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Water-Soluble Dendronized Polyfluorenes with an Extremely High Quantum Yield in Water

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ABSTRACT: A set of water-soluble dendronized polyfluorenes bearing peripheral charged amino groups were synthesized by two steps: (1) Suzuki polycondensation of dendritic macromonomers carrying peripheral Boc-protected amino groups with 1,4-benzenediboronic acid propanediol ester; (2) the deprotection of the resulting Boc-protected dendronized polymers with aqueous HCl. All the protected dendronized polyfluorenes displayed good solubility in common organic solvents such as THF, chloroform, and methylene chloride. After deprotection, the zero generation polymers were only partially soluble in water, but the first and the second generation dendronized polymers were fully soluble in water. The optic properties of the protected and deprotected dendronized polymers were investigated. In solution, all these polymers exhibited bright blue emission. Unlike normal water-soluble conjugated polymer, the second generation deprotected dendronized polyfluorenes exhibited a quite high quantum yield ($\Phi_F = 94\%$) in water.

Introduction

Conjugated polymers are being extensively investigated for their potential applications in the fields of optoelectronics, microelectronics,[1] and chemical and biological sensors.[2] Conjugated polymers based on poly(*p*-phenylene)s,[3] poly(*p*-phenylene−vinylene)s,[4] poly(*p*-phenylene−ethynylene)s,[5] poly(triacetylene)s,[6] poly(acetylene)s,[7] and poly(fluorene)s[8] have been well developed in the past decade. Among them, polyfluorenes are considered to be promising blue-light-emitting materials due to their exceptionally high solution quantum efficiencies as well as their excellent chemical properties and thermal stabilities.[9] However, polyfluorenes, like many other conjugated polymers, have a strong tendency to aggregate, resulting in self-quenching their fluorescence in some extent. Many efforts have been devoted to overcome this drawback. Hence, dendronized polymers have been developed and highlighted.[10]

Dendronized polymers are polymers carrying lateral dendron(s) at each repeat unit. For higher generation dendronized polymers, the polymer backbones are fully encapsulated into dendritic envelopes. The “site isolation” effect of the dendritic envelope can effectively prevent the polymer backbone from aggregating and doing cross-talk.[11] As an important family member, dendronized polyfluorenes have also been synthesized, and their luminescent properties have been investigated as the conjugated main chains are wrapped with a variety of dendritic segments. For higher generation dendronized polyfluorenes, the photoluminescent quantum efficiency can be very high due to the polyfluorene backbones are fully isolated by the dendritic wedges.[11]

Water-soluble conjugated polymers, generally realized by the addition of charged groups in the polymers’ side chains, greatly combining the remarkable advantages of conjugated polymers and polyelectrolytes, are being studied for their applications in the fields of electrooptical devices,[12] chem- and biosensors, and drug delivery.[13] The syntheses of various water-soluble conjugated polymers[14] and the investigations of the excitation energy transfer[15] have been reported. Since the aggregation of conjugated polymer chains in aqueous media leads to the reducing of their luminescent and the decreasing of their PL quantum efficiency, most of fluorene-based polyelectrolytes reported in the literature did not show PL quantum efficiencies as high as those of typical fluorene-based polymers in organic solvents.[14c,16]

We report here the synthesis of a series of cationic water-soluble dendronized polyfluorenes carrying peripheral charged amino groups. The introduction of lateral dendrons, as expected, should not only provide the conjugated polymers with good solubility in water through the charged amino groups but also reduce the aggregation of polymers through the “site isolation” effect. An investigation of the photophysical properties revealed that the second generation water-soluble dendronized polyfluorenes were of extremely high PL quantum efficiency in water solution.

Experimental Section

Materials. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature[17] and stored in a Schlenk tube under nitrogen. 2,7-Dibromofluorene (**1**), *tert*-butyl-3-chloropropylcarbamate (**2**), 3,5-bis(3-*tert*-butoxycarbonylaminopropoxy)benzoic acid (**3**), 3,5-bis{3-[3,5-bis(3-*tert*-butoxycarbonylaminopropoxy)benzoylamino]propoxy}benzoic acid (**4**), and 1,4-benzenediboronic acid propanediol ester (**5**) were purchased from Synwit Technology. 1-Hydroxybenzotrizole (HOBt) and 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC·HCl) were purchased from Shanghai Medpep. Solvents were dried according to standard procedures.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 or a Bruker DM300 spectrometer in $CDCl_3$ or DMSO-d_6. The GPC measurements were performed on Waters 410 system against polystyrene standards with THF as an eluent. UV−vis absorption spectra were obtained on a Shimadzu UV−vis spectrophotometer model UV-1601 PC. Fluorescence spectra were recorded on a Varian Cary-Eclipse spectrophotometer. Elemental analyses were performed on a Flash EA 1112 analyzer.

