Articles

Amplified Fluorescence Quenching and Electroluminescence of a Cationic Poly(*p*-phenylene-*co*-thiophene) Polyelectrolyte

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ABSTRACT: A water-soluble conjugated polymer was developed that displays significant fluorescence quenching (25% quenching of polymer's fluorescence at quencher concentrations of 500 nM) and forms well-defined multilayer structures via electrostatic deposition. The polymer contains alternating 2,5thienyl- and 2,5-bis[2-(N,N-diethylamine)-1-oxapropyl]-substituted 1,4-phenylene units formed by a Stille reaction protocol. Poly({2,5-bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4-phenylene}-alt-2,5-thienylene) (PPT-NEt₂) was synthesized in 80% yield from 2,5-bis(trimethylstannyl)thiophene and the reactive diiodinated species 2,5-bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene. The neutral polymer was soluble in THF, chloroform, and 1 M HCl (aq). A number-average molecular weight of 5300 g mol⁻¹ (ca. 40 rings) was measured by GPC (relative to polystyrene standards). PPT-NEt₂ is easily converted to the watersoluble polymer, poly{2,5-bis[2-(N,N,N-triethylammonium)-1-oxapropyl]-1,4-phenylene-alt-2,5-thienylene} dibromide (PPT-NEt $_3^+$), by quaternization with bromoethane. The polymer's electronic absorption is dependent on quaternization with absorption/emission wavelength maxima (λ_{max}) corresponding to 460/ 519 nm for the neutral polymer and 411/495 nm for the quaternized version in the appropriate solvent. Well-defined, thin multilayer films of PPT-NEt₃⁺, alternating with poly(acrylic acid)[PAA] or poly(styrene sulfonic acid)[PSS], were deposited via electrostatic deposition onto indium tin oxide coated glass. Polymer light-emitting diodes prepared from PPT-NEt₃⁺/PSS exhibited the best results with a λ_{max} of absorption and emission equal to 450 and 558 nm, respectively, external quantum efficiency of 0.017%, and light output of 110 nW.

Introduction

Conjugated polyelectrolytes (CPE's) are an interesting class of polymers that combine the optoelectronic and redox properties of traditional conjugated polymers with the aqueous solubility and ionic nature of polyelectrolytes with potential uses in electroluminescent and electrooptic devices.¹ With appropriate substitution, numerous conjugated polymers have been prepared that are soluble in organic media. Water-soluble polyelectrolytes (PE's) are known for their uses in redox and electroactive systems,² concentration control of ionic reactants in chemical reactions,3 and photoinduced electron-transfer events.⁴ Careful incorporation of anionic or cationic functionality into a CPE yields a material that possesses the beneficial properties of a conjugated polymer with the aqueous solubility/processability of a PE. The conducting and luminescent properties of conjugated polymers, including CPE's, have been exploited for use in detection devices for a wide range of chemical and biological agents.⁵

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Wegner and Rehahn et al. reported the synthesis and characterization of substituted poly(p-phenylene's) (PPP's) that mimic "true" PPP but possess solubility in organic or aqueous media.⁶ Novak et al. investigated watersoluble PPP's functionalized with carboxylic acid groups.⁷ Our group reported the synthesis of sulfonatopropoxysubstituted poly(p-phenylene) (PPP-ORSO₃)⁸ along with the cationic quaternary ammonium-substituted poly-[2,5-bis(2-{*N*,*N*,*N*-triethylammonium}-1-oxapropyl)-1,4phenylene-alt-1,4-phenylene] dibromide (PPP-NEt₃⁺).⁹ PPP-ORSO₃ has been used to create self-assembled multilayer LED devices.¹⁰ PPP-NEt₃⁺ has been used as a buffer layer for hybrid ink-jet printing of pixylated LED's using sulfonatopropoxy-substituted poly(phenvlenevinylenes)11a and for amplified fluorescence quenching studies with several anionic quenchers, including $Ru(phen')_{3}{}^{4-}$ and $Fe(CN)_{6}{}^{4-},$ in aqueous solution (phen' = 4,7-bis(4-sulfophenyl)-1,10-phenanthroline). 11b

While PPP-NEt₃⁺ is a strong blue-emitting polymer, it is desirable to have structurally similar materials with a range of emission wavelengths. Yu and coworkers reported on the Stille synthesis of phenylene*co*-thienylene polymers with emission wavelengths in the green region which were soluble in organic solvents,^{12a-c} while Wang et al. reported on the synthesis

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Scheme 1. Synthesis of 2,5-Bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt₂)



and electrochromic properties of linear and star branched poly(3,4-ethylenedioxythiophene-*co*-didocyloxybenzene) polymers.^{12d} Herein, we utilize a modified Stille reaction¹³ protocol in the synthesis of poly({2,5-bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-2,5-thienylene) (PPT-NEt₂), which is easily converted to the CPE quaternary ammonium salt, poly{2,5-bis[2-(N,N,N-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-2,5-thienylene} dibromide (PPT-NEt₃⁺).

 $PPT-NEt_3^+$ is highly water soluble and forms uniform thin-layer structures over a wide pH range upon electrostatic deposition with poly(acrylic acid) [PAA] or poly-(styrene sulfonic acid) [PSS]. The layer-by-layer, thin film processing technique provides a simple means of creating multilayer films with molecular-level control.¹⁴ This technique is based on the spontaneous adsorption of oppositely charged polymers or molecules from aqueous solution. The adsorption cycle can be repeated to create a highly uniform multilayer film. This technique has been applied to organic light-emitting device (LED) technology^{10,15,16} and is particularly attractive because of its ease of use and flexibility as well as the high control over molecular architecture and the potential for uniform large-area coverage. Conjugated polyelectrolytes provide a means to create highly molecularly controlled conducting layers in an environmentally sound setting. We previously demonstrated layer-bylayer assembled green-emitting LEDs containing poly- $(p-phenylenevinylene)(PPV)^{15}$ as well as blue-emitting LEDs containing poly(p-phenylene)¹⁰ derivatives. The LED and amplified fluorescence quenching characteristics of a green-luminescent cationic poly(p-phenyleneco-thiophene) (PPT-NEt₃⁺) polyelectrolyte synthesized via the Stille-coupling reaction will be demonstrated.

Results and Discussion

Monomer Synthesis. To effectively synthesize PPT-NEt₃⁺ of high molecular weight via a Stille polymerization, we selected 2,5-bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt₂) and 2,5-bis(trimethylstannyl)thiophene (**5**) as co-monomers. A diiodobenzene monomer was chosen over a dibromo reagent due to its higher reactivity in Pd coupling reactions. The use of a diiodo monomer was necessitated by the fact that the aryl tin reagents used in the Stille reaction are somewhat less reactive than the aryl boronic acids used in the Suzuki coupling reaction. Particular attention was paid to the stringent monomer purification requirements needed for complete conversion of functional groups.

