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A rare (3,12)-connected zirconium metal-organic framework with efficient iodine adsorption capacity and pH sensing

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We synthesized a rare (3,12)-connected zirconium metal-organic framework with sky topology showing efficient iodine adsorption and pH sensing capacity

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ABSTRACT: We report here a stable rare zirconium metal-organic framework (MOF) exhibiting sky topology $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$ (ITTC)₄ (**UPC-158**) (where H₃ITTC = 4,4',4''-(1H-imidazole-2,4,5-triyl)tribenzoic acid) established by $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(-COO)_{12}$ clusters and 4,4',4''-(1H-imidazole-2,4,5-trivl)tribenzoic acid with abundant π -electron as an ideal material for removing iodine vapor-a major radioactive fission waste. The iodine adsorption effect of the acid-treated UPC-158-HX series has a substantial improvement compared with the parental UPC-158 (1.77 g·g⁻¹), and the iodine vapor uptake of 2.92 g·g⁻¹ at 343.15 K for UPC-158-HCl has reached the maximum value among the reported MOF materials. In addition, the protonation and deprotonation of imidazole nitrogen alter the symmetry of internal structures, resulting in a strong fluorescence enhancement of the material in the pH range from 10~11, making it a potentially precise pH meter. This work not only provides insights into the discovery of unprecedented structures and topologies through the rational choice of organic linkers via experimental and simulation method but also pave the way to understand the structure related functional applications. It also opens up a window for the design and construction of highly complicate porous and stable structures for sophisticated applications.

Introduction

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As an emerging class of crystalline porous materials, metal-organic frameworks (MOFs) constructed from inorganic metal ions or clusters and organic linkers via coordination bonds have attracted considerable interest in the past decades.^{1, 2} On account of their structural and functional tunability, high surface area as well as suitable pore size, MOFs have shown great promise in multifarious fields, such as gas storage and separation,^{3, 4} sensing,⁵⁻⁷ heterogeneous catalysis,^{8, 9} and biochemical systems.¹⁰⁻¹³ So far, more and more MOFs with high tunability of surface chemistry environments and pore textural properties have been synthesized for targeted applications. However, the stability of MOFs, especially under harsh conditions, has become an important obstacle, hindering their further applications and the rational design and synthesis of highly stable MOFs remain a challenge.14-17

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According to the soft and hard acid-base theory,^{18, 19} the MOFs based on carboxylates linkers and with high oxidation state metal ions or clusters have shown high chemical stability than those that constructed from low oxidation transition element / earth element metal and carboxylates linkers. Thus, chemists devoted their efforts to MOFs with high-valence metals (Fe³⁺, Al³⁺, Cr³⁺, Re³⁺, Zr⁴⁺), such as MIL-101 series,²⁰ UiO-66,²¹ PCN series,^{22, 23} MOF-525-545²⁴ and their stabilities were improved significantly. Among them, due to its extremely high valence state, the tetravalent zirconium MOF was easier forming into strong metal coordination bonds with carboxylic acid ligands, enabling its remarkable stability, offering Zr-MOF an advantage in practical applications.

In the process of designing stable zirconium MOFs, 2-, 3-, 4connected ligands are mostly used, and 4-connected linker could take two configuration modes: square or tet-; the cluster shows 4-c, 6-, 8-, 10-, 12- connected, and highly symmetrical 12-c cluster has multiple transformation configurations such as cuo, ico hpr, tte.17, 25 Types of linkers or SBUs (secondary building units) depend on the connections. Therefore, combined flexibility of cluster and linker makes topology prediction a great challenge for MOFs.²⁶

Among all the reported Zr-MOFs, compared to 2- and 4connected linkers, only few 3-connected linkers have been used to build Zr-MOFs. H₃TATB (H₃TATB = 4,4',4''-(1,3,5-triazine-2,4,6triyl)tribenzoic acid),²⁷ H_3BTB ($H_3BTB = 5'-(4-carboxyphenyl)-$ [1,1':3',1"-terphenyl]-4,4"-dicarboxylate)²⁸ usually exhibit coplanar with D_{3h} symmetry to construct (3, 6)-c Zr-MOF with D_{3d} symmetry

