Sulfur-tagged metal-organic frameworks and their post-synthetic oxidation

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Supplementary information

General experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV300 spectrometer operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C, or a Bruker AV250 spectrometer operating at 250 MHz for ^{1}H. Spectra were referenced to 7.26 ppm and 77.0 ppm in $CDCl_3$ and 2.50 ppm and 39.6 ppm in DMSO-d_6, for ^{1}H and ^{13}C spectra, respectively. Microanalyses were recorded by Alan Carver (University of Bath Microanalysis Service) and Gillian Maxwell (University College London Microanalysis Service). Yields of **1-4** were around 40 % based on the dicarboxylic acid. The MOF samples for microanalysis were ground in a pestle and mortar, then dried at 100 °C for 1 hour under reduced pressure (0.1 mm Hg).

Mass spectra were recorded on a Bruker micrOTOF (ESI-TOF) spectrometer. Single crystals were analysed using a Nonius Kappa CCD diffractometer and Mo-K_α radiation (λ = 0.71073 Å). Powder diffraction data were recorded on a Bruker D8 diffractometer fitted with Goebal mirrors and a 0.2 mm beam slit. IR spectra were recorded on a Bruker Nexus FTIR spectrometer as KBr disks.

Chemicals were obtained from Fisher Scientific or Sigma-Aldrich and used as received unless noted. DMDO was generated as an acetone solution (0.05 mol dm^{-3}) following the method of Adam *et al.*[1] and the concentration determined by assay against PPh_3. MOF digestion studies were carried out using the method of Cohen and co-workers.[2]

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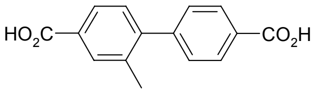
[1] W. Adam, Y.-Y. Chan, D. Cremer, J. Gauss, D. Scheutzow and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800.
[2] Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2007, **129**, 12368.

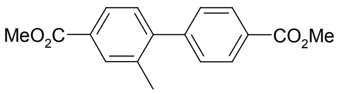
Synthesis of 2-(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid, H_2L^1

1. Synthesis of 2-methylbiphenyl-4,4'-dicarboxylic acid



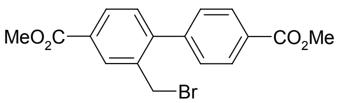
DMF (35 cm^3) and then 2M Na_2CO_3 (17.5 cm^3, 35 mmol) were added by syringe to 4-bromo-3-methylbenzoic acid (2.15 g, 10 mmol), 4-carboxyphenylboronic acid (2.07 g, 12.5 mmol) and [$PdBr_2$(dppf)] (0.25 g, 4 mol%) with stirring under an atmosphere of N_2. The mixture was heated at 90 °C for 3 h, cooled, and filtered over Celite®. The filter pad was washed with 0.1 N NaOH (50 cm^3) and H_2O (50 cm^3) and the combined washings and filtrate extracted once with EtOAc (75 cm^3). The aqueous layer was acidified with conc. HCl to precipitate the product, which was collected by filtration, washed with H_2O and oven dried (80 °C). Yield 2.83 g. A small portion was crystallised from hot DMSO/H_2O for analytical purposes. Found: C, 70.2; H, 4.73. $C_{15}H_{12}O_4$ requires C, 70.3; H, 4.72. δ_H (300 MHz; DMSO-*d*$_6$) 2.28 (3 H, s), 7.35 (1 H, d, *J* = 7.9 Hz), 7.50 (2 H, d, *J* = 8.3 Hz), 7.83 (1 H, dd, *J* = 7.9, 1.2 Hz), 7.90 (1 H, s), 8.02 (2 H, d, *J* = 8.3 Hz), 13.04 (2 H, s(br)); δ_C (75.5 MHz, DMSO-*d*$_6$) 20.19, 127.12, 129.25, 129.46, 129.88, 129.92, 130.21, 131.47, 135.41, 144.75, 144.86, 167.23, 167.28.

2. Synthesis of 2-methylbiphenyl-4,4'-dicarboxylic acid dimethyl ester



Crude 2-methylbiphenyl-4,4'-dicarboxylic acid (2.83 g) was refluxed overnight with MeOH (35 cm^3) and conc. H_2SO_4 (0.75 cm^3). The reaction was cooled then concentrated by removing approximately half the solvent by rotary evaporation and then chilled in a freezer. The crystallised material was collected by filtration and washed sparingly with fresh MeOH. Yield 2.42 g (85% over 2 steps). Found: C, 71.7; H, 5.64. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.67. δ_H (300 MHz; $CDCl_3$) 2.28 (3 H, s), 3.94 (3 H, s), 3.95 (3 H, s), 7.29 (1 H, d, *J* = 7.9 Hz), 7.40 (2 H, d, *J* = 8.5 Hz), 7.91 (1 H, dd, *J* = 7.9, 1.4 Hz), 7.96 (1 H, s), 8.10 (2 H, d, *J* = 8.5 Hz); δ_C (75.5 MHz, $CDCl_3$) 20.33, 52.15, 52.20, 127.05, 128.97, 129.12, 129.41, 129.52, 129.63, 131.60, 135.51, 145.37, 145.61, 166.85, 166.97. *m/z* (ESI) 307.0927 ($[M + Na]^+$. $[C_{17}H_{16}O_4 + Na]^+$ requires 307.0946).

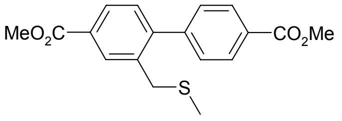
3. Synthesis of 2-(bromomethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester



2-Methylbiphenyl-4,4'-dicarboxylic acid dimethyl ester (1.69 g, 5.9 mmol), *N*-bromosuccinimide (1.16 g, 6.5 mmol) and VAZO® (0.16 g, 0.65 mmol) were refluxed in benzene (25 cm^3) overnight. The volatiles were removed by rotary evaporation and the residue triturated with CH_2Cl_2 (10 cm^3) and filtered. The filtered material was washed sparingly with fresh CH_2Cl_2 (5 cm^3) and the combined filtrates were loaded directly onto a column of silica gel and eluted with CH_2Cl_2. The recovered product (R_f ~0.45) crystallised from CH_2Cl_2/hexane as colourless crystals. Yield 1.40 g (65%). Found: C, 56.2; H, 4.16. $C_{17}H_{15}O_4Br$ requires C, 56.2; H, 4.16. δ_H (300 MHz; $CDCl_3$) 3.96 (6 H, s), 4.42 (2 H, s), 7.33 (1 H, d, *J* = 8.0 Hz), 7.53 (2 H, d, *J* = 8.6 Hz), 8.02 (1 H, dd, *J* = 8.0, 1.7 Hz), 8.14 (2 H, d, *J* = 8.6 Hz), 8.22 (1 H, d,

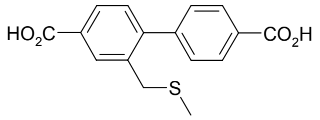
J = 1.7 Hz); δ_C (75.5 MHz, $CDCl_3$) 30.76, 52.25, 52.33, 128.83, 129.54, 129.73, 129.84, 130.39, 130.44, 132.29, 135.61, 143.85, 145.35, 166.22, 166.68. *m/z* (ESI) 385.0050 ($[M + Na]^+$. $[C_{17}H_{15}BrO_4 + Na]^+$ requires 385.0051).

4. Synthesis of 2-(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester



NaSMe (1.37 g, 19.6 mmol) was added as a solid to 2-(bromomethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester (2.84 g, 7.8 mmol) in THF (35 cm^3) and the mixture stirred overnight. The suspension was diluted with EtOAc (150 cm^3) and filtered. The filtrate was washed with H_2O (2 × 50 cm^3), brine (30 cm^3), dried over Na_2SO_4 and the solvent removed by rotary evaporation. The residue was taken up in CH_2Cl_2–petroleum ether (1:1) and passed through a silica gel plug eluting with the same mixture. The recovered product (R_f ~0.40) was sonicated/triturated with MeOH and collected by filtration. Yield 1.87 g (72%). Found: C, 65.4; H, 5.62. $C_{18}H_{18}O_4S$ requires 65.4; H, 5.49. δ_H (300 MHz; $CDCl_3$) 1.97 (3 H, s), 3.64 (2 H, s), 3.94 (3 H, s), 3.95 (3 H, s), 7.31 (1 H, d, J = 8.0 Hz), 7.48 (2 H, d, J = 8.5 Hz), 7.97 (1 H, dd, J = 8.0, 1.8 Hz), 8.11 (3 H, m); δ_C (75.5 MHz, $CDCl_3$) 15.69, 35.80, 53.21, 52.22, 128.14, 129.16, 129.45, 129.55, 129.75, 130.23, 131.35, 136.02, 144.77, 145.53, 166.64, 166.79.

