Supporting Information

Two Novel MOF-74 Analogs Exhibiting Unique Luminescent Selectivity

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Section 1. Materials and Instrumentation.

All reagents and solvents were used as received from commercial suppliers without further purification. (E)-3-(2-hydroxyl-phenyl)-acrylic acid, (E)-3-(3-hydroxyl-phenyl)-acrylic acid and 4,4'-pyridine were purchased from the company of Alfa Aesar China (Tianjin). Organic solvents with analytical purity were supplied by commercial sources and used as received. Elemental analyses (C, H, N) were performed on a Flash EA1112 microanalyzer at the Beijing Institute of Technology. FT-IR spectrum is recorded in the Nicolet-360 FT-IR spectrometer as KBr pellets in the 4000–400 cm⁻¹ region. The UV-vis absorption spectra were examined on a JASCO UV-1901 spectrophotometer in the wavelength range of 200–800 nm. The photoluminescence (PL) spectra were recorded by using a Hitachi F-7000 luminescence spectrophotometer equipped with a 450 W xenon lamp as the excitation source, and the measurements were performed at room temperature. The photomultiplier tube voltage was 700 V, the scan speed was 12000 mm/min, and the slit width was 2.5 nm. Thermo-gravimetric analysis (TGA) were carried out on a SEIKO TG/DTA 6200 thermal analyzer from room temperature to 1000 °C at a ramp rate of 10 °C/min in a flowing 150 mL/min nitrogen atmosphere. X-ray powder diffraction (XPRD) of samples were measured using a Japan Rigaku D/max γ A X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 0.154060 nm). Nitrogen adsorption experiments and micropore analysis were conducted at 77K using a TriStarII3020 (Micromeritics Instrument Corporation) apparatus. Before adsorption measurements, the samples were degassed in vacuum at 333K for 2h and 403K for 6h. The specific surface areas (SSAs) of the freeze-dried samples were calculated by Brunauer Emmett Teller (BET) analyses of their adsorption isotherms.

Section 2. Synthesis of compounds 1, 2, 1−Solvents and 2−Solvents.

Synthesis of [(Zn(OCA−OH)₂(4,4'-bipy)₀.₅]·1.₆₇H₂O (1). A mixture of OCA-OH (0.025g, 0.15mmol) and triethlamine (15.1mg, 0.15 mmol) was dissolved in methanol solution (6 mL) to bring the pH of the solution to about 7 with constantly stirring for thirty minutes and then a methanol solution (6 mL) of Zn(ClO₄)₂·6H₂O (0.027g, 0.075mmol) was added whilst stirring. To this solution 4-4'-bipyridine (7.8 mg, 0.05 mmol) in Dimethyl sulfoxide solution (1mL) was added with stirring for 30 minutes. The result solution was then filtered and left at ambient condition for three days and the colorless prism single crystals suitable for X-ray diffraction were obtained with the yield of 63% based on Zn(ClO₄)₂·6H₂O. Anal. Caled for C₂₅H₂₁.₃₃NZnO₇.₆₇: C, 55.23; H, 4.30; N, 2.80. Found: C, 55.86; H, 4.13; N, 2.99.

Synthesis of [(Zn(MCA−OH)₂(4,4'-bipy)₀.₅]·0.₅CH₃OH·H₂O (2). A solution of Zn(ClO₄)₂·6H₂O (0.054g, 0.15mmol) in CH₃OH (6ml) was added to the solution of (E)-3-(3-hydroxyl-phenyl)-acrylic acid (MCA-OH) (0.049g, 0.30mmol)in CH₃OH (6ml) adjusted with triethylamine(0.30mmol) to pH ≈ 7 with constantly stirring for thirty minutes. Then, a solution of 4,4'-bipyridine(0.015g, 0.10mmol) was added to the mixture with constantly stirring for fifteen minutes. The result solution was then filtered and left at room temperature. The single crystals (colorless prisms)
suitable for X-ray diffraction were obtained by slow evaporation for three days and washed with CH$_3$OH several times to give [Zn(MCA−OH)$_2$(4,4'-bipy)$_0.5$]·0.5CH$_3$OH·H$_2$O, yield 75%. Anal. Calcd for C$_{23.5}$H$_{22}$N$_2$ZnO$_7.5$: C, 55.98; H, 4.40; N, 2.78. Found: C, 57.05; H, 3.83; N, 2.94.

