

Supplementary information

Generation of thiyl radicals in a zinc(II) porous coordination polymer by light-induced post-synthetic deprotection

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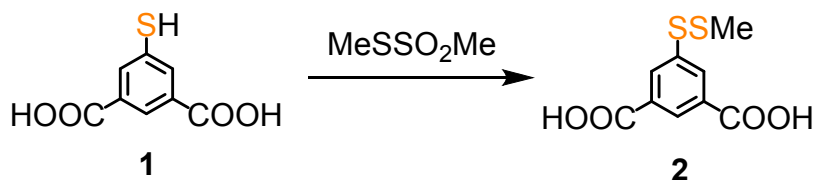
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Materials and methods

All commercially available chemicals were purchased and used as received. NMR spectra were recorded on a JEOL ECA-400 spectrometer. Single-crystal X-ray diffraction (SXRD) measurement were performed on a Rigaku Saturn 724 diffractometer equipped with a Dectris PILATUS 200 K detector, using a VariMax Mo Optic with Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$) and a confocal monochromator. The structure was solved using direct methods and refined by full-matrix least-squares cycles in SHELXL2016.¹ For **SEC-1**, all non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were located at geometrically calculated positions. The guest solvent molecules in the pores were severely disordered and the SQUEEZE command was employed in the refinement. For **SEC-2**, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions except for coordinated DMF molecules, and refined with isotropic thermal parameters. The position of sulfur atoms derived from methylthio protecting group were assigned by Q-peak at the reasonable positions and refined using free-variable. Methyl moieties of methylthio groups were not assigned due to low electron density. The deprotection ratio was calculated from the sum of the occupancies of remaining methylthio groups (Figure S7). Solvent molecules in the pore were severely disordered and were not assigned, and also SQUEEZE command was not employed, thus checkcif alerts "VERY LARGE solvent accessible voids". Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku SmartLab X-ray diffractometer using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) in the 2θ range of 3–40° with a scanning rate of 5° min⁻¹. Both solution and solid state UV-vis absorption spectra were recorded on a JASCO V-670 spectrometer. Adsorption experiment was performed on a Microtrac-BEL BELmax automatic adsorption analyser equipped with a cryostatic temperature controller using 99.9999% CO₂ as an adsorbate. Electron spin resonance (ESR) spectra were recorded on a JEOL JES-X320 spectrometer. The temperature was controlled by a heater under liq. N₂ steam (low temperature) or air flowing (high temperature). Magnetic field was scanned from 310 to 360 mT over 2 min with the modulation width of 0.1 mT, at the constant microwave frequency of 9.095 GHz.

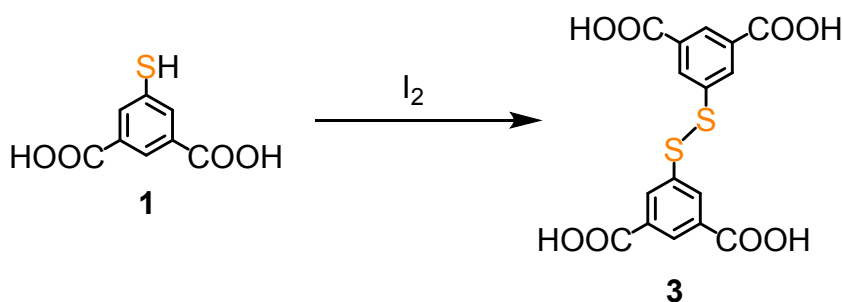
Synthesis of ligand 2



A MeOH (63 mL) solution of 5-mercaptoisophthalic acid² **1** (990 mg, 5.00 mmol) was added S-methylthio methanethiosulfonate (540 mL, 5.00 mmol) and refluxed 14 h under N₂ atmosphere. The reaction mixture was cooled to room temperature and the solvent was evaporated to dryness. The residue was recrystallised with MeOH and H₂O and was vacuum dried to give **2** (1.14 g, 93%).

¹H NMR for **2** (CD₃OD) δ 8.48 (t, *J* = 1.6 Hz, 1H), 8.34 (d, *J* = 1.6 Hz, 2H), 2.49 (s, 3H).

Synthesis of 3



An EtOH (30 mL) solution of **1** (396 mg, 2.00 mmol) was added to an EtOH (40 mL) solution of I₂ (370 mg, 3.00 mmol) which was further refluxed 20 min. After cooling to room temperature, the mixture was added sodium hydrogensulfite (110 mg, 1.06 mmol) and evaporated. The residue was recrystallised with EtOH/H₂O, washed with H₂O and vacuum dried to give **3** (356 mg, 90.3%) as white solids.

