Chem. Mater. **2001,** *13,* 4635−4641

Synthesis and Properties of Polyimide with Diazacrown Ether Moiety and the Corresponding Polymer Barium Complexes

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Received April 23, 2001. Revised Manuscript Received August 14, 2001

A series of polyimides with diaza-18-crown-6 moieties on the main chain were synthesized by the reaction between 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and different macrocyclic diamine monomers. The polyimide barium complexes were also synthesized from the corresponding monomeric barium complexes. An X-ray crystal structure of one of the monomers was also determined. Good quality, free-standing polymer films were obtained by thermal imidization of the poly(amic acid) presursors. No decomposition of the barium complexes was found during the thermal imidization processes. The polyimides and their barium complexes exhibit different electronic absorption properties, which is attributed to the formation of charge-transfer excited states. The binding of barium ion to the polymer main chain may affect the energy level of the resulting charge transfer states. In addition, the emission properties of the polyimides with and without barium ion are also different. Changes in the emission spectrum were observed when the metal-free polyimide film was immersed in barium solution. These materials may serve as potential candidates as sensors for barium or other alkaline earth metals.

Introduction

Polyimides are a class of polymers that have been used extensively in microelectronics and in a variety of advanced technologies. The studies of these materials have mainly focused on the electronics, coating, composites, gas separation, and fiber applications.[1] Most of the polyimides reported to date were based on pure organic systems. Recently, research in studying the interaction of polyimides with metals, particularly the adhesion of polyimides to various metal substrates, has drawn significant attention due to their potential applications as interlayer dielectric materials in microelectronic industry.[2] On the other hand, relatively little attention was paid to polyimides functionalized with metal complexes. There are several examples of doping metal salts or metal complexes into polyimide matrixes. By doping gold or silver compounds to poly(amic acid) precursor followed by thermal treatment, optically reflective/electrical conductive polyimide thin films were obtained.[3] Other polyimides doped with zirconium,[4] rare earth metals,[5] iron, palladium, aluminum, and copper complexes[6] have also been reported. The metal complexes are able to modify the physical properties or to perform some specific functions such as ionic conduction, sensing, and catalytic activities.

Our research effort has been focused on studying the role of metal complexes present in polymeric systems. Different physical properties such as photosensitivity, charge mobility, and luminescence can be tuned by incorporating different metal complexes into the polymers. A number of metal-containing block copolymers,[7] conjugated polymers,[8] polyimides,[9] and polyamides[10] based on diimine complexes of d^6 transition metals have been synthesized and their optoelectronic properties were reported.[11] In our previous paper, we turned our attention to a diazacrown ether containing conjugated

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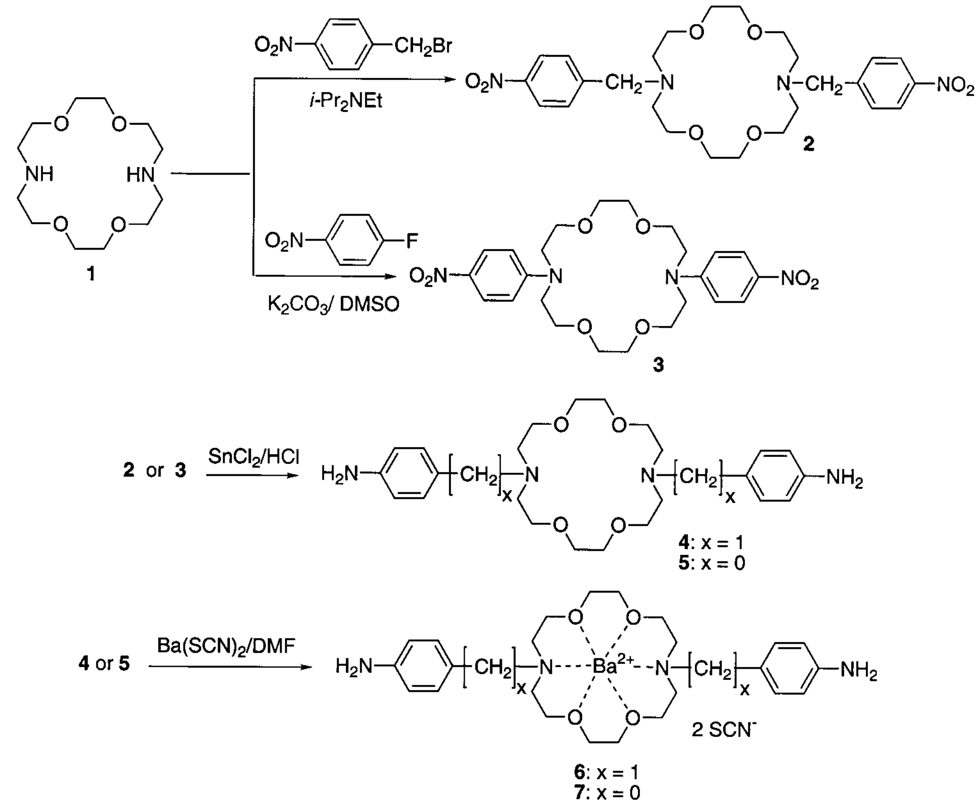

Scheme 1. Synthesis of Diamine Monomers with and without the Coordinated Barium Ion

polymers and their alkaline earth metal complexes.[12] In the solid state, the emission properties of these polymers were affected by the alkaline earth metals. In this paper, we report the synthesis of polyimides that contain the diaza-18-crown-6 moiety on the polymer main chain. It was found that the monomeric barium complexes can be polymerized and thermally imidized to yield the target polyimides. The effect of the barium metal on the electronic transition properties has been studied.

