Metallo Supramolecular Assemblies of Bis-squaraines by Allosteric Ca²⁺ 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 xerographic² 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 Ca²⁺ and Mg²⁺ 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 polymethylenebridged 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 CHCl₃/CH₃CN 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 Ca²⁺. The electronic absorption spectral changes

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

of **1a** in CHCl₃/CH₃CN (3/1, v/v) in the presence of varying concentrations of Ca(ClO₄)₂ are shown in Figure 2. As the



Figure 2. Electronic absorption spectral changes of **1a** in CHCl₃/ CH₃CN (3/1, v/v) at 293 K upon addition of varying concentrations of Ca(ClO₄)₂ ([Ca²⁺]/[**1a**] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0). [**1a**] = 4.0×10^{-6} M.

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.

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-(ClO₄)₂; [**1a**] = 4.0×10^{-6} M. The inset shows the Job's plot for the **1a**-Ca²⁺ system; [**1a**] + [Ca²⁺] = 4.0×10^{-6} M.

H-aggregate formation was caused not only by a simple 1:1 complexation between **1a** and Ca²⁺ 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 Ca²⁺ Complexes in CHCl₃/CH₃CN (3/1, v/v) at 298 K^{*a*}

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

 a 4.0 \times 10⁻⁶ M. b 8.0 \times 10⁻⁶ M. c No spectral change was observed. $^dA_{\rm complex}$ and $A_{\rm free}$ are absorbances at $\lambda_{\rm max}$ of H-aggregate (ca. 575 nm) and metal-free dye (ca. 640 nm), respectively.

As summarized in Table 1, similar Ca²⁺-induced spectral changes were observed in the other dimers, although the ratio

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of the absorbance of the H-aggregate to that of the cationfree 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 CHCl₃ 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 Ca²⁺ (see Supporting Information). This result indicates that the bound Ca²⁺ should interact with the negatively charged oxygen atoms of the cyclobutenoate core. Thus, one can see that



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

chelation of the two squaraine moieties in the dimer to a Ca^{2+} affords the H-foldamer (Figure 4a). This folded "unit

⁽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 absorbance 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 Ca²⁺ 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 onedimensional array of the H-type folded aggregates of the Ca²⁺ 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(ClO₄)₂ in CHCl₃/CH₃CN (3/1, v/v) is shown in Figure 5. Parent peaks assigned to the supramolecular



Figure 5. ESI-MS spectrum of 1a with 3 molar equiv of Ca(ClO₄)₂ in CHCl₃/CH₃CN (3/1, v/v). [1a] = 4.0×10^{-4} M.

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 Ca²⁺ 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 Ca²⁺ binding facilitated by the preorganized chelating sites of the initially formed folded H-aggregates.

The complexation-induced formation of the supramolecular assemblies of the folded H-aggregate was also examined

Table 2. Assignment of ESI-MS Peaks of Dye-Ca²⁺ Complexes in CHCl₃/CH₃CN (3/1, v/v)

molecular	m/z (relative intensity)			
composition	1a	1b	1c	
[M+Ca+ClO ₄] ⁺	1029	1071	1113	
	(29%)	(11%)	(21%)	
$[2M+Ca]^{2+}$	910	952	994	
	(18%)	(22%)	(17%)	
$[2M+Ca+ClO_4]^+$	1919	2003	2087	
	(20%)	(6%)	(3%)	
[3M+Ca] ²⁺	1355	1418	1481	
	(55%)	(54%)	(31%)	
[3M+2Ca+2ClO ₄] ²⁺	1474	1537	1600	
	(7%)	(9%)	(9%)	

with other alkali and alkaline earth metal cations (using perchlorates of Li⁺, Na⁺, K⁺, Mg²⁺, and Sr²⁺). Only small electronic absorption spectral changes were observed for the dimers **1a**-**c** and **2** upon addition of Mg²⁺ and Sr²⁺, 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 Ca²⁺ is a good trigger for the formation of the metallo supramolecular assemblies of the folded H-aggregates.

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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