Electronic Supplementary Material (ESI) for Dalton Transactions

New Metal-Organic Frameworks from Triptycene: Structural Diversity from Bulky Bridges

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1 Equipment

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. ^{13}C NMR spectra were recorded using a proton decoupled pulse sequence. ^{1}H and ^{13}C NMR spectra were calibrated to the residual protonated solvent at δ 7.27 and δ 77.23, respectively, for $CDCl_3$, or at δ 2.50 and δ 39.51, respectively, for DMSO-d_6. IR spectra were obtained neat with a Thermo Nicolet 6700 FT-IR with a Smart Orbit attenuated total reflectance (ATR) accessory. Electron impact (EI) mass spectra were obtained at the UBC Microanalytical Services Laboratory using a double focussing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of source temperatures 120-180 °C and ionization energy of 70 eV. Elemental analyses (C, H, N) were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John's melting point apparatus and corrected according to the appropriate calibration. Single crystal X-ray diffraction (SCXRD) experiments were performed on a Bruker X8 APEX CCD with MoKα radiation or a Bruker APEX DUO with MoKα or CuKα radiation Powder X-ray diffraction experiments were performed on a Bruker D8 Advance with a CuKα sealed tube X-ray source and a NaI scintillation detector. Thermogravimetric analysis data were obtained using a Perkin Elmer TGA6 instrument. Gas (N_2) adsorption data were obtained using a Micromeritics ASAP 2010 analyzer; analyses were carried out at 77 K.

2 Single crystal x-ray diffraction analysis (SCXRD)

Suitable crystals of **TMOF-1** and **TMOF-2** were mounted on a glass fibre with oil. In the case of **TMOF-2**, three different suitable crystals were isolated, giving rise to structures for **TMOF-2a**, **TMOF-2b**, and **TMOF-2c**. Structure solutions were refined using the SHELXL software.[1]

2.1 SCXRD of TMOF-1

Crystals of **TMOF-1** suitable for X-ray diffraction were grown by slow vapor-diffusion of pyridine/toluene into a DMF/chlorobenzene solution over 2 months. All measurements were made on a Bruker X8 APEX diffractometer at 100 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 30.09° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 189824 reflections that were collected, 57091 were unique ($R_{int} = 0.072$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.[2] Data were corrected for absorption effects using a multi-scan technique (SADABS),[3] with max and min transmission coefficients of 0.809 and 0.483, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[4] Disorder and partial occupancy is present in solvent DMF and water molecules filling the void space left by the porous structure. Modelling such solvent molecules was performed to partially account for electron density in the void spaces using OLEX[5]. Further electron density was removed using PLATON[6] SQUEEZE[7]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 57091 reflections and 2371 variable parameters and converged. (largest parameter shift was 0.169 per esd).

2.2 SCXRD of TMOF-2a

Crystals of **TMOF-2a** suitable for x-ray diffraction were grown by slowly cooling a dimethylformamide solution of **TMOF-2** heated to 110 °C in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 22.52° in a series of φ and ω scans in .50° oscillations with 60 s exposures. Of the 32208 reflections that were collected, 10441 were unique (R_{int} = 0.087); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.[2] Data were corrected for absorption effects using a multi-scan technique (SADABS),[3] with max and min transmission coefficients of 0.996 and 0.858, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[4] Disorder is present in solvent DMF molecules filling the void space left by the porous structure. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 10441 reflections and 1111 variable parameters.

2.2 SCXRD of TMOF-2b

Crystals of **TMOF-2b** suitable for x-ray diffraction were grown by slowly cooling a dimethylformamide solution of **TMOF-2** heated to 110 °C in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 1 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 26.32° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 119076 reflections that were collected, 31729 were unique (R_{int} = 0.072); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.[2] Data were corrected for absorption effects using a multi-scan technique (SADABS),[3] with max and min transmission coefficients of 0.975 and 0.813, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[4] All non-hydrogen atoms were refined anisotropically. Disorder is present in solvent DMF molecules filling the void space left by the porous structure. Disorder and partial occupancy is present in solvent DMF and water molecules filling the void space left by the porous structure. Modelling such solvent molecules was performed to partially account for electron density in the void spaces. Natural void spaces occurred within the structure; PLATON[6] SQUEEZE[7] was not used. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 31729 reflections and 1915 variable parameters and converged (largest parameter shift was 0.012 per esd).

