Copper cyanide polymers – new directions

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Our original goal was the designed synthesis and X-ray structure determination of neutral mixed-valence copper cyanide polymers with Cu^{II} complexed with amine bases, and a $Cu^{I}Cu^{II}CN$ framework. We determined the X-ray structures of a number of 1D, 2D and 3D mixed valence polymers of this type. Some syntheses, however, led to unexpected products that could not contain Cu^{II} as they were colorless. X-ray structural analyses indicated anionic 2D or 3D Cu^{I} networks with guest cations, and suggested further systematic study. By altering reaction conditions to produce intentionally more compounds of this type, we have characterized a number of new polymeric anionic $Cu^{I}CN$ structures, with charge neutrality obtained by various protonated guest amines and diamines. For instance, whereas crystallization of $Cu(CN)_x^{1-x}$ mixtures in the presence of N-ethylethylenediamine (eten) affords large blue crystals of $Cu_2(CN)_3eten_2$ via air-oxidation, at lower pH we obtain colorless needles of $[etenH][etenH_2].[Cu_4(CN)_7]$ with the anionic CuCN framework shown. We will present the new structures and discuss how different bases can drive formation of different topologies for the CuCN frameworks.