Results and Discussion

Synthesis of Monomers and Polymers. The diamine monomers **4** and **5** with diazacrown ether moieties were conveniently synthesized by the reaction between the commercially available 4,13-diaza-18-crown-6 (**1**) with either 4-nitrobenzyl bromide or 1-fluoro-4-nitrobenzene, followed by the reduction of the nitro group with tin(II) chloride (Scheme 1). These monomers differ from each other by a methylene linkage between the phenylene group and the nitrogen atom on the crown ether. The corresponding barium complexes **6** and **7** were synthesized by the reaction with barium thiocyanate in high yield. Thiocyanate was chosen as the counteranion because of its higher solubility in organic solvents. In addition, it shows a very characteristic infrared absorption band at ca. 2020–2060 cm^{-1}, and the presence of this anion can be easily identified. In the metal complexation reaction, a slight excess of the macrocycle ligand was used in order to drive the reaction to completeness. The excess ligand can be conveniently removed by washing with hot chloroform, in which the target complexes do not dissolve. This type of metal complexes is uaually synthesized by using acetonitrile as the solvent. However, monomer **4** has very low solubility in acetonitrile, and DMF was used as the solvent instead. We have also synthesized several other macrocyclic complexes based on other alkaline or alkaline earth metal such as potassium and strontium. Although these complexes can be prepared readily by similar procedures, it was found that the metal ions detached from the crown ether in the subsequent polymerization reaction. Therefore, our studies were mainly focused on the barium complexes.

The polymerization was performed using the conventional two-stage reaction (Scheme 2). The intermediate poly(amic acid)s were obtained by the reaction between the diamine monomers and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in NMP. This dianhydride monomer gave the final polyimides with the best solubility and processing properties. The poly(amic acid)s can be isolated by precipitation in methanol for characterization. In general, the polyimide film was obtained by directly casting the NMP solution of the poly(amic acid) precursor in situ on a glass or quartz substrate, which was then subjected to thermal imidization. The poly(amic acid)s were subjected to thermal imidization at 100 °C for 15 h and then at 200 °C for 10 h under vacuum. TGA studies revealed that no thermal decomposition occurred nor solvent residue was left under these conditions. The polyimides obtained were only soluble in NMP, and the barium-containing polyimides had higher solutility due to the presence of ionic species in the polymer. We also tried the chemical imidization method by heating the poly(amic acid)

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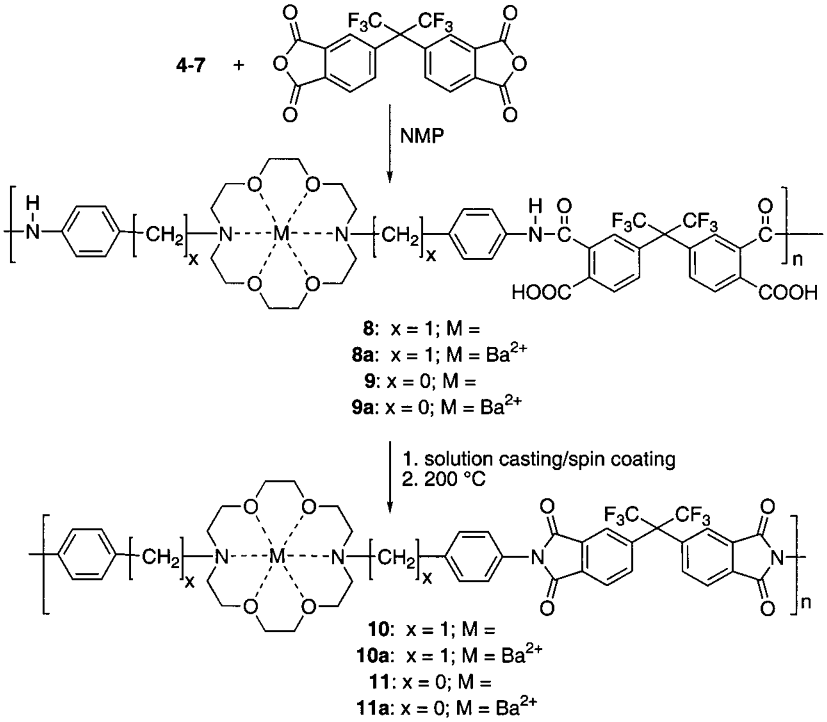
Scheme 2. Synthesis of Poly(amic acid)s and Polyimides and Their Polymer Barium Complexes



8: x = 1; M =
8a: x = 1; M = Ba^{2+}
9: x = 0; M =
9a: x = 0; M = Ba^{2+}

10: x = 1; M =
10a: x = 1; M = Ba^{2+}
11: x = 0; M =
11a: x = 0; M = Ba^{2+}

solution with a mixture of pyridine and acetic anhydride at 90 °C. However, decomposition of the metal complex was observed under this condition.

