

Electronic Supplementary Material (ESI) for *Dalton Transactions*

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**A novel zirconium-based metal-organic framework covalently
modified by methyl pyridinium bromide for mild and co-catalyst free
conversion of CO₂ to cyclic carbonates**

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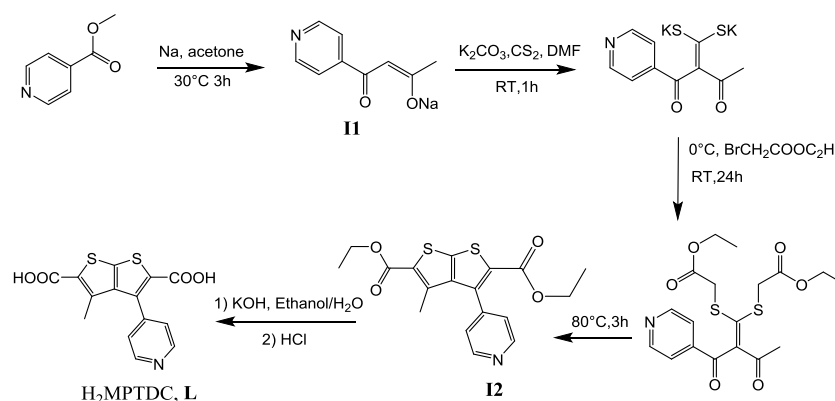
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I. Experimental section

Synthesis of H₂MPTDC



Scheme S1 The synthetic route of H₂MPTDC.

The ligand H₂MPTDC was synthesized according to a similar route from the reference with appropriate modifications.^{S1-S4}

Synthesis of MPTDC-C₂H₅. The mixture of 13.2 mL methyl isonicotinate (15.00 g, 0.11 mol), 9.50 mL acetone (7.50 g, 0.13 mmol) and 50 mL anhydrous ether was added into a 100mL three-necked flask and then cooling to 0~2 °C, under the protection of nitrogen, 2.50 g (0.11 mol) of newly cut metal sodium tablets were added in batches with continuous stirring at room temperature for 3h. The reaction mixture was filtered by suction, the filter cake was washed with a small amount of ethyl acetate, and the obtained solid was dried in vacuum to obtain powdery yellow solid 1-(pyridin-4-yl)-1,3-butanedione sodium salt I1. Subsequently, intermediate 1 (1.85 g, 10 mmol), K₂CO₃ (8.28 g, 60 mmol) in 10 mL DMF were well mixed at ice bath in a 100 mL three-necked flask. Controlled the temperature of mixture at 0~5 °C, and slowly added 0.6mL CS₂ (0.76 g, 10 mmol), and stirred for 1 h at 20 °C. Under the condition of ice bath, ethyl bromoacetate (2.22 mL, 20 mmol) and 10 mL DMF were added dropwise, stirred at room temperature for 24 hours, and then heated to 80 °C for 3h. The reaction solution was poured into ice deionized water, then the solid was precipitated. The reaction mixture was filtered by suction, and purified by column chromatography with ethyl acetate/petroleum ether (1/3), and the light yellow solid powder 3-methyl-4-pyridin-4-yl-thieno [2,3-b] thiophene-2,5-di carboxylic acid diethyl ester (MPTDC-C₂H₅) (I2) was obtained with a yield of 30%. FT-IR (KBr, cm⁻¹): 2981 (m), 1718 (vs), 1598 (m), 1483 (s), 1419 (m), 1373 (m), 1294 (vs), 1224 (s), 1166 (s), 1091 (s), 1024 (s), 846 (m), 763 (w), 626 (w) (Fig. S1). ¹H NMR (500 MHz, CDCl₃) δ 8.73 (d, J = 6.0 Hz, Ar(14,16)-H, 2H), 7.38 (d, J = 5.4 Hz, Ar(13,17)-H, 2H), 4.35 (d, J = 7.1 Hz, C21-H, 2H), 4.18 (d, J = 7.1 Hz, C24-H, 2H), 2.13 (s, C10-H, 3H), 1.37 (t, J = 7.1 Hz, C22-H, 3H), 1.15 (t, J = 7.1 Hz, C25-H, 3H) (Fig. S3). ¹³C NMR (126 MHz, CDCl₃) δ 162.19(C12), 161.25(C9), 149.30(C14,16), 145.86(C8), 145.13(C11), 143.70(C1), 140.00(C5), 139.12(C4), 132.71(C2), 131.00(C7), 124.26(C13,17), 61.48(C21), 61.25(C24), 14.29(C22), 14.17(C25), 13.82(C10) (Fig. S4).