Synthesis of 1$\supset$Solvents and 2$\supset$Solvents. In a Pyrex reaction tube, dried complex 1 (30mg) was prepared by evacuation at 60 °C for 2 h, and then 130 °C for 5 h; subsequently, it was immersed in CH$_3$CN (1 ml) at room temperature. After excess CH$_3$CN was completely removed by evacuation at room temperature for 5 h, the reaction tube was filled with nitrogen. 1$\supset$CH$_3$OH, 1$\supset$CH$_3$CH$_2$OH, 1$\supset$acetone, 1$\supset$CH$_2$Cl$_2$, 1$\supset$H$_2$O, 1$\supset$THF, 1$\supset$cyclohexane, 2$\supset$CH$_3$CN, 2$\supset$CH$_3$OH, 2$\supset$CH$_3$CH$_2$OH, 2$\supset$acetone, 2$\supset$CH$_2$Cl$_2$, 2$\supset$H$_2$O, 2$\supset$THF, 2$\supset$cyclohexane, 2$\supset$C$_6$H$_6$, 2$\supset$C$_6$H$_5$CH$_3$, 2$\supset$C$_6$H$_5$I and 2$\supset$C$_6$H$_6$NO$_2$ were prepared same way by using corresponding guest solvent molecules, respectively.

Section 3. Single-crystal X-ray crystallography.

Suitable single crystals with dimensions of 0.25 × 0.07 × 0.07 mm and 0.50 × 0.14 × 0.14 mm for compounds 1 and 2 were selected for single-crystal X-ray diffraction analysis respectively. Data collection were performed on a Rigaku RAXIS-RAPID CZN diffractometer equipped with a graphite-monochromatic Mo Kα radiation (λ =0.71073 Å) using an ω scan mode for compounds 1 and 2 at 153(2) K. Unit-cell parameters were determined from automatic centering of 25 reflections and refined by a least-squares method. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques with I > 2σ(I). All refinements were performed using SHELXTL 97. The isolated solvent atom O9 and O7 are disordered to three positions (O9/O9'/O9'' and O7/O7'/O7'') in compounds 1 and 2 respectively. In compound 1, the restraint command “ISOR” was applied to the disordered O9 atom for obtaining reasonable thermal parameters. In compound 2, the restraint command “ISOR” was applied to the disordered C2, C6, C6’, C7, C7’, O7”, O8, C24 and C24’ atoms, and the restraint command “EADP” is applied to the disordered O4, O4’, C7, C7’, C24 and C24’ atoms for obtaining reasonable thermal parameters. The bond distance restraint command “DFIX” is applied to the bonds C24−O8, C24’−O8, C7−C8 and C7’−O8 for obtaining reasonable bond distances. In compound 2, the two MCA-OH ligands are each equally disordered over two orientations, the refined occupancies have values 0.502(7) and 0.498(7) which do not differ from an exact 0.5 value. It is acceptable to only refine half-occupancy O and C atoms isotropically. CCDC-890826 (1) and CCDC-890827 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Section 4. Experiment of Photoluminescence (PL) investigations.

The fluorescence properties of compounds 1, 2, 1a and 2a in the solid state, and those of
desolvated 1 and 2 in various solvent emulsions (designated as 1a-solvent and 2a-solvent respectively) were investigated at room temperature. Desolvated 1 and 2 were prepared as follows: after immersed in CH$_3$OH for 3 days, the sample was evacuated at 60 °C for 1 h and then 120 °C for over 3 h. The 1a-solvent and 2a-solvent emulsions were prepared by introducing 1.0 mg of 1a-solvent and 2a-solvent fine powder into 50 mL of MeOH, EtOH, CH$_3$CN, CH$_2$Cl$_2$, DMF, DMSO, THF, distilled water, acetone, or cyclohexane respectively. After sonication treatment, aging for over 24 h and shaking, the fluorescence spectra were measured. For sensing properties with respect to solvents, desired amounts of desolvated-1 emulsion in distilled water (0.4 mg of fine powder of desolvated-1 in 10 mL of distilled water) were added into a certain requirement amount of desolvated-1 emulsion in acetone (0.4 mg of fine powder of desolvated-1 in 10 mL of acetone), and desired amounts of desolvated-2 emulsion in distilled water (0.4 mg of fine powder of desolvated-2 in 10 mL of distilled water) were added into a standard desolvated-2 emulsion in acetonitrile (0.4 mg of fine powder of desolvated-2 in 10 mL of acetonitrile). The photoluminescence spectra were investigated after sonication treatment, one-day aging and shaking vigorously before testing.

