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# Water-Soluble and Blue Luminescent Cationic Polyelectrolytes Based on Poly(*p*-phenylene)

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ABSTRACT: Two new (dialkylamino)ethoxy-substituted poly(*p*-phenylene)s (PPP) have been prepared, poly[2,5-bis(3-{*N*,*N*-diethylamino}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] (P−NEt$_2$) and poly[2,5-bis(3-{*N*,*N*-dimethylamino}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] (P−NMe$_2$). These PPPs were synthesized via Pd-catalyzed Suzuki polymerization and are soluble in organic solvents (THF, chloroform) and dilute aqueous acid. Water-soluble quaternary ammonium functionalized PPPs, poly[2,5-bis(3-{*N*,*N*,*N*-triethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (P−NEt$_3^+$) and poly[2,5-bis(3-{*N*,*N*,*N*-trimethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (P−NMe$_3^+$), were easily prepared from the neutral polymers. Number-average molecular weights ranging from 5000 to 19 000 g mol$^{-1}$ were measured by GPC (relative to PS standards), and these values were standardized to PPP's via universal calibration. The neutral polymer is stable to over 300 °C by TGA, while the alkylated polymers begin to dealkylate at 230 °C. The polymer's electronic absorption is dependent on quaternization with the neutral polymer having a $\lambda_{\max}$ at 350 nm, while the triethyl quaternized polymer's $\lambda_{\max}$ shifts to 330 nm. This corresponds to an electronic band gap ($E_g$) shift from 3.0 to 3.3 eV where $E_g$ is defined as the onset of the $\pi$ to $\pi$* transition. The polymers luminesce blue light with an intensity that is a function of ionic composition, allowing them to be used as emitting materials in LED's constructed by both layer-by-layer electrostatic deposition and hybrid ink jet printing methods.

## Introduction

The ionic nature, induced electrostatic potentials, and broad range of microscopic architectures available with polyelectrolytes (PE's) make them interesting candidates for use in a variety of redox and electroactive systems,[1] including solid-state device applications. PE's can enhance or hinder chemical reactions by their ability to increase or decrease the concentration of ionic reactants.[2,3] PE's have also proven useful as reaction media for photoinduced electron-transfer events; photoinduced charge separation has been enhanced in the presence of PE's which may retard back electron transfer.[4,5]

Previously, our group has reported the synthesis of rigid anionic PE's based on sulfonated poly(benzobisthiazole)s[6] and poly(*p*-phenylene)s (PPP's).[7] Such rigid systems provide an additional degree of order due to their possible lyotropic nature in water, and they hold great potential for formation of tough composite materials. The sulfonatoalkoxy PPP derivative, poly[2,5-bis-(3-sulfonatopropoxy-1,4-phenylene-*alt*-1,4-phenylene] disodium salt (PPP−OPSO$_3$), luminesces blue under UV illumination and has been utilized for the formation of self-assembled multilayer LED devices.[8] Recent publications have shown that PPP polyelectrolytes can be obtained with high molecular weight, controlled physical properties, and desired solubility.[9]

Two new polyelectrolytes based on PPP have been synthesized as cationic counterparts to our above-mentioned anionic PPP. These are poly[2,5-bis(3-{*N*,*N*,*N*-triethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (P−NEt$_3^+$) and its neutral analogue poly[2,5-bis(3-{*N*,*N*-diethylamino}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] (P−NEt$_2$), along with poly[2,5-bis(3-{*N*,*N*,*N*-trimethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (P−NMe$_3^+$) and its neutral analogue poly[2,5-bis(3-{*N*,*N*-dimethylamino}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] (P−NMe$_2$). We find these polymers to be highly water-soluble and luminesce blue with an intensity that is a function of ionic composition. These polymers form compatible blue-emitting solid-state devices via layer-by-layer polyelectrolyte self-assembly with the sulfonatopropoxy PPP and have been used as a buffer layer for hybrid ink jet printing creation of pixylated LED's using sulfonatopropoxy-substituted poly(phenylenevinylenes).[10]

## Results and Discussion

**Monomer Synthesis.** The synthesis of the monomers M−NMe$_2$, 2,5-bis(3-[*N*,*N*-dimethylamino]-1-oxapropyl)-1,4-dibromobenzene, and M−NEt$_2$**,** 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene, is illustrated in Scheme 1. Dibromohydroquinone (**1**) was treated with 2-chloroethyldimethylamine hydrochloride (**2**) or 2-chlorotriethylamine hydrochloride (**3**) in refluxing acetone in the presence of excess anhydrous potassium carbonate. Overall unoptimized yields of M−NMe$_2$ and M−NEt$_2$ were 29% and 38%, respectively. The reactions are presumed to proceed through the in situ formation of aziridinium ions **4** and **5**. The syntheses of **1** and bisneopentylglycol-1,4-phenylene diboronate (**6**) are described elsewhere.[11] M−NEt$_2$ was quaternized by stirring at room temperature for 30 days with bromoethane (see Scheme 2), and the product, M−NEt$_3^+$, was found to be ca. 98% quaternized by elemental analysis. Alternatively, stirring M−NEt$_2$ for 5 days in acetonitrile with excess bromoethane leads to nearly quantitative quaternization.

**Polymer Synthesis.** Neutral tertiary amine carrying PPPs were synthesized via variations of the Suzuki coupling reaction according to Scheme 3. P1−NEt$_2$ was synthesized under conditions of stoichiometric balance of monomers by Pd(OAc)$_2$-catalyzed Suzuki cross-

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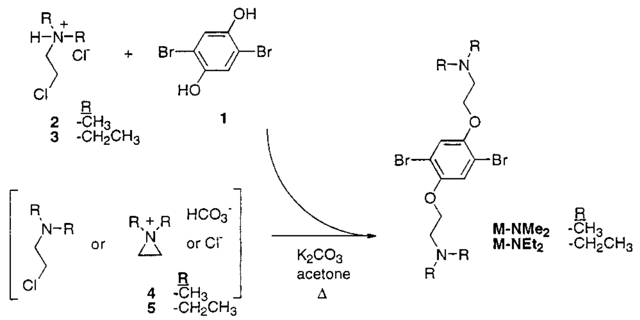
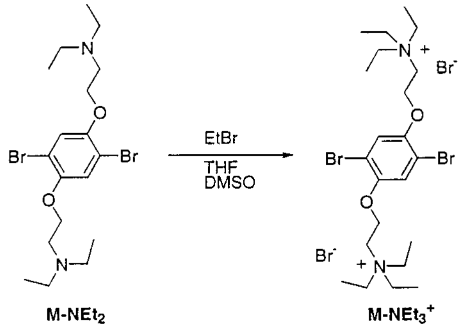
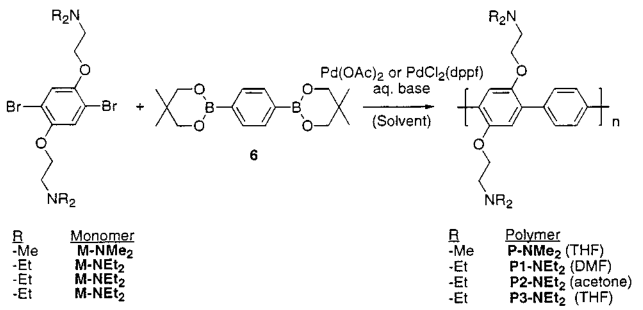
**Scheme 1**



**Scheme 2**



**Scheme 3**



coupling polymerization of M−NEt$_2$ with **6** in aqueous DMF in 76% yield. P2−NEt$_2$ was synthesized in aqueous acetone in 91% yield by reaction of M−NEt$_2$ with **6** in the presence of monofunctional ethylene-4-methylphenylboronate under conditions of stoichiometric imbalance (theoretical $\bar{X}_n = 15$, 30 rings). P1−NMe$_2$ was synthesized under conditions of stoichiometric balance in aqueous THF in 38% yield. P3−NEt$_2$ was synthesized in aqueous THF with stoichiometric balance between M−NEt$_2$ and **6** in 95% yield with PdCl$_2$(dppf) as catalyst. Elemental analyses for the monomers and neutral polymers are given in Table 1. While the monomers are all analytically pure, it can be seen that small quantities of Br remain in the polymers which can be attributed to end groups.

