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ARTICLE TYPE

Fabrication of Multi-Charges Generable Poly(phenyl isocyanide)-block-Poly(3-hexylthiophene) Rod-Rod Conjugated Copolymer

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A facile construction of diverse polymeric nanostructures was reported by simple quaternization reaction and UV irradiation starting from the same rod-rod conjugated poly(4-isocyano-benzoic acid 5-(2-dimethylamino-ethoxy)-2-nitro-benzyl ester)-*b*-poly(3-hexylthiophene) (PPI(-DMAENBA)-*b*-P3HT) diblock copolymers, which prepared by sequential living copolymerization of 4-isocyano-benzoic acid *tert*-butyl ester (PI) and 3-hexylthiophene (3HT) by using Ni(dppp)Cl_2 as a catalyst in one-pot and subsequent chemical modification. Facile quaternization reaction and UV irradiation upon PPI(-DMAENBA)-*b*-P3HT could afford quaternized PPI(-DMAENBA)-*b*-P3HT (PPI(-QDMAENBA)-*b*-P3HT) and poly(4-isocyano-benzoic acid)-*b*-poly(3-hexylthiophene) (PPI(-AA)-*b*-P3HT) copolymers. Two different polymeric micellar supramolecular structures with cationic and anionic surface properties, respectively, could be obtained by direct dispersion of positively PPI(-QDMAENBA)-*b*-P3HT and negatively charged PPI(-AA)-*b*-P3HT copolymers into water. Interestingly, the resultant PPI(-QDMAENBA/DMAENBA)-*b*-P3HT block copolymers with 40% degree of quaternization were found to exhibit unique light emissions with the color transformed from luminous yellow to pink depending on the solvent ratio of THF and water used. Almost neutral and ordered thin film was achieved on the exact stoichiometric charge balance between these two kinds of oppositely charged micelles, which highlights the potential to incorporate conjugated copolymers into the assembled block copolymer micelles (BCMs) to yield multifunctional ordered films and relevant applications.

