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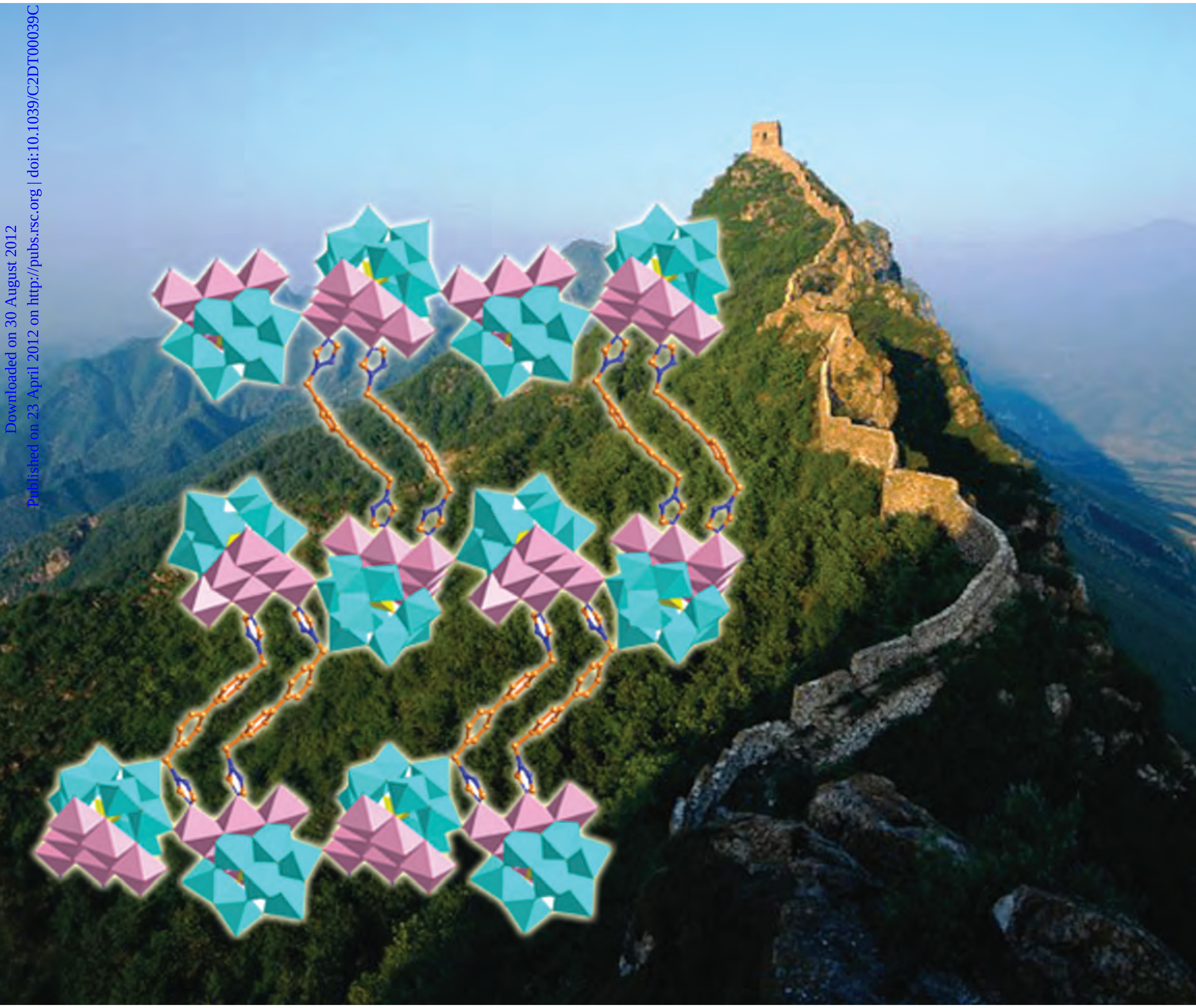

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COMMUNICATION

A novel 2D → 3D $\{Co_6PW_9\}$-based framework extended by semi-rigid bis(triazole) ligand†

Xiuli Wang,* Xiaojing Liu, Aixiang Tian, Jun Ying, Hongyan Lin, Guocheng Liu and Qiang Gao

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The building blocks $\{Co_6PW_9\}$ converging lacunary polyoxometalates and high-nuclear $\{Co_6\}$ clusters are furtherlinked by semi-rigid bis(triazole) ligands to construct a 2D → 3D framework under hydrothermal conditions, $[Co_6(\mu_3\text{-}OH)_3(H_2O)_9L(PW_9O_{34})]$ (1) (L = 4,4′-bis(1,2,4-triazol-1-ylmethyl) biphenyl).

