

Supporting information

Anionic effects on third-order nonlinear optical properties of ultrathin films containing cationic phthalocyanine and Keggin polyoxometalates fabricated using layer-by-layer deposition from aqueous solution

Hafiz Muhammad Asif,[†] Ningning Qu,[†] Yunshan Zhou,^{*} Lijuan Zhang,^{*} Farooq Khurram Shehzad, Zonghai Shi, Yi Long, Sadaf Ul Hassan

State Key Laboratory of Chemical Resource Engineering, Institute of Science, Beijing
University of Chemical Technology, Beijing 100029, P. R. China

1. UV-vis. spectra of AB and Keggin type POMs in H₂O

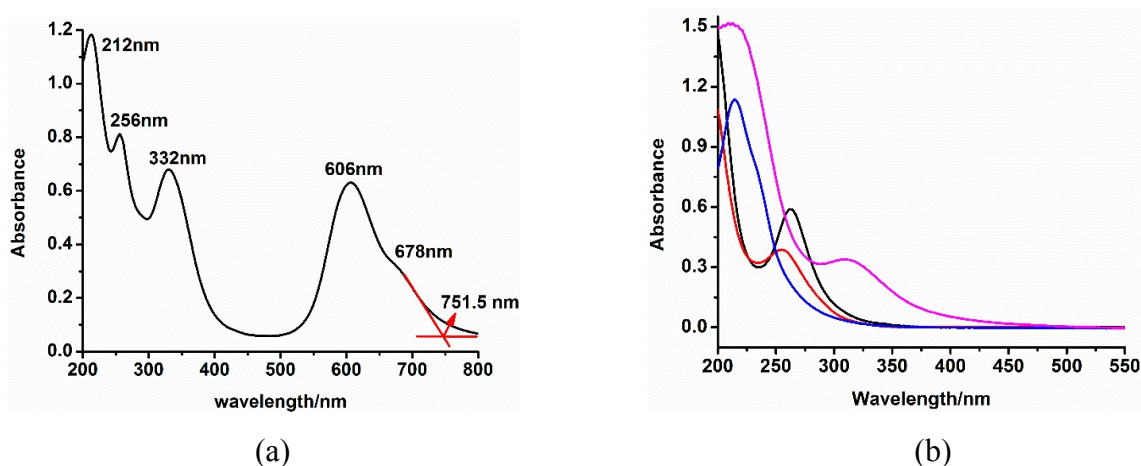
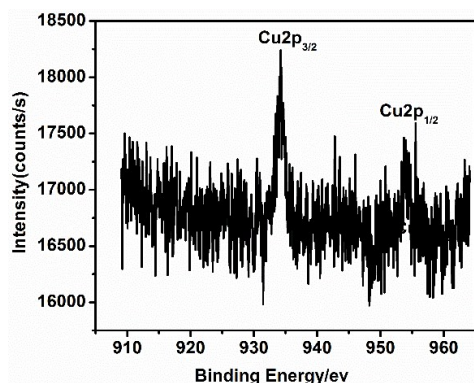


Figure S1. UV-vis spectra of AB (a) and Keggin type POMs (b) in H₂O where SiW₁₂ (black); PW₁₂ (red); PMO₁₂ (blue); PMO₁₀V₂ (pink)

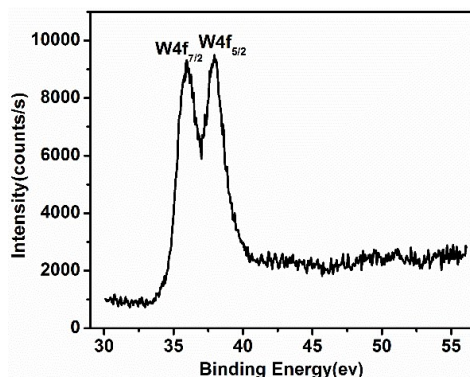
Figure S1 shows the UV-vis absorption spectra of AB in aqueous solution. The absorbance at about 332 nm (B-band) in the ultraviolet region (before 380 nm) the transition arises from the lower LUMO π -levels. The absorption of Q-band resulted from the transition between the highest occupied molecular orbital a_u and the lowest excited orbital (e_g) have two peaks at approximately 678 nm and 606 nm, which are due to monomer and aggregate of AB, respectively. The above absorption peaks are characteristic in phthalocyanine materials¹⁻³. Figure 3b shows the UV-vis absorption spectra of Keggin type POMs in aqueous solution.⁴ The maximum absorption peak appearing at 263 nm for SiW₁₂, 255 nm for PW₁₂, 214 nm for PMO₁₂