Scheme 1 illustrates the three-step synthesis of 2,5bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt₂). 1,4-Dimethoxybenzene (1) was iodonated under acidic conditions using potassium periodate, iodine, and a mixed-solvent system consisting of 90:7:3 $HOAc/H_2O/H_2SO_4$ by volume with heating to yield 2,5dimethoxy-1,4-diiodobenzene (2).17 Compound 2 was reacted with boron tribromide in methylene chloride at -78 °C, producing 2,5-diiodohydroquinone (3).¹⁸ The desired diiodo, dialkoxyamine product, 2,5-bis(3-[N,Ndiethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt2), was synthesized by the Williamson etherification of 3 by refluxing in acetone for 3 days with 2-chloroethyldiethylamine hydrochloride and potassium carbonate. The overall yield for DINEt₂ based on dimethoxybenzene (1)was 46%.

Polymer Syntheses. To compare the relative reactivity of the new DINEt₂ monomer with its dibromo analogue (DBrNEt₂), a Suzuki coupling polymerization (see Scheme 2) was conducted to synthesize $poly({2,5$ bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4-phenylene}alt-1,4-phenylene) (PPP-NEt₂), described previously by our group.⁹ Using identical protocols, reactions were conducted to couple DINEt2 and DBrNEt2 with bisneopentylglycol-1,4-phenylene diboronate (4) via a Suzuki protocol. Both reactions were quenched by precipitation into MeOH after 3 h. GPC results in chloroform (vs polystyrene [PS] standards) revealed low molecular weight oligomers ($\bar{M}_{\rm n}$ < 1500 g mol⁻¹ , multimodal) for the reaction using the dibromonated species [PPP-NEt₂-(Br-3)], while the polymer prepared using the diiodonated reagent [PPP-NEt₂(I-3)] reached a $\overline{M}_n = 10\ 900$ g mol⁻¹ (unimodal). Published results using DBrNEt₂ in the reaction for 72 h showed $\bar{M}_{
m n} = 15~900~{
m g~mol^{-1}}$ for the resulting polymer [PPP-NEt₂(Br-72)].⁹ The GPC results are summarized in Table 1. Longer reaction times (complete polymerization stopped after 24 h) with DINEt₂ [PPP-NEt₂ (I-24); $\overline{M}_n = 15\ 900\ \text{g mol}^{-1}$] approached the molecular weight values reported for PPP-NEt₂(Br-72). The use of DINEt₂ leads to formation of a polymer with similar molecular weight properties to PPP-NEt₂(Br-72) in a shorter amount of time. Once the polymer has reached a certain molecular weight, it begins to precipitate out of solution, terminating polymer growth and negating the advantages of the more reactive iodine reagent at longer reaction times.

Scheme 2. Synthesis of PPP-NEt₂ via a Suzuki Coupling Protocol



Table 1. Gel Permeation Chromatog	raphy Results
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polymer	reaction solvent	reaction type	reaction time (h)	$ar{M}_{ m n}$ (kg mol $^{-1}$)	$MP \ { m kg \ mol^{-1}}$	$ar{M}_{ m w}$ (kg mol $^{-1}$)	$ar{M}_{ m w}/ar{M}_{ m n}$
PPP-NEt ₂ (Br-72) ^a	DMF/H ₂ O	Suzuki	72	15.9	24.3	35.0	2.20
$PPP-NEt_2(I-3)^a$	DMF/H ₂ O	Suzuki	3	10.9	13.3	16.6	1.52
$PPP-NEt_2 (I-24)^a$	DMF/H ₂ O	Suzuki	24	15.3	19.5	27.5	1.80
$PPT-NEt_2(48)^b$	DMF	Stille	48	3.2	4.3	5.2	1.70
$PPT-NEt_2(96)^b$	DMF	Stille	96	4.1	5.8	6.9	1.68
$PPT-NEt_2(240)^b$	DMF	Stille	240	4.2	5.4	7.2	1.71
$PPT-NEt_2(96-drop)^b$	DMF	Stille (dropwise)	96	5.3	6.9	9.0	1.70

^a Indicates CHCl₃ as solvent for GPC analysis. ^b Indicates THF as solvent for GPC analysis.

Elemental analysis data for the neutral PPP-NEt₂-(Br-72) and PPP-NEt₂(I-3,24) is provided as Supporting Information (Table S1) and indicates only a small percentage of Br or I end groups remained in the final polymer. Taking into account the different atomic weights of Br and I with the associated error in elemental analysis, $\pm 0.04\%$, the percentage of each element found in PPP-NEt₂(Br-72), [Br = 0.54%] and PPP-NEt₂(I-24), [I = 0.76%], are indicative of materials with approximately 0.025 halogen atoms per polymer repeat unit. Solution UV-vis absorption properties $(\lambda_{\rm max} = 349 \text{ nm}; \text{molar absorptivity} \approx 8,000 \text{ L mol}^{-1} \text{cm}^{-1}$ in THF) for both PPP-NEt₂(Br-72) and PPP-NEt₂(I-24) were identical. DINEt₂ proved to be a more active halogenated species for Suzuki coupling reactions, and these results indicate that DINEt₂ should be a more effective monomer when used in the Stille polymerization protocol as compared to DBrNEt₂.

The Stille coupling polymerization used in the synthesis of poly({2,5-bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4-phenylene}-alt-2,5-thienylene) (PPT-NEt₂) is depicted in Scheme 3. Compound 5 was easily prepared in good yield using a literature methodology¹⁹ and purified by vacuum distillation followed by two recrystallizations from pentane. Elemental analyses for the subsequent polymerization experiments described herein are presented in the Supporting Information (Table S1). It should be noted that the carbon analyses are somewhat lower than expected. One possible explanation of this is that these highly aromatic polymers are difficult to fully combust and some carbonization may have occurred during the measurements. A second possible explanation of the lowered carbon percentages is that in Stille polymerizations hydrolyzed tin byproducts can remain trapped in the resulting polymer. In the PPP's prepared via Suzuki polymerization, where tin contamination was not possible, carbon analysis was similarly low, and if tin-contaminated PPT samples were present





