

A Controlled Supramolecular Approach toward Cation-Specific Chemosensors: Alkaline Earth Metal Ion-Driven Exciton Signaling in Squaraine Tethered Podands

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Abstract: Three different squaraine tethered bichromophoric podands 3a-c with one, two, and three oxygen atoms in the podand chain and an analogous monochromophore 4a were synthesized and characterized. Among these, the bichromophores 3a-c showed high selectivity toward alkaline earth metal cations, particularly to Mg2+ and Ca2+ ions, whereas they were optically silent toward alkali metal ions. From the absorption and emission changes as well as from the Job plots, it is established that Mg²⁺ ions form 1:1 folded complexes with 3a and 3b whereas Ca2+ ions prefer to form 1:2 sandwich dimers. However, 3c invariably forms weak 1:1 complexes with Mg²⁺, Ca²⁺, and Sr²⁺ ions. The signal output in all of these cases was achieved by the formation of a sharp blue-shifted absorption and strong quenching of the emission of 3a-c. The signal transduction is achieved by the exciton interaction of the face-to-face stacked squaraine chromophores of the cation complex, which is a novel approach of specific cation sensing. The observed cation-induced changes in the optical properties are analogous to those of the "H" aggregates of squaraine dyes. Interestingly, a monochromophore 4a despite its binding, as evident from ¹H NMR studies, remained optically silent toward Mg²⁺ and Ca²⁺ ions. While the behavior of 4a toward Mg²⁺ ion is understood, its optical silence toward Ca2+ ion is rationalized to the preferential formation of a "Head-Tail-Tail-Head" arrangement in which exciton coupling is not possible. The present study is different from other known reports on chemosensors in the sense that cation-specific supramolecular host-guest complexation has been exploited for controlling chromophore interaction via cation-steered exciton coupling as the mode of signaling.

Introduction

Supramolecular host-guest interaction and molecular recognition, particularly cation binding, is a subject of considerable interest due to its implications in many fields such as chemistry, biology, medicine, and environmental studies.¹ Such interactions will become useful when the host molecules are able to express the recognition event in the form of a measurable signal, invoking a change in one or more properties of the system such as redox potentials, absorption, or emission characteristics. The design of such molecular systems, chemosensors, the usual configuration of which consists of a macrocyclic receptor (ionophore) unit, integrated to an organic chromophore (fluorophore), is a topic of considerable interest.² Among various chemosensors, the design of cation-specific sensors for the selective detection of biologically important cations such as Na⁺, K^+ , Mg^{2+} , Ca^{2+} , and Zn^{2+} is of extreme importance.³ In this context, designing chemosensors for the specific recognition between alkali and alkaline earth metal cations is a challenging task.

There are several reports in the literature which pertain to chemosensors that selectively detect alkaline earth metal ions.⁴ Even though macrocyclic receptors are the widely used cation binding sites in these systems, reports on chromophore-linked pseudomacrocycle- or podand-based chemosensors are relatively few.^{5,6} For example, Nakamura et al. have reported several anthracene- or pyrene-linked podands, which specifically detect alkaline earth metal ions.⁶ In addition, there are a few recent

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Figure 1. Schematic representation of a chemosensor based on a cation-driven, exciton interaction in a dye-linked podand.

reports which pertain to macrocycle- and pseudomacrocyclebased ion recognition systems in combination with the supramolecular approach.⁷ Although none of these latter systems have been projected as chemosensors, they are interesting from the viewpoint of specific supramolecular recognition-induced allosteric effects,^{7a} chirality transfer,^{7b} and photochemistry.^{7c}

Signal transduction in most of the chemosensors is achieved either by photoinduced electron,^{5e-g,8} energy,^{5f} or charge-transfer processes,^{5a-c,9} by excimer formation,^{4h,6,10} or by conformational restrictions.¹¹ Therefore, the design of cation-specific chemosensors, which work on alternate ways of signal transduction, is

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of fundamental importance. This has prompted us to think of exciton interaction in organic dye aggregates as a potential signaling process of a specific cation binding event. The idea involves a cation-induced folding or dimerization of dye-linked podands to form complexes akin to organic dye aggregates in which exciton interaction in the bound complex produces measurable changes in optical and photophysical properties (Figure 1). We speculated that if face-to-face interactions of organic dyes similar to those of an "H" aggregate can be induced by a metal ion, the binding event could be expressed in the form of a measurable optical signal. For this purpose, we have selected squaraine dyes as the signal transducing chromophore for several reasons.

