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PAPER

## Dye-sensitized polyoxometalate for visible-light-driven photoelectrochemical cells

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A simple and facile one-step method for the synthesis of organic dye-functionalized polyoxometalate (POM) hybrid with visible-light photo-response was reported. The POM hybrid was fully characterized via single crystal XRD, powder XRD, FTIR and elemental analysis. The reaction of organic dye with inorganic salts gave the dye-functionalized POM (**MoBB3**), in which the POM cluster was formed *in situ*. The electronic absorption peak of this hybrid was successfully extended beyond 680 nm. Photoelectrochemical measurement indicated that **MoBB3** was photoresponsive under visible-light illumination, suggesting that it is an n-type (electron conductive) semiconducting material. This result might offer a method for the design of novel organic dye-functionalized POMs for photoelectric applications.

### Introduction

As a rich family of early transition metal-oxygen anion clusters, polyoxometalates (POMs) have attracted tremendous attentions over the past decades due to their promising applications in catalysis, biology, magnetism, optics, material science and medicinal chemistry.<sup>1-14</sup> Especially, their nanosized geometry, unique optical characteristics, electronic properties, and excellent chemical reactivity make POMs more promising for the applications in photocatalysis and photovoltaics.<sup>15-21</sup> However, one major drawback of POMs for photoelectronic applications is their low or negligible absorption in the visible light region, which poses a limitation for the utilization of solar energy.

Recently, more and more studies focus on organic dye-functionalized POM hybrids, which can offer new opportunities to harvest light energy in the entire visible region of solar spectrum, as these hybrids have tunable band-edge potentials and strong absorption in the visible-light region.<sup>22-26</sup> In addition, the electrical and optical properties of POMs could be dramatically enhanced by the large planar conjugated  $\Pi$  system of organic dyes. Obviously, organic dye-functionalized POM hybrids would show promising applications in functional devices for the photoconversion of light into energy such as artificial photosynthetic devices and photovoltaic cells.<sup>27-30</sup> There are two methods for the functionalization of POMs with organic dyes. One is to directly attach organic dyes onto the surface of POMs through covalent bonds.<sup>31-34</sup> However, this strategy usually involves complicated synthetic work, such as harsh reaction conditions and inefficient purification processes. The other way to introduce organic dyes into POM system is to employ the electronic interactions between dye cations and POM anions. This approach involves two steps: the synthesis of anionic POMs with

inorganic ions as cations, followed by exchanging the cations with positively-charged organic dyes.<sup>35-40</sup> Owing to its simplicity, the second method, which holds great potential for large-scale reproduction, is far more attractive. However, this method is still in its infancy at current stage, and strong efforts are required to explore this method deeply.

Here, a one-step method for the synthesis of organic dye-sensitized POMs, which showed the response to visible-light illumination, is reported. The reaction between organic dye and inorganic salts leads to the formation dye-functionalized POM hybrid, in which the POM clusters were formed *in situ*. The UV-vis absorption of the as-prepared POM hybrid was successfully extended to visible-light region and showed an efficient photo-response with an n-type semiconductor characteristics.<sup>41-46</sup>

