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Facile Synthesis of 3,8-Dibromo-Substituted Phenanthridine Derivatives and Their Conjugated Polymers

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ABSTRACT: We present an efficient and convenient synthesis of 3,8-dibromophenanthridine derivatives and their conjugated polymers and demonstrate that phenanthridine-containing conjugated polymers can be used as luminescent chemosensor materials. High molecular weight poly(phenanthridine-*co*-fluorene)s (**P1**, **P2**) and poly(phenanthridine-*co*-*p*-phenylene) (**P3**) were synthesized by palladium-catalyzed Suzuki−Miyaura−Schlüter polycondensation (SMSPC). These phenanthridine-containing polymers are of high quantum yields in solution and show reversible optical response to protonation and deprotonation of the phenanthridine rings.

Introduction

Conjugated polymers have received a great deal of interest for a variety of potential applications, such as optoelectronics, microelectronics,[1] and chemical and biological sensors.[2] To meet diverse demands for different uses, incessant exploration of new conjugated polymer materials is highly required.[3] Phenanthridine is a fused aromatic compound with an electron-withdrawing nitrogen atom in scaffold,[4] which has been synthesized in 1930s.[5] However, there is no report on this chromophore as a building block for the construction of conjugated polymers.

Bischler−Napieralski cyclization was first reported more than a century ago[6] and has been widely used in synthesis of pharmaceutically interesting nitrogen-containing heterocyclic compounds in synthetic organic and medical chemistry.[7] Here, we report the facile synthesis of 3,8-dibromo-substituted phenanthridine derivatives using Bischler−Napieralski cyclization as the key step. A set of 6-substituted 3,8-dibromophenanthridine monomers has been synthesized. Suzuki−Miyaura−Schlüter polycondensation (SMSPC) of 3,8-dibromophenanthridine-based monomers and aryldiboronic ester monomers afforded high molecular weight conjugated polymers with phenanthridine units in polymer main chains. Photophysical properties of these polymers were also studied. To the best of our knowledge, this is the first report on the synthesis of phenanthridine-containing conjugated polymers.

Experimental Section

Materials. Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Phosphoryl trichloride was freshly distilled before use. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200−300 mesh). The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature[8] and stored in a Schlenk tube under nitrogen. 2-Nitro-4,4′-dibromobiphenyl (**1**),[9] 9,9-dioctylfluorene-2,7-diboronic pinacol ester (**5**),[10] and 2,5-dihexylphenyl-1,4-diboronic acid ester (**6**)[11] were prepared according to literature procedures.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 or an AV600 spectrometer. Gel permeation chromatography (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 Hitachi F-4500 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) of the samples in THF were measured by using 9,10-diphenylanthracene ($\Phi_F = 0.9$) as a standard.[12] Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The powder X-ray diffraction (XRD) patterns were collected using monochromated Cu Kα radiation (λ = 1.540 56 Å) on a Rigaku D/max-2500 diffractometer. Polarized light micrography was performed on an Olympus BH-2 optical microscope with a Mettler hot stage (FP-52) and an automatic camera (heating rate: 10 °C/min). HOMO levels of the polymers were determined by the ultraviolet photoelectron spectroscopy (UPS) measurements of a bulk thin film spin-coated on ITO. UPS characterizations (binding energy error of about 100 meV) were carried out with monochromatized HeI radiation at 21.2 eV in ultrahigh vacuum. The highest occupied molecular orbital (HOMO) values are here defined as the vertical ionization potential derived from UPS.

2-Amino-4,4′-dibromobiphenyl (2). To a solution of **1** (15.0 g, 42.0 mmol) in 160 mL of ethanol was added aqueous HCl (80 mL, 32%). Tin powder (10.0 g, 84.0 mmol) was then added portionwise over 10 min, and the reaction mixture was heated to reflux overnight. After cooling, the mixture was poured into ice water (400 mL) and then made alkaline with aqueous NaOH solution (20%) until the pH was 9.0. The precipitate was collected by filtration and dried under vacuum to give the product as a colorless solid that could be used for next step without further purification (13 g, 95%). ^1H NMR

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($CDCl_3$, 400 MHz): δ 7.57 (d, 2H, ArH), 7.29 (d, 2H, ArH), 6.93 (s, 2H, ArH), 6.91 (s, 1H, ArH), 3.77 (s, 2H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.85, 137.46, 132.25, 131.63, 130.75, 125.20, 122.52, 121.75, 121.70, 118.29. Anal. Calcd for $C_{12}H_9NBr_2$: C, 44.07; H, 2.77; N, 4.28. Found: C, 44.21; H, 2.86; N, 4.12.

General Procedure for Synthesis of Amide-Substituted Biphenyl Derivatives 3a−g. To a dry THF solution of **2** and triethylamine (3 mL) was added dropwise a dry THF solution (35 mL) of the respective acyl chloride at 0 °C. After stirring at room temperature for 24 h, the solution was poured into water (80 mL) and extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by recrystallization from CH_2Cl_2/*n*-Hex or chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2.

