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New organic-inorganic hybrid compounds constructed from polyoxometalates and transition metal mixed-organic-ligand complexes

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Five new organic-inorganic hybrid compounds based on different polyoxoanions $[H_xGeW_{12}O_{40}]^{n-}$ or $[H_3As_2W_{18}O_{62}]^{3-}$ (x=0, 2; n=4, 2), namely $[Cu_3(2,2'\text{-bpy})_3(\text{inic})(OH)(H_2O)][GeW_{12}O_{40}]\cdot 1.5H_2O$ **(1)**, $[Cu_2(\text{phen})_2(\mu_2\text{-}Cl)_2(\text{inic})]_2[H_2GeW_{12}O_{40}]\cdot 2H_2O$ **(2)**, $[Cu_2(\text{phen})_2(\mu_2\text{-}Cl)Cl(\text{nic})]_2[H_2GeW_{12}O_{40}]$ **(3)**, $[Cu_2(2,2'\text{-bpy})_2(\text{hnic})Cl]_2[H_2GeW_{12}O_{40}]$ **(4)**, $[Cu(\text{phen})(\text{inic})H_2O][Cu_2(\text{phen})_2(\text{inic})_2(H_2O)][H_3As_2W_{18}O_{62}]\cdot 3H_2O$ **(5)** (inic = isonicotinic acid, nic =nicotinic acid, hnic = 2-hydroxy-nicotinic acid, 2,2'-bpy=2,2'-bipyridine, phen=1,10-phenanthroline) have been synthesized and characterized by IR, UV-Vis, XRD, cyclic voltammetric measurements and single crystal x-ray diffraction analysis. Single crystal x-ray analysis reveals that compound **1** is isomorphous and isostructural with a compound we reported recently, the main difference between the two is the heteroatom of the polyoxoanions in the two compounds. Compound **2** is a supramolecular structure constructed from polyoxoanions and transition metal mixed-organic-ligand complexes. Compound **3** is a novel polyoxoanion bi-supported transition metal mixed-organic-ligand complex. Compound **4** is a 1-D chain structure constructed from polyoxoanions and transition metal mixed-organic-ligand complexes. The photodegradation properties of compounds **1-5** have been analyzed.

Introduction

Polyoxometalates (POMs) form a distinctive class of inorganic metal-oxygen cluster compounds of electronic versatility and structural variation, with impacts ranging from catalysis, analysis, biochemistry, materials science and medicine.[1] Though the class of POMs has been known for almost 200 year,[2] it continues to be a focus in the ongoing research because of the progressive development of POM structures and properties. Many of fundamental properties of POM that have impact on its applications, including elemental composition, solubility, redox potential(s), charge density, size, and shape, can be systematically altered to a considerable degree.[3]

Current research interests are mainly driven by the combination of POMs and N-containing organic moieties or transition metal N-containing organic complexes into POM-based hybrids.[1i, 4] Our group has focused on the preparations, structures and properties of hybrids constructed from POMs and transition metal N-containing organic complexes for several years.[5] Based on an analysis of the literatures hitherto reported,[4, 5] we find that the transition metal complex (TMC) of above-mentioned POM-based organic-inorganic hybrids is almost always comprised of a metal ion and a type of organic ligands. That is to say, hybrids formed by POMs and transition metal mixed-organic-ligand complexes (TMMCs) are very rare. It is worthy to note that the direct introduction of N-containing organic moieties or transition metal N-containing organic ligand complexes to POMs can not only enrich POM structures, but also ameliorate their polar, electricity, acid, and redox properties.[6] The introduction of TMMCs thereby may give rise to compounds with more interesting structures, topologies, and properties.

According to different TMMC organic ligands, the POM-based hybrids containing TMMCs could be divided into three types: namely type **1**, type **2** and type **3**. Type **1** hybrids contain more than one type of TMMC N-containing organic ligands;[7] type **2** hybrids contain more than one type of TMMC carboxylates; type **3** hybrids contain more than one type of TMMC organic ligands being composed of both N-containing organic ones and carboxylates.[8, 9] To our knowledge, although several type **1** hybrids were synthesized;[7] still no type **2** hybrids have been reported; type **3** compounds have been only rarely reported,[8,9].

We have recently synthesized some type **1** and type **3** hybrids,[5k, 5m] and we attempt to synthesize all the above-mentioned three types of hybrids. We have pointed out that the synthesis of compounds constructed from POMs and TMMCs of a N-containing ligand and a pyridinecarboxylate should be the breakthrough point for the synthesis of the above-mentioned second and third types of compounds.[5m] After the syntheses of the compounds containing pyridinecarboxylates,[5m] then we further our study by introducing apy (apy = 2-aminopyridine), 2,2'-bpy, and phen as N-containing organic ligands (secondary organic ligands) with picolinic acid to explore the roles of these selected secondary organic ligands in the synthesis of the hybrids.[10]

In this paper, we report the synthesis and characterizations of another five new compounds based on POMs and TMMCs, namely $[Cu_3(2,2'\text{-bpy})_3(inic)(OH)(H_2O)][GeW_{12}O_{40}]\cdot 1.5H_2O$ **(1),** $[Cu_2(phen)_2(\mu_2\text{-}Cl)_2(inic)]_2[H_2GeW_{12}O_{40}]\cdot 2H_2O$ **(2),** $[Cu_2(phen)_2(\mu_2\text{-}Cl)Cl(nic)]_2[H_2GeW_{12}O_{40}]$ **(3),** $[Cu_2(2,2'\text{-bpy})_2(hnic)Cl]_2[H_2GeW_{12}O_{40}]$ **(4),** $[Cu(phen)(inic)H_2O][Cu_2(phen)_2(inic)_2(H_2O)][H_3As_2W_{18}O_{62}]\cdot 3H_2O$ **(5)** Compound **1** which is based on $[GeW_{12}O_{40}]^{4-}$, is isostructural and isomorphous with $[Cu_3(2,2'\text{-bpy})_3(inic)(\mu_2\text{-}OH)(H_2O)][SiW_{12}O_{40}]\cdot 2H_2O$ we reported very recently.[5m] Compound **2**-**4** are all similar to the previously reported compounds which are based on $[XM_{12}O_{40}]^{4-}$ (X=Si, Ge, M=Mo, W),[5m] but each of which exhibits distinctly different structure from the previously reported compounds. The reason lies in that the TMMC in each of the three compounds not only contains two different organic ligands, but also contains extra chloride ions as the third ligands. We have synthesized a series of compounds based on the combination of an organic ligand and chloride ions.[11] And also we synthesized several type **3** compounds in which their TMMCs contain extra chloride ions.[5m] The introduction of extra chloride ions no doubt makes the structures of TMMCs more diverse and complex. Most interestingly, compound **5** is based on the Dawson POM $[H_3As_2W_{18}O_{62}]^{3-}$, exhibiting a novel structure in which the Dawson POM supports two different TMMCs. To our knowledge, two type **1** compounds based on Dawson POMs and TMMCs were reported previously, in which the two TMMCs are based on methylimidazol, 1,1-(1,4-butanediyl)-bis(imidazole)) and 1,4-bis(triazol-1-ylmethyl)benzene, 1,3-Bis-(1,2,4-triazol-1-yl)propane, respectively.[7f] Three type **3** isostructural compounds based on Dawson POMs and TMMCs of oxalic group and 4,4'-bpy have been reported,[8d, 8e] the difference of compound **5** and the reported compounds is that the TMMC in the reported compounds are based on oxalic group and 4,4'-bpy and the POM of the three have no covalent interactions with the TMMCs. Compared with the previous reported Dawson POM-TMMC hybrids, compound **5** exhibits some unprecedented structural features: 1. The carboxylate used in compound **5** is an aromatic acid, but the acid used in the previously reported compounds is an aliphatic one; 2, there are two different coexisting type **3** TMMCs in compound **5**; 3 the Dawson POM supports the two TMMCs simultaneously. The introductions of both chloride ions and different POMs give new impetuses to the development of hybrids based on POMs and TMMCs.

