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Helical Structures

Self-Assembly of Tripodal Squaraines: Cation-Assisted Expression of Molecular Chirality and Change from Spherical to Helical Morphology**

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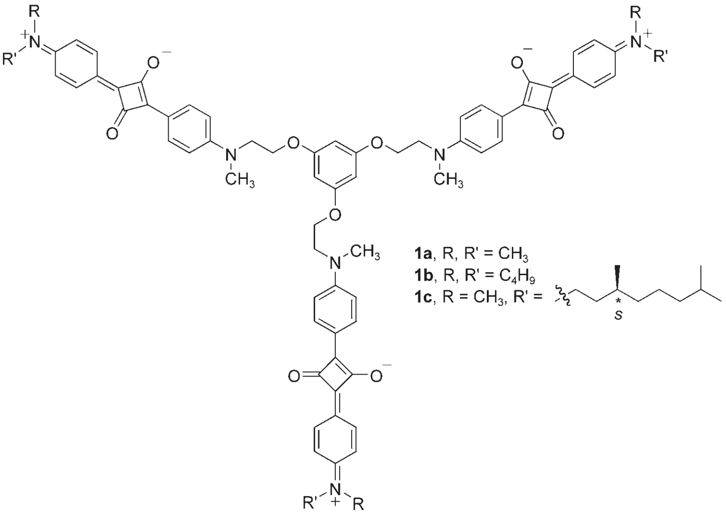
Inspired by the elegance and complexity of natural helical assemblies, from the nanoscopic DNA double helix and collagen triple helix to microscopic viruses and macroscopic sea shells, chemists have been trying to mimic the structure and functions of biological macromolecules in self-assembled synthetic molecules.[1–7] The most challenging task in these studies is the control of the overall morphology and the supramolecular chirality of the self-assembled architectures within the nanometer-to-micrometer length scale.[8] Although a few reports on reversible morphology transitions caused by external stimuli have appeared,[9] a spherical-to-helical change induced by a cation was previously unknown. However, in an interesting report Nolte and co-workers described the loss of helicity in a phthalocyanine-derived self-assembly in the presence of potassium ions.[10] Herein we report an unprecedented self-assembly of tripodal squaraine dyes, which form vesicular structures upon evaporation of the solvent from a solution of the dye and helical architectures through the expression of molecular chirality into supramolecular helicity upon a specific cation binding.[11]

The supramolecular chemistry of functional dyes is at center stage in the "bottom-up" creation of nanoarchitectures.[12] Squaraines, a class of zwitterionic dyes, are well known for their tendency to form aggregates under the influence of certain solvent mixtures and cations.[13,14] Although these dyes have been studied extensively owing to their fundamental and technological significance, they are rarely exploited for the crafting of supramolecular architectures. The propensity of these dyes to aggregate to form hierarchical assemblies could be enhanced by confining the chromophores to an aromatic platform, thereby making interchromophore interaction possible. As a proof of principle of this hypothesis, we designed the three tripodal squaraines **1a–c**, which we then synthesized by the reaction of 1,3,5-tris(2-(*N*-methyl-*N*-phenylamino)ethoxy)benzene with the corresponding *N*,*N*-(dialkylaminophenyl)-4-hydroxycyclobut-3-ene-1,2-dione and characterized by spectral analysis. The UV/Vis spectra of these dyes show strong absorption but weak emission. For example, **1c** has an absorption maximum in chloroform at 647 nm (6.2×10^{-7} M, $\varepsilon_{651\,\text{nm}} = 8.9\times10^{5}\,\text{M}^{-1}\,\text{cm}^{-1}$) with a shoulder at 617 nm, whereas in acetonitrile, in addition to the $\lambda_{\max}$ absorption at 651 nm (8.3×10^{-7} M, $\varepsilon_{651\,\text{nm}} = 2.5\times10^{5}\,\text{M}^{-1}\,\text{cm}^{-1}$) and the shoulder at 614 nm, another band was observed at 578 nm. The emission maximum of **1c** when excited at 570 nm in chloroform or acetonitrile occurred at 662 and 663 nm with quantum yields of 0.01 and 0.004, respectively (relative to bis(4-(dimethylamino)phenyl)squaraine in chloroform as the standard). These observations support intramolecular chromophore interaction in acetonitrile and the consequent exciton coupling of the confined chromophores.[15]



