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Chiral Supramolecular Assemblies of a Squaraine Dye in Solution and Thin Films: Concentration-, Temperature-, and Solvent-Induced Chirality Inversion

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Abstract: We prepared novel cholesterol-appended squaraine dye **1** and model squaraine dye **2** and investigated their aggregation behavior in solution and thin films using photophysical, chiroptical, and microscopic techniques. Investigations on the dependence of aggregation on solvent composition (good/poor, $CHCl_3/CH_3CN$) demonstrated that squaraine dye **1** forms two novel H-type chiral supramolecular assemblies with opposite chirality at different good/poor solvent compositions. Model compound **2** formed J-type achiral assemblies under similar conditions. The supramolecular assembly of **1** observed at lower fractions of the poor solvent could be assigned to the thermodynamically stable form, while a kinetically controlled assembly is formed at higher fractions of the poor solvent. This assignment is evidenced by temperature- and concentration-dependent experiments. With increasing temperature, the chirality of the kinetically controlled aggregate was lost and, on cooling, the aggregate with the opposite chirality was formed. On further heating and cooling the aggregates thus formed resulted in no significant changes in chirality, that is they are thermodynamically stable. Similarly, at lower concentrations, the thermodynamically stable form exists, but at higher concentration aggregation was found to proceed with kinetic control. Based on these observations it can be assumed that formation of the kinetically controlled assembly might be largely dependent on the presence of the nonpolar cholesterol moiety as well as the amount of poor solvent present. However, under solvent-free conditions, structurally different aggregates were observed when drop cast from solutions containing monomer, whereas a left-handed CD signal corresponding to the thermodynamically controlled assemblies was observed from pre-aggregated solutions.

Keywords: aggregation · chirality · dyes/pigments · helical structures · supramolecular chemistry

Introduction

Squaraine dyes have been the subject of many recent investigations.[1] The current interest in these dyes may be attributed to their interesting photophysical and photochemical properties[2] which make them suitable for a variety of applications. These include photoconductors in organic solar cells,[3] photoreceptors in copiers and laser printers,[4] IR absorbers in organic optical disks,[5] sensors for metal ions[1g] and proteins,[6] and sensitizers in photodynamic therapeutic (PDT) applications.[7] These dyes are known to form aggregates in solution, organized media, Langmuir–Blodgett films, and microcrystals.[8] Depending on the nature of the substituents and the medium, these dyes form both H- (pack-of-cards) and J-type (end-to-end) aggregates.[8,9]

Recently, dye aggregates have received considerable attention in the fields of highly sensitive biosensors,[10] field-effect transistors,[11] and supramolecular electronics.[1a] Dye aggregates that can form chiral assemblies are particularly important, since switching between the different supramolecular chiral states could, in principle, have potential applications in data storage, optical devices, LCDs, and chromatographic chiral separation.[12] Moreover, stable chiral aggregates with favorable photophysical properties that exhibit reversible switching between P (plus, right-handed) and M (minus, left-handed) supramolecular assemblies could have applications as chiroptical materials.[13,14]

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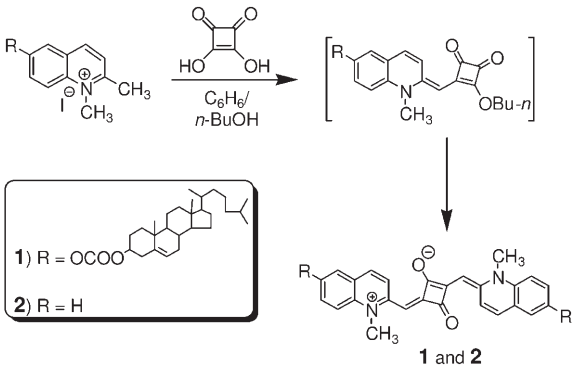
Reversible P–M transitions driven by external stimuli such as temperature,[15] light,[16] and additives[17] have been reported in synthetic helical polymers. More recently, Würthner and co-workers reported formation of supramolecular chiral assemblies derived from merocyanine dyes which exhibit irreversible stereomutation of one form (kinetically controlled) to another, thermodynamically stable form.[18] However, chiral aggregates derived from squaraine dyes and their chiroptical applications have received less attention.[1a,9b] In this context, our objective has been to design novel squaraine dyes that can form chiral assemblies and to further understand the chiral inversion in such assemblies. For the present study, we prepared cholesterol-appended quinoline-based squaraine dye **1** (Scheme 1) and, for comparison, model compound **2** and investigated their aggregation behavior under different conditions using photophysical, chiroptical, and microscopic techniques. Our results indicate that the cholesterol-linked squaraine dye **1**, which exhibits favorable photophysical properties, forms two novel H-type chiral supramolecular assemblies, the chiral state of which can be controlled by temperature, solvent polarity, and concentration.

