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Metallo Supramolecular Assemblies of Bis-squaraines by Allosteric Ca^{2+} Ion Binding

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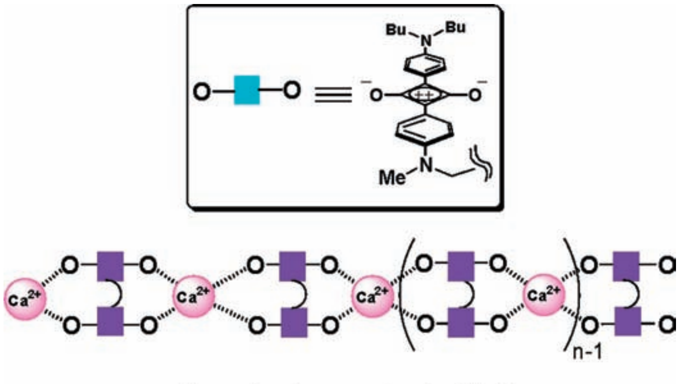
ABSTRACT



one-dimensional supramolecular H-foldamers

Alkyl chain tethered bis-squaraines bind to Ca^{2+} ions through the participation of the negatively charged oxygen of the central cyclobutene moiety to form folded H-type aggregates. The initially formed Ca^{2+} complex is preorganized to facilitate cooperative allosteric binding of Ca^{2+}, resulting in the formation of extended supramolecular arrays. The electronic absorption, IR, and ESI-MS studies support the formation of metallo supramolecular architectures of the folded H-type dimers of the bis-squaraines.

Squaraine dyes (squarylium dyes) are zwitterionic dyes consisting of aromatic or heterocyclic π-electron systems at both ends of a cyclobutenoate core that exhibit unique optical and electrochemical properties.[1] They have been receiving much attention from fundamental and technological viewpoints and have been extensively used in xerographic[2] and electroluminescent devices,[3] organic solar cells,[4] chemosensors,[5] and so on. Due to their planar structures, squaraine dyes often form aggregates in solutions as well as in solid states.[6] Such aggregate formation significantly affects the optical and electronic properties of the dyes due to excitonic interaction among the constituent chromophores. Thus,

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controlling the aggregate formation is one of the important issues to optimize the performance of the materials based on organic functional dyes. In general, two type of aggregates, H- and J-types, are formed, where the dye molecules are aligned in card-pack and slipped-stack manners, respectively, resulting in different types of excitonic interactions of the chromophores.[7] The H-type aggregation, in which the transition dipole moments of the chromophores are arranged in a parallel mode, yields a hypsochromic shift of the electronic absorption band. On the other hand, in the J-type aggregates, the transition dipoles are arranged in a head-to-tail manner, leading to a bathochromic shift.[8] Recently, Ajayaghosh and co-workers have exploited exciton interaction in a series of squaraine-tethered podands to colorimetric sensing of Ca^{2+} and Mg^{2+} ions.[9] In these cases, the podand chains play a crucial role in the binding of the cations. However, in an unprecedented way, we found another type of metal-cation-induced H-aggregate formation of squaraine dimers. Herein we report that polymethylene-bridged squaraine dimers form metallo supramolecular assemblies through extended allosteric chelation of the folded H-aggregates in which the negatively charged oxygens in the central cyclobutene ring of the squaraine skeleton play a crucial role.[10]

The polymethylene-bridged squaraine dimers **1a**−**c** (Figure 1) with varying spacer length were prepared from 4-[4-(*N*,*N*-dibutylamino)phenyl]-3-hydroxy-3-cyclobutene-1,2-dione and the corresponding *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-α,*ω*-alkanediamines in 42−58% yields, using triethyl orthoformate as a dehydrating reagent (see Supporting Information). The synthesis of the dimer **2** was reported previously.[11] The dimers **1** and **2** exhibit their absorption maxima at 640−645 nm in $CHCl_3/CH_3CN$ solutions, similar to that of the squaraine monomer **3**. On the other hand, the dimers exhibit large hypsochromic shifts upon addition of increasing amounts of Ca^{2+}. The electronic absorption spectral changes of **1a** in $CHCl_3/CH_3CN$ (3/1, v/v) in the presence of varying concentrations of $Ca(ClO_4)_2$ are shown in Figure 2. As the concentration of Ca^{2+} increased, the absorbance at 645 nm decreased, and a new absorption band appeared at 574 nm, accompanied by two isosbestic points at 614 and 677 nm. These spectral changes were similar to those observed in the cation-induced H-type foldamer formation previously reported by Ajayaghosh et al.[9] Taking into consideration that Ca^{2+}-induced spectral changes were not observed in the case of the monomer **3**, the hypsochromic shift indicates that the complexation of **1a** with Ca^{2+} led to formation of the H-foldamer.

