# **Electronic Supplementary Information**

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#### **General Methods**

A rotary evaporator was employed for concentrating organic solvents and dried under vacuum at <1 torr. Bruker FT AM400 (400 MHz for <sup>1</sup>H & 100 MHz for carbon) and FT AM500 (500 MHz for hydrogen & 125 MHz for <sup>13</sup>C) were employed for NMR spectroscopy. Chemical shifts ( $\delta$ ) were quoted based on the parent solvent peaks (CHCl<sub>3</sub> or (CH<sub>3</sub>)<sub>2</sub>SO) or TMS (tetramethylsilane) for 0 with part per million (ppm) units. The peak patterns of <sup>1</sup>H NMR spectra were assigned with standard abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Broad band decouplings were employed for fully H-C decoupled <sup>13</sup>C NMR. A triplet at 77.0 ppm for chloroform-*d* and a septet at 39.52 ppm for DMSO-*d*<sub>6</sub> were used for a reference peak in <sup>13</sup>C NMR spectra. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-7800F Prime operating at 5 kV. High-resolution transmission electron microscopy (HR-TEM) images obtained with a JEOL JEM-2100F microscope.

#### Materials

All reagents and solvents from commercial sources were used without further purifications unless otherwise mentioned. All chemicals were purchased from Sigma-Aldrich, TCI, Alfa-Aesar, Daejung, Samchun chemical companies.



#### **Overall Scheme for Target Ligand Synthesis**

D-II, BDCE-2,5-(NO<sub>2</sub>)(OH) E-II, BDCE-2,5-(NH<sub>2</sub>)(OH) 2, BDC-2,5-(NH<sub>2</sub>)(OH)

Scheme S1. Reaction schemes for BDC-2,3-(NH<sub>2</sub>)(OH) (1) and BDC-2,5-(NH<sub>2</sub>)(OH) (2).

#### **Detail Procedures of Ligand Synthesis**



Synthesis of 2-hydroxyterephthalic acid (BDC-OH, B)

BDC-NH<sub>2</sub> (**A**, 2.0 g, 11 mmol) were dissolved in H<sub>2</sub>O (30 mL). Then 2.0 g aqueous NaOH (50 wt%) solution was added to the suspension. After stirring of solution at 0 °C to clear solution, 1.2 g NaNO<sub>2</sub> (dissolved in 2 mL distill water) was added to the mixture. Then, the solution mixture was diluted with 16 mL of distilled water, and 8 mL of conc. HCl was slowly added. After HCl addition, the solution turns beige color. After stirring for 4 h at room temperature, CuSO<sub>4</sub> was added, and heated at 85 °C for 24 h. After completion, the solid was obtained by filtration and washed with distilled water (30 mL, 3 times). Target BDC-OH (**B**) was obtained as a colorless solid (1.8 g, 90%).

2-Hydroxyterephthalic acid (**B**): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500MHz, ppm.)  $\delta$  7.88 (1H, d, *J* = 8.15 Hz), 7.45 (1H, dd, *J* = 1.6 Hz), 7.42 (1H, d, *J* = 1.45 Hz); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz, ppm)  $\delta$  166.4, 160.6, 136.9, 130.8, 119.6, 117.8.



Synthesis of dimethyl 2-hydroxyterephthalate (BDCE-OH, C)

BDC-OH (**B**, 2.0 g, 11 mmol) were dissolved in MeOH (100 mL), and 5 mL conc.  $H_2SO_4$  was added to the solution. The mixture was stirred at 50 °C for 24 h. After completion (monitored by TCL), the solution was extracted with ethyl acetate and distill water. To the combined organic layer, MgSO<sub>4</sub> was added to remove residual water. After filtration to remove inorganic salts, the organic solvent was evaporated. The mixture solid was purified by column chromatography with SiO<sub>2</sub> (10% EtOAc/*n*-hexane) and the target product, dimethyl 2-hydroxyterephthalate (BDCE-OH, **C**, 1.3 g, 56%) were obtained.