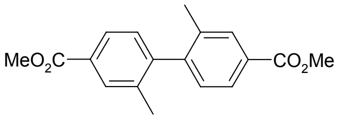
5. Synthesis of 2-(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid



1 N NaOH (8 cm^3, 8 mmol) was added to 2-(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester (1.00 g, 3.0 mmol) in a solvent mixture of MeOH–THF (1:1, 12 cm^3) and the mixture stirred overnight. The solution was reduced to dryness by rotary evaporation and the residual solid taken up in H_2O (20 cm^3) and THF (4 cm^3) before acidification with 1 N HCl. The precipitated solid was collected by filtration, washed with H_2O (3 × 10 cm^3) and recrystallised from DMF/H_2O and oven dried (85 °C). Yield 0.797 g (87%). Found: C, 63.2; H, 4.69. $C_{16}H_{14}O_4S{\cdot}0.1H_2O$ requires 63.2; H, 4.71. δ_H (300 MHz; DMSO-d_6) 1.91 (3 H, s), 3.71 (2 H, s), 7.37 (1 H, d, J = 7.9 Hz), 7.55 (2 H, d, J = 8.4 Hz), 7.89 (1 H, dd, J = 7.9, 1.7 Hz), 8.03 (2 H, d, J = 8.4 Hz), 8.05 (1 H, s); δ_C (75.5 MHz, DMSO-d_6) 14.99, 34.84, 127.98, 129.27, 129.42, 130.09, 130.33, 130.40, 131.15, 136.18, 144.18, 144.84, 167.03, 167.15. *m/z* (ESI) 301.0537 ($[M - H]^-$. $[C_{16}H_{14}O_4S - H]^-$ requires 301.0534).

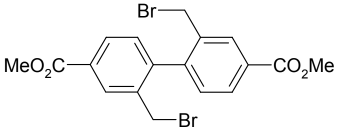
Synthesis of 2,2'-bis(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid, H_2L^2

1. Synthesis of 2,2'-dimethylbiphenyl-4,4'-dicarboxylic acid dimethyl ester



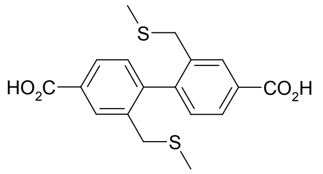
Dry DMSO (15 cm^3) was added by syringe to 4-bromo-3-methylbenzoic acid methyl ester (2.29 g, 10.0 mmol), bis(pinacolato)diboron (1.20 g, 4.7 mmol), $[PdBr_2(dppf)]$ (0.32 g, 4 mol%) and K_2CO_3 (4.15 g, 30 mmol) under an atmosphere of N_2 and the mixture was stirred and heated at 85 °C overnight. The cooled reaction mixture was poured into H_2O (150 cm^3) and extracted with CH_2Cl_2 (3 × 40 cm^3). The combined extracts were washed with H_2O (50 cm^3), brine (50 cm^3) and dried over Na_2SO_4. The solution was concentrated by rotary evaporation and loaded onto a column of silica gel and the product (R_f ~0.45) was obtained by eluting with CH_2Cl_2 and removal of the solvent. Yield 1.16 g (82%). Found: C, 74.5; H, 6.06. $C_{18}H_{18}O_4$ requires C, 74.5; H, 6.08. δ_H (300 MHz; $CDCl_3$) 2.07 (6 H, s), 3.94 (6 H, s), 7.15 (2 H, d, J = 7.9 Hz), 7.90 (2 H, dd, J = 7.9, 1.7 Hz), 7.96 (2 H, s). δ_C (75.5 MHz, $CDCl_3$) 19.64, 52.13, 126.95, 128.95, 129.40, 131.13, 135.87, 145.42, 167.05. *m/z* (ESI) 321.1102 ([M + Na]$^+$. $[C_{18}H_{18}O_4 + Na]^+$ requires 321.1103).

2. Synthesis of 2,2'-bis(bromomethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester



2,2'-dimethylbiphenyl-4,4'-dicarboxylic acid dimethyl ester (2.09 g, 7.0 mmol), *N*-bromosuccinimide (2.62 g, 14.7 mmol) and VAZO® (10 mol%) were refluxed together in benzene (40 cm^3) for 3 h. The volatiles were removed by rotary evaporation and the residue treated with two portions of CH_2Cl_2 (10 cm^3 and 5 cm^3) and these combined portions loaded directly onto a small column of silica gel and eluted with CH_2Cl_2. The product (R_f ~0.5) was obtained as an oil after removal of solvent and used in further reactions without purification. Yield 3.47 g. δ_H (300 MHz; $CDCl_3$) 3.96 (6 H, s), 4.16 (2 H, d, J = 10.3 Hz), 4.33 (2 H, d, J = 10.3 Hz), 7.36 (2 H, d, J = 8.0 Hz), 8.05 (2 H, dd, J = 8.0, 1.7 Hz), 8.23 (2 H, d, J = 1.7 Hz).

3. Synthesis of 2,2'-bis(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid

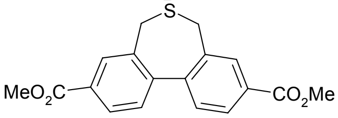


NaSMe (0.62 g, 8.8 mmol) was added as a solid to 2,2'-bis(bromomethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester (1.01 g, 2.2 mmol) in THF (35 cm^3) and the mixture stirred overnight. The suspension was diluted with EtOAc (100 cm^3) and filtered. The filtrate was washed with H_2O (2 × 50 cm^3), brine (30 cm^3), dried over Na_2SO_4 and the solvent removed by rotary evaporation. The residual yellow oil was taken up in CH_2Cl_2 and passed through a silica gel plug and the solvent removed. The recovered 2,2'-bis(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester (R_f ~0.80 (CH_2Cl_2); 0.75 g) was taken up in MeOH-THF (1:1, 8 cm^3) and 1 N

NaOH (5 cm^3, 5 mmol) was added and the mixture stirred overnight. The solution was reduced to dryness by rotary evaporation and the residual solid taken up in THF (3 cm^3) and diluted with H_2O (25 cm^3) before acidification with 1 N HCl. The suspension was extracted with Et_2O (3 × 20 cm^3) and the combined extracts dried over Na_2SO_4 before removing the solvent and triturating the residue with Et_2O/hexane and collecting the yellow solid by filtration. Yield 0.526 g (65% over 2 steps). Found: C, 59.9; H, 5.01. $C_{18}H_{18}O_4S_2$ requires C, 59.7; H, 5.01. δ_H (300 MHz; DMSO-*d*$_6$) 1.89 (6 H, s), 3.37 (4H, d, *J* = 13.3 Hz), 3.57 (2 H, d, *J* = 13.3 Hz), 7.31 (2 H, d, *J* = 7.9 Hz), 7.89 (2 H, dd, *J* = 7.9, 1.7 Hz), 8.07 (2 H, d, *J* = 1.7 Hz); δ_C (75.5 MHz, DMSO-*d*$_6$) 14.97, 35.02, 127.58, 130.27, 130.48, 130.54, 136.69, 143.52, 167.11. *m/z* (ESI) 361.0585 ($[M-H]^-$. $[C_{18}H_{18}O_4S_2-H]^-$ requires 361.0568).

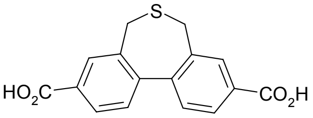
Synthesis of 5,7-dihydrodibenzo[*c*,*e*]thiepine-3,9-dicarboxylic acid, H_2L^3

1. Synthesis of 5,7-dihydrodibenzo[c,e]thiepine-3,9-dicarboxylic acid dimethyl ester



$Na_2S\cdot9H_2O$ (2.29 g, 9.5 mmol) was added to crude 2,2'-bis(bromomethyl)biphenyl-4,4'-dicarboxylic acid dimethyl ester (3.47 g, 7.6 mmol) in DMF (13 cm^3) and the mixture heated with stirring at 100 °C for 30 min. The cooled solution was poured into H_2O (150 cm^3) and extracted with Et_2O (3 × 50 cm^3). The combined extracts were washed with H_2O (2 × 50 cm^3), brine (30 cm^3) and dried over Na_2SO_4 before removing the solvent by rotary evaporation. The residue was taken up in CH_2Cl_2 and passed through a silica gel plug (R_f ~0.5), concentrated, and crystallised from CH_2Cl_2/MeOH to give the product as pinky white crystals. Yield 1.38 g (55 % over 2 steps). Found: C, 65.6; H, 4.71. $C_{18}H_{16}O_4S\cdot0.125H_2O$ requires C, 65.8; H, 4.91. δ_H (300 MHz; $CDCl_3$) 3.44 (4 H, m), 3.95 (6 H, s), 7.40 (2 H, d, *J* = 7.9 Hz), 8.04 (2 H, d, *J* = 1.6 Hz), 8.07 (2 H, dd, *J* = 7.9, 1.6 Hz); δ_C (75.5 MHz, $CDCl_3$) 31.05, 52.26, 128.63, 129.01, 129.84, 130.84, 135.89, 144.19, 166.51. *m/z* (ESI) ($[M + Na]^+$ 351.0659. $[C_{18}H_{16}O_4S + Na]^+$ requires 351.0667).

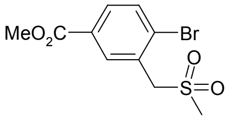
2. Synthesis of 5,7-dihydrodibenzo[c,e]thiepine-3,9-dicarboxylic acid



1 N NaOH (6 cm^3, 6 mmol) was added to 5,7-dihydro-dibenzo[*c*,*e*]thiepine-3,9-dicarboxylic acid dimethyl ester (0.763 g, 2.3 mmol) in a solvent mixture of MeOH–THF (1:1, 12 cm^3) and the mixture stirred overnight. The volume of solution was reduced to 3-4 cm^3 by rotary evaporation and the solution filtered and diluted with H_2O (30 cm^3). Acidification with 1 N HCl precipitated a solid and this was collected by filtration, washed with H_2O (3 × 10 cm^3), dried in a fume hood overnight and finally oven dried (80 °C / 1 h). Yield 0.682 g (91%). Found: C, 63.5; H, 4.08. $C_{16}H_{12}O_4S\cdot0.125H_2O$ requires C, 63.5; H, 4.01. δ_H (300 MHz; D_2O/KOH) 3.40 (4 H, m), 7.35 (2 H, d, *J* = 7.8 Hz), 7.85 (2 H, dd, *J* = 7.8, 1.5 Hz), 7.90 (2 H, d, *J* = 1.5 Hz); δ_H (300 MHz; DMSO-d_6) 3.24 (2 H, d, *J* = 11.4 Hz), 3.67 (2 H, d, *J* = 11.4 Hz), 7.47 (2 H, d, *J* = 7.8 Hz), 7.99 (2 H, dd, *J* = 7.8, 1.5 Hz), 8.01 (2 H, d, *J* = 1.5 Hz); δ_C (75.5 MHz, DMSO-d_6) 29.92, 128.87, 128.95, 129.63, 131.46, 135.96, 143.78, 167.03. *m/z* (ESI) 299.0372 ($[M – H]^-$. $[C_{16}H_{12}O_4S – H]^-$ requires 299.0378).

