Supporting Information

Phenothiazine-dioxide-based Cu-MOFs: Preserving Porosity through the Incorporations of Substituents into Organic Linkers

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General procedures

¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were measured in CDCl₃ and dimethylsulfoxide- d_6 on a JEOL JNM ECS-400SS spectrometer. A signal arising from residual CHCl₃ (7.26 ppm) in CDCl₃ and C₂D₅HSO in DMSO- d_6 were used as an internal standard for the ¹H NMR spectra. Powder X-ray powder diffraction (PXRD) patterns were recorded on a Rigaku Miniflex (scanning range: 3-40°; scanning increments: 0.01°). IR spectra were recorded in a JASCO FT/IR-4200 type A Fourier transform infrared spectrometers with KBr pellets. Gas Sorption isotherms for pressures in the range 0-1.0 bar were measured by a volumetric method using Micromeritics Tristar-II instruments. >99.999% purity He, H₂, CO₂ and N₂ were used for all measurements. >99.999% H₂ gas was generated0 by Yanaco RHG-200 hydrogen generator. A typical sample of 30-100 mg of Cu-ArPTDO was transferred to a preweighed analysis tube and evacuated by heating at 135 °C under dynamic vacuum for 6 h. The evacuated analysis port of the gas sorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas. Nitrogen gas sorption isotherms at 77 K were measured in liquid nitrogen. BET surface areas were determined from N₂ adsorption data at 77 K using Micromeritics software. The heat of adsorption can be directly calculated for each isostere on plot by using a derivation of the van't Hoff equation:

$$\ln\left(P\right) = \frac{-\Delta(H)}{RT} + \frac{\Delta S}{R}$$

where: *H* is heat of adsorption in kJ/mol, *S* is entropy of sorption in kJ/mol*K, *P* is the pressure in Torr, and *R* is the gas constant, 0.0083144 kJ/mol*K.

Ligand Synthesis



1-1. 1,4-di(10H-phenothiazin-10-yl)benzene (R = H)

Under nitrogen atmosphere, dry toluene solution (100 mL) of 1,4-dibromobenzene (1.35 g, 5.72 mmol), Pd₂dba₃ (0.23 g, 0.25 mmol), *t*Bu₃PHBF₄ (0.073 g, 0.25 mmol), NaO*t*Bu (2.88 g, 30.0 mmol), and phenothiazine (2.2 g, 11.0 mmol) were stirred at 100 °C for 24 h. The mixture was cooled to room temperature, quenched with 1N HCl aq. and diluted with CHCl₃ then filtered through Celite. The organic layer was washed with brine and dried over MgSO₄. After removal solvent, the resulting residue was purified by SiO2 column chromatography (CHCl₃ : Hexane = 1 : 1) afford to 1,4-di(10H-phenothiazin-10-yl)benzene (**HPT**) as a colorless solid (2.60 g, 5.50 mmol, 96.2%). ¹H-NMR (396 MHz, CHLOROFORM-D) δ 1.78 (s, 4H), 1.41 (dd, *J* = 7.5, 1.6 Hz, 4H), 1.30-1.26 (m, 4H), 1.20 (td, *J* = 7.5, 1.1 Hz, 4H), 0.80 (dd, *J* = 8.2, 1.4 Hz, 4H). HRMS (DART) found: *m/z* 473.1106 ([M+H]⁺). Calcd for C₃₀H₂₀N₂S₂: 473.1146 ([M+H]⁺).

1-2. 10,10'-(2,5-dimethyl-1,4-phenylene)bis(10H-phenothiazine) (R = Me)

The procedure for **HPT** was followed: 1,4-dibromo-2,5-dimethylbenzene (1.25 g, 5.00 mmol), Pd_2dba_3 (0.11 g, 0.125 mmol), tBu_3PHBF_4 (0.036 g, 0.125 mmol), NaOtBu (1.44 g, 15.0 mmol), and phenothiazine (1.1 g, 5.5 mmol) and toluene 50 mL The crude mixture was purified by SiO2 column chromatography yielding pure **MePT** as colorless powder (1.02 g, 2.00 mmol, 80.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.46 (s, 2H), 7.01-6.99 (m, 4H), 7.55-7.51 (m, 6H), 6.90 (m, 4H), 6.84-6.82 (m, 4H), 6.14, 6.12 (dd, *J* = 1.2, 1.6 Hz, 4H), 2.25 (s, 6H). HRMS (DART) found: *m/z* 501.1461 ([M+H]⁺). Calcd for $C_{32}H_{24}N_2S_2$: 501.1459 ([M+H]⁺).

1-3. 10,10'-(2,5-dimethoxy-1,4-phenylene)bis(10H-phenothiazine) (R = MeO)

The procedure for **HPT** was followed: 1,4-dibromo-2,5-dimethoxybenzene (0.66 g, 2.5 mmol), Pd_2dba_3 (0.23 g, 0.25 mmol), tBu_3PHBF_4 (0.073 g, 0.25 mmol), NaOtBu (2.88 g, 30.0 mmol), and phenothiazine (2.2 g, 11.0 mmol) and toluene 100 mL The crude mixture was purified by SiO2 column chromatography yielding pure **MeOPT** as colorless powder (0.55 g, 1.02 mmol, 20.5%). 1H NMR (400 MHz, CDCl3): $\delta7.19$ (s, 2H), 7.06-7.04 (m, 4H), 6.96-6.93 (m, 4H), 6.87-6.84 (m, 4H), 6.21, 6.19 (d, J = 0.08, 1.2, 4H), 3.74 (s, 6H) HRMS (DART) found: m/z 533.1339 ([M+H]⁺). Calcd for $C_{32}H_{24}N_2O_2S_2$: 533.1357 ([M+H]⁺).

