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Water-Soluble Multifunctional Cross-Conjugated Poly(*p*-phenylenes) as Stimuli-Responsive Materials: Design, Synthesis, and Characterization

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ABSTRACT: The design, synthesis, and characterization of a series of thermally stable water-soluble polymers with cross-conjugation and multiple functional groups are reported. All copolymers were characterized by means of FT-IR, GPC, ^{1}H and ^{13}C NMR, UV−vis, and fluorescence spectroscopy. Photophysical properties showed collective responses from their respective conjugated segments. Titration studies showed that such polymers have good sensitivity for both cationic and anionic quenchers in fluorescence decay, with an average Stern−Volmer constant of 10^5 M^{-1}. Besides fluorescence quenching, significant shifts in absorption and emission maxima upon addition of small molecules were also observed. High concentration of small molecular quenchers induced aggregation of the polymers. All polymers were able to form highly fluorescent, flexible, free-standing thin films via evaporation of the solvent. Hence, by attaching cationic and anionic groups on a cross-conjugated water-soluble structure, a multifunctional CP system was developed for potential applications.

Introduction

Conjugated polymers are used in a variety of applications such as sensors and other devices.[1] The sensing principle of conjugated polymers (CPs) is based on the photon-induced fast electron transfer to the trapping site formed by electrostatic complexation between the polymer and analyte, which leads to effective quenching of fluorescence.[1] A key advantage of CP-based sensors over small molecules is the potential of the CP to exhibit additive properties that are sensitive to tiny perturbations from environment. In particular, the electron transport properties, electrical conductivity, or rate of energy migration on the conjugated polymer backbone provides amplified sensitivity.[2] Polymer-based sensors have been fabricated and used for applications such as conductometric sensors,[3,4] potentinometric sensors,[5] colorimetric sensors,[6] and fluorescence sensors.[7,8] Fluorescent sensors offer special advantagtes in sensitivity and fast response. This method offers diverse transduction schemes based upon changes in intensity, energy transfer, wavelength (excitation and emission), and lifetime. There are advantages to using CPs in fluorescent sensors owing to amplification resulting from efficient energy migration. Enhanced sensitivity of the CPs results from the fact that complete quenching does not require all acceptors on CPs to be occupied by analytes, as opposite to the small molecules.[9,10] Combination of the amplification and sensitivity in CP-based sensors produces new systems of high sensitivity.[7,8] In recent years, water-soluble CPs-based sensors gained much attention due to potential applications in biosystems.[11−14] In general, water-soluble conjugated polymers are synthesized by attaching polar functional groups such as carboxylates,[15−17] sulfonates,[18−20] phosphonates,[21] and quaternary ammonium salts[22−26] on the polymer backbone. Synthesis and characterization of poly(*p*-phenylenes) (PPP) derivatives have been widely investigated owing to its high fluorescence intensity, thermal and chemical stability, high quantum efficiency, flexibility of chemical modification, and easy processing.[27−33]

Recently, cross-conjugated polymers are designed and developed to fine-tune the electrical and optical properties in polymers[34−36] and dendrimers.[37−40] Extended conjugation in these macromolecules leads to strong intermolecular interactions via $\pi-\pi$ stacking. Following the first report by Novak et al. on water-soluble PPPs,[15] numerous linear polymers haven been published. In this investigation, design, synthesis, and characterization of a series of novel two-dimensional water-soluble conjugated PPPs are described. The polymers are designed with intention to expand the conjugation and to facilitate electron/charge transport across the 2D architecture, as shown by a cartoon in Figure 1. The molecular structures of the target polymers are given in Figure 2.

Experimental Section

Chemicals and Instrumentation. All reagents were purchased from Sigma-Aldrich, Fluka, Lancaster, and TCI Chemicals and were used without further purification unless otherwise stated; snake skin pleated dialysis tubing with MW cutoff value of 3500 was purchased from Pierce. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Silica gel was used as packing material for column purification. Tetrahydrofuran (THF) was purified via distillation over sodium wires under nitrogen atmosphere. The NMR spectra were collected on a Bruker ACF 300 spectrometer in chloroform-*d*, acetone-d_6, D_2O, and DMSO-d_6 as solvent and tetramethylsilane as internal standard. FT-IR spectra were recorded on a Bio-Rad FTS 165 spectrophotometer using KBr matrix. UV−vis spectra were recorded on a Shimadzu 3101 PC spectrophotometer, and fluorescence measurements were carried out on a RF-5301PC Shimadzu spectrofluorophotometer; the excitation width and emission width were all set as 3 nm. Thermogravimetric analyses were done using a TA Instruments SDT 2960 with a heating rate of 10 °C/ min up to 1000 °C under a nitrogen atmosphere. Gel permeation chromatography (GPC) was used to obtain the molecular weight of precursor polymers with reference to poly(ethylene glycol) standards using dimethylformamide (DMF) as solvent with a flow

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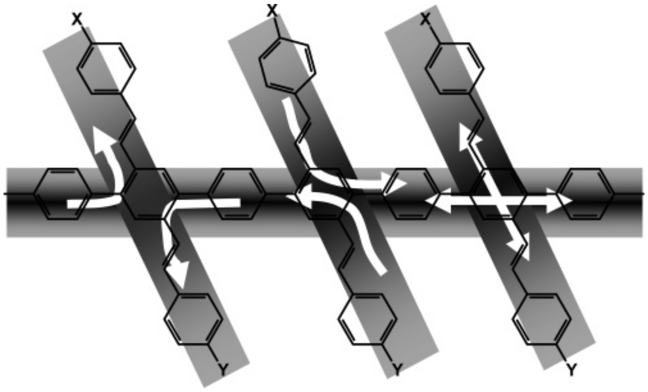

Figure 1. A cartoonistic representation of various pathways for electronic conjugations in 2D polymers; X and Y represent donor−acceptor type functional groups.

rate of 0.8 mL/min. Phenogel 10 linear columns (S/N GP3673, GP42637) were used and hyphenated with a Waters 410 differential refractometer and a Waters 515 HPLC pump. Elemental analyses were performed using a Perkin-Elmer CHNS autoanalyzer. EM images were taken with a JEOL JSM 6700 scanning electron microscope (SEM). The samples were carefully mounted on copper stubs with a double-sided conducting carbon tape and sputter-coated with 2 nm platinum before examination. For the fluorescence imaging, a Carl Zeiss LSM 510 laser scanning microscope with an excitation wavelength of 365 ± 12 nm was used. Dynamic light scattering (DLS) studies were carried out with a 5 W and 514 nm argon ion laser (Brookhaven Instruments) and a BI-200Sm goniometry coupled to BI-9000AT digital correlators and other accessories. The power of the laser was varied from 50 to 500 mW depending on the concentration. The data were collected at a scattering angle of 90° to the incident laser beam with a pulse time of 0.8 μs. The polymer concentration was kept constant at 20 mg/L. The CONTIN method was used to analyze the first-order field correlation function for size distribution.[41−42]

Synthesis. All polymers possess cross-conjugated backbones, as shown in Figure 2. Polymers **P1**−**P6** contain two different functional groups with polar water-soluble groups, which are structurally different from linear water-soluble polymers reported earlier.[15−26] The synthetic routes for all polymers are given in Scheme 1. 4-(3-Sulfonatopropoxy)benzaldehyde **(1)** and 4-(2-(diethylamino)ethoxy)benzaldehyde **(2)** were synthesized from 4-hydroxybenzaldehyde,[43] and 4-pyridylacrolein (**3**) was purchased from Lancaster. Bromination of 1,4-dibromo-*p*-xylene using NBS gave 1,4-dibromo-2,5-bisbromomethylbenzene **(4)**.[44] 2,7-Dibromo-9-bis(3-(*N*,*N*-dimethylamino)propyl)-9*H*-fluorene **(8)** was synthesized from 2,7-dibromofluorene and (*N*,*N*-dimethylamino)propyl bromide in DMF with 50% NaOH aqueous solution.[45] Two boronic acids **9**[46] and **10**[47] were synthesized from dibromide using *n*-BuLi in THF solution at −78 °C followed by addition of triisopropylborate. 2,5-Bis(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-pyridine **(11)** was synthesized according to reported procedures.[48]

