Dramatic Improvement of Stability by In-Situ Linker Cyclization of a Metal-Organic Framework

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Experimental details

General procedure. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich and J&K) and used without further purification. 4-Trimethylsilylethynyl-1-methylthiobenzene was prepared according to the reported procedure (*CrystEngComm*, 2004, 6, 184). Bis(triphenylphosphine)palladium(II) chloride and trimethylsilylacetylene were purchased from Meryer and used without further purification. Solution nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Mercury VX-300 spectrometers, with working frequencies of 300 and 400 MHz for ^{1}H and 75 and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents, with tetramethylsilane (TMS) as the internal standard. Solid state ^{13}C NMR CP-MAS measurements were carried out using a Bruker Advance 400 spectrometer operating at 100.6 MHz for ^{13}C using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 10-12.5 kHz.

Powder X-ray diffraction data were collected in the reflection mode at room temperature on a Bruker D2 Phaser X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) operating at 30 kV and 10 mA, respectively. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analyses (TG) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with heating program described in the respective TGA figure captions (e.g., 2 ℃/min). Diffuse reflection spectrum was collected in the UV-Visable Near Infra-red Spectrophotometer with Integrating Sphere (PE Lamda 750).

The structural models of Zr-**L1** and Zr**L1**-320 (from which Figures 1 and 2 were prepared), including cell parameters and atomic positions, was generated using Materials Studio (v6.1.0)

suit of programs by Accelrys. For Zr**L1**, a crude structure model was obtained by lowering the symmetry of Lin's MOF (*Chem. - Eur. J.* **2014,** *20,* 14965) to *P*1 and substituting the ligand with **L1** while maintaining a geometrical arrangement of organic linkers and zirconium clusters, followed by Geometry Optimization of Forcite Calculation in Materials Studio by Accelrys. For Zr**L1**-320, a crude structure model was obtained by substituting the ligand of Zr**L1** with **L1**-320 while maintaining a geometrical arrangement of organic linkers and zirconium clusters, followed by Geometry Optimization of Forcite Calculation in Materials Studio by Accelrys. The lattice parameters were then modified with the PXRD pattern indexing results, and the structures were subjected to geometry optimization under the constraint of fixed lattice geometry. No refinement of atomic positions against the PXRD data was applied.

Synthesis of SM1. Methyl 4-amino-3,5-dibromobenzoate (**SM1**) was prepared based on a modified literature method (Eur. Pat. Appl., 1986, 188351). Methyl 4-aminobenzoate (10.0 g, 66.2 mmol) was added to a round-bottom flask charged with a magnetic stirring bar and dissolved in acetic acid (30 mL). A mixture of acetic acid (30 mL) and bromine (23 g, 146 mmol) was added dropwise into the flask. After stirring at room temperature for 12 hours, the reaction mixture was poured into deionized water (500 mL). The precipitate was filtrated and re-dissolved in dichloromethane (DCM) and dried over anhydrous MgSO4. After removal of the solvent, the residue was purified by column chromatography (silica gel, 1:1 *n*-hexane/DCM as the eluent) to provide **SM1** as a white powder (18.0 g, yield 90% based on methyl 4-aminobenzoate). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.07 (s, 2H, CHAr), 5.00 (s, 2H, NH_2), 3.86 (s, 3H, CH_3).

Synthesis of SM2. To a stirred mixture of methyl 4-amino-3,5-dibromobenzoate (8.0 g, 26 mmol), 98% H_2SO_4 (10 mL) and glacial acetic acid (50 mL) was added dropwise a solution of $NaNO_2$ (2.0 g, 29 mmol) in water (25 mL) over 1 h below 5 ℃ in an ice-salt bath. Then a

solution of KI (43 g, 260 mmol) in water (30 mL) was added, and the mixture was stirred at room temperature for an additional 30 min. After neutralization with saturated aqueous NaOH, the organic mixture was extracted with CH_2Cl_2 (×3), and the organic phase was washed with Na_2SO_3 aqueous solution and dried over MgSO4. After removal of the solvent on a rotary evaporator, 9.6 g of pure orange solid were obtained (88% yield based on **SM1**). ^{1}H NMR (400 MHz, $CDCl_3$):): δ = 8.16 (s, 2H, CHAr), 3.93 (s, 3H, CH_3).

Synthesis of SM3. A mixture of **SM2** (4.0 g, 9.8 mmol), bis(triphenylphosphine)palladium(II) chloride (330 mg, 0.44 mmol), triphenylphosphine (250 mg, 0.93 mmol) and copper(I) iodide (180 mg, 0.90 mmol) were added to a 50-mL Schlenk tube and the tube was connected to a nitrogen manifold. Diisopropylamine (12.0 mL) and THF (12.0 mL), each previously purged by bubbling nitrogen gas for 5 minutes, were then transferred into the tube via a cannula. After trimethylsilylacetylene (2.7 mL, 19.6 mmol) was injected, the tube was screw-capped and stirred at 85 ^{o}C in an oil bath under nitrogen protection for 12 hours. After cooling to room temperature, the solvents were removed by a rotary evaporator and the resulting residue was purified by column chromatography (eluent: hexanes/EA, 2:1) to yield **SM3** as an orange solid (3.0 g, 80% yield based on **SM2**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.18 (s, 2H, CHAr), 3.92 (s, 3H, CH_3).

Synthesis of SM4. A mixture of **SM3** (500 mg, 1.3 mmol), bis(triphenylphosphine)palladium(II) chloride (38.0 mg, 0.05 mmol), triphenylphosphine (30.0 mg, 0.11 mmol) and copper(I) iodide (16.0 mg, 0.08 mmol) were added to a 20 mL Schlenk tube and the tube was connected to a nitrogen manifold. Diisopropylamine (3.0 mL) and THF (3.0 mL), each previously purged by bubbling nitrogen gas for 5 minutes, were then transferred into the tube via a cannula. After 4-trimethylsilylethynyl-1-methylthiobenzene (800 mg, 5.4 mmol) was added, the tube was screw-

capped and stirred at 85 ^{o}C in an oil bath under nitrogen protection for 12 hours. After cooling to room temperature, the solvents were removed by a rotary evaporator and the residue was purified by column chromatography (eluent: hexanes/DCM, 3:1) to yield **SM4** as an orange solid (565 mg, 89% yield based on **SM3**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.18 (s, 2H, CHAr), 7.47-7.49 (d, *J* = 8.5 Hz, 4H, CHAr), 7.21-7.24 (d, *J* = 8.5 Hz, 4H, CHAr), 3.95 (s, 3H, $COOCH_3$), 2.52 (s, 6H, SCH_3), 0.31 (s, 9H, $SiCH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.52, 140.19, 132.07, 131.72, 129.43, 126.98, 125.73, 119.00, 106.58, 101.60, 94.41, 87.37, 52.55, 15.28.

