

Chemistry of Squaraine-Derived Materials: Near-IR Dyes, Low Band Gap Systems, and Cation Sensors

AYYAPPANPILLAI AJAYAGHOSH*

Photosciences and Photonics Division, Regional Research Laboratory, CSIR, Trivandrum, 695019, India

Received October 18, 2004

ABSTRACT

Squaraines belong to an important class of organic dyes with intense absorption and emission properties in the visible to near-IR wavelength range. The optical properties of squaraines, which are sensitive to the surrounding medium, make them ideal candidates to photophysicists to study the excited-state properties and to material chemists for designing a variety of materials that are useful for wide-ranging applications. The present Account pertains to the recent developments in the materials chemistry of squaraines, highlighting our contributions to the study of squaraine-based near-IR dyes, low band gap polymers, and cation sensors.

Introduction

The quest for technological innovations is never-ending, which ensures the design of a plethora of advanced materials with new or improved properties for optimum device performance. The chemistry of functional organic dyes has made significant contributions to the development of electronic devices of modern times, particularly in the area of photon-based technologies such as optical data storage, imaging, and communications.¹ Squaraines are a novel class of organic dyes that play a crucial role in the design of a variety of photonic materials that are used for applications such as imaging, nonlinear optics, photovoltaics, biological labeling, and photodynamic therapy. The intense absorption and emission properties of squaraines, which are associated with the donor–acceptor–donor-type charge-transfer interaction, is ideally suited for applications related to the photosensitization phenomenon.² Therefore, in recent years, squaraine chemistry is at the center stage of research from fundamental and technological viewpoints.

Ayyappanpillai Ajayaghosh was born (1962) in Kerala, the southwest coastal state of India. After obtaining his Masters (1984) and Ph.D. (1988) in Chemistry from Calicut University, he joined the Regional Research Laboratory as a scientist. Subsequently, he was an Alexander von Humboldt Fellow at the Maxplanck Institut fuer Starhlenchemie, Muelheim an der Ruhr, Germany (1994–1996) and a visiting scientist to many universities in Germany, Japan, and The Netherlands. He is a recipient of the Young Scientist award of the Indian Science Congress Association (1988), Young Scientist Medal of the Indian National Science Academy (1991), and the Bronze Medal of the Chemical Research Society of India (2002). His research interests are in the broad area of organic and macromolecular materials chemistry, particularly the chemistry of π -conjugated systems, supramolecular chemistry, organic nanostructures, organogels, and chemosensors. Currently, he is a senior scientist of the Regional Research Laboratory and an Adjunct Professor of the Material Research Program of the Indian Institute of Technology, Kanpur, India.

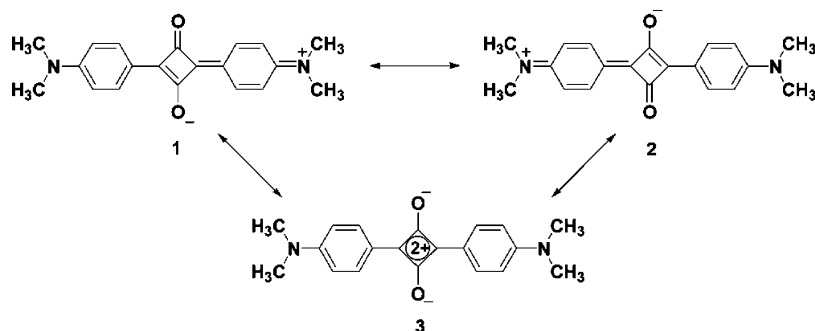
Squaraines belong to the class of polymethyne dyes with resonance-stabilized zwitterionic structures, a classical example of which is shown in Scheme 1. The genesis of squaraine dyes can be traced back to 1965 in the report of Triebs and Jacob,³ which pertains to the reaction of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid) with pyrrole (Scheme 2). Later, reports started appearing in the literature giving birth to a novel class of intensely colored organic dyes, which are generally prepared by the condensation of electron-rich aromatic or heterocyclic compounds such as *N,N*-dialkylanilines, benzothiazoles, phenols, azulenes, and pyrroles with squaric acid.⁴ It is Schmidt who coined the widely accepted name “squaraine” for this class of zwitterionic dyes.⁵ Access to the synthesis of a variety of electron-rich aromatic and heterocyclic systems, which react with squaric acid, facilitated the design of a variety of symmetrical and unsymmetrical squaraines with tunable optical properties. In the solid state, because of intermolecular interactions and aggregation, the absorption spectra ($\epsilon > 10^5$ L mol⁻¹ cm⁻¹) of these dyes are generally broad and red-shifted to the near-IR wavelength range. Most of these dyes emit in the far-visible to the near-IR region and are photostable. These properties of squaraines have generated considerable interests in the design of squaraine-based near-IR dyes because of their potential application in photonic devices.

Squaraine-Based π -Extended Dyes

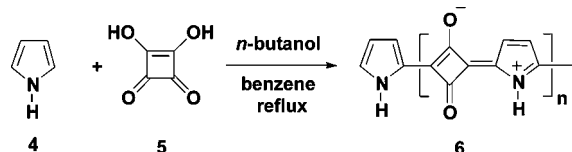
Near-IR absorbing squaraine dyes are important in optical recording devices based on gallium-arsenide diode lasers (780–803 nm), neodymium-YAG lasers (1064 nm), and in the imaging of biological specimen. Optical absorption of squaraines can be pushed toward the long wavelength region either by the use of strong electron donors or by the extension of conjugation. Using this approach, a large number of squaraines with near-IR absorption and emission have been synthesized.^{6–17} Several of these dyes have potential application as photoreceptors for diode lasers, laser optical recording, laser printing, photolabeling, and DNA sequencing. Recently, we have shown that extension of conjugation in squaraine dyes through vinylaromatic end groups imparts interesting optical and redox properties.¹⁸ For example, incorporation of two vinylbenzene moieties to the simple *N*-alkylpyrrole-based squaraine dye **11** (Chart 1), resulted in dye **7** that featured a red shift in the absorption maximum from 547 to 687 nm in toluene. The squaraine dye **8** showed a further red shift of 13–20 nm in toluene, depending upon the length of the alkyl side chains. Interestingly, in the solid state, they showed broad absorption from the 600 to 1000 nm range with different absorption maxima, the intensities of which are dependent upon the length of the side chains. Among these molecules, the dye **10** showed interesting redox behavior characteristic of a class III mixed-valence system. Cyclic voltammograms (Figure 1) reveal that the squaraine

* To whom correspondence should be addressed. Fax: +91 471 2491712. E-mail: aajayaghosh@rediffmail.com.

