Electroconductive $\pi$-junction Au Nanoparticles
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Electrodes and circuits are necessary in all types of electric devices such as transistors, photovoltaic cells, and light-emitting devices. These devices are commonly fabricated by employing expensive vacuum deposition processes. A promising alternative that is cheaper and faster for fabricating devices is wet printing using material from specially designed solutions. Many examples of solution processes for transistors, photovoltaic cells, and light-emitting devices have been reported. However, in order to achieve high efficiency and reliable devices, vacuum-processed metals and conductive metal oxides electrodes must be used, thereby producing only partially solution-processed devices. To realize the fabrication of all-solution-processed devices, electrodes must be fabricated at relatively low temperatures from a solution, and the resultant electrode must fulfill three requirements: they must have (1) good contacts, i.e., low resistance at the semiconductor–electrode interface, (2) high electroconductivity, and (3) high oxidation stability. In this study, we report that the $\pi$-junction Au nanoparticles (NPs) possessing orbital hybridization between the Au core and relatively large aromatic molecules meet these three requirements, and consequently, produce reliable electrodes that are comparable to vacuum-deposited Au electrodes.

We synthesized two Pc derivatives, 2,3,9,10,16,17,23,24-octakis(2-N,N-dimethylaminoethylthio) phthalocyanine (OTAP) and 2,3,11,12,20,21,29,30-octakis(2-N,N-dimethylaminoethylthio)naphthalocyanine (OTAN). Eight substituted thioether groups elevate the highest occupied molecular orbital (HOMO) level of the ligands to provide the Pc ring with the ability to coordinate with Au NPs. Terminal dimethylamino groups cause Pc-coordinated Au NPs to dissolve in aqueous solution under acidic conditions. OTAP- and OTAN-protected Au (OTAP–Au and OTAN–Au) NPs were prepared by a ligand-exchange reaction using conventional citrate-capped Au NPs having a diameter of 14.3 ± 2.2 nm. The synthesized NPs showed good solubility in water under acidic conditions and no solubility under basic conditions, which indicate a successful ligand exchange. We found that an acidic aqueous formic acid solution of OTAP–Au and OTAN–Au NPs could be used as a printable electroconductive material without post-treatment. The purple aqueous solutions of OTAP–Au and OTAN–Au NPs became metallic gold in color after deposition and drying on the substrate under ambient conditions. OTAP–Au and OTAN–Au NP thin films, dried at 55 °C for 10 min to remove the remaining solvent, exhibited electric conductivities of 1560 and 6600 S/cm, respectively. The all-solution-processed organic field-effect transistor (OFET) fabricated under ambient conditions exhibits mobility values as high as 2 cm$^2$/Vs, the value of which is comparable to OFET devices having vacuum-deposited Au electrodes.

Figure. (a) Chemical structure of OTAN, (b) schematic illustration of phthalocyanine coordinated $\pi$-junction Au nanoparticle, (c) the all-solution-processed organic field-effect transistor (OFET).