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Nanoporous Ag(I)-MOF showing unique selective adsorption of benzene among its organic analogues

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A stable porous Ag(I)-MOF with new topology is constructed from AgSbF₆ and 3,6-bis[2-(4-oxide-quinoxaline-yl)]-4,7,5-diaza-3,5-octadiene (L). This compound can be a highly selective porous MOF material to effectively separate benzene from its six-membered cyclic organic analogues such as cyclohexane, cyclohexene and *o*-, *m*-, *p*-xylene under ambient conditions in both vapor and liquid phases.

It is well known that benzene, as a very important chemical, is a typical volatile organic compound (VOC) of great social and environmental significance.¹ Benzene, however, often coexists with other aliphatic or aromatic analogues such as cyclohexane, cyclohexene and *o*-, *m*-, *p*-xylene species, and some of them have very similar boiling points. So its separation is a technical challenge. On the other hand, metal-organic frameworks (MOFs),² as an emerging class of hybrid porous materials, exhibit a promising application for molecular adsorption and separation.^{2a,3} In principle, suitable MOFs, which are able to selectively absorb benzene in the presence of other competitors, could be constructed by the rational combination of subtly designed organic ligands and metal ions. Additionally, adsorption separation based on MOF adsorbents might be a more energy efficient approach than that of distillation, so the development of new types of MOF adsorbents is very significant.

In this contribution, we report a novel porous Ag(I)-MOF which is generated from a new Schiff-base bridging *N,N'*-dioxides (ESI) and AgSbF₆. Furthermore it is able to reversibly absorb and separate benzene from its six-membered ring organic analogues, such as cyclohexane, cyclohexene, *o*-, *m*- and *p*-xylene, in both liquid and vapor phases.

L was prepared in 85% yield by the Schiff-base condensation reaction of 2-propionyl-quinoxaline-*N*-oxide with hydrazine (80 wt % solution in water) in ethanol at room temperature.⁴ Crystallization of L with AgSbF₆ in a CHCl₃/CH₃OH mixed solvent system at room temperature afforded **1** as yellow crystals in 61% yield †.

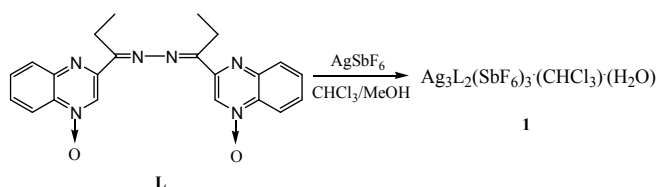
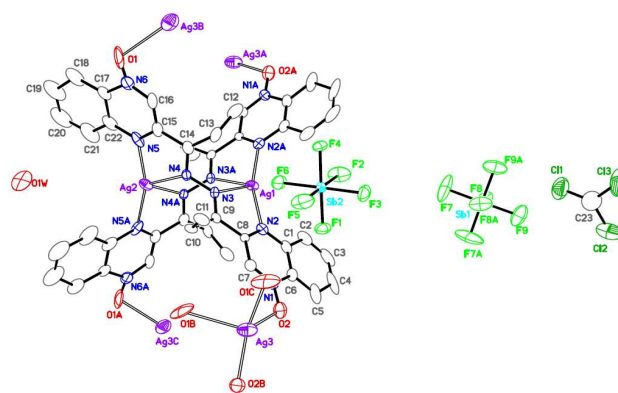
Scheme 1. Synthesis of **1**.

Fig. 1 The ORTEP figure of **1** (displacement ellipsoids drawn at the 30% probability level). The TEM image (Fig. S4) indicates that the obtained crystalline sample of **1** is high quality.

The X-ray single-crystal structural analysis† revealed that **1** crystallized in the hexagonal space group *P6(5)22*. As shown in Fig. 1, there are three types of crystallographically independent Ag(I) ions ($\{\text{Ag}(1)\text{N}_4\}$, $\{\text{Ag}(2)\text{N}_4\}$ and $\{\text{Ag}(3)\text{O}_4\}$) in **1**, and they all lie in a distorted tetrahedral coordination environment. The ligand is six-dentate and provides two pairs of chelating N-donors in the middle and two *exo*-monodentate O-donors at the ends. Fig. 1 shows that two 2-fold symmetry related Ag(I) centers are held together by two L ligands through the middle chelating nitrogen donors, affording a "X-shaped" binuclear unit Ag₂L₂ in which the Ag(1)⋯Ag(2) distance is 4.46 Å.

