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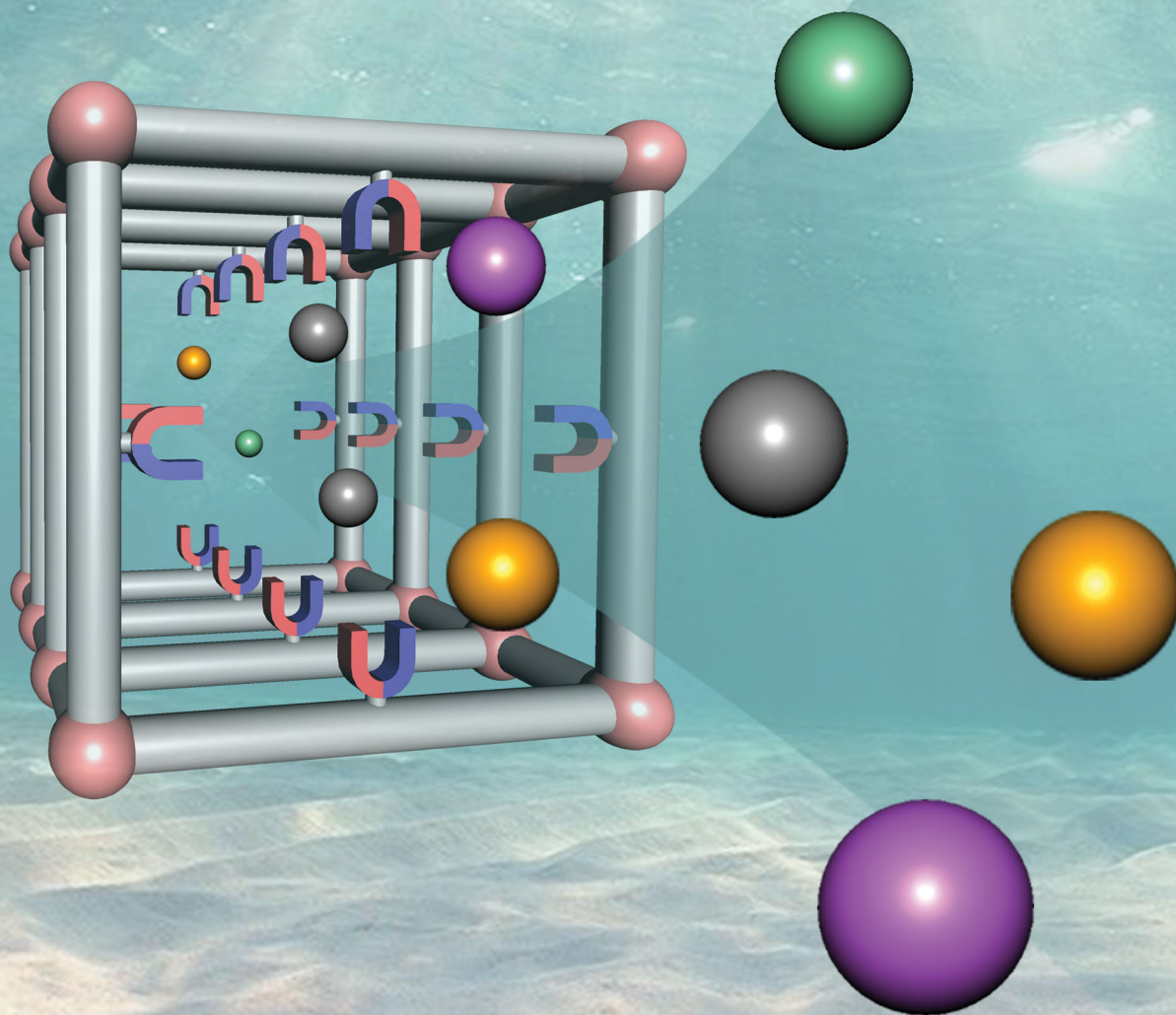
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A non-interpenetrating lead-organic framework with large channels based on 1D tube-shaped SBUs†

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This work presents the construction of a porous lead-organic framework (UPC-10) with large channels of $\sim$24 Å. UPC-10 shows efficient adsorption of I_2 and selective adsorption of some dyes containing the SO_3^- group. After the adsorption of dyes, UPC-10 exhibits a CO_2 gas uptake ability. Furthermore, UPC-10 could be transformed into PbS in a H_2S atmosphere, and the derived PbS manifests N_2 and CO_2 uptake abilities.

