

Supporting Information for  
**A New Strategy to Construct Metal-Organic Frameworks with  
Ultrahigh Chemical Stability**

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## S1. Chemicals and Instrumentation.

Commercially available reagents were purchased as analytical grade and used without further purification unless otherwise stated. *meso*-tetra(4-imidazolyl)porphyrin was prepared according to the procedures that described in S2. Pyrrole was purchased from Aladdin Inc., 4-imidazolecarboxaldehyde was purchased from Sigma-Aldrich; other reagents were purchased from Sinopharm Chemical Reagent Co.,Ltd.

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-Advance diffractometer at room temperature with a Cu sealed tube ( $\lambda=1.54178 \text{ \AA}$ ) at 40 kV and 40 mA. Elemental analysis (C, H and N) was performed by Vario EL III (Elementar Analysen System GmbH). Thermogravimetry analysis (TGA) was conducted on a Perkin-Elmer Diamond TG/DTA instrument. Fourier transform infrared spectra (FT-IR) were recorded as KBr pellets on a Bruker Tensor 27 FT-IR spectrometer in the range of 4000 to 400  $\text{cm}^{-1}$ . Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) data were collected on Bruker Avance 400 Spectrometer and the chemical shifts were reported relative to the internal standard TMS (0 ppm). The UV-visible spectra were recorded on Varian Cary 5000 UV-Vis-NIR Spectrophotometer; fluorescence spectra was acquired using a Perkin-Elmer LS-50B Fluorescence spectrometer.

## S2. Synthesis of *meso*-tetra(4-imidazolyl)porphyrin.

*meso*-tetra(4-imidazolyl)porphyrin was prepared according to the method described as below. Typically, 200 mL of propionic acid, 0.35 g of 4-imidazolecarboxaldehyde and 0.80 mL of freshly distilled pyrrole were added into a 250 mL round-bottomed flask. The solution was refluxed at 105 °C for 30 minutes under vigorous stirring. After the resulting solution cooled to room temperature, silica gel column chromatography was used for purification. ~150 mL  $\text{CHCl}_3$  was firstly used to elute the mixture and then anhydrous ethanol was used as eluent. The dark-pink liquid was collected and filtered with a millipore filter. Then the collection was concentrated and dried at 150 °C for 5 hours, dark-purple powder of *meso*-tetra(4-imidazolyl)porphyrin was obtained. Yield: ~110 mg, 13.8%. Elemental Analysis, Found: C, 65.24; H, 4.31; N, 28.91 %. Anal. Calcd for  $\text{C}_{32}\text{H}_{22}\text{N}_{12}\cdot\text{H}_2\text{O}$ : C, 64.86; H, 4.05; N, 28.38 %,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 25 °C):  $\delta$ , ppm -2.70 (s, 2H), 7.97 (s, 4H), 8.26 (s, 4H), 9.25 (s, 8H), 12.91 (s, 4H). FT-IR (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu$  = 3450 (s), 2920 (w), 2850 (w),

1640 (m), 1550 (w), 1470 (w), 1410 (w), 1380 (w), 1300 (w), 1080 (w), 947 (w), 621 (w).

### S3. Synthesis of NJNU-1.

Ferrocene was selected as Fe source to synthesis NJNU-1. *meso*-tetra(4-imidazolyl)porphyrin (28.8 mg, 0.05 mmol) and ferrocene (9.3 mg, 0.05 mmol) were added into *N,N*-dimethylformamide (DMF, 14 mL) in a small capped vial and sonicated for ten minutes for dissolution. 0.5 mL deionized water was added into the above solution afterward, further sonication for ten minutes. The vial was placed into a Teflon lined acid-digestion bomb and heated at 125 °C for five days, then it was allowed to cool to room temperature naturally. Small dark-purple crystals (0.1×0.1×0.02 mm, Fig. S1) were obtained followed by washing several times with DMF, ethanol and anhydrous ether, respectively. Yield: ~6 mg (34.8 %, based on porphyrin). Anal. Calcd for C<sub>34</sub>H<sub>28</sub>FeN<sub>13</sub>O·2H<sub>2</sub>O: C, 56.16; H, 4.41; N, 25.05 %, Found: C, 56.22; H, 4.23; N, 25.17 %. FT-IR (KBr pellet, cm<sup>-1</sup>):  $\nu = 3446(s), 2925(w), 1652(m), 1436(w), 1384(w), 1255(w), 1199(w), 1110(m), 1102(w), 968(m), 827(w), 794(w), 711(w), 653(w)$ .