¹H NMR for **3** (CD₃OD) δ 8.51 (t, *J* = 1.6 Hz, 1H), 8.34 (d, *J* = 1.6 Hz, 2H).

Synthesis and treatment of SEC-1

A mixture of ligand **2** (24 mg, 9.9 μmol), zinc(II) acetate hydrate (22 mg, 10 μmol) in water (2 mL) and MeOH (2 mL) was heated at 80 °C in a capped glass vial for 2 days. As-synthesized colorless block crystals formed (8.0 mg yield when collected by filtration) were directly used for single-crystal X-ray diffraction (SXRD). The reaction mixture was decanted and the crystals were washed

with DMF for 3 times and stored in DMF for 1 day, which were used for powder X-ray diffraction (PXRD) and photo-irradiation study.

Table S1. Crystallographic parameters for **SEC-1** and **SEC-2**

	SEC-1	SEC-2
Empirical formula	C ₉₂ H ₆₆ O ₅₂ S ₂₀ Zn ₁₂	C ₈₆ H ₃₀ N ₂ O ₅₂ S _{13.97} Zn ₁₂
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2	<i>P</i> 2
<i>a</i> / Å	23.7128(4)	23.5616(11)
<i>b</i> / Å	10.8050(2)	10.8170(4)
<i>c</i> / Å	28.5974(5)	28.5728(9)
α / °	90	90
β / °	90.017(2)	90.096(3)
γ / °	90	90
Volume / Å ³	7327.13	7282.22
<i>Z</i>	2	2
Data/restraints/parameters	33785/3530/1693	27641/3525/1562
Flack parameter	0.065(3)	0.017(7)
Goodness-of-fit on <i>F</i> ²	1.036	1.067
<i>R</i> [<i>I</i> > 2σ (<i>I</i>)]	0.0695	0.1039
<i>wR</i> ² [all data]	0.1988	0.3137

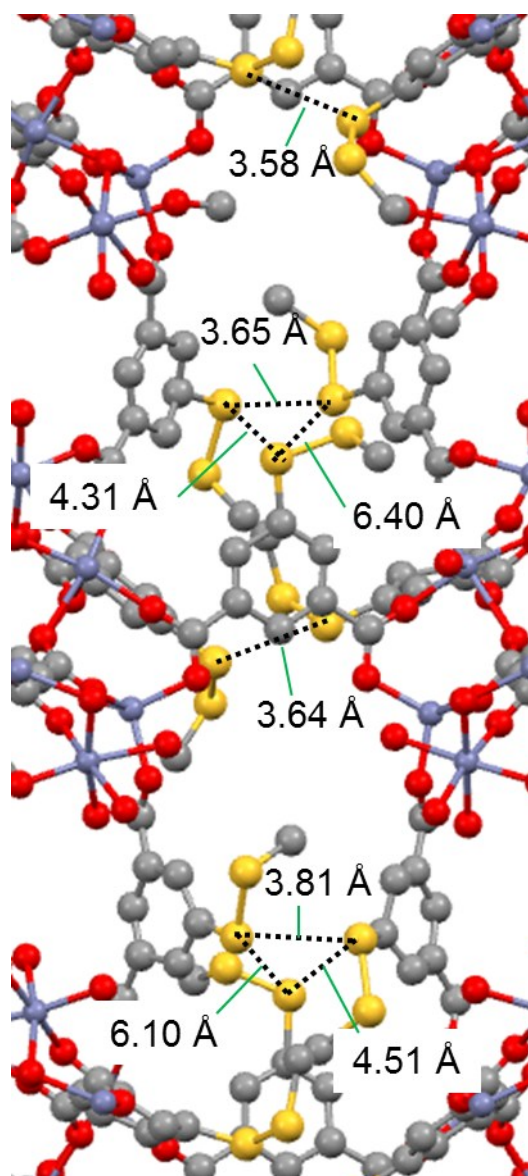


Figure S1. Selected sulfur-sulfur atomic distances in the crystal structure of SEC-1.

