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Solvent-Induced Aggregation and Cation-Controlled Self-Assembly of Tripodal Squaraine Dyes: Optical, Chiroptical and Morphological Properties

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The synthesis, characterisation, optical, chiroptical, aggregation, and alkaline earth metal cation assisted self-assembly properties of tripodal squaraine dyes have been described. In the tripodal geometry, these dyes exhibit three absorption bands around 650, 620 and 580 nm in contrast to the single, sharp absorption of a simple dye (**SQ**) at 640 nm. The fluorescence quantum yield of the squaraine dyes are 25–30 times lower when compared to that of **SQ**, which indicates intramolecular exciton interaction as a result of the confinement of the dyes. The evaporation of an acetonitrile solution of the dye resulted in the formation of vesicular objects as confirmed by AFM and TEM analyses. However, evaporation of an acetonitrile solution containing 10–12 % water gave short fibrous aggregates. In the presence of Ca^{2+} or Mg^{2+} ions, the dyes exhibit an intense and sharp absorption band at 547 nm with a concomitant decrease of the native absorption. Interestingly, the dye with chiral groups failed to give a circular dichroic signal during aggregation in solvent mixtures, whereas strong signals were observed in the presence of Ca^{2+} and Mg^{2+} ions. AFM and TEM analyses of the corresponding cation complexes revealed the formation of worm like nanohelices. However, addition of EDTA to the Ca^{2+} or Mg^{2+} complex exhibited a reversal of the absorption, emission, and circular dichroic spectra to that of the native dye, indicating decomplexation. AFM analyses revealed the transformation of the helices to particles. These observations reveal the difference in the nature and properties of the simple aggregates formed in solvent mixtures and those formed in the presence of cations. In the present study, we were able to establish the importance of specific cation binding in controlling the size, shape, and properties of the hierarchical assemblies of tripodal squaraines.

Keywords: aggregation · dyes/pigments · self-assembly · supramolecular chemistry · vesicles

Introduction

Aggregation of organic dyes is a phenomenon of interest, both from the fundamental and technological points of view. As a result of exciton interaction, the absorption and emission properties of aggregates will be different from those of the corresponding monomers. This phenomenon usually leads to low-order structures such as dimers, trimers, tetramers, or pentamers. Aggregation of a variety of functional dyes such as cyanines,[1] merocyanines[2] porphyrins,[3] perylenes,[4] and squaraines[5] has been reported, which occurs because of π-interaction and solvophobic assistance. On the other hand, use of hydrogen bonding and metal ion coordination along with π-stacking facilitates self-assembly of the dye leading to supramolecular architectures with definite shape and size. In this way, different morphologies such as vesicles, micelles, tubes, rods, and fibers of functional dyes could be possible in solvents of varying polarity.[6] In this context, supramolecular dye chemistry has been attracting significant attention in recent years.[7]

Squaraines are a well-studied class of organic dyes for both fundamental, and technological reasons.[8] They are extensively used in electrophotography,[9] organic solar cells,[10] non-linear optics,[11] optical data storage,[12] cation sensing,[13] two-photon studies[14] and in photodynamic therapy.[15] Even though the aggregation behavior of squaraine dyes are well-

