# Controlled self-assembly of squaraines to 1D supramolecular architectures with high molar absorptivity†‡

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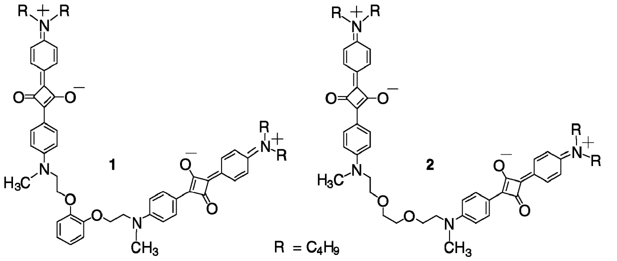
**A tailor made squaraine dye 1 upon binding with $Ca^{2+}$ self-assembles to form a spherical micellar assembly that reorganises to thermodynamically stable 1D cylindrical rods with high molar absorptivity.**

Self-assembly of functional dyes is a topic of current interest in the 'bottom-up' creation of nanoarchitectures due to their importance in the mimicry of natural processes and to the design of organic electronic devices.[1,2] Of particular importance is the self-assembly of organic dyes to 1D structures with high aspect ratio.[3] A variety of organic dyes, such as porphyrins,[4] phthalocyanines,[5] merocyanines,[6] perylenes[7] and squaraines,[8] have been reported as versatile synthons for the creation of functional supramolecular assemblies. Though extensive reports are available on the aggregation of squaraines, only a few examples are known of extended self-assembly leading to supramolecular architectures.[8,9] Herein we report an unprecedented effect of a cation binding to the self-assembly pathway and optical properties of a catechol-linked bis-squaraine dye **1**. Such an effect leading to a 0–1D structural change with strongly enhanced visible absorption upon cation complexation has not been reported previously.



In this work we explore the $Ca^{2+}$ and $Mg^{2+}$ binding ability of flexible chain-linked bis-squaraines.[10] The bis-squaraines **1** and **2** were synthesized and characterized by NMR and mass spectral analyses.[11] **1** in acetonitrile ($1 \times 10^{-6}$ M) exhibited an absorption maximum at 650 nm with two additional bands at 619 and 580 nm. The emission of the dye occurs at around 670 nm with a quantum yield of 0.004. On the other hand, the dye **2** with a flexible podand chain showed a relatively broad absorption with a better fluorescence quantum yield (0.014). These observations indicate a strong excitonic interaction between the dye moieties in **1** due to the positional confinement on an aromatic platform.

Titration of $Ca(ClO_4)_2{\cdot}4H_2O$ to a solution of **1** ($1.8 \times 10^{-6}$ M) in acetonitrile exhibited a decrease in the intensity of the absorption maximum at 651 nm with the formation of a new band at 547 nm (Fig. 1a). The Job plot revealed a 1 : 1 binding of the cation with the dye. Addition of $Mg^{2+}$ caused a similar effect, however $Sr^{2+}$ and $Ba^{2+}$ showed relatively weak changes to the absorption and emission spectra.[11] The dye **2** exhibited a relatively weak response towards $Ca^{2+}$. The absorption maximum of $\mathbf{2}{\cdot}Ca^{2+}$ occurred at 560 nm which is *ca.* 13 nm red-shifted with relatively weak molar absorptivity

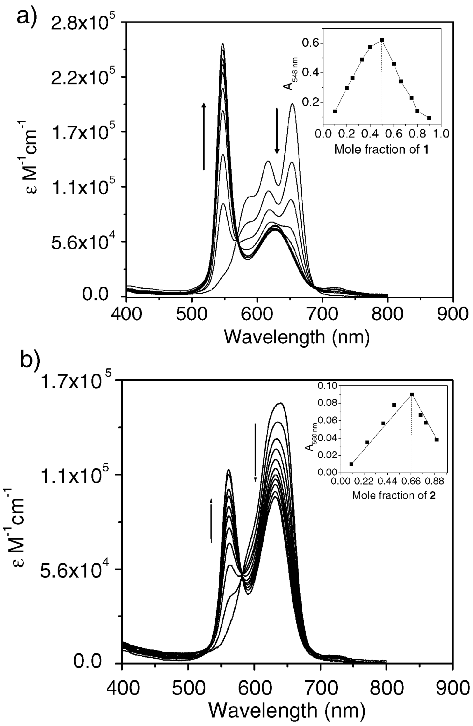


**Fig. 1** Absorption spectral change of (a) **1** and (b) **2** ($1.8 \times 10^{-6}$ M) in acetonitrile upon addition of $Ca(ClO_4)_2{\cdot}4H_2O$ (0–$2 \times 10^{-6}$ M) in acetonitrile. Insets show the corresponding Job plots.