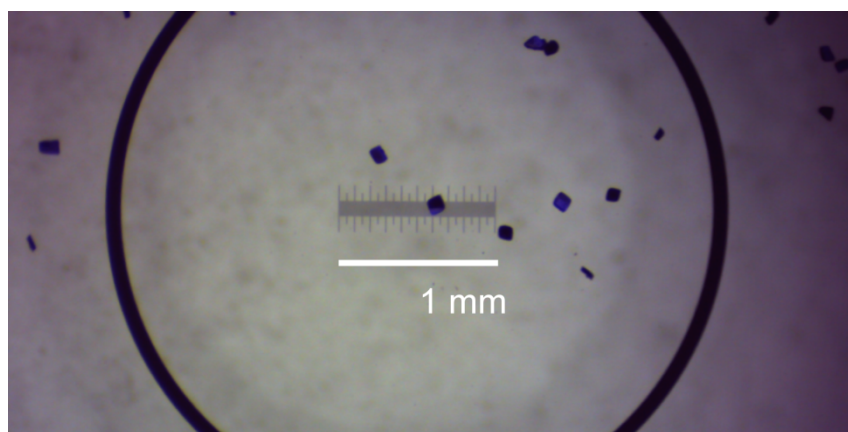


Fig. S1 Optical microscopy image of the obtained small crystals of NJNU-1.

### S4. Crystallography.

Diffraction measurement were carried out on a Bruker Smart APEX II CCD with with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using  $\omega$ -2 $\theta$  scan method, a long X-ray exposure time of 25 s/frame was required due to the weak diffraction. The single crystal of NJNU-1 was chosen onto a thin glass fiber by epoxy glue in air for

data collection. Data reductions and absorption corrections were performed using the SAINT and SADABS programs,<sup>1</sup> respectively. All structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on  $F^2$  using the SHELXL-97 program.<sup>2</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in geometrically calculated positions.

Crystallographic data for NJNU-1 described in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC-904982. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

**S5.** Illustration of the two disordered uncoordinated imidazolyl groups.

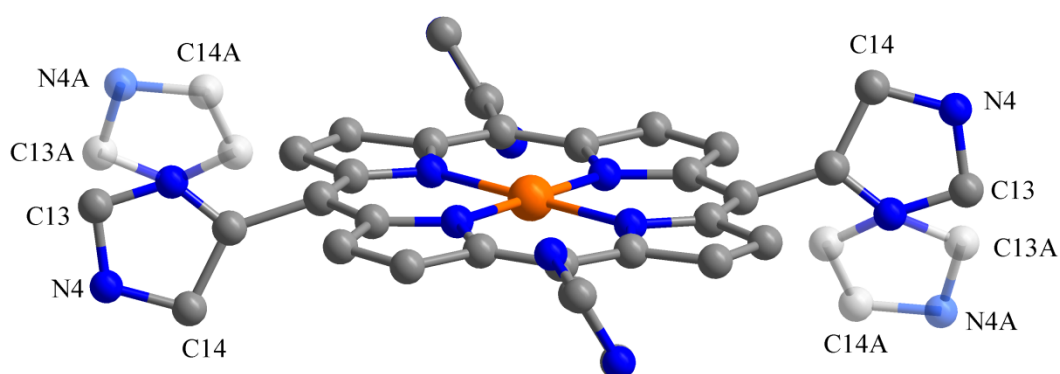


Fig. S2 Illustration of the two disordered uncoordinated imidazolyl groups, hydrogen atoms are omitted for clarity.

S6. Simulated and as-synthesized PXRD patterns of NJNU-1.