Crystal Structure Determination. Single crystals of **6·H$_2$O** were obtained by vapor diffusion of diethyl ether into a DMF solution of the complex. The barium ion locates at the center of the macrocyclic crown ether moiety and is at the same level with the two nitrogen atoms on the ring with a N(1)−Ba(1)−N(1) angle of 175.7(2)°. The two thiocyanate counteranions attached to the barium atom from the other side of the ring. In addition, a water molecule is also found in the structure. It was observed that the hydrogen atom on the water molecule forms hydrogen bonds with the nitrogeon atom on the adjacent amino group, with a bond distance of 2.068 Å. The geometry of this complex is very similar to those of the iodobenzyl-substituted diazacrown ethers reported by us.[12] A perspective drawing of **6** with atomic numbering is depicted in Figure 1. Selected bond distances and angles are summarized in Table 1.

Characterization of Monomers and Polymers. After the thermal imidization process, the resulting polyimides could be peeled off directly from the supporting glass slide. They can form free-standing films that were used for subsequent physical characterization. The inherent viscosities of the polyimides were measured in the range between 0.2 and 0.7 dL/g, except for polyimide **10**, which shows a viscosity value of 2.0 dL/g (Table 2). It is because polyimide **10** was not completely soluble in NMP and only the soluble component was used for measurement. All polyimides did not show a clear glass transition process up to 300 °C. Polyimide **11** shows a higher thermal stability than **10** owing to the absence of a methylene linkage that makes the polymer main chain more flexible. In addition, the

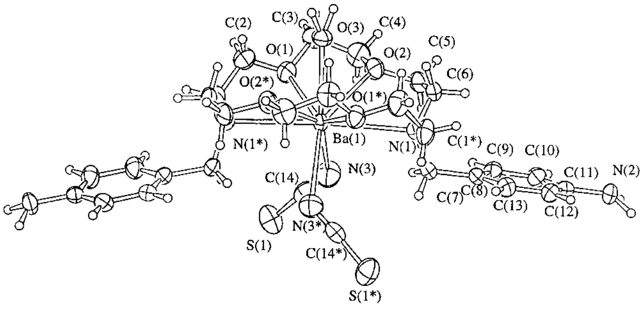


Figure 1. Perspective drawing of **6·H$_2$O** with the atomic numbering scheme.

Table 1. Selected Geometric Data for Barium Complex 6·H$_2$O

	Bond Lengths (Å)		
Ba(1)−N(1)	2.969(4)	Ba(1)−O(1)	2.838(4)
Ba(1)−O(2)	2.793(4)	Ba(1)−O(3)	2.706(5)
Ba(1)−N(3)	2.849(6)	N(1)−C(7)	1.489(7)
N(3)−C(14)	1.136(8)	S(1)−C(14)	1.619(7)
	Bond Angles (deg)		
N(1)−Ba(1)−N(1*)	175.7(2)	O(1)−Ba(1)−O(1*)	143.7(2)
O(1)−Ba(1)−O(2)	59.6(1)	O(1)−Ba(1)−O(2*)	104.1(1)
O(1)−Ba(1)−O(3)	71.84(9)	N(1)−Ba(1)−O(1)	121.0(1)
N(1)−Ba(1)−O(1*)	60.5(1)	N(1)−Ba(1)−O(2)	62.1(1)
N(1)−Ba(1)−O(2)	119.9(1)	N(1)−Ba(1)−O(3)	92.15(10)
N(1)−Ba(1)−N(3)	88.4(2)	N(3)−Ba(1)−N(3*)	80.3(3)
N(3)−Ba(1)−O(3)	139.9(1)	N(1)−C(7)−C(8)	117.4(4)

Table 2. Properties of Polyimides

polyimide	yield (%)	η_{inh} (dL/g)[a]	T_d (°C)[b]
10	90	2.0[c]	302
10a	81	0.22	276
11	76	0.55	410
11a	72	0.67	322

[a] Inherent viscosity measured in NMP solution at 30 °C with concentration $c = 0.5$ g/dL. [b] Decomposition temperature measured with TGA. The onset of weight loss was taken as the decomposition temperature. [c] The polyimide was not completely soluble in NMP and only the soluble component was used for viscosity measurement. Therefore, the viscosity value measured may not be accurate.