Synthesis of H₂MPTDC. MPTDC-C₂H₅ (1 g) and KOH (1 g) were added into mixed solution of 10 mL deionized water and 10 mL ethanol in a 100 mL flask, then heated and refluxed for 3 h, after slowly cooling to ambient temperature and adjusted the pH value to 2 with 2M HCl, a large amount of pale yellow solid separated, then filtered and washed it to neutrality. The light yellow solid of H₂MPTDC was obtained with 95% yield. FT-IR (KBr, cm⁻¹): 1689 (m), 1623 (s), 1496 (s), 1352 (s), 1244 (vs), 880 (m), 835 (m), 756 (s), 632 (w) (Fig. S2). ¹H NMR (500 MHz, DMSO-d₆) δ 13.25 (s, O(17,20)-H, 2H), 8.64 (d, J = 6.1 Hz, Ar(12,14)-H, 2H), 7.44 (d, J = 6.0 Hz, Ar(11,15)-H, 2H), 2.01 (s, C9, 3H) (Fig. S5). ¹³C NMR (126 MHz, DMSO-d₆) δ 163.86(C19), 162.72(C16), 149.14(C12,14), 145.77(C8), 144.43(C10), 144.01(C1), 138.99(C4), 138.88(C5), 134.05(C2), 132.17(C7), 125.13(C11,C15), 14.05(C9) (Fig. S6).

II. Supplementary illustrations and explanations

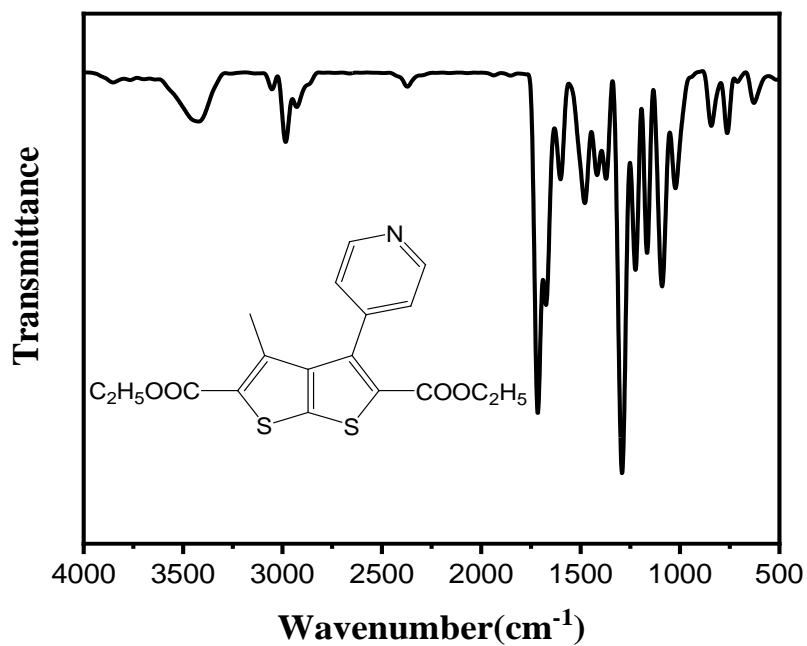


Fig. S1 The FT-IR spectrum of intermediate I2.