1-4. 10,10'-(2,5-diisopropyl-1,4-phenylene)bis(10H-phenothiazine) (R = *i*Pr)

The procedure for **HPT** was followed: 1,4-dibromo-2,5-diisopropylbenzene (0.96 g, 3.00 mmol), Pd_2dba_3 (0.14 g, 0.15 mmol), tBu_3PHBF_4 (0.044 g, 0.15 mmol), NaOtBu (1.73 g, 18.0 mmol), and phenothiazine (1.32 g, 6.6 mmol) and toluene 30 mL The crude mixture was purified by SiO₂ column chromatography yielding pure *i***PrPT** as colorless powder (1.14 g, 2.05 mmol, 68.3%). ¹H NMR (400 MHz, CDCl3): δ 7.50 (s, 2H), 7.04-7.02 (m, 4H), 6.93-6.89 (m, 4H), 6.85-6.82 (m, 4H), 6.16 (d, J = 8.0 Hz, 4H), 3.41-3.37 (m, 2H), 1.11 (d, J = 6.8 Hz, 12H). HRMS (DART) found: *m/z* 557.2108 ([M+H]⁺). Calcd for C₃₆H₃₂N₂S₂: 557.2085 ([M+H]⁺).

1-5. 10,10'-(2,5-di-tert-butyl-1,4-phenylene)bis(10H-phenothiazine) (R = *t*Bu)

The procedure for **HPT** was followed: 1,4-dibromo-2,5-di-*tert*-butylbenzene (1.54 g, 4.4 mmol), Pd₂dba₃ (0.20 g, 0.22 mmol), tBu_3PHBF_4 (0.064 g, 0.22 mmol), NaOtBu (2.50 g, 26.4 mmol), and phenothiazine (1.99 g, 10.0 mmol) and dioxane 50 mL The crude mixture was purified by SiO₂ column chromatography yielding pure *t*BuPT as colorless powder (0.256 g, 0.44 mmol, 9.9 %). ¹H NMR (400 MHz, CDCl₃): δ 7.45 (s, 2H), 7.15-7.13 (m, 4H), 6.97-6.95 (m, 4H), 6.92-6.90 (m, 4H), 6.25 (dd, *J* = 1.2, 1.2 Hz, 4H), 1.33 (s, 18H). HRMS (DART) found: *m/z* 585.2352 ([M+H]⁺). Calcd for C₃₈H₃₆N₂S₂: 585.2398 ([M+H]⁺).

1-6. 10,10'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(10H-phenothiazine) (DurPT)

The procedure for **HPT** was followed: 9,10-dibromodurene (0.88 g, 3.0 mmol), Pd₂dba₃ (0.174 g, 0.19 mmol), *t*Bu₃PHBF₄ (0.055 g, 0.15 mmol), NaO*t*Bu (1.73 g, 18.0 mmol), and phenothiazine (1.31 g, 6.60 mmol) and dioxane 60 mL The crude mixture was purified by SiO₂ column chromatography yielding pure **DurPT** as pale yellow powder (1.04 g, 1.97 mmol, 65.7 %). ¹H NMR (400 MHz, CDCl₃): δ 6.94- 6.96 (m, 4H), 6.79- 6.87 (m, 4H), 6.76- 6.80 (m, 4H), 5.91 (d, *J* = 7.9 Hz, 4H), 2.23(s, 12H). HRMS (ESI) found: *m/z* 529.1781 ([M+H]⁺). Calcd for C₃₄H₂₈N₂S₂: 529.1772 ([M+H]⁺).

1-7. 9,10-di(10H-phenothiazin-10-yl)anthracene (AntPT)

The procedure for **HPT** was followed: 9,10-dibromoanthracene (2.2 g, 6.6 mmol), Pd_2dba_3 (0.137 g, 0.15 mmol), tBu_3PHBF_4 (0.044 g, 0.15 mmol), NaOtBu (1.73 g, 18.0 mmol), and phenothiazine (0.96 g, 3.00 mmol) and dioxane 30 mL The crude mixture was purified by SiO₂ column chromatography yielding pure **AntPT** as pale yellow powder (1.05 g, 1.83 mmol, 61.1 %). ¹H NMR (400 MHz, CDCl₃): δ 8.45-8.42 (m, 4H), 7.56-7.53 (m, 4H), 7.11-7.09 (m, 4H), 6.83-6.79 (m, 4H), 6.83-6.79 (m, 4H), 5.85-5.83 (m, 4H).

HRMS (DART) found: *m*/*z* 573.1486 ([M+H]⁺). Calcd for C₃₈H₂₄N₂S₂: 573.1459 ([M+H]⁺).



2-1. 1,1',1'',1'''-(1,4-phenylenebis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = H)

Acetyl chloride (1.96 g, 25.0 mmol) was added dropwise to dichloromethane suspension (20 mL) of AlCl₃ (1.67 g, 12.5 mmol) at room temperature. Solution of **HPT** in 20 mL of dichloromethane was added to the reaction mixture at 0 °C. After the stirring at room temperature for 3 h, the reaction mixture was poured into H₂O to precipitate the product. Vacuum filtration afforded **Ac₄HPTDO** (1.30 g, 1.84 mmol, 92.2%) as an orange solid. m.p. >300 °C, ¹H-NMR (396 MHz, CHLOROFORM-D) δ 7.72 (s, 4H), 7.65 (d, J = 1.8 Hz, 4H), 7.55 (d, J = 9.1 Hz, 4H), 6.24 (d, J = 8.6 Hz, 4H), 2.50 (d, J = 12.7 Hz, 12H).

2-2. 1,1',1'',1'''-((2,5-dimethyl-1,4-phenylene)bis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = Me)

The procedure for Ac4HPTDO was followed: MePT (0.750 g, 1.50 mmol), acetylchloride (1.47 g, 6.00 mmol), AlCl₃ (1.33 g, 10.0

mmol), and dichloromethane 12 mL. The crude mixture was washed with MeOH yielding pure **MemCBAc₄** as colorless powder (0.826 g, 1.13 mmol, 75.1%). ¹H NMR (400 MHz, CDCl₃): δ 7.59 (s, 4H), 7.53-7.48 (m, 6H), 6.06 (d, *J* = 8.8 Hz, 4H), 2.51 (s, 12H), 2.26 (s, 6H).

2-3. 1,1',1'',1'''-((2,5-dimethoxy-1,4-phenylene)bis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = MeO)

The procedure for Ac₄HPTDO was followed: MeOPT (533 g, 1.0 mmol), acetylchloride (1.08 g, 12.5 mmol), AlCl₃ (0.85 g, 6.25 mmol), and dichloromethane 10 mL. The crude mixture was washed with MeOH yielding pure Ac₄MeOPTDO as a yellow powder (0.533 g, 0.697 mmol, 69.7%). ¹H NMR (400 MHz, CDCl₃): δ 7.64 (s, 4H), 7.56 (d, *J* = 8.8 Hz, 4H), 7.20 (s, 2H), 6.14 (d, *J* = 8.8 Hz, 4H), 3.78 (s, 6H), 2.52 (s, 12H).

