



Cationic Fluorene-Thiophene Diblock Copolymers

Abstract

Water-soluble conjugated copolymers are currently of considerable interest for applications in areas such as fluorescent chemical and biological sensors or components for optoelectronic systems. We have focused on novel cationic conjugated block copolymers involving fluorene and thiophene units, which have been synthesised in three steps. In the first step, monobromo terminated poly(3-bromohexylthiophene) Br-P3BrHT was prepared with a mean average molecular weight ca. 10 000 in a protocol first described by McCullough et al^[1].

The second step involves a Suzuki-type cross coupling of 2-bromo-9,9-bis(2-ethylhexyl)fluorene-7-boronic ester using Pd(PPh₃)₄ as a catalyst and Br-P3BrHT as a macromolecular end-capper^[2]. The number average molecular weight of the final diblock copolymer **P1** was ca. 18 000, giving ca. 8 000 as the molecular weight of the polyfluorene segment. The final step in synthesis of the cationic copolymers **P2** and **P3** involved quaternization of the bromoalkyl functions of the non-ionic precursor with trimethylamine^[3] or pyridine.

Synthesis + UV/Vis and PL Spectra

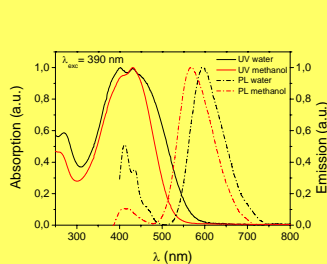
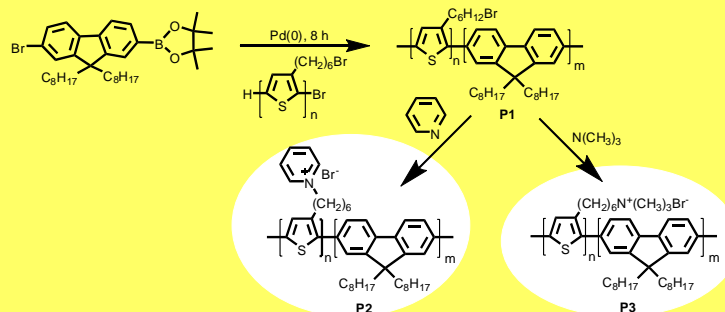


Fig. 1: UV/Vis and photoluminescence (PL) spectra of the block copolymer **P3** in water and methanol.



Scheme 1: Structure and reaction scheme of the polyfluorene-polythiophene block copolymer **P1** and polyelectrolytes **P2** and **P3**.

Atomic Force Microscopy

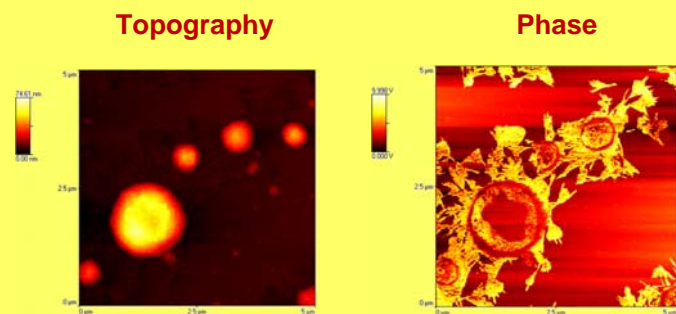


Fig. 2 and 3: Tapping-mode atomic force microscopy (AFM) images of drop-cast thin layers of **P2** onto a glass slide from methanol (0.08 mg/ml). (left: topography; right: phase).

Addition of Surfactant

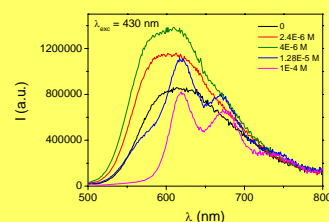


Fig. 4: Emission spectra of the ionic polythiophene blocks of **P3** for the addition of sodium dodecyl sulfate (SDS) to aqueous solutions of **P3** (polymer concentration: 2×10^{-6} M).

Polarity Effect

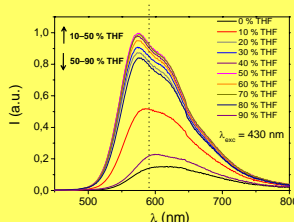


Fig. 5: Normalised fluorescence spectra of **P3** (polymer concentration: 2×10^{-6} M) in aqueous solution and in 10, 20, ... 90 % THF mixtures.

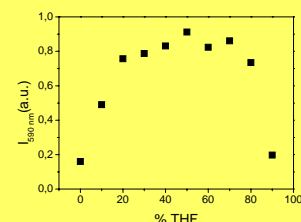


Fig. 6: Fluorescence intensity at emission maximum of **P3** (polymer concentration: 2×10^{-6} M) as a function of THF-water composition.

Conclusions

- Cationic, water-soluble fluorene-thiophene diblock copolymers have been synthesised and its spectral behaviour studied.
- The compounds are weakly fluorescent in water but more strongly emissive in organic solvents such as methanol, THF and acetone.
- Solvatochromic changes both in emission and absorption may be attributed to changes in the polythiophene conformation and aggregation.
- With anionic surfactants, i. g. SDS, marked spectral changes are seen that reflect the formation of well-ordered aggregates.

References

- [1] I. Zhai, R. D. McCullough, *Adv. Mater.*, **14** (2002) 901; [2] G. Tu, H. Li, M. Forster, R. Heiderhoff, L. J. Balk, R. Sigel, U. Scherf, *Small*, **3** (2007) 1001; [3] U. Scherf, A. Gutacker, N. Koenen, *Acc. Chem. Res.*, (2008) DOI: 10.1021/ar7002539; *Macromol. Rapid. Commun.* asap.