Supporting information

Organic-inorganic hybrid assemblies based on Ti-substituted polyoxometalates for photocatalytic dye degradation

Li-Jie Xu, Wen-Zhe Zhou, Li-Yuan Zhang, Bin Li, Hong-Ying Zang*, Yong-Hui Wang, Yang-Guang Li*

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1. Additional structural figures for compounds 1-2



Fig. S1 (a) ORTEP diagram of structure of 1 with thermal ellipsoids at 30% probability displacement. All H atoms are omitted for clarity; (b) The polyoxoanion structure in 1; (c) The [CuLo] metal-organic unit in 1.



Fig. S2. Ball-and-stick view of 1-D chain in 1, showing the connection mode between double-Keggin-type POM units and the [CuLo] units. The atoms with the prime (') character indicates that these atoms are at equivalent position (3/2 - x, 1/2 + y, 1/2 - z).



Fig. S3. (a) Packing arrangement of compound 1 viewed along a axis; (b) The packing mode of adjacent 1-D chains in one supramolecular layer viewed along c axis.



Fig. S4 (a) ORTEP diagram of structure of 2 with thermal ellipsoids at 30% probability displacement. All H atoms are omitted for clarity; (b) The polyoxoanion structure in 2; (c) The [CuLo] metal-organic unit in 2.



Fig. S5. Ball-and-stick view of square plane cluster in **2**, showing the connection mode between double-Keggin-type POM units and the [CuLo] units. (The equivalent-position information, A: x, 1+y, z; B: 2-x, -y, 1-z; C: 2-x, 1-y, 1-z)



Fig. S6. Packing arrangement of compound 2 viewed along *a* axis (a) and along [110] direction (b). The cations and lattice water molecules are omitted for clarity.

2. Selected bond lengths and angles for compounds 1-2

Cu(1)-N(2)	1.953(16)	Cu(1)-N(4)	1.971(13)
Cu(1)-N(5)	2.0004(15)	Cu(1)-N(3)	2.052(17)
Cu(1)-O(21)	2.476(5)	Cu(1)-O(77)	2.767(7)
Ti(1)-O(20)	1.797(13)	Ti(1)-O(31)	1.891(11)
Ti(1)-O(22)	1.918(12)	Ti(1)-O(79)	1.932(11)
Ti(1)-O(64)	1.947(12)	Ti(1)-O(83)	2.373(12)
Ti(2)-O(20)	1.758(13)	Ti(2)-O(48)	1.903(13)
Ti(2)-O(81)	1.912(12)	Ti(2)-O(80)	1.932(12)
Ti(2)-O(61)	1.946(12)	Ti(2)-O(8)	2.42(3)
Ti(2)-O(1)	2.427(17)	N(5)-Cu(1)-N(3)	147.8(6)
N(2)-Cu(1)-N(4)	164.2(6)	N(2)-Cu(1)-N(5)	101.1(7)
N(4)-Cu(1)-N(5)	81.1(6)	N(2)-Cu(1)-N(3)	82.8(6)
N(4)-Cu(1)-N(3)	103.7(6)	O(20)-Ti(1)-O(31)	101.0(6)
O(20)-Ti(1)-O(22)	102.4(6)	O(31)-Ti(1)-O(22)	86.0(5)
O(20)-Ti(1)-O(79)	100.9(6)	O(31)-Ti(1)-O(79)	158.1(5)
O(22)-Ti(1)-O(79)	89.5(5)	O(20)-Ti(1)-O(64)	100.8(6)
O(31)-Ti(1)-O(64)	89.7(5)	O(22)-Ti(1)-O(64)	156.8(5)
O(79)-Ti(1)-O(64)	86.1(5)	O(20)-Ti(1)-O(83)	171.4(5)
O(31)-Ti(1)-O(83)	84.7(5)	O(22)-Ti(1)-O(83)	84.3(5)
O(79)-Ti(1)-O(83)	73.5(5)	O(64)-Ti(1)-O(83)	72.6(4)
O(20)-Ti(2)-O(48)	102.9(7)	O(20)-Ti(2)-O(81)	100.2(6)
O(48)-Ti(2)-O(81)	86.4(5)	O(20)-Ti(2)-O(80)	100.1(6)
O(48)-Ti(2)-O(80)	156.9(7)	O(81)-Ti(2)-O(80)	88.1(5)
O(20)-Ti(2)-O(61)	102.3(6)	O(48)-Ti(2)-O(61)	89.6(5)
O(81)-Ti(2)-O(61)	157.5(7)	O(80)-Ti(2)-O(61)	87.1(5)
O(20)-Ti(2)-O(8)	156.7(8)	O(48)-Ti(2)-O(8)	63.3(8)
O(81)-Ti(2)-O(8)	62.0(8)	O(80)-Ti(2)-O(8)	94.4(8)
O(61)-Ti(2)-O(8)	96.5(8)	O(20)-Ti(2)-O(1)	163.8(6)
O(48)-Ti(2)-O(1)	90.1(6)	O(81)-Ti(2)-O(1)	90.0(6)
O(80)-Ti(2)-O(1)	67.5(6)	O(61)-Ti(2)-O(1)	67.8(6)
O(8)-Ti(2)-O(1)	39.2(7)	Ti(2)-O(20)-Ti(1)	158.7(8)