Squaraine dyes are a well-studied class of organic dyes having interesting optical and photophysical properties which are sensitive to the surrounding media.¹² This property of squaraine dyes has made them suitable for the design of a variety of materials including cation sensors.^{12d,13–15} However, the selectivity and sensitivity of these chemosensors to a specific analyte is very poor except in a few cases.^{15b,c} Recently, we have reported squaraine oligomer-based cation sensors, which are selective and sensitive, by applying Swager's concept of molecular wire-based signal amplification.^{16,17} Another striking property of squaraine dyes is their ability to form "J" (red-shift) or "H" (blue-shift) aggregates in appropriate solvent media.¹⁸ In the majority of the cases, they form "H" aggregates with a blue-shifted absorption band relative to the monomer.¹⁹ Re-

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Scheme 1



cently, Liang et al. have reported that squaraines, which are linked to flexible alkyl chains in a bichromophoric fashion, show exciton coupled spectral changes, depending upon the length of the alkyl chain.²⁰ However, this property of squaraine dyes has never before been exploited in the designing of chemosensors, until recently when we reported the Ca2+ ion-specific exciton interaction in a squaraine foldamer.²¹ In the present study, we illustrate a supramolecular approach in combination with cation-driven exciton interaction for the signaling of a specific cation binding, where the mode of complexation and chromophore interaction are controlled by the nature of the host and guest molecules.

Results and Discussion

Synthesis and Characterization of Squaraine Bichromophores 3a-c and the Monochromophore 4a. The bisaniline derivatives 1a-c and the squaric acid derivatives 2a and **2b** were prepared as per reported procedures.^{22,23} Reaction of 1a-c with the semisquaraine derivative 2a or 2b in a 1:2 stoichiometry, under reflux conditions in 2-propanol using tributyl orthoformate as catalyst, resulted in the formation of the bichromophores 3a-c in 20-25% yields along with small amounts of the monochromophores 4a-c (Scheme 1). In a separate experiment, the monochromophore 4a was synthesized in 32% yield by a controlled reaction between 1a and 2b in a 1:1 stoichiometry. FT-IR spectra of **3a-c** and **4a** showed a sharp band at 1590 cm⁻¹, characteristic of the C–O⁻ stretching of the zwitterionic squaraine dyes. ¹H NMR spectra of 3a-c in CDCl₃ showed resonance signals corresponding to -NCH₃, $-OCH_2$, and $-NCH_2$ protons at δ 3.1, 3.54, and 3.65 ppm,

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Table 1. Absorption and Emission Parameters for Compounds 3a-c and 4a in Acetonitrile

	absorption		emission ^a	
compound	λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ _{max} (nm)	$\Phi_{\mathrm{f}}{}^{b}$
3a	652 618 587 (sh)	120 226	664	0.008
3b	644 625	134 896	663	0.014
3c 4a	630 637	138 038 229 086	654 664	0.023 0.06

^a Solutions were excited at 570 nm, and emission was monitored in the region 600–750 nm for estimating $\Phi_{\rm f}$. ^b Fluorescence quantum yields were determined using 4,4-[bis-(N,N-dimethylamino)phenyl]squaraine dye as the standard ($\Phi_f = 0.7$ in CHCl₃), error limit $\pm 5\%$.

respectively. Due to the symmetry of the charge-delocalized zwitterionic structures of 3a-c, the aromatic protons appeared as two sets of four protons each at δ 6.7 and 8.3 ppm. The ¹H NMR spectrum of 4a in CDCl₃ showed two characteristic singlets at δ 3.1 and 2.86 ppm, corresponding to three protons each of the two -NCH₃ groups. The -NCH₂ and -OCH₂ protons appeared as multiplets around δ 3.5–3.75 ppm. In the aromatic region, five different signals could be seen. Signals at δ 8.2 and 6.7 ppm, which correspond to four protons, are assigned to the squaraine moiety. Signals at δ 7.2 and 6.7 ppm, corresponding to two protons each, and the signal at δ 6.6 ppm corresponding to a single proton are assigned to the aniline moiety. ¹³C NMR spectra of 3a-c and 4a, high-resolution mass spectra, and the elemental analyses data were in agreement with their assigned structures. The high-resolution mass spectra of $3\mathbf{a}-\mathbf{c}$ showed the characteristic $[M]^+$ ion peak, whereas the MALDI-TOF mass spectra showed the $[M + H]^+$ ion peak along with $[M + Na]^+$ and $[M + K]^+$ peaks.