Porous metal–organic frameworks (MOFs) are a class of newly developed materials formed by metal ions or clusters as nodes and organic ligands as linkers.[1–5] The structures of the porous MOFs are highly determined by the coordination geometry of the metal ions or clusters and the coordination mode of the organic ligands.[6–8] Normally, some transition metal ions such as Zn^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, *etc.*, exhibit 4–6 coordination numbers with tetrahedral, square planar, tetragonal pyramidal, and octahedral geometries, and tend to form stable secondary building units (SBUs),[9–11] which can be further connected by organic ligands to generate high-dimensional open frameworks. In the past few decades, a large number of porous MOFs based on these series of transition metal ions and multifunctional organic ligands were synthesized and characterized, and their properties such as gas storage and catalysis were also widely studied.[12–15] However, there have been only a few reports on porous lead-organic frameworks with adsorption properties to date; the reason may be that lead ions possess a special coordination sphere (flexibility) and electronic structure ($6S^2$ outer electron configuration), and it is difficult for them to form stable SBUs.[16–19] Hence, the construction of porous lead-organic frameworks is still a great challenge.

On the other hand, due to the flexibility of the Pb^{2+} coordination sphere and the non-stereospecific nature of the halide

anions, the Pb^{2+} ions can be easily connected by halide anions to form 1D chains or 2D layer frameworks balanced by protonated amines, as observed in halo plumbate(II) systems.[20] Thus, with the help of halide anions, they may generate stable Pb^{2+} SBUs, which can be further linked by organic ligands to form high-dimensional open frameworks. In this communication, an unprecedented porous lead-organic framework, $[Pb_{1.5}ClL(H_2O)]\cdot(EtOH)_2\cdot DMF$ (**UPC-10**, H_2L = 2′-amino-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid (Fig. 1a), where EtOH = ethanol and DMF = *N,N*-dimethylformamide) based on 1D $[PbCl]_n$ tube-shaped SBUs, is reported. **UPC-10** exhibits efficient adsorption of I_2 molecules and selective adsorption of SO_3^--containing dyes (Fig. 1b–d).

A solvothermal reaction of $PbCl_2$ with H_2L in DMF/EtOH solvent at 120 °C for 3 days gave rise to yellow crystals of **UPC-10**, which is structurally characterized by single-crystal X-ray diffraction, elemental analysis (EA) and thermogravimetric analysis (TGA). Single-crystal X-ray diffraction reveals that **UPC-10** is a 3D open framework based on 1D infinite tube-shaped SBUs (Fig. 2a). The asymmetric unit consists of one and a half lead ions (1 Pb1 and 0.5 Pb2), one chloride ion, one **L** ligand and one
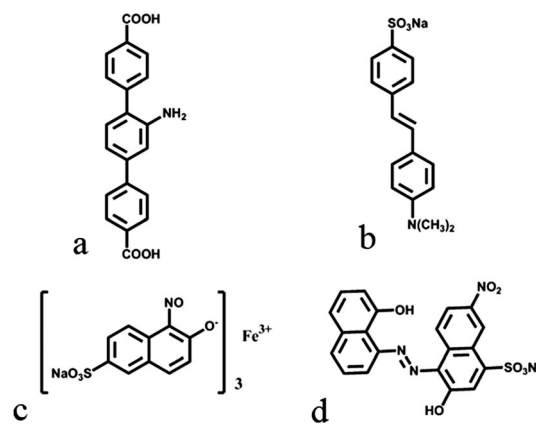
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Fig. 1 Molecular structures of (a) the 2′-amino-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid ligand (H_2L), (b) Eriochrome Black T (EBT), (c) Naphthol Green B (NG), and (d) Methyl Orange (MO).
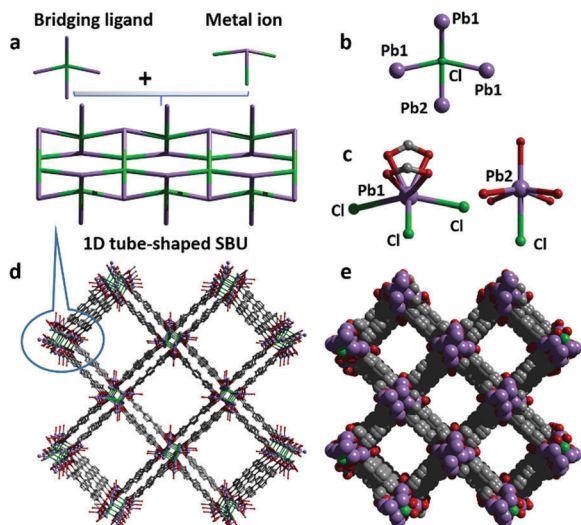
Fig. 2 (a) The 1D tube-shaped SBU, (b) and (c) Cl$^-$ and Pb^{2+} ions showing the coordination modes, (d) the 3D non-interpenetrating framework showing large pores, and (e) space-filling representation of the 3D porous framework.