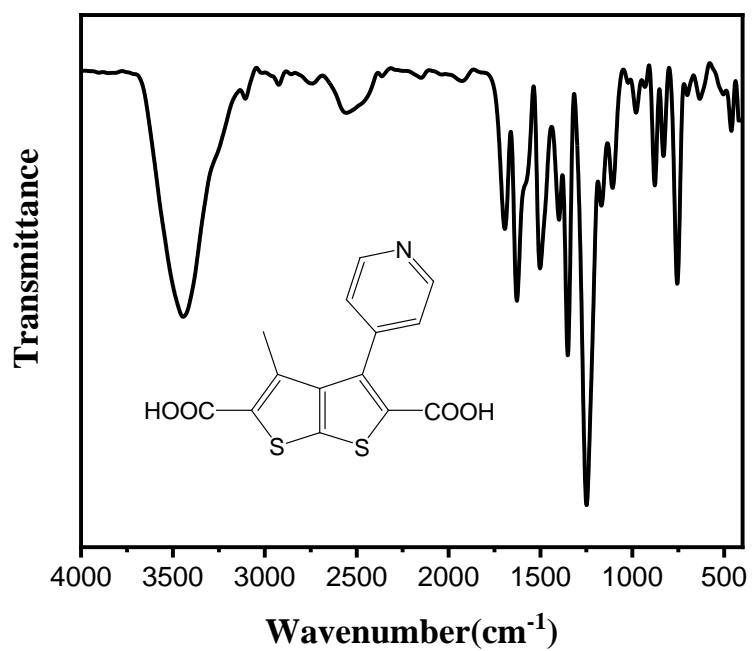


Fig. S2 The FT-IR spectra of ligand H₂MPTDC.

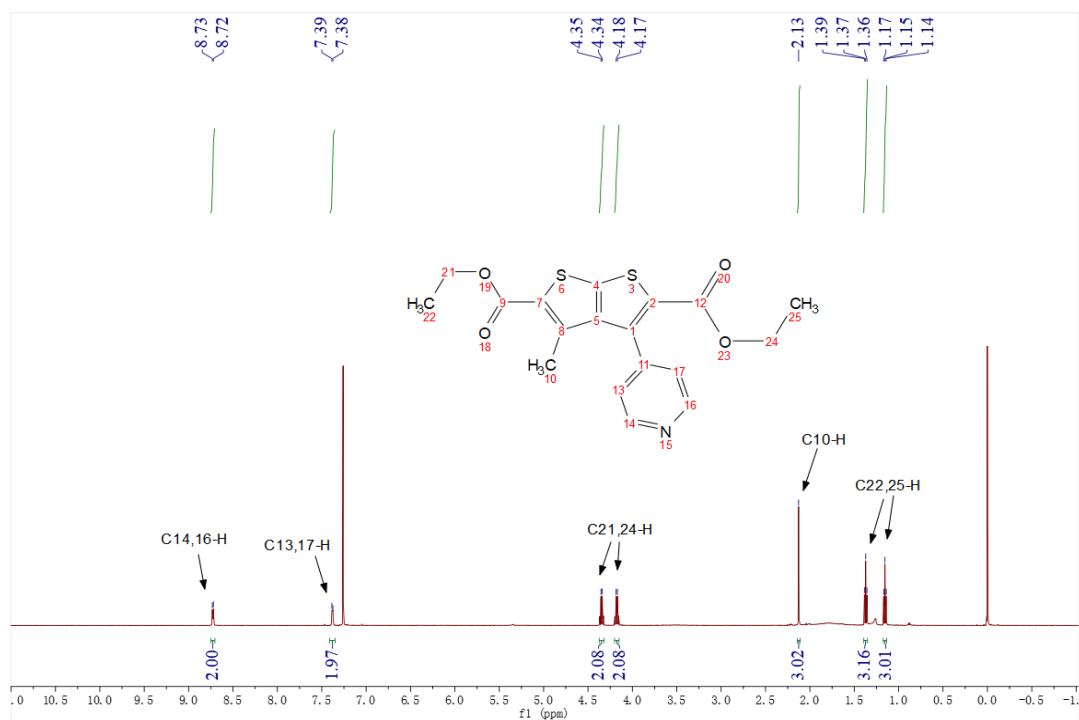


Fig. S3 ^1H NMR spectra of Intermediate I2.