Synthesis of SM5. A mixture of **SM4** (280.0 mg, 0.53 mmol) and anhydrous potassium carbonate (0.380 g, 2.80 mmol) in a solution of DCM (2.0 mL) and methanol (2.0 mL) was stirred at room temperature for 1 hours. After removal of the solvent, the product was extracted with DCM (3 × 30 mL), filtered, and the resulting organic filtrate was washed by distilled water (3 × 30 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, an orange solid thus obtained was used directly in the next step (216.0 mg, 90% based on **SM4**).

Synthesis of Me_2L1. A round-bottom flask charged with compound **SM5** (216 mg, 0.48 mmol), copper(II) acetate monohydrate (270 mg, 0.48 mmol) and acetonitrile (7.0 mL) was stirred at 70 ^{o}C in an oil bath for 5 hours. Afterward, the solvents were removed by a rotary evaporator and distilled water (50 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL) and the combined organic layers were washed by distilled water (3 × 30 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (eluent: hexanes/DCM, 1:1; DCM being dichloromethane) to provide Me_2**L1** as a light yellow powder (190 mg, 85% based on **SM5**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (s, 4H, CHAr), 7.39-7.41 (d, *J* = 7.6 Hz, 8H, CHAr), 6.98-6.99 (d, *J* = 7.6 Hz, 8H, CHAr), 3.98 (s,

6H, $COOCH_3$), 2.39 (s, 12H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.40, 140.35, 132.12, 131.32, 130.28, 128.12, 125.61, 118.22, 95.86, 86.91, 83.96, 82.49, 52.69, 15.15.

Synthesis of H_2L1. Compound Me_2**L1** (190.0 mg, 0.21 mmol) was added to a two-neck round-bottom flask charged with a magnetic stirring bar and connected to a nitrogen manifold. An aqueous solution mixture of KOH (0.4 M, 12 mL in THF/H_2O, 2:1, v:v) was bubbled by N_2 for 5 minutes and then transferred to the flask via cannula under N_2 protection. The mixture was stirred at 60 ^oC for 12 hours. After cooling to room temperature, THF was removed by a rotary evaporator and distilled water (50 mL) was added, the resulting mixture was acidified with 10% HCl to attain a pH value lower than 2. An orange precipitate was formed, collected by filtration, and washed extensively with distilled water, yielding H_2**L1** as a yellow solid (175 mg, 95% based on Me_2**L**). ^1H NMR (300 MHz, DMSO-d_6): δ = 8.06 (s, 4H, CHAr), 7.42-7.44 (d, J = 7.9 Hz, 8H, CHAr), 7.08-7.09 (d, J = 7.8 Hz, 8H, CHAr), 2.41 (s, 12H, SCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 166.02, 140.99, 132.23, 132.14, 127.01, 126.01, 125.85, 117.77, 95.10, 87.62, 82.61, 82.16, 14.58.

Crystallization and activation of ZrL1. Molecule H_2**L1** (20 mg, 0.023 mmol) and a *N*,*N*-diethylformamide (DEF, 0.56 mL) solution of $ZrCl_4$ (5.2 mg, 0.022 mmol) and acetic acid (256 mg, 4.3 mmol, about 195 molar equivalents to $ZrCl_4$) were added in a Pyrex glass tube (soda lime, 10 mm OD, 6 mm ID). The tube was flame-sealed and heated at 120 ℃ in an oven for 48 hours, followed by programmed cooling to room temperature over 18 hours to afford orange truncated octahedron-shaped crystals (0.1-0.2 mm). For elemental analysis, the crystals were washed by DMF (3 × 2 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile every hour). The resulting crystals were further washed by acetone (3 × 2 mL), filtered and then evacuated at 70 ℃ for 8 hours. Elemental analysis found [C (60.14%), H (3.67%), N (0.08%)]; a

fitting formula can be determined to be $Zr_6O_4(OH)_8(H_2O)_4(C_{54}H_{32}O_4S_4)_4 \cdot H_2O$ (mw 4330), which gives a calculated profile as [C (59.92%), H (3.40%)]. The Zr**L1** solid sample was also characterized by TGA (see Figure S8).

Solvent-induced "shrinking and breathing" of ZrL1 crystals. As-made crystals 30 mg were washed by DMF (3 × 2 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile after 12 hours each time). The resulting crystals were filtered and then evacuated at 70 ℃ for 8 hours. Then the solvent 0.5mL (water, methanol, hexane, acetonitrile, benzonitrile and DMF) was added into the above sample 5mg in a glass vial, respectively. The crystal solution allowed to stand at room temperature for 24 hours, followed by the PXRD measurement of the wet crystal sample (the crystals were covered by a thin layer of the solvent during the scanning period).

Thermocyclization of ZrL1 crystals. As-made crystals 100 mg were washed by DMF (3 × 2 mL) and soaked in acetonitrile (3 × 3 mL, replaced by fresh acetonitrile after 12 hours each time). The resulting crystals were filtered and then evacuated at 70 ℃ for 8 hours. Then the crystal sample was heated in oven at an argon atmosphere at 320℃ for 3 hours. Heating rate: 3 ℃ /minutes.

Trapping and characterization of emitted molecules. To further characterize the emitted molecules from the thermal treatment, a sample of ZrL1-ac (18 mg) was flame-sealed under vacuum in a glass tube (ID, 6 mm; OD, 10 mm; length, ~10 cm), and heated at 320 ℃ for 3 hours before cooling back down to room temperature. The tube was then opened, and $CDCl_3$ (0.5 ml) was immediately added and the tube quickly sealed by parafilm. The tube was then tilted a few times to spread the liquid along the tube (to facilitate the liquid-gas contact). After about 10

minutes, the solid product was filtered off, and the $CDCl_3$ solution was collected for ^1H NMR measurement.

