Macromolecules

Cationic Polyfluorene-*b*-Neutral Polyfluorene "Rod–Rod" Diblock Copolymers

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ABSTRACT: All-conjugated "rod—rod" diblock copolymers are an emerging class of polymeric materials of considerable interest for applications in chemical and biological sensors or as components for optoelectronic devices. Here, we report a novel cationic diblock copolymer containing a neutral polyalkylfluorene block covalently bound to a polar polyfluorene counterpart poly[9,9-bis(6-trimethylammoniumhexyl)-2,7-fluorene]-*b*-poly(3hexyl-2,5-thiophene) (PF6NBr-*b*-PF8)—which was synthesized in a sequential Suzuki–Miyaura polymerization and was made ionic with trimethylamine in a subsequent quaternization step. The optical properties of this material were investigated by UV/ vis and photoluminescence spectroscopies in three different



solvents: methanol, THF and THF/methanol 1:1. Atomic force microscopic (AFM) imaging experiments provided evidence for solvent-induced aggregation. The formation of vesicles and spherical particles is observed in layers from THF and methanolic solution.

■ INTRODUCTION

Block copolymers that contain two chemically different chains covalently bound to each other are an important topic of synthetic macromolecular science.¹ All-conjugated block copolymers are a recent development.^{2,3} These systems often exhibit nanophase separation of the two segments, both in solution and in the solid state, thus giving rise to new properties and therefore have the potential to access new types of applications.^{4–6} In all-conjugated rod—rod block copolymers both blocks are rigid rods. This fact influences their self-assembling behavior by favoring aggregation into low curvature nanostructures.⁴ For tuning their electrical, optical, and self-assembly properties, the structure of the conjugated blocks can be modified by introducing different functional groups.

An essential synthetic enabler toward all-conjugated block copolymers is the application of transition-metal-mediated coupling reactions. In 2007, Tu et al.² described a first all-conjugated block copolymer, which contains one hydrophobic and one hydrophilic block, each with their different electronic properties. The key step of the preparative procedure utilizes a Suzuki-type cross-coupling in the presence of a macromolecular P3HT end-capped unit, occurring as a step-growth poly-condensation⁷ and yielding a poly[9,9-bis(2-ethylhexyl)-fluorene]-*b*-poly[3-(6-bromohexyl)thiophene] (PF2/6-*b*-P3BrHT) diblock copolymer. Phosphorylation in a subsequent Arbuzov reaction provides the amphiphilic poly[9,9-bis(2-ethylhexyl)-fluorene]-*b*-poly[3-(6-diethylphosphonatohexyl)-thiophene] (PF2/6-*b*-P3PHT) diblock copolymer. The amphi-

philic, all-conjugated rod-rod block copolymer shows vesicle formation in mixtures of specific and nonspecific solvents with different arrangements of the hydrophilic and hydrophobic components, depending on the polarity of the medium.

Related systems such as the cationic poly[9,9-bis(2ethylhexyl)fluorene]-*b*-poly[3-(6-trimethylammoniumhexyl)thiophene] (PF2/6-b-P3AHT) polyelectrolyte with cationic alkylammonium side groups also showed the formation of bilayer-based, micrometer-sized vesicles (polymersomes).⁸ Higher concentration led to the observation of a transition into layered (lamellar) aggregates.9 The tendency to selfassemble into low curvature nanostructures appears to be independent of size and composition of the block copolymers.^{2,10} Similar self-assembling behavior has been observed for poly(3-alkylthiophene)-b-poly(3-alkylthiophene) (P3AT-b-P3AT) diblock copolymers in which the chemical identity of the alkyl groups is different.¹¹ For the preparation of these materials, poly(3-hexylthiophene)-*b*-poly[3-(2-ethylhexyl)thiophene] (P3HT-b-P3EHT)s was accessed in a controlled chain growth polymerization as described by McCullough et al.¹² and Yokozawa et al.¹³ with excellent control over the molecular weight. This effort requires the use of catalysts that allow selective catalyst transfer to the terminus of the polymer chain after each coupling step.¹⁴ Subsequent reports have

