

Polyfluorene Nanoparticles and Quantum Dot Hybrids via Miniemulsion Polymerization

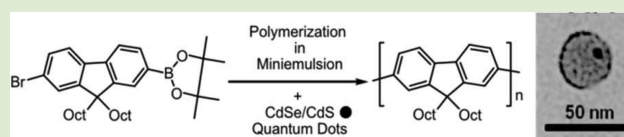
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Supporting Information

ABSTRACT: Suzuki–Miyaura polycondensation of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-bromo-9,9-dioctylfluorene in aqueous miniemulsion with only two equivalents of NaOH as a base yields colloidally stable nanoparticles of polyfluorene with M_n ca. 2×10^4 g mol⁻¹ and particle sizes of 40–85 nm, depending on the surfactant concentration.

Polymerization in the presence of CdSe/CdS core/shell quantum dots affords hybrid nanoparticles of nonaggregated quantum dots, in particular nanoparticles composed of a single quantum dot embedded in a polyfluorene shell. Microphotoluminescence spectroscopy on single hybrid particles reveals an enhanced photostability of the quantum dots and indicates an efficient Förster energy transfer from the polyfluorene shell to the quantum dot.



Luminescent nanoparticles based on conjugated polymers feature large absorption cross sections, high fluorescence intensities, photostability, and toxicological safety. This combination compares favorably to other materials. Thus, conjugated polymer nanoparticles have emerged as luminescent probes.^{1–6} They are currently studied, for example, in live biological imaging^{7–9} or sensors.^{10–12} Most frequently, studies of such luminescent particles have employed polyfluorene as the conjugated polymer. These particles were generated by postpolymerization methods, namely, secondary dispersion by emulsification of a polymer solution in a water-insoluble solvent^{13,14} or a “reprecipitation” approach, in which a dilute solution of polyfluorene in a water-soluble organic solvent is injected manually into excess water. Here, we report a different approach, the direct synthesis of polyfluorene dispersions by Suzuki–Miyaura cross-coupling polycondensation in miniemulsion. This approach is further elaborated to the preparation of well-defined hybrid semiconductor quantum dot/polyfluorene particles, which are exceptionally suited for quantum optics experiments with single nanoemitters.^{15–19}

Miniemulsions most commonly employ anionic surfactants, like sodium dodecyl sulfate (SDS), to stabilize the particles being formed. However, such a stabilization is very sensitive to the ionic strength of the aqueous phase.²⁰ In Suzuki polycondensation protocols, an excess of base of up to 30 wt % concentration of the aqueous phase²¹ is not unusual to yield high conversions and thus high molecular weights. According to the established mechanistic picture, the catalytic reaction requires two equivalents of base, one for the metathesis of the organopalladium halide species to the organopalladium hydroxide or alkoxide species and another one for the quaternization of the boronic acid.^{22,23} Therefore, we employed a bimolar excess of NaOH only with respect to the monomer. Miniemulsions were generated by ultrasonication of a mixture of a basic (0.06 wt % NaOH, 14 mg) 1 wt % aqueous SDS

solution, with a toluene solution of the bifunctional AB-monomer 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-bromo-9,9-dioctylfluorene, 1 mol % [Pd(PPh₃)₄], and hexadecane as a hydrophobe as the oil phase. Heating to 85 °C for 20 h resulted in polymerization to afford a stable, virtually transparent dispersion. The number average particle sizes determined by dynamic light scattering (DLS) are typically on the order of 40 nm. GPC vs polystyrene standards revealed a polymer molecular weight (M_n) of ca. 2.3×10^4 g mol⁻¹. This compares to molecular weights obtained with standard Suzuki polymerization protocols,²⁴ indicating that very low base concentrations can sufficiently promote the Suzuki polycondensation in miniemulsion.

Higher amounts of base (50 mg of NaOH, 0.2 wt % aqueous solution, 7-fold excess over monomer) did not afford stable dispersions, underlining the need of appropriately chosen reaction conditions compatible with colloidal stabilization. Only a 1:1 molar ratio of base:monomer (7 mg of NaOH) yielded dispersions with a polymer molecular weight (M_n) of 1.9×10^4 g mol⁻¹, indicating that one equivalent of base is still adequate for an efficient catalysis, irrespective of the aforementioned mechanistic considerations. At this low base concentration, particles with a more uniform shape (Figure S1D in Supporting Information) are formed. This can be related to a better emulsion and particle stability at this lower concentration of added NaOH electrolyte. In the absence of any NaOH, no polymer was obtained, confirming the crucial role of the base for the polymerization.