Scheme 1



Scheme 2



10 possesses maximum reversibility, indicating the role of the phenylanthracenyl unit in the stabilization of the radical cations and dications.

The cyclic voltammogram of **10** showed limited electrochemical but full chemical reversibility. It is assumed that oxidation leads to an electronic situation at the mixed-valence radical cation stage in which the positive charge is localized on the vinylpyrrole subunits. AM1 level quantum mechanical calculations of the geometries and charge distribution of **10** in different oxidation states suggest that the pyrrole-vinyl subunit has to be regarded as an effective redox center in the oxidative process. The calculations also predict that the spreading of the positive charge is extended further to the anthracene substructures (Figure 2). This is in agreement with the finding of reduced stability of the oxidized forms of compounds **7** and **9**. The promising optical and redox properties of squaraine dyes and the observation that extension of conjugation has significant effect in the absorption properties are signs of potential use as building blocks to the design of oligomers and polymers with intrinsic semiconducting properties.

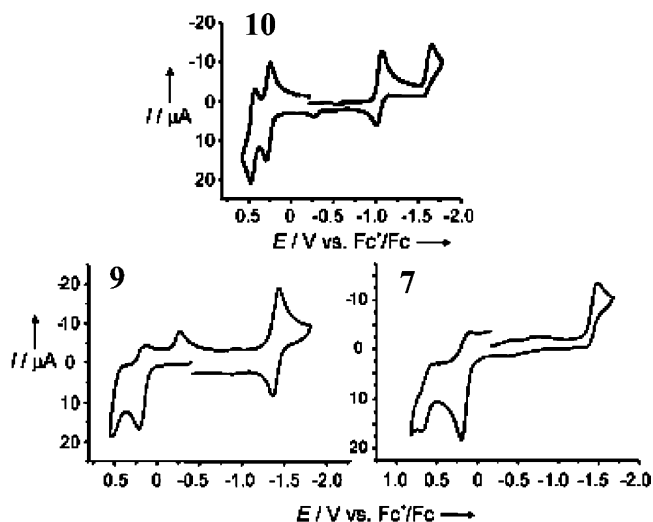
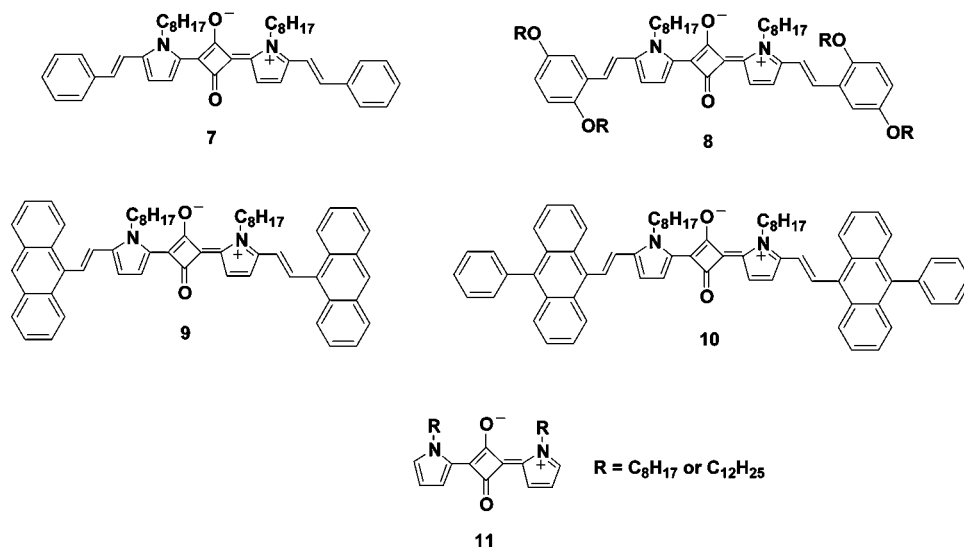


FIGURE 1. Cyclic voltammograms of squaraine dyes **7**, **9**, and **10** in dichloromethane using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte; scan rate, 250 mV/s (adapted from ref 18).

Squaraine-Based Low Band Gap Polymers

Design of π -conjugated polymers with low optical band gaps are important because of intrinsic semiconducting properties.¹⁹ Use of organic dyes with inherently low HOMO–LUMO energy gap as building blocks for conjugated polymers will lead to strong absorption in the near-

Chart 1



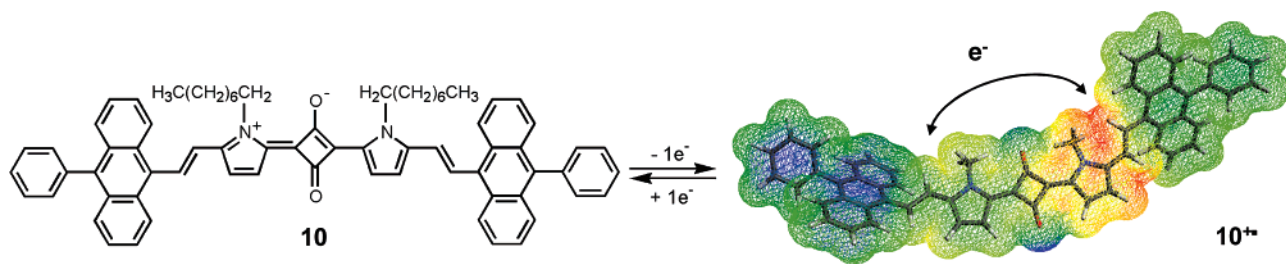
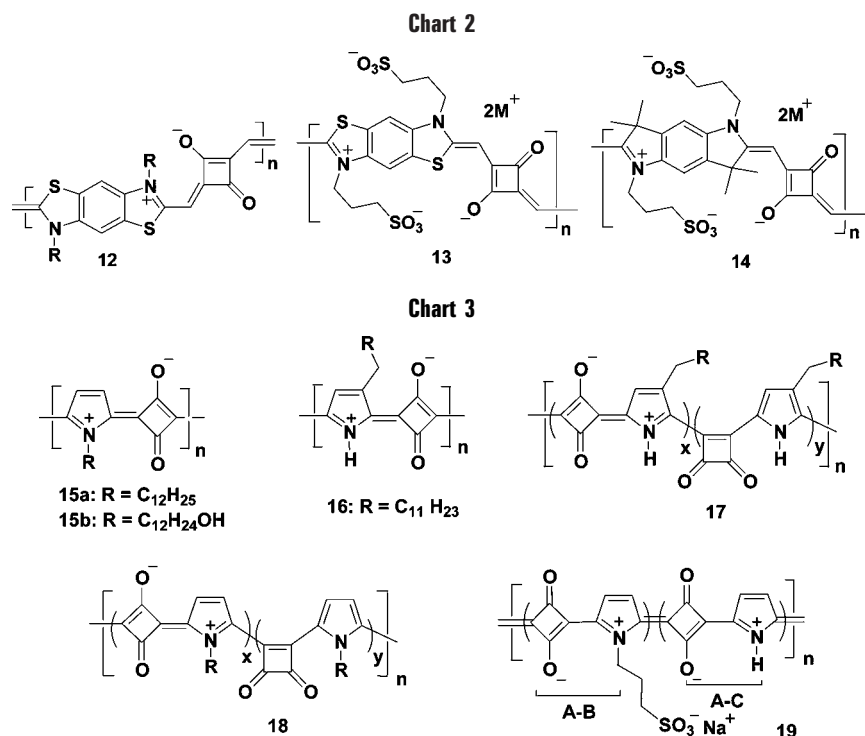


