Efficient Charge Transport by Multiple Inelastic Cotunneling in Indium Tin Oxide Nanocrystal Thin-Films Functionalized with M-Tetraaminophthalocyanine (M = Cu, Co, Fe, Ni, Zn)

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Macroscopic superlattices of tin-doped indium oxide (ITO) nanocrystals (NCs) are prepared by self-assembly at the air/liquid interface followed by simultaneous ligand exchange with the organic semiconductors M-4,4`,4``,4```-tetraaminophthalocyanine (M4APc, M = Cu, Co, Fe, Ni, Zn). By using X-ray photoelectron spectroscopy (XPS), grazing-incidence small-angle X-ray scattering (GISAXS), ultraviolet-visible-near infrared (UV–vis–NIR) spectroscopy, we demonstrate that the semiconductor molecules largely replace the native surfactant from the ITO NC surface and act as cross-linkers between neighboring particles. Transport measurements, focusing on the effect of the metal center of the ligand, reveal a ligand-dependent increase in electrical conductance by 6-9 orders of magnitude, suggesting that M4APc provides efficient electronic coupling for neighboring ITO NCs. The resulting I–V characteristics as well as the temperature dependence (7 - 300 K) of the zero-voltage conductance indicates that at low temperatures, transport across the arrays occurs via a sequence of inelastic cotunneling events, each involving ~3 ITO NCs.

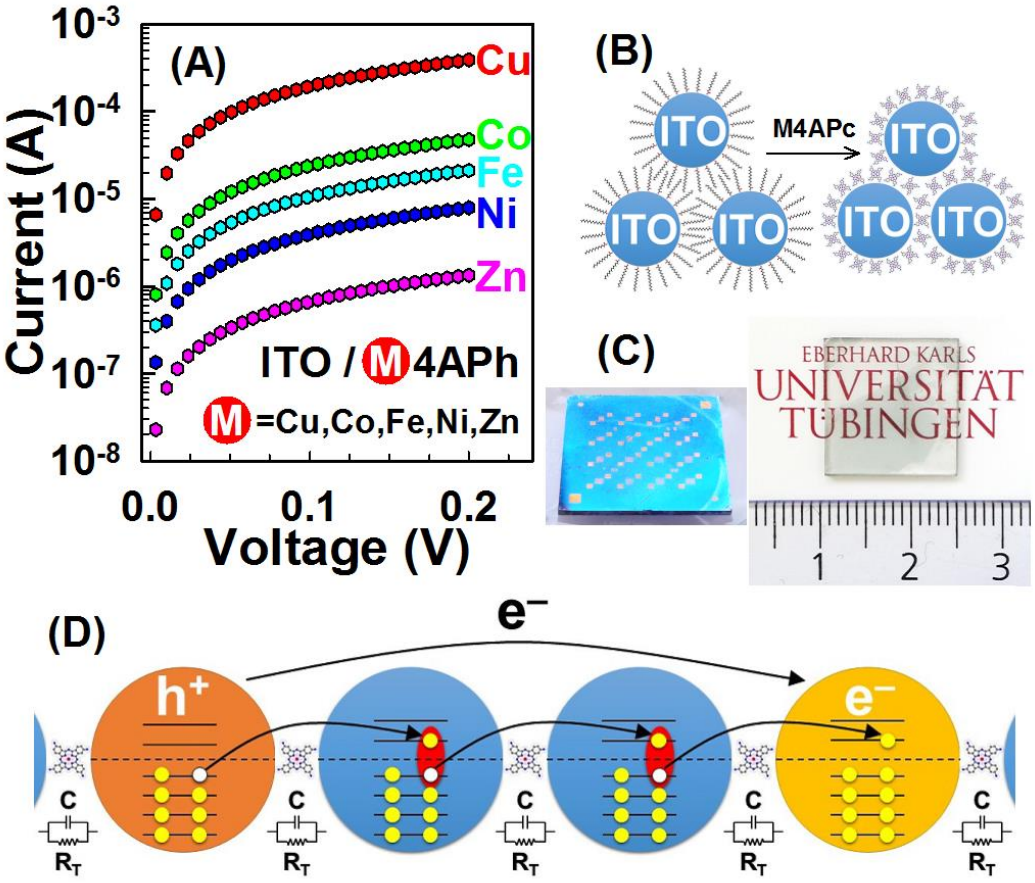

Fig. 1 (A) Current–voltage (I–V) characteristics as well as the sheet resistance measured for ITO NC thin-films functionalized with Cu-, Co-, Fe-, Ni-, and Zn4APc. (B) Schematic representation of the ligand exchange process (C) Photograph of the macroscopic, transparent, crack-free film of ITO NC / M4APc superlattice on a gold-patterned silicon and a glass substrate (D) Schematic representation of the inelasic cotounelling transport in nanocrystals.