Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPORTING INFORMATION

Iodine Sequestration by Thiol-Modified MIL-53(Al)

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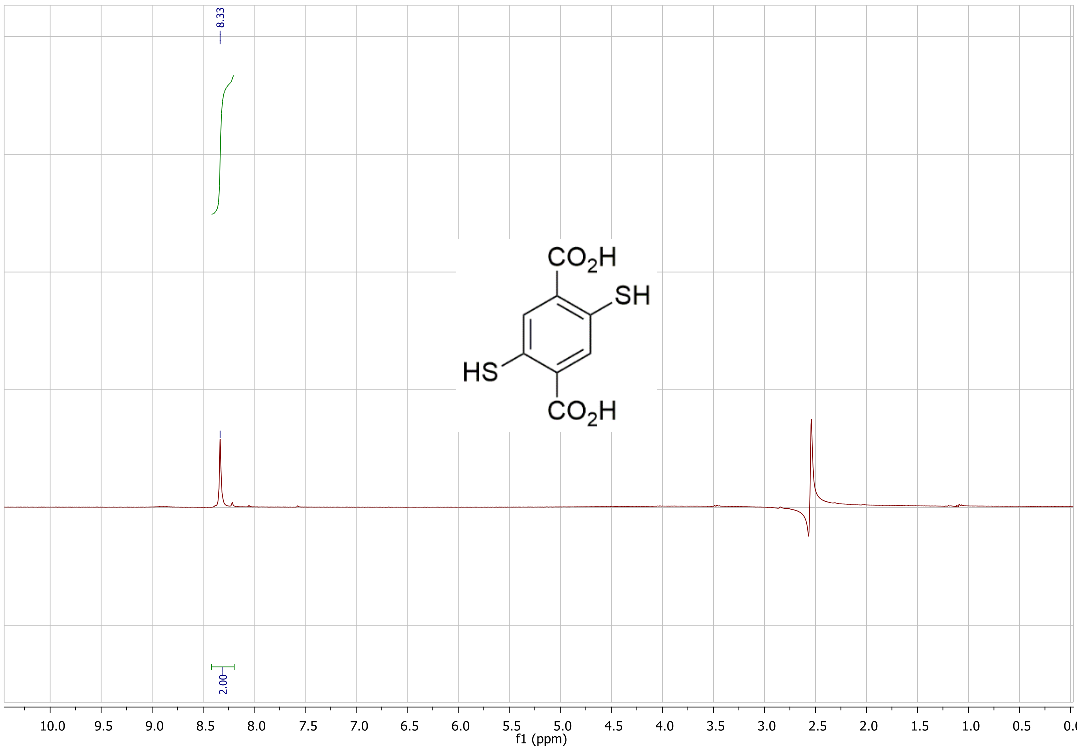

Figure S1: ^{1}H NMR of 2,5-dithiol-1,4-benzenedicarboxylic acid (300 MHz, DMSO)

Figure S2: Photographs of thiol-modified MIL-53(Al) (Product B) before (a) and after addition of iodine (b) from chloroform solution and (c) from vapour.