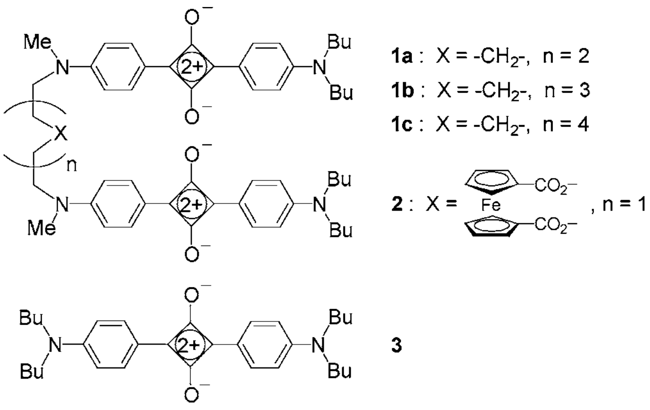

Figure 1. Squaraine dimers **1** and **2** and monomer **3**.

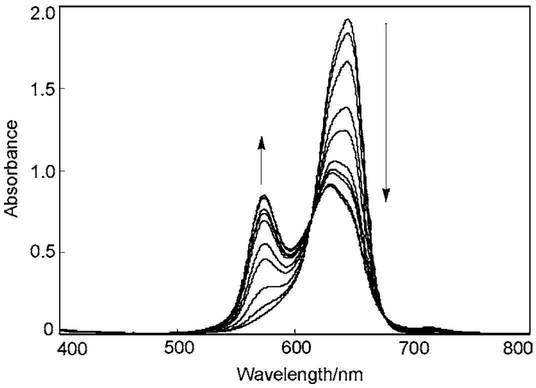

Figure 2. Electronic absorption spectral changes of **1a** in $CHCl_3/CH_3CN$ (3/1, v/v) at 293 K upon addition of varying concentrations of $Ca(ClO_4)_2$ ($[Ca^{2+}]/[\mathbf{1a}] = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0). $[\mathbf{1a}] = 4.0 \times 10^{-6}$ M.

The plot of the absorbance at 574 nm of the H-aggregate of **1a** upon titration with $Ca(ClO_4)_2$ is shown in Figure 3. The absorbance change reached a plateau when an equimolar amount of $Ca(ClO_4)_2$ was added, indicating that the stoichiometry of the dimer−Ca^{2+} complexation is 1:1. The Job's analysis also supported 1:1 stoichiometry. However, the sigmoidal profile of the absorbance changes implied that the

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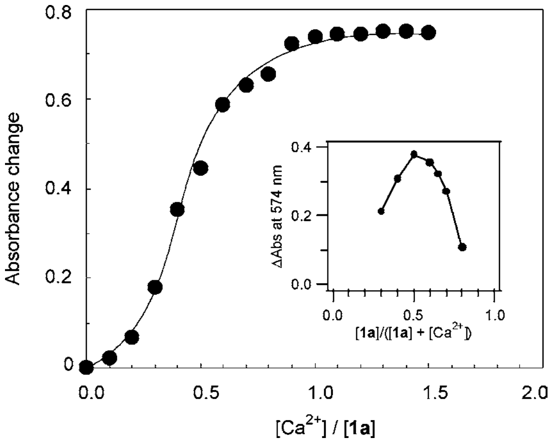

Figure 3. Absorbance changes at 574 nm of **1a** titrated with Ca$(ClO_4)_2$; [**1a**] = 4.0 × 10^{-6} M. The inset shows the Job's plot for the **1a**−Ca^{2+} system; [**1a**] + [Ca^{2+}] = 4.0 × 10^{-6} M.

H-aggregate formation was caused not only by a simple 1:1 complexation between **1a** and Ca^{2+} but also by their cooperative supramolecular assembly. This cooperative assembling behavior was also indicated by the Hill's analysis, where the Hill's constant, n, and the logarithm of the apparent association constant, log K_{app}, were determined as 4.4 (SD = 0.1) and 25.7 (SD = 0.6), respectively.[12,13]

Table 1. Electronic Absorption Spectral Properties of the Squaraine Dimers and Their Ca^{2+} Complexes in $CHCl_3/CH_3CN$ (3/1, v/v) at 298 K[a]

	metal-free		complex	
compound	λ_{max} (nm)	ϵ ($\times 10^{-5}$ M cm^{-1})	λ_{max} (nm)	$A_{complex}/A_{free}$[d]
1a	645	4.8	574	0.85
1b	641	4.7	575	0.27
1c	640	4.3	577	0.16
2	640	4.2	564	1.2
3	644	2.6[b]	c	c

[a] 4.0 × 10^{-6} M. [b] 8.0 × 10^{-6} M. [c] No spectral change was observed. [d] $A_{complex}$ and A_{free} are absorbances at λ_{max} of H-aggregate (ca. 575 nm) and metal-free dye (ca. 640 nm), respectively.