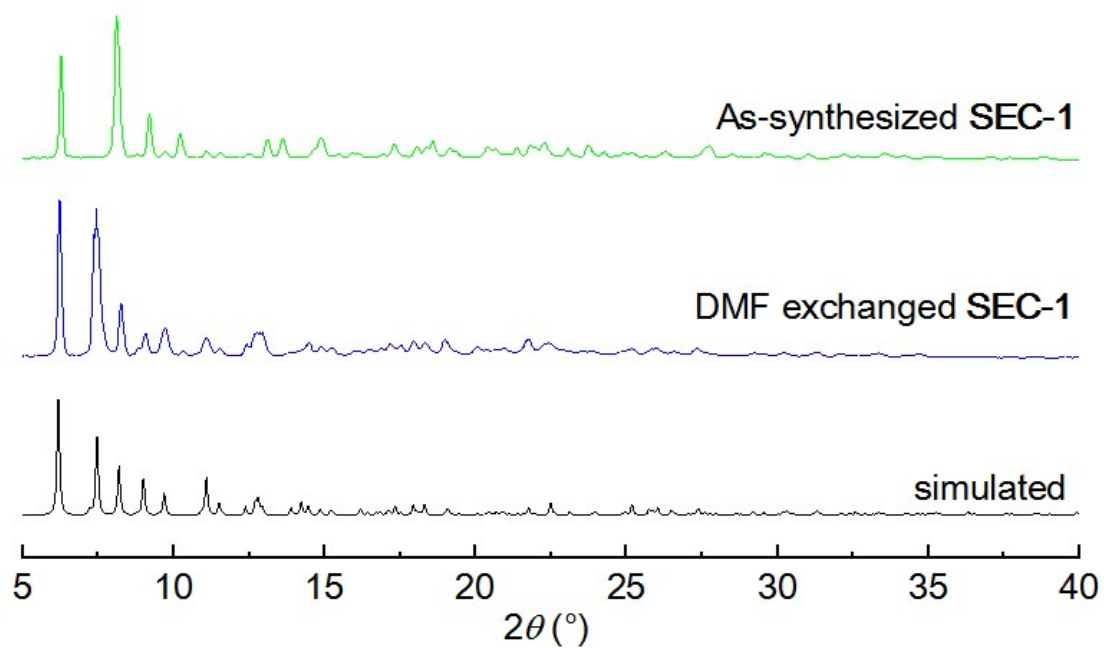


Figure S2. PXRD patterns of SEC-1 (simulated pattern of the as-synthesized sample (black), DMF exchanged sample (blue) and the as-synthesized sample (green)).

Light irradiation

SEC-1 (8 mg) crystals were synthesized by the procedure above, which were immersed in DMF (3 mL) for 1 day to exchange crystal solvent. The supernatant was removed by decantation and the crystals were dispersed in fresh DMF (3 mL) in quartz fluorescence cell. The solvent was degassed by N₂ bubbling for 20 minutes, and the cell was capped and irradiated by UV-light (HITACHI FL8BL-B black light, $\lambda = 350$ nm, total UV emission power of $0.80 \text{ W} \times 10 = 8 \text{ W}$) for 2 days inside a stainless box ($30 \times 30 \times 20 \text{ cm}^3$) equipped with an exhaust fan. After irradiation, the supernatant was removed by decantation and crystals were immersed in DMF for 1 day. The crystals were analysed by ¹H NMR or SXR D after collection. ¹H NMR sample was prepared by immersing the ~5 mg of crystals in CD₃OD and added one drop of 35% DCl in D₂O, which was sonicated until no solid precipitates were visible. The product yields were determined as **1** (29%) and **3** (22%) from the integral of peaks corresponding to isophthalic acids, assuming that the solution contains only **1**, **2** and **3**.

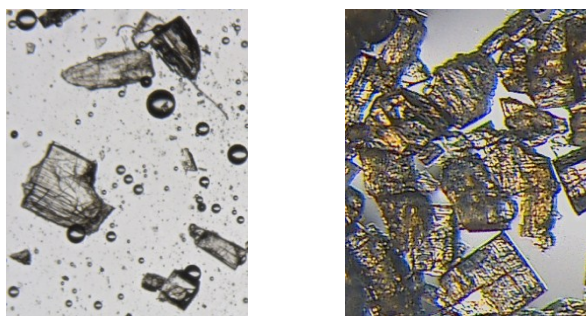


Figure S3. Optical microscopic images for **SEC-1** (left) and **SEC-2** (right).