Table S1. Selected bond lengths (Å) and angles (deg) of 1.

Cu(1)-N(5)	1.935(16)	Cu(1)-N(4)	1.951(17)
Cu(1)-N(2)	1.973(17)	Cu(1)-N(1)	2.031(17)
Cu(1A)-O(14)	2.689(2)	Cu(1A)-O(54C)	2.634(2)
Ti(1)-O(59)	1.801(17)	Ti(1)-O(29)	1.873(19)
Ti(1)-O(28)	1.914(16)	Ti(1)-O(15)	1.926(18)
Ti(1)-O(17)	1.938(16)	Ti(1)-O(12)	2.364(16)
Ti(2)-O(59)	1.794(18)	Ti(2)-O(40)	1.915(16)
Ti(2)-O(64)	1.945(19)	Ti(2)-O(53)	1.958(17)
Ti(2)-O(63)	2.01(2)	Ti(2)-O(38)	2.34(2)
N(5)-Cu(1)-N(4)	82.1(8)	N(5)-Cu(1)-N(2)	103.0(8)
N(4)-Cu(1)-N(2)	154.8(8)	N(5)-Cu(1)-N(1)	154.8(8)
N(4)-Cu(1)-N(1)	105.7(8)	N(2)-Cu(1)-N(1)	80.3(8)
O(59)-Ti(1)-O(29)	101.4(8)	O(59)-Ti(1)-O(28)	102.5(8)
O(29)-Ti(1)-O(28)	84.0(8)	O(59)-Ti(1)-O(15)	100.5(8)
O(29)-Ti(1)-O(15)	158.0(7)	O(28)-Ti(1)-O(15)	91.7(8)
O(59)-Ti(1)-O(17)	99.8(8)	O(29)-Ti(1)-O(17)	89.5(8)
O(28)-Ti(1)-O(17)	157.6(7)	O(15)-Ti(1)-O(17)	86.3(7)
O(59)-Ti(1)-O(12)	171.5(8)	O(29)-Ti(1)-O(12)	84.9(7)
O(28)-Ti(1)-O(12)	83.7(7)	O(15)-Ti(1)-O(12)	73.2(6)
O(17)-Ti(1)-O(12)	74.3(6)	O(59)-Ti(2)-O(40)	99.1(8)
O(59)-Ti(2)-O(64)	102.1(8)	O(40)-Ti(2)-O(64)	87.1(9)
O(59)-Ti(2)-O(53)	98.9(8)	O(40)-Ti(2)-O(53)	89.9(8)
O(64)-Ti(2)-O(53)	159.0(8)	O(59)-Ti(2)-O(63)	100.7(8)
O(40)-Ti(2)-O(63)	160.1(8)	O(64)-Ti(2)-O(63)	90.7(8)
O(53)-Ti(2)-O(63)	85.0(7)	O(59)-Ti(2)-O(38)	170.6(8)
O(40)-Ti(2)-O(38)	73.4(7)	O(64)-Ti(2)-O(38)	72.3(7)
O(53)-Ti(2)-O(38)	86.9(7)	O(63)-Ti(2)-O(38)	87.0(7)
Ti(2)-O(59)-Ti(1)	149.2(12)		

Table S2. Selected bond lengths (\AA) and angles (deg) of 2.

Symmetry transformations used to generate equivalent atoms, A: x, 1+y, z; C: 2-x, 1-y, 1-z

3. Synthesis, crystal data and crystal structure of compound 3

3.1. Synthesis of compound 3

[CuLo]₄[PW^VW^{VI}₁₁O₄₀] (3) . The mixture of $[(CH_3)_4N]_7$ [PTi₂W₁₀O₄₀]·4H₂O (0.3125g, 0.1 mmol) and CuCl (0.05g, 0.5mmol) was dissolved in 10 mL of distilled water at room temperature and stirred for 30 min. The pH of above mixture was adjusted to 5.0 with 1M HCl. Then, the above solution and Lo (0.039g, 0.1mmol) were sealed into a Teflon-lined autoclave and kept under autogenous pressure at 180 °C for 5 days. After slow cooling to room temperature, black block crystals were filtered and washed with distilled water (60% yield based on W). Anal. Calcd for $C_{96}H_{80}N_{24}O_{40}PW_{12}Cu_4$: C 24.5, H 1.70, O 7.15. Found: C 24.3, H 1.40, O 7.00. Selected IR (KBr pellet, cm⁻¹): 3648(s), 3108(s), 1606(m), 1498(m), 1437(w), 1364(m), 1228(m), 1159(s), 1079(w), 976(w), 897(w), 816(w).