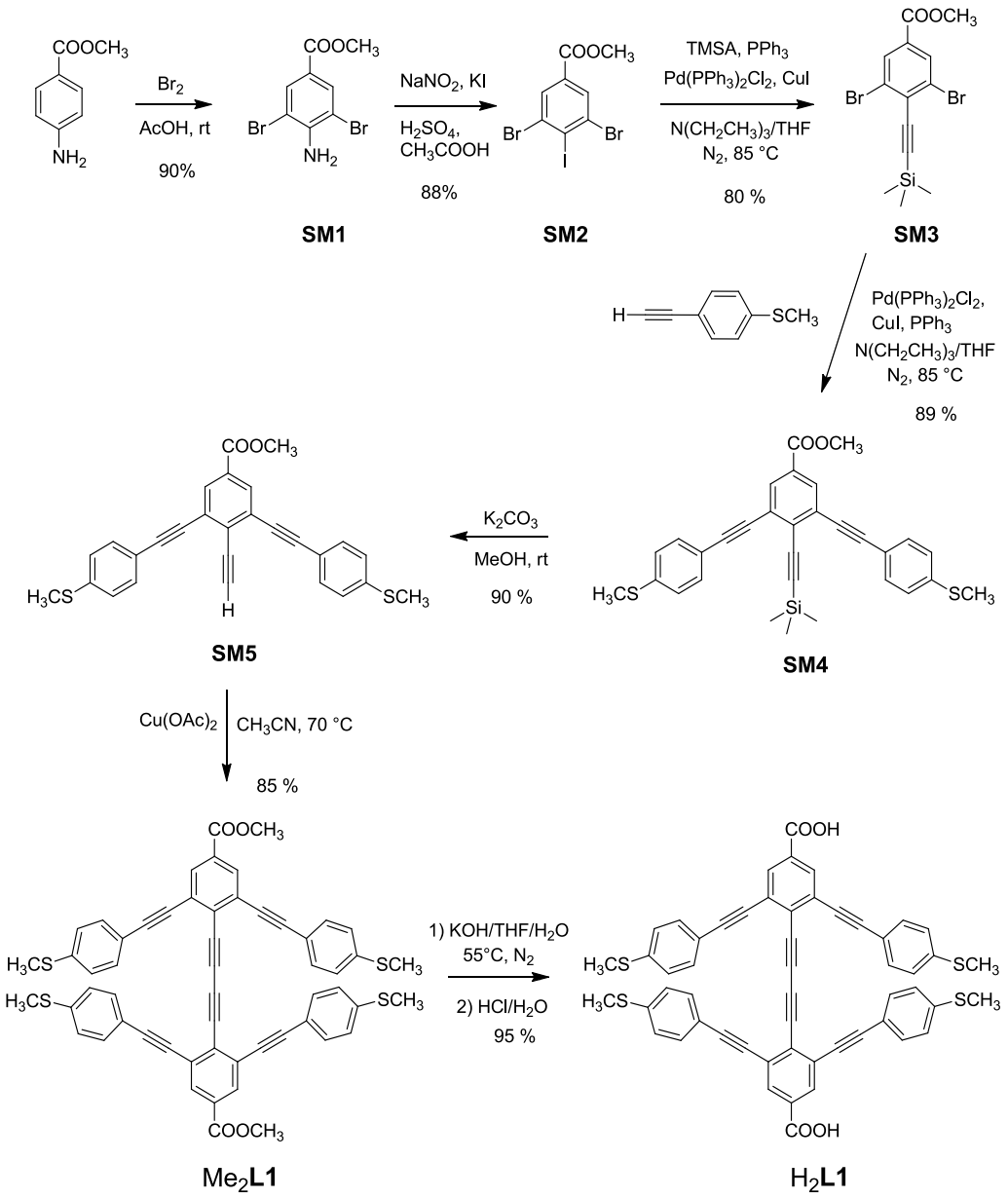

Figure S1. The synthetic steps for H_2**L1**.

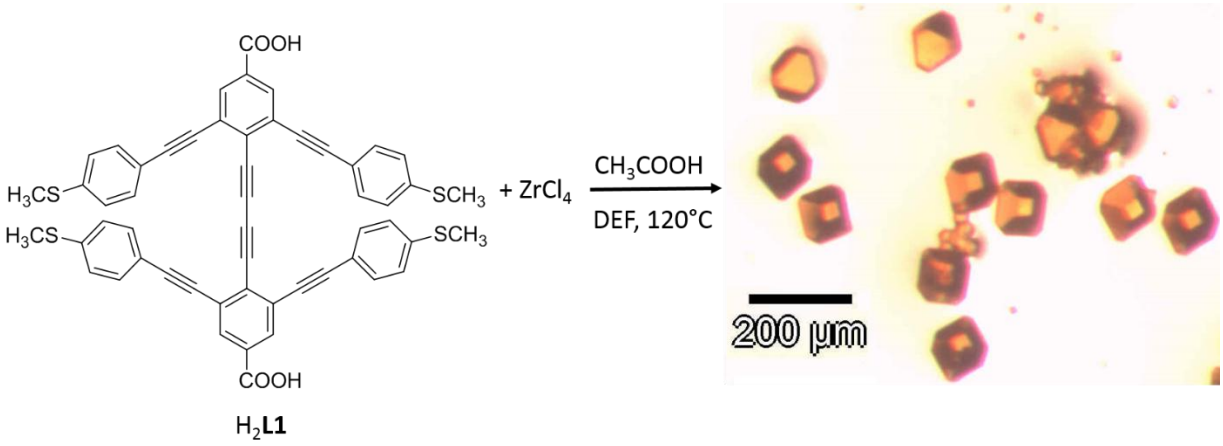

Figure S2. A reaction scheme for the crystallization of Zr**L1**, with a photograph of the crystals on the right.