3a. Compound **2** (4.0 g, 12.2 mmol) and decanoyl chloride (3.5 g, 18.3 mmol) were used. The crude product was recrystallized from CH_2Cl_2/*n*-Hex and dried under high vacuum to afford **3a** as a colorless solid (4.3 g, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.53 (s, 1H, NH), 7.62 (d, 2H, ArH), 7.30 (dd, 1H, ArH), 7.21 (d, 2H, ArH), 7.05 (d, 1H, ArH), 7.00 (s, 1H, ArH), 2.20 (t, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.32−1.25 (m, 12H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.37, 136.21, 135.89, 132.57, 131.08, 130.90, 129.69, 127.47, 124.64, 122.81, 122.65, 37.83, 31.97, 29.51, 29.43, 29.38, 29.21, 25.47, 22.78, 14.22. Anal. Calcd for $C_{22}H_{27}NBr_2O$: C, 54.90; H, 5.65; N, 2.91. Found: C, 54.94; H, 5.72; N, 2.76.

3b. Compound **2** (0.5 g, 1.5 mmol) and 4-methylbenzoyl chloride (0.35 g, 2.3 mmol) were used. The crude product was purified by chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2 (v:v, 1:1) to afford **3b** as a colorless solid (0.61 g, 90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.72 (s, 1H, NH), 7.82 (s, 1H, ArH), 7.64 (d, 2H, ArH), 7.49 (d, 2H, ArH), 7.33 (dd, 1H, ArH), 7.28 (d, 2H, ArH), 7.22 (d, 2H, ArH), 7.10 (d, 1H, ArH), 2.39 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): qδ 165.10, 142.93, 136.19, 136.09, 132.68, 131.43, 131.14, 130.96, 129.93, 129.73, 127.58, 126.93, 124.47, 122.94, 122.79, 21.59. Anal. Calcd for $C_{20}H_{15}NBr_2O$: C, 53.96; H, 3.40; N, 3.15. Found: C, 54.03; H, 3.44; N, 2.92.

3c. Compound **2** (1.2 g, 3.7 mmol) and 4-*tert*-butylbenzoyl chloride (1.2 g, 6.1 mmol) were used. The crude product was recrystallized from CH_2Cl_2/*n*-Hex and dried under high vacuum to afford **3c** as a colorless solid (1.6 g, 89%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.75 (s, 1H, NH), 7.87 (s, 1H, ArH), 7.65 (d, 2H, ArH), 7.54 (d, 2H, ArH), 7.44 (d, 2H, ArH), 7.33 (dd, 1H, ArH), 7.29 (d, 2H, ArH), 7.10 (d, 1H, ArH), 1.33 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.11, 156.08, 136.33, 136.21, 132.81, 131.42, 131.29, 131.08, 129.99, 127.66, 126.91, 126.15, 124.54, 123.06, 122.91, 35.26, 31.33. Anal. Calcd for $C_{23}H_{23}NBr_2O$: C, 56.70; H, 4.34; N, 2.87. Found: C, 56.62; H, 4.35; N, 2.87.

3d. Compound **2** (1.0 g, 3.1 mmol) and 4-bromobenzoyl chloride (1.0 g, 4.5 mmol) were used. The crude product was purified by chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2 (v:v, 1:1) to afford **3d** as a colorless solid (1.2 g, 77%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H, NH), 7.80 (s, 1H, ArH), 7.64 (d, 2H, ArH), 7.56 (d, 2H, ArH), 7.45 (d, 2H, ArH), 7.35 (dd, 1H, ArH), 7.27 (d, 2H, ArH), 7.11 (d, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.33, 136.10, 135.77, 133.15, 132.85, 132.43, 131.33, 131.00, 130.31, 128.59, 128.12, 127.26, 124.76, 123.20, 122.90. Anal. Calcd for $C_{19}H_{12}NBr_3O$: C, 44.74; H, 2.37; N, 2.75. Found: C, 44.77; H, 2.57; N, 2.82.

3e. Compound **2** (1.0 g, 3.1 mmol) and 4-nitrobenzoyl chloride (0.74 g, 4.0 mmol) were used. The crude product was recrystallized from CH_2Cl_2/*n*-Hex and dried under high vacuum to afford **3e** as a yellow solid (1.06 g, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.66 (s, 1H, NH), 8.28 (d, 2H, ArH), 7.84(s, 1H, ArH), 7.77 (d, 2H, ArH), 7.66 (d, 2H, ArH), 7.40 (dd, 1H, ArH), 7.28 (d, 2H, ArH), 7.14 (d, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.98, 149.83, 139.54, 135.61, 135.07, 132.70, 131.20, 130.69, 130.27, 128.38, 127.98, 124.56, 124.17, 123.15, 122.71. Anal. Calcd for $C_{19}H_{12}N_2Br_2O_2$: C, 47.93; H, 2.54; N, 5.88. Found: C, 47.58; H, 2.71; N, 5.79.

3f. Compound **2** (2.0 g, 6.1 mmol) and thiophene-2-carbonyl chloride (1.2 g, 8.1 mmol) were used. The crude product was recrystallized from CH_2Cl_2/*n*-Hex and dried under high vacuum to afford **3f** as a colorless solid (2.0 g, 75%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.69 (s, 1H, NH), 7.71 (s, 1H, ArH), 7.67 (d, 2H, ArH), 7.52 (d, 1H, ArH), 7.34 (dd, 1H, ArH), 7.29 (d, 2H, ArH), 7.23 (d, 1H, ArH), 7.11(d, 1H, ArH), 7.07 (t, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.41, 138.68, 135.78, 135.52, 132.59, 131.30, 130.98, 130.84, 129.45, 128.45, 128.02, 127.52, 124.06, 122.89, 122.68. Anal. Calcd for $C_{17}H_{11}NBr_2SO$: C, 46.71; H, 2.54; N, 3.20. Found: C, 46.38; H, 2.57; N, 3.33.