3.2 Crystal structure of compound 3

Compound **3** crystallizes in monoclinic space group $P2_1/n$. In the compound **3**, the basic structural unit consists of 1-D helical chains $[Cu^{I}Lo]_{\infty}$ and a typical α -Keggin-type one-electron-reduced $[PW_{12}O_{40}]^{4-}$ unit. In the Keggin-type $\{PW_{12}O_{40}\}$ cluster, the central P1 atom of the $\{PW_{12}O_{40}\}$ moiety lies on an inversion center. The four oxygen atoms bonded to P atoms exhibit a two-fold disorder with 50% of site-occupancies for each oxygen group. The 1-D helical chain $[Cu^{I}Lo]_{\infty}$ is composed of two Cu^I centers and Lo ligands with two different configurations. Each Cu^I center exhibits the tetra-coordinated environment with four N atoms derived from two different Lo ligands (Fig. S7). The bond lengths of Cu-N range from 1.943(8) to 2.123(9) Å. Both types of Lo ligands are "anti"-style, as shown in Fig. S8. The distances between two adjacent Cu^I centers are 10.171(7) Å and 7.751(8) Å, respectively. Furthermore, Lo¹ and Lo² ligands are alternately bonded by the Cu^I centers to form the final helical chains along *b* axis with a screw pitch of 16.019(8) Å (Fig. S9). The left- and right- helical chains are parallel with each other along the *bc* plane to form a supramolecular 2-D network. The central space is filled by the Keggin-type polyoxoanions.



Fig. S7. Ball-and-stick view of 1-D helical chain in **3**. The two types of L*o* are colored by red and purple respectively.



Fig. S8. Lo ligands with (a) Lo^1 and (b) Lo^2 configurations in **3**



Fig. S9. One pair of left- and right-helical chains in **3** arranged on the *bc* plane, and the cavities are occupied by the Keggin-type polyoxoanions.

3.3 Crystal data of compound 3

Compounds	3
Formula	$C_{96}H_{80}N_{24}O_{40}PW_{12}Cu_4$
Mr	4701.17
<i>T</i> /K	296(2)
Cryst. Syst.	Monoclinic
Space group	$P2_{1}/n$
a/Å	15.9375(9)
<i>b</i> /Å	16.0198(9)
$c/\text{\AA}$	23.1712(14)
a (°)	90
β (°)	91.9510(10)
γ (°)	90
$V/\text{\AA}^3$	5912.5(6)
Ζ	2
μ/mm^{-1}	12.423
<i>F</i> (000)	4326
Refls	43680
R _{int}	0.0893
GOF	0.994
$R_1 [I > 2 \sigma (I)]^a$	0.0481
w $R_2(all data)^b$	0.1209
$\Delta \rho_{\text{max.min}}/\text{e} \text{ Å}^{-3}$	1.556 and -1.675

Table S3 Crystal data and structure refinement for 3

 $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; {}^{b} w R_2 = \Sigma [w(F_o{}^2 - F_c{}^2)^2] / \Sigma [w(F_o{}^2)^2]^{1/2}$

Table S4 Selected bond lengths (Å) and angles (deg) of $\mathbf{3}$

Cu(1)-N(6)	1.943(8)	Cu(1)-N(4)	2.010(9)
Cu(1)-N(5)	2.030(10)	Cu(1)-N(7)	2.123(9)
Cu(2)-N(12)	2.020(9)	Cu(2)-N(2)#2	2.038(8)
Cu(2)-N(9)#2	2.043(10)	Cu(2)-N(11)	2.055(9)
N(6)-Cu(1)-N(4)	134.4(4)	N(6)-Cu(1)-N(5)	133.7(4)
N(4)-Cu(1)-N(5)	82.0(4)	N(6)-Cu(1)-N(7)	80.6(3)
N(4)-Cu(1)-N(7)	114.0(4)	N(5)-Cu(1)-N(7)	113.6(4)
N(12)-Cu(2)-N(2)#2	118.2(4)	N(12)-Cu(2)-N(9)#2	125.8(4)
N(2)#2-Cu(2)-N(9)#2	79.9(4)	N(12)-Cu(2)-N(11)	79.9(4)
N(2)#2-Cu(2)-N(11)	136.0(4)	N(9)#2-Cu(2)-N(11)	123.8(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z; #2 -x+1/2,y+1/2,-z+1/2

