Electronic Supplementary Material (ESI) for CrystEngComm

Metal-Organic Frameworks from Novel Flexible Triptycene- and Pentiptycene-Based Ligands

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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 $CDCl_3$, δ 5.32 and δ 54.00, respectively, for CD_2Cl_2, 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 (SCXRD) analysis

Suitable crystals of **3Me$_2$**, **3H$_2$**, **5H$_2$**, **TMOF-3**, **TMOF-3-*bipy***, **TMOF-4** and **PMOF-1** were mounted on a glass fibre with oil. Structure solutions were refined using the SHELXL software.[1]

2.1 SCXRD of 3Me$_2$

Crystals of **3Me$_2$** suitable for X-ray diffraction were grown by slow evaporation from DCM/hexanes. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 60.078° in a series of φ and ω scans in 0.50° oscillations with 3 s exposures. Of the 33845 reflections that were collected, 4253 were unique (R_{int} = 0.0328); 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 1.0090 and 0.9674, 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. 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 4253 reflections and 200 variable parameters and converged. (largest parameter shift was 0.001 per esd).

2.2 SCXRD of 3H$_2$

Crystals of $\mathbf{3H_2}$ suitable for X-ray diffraction were grown by slow evaporation from THF. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 58.39° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 107574 reflections that were collected, 33613 were unique (R_{int} = 0.0352); 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 1.015 and 0.833, 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 THF 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 33613 reflections and 1767 variable parameters and converged. (largest parameter shift was 0.001 per esd).

2.3 SCXRD of 5H$_2$

Crystals of $\mathbf{5H_2}$ suitable for X-ray diffraction were grown by slow evaporation from THF/hexanes. All measurements were made on a Bruker X8 APEX CCD diffractometer at 100 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 54.97° in a series of φ and ω scans in 0.50° oscillations with 10 s exposures. Of the 23637 reflections that were collected, 5931 were unique (R_{int} = 0.0546); 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 0.9879 and 0.8935, 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 hexane 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 5931 reflections and 352 variable parameters and converged. (largest parameter shift was 0.005 per esd).

2.4 SCXRD of TMOF-3

Crystals of **TMOF-3** suitable for X-ray diffraction were grown by slow cooling a DMF solution of $\mathbf{3H_2}$ and $Zn(NO_3)_2{\bullet}6H_2O$ in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 51.08° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 26585 reflections that were collected, 8086 were unique (R_{int} = 0.0543); 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

0.9526 and 0.8142, 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 framework and solvent DMF and water 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 8086 reflections and 604 variable parameters and converged. (largest parameter shift was 0.001 per esd).

2.5 SCXRD of TMOF-3-*bipy*

Crystals of **TMOF-3-*bipy*** suitable for X-ray diffraction were grown by slow cooling a DMF solution of $\mathbf{3H_2}$, 4,4'-bipyridine, and $Zn(NO_3)_2$•$6H_2O$ in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (1.54178 Å). Data were collected to a maximum 2θ value of 131.305° in a series of φ and ω scans in 0.50° oscillations with 5 s exposures. Of the 41065 reflections that were collected, 15214 were unique (R_{int} = 0.0629); 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 0.6786 and 0.5143, 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 the framework and solvent DMF, chlorobenzene, and water 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 15214 reflections and 1358 variable parameters and converged. (largest parameter shift was 0.030 per esd).

2.6 SCXRD of TMOF-4

Crystals of **TMOF-4** suitable for X-ray diffraction were grown by slow cooling a 1:1 DMF:PhCl solution of $\mathbf{3H_2}$ and $Zn(NO_3)_2$•$6H_2O$ in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Cu Kα radiation (1.54178 Å). Data were collected to a maximum 2θ value of 112.605° in a series of φ and ω scans in 0.50° oscillations with 120 s exposures. Of the 8726 reflections that were collected, 8726 were unique (R_{int} = 0.000); 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 1.193 and 0.854, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[4] Electron density resulting from disordered solvent molecules was removed using an 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 8726 reflections and 788 variable parameters and converged. (largest parameter shift was 0.000 per esd).

2.7 SCXRD of PMOF-1

Crystals of **PMOF-1** suitable for X-ray diffraction were grown by slow cooling a DMF solution of **$5H_2$** and $Zn(NO_3)_2$•$6H_2O$ in a sealed Parr pressure vessel. All measurements were made on a Bruker APEX DUO diffractometer at 90 ± 2 K using graphite monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 49.802° in a series of φ and ω scans in 0.50° oscillations with 30 s exposures. Of the 84407 reflections that were collected, 22294 were unique (R_{int} = 0.0535); 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 0.887 and 0.752, 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. 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 22294 reflections and 2167 variable parameters.