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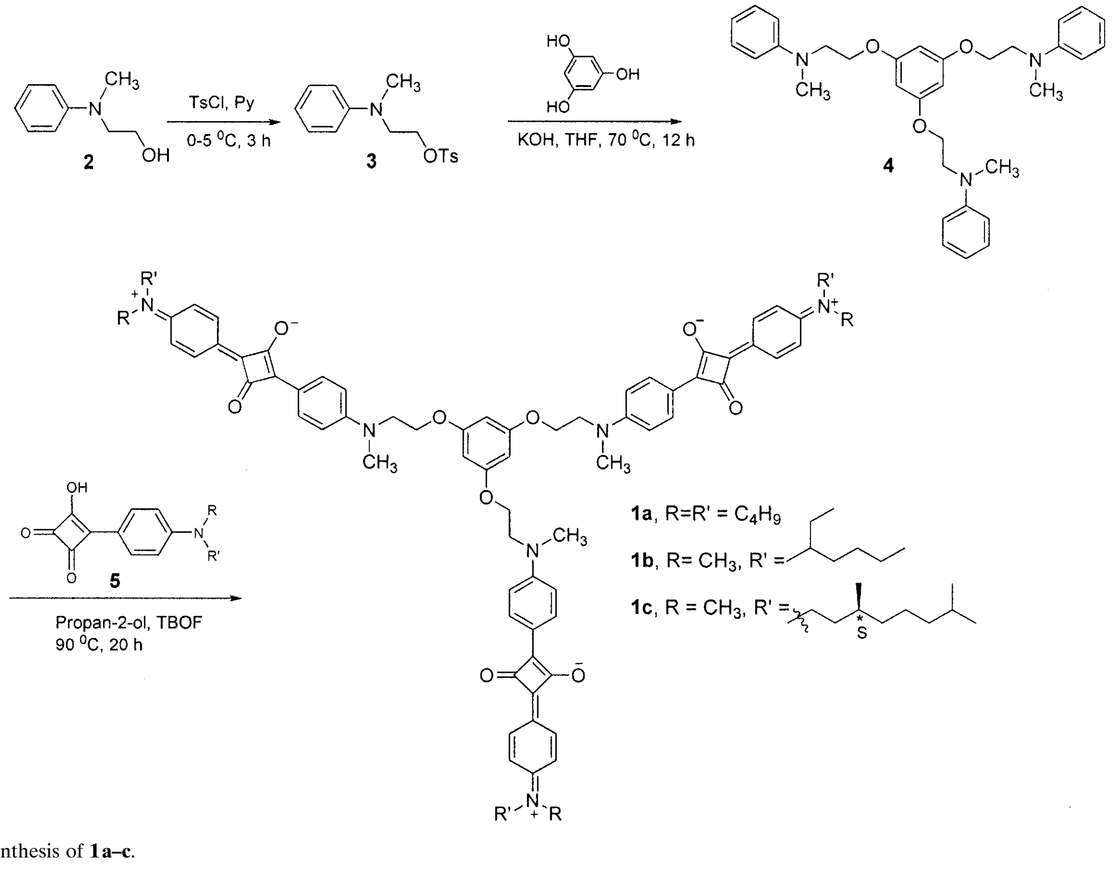
understood, studies pertaining to the self-assembly of these dyes to supramolecular architectures are very few.[16–19] Whitten and co-workers have earlier reported the organo gel formation of cholesterol linked squaraine dyes because of the formation of micrometer sized fiber networks.[16] Recently we have demonstrated cation assisted amplification of chirality and morphology change from spheres to helices in a chiral tripodal squaraine upon complexation with Ca^{2+}.[17] Herein, we present the detailed results on the aggregation and self-assembly of a few tripodal squaraines, induced by solvophobic effects and cations, leading to significant changes in the optical, chiroptical, and morphological properties.

Results and Discussion

The tripodal dyes **1a**–**c** were synthesized according to Scheme 1 with the speculation that confinement of the dyes on a rigid aromatic core might enhance the propensity of aggregation leading to hierarchical assemblies. The precursor **4** was obtained by the reaction of **3** with phloroglucinol which, on further reaction with 3.3 equivalents of the corresponding *N,N*-(dialkylaminophenyl)-4-hydroxycyclobut-3-en-1,2-dione in propan-2-ol in the presence of a catalytic amount of tributyl orthoformate, gave the dyes **1a**–**c** in 11–25 % yields. The purified compounds were characterized by NMR and mass spectral analyses.

Optical Properties

The absorption and emission spectra of **1a–c** and their fluorescence quantum yields in acetonitrile are shown in Table 1. These dyes showed three clear absorption bands in acetonitrile when compared to the single sharp absorption band of an analogous model dye **SQ** obtained from *N,N*-dibutylaniline and squaric acid.[20] The fluorescence quantum yields of **1a–c** are nearly 25–30 times lower than that of the **SQ** dye. The absorption and emission spectra of **1b** in different solvents are shown in Figure 1a and 1b. In acetonitrile, **1b** exhibited an absorption maximum at 651 nm with two absorption shoulders at 619 and 580 nm (Figure 1a). In chloroform, apart from the strong sharp absorption at 647 nm there was an absorption shoulder at around 616 nm. In DMSO, the dye exhibited a broad absorption at 665 nm. The emission spectra showed a maximum at 666 nm in chloroform which was red shifted by 19 nm in DMSO (685 nm). The presence of two clear shoulder bands in the absorption spectra of the dyes in acetonitrile, in addition to the absorption maximum, indicates solvent dependent exciton coupling in **1a–c** as a result of intramolecular interactions of the conformationally confined dye molecules.[21] Increasing the concentration of the dye in acetonitrile (10^{-6}–



Scheme 1. Synthesis of **1a–c**.

Table 1. Absorption, emission and quantum yields of **1a–c** and a model dye **SQ** in acetonitrile.

Compound	Abs λ_{max} [nm]	ε [10^5 M^{-1} cm^{-1}]	Ems λ_{max} [nm]	Quantum yield (Φ)[a]
1a	651,620,580	6.9	668	0.004
1b	650,619,580	7.2	668	0.006
1c	650,620,579	8.9	670	0.004
SQ	640	3	660	0.15

[a] Fluorescence quantum yields are calculated using 4,4-[bis-(*N,N*-dimethylamino)phenyl]squaraine dye as standard ($\Phi = 0.7$ in $CHCl_3$), excited at 570 nm.