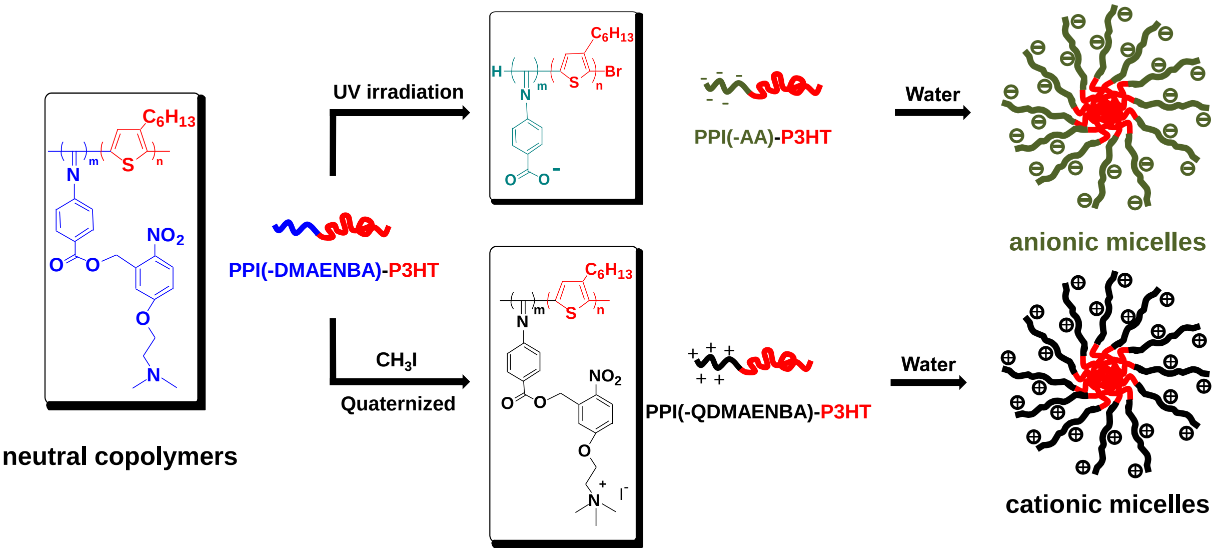
Introduction

The Conjugated polymers have attracted considerable attention as potential materials for organic photoelectronic device applications, such as organic photovoltaic devices (OPVs),[1-5] light-emitting diodes (LEDs),[6-9] and field-effect transistors (FETs).[10-13] Among the numerous synthetic π-conjugated polymers, polythiophene as well as its derivatives, for example poly(3-hexylthiophene) (P3HT), are well-known as fluorescent conjugated polymers, and have been widely studied in theory or used in practical applications due to their high chemical resistance, synthetic accessibility, and excellent electronic properties.[14-17] Up to now, P3HT incorporated block copolymers, such as P3HT-*b*-poly(acrylic acid), P3HT-*b*-polystyrene, P3HT-*b*-poly(perylenebisimide acrylate), P3HT-*b*-fullerene, P3HT-*b*-polylactide, P3HT-*b*-poly(2-vinylpyridine), P3HT-*b*-poly(benzyl L-glutamate),[18-24] and others,[25-30] had been designed and prepared to precise control of the optical properties through self-assembling morphology or to optimize the optoelectronic properties in further practical applications.[25, 31-33]

Recently, a convenient synthetic approach, which has been demonstrated to be proceeded in a controlled chain-growth mechanism, for the construction of well-defined block copolymers by using Ni(II) complex as catalyst with sequential monomer addition in a single pot was established.[34-35] By taking advantage of this modern polymerization methodologies, block copolymers containing P3HT as building blocks possessing capability for supramolecular assembly in selective solvents were synthesized, such as P3HT-*b*-poly(phenyl isocyanide),[36-37] P3HT-*b*-poly(quinoxaline-2,3-diyl),[38] and P3HT-*b*-poly(hexadecyloxylallene).[39] Among them, poly(phenyl isocyanide)s (PPIs), due to their unique helical structure of the main chain, have been the focus of intense research efforts.[40-41] Yashima and co-workers had demonstrated that PPIs bearing amide group as side pendants possessing a rigid-rod helical conformation through intramolecular hydrogen bonding (H-bond) between the adjacent repeating units.[42-43] PPIs could be prepared from tremendous readily available monomers and had been testified to self-assembly into different well-defined supramolecular architectures. Recent literature had also reported their utility in OPV devices.[44] Hence, block copolymers containing P3HT and PPI are attractive targets for study in various electronic applications.

In the past few years, functional thin films have attracted considerable attention due to their potential application as sensors,[45-46] catalysts,[47-48] and electronic devices.[49-50] The assembly method offers versatile opportunities to prepare thin films with multifunctional properties. Previously, polyelectrolytestabilized surfactant micelles and block copolymer micelles had been used as building blocks to fabricate layer-by-layer (LBL) assembled multilayers.[51-55] Then, the formation of multilayers exclusively from micelle aggregates were appeared through entirely of oppositely charged block copolymer micelles (BCMs) possessing polycation or polyanion coronae.[56-60] For example, Cho and Char *et al*. introduced a versatile approach for preparing self-assembled multilayered films through protonated polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) and anionic polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) BCMs governed by electrostatic interactions between the opposite BCMs.[56] Both film porosity and thickness were dependent upon the charge density of the micelles. The possibility of controlling film structure and function by combining different BCMs endowed the BCMs-based multilayer films attractive candidates for constructing highly functional assemblies. As far as we know, functional films constructed with conjugated diblock copolymer based micelles with opposite surface charges originated from the same diblock copolymer is rare.