Absorption and Emission Properties of 3a-c and 4a. The absorption and emission maxima and the fluorescence quantum

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Figure 2. Changes in the (a) absorption and (b) emission spectra of **3a** (3.6 μ M) in acetonitrile with the addition of Mg(ClO₄)₂. The arrows indicate the changes that result from progressively increasing the concentration of Mg(ClO₄)₂. Insets show variation of (a) absorbance at 548 nm and (b) fluorescence intensity at 664 upon increasing the ratio [Mg(ClO₄)₂]/[**3a**].

yields of 3a-c and 4a in acetonitrile are presented in Table 1. The bichromophore 3a showed an intense absorption maximum at 652 nm with two strong shoulders around 620 and 585 nm (Figure 2a). The fluorescence emission spectrum of 3a in acetonitrile $(3.6 \times 10^{-6} \text{ M})$ showed a maximum at 664 nm with a low quantum yield of 0.008 (Figure 2b). The absorption spectrum of 3b having two oxygen atoms in the podand chain exhibited two close maxima at 644 and 625 nm with a weak shoulder around 590 nm. The emission maximum of 3b was at 663 nm with a quantum yield of 0.014. Interestingly, 3c showed a sharp spectrum with absorption maximum at 630 nm and an emission maximum at 654 nm. The fluorescence quantum yield of 3c is 0.023, which is higher than those of 3a and 3b. The absorption and emission maxima of 4a in acetonitrile occurred at 637 and 664 nm, respectively, with a fluorescence emission quantum yield of 0.06, which is almost 8 times higher than that of 3a. The differences in the spectral pattern and the quantum yields of 3a-c are attributed to the oxyethylene chaindependent chromophore interaction, in analogy to the report by Liang et al.20

Cation Binding Properties of 3a-c: Changes in the Absorption and Emission Spectra. Changes in the absorption and emission spectra of 3a in acetonitrile (3.6×10^{-6} M) upon the addition of aliquots of Mg(ClO₄)₂ are shown in Figure 2. With an increasing amount of Mg(ClO₄)₂, the intensity of the absorption maximum at 652 nm is decreased with the concomitant growth of a new sharp band at 548 nm, through an isosbestic point at 570 nm. The inset of Figure 2a shows a plot of the absorbance at 548 nm against the ratio of the concentrations of Mg(ClO₄)₂ and 3a, which gets saturated when the concentration of the metal salt equals that of 3a indicating a 1:1 complexation



Figure 3. Changes in (a) absorption and (b) emission spectra of **3a** (3.6 μ M) in acetonitrile with the addition of Ca(ClO₄)₂. The arrows indicate the changes that result from progressively increasing the concentration of Ca(ClO₄)₂. Insets show variation of (a) absorbance at 548 nm and (b) fluorescence intensity at 664 nm with the ratio [Ca(ClO₄)₂]/[**3a**].

between the two. Similarly, upon addition of Mg(ClO₄)₂, the intensity of the emission band at 664 nm ($\Phi_f = 0.008$) gradually decreased with a marginal blue-shift (8 nm) when excited at 570 nm (Figure 2b). The quenching of the emission gets saturated ($\Phi_f = 0.004$) when the concentration of Mg(ClO₄)₂ reached nearly that of **3a**, indicating a 1:1 stoichiometry of binding (Figure 2b, inset).

Changes in the absorption and emission spectra of 3a (3.6 \times 10^{-6} M) induced by the addition of Ca(ClO₄)₂ in acetonitrile are shown in Figure 3, which are identical as in the case of $Mg(ClO_4)_2$. However, in the case of $Ca(ClO_4)_2$, the plot of absorbance at 548 nm reached a maximum when the ratio of the concentrations of the metal salt and **3a** reached a value of 0.5 (Figure 3a, inset). A same effect is observed when the ratio of the fluorescence intensities (I/I_0) was plotted against the ratio of concentration of Ca(ClO₄)₂ and **3a**, indicating a 2:1 stoichiometry for the complexation of 3a with Ca^{2+} ion. Similar changes in the absorption and emission spectra could be obtained when $Sr(ClO_4)_2$ was added to an acetonitrile solution of **3a**. However, addition of Ba(ClO₄)₂ to **3a** showed weak changes, indicating a very loose interaction between the two. Interestingly, addition of LiClO₄, NaClO₄, and KClO₄ did not induce any change in the absorption or emission properties of **3a**, revealing its high specificity toward alkaline earth metal cations. These observations are justified by a comparison of the plots of the fluorescence quantum yields (Φ_f) against the ratio of the concentrations of metal salt to the bichromophore **3a** (Figure 4).

