

Bio-inspired stabilization of sulfenyl iodide RS-I in a Zr(IV)-based metal-organic framework

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Supporting Information



Figure S1. Photographs of (a) an as-made sample of ZrDMBD; (b) an I₂-treated sample ZrDMBD-I₂; and (c) sample b treated with 1,2-ethanedithiol (EDT), i.e., the regenerated sample ZrDMBD-2.

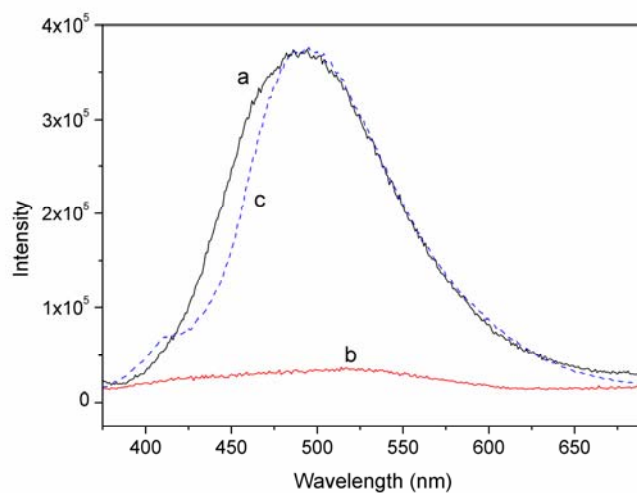


Figure S2. Room-temperature solid-state emission spectra from (a) an as-made ZrDMBD solid; (b) an I_2 -treated sample ZrDMBD- I_2 ; (c) sample b treated with EDT, i.e., the regenerated sample ZrDMBD-2 (excitation wavelength $\lambda_{\text{ex}} = 365$ nm).

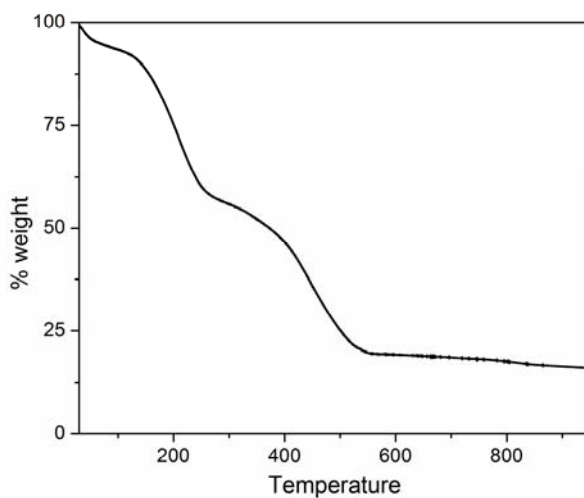


Figure S3. A thermogravimetric analysis (TGA) plot of a ZrDMBD- I_2 sample. Heating rate: 2 °C/min.

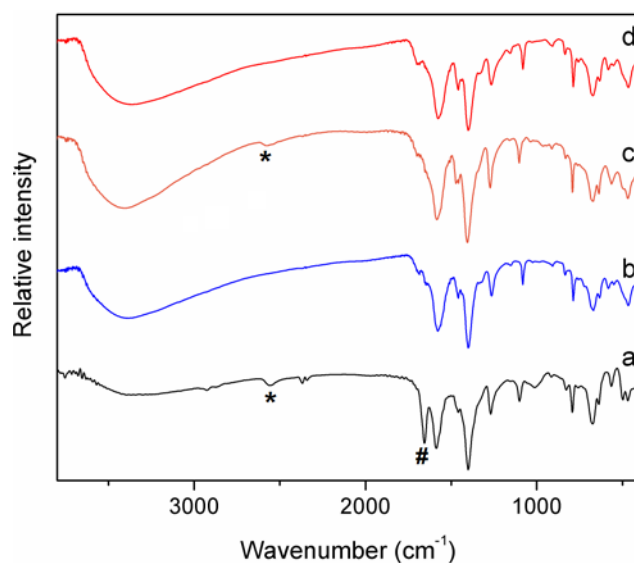


Figure S4. The IR spectra of (a) an as-made ZrDMBD solid; (b) an I₂-treated sample ZrDMBD-I₂; (c) sample b treated with EDT, i.e., the regenerated sample ZrDMBD-2; (d) sample c after being treated by I₂, i.e., the ZrDMBD-I₂-2 sample. The S-H stretching peaks (a and c) at 2560 cm⁻¹ are asterisked. The peak at 1680 cm⁻¹ in spectrum a (marked by #) is due to DMF—this peak consequently weakens in spectra b-d.