FIGURE 2. Redox behavior of **10** and the calculated charge distribution of **10⁺**. The double-headed arrow represents intramolecular electron hopping from the radical cation subunit to the bridge.



IR region, which is a signature of the low optical band gap. Although a variety of near-IR absorbing organic dyes are known, π -conjugated polymers that absorb in the near-IR wavelength are rare.²⁰ Squaraines, by virtue of favorable optical properties and immense flexibility for synthetic manipulation, are suitable for the design of polymers with low optical band gaps. This assumption is supported by the theoretical calculations of Brocks and Tol who predicted low band gaps in polysquaraines.²¹ Bifunctional heterocyclic aromatic compounds such as pyrrole, carbazole, and benzothiazoles are suitable substrates, which, on polycondensation with squaric acid, form either oligomers or polymers with squaraine backbones. The early attempts to the synthesis of polysquaraines were not promising because of the insoluble and intractable nature of the resulted materials.^{3,22} Later, benzobisthiazoles and benzobispyrrolines were shown to condense with squaric acid to form polysquaraines (**12–14**) with low optical band gaps (Chart 2).^{23–25} The polysquaraine **12** had an optical band gap of 1.2 eV with conductivity in the range of 10^{-6} – 10^{-5} S/cm. The water-soluble polysquaraine **13** and **14** showed band gaps of 0.7 and 1.2 eV, respectively. According to Havinga et al., the low band gaps in these polymers are due to the conjugated main chain with

alternation of strong electron withdrawing and donating moieties that represent the one-dimensional analogue of an n-i-p-i semiconductor super lattice structure.²⁶

Pyrrole derivatives have been extensively used for the synthesis of polysquaraines, in anticipation of semiconducting and near-IR optical properties.^{27,28} Reaction of *N*-alkyl- or 3-alkyl-substituted pyrroles with squaric acid provided polysquaraines **15–19** (Chart 3), the structure and properties of which vary depending upon reaction conditions.^{28c} For example, in the *n*-butanol-benzene mixture under azeotropic reflux conditions, the condensation between pyrrole derivatives and squaric acid resulted mainly the 1,3-substituted zwitterionic products **15** and **16**, whereas in DMSO, polymers with a mixture of the 1,3-zwitterionic and 1,2-diketonic repeat units were formed. Properties of the resulting polymers were influenced by the ratio between the two repeat units. The water-soluble copolymer **19** showed conductivities in the range of 10^{-5} S/cm⁻¹ depending upon the copolymer composition.

Although pyrrole-based polysquaraines were expected to have near-IR absorption and low optical band gaps, their absorption maxima were not much different from the corresponding monomeric dye units. For example, the squaraine dye **11** has an absorption maximum of 547 nm,

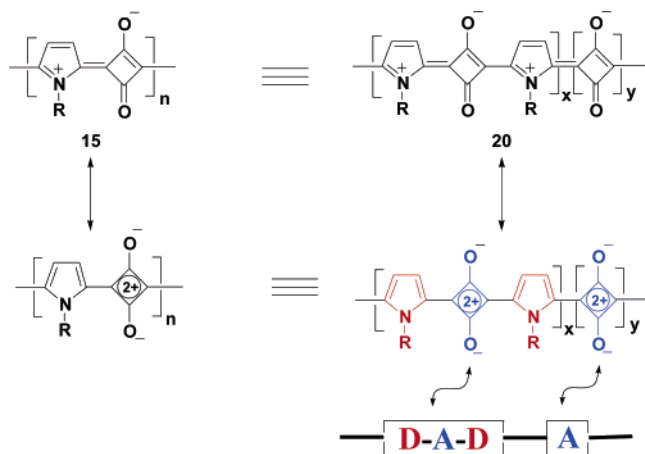


FIGURE 3. Pyrrole-based polysquaraine, represented as a copolymer of D-A-D squaraine dye and an electron-deficient cyclobutane diolate dianion unit.

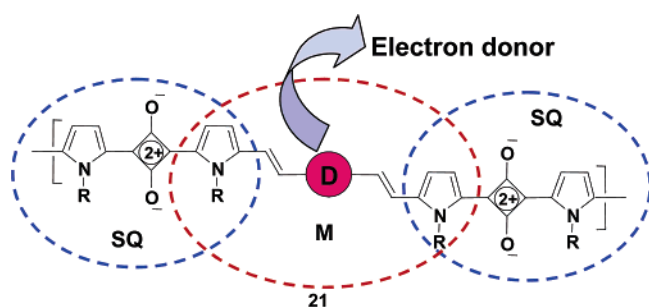


FIGURE 4. Structure of a modified polysquaraine with low optical band gap.