2.2 SCXRD of TMOF-2c

Crystals of **TMOF-2c** suitable for x-ray diffraction were grown by slowly cooling a dimethylformamide solution of **TMOF-2** heated to 110 °C in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 1 K using graphite monochromated Cu Kα radiation (1.54178 Å). Data were collected to a maximum 2θ value of 67.17° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 178548 reflections that were collected, 29024 were unique ($R_{int} = 0.054$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.[2] Data were corrected for absorption effects using a multi-scan technique (SADABS),[3] with max and min transmission coefficients of 0.813 and 0.725, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[4] Disorder and partial occupancy is present in solvent DMF molecules filling the void space left by the porous structure. Modelling such solvent molecules was performed to partially account for electron density in the void spaces. Further electron density was removed using OLEX[5] solvent mask. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full matrix least-squares refinement on F^2 was based on 29024 reflections and 1960 variable parameters and converged (largest parameter shift was 0.004 per esd).

3 ^{1}H NMR Spectra

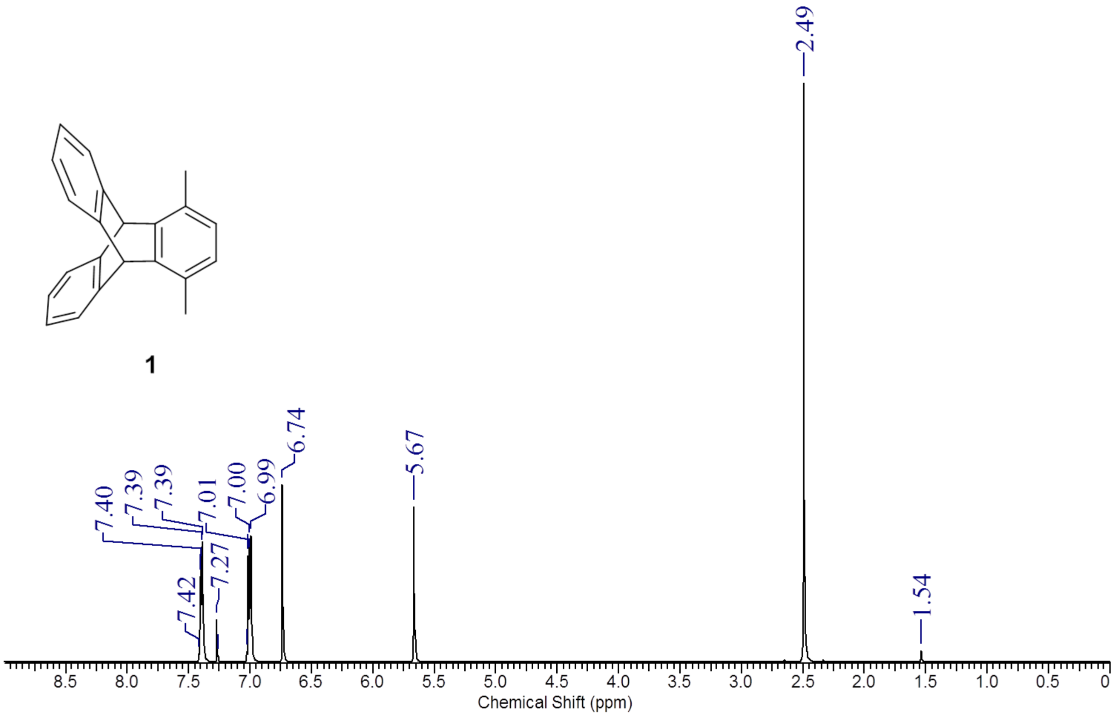

Figure S1. ^{1}H NMR spectrum of 1,4-dimethyltriptycene, **1** ($CDCl_3$, 298 K). The peak at 1.54 ppm is residual water in the solvent.