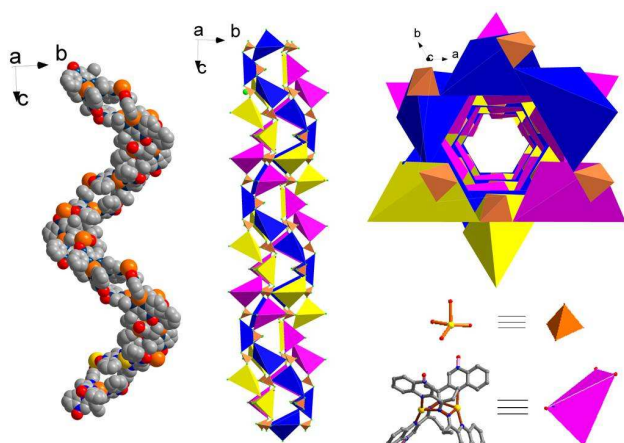


Fig. 2 Left: Space-filling view of single helical chain. Right: Side and top views of single nanotube consisting of three sets of helical chains in **1**.

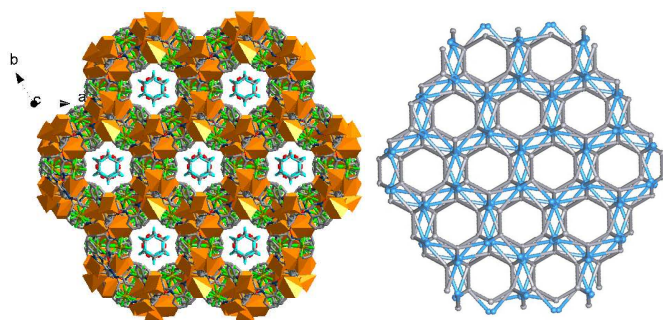


Fig. 3 3D framework containing disordered CHCl_3 and H_2O solvent molecules (left) and schematic representation (right) of 3D net of **1**.

As shown in Fig. 2, these binuclear helical units $\{\text{Ag}(1)\text{Ag}(2)\text{L}_2\}$ act as the secondary building blocks that can continue to bind $\text{Ag}(3)$ ions to generate a huge left-handed helical chain with a pitch of $44.26(6)$ Å. Three strands are interlocked by $\text{Ag}(3)\text{-O}(2)$ to eventually form a hexagon-like nanotube (Fig. 2). All the nanotubes are further crosslinked together in the crystallographic ab plane by $\text{Ag}(3)\text{-O}(1)$ into a non-interpenetrating 3D porous framework. The open tubular channels (ca. 10×10 Å) are filled with disordered CHCl_3 and H_2O guest molecules. The SbF_6^- ions are dispersed in the framework (Fig. 3). This is a very unusual network (Schläfli symbol $\{4^2.6\}_2\{4^4.6^2.7^4.8^3.9\}$) and we are unaware of a precedent despite some of the networks based on binuclear helical units reported in the literature (Fig. 3).^{4,5} In addition, Brunauer–Emmett–Teller (BET) measurement readily revealed the microporous character of the $\text{Ag}(I)$ -framework. The surface area calculated from the CO_2 adsorption isotherm was estimated to be $232 \text{ m}^2\text{g}^{-1}$ (ESI, Fig. S5).

The encapsulated CHCl_3 and H_2O guest molecules can be removed by heating the crystals of **1** at 200°C for 24h to generate guest-free framework of **1'**, which is clearly confirmed by thermogravimetric analyses (TGA) and ^1H NMR spectra (Fig. 4). The corresponding XRPD pattern of **1'** is identical to that of **1** (Fig. 4), indicating that guest loss does not result in symmetry change or cavity volume collapse. Notably, the single crystals of **1** are highly thermal stable and their

single crystallinity can be maintained during the process for removal of guest species by heating (Fig. 5)†.