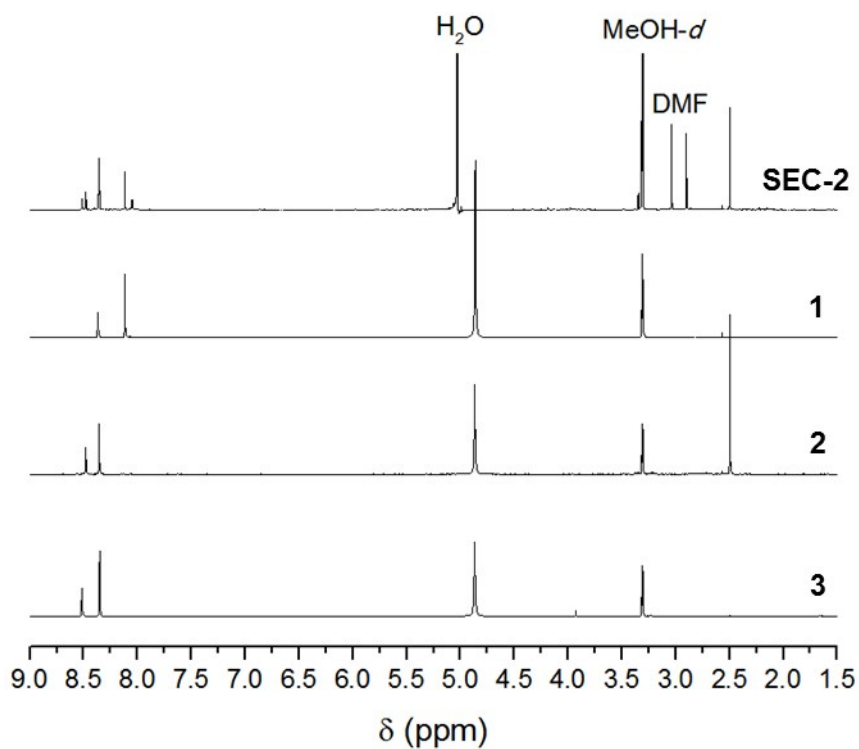


Figure S4. ^1H NMR spectra for SEC-2, 1, 2, 3 in DCI/CD₃OD.

