

Enhanced Sensitivity and Selectivity in Lithium Ion Recognition Property of an Oligomeric Squaraine Dye Based Fluorescent Sensor

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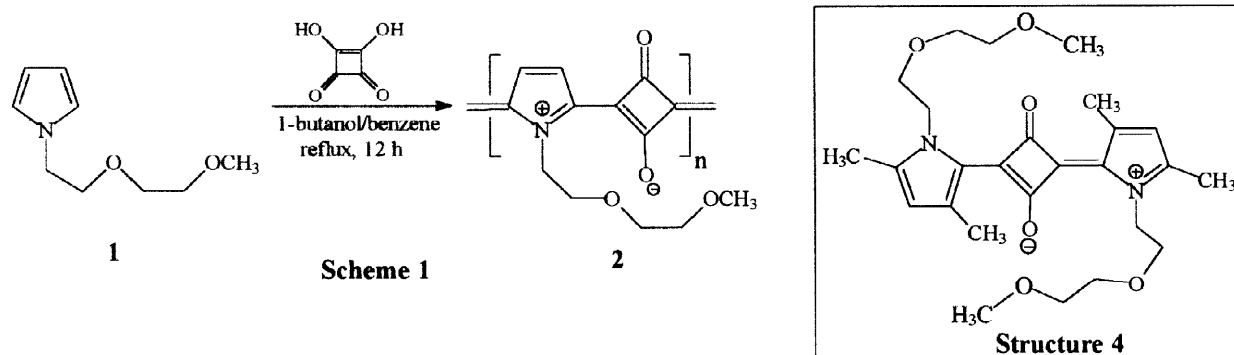
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Abstract: A novel fluorescent sensor based on a pyrrole-derived π -conjugated oligosquaraine containing diethylene glycol monomethyl ether side chain has been synthesized. This molecular wire based fluorescent sensor showed enhanced sensitivity and specificity towards the recognition of Li^+ when compared to Na^+ and K^+ . An analogous simple squaraine dye could not sense any of the metal ions. © 1998 Elsevier Science Ltd. All rights reserved.

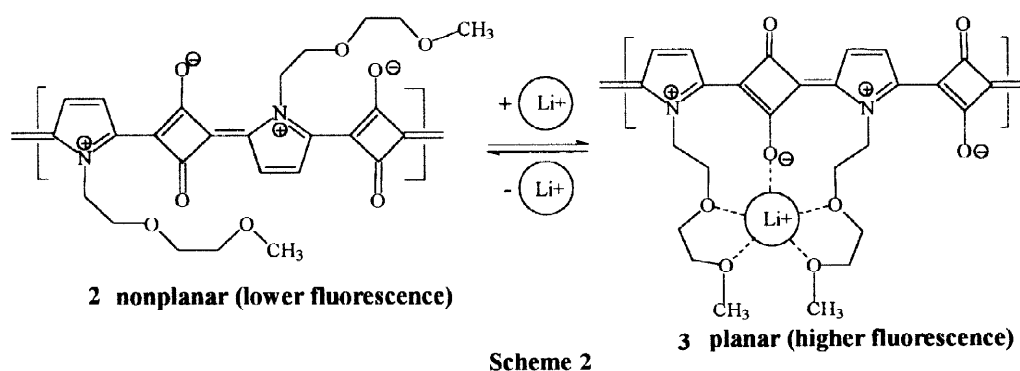
Molecule-based sensory devices such as fluorescent chemosensors have received considerable attention in recent years due to their potential use in several analytical applications.¹ Sensitivity enhancement in the reversible binding of an analyte by such systems to facilitate the real-time assay using simple analytical methods is a challenging area of research. A novel approach towards this direction is the use of π -conjugated polymers (molecular wires) containing covalently linked binding sites.^{2,3} When compared to the sensitivity of a single receptor sensory molecule, a molecular wire based sensory device shows enhanced response to a recognition event. The origin of this effect is attributed to the facile energy migration and/or conformational changes associated with the conjugated polymer backbone which become a collective response rather than that of the discrete units of the polymer.

Even though several conventional conducting polymer based chemoresistive and ionoresistive sensors are reported, a molecular wire based metal ion sensor in which a recognition event is detected through the response in its optical absorption or emission, are rather limited. In this context, metal ion sensors based on organic dye molecules having extended conjugation have great importance due to their interesting optical properties. Squaraine dyes would be appropriate candidates due to their strong absorption and emission properties in the visible and near infrared region.⁴ There are a few recent reports pertaining to the metal ion recognition properties of squaraine dye based fluoroionophores.⁵ The transduction mechanism in these systems are based on the fluorescence quenching of the fluoroionophore upon metal ion binding. We report here the use of a squaraine molecular wire which shows significant enhancement in its fluorescence emission which is specific for Li^+ in micromolar quantities.

The synthetic route for the new sensor **2** is shown in Scheme 1. The pyrrole derivative **1** was prepared as per literature procedures.^{2e,6} The polycondensation reaction of **1** with squaric acid was carried in a 1:1 mixture of 1-butanol and benzene, under azeotropic removal of water. The molecular wire **2** was



obtained in 62% yield. The molecular weight of **2**, determined by gel permeation chromatography (polystyrene standards, THF eluent) showed number average molecular weight around 1800 atomic mass unit. This corresponds to a molecular wire consisting of an average of 7-8 repeat units as shown in structure **2**. The IR spectrum of **2** showed strong absorption peak of the cyclobutane 1,3-diolate anion moiety around 1620 cm^{-1} which is characteristic of the resonance stabilized zwitterionic structure of squaraine dyes in general. The structure of **2** was proved by comparing its NMR spectral data with those of analogous macromolecular squaraine dyes, the structure of which are reported earlier by us.^{7,8} The absorption spectrum of **2** in DMSO showed a broad maximum at 564 nm with a shoulder around 602 nm. The emission spectrum of **2** in DMSO showed maxima around 574 nm with a Stoke shift of nearly 10 nm at an excitation wavelength of 520 nm.