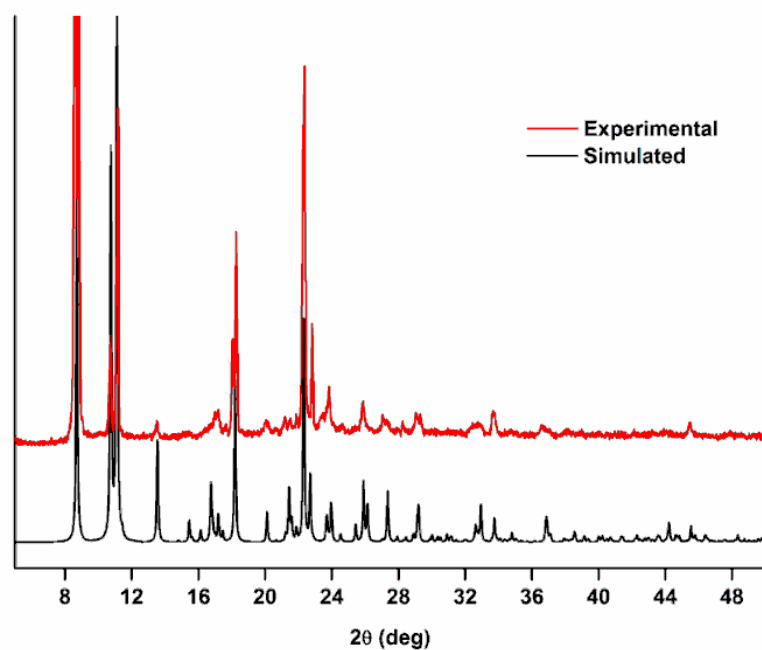


Fig. S3 PXRD patterns of NJNU-1 simulated and as-synthesized.

S7. FT-IR spectroscopy of NJNU-1 and TImP.

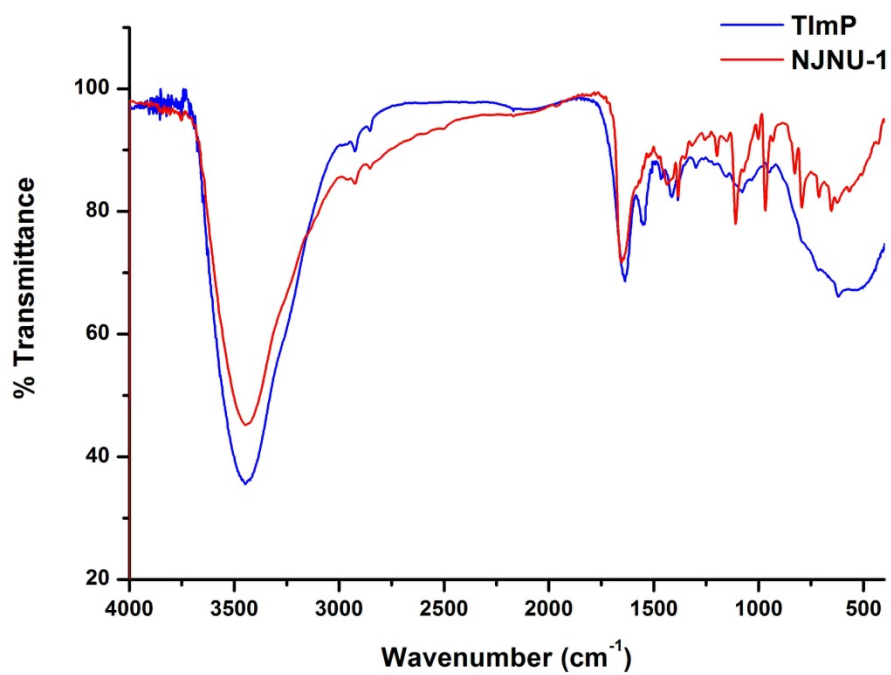


Fig. S4 FT-IR spectroscopy of NJNU-1 and TImP on KBr pellets.

### S8. TGA profile of NJNU-1.

Thermogravimetric analyses (TGA) of fresh NJNU-1 were conducted to examine the thermal stability of the structure. The first weight loss of  $\sim 7.2\%$  (calcd  $7.4\%$ ) from room temperature to *ca.*  $150\text{ }^{\circ}\text{C}$  corresponding to release of three  $\text{H}_2\text{O}$  molecules that trapped in the crystal pores and absorbed on the crystal surfaces. Successive  $\sim 9.5\%$  and  $\sim 8.9\%$  weight losses in the ranges  $165\text{--}280\text{ }^{\circ}\text{C}$  and  $420\text{--}550\text{ }^{\circ}\text{C}$ , followed by  $\sim 18.0\%$  weight loss up to  $900\text{ }^{\circ}\text{C}$  were attributed to lose one, one (calcd  $9.4\%$ ), two (calcd  $18.7\%$ ) imidazolyl groups, respectively. No obvious weight loss was observed after  $900\text{ }^{\circ}\text{C}$  from the TGA profile.

