Supporting Information

A Highly Stable and Hierarchical Tetrathiafulvalene-based Metal-Organic Framework with Improved Performance as Solid Catalyst

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1. General methods and materials

All reagents and solvents employed for the syntheses were of high purity grade and were purchased from Sigma-Aldrich Co., and TCI. \(^1\)H NMR spectra were recorded using a Bruker DPX300 (300 MHz) spectrometer and Me\(_4\)Si as an internal standard. Infrared spectra were recorded in a FT-IR Nicolet 5700 spectrometer in the 4000-400 cm\(^{-1}\) range using powdered samples diluted in KBr pellets. Thermogravimetric analysis was carried out with a Mettler Toledo TGA/SDTA 851 apparatus in the 25-600 °C temperature range under a 10 °C/min scan rate and a N\(_2\) flow of 30 mL·min\(^{-1}\). Powder X-ray diffraction spectra were recorded using 0.7 mm borosilicate capillaries that were aligned on an Empyrean PANalytical powder diffractometer, using Cu K\(\alpha\) radiation (\(\lambda = 1.54056 \) Å).

2. Synthesis of Et\(_4\)TTFTB

\[
\begin{align*}
\text{C}_6\text{H}_4\text{S}_4 &\quad \text{EtOOC} \\
204.36 \text{ g mol}^{-1} &\quad \text{EtOOC} \\
\text{C}_6\text{H}_5\text{BrO}_2 &\quad \text{COOEt} \\
229.07 \text{ g mol}^{-1} &\quad \text{COOEt} \\
\end{align*}
\]

Pd(OAc)\(_2\) (84 mg, 0.38 mmol), P\(\text{Bu}_3\)•HBF\(_4\) (326 mg, 1.1 mmol), and Cs\(_2\)CO\(_3\) (2444 mg, 7.5 mmol) were placed in a 50-mL reaction flask under Argon. THF (10.0 mL) was added and the mixture was stirred for 10 min with heating. A solution of tetrathiafulvalene (307 mg, 1.5 mmol) and ethyl 4-bromobenzoate (1718 mg, 7.5 mmol) in THF (10.0 mL) was added. The mixture was heated at reflux for 15 h. The organic compounds were extracted with chloroform three times. The combined organic part was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo. Chromatographic purification on silica gel by using hexane/dichloromethane as an eluent afforded 2,3,6,7-tetra(4-ethoxycarbonylphenyl) tetrathiafulvalene (Et\(_4\)TTFTB) (840 mg, 1.1 mmol, 70%) as a dark red solid. Characterization: \(^1\)H NMR (CDCl\(_3\)): \(\delta = 1.37\) (t, \(J = 7.1 \) Hz, 12H), 4.36 (q, \(J = 7.1 \) Hz, 8H), 7.25–7.27 (m, 8H), 7.91 (dt, \(J = 8.7, 1.8 \) Hz, 8H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 14.51, 61.42, 108.92, 129.06, 130.06, 130.19, 130.80, 136.82, 166.02\). IR (v cm\(^{-1}\)): 1716 (s, C=O); 1696 (m); 1275 (s); 1101 (s).
3. Synthesis of $\text{H}_4\text{TTFTB}$

A 50-mL flask was charged with $\text{Et}_4\text{TTFTB}$ (734 mg, 0.921 mmol) and subjected to three cycles of evacuation and refilling with Ar. Degassed MeOH (7 mL) and THF (7 mL) were added to generate a suspension. In a separate flask, NaOH (466 mg, 11.6 mmol) was dissolved in degassed water (5 mL). The sodium hydroxide solution was added to $\text{Et}_4\text{TTFTB}$ under Ar and the reaction was heated to reflux for 12 hours. The reaction was then cooled to room temperature and the volatiles were removed in vacuo. A 1M solution of HCl (30 mL) was added to afford a maroon precipitate, which was collected by filtration and washed with water (50 mL). The product was collected and dried under high vacuum for 12 hours to afford $\text{H}_4\text{TTFTB}$ as a maroon solid (556.5 mg, 0.813 mmol, 88% yield). $^1$H NMR (DMSO-$d_6$): $d =$ 13.14 (br s, 4H, CO$_2$H), 7.87 (dt, 8H, J = 8.3 Hz, 1.8 Hz, CHCCO$_2$H), 7.35 (dt, 8H, J = 8.4 Hz, 1.8 Hz, SCCCH). $^{13}$C NMR (DMSO-$d_6$): $d =$ 166.5, 135.5, 131.2, 129.9, 129.2, 129.1, 107.7. IR (ν cm$^{-1}$): 3420 (s, OH); 1686 (s, C=O); 1602 (s); 1412 (m); 1265 (m).