Addition of micromolar quantities of alkali metal ions such as Li^+ , K^+ and Na^+ to a DMSO solution of **2** enhanced the absorption maxima with a marginal red shift. On the other hand, the squaraine molecular wire **2** showed significant change in its fluorescence emission behaviour upon addition of micromolar quantities of Li^+ (Figure 1). Interestingly, addition of micromolar quantities of K^+ and Na^+ did not show any considerable change to the emission property of **2**. The effect of various metal ions on the fluorescence quantum yield of **2** is shown in Figure 2. The squaraine molecular wire **2** showed a 92%

enhancement in the fluorescence quantum yield (Φ_f) upon addition of 40 μM of LiClO_4 , whereas addition of 40 μM KClO_4 or NaClO_4 induced only 8% enhancement in Φ_f . The observed specificity of **2** towards Li^+ can be attributed to the optimum chain length of the binding sites and the electron affinity of Li^+

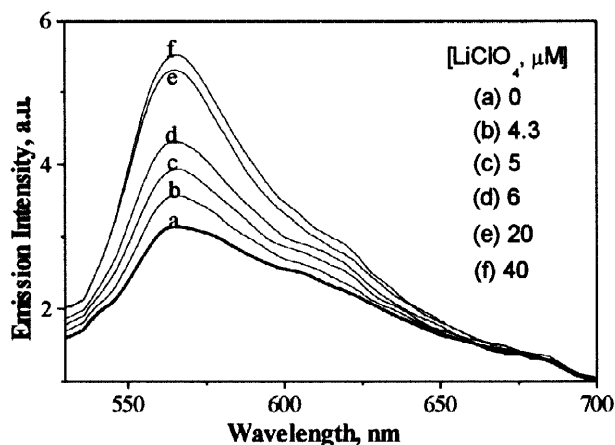


Figure 1. Effect of LiClO_4 on the fluorescence emission intensity of **2** in DMSO ($\lambda_{\text{exc}} = 520 \text{ nm}$).

which facilitate a better complexation. A model squaraine fluoroionophore **4**⁹ which was prepared by the condensation of squaric acid and N-[[[(methoxyethoxy)ethoxy]ethyl]-2,4-dimethylpyrrole under identical experimental conditions as that of **2**, showed only a marginal change to its fluorescence emission

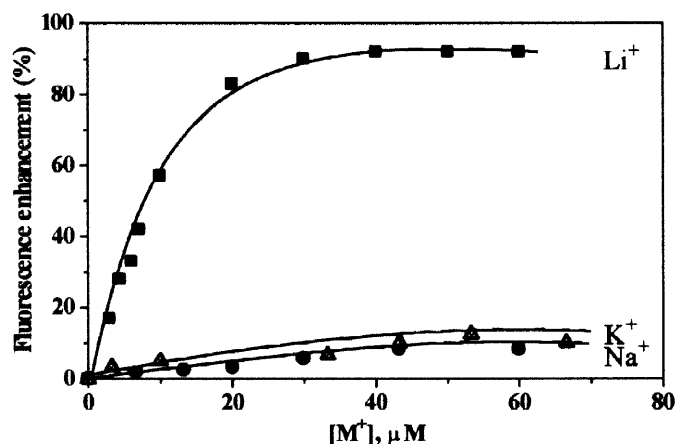


Figure 2. Plot of various alkali metal ion concentrations vs % fluorescence quantum yield enhancement ($\lambda_{\text{exc}} = 520 \text{ nm}$).

intensity upon the addition of micromolar quantities of alkali metal ions. The enhanced response of **2** towards Li^+ when compared to that of **4** can be attributed to the collective response associated with non-planar to planar conformational change of the repeat units of **2** which are wired together through extended π -conjugation. Even a small perturbation on the backbone conformation of the molecular wire **2** can bring about large changes to its optical emission properties.

In conclusion, we have designed a novel squaraine dye based molecular wire which shows enhanced sensitivity and significant selectivity in the recognition of Li^+ over Na^+ and K^+ when compared to a non-

wired squaraine dye **4**. Our preliminary results may lead to the designing of several related squaraine molecular wire based fluorescent sensors for the selective real-time assay of metal ions. Work in this direction is in progress.

ACKNOWLEDGMENTS

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8. Characterization data for **2**: IR ν_{\max} (KBr) 2878, 1776, 1620, 1519, 1351, 1197, 1106, 846 cm^{-1} ; ^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. calcd for $(\text{C}_{13}\text{H}_{13}\text{NO}_4)_n$: C, 63.16; H, 5.26; N, 5.67. Found C, 64.1; H, 5.73; N, 5.04.
9. Characterization of **4**: mp 95-96 $^\circ\text{C}$; IR ν_{\max} (KBr) 2913, 1714, 1605, 1541, 1457, 1394, 1350, 1215, 1114, 963, 843 cm^{-1} ; UV λ_{\max} (CH_3CN) 574 nm ($13\ 800\ \text{M}^{-1}$), DMSO 583 nm ($79\ 700\ \text{M}^{-1}$); ^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, s, OCH_2), 3.67 (4 H, t, $J = 4.5\ \text{Hz}$, CH_2), 4.85 (4 H, t, $J = 4.5\ \text{Hz}$, 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 $\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_6$: C, 66.10; H, 7.63; N, 5.93. Found: C, 66.22; H, 7.81; N, 5.73.