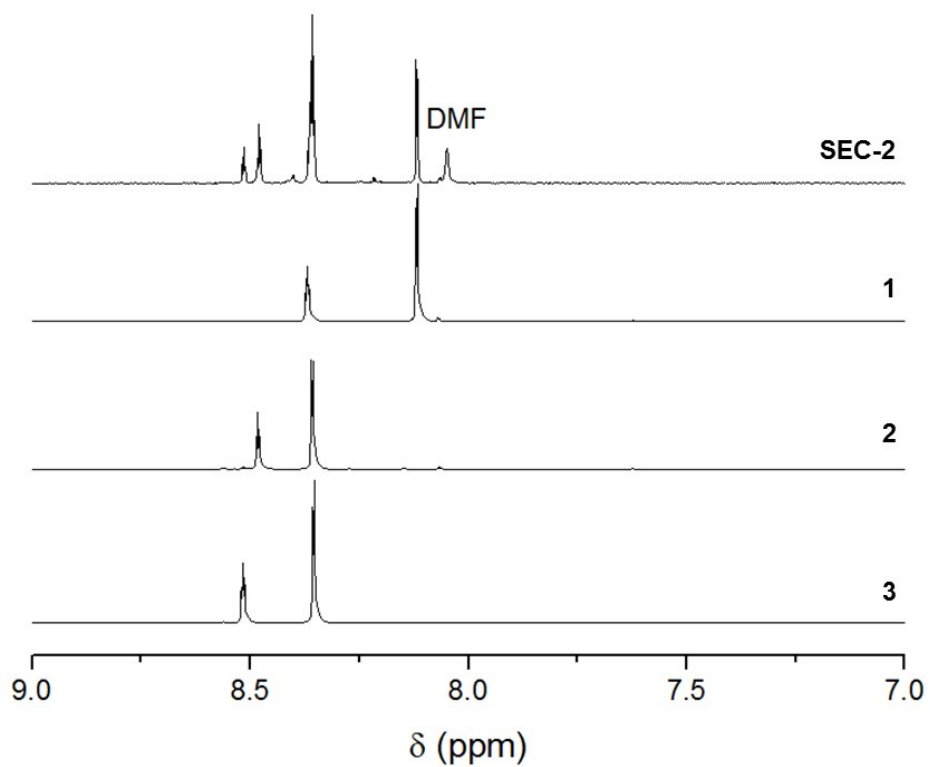


Figure S5. Zoom-up ^1H NMR spectra for SEC-2, 1, 2, 3 around aromatic region

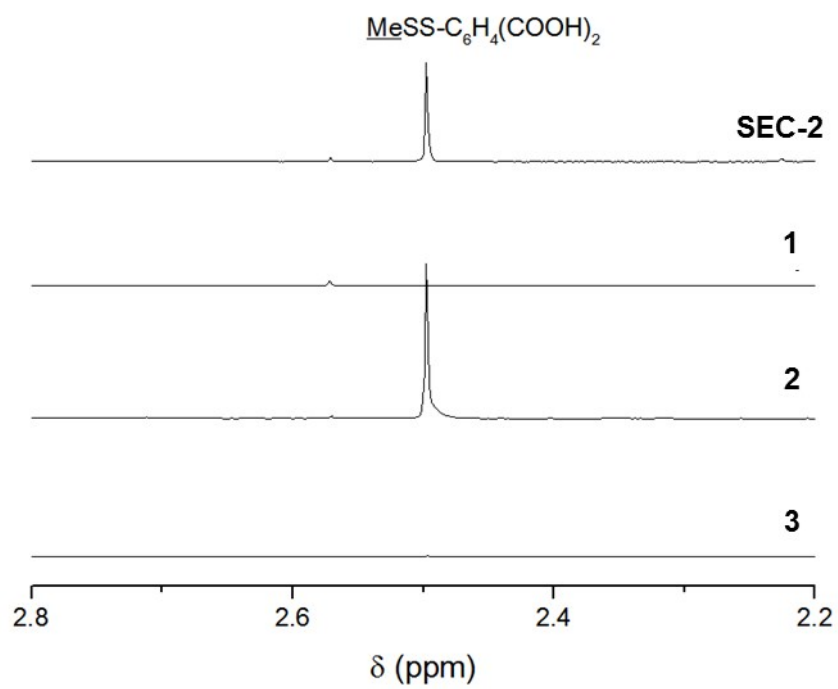


Figure S6. Zoom-up ^1H NMR spectra for SEC-2, 1, 2, 3 around aliphatic region

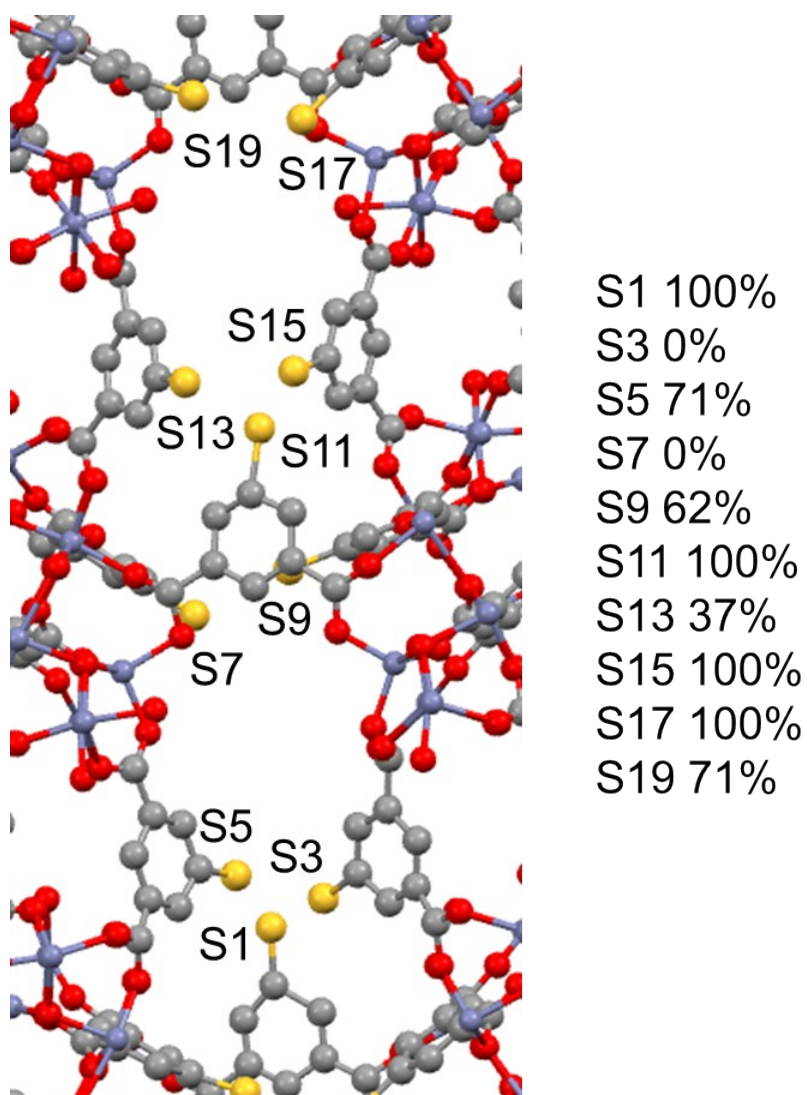


Figure S7. Crystallographically estimated position dependent deprotection ratio of disulfides in **SEC-2**. 100% means that there is no high Q-peak at around sulfur atoms and thus no additional sulfur atoms were assigned in the structural analysis. In **SEC-1**, S1, S3, S5, S7 and S9 are almost equivalent to S11, S13, S15, S17 and S19 respectively, while deprotection ratio in S1-S9 are lower than S11-S19. This is due to asymmetric shrinkage of the pore, and the former is narrower (e.g., atomic distance of S3-S5 is 3.45 Å, while that of S13 and S15 is 3.85 Å) so that diffusion elimination of the protecting group is suppressed and exhibits lower deprotection ratio.

