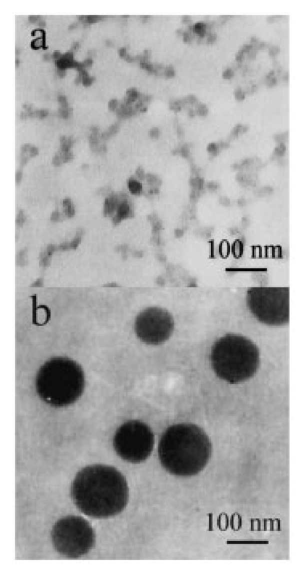
Summary: Novel non-covalently connected water-soluble nanoparticles that contain poly(fluorene-*co*-phenylene) with hydroxy-capped alkoxy side chains (PF3BOH) and poly(acrylic acid) (PAA) have been obtained and characterized. With different proportions of PF3BOH and PAA, the shape and size of the nanoparticles can be regulated. The nanoparticles are quite stable in water with no precipitate being observed after weeks. Transmission electron microscopy and dynamic laser light scattering are used to confirm the morphology of the PF3BOH/PAA nanoparticles. Their optical properties have been investigated and show similar optoelectronic properties to a PF3BOH solid film although they do not undergo aggregation.



TEM images of the nanoparticles obtained upon varying the PAA/PF3BOH content.

Novel Water-Soluble Shape-Regulatable Luminescent Nanoparticles by Non-Covalently Bonded Self-Assembly

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Introduction

In recent years great efforts have been devoted to the synthesis of conjugated polymers and their application as fluorescent chemosensors or biosensors.[1] In this field, water-soluble conjugated polymers have attracted increasing attention as good sensory materials to detect chemical or bioactive species, such as proteins, DNA, and RNA.[2]

To be good candidates for biosensors, the water solubility of the conjugated polymers must be realized since most biomolecules are dissolved in water. The first water-soluble conjugated polymer reported was a 3-substituted polythiophene[3] and subsequently a series of conjugated polyelectrolytes have been developed, such as poly(phenylene ethylene),[4] poly(phenylene vinylene),[5] and polyfluorene.[6] Their water solubility has been achieved by introducing ionic functional groups to their side chains. Another way to achieve water solubility is by the formation of a block copolymer, e.g., by combining neutral conjugated polymer segments with water-soluble polymer segments. Our group was the first to reported the formation of water-soluble conjugated-acidic and conjugated-ionic block copolymers by atom transfer radical polymerization (ATRP) with a polyfluorene-based macroinitiator.[7,8] All the methods mentioned above depend on covalent bonding to connect the conjugated polymers with water-soluble groups or segments, which need complicated synthetic routes to obtain the target water-soluble polymers. Recently, self-assembly by non-covalent bonding, a facile way to produce water-soluble micelles and other nanostructures, has been applied in the area of nanotechnology.[9,10] For example, Yoshida et al. reported the micelle formation of a non-amphiphilic diblock copolymer by non-covalently bonded cross-linking in 1,4-dioxane.[10] Jiang et al. demonstrated the formation of a series of spherical micelles obtained from polyimide (PI) with carboxy end-groups, a rigid polymer, and poly(4-vinylpyridine) (PVPy) in a common solvent of the two polymers.[9] Unlike the other methods to produce water-soluble polymers mentioned above, our water-soluble materials can be realized directly from water-insoluble conjugated polymers by the assistance of some water-soluble polymers and do not need any further chemical modification of their polymer chain.[10] As a significant advantage in a 'block-copolymer-free' strategy[9] to prepare water-soluble nanoparticles, herein a new approach for the preparation of water-soluble luminescent materials self-assembled by hydrogen bonding between poly(fluorene-*co*-phenylene) (PF3B) and poly(acrylic acid) (PAA) is reported. The luminescence and water solubility are attributable to the luminescent character of PF3B and the hydrogen bonding between PF3B and PAA.[9]