2-4. 1,1',1''-((2,5-diisopropyl-1,4-phenylene)bis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = *i*Pr)

The procedure for Ac₄HPTDO was followed: *i*PrPT (0.557 g, 1.00 mmol), acetylchloride (1.57 g, 20.0 mmol), AlCl₃ (1.33 g, 10.0 mmol), and dichloromethane 30 mL. The crude mixture was washed with MeOH yielding pure Ac₄*i*PrPTDO as a yellow powder (0.680 g, 0.862 mmol, 86.2%). M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (s, 4H), 7.53-7.49 (m, 6H), 6.08 (d, *J* = 8.8 Hz, 4H), 3.32-3.25 (m, 2H), 2.51 (s, 12H), 1.15-1.13 (m, 12H).

2-5. 1,1',1'',1'''-((2,5-di-tert-butyl-1,4-phenylene)bis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = tBu)

The procedure for Ac₄HPTDO was followed: *t*BuPT (0.426 g, 0.728 mmol), acetylchloride (0.785 g, 10.0 mmol), AlCl₃ (0.655 g, 5.0 mmol), and dichloromethane 10 mL. The crude mixture was washed with MeOH yielding pure Ac₄*t*BuPTDO as a yellow powder (0.467 g, 0.572 mmol, 78.5%). ¹H NMR (400 MHz, CDCl₃): δ 7.23 (s, 4H), 7.46 (s, 2H), 6.18 (d, *J* = 8.8 Hz, 4H), 2.54 (s, 12H), 1.34 (s, 18H).

2-6. 1,1',1'',1'''-((2,3,5,6-tetramethyl-1,4-phenylene)bis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = Dur)

The procedure for Ac₄HPTDO was followed: DurPT (0.529 g, 1.00 mmol), acetylchloride (0.985 g, 12.5 mmol), AlCl₃ (0.835 g, 6.25 mmol), and dichloromethane 20 mL. The crude mixture was washed with MeOH yielding pure Ac₄DurPTDO as a yellow powder (0.460 g, 0.600 mmol, 60%). ¹H NMR (400 MHz, CDCl₃): δ 1.94 (s, 12H), 7.00 (d, *J* = 9.1 Hz, 4H), 8.21 (d, *J* = 8.3 Hz, 4H), 8.63 (s, 4H).

2-7. 1,1',1'',1'''-(anthracene-9,10-diylbis(5,5-dioxido-10H-phenothiazine-10,3,7-triyl))tetrakis(ethan-1-one) (R = Ant) The procedure for Ac₄HPTDO was followed: AntPT (0.400 g, 0.700 mmol), acetylchloride (0.785 g, 10.0 mmol), AlCl₃ (0.655 g, 5.0 mmol), and dichloromethane 10 mL. The crude mixture was washed with MeOH yielding pure Ac₄AntPTDO as a yellow powder (0.486 g, 0.604 mmol, 86.3%). ¹H NMR (400 MHz, CDCl₃): δ 8.36- 8.34 (m, 4H), 7.71 (s, 4H), 7.71-7.63 (m, 4H), 7.31-7.28 (m, 4H), 5.77 (d, *J* = 8.7 Hz, 4H), 2.45 (s, 12H).



3-1. 10,10'-(1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = H)

Br₂ (2.1 mL, 40.0 mmol) was added dropwise to 5 M NaOH aqueous solution (40 mL) at 0 °C. After stirring for 0.5 h, the resulted yellow solution was added to suspension of **Ac₄HPTDO** (0.486 g, 0.69 mmol) in 100 mL of Dioxane at room temperature. The mixture was heated at 80 °C for overnight. The reaction mixture was cooled to room temperature, and then quenched with saturated Na₂SO₃ aqueous solution. The solution was acidified with conc. Hydrochloric acid to give colorless precipitate, which was filtered and washed with water several times. The precipitate was dried in vacuo to give **H₄HPTDO** (0.440 g, 0.617 mmol, 89.5%) as a pale-yellow solid. m.p. >300 °C, ¹H-NMR (396 MHz, DMSO-D6) δ 13.47 (s, 4H), 8.60 (d, *J* = 2.4 Hz, 4H), 8.20 (dd, *J* = 9.1, 1.8 Hz, 4H), 8.04 (s, 4H), 7.08 (d, *J* = 9.1 Hz, 4H), ¹³C-NMR (100 MHz, DMSO-D₆) δ 165.5, 142.4, 139.4, 134.3, 133.7, 125.6, 124.4, 122.1, 118.9. HRMS (ESI-negative) found: *m/z* 711.0365 ([M-H]⁻). Calcd for C₃₄H₂₀N₂O₁₂S₂: 711.0379 ([M-H]⁻).

3-2. 10,10'-(2,5-dimethyl-1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = Me) The procedure for **H**₄**HPTDO** was followed: **Ac**₄**MePTDO** (0.669 g, 1.00 mmol), Br₂ (6.4 g, 2.1 mL, 40.0 mmol), 5 M NaOH (40 mL), and Dioxane 100 mL. The crude mixture was washed with MeOH yielding pure **H**₄**MePTDO** as a pale-yellow powder (0.558 g, 0.753 mmol, 75.3%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.63-8.62 (m, 4H), 8.23 (m, 4H), 7.92 (s, 2H), 7.10 (d, J = 9.2, 4H), 2.01 (s, 6H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.4, 141.3, 138.1, 137.7, 134.7, 134.3, 125.8, 124.5, 122.2, 118.2, 16.2. HRMS (ESI-negative) found: *m/z* 739.0659 ([M-H]⁻). Calcd for C₃₆H₂₄N₂O₁₂S₂: 739.0692.