G0Boc. A mixture of **1** (4.35 g, 13.4 mmol), **2** (5.72 g, 29.5 mmol), $PhCH_2NEt_3Cl$ (0.4 g, 1.47 mmol), and DMSO (200 mL)

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was carefully degassed and charged with nitrogen. To the mixture was added in dropwise a degassed aqueous NaOH solution (15 mL, 40 wt %). The mixture was stirred at room temperature for 48 h. Water was added, and the mixture was extracted with ether. The ether layer was separated, washed with aqueous NaOH (5 wt %) and water each for three times, and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel column eluting with CH_2Cl_2/CH_3OH (v:v, 20:1) to afford **G0Boc** a pale yellow solid (5.92 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52 (d, 2H), 7.47 (d, 2H), 7.43 (s, 2H), 4.24 (s, 2H), 2.88 (s, 4H), 1.96 (t, 4H), 1.39 (s, 18H), 0.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.73, 151.27, 138.95, 130.61, 125.99, 121.76, 121.26, 79.03, 54.84, 40.32, 37.08, 28.30, 24.44. Anal. Calcd for $C_{29}H_{38}Br_2N_2O_4$: C, 54.56; H, 6.00; N, 4.39. Found: C, 53.62; H, 5.91; N, 4.29.

G0·HCl. To a solution of **G0Boc** (2.5 g, 3.92 mmol) in THF (5.0 mL) was added hydrochloric acid (15 mL, 5 M). The mixture was stirred at room temperature for 24 h. After the addition of acetone (30 mL), the mixture was then placed in a fridge overnight. A large amount of white precipitates were formed; filtration and washing with acetone afforded **G0·HCl** as a white solid (2.0 g, 95%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.87 (d, 2H), 7.75 (s, 2H), 7.60 (d, 2H), 7.46 (s, 6H), 2.54 (m, 4H), 2.09 (m, 4H), 0.73 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 151.9, 139.6, 131.4, 127.4, 127.2, 122.1, 55.6, 45.6, 36.3, 22.7.

G1Boc. A mixture of **G0·HCl** (400 mg, 0.78 mmol), **3** (912 mg, 1.95 mmol), HOBt (320 mg, 2.37 mmol), and 150 mL of anhydrous CH_2Cl_2 was carefully degassed and charged with N_2. The mixture was cooled to 0−5 °C in an ice water bath; Et_3N (1.2 mL) and EDC·HCl (600 mg, 3.13 mmol) were added. The mixture was stirred at room temperature overnight and then poured into 50 mL of aqueous $NaHCO_3$. The organic layer was separated, washed with aqueous NaCl, and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel column eluting with CH_2Cl_2/CH_3OH (10:1) to afford **G1Boc** as a white solid (692 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53 (d, 2H), 7,47 (d, 2H), 7.46 (s, 2H), 6.78 (s, 4H), 6.52 (s, 2H), 5.96 (s, 2H), 4.70 (s, 4H), 3.99 (t, 8H), 3.29 (m, 8H), 3.20 (m, 4H), 2.05 (m, 4H), 1.94 (m, 8H), 1.59 (s, 36H), 0.89 (t, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.18, 160.08, 156.15, 151.39, 139.17, 136.83, 130.93, 126.23, 122.05, 121.56, 105.73, 104.59, 79.40, 66.04, 55.09, 40.03, 37.94, 37.41, 29.63, 28.55, 24.38. Anal. Calcd for $C_{65}H_{90}Br_2N_6O_{14}$: C, 58.29; H, 6.77; Br, 11.93; N, 6.28. Found: C, 58.04; H, 6.77; Br, 12.04; N, 6.15.

G2Boc. A mixture of **G0·HCl** (50 mg, 0.0978 mmol), **4** (286 mg, 0.245 mmol), HOBt (33 mg, 0.245 mmol), and anhydrous CH_2Cl_2 (40 mL) was degassed and charged with N_2. The mixture was cooled to 0−5 °C in an ice water bath; Et_3N (0.13 mL) and EDC·HCl (56 mg, 0.294 mmol) were added. The mixture was stirred at room temperature overnight and then poured into 15 mL of aqueous $NaHCO_3$. The organic layer was separated, washed with aqueous NaCl, and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel column eluting with CH_2Cl_2/CH_3OH (10:1) to afford **G2Boc** as a white solid (198 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (d, 2H), 7.39 (broad, 4H), 7.29 (s, 4H), 6.89 (s, 2H), 6.87 (s, 8H), 6.79 (s, 4H), 6.46 (s, 4H), 6.39 (s, 2H), 5.01 (s, 8H), 3.91 (s, 24H), 3.54 (s, 8H), 3.22 (s, 16H), 3.17 (s, 4H), 2.00 (m, 12H), 1.89 (m, 16H), 1.41 (s, 72H), 0.93 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.42, 167.14, 159.80, 159.63, 156.09, 151.44, 138.83, 136.53, 130.54, 126.00, 121.63, 121.32, 105.69, 104,34, 79.10, 66.99, 66.03, 65.71, 54.78, 39.89, 37.64, 37.41, 29.51, 28.82, 28.34, 24.07. Anal. Calcd for $C_{137}H_{194}Br_2N_{14}O_{34}$: C, 60.03; H, 7.13; Br, 5.83; N, 7.15. Found: C, 60.02; H, 7.34; Br, 5.99; N, 6.77.

