

Precursor Engineering for Soft Selective Synthesis of Phase Pure Metal-Rich Digenite (Cu₉S₅) and Djurleite (Cu₃₁S₁₆) Nanocrystals and Investigation of Their Photo-Switching Characteristics

Suraj Peerappa Yadav^{a, #}, Gourab Karmakar^{b, #}, Alpa Y. Shah^b, Bal Govind Vats,^c Ankita Pathak,^d Adish Tyagi^{b, *}, Rohit Singh Chauhan^{a, *}, Vishal Singh^e

^a*Department of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai, 400077, India.*

^b*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India.*

^c*Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India.*

^d*Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai- 400085, India.*

^e*Materials Science Division, Bhabha Atomic Research Centre, Trombay, Mumbai- 400085, India.*

[#]Authors contributed equally

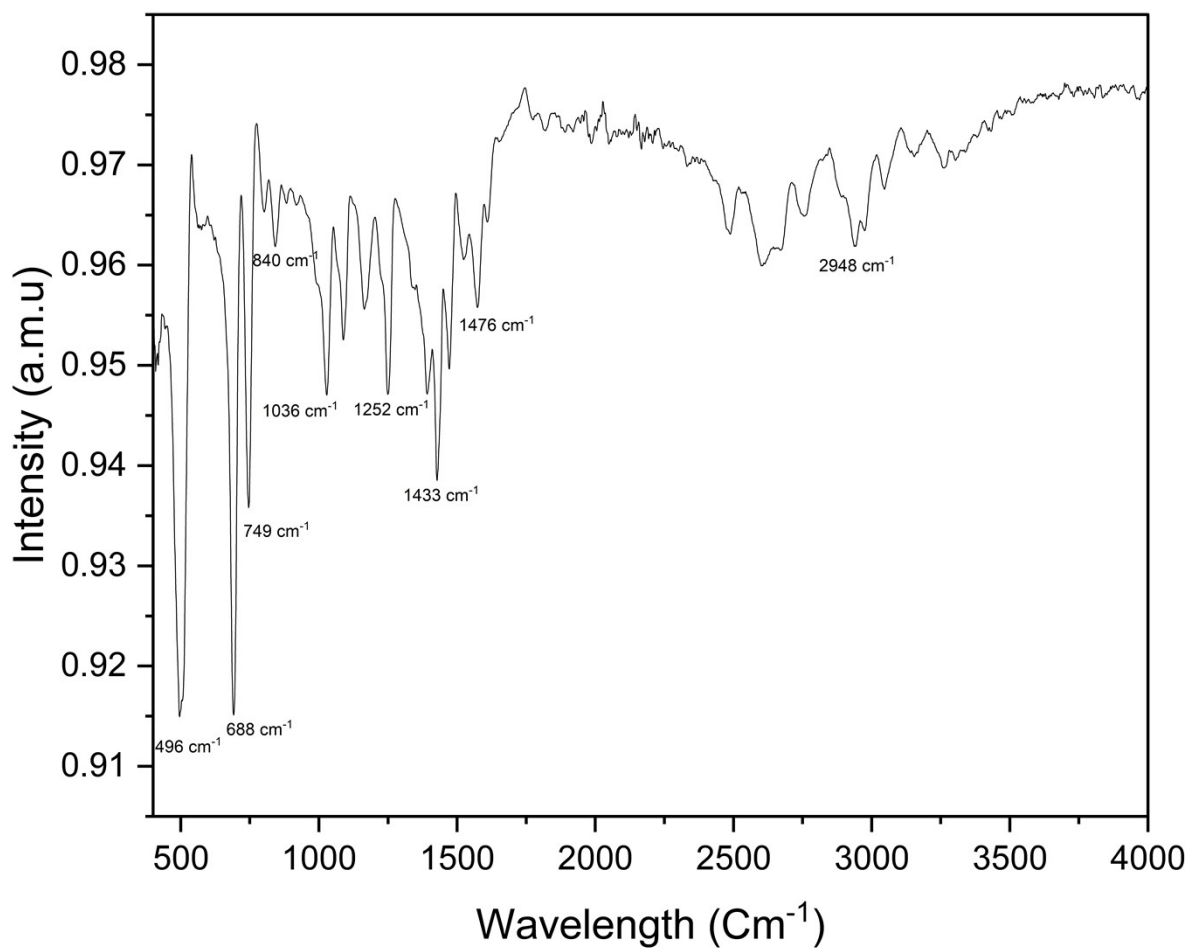


Fig. S1. IR spectra of CuCl(dmpymSH)(PPh₃)₂ (**1**)