In this contribution, a new type of PPI derivative and P3HT incorporated diblock copolymers, poly(4-isocyano-benzoic acid 5-(2-dimethylamino-ethoxy)-2-nitro-benzyl ester)-*b*-poly(3-hexylthiophene) (PPI(-DMAENBA)-*b*-P3HT), were synthesized. The pendent side groups, 5-(2'-(dimethylamino)ethoxy)-2-nitrobenzyl ester (DMAENBE), on PPI blocks allowed further chemical modification to yield quaternized PPI(-DMAENBA)-*b*-P3HT (PPI(-QDMAENBA)-*b*-P3HT) and negatively charged poly(4-isocyano-benzoic acid)-*b*-poly(3-hexylthiophene) (PPI(-AA)-*b*-P3HT) copolymers by facile quaternization reaction with methyl iodide or upon UV irradiation, as illustrated in Scheme 1. The entire modification process from the same nonionic PPI(-DMAENBA)-*b*-P3HT copolymers to diverse anionic and cationic copolymers bypasses the conventional procedures and have greatly facilitated the preparation of complex polymeric materials, which is a challenging aim to construct a system that serves as a versatile platform toward multifunctional materials with tunable properties both for fundamental studies and also toward a wide variety of applications. Light emissions with the color transformed from luminous yellow to pink was observed for positively charged PPI(-QDMAENBA)-*b*-P3HT (40% degree of quaternization) in the mixing solvent of THF and water. Moreover, almost neutral and ordered thin film was achieved from these two different polymeric micellar supramolecular structures with cationic and anionic surface properties, respectively, obtained by direct dispersion of positively charged PPI(-QDMAENBA)-*b*-P3HT and negatively charged PPI(-AA)-*b*-P3HT copolymers into water. This facial fabrication process highlights the possibility to incorporate conjugated copolymers into the assembled block copolymer micelles (BCMs) to yield multifunctional ordered films and relevant applications.

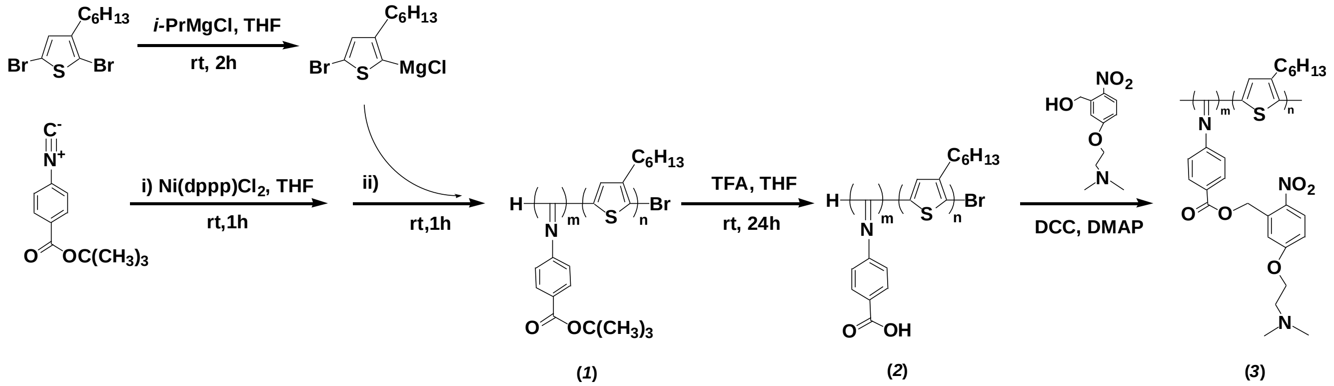


Scheme 1. Schematic Illustration of Tuning the Charges of P3HT Incorporated Diblock Copolymers as well as the Self-Assembly in Water to Afford Micelles with Polycation and Polyanion Coronas.

Results and discussion

The well-defined PPI(-DMAENBA)-*b*-P3HT block copolymers with controlled compositions were prepared according to Scheme 2. First of all, 4-isocyano-benzoic acid tert-butyl ester (PI monomer; compound *d* in Figure S1, see Supporting Information) was synthesized according to previously reported literature with little modification.[42] The employed synthetic routes and chemical structure of final product as well as mediators in each steps confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) were shown in Supporting Information Figures S1 and S2. Moreover, the synthetic routes employed for the photo-sensitive precursor 5-(2'-(dimethylamino)ethoxy)-2-nitrobenzyl alcohol (DMAENBA) were referred to our previous reported literature,[61] and corresponding ^{1}H NMR spectra were shown in Supporting Information Figure S3.