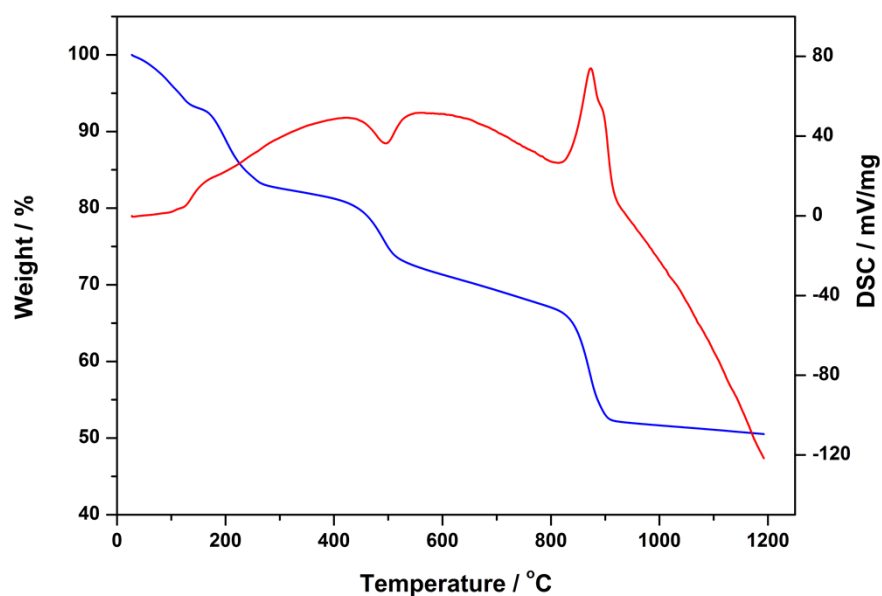


Fig. S5 TGA profile of NJNU-1 measured from room temperature to  $1200\text{ }^{\circ}\text{C}$  at a ramp rate of  $10\text{ }^{\circ}\text{C} / \text{min}$  under  $\text{N}_2$  with  $100\text{ mL} / \text{min}$  flow speed.

**S9.** Solid-state UV-vis spectra of TImP and NJNU-1.

In solid-state UV-vis spectra, TImP show one intense Soret band at 379 nm and four Q bands at *ca.* 523, 567, 601, 658 nm, NJNU-1 show Soret band at 384 nm and two Q bands at 560 nm and 594 nm. Compared with TImP, the slight red shift of the Soret band and reduction of Q bands from four to two of NJNU-1 was in good agreement with literatures.<sup>3, 4</sup>

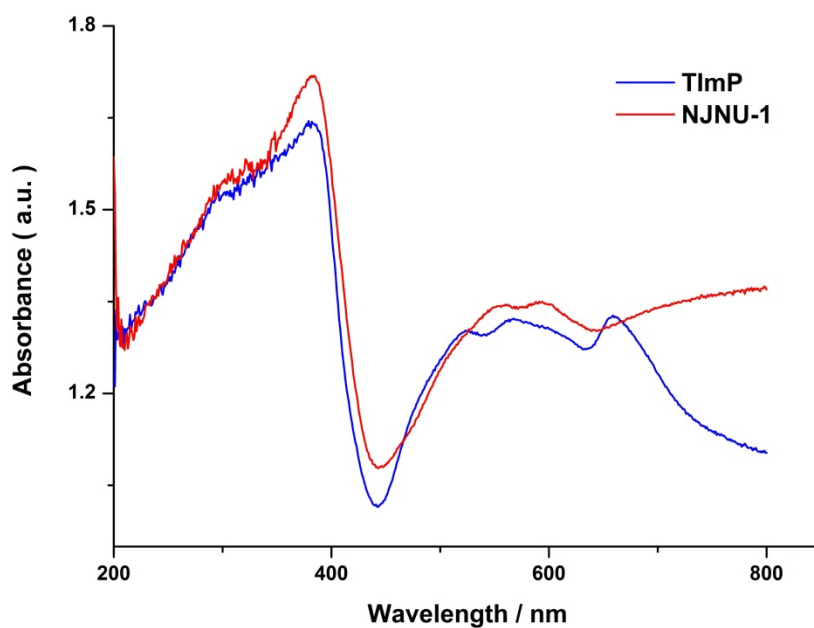


Fig. S6 Solid-state UV-vis spectra of TImP and NJNU-1.