The neutral polymers were then quaternized by treatment with an alkyl halide as shown in Scheme 4. Conversion of the P−NEt$_2$ polymers to P−NEt$_3^+$ was achieved by treatment with bromoethane in dimethyl sulfoxide (DMSO) or tetrahydrofuran (THF). In THF, approximately 80% of the functional groups were quaternized after 5 days of room temperature stirring while over 90% quaternization could be accomplished in DMSO. Although elemental analyses showed quantitative conversion (see Table 1), $^1$H NMR indicated conversion was not complete, suggesting the alkylation may be reversible in solution. P1−NMe$_2$ was first converted to the water-insoluble ammonium iodide by treatment with iodomethane in DMSO, which formed a gel during the conversion process. Following isolation by acetone precipitation, the water-insoluble product was dissolved in aqueous HBr and reprecipitated in acetone. Following two iterations, P1−NMe$_3^+$ was isolated as the predominantly bromide salt with nearly quantitative quaternization. As an alternative method, P4−NEt$_3^+$ was synthesized directly in 45% yield by the polymerization of M−NEt$_3^+$ with **6** in aqueous DMF solution (see Scheme 5). The polymer was collected by precipitation in acetone and, as such, contained small amounts of residual salts.

**Polymer Characterization.** The $^1$H and $^{13}$C NMR spectra of the neutral polymers described in this section are similar to those of other PPPs synthesized by Pd(OAc)$_2$-catalyzed polymerization.[10a] It was found that changes in the solvent and/or ionic strength of the NMR solution, and the mobility of the polymers, contribute to spectral changes. The $^1$H NMR spectra of P1−NMe$_2$ and P1−NMe$_3^+$ are shown in Figures 1 and 2, respectively. The features of the two $^1$H NMR spectra are similar, with the alkyl peaks of P1−NMe$_3^+$ shifted downfield relative to those of the neutral polymer. From the relative integrals of the methylene and methyl peaks, it can be seen that a high degree of quaternization exists in P1−NMe$_3^+$.

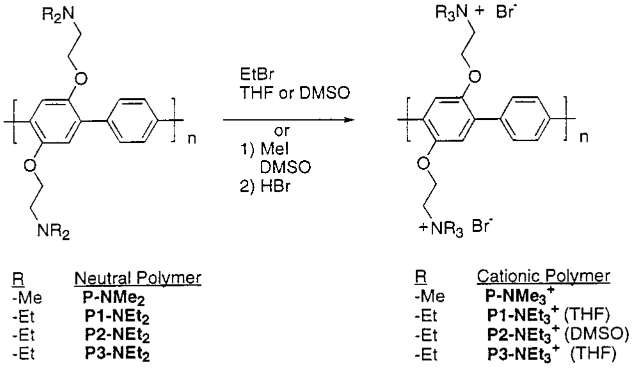
A possible benefit of a direct synthesis of dicationic PPP from a dicationic monomer is a higher level of quaternization. Obtaining salt-free polymers by this route would require that polymers be purified by dialysis. It is difficult to determine the molecular weight of the cationic P−NEt$_3^+$ and P−NMe$_3^+$ polymers due to difficulties in direct analysis of polyelectrolytes. A benefit of the initial synthesis of the neutral amine derivatized polymer lies in the ease with which it can be purified and analyzed by conventional means. The neutral P−NEt$_2$ and P−NMe$_2$ polymers are soluble in many standard organic solvents and aqueous acid through protonation but are insoluble in neutral water. Though the neutral polymers were poorly soluble in THF at room temperature, they were readily soluble in warm THF and CHCl$_3$ allowing acquisition of the GPC results in Table 2. Universal calibration has been developed for functionalized PPPs in THF solution.[12] While the results are not directly applicable to chloroform, application of the method provides a better indication of molecular weight than comparison to polystyrene standards alone. Accordingly, P1−NMe$_2$ had a $\bar{M}_n$ of 4000 g mol$^{-1}$ (approximately 25 rings) with a polydispersity index (PDI) of 3.3. P1−NEt$_2$ and P2−NEt$_2$ had $\bar{M}_n$ values approximately doubled at 10 000 and 9000 g mol$^{-1}$, respectively, with PDI's near 2. Thus, higher yields and molecular weights were obtained in polar aprotic solvents than in the lower dielectric solvent, THF. Use of the more active palladium catalyst, PdCl$_2$(dppf),[9c] in THF led to a higher yielding polymerization, producing a polymer of somewhat higher $\bar{M}_n$ (12 400 g mol$^{-1}$) and a much narrower PDI of 1.2. The PdCl$_2$(dppf) catalyst also has the advantage of preventing the precipitation of Pd(0) from the reaction solution. This was found to be troublesome in purification of the polymers synthesized using Pd(OAc)$_2$.

**Electronic Spectra.** Another benefit in the synthesis of the neutral polymer is that it becomes possible to explore the evolution of the absorption and luminescence properties as a function of solvent and/or pH. For

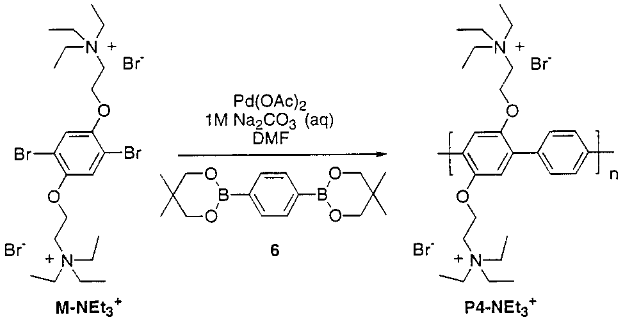
**Table 1. Elemental Analysis Results for the Diamino-PPP Monomers and Polymers**

| anal. calcd for | [anal. found for] | C, % | H, % | N, % | Br, % | FW |
|---|---|---|---|---|---|---|
| $C_{14}H_{22}N_2O_2Br_2$ | | 41.00 | 5.41 | 6.83 | 38.96 | 410.15 |
| | M−NMe$_2$ | 41.13 | 5.44 | 6.71 | | |
| $C_{20}H_{26}N_2O_2$ | | 73.59 | 8.03 | 8.58 | | 326.44 |
| | P1−NMe$_2$ | 70.64 | 7.59 | 7.58 | 1.23 | |
| $C_{22}H_{32}N_2O_2Br_2$ | | 51.18 | 6.25 | 5.43 | 30.95 | 516.32 |
| | P1−NMe$_3^+$ | 51.24 | 6.21 | 4.76 | 30.95 | |
| $C_{18}H_{30}N_2O_2Br_2$ | | 46.37 | 6.49 | 6.01 | 34.27 | 466.26 |
| | M−NEt$_2$ | 46.43 | 6.41 | 5.89 | | |
| $C_{18}H_{30}N_2O_2Br_2{\cdot}2BrC_2H_5$ | | 38.62 | 5.89 | 4.09 | 46.71 | 684.2 |
| $C_{18}H_{30}N_2O_2Br_2{\cdot}2BrC_2H_5{\cdot}1.6H_2O$ | | 37.06 | 6.11 | 3.93 | 44.83 | 713 |
| $C_{18}H_{30}N_2O_2Br_2{\cdot}1.96BrC_2H_5{\cdot}1.6H_2O$ | | 37.15 | 6.12 | 3.95 | 44.65 | 709 |
| | M−NEt$_3^+$ | 37.25 | 5.85 | 3.76 | 44.47 | |
| $C_{24}H_{34}N_2O_2Br_{0.026}$ | | 74.95 | 8.91 | 7.28 | 0.53 | 383 |
| | P3−NEt$_2$ | 75.21 | 8.94 | 8.01 | 0.45 | |
| | P1−NEt$_2$ | 75.09 | 8.92 | 8.05 | 0.54 | |
| $C_{24}H_{34}N_2O_2Br_{0.026}{\cdot}1.6C_2H_5Br$ | | 58.54 | 7.57 | 5.01 | 23.24 | 559 |
| $C_{24}H_{34}N_2O_2Br_{0.026}{\cdot}1.6C_2H_5Br{\cdot}2.54H_2O$ | | 54.02 | 7.85 | 4.63 | 21.48 | 605 |
| | P1−NEt$_3^+$ | 53.44 | 7.52 | 4.34 | 21.12 | |
| | P3−NEt$_3^+$ | 52.35 | 7.61 | 4.31 | 21.40 | |
| $C_{24}H_{34}N_2O_2$ | | 75.35 | 8.96 | 7.32 | | 382.6 |
| $C_{24}H_{34}N_2O_2{\cdot}0.33H_2O$ | | 74.20 | 8.99 | 7.21 | | 388 |
| | P2−NEt$_2$ | 74.18 | 8.78 | 6.88 | <0.02 | |
| $C_{24}H_{34}N_2O_2{\cdot}2C_2H_5Br$ | | 56.01 | 7.39 | 4.67 | 26.61 | 600.5 |
| $C_{24}H_{34}N_2O_2{\cdot}2C_2H_5Br{\cdot}3H_2O$ | | 51.38 | 7.70 | 4.28 | 24.42 | 655 |
| $C_{24}H_{34}N_2O_2{\cdot}2C_2H_5Br{\cdot}1.8H_2O$ | | 53.14 | 7.58 | 4.43 | 25.25 | 633 |
| | P2−NEt$_3^+$ | 52.45 | 6.98 | 4.59 | 26.84 | |
| $C_{24}H_{34}N_2O_2{\cdot}1.9C_2H_5Br$ | | 56.63 | 7.44 | 4.75 | 25.75 | 590 |
| $C_{24}H_{34}N_2O_2{\cdot}1.9C_2H_5Br{\cdot}3H_2O$ | | 51.88 | 7.75 | 4.35 | 23.59 | 644 |
| | P4−NEt$_3^+$ | 51.84 | 7.64 | 3.90 | 23.49 | |

