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^{1}H NMR Spectral Evidence for a Specific Host–Guest Complexation Induced Charge Localization in Squaraine Dyes

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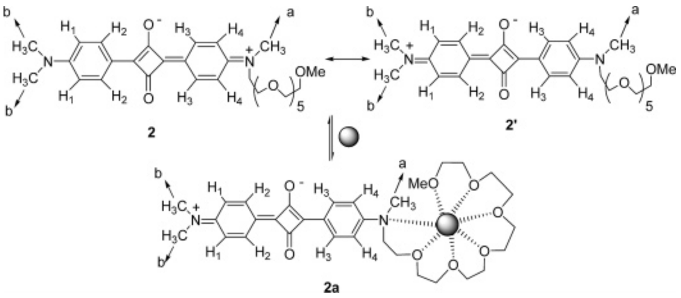
ABSTRACT



Experimental support is provided for the charge localization in squaraines, a class of fundamentally and technologically important organic dyes, by ^{1}H NMR analysis through a host–guest complexation approach. Specific binding of Ca^{2+} ions to the squaraine 2 with a podand sidearm resulted in a charge-localized structure 2a with dramatic shifts and resolution of the proton signals when compared to those of 2.

Squaraine dyes are important from both fundamental and technological viewpoints. They are extensively used in imaging process,[1] photovoltaics,[2] nonlinear optics,[3] sensor design,[4] photoconducting devices,[5] photodynamic therapy,[6] and the design of conjugated polymers.[7] They show sharp and intense absorption bands from visible to the near-IR wavelengths, depending upon the structure, due to a donor−acceptor−donor type of charge transfer and also due to the extensive conjugation.[8] Theoretical studies have proved that squaraine dyes show significant bond delocalization.[9] From crystallographic studies Dirk et al. have reported that the average C−C bond length in squaraines lies between single and double bonds, suggesting that there is an extensive delocalization of the electronic charge along the molecule, resulting in resonance structures as shown in Scheme 1.[10] Kazmaier et al. have demonstrated that a dipolar cyanine structure and not a cyclobutene diylium structure best

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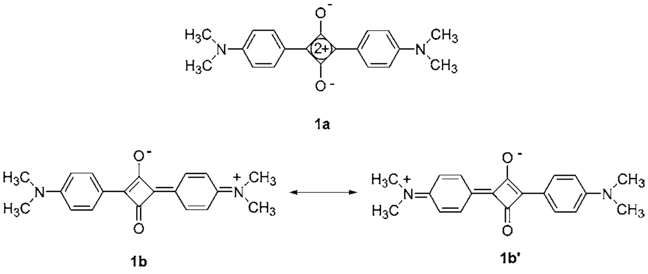
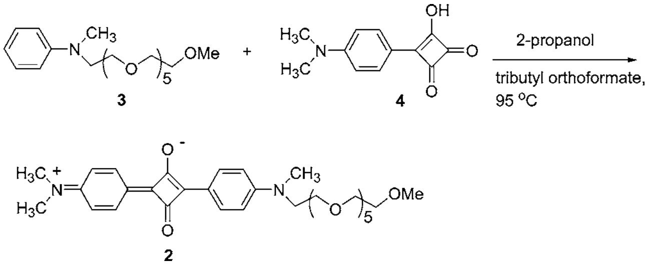
Scheme 1



represents the electronic configuration of these compounds.[11] They have been able to support the dipolar canonical structure with partial double bond character to the bond connecting the four-membered ring and the six-membered aromatic ring. These studies have established the zwitterionic structure that is the preferred structure for squaraines. Herein, we provide ^1H NMR experimental evidence for the charge localization, which is an indirect support for the zwitterionic structure of squaraines.

