

A 3D porous metal–organic framework constructed of 1D zigzag and helical chains exhibiting selective anion exchange†

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Slow diffusion of AgClO_4 with $\text{Me}_2\text{Si}[(4\text{-Im-1-yl)Ph}]_2$ (BIPS) yields the crystalline complex **1 with a 3D-braided porous metal–organic framework via self-assembly of two series of 1D polymer chains through both braiding and interpenetrating. Complex **1** consists of two distinct kinds of channels with different sizes and shapes along *a* and *b* directions occupied by perchlorate anions and water molecules.**

The design and construction of functional metal–organic frameworks (MOFs) with specific motifs is a fascinating area because of their interesting molecular topologies and potential applications such as photoelectronic devices, molecular recognition, molecular separation, ion exchanges, luminescent sensors and catalysts.^{1–3} On the basis of current research on MOFs, two effective strategies can be achieved to construct functional high-dimensional MOFs: (1) the use of multi-topic bridging organic ligands to connect metal ions through covalent bonds to generate 3D MOFs and (2) interpenetrating or braiding between low-dimensional coordination polymers to form 3D MOFs with interesting structural topologies. In the past decades, many functional MOFs constructed from multi-topic bridging ligands such as carboxylate- and pyridine-based ligands have been widely synthesized and reported based on the former strategy.⁴ However, construction of porous MOFs based on the latter strategy is somewhat rare.⁵ In 2004, Suh and co-workers reported an attractive porous material constructed of linear coordination polymer chains, in which three linear polymer chains extend in different directions to braid a 3D porous framework.⁶ In this communication, a novel 3D porous framework, $[\text{Ag}(\text{BIPS})]_{0.5}[\text{Ag}(\text{BIPS})]_2 \cdot 2.5\text{ClO}_4 \cdot 5\text{H}_2\text{O}$ (**1**), constructed of 1D linear polymer chains through both braiding and interpenetrating is reported.

To braid 1D polymer chains to generate high-dimensional frameworks, the 1D polymer chain should possess certain flexibility in order to avoid the space hindrance generated between the chains. Thus, the selection of an organic ligand with appropriate flexibility would be a crucial step. The semi-rigid ligand, bis(4-(imidazol-1-yl)phenyl)dimethylsilane (BIPS), which is synthesized via Ullmann condensation reaction, is our choice for constructing braided MOFs (Scheme 1). Compared to carbon analogues, tetrahedral silicon

centers are, in general, more synthetically accessible. The longer bond length and increased bond angle to silicon as well as the decreased conformational rigidity in these molecules result in greater flexibility which can affect strain and hence supramolecular geometry.⁷ In addition, electrons within these molecules commonly exhibit higher delocalization due to the electron-releasing nature of silicon atom from an electronic standpoint. Thus, a variety of multi-topic ligands with silicon as a linking moiety including pyridine rings,⁸ monothioether alkyl chains,⁹ cyclopentadienyl rings¹⁰ and carboxylate groups¹¹ have been synthesized and used for the construction of MOFs materials. However, to our best knowledge, there is no report on the exploitation of silicon-based imidazole-containing units.

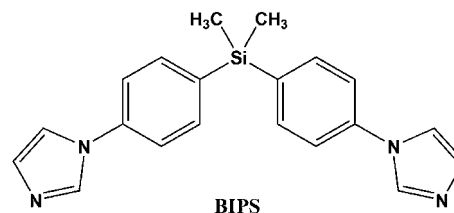
Single-crystal analysis on BIPS shows that the ligand in the bent conformation lies across a mirror plane and presents a tetrahedral structure around the silicon atom with the average Si–C distance of 1.86 Å and the average dihedral angle of 41.024° between the imidazole ring and the phenyl ring (ESI, Fig. S1†), which is significantly different from other rigid conformation-restricted imidazole-containing linkers.¹²

The slow diffusion of a methanol solution of AgClO_4 into a dichloromethane solution of BIPS ligand afforded a large amount of colourless block crystals of **1**. The crystalline product is air-stable at room temperature and insoluble in water and common organic solvents. Single-crystal X-ray characterization reveals that complex **1** is a coordination polymer with a metal-to-ligand ratio of 1 : 1 and crystallizes in the orthorhombic system space group *Pnma*. The asymmetric unit of **1** consists of two and a half silver ions, two and a half BIPS ligands, two and a half ClO_4^- anion and half uncoordinated water molecules and the Ag3, Si3 and Cl3 atoms lie in space-group-imposed twofold symmetry (ESI, Fig. S2†). The central silver ions adopt linear geometries coordinated by two nitrogen atoms from different BIPS ligands with the average Ag–N distances of 2.078 Å. The BIPS ligands in **1** possess similar conformation with the free BIPS ligand, except that the average dihedral angle between phenyl rings and imidazole rings changed from 1.905° to 15.960°. Each BIPS ligand adopts bidentate bridging mode to connect two Ag ions and every Ag ion attaches to two BIPS ligands to result in the formation of two different one-dimensional chains: 1D helical chain and zigzag

