Synthesis of Oligothiophene Dendron-Modified Au Nanoparticles and Their Effects on Optical Properties and Self-Assembled Structures

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Au nanoparticles (NPs) exhibit localized surface plasmon resonance (LSPR) in the visible region, facilitating interactions with various optical materials. Among organic soft materials, oligothiophene dendrons [1] have π-conjugated moieties that enable wavelength-tunable photoluminescence (PL) [2]. Our previous study demonstrated that CdS quantum dots modified with phenylethyl ether-based liquid crystalline (LC) dendron exhibited energy transfer from the band edge of CdS to lower-energy states originating from π–π stacking of the dendrons [3]. Furthermore, LC dendron-modified Au NPs were found to self-assemble into a hexagonal phase, which transforms into a cubic LC phase at 150 °C [4]. Based on these findings, this study investigates the synthesis, optical properties, and self-assembled structures of oligothiophene dendron-modified Au NPs (Fig. (i)).

1-Dodecanethiol (DT) modified Au NPs (**A**) and oligothiophene dendron (**T7**) and DT -modified Au NPs (**DA**) were synthesized in three different initial ligand ratios (**T7** :DT = 25:75(**DA25**), 50:50(**DA50**), 75:25(**DA75**). Transmission electron microscopy images of **A** and each **DA** show similar particle sizes of approximately 4.6 nm, while the interparticle distances increased with increasing **T7** content (Fig. (ii)). The optical property of **DA50** , **T7** , and mixture of Au NPs and **T7** with a protected thiol group (**A+T7-THP**) were evaluated via PL measurement in chloroform (Fig. (iii)). While the PL of **A+T7-THP** was quenched relative to an equivalent amount of **T7** , the PL from **T7** covalently bound to the Au core in **DA** showed a more significant quenching of 91%. This indicates the occurrence of energy transfer from **T7** to the Au core, which is significantly enhanced by direct binding of **T7** . Additionally, small-angle X-ray scattering of **DA50** film confirmed a structural phase transition into a face-centered cubic structure at 150 °C. The effect of the **T7** modification ratio on the self-assembled structures will also be discussed.

Keywords:
Au nanoparticles, Oligothiophene dendron, Optical property, Energy transfer, Self assembly

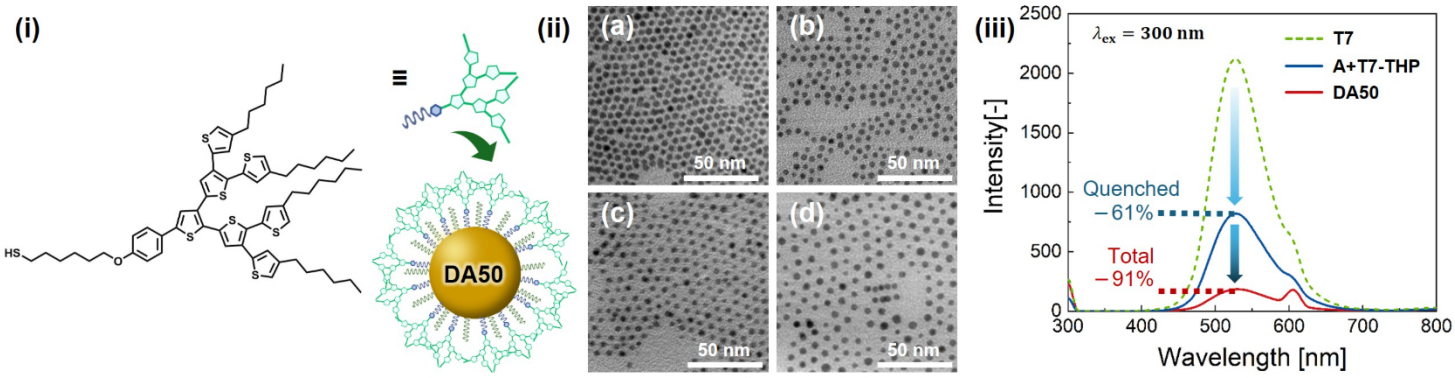

Fig. (i) A molecular structure of T7 and schematic image of DA, (ii) TEM images of (a) A, (b) DA25, (c) DA50, and (d) DA75, and (iii) PL spectra of T7, A+T7-THP, and DA50.

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