3g. Compound **2** (1.2 g, 3.7 mmol) and 5-bromothiophene-2-carbonyl chloride (1.0 g, 4.4 mmol) were used. The crude product was recrystallized from CH_2Cl_2/*n*-Hex and dried under high vacuum to afford **3g** as a colorless solid (1.0 g, 53%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.59 (s, 1H, NH), 7.66 (d, 2H, ArH), 7.60 (s, 1H, ArH), 7.34 (d, 1H, ArH), 7.27 (d, 2H, ArH), 7.11 (d, 1H, ArH), 7.02 (d, 1H, ArH), 6.9 (d, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.33, 140.13, 135.65, 135.13, 132.63, 131.05, 130.97, 130.77, 129.60, 128.17, 127.79, 124.21, 122.99, 122.67, 119.57. Anal. Calcd for $C_{17}H_{10}NBr_3SO$: C, 39.57; H, 1.95; N, 2.71. Found: C, 39.33; H, 2.23; N, 2.88.

General Procedure for Synthesis of 3,8-Dibromo-6-Substituted Phenanthridine Derivatives 4a−g. A solution of amide-substituted biphenyl derivatives (**3a−g**) and P_2O_5 in freshly distilled $POCl_3$ was stirred under reflux for 30 h. The mixture was concentrated under vacuum, the residue was diluted with ethyl acetate (15 mL), and water (15 mL) was added slowly. The aqueous layer was adjusted to pH = 10 with NaOH solution (5 M) and extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was chromatographically purified on silica gel column eluting with petroleum ether/CH_2Cl_2.

4a. Compound **3a** (0.98 g, 2.0 mmol), P_2O_5 (2.2 g, 15.5 mmol), and $POCl_3$ (40 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4a** as a colorless solid (0.920 g, 98%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.39 (d, 1H, ArH), 8.33 (d, 1H, ArH), 8.28 (d, 1H, ArH), 8.27 (d, 1H, ArH), 7.89 (dd, 1H, ArH), 7.68 (dd, 1H, ArH), 3.27 (t, 2H, CH_2), 1.88 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.36−1.27 (m, 8H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.58, 144.70, 133.89, 132.38, 131.27, 129.92, 129.06, 126.67, 124.31, 123.30, 122.77, 121.94, 121.78, 36.15, 32.01, 29.91, 29.65, 29.61, 29.43, 29.08, 22.80, 14.24. Anal. Calcd for $C_{22}H_{25}NBr_2$: C, 57.04; H, 5.44; N, 3.02. Found: C, 56.98; H, 5.51; N, 3.07.

4b. Compound **3b** (0.4 g, 0.90 mmol), P_2O_5 (1.0 g, 7.0 mmol), and $POCl_3$ (20 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4b** as a colorless solid (0.350 g, 91%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.49 (d, 1H, ArH), 8.40 (d, 1H, ArH), 8.38 (d, 1H, ArH), 8.28 (d, 1H, ArH), 7.94 (dd, 1H, ArH), 7.76 (dd, 1H, ArH), 7.60 (d, 2H, ArH), 7.39 (d, 2H, ArH), 2.49 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.41, 144.81, 139.42, 135.98, 134.21, 132.99, 131.96, 131.50, 130.51, 129.71, 129.49, 126.66, 124.09, 123.36, 123.03, 122.06, 121.69, 21.54. Anal. Calcd for $C_{20}H_{13}NBr_2$: C, 56.24; H, 3.07; N, 3.28. Found: C, 56.05; H, 3.09; N, 3.13.

4c. Compound **3c** (0.24 g, 0.49 mmol), P_2O_5 (0.4 g, 2.8 mmol), and $POCl_3$ (12 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4c** as a colorless solid (0.230 g, 100%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.49 (d, 1H, ArH), 8.40 (d, 1H, ArH), 8.38 (d, 1H, ArH), 8.33 (d, 1H, ArH), 7.94 (dd, 1H, ArH), 7.76 (dd, 1H, ArH), 7.65 (d, 2H,

ArH), 7.60 (d, 2H, ArH), 1.42 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.40, 152.54, 144.81, 135.93, 134.23, 132.99, 131.96, 131.51, 130.49, 129.49, 126.60, 125.85, 124.10, 123.36, 123.02, 122.04, 121.69, 34.98, 31.46. Anal. Calcd for $C_{23}H_{19}NBr_2$: C, 58.87; H, 4.08; N, 2.99. Found: C, 58.27; H, 4.10; N, 3.12.

4d. Compound **3d** (0.3 g, 0.59 mmol), P_2O_5 (0.42 g, 2.9 mmol), and $POCl_3$ (12 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4d** as a colorless solid (0.277 g, 96%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, 1H, ArH), 8.40 (d, 1H, ArH), 8.38 (d, 1H, ArH), 8.19 (d, 1H, ArH), 7.96 (dd, 1H, ArH), 7.79 (dd, 1H, ArH), 7.73 (d, 2H, ArH), 7.59 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.92, 144.47, 137.54, 134.33, 132.87, 131.89, 131.84, 131.26, 130.86, 130.76, 126.10, 124.10, 123.79, 123.27, 123.10, 121.98, 121.78. Anal. Calcd for $C_{19}H_{10}NBr_3$: C, 46.38; H, 2.05; N, 2.85. Found: C, 45.95; H, 2.03; N, 2.74.