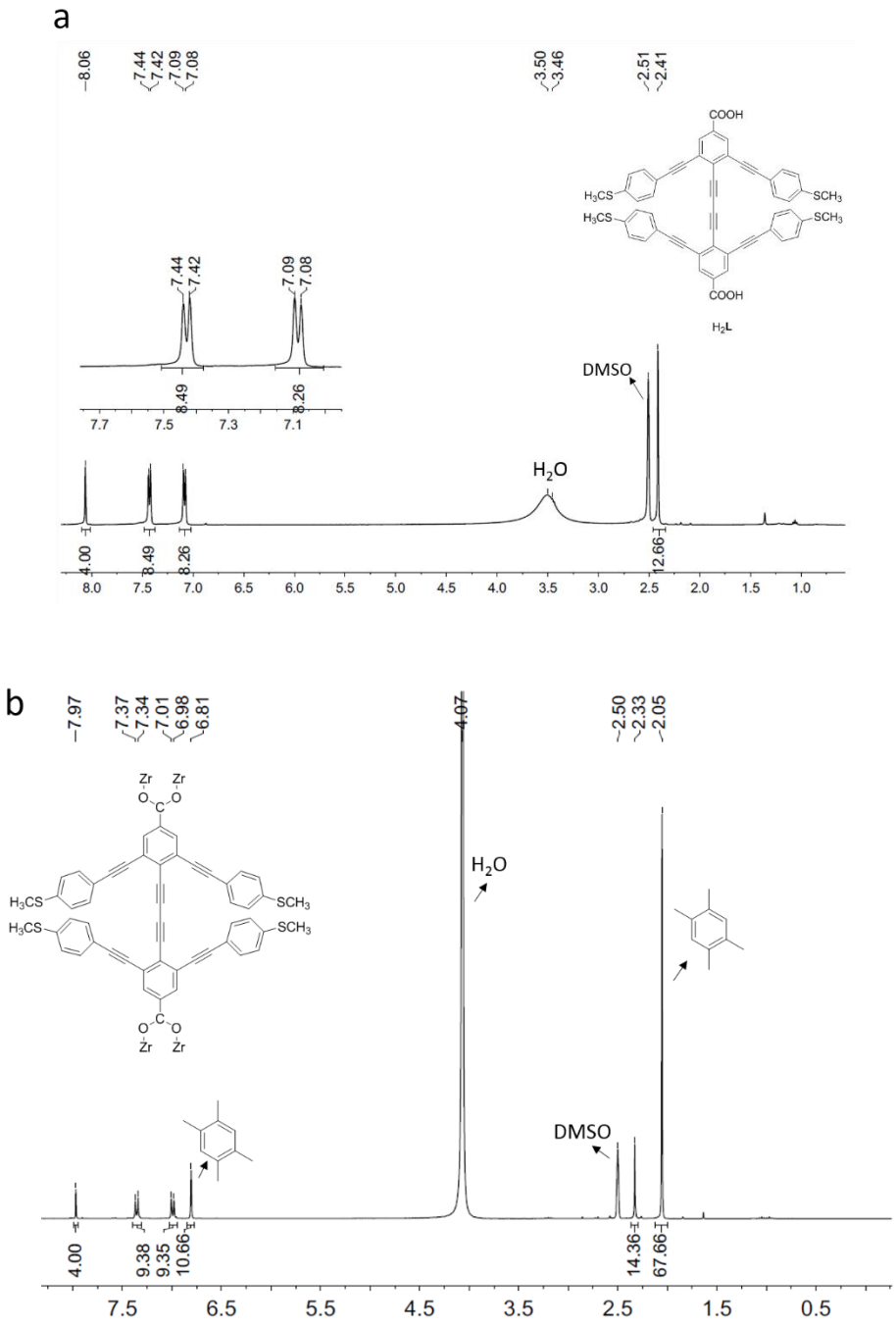

Figure S3. Solution ^{1}H-NMR spectra of the ligand H_2**L1** in DMSO-d_6 (a) and the activated sample of Zr**L1** (preparation of the solution: the activated Zr**L1** crystals were shaken with a mixture of saturated K_3PO_4/D_2O and DMSO-d_6 (1:1, v:v) for 0.5 hours, and the top layer (i.e., the DMSO layer) organic phase was isolated and used for NMR analysis (b).

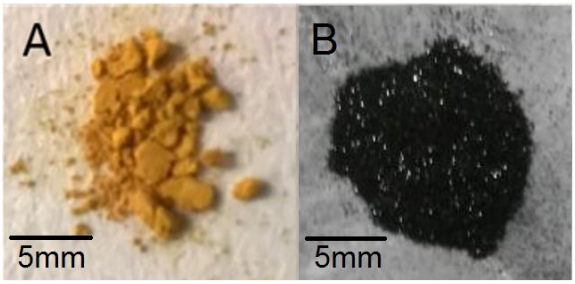

Figure S4. Photographs of an as-made bulk sample of Zr**L1** (panel a) and a sample of Zr**L1**-320 (panel b)—i.e., Zr**L1** after heating at 320 ℃.

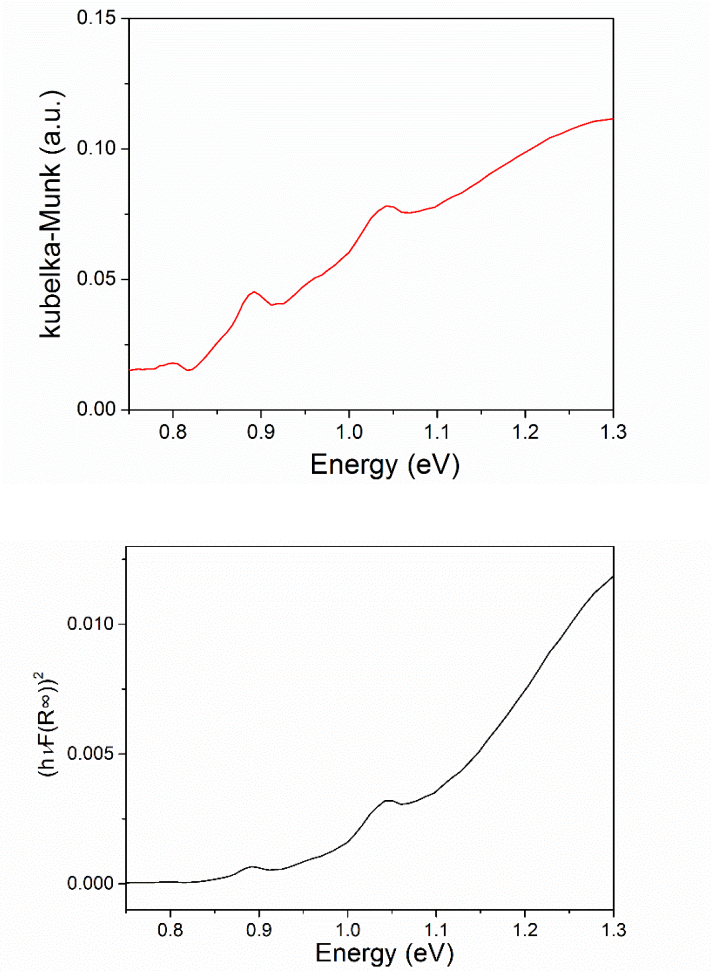

Figure S5. A Kubelka-Munk-transformed reflectance spectrum (top) and the corresponding Tauc plot (bottom; as direct bandgap semiconductor) for a solid sample of Zr**L1**-320 (the 320 ℃-treated sample). The optical band gap was estimated to be below ca 1.0 eV.

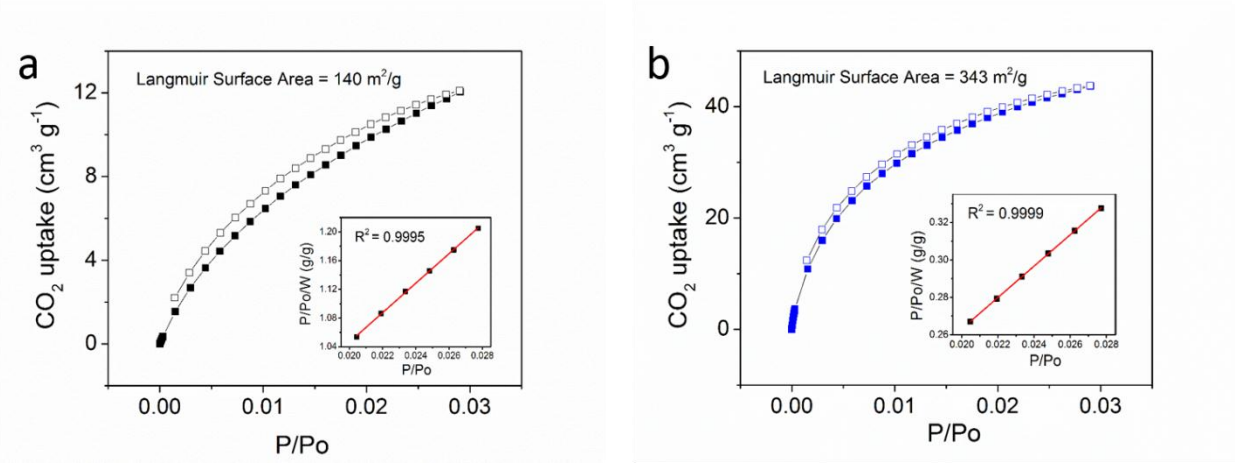

Figure S6. CO_2 sorption isotherms at 273 K for an activated sample of Zr**L1** (panel a) and Zr**L1**-320 (panel b). The Zr**L1** samples were first solvent-exchanged with acetonitrile and then evacuating at 120 ℃ for activation. Insets: Langmuir plot of Zr**L1** and Zr**L1**-320.