General Procedure for the Synthesis of Dendronized Polymers (PG0Boc, PG1Boc, and PG2Boc). A mixture of the dendritic monomer (**G0Boc** or **G1Boc** or **G2Boc**), **5**, $NaHCO_3$, THF, and H_2O was carefully degassed before and after $Pd(PPh_3)_4$ was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. CH_2Cl_2 (100 mL) was added, and the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was redissolved in a small amount of CH_2Cl_2, the obtained solution was dropped into diethyl ether, and the formed precipitate was recovered by centrifugation. This procedure was repeated two times. The collected precipitate was dried under high vacuum to afford the desired dendronized polymers (**PG0Boc**, **PG1Boc**, and **PG2Boc**).

PG0Boc. G0Boc (200 mg, 0.31 mmol), **5** (77 mg, 0.31 mmol), $NaHCO_3$ (0.3 g, 3.57 mmol), $Pd(PPh_3)_4$ (3.6 mg, 3.12 μmol), THF (10 mL), and water (4 mL) were used. **PG0Boc** was obtained as a slightly yellow solid (148 mg, yield 83%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85−7.80 (broad, 6H), 7.70 (d, 2H), 7.65 (s, 2H), 4.27 (s, 2H), 2.95 (broad, 4H), 2.15−2.07 (broad, 4H), 1.38 (s, 18H), 0.95 (broad, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.85, 150.54, 140.14, 132.07, 128.86, 128.52, 127.66, 127.58, 127.08, 121.29, 120.31, 115.83, 79.05, 54.66, 40.69, 37.51, 28.38, 24.79. Anal. Calcd for $[C_{35}H_{42}N_2O_4]_n$: C, 75.78; H, 7.63; N, 5.05. Found: C, 73.43; H, 7.38; N, 5.17.

PG1Boc. **G1Boc** (103 mg, 0.077 mmol), **5** (19 mg, 0.078 mmol), $NaHCO_3$ (0.2 g, 2.38 mmol), $Pd(PPh_3)_4$ (0.9 mg, 0.78 μmol), THF (10 mL), and water (4 mL) were used. **PG1Boc** was obtained as a slightly yellow solid (87 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81−7.62 (broad, 10H), 6.76 (s, 4H), 6.45−6.41 (broad, 4H), 5.01 (broad, 4H), 3.87 (broad, 8H), 3.21 (broad, 12H), 2.19 (broad, 4H), 1.86 (broad, 8H), 1.39 (s, 36H), 1.04 (broad, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.7, 158.5, 154.8, 140.8, 138.9, 138.5, 135.4, 135.2, 126.1, 104.2, 103.1, 77.8, 64.5, 64.3, 36.3, 28.0, 27.0, 26.6, 20.7, 13.9. Anal. Calcd for $[C_{71}H_{94}N_6O_{14}]_n$: C, 67.92; H, 7.55; N, 6.69. Found: C, 67.10; H, 7.77; N, 6.42.

PG2Boc. **G2Boc** (100 mg, 0.036 mmol), **5** (9 mg, 0.037 mmol), $NaHCO_3$ (0.2 g, 2.38 mmol), $Pd(PPh_3)_4$ (0.5 mg, 0.43 μmol), THF (10 mL), and water (4 mL) were used. **PG2Boc** was obtained as a slightly yellow solid (86 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61 (broad, 14H), 6.89 (broad, 10H), 6.75 (s, 4H), 6.44 (broad, 6H), 5.13 (broad, 8H), 3.86 (broad, 24H), 3.48 (broad, 8H), 3.19 (broad, 20H), 1.94−1.85 (broad, 28H), 1.39 (s, 72H), 1.91 (broad, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.22, 160.41, 156.84, 137.18, 106.50, 79.78, 66.40, 38.39, 30.15, 29.58, 29.08, 15.92. Anal. Calcd for $[C_{143}H_{198}N_{14}O_{34}]_n$: C, 64.64; H, 7.51; N, 7.38. Found: C, 62.95; H, 7.40; N, 6.63.