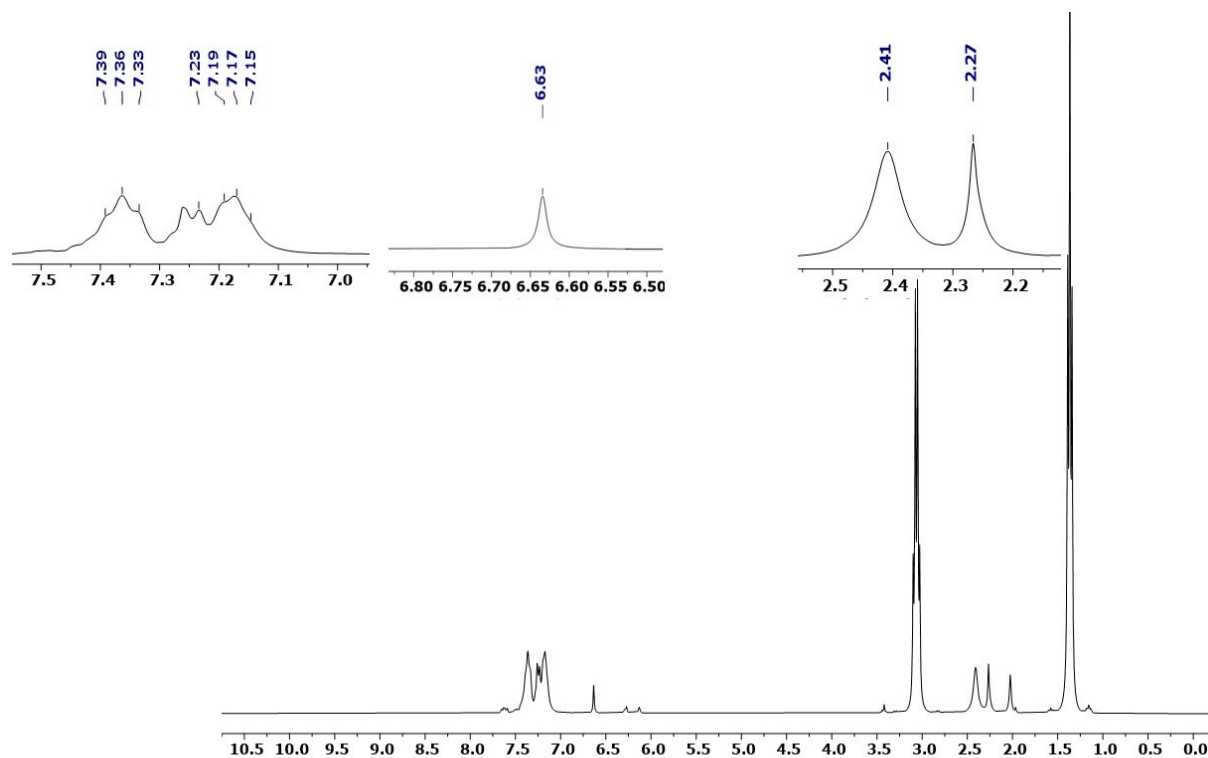


Fig. S2. ^1H NMR spectra of $\text{CuCl}(\text{dmpymSH})(\text{PPh}_3)_2$ (**1**)