and 213 nm for $\text{PMo}_{10}\text{V}_2$ are assigned to bridge oxygen to tungsten/molybdenum charge transfer transition. The absorbance at 312 nm for $\text{PMo}_{10}\text{V}_2$ is the typical absorption of polyoxometalates containing vanadium⁵⁻⁶.

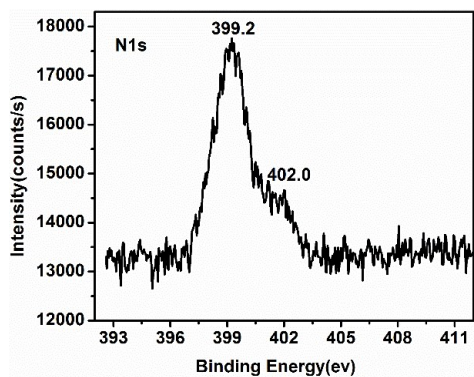
2. XPS of composite films



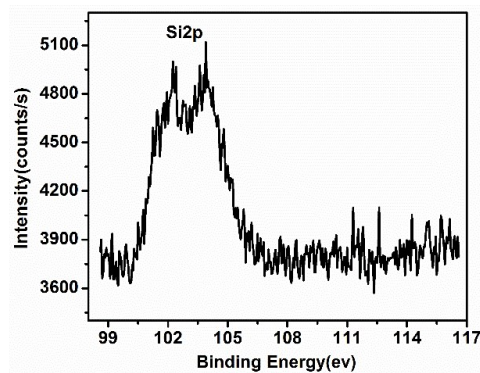
(a)



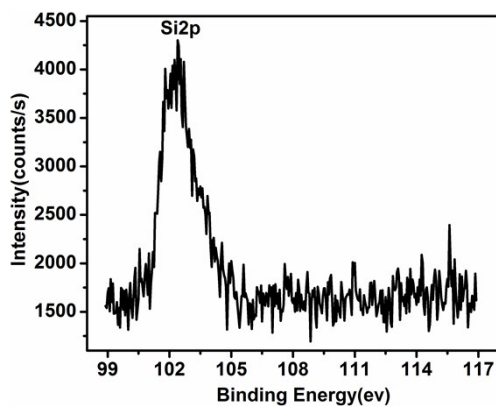
(b)



(c)



(d)



(e)

Figure S2. XPS spectra of (PAH/PSS)₃(AB/SiW₁₂)₈ multilayers films: Cu2p (a), W4f (b), N1s (c) and Si2p (d). For comparison the XPS spectra of Si in glass substrate is also shown (e).

It should be mentioned that the peak of Si2p in the glass substrate appears at 102.4 eV (Figure S2(e), while there are two peaks appearing at 102.3 eV and 103.9 eV for Si2p in the films (Figure S2(d), showing that former one is from the glass substrate and the latter one is from the SiW₁₂ of the (PAH/PSS)₃(AB/SiW₁₂)₈ multilayered films.

