

Electronic Supplementary Information

Vis/NIR Light Driven Mild and Clean Synthesis of Disulfides in the presence of $\text{Cu}_2(\text{OH})\text{PO}_4$ under Aerobic Condition

Sk. Sheriff Shah,^a S. Karthik,^a and N. D. Pradeep Singh^a

Department of Chemistry, Indian Institute of Technology Kharagpur, West Bengal, India, 721302

Table of Contents

General Information	S2
Synthesis of catalyst	S2
Characterization of catalyst	S3
Disulfide synthesis	S5
Reusability of the photocatalyst	S6
Study of reaction mechanism	S7
¹ H NMR and ¹³ C NMR of the disulfides	S8
References	S10

General Information

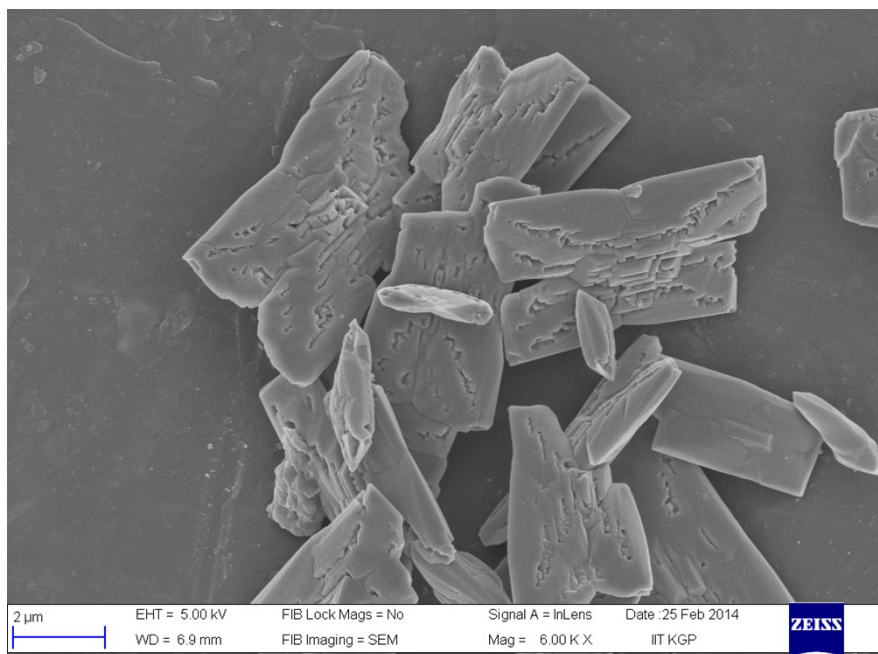
Methyl thioglycolate (Aldrich, 95%) and other thiol compounds were purchased from Sigma-Aldrich. Other chemicals are of analytical grade and used without further purification unless otherwise noted. UV-Vis-NIR absorption spectra were recorded with a Varian, Inc. (Carry, 4000i) spectrophotometer. Scanning electron microscopy (SEM) was performed on a ZEISS EVO 60 (Carl ZEISS SMT, Germany). The Microscope works with tungsten filament and maximum acceleration voltage of 30 kV. For NIR excitation we used a diode laser with wavelength 828 nm. All Reactions were carried out in presence of air. Column chromatography was carried out on silica gel. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 200 in solvents as indicated. Chemical shift are reported in ppm from CDCl_3 using TMS as internal standard.

Synthesis of catalyst

$\text{Cu}_2(\text{OH})\text{PO}_4$ was synthesized according to the reported method,¹ briefly stoichiometric amounts of $\text{Cu}(\text{NO}_3)_2$ and Na_2HPO_4 were mixed into 100 ml of deionized water under constant stirring for 1 h, and then the pH of the suspension was adjusted to seven. The suspension was transferred into a teflon-lined autoclave and followed by hydrothermal treatment at 120°C for 6 h. The sample was collected by filtration, then thoroughly washed with deionized water and ethanol, and finally dried in an oven at 60°C overnight.