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focused on the nanophase separation in (P3HT-*b*-P3EHT) into crystalline P3HT and amorphous P3EHT domains.¹⁵ Similar self-assembly behavior was also seen for the all-conjugated poly(3-hexylthiophene)-*b*-poly(3-phenoxymethylthiophene) (P3HT-*b*-P3PT) after thermal annealing of the films.¹⁶ Recent work by Wu et al.¹⁷ and Ge et al.¹⁸ reported other types of diblock copoly(3-alkylthiophene)s with high degrees of internal order.

Motivated by these reports, we now studied the chain-growth synthesis as well as the optical and self-assembling properties of a diblock copolymer composed of a neutral poly-(dialkylfluorene) (PF) segment bound to a cationic poly-(fluorene) counterpart. Because of the strong blue fluorescence¹⁹ and the unique self-organization properties²⁰ of polyfluorenes, these diblock PFs are attractive objects of potential use in the fabrication of optoelectronic devices and expected to undergo a controlled nanophase separation dependent on the polarity of the surrounding medium. Recently, conjugated polyelectrolytes (CPEs) like cationic poly[3-(6-trimethylammoniumhexyl)thiophene] (P3TMAHT) and poly[9,9-dialkylfluorene]-b-poly[3-(6trimethylammoniumhexyl)thiophene] (PF2/6-b-P3TMAHT) have been tested as electron extraction interlayers of organic bulk heterojunction (BHJ)-type solar cells. Bazan et al. reported that the introduction of P3TMAHT or PF2/6-b-P3TMAHT as thin interlayers lead to an increase of the power conversion efficiency (PCE), from ca. 5.3% to ca. 6.5%.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of poly(fluorene)-based diblock copolymers has been made considerably simpler by using a catalyst-transfer, Suzuki–Miyaura type polycondensation method. Specifically, Yokozawa et al.²² reported the polymerization of 7-bromo-9,9-dialkyl-fluorene-2-ylboronic acid ester using Hartwig's (t-Bu₃P)Pd-(C_6H_5)Br²³ as the arylpalladium catalyst. Unlike "classical" Suzuki–Miyaura coupling reactions²⁴ of aromatic dihalides and corresponding arylenediboronic esters, the polymeric products of the catalyst-transfer process exhibit narrow molecular weight distributions with polydispersity indices (PDIs) of <1.3.

Our initial targets were poly(dialkylfluorene)-*b*-poly-(dialkylfluorene) diblock copolymers in which one of the polyfluorene blocks contains bromoalkyl substituents in the 9,9positions of the repeat units. The overall strategy is illustrated in Scheme 1. Complete details are found in the Experimental Part.

Two AB-type monomers 2-(4',4',5',5'-tetramethyl-1',3',2'dioxaborolane-2'-yl)-7-bromo-9,9-bisoctylfluorene (F8) and 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9bis(6-bromohexyl)fluorene (F6Br) were made starting from the known dibromo monomers by metal-halogen exchange and borolation.²⁵ As shown in Scheme 1, the nonionic poly(9,9bis(6-bromohexyl)-2,7-fluorene)-b-poly(9,9-bisoctyl-2,7-fluorene) (PF6Br-b-PF8) can be generated in a chain-growth polycondensation²² by subsequent addition of the two AB-type monomers F8 and F6Br. Optimization of reaction conditions was accomplished by varying reaction time (from 0.5 to 60 min), catalyst concentration (2.5-10 mol %), and the order of monomer addition. We found that the optimum results are obtained by (i) polymerizing F8 first with 10 mol % of (t- $Bu_3P)Pd(C_6H_5)Br$ in aqueous sodium carbonate solution/THF for 10 min at room temperature and (ii) adding the second monomer F6Br dissolved in THF and stirring the mixture for