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† Electronic supplementary information (ESI) available: Synthetic procedures, emission change of **1** with $Ca^{2+}$, absorption changes of **1** with $Mg^{2+}$, $Sr^{2+}$, $Ba^{2+}$, mass spectra of **1** before and after complexation with $Ca^{2+}$, AFM images of $\mathbf{1}{\cdot}Ca^{2+}$ complex after 9 h, TEM image of **2**. See DOI: 10.1039/b718054c

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in a 2 : 1 complexation mode when compared to those of **1**·Ca$^{2+}$, indicating a weak complexation in the former (Fig. 1b). This is clear from the comparison of $A_{547}/A_{651}$ for **1**·Ca$^{2+}$ and $A_{560}/A_{640}$ for **2**·Ca$^{2+}$, which are 1.31 and 0.74, respectively. Binding of Ca$^{2+}$ to the dye **1** is confirmed by mass spectral (FAB) analyses which gave values of 944.13 (M + 2H) for **1** and 982.33 (M + Ca$^{2+}$) for **1**·Ca$^{2+}$.[11]

Surprisingly, after the addition of $Ca(ClO_4)_2{\cdot}4H_2O$ to **1**, a three-fold increase in the intensity of the absorbance is observed within a time span of 10 h (Fig. 2). Such a persistent increase in the absorbance of a supramolecular dye–cation complex with time (hyperchromism) has not been reported previously. This phenomenon is attributed to the difference in the dipole orientation of the chromophores with time.[12] In such a situation we speculated that the initially formed kinetically controlled aggregates may change to thermodynamically favored structures in which the dipole orientation of the dye may change significantly. In addition, a considerable decrease in molecular shadowing may be possible when the morphology changes to cylindrical rods from spherical micelles.[13] Insight into this hypothesis is obtained by the detailed atomic force microscopic (AFM) and transmission electron microscopic (TEM) analyses of **1** in the absence and presence of Ca$^{2+}$. Interestingly, the Ca$^{2+}$ complex of the dye **2** did not show any change in the absorption spectra even on standing for several hours.

AFM images of the dried samples of **1** prepared from acetonitrile ($1.8 \times 10^{-6}$ M) in the presence of one equivalent of $Ca(ClO_4)_2{\cdot}4H_2O$ on freshly cleaved mica substrates showed spherical particles of 5–200 nm in diameter after deducting the tip broadening factor (Fig. 3a).[14] The corresponding histogram reveals an average particle size of 60 nm. AFM images after 6 h revealed the complete transformation of the spheres into extended assemblies of 10–100 nm in width and micrometres in length with an average height of 15 nm (Fig. 3c). The broad distribution of the width of the fibers indicates the formation of elementary 1D fibers that tend to form large bundles on the mica substrate. The morphology remained almost unchanged when imaged after 6 h.[11]

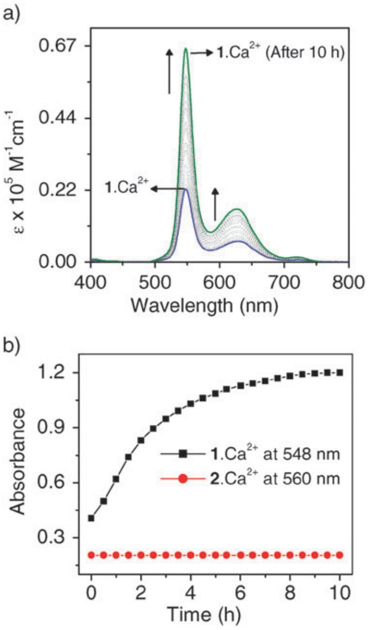

**Fig. 2** (a) Time dependent absorption spectral change of **1** ($1.8 \times 10^{-6}$ M) in acetonitrile after the addition of one equivalent of $Ca(ClO_4)_2{\cdot}4H_2O$. (b) Comparison of plots of the absorbance at 548 nm of **1**·Ca$^{2+}$ and at 560 nm of **2**·Ca$^{2+}$ against time showing the hyperchromic effect of the former.

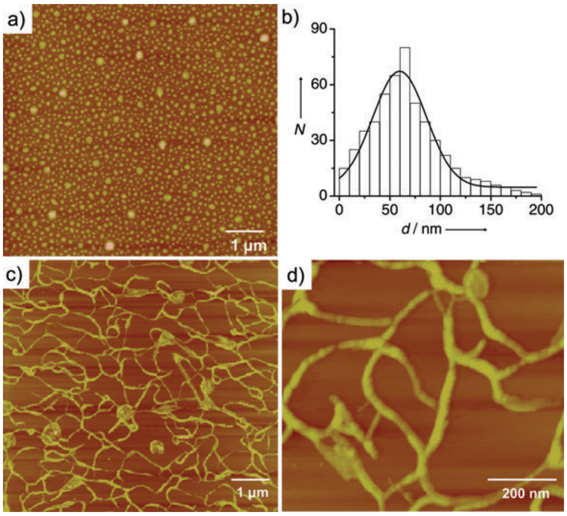

**Fig. 3** Tapping mode AFM images of **1**·Ca$^{2+}$ recorded after different intervals; (a) initial micellar assemblies, (b) histogram showing the particle distribution (Gaussian fit, $R^2 = 0.9510$) of the spherical assemblies of **1**·Ca$^{2+}$, (c) after 6 h and (d) zoomed image of the same. AFM samples were prepared by casting an acetonitrile solution ($1.8 \times 10^{-6}$ M) over a mica surface after adding an equivalent amount of $Ca(ClO_4)_2{\cdot}4H_2O$, *z*-scales of AFM images: (a) 10 nm and (c), (d) 30 nm.

