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Preparation of Poly(silylene-*p*-phenylene)s Bearing a Benzo Crown Pendant Group and Their Iono- and Solvatochromic Behavior in the Emission Spectra

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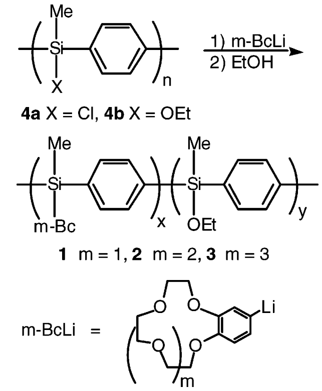
Poly(silylene-*p*-phenylene)s bearing a benzo crown pendant group were obtained as colorless solids in moderate yield by the reactions of poly[chloromethyl- or ethoxymethylsilylene-*p*-phenylene] with lithiated benzo crown ethers in THF. The benzo crown substituted polymers responded to selected alkali-metal or alkaline-earth-metal ions in the emission spectra, depending on the crown ether ring size. Thus, when appropriate metal ions were added to the polymer solutions, the intensity of a maximum broad emission band around 400 nm decreased and a band at about 320 nm was markedly enhanced. Similar chromism of the polymers was also observed, depending on the solvent polarity in the absence of metal ions.

Introduction

Several approaches have been made to develop π-conjugated polymers that respond to metal ions for use as ion-sensing materials, since ionochromic optical properties were initially observed for poly(thiophene)s featuring ether side chains.[1] Recent examples involve π-conjugated polymers with carboxylic acid units,[2] hydroxy groups,[3] and ether chains[4] as the ion-capturing side groups. Polymers bearing π-conjugated chromophores bridged by a coordinating bipyridyl unit[5] and ether linkage[6] also were synthesized. These polymers undergo stacking of the chromophores and/or conformational changes reversibly upon interaction with metal ions, which results in their ionochromic behaviors. Silicon-based ion-sensing polymeric systems have also been studied by West and co-workers.[7] They found that an ether-substituted polysilane responds to Li^+, with respect to both the absorption and emission spectra.

On the other hand, there has been recent interest in polymers whose backbone is composed of an alternating arrangement of an organosilanylene group and a π-conjugated organic unit, because they may be used as functional materials, such as, for example, organic semiconductors, hole-transport materials, photoconductors, and heat-resistant materials.[8] In the hope of developing novel ion-sensing materials based on the Si−π alternating system, we recently synthesized silylene-2,5-thienylene alternating oligomers having an ether side chain.[9] Although these oligomers exhibit unique solvatochromic behaviors in the emission spectra, they do not respond to metal ions. Here, we report the synthesis and iono- and solvatochromic behaviors of poly(silylene-*p*-phenylene)s having a benzo crown ether group as the pendant group, which is anticipated to interact with metal ions more tightly than linear ether side chains. In these polymers, electron-donating silyl substitution on the benzo crown unit would even facilitate the coordination to the metal ions.[10] As expected, the polymers exhibited clear ionochromism in the emission spectra toward selected alkali-metal and alkaline-earth-metal ions, depending on the ring size of the crown ether. Solvatochromic behavior of the polymers also is described.

Scheme 1



Results and Discussion

Polymer Synthesis. Poly(silylene-*p*-phenylene)s bearing a benzo crown pendant group (**1**−**3**) were readily accessible by substitution reactions of chlorosilylene− and ethoxysilylene−phenylene polymers,[11] as shown in Scheme 1. Thus, reactions of poly(chloromethylsilylene-*p*-phenylene) (**4a**; $M_w = 11\,000$,

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Table 1. Preparation of Polymers 1−3

polymer	amt of m-BcLi/equiv	x/y[a]	yield/ %[b]	mp/°C	UV λ_{max}/ nm[c]
1	1.6	79/21	51	>300	285
2a	1.3	74/26	85	110−114	280
2b	1.1	49/51	45	109−113	279
2c	0.4	25/75	45	108−113	278
3	1.5	89/11	38	135−141	281

[a] Determined by the ^{1}H NMR spectrum. [b] After reprecipitation from methanol/chloroform, based on the starting polymer used. [c] In 1/1 THF/acetonitrile.