4. Synthesis of trinuclear $\text{Fe}_3\text{O}$

1.1 g of $\text{Fe}^0$ (0.02 mol) were dissolved in 10 ml of water (MQ) and 5.6 ml of $\text{HClO}_4$ (60 %) were added dropwise and the solution was stirred at 50-60°C during 2 hours. The blue solution was cooled at room temperature and stirred overnight. Then 3.5 ml of $\text{H}_2\text{O}_2$ (35 %) and 0.6 ml of water were added dropwise to the solution with an ice bath and the solution change from blue to orange. Finally, 3.3 of $\text{CH}_3\text{COONa}$ (0.04 mol) were carefully added at 0-5 °C to the solution that became dark reddish. The solution was collected in a Petri dish and dark red crystals of [Fe$_3$O(CH$_3$COO)$_6$]ClO$_4$ appeared after slow evaporation at room temperature and were collected by filtration.
5. Synthesis of MUV-2

**Single crystal:** The procedure was adapted from ref. 5. H$_4$TTFTB (5 mg), [Fe$_3$O(CH$_3$COO)$_6$]ClO$_4$ (5 mg) and acetic acid (0.2 ml) in 1 ml of DMF were ultrasonically dissolved in a 4 ml Pyrex vial. The mixture was heated in an oven at 90 °C for 72 h. After cooling down to room temperature, dark red crystals were collected by filtration.

**Bulk powder:** 20 mg of H$_4$TTFTB, 20 mg of [Fe$_3$O(CH$_3$COO)$_6$]ClO$_4$ and 0.8 ml of acetic acid were dissolved in 4 ml of DMF in a 10 ml Pyrex vial. The mixture was heated in an oven at 90°C for 72 h. After cooling down to room temperature, dark brown powder was collected by filtration. The powder was washed with large amount of DMF in order to remove the unreacted ligand and [Fe$_3$O(CH$_3$COO)$_6$]ClO$_4$ and immersed in DMF during one night. Finally, the product was immersed in EtOH during 3 h at 65°C, washed and collected by filtration (19.6 mg; 80 %).

6. IR of MUV-2

The infrared spectrum of MUV-2 clearly shows the presence of the vibrational bands characteristic of the framework -(O-C-O)- groups around 1550 and 1430 cm$^{-1}$ confirming the presence of the dicarboxylate within the solid. On the other hand, the band at 1700 cm$^{-1}$ characteristic of free C=O groups was not observed for washed MUV-2 which is in agreement with the absence of free acid within the pores for this solid.  

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**Fig. S1.** IR of H$_4$TTFTB ligand and washed MUV-2.
7. Crystallographic data

Data Collection. X-ray data for compound MUV-2 was collected at a temperature of 100 K using a synchrotron radiation at single crystal X-ray diffraction beamline I19 in Diamond light Source,7 equipped with an Pilatus 2M detector and an Oxford Cryosystems nitrogen flow gas system. Data was measured using GDA suite of programs.

Crystal structure determinations and refinements. X-ray data were processed and reduced using CrysAlisPro suite of programmes. Despite of using Diamond Light Source synchrotron radiation, crystals of MUV-2 only diffracted to 1.2 Å of resolution. Thus, the data was trimmed accordingly. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The crystal was found to be an inversion twin with a twin law of (-1, 0, 0, -1, 0, 0, -1) and a BASF of 0.50(4). The crystal structure was solved and refined against all \( F^2 \) values using the SHELXL and Olex2 suite of programmes.8,9 All atoms were refined anisotropically with the exception of the [Fe₃O(O₂CCH₃)₆(H₂O)]₃⁺ cations. Hydrogen atoms were placed in the calculated positions. Starting material [Fe₃O(O₂CCH₃)₆(H₂O)]₃⁺ clusters were found disordered and modelled over six positions in the pores. The C-O distances and O-C-C angles were restrained using SADI and DFIX commands. The crystal was found to be an inversion twin with a twin law of (-1, 0, 0, -1, 0, 0, -1) and a BASF of 0.50(4). The crystal structure was solved and refined against all \( F^2 \) values using the SHELXL and Olex2 suite of programmes.8,9