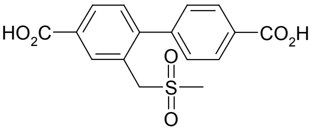
Synthesis of 2-(methylsulfonylmethyl)biphenyl-4,4'-dicarboxylic acid, H_2L^4

1. Synthesis of 4-bromo-3-(methylsulfonylmethyl)benzoic acid methyl ester



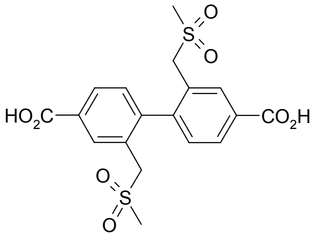
4-Bromo-3-methylbenzoic acid methyl ester (6.76 g, 28 mmol), *N*-bromosuccimimide (5.24 g, 29 mmol) and VAZO® (0.66 g, 10 mol%) were refluxed in benzene (70 cm^3) for 1 h. The volatiles were removed by rotary evaporation and the residue treated with CH_2Cl_2 (15 cm^3) and filtered. The filtrate was passed through a plug of silica gel eluting with CH_2Cl_2 and the solvent removed to give 4-bromo-3-bromomethylbenzoic acid methyl ester and 4-bromo-3-methylbenzoic acid methyl ester in a 9:1 ratio by ^{1}H NMR analysis (7.96 g). These compounds were taken up in THF (40 cm^3) and NaSMe (1.95 g, 28 mmol) was added as a solid and the reaction stirred for 5 h. The suspension was diluted with EtOAc (150 cm^3) and washed with H_2O (2 × 40 cm^3), brine (30 cm^3), dried over Na_2SO_4 and the solvent removed by rotary evaporation. ^{1}H NMR analysis indicated a 1:1 ratio of 4-bromo-3-methylsulfanylmethyl-benzoic acid methyl ester and 4-bromo-3-methyl-benzoic acid methyl ester, which TLC indicated could not be separated by chromatography. These compounds were dissolved in AcOH (25 cm^3) and 30% H_2O_2 solution (15 cm^3) was added over the period of an hour. The solution was heated at 90 °C for 2 h, cooled and diluted with H_2O (200 cm^3). The precipitated material was collected by filtration and the product was obtained after crystallisation from boiling MeOH. Yield 3.03 g (35% over 3 steps). Found: C, 39.1; H, 3.63. $C_{10}H_{11}BrO_4S$ requires C, 39.1; H, 3.61. δ_H (300 MHz; $CDCl_3$) 2.86 (3 H, s), 3.93 (3 H, s), 4.55 (2 H, s), 7.74 (1 H, d J = 8.4 Hz), 7.91 (1 H, dd, J = 8.4, 2.0 Hz), 8.23 (1 H, d, J = 2.0 Hz); δ_C (75.5 MHz, $CDCl_3$) 40.14, 52.54, 60.11, 128.97, 130.20, 130.43, 131.48, 133.69, 133.81, 165.54. *m/z* (ESI) 328.9447 ($[M + Na]^+$. $[C_{10}H_{11}BrO_4S + Na]^+$ requires 328.9459).

2. Synthesis of 2-(methylsulfonylmethyl)biphenyl-4,4'-dicarboxylic acid



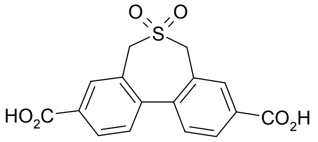
DMF (12 cm^3) and then 2 M Na_2CO_3 (4 cm^3, 8 mmol) were added by syringe to 4-bromo-3-(methylsulfonylmethyl)benzoic acid methyl ester (0.95 g, 3.1 mmol), 4-carboxyphenylboronic acid (0.64 g, 3.9 mmol) and $[PdBr_2(dppf)]$ (0.10 g, 4 mol%) with stirring under an atmosphere of N_2. The mixture was heated at 90 °C for 2 h and cooled to room temperature before 1 N NaOH (10 cm^3, 10 mmol) was added and the mixture stirred 3 h before dilution with H_2O (25 cm^3) and filtration over Celite®. The pad was washed with H_2O (10 cm^3) and the washings and filtrate diluted with H_2O and acidified with 2 N HCl to precipitate the product, which was collected by filtration and washed with H_2O. The product was purified by crystallisation from hot DMF/H_2O and oven dried (85°C). Yield 0.68 g (65%). Found: C, 56.2; H, 4.29. $C_{16}H_{14}O_6S\cdot 0.4H_2O$ requires C, 56.3; H, 4.37. δ_H (300 MHz; DMSO-d_6) 2.89 (3 H, s), 4.53 (2 H, s), 7.46 (1 H, d, J = 8.1 Hz), 7.55 (2 H, d, J = 8.1 Hz), 8.02 (3 H, m), 8.21 (1 H, d, J = 1.4 Hz); δ_C (75.5 MHz; DMSO-d_6) 40.65, 56.12, 126.36, 129.36, 129.54, 129.60, 130.26, 130.36, 130.87, 133.16, 143.67, 146.63, 166.84, 167.18. *m/z* (ESI) 333.0434 ($[M - H]^-$. $[C_{16}H_{14}O_6S - H]^-$ requires 333.0433).

Synthesis of 2,2'-bis(methylsulfonylmethyl)biphenyl-4,4'-dicarboxylic acid, H_2L^5



KOH (0.052 g, 0.93 mmol) was added to 2,2'-bis(methylsulfanylmethyl)biphenyl-4,4'-dicarboxylic acid (0.133 g, 0.37 mmol) in H_2O (2 cm^3) and the mixture ultrasonicated until a clear yellow solution was obtained and then diluted with H_2O (2 cm^3). To this stirred solution was added $KHCO_3$ (0.400 g) and Oxone® (0.98 g, 1.60 mmol) and the frothy mixture was stirred for 30 minutes. The reaction was then filtered and the filter pad washed with water (1 cm^3) and the combined filtrates acidified with 12 M HCl to pH = 1. The solution was extracted with Et_2O/THF (4:1, 3 × 5 cm^3) and the combined extracts dried over Na_2SO_4 before removing the solvent to give the product as a foamy solid. This was quickly crystallised by taking up in hot EtOH and leaving to cool. Yield 0.111 g (71 %). Found: C, 50.8; H, 4.60. $C_{18}H_{18}O_8S_2$ requires C, 50.7; H, 4.25. δ_H (300 MHz; DMSO-*d*$_6$) 2.92 (6 H, s), 4.15 (2 H, d, J = 13.3 Hz), 4.37 (2 H, d, J = 13.3 Hz), 7.45 (2 H, d, J = 7.9 Hz), 7.98 (2 H, dd, J = 7.9, 1.7 Hz), 8.23 (2 H, d, J = 1.7 Hz). δ_C (75.5 MHz; DMSO-*d*$_6$) 56.76, 127.75, 129.17, 130.97, 131.46, 132.95, 144.84, 167.13. *m/z* (ESI) 425.0381 ($[M - H]^-$. $[C_{18}H_{18}O_4S_2 - H]^-$ requires 425.0365).

Synthesis of 5,7-dihydrodibenzo[*c*,*e*]thiepine-*S*,*S*-dioxide-3,9-dicarboxylic acid, H_2L^6



KOH (0.032 g, 0.57 mmol) was added to 5,7-dihydrodibenzo[*c*,*e*]thiepine-3,9-dicarboxylic acid (0.064 g, 0.22 mmol) in H_2O (2 cm^3) and the mixture ultrasonicated until a clear yellow solution was obtained. To this stirred solution was added $KHCO_3$ (0.120 g) and Oxone® (0.280 g, 0.44 mmol) and the frothy mixture was stirred for 30 min. The reaction was then filtered and the filter pad washed with water (1 cm^3) and the combined filtrates acidified with 12 M HCl to precipitate a solid. The solid was collected by filtration, washed with H_2O (6 × 0.5 cm^3), dried in a fume hood overnight and finally oven dried (80 °C / 2 h). Yield 0.059 g (83 %). Found: C, 56.2; H, 3.71. $C_{16}H_{12}O_6S\cdot 0.5H_2O$ requires C, 56.3; H, 3.84. δ_H (300 MHz; DMSO-*d*$_6$) 3.91 (2 H, d, J = 14.6 Hz), 4.70 (2 H, d, J = 14.6 Hz), 7.72 (2 H, d, J = 8.0 Hz), 8.10 (2 H, dd, J = 8.0, 1.5 Hz), 8.18 (2 H, d, J = 1.5 Hz); δ_C (75.5 MHz, DMSO-*d*$_6$) 56.08, 129.22, 130.00, 130.10, 131.44, 131.82, 143.17, 166.70. *m/z* (ESI) 331.0280 ($[M-H]^-$. $[C_{16}H_{12}O_6S - H]^-$ requires 331.0270).