whereas the corresponding polysquaraine **15a** has an absorption maximum of 580 nm. This observation revealed that a mere extension of conjugation in these systems is not sufficient to lower the band gaps. This is rationalized by representing the structure of the polysquaraine **15** as a donor-acceptor-donor (D-A-D)-type squaraine dye repeating unit, which is bridged through an electron-deficient cyclobutene moiety (A), as shown in Figure 3. Therefore, the D-A-D interactions of the squaraine unit in polysquaraines are significantly weakened, which in turn influence the optical properties. From this viewpoint, it is reasonable to argue that introduction of an electron-rich bridging group may considerably improve the optical and electronic properties of the resulting polymers. The conjugated donor bridge will strengthen the D-A-D interaction of the organic dye moiety, leading to a quinoid-type resonance structure, thereby improving the effective conjugation length and thus lowering the optical band gap.²⁹

A rational approach to the design of low band gap polysquaraines is the use of a bifunctional monomer (**M**) with two reactive end groups that are connected to an electron-rich conjugated bridging unit **D** as shown in Figure 4. Reaction of such a monomer with squaric acid can lead to a polysquaraine through the *in situ* generation of squaraine dye units (**SQ**) at definite positions of the polymer backbone. This is illustrated using a variety of bispyrroles, bridged with electron-rich dialkoxydivinylbenzene moiety as the building block. Polycondensation

of bispyrroles **22–26** with squaric acid resulted in the formation of polysquaraines **27–31** (Scheme 3), which absorb in the near-IR wavelength, indicating low optical band gap in these polymers.^{30–32} The gel permeation chromatography in THF showed broad elution peaks, indicating high polydispersity values (M_w/M_n), which could be due to the strong tendency of these polymers to aggregate in solvents. The absorption spectra of **27–31** are strongly influenced by the electronic properties of the bridging unit and the length of the aliphatic side chains of the polymer backbone. For example, the polysquaraine **29** with the dialkoxybenzene unit showed the maximum shift of the absorption toward the long wavelength region. Interestingly, **29a** with short side chains on the pyrrole nitrogen atom showed a broad spectrum with several absorption shoulders, whereas **29d** with long side chains showed a relatively narrow spectrum (Figure 5). The broad window of the absorption spectra starting from 500 nm down to 1200 nm in these cases is remarkable when compared to the absorption properties of the polysquaraine **15a** obtained from the reaction of *N*-alkylpyrrole with squaric acid, which has a narrow absorption spectrum with a maximum at 581 nm (Figure 5). The strong donor-acceptor interaction in these polymers may facilitate the resonance-stabilized quinoid structures,²⁹ which may be responsible for the observed long wavelength optical absorption (Scheme 4).

The solution and solid-state band gaps of **29a–d**, which are calculated from the onset of the absorption spectra, are in the range of 1–1.1 eV. The intrinsic conductivities of these polymers were in the order of 10^{-4} – 10^{-7} S/cm. The important observation of the study is that, although the band gaps of the polysquaraines **29a–d** are very close to each other, the intrinsic conductivities showed considerable variation. This indicates that the length of the side chains has considerable influence on the solid-state molecular packing of the polymer chains. A comparison of the band gap and conductivity data reveal that among polysquaraines of comparable band gaps, conductivity can be tuned by proper tailoring of the side chains. This is established by the powder X-ray diffraction data of **29a–d**, which showed interdigitated packing, the spacing of which varies with the length of the side chains.

Squaraine-Based Ion Probes (Chemosensors)

Chemosensors, the usual configuration of which consists of an ionophore unit, integrated to a chromophore, is a topic of considerable interest because of their importance in specific detection of analytes in different fields such as chemistry, biology, medicine, and environmental studies. Organic dyes are extensively used as the signaling units in chemosensor design because of their intense absorption and emission properties, which are sensitive to external inputs.³³ Squaraine dyes are ideally suited for this purpose because of their favorable optical properties associated with the peculiar zwitterionic structure, which gets perturbed with the polarity of the medium, temperature, pH, and other additives. Therefore, ionophores which are

Scheme 3

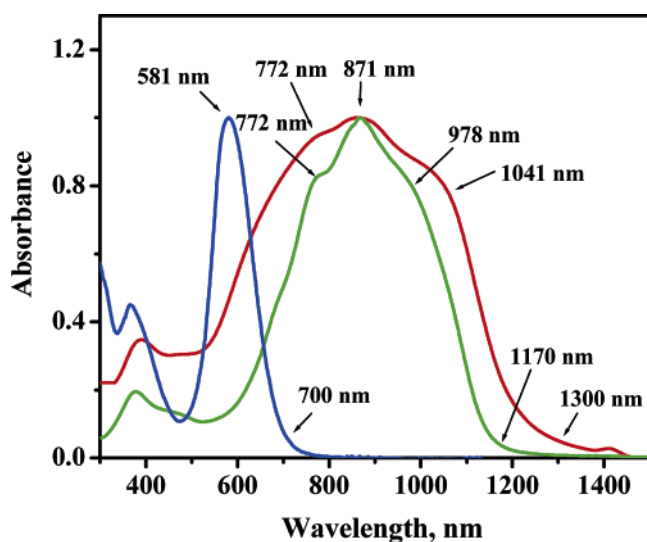
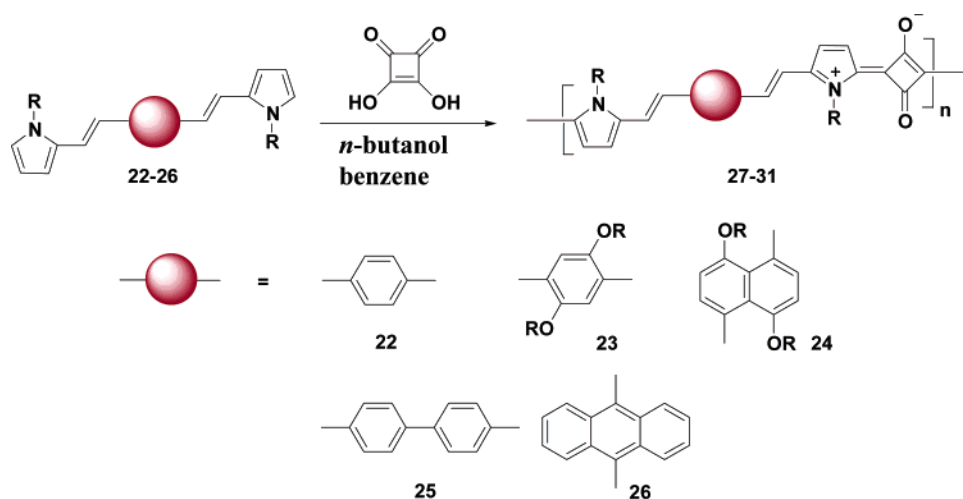


FIGURE 5. Absorption spectra of polysquaraines **15a** (blue), **29a** (red), and **29d** (green), which show the remarkable shift in the absorption spectra of **29a** and **29d**.

integrated to squaraine dyes, can signal the binding event in the form of measurable changes in the absorption or emission properties.