$M_n = 5800$)[12] with lithiated benzo crown ethers (1-BcLi and 3-BcLi) in THF at −90 °C, followed by treatment of the resulting mixtures with ethanol in large excess, gave polymers **1** and **3**, having benzo-12-crown-4 and benzo-18-crown-6 units, respectively. However, similar reactions of **4a** with 2-BcLi gave colorless solids that were insoluble in organic solvents. Changing the reaction conditions and the ratio of the reactants did not affect the results. Finally, soluble polymer **2a** with a benzo-15-crown-5 pendant group was obtained by a reaction of poly(ethoxymethylsilylene-*p*-phenylene) (**4b**; $M_w = 19\,000$, $M_n = 10\,500$) with 2-BcLi. Table 1 summarizes yields and some properties of the polymers, after purification by reprecipitation from methanol/chloroform. The ratios of the introduction of benzo crown units into the polymers were determined to be x/y = ca. 7/3 to 9/1 on the basis of the ^{1}H NMR spectra (see the Supporting Information). Controlled introduction of the benzo crown unit was also possible, and less substituted polymers **2b** ($x/y = 49/51$) and **2c** ($x/y = 25/75$) were obtained from the reactions of **4b** with smaller amounts of 2-BcLi (Table 1).

The molecular weight of polymer **1** was determined to be $M_w = 3500$ and $M_n = 3200$ (degree of polymerization ca. 10) by gel permeation chromatography (GPC) with THF as eluent, relative to polystyrene standards. These values were smaller than those expected from the molecular weight of the starting material **4a**, indicating that cleavage of the polymer backbone was involved to an extent in the reaction of **4a** with 1-BcLi. Polymers **2** and **3** underwent decomposition when subjected to GPC, giving unresolved, very broad peaks, even when the chromatography was carried out using dry solvent, in contrast to the GPC of **1**, which revealed a clear monomodal profile. Changing the solvent from THF to chloroform did not affect the results. We therefore could not determine the molecular weights of **2** and **3** by GPC analysis. However, the fact that no clear signals assignable to possible end groups, such as SiH, SiOH, SiMe$(OEt)_2$, and terminal Ph−Si, were observed in the NMR and IR spectra seems to indicate that polymers **2** and **3** must have moderately high molecular weights, similar to polymer **1**. Polymers **2** and **3** melted without decomposition, as shown in Table 1, while **1** did not melt up to 300 °C. Polymers **1−3** are colorless solids and are soluble in a wide variety of organic solvents, such as THF, ether, aromatic compounds, and chlorocarbons, but barely soluble in saturated hydrocarbons and alcohols alone. They are rather stable and can be handled in air without special care. Even when the polymers were purified by reprecipitation from methanol/chloroform, no ethoxy−methoxy exchange occurred. However, storing the polymers in air for several months led to the formation of insoluble substances, probably due to hydrolysis of ethoxy−Si bonds producing cross-linking siloxane units. Integration of ethoxy methyl protons in the ^{1}H NMR spectra of the freshly prepared polymers was slightly smaller than expected, suggesting that hydrolysis of ethoxy−Si bonds to form siloxane units had already occurred to an extent during the workup process.

