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Molecular assemblies based on the template-directing effect of anionic polyoxometalate clusters and organic cationic flexibility

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ABSTRACT

Molecular assembly processes by utilizing the template-directing effect of anionic polyoxometalate clusters and the flexible organic cation have achieved three hybrids: $(H_2bpp)(Hbpp)[PMo_{12}O_{40}]\cdot 3DMF$ (**1**), $(H_2bpp)(Hbpp)(bpp)_2$ $[PMo_9V_3O_{40}(VO)_2]_2$ (**2**), and $(H_2bpp)_2[\beta\text{-}Mo_8O_{26}]$ (**3**) (bpp = 1,3-bis(4-pyridyl)propane). Three compounds were characterized using single crystal X-ray crystallography, elemental analysis, IR, XPS, EPR, voltammetric behavior and TGA. Crystal structural analyses revealed that compounds **1**–**3** were all constructed from protonated organic bpp cations with different POM clusters: isolated α-Keggin P–Mo cluster in **1**; dimer of bi-capped α-Keggin P–Mo–V anions linked through a $\{V_2O_2\}$ unit in **2**; β-octamolybdate isopolyanion in **3**, respectively. All three assemblies demonstrated a higher thermal stability. The protonated bpp cations lost at temperature higher than 300 °C that the strong intermolecular interactions may account for the high initial temperature of weight loss. The electrochemistry property of compound **2** modified carbon paste electrode was also studied in 1 M H_2SO_4 aqueous.

1. Introduction

Polyoxometalate (POM) clusters with unrivalled structural diversity offer interesting and exciting perspectives for the design of hybrid materials. POMs have been investigated in many important aspects of chemistry such as catalysis, non-linear optical materials, and medicine [1–5]. POMs have been employed as important inorganic building blocks for constructing novel hybrid materials with various organic molecules [6–11]. In this respect, supramolecular assemblies are of interest because their intriguing physical properties result from their versatile architectures and weak intermolecular interactions. Such assemblies not only combine the advantages of organic molecules, such as structural fine-tuning, but also the close interaction and synergistic effect of organic group and metal-oxo cluster [12,13]. A current development is to explore novel lattice architectures resulting from the association of organic molecules and POM anions. POM chemistry has also become one of many areas in inorganic chemistry that is developing most rapidly [14–16].

Supramolecular chemistry has been defined as the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties [17–19]. Plenty of oxygen atoms located on the spherical surface of POMs offer better opportunities to fabricate hydrogen bonds with organic moieties. Therefore, POM anions as a template agent may direct the ordered assembly of organic moieties through directional hydrogen bonds involving N–H···O and C–H···O. We are interested in the 'template' synthesis of new POM-based supramolecular assemblies through weak non-covalent interactions which occur between surface oxygen atoms of POMs and organic molecules containing phenyl, pyridine, and/or carboxylate groups. In our ongoing efforts to develop synthetic and functional analogues of POM-based hybrids [20,21], we previously reported a new family of supramolecular architectures based on POM anions and decorated bipyridine cations with rigid and conjugated structures such as 2,4′-bipyridine (bpy), 4-(5-chloropyridin-2-yl)pyridine (cpy), 4-(5-phenylpyridin-2-yl)pyridine (ppy), and 4-(5-(4-bromophenyl)pyridin-2-yl)pyridine (bppy). The results illustrate that POM anions can structure this kind of rigid and conjugated organic molecules into a parallel and ordered arrangement. In current work, organic molecule 1,3-bis(4-pyridyl)propane (bpp) with a flexible unit structure is explored as organo-cation to assemble POM clusters. Three compounds with formulas: $(H_2bpp)(Hbpp)$ $[PMo_{12}O_{40}]\cdot 3DMF$ (**1**), $(H_2bpp)(Hbpp)(bpp)_2[PMo_9V_3O_{40}(VO)_2]_2$ (**2**), and $(H_2bpp)_2[\beta\text{-}Mo_8O_{26}]$ (**3**) have been prepared and characterized. Their structural features have been investigated, revealing that the structural flexibility of bpp prefers to wrap around POM anion to form a supramolecular core–shell inclusion structure. Structure-directing template effects of inorganic anions play

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important roles in the self-organization process of these assemblies.

2. Experimental

2.1. Materials and physical measurements

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses were carried on a Perkin–Elmer 2400 CHN elemental analyzer. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT-IR spectrophotometer using a KBr pellet. XPS spectrum was recorded on an ESAY ESCA spectrometer with a Mg Kα achromatic X-ray source. EPR spectrum was recorded on a Japanese JES-FW3AX spectrometer at room temperature. TG-DTA analyses were performed on a Perkin–Elmer Pyris Diamond TG/DTA instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Hydrothermal syntheses were carried out in 20 mL Teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to approximately 70% volume capacity. Cyclic voltammograms (CV) were recorded on a 384B polarographic analyzer. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was a modified CPE. An Ag/AgCl (saturated KCl) electrode was used as a reference electrode and a Pt gauze as a counter electrode. All potentials were measured and reported versus the Ag/AgCl electrode.