Characterization of catalyst

a)



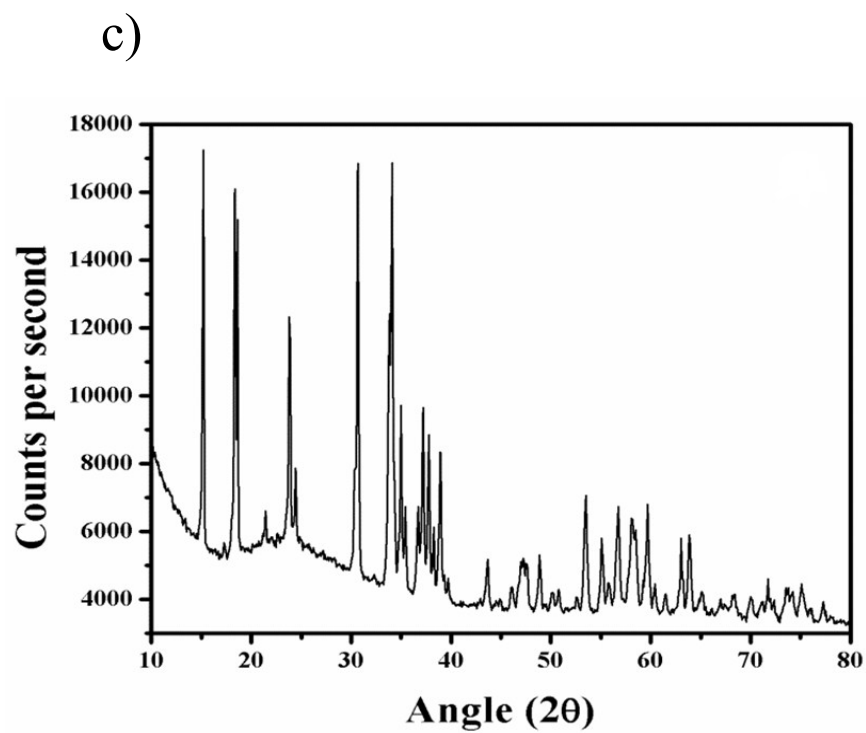
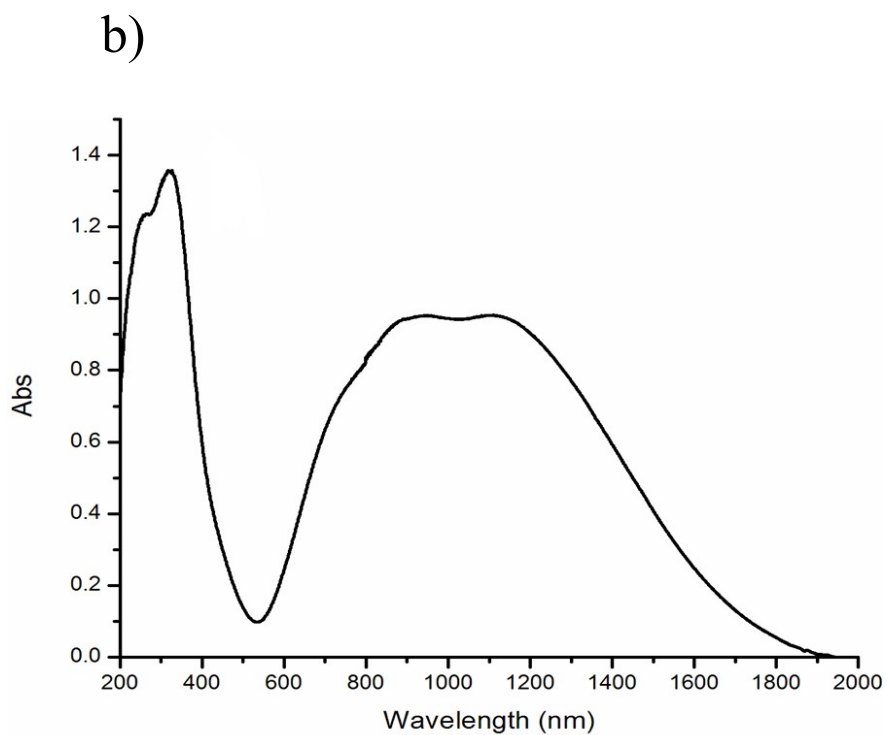


Figure S1. Characterization of catalyst a) scanning electron microscopy (SEM) image. b) UV/Vis/NIR absorption spectrum. c) XRD of $\text{Cu}_2(\text{OH})\text{PO}_4$.