**Scheme 4**



**Scheme 5**



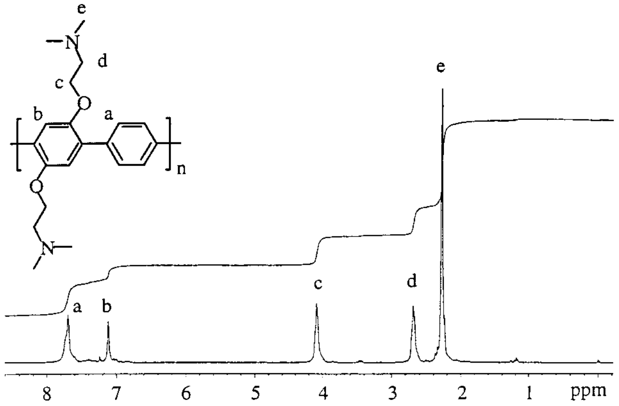


**Figure 1.** Proton NMR spectrum of P1−NMe$_2$ in CDCl$_3$.

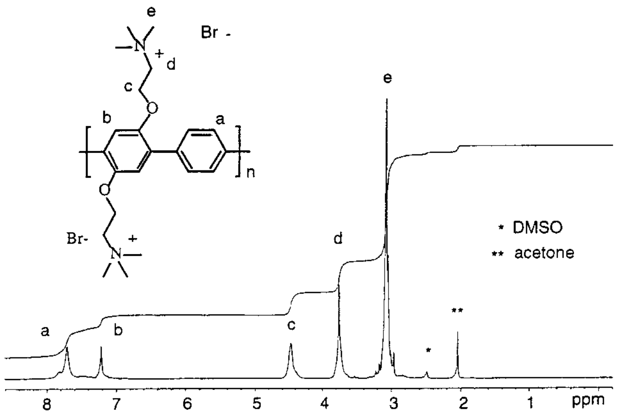


**Figure 2.** Proton NMR spectrum of P1−NMe$_3^+$ in ca. 30/70 DMSO-$d_6$/D$_2$O.

example, the properties of a single polymer sample can be examined in both aqueous and nonaqueous media. Figure 3 shows the electronic spectra of P2−NEt$_2$ in THF, protonated P2−NEt$_2$ in 1 M aqueous HCl, and P2−NEt$_3^+$ in H$_2$O. The molar absorptivity of the polymers range from a maximum of about 21 000 L mol$^{-1}$ cm$^{-1}$ in water to a minimum of 8000 L mol$^{-1}$ cm$^{-1}$ in THF (based on polymer repeat MW). It can be seen that the ratio of the absorptivities of the $\pi$ to $\pi^*$ band for the neutral polymer in THF, relative to the band at ca. 290 nm, is smaller for the neutral polymer relative to either of the cationic derivatives.[13] Similar solvent-induced changes in intensity have been observed for the low-energy $\sigma \rightarrow \sigma^*$ transition of poly[bis(*p*-alkoxyphenyl)silylene]s.[14]

**Table 2. Gel Permeation Chromatography Results in Chloroform**

| polymer | reaction solvent | yield, % | calibration method | $\bar{M}_n$, kg mol$^{-1}$ | MP, kg mol$^{-1}$ | $\bar{M}_w$, kg mol$^{-1}$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|---|
| P1−NMe$_2$ | THF | 38 | PS | 5.0 | 4.8 | 19.5 | 3.91 |
| | | | PPP[a] | 3.9 | 3.8 | 12.9 | 3.29 |
| P1−NEt$_2$ | DMF | 76 | PS | 15.9 | 24.3 | 35.0 | 2.20 |
| | | | PPP | 10.8 | 15.6 | 21.5 | 1.99 |
| P3−NEt$_2$ | THF | 95 | PS | 18.7 | 19.4 | 22.1 | 1.18 |
| | | | PPP | 12.4 | 12.8 | 14.4 | 1.16 |
| P2−NEt$_2$ | acetone | 92 | PS | 12.6 | 21.4 | 28.6 | 2.27 |
| | | | PPP | 8.8 | 14.0 | 18.0 | 2.05 |

[a] Universal calibration using values derived for PPP in THF (from ref 12).

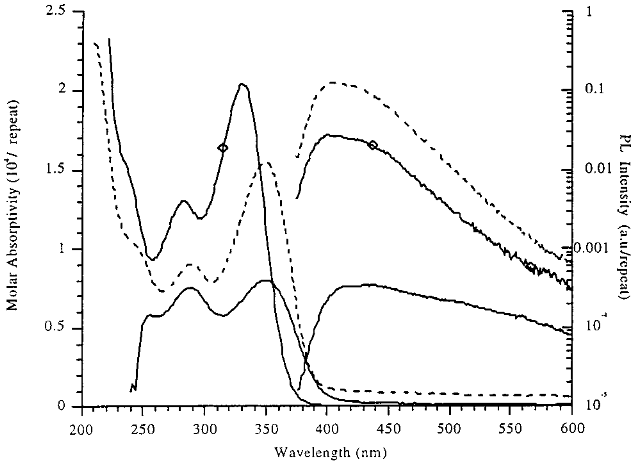


**Figure 3.** UV−vis absorption and PL emission spectra of (—) P2−NEt$_2$ in THF, (- - -) P2−NEt$_2$ in HCl(aq), and (◇) P2−NEt$_3^+$ in H$_2$O.

A more intriguing feature observed in comparison of the absorption spectra of P2−NEt$_2$ and P2−NEt$_3^+$ is the solvatochromic effect on the $\lambda_{max}$ of the $\pi$ to $\pi^*$ transition. The $\lambda_{max}$ of P2−NEt$_2$ is similar in THF (350 nm) to the protonated derivative in 1 M aqueous HCl solution (349 nm). However, when quaternized, the $\lambda_{max}$ of the polymer blue shifts to 330 nm. While solvatochromic effects are observed in conjugated polymers, such as poly(diacetylene)[15] and substituted polythiophenes,[16] this is attributed to a change in solvent polarity bringing about conformational changes that either enhance or decrease the effective conjugation length.[17] A process that results in an increased torsional angle between adjacent rings would result in a blue shift in the $\pi$ to $\pi^*$ transition. It is possible that, for the alkylated polymer in a polar medium of low ionic strength, the mutual repulsion of positive charges housed on alternate rings leads to a lowest energy conformation where the torsional angle is increased. This is analogous to the argument made for chain extension observed with flexible polyelectrolytes under similar conditions, namely, the polyelectrolyte effect. The ability to alter the ionic nature of these polymers, without greatly affecting the chain end-to-end distance, makes them well-suited for a variety of polymer solution property studies.