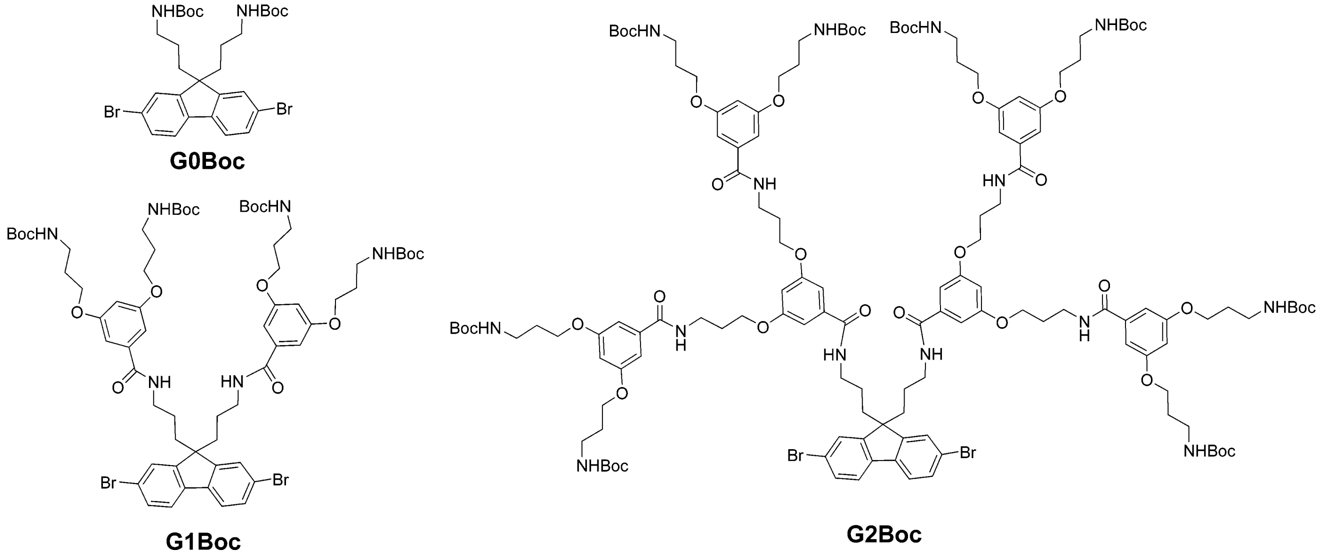
General Procedure for the Synthesis of Water-Soluble Dendronized Polymers (**PG0·HCl**, **PG1·HCl, and PG2·HCl**). To a solution of 50 mg of the dendronized polymer (**PG0Boc** or **PG1Boc** or **PG2Boc**) in 3 mL of THF was added hydrochloric acid (10 mL, 5 M). After stirring at room temperature overnight, to the mixture was added 30 mL of acetone and placed in fridge until a large amount of precipitate formed. The formed precipitate was recovered by filtration and washed with acetone three times to afford the desired water-soluble dendronized polymers (**PG0·HCl** or **PG1·HCl** or **PG2·HCl**).

PG0·HCl. **PG0·HCl** was obtained as a slightly yellow solid (34 mg, 89%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.01−7.93 (broad, 16H), 2.68−2.62 (broad, 4H), 2,34−2.28 (broad, 4H), 1.01 (broad, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 150.80, 139.95, 129.50, 127.93, 126.52, 122.21, 121.20, 60.35, 56.31, 54.79, 36.43, 32.58, 30.07, 22.65, 13.25.

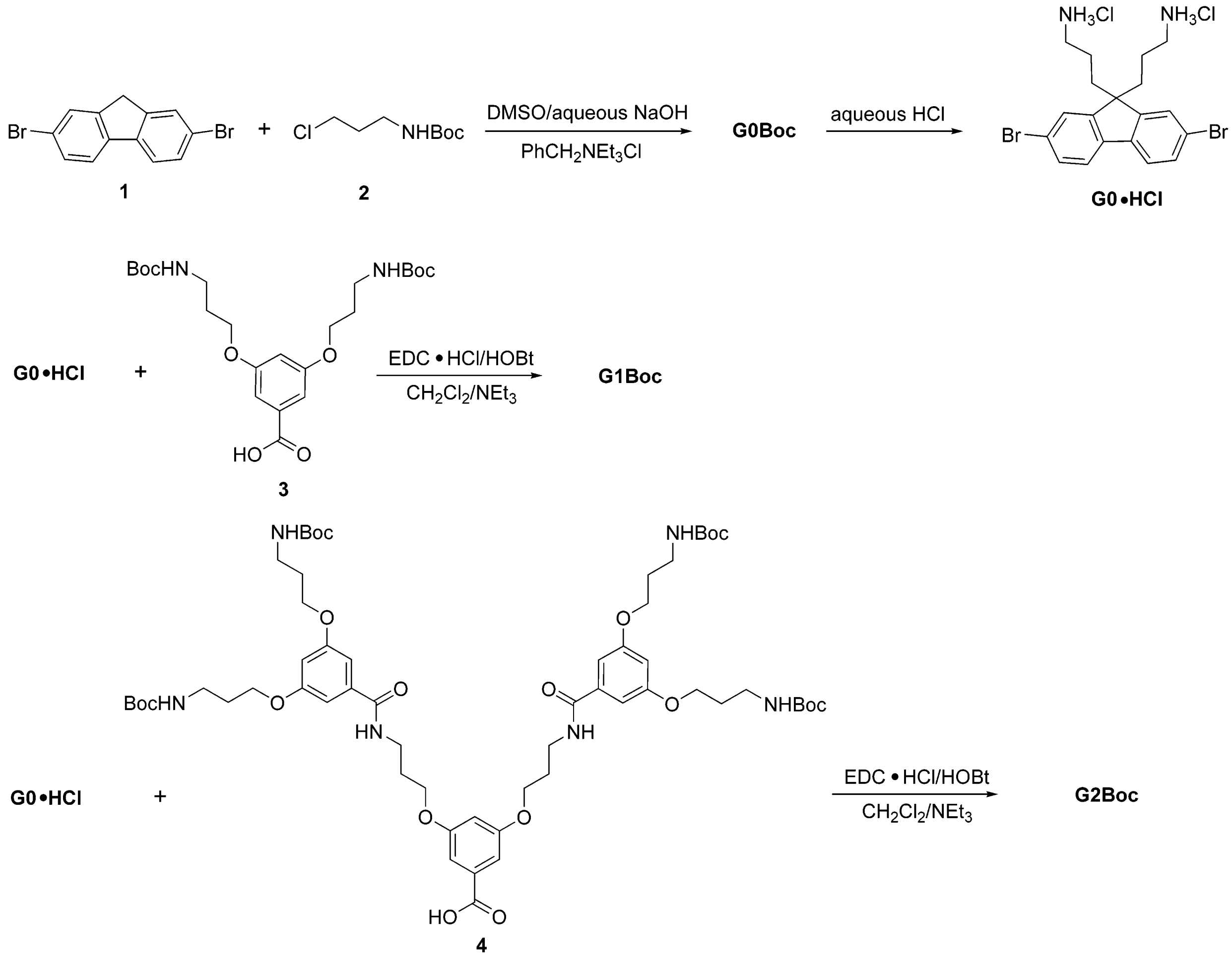
PG1·HCl. **PG1·HCl** was obtained as a slightly yellow solid (34 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.24−7.91 (broad, 24H), 7.01 (s, 4H), 6.66 (s, 2H), 4.09 (broad, 8H), 2.94 (broad, 12H), 2.05 (broad, 12H), 0.95 (broad, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 160.34, 140.87, 137.57, 128.49, 107.03, 66.14, 37.22, 27.80, 1.22.