To determine the role of the podand chain length on the cation sensing properties, the bichromophores **3b** and **3c** were subjected to detailed metal ion titration studies. Changes in the absorption



Figure 4. Plot of Φ_f versus the ratio of [metal salt] to [**3a**] illustrating the variation of fluorescence quantum yield of the bichromophore with various metal cations such as Ca²⁺ (**I**), Mg²⁺ (**O**), Sr²⁺ (**A**), Ba²⁺ (**V**), Na⁺ (**A**), K⁺ (**A**), and Li⁺ (**O**).



Figure 5. A 3D plot showing the selectivity and sensitivity of 3a-c toward various metal cations.

and emission spectra of 3b upon gradual addition of Mg(ClO₄)₂ and Ca(ClO₄)₂ are presented in the Supporting Information. Although these changes of 3b are similar to those of 3a, the former showed better selectivity and sensitivity toward Ca²⁺ ion. Addition of Sr(ClO₄)₂ and Ba(ClO₄)₂ showed weak response, whereas LiClO₄, NaClO₄, and KClO₄ had hardly any effect. The bichromophore 3b also formed a 1:1 complex with Mg^{2+} , whereas Ca^{2+} and Sr^{2+} ions showed a 1:2 complexation mode as in the case of 3a. In contrast to the behavior of 3a and 3b, the bichromophore 3c having a long podand chain (three oxygen atoms) invariably showed a 1:1 binding with $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, and $Sr(ClO_4)_2$. However, in these cases, the response toward the metal cations was relatively weaker when compared to those of 3a and 3b. A 3D plot of the percentage of fluorescence quantum yields of 3a-c against various metal cations reveals the effect of the podand chain on the selectivity and sensitivity on cation binding (Figure 5). From the fluorescence quenching data, the maximum sensitivity and selectivity are obtained for 3b. In all cases, the sensitivity was in the order $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$.

The difference in the complexation modes of 3a-c with Mg²⁺ and Ca²⁺ was confirmed by the corresponding Job plots.^{24,25} For example, the Job plots of 3a with Mg²⁺ and Ca²⁺ ions are shown in Figure 6. In the case of Mg²⁺ binding, the maximum absorbance of the complex is obtained when the mole fraction of the host (**3a**) has reached 0.5, which is a signature of a 1:1 stoichiometry (Figure 6a). However, for Ca²⁺, the maximum absorbance at 548 nm could be seen when the mole fraction of **3a** was at 0.66, which is characteristic of a host–guest binding in a 2:1 stoichiometry (Figure 6b). Similar results were obtained for **3b**. The Benesi–Hildebrand²⁶ plot for Mg²⁺ binding showed a good linear relationship of a 1:1 complexation with a binding constant of $6.15 \times 10^5 \text{ M}^{-1}$ for **3a** and $1.04 \times 10^6 \text{ M}^{-1}$ for **3b**. It must be noted here that in acetonitrile ($\epsilon = 38.8$) ambiguity exists regarding the complete dissociation of the metal salts. However, for bivalent metal cations in micromolar concentrations, we assume the complete dissociation of the metal salts and the resultant complexes are not ion paired.²⁷

¹H NMR Binding Studies of 3a with Ca(ClO₄)₂ and Mg- $(ClO_4)_2$. The effect of the addition of Mg $(ClO_4)_2$ and Ca $(ClO_4)_2$ to the ¹H NMR spectrum of **3a** in a mixture of 30% CD₃CN and 70% CDCl₃ is shown in Figure 7. After the addition of an equivalent amount of Mg(ClO₄)₂ or Ca(ClO₄)₂, the well-resolved resonance signals of 3a (Figure 7a) became broad and shifted toward upfield. For example, the signals at δ 8.3 and 6.8 ppm, which correspond to the squaraine aromatic protons, became very broad between δ 7.7–9.0 and δ 5.5–7.0 ppm, respectively. Similarly, signals corresponding to -NCH₃, -OCH₂, and $-NCH_2$ protons at δ 3.1, 3.54, and 3.65 ppm, respectively, were shifted toward lower δ values and merged to form broad signals. A considerable shift could also be noticed for the water signal at δ 2.1 ppm, toward low field after the addition of metal perchlorates, indicating the involvements of water molecules in the metal ion coordination processes. Interestingly, addition of LiClO₄, NaClO₄, or KClO₄ to **3a** did not show any change in the NMR spectrum, revealing no interaction between these cations with 3a, which is in agreement with the absorption and emission spectral studies.

