## **Electronic Supplementary Information (ESI)**

# Covalent organic frameworks as pH responsive signaling

### scaffolds

Yuwei Zhang<sup>a,d</sup>, Xiaochen Shen<sup>a</sup>, Xiao Feng<sup>b</sup>, Hong Xia<sup>c</sup>, Ying Mu<sup>a</sup>\* and Xiaoming Liu<sup>a</sup>\*

<sup>a</sup>State Key Laboratory for Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P.R. China.

<sup>b</sup> School of Chemistry, Beijing Institute of Technology, Beijing, 100081, P.R. China.

<sup>c</sup> State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Technology, Jilin University, Changchun 130012, P.R. China.

<sup>d</sup> College of Resourcees and Environmnet, Jilin Agricultural University, Changchun 130118, P.R. China

Email: xm\_liu@jlu.edu.cn

#### **Materials and Methods**

The 1,4-dimethoxybenzene, bromine, magnesium, hydrazine hydrate were obtained from Aldrich. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

<sup>1</sup>H spectra were recorded on a Bruker AVANCE III HD 400M spectrometer, where chemical shifts ( $\delta$  in ppm) were determined with a residual proton of the solvent as standard. The infrared spectra were recorded from 400 to 4000 cm<sup>-1</sup> on an Avatar FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer diffractometer by depositing powder on glass substrate, from  $2\theta = 2.0^{\circ}$  to  $45^{\circ}$  with 0.02° increment at 25 °C. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer within the wavelength range 200-800 nm. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the NLDFT method was applied for the estimation of pore size distribution. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 by using an integrating sphere. Photoluminescence measurements at room temperature were taken on a Cary Eclipse Fluorescence Spectrophotometer.

#### Syntheses and Characterization

Scheme S1: Synthetic route for monomer



Synthesis of 1,4-dibromo-2,5- dimethoxybenzene (1):

1,4-dimethoxybenzene (1.5 g, 10.8 mmol) was dissolved in CHCl<sub>3</sub> (10 mL) and cooled to 0 °C under N<sub>2</sub>, and the pressure was vented through a 10% aq Na<sub>2</sub>SO<sub>3</sub> solution (200 mL). Bromine (1.39 mL, 27.0 mmol) was added dropwise via syringe. The reaction mixture continued to stir at room temperature for 5 h. Then the reaction was quenched with 10% aq Na<sub>2</sub>SO<sub>3</sub> (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The organic layer was washed with brine (3 × 30 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give 2.47 g of product as white crystals (yield 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.10 (s, 2H), 3.84 (s, 6H) ppm. IR (KBr): 2969, 2937, 2839, 1700, 1494, 1435, 1359, 1278, 1211, 1179, 1062, 1017, 855, 761 and 442.

#### Synthesis of 2,5-dimethoxyterephthalic acid (2):

The 1-2 grains of iodine was added to a flask with a mixture of magnesium (0.97 g, 40 mmol) and dry THF (15 mL) under a nitrogen atmosphere. The solution of 1, 4-dibromo-2, 5-dimethoxybenzene (3.0 g, 10 mmol) in 20 mL of dry THF was added slowly the flask through a syringe. The solution was allowed to stir at 40 °C for 6 h. The obtained grayish solution was cooled to 0 °C, and then carbon dioxide gas was passed slowly into the reaction flask, the mixture was stirred at 0 °C for 30 minutes.

The white solid was filtered and dissolved in water (15 mL). Then the solution was acidified with dilute sulfuric acid (5 mL, 10%) and the mixture was stirred at room temperature for 30 minutes. A light yellow precipitate was collected by filtration. The solid was washed with water three times and dried in air. Yield: 1.5 g, 65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (s, 2H), 4.14 (s, 6H) ppm. IR (KBr): 3225, 2959, 1732, 1494, 1417, 1341, 1211, 1166, 1017, 905, 811, 788, 725, 590, 549 and 464.

#### Synthesis of diethyl-2,5-dimethoxyterephthalate (3):

2, 5-Dimethoxyterephthalic acid (1.0 g, 4.42 mmol) was added into a flask with dry ethanol (30 mL) and two drops of concentrated H<sub>2</sub>SO<sub>4</sub>. The mixture was refluxed for 24 h until it completely dissolved. The reaction mixture was poured in cold water (10 mL)and a large number of white solid precipitated. Then the mixture was neutralized by sodium bicarbonate and the solid was collected by filtration, washed three times with water and dried in air. Yield: 0.89 g, 72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (s, 2H), 4.38 (q, *J* = 8 Hz, 4H), 3.89 (s, 6H) and 1.39 (t, *J* = 8 Hz, 6H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  165.3, 152.1, 124.1, 115.1, 61.1, 56.5 and 13.9 ppm. IR (KBr): 2923, 2854, 1718, 1507, 1466, 1380, 1317, 1247, 1206, 1182, 1092, 1023, 885, 788, 767 and 605.

#### Synthesis of diethyl-2,5-dimethoxyterephthalate (4):

Diethyl-2,5-dimethoxyterephthalate (0.5 g, 1.7 mmol) was dissolved in ethanol (20 mL) in a round bottom flask. Hydrazine hydrate (8.5 mL, 174 mmol) was added into the flask, and then the reaction mixture was heated to reflux for 10 h. The flask was cooled to room temperature, and white precipitate formed. The flask was placed in the freezer overnight until white solid completely precipitated. The crude product was collected by filtration, washed three times with ethanol, and dried under vacuum. Yield: 0.38 g, 84%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.31 (s. 2H), 7.39 (s, 2H), 4.56 (s, 4H), 3.84 (s, 6H) ppm. IR (KBr): 3299, 3195, 2971, 2934, 2845, 1639, 1477, 1300, 1211, 1143, 1112, 1033, 966, 892, 757, 714, 605 and 412.