The absorption spectra of **1a–c** in acetonitrile–water mixtures of different compositions showed significant changes. For example, the addition of an increasing amount of water (0–12 %) to a solution of **1c** in acetonitrile ($c = 3.6\times10^{-6}$ M) led to a gradual decrease in the intensities of the bands at 651 and 614 nm with a simultaneous increase in the intensity of the band at 578 nm through an isosbestic point at 596 nm (Figure 1a). The intensity of the emission decreased as the percentage of water in the solution was increased. These changes are similar to those observed in the H aggregation of analogous squaraine dyes.[13b,c] However, the addition of $Ca(ClO_4)_2$ or $Mg(ClO_4)_2$ (0–4×10^{-6} M) to **1c** ($3.6\times$

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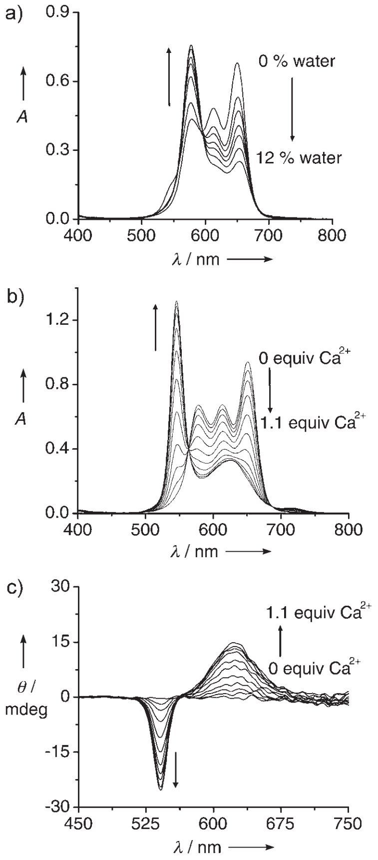

Figure 1. Changes in the absorption spectra of **1c** (3.6×10^{-6} M): a) in acetonitrile–water mixtures of different compositions and b) with an increasing concentration of $Ca(ClO_4)_2$ ($0–4\times10^{-6}$ M) in acetonitrile. c) Induced CD of **1c** (3.6×10^{-6} M) with an increasing concentration of $Ca(ClO_4)_2$ ($0–4\times10^{-6}$ M) at 298 K (path length: 10 mm).

10^{-6} M) in acetonitrile led to a decrease in the intensities of the initial absorption bands with the concomitant growth of an intense blue-shifted band at 547 nm through an isosbestic point at 563 nm; saturation occurs at a cation concentration of 3.6×10^{-6} M (Figure 1b). During the process the initial excitonic features are lost, and the color of the dye changes from light blue to an intense purple-blue. These changes are relatively weaker for Sr^{2+} and Ba^{2+}, whereas the addition of alkali metal salts had no effect on the optical properties of **1a–c**. Job and Benesi–Hildebrand analyses indicated a 1:1 stoichiometry.[16]

The chiral dye **1c** is CD silent up to a concentration of 3.6×10^{-6} M in acetonitrile. However, upon the addition of $Ca(ClO_4)_2$ a CD couplet with a first positive Cotton effect at 622 nm followed by a negative Cotton signal at 541 nm with zero crossing at 564 nm is observed (Figure 1c). The negative sign of the couplet corresponds to the absorption of the blue-shifted band at 547 nm, and the zero crossing matches with the isosbestic point at 563 nm. The CD intensity increases gradually with an increasing concentration of $Ca(ClO_4)_2$ and becomes saturated at an equimolar concentration of the metal salt and **1c**. Induced CD was also observed upon the addition of Mg^{2+}, although the signal intensities were weaker than with Ca^{2+}. With Sr^{2+} and Ba^{2+} the CD signals were very weak.

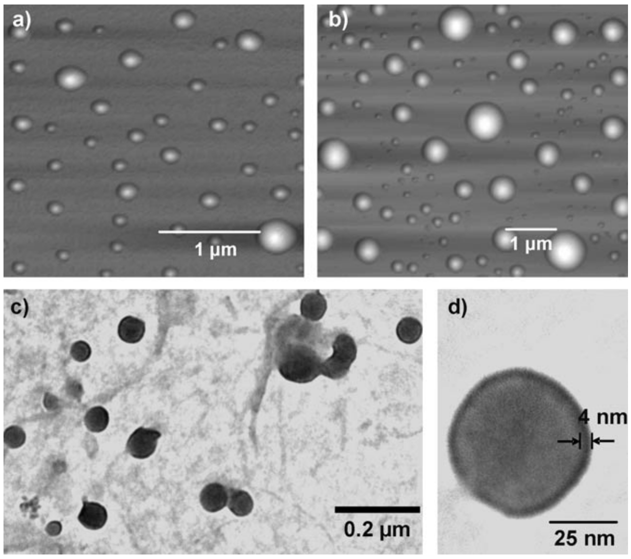

Figure 2. Height images acquired by tapping-mode AFM of a) **1b** (z scale = 100 nm) and b) **1c** (z scale = 200 nm). c) TEM image of **1c** on a carbon-coated grid. d) A magnified TEM image of a vesicular assembly. Blank experiments were carried out with neat acetonitrile evaporated from mica or a carbon grid to rule out the possibility of any artifacts.

