Supporting Information

Pore-coordination sphere facilitated ratiometric fluorescent detection of organic amines in a substitutional metal–organic matrix

Kai Xing,*a Xiao-Yuan Liu,*b Cheng-Shan Ji,c and Jing Li*db

a Department of Chemistry, College of Basic Medicine, Third Military Medical University (Army Medical University), Chongqing, 400038, P.R. China
b Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic University, 7098 Liuxian Blvd, Nanshan District, Shenzhen, 518055, P.R. China
c MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, P. R. China
d Department of Chemistry and Chemical Biology, Rutgers University, 123 Bevier Road, Piscataway, New Jersey, 08854, United States
Contents

Section 1. Materials and Methods ........................................................3

Section 2. Structural Information..........................................................4

Section 3. General Characterization......................................................5

Section 4. Fluorescent Measurements ..................................................8

References ........................................................................................20
Section 1. Materials and Methods

Chemical stability

10 mg finely ground HIAM-3001, HIAM-3002 and HIAM-3001-PNT-25% powders were immersed in 5 mL of deionized water for 72 h; then the MOF powders were centrifuged and used to measure the PXRD patterns.

Computational Methods

The geometries of PBT and PNT without and with methylamine were performed with Gaussian09 program. To the ground state, the density functional theory (DFT) were applied using range-separated CAM-B3LYP functional together with 6-31g+(d,p) basis set in the conductor-like polarizable continuum model (CPCM) after considering the solvent effects of water (ε = 78.36). Accordingly, the geometries of excited states were optimized using the time-dependent density functional theory (TDDFT) with CAM-B3LYP functional and 6-31g+(d,p) basis set.
Section 2. Structural Information

Fig. S1 Standard curve for quantification of PNT by UV-Vis spectra.

Fig. S2 (a) Solvent accessible void space of HIAM-3001; (b) Solvent accessible void space of HIAM-3002 (gray: outer site of the pore and green: inner site of the pore).
Section 3. General Characterization

Thermogravimetric Analysis

Fig. S3 TGA curves of HIAM-3001 and HIAM-3001-PNT-25%.
Powder X-ray Diffraction Patterns

**Fig. S4** (a) Scheme of PNT ligand doping in pristine HIAM-3001 matrix; (b) PXRD patterns of the as-synthesized HIAM-3001-PNT-25%, the simulated HIAM-3001 and HIAM-3002; (c) PXRD patterns of the as-synthesized HIAM-3001-PNT-25% and HIAM-3001-PNT-25% after treatment in water for 72 h, in comparison with those of simulated and as-synthesized HIAM-3001.

**Fig. S5** (a) PXRD profiles of HIAM-3001 and HIAM-3001-PNT-25% (inset: crystal pictures); (b) schematic illustration of the framework change of HIAM-3001 after ligand doping.
Hirshfeld surfaces analysis

Fig. S6 The bar chat of relative contributions for HIAM-3001 and HIAM-3002 to the Hirshfeld surface area for the various close intermolecular contacts.
Section 4. Fluorescent Measurements

Fig. S7 Emission spectra of fluorescence mapping of HIAM-3001-x% with different ratios.

Fig. S8 Emission spectra of HIAM-3001 (solid line) and UV absorbance of PNT (dashed dot line).
Fig. S9 Calculated HOMO and LUMO orbitals of PBT and PNT and their HOMO-LUMO energy gap, plotted with an isovalue of 0.04.

Fig. S10 (a) The emission, (b) relative intensity of HIAM-3001 in different solvents.
Fig. S11 (a) The emission, (b) relative intensity of **HIAM-3002** in different solvents.

Fig. S12 (a) The emission, (b) relative intensity of **HIAM-3001-PNT-25%** in different solvents.
Fig. S13 The relation between relative intensity and corresponding different solvent parameters for various solvents with different protic property for **HIAM-3001**.

Fig. S14 The relation between relative intensity and corresponding different solvent parameters for various solvents with different protic property for **HIAM-3002**.
**Fig. S15** The relation between relative intensity and corresponding different solvent parameters for various solvents with different protic property for **HIAM-3001-PNT-25%**.

