Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Encapsulation of Large Dye Molecules in Hierarchically Superstructured Metal-Organic Frameworks

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1. Experimental and measurements

Materials. The ligand of 1,4-benzenedicarboxylic acid (H_2BDC), 2-amino-1,4-benzenedicarboxylic acid (NH_2H_2BDC), 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC), Rhodamine B (RB), and solvent (dimethylformamide, DMF) and metal salts (zinc acetate and copper acetate) were purchased from Aldrich Chemical Co. Inc.. All materials were used without further purification.

Synthesis of hierarchical IRMOF-3. A 20 mL DMF solution of NH_2H_2BDC (0.10 g, 0.55 mmol) was added to a 20 mL DMF solution of 0.343 g, 1.57 mmol, $Zn(OAc)_2 \cdot 2H_2O$ under stirring. The mixture was stirred for 4 hours at room temperature, with the speed of magnetic bar being 1200 cycles/minute. The resulting white-off precipitate was separated by centrifugation, washed with dimethylformamide and methanol, subsequently dried under vacuum at 60 ^{o}C overnight before characterizations.

Synthesis of hierarchical Cu-BDC. A 20 mL DMF solution of H_2BDC (0.166 g, 1.0 mmol) was added to a 20 mL DMF solution of 0.199 g, 1.0 mmol, $Cu(OAc)_2 \cdot H_2O$ under stirring. The mixture was stirred for 48 hours at room temperature, with the speed of magnetic bar being 1200 cycles/minute. The resulting blue precipitate was separated by centrifugation, washed with dimethylformamide and methanol subsequently; then the solid was dried under vacuum at 60 ^{o}C overnight before characterizations.

Synthesis of hierarchical Cu-BTEC. A 20 mL DMF solution of H_4BTEC (0.254 g, 1.0 mmol) was added to a 20 mL DMF solution of 0.498 g, 2.5 mmol, $Cu(OAc)_2 \cdot H_2O$ under stirring. The mixture was stirred for 24 hours at room temperature, with the speed of magnetic bar being 1200 cycles/minute. The resulting blue precipitate was separated by centrifugation, washed with DMF and methanol, subsequently dried under vacuum at 60 ^{o}C overnight.

Synthesis of RB@hierarchical IRMOF-3. A 20 mL DMF solution of NH_2H_2BDC (0.10 g, 0.55 mmol) and 0.05 g Rhodamine B was added to a 20 mL DMF solution of 0.343 g, 1.57 mmol, $Zn(OAc)_2 \cdot 2H_2O$ under stirring. The mixture was stirred for 4 hours at room temperature, with the speed of magnetic bar being 1200 cycles/minute. The resulting precipitate was separated by centrifugation, washed with dimethylformamide and methanol, subsequently dried under vacuum at 60 ^{o}C overnight before characterizations.

Powder X-ray Diffraction (XRD). Powder X-ray Diffraction (XRD) analysis of these nanoporous materials was used to confirm the crystallinity as well as the phase purity of the bulk materials. Powder XRD patterns were recorded on a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å).

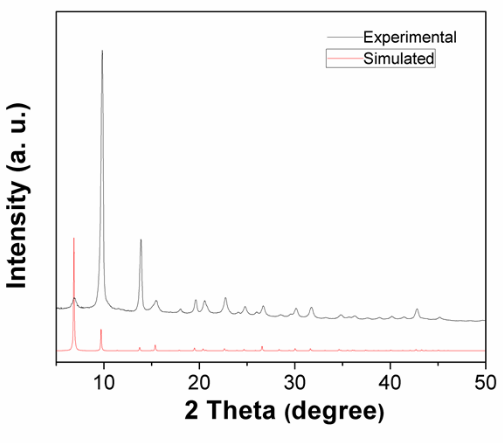
Gas Adsorption Analysis. Gas adsorption studies were done to confirm the permanent porosity of the nanoporous MOF materials as well as to determine the surface area. Gas adsorption experiments were performed on a Micromeritics Tristar 3000 at 77 K. Samples (around 100 mg) were activated for 6 hours at 150 °C under nitrogen flow and subsequently loaded for adsorption analysis.

Scanning Transmission Electron Microscopy (STEM). Scanning transmission electron microscope (STEM) images were recorded using a Hitachi HD2000 STEM microscope operating at 200 kV. Samples for STEM analysis were prepared by drop casting: one drop of the sample dispersion in ethanol was dropped onto a copper grid and allowed to dry at ambient temperature before being subjected to STEM analysis.