To prepare the PPI(-DMAENBA)-*b*-P3HT diblock copolymers, well-defined PPI-*b*-P3HT block copolymer was firstly prepared through the sequential living polymerization of PI and 3HT monomers in a single pot *via* distinct mechanism. This methodology is more advantageous than the conventional chain extension from purified macroinitiator, which always accompanied by the existence of inseparable homopolymer impurities. After the complete conversion of the first PI monomer and no further molecular weight increase was observed as monitored by size exclusion chromatography (SEC), the second 3HT monomer activated in advance was added into the reaction mixture to yield PPI-*b*-P3HT diblock copolymers (1). However, successful chain extension could also be achieved when the addition order of the two monomers in the sequential polymerization was reversed as reported in our previous literatures.[36-37] Hydrolysis reaction was then performed under the introduction of trifluoroacetic acid to afford carboxyl group functionalized PPI(-AA)-*b*-P3HT diblock copolymers (2). In order to achieve the multi-charges generable character, DMAENBA moieties were grafted onto the PPI(-AA) blocks by condensation reaction to yield targeted PPI(-DMAENBA)-b-P3HT diblock copolymers (3).



Scheme 2 Synthetic Routes Employed for the Synthesis of Nonionic PPI(-DMAENBA)-*b*-P3HT Diblock Copolymers (3).

SEC analysis was first used to confirm the structure of these three diblock copolymers. As shown in Figure 1a, the aliquot of PPI homopolymers removed from the reaction mixture obviously revealed monomodal elution peak. All the three diblock copolymers, PPI-*b*-P3HT, PPI(-AA)-*b*-P3HT, and PPI(-DMAENBA)-*b*-P3HT exhibited monomodal elution peaks on SEC traces. Each of the diblock copolymer was of higher number-average molecular weight (M_n) than its respective precursor and kept the narrow molecular weight distributions (M_w/M_n), that the PPI(-DMAENBA)-*b*-P3HT copolymer had the highest molecular weight (M_n = 26.1 kDa; M_w/M_n = 1.22) than that of the PPI(-AA)-*b*-P3HT precursor (M_n = 15.7 kDa; M_w/M_n = 1.21) and the original PPI-*b*-P3HT copolymer (M_n = 18.6 kDa; M_w/M_n = 1.20). All these diblock copolymers exhibited single modal SEC traces, indicating that no chain termination or chain transfer took place during the progress of the block copolymerization. Then, the chemical structure of PPI(-DMAENBA)-*b*-P3HT was characterized by ^{1}H NMR analysis (Figure 1b) as the proton signals attributable to both PPI(-DMAENBA) and P3HT blocks could be distinguished. The ^{1}H NMR spectra obtained in $CDCl_3$ at room temperature for PPI-*b*-P3HT and PPI(-AA)-*b*-P3HT diblock copolymers were shown in Figure S4 (see Supporting Information). Moreover, differential scanning calorimetric (DSC) was further used to confirm the existence of PPI(-DMAENBA) and P3HT blocks, because glass transition temperature (T_g) and melting point (T_m) are basic physical parameters of polymers and both molecular weight or chain topology can considerably affect these two values.[62] In Figure 1c, the DSC curve for PPI(-DMAENBA)-*b*-P3HT displayed two T_g values at 86.9 and 140.2 °C as well as two endothermic peaks at 225.6 and 297.4 °C, with the lower temperatures corresponding to the P3HT segments and the higher temperatures to the PPI(-DMAENBA) segments. As T_g temperatures assignable to both PPI(-DMAENBA) and P3HT phases could be distinguished obviously, this DSC curve provided further evidence suggesting that the targeted diblock copolymer has been successfully obtained and the microphase separation occurred in the bulk state, resulting from the intrinsic immiscibility between PPI(-DMAENBA) and P3HT blocks.

