Supporting Information

A copper cluster protected with phenylethanethiol

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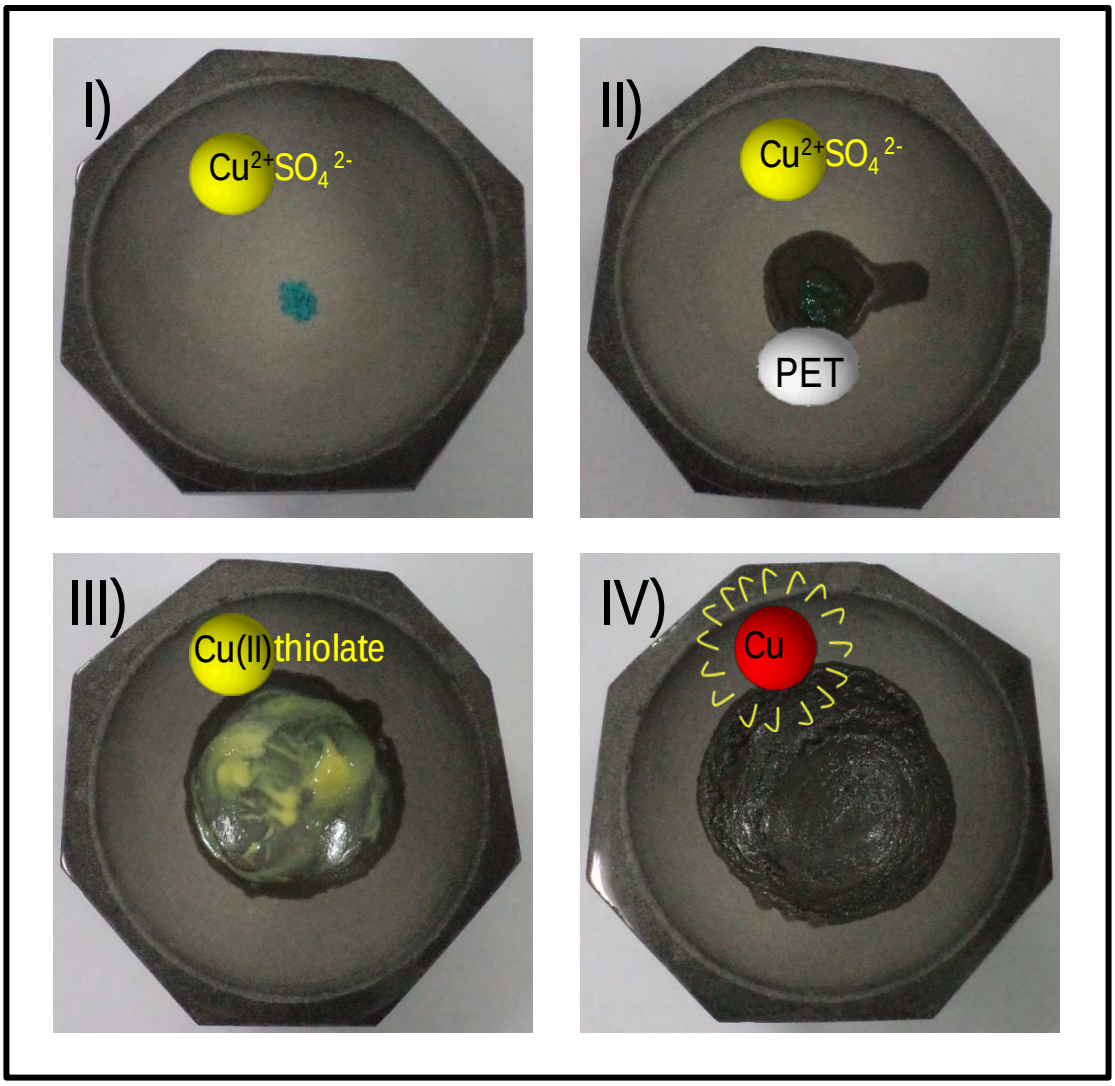


Fig. S1. Top view of different stages during synthesis of the copper cluster. I) $CuSO_4.5H_2O$ in the mortar. II) Immediately after the addition of 2-Phenylethanethiol to copper sulphate. III) Cu-thiolate formed after grinding the copper sulphate - PET mixture for ten minutes. IV) Black paste formed after grinding copper thiolate with $NaBH_4$ for about 3 minutes.