Dimethyl 2-hydroxyterephthalate (**C**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  10.74 (1H, s), 7.90 (1H, d, *J* = 3.0 Hz), 7.63 (1H, d, *J* = 15.6 Hz), 7.52 (1H, dd), 3.98 (3H, s), 3.92 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  169.9., 166.0, 161.3, 136.4, 130.0, 119.7, 118.9, 115.7, 52.6, 52.5.



Synthesis of dimethyl 2-hydroxy-3-nitroterephthalate (BDCE-2,3-(NO<sub>2</sub>)(OH), **D-I**) and dimethyl 2-hydroxy-5-nitroterephthalate (BDCE-2,5-(NO<sub>2</sub>)(OH), **D-II**)

BDCE-OH (C, 1.0 g, 5 mmol) were dissolved in conc. H<sub>2</sub>SO<sub>4</sub> (30 mL) at 0 °C, and 60%

nitric acid (0.35 mL) was quickly added to solution mixture. And the solution was stirred at 0 °C for 5 min (Note: keeping reaction temperature at 0 °C is critical to obtain two regioisomers). After completion (monitored by TLC), the reaction was quenched by adding ice. The crude yellow solid mixture was purified by column chromatography with SiO<sub>2</sub> (5% EtOAc/*n*-hexane). Each target products, dimethyl 2-hydroxy-3-nitroterephthalate (BDCE-2,3-(NO<sub>2</sub>)(OH), **D-I**, 450 mg, 36%) and dimethyl 2-hydroxy-5-nitroterephthalate (BDCE-2,5-(NO<sub>2</sub>)(OH), **D-II**, 240 g, 20%), were obtained as pale-yellow solids.

Dimethyl 2-hydroxy-3-nitroterephthalate (**D-I**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  11.32 (1H, s), 8.01 (1H, d, *J* = 3.0 Hz), 7.47 (1H, d, *J* = 3.0 Hz), 4.03 (3H, s), 3.90 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  168.9, 162.9, 153.1, 140.1, 131.4, 128.7, 120.1, 117.6, 53.5, 53.4.

Dimethyl 2-hydroxy-5-nitroterephthalate (**D-II**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  11.41 (1H, s), 8.62 (1H, s), 7.14 (1H, s), 4.04 (3H, s), 3.94 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  168.7, 165.6, 165.3, 138.3, 135.8, 127.6, 118.7, 113.2, 53.6, 53.5.



Synthesis of dimethyl 2-amino-3-hydroxyterephthalate (BDCE-2,3-(NH<sub>2</sub>)(OH), **E-I**) and dimethyl 2-amino-5-hydroxyterephthalate (BDCE-2,5-(NH<sub>2</sub>)(OH), **E-II**)

BDCE-2,3-(NO<sub>2</sub>)(OH) or BDCE-2,5-(NO<sub>2</sub>)(OH) (**D-I** or **D-II**, 600 mg, 2.4 mmol) and 10 wt% Pd/C (60 mg) were poured in EtOH/EtOAc (EtOAc:EtOH = 4 mL:16 mL) mixture. The heterogeneous mixture was stirred for 24 h under H<sub>2</sub> atmosphere condition (by balloon) at 50 °C. After completion (monitored by TLC), the solid materials were removed by celite S5 filtration, and organic solvent was evaporated. The crude solid mixture was purified by column chromatography with SiO<sub>2</sub> (20% EtOAc/*n*-hexane) and the desired products, dimethyl 2-amino-3-hydroxyterephthalate (BDCE-2,3-(NH<sub>2</sub>)(OH), **E-I**, 320 mg, 60%) or dimethyl 2-amino-5-hydroxyterephthalate (BDCE-2,5-(NH<sub>2</sub>)(OH), **E-II**, 350 mg, 65%) were obtained as pale-yellow solids.

Dimethyl 2-amino-3-hydroxyterephthalate (**E-I**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  11.14 (1H, s), 7.35 (1H, d, *J* = 2.8 Hz), 7.04 (1H, d, *J* = 2.8 Hz), 5.92 (2H, s), 3.94 (3H, s), 3.88 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  170.9, 168.1, 150.4, 140.8, 120.1, 114.4, 113.2, 113.1, 52.6, 51.9.