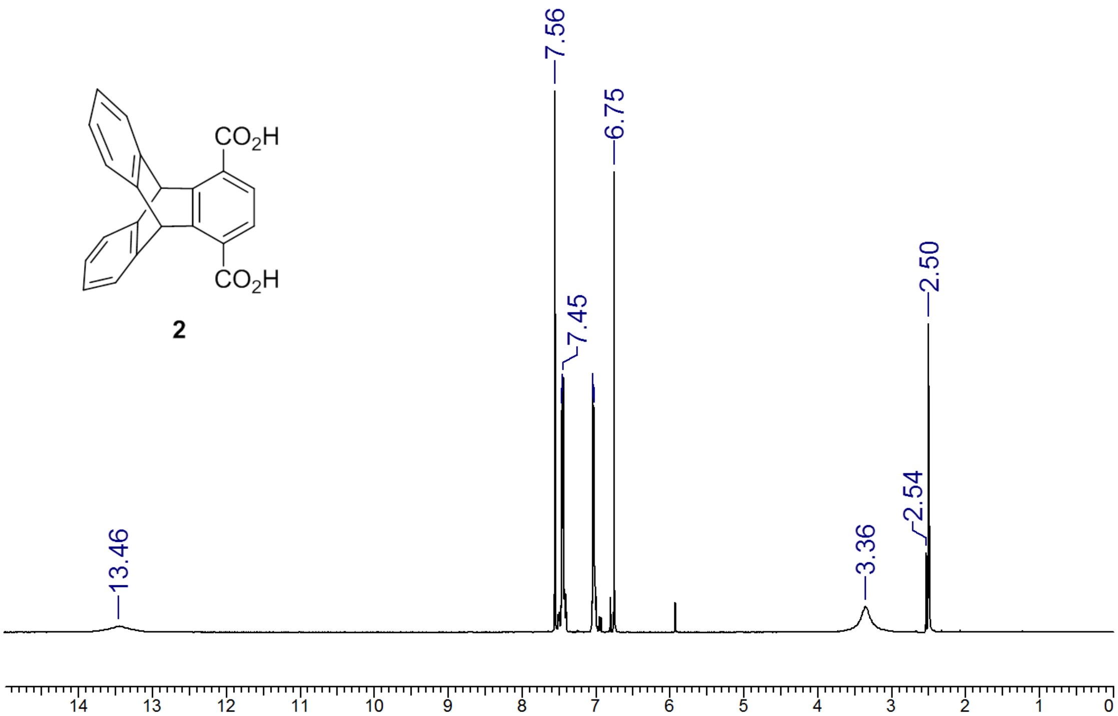

Figure S2. ^{1}H NMR spectrum of triptycene-1,4-dicarboxylic acid, **2** (DMSO-d_6, 298 K). The peak at 3.36 ppm is residual water and 2.54 ppm is residual dimethyl sulfoxide in the solvent.