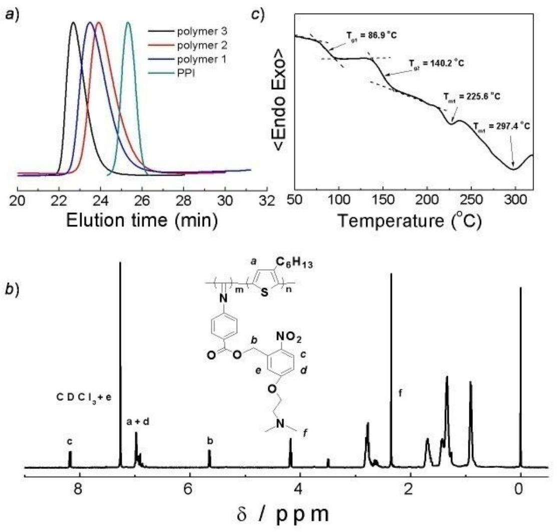


Fig. 1. (a) Size exclusion chromatograms (SEC) traces obtained for PPI homopolymer, PPI-*b*-P3HT (polymer 1), PPI(-AA)-*b*-P3HT (polymer 2), and PPI(-DMAENBA)-*b*-P3HT (polymer 3) diblock copolymers. (b) ^{1}H NMR spectrum and (c) DSC curve recorded for PPI(-DMAENBA)-*b*-P3HT diblock copolymers.

The introduction of 2-nitrobenzyl ester moieties covalently linked to the polymers endow them photo-triggered charge generation ability.[63] In the current work, the solution of PPI(-DMAENBA)-*b*-P3HT copolymer was firstly subjected to irradiation under UV light (365 nm) for 2.5 h. UV-Vis spectra of copolymer solution obtained before and after UV irradiation clearly revealed that UV absorbance before 290 nm decreased, accompanied with the increase of absorbance after 290 nm (see

Supporting Information; Figure S5), no further change was observed even increasing the irradiation time over 2.5 h. This difference before and after UV irradiation was well accordance with the results as reference reported, which suggested the photo-triggered cleavage of 2-nitrobenzyl ester moieties and the generation of 2-nitrosobenzaldehyde derivatives and carboxylate residues.[61] Therefore, the initial nonionic PPI(-DMAENBA)-*b*-P3HT copolymers could bear net negative charges within PPI(-DMAENBA) blocks upon UV irradiation and form amphiphilic copolymer, namely PPI(-AA)-*b*-P3HT. On the other hand, PPI(-QDMAENBA)-*b*-P3HT copolymer could be obtained from the same diblock copolymer of PPI(-DMAENBA)-*b*-P3HT by quaternization of PPI(-DMAENBA) blocks with excess of methyl iodide (CH_3I), which gave rise to net positive charges generated. Therefore, both of PPI(-AA)-*b*-P3HT and PPI(-QDMAENBA)-*b*-P3HT could be considered as amphiphilic copolymers.

As we all known, amphiphilic copolymers can self-assemble into various well-defined supramolecular structures such as spherical, hollow, or rod-like aggregates in selective solvent, depending on the relative lengths of two types of blocks.[64-67] In this study, amphiphilic PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT copolymers possess the same hydrophobic P3HT block but different in hydrophilic segment. PPI(-QDMAENBA)-*b*-P3HT possessing positive charged PPI(-QDMAENBA) block as hydrophilic blocks, while PPI(-AA)-*b*-P3HT have a negative charged PPI(-AA) blocks. Using a cosolvent approach, stable aggregates in aqueous solution could be obtained on the basis of the characteristics of surface charged BCMs in aqueous solution. The final equilibrium concentration of micellar solution is fixed at 0.1 g/L, higher than that CMC values of 0.035 g/L for PPI(-QDMAENBA)-*b*-P3HT and 0.037 g/L for PPI(-AA)-*b*-P3HT copolymers, respectively (see Supporting Information; Figure S6). The structural examinations of PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT aggregates were performed by transmission electron microscopy (TEM). The typical TEM images formed from fully quaternized PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT diblock copolymers were shown in Figures 2a and 2c, respectively. These figures indicated the self assembly of spherical nanoparticles from both diblock copolymers. The cationic and anionic surface charged micelles with hydrodynamic diameters of ~75 nm and ~80 nm and could be facilely formed by suspending these two diblock copolymers into water. Dynamic light scattering (DLS) measurement of the aggregates further confirmed the average dimension of the supramolecular structures to be ~94 nm for cationic surface charged micelles and ~100 nm for anionic surface charged micelles, and both as symmetric and single model trace, shown in Figures 2b and 2d, with consistent diameter to that obtained from TEM. On the basis of chemical intuition, the formed cationic micelles should consist of P3HT cores and quaternized PPI(-QDMAENBA) coronas, while anionic micelles consist of P3HT cores and PPI(-AA) coronas.