More specifically, the samples were solvent-exchanged with acetonitrile and degassed in vacuo at 120 ℃ for 10 hours. CO_2 sorption experiments at 273 K (pressure range: from 8×10^{-3} to 780 mmHg) on Zr**L1** and Zr**L1**-320 crystals revealed a typical type-I gas adsorption isotherm (CO_2 gas, 273 K) with a Langmuir surface area of 140 m^2/g and 343 m^2/g.

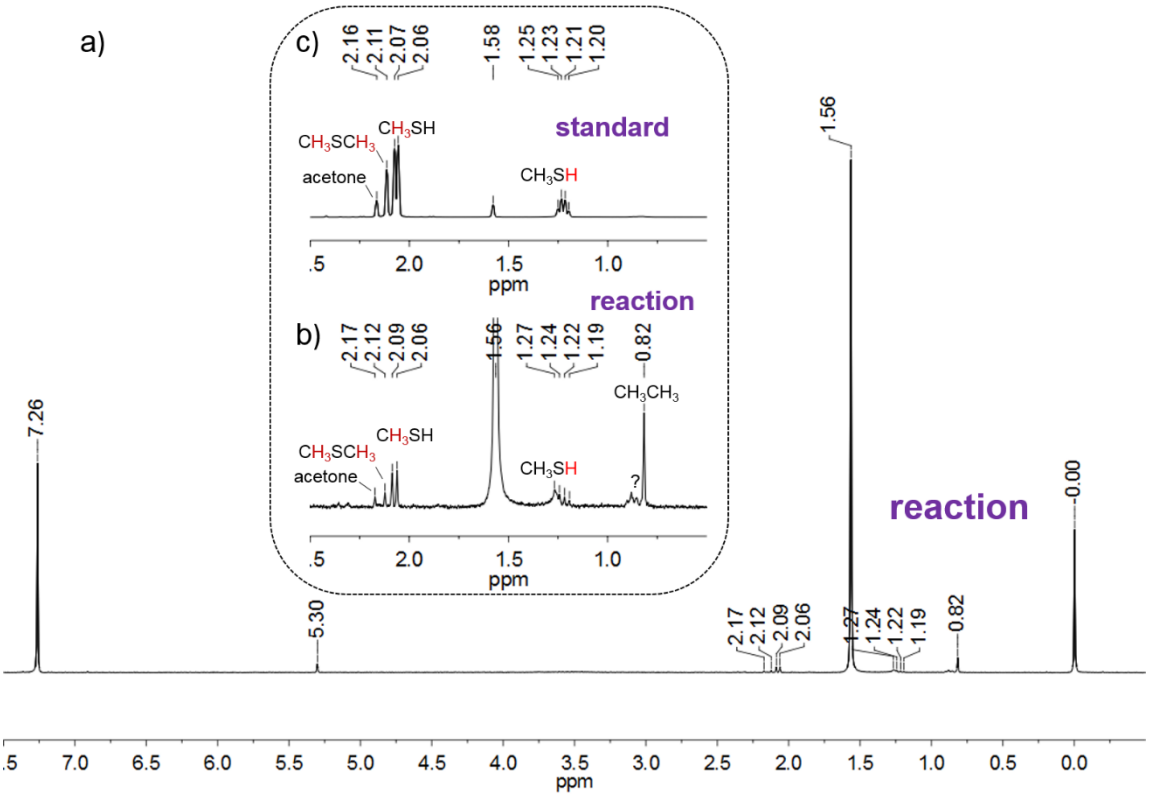

Figure S7. Solution ^{1}H NMR spectra (in $CDCl_3$) for characterizing the molecules emitted from the thermal treatment (to convert Zr**L1**-ac into Zr**L1**-320): a) the spectrum of the solution obtained by adding $CDCl_3$ to a reaction tube for collecting the emitted molecules (see above the detailed procedure); b) an amplified portion of (a) for the chemical shift δ range 0.5-2.5; c) the same portion of the spectrum of a $CDCl_3$ solution containing the standard samples of CH_3SH and CH_3SCH_3. The assignment of the signals are also presented, i.e., the doublet (δ, 2.08 and 2.06) and quadruplet (δ, 1.20, 1.22, 1.24 and 1.26) from CH_3SH, and the singlet (δ, 2.17) from CH_3SCH_3. The singlet at 0.82 observed in (a) and (b) appears to be from CH_3CH_3, which could arise from demethylation of the MeS- groups (further study on the origin of this NMR peak is however needed).