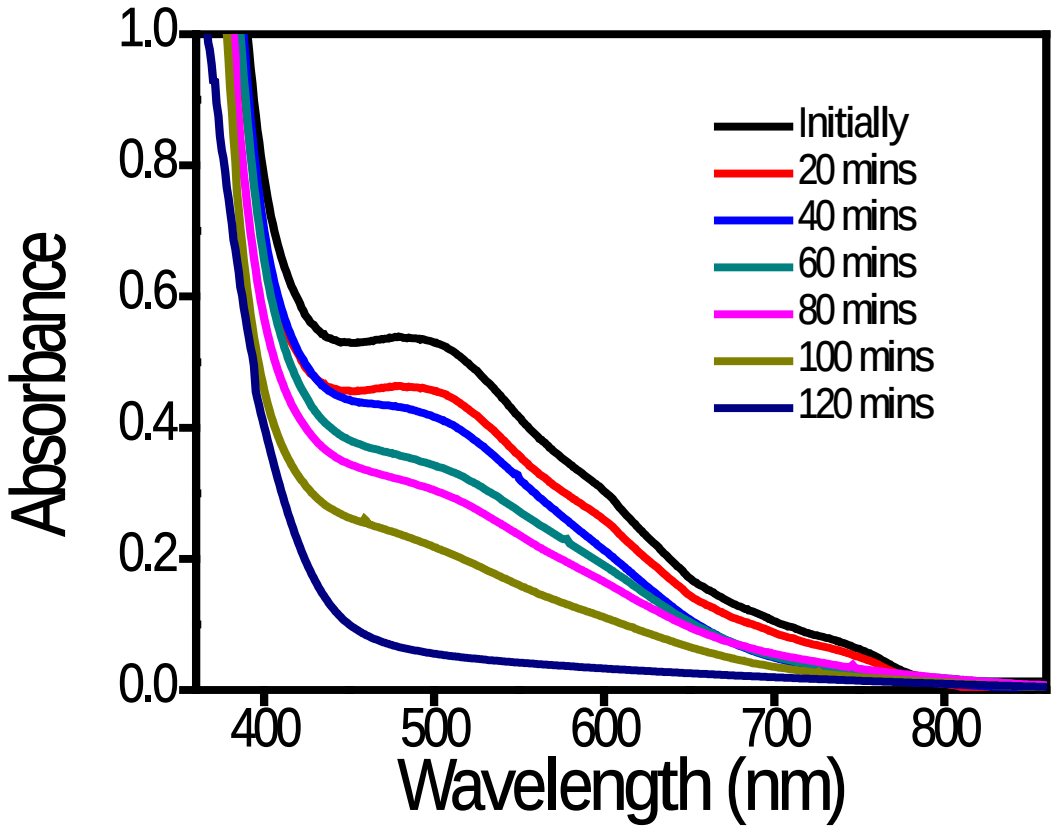


Fig. S2. Time dependent UV/Vis spectra of as-synthesized Cu@PET cluster. Initially, three features at 500, 600 and 750 nm are seen. By about 40 minutes, the humps at 600 and 750 nm have nearly disappeared. Also, from the beginning, the intensity of the hump at 500 nm keeps decreasing, finally merging with the baseline in about 120 minutes.