1,4-Dibromo-2,5-bis[2-(4-(3-sulfonatopropoxy)phenyl)vinyl]-benzene (5). A mixture of compound **4** (2 g, 4.8 mmol) and triethylphosphine (3.3 mL, 19.2 mmol) was refluxed for 6 h without solvent; excess triethylphosphine was removed under reduced pressure. The obtained ylide was mixed with DMF, potassium *tert*-butoxide (1.8 g, 19.2 mmol), and compound **1** (5.4 g, 19.2 mmol) at 0 °C and stirred overnight at room temperature, poured into acetone, and filtered, and the crude solid was recrystallized from methanol to get a yellow product in 75% yield. ^{1}H NMR (DMSO-d_6, δ ppm): 8.09 (s, 2H, central Ar−**H**), 7.56 (d, J = 9 Hz, 4H terminal Ar−**H**), 7.37 (d, J = 17 Hz, 2H C**H**═CH), 7.17 (d, J = 12 Hz, 2H CH═C**H**), 6.98 (d, J = 9 Hz, 4H, H2 and H6 Ar−**H**), 4.10 (t, J = 6 Hz, 4H C$\mathbf{H_2}$O), 2.56 (t, J = 6 Hz, 4H C$\mathbf{H_2}$N), 2.01 (q ,J = 6 Hz, 4H −C$\mathbf{H_2}$−). ^{13}C NMR (DMSO-d_6, δ ppm): 162.5, 136.2, 132.2, 129.2, 128.2, 127.8, 121.8, 121.5, 114.3, 67.2, 47.2, 24.7. FTIR (KBr, cm^{-1}): 3036, 2940, 2869, 1671, 1604, 1473, 1366, 1253, 1202, 1050, 955, 816, 733, 619, 584, 530. Elemental analysis: C: 42.43, H: 3.31. Found: C: 42.14, H: 3.38.

1,4-Dibromo-2,5-bis[2-(4-(2-(*N*,*N*-diethylamino)ethoxy)phenyl)-vinyl]benzene (6). ^{1}H NMR (CDCl$_3$, δ ppm): 8.01 (s, 2H, central Ar−**H**), 7.48 (d, J = 9 Hz, 4H, H3 and H5 terminal Ar−**H**), 7.09 (d, J = 12 Hz, 2H C**H**═CH), 6.91 (d, J = 12 Hz, 2H CH═C**H**), 6.84 (d, J = 9 Hz, 4H, terminal Ar−**H**), 3.99 (t, J = 4 Hz, 4H C$\mathbf{H_2}$O), 2.87 (t, J = 4 Hz, 4H C$\mathbf{H_2}$N), 2.64 (q, J = 4 Hz, 4H, N(C$\mathbf{H_2}$CH$_3$)$_2$), 1.05 (t, J = 5 Hz, 6H, N(CH$_2$C$\mathbf{H_3}$)$_2$). ^{13}C NMR (CDCl3, δ ppm): 158.7, 137.2, 131.5, 129.9, 128.2, 123.6, 122.7, 114.8, 68.7, 51.5, 47.7, 11.6. FTIR (KBr, cm^{-1}): 2964, 2935, 2817, 1628, 1602, 1512, 1458, 1367, 1292, 1254, 1176, 1046, 958, 851, 805, 606, 553, 523. Elemental analysis: C: 60.90, H: 6.31. Found: C: 60.78, H: 6.27.

1,4-Dibromo-2,5-bis(4-pyridylbuta-1,3-dienyl)benzene (7). ^{1}H NMR (CDCl$_3$, δ ppm): 8.49 (d, J = 5 Hz, 4H, Py−**H**), 8.05 (s, 2H central Ar−**H**), 7.52 (d, J = 7 Hz, 4H, Py−**H**), 7.14 (d, J = 17 Hz, 2H, CH═C**H**−CH═CH), 7.02 (d, J = 15 Hz, 2H, CH═CH−CH═C**H**), 6.75 (d, J = 15 Hz, 2H, CH═CH−C**H**═CH), 6.68 (d, J = 14 Hz, 2H, C**H**═CH−CH═CH). ^{13}C NMR (CDCl$_3$, δ ppm): 150.2, 142.9, 137.7, 135.5, 133.2, 131.5, 127.8, 126.9, 123.9, 107.7. FTIR (KBr, cm^{-1}): 2962, 2925, 2853, 1707, 1634, 1474, 1416, 1364, 1260, 1056, 1025, 966, 804, 706, 619, 525. Elemental analysis: C: 58.33, H: 3.67. Found: C: 58.15, H: 3.69.

Poly{2,5-bis[2-(4-(3-sulfonatopropoxy)phenyl)vinyl]-1,4-benzene-*alt*-9-bis(3-(*N*,*N*,*N*-trimethylamino)propyl)-9*H*-2,7-fluorene} (P1). Compounds **5** (0.93 g, 1.18 mmol) and **9** (0.5 g, 1.18 mmol) were dissolved in 30 mL of DMF. K$_2$CO$_3$ solution (2 M, 20 mL) was added to this mixture followed by tetrakis(triphenylphosphino)palladium(0) (3 mol %) as catalyst and cetyltrimethylammonium bromide (30 mol %) as phase transfer agent to increase the solubility. The mixture was stirred at 80 °C for 3 days, concentrated under reduced pressure, and precipitated twice from methanol; the crude product was directly treated with excess CH$_3$I in DMSO for 2 days. 250 mL of H$_2$O was added followed by filtration, and the filtrate was dialyzed using snake skin pleated dialysis tubing with MW cutoff value of 3500 for 3 days with H$_2$O changed twice per day. The concentrated polymer solution was passed through a syringe filter with a pore diameter of 0.25 μm and lyophilized to get a dark brown solid in 40% yield. ^{1}H NMR (D$_2$O, δ ppm): 7.92 (b, Ar−**H**), 7.53 (b, Ar−**H**), 7.24 (b, Ar−**H**, C**H**═C**H**), 6.96 (b, Ar−**H**), 6.77 (b, C**H**═C**H**), 3.60 (b, C$\mathbf{H_2}$), 2.94 (b, C$\mathbf{H_2}$), 2.85 (b, C$\mathbf{H_2}$), 2.17 (b, C$\mathbf{H_3}$), 1.98 (b, C$\mathbf{H_2}$). ^{13}C NMR (D$_2$O, δ ppm): 162.1, 150.1, 141.8, 140.4, 140.2, 140.0, 137.7, 135.0, 130.2, 129.6, 128.9, 128.5, 128.3, 128.0, 127.7, 127.3, 124.6, 116.0, 115.5, 114.4, 68.6, 66.7, 62.3, 56.4, 53.4, 47.9, 38.4, 33.0, 26.6, 22.2. FTIR (KBr, cm^{-1}): 2969, 2884, 2786, 2451, 2361, 2273, 2204, 2074, 1964, 1681, 1605, 1512, 1473, 1410, 1342, 1255, 1024, 960, 831, 793, 765, 615, 526. Elemental analysis: C: 63.82, H: 6.27. Found: C: 63.03, H: 6.42.

Poly{2,5-bis[2-(4-(2-(*N*,*N*-diethylmethylamino)ethoxy)phenyl)-vinyl]-1,4-benzene-*alt*-2,5-bis(3-sulfonatopropoxy)-1,4-benzene} (P2). After Suzuki coupling as described above, the copolymer was deprotected using hydrogen gas and Pd/C as catalyst in THF solution for 2 weeks (crude NMR was taken periodically to monitor the deprotection). The solution was passed through celite filter gel to remove the catalyst and concentrated to get a solid. The solid was dissolved in DMSO mixed with excess 1,3-propane sultone at 55 °C, and the solution was stirred for another 3 days. The mixture was cooled to room temperature, and excess CH$_3$I was added for quarternization. The solution was stirred for three more days and purified as discribed for **P1**. ^{1}H NMR (D$_2$O, δ ppm): 7.44 (b, Ar−**H**, C**H**═C**H**), 7.05 (b, Ar−**H**), 6.92 (b, Ar−**H**), 6.85 (b, C**H**═C**H**), 3.98 (b, C$\mathbf{H_2}$), 3.75 (b, C$\mathbf{H_2}$), 3.00 (b, C$\mathbf{H_2}$), 2.81 (b, C$\mathbf{H_2}$), 2.11 (b, C$\mathbf{H_3}$), 2.00 (b, C$\mathbf{H_2}$), 1.16 (b, C$\mathbf{H_3}$). ^{13}C NMR (D$_2$O, δ ppm): 152.7, 152.5, 149.6, 136.5, 134.9, 131.8, 130.9, 129.1, 128.3, 125.9, 117.2, 116.0, 116.3, 68.5, 67.4, 48.2, 47.8, 39.5, 39.2, 38.7, 26.5, 24.5, 7.24. FTIR (KBr, cm^{-1}): 2963, 2881, 2449, 2363, 2270, 2201, 2071, 1961, 1647, 1610, 1509, 1407, 1385, 1341, 1238, 1031, 957, 798, 762, 735, 617,