Table S1. Crystallographic information for MUV-2.

| Crystal colour | red |
|----------------|-----|
| Crystal size (mm) | 0.18 × 0.03 × 0.02 |
| Crystal system | Hexagonal |
| Space group, \( Z \) | P-62m, 2 |
| \( a \) (Å) | 33.298(3) |
| \( c \) (Å) | 12.3958(7) |
| \( V \) (Å³) | 11903(2) |
| Density (Mg.m⁻³) | 0.429 |
| Wavelength (Å) | 0.6889 |
| Temperature (K) | 100 |
| \( \mu \) (Mo-Kα) (mm⁻¹) | 0.316 |
| 2Θ range (°) | 3.622 to 33.358 |
| Refls collected | 22307 |
| Independent reflns (\( R_{int} \)) | 2697 (0.2068) |
| L.S. parameters, \( p \) | 215 |
| No. of restraints, \( r \) | 199 |
| \( R1(F) \) \( F > 2.0σ(F) \) | 0.0324 |
| \( wR2(F^2) \), all data | 0.0929 |
| \( S(F^2) \) | 0.671 |

[a] \( R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| \); [b] \( wR^2(F^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]^{1/2} \); [c] \( S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2} \)
**Fig. S2.** Schematic representation of the 4,6-connected network with ttp topology

**Fig. S3.** Partial views of the crystal structure of TTFTB in MUV-2 highlighting the dihedral angles.
8. Mössbauer of MUV-2

Mössbauer spectra were collected in the temperature range 295–4 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi $^{57}$Co source in a Rh matrix. The velocity scale was calibrated using α-Fe foil. Isomer shifts, IS, are given relative to this standard at room temperature. The absorber was obtained by packing the powder samples into a Perspex holder. The absorber thickness was calculated on the basis of the corresponding electronic mass-absorption coefficients for the 14.4 keV radiation.\(^\text{10}\) The low temperature spectra were collected in a bath cryostat with the sample immersed in liquid He at 4 K or in He exchange gas at 50 K. The spectra were fitted to Lorentzian lines using a non-linear least-squares method.\(^\text{11}\)

The Mössbauer spectra (Fig. S4) of MUV-2 in the temperature range 4-295 K consist of two absorption peaks. At 295 and 50 K they may be fitted by a single, symmetric, quadrupole doublet. The estimated isomer shifts relative to metallic Fe at room temperature, IS, are consistent with S=5/2 Fe(III) ion in an octahedral oxygen environment\(^\text{12}\) and similar to those reported for other Fe(III) trinuclear complexes.\(^\text{13-16}\) Considering that S=5/2 Fe(III) has significantly lower quadrupole splittings than S=2 Fe(II),\(^\text{12}\) if Fe in this electronic state was present it would give rise to one resolved peak located at a higher velocity than the S=5/2 Fe(III) peaks. The room temperature spectrum was accumulated during a long time in order to improve the statistics, so the dispersion of the base line counts is narrow enough to allow the detection of this S=2 Fe(II) peak if it had > 1% of the total absorption area. Since this peak was not observed, if there is any S=2 Fe(II) in the sample its content should be ≤ 2% of the total Fe. The occurrence of a single doublet is in fair agreement with the similarity of the first coordination spheres of the Fe(III) cations in the three different crystallographic sites. The increase in IS with decreasing temperature is due to the second order Doppler shift.

The line widths, Γ, at 4 K are significantly larger than at room temperature and 50 K. Furthermore, the doublet is clearly asymmetric. These features may be explained by a decrease of the relaxation frequency of the direction of the Fe(III) magnetic moments due to the presence of strong AFM interactions (see below magnetic measurements).\(^\text{12,13,15,16}\) The relaxation frequency, however, is not low enough to allow the observation of magnetic splitting, which implies that no long range magnetic correlations are established.

