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Ultrafast Energy Migration in Chromophore Shell−Metal Nanoparticle Assemblies

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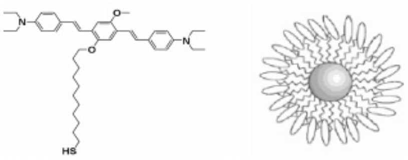
There is great interest in ligand-coated nanoparticles for a variety of sensing and imaging applications.[1] The ability to attach functional ligands, including chromophoric ligands, to nanoparticles offers opportunities to prepare multifunctional systems with a high local concentration of chromophores, and such systems could have interesting light harvesting properties.[2] Stellacci et al.[3] have reported on silver nanoparticles coated with a self-assembled shell of thiol-functionalized bis-1,4-(4-nitrostyryl)benzene chromophores, with an average of ~2000 chromophores per particle. These nanoparticles exhibited a large two-photon absorption cross section, δ, of $\sim 2.7 \times 10^{-45}$ cm^4 s, which corresponds roughly to a linearly additive contribution of individual molecules on the surface.[3] Interestingly, the chromophores on the particles exhibited little fluorescence quenching (quantum yield = 0.33 vs 0.47 for free chromophore) despite the high local concentration of the chromophore, which frequently leads to self-quenching interactions. Recently, chromophore-coated silver nanoparticles with greatly increased solubility have been synthesized,[4] and these particles are highly fluorescent ($\Phi = 0.5$), again with little fluorescence quenching. Given the high local concentration of chromophores and efficient fluorescence, we performed studies utilizing ultrafast time-resolved spectroscopic methods to probe whether interactions between chromophores could lead to energy migration on the surface of the particle.

The structure of the 11-(2,5-bis(4-(diethylamino)styryl)-4-methoxyphenoxy)undecane-1-thiol chromophore, **1**, and a schematic of the silver particle−chromophore assembly are shown in Scheme 1. From estimates based on chemical analysis and transmission electron microscopy (TEM), the number of chromophores on the particle is on the order of ~2000.

Similar to the previously examined system,[3] this silver−chromophore assembly exhibits a very large δ (1.5×10^{-44} cm^4 s) and relatively high fluorescence quantum yield of 0.42 (0.8 for the free dye) in toluene.[4] The linear absorption and fluorescence spectra of a solution of the chromophore−shell silver particles system, and the free dye[5] in dilute and concentrated solutions is shown in Figure 1. In this system, the silver core acts primarily as a center for assembly of the chromophores. We observe essentially no evidence of significant local field effects on the two-photon spectrum or peak cross section or on the fluorescence spectrum or radiative decay,[4] which may be due in part to the distance of the chromophore from the surface (about 1.5 nm,) its orientation relative to the surface, and the detuning from the plasmon resonance. The absorption and fluorescence spectra for the dilute and concentrated solutions of the free chromophore are very similar. There is not a significant shift in the spectra even when the concentration is changed by more than 5 orders of magnitude.

Scheme 1. Structure of Thiolated Chromophore **1** and Schematic of Chromophore−Silver Particle Assembly



The fluorescence intensity exhibits a linear increase as a function of the concentration of chromophores (over the range of 2×10^{-6} M to 10^{-1} M), which is consistent with weakly interacting chromophores. This behavior is in contrast to that of many other chromophore systems with highly polarizable π-electron systems that show significant spectral shifts and self-quenching at large molar concentration.[6]

To probe the excited state dynamics of the chromophore, time-resolved fluorescence upconversion measurements[7] were carried out in dilute and concentrated chromophore solutions as well as the chromophore−silver particle assembly using the second harmonic of a Ti−sapphire femtosecond laser for excitation (λ_{ex} = 400 nm). For the dilute chromophore solutions, one observes a short rise-time feature (~150 fs), as shown in Figure 2, that is similar to what has been reported previously with other distyrylbenzene chromophores.[8] For highly concentrated solutions (10^{-1} M), an additional rise-time component of 1.3 ps that is thought to be associated with dye−dye energy transfer is observed (Figure 2). The chromophore/metal particle assembly showed different dynamics with no detectable rise-time component. Comparison of this result with that of the concentrated dye suggests a much faster energy transfer time for the metal particle system. These results are consistent with a relatively dense chromophore packing, in accord with the large number of chromophores estimated by elemental and TEM analysis.[4] The different dynamics for the dye−nanoparticle assembly as compared to the diluted dye may also reflect the different solvation environment for densely packed

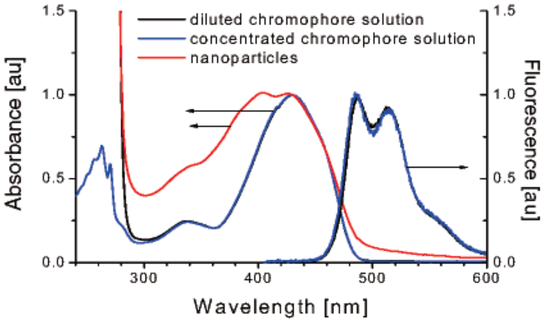


Figure 1. Normalized absorption and fluorescence spectra of silver particle assemblies (dilute) and free dye (dilute: 2×10^{-6} M and concentrated: 10^{-1} M) in toluene solution.

