

## Highlights of recent advances in functional coordination polymers made in China

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Coordination polymers (or metal-organic frameworks, MOFs), as one of the essences of crystal engineering and coordination chemistry, have attracted considerable attention from chemists, physicists, and materials scientists for the development of hybrid crystalline solids with novel supramolecular structures and physicochemical properties. In particular, research on functional coordination polymers has evolved considerably during the last decade [1]. In this context, *Science China Chemistry* and *Chinese Science Bulletin*, as internationally recognized and influential academic journals, have provided a stage for chemists in China to demonstrate their significant contributions to this field. Current research is mostly concentrated on the potential applications of such network-based complexes as magnetic, fluorescent, adsorption, optoelectronic, drug delivery, and multifunctional molecule-based materials.

One of the flourishing themes in coordination polymers is the design and synthesis of diversiform molecule-based magnetic materials with interesting structures and properties [2]. In this regard, Gao et al. [3] have successfully prepared two three-dimensional (3D) Mn<sup>II</sup>-W<sup>IV</sup> and Cu<sup>II</sup>-W<sup>IV</sup> coordination systems based on octacyanotungstate (IV) and 4,4'-bipyridine dioxide. Antiferromagnetic coupling is observed between the Mn<sup>II</sup> ions, while a weak ferromagnetic interaction exists between the Cu<sup>II</sup> centers. In a similar vein, Song and co-workers synthesized two bimetallic Mn<sup>II</sup>-W<sup>IV</sup> coordination polymers with 1D chain and 3D open network structures [4]. Both complexes show weak antiferromagnetic interactions between adjacent Mn<sup>II</sup> ions because of the presence of long diamagnetic bridges. In addition, a novel heterospin 1D polymeric chain generated from Cu<sup>II</sup> and nitroxide radicals has been reported by Liao's group [5].

This complex displays a ferromagnetic interaction between Cu<sup>II</sup> and nitroxide radicals, as well as a weak antiferromagnetic interaction between the Cu<sup>II</sup> centers.

Carboxylate-based polymeric coordination complexes represent an important class of magnetic materials. For example, Bu and co-workers [6] synthesized two isomorphous 3D Mn<sup>II</sup> and Co<sup>II</sup> coordination polymers using a mixture of benzoimidazol-1-yl-acetate and formate ligands. Both complexes display a new (3,6)-connected topological network and distinct magnetic behaviors, that is, spin-canted antiferromagnetism for the Mn<sup>II</sup> complex and antiferromagnetic coupling for the homologous Co<sup>II</sup> species, which are essentially based on the interactions between the metal ions and bridging carboxylate groups. Feng and co-workers [7] prepared a 2D Mn<sup>II</sup> coordination polymer hydrothermally using 1,4-benzenedis(thioacetic acid) as bridging tectons and 1,10-phenanthroline as a chelating co-ligand. The layered structure contains linear trinuclear Mn<sup>II</sup> subunits that display weak antiferromagnetic interactions. Zuo and co-workers [8] prepared a 1D chain-like Co<sup>II</sup> coordination polymer with tetrathiafulvalene carboxylate that exhibits ferromagnetic interactions at low temperature between intrachain Co<sup>II</sup> ions bridged by carboxylate groups. The presence of bulky crown-ether segments and weak intermolecular S...S interactions causes this complex to have low electric conductivity. A 3D porous Cu<sup>II</sup> MOF containing tris(2-carboxyethyl)isocyanurate and piperazine was prepared by Hou and co-workers under hydrothermal conditions [9]. In the resulting (3,8)-connected network, the planar tetranuclear Cu<sup>II</sup> clusters formed *via* bridging hydroxyl and carboxylate anions act as 8-connected nodes and exhibit antiferromagnetic interactions. Using the connectivity of both carboxylate and triazole groups in 1H-1,2,3-triazole-4,5-dicarboxylic acid, Su and co-workers [10] constructed a 3D

