

Electronic Supplementary Information (ESI)

Metallosalen-based microporous organic polymers: synthesis and carbon dioxide uptake

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Section A. Synthesis of Salen Monomers

Synthesis of Salen ligand.

A solution of ethylenediamine (0.5 mL, 7.5 mmol) in ethanol (10 mL) was added to a solution of 5-bromosalicylaldehyde (3.0 g, 15 mmol) in ethanol (30 mL) at room temperature. The mixture was refluxed and stirred for 6 h. After the mixture was cooled to room temperature, the precipitate was filtered off and washed with ethanol (50 mL). After drying in vacuum, *N,N'*-bis(5-bromosalicylidene)-1,2-ethylenediamine (Salen ligand) was obtained as a light yellow powder (3.1 g, 7.27 mmol, 96.8%). ¹H NMR (400 MHz, CDCl₃) δ: 3.96 (s, 4H, CH₂), 6.85 (d, 2H, *J* = 8.76 Hz, *Ph*-H), 7.34 (d, 2H, *J* = 1.80 Hz, *Ph*-H), 7.38 (dd, 2H, *J* = 1.80, 8.80 Hz, *Ph*-H), 8.29 (s, 2H, CH=N), 13.15 (s, 2H, OH) ppm. Anal. Calcd for C₁₆H₁₄Br₂N₂O₂ (426.1): C, 45.10; H, 3.31; N, 6.57; Found: C, 45.01; H, 3.38; N, 6.64.

Synthesis of Salen-Zn.

A solution of Zn(OAc)₂·2H₂O (0.21 g, 0.94 mmol) in methanol (10 mL) was added to a solution of Salen (0.40 g, 0.94 mmol) in dichloromethane (30 mL) at room temperature. Then the mixture was refluxed and stirred for 4h. After the mixture was cooled to room temperature, the precipitate was filtered off and washed with methanol (40 mL). After drying in vacuum, Salen-Zn was obtained as a yellow powder (0.37 g, 0.76 mmol, 81.4%). ¹H NMR (400 MHz, DMSO) δ: 3.72 (s, 4H, CH₂), 6.58 (d, 2H, *J* = 8.76 Hz, *Ph*-H), 7.21 (dd, 2H, *J* = 2.93, 8.94 Hz, *Ph*-H), 7.34 (d, 2H, *J* = 2.96 Hz, *Ph*-H), 8.42 (s, 2H, CH=N) ppm. Anal. Calcd for C₁₆H₁₂Br₂N₂O₂Zn (489.5): C, 39.26; H, 2.47; N, 5.72; Found: C, 39.14; H, 2.53; N, 5.85. IR (KBr): ν 412, 464, 498, 541, 635, 687, 787, 819, 872, 972, 1028, 1089, 1135, 1176, 1300, 1371, 1459, 1520, 1587, 1626, 2899 cm⁻¹.

Synthesis of Salen-Ni.

A solution of Ni(OAc)₂·4H₂O (0.23 g, 0.94 mmol) in methanol (15 mL) was added to a solution of Salen (0.40 g, 0.94 mmol) in dichloromethane (30 mL) at room temperature. Then the mixture was refluxed and stirred for 4h. After the mixture was cooled to room temperature, the precipitate was filtered off and washed with methanol (40 mL). After drying in vacuum, Salen-Ni was obtained as a brown powder (0.39 g, 0.82 mmol, 87.3%). ¹H NMR (400 MHz, DMSO) δ: 3.43 (s, 4H, CH₂), 6.67 (d, 2H, *J* = 9.04 Hz, *Ph*-H), 7.26 (dd, 2H, *J* = 2.93, 8.94 Hz, *Ph*-H), 7.34 (d, 2H, *J* = 2.96 Hz, *Ph*-H), 8.42 (s, 2H, CH=N) ppm. Anal. Calcd for C₁₆H₁₂Br₂N₂O₂Ni (482.8): C, 39.81; H, 2.51; N, 5.20; Found: C, 39.05; H, 2.60; N, 5.31. IR (KBr): ν 414, 464, 499, 618, 653, 698, 752, 822, 867, 950, 1067, 1092, 1134, 1181, 1241, 1305, 1372, 1422, 1455, 1525, 1625, 2910 cm⁻¹.

Synthesis of Salen-Pt.

