Squaraine Dye Based Molecular Wires Containing Flexible Oxyethylene Chains as Sensors. Enhanced Fluorescence Response on Li^+ Recognition†

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ABSTRACT: Two new pyrrole-derived squaraine molecular wires **4a** and **4b** containing flexible oxyethylene side chains have been prepared and characterized. GPC analysis of **4a** and **4b** showed molecular weights of nearly 1800 g/mol. The UV−vis absorption maxima of these molecular wires were broad and red-shifted (11−12 nm) when compared to that of a model squaraine dye **7a**. Nevertheless, the absorption maxima of the molecular wires **4a** and **4b** were much lower than the expected values despite their extended conjugation which could be due to the reduced charge-transfer interactions in these systems. Addition of alkali metal ions such as Li^+, Na^+, and K^+ could not produce considerable changes in the absorption properties of the molecular wires except a marginal change in the case of **4a** on addition of Li^+. However, significant changes in the emission characteristics could be noticed in the case of **4a** upon addition of Li^+, whereas addition of K^+ and Na^+ did not produce any measurable response. Interestingly, the absorption and emission characteristics of the monomeric squaraine dyes **7a** and **7b** showed only marginal response upon the addition of Li^+, Na^+, and K^+. The enhanced response of the molecular wire **4a** over the monomeric squaraine dye **7a** has been explained on the basis of the optimum chain length of the flexible binding site and due to a collective system response of the molecular wire, which is associated with a flexible to a rigid conformational change upon the alkali metal ion binding.

Introduction

Recent developments in the synthesis and studies of π-conjugated polymers have led to the design of novel macromolecular materials with tailored properties for advanced technological applications. A promising development in this direction is the designing of macromolecular wire based sensory devices for the detection of metal ions and organic molecules.[1] In addition to the numerous reports on single molecule based chemosensory systems that are capable of detecting analytes in both real-time and reversible fashion,[2] considerable effort has been directed toward the design and synthesis of conjugated polymer based metal ion sensors.[3] Besides the ease of fabrication, advantages of the polymer based sensors over the corresponding single molecule based sensors are their enhanced signal amplification during the analyte recognition. The origin of this effect is attributed to the facile energy migration and/or conformational changes associated with the conjugated polymer backbone upon a recognition event.[4]

There have been several reports pertaining to polythiophene and polypyrrole based sensory polymers.[3,5] Most of these systems make use of the changes in the electronic mobility (conductivity) or redox property for the signal transduction. On the other hand, a molecular wire based sensor in which a recognition event is detected through the response in its optical absorption or emission is rather simple and easy to operate.[6,7] In this context, conjugated polymer based optical sensors derived from organic dye molecules have great significance due to their novel optical and electronic properties. Squaraine dyes would be ideal candidates toward this end due to their intense absorption and emission properties in the visible and near-infrared region.[8] These properties of squaraine dyes have already been exploited in the designing of a few metal ion sensors.[9] Previous reports on the synthesis and properties of squaraine dye based conjugated oligomers and polymers derived from pyrrole derivatives[10,11] have prompted us to utilize these materials for the designing of squaraine molecular wire based fluorescent sensors for the detection of alkali metal ions.[12] In the present study we report that the squaraine molecular wire **4a** containing flexible methoxyethoxyethyl side chains show enhanced fluorescence sensitivity and specificity toward Li^+ over Na^+ and K^+ when compared to the molecular wire **4b** with a more labile methoxyethoxy−ethoxyethyl side chains and with the monomeric model squaraine dye **7a**.

Results and Discussion

Synthetic route for the molecular wires **4a** and **4b** are shown in Scheme 1. The bromo derivatives **2a** and **2b** of diethylene glycol monomethyl ether **1a** and triethylene glycol monomethyl ether **1b** were prepared as per known procedures in 71% and 67% yields, respectively.[7a] The [(*N*-methoxyethoxy)ethyl]pyrrole **3a** and [[*N*-[(methoxyethoxy)ethoxy]ethyl]pyrrole **3b** were obtained by the reaction of pyrrole with **2a** and **2b** in 67% and 64% yields, respectively.[7a,13] The polycondensation reactions of **3a** or **3b** with squaric acid in 1:1 mole ratio were carried out in a mixture of 1-butanol and benzene (1:1) by azeotropic removal of water from the reaction mixture. The crude products were purified by reprecipitation from DMSO solutions by hexane to get 62% and 56% yields of **4a** and **4b**, respectively.