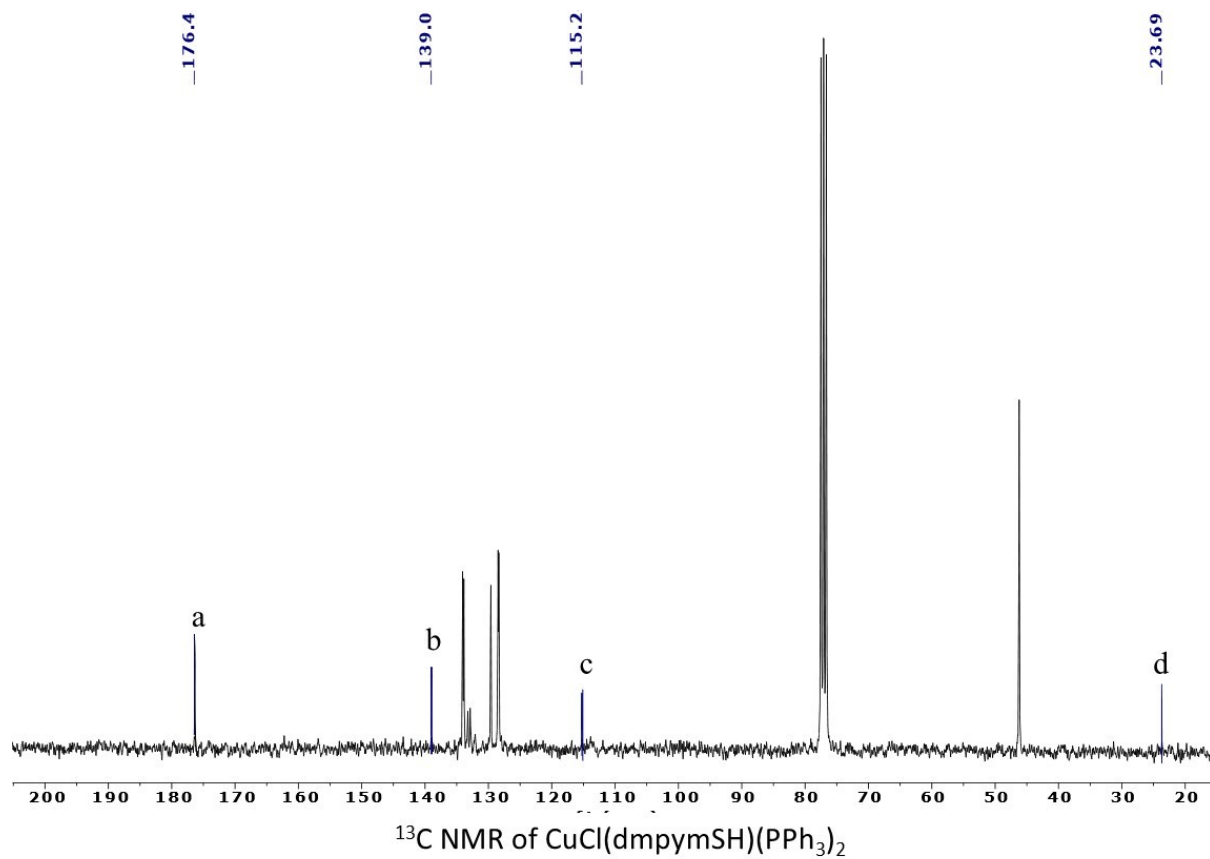


Fig. S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{CuCl}(\text{dmpymSH})(\text{PPh}_3)_2$ (**1**)

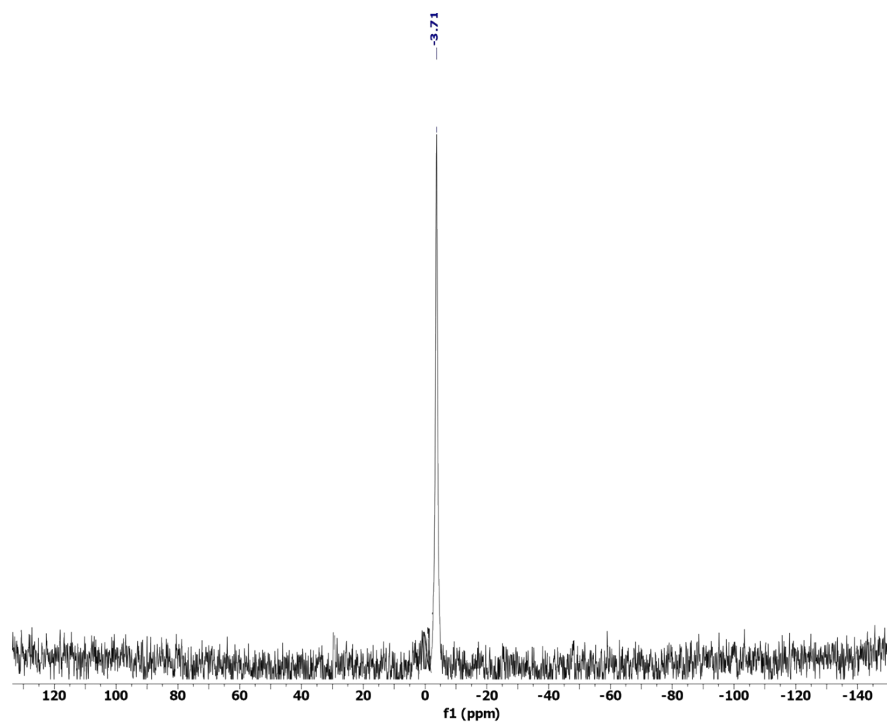


Fig. S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{CuCl}(\text{dmpymSH})(\text{PPh}_3)_2$ (**1**)