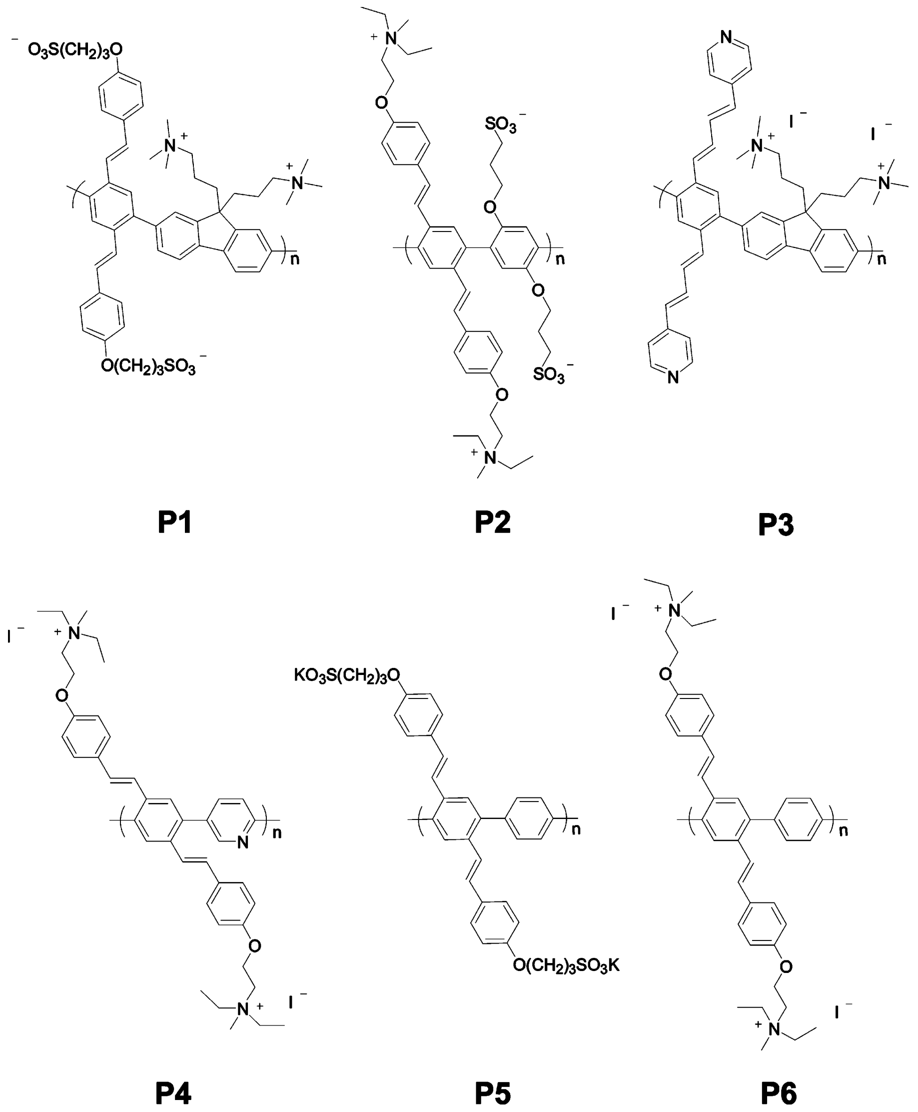

Figure 2. Molecular structures of target polymers.

529. Elemental analysis: C: 59.48, H: 6.45. Found: C: 58.23, H: 6.65.

Poly{2,5-bis(4-pyridylbuta-1,3-dienyl)-1,4-benzene-*alt*-9-bis-(3-(*N*,*N*,*N*-trimethylamino)propyl)-9*H*-2,7-fluorene} (P3). The polymer was obtained following the same procedure used for **P1**. ^{1}H NMR (D$_2$O, δ ppm): 8.49 (b, Py−**H**), 7.88 (b, Py−**H**), 7.61 (b, Py−**H**), 7.50 (b, Ar−**H**, Py−**H**), 7.28 (b, Ar−**H**, C**H**=CH−C**H**=C**H**), 6.70 (b, Ar−**H**, C**H**=CH−CH=C**H**), 2.95 (b, C**H**$_2$), 2.72 (b, C**H**$_2$), 2.45 (b, C**H**$_2$), 2.30 (b, C**H**$_3$). ^{13}C NMR (D$_2$O, δ ppm): 150.1, 144.9, 144.1, 143.3, 141.3, 141.0, 136.7, 136.3, 133.3, 132.9, 132.7, 131.8, 130.6, 130.3, 129.3, 128.7, 128.2, 127.7, 127.1, 124.9, 122.9, 122.6, 120.2, 116.9, 111.7, 68.3, 52.4, 48.0, 39.4, 38.5, 22.3. FTIR (KBr, cm^{-1}): 3013, 2951, 2925, 2864, 1617, 1475, 1411, 1385, 1237, 1054, 1025, 966, 911, 818, 789, 705, 672, 617, 538. Elemental analysis: C: 84.20, H: 7.79. Found: C: 83.37, H: 8.01.

Poly{2,5-bis[2-(4-(2-(*N*,*N*-diethylmethylamino)ethoxy)phenyl)-vinyl]-1,4-benzene-*alt*-2,5-pyridine} (P4). The polymer was obtained following the same procedure used for **P1**. ^{1}H NMR (DMSO-*d*$_6$, δ ppm): 8.40 (b, Py−**H**), 7.97 (b, Ar−H), 7.70 (b, Ar−H), 7.68 (b, Ar−H), 7.52 (b, Ar−H), 7.34 (b, Ar−**H**, C**H**=C**H**), 6.89 (b, C**H**=C**H**), 4.30 (b, C**H**$_2$), 3.74 (b, C**H**$_2$), 3.48 (b, C**H**$_2$), 2.25 (b, C**H**$_3$), 1.27 (b, C**H**$_3$). ^{13}C NMR (DMSO-*d*$_6$, δ ppm): 158.1, 151.4, 142.4, 140.3, 137.1, 132.6, 130.6, 130.3, 129.0, 128.7, 123.1, 122.8, 120.4, 115.5, 61.9, 59.0, 57.0, 26.5, 8.24. FTIR (KBr, cm^{-1}): 2964, 2936, 2818, 1631, 1603, 1513, 1458, 1389, 1367, 1348, 1293, 1255, 1176, 1046, 958, 852, 824, 607, 543, 523. Elemental analysis: C: 79.70, H: 8.32. Found: C: 78.91, H: 8.47.

Poly{2,5-bis[2-(4-(3-sulfonatopropoxy)phenyl)vinyl]-1,4-benzene-*alt*-1,4-benzene} (P5). The polymer was obtained following the same procedure as for **P1**. ^{1}H NMR (D$_2$O, δ ppm): 7.85 (b, Ar−**H**), 7.75 (b, Ar−**H**), 7.70 (b, Ar−**H**), 7.66 (b, Ar−**H**), 7.57 (b, Ar−**H**), 7.33 (b, Ar−**H**, **CH=CH**), 6.91 (b, C**H**=C**H**), 3.61 (b, C**H**$_2$), 2.92 (b, C**H**$_2$), 1.98 (b, C**H**$_2$). ^{13}C NMR (D$_2$O, δ ppm): 163.5, 158.9, 140.5, 132.2, 131.7, 130.4, 129.8, 129.6, 128.4, 127.8, 127.4, 127.2, 114.9, 102.1, 68.6, 65.6, 47.8, 46.0, 28.6, 24.5. FTIR (KBr, cm^{-1}): 3036, 2941, 2869, 1670, 1604, 1574, 1512, 1473, 1388, 1366, 1254, 1206, 1050, 956, 889, 850, 814, 737, 619, 585, 530. Elemental analysis: C: 57.60, H: 4.27. Found: C: 56.71, H: 4.40.