3-3. 10,10'-(2,5-dimethoxy-1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = OMe) The procedure for **H**₄**HPTDO** was followed: **Ac**₄**MeOPTDO** (0.533 g, 0.70 mmol), Br₂ (6.40 g, 2.1 mL, 40.0 mmol), 5 M NaOH (40 mL), and Dioxane 100 mL. The crude mixture was washed with MeOH yielding pure **H**₄**MeOPTDO** as a pale-yellow powder (0.538 g, 0.697 mmol, 99%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.60 (s, 4H), 8.25-8.22 (m, 4H), 7.81 (s, 2H), 7.15 (d, *J* = 9.2 Hz, 4H), 3.65 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.5, 151.1, 141.7, 134.6, 127.4, 125.6, 124.5, 122.1, 118.5, 116.8, 56.9. HRMS (ESI-negative) found: *m/z* 771.0513 ([M-H]⁻). Calcd for C₃₆H₂₄N₂O₁₄S₂: 771.0591.

3-4. 10,10'-(2,5-diisopropyl-1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = *i*Pr)

The procedure for **H**₄**HPTDO** was followed: **Ac**₄*i***PrPTDO** (0.552 g, 0.70 mmol), Br₂ (6.4 g, 2.1 mL, 40.0 mmol), 5 M NaOH (40 mL), and Dioxane 100 mL. The crude mixture was washed with MeOH yielding pure **H**₄*i***PrPTDO** as a pale-yellow powder (0.528 g, 0.663 mmol, 94.7%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.63-8.62 (m, 4H), 8.28-8.26 (m, 4H), 7.04 (s, 2H), 7.04-7.02 (m, 4H), 2.51-2.49 (m, 2H) 0.10-0.96 (m, 12H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.5, 148.2, 142.3, 136.9, 134.5, 133.4, 125.7, 124.5, 122.2, 118.4, 27.8, 23.1. HRMS (ESI-negative) found: *m/z* 795.1296 ([M-H]⁻). Calcd for C₄₀H₃₂N₂O₁₂S₂: 795.1318.

3-5. 10,10'-(2,5-di-tert-butyl-1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = *t*Bu)

The procedure for **H**₄**HPTDO** was followed: **Ac**₄*t***BuPTDO** (0.409 g, 0.50 mmol), Br₂ (6.4 g, 2.1 mL, 40.0 mmol), 5 M NaOH (40 mL), and Dioxane 50 mL. The crude mixture was washed with MeOH yielding pure **H**₄*t***BuPTDO** as a pale-yellow powder (0.360 g, 0.436 mmol, 87.3%). M.p. >300 °C. ¹H NMR (396 MHz, DMSO-D6) δ 8.61 (d, *J* = 2.3 Hz, 3H), 8.27 (dd, *J* = 2.5, 8.7 Hz, 3H), 7.83 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 3H), 1.05 (s, 18 H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.6, 149.4, 144.0, 137.1, 135.3, 134.2, 125.8, 124.1, 122.4, 119.1, 35.5, 30.7. HRMS (ESI-negative) found: *m/z* 823.1677 ([M-H]⁻). Calcd for C₄₂H₃₆N₂O₁₂S₂: 823.1631.

3-6. 10,10'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = Dur)

The procedure for **H**₄**HPTDO** was followed: **Ac**₄**DurPTDO** (0.402 g, 0.50 mmol), Br₂ (3.20 g, 1.1 mL, 20.0 mmol), 5 M NaOH (20 mL), and Dioxane 50 mL. The crude mixture was washed with MeOH yielding pure **H**₄**DurPTDO** as a yellow powder (0.320 g, 0.394 mmol, 78.7%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.63 (s, 4H), 8.21 (d, *J* = 8.3 Hz, 4H), 7.00 (d, *J* = 9.1 Hz, 4H), 1.94 (s, 12H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.0, 141.2, 136.8, 136.7, 135.4, 126.7, 125.1, 125.0, 122.9, 118.5, 15.1. HRMS (ESI-negative) found: *m/z* 767.1047 ([M-H]⁻). Calcd for C₃₈H₂₈N₂O₁₂S₂: 767.1005.

3-7. 10,10'-(anthracene-9,10-diyl)bis(10H-phenothiazine-3,7-dicarboxylic acid 5,5-dioxide) (R = Ant)

The procedure for **H**₄**HPTDO** was followed: **Ac**₄**AntPTDO** (0.402 g, 0.50 mmol), Br₂ (3.20 g, 1.1 mL, 20.0 mmol), 5 M NaOH (20 mL), and Dioxane 50 mL. The crude mixture was washed with MeOH yielding pure **H**₄**AntPTDO** as a yellow powder (0.320 g, 0.394 mmol, 78.7%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.71 (s, 4H), 8.00-7.97 (m, 4H), 7.89, 7.87 (m, 4H), 7.69-7.67 (m, 4H), 6.74 (d, J = 9.2 Hz, 4H)., ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.4, 142.8, 135.2, 131.8, 130.4, 126.6, 123.7, 123.6, 119.4. HRMS (ESI-negative) found: *m/z* 811.0714 ([M-H]⁻). Calcd for C₄₂H₂₄N₂O₁₂S₂: 811.0692.

4. 4,4',4'',4'''-(anthracene-9,10-diylbis(azanetriyl))tetrabenzoic acid (H₄TCPADA)



The procedure for H_4HPTDO was followed: 9,10-dibromoanthracene (1.01 g, 3.0 mmol), Pd₂dba₃ (0.14 g, 0.15 mmol), tBu_3PHBF_4 (0.044 g, 0.15 mmol), NaOtBu (1.73 g, 18.0 mmol), and diphenylamine (1.12 g, 6.6 mmol) and toluene 30 mL The crude mixture was purified by SiO₂ column chromatography yielding pure **ADA** as colorless powder (1.19 g, 2.32 mmol, 77.4 %). ¹H NMR (400 MHz, CDCl₃): δ 8.20-8.17 (m, 4H), 7.36-7.34 (m, 4H), 7.26-7.18 (m, 8H), 7.13-7.10 (m, 8H), 6.92-6.89 (m, 4H).

ADA (0.769 g, 1.50 mmol), acetylchloride (2.36 g, 30.0 mmol), AlCl₃ (2.00 g, 15.0 mmol), and dichloromethane 30 mL. The crude mixture was washed with MeOH yielding pure **Ac₄ADA** as colorless powder (1.00 g, 1.47 mmol, 97.9%). ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.06 (m, 4H), 7.88-7.86 (m, 8H), 7.45-7.28 (m, 4H), 7.17-7.15 (m, 8H), 2.53 (s, 12H).

