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## COMMUNICATION

## Two hybrid materials assembled from transition metal mono-substituted Keggin polyoxoanions as photocatalyst under visible light

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**Two 2D isostructural organic–inorganic hybrid solid materials based on transition metal mono-substituted Keggin polyoxotungstate with an antenna molecule were synthesized under hydrothermal condition. Compound 2 with the Co(II) substituted exhibits good photocatalytic activity in the degradation of rhodamine-B (RB) under visible light irradiation.**

Polyoxometalates (POMs) are a unique family of metal-oxygen clusters, which exhibit structural diversity and tunable properties, and have found numerous applications in analytical chemistry, material science, magnetism, catalysis and medicine.<sup>1</sup> The incorporation of d-block metal atoms in vacant POM matrices is one of the oldest and most studied reactions in POM chemistry.<sup>2</sup> More recently, introduction of organic ligands in such inorganic systems has been developed by several groups.<sup>3</sup> Especially, the synthesis of Keggin-based transition-metal monosubstituted POMs (Keggin–TPOMs) with an organic ligand coordinated to the transition metal ion as a pendant or antenna is of special significance because of their wide applications.<sup>4</sup> These derivatives have been recognized as inorganic analogs of metalloporphyrin complexes, but the former have distinct advantages over the latter, e.g. they are rigid, hydrolytically stable and thermally robust.<sup>5</sup> Such organic–inorganic hybrid materials can combine the key merits of both sources, for example, magnetic and catalytic properties, as well as new properties arising from the synergistic interplay of the two components.<sup>6</sup>

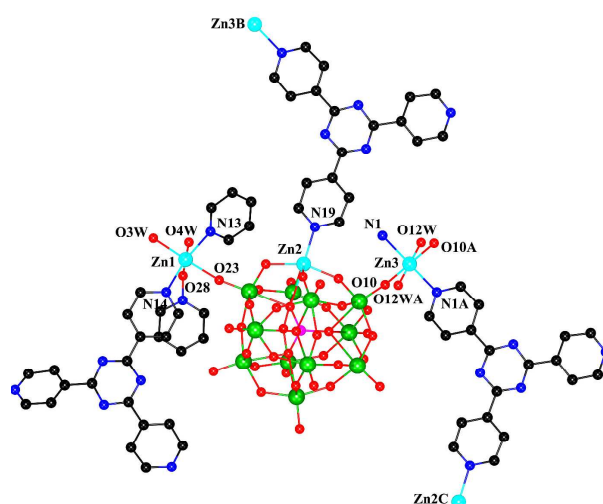
However, it represents a remarkable challenge to synthesize and characterize monolacunary Keggin POMs bearing a transition metal with an organic ligand.<sup>7</sup> In fact, many metal-substituted lacunary POMs (LPAs) with antenna ligands reported previously, formulated as

$[\alpha\text{-XW}_{11}\text{O}_{39}\text{ML}]^n$  (X = P or Si, L = N-, S- or C-donor ligand, M = Sn, Ti, Rh, Ru, Re or Os), were synthesized in organic solvents, and were characterized by NMR instead of single crystal X-ray crystallographic analysis.<sup>8</sup> According to the literatures, only very few single crystal structures of metal-substituted LPAs with an organic antenna ligand have been reported and in these scarce cases, the heteroatom metal is always a second series transition metal or a rare earth metal as in the series.<sup>9</sup> Even so, longstanding problems in these single crystal structures still exist: the crystallographic disorder between the substituted metal site and the intrinsic metal ions in the polyanion because of the high symmetry of the polyanion units themselves and the nearly identical geometrical features of the two metal ions. Many studies have focused on obtaining structures of disorder-free mono-substituted Keggin complexes by X-ray diffraction but with only very limited success. In this field, Hill,<sup>10</sup> Kortz,<sup>11</sup> Proust,<sup>8b</sup> Drain, Francesconi,<sup>12</sup> and Peng<sup>13</sup> groups reported several rare examples of mono-substituted Keggin without positional disorder of the incorporated transition-metal center. Among these, Peng et al. prepared the first crystallographically characterized examples of monolacunary Keggin POMs bearing a 3d transition metal with imidazole and 4,4'-bipyridine as pendant ligands. Although it is common that imidazole and 4,4'-bipyridine show high affinity to some 3d transition-metal ions which can favour the formation of high dimensional transition-metal complexes,<sup>14</sup> in their work, the remaining nitrogen atom from the imidazole or pyridine is naked which makes the whole structure isolated. Unfortunately, up to now, no related works have been reported to extend these isolated subunits into high dimensional structures.<sup>15</sup>