In recent years, polyoxometalates (POMs) have received great attention because of their various structures and extensive application in the field of crystal engineering and functional materials.[1] Two remarkable branches have arisen in the POMs' development. One branch is the introduction of POMs to metal–organic frameworks (MOFs) to construct high dimensional inorganic–organic hybrid frameworks with novel topologies, such as interpenetration, polycatenation and polythreading.[2] In this series, POMs are almost the classical saturated ones.[3] The other branch is the design and syntheses of novel topological structures based on new lacunary type POMs and their derivatives.[4] Though lacunary POMs exhibit strong coordination ability by exposing more active coordination sites,[5] the synthetic conditions of this kind of compounds are relatively rigorous in an aqueous solution under a non-pressure process. Up to now, there are rare reports about the MOFs constructed from lacunary type POMs derivatives and organic ligands especially under hydrothermal condtions,[6] which may become a challenge in the POMs' field.

The reported lacunary POMs show a wide variety, such as classical mono-, bi- and tri-lacunary types, and usually act as excellent inorganic ligands. The metal ions insert into the active lacunary sites to build saturated mixed POMs. Up to now, those compounds constructed from the saturated mixed POMs and organic ligands under hydrothermal conditions were mostly reported by Yang's group.[7] They have done outstanding and systemic work in this field and reported a series of secondary building units (SBUs) based on saturated mixed POMs.[8] For example, a $\{Ni_6PW_9\}$-based compound, $[Ni(en)_2(H_2O)_2]_6\{Ni_6(Tris)(en)_3(BTC)_{1.5}\text{-}(B\text{-}\alpha\text{-}PW_9O_{34})\}_8\cdot 12en\cdot 54H_2O$ (en = ethylenediamine, BTC = 1,3,5-benzenetricarboxylate), has been reported as an organic molecular cage with a super large size.[9] However, in the reports of Yang's group, small multidentate amines and benzenetricarboxylate-type ligands were usually chosen as organic moieties of MOFs for grafting on lacunary POMs.[10] As is known, the selection of proper organic ligands is very important in construction of novel POM-based frameworks.[11] In the previous work, our group used flexible/semi-rigid N-donor ligands with large dimensions to obtain some new saturated POM-based structures,[12] which has been confirmed to be an effective strategy for construction of novel topological frameworks. Thus, in this work, we attempt to introduce a semi-rigid bis(triazole) ligand 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl (**L**) (Chart S1†) to lacunary POMs, which has unique merits: more N donors for enhancing the coordination ability, the biphenyl group with a large dimension for strengthening the rigidness, and two $-(CH_2)-$ spacers for endowing some flexibility.[13] Furthermore, the transition metal ions in the tri-substituted Keggin anions reported by Yang's group are mostly based on Cu, Fe and Ni atoms. In this work, we select cobaltous acetate as the reactant aiming for construction of co-substituted POM-based compounds. Fortunately, the expected novel framework $[Co_6(\mu_3\text{-}OH)_3(H_2O)_9$**L**$(PW_9O_{34})]$ (**1**) based on $[Co_6(\mu_3\text{-}OH)_3(H_2O)_9]\text{-}[PW_9O_{34}]$ (abbreviated to $\{Co_6PW_9\}$) building blocks further linked by semi-rigid bis(triazole) ligand **L** have been obtained, exhibiting a 2D → 3D framework.

Compound **1**‡ was prepared under hydrothermal conditions from heating a mixture of $H_3PW_{12}O_{40}$, $Co(CH_3COO)_2$ and **L** in water at 120 °C for 3 days. Single crystal X-ray structural analysis[14] reveals that compound **1** contains two motifs: a Co_6-substituted POM unit $\{Co_6PW_9\}$ (Fig. 1c) and a semi-rigid bis (triazole) ligand **L**.

