

## Quantum Dot on a Rope

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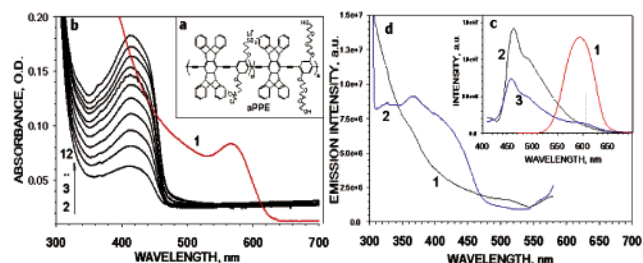
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Diversity of physical properties of nanoparticles (NPs) makes them attractive elements for the construction of new chemical assemblies. The conjugation of NPs with other building blocks such as proteins, metal complexes, carbon nanotubes, oligonucleotides, other NPs, and so forth yields supramolecular materials which display unique optical and electronic effects.<sup>1</sup> Once formed, these NP assemblies are typically fairly rigid, and the electronic coupling between the NP and other structural units of these compounds is fixed by covalent bonds. The dynamic NP systems with interunit coupling that can be modulated by an experimentalist represent an interesting chemical problem because their realization should rely on fairly weak intermolecular forces. Such systems would also open a possibility of controlled energy/electron exchange between NPs and other structural blocks, which is of importance for fundamental studies of electronic processes in NP superstructures. As well, variable coupling offers a convenient structural platform for new nanotechnological devices.<sup>2</sup> Here, we report on a novel bichromophore system constructed from a quantum dot tethered to a semiconducting polymer. The efficiency of the energy-transfer coupling between them depends on the tether extension and, therefore, can be controlled by tether-solvent interactions (polymer brush).

The NP bichromophoric system was made on the basis of the layer-by-layer assembled (LBL) films<sup>3</sup> of anionic polyelectrolyte with poly(*p*-phenylene ethynylene) backbone, aPPE (Figure 1a).<sup>4</sup> The train of conjugated bonds in aPPE acts as a "molecular wire" imparting semiconductor properties to the polyelectrolyte.<sup>5</sup> Negatively charged aPPE can be LBL assembled with positively charged polyelectrolytes to produce strongly luminescent thin films (quantum yield 15%),<sup>4</sup> such as poly(allylamine hydrochloride) PAH, (MW 70 000, Aldrich).<sup>6</sup> The gradual rise of the absorption density of aPPE peak deposited on a glass slide (Figure 1b, traces 2–12) indicates the formation of the (aPPE/PAH)<sub>*m*</sub> LBL film, where *m* is the number of deposition cycles. The assembled films exhibit strong 460 nm luminescence (Figure 1c, trace 2). NPs of CdTe stabilized with thioglycolic acid<sup>7</sup> with UV-vis absorption peak at 570 nm (Figure 1b, trace 1) and strong luminescence at 600 nm (yield 20%) were used as aPPE counterpart. aPPE emission strongly overlaps with the absorption profile of the NPs, which makes the energy transfer from the excitonic level of aPPE to the excitonic level of CdTe quite efficient.

To conjugate CdTe NPs to the (aPPE/PAH)<sub>*m*</sub> LBL film, we took advantage of the reactive groups of NP stabilizer and the polyelectrolyte matrix. PAH polycation was chosen to be an LBL partner of aPPE because it has significant amount of nonionized -NH<sub>2</sub> groups (pH 6.8). Side reactions during aPPE synthesis make it difficult to introduce amino groups into the structure of this polyelectrolyte. Fortunately, strong interdigitation of polymers in



**Figure 1.** (a) Chemical structure of aPPE. (b) UV-vis absorption spectra of CdTe NP dispersion (1) and (aPPE/PAH)<sub>*m*</sub> LBL films, *m* = 2–12 (2–12). (c) Luminescence spectra of CdTe NP dispersion (1), (aPPE/PAH)<sub>2</sub> LBL film before (2) and after (3) NP tethering. (d) Excitation spectra of CdTe NP in dispersion (1) and after PEF tethering (aPPE/PAH)<sub>2</sub> LBL film (2).