Experimental

All chemicals used were of reagent grade without further purification. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer SPECTRUM ONE FTIR spectrophotometer. UV-Vis spectra in dimethyl sulfoxide (DMSO) solution were recorded on a Shimadzu UV3100 spectrophotometer. Powder XRD patterns were obtained with a Scintag X1 powder diffractometer system using Cu K_α radiation with a variable divergent slit and a solid-state detector.

$[Cu_3(2,2'\text{-bpy})_3(inic)(OH)(H_2O)][GeW_{12}O_{40}]\cdot 1.5H_2O$ (1) Compound **1** was synthesized hydrothermally by reacting of $Na_2WO_4\cdot 2H_2O$ (0.659g, 2.0mmol), GeO_2 (0.105g, 1.0mmol), $CuCl_2\cdot 2H_2O$ (0.171g, 1.0mmol), isonicotinic acid (0.062g, 0.50mmol), 2, 2'-bpy (0.077g, 0.50mmol), SeO_2 (0.111g, 1.0mmol) and distilled water (15ml) in a 18ml Teflon-lined autoclave. The resulting suspension was stirred for 3h and the pH of the mixture was necessarily adjusted to 2 with HCl solution. The mixture was heated under autogenous pressure at 160°C for 5 days and then left to cool to room temperature. Lyons blue block crystals of **1** were filtered washed with water and dried at room temperature. Yield: 19% (based on W). Anal. Calcd for $C_{36}H_{34}Cu_3N_7O_{45.5}Ge_1W_{12}$: W, 58.64; Cu, 5.07; C, 11.49; H, 0.91; N, 2.61%. Found: W, 58.43; Cu, 4.80; C, 11.31; H, 1.03; N, 2.74%.

$[Cu_2(phen)_2(\mu_2\text{-}Cl)_2(inic)]_2[H_2GeW_{12}O_{40}]\cdot 2H_2O$ (2) Compound **2** was synthesized hydrothermally by reacting of $Na_2WO_4\cdot 2H_2O$ (0.659g, 2.0mmol), GeO_2 (0.105g, 1.0mmol), $CuCl_2\cdot 2H_2O$ (0.171g, 1.0mmol), isonicotinic acid (0.062g, 0.50mmol), phen (0.099g, 0.50mmol), SeO_2 (0.111g, 1.0mmol) and distilled water (15ml) in a 18ml Teflon-lined autoclave. The resulting suspension was stirred for 3h and the pH of the mixture was necessarily adjusted to 2.5 with HCl solution. The mixture was heated under autogenous pressure at 160°C for 5 days and then left to cool to room temperature. Green block crystals of **2** were filtered washed with water and dried at room temperature. Yield: 29% (based on W). Anal. Calcd for $C_{60}H_{42}Cl_4Cu_4GeN_{10}O_{46}W_{12}$: W, 51.09; Cu, 5.89; C, 16.69; H, 1.07; N, 3.24%. Found: W, 50.58; Cu, 5.74; C, 16.34; H, 0.86; N, 3.11%.

$[Cu_2(phen)_2(\mu_2\text{-}Cl)Cl(nic)]_2[H_2GeW_{12}O_{40}]$ (3) Compound **3** was synthesized hydrothermally by reacting of $Na_2WO_4\cdot 2H_2O$ (0.661g, 2.0mmol), GeO_2 (0.110g, 1.0mmol), $CuCl_2\cdot 2H_2O$ (0.342g, 2.0mmol), nicotinic acid (0.124g, 1.0mmol), phen (0.10g, 0.50mmol), NaOH (0.081g, 2.0mmol) and distilled water (15ml) in a 18ml Teflon-lined autoclave. The resulting suspension was stirred for 3h and the pH of the mixture was necessarily adjusted to 1.5 with HCl solution. The mixture was heated under autogenous pressure at 160°C for 3 days and then left to cool to room temperature. Blue block crystals could be isolated in about 33% yield (based on W). Anal. Calcd for $C_{60}H_{42}Cl_4Cu_4GeN_{10}O_{44}W_{12}$: W, 51.52; Cu, 5.94; C, 16.83; H, 0.99; N, 3.27%. Found: W, 51.27; Cu, 5.63; C, 16.86; H, 1.15; N, 3.11%.

$[Cu_2(2,2'\text{-bpy})_2(hnic)Cl]_2[H_2GeW_{12}O_{40}]$ (4) Compound **4** was synthesized hydrothermally by reacting of $Na_2WO_4\cdot 2H_2O$ (0.660g, 2.0mmol), GeO_2 (0.112g, 1.0mmol), $CuSO_4\cdot 5H_2O$ (0.500g, 2.0mmol), nicotinic acid (0.063g, 0.51mmol), 2,2'-bpy (0.079g, 0.50mmol), NaOH (0.085g, 2.0mmol) and distilled water (15ml) in a 18ml Teflon-lined autoclave. The resulting suspension was stirred for 3h and the pH of the mixture was necessarily adjusted to 3.0 with HCl solution. The mixture was heated under autogenous pressure at 160°C for 3 days and then left to cool to room temperature. Blue block crystals could be isolated in about 35% yield (based on W). Anal. Calcd for $C_{52}H_{40}Cl_2Cu_4GeN_{10}O_{46}W_{12}$: W, 53.23; Cu, 6.13; C, 15.07; H, 0.97; N, 3.38%. Found: W, 53.49; Cu, 6.00; C, 15.33; H, 0.78; N, 3.09%.

$[Cu(phen)(inic)H_2O][Cu_2(phen)_2(inic)_2(H_2O)][H_3As_2W_{18}O_{62}]\cdot 3H_2O$ (5) Compound **5** was synthesized hydrothermally by reacting of $Na_2WO_4\cdot 2H_2O$ (0.660g, 2.0mmol), $NaAsO_2$ (0.130g, 1.0mmol), $CuCl_2\cdot 2H_2O$ (0.350g, 2.0mmol), isonicotinic acid (0.061g, 0.50mmol), phen (0.099g, 0.50mmol) and distilled water (15ml) in a 18ml Teflon-lined autoclave. The resulting suspension was stirred for 3h and the pH of the mixture was necessarily adjusted to 3 with HCl solution. The mixture was

Table 1. Crystal data and structural refinements for compounds **1** - **5**.

Empirical formula	$C_{36}H_{34}GeCu_3N_7O_{45.5}W_{12}$	$C_{60}H_{46}Cl_4Cu_4GeN_{10}O_{46}W_{12}$	$C_{60}H_{42}Cl_4Cu_4GeN_{10}O_{44}W_{12}$	$C_{52}H_{40}Cl_2Cu_4GeN_{10}O_{46}W_{12}$	$C_{54}H_{49}As_2Cu_3N_9O_{73}W_{18}$
Formula weight	3762.11	4317.82	4281.78	4144.73	5641.78
Crystal system	Monoclinic	Orthorhombic	triclinic	monoclinic	monoclinic
space group	P2(1)/c	Pbca	P-1	P2(1)/c	P2(1)/m
a (Å)	23.410(3)	20.681(4)	11.475(2)	15.1378(9)	16.729(3)
b (Å)	12.970(2)	13.187(3)	12.627(3)	13.5053(8)	18.897(4)
c (Å)	22.779(3)	32.788(7)	15.450(3)	23.978(1)	17.003(3)
α (˚)	90	90	88.57(3)	90.00	90
β (˚)	109.576(2)	90	68.68(3)	128.069(3)	103.82(3)
γ (˚)	90	90	87.78(3)	90.00	90
Volume ($Å^3$)	6516.3(13)	8942(3)	2083.7(8)	3859.2(4)	5219.5(18)
Z	4	4	1	2	2
D_C ($Mg\cdot m^{-3}$)	3.835	3.207	3.412	3.567	3.590
μ (mm^{-1})	22.600	16.839	18.062	19.433	21.074
F(000)	6680	7792	1928	3720	5010
θ for data collection	1.82 to 25.04	3.09 to 27.49	3.17 to 27.48	2.94 to 25.35	3.02 to 27.48
Reflections collected	33282	79213	20607	19015	47689
Reflections unique	11518	10201	9418	7059	12254
R(int)	0.1032	0.0905	0.0692	0.0440	0.0825
Completeness to θ	99.7	99.9	99.8	99.9	99.7
parameters	946	637	628	592	874
GOF on F^2	1.009	1.072	1.060	1.056	1.017
R^a [I>2σ(I)]	$R_1 = 0.0526$	$R_1 = 0.0626$	$R_1 = 0.0753$	$R_1 = 0.1040$	$R_1 = 0.0463$
R^b (all data)	$\omega R_2 = 0.0992$	$\omega R_2 = 0. 1300$	$\omega R_2 = 0.1776$	$\omega R_2 = 0.2306$	$\omega R_2 = 0.1143$

[a] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$. [b] $\omega R_2 = \{\sum [w (F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

heated under autogenous pressure at 160°C for 5 days and then left to cool to room temperature. Dark green block crystals could be isolated in about 27% yield (based on W). Anal. Calcd for $C_{54}H_{49}As_2Cu_3N_9O_{73}W_{18}$: W, 58.66; Cu, 3.38; As, 2.66; C, 11.50; H, 0.88; N, 2.23%. Found: W, 58.42; Cu, 3.10; As, 2.44; C, 11.36; H, 0.88; N, 2.08%.

