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# Construction and catalytic activities of polyoxometalate-based compound containing helical chains

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A polyoxometalate-based, inorganic-organic hybrid compound containing a helical structure along the *a* axis,  $[Ag(pyttz)_2][H_2PW_{12}O_{40}]\cdot 2H_2O$  (*p*-pyttz = 3-(pyrid-4-yl)-5-(1H-1,2,4-triazol-3yl)-1,2,4-triazolyl), has been isolated and structurally characterized. Single-crystal X-ray diffraction analysis reveals that the new compound possesses two helical channels constructed by the left- and right-handed helical chains, respectively, which are fused together through sharing POMs dimer fabricating a 3D framework with  $\{4^4 \cdot 5^3 \cdot 6^3\}$  { $4^4 \cdot 5^3 \cdot 6^3$ } topolopy. The new compound displays good acid-catalytic activity toward the synthesis of Aspirin and good oxidation-catalytic activity to the decomposition of Rhodamine B dye; the catalytic reaction kinetics are discussed.

Keywords: Polyoxometalates; Supramolecule; Helix; Acid-catalysis; Oxidation-catalysis

#### 1. Introduction

Supramolecular chemistry, an important part of crystal engineering, has been defined as understanding chemistry beyond the molecule [1-4]. Compared to discrete compounds, combination of molecules through non-covalent bonds can enhance or even generate new properties [5, 6], such as conductivity, porosity, magnetism and nonlinear optical properties [7-10]. Although non-covalent bonds are weak bonds, they are very important in crystallography,

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supporting the dimensionality and stabilization of the crystal structure. Many biological macromolecules, such as proteins and nucleic acids, use all kinds of intermolecular or intramolecular non-covalent bonds to achieve a high degree of order and advanced structure [11-13]. One of the goals in supramolecular synthesis is to construct highly complex hybrid compounds depending on intermolecular forces [14, 15], such as hydrogen bonding (O–H···O, C–H···N, N–H···O, O–H···N, C–H···O, *etc.*), aryl packing ( $\pi$ ··· $\pi$ , C–H··· $\pi$  and N–H··· $\pi$ ) and other short-range forces [16-18].

Inorganic-organic hybrid supramolecular compounds have captivated interest due to the range of applications [19-21]. Polyoxometalates (POMs), as significant metal oxide clusters with nanosizes and abundant properties, can be viewed as versatile building blocks for construction of new supramolecular materials [22-25]. POMs have been employed for constructing supramolecular arrays with various organic and transition-metal complexes (TMCs) [26, 27]. A current development is to fabricate helical supramolecular polymers [28, 29], because living organisms utilize helices to store and transmit genetic information, and these helical compounds have applications in optical devices and asymmetric catalysis [30-32]. Although a number of supramolecular compounds based on POMs (POMSCs) have been assembled, POMSCs with helical structures are scarce. The first such structure was the vanadium phosphate based architecture reported by Zubieta in 1993 [33]. In 2006, two new enantiomerically pure 3D POMs-based frameworks were described by E.B. Wang [34], and the first POM-templated 3D frameworks were obtained by G.Y. Yang in 2009 [35, 36]. Since then, some POM-based compounds with helical features have been reported [37, 38]. Our group also synthesized a series of helical POM-based compounds [39-44]; the p-pyttz ligand (3-(pyrid-4-yl)-5-(1H-1,2,4-triazol-3-yl)-1,2,4-triazolyl) (scheme S1) is advantageous to construct a helix owing to the conjugated heterocycle with rigid plane and abundant coordinated nitrogens. Inspired by the aforementioned considerations, herein, we chose classical Keggin POMs and Ag/pyttz as modifiers to construct the inorganic-organic hybrid compound with helical structure. A new supramolecular compound with left- and right-handed helical channels,  $[Ag(pyttz)_2][H_2PW_{12}O_{40}]\cdot 2H_2O$ , was isolated. In addition, the acid-catalytic and oxidation-catalytic activities of the new compound were discussed.

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#### 2. Experimental

#### 2.1. Materials and general procedures

The *p*-pyttz was purchased from the chemical company of Jinan Henghua and other reagents were commercially available and used without purification. Elemental analyses (C, H and N) were obtained on a Perkin Elmer 2400 CHN Elemental analyzer. The IR spectrum was obtained on an Alpha Centaurt FT/IR spectrometer as a KBr pellet from 400–4000 cm<sup>-1</sup>. The XRPD was obtained with a Rigaku D/max 2500V PC diffractometer with Cu-K $\alpha$  radiation with scanning rate of 4°/s, 2 $\theta$  ranging from 5-40°. The thermogravimetric analysis was carried out on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 °C·min<sup>-1</sup>. UV-vis absorption spectra were recorded on a 756 CRT UV-vis spectrophotometer.

