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A 4 + 4 strategy for synthesis of zeolitic metal–organic frameworks: an indium-MOF with SOD topology as a light-harvesting antenna†

Libo Sun,[a] Hongzhu Xing,[b] Zhiqiang Liang,*[a] Jihong Yu*[a] and Ruren Xu[a]

A zeolitic metal–organic framework with a SOD topology, (Et_2NH_2)-$[In(BCBAIP)]\cdot 4DEF\cdot 4EtOH$ ($H_4BCBAIP$: 5-(bis(4-carboxybenzyl)amino)-isophthalic acid) (1), has been constructed by a 4 + 4 synthetic strategy from tetrahedral organic building units and In^{3+} ions. Compound 1 could adsorb organic dyes and be used as a light-harvesting antenna.

Zeolites are a class of porous crystalline materials with excellent thermal and chemical stable properties, and are widely used in industrial applications, such as catalysis, ion exchange and adsorption.[1] A fundamental strategy for the construction of traditional zeolitic materials is based on the rational selection of four-connected tetrahedral nodes (TO_4, T = Si^{4+}, Ge^{4+}, Al^{3+}, Ga^{4+}, Be^{2+}, B^{3+}, Zn^{2+} *etc.*) with right T–O–T angles,[2] where the O^{2-} anion can act as a bridging atom. Up to now, 206 kinds of zeolitic topologies have been identified.[3] In recent decades, zeolitic metal–organic frameworks (ZMOFs)[4] have attracted increasing interest due to their potential applications in catalysis,[5] gas storage[6] and separation.[7] As one kind of porous material different from zeolites, the construction of MOFs can be divided into two parts: the choosing of organic ligands and the selection of metal ions.[8] In order to construct ZMOFs, the 4 + 2 synthetic strategy, which is very popular and widely used up to now, is employed.[9,10] In fact, with judicious selection of metals and ligands, most types of ZMOFs were synthesized based on the mimicking of the Si–O–Si angle of approximately 145° by T–L–T angles through the 4 + 2 strategy.[10] This strategy has led to the imidazolate type ZIFs and heterocyclic carboxylate ZMOFs.[10,11] In addition, Zheng *et al.* utilized the bent carboxylate ligand instead of the heterocyclic ligand to generate a suitable T–L–T angle and successfully synthesized a series of ZMOFs.[12] On the other hand, it is not surprising that ZMOF materials can be prepared by the connection of inorganic and organic tetrahedral nodes through direct coordination interaction. For using such a 4 + 4 strategy, it is necessary to design and synthesize organic ligands as tetrahedral nodes in the final crystal structure. So far only two isostructural ZMOFs have been reported that have four-connected boron imidazolate complexes and four-connected Li^+ or Cu^+ ions.[4f]

Recently, we have focused on the design and synthesis of novel ligands based on isophthalic acid, which were used to construct MOFs with interesting properties.[13] In this work, a tetracarboxylate ligand 5-(bis(4-carboxybenzyl)amino)isophthalic acid (**H_4BCBAIP**) was designed and synthesized as the four-connected tetrahedral linker. In the ligand, the centered N atom plays a crucial role in the conformation, and the ligand can be considered as an organic tetrahedral node with four carboxylate groups as the vertices of the tetrahedron. It is well known that metal ions show different coordination ability and could be simplified as various inorganic topological nodes in the MOF structures. Notably, the In^{3+} ion shows great facility to coordinate to four carboxylate groups to form a tetrahedral four-connected $\{In(O_2C)_4\}$ group,[14] which was also reported in the ZMOFs obtained by using the 4 + 2 synthetic strategy.[12] With above considerations, we have successfully synthesized a zeolitic metal–organic framework compound with SOD topology, (Et_2NH_2)-$[In(BCBAIP)]\cdot 4DEF\cdot 4EtOH$ (**1**) by using this 4 + 4 strategy. Compound **1** exhibits dye-adsorption and light-harvesting properties.

1 was synthesized by a solvothermal reaction of $InCl_3\cdot 6H_2O$ and **H_4BCBAIP** in a mixture of *N*,*N*-diethylformamide (DEF) and C_2H_5OH at 95 °C. Light brown block shaped crystals were obtained after 72 h. The crystal structure of **1** was determined using single-crystal X-ray diffraction.‡ The purity of the samples was proven by the powder X-ray diffraction pattern, which matches well with the simulated one (Fig. S9, ESI†).