Inspired by one similar work in which organoimido derivatized hexamolybdate containing carboxyl terminus acts as a ligand to

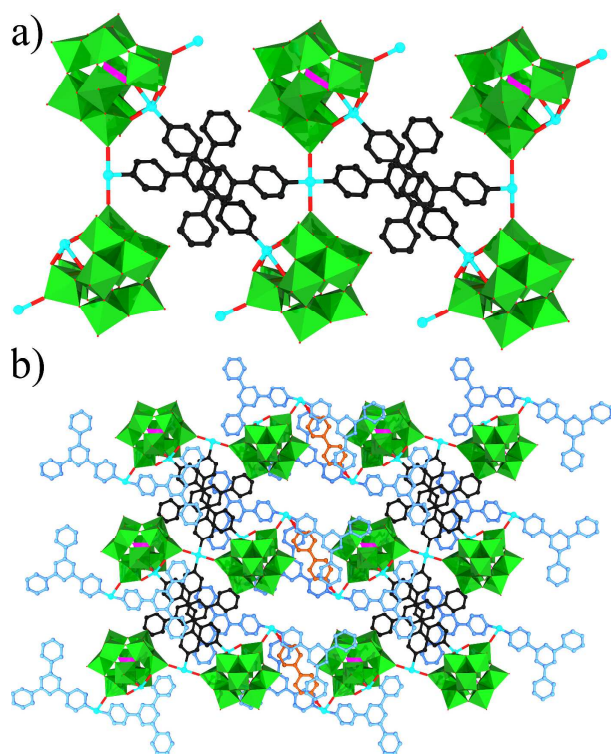
coordinate with Cu(II) ions to form a paddle-wheel structure,<sup>16</sup> we think two strategies can be adopted to obtain high dimensional structures in which the monolacunary Keggin POM bearing a disorder-free transition metal with pendant ligands services as a building block. One strategy is to use a multidentate ligand to coordinate with the transition metal ion incorporated in the LPAs which will increase the opportunity of the ligand coordinating with other transition metal ions; The other one is to employ the auxiliary ligand to connect the subunits. Herein, two 2D isostructural organic-inorganic hybrid materials based on 3D-transition metal mono-substituted Keggin polyoxotungstate with an antenna molecule,  $\{[M(H_2tpt)_2(dpdo)_{0.5}(H_2O)_2][M_{0.5}(H_2O)]PW_{11}M(tpt)O_{39}\} \cdot 11H_2O$  [ $M = Zn$ , **1**;  $M = Co$ , **2**;  $tpt = \text{tris}(4\text{-pyridyl})\text{triazine}$ ;  $dpdo = 4,4'$ -bipyridine- $N,N'$ -dioxide], have been hydrothermally synthesized and fully characterized. In **1** and **2**, the Zn(II) and Co(II) are disorder-free, and **2** shows efficient photocatalytic degradation of rhodamine-B (RB) under visible light irradiation.