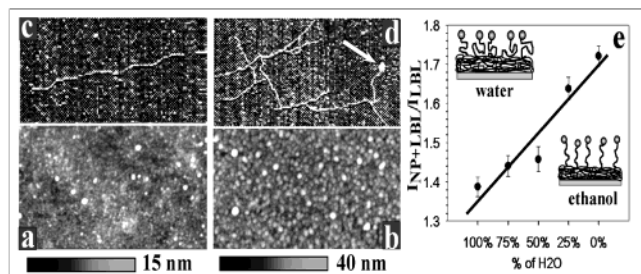
the LBL assembly<sup>3</sup> allows one to use functionalities of both polyelectrolytes after the assembly as if they belong to one polymer chain, which makes LBL films suitable for cross-linking<sup>8</sup> and uniquely convenient for surface modification reactions, which may be utilized for the attachment of quantum dots as well as other entities.

Tethering of CdTe NP with -COOH groups on their surface to -NH<sub>2</sub> functionalities of the LBL films can be accomplished by using PEG chains with reactive terminals such as *t*-BOC-NH-PEG-COO-NHS (MW 3400, Shearwater Polymers), where NHS and *t*-BOC stand for *N*-hydroxysulfosuccinimide and *tert*-butoxycarbonyl groups, respectively. Initially, the PEG tethers were attached to the polyelectrolyte film via reaction of its NHS end. The glass slides bearing (aPPE/PAH)<sub>2</sub> films were immersed for 24 h in a solution of 100 mg of *t*-BOC-NH-PEG-COO-NHS in 5.6 mL of deionized water and 1.4 mL of DMSO. This results in *t*-BOC-NH-PEG-CO-NH-(PAH) derivatization of the LBL film surface. Long reaction time and significant excess of -NHS reagent ensures virtually complete conversion of all accessible surface amino groups. After thorough rinsing with water and drying, the *t*-BOC protection of the terminal amine of PEG was removed by exposure to 10 mL of 99.5% trifluoroacetic acid for 20 min. The regenerated -NH<sub>2</sub> terminal of PEG can be conjugated to NPs via standard bioconjugation techniques. To 7.5 mL of CdTe NP solution with adjusted pH 6.5, 0.1 g (0.5 mmol) of 98% EDC and 5 mg (0.0025 mmol) of sulfo-NHS was added. Immediately after that, the PEG-derivatized slide was immersed into this solution for 2 h at 25 °C.

The evidence for successful conjugation of NP to the LBL films can be seen both in AFM images and in optical data. After the NP conjugation, the film acquires typical topographic pattern of NP monolayers (Figure 2a,b).<sup>9</sup> Particularly informative are the phase images of a rarified submonolayer of PAH. Before the modification, primarily single straight chains of the PAH can be seen (Figure 2c). After the conjugation, one can clearly see the appearance of short chains branching off the main backbone, which can be

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**Figure 2.**  $1 \mu\text{m} \times 0.5 \mu\text{m}$  AFM images of (aPPE/PAH)<sub>2</sub> LBL film before (a) and after (b) NP tethering.  $100 \text{ nm} \times 300 \text{ nm}$  phase images of PAH submonolayer before (c) and after (d) NP tethering. The submonolayer was made on Si wafers from 0.005% PAH (30 s, pH 6.8). (e) Effect of solvent composition on the 460 nm aPPE luminescence intensity with schematics of the tether extension.

attributed to PEG tethers (Figure 2d). In the end of some 50–60 nm branches (high end of the MW PEG distribution), objects with a height of 4–5 nm can be seen, which corresponds very well to CdTe NPs used here (marked by arrow in Figure 2d).