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Scheme 1 The structure of BIPS

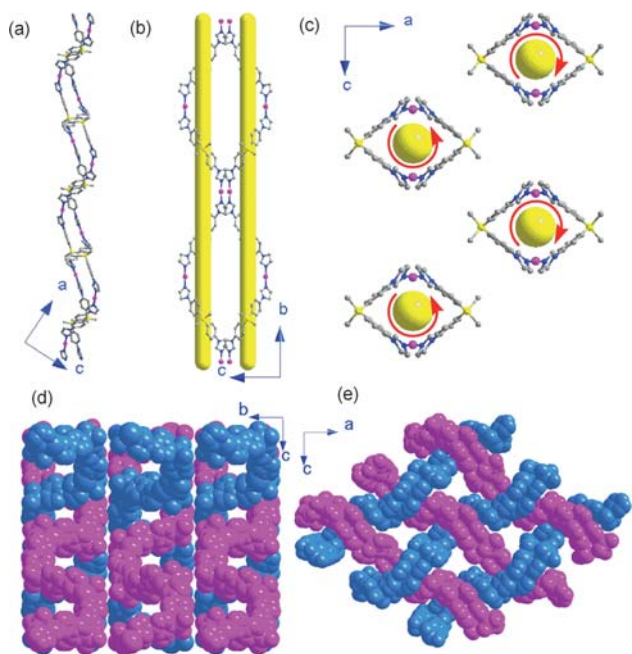


Fig. 1 (a) 1D double-stranded zigzag chains; (b) 1D helical left- and right-handed chains; (c) the equal arrangement of the 1D left- and right-handed helical chains along the *b* axis, resulting the whole molecule achiral; (d) and (e) the 2D braiding layers showing the rectangular channels and trigonal voids in the layers along the *a* and *b* axes, respectively.

chain (Fig. 1a, 1b and 1c). The 1D 2_1 helical chain is generated by BIPS ligands connecting Ag3 ions with the shortest intrachain Ag–Ag distance of 16.924 Å, while the zigzag chain is formed by BIPS ligands link Ag1 and Ag2 ions with the shortest intrachain Ag–Ag distance of 15.693 Å.

The whole structure of **1** contains a helical chain and a pair of zigzag chains extending in different directions. Two zigzag chains stack each other through π – π interactions between the imidazole rings (3.634 Å) to form a double-stranded chain with the shortest interchain Ag–Ag distance of 6.782 Å. Two series of double-stranded chains are extending in [101] and $[10\bar{1}]$ directions in the *ac* plane to braid one another through the π – π interactions between the imidazole rings and the benzene rings of BIPS ligands in different double-stranded chains, resulting in the formation of a two-dimensional layer containing rectangular channels (5.1 × 6.6 Å) along the *a* axis and trigonal voids (14.8 × 18.3 Å) along the *b* axis (Fig. 1d and 1e). The ClO₄[−] anions, located in the rectangular channels, balance the charge. In particular, one of ClO₄[−] anions has weak interaction with Ag2 ion with the Ag–O distance of 3.208 Å. (It is shorter than the sum of the van der Waals radii for silver and oxygen (3.24 Å)¹³.)

The 1D helical chains are extending along *b* axis and interpenetrating with the 2D layers, giving rise to a 3D porous metal–organic framework (Fig. 2). The interpenetration between the 2D layers and the 1D helical chains partly block the trigonal voids with the dimensions of the resulting rectangular channels of 4.5 × 11.5 Å, in which the uncoordinated water molecules reside (Fig. 2c). However, the interpenetration does not have any influence on the dimensions of the rectangular channels in the 2D layer, as shown in Fig. 2b.

The thermogravimetric analysis (TGA) for compound **1** shows that the skeleton is thermally stable up to 305 °C (ESI, Fig. S5†). A

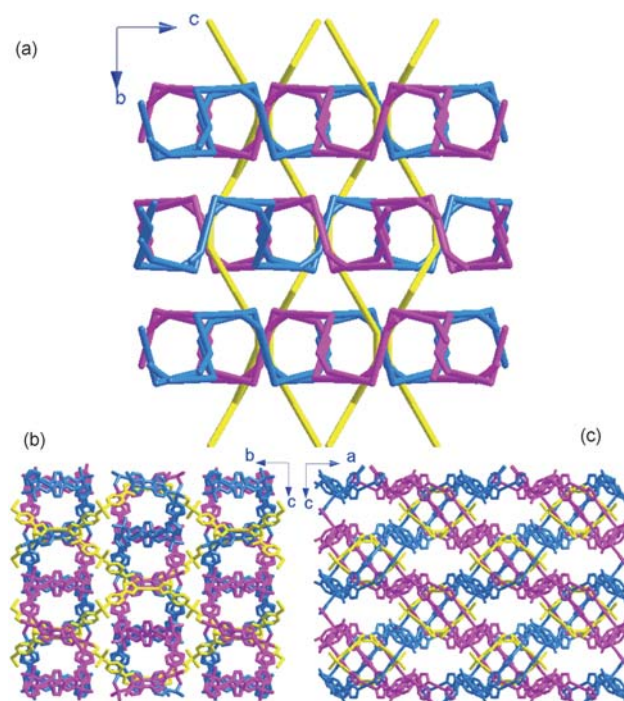


Fig. 2 (a) Schematic representation of the 3D framework of **1**; (b) and (c) the 3D porous framework of **1** along the *b* and *a* axes, respectively. Perchlorate anions and water molecules are omitted for clarity.