For further detecting the sensing properties with respect to solvents, desired amounts of desolvated-1 emulsion in DMSO (0.4 mg of fine powder of desolvated-1 in 10 mL of DMSO) were added into a certain requirement amount of desolvated-1 emulsion in acetone (0.4 mg of fine powder of desolvated-1 in 10 mL of acetone), and desired amounts of desolvated-1 emulsion in distilled water (0.4 mg of fine powder of desolvated-1 in 10 mL of distilled water) were added into a standard desolvated-1 emulsion in methanol (0.4 mg of fine powder of desolvated-2 in 10 mL of methanol). The photoluminescence spectra were investigated after sonication treatment, one-day aging and shaking vigorously before testing.

To detect luminescence diminishment properties of acetone to 1a, a small amount of acetone were added into a certain requirement amount of desolvated-1 emulsion in DMSO and H$_2$O (0.4 mg of fine powder of desolvated-1 in 10 mL of DMSO and H$_2$O respectively). The photoluminescence spectra were investigated after shaking vigorously.

To detect the solid-state PL properties of guest-free framework 2a upon immersing to the two different categories of aromatic compounds, namely, compounds containing electron-withdrawing groups such as nitroaromatics (group A) and those having electron-donating groups such as CH$_3$ (group B), the fine powder of 2=S$_6$H$_6$, 2=S$_6$H$_6$CH$_3$, 2=S$_6$H$_6$I and 2=S$_6$H$_6$NO$_2$ with the same amount and similar particle size (the good agreement of the XRPD patterns in intensity and position demonstrates that these powder have similar particle size) were investigated at room temperature.

Luminescence control experiments were done in different small solvent molecules by using the ligands (OCA-OH+4,4′-bipy and MCA-OH+4,4′-bipy), ligands+metals (OCA-OH+4,4′-bipy+Zn(ClO$_4$)$_2$$\cdot$$\delta$H$_2$O and MCA-OH+4,4′-bipy+Zn(ClO$_4$)$_2$$\cdot$$\delta$H$_2$O) to compare with the emission properties of MOF-desolvated (Zn-OCA-MOF-desolvated (1a) and Zn-MCA-MOF-desolvated
(2a)) at the same concentration, to see the solvent effect on these different systems.

Section 5. Crystal Data and Selected Bond Distances and Angles of 1 and 2.

Table S1 Crystal Data and Structure Refinement of Compounds 1 and 2.

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<thead>
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<th>Compounds</th>
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<th>2</th>
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<tr>
<td>Formula</td>
<td>C_{23}H_{21.33}NO_{7.67}Zn</td>
<td>C_{23.5}H_{22}NO_{7.5}Zn</td>
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<tr>
<td>Fw</td>
<td>499.78</td>
<td>503.79</td>
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<tr>
<td>T(K)</td>
<td>153(2)</td>
<td>93(2)</td>
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<td>Wavelength (Å)</td>
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<td>0.71073</td>
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<td>Crystal system</td>
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<td>Rhombohedral</td>
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<td>Space group</td>
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<td>R-3</td>
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<td>a (Å)</td>
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<td>31.8565(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>31.864(5)</td>
<td>31.8565(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.846(3)</td>
<td>12.6269(6)</td>
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<td>90.00</td>
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<td>β (°)</td>
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<td>90.00</td>
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<td>120.00</td>
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<td>11097.5(7)</td>
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<td>18</td>
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<td>(\rho) (calculated)/g·cm(^{-3})</td>
<td>1.322</td>
<td>1.346</td>
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<td>(\mu) (Mo-K(\alpha))/mm(^{-1})</td>
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<td>(F(000))</td>
<td>4632</td>
<td>4608</td>
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<td>θ Range /°</td>
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<td>3.11 – 25.02</td>
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<td>Reflns collected</td>
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<td>Independent reflns</td>
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<td>Obsd data [I&gt;2σ(I)]</td>
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<td>4123</td>
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<tr>
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<td>4319 / 59 / 387</td>
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<td>GOF on (F^2)</td>
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<td>1.083</td>
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<tr>
<td>R1, wR2 [I &gt; 2σ(I)]</td>
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<td>R1, wR2 (all data)</td>
<td>0.0708, 0.1585</td>
<td>0.0829, 0.1870</td>
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<td>(\Delta\rho_{\text{max}}, \text{min}/\text{eÅ}^{-3})</td>
<td>1.007, -0.490</td>
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Table S2 Selected Bond Distances (Å) and Angles (deg) for 1