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of Zr₆ cluster. Recently, Li and co-authors introduced three methyl group into the meta-position of H₃BTB to rotate the carboxyl-linked benzene ring to form a D_{3h} -symmetric H₃CTTA (H₃CTTA = 5'-(4-carboxyphenyl)-2',4',6'-trimeth-yl-[1,1':3',1''-terphenyl]-4,4''-

dicarboxylic acid).²⁹ As the symmetry of the ligand decreases, the Zr_6 cluster occupies a higher D_{4h} symmetry mode, thus constructing a (3,8)-connected Zr-MOF. More connections of the Zr_6 cluster contribute to higher stability of the Zr-MOFs. Mohamed Eddaoudi pointed out the combination of *cuo-*12-connected MBBs (molecular building blocks) with either linear (2-connected) or square (3connected) MBBs leads to the formation of fcu or ftw net, respectively, and that no structure can be formed when it combined with a 3-connected unit. Apparently, it is not compatible to 12connected Zr₆ cluster combined with triangular ligands.³⁰ Very recently, Yaghi reported the only (3,12)-connected sky net, named MOF-1004, which contributes to the twist of longer linkers (H₃BTE = 4,4',4"-[benzene-1,3,5-triyltris(ethyne-2,1-diyl)]tribenzoate) with more flexible and longer than the previously reported backbone.³¹ However, associated with the flexible long linkers, there is an unknown phase formed in MOF-1004 produces, impeding the further characterization and applications.

Inspired by the above researches, saturated Zr clusters can be achieved under high stability multi-linkage number, and we assembled (3,12)-c Zr-MOF with a tricarboxylic acid ligand containing modifiable active sites (N, S et al) and strong conjugate electron, interacting with a guest molecule or facilitating postmodification, to achieve such stable MOFs. Herein, we reported a simple and economical reaction where the methyl pformylbenzoate was the main reaction material to form the new imidazole-tricarboxylate linker H_3 ITTC (H_3 ITTC = 4,4',4''-(1Himidazole-2,4,5-triyl)tribenzoic acid) (Scheme S1), in which imidazole ring acts as an equatorial plane, and the three benzene rings connected thereto deviate from the same side of the equatorial plane by 5.741, 41.887, 41.888 degrees, respectively (Fig. S4). The angles of the benzene rings in the ligands are slightly twisted to 8.926, 15.183, 15.183 degrees, respectively (Fig. S5), combined with Zr₆ clusters to generate a high-symmetry MOF (UPC-158) that enables a robust porous framework owing to the strong affinity between Zr(IV) and carboxylate-O.18 UPC-158 exhibits a fluorescence-pH dependent relationship after varying degrees of protonation, which makes it a potentially precise pH meter. Moreover, UPC-158-HX exhibits different iodine adsorption capacity after treatment with different halogen acids.

Experimental Section

Materials and Methods.

All the reagents and solvents were used as received from commercial suppliers without further purification. Single crystal data were collected by X-ray diffractometer with a Cu sealed tube (λ = 1.5406) at 40 kV and 40 mA. Powder X-ray diffraction (PXRD) was carried out on a BRUKER D8-Focus Bragg-Brentano X-ray powder

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diffractometer equipped with a Cu sealed tube ($\lambda = 1.54478$, Å) at 40 kV and 40 mA. Nuclear magnetic resonal 62: (NMR)/Gata^O Were collected on a Mercury 400 NMR spectrometer. Thermogravimetric analysis (TGA) data were obtained on a Mettler Toledo thermogravimetric analyzer at a rate of 10 K·min⁻¹ under nitrogen atmosphere (100 mL·min⁻¹). N₂ adsorption-desorption isotherms were measured using a Micrometritics ASAP 2020 system at 77 K. The UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. SEM and TEM images were collected via a scanning electron microscope (Philips XL30 FEG SEM) and transmission electron microscope (JEOL JEM-2100TEM). X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo ESCALAB 250 surface analysis system.