For comparing the spectral properties and the alkali metal ion binding behavior of **4a** and **4b**, a model

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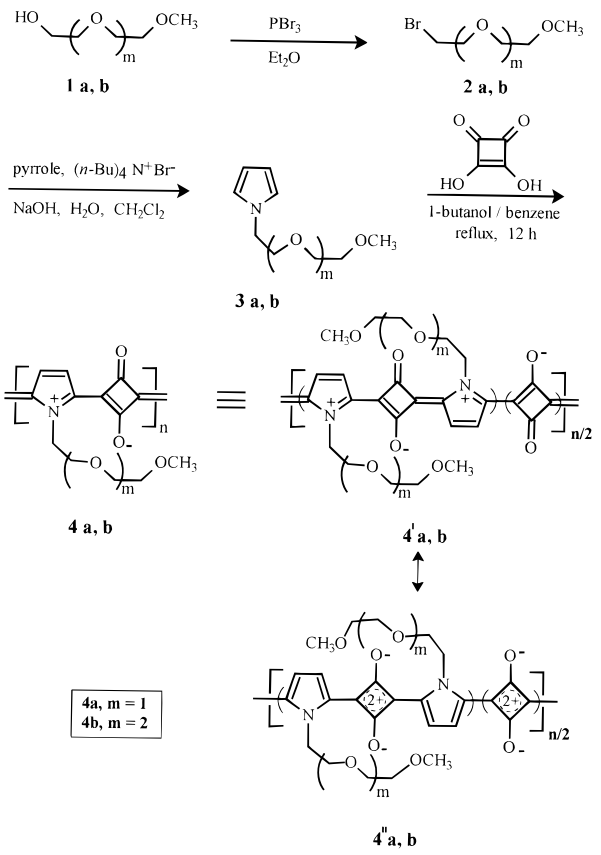
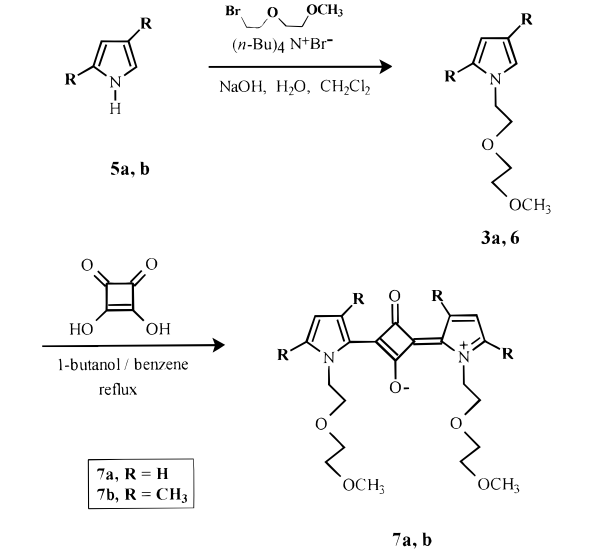
Scheme 1



Scheme 2



squaraine dye **7a** has been prepared by slow addition of squaric acid to a dilute solution of **3a** (1:2 mole ratio) followed by azeotropic removal of water (Scheme 2). A red dye with a sharp intense absorption around 553 nm was obtained in a 40% yield after purification of the reaction mixture on a silica column. The structure of **7a** is confirmed by FT-IR and ^{1}H NMR spectral data. The UV−vis spectrum of **7a** showed slow change in the absorption maxima under elevated temperatures and while keeping in solvents such as DMSO probably due to further polymerization. Therefore, we have prepared another dye **7b** in a 67% yield by the reaction of 2-(*N*-methoxyethoxy)ethyl-2,4-dimethylpyrrole (**3a**). This dye was fairly stable and did not undergo any polymerization due to presence of a methyl group at the 2-position of the pyrrole ring. The IR spectra of **7a** and **7b** were comparable with those of the molecular wires **4a** and **4b** which showed the characteristic absorption of the resonance-stabilized cyclobutene-1,3-diolate dianion around 1620 cm^{-1}, indicating the zwitterionic 1,3-substituted squaraine structure. The ^{1}H NMR spectrum of **7b** showed two singlets at δ 2.35 and 2.63, corresponding to the four CH_3 groups attached to the two pyrrole moieties. The protons attached to the OCH_3 groups appeared as a singlet at δ 3.29. The multiplets around δ 3.42 correspond to protons of the two oxyethylene side chains. The two triplets at δ 3.67 and 4.85 are assigned to the OCH_2 and NCH_2 protons, respectively. The aromatic protons of the two pyrrole rings appeared as a singlet at δ 6.0. The ^{13}C NMR spectrum of **7b** showed a total of 13 carbon signals which are exactly half of the total number of 26 carbon atoms present, indicating that each half of the molecule is identical.

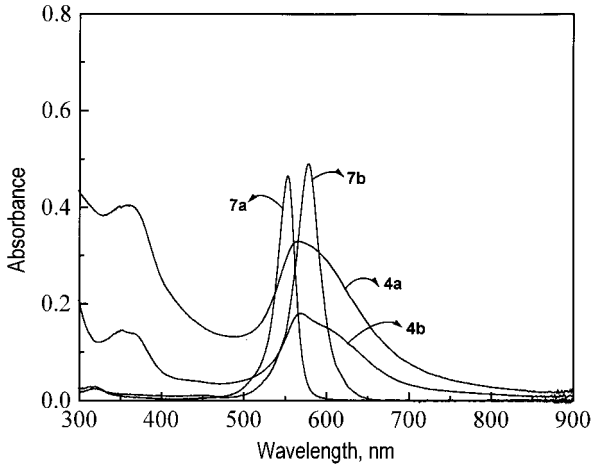


Figure 1. UV−vis absorption spectra of the squaraine molecular wires **4a, 4b** and the model squaraine dyes **7a, 7b** in DMSO.