Synthesis of $[Zn_4O(L^1)_3(DMF)_2]\cdot 4DMF$ 1

$H_2\mathbf{L}^1$ (0.105 g, 0.35 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.315 g, 1.06 mmol) were dissolved in either DMF or DEF (15 cm^3) and heated in an oven at 100 °C for 24 h. The reaction mixture was allowed to cool slowly to room temperature and the crystals were collected by filtration, washed with fresh solvent and air dried. Found: C, 43.65; H, 3.21; N, 0.00 %. $Zn_4O(\mathbf{L}^1)_3\cdot 8H_2O$ [$C_{48}H_{52}O_{21}S_3Zn_4$] requires C, 43.59; H, 3.96; N, 0.00 %. IR/cm^{-1}: 1654m, 1605s, 1545m, 1385s (Fig. S1).

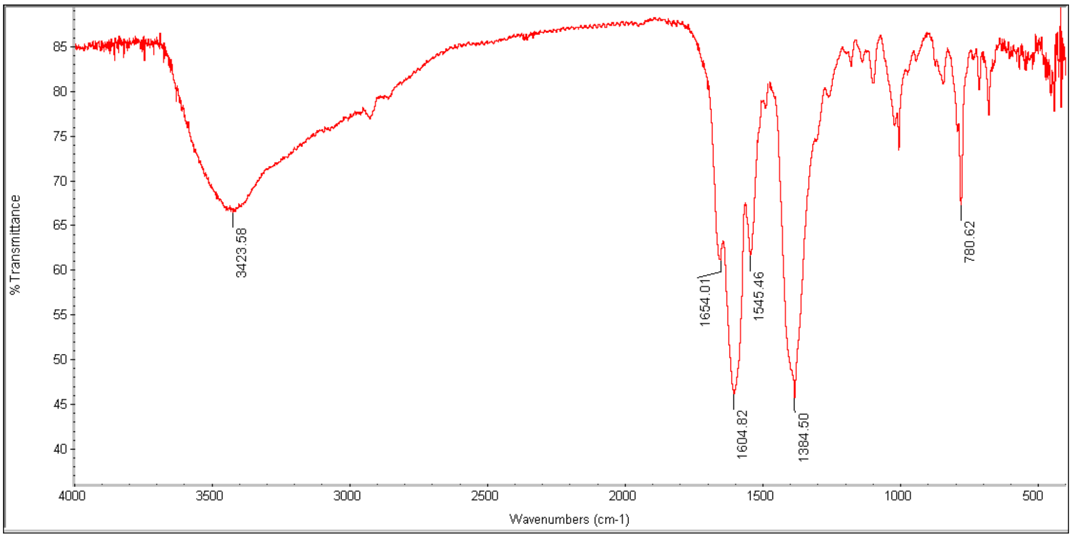


Figure S1. IR spectrum for **1**.

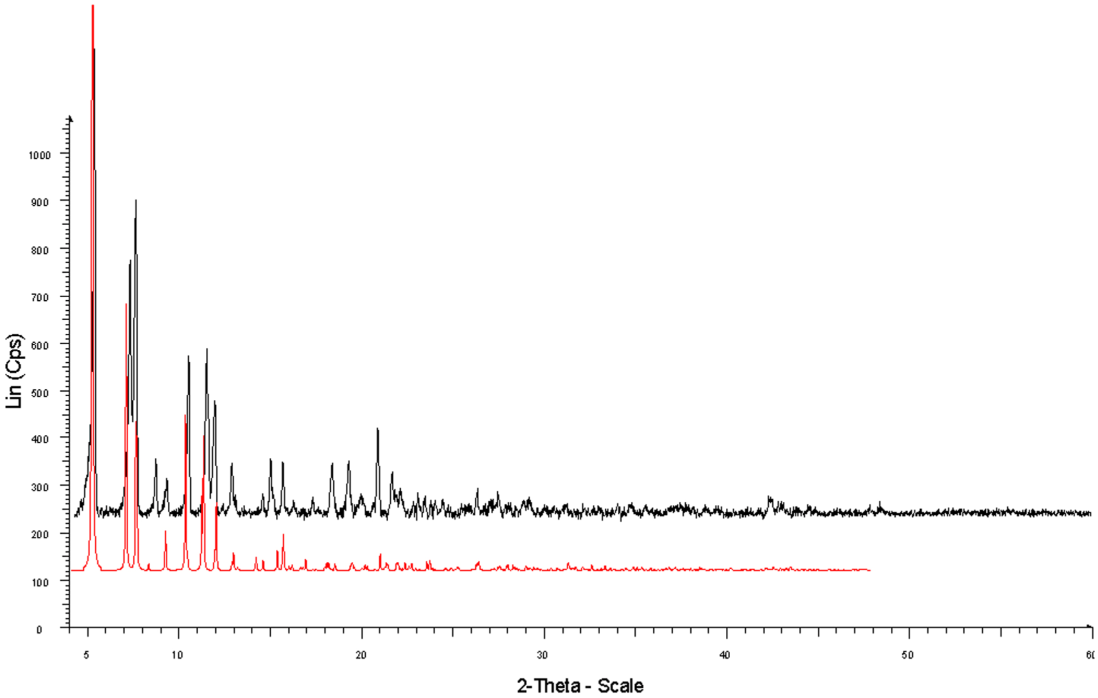


Figure S2. Comparison of the observed powder diffraction pattern for **1** (black) with that simulated from the single crystal data (red).

Synthesis of $[Zn_4O(\mathbf{L}^2)_3]\cdot 5DMF$ 2

$H_2\mathbf{L}^2$ (0.091 g, 0.25 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.223 g, 0.075 mmol) were dissolved in either DMF or DEF (7 cm^3) and heated in an oven at 100 °C for 24 h. The reaction mixture was allowed to cool slowly to room temperature and the crystals were collected by filtration, washed with fresh solvent and air dried. Found: C, 42.60; H, 3.36; N, 0.00 %. $Zn_4O(\mathbf{L}^2)_3\cdot 5H_2O$ $[C_{54}H_{58}O_{18}S_6Zn_4]$ requires C, 44.76; H, 4.03; N, 0.00 %. IR/cm^{-1}: 1654s, 1608s, 1549m, 1400s (Fig. S3).

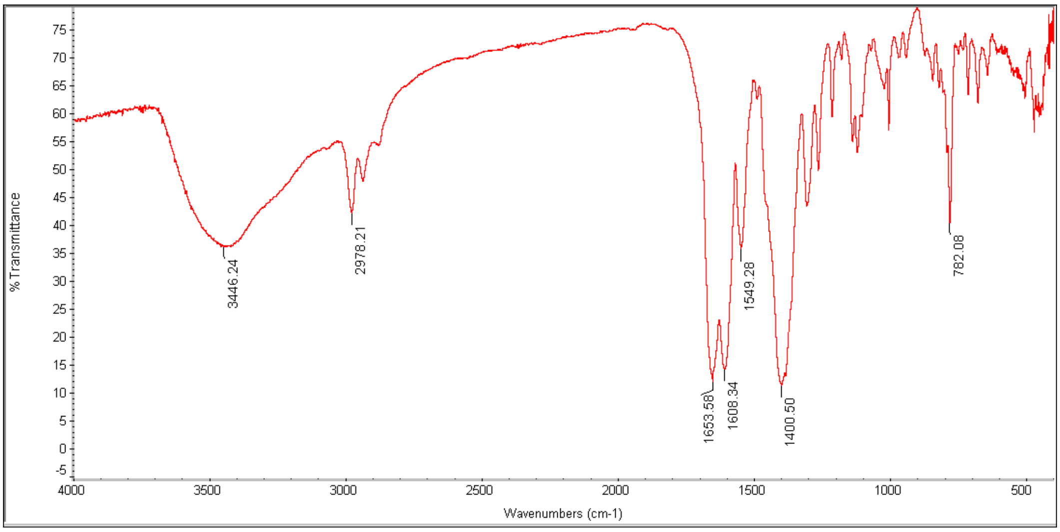


Figure S3. IR spectrum for **2**.

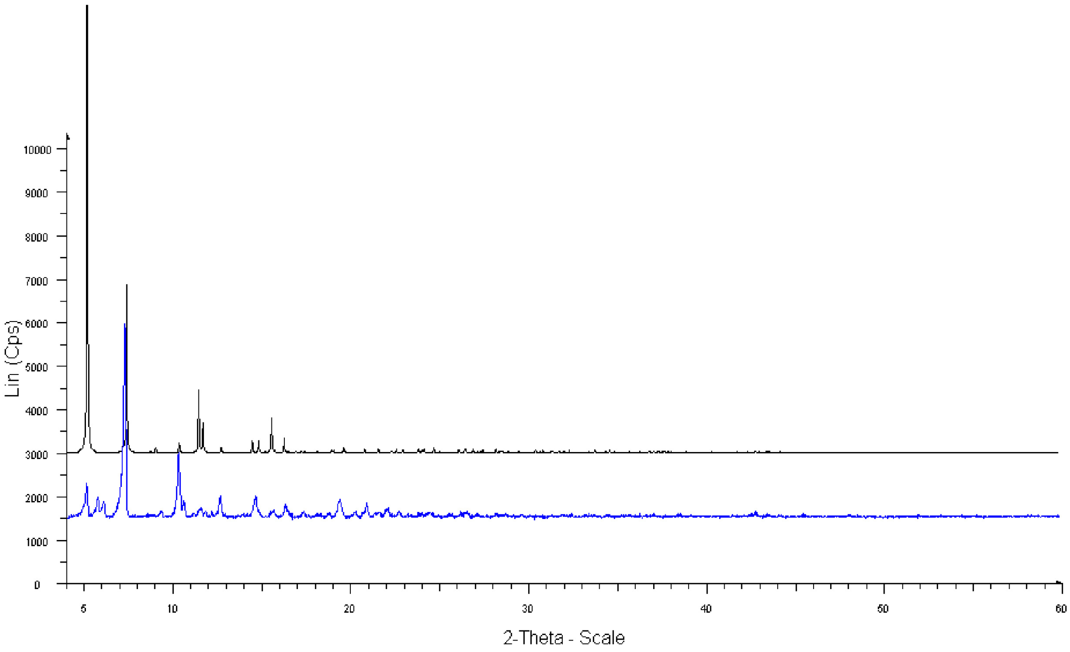


Figure S4. Comparison of the observed powder diffraction pattern for **2** (blue) with that simulated from the single crystal data (black). The poor agreement in peak heights is probably a consequence of orientational effects.