The most striking feature observed in the electronic spectra for these polymers is the tremendous range of intensities observed in the photoluminescence which differ by nearly 4 orders of magnitude. The highest intensity emission is observed for protonated P−NEt$_2$ in 1 M HCl solution, while the lowest is observed for P−NEt$_2$ in THF. We attribute this to interaction of the nonbonding electron pair on the nitrogen atom with the $\pi$ system, resulting in quenching of the excited state through intramolecular charge transfer.[18−20] As such, PPP−NR$_2$ polymers have the potential for use as luminescent photoinduced electron transfer (PET) pH sensors.[21]

The fact that these cationic PPP's have the same backbone structure as the anionic PPP−OPSO$_3$ allows them to be used in layer-by-layer self-assembly to form electroluminescent devices in which each layer (anion or cation) contributes to the overall emission. EL devices constructed in this manner are over an order of magnitude more luminescent than devices in which PPP−OPSO$_3$ is assembled with nonluminescent polycations.[10a] In addition, these PPP−NR$_3^+$ polymers can serve as buffer layers for hybrid ink jet printed emitting devices where a lower gap polyelectrolyte can be patterned onto the higher gap PPP. Pixelated devices have been constructed that emit both blue and red-orange light.[10b]

**Thermal Analysis.** LEDs operating under a high bias are typically limited in lifetime by thermal and electric field induced degradation, making materials with low barriers to thermal degradation of limited use. From the perspective of device applications, the most important degradation event is the one that occurs first. If the first degradation occurs at the device operating temperature, and does not disrupt device functon or lifetime, the material can still be useful in this application.

The thermal stability of P2−NEt$_2$ and P2−NEt$_3^+$ was studied by TGA in a nitrogen atmosphere in order to obtain a better understanding of degradation mechanisms. The temperature was ramped from 50 to 1000 °C at 10 °C/min, and the weight loss was observed with time. In a second set of experiments, the polymers were heated at the same rate from 50 to 400 °C under high vacuum in the probe of a mass spectrometer. Mass spectral thermograms were obtained which corresponded with the TGA thermograms. Representative mass spectra were obtained during the course of decomposition and fragmentation patterns identified. It should be noted that the experimental design did not allow for discernment between fragmentation events that occur prior to ionization and those that occur after.

The TGA thermogram for the neutral P2−NEt$_2$ and the mass spectrum associated with the first degradation event are shown in Figure 4. P2−NEt$_2$ displayed an onset to decomposition over 300 °C, whereupon it suffered a rapid mass loss indicative of side chain cleavage to a quinone or hydroquinone type structure. Four major fragment ions were associated with this event. The peaks were identified as originating from within the side chain on the basis of the fragmentation patterns shown in Figure 4. Absent from the mass spectrum are larger fragments containing oxygen or phenyl rings. Following the initial mass loss, two

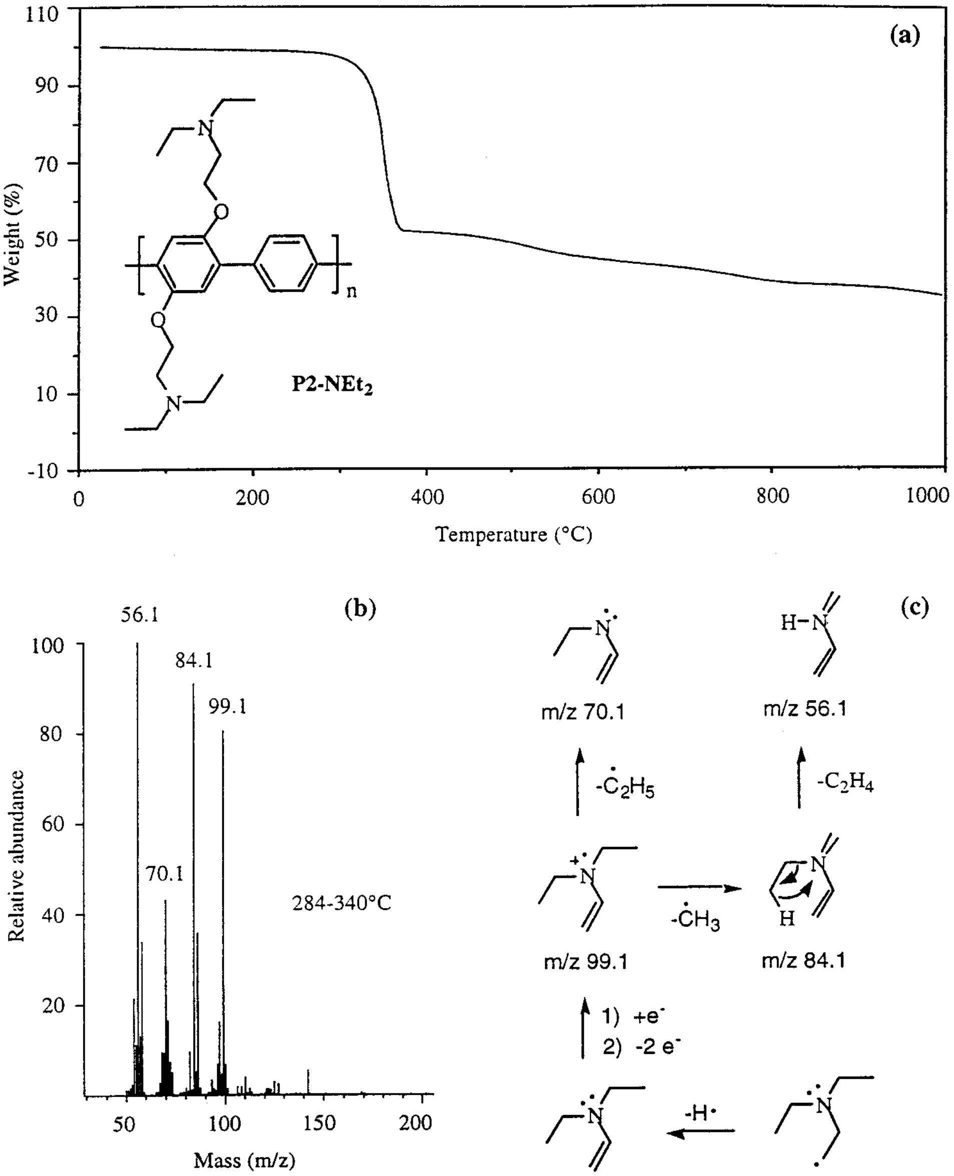


**Figure 4.** Analysis of the thermal decomposition of P−NEt$_2$: (a) TGA thermogram in nitrogen at 10 °C/min; (b) mass spectrum of the volatile products associated with decomposition over the 284−340 °C temperature range; (c) fragmentation pattern proposed for the identification of the volatile organic products produced during the thermal decomposition of P−NEt$_2$ in a nitrogen atmosphere.

smaller transitions which provide mass losses approximately that of carbon monoxide occur at ca. 500 and 700 °C, leaving a 34−37% residual at 800 °C.

The TGA thermogram and associated mass spectra showing the thermal decomposition of P2−NEt$_3^+$ are provided in Figure 5. The quaternized materials begin decomposition at ca. 230 °C (with a small amount of $H_2O$ loss at lower temperatures), with the first mass loss corresponding to loss of ethyl bromide, which was confirmed by TGA-MS. A second major transition occurs in the vicinity of the first transition of the neutral polymer, again due to side chain cleavage. Likewise, two minor transitions follow at ca. 500 and 700 °C. A residual mass, approximately 24−26% of the starting mass, remained at 800 °C.