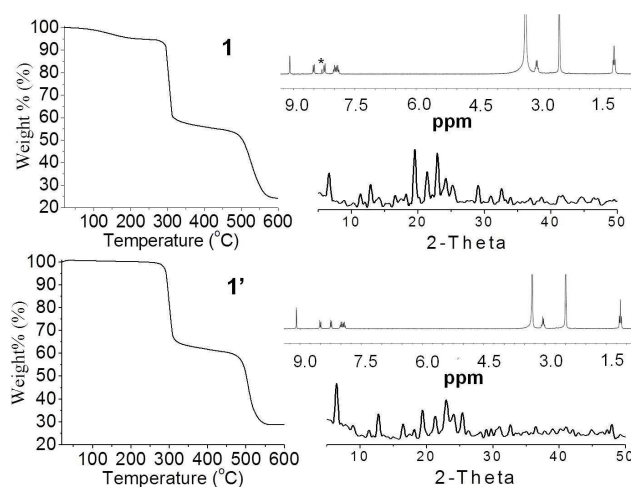


Fig. 4 TGA traces, ^1H NMR ($\text{DMSO}-d_6$) spectra and XRPD patterns of **1** (top) and **1'** (bottom). For TGA measurement of **1**, the observed solvent mass loss is 5.2% (calculated 6.9%). The XRPD pattern indicated that the framework of **1** is stable up to $\sim 250^\circ\text{C}$ (Fig. S6). No solvent mass loss for **1'** was observed. The signal (8.30 ppm) for encapsulated CHCl_3 guest molecules was marked in ^1H NMR spectrum.

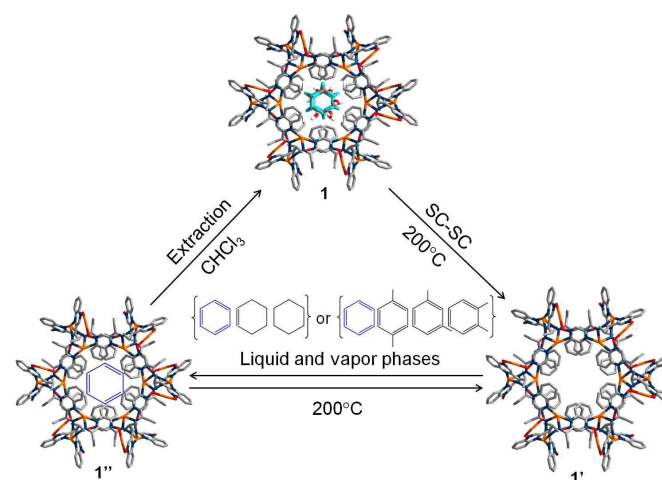


Fig. 5 Reversible selective adsorption of benzene among other organic analogues in liquid and vapor phases.

According to our previous study,⁶ the tubular channel of **1**, with crystallographic dimensions of ca. 10×10 Å², might be suitable for accommodation of $\text{C}_6\text{-C}_8$ cyclic organic compounds. Indeed, our experiments demonstrated that **1'** is able to reversibly uptake benzene and its six-membered ring analogues such as cyclohexane, cyclohexene and *o*-, *m*-, *p*-xylene in both liquid and vapor phases. For example, when the crystals of **1'** were respectively immersed in benzene, cyclohexane, cyclohexene, *o*-, *m*-, and *p*-xylene for a week, the corresponding ^1H NMR spectra indicated that all the compounds can be uploaded (ESI). On the other hand, the uploaded guest molecules can be further removed by either heating (200°C) or extracting (by CHCl_3) to regenerate the guest-free framework. So the

framework of Ag_3L_2 is reusable. The single crystallinity of $\mathbf{1}'$, however, cannot be maintained any longer during the process.

The major hurdle in molecular recognition based on MOFs is selectivity, that is, the preparation of a host framework that responds to a specific substrate in the presence of other different competitors. As we know, the separation of benzene from cyclohexane and cyclohexene based on distillation is very difficult due to their quite similar boiling points (benzene 80.1°C , cyclohexane 80.7°C , and cyclohexene 83°C). The separation of benzene from cyclohexane and cyclohexene, however, is very important for polyamide production based on cyclohexene hydration method.⁷ To explore the selectivity of $\mathbf{1}$, an experiment was designed to test the binding affinity for benzene in the presence of cyclohexane and cyclohexene species (Fig. 5).