Synthesis of [$Zn_4O(L^3)_3$] 3

H_2**L**^{3} (0.097 g, 0.32 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.276 g, 0.93 mmol) were dissolved in DMF (10 cm^3) and heated in an oven at 100 °C for 36 h. The reaction mixture was allowed to cool slowly to room temperature and the crystals were collected by filtration, washed with fresh DMF and air dried. Found: C, 42.77; H, 3.31; N, 0.98 %. Zn_4O(**L**^{3})$_3{\cdot}10H_2O{\cdot}$DMF [$C_{51}H_{57}O_{24}S_3Zn_4$] requires C, 42.96; H, 4.03; N, 0.98 %. IR/cm^{-1}: 1654s, 1601s, 1540m, 1419s, 1388s (Fig. S5).

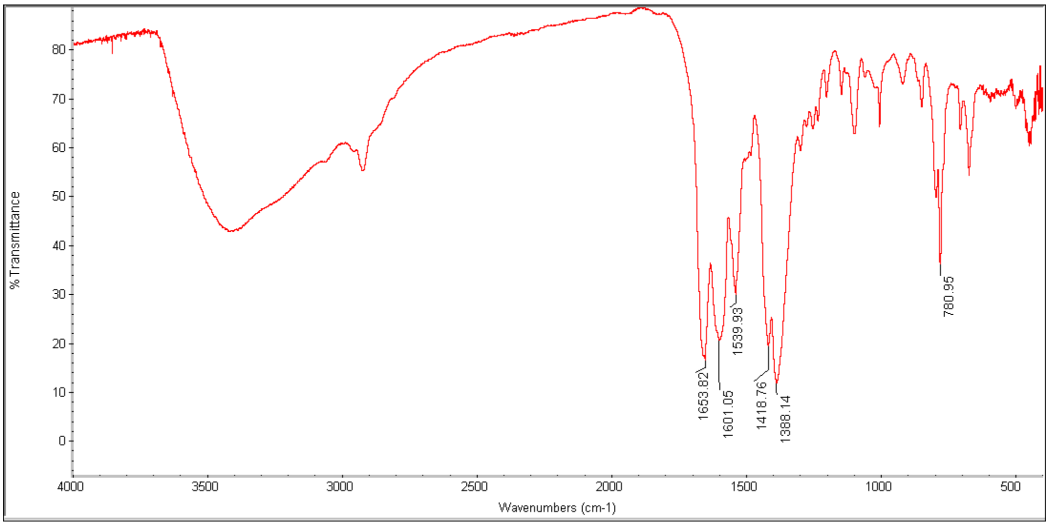


Figure S5. IR spectrum for **3**.

Synthesis of [$Zn_4O(L^4)_3(DMF)_2$]·2DMF 4

H_2**L**^{4} (0.167 g, 0.50 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.447 g, 1.50 mmol) were dissolved in either DMF or DEF (20 cm^3) and heated in an oven at 100 °C for 12 h. The reaction mixture was allowed to cool slowly to room temperature and the crystals were collected by filtration, washed with fresh solvent and air dried. Found: C, 42.27; H, 3.33; N, 0.00 %. Zn_4O(**L**^{4})$_3{\cdot}5H_2O$ [$C_{48}H_{46}O_{24}S_3Zn_4$] requires C, 42.25; H, 3.40; N, 0.00 %. IR/cm^{-1}: 1653s, 1606s, 1546m, 1385s, 1308m, 1139m, 1124m (Fig. S6).

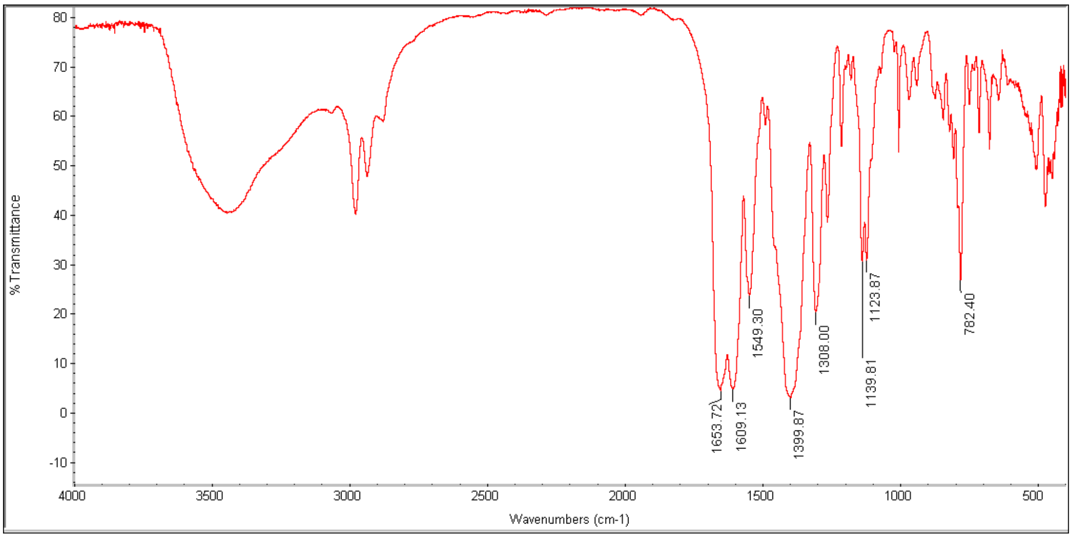


Figure S6. IR spectrum for **4**.

Post-synthetic oxidation of 1 to 1'

A sample of **1** (0.044 g, 0.027 mmol) was soaked in portions of acetone (3 × 3 cm^3) over 1.5 h to exchange DMF for acetone. The crystals were then covered with a solution of DMDO in acetone (5 cm^3 of 0.05 M solution), and the solution allowed to stand at 4 °C. Individual crystals were taken out after 30 min, 1 h, 2 h and overnight. These were digested in HCl/H_2O and the resulting solutions analysed by ESI-MS (Fig. S7). The proportion of $\mathbf{L}^4$ to $\mathbf{L}^1$, as judged by the relative intensities of the peaks for $[H\mathbf{L}^1]^-$ (*m/z* 301.05) and $[H\mathbf{L}^4]^-$ (*m/z* 333.04), increased as the reaction proceeded.

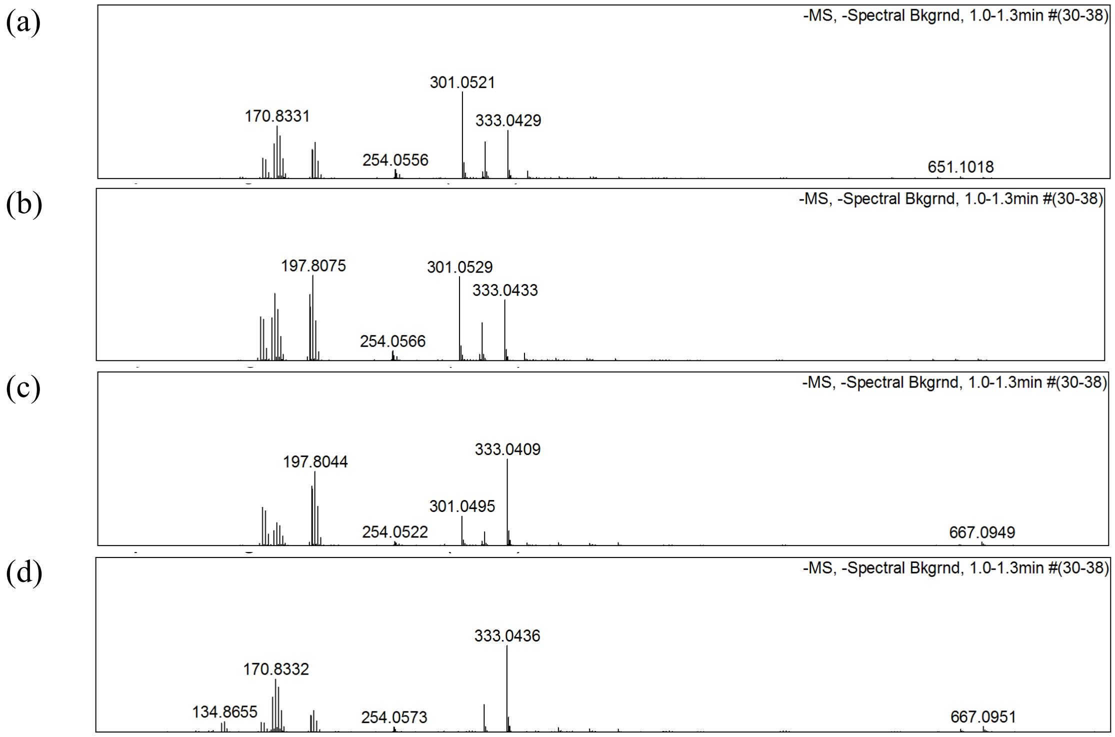


Figure S7. ESI-MS recorded on individual crystals of **1**, extracted from the reaction mixture with DMDO after (a) 30 min, (b) 1 h, (c) 2 h, (d) overnight, and digested in HCl/H_2O.