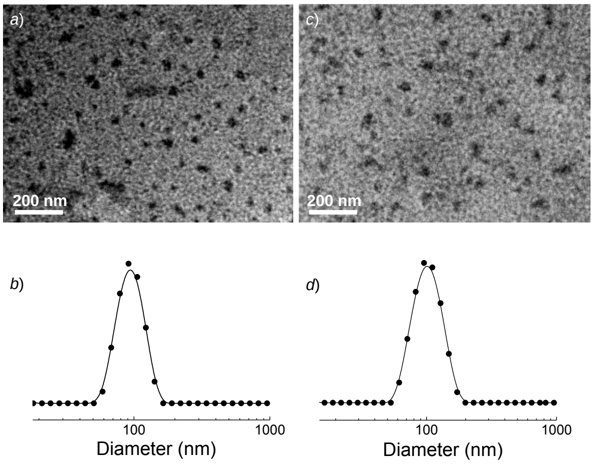


Fig. 2. Typical TEM images (a and c) and DLS spectra (b and d) obtained for PPI(-QDMAENBA)-*b*-P3HT (a and b) and PPI(-AA)-*b*-P3HT (c and d) copolymer micelles in water at room temperature, respectively. The concentration of micellar solution is fixed at 0.1 g/L.

Additionally, the degree of surface charges characterized for the resulting PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT micelles were measured as ζ-potential values in aqueous solutions, which were shown in Figure 3. As expected, cationic micelles formed from quaternized PPI(-QDMAENBA)-*b*-P3HT copolymers led to strongly cationic character with zeta potential values ranging from 0 to +35.9 mV because of a higher extent of quaternization from 0 to 100% to yield quaternary ammonium salt. On the other hand, anionic character was observed for anionic micelles formed from PPI(-AA)-*b*-P3HT copolymers with zeta potential values ranging from 0 to -28.4 mV due to the higher creation of carboxylic groups within side chains with increasing UV irradiation time from 0 to 2.5 h.

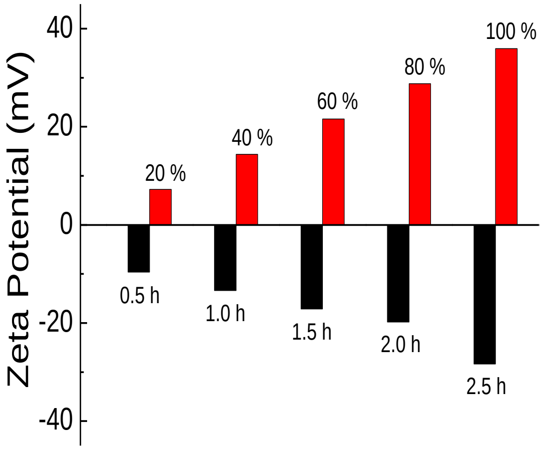


Fig. 3. ζ -Potential values obtained by quaternization of PPI(-DMAENBA)-*b*-P3HT diblock copolymer with various amount of methyl iodide (red column) or after UV irradiation (365 nm) for different times (black column).

