Supporting Information

Enhanced gas sorption and breathing properties of the new sulfone functionalized COMOC-2 metal organic framework

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Figure S7. V K-edge XANES spectra of reference compounds with varying V oxidation states. From bottom to top, nominal oxidation state in parenthesis: V_2O_5 (black, +5), V_6O_{13} (green, +4.3), VO_2 (red, +4) and V_2O_3 (blue, +3). A line guide is displayed to show the relation between V oxidation state and main edge position.

Figure S8. Position of the V K-edge XANES main edge for the pure vanadium oxides V_2O_5 , V_6O_{13} , VO_2 and V_2O_3 as a function of vanadium oxidation state. Energy positions are relative to the V-foil offset.

Figure S9. Isosteric heat of CO₂ adsorption of SO₂-COMOC-2 (Red) and COMOC-2 (Black)



Figure S1. Narrow pore phase of COMOC- $2(V^{IV})$ (left) and large pore structure of COMOC- $2(V^{IV})$, view along the V-O axis.

Synthesis and characterization of the ligand 4,4'-bibenzoic acid-2,2'-sulfone $(H_2BPDC-SO_2)$: A slightly modified recipe was employed in comparison to the procedure published elsewhere to synthesize the SO_2 based organic ligand.¹ 2 g 4,4'-biphenyldicarboxylic acid and 20 mL fuming sulfuric acid were added into a 50 mL round-bottom flask equipped with a magnetic stirrer and the mixture was refluxed at 120 °C overnight. The resulting solution was cooled down to room temperature and then slowly poured into a beaker containing 150 mL deionized water under vigorous stirring. The obtained white precipitate was isolated by filtration and washed with copious amount of water and dried under vacuum. Yield, 1.91g, 76 %, based on 4,4'-biphenyldicarboxylic acid. Elemental Analysis for H₂BPDC-SO₂: calcd (%), C, 55.26; H, 2.63; S, 10.53; found (%), C, 53.98; H, 2.68; S, 10.24. 1H NMR (300 MHz, DMSO-d₆, δ , ppm):H1, 8.34, 2H; H2, 8.37-8.39, 2H; H3, 8.41-8.44, 2H (Figure S2). 13C NMR (300MHz, DMSO-d₆, δ, ppm): C1, 122.46; C2, 124.07; C3, 133.54; C4, 133.89; C5, 135.51; C6, 137.98; C7, 165.41 (Figure S3). IR spectrum (cm⁻¹, KBr pellet): 1137 (s), 1303 (m) (O=S=O of sulfone group), 1602 (s), 1480 (m) (carboxylate groups) (Figure S4).



Figure S2. ¹H NMR (300MHz, DMSO-d₆) spectrum of H_2BPDC -SO₂ ligand: 8.44-8.34 (m, 6H).



Figure S3. ¹³C NMR (300MHz, DMSO-d₆) spectrum of H₂BPDC-SO₂ ligand



Figure S4. IR spectra of the H₂BPDC-SO₂ ligand (Black) and BPDC ligand (Red).



Figure S5. TGA curves of COMOC-2 (Black) and SO₂-COMOC-2 (Red) measured under an air flow



Figure S6. IR spectra of COMOC-2 (Top) and SO₂-COMOC-2 (Bottom).



Figure S7. V K-edge XANES spectra of reference compounds with varying V oxidation states. From bottom to top, nominal oxidation state in parenthesis: V_2O_5 (black, +5), V_6O_{13} (green, +4.3), VO_2 (red, +4) and V_2O_3 (blue, +3). A line guide is displayed to show the relation between V oxidation state and main edge position



Figure S8. Position of the V K-edge XANES main edge for the pure vanadium oxides V_2O_5 , V_6O_{13} , VO_2 and V_2O_3 as a function of vanadium oxidation state. Energy positions are relative to the V-foil offset.



Figure S9. Isosteric heat of CO₂ adsorption of SO₂-COMOC-2 (Red) and COMOC-2 (Black)

The isosteric heat of CO_2 adsorption (Q_{st}) was calculated from the obtained CO_2 adsorption isotherms at different temperatures by employing the Clausius-Clapeyron equation:

$$Q_{st} = -R[\frac{\partial(\ln P)}{\partial(1/T)}]_n$$

Where P is the pressure, n is the amount adsorbed, T is temperature, R is the universal gas constant. We plotted lnP versus 1/T for different temperatures and the slope of these lines was used to determine the isosteric heat of adsorption at each pressure point.

As shown in Figure S9, the Q_{st} values of CO₂ for SO₂-COMOC-2 significantly increased compared with that of the pristine COMOC-2. Typically, the CO₂ Q_{st} of COMOC-2 at low uptake is 29.4 kJ/mol, while the CO₂ Q_{st} for SO₂-COMOC-2 reaches 43 kJ/mol. As loading increases, the isosteric heat drops to 32 kJ/mol and 25 kJ/mol for SO₂-COMOC-2 and COMOC-2, respectively.

References

 E. Neofotistou, C. D. Malliakas and P. N. Trikalitis, *Chemistry – A European Journal*, 2009, 15, 4523-4527.