Scheme 1. Synthesis of the Cationic Diblock Copolymer PF6NBr-*b*-PF8 in a Polymer-Analogous Derivatization of the Nonionic Diblock Copolymer PF6Br-*b*-PF8



an additional 30 min. The inverse order of monomer addition (first F6Br, then F8) led to insufficient results. Afterward, the mixture was poured into a solution of acidified methanol and the precipitate was purified by Soxhlet extraction with methanol. The polymer PF6Br-*b*-PF8 was obtained as a light yellow solid. GPC analysis versus polystyrene (PSS) provided a number-average weight (M_n) of 18 100 and a PDI of 1.27 (yield: 82%; see Table 1 for a summary of the molecular weight

Table 1. M_n, M_w, and PDI of PF8, PF6Br, and PF6Br-b-PF8

polymer	time (min)	$M_{ m n}$	$M_{ m w}$	PDI
PF8	10	8 100	10 200	1.26
PF6Br	30	10 000	12 700	1.27
PF6Br-b-PF8	10 + 30	18 100	22 900	1.27

characteristis of all polymers). To calculate the average molecular weights of both blocks, a small sample was analyzed before the second monomer F6Br was added. The PF8 block showed a M_n of 8100 (ca. 20 repeat units, $m \sim 20$) and the PF6Br block a M_n of 10 000 ($n \sim 20$) with the GPC results in good agreement with ¹H NMR data. PF6Br-b-PF8 is soluble in typical organic solvents, such as chloroform, tetrachloroethane, or chlorobenzene.

The resulting nonionic PF6Br-*b*-PF8 is further treated with trimethylamine in a quaternization reaction to obtain the target all-conjugated, cationic diblock copolymer PF6NBr-*b*-PF8. The cationic diblock copolymer PF6NBr-*b*-PF8 is soluble in polar solvents and solvent mixtures, including methanol and THF– water as well as in organic solvents such as chloroform and THF.

Optical Spectroscopy. Figure 1a shows the normalized absorption spectra of PF6NBr-*b*-PF8 in three solvents: methanol, THF/methanol 1:1, and THF. One major absorption band is observed in THF, with an absorption maximum at about 390 nm, as is typical for PF-type polymers. In methanol and THF/methanol 1:1 one observes the emergence of an additional sharp peak at about 430 nm in addition to the broad band observed in THF. The lower energy peak at 430 nm has been previously assigned to the β -phase of PF.^{20,26} Nothofer described that treating poly(dialkylfluorene)s



Figure 1. UV/vis spectra of PF6NBr-*b*-PF8 in methanol, THF/ methanol 1:1, and THF (a). PL spectra of PF6NBr-*b*-PF8 in methanol, THF/methanol 1:1, and THF (λ_{exc} = 380 nm) (b).

with solvent/nonsolvent mixtures of increasing nonsolvent content leads to aggregation and β -phase formation with their unique packing behavior.²⁷ The so-called β -phase shows a distinct red-shift of absorption and emission with well-resolved vibronic side bands caused by the planarization of the PF backbone. For our amphiphilic PF-b-PF β -phase formation is observed with increasing solvent polarity (as well as in the solid state).

The photoluminescence spectra obtained by excitation at 380 nm are shown in Figure 1b. The PL spectra in THF show characteristic polyfluorene emission bands at 414, 437, and 464 nm (414 nm: 0–0 α -phase; 437 nm: 0–0 β -phase).^{19a,28} In methanol stronger peaks at 437 and 464 nm, as compared to the emission band at 414 nm, indicate favored β -phase formation.²⁹ The photoluminescence in methanol and the

THF/methanol mixture (1:1) are similar. In polar solvents β -phase formation (most probably of the PF8 block) is observed as described for the PF8 homopolymer.²⁰ Whereas, we suppose the PF8 block is the most reasonable segment where such an arrangement of chains can take place but we might be wrong.