In our work, a saturated Keggin type anion $[PW_{12}O_{40}]^{3-}$ was chosen as the precursor for losing a $\{W_3O_{13}\}$ cluster to form a $[PW_9O_{34}]^{9-}$ (abbreviated as $\{PW_9\}$) unit, which was conduced to convert under basic conditions. The $\{PW_9\}$ unit is a good inorganic ligand by offering seven active O coordination sites. In Fig. 1a–c, the $\{PW_9\}$ unit is capped by a triangular $[Co_6(\mu_3\text{-}OH)_3(H_2O)_9]^{9+}$ (abbreviated as $\{Co_6\}$) cluster to generate a $\{Co_6PW_9\}$ secondary building unit (SBU). In the $\{Co_6\}$ cluster, it shares seven terminal O atoms with a $\{PW_9\}$ unit. Each Co atom shows an octahedral coordination geometry and has a different coordination environment. Six Co atoms are in the same plane through sharing O atoms to form a triangular structure. The valence sum calculations[15] show that all the Co atoms

Department of Chemistry, Bohai University, Jinzhou, 121000, P.R. China. E-mail: wangxiuli@bhu.edu.cn; Fax: +86-416-3400158; Tel: +86-416-3400158

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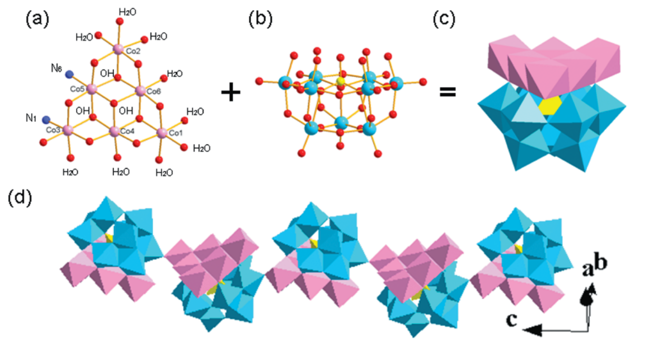

Fig. 1 (a) Ball-and-stick views of {Co_6}. (b) $[PW_9O_{34}]^{9-}$ unit. (c) Polyhedral view of the structure of {Co_6PW_9} and (d) Fragment of the 1D inorganic chain consisting of {Co_6PW_9} units. CoO_6–CoO_5N: rose; PO_4: yellow; WO_6: blue.

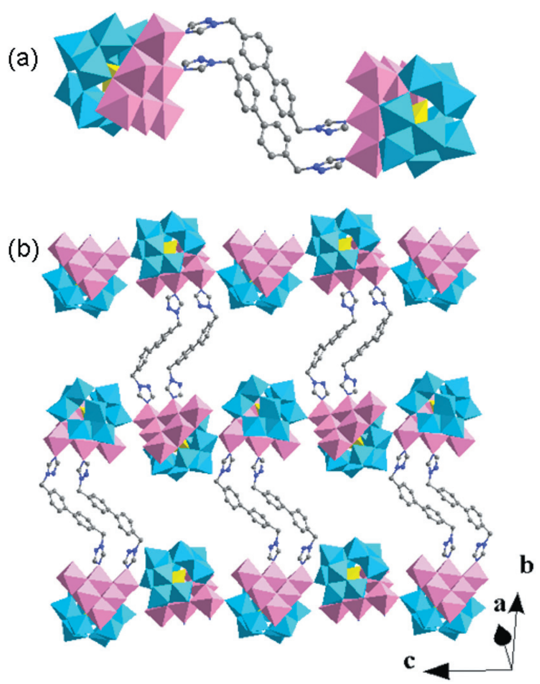

Fig. 2 (a) Two {Co_6PW_9} units linked by two bridging **L** ligands of **1**. (b) The view of the 2D sheet constructed from 1D {Co_6PW_9} chains linked by **L** ligands.

are in +II oxidation states and all the W atoms are in +VI oxidation states. In a word, the formation of {Co_6PW_9} becomes the first feature of **1**, especially obtained under hydrothermal conditions.