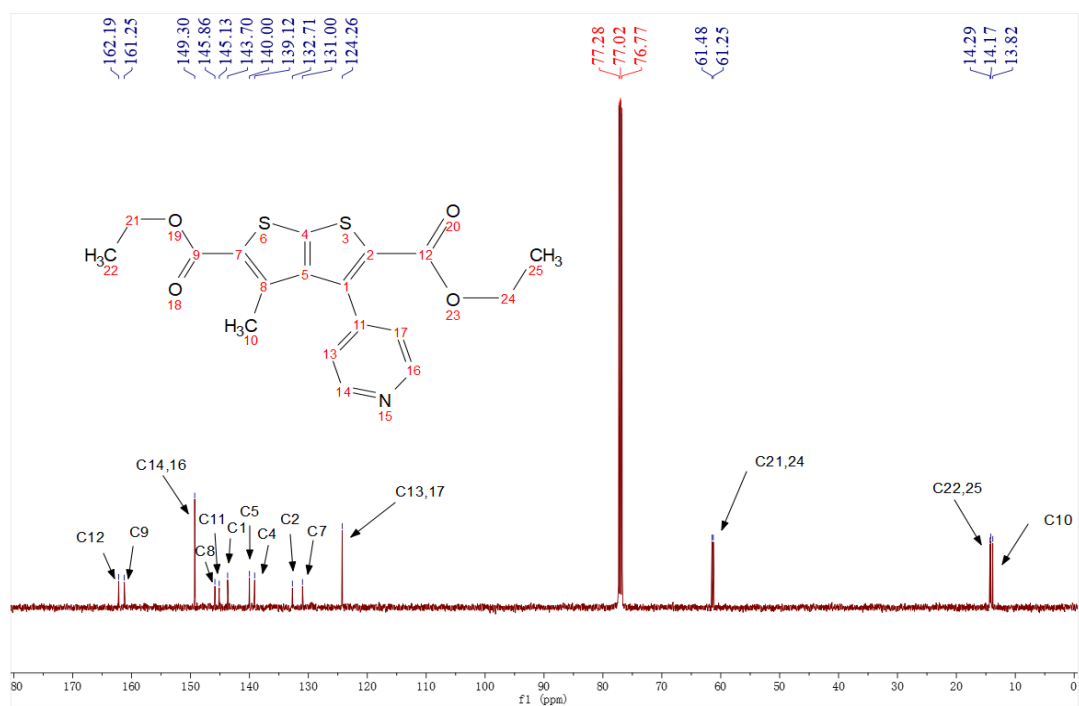


Fig. S4 ^{13}C NMR spectra of Intermediate I2.