Dimethyl 2-amino-5-hydroxyterephthalate (**E-II**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  9.75 (1H, s), 7.51 (1H, s), 7.2 (1H, s), 3.94 (3H, s), 3.88 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  169.6, 167.5, 151.3, 142.3, 118.9, 117.9, 117.6, 117.2, 52.6, 52.1.



Synthesis of 2-amino-3-hydroxyterephthalic acid (BDC-2,3-(NH<sub>2</sub>)(OH), **1**) and 2-amino-5hydroxyterephthalic acid (BDC-2,5-(NH<sub>2</sub>)(OH), **2**)

BDCE-2,3-(NH<sub>2</sub>)(OH) or BDCE-2,5-(NH<sub>2</sub>)(OH) (**E-I** or **E-II**, 225 mg, 1 mmol) was dissolved in anhydrous THF (5 mL), and 5 mL of a 4% LiOH aqueous solution was added to the THF solution. The solution was stirred at 66 °C for 24 h. After completion (monitored by TLC), the solvent was evaporated, and acidified with a 1.0 M HCI aqueous solution. The pale-

yellow precipitate was collected by filtration, and washed with distilled water for several times. After drying under vacuum, the target product was obtained; 2-amino-3-hydroxyterephthalic acid (BDC-2,3-(NH<sub>2</sub>)(OH), **1**, 150 mg, 76%) and 2-amino-5-hydroxyterephthalic acid (BDC-2,5-(NH<sub>2</sub>)(OH), **2**, 170 mg, 86%).

2-Amino-3-hydroxyterephthalic acid (1): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500MHz, ppm.)  $\delta$  7.27 (1H, d, J = 2.9 Hz), 6.93 (1H, d, J = 2.9 Hz); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz, ppm)  $\delta$  172.4, 169.2, 150.0, 141.3, 120.1, 113.4, 113.3, 112.3; HR-MS Calculated for [M-H]<sup>-</sup>, C<sub>8</sub>H<sub>6</sub>NO<sub>5</sub><sup>-</sup> 196.0251, Found: 196.0251.

2-Amino-5-hydroxyterephthalic acid (**2**): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500MHz, ppm.) δ 7.24 (1H, s), 7.14 (1H, s); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz, ppm) δ 170.8, 168.6, 149.4, 143.1, 120.1, 117.8, 117.3, 115.8; HR-MS Calculated for [M-H]<sup>-</sup>, C<sub>8</sub>H<sub>6</sub>NO<sub>5</sub><sup>-</sup> 196.0251, Found: 196.0251.

#### **Detail Procedures for MOF Synthesis**

Preparation of UiO-66-2,3-(NH<sub>2</sub>)(OH)

COOH  $ZrOCl_2 \cdot 8H_2O$ OH formic acid, DMF,  $H_2O$  $NH_2$  120 °C, 3 h, reflux  $UiO-66-2,3-NH_2OH$ 

BDC-2,3-(NH<sub>2</sub>)(OH) (**1**, 56.3 mg, 0.25 mmol) and ZrOCl<sub>2</sub>•8H<sub>2</sub>O (80.6 mg, 0.25 mmol) were dissolved in 2.5 mL of formic acid. To this solution mixture, H<sub>2</sub>O (0.25 mL) and DMF (2.5 mL) were added. The solution was heated and stirred at 120 °C. After 3 h reaction, the mixture was cooled to room temperature. The resulting crude powder mixture was washed with distilled water (5 mL, 3 times) with centrifugation. Then, MOF material was washed by MeOH (5 mL) over three days (for solvent exchange), replacing the old MeOH with fresh MeOH for every 24 h.

Preparation of UiO-66-2,5-(NH<sub>2</sub>)(OH)



BDC-2,5-(NH<sub>2</sub>)(OH) (**2**, 56.3 mg, 0.25 mmol) and ZrOCl<sub>2</sub>•8H<sub>2</sub>O (80.6 mg, 0.25 mmol) were dissolved in 2.5 mL of formic acid. To this solution mixture, H<sub>2</sub>O (0.25 mL) and DMF (2.5 mL) were added. The solution was heated and stirred at 120 °C. After 3 h reaction, the mixture was cooled to room temperature. The resulting crude powder mixture was washed with distilled water (5 mL, 3 times) with centrifugation. Then, MOF material was washed by MeOH (5 mL) over three days (for solvent exchange), replacing the old MeOH with fresh MeOH for every 24 h.