Steric stabilization is less sensitive than electrostatic stabilization toward additional electrolytes, like the added

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NaOH base. To this end, substitution of the anionic SDS for the nonionic surfactants Tween 80 or Span 80 afforded polyfluorene nanoparticles which precipitated within a few days. By comparison, SDS stabilized nanoparticles were stable for months or longer. Even at a low SDS concentration of 0.08 wt %, stable dispersions with particle sizes of 85 nm were obtained (Table 1). As expected, particle sizes decrease with

Table 1. Effect of Surfactant Concentration on Particle Size and Molecular Weight in Suzuki Miniemulsion Polymerizations^a

entry	amount of SDS	particle size ^b	M_n^c	M_w/M_n^c
1	20 mg	85 nm	1.3×10^4	2.1
2	50 mg	70 nm	9.0×10^3	2.5
3	125 mg	55 nm	1.7×10^4	2.3
4	250 mg	39 nm	2.3×10^4	2.5

^aReaction conditions: 100 mg of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-bromo-9,9-dioctylfluorene, 1 mol % $[\text{Pd}(\text{PPh}_3)_4]$, 0.05 mL of hexadecane, 1 mL of toluene, 25 mL of H_2O , 14 mg of NaOH, 2 min ultrasonication, and 20 h at 85 °C. ^bNumber average particle size determined by DLS ^cDetermined by GPC in THF vs polystyrene standards.

increasing surfactant concentration. This effect goes along with an increase in polymer molecular weight (Table 1). It can be related to a more efficient reaction between the various polar and apolar reagents with decreasing droplet size and increasing aqueous–organic interface, resulting in a higher degree of functional group conversion. Particle sizes from transmission electron microscopy (TEM, Figure 1 and Figure S1, Supporting Information) agree reasonably well with DLS results.

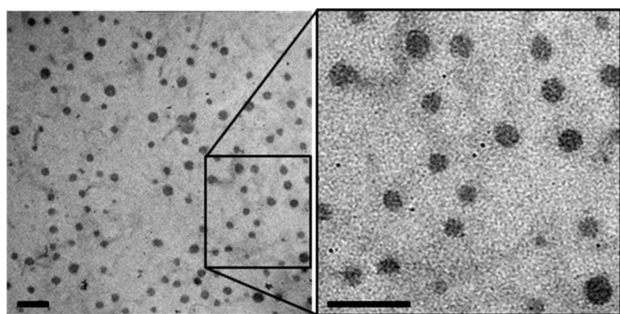


Figure 1. Transmission electron micrograph of polyfluorene nanoparticles prepared by miniemulsion polymerization (0.06 wt % = 2 equiv of NaOH and 1 wt % aqueous SDS). The scale bars correspond to 100 nm.

Fluorescence spectroscopy revealed the bright blue luminescence of the polyfluorene dispersions to be composed of three distinct peaks, corresponding to the 0–0 electronic transition band and the first and second vibronic side bands. As expected, the emission spectrum is red-shifted (by ca. 20 nm) by comparison to solution spectra of the same polymer (Figure S2, Supporting Information). Enhanced inter- and intrachain interactions in the solid state by comparison to solutions are often observed to promote energy transfer to lower energy chromophores in conjugated polymer particles.^{25,26} Likely more relevant here, polyfluorene can assume a metastable β -phase morphology when processed from toluene which goes along with a red-shift of the magnitude observed.^{27,28} Typical fluorescence quantum yields for the particle dispersions amount

to $\Phi \approx 40\%$, which is remarkably high for conjugated polymer nanoparticles.^{5,6}

Miniemulsion processes are uniquely suited for the preparation of highly disperse hybrid materials.^{29,30} Hybrids of conjugated polymers with inorganic semiconductors are of broad interest due to charge and energy transfer phenomena between the phases.³¹ This fact is underlined by Chiu's recent study of poly[(9,9-dioctylfluorene-2,7-diyl)-*co*-4,7-benzothiadiazole] (PFBT)/CdSe quantum dot hybrid nanoparticles. These particles, generated by a postpolymerization procedure, contained multiple (ca. 30) quantum dots per particle.³²

Suzuki polycondensation in the presence of core/shell CdSe/CdS quantum dots in the oil phase along with the monomer, catalyst, and hydrophobe afforded stable dispersions of hybrid particles (cf. Supporting Information for details). The progress of the reaction can be monitored by illumination with UV light. Upon heating the miniemulsion to the polymerization temperature, the red fluorescence of the quantum dots is rapidly dominated by the blue fluorescence of the forming polyfluorene. TEM (Figure 2) reveals the quantum dots to be