Polyfluorenes and poly(fluorene-*co*-phenylene)s, the high-performance blue-luminescent polymers with high chemical and thermal stability, have attracted great interest.[11] Water-soluble luminescent polymers have been widely investigated as highly sensitive materials in biosensors. Bazan et al. have reported using water-soluble polyfluorenes as the platforms for multicolored biosensors to detect DNA.[12] The water-soluble polyfluorenes were all acquired by means of attaching ionic groups on the side chains.[6–8] However, as far as we know, using self-assembly by non-covalent bonds (such as hydrogen bonds) to achieve water-soluble light-emitting materials has seldom been reported. In this paper, aqueous nanoparticles that contain poly(fluorene-*co*-phenylene)s have been successfully prepared by self-assembly by hydrogen bonding between hydroxy-capped groups on the side chains and the carboxy groups on the PAA side chains. Their water-solubility, optical properties, and morphologies have been investigated and the corresponding results indicate that many other types of water-soluble luminescent materials can be conveniently and efficiently obtained by this method.

Experimental Part

Materials

2,7-Dibromofluorene (97%), 1-bromooctane (97%), 4-methoxyphenol (99%), 1,6-dibromohexane (99%), butyllithium (1.6 M solution in hexanes), tetrabutylammonium bromide (99%), trimethyl borate (98+%), magnesium turnings, poly(acrylic acid) $\overline{M}_n = 15\,000$, and tetrakis(triphenylphosphine)palladium(0) (99%) were purchased from Aldrich Chemical Co. Tetrahydrofuran (THF, 99%, Sinopharm) was distilled from sodium/benzophenone, and *o*-dichlorobenzene(99%, Acros) was distilled from calcium hydride and stored under argon. Potassium hydrate, propane-1,3-diol, bromine, potassium acetate, and acetic anhydride were purchased from Shanghai Chemical Reagent Co. Ltd. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All chemicals used were further purified before use.

Characterization

^{1}H and ^{13}C NMR spectra were collected on a Varian Mercury plus 400 spectrometer with chemical shifts being referenced against tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) analysis was conducted with a Shimadzu Lc-VP system using polystyrenes as the standard and THF as the eluent at a flow rate of 0.8 $\text{mL} \cdot \text{min}^{-1}$ and 40 °C. The transmission electron microscopy (TEM) image was taken on a Hitachi H-600 electron microscope operated at 75 kV. UV-vis absorption spectra were recorded with a Shimadzu UV-2450 UV-vis-NIR spectrophotometer. Photoluminescence spectra were performed with a Shimadzu RF-5301PC fluorescence spectrometer. Film samples for PL spectra were prepared by casting the polymer from its THF solution onto a clean quartz substrate.

Synthesis

1-(6-Bromohexyloxy)-4-methoxybenzene (**2**)

1,6-Dibromohexane (55.5 g, 35.0 mL) was added to a mixture of 4-methoxyphenol (10.00 g, 0.08 mol) and potassium hydrate (4.6 g, 0.8 mol) in ethanol (200 mL). The reaction mixture was stirred at 90 °C for 4 h. The organic layer was separated, washed with brine, and dried with sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to yield **2** (15.4 g, 67%).

^{1}H NMR (CDCl$_3$): $\delta = 6.83$ (s, phenyl H, 4H), 3.91 (t, –OCH$_2$–, 2H), 3.77 (s, –OCH$_3$, 3H), 3.43 (t, –CH$_2$–Br, 2H), 1.92–1.86 (m, –C*H*$_2$CH$_2$Br, 2H), 1.75–1.80 (m, –OCH$_2$C*H*$_2$–, 2H), 1.53–1.46 (m, –(C*H*$_2$)$_2$–CH$_2$CH$_2$Br, 4H).

^{13}C NMR (CDCl$_3$): $\delta = 154.11$ (phenyl q-C), 153.33 (phenyl q-C), 115.76 (phenyl H-C), 114.93 (phenyl H-C), 67.78 (–OCH$_2$–), 55.96 (–OCH$_3$), 33.73 (–CH$_2$Br), 32.72 (–CH$_2$–), 29.78 (–CH$_2$–), 28.24 (–CH$_2$–), 25.15 (–CH$_2$–).