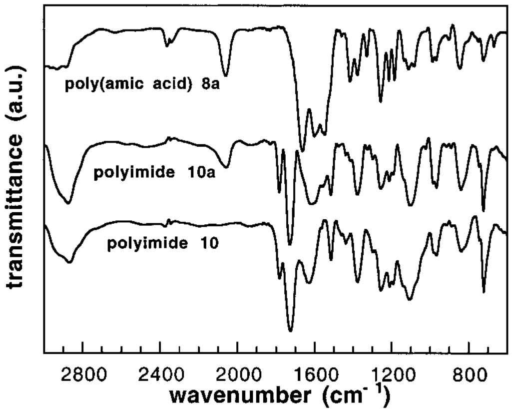


Figure 2. FTIR spectra of poly(amic acid) **8a** and polyimides **10** and **10a**.

polyimide barium complexes **10a** and **11a** show lower decomposition temperatures compared to their metal-free counterparts. This is due to the presence of thiocyanate anions, which first decompose when subjected to heating.

All the intermediates and monomers were fully characterized by conventional spectroscopic methods and elemental analysis. The FTIR spectra of poly(amic acid) **8a** and polyimides **10** and **10a** are shown in Figure 2. Monomer **6** shows the amine N−H and thiocyanate CN stretching band at ca. 3400 and 2060 cm^{-1}, respectively. Two other intense characteristic bands due to the C−O stretching of the crown ether moiety were also found at ca. 1100 and 1070 cm^{-1}. For the poly(amic acid) precursor, the carbonyl C═O stretching band due to the amide linkage appeared at 1660 cm^{-1}. After the imidization, this absorption band disappeared. Two new C═O stretching bands due to the imide unit were found at 1780 and 1720 cm^{-1}. The absorption band due to the thiocyanate anion was preserved in the polyimides barium complexes. These results indicate that the imidization process was complete and the barium complexes survived in the polymerization. The infrared spectra of these polyimide barium complexes in other region are quite similar to those of barium-free polyimides.

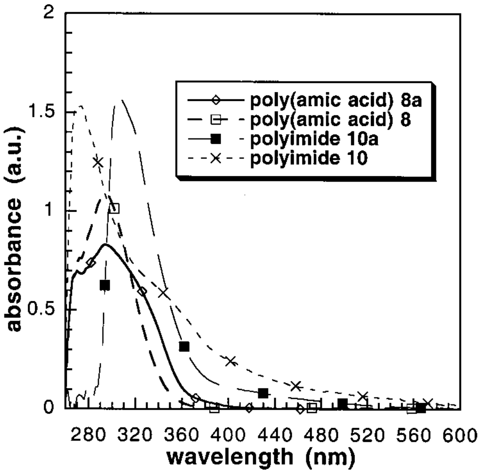


Figure 3. UV−vis absorption spectra of some poly(amic acid)s and polyimides in NMP solution.

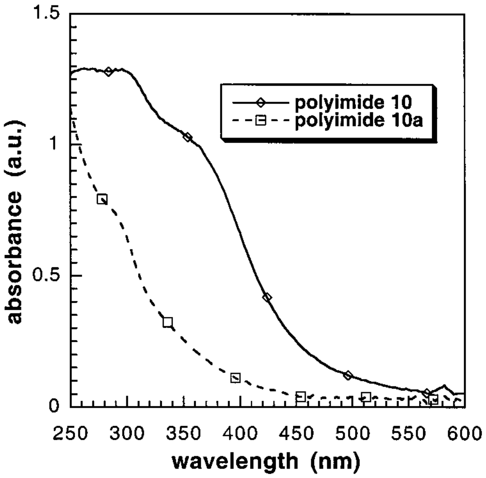


Figure 4. UV−vis spectra of the thin films of polyimides **10** and **10a**.

Effect of Barium Complexes on Electronic Properties. The UV−vis absorption spectra of some poly(amic acid)s and polyimides in dilute NMP solution (10−50 μg/mL) are shown in Figure 3. There are little differences between the absorption spectra of poly(amic acid)s **8** and **8a**, and both of them show an absorption peak at 290 nm. After the formation of polyimides, the differences in their absorption spectral features were more significant. The barium-free polyimide **10** shows an absorption maxima at 275 nm and a shoulder is observed at 360 nm. On the other hand, the absorption maxima of the barium-containing polyimide **10a** exhibits a significant red shift and is found at 320 nm. No shoulder was observed in the absorption band. Both polyimides exhibit long absorption tails that extend to the visible region. With reference to the absorption spectra of other polyimides,[13] this is possibly due to the formation of charge transfer (CT) complexes. The charge-transfer transitions are responsible for the low-energy electronic transitions. In dilute solution, intermolecular interactions are minimized, and the electronic transitions are dominated by intramolecular charge-transfer complex formation. Figure 4 shows the absorption spectra of polymer films cast from **10** and **10a**. The absorption tail of of polyimide **10** extends to longer wavelength, with a clear shoulder observed at 400 nm. The lower energy electronic transition is attributed to the CT states contributed by intermolecular interaction. On the other hand, such transition was not found in the barium-containing polyimide **10a**. We suggest that the presence of ionic species on the polymer main chain could affect the CT complex formation by changing the conformation of the polymer main chian. The mobility of the diazacrown moiety is reduced by the barium ion that “locks” the coordinating nitrogen and oxygen atoms. From the monomer crystal structure, the presence of the bulky thiocyanate anion may also prevent the polymer molecules from approaching each other. As a result, the energy levels of the CT states in these polyimides were changed after the formation of barium complex. It should be noted that the intra- and intermolecular interactions are very difficult to isolate, and both of them may give rise to the electronic transitions in solid state. The UV−vis absorption spectra of polyimides **11** and **11a** are shown in Figure 5. Both of them show very similar spectral features with an absorption