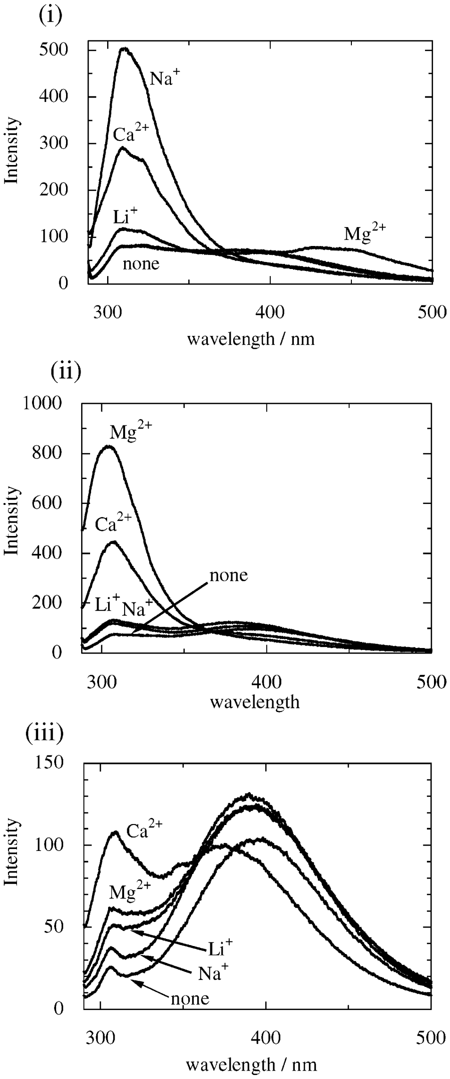

Figure 1. Emission spectra of polymers (i) **1**, (ii) **2a**, and (iii) **3** ([polymer unit] = 2 × 10^{-5} M in 1/1 THF/acetonitrile) in the presence or absence of a large excess of metal ions (0.2 M).

Chromic Behaviors of Polymers 1−3. UV spectra of polymers **1−3** showed an absorption band at λ_{max} ca. 280 nm in THF/acetonitrile (1/1), independent of the benzo crown ring size (Table 1), which was slightly red-shifted from those of benzo crown ethers (λ_{max} ca. 260 nm). The emission spectra of the polymers in THF/acetonitrile showed a broad band around 400 nm, together with a small peak or a shoulder at 310−320 nm. When appropriate metal ions were added to the solutions, distinct changes were observed in the emission spectra. Figure 1 depicts the spectral changes on addition of some metal perchlorates to the polymer solutions in large excess. As can be seen in Figure 1i, polymer **1** responded to Na^+ most

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(12) Although the Si−Cl bond is moisture sensitive and poly(chloromethylsilylene-*p*-phenylene) must be handled under an inert atmosphere, its molecular weight is readily determined by GPC. In fact, it was found that treatment of the Si−Cl-containing polymer with organolithium reagents gave the substituted polymers with molecular weights close to those calculated from that of the starting poly(chloromethylsilylene-*p*-phenylene).[11a]

