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Morphologically induced polychromism of MEH-PPV nanoparticles prepared using amphiphilic comb-polymer as encapsulation matrix

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ABSTRACT

Control over the photophysical properties of aqueous dispersions of conjugated polymers is of interest for biosensing and bioimaging applications and of paramount importance in the fabrication of optoelectronic devices. We demonstrate that an amphiphilic comb-polymer obtained from a poly(maleic anhydride-*alt*-1-octadecene) precursor can be used as effective transfer agent to bring hydrophobic poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-1,4-phenylenevinylene] (MEH-PPV) from the organic to the aqueous phase. Both the reprecipitation and miniemulsion methods results in MEH-PPV dispersed in water. The reprecipitation method results in bathochromically shifted emission relative to the emission of MEH-PPV in tetrahydrofuran. However, the miniemulsion method results in a hypsochromic shift in the emission of MEH-PPV relative to the emission of the polymer in chloroform.

1. Introduction

Aqueous dispersions of hydrophobic conjugated polymers are of interest for bioimaging [1–4] and biosensing [5] applications, and for the fabrication of optoelectronic devices [6]. To this end, the polymers can be polymerized directly in water [7] or a presynthesized polymer can be transferred to aqueous medium via the reprecipitation [8] or miniemulsion methods [9,10]. Reprecipitation of conjugated polymers in water may lead at low concentrations to dispersed collapsed polymer chains; however, such dispersions are highly unstable. To stabilize the hydrophobic conjugated polymers in water a surfactant, or a transfer matrix, is often used, such as sodium dodecyl sulfate [11], short linear PEG chains [1,12], modified lipids [13,14], or block copolymers of varying chemical composition and block length [4,15,16].

The optical properties of conjugated polymer (CP) aqueous dispersions are primarily controlled by the chemistry of the luminescent polymer defining the energy levels of the ground and excited states. Nonetheless, polymer chain conformation and morphology are also largely responsible for the polymer photophysical properties in solution and in the solid state. Indeed, the absorption and emission spectra of CPs have been shown to exhibit bathochromic and hypsochromic shifts depending on the solvents [17–19] or on the type of polymeric matrix [20] and degree of aggregation [20,21] in thin films, with evidence for memory of the solution conformation geometry [17,22,23]. Intrachain and interchain interactions influencing the ground and excited electronic states, effective conjugation lengths and therefore chromophore sizes, and concomitant energy transfer pathways were often invoked to explain shifts in the optical spectra for conjugated polymer nanoparticles [24].

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In this contribution, we demonstrate that an amphiphilic comb-polymer obtained from a poly(maleic anhydride-*alt*-1-octadecene) (PMAOD) precursor serves as an effective agent in the preparation of stable aqueous dispersions made of poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-1,4-phenylenevinylene] (MEH-PPV). The polymeric amphiphile is shown to effectively transfer MEH-PPV into water yielding optically clear and stable aqueous dispersions on the sub-100 nm lengthscale. The choice of the phase transfer protocol results however in morphologically induced polychromism. While the reprecipitation method from a solvent that is miscible with water leads to a bathochromic shift of the emission, we report an unusually large hypsochromic shift in the fluorescence emission and long fluorescence lifetime of MEH-PPV transferred to water from chloroform *via* a miniemulsion method.

2. Experimental

2.1. Materials

The conjugated polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-1,4-phenylenevinylene] (MEH-PPV) was obtained from American Dye Source or synthesized in the lab. In general, a solution of potassium *tert*-butoxide in tetrahydrofuran (THF) (5 mL, 1.0 M) was added into 20 mL anhydrous THF in 100 mL round bottom flask under N_2 atmosphere. Next, a solution of α,α′-dibromo-2-methoxy-5-(2-thylhexyloxy) xylene (506 mg, 1.2 mmol) in anhydrous THF (20 mL) was added drop-wise. Above mixture solution was stirred for 24 h at room temperature. The reaction was quenched by pouring the solution into rapidly stirred methanol and the resulting polymer precipitate was collected by filtration. The polymer was further purified by two additional precipitations from THF into methanol and dried under reduced pressure to give 150 mg of MEH-PPV (50%). ($M_n = 2 \times 10^5$ g/mol, PDI = 2). Poly(maleic anhydride-*alt*-1-octadecene) (PMAOD) was purchased from Sigma–Aldrich. Anhydrous THF and chloroform ($CHCl_3$) were obtained from Merck. Milli-Q water (18 MΩ) was used in all the experiments for aqueous solution.