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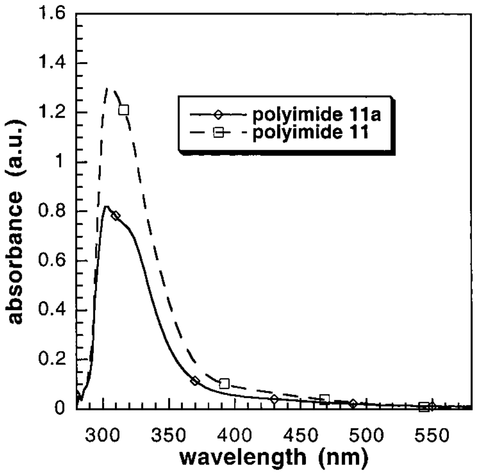

Figure 5. UV−vis absorption spectra of polyimides **11** and **11a** in NMP solution.

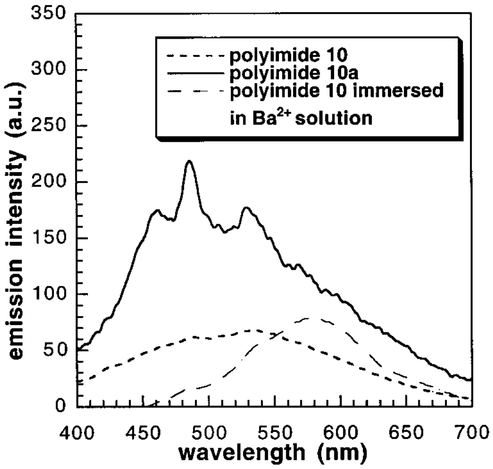

Figure 6. Emission spectra of polyimide **10** and its polymer barium complex **10a**. The emission spectrum of **10** after being immersed in methanolic barium thiocyanate solution (10 mM) is also shown.

tail at the visible region, indicating that they both form CT states with similar energy levels. In these polyimides, the absence of a methylene linkage on the main chain makes both of them more rigid in nature. As a result, there was little difference in CT states before and after the formation of barium complexes. The more rigid conformation may also inhibit the formation of CT complexes.

It has been suggested that polyimides can exhibit fluorescence from the CT states.[14] We have studied the effect of barium ion on the emission properties of the polyimides. Figure 6 shows the emission spectra of polyimides **10** and **10a** when excited at 250 nm. The spectra were collected on free-standing polymer films that were obtained by thermal imidization. Polyimide **10** exhibits a broad emission band centered at ca. 530 nm and the polymer is not strongly emissive. This phenomenon is similar to the emission from some polyimide,[15] which was interpreted to be intramolecular charge-transfer transition with electron density shifting from the amine to the imide unit. On the other hand, the barium-containing polyimide **10a** shows completely different spectral properties. A new emission peak was observed at 490 nm and the polymer film was more emissive. For polyimides **11** and **11a**, they are typically nonemissive polymers and their fluorescence properties were not studied.

Polyimide **10** is a potential barium-sensing material, as there are significant changes in fluorescence after coordination to barium ion. To explore the feasibility of utilizing these polyimides as a metal ion sensor, we compared the emission spectra of the polyimide film before and after immersion in a methanolic barium thiocyanate solution (10 mM). After immersion, the emission peak of the resulting polymer film showed a red shift with a maxima at ca. 580 nm (Figure 6). Interestingly, this is quite different from the spectral properties of polyimide **10a**. We suggest that by immersing the polymer film in barium solution, only the crown ether moieties near the film surface can be binded with barium, while the emission of the bulk polymer film was not affected. Nevertheless, it demonstrates that it is possible to probe the barium ion content in a solution by using this polymer.

Conclusions

We have developed two series of polyimides based on diaza-18-crown-6 on the polymer main chain. Their corresponding polymer barium complexes were also synthesized from the monomeric barium complexes. It was found that the barium-free and barium-containing polyimides exhibit different electronic absorption and emission properties. Such differences are attributed to the formation of charge-transfer complexes, whose energy levels are dependent on the conformation of polymer and the presence of barium ion. This enormous difference in electronic properties implies possible technological application such as metal ion sensing. Determination of the nature of the charge transfer states would constutute another research project, which is being undertaken in our group.