Compounds **1** and **2** crystallized isostructurally in the triclinic, space group P-1. We therefore focus on the structure description of **1** as representative. The asymmetric unit of **1** contains one  $[PW_{11}O_{39}Zn(tpt)]$  unit, two Zn(II) ions, two TPT ligands, three coordinated and eleven lattice water molecules. As shown in Fig. 1, Zn1 has a six-coordinated octahedral geometry which is defined by two oxygen atoms from two different water molecules ( $Zn-O = 2.094(3)\text{-}2.105(3)$  Å), one oxygen atom from the  $dpdo$  ( $Zn-O = 2.105(3)$  Å), one oxygen atom from the terminal oxygen atoms of the  $[PW_{11}O_{39}Zn(tpt)]$  unit ( $Zn-O = 2.141(3)$  Å), two nitrogen atoms from two different TPT ligands ( $Zn-N = 2.155(4)$  and  $2.178(4)$  Å); Zn2 is embedded in the vacancy of  $\{PW_{11}\}$  with its outside axial site coordinated by one nitrogen atom from the  $tpt$  ligand to complete the octahedral environment; while, Zn3, lying on independent inversion center, shows an octahedral environment which is formed by two different nitrogen atoms from two different  $tpt$  ligands, two oxygen atoms from two different water molecules, two oxygen atoms from the terminal oxygen atoms of two different  $[PW_{11}O_{39}Zn(tpt)]$  units. In  $[PW_{11}ZnO_{39}]$  polyanion, the central P atom is surrounded by four oxygen atoms ( $O_1$ ,  $O_2$ ,  $O_3$ , and  $O_4$ ). Average distance of the P-O bonds is in the usual region of  $1.531$  Å, and the O-P-O bond angle is in the range of  $107.7(4)\text{-}110.5(4)$ . According to the coordination mode, there are three kinds of oxygen atoms in the cluster: terminal oxygen atoms ( $O_t$ ), bridging oxygen atom ( $O_b$ ), and central oxygen atoms ( $O_c$ ). Therefore, the distances of the W-O bonds can be divided into three groups:  $W-O_t$ ,  $1.693(8)\text{-}1.735(8)$  Å;  $W-O_b$ ,  $1.777(8)\text{-}2.054(7)$  Å;  $W-O_c$ ,  $2.333(7)\text{-}2.494(8)$  Å, which is in the range of reported monovacant Keggin polyoxoanions.<sup>17</sup> Bond-valence-sum calculations show that all of the tungsten sites exhibit a 6+ oxidation state and all of the zinc ions have a 2+ oxidation state in the  $[PW_{11}ZnO_{39}]$  unit. In compound **1**, it is interesting that  $PW_{11}$  is formed from the saturated Keggin cluster  $PW_{12}$  under hydrothermal conditions. Another outstanding feature is that the encapsulated zinc ion (Zn2) is disorder-free, which is ascribed to special coordination environment.



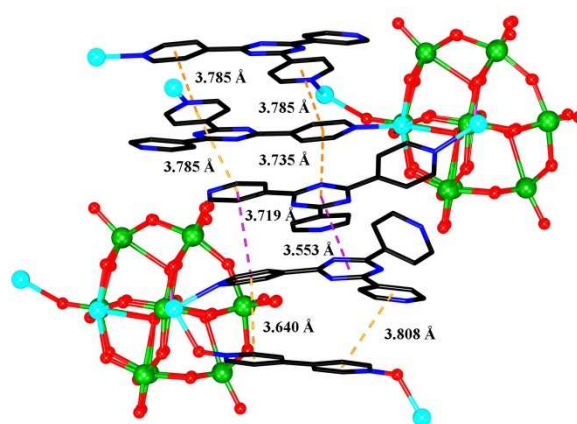
**Fig. 1** The  $[PW_{11}Zn(tpt)O_{39}]$  unit and the coordination environment of Zn(II) ions in **1**. Hydrogen atoms were omitted for clarity. Note: one  $\mu_1$ -TPT was simplified as a pyridine (N13) for clarity.

In the whole structure of **1**,  $tpt$  ligands demonstrate two different kinds of coordinated mode. One acts as monodentate ligand ( $\mu_1$ - $tpt$ ), in which only one pyridine on the  $tpt$  participates in coordination with Zn1 which is grafted on the surface of  $[PW_{11}ZnO_{39}]$  unit. The other one acts as bidentate ligand ( $\mu_2$ - $tpt$ ), in which two pyridines coordinate with Zn2 and Zn3. Briefly, the  $\mu_2$ - $tpt$  ligand can be considered as a V-shaped ligand to connect the zinc ion (Zn2) encapsulated in one LPA and the zinc ion (Zn3) grafted on the surface of adjacent LPA (Fig. S1, ESI). As a result, a subunit is formed in which four  $[PW_{11}ZnO_{39}]$  units are connected by two  $\mu_2$ - $tpt$  ligands (Fig. 2a). Given the configuration of the two  $\mu_1$ - $tpt$  ligands coordinating with Zn1, they can be viewed as cantilevers which are arrayed along the two sides of the subunit. Next, the auxiliary ligand,  $dpdo$ , as a linker, bounded to the Zn1 ions and links the adjacent subunits into a 2D layer (Fig. 2b, S2). To the best of our knowledge, this is the first example of 2D organic-inorganic hybrid material constructed by a building block of monovacant Keggin POMs bearing a disorder-free 3d transition metal with pendant organic ligands.