Preparations of 1-, 2-, 3-, 4- and 5-CPEs. The compound **1**-modified carbon-paste electrode (**1**-CPE) was fabricated as follows: 6 mg graphite powder, 1 μL of Nujol and 3 mg compound **1** were blended and grounded thoroughly in an agate mortar. Then the homogeneous mixture was packed into a poly(tetrafluoroethylene) tube with a 1.5 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a Cu rod through the back of the electrode. In a similar manner, **2**-, **3**-, **4**-, and **5**-CPEs were made with compounds **2-5**. Electrochemical measurements were performed with a CHI 660b electrochemical workstation. A conventional three-electrode system was used with Ag/AgCl as a reference electrode and Pt wire as a counter electrode. Chemically bulk-modified CPEs were used as the working electrodes. CV measurements are carried out in a 1 mol/L H_2SO_4 aqueous solution.

Rhodamine B (RhB) is a typical dye contaminant that can be used for evaluating the activity of photocatalysts for the purification of waste water.[12] In a typical process, compound **1** (4.8mg, 1.3×10-3mmol), **2** (5.0mg, 1.2×10-3mmol), **3** (5.0mg, 1.2×10-3mmol), **4** (4.8mg, 1.2×10-3mmol) or **5** (6.4mg, 1.1×10-3mmol) was ground for about 10min with an agate mortar to obtain a fine powder, and then the powder was dispersed in 100 mL RhB solutions (1.0×10-5mol·L-1). The suspension was agitated in an ultrasonic bath for 20min in the dark and then magnetically stirred in the dark for about 30min. The suspension was finally exposed to irradiation from a 400W Xe lamp at a distance of about 4-5 cm between the liquid surface and the lamp. The suspension was stirred during irradiation at a stirring rate of about 790-800 rpm. At 30min intervals, 5mL of samples were taken out from the beaker, which was clarified by centrifugation at 10000 rpm for 5 min, and subsequently analyzed by UV-Vis spectroscopy.

Reflection intensity data for compound **1** were measured on a Bruker Apex II diffractometer with a graphite monochromated Mo K_α (λ = 0.71073Å) radiation source and reflection intensity data for compound **4** were measured on an Agilent Technology SuperNova Eos Dual system with a Mo K_α (λ = 0.71073Å) microfocus source and focusing multilayer mirror optics, whereas reflection intensity data for compound **2**, **3** and **5** were measured on a Rigaku R-AXIS RAPID IP diffractometer with a graphite monochromated Mo K_α (λ = 0.71073Å) radiation source. None of the crystals showed evidence of crystal decay during data collections. Refinements were carried out with SHELXS-2014/7[13] and SHELXL-2014/7[13] using WinGX via the full matrix least-squares on F_2 method.[14] In the final refinements, all atoms were refined anisotropically in compounds **1-5**. A summary of the crystallographic data and structure refinements for compounds **1-5** is given in Table **1**. CCDC number: 1419955 for **1,** 1419956 for **2,** 1419957 for **3,** 1419958 for **4,** 1419959 for **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Description of the crystal structures

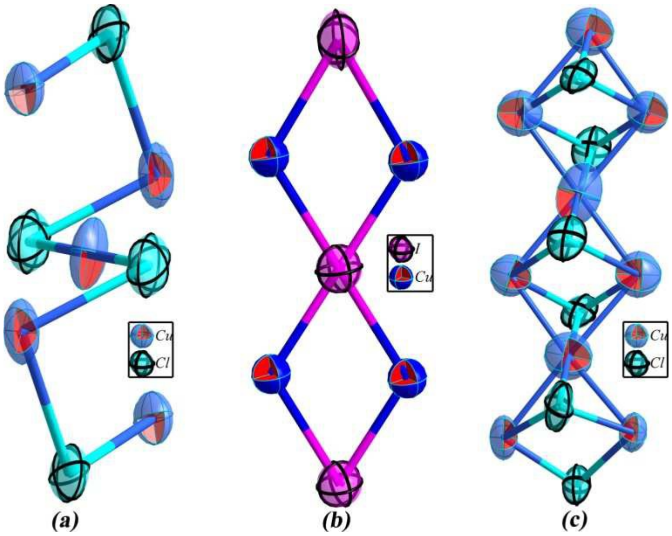


Fig. 1 Ellipsoid representation (50% probability) of metal-halide clusters reported previously by our group, carbons, hydrogens and nitrogens are omitted for clarity.

Our group has synthesized a series of organic-inorganic hybrids based on POMs and metal-chloride clusters.[11] Metal-chloride clusters in the previously reported compounds are based on one kind of organic ligands, one kind of metal ions and one kind of chloride ions. Therefore, from the standpoint of incorporated ligands, these reported metal-chloride clusters should be a special kind of TMCs. The coordination modes of chloride ions have been carefully discussed previously: the chloride ion can act as a terminal ligand coordinating to a metal ion or can act as a μ_2-bridge linking two metal ions (Fig. 1(a) and (b)). The chloride ion can also adopt a μ_4-bridging coordination mode with four metal centers. Except the three modes, one more mode was also observed in $[Cu_{11}Cl_7(Phen)_8]^{4+}$, the chloride ion of which serves as a μ_3-bridge linking three metal ions (Fig. 1(c)).[11] Wang et al also reported a novel hybrid based on POMs and metal-chloride clusters, in which chloride ions adopt two different coordination modes: one is a μ_3-bridging mode and the other is a μ_4-bridging mode.[15] However, all the previously reported compounds are based on the traditional metal complexes of one kind of organic ligands and the successful synthesis of these compounds demonstrated that the introduction of chloride ions can dramatically increase the structural complexity of the hybrids based on POMs and TMCs. Thus from the structural standpoint, it is obvious that the introduction of chloride ions into the TMMC would increase the structural complexity of the hybrids based on POMs and TMMCs.