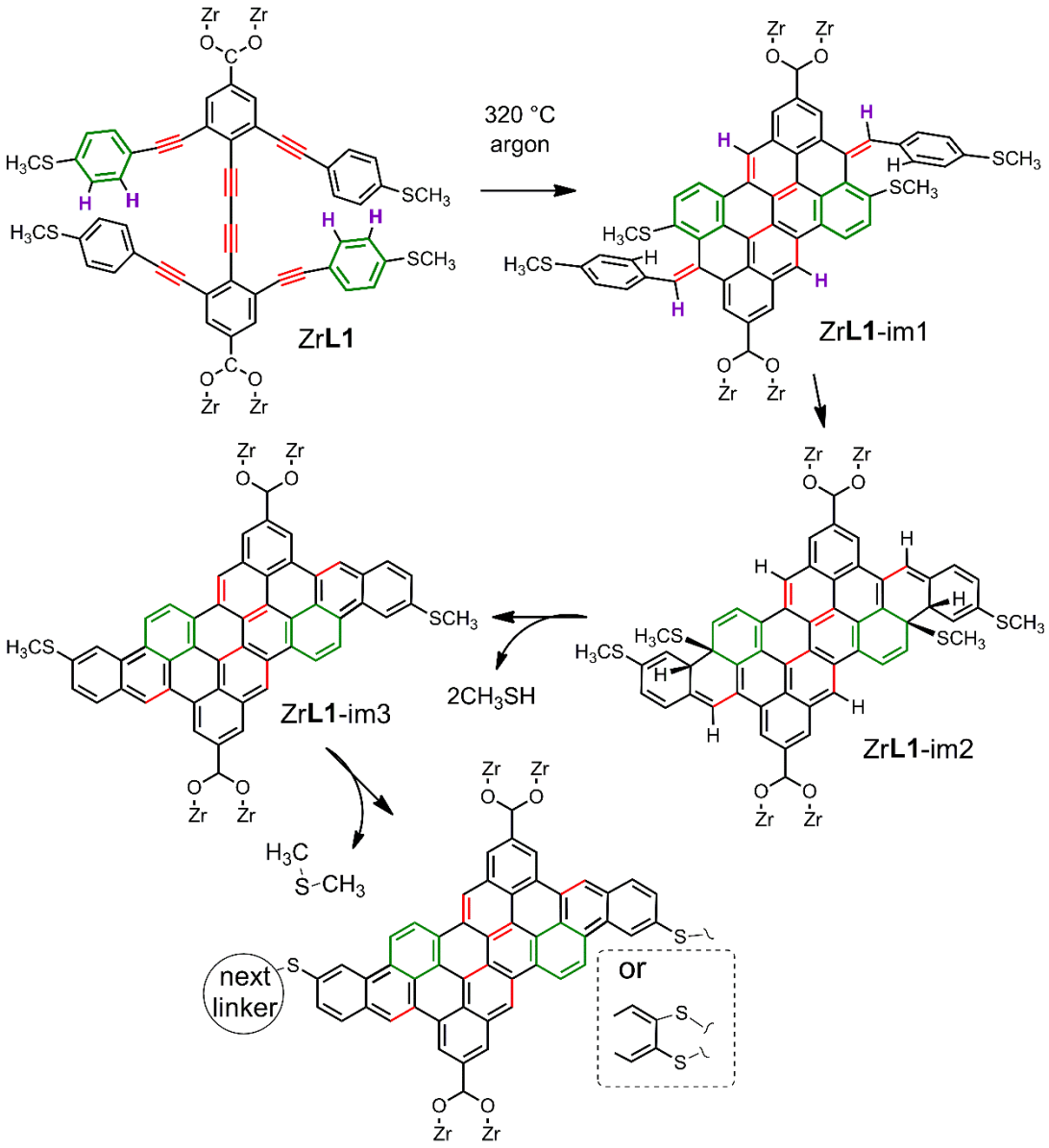

Figure S8. A proposed reaction pathway, featuring the elimination of CH_3SCH_3 and CH_3SH molecules as observed by NMR characterization of the trapped small-molecule products. The inset at lower right represents an alternative motif of crosslink in the product, but further characterization of the sulfur bonding features is still needed. For a cyclization reaction that also eliminates the methythio (-CH3S-) group, see Figure 20 of: Woodward, R. B. (1973). "The total synthesis of vitamin B12". *Pure Appl. Chem.* **33** (1), 145–178. doi:10.1351/pac197333010145

As-made

Elem	Wt %	At %
C K	54.39	71.86
O K	18.49	18.34
ZrL	11.26	1.96
S K	15.86	7.85
Total	100.00	100.00

Elem	Wt %	At %
C K	55.21	72.72
O K	17.92	17.72
ZrL	11.57	2.01
S K	15.30	7.55
Total	100.00	100.00

S/Zr = 3.85/1

320 °C

Elem	Wt %	At %
C K	52.06	69.32
O K	22.54	22.53
ZrL	14.00	2.45
S K	11.41	5.69
Total	100.00	100.00

Elem	Wt %	At %
C K	52.93	69.58
O K	23.07	22.77
ZrL	13.05	2.26
S K	10.95	5.39
Total	100.00	100.00

S/Zr = 2.38/1

Figure S9. Elemental profiles as found by EDX measurements on the as-made Zr**L1** sample and Zr**L1**-320 (two parallel measurements for each sample). The elemental analysis results from EDX measurements are semi-quantitative, but serve to indicate smaller sulfur content in the thermally treated sample of Zr**L1**-320, i.e., to result in a S/Zr ratio of 3.85/1, as compared with S/Zr = 2.38/1 found for as-made Zr**L1**.

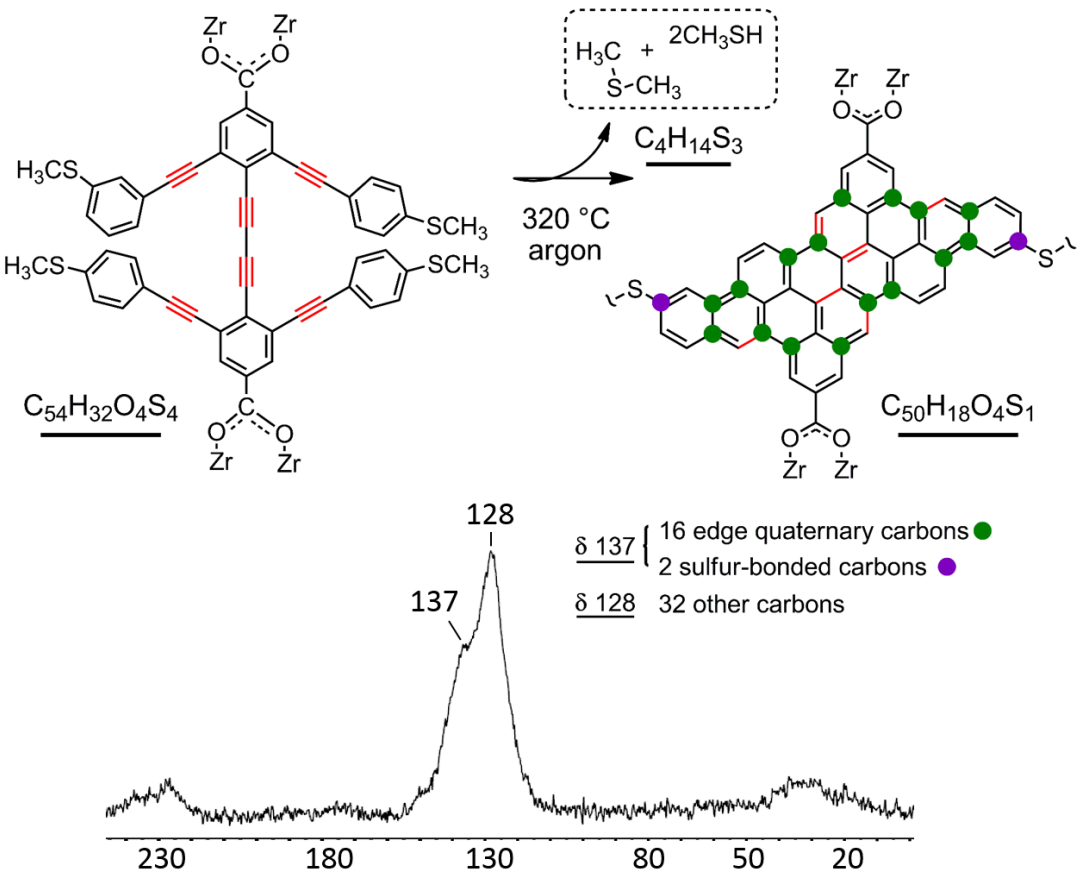

Figure S10. A solid state ^{13}C NMR (100.6 MHz) spectrum of a solid sample of Zr**L1**-320 (the 320 ℃-treated sample).