Poly{2,5-bis[2-(4-(2-(*N*,*N*-diethylmethylamino)ethoxy)phenyl)-vinyl]-1,4-benzene-*alt*-1,4-benzene} (P6). The polymer was obtained following the same procedure as for **P1**. ^{1}H NMR (DMSO-*d*$_6$, δ ppm): 7.57−7.61 (b, Ar−**H**), 7.32 (b, Ar−**H**), 7.44 (b, Ar−**H**), 7.26 (b, Ar−**H**, **CH=CH**), 6.94 (b, C**H**=C**H**), 4.40 (b, C**H**$_2$), 3.41 (b, C**H**$_2$), 3.03 (b, C**H**$_2$), 2.81 (b, C**H**$_3$), 1.25 (b, C**H**$_3$). ^{13}C NMR (DMSO-*d*$_6$, δ ppm): 157.0, 139.2, 135.6, 132.0, 131.5, 131.1, 130.8, 129.6, 129.4, 129.0, 128.8, 127.8, 127.6, 114.9, 61.2, 58.6, 56.4, 47.2, 11.7, 7.6. FTIR (KBr, cm^{-1}): 2975, 2927, 1701, 1654, 1604, 1510, 1465, 1395, 1304, 1241, 1176, 1115, 1059, 1013, 961, 833, 704, 619, 534. Elemental analysis: C: 81.78, H: 8.50. Found: C: 81.51, H: 8.59.

Scheme 1. Synthetic Routes for P1−P6

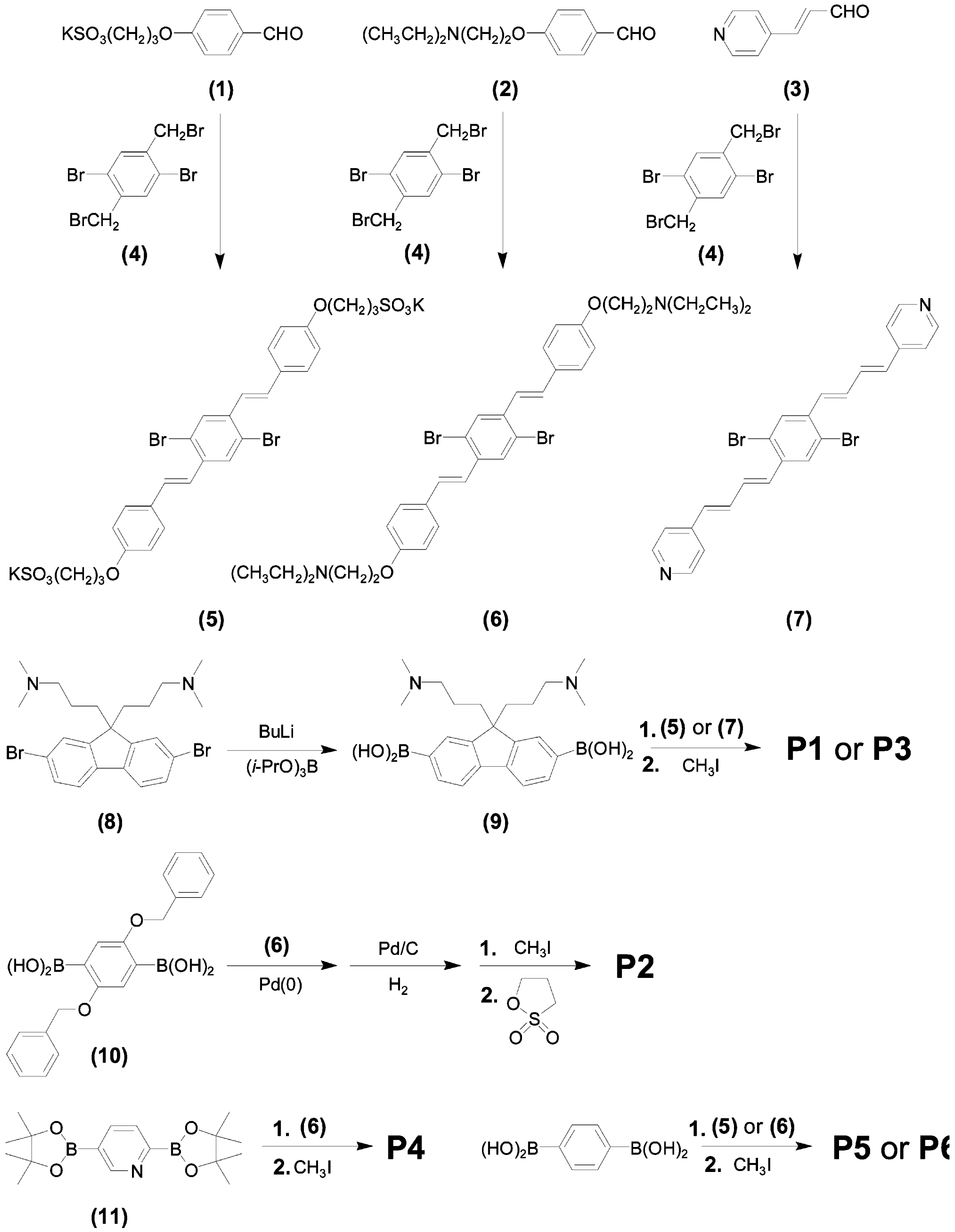

Table 1. GPC, TGA, UV−vis Absorption, and Emission Maxima of P1−P6

polymer	M_n	M_w	PDI	T_{decomp} (°C)	absorption max (nm)	emission max (nm)
P1	7400	8000	1.08	237	326	454
P2	8900	10000	1.12	290	313	449
P3	9800	15100	1.54	238	359	407, 428
P4	9200	17300	1.88	212	349	435
P5	37600	62300	1.66	377	277	468
P6	11200	21900	1.96	285	283, 324	448

Characterization. All polymers were soluble in water and partially soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), except **P4** and **P6**, which were readily soluble in all three solvents. Molecular weights of the polymers were determined using gel permeation chromatography with reference to poly(ethylene glycol) standards and DMF as eluent, and the observed values were within the range of 7440−37640 (Table 1). Owing to the polar nature and presence of many ligating groups on the polymer backbone, increasing the molecular weight was difficult. **P1**, for example, has the lowest molecular weight with the number of repeating unit of ca. 8. Solubility of one of the intermediate **5** was poor in DMF while the other intermediate **9** was readily soluble, which caused significant difference in the effective concentrations of both compounds in DMF solution. This may be the reason for observing the low molecular weight. On the other hand, **P1** and **P2** showed considerably narrow PDIs, owing to the removal of highly soluble low molecular weight fractions (i.e., during dialysis with MWCO membrane with 3.5 K cutoff to remove the low MW fractions) and less soluble high molecular weight fractions during the filtration prior to the GPC analysis. Other solvents (e.g., piperidine) and phase transfer catalysts (tetrabutylammonium bromide) were also used with no obvious improvement in the molecular weight. It is expected that after a certain critical value the molecular weight may not have a significant influence on the photophysical properties. Many conjugated polymers have structural defects which disrupt the effective conjugation length.[49−56]

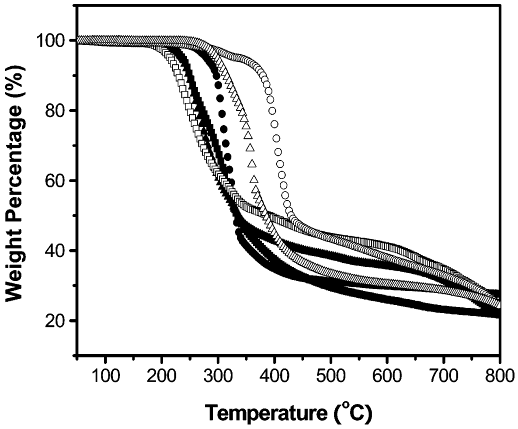

Figure 3. TGA results of **P1** (■), **P2** (●), **P3** (▲), **P4** (□), **P5** (○), and **P6** (△).