in this study, one would expect a deviation for all elemental percentages analyzed. The iodine elemental analyses provide a rough method for approximating the degrees of polymerization. Using PPT-NEt₂(96-drop) as an example, elemental analysis showed 0.97% iodine in the polymeric sample, resulting in a theoretical repeat unit formula of C₂₂H₃₂N₂O₂SI_{0.030}. If the polymer sample consisted solely of chains terminated with one iodophenylene group, a degree of polymerization of approximately $33 (\sim 66 \text{ rings})$ would be necessary to result in an iodine elemental percentage of 0.97%. If the polymer sample consisted solely of chains terminated with two iodophenvlene groups, a degree of polymerization of approximately 66 (\sim 132 rings) would result. More likely, the individual polymer molecules are a mixture of chains terminated with one and two iodophenylene groups or with two thienyl groups. Chains with double thienyl termination would show no iodine in their elemental

analysis, even if they were of very small molecular weight. Taking the double thienyl termination into account, the perceived degree of polymerization (33-66 repeat units) based on elemental iodine analysis alone would be higher than the actual value. Gel permeation chromatography (GPC) analysis revealed $\overline{M}_{\rm n} = 5300 \text{ g mol}^{-1}$ for sample PPT-NEt₂(96-drop), corresponding to a degree of polymerization of approximately 15 repeat units (30 rings) [see Table 1]. A general trend observed among the different PPT-NEt₂ samples was that as the percent of iodine decreased in a polymer sample, the degree of polymerization of the sample, as determined by GPC, was proportionately higher as well, thus allowing iodine analysis to provide a relative indication of the degree of polymerization between samples.

PPT-NEt₂ molecular weight optimization was carried out by varying polymerization conditions. Initial polymerization reactions consisted of adding the stannylated compound, DINEt₂, and DMF to an appropriately sized flask under argon with heating to 70 °C. A catalytic amount of PdCl₂(PPh₃)₂ was added in one portion to the reaction flask. PPT-NEt₂(48) and PPT-NEt₂(96) were synthesized with 48 and 96 h reaction times followed by precipitation into MeOH. The precipitated material was extracted with MeOH and acetone for 24 h, separately, via Soxhlet extraction to remove low molecular weight species. The remaining polymeric solid was extracted with chloroform. The chloroform-soluble fraction of polymer was used for all subsequent characterizations and analyses. PPT-NEt₂(48) was collected in 75% yield with $\bar{M}_n = 3200 \text{ g mol}^{-1}$, while PPT-NEt₂(96) was collected in 80% yield with $\bar{M}_n = 4100 \text{ g mol}^{-1}$ (see Table 1). Polydispersities of 1.7 were found for both. Doubling the reaction time led to modest improvements in both yield and \overline{M}_n , while increasing the reaction time to 10 days in PPT-NEt₂(240) led to no appreciable molecular weight enhancement ($\bar{M}_n = 4200 \text{ g mol}^{-1}$).

Structural Characterization. ¹H and ¹³C NMR analysis of the recovered PPT-NEt₂ polymers gave expected shift values with the proton peaks appearing as broad multiplets (see Figure 1 and Experimental Section). Expansion of the aromatic region of the ¹H NMR (ppm > 7.0) spectrum did not reveal the presence of terminal thienyl protons, although the peaks may be hidden under the broadened aromatic peaks from the backbone protons (Ha and Hb). ¹H peaks were not present for the methylene protons of trimethylstannyl groups (~0.38 ppm) or tolylene protons (~2.35 ppm), which would have resulted from an unreacted trimethylstannyl group or the transfer of a methyl group from the 2,5-bis(trimethylstannyl)thiophene to an iodophenylene ring during the catalytic cycle. If signals from any of the above-mentioned end-group protons were readily visible, a low molecular weight polymer would have been indicated. The ¹³C NMR spectrum shows a small peak slightly upfield from the peak #3, 126.49 ppm, which most likely corresponds to the carbon atom beta to the sulfur atom on terminal thienyl groups. No other ¹³C peaks were evident for perceived chain-terminating carbons. Due to the relatively low-intensity ¹³C peak at \sim 126 ppm, as compared to the signals from the major backbone aromatic carbons, a polymer sample consisting of low molecular weight oligomers can be excluded.

On the basis of the ¹³C NMR results which indicated that thienyl end groups were present in the final polymeric materials, it was hypothesized that 2,5-bis-



Figure 1. (a) ¹H NMR and (b) ¹³C NMR for **PPT-NEt₂** in $CDCl_3$.

(trimethylstannyl)thiophene (5) was degrading when exposed to the elevated reaction temperatures for extended periods of time. PPT-NEt₂(96-drop) was synthesized by slow dropwise addition of 5 (dissolved in DMF) to a solution of catalyst, DINEt₂, and DMF over the course of 24 h. The reaction was allowed to remain at 70 °C for an additional 72 h. The polymer was isolated as described previously for PPT-NEt₂(96) and exhibited a \overline{M}_n of 5300 g mol⁻¹ (GPC versus PS standards). This methodology produced a polymer with the lowest percent of halogentated end groups (wt % I = 0.98) and highest molecular weight by GPC of all trials. Slow addition of the more reactive tin compound allows for immediate coupling of the thiophene to DINEt₂, thereby limiting exposure of the stannylated thiophene compound to elevated temperatures, which would promote destannylation of the thiophene and result in a loss of stoichiometric balance between the halogen and trimethylstannyl functional groups.

The dropwise addition of bis(trimethylstannyl)thiophene (5) led to the highest degree of polymerization for the PPT-NEt₂ polymers prepared. These molecular weights are lower than those reported by Yu and coworkers for poly(*p*-phenylene-*co*-thiophene)'s (\overline{M}_n of 14 000 g mol⁻¹), which had longer alkoxy groups as side chains, thereby increasing the polymer solubility in DMF.^{12b} Onset of polymer precipitation from the reac-





tion media was observed after approximately 40 h for all PPT-NEt_2 reactions and appears to be the predominant mechanism of molecular weight limitation for our systems.

Cationic, water-soluble polymers are easily formed from the neutral PPT-NEt₂ by guaternization with bromoethane in THF as shown in Scheme 4. The quaternized polymer, PPT-NEt₃⁺, was precipitated into acetone, collected, and dried at 50 °C under vacuum. The elemental analysis results for PPT-NEt₃⁺⁽⁹⁶⁾ and PPT-NEt₃⁺(96-drop), which are the quaternized forms of PPT-NEt₂(96) and PPT-NEt₂(96-drop), respectively, are provided as Supporting Information (Table S1). Bromine elemental analysis provides one method of determining the quaternization efficiency of the reaction between the neutral polymers and bromoethane. PPT-NEt₃⁺(96-drop) would reflect a theoretical 26.24% Br by weight for complete alkylation compared to the 23.62% Br found, and PPT-NEt₃⁺(96) would reflect a theoretical 26.20% Br by weight for complete alkylation compared to the 24.18% Br found. Elemental analysis indicates quaternization of approximately 90% of the available amine sites. This is in good agreement with ¹H NMR integration determination of quaternization efficiency which was on the order of 80-90% per sample. The quaternized polymers are soluble in acidic and neutral aqueous solutions.