As shown in Fig. 1d, the {Co_6PW_9} units in compound **1** are further linked with each other to form an infinite 1D inorganic chain, through sharing Co3–O34–W8 bonds. The adjacent {Co_6} clusters are in an up–down style. As expected, the **L** molecule acts as a bridging ligand by providing two apical N donors (N1 and N6) to coordinate with Co3 and Co5 atoms from two different {Co_6PW_9} units, that is to say, two {Co_6PW_9} units can be fused by two bridging **L** ligands (Fig. 2a). The **L** ligand presents a 'S'-type conformation (Fig. S1†). Thus, the 1D inorganic chains composed by {Co_6PW_9} units are further

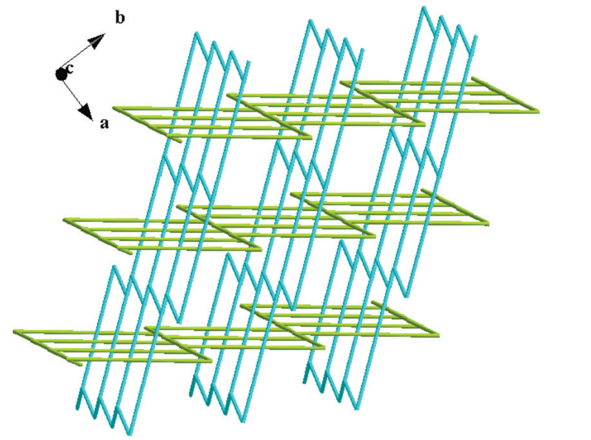

Fig. 3 The multi-fold interpenetrating 3D topology framework of compound **1**.

extended to a 2D sheet by bridging **L** ligands (Fig. 2b). The participation of **L** ligand with large dimensions for linking {Co_6PW_9} units becomes the second feature for construction of compound **1**. In the 2D sheet, the grid is too big that may induce the instability of the whole structure. Thus, each 2D sheet interpenetrates with each other (Fig. S2†) to generate a multi-fold interpenetrating 3D framework (Fig. S3†). Further insight into the architecture can be described by a simple node-and-linker reference nets, namely, an intriguing topology shown in Fig. 3. The 2D sheet is a (6^3)-connected topology through assigning the {Co_6PW_9} units as nodes, and the bis(triazole) ligands as the linkers. The construction of the multi-fold interpenetrating 3D framework by 2D sheets can be viewed as the third feature of compound **1**, achieving the conversion of 2D to 3D.

The electrochemical property of compound **1** was studied in 1 M H_2SO_4 aqueous solution.[16] At different scan rates, there are three reversible redox peaks appearing in the potential range of 300–750 mV (Fig. S4a†). The redox peaks I–I′, II–II′ and III–III′ with the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ approximately at −197 (I–I′), −451 (II–II′) and −634 (III–III′) mV (scan rate: 60 mV s^{-1}) are attributed to the redox of the {PW_9} polyanion. Fig. S4b† shows cyclic voltammograms for the electrocatalytic reduction of nitrite at **1**-CPE in 1 M H_2SO_4 aqueous solution. With the addition of nitrite, all three reduction peak currents gradually increase, while the corresponding oxidation peak currents decrease with the scan rate of 200 mV s^{-1}. It shows that compound **1** has good electrocatalytic activity toward the reduction of nitrite in 1 M H_2SO_4 aqueous solution.

The photocatalytic property of compound **1** was investigated in the methylene blue (MB) solution (1 mol L^{-1}) under UV irradiation from an Hg lamp, as shown in Fig. S5.†[17] It can be clearly observed that the absorbance peak of MB is decreased obviously from 1.97 to 0.26 for compound **1** after 90 min, and the calculation reveals that the conversion of MB is 91.9% for compound **1**. The result indicates that compound **1** shows an excellent photocatalytic activity for the degradation of MB.