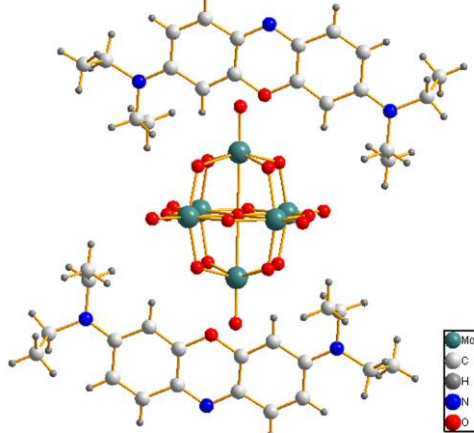
### Results and Discussion

#### Synthesis and characterization of **MoBB3**.

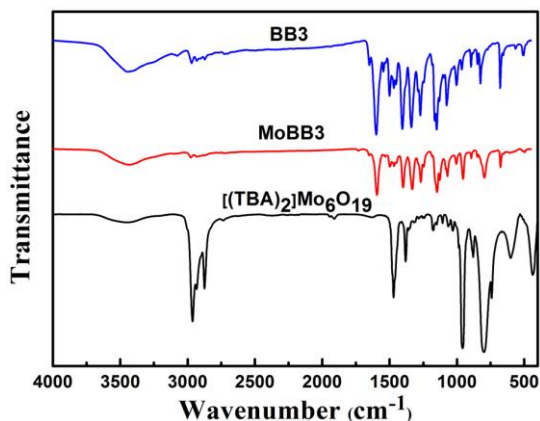
The Lindqvist-type  $\text{Mo}_6\text{O}_{19}^{2-}$ -based hybrid POM [(C<sub>20</sub>H<sub>26</sub>N<sub>3</sub>O)<sub>2</sub>Mo<sub>6</sub>O<sub>19</sub>] (**MoBB3**) was obtained through the facile synthetic approach by mixing basic blue 3 (**BB3**) and Na<sub>2</sub>MoO<sub>4</sub> in aqueous solution. The product precipitated from the solution immediately as dark blue solid, where  $\text{Mo}_6\text{O}_{19}^{2-}$  cluster was formed *in situ*. The suitable crystals of **MoBB3** for single crystal X-ray diffraction analysis were prepared by the slow diffusion of ethanol into the *N,N*-dimethylformamide (DMF) solution of **MoBB3**.

The single-crystal structure analysis shows that **MoBB3** crystallizes in the monoclinic space group P2(1)/n with cell parameter as  $a = 10.92 \text{ \AA}$ ,  $b = 19.22 \text{ \AA}$ ,  $c = 11.96 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 101.1^\circ$ ,  $\gamma = 90^\circ$ , and volume =  $2465.0(2) \text{ \AA}^3$ . The crystal structure of **MoBB3** is displayed in **Figure 1**. The asymmetric unit for

**MoBB3** is constituted of a Lindqvist anion  $\text{Mo}_6\text{O}_{19}^{2-}$  and two **BB3** cation ( $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}^+$ ). The average bond lengths of  $\text{Mo}-\text{O}_t$  (terminal oxygen),  $\text{Mo}-\text{O}_b$  (bridge oxygen) and  $\text{Mo}-\text{O}_c$  (center oxygen) are 1.69, 1.92 and 2.32 Å, respectively. These values are quite consistent with the values of prototypical compound  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  (TBA: tetrabutyl ammonium).<sup>34</sup> In the crystal structure, all the basic blue cations are aligned regularly with planar conjugated structures vertical to the z-axis (Figure S1). Details of the crystal structure and refinement data are provided in supporting information (Table S1). The experimental powder XRD patterns for **MoBB3** (Figure S2) confirmed the phase purity of the bulk materials. The IR spectra of **MoBB3**, **BB3** and  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  with prototypical Lindqvist structure are displayed in Figure 2. The band-pattern characteristic for the Lindqvist structure was described in the low wavenumber region of spectra (below  $1000\text{ cm}^{-1}$ ). The  $\nu(\text{Mo}-\text{O}_t)$  and  $\nu(\text{Mo}-\text{O}_b)$  bands of  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  are located at  $957\text{ cm}^{-1}$  and  $799\text{ cm}^{-1}$ , which is similar to the previous report.<sup>47,48</sup> In the spectra of **MoBB3**, the peak near  $955\text{ cm}^{-1}$  and  $796\text{ cm}^{-1}$  can be assigned to the  $\nu(\text{Mo}-\text{O}_t)$  and  $\nu(\text{Mo}-\text{O}_b)$  bands, confirming the formation of  $\text{Mo}_6\text{O}_{19}^{2-}$  cluster in the product. Almost all the peaks appeared in **BB3** could be found in the IR spectra of **MoBB3**, indicating the existence of **BB3** part in the product.



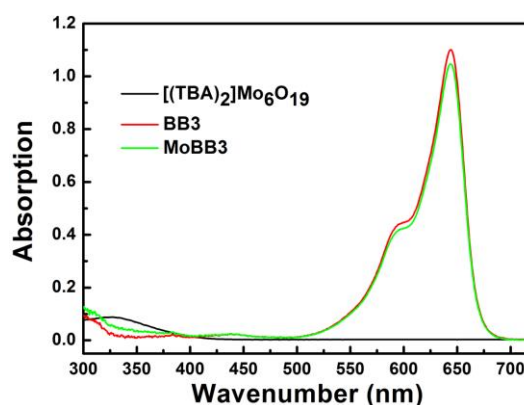
**Figure 1.** Crystal structure of the POM hybrid **MoBB3** shown in combined Ball-and Stick representation.