These results show that the alkylated polymers, which are useful for the preparation of multilayer light-emitting films by electrostatic deposition, thermally dealkylate. As the layer-by-layer electrostatic deposition method eliminates most of the free salt, the thermal loss of bromoethane will not be possible in devices, and thus the degradation processes observed for the neutral polymer will control the upper temperature limits for device operation. The fact that the thermal degradation of these alkoxy-substituted PPPs is a relatively clean process may provide a route to hydoxylated PPP's.

## Experimental Section

**Reagents and Solvents.** All reagents and solvents were purchased from Aldrich or Fisher unless otherwise noted. 1,4-Dibromobenzene (Aldrich) was recrystallized from hot pentane. Tetrahydrofuran (THF) and diethyl ether used in Grignard, alkyllithium reactions, and/or Suzuki coupling reactions were distilled from NaK/benzophenone under nitrogen unless otherwise noted.

**Instrumentation.** Elemental analysis was performed by Robertson Microlit, Inc., or in-house by combustion with a Fisons/Carlo-Erba 1106 and 1108. Ultraviolet−visible (UV−vis) spectra were recorded using either a Varian Cary 5E UV−vis−NIR spectrophotometer or a HP 8452A diode-array spectrophotometer. Fluorescence data were obtained with a Spex

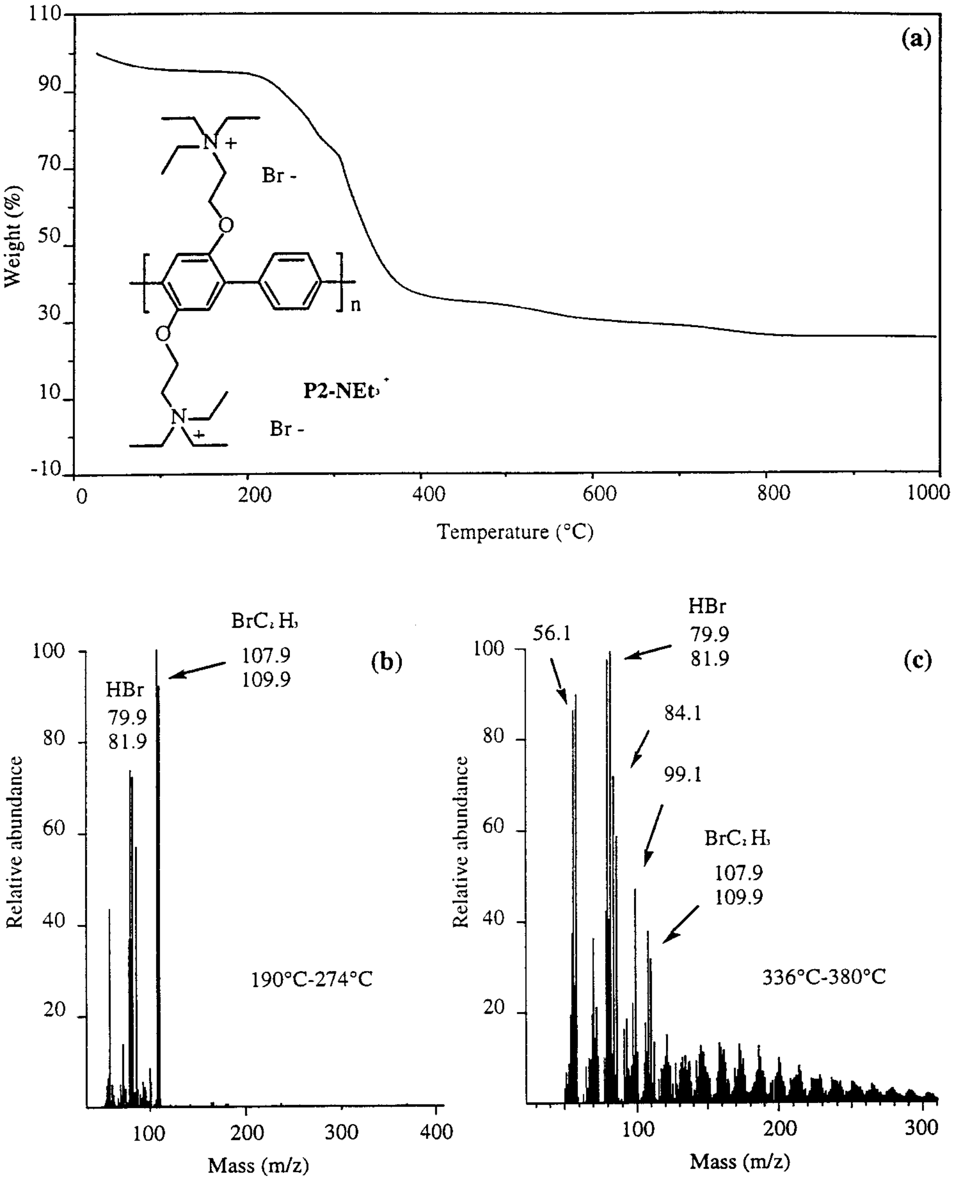


**Figure 5.** Analysis of the thermal decomposition of P2$-$NEt$_3$$^+$: (a) TGA thermogram in nitrogen at 10 °C/min; (b) mass spectrum of the volatile products associated with decomposition over the 190$-$274 °C temperature range; (c) mass spectrum of the volatile products associated with decomposition over the 366$-$380 °C temperature range.

F-112 photon counting fluorimeter at room temperature. NMR spectra were obtained with a Varian VXR-300 or with a Varian Gemini-300. Gas$-$liquid chromatograms were recorded with a HP 5880A series gas chromatograph. FT-IR spectra of samples prepared as thin films on NaCl plates and as pressed pellets in KBr were obtained using a Perkin-Elmer 1640. Melting points under 200 °C were observed in a Thomas-Hoover capillary melting point apparatus. Melting points over 200 °C were observed with a Laboratory Devices Mel-Temp melting point apparatus. Differential scanning calorimetry was obtained with either a Perkin-Elmer DSC 7 differential scanning calorimeter or a Du Pont Instruments DSC 2910 differential scanning calorimeter. Thermogravimetric analysis was performed with a Du Pont Instruments HI-Res TGA 2950 thermogravimetric analyzer. Polymer degradation studies were performed using a Finnigan MAT95Q mass spectrometer (Finnigan MAT, San Jose, CA) in low-resolution mode. Polymer samples were thermally decomposed, and the degradation products were ionized by electron impact ionization and monitored over time. Low-resolution GC/MS spectra were recorded using a Finnigan GCQ mass spectrometer with electron impact ionization. GPC results were obtained with a system consisting of a Waters model 590 pump, a suitable size exclusion column, a Spectraflow 757 tunable UV$-$vis detector, and a Perkin-Elmer LC-25 refractive index detector. Chromatographs in tetrahydrofuran were obtained using tandem 300 × 7.8 mm, 10 $\mu$m particle size Phenomonex Phenogel columns (500 Å + 5000 Å or 500 Å + 5000 Å + 50 000 Å). Chromatographs in chloroform were obtained using a 300 × 7.5 mm Polymer Laboratories linear mixed bed (Plgel 5 $\mu$m mixed-C) column. Polymer samples were prepared by dissolving ca. 10 mg of polymer in 1 mL of the eluent, which was taken from the pump stream. Samples were passed through membrane filters prior to injection.

**General Procedure for 2,5-Bis(3-[*N*,*N*-dialkylamino]-1-oxapropyl)-1,4-dibromobenzenes.** A 500 mL round-bottom flask with magnetic spin bar was charged with anhydrous potassium carbonate, 2-chlorotriethylamine hydrochloride, and 300 mL of acetone. The stirred mixture was sparged with nitrogen for 15 min followed by addition of 2,5-dibromohydroquinone (**1**). After 15 min additional sparging the reaction was brought to reflux for 2 days. The reaction mixture was diluted with 300 mL of water, dissolving all salts. The product was extracted with ether (1 × 300, 2 × 200 mL), and the combined organics were washed with 10% NaOH(aq) (2 × 50 mL), water (2 × 200 mL), and brine (1 × 200 mL). The solution was dried over MgSO$_4$, filtered, and stripped of solvent by vacuum evaporation to yield crude oily solids. The crude product was recrystallized from MeOH/H$_2$O and then from EtOH/H$_2$O to give a white microcrystalline product which was dried in vacuo over KOH for 4 days.