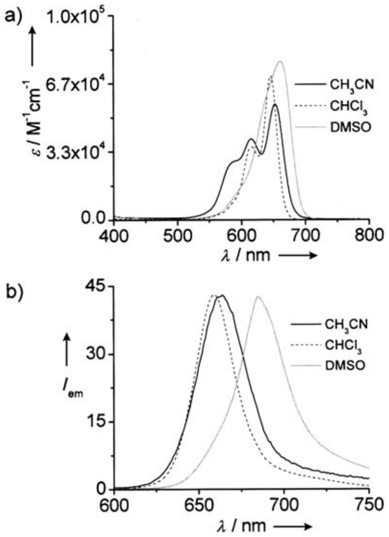


Figure 1. a) Absorption and b) emission spectra of **1b** in chloroform, DMSO and acetonitrile (10^{-6} M).

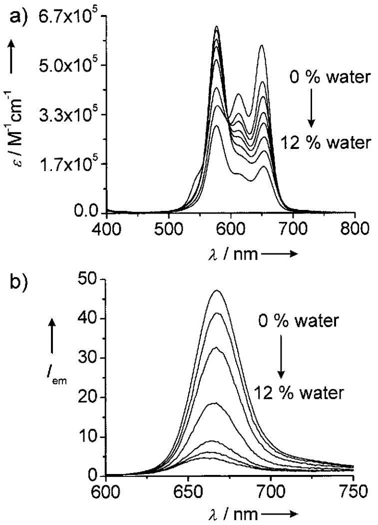


Figure 2. Absorption and emission spectral changes of **1b** (1.2×10^{-6} M) in different acetonitrile–water compositions.

10^{-4} M) did not show any considerable change in the absorption and emission spectra, thus ruling out any intermolecular processes.

Solvent Induced Changes in the Optical Properties

Optical properties of the squaraines are known to be strongly influenced by solvent polarity as well as solvent composition as a result of the aggregation of molecules.[5] These are mainly intermolecular aggregation leading either to "H"- or "J"-type aggregates. In the case of dyes **1a–c**, the absorption spectra indicate intramolecular exciton interaction, which is strong in acetonitrile. Since water is known to induce aggregation of the squaraine dyes, the absorption spectral changes of **1a–c** were monitored in solutions of acetonitrile and DMSO having different compositions of water. The absorption spectral changes of **1b** in acetonitrile having 0–12% (v/v) water are shown in Figure 2. The major absorption band of **1b** at 651 nm decreases in intensity with a concomitant increase in intensity of the shoulder band at 580 nm as the water content in the mixture is gradually increased to 12%. Increase in temperature from 25–70 °C showed only a slight decrease in the intensity of the peak at 580 nm, which indicates that the aggregates of **1b** are fairly stable. In the emission spectra, the intensity of emission at 660 nm decreases as the water percentage in acetonitrile is increased (Figure 2b). These changes in the absorption and emission properties of **1b** are in accordance with the formation of "H"-type aggregates. In a 12% water–acetonitrile mixture, the dye **1b** showed an additional weak band at 540 nm. However, the nature of this band could not be studied because a further increase in the water content induced precipitation of the aggregates. For an insight on the phenomenon, DMSO–water mixtures of different compositions were chosen. Initially, the dye in DMSO (1.2×10^{-6} M) exhibited a broad absorption centred at 668 nm. However, increasing the water content from 0–14% resulted in a decrease in the intensity of the absorption at 668 nm with the growth of a new blue-shifted absorption at 597 nm (Figure 3a).

Interestingly, increasing the water content from 14–20% resulted in a decrease in the intensity of the absorption at 597 nm with a sharp rise in the absorption at 537 nm (Figure 3a). Again, further increase in the water content lead to precipitation of the dye. The color of these aggregates at different water compositions are shown in Figure 3d. In DMSO, the dye is green in color whereas the aggregates in 10% and 15% water in DMSO appeared light blue and purple respectively. The emission of the dye in DMSO at 685 nm was quenched as the water composition increased (Figure 3b), with a slight blue shift (685–681 nm).

The absorption spectrum of **1b** in DMSO with 12–14% water content showed a time-dependent increase in the intensity of the band at 537 nm. The intensity of the absorption at 595 nm rapidly decreased in a 14% water solution reaching equilibration within a time span of around 8 min.

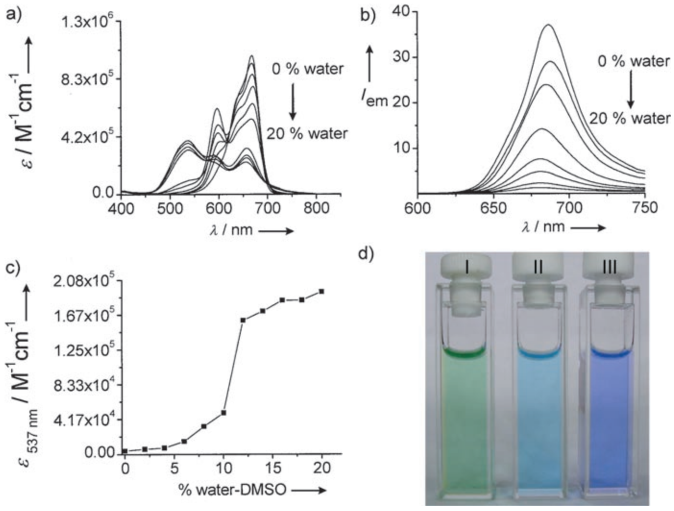


Figure 3. Aggregation of **1b** (1.2×10^{-6} M) in various composition of DMSO–water. a) Absorption and b) emission spectral changes of **1b** in 0–20 % water–DMSO, c) variation of absorbance at 537 nm at various water–DMSO compositions. d) Photograph of the aggregates of **1b** formed at different water–DMSO composition: I) 0 % water, II) 10 % water–DMSO and III) 15 % water–DMSO.

