Electronic Supplementary Information

Facile Synthesis of Nanocrystals of Microporous Metal-Organic Framework by Ultrasonic Method and Selective Sensing of Organoamines

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Experimental

Instruments: Infrared spectra (IR) (KBr pellets) were recorded in the 400-4000 cm^{-1} range using a Nocolet Nexus 870 FTIR spectrometer. The elemental analyses of C and H were carried out on a Perkin-Elmer 2400 elemental analyzer. Fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Powder X-ray diffraction (XRD) data were recorded using a step scan with a range of 5-50 degrees 2θ on a Philips-1700X diffractometer (Cu-Kα radiation, λ = 0.154178 nm), and the morphologies and size or nanostructure of the products were characterized on a JEOL JEM-100SX transmission electron microscope (TEM).

Synthesis of 1: Hydrothermal synthesis of $Zn_3(BTC)_2\cdot 12H_2O$ (**1**) was carried out according to reference [12]. Ultrasonic syntheses of **1** were carried out under ultrasonic irradiation at a frequence of 40 KHz (JL-60DTH, J&L Shanghai Ultrasonics) at ambient temperature and atmospheric pressure for 5, 10, 30, and 90 min, respectively, and the ultrasonic output was kept to be 60 W in all experiments. Generally speaking, 2 mL of ethanol solution of H_3BTC (0.105 g, 0.5 mmol) was added into an aqueous solution (5 mL) of zinc acetrate dihydrate (0.181 g, 0.83 mmol) in a test tube (20 mL), and then the test tubes were fixed in the bath of the ultrasonic generator. After the ultrasonic irradiation for different reaction times, the resulting products were filtered. The products were isolated by filtering the precipitation from reaction mixture, and the precipitation washed with water (50 mL) and ethanol (10 ml × 3) and then dried at 70 °C in vacuum (0.01 MPa). Although nanocrystals of MOF **1** are very fine, a tendency of aggregation of these nanocrystals leads to precipitation of the product. After the filtration, nanocrystals can be re-dispersed in ethanol as demonstrated by TEM in the manuscript. Yield of **1** varied from 75.3-86.3 % depending on different reaction times, and their structures were confirmed by IR, elemental analysis and Rietveld analysis of powder X-ray diffraction (XRD) paterns (see Table S1).

***1**-HT* (sample synthesized using hydrothermal method): Elemental analysis calcd (%) for $Zn_3(BTC)_2 \cdot 12H_2O$: $C_{18}H_{30}O_{24}Zn_3$, C 26.16, H 3.66; found: C 26.37, H 3.19; IR (KBr, cm^{-1}): 3451(vs, broad), 1617(vs), 1560(vs), 1438(vs), 1368(vs), 1109(w), 984(w), 758(s), 729(vs), 561(m), 419(w).

***1**-US(5)* (sample prepared using ultrasonic method for 5 min): Elemental analysis calcd (%) for $Zn_3(BTC)_2 \cdot 12H_2O$: $C_{18}H_{30}O_{24}Zn_3$, found: C 26.41, H 3.58; IR (KBr, cm^{-1}): 3447(vs, broad), 3179(s, broad), 1615(vs), 1559(vs), 1436(vs), 1368(vs), 1111(w), 761(s), 730(vs), 562(m), 461(w), 423(w).

***1**-US(10)* (ultrasonic method for 10 min): Elemental analysis calcd (%) for $Zn_3(BTC)_2 \cdot 12H_2O$: $C_{18}H_{30}O_{24}Zn_3$, found: C 26.22, H 3.69; IR (KBr, cm^{-1}): 3447(vs, broad), 1617(vs), 1568(vs), 1440(vs), 1369(vs), 1113(w), 764(s), 730(vs), 557(m), 461(w), 423(w).

***1**-US(30)* (ultrasonic method for 30 min): Elemental analysis calcd (%) for $Zn_3(BTC)_2 \cdot 12H_2O$: $C_{18}H_{30}O_{24}Zn_3$, found: C 26.51, H 3.37; IR (KBr, cm^{-1}): 3448(vs, broad), 1617(vs), 1560(vs), 1437(vs), 1369(vs), 1111(w), 758(s), 730(vs), 562(m), 462(w).

***1**-US(90)* (ultrasonic method for 90 min): Elemental analysis calcd (%) for $Zn_3(BTC)_2 \cdot 12H_2O$: $C_{18}H_{30}O_{24}Zn_3$, found: C 26.23, H 3.68; IR (KBr, cm^{-1}): 3448(vs, broad), 1617(vs), 1569(vs), 1438(m), 1369(vs), 1113(w), 761(s), 730(vs), 560(m), 462(w), 419(w).