#### 2.2. Synthesis of $[Ag(pyttz)_2][H_2PW_{12}O_{40}]$ $\Box H_2O(1)$

A solution of  $H_3PW_{12}O_{40}$  (600 mg),  $H_2pyttz$  (90 mg), AgNO<sub>3</sub> (200 mg), NH<sub>4</sub>VO<sub>3</sub> (20 mg) and  $H_2O$  (12 mL) was stirred for 30 min at room temperature, and the pH was then adjusted to 4.5 with 1M HCl, and the mixture was transferred to a 20 mL Teflon-lined reactor. After 3 days heating at 180 °C, the reactor was slowly cooled to room temperature. Red block crystals of **1** were filtered, washed with water, and dried at room temperature (30% yield based on Ag). *Anal.* Calc. for  $C_{18}H_{18}W_{12}AgN_{14}O_{42}P$  (3447.38): found C, 6.27; H, 0.52; N, 5.69 %; calcd. C, 6.30; H, 0.65; N, 5.71%.

#### 2.3. X-ray crystallography

Crystal data for **1** was collected on an Agilent Technology Eos Dual system with focusing multilayer mirror optics and a Mo-K $\alpha$  source ( $\lambda = 0.71073$  Å). Empirical absorption corrections were applied to the intensities using SADABS [45]. The structure was solved by direct methods and refined by full matrix least squares on F<sup>2</sup> using the SHELXTL crystallographic software package [46, 47]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. All hydrogens of *p*-pyttz were included in their idealized positions. To solve problems of ADP, the command "ISOR" was used to restrain the non-H atoms such as O2, O4, O11, C1. The crystal data and structure refinements are summarized in table 1.

#### 2.4. Catalytic degradation of Rhodamine-B

Compound **1** (50 mg) was mixed with 100 ml of  $1.0 \times 10^{-5}$  mol/L (C<sub>0</sub>) RhB solution in a beaker by ultrasonic dispersion for 10 min. The mixture was stirred for 0.5 h in the dark to reach surface-adsorption equilibrium on particles of **1**. Then, the mixture was stirred continuously under ultraviolet (UV) irradiation from a 125 W high pressure Hg lamp. At 0, 10, 20, 30, 40, 50, 60 and 90 min, 3 ml of the sample was taken from the beaker, followed by several centrifugations to remove **1** and a clear solution obtained for UV-vis analysis.

#### 2.5. Catalytic synthesis of Aspirin

1.5 g of salicylic acid was transferred to a 50 mL dry three-necked flask, to which 3.0 mL of acetic anhydride and 0.04 mg of **1** were added. The reaction was then carried out in a water bath (70-90 °C) for 60 min. During each 5 min interval, 10  $\mu$ l of sample was taken out and diluted with PBS for UV-vis analysis. The contents of salicylic acid (SA) and Aspirin (ASP) were measured by ultraviolet two-wavelength isoabsorption spectrophotometry, which has been proved to be highly reliabile, accurate, reproducible, and easy (ESI<sup>+</sup> and equations 1 and 2).

 $C_{SA} = 43.787A_{297} - 16.609A_{270} + 0.548$  (1)

 $C_{ASP} = 378.103A_{270} - 86.207A_{297} - 3.739 \quad (2)$ 

#### 3. Results and discussion

During synthesis of **1**, parallel experiments indicate that the use of NH<sub>4</sub>VO<sub>3</sub> is necessary for isolation of the compound, although it was not involved in the final structure. NH<sub>4</sub>VO<sub>3</sub> may play a role of mineralization. The bond valence sum (BVS) calculations [48] (S = exp[ $\sum$ -(R-Ro)/B]; S = bond valence, R = bond length) indicate all Ag ions are +1 and twelve W +6 oxidation states. Combining the results of elemental analysis, bond valence sum (BVS) calculations, coordination geometries and charge balance, **1** is formulated as [Ag(pyttz)<sub>2</sub>][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>]·2H<sub>2</sub>O.