Experimental Section

Materials. 4,13-Diaza-18-crown-6 (**1**), 4-nitrobenzyl bromide, 1-fluoro-4-nitrobenzene, and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from Aldrich Chemical Co. Cesium fluoride, tin(II) chloride, and barium thiocyanate were purchased from Strem Chemical Co. All the chemcials were used as received, unless otherwise specified. *N*-Methylpyrrolidinone (NMP) was distilled over calcium hydride under reduced pressure.

Instruments. Melting point and other thermal properties were determined by a Perkin-Elmer DSC7 and TGA7 thermal analyzer with a heating rate of 10 and 15 °C/min, respectively. ^{1}H and ^{13}C NMR spectra were collected on a Bruker 300 DPX NMR spectrometer. FTIR spectra (KBr pellet) were collected on a Bio-Rad FTS-7 FTIR spectrometer. UV−vis spectra were collected on a Hewlett-Packard HP8452 photodiode array spectrophotometer. Emission and excitation spectra were collected on a Perkin-Elmer LS-50B luminescence spectrophotometer. Mass spectrometry was performed on a high-resolution Finnigan MAT-95 mass spectrometer. The viscosity measurements were performed in a constant-temperature bath (30 °C) using an Ubbelohde viscometer, with the polymer concentration of 0.5 g/dL in NMP.

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***N*,*N*′-Bis(4-nitrobenzyl)-4,13-diaza-18-crown-6 (2).** A mixture of 4-nitrobenzyl bromide (6.13 g, 28 mmol), 4,13-diaza-18-crown-6 (3.72 g, 14 mmol), and *N*,*N*-diisopropylethylamine (18.4 g, 0.14 mol) was heated under reflux in ethanol (30 mL) for 3 h. After cooling, the solvent was removed under reduced pressure. The residue was extracted with $CHCl_3$ (100 mL), washed with water (3 × 10 mL), and dried over $MgSO_4$. The organic layer was evaporated and the orange solid was purified by heating with hot methanol. Yield: 7.29 g (96%). Mp: 116 °C. ^{1}H NMR ($CDCl_3$), δ: 8.15 (d, $J = 8.7$ Hz, 4 H, aryl), 7.56 (d, $J = 8.7$ Hz, 4 H, aryl), 3.8 (s, 4 H, benzyl CH_2), 3.64−3.60 (m, 16 H, crown ether OCH_2CH_2O), 2.83 (t, $J = 5.7$ Hz, 8 H, crown ether CH_2N). ^{13}C NMR ($CDCl_3$), δ: 147.6, 128.6, 122.9, 70.2, 69.4, 58.8, 53.6, 26.0, FTIR (KBr), cm^{-1}: $\nu = 2962$, 2839 (C−H stretching), 1605 (C=C stretching), 1517, 1346 (NO_2), 1128, 1099 (ether C−O stretching), 812 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis ($CHCl_3$): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 299 (9400). FAB-MS, *m*/*e*: 534 (M$^+$). Anal. Calcd for $C_{26}H_{36}N_4O_8$: C, 58.58; H, 6.76; N, 10.51. Found: C, 57.72; H, 6.59; N, 10.25.

***N*,*N*′-Bis(4-nitrophenyl)-4,13-diaza-18-crown-6 (3).** A mixture of 1-fluoro-4-nitrobenzene (1.74 g, 12 mmol), 4,13-diaza-18-crown-6 (1.53 g, 5.8 mmol), anhydrous potassium carbonate (4.02 g, 29 mmol), and DMSO (20 mL) was heated at 90 °C for 4 days. After cooling, the mixture was poured into water. The yellow solid was collected by filtration and washed with hot methanol. Yield: 1.46 g (50%). Mp: 209 °C. ^{1}H NMR ($CDCl_3$), δ: 8.10 (d, $J = 9.4$ Hz, 4 H, aryl), 6.62 (d, $J = 9.4$ Hz, 4 H, aryl), 3.72 (m, 16 H, crown ether OCH_2CH_2O), 3.65 (s, 8 H, crown ether CH_2N). ^{13}C NMR ($CDCl_3$), δ: 161.8, 125.7, 109.7, 70. 5, 68.1, 51.2. FTIR (KBr), cm^{-1}: $\nu = 2911$, 2877 (C−H stretching), 1595 (C=C stretching), 1513, 1328 (NO_2), 1108, 1072 (ether C−O stretching), 824 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis ($CHCl_3$): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 393 (45 000). FAB-MS, *m*/*e*: 505 (M$^+$). Anal. Calcd for $C_{24}H_{32}N_4O_8$: C, 57.08; H, 6.34; N, 11.10. Found: C, 56.91; H, 6.34; N, 10.99.