Chloride ions in the previously reported compound $[Cu_6(phen)_6(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2Cl_2(inic)_2][SiW_{12}O_{40}]\cdot 6H_2O$ **(6)** shows three different coordination modes: μ_3-bridging, μ_2-bridging and monodentate terminal modes.[5m] Chloride ions in compounds $[Cu_2(hnic)(2,2'\text{-}bpy)_2Cl]_2[H_2SiW_{12}O_{40}]$ **(7),** $[Cu_2(nic)(phen)_2Cl_2]_2[SiW_{12}O_{40}]$ **(8)** and $[Cu_2(pic)(2,2'\text{-}bpy)_2Cl]_2[SiW_{12}O_{40}]$ **(9)** only show a monodentate terminal mode.[5m]

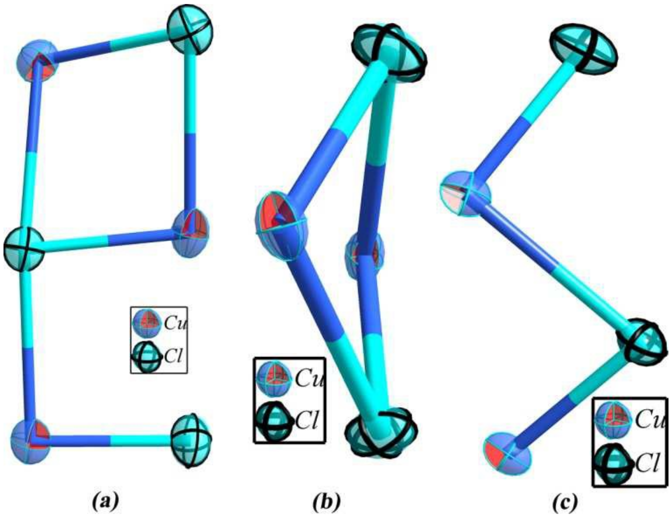
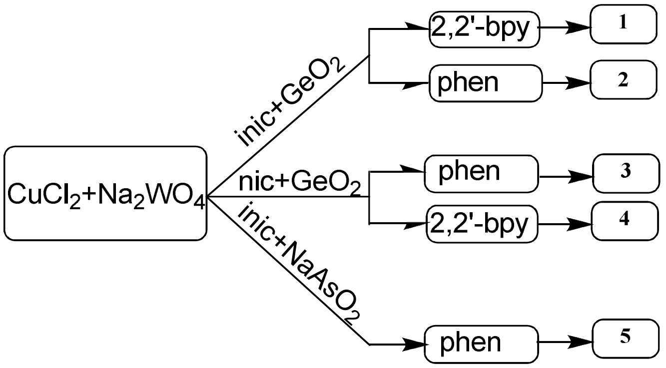


Fig. 2 Ellipsoid representation (50% probability) of metal-halide clusters in compound **6** (a), compound **2** (b) and compound **3** (c), carbons, hydrogens and nitrogens are omitted for clarity.

Though compounds **2** and **3** are very similar to each other, their final structures are thoroughly different. One of the main reasons perhaps lies in the different coordination modes of the chloride ions in the two. The metal chloride clusters in compounds **2** and **3** are shown in Fig. 2, chloride ions in compound **2** exhibits the μ_2-bridging mode linking metal ions into a binuclear metal chloride cluster (Fig. 2(b)), whereas chloride ions in compound **3** adopt both μ_2-bridging and monodentate terminal mode linking metal ions into a different bi-nuclear metal chloride cluster as shown in Fig. 2(c). However, the mechanism of the formation of the different modes is still elusive.



Scheme 1. Summary of the reactions of compounds **1-5**.

As shown in scheme 1, compounds **1** and **2** were synthesized under similar conditions; especially the molar ratios of Na_2WO_4/GeO_2/pyridinecarboxylate /$CuCl_2\cdot 2H_2O$/ N-containing ligand for the two compounds are identical, which are 4:2:1:2:1. The difference between the two sets of starting materials is the different N-containing ligand used. Therefore, the different starting materials used are very important for the final products. It should be noted that the compound which is isostructural and isomorphous with compound **1** have been reported by our group very recently,[5m] the main difference between the two sets of starting materials is that GeO_2 used for the preparation of compound **1** replaces SiO_2 used for the preparation of the compound reported.

The molar ratios of Na_2WO_4/GeO_2/pyridinecarboxylate/$CuCl_2·2H_2O$/ N-containing ligand for compounds **3** and **4** are 4:2:2:4:1 and 4:2:1:4:1, respectively. The N-containing ligands used for compounds **3** and **4** are also different, therefore, the final structures of compounds **3** and **4** are thoroughly different. It should be noted that compound **7** containing $hnic^{2-}$ which is a result of *in situ* hydroxylation of the nicotinic acid has been reported by our group recently.[5m] The starting material is the nicotinic acid. However, the organic component in the resulting hybrid becomes a $hnic^{2-}$ group. Hydroxylation of the nicotinic acid leading to the $hnic^{2-}$ group in compounds **4** and **7** is the result of nucleophilic attack of hydroxide ions. It should be noted that the molar ration of Na_2WO_4/SiO_2/pyridinecarboxylate acid/$CuCl_2·2H_2O$/ N-containing ligand for compound **7** is 4:2:1:4:1, too, which is identical to that of compound **4**. Though the synthesis procedures of compounds **4** and **7** are very similar to each other, the final structures of the two are thoroughly different.

Crystal structure of 1 Single crystal X-ray analysis reveals that the POM in compound **1** is $[GeW_{12}O_{40}]^{4-}$, which was detailedly described below. The structure of the Keggin core in compound **1** includes a central $\{GeO_4\}$ tetrahedron surrounded by twelve $\{WO_6\}$ octahedra arranged in four groups of three edge-sharing octahedra units $\{W_3O_{13}\}$. W-O bonds can be classified into three sets: W-O_t (terminal oxygens) with distances of 1.66(1)-1.73(1)Å, W-O_b (bridging oxygens) with distances of 1.89(1)-1.97(1)Å and W-O_c (central oxygens) with distances of 2.27(1)-2.33(1)Å. Oxidation states for the W atoms in compound **1** were calculated using the parameters given by Brown.[18] Results indicate that all the tungsten atoms are in the +6 oxidation state.

X-ray analysis of compound **1** reveals that compound **1** was isostructural and isomorphous with $[Cu_3(2,2'\text{-bpy})_3(\text{inic})(\mu_2\text{-OH})(H_2O)][SiW_{12}O_{40}]·2H_2O$ we reported very recently.[5m] The main difference between the two compounds is the heteroatoms of the Keggin POMs of the two: one is Ge and the other is Si.

Crystal structure of 2 Single crystal X-ray analysis reveals that the POM in compound **2** is $[H_2GeW_{12}O_{40}]^{2-}$. The structure of $[H_2GeW_{12}O_{40}]^{2-}$ is almost identical to the structure of $[GeW_{12}O_{40}]^{4-}$ in compound **1**. Oxidation states for the W atoms in compound **2** were calculated using the parameters given by Brown.[18] Results indicate that all the tungsten atoms are in the +6 oxidation state.

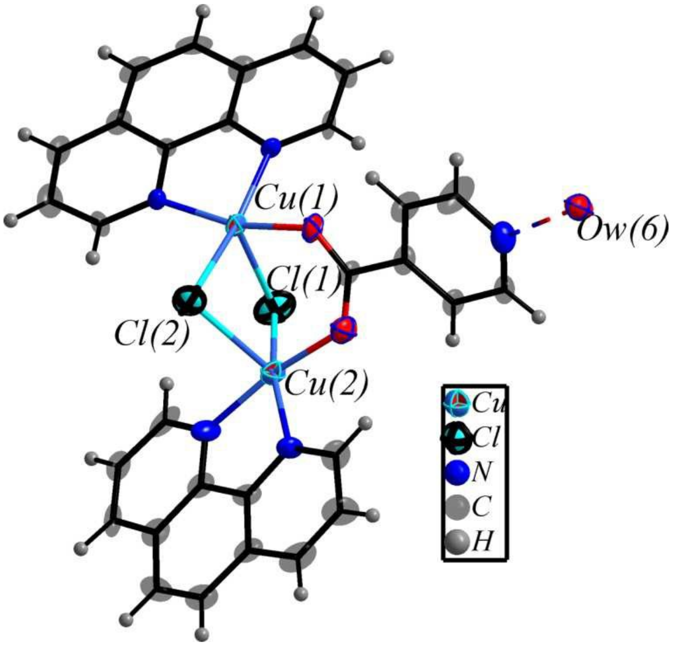


Fig. 3 Ellipsoid representation (50% probability) of the TMMC in compound **2**.