**Fig. 2** a) Subunit formed from four  $[PW_{11}ZnO_{39}]$  connected by two  $\mu_2$ -tpt (black), containing eight  $\mu_1$ -tpt (light blue); b) dpdo (orange) as a string to connect adjacent subunits presented in a. Hydrogen atoms were omitted for clarity.

Further study into the nature of this 2D architecture, two kinds of strong offset  $\pi$ - $\pi$  stacking interactions are observed in the single 2D layer structure. The first one is formed between the  $\mu_1$ -tpt and  $\mu_2$ -tpt,  $\mu_2$ -tpt and  $\mu_2$ -tpt ligand (centroid-centroid distances from 3.735 to 3.785 Å); The second one is formed between  $\mu_1$ -tpt and  $\mu_2$ -dpdo ligand (centroid-centroid distances from 3.640 to 3.808 Å). More importantly, the offset  $\pi$ - $\pi$  stacking interactions between two  $\mu_1$ -tpt ligand from two different single 2D layer (centroid-centroid distances from 3.553 to 3.719 Å) extend the 2D architecture into 3D supramolecular structure (Fig. 3, S3). The special packing model and the strong  $\pi$ - $\pi$  stacking interactions result in a stable organic-inorganic hybrid material. TG data indicate that compound **1** is thermally robust. The TG curve of **1** demonstrates an initial weight loss of ca. 4.86% between 50 °C and 300 °C corresponding to the remove of free and coordinated water molecules (Fig. S4). The decomposition of the whole framework starts at 400 °C. The phase purity of the as-synthesized material is confirmed by the PXRD pattern (Fig. S5).

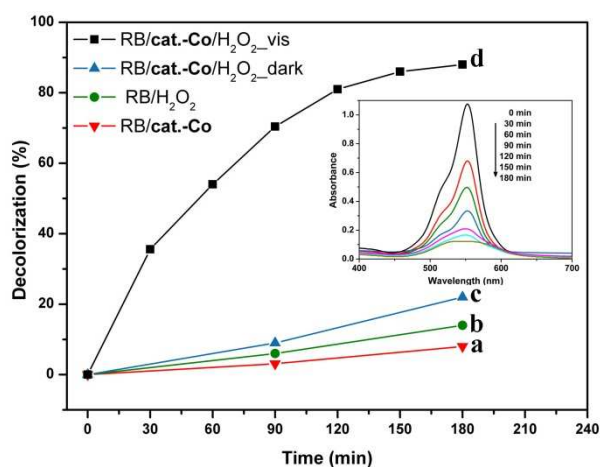


**Fig. 3** The strong offset  $\pi$ - $\pi$  stacking interactions observed in **1**. The orange dash lines represent the  $\pi$ - $\pi$  stacking interactions in the single layer; The pink dash lines represent the  $\pi$ - $\pi$  stacking interactions between two layers. Hydrogen atoms were omitted for clarity.

Photosensitization as an approach can extend the photosensitivity of POMs with high energy gap into the visible region.<sup>18</sup> Highly conjugated aromatic N-heterocyclic molecules are well-known light sensitizing reagents, which have been used in solar energy conversion systems.<sup>19</sup> It has been well documented that the N-heterocyclic tpt molecule has the maximum absorption locating at 309 nm and 410 nm.<sup>20</sup> This character makes the tpt molecule as an antenna to absorb effective light energy for the catalytic cluster,<sup>21</sup> which will be beneficial for solar light utilization and photocatalytic efficiency enhancement; The photocatalytic activity of as-prepared **1** and **2** (denoted as **cat.-Zn** and **cat.-Co** hereafter) were tested by degradation of organic dye solutions under visible light, which is one of the effective ways to eliminate environmental pollutants.<sup>22</sup> The results demonstrated that **cat.-Co** showed good photo-catalytic activity of rhodamine-B (RB) degradation under visible light. The reaction was stirred mechanically during the whole process and the photocatalytic degeneration was monitored by ultraviolet-visible spectroscopy. The decolorization rate of RB solution under various conditions is plotted in Fig. 4. References were made with different reaction systems to compare the catalytic ability under different conditions. Experimental results show that barely degradation of RB can be detected when only **cat.-Co** or  $H_2O_2$  is added to the reaction solution. Even in the reaction system of **cat.-Co** and  $H_2O_2$  coexisting in the dark, the degradation rate is fairly low. By comparison, the degradation rate increases dramatically with the combination of **cat.-Co** and  $H_2O_2$  under the visible light. The characteristic absorbance at 553 nm of RB in aqueous solution decreased with increasing time of visible light irradiation. The decoloration rate of RB reached 88.1% after 180 min (3 h) of visible light irradiation. However, under the same experimental conditions, when **cat.-Zn** was used as the catalyst, the decoloration rate of RB only reached 47% (Fig. S6). The UV-vis spectrum of compound **1** shows no absorption bands in the visible region, while for compound **2**, the spectrum shows obvious absorption from 400-800 nm, which indicates the charge transfer between the metal-organic fragments and the POM in compound **2** (Fig. S7).<sup>18a</sup> In other words, the Co-tpt coordination fragments in **2** acting as sensitizer can be induced by visible light. On the other hand, the dye RhB has strong absorption for visible light and its excited state has a