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<th>Bond</th>
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<td>Zn(1)-O(1)</td>
<td>1.949(3)</td>
<td>1.980(3)</td>
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<tr>
<td>Zn(1)-O(3)</td>
<td>1.953(3)</td>
<td>2.052(3)</td>
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<tr>
<td>C(19)-N(1)-Zn(1)</td>
<td>121.2(3)</td>
<td>121.3(3)</td>
</tr>
<tr>
<td>C(1)-O(1)-Zn(1)</td>
<td>116.9(3)</td>
<td>136.7(3)</td>
</tr>
<tr>
<td>C(10)-O(3)-Zn(1)</td>
<td>108.9(3)</td>
<td>128.29(12)</td>
</tr>
<tr>
<td>O(1)-Zn(1)-O(2)</td>
<td>96.05(12)</td>
<td>118.41(12)</td>
</tr>
<tr>
<td>O(1)-Zn(1)-N(1)</td>
<td>113.65(13)</td>
<td>97.94(13)</td>
</tr>
<tr>
<td>O(2)-Zn(1)-N(1)</td>
<td>99.88(13)</td>
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#3 Symmetry code: -x+y-1/3,-x+1/3,z+1/3

Table S3 Selected Bond Distances (Å) and Angles (deg) for 2

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<tr>
<th>Bond/Angle</th>
<th>Distance (Å)</th>
<th>Angle (deg)</th>
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<td>Zn(1)-O(5)</td>
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<td>Zn(1)-O(2)</td>
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<tr>
<td>Zn(1)-O(6')</td>
<td>2.122(4)</td>
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<td>O(3)#1-Zn(1)</td>
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<td>O(2)-Zn(1)-N(1)</td>
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<td>O(3)#1-Zn(1)-O(6')</td>
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<td>C(9)-O(2)-Zn(1)</td>
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<tr>
<td>C(23)-N(1)-Zn(1)</td>
<td>122.0(4)</td>
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#1 Symmetry code: -y+2/3,x-y-2/3,z+1/3   #2 Symmetry code: -x+y+4/3,-x+2/3,z-1/3

Section 6. Structural Information for 1 and 2.

Scheme S1. Lengths of 4,4'-bipy and mono-dentate OCA–OH and MCA–OH ligands in compounds 1 and 2.

Figure S1. View of the coordination environments of Zn and ligands in (a) 1 and (b) 2.
Figure S2. View of (a) the 3D network in 1 along c-axis. The different helical chains are highlighted with violet and plum, respectively. (b) View of the 1D left-hand helical chain formed by Zn(II), 4,4'-bipy and OCA-OH ligands in 1, and (c) the 1D extended chain of Zn(II) ions, and (d) the polyhedral presentation of 1D extended chain of Zn(II) ions, and (e) the left-hand helical presentation in 1. (f) View of the 1D right-hand helical chain formed by Zn(II), 4,4'-bipy and OCA-OH ligands in 1, and (g) the 1D extended chain of Zn(II) ions, and (h) the polyhedral presentation of 1D extended chain of Zn(II) ions, and (i) the right-hand helical presentation in 1. H atoms have been omitted for clarity.
**Figure S3.** View of the 1D channel presented in (a) 1 which was filled with H$_2$O solvent molecules. (b) View of the sandwich structure formed by OH groups which showing a chair-shaped configuration and free H$_2$O molecules in the 1D channel of 1. (c) View of the space-filling picture of H$_2$O solvent molecules (red) and OH groups (dark red) along $b+40^\circ$ in the 1D channel of 1. For clarity, the only position was kept for the disordered O atom of H$_2$O solvent molecules.