#### 3.1. Structure description of 1

Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** is made up of one Ag ion, two pyttz molecules, one  $[PW_{12}O_{40}]^{3-}$  polyoxoanion  $(PW_{12})$  and two water molecules (figure 1). There are two crystallographically unique pyttz molecules, which coordinate with Ag

ions  $[Ag(pyttz)_2]^+$ , and the length of Ag-N bonds are 2.24(1) – 2.47(2) Å ( $d_{Ag1...N6} = 2.248$  Å,  $d_{Ag1...N12} = 2.290$  Å,  $d_{Ag1...N9} = 2.417$  Å,  $d_{Ag1...N4} = 2.463$  Å).

Supramolecular interactions play vital roles to stabilize the whole structure of 1 (figure S1), provided in table 2. As shown in figure 2, each  $PW_{12}$  cluster links with three  $[Ag(pyttz)_2]^+$  subunits and another two PW<sub>12</sub> clusters via O···C, O···N and O···O bonds. Each  $[Ag(pyttz)_2]^+$  subunit connects with three PW<sub>12</sub> clusters and another  $[Ag(pyttz)_2]^+$  subunit via O…C, O…N and N…C bonds. As a result, PW<sub>12</sub> clusters and [Ag(pyttz)<sub>2</sub>]<sup>+</sup> subunits alternately array through intermolecular and intramolecular bonds (O29...N10, O5...C7,O6...C8, O28...C1, O8...N7, O22...C18) forming two kinds of 1D supramolecular chains with different orientation along the *a* axis. Then 1D chains with different orientation link through aryl stacking  $(d_{C3}...D_2 =$  $3.596 \text{ Å}, d_{C2...D2} = 3.641 \text{ Å}, d_{N11...D3} = 3.681 \text{ Å}, d_{1\#N13...D4} = 3.791 \text{ Å}, d_{2\#N13...D1} = 3.791 \text{ Å},$  $d_{N14...D1} = 3.829$  Å,  $d_{D2...D5} = 3.939$  Å) in a manner of "clothes buttons" obtaining 1D double chains (figure 3a). Furthermore, adjacent 1D double chains fuse through short contact bonds  $(d_{09}..._{025} = 2.913 \text{ Å})$  forming 2D sheets (figure 3b), Finally, 2D sheets are stacked stabilizing the whole 3D framework *via* short-range forces ( $d_{O16}$ ... $c_{15}$  = 3.792 Å,  $d_{O33}$ ... $o_{n13}$  = 3.124 Å,  $d_{O35...N1} = 3.550$  Å and  $d_{O25...O5} = 3.037$  Å) (figure 3c). To simplify the structure, the PW<sub>12</sub> cluster and  $[Ag(pyttz)_2]^+$  subunit as 5-connected, the 3D structure can be rationalized as a (5,5) connecting network with  $\{4^4 \cdot 5^3 \cdot 6^3\}$   $\{4^4 \cdot 5^3 \cdot 6^3\}$  topolopy (figure 3d).

Further investigation reveals that the 3D supramolecular network of **1** possesses a helical channel. More specifically,  $PW_{12}$  clusters and  $[Ag(pytz)_2]$  subunits alternately array fabricating left- and right-handed helical chains with 13.568 Å pitch of screw along the *a* axis *via* the Ag-Ag-Ag-POMs-POMs-Ag- Ag-Ag-POMs shown in figure 4. Although the left- and right-handed helical chains are composed of the same components, the spatial positions of  $PW_{12}$  clusters result in different helical structures. There are two types of spatial positions of POMs (position A and B) shown in figure 5a, which are connected through O9...O25 short range bond forming a POM dimer. The structures are complementary contrary and can convert through two mirror symmetries shown in figure 5b. As a result, two  $PW_{12}$  clusters of different position link with  $[Ag(pyttz)_2]$  subunits along different directions forming left- and right-handed helical chains are perfectly enclosed by sharing a POM dimer giving the final 3D framework (figure 5d).

#### 3.2. XRPD and FT-IR characterization

The XRPD pattern for **1** is presented in figure S2. The diffraction peaks of both simulated and experimental patterns match well, except for a little difference in reflection intensities, indicating that **1** is a pure phase. The difference may be due to different orientation of the crystals in the powder samples. The IR spectrum is shown in figure S3. Characteristic bands at 1072, 957 and 792 cm<sup>-1</sup> are attributed to v(P-O), v(W=O) and v(W-O-W), respectively. Bands from 1610-1299 cm<sup>-1</sup> are attributed to pyttz. XRPD and IR of **1** have similar peak position and intensity before and after photodegradation of RhB shown in figures S2 and S3, which confirms the stability and purity of **1** as photocatalyst.