Exciton Coupled Signaling of the Cation Binding Events. From the detailed analysis of the changes in the absorption and emission properties, and from the Job plots, it is clear that **3a** and **3b** form 1:1 complexes with Mg²⁺ ion whereas Ca²⁺ and Sr²⁺ ions prefer to form 1:2 complexes (Schemes 2 and 3). Mg²⁺ ion induces the folding of **3a** to form a foldamer, **5**, in a 1:1 stoichiometry, whereas Ca²⁺ ion prefers to form a 1:2 sandwich dimer, **6**, with **3a**. The difference in the absorption and emission properties of the cation complexes **5** and **6** from that of **3a** can be rationalized on the basis of the exciton interaction in the face-to-face stacked squaraine chromophores of the former. It is interesting to mention here that the cation-induced changes in the optical properties of **3a**–**c** are similar to those of the "H" aggregates of analogous squaraine dyes.¹⁹

In analogy to the exciton theory of dye aggregation, the cation-induced folding or dimerization of 3a-c results in the splitting of the excited-state energy levels of the complex into two, one of which is higher in energy and the other lower in

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Figure 6. Job plots for the binding of 3a with Mg^{2+} and Ca^{2+} ions: (a) 1:1 complexation with Mg^{2+} ; (b) 2:1 complexation with Ca^{2+} .



Figure 7. ¹H NMR spectra in 30% CD₃CN-70% CDCl₃ of **3a** (a) before addition of metal perchlorates (2.3 mM), (b) with 2.3 mM Mg(ClO₄)₂, and (c) with 2.3 mM Ca(ClO₄)₂.

energy.²⁸ The spectral shift $(\Delta \nu)$ associated with the electronic transition in such cases will be determined by the tilt angle α of the transition dipole moments of the cation-complexed chromophores with the line of centers, which is given by the equation,

$$\Delta\nu \text{ (dimer)} = h^{-1} \langle m^2 \rangle (1 - 3\cos^2\alpha)/r^2 \tag{1}$$

where *h* is Planck's constant, *r* is the separation of the molecular centers, and $\langle m^2 \rangle$ is the dipole moment of the dye monomer.²⁹ From this relationship, it can be seen that when α becomes greater than 54°44′, the value of $\Delta \nu$ changes to positive, indicating a hypsochromic shift, and reaches a maximum when α becomes 90°. In the case of the folded complex **5** and the sandwich dimer **6**, the squaraine chromophores are face-to-face stacked as in the case of "H" aggregates where α tends to approach 90°. As a result, the excited state of the complex will

be shifted to higher energy, resulting in a blue-shifted absorption. Consequently, the emission of the bound complexes is weak because the internal conversion from the upper excited state to the lower one is very fast and the emission from the lower excited state is theoretically forbidden.

Cation Binding Property of the Monochromophore 4a. In light of the cation binding behavior of the bichromophores 3a-c, we speculated that a monochromophore 4a might be able to distinguish between Mg²⁺ and Ca²⁺ ions. The rationale for this speculation was that signaling would not be possible in the 1:1 folded complex of 4a with Mg^{2+} where exciton coupling is not possible. However, signaling will be possible in a 1:2 complex of 4a with Ca²⁺, in the event of a face-to-face stacking of the squaraine chromophore. However, 4a was optically silent toward both Mg²⁺ and Ca²⁺ ions. While this is understood for Mg²⁺ ions, the silence of Ca²⁺ ions against **4a** was surprising, which is rationalized by considering the two statistical complexation modes of 4a with Ca^{2+} ions as shown in Scheme 4. The "Head-Tail-Head-Tail" (H-T-H-T) arrangement 7 is expected to give an exciton coupled blue-shifted spectrum with Ca²⁺ ion, whereas the "Head-Tail-Head" (H-T-T-H) arrangement 8 should be optically silent. Because the absorption or emission spectra of 4a did not change upon addition of Ca(ClO₄)₂, it is reasonable to assign the "H-T-T-H" assembly 8 for the 2:1 complex of 4a with Ca^{2+} ion in which the two squaraine chromophores are positioned away from each other, thereby preventing exciton interaction between the chromophores.