**Figure S4.** View of the 1D channel presented in (a) 2 which was filled with H$_2$O and CH$_3$OH solvent molecules. (b) View of the sandwich structure formed by OH groups which showing a chair-shaped configuration and free H$_2$O and CH$_3$OH molecules in the 1D channel of 2. (c) View of the space-filling picture of H$_2$O and CH$_3$OH solvent molecules (O, red; C, olive green) and OH groups (dark red) along $b+30^\circ$ in the 1D channel of 2. For clarity, the only position was kept for the disordered MCA-OH ligand and O atoms of H$_2$O solvent molecules.
Figure S5. A view showing the different size of 9.7508 Å (a) and 8.9004 Å (b) surrounded by OH groups, and the different dextral (b) and levorotary (d) propeller shape of the H$_2$O and H$_2$O, CH$_3$OH solvent molecules in the 1D channel of 1 and 2 respectively.

Figure S6. View of the 3D network of 2 along c-axis. The different helical chains are highlighted with teal (right-hand) and light blue (left-hand), respectively. For clarity, the only position was kept for the disordered MCA-OH ligands.
Section 7. IR spectrum, TGA Curves and PXRD patterns for 1 and 2.

Figure S7. IR spectra for (a) as-synthesized 1 and desolvated-1, and (b) as-synthesized 2 and desolvated-2.
Figure S8. TG curves for compounds 1 and 2.

Figure S9. Powder XRD profiles of simulated 1, experimental 1, desolvated-1, simulated 2, experimental 2 and desolvated-2.
Figure S10. Powder XRD profiles of (a) simulated 1, (b) experimental 1, (c) desolvated-1 for fluorescence examination and desolvated-1 immersed in different solvents for 2 days: (d) acetone, (e) cyclohexane, (f) EtOH, (g) THF, (h) CH₂Cl₂, (i) CH₃CN, (j) CH₃OH, and (k) H₂O.

Figure S11. Powder XRD profiles of (a) simulated 2, (b) experimental 2, (c) desolvated-2 for fluorescence examination and desolvated-2 immersed in different solvents for 2 days: (d) CH₃CN, (e) THF, (f) CH₃OH, (g) EtOH, (h) acetone, (i) CH₂Cl₂, (j) cyclohexane, and (k) H₂O.
**Figure S12.** Powder XRD profiles of (a) simulated 2, (b) experimental 2, (c) desolvated-2 for solid-state fluorescence examination and desolvated-2 immersed in different solvents for 2 days: (d) C₆H₆ (benzene), (e) C₆H₅CH₃ (toluene), (f) C₆H₅I (iodobenzene), and (g) C₆H₅NO₂ (nitrobenzene).

**Section 8.** UV-vis and PL spectra of 1 and 2.

**Figure S13.** UV-vis spectra of compound 1 introduced into various pure solvents.
Figure S14. UV-vis spectra of compound 2 introduced into various pure solvents.

Figure S15. The PL spectra of 1a methanol emulsion in the presence of various amounts of H₂O under λₑₓ = 286 nm.
Figure S16. The PL spectra of 1a DMSO solution and 1a acetone emulsion in the presence of various amounts of DMSO under $\lambda_{ex} = 286$ nm.

Figure S17. The PL spectra of 1a H$_2$O solution and 1a acetone emulsion in the presence of various amounts of H$_2$O under $\lambda_{ex} = 286$ nm.
Figure S18. Photographs of fluorescence emission of 1a taken during PL spectra collection in different solvents for sensing properties with respect to (a) H₂O and methanol, (b) DMSO and acetone, and (c) H₂O and acetone.

Figure S19. The PL spectra of 1a DMSO solution in the presence of various amounts of acetone under $\lambda_{ex} = 286$ nm.
**Figure S20.** The PL intensity of 1a DMSO solution as a function of acetone content.