### S10. Solid-state fluorescence emission spectra of NJNU-1 and TImP.

Upon excitation at 280 nm, TImP displays a main emission band at 428 nm and a weaker band at 482 nm in the solid-state fluorescence spectra, while NJNU-1 show a broad emission band located at 394 nm, which was due to the intra-ligand  $\pi$ - $\pi^*$  or  $\pi$ - $n^*$  transitions.<sup>5</sup> Compared to TImP, the main emission band of NJNU-1 was 34 nm blue shifted that can be ascribed to the metalation of porphyrins.<sup>5-7</sup>

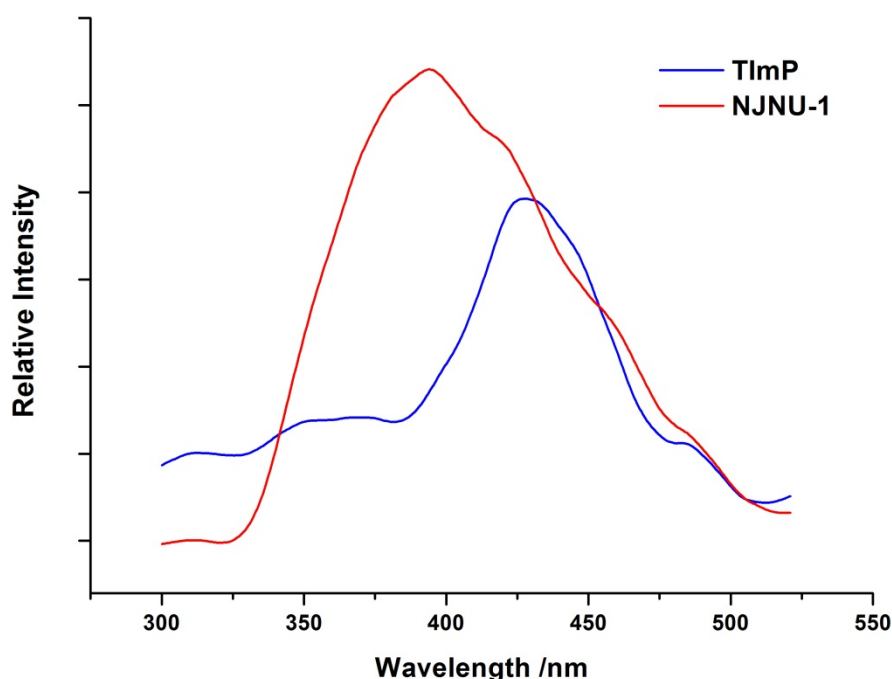
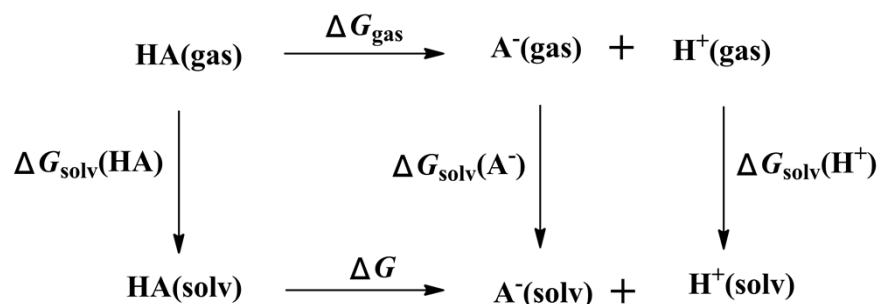


Fig. S7 Solid-state emission spectra of NJNU-1 and TImP ( $\lambda_{\text{ex}} = 280$  nm).