Thermogravimetric analysis was used to probe the thermal stability of both the PPT-NEt₂ and PPT-NEt₃⁺ polymers. Thermal dealkylation of the amine sites is the initial degradation event of the polymers as evidenced

in the TGA (see Supporting Information, Figure S1) with loss of triethylamine fragments occurring at 200 and 250 °C for PPT-NEt₃⁺ and PPT-NEt₂, respectively. Both polymers have a final degradation occurring over 400 °C, attributed to the breakdown of the conjugated backbone with little residual mass remaining at a temperature of 650 °C.

Absorption, Emission, and PL Quenching. Figure 2 shows the UV-vis absorption and photoluminescence spectra for PPT-NEt₂ in THF and PPT-NEt₃⁺ in H_2O (normalized for convenience). It is interesting to note the shift in absorption maxima between the neutral and charged polymers. PPT-NEt₂ exhibits a λ_{max} at 460 nm with a corresponding molar absorptivity of about 18 000 L mol⁻¹ cm⁻¹, while PPT-NEt₃^{+'}s λ_{max} is blue shifted 49 nm to 411 nm with a corresponding molar absorptivity of about 16 000 L mol⁻¹ cm⁻¹. The blue shift of the π to π^* transition for these polymers may be due to a solvatochromic effect as seen in substituted polythiophenes²⁰ and poly(diacetylene).²¹ Fine tuning of λ_{max} could be achieved by controlling the extent of quaternization as incomplete quaternization leads to a lower extent of hypsochromic shift.

Solution photoluminescence experiments revealed peak emission wavelengths of 519 and 494 nm for PPT-NEt₂ in THF and PPT-NEt₃⁺ in H₂O, respectively, when excited at the λ_{max} of absorption. PPT-NEt₃⁺ exhibited a fluorescence quantum efficiency of 10% in water. The spectra display the typical characteristics of conjugated polymers in solution with a Stoke's-shifted emission maximum tailing broadly to higher wavelengths. Table S2 (Supporting Information) summarizes the optical properties for both the neutral and water-soluble PPP-NEt and PPT-NEt polymers.

In a previous study, the fluorescence quenching of the poly(*p*-phenylene)-type polyelectrolyte, PPP-NEt₃⁺, by oppositely charged metal complexes $\operatorname{Ru}[(4,7-\operatorname{bis}(4-\operatorname{sulfophenyl})-1,10-\operatorname{phenanthroline}]_3^{4-}$ (Ru(phen)₃⁴⁻) and potassium ferrocyanide (Fe(CN)₆⁴⁻) via an energy-transfer mechanism was investigated.^{11b} Quenching by photoinduced electron transfer was also observed when the anionic electron acceptors, sodium anthraquinone-2,6-disulfonate (AQS) and sodium 1,4,5,8-naphthalene-diimide-*N*,*N'*-bis(methylsulfonate) (NDS), electrostatically bind to the polymer chain.

In the present investigation three anionic quenchers, $Fe(CN)_6^{4-}$, AQS, and NDS, were used to study the solution quenching behavior of PPT-NEt₃⁺. The results



Figure 2. Normalized UV–vis absorption and PL emission spectra for the PPT derivatives. (A) PPT-NEt₂ absorption (-) and emission (\square) in THF. (B) PPT-NEt₃⁺ absorption (\bigcirc) and emission (\triangle) in H₂O.



Figure 3. UV–vis absorption spectra of 10 μ M PPT-NEt₃⁺ with addition of Fe(CN)₆⁴⁻. Each curve corresponds to an Fe(CN)₆⁴⁻ concentration increment of 0.2 μ M. Arrows indicate direction of change in absorbance with addition of Fe(CN)₆⁴⁻. [Fe(CN)₆⁴⁻ concentration range 0–2 μ M].

show that the quenching efficiency is strongly dependent on ion-pair association of the cationic polymer and anionic quenchers. However, electrostatic interaction may not be the only contribution for the ground-state complexation, as hydrophobic and charge-transfer interactions between the polymer chain and quencher may also contribute to the binding. Because of the different charges and different hydrophobic character of these three quenchers, their ability to bind to the polymer is different. From the UV-vis absorption spectra of the titrations of PPT-NEt₃⁺ with $Fe(CN)_6^{4-}$ (Figure 3), it is evident that there is a decrease in intensity of the 415 nm absorption band along with formation of a redshifted band with a maximum absorbance at 452 nm. The clear isosbestic point at 430 nm suggests that complexation induces a change between two distinct chromophoric states of the PPT-NEt₃⁺ polymer chain. A possible cause for the change in absorption could be that the polyvalent ion induces aggregation of the PPT-NEt₃⁺ chains. Interactions could result in a planarization of the backbone, increasing the effective conjugation length. Similar red shifts in absorption are observed when polyvalent ions are added to solutions of poly-(phenyleneethynylene)-conjugated polyelectrolytes.^{5h} A binding constant of $3 \times 10^5 \, \mathrm{M^{-1}}$ was determined for the complex using a Scatchard plot (See Supporting Information, Figure S2) with the assumption that the absorption band at 415 nm is from the free polymer chain and the red-shifted band at 452 nm is from the PPT-NEt₃⁺/Fe(CN)₆⁴⁻ complex.

Similar phenomena, including the decrease of the polymer absorption band at 415 nm and the formation of a red-shifted band, can be seen in the UV-vis absorption spectra of mixtures of PPT-NEt₃⁺ with AQS or NDS (Figure 4). For the AQS system an isosbestic point is observed at 460 nm and the red-shifted band appears at a $\lambda_{max} = 490$ nm, whereas for the NDS system an isosbestic point at 480 nm and a red-shifted band with $\lambda_{max} = 500$ nm is seen. The λ_{max} of the red shift that occurs on addition of NDS and AQS is greater than that in the $Fe(CN)_6^{4-}/PPT-NEt_3^+$ complex. There are reasons why the absorption shift is larger for AQS and NDS addition. First, these quenchers feature large hydrophobic planar π -electron systems resulting in a face-to-face association with the polymer. This association leads to a conformational change in the polymer structure. Second, both AQS and NDS are strong



Figure 4. (a) UV–vis absorption spectra of pure AQS at 7 μ M (-···-), pure PPT-NEt₃⁺ at 10 μ M (-), and two PPT/AQS mixtures at the same PPT-NEt₃⁺ concentration of 10 μ M and two different AQS concentrations of 3.6 μ M (···) and 5.4 μ M (- -), respectively. (b) UV–vis absorption spectra of pure NDS at 20 μ M (-···), pure PPT-NEt₃⁺ at 10 μ M (-), and two PPT/NDS mixtures at the same PPT-NEt₃⁺ concentration of 10 μ M and two different NDS concentrations of 3.6 μ M (···) and 5.4 μ M (- -), respectively.

electron acceptors. Thus, it is reasonable to argue that these molecules interact with PPT-NEt₃⁺ in a donor– acceptor manner and contribute a charge-transfer component to the red-shifted absorption band.