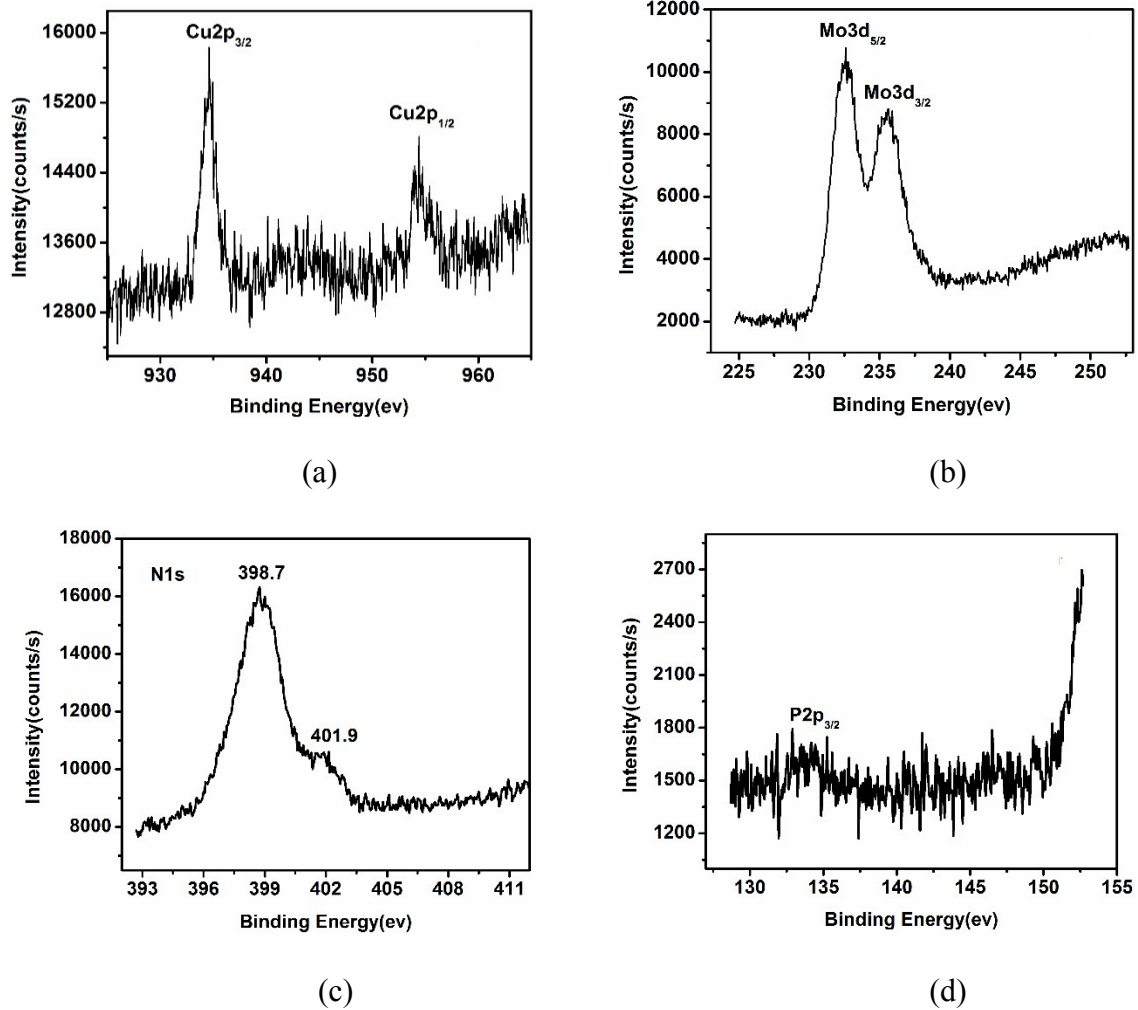
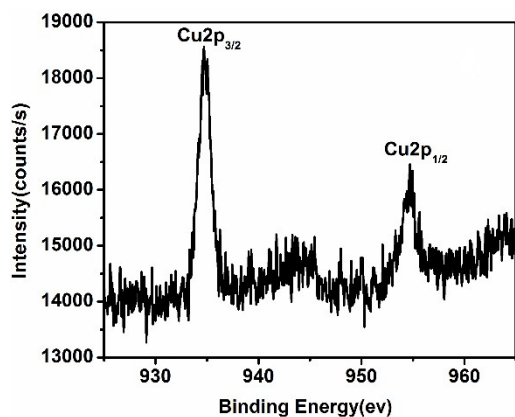
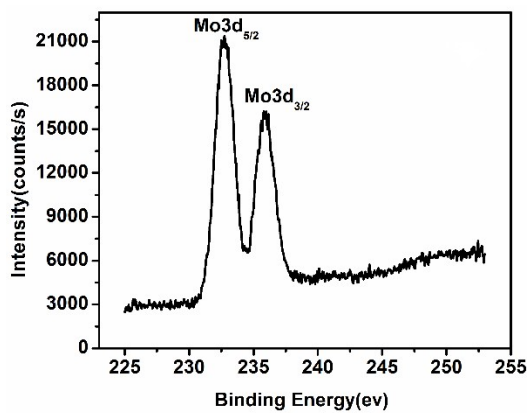