coordinated water molecule. The Pb1 ion sits in an irregular environment hepta-coordinated by three chloride ions and four oxygen atoms from two carboxylate groups in a chelating mode, and Pb2 is six-coordinated by one chloride ion, one coordinated oxygen atom from a coordinated water molecule, and four oxygen atoms from four carboxylate groups of different **L** ligands (Fig. 2c). The Pb–O [from 2.406 to 2.703 Å] and Pb–Cl [3.012 and 2.910 Å] distances are comparable to those reported in other Pb^{2+} coordination polymers.[21]

The chloride ion in **UPC-10** plays an important role in the formation of 1D tube-shaped SBUs, as well as the final 3D open framework. Each Cl$^-$ ion adopts a μ_4-coordination mode (Fig. 2b) to connect four Pb^{2+} ions and every Pb1 ion attaches to three Cl$^-$ ions in a T-shaped geometry (Fig. 2c) to generate a 1D tube-shaped SBU with dimensions of 5.0×5.0 Å^2. In the past few decades, although many porous MOFs based on various SBUs such as [Cu$_2$(COO)$_4$] paddlewheel SBUs,[22] trinuclear SBUs,[23–25] [Zn$_4$O(COO)$_6$] tetrahedral SBUs,[26] high-nuclear SBUs,[27] and infinite 1D rod-shaped SBUs[28–30] have been widely documented, porous MOFs with 1D tube-shaped SBUs are rare and they will show great potential for structural diversity.

The 1D tube-shaped SBU was further connected by the **L** ligands along four directions to generate a 3D framework with 1D square double-walled channels along the [001] direction (Fig. 2d). The square channel (inner wall) is made up of four lead ions and four **L** ligands with the dimensions being 20.2×20.2 Å^2 in side length and 24.0×24.0 Å^2 diagonally (from lead ion to lead ion). The presence of the 1D tube-shaped SBU and the double walls prevents interpenetration; hence, **UPC-10** is a non-interpenetrating net with large channels (Fig. 2e). A large amount of uncoordinated solvates such as DMF and EtOH molecules reside in the channels. The total solvent-accessible volume fraction of **UPC-10** calculated using PLATON is 50.2% (6507.2 Å^3 per unit cell), which is comparable to MOF-5,

HKUST, *etc.*[31,32] TGA measurements show that **UPC-10** loses uncoordinated solvents below 300 °C and can be stable up to 370 °C (Fig. S1, ESI†).

The purity of **UPC-10** was confirmed by comparison of its simulated and experimental powder X-ray diffraction (Fig. S2, ESI†). It is known that porous MOFs can encapsulate some colored guest molecules, owing to it is easy to be detected by colour change when adsorbed into a colorless or light-colored crystal.[33–38] Due to the existence of large channels with double walls, adsorption experiments such as the adsorption of I$_2$ and dye molecules were carried out. **UPC-10** can effectively adsorb I$_2$ molecules in cyclohexane solution; more interestingly, the selective adsorption of SO$_3^-$-containing dye molecules, such as Eriochrome Black T (EBT), Naphthol Green B (NG) and Methyl Orange (MO) (Fig. 1b–d), was observed in **UPC-10**.

