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ARTICLE TYPE

A New Strategy to Construct Metal-Organic Frameworks with Ultrahigh Chemical Stability

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A novel two-dimensional metal-organic frameworks has been constructed from Fe^{3+} and *meso*-tetra(4-imidazoyl)porphyrin, and it can stand in saturated (~27.5 M) NaOH solutions for a week. To the best of our knowledge, this is the first report of a stable MOF in saturated NaOH solution. The utilizing of imidazolyl-based porphyrin ligand and high-valence metal is a new and promising strategy to construct porphyrinic MOFs with ultra-high stability.

Porphyrins and metalloporphyrins which are biologically-relevant macrocycles play an important role in catalysis, sensors, photonic devices due to their special photochemical, electronic and catalytic properties.[1] Since the first metal-organic frameworks (MOFs)[2] assembled by tetra-pyridylporphyrin and Cd that reported by Robson,[3] porphyrinic MOFs (porphyrins serve as nodes or linkers) and porphyrin@MOFs (porphyrins are encapsulated in MOFs)[4] have been intensely investigated for their potential applications as gas storage,[5] light harvest,[6] selective sorption,[7] sensing[8] and heterogeneous catalysis.[9, 10] However, compared with the fast-developing porphyrin chemistry, the field of porphyrinic MOFs and its application is still in the infancy.[10, 11] Though thousands of MOFs have been reported in recent year, the number of porphyrinic MOFs keeps relatively rare hitherto.[10] Porphyrin is facile synthesis and functionalization. Indeed, by introducing multifarious functional peripheral substituents at the β-pyrrolic or/and *meso*-positions or adding different central metals to the porphyrin core, porphyrin exhibits multi-functional properties.[12] Among the reported porphyrinic MOFs, almost all the ligands are pyridyl or carboxyphenyl substituted porphyrins or their derivatives (Fig. 1a, 1b),[10, 13] ligands other than those mentioned above are quite rare. Imidazole and its derivatives have been shown to be versatile ligands for constructing MOFs, especially the metal-imidazolate frameworks usually show high thermal or chemical stability,[14] which will benefit the potential applications of MOFs. Indeed, the stability of MOFs is always the bottleneck of its development. It is reasonable to suppose that not only high stability, but also interesting properties would be achieved if imidazolyl-porphyrin based ligands have been used to construct MOFs. However, to the best of our knowledge, there are no MOFs assembled from imidazolyl-porphyrin to be reported. In order to obtain porphyrinic MOFs with high stability, herein, we present the structure of the first example of imidazolyl-porphyrin MOFs constructed from *meso*-tetra(4-imidazolyl)porphyrin (hereafter, TImP, Fig. 1c), and its ultra-high chemical stability in alkaline solutions.

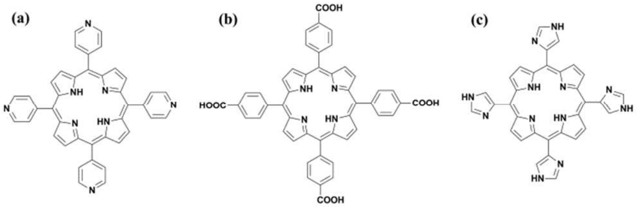

Fig. 1 (a) and (b), *meso*-tetra(4-pyridyl)porphyrin (TPyP) and *meso*-(4-carboxyphenyl)porphyrin (TCPP) which were mostly used to construct MOFs. (c), *meso*-tetra(4-imidazoyl)porphyrin (TImP) used in this work.

Small dark-purple crystals of $[Fe(C_{32}H_{18}N_{12})][Me_2NH_2]$ (NJNU-1, NJNU = Nanjing Normal University) were obtained via solvothermal reaction (S3, ESI†). Single-crystal X-ray crystallographic studies revealed that NJNU-1 crystallized in the monoclinic $P2_1/n$ space group, forming two-dimensional frameworks composed of porphyrin and Fe^{3+} linked through imidazolyl groups. The coordination environment of porphyrin with Fe^{3+} is illustrated in Fig. 2a. We can see that each TImP behaves as a di-dentate entity and coordinates to three Fe atoms, one Fe atom is located in the center of the porphyrin unit, two *trans*-related imidazolyl groups of each porphyrin coordinate to other two Fe atoms of two adjacent porphyrin units by its N6 atoms (Fig. 2b), and the dihedral angles between the porphyrin plane and the coordinated imidazolyl plane is 58.34 °. The two uncoordinated imidazolyl groups are disordered (Fig. S2, ESI†) and these imidazolyl plane tilted to the porphyrin plane by 79.22 °. Each Fe atom is located almost at the center of the porphyrin core and coordinated by six N atoms with an octahedral geometry, in which four N atoms are from the pyrrolic units with two types of Fe–N_{py} distance, 1.984 Å and 2.000 Å, and two axial N atoms of imidazolyl which belongs to the neighboring TImP ligand with identical Fe-N_{im} distance of 1.993 Å. Thus, each Fe-TImP unit is connected to four neighboring ones: two through the Fe^{3+} center and the other two through its imidazolyl arms (Fig. 2b). Adjacent porphyrin planes are mutually tilted and the dihedral angle is 67.90 °.