Thermogravimetric analysis (TGA) was done using a heating rate of 10 °C/min up to 1000 °C under a N_2 atmosphere. All polymers showed reasonably good thermal stability (Table 1 and Figure 3). It is interesting to note that **P1**, **P2**, **P3**, and **P6** showed similar thermal stability; **P4** showed lowest stability close to **P2** and **P6**, while **P5** was the most stable one among the polymers. In view of the structures, **P1** and **P3** are incorporated with 3-(*N*,*N*,*N*-trimethylamino)propyl-9*H*-2,7-fluorene, and **P2**, **P4**, and **P6** contain 2-(*N*,*N*-diethylmethylamino)ethoxy groups along the polymer backbone. Therefore, these groups decompose/degrade readily at high temperatures. **P1**−**P6** showed similar thermal stability compared with previously reported linear PPP polymers.[22,24,57]

Photophysical Properties

Absorption and Emission Spectra. As seen in the case of TGA results, polymers having similar functional groups showed comparable absorption and emission properties. UV−vis absorption and emission spectra of **P1**−**P6** are shown in Figure 4, and peak maxima are summarized in Table 1. All characterizations were done in aqueous solution with a polymer concentration of 20 mg/L. All polymers showed absorption maxima between 325 and 360 nm, which corresponds to a $\pi-\pi^*$ transition and a red shift in $\lambda_{\max}$ ($\Delta\lambda_{\max} \sim 25$ nm), as compared with linear water-soluble PPPs without conjugated side chain.[18] **P2** and **P6** with a 2-(*N*,*N*-diethyl-*N*-methylamino)ethoxy group showed absorption maxima in the range of 280−320 nm; **P3** and **P4** with pyridyl groups gave absorption maxima at 355 nm, which is red-shifted as compared to other linear PPP polymers. This may be due to the strong electron-withdrawing effect of pyridine ring, lowering the LUMO energy and band gap. Absorption spectra of **P5** and **P6** were broad indicating possible aggregation in solution. **P1** showed a blue shift in the emission maximum (452 nm) as compared with that of **P5** (468 nm), indicating its lack of planarity caused by the bulky 3-(*N*,*N*,*N*-trimethylamino)propyl-9*H*-2,7-fluorene unit. **P3** showed two emission maxima (407 and 428 nm), while the emission maximum for **P4** was at 434 nm. Compared with the linear water-soluble sulfonated PPPs[18] which showed emission maxima around 400 nm, a significant red shift of 25−65 nm was observed for all polymers owing to the extended π-conjugation. Compound **5** with the phenylenevinylene unit (Scheme 1) showed a blue shift in emission maximum (396 nm) as compared with the corresponding polymers **P1** (452 nm) and **P5** (468 nm), possibly due to reduced conjugation. However, the formation of excimer could not be neglected in our studies.[58] The emission measurements were also done in dilute solution, but no significant peak shift was observed (see Supporting Information).

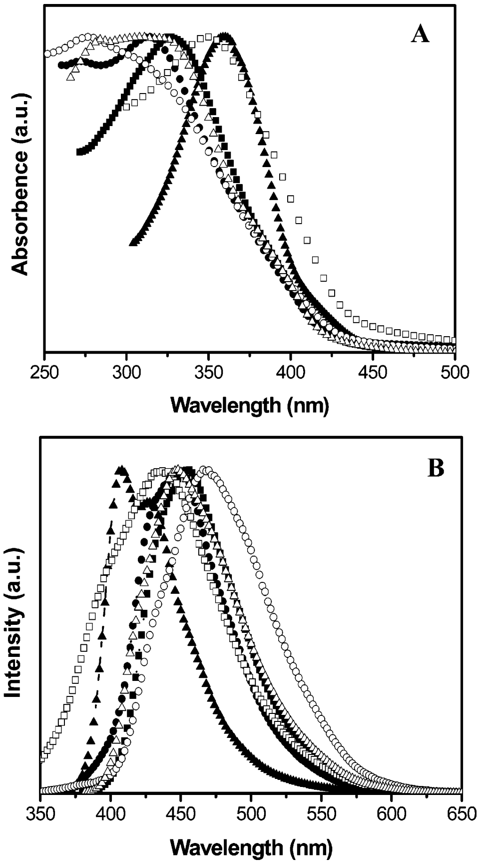

Figure 4. Normalized absorption (A) and emission (B) spectra of **P1** (■), **P2** (●), **P3** (▲), **P4** (□), **P5** (○), and **P6** (△) in water (20 mg/L).

Titration Studies. Target polymers functionalized with different binding groups should possess sensing behavior for various charged molecules. Five commercially available quenchers were used in these studies, including acid blue 45 (50% dye content (AB)), 9,10-anthraquinone-2,6-disulfonic acid disodium salt (AD), potassium hexacyanoferrate (III) (PF), benzyl viologen (BV), and ferrous chloride (FC). The first three are anionic, and the rest are cationic in nature. All fluorescence quenching studies with different quenchers were carried out in aqueous solution with a polymer concentration of 20 mg/L. The concentrations of the quenchers varied in micromolar level based on the sensitivity of each polymer. The results are illustrated in Figure 5 and in the Supporting Information (Figures S1−S5). The static quenching through the formation of a complex is assumed to be the only way in our system due to strong electrostatic interactions between the polymer and small molecular quenchers; the quenching efficiency was expressed by the following Stern−Volmer equation.[59]

$$F_0/F = 1 + K_{sv}[Q]$$

Some of the data collected from titration experiments showed upward curves at high concentrations of the quenchers (Figure 5F); the values of K_{sv} calculated were based on the linear region at low concentrations. Ideally speaking, binding of one quencher molecule to one polymer chain is sufficient for quenching the fluorescence of that chain.[60] However, if we take into account the aggregation induced self-quenching, which is quite significant in the case of **P1**−**P6** (see discussion below), the K_{sv} constants reported in Table 2 could be underestimated. Polymers **P1** and **P2** have been functionalized with both cationic and anionic groups which enhance the sensing properties through