3 ^{1}H NMR Spectra

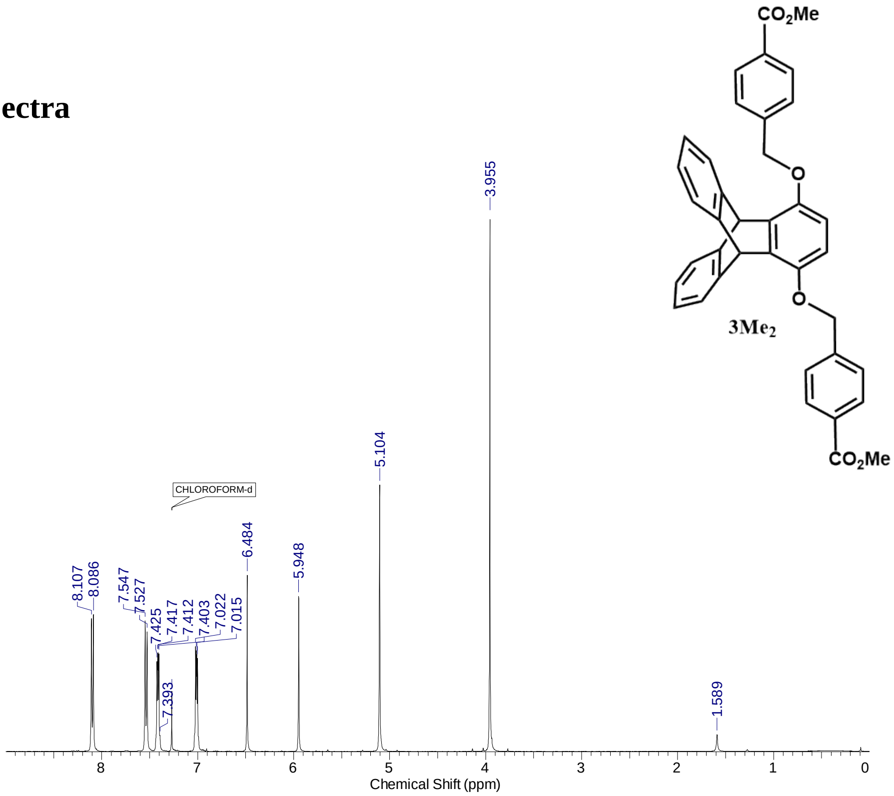

Figure S1. ^{1}H NMR spectrum of **$3Me_2$** ($CDCl_3$, 298 K). The peak at 1.589 ppm is residual water in the solvent.

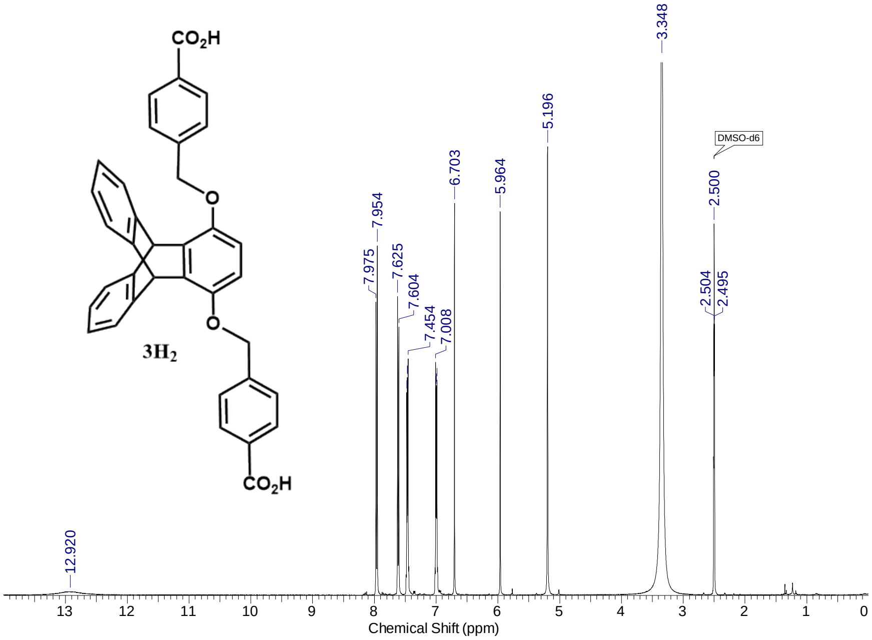

Figure S2. ^{1}H NMR spectrum of **$3H_2$** (DMSO-d_6, 298 K). The peak at 3.348 ppm is residual water in the solvent.

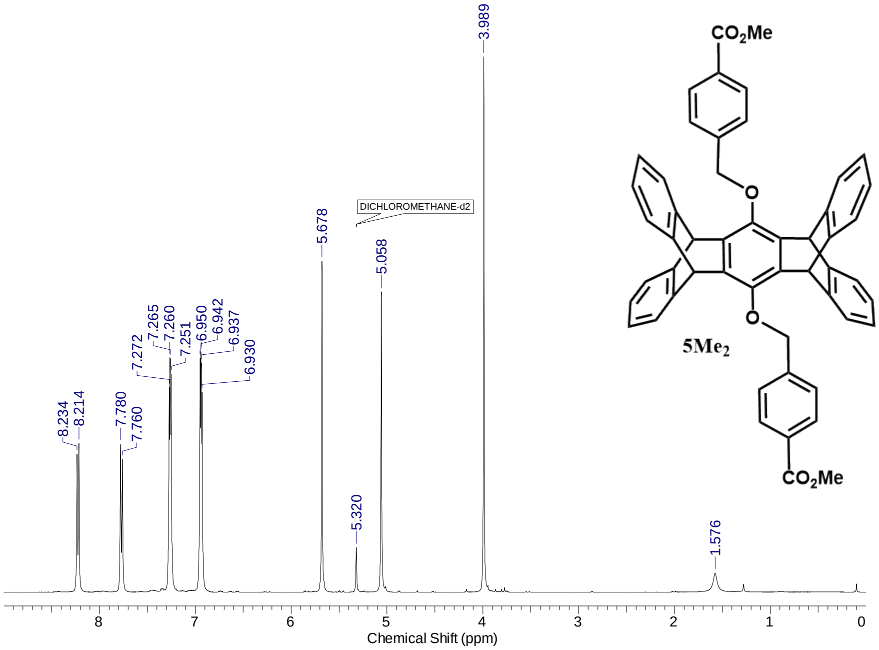

Figure S3. ^{1}H NMR spectrum of **$5Me_2$** (CD_2Cl_2, 298 K). The peak at 1.576 ppm is residual water in the solvent.