rather low redox potential which means, in our system, the dye RhB itself can act as sensitizer.<sup>23</sup> As a result, for **cat.-Zn**, combined with the result of UV-vis spectrum, we can suppose, in the catalytic reaction process, only one sensitizer exists: the dye RhB. While for **cat.-Co**, during the whole catalytic reaction process, two sensitizers coexist: the dye RhB and the Co-tpt coordination fragments, the latter can be concluded from UV-vis spectrum of **cat.-Co** which shows absorption in the visible region.<sup>21</sup> So, after 180 min (3 h) of visible light irradiation, the decoloration rate of RB is much higher when **cat.-Co** was used as the photocatalyst. A proposed photodegradation mechanism of organic dyes is deduced that after excited by visible light, the excited sensitizer injected electrons into the LUMO of the POM, and then these electrons were trapped by H<sub>2</sub>O<sub>2</sub> to yield the oxidizing species OH<sup>•</sup>, further, radicals attack organic substrates and degrade dye (Fig. S8).<sup>28a</sup> The interesting feature of **cat.-Co** lies in the fact that the catalytic unit is decorated by light sensitizing fragments Co-tpt, also called antenna, which strengthens light absorption for the catalytic center and thus increases the photocatalytic yield.



**Fig. 4** Decolorization rates of RB in different reaction systems. Initial concentrations: RB (15 mg L<sup>-1</sup>), **cat.-Co** (0.6 g L<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub> (1.5 mmol L<sup>-1</sup>). (a) RB/**cat.-Co**; (b) RB/H<sub>2</sub>O<sub>2</sub>; (c) RB/**cat.-Co**/H<sub>2</sub>O<sub>2</sub>\_dark; (d) RB/**cat.-Co**/H<sub>2</sub>O<sub>2</sub>\_vis; Inset: UV-vis spectra of the RB solutions after different times of visible light irradiation.

## Conclusions

In conclusion, the strategy of using multidentate ligand and auxiliary ligand is developed to construct the rare 2D organic-inorganic hybrid materials formed by a building block of monovacant Keggin POM bearing a disorder-free 3d transition metal with pendant organic ligands. The special packing model and the strong  $\pi$ - $\pi$  stacking interactions result in a highly stable framework. Due to the tpt molecules as an light harvesting antenna, the framework exhibit good visible light photocatalytic activity in the degradation of rhodamine-B (RB) in the presence of H<sub>2</sub>O<sub>2</sub>. The fabrication of 3D supramolecular framework of this type may find more practical application in POM chemistry and the related work is ongoing.