TEM characterization: The morphologies and size or nanostructure of the products were characterized on a JEOL JEM-100SX (TEM). Samples for the TEM were prepared by ultrasonically dispersing the as-synthesized products into absolute ethanol, then placing a drop of this suspension onto a copper grid coated with an amorphous carbon film, and then drying the sample in air.

Sensing of organoamines: For the sensing of organoamines in acetonitrile solution, corresponding fluorescence spectra of **1** was recorded upon exictation at 327 nm after injecting various amounts of organoamines into a 1-cm cuvette containing 2.00 mL of acetonitrile, in which a slice of glass coated with nanocrystals of **1** was fixed (see Figure S1). To have a better understanding on possible influence of solvents on the sensing studies and select a proper solvent for the sensing of organoamines, solvent effect on solid state fluorescence of nanocrystals of **1** obtained for 90 min was investigated before the fluorescence spectrometric titration experiments. It was found that fluorescent intensity of **1** in different solvents followed the order *iso*-propanol, acetonitrile, enthanol, cyclohexane, N,N-dimethylformamide (DMF), toluene, and acetone (see Fig. S3). As a result, to obtain a high sensitivity for the sensing amines, acetonitrile was selected as the solvent in the present work due to a relatively high fluorescent intensity of nanocrystals of **1** in this solvent.

Table S1

Crystallograpgic data for crystals of **1** obtained by Rietveld analysis using powder XRD data.[a]

	$Co_3(BTC)_2{\cdot}12H_2O$ [b]	**1**-HT	**1**-US(10)	**1**-US(30)	**1**-US(90)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a, Å	17.482	17.501	17.460	17.418	17.464
b, Å	12.963	12.942	12.960	12.920	12.953
c, Å	6.559	6.588	6.590	6.573	6.595
α,°	90.00	90.00	90.00	90.00	90.00
β,°	112.04	112.38	111.97	111.90	112.04
γ,°	90.00	90.00	90.00	90.00	90.00
V, $Å^3$	1377.8	1379.7	1382.8	1372.4	1382.8
M[20][c]		11.6	12.5	10.3	12.0
F[20][c]		20.3	13.5	18.4	12.7

[a] Samples synthesized using hydrothermal method is designated as **1**-HT, and those prepared using ultrasonic method for 10, 30, and 90 min are designated as **1**-US(10), **1**-US(30), and **1**-US(90), respectively. [b] Data from reference [12]. [c] See ref. [13].

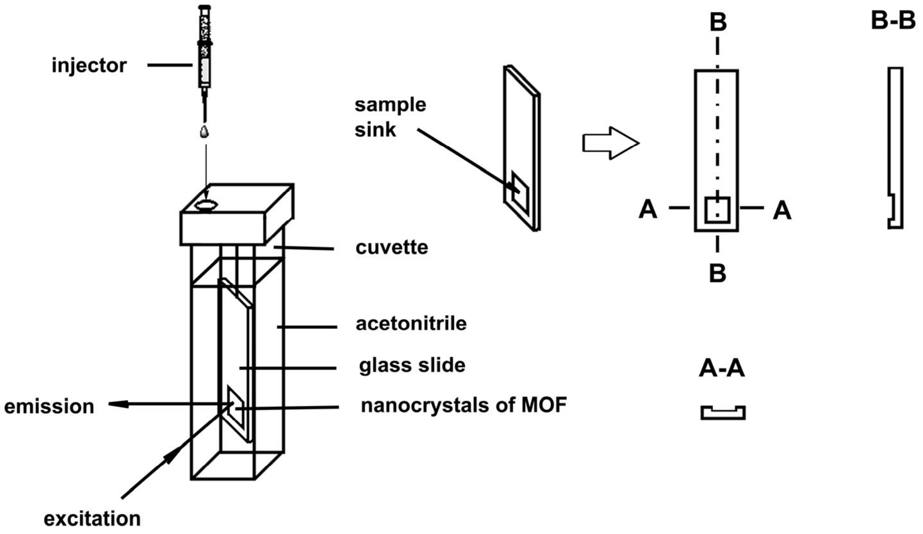

Fig. S1 Illustration of devices for fluorescence spectrometric titration experiments for the sensing of organoamines in acetonitrile solution.