As summarized in Table 1, similar Ca^{2+}-induced spectral changes were observed in the other dimers, although the ratio of the absorbance of the H-aggregate to that of the cation-free dimer varied with the alkyl and ferrocene linkages. As the length of the alkyl linker is increased in **1a**−**c**, the formation of the H-foldameric aggregates is suppressed. One might see that the entropic disadvantage upon the complexation may reduce the stability of the H-foldamer. The H-aggregate formation was remarkable on **2** compared to that of **1**. We previously reported that **2** showed the broader absorption band in $CHCl_3$ solution than the monomeric squaraine dye, due to the intramolecular interaction between two squaraine chromophores.[11] Thus, the chromophores in **2** might be more preorganized by the ferrocene linkage, preferably due to the complexation-induced formation of the folded H-aggregate.

In order to confirm the complexation mode between the dimers and Ca^{2+} ions, the IR spectroscopic study and electrospray ionization mass (ESI-MS) measurements were performed. The IR absorption bands assigned to squaraine moieties of the metal-free dimers, including C═O stretching at the cyclobutenoate core, were observed as strong peaks at 1582−1616 cm^{-1},[14] whereas these peaks coalesced into one at ca. 1590 cm^{-1} upon complexation with Ca^{2+} (see Supporting Information). This result indicates that the bound Ca^{2+} should interact with the negatively charged oxygen atoms of the cyclobutenoate core. Thus, one can see that chelation of the two squaraine moieties in the dimer to a Ca^{2+} affords the H-foldamer (Figure 4a). This folded "unit

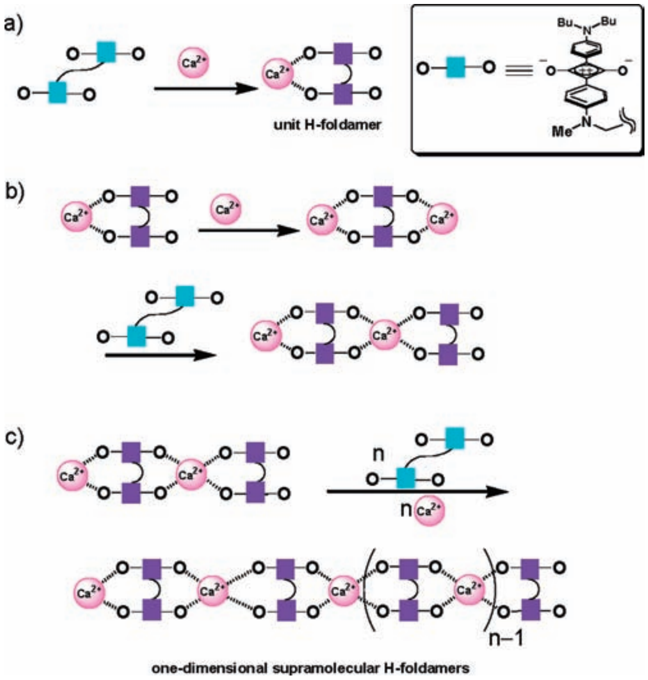

Figure 4. A possible structure of the H-aggregate supramolecule of squaraine dimer with an alkaline earth metal cation.

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(12) The Hill's analysis was carried out according to the equation: log[$Y/(1 - Y)$] = n log[Ca^{2+}] + log K_{app}, where Y, n, [Ca^{2+}], and K_{app} represent the fractional saturation (occupancy of the binding sites), the Hill's constant, the concentration of Ca^{2+}, and the apparent association constant, respectively. Monitoring the absorbance changes of **1a** at 574 nm, Y was determined by the equation of $(A - A_0)/(A_{max} - A_0)$, where A_0, A, and A_{max} are the absorbance in the absence of Ca^{2+}, the absorbance in the presence of Ca^{2+}, and the absorbance upon addition of an excess amount of Ca^{2+}, respectively. See also ref 13.