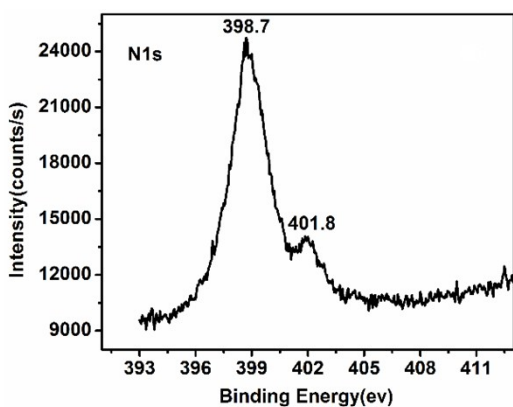
Figure S3. XPS spectra of (PAH/PSS)₃(AB/PMo₁₂)₈ films, (a): Cu2p; (b): Mo3d; (c): N1s; (d): P2p.



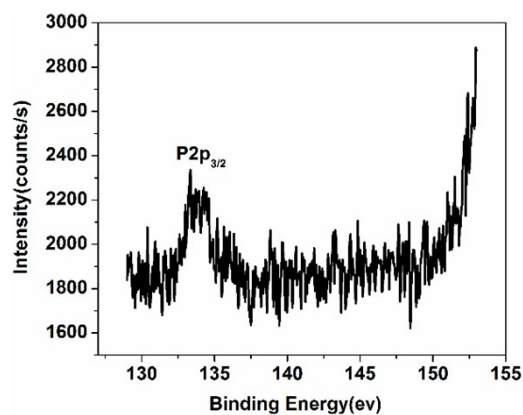
(a)



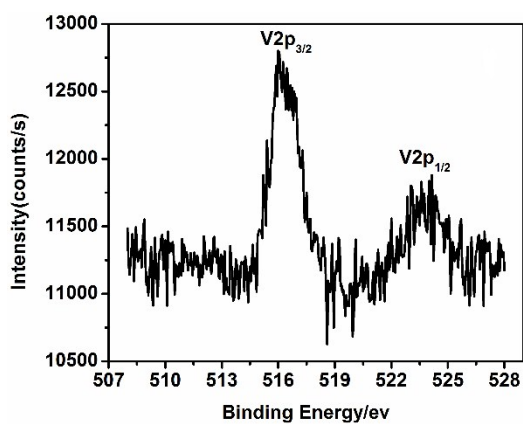
(b)



(c)



(d)



(e)

Figure S4. XPS spectra of (PAH/PSS)₃(AB/PMo₁₀V₂)₈ films. (a): Cu2p; (b): Mo3d; (c): N1s; (d): P2p; (e): V2p.