In order to maintain the charge balance, one of the 3 coordinated H$_2$O molecules in the cluster [Fe$_3$(µ$_3$-O)] is present as a negatively charged hydroxide OH$^-$ and the formula for a neutral MUV-2 is (C$_{34}$H$_{16}$O$_8$S$_4$)$_3$(Fe$_3$O)$_2$(H$_2$O)$_4$(OH)$_2$.

**Table S2.** Estimated parameters from the Mössbauer spectra of MOF based on Fe$_3$O trimers sample taken at different temperatures.

| T     | IS (mm/s)$^a$ | QS (mm/s)$^b$ | Γ (mm/s)$^c$ |
|-------|---------------|---------------|--------------|
| 295 K | 0.41          | 0.71          | 0.54         |
| 50 K  | 0.54          | 0.73          | 0.68         |
| 4 K   | 0.54          | 0.82          | 0.98         |

[a] IS (mm/s) isomer shift relative to metallic α-Fe at 295 K; [b] QS (mm/s) quadrupole splitting; [c] Γ peak width. Estimated errors are ≤ 0.02 mm s$^{-1}$ for IS and QS, Γ.
Fig. S4. Mössbauer spectra of MUV-2 taken at different temperatures.

9. SQUID of MUV-2

The temperature dependence of the magnetic susceptibility (Figure S5) shows that $\chi T$ product of MUV-2 at 300 K ($11.9 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$) is close to the theoretical expected value for three Fe(III) non-interacting $S = 5/2$ spins ($\chi T = 13.125 \text{ cm}^3\text{K}\cdot\text{mol}^{-1}$). Upon cooling, $\chi T$ strongly decreases when lowering the temperature in agreement with the strong antiferromagnetic coupling within the quasi-isolated Fe(III) trimers.

Fig. S5. Magnetic susceptibility $\chi$ (black line) and $\chi T$ (red line) versus temperature variation of MUV-2.
10. CV of MUV-2

Solid-state cyclic voltammetry (CV) of MUV-2 (Figure S6) was recorded in the potential range of –1.2 to 1.6 V and exhibited one reversible reduction peak at –0.77 corresponding to the Fe$^{3+}$/Fe$^{2+}$ reduction. Surprisingly, it was not observed any peak corresponding to the oxidation process of the electroactive TTF ligand. As it has been previously reported for other bent TTF derivatives,$^{17,18}$ the significant deviation from planarity of the TTF unit destroys its donor ability by preventing efficient 6-π electron delocalization (heteroaromaticity) within the dithiolium cation formed in the TTF$^+$ radical cation. Moreover, the oxidation of TTF ligand of MUV-2 with iodine was not successful as confirmed by Raman spectroscopy (see below).

![Solid-state cyclic voltammetry of MUV-2](image)

**Fig. S6.** Solid-state cyclic voltammetry of MUV-2 collected at 0.05 V/s in TBAPF$_6$/CH$_3$CN 0.1 M electrolyte using a platinum wire as the counter electrode, and a silver wire as the pseudoreference electrode. Ferrocene was added as an internal standard upon completion of each experiment. All potentials are reported in V versus Ag/AgCl.
11. Raman of MUV-2

Raman spectrum of MUV-2 shows that the peak assigned to C=C stretch of the neutral TTF core which appears at 1605 cm\(^{-1}\) for the ligand slightly shift to 1609 cm\(^{-1}\) for MUV-2 confirming that the TTF remains in the neutral state (Figure S7).\(^{19}\) Moreover, it was intended to chemically oxidize the TTF ligands of MUV-2 via iodine doping by immersing the crystals in a solution of iodine in cyclohexane as it has been reported for other TTF-based MOF.\(^{19}\) However, Raman peaks assigned to the C=C ring stretch of the TTF moiety in MUV-2@I\(_2\) remained identical and didn’t shift towards lower frequencies confirming that it was not possible to oxidize the TTF units with iodine (Figure S8).

