

Controlling Intermolecular Interactions, Optical Property, and Charge Transport in Conjugated Polyelectrolytes for Applications in Opto-electronic Devices

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Introduction

Conjugated polymers are materials that combine the optical and electrical properties of semiconductors with the mechanical properties of plastics. The emission color and electronic properties can be controlled by molecular structure. In recent years, a new class of conjugated polymers, *charged conjugated polymers or conjugated polyelectrolytes (CPs)*, has reported by several research groups. The charged CP has a hydrophobic conjugated backbone and anionic or cationic side groups. Therefore, these polymers are soluble in water and polar solvents such as methanol, dimethylformamide (DMF), and dimethylsulfoxide (DMSO). CPs have been used mainly as an optical component for the amplification of fluorescent biosensors [1] and recently there are few reports using charged CPs as electron transporting layers in multilayer polymer LEDs [2] and as an active layer in polymer solar cells [3] and light-emitting electrochemical cells (LECs) [4]. Because of their solubility in polar solvents, it is possible to use CPs in combination with neutral, organic soluble, conjugated polymers to fabricate multilayer polymer LEDs by alternating spin-coating techniques. Thus, understanding the polymer conformation in solution, polymer photophysics, and charge transport properties should aid in improving the performance of opto-electronic devices. In this work, we provide a straightforward anion exchange method and characterization procedure and use the resulting materials to examine how the molecular properties of different counteranions (CAs) affect the solid state photoluminescence (PL) quantum yields, the nanoscale charge transport properties, and the aggregation of the chains in solution. We will take advantage of a typical cationic CP framework, namely poly[(9,9-bis(6'-N,N,N-trimethylammonium)hexyl)fluorene-alt-4,7-(2,1,3-benzothiadiazole)] (PFBT-X, where X corresponds to the charge compensating anion, see Figure 1), as the subject of our studies.

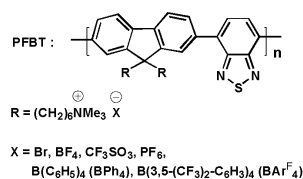


Figure 1. Chemical structures of the polymer and counteranions used in this work.

Experimental

The synthesis of PFBT-Br was adapted from the literature [5].

General anion exchange procedure. Poly[(9,9-bis(6'-N,N,N-trimethylammonium bromide)hexyl)fluorene-alt-4,7-(2,1,3-benzothiadiazole)] (PFBT-Br) 56 mg (0.075 mmol in repeat units) was dissolved in 10 mL methanol. Subsequently, a solution of the corresponding salt (0.45 mmol) in 10 mL water and/or methanol was added. The mixture was stirred for two days at room temperature. After removal of methanol under reduced pressure, deionized water was added several times to wash the residue. The overall procedure can be repeated until the majority of the bromide is removed. Finally, the resulting polymer was dried under vacuum. The anion exchange was confirmed by X-ray photoelectron spectroscopy.

Scanning probe measurements. All measurements were done under ambient conditions and in the dark using a commercial scanning probe microscope (MultiMode equipped with Conducting Atomic Force Microscopy, C-AFM, module and the Nanoscope Controller IIIa, Veeco Inc.). Platinum-coated Si tips with spring constant of 0.2 N/m and the tip radius of 25 nm were used.

Results and discussion

Table 1. Summary of absorption and PL spectra and the PL quantum yield, Φ , of PFBT-CA in methanol solutions and films.

CA	MeOH			Film		
	UV	PL		UV	PL	
	λ_{abs} (nm)	λ_{PL} (nm)	Φ (%)	λ_{abs} (nm)	λ_{PL} (nm)	Φ (%)
Br ⁻	446	568	29	467	574	5
BF ₄ ⁻	444	562	31	449	570	8
CF ₃ SO ₃ ⁻	451	565	34	463	578	12
PF ₆ ⁻	443	564	29	449	574	11
BPh ₄ ⁻	449	568	28	460	570	15
BArF ₄ ⁻	450	563	36	457	560	41

For both the solutions and films, the PL quantum yield increases as large CAs are used. More pronounced changes occur in the Φ s of the films, where values span from 5% (Br⁻) to 41% (BArF₄⁻). These solid state measurements involved examination of films spun from methanol, optical excitation at 364 nm and collection of emission using an integrating sphere. The most plausible explanation is that the size of the CA modulates the separation between polymer chains, thereby reducing the extent of PL quenching by the aggregates. The hole mobility is $9.4 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ for PFBT-BArF₄⁻ and $9.4 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ for PFBT-Br. More intimate chain contacts can account for the increased mobility for PFBT-Br, relative to PFBT-BArF₄⁻. The CAs are useful not only for modulating optical properties and charge mobility, but also for changing the charge injection barriers.

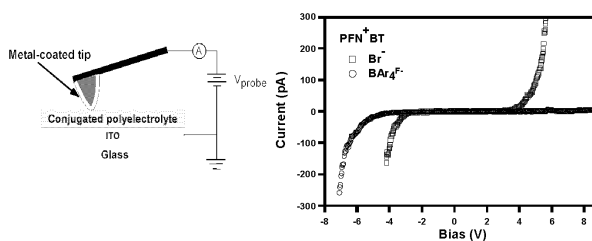


Figure 2. (Right) Representative I-V curves for PFBT-Br (black) and PFBT-BArF₄ (blue) and (left) a schematic of C-AFM experimental setup.

Conclusions

In summary, a simple protocol is provided for exchanging CAs in conjugated polyelectrolytes. This method was demonstrated with PFBT, but should prove equally effective for other cationic and anionic conjugated polyelectrolytes. Examination of the effect of CAs on the optical, charge transport, and aggregation properties of PFBT shows that the solid-state PL quantum yield values and the charge mobilities can be varied by close to an order of magnitude. It is note worthy that improvements in emission output in the solid-state could impact the types of technological applications of conjugated polyelectrolytes, for example their use as the emissive layers in organic LEDs and the fabrication of more efficient single component LECs. For applications requiring high charge mobility such as ETL or HTL in LEDs, field effect transistors or photovoltaic devices, PFBT-Br should prove more useful than PFBT-BArF₄.

References

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