***N*,*N*′-Bis(4-aminobenzyl)-4,13-diaza-18-crown-6 (4).** Tin(II) chloride dihydrate (10.37 g, 46 mmol) was added slowly into a mixture of **2** (3.05 g, 5.7 mmol), concentrated hydrochloric acid (75 mL), and ethanol (40 mL). The mixture was heated under reflux for 24 h. After cooling, aqueous sodium hydroxide solution (50%) was added in dropwise into the mixture under a nitrogen atmosphere. After the solution had been neutralized, the solution was filtered. The white solid obtained was washed with water, and the crude product was recrystallized with methanol. Yield: 2.3 g (85%). Mp: 149 °C. ^{1}H NMR (DMSO-d_6), δ: 6.91 (d, $J = 8.1$ Hz, 4 H, aryl) 6.47 (d, $J = 8.1$ Hz, 4 H, aryl), 4.89 (s, 4 H, NH_2), 3.46 (m, 16 H, crown ether OCH_2CH_2O), 3.39 (s, 4 H, benzyl CH_2), 2.61 (t, $J = 5.8$ Hz, 8 H, crown ether CH_2N). ^{13}C NMR (DMSO-d_6), δ: 147.2, 129.3, 126.2, 113.5, 69.8, 69.2, 58.9, 52.9. FTIR (KBr), cm^{-1}: $\nu = 3377$ (N−H stretching), 2968, 2853 (C−H stretching), 1653 (N−H bending), 1613 (C=C stretching), 1130, 1106 (crown ether C−O stretching), 836 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis (DMF): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 300 (3900). MS, *m*/*e*: 472.304 956; $C_{26}H_{40}N_4O_4$ requires 472.304 955 6.

***N*,*N*′-Bis(4-aminophenyl)-4,13-diaza-18-crown-6 (5).** Tin(II) chloride (10.23 g, 45 mmol) was added slowly into a mixture of **2** (2.86 g, 5.7 mmol), concentrated hydrochloric acid (60 mL), and ethanol (40 mL). The solution was heated under reflux for 24 h, and the workup procedure was similar to that of **4**. The crude product was purified by washing in hot ethanol. Yield: 2.0 g (79%). Mp: 108 °C. ^{1}H NMR (CD_3CN), δ: 6.60−6.52 (m, 8 H, aryl), 3.62−3.55 (m, 16 H, crown ether OCH_2CH_2O), 3.42 (t, $J = 5.9$ Hz, 8 H, crown ether CH_2N). ^{13}C NMR (CD_3CN), δ: 161.8, 115.4, 114.5, 69.9, 68.5, 51.3. FTIR (KBr), cm^{-1}: $\nu = 3411$, 3336 (N−H stretching), 2873 (C−H stretching), 1624 (C=C stretching), 1116, 1075 (crown ether C−O stretching), 816 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis (DMF): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 339 (3000). MS, *m*/*e*: 444 (M$^+$). Anal. Calcd for $C_{24}H_{36}N_4O_4$: C, 64.78; H, 8.10; N, 12.60. Found: C, 64.12; H, 8.36; N, 12.29.

[*N*,*N*′-Bis(4-aminobenzyl)-4,13-diaza-18-crown-6]-barium Thiocyanate Monohydrate (6·H_2O). A mixture of barium thiocyanate trihydrate (0.4 g, 1.3 mmol) and **4** (0.51 g, 1.1 mmol) was warmed in DMF (5 mL) at 50 °C for 24 h. After cooling, the solution was poured into water and then filtered. The white complex was further washed with hot $CHCl_3$ and then filtered. It was dried at 80 °C in vacuo for 24 h. Yield: 0.68 g (81%). Mp: >340 °C. ^{1}H NMR (DMSO-d_6), δ: 6.91 (d, $J = 8.3$ Hz, 4 H, aryl), 6.47 (d, $J = 8.3$ Hz, 4 H, aryl), 4.91 (s, 4H, NH_2), 3.48 (m, 16 H, crown ether OCH_2CH_2O), 3.41 (s, 4 H. benzyl CH_2), 2.61 (t, $J = 5.8$ Hz, 8 H, crown ether CH_2N). ^{13}C NMR (DMSO-d_6), δ: 147.4, 129.8, 129.5, 113.5, 69.8, 68.8, 52.6. FTIR (KBr), cm^{-1}: $\nu = 3367$ (N−H stretching), 2850 (C−H stretching), 2057 (thiocyanate CN stretching), 1612 (C=C stretching), 1089 (crown ether C−O stretching), 832 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis (DMF): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 300 (4000). FABMS, *m*/*e*: 668 (M$^+$ − SCN). Anal. Calcd for $C_{28}H_{40}N_6O_4S_2Ba \cdot H_2O$: C, 45.15; H, 5.68; N, 11.29. Found: C, 44.85; H, 5.51; N, 11.04.