As shown in Fig. 2b and 2c, the total arrangements of Fe^{3+} and TImP give infinite 2D frameworks with paddle-wheel-like pattern, which is similar to the reported Fe-TPyP structure[15] with a shorter 'paddle' depth of 13.99 Å. The adjacent layers give a ···AA··· packing sequence with the interlayer distance of 10.15 Å (Fig. 2c). Upon stacking, small parallel channels (8.97 × 5.24 Å^2, nearest atom to atom distance within the channel, Fig. 2d) were formed that propagate along the *c*-axis. However, unlike pyridyl groups of TPyP that coordinate to metal without deprotonation; N atoms of imidazolyl in this work need to depreciate to coordinate with Fe^{3+}. Each TImP ligand deprotonates four H atoms that two from the pyrrolic units and two from the coordinated imidazolyl groups to form anion frameworks together with Fe^{3+} ions. As shown in Fig. 2c and 2d, the negative charge of the frameworks is balanced by incorporation disordered $[NH_2Me_2]^+$ cations, which was formed through hydrolysis of DMF.[16] Unfortunately, but unsurprisingly, the presence of large disordered $[NH_2Me_2]^+$ cations as well as solvent water molecules in the channels leads to no accessible void space as calculated by PLATON.[17]

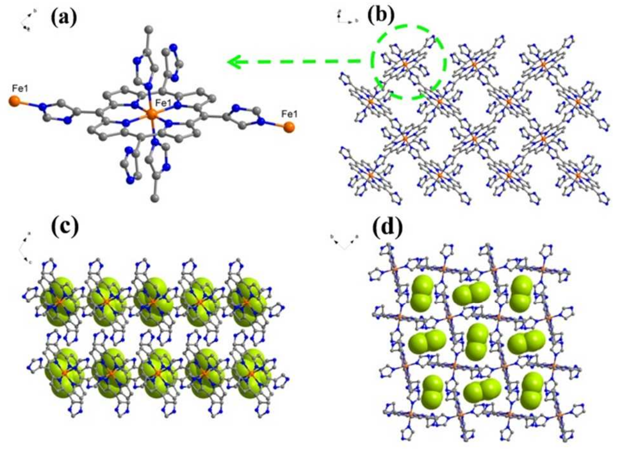

Fig. 2 (a) coordination mode of TImP and Fe^{3+} in NJNU-1; (b) the 2D lamellar network of NJNU-1; (c) packing mode of the 2D network and the presentation of the disordered $[NH_2Me_2]^+$ cations (space filling style); (d) top view of the 1D channels and disordered $[NH_2Me_2]^+$ cations trapped in these channels. Color codes: Fe, orange; N, blue; C, gray; $[NH_2Me_2]^+$ cations, light-green.

For viable applications of MOFs in industry, the chemical stability is essential as most of the chemical processes are carried out in acidic or basic conditions.[18] Unfortunately, most MOFs were unstable in acid and base or even in moist air, the chemical stability of MOFs always be an obstacle for its application. Remarkably, and as expected, NJNU-1 demonstrates ultrahigh chemical stability. At ambient conditions, NJNU-1 was placed in the open air for two months and immersed in common solvents such as chloroform, acetonitrile, dimethyl sulfoxide, methanol, benzene, boiling water, pH = 2, pH = 3, pH = 4 HCl and 5 M, 10 M, 20 M, saturated (20 °C, ~27.5 M) NaOH solutions for a week; the crystal retains its crystallinity as checked by PXRD shown in Fig. 3 (more PXRD patterns and optical microscopy images see Fig. S9 and Fig. S10, ESI†), demonstrated NJNU-1 was stable in air, common solvents and show exceptional resistance to acid and alkali solutions. It is worth noting that NJNU-1 would be the first porphyrinic MOFs that can survive in such an extensive pH ranges (from pH = 2 to saturated NaOH solution). Before this work, PCN-222 was reported can retain its structure in aqueous solutions with pH ranging from 0 to 11.[19] The strong alkali resistance of NJNU-1 is also outstanding among the reported MOFs so far, for example, Cu-imidazolate structure is found stable in 1 M NaOH,[20] ZIF-8 can retain its crystallinity after immersed in 8 M NaOH,[21] and MOP-100 is stable in 8 M KOH.[22] However, to the best of our knowledge, no MOFs that could sustain the alkalinity of saturated NaOH for a week has been reported yet.