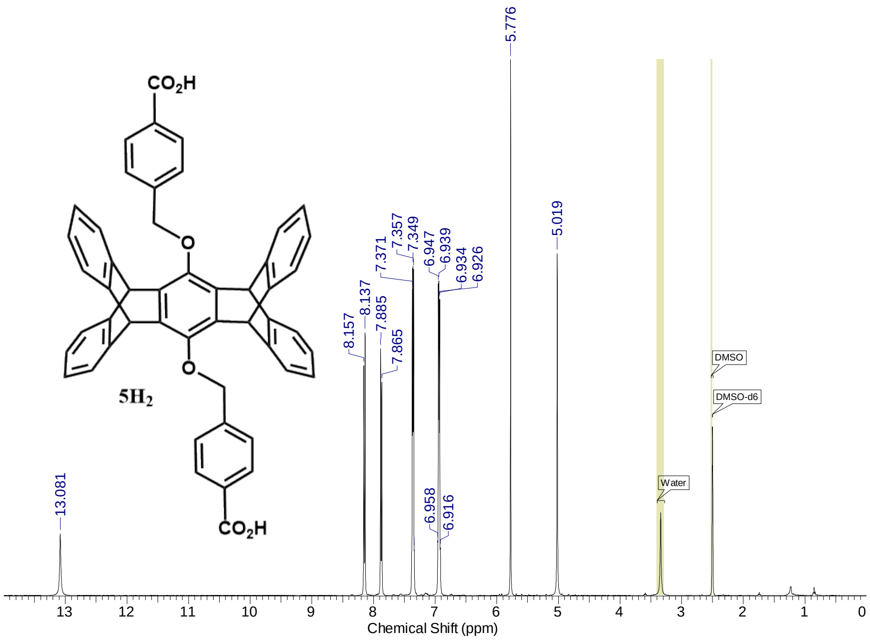

Figure S4. ^{1}H NMR spectrum of **$5H_2$** (DMSO-d_6, 298 K). The peak at 3.341 ppm is residual water in the solvent.

4 ^{13}C NMR Spectra

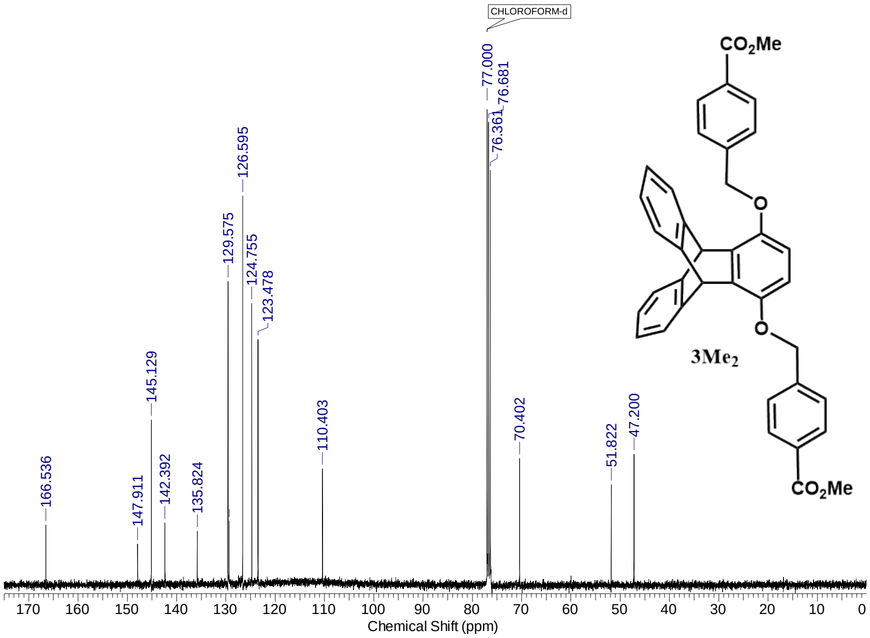

Figure S5. ^{13}C NMR spectrum of **$3Me_2$** ($CDCl_3$, 298 K).

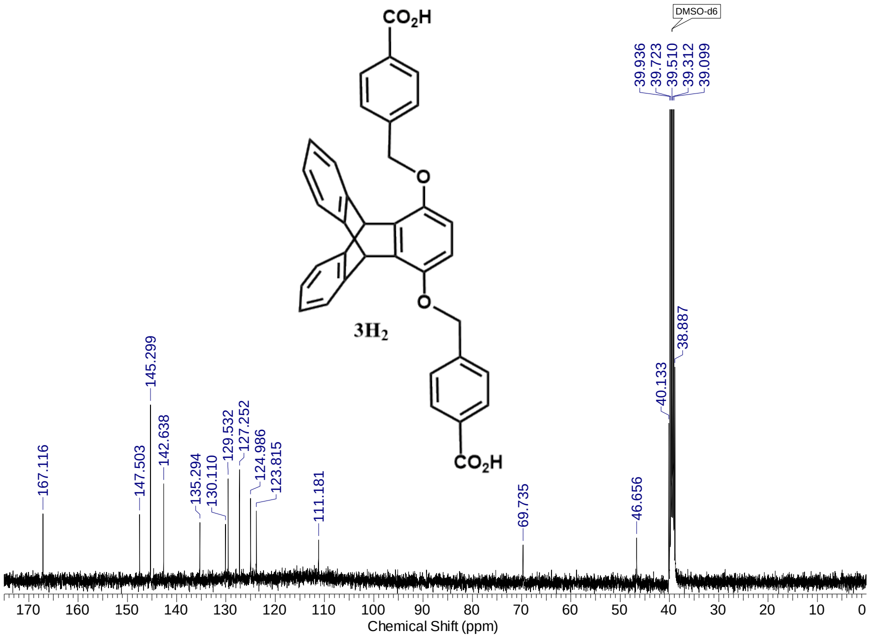

Figure S6. ^{13}C NMR spectrum of **3H$_2$** (DMSO-d_6, 298 K).