**Figure 2.** FT-IR spectra of **MoBB3**,  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  and **BB3**.

### Electronic and photoelectrochemical properties.

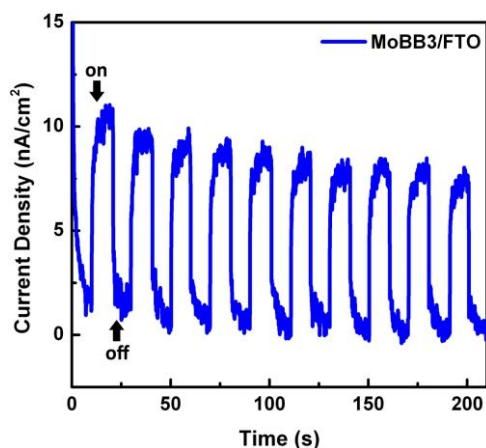
The electronic properties of **MoBB3** were studied in acetonitrile solution by the UV-vis absorption spectrum, and compared with the starting materials **BB3** and  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  (Figure 3).  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  showed lowest energy electronic transition absorption at 325 nm, which could be assigned to the charge transfer transitions from the  $\pi$ -type HOMO orbital of oxygen to the  $\pi$ -type LUMO orbital of molybdenum. No absorption in the visible region was observed in the spectrum of  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$ , while the maximum optical absorption of **MoBB3** is at 644 nm, which originated from the **BB3** molecules since **BB3** showed strong absorption in the visible-light region with a maximum at 644 nm and a shoulder at 596 nm. Our results clearly demonstrated that the absorption of POM complex was successfully extended from the UV region to the visible light area.



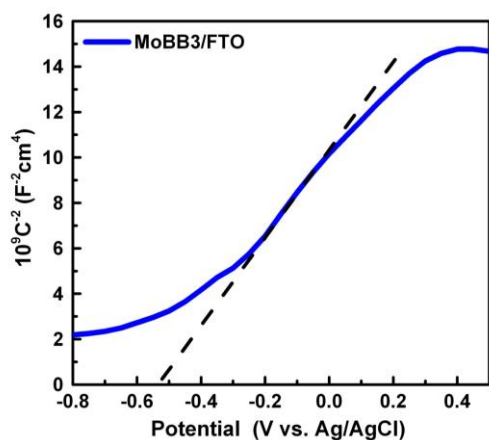
**Figure 3.** The UV-vis absorption of **MoBB3**,  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$  and **BB3** in acetonitrile solution with a concentration of  $1.0 \times 10^{-5}\text{ mol L}^{-1}$ .

The photoelectrochemical properties of **MoBB3** were studied in a three-electrode set-up. **Figure 4** shows the photocurrent responses of **MoBB3**/FTO photoelectrode under zero-biased condition, indicating that the **MoBB3** is active towards visible light ( $\lambda > 400\text{ nm}$ ) illumination. The repeatable anodic photocurrent responses indicate that **MoBB3** is an n-type (electron conductive) semiconducting material. The amplitude of the photocurrent is  $\sim 10\text{ nA/cm}^2$ . **Figure S3** shows the photocurrent-voltage (J-V) behavior of **MoBB3**/FTO collected using linear sweep voltammetry in  $0.5\text{ M Na}_2\text{SO}_4$  solution. The generated photocurrent increases with increasing applied bias potential, and can produce a photocurrent density of  $21\text{ nA/cm}^2$  at  $\sim 0.45\text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ ). No photocurrent responses under visible light illumination were observed for **BB3** dye and the Lindqvist POM  $[(\text{TBA})_2]\text{Mo}_6\text{O}_{19}$ . The possible mechanism for visible-light-driven photoresponse of **MoBB3** could be as following: organic dye will accept photons and electrons in HOMO of the dye will be excited to LUMO. Then, the excited electrons would be injected into POM clusters, which could be transferred to electrode through hopping mechanism from one cluster to another cluster. This electron transfer process from the organic dyes to inorganic POM cluster was observed in many dye-functionalized POMs.<sup>4-6,34</sup> To further investigate the conductivity type and flat-band potential of **MoBB3**, Mott-Schottky measurement was also

performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. As shown in **Figure 5**, the positive slope of the linear region on the M-S plot indicates that MoBB3 is n-type conductive, which is consistent with the result in photoelectrochemical measurements. The flat-band potential of this material is around 0.103 V vs. RHE.