4 ^{13}C NMR Spectra

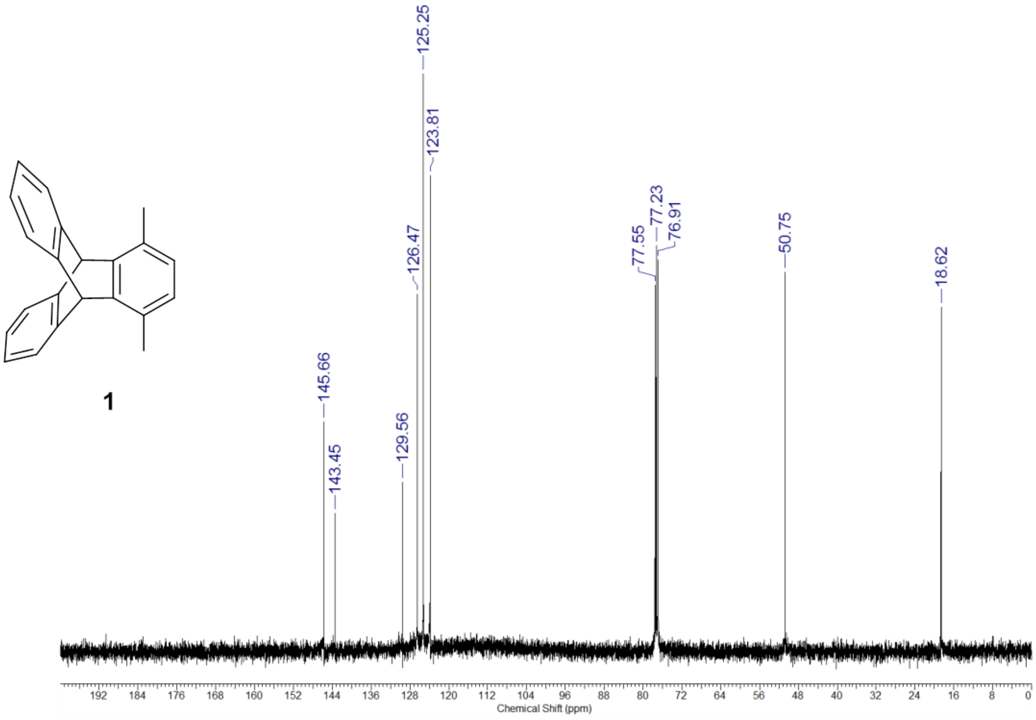

Figure S3. ^{13}C NMR spectrum of 1,4-dimethyltriptycene, **1** (CDCl$_3$, 298 K).

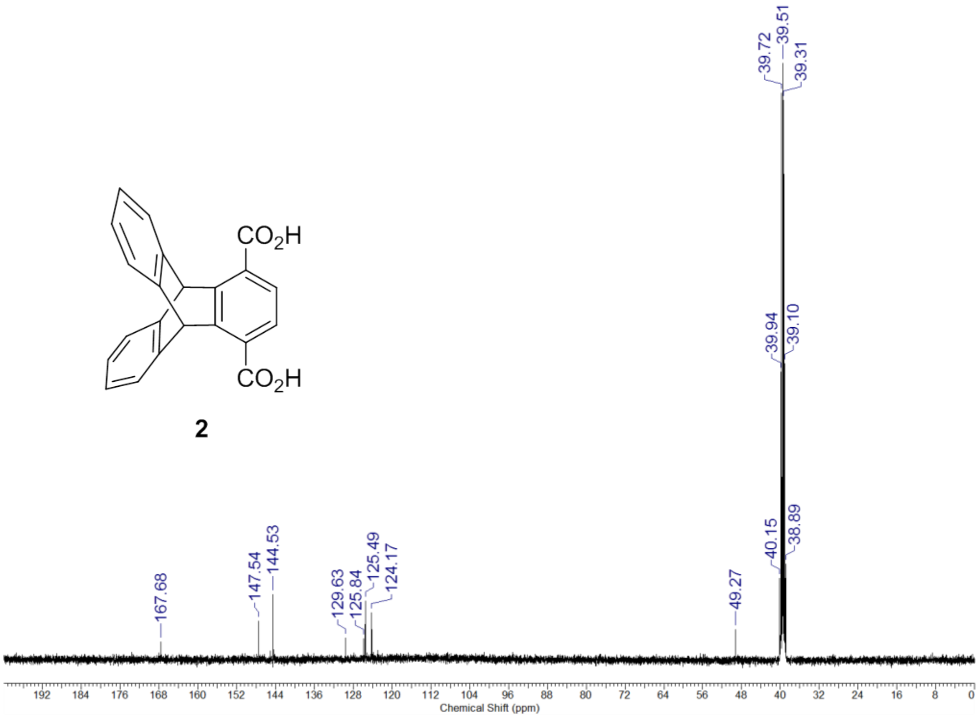

Figure S4. ^{13}C NMR spectrum of triptycene-1,4-dicarboxylic acid, **2** (DMSO-d_6, 298 K).