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(3,4)-connected  $\text{Co}^{\text{II}}$  coordination polymer that displays antiferromagnetic coupling between the  $\text{Co}^{\text{II}}$  ions. More interestingly, Zheng et al. [11] synthesized a 1D  $\text{Co}^{\text{II}}$  helical complex with 6-phosphononicotinic acid, in which the metal centers bridged by phosphonate groups show antiferromagnetic interactions. After excluding coordinated and lattice water, visible changes are observed in the color and structure of the dehydrated material, which shows the metamagnetic behavior at low temperature. Coordination polymers containing metal ions other than those of transition metals have also been prepared. Zhao and co-workers [12] produced a 3D  $\text{Gd}^{\text{III}}$  coordination framework with 1D channels, in which ferromagnetic coupling exists between adjacent metal centers bridged by the carboxylate groups of 2,6-naphthalenedicarboxylate ligands. Two porous  $\text{Ce}^{\text{III}}$  MOFs containing two different carboxylic acid derivatives have been reported by Wang et al. [13]. The magnetic properties of both pillared-layer coordination frameworks were also studied.

On the other hand, fluorescent MOFs are of great significance because of their high thermal stability and favorable metal-ligand interactions for structural and functional regulation. As a representative type of photoluminescent material, coordination polymers containing  $d^{10}$  metal ions have received particular consideration. For example, Sun and co-workers have reported two novel  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  coordination polymers containing 4-imidazole-benzoate, which display a 2-fold interpenetrating 2D (4,4) layered structure that crystallizes in the chiral group  $P4_122$ , and a 4-fold interpenetrating 3D porous framework with diamond topology, respectively. The acentric  $\text{Zn}^{\text{II}}$  coordination polymer shows modest powder second-harmonic-generation (SHG) activity, making it a good candidate for non-linear optical applications. With regard to their photoluminescence properties, only the  $\text{Cd}^{\text{II}}$  species exhibits enhanced ligand-based fluorescent emission at 480 nm [14]. Cheng and co-workers [15] prepared two 1D zigzag  $\text{Zn}^{\text{II}}$  coordination polymers and one 2D grid-like layered  $\text{Cd}^{\text{II}}$  complex using 2,5-dihydroxy-*p*-benzenediacetic acid and different  $\text{N},\text{N}'$ -chelating co-ligands. These polymeric materials exhibit solid state fluorescent emissions that originate from charge transfer between the metal centers and organic ligands. Likewise, Wang and co-workers prepared two 2D  $\text{Zn}^{\text{II}}$  coordination polymers with different helical subunits as well as one 1D helical coordination array using 5,5'-dithiobis(2-nitrobenzoic acid) and secondary N-donor bridging or chelating co-ligands. All the complexes exhibit ligand-based solid state fluorescent emission where the metal ions enhance the intensity of emission [16]. Chen et al. [17] also demonstrated that rigid dicarboxylate building blocks could facilitate fluorescent enhancement, by exploring the luminescent properties of three  $\text{Cd}^{\text{II}}$  coordination polymers containing different rigid/flexible dicarboxylate species and N-donor chelating co-ligands. The two 2D layered  $\text{Cd}^{\text{II}}$  coordination polymers based on 2-(2-pyridinyl-benzimidazolyl)acetic acid and

5-hydroxy-isophthalic acid as a co-ligand prepared by Zheng and co-workers [18] exhibit red shifts of fluorescence maxima compared with that of the free ligand. Su's research group [19] obtained a 3D MOF from the hydrothermal reaction of  $\text{Zn}^{\text{II}}$  with 5-aminotetrazole that shows a diamond network topology, hexagonal channels, and strong blue fluorescence at room temperature. In addition, Lang and co-workers [20] prepared four different 1D and 2D  $[\text{Cu}_n\text{I}_n]$ -based coordination polymers using flexible benzimidazolyl derivatives. These polymeric complexes exhibit strong solid state emissions at 507–597 nm with different origins, so may be used as green-emitting luminescent materials. As well as  $d^{10}$  coordination systems, lanthanide-organic frameworks can also display attractive photoluminescence behavior. For example, Zhao et al. [12] reported a 2D  $\text{Eu}^{\text{III}}$  coordination polymer that exhibits the characteristic red emission of  $\text{Eu}^{\text{III}}$  in DMF solution.