**2,5-Bis(3-[*N*,*N*-dimethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NMe$_2$).** Anhydrous potassium carbonate (34.7 g, 251 mmol), 2-chlorotrimethylamine hydrochloride (**2**, 18.09 g, 126 mmol), and 2,5-dibromohydroquinone (**1**, 13.46 g, 50.2 mmol). Yield 5.88 g [29%], mp 76−78 °C. Anal. Calcd for $C_{14}H_{22}N_2O_2Br_2$: C, 41.00; H, 5.41; N, 6.83. Found: C, 41.13; H, 5.44; N, 6.71. $^1$H NMR (300 MHz, CDCl$_3$): 7.12 (s, 2 H), 4.05 (t, $J = 5.4$ Hz, 4 H), 2.75 (t, $J = 5.8$ Hz, 4 H), 2.34 (s, 12 H) ppm. $^{13}$C NMR (75.4 MHz, CDCl$_3$): 150.55, 119.37, 111.61, 69.39, 58.18, 46.02 ppm.

**2,5-Bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$).** Anhydrous potassium carbonate (72.0 g, 521 mmol), 2-chlorotriethylamine hydrochloride (**3**, 22.56 g, 131 mmol), and 2,5-dibromohydroquinone (**1**, 15.0 g, 56.0 mmol). Yield 9.56 g [37%], mp 64−65 °C. Anal. Calcd for $C_{18}H_{30}N_2O_2Br_2$: C, 46.37; H, 6.49; N, 6.01. Found: C, 46.43; H, 6.41; N, 5.89. $^1$H NMR (300 MHz, CDCl$_3$): 7.12 (s, 2 H), 4.02 (t, $J = 6.0$ Hz, 4 H), 2.90 (t, $J, = 6.2$ Hz, 4 H), 2.65 (q, $J = 7.1$ Hz, 8 H), 1.07 (t, $J = 7.0$ Hz, 12 H) ppm. $^{13}$C NMR (75.4 MHz, CDCl$_3$): 150.02, 118.39, 110.92, 69.92, 51.44, 47.90, 12.06 ppm.

**2,5-Bis(3-[*N*,*N*,*N*-triethylammonium]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_3^+$, Method A).** A solution of 1.047 g (2.25 mmol) of 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$) in 10 mL of bromoethane was stirred for 30 days. Hexane (20 mL) was added and the product collected on a frit at reduced pressure, dried in an air stream, and then in vacuo at 56 °C for 2 days. Yield: 1.45 g [94%], mp 246−248 °C (dec). Anal. Calcd for $C_{18}H_{30}N_2O_2{\cdot}1.96BrC_2H_5{\cdot}1.6H_2O$: C, 37.06; H, 6.11; N, 3.95; Br, 44.65. Found: C, 37.25; H, 5.85; N, 3.76; Br, 44.47.

**2,5-Bis(3-[*N*,*N*,*N*-triethylammonium]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_3^+$, Method B).** A solution of 1.916 g (4.109 mmol) of 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$) in 50 mL of acetonitrile with 10 mL of bromoethane was stirred for 5 days at room temperature. The resulting precipitate was collected on a frit at reduced pressure and dried in an air stream and then in vacuo at 56 °C for 2 days. Yield: 2.62 g [93%], mp 252−253 °C (dec). Anal. Calcd for $C_{22}H_{40}N_2O_2Br_4$: C, 38.62; H, 5.89; N, 4.09; Br, 46.71. Found: C, 38.33; H, 5.98; N, 4.05; Br, 46.31. $^1$H NMR (300 MHz, D$_2$O/DMSO-$d_6$, 80 °C): 7.33 (s, 2 H), 4.31 (s, 4 H), 3.60 (s, 4 H), 3.32 (d, $J = 7.2$ Hz, 12 H), 1.21 (s, 18 H) ppm. $^{13}$C NMR (75.5 MHz, D$_2$O/DMSO-$d_6$, 80 °C): 150.29, 119.88, 111.64, 64.50, 56.47, 54.79, 8.12 ppm.

**Poly({2,5-bis[3-(*N*,*N*-dimethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-1,4-phenylene) (P1−NMe$_2$).** A 500 mL round-bottom flask with magnetic spin bar and airless adapter was charged with M−NMe$_2$ (2.0372 g, 5.00 mmol), **6** (1.5000 g, 5.00 mmol), Na$_2$CO$_3$ (3.207 g, 30.25 mmol), and Pd(OAc)$_2$ (38 mg, 0.36 mmol, 7 mol %). The flask was evacuated for 30 min and then back-filled with argon. Deaerated (30 min of argon sparge) THF (350 mL of distilled-off Na/benzophenone) and 50 mL of water were added via cannula. The reaction mixture was heated to 60 °C under argon, vigorously stirred for 64 h, and then filtered through a medium-porosity frit under reduced pressure. Polymer was precipitated in 800 mL of water, collected by filtration, and washed with water (2 × 200 mL) and with MeOH (200 mL). Following the MeOH wash, MeOH-soluble oligomer precipitated in the filter flask. This fraction was collected separately. The polymer samples were soaked in Et$_2$O, dried in an air stream, and then dried in vacuo at 56 °C. Yield, MeOH-insoluble fraction, P1−NMe$_2$: 0.35 g (22%). $^1$H NMR (300 MHz, CDCl$_3$): 8.0−6.8 {6.3 H [7.70 (bm, 4.30 H), 7.12 (s, 1.73)]}, 4.09 (s, 4 H), 2.69 (s, 4 H), 2.89 (s, 12 H) ppm. $^{13}$C NMR [75 MHz, CDCl$_3$ (end groups)]: 150.81, (153.65), 150.81, (139.63), (138.42), (137.42), 137.07, (132.44), 131.18, (130.97), (129.95), (129.53), 129.10, (127.91), (127.40), (126.58), 117.19, (115.30) ppm. GPC (CHCl$_3$ vs PS): $\bar{M}_n = 4985$ g mol$^{-1}$, MP = 4830 g mol$^{-1}$, $\bar{M}_w = 19\,500$ g mol$^{-1}$, $\bar{M}_w/\bar{M}_n = 3.9$. UV−vis (THF) $\lambda_{max} = 337$ nm. Yield, MeOH-soluble fraction: 0.27 g (16%). Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59; H, 8.03; N, 8.58. Found: C, 70.64; H, 7.59; N, 7.58; Br, 1.23.

**Poly({2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-1,4-phenylene) (P1−NEt$_2$).** A 200 mL Schlenk flask with a magnetic spin bar was charged with 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$, 0.976 g, 2.09 mmol), bisneopentylglycol 1,4-phenylene diboronate (**6**, 0.632 g, 2.09 mmol), 12 mL of mM Na$_2$CO$_3$(aq), and 24 mL of DMF. The reaction mixture was sparged with argon for 30 h. Pd(OAc)$_2$ (20 mg, 4 mol %) was added and the reaction mixture stirred vigorously for 24 h at 80 °C. A second portion (20 mg) of Pd(OAc)$_2$ was added and stirring continued at 80 °C for another 24 h. The reaction mixture was diluted with 50 mL of acetone and 100 mL of water. EDTA (5 g) was added and stirring continued for 12 h at 60 °C. The reaction mixture was filtered and then concentrated NH$_4$OH(aq) added until polymer precipitated. An additional 5 mL of concentrated NH$_4$OH (aq) was added, and the polymer collected on a frit at reduced pressure. The tan material was washed liberally with water, rinsed with methanol, dried in an air stream, and then dried in vacuo at 56 °C. Yield: 0.61 g [76%]. Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.09; H, 8.92; N, 8.05; Br, 0.54. $^1$H NMR (300 MHz, CDCl$_3$): 7.71 (bm, 4 H), 7.13 (bm, 2 H), 4.11 (bm, 4 H), 2.87 (bm, 4 H), 2.62 (bm, 8 H), 1.05 (bm, 12 H) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): 150.41, 136.98, 130.53, [129.96], 129.10, [127.93], [126.61], 116.32, 68.32, 51.98, 47.82, 12.03 ppm [end groups]. GPC (THF vs PS) $\bar{M}_n = 3283$ g mol$^{-1}$, MP = 4653 g mol$^{-1}$, $\bar{M}_w = 5517$ g mol$^{-1}$, $\bar{M}_w/\bar{M}_n = 1.7$; excludes secondary peak, MP = 263. GPC (CHCl$_3$ vs PS): $\bar{M}_n = 15\,900$ g mol$^{-1}$, MP = 24 300 g mol$^{-1}$, $\bar{M}_w = 35\,000$ g mol$^{-1}$, $\bar{M}_w/\bar{M}_n = 2.20$.