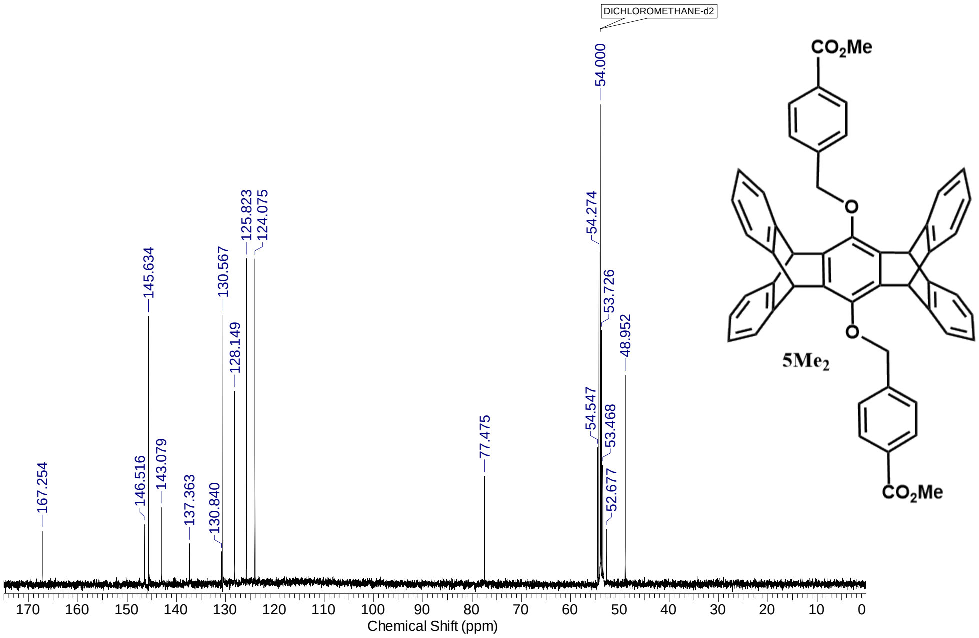

Figure S7. ^{13}C NMR spectrum of **5Me$_2$** (CD$_2$Cl$_2$, 298 K).

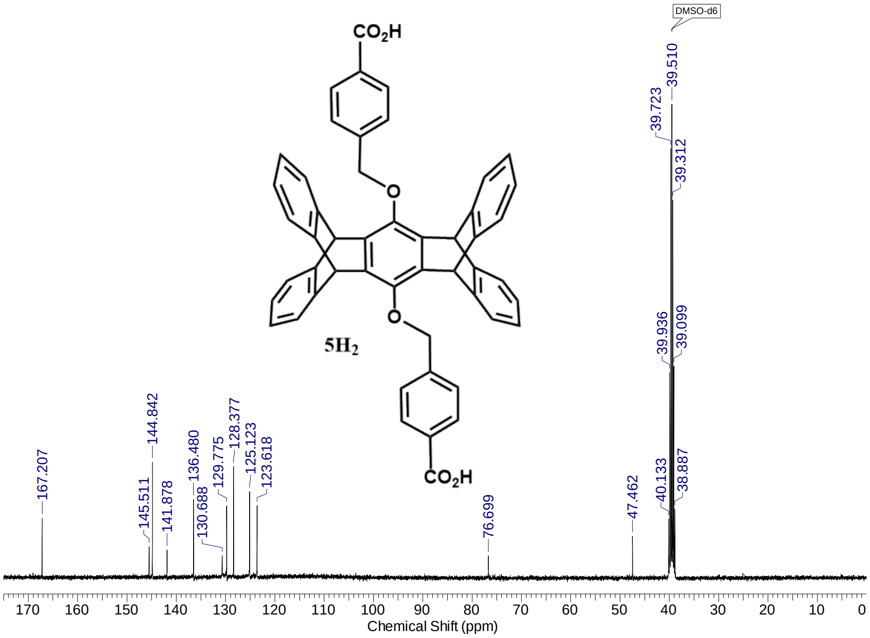

Figure S8. ^{13}C NMR spectrum of **$5H_2$** (DMSO-d_6, 298 K).