Sodium acetate (0.041 g, 0.5 mmol) was suspended in a solution of Salen (0.10 g, 0.25 mmol) in DMF (8 mL). K₂PtCl₄ (0.10 g, 0.25 mmol) dissolved in DMSO (2 mL) was added dropwise to the suspension at 70°C and the resulting mixture was stirred

for 15 h at the same temperature. After the mixture was cooled to room temperature, diethyl ether (25 mL) was added to the mixture to afford an orange precipitate. The solid product was filtered and washed with Et₂O (5 × 5 mL). After drying in vacuum, Salen-Pt was obtained as an orange powder (0.13 g, 0.21 mmol, 84.4%). ¹H NMR (400 MHz, DMSO) δ: 3.83 (s, 4H, CH₂), 6.88 (d, 2H, *J* = 9.08 Hz, *Ph*-H), 7.53 (dd, 2H, *J* = 2.68, 9.10 Hz, *Ph*-H), 7.72 (d, 2H, *J* = 2.68 Hz, *Ph*-H), 8.57 (s, 2H, CH=N) ppm. Anal. Calcd for C₁₆H₁₂Br₂N₂O₂Pt(619.2): C, 31.04; H, 1.95; N, 4.52; Found: C, 31.11; H, 2.13; N, 4.35. IR (KBr): ν 475, 556, 620, 669, 701, 815, 928, 1082, 1146, 1170, 1292, 1338, 1378, 1416, 1460, 1524, 1592, 1629 cm⁻¹.

Section B. The Stability of MsMOPs

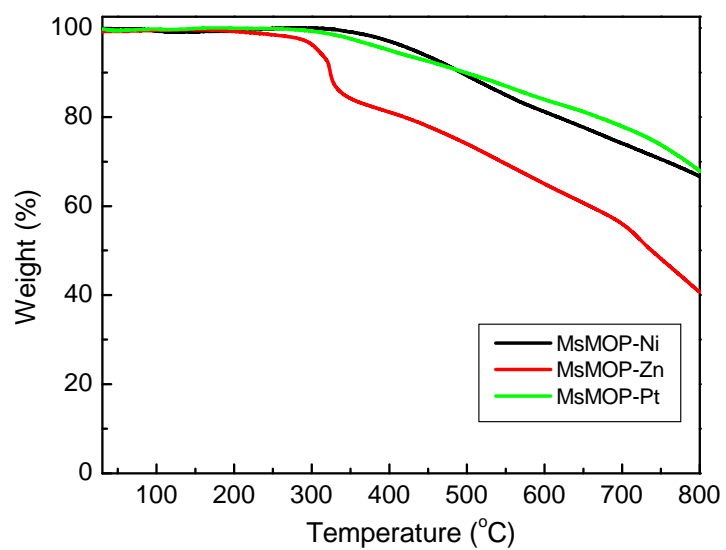


Fig. S1 TGA curves of MsMOPs under nitrogen.