The height images obtained by tapping-mode atomic force microscopy (AFM) of **1b** and **1c** after the evaporation of the solvent from a solution of each dye (2×10^{-6} M) in acetonitrile on freshly cleaved mica sheets showed the formation of nano- to microsized spherical assemblies (Figure 2a,b). The diameter of the spherical assemblies of **1b** varied from 90 nm to 2.3 µm with heights in the range of 8 to 150 nm. Spheres of the chiral dye **1c** had diameters ranging from 75 nm to 2.6 µm and heights of 10 to 350 nm. These differences in the diameter and height indicate a flattening of the objects as a result of either the evaporation of the solvent or the local force exerted by the AFM tip.[17] Analysis of **1c** on carbon-coated grids by transmission electron microscopy (TEM) showed the formation of relatively smaller spherical assemblies with a better size control (Figure 2c,d). This observation indicates that the surface influences particle formation during the evaporation of the solvent. The TEM images reveal the hollow nature of the spherical assemblies through the contrast difference between the periphery and the inner part of the spheres. This structure is clear from a magnified image of a vesicle (Figure 2d). Its wall thickness of approximately 4 nm is very close to the calculated bilayer thickness of two π-stacked tripodal dyes if the length of the terminal alkyl chain is subtracted. The X-ray diffraction (XRD) patterns of **1c** showed a sharp peak at 2.88 nm with periodic second- and third-order reflections at 1.44 and 0.7 nm.[16] Although a few reports on the morphology of squaraine-dye aggregates have appeared in the literature,[18] the formation of vesicular assemblies of squaraines from pure acetonitrile has not been reported.

The AFM images of **1b** in the presence of Ca^{2+} or Mg^{2+} showed an unexpected morphology change from spheres to extended structures of nanometer dimensions (Figure 3a).

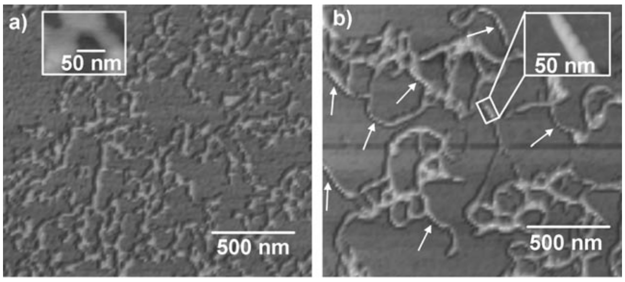

Figure 3. Height images acquired by tapping-mode AFM of a) **1b**–Ca^{2+} and b) **1c**–Ca^{2+}. Insets show zoomed images of selected parts (*z* scale = 15 nm). Arrows indicate helical bias.

More importantly, **1c** formed nanohelices upon the addition of Ca^{2+} or Mg^{2+} (Figure 3b). Section analysis of the images of **1c** revealed helical structures of micrometer length and (28 ± 15) nm in width with a height of (3.5 ± 0.5) nm after subtracting the broadening factor due to the AFM tip.[19] A zoomed image of a helix showed a right-handed bias with a helical pitch of 90 nm. In the present system the helicity is clear, in contrast to many reported cases in which the helical morphology is not visible in the AFM images despite the exhibition of strong CD signals.[20]

Strikingly, the CD signals of aggregates of **1c** ($c = 3.6 \times 10^{-6}$ M) formed from acetonitrile–water mixtures of different compositions were negligible, thus indicating that complexation with cations is crucial for the expression of the molecular chirality.[16] Moreover, the AFM images of the dye structures formed from acetonitrile–water mixtures show agglomerated nanoaggregates without visible helicity.[16] The amplification of CD and the supramolecular helicity exclusive to the cation-complexed chiral dye indicate that the presence of cations is necessary for the induction of a helical bias in the self-assembly of **1c**. The intensity of the blue-shifted absorption band at 547 nm and of the induced CD of the cation-complexed dye decrease upon titration with ethylenediaminetetraacetic acid disodium salt (EDTA), which facilitates the decomplexation of Ca^{2+} from the dye. Thus, at 1 equivalent of EDTA the original spectra are obtained (Figure 4a,b). The AFM image of **1c**–Ca^{2+} after the addition of EDTA showed the deformation of the helical structures and the formation of spherical assemblies. Figure 4c shows the regeneration of the spherical aggregates from the destroyed helical structures, which subsequently change completely into spherical assemblies (Figure 4d). These changes in the optical, chiroptical, and morphological properties indicate that cation complexation is essential for the formation of extended helical structures.