In the context of the above observations, it is important to see that **4a** is optically silent toward Mg²⁺ and Ca²⁺ ions despite their binding to 4a. This is proved by the ¹H NMR studies of 4a in CD₃CN in the presence of Mg^{2+} and Ca^{2+} ions (Figure 8). In both cases, considerable changes to the resonance signals could be noticed upon addition of the metal perchlorates. Signals corresponding to the aromatic protons of the squaraine moiety at δ 6.87 and δ 8.2 ppm became broad and weak. The signal at δ 3.1 ppm corresponding to the N-CH₃ protons, attached to the squaraine moiety, is shifted upfield and merged with the N-CH₃ protons of the aniline moiety, which appeared at δ 2.86 ppm. The multiplets at δ 3.44–3.65 ppm corresponding to the -OCH₂ and -NCH₂ protons underwent considerable shift toward high field, particularly the -NCH₂ protons. It is interesting to note that the resonance signals at δ 6.6–6.68 and δ 7.14 ppm, which correspond to the aromatic protons of the aniline moiety of 4a, did not show many changes in the presence of Ca(ClO₄)₂ whereas addition of Mg(ClO₄)₂ induced consider-

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Scheme 2. Mg2+ Ion Induced Folding of 3a to a 1:1 Folded Dimer



Scheme 3. Ca2+ Ion Binding of 3a To Form a 2:1 Sandwich Dimer



able broadening. These observations indicate that, in the 1:1 folded complex of **4a** with Mg²⁺, the aniline moiety experiences considerable interaction with the squaraine moiety whereas in the case of the "H-T-T-H" sandwich dimer of **4a** with Ca²⁺, the aniline moieties seem to be slightly displaced from the squaraine chromophore. Thus, while the NMR experiments clearly support the binding of Ca²⁺ to **4a**, the absorption and emission studies strongly favor the "H-T-T-H" arrangement for the complex where there is no possibility for exciton interaction as shown in Scheme 4, which justify its optical silence toward the Ca²⁺ ion.

Conclusions

In the present study, we have illustrated a rational supramolecular approach in controlling and expressing the binding of specific cations, invoking exciton interaction as the mode of optical signaling, which is different from other known signaling mechanisms. The results obtained from the absorption, emission, and ¹H NMR studies revealed the difference in the supramolecular control of the binding modes of the bichromophores

3a-c and the monochromophore 4a with Mg²⁺ and Ca²⁺ ions. From the absorption and emission changes and from the Job plots, it is clear that **3a** and **3b** bind with Mg²⁺ ion to form intramolecular 1:1 foldamers whereas Ca2+ ion prefers to bind in a 1:2 stoichiometry leading to intermolecular sandwich dimers. However, the bichromophore 3c invariably forms 1:1 folded complexes with Mg²⁺ and Ca²⁺ ions. However, addition of LiClO₄, NaClO₄, or KClO₄ did not bring any difference in the absorption or emission properties of 3a-c, making them selective toward alkaline earth metal ions. Interestingly, the monochromophore 4a is optically silent toward Mg²⁺ and Ca²⁺ ions. While this is clear in the case of Mg²⁺ ion, the optical silence of 4a toward Ca²⁺ ion is rationalized on the basis of the preferential complexation in a "H-T-T-H" arrangement where exciton coupling of the chromophore is not allowed. The present study is different from other reports on chemosensors in the sense that the cation-specific supramolecular host-guest interaction has been exploited for controlling and expressing ion recognition via chromophore interaction, which in turn



Figure 8. ¹H NMR spectral changes (300 MHz, 300 K) of **4a** (3.52 mM) in CD₃CN (a) before addition of metal perchlorates, (b) after addition of Ca(ClO₄)₂ (3.52 mM), and (c) after addition of Mg(ClO₄)₂ (3.52 mM).