#### **Detail Procedures for PSMs**





BDCE-2,3-(NH<sub>2</sub>)(OH) (**E-I**, 56.3 mg, 0.25 mmol) was mixed with CH(OEt)<sub>3</sub> (0.7 mL) in microwave reactor vial, and stirred in the microwave reactor at 100 °C for 1 h. After completion (monitored by TLC), the solid mixture was with MeOH, and then crude solid was purified by column chromatography with SiO<sub>2</sub> (30% EtOAc/*n*-hexane) and the desired product, dimethyl benzo[d]oxazole-4,7-dicarboxylate (**F**, 87 mg, 77%) were obtained.

Dimethyl benzo[*d*]oxazole-4,7-dicarboxylate (**F**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  8.35 (1H, s), 4.06 (3H, s), 4.03 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  164.8 163.7, 154.8, 149.5, 140.6, 127.3, 126.9, 126.6, 118.8, 52.9, 52.8; HR-MS Calculated for [M+Na]<sup>+</sup>, C<sub>11</sub>H<sub>9</sub>NNaO<sub>5</sub><sup>+</sup> 258.0373, Found: 258.0377.

Preparation of Ligand G: Formamide Formation on Ligand Status



BDCE-2,5-(NH<sub>2</sub>)(OH) (**E-II**, 56.3 mg, 0.25 mmol) was mixed with CH(OEt)<sub>3</sub> (0.7 mL) in microwave reactor vial, and stirred in the microwave reactor at 100 °C for 1 h. After completion (monitored by TLC), the solid mixture was with MeOH, and then crude solid was purified by column chromatography with SiO<sub>2</sub> (30% EtOAc/*n*-hexane) and the desired product, dimethyl 2-formamido-5-hydroxyterephthalate (**G**, 75 mg, 63%) were obtained.

Dimethyl 2-formamido-5-hydroxyterephthalate (**G**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz, ppm.)  $\delta$  10.51 (1H, s), 9.16 (1H, s) 8.46 (1H, d), 7.65 (1H, s), 3.98 (3H, s), 3.95 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm)  $\delta$  169.8, 167.5, 159.2, 156.4, 131.5, 122.7, 122.1, 119.8, 116.8, 53.0, 29.8; HR-MS Calculated for [M+Na]<sup>+</sup>, C<sub>11</sub>H<sub>11</sub>NNaO<sub>6</sub><sup>+</sup> 276.0479, Found: 276.0479.

Preparation of UiO-66-Benzoxazole through PSM



UiO-66-2,3-(NH<sub>2</sub>)(OH) (18.5 mg, 0.01 mmol) was added to CH(OEt)<sub>3</sub> (0.12 mL, 0.6 mmol) in microwave reactor vial, and NaCN (3mg, 0.06 mmol) was added to mixture. After performing microwave irradiation at 100 °C for 12 h, MOF materials (UiO-66-Benzoxazole) were washed with MeOH for several times by centrifugation, and dried under vacuum for further analysis.



UiO-66-2,5-(NH<sub>2</sub>)(OH) (18.5 mg, 0.01 mmol) was added to CH(OEt)<sub>3</sub> (0.12 mL, 0.6 mmol) in a microwave reactor vial, and microwave irradiation was performed at 180 °C for 3 h. After completion, MOF materials (UiO-66-2,5-(Formamide)(OH)) were washed with MeOH for several times by centrifugation, and dried under vacuum for further analysis.

#### **MOF** characterization

#### Acid Digestion of UiO-66 Series for <sup>1</sup>H NMR Analysis

Fully dried (under vacuum) UiO-66 MOF (approximately 10-20 mg) was poured into 590  $\mu$ L of DMSO-*d*<sub>6</sub>, and 10  $\mu$ L of HF was added to the solution mixture. The mixture was sonicated until obtaining clear solution.