After 2 h, several crystals were removed and allowed to stand over DMF overnight. The powder X-ray diffraction pattern was recorded on these crystals (Fig. S8). The product was separated by filtration and the crystals were dried under reduced pressure. A sample was digested in $DCl/D_2O/d_6$-DMSO and analysed by ^1H NMR spectroscopy (see Fig. S9).

Found: C, 44.12; H, 2.95; N, 0.00 %. $Zn_4O(\mathbf{L}^4)_3 \cdot 2H_2O$ [$C_{48}H_{40}O_{21}S_3Zn_4$] requires C, 43.99; H, 3.08; N, 0.00 %. A sample was left in air for three weeks and re-analysed. Found: C, 42.37; H, 3.29; S, 7.24 %. $Zn_4O(\mathbf{L}^4)_3 \cdot 5H_2O$ [$C_{48}H_{46}O_{24}S_3Zn_4$] requires C, 42.25; H, 3.40; S, 7.05 %. The lower value of %C and higher value of %H is consistent with adsorption of atmospheric water.

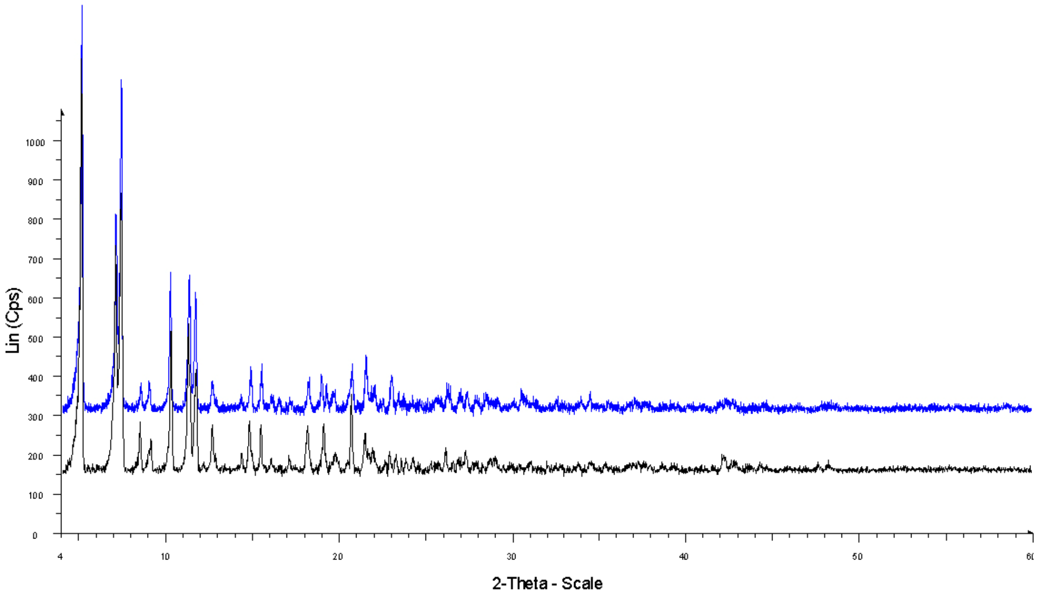


Figure S8. Comparison of the powder diffraction pattern for **1** (black) with that for **1'** (blue).

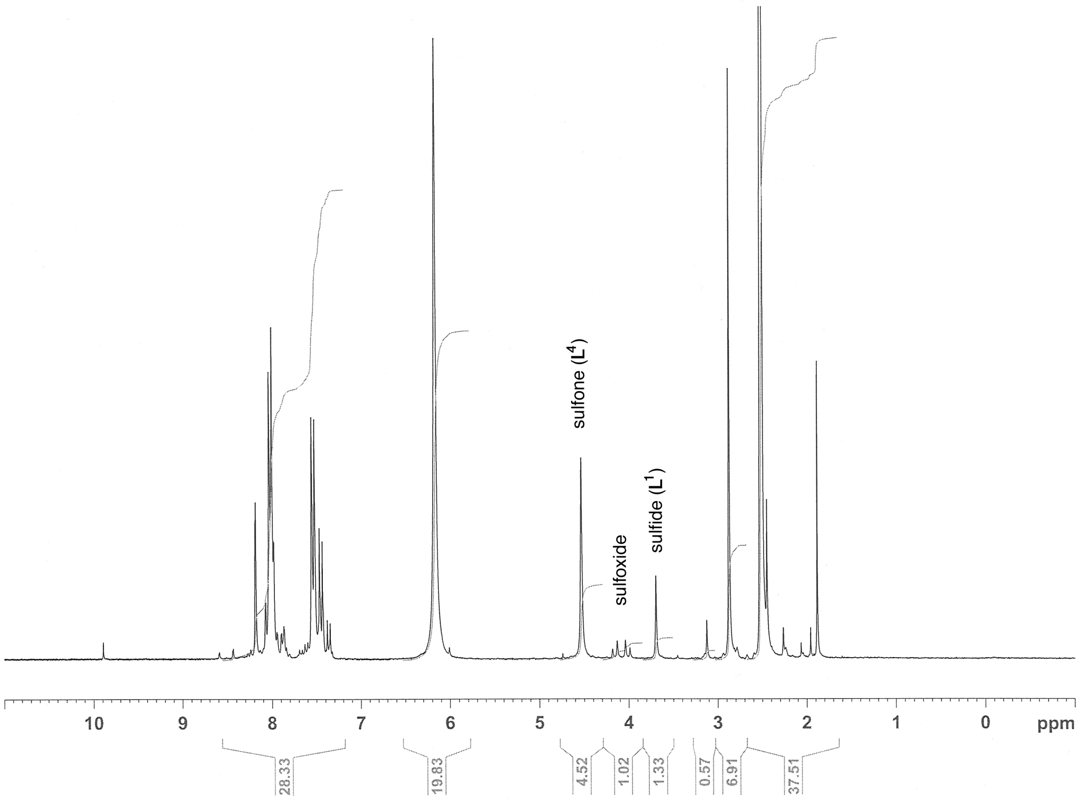


Figure S9. ^{1}H NMR spectrum of a bulk sample of **1'** digested in DCl/D_2O/d_6-DMSO. The methylene protons, labeled on the spectrum, are well separated and provide a good measure of the degree of the PSM reaction. In this case the sulfone : sulfoxide : sulfide ratio is 66:15:19. The minor peak at δ 3.1 is likely to be caused by a trace amount of dimethylsulfone.

Post-synthetic oxidation of 3 to 3'

This was undertaken in a similar manner to the conversion of **1** to **1'**. A crystal was taken out after 3 h, digested in HCl/H_2O and the resulting solution analysed by ESI-MS. The spectrum showed the presence of $[H\mathbf{L}^6]^-$ (*m/z* 331.03), with no evidence for $[H\mathbf{L}^3]^-$ (Fig. S10).

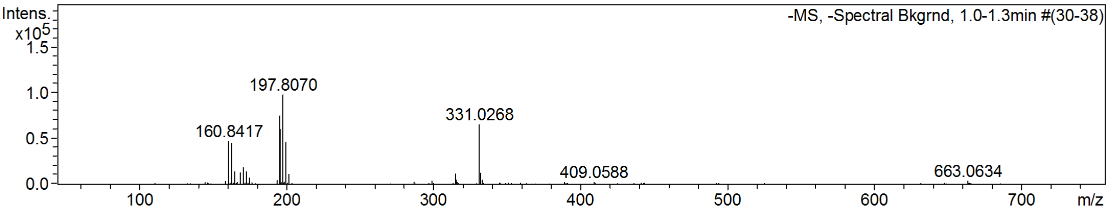


Figure S10. ESI-MS recorded on an individual crystal of **3'**, extracted from the reaction mixture of **3** with DMDO after 2 h and digested in HCl/H_2O.

The solvent was removed from the bulk sample by decantation, and the crystals washed with acetone and dried under reduced pressure. A sample was digested in DCl/D_2O/*d*$_6$-DMSO and analysed by ^1H NMR spectroscopy (Fig. S11). The spectrum indicates complete conversion of $\mathbf{L}^3$ to $\mathbf{L}^6$ has occurred (Fig. S12 shows, for comparison, the ^1H NMR spectrum of $H_2\mathbf{L}^3$).

Found C, 44.14; H, 2.45; N, 0.00 %. $Zn_4O(\mathbf{L}^6)_3 \cdot 2H_2O$ [$C_{48}H_{34}O_{21}S_3Zn_4$] requires C, 44.19; H, 2.63; N, 0.00 %. A sample was left in air for three weeks and re-analysed. Found: C, 39.96; H, 3.19; S, 6.56 %. $Zn_4O(\mathbf{L}^4)_3 \cdot 9H_2O$ [$C_{48}H_{48}O_{28}S_3Zn_4$] requires C, 40.30; H, 3.38; S, 6.72 %. The lower value of %C and higher value of %H is consistent with adsorption of atmospheric water.