Synthesis of compounds.

Synthesis of ligand: The synthesis of H_3 ITTC (4,4',4''-(1H-imidazole-2,4,5-triyl)tribenzoic acid) is based on the method of the previous literatures.³² (See supporting information Section 1 for details)

Synthesis of ligand single crystal (UPC-157): 5.0 mg H_3 ITTC was dissolved in 2.0 mL mixed solution of methanol and acetonitrile (1:1), and heated at 75 °C for two days to precipitate a single crystal of the ligand.

Synthesis of UPC-158: 0.024 g of $ZrCl_4$ and 0.010 g H₃ITTC were dissolved in 3.0 ml DMF solution with 1.1 mol/L benzoic acid. Then, the solution was heated in a vacuum oven at 120 °C for 48 h under constant pressure. After cooling, triangular prism-shaped crystals were obtained. The sample was purified with fresh DMF three time to remove the benzoic acid and unreacted raw material, then methanol solution (95%) was used three times to make sure that the occluded DMF molecules were totally exchanged. After drying, UPC-158 was obtained under vacuum at 100 °C for 10 h.

Preparation of UPC-158-HX(X = F, Cl, Br, l): The fresh crystals of **UPC-158** were washed with DMF several times, then, soaked with HX aqueous solution (pH = 3) for two days, during which the solvent was removed and replenished two times. After that, the solvent was decanted, soaking in methanol for two days and changed the fresh methanol three times a day. After drying, **UPC-158-HX** was obtained under vacuum at 100 °C for 10 h.

Results and discussion

Structure description

Colorless triangular prism-shaped of **UPC-158** was obtained via solvothermal reactions of $ZrCl_4$ with H₃ITTC ligand in DMF at 120 °C for 72 h by using benzoic acid as a modulator. Single-crystal X-ray diffraction reveals that **UPC-158** crystallizes in the cubic crystal system with $Pm\overline{3}n$ space group and is composed of the *cuo*-12-connected $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(-COO)_{12}$ clusters connected by tritopic H₃ITTC linker to form the 3-D network. As shown in Fig. 1, $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(-COO)_{12}$ cluster in **UPC-158** adopts O_h symmetry and

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each edge of the Zr₆ cube is linked by one carboxylate from a ITTC³⁻ ligand and each triangular face is bridged by (μ_3 -O) and (μ_3 -OH) group, which is similar to that of UiO series,²¹ PCN-221,³³ PCN-228-230,³⁴ PCN-56,³⁵ and MOF-525.²⁴ Surprisingly, the symmetry of H₃ITTC ligand is reduced to the lowest *C*_s symmetry to connect three Zr₆ clusters, which is different from the *D*_{3h} symmetry in MOF-808,³⁶ PCN-777,²⁷ BTU-12-13²⁸ and *C*₁ in Zr-BTB.²⁹ This symmetry reduction contributes to the triangular ligand symmetrically compatible with the Zr₆(μ_3 -O)₄(μ_3 -OH)₄(-COO)₁₂ clusters. Moreover, there exist two kinds of cages in the sizes of around 12.69 and 20.00 Å in **UPC-158**, respectively. As we predicted, the combination of the unique linker and the Zr₆ clusters results in a *sky* topology in the Reticular Chemistry Structure Resource with {4²⁰6²⁴8²²}{4³₄} topology.



Fig. 1 Crystal structure of **UPC-158**: (a) 3-connected organic ligand; (b) *cuo* 12-connected Zr_6 cluster; (c) simplified 3-connected linker; (d) 12-connected node; (e) 3D network; (f) sky topology; (g)(f) big cage in **UPC-158**; (h)(j) small cage in **UPC-158**.