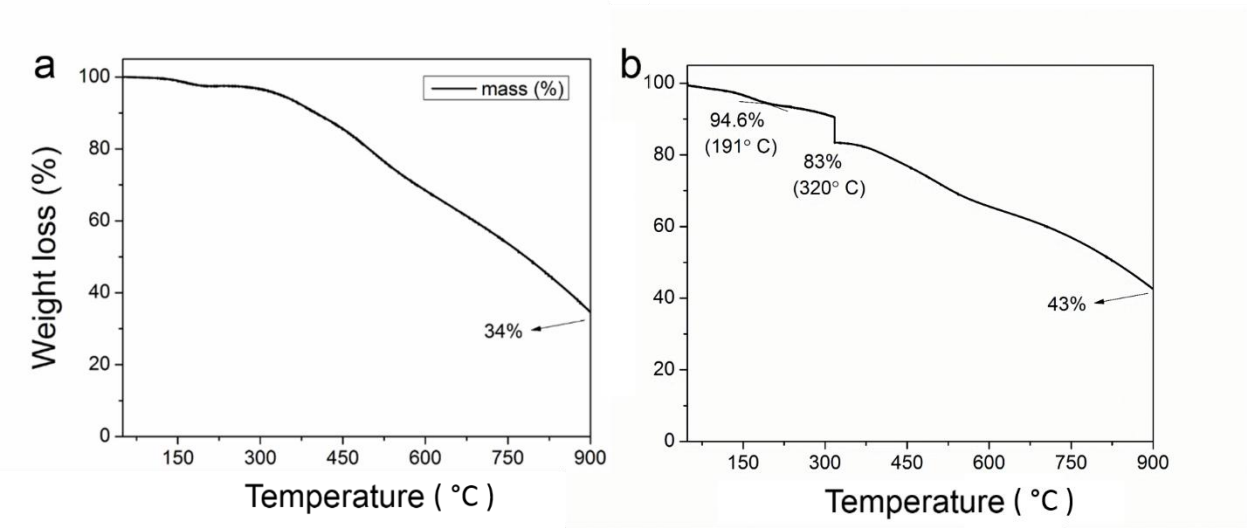

Figure S11. Two thermogravimetric analysis (TGA) plots of Zr**L1** (as-made sample washed with DMF and CH_3CN three times each, then air-dried at room temperature overnight). Temperature programs: a) 30 min at 50 ℃, then heat to 900 ℃ at 2 ℃/min; b) 30 min at 50 ℃, then heat to 320 ℃ at 2 ℃/min and stay at 320 ℃ for 3 hours, then heat to 900 ℃ at 2 ℃/min. The initial weight loss (e.g., up to 180 ℃) of about 5.0% can be ascribed to the departure of the guest molecules (e.g., water and DMF). In (b), the weight loss from 191 to 320 ℃ (3hrs) involves the departure of the small molecules from the cyclization and crosslinking processes outlined in Figure S8.

The residual readings (plot a: 34%; and plot b: 43%) at 900 ℃ substantially outweighs the value (16.8%) calculated for the formation of ZrO_2, pointing to carbon-containing residue (with EDX indicating, semi-quantitatively, the presence of about 40% w/w of carbon and 9.5% w/w of sulfur in the residue). The residual weight of 43% in (b) is greater than the 34% of (a): apparently, the extra 3 hours maintained at 320 ℃ for sample (b) allows for the cyclization and crosslinking to occur more extensively and therefore results in less fragmentation in the higher temperature regime.

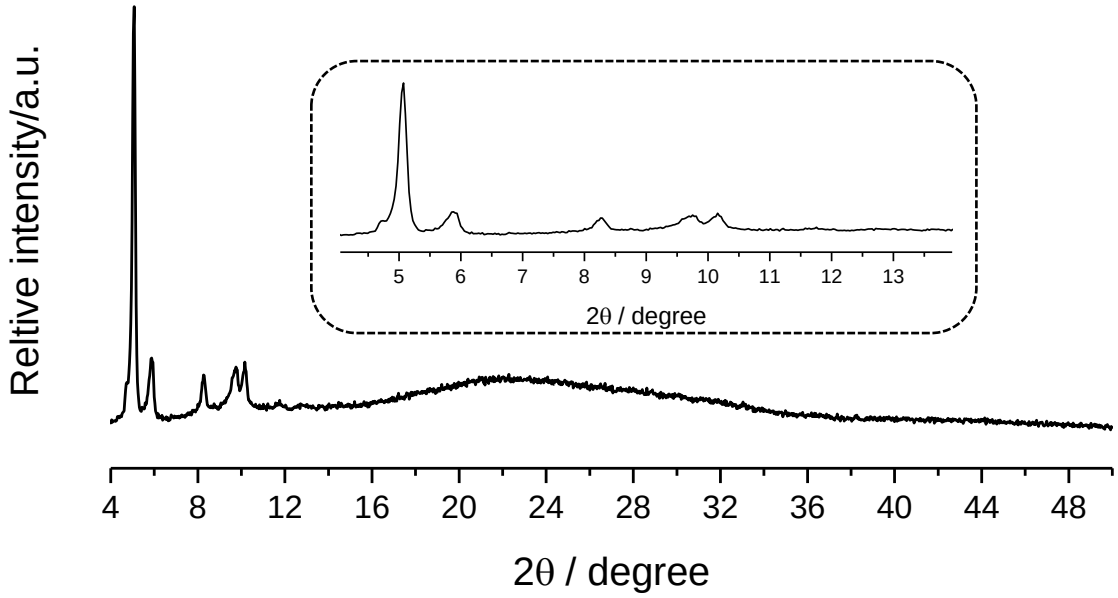

Figure S12. X-ray diffraction pattern (collected on an Inel Equinox 1000 X-ray diffractometer equipped with a CPS 180 detector using monochromated Cu-Kα1 radiation, λ = 1.5418 Å) of Zr**L**$_1$-320 soaked in DMF at r.t. for 24 hr. The inset is an amplification of higher angle region

Refinement details of the PXRD patterns of Figure 3.

(a) Pattern a is calculated from a model structure; no indexing is needed.

(b) As-made Zr**L1** (Fig. 3, pattern b):

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asmade-wet.dif

Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  24.3000  24.3000  32.5000  90.00  90.00  90.00  19190.92
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     4.5270       4.5270     4.5403    -0.0133
    1    1    0     5.1540       5.1540     5.1429     0.0111
    0    0    2     5.4380       5.4380     5.4383    -0.0003
    0    2    0     7.2780       7.2780     7.2756     0.0024
    1    1    2     7.4800       7.4800     7.4876    -0.0076
    1    2    1     8.5730       8.5730     8.5793    -0.0063
    1    0    3     8.8960       8.8960     8.9370    -0.0410
    0    2    2     9.0380       9.0380     9.0878    -0.0498
    2    2    0    10.2910      10.2910    10.2961    -0.0051
    0    1    4    11.4450      11.4450    11.4833    -0.0383
    1    3    2    12.6980      12.6980    12.7427    -0.0447
    2    3    1    13.3660      13.3660    13.4169    -0.0509
    1    2    4    13.5480      13.5480    13.6072    -0.0592

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0359
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0330

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  24.3417  24.3417  32.6451  90.00  90.00  90.00  19342.75
  0.0000 0.00000   0.0592   0.0000   0.0073   0.000  0.000  0.000   47.252


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     4.5270       4.5270     4.5281    -0.0011
    1    1    0     5.1540       5.1540     5.1341     0.0199
    0    0    2     5.4380       5.4380     5.4141     0.0239
```