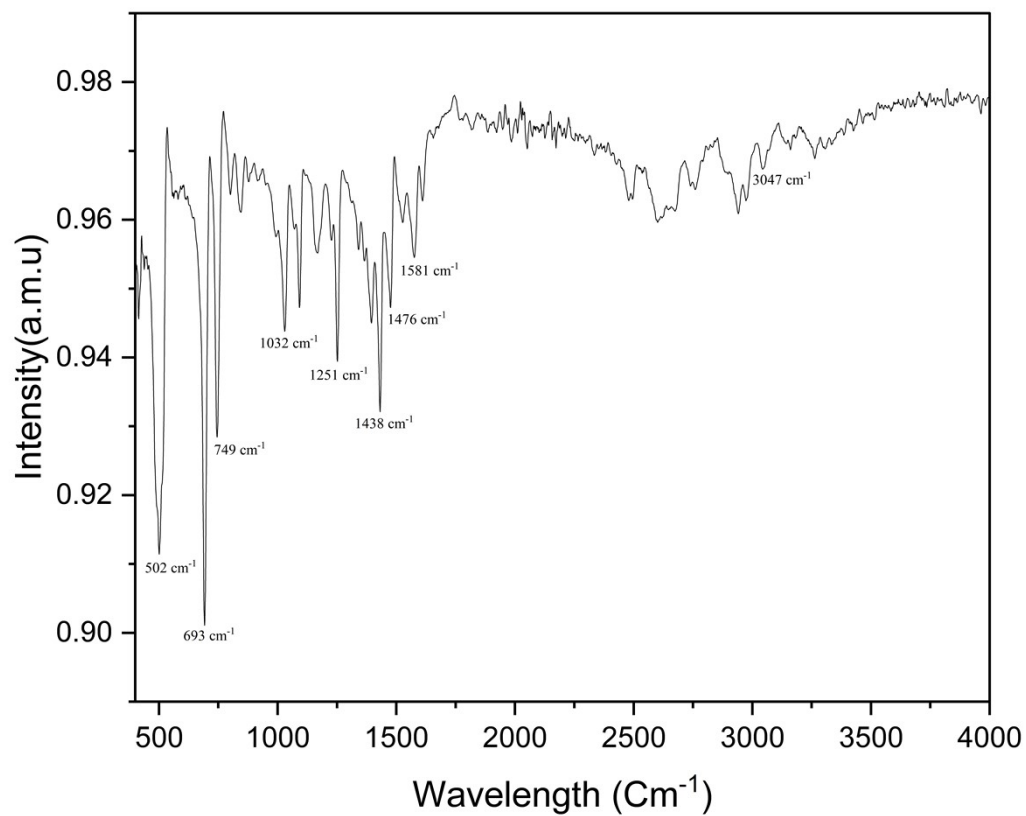
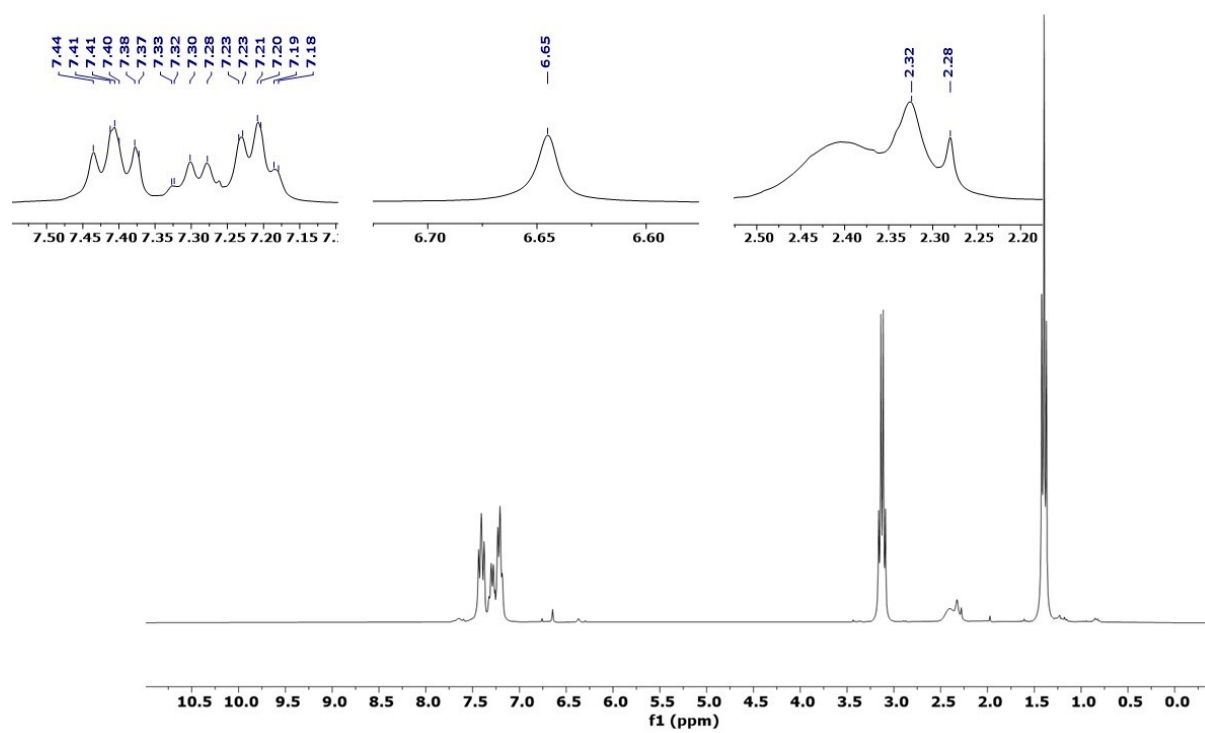