DFT calculation on ligand energy barrier

The density functional theory (DFT) calculations were used to interpret the successful formation of (3,12)-connected *sky* net in **UPC-158** at the level of M06-2X-D3/6-311+G(2d,2p) in the SMD solvent mode using Gaussian 09 D.01.³⁷ To simplify the calculations, the effect of Zr_6 clusters on energy barrier was ruled out and the crystal structure of H₃ITTC linker was also performed as a reference. Thus, DFT calculations were carried out on the ligands with different configurations. One is free state in **UPC-157** and the other is in **UPC-158**. As depicted by DFT calculations, the energy barrier (ΔG) between two states is 28.73 kcal/mol, which can be easily overcome. Thus, it is suggested that the rational choice of organic linkers is the key factor to construct rare (3,12)-connected *sky* net.

Thermal and chemical stability analysis.

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To explore the thermal stability of **UPC-158**, TGA curves were measured, indicating that **UPC-158** is stable up to about 500 °C (Fig. S7). PXRD patterns of **UPC-158** at different temperatures were performed to further demonstrate thermal stability. As shown in Fig. 2a, **UPC-158** maintains its crystallinity after heating at 450 °C for 1 h in N₂. Apart from the high thermal stability, **UPC-158** also possesses excellent chemical stability. **UPC-158** was separated into solutions with different pH (0.5, 1, 2, 7, 10, 11 and 12) for 24 hours, PXRD results prove that **UPC-158** remains intact between pH = 0-11. Surprisingly, UPC-158 can maintain unchanged in 3 M HCl aqueous solutions (Fig. S8).

Thus, the chemical stability of **UPC-158** towards halogen acid is investigated by immersing them into different aqueous solutions of halogen acid (pH = 3) for two days. The resultant PXRD patterns are very consistent with the simulated ones, demonstrating that **UPC-158** can survive in halogen acids (Fig. 2b). The excellent thermal and chemical stability are attributed to the saturated multi-coordination number and strong coordination capacity between Zr_6 and carboxylate group based on Hard-Soft-Acid-Base theory. Other reasons may arise from deprotonation of imidazole group of H₃ITTC ligand involved in the **UPC-158** framework. When the pH is acidic, -N group in imidazole will obtain an H⁺, forming protonation format. In comparison, when the pH is basic, -NH group in imidazole will lose an H⁺, forming deprotonation format (Fig. 2c).



Fig. 2 (a) PXRD of UPC-158 treated through Different temperature (30~480 °C). (b) PXRD of UPC-158 treated with different halogen acid solutions at pH = 3. (c) Protonation and deprotonation processes of porphyrin involved in UPC-158 framework in experimental acidic and basic media (pH = 0-11). (d) N₂ adsorption isotherms for UPC-158 and UPC-158-HX (X = F, Cl, Br, I).

To assess the porosities of **UPC-158** and **UPC-158-HX** (X = F, Cl, Br, I), we investigated N₂ sorption experiments at 77 K (Fig.2d). **UPC-158** and **UPC-158-HX** exhibit a type-I isotherm of N₂ sorption with N₂ uptakes of ~600 cm³/g at 1 bar, implying the existence of micropores in **UPC-158**. Indeed, the pore size distribution shows the presence of two pore sizes of 12 Å and 20 Å. The resulting 3D **UPC-**

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158 exhibits high specific surface area. The experimental Brunauer–Emmett–Teller surface areas of **UPC-158**, **UPC-158-HF**, **UPC-158-HCI**, **UPC-158-HBr** and **UPC-158-HI** are 2170.16 m²·g⁻¹, 2136.72 m²·g⁻¹, 2289.13 m²·g⁻¹, 2151.35 m²·g⁻¹, 1953.55 m²·g⁻¹, respectively, and their porosities are 0.928591, 0.956570, 0.992850, 0.931357, 0.853214 cm³/g, in good agreement with the results calculated using the non-disordered structure. Therefore, the high porosity of **UPC-158** can be used to carry out the adsorption and encapsulation experiment of difficult-to-capture guest molecules.