PG2·HCl. **PG2·HCl** was obtained as a white solid (35 mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.71 (broad, 4H), 8.31 (broad, 30H), 7.85 (broad, 6H), 7.12−6.97 (broad, 12H), 6.70−6.64 (broad, 6H), 4.14 (broad, 28H), 2.97 (broad, 24H), 2.08 (broad, 28H), 0.95 (broad, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 166.79, 160.62, 160.41, 137.62, 107.17, 105.26, 66.87, 66.21, 37.54, 37.25, 29.93, 27.81, 1.23.

Chart 1. Chemical Structures of the Dendritic Macromonomers G0Boc, G1Boc, and G2Boc



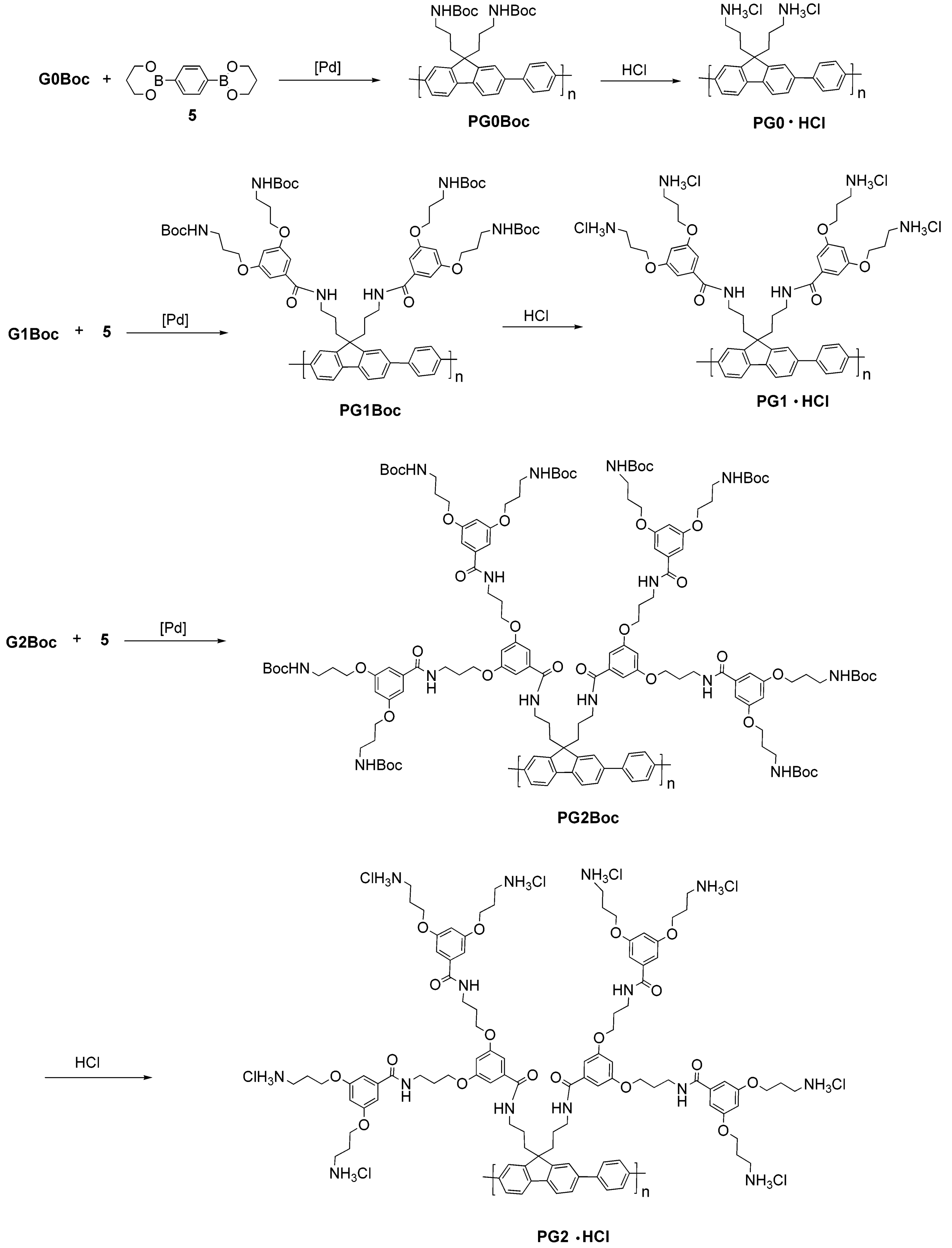
Scheme 1. Synthesis of the Dendritic Macromonomers G0Boc, G1Boc, and G2Boc



