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Short communication

3D porous Mn(II) coordination polymer with left-handed 4_1 helical chains as building subunits: Selective gas adsorption of CO_2 over CH_4 and anticancer activity evaluation

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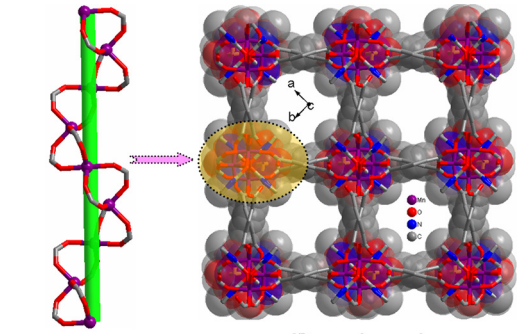
GRAPHICAL ABSTRACT

Presented here is a new Mn(II) coordination polymer, namely $[Mn(bptc)_{0.5}(e\text{-urea})]_n$ (**1** H_4bptc = biphenyl-3,3′,5,5′-tetracarboxylic acid, e-urea = 2-imidazolidone), which features a homochiral 3D porous framework based on left-handed 4_1 helical Mn(II)-carboxylate chains as building subunits.



Left-handed 4_1 helical chain 3D porous framework

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ABSTRACT

A new Mn(II) coordination polymer, namely $[Mn(bptc)_{0.5}(e\text{-urea})]_n$ (**1** H_4bptc = biphenyl-3,3′,5,5′-tetracarboxylic acid, e-urea = 2-imidazolidone), was urothermally synthesized by the self-assemble reaction of $MnCl_2{\cdot}4H_2O$, H_4bptc and e-urea. Single crystal X-ray structural analysis revealed that compound **1** features a 3D porous framework with 1D left-handed 4_1 helical chains as building subunits. Gas sorption properties investigations indicated that compound **1** shows high adsorption selectivity for CO_2/CH_4. In addition, the anticancer activity of the newly prepared compound **1** has been evaluated against the human cancer cells HeLa and Hep G2 via the MTT assay method.

Porous metal-organic frameworks (PMOFs), which can be considered as promising candidate for gas storage and separation because of their permanent microporosities and large internal surface areas, have gained tremendous interest [1–5]. The recent progress in this area has generated numerous PMOFs, most of which are interpenetrated with low porosity, small internal surface areas and low thermal stability [6–10]. Therefore, how to obtain non-interpenetrated PMOFs with high stability is challenging and significant. In order to avoid interpenetration in the construction of MOFs, an effective way reported by Yaghi and his co-workers was well established, which exploit in situ generated rod-shaped metal-carboxylate chains as second building subunits (SBUs) [11]. The cross-linking of these rod-shaped SBUs can effectively avoids the occurrence of interpenetration in MOFs owing to its intrinsic geometry and rigidity. In addition, the selection of a suitable

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polycarboxylate ligands is also crucial for the construction PMOFs in that the carboxylate groups can easily bridge metal ions into a rod-shaped metal-carboxylate chains [12].

As a symmetrical carboxylate ligand, biphenyl-3,3′,5,5′-tetracarboxylic acid (H_4L) has four carboxylate groups, and has been widely used to construct PMOFs with excellent gas adsorption properties and drug delivery capacity [13–15]. In viewing of the superior structural characteristic of H_4L for the construction of PMOFs, in this work, we also selected H_4L as the organic building block to react with Mn(II) ions under urothermal conditions. Successfully, we obtained a new Mn(II) coordination polymer, namely $[Mn(bptc)_{0.5}(e\text{-urea})]_n$ (**1** H_4bptc = biphenyl-3,3′,5,5′-tetracarboxylic acid, e-urea = 2-imidazolidone). Single crystal X-ray diffraction analysis revealed that compound **1** features a 3D porous framework with left-handed 4_1 helical chains as building subunits. In addition, the anticancer activity of the newly prepared compound **1** has been evaluated against the human cancer cells HeLa and Hep G2 via the MTT assay method.

Urothermal reactions of $MnCl_2{\cdot}4H_2O$, H_4bptc and 2-imidazolidone afforded a new crystalline materials of $[Mn(bptc)_{0.5}(e\text{-urea})]_n$. Single crystal X-ray structural analysis revealed that compound **1** crystallizes in the tetragonal chiral $P4_122$ space group, presenting a 3D porous framework with 1D Mn(II)-carboxylate left-handed helical chains as building subunits. The asymmetric unit of **1** contains one Mn(II) ion with 0.5 occupancy, a quarter of the L^{4-} ligand, and half of coordinated e-urea molecule. As shown in Fig. 1, each Mn(II) ion is coordinated to five carboxylate oxygen (O1, O1a, O2c, O3c and O2b) atoms from five L^{4-} ligand and one coordinate e-urea molecule (O3) to form a slightly distorted octahedral coordination geometry. The Mn−O distances are in the range of 2.106(4)–2.269(4) Å, and the O−Mn−O bond angles vary from 87.57(17)° to 173.0(2)° (Table S1), which are comparable to that of previously reported Mn(II)-carboxylate compounds [16]. The H_4L ligand are fully deprotonated in the self-assemble process, and further links eight individual Mn(II) ions with its four carboxylate groups in uniform bis-monodentate mode (Fig. S1). Interestingly, two adjacent Mn(II) ions with the separation of 3.753 Å are bridged by two carboxylate groups, further extending into a 1D left-handed 4_1 helical chains with a pitch of 9.597 Å (Fig. 2a). These adjacent left-handed helical chains are further linked by the L^{4-} ligands together, giving rise to a complicated 3D framework with 1D nano-sized channels along crystallographical *c* axis (Fig. 2b). The diameter of the 1D nano-sized channel is 11.13 Å. The total solvent-accessible volume is estimated to be about 36.3% calculated by the PLATON program.