### S11. Method and results of $pK_a$ calculation of TImP.

All calculations were performed with Gaussian 09 package.<sup>8</sup> A full structure optimization for both neutral and anionic species in gas phase were carried out at the DFT B3LYP/6-31+G(d, p) level of theory. All calculated structures were true minima, *i.e.*, no imaginary frequencies were observed. Solvation Gibbs energies ( $\Delta G_{\text{solv}}$ ) in water were obtained using SMD developed by the Truhlar/Cramer group,<sup>9</sup> which is recommended choice for computing  $\Delta G_{\text{solv}}$  in Gaussian 09. The calculation of  $pK_a$  values usually employ some thermodynamic cycles.<sup>10, 11</sup> Here we applied a standard thermodynamic cycle named Born-Haber cycle as reported method (scheme below and equations 1-5).<sup>12, 13</sup>





$$pK_a = \Delta G / 2.303 RT \quad 1$$

$$\Delta G = \Delta G_{\text{gas}} + \Delta G_{\text{solv}}(\text{A}^{-}) + \Delta G_{\text{solv}}(\text{H}^{+}) - \Delta G_{\text{solv}}(\text{HA}) \quad 2$$

$$\Delta G_{\text{gas}} = G_{\text{gas}}(\text{A}^{-}) + G_{\text{gas}}(\text{H}^{+}) - G_{\text{gas}}(\text{HA}) \quad 3$$

$$\Delta G_{\text{gas}}(1 \text{ M}) = \Delta G_{\text{gas}}(1 \text{ atm}) + RT \ln(24.46) \quad 4$$

$$pK_a = [G_{\text{gas}}(\text{A}^{-}) - G_{\text{gas}}(\text{HA}) + \Delta G_{\text{solv}}(\text{A}^{-}) - \Delta G_{\text{solv}}(\text{HA}) - 268.38] / 1.364 \quad 5$$

$\Delta G_{\text{gas}}(\text{H}^{+}) = -6.28 \text{ kcal mol}^{-1}$  and  $\Delta G_{\text{solv}}(\text{H}^{+}) = -264.0 \text{ kcal mol}^{-1}$  that derived from experiment were used in our calculations.<sup>14</sup> Converting the  $\Delta G_{\text{gas}}$  reference state (22.46 L at 298.25 K) from 1 atm to 1 M is accomplished using equation 4. Based on equations 1-4, the  $pK_a$  values using the thermodynamic cycle are derived as shown in equation 5.<sup>12</sup>

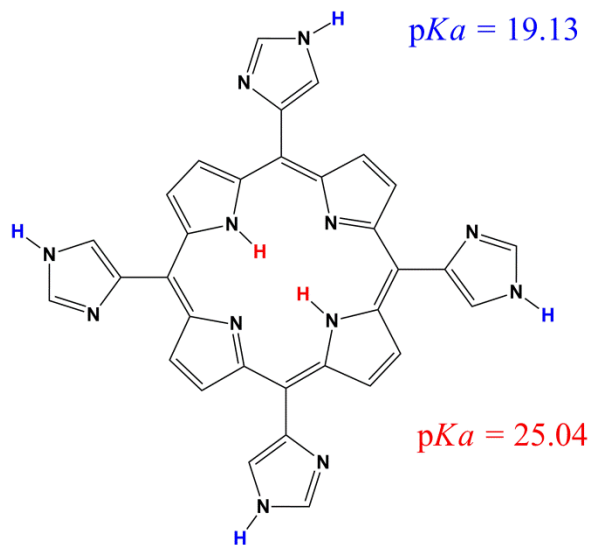


Fig. S8 calculated  $pK_a$  values of TImP ligand.

**S12.** Stability measurements and PXRD patterns, optical microscopy images of NJNU-1 at different conditions.

Acidic solutions (pH = 2, pH = 3, pH = 4) and alkaline solutions ( $C_{\text{NaOH}} = 5 \text{ M}, 10 \text{ M}, 20 \text{ M}, \sim 27.5 \text{ M}$ ) were firstly prepared. Then about 20 mg of sample was soaked in the acidic or alkaline solutions and different organic solutions as well as boiling water for a week. After that, all the samples were filtered and washed with ethanol and anhydrous ether. For the sample in open air, about 20 mg of sample was put in a small beaker and put this beaker in ventilation place for two months. Then samples were taken pictures. After that, PXRD measurement was performed to check the structural stability of all samples.