**Figure 4.** The photocurrent responses of MoBB3/FTO photoelectrode under zero-bias condition.



**Figure 5.** Mott-Schottky plot of the MoBB3 measured at a frequency of 1000 Hz.

## Conclusions

In summary, a new organic dye-sensitized POM was synthesized via a simple and facile one-step method. The reaction between BB3 and Na<sub>2</sub>WO<sub>4</sub>, where the Lindqvist type Mo<sub>6</sub>O<sub>19</sub><sup>2-</sup>-based hybrid POM was formed *in situ*. The electronic absorption peak of this hybrid was successfully extended to the visible region (beyond 680 nm). Photoelectrochemical study indicated that MoBB3 was photo-responsive under visible-light illumination and should be a n-type (electron conductive) semiconducting material. Our result might offer a new strategy to design and prepare organic dye-sensitized POMs for photoelectrochemical applications and photoelectric devices.

## Experimental Section

**Materials.** All chemicals (except acetonitrile) were purchased

from Alfa Aesar, TCI chemical and Aldrich and used without further purification. Acetonitrile was distilled over drying agents before used. [(TBA)<sub>2</sub>Mo<sub>6</sub>O<sub>19</sub>] was synthesized according to the literature procedure.<sup>6</sup>

**Synthesis of MoBB3.** A solution of 5 mmol (1.25 g) of sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) was dissolved in 12 mL of water, then acidified with 1.3 ml of 6.0 M aqueous HCl in a 50 ml flask with rigorous stirring over a period of 10 min at room temperature. A solution of 12 mmol (0.39 g) Basic Blue 3 (C<sub>20</sub>H<sub>26</sub>N<sub>3</sub>OCl) in 10 mL of water was then added with rigorous stirring to cause immediate formation of a blue precipitate. The precipitate was washed with ethanol and dried in the oven. The as-obtained product was obtained as dark blue powder. Yield: 56% (based on Mo). Dark blue single crystals were formed by the liquid-liquid diffusion of methanol to the DMF solution. Anal. Calcd (%) for Mo<sub>6</sub>O<sub>21</sub>C<sub>40</sub>H<sub>52</sub>N<sub>6</sub>: C, 31.43; H, 3.43; N, 5.50. Found: C, 31.38; H, 3.49; N, 5.38.

**Characterization.** UV-vis absorption spectra were obtained using a Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence was measured on a Shimadzu RF-5301pc spectrofluorophotometer. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Elemental analyses were obtained from a EuroVector Euro EA elemental analyzer.

**Crystallographic measurements.** Dark Blue crystals of MoBB3 were grown through diffusing methanol into DMF solution at room temperature. Data collection was carried out on Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized MoK $\alpha$  radiation source ( $\lambda=0.71073$  Å) at 293 K. Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHRLX-TL program package. All hydrogen atoms were calculated and refined using a riding model. CCDC number for compound MoBB3 is 1060702.

**Photoelectrochemical measurements.** The photoelectrochemical tests were performed in a 22.5 ml extrasil quartz cell filled with 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 7.02), using an electrochemical workstation (CHI 760E). Prior to the measurement, the electrolyte was deaerated by purging with argon continuously for 30 minutes. A 300 W xenon lamp (Newport) coupled to an AM 1.5G filter was used as the standard light source, and the illumination intensity on the surface of the photoelectrode was  $\sim 100$  mW/cm<sup>2</sup>, calibrated using a standard silicon photodiode. Three-electrode set-up, with a platinum plate (1.0  $\times$  2.0 cm<sup>2</sup>) and a silver-silver chloride electrode (Ag/AgCl, in 3 M KCl) as the counter and reference electrodes respectively, to study the photocurrent responses and linear sweep voltammetry.

### Mott-Schottky Measurement

The Mott-Schottky plots of different samples were generated using impedance-potential technique. The capacitance of the semiconductor-electrolyte interface was collected at 1 kHz, with 10 mV AC voltage amplitude, in the same electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 7.02) and setup for PEC measurements. For estimating the flat-band potential of the samples, the measured voltage was converted into RHE scale by applying the following calculation:

$$V_{RHE} = V_{measured} + V_{Ag/AgCl}^0 + 0.059 \times pH$$

Where  $V_{RHE}$  is the converted potential,  $V_{measured}$  is the potential

reading from potentiostat and  $V_{\text{Ag/AgCl}}^0$  is the potential difference between Ag/AgCl reference electrode and standard hydrogen electrode (SHE).

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## Notes and references

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## Dye-sensitized polyoxometalate for visible-light-driven photoelectrochemical cells

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A simple and facile one-step method for the synthesis of organic dye-functionalized polyoxometalate (POM) hybrid with visible-light photo-response was reported.

