S1) HR TEM images and d-spacing measurements for a) Cu₆PS₅Cl and b) Cu₃PS₄. These measurements agree with standard crystallography data.
S2) Rietveld fits for PXRD spectra a) Cu₆PS₅Cl nanoparticles using both Cu₃PS₄ and Cu₆PS₅Cl standards b) Cu₃PS₄ nanoparticles using both Cu₃PS₄ and Cu₆PS₅Cl standards c) and Cu₆PS₅Cl nanoparticles using Cu₆PS₅Cl standard. Due to the lack of any visible Cu₃PS₄ peak in the Raman spectra of the Cu₆PS₅Cl nanoparticles and that the Rietveld fitting for the Cu₆PS₅Cl nanoparticles using only the Cu₆PS₅Cl standard is able to account for all visible peaks, means that we believe the <1% Cu₃PS₄ reported in the quantitative analysis is likely due to experimental error and not the presence of any actual Cu₃PS₄. For the Cu₃PS₄ spectra, the refinement calculated 0% Cu₆PS₅Cl. (Cu₃PS₄ standard JCPDS: 01-071-3306, Cu₆PS₅Cl standard JCPDS: 01-073-5736)
S3) Data taken from an aliquot of the Cu$_3$PS$_4$ synthesis just after it reached 250 °C. From the Raman spectra shown in figure 4b) 250 °C, we expect both Cu$_6$PS$_5$Cl and Cu$_3$PS$_4$ to be present in the sample. a) Shows the PXRD spectra for this sample along with standards for both Cu$_3$PS$_4$ and Cu$_6$PS$_5$Cl (Cu$_3$PS$_4$ standard JCPDS: 01-071-3306, Cu$_6$PS$_5$Cl standard JCPDS: 01-073-5736) b) HAADF TEM image of the particles.