

Synthesis of Bis(tetra-n-butylammonium) tetrakis-[benzenethiolato- μ_3 -sulphido-iron], $[\text{N}^+\text{Bu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$: The precursor was synthesized in anaerobic conditions following reported procedure.¹³ Briefly, to a 40 ml methanolic solution containing 40 mmol of Na, 40 mmol of thiophenol was added, followed by a 25 ml methanol solution containing 10 mmol of anhydrous FeCl_3 . The mixture was stirred till a yellow-black solution was obtained. This was followed by the addition of 10 mmol of S powder. The stirring was continued till the S was completely digested (typically in 12 hours). The resulting solution was filtered into a methanolic solution containing 7.5 mmol of tetra-n-butylammonium iodide to obtain a black precipitate. The precipitate was filtered and dissolved in warm acetonitrile and re-crystallized by cooling. The crystallites upon dissolution in DMSO revealed the absorption band characteristic of the $[\text{FeS}_4(\text{SPh})_4]$ cluster.¹³ [Calcd. for $\text{C}_{56}\text{H}_{92}\text{Fe}_4\text{N}_2\text{S}_8$, C, 52.5%; H, 7.2%; Fe, 17.5%; N, 2.2%; S, 20.1%, Found: C: 53.0; H: 7.1; Fe: 17.4; N: 2.3; S: 20.2].

Synthesis of the Iron-sulfide nanocrystals: Nanocrystals of Fe-S were synthesized by injecting a solution of the precursor into a hot coordinating solvent followed by extended periods at elevated temperatures. In a typical preparation, 0.1 mmol of the cluster dissolved in 5 ml of octylamine was injected under vigorous stirring into a 15 ml octylamine heated to 180 °C in a N_2 atmosphere. The heating and stirring was continued for a further period of 12-16 hours. When the reaction vessel was cooled to room temperature, a portion of nanoparticles in the form of a black precipitates were adherent to the stir-bar. Copious amount of methanol was added to complete the precipitation of particles. The precipitates were centrifuged and dispersed in chloroform. The particulate dispersions were filtered and the clear solutions obtained were used for all further characterization and studies. We find that the precipitates could also be dispersed in octylamine.

The particulates were characterized by X-ray diffraction, Transmission electron microscopy, Energy dispersive X-ray analysis and Magnetic measurements. Magnetic measurements were carried out on dried dispersions of nanocrystals blended with eicosan.