The structure analysis reveals that **1** crystallizes in the hexagonal $R\bar{3}c$ space group. The detailed coordination environment is depicted in Fig. S1 (ESI†). In each asymmetric unit, there exists half one independent In^{3+} ion, half one organic **$BCBAIP^{4-}$** anion, and the negative charge of the framework is balanced by half one $Et_2NH_2^+$ cation, which was generated from the decomposed DEF. Both of the In^{3+} ion and the centered N atom of the **$BCBAIP^{4-}$** ligand are located on the crystallographically-imposed 2-fold axis. Each In^{3+}

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[a] State Key Lab of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, 130012, China. E-mail: liangzq@jlu.edu.cn, jihong@jlu.edu.cn; Fax: +86-431-85168608; Tel: +86-431-85168608

[b] College of Chemistry, Northeast Normal University, Changchun, China

† Electronic supplementary information (ESI) available: Experimental details, IR, TGA, UV-vis, luminescence, dyes adsorption, gas sorption, fluorescence decay, crystallographical data, selected bond lengths and angles for compound **1**. CCDC 918529. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43383h

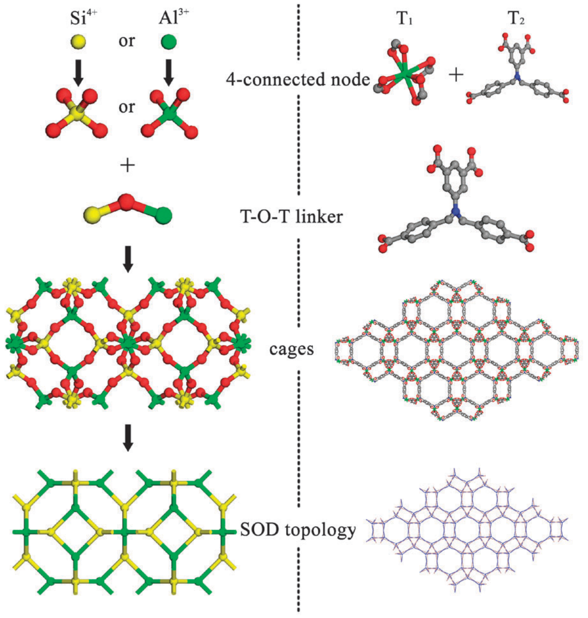

Fig. 1 The structure analogy between aluminosilicate zeolite sodalite and compound **1**.

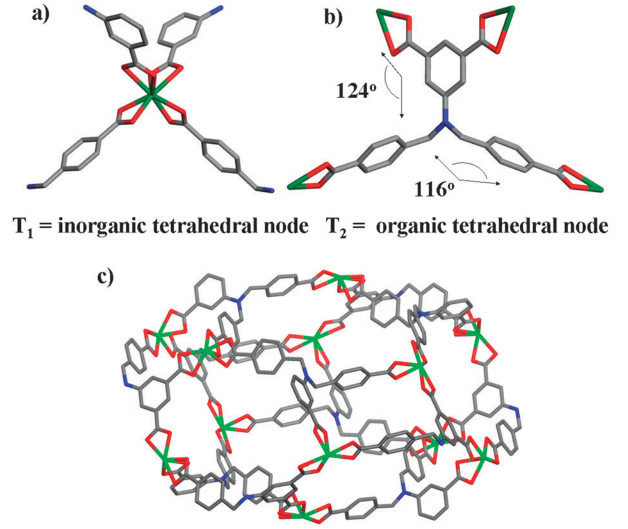

Fig. 2 (a) The $In(O_2C)_4$ unit as the $\mathbf{T_1}$ node; (b) the **BCBAIP**$^{4-}$ anion as the $\mathbf{T_2}$ node; (c) the sodalite cage of compound **1**.

ion is bonded to four carboxylates to form a four-connected $\{In(O_2C)_4\}$ group, while each ligand serves as a four-connected linker to bridge four In^{3+} ions. Assuming the In^{3+} ions and the ligand as four-connected nodes, the TOPOS analysis of this network results in a zeolitic SOD topology with a point symbol of $(4^2{\cdot}6^4)$ (Fig. 1). The void volume of **1** calculated using PLATON/SQUEEZE is 75.2% of the unit cell volume upon removal of the $Et_2NH_2^+$ cations and guest solvent molecules.[15] Fig. S2 (ESI†) illustrates the framework viewed along the [001] direction and shows two kinds of windows. The hexagonal window is constructed by three ligands and three $\{In(O_2C)_4\}$ units with a size of *ca.* 14 × 14 Å. The relatively smaller rectangle window (*ca.* 7.5 × 10.5 Å) is formed by two ligand molecules and two $\{In(O_2C)_4\}$ units. The sodalite cage formed in the framework has a size of *ca.* 26 × 26 × 8.2 Å.