4e. Compound **3e** (0.3 g, 0.63 mmol), P_2O_5 (0.45 g, 3.2 mmol), and $POCl_3$ (12 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:3) afforded **4e** as a yellow solid (0.197 g, 68%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, 1H, ArH), 8.46 (d, 2H, ArH), 8.44 (d, 1H, ArH), 8.39 (d, 1H, ArH), 8.11 (d, 1H, ArH), 8.00 (dd, 1H, ArH), 7.59 (d, 2H, ArH), 7.84 (dd, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.64, 148.31, 144.87, 144.29, 134.67, 132.99, 131.89, 131.32, 130.75, 130.34, 125.76, 124.30, 123.91, 123.36, 122.15, 122.08. Anal. Calcd for $C_{19}H_{10}N_2Br_2O_2$: C, 49.81; H, 2.20; N, 6.12. Found: C, 49.84; H, 2.11; N, 5.83.

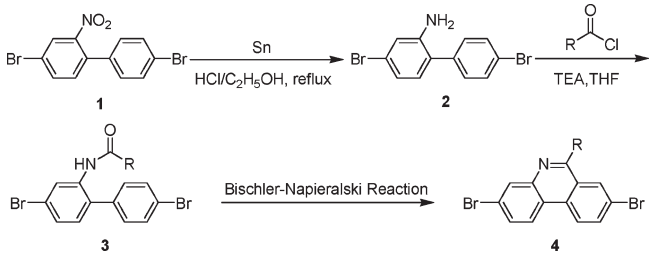
4f. Compound **3f** (0.31 g, 0.71 mmol), P_2O_5 (0.51 g, 3.6 mmol), and $POCl_3$ (12 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4f** as a yellow solid (0.256 g, 86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.70 (s, 1H, ArH), 8.46 (d, 1H, ArH), 8.35 (d, 1H, ArH), 8.34 (d, 1H, ArH), 7.95 (d, 1H, ArH), 7.74 (d, 1H, ArH), 7.64 (d, 1H, ArH), 7.61 (d, 1H, ArH), 7.27 (t, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.55, 145.21, 142.61, 134.97, 133.45, 132.70, 131.36, 131.32, 130.55, 129.76, 128.62, 126.49, 124.84, 123.93, 123.90, 122.89, 122.43. Anal. Calcd for $C_{17}H_9NSBr_2$: C, 48.72; H, 2.16; N, 3.34. Found: C, 48.94; H, 2.38; N, 3.32.

4g. Compound **3g** (0.3 g, 0.58 mmol), P_2O_5 (0.42 g, 2.9 mmol), and $POCl_3$ (12 mL) were used. Chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) afforded **4g** as a yellow solid (0.212 g, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, 1H, ArH), 8.48 (d, 1H, ArH), 8.34 (d, 1H, ArH), 8.32 (d, 1H, ArH), 7.96 (dd, 1H, ArH), 7.75 (dd, 1H, ArH), 7.41 (d, 1H, ArH), 7.21 (d, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.52, 144.33, 143.59, 134.35, 132.65, 132.60, 132.11, 130.76, 130.60, 130.07, 129.86, 125.29, 124.25, 123.19, 122.17, 121.73, 116.69. Anal. Calcd for $C_{17}H_8NSBr_3$: C, 41.00; H, 1.62; N, 2.81. Found: C, 40.95; H, 1.63; N, 2.95.

General Procedure for Synthesis of Phenanthridine-Containing Polymers P1−3. A mixture of 2,8-dibromophenanthridines, aryldiboronic acid esters, $NaHCO_3$, THF, toluene, 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. The reaction mixture was extracted with $CHCl_3$ (2 × 50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After the removal of most of solvent, the residue was precipitated into methanol, and the resulted precipitate was collected by filtration and dried under vacuum to give polymers **P1−3**.

*Polymer **P1***. Compound **4a** (0.10 g, 0.22 mmol), 9,9-dioctylfluorene-2,7-diboronic pinacol ester (0.14 g, 0.22 mmol), $NaHCO_3$ (0.73 g), $Pd(PPh_3)_4$ (2.49 mg), THF (10 mL), toluene (10 mL), and H_2O (6 mL) were used. **P1** was obtained as an off-white solid (0.14 g, 93%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.76 (broad, 1H), 8.65 (broad, 1H), 8.55 (broad, 2H), 8.19 (broad, 1H), 8.03 (broad, 1H), 7.91−7.39 (broad, 6H), 3.53 (broad, 2H), 2.08 (broad, 4H), 1.64 (broad, 8H), 1.31−1.14 (broad, 30H), 0.90 (broad, 3H), 0.79 (broad, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.52, 152.37, 152.20, 151.95, 144.34, 141.77, 140.65, 139.57, 132.03, 130.02, 128.95, 127.38, 126.71, 125.77, 124.78, 123.36, 122.74, 121.94, 120.59, 55.68, 40.73, 36.94, 32.10, 31.94, 30.28, 29.81, 29.55, 29.44, 24.15, 22.88, 22.76, 14.30, 14.22, 14.07.