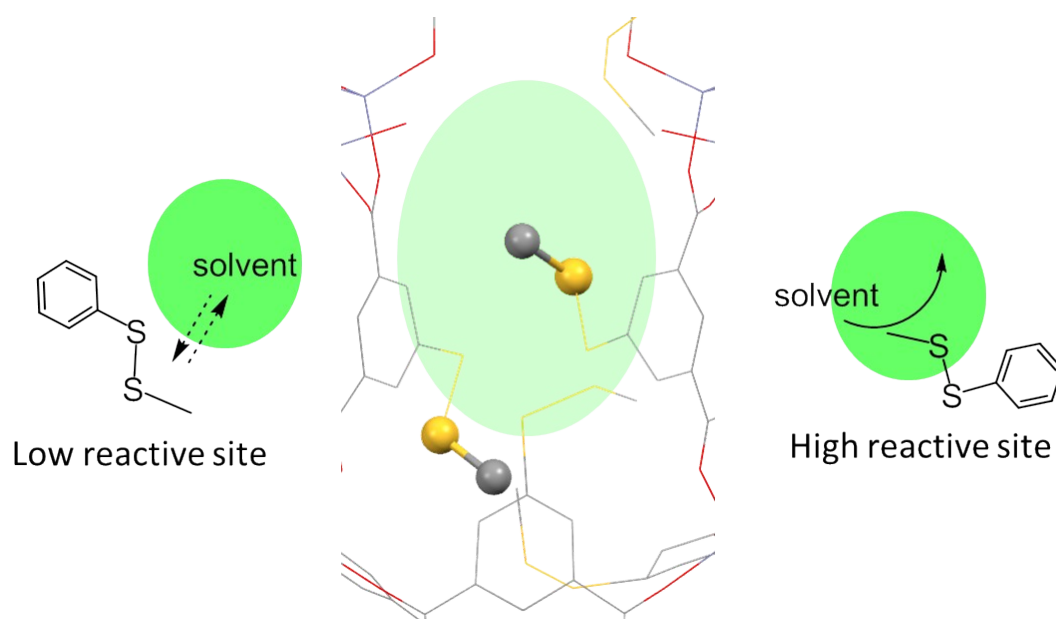


Figure S8. Plausible schematic representation of the relationship between reactivity of disulfides and orientation of disulfide bonds around the pore at low reactive (e.g. S3 and S13) and high reactive sites (e.g. S5 and S15).

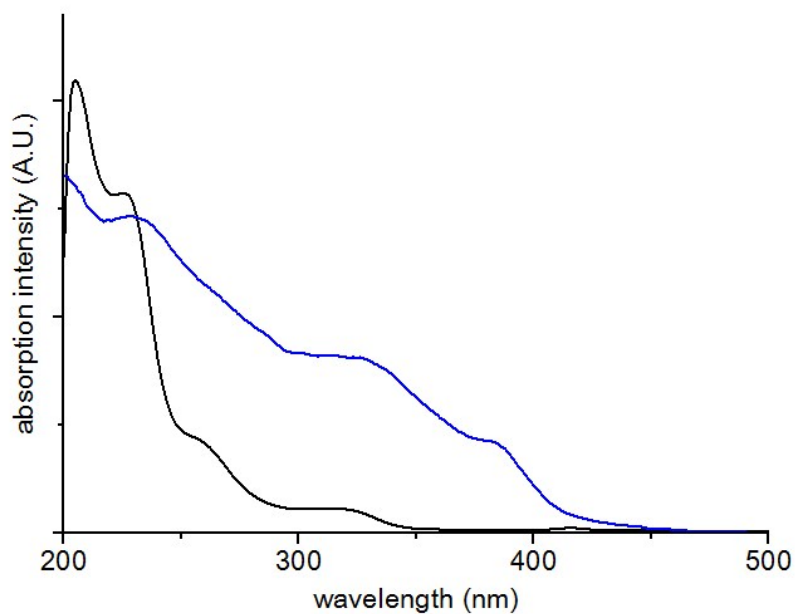


Figure S9. UV-vis absorption spectra for ligand **2** in MeOH solution (black) and SEC-1 powders diluted with BaSO₄ (blue).