The absorption spectra of PPI(-QDMAENBA/DMAENBA)-*b*-P3HT (40% degree of quaternization) in pure THF shows maximum absorption appeared at 427 nm (see Supporting Information; Figure S6c), similar to that of analogous P3HT-incorporated block copolymers reported previously.[36-37] However, it showed a red shift upon the gradual addition of water,[68] shown in Figure 4a, the absorption spectra kept change until the content of water increase to 40% with the maximum absorption appeared at 464 nm and were saturated at this stage. Added more water to the THF solution could not induce any changes on the absorption spectra, while the block copolymers were precipitated when the content of water was more than 40%. This is absolutely different from the absorption spectra of PPI(-DMAENBA)-*b*-P3HT and PPI(-QDMAENBA/DMAENBA)-*b*-P3HT (40% degree of quaternization) diblock copolymers in pure THF (see Supporting Information; Figure S7), that both of the absorption intensities at 437 nm and 427 nm before and after quaternization exhibited prominent linear increase to the concentration of the two diblock copolymers from 0.01 to 0.1 mg/mL, and no tendency to stabilize or wavelength shift were observed in current situation.

Inspired by existing references, the light emission properties of block copolymer was depending on the self-assembled structures.[37,69,70] Herein, the emission properties of PPI(-QDMAENBA/DMAENBA)-*b*-P3HT block copolymer with 40% degree of quaternization were investigated in the mixture solvents of THF and water. In Figure 4b, it showed a luminous yellow emission under UV illumination at 365 nm and no remarkable changes could be observed when the content of added water in the THF solution was less than 5%, distinct from the pink color light emitting when 40% water contained. This indicated that the small amount of water could not induce any assembly of the amphiphilic PPI(-QDMAENBA/DMAENBA)-*b*-P3HT block copolymers. The emission properties were further confirmed by fluorescent spectra (Figure 4c). Upon the solvent transmitted from pure THF to 40% water contained mixture solvent, the maximum emission peak at 560 nm was shift to 586 nm, accompanied by the obviously decease of long wavelength emission peaks and the slightly increase of the short wavelength emission peaks at 410, 435, and 460 nm (inserted in Figure 4c). The remarkably fluorescence quenching could be ascribed to the assembly induced quenching site enhancement, that the diffusion of solvent molecules out of the assembly led to the formation of intramolecular stack structure of thiophene rings.[37, 71] This phenomenon is well accordance with the reported poly(3-triethylene glycol thiophene) (P3(TEG)T) homopolymer when the solvent is transferred from THF to methanol.[37] Simultaneously, these short wavelength emission peaks were similar to that of the thiophene oligomers, that the conjugation length of some P3HT was partially reduced by rotational defects in the micellar aggregates, which disrupts the planarity of P3HT. Moreover, a new absorption peak located at 605 nm was observed with the gradual increase of water content, which had been reported to be indicative of the strong intermolecular π-π interaction because of the aggregation of P3HT moieties.[36]

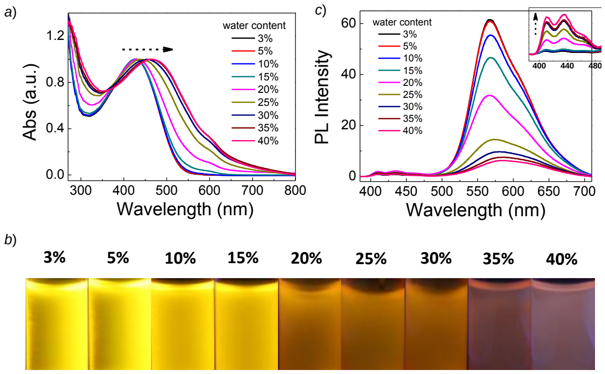


Fig. 4. (a) Absorption, (b) distinct photographs (under 365 nm UV light), and (c) fluorescent spectra recorded for PPI(-QDMAENBA/DMAENBA)-*b*-P3HT (40% degree of quaternization) diblock copolymers in THF upon addition of various amount of water.