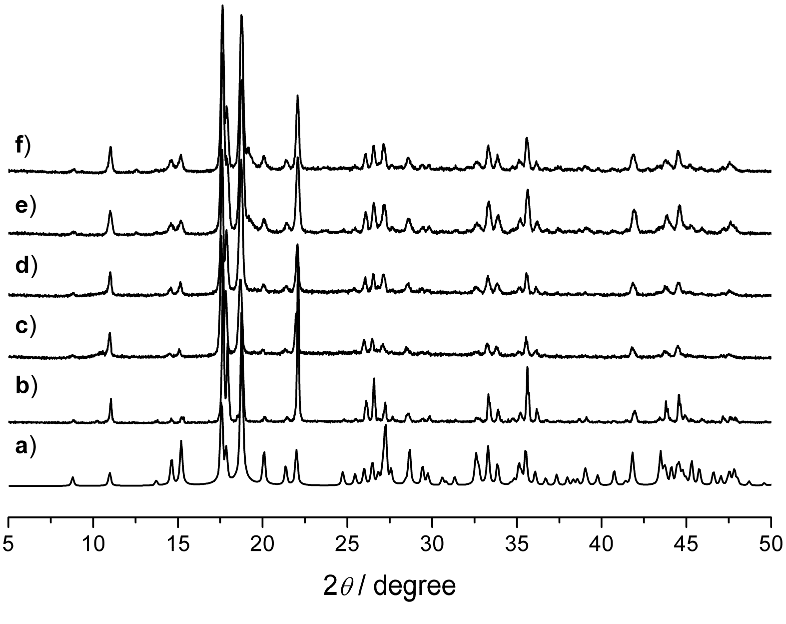

Fig. S2 Powder X-ray diffraction patterns of a) simulated from the crystallographic data of $Co_3(BTC)_2 \cdot 12H_2O$ obtained from single crystal X-ray diffraction, b) synthesized using hydrothermal method, and c) to f) synthesized by using ultrasonic method for 5, 10, 30, and 90 min, respectively.

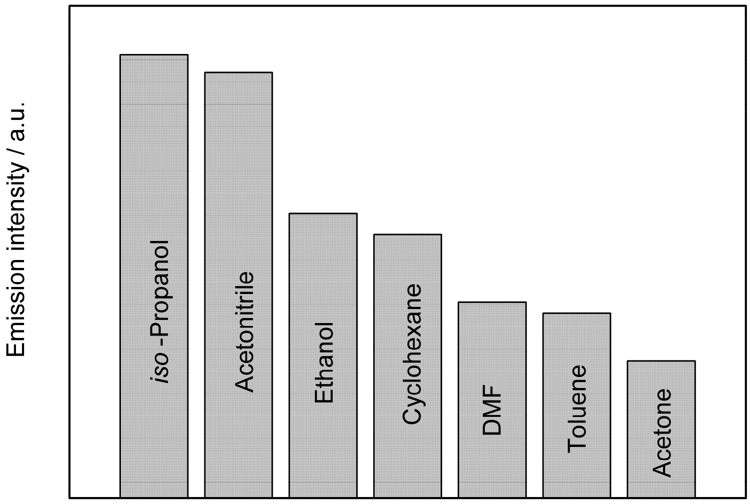

Fig. S3 Solid state fluorescence intensity of **1** in different solvents, showing solvent-dependent fluorescence property of the framework.

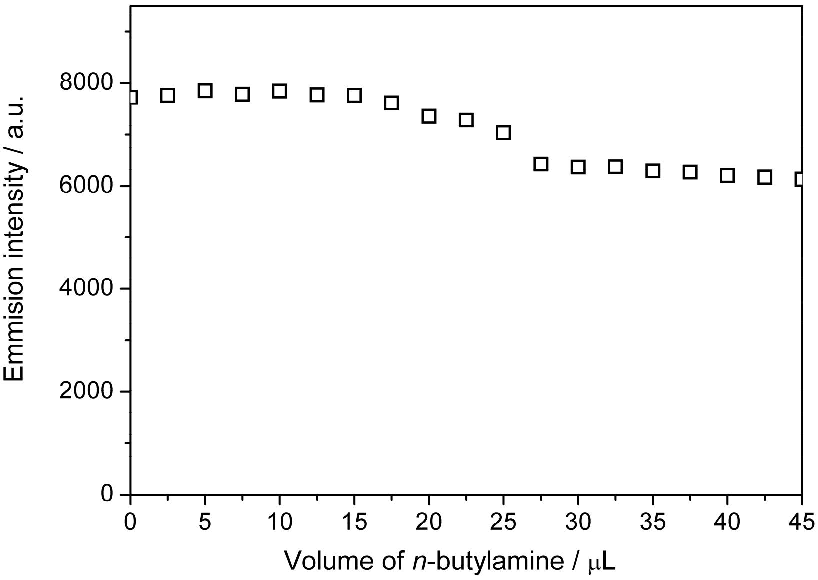

Fig. S4 Emission intensity of **1** at 414 nm against volume of *n*-butylamine in 2 mL of acetronitrile, showing weak fluorescence quench effect at high concentrations of amine.