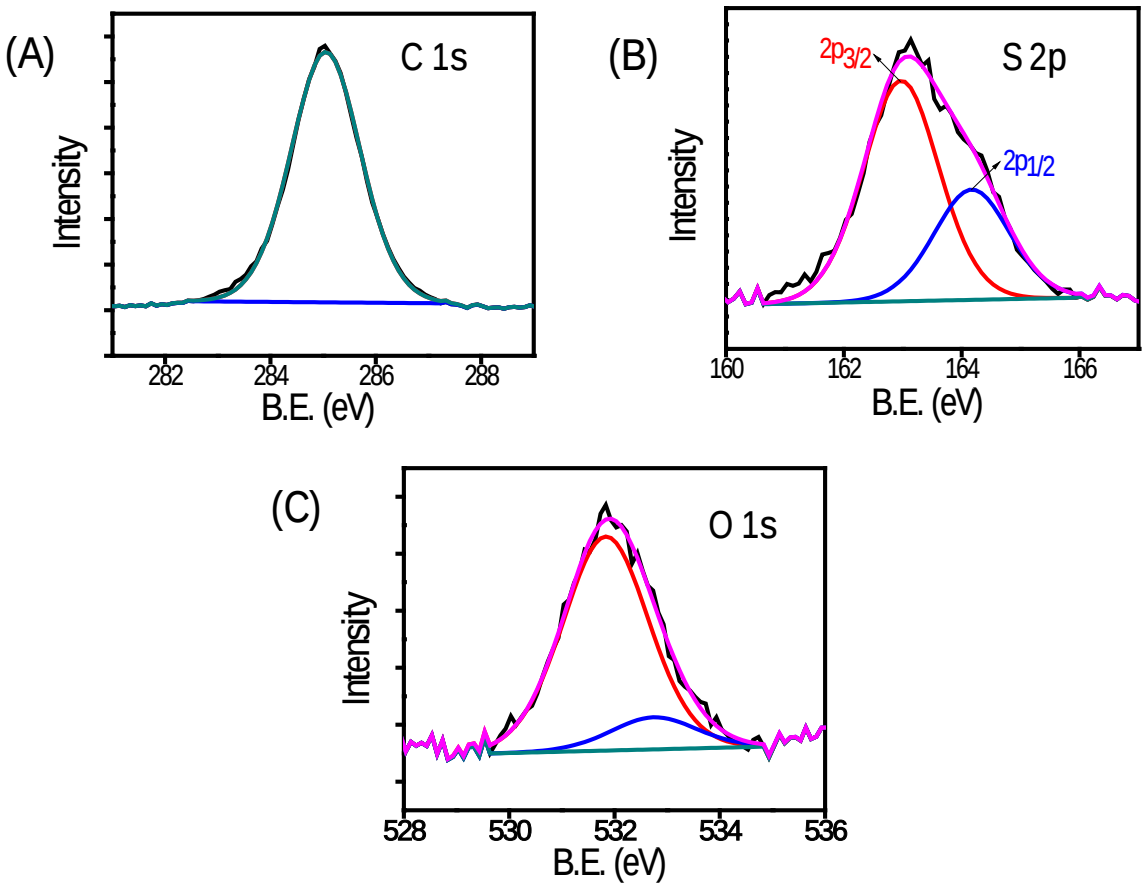


Fig. S3. A, B, and C are the expanded regions in the XPS for C 1s, S 2p, and O 1s, respectively. All the spectral features are fitted to the chemical species expected.