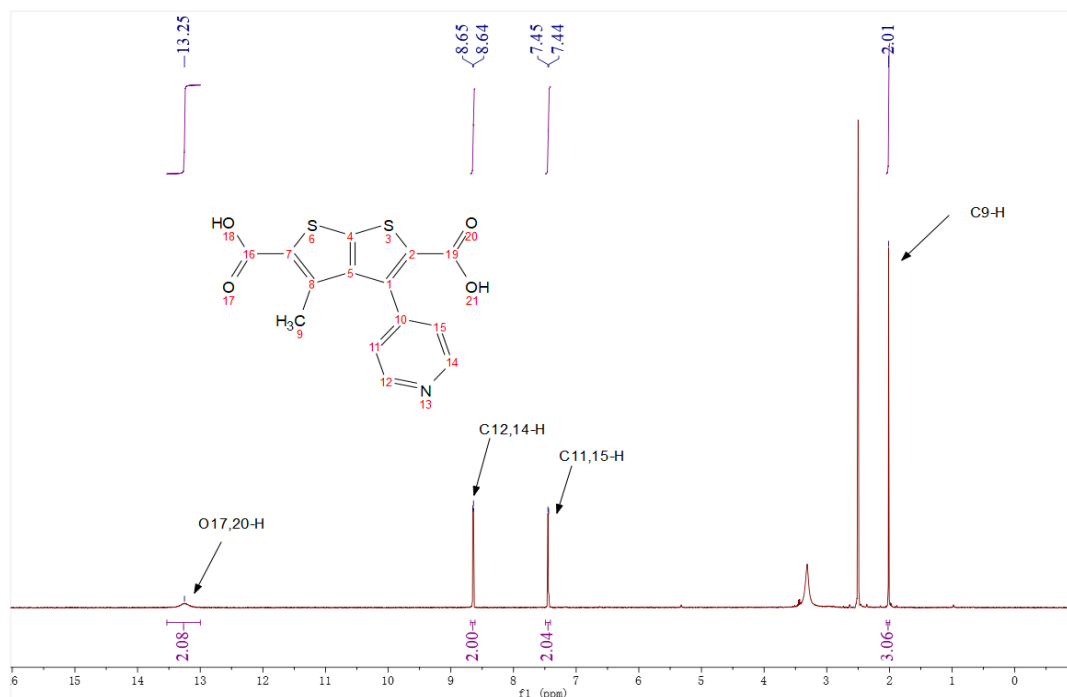


Fig. S5 1H NMR spectra of ligand H_2MPTDC .

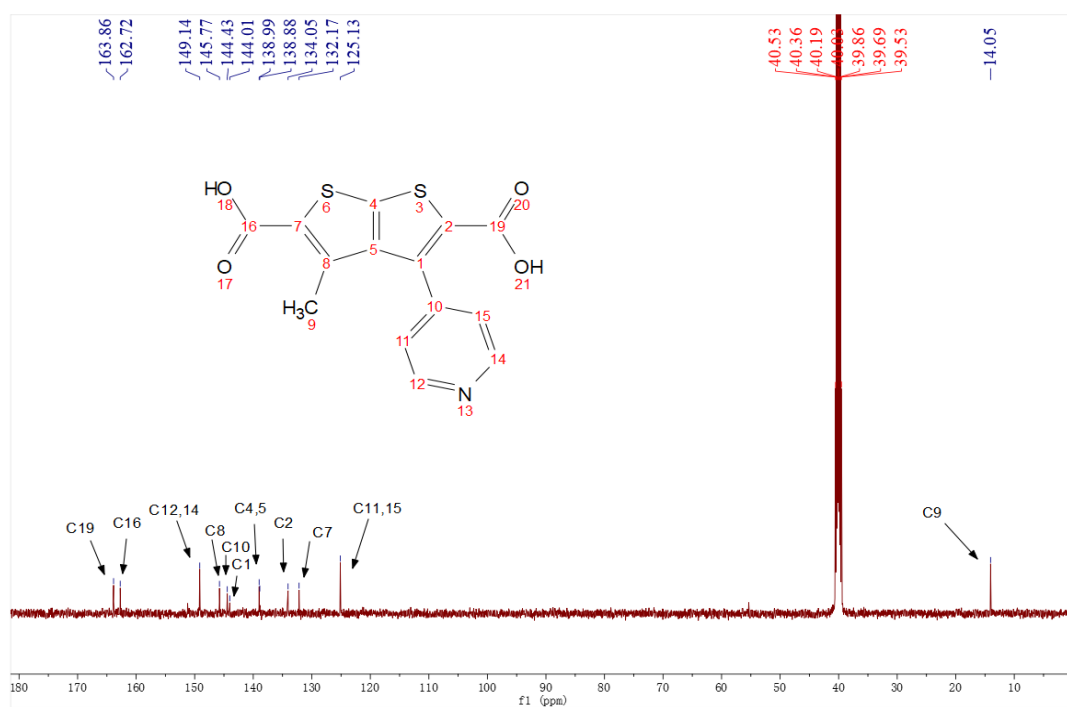


Fig. S6 ^{13}C NMR spectra of ligand H_2MPTDC .