Ac₄ADA (0.681 g, 1.00 mmol), Br₂ (6.4 g, 2.1 mL, 40.0 mmol), 5 M NaOH (40 mL), and Dioxane 100 mL. The crude mixture was washed with MeOH yielding pure H₄TCPADA as yellow powder (0.300 g, 0.436 mmol, 43.6%). ¹H NMR (400 MHz, DMSO- d_6): δ 8.08-8.05 (m, 4H), 7.84 (d, J = 9.2 Hz, 4H), 7.56-7.53 (m, 4H), 7.15 (d, J = 8.4 Hz, 8H).















¹³C NMR of H₄MepPTDO ¹H NMR of MeOpPT



Figure S10. ¹H NMR of Ac₄MeOpPT









Figure S18. ¹H NMR of Ac₄*t*BupPTDO



Figure S20. ¹³C NMR of H₄*t*BupPTDO



Figure S22. ¹H NMR of Ac₄DurPTDO





Figure S26. ¹H NMR of Ac₄AntPTDO



Figure S28. ¹³C NMR of H₄AntPTDO









Single X-Ray Diffraction Analysis of M-ArPTDO

Single-crystal X-ray diffraction (SC-XRD) data of Zn-MeOPTDO, Zn-*t*BuPTDO, Zn-DurPTDO, Zn-AntPTDO, and Zn-TCPADA was collected at 233 K using a Bruker-D8 Quest diffractometer equipped with a PHOTON-III detector, and Graphite monochromated Mo K α radiation ($\lambda = 0.7103$ Å) I μ S microfocus source. The diffraction data for Zn-HPTDO, Zn-MePTDO, Zn-*i*-PrPTDO, Cu-HPTDO, Cu-AntPTDO, and CuTCPADA was collected at the BL02B1 beamline of Spring-8 on Piratus3 X CdTe Ditector (Dectris) using synchrotron radiation The structures were determined by intrinsic phasing (SHELXT 2018/2)³ and refined by full-matrix least-squares refinement (SHELXL-2018/3)⁴ using the yadokari⁵ software package and Olex2.⁶ The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program.⁷ Refinement results are summarized in Tables S1. Deposition numbers Zn-HPTDO (2367252), Zn-MePTDO (2367255), Zn-MeOPTDO (2367254), Zn-*i*-PrPTDO (2367253), Zn-*t*BuPTDO (2367256), Zn-DurPTDO (2367257), and Cu-TCPADA (2367250), Cu-HPTDO (2367248), Cu-HPTDO-II (2409246), Cu-AntPTDO (2367247), Zn-TCPADA (2367257), and Cu-TCPADA (2367249) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.).

In the crystallographic refinement of Zn-MePTDO, Zn-MeOPTDO, and Zn-*i*-PrPTDO, the substituents on the benzene rings—methyl (Me), methoxy (MeO), and isopropyl (i-Pr), respectively—exhibited significant positional disorder. Due to this disorder, it was not feasible to assign both the hydrogen atom and the substituent to the same carbon atom with confidence. Consequently, no detailed disorder modeling was conducted for these groups. To address the refinement challenges posed by the disordered substituents, several restraint commands were applied: **SIMU**: to restrain the atomic displacement parameters (ADPs) of neighboring atoms to be similar. **DELU**: to restrain the anisotropic displacement parameters of bonded atoms. **ISOR**: to enforce near isotropic ADPs for certain atoms, particularly where high anisotropy was observed due to disorder. Additionally, selected bond lengths within the benzene rings were constrained using **DFIX** restraints to maintain chemically reasonable bond distances, especially where electron density was ambiguous due to substitution disorder. The residual electron density map, as shown in Figure S33, further supports the presence of this disorder and justifies the applied restraints. All structural models were refined using these restraint strategies to ensure convergence and chemically meaningful geometry despite the presence of unresolved disorder. In Cu-AntPTDO (CCDC 2367247), the residual density map showed evidence of disorder for the SO2 group, this modelled to ~9%. A decision was made not to model the ring systems as disordered due to the extensive restraints that would be required. Consequently the geometry of the SO2 in part 2 as shown is out of the plane of the ring, but this is not the actual case.

Table S1. Crystal data and data collections of M_ArPTDO.

	Zn-HPTDO	Zn-MePTDO	Zn-MeOPTDO	Zn- <i>i</i> PrPTDO	Zn-tBuPTDO	Zn-DurPTDO
empirical formula	$C_{34}H_{18}N_2O_{14}S_2Zn_2$ ·5DMF	$C_{36}H_{22}N_2O_{14}S_2Zn_2 \cdot 10DM$	FC ₃₆ H ₂₂ N ₂ O ₁₆ S ₂ Zn ₂ ·5DMF	FC40H28N2O14S2Zn2·6DMF	$C_{42}H_{32}N_2O_{14}S_2Zn_2\cdot 5DMF$	$C_{38}H_{26}N_2O_{14}S_2Zn_2 \cdot 12DMF$
formula weight	1234.81	1626.32	1296.88	1394.08	1349.03	1950.79
color	colorless	colorless	colorless	colorless	colorless	colorless
temp (°C)	-40	-40	-40	-40	-40	-40
crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal
space group	R-3m	R-3m	R-3m	R-3m	R-3m	R-3m
unit-cell dimentions						
a(Å)	29.3386(4)	29.3296(19)	29.123(2)	29.2673(6)	29.2864(12)	29.279(2)
b(Å)	29.3386(4)	29.3296(19)	29.123(2)	29.2673(6)	29.2864(12)	29.279(2)
c(Å)	29.3136(10)	30.881(2)	30.375(2)	31.1360(8)	30.3936(16)	30.170(3)
$\alpha(^{\circ})$	90	90	90	90	90	90
$\beta^{(0)}$	90	90	90	90	90	90
$\gamma(^{\circ})$	120	120	120	120	120	120
$V(Å^3)$	21851	23005(3)	22311(4)	23097.2(11)	22576(2)	22398(4)
Ζ	9	9	9	9	9	9
$D(g/cm^3)$	0.845	1.056	0.869	0.902	0.893	1.302
independent reflections	4731	2889	3781	3293	2836	2804
parameters	136	145	148	163	157	148
R1, wR2	0.0786, 0.2741	0.0583, 0.1626	0.0797, 0.2580	0.0681, 0.2153	0.0643, 0.1855	0.0554, 0.1712
goodness-of-fit on F^2	1.138	1.000	1.054	1.102	1.078	1.057
CCDC	2367252	2367255	2367254	2367253	2367256	2367251