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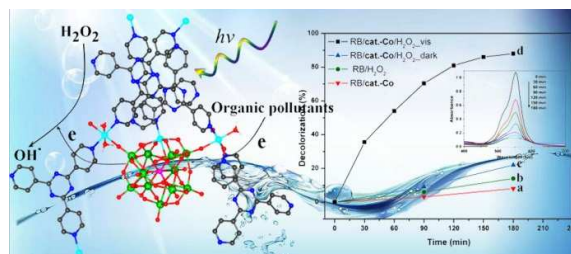
## Notes and references

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† Electronic Supplementary Information (ESI) available: Schemes, figures and CIF files giving additional structural figures, PXRD, TGA, IR and crystallographic data (CCDC 1004589-1004590), and details of experiments. See DOI: 10.1039/b000000x/

- (a) M. T. Pope, Y. Jeannin and M. Fournier, *Heteropoly and isopoly oxometalates*, Springer-Verlag, New York, 1983; (b) M. Pope and A. Müller, *Polyoxometalate chemistry from topology via self-assembly to applications*, Academic Press, Netherlands, 2001; (c) J. J. Borrás-Almenar, E. Coronado and M. Pope, *Polyoxometalate molecular science*, Kluwer Academic Publishers., Dordrecht, The Netherlands, 2003; (d) M. T. Pope and A. Müller, *Angew. Chem. Int. Ed.*, 1991, **30**, 34-48; (e) D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.*, 2010, **49**, 1736-1758; (f) P. Kogerler, B. Tsukerblat and A. Muller, *Dalton Transactions*, 2010, **39**, 21-36; (g) N. Mizuno, K. Yamaguchi and K. Kamata, *Coord. Chem. Rev.*, 2005, **249**, 1944-1956; (h) J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, *Chem. Rev.*, 1998, **98**, 327-358.
- (a) P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77-112; (b) A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009-6048; (c) L. Chen, D. Shi, J. Zhao, Y. Wang, P. Ma, J. Wang and J. Niu, *Crystal Growth & Design*, 2011, **11**, 1913-1923.
- (a) O. Oms, A. Dolbecq and P. Mialane, *Chem. Soc. Rev.*, 2012, **41**, 7497-7536; (b) A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh and G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605-7622.
- (a) I. Bar-Nahum and R. Neumann, *Chem. Commun.*, 2003, 2690-2691; (b) I. Bar-Nahum, H. Cohen and R. Neumann, *Inorg. Chem.*, 2003, **42**, 3677-3684; (c) S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacôte, S. Thorimbert and M. Malacria, *J. Am. Chem. Soc.*, 2005, **127**, 6788-6794.
- (a) R. Neumann, A. M. Khenkin and M. Dahan, *Angew. Chem. Int. Ed.*, 1995, **34**, 1587-1589; (b) C. Rong and M. T. Pope, *J. Am. Chem. Soc.*, 1992, **114**, 2932-2938.
- (a) R. Neumann and M. Dahan, *Nature*, 1997, **388**, 353-355; (b) H. Miao, X. Xu, W.-W. Ju, H.-X. Wan, Y. Zhang, D.-R. Zhu and Y. Xu, *Inorg. Chem.*, 2014, **53**, 2757-2759.
- (a) C. Dablemont, C. G. Hamaker, R. Thouvenot, Z. Sojka, M. Che, E. A. Maatta and A. Proust, *Chemistry – A European Journal*, 2006, **12**, 9150-9160; (b) P. Gouzerh, R. Villanneau, R. Delmont and A. Proust, *Chemistry – A European Journal*, 2000, **6**, 1184-1192; (c) J. F. W. Keana, M. D. Ogan, Y. Lu, M. Beer and J. Varkey, *J. Am. Chem. Soc.*, 1986, **108**, 7957-7963.
- (a) V. Lahootun, C. Besson, R. Villanneau, F. Villain, L.-M. Chamoreau, K. Boubekeur, S. Blanchard, R. Thouvenot and A. Proust, *J. Am. Chem. Soc.*, 2007, **129**, 7127-7135; (b) V. Artero, D. Laurencin, R. Villanneau, R. Thouvenot, P. Herson, P. Gouzerh and