The applications of coordination polymers have recently been extended to areas such as gas adsorption, drug carriers, and semiconductors. In this context, a novel 2D layered  $\text{Ni}^{\text{II}}$  organo-diphosphonate containing 4,4'-bipyridine co-ligand with the capability to adsorb alkaline gas was recently produced by hydrothermal synthesis [21]. Sun and co-workers reported four 2D and 3D bismuth citrate coordination polymers based on dimeric building units, with the inclusion of protonated ethylenediamine and pyridine guest moieties [22]. A possible pharmacokinetic pathway for bismuth citrate-based drugs was proposed, in which release of encapsulated drugs from the porous matrix of bismuth citrate may occur at low pH value. As a result, these polymeric systems can be considered as a new type of hybrid material with potential application in drug carrier. Niu and co-workers [23] prepared two 1D  $\text{Fe}(\text{II/III})$  coordination polymers with mixed ligands. These complexes show *p*-type semiconductor characteristics, as confirmed by their surface photovoltage spectra exhibiting positive surface photovoltaic responses in the range of 300–600 nm. These results may aid in developing novel photoelectric materials.

Very recently, the rational design and preparation of coordination polymers with multiple functions has received increasing research interest [1]. With this in mind, Qiu's group [24] prepared a 3D  $\text{Mn}^{\text{II}}$  coordination framework with rutile-type network topology using 8-hydroxyquinoline-5-sulfonate. This framework exhibits strong antiferromagnetic interactions between adjacent  $\text{Mn}^{\text{II}}$  centers and also fluoresces intensely at 568 nm because of ligand-to-metal charge transfer. Chen and co-workers [25] synthesized a 3D rutile-type  $\text{Zn}^{\text{II}}$  coordination polymer with 1,3,5-benzenetricarboxylate, in which DMF solvent molecules and  $\text{Me}_2\text{NH}_2^+$  cations are accommodated. After removing the DMF molecules by heating at 160°C, a structural transformation occurs to afford a new phase that exhibits proton conductivity. Further heat treatment at 260°C induces the release of counter cations in their neutral form through a proton transfer process. The resulting porous solid shows a

moderate uptake of CO<sub>2</sub> gas, and can adsorb methanol and exclude acetone molecules. The same group also prepared a (3,12)-connected porous framework with octacobalt clusters from CoSO<sub>4</sub> and 2,6-di-*p*-carboxyphenyl-4,4'-bipyridine. This framework displays spin-glassy behavior as well as gas adsorption properties toward N<sub>2</sub> and H<sub>2</sub> after activation by heating [26]. Additionally, Cao and co-workers [27] synthesized a 3D porous coordination framework from Zn<sup>II</sup> and tetrakis[4-(carboxyphenyl)oxamethyl]methane acid with chiral building units, which can be regarded as a multifunctional crystalline material with ferroelectric and SHG activity as well as gas adsorption properties. Wang et al. [28] showed that metal-formate coordination frameworks may exhibit diverse topological networks depending on the size, shape, charge, and H-bonding geometries of the protonated amine templates. These molecule-based materials display promising magnetic, dielectric, porous, and optical properties.

The enormous attention devoted to coordination polymers originates from their diverse and adjustable network architectures as well as their associated properties and potential applications. The current research developments in this field, both at home and abroad, indicate a clear trend away from the initial random synthesis and structural characterization of coordination polymers to the design, prediction, and controlled preparation of desired functional systems. The latest progress has been production of advanced crystalline materials with multiple functions. Undoubtedly, the original results published in journals such as *Science China Chemistry* and *Chinese Science Bulletin* by Chinese chemists are of great significance and influence the overall direction of research in this field, where an abundance of developments remain to be made.

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