There are two factors that contribute to the ultra-stability of NJNU-1. The first one is the strong metal-nitrogen bonds generated by metal-imidazolate networks.[14] It is believed the strength of the resulting metal-nitrogen bonds can be predicted to be closely related to the p*Ka* values for the deprotonation of the N–H bond, the higher the p*Ka* value, the stronger the metal-nitrogen bonds, which will generate more stable structures.[23, 24] From this point, we have calculated the p*Ka* value of TImP ligand (S11, ESI†) and the calculation results demonstrated that the p*Ka* values of imidazolyl groups and porphyrin macrocycle of TImP are 19.13 and 25.04, respectively, It is obvious that these p*Ka* values of TImP ligand are higher than that of 1,2,3-triazole (p*Ka* = 13.9), imidazole (p*Ka* = 18.6), and pyrazole (p*Ka* = 19.8), which are always used to generate highly stable MOFs.[23] The second one is that the high-valence metals such as Al^{3+}, Fe^{3+}, In^{3+}, Zr^{4+}, Ti^{4+} can considerably increase the chemical stability of the frameworks,[25] for previous reported Fe^{2+}-TCPP frameworks would be oxidized to an amorphous phase at room temperature.[26] Thus trivalent Fe atoms together with the higher p*Ka* value of TImP ligand result in the ultrahigh chemical stability of NJNU-1.

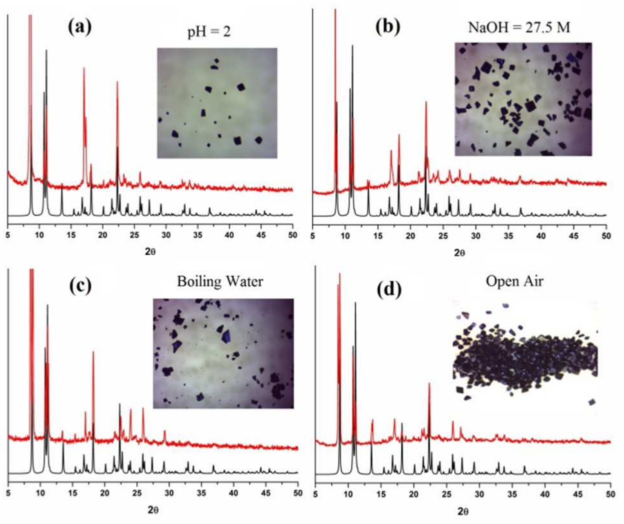

Fig. 4 Simulated (black), experimental (red) PXRD patterns and optical microscopy images of NJNU-1 at different conditions.

The phase purity of bulk NJNU-1 was confirmed by powder X-ray diffraction (PXRD) studies (Fig. S3, ESI†). The thermogravimetric analyses (Fig. S5, ESI†), solid-state UV-vis spectra (Fig. S6, ESI†) and the solid-state fluorescence spectra (Fig. S7, ESI†) of fresh NJNU-1 were also characterized, respectively (please see details in supporting information).

In summary, the two-dimensional metal-organic frameworks presented here is the first example of MOFs constructed from imidazolyl-based porphyrin ligand. The ultra-high stability of NJNU-1 indicates that the use of imidazolyl-based porphyrin

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ligand and high-valence metals would provide an opportunity to construct MOFs with ultra-high stability, and this will undoubtedly facilitate the application of MOFs. The discovery of more imidazolyl-based porphyrin MOFs with diversity structures and properties are ongoing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Procedures for the synthesis of TImP and NJNU-1, single crystal X-ray diffraction experiment, PXRD pattern, TGA, UV-Vis, FL profiles, Method and results of p*Ka* calculation, stability measurements as well as crystallographic data in CIF format. CCDC 904982. See DOI: 10.1039/b000000x/

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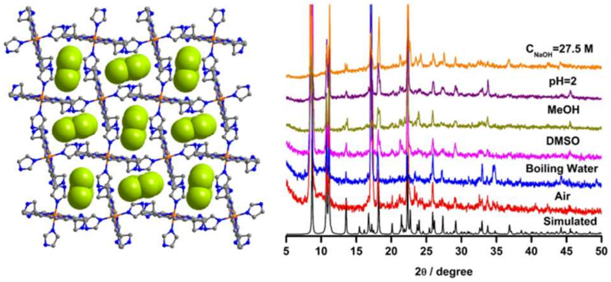
Graphic Abstract



By using a new strategy, a novel 2D MOF constructed from Fe^{3+} and imidazoyl base porphyrin ligand has ultra-high stability and it can stand in saturated (~27.5 M) NaOH solution for a week.