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To boost the design of microporous solids, we integrated the two-faced shape (as in cucurbiturils and cyclodextrins) into building blocks of framework materials. Reported here is a planar tritopic carboxyl linker with secondary tripod donors sprouting off both sides at the core region. The two-faced, barrel-like core region imparts a rugged 3D character to the linker architecture, obviating close packing and creating complex-shaped cavities in an Eu(III)-carboxylate network. The merits extend beyond the pleasing shape of the multiple tripod: e.g., the two sets of sulfur tripods at the barrel region, together with the triazine center, offer a rich array of donors for adsorbing Hg(II) ions. The microporous solid also removes iodine from vapor and water, and can be easily cycled in column chromatography.

Postsynthetic metalation of metal-organic frameworks (MOF) is topical,[1] because of the versatile catalytic and electronic properties that can potentially be imparted by the metal guests. To optimize such properties, it is imperative to understand how metal species interact with complex porous materials. The sophisticated functionalities that can be accommodated by the crystalline MOF matrix offer rich opportunities for such fundamental studies. For example, Pardo *et al.* exploited MOF hosts based on methionine and other sulfur-containing biomolecules to effect metalation;[2] also, bioinspired catalyses emulating methane monooxygenase[3] and scorpionate-like binding sites[4] were recently accessed in MOF solids. The field, however, is still emerging, and the design of new binding motifs for probing metal-host interactions remains relevant.

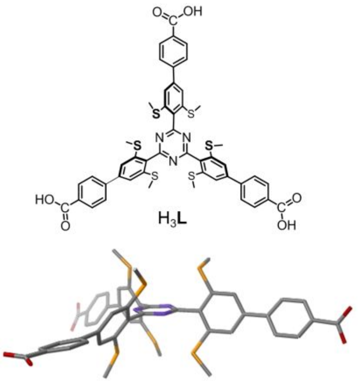

Fig. 1 The triple tripod molecule H_3**L** and an X-ray conformation.

In this regard, the rigid tritopic carboxylic acid H_3**L** (Fig. 1), with the dense array of S and N donor sites, is of interest. In particular, the methylsulfanyl (MeS) units, grouping into trios on both sides of a triazine core, conjure up a double-faced “Janus” molecule. Together with the three extended carboxyl arms, one obtains a distinct multiple tripod that connects simultaneously to the topical areas of MOF construction[5] and supramolecular assemblies.[6] Already, two-faced molecules such as cucurbiturils,[6c,7] pillararenes,[8] and a recent Janusarene by Wang *et al.*,[9] have fomented various investigations on host-guest chemistry. Also known are doubly tripodal molecules resembling the MeS-triazine core of H_3**L**, which include hexakis(arylthio)arenes[10] and the Walsdorff hexathiol.[11] The attachment of polytopic donor arms onto a double-faced core (e.g., to form the triple tripod H_3**L**), however, is unexplored, in spite of its relevance to MOFs and other porous materials.[8c,12] The rich host-guest chemistry spawned by the double-faced molecules, therefore, motivates us to integrate these versatile motifs into the bustling field of MOF chemistry.

Reported here is a microporous Eu(III)-carboxylate framework (denoted GDUT-7, Fig. 2) based on the triple tripod molecule H_3**L**. Notably, GDUT-7 sports diverse and extensive