Results and Discussion

Synthesis of Monomers and Polymers. The chemical structures of dendritic monomers **G0Boc**, **G1Boc**, and **G2Boc** are shown in Chart 1. The synthetic routes are shown in Scheme 1. **G0Boc** was accomplished in a yield of 69% by the reaction of 2,7-dibromofluorene (**1**) and *tert*-butyl-3-chloropropylcarbamate (**2**) in DMSO with aqueous NaOH as a base and triethylbenzylammonium chloride as a phase transfer catalyst. The deprotection of **G0Boc** with aqueous HCl afforded **G0·HCl** in a yield of 95%. Dendritic monomers **G1Boc** and **G2Boc** were prepared by the coupling of **G0·HCl** with **3** and **4**, respectively, using 1-hydroxybenzotriazole (HOBt) and 1-ethyl-3-(3-dimethylamino)propylcarbodiimide hydrochloride (EDC·HCl) as mild coupling reagents for the formation of amide linkage. After purification by normal silica gel chromatography, pure macromonomer **G1Boc** and **G2Boc** were obtained in yields of 66% and 74%, respectively. The high purity of the dendritic monomers was

Scheme 2. Synthesis of Dendronized Polymers PG0Boc, PG1Boc, PG2Boc, PG0·HCl, PG1·HCl, and PG2·HCl



proved by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

Suzuki polycondensation (SPC) of the dendritic macromonomers (**G0Boc**, **G1Boc**, and **G2Boc**) with 1,4-benzenediboronic acid propanediol ester (**5**) was done in a biphasic system (THF/aqueous $NaHCO_3$) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor (Scheme 2). Reactions were kept stirring at reflux for 96 h. Standard workup afforded dendronized polymers **PG0Boc**, **PG1Boc**, and **PG2Boc** as amorphous, slightly yellow solids in yields of 83%, 90%, and 89%, respectively. The molecular weights determined by GPC against polystyrene standards are summarized in Table 1. The structure of Boc-protected dendronized polymers (**PG0Boc**, **PG1Boc**, and **PG2Boc)** was also fully characterized by ^{1}H and ^{13}C NMR

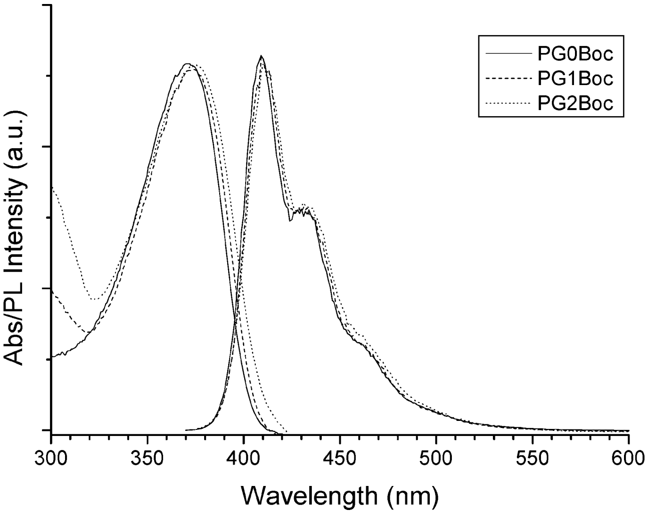


Figure 1. UV−vis absorption and PL spectra (excited at 360 nm) of dendronized polymers **PG$_0$Boc**, **PG$_1$Boc**, and **PG$_2$Boc** in THF (1 μg/mL).