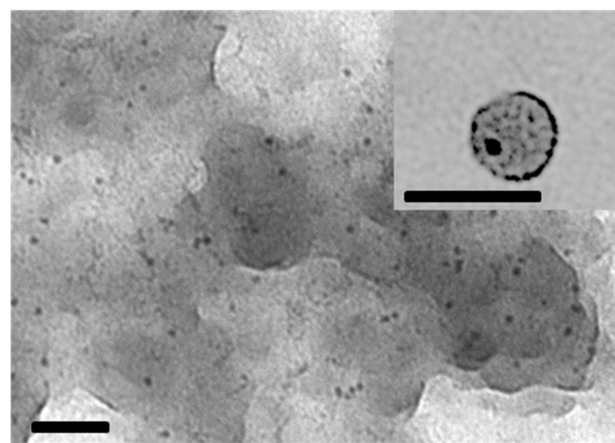


Figure 2. Transmission electron micrograph (TEM) of polyfluorene/quantum dot hybrid nanoparticles. Inset: individual core/shell hybrid particle (in a TEM sample prepared from a dilute dispersion). The scale bars correspond to 50 nm.

dispersed in the polymer particles in an isolated and nonaggregated way. This finding is remarkable since aggregation of quantum dots is a notorious problem in the preparation of hybrid materials in general and during polymerization steps in particular.^{33,34} Nonetheless, this miniemulsion polymerization procedure provides access to hybrid particles containing an individual quantum dot, as shown in the inset of Figure 2.

For example, such particles enable the exploration of single few-fermion systems having a restricted, electron-donating surrounding. To this end, we used CdSe/CdS quantum dots with high optical quality synthesized similar to a known procedure (cf. Supporting Information),³⁵ which were incorporated into hybrid particles with a polyfluorene shell by the miniemulsion procedure. Single hybrid particles were studied at room temperature and in air using a microphotoluminescence setup. To ensure the observation of single particles, a highly diluted solution of quantum dot/polyfluorene hybrid particles in water was spincoated on a quartz glass substrate pre-cleaned in plasma. Exciting the sample with a frequency-doubled Nd:YAG laser at a wavelength of 532 nm, we observed different

signals depending on whether the polyfluorene particle was loaded with a nanoemitter or not. Empty particles showed a broad red emission (Figure 3(a)) that can be assigned to the

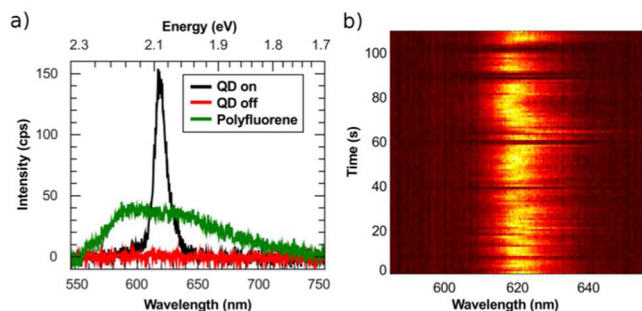


Figure 3. (a) Emission spectra of a hybrid quantum dot/polyfluorene particle containing a quantum dot in an “on” state (black) and in an “off” state (red) and of an empty polyfluorene particle (green). (b) Time trace of a single quantum dot/polyfluorene particle excited at 532 nm.

low-energy tail of the polyfluorene spectrum passing through the long pass filter at 575 nm. For hybrid particles, we observed the typical narrowband emission and blinking behavior of a single quantum dot. Figure 3(b) shows the spectrally resolved time evolution of the luminescence of a single quantum dot embedded into a polyfluorene shell. The extracted on and off state spectra are shown in Figure 3(a). In the on state one can see a clear narrow peak emission without any polyfluorene background. The emission of the shell is suppressed via an effective Förster energy transfer (also cf. Figure S3, Supporting Information) to the dot which was observed before in ensemble systems.³² In the off state of the quantum emitter, this energy transfer remains effective, but the recombination channel in the quantum dot is nonradiative, leading to a completely dark particle. Additionally, the embedding of the nanocrystals leads to a higher stability against photochemical oxidation. That is, the incorporation of quantum dots into polyfluorene particles leads to well-protected quantum systems having a functionalized electron-donating surrounding. It is worth noting that the quantum dots do not lose their colloidal nature in terms of single addressability and manipulability and that no broad band emission hinders their use for quantum optical experiments.

In conclusion, Suzuki–Miyaura polycondensation in mini-emulsion is a viable route to synthesize polyfluorene nanoparticles. The utilization of a sufficient, but otherwise low, amount of base was found to be critical. Strongly fluorescing nanoparticles of polyfluorene with a molecular weight exceeding 10^4 g mol⁻¹ are obtained. The versatility of this approach is demonstrated by the preparation of hybrid nanoparticles which contain single inorganic semiconductor quantum dots. Optical studies showed that the shell material provides protection and functionalization without any disturbing luminescence. This fact makes these CdSe/CdS/polyfluorene core/shell particles promising systems for quantum optics.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details of synthetic procedures, characterization data, and supplemental figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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