Further insight into the structure of **1** explains the 4 + 4 strategy by the judicious selection of the **H$_4$BCBAIP** ligand and the indium ion. **1** is constructed by two kinds of different T nodes from the simplified form. One is from $\{In(O_2C)_4\}$ ($\mathbf{T_1}$) and the other is from the ligand ($\mathbf{T_2}$) (Fig. 2a and b). The linkage of these two kinds of T nodes forms a distorted SOD cage (Fig. 2c and Fig. S3, ESI†). The design of the **H$_4$BCBAIP** ligand with the T node and the suitable T–O–T angles is the key for the 4 + 4 strategy. The crystal structure of pure **H$_4$BCBAIP** reveals that the ligand adopts a tetrahedral configuration in the structure (Fig. S4, ESI†), and the centered N atom could be seen as a T node. By mimicking the T–O–T angles in the zeolite structures, the **H$_4$BCBAIP** ligand itself as the T node can supply suitable T–L–T angles (116–124°) for the construction of **1** (Fig. 2b). In order to further investigate the influence of T–L–T angles of the ligand on the formation of **1**, we have designed another tetracarboxylate ligand 5-(bis(3-carboxybenzyl)amino)isophthalic acid (**H$_4$BCBAIP′**), which is similar to **H$_4$BCBAIP** except for the position of carboxylate acid of the carboxybenzyl group. The solvothermal reaction of **H$_4$BCBAIP′** with indium salt only yielded a 2D In-MOF (Fig. S5, ESI†). In this compound, the T–L–T angles of the **BCBAIP′**$^{4-}$ anion are 116° and 80° (Fig. S6, ESI†). The linkage of the $\{In(O_2C)_4\}$ group and **BCBAIP′**$^{4-}$ results in a 2D In-MOF with **sql** topology. The failure in the formation of ZMOFs can be ascribed to the unsuitable angles in the **H$_4$BCBAIP′** ligand.

To evaluate the porosity of compound **1**, nitrogen (at 77 K) and carbon dioxide (at 273 K) adsorption experiments were performed by using the samples activated at 85 °C (Fig. S9b, ESI†). Unfortunately, the Brunauer–Emmett–Teller (BET) surface area is rather low (209 $m^2\ g^{-1}$, Fig. S10, ESI†), and this may be caused by the cationic $Et_2NH_2^+$ blocked in the cages. The CO_2 uptake of **1** at 273 K and 722 mmHg is 37.6 $cm^3\ g^{-1}$. In order to testify the accessibility of the porosity of **1**, the dye-adsorptions were measured using a range of different dyes.[16] When immersed into the methanol solutions of Methylene Blue (MB), Rhodamine B (RB), Rhodamine 6G (R6G), Coumarin 343 (**C343**) and Coumarin 6 (**C6**) for 6 h at room temperature, respectively, **1** presents different kinetic adsorption behavior toward these dyes as monitored using UV-vis absorption spectroscopy (Fig. S11, ESI†), in the order of MB > RB > R6G > **C343** ≈ **C6**, which could be mainly ascribed to the anionic nature of the framework of **1**. The $Et_2NH_2^+$ ions in the channels can be rapidly exchanged by cationic MB, RB and R6G, while the neutral **C343** and **C6** are not the favored dyes for the exchange. Since the size of MB is smaller than that of RB and R6G, it exhibits the most rapid adsorption rate.