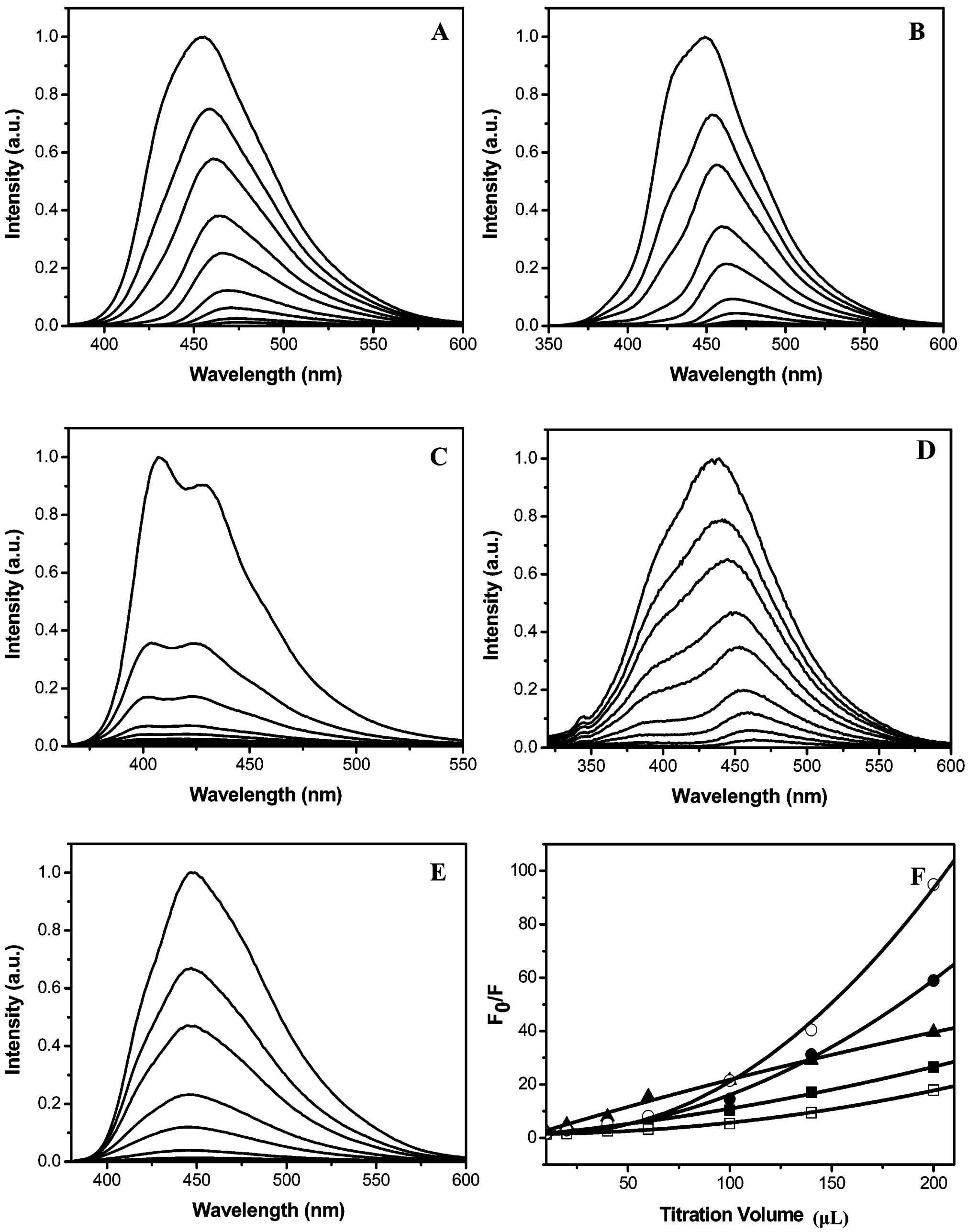

Figure 5. Fluorescence spectra of **P1** (A; 0, 5, 10, 16, 33, 66, 132, 200, and 333 μM), **P2** (B; 0, 0.5, 1, 1.6, 3.3, 6.6, 13.2, 20, and 33 μM), **P3** (C; 0, 0.05, 0.1, 0.16, 0.33, 0.66, 1.32, 2, and 3.3 μM), **P4** (D; 0, 0.5, 1, 1.6, 3.3, 6.6, 13.2, 20, and 33 μM), and **P6** (E; 0, 0.5, 1, 1.6, 3.3, 6.6, 13.2, 20, and 33 μM) with titration of potassium hexacyanoferrate(III) and corresponding titration curves **P1** (○), **P2** (●), **P3** (▲), **P4** (□), and **P6** (■) (F) in water solution. Polymer concentration was 20 mg/L. Quencher concentrations were indicated in the each figure and parenthesis.

Table 2. Stern−Volmer Constant (K_{sv}) for P1−P6 with Titration of Five Different Quenchers in Water

	K_{sv} (M^{-1})					
quenchers	P1	P2	P3	P4	P5	P6
AB	6.4×10^4	1.6×10^5	5.5×10^6	7.0×10^5	N/A	3.7×10^5
AD	4.0×10^4	7.2×10^5	4.5×10^6	3.1×10^5	N/A	9.6×10^5
PF	5.4×10^4	3.6×10^5	6.3×10^6	2.2×10^5	N/A	3.4×10^5
BV	2.2×10^5	4.6×10^5	6.2×10^4	8.0×10^4	5.4×10^5	N/A
FC	1.5×10^5	1.6×10^5	2.5×10^5	1.2×10^5	4.8×10^5	N/A

electrostatic interactions. **P3** and **P4** are interesting because of the presence of pyridyl groups on the polymer backbone which is highly sensitive to metal ions. However, the pyridyl moiety alone did not enhance solubility of polymers in water; hence, quaternary ammonium groups were incorporated on the side chains.

All polymers showed good sensitivity to the quenchers with an average value of K_{sv} around 10^5 (Table 2). **P1** and **P2** showed lower sensitivities, which was explained using two factors. First, the low molecular weights might reduce the effective conjugation length, depressing the signal amplification; it is also possible that the zwitterionic character of the polymers results in competing electrostatic interactions: attraction and repulsion. The repulsion force inevitably prevents the analytes from approaching closer to a donor−acceptor distance (r) to the functional groups participating in the complexation. According

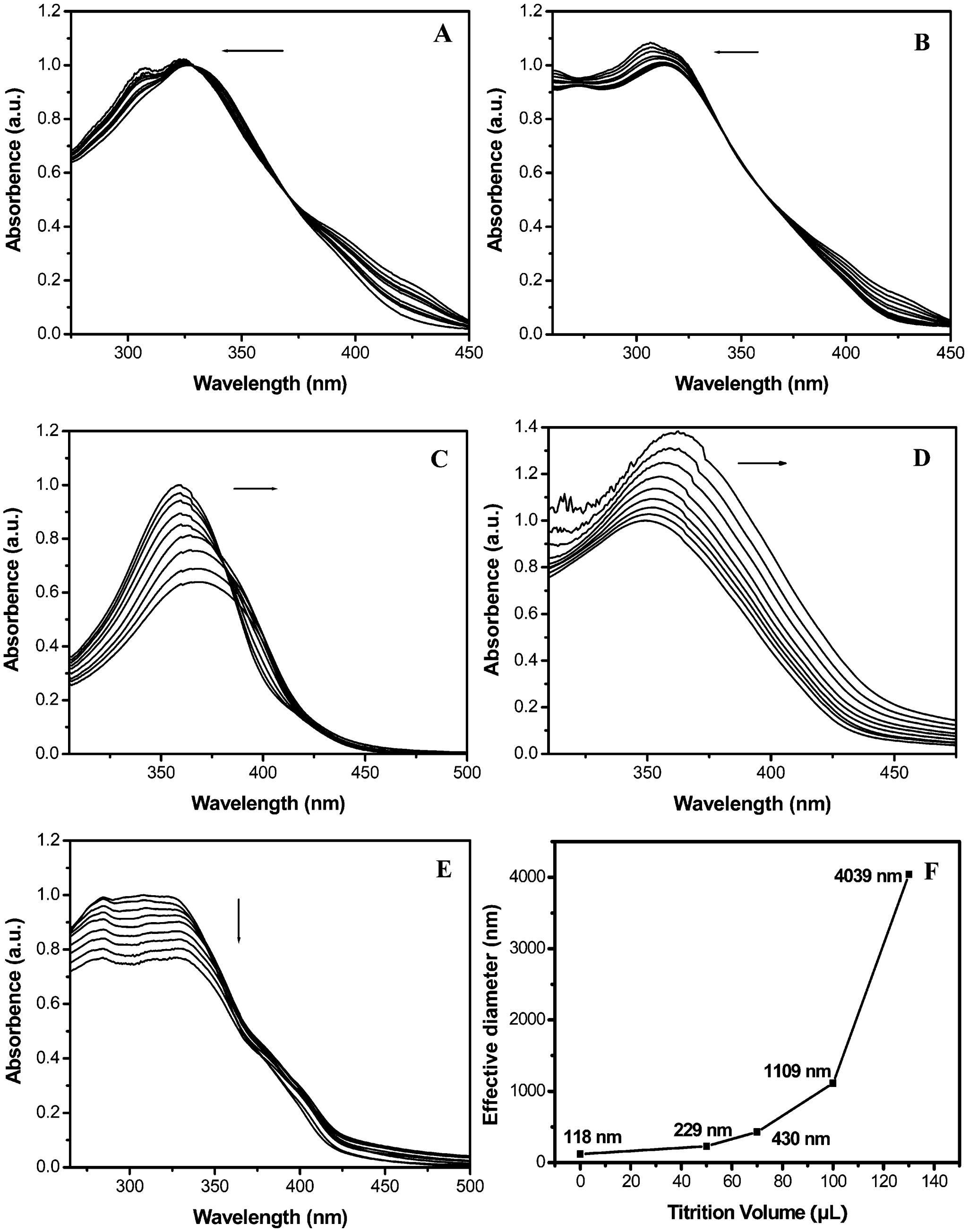

Figure 6. UV−vis absorption spectra of **P1** (A), **P2** (B), **P3** (C), **P4** (D), and **P6** (E) with titration of potassium hexacyanoferrate(III) (PF). Hydrodynamic diameter profile obtained from DLS for **P2** with titration of 9,10-anthraquinone-2,6-disulfonic acid disodium salt (AD) (F) in water. Polymer concentration was 20 mg/L. Quencher concentrations were same as the corresponding ones given in Figure 5.