4. Additional measurements for compounds 1-3



4.1 XPS spectra

Fig. S10 XPS spectra of W4f level of compound **3**. The XPS of **3** show four partially overlapped peaks, and the fit of curve provides with positions of these four peaks at 37.46, 36.95, 35.3 and 34.8 eV attributing to $W^{VI} 4f_{5/2}$, $W^{V} 4f_{5/2}$, $W^{VI} 4f_{7/2}$ and $W^{V} 4f_{7/2}$, respectively. The ratios of the peak are for W^{V} to W^{VI} is ca. 1 : 11.

4.2 IR spectra of compound 1-3

In the IR spectra of compound 1, there are four characteristic peaks which can be attributed to v(P-O), v(W=Od), v(W-Ob-W) and v(W-Oc-W), appearing at 1069, 966, 892, and 810 cm⁻¹, respectively. The peaks in the regions of 1614-1162 cm⁻¹ are belong to the vibrations of the v(C=C), v(C=N) and v(C=N) in phenyl, pyridyl and pyrazole rings of Lo ligand. The peak at 3417 cm⁻¹ is attributed to the vibration of $v(H_2O)$.



Fig. S11 IR Spectrum of compound 1.

In the IR spectra of compound **2**, there are four characteristic peaks which can be attributed to v(P-O), v(W=Od), v(W-Ob-W) and v(W-Oc-W), appearing at 1071, 969, 891, and 809 cm⁻¹, respectively. The peaks in the regions of 1614-1234 cm⁻¹ are belong to the vibrations of the v(C=C), v(C=N) and v(C=N) in phenyl, pyridyl and pyrazole rings of L*o* ligand. The peak at 3447 cm⁻¹ is attributed to the vibration of v(H₂O).



Fig. S12 IR Spectrum of compound 2.

In the IR spectra of compound **3**, there are four characteristic peaks which can be attributed to v(P-O), v(W=Od), v(W-Ob-W) and v(W-Oc-W), appearing at 1079, 976, 897, and 816 cm⁻¹, respectively. The peaks in the regions of 1606-1159 cm⁻¹ are belong to the vibrations of the v(C=C), v(C=N) and v(C=N) in phenyl, pyridyl and pyrazole rings of Lo ligand. The peak at 3442 cm⁻¹ is attributed to the vibration of v(H₂O).



Fig. S13 IR Spectrum of compound 3.

4.3 TG analyses of compound 1-3

The TG curve of compound **1** suggests that the first weight loss is 1.29 % from 90-120 °C, attributed to the loss of lattice water molecules (calc. 1.12 %). The following two-step continuous weight losses of 13.77 % from 300-750 °C is ascribed to the decomposition and loss of L*o* ligand and $[(CH_3)_4N]^+$ cations (calc. 12.99 %) (**Fig. S14**). The TG curve of co mpound **2** shows the first weight loss of 0.43 % in the temperature range of 90-110 °C, ascribed to the loss of lattice water molecules (calc. 0.4 %). The following two-step continuous weight losses are 14.78 % from 340-780 °C, attributed to the decomposition and loss of L*o*, bpp and $[(CH_3)_4N]^+$ cations (calc. 14.77 %) (**Fig. S15**). The TG curve of compound **3** exhibits two-step continuous weight losses (33.55 %) from 310 to 850 °C, corresponding to the loss of L*o* ligand (33.34 %) (**Fig. S16**).



Fig.S14 TG curve of compound 1.



Fig. S15 TG curve of compound 2.



Fig. S16 TG curve of compound 3.

4.4 The PXRD patterns of compound 3.



Fig. S17 The PXRD patterns of compound**3** with simulated (black, below), as-synthesized (Orange) and blue curve (after four-circle of catalytic process)

5. Four-cycle photocatalytic experiment results of compounds 1-3



Fig. S18 Four-cycle photocatalytic experiment results for compound 1.



Fig. S19 Four-cycle photocatalytic experiment results for compound 2.



Fig. S20 Four-cycle photocatalytic experiment results for compound 3.



Fig. S21 Photocatalytic degradation of MB over compound **2** photocatalyst alone and with the addition of IPA or BQ.