General procedure for disulfide synthesis:

Solvent-rich disulfide synthesis: Disulfides were synthesized using a 125 W medium pressure mercury lamp (using 10% NaNO₂ solution as cut-off filter), for NIR light source we used an 828 nm diode laser. Desired thiol (1.6 mmol) was dissolved in 10 ml of water (in case of non-solubility instead of water we used 1:1 THF/water mixture) in a 25 ml of round bottom flask and to it the catalyst (0.042 mmol) was added. The solution was stirred in the dark for an hour and then exposed to light for about 1-2 hours in the presence of air at room temperature. Progress of the reaction was monitored by TLC plates. After completion of the reaction, the catalyst was separated by centrifugation and the residue was extracted with ethyl acetate three times (3×15 ml). The disulfide solution was concentrated under reduced pressure on a Büchi rotary evaporator. The disulfide was purified by flash chromatography on silica gel (Fluka, 230-400 mesh) using ethyl acetate/pet ether as eluent. Identification of the disulfides were carried out by comparison of their physical properties (color and physical state), melting points and spectral (¹H and ¹³C NMR) data with those reported in the literature, and they were further identified by GC-MS.

Solvent-free disulfide synthesis: In case of solvent-free reactions, the desired thiol (1.6 mmol) was mixed properly with the catalyst (0.042 mmol) in a 15 ml glass vial (Borosilicate glass) using a glass rod, then the reaction mixture was kept in the dark for an hour under constant stirring using magnetic stirrer and finally exposed to visible light under constant stirring ($\lambda > 400$ nm) for about 3-4 hours in the presence of air at room temperature. Progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was washed several times with ethyl acetate. The disulfides were purified and characterized by the above mentioned methods.

Grinding method for disulfide synthesis: The desired thiol (1.6 mmol) was grinded properly with the catalyst (0.042 mmol) in a mortar and pestle. The reaction mixture was then transferred to a 15 ml glass vial (Borosilicate glass), and then the reaction mixture was kept in the dark for an hour and finally exposed to light for about 3-4 hours in the presence of air at room temperature. Progress of the reaction was monitored by TLC. After completion of the reaction,

the reaction mixture was washed several times with ethyl acetate. The disulfides were purified and characterized by the above mentioned methods.

Reusability of the photocatalyst

The reusability of $\text{Cu}_2(\text{OH})\text{PO}_4$ was tested for the aerobic oxidative coupling of methyl thioglycolate. At the end of the reaction, the catalyst was separated by centrifugation, and then thoroughly washed with ethyl acetate to extract the disulfide before the next run. The recovered catalyst was dried, and then reused without further purification for the second run with fresh methyl thioglycolate. Further, we compare the XRD pattern of the fresh catalyst and the reused catalyst as shown below.

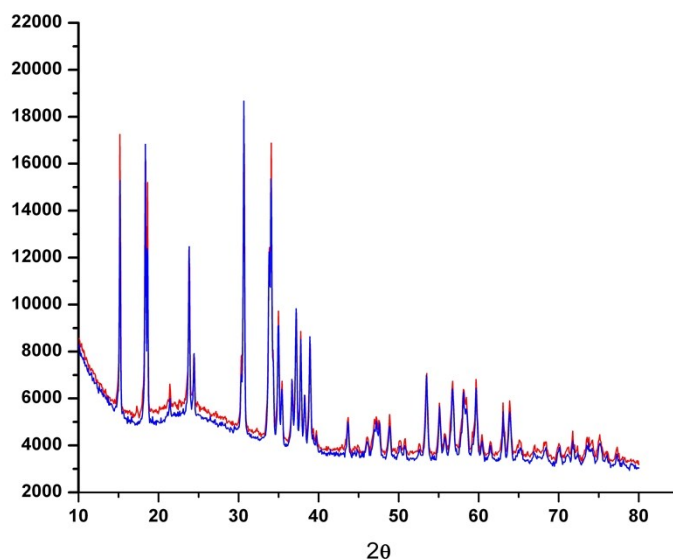


Figure S2. Comparison of the XRD pattern of the fresh catalyst (blue line) and the reused catalyst (red line).