**Figure S21.** The PL spectra of 1a H₂O emulsion in the presence of various amounts of acetone under $\lambda_{ex} = 286$ nm.
Figure S22. The PL intensity of 1a H₂O solution as a function of acetone content.

Figure S23. Fluorescence spectra of desolvated-2 (2a) introduced into various pure solvents when excited at 286 nm.
**Figure S24.** PL spectra of 2a water emulsion in the presence of various amounts of CH$_3$CN under $\lambda_{ex} = 286$ nm.

**Figure S25.** Solid-state UV-vis spectra of compound 2.
Figure S26. Solid-state fluorescence spectra picture of 4,4'-bipy.

Figure S27. Solid-state fluorescence spectra picture of OCA-OH.
Figure S28. Solid-state fluorescence spectra picture of MCA-OH.

Figure S29. Solid-state fluorescence spectra pictures of compounds 1, desolvated-1 (1a), 2 and desolvated-2 (2a).
Figure S30. Solid-state fluorescence spectra pictures of desolvated-2 (2a), desolvated-2 immersed in C₆H₆ (benzene), C₆H₅CH₃ (toluene), C₆H₅I (iodobenzene), and C₆H₅NO₂ (nitrobenzene) for 2 days.

Section 9. PL spectra of ligands, ligands+metals and normalized PL spectra of ligands, ligands+metals and MOF-desolvated

Figure S31. Emission spectra of ligands(OCA-OH and 4,4'-bipy) + metals(Zn(ClO₄)₂·6H₂O) introduced into various pure solvents (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.
**Figure S32.** Emission spectra of ligands (OCA-OH and 4,4'-bipy) introduced into various pure solvents ($4 \times 10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.

**Figure S33.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO$_4$)$_2$·6H$_2$O) and desolvated-1 (1a) introduced into DMF pure solvent ($4 \times 10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.
**Figure S34.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-1 (1a) introduced into DMSO pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

**Figure S35.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-1 (1a) introduced into H₂O pure solvent.
solvent($4 \times 10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.

**Figure S36.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO$_4$)$_2$·6H$_2$O) and desolvated-1 (1a) introduced into MeOH pure solvent($4 \times 10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.

**Figure S37.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO$_4$)$_2$·6H$_2$O) and desolvated-1 (1a) introduced into MeOH pure solvent($4 \times 10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.
and 4,4'-bipy)+ metals (Zn(ClO₄)₂·6H₂O) and desolvated-1 (1a) introduced into CH₃CN pure solvent(4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

Figure S38. Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-1 (1a) introduced into CH₂Cl₂ pure solvent(4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.
**Figure S39.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO$_4$)$_2$$\cdot$6H$_2$O) and desolvated-I (1a) introduced into THF pure solvent ($4\times10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.

**Figure S40.** Normalized emission spectra of ligands (OCA-OH and 4,4'-bipy), ligands (OCA-OH and 4,4'-bipy) + metals (Zn(ClO$_4$)$_2$$\cdot$6H$_2$O) and desolvated-I (1a) introduced into EtOH pure solvent ($4\times10^{-5}$ mol·L$^{-1}$) when excited at 286 nm.
**Figure S41.** Emission spectra of ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) introduced into various pure solvents (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

**Figure S42.** Emission spectra of ligands (MCA-OH and 4,4'-bipy) introduced into various pure solvents (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

**Figure S43.** Normalized emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH
and 4,4'-bipy)+metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into CH₃CN pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

**Figure S44.** Normalized emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into THF pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.
**Figure S45.** Emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into DMF pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

**Figure S46.** Emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into MeOH pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.
Figure S47. Emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into DMSO pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

Figure S48. Emission spectra of ligands (MCA-OH and 4,4'-bipy), ligands (MCA-OH and 4,4'-bipy) + metals (Zn(ClO₄)₂·6H₂O) and desolvated-2 (2a) introduced into EtOH pure solvent (4×10⁻⁵ mol·L⁻¹) when excited at 286 nm.

Section 10. TGA Curves of 1⊃Solvents and 2⊃Solvents
Figure S49. TG analysis of H\textsubscript{2}O adsorbed form, 1⊃H\textsubscript{2}O. The observed weight loss (1.78\%) is the weight of 0.50 H\textsubscript{2}O molecules.