The probable self-assembly pathways of the chiral tripodal dye are shown in Figure 5. Evaporation of the solution of the dye in the absence of Ca^{2+} facilitates the formation of vesicular assemblies as a result of a bilayer arrangement of the tripodal dyes, as confirmed by TEM analysis. The observed wall thickness of 4 nm agrees approximately with the calculated length of two π-stacked tripodal squaraine moieties. Complexation with Ca^{2+} does not favor such an assembly because of the cationic charge repulsion, and extended packing of the cation-complexed rigid chromophore is facilitated. Such packing in the case of **1c** leads to a helical arrangement of the molecules owing to the presence of the chiral handles and results in helical supramolecular structures.

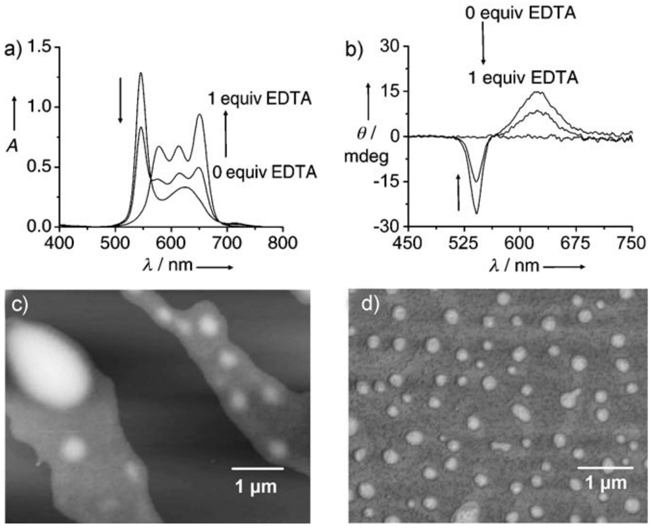

Figure 4. Reversal of a) absorption and b) CD spectra of **1c**–Ca^{2+} (3.6×10^{-6} M) with an increasing amount of EDTA (0, 1.8, 3.6×10^{-6} M). c),d) AFM images that show the morphology change under ambient conditions of **1c**–Ca^{2+} after the addition of an equimolar amount of EDTA (*z* scale = 75 and 50 nm for c and d, respectively).

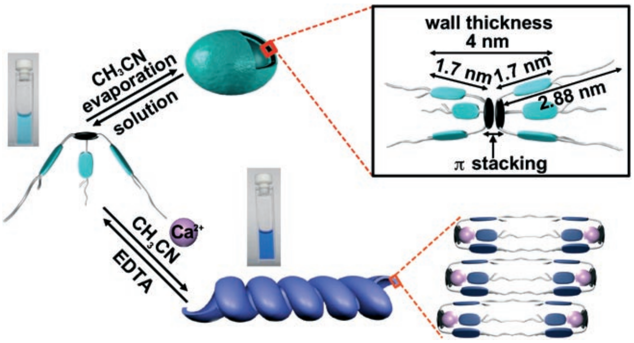

Figure 5. A cartoon representation of the self-assembly processes and morphology changes of **1c**. The solutions in the cuvettes show the actual colors of the tripodal dye before (light blue) and after (dark blue) the addition of Ca^{2+}.

In conclusion, we have demonstrated the self-assembly of tripodal squaraines from acetonitrile into hollow spherical structures that change to form linear structures upon binding with Ca^{2+} or Mg^{2+}. This unprecedented cation-controlled morphology change has been exploited for the design of nanohelices of a chiral tripodal squaraine dye. Surprisingly, CD signals and supramolecular helicity are observed only for the cation-complexed chiral dye and not for the aggregates from acetonitrile–water mixtures. This is the first example of a cation-induced morphology change of spherical assemblies into nanosized helical structures through expression of molecular chirality in a functional tripodal dye and has implications in the broad area of supramolecular dye chemistry and functional nanoarchitectures.

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