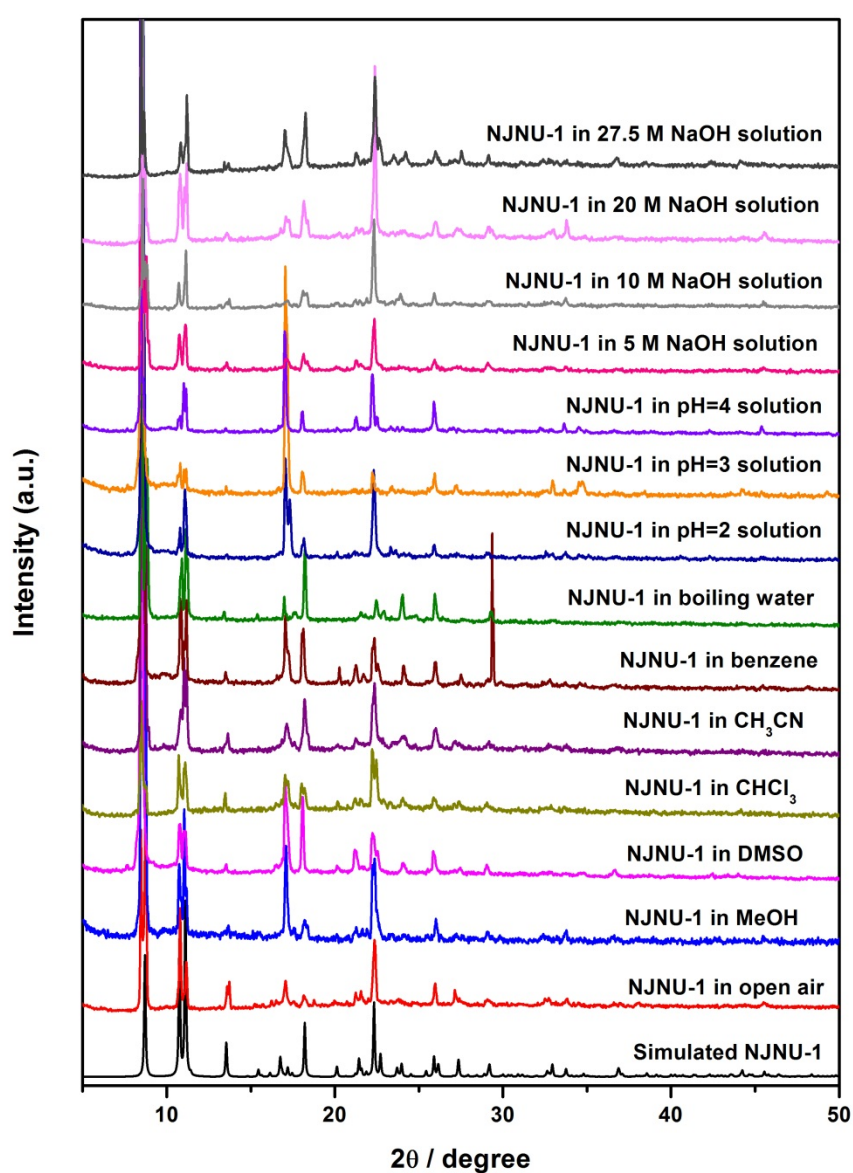


Fig. S9 PXRD patterns of NJNU-1 in different concentrations of HCl, NaOH,

different solvents for a week and open air for two months.