Scheme 1. Synthesis of 3,8-Dibromo-6-Substituted Phenanthridine Derivatives



*Polymer **P2***. Compound **4b** (0.10 g, 0.23 mmol), 9,9-dioctylfluorene-2,7-diboronic pinacol ester (0.15 g, 0.23 mmol), $NaHCO_3$ (0.78 g), $Pd(PPh_3)_4$ (2.70 mg), THF (10 mL), toluene (10 mL), and H_2O (6 mL) were used. **P2** was obtained as an off-white solid (0.15 g, 97%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.84 (broad, 1H), 8.73 (broad, 1H), 8.64 (broad, 1H), 8.47 (broad, 1H), 8.23 (broad, 1H), 8.10 (broad, 1H), 7.89−7.80 (broad, 4H), 7.79 (d, 2H),7.65 (broad, 2H), 7.44 (d, 2H), 2.52 (s, 3H), 2.08 (broad, 4H), 1.56 (broad, 4H), 1.26−1.10 (broad, 20H), 0.78 (broad, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.30, 152.29, 144.55, 140.78, 140.58, 130.14, 129.96, 129.74, 129.55, 129.43, 128.32, 127.44, 126.35, 125.99, 123.08, 122.93, 122.77, 122.05, 122.00, 121.90, 120.59, 55.65, 40.79, 31.98, 30.30, 30.14, 29.92, 29.76, 29.47, 24.16, 22.82, 21.67, 14.27.

*Polymer **P3***. Compound **4a** (0.10 g, 0.22 mmol), 2,5-dihexylphenyl-1,4-diboronic 1,3-propanediol ester **6** (0.09 g, 0.22 mmol), $NaHCO_3$ (0.73 g), $Pd(PPh_3)_4$ (2.49 mg), THF (10 mL), toluene (10 mL), and H_2O (6 mL) were used. **P3** was obtained as a grayish solid (0.10 g, 84%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.80 (broad, 1H), 8.68 (broad, 1H), 8.29 (d, 2H), 7.95 (s, 1H), 7.76 (s, 1H), 7.40−7.35 (broad, 2H), 3.45 (broad, 2H), 2.73 (broad, 4H), 2.02 (broad, 2H), 1.59 (broad, 8H), 1.28−1.19 (broad, 20H), 0.87 (broad, 3H), 0.78 (broad, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.03, 143.82, 142.64, 140.82, 138.04, 131.98, 131.59, 131.45, 129.97, 128.13, 126.76, 125.16, 122.37, 121.62, 36.70, 32.86, 31.94, 31.61, 30.15, 29.90, 29.72, 29.67, 29.40, 22.74, 22.56, 14.17, 14.06.

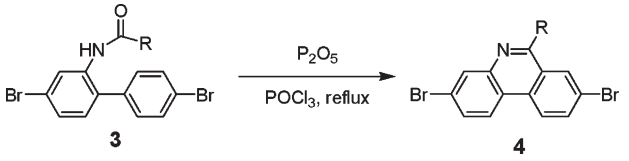
Results and Discussion

Synthesis of 3,8-Dibromo-6-Substituted Phenanthridine Derivatives. As shown in Scheme 1, the synthetic route for 3,8-dibromophenanthridines is rather straightforward. Starting from 4,4′-dibromo-2-nitrobiphenyl (**1**), reduction of the nitro group with Sn/H^+ afforded the corresponding 2-amino-4,4′-dibromobiphenyl (**2**) in a yield of 95%. The reaction of compound **2** with acyl chlorides in a solvent mixture of tetrahydrofuran (THF) and triethylamine (TEA) afforded amides **3** in yields of 53−90%. The conversion of compounds **3** to 3,8-dibromophenanthridines **4** was accomplished with Bischler−Napieralski cyclization. The conversion of **3b** to **4b** was investigated using different reaction conditions. The cyclization was screened using $POCl_3$ as the solvent and PCl_3,[13] PCl_5,[14] or P_2O_5[15] as the catalyst at refluxing. The cyclization is very sensitive to the catalyst. No product was detected, when PCl_3 or PCl_5 was used as the catalyst; whereas when P_2O_5 was used as the catalyst, the cyclization yields were in the range of 90% to almost 100%. The optimized cyclization conditions are feasible for the synthesis of various 3,8-dibromophenanthridine derivatives. The results are shown in Table 1. The cyclization yields range between 68 and 99% for various substituents in the

6-position of phenanthridine.[7f,16] The purification of 3,8-dibromophenanthridine derivatives only requires simple chromatography on silica gel column. All compounds obtained were unambiguously characterized with ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. This approach is suitable for the preparation of 3,8-dibromophenanthridine derivatives on a large scale.