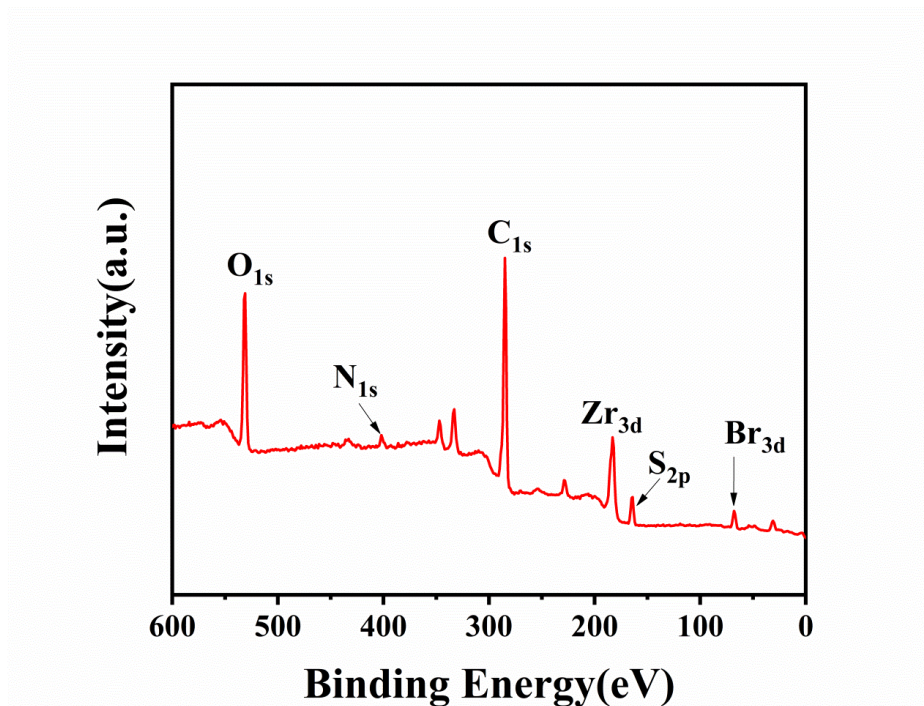


Fig. S7 The XPS of $(\text{Br}^-)\text{CH}_3\text{-Pyridinium-MOF-1}$.