to Förster theory of dipole−dipole interaction,[61] the rate of energy transfer (k) is inversely proportional to r^6, expressed as the following equation:

$$k \propto \frac{1}{r^6} k^2 J(\lambda)$$

The electrostatic attraction might not be as “strong” as the case in other polymers. **P3** and **P4** showed different sensitivities to anionic and cationic species. During the titration experiments of **P3** with Fe^{2+}, the coordination of Fe^{2+} to nitrogen atom of the pyridyl group occured on a fast time scale. Both **P3** and **P4** showed low response to organic cations such as benzyl viologen as compared with inorganic Fe^{2+} ion. This may be due to several competing factors such as steric hindrance of benzyl groups of benzyl viologen, hydrophobicity, and high degree of solvation of viologen moiety.[62]

Complexation also induced a significant shift in the fluorescence maxima, λ_{emiss} (for some polymers), along with quenching (Figures 6 and S1−S5). In the case of **P2**, titration of acid blue 45 (AB) and benzyl viologen (BV) induced blue shift, while titration of potassium hexacyanoferrate (PF) showed a red shift in λ_{emiss} along with decrease in intensity. Similar results observed for other polymers and the values are summarized in Table 3. From the above studies, it is possible to summarize the following: (i) the acid blue 45 induced a blue shift in λ_{emiss} for all polymers; (ii) only potassium hexacyanoferrate induced a red shift in λ_{emiss} for a few polymers (**P1**, **P2**, and **P4**); (iii) ferrous chloride induced no shift in λ_{emiss}, except **P5**; (iv) complexation with pyridine did not affect the λ_{emiss}, but the emission of **P3** changed to a single broad peak in presence of benzyl viologen; (v) **P5** and **P6** with single functional groups showed a blue shift in the λ_{emiss} value.

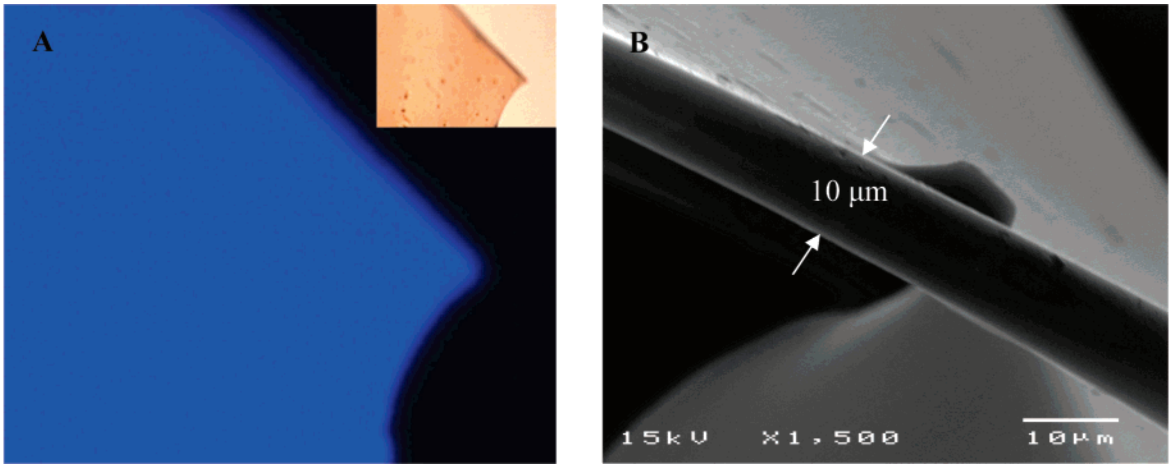

Figure 7. Confocal (excited with UV light) and optical (inset) micrographs of thin films of **P1** prepared from a water solution with a concentration of 10 mg/mL on a glass plate (A) and an SEM micrograph of the edge indicating the thickness of the film (B).

Table 3. Changes in Emission Maxima in Presence of Added Quenchers in Water[a]

quenchers	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
AB	B (26 nm)	B (23 nm)	B (16 nm)	B (20 nm)	N/A	B (10 nm)
AD	N	N	B (14 nm)	N	N/A	B (10 nm)
PF	R (22 nm)	R (24 nm)	B (16 nm)	R (30 nm)	N/A	N
BV	N	B (10 nm)	M	N	B (19 nm)	N/A
FC	N	N	N	N	B (12 nm)	N/A

[a] B = blue shift, R = red shift, N = no change, and M = merging of peaks. Shifting values after complete quenching are indicated in parentheses.

Water-soluble CPs show aggregation in water,[18] which should also be the case with our zwitterionic cross-conjugated systems. Furthermore, there are two interesting but contradictory phenomena: first, the aggregation of polymer chains was confirmed by the blue shift in λ_{emiss} in the presence of charged quenchers (usually organic) which may act as cross-links between polymer chains. It may also disrupt the order of the stacked polymer chains. Second, aggregation of polymer chains with certain degree of order is also possible (red shift in λ_{emiss}) with the addition of the highly charged quenchers like $[Fe(CN)_6]^{3-}$ which reduce the repulsion of the similar functional groups along the polymer chain. Thus, the preliminary data collected here shall imply an alternative way for fine-tuning photophysical properties of the cross-conjugated polymers.

UV–vis titration studies were done under exactly the same conditions as that of fluorescence. The results showed that, except for **P6,** all polymers showed shift in absorption maxima (λ_{max}) after complexation with ionic species, but the directions of shift depend on the respective systems. For **P1** and **P2**, addition of anionic species resulted in less planar cross-conjugated structures, whereas cationic species induced a red shift. In the case of **P3** and **P4**, anionic species induced more planarity of the polymer backbone through strong electrostatic interaction which led to a red shift, while addition of cations did not show an obvious shift in the absorption maxima. The results are consistent with the fact that the static quenching results from complexation of the analyte to the receptor sites, which leads to the relaxation or energy transfer processes that favor nonradiative decay or through a new excitation/emission behavior.[63,64] For **P2** and **P4**, a significant decrease in λ_{max} at highest quencher concentration (tens of μM) of AD was observed (Figures S7B and S9B, Supporting Information), which may be due to the strong aggregate formation.

Titration studies in aqueous solution with 20 mM NaCl and 100 mM NaCl were carried out to examine the role of ionic strength in fluorescent quenching. It was observed that with increasing ionic strength the sensitivity, i.e., value of Stern–Volmer constant, was decreased. A significant decrease in K_{sv} was observed in the case of **P2** with addition of AB in 100 mM saline compared with the values obtained from pure water (Tables S1 and S2 in the Supporting Information). This is because the presence of salt leads to disaggregation or decomplexation of the polymer in solution, which become stronger with increase in ionic strength. The titration study could not be conducted in buffer solutions such as PBS or SSC due to strong quenching by phosphate and citrate anions present in the buffer solution.

DLS Studies. The aggregation behavior of **P2** induced by the sodium salt of 9,10-anthraquinone-2,6-disulfonic acid (AD) was studied using DLS (Figures 6F and S11) in water with polymer concentration of 20 mg/L. The pure polymer solution showed the mean hydrodynamic diameter around 118 nm, indicating the mild aggregation of polymer chains. With increasing the concentration of quencher, the effective diameter increased almost exponentially, indicating significant aggregation. Notably the hydrodynamic diameter of the aggregates was increased to 4 μm when the quencher concentration was 43.3 μM, and the solution became turbid, which was consistent with the UV–vis results (Figure S7B, Supporting Information). We also found that, unlike fluorescence quenching, the aggregation process was not instantaneous; therefore, the solutions were mixed well and incubated for 3 min before each measurement. Aggregation often reduces the quantum efficiency of the emission via strong intermolecular charge transfer, which should provide added quenching efficiency. However, the values of Stern–Volmer constants were close to values reported for sulfonated PPPs,[18] probably due to partial self-quenching among the polymer chains.