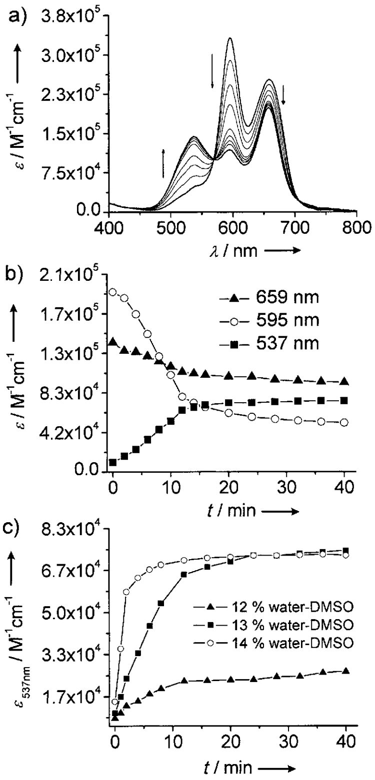


Figure 4. Time-dependent absorption spectral changes of the aggregate of **1b** (1.2×10^{-6} M) in a) 13 % water–DMSO, b) corresponding variation of absorbance at 659, 595 and 537 nm with time and c) variation of absorbance at 537 nm of aggregates in 12, 13 and 14 % water–DMSO.

The same phenomenon was observed in the case of the 13 % water solution; however the process was comparatively slow and required 14 min for equilibration (Figure 4c). During the process, the intensity of the absorption at 659 nm also decreased (Figure 4a) with an isosbestic point at 570 nm. The plot of the intensity of the 537 nm band versus time (Figure 4c) reveals that the water content in DMSO plays a crucial role in the time-dependent conversion of aggregates. Similar observation of time-dependent change in the aggregate bands of squaraines in DMSO–water has been reported, and was attributed to the dynamic conversion of "kinetically" to "thermodynamically" preferred aggregates.[22] The formation of the blue-shifted band at 537 nm suggests further aggregation processes occur with time to form more stable assemblies.

Cation Induced Changes in the Optical Properties

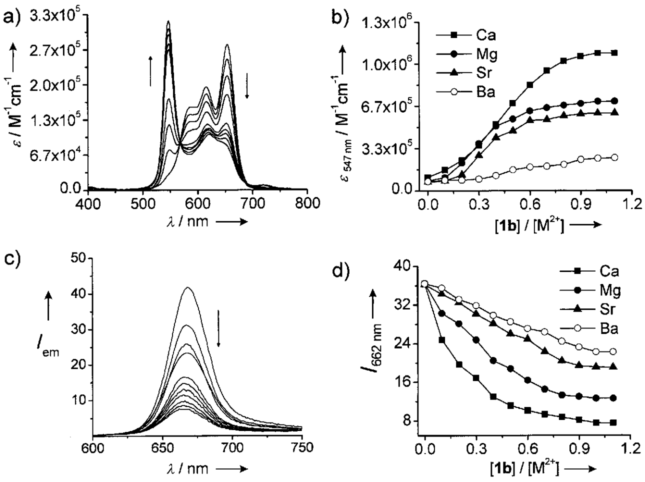


Figure 5. a) Absorption and b) emission spectral changes of **1b** (1.2×10^{-6} M) in acetonitrile on addition of $Ca(ClO_4)_2{\cdot}4H_2O$ ($0–4\times10^{-6}$ M) at 298 K (path length: 10 mm)

Alkaline earth metal cations, particularly Ca^{2+} and Mg^{2+} ions are known to strongly bind to podands and polymethylene linked squaraines, inducing a significant blue shift of the absorption spectrum.[23] The cations are shown to induce folding of the flexible chains leading to "H"-type intramolecular dimers. In some cases, the cation bound complex leads to the formation of metallo supramolecular arrays.[24] The tripodal dyes **1a**–**c** showed a similar decrease in the original absorption with the formation of a new band at 547 nm and an isosbestic point at 563 nm upon addition of $Ca(ClO_4)_2{\cdot}4H_2O$. The emission spectrum showed a gradual quenching of the maximum at 670 nm with the addition of the cation salt. These changes for **1b** are shown in Figure 5a and 5c. Although other alkaline earth metal ions such as Mg^{2+}, Ba^{2+}, and Sr^{2+} exhibited changes in the absorption and emission spectra, these changes were comparatively weaker than those induced by the Ca^{2+} ion and decreased in the order $Mg^{2+} > Sr^{2+} > Ba^{2+}$ (Figure 5b and d). The difference in the binding affinity may be as a result of the difference in the size and charge density of the cations. Ca^{2+} and Mg^{2+} ions are known to strongly bind with negatively charged chelating agents.