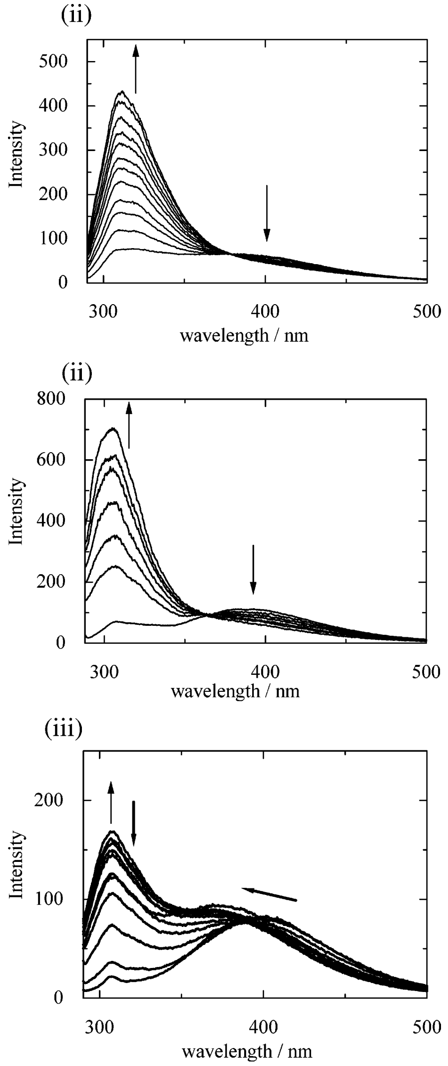

Figure 2. Emission spectral changes of polymers (i) **1**, (ii) **2a**, and (iii) **3** ([polymer unit] = 2 × 10^{-5} M in 1/1 THF/acetonitrile) in the presence or absence of metal perchlorates. [sodium or magnesium perchlorate]/[polymer unit] = 0, 100, 200, 500, 1000, 2000, 5000 for (i) and (ii). [calcium perchlorate]/[polymer unit] = 0, 1, 2, 5, 10, 20, 50, 500, 1000, 5000 for (iii).

sensitively among the metal ions examined, and the peak at 310 nm was markedly enhanced and the original broad band around 400 nm nearly disappeared. Similar spectral changes of **1** also were observed in response to Ca^{2+} and Li^{+}, but to a much lesser degree. The sensitivity decreased in the order $Na^{+} > Ca^{2+} \gg Li^{+}$. Addition of K^{+} and Al^{3+} affected the emission profile of **1** only slightly. Interaction of **1** with Mg^{2+} occurred in a different manner, giving rise to new broad bands at about 420 and 450 nm.

Polymer **2a** responded to Mg^{2+} most sensitively, and the sensitivity was reduced in the order $Mg^{2+} > Ca^{2+} \gg Li^{+} > Na^{+}$. No significant changes were observed when K^{+} and Al^{3+} were added to the solution of **2a**. Polymer **3** exhibited clear spectral changes only with Ca^{2+}. These ionochromic processes were reversible, and the polymers could be recovered by adding chloroform to their solutions followed by washing with water several times. The spectra of **1** underwent continuous changes through an isosbestic point upon titration with $NaClO_4$, indicating the usefulness of this polymer for Na^{+} sensing (Figure 2i). Similar simple and smooth changes in the emission spectra were observed for titration of polymer **2a** with Mg^{2+} (Figure 2ii). On the other hand, emission spectra of polymer **3** underwent ionochromic changes with Ca^{2+} in two steps. Thus, the signal in the high-energy region was enhanced in the first step to reach a maximum intensity ($[Ca(ClO_4)_2]$/[polymer unit] ≤ 20), which was then weakened on further addition of Ca^{2+} (Figure 2iii).

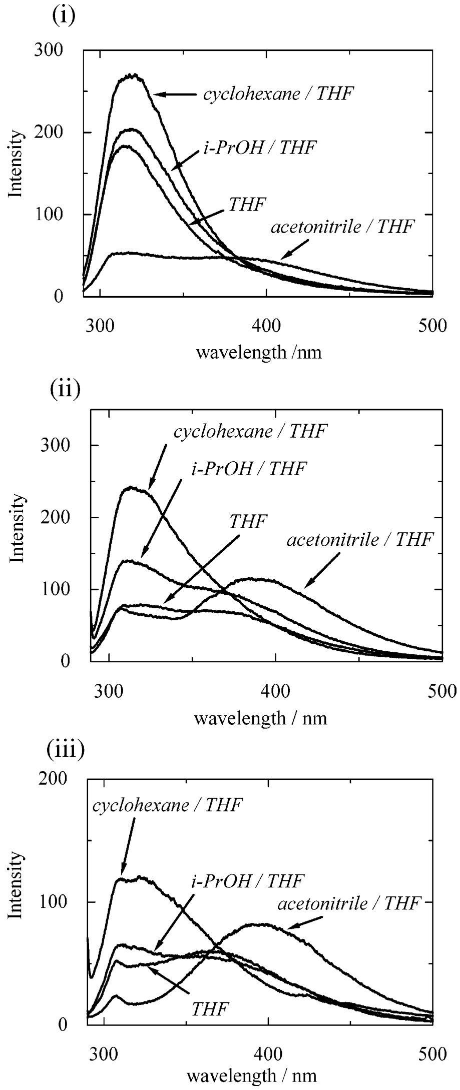

Figure 3. Solvent dependence of emission spectra of polymers (i) **1**, (ii) **2a**, and (iii) **3**.