The binding constant for AQS and PPT-NEt₃⁺ is approximately $1.0 \times 10^5 \, M^{-1}$. The difference in binding constants between Fe(CN)_6^4-/PPT-NEt_3^+ and AQS/PPT-NEt_3^+ is mostly likely due to the different charge of the anionic quenchers as the more negatively charged Fe(CN)_6^4- displays a stronger binding with the polymer. The complexation of NDS and PPT-NEt_3^+ results in partial precipitation in solution at concentrations higher than 5 μM , thereby precluding determination of a binding constant.

The fluorescence quenching of PPT-NEt₃⁺ by Fe- $(CN)_6^{4-}$, AQS, and NDS was investigated, and the Stern-Volmer (SV) quenching plots are shown in Figure 5. At very low quencher concentrations (<600 nM) the SV plots are linear and the $K_{\rm sv}$ values for all three quenchers are similar ($K_{\rm sv} = 1.2 \times 10^6 \,{\rm M}^{-1}$, $K_{\rm sv} = 0.6 \times 10^6 \,{\rm M}^{-1}$, and $K_{\rm sv} = 0.5 \times 10^6 \,{\rm M}^{-1}$ for Fe(CN)₆^{4–}, AQS, and NDS, respectively). Note that quenching is very efficient in all three cases with 25% of the polymer's fluorescence being quenched with quencher concentrations of 500 nM. This corresponds to a polymer repeat unit to quencher ratio of 20:1. The efficient quenching arises because the quenchers are associated with the polymer chains and because the fluorescent exciton is strongly delocalized and able to diffuse along the chain to the quencher unit rapidly.²² At higher quencher concentration the SV plots for $Fe(CN)_6^{4-}$ and AQS display upward curvature, whereas the plot for NDS



Figure 5. Stern–Volmer plots of 10 uM PPT-NEt₃⁺ quenching by $Fe(CN)_6^{4-}(\bullet)$, AQS (\bigcirc), and NDS(\checkmark).



Figure 6. Bilayer composition of PPT-NEt₃⁺/PAA films as a function of PAA pH at a fixed PPT-NEt₃⁺ solution pH of 5.0.

remains nearly linear. The upward curvature observed in the SV plots indicates that an additional quenching pathway becomes active. On the basis of previously reported investigations of other conjugated polyelectrolyte/quencher systems,²² we suspect that the additional mechanism involves quencher-induced aggregation of the PPT-NEt₃⁺ chains. Quenching is more efficient in the aggregates because intrachain exciton migration becomes important, allowing more efficient trapping of the excitation by the quencher sites.

Layer-by-Layer Films and PLED's. Luminescent layer-by-layer-assembled PPT-NEt₃⁺-based multilayer films were created via incorporation of the polyanion poly(styrene sulfonic acid) (PSS) and poly(acrylic acid) (PAA). Aqueous solutions were prepared in deionized Milli-Q water and filtered through 0.45 μ m cellulose acetate filters. In the case of the polyanion solutions and PPT-NEt₃⁺, the concentrations were $\sim 1 \times 10^{-2}$ M and ${\sim}5~{\times}~10^{-3}$ M, respectively (based on the repeat unit molecular weight). Solution pH was adjusted to the desired value with dilute HCl or NaOH. Polymer lightemitting diodes (PLEDS) were prepared using cleaned ITO-patterned glass obtained from DCI incorporated.^{15g} The PPT-NEt₃⁺-based multilayers were assembled on cleaned glass and silicon substrates, while film growth was monitored by profilometry, ellipsometry, and UVvis spectroscopy.

The film growth characteristics were investigated for the PPT-NEt₃⁺ aqueous solution at pH 4.0 and 5.0, PAA pH varying between 3.0 and 4.5, and PSS at pH 3.5. Linear, highly uniform, reproducible growth was achieved over the pH range studied. There was virtually no multilayer buildup when the PAA solution pH was set above 5.0 and below 2.5. Figure 6 illustrates the bilayer composition of PPT-NEt₃⁺/PAA films as a function of



Figure 7. Normalized absorbance and electroluminescence spectra of a typical PPT-NEt₃⁺/SPS multilayer PLED.

PAA pH at a fixed PPT-NEt₃⁺ solution pH of 5.0. Similar trends have been previously studied²³ and will only be briefly summarized here. As the pH of the PAA solution, which has a weak carboxylic acid functional group, is increased for a given PPT-NEt₃⁺ pH, the PAA polymer chains attain a higher degree of ionization and acquire a more extended conformation and thinner bilayers result. For the various pH conditions studied film growth was linear in the thickness ranges investigated, which were as high as 3000 Å with bilayer thicknesses ranging from 18 to 100 Å at various pH conditions. PPT-NEt₃⁺-based films were of remarkably high quality with no observable pinholes or uniformity defects.

Polymer light-emitting diodes (PLEDs) were created by first assembling the green-emitting PPT-NEt₃⁺/PSS or PPT-NEt₃⁺/PAA multilayers on ITO-patterned glass and the subsequent evaporation of 2000 Å thick Ag electrodes on top of the structure. Prior to evaporation of the metal electrode the films were dried under vacuum for 2 h at 90 °C. PLEDs were stored and tested in a drybox under a nitrogen atmosphere. PPT-NEt₃^{+/} PSS and PPT-NEt₃⁺/PAA devices in the range of 800-1100 Å thick were made at various pH conditions. PPT-NEt₃⁺/PSS devices showed superior performance to those made from PPT-NEt₃⁺/PAA. The best device performances were observed for the PPT-NEt₃⁺/PSS system at pH conditions of 5.0 and 3.5 for the PPT- NEt_3^+ and PSS, respectively. This corresponds to a bilayer thickness of ~ 15 Å (± 2 Å) and approximately 45% PPT-NEt₃⁺ in the structure. Light emission in the PPT-NEt₃⁺/PSS PLEDs was observed only under forward bias, i.e., the ITO electrode biased positive with respect to the metal electrode and devices had external quantum efficiencies as high as 0.017%.