Thin Film Studies. For the device fabrications, it is important that the polymer should be soluble and processable. Enhancement of performance may be realized in the solid state due to close proximity of the polymer chains, facilitating the exciton diffusion.[65] Thin films were prepared from all water-soluble polymers formed via slow evaporation of the aqueous polymer solutions on various substrates. The film had smooth and uniform morphology and intense blue emission after exposure to UV light (Figure 7A). The thickness of the films can be varied by varying the concentration of the polymer solution and fabrication methodologies. A self-supporting film with an average thickness around 10 μm is shown in Figure 7B. The films prepared from **P3**, **P4**, and **P6** were highly flexible, and further improvement in film quality can be achieved by blending the polymers with other polymers such as poly(vinyl alcohol) (PVA). Therefore, it is possible to use the polymers either in solution or in solid states. Removal of water after casting the film under different concentrations, temperatures, and pressures was investigated, but no significant changes in optical or morphological properties of the film were observed.

Conclusion

A series of water-soluble cross-conjugated PPP derivatives have been synthesized and fully characterized. All polymers incorporated with multiple functional groups on the backbone and conjugated side chain are thermally stable. Optical studies indicated an extended conjugated π-electron system with collective response arising from the respective chromophores. Cross-conjugated structures offer possible exciton migration pathways in presence of a quencher. Titration studies with various organic and inorganic compounds showed good sensitivity to the analytes at the micromolar concentration, as indicated by fluorescence quenching. The aggregation of the polymer was investigated using dynamic light scattering technique. Complexation also induced blue or red shift of $\lambda_{\max}$, depending on concentration of the quencher, structure of the polymer, and added quencher molecules. All polymers formed thin, smooth, and uniform films with high emission characteristics. These results contribute a novel way to extend the capability of CPs in chemo- and biosensor applications.

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Supporting Information Available: Absorption and emission spectra for all polymers along with DLS data on aggregation of **P2** in the presence of quenchers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; p 203.
(2) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.
(3) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.
(4) Kittlesen, G. P.; White, H. S.; Erighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389.
(5) Janata, J.; Josowicz, M. *Acc. Chem. Res.* **1998**, *31*, 241.
(6) Kim, J. M.; Lee, J. S.; Choi, H.; Sohn, D.; Ahn, D. J. *Macromolecules* **2005**, *38*, 9366.
(7) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321.
(8) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.
(9) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017.
(10) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.
(11) Lu, L.; Rininsland, F. H.; Wittenburg, S. K.; Achyuthan, K. E.; McBranch, D. W.; Whitten, D. G. *Langmuir* **2005**, *21*, 10154.
(12) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 10954.
(13) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 896.
(14) Liu, B.; Bazan, G. C. *Chem. Mater.* **2004**, *16*, 4467.
(15) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.
(16) Kim, I. -B.; Dunkhorst, A.; Gilbert, J.; Bunz, U. H. F. *Macromolecules* **2005**, *38*, 4560.
(17) Ksenijia, H. G.; Pinto, M. R.; Tan, C. Y.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 14964.
(18) Vetrichelvan, M.; Li, H. R.; Renu, R; Valiyaveettil, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3763.
(19) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975.
(20) Chem, L.; McBranch, D. W.; Wang, H.; Helgeson, R.; Wudl, F.; Whitten, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287.
(21) Pinto, M. R.; Kristal, B. M.; Schanze, K. S. *Langmuir* **2003**, *19*, 6523.
(22) Fan, Q. L.; Lu, S.; Lai, Y. H. *Macromolecules* **2003**, *36*, 6976.
(23) Harrison, B. S.; Ramey, M. B.; Reynolds, J. R.; Schanze, K. S. *J. Am. Chem. Soc.* **2000**, *122*, 8561.
(24) Balanda, P. B.; Ramey, M. B.; Reynolds, J. R. *Macromolecules* **1999**, *32*, 3970.
(25) Patil, A. O.; Ikeniue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
(26) Pickup, P. *J. Electroanal. Chem.* **1987**, *225*, 273.
(27) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.
(28) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.
(29) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.
(30) Rau, I. U.; Rehahn, M. *Acta Polym.* **1994**, *45*, 3.
(31) Brodowski, G.; Horvath, A.; Ballauf, M.; Rehan, M. *Macromolecules* **1996**, *29*, 6962.
(32) Rulkens, R.; Schulze, M.; Wegner, G. *Makromol. Rapid Commun.* **1994**, *15*, 669.
(33) Kim, S.; Jackiw, J.; Robinson, E.; Schanze, K. S.; Reynolds, J. R.; Baur, J.; Rubner, M. F.; Boils, D. *Macromolecules* **1998**, *31*, 964.
(34) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681. Zucchero, A. J.; Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11872.
(35) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrel, T. *J. Am. Chem. Soc.* 2**006**, *128*, 3914. Pina, J.; Seixas de Melo, J.; Burrows, H. D.; Bilge, A.; Farrel, A.; Forster, M.; Scherf, U. *J. Phys. Chem. B* **2006**, *110*, 15100.
(36) Diez-Barra, E.; Garcia-Martinez, J. C.; Rodriguez-Lopez, J. *J. Org. Chem.* **2003**, *68*, 832. Fan, Q. L.; Lai, Y. H.; Hou, X.Y.; Huang, W. *Macromolecules* **2003**, *36*, 6976.
(37) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.
(38) Smith, D. K.; Diederich, F. *Chem.—Eur. J.* **1998**, *4*, 1353.
(39) Miller, L. L.; Duan, R. G.; Tully, D. C.; Tomalia, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 1005.
(40) Diez-Barra, E.; Garcia-Martinez, J. C.; Merino, S.; del Rey, R.; Rodriguez-Lopez, J.; Sanchez-Verdu, P.; Tejeda, J. *J. Org. Chem.* **2001**, *66*, 5664.
(41) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.
(42) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.
(43) Campbell, L. J.; Borges, L. F.; Heldrich, F. J. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2627.
(44) Otsubo, T.; Kohda, T.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 512.
(45) Shen, H. L.; Huang, F.; Hou, L. T.; Wu, H. B.; Cao, W.; Yang, W.; Cao, Y. *Synth. Met.* **2005**, *152*, 257.
(46) Ma, W. L.; Iyer, P. K.; Gong, X.; Liu, B.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2005**, *17*, 274.
(47) Baskar, C.; Lai, Y. H.; Valiyaveetil, S. *Macromolecules* **2001**, *34*, 6255.
(48) Mandolesi, S. D.; Vaillard, S. E.; Podesta, J. C.; Rossi, R. A. *Organometallics* **2002**, *21*, 4886.
(49) Franco, I.; Tretiak, S. *Chem. Phys. Lett.* **2003**, *372*, 403.
(50) Chen, Y. S.; Meng, H. F. *Phys. Rev. B: Conden. Matter Mater. Phys.* **2002**, *66*, 035202/1.
(51) Grozema, F. C.; van Duijnen, P. Th.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2002**, *106*, 7791.
(52) Freo, L. D.; Painelli, A.; Girlando, A.; Soos, Z. G. *Synth. Met.* **2001**, *116*, 259.
(53) Yurtsever, E.; Yurtsever, M. *Synth. Met.* **1999**, *101*, 335.
(54) Baughman, R. H.; Shacklette, L. W. *J. Chem. Phys.* **1989**, *90*, 7492.
(55) Kürti, J.; Kuzmany, H.; Nagele, G. *J. Mol. Electron.* **1987**, *3*, 135.
(56) Baughman, R. H.; Chance, R. R. *J. Appl. Phys.* **1976**, *47*, 4295.
(57) Huang, F.; Wu, H. B.; Wang, D. L.; Yang, W.; Cao, Y. *Chem. Mater.* **2004**, *16*, 708.
(58) Ding, L.; Egbe, D. A. M.; Karasz, F. E. *Macromolecules* **2004**, *37*, 6124.
(59) Pesce, A. J. In *Fluorescence Spectroscopy*; Pesce, A. J., Rosen, C. G., Pasby, T. L., Eds.; Marcel Dekker: New York, 1971.
(60) Thomas III, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.

(61) Förster, Th. *Naturwissenschaften* **1946**, *33*, 166.

(62) Fan, C. H.; Hirasa, T.; Plaxco, K. W.; Heeger, A. J. *Langmuir* **2003**, *19*, 3554.

(63) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Plenum Press: New York, 1999.

(64) Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E. Jr. *J. Phys. Chem. B.* **2004**, *108*, 1537.

(65) Nesterov, E. E; Zhu, Z. Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 10083.

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