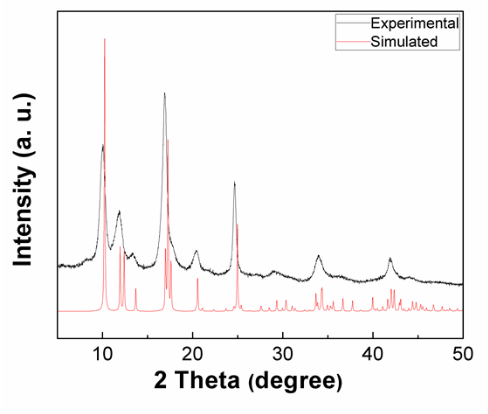
The Photoluminescence (PL) Spectra. The RB@IRMOF3 were exposed to different solvents, such as orthodichlorobenzene, chlorobenzene, benzene, toluene, *p*-xylene, methanol, and ethanediol for 10 min, then the luminescent spectra for the samples were recorded by a Hitachi F4600 fluorescence spectrometer. The photomultiplier tube voltage was 750 V and the scan speed was 240 nm/min, while the slit widths of excitation and emission spectra were 2.5 nm and 2.5 nm.

2. Powder XRD patterns of mesoporous MOFs

a



b



c

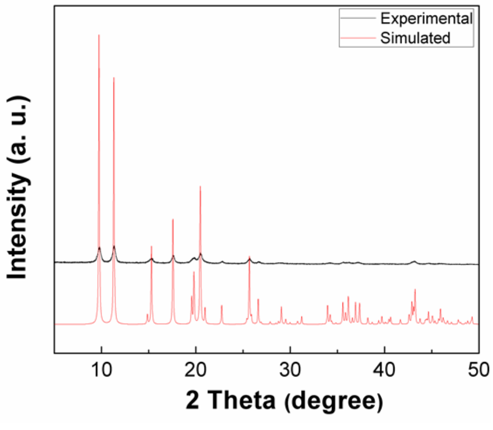


Figure S1. Powder XRD patterns of IRMOF-3 (*a*), Cu-BDC (*b*), and Cu-BTEC (*c*).

3. Powder XRD patterns of RB@IRMOF-3 composite

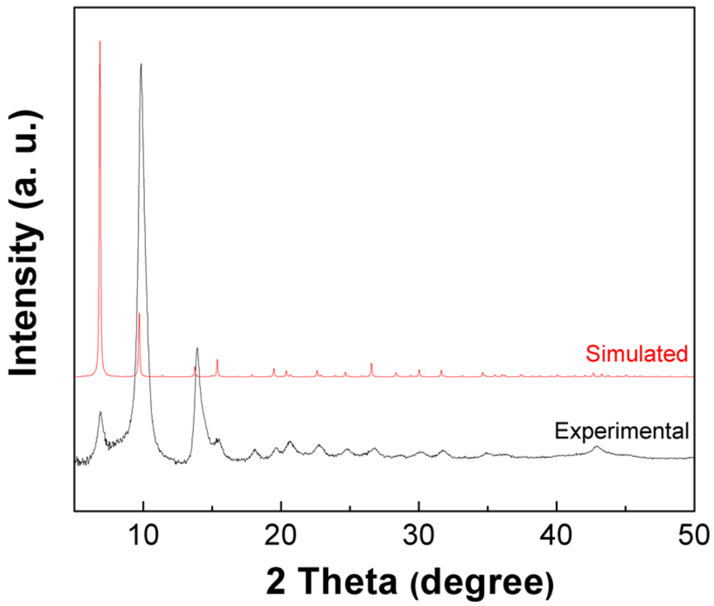


Figure S2. Powder XRD patterns of RB@IRMOF-3 composite.