Synthesis of Phenanthridine-Containing Polymers. As shown in Scheme 2, three phenanthridine-containing conjugated polymers were prepared by palladium-catalyzed Suzuki−Miyaura−Schlüter polycondensation. The polymerization of 6-substituted 3,8-dibromophenanthridines with 9,9-dioctylfluorene-2,7-diboronic pinacol ester (**5**) or 2,5-dihexylphenyl-1,4-diboronic 1,3-propanediol ester (**6**) was carried out in a biphasic mixture of aqueous $NaHCO_3$ and THF/toluene with freshly prepared $Pd(PPh_3)_4$ as the catalyst precursor. The reaction was kept stirring under N_2 at reflux for 4 days. During the reaction, only **P2** precipitated from the reaction mixture in about 2 days. And all precipitated polymers could be fully redissolved in common organic solvents, such as chloroform and THF. Standard work-up afforded polymers **P1**, **P2**, and **P3** as amorphous, gray solids in yields of 93%, 97%, and 84%, respectively. The molecular weights determined by gel permeation chromatography (GPC) against polystyrene standards are shown in Figure 1 and Table 2. These data show that high molecular weights were achieved. The weight-average molecular weights (M_w) for **P1**, **P2**, and **P3** were found up to 82, 180, and 67 kg/mol, respectively. GPC is known not to be a good method to determine the actual molecular weight of rodlike polymers; the number presented here should be treated with carefulness. The polymers were unambiguously characterized with ^{1}H and ^{13}C NMR spectroscopy.

Table 1. Isolated Yields of 3,8-Dibromo-6-Substituted Phenanthridines (4a−g) by Cyclization of 4,4′-Dibromo-2-acylbiphenyls (3a−g)

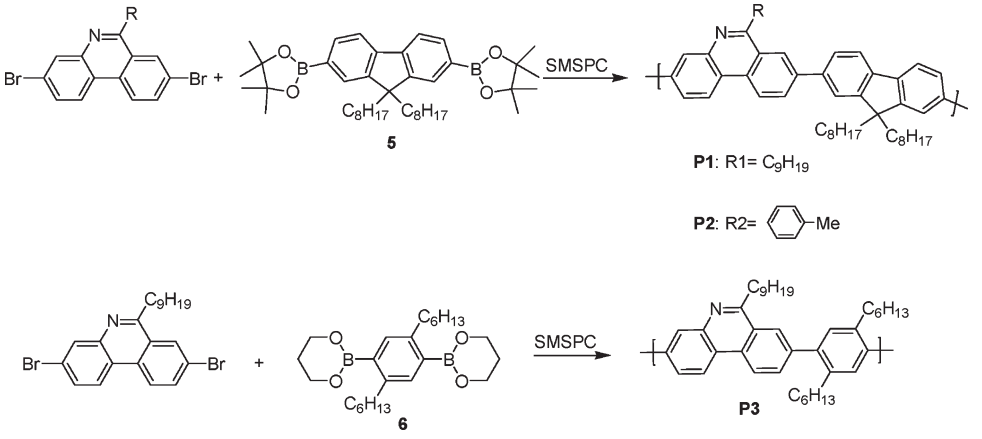


entry	R	compd/yield (%)
1	C_9H_{19}—	**4a**/98
2	H_3C—	**4b**/91
3		**4c**/100
4	Br—	**4d**/96
5	O_2N—	**4e**/68
6		**4f**/86
7	Br—	**4g**/73

The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Figure 2, all these polymers **P1**−**3** exhibit good thermal stability. They showed less than 5% decomposition up to 400 °C and a residual weight of about 50−60% at 800 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. The 5% weight loss temperatures (T_d) of polymers are also included in Table 2. For **P1** and **P2**, no distinct glass transition was observed from 35 to 350 °C in their DSC curves of the second heating and cooling runs (10 °C/min), which suggested that they were amorphous (Figure S1).[17] As shown in Figure S1c, **P3** exhibited a distinct endothermal peak at about 106 °C in the DSC trace of second heating and a distinct exothermic peak at about 93 °C in the trace of second cooling at a rate of 10 °C/min. However, no distinct morphology change was observed by polarized light micrography in the second cooling and heating runs from the temperature range of 35−320 °C (Figure S2). Therefore, the above observed endothermal and exothermic peaks are probably ascribed to an undefined solid to solid transition.[18]

Optical and Electrical Properties of Polymers P1−3. All the three polymers could be readily dissolved in common organic solvents, such as methylene chloride, chloroform, toluene, and THF. The UV−vis absorption and photoluminescent (PL) spectra of **P1**−**P3** in dilute THF solution are shown in Figure 3a. **P1** and **P2** exhibit strong absorption in the ultraviolet region ranging from 320 to 410 nm with a maximum at around 386 nm. **P3** absorbs in the range of 250−370 nm with two peaks at about 284 and 305 nm.