Fig. 3 (a) Blue points showed the normalized fluorescence intensity at ~448 nm in different pH solution; (b) Normalized to show blue shift (pH > 9.7) of the fluorescence emission wavelength; (c) Fluorescence lifetime of UPC-158 in different pH solutions; (d) The quantum yield of UPC-158 in different pH solutions.

pH sensing analysis

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Fluorescent pH sensors have certain advantages in electrode and current wide range of environmental analysis, bioanalytical chemistry for medical diagnostics, etc.³⁵ However, only a few MOFs as pH-dependent fluorescence sensors have been reported (Table S2). The excellent chemical stability towards acid and base has propelled us to use UPC-158 as a potential pH detector. UPC-158 shows strong fluorescence emission of H₃ITTC ligand at 448 nm at room temperature with $\lambda ex = 350$ nm, owing to π^* - π transition between intraligands (Fig. S9). The coordination with Zr₆ clusters with linkers did not affect the fluorescence emission, and there is no electron and long range energy transfer processes between Zr₆ and linkers. Furthermore, the pH dependent fluorescence properties of UPC-158 were investigated by exposing UPC-158 to aqueous solution with different pH values. Interestingly, the fluorescence intensity of UPC-158 is in close association with pH changes of the dispersed solutions (pH range from 0 to 12.2) (Fig. 3a, S10, 11). Altogether, UPC-158 exhibits weak fluorescence in acidic solution while strong fluorescence in basic solution with the highest intensity in pH = 11.08. When the pH < 1.04, which is characteristic of protonation of the imidazole ring, the increasing pH causes a slight increase of the fluorescence emission intensity. When the pH is acidic, -N group in imidazole will obtain an H⁺, forming protonation format, destroying the π system of imidazole and thus resulting in significant fluorescence quenching, and the

symmetry of ligands changes from C_s to C_s . In comparison, when the pH is higher than 10, the fluorescence intersity of UPC 158 Hises gradually in line with the increment of pH and reaches up to the maximum when the pH is 11.08. It is noted that an obvious blue shift of 13 nm (pH > 9.7) of emission maxima was detected (Fig. 3b). The fluorescence enhancement and blue-shift in pH (9.7-11.2) solution arise from deprotonation of N-H group of imidazole and the symmetry of ligands changes to chiral symmetric structure again. After that, the fluorescence decrease gradually accompanied by the partially destroy of UPC-158. Significantly, the correlation relationship between fluorescence intensity and pH values can be divided into three pieces: When pH varies from 0-1.04, a simple linear relationship with slope is 0.08489. And when the pH is in the range of 1.04-10.2, the fluorescence intensity keeps constant. However, when the pH is between 10.2-11.08, another linear relationship appears with slope is 1.07825.

To further analyze the changes in fluorescence intensity, the fluorescence lifetime and quantum yield tests were recorded. As depicted in Fig. 3c, in pH < 9 solution, their fluorescence lifetime are maintained at approximately 2.7 ns, When the pH is between 10 and 11, the fluorescence lifetime is extended to 3.13 ns. At the same time, the quantum yield is correspondingly increased from 5% to 30%, which is consistent with the fluorescent mutation region (Fig. 3d). The excellent pH sensing properties make **UPC-158** be a potentially precise pH meter, especially in the range of pH = 10~11.



Fig. 4. XPS high-resolution spectra of the F 1s region (a); Cl 2p region; (b) Br 3d region; (c) and I 3d region (d).

Adsorption and release of iodine.

Due to the ultra-high energy density and low carbon emissions of nuclear power, it has become an important and widely used energy source.³⁸ The radionuclides ¹²⁹I and ¹³¹I are nuclear waste streams generated by nuclear power. The colored guest iodine molecules can be encapsulated by suitable multi-stage channels in MOFs. The active site "N" and the strong conjugated π -electrons of the ligands provide possibilities to interact strongly with guest molecules. Moreover, **UPC-158** crystals with large specific surface areas and porous channels also make **UPC-158** performing high guest molecule-capturing. Although previous reports have focused on

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how to design porous materials with high capacity, ultra high stability, and easy reusability, few studies have explored the ability to affect iodine adsorption differently modified materials.