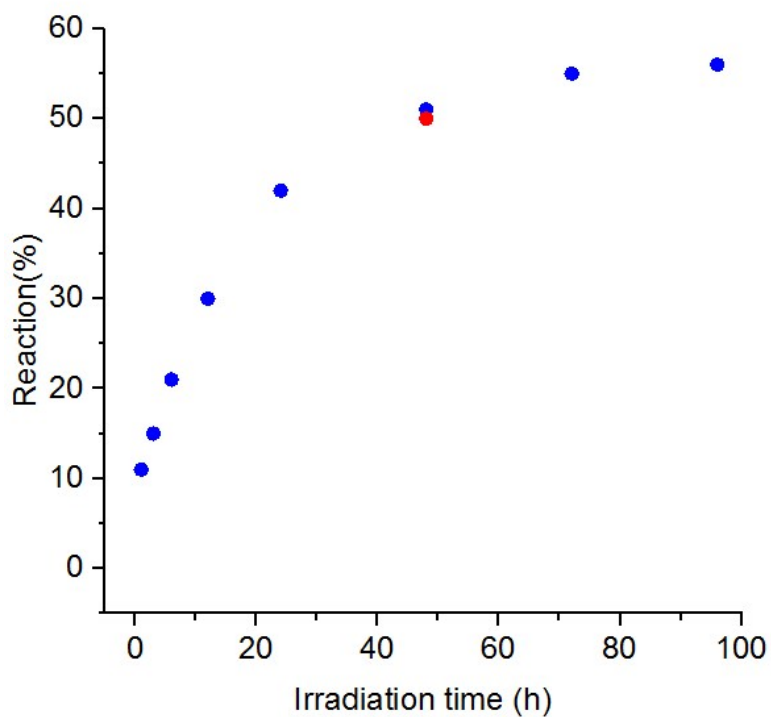


Figure S10. Time-course conversion transition for deprotection of **SEC-1**. Light irradiation experiments were performed as above by changing the irradiation time. Blue markers indicate the reaction completion determined using the integral of the peaks of **1**, **2** and **3** in ^1H NMR of UV-irradiated **SEC-1** in DMF. Red marker indicates the completion of the deprotection reaction **SEC-1** ground in DMF suspension.

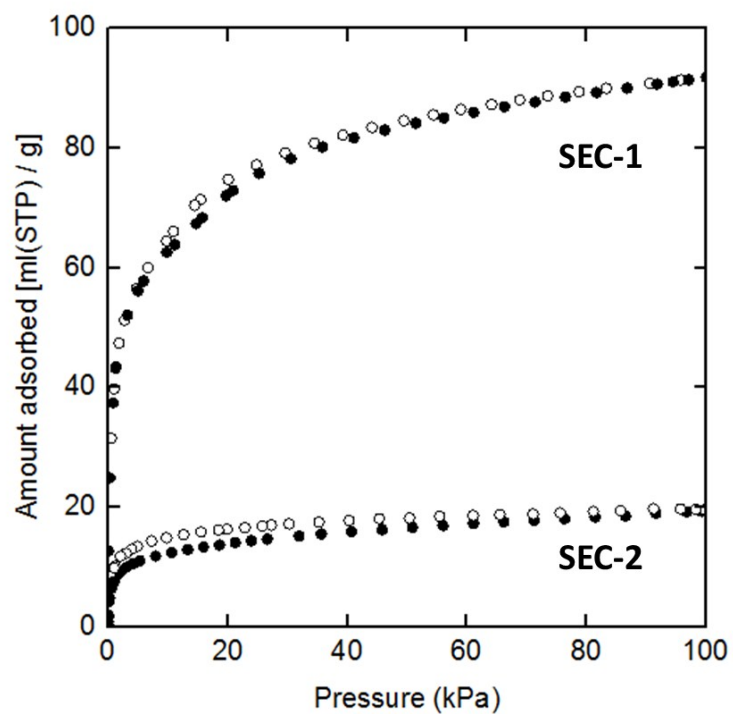


Figure S11. CO₂ adsorption isotherms (195 K) of SEC-1 and SEC-2. Both samples were soaked in methanol for 1 day and activated by vacuum heating at 100 °C for 16 h prior to the adsorption experiment.

ESR study

As-synthesized **SEC-1** crystals were washed with MeOH and placed in a quartz ESR sample tube connected with a vacuum pump. The sample was activated at 80 °C under dynamic vacuum for 4 h. The sample was then cooled to 95 K, and the ESR spectrum showed no signal (Figure S8, black line). Then, the ESR spectra were recorded under UV light irradiation using a high-pressure mercury lamp (Figure S8, blue line). Irradiation was stopped after 1 h and the sample was recovered to room temperature then ESR was measured (Figure S8, red line). We also note that no ESR signal could be observed by irradiation of UV light at room temperature, indicating that thiyl radicals were thermally unstable and recombined very fast.