Fig. S5. IR spectra of $\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2$ (**2**)



^1H NMR of $[\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2]$

Fig. S6. ^1H NMR spectra of $\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2$ (**2**)

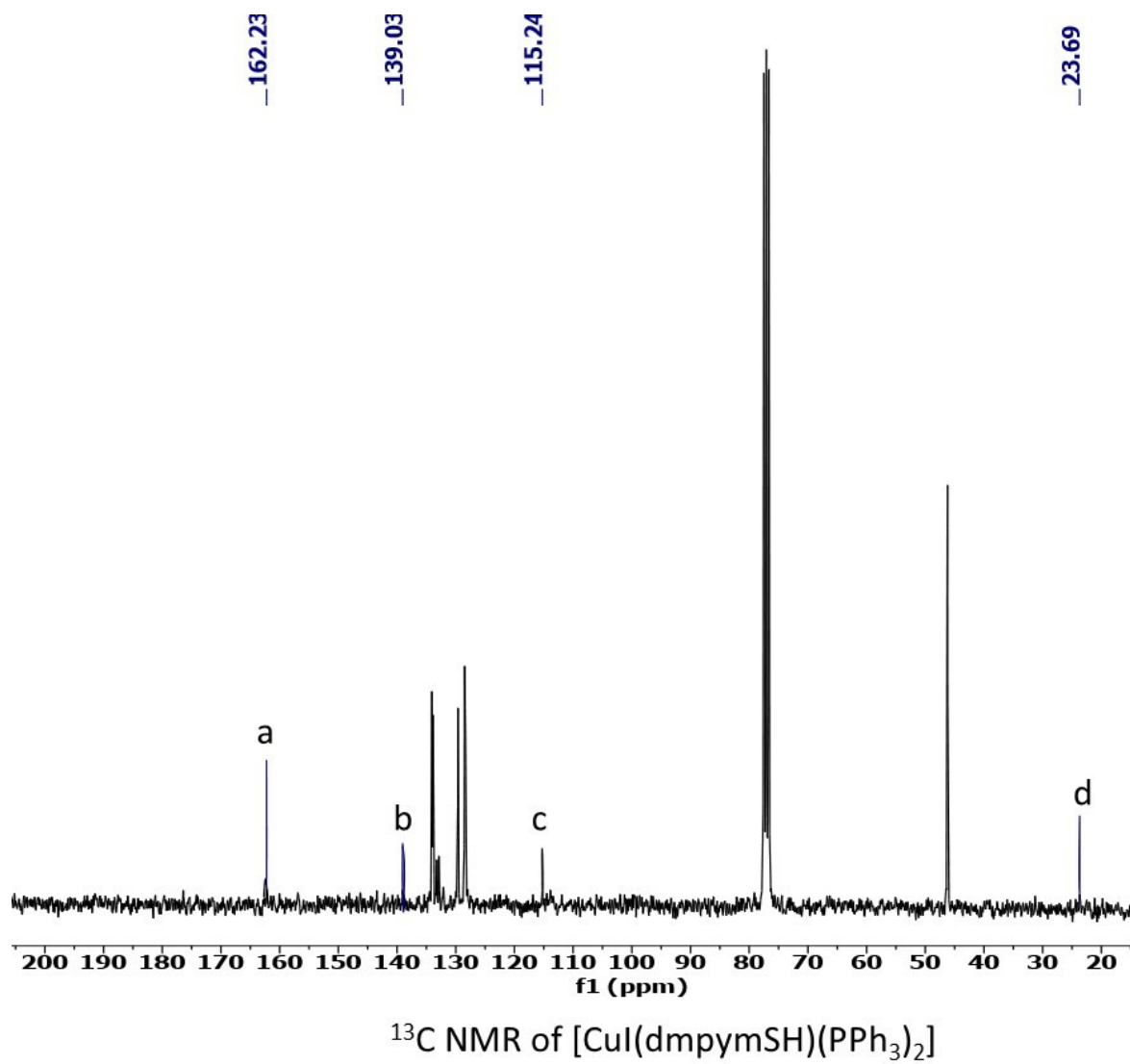


Fig. S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2$ (**2**)

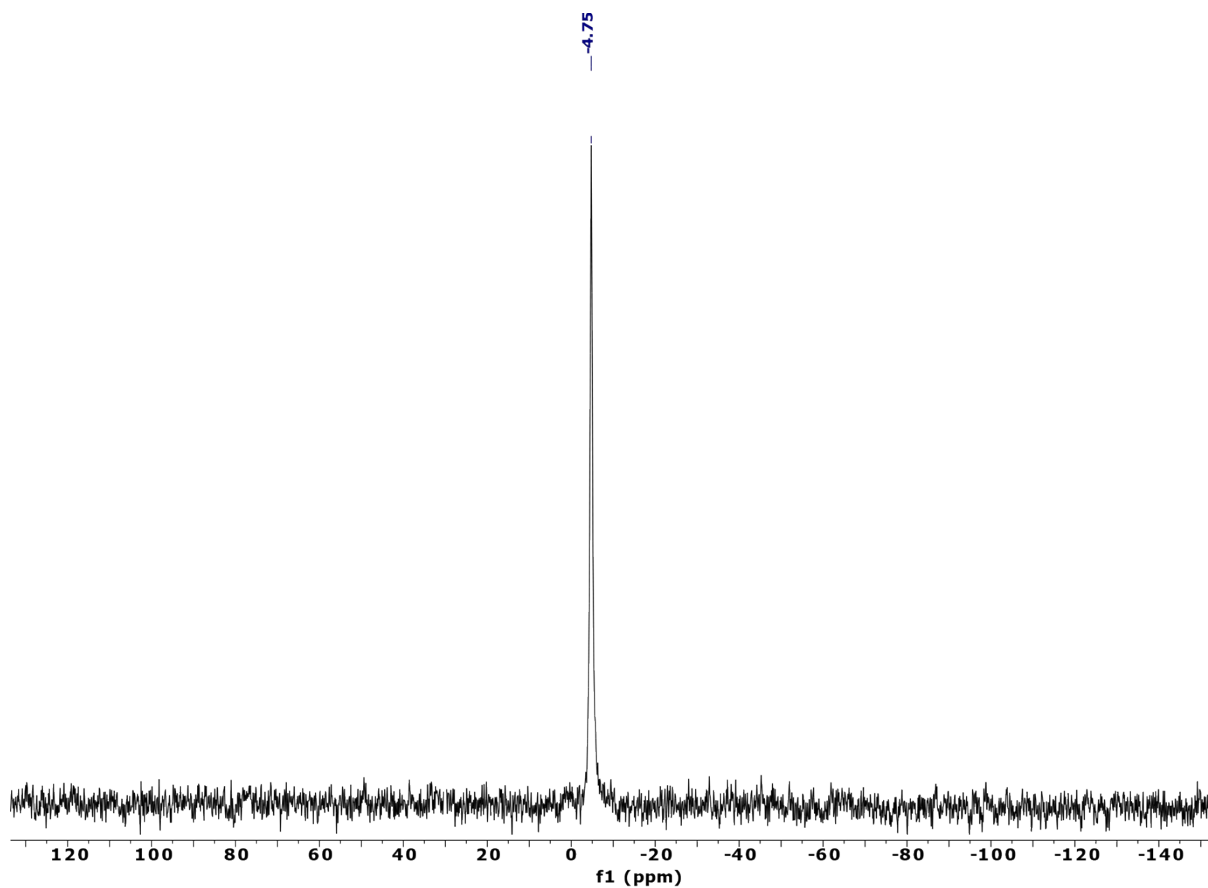


Fig. S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2$ (**2**)