**Poly({2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-1,4-phenylene), P3−NEt$_2$.** A 50 mL aliquot of THF and 10 mL of H$_2$O were sparged with argon under reflux for 1 h. A 200 mL Schlenk flask with a magnetic spin bar was charged with 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$, 1.995 g, 4.28 mmol), bisneopentylglycol 1,4-phenylene diboronate (**6**, 1.293 g, 4.28 mmol), 3.60 g of NaHCO$_3$, and PdCl$_2$(dppf) (35 mg, 1 mol %) [Strem Chemicals Inc.]. The flask was evacuated and back-filled with argon three times. The THF/H$_2$O solvent solution was added via cannula to the flask, and the reaction was heated to 75 °C and stirred for 3 days. The solution was precipitated into 200 mL of cold methanol and collected on a glass frit. The polymer was washed with methanol and then water, dried in an air stream, and then dried in vacuo at 56 °C overnight. Yield: 1.552 g [95%]. Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.21; H, 8.94; N, 8.01; Br, 0.45. $^1$H NMR (300 MHz, CDCl$_3$): 7.71 (bm, 4 H), 7.13 (bm. 2 H), 4.11 (bm, 4 H), 2.87 (bm, 4 H), 2.62 (bm, 8 H), 1.05 (bm, 12 H) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): 150.41, 136.98, 130.53, 129.10, 116.32, 68.32, 51.98, 47.82, 12.03 ppm. GPC (CHCl$_3$ vs PS) $\bar{M}_n = 18\,700$ g mol$^{-1}$, MP = 19 400 g mol$^{-1}$, $\bar{M}_w = 22\,100$ g mol$^{-1}$, $\bar{M}_w/\bar{M}_n = 1.18$. UV−vis (THF): $\lambda_{max} = 350$ nm, log $\epsilon_{max} = 3.84$; $\lambda_{max} = 290$ nm, log $\epsilon_{max} = 3.74$. UV−vis (1 M HCl): $\lambda_{max} = 352$ nm, log $\epsilon_{max} = 3.98$; 290 nm, log $\epsilon_{max} = 3.64$. PL (THF with 370 nm excitation): $\lambda_{max} = 435$ nm. PL (1 M HCl with 370 nm excitation): $\lambda_{max} = 408$ nm.

**Polymerization of M−NEt$_2$ with Stoichiometric Imbalance (P2−NEt$_2$).** A 200 mL Schlenk flask with a magnetic spin bar was charged with 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (M−NEt$_2$, 2.1073 g, 4.520 mmol), bisneopentylglycol 1,4-benzenediboronate (**6**, 1.2739 g, 4.218 mmol), ethylene 4-tolueneboronate (**7**, 0.0971 g, 0.6027 mmol), Na$_2$CO$_3$ (2.66 g, 25.3 mmol), and Pd(OAc)$_2$ (30 mg, 3 mol %). The flask was evacuated. Deaerated (30 min argon sparge) solvent (80 mL of acetone, 20 mL of H$_2$O, and 20 mL of MeOH) was added via cannula and the reaction mixture vigorously stirred at 50 °C under argon for 48 h. The polymer was precipitated in 800 mL of H$_2$O, collected on a glass frit, and washed with water (2 × 200 mL) and then MeOH (1 × 200 mL). The product was dissolved in 400 mL of chloroform, stirred with activated carbon for 24 h, and then filtered through Celite. The chloroform was concentrated to 50 mL and the polymer reprecipitated in 600 mL of MeOH/100 mL of $H_2O$. The product was collected by centrifugation, washed with $Et_2O$, and dried in vacuo at 56 °C for 24 h to give a waxy tan solid Yield: 1.58 g [91%]. Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 74.18; H, 8.78; N, 6.88; Br, <0.02. $^1H$ NMR (300 MHz, $CDCl_3$, 60 °C): 7.69 (s, 3.5 H), 7.11 (s, 1.8 H), 4.07 (cm, 4 H), 2.84 (cm, 4 H), 2.57 (cm, 8 H), 1.02 (cm, 12 H) {end groups: 7.77 (s, 0.1 H), 7.51 (d, $J = 8.0$ Hz, 0.2 H), 7.22 (d, $J = 8.1$ H, 0.2 H), 7.02 (s, 0.1 H), 2.49 (s, 0.3 H)} ppm. $^{13}C$ NMR (75.5 MHz, $CDCl_3$, 60 °C): 150.72, 137.17, 130.97, 129.13, 116.81, 68.96, 52.34, 47.97, 12.18 ppm. GPC ($CHCl_3$ vs PS): $\bar{M}_n = 12\,600$ g mol$^{-1}$, MP = 21 400 g mol$^{-1}$, $\bar{M}_w =$ 28 600 g mol$^{-1}$, $\bar{M}_w/\bar{M}_n = 2.3$. GPC (THF vs PS): $\bar{M}_n = 4700$ g mol$^{-1}$, MP = 7100 g mol$^{-1}$, $\bar{M}_w = 12\,500$ g mol$^{-1}$, $\bar{M}_w/\bar{M}_n =$ 2.6. UV−vis (THF): $\lambda_{max} = 350$ nm, $\log \epsilon_{max} = 3.97$; $\lambda_{max} =$ 290 nm, $\log \epsilon_{max} = 3.87$. UV−vis (1 M HCl): $\lambda_{max} = 352$ nm, $\log \epsilon_{max} = 4.03$; 290 nm, $\log \epsilon_{max} = 3.78$. PL (THF with 370 nm excitation): $\lambda_{max} = 435$ nm. PL (1 M HCl with 370 nm excitation): $\lambda_{max} = 408$ nm.

**Poly{2,5-bis[3-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-1,4 phenylene} Dibromide via Polymerization of 2,5-Bis(3-[*N,N,N*-triethylammonium]-1-oxapropyl)-1,4-dibromobenzene Dibromide (M−$NEt_3^+$) with Bisneopentylglycol 1,4-Benzenediboronate (6) (P4−$NEt_3^+$).** A 100 mL Schlenk tube with a magnetic spin bar was charged with M−$NEt_3^+$ (0.902 g, 1.324 mmol), bisneopentylglycol 1,4-benzenediboronate (**6**, 0.400 g, 1.325 mmol), 8 mL of 1 M $Na_2CO_3$(aq), and 16 mL of DMF. The stirred reaction mixture was sparged with argon for 1 h. Following Schlenk transfer of $Pd(OAc)_2$ (12 mg, 4 mol %) to the reaction flask, the reaction flask was subjected to six rapid evacuation/argon fill cycles, and the reaction mixture was stirred vigorously under argon at 80 °C. After 24 h a second aliquot of $Pd(OAc)_2$ was added, and after a total of 48 h the dark brown/black reaction mixture was poured into 400 mL of water. The solution was filtered through a fine-porosity sintered glass funnel, acidified with HBr (aq), and treated with 1 g of EDTA. The mixture was stirred overnight and then filtered through a medium-porosity sintered glass funnel to give a clear, but still gray, solution, which was concentrated to 100 mL on the rotovap. Polymer was precipitated by pouring the aqueous solution into 600 mL of acetone. The solids were collected by centrifugation and dried in vacuo for 2 days at 56 °C to give P4−$NEt_3^+$ as a hard gray (catalyst residues) solid. Yield: 0.36 g [45%]. Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 1.9C_2H_5Br$: C, 56.63; H, 7.44; N, 4.75; Br, 25.75. Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 1.9C_2H_5Br \cdot 3H_2O$: C, 51.88; H, 7.64; N, 4.35; Br, 23.59. Found: C, 51.84; H, 7.64; N, 3.90; Br, 23.49. $^1H$ NMR (300 MHz, $D_2O$): 8.01 (bm, 2.7 H), 7.50 (bm, 2 H), 4.70 (bm, 4 H), 3.94 (bm, 4 H), 3.63 (bm, 11.3 H), [3.31 (bm, 0.6 H)], 1.51 (bm, 17.6 H) ppm.

