Supplementary Material (ESI) for Chemical Communications

Supporting Information

Aerobic oxidation of thiols to disulfides using iron metal organic frameworks as solid redox catalyst

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Experimental

General procedures

All reagents, starting materials and MOFs were obtained commercially from Aldrich (see Table S1) and used without any further purification unless otherwise noted. Fe(BTC) was characterized by chemical analysis, isothermal gas adsorption, IR, EPR and XRD. The percentage conversion, purity and relative yields of the final products were determined using Hewlett Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by GC–MS using a Hewlett Packard 6890 series spectrometer. Powder XRD patterns of fresh and reused Fe(BTC) were recorded in a Philips X'Pert diffractometer using the CuK_α radiation at a scan rate of 0.2 ^{o} min^{-1}. ESR spectra were recorded using a Bruker EMX, with the following settings: frequency 9.476 GHz, sweep width 6900 G, modulation frequency 100 kHz, modulation width 1 G, microwave power 19.93 mW.

Typical procedure for aerobic oxidation of thiophenol

To a stirred solution of 2.27 mmol of thiophenol in 4 mL of acetonitrile, 100 mg of Fe(BTC) was charged and the temperature was raised to 70^{o}C. To this heterogeneous reaction mixture, oxygen was purged through balloon and the reaction continued for the required time (1-2 h). After completion of reaction, the reaction mixture was filtered and the solid catalyst was washed three times with acetonitrile (3 mL) to extract thoroughly the adsorbed disulfide. The combined organic solutions (pale yellow) were injected in GC to check the purity of the products. Typically diphenyldisulfide and the other aromatic disulfides were isolated as white solids in high purity by simple evaporation of the solvent without any further chromatographic purification. The mass balances of the recovered reaction mixture accounted for more than 95 % of the initial substrate as confirmed by GC using nitrobenzene as internal standard. The products were analyzed by GC and characterized by GC–MS. The yields of the product were determined using nitrobenzene as internal standard considering the response factors unity. Similar procedure was followed for other catalyst $Fe(NO_3)_2.9H_2O$ maintaining the same iron to substrate ratio as for the experiments using Fe(BTC) as catalyst.

Experimental procedure for reusability tests

The reusability of Fe(BTC) was tested for the aerobic oxidation of thiophenol. At the end of the reaction, the solid catalyst was allowed to settle completely and the supernatant liquid was filtered. The catalysts were thoroughly washed with acetonitrile to extract almost completerly the disulfide before the next run. The recovered catalyst was dried, then reused without further purification for the second run with fresh thiophenol.

Table S1. BET surface area and catalog code of the three MOFs used in the present work (data supplied by Aldrich).

MOF	BET surface area m^2/g	Aldrich product No.
Fe(BTC)	1300-1600	690872
$Cu_3(BTC)_2$	1500-2100	688614
$Al_2(BDC)_3$	1100-1500	688738