Table 1. Molecular Weights of Dendronized Polymers

	M_n	P_n	M_w	P_w	M_w/M_n
PG$_0$Boc	27 000	50	56 000	102	2.05
PG$_1$Boc	28 000	23	60 000	48	2.10
PG$_2$Boc	31 000	12	52 000	20	1.70

spectroscopy as well as elemental analysis. The deprotection of the dendronized polymers **PG0Boc**, **PG1Boc**, and **PG2Boc** was accomplished by stirring their THF solutions with concentrated aqueous HCl to afford the desired water-soluble dendronized polymers **PG0·HCl**, **PG1·HCl**, and **PG2·HCl** in yields of 89%, 85%, and 86%, respectively. Their structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Optical Properties. Boc-protected dendronized polymers **PG0Boc**, **PG1Boc**, and **PG2Boc** were readily soluble in common organic solvents such as methylene chloride, toluene, and THF and exhibited bright blue fluorescence in solution, whereas the deprotected dendronized polymers **PG1·HCl** and **PG2·HCl** were soluble in polar solvents such as water and DMSO. Zero generation polymer **PG0·HCl** was only partially soluble in water but fully soluble in DMSO. The solubility of the deprotected dendronized polymers in water increases with the increasing of their generation. The absorption and photoluminescent (PL) spectra of the Boc-protected dendronized polymers in dilute THF solutions and the deprotected dendronized polymers in deionized water solutions are shown in Figure 1 and Figure 2, respectively. The maximum absorption and emission wavelengths, as well as the PL quantum efficiencies (Φ_F), are listed in Table 2.

In THF solution, dendronized polymers **PG0Boc**, **PG1Boc**, and **PG2Boc** exhibited typical absorption and emission spectra of fluorene−phenylene-based polymers as reported in the literature. All the polymers exhibited an absorption maximum ranging from 372 to 376 nm and an emission maximum at about 409 nm and a shoulder at about 432 nm. The quantum yields of **PG0Boc**, **PG1Boc**, and **PG2Boc** in dilute THF solution were measured to be 95%, 99%, and 77%, respectively, by using 9,10-diphenylanthracene as a reference standard ($\Phi_F = 90\%$). The decreasing of quantum efficiency for **PG2Boc** is probably due to the twisting of the backbone caused by the steric congestion of the lateral dendrons. The same phenomenon has been observed in a similar system as reported in our previous paper.[11d]

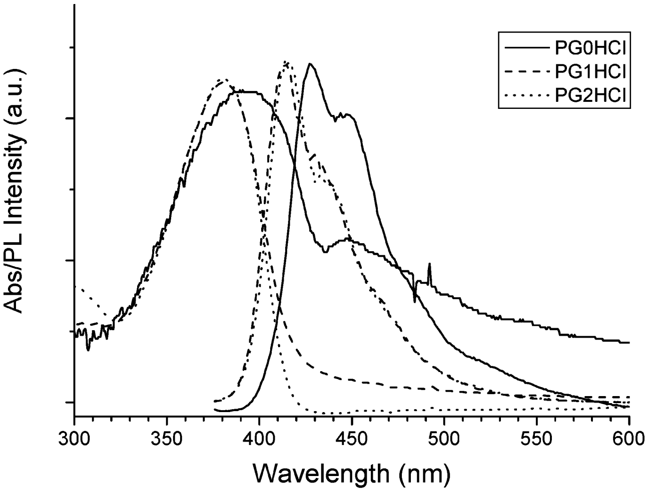


Figure 2. UV−vis absorption and PL spectra (excited at 360 nm) of dendronized polymers **PG$_0$·HCl**, **PG$_1$·HCl**, and **PG$_2$·HCl** in water (1 μg/mL).

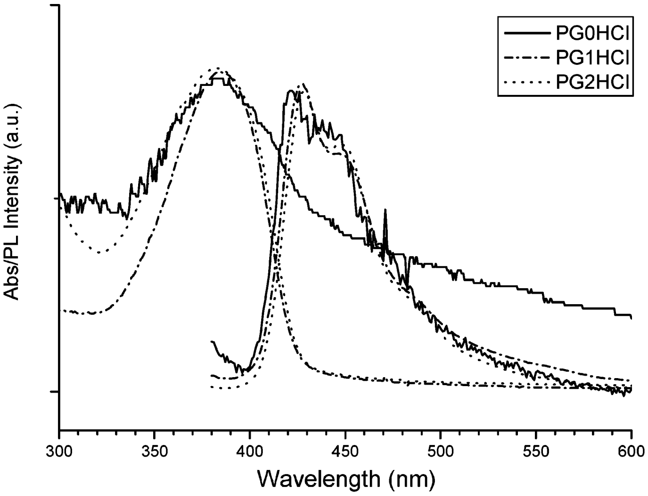


Figure 3. UV−vis absorption and PL spectra (excited at 360 nm) of water-soluble dendronized polymers **PG$_0$·HCl**, **PG$_1$·HCl**, and **PG$_2$·HCl** in films.