Before performing the adsorption property test, the as-synthesized crystals of **UPC-10** were immersed in cyclohexane for two days to remove the guest solvent molecules. The solvent-exchanged sample was suspended in a cyclohexane solution containing I$_2$. The colour of the solution changed from deep purple through pink to light pink with time (Fig. 3a). At the same time, the crystals changed from light yellow to deep brown (Fig. 3c), but their form and size remained unchanged during the adsorption process. The single crystal X-ray diffraction on the I$_2$-loaded crystals of **UPC-10** can give the same crystal cell with the as-synthesized one; however, due to the weak diffraction of the crystal, the resolution of the structure was poor. The XRD pattern of **UPC-10** before and after adsorption of I$_2$ confirmed its crystalline status (Fig. S2, ESI†). The photoluminescence measurement revealed that the emission for the iodine-loaded samples changed dramatically and the intensity reduced significantly compared to the as-synthesized sample, which indicates that the adsorbed iodine molecules partly quenched the fluorescence of **UPC-10** (Fig. S3, ESI†). The release of I$_2$ molecules from **UPC-10** was performed in cyclohexane solution. With the time increasing, the colourless solution of cyclohexane changed to pink (Fig. 3b), indicating that the I$_2$ molecules can be slowly released from the channels of **UPC-10**.

Dye molecules, as widely used chemicals in many industries, have caused environmental pollution due to their poor
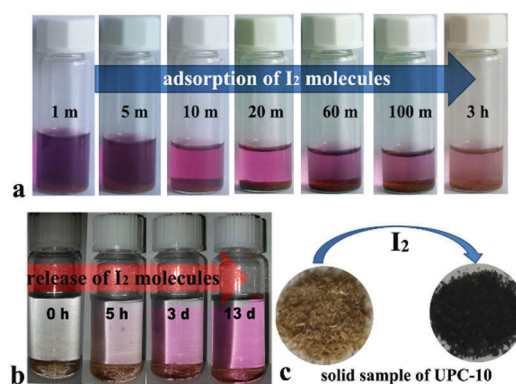

Fig. 3 (a) The I$_2$ adsorption in cyclohexane, (b) the I$_2$ release in clean cyclohexane, and (c) the colour change of the **UPC-10** solids.

biodegradability.[39] Thus, the selective removal/enrichment or degradation of dye molecules is very important for environmental protection. **UPC-10** shows selective adsorption of SO_3^--containing dye molecules, such as EBT, NG and MO, although the adsorption capacity is somewhat lower than some other reported results.[40–43] When the crystals of **UPC-10** were soaked in solutions of the dyes, the colourless crystals gradually became coloured (showing the dye molecules' colour) in 96 hours and the colour of the solution faded, indicating that the EBT, NG and MO could be adsorbed by the crystals of **UPC-10** (Fig. 4a–c). As mentioned above, **UPC-10** maintains large channels, so we failed to obtain its gas adsorption behaviour. Interestingly, we found that, after the adsorption of the above dyes, **UPC-10** could adsorb CO_2 molecules (19.16 cm^3 g^{-1}, 16.54 cm^3 g^{-1} and 25.57 cm^3 g^{-1} after being soaked in EBT, NG and MO, respectively). This could be derived from the fact that the solvent molecules have been exchanged by the dye molecules, and there are well fixed pores for the CO_2 molecules (Fig. 4d–f). The XRD patterns of **UPC-10** after the adsorption of the three dyes are shown in Fig. S5–S7 (ESI†); although the crystallinity of **UPC-10** after the adsorption of NG or MO is slightly declined, the constructed MOFs after the adsorption of the dyes are still maintained. We have also tried other dyes such as methyl yellow, crystal violet, diphenylthiocarbazone, methyl red, and methyl violet, but failed to obtain similar adsorption behaviour. Based on the characteristic nature of the structures of **UPC-10** and dye molecules, we speculate that the selectivity to the three dye (EBT, NG and MO) molecules may be derived from the electrostatic forces between the SO_3^- anions in the dye molecules and the NH_3^+ cations in the framework of **UPC-10**.