5 IR Spectra

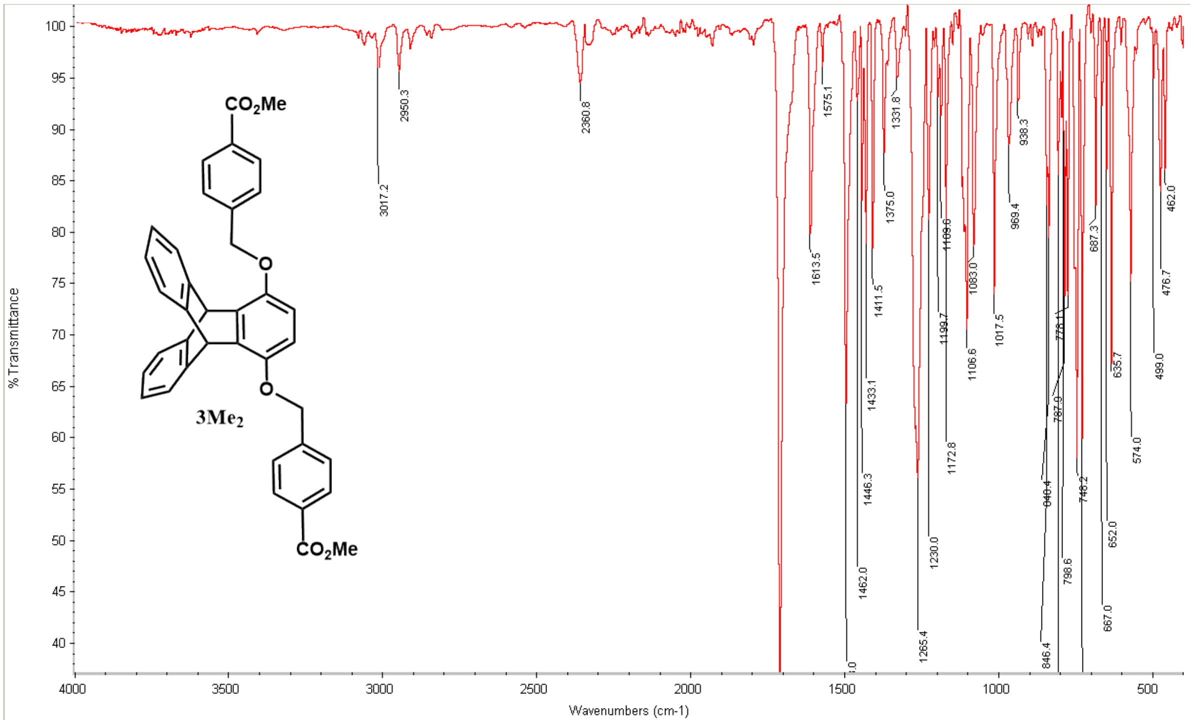

Figure S9. IR spectrum of **$3Me_2$**.

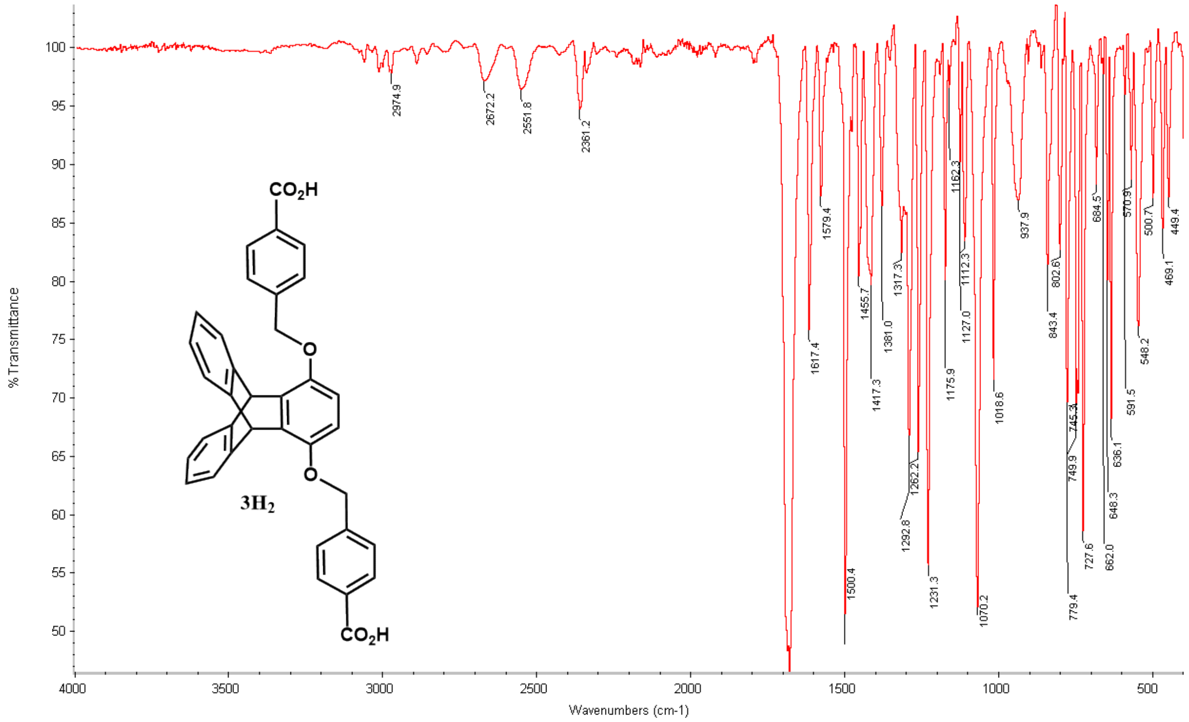

Figure S10. IR spectrum of **$3H_2$**.