Section C. FT-IR Spectra

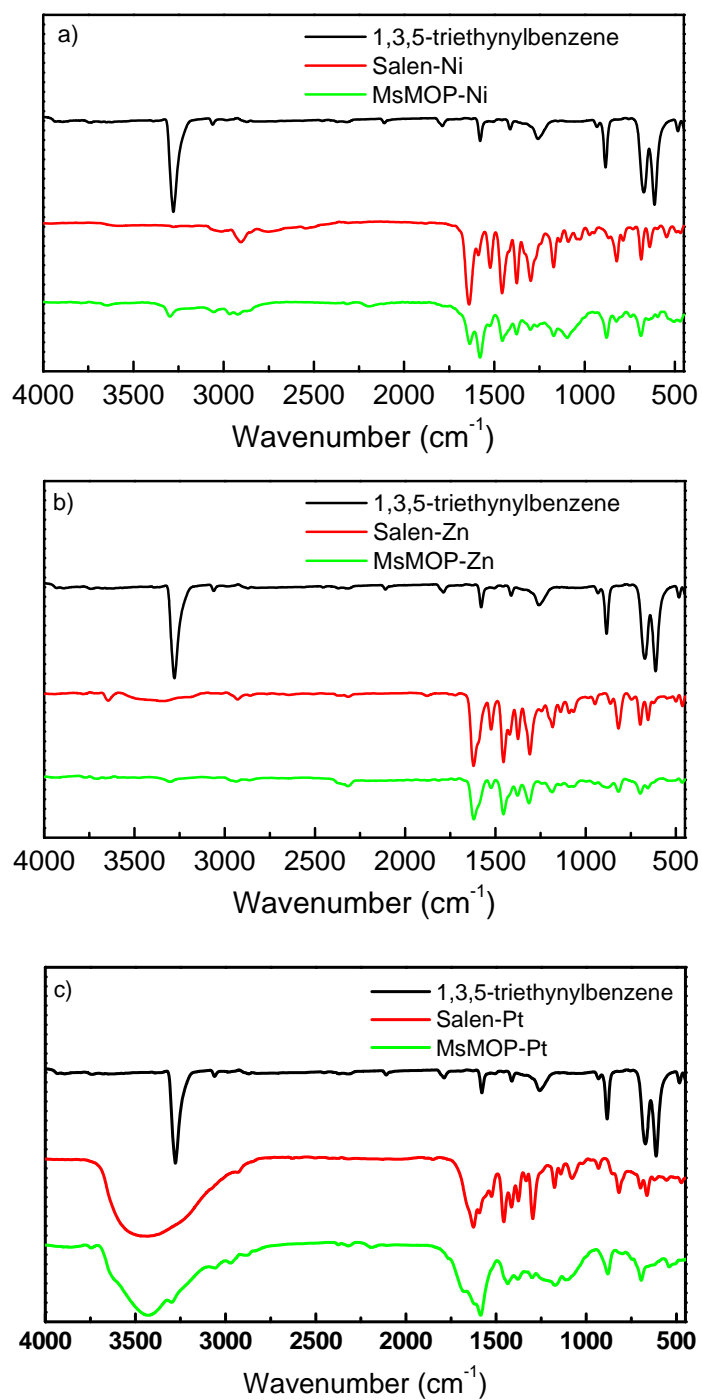


Fig. S2 The FT-IR spectra of MsMOPs and monomers.

Section D. The UV Spectra

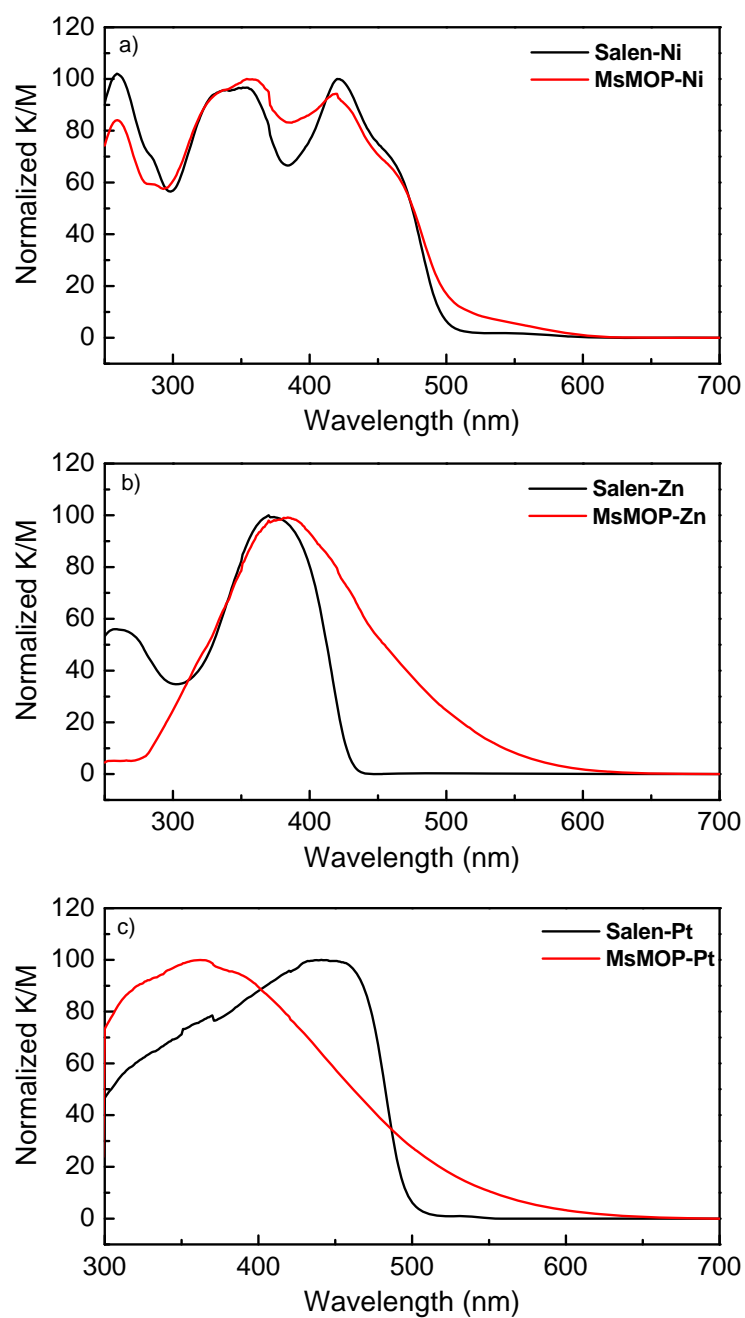


Fig. S3 UV-Vis spectra of MsMOPs and the corresponding metallosalen monomers.