Comparison of the IR and NMR spectral data of the new squaraine molecular wires **4a** and **4b** with those of the model compounds **7a** and **7b** has revealed that the former have the alternate donor−acceptor 1,3-zwitterionic repeating units (Scheme 1). Alternatively, the structures of **4a** and **4b** can be written as **4′a** and **4′b** in the form of squaraine dye repeating units which are separated by the electron-deficient C_4O_2 spacers. The structures **4′a** and **4′b** can be in resonance with structures **4″a** and **4″b** as shown in Scheme 1. The molecular weight analysis of **4a** and **4b** by gel permeation chromatography (GPC) showed number-average molecular weights of approximately 1800 g/mol with a polydispersity of 1.8.[14] This corresponds to molecular wires consisting of an average of four squaraine dye units, each separated by an alternate C_4O_2 moiety. The average length of the molecular wires **4a** and **4b** are calculated from their minimum-energy conformations using semiempirical calculations, which are found to be approximately 6 nm.

The UV−vis absorption spectra of **4a, 4b**, **7a**, and **7b** are shown in Figure 1. The absorption maxima of **4a, 4b**, and **7b** are red-shifted when compared to that of **7a**. The broad and red-shifted absorption maxima of **4a** and **4b** when compared to the intense sharp and blue-shifted absorption maximum of **7a** indicate the oligomeric nature of the former. The bathochromic shift in

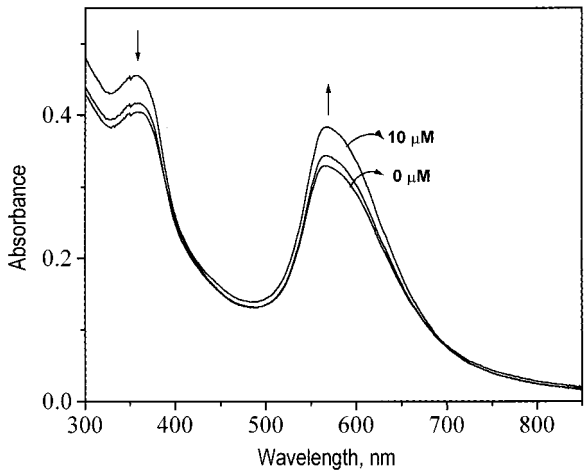


Figure 2. Effect of addition of $LiClO_4$ on the UV−vis absorption spectrum of the squaraine molecular wire **4a**.

the absorption maximum of the monomeric dye **7b,** when compared to that of **4a, 4b**, and **7a**, can be attributed to the strong charge-transfer interaction in **7b** due to the presence of four methyl groups on the two pyrrole rings. Introduction of electron-donating methyl groups are known to shift the absorption maxima of the pyrrole-derived squaraine dyes to the longer wavelength region.[15] The observed red shift of nearly 11−12 nm of the molecular wires **4a** and **4b** when compared to the model dye **7a** is far below the expected value for an extensively conjugated system. This can be explained due to the presence of the electron-deficient C_4O_2 spacer between each squaraine repeating unit as in **4′a** and **4′b** which may contribute significantly in reducing the charge-transfer interactions.

The alkali metal ion sensing abilities of the squaraine molecular wires **4a** and **4b** and the monomeric squaraine dye **7a** were studied, making use of their response toward the absorption and emission properties upon metal ion recognition. The absorption spectral changes of **4a** on addition of micromolar quantities of $LiClO_4$ are shown in Figure 2. Even though the changes in the absorption maximum at 564 nm are not very predominant, noticeable increase in the intensity of absorption with a marginal red shift of nearly 5 nm could be observed on addition of $LiClO_4$ in micromolar quantities. However, no change in the absorption spectrum could be seen on addition of $NaClO_4$ or $KClO_4$. On the other hand, in the case of **4a**, addition of micromolar quantities of $LiClO_4$ and $KClO_4$ resulted in very weak changes in the absorption spectra of **4b**, whereas addition of $NaClO_4$ did not produce any change.

