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Fractal-like Self-Assembly of Oligo(*p*-phenylene vinylene) Capped Gold Nanoparticles

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Hybrid materials containing inorganic nanoparticles and π-conjugated polymers have unique properties, and application of these materials in optoelectronic devices is being explored intensively.[1] The internal organization of such materials on the nanometer-length scale is often crucial in determining the desired properties.[2] An attractive approach to control this organization involves self-assembly. For π-conjugated molecules[3] and inorganic nanoparticles[4,5] themselves, routes to self-assembly have been established. For hybrid nanoparticles consisting of an inorganic core functionalized with π-conjugated oligomers, self-organization has hardly been explored.[6] Here, we report on the reversible self-assembly[7] of oligo(*p*-phenylene vinylene) (OPV) functionalized gold nanoparticles into fractal-like objects and show that the same principles that have been used previously to organize (dendritic) π-conjugated systems can be applied to hybrid nanoparticles.[3]

OPV−gold nanoparticle adducts (**OPV−Au**) with different gold core sizes (diameter $d_{Au} = 1.6 \pm 0.3$, 4.1 ± 0.6 nm) were obtained via standard methods.[8−10] **OPV**, an oligomer with a disulfide moiety, was synthesized in two steps using literature procedures (Figure 1).[10,11]

The interparticle aggregation of the **OPV−Au** particles with $d_{Au} = 4.1$ nm was investigated in detail. UV−vis absorption studies in toluene indicate a single, isolated species featuring a surface plasmon (SP) absorption band with a maximum at $\lambda = 525$ nm (Figure 1) and an OPV absorption band at 404 nm. Transmission electron microscopy (TEM)[10] and atomic force microscopy (AFM)[10] on samples cast from toluene confirm the presence of isolated particles, but also show some small clusters that may have formed during solvent evaporation. In *n*-butanol, however, we find that the particles self-organize into larger structures in a reversible manner. Evidence for this comes from the observation of a red-shifted SP band of **OPV−Au** in butanol with a maximum at $\lambda = 720$ nm (Figure 1). When heating the butanol solution above 80 °C, the SP band shifts back to 525 nm, a spectral position similar to that found for toluene. Upon cooling, the SP band reappears at 720 nm.[12] We ascribe the red shift to a reversible transition from nonaggregated to aggregated hybrid nanoparticles. The red shift can be interpreted in terms of the Mie scattering theory and results from coupling of the transition dipoles associated with the SP band of metal particles at close distance.[13] Our assignment is supported by dynamic light scattering (DLS) experiments that reveal the formation of spherical objects with an average diameter of 0.8 μm in butanol, which break up at a temperature above 80 °C (Figure 2a). Remarkably, the transition from aggregated to isolated hybrid particles takes place in a very narrow temperature window (~10 °C), indicating a cooperative nature for the aggregation process.

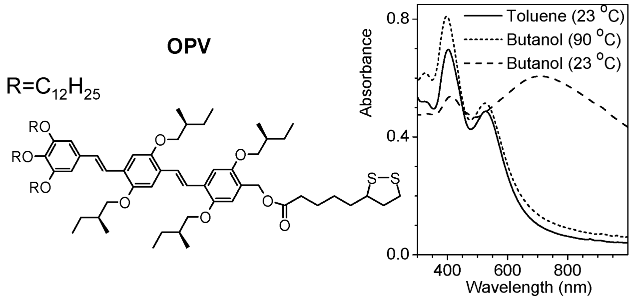

Figure 1. Chemical structure of **OPV**. UV−vis absorption of **OPV−Au** ($d_{Au} = 4.1$ nm, optical path length 1 mm, [**OPV−Au**] = 0.5 μM) in toluene and butanol.

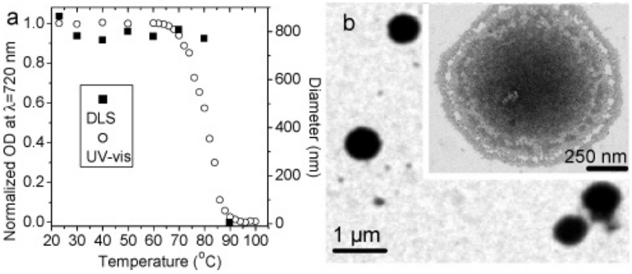

Figure 2. (a) Temperature dependence of the optical density (OD) at $\lambda = 720$ nm and diameter of the aggregates from DLS on **OPV−Au** ($d_{Au} = 4.1$ nm) in *n*-butanol ([**OPV−Au**] = 0.5 μM). (b) TEM pictures of **OPV−Au** cast from butanol ([**OPV−Au**] = 0.3 μM).

AFM investigation of a film of **OPV−Au** deposited on glass from butanol shows features of ~0.01-μm size in the phase contrast image (Figure 3A), which may be assigned to individual **OPV−Au** particles. When zooming out, the particles remain visible in the phase image (Figure 3B), but the corresponding height image shows that the particles are clustered into features with ~0.15-μm diameter (Figure 3C). When scanning an even larger area, it appears that the ~0.15-μm objects are grouped into super structures with a diameter of ~1 μm (Figure 3D). The latter object size is also observed with DLS. Thus, the material shows a fractal-like structure displaying limited self-similarity, featuring spherical objects with diameters on the 0.01-, 0.1-, and 1-μm length scale. Previously, we found that OPV-terminated poly(propylene imine) dendrimers self-assemble into fiberlike structures in alcohol solution.[14] This illustrates self-assembly driven by peripheral OPVs, and the difference in flexibility of the core may induce a different supramolecular architecture.

