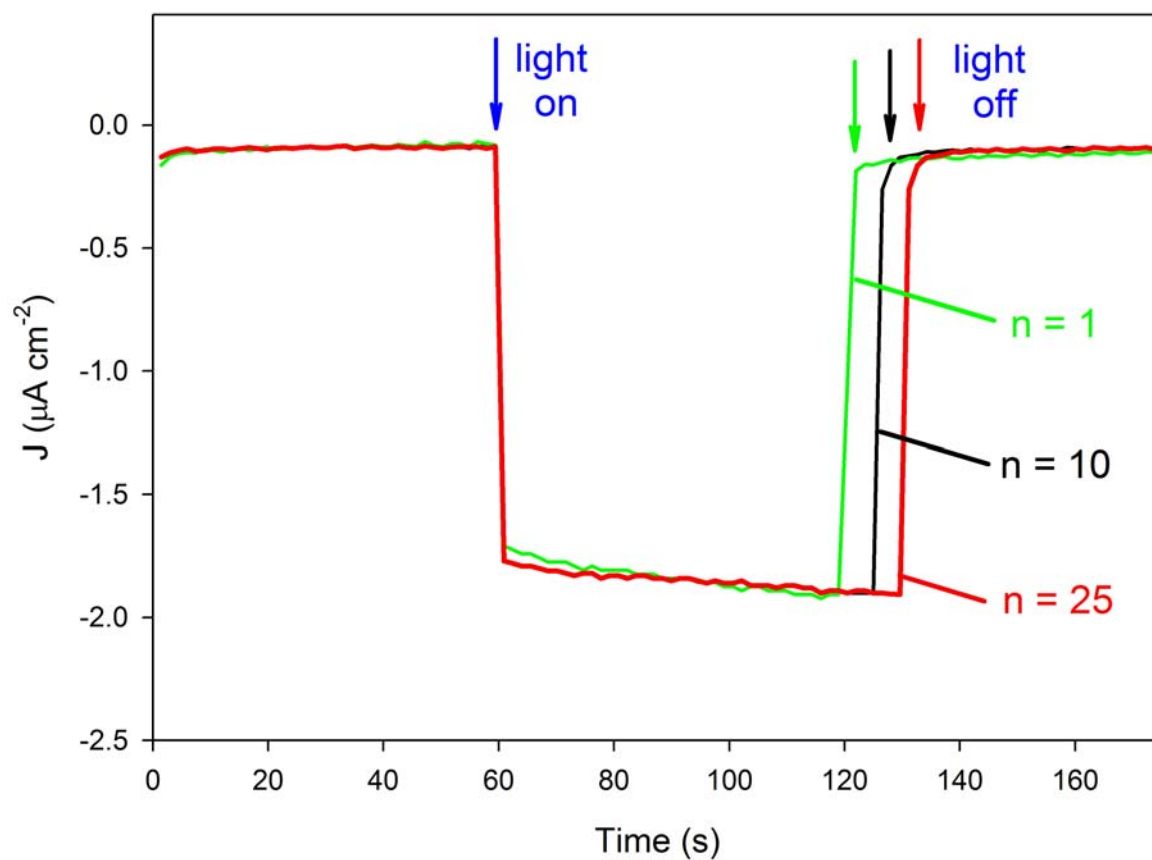


Fig. S8. Photocurrent-time curves generated for the $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-} / \text{H}_2\text{TN}(\text{Me})_3\text{PhP}^{4+}]_n$ film on a ITO substrate using $n=1, 10, 15$ and 20 deposition cycles. Applied potential -0.1 V.