4. Nitrogen – 196 ^{o}C isotherms of RB@IRMOF-3 composite

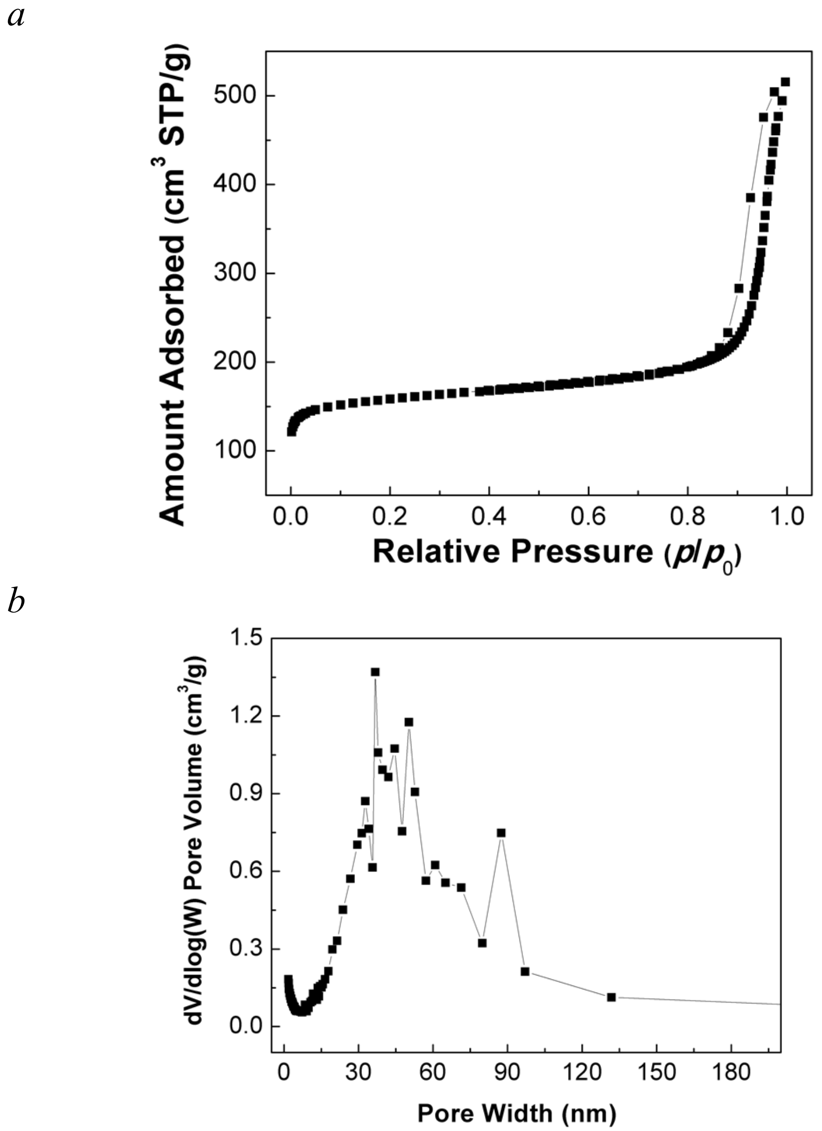


Figure S3. Nitrogen – 196 ^{o}C isotherms of RB@IRMOF-3 composite (*a*) and PSD curve (*b*).

5. Emission spectra of RB solution in ethanol and RB@IRMOF-3 composite

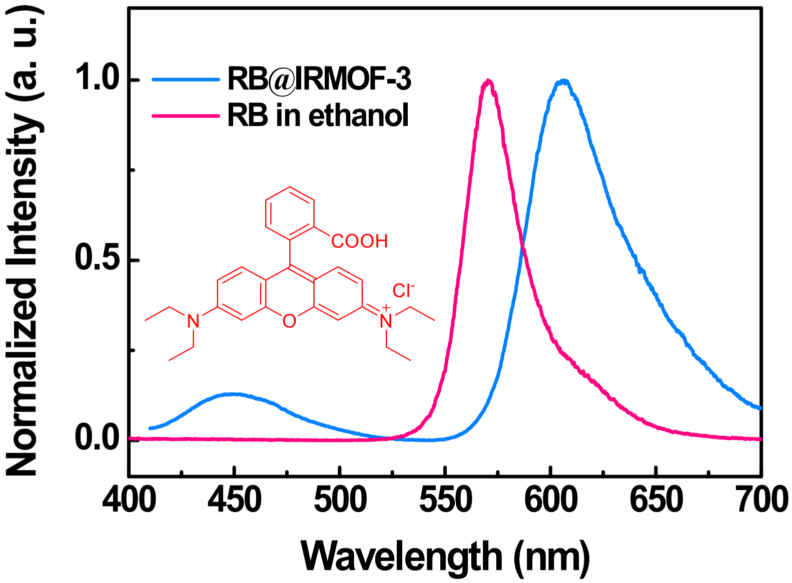


Figure S4. Emission spectra of RB solution in ethanol and RB@IRMOF-3 excited at 355 nm; the molecular structure of PB (inset)