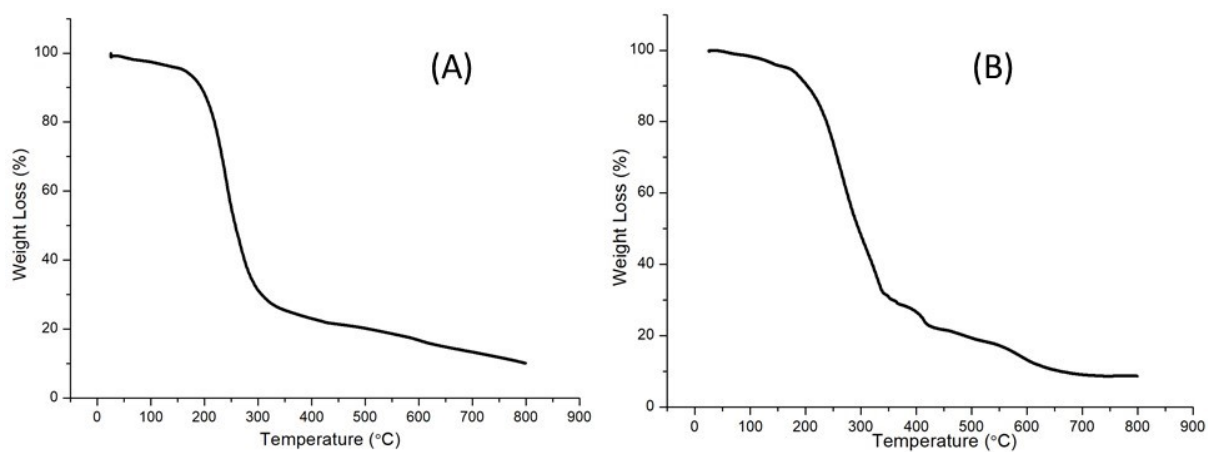


Fig. S9. TG analysis of (a) $\text{CuCl}(\text{dmpymSH})(\text{PPh}_3)_2$ (**1**) and (b) $\text{CuI}(\text{dmpymSH})(\text{PPh}_3)_2$ (**2**).

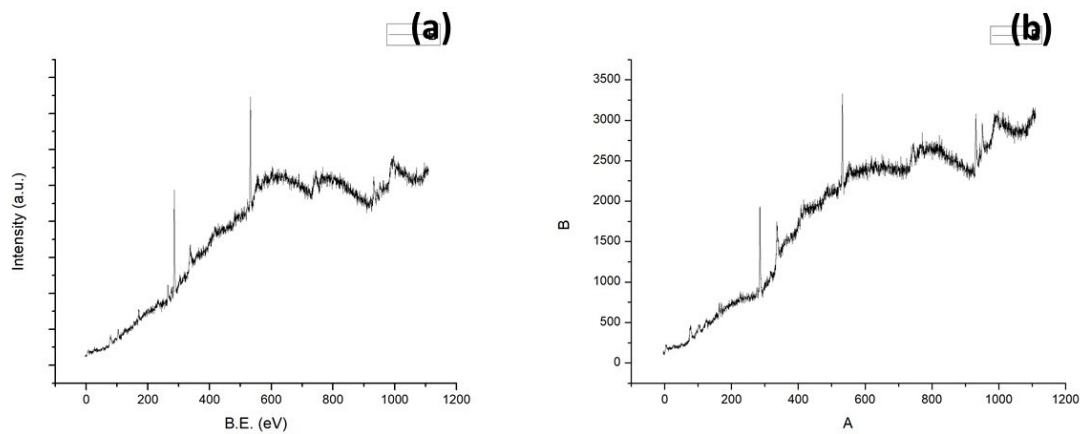


Fig. S10. XPS survey spectra respectively for (a, b) Cu_9S_5 and (c, d) $\text{Cu}_{31}\text{S}_{16}$ nanostructures.