1,4-Dibromo-2-(6-bromohexyloxy)-5-methoxybenzene (**3**)

Bromine (6.20 mL, 0.12 mol) in chloroform (40 mL) was added dropwise to **2** (14.4 g, 0.05 mol) in chloroform (200 mL). The mixture was stirred for 12 h, and the produced HBr gas was collected in saturated aqueous sodium hydrate. The organic layer was separated, washed with brine, and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to afford **3** (19.5 g, 87%).

^{1}H NMR (CDCl$_3$): $\delta = 7.09$ (s, phenyl H, 2H), 3.96 (t, –OCH$_2$–, 2H), 3.85 (s, –OCH$_3$, 3H), 3.42 (m, –CH$_2$Br, 2H), 1.94–1.80 (m, $-OCH_2CH_2(CH_2)_2CH_2CH_2Br$, 4H), 1.57–1.45 (m, $-OCH_2CH_2(CH_2)_2CH_2CH_2Br$, 4H).

^{13}C NMR ($CDCl_3$): $\delta = 150.92$ (phenyl C–OCH_3), 150.03 (phenyl C–OCH_2–), 118.81 (phenyl C–H), 117.25 (phenyl C–H), 111.57 (phenyl C–Br), 110.79 (phenyl C–Br), 69.54 (–OCH_2–), 57.26 (–OCH_3), 33.78 (–CH_2Br), 32.73 (–CH_2–), 29.79 (–CH_2–), 28.13 (–CH_2–), 25.16 (–CH_2–).

6-(2,5-Dibromo-4-methoxyphenoxy)hexyl acetate (**4**)

A mixture of potassium acetate (5.9 g, 60.0 mmol), **3** (13.4 g, 30.0 mmol), and acetic anhydride (5.0 mL) in acetic acid (100 mL) was stirred and refluxed for 1 d. The precipitate of KBr was filtered off, and the excess acetic acid was removed by evaporation. The residue was then washed with a large amount of water. The mixture was extracted with chloroform, and the organic layer was washed with brine and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to afford **4** (10.6 g, 83.3%).

^{1}H NMR ($CDCl_3$): $\delta = 7.09$ (s, phenyl H, 2H), 4.07 (t, –CH_2OAc), 2H), 4.96 (t, –OCH_2–, 2H), 3.84 (s, –OCH_3, 3H), 2.05 (s, –$COCH_3$, 3H), 1.86–1.78 (m, –OCH_2CH_2–, 4H), 1.71–1.63 (m, –CH_2CH_2OAc), 1.57–1.39 (m, –$OCH_2CH_2(CH_2)_2CH_2$-CH_2OAc, 4H).

^{13}C NMR ($CDCl_3$): $\delta = 171.91$ (C=O), 151.53 (phenyl C–OCH_3), 150.75 (phenyl C–OCH_2–), 119.52 (phenyl C–H), 117.87 (phenyl C–H), 112.18 (phenyl C–Br), 111.20 (phenyl C–Br), 70.53 (–OCH_2–), 64.87 (–CH_2OAc), 57.84 (–OCH_3), 29.79 (–CH_2–), 29.12 (–CH_2–), 26.55 (–CH_2–), 26.18 (–CH_2–), 21.83 (–$COCH_3$).

6-(2,5-Dibromo-4-methoxyphenoxy)hexan-1-ol (**5**)

A mixture of **4** (2.5 g, 5.9 mmol) and sodium hydrate (1.0 g, 25.0 mmol) in methanol (200 mL) was stirred for 3 h at room temperature. The excess methanol was evaporated and the residue was poured into a large amount of water and then extracted with the petroleum ether. The organic layer was washed with brine and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to afford **5** (2.1 g, 93%).