Polymers **1**−**3** showed clear solvatochromism in the emission spectra. As shown in Figure 3, decreasing the solvent polarity[13] resulted in enhancement of the band at about 320 nm and a decrease of the intensity of the broad band around 400 nm, similar to their ionochromism.

In contrast to the emission spectra, no significant changes occurred in the UV absorption spectra of **1**−**3** on adding metal perchlorates (metal = Li, Na, K, Mg, Ca, Al) to the polymer solutions and also on changing the solvent polarity. Only a slight blue shift was always observed, at most by 4 nm when $LiClO_4$ was added to a solution of **1** in large excess. Polymer **4b**, which has no benzo crown side group, exhibited neither iono- nor solvatochromic behavior in the UV (λ_{max} 238 nm) and emission spectra (λ_{max} 320 nm). In addition, benzo crown ethers exhibited a far different type of ionochromism, including enhancement and slight blue shifts of the emission bands around 300 nm on contact with metal ions. For example, interaction with $MgClO_4$

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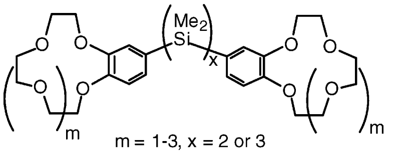
[13] The dielectric constants (ϵ) 36.64 for acetonitrile, 20.18 for 2-propanol, 7.52 for THF, and 2.02 for cyclohexane are given in: *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: New York, 1995.

Chart 1



led to a ca. 10 nm blue shift and an approximate 2 times enhancement of the emission band of benzo-15-crown-5 in THF/acetonitrile. These results indicate that the chromic behavior of polymers **1**−**3** is a function of their benzo crown substituted polymeric structures. Presumably, stacking of chromophores, the benzo crown and silylenephenylene units, leads to red-shifted broad emission bands of the polymers in the absence of metal ions in polar solvents through the intramolecular formation of excimers and/or exciplexes. Adding metal ions and decreasing the solvent polarity would cause the deformation of the stacking of the chromophores, leading to the enhancement of the bands at higher energies. Similar preferential stacking of chromophores in polar solvents has been reported previously for poly(silylenethienylene)s bearing ether side chains.[9]

Recently, we found that disilanylene- and trisilanylene-bridged benzo crown derivatives shown in Chart 1 exhibited ionochromic behaviors responding to alkali and alkaline-earth-metals.[10] However, in contrast to the present polymers, the silanylene-bridged benzo crown derivatives showed the emission maximum at about 320 nm in the absence of metal ions; addition of metal ions to the solutions led to a decrease of the emission intensity of the original band, together with enhancement of a new broad band centered at 400 nm. To understand the ionochromism of the silanylene-bridged benzo crown derivatives, we assume that the benzo crown units coordinate with the metal ion in a chelate fashion to form $\pi-\pi$ stacking that would be responsible for the appearance of the new band at the low-energy region. In the present polymers, the neighboring benzo crown units, which are linked by the silylenephenylene unit, may be too distant to form $\pi-\pi$ stacking. In fact, polymers **2b**,**c** showed ionochromic behavior similar to that of **2a**, indicating that the degree of introduction of benzo crown unit did not affect the ionochromism in the range of $x/y = 25/75$ to 74/26. Presumably, $\pi-\pi$ stacking between neighboring benzo crown chromophores did not take place, but stacking occurred between any other chromophores in the polymer rod, making the chromic properties different from those of the silanylene-bridged benzo crown derivatives.