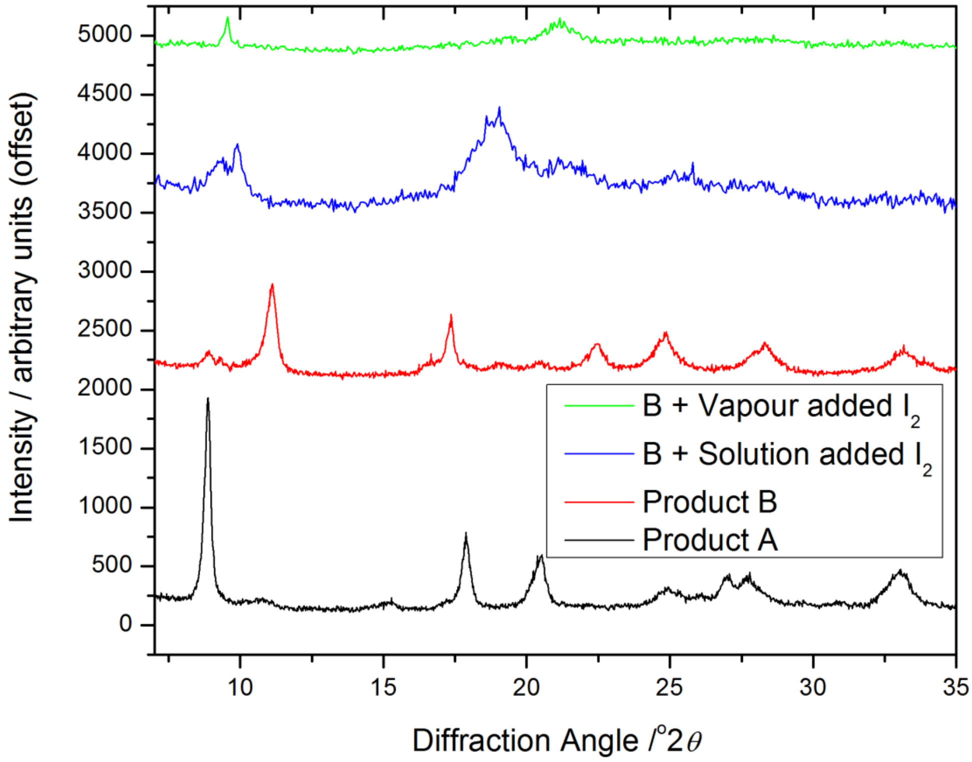

Figure S3: Powder XRD of the materials after iodine addition (Product B + iodine from vapour phase and from chloroform solution) compared to the patterns of Product A and Product B).

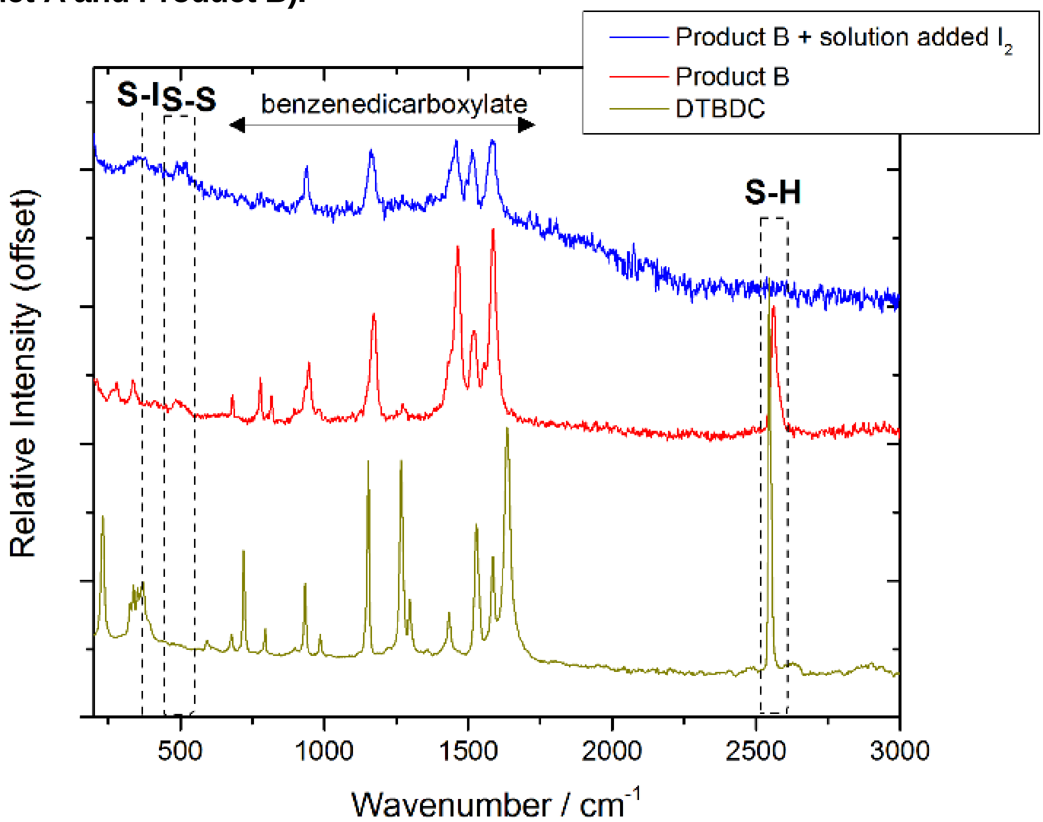

Figure S4: Raman spectra of the linker precursor 2,5-dithiol-1,4-benzenedicarboxylic acid (DTBDC), Product B and Product B after iodine addition from solution.

The Raman band for S-I in sulfenyl iodides[1] is expected at 340 cm^{-1}, while S-S stretches in organic disulfides[2] fall in the region 450 - 550 cm^{-1}. The S-H stretch is expected at ~2550 cm^{-1} as a strong Raman band.[3]

1. K. K. Yee, Y. L. Wong and Z. T. Xu, *Dalton Trans.*, 2016, **45**, 5334-5338.
2. H. E. Van Wart and H. A. Scheraga, *J. Phys. Chem.*, 1976, **80**, 1812-1823.
3. W. Qian and S. Krimm, *Biopolymers*, 1992, **32**, 1503-1518.