^{1}H NMR ($CDCl_3$): $\delta = 7.09$ (d, phenyl H, 2H), 3.96 (t, –OCH_2–, 2H), 3.84 (s, –OCH_3, 3H), 3.66 (t, –CH_2OH, 2H), 1.86–1.78 (m, –OCH_2CH_2–, 2H), 1.65–1.41 (m, –$(CH_2)_3$-CH_2OH, 6H).

^{13}C NMR ($CDCl_3$): $\delta = 151.42$ (phenyl C–OCH_3), 151.25 (phenyl C–OCH_2–), 119.12 (phenyl C–H), 117.67 (phenyl C–H), 111.83 (phenyl C–Br), 110.95 (phenyl C–Br), 70.77 (–OCH_2–), 63.23 (–CH_2OH), 57.64 (–OCH_3), 32.51 (–CH_2–), 29.68 (–CH_2–), 28.25 (–CH_2–), 25.23 (–CH_2–).

9,9-Dioctyl-2,7-dibromofluorene (**7**)

A mixture of 2,7-dibromofluorene (9.7 g, 30 mmol) and catalytic amounts of tetrabutylammonium bromide (0.6 g, 2.0 mmol) in 50 mL of dimethyl sulfoxide (DMSO) was stirred for 30 min at room temperature. 1-Bromooctane (13.5 g, 70 mmol) was added to the reaction mixture, and the mixture was then treated with 15 mL of 50% aqueous KOH at 60 °C and stirred for 12 h. The residue was then washed with a large amount of water. The mixture was extracted with ether, and the organic layer was washed with brine and dried over sodium sulfate. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum ether as the eluent to afford **7** (15.2 g, 93%).

^{1}H NMR ($CDCl_3$): $\delta = 7.51$ (d, fluorenyl H, 2H), 7.46 (d, fluorenyl H, 2H), 7.44 (s, fluorenyl H, 2H), 1.91 (m, –$CH_2C_7H_{15}$, 4H), 1.32–0.57 (m, –$CH_2C_7H_{15}$, 30H).

^{13}C NMR ($CDCl_3$): $\delta = 152.34$ (fluorenyl q-C), 140.06 (fluorenyl q-C), 130.04 (fluorenyl C–H), 126.07 (fluorenyl C–H), 121.38 (fluorenyl C–H), 120.96 (fluorenyl C–Br), 55.56 ($C(Ph)_2(C_8H_{17})_2$), 40.02 (–CH_2–), 31.63 (–CH_2–), 29.78 (–CH_2–), 29.04 (–CH_2–), 29.01 (–CH_2–), 23.51 (–CH_2–), 22.47 (–CH_2–), 13.94 (–CH_3).

9,9-Dioctylfluorene-2,7-bis(trimethylene boronate) (**8**)

A solution of **7** (11.0 g, 20.0 mmol) in dry THF was added slowly to a stirred mixture of magnesium turnings (1.2 g, 50.0 mmol) in dry THF that contained a catalytic amount of iodine under nitrogen to form the Grignard reagent. The Grignard reagent solution was slowly dropped into a stirred solution of trimethyl borate (11.5 mL, 100 mmol) in dry THF at −78 °C over a period of 1.5 h and was then slowly warmed to room temperature. The mixture was stirred (vigorous stirring was required to avoid gel formation) at room temperature for three days and was then poured onto a mixture of crushed ice containing sulfuric acid (5%) with stirring. The mixture was extracted with ether, and the combined extracts were evaporated to give 9,9-dioctylfluorene-2,7-diboronic acid. The crude acid was washed with hexane to give a white solid (4.3 g, 45%). The diboronic acid was then refluxed with propane-1,3-diol (1.2 g, 20 mmol) in toluene for 10 h. After work up, the crude product was recrystallized from hexane to afford 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (3.6 g, 72%) as white crystals.

^{1}H NMR ($CDCl_3$): $\delta = 7.75$ (d, fluorenyl H, 2H), 7.72–7.67 (m, fluorenyl H, 4H), 4.21 (t, –$B(OCH_2)_2$–, 8H), 2.10 (m, –$CH_2C_7H_{15}$, 4H), 1.98 (m, $CH_2(CH_2O)_2B$–, 4H), 1.23–0.52 (m, –$CH_2C_7H_{15}$, 30H).