The changes get saturated upon addition of one equivalent of the calcium salt as can be seen from the plots of absorbance at 547 nm against the ratio of the dye and the cation (Figure 5b). Job plots revealed 1:1 complexation between the cation and the dye. The dyes **1a** and **1c** showed a similar trend in the absorption and emission spectra with different alkaline earth cations. It is interesting to note that the absorption maxima of the Ca^{2+} and the Mg^{2+} complexes of **1a–c** fall very close to that of the aggregate band in acetonitrile and DMSO with a higher water (>12%) composition. However, the absorption bands of the cation complexes are more intense and sharp when compared to those of the aggregates obtained from the solvent mixtures, which indicates a more organized self-assembly in the former. In order to get more insight into this hypothesis, we have used the dye **1c** having a chiral handle. In this case, circular dichroism (CD) becomes a powerful tool to probe the difference in the nature of the aggregates formed in solvent mixtures and with cations.

Chiroptical Properties

In the case of chromophores having chiral centres, a CD signal arises as a result of biased interchromophore aggregation leading to organized hierarchical helical assemblies with a preferred handedness. Recently, Hecht and co-workers have shown that a chiral squaraine dye which forms both blue- and red-shifted aggregates from acetonitrile–water mixtures exhibit CD signals indicating helical aggregates.[25] However, in this case the observed strong CD signal corresponds to the red-shifted aggregate band. In the case of **1c**, the CD signal was negligible in acetonitrile at a concentration of 3.6×10^{-6} M, which indicates the absence of interchromophore aggregation. Surprisingly, in solvent mixtures, even though aggregation is evident from the absorption spectrum, we could not see any considerable CD response. From this observation it can be inferred that in solvent mixtures, the tripodal geometry of **1c** facilitates the collapse of the dye moieties, resulting in ill-defined aggregates without a helical twist. However, addition of Ca^{2+} or Mg^{2+} ions to a solution of **1c** in acetonitrile (3.6×10^{-6} M) resulted in a CD couplet with a first positive Cotton effect at 622 nm followed by a negative one at 541 nm through zero crossing at 565 nm (Figure 6a). The increase in the intensity of the CD signal gets saturated after the addition of one equivalent of the metal salt. The CD intensities on complexation with alkaline earth metal ions varies in the order $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$ (Figure 6c). These observations are in agreement with the absorption and emission spectral changes. Furthermore, the observed difference in the CD response of the aggregates of **1c** formed in solvent mixtures and in the presence of the cations, indicates the remarkable difference in their supramolecular organization and morphology. It is obvious that cation complexation is crucial for the expression of chirality and helps the dye molecules in **1c** to form aggregates with a helical bias leading to supramolecular helicity.

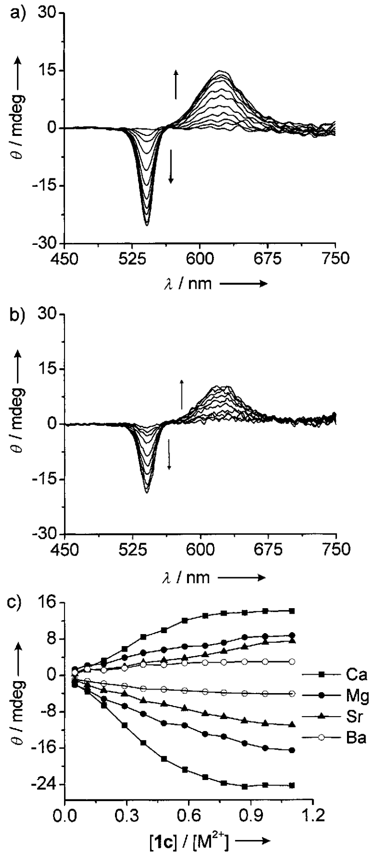


Figure 6. Circular dichroism spectral changes of **1c** (3.6×10^{-6} M) in acetonitrile on addition of a) $Ca(ClO_4)_2{\cdot}4H_2O$ and b) $Mg(ClO_4)_2{\cdot}4H_2O$ (0–4×10^{-6} M) at 298 K. c) Plots corresponding to the intensities of the positive and negative CD signals against the ratio of the dye to the cations.