It should be pointed out that **UPC-10** could be transformed into PbS in a pure H_2S atmosphere, and Fig. S4 (ESI†) shows the XRD patterns of PbS and the standard data for PbS as well. The results of the XRD indicate that the PbS samples are well
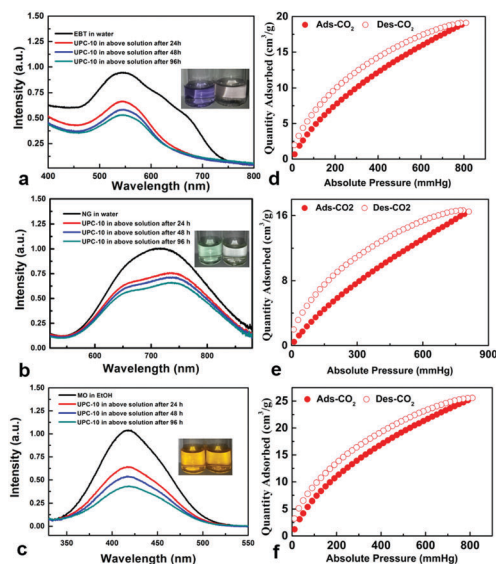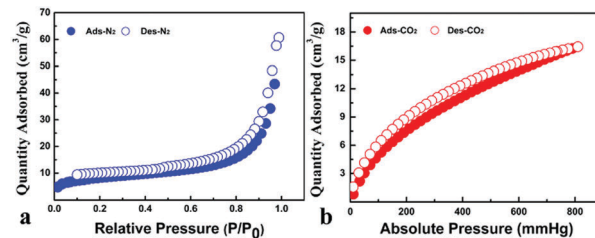

Fig. 5 Sorption isotherms for the generated PbS from **UPC-10**: (a) N_2 at 77 K and (b) CO_2 at 273 K.

crystallized, and their patterns are in good agreement with the bulk cubic PbS crystal phase (JCPDS 05-0592). The five major peaks can be indexed to 111, 200, 220, 311, and 222, respectively. No peaks of other impurities were detected. As H_2S gas is a potent neurotoxin, which will cause a stimulation of the mucosa, the experiment should be conducted in a fume hood. The H_2S gas was prepared by the reaction of FeS with H_2SO_4 ($H_2SO_4 : H_2O$ = 2 : 3 [v/v]) in a flask, and collected through a desiccant of P_2O_5 for an hour and waste gas was absorbed by NaOH solution at the end of the equipment. By using volumetric gas adsorption measurements, we found that the PbS generated from **UPC-10** showed gas adsorption abilities (Fig. 5); the N_2 uptake capacity at 77 K and CO_2 uptake capacity at 273 K are 60.46 cm^3 g^{-1} and 16.40 cm^3 g^{-1}, respectively. As we know, PbS thin films or PbS nanoparticles usually show gas-sensing properties,[44–47] but reports on their gas adsorption ability are still rare. MOF-derived porous materials normally exhibit interesting properties and have become a hot research topic.[48–50] We believe that the present study of porous PbS with gas adsorption abilities is interesting and will provide new inspiration for MOF derived materials. Further study on **UPC-10**-derived PbS materials is currently underway in our lab.

In summary, a non-interpenetrating porous lead-organic framework (**UPC-10**) with large channels of ∼24 Å based on a NH_2-decorated dicarboxylate ligand has been synthesized and characterized. The 1D tube-shaped $[PbCl]_n$ SBUs are crucial to the formation of the non-interpenetrating framework. The adsorption and release of I_2 in **UPC-10** were also studied. **UPC-10** exhibits selectivity to SO_3^--containing dye molecules (EBT, MO, and NG). Our results presented here may provide a strategy for the construction of non-interpenetrating Pb-MOFs with large channels based on 1D tube-shaped SBUs.

Fig. 4 (a), (b) and (c) UV–vis spectra of **UPC-10** soaked in EBT, NG and MO solutions, respectively. (d), (e) and (f) CO_2 sorption isotherms for **UPC-10** after adsorption of EBT, NG and MO, respectively.

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