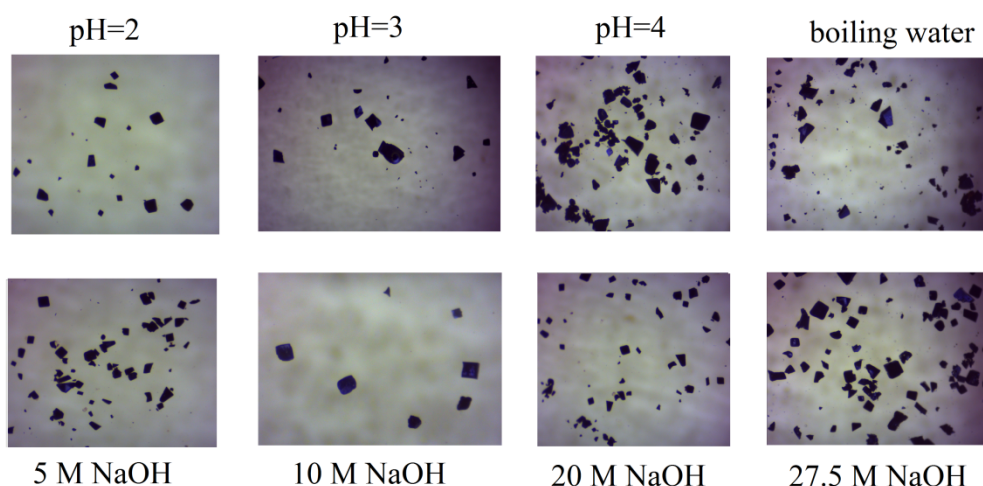


Fig. S10 Optical microscopy images of NJNU-1 in pH = 2, pH = 3, pH = 4 HCl solutions, 5 M, 10 M, 20 M, saturated ( 20 °C, ~27.5 M ) NaOH solutions and boiling water after a week.

### S13 Tables of crystal data, selected bond length and angle for NJNU-1.

Table S1. Crystal data and structure refinements for NJNU-1.

NJNU-1	
Empirical formula	C <sub>34</sub> H <sub>27</sub> Fe N <sub>13</sub> O
Formula weight	689.54
Temperature	110(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions	a = 11.734(5) Å α = 90 ° b = 11.967(5) Å β = 114.528(7) ° c = 12.461(5) Å γ = 90 °
Volume	1591.9(12) Å <sup>3</sup>
Z	2
Calculated density (mg/m <sup>3</sup> )	1.439
Absorption coefficient (mm <sup>-1</sup> )	0.526
F(000)	712
Crystal size (mm)	0.16 x 0.14 x 0.05
Theta range for data collection (°)	2.01 to 25.02
Reflections collected / unique	11638 / 2767 [ <i>R</i> (int) = 0.0764]
Completeness to theta = 25.02	98.6 %
Max. and min. transmission	0.9396 and 0.9206
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2767 / 133 / 277
Goodness-of-fit on <i>F</i> <sup>2</sup> , <i>S</i>	1.052
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0886, <i>wR</i> <sub>2</sub> = 0.2324
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1352, <i>wR</i> <sub>2</sub> = 0.2635
Largest diff. peak and hole	0.814 and -0.618 e.Å <sup>3</sup>

$$R_1 = \frac{\sum(F_o - F_c)}{\sum F_o}, wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Table S2. Selected bond lengths (Å) and angles (°) for NJNU-1.

Fe(1)-N(2)	1.984(4)	Fe(1)-N(1)#1	2.000(3)
Fe(1)-N(2)#1	1.984(4)	Fe(1)-N(1)	2.000(3)
Fe(1)-N(6)#2	1.993(3)	N(6)-Fe(1)#4	1.993(3)
Fe(1)-N(6)#3	1.993(3)		
N(2)-Fe(1)-N(2)#1	180.0	N(6)#2-Fe(1)-N(1)#1	90.93(13)
N(2)-Fe(1)-N(6)#2	91.38(13)	N(6)#3-Fe(1)-N(1)#1	89.07(13)
N(2)#1-Fe(1)-N(6)#2	88.62(13)	N(2)-Fe(1)-N(1)	89.58(14)
N(2)-Fe(1)-N(6)#3	88.62(13)	N(2)#1-Fe(1)-N(1)	90.42(14)
N(2)#1-Fe(1)-N(6)#3	91.38(13)	N(6)#2-Fe(1)-N(1)	89.07(13)
N(6)#2-Fe(1)-N(6)#3	180.000(1)	N(6)#3-Fe(1)-N(1)	90.93(13)
N(2)-Fe(1)-N(1)#1	90.42(14)	N(1)#1-Fe(1)-N(1)	180.0
N(2)#1-Fe(1)-N(1)#1	89.58(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+1/2,y+1/2,-z+1/2; #3 x+1/2,-y+1/2,z+1/2; #4 -x+1/2,y-1/2,-z+1/2; #5 -x,-y+1,-z

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