Morphological Properties

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) analyses of the acetonitrile solutions of **1a–c** after evaporation on a mica surface and carbon coated grids, showed spherical structures (Figure 7). The AFM analysis of **1c** from acetonitrile revealed spheres with a diameter in the range of 80 nm–2.3 μm after reducing the tip broadening factor (Figure 7a).[26] Detailed particle size analysis revealed an average size of 518 nm as shown in the histogram (Figure 7b). The height of these spheres was in the range of 10–350 nm, which indicated considerable flattening of the objects. This phenomenon is common in organic soft self-assemblies which is caused by the local force exerted by the AFM tip.[27] Since we could not observe any major changes in the absorption spectra of **1a–c** in acetonitrile at different concentrations and temperatures, it was clear that these dyes do not form any type of hierarchical assemblies in solution. This hypothesis is supported by the fact that dynamic light scattering (DLS) failed to show the presence of particles in solution. Therefore, particle formation could be

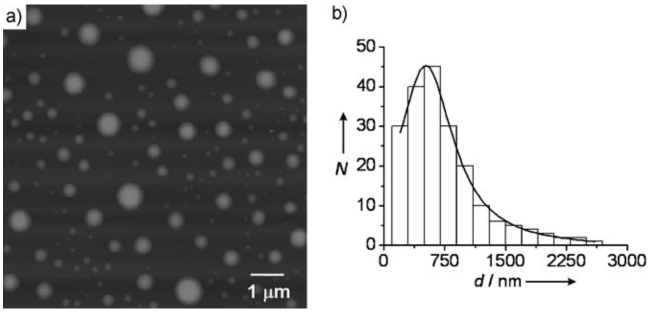


Figure 7. a) AFM height image of **1c** from acetonitrile (2×10^{-6} M) evaporated on mica surface. Z-scale: 250 nm. b) Histogram showing the particle distribution with an average size of 518 nm (Lorentzian fit, $R^2=0.9948$).

as a result of the slow evaporation of the solvent on the mica surface.

TEM images of a dried solution of **1c**, dip cast on a carbon coated grid showed particles of 40–80 nm in size (Figure 8a). These particles are vesicular, as could be seen from a zoomed part of the image which shows a clear difference in contrast to the periphery and the inner part of the spheres (Figure 8b). The wall thickness of these images are of ca. 4–5 nm (Figure 8b, inset), which agrees with the calculated bilayer thickness of two stacked tripodal dye units after deducting the length of the alkyl chains. The large difference in the particle size observed in the AFM images may arise from the fusion of small vesicles during the slow evaporation of the solvent on the mica surface.

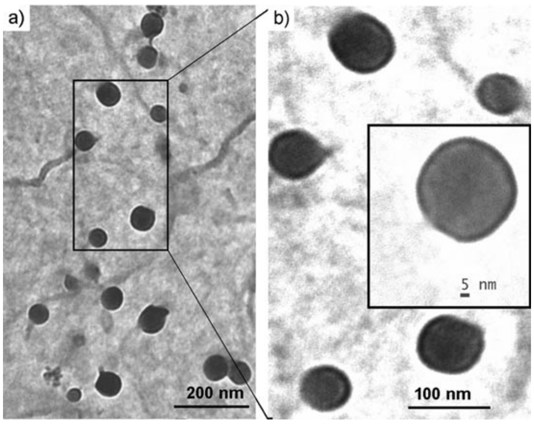


Figure 8. a) TEM image of the nanospheres obtained by the dip coating of an acetonitrile solution of **1c** on carbon coated grid (inset: image of a fused vesicle). b) Zoomed images of the marked area showing the vesicular nature (inset: zoomed image of a single vesicle showing the wall thickness).

The AFM images of **1c** obtained by the evaporation of its solution in acetonitrile containing 10% water (v/v), drop cast on a mica surface are shown in Figure 9. The images 9a and 9b are taken from two different places of the same sample which indicate a large variation in the morphology. In many places, short fibrous structures of 50–100 nm in width could be seen. It must be remembered that the CD spectra of **1c** did not show any response in the same solvent mixture indicating the absence of chiral assemblies. Therefore, the structures seen on the mica surface must have been formed from the organization of the elementary aggregates upon evaporation of the solvent. Thus a change of solvent from pure acetonitrile to 10% water–acetonitrile had a profound influence on the morphology, namely, from vesicles to fibres. Unfortunately, we failed to acquire good TEM images of these aggregates even after repeated attempts.

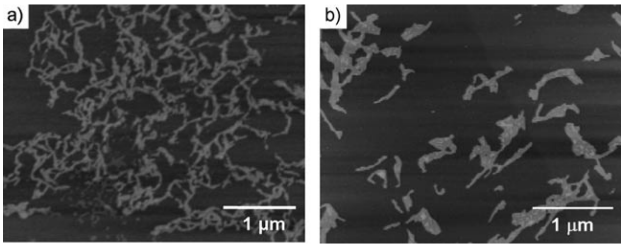


Figure 9. AFM height images of the aggregates of **1c** in 90% acetonitrile-water casted on mica surface. Images are obtained from two different places of the sample. z-scale: a) and b) 20 nm.