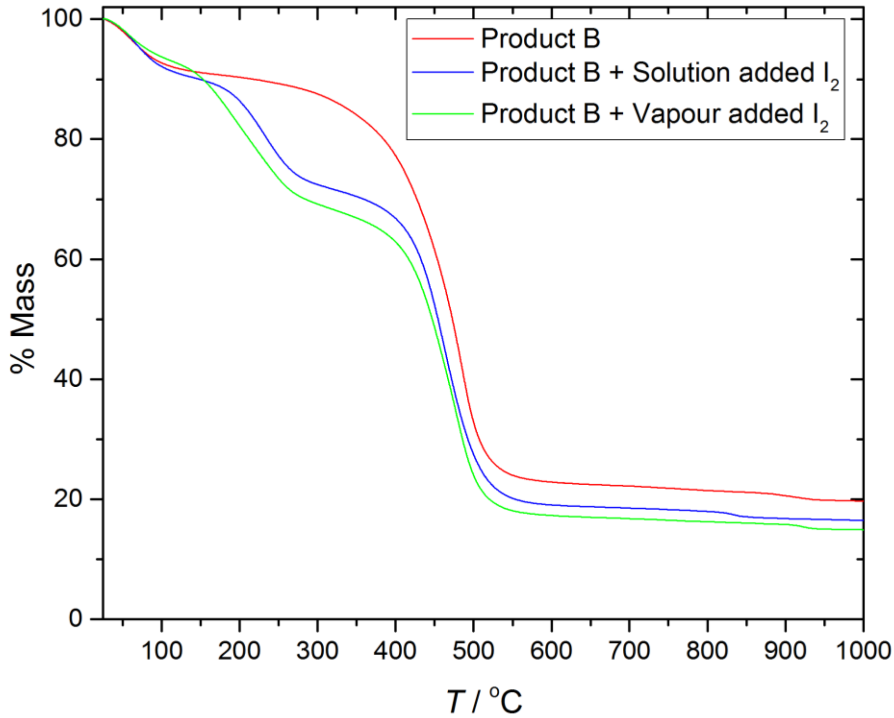

Figure S5: Thermogravimetric analysis (in flowing air 10 °C.min^{-1}) of the two iodine modified materials compared to Product B.

Assignment of the TGA of the two iodine modified materials is complicated by the presence of disulfide, inferred from the S K-edge XANES. Therefore we must assume (1) the same saturation iodine uptake as the assumed iodine content (1 I per 3 S), (2) that all thiol is either converted to sulfenyl iodide or disulfide, and (3) that the materials contain a similar amount of water as Product **B**. Importantly the TGA traces of both iodine modified materials are similar to each other and rather different to Product B, showing an additional mass loss around 200 – 300 °C. If we then further assume this intermediate mass loss is due to loss of iodine, then a reasonable match to the TGA can be obtained as shown in the following tables. The loss of iodine is likely to be accompanied by formation of further S-S bonds to charge balance and collapse of the structure

Table S1: Assignment of TGA of Product B

***T* / °C**	**Assumed Formula**	**% Mass Expected**	**% Mass Observed**
25	$Al[C_8H_2(SH)_2](OH)_2{\cdot}H_2O$	100	100
100	$Al[C_8H_2(SH)_2](OH)_2$	93.6	92.7
1000	½ Al_2O_3	19.7	19.7

Table S2: Assignment of TGA of Product B + Vapour Added I_2.

T / °C	Assumed Formula	% Mass Expected	% Mass Observed
25	$Al[C_8H_2(SI)_{0.67}S_{1.33}](OH)_2 \cdot H_2O$	100	100
100	$Al[C_8H_2(SI)_{0.67}S_{1.33}] (OH)_2$	95.2	93.7
300	$Al[C_8H_2S_2](OH)_2$	72.4	69.2
1000	½ Al_2O_3	13.7	14.9

Table S3: Assignment of TGA of Product B + Solution Added I_2.

T / °C	Assumed Formula	% Mass Expected	% Mass Observed
25	$Al[C_8H_2(SI)_{0.67}S_{1.33}](OH)_2 \cdot H_2O$	100	100
100	$Al[C_8H_2(SI)_{0.67}S_{1.33}](OH)_2 \cdot 0.33I_2$	95.2	92.1
300	$Al[C_8H_2S_2](OH)_2$	72.4	72.5
1000	½ Al_2O_3	13.7	16.5