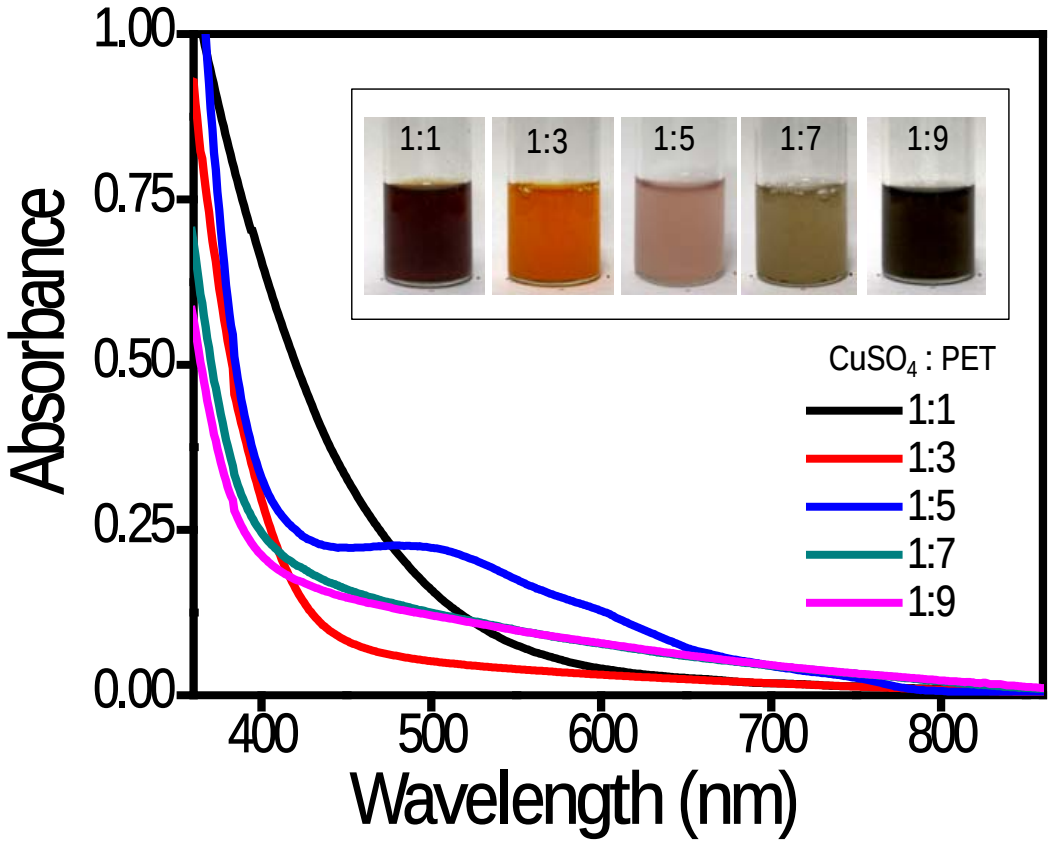


Fig. S4. UV/Vis absorption spectra for preparations with different copper sulphate to PET ratios. Among the five, only the 1:5 sample produced the cluster with features at 500, 600, and 750 nm. Inset shows the photographs after extraction in ethanol.

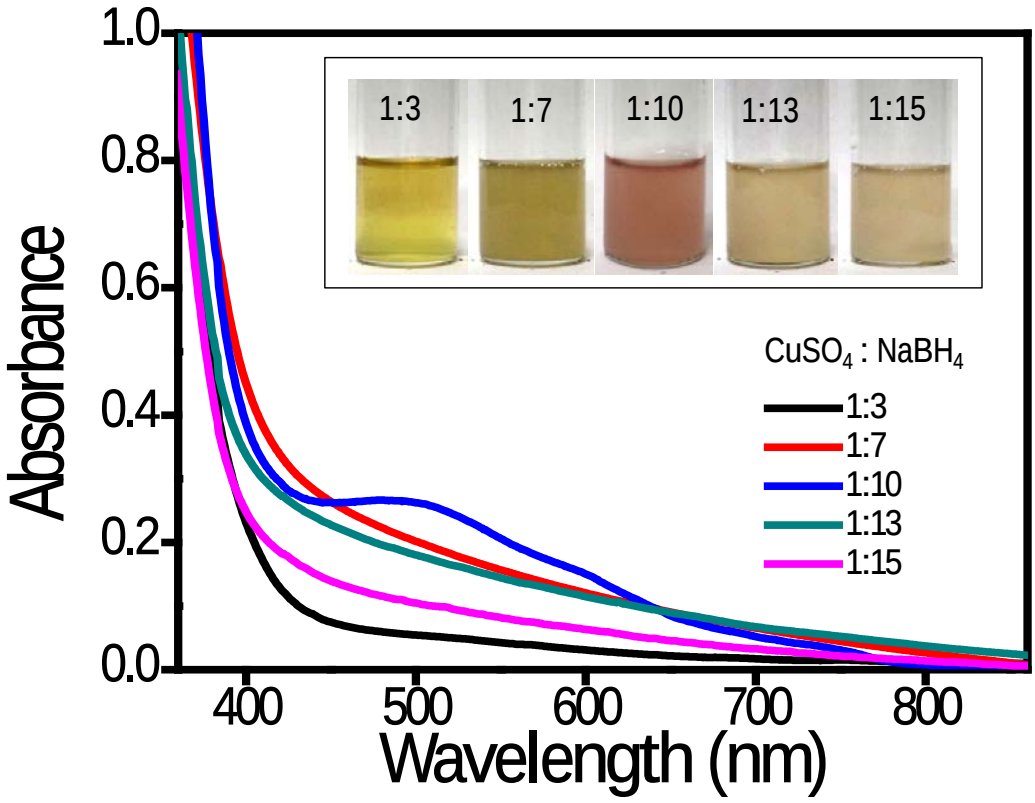


Fig. S5. UV/Vis absorption spectra for the preparations with different copper sulphate to $NaBH_4$ ratios. Among the five, only that with a ratio of 1:10 produced the cluster, $Cu_{38}(PET)_{25}$ with features mentioned earlier. Inset shows photographs of the preparations after extraction in ethanol.