8. Potential dependence

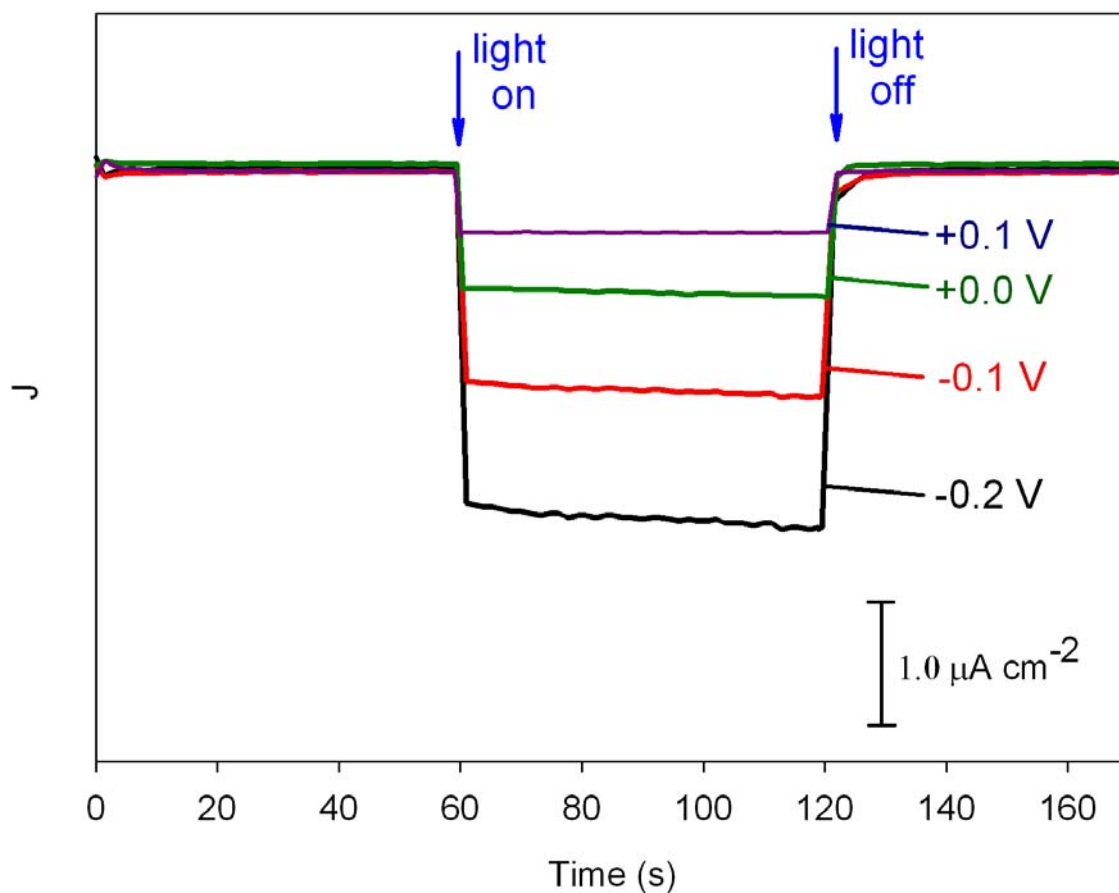


Fig. S9. Photocurrent density under visible light illumination from 300 W Xe arc lamp (with $\lambda > 385$ nm long pass filter) in acetonitrile containing I_3^- 0.1 mol L^{-1} and I^- 0.5 mol L^{-1} versus applied potential for the $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-} / \text{H}_2\text{TN}(\text{Me})_3\text{PhP}^{4+}]_{25}$ film ($n=25$ being the number of deposition cycles).

9. Permeability of the Films. The permeability of these films toward electrochemically active probe molecules has been also studied. Figure S10 shows the electrochemical response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe at ITO electrodes modified with films constituted of various numbers n of deposition cycles of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-} / \text{H}_2\text{TN}(\text{Me})_3\text{PhP}^{4+}]_n$.

For bare ITO electrode (non-modified), the redox probe shows a quasi-reversible cyclic voltammetry (peak-to-peak separation 219 mV, full line), indicating that the probe diffuses freely to the ITO electrode surface and undergoes electron-transfer at the electrode. In contrast, in the presence of $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-} / \text{H}_2\text{TN}(\text{Me})_3\text{PhP}^{4+}]_n$ films, it becomes almost impermeable to the probe molecule when n is equal to 1. Indeed, the peak current decreases and reaches zero when the number n of deposition cycles increases.

These results indicate a good quality of the films with the absence of pores which is in agreement with the AFM study.

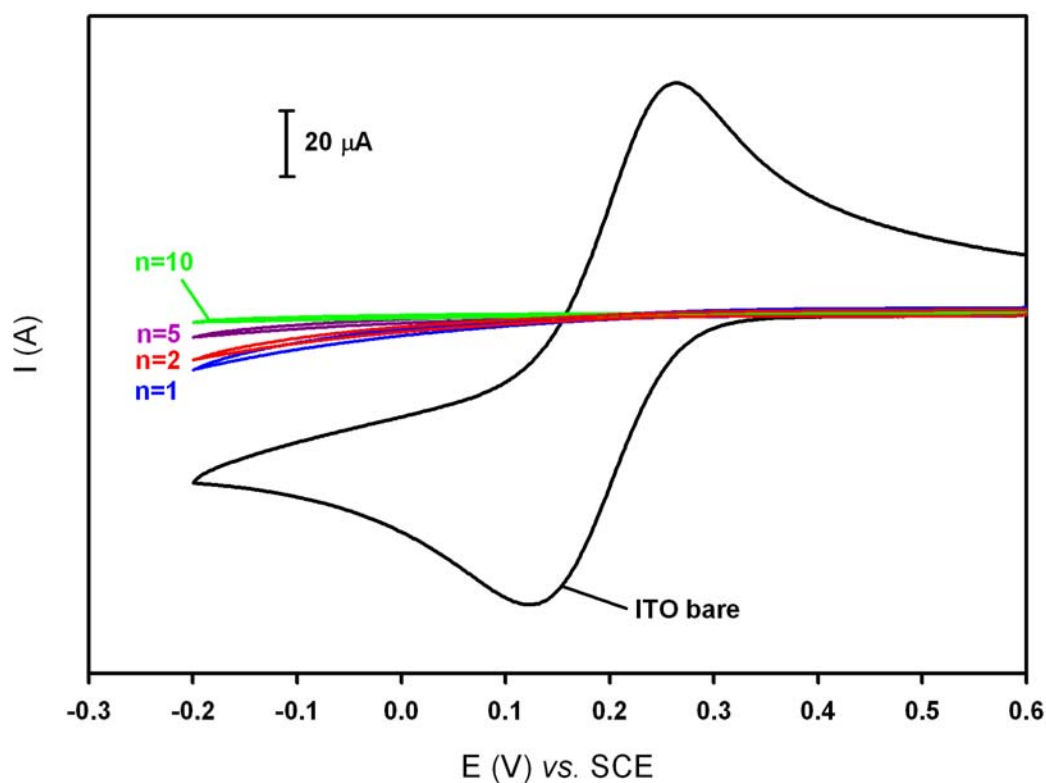


Fig. S10. Cyclic voltammograms of 1 mM of $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.5 M Na_2SO_4 at modified ITO electrode with $[\alpha_2\text{-Fe}^{\text{III}}\text{P}_2\text{W}_{17}\text{O}_{61}^{7-} / \text{H}_2\text{TPhN}(\text{Me})_3\text{P}^{4+}]_n$ films: blue line, $n=1$; red line, $n=2$; violin line, $n=5$ and green line, $n=10$ (black line, noncoated ITO electrode). $v=100 \text{ mV s}^{-1}$.