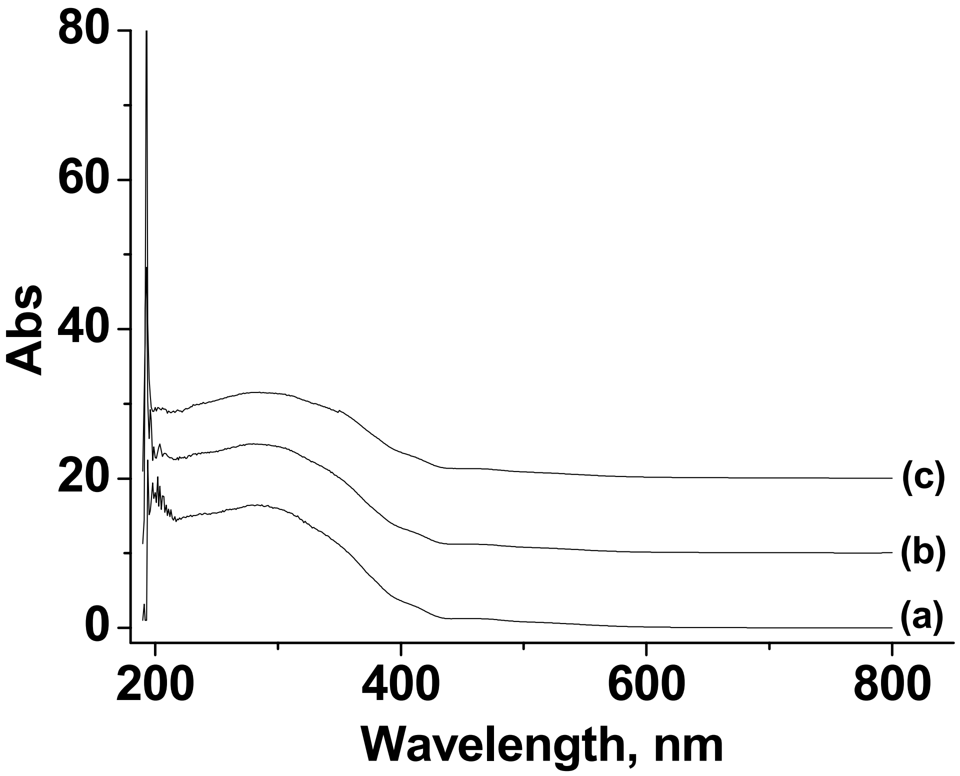

Figure S1. Diffuse reflectance spectra of (a) Fe(BTC), Fe(BTC) (100 mg) stirred with thiophenol (250 mg) at 70 °C for 5 min (b) and 60 min (c).