A variety of squaraine-based sensors are known in the literature, the selectivity and sensitivity of which are relatively low when compared to several of the other classes of chemosensors.^{34,35} In an attempt to improve the performance of squaraine-based sensors, we have applied Swager's concept of molecular wire-based signal amplification³⁶ in pyrrole-based polysquaraines.^{37,38} This was illustrated using polysquaraines **32** and **33** and a model dye **34** containing flexible oxyethylene chains that reversibly bind specific cations (Chart 4).

The polysquaraine **32** showed enhanced sensitivity and selectivity to Li^+ over Na^+ and K^+ . Although the absorption spectrum of **32** remains unperturbed, considerable enhancement in the fluorescence emission is observed upon Li^+ binding (Figure 6a). However, the model squaraine dye **34** showed a very weak response to Li^+ , revealing the crucial role of the conjugated polysquaraine backbone in the signal amplification process (Figure 6b). This is

rationalized based on the collective and cooperative impact of the Li^+ binding, leading to a flexible to rigid conformational locking of the polymer backbone (Figure 7).

The signal transduction in chemosensors is usually achieved by the change in the absorption or emission properties associated with an analyte-induced electron-transfer, energy-transfer, or charge-transfer interaction or by conformational restrictions. The weak changes in the optical properties have necessitated an alternate approach toward selective and sensitive signaling in squaraine-based sensors. This has prompted us to think of exciton interaction in squaraine aggregates as a potential signaling pathway of a specific cation-binding event. The idea involves a cation-induced folding or dimerization of a squaraine dye-linked podand to form a folded complex, similar to the "H" aggregate in which exciton interaction between the chromophores in the bound complex induces measurable changes in the optical properties as shown in Figure 8. This has been illustrated with the help of a number of squaraine-tethered bichromophoric podands **35a–g** (Chart 5) and the analogous monochromophores **36a–c**.^{39–41}

The bichromophores **35a–g** showed strong perturbation in the absorption and emission spectra with high selectivity toward alkaline earth metal cations, particularly to Mg^{2+} and Ca^{2+} ions, whereas no optical response was noticed against alkali metal ions. Although the bichromophore **35a** and **35b**, having short podand chains, showed similar changes in the absorption spectra with Mg^{2+} and Ca^{2+} (Figure 9), Job plots (insets of Figure 9) revealed the preferential formation of a 1:1-folded complex with Mg^{2+} and 1:2 sandwich dimer with Ca^{2+} as shown in Scheme 5. However, **35c** invariably forms 1:1 complexes with Mg^{2+} , Ca^{2+} , and Sr^{2+} .

The binding of Ca^{2+} and Mg^{2+} to the bichromophores was confirmed by the change in the characteristic proton signals in the ^1H NMR spectra after the addition of metal salts. Cyclic voltammograms in the presence of Ca^{2+} showed shifts in the oxidation potentials toward more positive values. This is attributed to the coordination of

Scheme 4

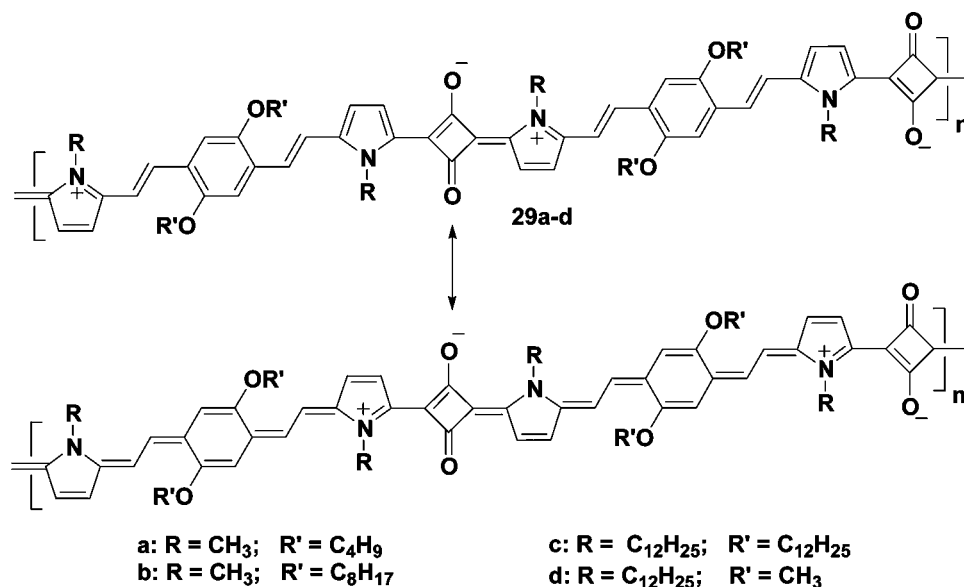
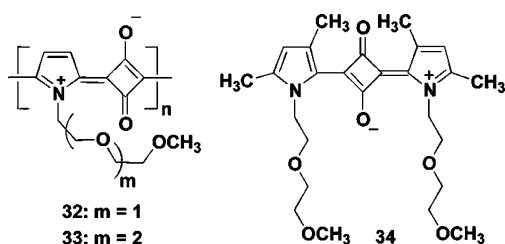


Chart 4



the nitrogen lone pair of electrons with Ca²⁺, which decreases the charge-transfer character of the chromophore. However, at this point, it is not clear to us whether the oxygen atom in the central cyclobutene ring of the squaraine chromophore has any role in the binding. Increase of the temperature in the presence of Ca²⁺ showed an increase in the long wavelength absorption band with a concomitant decrease in the short wavelength band, indicating a thermoreversible binding of the cation. Addition of EDTA, which is a strong complexing agent, reinstated the original absorption spectrum of the bichromophore, indicating the decomplexation of Ca²⁺. Three dimensional plots of the percentage fluorescence quantum yields (ϕ_F) of **35a–c** against various metal cations are

shown in Figure 10 and reveal the selectivity of alkaline earth metal cations over alkali metal cations.