Section E. The ^{13}C CP/MAS NMR Spectra

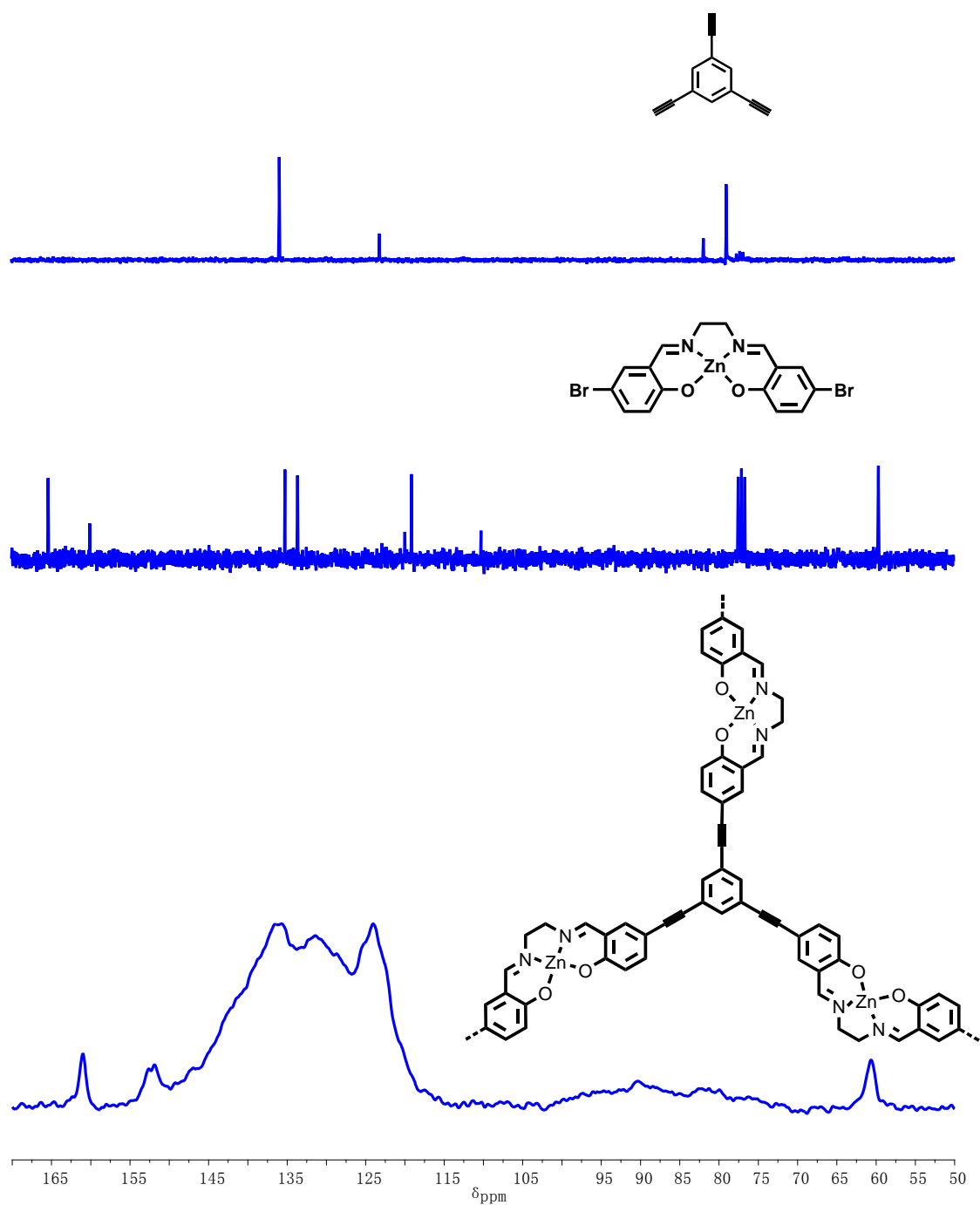


Fig. S4 ^{13}C CP/MAS NMR spectroscopy of MsMOP-Zn and ^{13}C NMR spectra of Salen-Zn and 1,3,5-triethynylbenzene.