^{13}C NMR ($CDCl_3$): $\delta = 151.11$ (fluorenyl q-C), 140.23(fluorenyl q-C), 139.48 (fluorenyl C–H), 132.24 (fluorenyl C-B), 128.37 (fluorenyl C–H), 123.33 (fluorenyl C–H), 67.83 (–$B(OCH_2)_2$–), 55.39 ($C(Ph)_2(C_8H_{17})_2$), 40.18 (–CH_2–), 31.63 (–CH_2–), 30.72 (–CH_2–), 29.42 (–CH_2–), 29.14 (–CH_2–), 28.75 (–CH_2–), 23.86 (–CH_2–), 22.78 (–CH_2–), 13.91 (–CH_3).

Preparation of PF3BOH (9)

A mixture of **5** (1.0 g, 2.6 mmol), **7** (1.4 g, 2.6 mmol), **8** (2.9 g, 5.2 mmol), toluene (50 mL), potassium carbonate (2 M, 50 mL), $Pd(PPh_3)_4$ (0.20 g, 0.17 mmol), and tetrabutylammonium bromide (0.3 g, 1.0 mmol) was stirred for 2 d at 90 °C in the dark. The reaction mixture was cooled to room temperature and precipitated into a mixture of MeOH and H_2O. The crude polymer was collected, washed with excess MeOH, redissolved in THF, and then precipitated into MeOH. Finally, the polymer was washed with acetone for 48 h with a Soxhlet apparatus and then dried under vacuum to yield PF3BOH (4.8 g, 90%).

^{1}H NMR ($CDCl_3$): $\delta = 7.85-7.59$ (m, fluorenyl H, 18*n*H), 7.10 (s, phenyl H, 2*n*H), 3.99 (t, $-OCH_2-$, 2*n*H), 3.85 (s, $-OCH_3$, 3*n*H), 3.61 (m, $-CH_2OH$, 2*n*H), 2.10 (m, $-CH_2C_7H_{15}$, 12*n*H), 1.80–1.34 (m, $-OCH_2(CH_2)_4CH_2OH$, 8*n*H), 1.30–0.60 and 1.32–0.57 (m, $-CH_2C_7H_{15}$, 90*n*H).

^{13}C NMR ($CDCl_3$): $\delta = 152.03$ (phenyl *C*–OCH_3), 151.36 (phenyl *C*–OCH_2–), 150.72 (fluorenyl q-C), 140.78 (fluorenyl q-C), 140.24 (fluorenyl q-C), 128.22 (fluorenyl C–H), 126.43 (fluorenyl C–H), 124.89 (fluorenyl C–H), 121.70 (phenyl q-C), 120.23 (phenyl q-C), 117.04 (phenyl C–H), 115.37 (phenyl C–H), 70.09 ($-OCH_2-$), 63.13 ($-CH_2OH$), 57.03 ($-OCH_3$), 55.65 ($C(Ph)_2(C_8H_{17})_2$), 40.68 ($-CH_2-$), 33.03 ($-CH_2-$), 32.05 ($-CH_2-$), 30.49 ($-CH_2-$), 30.36 ($-CH_2-$), 30.02 ($-CH_2-$), 29.65 ($-CH_2-$), 29.48 ($-CH_2-$), 26.26 ($-CH_2-$), 25.79 ($-CH_2-$), 24.21 ($-CH_2-$), 14.36 ($-CH_3$).

$\overline{M}_n$ (GPC) = 29 500, $\overline{M}_w/\overline{M}_n = 2.19$.