The asymmetric unit of compound **2** is composed of half a $[H_2GeW_{12}O_{40}]^{2-}$, a copper-chloride-isonicotinic-phenanthroline complex $[Cu_2(\text{phen})_2(\mu_2\text{-Cl})_2(\text{inic})]^+$ and a lattice water molecule. $[Cu_2(\text{phen})_2(\mu_2\text{-Cl})_2(\text{inic})]^+$ consists of two copper ions, two phen ligands, two chlorides and one inic^-. As shown in Fig. 3, two phens form two chelate complexes with two coppers with Cu-N distances of 2.00(1)-2.02(1)Å, respectively. Two chloride ions each join the two coppers too, Cu-Cl distances are in the range of 2.260(4)-2.645(4)Å. inic^- coordinates to the two coppers via its two carboxylate oxygens in a bis-monodentate coordination mode with Cu-O distances of 1.949(9)-1.95(1)Å, indicating that inic^- acts as a μ_2-bridge linking the two coppers. Thus, inic^- and chloride ions play the most important roles in the formation of TMMC in compound **2**.

As shown in Fig. 3, inic^- in TMMC in compound **2** has a strong O-H···N interaction with the lattice water molecule in compound **2**. The nitrogen of inic^- acts as the hydrogen acceptor and O(1w) acts as the hydrogen donor with the N···O distance of 2.7771(4)Å, which means that the O-H···N interaction are very strong. The existence of the O-H···N interaction here demonstrated that the existence of inic^- in compound **2**: the O-H···N interaction demonstrated that the heterocyclic nitrogen is located at the para-position of the carboxylate group.

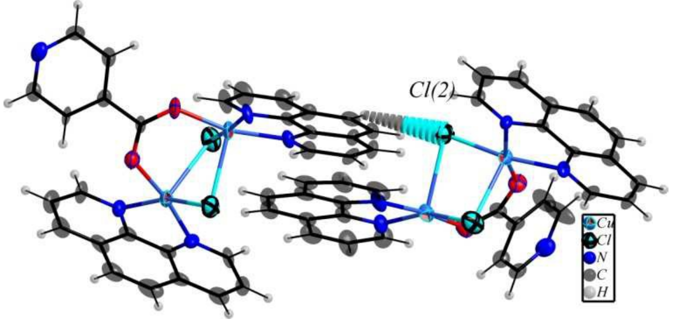


Fig. 4 the 1-D chain structure formed via intramolecular C-H···Cl interactions in compound **2**.

There also exist strong C-H···Cl interactions, which play an important role in the formation of the supramolecular structure in compound **2**. As shown in Fig. 4, C-H···Cl interactions in compound **2** can be grouped into two types, one type is intramolecular and the other is intermolecular. C(2), C(29) as hydrogen donors and Cl(2), Cl(1) as hydrogen accepters form intramolecular C-H···Cl interactions with C···Cl distances of 3.3002(5)-3.3517(5)Å. The intramolecular interactions increased the stability of TMMC in compound **2**. There is only one type of intermolecular C-H···Cl interaction, of which C(17) serves as the hydrogen donor and Cl(2) serves as the hydrogen acceptor with a C···Cl distance of 3.4609(6)Å. Via the strong intermolecular C-H···Cl interaction, TMMCs in compound **2** are linked into a novel supramolecular chain structure running along the *a* axis (Fig. 4).

There also is a C-H···O interaction between O(15) of $[H_2GeW_{12}O_{40}]^{2-}$ and C(12a, a: 1-x, 0.5+y, -0.5-z) of TMMC. C···O distances of the C-H···O interaction is 3.0930(5)Å. Through the C-H···O interaction, each POM is linked to two TMMCs. Then POMs and TMMCs are linked into a 2-D supramolecular structure via both C-H···Cl and C-H···O interactions.

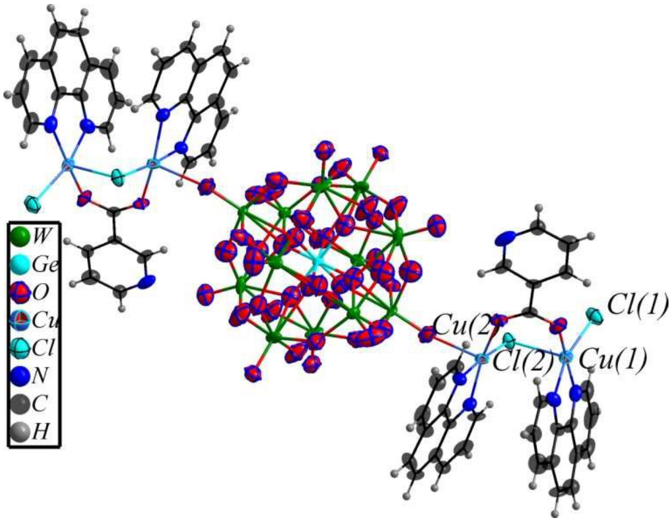


Fig. 5 the POM bi-supported TMMC in compound **3**.

Crystal structure of 3 The asymmetric unit of compound **3** is composed of half a $[H_2GeW_{12}O_{40}]^{2-}$ and a copper-chloride-nicotinic-phenanthroline complex $[Cu_2(phen)_2(\mu_2\text{-}Cl)Cl(nic)]^{+}$. The formula of the TMMC in compound **3** is very similar to that of the TMMC in compound **2** except that nic^- takes the place of $inic^-$. However, the structures of the two TMMCs are thoroughly different from each other. As shown in Fig. 5, $[Cu_2(phen)_2(\mu_2\text{-}Cl)Cl(nic)]^{+}$ in compound **3** is comprised of two coppers, two chlorides, two phens and a nic^-. As shown in Fig. 5, the two phens adopting an N, N-chelating mode coordinate to two coppers with Cu-N distances of 1.97(2)-2.04(2)Å, respectively, nic^- adopting a bis-monodentate coordination mode links the two coppers with Cu-O distances of 1.94(1)-1.97(1)Å. It should be noted that the roles of both phen and nic^- in compound **3** are almost identical to those of phen and $inic^-$ in compound **2**. However, the roles of the two chlorides in compound **3** are distinctly different from those of the two in compound **2**. One of the two chlorides as a μ_2-bridege connects the two coppers with Cu-Cl distances of 2.222(5)-2.707(5)Å, but the other of the two only serves as a terminal ligand coordinating to one copper of the TMMC with a Cu-Cl distance of 2.252(6)Å. Therefore, the core of the TMMC in compound **2** is a Cu_2Cl_2 cluster; however, the core of the TMMC in compound **3** is a Cu-Cl-Cu-Cl zigzag chain. It is still elusive what causes the difference between the two. Perhaps it is the pyridinecarboxylate that make the difference between the two; however, the mechanism is still elusive. The successful synthesis of compounds **2** and **3** demonstrated that different coordination modes of chloride ions will have a strong influence on the structures of compounds.

The two coppers in compound **2** exhibit a square-pyramidal geometry, the two of TMMC in compound **3** adopt a square-pyramidal geometry too. The two geometries in compound **2** are identical to each other with a Cl_2N_2O donor set. However, only one of the two geometries in compound **3** is identical to that of compound **2**, the other is defined by an O_2N_2Cl donor set with the apical position is occupied by an oxygen atom from $[H_2GeW_{12}O_{40}]^{2-}$ replacing the chloride ion with a Cu-O distance of 2.38(2)Å. That is to say, the POM acting as a ligand coordinates to the TMMC via a terminal oxygen to form a POM supported TMMC. It should be noted that there are two TMMCs disposed at the two opposite sides of $[H_2GeW_{12}O_{40}]^{2-}$, forming a novel POM bi-supported TMMC.

C-H···Cl interactions in compound **3** also play an important role in the formation of the supramolecular structure of compound **3**. There are also two types of C-H···Cl interactions, one type is intramolecular, and the other is intermolecular. The intramolecular interactions include C(29)-H(29)···Cl(2) and C(16)-H(16)···Cl(1) with C···Cl distances of 3.283(1)-3.3292(9)Å. The intermolecular ones include C(28)-H(28)···Cl2a(a: 5-x, -y, -z), C(23)-H(23)···Cla (a, x, 1+y, z) with C···Cl distances of 3.5030(9)-3.621(1)Å. There also exist complex C-H···O interactions in compound **3** with C···O distances in the range of 2.961(1)-3.0723(8)Å. Via both C-H···Cl and C-H···O interactions, POM bi-supported TMMCs are linked into a 3-D supramolecular structure.