The changes in the fluorescence spectra of **4a** and **4b** (Φ_f = 0.012) in DMSO upon addition of micromolar quantities of $LiClO_4$ and $KClO_4$ are shown in Figures 3 and 4, respectively. The fluorescence spectra of **4a** and **4b** in DMSO in the absence of metal ions showed emission maxima at 574 and 575 nm at an excitation wavelength of 520 nm. Effects of addition of Li^+, Na^+, and K^+ on the fluorescence quantum yields and percentage fluorescence enhancement of **4a** and **4b** are shown in Table 1. The most significant response was noticed for the molecular wire **4a** against Li^+ as evident from a nearly 2-fold enhancement in fluorescence quantum yield. This is clear from the plot of the relative fluorescence quantum yields of **4a** against the metal ion concentration as shown in Figure 5. In the case of Na^+ and K^+ no major response in the fluorescence emission

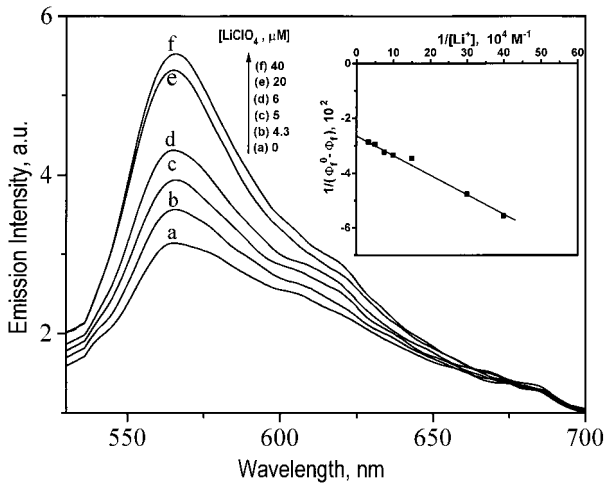


Figure 3. Change in the emission intensity of the squaraine molecular wire **4a** as a function of increasing Li^+ concentration (λ_{exc} = 520 nm). The inset shows the plot of $1/(\Phi_f^0 - \Phi_f)$ against $1/[Li^+]$.

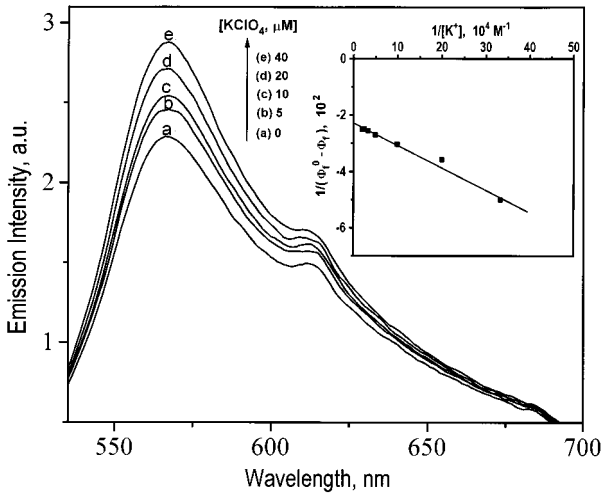


Figure 4. Change in the emission intensity of the squaraine molecular wire **4b** as a function of increasing K^+ concentration (λ_{exc} = 520 nm). The inset shows the plot of $1/(\Phi_f^0 - \Phi_f)$ against $1/[K^+]$.

Table 1. Effect of Addition of (40 μM) Li^+, Na^+, and K^+ on the Fluorescence Quantum Yield and Relative Fluorescence Enhancement of 4a, 4b, and 7a in DMSO

		$\Phi_f \times 10^2$			rel fluorescence enhancement		
substrate	$\Phi_f^0 \times 10^2$	Li^+	Na^+	K^+	Li^+	Na^+	K^+
4a	1.2	2.3	1.3	1.3	1.92	1.08	1.08
4b	1.4	1.7	1.43	1.8	1.21	1.02	1.28
7a	6.6	7.3	6.8	6.9	1.1	1.03	1.02

is observed. A similar plot for **4b** which is shown in Figure 6 revealed that both Li^+ and K^+ have shown some responses that are comparatively smaller than the response of **4a** against Li^+. Interestingly, addition of Na^+ could not make any significant change in the fluorescence emission of **4b** as in the case of **4a**. These observations reveal that **4a** shows a strong response which is specific to Li^+ whereas **4b** shows relatively weak responses against both Li^+ and K^+.

We have analyzed the stability constants and the nature of binding by applying the Benesi−Hildebrand equation to the fluorescence emission data obtained at various metal ion concentrations. A plot of $1/(\Phi_f^o - \Phi_f)$ versus the reciprocal of the metal ion concentration was

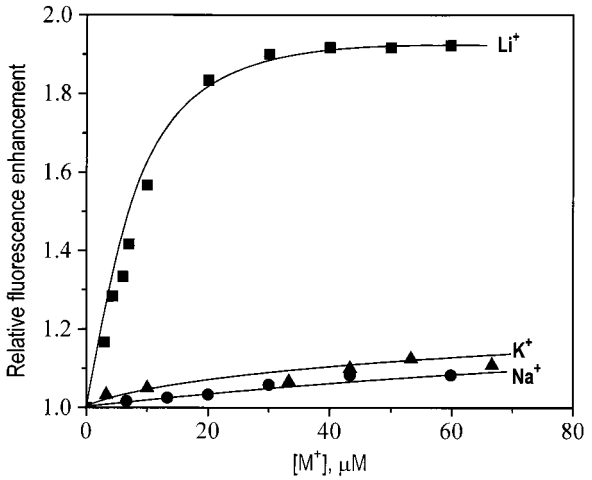


Figure 5. Effect of various alkali metal ion concentrations on the fluorescence quantum yield of **4a** (λ_{exc} = 520 nm).