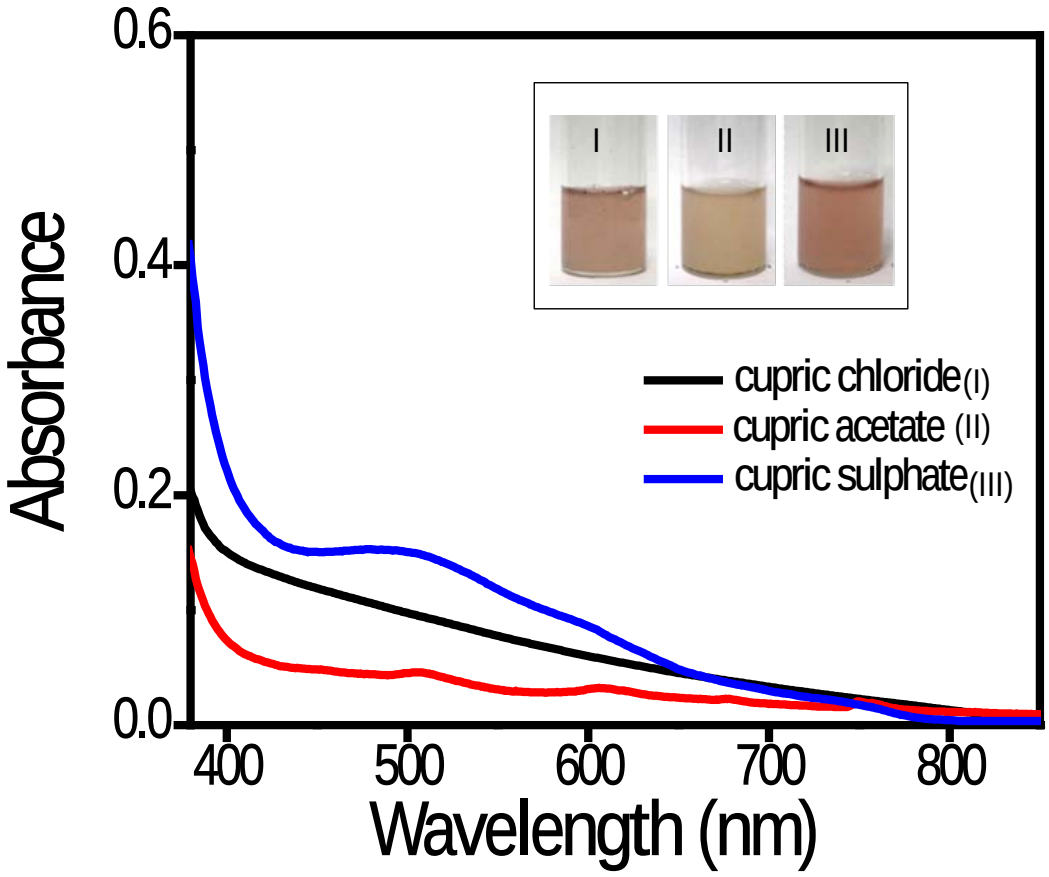


Fig. S6. UV/Vis absorption spectra for preparations with different salt precursors. Sample prepared from copper acetate shows features of $Cu_{38}(PET)_{25}$ though it is weak with respect to the preparation from copper sulphate. On the other hand, sample from $CuCl_2$ does not have the desired features of $Cu_{38}(PET)_{25}$. However, all ethanolic extracts are pink in color (Inset).

