Supporting Information

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

Guangbo Wang\textsuperscript{a}, Karen Leus\textsuperscript{a}, Sarah Couck\textsuperscript{b}, Pieter Tack\textsuperscript{c}, Hannes Depauw\textsuperscript{a}, Ying-Ya Liu\textsuperscript{d}, Laszlo Vincze\textsuperscript{c}, Joeri F. M. Denayer\textsuperscript{b} and Pascal Van Der Voort*\textsuperscript{a}

\textsuperscript{a} COMOC - Center for Ordered Materials, Organometallics and Catalysis, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium

\textsuperscript{b} Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

\textsuperscript{c} X-ray Imaging and Spectroscopy Group, Ghent University, Krijgslaan 281-S12, 9000 Ghent, Belgium

\textsuperscript{d} State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116024, Dalian, P. R. China

E-mail: pascal.vandervoort@ugent.be

Tel: (+)32-92644442; Fax: (+)32-92644983.
**Figures**

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.

Figure S2. $^1$H NMR (300MHz, DMSO-d$_6$) spectrum of H$_2$BPDC-SO$_2$ ligand: 8.44-8.34 (m, 6H).

Figure S3. $^{13}$C NMR (300MHz, DMSO-d$_6$) spectrum of H$_2$BPDC-SO$_2$ ligand.

Figure S4. IR spectra of the ligands of H$_2$BPDC-SO$_2$ (Black) and BPDC (Red).

Figure S5. TGA curves of COMOC-2 (Black) and SO$_2$-COMOC-2 (Red) measured under an air flow.

Figure S6. IR spectra of COMOC-2 (Top) and SO$_2$-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$_2$O$_5$ (black, +5), V$_6$O$_{13}$ (green, +4.3), VO$_2$ (red, +4) and V$_2$O$_3$ (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$_2$O$_5$, V$_6$O$_{13}$, VO$_2$ and V$_2$O$_3$ as a function of vanadium oxidation state. Energy positions are relative to the V-foil offset.

Figure S9. Isosteric heat of CO$_2$ adsorption of SO$_2$-COMOC-2 (Red) and COMOC-2 (Black)
Figure S1. Narrow pore phase of COMOC-2(VIV) (left) and large pore structure of COMOC-2(VIV), view along the V-O axis.

Synthesis and characterization of the ligand 4,4'-bibenzoic acid-2,2'-sulfone (H2BPDC-SO2): A slightly modified recipe was employed in comparison to the procedure published elsewhere to synthesize the SO2 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, 1.91 g, 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. $^1$H NMR (300MHz, DMSO-d$_6$) spectrum of H$_2$BPDC-SO$_2$ ligand: 8.44-8.34 (m, 6H).

Figure S3. $^{13}$C NMR (300MHz, DMSO-d$_6$) spectrum of H$_2$BPDC-SO$_2$ ligand
Figure S4. IR spectra of the H$_2$BPDC-SO$_2$ ligand (Black) and BPDC ligand (Red).

Figure S5. TGA curves of COMOC-2 (Black) and SO$_2$-COMOC-2 (Red) measured under an air flow.
Figure S6. IR spectra of COMOC-2 (Top) and SO$_2$-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 CO$_2$ adsorption of SO$_2$-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:

$$Q_{st} = -RT \left(\frac{\partial \ln P}{\partial (1/T)}\right)_n$$

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 CO$_2$ for SO$_2$-COMOC-2 significantly increased compared with that of the pristine COMOC-2. Typically, the CO$_2$ $Q_{st}$ of COMOC-2 at low uptake is 29.4 kJ/mol, while the CO$_2$ $Q_{st}$ for SO$_2$-COMOC-2 reaches 43 kJ/mol. As loading increases, the isosteric heat drops to 32 kJ/mol and 25 kJ/mol for SO$_2$-COMOC-2 and COMOC-2, respectively.

References