The successful loading of **C6** and **C343** into **1** (**C6@1** and **C343@1**), as confirmed using the UV-vis absorption spectroscopy (Fig. 3 and 4), inspired us to further study their light-harvesting properties.[17] As shown in Fig. 3 and 4, the emission of **1** (donor) in the solid state overlap well with the absorption spectra of the two dyes (acceptor) in methanol, which favors the energy transfer process. In the case of **C6@1** and **C343@1**, when excited at 381 nm in the solid state, the emission of the host framework is quenched while the emissions of **C6** and **C343** dyes could be enhanced, respectively. These results indicate that the excitation energy is transferred from the host framework to the guest dyes. Compared with the lower emissions of dyes (dispersed in SiO_2, *ca.* 0.1 wt%, excited at 381 nm), the ordered porous structure of **1** for

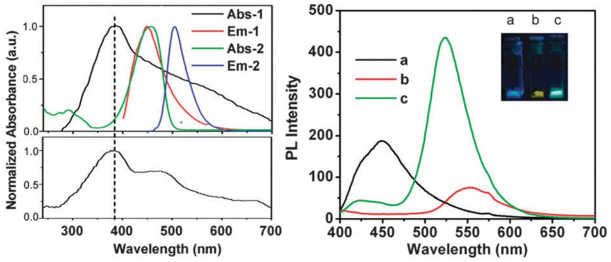

Fig. 3 (Left, top) Normalized UV-vis absorption and PL spectra of **1** (Abs-1, Em-1) in solid and Coumarin 6 (Abs-2, Em-2) in MeOH; (left, bottom) UV-vis spectrum of **C6@1** (0.087 wt%); (right) the emission spectra of **1** (a), **C6@SiO$_2$** (b, 0.1 wt%), **C6@1** (c, 0.087 wt%), λ_{ex} = 381 nm. The inset shows the PL images under 365 nm UV light.

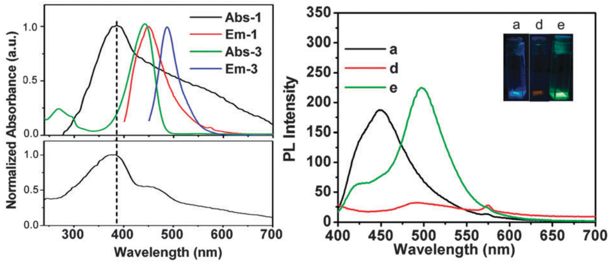

Fig. 4 (Left, top) Normalized UV-vis absorption and PL spectra of **1** (Abs-1, Em-1) in solid and Coumarin 343 (Abs-3, Em-3) in MeOH; (left, bottom) UV-vis spectrum of **C343@1** (0.072 wt%); (right) the emission spectra of **1** (a), **C343@SiO$_2$** (d, 0.1 wt%), **C343@1** (e, 0.072 wt%,), λ_{ex} = 381 nm. The inset shows the PL images under 365 nm UV light.

the spatial confined dyes decreases the quenching within the dyes during the energy transfer process.[18] The synthesis of different amounts of **C6@1** and **C343@1** has been achieved by immersing **1** in the methanol with different concentrations of dyes for about 24 h (Fig. S12, ESI†). From the descending peak of **1** accompanied with the ascending peaks of different amounts of dyes, further evidence for the energy transfer process could be obtained, which could be proved by the time-resolved fluorescence decay curves of **1**, **C6@1** and **C343@1** (Fig. S13, ESI†).

In conclusion, we have designed and synthesized a SOD-type ZMOF $(Et_2NH_2)[In(BCBAIP)]\cdot 4DEF\cdot 4EtOH$ through the 4 + 4 synthetic strategy by cross-linking the designed four-connected tetracarboxylate ligand **H$_4$BCBAIP** with the four-connected In^{3+} ion. This compound possesses an anionic framework and a nano-sized sodalite cage, which enable it to adsorb dyes, especially cationic dyes. Importantly, **C6** and **C343** loaded compound **1** exhibits efficient light-harvesting properties. The effective 4 + 4 strategy for the construction of ZMOFs by using a novel tetracarboxylate ligand with tetrahedral configuration and four-connected metal ions would expand the versatility and utility of the ZMOFs.

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Notes and references

‡ Crystal data for **1:** $C_{56}H_{95}N_6O_{16}In$, M = 1223.20, trigonal, space group $R\bar{3}c$, a = 38.2369(10) Å, b = 38.2369(10) Å, c = 22.7356(12) Å, V = 28787.4(19) Å^3, Z = 18, D_c = 1.270 g cm^{-3}, μ = 0.436 mm^{-1}, T = 296(2) K, $F(000)$ = 11 700, 69 588 reflections collected, 7969 independent reflections (R_{int} = 0.0947) which were used in all the calculations. After the refinement cycles, reliability factors were R_1 = 0.0448, wR_2 = 0.0788 for $[I > 2\sigma(I)]$, and R_1 = 0.1513, wR_2 = 0.0878 for all 7969 data.

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