Table S1. continue

	Zn-AntPTDO	Cu-HPTDO	Cu-AntPTDO	Zn-TCPADA	Cu-TCPADA	Cu-HPTDO-II
empirical formula	$C_{42}H_{22}N_2O_{14}S_2Zn_2\cdot 8DMF$	C ₃₄ H ₁₈ Cu ₂ N ₂ O ₁₄ S ₂ ·5DMF	FC42H22Cu2N2O14S2·10DM	$HC_{42}H_{26}N_2O_{10}Zn_2 \cdot 10DMF$	C42H26Cu2N2O10.2.5DM	MC ₃₄ H ₁₈ Cu ₂ N ₁₄ O ₁₄ S ₂ ·6DMF
formula weight	1524.22	1233.16	1694.72	1578.33	1026.45	1308.28
color	colorless	green	green	colorless	green	green
temperature (°C)	-40	-40	-40	-40	-40	-40
crystal system	Trigonal	Trigonal	Trigonal	Monoclinic	Monoclinic	Hexagonal
space group	R-3m	R-3m	R-3m	C2/c	C2/c	P63/mmc
unit-cell dimentions						
<i>a</i> (Å)	29.3475(6)	28.9680(9)	29.1655(5)	36.431(3)	36.468(9)	29.8395(10)
b(Å)	29.3475(6)	28.9680(9)	29.1655(5)	16.6320(7)	16.549(3)	29.8395(10)
<i>c</i> (Å)	30.1175(9)	31.2872(11)	31.1656(8)	23.621(2)	23.765(6)	43.3839(12)
$\alpha(^{\rm o})$	90	90	90	90	90	90
$\beta^{(0)}$	90	90	90	132.306(14)	132.62(4)	90
γ(⁰)	120	120	120	90	90	120
$V(Å^3)$	22464.2(11)	22737.1(16)	22958.6(10)	10585(2)	10554(7)	33454(2)
Ζ	9	9	9	4	4	12
$D(g/cm^3)$	1.014	0.811	1.103	0.990	0.646	0.779
independent reflections	5434	3188	3913	7606	5517	6369
parameters	163	155	182	253	253	282
R1, wR2	0.0538, 0.1751	0.0829, 0.2554	0.0455, 0.1463	0.0760, 0.2404	0.1256, 0.3396	0.0599, 0.1842
goodness-of-fit on F^2	1.088	1.029	1.148	1.030	1.016	1.052
CCDC	2367250	2367248	2367247	2367257	2367249	2409246



Figure S33.

Residual electron density maps of Zn-MePTDO (left), Zn-MeOPTDO (center), and Zn-iPrPTDO (right)



Figure S34. Asymmetric Structure of Zn-HPTDO







Figure S36. Asymmetric Structure of Zn-MeOPTDO



Figure S37. Asymmetric Structure of Zn-*i*PrPTDO



Figure S38.Asymmetric Structure of Zn-tBuPTDO



Figure S39. Asymmetric Structure of Zn-DurPTDO







Figure S41. Asymmetric Structure of Zn-TCPADA



Figure S42. Asymmetric Structure of Cu-HPTDO



Figure S43. Asymmetric Structure of Cu-AntPTDO



Figure S44. Asymmetric Structure of Cu-TCPADA



Figure S45. Asymmetric Structure of Cu-HPTDO-II

Topology Analysis of MOFs by ToposPro

Cu-HPTDO

Point symbol for net: {6⁴.8²}

4-c net; uninodal net

Topological type: nbo;



Figure S46. Topological structure of Cu-HTPDO

Cu-TCPADA

Point symbol for net: {4².8⁴} 4-c net; uninodal net

Topological type: lvt; 4/4/t1.

Figure S47. Topological structure of Cu-TCPADA

Figure S50. PXRD patterns of Cu-ArPTDO.

Figure S51. PXRD patterns of the bulk sample of Zn-TCPADA under several conditions.

Figure S52. PXRD patterns of the bulk sample of Cu-TCPADA under several conditions.

Purity of Cu-HPTDO

To investigate the purity of the balk sample of Cu-HPTDO, an SC-XRD analysis of the newly discovered the hexagonal crystals of Cu-HPTDO-II was performed (Figure S43 and Table S1). The chemical formula of Cu-HPTDO-II is the same as that of Cu-HPTDO, but they have different space groups ($P6_3/mmc$ for Cu-HPTDO-II, R-3m for Cu-HPTDO). The PXRD pattern of as-synthesized samples is consistent with that of the mixture of simulated patterns of Cu-HPTDO and Cu-HPTDO-II by SC-XRD analysis (Figure S51). We attempted synthesis of phase pure samples of Cu-HPTDO or Cu-HPTDO-II, but it could not be achieved.

Figure S53. Comparison of PXRD patterns of Cu-HPTDO and Cu-HPTDO-II.

Stability of MOFs

To investigate the stability of the bulk sample of Cu-AntPTDO, the PXRD analysis of Cu-AntPTDO under several conditions was measured. As shown in Figure S52, the PXRD pattern of Cu-AntPTDO in organic solvent unchanged. Although the pattern of the dried sample at room temperature under vacuum condition is also no change, the sample in the air after 30 min showed significant broadened pattern. Moreover, the activated sample at 135 °C for 6h exhibits broadened one, indicating moisture sensitivity of the bulk sample of Cu-AntPTDO.

The patterns of Zn- and Cu-TCPADA were inconsistent with their simulated patterns from SC-XRD. As shown in Figures S52 and S53, they exhibited sensitivity to external stimuli, such as solvent exchange and drying, indicating their instability.

Figure S54. Comparison of PXRD patterns of the bulk sample of Cu-AntPTDO under several conditions.

Gas Adsorption/desorption Experiments

Figure S55.

N₂ adsorption/desorption experiments of Zn-ArPTDO at 77 K.

Figure S56. N₂ adsorption/desorption experiments of Cu-ArPTDO at 77 K.