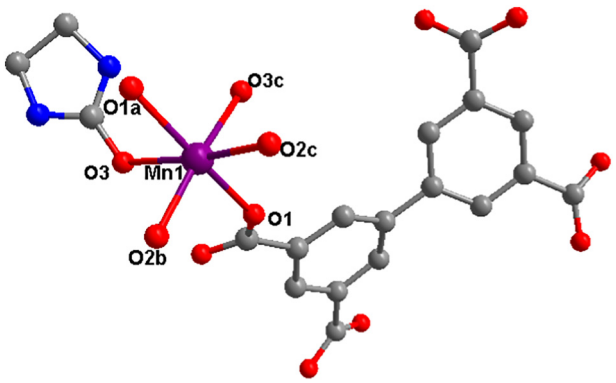

Fig. 1. Perspective view of the coordination environments of Mn(II) ion in compound 1. symmetry codes: (a) –1 + *x*, 1 + *y*, 1 − *z*; (b) 0.5 − *x*, *y*, 0.75 − *z*; (c) –0.5 − *x*, 1 + *y*, 0.25 + *z*.

The phase purity of compound **1** was confirmed by the similarity of the experimental and simulated X-ray diffraction patterns (Fig. S2a). Thermogravimetric analysis indicated that compound **1** can be stable up to 350 °C, and after that, the framework of **1** begins to collapse owing to the decomposition of the organic ligand. The final residues of 23.73% may be powder MnO (calcd: 23.32%) (Fig. S2b). The high thermal stability of **1** was also confirmed by the variable powder X-ray diffraction experiment (Fig. S2a).

Considering the porous structural feature of **1**, the gas adsorption properties were investigated to evaluate the porosity of the as-synthesized samples. The as-synthesized samples of **1** were firstly activated under vacuum at 100 °C for about 2 h before the gas adsorption experiment. The permanent porosity of **1** was evaluated by the N_2 sorption isotherms at 77 K (Fig. 3a), which exhibits a typical-I sorption behavior with N_2 uptake capacity of 147.6 cm^3/g at 1 atm, giving the giving BET and Langmuir surface areas of 729.1 and 867.8 m^2/g, respectively. In addition, the adsorption isotherms of CO_2 and CH_4 for **1** were also measured up to 1 atm at 273 K and 298 K (Fig. 3b). The CO_2 adsorption values of **1** are 52.2 cm^3/g at 273 K and 31.7 cm^3/g at 298 K under 1 atm pressure, respectively, which are comparable with previously reported well known porous crystalline materials [17,18]. The CH_4 adsorption capacities are 13.9 cm^3/g and 6.1 cm^3/g at 273 K and at 298 K under 1 atm pressure, respectively, which are far less than that of the CO_2 adsorption values under the same conditions. The heat of adsorption (Q_{st}) values of CO_2 and CH_4 were calculated based on the adsorption data collected at 273 K and 298 K. At zero coverage, the Q_{st} of CO_2 and CH_4 are 28.94 kJ/mol and 17.8 kJ/mol, respectively, indicating that there exist strong interactions between CO_2 molecules and the framework of the title compound. To further evaluate the gas separation ability of **1**, the adsorption selectivity of CO_2/CH_4 (equimolar binary mixtures) was calculated by the "ideal adsorbed solution theory" (IAST) model, which was a method used to determine the gas selectivity of porous crystalline materials. As shown in Fig. S3, the CO_2/CH_4 adsorption selectivity of **1** is 7.8 and 9.2 at 273 K and 298 K, respectively, which are higher than that of MAF-66 and LIFM-10 [19,20]. Such high selectivity indicates that this Mn(II) MOF can serve as a potential separation material for CO_2/CH_4.

The interesting structural features of compound **1** encouraged us to test its cytotoxicity against a panel of human cancer cell lines HeLa and Hep G2 by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay method. Compounds were dissolved in DMSO and blank samples containing the same volume of DMSO were taken as controls to identify the activity of solvent in this cytotoxicity experiment. Cisplatin was used as a positive control to assess the cytotoxicity of the test compounds. The results were analyzed by means of cell inhibition expressed as IC_{50} values and they are shown in Fig. 4. The IC_{50} value showed that the Mn(II) complex exhibited significant activity against the tested cancer cells which is almost equal to the activity of well-known anticancer drug cisplatin. It is to be noted that the ligand and $MnCl_2$ did not show any significant activity on all the cancer cells, which confirmed that the chelation of the ligand with the Mn(II) ion is the only responsible factor for the observed cytotoxic properties of the compound **1**.

In summary, we successfully obtained a new 3D porous Mn(II) coordination polymer, which contains left-handed 4_1 helical Mn(II)-carboxylate chains as building subunits. Gas adsorption properties investigations indicated that this Mn(II) compound exhibits high adsorption selectivity for CO_2/CH_4 and promising anticancer activity against the cancer cells tested. Further works for developing new porous crystalline materials are ongoing in our laboratory.