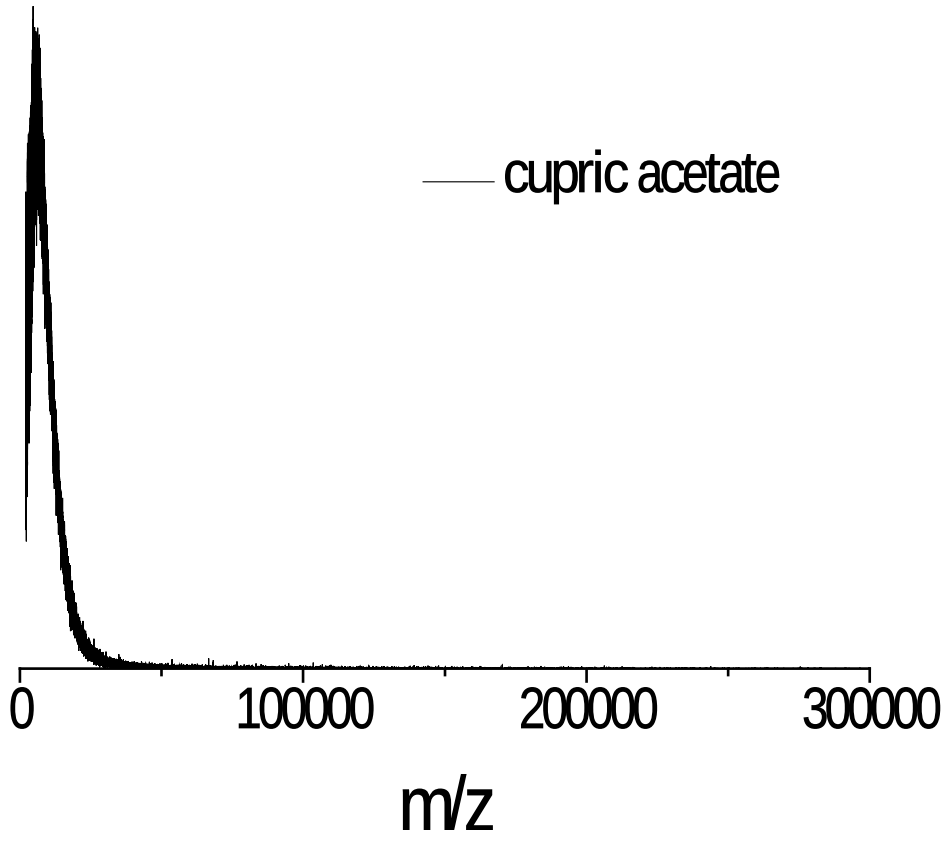


Fig. S7. MALDI mass spectrum of Cu@PET clusters, prepared from copper acetate as the precursor. This shows a molecular ion peak in the negative mode at m/z 5800.