Section F. The Crystalline of MsMOPs

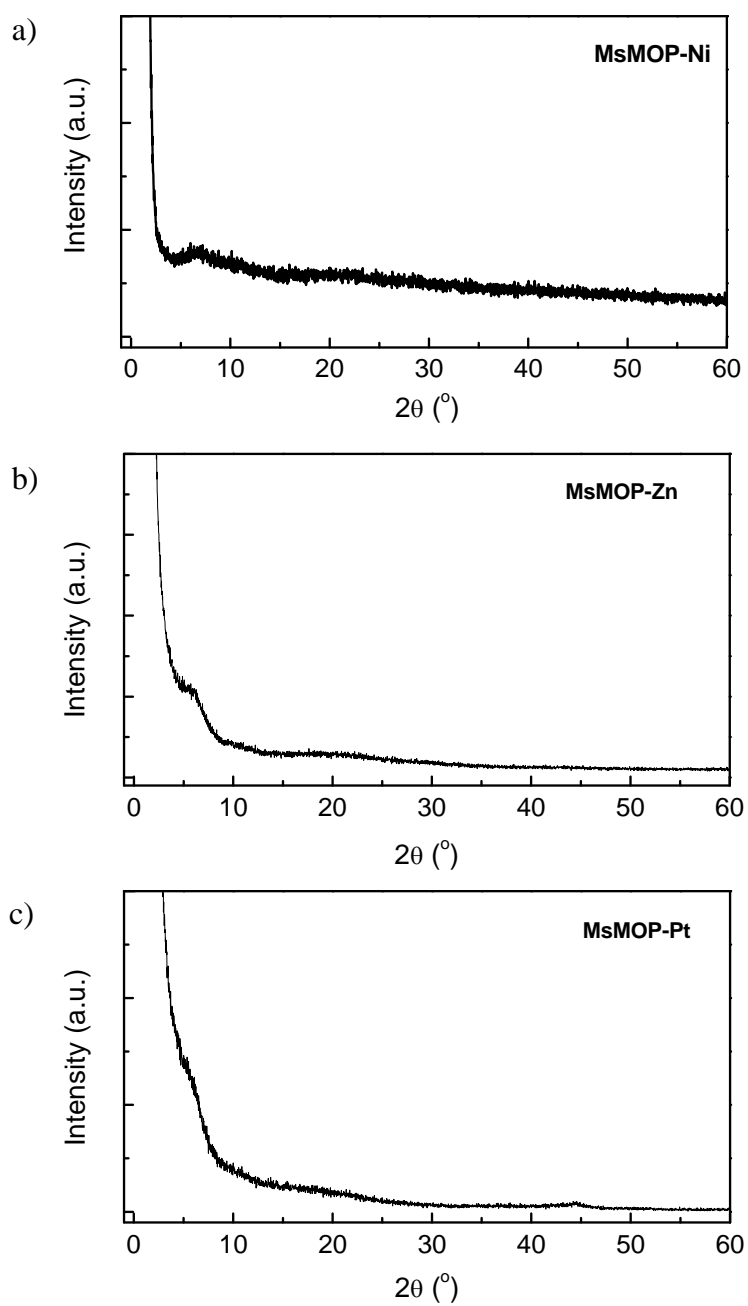


Fig. S5 PXR curves of MsMOPs.

Section G. XPS Spectra of MsMOPs

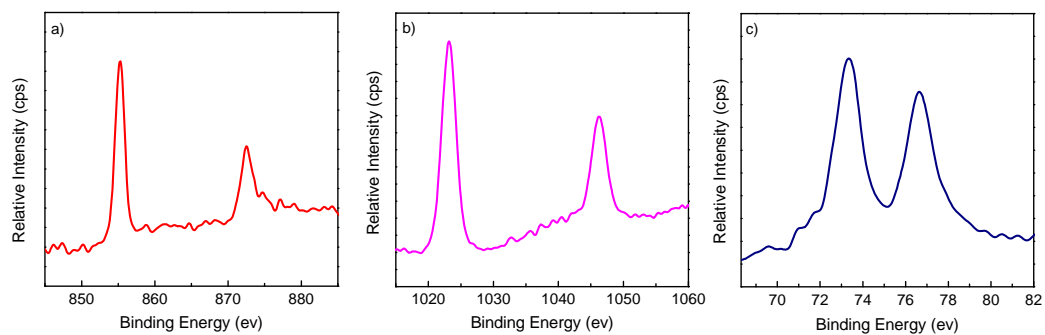


Fig. S6 XPS spectra taken for the Ni 2p region of MsMOP-Ni (a), the Zn 2p region of MsMOP-Zn (b), and the Pt 4f region of MsMOP-Pt (c).