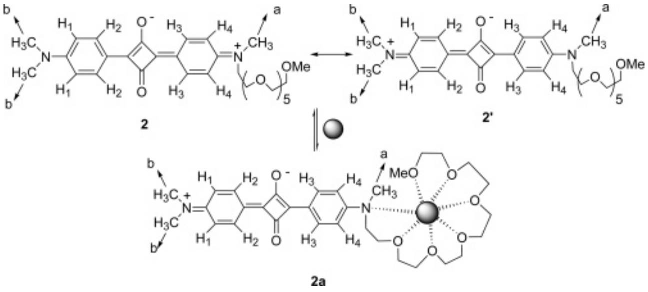
On the basis of our recent findings on squaraine foldamers as cation probes,[12,13] we speculated that an unsymmetrical squaraine dye with a podand sidearm upon binding of Ca^{2+} may localize the charge to the opposite nitrogen atom of the dye. To verify this hypothesis we studied Ca^{2+}-induced changes in the ^1H NMR spectrum of the squaraine dye **2**, which is prepared as shown in Scheme 2.

Scheme 2



Synthesis of **2** started with the preparation of *N*-(hexa(ethyleneoxy)methyl)-*N*-methylaniline **3** according to standard procedures starting from *N*-methyl aniline in 65% yield. The squaryl derivatve **4** was obtained by the reaction between *N*,*N*-dimethyl aniline and squaryl chloride.[14] Reaction between **3** and **4** in 2-propanol under refluxing in the presence of tributyl orthoformate yielded the squaraine dye **2** (32%, Scheme 2), which is characterized using FT-IR, ^1H, ^{13}C, $^1H-^1H$ COSY, NOESY, and ROESY NMR spectroscopic techniques, HRMS, and elemental analysis. The FT-IR and NMR spectral data indicate considerable charge delocalization in **2**, which could be due to the resonance hybridized canonical forms, **2** and **2′**, as shown in Scheme 3. There are

Scheme 3



four pairs of aromatic protons H1, H2, H3, and H4 and two different types of NCH_3 protons as indicated in Scheme 3.

The ^1H NMR spectrum of **2** in CD_3CN (Figure 1) shows two peaks at δ 3.18 and 3.17 ppm for the $-NCH_3$ (a) and $-NCH_3$ (b), respectively, corresponding to a total of nine protons. The singlet at δ 3.27 ppm is assigned to $-OCH_3$ protons. The multiplet observed at δ 3.69−3.72 ppm is attributed to $-NCH_2$ protons and the neighboring $-OCH_2$ protons. The multiplet at δ 3.42−3.57 ppm is due to the $-OCH_2$ protons. Two quartet like peaks observed at δ 7 and 8.2 ppm, which are comprised of four doublets, correspond to the four different pairs of aromatic protons H1, H2, H3, and H4. Each proton is characterized using $^1H-^1H$ COSY, NOESY, and ROESY analyses (Figures S1 and S2, Supporting Information). ^1H NMR ROESY and NOESY spectra indicate that $-NCH_3$ (a), and $-NCH_2$ proton signals couple with the H4 aromatic protons. The $^1H-^1H$ COSY experiments reveal that the H1 protons couple with H2 protons, indicating that they are neighboring pairs. Similarly H3 and H4 protons couple each other since they are a neighboring pair of aromatic protons.

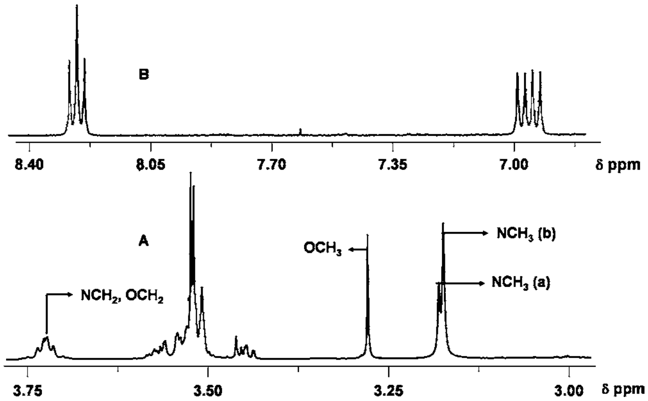


Figure 1. ^1H NMR spectrum of **2** (8.5 mM) in CD_3CN. (A) Aliphatic region. (B) Aromatic region.