Addition of $Ca(ClO_4)_2{\cdot}4H_2O$ to a solution of **1a–c** resulted in uniformly distributed fibres having a width of (28 ± 15) nm and a height of (3.5 ± 0.5) nm, as visualised from the AFM image. In the case of **1c** these fibres are helical in nature (Figure 10). They appear to be worm like with a near uniform width of ca. 50 nm with a right handed helical pitch of 90 nm. TEM images showed a comparable morphology and size even though the helicity was not very clear (Figure 11). The size of the supramolecular structures found in the AFM and TEM images in the presence of the cations are comparable to each other. This could be attributed to the possible formation of the self-assembly in the solution itself and evaporation of the solvent on the mica surface may not have much influence on deciding the size and the morphology. It must be recalled that **1c** in the presence of Ca^{2+} exhibited a strong CD signal in solution, which indicates the formation of a helical assembly. The morphology

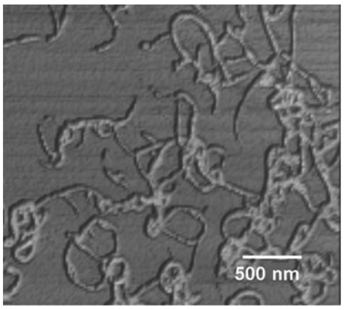


Figure 10. AFM images of **1c**.Ca^{2+} on mica substrate cast from acetonitrile solution (1.8×10^{-6} M).

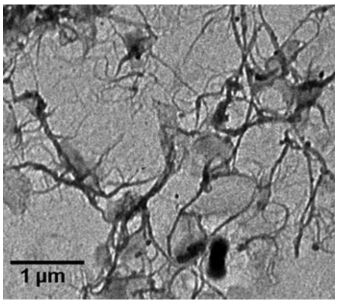


Figure 11. TEM images of **1c**.Ca^{2+} complex on carbon coated grid casted from acetonitrile solution (1.8×10^{-6} M).

of the Mg^{2+} complex was almost similar to that of the Ca^{2+} complex as evident from the AFM images except that the length of the fibres are relatively shorter in the case of the Mg^{2+} complex (Figure 12).

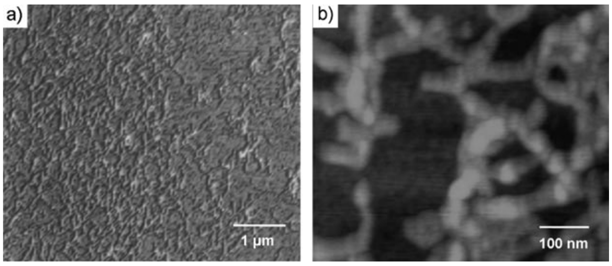


Figure 12. AFM images of **1c**.Mg^{2+} complex cast from acetonitrile solution on mica surface at two different magnifications and view. z-scale: a) 25 nm and b) 20 nm.

An interesting feature of **1a–c** is the reversibility of the cation complexation in the presence of EDTA. Addition of an equivalent amount of EDTA, which is a better chelator of Ca^{2+} and Mg^{2+}, facilitates decomplexation leading to the reversal of the absorption, emission, and CD spectra to the initial state of the dye (Figure 13). AFM analysis of the **1c**·Ca^{2+} complex in acetonitrile after addition of an equivalent amount of EDTA resulted in the complete transformation of the helical structures to disc like objects (Figure 13c). This change in the morphology indicates that cation complexation is essential for the formation of nanohelices.

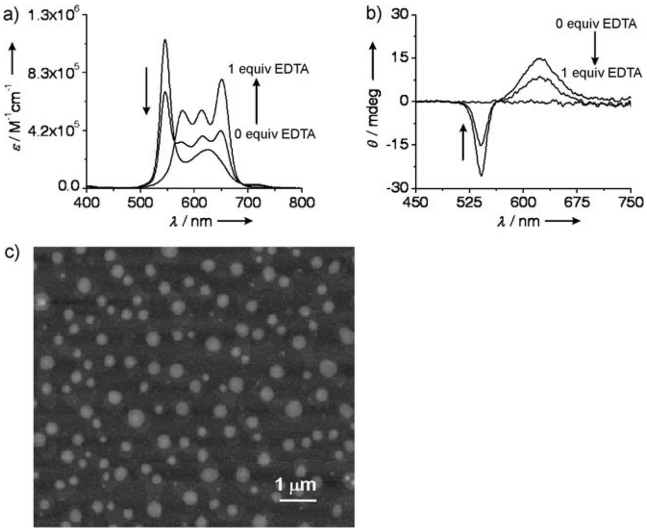


Figure 13. a) Absorption and b) CD spectral changes of **1c**.Ca^{2+} on addition of EDTA. c) AFM images of **1c**.Ca^{2+} on addition of equivalent amount of EDTA showing morphology change from helical fibres to particles. z-scale: c) 50 nm.