Conclusions

We prepared and characterized a series of benzo crown substituted poly(methylsilylene-*p*-phenylene)s that were able to respond selectively to alkali-metal and alkaline-earth-metal ions and also to the solvent polarity. The ring size of the ether unit exerted a crucial influence on the selectivity toward the ions. The polymers emitted visible luminance in the absence of ions in polar solvents when irradiated with a low-pressure mercury lamp (254 nm), which disappeared on adding the ions or on replacement of the solvent with less polar ones. It is noteworthy that the present polymers underwent deformation of stacking of the chromophores when they interacted with metal ions, as evidenced by suppression of the emission band in the lower energy region. In contrast, the interaction of poly(ethynylene-*p*-phenylene)[4f] and poly(ethenylene-*p*-phenylene)[4g] which have crown ether units with metal ions causes stacking of the chromophores.

Experimental Section

Materials. THF used as the reaction solvent was dried over sodium−potassium alloy and distilled just before use. Poly(chloromethylsilylene-*p*-phenylene) was prepared by stirring poly(ethoxymethylsilylene-*p*-phenylene) in an excess of acetyl chloride at room temperature for more than 20 h, followed by removal of the excess acetyl chloride and the resulting ethyl acetate under reduced pressure.[11a,12] The chlorosilylene polymer thus obtained was subjected to the following reactions without purification. 3,4-(1-Bromobenzo)-crown ethers were prepared as reported in the literature.[14]

Preparation of Polymers 1−3. In a 30 mL two-necked flask was placed 0.40 g (1.32 mmol) of 3,4-(1-bromobenzo)-12-crown-4 and 5.0 mL of THF, and the flask was cooled to −90 °C. To this mixture was added dropwise 0.84 mL (1.32 mmol) of a 1.57 M butyllithium−hexane solution, and the resulting mixture was stirred at this temperature for 10 min. A solution of poly(chloromethylsilylene-*p*-phenylene), prepared from 0.14 g of poly(ethoxymethylsilylene-*p*-phenylene), in 10 mL of THF was added slowly to the mixture, and it was then warmed to room temperature. After 5 mL of ethanol was added to the mixture, the solvent was evaporated and the resulting residue was reprecipitated from methanol−chloroform to give 0.13 g (51% yield based on the ethoxysilylene polymer) of polymer **1**.