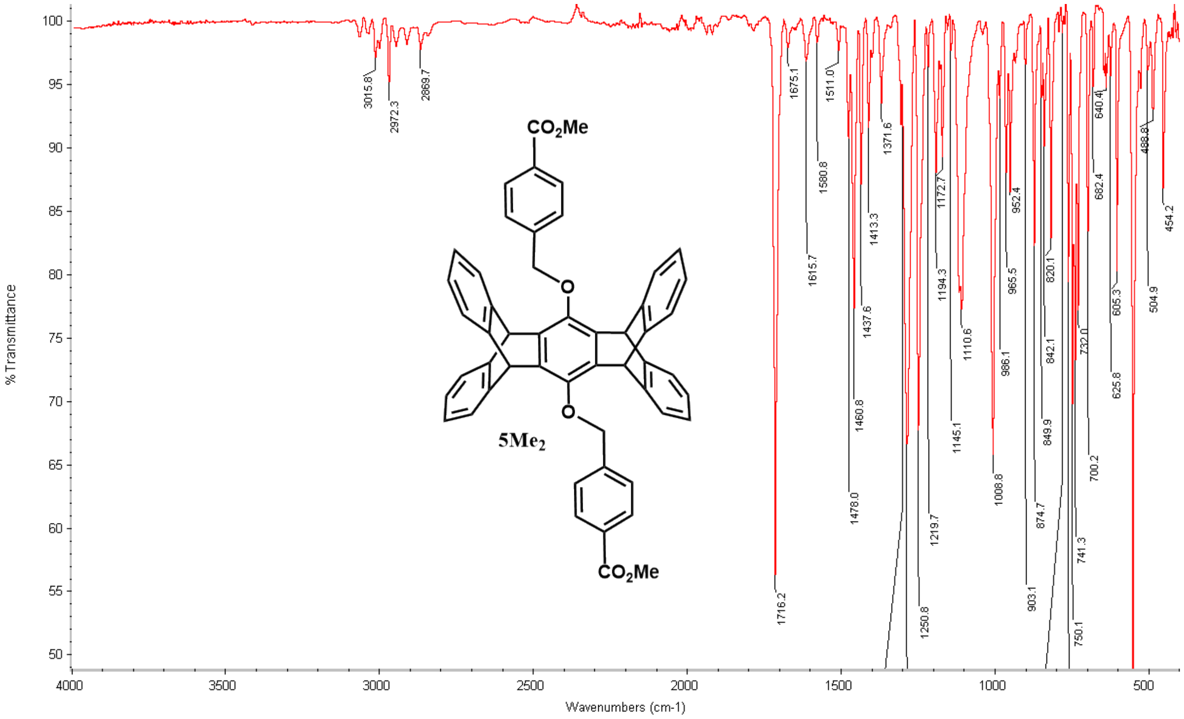

Figure S11. IR spectrum of **$5Me_2$**.

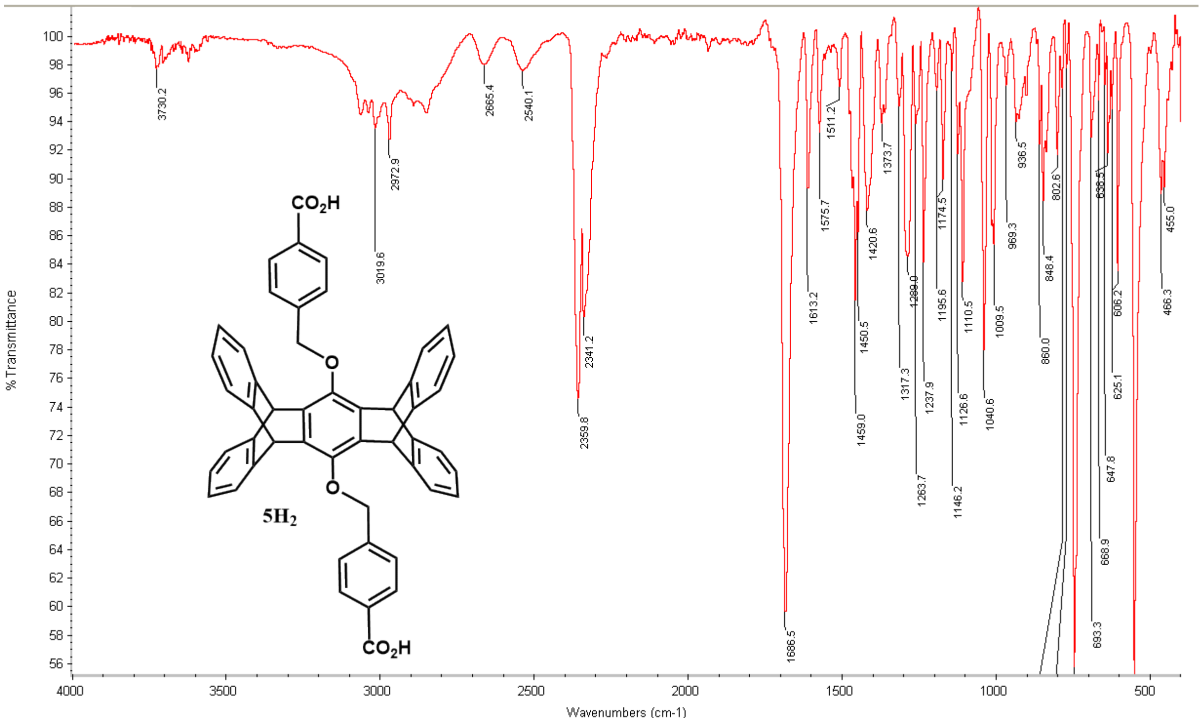

Figure S12. IR spectrum of **$5H_2$**.