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In view of the fact that neutral **UPC-158** can be protonated in the acidic environment, it is bound to change the electrical properties of the skeleton. To investigate the effects on the iodine adsorption capacity of protonated **UPC-158**, we compared the effects of protonated cation skeleton of **UPC-158-HX** (F, Cl, Br, I) on the ability to adsorb iodine. The characterization results of XPS (Fig. 4) and EDS-mapping (Fig. S13~18) proved the entry of halogen elements. Therefore, based on the above characteristics, and iodine adsorption experiments were carried out.



Fig. 5. (a) Time-dependent iodine vapor capture capacities of **UPC-158** and **UPC-158-HX** (X=F, Cl, Br, I); The colour change of **UPC-158** (a)sample and single crystal during iodine adsorption for 3h, respectively; (c) Color transformation from dark red to colorless of a single crystal of **UPC-158**.

In this work, the stable ¹²⁷I was substitute to radioactive ¹²⁹I and ¹³¹I, because these isotopic iodine elements possess nearly identical chemical behaviour. When the activated UPC-158 series were exposed to iodine vapor environment of 343.15 K and 1 bar, its colour changes from colorless to red until the final black throughout (Fig. 5a, 5b). The weight of the corresponding iodine-loaded adsorbent also gradually increases in the surrounding environment. The results show the introduction of different halogens F-,Cl-, Brand I⁻ did make the iodine adsorption of UPC-158 increase, from the original 178% to 219%, 292%, 275% and 259%, respectively (Fig. 5c), in line with the TGA results (Fig. S19-23). It is worth noting that the iodine adsorption capacity of the crystal after protonatied by HCl is significantly improved to 292%, which was the highest among MOFs, and the equilibrium uptake for UPC-158 series were reached guickly within 4 h, and no further changes in the iodine loading amounts were observed after 20 h, indicating that the iodine uptake in the system was basically saturated. In addition, we can clearly see the iodine particles adsorbed in UPC-158-HF by high-power transmission electron microscopy (Fig. S18). The XRD results of

UPC-158-HX show that the materials were stable after the iodine adsorption (Fig. S24). This sorption was kinetic¹faster/faalother observed in most porous iodine MOFs,³⁹⁻⁴⁵ some CMP ⁴⁶⁻⁴⁸ and traditional activated carbon adsorbent (Table S3).^{49, 50} XPS was implemented to further verify the morphology of iodine in **UPC-158** series (Fig. S25). Peak splitting originates from the 3d_{3/2} and 3d_{5/2} orbitals of iodine, which correspond to the binding energy peaks at 630.6 and 619.2 eV, respectively. The peaks at ~630.2 and ~618.8 eV of **UPC-158** series are attributed to covalently bound to iodine.



Fig. 6. The electronic static potential of neutral and acid state H_3 ITTC and I_2 molecule, and their corresponding adsorption energies to I_2 molecule.

DFT calculation on Iodine adsorption

To clarify the different absorption ability between the neutral and halogenated and protonated state, density function theory (DFT) calculations were carried out on the basis of M06-2X-D3/6-311G(d,p)/SDDALL//6-311G+(2d,2p)/SDDALL using Gaussian 09 D.01 software package.³⁷ The electrostatic potential (ESP) populations of neutral, protonated and halogenated state of MOFunit together with I₂ molecule are calculated and the results are shown in Table 1: the binding energy of H₃ITTC-HX to the iodine molecule is HCl > HBr > HI > HF > netural. The H₃ITTC is overall neutral among the molecule. After protonation, the entire imidazole molecule is positively charged. On the other hand, the entirety of the iodine molecule exhibits a weaker electronegativity, except that the two sides exhibit a strong positive charge. As a consequence, the iodine molecule can not only interact with positive charges, but also generate mutual electrostatic forces with halogen ions. The calculation results show that both iodine molecules and neutral and protonated/halogenated HaITTC can be electrostatically adsorbed. For the purpose of further measuring the adsorption capacity of the iodine molecule and the H₃ITTC in both states, we also calculated the binding energy of the two molecules in the two states. As presented in Fig. 6, the physical adsorption between I₂ molecule and H₃ITTC are favourable in both states. Undoubtedly, the adsorption of iodine molecules with protonated imidazole ligands is stronger than that of neutral imidazole ligands, which is consistent with the experimental observations. The introduction of protonation and halogenation increases the force of the iodine molecular guest and the skeleton to varying degrees, thereby increasing the adsorption of iodine (The role of iodine and ITTC in different states can be found in detail in supporting information Section 6).