3. The calculation formulas of third-order nonlinear optical parameters

The following formula are used to calculate the third-order nonlinear refractive index n_2 (esu), the nonlinear absorption coefficient β (esu) and the third-order optical nonlinear susceptibility $\chi^{(3)}$ (esu).⁷

$$\Delta T_{P-V} = 0.406(1 - S)^{0.25} |\Delta\phi_0| \quad (1)$$

$$\Delta\phi_0 = kL_{eff}\gamma I_0 \quad (2)$$

$$L_{eff} = (1 - e^{-\alpha_0 L}) / \alpha_0 \quad (3)$$

$$n_2(esu) = \frac{cn_0}{40\pi} \gamma (m^2 / W) \quad (4)$$

where, ΔT_{P-V} is the normalized peak-valley difference, $\Delta\phi_0$ is the phase shift of the beam at the focus, $K = 2\pi/\lambda$ is the wave vector, I_0 (unit: W/m²) is the intensity of the light at focus, L_{eff} is the effective length of the sample defined in terms of the linear-absorption coefficient α_0 and the true optical path length through the sample, n_0 is the linear refractive index, and γ is optical Kerr constant. The conversion can be realized between n_2 (esu) and γ (m²/W) by eq (4).

When the sample is measured under open aperture, the normalized transmittance T ($z, s = 1$) can be expressed as

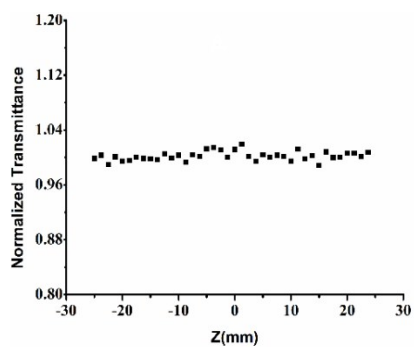
$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad (5)$$

Where $q_0(z) = \frac{\beta I_0 L_{eff}}{(1 + z^2/z_0^2)}$, β is nonlinear absorption coefficient.

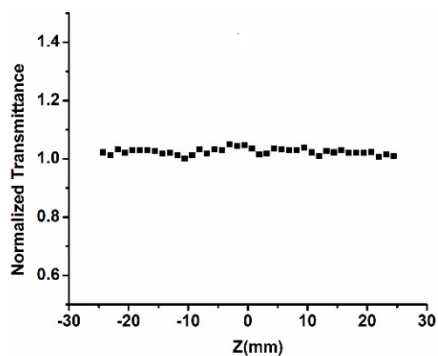
From eq (5) we can get β . From eq (6), we can get the third-order optical nonlinear susceptibility $\chi^{(3)}$.

$$\chi^{(3)} = \sqrt{\left(\frac{cn_0}{160\pi^2} \gamma\right)^2 + \left(c\beta n_0^3 \lambda / 64\pi^3\right)^2} \quad (6)$$

3. The Z-scan curves

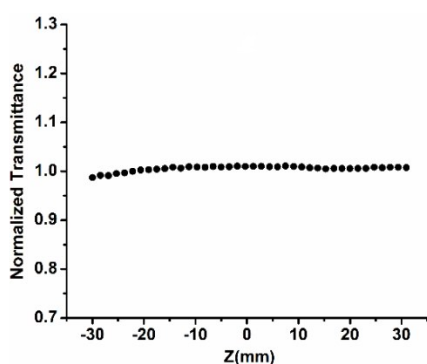


(a)

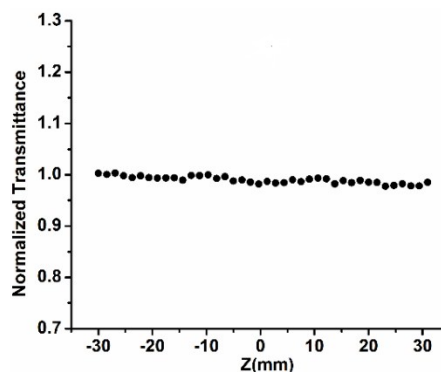


(b)

Figure S5. Z-scan curves of precursor films (PAH/PSS)₃ modified quartz substrate, (a) the open-aperture configuration (b) the closed-aperture configuration, $E = 9.99\mu\text{J}$.