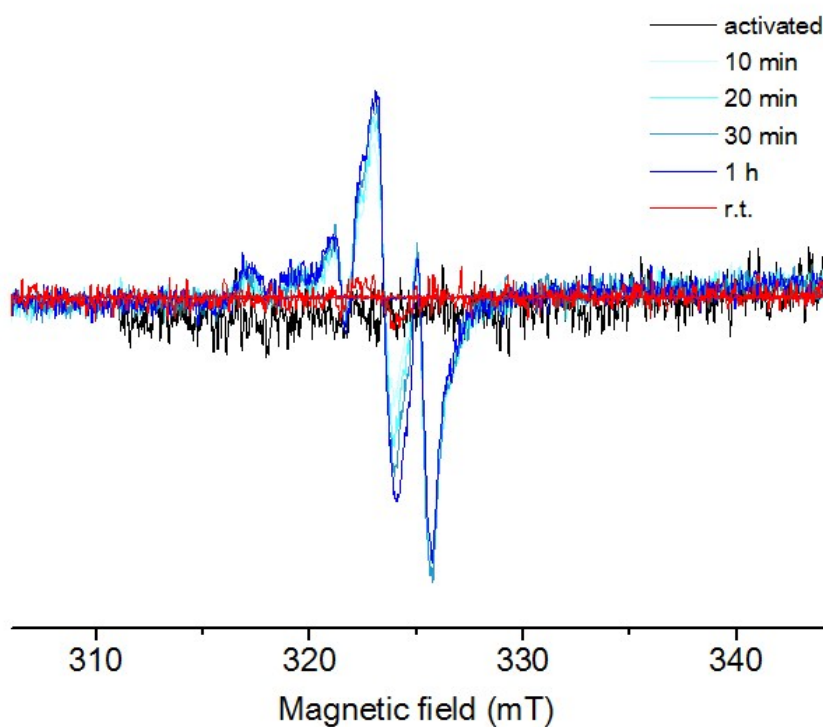


Figure S12. The ESR spectra for **SEC-1** under irradiation of UV light at 95 K and that after returned to room temperature under dark.

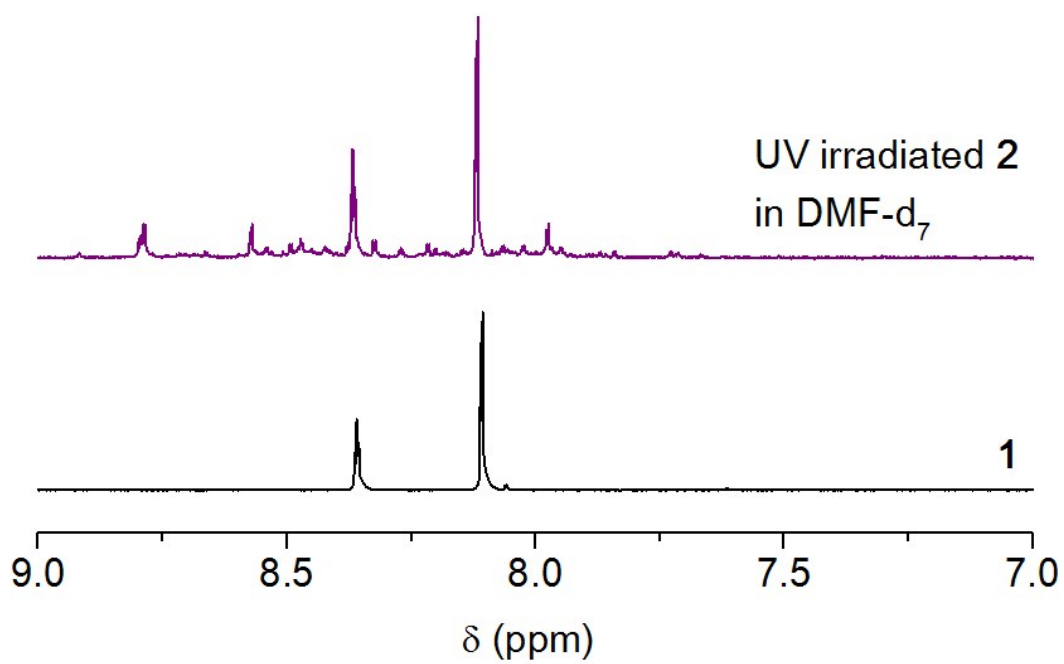


Figure S13. ¹H NMR spectra for disulfide **2** irradiated by UV-light in solution (purple) and thiol **1** (black)

References

1. G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3.
2. A. Dahan, A. Weiss and M. Portnoy, *Chem. Commun.* 2003, 1206-1207.