Compared with the absorption spectra of the Boc-protected dendronized polymers **PG0Boc**, **PG1Boc**, and **PG2Boc** in THF solution, the absorption spectra of the deprotected polymers **PG0·HCl**, **PG1·HCl**, and **PG2·HCl** in water solution were red-shifted. The red shift of the absorption is probably caused by the solvatochromism of the conjugated polyfluorene−phenylene backbone in more polar solvent (water). In water solution, the deprotected polymer **PG0·HCl** displayed a very broad absorption peak centered at 394 nm and a shoulder peaked at 448 nm. The red-shifted and broadened absorption of **PG0·HCl** is probably due to the formation of J-aggregations of the hydrophobic conjugated polymer chains in water solution. For polymers **PG1·HCl** and **PG2·HCl**, as expected, the “site-isolation” effect of the larger lateral dendritic wedges effectively prevented the backbones from forming aggregation. The isolation of backbones by the dendritic envelope in the case of higher generation dendritic polymers **PG1·HCl** and **PG2·HCl** resulted in narrower absorption peaks. In water solution, the deprotected polymer **PG0·HCl** exhibited a blue emission peak at 427 nm and a shoulder at 447 nm, which is probably from the J-aggregates. The deprotected dendronized polymers **PG1·HCl** and **PG2·HCl** showed almost superimposable emission spectra in water solution, which had an emission peak at 415 nm and a shoulder at about 433 nm. The PL quantum efficiencies of the dendronized polymers in water solution were measured by using quinine sulfate as a reference standard, and the results

Table 2. UV−vis Absorption and Photoluminescent Properties of Dendronized Polymers in Solutions

polymers	$\lambda_{\max,\mathrm{abs}}$ (nm)	$\lambda_{\max,\mathrm{em}}$ (nm)	Φ_F (%)	solvent	standard
PG$_0$Boc	372	409	95	THF	9,10-diphenylanthracene ($\Phi_F = 0.9$)
PG$_1$Boc	375	410	99		
PG$_2$Boc	376	410	77		
PG$_0$·HCl	391	427	17	water	quinine sulfate ($\Phi_F = 0.55$)
PG$_1$·HCl	381	415	85		
PG$_2$·HCl	382	415	94		

Table 3. UV−vis Absorption and Photoluminescent Properties of Water-Soluble Dendronized Polymers in Films

polymer	$\lambda_{\max,\mathrm{abs}}$ (nm)	$\lambda_{\max,\mathrm{em}}$ (nm)	Φ_F (%)	standard
PG$_0$·HCl	385	421	6	polyfluorene ($\Phi_F = 0.55$)
PG$_1$·HCl	384	427	10	
PG$_2$·HCl	382	429	21	

are listed in Table 2. Because of the strong aggregation tendency of **PG0·HCl** in water solution, the quantum yield of **PG0·HCl** is relatively low (17%). Polymers **PG1·HCl** and **PG2·HCl**, as expected, had remarkably high PL quantum efficiencies of 85% and 94% in water, respectively. Although this relative method could only give an estimation of the fluorescence quantum yield, these data still indicated that the introducing of dendritic wedges onto the fluorene−phenylene backbones highly enhanced the PL quantum yields of the dendronized polymers, which realized our foremost expectations very well.

Solid films on quartz plates used for UV−vis absorption and fluorescence spectroscopy measurements were prepared by dip-coating with water solutions of the deprotected dendronized polymers (1.0 mg/mL). Figure 3 shows the UV−vis absorption and fluorescence spectra of the water-soluble dendronized polymers **PG0·HCl**, **PG1·HCl**, and **PG2·HCl** in films. Compared with their corresponding absorption spectra in water solutions, the absorption maximum of **PG0·HCl** in film blue-shifted for about 6 nm, the absorption maximum of **PG1·HCl** in film red-shifted for about 2 nm, and the absorption maximum of **PG2·HCl** in film was almost unchanged. In comparison with the film absorption spectrum of **PG0·HCl**, the film ones of **PG1·HCl** and **PG2·HCl** were much narrower. These results also indicated that higher generation dendritic envelop could effectively reduce the aggregation of the conjugated polymer chains in solid films. Compared with their corresponding emission spectra in water solutions, the emission maximum of **PG0·HCl** in film blue-shifted for about 6 nm, the emission maximum of **PG1·HCl** red-shifted for about 12 nm, and the emission maximum of **PG2·HCl** red-shifted for about 14 nm. The fluorescence quantum yields of the dendronized polymers in films were estimated by comparing the fluorescence intensity of the dendronized polymers with that of a sample of poly(2,7-(9,9-dioctyl)fluorene) (POF) excited at 384 nm ($\Phi_F = 0.55$).[11a,d] The results are listed in Table 3. This relative method can only give an estimation of the fluorescence quantum yields of the polymers in films. The fluorescence quantum yields of the dendronized polymers in films increased with the increasing of the generation of the lateral dendrons, and the second generation dendronized polymer **PG2·HCl** in film had the highest quantum yield.

In conclusion, a novel series of water-soluble dendronized poly(fluorene−phenylene)s were designed and synthesized. Preliminary studies showed that the solubility and PL quantum efficiencies of these polymers in water got notably better and higher as the size of the attached dendrons got larger. The deprotected dendronized polymers **PG1·HCl** and **PG2·HCl** exhibited remarkably high PL quantum efficiencies in water. Further experiments on the pH-depended aggregation and self-assembly behaviors, as well as detailed investigations on the applications in the field of chem- and biosensors and light-emitting materials, are in progress.

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