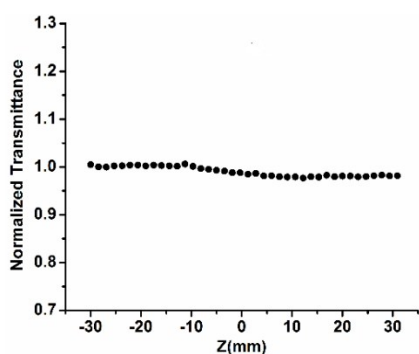


(a)

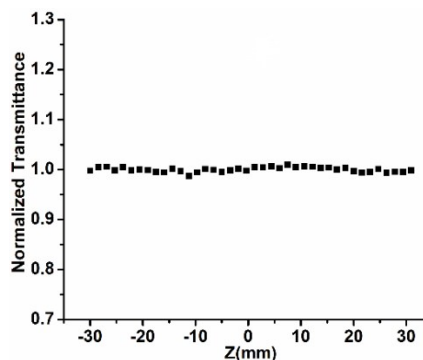


(b)

Figure S6. Z-scan curves of SiW_{12} in H_2O (10^{-3} M), (a) the open-aperture configuration (b) the closed-aperture configuration, $E = 10.4\mu\text{J}$.

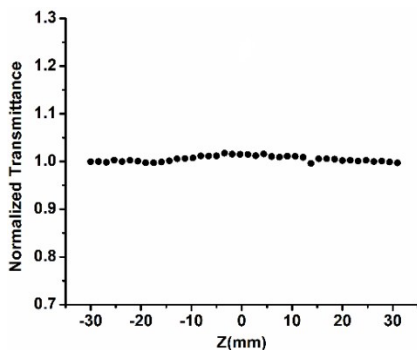


(a)

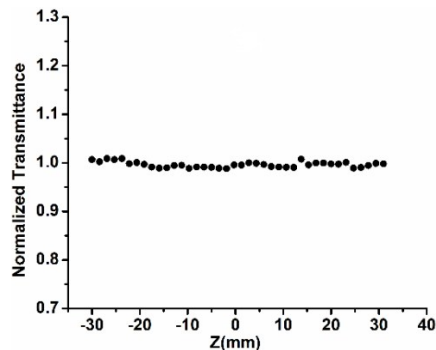


(b)

Figure S7. Z-scan curves of PW_{12} in H_2O (10^{-3} M), (a) the open-aperture configuration (b) the closed-aperture configuration, $E = 10.19\mu\text{J}$.

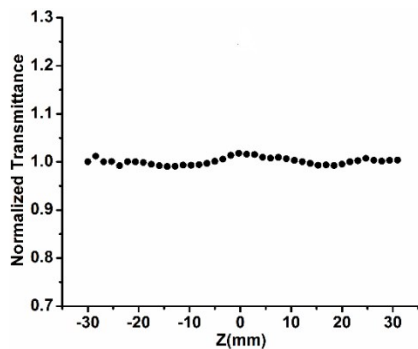


(a)

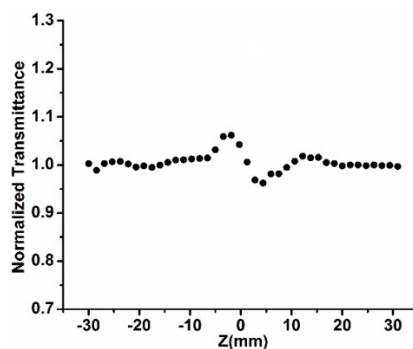


(b)

Figure S8. Z-scan curves of PMo_{12} in H_2O (10^{-3} M), (a) the open-aperture configuration (b) the closed-aperture configuration, $E = 10.1\mu\text{J}$.



(a)



(b)

Figure S9. Z-scan curves of $\text{PMo}_{10}\text{V}_2$ in H_2O (10^{-3} M), (a) the open-aperture configuration (b) the closed-aperture configuration, $E = 9.7\mu\text{J}$.