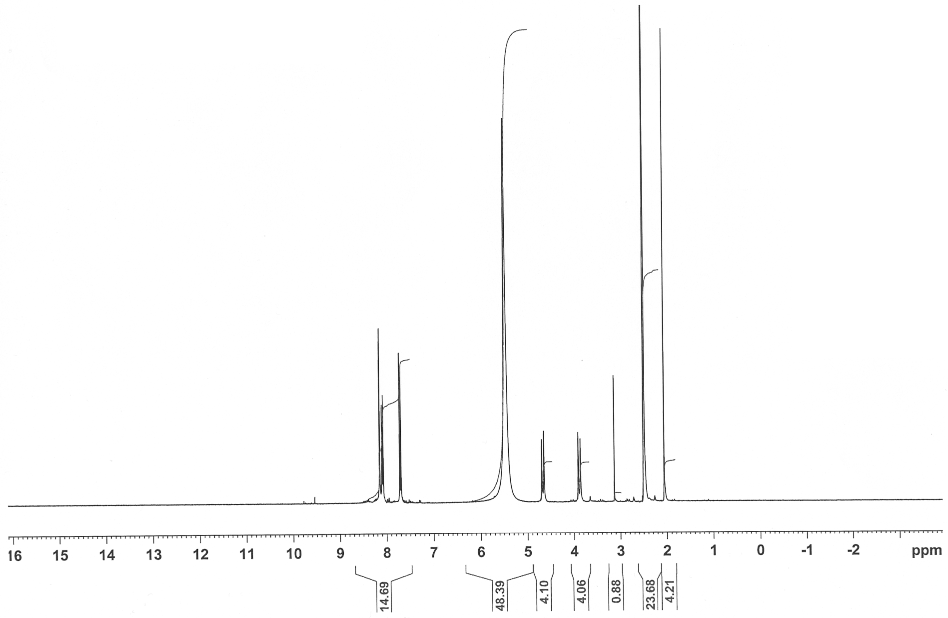


Figure S11. ^1H NMR spectrum of a bulk sample of **3'** digested in DCl/D_2O/KOH. The methylene protons are observed as a well-separated AB system at δ 3.91 and δ 4.70. The peak at δ 3.1 is likely to be caused by a small amount of dimethylsulfone.

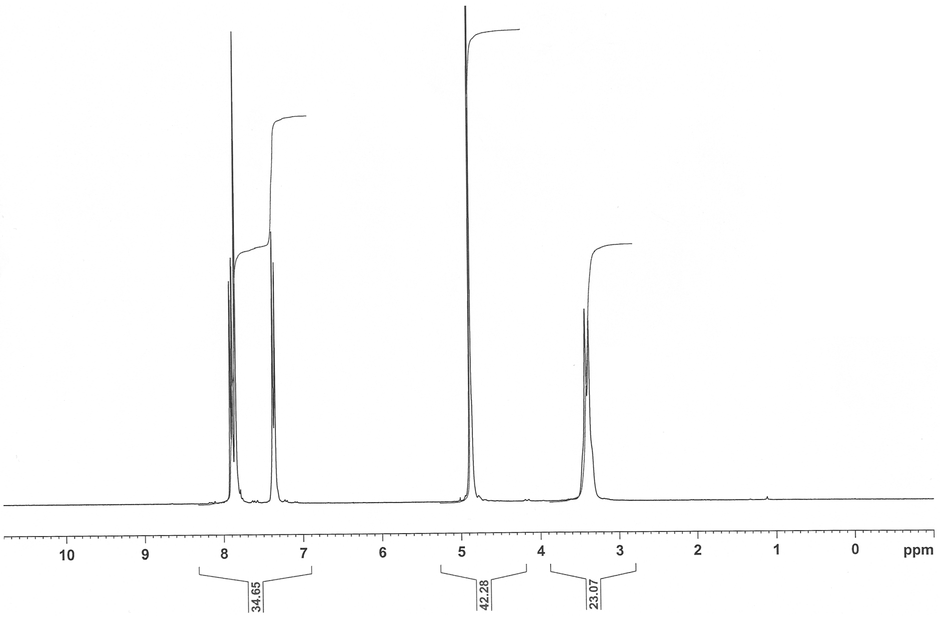


Figure S12. ^{1}H NMR spectrum of $H_2\mathbf{L}^3$ in d_6-DMSO. The methylene protons are observed as a close-spaced AB system centred at δ 3.40.

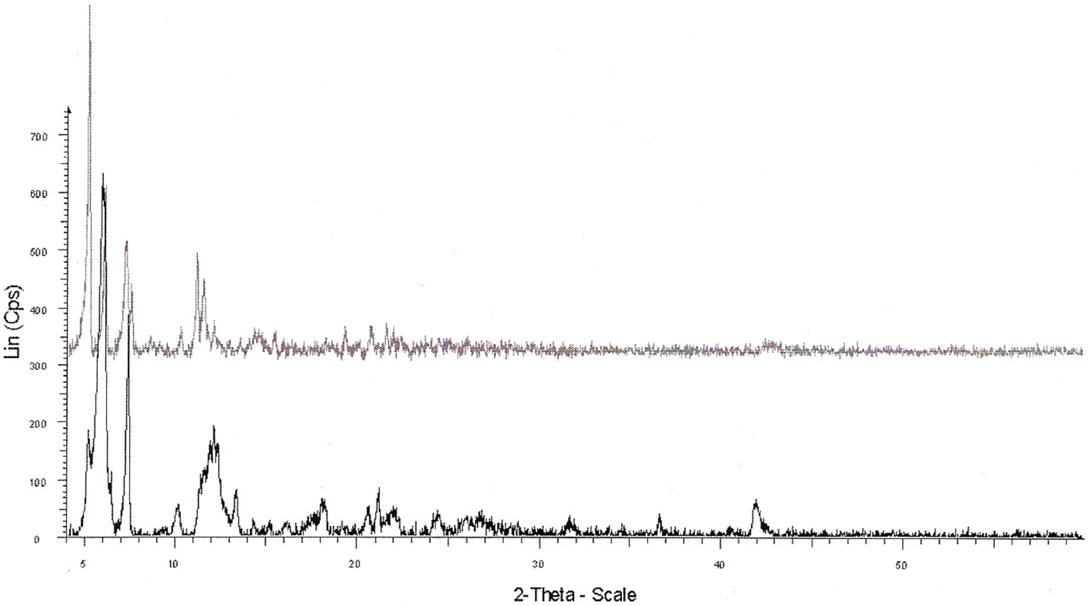


Figure S13. Comparison of the powder diffraction pattern for **3** (black) with that for **3'** (grey). The broadness of the pattern for **3** is due to some loss of crystallinity on sample preparation.

X-ray crystallographic analyses

Summary

1	*C*2/*m*	*a* = 25.0111(9), *b* = 22.9843(9), *c* = 17.1959(3) Å, β = 96.404(4)°
2	*R*–3*m*	*a* = 23.8212(3), *c* = 30.2938(11) Å
3	*P*-4 2_1*m*	*a* = 17.096, *c* = 16.949 Å
4	*C*2/*m*	*a* = 25.1670(4), *b* = 23.2000(3), *c* = 17.1020(3) Å, β = 93.561(1)°

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{66}H_{78}N_6O_{19}S_3Zn_4$
Formula weight	1617.00
Temperature	170 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*m*
Unit cell dimensions	*a* = 25.0111(9)Å α = 90°
	b = 22.9843(9)Å β = 96.404(4)°
	c = 17.1959(3)Å γ = 90°
Volume	9823.6(5) Å^3
Z	4
Density (calculated)	1.093 Mg/m^3
Absorption coefficient	1.082 mm^{-1}
F(000)	3344
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	3.52 to 26.70°
Index ranges	-31<=h<=31; -28<=k<=28; -21<=l<=21
Reflections collected	83061
Independent reflections	10421 [R(int) = 0.0698]
Reflections observed (>2σ)	6615
Data Completeness	0.975
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.82 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10421 / 12 / 334
Goodness-of-fit on F^2	0.997
Final R indices [I>2σ(I)]	R1 = 0.0765 wR2 = 0.2190
R indices (all data)	R1 = 0.1006 wR2 = 0.2346
Largest diff. peak and hole	1.080 and -0.844 eÅ^{-3}

The asymmetric unit in this network contains one full occupancy zinc (Zn2) and two half-occupancy zincs (Zn1 and Zn3), one full occupancy $\mathbf{L^1}$ ligand, half of an additional $\mathbf{L^1}$ ligand (wherein O2, O3, C17, C18 C21, C22 C25 and C29 are located on a crystallographic mirror plane), one half-occupancy oxygen atom (at the centre of the SBU) and two DMF ligands attached to Zn3. The partial zinc atoms and ligand atoms bearing half occupancy are located on a crystallographic mirror plane, with the exceptions of carbons 2-7, which closely straddle this symmetry element.

The data for this sample were good quality but, nevertheless, the refinement presented the usual issues that bedevil symmetrical 3-D MOF structures. In particular, the DMF ligand based on O8 was disordered over 2 sites, electron-density in this region of the map was modeled subjects to distance restraints in the solvent fragment. O9 forms the basis of the second DMF ligand, and while credible residual density was observed for the remaining atoms in this ligand, refinement in this area did not succeed – probably due to disorder coupled with the proximity to the crystallographic mirror plane. There was rotational motion observable along the spine of each of the **L**^{1} ligands, with ADP values increasing proportionally to the distance of atoms from the spine. In the case of the ligand straddling the mirror plane, 50:50 disorder was successfully modeled, the presence of which necessarily demands that the sulfur tag to be similarly disordered. Distance restraints were also applied in this part of the model to aid convergence. Overall however, the CH_2SCH_3 groups are remarkably ordered in this structure, given the possibilities for additional disorder in each ligand.