**Quaternization of Polymeric Amino-Functionalized Poly(*p*-phenylene)s. A. Poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-1,4 phenylene} Dibromide via Postpolymerization Alkylation of Poly{2,5-bis[3-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene-*alt*-1,4-phenylene} with Bromoethane. P2−$NEt_3^+$, Method A.** A 125 mL Erlenmeyer flask with a magnetic spin bar was charged with P2−$NEt_2$ (0.329 g, 0.860 mmol based on repeat). The polymer was dissolved in 90 mL of THF. To this was added bromoethane (0.900 g, 8.26 mmol) and 30 mL of DMSO. The solution was stirred at 50 °C for 2 days, at which time most of the bromoethane and THF had evaporated. Polymer was precipitated by the addition of ca. 80 mL of acetone, collected by centrifugation, and dried overnight in vacuo at 56 °C (0.408 g, 79%). Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 2C_2H_5Br$: C, 56.01; H, 7.39; N, 4.67; Br, 26.61. Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 2C_2H_5Br \cdot 1.8H_2O$: C, 53.14; H, 7.58; N, 4.43; Br, 25.25. Found: C, 52.45; H, 6.98; N, 4.59; Br, 26.84. $^1H$ NMR (300 MHz, 70/30 DMSO-$d_6$/$D_2O$): 7.62, (bm, 4.2 H), 7.08 (bm, 2.4 H), 4.29 (bm, 4 H), 3.51 (bm, 1.44 H), 3.39 (bm, 2.56 H), 3.16 (d, $J = 6.3$ Hz, 3.29 H), 3.06 (d, $J = 6.9$ Hz, 5.27 H), 2.43 (s, 1.21 H), 1.06 (m, 13.22 H) ppm. UV−vis ($H_2O$): $\lambda_{max} = 330$ nm, $\log \epsilon_{max} = 4.30$; $\lambda_{max} =$ 282 nm, $\log \epsilon_{max} = 4.12$. PL ($H_2O$ with 380 nm excitation): $\lambda_{max}$ = 401 nm.

**P3−$NEt_3^+$, Method A.** P3−$NEt_2$ (1.32 g, 3.46 mmol) was quaternized following the above procedure with nearly identical quaternization results based on $^1H$ NMR results.$^1H$ NMR (300 MHz, $D_2O$): 7.9−6.5 (bm, 6 H), 4.5−3.8 (bm, 4 H), 3.8−2.5 (bm, 16 H), 1.5−0.4 (bm, 16.38 H [theoretical 18 H]]) ppm. Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 1.6C_2H_5Br \cdot 2.54H_2O$: C, 54.02; H, 7.85; N, 4.63; Br, 21.48. Found: C, 52.35; H, 7.61; N, 4.31; Br, 21.40. UV−vis ($H_2O$): $\lambda_{max} = 330$ nm, $\log \epsilon_{max} = 4.17$; $\lambda_{max} =$ 282 nm, $\log \epsilon_{max} = 4.02$. PL ($H_2O$ with 380 nm excitation): $\lambda_{max}$ = 401 nm.

**B. Poly{2,5-bis[3-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-1,4 phenylene} Dibromide via Postpolymerization Alkylation of Poly{2,5-bis[3-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene-*alt*-1,4-phenylene} with Bromoethane. P1−$NEt_3^+$, Method B.** P1−$NEt_2$ (0.164 g, 0.429 mmol) was stirred at room temperature with bromoethane (5 mL) in THF (20 mL) in a sealed flask. The partially quaternized amine polymer **P2−$NEt_3^+$** precipitated out of solution such that, after stirring 5 days at room temperature, about 80% conversion of functional groups was obtained. Anal. Calcd for $C_{24}H_{34}N_2O_2 \cdot 1.6C_2H_5Br \cdot 2.54H_2O$: C, 54.02; H, 7.85; N, 4.63; Br, 21.48. Found: C, 53.44; H, 7.52; N, 4.34; Br, 21.12. The water included in the elemental analysis results was based on early mass loss in the TGA. $^1H$ NMR (300 MHz, $D_2O$): 7.9−6.5 (bm, 6 H), 4.5−3.8 (bm, 4 H), 3.8−2.5 (bm, 16 H), 1.5−0.4 (bm, 17 H [theoretical 18 H]]) ppm. UV−vis ($H_2O$): $\lambda_{max} = 330$ nm, $\log \epsilon_{max} = 4.26$; $\lambda_{max} = 282$ nm, $\log \epsilon_{max} = 4.11$. PL ($H_2O$ with 370 nm excitation): $\lambda_{max}$ = 410/417 (sh) nm.

**Poly{2,5-bis[3-(*N,N,N*-trimethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-1,4 phenylene} Dibromide (P1−$NMe_3^+$) via Postpolymerization Alkylation of Poly{2,5-bis[2-(*N,N*-diethylamino)ethyoxy]-1,4-phenylene-*alt*-1,4-phenylene}.** A glass vial with magnetic spin bar was charged with P1−$NMe_2$ (0.306 g, 0.937 mmol) and iodomethane (1.0 mL, 16.1 mmol) in 10 mL of DMSO. The vial was tightly capped, and the contents were stirred at 60 °C overnight. During this time gel formation occurred. The addition of 20 mL of DMSO failed to dissipate the gel; a viscous dispersion was formed. A second 1.0 mL portion of iodomethane was added, and the mixture was again stirred overnight. The contents of the vial were transferred to a 250 mL Erlenmeyer flask, and quaternized polymer precipitated with 150 mL of acetone as an iodide salt. The polymer was allowed to settle, and the majority of the liquid decanted off. Water (10 mL) was added. The polymer did not dissolve but was dissolved by the addition of 48% aqueous HBr (20 mL). To the flask was added 150 mL of acetone, which resulted in polymer precipitated. After settling, the solvent was decanted off. Water (10 mL) was added. The polymer dissolved, indicating that most of the iodide was displaced by bromide. Aqueous 48% HBr (20 mL) was again added, followed by acetone (150 mL). After settling the solvents were decanted. Fresh acetone (2 × 150 mL) was added to wash the precipitated polymer. Following the second acetone wash, the polymer was collected by centrifugation and dried in vacuo overnight at 56 °C. Yield: 0.44 g of dark tan glassy solid (92%). Anal. Calcd for $C_{22}H_{32}N_2O_2Br_2$: C, 51.18; H, 6.25; N, 5.43; Br, 30.95. Found: C, 51.24; H, 6.21; N, 4.76; Br, 26.25. $^1H$ NMR (300 MHz, $D_2O$): 8.0−6.8 {7.4 H [7.71 (bm, 4 H), 7.22 (s, 2 H)]}, 4.73 (bm, 4 H), 3.75 (bm, overlapping $D_2O$, 5.4 H [4 + 1.4]), 3.09 (cm, 18 H) ppm. $^{13}C$ NMR [75 MHz, $D_2O$ (end groups)]: 150.17, (139.57), 136.94, 131.26, (130.69), 129.94, (128.99), (127.20), 117.01 ppm. UV−vis ($H_2O$): $\lambda_{max} = 330$ nm, $\log \epsilon_{max} = 4.25$; $\lambda_{max} = 286$ nm, $\log \epsilon_{max} = 4.06$. PL ($H_2O$ with 380 nm excitation): $\lambda_{max}$ = 410/717 (sh) nm.

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