TEM on samples cast from butanol also shows aggregates with an average diameter of 1 μm (Figure 2b) composed of **OPV−Au** particles, in agreement with AFM and DLS measurements. The edge-to-edge distance of the gold cores in the cluster is 3.3 ± 0.8 nm, implying intercalation of the **OPV** ligands.[10] At higher magnification, TEM reveals that the 1-μm circular objects have an internal structure (Figure 2b). Clustering of **OPV−Au** with a typical size of 0.1 μm can be discerned at the edge of the object.

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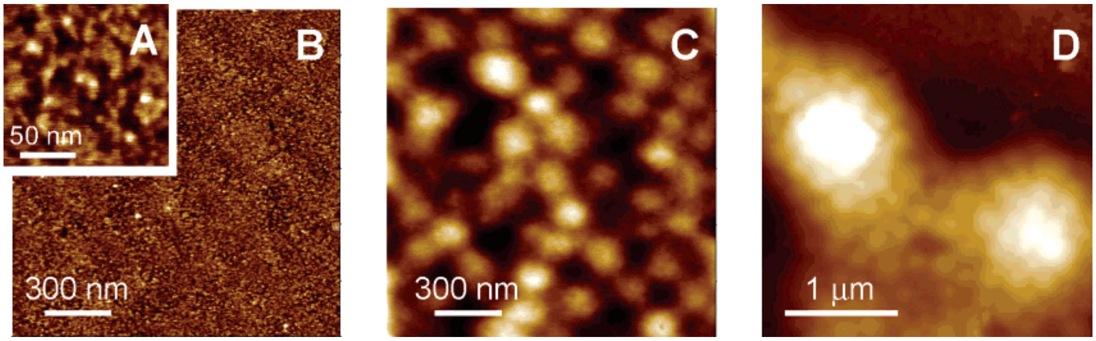

Figure 3. AFM images of **OPV−Au** ($d_{\mathrm{Au}} = 4.1$ nm) deposited on glass from butanol ([**OPV−Au**] = 0.5 μM). (A,B) Phase contrast image. (C,D) Height image.

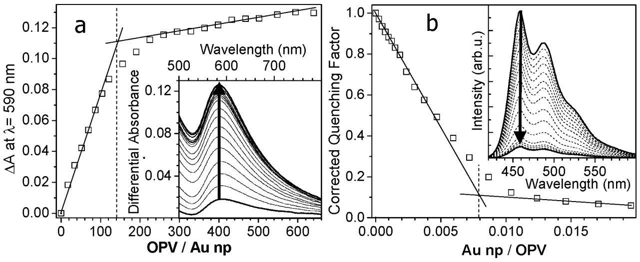

Figure 4. (a) Titration adding **OPV** to **TOAB−Au** while monitoring the differential absorbance (Δ*A*) of the SP band of the gold core induced by addition of **OPV** in toluene. (b) Titration adding **TOAB−Au** to **OPV** monitoring the **OPV** fluorescence. All experiments were carried out in toluene.

Concentration-dependent absorption measurements in combination with TEM indicate that the 1-μm-sized spheres are only formed when the **OPV−Au** concentration is above 0.2 μM.[10] At a concentration of 0.1 μM, only 0.1-μm clusters are observed that may correspond to the 0.1-μm structural subunit in the fractal-like assembly.[10] When **OPV** is replaced by 1-dodecanethiol, clustering also occurs in butanol at 0.5 μM particle concentration, but TEM shows only small clusters with 0.03-μm diameter.[10] **OPV−Au** does not aggregate in apolar solvents.[10]

Surprisingly, the 1.6-nm **OPV−Au** particles do not aggregate in butanol, and a structural difference in the organic shell may explain the size-dependent behavior.[15,16] Therefore, we have investigated the packing of the organic shell in our 1.6- and 4-nm particles using spectroscopic techniques. When **OPV−Au** particles are prepared via the ligand exchange method,[10] the stepwise functionalization of tetra-*n*-octylammonium bromide capped gold nanoparticles (**TOAB−Au**) with **OPV** can be followed with UV−vis absorption and fluorescence measurements (Figure 4a and b), revealing that approximately 1.4×10^2 **OPV**s are bound to the Au particle.[10] The area available per **OPV** on a spherical metal surface is then 49 Å^2, while the area per sulfur atom in an alkanethiol self-assembled monolayer on gold is 22 Å^2.[17] This is consistent with bidentate coordination of the **OPV** with the sulfur atoms forming a nearly close packed array.[10] For the smaller 1.6-nm core, the organic shell contains ~13 **OPV**s corresponding to an area of 63 Å^2 per **OPV** on the metal surface.[10] Combined with the stronger curvature, this implies a less densely packed organic shell, which could presumably change the driving force for aggregation.[15,16]

In summary, we have demonstrated a principle for organization of inorganic/π-conjugated nanoparticles involving self-assembly of peripheral π-conjugated ligands.

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Supporting Information Available: Detailed experimental procedures, synthesis and characterization of **OPV** and the gold nanoparticles, AFM and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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