- A. Proust, *Inorg. Chem.*, 2005, **44**, 2826-2835; (c) Y. Sakai, A. Shinohara, K. Hayashi and K. Nomiya, *Eur. J. Inorg. Chem.*, 2006, **2006**, 163-171; (d) M. Sadakane, D. Tsukuma, M. H. Dickman, B. Bassil, U. Kortz, M. Higashijima and W. Ueda, *Dalton Transactions*, 2006, 4271-4276.
- 9 (a) J.-P. Wang, J.-W. Zhao, X.-Y. Duan and J.-Y. Niu, *Crystal Growth & Design*, 2006, **6**, 507-513; (b) H. Liu, C. Qin, Y.-G. Wei, L. Xu, G.-G. Gao, F.-Y. Li and X.-S. Qu, *Inorg. Chem.*, 2008, **47**, 4166-4172; (c) S.-T. Zheng, J. Zhang and G.-Y. Yang, *Angew. Chem. Int. Ed.*, 2008, **47**, 3909-3913; (d) S.-T. Zheng, J. Zhang, X.-X. Li, W.-H. Fang and G.-Y. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 15102-15103.
- 10 R. Cao, K. P. O'Halloran, D. A. Hillesheim, K. I. Hardcastle and C. L. Hill, *CrystEngComm*, 2010, **12**, 1518-1525.
- 11 L.-H. Bi, U. Kortz, B. Keita and L. Nadjo, *Dalton Transactions*, 2004, 3184-3190.
- 12 A. Falber, B. P. Burton-Pye, I. Radivojevic, L. Todaro, R. Saleh, L. C. Francesconi and C. M. Drain, *Eur. J. Inorg. Chem.*, 2009, **2009**, 2459-2466.
- 13 (a) H. Liu, C. J. Gomez-Garcia, J. Peng, J. Sha, Y. Li and Y. Yan, *Dalton Transactions*, 2008, 6211-6218; (b) H. Liu, C. J. Gómez-García, J. Peng, J. Sha, L. Wang and Y. Yan, *Inorg. Chim. Acta*, 2009, **362**, 1957-1962.
- 14 T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2012, **113**, 734-777.
- 15 (a) P.-Q. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2005, **44**, 1190-1192; (b) Y. Wang, F.-Q. Wu, L. Ye, T.-G. Wang, G.-W. Wang, S.-Y. Shi, L.-N. Xiao, X.-B. Cui and J.-Q. Xu, *Inorg. Chem. Commun.*, 2010, **13**, 703-705.
- 16 Y. Zhu, P. Yin, F. Xiao, D. Li, E. Bitterlich, Z. Xiao, J. Zhang, J. Hao, T. Liu, Y. Wang and Y. Wei, *J. Am. Chem. Soc.*, 2013, **135**, 17155-17160.
- 17 Y. Wang, Y. Peng, L.-N. Xiao, Y.-Y. Hu, L.-M. Wang, Z.-M. Gao, T.-G. Wang, F.-Q. Wu, X.-B. Cui and J.-Q. Xu, *CrystEngComm*, 2012, **14**, 1049-1056.
- 18 (a) H. Yang, T. Liu, M. Cao, H. Li, S. Gao and R. Cao, *Chem. Commun.*, 2010, **46**, 2429-2431; (b) J. Lu, J.-X. Lin, X.-L. Zhao and R. Cao, *Chem. Commun.*, 2012, **48**, 669-671.
- 19 (a) L. Qin, Q. Zhang, W. Sun, J. Wang, C. Lu, Y. Cheng and L. Wang, *Dalton Transactions*, 2009, 9388-9391; (b) K. Kalyanasundaram and M. Grätzel, *Coord. Chem. Rev.*, 1998, **177**, 347-414.
- 20 (a) Z. Fu, Y. Chen, J. Zhang and S. Liao, *J. Mater. Chem.*, 2011, **21**, 7895-7897; (b) J. Zhang, Z. Yao, S. Liao, J. Dai and Z. Fu, *Journal of Materials Chemistry A*, 2013, **1**, 4945-4948.
- 21 A. Hiskia, A. Mylonas and E. Papaconstantinou, *Chem. Soc. Rev.*, 2001, **30**, 62-69.
- 22 (a) C. Chen, W. Zhao, P. Lei, J. Zhao and N. Serpone, *Chemistry – A European Journal*, 2004, **10**, 1956-1965; (b) C. Chen, Q. Wang, P. Lei, W. Song, W. Ma and J. Zhao, *Environmental Science & Technology*, 2006, **40**, 3965-3970; (c) Z. Fu, Y. Zeng, X. Liu, D. Song, S. Liao and J. Dai, *Chem. Commun.*, 2012, **48**, 6154-6156.
- 23 T. Takizawa, T. Watanabe and K. Honda, *The Journal of Physical Chemistry*, 1978, **82**, 1391-1396.



Two novel hybrid materials assembled from transition metal mono-substituted Keggin polyoxoanions with antenna molecule were obtained and show photocatalytic activity under visible light.