Scheme 4. Possible Complexation Modes of 4a with Ca(CIO₄)₂



Head-Tail-Tail-Head arrangement

becomes the key process in the signal transduction. The present approach successfully could translate changes in the photophysical properties associated with a dye aggregation to a measurable signal, making use of the cation-specific supramolecular organization of chromophore-linked podands. In addition, the present study demonstrates how organic dye aggregation, a well-studied phenomenon with respect to organic semiconducting devices³⁰ and supramolecular chemistry,³¹ becomes important in the design of cation selective chemosensors.

Experimental Section

Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents used were purified and dried by standard methods prior to use. Melting points were determined with a Mel-Temp-II melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Nicolet Impact 400D infrared spectrophotometer. ¹H and ¹³C NMR spectra were measured on a 300 MHz Bruker Avance DPX spectrometer using TMS as internal standard. High-resolution mass spectra were recorded in a Finnigan MAT 95 instrument using xenon as ionization gas. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Perseptive Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. Elemental analyses were done using a Perkin-Elmer series-II 2400 CHN analyzer. The emission spectra were measured on a Spex-Fluorolog F112X spectrofluorimeter. Fluorescence quantum yields were determined in spectroscopic grade CH₃CN using optically matching solutions

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of 4,4-[bis-(*N*,*N*-dimethylamino)phenyl]-squaraine dye ($\Phi_f = 0.70$ in chloroform) as standard. The stability constants (K_s) were determined from the absorption spectral changes using the equation,

$$\frac{A_0}{(A_0 - A)} = \frac{\epsilon_{\rm L}}{\epsilon_{\rm L} - \epsilon_{\rm ML}} \left(\frac{1}{K_{\rm s}[{\rm M}]} + 1 \right)$$

where ϵ_L and ϵ_{ML} are the molar extinction coefficients of the ligand and the complex, respectively. The quantity $A_0/(A_0 - A)$ is plotted versus 1/[M], and the stability constant is then obtained from the ratio intercept/ slope.

General Procedure for the Metal Ion Binding Studies. Metal perchlorate solutions were prepared in spectroscopic grade acetonitrile. The bichromophores 3a-c were dissolved in acetonitrile under sonication and warming in a water bath. Metal ion titrations were carried out by adding small volumes $(1-5 \ \mu L)$ of the metal salt solutions $(10^{-6} \text{ M in CH}_3\text{CN}, 4 \text{ mL})$ in a quartz cuvette. After the addition of metal perchlorate solution to the cuvette using a microliter syringe, the solution was shaken well and was left to stand for 1 min before recording the absorption and emission spectra of the metal complexed dye.

General Procedure for the Preparation of the Bichromophores 3a-c. To a 100 mL round-bottomed flask containing 50 mL of 2-propanol were added the appropriate bisaniline derivative (0.35 mmol), *N*,*N*-(dialkylamino)phenyl-4-hydroxy cyclobut-3-ene-1,2-dione (0.86 mmol), and tributyl orthoformate (1 mL). The reaction mixture was then refluxed for 20 h. The hot reaction mixture was filtered, and the solid was washed with 2-propanol until the filtrate was almost colorless. Column chromatography (chloroform/methanol, 9:1) of the crude product over silica gel (100–200 mesh) gave the pure product. Yields, melting points, and spectral details of each product are given below.

3a. Yield: 25%. mp 230–232 °C. FT-IR (KBr): $\nu = 1590$, 1481, 1398, 1351, 1175, 1113, 984, 917, 839, 787 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.96–1.01 (t, J = 7.28 Hz, 12H, –CH₃), 1.36–1.6 (m, 16H, –CH₂), 3.10 (s, 6H, –NCH₃), 3.41–3.46 (m, 8H, –NCH₂), 3.65–3.67 (m, 8H, –NCH₂, –OCH₂), 6.70–6.77 (dd, J = 1.23, 9.3 Hz, 8H, aromatic), 8.35–8.39 (dd, J = 2.4, 9.2 Hz, 8H, aromatic) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 13.8, 20.2, 29.6, 39.5, 51.2, 52.3, 69, 112.3, 112.4, 119.5, 120.2, 132.8, 133.6, 153.8, 183.3, 187.5, 189.3 ppm. HRMS-FAB: [M]⁺ calcd for C₅₄H₆₆N₄O₅, 851.5111; found, 851.5103.