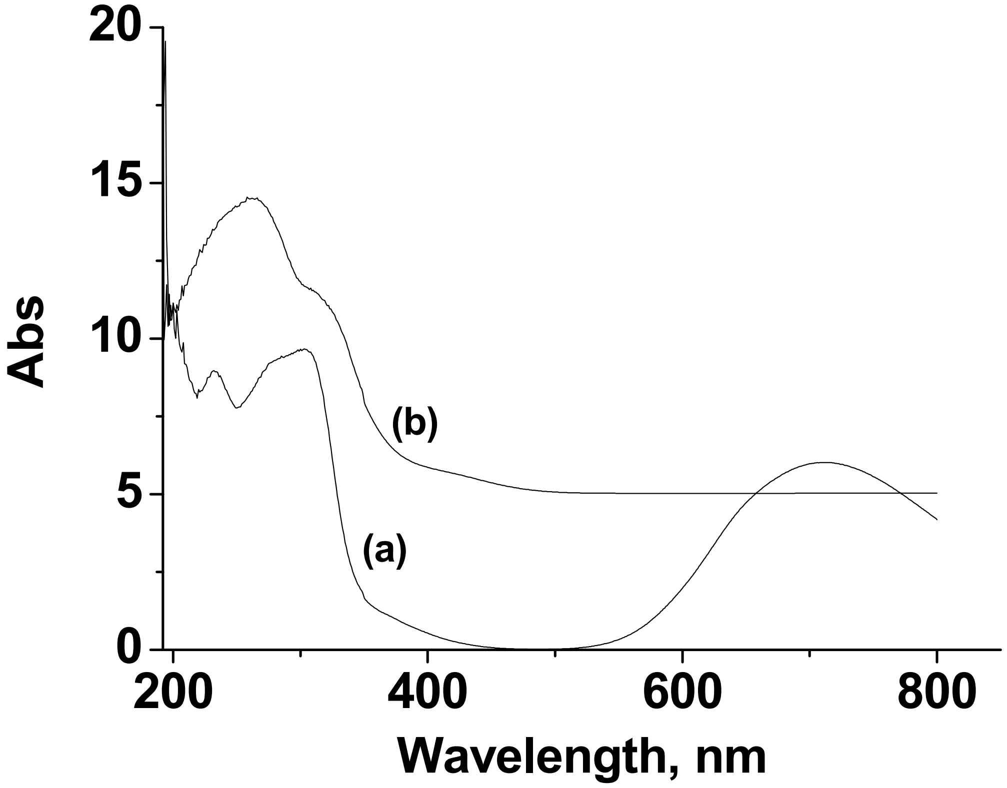

Figure S2. Diffuse reflectance spectra of (a) fresh $Cu_3(BTC)_2$, (b) $Cu_3(BTC)_2$ (100 mg) stirred with thiophenol (250 mg) at 70 °C for 60 min. Notice the disappearance of the typical Cu^{2+} visible band after heating with thiophenol.

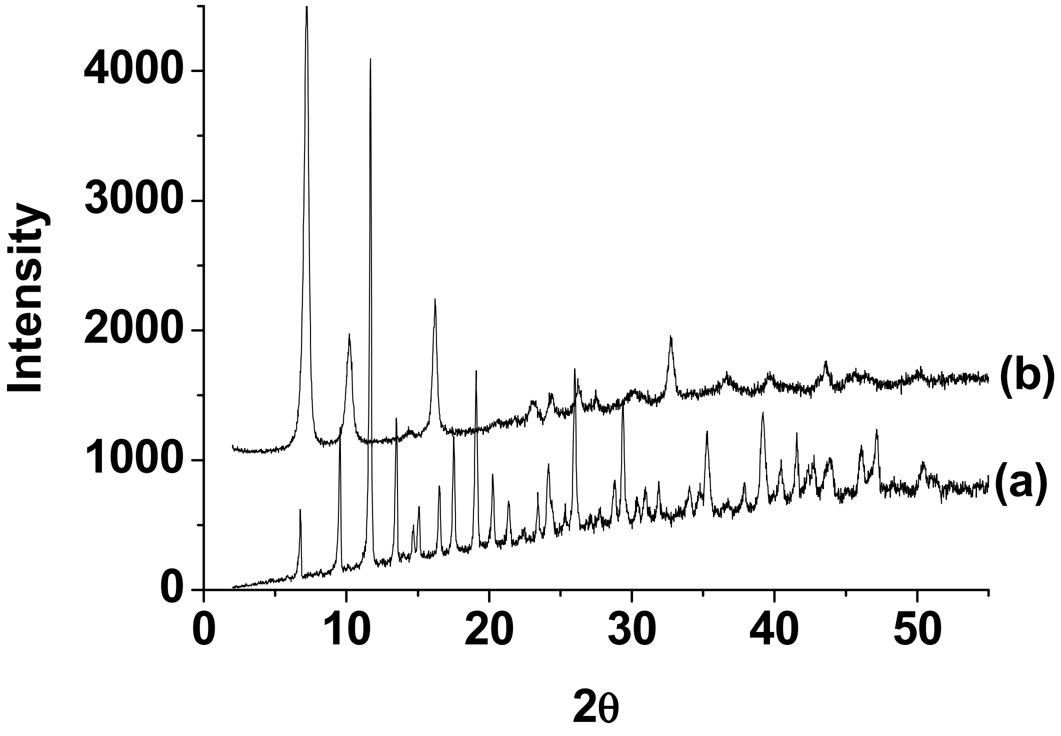

Figure S3. Powder XRD of $Cu_3(BTC)_2$ (a) fresh and (b) after reaction with thiophenol. Reaction conditions: Thiophenol (0.250 mL), $Cu_3(BTC)_2$ (100 mg), 70 °C, acetonitrile (4 mL), 1 h.