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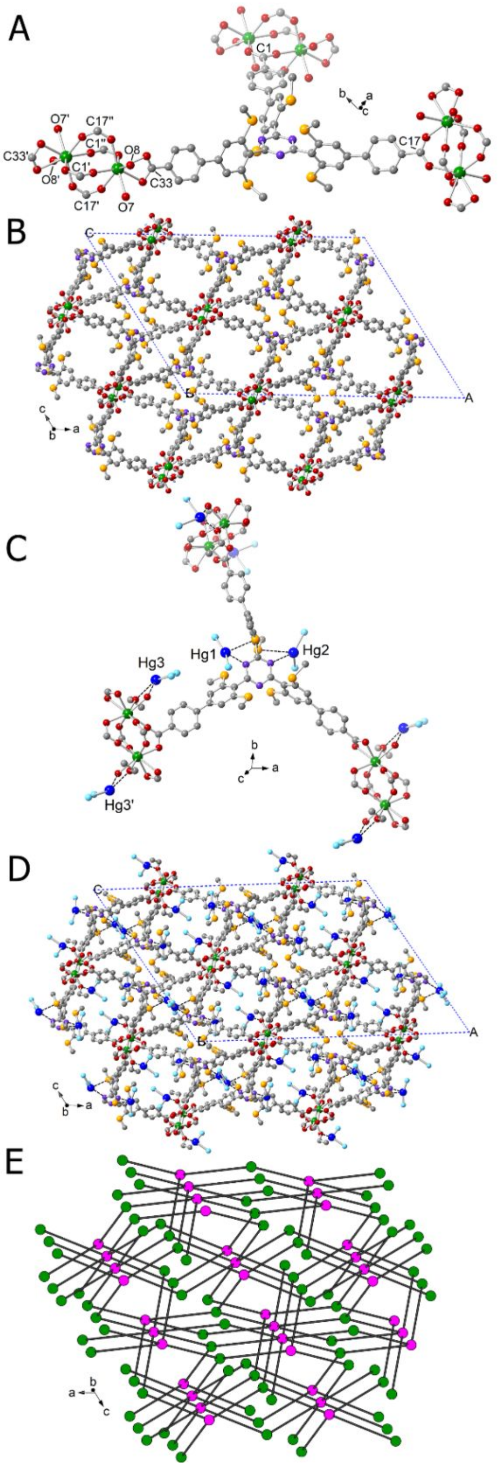

Fig. 2 Crystal structures of GDUT-7 and GDUT-7-$HgCl_2$: a) Linker **L** and its three Eu(III) clusters in GDUT-7, with selected crystallographic atom labeling; the DMF and H_2O molecules bonded to the Eu sites are only partially shown. b) A view of GDUT-7 along the *b* axis. c) Linker **L**, its three Eu(III) clusters and the three $HgCl_2$ guests in GDUT-7-$HgCl_2$. d) A view of GDUT-7-$HgCl_2$ along the *b* axis. e) Topology of the Eu-carboxyl net. Purple sphere: center of Eu cluster; green sphere: center of linker **L**.

interactions with metal and iodine guests. For example, an $HgCl_2$-treated sample was found by single crystal X-ray diffraction (SCXRD) to contain a total of three distinct $HgCl_2$ sites located in the unit cell: besides two associated with the soft S and N donors at the Janus core, another one peculiarly links to the Eu(III) center via bridging O atoms from water and ethanol ligands. Apart from distinct coordination bonding with the $HgCl_2$ guests, their snug fit into the microporous matrix of GDUT-7 suggests van der Waals pockets also help sequester the $HgCl_2$ guests. Besides the relevance to heavy metal removal[1e,13] and iodine sequestration,[14] the diverse host–guest interactions unveiled in the GDUT-7-$HgCl_2$ system offers insight into how microporous solids interact with metal guests.

H_3**L** was synthesized as follows (Fig. S1): nitrile trimerization first forms the triazine core (the modest yield of 25% is likely due to the electron-withdrawing and steric effects from the crowded F atoms), followed by a Suzuki coupling to install the carboxyl arms, and the replacement of the F groups by the strong nucleophile thiomethoxide. By comparison, crystallizing framework GDUT-7 is simpler, i.e., by solvothermally reacting H_3**L** and $EuCl_3 \cdot 6H_2O$ in 1:1 water and DMF (*N*,*N*-dimethylformamide). The single crystal X-ray structure reveals a composition of Eu·**L**·$(DMF)_{3.5}\cdot(H_2O)_4$, which is also consistent with the results of CHN elemental analysis, solution ^1H NMR (Fig. S10) of the dissolved the GDUT-7 solid in DCl/DMSO-d_6 and thermogravimetric analysis (TGA, Fig. S11) (see ESI for details).