```
    0    2    0     7.2780       7.2780     7.2631     0.0149
    1    1    2     7.4800       7.4800     7.4639     0.0161
    1    2    1     8.5730       8.5730     8.5622     0.0108
    1    0    3     8.8960       8.8960     8.9013    -0.0053
    0    2    2     9.0380       9.0380     9.0633    -0.0253
    2    2    0    10.2910      10.2910    10.2785     0.0125
    0    1    4    11.4450      11.4450    11.4353     0.0097
    1    3    2    12.6980      12.6980    12.7145    -0.0165
    2    3    1    13.3660      13.3660    13.3923    -0.0263
    1    2    4    13.5480      13.5480    13.5599    -0.0119

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0181
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0166
```

(c) Zr**L1**-ac (Fig. 3, pattern c):

```
CELREF Version 3.  11/2/2017 1:37:23 PM
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asmade-70.dif

Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda      a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  28.6000  28.6000  36.0000  90.00  90.00  90.00  29446.56
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     5.0530       5.0530     5.0118     0.0412
    0    1    2     5.7610       5.7610     5.8013    -0.0403
    0    2    0     6.2260       6.2260     6.1805     0.0455
    0    1    3     7.9860       7.9860     7.9898    -0.0038
    2    2    0     8.7140       8.7140     8.7448    -0.0308
    0    3    1     9.5230       9.5230     9.5969    -0.0739
    1    3    1    10.0690      10.0690    10.0841    -0.0151
    0    0    5    12.3140      12.3140    12.2928     0.0212

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0456
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0395

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda      a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  28.6483  28.6483  35.9841  90.00  90.00  90.00  29533.12
  0.0000 0.00000   0.2513   0.0000   0.0224   0.000  0.000  0.000  259.743


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     5.0530       5.0530     5.0059     0.0471
    0    1    2     5.7610       5.7610     5.8003    -0.0393
```

```
    0    2    0     6.2260       6.2260     6.1701     0.0559
    0    1    3     7.9860       7.9860     7.9907    -0.0047
    2    2    0     8.7140       8.7140     8.7300    -0.0160
    0    3    1     9.5230       9.5230     9.5820    -0.0590
    1    3    1    10.0690      10.0690    10.0683     0.0007
    0    0    5    12.3140      12.3140    12.2983     0.0157

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0426
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0369
```

(d) Zr**L1**-DMF*rg* (Fig. 3, pattern d):

```
CELREF Version 3.  2017/11/3 22:31:00
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Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda      a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  33.8132  33.8132  34.2775  90.00  90.00  90.00  39190.58
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     4.5070       4.5070     4.5059     0.0011
    0    0    2     5.1490       5.1490     5.1561    -0.0071
    2    2    0     7.3790       7.3790     7.3945    -0.0155
    1    3    1     8.6530       8.6530     8.6625    -0.0095
    2    2    2     9.0170       9.0170     9.0188    -0.0018
    1    5    1    13.6280      13.6280    13.6003     0.0277

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0170
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0138

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda      a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  33.8043  33.8043  34.2763  90.00  90.00  90.00  39168.63
  0.0000 0.00000   0.1180   0.0000   0.0577   0.000  0.000  0.000  151.802


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    1    1    1     4.5070       4.5070     4.5067     0.0003
    0    0    2     5.1490       5.1490     5.1562    -0.0072
    2    2    0     7.3790       7.3790     7.3965    -0.0175
    1    3    1     8.6530       8.6530     8.6646    -0.0116
    2    2    2     9.0170       9.0170     9.0205    -0.0035
    1    5    1    13.6280      13.6280    13.6038     0.0242

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0165
```

```
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0135
```

(e) Zr**L1**-320 (Fig. 3, pattern e):

```
CELREF Version 3.  11/2/2017 8:58:19 PM
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320.dif

Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.4000  21.4000  29.3000  90.00  90.00  90.00  13418.23
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.1140       5.1140     5.1135     0.0005
    0    0    2     6.0040       6.0040     6.0327    -0.0287
    0    2    0     8.2690       8.2690     8.2631     0.0059
    1    0    3     9.9280       9.9280     9.9549    -0.0269
    0    2    2    10.2310      10.2310    10.2372    -0.0062

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0232
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0180

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.3530  21.3530  29.4092  90.00  90.00  90.00  13409.10
  0.0000 0.00000   0.1711   0.0000   0.0202   0.000  0.000  0.000  107.862


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.1140       5.1140     5.1142    -0.0002
    0    0    2     6.0040       6.0040     6.0103    -0.0063
    0    2    0     8.2690       8.2690     8.2813    -0.0123
    1    0    3     9.9280       9.9280     9.9280    -0.0000
    0    2    2    10.2310      10.2310    10.2387    -0.0077

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0092
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0071
```

(f) sample (e) immersed in a saturated (4% w/w) NaF solution (Fig. 3, pattern f):

```
CELREF Version 3.  12/14/2017 5:13:03 PM
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320-NaF.dif

Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.1000  21.1000  31.4000  90.00  90.00  90.00  13979.59
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.0530       5.0530     5.0457     0.0073
    1    1    0     5.9230       5.9230     5.9235    -0.0005
    1    1    2     8.1680       8.1680     8.1749    -0.0069
    0    2    2    10.0890      10.0890    10.1013    -0.0123

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0112
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0079

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.0997  21.0997  31.4629  90.00  90.00  90.00  14007.18
  0.0000 0.00000   0.0545   0.0000   0.0441   0.000  0.000  0.000   41.183


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.0530       5.0530     5.0427     0.0103
    1    1    0     5.9230       5.9230     5.9236    -0.0006
    1    1    2     8.1680       8.1680     8.1672     0.0008
    0    2    2    10.0890      10.0890    10.0951    -0.0061

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0085
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0060
```

(g) sample (e) immersed in H_3PO_4 (10% w/w) for 24 hours (Fig. 3, pattern g):

```
CELREF Version 3.  12/14/2017 5:19:48 PM
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320-H3PO4.dif

Initial values    : (Refinement keys on 2nd line)
--------------    :
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.4000  21.4000  30.1000  90.00  90.00  90.00  13784.60
   0      0         1        0        1        0      0      0

    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.0730       5.0730     5.0666     0.0064
    1    1    0     5.8420       5.8420     5.8404     0.0016
    0    2    2    10.1300      10.1300    10.1431    -0.0131

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0147
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0085

Final values      : (Standard errors on 2nd line)
------------
  Zero    Lambda       a       b       c      alpha  beta   gamma   volume
   0.000 1.54180  21.3940  21.3940  30.1868  90.00  90.00  90.00  13816.67
  0.0000 0.00000   0.0848   0.0000   0.0922   0.000  0.000  0.000   69.131


    H    K    L    2Th(obs) 2Th_obs-shift 2Th(Calc)    diff.

    0    1    1     5.0730       5.0730     5.0626     0.0104
    1    1    0     5.8420       5.8420     5.8420     0.0000
    0    2    2    10.1300      10.1300    10.1352    -0.0052

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar)) : 0.0116
Sqrt(Sum(2Th O-C)**2)/Nref       ) : 0.0067
```