Onset of light output for PPT-NEt₃⁺/PSS PLEDs occurred at ~11 V with a maximum light output of 110 nW (current = 30 mA/cm²) at a peak voltage of 15 V. Figure 7 shows a typical normalized absorbance spectrum of the multilayer film and electroluminescence spectrum of the PLEDs. The λ_{max} of absorption and emission is centered around 450 and 558 nm, respectively, and are red shifted as expected from the values obtained from solution photoluminescence measurements (λ_{max}^{abs} 411 nm; λ_{max}^{em} 494 nm). The emitted light was observed to be of a yellow/orange coloration.

Conclusions

A new water-soluble, substituted cationic poly(p-phenylene-co-thiophene), PPT-NEt₃⁺, was prepared via postpolymerization quaternization of alkylamine sites along the polymer backbone. The mild conditions used

for quaternization prevent polymer chain breakage and thus allow for molecular weight characterizations of the neutral polymers to be extended to the water-soluble species with the realization that additional molecular weight is added to the polymer after quaternization. This methodology offers the ability to avoid the direct molecular weight characterization of a polyelectrolyte. The conjugated, water-soluble PPT-NEt₃⁺'s absorption, emission, binding, and thin-layer-forming properties were exploited in order to create new electrostatically deposited polymer light-emitting diodes and to demonstrate the ability of PPT-NEt₃⁺ to function as an extremely sensitive sensor for known anionic quenchers. These initial discoveries provide insight into the chemical behavior of the conjugated polyelectrolye, PPT- NEt_3^+ , and will stimulate continued research into the development of water-soluble polymers for a variety of optical and sensing technologies.

Experimental Section

Materials. THF and TMEDA were purified by distillation over sodium and benzophenone. Thiophene was distilled under argon from KOH pellets. Anhydrous DMF was used as supplied by Aldrich Chemical Co. Palladium catalysts were used as received from Strem Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted. 2,5-Bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (DBrNEt₂) was synthesized as previously reported.⁹ Bisneopentylglycol-1,4-phenylene diboronate (4) was prepared by the literature procedure²⁴ for the synthesis of phenylene diboronic acid, followed by esterification with neopentyl glycol in refluxing toluene.

General Methods. NMR spectra were obtained with a Varian VXR-300 or a Varian Gemini-300. Elemental analyses were 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 a Varian Cary 5E UV-Vis-NIR spectrophotometer. Fluorescence results were obtained with a Spex F-112 photon-counting fluorimeter at room temperature. TGA was performed under N₂ with a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. The temperature was ramped from 50 to 800 °C at 10 °C/min under N2 atmosphere. GPC results were obtained with a system consisting of a Waters model 590 pump and two 300×7.5 mm Polymer Laboratories Linear Mixed Bed (Plgel 5µm mixed-C) columns in series using a Spectraflow 757 Tunable UV-Vis Detector. Polymer light-emitting diodes (PLEDS) were prepared using cleaned ITO-patterned glass obtained from DCI incorporated. The luminescent multilayer systems were assembled with a programmable Zeiss glass stainer via the alternate dipping of the substrate into the polycation and polyanion for 15 min each followed by three rinsing steps in deionized Milli-Q water for a total of 6 min. The cleaning process involved a 1 min etch in 1 M HCl, a 10 min sonification in a detergent solution, a 15 min sonification in deionized water, and a 2 min plasma etch. Voltage, current, and light output of LED devices were measured using an HP3245A universal source, an HP34401A multimeter, and a Newport 1830-C optical power meter controlled by LabView (National Instruments).

2,5-Dimethoxy-1,4-diiodobenzene (2).²⁵ Following an iodination procedure outlined by West et al.,¹⁷ a 250 mL threeneck round-bottom flask was charged with 1,4-dimethoxybenzene (1) (10.48 g, 75.85 mmol) and 100 mL of 90:7:3 HOAc/ H₂O/H₂SO₄ by volume solution. The reaction mixture was stirred under Ar until the 1,4-dimethoxybenzene dissolved completely. I₂ (23.66 g, 91.02 mmol) and KIO₄ (20.93 g, 91.02 mmol) were added, and the reaction was heated to 70 °C overnight. The reaction was cooled and poured into 500 mL of H₂O, and a crude orange solid was collected. The crude solid was recrystallized from THF/H₂O, yielding a light yellow solid (24.03 g, 81% yield). mp 168–170 °C (lit. mp²⁶ 169 °C). ¹H NMR (300 MHz, CDCl₃) 7.20 (s, 2 H), 3.83 (s, 6 H) ppm. ¹³C NMR (75.5 MHz, CDCl₃) 153.29, 121.57, 85.44, 57.17 ppm. Anal. Calcd for $C_8H_8O_2I_2$: C, 24.62; H, 2.05. Found: C, 24.31; H, 1.89. EI-LRMS calcd for $C_8H_8O_2I_2$: 389.9, found 390.

1.89. EI-LRMS calcd for $C_8H_8O_2I_2$: 389.9, found 390. **2,5-Diiodohydroquinone (3).**¹⁸ 2,5-Dimethoxy-1,4-diiodobenzene (10.00 g, 25.60 mmol) was dissolved in 50 mL of dichloromethane and cooled in a dry ice/acetone bath. Boron tribromide (26.50 g, 105.80 mmol) in 15 mL of dichloromethane was added dropwise via an addition funnel to the solution with stirring. The reaction mixture was held at -78 °C for 30 min and then allowed to warm to room temperature overnight. The reaction was added slowly to 300 mL of ice water. A white precipitate was collected and recrystallized from THF/H₂O (7.05 g, 76% yield). mp 192–193 °C. ¹H NMR (300 MHz, acetone- d_6) 8.75 (s, 2 H), 7.30 (s, 2 H) ppm. ¹³C NMR (75 MHz, acetone- d_6) 151.58, 124.93, 84.25 ppm. Anal. Calcd for $C_6H_4O_2I_2$: C, 19.90; H, 1.11. Found: C, 19.73; H, 1.08. EI-LRMS calcd for $C_6H_4O_2I_2$: 361.8, found 362.