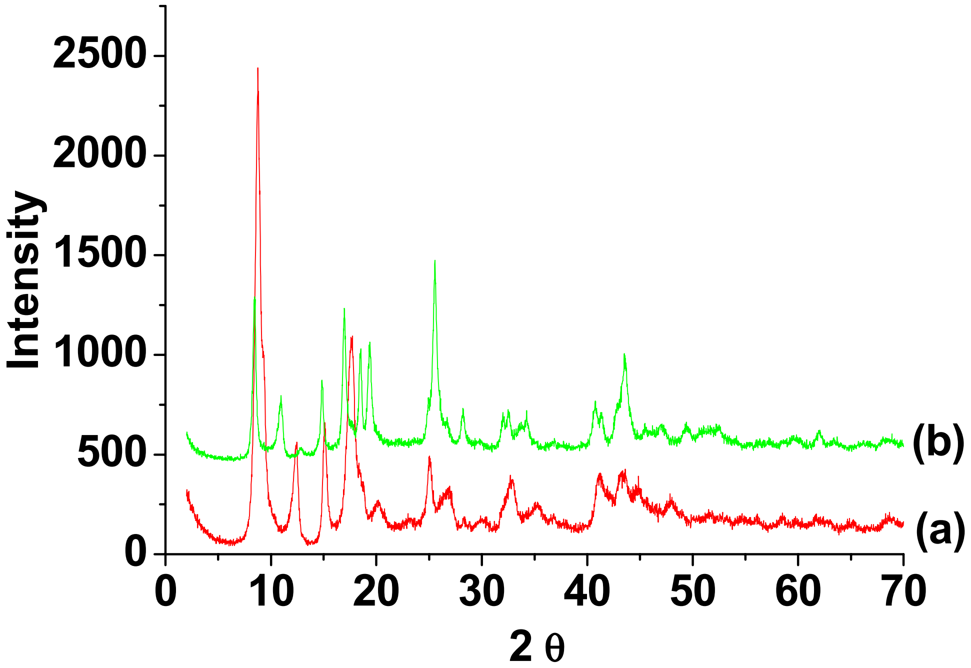

Figure S4. Powder XRD of $Al_2(BDC)_3$ (a) fresh and (b) after reaction with thiophenol. Reaction conditions: Thiophenol (0.250 mL), $Al_2(BDC)_3$ (100 mg), 70 °C, acetonitrile (4 mL), 1 h.