5 IR Spectra

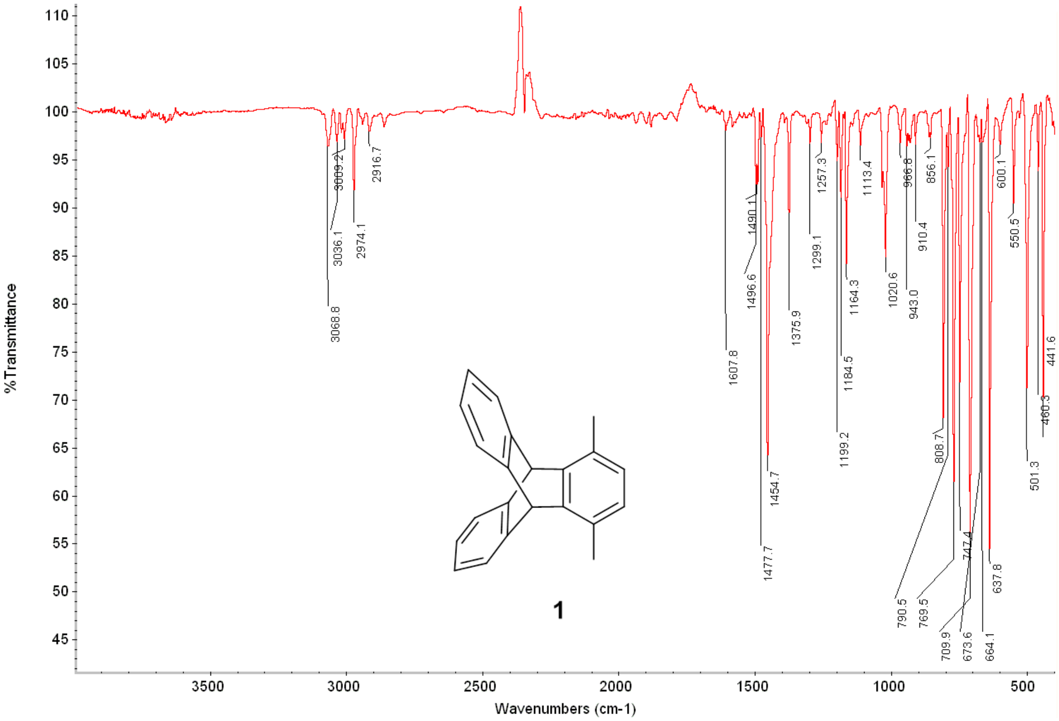

Figure S5. IR spectrum of 1,4-dimethyltriptycene, **1**.