The quaternized PPI(-QDMAENBA)-*b*-P3HT and anionic PPI(-AA)-*b*-P3HT BCMs could be further used as building blocks to afford P3HT incorporated films, which is governed by electrostatic interactions between the opposite charged BCMs and opens new opportunities in designing functional films capable of potential application. Assembly of two different polymer micelles was realized through mixing of micelles with polyanion or polycation corona simultaneously. In the case of aggregates formation, the positive charge of quaternary ammonium groups and the negative charge of carboxylic groups counteracted each other. Exact stoichiometric balance of oppositive charges resulted in almost neutral assembled film with zeta potential value as low as ~+0.1 mV (data not shown).

Moreover, the surface morphology of the films was observed using scanning electron microscope (SEM). Although the electrostatic interaction behavior originating from such charged BCMs is similar to that of conventional polyelectrolytes, the surface morphology obtained from the micelle/micelle assembly should be significantly different from that observed for polyelectrolyte films. Figure 5 showed a representative image obtained by direct casting of the assembled film on a silicon wafer. The compact small spherical features could be seen within the film, which were similar to the micelles observed on TEM and DLS (Figure 2), suggested that individual BCMs are involved in the film, which is attributed to the high degree of interdigitation between the adjacent coronas, thus creating closely packed between the micelles. This observation could be explained by the fact that the relatively short chain length of charged coronas could not penetrate the shells of adjacent micelles to a larger extent, yielding sparse vacancy between the neighboring micelles. Another image obtained at a larger scale was shown in Figure S8 (see Supporting Information).

It is worthy of noting that the surface morphology was different from that formed by the conventional LBL assembly approach, whose substrates were always not completely covered with BCMs to form so called "defects". These defects should be ascribed to the lack of micellar mobility at the surface, which was required for the formation of highly packed micelle monolayer, and the adsorption of later arriving micelles was hindered due to the insufficient size of landing spots remaining in between surface-bound micelles.[72]

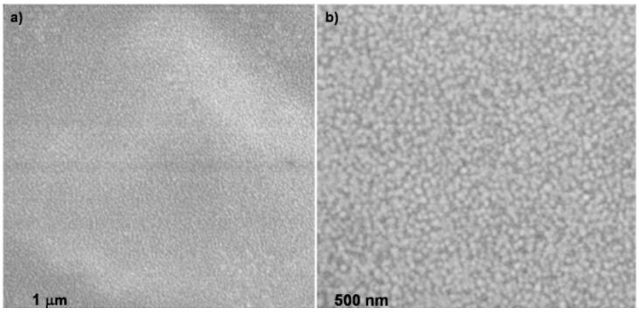


Fig. 5. SEM images obtained for conjugated copolymer micelles based film by directed fabrication from micelles with polycation and polyanion coronas.

Conclusion

Positively charged PPI(-QDMAENBA)-*b*-P3HT and negatively charged PPI(-AA)-*b*-P3HT copolymers were reported to fabricate from rod-rod conjugated PPI(-DMAENBA)-*b*-P3HT diblock copolymers with the same backbone by facile quaternization reaction and UV irradiation, respectively. The former could form micellar structure with hydrophobic P3HT core and positively charged PPI(-QDMAENBA) corona, while the latter formed micelles with P3HT core and negatively charged PPI(-AA) corona. What is interesting is that the light-emitting properties of the PPI(-QDMAENBA/DMAENBA)-*b*-P3HT block copolymers with 40% degree of quaternization could be tuned just by controlling the mixing ratio of solvents utilized without altering the molecular structure, demonstrating that self-assembly can be used to manipulate the properties of conjugated materials in a controllable manner. The direct assembly of these two kinds of polymeric micelles with equal opposite charges could achieve an almost neutral and ordered assembled film, which opens a general, versatile, and robust route to construct conjugated polymer incorporated layered or ordered thin films. We believe the present studies will provide a general method to construct diversiform functional structures and enrich the potential applications.

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Notes and references

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