#### 3.3. Thermal properties

The thermal analysis of **1** (figure S4) gives a total loss of 13.42% from 279-760 °C, which agrees with the calculated weight loss of 13.35%. The first weight loss of 1.05% at 270-320 °C corresponds to loss of water molecules (calc. 1.04%). The second weight loss of 12.37% at 350-760 °C arises from decomposition of pyttz molecules (cale. 12.31%). The results further confirm the formula of **1**.

#### 3.4. Photo-catalytical degradation of RhB

To investigate the photocatalytic activities of **1** as catalyst, the photodecomposition of Rhodamine-B (RhB) is evaluated under UV light irradiation. As shown in figure 6, after 90 min the photocatalytic decomposition rate, defined as  $1-C/C_0$ , is 67.7%. However the decomposition rate is 50.8% using (NBu<sub>4</sub>)<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] as catalyst and 13% without catalyst at the same conditions, which indicates that the formation of hybrid compound improves the photocatalytic performance of the POMs. Comparing with other similar POM-based compounds containing Keggin polyoxoanion, the different photocatalytic activities (*ca*. 60-80% for XY<sub>12</sub>O<sub>40</sub> [49-51], (X = P or Si; Y = W or Mo) may arise from the different TMCs acting as photosensitizer under UV light, which leads to inequivalent transition of electrons to POMs.

In order to quantitatively understand the reaction kinetics for degradation of RhB dye, we applied pseudo-first order model (the initial concentration of pollutant is low  $(1.0 \times 10^{-5})$ ) [52] as expressed by equation 3 to obtain the rate constant (k):

$$-\ln\left(\frac{C_n}{C_0}\right) = kt(3)$$

where  $C_0$  is the initial concentration (0 min) of the RhB aqueous solution and  $C_n$  is the concentration of the RhB aqueous solution for different times, t is the time and the rate constant k is pseudo-first order. According to equation 3, k values for degradation of RhB solutions are 0.013 and 0.008 for **1** and matrix, respectively. These results also illustrate that formation of organic-inorganic hybrid compounds can improve the photocatalytic performance of POMs. Compound **1** is readily isolated from the reaction mixture by filtration and the catalytic activity for subsequent runs show little changes (67.7% for the first cycle, 66.3% for the second cycle, 66.1% for the third cycle, 65.3% for the fourth cycle, 64.6% for the fifth cycle), indicating **1** is stable and may be a potential photocatalyst to decompose some organic dyes.

#### 3.5. Acid-catalytic synthesis of Aspirin

The influence of reaction temperature and time on catalytic synthesis of Aspirin are shown in figure 7 and tables S3 and S4 (Supporting Information). From figure 7, at the same reaction time, the higher temperature gives higher conversion rate of salicylic acid, better reaction yield of Aspirin and selectivity of catalyst. The conversion rate of salicylic acid, the yield of Aspirin, and the selectivity of catalyst are significantly increased with increasing time during the initial period of 5-40 min. The three physical quantities increase slowly with the temperature rising after 40 min. When the reaction temperature is higher than 90 °C, the yield of Aspirin changes in an irregular manner, perhaps due to side effects. So reaction time of 40 min and temperature of 85 °C were employed in the system, resulting in conversion rate of salicylic acid of 97.37%, yield of Aspirin of 80.56%, and selectivity of catalyst of 82.73%.

In order to quantitatively understand the reaction kinetics for the synthesis of Aspirin by using **1** as catalyst, the reaction rate equation model is set up to obtain the rate constant (k) and reaction order (n):

 $r_{SA} = d C_{SA}/dt = k C_{SA}^{n} \quad (4)$ 

 $\ln(dCSA/dt) = \ln k + n\ln CSA(5)$ 

where  $C_{SA}$  is the concentration of the salicylic acid aqueous solution for different time and t is the time, respectively. Figure 8 shows the reaction kinetic analysis at 85 °C; the k and n values are 0.1672 and 1.3891, respectively. The correlation coefficient (R) also shows good statistics values. The rate equation is obtained as:

$$r_{\rm SA} = 0.1672 \, {\rm C_{SA}}^{1.3891} \quad (6)$$

#### 4. Conclusion

A new supramolecular compound with helical configuration based on  $PW_{12}$  clusters and Ag-pyttz subunits has been synthesized under hydrothermal conditions. The pyttz and POMs are excellent supramolecular synthons, which can generate hydrogen bonds to increase the stability of a supramolecular network. The new compound exhibits good acid- and oxidation-catalytic activities, revealing potential applications of various POM-based compounds in catalysis.

#### Appendix A. Supplementary data

Crystallographic data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data\_request/cif. X-ray crystallographic files, IR, XRPD, TG, structural figures and tables for **1** are also avaliable free of charge *via* http://pubs.acs.org.