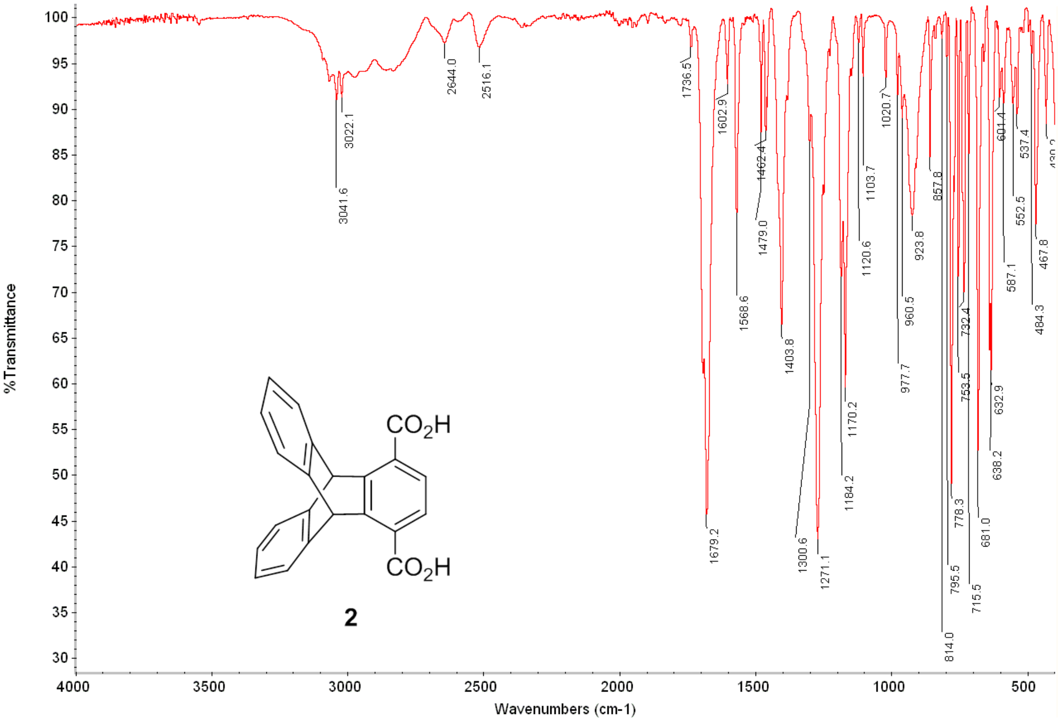

Figure S6. IR spectrum of triptycene-1,4-dicarboxylic acid, **2**.

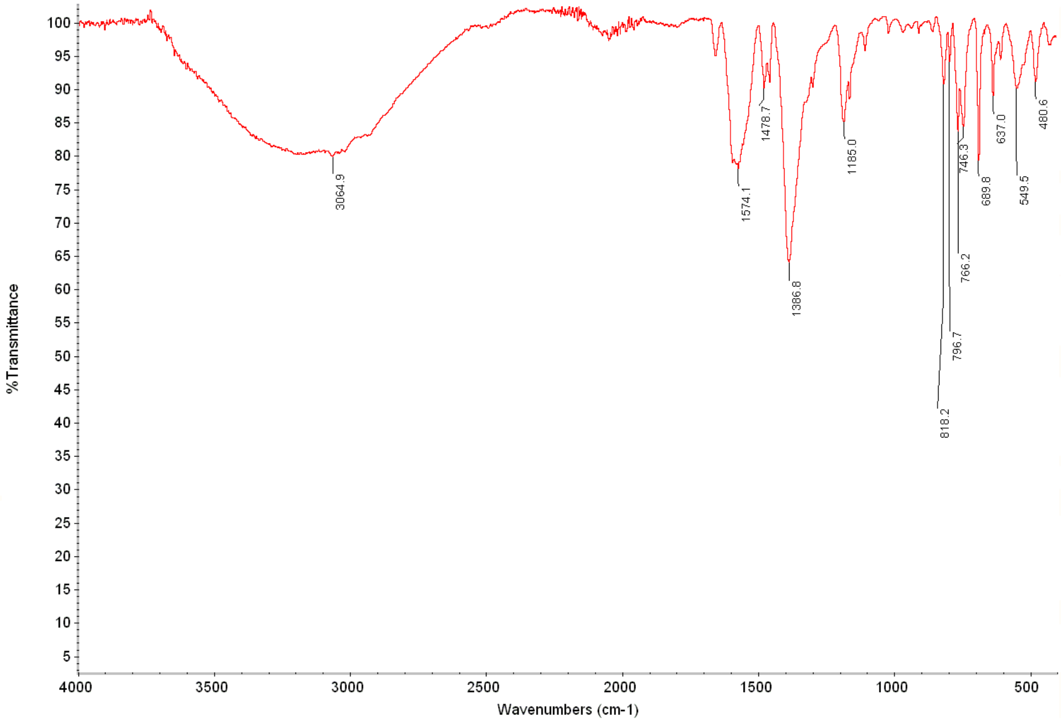

Figure S7. IR spectrum of bulk **TMOF-2** after being dried under vacuum at 120 °C.

References

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