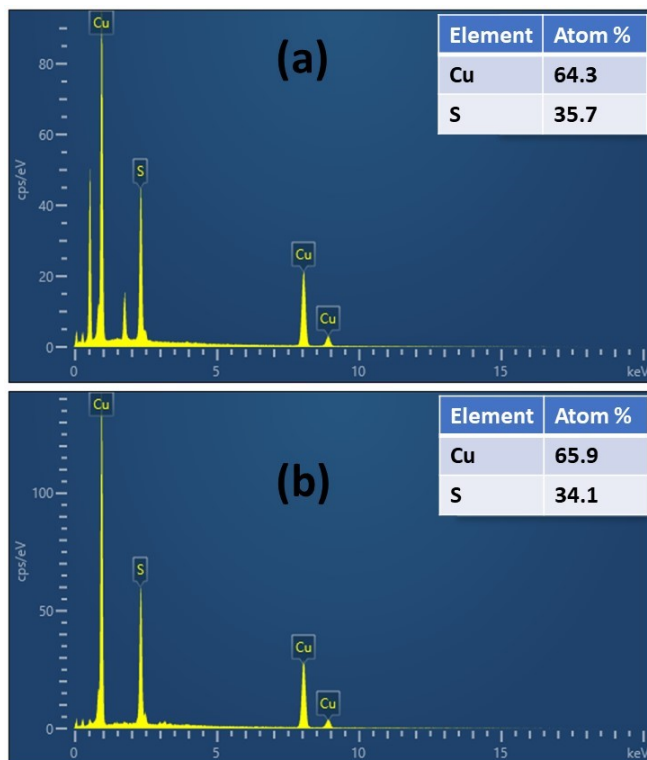


Fig. S11. EDS spectra of (a) Cu_9S_5 and (b) $\text{Cu}_{31}\text{S}_{16}$ nanoparticles respectively.

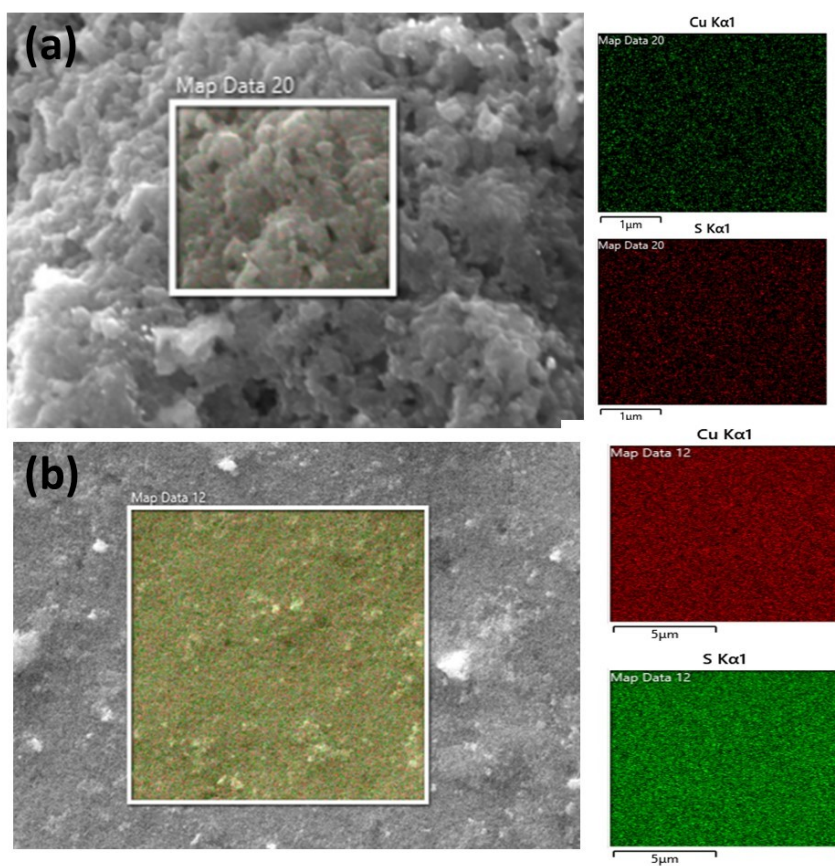


Fig. S12. 2D elemental mapping of (a) Cu_9S_5 and (b) $\text{Cu}_{31}\text{S}_{16}$ nanoparticles respectively.