^{1}H NMR spectra of polymers **1**−**3** contain overlapped signals ascribed to the ethoxy and benzo crown group substituted units, the former of which appeared at the same positions as those of polymer **4b** reported previously,[11a] and are not included in the following data. Signals attributed to the ethoxysilylene unit could not be observed in the ^{13}C and ^{29}Si NMR spectra of **1**−**3**, presumably due to the low intensities. Data for **1**: ^{1}H NMR (δ in $CDCl_3$) 0.75 (s, 3H, MeSi), 3.76 (br s, 6H, $C_6H_3OCH_2\mathit{CH_2}O\mathit{C_2}H_4$), 3.84 (br s, 2H, $C_6H_3OCH_2\mathit{CH_2}$), 4.09 (br s, 2H, $C_6H_3O\mathit{CH_2}$), 4.14 (br s, 2H, $C_6H_3O\mathit{CH_2}$), 6.91 (d, 1H, $J = 7.9$ Hz, H on C6), 7.07 (d, 1H, $J = 7.9$ Hz, H on C5), 7.09 (s, 1H, H on C3), 7.45 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.34 (MeSi), 69.90, 71.02, 71.38, 72.54 (2C) (crown ether), 116.84, 125.45, 128.97, 130.58, 149.97, 152.11 (benzocrown sp^2 carbons), 133.19, 134.48 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −11.53. Anal. Calcd for $((C_{19}H_{22}O_4Si)_{0.79}\ (C_9H_{12}OSi)_{0.21})_n$: C, 66.54; H, 6.58. Found: C, 64.32; H, 6.53. Data for **2a**−**c**: ^{1}H NMR (δ in $CDCl_3$) 0.76 (s, 3H, SiMe), 3.76 (br s, 8H, $O\mathit{CH_2}CH_2O$), 3.86 (br s, 4H, $C_6H_3OCH_2\mathit{CH_2}$), 4.04 (br s, 2H, $C_6H_3O\mathit{CH_2}$), 4.11 (br s, 2H, $C_6H_3O\mathit{CH_2}$), 6.84 (d, 1H, $J = 7.6$ Hz, H on C6), 6.98 (s, 1H, H on C3), 7.02 (d, 1H, $J = 7.6$ Hz, H on C5), 7.46−7.58 (m, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.30 (SiMe), 68.70, 69.38, 69.60, 69.69, 70.55, 70.68, 71.14 (2C) (crown ether), 113.50, 120.92, 128.32, 129.36, 148.70, 150.60 (benzocrown sp^2 carbons), 133.26, 133.57 (phenylene); ^{29}Si NMR (δ in $CDCl_3$): δ −11.30. Anal. Calcd for **2a** $((C_{21}H_{26}O_5Si)_{0.74}(C_9H_{12}OSi)_{0.26})_n$: C, 65.32; H, 6.86. Found: C, 63.54; H, 6.81. Calcd for **2b** $((C_{21}H_{26}O_5Si)_{0.49}(C_9H_{12}OSi)_{0.51})_n$: C, 65.42; H, 6.96. Found: C, 63.33; H, 6.96. Calcd for **2c** $((C_{21}H_{26}O_5Si)_{0.25}(C_9H_{12}OSi)_{0.75})_n$: C, 65.56; H, 7.11. Found: C, 62.38; H, 7.06. Data for **3**: ^{1}H NMR (δ in $CDCl_3$) 0.75 (s, 3H, SiMe), 3.65 (br s, 4H, $C_6H_3OC_2H_4OC_2H_4O\mathit{C_2}H_4$), 3.69 (br s, 4H, $C_6H_3OC_2H_4OCH_2\mathit{CH_2}$), 3.72 (br s, 4H, $C_6H_3OC_2H_4O\mathit{CH_2}$), 3.84 (br s, 2H, $C_6H_3OCH_2\mathit{CH_2}$), 3.90 (br s, 2H, $C_6H_3OCH_2\mathit{CH_2}$), 4.06 (br s, 2H, $C_6H_3O\mathit{CH_2}CH_2O$), 4.13 (br s, 2H, $C_6H_3O\mathit{CH_2}CH_2O$), 6.84 (d, 1H, $J = 7.6$ Hz, H on C6), 6.99 (s, 1H, H on C3), 7.01 (d, 1H, $J = 7.6$ Hz, H on C5), 7.45 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.26 (SiMe), 68.63, 69.24, 69.53, 69.65, 70.67, 70.75 (2C) (crown ether), 113.31, 120.81, 127.47, 129.35, 148.36, 150.30 (benzocrown sp^2 carbons), 133.21, 134.43 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −11.37. Anal. Calcd for **3** $((C_{23}H_{30}O_6Si)_{0.89}(C_9H_{12}OSi)_{0.11})_n$: C, 64.23; H, 7.04. Found: C, 62.79; H, 7.00. The combustion elemental

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analysis of the polymers always determined the carbon contents to be lower than the theoretical values. This is probably due to both the contamination of siloxane units in the polymers and the formation of carbon-containing inorganic substances during the analysis. Indeed, EDS analysis of the ash obtained by heating polymer **2a** at 1000 °C in air indicated a content of carbon of about 6 atom % (see the Supporting Information).

Measurements of Emission Spectra. Emission spectra were obtained for polymer solutions with [polymer unit] $= 2 \times 10^{-5}$ M in 1/1 THF/acetonitrile in the presence or absence of metal perchlorates at room temperature. Photoexcitation was carried out at the absorption λ_{max} of the polymers. For titration experiments, the perchlorates were added as acetonitrile solutions.

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Supporting Information Available: Figures giving ^{1}H NMR spectra of polymers **1**, **2a**, and **3** in $CDCl_3$ and EDS data for the ash obtained by combustion of polymer **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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