couple of slight endothermic and exothermic peaks of the differential scanning calorimetry (DSC) curve were observed around 230 °C, indicating that a slight structure change without any weight loss. The two peaks may be attributed to slight deviation and return of the uncoordinated ClO₄[−] anions in the channels. The first TGA and DSC changes are obviously associated with the removal of the lattice water molecules between 25 and 95 °C by 5.9% weight (calcd 6.1%), which indicates that water molecules could easily escape from the crystal lattice of **1**.

To investigate the porous properties, anion exchange of **1** with CF₃SO₃[−] and PF₆[−] was accomplished. The anion exchange was monitored by the enhanced intensity at 1265 cm^{−1} of the CF₃SO₃[−] bending band and appearance of the PF₆[−] at 834 cm^{−1}, as well as the

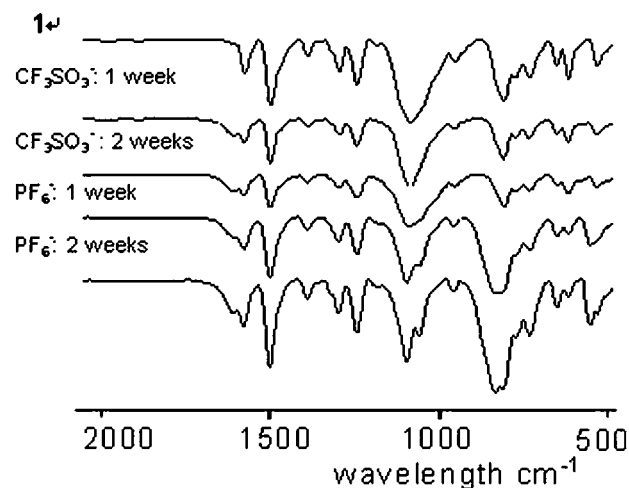


Fig. 3 Anion exchange with CF₃SO₃[−] and PF₆[−] for compound **1**.

reduced intensity at 1096 cm^{-1} and 622 cm^{-1} of ClO_4^- . The anion exchange of **1** with CF_3SO_3^- does not occur even after immersing crystals of **1** in methanol solution containing NaCF_3SO_3 for two weeks, which may be due to the large size for the triflate anions. The ClO_4^- anions could be slowly and partly exchanged by PF_6^- after two weeks (Fig. 3). There is no characteristic signal for CF_3SO_3^- in the ^{19}F NMR spectra for the exchange products. However, the appearance of chemical shift at -70.2 confirmed the existence of PF_6^- , in agreement with the results monitored by IR (ESI, Fig. S3†). As mentioned above, one of ClO_4^- anions has a weak interaction with the Ag ion and is hardly exchanged by PF_6^- . XRD results indicate the framework for **1** can be still sustained as the exchange products showing similar patterns with **1** (ESI, Fig. S4†). Thus, the present anion exchange seems to be affected by both the cavity size and the nature of anions.

Photoluminescence property of compound **1** and BIPS has been measured at the room temperature in the solid state. The free BIPS ligand exhibits a strong violet emission with maximum at 337 nm, which is assigned to the $\pi \rightarrow \pi^*$ transitions ($\lambda_{\text{ex}} = 290$ nm). Compared with the BIPS ligand, the emission spectra of compound **1** is red-shifted with the emission maxima at 353 nm (ESI, Fig. S6†), which can be attributed to the ligand to metal charge transfer (LMCT).¹⁴ In addition, compound **1** exhibits much weaker emission than BIPS, which may be a result of the heavy-atom effect of Ag ion.¹⁵

In conclusion, we have synthesized and characterized a novel porous metal-organic framework based on a new silicon-based imidazole-containing ligand. Complex **1** features a remarkable and unique braided 3D framework containing two distinct 1D channels along *a* and *b* axes, in which perchlorate anions and uncoordinated water molecules reside. Complex **1** possesses selective anion exchange with PF_6^- anions over $\text{CF}_3\text{SO}_3^-/\text{PF}_6^-$. In the past decades, many functional interpenetrating MOFs constructed from multitopic ligand with special properties have been documented, however, reports on porous MOFs constructed of 1D coordination polymers through braiding are quite rare. To the best of our knowledge, complex **1** represents the first example constructed of 1D coordination polymer through both braiding and interpenetrating, and possessing selective anion exchange. Further studies will focus on the synthesis of other functional MOFs based on this novel silicon-based building block and examining their enormous potentials such as adsorption-desorption, ion exchanges *etc.*

Acknowledgements

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