In light of the cation-binding behavior of the bichromophores **35a–c**, we studied the effect of the addition of metal salts to the monochromophore **36a–c**. Although the ¹HNMR studies showed binding of Ca²⁺ and Mg²⁺ to **36a–c**, they failed to show any change in the absorption or emission spectra. Thus, the optical response of **35a–c** and the optical silence of **36a–c** with Mg²⁺ and Ca²⁺ lead us to conclude that the monochromophores preferentially form complexes having “Head–Head” arrangements (Scheme 6). These observations are in full support of the folded and sandwiched conformations of the metal complexes of **35a** as shown in Scheme 5. Mg²⁺ and Ca²⁺ complexes of **35a** have similar properties to that of the “H” aggregates of squaraines, where the exciton interaction between the chromophore results in the blue shift of the absorption bands, while such an interaction is not possible in the “Head–Head” arrangement of **36a** with Ca²⁺.

Although **35a–c** showed selectivity toward alkaline earth metal ions, the ultimate aim of the study was the specific detection of one of these metal ions. Interestingly,

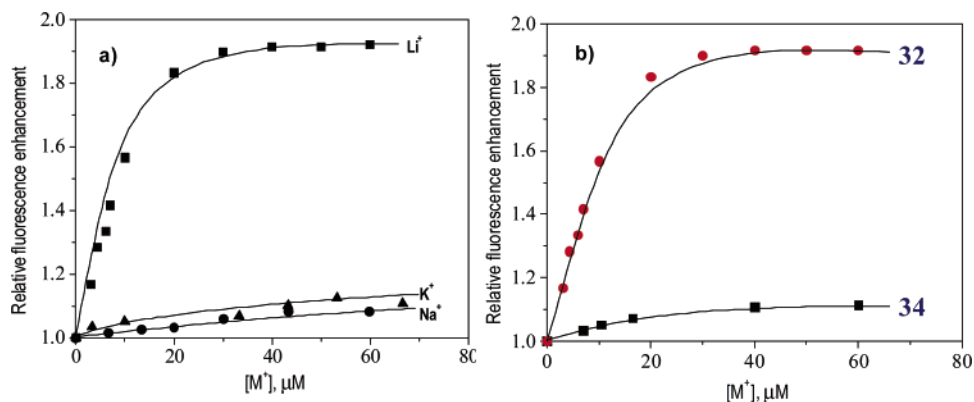


FIGURE 6. (a) Effect of various alkali metal ion concentrations on the fluorescence emission of **32**. (b) Effect of Li⁺ concentrations on the fluorescence emission of the squaraine molecular wire **32** and the model squaraine dye **34** (adapted from ref 38).

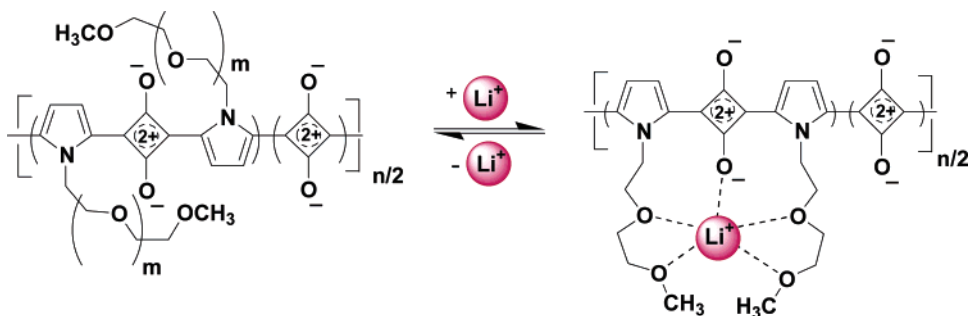


FIGURE 7. Li^+ -induced rigidisation of the polysquaraine **32**.

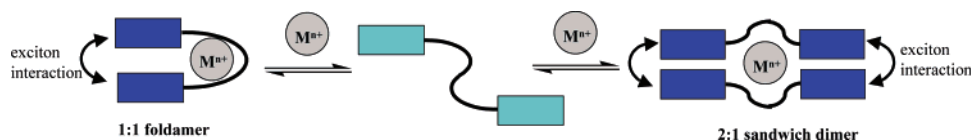


FIGURE 8. Schematic representation of a chemosensor based on cation-driven exciton interaction.

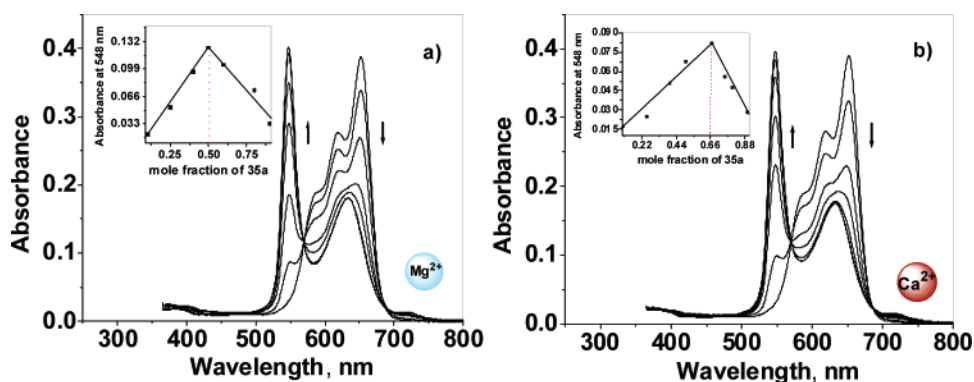
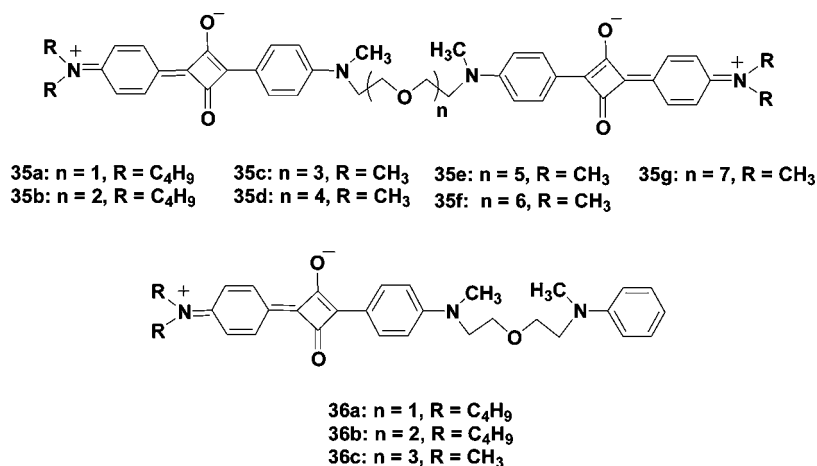


FIGURE 9. Changes in the absorption spectra of **35a** in acetonitrile with addition of (a) $\text{Mg}(\text{ClO}_4)_2$ and (b) $\text{Ca}(\text{ClO}_4)_2$ (adapted from ref 40).