Atomic Force Microscopy of Thin Films. Having first indications for aggregation from the optical spectra, we also investigated the all-conjugated, cationic diblock copolymer PF6NBr-*b*-PF8 by using atomic force microscopy (AFM). Here, the self-assembling behavior of PF6NBr-*b*-PF8 in a selective solvent for the polar block (methanol) and a nonselective solvent (THF) for both blocks will be discussed in detail. Films spin-casted on mica from dilute methanolic solution (0.1% of PF6NBr-*b*-PF8 by weight) show the occurrence of isolated vesicular aggregates with a diameter of 20-100 nm (Figure 2a,b) as already described for other allconjugated diblock copolymers.^{2,30}

AFM experiments of copolymer films casted onto mica from THF solution of identical concentration (0.1%) show a denser coverage of the substrate most probably to a preaggregation process during sample preparation (Figure 2c,d). However, the larger agglomerates contain smaller, individual particles, probably also vesicles that are partially fused (as indicated in the phase image).

Further investigating the structure of the nanoobjects, scanning surface potential measurements were carried out for both samples. In this mode, a Pt-coated silicon tip is scanned while a bias is applied to the sample to map the electrostatic potential on the sample surface. The first scan is used to obtain the surface topography, and the second scan is lifted above the surface to obtain the local surface potential image. The presence of charges on a surface will reduce the potential difference between the substrate and the tip, and as the result, low surface potential should be observed. Films from dilute methanolic solution (0.1% of PF6NBr-b-PF8) show the occurrence of isolated vesicular/spherical particles with a diameter of ~50 nm. Figure 3a gives an exemplary illustration for this. We already mentioned that the self-assembly of such rod–rod all-conjugated diblock copolymers should be mainly



Figure 2. Topographic (a, c) and phase (c, d) AFM images of 0.1% PF6NBr-*b*-PF8 spin-casted on mica from methanol (a, b) and THF (c, d) of PF6NBr-*b*-PF8 (image size 2 μ m × 2 μ m).



Figure 3. AFM topography (a, c) and surface potential (b, d) images of ITO/PF6NBr-*b*-PF8 films spun from 0.1% in methanol (a, b) and 0.1% THF (c, d) solutions (image size: $2 \ \mu m \times 2 \ \mu m$).

independent from the molecular weight of the diblock copolymers and the block length ratio.² In methanol, one would expect the charge blocks located on the outside in contact with the polar solvent and shielding the neutral block in the interior from the polar solvent. Next, we dissolved 0.1% of the polyelectrolyte diblock copolymer PF6NBr-b-PF8 in THF. Figure 3c shows the surface topography of THF cast film. The surface comprises of nanofibers with the average width of ~ 30 nm. The nanofibers are necklaces of individual spherical objects. Please note that this second series of AFM investigations was carried out on ITO-coated substrates with block copolymer solutions in THF that have been preaged for 10 days. This may explain the rather different morphology of the aggregate morphology (compare Figures 2c and 3c). We expected that the nanostructures are now reversed with the neutral block on the outside thus shielding the charged block from the nonpolar medium. So, a high surface potential should result since the surface is now neutral. Figures 3b and 3d show the surface potential images of methanol and THF cast films, respectively. The film cast from methanol shows low surface potential whereas the nanofibers observed in the THF cast film have much higher surface potential. This difference in surface potential is the result of different surface coverage: charged versus hydrophobic surfaces. The occurrence of inverse block morphologies as a function of solvent polarity has been previously discussed by Scherf et al. for the poly[9,9-bis(2ethylhexyl)fluorene]-b-poly[3-(6-diethylphosphonatohexyl)thiophene] (PF2/6-b-P3PHT) system when applying different mixtures of selective and nonselective solvents (THF/water vs THF/hexane).²

CONCLUSION

In summary, we have studied the synthesis of a novel allconjugated, cationic PF6NBr-*b*-PF8 diblock copolymer, its photophysical properties, and its aggregation behavior. We could observe evidence of nanophase separation and selfassembly into vesicles especially in methanol and THF.