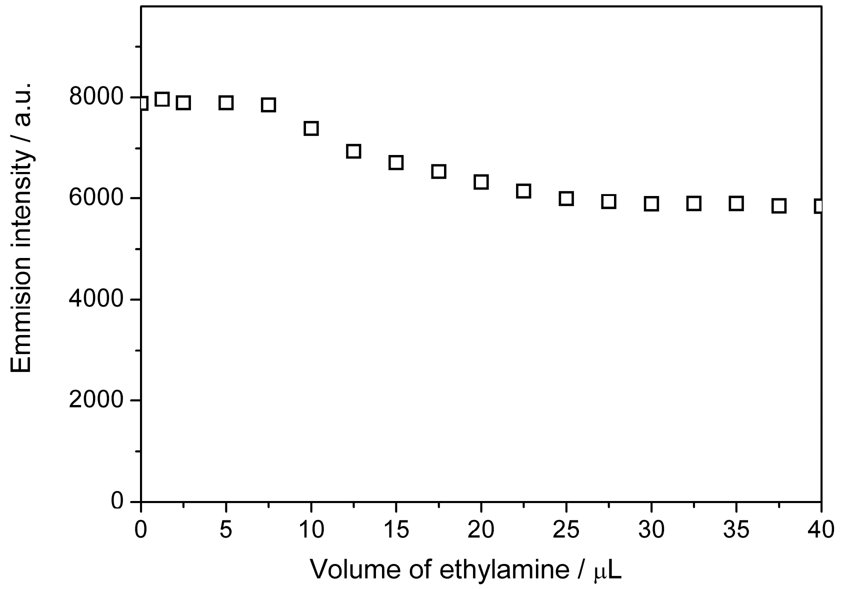

Fig. S5 Emission intensity of **1** at 414 nm against volume of *n*-propylamine in 2 mL of acetronitrile, showing weak fluorescence quench effect when concentration of propylamine is larger than 7.5 μL.

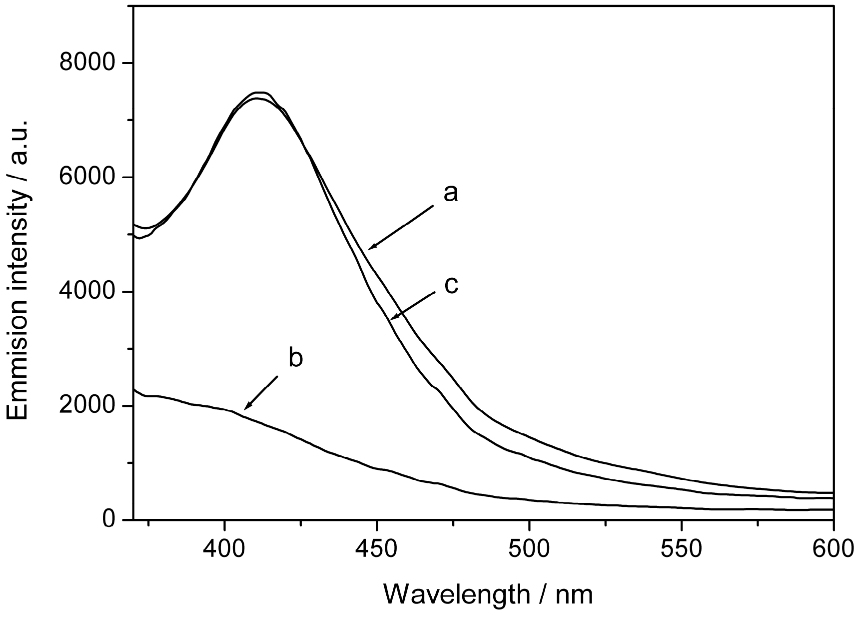

Fig. S6 Emission spectra of sample of **1** a) in acetronitrile, b) after 17.5 μL of ethylamine was added into acetronitrile, and c) after drying.