Luminescence spectra after the conjugation displays a new peak at 600 nm, identical to the emission peak of CdTe dispersions (Figure 1c, traces 1 and 3). Importantly, the excitation spectrum of CdTe-PEG-aPPE registered at 600 nm reveals a strong new band at 400 nm, which matches the absorption band of aPPE LBL films (Figure 1b, traces 2–12). This indicates that the light quanta emitted by the NP originate from the light absorption of the polymer film, which proves the presence of the aPPE → NP energy transfer process. As expected, the total emission intensity of aPPE is significantly quenched after the NP conjugation (Figure 1c, trace 3).

The average separation distance between the NP tethered to the LBL films can be changed by altering the dielectric properties of the media which affects the coiling of the PEG “rope”: it becomes more extended in “good” solvents and shorter in “bad” ones. Since the efficiency of dipole–dipole coupling in the Förster resonance energy transfer exponentially falls with the increase of interchromophor distance, the conformation of the PEG tether should strongly alter the energy-transfer coupling between aPPE and CdTe NPs. This may be observed by varying the composition of, for instance, a water–ethanol mixture and monitoring the concomitant change of emission intensity. A corresponding experiment was carried out with a glass slide tightly fitted diagonally into a  $1 \text{ cm} \times 1 \text{ cm}$  cuvette at a ca.  $40^\circ$  to the incident beam. Different water–ethanol mixtures were sequentially injected into the cuvette. The gradual increase of the luminescence intensity of aPPE was observed, when water was replaced by ethanol (Figure 2e). The plot in Figure 2e shows 460 nm emission intensity in the tethered system divided by the luminescence at the same wavelength for (aPPE/PAH)<sub>2</sub> samples without NPs obtained under the same conditions. This was done to eliminate possible media influence on the intrinsic photophysics of aPPE and to elucidate tether effects. Ethanol is a better solvent for PEG than water,<sup>10</sup> and therefore, its chain acquires progressively more extended conformation in ethanol-rich solvent compositions. Concomitantly, the energy-transfer quenching of aPPE luminescence is reduced, which shows as 400 nm luminescence enhancement (Figure 2e). The tether extension is totally reversible, and the original luminescence intensity can be recovered by the similar solvent replacement back to water. Discussing the nature of the observed optical effects, two additional points need to be made. (1). The influence of media on the through-space dipole coupling is not responsible for observed

luminescence changes because it would have led to stronger quenching in low dielectric constant environment (ethanol), provided that the interchromophor separation distance remains constant. (2). Besides PEG solvation, solvent-related changes in the Coulombic interaction between highly charged NPs and LBL film surface and the degree of ionization of the chromophors are also convoluted into the tether extension. High dielectric-constant media, such as water, should reduce the electrostatic forces while increasing the degree of ionization of the surface groups. Therefore, both factors partially compensate each other in the experiments described. The presence of long-range Coulombic interaction, however, affords the realization electrostatic-field-modulated optical coupling when CdTe-PEG-aPPE system is assembled on an electrode.

Thus, CdTe-PEG-aPPE is an example of an organized NP system with tunable optical coupling, which is gradual and experimentally straightforward. Since the distance control is not fixed by the synthetic protocol as in molecular systems with constant-length spacers,<sup>11</sup> the coupling can be modulated in situ. This is an essential quality for various NP-based and hybrid molecular devices, for which spatial control translates into a higher level of sophistication. It is also necessary to point out that protein-oriented chemistry of PEG with reactive terminals affords a wide variety of polymer chain configurations, which makes possible the preparation of diverse NP superstructures.

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- 0.01 mg aPPE dissolved in 5 mL of DMF was diluted 10 times with deionized water. Substrates were sequentially immersed into aqueous solution of 0.5% PAH in 1.5 M NaCl, pH 6.2, and aPPE, pH 6.8, for 5 min each. Between polyelectrolyte baths, the substrates were rinsed with deionized water for at least 20 s.
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