3b. Yield: 27%. mp 236–238 °C. FT-IR (KBr): $\nu = 1589$, 1460, 1390, 1367, 1181, 1129, 875 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.907–0.99 (t, J = 7.27 Hz, 12H, –CH₃), 1.37–1.63 (m, 16H, –CH₂), 3.14 (s, 6H, –NCH₃), 3.42–3.64 (m, 20H, –NCH₂, and –OCH₂), 6.69–6.77 (dd, J = 1.4, 9.32 Hz, 8H, aromatic), 8.33–8.36 (dd, J = 2.3, 9.25 Hz, 8H, aromatic) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 13.8, 20.2, 29.4, 39.5, 51.2, 52.3, 68.7, 70.93, 112.4, 112.9, 119.5, 120, 132.8, 133.5, 153.8, 183.4, 187.6, 189.2 ppm. Anal. Calcd for C₅₆H₇₀N₄O₆: C, 75.14; H, 7.88; N, 6.26. Found: C, 74.96; H, 7.96;

N, 6.10. HRMS-FAB: $[M]^+$ calcd for $C_{56}H_{70}N_4O_6$, 895.5374; found, 895.5385.

3c. Yield: 18%. mp 265–268 °C. FT-IR (KBr): $\nu = 1588$, 1483, 1365, 1176, 1120, 938, 833, 784 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 3.14–3.16 (m, 18H, –NCH₃), 3.54–3.65 (m, 16H, –NCH₂, and –OCH₂), 6.73–6.78 (dd, J = 1.35, 9.3 Hz, 8H, aromatic), 8.3–8.36 (dd, J = 2.25, 9.1 Hz, 8H, aromatic). ¹³C NMR: δ 39.66, 40.29, 52.38, 68.53, 70.52, 70.58, 70.63, 70.89, 112.35, 112.53, 119.86, 120.2, 133.17, 154.77, 154.98, 183.36. MALDI-TOF MS (MW = 770.922): $m/z = 771.09 [M + H]^+$. Anal. Calcd for C₄₆H₅₀N₄O₇: C, 71.67; H, 6.54; N, 7.27. Found: C, 71.36; H, 6.78; N, 7.06.

Preparation of the Monochromophore 4a. To a 100 mL roundbottomed flask containing 50 mL of 2-propanol were added 1a (100 mg, 0.35 mmol), 2b (105 mg, 0.35 mmol), and tributyl orthoformate (1 mL). After being refluxed for 12 h, the hot reaction mixture was filtered, and the solid was washed with 2-propanol until the filtrate was almost colorless. Column chromatography (chloroform/methanol, 95:5) of the crude product over silica gel (100-200 mesh) gave the pure product 4a. Yield: 32%. mp 112–114 °C. FT-IR (KBr): $\nu =$ 1580, 1351, 1270, 1169, 1108, 784 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): $\delta 0.96 - 1.01$ (t, J = 7.26 Hz, 6H, $-CH_3$), 1.25 - 1.43 (m, 8H, -CH₂), 2.92 (s, 3H, -NCH₃), 3.13 (s, 3H, -NCH₃), 3.41-3.65 (m, 12H, -NCH₂, and -OCH₂), 6.7-6.77 (m, 7H, aromatic), 7.18-7.25 (t, J = 7.9 Hz, 2H, aromatic), 8.36–8.39 (dd, J = 2.35, 9.35 Hz, 4H, aromatic) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 13.8, 20.2, 29.6, 38.9, 39.5, 51.2, 52.3, 52.4, 68.7, 69.1, 112.1, 112.2, 112.3, 116.3, 119.4, 122.03, 129.1, 132.8, 133.5, 153.7, 183.4 ppm. MALDI-TOF MS (MW = 567.7): m/z = 568.3 [M + H]⁺. Anal. Calcd for C₅₆H₇₀N₄O₆: C, 76.16; H, 7.99; N, 7.40. Found: C, 75.84; H, 8.19; N, 7.54.

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Supporting Information Available: Synthetic details of **1a**-c, **2a**, and **2b**, changes in the absorption and emission properties of **3a** with $Sr(ClO_4)_2$, $Ba(ClO_4)_2$, $LiClO_4$, $NaClO_4$, and $KClO_4$, **3b** with $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$, and **3c** with $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$, plots of variation of quantum yield with $[M^{n+}]$, Job plots of **3b** with Mg^{2+} and Ca^{2+} ions, and Benesi-Hildebrand plots of **3a** and **3b** with Mg^{2+} ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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