Conclusions

With the help of a few tripodal squaraine dyes, we have illustrated that confinement of the dye moieties on an aromatic platform strongly influences the optical, chiroptical, and morphological properties. We could establish significant differences in the properties of the aggregates, which are induced by solvents and cations. The tripodal dyes gave vesicular assemblies when evaporated from acetonitrile while forming fibrous aggregates on evaporation from acetonitrile–water mixtures. On the other hand, in the presence of Ca^{2+} or Mg^{2+} ions, nanosized fibrous self-assemblies are formed. In the case of a chiral dye, amplification of chirality was observed upon cation binding, whereas the solvent induced aggregates were optically inactive by circular dichroism. The worm like nanohelices formed with cations are deformed into particles upon addition of EDTA. These results reveal that in the present systems, cations play an important role in the expression of molecular chirality to supramolecular helicity. The clear difference in the nature and properties of solvent and cation induced aggregates suggest that an appropriate cation binding is essential for an organized self-assembly of the tripodal squaraines, leading to supramolecular architectures with controlled shape and size.

Experimental Section

General experimental details including the instrumentation and methods are given in the Supporting Information.

Synthesis of 1a–c: 1,3,5-tris[(2-(*N*-methyl-*N*-phenyl)amino)ethoxy]benzene (**4**) was refluxed with 3.3 equivalents of the corresponding *N,N*-(dialkylaminophenyl)-4-hydroxycyclobut-3-en-1,2-dione in propan-2-ol (50 mL) in the presence of tributyl orthoformate (TBOF, 1 mL) for 20 h, which resulted in the formation of the squaraine dyes **1a–c**. The crude products were purified over silica gel (100–200 mesh) using chloroform/methanol (9:1) as the eluent.

1a: Yield: 11 %; m.p. >320 °C (decomp); FT-IR (KBr) $\nu_{max}=3513$, 2955, 1710, 1587, 1402.3, 1349, 1182, 834, 786.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta=0.96$(t, $J=8$ Hz, 18 H, $-CH_3$), 1.31–1.43 (m, 24 H, $-CH_2$), 3.1 (s, 9 H, $-NCH_3$), 3.41–3.67 (m, 24 H, $-NCH_2$ and $-OCH_2$), 6.1(s, 3 H, aromatic), 6.71–6.78 (m, 15 H, aromatic), 8.36–8.39 ppm (m, 12 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=13.8$, 20.2, 29.5, 39.6, 51.2, 76.9, 106.9, 112.3, 112.4, 120.1, 132.7, 133.6, 153.8, 183.3, 187.3 ppm; elemental analysis: calcd (%) for $C_{87}H_{102}N_6O_9$: C 75.95, H 7.47, N 6.11; found: C 75.86, H 7.50, N 6.09.

1b Yield: 25 %; mp >320 °C (decomp); FT-IR (KBr) $\nu_{max}=2954$, 2914, 2670, 1718, 1581.4, 1429, 1389, 1351.3, 1286.5, 1178, 1126.4, 932, 840, 787, 501.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.91$(t, J=8.1 Hz, 18H, $-CH_3$), 1.41–1.44(m, 27H, $-CH_2$), 3.1 (s, 18H, $-NCH_3$), 3.39–3.67(m, 18H, $-NCH_2$ and $-OCH_2$), 6.75–6.78 (m, 15H, aromatic), 8.36–8.39 ppm (d, 12H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 10.66$, 14.00, 23, 23.90, 28.61, 30.57, 37.8, 38.2, 39.61, 40.11, 52.27, 56.63, 56.95, 69, 104.3, 105.63, 107.73, 110.4, 110.8, 111, 111.95, 112.3, 114.7, 118.32, 119.69, 120, 131.9, 154.9, 183.3, 187.7 ppm; elemental analysis: calcd (%) for $C_{90}H_{108}N_6O_9$: C 76.24, H 7.68, N 5.93; found: C 76.36, H 7.59, N 6.01.

1c:Yield: 21%; m.p. >320°C (decomp); FT-IR (KBr) $\nu_{max} = 2953$, 2924, 2673, 1720, 1587.4, 1435, 1384, 1355.3, 1284.5, 1182, 1126.4, 933, 835, 785, 503.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.86$–0.88(d, 18H, $-CH_3$), 0.96–0.98(d, 9H, $-CH_3$), 1.25–1.71 (m, 30H, $-CH_2$), 3.1 (s, 18H, $-NCH_3$), 3.51–3.67(m, 18H, $-NCH_2$ and $-OCH_2$), 6.72–6.78 (m, 15H, aromatic), 8.35–8.4 ppm (d, 12H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 15.2, 19.6, 22.6, 24.6, 27.9, 29.6, 30.9, 33.9, 37.1, 39.6, 52.3, 69, 92.8, 94.6, 96.4, 104.4, 107.4, 110.8, 113, 119, 120.1, 124, 128.7, 132.9, 133.5, 183.3, 194.3, 197.2, 199.3 ppm. MALDI-TOF MS (MW=1500.99): $m/z = 1501.07$ $[M]^+$.

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