![Graph showing TG analysis for Zn-OCA-MOF-CH\textsubscript{3}OH](image)

2.36\% (Calcd. 2.37\% for the weight loss of 0.37 CH\textsubscript{3}OH molecule)

Figure S50. TG analysis of CH\textsubscript{3}OH adsorbed form, 1⊃CH\textsubscript{3}OH. The observed weight loss (2.36\%) is the weight of 0.37 CH\textsubscript{3}OH molecules.

![Graph showing TG analysis for Zn-OCA-MOF-CH\textsubscript{3}CN](image)

3.52\% (Calcd. 3.53\% for the weight loss of 0.43 CH\textsubscript{3}CN molecule)

Figure S51. TG analysis of CH\textsubscript{3}CN adsorbed form, 1⊃CH\textsubscript{3}CN. The observed weight loss (3.52\%) is the weight of 0.43 CH\textsubscript{3}CN molecules.
Figure S52. TG analysis of CH₂Cl₂ adsorbed form, 1⊃CH₂Cl₂. The observed weight loss (3.35%) is the weight of 0.20 CH₂Cl₂ molecules.

Figure S53. TG analysis of CH₃CH₂OH adsorbed form, 1⊃CH₃CH₂OH. The observed weight loss (2.17%) is the weight of 0.24 CH₃CH₂OH molecules.
Figure S54. TG analysis of acetone adsorbed form, 1$\supset$acetone. The observed weight loss (2.86%) is the weight of 0.25 acetone molecules.

Figure S55. TG analysis of CH$_3$CN adsorbed form, 2$\supset$CH$_3$CN. The observed weight loss (2.30%) is the weight of 0.28 CH$_3$CN molecules.
Figure S56. TG analysis of THF adsorbed form, $2\supset$THF. The observed weight loss (2.68%) is the weight of 0.20 THF molecules.

Figure S57. TG analysis of CH$_3$OH adsorbed form, $2\supset$CH$_3$OH. The observed weight loss (3.17%) is the weight of 0.50 CH$_3$OH molecules.
Figure S58. TG analysis of CH$_3$CH$_2$OH adsorbed form, 2$\supset$CH$_3$CH$_2$OH. The observed weight loss (3.70%) is the weight of 0.41 CH$_3$CH$_2$OH molecules.

Figure S59. TG analysis of cyclohexane adsorbed form, 2$\supset$cyclohexane. The observed weight loss (2.93%) is the weight of 0.21 cyclohexane molecules.
**Figure S60.** TG analysis of H$_2$O adsorbed form, 2$\rightarrow$H$_2$O. The observed weight loss (5.23%) is the weight of 1.46 H$_2$O molecules.

**Figure S61.** TG analysis of CH$_2$Cl$_2$ adsorbed form, 2$\rightarrow$CH$_2$Cl$_2$. The observed weight loss (1.91%) is the weight of 0.11 CH$_2$Cl$_2$ molecules.
**Figure S62.** TG analysis of C₆H₆CH₃ adsorbed form, 2⇌C₆H₆CH₃. The observed weight loss (1.53%) is the weight of 0.08 C₆H₆CH₃ molecules.

**Figure S63.** TG analysis of C₆H₆ adsorbed form, 2⇌C₆H₆. The observed weight loss (2.30%) is the weight of 0.15 C₆H₆ molecules.
**Figure S64.** TG analysis of C₆H₆I adsorbed form, 2⇌C₆H₆I. The observed weight loss (1.91%) is the weight of 0.05 C₆H₆I molecules.

**Figure S65.** TG analysis of C₆H₆NO₂ adsorbed form, 2⇌C₆H₆NO₂. The observed weight loss (1.85%) is the weight of 0.08 C₆H₆NO₂ molecules.
Section 11. Gas sorption isotherms of MOF 1a and 2a for N₂

Figure S66. Gas sorption isotherms of MOF 1a for N₂ (Surface Area = 26.982 m²/g).

Figure S67. Gas sorption isotherms of MOF 2a for N₂ (Surface Area = 23.542 m²/g).