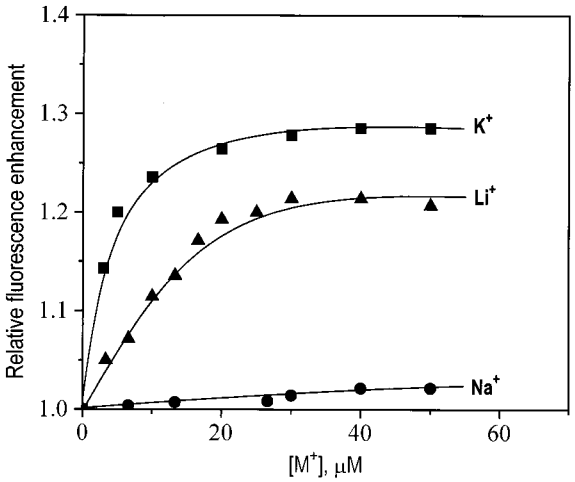
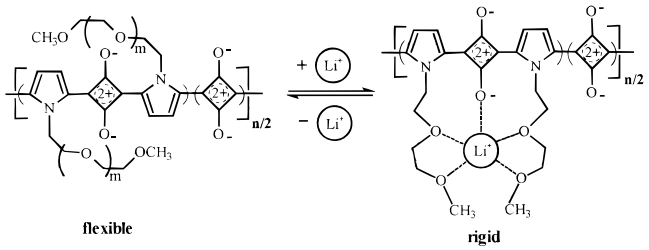


Figure 6. Effect of various alkali metal ion concentrations on the fluorescence quantum yield of **4b** (λ_{exc} = 520 nm).

Scheme 3



found to be linear as shown in the insets of Figures 3 and 4, which indicate the characteristic of a 1:1 complexation between the metal ion and the squaraine dye repeating unit of the molecular wires **4a** and **4b** (Scheme 3). The calculated stability constant of Li^+ for **4a** ($K_s = 3.5 \times 10^5\ M^{-1}$) is much higher than that of **4b** ($K_s = 5.14 \times 10^4\ M^{-1}$), which indicates a strong complexation between **4a** and Li^+. The strong binding of Li^+ to **4a** could be explained on the basis of the oxyethylene chain length and the electron affinity of the metal ion.

To study the role of the oligomeric structure of the molecular wires **4a** and **4b** in alkali metal ion recognition, their emission spectral changes were compared with those of the model squaraine dyes **7a** and **7b**. Changes in the emission spectrum upon the addition of Li^+ to a solution of **7a** are shown in Figure 7. As in the

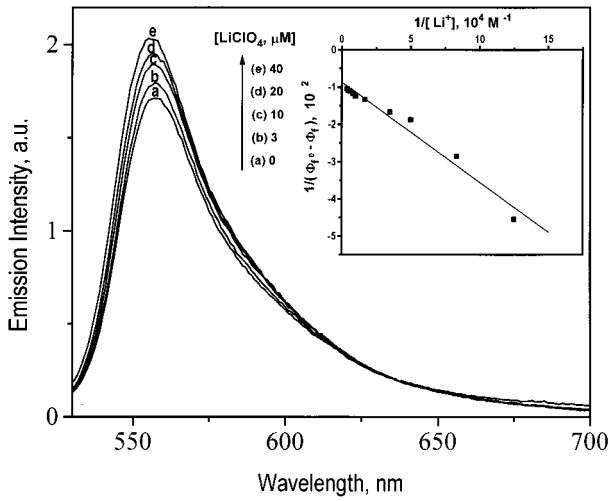


Figure 7. Change in the emission intensity of the model squaraine dye **7a** as a function of the Li^+ concentration (λ_{exc} = 520 nm). The inset shows the plot of $1/(\Phi_f^0 - \Phi_f)$ against $1/[Li^+]$.

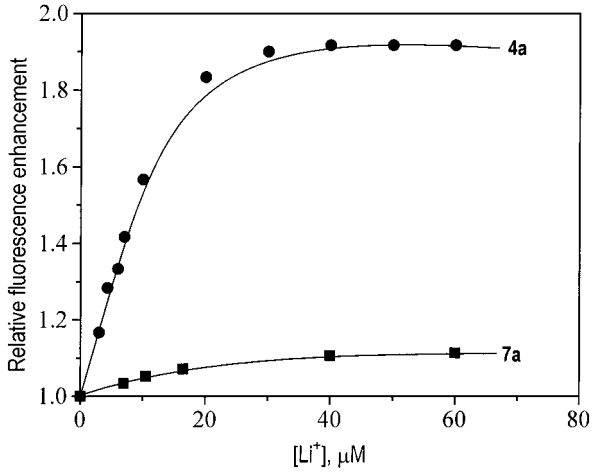


Figure 8. Comparison of the effect of Li^+ concentrations on the fluorescence emission quantum yields of the squaraine molecular wire **4a** and the model squaraine dye **7a**.