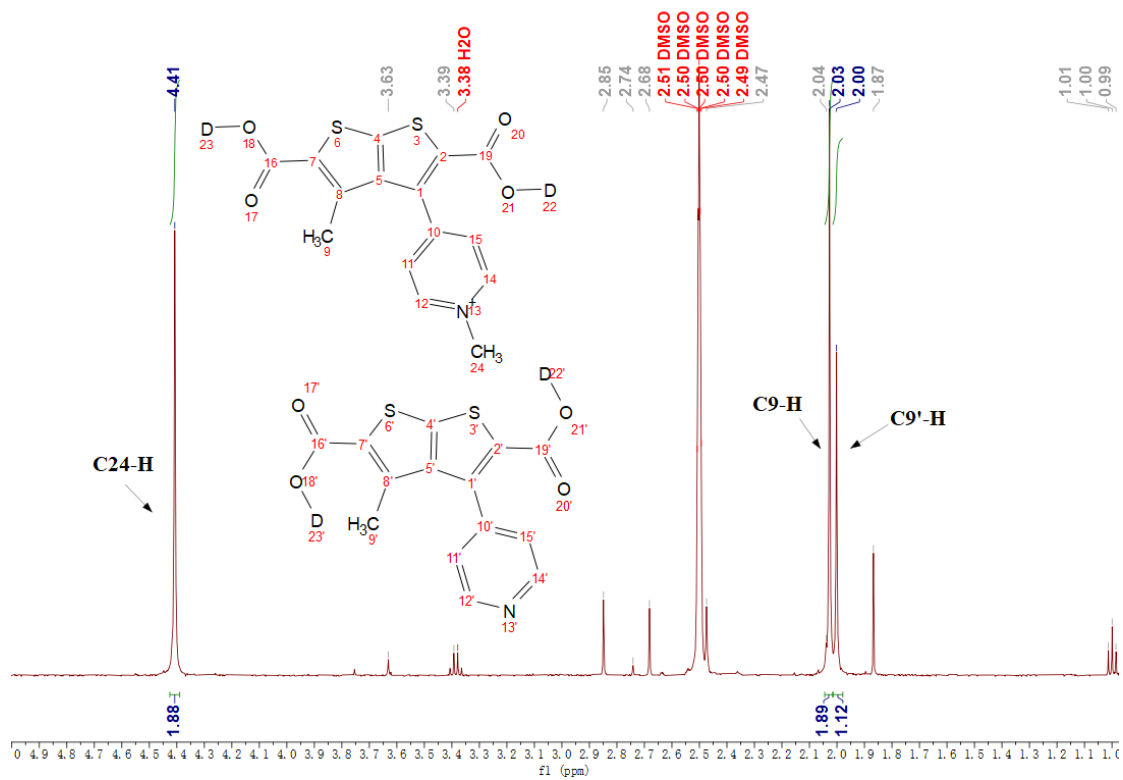


Fig. S8 ^1H NMR spectra of $(\text{Br}^-)\text{CH}_3\text{-Pyridinium-MOF-1}$.

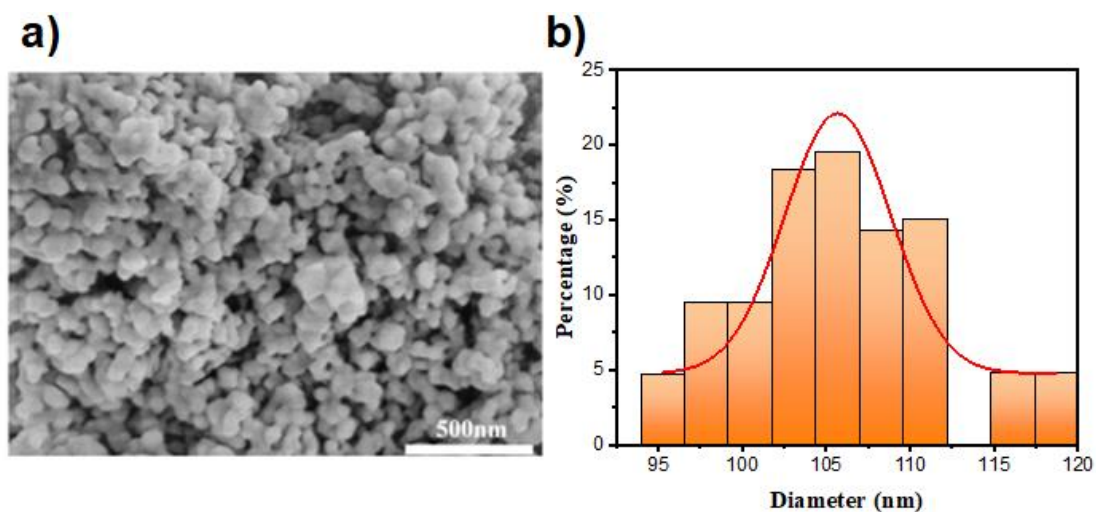


Fig. S9 (a) SEM image of $(\text{Br}^-)\text{CH}_3\text{-Pyridinium-MOF-1}$ and (b) analysis of particle size distribution in SEM.