Figure 4 depicts our structure model for the vesicle (polymersome) formation in methanol and THF. In methanol



Figure 4. Graphical illustration of the vesicle structure formed by PF6NBr-*b*-PF8 from methanol and THF (orange: PF8 block; black: PF6NBr block).

the core region of the amphiphilic bilayers (vesicle walls) is generated by aggregation of the nonionic, hydrophobic PF8 segments (in orange). The outer shell of the vesicle walls in the polar MeOH is formed by the ionic, hydrophilic PF6NBr segments (in black), with the rigid-rod diblock copolymer chains oriented perpendicular to the plane of the vesicle walls. Aggregation in methanol with the PF8 blocks as inner layer of the vesicles (Figure 4, top) supports β -phase formation (Figure 1). This indicates that the PF8 blocks and not the PF6Br blocks are responsible for β -phase formation. Aggregation in THF creates the reverse situation. Future work will focus on the application of the ionic diblock copolymers as charge injection/ charge extraction interlayers of organic electronics devices.

EXPERIMENTAL PART

Instruments. The ¹H and ¹³C NMR spectra were recorded on a either a Bruker Avance500 500 MHz or a Bruker Avance II 600 MHz NMR spectrometer with use of the solvent proton or carbon signals as internal standard. Elemental analyses were performed on a Vario EL II (CHNS) instrument. Gel permeation chromatography (GPC) measurements were carried out using a Waters 2695 Separation Module equipped with Column I-Series Mixed Bed High Molecular Weight Viscotek columns with separation range 1000–10 M (30 cm × 7.8 mm i.d.), a 2414 RI detector, and a 2996 photodiode array (PDA)

detector. THF was employed as the solvent and polystyrene (PSS) standards were used for calibration. The measurements were obtained at 30 °C. UV–vis absorption spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer at room temperature. Fluorescence measurements were carried out on a Shimadzu UV-2401 instrument at room temperature. Atomic force microscopy measurements were recorded using a under nitrogen environment using a commercial scanning probe microscope (MultiMode and Nanoscope Controller IIIa, Veeco Inc.). Surface potential measurements were collected using a Veeco diDimension Icon atomic force microscope instrument.

Materials. Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. All reactions were carried out using standard and Schlenk techniques under an argon atmosphere. The solvents were used as commercial p.a. quality.

2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7bromo-9,9-bisoctylfluorene (F8). Compound 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9-bisoctylfluorene was prepared according to the method described for 2-(4',4',5',5'tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9-bis(6bromohexyl)fluorene by using 2,7-bromo-9,9-bisoctylfluorene (6.0 g, 10.9 mmol) in diethyl ether (150 mL), 1.6 M n-buthyllithium (6.4 mL, 10.9 mmol), and an excess of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2dioxaborolane (3.8 mL, 16.4 mmol). Column chromatography (ethyl acetate/hexane = 95:5) followed by recrystallization from ethanol afford F8 (3.2 g, 49%) as a white solid. ¹H NMR (500 MHz, CDCl₃). δ (ppm): 7.81 (d, 1H, Ar–H), 7.72 (s, 1H, Ar–H), 7.66 (d, 1H, Ar– H), 7.57 (d, 1H, Ar-H), 7.46 (s, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 2.04-1.90 (m, 4H, Ar-CH₂), 1.39 (bs, 12H, OC(CH₃)₂C(CH₃)₂O), 1.29-1.00 (m, 20H, Alkyl-H), 0.82 (t, 6H, CH₂-CH₃), 0.64-0.47 (m, 4H, Alkyl-H). ¹³C NMR (125 MHz, $CDCl_3$): δ (ppm): 153.6, 149.5, 143.0, 140.0, 133.9, 129.9, 128.9, 126.2, 121.4, 119.0, 83.8, 55.5, 40.1, 31.8, 29.9, 29.1, 24.9, 23.6, 22.6, 14.0. Elemental analysis: C35H52BBrO2, calcd (%): C 70.59, H 8.80; measd (%): C 70.25, H 8.47