case of **4a**, the maximum response was observed against Li^+ whereas K^+ and Na^+ did not show any measurable change. Plots of the relative fluorescence quantum yield enhancement of the molecular wire **4a** and the model dye **7a** against the Li^+ concentration are shown in Figure 8 which reveals considerable signal amplification by the molecular wire **4a**. On the other hand, addition of Li^+, Na^+, and K^+ to a solution of **7b** did not show any measurable response either to the UV−vis spectrum or to the emission spectrum. These observations reveal that a mere complexation of the less conjugated model squaraine dyes with metal ion is not sufficient to produce a measurable response. Thus, it is apparent that the π-conjugated backbone of the molecular wires **4a** and **4b** has a significant role in amplifying the recognition event of a metal ion. This can be attributed to either a nonplanar to a near-planar or flexible to a rigid conformational changes associated with the strong binding of Li^+ which will become a collective amplified response when compared to the single molecular response of the monomeric squaraine dyes. However, the fact that the addition of metal ion could produce only a marginal response in the absorption spectrum of **4a** in contrast to its emission spectral changes reveals that a

nonplanar to planar conformational change is unlikely during the metal ion recognition. Therefore, the observed response in the emission properties of **4a** against Li^+ can be rationalized on the basis of a flexible to rigid conformational locking upon the metal ion binding as shown in Scheme 3. The observed low amplification and specificity of the molecular wire **4b** when compared to **4a** could be due to the increased flexibility of the binding sites of the former leading to more labile complexation.

In conclusion, we have prepared two new squaraine-based molecular wires **4a** and **4b**, and their alkali metal ion sensing behavior has been compared with the model squaraine dyes **7a** and **7b**. Even though addition of Li^+ produces only minor changes in the absorption spectra of both **4a** and **4b**, significant changes in the emission spectra could be noticed. The fluorescence spectrum of **4a** showed a selective and enhanced response toward Li^+ over Na^+ and K^+ whereas **4b** showed relatively weak responses toward Li^+ and K^+. Both **4a** and **4b** did not show any response toward Na^+. Surprisingly, the less conjugated model compounds **7a** and **7b** showed very marginal changes to their absorption or emission properties on adding Li^+, Na^+, or K^+. This observation reveals that conjugation to the extent of a few nanometers may be necessary to produce measurable changes in the emission signal at the event of an ion recognition.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer model 883 infrared spectrometer. The electronic absorption spectra were recorded on a GBC double beam UV−vis spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL EX90 spectrometer using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Molecular weights were determined on Shimadzu LC 6A GPC system equipped with a RI detector. Fluorescence measurements were performed on a SPEX fluorimeter. Quantum yields of fluorescence were measured by the relative method using optically dilute solutions with Rhodamine 6G ($\Phi_f = 0.9$) in ethanol as reference. Corrections have been made in fluorescence quantum yield measurements for the changes in the absorbance at the excitation wavelength. Spectroscopic solvents were used throughout. Metal ion binding studies were carried out in DMSO using the corresponding metal perchlorates unless otherwise stated.

Preparation of 2-(Methoxyethoxy)ethyl Bromide (2a). A dry, nitrogen-purged flask was charged with diethyl ether (100 mL) and diethylene glycol monomethyl ether (**1a**) (5.9 mL, 50 mmol), and the mixture was cooled to 0 °C. To this solution was added dropwise phosphorus tribromide (2.4 mL, 25 mmol). After the addition, the reaction mixture was stirred at 0 °C for 10 min. To this solution, methanol (7 mL) was added, and the reaction mixture was allowed to warm to room temperature. The stirring was continued for 30 min, and the reaction mixture was poured into water (10 mL). The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (5 × 10 mL). The combined organic extracts were washed with 5% sodium bicarbonate (1 × 10 mL) and brine (1 × 10 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure to afford 6.5 g (71%) of the title compound as a colorless clear liquid. IR: ν_{max} (neat) 2890, 1463, 1361, 1270, 1201, 1116, 981 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.35 (3 H, s, CH_3), 3.4−3.7 (6 H, m, CH_2), 3.75 (2 H, t, $J = 6.3$ Hz, CH_2Br). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 29.86, 58.68, 70.08, 70.8, 71.54. Mass spectrum: m/z 183 ($M^+ + 1$, 8), 181 (9), 153 (16), 151 (17), 109 (97), 107 (100), 89 (40), 87 (9).