![Solid state Raman spectra of the ligand H\(_4\)TTFTB and MUV-2 using a laser of \(\lambda = 785\) nm.](image)

![Solid state Raman spectra of MUV-2 and MUV-2@I\(_2\) using a laser of \(\lambda = 785\) nm.](image)
Fig. S9. Top: EDAX analysis of washed crystals of washed MUV-2 confirming the presence of all the elements (C, O, S, Fe) and the (S : Fe) ratio of (2 : 1). Bottom: Picture of SEM showing the length of the crystals (100-200 μm).
13. TGA of MUV-2

![TGA profile of washed MUV-2](image1)

**Fig. S10.** Thermogravimetric analysis (TGA) profile of washed MUV-2 at a heating rate of 5°C/min under a constant stream of N₂ (black) and DTG curve (red).

![Powder X-ray diffraction patterns](image2)

**Fig. S11.** Powder X-ray diffraction patterns of simulated, as-synthesised, desolvated and resolvated (DMF) of MUV-2.
14. Chemical stability of MUV-2

![X-ray diffraction patterns](image)

**Fig. S12.** Powder X-ray diffraction patterns of washed MUV-2 and after treatment with aqueous solutions of pH = 2, 7 and 11, and with different organic solvents (CH$_2$Cl$_2$, toluene, EtOH) for 24 h. Concentration: 5 mg of MUV-2 / 5 ml buffer solution.

15. Adsorption measurements of MUV-2

![Nitrogen adsorption isotherm](image)

**Fig. S13.** Nitrogen adsorption isotherm at 77 K on MUV-2.

The BET surface area was determined applying the theory of Brunauer, Emmett, and Teller, but fulfilling the criterion established by Rouquerol et al. (Figure S11), according to which the relative pressure range for BET surface area determination was limited to 0-0.08.
Fig. S14. $v(1-p/p_0)$ vs $p/p_0$ (left) and BET plot for the 0-0.08 relative pressure range (right).

The pore size distribution was obtained by means of the Barrett-Joyner-Halenda (BJH) method and the Harkins-Jura statistical film thickness curve ($t$-curve), shown in Figure S15. The average pore diameter was 38.7 Å.

![Figure S15](image)

Fig. S15. BJH pore size distributions for MUV-2.

The surface area of MUV-2 was also calculated through the monolayer capacity of CO$_2$ at 298 K by using Dubinin-Astakhov equation. In this case, it was assumed that the molecular sectional area of CO$_2$ at 298 K is 0.195 nm$^2$. The surface area of MUV-2 calculated via the CO$_2$ Dubinin-Astakhov approach is 1425 m$^2$/g at 298 K (Figure S16). This value is in good agreement with the corresponding obtained with the N$_2$ isotherm at 77 K and the BET model.
Fig. S16. Dubinin-Astakhov plot for CO\textsubscript{2} adsorption at 298 K on MUV-2.

The experimental isotherms were fitted by using a fourth grade virial equation: \(^{24}\)

\[
\ln \left( \frac{P}{Q} \right) = A_0 + A_1 Q + A_2 Q^2 + A_3 Q^3 + A_4 Q^4
\]

Fig. S17. Gas adsorption isotherms of CO\textsubscript{2} (left) and CH\textsubscript{4} (right) on MUV-2 at different temperatures. Points are experimental uptakes and lines are virial fittings.

The isosteric heats of adsorption of CO\textsubscript{2} and CH\textsubscript{4} were calculated from sets of fitted isotherms according to the Clausius-Clapeyron equation: \(^{25}\)

\[
q_{st} = R \cdot T^2 \cdot \left[ \frac{\partial \ln P}{\partial T} \right]_{Q=\text{cte}} = -R \cdot \left[ \frac{\partial (\ln P)}{\partial (1/T)} \right]_{Q=\text{cte}}
\]

The isosteric heat of adsorption (q\textsubscript{st}) of CO\textsubscript{2} decreases from 30 to 20 kJ/mol, which remains constant in the case of CH\textsubscript{4} at around 16 kJ/mol within the studied loading range (Figure S18). These values clearly indicate the highest affinity of MUV-2 for the CO\textsubscript{2}, rather than for the...
CH₄. The isosteric heat of adsorption of CO₂ at zero coverage (q̂st₀) of MUV-2 is comparable to that of a LTA zeolite of Si/Al ratio of around 6.²⁶