Crystal structure of 4 The asymmetric unit of compound **4** is composed of half a $[H_2GeW_{12}O_{40}]^{2-}$ and a copper-2,2'-bipyridine-chloride-hydroxyl-nicotinic complex $[Cu_2(2,2'\text{-}bpy)_2(hnic)Cl]^{+}$.

In addition, one interesting feature of compound **4** is that the nicotinic acid transforms to the $hnic^{2-}$ group via *in situ* hydroxylation. A variety of novel hybrid complexes involving *in situ* synthesized ligands were documented. To date, more than 10 types of ligand *in situ* formation reactions have been reported.[16] The starting material used is nicotinic acid. However, the corresponding organic component in the resulting hybrid becomes $hnic^{2-}$. Hydroxylation of the nicotinic acid leading to $hnic^{2-}$, which was reported only very recently by our group, is the result of nucleophilic attack of hydroxide ions.[5m]

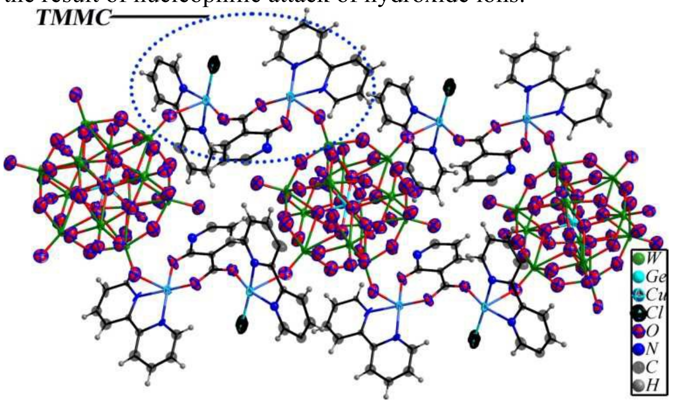


Fig. 6 Ellipsoid representation (50% probability) of the 1-D chain structure in compound **4**.

Hnic^{2-} in compound **4** adopts an identical coordination mode to that of compound **7** we reported recently. Moreover, the TMMC in compound **4** made up of copper, hnic^{2-}, phen and chloride ions is also almost identical to that of compound **7** we reported with only slight differences in bond lengths and angles. Thus, the two TMMCs in the above-mentioned two compounds are almost identical. The POM in compound **4** is also almost identical to that of compound **7** we reported recently except that the heteroatom is Ge replacing Si.[5m] Both the POM and TMMC in compound **4** are almost identical to those in compound **7**, therefore, the 1-D chain structure constructed form POMs and TMMCs in compound **4** (Fig. 6) are almost identical to that of compound **7**.[5m]

However, it is strange to find that compound **7** and compound **4** are not isostructural and isomorphous. The two compounds crystalize in the space groups P2(1)/n and P2(1)/c, and more importantly, the cell parameters of the two compounds are thoroughly different from each other, which are 15.070(4)Å, 13.496(3)Å, 18.814(5)Å, 90º, 90.953(4)º, 90º for compound **7** and 15.1378(9)Å, 13.5053(8)Å, 23.978(1)Å, 90º, 128.069(3)º, 90º for compound **4**. The relationship of compounds **7** and **4** is reminiscent of the compounds which are polymorphs of each other.[15] If the heteroatom of compound **4** is replaced by Si, the Si-compound which is isostructural with compound **4** will be a polymorph of compound **7** we reported recently, for the two compounds have the identical chemical formula but different crystal structures.

Polymorphism, defined as the phenomenon of a chemical species having more than one crystal forms,[17] is attracting much attention because different forms maybe result in significantly difference in terms of both their structures and physical and chemical properties of compounds. To this date, several polymorphs based on different POMs have been reported in literatures.[18]

However, compounds **4** and **7** are not polymorphs of each other; it should be said that the Si-compound which is isostructural with compound **4** and compound **7** we reported recently are polymorphs of each other. Thus, we can say that compounds **4** and **7** are almost polymorphs of each other.

Crystal structure of 5 The structure of compound **5** is the most interesting one in the five compounds reported here, all the other compounds here and compounds we reported recently are all based on the Keggin POM, however, compound **5** is a hybrid which is based on Dawson POMs and TMMCs.

The asymmetric unit of compound **5** is comprised of half a Dawson POM $[H_3As_2W_{18}O_{62}]^{3-}$, half a $[Cu(phen)(inic)(H_2O)]^+$, half a $[Cu_2(phen)_2(inic)_2(H_2O)]^{2+}$ and one and a half of water molecules. The $[H_3As_2W_{18}O_{62}]^{3-}$ anion contains two $[\alpha\text{-A-}AsW_9O_{34}]^{9-}$ units derived from the α-Keggin anion by removal of a set of three corner-shared WO_6 octahedra. The As-O distances are in the range of 1.67(1)-1.721(9)Å, W-O distances are comparable to those of compounds **1**-**4**.

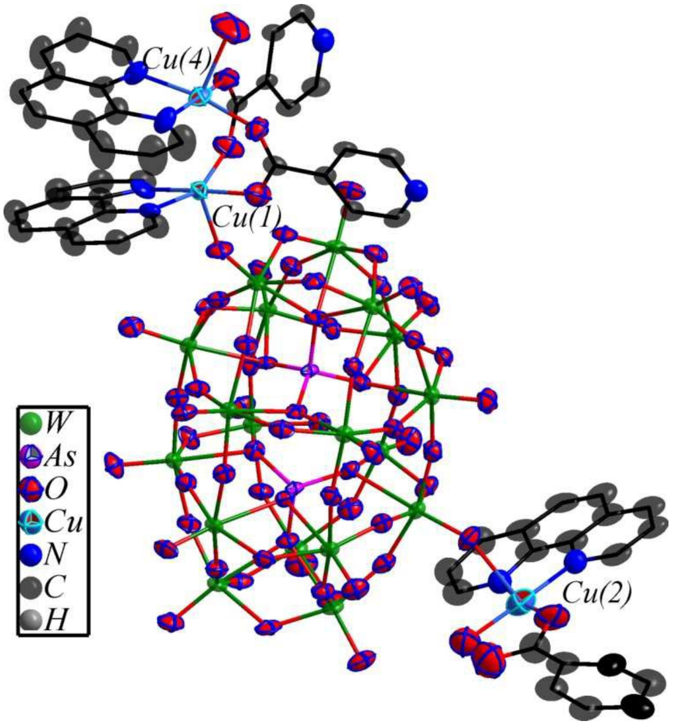


Fig. 7 Ellipsoid representation (50% probability) of the novel POM bi-supported TMMC in compound **5,** hydrogen atoms were omitted for clarity.

In contrast to TMMCs in compounds **1**-**4**, there are two different TMMCs in compound **5**, as shown in Fig. 7. One is $[Cu(phen)(inic)(H_2O)]^+$, and the other is $[Cu_2(phen)_2(inic)_2(H_2O)]^{2+}$. $[Cu(phen)(inic)(H_2O)]^+$ comprises a copper, a phen, an inic$^-$ and a water molecule, the copper exhibits a square-pyramidal geometry, in which the cooper is coordinated by a phen with Cu-N distances of 1.95(1)-1.99(2)Å, an inic$^-$ adopting a monodentate coordination mode via a carboxylate oxygen, a water molecule and a terminal oxygen from $[H_3As_2W_{18}O_{62}]^{3-}$ with Cu-O distances of 1.93(2)-2.399(9)Å. Via the contact between copper and the terminal oxygen of $[H_3As_2W_{18}O_{62}]^{3-}$, $[Cu(phen)(inic)(H_2O)]^+$ is linked to $[H_3As_2W_{18}O_{62}]^{3-}$ to form a novel POM supported TMMC. $[Cu_2(phen)_2(inic)_2(H_2O)]^{2+}$ is made up of two coppers, two phens, two inic$^-$ and a water molecule, the two coppers exhibit similar square-pyramidal geometries, one of which is defined by two nitrogens from a phen with Cu-N distances of 1.96(1)-2.04(1)Å, two carboxylate oxygens from two inic$^-$ ligands and one terminal oxygen from $[H_3As_2W_{18}O_{62}]^{3-}$ with Cu-O distances of 1.930(9)-2.17(1)Å, the other of which is defined by two nitrogen from a phen with a Cu-N distance of 2.02(1)Å, two carboxylate oxygens from two inic$^-$ ligands and one water molecule with Cu-O distances of 1.946(9)-2.29(2)Å. It is clear that the main difference between the two square-pyramids is that the water molecule at the apical position of one pyramid replaces the corresponding terminal oxygen of $[H_3As_2W_{18}O_{62}]^{3-}$ of the other pyramid. Each inic$^-$ adopting a bis-monodentate coordination mode is bound to two copper ions, therefore, each inic$^-$ serving as a linking agent joining the two copper complexes into a TMMC. One copper of $[Cu_2(phen)_2(inic)_2(H_2O)]^{2+}$ interacts with $[H_3As_2W_{18}O_{62}]^{3-}$ via Cu-O contact, that is to say, $[H_3As_2W_{18}O_{62}]^{3-}$ as a ligand coordinates to the copper of the TMMC, forming a POM supported TMMC. Thus, there are two different TMMCs supported by $[H_3As_2W_{18}O_{62}]^{3-}$, forming a novel POM bi-supported TMMC.