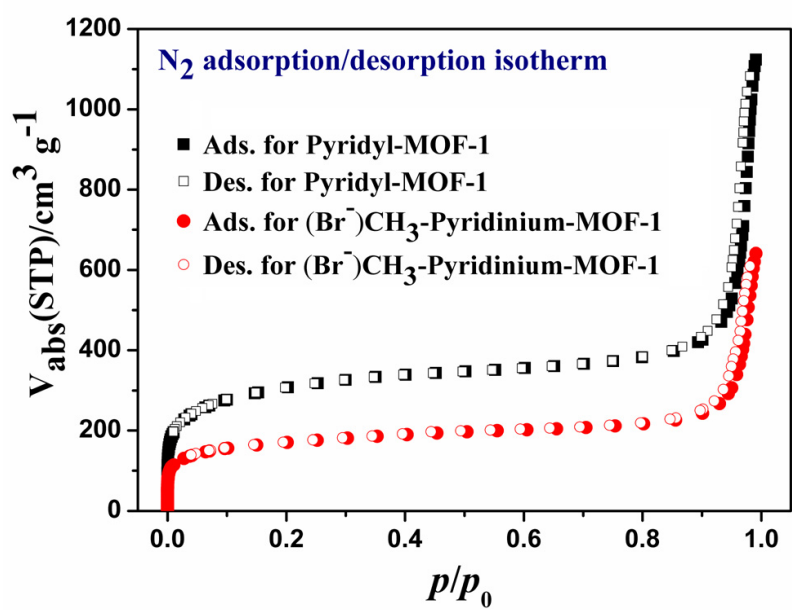


Fig. S10 N_2 Adsorption isotherms of Pyridyl-MOF-1 and $(\text{Br}^-)\text{CH}_3\text{-Pyridinium-MOF-1}$.

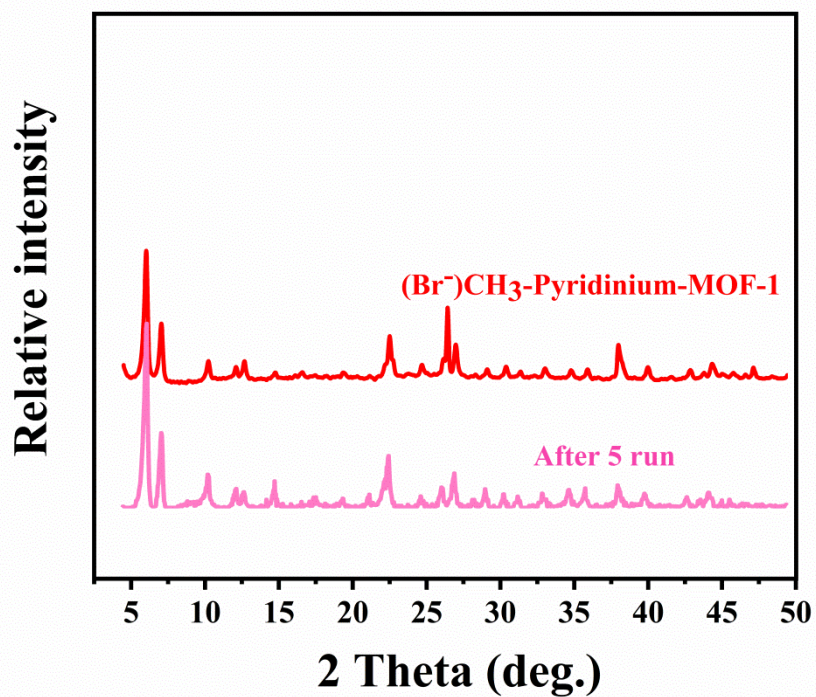


Fig. S11 Recycled experiments of (Br⁻)CH₃-Pyridinium-MOF-1.

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