The BET transformation is calculated as:

$$B_1 = \frac{P_{rel}}{(1 - P_{rel}) \times N_{ads}}$$
A least-squares fit is performed on the **P**_{rel}, **B**₁. The following are calculated:

a. Slope (S g/cm³ STP), b. Y-intercept (Y_{INT} g/cm³ STP), c. Uncertainty of the slope (S_{ERR} g/cm³ STP), d. Uncertainty of the Y-intercept (YI_{ERR} g/cm³ STP), e. Correlation coefficient (Cc), f. Molecular Cross-Sectional Area (CSA): 0.1620 nm² Using the results of the above calculations, the following can be calculated:

$$BET \text{ Surface Area (SA_{BET})} = \frac{CSA \times (6.023 \times 10^{23})}{(22414 \text{ } cm^3 \text{ } STP) \times \left(10^{18} \frac{nm^2}{m^2}\right) \times (S + Y_{INT})}$$

BET C value (C) = $\frac{S}{Y_{INT}} + 1$

Quantity in the monolayer (Qm) = $\frac{1}{C \times Y_{INT}} = \frac{1}{S + Y_{INT}}$

$$\frac{SA_{BET} \times \sqrt{S_{ERR}^2 + YI_{ERR}^2}}{S + Y_{INT}} \mathbf{o}/$$

Error of the BET Surface Area (u(As)) =

Table S2. BET Report on Cu-ArPTDO

Cu-ArPTDO	Н	Me	OMe	iPr
BET Su	rface Area 821.7957 ± 4.7990 $(m^2/g):$	1362.7037 ± 5.2278	899.9441 ± 0.9957	1366.5927 ± 2.4770
Slope (g/	/cm ³ STP): 0.005292 ± 0.000031	0.003191 ± 0.000012	0.004834 ± 0.000005	0.003183 ± 0.000006
Y-Intercept (g/	/cm ³ STP): 0.000004 ± 0.000000	0.000003 ± 0.000000	0.000003 ± 0.000000	0.000002 ± 0.000000
	C:1233.912840	1077.033489	1855.971663	1749.230768
Qm (cr	m ³ /g STP):188.8067	313.0797	206.7612	313.9731
Correlation C	Coefficient: 0.9998805	0.9999337	0.9999945	0.9999852

Table S2. Continued.

Cu-ArPTDO	<i>t</i> Bu	Dur	Ant
BET Surface Area	(m^2/g) : 1680.4554 ± 3.0515	1659.2806 ± 2.4622	1950.3000 ± 2.9733
Slope (g/cm	3 STP): 0.002589 ± 0.000005	0.002622 ± 0.000004	0.002231 ± 0.000003
Y-Intercept (g/cm	³ STP): 0.000002 ± 0.000000	0.000002 ± 0.000000	0.000001 ± 0.000000
	C:1706.665234	1731.967619	2587.451124
Qm (cm ³ /2	g STP): 386.0828	381.2179	448.0793
Correlation Coef	ficient: 0.9999851	0.9999901	0.9999895

Qm: Quantity in the monolayer

Figure S57. Liner Brunauer-Emmett-Teller (BET) plot, i.e., 1/W(P0/P-1) vs Relative pressure (P/P0) from N₂ adsorption isotherm of a) Cu-HPTDO, b) Cu-MePTDO, c) Cu-MeOPTDO, d) Cu-iPrPTDO, e) Cu-tBuPTDO, f) Cu-DurPTDO, and g) Cu-AntPTDO.

Pore size distribution of Cu-ArPTDO.

Figure S59. N₂ adsorption/desorption experiments of Cu-ArPTDO at 298 K.

Figure S60.

N₂ adsorption/desorption experiments of Cu-ArPTDO at 273 K.

Figure S61. CO₂ adsorption/desorption experiments of Cu-ArPTDO at 298 K.

CO₂ adsorption/desorption experiments of Cu-ArPTDO at 273 K.

Figure S63. H₂ adsorption/desorption experiments of Cu-ArPTDO at 77 K.

Figure S64. N₂ adsorption/desorption experiments of Cu-TCPADA at 77 K.

Figure S65. H₂ adsorption experiments of Cu-TCPADA at 77 K.

IAST fitting

Li(P) for species I follows Henry's Law isotherm with Henry's constant K_H and pressure P: $Li(P) = K_H P$

Li(P) for species I follows a Langmuir isotherm with saturation loading M and Langmuir constant Ki:

$$Li(P) = M \frac{KiP}{1 + KiP'}$$

Figure S66. Langmuir fitting (red line) for CO₂ (dark blue square) and Langmuir fitting (yellow line) for N₂ (green square) isotherm measured at 298 K in Cu-AntPTDO.

	K_H	М	Ki
CO ₂		271.0477862	0.002322685
N ₂	0.0311907115253434		

Figure S67. Langmuir fitting (red line) for CO₂ (dark blue square) and N₂ (green square) isotherm measured at 298 K in Cu-DurPTDO.

Figure S68. Langmuir fitting (blue line) for CO₂ (black circle) and (yellow line) for N₂ (black circle) isotherm measured at 298 K in Cu-*t*BuPTDO.

Figure S69. Calculated IAST selectivity of **CuArPTDO** for a range of total pressures (0-100 kPa) at a molar CO₂/N₂ ratio of 15/85 at 298 K.

Figure S70. Heat of CO₂ adsorption of Cu-ArPTDO.

Estimation of pore-size retention (PSR)

The PSR (%) values were calculated based on the actual pore size (cm³ g⁻¹) estimated from the gas-adsorption experiments on MOFs and the ideal pore size (cm³ g⁻¹) estimated from the single-crystal XRD analysis of the MOFs. The actual pore size was estimated by the Horvath-Kawazoe method using N₂-adsorption isotherms at 77 K.

$$ln\frac{P}{P_{0}} = \frac{K}{RT} \times \frac{IP \times 10^{23} JA^{4} / J cm^{4}}{\sigma^{4} \times (L - 2d_{0})} \times \left[\frac{\sigma^{4}}{3 \times (L - d_{0})^{3}} - \frac{\sigma^{10}}{9 \times (L - d_{0})^{9}} - \frac{\sigma^{4}}{3 \times d_{0}^{3}} - \frac{\sigma^{10}}{9 \times d_{0}^{9}}\right]$$
$$Z_{S} - Z_{A}$$

 σ = gas solid nuclear separation at zero interaction energy (Å), 2

Z_S = sample equilibrium diameter at zero interaction energy (Å) from the Horvath-Kawazoe physical properties window

Z_A = zero interaction energy diameter from the Horvath-Kawazoe physical properties window

$$K = 6.023 \text{ x} 10^{23}$$

 $R = (ergs/mol K): 8.314 \times 10^7$

IP = interaction parameter (erg-cm⁴) from the Horvath-Kawazoe report options window

$$d_0(\text{\AA}) = \frac{D_S - D_A}{2}$$

D_s = molecular diameter from the Horvath-Kawazoe Physical Properties window

D_A = diameter of sample atom from the Horvath-Kawazoe Report Options window

L(Å) = pore width

P (mmHg) = equilibrium pressure

 P_0 = saturation pressure

Table S3. Horvath-Kawazoe pore-volume report of Cu-ArPTDO.