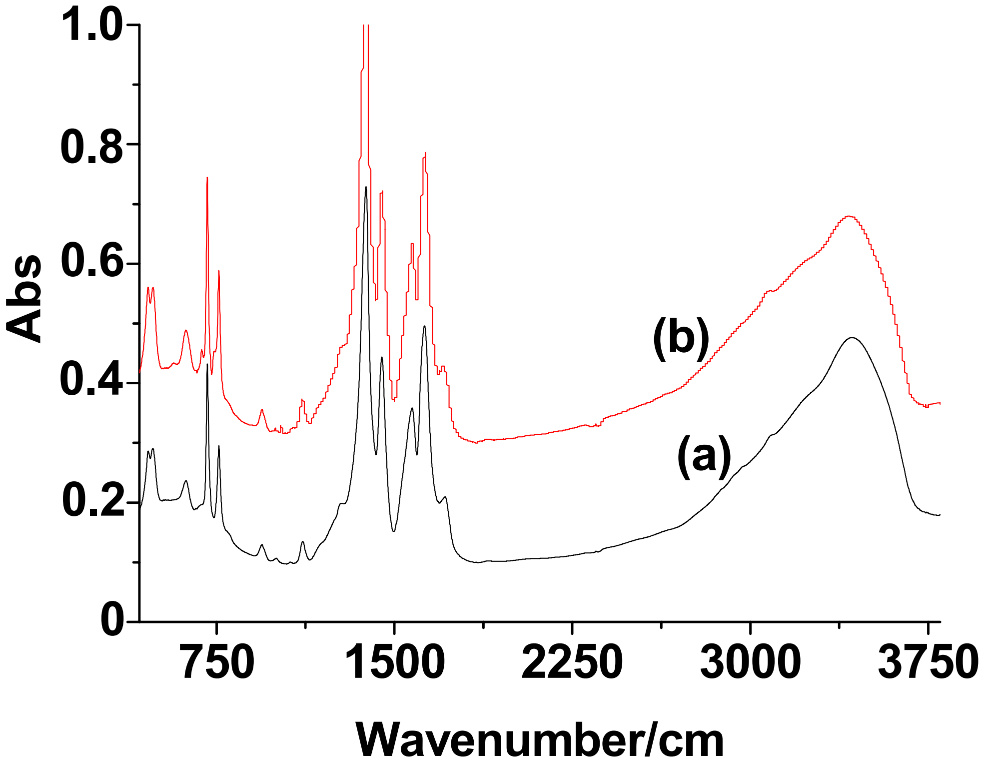

Figure S5. FT-IR spectra of Fe(BTC) (a) fresh and (b) two times used. Reaction conditions: Thiophenol (0.250 mL), Fe(BTC) (100 mg), 70 ^{o}C, acetonitrile (4 mL), 1 h.

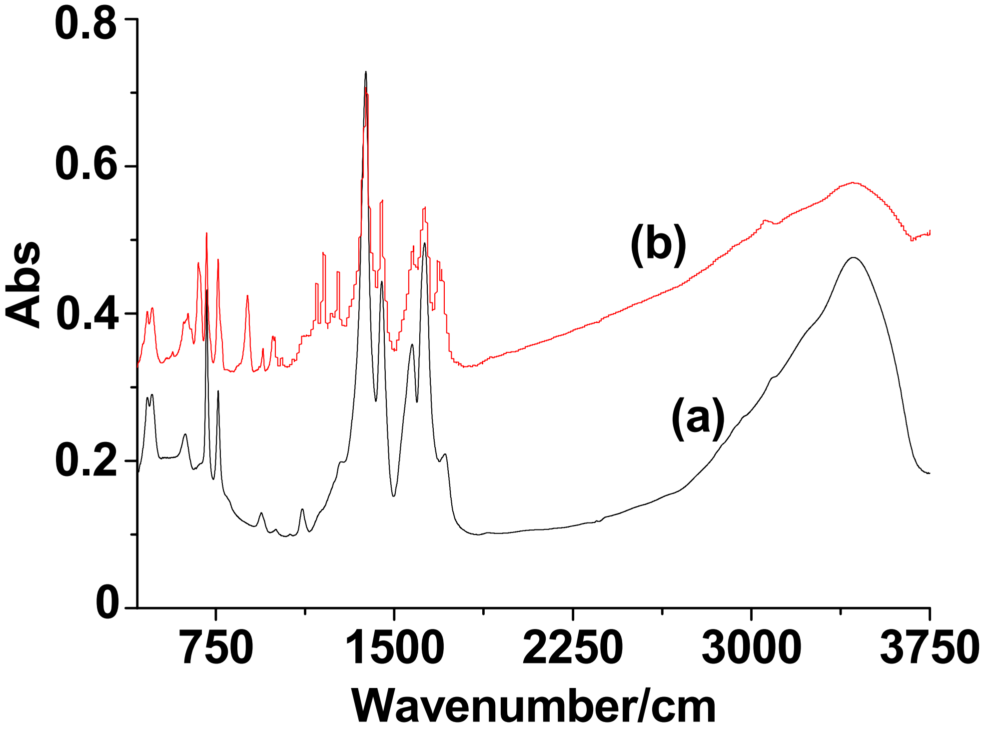

Figure S6. FT-IR spectra of Fe(BTC) (a) fresh and (b) after reaction with thiobenzoic acid. Reaction conditions: Thiobenzoic acid (0.250 mL), Fe(BTC) (100 mg), 70°C, acetonitrile (4 mL), 1 h. Notice the remarkable changes particularly in the aromatic region (1600-1350 cm^{-1}) of the solid after being used in the reaction with thiobenzoic acid.