2.2. Preparation of MPP1

MPP1 was prepared using a modified reprecipitation protocol found in the literature [8]. Equal amounts of MEH-PPV and PMAOD were co-dissolved in 5 mL THF to form a 0.01 mg/mL solution. The solution was then added drop wise to 10 mL of a 0.01 M sodium hydroxide solution (pH = 10) during probe ultrasonication (Sonics Vibracell ultrasonic processor) at 9.5 W for 4 min. The solution was further ultrasonicated for 10 min at 15 W. After sonication, the homogenous solution was transferred to a round bottom flask to evaporate THF using rotary evaporator resulting in an optically clear MPP1 aqueous solution, which was then stored in glass vials in the dark.

2.3. Preparation of MPP2

MPP2 was prepared using a modified miniemulsion protocol found in the literature [9,10]. PMAOD was first dissolved in 10 ml of a 0.01 M sodium hydroxide solution (pH = 10) at a concentration of 0.005 mg/mL. An ultrasonic probe was immersed into the solution and a 0.01 mg/mL solution of MEH-PPV in $CHCl_3$ was added drop wise during ultrasonication at 9.5 W for 4 min. The solution was further ultrasonicated for 10 min at 15 W. The resulting microemulsion was transferred to a round bottom flask to evaporate $CHCl_3$ using a rotary evaporator resulting in an optically clear MPP2 aqueous solution, which was then stored in glass vials in the dark.

2.4. Characterization methods

The UV–visible absorption spectra of MPP1 and MPP2 were obtained using a Shimadzu UV-3150 spectrometer and the emission spectra were acquired using a Shimadzu RF-5301PC spectrophotometer. The fluorescence emission quantum yields were obtained by measuring the fluorescence emission relative to emission of a dye fluorescein (Sigma–Aldrich) as the standard (QY_{st} = 95%, 0.1 M NaOH). Quantum yield was computed using the following equation:

$$QY_s = \left(\frac{Abs_{st}}{Abs_s}\right) \times \left(\frac{n_s^2}{n_{st}^2}\right) \times \left(\frac{I_s}{I_{st}}\right) \times QY_{st} \qquad (1)$$

where *Abs* is the absorbance, *n* is the refractive index of the solvent, *I* is the integrated area under the fluorescence emission spectra, and the subindices *s* and *st* correspond to the sample and the standard, respectively. Transmission Electron Microscopy (TEM) was performed using a Philips CM300 FEG. For TEM measurements, a droplet of the MPP1 and MPP2 solutions was placed onto carbon coated copper grids and dried in vacuum. The average particle size and size distribution were determined by dynamic light scattering (DLS) with a particle size analyzer (90 Plus, Brookhaven Instruments Co., USA) at a fixed angle of 90° at room temperature.

For AFM measurements, dilute solutions were drop-casted onto clean glass cover slips and dried in air. Topography imaging was performed with a Veeco Bioscope II Atomic Force Microscope, equipped with a Nano Scope IIIa controller, in the tapping mode using standard single beam silicon cantilevers with a nominal spring constant of 42 nN/nm (Nanosensors, Germany). All AFM experiments were performed at ambient conditions in air.

2.5. Sonodegradation of MEH-PPV

Sonodegradation testing was performed by dissolving the same amount of MEH-PPV as used during the preparation of MPP2 in chloroform and sonicating the solution for 20 min at 15 W. Fluorescence spectra of MEH-PPV were taken before and after sonication for comparison.