**Fig. S18.** Isosteric heat of adsorption of CO₂ and CH₄ on MUV-2.

**Fig. S19.** PXRD of activated MUV-2 before and after adsorption measurements.

**Fig. S20.** Gas adsorption isotherms of CO₂ on MUV-2 after treatment with pH = 2 and 11 aqueous solution.
Catalytic activity of MUV-2

Materials

DBT (99%), DBTO$_2$ (97%), 4-methyl DBT (96%) and 4,6-dimethyl DBT (97%) and $n$-dodecane were of analytical grade and supplied by Sigma-Aldrich.

Catalytic experiments

5 mg of catalyst was placed on a round-bottom flask (25 mL). Activation of the MUV-2 catalyst was carried out by heating at 150 °C under vacuum overnight. Subsequently, the reaction temperature was fixed at 140 °C and the required reaction atmosphere was obtained by purging the system with a balloon containing O$_2$ under atmospheric pressure. The reaction time started by addition of a solution of DBT (200 mg L$^{-1}$ of S) in 10 mL of the reaction solvent to the preheated round-bottom flask. As reaction solvent, $n$-dodecane or commercial diesel (Repsol) were used. The mixture was continuously stirred magnetically at 500 rpm. The course of the reaction was followed by sampling 250 µl of the reaction mixture that was diluted with 250 µl of anisole and injected in a GC having a FI detector and a 30 m capillary column of 5% crosslinked phenyl methyl silicone. At the end of the reaction, the mixture was filtered to remove the solid while still hot and the organic phase was washed with three aliquots of 20 ml of water to remove the DBTO$_2$ product formed in the process. Selective radical quenching experiments using $p$-benzoquinone or DMSO were carried out as described above but with the addition of 20 mol% of these reagents with respect to the initial DBT at 1.5 h of the reaction time.

Raman measurements

Raman spectra were recorded with a 514 nm laser excitation on a Renishaw Raman Spectrometer (“Refelx”) equipped with a CCD detector. The laser power on the sample was 25 mW and a total of 50 acquisitions were taken for each spectrum. A commercial Linkam cell (THMS600) was used for collecting spectra under controlled conditions. Thus, the sample was first subjected to a Ar flow (20 ml min$^{-1}$) at 220 °C for ~5 h. Afterwards the temperature was lowered to 140 °C in Ar, and then the gas was changed to O$_2$ (20 ml min$^{-1}$) at the same temperature. Finally, the gas was changed to Ar.

Table S3. Comparison of pore sizes and pore windows between the different MOFs MIL-100, MIL-101 and MUV-2.

|       | MIL-100                   | MIL-101                   | MUV-2                      |
|-------|---------------------------|---------------------------|----------------------------|
| Pore window | Pentagonal: 4.7 x 5.5 Å | Pentagonal:12 x 12 Å     | Hexagonal: 33 x 33 Å     |
|        | Hexagonal: 8.6 x 8.6 Å   | Hexagonal: 16 x 15 Å     | Trigonal: 12 x 9.5 Å     |
| Pore size | 25 - 29 Å                 | 29 - 34 Å                 | 33 Å                      |
16.1. Study of the induction period

To gain understanding on the origin of the induction period, providing evidence of the favorable role of MUV-2 mesoporosity explaining its higher catalytic activity, three control experiments were carried out in where MUV-2 was contacted with n-dodecane containing DBT in the absence of oxygen for 2 h and then oxygen was admitted or MUV-2 was boiled at the reaction temperature in n-dodecane under oxygen and then DBT was added after 2 h. In a third experiment, MUV-2 was heated in n-dodecane under Ar for 2 h and then O₂ and DBT were added simultaneously. The results obtained (see Figure S21) clearly indicate that the induction period is significantly reduced to about one half when either DBT or O₂ are already present in the system and it is unchanged when both, DBT and O₂ are introduced in the system even if MUV-2 was already equilibrated in n-dodecane. Therefore, these variations in the induction period indicate that diffusion of DBT and O₂ are responsible for the delay in observing DBT consumption or DBTO₂ appearance. Thus, the large pore size of MUV-2 should be responsible for the shortened induction period observed for this hierarchical MOF respect to MIL-100 and MIL-100.