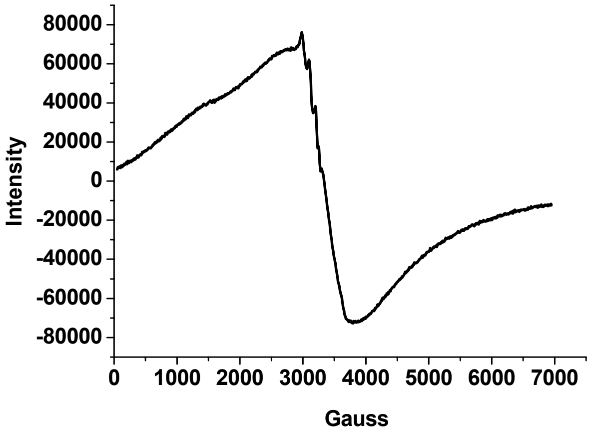

Figure S 7. EPR spectrum recorded for Fe(BTC) in solid state at room temperature.

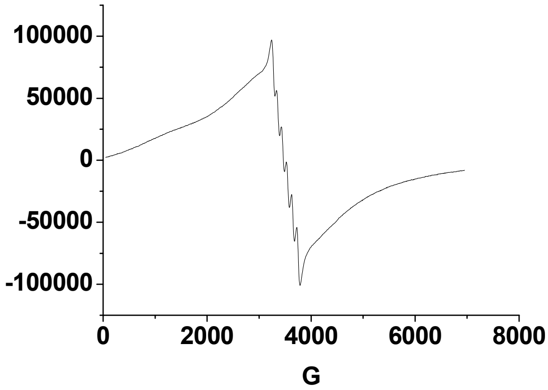

Figure S 8. Room-temperature EPR spectrum of a solid Fe(BTC) sample that was used twice as catalyst for the oxidation of thiophenol.

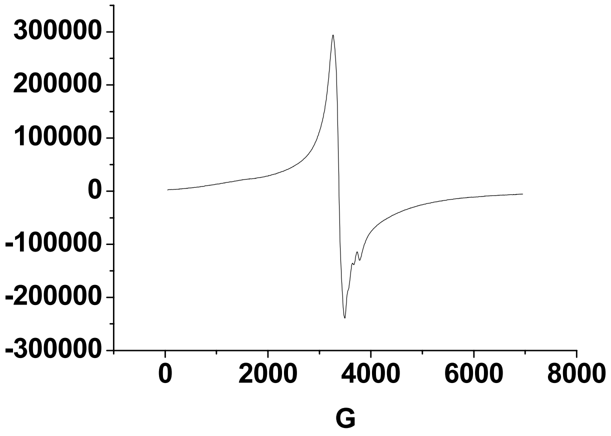

Figure S 9. Room-temperature EPR spectrum of a Fe(BTC) sample used for the oxidation of thiobenzoic.

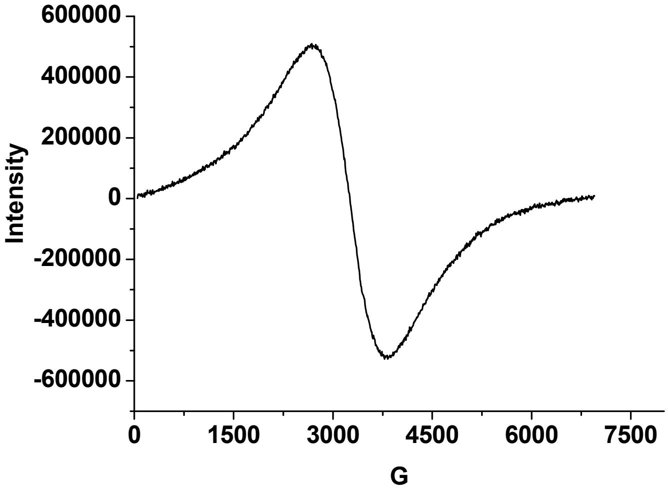

Figure S10. EPR spectrum of fresh $Cu_3(BTC)_2$.