#### Thermogravimetric Analysis (TGA)

Fully dried (under vacuum) UiO-66 MOF (*e.g.*, after BET analysis) around 10 mg was used for thermogravimetric analysis. Running temperature range was room temperature to 800 °C with N<sub>2</sub> stream (scan rate of 5 °C/min).

#### Powder X-ray Diffraction (PXRD)

Fully dried (under vacuum) UiO-66 MOF (approximately 10-20 mg) was used for PXRD analysis. PXRD data were collected on a Rigaku Miniflex (40 kV, 40 mA for CuKa ( $\lambda$  = 1.5406 Å)) with a 20 range of 5-30° at ambient condition.



Fig. S1 <sup>1</sup>H NMR spectra of (a) UiO-66-2,3-(NH<sub>2</sub>)(OH) and (b) UiO-66-2,5-(NH<sub>2</sub>)(OH) after acid digestion.



Fig. S2 N<sub>2</sub> sorption isotherms at 77K and Brunauer-Emmett-Teller surface area for (a) UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-2,5-(NH<sub>2</sub>)(OH), (c) UiO-66-Benzox, and (d) UiO-66-2,5-(Formamide)(OH).



**Fig. S3** Non-local density functional theory (NLDFT) pore size distribution for (a) UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-2,5-(NH<sub>2</sub>)(OH), (c) UiO-66-Benzox, and (d) UiO-66-2,5-(Formamide)(OH).



Fig. S4 SEM images of (a) UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-2,5-(NH<sub>2</sub>)(OH), (c) UiO-66-Benzox, and (d) UiO-66-2,5-(Formamide)(OH).



**Fig. S5** HR-TEM images of (a) UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-2,5-(NH<sub>2</sub>)(OH), (c) UiO-66-Benzox, and (d) UiO-66-2,5-(Formamide)(OH).



Fig. S6 TGA traces of (a) UiO-66-2,3-(NH<sub>2</sub>)(OH) and (b) UiO-66-2,5-(NH<sub>2</sub>)(OH).



Scheme S2. Ring-opening of benzoxazoles under acidic or basic conditions. S1,S2



**Fig. S7** <sup>1</sup>H NMR spectra (after acid digestion) of (a) UiO-66-Benzox after PSM of UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-(Formamide)(OH) after PSM of UiO-66-2,5-(NH<sub>2</sub>)(OH).



**Fig. S8** TGA traces of (a) UiO-66-Benzox after PSM of UiO-66-2,3-(NH<sub>2</sub>)(OH), (b) UiO-66-(Formamide)(OH) after PSM of UiO-66-2,5-(NH<sub>2</sub>)(OH).



**Scheme S3**. Triethyl orthoformate reactions with BDCE-2,3-(NH<sub>2</sub>)(OH) and BDCE-2,5-(NH<sub>2</sub>)(OH).

### **References for ESI**

S1. R. S. Sanchez, F. A. Zhuravlev, J. Am. Chem. Soc. 2007. 129, 5824.

S2. J. M, R. Merugu, Asian J. Pharm. Clin. Res. 2017, 10, 48.

# Appendix

# <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR data for obtained compounds

# 2-Hydroxyterephthalic acid (BDC-OH, B)













# Dimethyl 2-hydroxy-3-nitroterephthalate (BDCE-2,3-(NO<sub>2</sub>)(OH), D-I)





Dimethyl 2-hydroxy-5-nitroterephthalate (BDCE-2,5-(NO<sub>2</sub>)(OH), D-II)





# Dimethyl 2-amino-3-hydroxyterephthalate (BDCE-2,3-(NH<sub>2</sub>)(OH), E-I)





Dimethyl 2-amino-5-hydroxyterephthalate (BDCE-2,5-(NH<sub>2</sub>)(OH), E-II)



# 2-Amino-3-hydroxyterephthalic acid (BDC-2,3-(NH<sub>2</sub>)(OH), 1)











# Dimethyl benzo[d]oxazole-4,7-dicarboxylate (F)







Dimethyl 2-formamido-5-hydroxyterephthalate (G)

90 80 70 60 50 40 30 20 10 (

150 140 130 120 110 100 f1 (ppm)

0 190 180 170 160

