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Supporting Information

Rational Design on the MOFs Constructed from Modified Aromatic Amino Acids

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Ligand Synthesis:

Compound R-B (2R-acetylamino-3-(4-nitro-phenyl)-propionic acid methyl ester): A mixture of R-**A** (2R-amino-3-(4-nitro-phenyl)-propionic acid methyl ester hydrochloride salt) (1.9 g, 7.3 mmol), acetyl chloride (0.60 mL), CH_2Cl_2 (25 mL), Et_3N (2.4 mL) was stirred at 0 °C for 1 hour. The resulting mixture was washed with water and dried with $MgSO_4$, and the solvents were evaporated in vacuum. The yellow oil was purified by column chromatography (petroleum ether/ethyl acetate = 20/80) to give pure product R-**B** as yellow solid in 95 % yield. S-**B** and R, S-**B** were obtained under the same process. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 2.01 (s, 3H), 3.15-3.33 (m, 2H), 3.76 (s, 3H), 4.89-4.96 (m, 1H), 6.04 (d, 1H), 7.30 (d, 2H), 8.17 ppm (d, 2H). FT-IR (KBr): n bar = 3279, 1737, 1645, 1551, 1518, 1347, 1281, 1233, 1179, 704, 524 cm^{-1}.

Compound R-C (2R-acetylamino-3-(4-amino-phenyl)-propionic acid methyl ester): A mixture of R-**B** (1.3 g, 5.0 mmol), 10 % Pd/C (0.25g), CH_3OH (20 mL), $HCOONH_4$ (1.5 g, 23 mmol) was stirred in N_2 at 25 °C for 5 hours. Then the mixture was filtered and the organic solvent was evaporated in vacuum. Water was added into the mixture and CH_2Cl_2 was used to extract the aqueous layer. The resulting organic phase was dried with $MgSO_4$, and the solvents were evaporated in vacuum. The crude product was purified by column chromatography (ethyl acetate) to give pure product R-**C** as yellow oil in 65 % yield. S-**C** and R, S-**C** were obtained under the same process. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 1.82 (s, 2H), 1.97 (s, 3H), 3.00 (d, 2H), 3.47 (s, 2H), 3.72 (s, 3H), 4.79-4.81 (m, 1H), 5.92 (d, 1H), 6.61 (d, 2H), 6.87 ppm (d, 2H). ^{1}H-NMR (300 MHz, D_2O, 25 °C, TMS): d = 1.92 (s, 3H), 2.86-3.08 (m, 2H), 3.70 (s, 3H), 4.54-4.59 (m, 1H), 6.78 (d, 2H), 7.05 ppm (d, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 23.15, 37.10, 52.30, 53.40, 115.39, 125.56, 130.16, 145.49, 169.77, 172.43 ppm. FT-IR (KBr): n bar = 3423, 1743, 1656, 1543, 1374, 1218, 1014, 701, 597 cm^{-1}. HPLC (OD-H

chiral column, isopropyl alcohol/n-hexane=30/70, V = 0.5 ml/min): R. T of R-**C** = 23.8 min, R. T of S-**C** = 29.1 min.

Compound R-E (3E- [5-(2R-acetylamino-2-methoxycarbonyl-ethyl) -2-methoxy-phenyl]- acrylic acid methyl ester): A mixture of R-**D** (2R -acetylamino-3-(3-iodo -4-methoxy -phenyl)- propionic acid methyl ester) (0.56 g, 1.5 mmol), acrylic acid methyl ester (0.24 g, 2.8 mmol), $Pd(OAc)_2$ (0.016 g, 0.070 mmol), PPh_3 (0.037 g, 0.14 mmol), DMF (10 mL), Et_3N (1.0 mL) was stirred in N_2 at 120 °C for 10 hours. Then the mixture was filtered and the organic solvent was evaporated in vacuum. Water was added into the mixture and $CHCl_3$ was used to extract the aqueous layer. The resulting organic phase was dried with $MgSO_4$, and the solvents were evaporated in vacuum. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 30/70) to give pure product R-**E** as yellow solid in 58 % yield. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 2.00 (s, 3H), 3.00-3.10 (m, 2H), 3.74 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 4.84-4.87 (m, 1H), 5.98 (d, 1H), 6.46 (d, 1H), 6.82 (d, 1H), 7.10 (d, 1H), 7.20 (s, 1H), 7.90 ppm (d, 1H). FT-IR (KBr): n bar = 3311, 2953, 1745, 1713, 1652, 1552, 1500, 1434, 1375, 1329, 1274, 1252, 1191, 1169, 1121, 1027, 989, 864, 815, 707, 605, 534 cm^{-1}.