Section H. EDS Spectra of MsMOPs

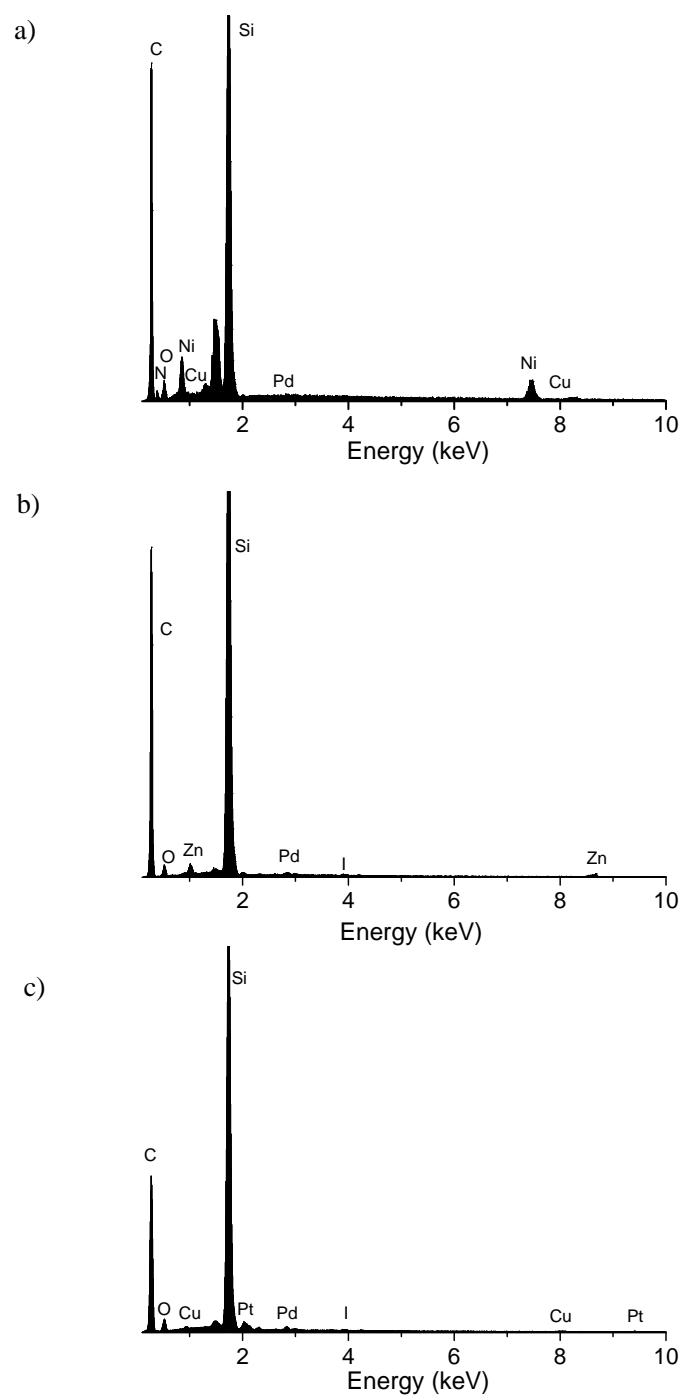


Fig. S7 EDS spectra of MsMOPs. The low palladium and copper contents are due to the incomplete washing after cross-coupling reaction. The silicon element is from silicon substrate.