6. Fluorescence spectra of RB@IRMOF3 treated with methanol and ethanediol

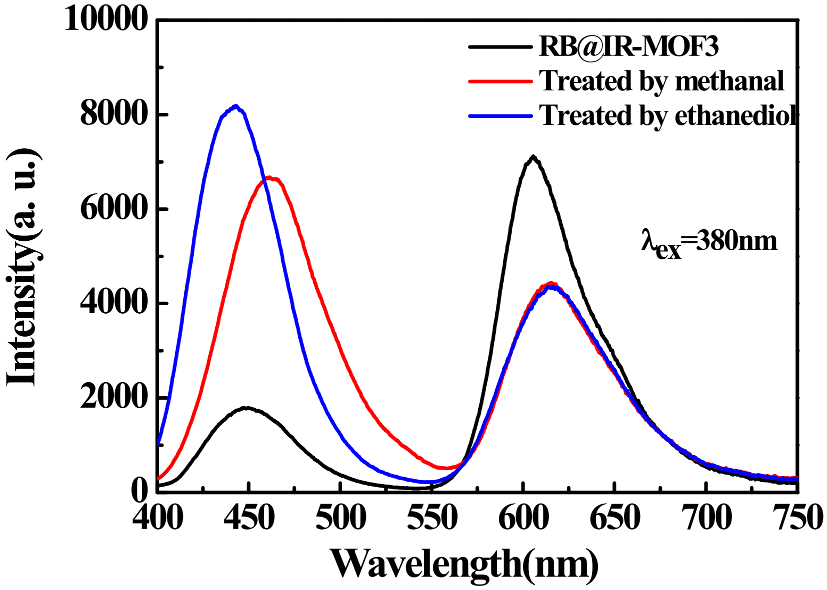


Figure S5. Fluorescence spectra of RB@IRMOF-3 treated with methanol and ethanediol.

7. The emission peak-height ratios between ligand and dye moieties

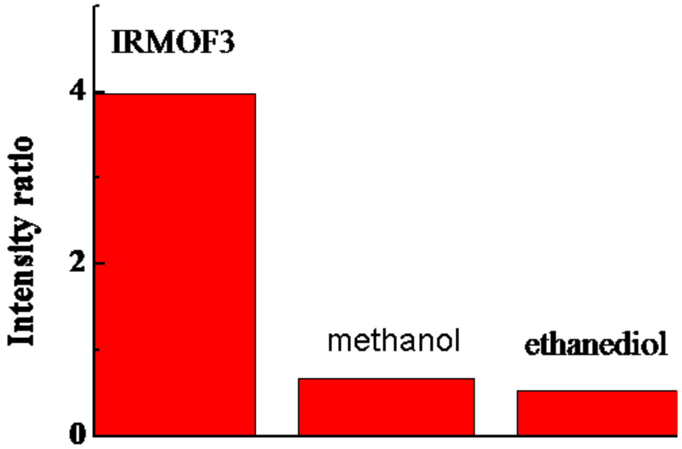


Figure S6. The emission peak-height ratios between ligand and dye moieties in RB@IRMOF-3 treated with methanol, ethanediol excited at 380 nm in the solid state at room temperature.

8. Table S1. The porosity details of hierarchical MOF materials[†]

Samples	V_{SP} **(cm^3/g)**[a]	S_{BET} **(m^2/g)**[b]	V_{mi} **(cm^3/g)**[c]	***100(V_{mi}/V_{SP})***[d]	***w*** **(nm)**[e]
IRMOF-3	0.41	248.4	0.05	12	19.4
Cu-BDC	0.23	107	0.01	4	13.7
Cu-BETC	0.38	226	–[f]	–	8.1
RB@IRMOF-3	0.76	541.1	0.19	0.25	36.7

[†][a]single point pore volume taken at $p/p_0 \sim 0.98$; [b]specific surface area calculated in the p/p_0 range of 0.05 – 0.20; [c]micropore volume calculated in the *t*-plot range of 0.35–0.5; [d]approximate *t*-plot micropore to total pore volume percent ratio; [e]mesopore width from the maximum of the calculated PSDs; [f]data not obtained due to have no micropores in the product.