The phenol ring of the $inic^-$ and the phen phenol rings of $[Cu(phen)(inic)(H_2O)]^+$ are not coplanar, but are twisted with a dihedral angle of about 30º, whereas the phenol ring of the two $inic^-$ ligands and the phen phenol rings of $[Cu_2(phen)_2(inic)_2(H_2O)]^{2+}$ are twisted with a dihedral angle of about 90º. The different dihedral angles in the two TMMCs should be the main reason that causes the different structures of the two TMMCs. However, the mechanism of the formation is still elusive.

It should be noted that POM supported TMCs are ordinarily observed, and POM mono-, bi-, tri-, tetra- and penta- supported TMCs have been reported previously.[8a, 19] However, POM supported TMMCs were rarely reported. To our knowledge, compound **5** is not only the first example of compounds based on Dawson POMs and TMMCs of aromatic carboxylates and N-containing ligands, but also the first example of compounds in which the POM supports two different TMMCs.

FT-IR spectra

Compounds **1-4** contain the identical Keggin POM $[GeW_{12}O_{40}]^{4-}$, therefore, the IR spectra of them are very similar. The IR spectrum of compound **1** was detailedly described below as an example. The IR spectrum of compound **1** is shown in Fig. s1, of which the characteristic bands at 978 and 955cm^{-1} are attributed to υ(W-O$_t$), the band at 886 cm^{-1} is ascribed to υ(W-O$_b$-W), and the band at 783cm^{-1} is due to υ(W-O$_c$), respectively. The stretching of Ge-O bonds is observed at the spectrum band of 830cm^{-1}.[20] The absorption bands at 1584-1108cm^{-1} are due to vibrations of 2,2'-bpy and isonicotinate ligands in compound **1**. The IR spectra of compounds **2-4** are similar to that of compound **1**. They exhibit characteristic bands at 968, 887, 830, 777cm^{-1} for **2**, 971, 887, 830, 784cm^{-1} for **3**, 960, 877, 833, 770cm^{-1} for **4** ascribed to υ(W-O$_t$), υ(W-O$_b$-W), υ(Ge-O$_c$) and υ(W-O$_c$), respectively,[20] while bands at 1604-1108cm^{-1}, 1634-1108cm^{-1} and 1639-1104cm^{-1} are assigned to phen and isonicotinate in compound **2**, phen, nicotinate in compound **3** and 2,2'-bipy, 2-hydroxy-nicotinate in compound **4**, respectively. The POM in compound **5** is different from those of compounds **1-4**, thus the IR spectrum of compound **5** is different from those of compounds **1-4**. The characteristic bands of compound **5** at 965, 897, 866, 831 and 759cm^{-1} should be ascribed to υ(W-O$_t$), υ(W-O$_b$-W), υ(As-O$_c$) and υ(W-O$_c$), respectively.[21]

XRD patterns

The X-ray powder diffraction patterns of compounds **1-5** are all in good agreement with the simulated XRD patterns, confirming the phase purity of all the five compounds (Fig. s2). The differences in reflection intensities are probably due to preferential orientations in the powder samples of compounds **1-5**.

UV-Vis spectra

UV-Vis spectra of compounds **1-5**, in the range of 250-400 nm, are presented in Fig. s3. The UV-Vis spectrum of compound **1** displays an intense broad absorption peak centered about 257nm with two shoulder peaks at about 303 and 313nm assigned to O→W charge transfer and n→ π * transitions of phen and $inic^-$ ligands in compound **1**. The UV-Vis spectrum of compounds **4** exhibits very similar intense broad absorption peaks and shoulder peaks to those of compound **1** centered about 255, 303, 313nm, respectively, which should be ascribed to transfer bands of O→W and n→ π * transitions of organic ligands in compound **4**. However, the UV-Vis spectra of compounds **2** and **3** show some difference from those of compounds **1** and **4** which exhibit peaks and shoulder peaks at 255, 272, 296 and 255, 273, 296nm, respectively, which should also be due to the transfer bands of O→W and n→ π * transitions of 2,2'-bpy, nic^- and $hnic^{2-}$ ligands. Though the POM in compound **5** is different from those of all the other four compounds, the UV-Vis characteristic peaks of compound **5** is located at 255, 274 and 296nm, which are very similar to those of compounds **2** and **3**. It should be noted that the peaks of compound **5** should also be ascribe to O→W and n→ π * transitions of phen and pic^- ligands. Thus we can concluded that both Keggin and Dawson tungstates exhibit the characteristic band at about 255nm, compounds containing phen ligands exhibits the characteristic band at about 273nm and compounds containing 2,2'-bpy ligands show the characteristic band at 303nm.

Cyclic voltammograms

Fig. s4 shows the cyclic voltammogram of compound **1** in 1mol/L H_2SO_4 solution at the scan rate of 100mV·s^{-1}. It is clearly seen that in the potential range -600 to 0mV, three pairs of redox peaks appeared. Mean peak potentials $E_{1/2}=(E_{pa}+E_{pc})/2$ were -501, -349 and -151mV. The redox peaks correspond to one two-electron and two consecutive one-electron processes of W in compound **1**.[22]

The cyclic voltammograms of compounds **2**, **3** and **4** in 1mol/L H_2SO_4 solutions at the scan rate of 100mV·s^{-1} are presented in the potential range of -600 to 0mV (Fig. s4), too. There exist three reversible redox peaks with half-wave potentials ($E_{1/2}=(E_{pa}+E_{pc})/2$) at -506, -349 and -176mV for compound **3**, -497, -337 and -141mV for compound **4**, respectively. The redox peaks correspond to one two-electron and two consecutive one-electron processes of W in compounds **3** and **4**.[22] However, There exists only two reversible redox peaks with half-wave potentials ($E_{1/2}=(E_{pa}+E_{pc})/2$) at -500 and -336mV for compound **2**, and the peaks with half-wave potentials at about -160mV are very weak and are very difficult to identify.[23]

The cyclic voltammogram of compound **5** in 1mol/L H_2SO_4 solutions at the scan rate of 100mV·s^{-1} are presented in the potential range of -600 to 100mV (Fig. s4). Three pairs of redox peaks with mean peak potentials $E_{1/2}=(E_{pa}+E_{pc})/2$ -518, -282 and -55mV appeared. The redox peaks correspond to three two-electron processes of W in compound **5**.[22]

Photodegradation properties

The performance of compounds **1-5** for photocatalytic degradation of RhB has been investigated (Fig. 8). Blank tests show that with catalysts but no light, RhB solution is not discolored; the photodegradation process of RhB without any photocatalyst has also been studied for comparison, and only 23% of RhB was photodegraded after 360min. Changes in C_t/C_0 plot of RhB solutions versus reaction time were shown in Fig. 8. Compared with RhB without any photocatalyst, the absorption peaks of compounds **1-5** decreased upon irradiation, indicating that these compounds have photocatalysis properties. It also reveals that compounds **1-5** are photocatalysts for photocatalytic degradation of RhB.