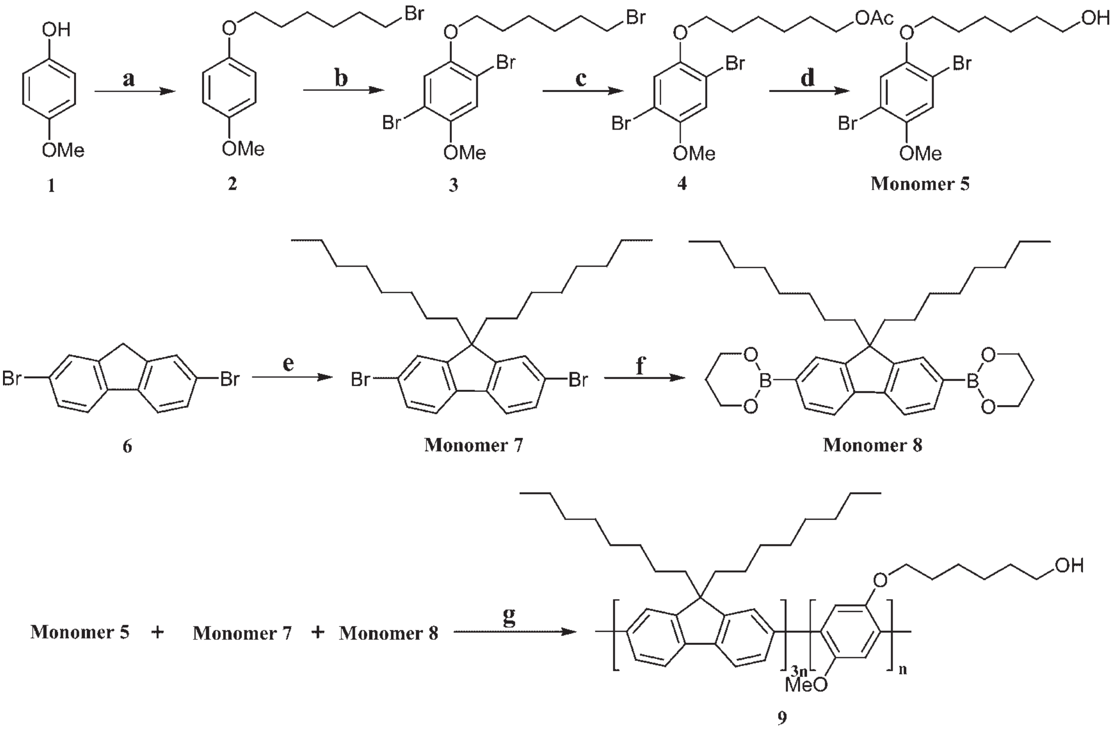
Preparation of Nanoparticles by Non-Covalently Bonded Self-Assembly

In a typical procedure to prepare the nanoparticles, a desired amount of PF3BOH (about 21 OH groups in every molecule) in THF was added dropwise to dilute PAA ($\overline{M}_n = 15\,000$, about 208 COOH groups in every molecule) aqueous solution directly under ultrasonic conditions (about one drop per ten seconds). In the procedure to prepare sample **M1**, the hydroxy-group number (n_{OH}) of PF3BOH was equal to the molecular number (n_{PAA}) of PAA, 0.3 mL of PAA (1.0 $mg \cdot mL^{-1}$ in water) was added to 2 mL of H_2O under ultrasonication for 5 min and then 0.2 mL of PF3BOH (0.1 $mg \cdot mL^{-1}$ in THF) was added dropwise under ultrasonication for 5 min. A similar procedure was used to make sample **M2**, where the molecular number (n_{PF3BOH}) of PF3BOH was equal to the molecular number (n_{PAA}) of PAA, such that 0.1 mL of PAA (0.1 $mg \cdot mL^{-1}$ in water) was added into 2 mL of H_2O under ultrasonication for 5 min and then 0.2 mL PF3BOH (0.1 $mg \cdot mL^{-1}$ in THF) was added dropwise under ultrasonication for 5 min. The concentrations of PF3BOH in **M1** and **M2** were about 3.3×10^{-7} $mol \cdot L^{-1}$. The resultant nanoparticles were characterized by dynamic light scattering (DLS) (Table 1).

Table 1. DLS characterization data of the nanoparticles and the proportion of PF3BOH and PAA.