Study of reaction mechanism

$\text{Cu}_2(\text{OH})\text{PO}_4$ catalyst solution was stirred for half an hour in the dark in two different vials. In one vial we added methyl thioglycolate and another we added 2-mercaptoethanol, the reaction mixture were stirred for another half an hour in the dark to allow maximal complexation between the catalyst and the thiol, then we added both the reaction mixture to a single vial and irradiated with visible light in presence of air for about 2 hours, methyl glycolate disulfide and bis(2-hydroxyethyl) disulfide were formed exclusively. We have not observed any heterocoupling during the course of the reactions.

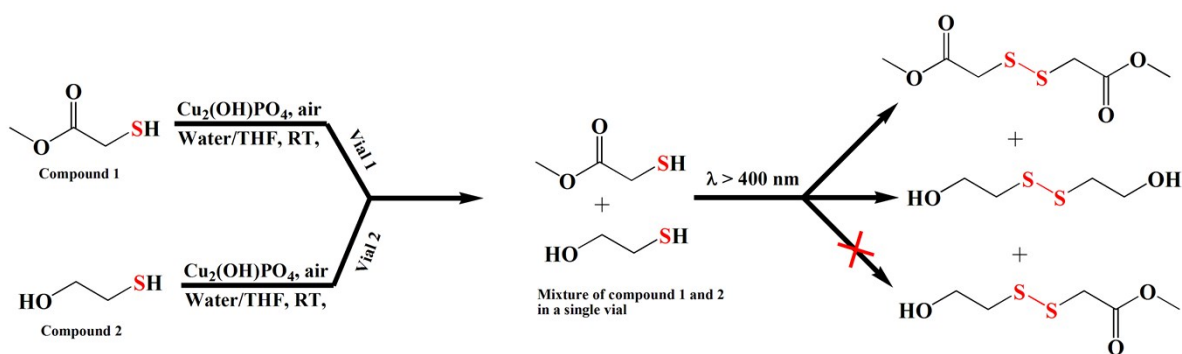
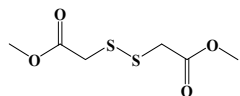


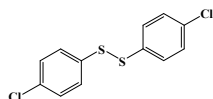
Figure S3. Photocatalytic homocoupling of disulfides.

Methyl glycolate disulfide



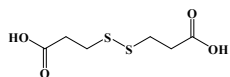
Colorless oil; $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 3.76$ (s, 6H), 3.58 (s, 4H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 170.0, 52.7, 41.3$ ppm; MS (EI) m/z (relative intensity) 210.0 (50) $[\text{M}]^+$; Ethyl acetate: pet ether, 1:1.

Bis(4-chlorophenyl) disulfide²



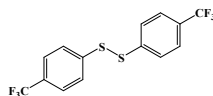
Colorless solid, mp 65-63 $^{\circ}\text{C}$ (lit.⁴ mp 65-66 $^{\circ}\text{C}$); $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 7.44$ -7.38 (m, 4H), 7.29 (d, $J = 8.6$ Hz, 4H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 135.3, 133.8, 129.4, 129.4$; MS (EI) m/z (relative intensity) 285.9 (50) $[\text{M}]^+$; Ethyl acetate: pet ether, 1:9.

3,3'-Dithiodipropanoic Acid²



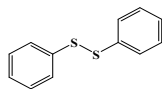
Colorless solid, mp 145-150 $^{\circ}\text{C}$ (lit. mp 155-158 $^{\circ}\text{C}$); $^1\text{H NMR}$ (200 MHz, CD_3OD): $\delta = 2.97$ (t, $J = 7.3$ Hz, 4H), 2.81 (t, $J = 7.4$ Hz, 4H); $^{13}\text{C NMR}$ (50 MHz, CD_3OD): $\delta = 173.9, 34.7, 34.1$; MS (EI) m/z (relative intensity) 210.0 (100) $[\text{M}]^+$; Ethyl acetate: pet ether, 1:1.