2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7bromo-9,9-bis(6-bromohexyl)fluorene (F6Br). 2,7-Bromo-9,9-bis-(6-bromohexyl)fluorene (10.0 g, 15.4 mmol) dissolved in dry, degassed diethyl ether (300 mL) was placed in a 500 mL round bottom flask. The solution was cooled to -78 °C, and 1.7 M tertbutyllithium (8.7 mL, 15.1 mmol) was added dropwise. After stirring the reaction mixture for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2dioxaborolane (12.6 mL, 61.5 mmol) was added in one shot and stirred one more hour at -78 °C. After the mixture had been warmed up to room temperature overnight, the reaction was quenched with water. The residue was extracted with dichloromethane, and the combined organic layers were washed with water and brine and dried over magnesium sulfate. The solvent was removed, and yellow oil was purified by silica gel column chromatography (ethyl acetate/hexane = 95:5) to afford F6Br (5.6 g, 52%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.82 (d, 1H, Ar–H), 7.72 (s, 1H, Ar–H), 7.66 (d, 1H, Ar-H), 7.77 (d, 1H, Ar-H), 7.46 (d, 2H, Ar-H), 3.30 (t, 4H, CH₂-Br), 2.00 (m, 4H, CH₂), 1.67 (quint, 4H, CH₂), 1.42 (s, 12H, OC(CH₃)₂C(CH₃)₂O), 1.21 (quint, 4H, CH₂), 1.09 (quint, 4H, CH₂), 0.60 (quint, 4H, CH₂). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 171.3, 153.3, 149.3, 142.9, 140.0, 134.0, 130.2, 129.0, 126.3, 121.8, 121.7, 119.2, 83.9, 60.6, 55.4, 39.9, 34.6, 32.8, 29.1, 27.9, 25.1, 23.6, 21.3, 14.5. Elemental analysis: C₃₁H₄₂BBr₃O₂, calcd (%): C 53.40, H 6.07; measd (%): C 53.44, H 6.08.

Poly(9,9-bisoctyl-2,7-fluorene) (PF8). Aqueous 2 M sodium carbonate solution (5 mL) was added into a mixture of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9-bisoctylfluorene (F8) (150 mg, 0.25 mmol) in freshly distilled THF (6 mL) in a Schlenk tube under argon. The catalyst (t-Bu₃P)Pd(C_6H_5)Br (5 mg, 0.013 mmol) in THF (2 mL) was added via a syringe, and the mixture was stirred for 10 min at room temperature. For quenching the polymer solution was poured into a mixture of methanol (500 mL) and hydrochloric acid (50 mL), and the residue was filtered and purified via a Soxhlet extraction with methanol. The residue was extracted again with chloroform using a Soxhlet. The chloroform was

removed by evaporation under reduced pressure, and the polymer was dried under reduced pressure to give PF8 as a light yellow solid (87 mg, 92%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.86 (m, 2H, Ar–H), 7.71 (m, 4H, Ar–H), 2.15 (bs, 4H, CH₂), 1.29–1.70 (m, 20H, Alkyl–H), 0.85 (m, 10H, Alkyl–H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 151.8, 140.5, 140.0, 126.2, 121.5, 120.0, 55.4, 40.5, 31.9, 30.0, 29.3, 28.0, 23.8, 22.6, 14.0. GPC (THF): M_{0} = 8100, PDI = 1.26.²⁷