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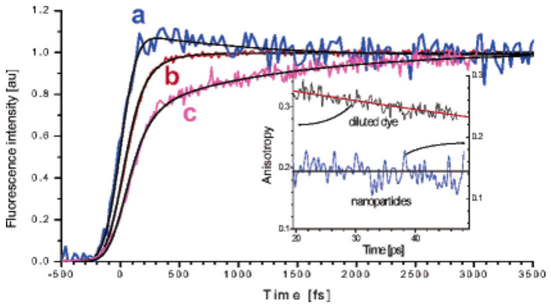

Figure 2. Time-resolved isotropic fluorescence decay of (a) chromophore−shell nanoparticles, (b) dilute, and (c) concentrated chromophore solutions in toluene (concentrations as in Figure 1). Inset: long time scale fluorescence anisotropy decays for dilute dye and chromophore−nanoparticle assembly (*Y*-axis slightly shifted for clarity).

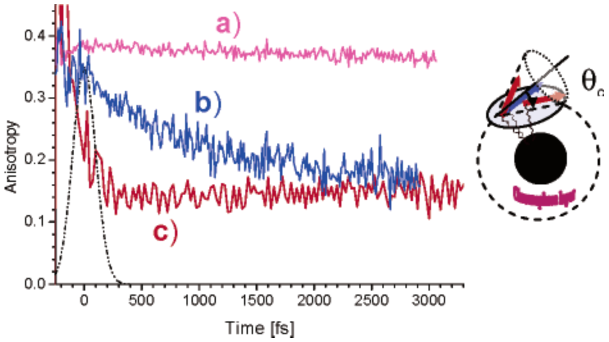

Figure 3. Fluorescence anisotropy decay of the dilute chromophore solution (a), the concentrated solution (b), and the metal particle−chromophore assembly (c). Instrument response function for fluorescence intensity (rescaled) is also shown (dash−dot).

chromophores. A small picosecond decay component is also seen in the chromophore−nanoparticle system, which indicates that a small fraction of the population of dyes undergoes a fast quenching process.

To probe possible energy transfer processes of the chromophore−particle assemblies, time-resolved fluorescence anisotropy measurements were carried out in combination with ultrafast single-color transient absorption anisotropy measurements. The dilute chromophore system shows the expected slow anisotropy decay ($\tau_{\text{rot}} \cong$ 200ps), which is due to rotational diffusion, with an initial anisotropy close to 0.4 (Figure 3). However, the highly concentrated dye solution shows a faster decay on this time scale, which may be explained by efficient self-energy transfer among the chromophores. Interestingly, the chromophore−nanoparticle assembly, with a larger local concentration of dye on the surface of the particle, shows a large decay component with an ultrafast anisotropy decay time ($\tau_{\text{np}} \leq$ 200 fs) followed by a long decay time component.

Considering the particle size and the dense arrangement of chromophores on the surface, one can essentially rule out an orientational mechanism for the ultrafast anisotropy decay for the chromophore particle assembly. The hydrodynamic volume of the single assembly was estimated to be ~435 nm^3, which leads to a reorientational time of >50 ns in toluene based on the Stokes' formula.[9,10] Given the rotational diffusion time of 190 ps for the free dye in toluene (Figure 3), it is likely that reorientational motion of dyes on the surface would be slower and thus would not contribute to the observed ultrafast anisotropy decay.

To estimate the relative dipolar orientational characteristics of the assembled chromophores, we analyzed the fluorescence anisotropy decay of concentrated chromophore solution on the picosecond time scale using the theory for randomly oriented chromophores in solution.[11] A reasonably good fit for the concentrated solution was obtained using a Förster radius of 35.3 Å, which suggests that chromophores at this high concentration remain randomly distributed, showing no significant deviations from the theory related to aggregation.[10] This is in accordance with a very weak tendency to aggregation.

In the chromophore−nanoparticle assembly, the initial depolarization time, ≤50 fs, is much faster than that in concentrated dye solution, indicating inter-chromophore energy migration between densely packed chromophores with different transition dipole orientations. Both time-resolved fluorescence anisotropy (Figure 3) and degenerate pump−probe[10] experiments showed non-zero residual anisotropy after the initial fast decay, which can be an indication of either a contribution of the emission from some unbound dye (which is polarized on this time scale) or the presence of a limited angular distribution of transition moments for energy migration in a spatially restricted domain. As we mentioned above, our experiments showed no other indications of the free dye in the sample, so we rule out this possibility.

In summary, we have shown that this chromophore−metal particle assembly has impressive two-photon properties, and the level of interaction between chromophores may be related to formation of specific geometrical domains on the metal surface. We have observed evidence for ultrafast energy migration in this chromophore shell−metal nanoparticle system, and this is of potential interest for light harvesting and sensing applications.

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Supporting Information Available: Experimental details and characterizing data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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