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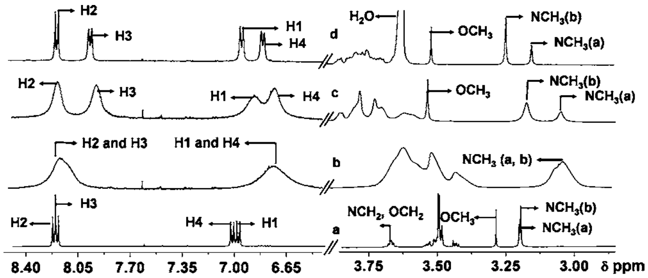

Figure 2. ^1H NMR spectral changes of **2** (8.55 mM) in CD_3CN before and after the addition of $Ca(ClO_4)_2$. [**2**:Ca^{2+}]: (a) [1:0], (b) [1:0.58], (c) [1:1.41], and (d) [1:10].

In acetonitrile, **2** showed an absorption maximum at 630 nm and an emission maximum at 657 nm with a quantum yield of 0.21. Addition of $Ca(ClO_4)_2$ to a solution of **2** in acetonitrile could not induce any changes in the absorption or emission properties, indicating that the structure or electronic properties of the molecule are not affected. However, ^1H NMR titration studies of **2** in the presence of $Ca(ClO_4)_2$ showed significant shift in the proton signals (Figure 2). During the initial additions, broadening and shift of the NMR signals were observed.[15] This could be due to the formation of complexes of different stoichiometry and due to the reversible exchange between the complexed and the uncomplexed states. However, subsequent additions of $Ca(ClO_4)_2$ clearly resolved the peaks due to the shift of the equlibrium toward complexation between the dye and $Ca(ClO_4)_2$. The most prominent changes are noticed for the H3 and H4 aromatic protons and the $-NCH_3$ (b) protons. The $-NCH_3$ protons that appeared together in the initial spectrum of the dye significantly resolved into two peaks at δ 3.12 ppm [$-NCH_3$ (a)] and δ 3.23 ppm [$-NCH_3$ (b)] after the addition of excess $Ca(ClO_4)_2$.

After the addition of 10 equiv of $Ca(ClO_4)_2$, $^1H-^1H$ NOESY (Figure 3) and $^1H-^1H$ ROESY (Figure S3, Supporting Information) spectra were recorded, which could distinguish between the aromatic protons H1, H2, H3, and H4 and the aliphatic protons, $-NCH_3$ (a), $-NCH_3$ (b), $-OCH_3$, and $-NCH_2$. Variable temperature NMR studies after adding $Ca(ClO_4)_2$ to **2** between 300 and 343 K showed a gradual change in the resonance signals of $-NCH_3$ protons, indicating the decomplexation of Ca^{2+} from the dye **2** (Figure 4). Binding of Ca^{2+} resulted in a downfield shift of the water peak from 2.13 to 3.68 ppm. This could be due to the coordination of the oxygen atom of the water molecule with Ca^{2+}, which weakens the O−H bond. Upon increasing the temperature, the water peak shifted toward upfield along with $-NCH_3$ protons to their initial position, suggesting the decomplexation of the metal ion at higher temperatures.

Since the positive charge of the dye **2** is equally distributed to the $-NCH_3$ (b) and $-NCH_3$ (a) moieties, these protons appeared together in the initial NMR spectrum as in Figure 1A. Upon Ca^{2+} binding, the positive charge is localized on the nitrogen atom opposite to the binding site. Consequently $-NCH_3$ (b) protons would be experiencing the least shielding, which is clearly exhibited by a downfield shift when compared to their original chemical shift value. On the other hand, the $-NCH_3$ (a) protons are shifted to the upfield relative to their initial chemical shift value. The separation of the H1, H4 and H2, H3 protons into four well-resolved doublets are a clear indication of the magnetic anisotropy of these protons due to the complexation-induced charge localization of the dye **2**. After complexation, protons on the aniline moiety, where the polyether chain is attached, experience more electron density than the uncomplexed state, as indicated by the upfield shift of these protons. Similarly the