In order to confirm the effect of the substrate on the morphology as well as the formation of a 1D self-assembly of **1**·Ca$^{2+}$ complex, transmission electron microscopy (TEM) studies were performed on carbon coated grids. TEM images of **1** ($1.8 \times 10^{-6}$ M) in acetonitrile in the presence of $Ca(ClO_4)_2{\cdot}4H_2O$ exhibited spherical structures that tended to agglomerate on the carbon grid (Fig. 4a). However, in the absence of the cation, no specific morphology could be seen.

The diameter of the smallest particle observed is *ca.* 4 nm which is twice the length of the molecule as determined from the energy minimized structure. This observation indicates the micellar nature of the self-assembly. The TEM images after 6 h revealed the transformation of the spherical micellar

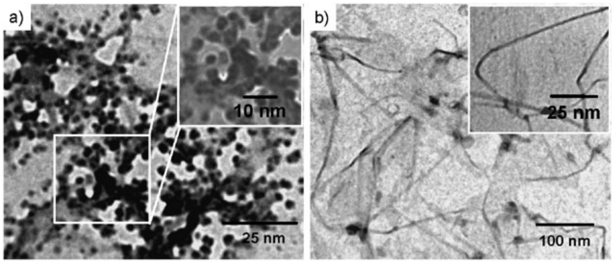

**Fig. 4** TEM (unstained) images of **1**·Ca$^{2+}$ recorded after different intervals; (a) initial micellar assemblies, and (b) after 6 h. Insets represent zoomed areas, highlighting different morphologies.

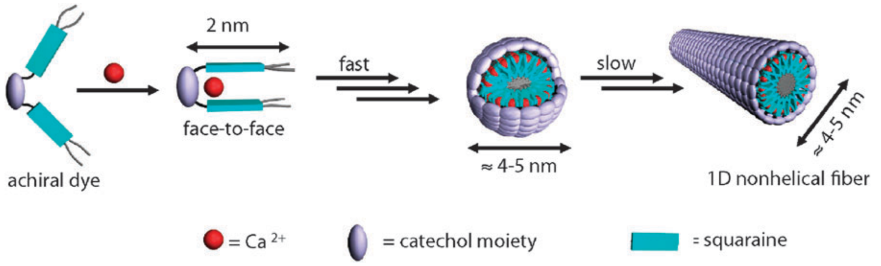

**Fig. 5** Schematic representation of $Ca^{2+}$ induced self-assembly processes in **1** leading to spherical and extended micellar structures.

aggregates to 1D nanostructures of *ca.* 4 nm in diameter and a few micrometres in length (Fig. 4b). After 6 h, the morphology remained more or less the same. Interestingly, the TEM analysis of the dye **2** showed spherical dye aggregates;[11] however, in the presence of $Ca(ClO_4)_2{\cdot}4H_2O$ no stable morphology could be seen, probably due to the weak complexation of **2** with $Ca^{2+}$. Thus the unusual hyperchromic behavior of **1**·$Ca^{2+}$ with time is in agreement with the morphology changes as observed by the AFM and the TEM analyses.

On the basis of the above observations, the self-assembly processes in dye **1** are rationalized as shown in Fig. 5. The amphiphilic nature of **1**·$Ca^{2+}$ allows initial self-assembly into the kinetically favored spherical micellar aggregates. Over a period of time the 0D spherical micelles rearrange into a thermodynamically stable 1D micellar assembly which is a slow process.[15] On the other hand, the dye **2** with a flexible podand chain forms a weak complex with $Ca^{2+}$ which neither shows a hyperchromic effect with time nor forms a stable self-assembly. These observations reveal that the confinement of the dye moieties on the aromatic platform as in **1** has a significant role in the hyperchromic effect and the self-assembly processes. In the case of the dye **1**, formation of the stable 1 : 1 complex may be partly assisted by the cation–arene interaction of the aromatic moiety of the podand chain. The initially formed stable complex facilitates the hierarchical assembly to spherical micelles and extended micellar structures through peripheral arene–arene interactions (Fig. 5). The weak 2 : 1 complexation in dye **2** with the cations does not allow these processes in the absence of the aromatic moiety of the podand chain.

In conclusion, we have illustrated that even a subtle variation in the structure of the dye has a significant impact on the hierarchical self-assembly, initially to 0D spherical and finally to 1D extended micellar structures, accompanied by a hyperchromic effect. The presence of the aromatic moiety of the catechol linker in dye **1** plays the key role in the cation controlled self-assembly process. This is clear from the fact that the dye **2** without the catechol linker did not show stable self-assembly or hyperchromism. The 1D structures of the dye **1** with high absorbance may find application in organic electronic and photonic devices that require a high molar absorption cross-section.

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