2,5-Bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt₂). A 250 mL three-neck round-bottom flask was equipped with a reflux condenser and Ar gas inlet. 2,5-Diiodohydroquinone (6.45 g, 17.82 mmol), 2-chlorotriethylamine hydrochloride (6.75 g, 39.21 mmol), K₂CO₃ (10.33 g, 74.85 mmol), and 150 mL of acetone (dried over $MgSO_4$) were added to the reaction flask and heated to reflux. After 3 days a yellow slurry was poured into 300 mL of H₂O and a solid precipitate collected. The precipitate was dissolved in Et₂O, and the filtrate was extracted with $Et_2O~(300~mL\,\times$ 1, 150 mL \times 1, 50 mL \times 1). The Et₂O solutions were combined and washed with 1 M NaOH (300 mL \times 1, 150 mL \times 1, 50 mL \times 1), H_2O (300 mL \times 1), and brine (300 mL \times 1). The Et₂O layer was dried over MgSO₄, and the solvent was removed under reduced pressure, leaving a yellowish-white solid. The solid was recrystallized twice from MeOH/H₂O (7.49 g, 75% yield). mp 79-80 °C. 1H NMR (300 MHz, CDCl₃) 7.21 (s, 2 H), 4.00 (t, J = 6.0 Hz, 4 H), 2.91 (t, J = 6.0 Hz, 4 H), 2.66 (q, J = 7.2)Hz, 8 H), 1.08 (t, J=7.2 Hz, 12 H) ppm. $^{13}\mathrm{C}$ NMR (75 MHz, CDCl₃) 152.84, 122.82, 86.02, 69.20, 51.49, 47.92, 12.09 ppm. Anal. Calcd for C₁₈H₃₁N₂O₂I₂: C, 38.59; H, 5.40; N, 5.00; I, 45.30. Found: C, 38.81; H, 5.53; N, 4.90; I, 45.10. FAB-HRMS $(M + H)^+$ calcd for $C_{18}H_{31}N_2O_2I_2$: 561.0475, found 561.0492.

2,5-Bis(trimethylstannyl)thiophene (5).¹⁹ The general preparation of this compound followed literature procedures, followed by a more rigorous purification needed for polymerization-quality monomer. The crude recovered product was distilled under vacuum (90 °C at 5×10^{-3} mmHg) and then recrystallized twice from pentane to yield a white crystalline solid. Yields for the reaction were slightly less than those reported in the literature due to the multiple purification steps employed (4.48 g, 69% yield). mp 100–102 °C (lit. mp¹⁹ 100–101.6 °C). ¹H NMR (300 MHz, CDCl₃) 7.40 (s, 2 H), 0.38 (s, 18 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 143.00, 135.80, -8.15 ppm. Anal. Calcd for C₁₀H₂₀SSn₂: C, 29.32; H, 4.92. Found: C, 29.65; H, 4.60. FAB–HRMS (M + H)⁺ calcd for C₁₀H₂₁SSn₂: 411.9330, found 411.9494.

Poly({2,5-bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4phenylene}-alt-1,4-phenylene). General Procedure. A 20 mL Schlenk flask with stir bar was charged with DINEt₂, bisneopentylglycol-1,4-phenylene diboronate (4), and NaHCO₃. The flask was evacuated and backfilled with Ar three times. A solvent system consisting of 25 mL of DMF and 5 mL of H_2O sparged with Ar for 30 min was transferred to the reaction flask via syringe, and the mixture was heated to 50 °C to dissolve all monomers. Pd(OAc)2 was added, and the temperature was raised to 70 °C for a variable number of hours. The reaction mixture was precipitated into 200 mL of MeOH and recovered as a tan solid. The polymer sample was redissolved in a minimal amount of hot CHCl₃ and precipitated into 200 mL of MeOH. The tan material was dried in vacuo at 60 °C overnight. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 150.41, 136.98, 130.53, 129.10, 116.32, 68.32, 51.98, 47.82, 12.03 ppm.

PPP-NEt₂(1-3). Reagents: $DINEt_2$ (1.0189 g, 1.819 mmol), bisneopentylglycol-1,4-phenylene diboronate (4) (0.5492 g,

1.819 mmol), NaHCO₃ (1.53 g, 18.21 mmol), and Pd(OAc)₂ (6.73 mg, 0.03 mmol). A 0.50 g amount of polymer was recovered (72% yield). Anal. Calcd for C₂₄H₃₄N₂O₂I_{0.045}: C, 74.24; H, 8.42; N, 7.22; I, 1.47. Found: C, 67.32; H, 8.42; N, 6.01; I, 1.48. GPC (CHCl₃ vs PS) $\bar{M}_n = 10\,900$ g mol⁻¹, $MP = 13\,300$ g mol⁻¹, $\bar{M}_w/\bar{M}_n = 1.52$.

PPP-NEt₂(**1**-24). Reagents: DINEt₂ (0.9589 g, 1.712 mmol), bisneopentylglycol-1,4-phenylene diboronate (4) (0.5169 g, 1.712 mmol), NaHCO₃ (1.44 g, 17.12 mmol). and Pd(OAc)₂ (6.73 mg, 0.03 mmol). A 0.52 g amount of polymer was recovered (80% yield). Anal. Calcd for C₂₄H₃₄N₂O₂I_{0.023}: C, 74.82; H, 8.83; N, 7.27; I, 0.76. Found: C, 71.85; H, 8.45; N, 6.78; I, 0.77. GPC (CHCl₃ vs PS) $\bar{M}_n = 15\,300$ g mol⁻¹, $MP = 19\,500$ g mol⁻¹, $\bar{M}_w/\bar{M}_n = 1.80$.

Poly({2,5-bis[2-(N,N-diethylamino)-1-oxapropyl]-1,4phenylene}-alt-2,5-thienylene) (PPT-NEt₂). Procedure for Synthesis (all reactants added at beginning of reaction). A 20 mL Schlenk flask with a stir bar was charged with DINEt₂ and 2,5-bis(trimethylstannyl)thiophene (5). The flask was evacuated and backfilled with Ar three times. A 20 mL amount of anhydrous DMF, previously sparged with Ar for 30 min, was added to the reaction flask via syringe. The reaction mixture was stirred and heated to 50 °C, allowing all monomers to dissolve. PdCl₂(PPh₃)₂ was added in one portion, and the reaction was heated at 70 °C for a variable number of hours. The DMF solution was concentrated to ~ 5 mL and precipitated into 150 mL of MeOH. A dark red solid was collected on a medium porosity glass frit, subsequently extracted with MeOH for 24 h and acetone for 24 h, and then collected by extraction with chloroform (via Soxhlet extraction). The chloroform-soluble fraction was collected by evaporation of the solvent and dried in vacuo at 50 °C overnight. ¹H NMR (300 MHz, CDCl₃) 7.63 (bm, 2 H), 7.34 (bm, 2 H), 4.24 (bm, 4 H), 3.04 (bm, 4 H), 2.69 (bm, 8 H), 1.11 (bm, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 149.53, 139.09, 126.49, 123.26, 113.26, 68.36, 52.09, 42.88, 12.01 ppm. UV-vis (THF) $\lambda_{max} = 460 \text{ nm}$, log ϵ_{max} = 4.26. PL (THF with 460 nm excitation) λ_{max} = 519 nm.