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H-type aggregate" possesses another preorganized chelating site to bind with one more Ca^{2+} ion, thereby resulting in the formation of a bimetallic H-aggregate (Figure 4b). This will further complex with another bis-squaraine dye, propagating a metallo supramolecular polymeric structure. Thus, a one-dimensional array of the H-type folded aggregates of the Ca^{2+} complex should be afforded (Figure 4c). This is supported by the ESI-MS study of the dimers **1a**−**c**. The ESI-MS spectrum of **1a** (4.0×10^{-4} M) in the presence of 3 molar equiv of $Ca(ClO_4)_2$ in $CHCl_3/CH_3CN$ (3/1, v/v) is shown in Figure 5. Parent peaks assigned to the supramolecular complexes ($[2M + Ca^{2+}]^{2+}$, $[2M + Ca^{2+} + ClO_4^-]^+$, $[3M + Ca^{2+}]^{2+}$, and $[3M + 2Ca^{2+} + 2ClO_4^-]^{2+}$) were observed in addition to the monomeric 1:1 complex ($[M + Ca^{2+} + ClO_4^-]^+$), indicating that three unit H-type folded aggregates were at least involved. Similar supramolecular complexes were also observed in the other dimers, but not observed in the monomer **3** (Table 2). Taking into account that the complexation-induced absorbance changes of squaraine dimers get saturated upon addition of 1 molar equiv of Ca^{2+} ion, the metallo supramolecular structures should involve the one-dimensional array of the folded H-aggregates (Figure 4c). The cooperative behavior observed in the electronic absorption spectroscopic titration is explained by the allosteric Ca^{2+} binding facilitated by the preorganized chelating sites of the initially formed folded H-aggregates.

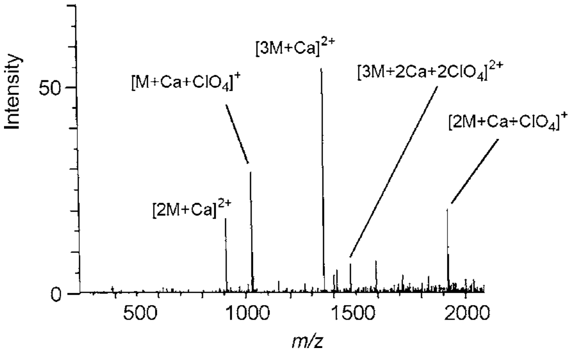

Figure 5. ESI-MS spectrum of **1a** with 3 molar equiv of $Ca(ClO_4)_2$ in $CHCl_3/CH_3CN$ (3/1, v/v). [**1a**] = 4.0×10^{-4} M.

The complexation-induced formation of the supramolecular assemblies of the folded H-aggregate was also examined with other alkali and alkaline earth metal cations (using perchlorates of Li^+, Na^+, K^+, Mg^{2+}, and Sr^{2+}). Only small electronic absorption spectral changes were observed for the dimers **1a**−**c** and **2** upon addition of Mg^{2+} and Sr^{2+}, where the absorbance ratios of the H-aggregates to the free dimers ranged from 0.07 to 0.16. On the other hand, addition of Li^+, Na^+, and K^+ did not show any change in the absorption spectrum. Thus, it was confirmed that Ca^{2+} is a good trigger for the formation of the metallo supramolecular assemblies of the folded H-aggregates.

Table 2. Assignment of ESI-MS Peaks of Dye−Ca^{2+} Complexes in $CHCl_3/CH_3CN$ (3/1, v/v)

molecular composition	m/z (relative intensity)		
	1a	**1b**	**1c**
$[M+Ca+ClO_4]^+$	1029 (29%)	1071 (11%)	1113 (21%)
$[2M+Ca]^{2+}$	910 (18%)	952 (22%)	994 (17%)
$[2M+Ca+ClO_4]^+$	1919 (20%)	2003 (6%)	2087 (3%)
$[3M+Ca]^{2+}$	1355 (55%)	1418 (54%)	1481 (31%)
$[3M+2Ca+2ClO_4]^{2+}$	1474 (7%)	1537 (9%)	1600 (9%)

In summary, we have demonstrated that the squaraine dimers with flexible alkyl chain linkers form H-type supramolecular aggregates by the extended complexation with Ca^{2+} cations. Chelation of the negatively charged oxygens in the central cyclobutenoate to Ca^{2+} ions is essential to the formation of the H-foldamer. This preorganized unit foldamer facilitates cooperative allosteric chelation to Ca^{2+} ions, resulting in the unprecedented formation of a metallo supramolecular one-dimensional array of squaraine H-aggregates. The present results provide new insights to explore the potential of squaraine dyes in the field of supramolecular dye chemistry.

Supporting Information Available: Experimentals and UV−vis spectral changes of the squaraine dimers upon addition of metal cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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