KI starch paper test for I₂ release. As shown in panel a of Figure S5, no color change was observed for the wet KI starch test paper placed over the Zr-DMBD-I₂ powder sample even after 20 hrs at room temperature, indicating minimal emission of I₂ species from the MOF-I₂ composite. (Zr-DMBD-I₂ therefore is found to be a suitable form of immobilizing I₂ at room temperature). We further heat the sample to 90 °C for 5 hours (at 1 atm), the color of KI starch test paper remain unchanged. Iodine molecules started to depart the solid matrix at 130 °C to cause the distinctive blue color on the test paper, as is seen in panel b of Figure S5.

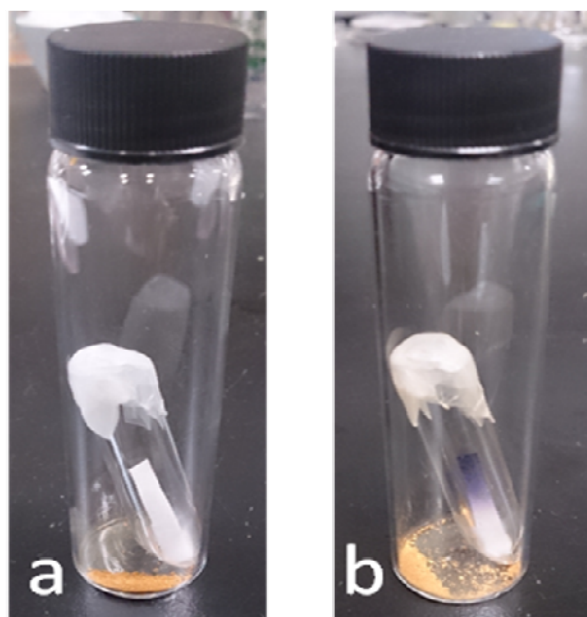
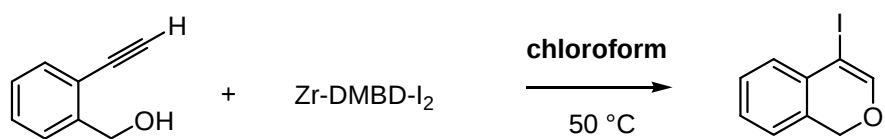


Figure S5. Photographs of the setup for testing I₂ emission from the ZrDMBD-I₂ solid. A powder sample of ZrDMBD-I₂ was placed in a capped vial; also placed in the vial is a strip of moist KI-starch test paper contained in a small glass cup that is loosely covered by paraffin film. (a) The setup after being left at room temperature for 20 hours; (b) after being heated at 130 °C for 10 min.

Cyclization of 2-ethynylbenzyl alcohol by Zr-DMBD-I₂ solid.



A powder sample of Zr-DMBD-I₂ (32 mg, equivalent to about 13 mg or 0.10 mmol of iodine), 2-ethynylbenzyl alcohol (5.0 mg, 0.038 mmol) and CDCl₃ (1.0 mL) were placed in a 7.5-ml glass vial. After being stirred at 50 °C for 12 hours, the suspension was centrifuged and the solution was collected for NMR analysis. The NMR spectrum shows that the conversion of 2-ethynylbenzyl alcohol to 4-iodo-1H-isochromene was over 93 %. ¹H NMR (CDCl₃, 400 MHz): δ = 7.56-7.54 (d, 1H), 7.43-7.39 (m, 1H), 7.36-7.32 (m, 1H), 7.31 (s, 1H), 7.14-7.12 (m, 1 H);

