Self-assembly of Lanthanide Double-Decker Crown-substituted Phthalocyaninates into 1D-Supramolecular Semiconductors

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Fabrication of organic semiconductors by self-assembly of supramolecular building blocks is an intensely developing field of modern material science. Herein we report a new strategy for fabricating conductive nanowires through self-assembly of lanthanide double-decker crown-substituted phthalocyaninate complexes (ML_2, where M = Lu, Ce, Tb) and potassium tetraphenylborate. The growth of supramolecular structure proceeds through a coordination of crown-ether groups of adjacent ML_2 complexes with potassium ions after the mixing of the ligand and salt in solution (Fig. 1a).

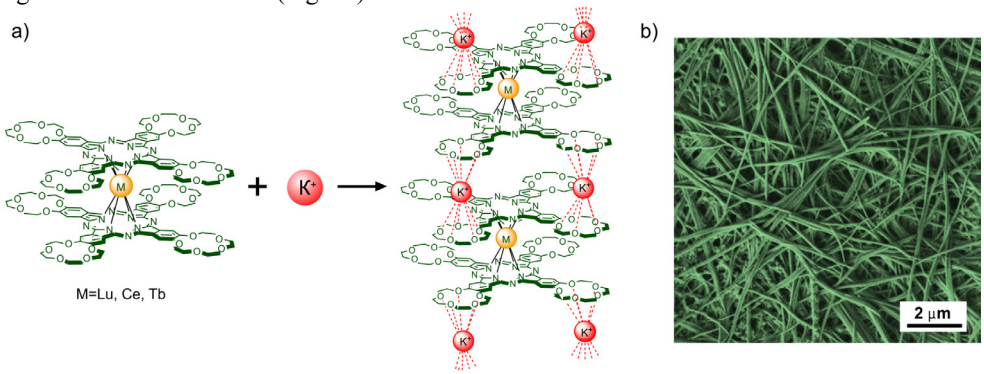

Fig. 1. a) Scheme of formation and b) SEM photo of supramolecular nanowires based on lanthanide bis(tetra-15-crown-5)phthalocyaninate) complexes.

The incorporation of large central metal ions such as Ce(III) or Tb(III) in ML_2 can increase the probability of intramolecular binding of K^+ ions instead of intermolecular coordination of complexes with smaller metal centers such as Lu(III). Spectrophotometric titration showed that the K^+-induced intermolecular binding dominates irrespective of the chemistry of central metal ion at high concentration of the potassium salt. The SEM investigation of the as-formed supramolecular structures deposited onto the solid supports via dip coating confirmed the formation of nanowires with an extraordinary high aspect ratio and length up to 50 microns (Fig. 1b). The electrical properties of these nanowires depend on the chemistry of central metal ion and dramatically decrease in the order Lu>Ce>Tb. The LuL_2-based nanowires exhibited better electrical properties than those of known conjugated polymer semiconductiors. The TbL_2-based 1D structures possessed insulator characteristics, whereas CeL_2-based wires showed semiconductor behaviour.
Our results is important for understanding how the composition of building blocks may affect the properties of resulting 1D supramolecular structures to optimize them for their integration with organic electronic devices.

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