## 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  $I_2$ -treated sample ZrDMBD- $I_2$ ; 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<sub>2</sub>-treated sample ZrDMBD-I<sub>2</sub>; (c) sample b treated with EDT, i.e., the regenerated sample ZrDMBD-2 (excitation wavelength  $\lambda_{ex} = 365$  nm).



**Figure S3.** A thermogravimetric analysis (TGA) plot of a ZrDMBD-I<sub>2</sub> sample. Heating rate: 2 °C/min.



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

**KI starch paper test for I**<sub>2</sub> **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-I<sub>2</sub> powder sample even after 20 hrs at room temperature, indicating minimal emission of I<sub>2</sub> species from the MOF-I<sub>2</sub> composite. (Zr-DMBD-I<sub>2</sub> therefore is found to be a suitable form of immobilizing I<sub>2</sub> 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  $I_2$  emission from the ZrDMBD- $I_2$  solid. A powder sample of ZrDMBD- $I_2$  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-I<sub>2</sub> solid.



A powder sample of Zr-DMBD-I<sub>2</sub> (32 mg, equivalent to about 13 mg or 0.10 mmol of iodine), 2-ethynylbenzyl alcohol (5.0 mg, 0.038 mmol) and CDCl<sub>3</sub> (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 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.56-7.54$  (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,);

4.71-4.60 (m, 2H) ppm. The solid color changed from orange brown to light yellow after the reaction was thus conducted.



**Figure S6.** The <sup>1</sup>H NMR spectrum of a CDCl<sub>3</sub> solution of 2-ethynylbenzyl alcohol being treated with a Zr-DMBD-I<sub>2</sub> (for the iodocyclization to form 4-iodo-1H-isochromene). The reaction scheme is also included, with the assignment of the NMR peaks. The integration indicates over 93% of the 2-ethynylbenzyl alcohol reactant has been converted into 4-iodo-1H-isochromene.

**Regeneration of the catalyst solid: re-loading of I<sub>2</sub>.** The Zr(IV)-based MOF solid (13 mg) after being used in the above catalytic reaction was placed in a 8-mL glass vial, to which ethane-1,2-dithiol (1 % w/w in CHCl<sub>3</sub>, 15 mL) was then added. After the mixture was stirred at 70°C for 12 hours, the solid was then collected by centrifugation and washed with chloroform (1.5 mL x 3). The resultant thiol-regenerated solid sample (ZrDMBD-2) was then placed in a chloroform solution of I<sub>2</sub> (0.75% w/w, 15 mL) to re-enter I<sub>2</sub> into the solid. The I<sub>2</sub>-reloaded sample (orange brown) was then used to repeat the above reaction (with similar conversion rate observed).