**Fig. S16** The PXRD profiles of **HIAM-3001-PNT-25%** after immersing in different solvents for 72 h.
Fig. S17 (a) Optical crystal photos of as-synthesized HIAM-3001-PNT-25%; (b) SEM image of HIAM-3001-PNT-25% after grinding.
Table S1 Solvent dependent luminescence properties of HIAM-3001, HIAM-3002 and HIAM-3001-PNT-25%.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent parameters</th>
<th>Luminescent property</th>
<th>Reichardt’s parameters</th>
<th>Gutmann’s parameters</th>
<th>HIAM-3001</th>
<th>HIAM-3002</th>
<th>HIAM-3001-PNT-25%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$E_N^N$</td>
<td>AN</td>
<td>Relative intensity</td>
<td>CIE X/CIE Y</td>
<td>Relative intensity</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.460</td>
<td>18.9</td>
<td>1.86</td>
<td>(0.15,0.11)</td>
<td>1.80</td>
<td>(0.41,0.54)</td>
<td>6.86</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.355</td>
<td>-</td>
<td>1.71</td>
<td>(0.15,0.10)</td>
<td>1.60</td>
<td>(0.42,0.55)</td>
<td>13.19</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.762</td>
<td>41.5</td>
<td>2.14</td>
<td>(0.15,0.09)</td>
<td>1.91</td>
<td>(0.41,0.56)</td>
<td>5.73</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.654</td>
<td>37.9</td>
<td>2.15</td>
<td>(0.15,0.10)</td>
<td>1.99</td>
<td>(0.41,0.55)</td>
<td>6.02</td>
</tr>
<tr>
<td>DMF</td>
<td>0.386</td>
<td>13.6</td>
<td>1.55</td>
<td>(0.16,0.12)</td>
<td>1.45</td>
<td>(0.44,0.54)</td>
<td>7.98</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1</td>
<td>54.8</td>
<td>1.0</td>
<td>(0.16,0.15)</td>
<td>1.0</td>
<td>(0.46,0.53)</td>
<td>1.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.77</td>
<td>0.72</td>
<td>0.60</td>
<td>(0.16,0.10)</td>
<td>0.80</td>
<td>(0.43,0.55)</td>
<td>1.75</td>
</tr>
</tbody>
</table>
**Fig. S18** ESP-mapped molecular $vdW$ surface and Electrostatic potential distribution of PBT (left) and PNT (right). (Significant surface local minima and maxima of ESP are represented as orange and azure spheres, respectively).

**Scheme S1** Structures of the selected organic amine analytes.
Fig. S19 (a) Effect on the fluorescence of HIAM-3001-PNT-25% dispersed in water upon the incremental addition of ammonia solution; (b) linear fit for the estimation of detection limit.

Fig. S20 (a) Effect on the fluorescent spectra of HIAM-3001-PNT-25% dispersed in water upon the incremental addition of methylamine; (b) linear fit for the estimation of detection limit.
**Fig. S21** (a) Effect on the fluorescence of HIAM-3001-PNT-25% dispersed in water upon the incremental addition of triethylamine; (b) linear fit for the estimation of detection limit.

**Fig. S22** (a) Effect on the fluorescence of HIAM-3001-PNT-25% dispersed in water upon the incremental addition of cadaverine; (b) linear fit for the estimation of detection limit.
Table S2 The limit of detection of selected analytes.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>The limit of detection (LOD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>0.299 ppm</td>
</tr>
<tr>
<td>Methylamine (MA)</td>
<td>0.681 ppm</td>
</tr>
<tr>
<td>Triethylamine (TA)</td>
<td>1.990 ppm</td>
</tr>
<tr>
<td>Cadaverine (PDA)</td>
<td>2.691 ppm</td>
</tr>
</tbody>
</table>

Fig. S23 PXRD profiles of HIAM-3001-PNT-25% before and after fluorescent sensing.
Fig. S24  (a) Optical image of HIAM-3001-PNT-25% coated filter paper strip in the presence of spoiled beef at room temperature; (b) images of HIAM-3001-PNT-25% coated filter paper before (top) and after (bottom) presenting in the spoiled beef.

Fig. S25  (a) Membrane exposure to the vapours from spoiled beef; (b) flexible membranes of HIAM-3001-PNT-25% before (top) and after (bottom) exposure to the vapours from spoiled beef.
References