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	Chemical formula	O42P1W12C18Ag1N14H18			
	Formula weight	3447.38			
	CCDC	966147			
	Temperature (K)	298(2)			
	Wavelength (Å)	0.71073			
	Crystal system	Orthorhombic			
	Space group	P -1			
	a (Å)	13.568 (5)			
	b (Å)	13.750(5)			
	c (Å)	17.143(5)			
	a (°)	77.429(5			
	β (°)	82.160(5)			
	γ (°)	62.938(5			
	V (Å <sup>3</sup> ) / Z	2777.2 / 4			
	Density (g⋅cm <sup>-3</sup> )	4.123			
	Abs. coeff. (mm <sup>-1</sup> )	15.533			
	F(000)	3020.0			
	Data collect θ range (°)	3.201 to 24.997			
	Refins. collected	18333			
	Independent refins.	9763			
	Rint	0.0436			
	Refinement method on F <sup>2</sup>	Full-matrix least-squares			
	Data / restraints / parameters	9763 / 42 / 783			
((	Goodness-of-fit on F <sup>2</sup>	1.046			
(C)	Final R indices $[I > 2\delta(I)]$	R1 = 0.0674, wR2 = 0.1747			
	R indices (all data)	R1 = 0.0837, wR2 = 0.1907			
$\vee$	Largest diff. peak and hole (e.Å <sup>-3</sup> )	5.564 and -6.106			
	$R_1 = \Sigma(  F_0  -  F_c  ) / \Sigma  F_0 , wR_2 = \Sigma w( F_0 ^2 -  F_c ^2)^2 / \Sigma w( F_0 ^2)^2]^{1/2}$				

Table 1. Crystal data and structure refinements for 1.

D…A	Å	D…A	Å	
02509	3.037	N5…C10	2.872	
020…05	2.913	N13…C9	3.265	/
O8…N7	3.444	N14…C9	3.517	
022…C18	3.442	O33…N13	3.124	
028…C1	3.525	O16…C16	3.792	
O29…N10	3.337	O5…C7	3.005	

Table 2. Distances involving short-range forces in 1.



Figure 1. (a) Ball/stick representation of the fundamental building block of **1**. Only Ag ions are labeled; water molecules and hydrogens are omitted for clarity. (b) Ball/stick representation of  $[Ag(pyttz)_2]^+$  subunits constructed by two pyttz ligands and Ag ions.



Figure 2. Ball/stick representation of the connection of  $PW_{12}$  cluster (left) and  $[Ag(pyttz)_2]$  subunit (right).

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Figure 3. Combined ball/stick/polyhedron representation of the formation of 3D supramolecular structure *via* intermolecular and intramolecular interactions. (a) 1D double chain constructed by 1D single chains with the different orientation through aryl stacking and hydrogen bond in a manner of "clothes buttons" (12). (b) 2D sheet through O9...O25 short contact bonds (3). (c) The whole 3D framework constructed by 2D sheets through intermolecular force (456). (d) Topological representations of the whole 3D framework.



Figure 4. Ball-and-stick and topological representations of left- and right-handed helical chains constructed by the [Ag(pyttz)<sub>2</sub>] subunits and POMs.



Figure 5. (a) Ball/stick representation of the complementary contrary POMs. (b) The transformation of position A and position B through twice mirror symmetry. (c) The formation of the left- and right-handed helical chains along different directions. (d) The whole 3D framework constructed by left- and right-handed helical chains by sharing POM dimer.



Figure 6. (a) Evolution of UV-vis absorption spectra 90 min of illumination for the photodegradation of RhB by 1 and  $(NBu_4)_3[PW_{12}O_{40}]$ . (b) Time dependence of RhB concentration over 1,  $(NBu_4)_3[PW_{12}O_{40}]$  and no catalyst. (c) Kinetics of weight-based photocatalytic degradation of RhB dye by the catalysts and first-order kinetics with catalysts. (d) Recycling experiments using 1 for photocatalytic degradation of MB solution.



Figure 7. Catalytic activity of **1**: Yield of Aspirin *vs* temperature (a) and time (d); conversion of salicylic acid *vs* temperature (b) and time (e); and catalytic selectivity *vs* temperature (c) and time (f).



Figure 8. Concentration and conversion change of salicylic acid with time (left) and the linear relation of  $\ln ( \Delta C_{SA} / \Delta t)$  with  $\ln C_{SA}$  at 85 °C.

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### Graphical abstract