#### Scheme S2: Synthetic route for model compound



#### Synthesis of model compound:

The reference compound was synthesized by the reaction between Triformylphloroglucinol (0.16 g, 0.76mmol) and hydrazone (0.38 g, 2.29 mmol) in 50 mL ethanol under refluxing condition for 24 h. After this time the solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol(20 mL  $\times$  3), and dried under vacuum to give 0.4 g (Yield: 80%) of an orange solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 13.97 (s, 3H), 11.87 (s, 3H), 8.87 (s, 3H), 7.68 (d, J = 8 Hz, 3H), 7.55 (t, J = 8 Hz, 13H), 7.20 (d, J = 8 Hz, 3H), 7.09 (t, J = 8 Hz, 3H), 3.92 (s, 9H) ppm. FT-IR (KBr): 3294, 2981, 2944, 2840, 1668, 1627, 1597, 1519, 1451, 1366, 1322, 1288, 1240, 1179, 1047, 1017, 949, 779, 749, 660, 586, 518 and 457 cm<sup>-1</sup>. UV-Vis ( $\lambda$ ; in solid state): 344 nm.

Scheme S3: Synthetic route for COF-JLU4



#### Synthesis of COF-JLU4:

A 4 mL pyrex tube was charged with triformylphloroglucinol (30 mg, 0.14 mmol), 2,5-dimethoxyterephthalohydrazide (54 mg, 0.21 mmol), mesitylene/dioxane (2 mL, 3:1 v/v) and AcOH (0.2 mL, 6 M), the mixture was sonicated for 1 minutes, degassed through three freeze–pump–thaw cycles, sealed under vacuum. The reaction was heated at 120 °C for 7 days yielding a pale-yellow solid at the bottom of the tube which was isolated by centrifugation and washed with anhydrous dioxane, anhydrous tetrahydrofuran and anhydrous acetone, and dried under vacuum at 50 °C for 10 h to afford pale yellow powder 67.4 mg in 84% isolated yield. For other solvent conditions, such as mesitylene, ethanol and mesitylene/dioxane (1/1 by vol.) followed the same experimental procedure to obtain the COF-JLU4s. Elemental analysis for the calculated C (53.63%), H (3.94%), N (15.64%) and observed C (51.36%), H (4.08%), N (13.77%).



**Figure S1.** (a) FT-IR spectra of COF-JLU4 (green line), model compound (blue line), its monomers 2,5-dimethoxy-terephthalohydrazide (black line) and 1,3,5-triformylphloroglucinol (red line). (b) FT-IR spectrum of COF-JLU4.



**Figure S2.** <sup>13</sup>C CP-MAS NMR spectrum of COF-JLU4, recorded at a CP contact time of 2 ms and a MAS rate of 15 kHz. Signals with \* symbols are side peaks.



Figure S3. (a) SEM and (b) TEM of COF-JLU4



**Figure S4.** (a)  $CO_2$  adsorption measurements for COF-JLU4. (b) The isosteric heat of  $CO_2$  adsorption.



Figure S5. TGA curve of the COF-JLU4 under a nitrogen atmosphere.



**Figure S6.** (a) XRD patterns and (b) FT-IR spectra of COF-JLU4 upon treatment 2 h in different solvents.



**Figure S7.** The electron absorption spectra of COF-JLU4 (green line), model compound (blue line), its monomers 2,5-dimethoxy-terephthalohydrazide (black line) and 1,3,5-triformylphloroglucinol (red line).



**Figure S8.** The PL spectra of COF-JLU4 (black line), its monomers 2,5-dimethoxyterephthalohydrazide (red line) and 1,3,5-triformylphloroglucinol (green line). Inset: Photograph of fluorescence emission of COF-JLU4 under a UV lamp with  $\lambda_{ex} = 365$  nm.



**Figure S9.** pH dependent fluorescence of model compound in the aqueous solutions with ranging from 0.8 to 12.0 measured under excitation of 340 nm.



**Figure S10.** (a) XRD patterns of fresh COF-JLU4 (black line), after recycling respond in the acidic solution (green line, intensity  $\times$  4), after recycling respond in the basic solution (red line, intensity  $\times$  4). (b) FT-IR spectra of of fresh COF-JLU4 (black line), after recycling respond in the acidic solution (green line), after recycling respond in the basic solution (red line).



**Figure S11.** Acid-base titration curve of COF-JLU4 (red) and first derivative curve (blue). The experimental pKa value for COF-JLU4 was approximately 6.45.

The pKa can be calculated via pH titration experiments.<sup>[1]</sup>

To achieve this, a 0.1 M NaOH solution was used to titrate a HCl polymer suspension. Equivalence points were obtained from the first derivative of the resulting titration curve of pH as a function of volume of titrant added, where the maximum points in the derivative curve correspond to inflection points and indicate equivalence points. pKa values were determined as the pH at one-half of the volume of titrant added to reach the equivalence point.

#### Reference

[1] R. C. Klet, Y. Liu, T. C. Wang, J. T. Hupp and O. K. Farha, *J. Mater. Chem. A*, 2016, 4, 1479-1485.