Compound R-F (3E-[5-(2R-amino-2-carboxy-ethyl)-2-methoxy-phenyl]-acrylic acid): A mixture of R-**E** (1.2 g, 3.4 mmol), 2M NaOH (15 mL), CH_3OH (20 mL), was stirred in N_2 at 110 °C for 16 hours. Then the HCl was added into the solution to mediate the pH value to 4. The white precipitates R-**F** in 35 % yield was filtered and dried in air. The solubility of R-**F** and its' potassium salt in general organic solvent is not good, so it could not be testifies by our HPLC system. $[a]_R^{20}$ = + 0.23°. ^{1}H-NMR (300 MHz, D_2O, 25 °C, TMS) of the potassium salt of R-**F**: d = 2.77-3.00 (m, 2H), 3.51 (t, 1H), 3.92 (s, 3H), 6.53 (d, 1H), 7.06 (d, 2H), 7.29 (d, 2H), 7.49 (s, 1H), 7.65 ppm (d, 2H). FT-IR (KBr): n bar = 3417, 2947, 1694, 1633, 1496, 1404, 1319, 1251, 1181, 1120, 1028, 987, 870, 816, 559 cm^{-1}.

Compound R-G (2R-(methoxycarbonylmethyl-amino)-3-(4-nitro-phenyl)-propionic acid methyl ester): A mixture of R-**A** (2R-amino-3-(4-nitro-phenyl)-propionic acid methyl ester hydrochloride salt) (1.0 g, 3.8 mmol), methyl chloroacetate (0.45 mL), CH_3CN (30 mL), K_2CO_3 (1.1 g, 8.0 mmol) was stirred in N_2 at 50 °C for 3 days. Then the mixture was filtered and the organic solvent was evaporated in vacuum. Water was added into the mixture and CH_2Cl_2 was used to extract the aqueous layer. The organic phase was washed with water and dried with $MgSO_4$, and the solvents were evaporated in vacuum. The yellow oil was purified by column chromatography (petroleum ether/ethyl acetate = 50/50) to give pure product R-**G** as yellow solid in 45 % yield. R, S-**G** was obtained under the same process. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 2.05 (s, 1H), 3.06-3.12 (m, 2H), 3.39-3.40 (d, 2H), 3.63 (t, 1H), 3.69 (s, 3H), 3.70 (s, 3H), 7.40 (d, 2H), 8.17 ppm (d, 2H). FT-IR (KBr): n bar = 3342, 2955, 1736, 1604, 1520, 1364, 1205, 1016, 857, 748, 699 cm^{-1}.

Compound R-H (3-(4-amino-phenyl)-2R-(methoxycarbonylmethyl-amino)-propionic acid methyl ester): A mixture of R-**G** (0.30 g, 1.0 mmol), 10 % Pd/C (0.20g), CH_3OH (10 mL), $HCOONH_4$ (0.30 g, 4.8 mmol) was stirred in N_2 at 25 °C for 5 hours. Then the mixture was filtered and the organic solvent was evaporated in vacuum. Water was added into the mixture and CH_2Cl_2 was used to extract the aqueous layer. The resulting organic phase was dried with $MgSO_4$, and the solvents were evaporated in vacuum. The crude product was purified by column chromatography (ethyl acetate) to give pure product R-**H** as yellow oil in 58 % yield. R, S-**H** was obtained under the same process. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 2.83-2.99 (m, 2H), 3.03 (s, 3H), 3.42 (d, 2H), 3.56 (t, 1H), 3.68 (s, 3H), 3.70 (s, 3H), 6.62 (d, 2H), 6.98 ppm (d, 2H). ^{1}H-NMR (300 MHz, D_2O, 25 °C, TMS): d = 2.95 (d, 2H), 3.45 (d, 2H), 3.67 (t, 1H), 3.71 (s, 3H), 3.74 (s, 3H), 6.82 (d, 2H), 7.07 ppm (d, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): d = 38.57, 48.94, 51.68, 51.72, 62.26, 115.19, 126.33, 129.94, 145.27, 172.01, 174.14 ppm. FT-IR (KBr): n bar = 3365, 2952, 1735, 1626, 1518, 1437, 1205, 1017, 825 cm^{-1}. HPLC (OD-H

chiral column, isopropyl alcohol/n-hexane=30/70, V = 0.5 ml/min): R. T of R-**H** = 51.8 min, R. T of S-**H** = 43.5 min.

Powder X-ray Diffraction:

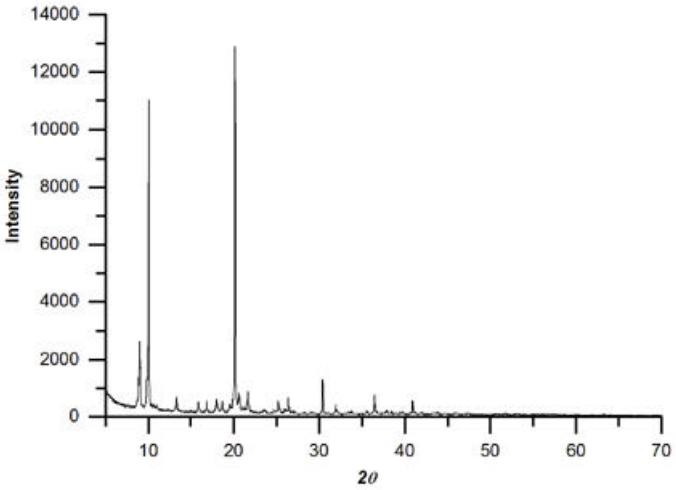

Figure S1. PXRD of compound R-**1**.