![Figure S21](image-url)

**Fig. S21.** Influence on the aerobic oxidation of DBT (▲) to DBTO₂ (Δ) using MUV-2 as a catalyst at various pretreatments in comparison to the general procedure of the aerobic oxidation of DBT (■) to DBTO₂ (□). (a) DBT in n-dodecane with MUV-2 under Ar at 140 °C for 2 h and then sudden addition of O₂ at 2 h; (b) suspending MUV-2 in n-dodecane under O₂ at 140 °C for 2 h and then addition of DBT at 2 h; (c) contacting MUV-2 in n-dodecane under Ar for 2 h at 140 °C and then sudden addition of DBT under an O₂ atmosphere at 2 h. Reaction conditions: catalyst (5 mg of MUV-2), DBT (1150 mg L⁻¹), n-dodecane (10 mL), O₂ (1 atm), 140 °C. Note that for ▲(a), ♦ (b) and ● (c), the initial reaction time was 2 h.
16.2. Reusability of MUV-2

Stability of MUV-2 as catalyst was addressed by performing a series of consecutive uses of the same sample recovered after each reaction, washed with anisole and then acetonitrile, dried and employed in a subsequent run under the general reaction conditions. The results comparing the time-conversion plot show that the induction period remains constant upon reuse, while, the reaction rate exhibits some decrease from the first to the third use (from 25.7 to 21.7 mgS h\(^{-1}\)) but it remains constant up to the fifth reuse (see Figure S22).

![Figure S22](image-url)

**Fig. S22.** Reusability of MUV-2 as catalyst in the aerobic oxidation of DBT (a) to DBTO\(_2\) (b). First use (■), third use (●) and fifth use (▲). Reaction conditions: catalyst (5 mg of MUV-2), DBT (1150 mg L\(^{-1}\)), \(n\)-dodecane (10 mL), O\(_2\) (1 atm), 140 °C.

16.3. Productivity test

MUV-2 stability of catalyst was also confirmed by performing a productivity test in where a large excess of DBT (1 g of S L\(^{-1}\)) was submitted to oxidation using a minor weight of catalyst (2 mg), allowing the reaction to progress for sufficiently long time. It was observed that a conversion about 95% of DBT can be achieved at 48 h reaction time even under these highly unfavourable conditions. (see Figure S23).

![Figure S23](image-url)

**Fig. S23.** Productivity test for the aerobic oxidation of DBT (■) to the corresponding sulfone (●) using MUV-2 as catalyst. Reaction conditions: catalyst (2 mg of MUV-2), DBT (5750 mg L\(^{-1}\)), \(n\)-dodecane (10 mL), O\(_2\) (1 atm), 140 °C.
16.4. Scope of the reaction

The general scope of MUV-2 as catalyst for the aerobic oxidation of DBTs was also evaluated by carrying out the oxidation of two derivatives containing one or two methyl groups (4-MeDBT and 4,6-Me₂DBT). As expected also for 4-MeDBT and 4,6-Me₂DBT oxidation to the corresponding sulfones proceeds in the presence of MUV-2 as catalyst, although a gradual increase in the induction period was observed due to the larger molecular dimensions of these derivatives, following the order DBT<4MeDBT<4,6Me₂DBT (see Figure S24).

[Fig. S24. (a) Aerobic oxidation of (■) DBT, (●) 4-MeDBT and (▲) 4,6-Me₂DBT to (b) the corresponding sulfones. Reaction conditions: catalyst (5 mg of MUV-2), DBT, 4-MeDBT and 4,6-Me₂DBT (1150 mg L⁻¹), n-dodecane (10 mL), O₂ (1 atm), 140 °C.]

