Controlled Self-Organization of Gold Nanorods in Aqueous Dispersion via Surface Modification with Oligo(ethylene glycol)-Based Ligands

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Gold nanorods (AuNRs) exhibit highly tunable localized surface plasmon resonance (LSPR) derived from their morphological anisotropy. To leverage their anisotropic optical properties, various strategies have been explored to achieve orientation control of AuNRs in dispersion, where their rotational freedom enables dynamic responses to environmental changes or external stimuli. Such structural freedom enables control not only over orientation but also over interparticle spacing, which significantly alters LSPR characteristics through near-field coupling and gives rise to collective responses. However, achieving well-ordered AuNR assemblies in dispersion, particularly with dynamic control by external stimuli, remains challenging.
In this study, we investigated the pH-responsive self-organization of AuNRs in aqueous dispersions by tuning ligand structures. Two kinds of carboxy-terminated thiols were employed as ligands for surface modification: 16-mercaptohexadecanoic acid (MHA) with a linear alkyl chain and 20-(11-mercaptoundecanyloxy)- 3,6,9,12,15,18-hexaoxaeicosanoic acid (C11EG6) with an oligo(ethylene glycol) (OEG) chain (Figure a). MHA-modified AuNRs, denoted as **CAR1** , and C11EG6-modified AuNRs, denoted as **CAR2** , were dispersed in water at 70 wt% and analyzed by small-angle X-ray scattering (SAXS).
CAR1 showed no scattering peaks assignable to ordered structures, whereas **CAR2** exhibited multiple peaks consistent with a hexagonal arrangement (Figure b). This difference is attributed to the OEG chains in C11EG6, which form a robust hydration layer [1] that suppresses irreversible aggregation and provides uniform surface coverage [2], thereby enabling uniform electrostatic repulsion from terminal carboxy groups. Furthermore, SAXS measurements under varying pH conditions revealed that **CAR2** formed highly ordered structures under strongly basic conditions (pH 12), where ten distinct sharp diffraction peaks assignable to a hexagonal structure were observed. These results suggest that the ionization state of surface ligands governs the self-organization of AuNRs in dispersion, highlighting the potential of ligand design for plasmonic nanoparticles in next-generation optical systems.

Keywords:
Organic-inorganic hybrid materials, Gold nanorods, Self-organization, Oligo(ethylene glycol)-based ligands, pH-responsiveness

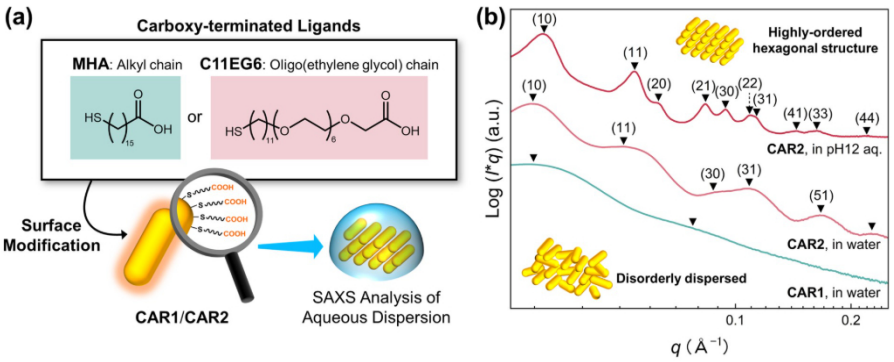

Figure. (a) Molecular structures of two ligands and a schematic illustration of this study; (b) SAXS patterns of CAR1 and CAR2 dispersed in water at 70 wt% and that of CAR2 dispersed at pH 12.

References:

[1] M. Sayin et al., *Phys. Chem. Chem. Phys.* 2020, **22** , 8088-8095. [2] E. Pellizzoni, et al., *J. Colloid Interface Sci.* 2022, **607** , 1373-1381.