Sample	Diameter nm	PI[a]	PAA/ PF3BOH[b]
M1	92.9	0.45	11:1
M2	138.2	0.16	1:2

[a] Polydispersity index.
[b] Weight ratio in water.



Scheme 1. Synthetic route to PF3BOH. Reagents and conditions: a) 1,6-dibromohexane, KOH, 90 °C; b) Br_2 (3 M in chloroform), room temperature; c) KOAc, 70 °C; d) KOH, room temperature; e) *n*-$C_8H_{17}Br$, 50% KOH aqueous solution, 60 °C; f) Mg, THF; $B(OCH_3)_3$, −78 °C; propane-1,3-diol, toluene, reflux; g) $Pd(PPh_3)_4$, Na_2CO_3 (2 M aqueous), 90 °C.

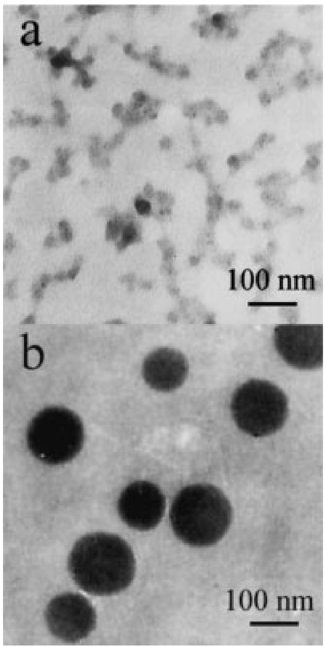


Figure 1. TEM images of the nanoparticles from a) sample **M1** and b) sample **M2**.

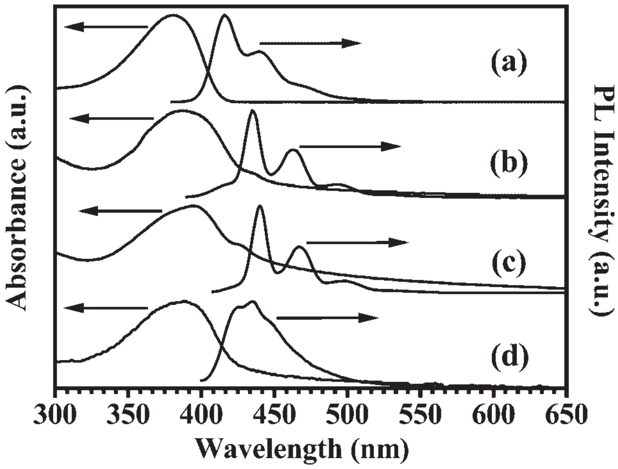


Figure 2. UV-vis absorption and PL (excited at 380 nm) spectra of a) PF3BOH in THF solution, b) aqueous sample **M1**, c) aqueous sample **M2**, and d) PF3BOH solid film.

Results and Discussion

The synthetic route to PF3BOH is illustrated in Scheme 1. Poly(fluorene-*co*-phenylene) with hydroxy-capped side chains (PF3BOH) is obtained by a Suzuki condensation reaction. All the structures of the monomers and PF3BOH have been confirmed by ^{1}H and ^{13}C NMR measurements. The number-average molecular weight of PF3BOH is about 29 500, as measured by GPC, and the number-average polymerization degree n of the PF3BOH has been calculated to be about 21.