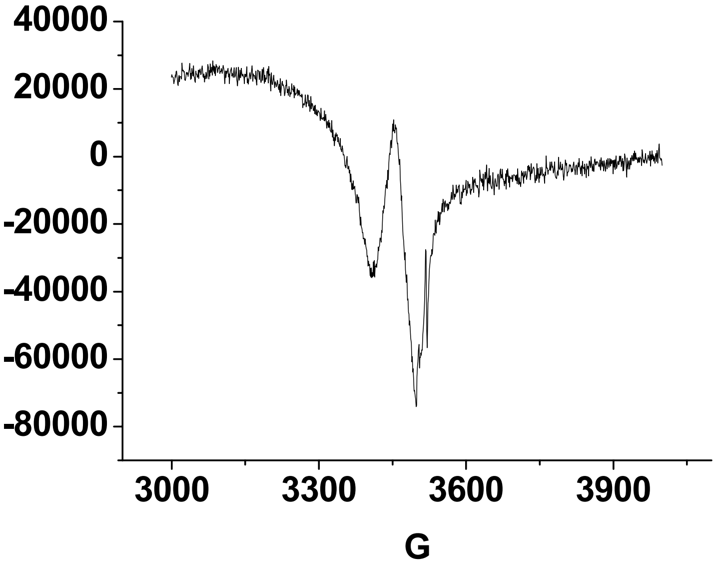

Figure S11. EPR spectrum of $Cu_3(BTC)_2$ after reaction with thiophenol.

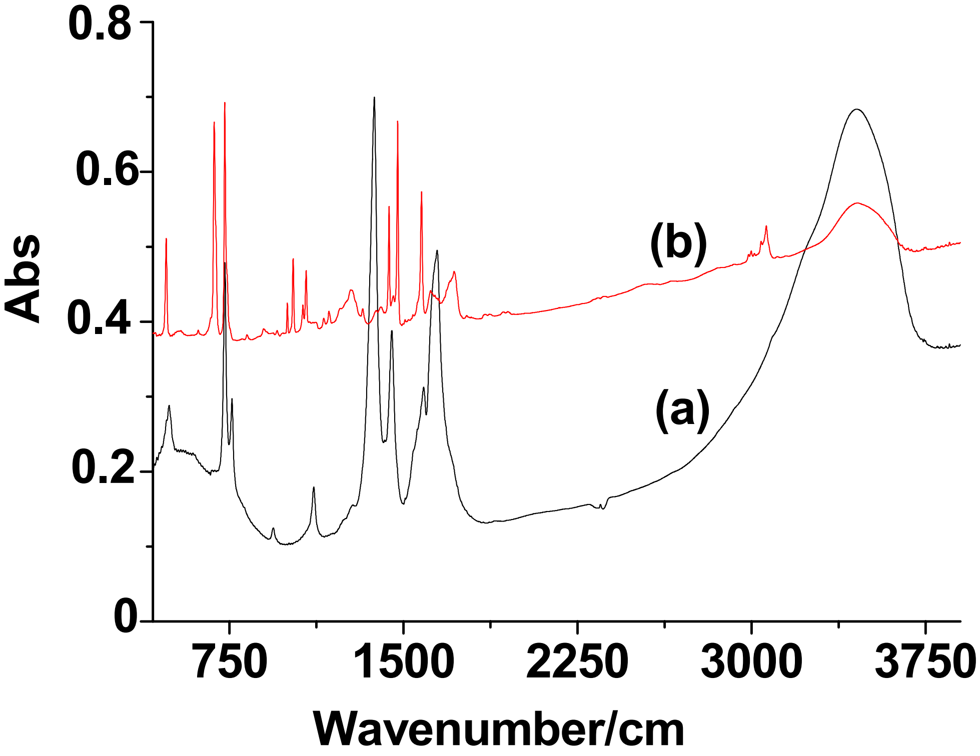

Figure S12. IR spectra of (a) fresh $Cu_3(BTC)_2$ and (b) after reaction with thiophenol.