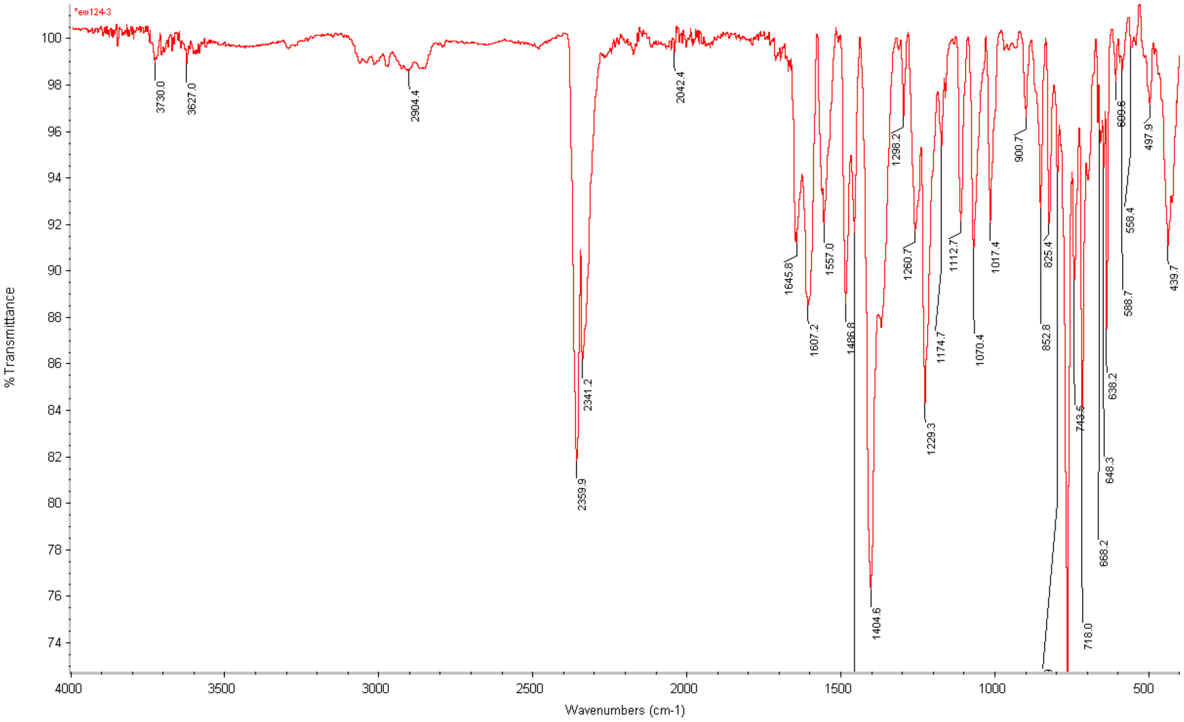

Figure S13. IR spectrum of bulk **TMOF-3** after being dried under vacuum at 120 °C.

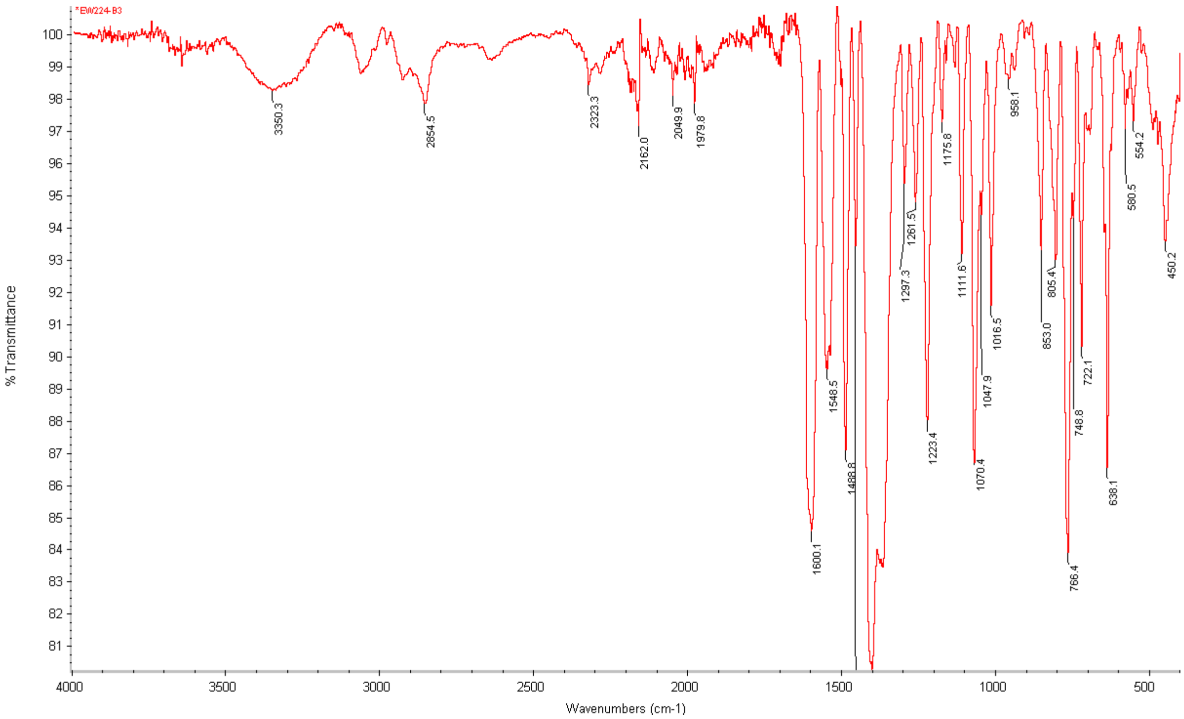

Figure S14. IR spectrum of bulk **TMOF-3-*bipy*** after being dried under vacuum at 120 °C.