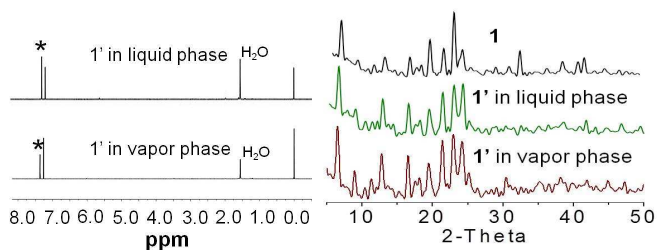


Fig. 6 Left: ^1H NMR spectra (CDCl_3) performed on CDCl_3 extract of $\mathbf{1}'$ obtained from liquid and vapor phases consisting of equimolar benzene-cyclohexane-cyclohexene, respectively. The proton peak of the encapsulated benzene is marked. Right: The corresponding XRPD patterns which are identical to that of $\mathbf{1}$.

When the desolvated sample of $\mathbf{1}'$ was immersed in a mixed-solvent system or exposed to a mixed-vapor that consists of equimolar benzene, cyclohexane and cyclohexene at room temperature for a week (no difference in binding was observed at the longer time), the ^1H NMR spectrum was performed on the CDCl_3 extract. As shown in Fig. 6, the single peak at 7.36 ppm indicates that only benzene was allowed into the pores of $\mathbf{1}'$ to result in a new host-guest complex benzene $\subset\text{Ag}_3\text{L}_2$ ($\mathbf{1}''$), whereas no observable proton resonances related to cyclohexane and cyclohexene were detected in the spectrum. Such binding preference of $\mathbf{1}'$ for benzene suggests that the guest species are encapsulated in the pores instead of on the surface. The Ag_3L_2 framework is maintained during the adsorption process, which is well supported by the corresponding XRPD patterns (Fig. 6).

In addition, the separation of benzene from its aromatic homologues of *o*-, *m*-, and *p*-xylene was also performed (Fig. 5). When $\mathbf{1}'$ was immersed in a mixed-solvent system consisting of benzene, *o*-, *m*- and *p*-xylene (molar ratio, 1:1:1:1) at room temperature for a week (no difference in binding was observed at the longer time), ^1H NMR spectrum performed on the CDCl_3 extract clearly evidences that benzene (single peak at 7.36 ppm),

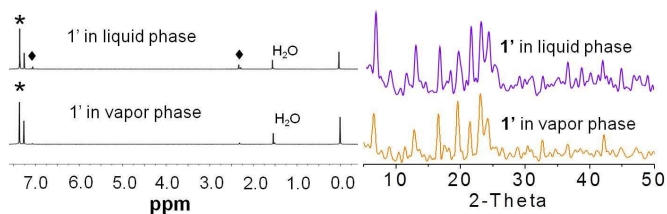


Fig. 7 Left: ^1H NMR spectra (CDCl_3) performed on CDCl_3 extract of $\mathbf{1}'$ obtained from liquid and vapor phases consisting of equimolar benzene and xylene isomers, respectively. The proton peak of the encapsulated benzene is marked. Right: The corresponding XRPD patterns which are identical to that of $\mathbf{1}$ (Fig. 6).

as the predominant species, exists in $\mathbf{1}'$, and only very tiny amount of *o*-, and *p*-xylene isomers were simultaneously uploaded (Fig. 7). Compared to the liquid phase, the separation efficiency is higher in vapor phase. In vapor phase (Fig. 7), the observable peaks related to xylene competitors are weaker than those of in liquid phase. Such difference might be caused by the different vapor pressures of the xylene isomers (bp: *o*-xylene 144.4°C ; *m*-xylene 139.1°C ; *p*-xylene 138.4°C). The different selectivity in liquid and vapor phases exhibited by $\mathbf{1}'$ is further supported by the gas chromatography (GC) measurement. The guest loaded samples obtained from liquid and vapor phases were extracted by chloroform, and the CHCl_3 -extractions were used for the GC analysis. In the CHCl_3 -extraction of $\mathbf{1}'$ obtained from liquid phase, the ratio of benzene/*o*-xylene/*m*-xylene/*p*-xylene is 10 : 1 : 0.71 : 0.93, while the corresponding ratio found in the CHCl_3 -extraction obtained from vapor phase is 10 : 1 : 0.36 : 0.70. Unfortunately, the Ag_3L_2 framework herein cannot effectively separate benzene and toluene (ESI), which reflect the affinity based on $\mathbf{1}'$ might be a size and shape controlled selectivity.