Scheme 2. Synthesis of Phenanthridine-Containing Polymers



In THF solution, **P1** and **P2** emit in blue region with a maximum at 409 and 411 nm and a shoulder at about 431 and 434 nm, respectively. **P3** emits in the ultraviolet region with a maximum of 369 nm and a shoulder at around 386 nm. The introduction of fluorene unit instead of 1,4-phenylene one into the polymer backbone results in obvious red-shifting of the absorption and emission spectra.[12,19] The quantum yields of **P1**, **P2**, and **P3** in dilute THF solution were measured to be 99%, 96%, and 81%, respectively, by using 9,10-diphenylanthracene as a reference standard ($\Phi_F = 0.9$). Solid films on quartz plates used for UV−vis absorption and fluorescence spectroscopy measurements were prepared by spin-coating with THF solutions of **P1**−**3** (1.0 mg/mL). Figure 3b shows the UV−vis absorption and fluorescence spectra of **P1**−**3** in films. The results are also listed in Table 3. In comparison with their absorption spectra in solution, the absorption peaks of all polymers **P1**−**3** are slightly broadening and red-shifted. In film, **P1** exhibits a featureless emission peak with a maximum at about 505 nm, which is red-shifted for about 96 nm in comparison with its solution emission spectrum. **P2** in film also displays a featureless emission spectrum peaked at about 452 nm, which is red-shifted for about 41 nm in comparison with its solution one. **P3** in film shows a very broad emission spectrum with two peaks at about 388 and 438 nm, which is also red-shifted in comparison with its solution one. The broadening and red-shifting of the absorption and emission spectra of conjugated polymers in film are usually ascribed to the formation of aggregation for conjugated polymer chains in the solid state.[2g,19,20] In THF solution, the PL spectra of **P1** and **P2** are similar because their chemical structures are almost the same except that the substituent on 6-position is different. However, the PL spectra of **P1** and **P2** in films are quite different, with **P1** emits much longer wavelength light than **P2**. This is probably due to the 6-position-substituted aryl group that usually has a dihedral angle with the phenanthridine ring, which can change the packing style of polymer chains in the solid state; thus, the formation of exciplexes may occur to a greater or lesser extent depending on the polymer structures.[2g] As revealed by the X-ray diffraction (XRD) patterns of the powdery sample of these polymers (as shown in Figure S3), the 6-position alkyl-substituted **P1** has apparently different packing style in comparison with the 6-position aryl-substituted **P2**.[3e] Therefore, it is possible to finely adjust the emission color and even to tune the morphological and charge transporting properties of phenanthridine-based conjugated polymers by selecting appropriate substituents on phenanthridine moiety.

The HOMO energy levels of **P1**−**3** bulk thin films spin-coated on ITO were estimated by ultraviolet photoelectron spectroscopy (UPS) to be -5.8 ± 0.1, -5.9 ± 0.1, and -6.4 ± 0.1 eV, respectively. The band gaps (E_g) were determined from the onset of the UV−vis absorption spectra, and the data are summarized in Table 3. According to the equation $E_{LUMO} = E_{HOMO} + E_g$, the LUMO energy levels were calculated to be 2.94 eV for **P1**, 3.03 eV for **P2**, and 2.91 eV for **P3**. These results imply that the three polymers have a similar electron-withdrawing ability while **P3** is poor in terms of electron-donating.[21]

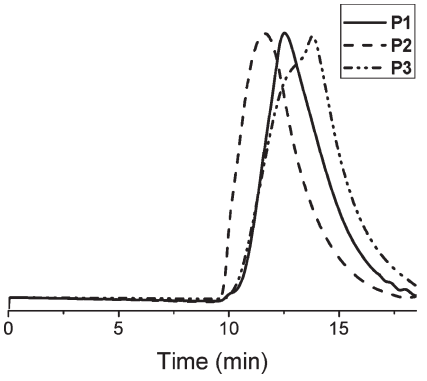


Figure 1. GPC elution traces of polymers **P1**−**3**.

Table 2. Molecular Weights and Thermal Properties of Polymers P1−3

polymer	M_n	P_n	M_w	P_w	M_w/M_n	T_g	T_d
P1	41 000	59	82 000	118	2.0	−	424
P2	83 000	126	180 000	287	2.3	−	417
P3	25 000	45	67 000	122	2.7	−	404

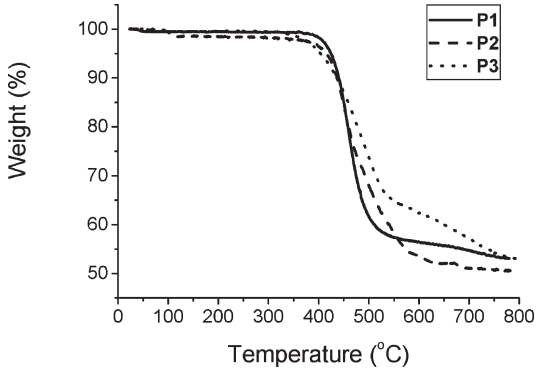


Figure 2. TGA traces of polymers **P1**−**3**.

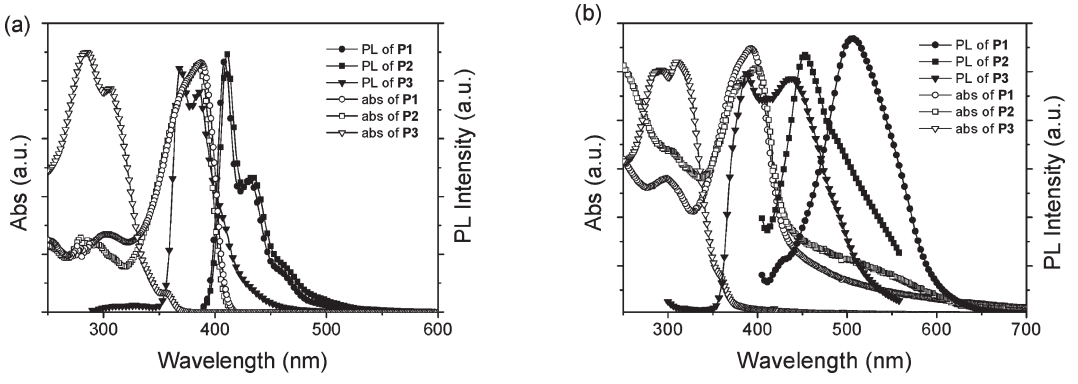


Figure 3. (a) Normalized solution absorption and PL spectra of polymers **P1**−**3** (10^{-5} M for repeating units) in THF. (b) Normalized film absorption and PL spectra of polymers **P1**−**3**.