The GDUT-7 crystal structure (space group: C2/c)[15] features a pair of Eu(III) centers straddled by four carboxyl groups from the **L** linker (Eu-O distances: 2.348, 2.423, 2.340, 2.408 Å); each Eu is also bonded by a chelating carboxyl (Eu-O: 2.536, 2.471 Å) group, and a DMF and water molecule at Eu-O distances of 2.457 and 2.466 Å, respectively (Fig. 2A). Overall, the Eu center is 8-coordinated and the Eu dimer centrosymmetric. With a total of six **L** linkers connected, the Eu dimer acts as a 6-connected node (Fig. 2D): together with the tritopic **L** linker, a 3D, non-interpenetrated (6,3)-net was generated; the topology had been reported,[16] and can be understood through subnet deconstruction,[17] namely, as two interesecting $ThSi_2$-type, (10, 3)-*b* subnets (see Fig. S12). The framework features small channels about 8.0 Å in diameter and smaller pockets aligned along the *b* axis (Fig. 2B): both types of voids are occupied by the DMF guests.

The colorless crystals of as-made GDUT-7 crystals turns yellow upon immersion in an ethanol (or water) solution of $HgCl_2$ (Fig. S13; see also Fig. S14 for the solid-state UV-Vis spectra), with concomitant suppression of the red photoluminescent emission (Fig. S15) from the Eu(III) centers. The Hg(II) adsorption isotherm (Fig. S16; aqueous solution, pH = 6.8) can be fitted against the Langmuir equation to yield an adsorption capacity q_{max} of 85 mg/g and a distribution coefficient K_d of 7.5×10^2 mL g^{-1}. Compared to other thioether-equipped MOF sorbents (e.g., q_{max} > 300 mg/g; $K_d > 10^4$), the Hg(II) uptake performance of GDUT-7 is modest; but one can imagine modifying the sulphur side groups of GDUT-7, e.g., with more donor atoms for a stronger chelation effect.

Higher Hg(II) loading, however, can be achieved under more forcing conditions, e.g., by immersing GDUT-7 crystals (6.0 mg) in a saturated EtOH solution (3.0 mL) of $HgCl_2$. GDUT-7-$HgCl_2$ thus obtained features the composition Eu(**L**)·$(HgCl_2)_{2.8}\cdot(EtOH)_{0.9}\cdot(H_2O)_{5.5}$ [calculated: C (29.97%), H (2.65%), N (2.11%), S (9.64%)], as per elemental analysis [found:

C (29.99%), H (2.64%), N (2.31%), S (9.57%)]. The EtOH content is also consistent with solution ^{1}H NMR (Fig. S17) of the GDUT-7-$HgCl_2$ solid dissolved in MeOH-d_4/DCl/DMSO-d_6; while the corresponding adsorption capacity (q_{max} = 214 mg/g) matches the TGA results (Fig. S11). The powder X-ray diffraction pattern (PXRD) of the GDUT-7-$HgCl_2$ solid indicates an intensity redistribution to higher angle (Fig. 3), as a result of the occupation of the void space by the heavy $HgCl_2$ guests.

The single crystal structure of GDUT-7-$HgCl_2$ indicates the DMF guests to be replaced by $HgCl_2$ and EtOH guests (see Fig. S17 for the ^{1}H NMR verification). Quantification of the guest species from the X-ray dataset, however, proves difficult, because of severe disorder and low occupancy of the guests. A total of three distinct $HgCl_2$ sites were identified in the unit cell (Figs. 2C and S18). Two of these are associated with the soft S and N donors at the Janus core, albeit at weak contacts (Hg1-N1, 2.788; Hg1-S3, 3.112; Hg2-N2, 2.938; Hg2-S4, 3.481 Å) considerably longer than typical Hg-N (about 2.0 Å) and Hg-S (2.3 Å) coordination distances. Both Hg1 and Hg2 sites are disordered over two sites, with total occupancy rates refined to be 0.33 for Hg1 and 0.087 for Hg2. Hg1 and Hg2 also each share the site with a disordered ethanol molecule (ccupancies: 0.17 and 0.63, respectively). The third $HgCl_2$ guest, being chemically soft, is peculiarly linked to the hard Eu(III) center via two bridging O atoms: one from a water ligand (Eu-O, 2.477; Hg-O, 3.214 Å) and the other from an ethanol ligand on Eu (Eu-O, 2.486; Hg-O, 2.662 Å). This $HgCl_2$ site is not disordered but is only 0.031-occupied and it also shares a site with an oxygen atom of another (more prevalent, with 0.67 occupancy) solvent molecule of ethanol. These local bonding features point to relatively weak binding of the $HgCl_2$ units, which is consistent with the modest K_d constant of 7.5×10^2 mL g^{-1} determined from the above sorption tests. All together, the X-ray structure features a formula Eu(**L**)·$(HgCl_2)_{0.44}$·$(EtOH)_{2.61}$, with an underestimated $HgCl_2$ content (compared with the above result from elemental analysis), suggesting that some of the $HgCl_2$ guests were too disordered to be located by SCXRD.