In summary, a highly thermal stable porous Ag(I)-MOF with new topology was successfully synthesized by the combination of AgSbF_6 and a new Schiff-base-bridged *N,N'*-dioxides ligand in solution. This compound is very stable and can retain its single crystallinity up to 200°C . Furthermore, it exhibits preferential affinity for benzene and can effectively separate benzene from its organic analogues under ambient conditions in both vapor and liquid phases.

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Notes and references

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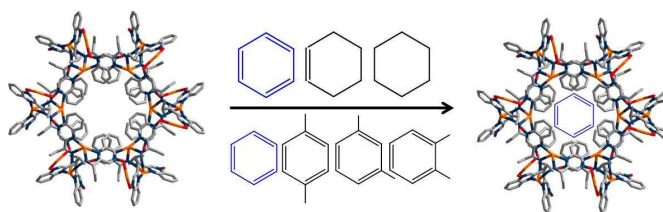
†Synthesis of $\mathbf{1}$. A CH_3OH solution (8 mL) of AgSbF_6 (20.6 mg, 0.06 mmol) was slowly diffused into a CHCl_3 solution (8 mL) of \mathbf{L}_2 (12.0 mg, 0.03 mmol). Yellow crystals formed in about 7 days (Yield, 61%, based on AgSbF_6). Elemental analysis (%) Calcd for $\text{Ag}_3\text{C}_{45}\text{H}_{43}\text{F}_{18}\text{N}_{12}\text{O}_5\text{Sb}_3$: C 27.44, H 2.20, N 8.53. Found: C 27.16, H 2.60, N 8.39. IR (KBr pellet cm^{-1}): 3415(m), 3123(m), 3078(m), 2926(w), 1793(w), 1604(s), 1488(s), 1410(s), 1365(s), 1291(s), 1275(s), 1174(s), 1090(s), 1064(s), 953(m), 889(s), 739(s), 664(vs), 558(s), 508(w). **Single-crystal structure determination.** Suitable single crystals of $\mathbf{1}$ and $\mathbf{1}'$ were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 123(2) or 173(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The raw frame data for $\mathbf{1}$ and $\mathbf{1}'$ were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.⁸ Corrections for incident and

diffracted beam adsorption effects were applied using SADABS.⁸ None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and structural analysis refined against F^2 by the full-matrix least squares technique. Crystal data for **1**: $C_{45}H_{43}Ag_3Cl_3F_{18}N_{12}O_5Sb_3$, $M_r = 1969.12$, hexagonal, $P6(5)22$, $a = 15.9174(15) \text{ \AA}$, $b = 15.9174(15) \text{ \AA}$, $c = 44.260(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 9711.5(18) \text{ \AA}^3$, $Z = 6$, $T = 123(2) \text{ K}$, $\rho_{\text{calcd}} = 2.020 \text{ g cm}^{-3}$, final R [$>2\sigma(I)$]: $R_1 = 0.0646$, $wR_2 = 0.1792$. Crystal data for **1'**: $C_{44}H_{40}Ag_3F_{18}N_{12}O_4Sb_3$, $M_r = 1831.74$, hexagonal, $P6(5)22$, $a = 15.825(5) \text{ \AA}$, $b = 15.825(5) \text{ \AA}$, $c = 43.703(19) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 9478(6) \text{ \AA}^3$, $Z = 6$, $T = 173(2) \text{ K}$, $\rho_{\text{calcd}} = 1.925 \text{ g cm}^{-3}$, final R [$>2\sigma(I)$]: $R_1 = 0.0507$, $wR_2 = 0.1237$. CCDC 999724-999725 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

‡ Electronic supplementary information (ESI) available: Synthesis and characterization data for ligand, adsorption of benzene and its analogies and separation of benzene from toluene, adsorption isotherm of benzene based on **1'**, CIF file and crystal data. See DOI: 10.1039/b000000x/

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For table content



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