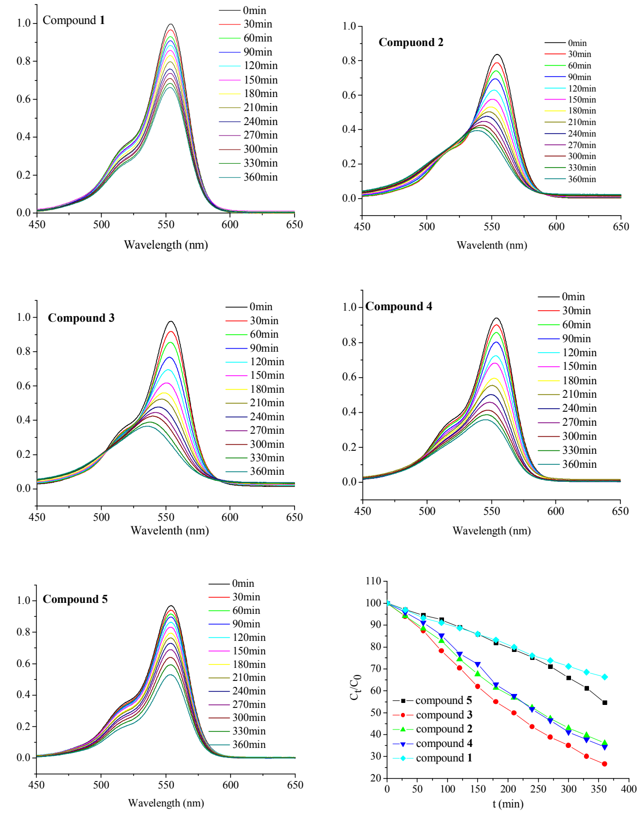


Fig. 8 photodegradation properties of compounds **1-5**.

Fig. 8 shows the reaction results of photodegradations of RhB over various catalysts at room temperature. As expected, all the catalysts are active for the photodegradation of RhB. Compound **1** catalyst shows the activity with 33.7% conversion after 360min. The photodegradations of RhB over [Cu$_3$(2,2'-bpy)$_3$(inic)(μ_2-OH)(H$_2$O)][SiW$_{12}$O$_{40}$]·2H$_2$O we reported recently that is isostructural and isomorphous with compound **1** has already been carried out, too. The reported compound shows the activity with 36.5% conversion, which is comparable to that of compound **1**. It should be noted that the only difference of the two compounds is that the heteroatom in compound **1** is Ge and the heteroatom in [Cu$_3$(2,2'-bpy)$_3$(inic)(μ_2-OH)(H$_2$O)][SiW$_{12}$O$_{40}$]·2H$_2$O is Si,[5m] indicating that the difference of heteroatom will have only slight influence to the photodegradation properties of compounds. Nevertheless, compound **5** shows a higher activity with 45.3% conversion. Compounds **2** and **4** show similar activities with 63.8% and 65.5% conversions, respectively, compound **3** shows the highest activity with the conversion (73.4%) of the five. It is worth noting that compounds **4** and **7** we reported recently are almost polymorphs of each other.[5m] However, compound **7** shows the activity with 42.3% conversion, which is much lower than that of compound **4**. The reason why compound **4** with Ge as heteroatom shows higher activity than compound **7** with Si as heteroatom is that the two are almost polymorphs of each other: two polymorphs can result in significantly difference in terms of both their structures and physical and chemical properties of compounds.

In the presence of equimolar amount H$_4$[GeW$_{12}$O$_{40}$][20] as a control experiment, about 70% of the dye was discolored within 240 min. The homogeneous catalyst H$_4$[GeW$_{12}$O$_{40}$] gave higher conversion (70% within 240 min, as shown in Fig. s5; by comparison, the conversion of compound **3** is 56.4% within 240min) under identical conditions; however, the recovery and recyclability of H$_4$[GeW$_{12}$O$_{40}$] was very difficult.[24]

Each catalyst used for degrading RhB solution is only about 5mg, which is hard to recover from the solution. For compound **3** exhibits the highest photodegradation efficiency and the amount of crystals of compound **3** is enough, compound **3** was selected to study its recyclability and reusability, including RhB conversion and catalyst recovery in three cycles. The same experimental conditions were used except that 30mg compound **3** was used as catalyst. It was found that with the increase of the amount of compound **3** the degradation rate of RhB increased. However, the increase of degradation rate of RhB is not proportional to the increase of amount of compound **3** used. The amount of compound **3** is increased to 30mg, about 90.5% of dye was discolored with the illumination time of 300min. by contrast, when the amount of compound **3** is 5mg, only 65.0% of RhB of dye was discolored.

The catalyst recovery was measured by the weight of the recovered catalyst. Generally, when using soluble heteropolyacid (e.g. H$_4$[GeW$_{12}$O$_{40}$]) as the catalyst, the used catalyst was recovered by precipitation and ion exchange[24]. In comparison, it was easy to separate and recycle compound **3**. The process of recovery possibly resulted in loss of approximately 5 wt.% after three consecutive cycles. RhB conversion dropped from 90.5% to 79.9% under the same experimental conditions

After three successive cycles for degradation experiments under the same conditions, the catalytic activity of residual amount of compound **3** were slightly decreasing, however it still can be well considered that the residual catalyst of compound **3** and the crystals used for X-ray powder diffraction are homogeneous (Fig. s6-7). Therefore, compound **3** exhibit superior stability in the catalytic processes.

Compounds **1-4** contain the identical Keggin ions. The photocatalytic reaction occurs in a adsorbed phase (on the surface of a catalyst), and the model of activation of catalysts is photonic activation by exciting a POM with light energy higher than the band gap of the POM, which leads to an intramolecular charge transfer and the formation of a excited-state species (POM*).[7f, 25] Therefore, POMs in catalysts are essentially important for their photodegradation properties. Identical POMs should be the main reason why compounds **2** and **4** exhibit very similar conversions.

The second main reason should be ascribed to the different packing structures of compounds **1-5**. The preferential orientations of crystal planes of compounds **1-5** should be different, thus the number of POMs on crystal planes should be different, and the difference will lead to their different photocatalytic properties. Therefore, the different photocatalytic properties of compounds **1**, **2** (**4**) and **3** can be due to the different packing structures of these compounds. Wang[26] and Wang[27] have also reported that the conversions of RhB over different compounds even containing identical Keggin species may not be the same.

In addition, the introduction of transition metal complexes should also have important influence on the catalytic activity. the hybridization between 3d orbit of Cu^{2+} and 2p orbit of O decreases the energy gap effectively,[28] enhancing the light absorption; and the organic ligand increases the adsorption capacity for substrate, which is in favor of the catalytic reaction.

Conclusions

Five new compounds based on polyoxometalates and TMMCs have been designed and synthesized. We not only introduced TMMCs into Dawson POMs but also carefully discussed the influence of chloride ions to the structures of TMMCs. It is very clear that the introduction of the new POM will increases the complexity of compounds based on POMs and TMMCs, and the introductions of both chloride ions and different POMs give new impetuses to the development of hybrids based on POMs and TMMCs.

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Notes and references

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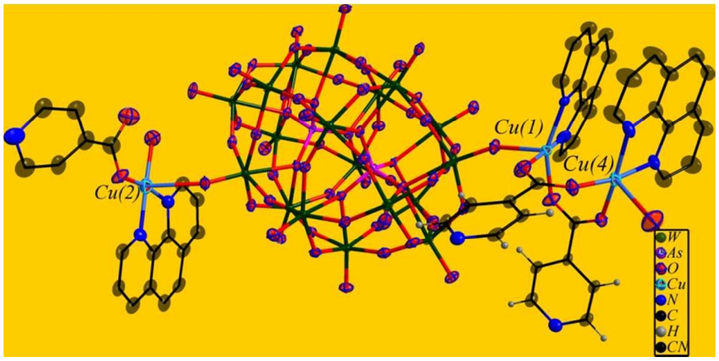

Five compounds constructed from different polyoxoanions and metal mixed-organic complexes of carboxylates and nitrogen-containing ligands have been synthesized and characterized.