[*N*,*N*′-Bis(4-aminophenyl)-4,13-diaza-18-crown-6]-barium Thiocyanate Monohydrate (7·H_2O). A mixture of barium thiocyanate trihydrate (0.21 g, 0.69 mmol) and **5** (0.30 g, 0.67 mmol) was added to acetonitrile (5 mL), and the resulting mixture was heated at 50 °C for 24 h. After cooling, the solvent was removed under reduced pressure. The white complex was washed with hot chloroform and filtered. It was further washed with water and then dried at 80 °C in vacuo for 24 h. Yield: 0.15 g (75%). Mp: >340 °C. ^{1}H NMR (CD_3CN), δ: 7.07 (d, $J = 8.5$ Hz, 4 H, aryl), 6.69 (d, $J = 8.5$ Hz, 4 H, aryl), 4.15 (br s, 4 H, NH_2), 3.63−3.72 (m, 16 H, crown ether OCH_2CH_2O), 3.18 (t, $J = 5.2$ Hz, 8 H, crown ether NCH_2). ^{13}C NMR (CD_3CN), δ: 116.2, 71.4, 69.9, 65.1, 57.7. FTIR (KBr), cm^{-1}: $\nu = 3448$, 3346 (N−H stretching), 2917, 2880 (C−H stretching), 2026 (thiocyanate CN stretching), 1622 (C=C stretching), 1114, 1079 (crown ether C−O stretching), 838 (C−H out-of-plane bending, 1,4-disubstituted benzene). UV−vis (DMF): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 338 (5800). FABMS, *m*/*e*: 640 (M$^+$ $^-$ SCN). Anal. Calcd for $C_{26}H_{36}N_6O_4S_2Ba \cdot H_2O$: C, 43.57; H, 5.31; N, 11.73. Found: C, 43.21; H, 4.94; N, 11.17.

Synthesis of Poly(amic acid). The synthesis of polyimide **10** is described as the general procedure. *N*,*N*′-Bis(4-aminobenzyl)-4,13-diaza-18-crown-6 (**4**) (0.11 g, 0.22 mmol) and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (0.096 g, 0.22 mmol) were dissolved in distilled NMP (2 mL) under a nitrogen atmosphere and the solution stirred at 0 °C for 1 h. The solution was then stirred at 25 °C for another 24 h. The polyamic acid can be obtained by pouring into methanol (100 mL) for characterization. A white solid was collected by filtration. For the preparation of polyimide film, the NMP solution obtained can be used in situ by solution casting without the isolation of the poly(amic acid) intermediate.

Preparation of Polyimide Films. The poly(amic acid) solution in NMP was casted on a glass or quartz substrate and the solution was evaporated slowly by heating on a hot plate at 80 °C for 2−4 h. The precursor poly(amic acid) film was thermally imidized in a vacuum oven at 100 °C for 15 h and then at 200 °C for 10 h. After the thermal imidization, the polyimide film can be peeled off from the substrate for further characterizations.

X-ray Crystallographic Studies. A colorless single crystal of **6** was obtained by slow diffusion of diethyl ether into DMF solution of the complex. The colorless crystal of $BaN_6S_2O_5C_{28}H_{42}$ having approximate dimensions of 0.21 × 0.22 × 0.25 mm was mounted in a glass capillary. The diffraction data was collected on at a temperature of 28 ± 1 °C on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0° and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 centered reflections in the range $13.47 < 2\theta < 16.67°$. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° with a takeoff angle of 6.0°. Scans of $(0.73 + 0.35 \tan \theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections (*I*

$< 10.0\sigma(I)$) were rescanned and the counts were accumulated to ensure good counting statistics. Stationary background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 9.0 mm (horizontal) and 13.0 mm (vertical). Crystal data for **6**: [$BaN_6S_2O_5C_{28}H_{42}$]; fw = 744.13, monoclinic, space group $C2/c$ (No. 15), $a = 17.727(7)$ Å, $b = 9.722(7)$ Å, $c = 20.761(6)$ Å, $\beta = 110.88(2)°$, $V = 3343(2)$ Å^3, $Z = 4$, $D_c = 1.478$ g/cm^3, μ(Mo Kα) = 13.56 cm^{-1}, $F(000) = 1520.00$. A total of 3243 reflections were collected, of which 3130 were unique ($R_{\rm int} = 0.032$). The intensities of three representative reflection were measured after every 250 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo Kα radiation is 13.6 cm^{-1}. An empirical absorption correction based on azimuthal scans reflections was applied that resulted in transmission factors ranging from 0.97 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Convergence for 191 variable parameters by least squares refinement on F with $w = 1/\sigma^2(F_0)$, where $\sigma_c(F_o)$ = esd based on counting statistics for 2065 observed reflections with $I > 3\sigma(I)$ was reached at $R = 0.041$ and $R_w = 0.036$ with a goodness of fit = 1.25. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.2 and −0.30 e/Å^3, respectively.

Acknowledgment. The work described in this paper has been substantially supported by the Research Grants Council of Hong Kong, China (Project Nos. HKU 7093/97P, HKU 7090/98P, and HKU 7096/00P). Partial financial support from the Committee on Conference and Research Grants (University of Hong Kong) is also acknowledged. S.H.C. thanks The Graduate School, University of Hong Kong for the award of the studentship.

Supporting Information Available: An X-ray crystallographic file in CIF format and tables listing detailed crystallographic data, atomic positional parameters, anisotropic temperature factors, and bond distances and angles for **6·H_2O** are available (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0103500

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