Section I. Gas Uptake and Selectivity of MsMOPs

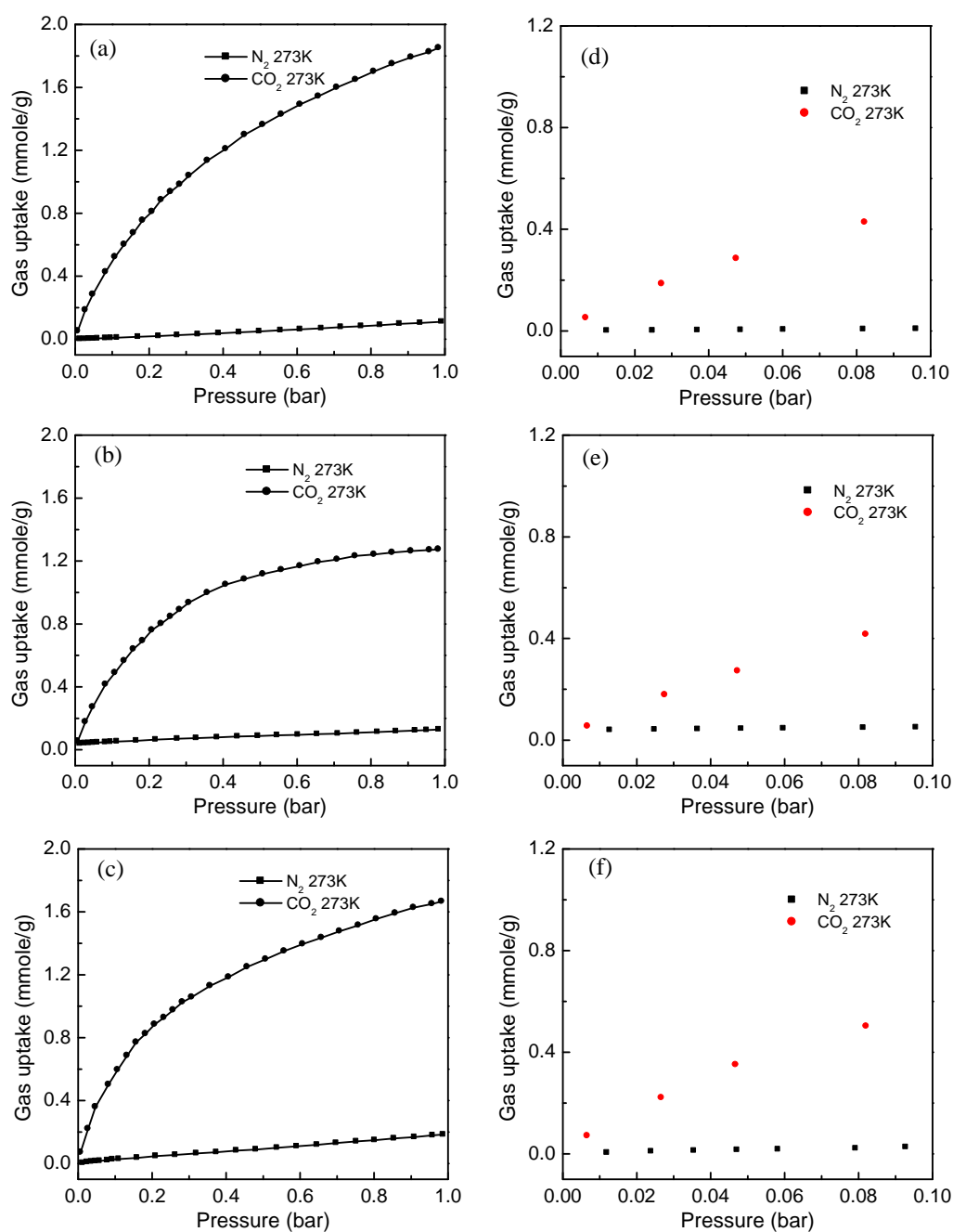


Fig. S8 CO_2 and N_2 adsorption isotherms of MsMOP-Ni (a), MsMOP-Zn (b) and MsMOP-Pt (c) at 273 K and the adsorption data of MsMOP-Ni (d), MsMOP-Zn (e) and MsMOP-Pt (f) at 0~0.1 bar.

Section J. N₂ Sorption Isotherms of MsMOP-Ni

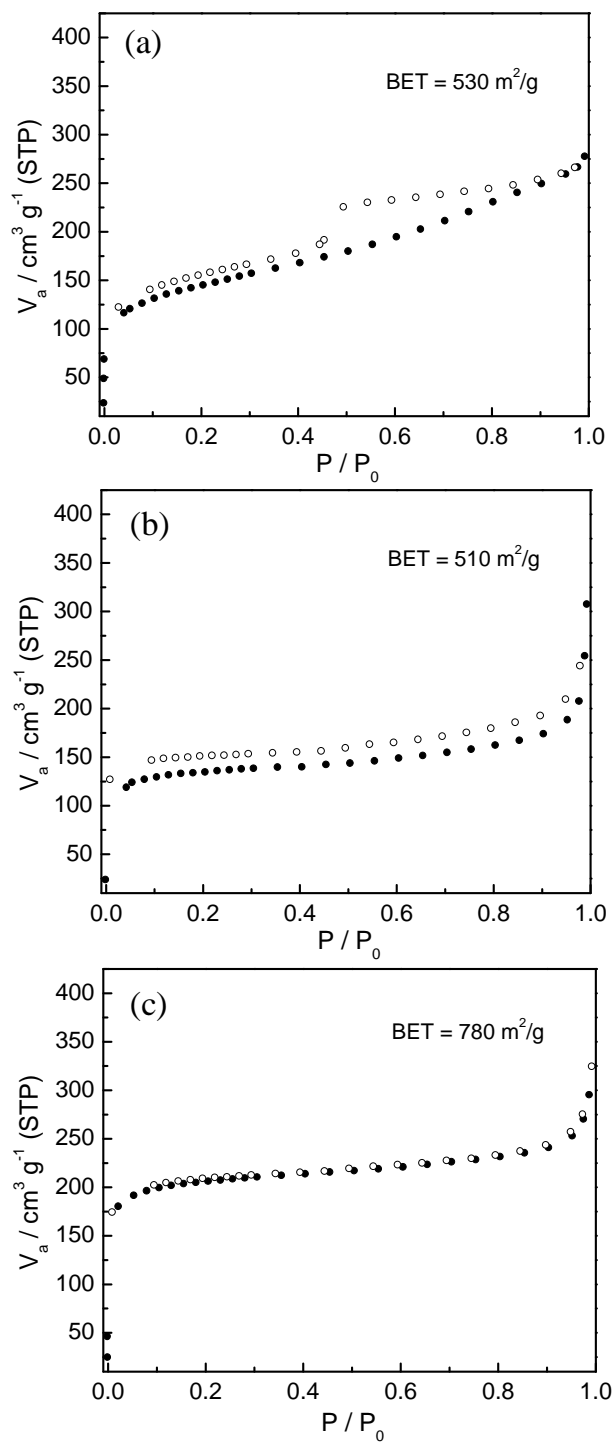


Fig. S9 Nitrogen adsorption-desorption isotherm and surface areas of MsMOP-Ni in the different solvent systems: toluene/TEA (a), dioxane/TEA (b) and DMF/TEA (c).

Section K. $^1\text{H-NMR}$ Spectra

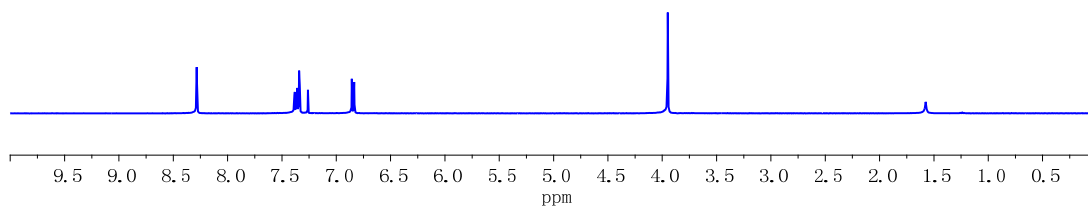


Fig. S10 $^1\text{H-NMR}$ spectra of Salen ligand.