PPT-NEt₂(48). Reaction time of 48 h. Reagents: DINEt₂ (1.0895 g, 1.945 mmol), 2,5-bis(trimethylstannyl)thiophene (**5**) (0.7967 g, 1.945 mmol), and 32 mg of PdCl₂(PPh₃)₂ (0.03 mmol). A 0.45 g amount of polymer was recovered (60% yield). Anal. Calcd for C₂₂H₃₂N₂O₂SI_{0.079}: C, 66.33; H, 8.04; N, 7.03; I, 2.52. Found: C, 65.23; H, 7.84; N, 6.65; I, 2.50. GPC (THF vs PS) $\bar{M}_n = 3200 \text{ g mol}^{-1}$, $MP = 4300 \text{ g mol}^{-1}$, $\bar{M}_w = 5200 \text{ g mol}^{-1}$, $\bar{M}_w = 1.70$.

PPT-NEt₂(96). Reaction time of 96 h. Reagents: DINEt₂ (1.2568 g, 2.243 mmol), 2,5-bis(trimethylstannyl)thiophene (**5**) (0.9191 g, 2.243 mmol), and 37 mg of PdCl₂(PPh₃)₂ (0.04 mmol). A 0.79 g amount of polymer was recovered (80% yield). Anal. Calcd for C₂₂H₃₂N₂O₂SI_{0.037}: C, 67.13; H, 8.14; N, 7.12; I, 1.19. Found: C, 63.64; H, 8.03; N, 6.46; I, 1.20. GPC (THF vs PS) $\bar{M}_n = 4100 \text{ g mol}^{-1}$, $MP = 5800 \text{ g mol}^{-1}$, $\bar{M}_w = 6900 \text{ g mol}^{-1}$, $\bar{M}_w / \bar{M}_n = 1.68$.

PPT-NEt₂(240). Reaction time of 240 h. Reagents: DINEt₂ (1.4298 g, 2.552 mmol), 2,5-bis(trimethylstannyl)thiophene (**5**) (1.0456 g, 2.552 mmol), and 35 mg of PdCl₂(PPh₃)₂ (0.05 mmol). A 0.81 g amount of polymer was recovered (82% yield). Anal. Calcd for C₂₂H₃₂N₂O₂SI_{0.037}: C, 67.13; H, 8.14; N, 7.12; I, 1.19. Found: C, 63.99; H, 7.99; N, 6.51; I, 1.22. GPC (THF vs PS) $\bar{M}_n = 4200$ g mol⁻¹, MP = 5400 g mol⁻¹, $\bar{M}_w = 7200$ g mol⁻¹, $\bar{M}_w / \bar{M}_n = 1.71$.

Procedure for Dropwise Synthesis. PPT-NEt₂(96drop). A 20 mL Schlenk flask with stir bar was charged with DINEt₂ (1.01 g, 1.80 mmol), 25 mg of PdCl₂(PPh₃)₂ (0.04 mmol), and 20 mL of anhydrous DMF, previously sparged with Ar for 30 min. The solution was warmed to 70 °C. 2,5-Bis(trimethylstannyl)thiophene (5) (0.74 g, 1.80 mmol) was dissolved in 15 mL of DMF and added to a 20 mL addition funnel attached to the Schlenk flask. Compound **5** was added dropwise over the course of 24 h. The reaction mixture was held at 70 °C for 96 h. The DMF solution was concentrated to ~ 5 mL and precipitated into 150 mL of MeOH. A dark red solid was collected on a medium porosity glass frit, subsequently extracted with MeOH for 24 h and acetone for 24 h, and then collected by extraction with chloroform (via Soxhlet extraction). The chloroform-soluble fraction was collected by evaporation of the solvent and dried in vacuo at 50 °C overnight. A 0.59 g amount of polymer was recovered (84% yield). ¹H NMR (300 MHz, CDCl₃) 7.63 (bm, 2 H), 7.34 (bm, 2 H), 4.24 (bm, 4 H), 3.04 (bm, 4 H), 2.69 (bm, 8 H), 1.11 (bm, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 149.53, 139.09, 126.49, 123.26, 68.36, 52.09, 42.88, 12.01 ppm. Anal. Calcd for C₂₂H₃₂N₂O₂SI_{0.030}: C, 67.38; H, 8.17; N, 7.15; I, 0.97. Found: C, 63.99; H, 8.02; N, 6.51; I, 0.98. GPC (THF vs PS) $\bar{M}_n = 5300 \text{ g mol}^{-1}$, $\bar{M}_P = 6900 \text{ g mol}^{-1}$, $\bar{M}_w = 9000 \text{ g mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.70$.

General Quaternization Procedure. Neutral alkoxyamine-containing polymers were stirred at room temperature with an excess of bromoethane in a minimal amount of THF under Ar with stirring. The partially quaternized amine polymers began to precipitate out of solution between 3 and 5 days at room temperature. The quaternized polymer solution was precipitated into acetone, collected on a glass frit, washed thoroughly with acetone, and dried in vacuo at 50 °C overnight.

Poly{2,5-bis[2-(*N*,*N*,*N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-2,5-thienylene} Dibromide (PPT-NEt₃⁺). ¹H NMR (300 MHz, D₂O) 7.22 (bm, 2 H), 6.90 (bm, 2 H), 3.96 (bm, 4 H), 3.12 (bm, 4 H), 2.70 (bm, 8 H), 0.55 (bm, 16.2 H) ppm. UV-vis (H₂O) $\lambda_{max} = 411$ nm, log $\epsilon_{max} = 4.20$. PL (H₂O with 411 nm excitation) $\lambda_{max} = 494$ nm.

 $PPT\text{-}NEt_8^+(96)\text{.}$ Anal. Calcd for $C_{22}H_{32}N_2O_2SI_{0.037}\text{-}2.0$ $C_2H_5\text{-}Br:\ C,\ 51.09;\ H,\ 6.88;\ N,\ 4.58;\ Br,\ 26.20.$ Found: C, 49.87; H, 6.48; N, 3.18; Br, 24.18.

 $PPT\text{-}NEt_8^+(\textbf{96-drop})\text{.}$ Anal. Calcd for $C_{22}H_{32}N_2O_2SI_{0.030}\text{-}2.0$ $C_2H_5Br:\ C,\ 51.16;\ H,\ 6.89;\ N,\ 4.59;\ Br,\ 26.24.$ Found: C, 49.73; H, 6.52; N, 3.29; Br,\ 23.62.

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Supporting Information Available: Elemental analysis results for the diamino PPP and PPT monomer and polymers (Table S1), Optical properties of PPP and PPT polymers in solution (Table S2), TGA thermogram of PPT-NEt₂ and PPT-NEt₃⁺ under N₂ at a heating rate of 10 °C/min (Figure S1), and Scatchard Analysis: Binding of Fe(CN)₆⁴⁻ to PPT-NEt₃⁺ (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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