After refinement of the network structure it was obvious that the cavities contained additional electron density. PLATON determined this solvent to be in the region of 10-11 DMF molecules per Zn_4O moiety. However, given precedent in network structures, the final least squares takes account of the presence of four molecules of solvent per Zn_4O moiety (as these materials do not normally have high densities, or hard-packed solvent in the pores).

Calculations for unit cell contents:

Ligand = C16 H12 O4 S1
Formula = ZnO4(L)3(DMF)2 = C54 H50 O5 S3 ZN4 N2
Additional DMF added after Squeeze = 4 molecules per Zn4O
Free solvent = C12 H28 N4 O4
Final formula = C66 H78 O19 N6 S3 Zn4

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	$C_{69}H_{83}N_5O_{18}S_6Zn_4$
Formula weight	1724.24
Temperature	170(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	*R*–3*m*
Unit cell dimensions	*a* = 23.8212(3)Å α= 90°
	b = 23.8212(3)Å β= 90°
	c = 30.2938(11)Å γ= 120°
Volume	14887.1(6) Å^3
Z	6
Density (calculated)	1.154 Mg/m^3
Absorption coefficient	1.135 mm^{-1}
F(000)	5352
Crystal size	0.38 x 0.25 x 0.20 mm
Theta range for data collection	3.58 to 26.45 °.
Index ranges	-29<=h<=29; -29<=k<=29; -37<=l<=37
Reflections collected	84171
Independent reflections	3663 [R(int) = 0.0999]

Reflections observed (>2σ)	1722
Data Completeness	0.995
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.81 and 0.69
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3663 / 28 / 112
Goodness-of-fit on F^2	0.954
Final R indices [I>2σ(I)]	R1 = 0.0666 wR2 = 0.1686
R indices (all data)	R1 = 0.1577 wR2 = 0.1994
Largest diff. peak and hole	0.484 and -0.288 eÅ^{-3}

The asymmetric unit in this structure contains half of a zinc (Zn2), one-sixth of a zinc (Zn1), one-sixth of an oxygen at the centre of the SBU (O1), a **L^2** ligand fragment in which O2, O3, C1-C8 and C11 and C12 are located on a crystallographic mirror plane, and approximately 2.5 molecules of DMF solvent. The data for this structure are high quality to the given resolution, given the usual issues with obtaining good data on highly symmetrical MOFs. Thus, it was frustrating not to be in a position to refine the tags on the ligand. Examination of the ADPs explains the issue in part, when taken in conjunction with the high symmetry present and the disorder. After refining the distances in the aromatic rings subject to some restraints based on ideal values, there was clear evidence for twisting of the these rings about the C1-C12 axis. In addition, the difference electron density maps (Fig. S14) suggest that the tags are disordered in a 50:50 ratio over two possible sites . These facts precluded reliable location and refinement of the fragments present, which is not untypical of this variety of MOFs.

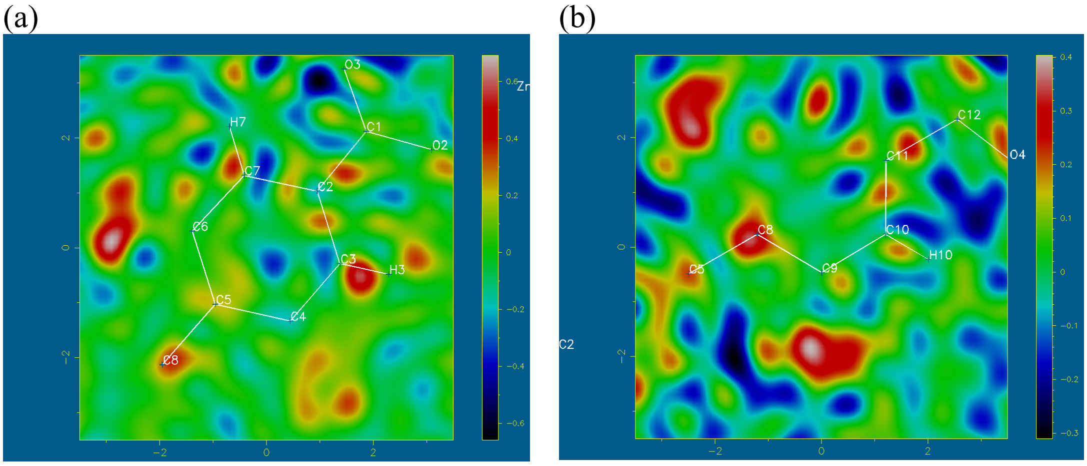


Figure S14. Fo-Fc maps taken perpendicular to the phenyl ring planes, showing the residual e-density due to the tag atoms in these planes (proximate to C4, C6, C9 and its symmetry-related counterpart). The diffuse nature of the residual near C4 is indicative of electron density smearing in the *z* direction.

After refinement of the network structure it was obvious that the cavities contained additional electron density. PLATON determined this solvent to be significantly higher than realistic – not aided by the fact that the un-modeled tag electron density contributes to the calculation. However, given precedent in network structure, the final least squares takes account of the presence of five molecules of solvent per Zn_4O moiety.

Crystallographic analysis of ***3***

The crystallographic analysis of **3** was hindered by space group ambiguity. Several possibilities were likely, all of which were examined on merit, with the optimum refinement in $P\text{–}4\ 2_1m$. Data resolution did not go beyond 1.2 Å and the crystal may have been twinned, though the quality of the data precluded finding a rational model for any twinning present. The combination of high symmetry, disorder and resolution in this particular case mitigated against a creditable refinement, though the gross structure, a doubly-interpenetrated cubic network, is unambiguous.

Table S3. Crystal data and structure refinement for **4**.

Empirical formula	$C_{60}H_{64}N_4O_{23}S_3Zn_4$
Formula weight	1566.81
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*m*
Unit cell dimensions	a = 25.1670(4)Å α= 90°
	b = 23.2000(3)Å β= 93.561(1)°
	c = 17.1020(3)Å γ= 90°
Volume	9966.1(3) Å^3
Z	4
Density (calculated)	1.044 Mg/m^3
Absorption coefficient	1.067 mm^{-1}
F(000)	3216
Crystal size	0.25 x 0.20 x 0.20 mm
Theta range for data collection	3.53 to 27.49°
Index ranges	-32<=h<=32; -30<=k<=30; -22<=l<=22
Reflections collected	88639
Independent reflections	11661 [R(int) = 0.0592]
Reflections observed (>2σ)	8102
Data Completeness	0.993
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.653 and 0.591
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11661 / 24 / 334
Goodness-of-fit on F^2	1.104
Final R indices [I>2σ(I)]	R1 = 0.0884 wR2 = 0.2743
R indices (all data)	R1 = 0.1159 wR2 = 0.2914
Largest diff. peak and hole	1.106 and -0.881 eÅ^{-3}

The asymmetric unit in this network contains one full occupancy zinc (Zn2) and two half-occupancy zincs (Zn1 and Zn3), one full occupancy $\mathbf{L}^4$ ligand, half of an additional $\mathbf{L}^4$ ligand (wherein C17, C18, C21, O7 and O8 are located on a crystallographic mirror plane), one half-occupancy oxygen atom (at the centre of the SBU) and two DMF ligands attached to Zn3. The partial zinc atoms are also located on a crystallographic mirror plane, as is the DMF ligand based on N1. Carbons 22-28 are refined at half occupancy, being very close to this same symmetry element.

The data for this sample were good quality but, nevertheless, the refinement presented the usual issues that bedevil symmetrical 3-D MOF structures. In particular, the DMF ligand based on O10 was disordered over two sites, and only the oxygen and one carbon atom therein could be reliably added to the atoms list for refinement. Electron density in the solvent ligand region of the map was modeled subjects to distance restraints within each fragment. There was rotational motion observable along the spine of each of the ligands, with ADP values increasing proportionally to the distance of atoms from this spine. In the case of the ligand straddling the mirror plane, 50:50 disorder was successfully modeled, the presence of which necessarily demands that the functional group is similarly disordered. The sulfur-containing functionality of the full occupancy $\mathbf{L}^4$ ligand was also disordered in a 1:1 ratio (S1/S1A) but this time the disorder was equally divided between both rings. Similarity distance restraints were applied to S-O and S-C distances within the functional groups. Only the sulfur atoms in the partial-occupancy $\mathbf{L}^4$ ligands were treated anisotropically. There is considerable ligand rotation of the $\mathbf{L}^4$ ligands about the long axis of each. Consequently, the aromatic rings were refined as hexagons where possible.

While the geometry about Zn1 and Zn2 are tetrahedral, Zn3 exhibits distorted octahedral geometry. The angles in the coordination sphere are not ideal, but a combination of thermal motion, disorder and lattice symmetry coalesced to preclude any reasonable additional modeling in this region.

After refinement of the network structure it was obvious that the cavities contained additional electron density. PLATON determined this solvent to be in the region of 2.7 DMF molecules per Zn_4O moiety. However, given precedent in network structures, the final least squares takes account of the presence of two molecules of solvent per Zn_4O moiety, the additional 0.7(DMF) being attributed to the atoms in the ligand based on O10, which could not be reliably included in the least-squares.

Calculations for unit cell contents:

Ligand = $C_{16} H_{12} O_6 S_1$
Formula = $Zn_4O(L)_3(DMF)_2$ = $C_{54} H_{50} O_{21} S_3 Zn_4 N_2$
Additional DMF added after SQUEEZE = 2 molecules per Zn_4O
Free solvent = $C_6 H_{14} N_2 O_2$
Final formula = $C_{60} H_{64} O_{23} N_4 S_3 Zn_4$