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Luminescent molecular wires that consist of up to eight copper atoms

Linear multi-atom complexes of Group 11 metals (Cu, Ag, Au) exhibit fascinating luminescence properties that make them highly interesting 1) for the systematic design of molecular wires in nanoelectronics and 2) their application as light-emitting building blocks in organic light-emitting devices/diodes (OLEDs). Since the light-emitting properties are specifically dependent on the number of metal atoms, these complexes can directly be applied in new tailored OLEDs, particularly in those that emit blue light – an urgent interest in the development of next-generation, energy-saving light sources.

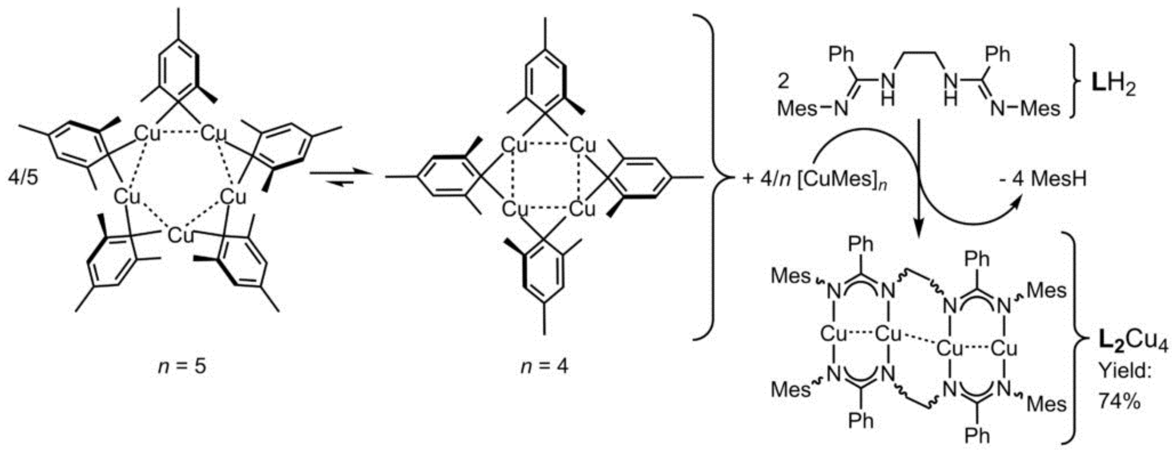

Fig. 1. Clean synthesis of L2Cu4 from mesitylcopper.

Previous methods to synthesize multi-atom complexes have shown that these compounds are usually available in only low yields, as contaminated product mixtures, or they are not accessible at all. We have utilized a new synthetic method to incorporate copper centers into a larger ligand framework L under ambient conditions and with excellent yields (Fig. 1). The star-shaped organometallic compound mesitylcopper, Cu_nMes_n (n = 4, 5), is a clean source of copper ions, since it serves as deprotonating base itself and produces only one volatile organic byproduct (mesitylene, MesH).

This new method allows us to control the size of (strictly linear or helically-bent) copper chain complexes: If L_2Cu_4 crystallizes from solution, it forms two different complexes 1 and 2 (Fig. 2), depending on how polar the solvent is. Toluene/hexanes mixtures yield both crystals of 1 and 2 simultaneously while more polar toluene/diethyl ether mixtures result in the exclusive formation of 2. As revealed by X-ray crystallography, a method to determine a molecular structure in the solid state, our new ligand L accommodates four copper atoms in a linear, coiling-like arrangement (1). Complex 1 can adopt a higher-level organization that creates an even longer chain of six copper atoms with two additional bridging central copper centers (2). To the best of our knowledge, this is the longest linear arrangement of copper atoms in a discrete molecule reported so far. An important criterion for a molecular wire are the distances between the metal atoms: If they are, in case of copper atoms, in the magnitude of –or smaller than– 2.8 Å (the sum of two copper van der Waals radii), then they undergo significant contact interactions.

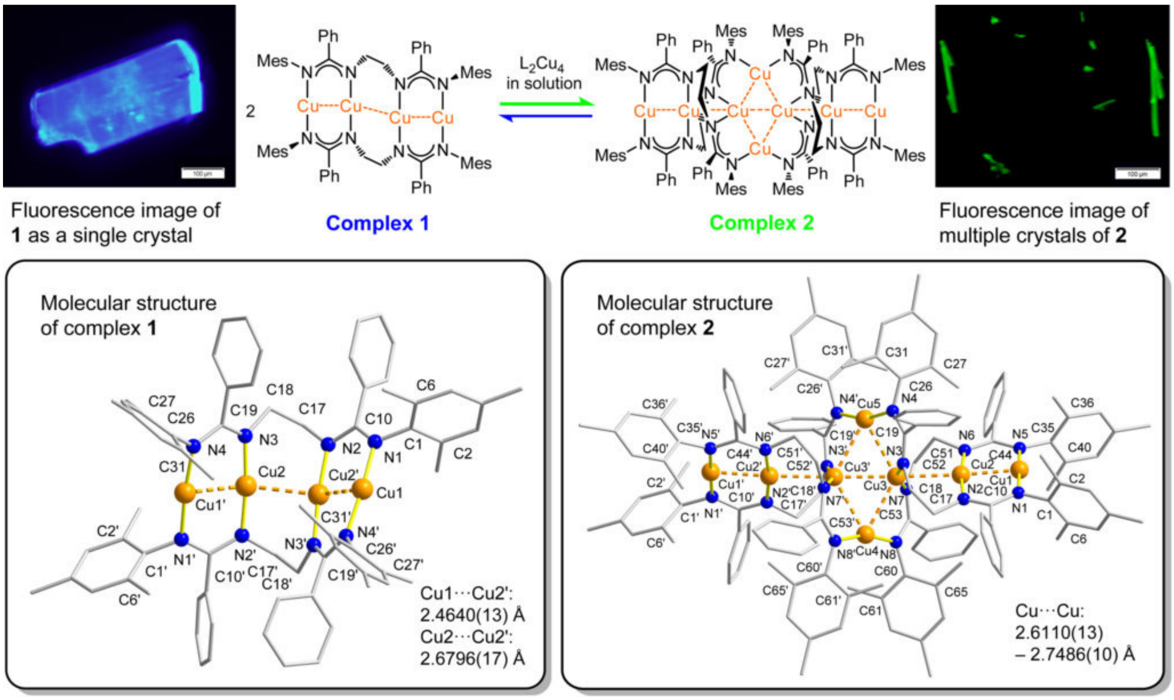

Fig. 2. Formation of complexes 1 and 2 as crystalline solids from L2Cu4 in solution. Fluorescence images of crystals of 1 and 2. Molecular structures of 1 and 2, determined by X-ray crystallography.

1 and 2 can directly be applied in OLEDs, since the two distinct crystal morphologies show blue (λ_{max} = 460 nm; 1) and green (λ_{max} = 495 nm; 2) light emissions (Fig. 2) in excellent singlet-to-triplet interconversions (a measure how efficient an emissive material is) – these are outstanding features for direct applications in OLEDs. Supported by computational calculations, we could demonstrate that the increased number of contacts between copper atoms from 1 to 2 result in the observed longer emission wavelength (so-called redshift).

Overall, we have applied an efficient method to synthesize two unique, highly luminescent multi-atom copper complexes that represent linear and coiling-like molecular wires. Both compounds are excellent candidates for applications in OLEDs and prospective multifunctional nanoelectronic devices.

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