Preparation of 2-[(Methoxyethoxy)ethoxy]ethyl Bromide (2b). Compound **2b** (7.5 g, 67%) was prepared from triethylene glycol monomethyl ether (8 mL, 50 mmol) and phosphorus tribromide (2.4 mL, 25 mmol) employing the same procedure used for the preparation of 2-(methoxyethoxy)ethyl bromide. IR: ν_{max} (neat) 2870, 1450, 1351, 1278, 1198, 112, 1025 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.36 (3 H, s, CH_3), 3.42−3.72 (10 H, m, CH_2), 3.78 (2 H, t, $J = 6.3$ Hz, CH_2Br). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 30.07, 42.39, 58.74, 70.35, 71.00, 71.18, 71.75. Mass spectrum: m/z 228 ($M^+ + 1$, 7), 226 (8), 181 (9), 153 (16), 151 (17), 109 (97), 10.7 (100), 89 (40), 87 (9).

Preparation of *N*-[(Methoxyethoxy)ethyl]pyrrole (3a). A nitrogen-purged flask equipped with a reflux condenser was charged with methylene chloride (10 mL), tetrabutylammonium bromide (3.71 g, 11.5 mmol), pyrrole (79 mL, 11.5 mmol), and 2-(methoxyethoxy)ethyl bromide (1.93 g, 10.52 mmol), and the mixture was cooled to 0 °C using an ice bath. To this solution was added dropwise 50% solutions of sodium hydroxide (10 mL). After the addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (5 mL), and the aqueous phase was extracted with ethyl acetate (5 × 5 mL). The combined organic extracts were washed with 3 N hydrochloric acid (1 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, ether/hexane (9:1)) to afford 1.2 g (67%) of the title compound as an yellow liquid, bp 103−110 °C/15 mm. IR: ν_{max} (neat) 3098, 2871, 1503, 1450, 1347, 1280, 1196, 934, 848, 725 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.35 (3 H, s, CH_3), 3.45−3.8 (6 H, m, CH_2), 4.05 (2 H, t, $J = 5.6$ Hz, NCH_2), 6.11 (2 H, t, $J = 2.1$ Hz, aromatic), 6.68 (2 H, t, $J = 2.1$ Hz, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 42.48, 58.89, 70.44, 71.27, 71.78, 107.99, 120.86. Mass spectrum: m/z 169 (M^+, 55) 137 (13), 124 (5), 111 (30), 94 (30), 80 (100), 67 (20).

Preparation of *N*-[[(Methoxyethoxy)ethoxy]ethyl]pyrrole (3b). This compound (1.45 g, 64%) was prepared from 2.38 g (10.52 mmol) of 2-[(methoxyethoxy)ethoxy]ethyl bromide and 0.77 g (10.52 mmol) of pyrrole using the same procedure described for the preparation of *N*-[(methoxyethoxy)ethyl]-pyrrole. IR: ν_{max} (neat) 3099, 2873, 1500, 1450, 1348, 1282, 1195, 1108, 934, 847, 723 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.36(3 H, s, CH_3), 3.61−3.50 (8 H, m, CH_2), 3.72 (2 H, t, $J = 5.6$ Hz, OCH_2), 4.04 (2 H, t, $J = 5.6$ Hz, NCH_2), 6.11 (2 H, t, $J = 2.1$ Hz , aromatic), 6.68 (2 H, t, $J = 2.1$ Hz). ^{13} C NMR ($CDCl_3$, 22.5 MHz): δ 49.66, 59.23, 70.75, 70.80, 70.85, 71.50, 72.15, 108.28, 121.19. Mass spectrum: m/z 213 (M^+, 15), 181 (3), 155 (15), 138 (9), 125 (6), 111 (20), 94 (47), 80 (100), 67 (31).

Preparation of the Squaraine Molecular Wire 4a. A dry, nitrogen-purged flask was charged with 20 mL of 1-butanol and 20 mL of benzene, 0.34 g (2 mmol) of *N*-[(methoxyethoxy)ethyl]pyrrole, and 0.22 g (2 mmol) of squaric acid. The reaction mixture was refluxed for 12 h, and the water formed was removed azeotropically. The reaction mixture was concentrated, and the pasty liquid was poured into excess of petroleum ether. The precipitated product was filtered, washed with hexane, and dissolved in the minimum amount of DMSO. The DMSO solution was poured into hexane, and the precipitated product was filtered and washed with hexane and diethyl ether. The solid product obtained was extracted thoroughly with methanol and chloroform. The combined extract was dried, and the solvent was removed under reduced pressure. The residue obtained was dried in a vacuum oven at 40 °C for 24 h to give 320 mg (62%) of **4a**. IR: ν_{max} (KBr) 2878, 1776, 1620, 1519, 1351, 1197, 1106, 846 cm^{-1}. λ_{max} (DMSO): 565 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.3−3.8 (9 H, m, CH_2), 4.80 (2 H, t, NCH_2), 6.20 (1 H, m, br, aromatic). Anal. Cacld for $(C_{13}H_{13}NO_4)_n$: C, 63.16; H, 5.26; N, 5.67. Found: C, 64.1; H, 5.73; N, 5.04.