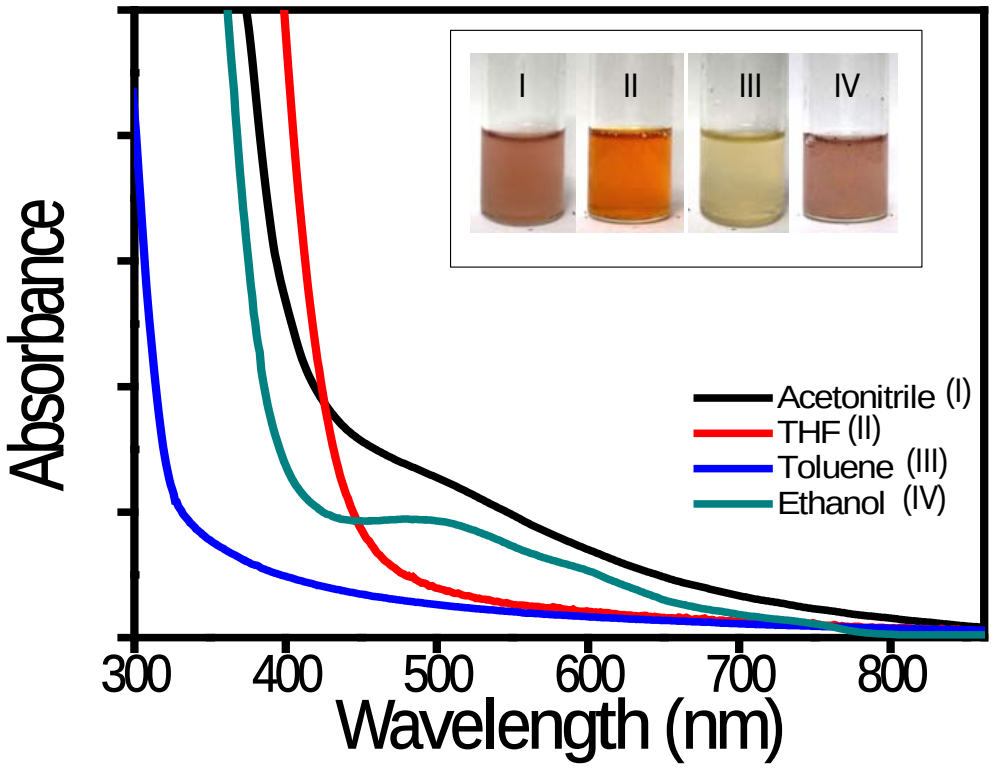
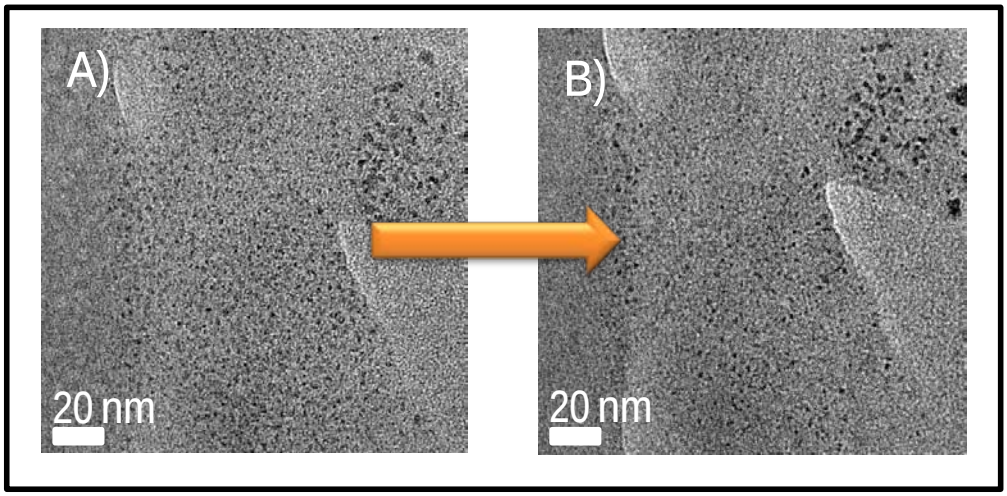


Fig. S8. UV/Vis absorption spectra for different solvents as the extraction media. Ethanol extract showed distinct features of $Cu_{38}(PET)_{25}$ while acetonitrile extract had a single hump at 500 nm. On the other hand, toluene and THF were not able to extract the cluster.



Cu:S = 1:0.67

C)

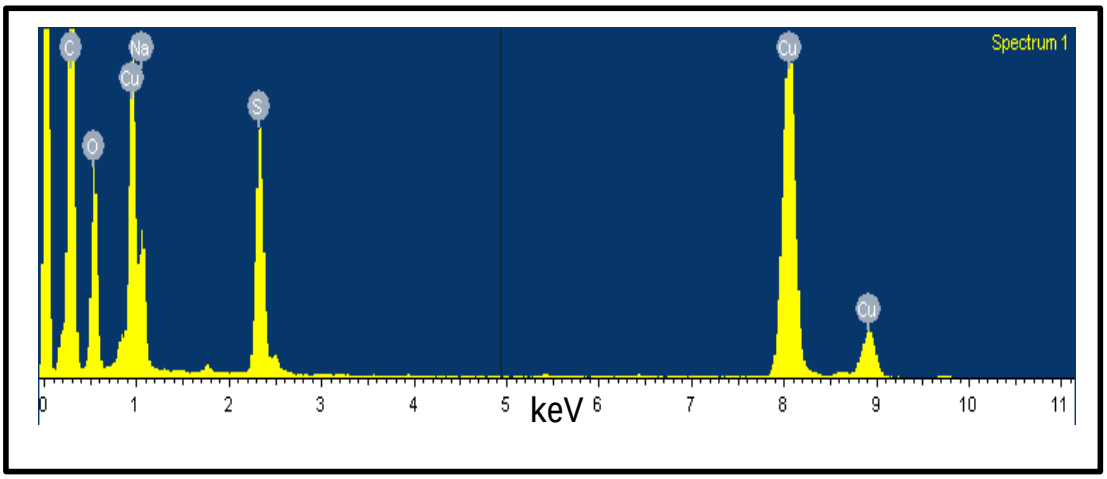


Fig. S9. HRTEM images of (A) as-synthesized $Cu_{38}(PET)_{25}$ cluster which appears as quantum dots, (B) after continued irradiation with electron beam, showing aggregates. (C) EDAX spectrum of the sample showing the elements: Cu, S, C, O, Na. Estimated Cu to S ratio from the spectrum is 1:0.67, consistent with theoretical ratio (1:0.65).