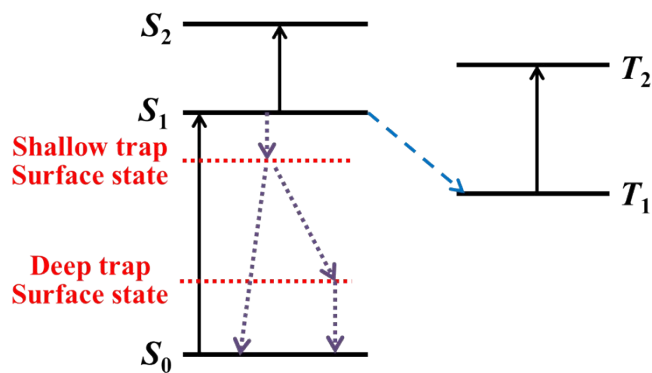
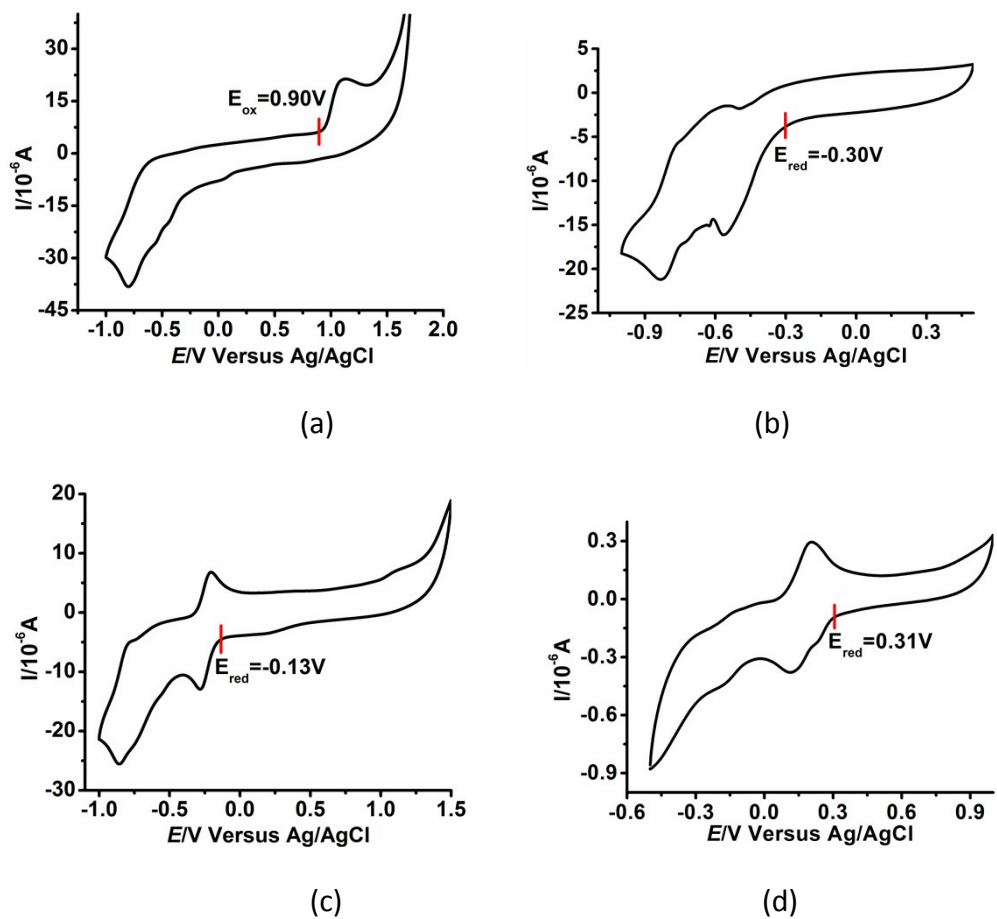
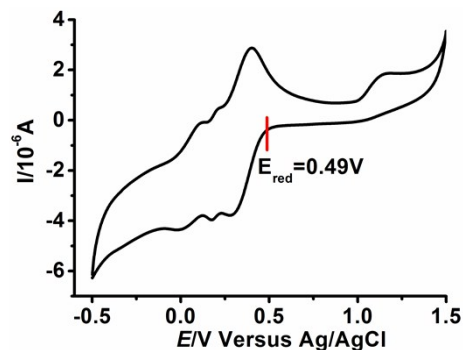


Figure S10. Schematic diagram of surface state trapping.