	-			
Cu-ArPTDO	Н	Me	OMe	<i>i</i> -Pr
Maximum pore volume:	0.317181 cm ³ /g	0.511538 cm³/g	0.341879 cm³/g	0.527014 cm³/g
at Relative Pressure:	0.148982026	0.148334798	0.148893980	0.148104181
Median pore width:	8.180 Å	8.093 Å	8.030 Å	8.026 Å
Relative pressure range:	1.946e-003 to 1.490e-001	1.772e-003 to 1.483e-001	1.652e-003 to 1.489e-001	1.644e-003 to 1.481e-001
Table S3. Continued.				_
Cu-ArPTDO	t-Bu	Dur	Ant	
Maximum pore volume:	0.645749 cm³/g	0.635268 cm³/g	0.737209 cm ³ /g	
at Relative Pressure:	0.148141871	0.148178934	0.147520581	
Median pore width:	7.839 Å	7.912 Å	7.858 Å	
Relative pressure range:	1.325e-003 to 1.481e-001	1.444e-003 to 1.482e-001	1.356e-003 to 1.475e-001	_
Diameter of adsorptive mo	lecule:	3.000 Å		
Diameter of adsorptive at z	ero interaction energy:	2.574 Å		
Diameter of sample atom:		3.040 Å		
Diameter of sample atom a	at zero interaction energy:	2.609 Å		
Interaction parameter:		3.49e-043 erg∙cm^4		
Density conversion factor:		0.0015468		

The ideal pore volume (cm³ g⁻¹) was calculated according to:

$$\frac{TSA \times 10^{-24} (cm^3) \times A (mol^{-1})}{M (g mol^{-1}) \times Z}$$

TSA = Total potential solvent area per unit cell (Å³) estimated by Platon Calc Solv command^[S6]

M = Formula weight (g/mol) per unit cell

$$A = 6.023 \times 10^{23}$$

Z = Asymmetric units per unit cell

Table S4. The ideal pore volumes of Cu-ArPTDO.

Zn-ArPTDO	н	Me	OMe	<i>i</i> -Pr	<i>t</i> -Bu	Dur	Ant
Ideal Pore volume	1.25	1.23	1.13	1.10	1.05	1.17	1.10
TSA (ų)	16311	16603.5	15825.3	15794.6	15504.1	16084.4	15934.1
FW (g mol ⁻¹)	435.69	451.74	467.74	479.79	493.81	460.72	485.75
Z	18	18	18	18	18	18	18

The pore size retention (%) was calculated according to:

 $\frac{Actual \text{ pore size estimated by Gas adsorption } (cm^3 g^{-1})}{Ideal \text{ pore size estimated by SCXRD } (cm^3 g^{-1})} = \frac{Maximum \text{ pore volume } (cm^3 g^{-1})}{Ideal \text{ pore volume } (cm^3 g^{-1})}$

Ideal pore size estimated by SCXRD (
$$cm^3 g^{-1}$$
)

Table S5. Pore-size retention (PSR) of Cu-ArPTDO.

Zn-ArPTDO	Н	Me	OMe	<i>i</i> -Pr	<i>t</i> -Bu	Dur	Ant
PSR(%)	25.32	41.59	30.20	47.84	61.47	54.38	67.16
Maximum pore volume	0.3172	0.5115	0.3419	0.5270	0.6457	0.6353	0.7372
Pore volume	1.25	1.23	1.13	1.10	1.05	1.17	1.10

Ex) PSR of hitherto reported MOFs

Table S6. Pore-size retention (PSR) of hitherto reported MOFs.

MOF	MOF-5	Zr-DBT	Zn-BrTrp
PSR (%)	96.87	98.25	101.77
Maxmum pore volume	1.2522	0.7687	0.4226
Ideal Pore volume	1.29	0.78	0.42
Reference	S8	\$9	S10

Table S7. Gas-adsorption data of hitherto reported MOFs

Zn-BrTrp	Zr-DBT	MOF-5	MOF
1116.1751 ± 3.1659	1959.5684 ± 4.3613	3483.0193 ± 124.2832	BET Surface Area (m ² /g):
0.003899 ± 0.000011	0.002220 ± 0.000005	0.001244 ± 0.000045	Slope (g/cm ³ STP):
0.000000 ± 0.000000	0.000001 ± 0.000000	0.000006 ± 0.000002	Y-Intercept (g/cm ³ STP):
11432.071643	1972.135415	205.247719	C:

Qm (cm ³ /g STP):	800.2198	450.2086	256.44			
Correlation Coefficient:	0.9936407	0.9999678	0.9999598			
Table S8. Ideal pore volume of hitherto reported MOFs.						
MOF	MOF-5	Zr-DBT	Zn-BrTrp			
Ideal Pore volume	1.29	0.78	0.42			
SA (A)	13219.700	11933.5	1198			
FW (g mol-1)	6159.11	1148.4	868.73			
Z	1	8	2			

Table S9. Maximum pore-volume Horvath-Kawazoe pore-volume report of Cu-ArPTDO.

MOF	MOF-5	Zr-DBT	Zn-BrTrp
Maximum pore volume:	1.252237	0.768659	0.422648
at Relative Pressure:	0.157124175	0.155452002	0.148713839
Median pore width:	9.259 Å	7.879 Å	8.569 Å
Relative pressure range:	1.318e-003 to 1.571e-001	1.390e-003 to 1.555e-001	2.873e-003 to 1.487e-001

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