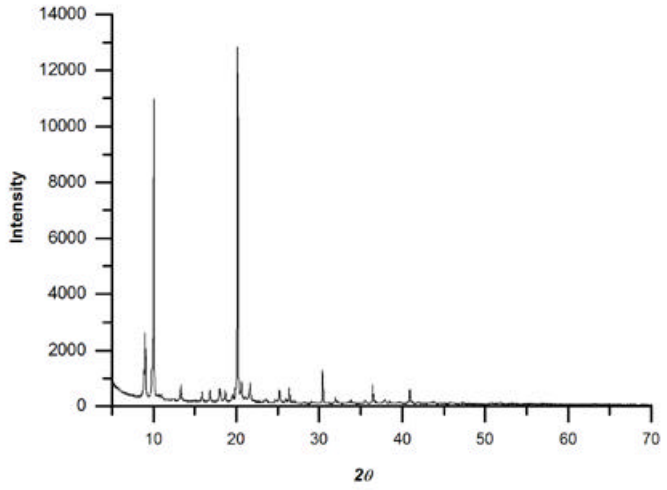

Figure S2. PXRD of inversion twin of compound R-**1**.

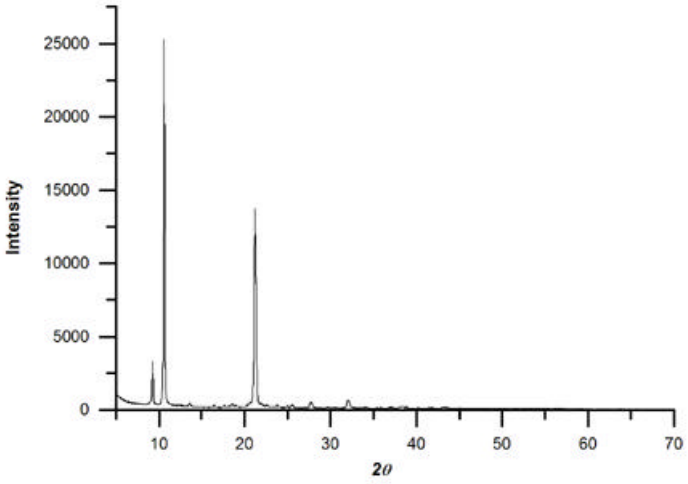

Figure S3. PXRD of compound S-**2**.

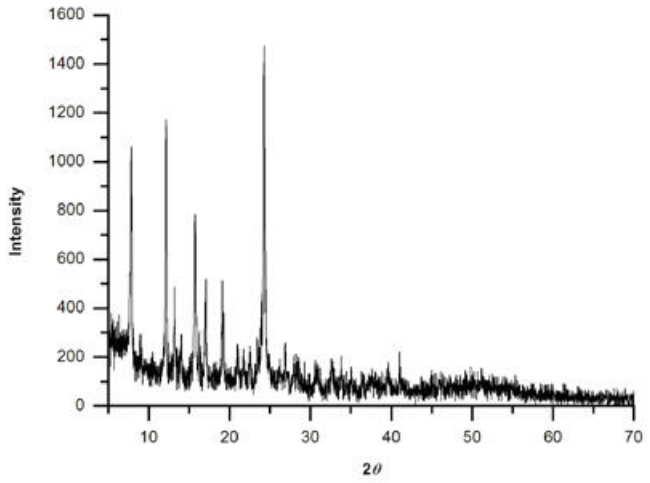

Figure S4. PXRD of compound R,S-**3**.

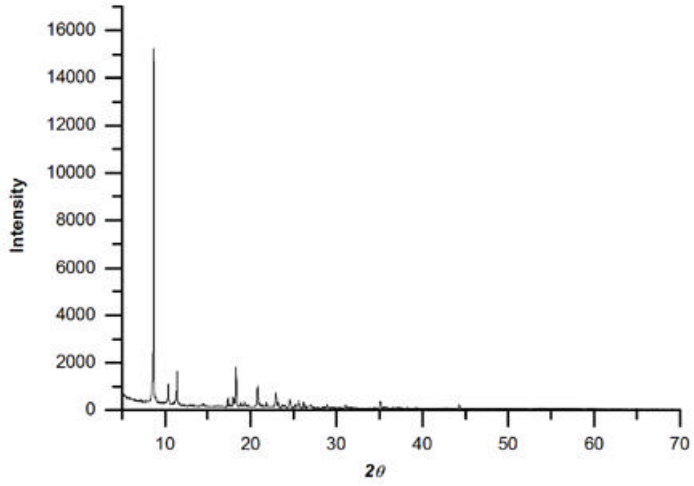

Figure S5. PXRD of compound R-**4**.