4. Cyclic voltammetry





(e)

Fig. S11. Cyclic voltammograms of AB (a), SiW₁₂ (b), PW₁₂ (c), PMo₁₂ (d), and PMo₁₀V₂ (e) in 0.1 mol/L DMF solution of TBAP (tetrabutylammonium hexafluorophosphate). All the compounds have the concentrations of 1 mM.

Cyclic voltammetry is used to calculate the HOMO-LUMO levels. The HOMO-LUMO gap E_g of AB is derived from the absorption edges of the spectra by equation $E_g = 1240/\lambda$ (λ is absorption edge).^{8, 9} Then the lowest unoccupied molecular orbital (LUMO) level of AB is obtained by $E_{\text{LUMO}} (\text{eV}) = -e (4.71 + E_{\text{ox}}) + E_g$ (4.71 is the vacuum level of Ag/AgCl electrode, E_{ox} is the onset of oxidation potential of AB), while the LUMO levels of the POMs were obtained by $E_{\text{LUMO}} (\text{eV}) = -e (4.71 + E_{\text{red}})$ (E_{red} is the onset of reduction potential of POMs).

References

1. Davidson, A. The Effect of the Metal Atom on the Absorption Spectra of Phthalocyanine Films. *J. Chem. Phys.*, 1982, **77**, 168-172.
2. Edwards, L.; Gouterman, M. Porphyrins: XV. Vapor Absorption Spectra and Stability: Phthalocyanines. *J. Mole. Spectro.*, 1970, **33**, 292-310.
3. De la Torre, G.; Vázquez, P.; Agullo-Lopez, F.; Torres, T. Role of Structural Factors in the Nonlinear Optical Properties of Phthalocyanines and Related Compounds. *Chem. Rev.*, 2004, **104**, 3723-3750.
4. Xin, F.; Pope, M. T., Polyoxometalate Derivatives with Multiple Organic Groups. 3. Synthesis and Structure of Bis(Phenyltin)Bis(Decatungstosilicate), [(PhSnOH₂)₂(Alpha-SiW₁₀O₃₆)₂]₁₀.

Inorg. chem., 1996, **35**, 5693-5695.

5. Contant, R.; Abbessi, M.; Thouvenot, R.; Hervé, G. Dawson Type Heteropolyanions. 3. Syntheses and ³¹P, ⁵¹V, and ¹⁸³W NMR Structural Investigation of Octadeca (Molybdo-Tungsto-Vanado) Diphosphates Related to the [H₂P₂W₁₂O₄₈]¹²⁻ Anion. *Inorg. chem.*, 2004, **43**, 3597-3604.

6. So, H.; Pope, M. T. Origin of Some Charge-Transfer Spectra. Oxo Compounds of Vanadium, Molybdenum, Tungsten, and Niobium Including Heteropoly Anions and Heteropoly Blues. *Inorg. Chem.*, 1972, **11**, 1441-1443.

7. Sheik-Bahae, M.; Said, A. A.; Van and Stryland E. W. High-sensitivity, Single-beam n₂ Measurements. *Opt. lett.*, 1989, **14**, 955-957.

8. Sun, X.; Liu, Y.; Chen, S.; Qiu, W.; Yu, G.; Ma, Y.; Qi, T.; Zhang, H.; Xu X. and Zhu, D. X-Shaped Electroactive Molecular Materials Based on Oligothiophene Architectures: Facile Synthesis and Photophysical and Electrochemical Properties. *Adv. Funct. Mater.*, 2006, **16**, 917-925.

9. Kuebler, S. M.; Denning R. G. and Anderson H. L. Large Third-Order Electronic Polarizability of a Conjugated Porphyrin Polymer. *J. Am. Chem. Soc.*, 2000, **122**, 339-347.