Preparation of the Squaraine Molecular Wire 4b. The molecular wire **4b** (0.5 g, 56%) was prepared from 0.63 g (3 mmol) of *N*-[[(methoxyethoxy)ethoxy]ethyl]pyrrole and 0.33 g (3 mmol) of squaric acid under the same conditions employed for the preparation of polymer **4a**. IR: ν_{max} (KBr) 2950, 1782, 1735, 1675, 1628, 567, 1488, 1441, 1299, 1114, 936 cm^{-1}. UV λ_{max} (DMSO): 564 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 3.30−

3.80 (13 H, m, CH_2), 4.04 (2 H, t, NCH_2), 6.2 (2 H, m, br, aromatic). Anal. Calcd for $(C_{15}H_{17}NO_5)_n$: C, 61.85; H, 5.84; N, 4.81; Found: C, 61.2; H, 5.04; N, 5.1.

Preparation of the Model Squaraine Dye 7a. In a RB flask containing 1-butanol and benzene in the ratio of 1:3 (60 mL) was added *N*-[(methoxyethoxy)ethyl]pyrrole (169 mg, 1 mmol) under a nitrogen atmosphere. To this, squaric acid (57 g, 0.5 mmol) was added in three portions over a period of 1 h under reflux. The refluxing was continued for 8 h while the water formed was removed azeotropically. The deep bluish red solution formed was cooled, and the benzene was removed under reduced pressure at low temperature. The residue was poured into water, and the dye was extracted with hexane. The crude product obtained was purified on a silica column using chloroform as the eluting solvent. Yield, 83 mg (40%); mp 86−87 °C. IR: ν_{max} (dichloromethane) 2880, 1625, 1526, 1480, 1410, 1392, 1359, 1107, 1075, 1043, 758, 620 cm^{-1}. UV: λ_{max}(DMSO) 553 nm. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.75 (2 H, t, aromatic), 7.44 (2 H, s, aromatic), 6.41 (2 H, q, aromatic), 4.81 (4 H, t, $N-CH_2$), 3.73 (4 H, t, $O-CH_2$), 3. 73 (4 H, t, $O-CH_2$), 3.4 (4 H, t, $O-CH_2$), 3.27 (6 H, s, OCH_3).

Preparation of *N*-[(Methoxyethoxy)ethyl]-2,4-dimethylpyrrole (6). Compound **6** (2 g, 67%) was prepared from 1.43 g (15 mmol) of 2,4-dimethylpyrrole and 2.75 g (15 mmol) of 2-(methoxyethoxy)ethyl bromide according to the procedure described for the preparation of 4-[(methoxyethoxy)ethyl]-pyrrole. IR: ν_{max} (neat) 2934, 1699, 1562, 1458, 1412, 1199, 1112, 915 cm^{-1} . ^1H NMR ($CDCl_3$, 90 MHz): δ 1.95 (3 H, s, CH_3), 2.05 (3 H, s, CH_3), 3.35 (3 H, s, CH_3), 3.4−3.75 (6 H, m, CH_2), 3.85 (2 H, t, J = 2.1 Hz, CH_2), 5.65 (1 H, s, aromatic), 6.3 (1 H, s, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 11.63, 11.72, 58.89, 70.47, 71.06, 71.21, 71.78, 108.03, 117.39, 117.87, 128.02.

Preparation of the Model Squaraine Dye 7b. A mixture of *N*-(methoxyethoxy)ethyl-2,4-dimethylpyrrole (1 g, 5 mmol) and of squaric acid (0.29 g, 2.5 mmol) in 20 mL of 1-butanol and 10 mL of benzene was refluxed for 6 h under nitrogen, and the water formed was removed azeotropically. The reaction mixture was cooled, and the benzene was removed under reduced pressure. The reaction mixture was poured into water and extracted with dichloromethane. The solvent was removed, and the crude dye was recrystallized from a mixture of petroleum ether and dichloromethane. The crystallized dye was dried in a vacuum oven at 45 °C for 24 h to give 0.8 g (67%) of **7**; mp 95−96 °C. IR: ν_{max} (KBr) 2913, 1714, 1620, 1541, 1457, 1394, 1350, 1215, 1114, 963, 843 cm^{-1}. UV: λ_{max} (CH_3CN) 574 nm (13 800 M^{-1}), DMSO 583 nm (79 700 M^{-1}). ^1H NMR ($CDCl_3$, 90 MHz): δ 2.35 (6 H, s, CH_3), 2.64(6 H, s, CH_3), 3.29 (6 H, s, OCH_3), 3.42 (8 H, m, OCH_2), 3.67 (4 H, t, J = 4.5 Hz, OCH_2), 4.85 (4 H, t, J = 4.5 Hz, NCH_2), 6.04 (2 H, s, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 13.75, 15.18, 47.17, 58.86, 70.47, 71.81, 117.73, 126.62, 139.27, 148.51, 173.96, 176.29. Anal. Calcd for $C_{26}H_{36}N_2O_6$: C, 66.10; H, 7.63; N, 5.93. Found: C, 66.22; H, 7.81; N, 5.73.

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