The GDUT-7 crystals also effectively take up I_2 molecules. For example, at 95 °C (2 hours), the crystals were impregnated by I_2 vapor to form the adduct Eu(**L**)·$(I_2)_{2.6}$ (I_2 content: 37.5%, as determined by elemental analysis and TGA, Fig. S19), while PXRD indicates the retention of the host lattice (Fig. S20). SCXRD on the I_2-loaded crystal revealed only the host net, indicating the I_2 guests to be highly disordered; while Raman spectra reveals the distinct peak of I_2 at 180 cm^{-1} (see Fig. S21). Further study (e.g., EXAFS; X-ray absorption fine structure) is needed for probing the I_2–host interactions. Besides the vapor phase, water offers an interesting medium for I_2 uptake tests,[18] because of the difficulty in removing I_2 contamination (e.g., the radioactive ^{131}I) by ion exchange or reverse osmosis. As most MOF solids are water-sensitive, the performance of GDUT-7 here merits attention. Specifically, shaking the crystals in an I_2-KI solution overnight leads to the adduct Eu(**L**)·$(I_2)_{1.2}$ (see ESI for elemental analysis, see Fig. S19 for TGA and Fig. S22 for PXRD), and uptake from non-polar solvents (e.g., petroleum ether) is also viable, leading to an even higher I_2 loading, as in Eu(**L**)·$(I_2)_{2.3}$ (see ESI for details). Sorbent regeneration is simple, as the I_2 guests can be readily eluted by ethanol (e.g., see the simple chromatography experiments of Fig. 4).

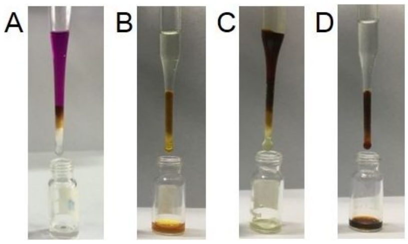

Fig. 4 Photographs of simple column chromatography (a pipette packed with crystalline powder of GDUT-7): a) a I_2 petroether solution being gravity-flown through; b) the pipette from step a being eluted by EtOH to regenerate the GDUT-7 sample; c) a Lugol (I_2-KI) solution being gravity-flown through; d) the pipette from step c being eluted by EtOH to regenerate GDUT-7.

In conclusion, the diverse guests--featuring the peculiar O-bound $HgCl_2$ and two other $HgCl_2$ units located by SCXRD--reflect the complex shapes and functions of the cavities in the triple-tripod-based MOF host. Besides the large number of donor functions (the S and N donors, as well as the O donors on the metal clusters), the non-planar, branchy and rigid triple tripod thwarts close packing, and forges various van der Waals pockets (micropores) for incorporating the guests. The extensive inclusion of $HgCl_2$ into this multiple-tripod-based MOF host is also in line with the propensity of other two-faced molecules (cucurbiturils, Janusarenes and pillararenes) to embrace guest molecules, pointing to the versatile guest-host chemistry that can be thus integrated into framework materials.

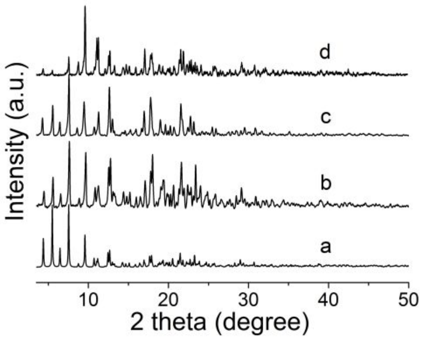

Fig. 3 PXRD patterns (Cu Kα, λ = 1.5418 Å) for GDUT-7 samples as: a) calculated from the crystal structure; b) of an as-made sample; c) of an activated sample; d) of GDUT-7 treated with excess $HgCl_2$ in ethanol.

Conflicts of interest

There are no conflicts to declare.

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15. CCDC 1888673 and 1888674 contain crystallographic data for GDUT-7 and GDUT-7-HgCl$_2$, respectively.

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