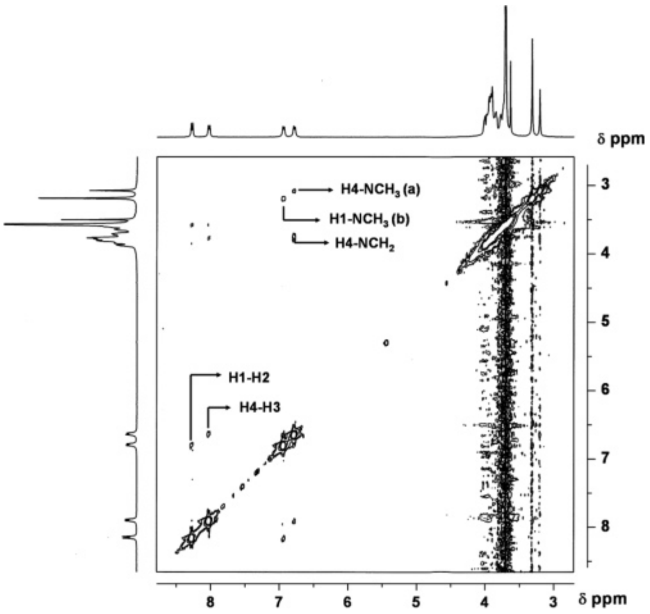

Figure 3. $^1H-^1H$ NOESY NMR spectra of the dye **2** (8.55 mM) after the addition of $Ca(ClO_4)_2$ (85.47 mM).

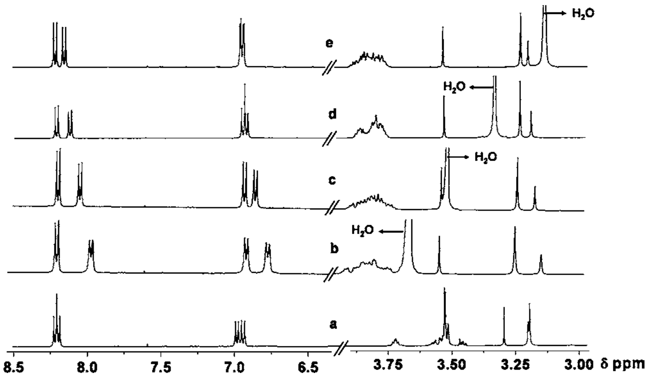

Figure 4. Temperature-dependent ^1H NMR spectra of **2** (8.55 mM) in CD_3CN (a) in the absence and in the presence of added $Ca(ClO_4)_2$ (85.47 mM) and measured at (b) 300, (c) 313, (d) 328, and (e) 343 K.

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[15] For similar observations, see: Kobiro, K.; Inoue, Y. *J. Am. Chem. Soc.* **2003**, *125*, 421.

-OCH_2 and -OCH_3 protons showed significant downfield shifts due to the decrease in electron density around the oxygen atom upon coordination with the Ca^{2+}. It must be noted that the neutral -OCH_3 protons experience more downfield shift when compared to that of the partly positive -NCH_3 (a) protons. These observations are in support of the involments of the -NCH_3 (a) group and the podand chain to the Ca^{2+} binding and the consequent charge localization as indicated in Scheme 3. Interestingly, addition of alkali metal salts such as $NaClO_4$ and $KClO_4$ did not show any change in the ^1H NMR spectrum of **2**, indicating that these metal ions do not bind with the dye.

In conclusion, through a rational approach, we provided experimental evidence for the charge localization in an unsymmetrical squaraine dye that specifically binds Ca^{2+} at the attached podand arm, which is an indirect support for the charge delocalized structure of squaraine dyes. ^1H NMR titration experiments of the dye in the presence of $Ca(ClO_4)_2$ showed remarkable resolution of the various proton signals as proof of the host−guest assisted charge localization within the dye molecule, thereby indicating that the initial ^1H NMR spectrum of the dye is an average of the charge delocalized resonance forms.

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Supporting Information Available: Synthetic details of **2**. NOESY, ROESY, and $^1H-^1H$ COSY NMR spectra and table showing change in the resonance signals of **2** with increasing Ca^{2+} ion concentration and temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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