Supposed Mechanism

$$POM + hv \rightarrow POM_{ox}^{*} \leftrightarrow POM(e^{-} + h^{+}) \quad (1)$$

$$POM_{ox}^{*} + MB \rightarrow POM_{red} + MB_{ox} \qquad (2)$$

$$POM_{ox}^{*} + H_{2}O \rightarrow POM_{red} + OH^{-} + H^{+} \qquad (3a)$$

$$OH^{-} + MB \rightarrow MB_{ox} \qquad (3b)$$

$$POM_{red} + O_{2} + 4H^{+} \rightarrow POM + H_{2}O \qquad (4)$$

$$\begin{array}{l}
O_2 + e^- \rightarrow & \cdot & O_2^- \\
 & \cdot & O_2^- + MB \rightarrow MB_{ox}
\end{array}$$
(5)

Polyoxometalates (POMs) have been observed to possess the similar photocatalytic properties with those of semi-conductors such as titanium oxide (TiO₂).^{1,2} In POM compounds, the energy level difference between HOMO and LUMO is analogous to the one between valence band (VB) and conductive band (CB) of semi-conductors. Thus, under light irradiation, the electron transferred to the M_{5d} orbits of POMs can be viewed as the photoelectron (e⁻), while the vacant site on the O_{2p} orbitals due to the electron-transition can be viewed as the photohole (h⁺), as shown in **equation (1)**. POM_{ox}^{*} represents the excited state of POM, which exhibits strong oxidative property and can directly oxidize the organic substrate (MB) (as shown in **equation (2)**). Furthermore, when water was used as the solvent media, the POM_{ox}^{*} species may also react with H₂O to form active hydroxyl radicals (OH[•]), which may also oxidize the MB into the degradative products (MB_{ox}) (as shown in **equation (3)**). In such reaction system, the reductive POM species (POM_{red}) exhibits no photocatalytic activity, and must be quickly oxidized into the POM_{ox} species again so as to continue the catalytic reactions. Generally, the O₂ in the reaction system can easily oxidize the POM_{red} species into the active POM species (as shown in **equation (4)**).

In order to confirm the above supposed mechanism, especially verify that the hydroxyl radicals (OH[•]) do emerge during the reaction process and participate in the catalytic reactions, we use the isopropyl alcohol (IPA) as the hydroxyl radical (OH[•]) scavenger and introduce IPA into the photocatalytic MB degradation reaction system.^{3,4} As shown in Fig. S21, the photocatalytic degradation of MB was dramatically depressed by the addition of 1 mM IPA (a quencher of OH[•]), which indicated that OH[•] radicals play a crucial role in the process of MB oxidation.

Moreover, the organic substrate (MB) could be also oxidized by the superoxide radical (O_2), which might formed in the reaction system by virtue of combination of photoelectron (e⁻) and O₂ molecule (see equation (5) and (6)). To verify such possible mechanism, the 1,4-benzoquinone (BQ) was introduced into the reaction system as the superoxide radical (O_2) scavenger. As shown in Fig. S21, the photocatalytic degradation of MB was just slightly depressed by the addition of 1 mM BQ, suggesting that no obvious superoxide radicals were generated, and the supposed mechanism may not involve in the reaction process of equation (5) and (6). Reference:

[1] O.M. Alfano, D. Bahnemann, R. Dillert, R. Goslich, Catal. Today, 2000, 58, 199.

[2] X. D. Yu, Y. N. Guo, L.L. Xu, X. Yang, Y. H. Guo, Colloids and Surfaces A: Physicochem. Eng. Aspects, 2008, 316, 110.

[3] T.G. Xu, L.W. Zhang, H.Y. Cheng, Y.F. Zhu, Appl. Catal. B: Environ. 2011, 101, 382.

[4] H.W. Huang, K. Liu, K. Chen, Y.L. Zhang, Y.H. Zhang, S.C. Wang, J. Phys. Chem. C., 2014, 118, 14379.



Fig. S22 Plot of C_t/C_0 of MB versus reaction time

The photocatalytic MB degradation activities of compounds **1**, **2**, **3** and P25-type TiO_2 were measured. As shown in Fig. S22, the photocatalytic activities of compounds **1** and **2** (Ti-based POMs) are better than the one of P25-type TiO_2 . The photocatalytic activity of compound **3** ($[PW_{12}O_{40}]$) is lower than the one of P25-type TiO_2 . Such experimental results suggest that the introduction of Ti elements into the POM structures may promote the electron transition and the easy generation of photoelectron (e⁻) and photohole (h⁺). Moreover, the introduced Ti element may help the separation of photoelectron (e⁻) and photohole (h⁺), or the Ti_2O groups that introduced owns the photocatalytic activity, which accelerate the photocatalytic reaction.