Chart 5

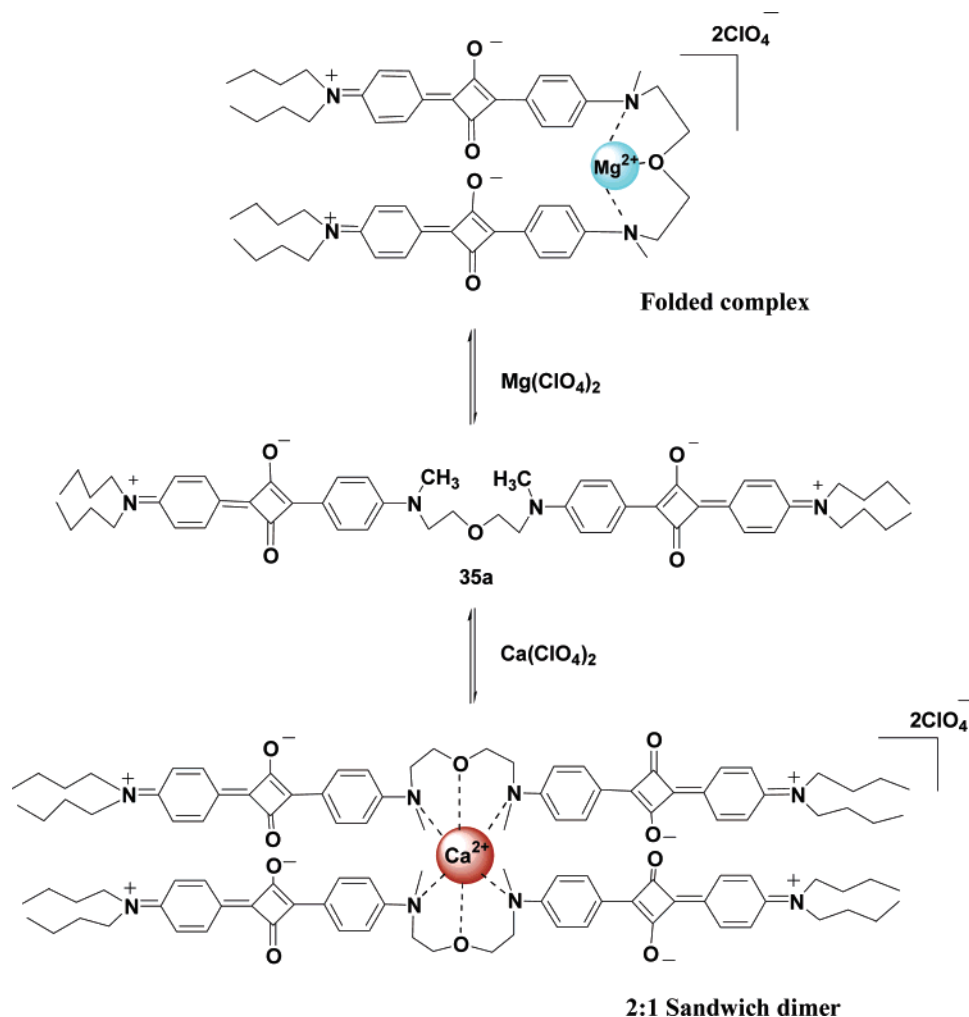


we have noted that the bichromophore **35e** with five oxygen atoms in the podand chain is highly selective toward Ca^{2+} . In this case, the light-blue color of **35e** became intense purple blue upon addition of $\text{Ca}(\text{ClO}_4)_2$, which is visible to the naked eyes (Figure 11). Addition of other cations such as Na^+ , K^+ , Mg^{2+} , Ba^{2+} , or Sr^{2+} did not show any visible color change, thus making **35e** a chromogenic Ca^{2+} ion sensor. The fluorescence emission of **35e** (1.75×10^{-5} M in acetonitrile), when excited at 580 nm, underwent considerable quenching upon addition of $\text{Ca}(\text{ClO}_4)_2$. The Benesi-Hildebrand and Job plots were in

agreement with a 1:1 complexation. The plots of the fluorescence quantum yields (ϕ_F) against the ratio between **35e** and the metal ions shown in Figure 12 indicate the high selectivity toward Ca^{2+} .

The observed changes in the absorption and emission properties of **35e** are rationalized by the cation-driven folding to form a complex akin to an "H" aggregate, where the two chromophores are stacked face-to-face (Figure 11). The exciton interaction in such a folded complex induces a blue shift of the absorption with concomitant quenching of the emission. The fluorescence emission of the folded

Scheme 5



complex is weaker than that of the unfolded bichromophore because of the fast internal conversion from the upper to the lower excited state from which emission is