2.2. Preparation

2.2.1. Synthesis of **1**

$H_7[PMo_{12}O_{40}]\cdot xH_2O$ (1 mmol) and NH_4VO_3 (0.5 mmol) were dissolved in DMF (10 mL) and acidified to pH 4 with 2 M HCl. A solution of bpp (0.5 mmol) in ethanol (10 mL) was added dropwise. The result solution was stirred for 2 h under a constant temperature of 75 °C. After slow cooling to room temperature, the precipitate was centrifuged and the clear solution was decanted into a clean beaker. The solution continued to precipitate but on leaving for 2 weeks produced red blocks, which were suitable for single crystal X-ray diffraction. Yield: ~20% (based on Mo); IR (cm^{-1}): 630(m), 858(s), 945(s), 1053(w), 1400(s), 1508(m), 1618(s), 3446(s); *Anal.* Calc. for $C_{35}H_{52}Mo_{12}N_7O_{43}P$: C, 17.22; H, 2.15; N, 4.02. Found: C, 17.12; H, 2.25; N, 4.00%.

2.2.2. Synthesis of **2**

A reaction mixture of $H_7[PMo_{12}O_{40}]\cdot xH_2O$ (1 mmol), V_2O_5 (0.5 mmol), bpp (0.5 mmol), and H_2O (10 mL) was neutralized to *ca.* pH 4.5 with dilute HCl solution. The result solution was stirred for *ca.* 20 min in air and then sealed in a reactor to heat at 165 °C for 4 days. After slow cooling (10 °C/h) to room temperature, black block crystals were obtained by hand; then are washed with distilled water and dried in air. Yield: ~40% (based on Mo); IR (cm^{-1}): 794(s), 869(m), 946(s), 1056(m), 1400(s), 1506(m), 1637(s), 3153(m), 3448(s); *Anal.* Calc. for $C_{52}H_{62}Mo_{18}N_8O_{84}P_2V_{10}$: C, 14.06; H, 1.41; N, 2.52. Found: C, 14.01; H, 1.51; N, 2.50%.

2.2.3. Synthesis of **3**

A reaction mixture of $Na_2MoO_4\cdot 2H_2O$ (1 mmol), bpp (0.5 mmol), and H_2O (10 mL) was neutralized to *ca.* pH 4.5 with dilute HNO_3 solution. The result solution was sealed in a reactor to heat at 160 °C for 4 days. Light yellow crystals were obtained. Yield: ~71% (based on Mo); IR (cm^{-1}): 622(m), 754(m), 827(m), 904(s), 945(s), 1203(w), 1364(m), 1400(s), 1506(m), 1635(s), 2362(m), 3149(m), 3413(s); *Anal.* Calc. for $C_{26}H_{32}Mo_8N_4O_{26}$(1584.08): C, 19.71; H, 2.04; N, 3.54. Found: C, 19.29; H, 2.35; N, 3.46%.

2.3. X-ray crystallography

The data for compounds **1–3** were collected at 293 K with a Bruker Smart Apex CCD diffractometer with Mo Kα monochromated radiation (λ = 0.71703 Å). Routine Lorentz and polarization corrections were applied. The structures of **1–3** were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL crystallographic software package [22]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. Protonated hydrogen atoms attached to nitrogen atoms were located from the difference Fourier map and were constrained. A summary of the crystallographic data and structural determination for **1–3** is provided in Table 1. Distances involving N–H···O and C–X···O weak interactions in **1–3** are shown in Table S1.

2.4. Preparation of compound **2** modified carbon paste electrodes (2-CPE)

Graphite powder (0.5 g) and 0.05 g of compound **2** were mixed, and ground together by agate mortar and pestle to achieve an even, dry mixture; to the mixture 0.50 mL paraffin oil was added under stirring with a glass rod; then the mixture was packed into 3 mm inner diameter glass tube, and the surface was pressed tightly onto weighing paper with a copper rod through the back. Electrical contact was established with copper rod through the back of the electrode.

3. Results and discussion

3.1. Synthesis

Here we show that it is possible to generate POM-based noncovalent assemblies by utilizing different synthetic routes. Gener-

Table 1
Crystal data and structure refinement for **1–3**.

Compounds	**1**	**2**	**3**
Formula	$C_{35}H_{52}N_7O_{43}PMo_{12}$	$C_{52}H_{62}N_8O_{84}P_2Mo_{18}V_{10}$	$C_{26}H_{32}N_4O_{26}Mo_8$
Mr (g mol^{-1})	2441.09	4441.36	1584.08
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*P2(1)/c*
a (Å)	12.3073(18)	11.3793(12)	10.5858(13)
b (Å)	13.0375(14)	12.7446(14)	10.0237(11)
c (Å)	24.031(2)	19.013(2)	19.653(2)A
α (°)	74.3510(10)	80.5410(10)	90
β (°)	88.482(2)	84.662(2)	100.938(2)
γ (°)	62.5270(10)	80.0250(10)	90
V ($Å^3$)	3272.5(7)	2672.8(5)	2047.5(4)
Z	2	1	2
D_{calc} (g cm^{-3})	2.477	2.759	2.569
μ (Mo Kα) (mm^{-1})	2.346	3.006	2.466
Independent reflections (R_{int})	11 263 (0.0340)	9081 (0.0549)	3602 (0.0246)
Data/ parameters	11 263/922	9430/776	3602/289
Goodness-of-fit	1.088	1.019	1.085
$R^a[I > 2\sigma(I)]$	$R_1 = 0.0990$ $wR_2 = 0.2041$	$R_1 = 0.0801$ $wR_2 = 0.2061$	$R_1 = 0.0246$ $wR_2 = 0.0594$
R^b [all data]	$R_1 = 0.1435$ $wR_2 = 0.2280$	$R_1 = 0.1643$ $wR_2 = 0.2408$	$R_1 = 0.0336$ $wR_2 = 0.0667$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.