Polyelectrolyte Complexes of a Cationic All Conjugated Fluorene Thiophene Diblock Copolymer with Aqueous DNA

We report on the structural and colorimetric effects of interaction of aqueous ∼0.06–1% poly[9,9-bis(2-ethylhexyl)fluorene]b-poly[3-6-trimethylammoniumhexyl]thiophene] bromide (PF2/6-P3TMAHT) with double-stranded DNA to form PF2/6-P3TMAHT(DNA)x where x is the molar ratio of DNA base pairs to P3TMAHT repeat units; x = 0.5 equals the nominal charge neutralization. PF2/6-P3TMAHT forms 20–40 nm sized particles with PF2/6 core and hydrated P3TMAHT exterior. The polymer particles form loose one-dimensional chains giving micrometer long branched chains (0.19 ≤ x ≤ 0.76) and subsequently randomly shaped aggregates (x = 1.89) upon DNA addition. Compaction of the P3TMAHT block and the 20–30 nm sized core is observed for x = 0.38–0.76 and attributed to the DNA merged within P3TMAHT domain with this structure disassembling with DNA excess. Structural transformations are followed by chromic changes seen as color changes from deep red (x < 0.076) to yellow (x = 0.19), nearly colorless (x = 0.38–0.76), and back to orange (x = 1.89). Both absorption and photoluminescence spectra display the distinct fluorene and thiophene bands and subsequent blue and red shifts when passing x = 0.5. Thiophene photoliminescence (PL) is significantly quenched by DNA with increasing x, and the changing P3TMAHT/PF2/6 band ratio allows quantitative DNA detection. Sixteen-fold dilution does not change aggregate structure, but PL is blue-shifted, indicating weakened intermolecular interactions.

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