Table 3. Summary of UV−vis Absorption and PL Maxima (λ), PL Quantum Yields (Φ_F), Optical Bandgaps (ΔE), and HOMO and LUMO Levels of Polymers P1−3

	λ_{abs} (nm)		λ_{PL} (nm)					
polymer	solution[a]	films	solution[a]	films	Φ_F[a]	ΔE (eV)[b]	HOMO[c] ± 0.1 (eV)	LOMO (eV)
P1	385	392	409	505	0.99	2.86	−5.8	−2.94
P2	386	398	411	452	0.96	2.87	−5.9	−3.03
P3	284, 305	292, 311	369, 386	388, 438	0.81	3.49	−6.4	−2.91

[a] Measured in THF. [b] Estimated from absorption onset. [c] Estimated from UPS.

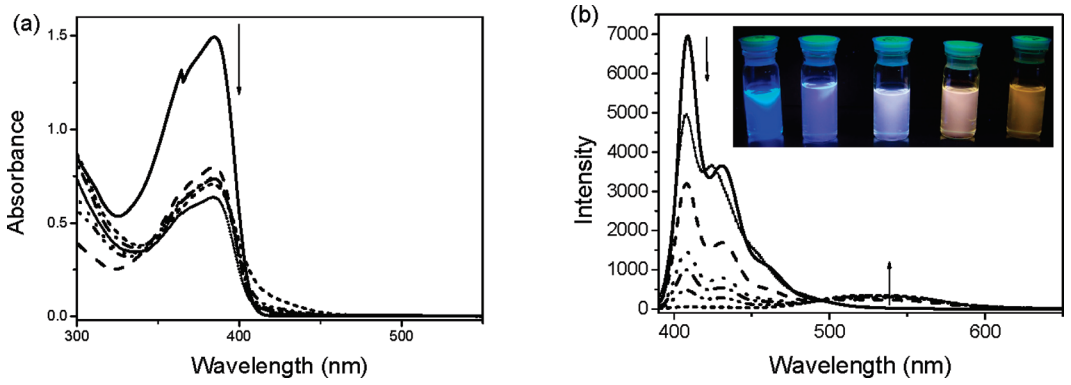


Figure 4. Changes in (a) UV−vis absorption and (b) PL spectra of **P1** (10^{-6} M (repeating unit)) in THF at various concentrations of TFA: [TFA] = 0, 4.0×10^{-3}, 6.0×10^{-3}, 8.0×10^{-3}, 2.4×10^{-2}, and 1.6×10^{-1} M. Dotted lines represent the partial recovery of the optical properties when the protonated **P1** solution in THF was titrated with a droplet of TEA. Inset shows the fluorescence images of **P1** in THF as the TFA concentration increased (taken under the illumination with 365 nm UV light).

Optical Response to Protic Acid. The nitrogen atom on the phenanthridine ring can be easily protonated and deprotonated, which should cause significant changes of their photoluminescent spectra due to the fact that the phenanthridine ring is in the polymer main chain.[2a,f,g,22] All the polymers can be effectively protonated with trifluoroacetic acid (TFA) and deprotonated with triethylamine (TEA). As shown in Figure 4 and Figure S4, the color changes of polymer solution and film upon the addition of TFA and TEA can be clearly seen by the naked eye. When adding TFA (from 0 to 1.6×10^{-1} M) to a solution of **P1** in THF (10^{-6} M), the color of polymer solution changed from colorless to orange. The color change is more evident under the illumination of UV light at the wavelength of 365 nm. UV−vis absorption spectra of **P1** in THF solution titrated with trifluoroacetic acid (TFA) are shown in Figure 4a. The intensity of absorption peak at 384 nm decreased upon the titration of the THF solution of **P1** with TFA. The photoluminescent spectra of polymer **P1**−**3** in THF solution titrated with trifluoroacetic acid (TFA) are shown in Figure 4b. When titrated with TFA, the intensity of the blue emission peak decreased dramatically and finally disappeared, and a new long wavelength emission band peaked at about 540 nm appeared and its intensity increased gradually. Partial recovery of the blue emission and complete disappearance of the long wavelength emission were observed, when the protonated **P1** solution in THF was titrated with a droplet of TEA. The appearance of the polymer solution changed from orange back to colorless. **P2** and **P3** also displayed similar optic properties (Figure S4). Our investigations have illustrated that these phenanthridine-containing polymers are promising light-emitting and protic acid sensitive materials.

Conclusions

In conclusion, we have demonstrated that Bischler−Napieralski cyclization is a very efficient approach to synthesize of 3,8-dibromophenanthridine derivatives. Suzuki−Miyaura−Schlüter polycondensation of 3,8-dibromophenanthridine monomers with 9,9-dioctylfluorene-2,7-diboronic ester or 2,5-dihexylphenyl diboronic acid ester afforded high molecular weight conjugated polymers with phenanthridine units in the polymer main chain. Photophysical studies indicated that these phenanthridine-containing polymers are promising light-emitting materials and pH sensors.

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Supporting Information Available: DSC data of **P1**−**3**, polarizing optical micrographs of **P3**, X-ray diffraction patterns of **P1**−**3**, and optical response to protic acid for **P2**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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