Poly[9,9-bis(6-bromohexyl)-2,7-fluorene] (**PF6Br**). Polymer PF6Br was prepared according to the method for PF8 by using 2 M sodium carbonate solution (5 mL) and 2-(4',4',5',5'-tetramethyl-1',3',2'dioxaborolane-2'-yl)-7-bromo-9,9-bis(6-bromohexyl)fluorene (F6Br) (150 mg, 0.22 mmol) in freshly distilled THF (6 mL) and (*t*-Bu₃P)Pd(C₆H₅)Br (8 mg, 0.022 mmol) in THF (2 mL). The reaction time was 30 min. Soxhlet extraction was done with methanol and chloroform. The chloroform fraction of the polymer gave PF6Br as a light yellow solid (85 mg, 86%).¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.87 (m, 2H, Ar–H), 7.72 (m, 2H, Ar–H), 3.32 (m, 4H, CH₂), 2.16 (m, 4H, CH₂), 1.71 (m, 4H, CH₂), 1.61 (m, 4H, CH₂), 1.26 (m, 4H, CH₂), 0.92 (m, 4H, CH₂). GPC (THF): $M_n = 10000$, PDI = 1.27.³¹

Poly(9,9-bis(6-bromohexyl)-2,7-fluorene)-b-poly(9,9-bisoctyl-2,7-fluorene) (PF6Br-b-PF8). Aqueous 2 M sodium carbonate solution (5 mL) was added into a mixture of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9-bisoctylfluorene (F8) (150 mg, 0,25 mmol) in freshly distilled THF (12 mL) in a Schlenk tube under argon. The catalyst (*t*-Bu₃P)Pd(C₆H₅)Br (9.6 mg, 0,025 mmol) in THF (4 mL) was added via syringe, and the mixture was stirred for 10 min at room temperature. After the addition of 2-(4',4',5',5'tetramethyl-1',3',2'-dioxaborolane-2'-yl)-7-bromo-9,9-bis(6bromohexyl)fluorene F6Br (176 mg, 0.25 mmol) in THF (2 mL) the mixture was stirred for 30 min at room temperature . For quenching the polymer solution was poured into a mixture of methanol (500 mL) and hydrochloric acid (50 mL), and the residue was filtered and Soxhlet extracted with methanol. The residue was extracted again with chloroform using a Soxhlet. The chloroform was removed by evaporation under reduced pressure, and the polymer was dried under reduced pressure to give PF6Br-b-PF8 as a light yellow solid (178 mg, 82%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.84 (m, 4H, Ar-H), 7.70 (m, 8H, Ar-H), 3.29 (m, 4H, CH₂), 2.13 (m, 8H, CH₂), 1.70 (m, 4H, CH₂), 1.22 (m, 32H, Alkyl-CH₂), 0.81 (m, 6H, CH₂-CH₃). Elemental analysis: C₅₂H₆₆Br₂, calcd (%): C 73.23, H 8.04; measd (%): C 73.11, H 7.87. GPC (THF): $M_n = 18100$, PDI = 1.27.

Poly[9,9-bis(6-trimethylammoniumhexyl)-2,7-fluorene]-bpoly(3-hexyl-2,5-thiophene) (PF6NBr-b-PF8). Condensed trimethylamine (2.5 mL) was added dropwise to a solution of neutral block copolymer PF6Br-b-PF8 (100 mg) in THF (50 mL) at -78 °C. The mixture was allowed to warm up to room temperature gradually. The solvent was removed by evaporation under reduced pressure. The precipitate was redissolved by addition of excess methanol, then an extra 2 mL of trimethylamine was added at -78 °C, and the mixture was stirred vigorously for 24 h at room temperature. After removal of most of the solvent the polymer was put in a dialysis membrane (cutoff 1000 g/mol) for further purification. After evaporation of the solvents the polymer was collected and dried under reduced pressure to give to give 104 mg (92%) of PF6NBr-*b*-PF8 as a yellow solid. ¹H NMR (600 MHz, MeOD) δ (ppm): 7.96-7.80 (m, 12H, Ar-H), 3.22 (m, 22H, N⁺(CH₃)₃ and N⁺-CH₂), 1.70-1.60 (m, 4H, Alkyl-CH₂), 1.31-1.17 (m, 32H, Alkyl-CH₂), 0.83 (m, 8H, Alkyl-CH₂), 0.14 (m, 6H, CH₂-CH₂).

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Notes

The authors declare no competing financial interest.

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