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Table 1. The combination energy between $H_3 ITTC$ and I_2 in neutral and acid state.

Processing conditions	Combination Energy	Amount of iodine adsorption
	(kcal/mol)	(g·g ⁻¹)
Neutral	-1.52	1.78
HF	-4.95	2.19
HCI	-19.40	2.92
HBr	-11.47	2.75
н	-9.22	2.59

The single crystal X-ray diffraction on the iodine-loaded crystals of **UPC-158-HX@l₂** can give the bigger crystal cell compared with the as-synthesized one; however, due to the weak diffraction of the crystal, the resolution of the structure was poor, and the single crystal XRD data of iodine-loaded crystals of UPC-158-HX@l₂ was not obtained. Neverthless, the XRD pattern of **UPC-158** before and after adsorption of l₂ confirmed its crystalline status.

In order to verify the recyclability of UPC-158, we implemented the iodine release experiments. The iodine-loaded sorbents UPC-158-HX@I2 were placed in dry methanol and the color of the solution slowly turned red to uniform (Fig. S26). After several times of washing, the solution turns to colorless and no longer changes. The crystal color of UPC-158-HX@I2 changes back to the near-white state, It is worth noting that the color of UPC-158 crystals without acid treatment is dark yellow (Fig. 27), indicating that part of the iodine molecules cannot be released. XRD curves of UPC-158 series after iodine release illustrate that the recovered material retains its crystalline stability after cycles (Fig. S28). The process of releasing iodine from UPC-158-HX@I2 was recorded by UV-vis absorption spectra. It can be concluded from the UV spectrum results that the release of iodine in methanol is in controlled release diffusion process of kinetic behavior, the iodine release rates of UPC-158, UPC-158-HF, UPC-158-HCl, UPC-158-HBr and UPC-158-HI were 78.56%, 96.51%, 95.78%, 97.53%, 95.78%, respectively (Fig. S29-40). That is, the acid-treated UPC-158 series provides a more complete release of iodine than the unacidified UPC-158. Because of the multiple supramolecular interactions generated between the aromatic ring-positively charged framework of UPC-158-HX and iodine, such as typical charge interactions between benzene and iodine molecules, N-H···I bonding interactions, and X···I interactions, the halogenated and protonated materials can adsorb more amounts of iodine. When the loaded-iodine material is immersed in the methanol solvent, the weak force between the material frame and the guest molecule iodine is destroyed,⁵¹ thereby achieving a high iodine adsorption function and a high recovery performance of the material.

Conclusions

In summary, a new porous and stable zirconium metal–organic framework $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(ITTC)_4$ (**UPC-158**), constructed by a O_h symmetry 12-connected Zr_6 cluster and a C_s symmetry 3-connected ligand, has been constructed. Based on the protonation and

deprotonation of nitrogen atom in the imidazole group article Chine exhibits pH-dependent fluorescence with the fludrescence interastiv increasing rapidly at pH = 9.7~11.2, which provides the basis for MOF as an accurate pH meter. Moreover, after treatment with different halogen acids, iodine absorption capacities of **UPC-158-HX** are greatly improved, and the iodine absorption capacity of **UPC-158-HCI** can reach up to 292%, which is the highest record among MOFs. These results on the structure–property relationships have the potential to guide future experimental syntheses of functional MOF materials with novel structures. Meanwhile, this research is of great significance to new functional porous material designs for pH sensing and iodine loading.

Conflicts of interest

There are no conflicts to declare

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