In the preparation of specimens to observe discrete nanoparticles, 5 μL of the nanoparticle solution is dropped on a carbon-coated copper grid, which is then frozen in liquid N_2 just before use, followed by solvent evaporation at room temperature. Figure 1 shows the TEM images of sample **M1** and **M2**, in which the fluorescent nanoparticles can be seen with catenarian and spherical shapes, and they have a narrow size distribution on the nanoscale, which is in accordance with the DLS data (Table 1). In Figure 1(a), vermiculate nanochains about 20 nm in width and hundreds of nanometers in length are observed. The diameter of 92.9 nm obtained by DLS is the mean of their width and length, and the PI of 0.45 is so large that it may also prove the structure of vermiculate nanochains indirectly. Because of an excess of PAA, the conjugated PF3B backbone with its hydroxy-capped side chains extends into the water, which prevents the formation of aggregates between conjugated PF3B backbones and confirms the existence of the interaction between PF3B and PAA through hydrogen bonding. On the contrary, in Figure 1(b), a series of pyrene-loaded nanoparticles are shaped and the mean diameter of the nanoparticles is around 90–120 nm. Because n_{PF3BOH} is equal to n_{PAA}, it is suggested that the isolated aggregates tend to coalesce together to form complex morphologies by further self-association behavior.[13] A similar feature has been observed in some water-soluble polymer systems.[14] Because of the ease of preparation, i.e., only using non-covalent bond (hydrogen bond) self-assembly, a series of water-soluble shape-regulatable nanoparticles has been prepared successfully.

The mixture of PF3BOH and PAA in water is quite stable and no precipitate is observed several weeks after preparation. On the other hand, precipitation occurs immediately when directly adding a THF solution of PF3BOH into pure water, and a similar phenomenon is observed when adding an unhydroxylated poly(fluorene-*co*-phenylene) solution into an aqueous PAA solution. These features manifest the existence of the interaction between PF3BOH and PAA through hydrogen bonding.

Table 2. UV maximum absorption and PL maximum emission data of all the samples.

Sample	UV_{max} nm	PL_{max} nm
PF3BOH in THF	381	416
PF3BOH solid film	390	435
M1 (3.3×10^{-7} mol · L^{-1})	390	435
Dilute **M1** (6.6×10^{-8} mol · L^{-1})	–	435
Dilute **M1** (1.3×10^{-8} mol · L^{-1})	–	435
M2 (3.3×10^{-7} mol · L^{-1})	393	440
Dilute **M2** (6.6×10^{-8} mol · L^{-1})	–	440
Dilute **M2** (1.3×10^{-8} mol · L^{-1})	–	440

In Figure 2, the UV-vis spectrum of PF3BOH shows a peak absorption at 381 nm in THF solution, which moves to 390 nm in the solid film (spin-cast from 5 $mg \cdot mL^{-1}$ PF3BOH in THF solution). In aqueous solutions of **M1** and **M2**, the maximal absorptions are observed at 390 and 393 nm, respectively. With an excitation wavelength of 380 nm, the solution of PF3BOH in THF shows a peak emission at 416 nm and distinct shoulders at 439 and 465 nm, while the solid film exhibits a broad and structureless emission around 435 nm (Table 2). This implied the existence of aggregation that results from interchain interactions in the solid state of PF3BOH, a phenomenon commonly observed in linear poly(9,9-dialkylated fluorene)s.[7,8] The photoluminescence (PL) spectra of aqueous solutions of **M1** and **M2** undergo a similar bathochromic shift, but retain their structure as in the solution PL spectrum of PF3BOH. Upon dilution (the concentration of PF3BOH is about 6.6×10^{-8} and 1.3×10^{-8} $mol \cdot L^{-1}$), the spectra do not show any appreciable change, and thus interchain aggregation can be excluded for the occurrence of such a red shift.[15] A likely explanation could be that the co-planarization of a single polymer chain of PF3BOH is increased upon interaction with PAA in water since the hydroxy groups of PF3BOH have to be 'positioned' towards the carboxylic groups of PAA to lead to a more 'regular' polymer chain of PF3BOH in **M1** and **M2**.[16]

Conclusion

In summary, novel water-soluble luminescent micelles containing PF3BOH and PAA have been successfully prepared by self-assembly through non-covalent bonds. TEM and DLS are used to confirm the morphology of the PF3BOH/PAA micelles. The micelles exhibit similar optoelectronic properties to a PF3BOH solid film although they do not undergo aggregation. Self-assembly by non-covalent bonds provides a novel and simple way to obtain water-soluble luminescent materials and to realize biomodification on conjugated polymers, which opens opportunities for potentially greatly improved conjugated-polymer-based biosensors. Further studies of the materials as biosensors are in progress.

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