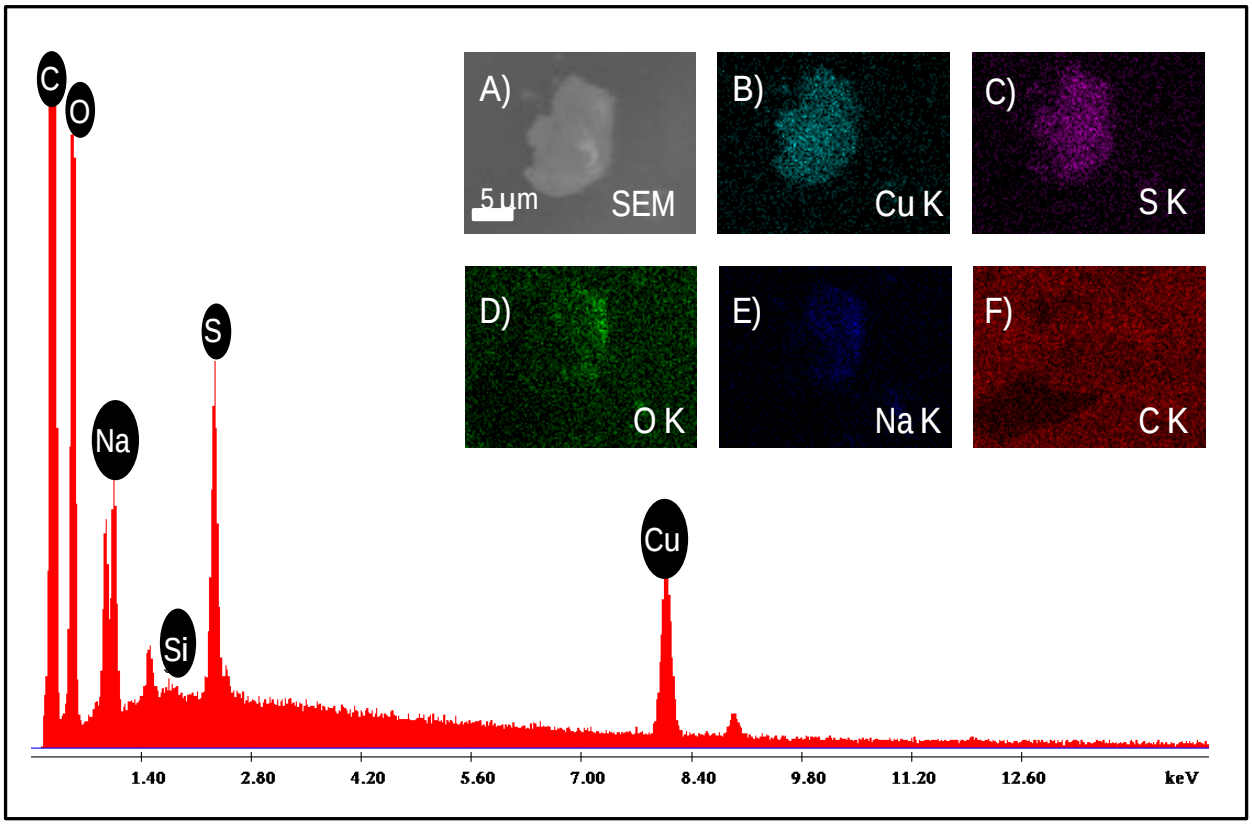


Fig. S10. EDAX spectrum of $Cu_{38}(PET)_{25}$ and Insets show the elemental mapping of a selected region. (A) SEM with (B) copper, (C) sulphur, (D) oxygen, (E) sodium and (F) carbon.