Bis(4-(trifluoromethyl)phenyl) disulfide²



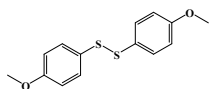
Colorless oil; $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 7.58$ -7.56 (m, 8H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 141.0, 129.9, 129.3, 128.6, 126.7, 126.4, 126.3, 126.2, 126.2, 121.3$; MS (EI) m/z (relative intensity) 353.9 (50) $[\text{M}]^+$; Ethyl acetate: pet ether, 1:9.

Bisphenyl disulfide³



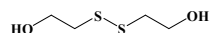
Colorless solid, mp 53-55 $^{\circ}\text{C}$ (lit.⁴ mp 51-52 $^{\circ}\text{C}$); $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 7.58$ (d, $J = 7.5$ Hz, 4H), 7.34 -7.25 (m, 6H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 137.0, 129.1, 127.5, 127.2$; MS (EI) m/z (relative intensity) 218.0 (100) $[\text{M}]^+$; Ethyl acetate: pet ether, 1:9.

Bis(4-methoxyphenyl) disulfide³



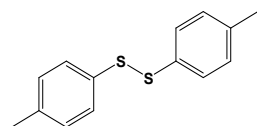
Colorless solid, mp 36-37 °C (lit.⁴ mp 34-35 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.43-7.39 (m, 4H), 6.86 (d, *J* = 8.8 Hz, 4H), 3.80 (s, 6H); ¹³C NMR (50 MHz, CDCl₃): δ = 159.9, 132.6, 128.4, 114.6, 55.3; MS (EI) *m/z* (relative intensity) 278.0 (90) [M]⁺; Ethyl acetate: pet ether, 1:9.

Di(2-hydroxyethyl) disulfide⁴



Colorless oil; ¹H NMR (200 MHz, CDCl₃): δ = 3.92 (t, *J* = 5.8 Hz, 4H), 2.91 (t, *J* = 5.8 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃): δ = 60.6, 41.4; MS (EI) *m/z* (relative intensity) 154.0 (30) [M]⁺; Ethyl acetate: pet ether, 3:7.

Bis(4-methylphenyl) disulfide⁴



Colorless solid, mp 53-55 °C (lit.⁴ mp 53-54 °C); ¹H NMR (200 MHz, CDCl₃): δ = 7.42 (d, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 7.9 Hz, 4H), 2.33 (s, 6H); ¹³C NMR (50 MHz, CDCl₃): δ = 137.6, 134.1, 129.9, 128.7, 21.2; MS (EI) *m/z* (relative intensity) 246.0 (100) [M]⁺; Ethyl acetate: pet ether, 1:9.

1,2-Dithiolane⁵



Colorless semi-solid; ¹H NMR (200 MHz, CDCl₃): δ = 2.71-2.60 (m, 4H), 1.99-1.86 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ = 37.4, 23.0; MS (EI) *m/z* (relative intensity) 106.0 (100) [M]⁺; Ethyl acetate: pet ether, 1:9.

References

1. G. Wang, B. Huang, X. Ma, Z. Wang, X. Qin, X. Zhang, Y. Dai, M. H. Whangbo, *Angew. Chem. Int. Ed.*, 2013, **52**, 4810.
2. X. B. Li, Z.J. Li, Y.J. Gao, Q.Y. Meng, S. Yu, R. G. Weiss, C.H. Tung, L.Z. Wu, *Angew. Chem. Int. Ed.*, 2014, **53**, 2085.
3. J. L. G. Ruano, A. Parra, J. Alem'an, *Green Chem.*, 2008, **10**, 706.
4. M. Oba, K. Tanaka, K. Nishiyama, W. Ando, *J. Org. Chem.* 2011, **76**, 4173.
5. N. A. Noureldin, M. Caldwell, J. Hendry, D. G. Lee, *Synthesis*, 1998, **11**, 1587.