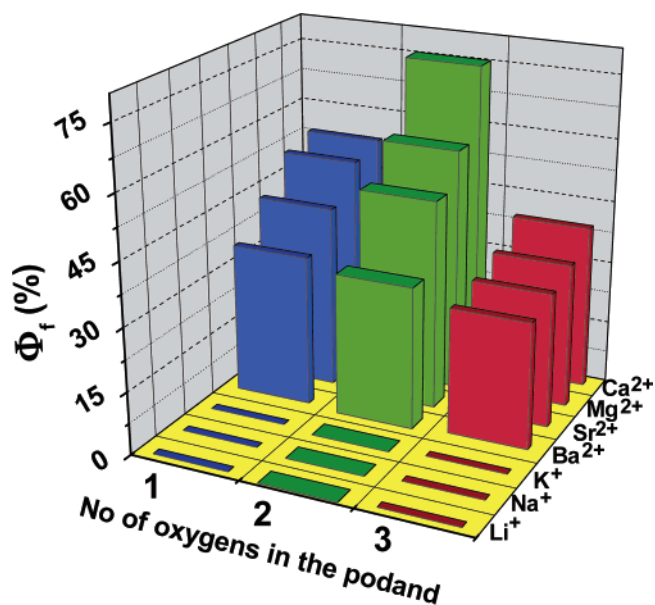
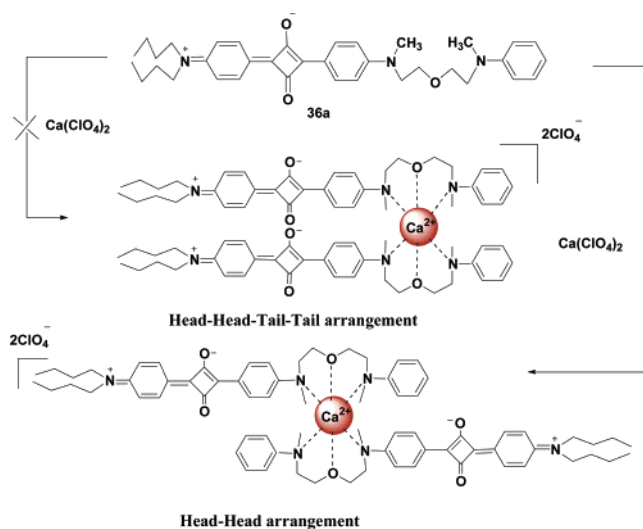


FIGURE 10. Three dimensional plot showing selectivity and sensitivity of **35a–c** toward various metal cations (adapted from ref 40).

Scheme 6



theoretically forbidden. Thus, using squaraines, it could be possible to control and express the binding of specific cations, invoking exciton interaction as the mode of signaling, which is different from other known signaling mechanisms resulting in a novel class of cation sensors. This concept is now explored by others in the design of

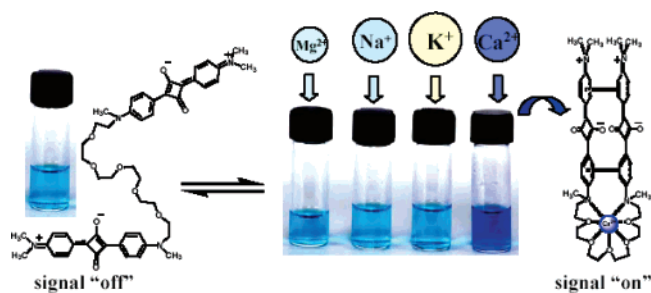


FIGURE 11. Visible color change of **35e** ($5.1 \mu\text{M}$) in acetonitrile upon addition of Ca^{2+} and the corresponding conformational change (adapted from ref 41).

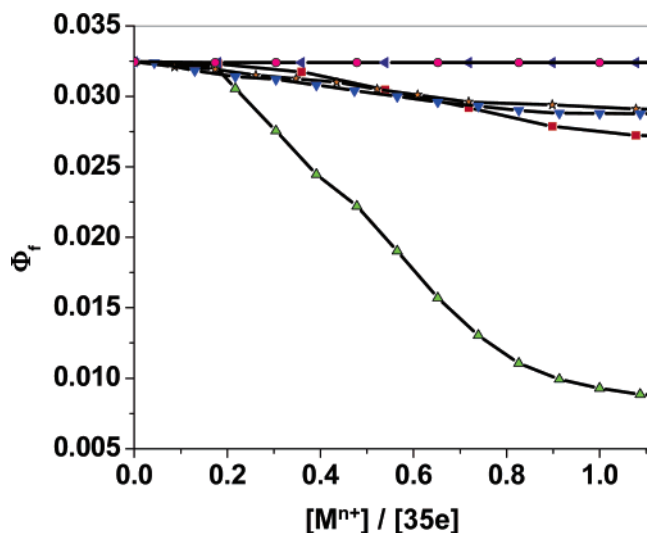


FIGURE 12. Plot of Φ_f versus the ratio between metal ion and **35e**, which illustrates the selectivity for Ca^{2+} (▲) over Na^+ (▲), K^+ (●), Mg^{2+} (■), Sr^{2+} (★), and Ba^{2+} (▼) (adapted from ref 41).

various cation probes.^{42–44} Recently, squaraines were shown to be useful as fluoro-chromogenic probes for the detection of CN^- ions,⁴⁵ as well as for thiol-containing compounds, which has significance to the detection of biorelevant thiols.⁴⁶ The latest result on the diverse application of squaraines pertains to the development of an ionically controlled nanoscopic molecular gate.⁴⁷ Thus, squaraines are reaching new heights with respect to the design of advanced smart materials with intriguing properties leaving the hope that several of such reports will appear soon.

Summary and Outlook

The present Account highlights our recent contributions that pertain to some aspects of the materials chemistry of squaraine dyes. Efforts have been made to bring light to the diverse scope and potential use of squaraines as scaffolds for the design of near-IR dyes, low band gap polymers, and cation probes. The novel strategy that we had demonstrated for the design of near-IR-absorbing polysquaraines with low optical band gap proved to be a successful approach and can be applied as a general procedure for the design of organic dye-based polymers. Although the optical properties of squaraines are ideal for the design of a variety of optoelectronic and stimuli

responsive materials, the bottleneck is the difficulty associated with the low solubility and processability. This is to be particularly tackled in the design of polysquaraine-based organic semiconductors and near-IR dyes. In the case of squaraine-derived ion probes, efforts are needed to design molecules that specifically detect biologically important cations under aqueous and physiological conditions. It is necessary to address this issue when squaraine-based ion probes and biological labels are being designed. Our strategy of specific cation-induced aggregation and the resultant exciton interaction in squaraine-based foldamers as the source of signaling are expected to make a significant impact in the design of cation sensors with better selectivity and sensitivity. In conclusion, squaraines are easily accessible organic dyes with useful optical properties and hence appear to be an ideal scaffold for the design of a variety of new optoelectronic and stimuli-responsive materials. Therefore, it is reasonable to conclude that the future of squaraine chemistry will continue to be bright and colorful.

The author gratefully acknowledges the contributions of co-workers whose names appeared in various references cited in this Account. Sincere gratitude to Professor Joerg Daub, University of Regensburg, for many fruitful discussions. The help rendered by my co-workers, Mr. V. K. Praveen and Ms. Priya Carol, is deeply appreciated. Financial support by the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India, are gratefully acknowledged. This is contribution number RRLT-PPD-201.

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AR0401000