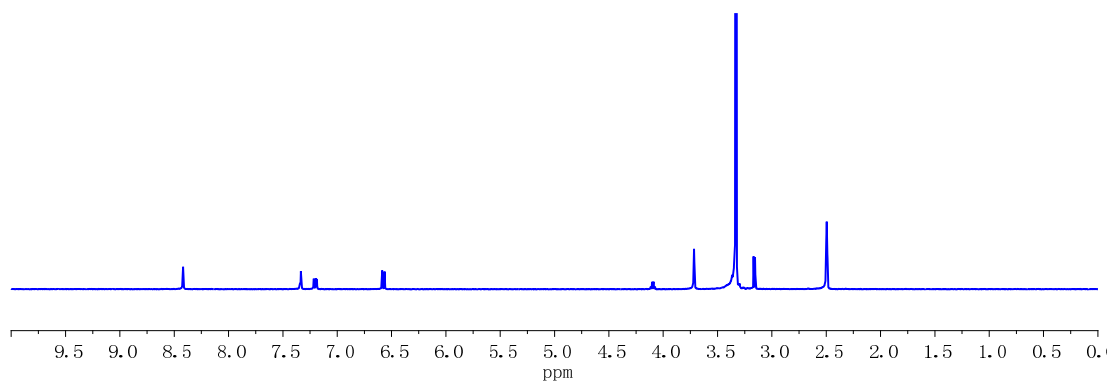


Fig. S11 $^1\text{H-NMR}$ spectra of Salen-Zn.

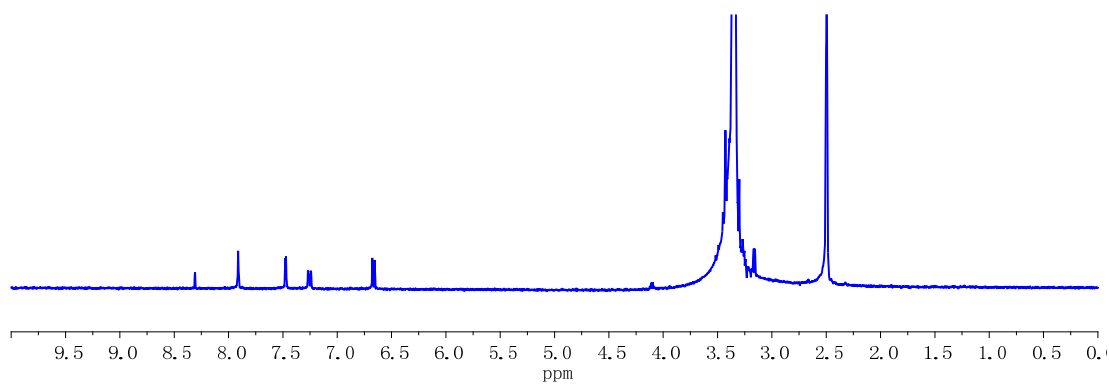


Fig. S12 $^1\text{H-NMR}$ spectra of Salen-Ni.

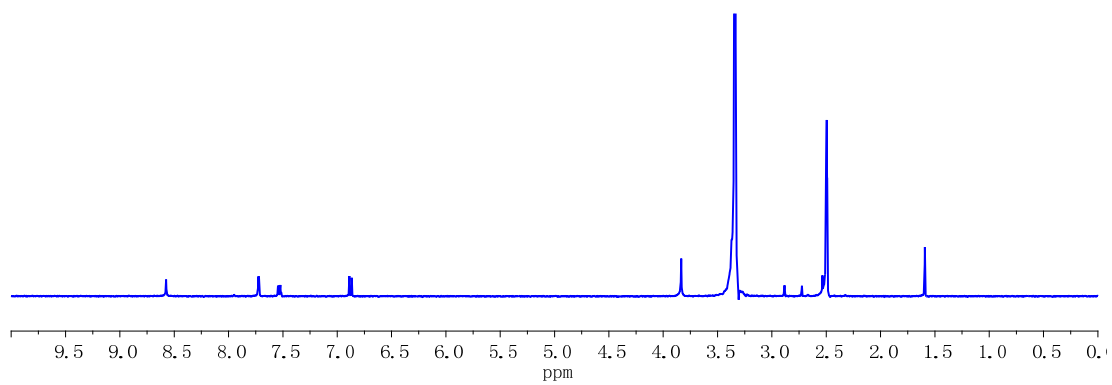


Fig. S13 $^1\text{H-NMR}$ spectra of Salen-Pt.