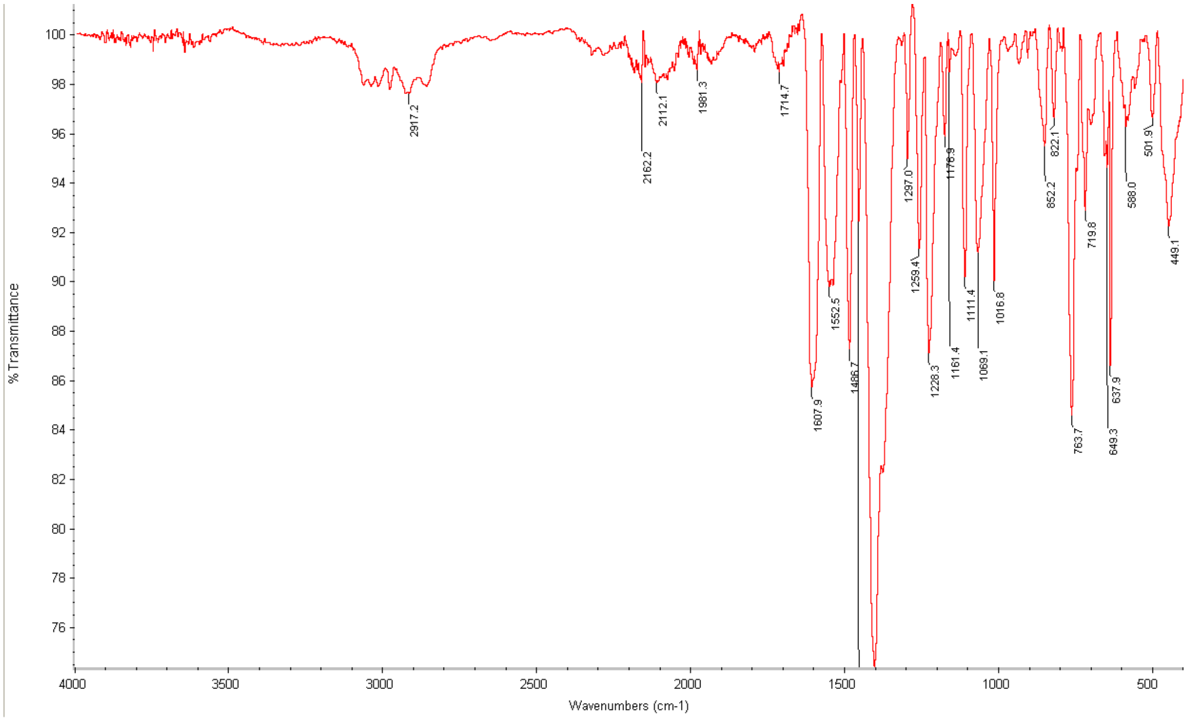

Figure S15. IR spectrum of bulk **TMOF-4** after being dried under vacuum at 120 °C.

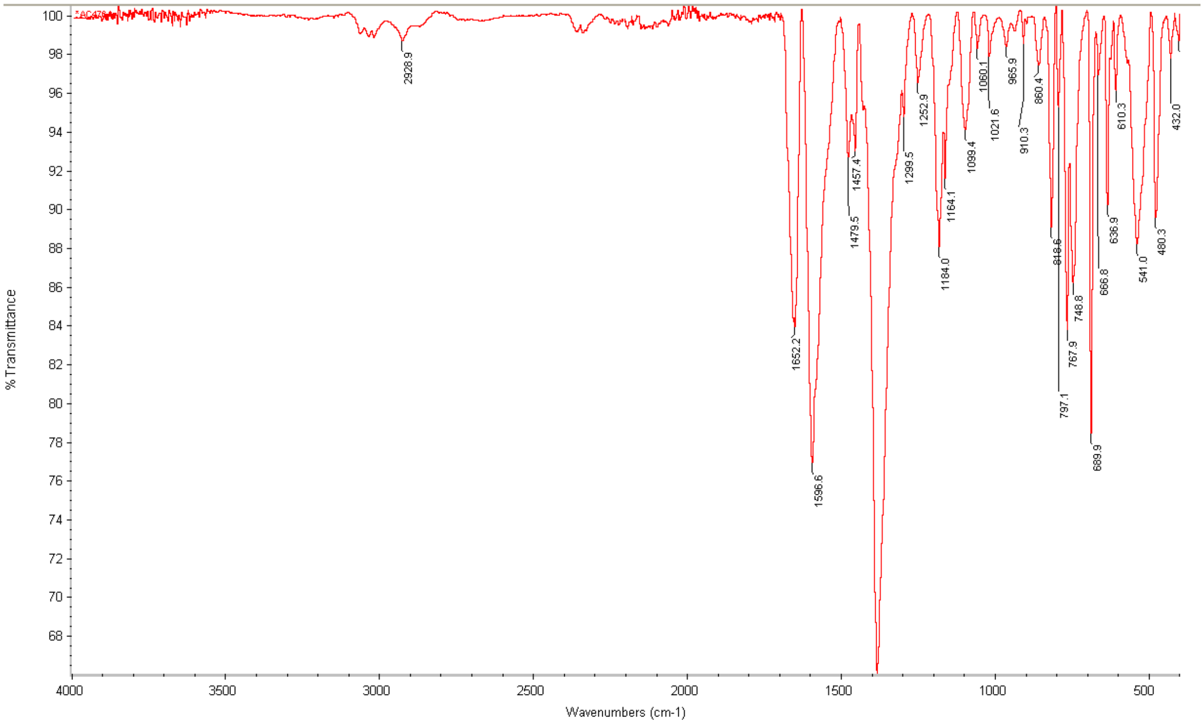

Figure S16. IR spectrum of bulk **PMOF-1** after being dried under vacuum at 120 °C.

References

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