Magnetic susceptibility of compound **1** was measured in the range of 2–300 K at 500 Oe. The $\chi_m T$ *vs.* T and χ_m^{-1} *vs.* T plots for compound **1** are shown in Fig. S8.† The $\chi_m T$ value at 300 K is 19.22 cm^3 mol^{-1} K, which is much higher than that of six spin-only Co^{II} ions (11.25 cm^3 mol^{-1} K), due to the spin–orbit coupling of Co^{II} ions. As cooling, the $\chi_m T$ value gradually increases to 19.91 cm^3 mol^{-1} K at 57 K, and then rapidly reaches a maximum of 28.37 cm^3 mol^{-1} K at 3.2 K that is well consistent with the value of the ground state of $S_{eff} = 3$ with $g_{eff} = 4.34$ due to the $S_{eff} = 1/2$ with $g_{eff} = 4.1–5.0$ for one Co^{II} ion at low temperature,[18] which indicates the global ferromagnetic interactions between Co^{II} ions. Finally, the magnetic susceptibility suddenly drops to 27.43 cm^3 mol^{-1} K at 2 K, which can be attributed to the anisotropy of Co^{II} ion and intercluster antiferromagnetic interactions. The magnetic data from 300 K to 50 K can be fitted to the Curie–Weiss law with a Weiss constant of 2.4 K for compound **1**. The small positive Weiss constant confirms the moderately ferromagnetic couplings between spin centers among the cluster units. The isothermal magnetization up to 50 KOe at 2 K is shown in Fig. S9.† The large slope at low field and the saturated values of 12.94 Nβ at 50 KOe (equal to $S_{eff} = 3$ with $g_{eff} = 4.32$) corroborate the ferromagnetic couplings between Co^{II} ions. Although tens of cobalt clusters from Co_5 to Co_{36} have been investigated,[19] most of them display 0 or small ground states because of antiferromagnetic couplings, while the ferromagnetic compounds are rarely reported. Compound **1** represents one of the rare ferromagnetic clusters in this system.

In summary, we have successfully synthesized a new 2D → 3D framework based on $\{Co_6\}$-substituted lacunary polyanions $\{Co_6PW_9\}$ and semi-rigid bis(triazole)-based ligand **L** under hydrothermal conditions. In compound **1**, the semi-rigid **L** ligands link the 1D inorganic chains composed by $\{Co_6PW_9\}$ units to construct a 2D sheet. Furthermore, these 2D sheets interpenetrate with each other to construct a 3D multi-interpenetrating framework. This work indicates that the employment of proper large N-donor ligands is an effective strategy for modifying lacunary POMs and obtaining multi-interpenetrating frameworks. Further study on modification of other lacunary POMs by large flexible/semi-rigid N-donor ligands is underway.

Acknowledgements

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Notes and references

‡ Synthesis of **1**: The mixture of $H_3PW_{12}O_{40}$ (0.58 g, 0.2 mmol), Co-$(CH_3COO)_2$ (0.18 g, 1 mmol), **L** (0.06 g, 0.2 mmol) was dissolved in 10 mL of distilled water at room temperature. After stirring for 30 min and adjusting the pH value of the mixture to about 5.8 with 1.0 mol L^{-1} HCl, the suspension was transferred to a Teflon-lined autoclave and kept under autogenous pressure at 120 °C for 3 days. After slow cooling to room temperature, red block crystals were obtained (30% yield based on W). Anal. Calcd for $C_{18}H_{16}Co_6N_6O_{46}PW_9$ (3091.48): Co 11.44, P 1.00, W 53.52, C 6.99, H 0.52, N 2.72%. Found: Co 11.32, P 1.08, W 53.98, C 6.86, H 0.91, N 2.69%. IR (KBr pellet, cm^{-1}): 3398(s), 2361(s), 1650 (w), 1533(m), 1454(m), 1390(m), 1031(s), 940(m), 790(w), 666(w).

Crystal data for **1**: $C_{18}H_{16}Co_6N_6O_{46}PW_9$, $M = 3091.48$, orthorhombic *Pbcn*, $a = 21.398(14)$ Å, $b = 32.298(14)$ Å, $c = 20.89(2)$ Å, $V = 14438(18)$ $Å^3$, $Z = 8$, $D_c = 2.845$ g cm^{-3}, $\mu = 15.720$ mm^{-1}, 79 188 reflections measured, 12 307 unique ($R_{int} = 0.0657$), final $R_1 = 0.0506$, w$R_2 = 0.1115$, GOF = 1.147, $T = 87$ K. CCDC reference number 856818.

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