16.5. Homogeneous, ligand and hot filtration test of MUV-2

Aerobic oxidation of DBT to DBTO₂ was also tested with the preformed cluster [Fe₃O(CH₃COO)₆]ClO₄ as homogeneous catalyst (Figure S25a, ●) using the same iron amount as that employed when using MUV-2 as heterogeneous catalyst (a, or with the iron amount determined during the leaching of MUV-2 (Figure S50a, □). Figure S50b show a blank control experiment where the ligand H₄TTFTB has been employed as homogeneous catalyst. Hot filtration test comparing the time-conversion plot of twin reactions in which for one of them the solid catalyst is removed by filtration at reaction temperature (140 °C), when conversion was about 40%, shows that the process is mainly heterogeneous (about 85%), taking place in the solid catalyst (see Figure S25c).
**Fig. S25.** a) Aerobic oxidation of DBT to DBTO₂ using the preformed cluster $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]\text{ClO}_4$ as catalyst with the amount of Fe present in MUV-2 (0.014 mmol) DBT (■), DBTO₂ (●); with the amount of Fe leached (0.00007 mmol) DBT (□), DBTO₂ (○), b) Aerobic oxidation of DBT to DBTO₂ using the ligand H₄TTFTB as catalyst with the amount of ligand present in MUV-2 (4 mg) DBT (■), DBTO₂ (●), c) Hot filtration test for the aerobic oxidation of DBT to DBTO₂ using MUV-2 as catalyst. In the presence of catalyst DBT (■), DBTO₂ (●); after catalyst filtration DBT (□), DBTO₂ (○) at 40 % conversion. Reaction conditions: catalyst (5 mg of MUV-2), DBT (1150 mg L⁻¹), n-dodecane (10 mL), O₂ (1 atm), 140 °C.

**16.6. Quenching experiments**

To address the reaction mechanism and, particularly, to determine the nature of the reactive oxygen species responsible for oxidation, a combination of quenching experiments and spectroscopic studies were carried out. Thus, while DMSO (a specific hydroxyl radical quencher) exerts a minor influence on the temporal profile of the oxidation, addition of p-benzoquinone (a scavenger of superoxide and hydroperoxyl radicals) has a strong influence decreasing significantly DBT conversion (see Figure S26).

**Fig. S26.** Aerobic oxidation of (a) DBT to (b) DBTO₂ in the absence of any quencher (■), in the presence of DMSO (●) or in the presence of p-benzoquinone (▲). Reaction conditions: catalyst (5 mg of MUV-2), DBT (1150 mg L⁻¹), n-dodecane (10 mL), O₂ (1 atm), 140 °C.
16.7. Raman spectra of MUV-2 with different atmospheres

Activation of molecular oxygen by Fe$_{3}$H$_{3}$O nodes was assessed by *in situ* Raman spectroscopy. Upon activation of MUV-2 at 220 °C under N$_{2}$ and subsequent admission of O$_{2}$ at 140 °C, appearance of two new vibration bands at 1502 and 1161 cm$^{-1}$ attributable to adsorbed O$_{2}$ and Fe-O-O, superoxo, respectively, was observed (see Figure S27). These characteristic vibration bands disappear and the Raman spectra of the original thermally treated MUV-2 Raman spectra is recovered by flushing N$_{2}$ on the sample, indicating that O$_{2}$ chemisorption was reversible.

**Fig. S27.** (1) Raman spectra of MUV-2 under N$_{2}$ flow at 140 °C after being activated at 220 °C under N$_{2}$ flow for 2 h. (2) Same sample of spectrum 1 that is submitted subsequently to O$_{2}$ at 140 °C for 2 h before recording the spectrum. (3) Sample of spectrum 2 that is submitted to N$_{2}$ at 140 °C for 2 h before recording the spectrum. Legend: iron-oxo (826 cm$^{-1}$), iron-superoxo (1161 cm$^{-1}$) and adsorbed O2 (1313 and 1502 cm$^{-1}$).
16.8. Diesel as solvent

**Fig. S28.** Aerobic oxidation of DBT using MUV-2 as catalyst (a) in n-dodecane (■) or diesel (▲) and (b) formation of the corresponding sulfone in n-dodecane (■) or in diesel (▲). Reaction conditions: catalyst (5 mg of MUV-2), DBT (1150 mg L\(^{-1}\)), n-dodecane or diesel (10 mL), \(\text{O}_2\) (1 atm), 140 °C.
17. References

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