Results

Synthesis of squaraine dyes 1 and 2: Dyes **1** and **2** were synthesized in good yields (85%) by condensation between squaric acid and the corresponding quinaldinium salt in 2:1 ratio in *n*BuOH/benzene (1/1) (Scheme 1). The squaraine



Scheme 1. Synthesis of quinaldine-based squaraine dyes **1** and **2**.

dye reaction proceeds via the intermediate semisquaraine dye, which under the reaction conditions reacts with another molecule of the quinaldinium salt resulting in the corresponding squaraine dye in good yields that depend on the substituents present.[19] The dyes were purified and characterized on the basis of spectral and analytical data (see Figure S1 in the Supporting Information).

Dependence of aggregation properties of 1 and 2 on solvent composition: Cholesterol-linked squaraine dye **1** exhibits good solubility in most nonpolar solvents. However, solutions in polar solvents do not obey the Beer–Lambert law at higher concentrations. Figure 1A shows absorption spectra

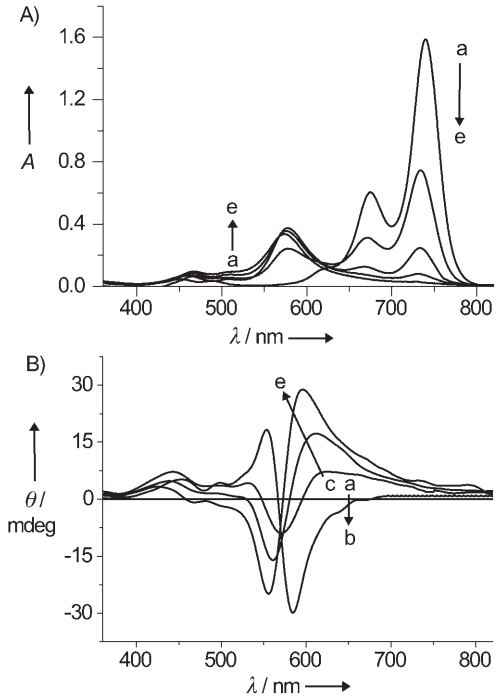


Figure 1. A) Absorption and B) corresponding CD spectra of dye **1** (7.2 μM) recorded in $CHCl_3/CH_3CN$ with increasing fraction of CH_3CN: a) 1/0, b) 1/1, c) 2/3, d) 3/7, and e) 1/4. All samples were equilibrated before recording the spectra.

of **1**, recorded in $CHCl_3$ with increasing content of CH_3CN (poor solvent). At 100% $CHCl_3$, the dye exhibits a sharp absorption maximum at 740 nm corresponding to the monomer ($\varepsilon = 2.2 \times 10^5\,M^{-1}cm^{-1}$). However, when the $CHCl_3/CH_3CN$ ratio was increased to 1/1 (v/v), a new broad band centered around 578 nm appeared in the absorption spectrum. With further increase in the fraction of CH_3CN, we observed a regular decrease in monomer absorption with a concomitant increase in absorption at 578 nm. The CD spectra (Figure 1B) recorded in a $CHCl_3/CH_3CN$ (1/1) showed a bisignate exciton-coupled CD signal with a negative Cotton effect (M), that is, the absorption at 578 nm is due to the formation of H-type aggregates in a left-handed helical pattern. However, when the $CHCl_3/CH_3CN$ ratio was increased to 2/3, we observed a shift in the zero crossing of the CD signal, indicative of weak exciton coupling between the individual chromophores. With further increase in the fraction of CH_3CN, we observed inversion of the CD signal from left-handed (*M*) to right-handed (*P*), that is, transformation between two aggregates having opposite handedness.

With a view to understanding the aggregation process, the time-dependent formation of the aggregates was monitored in $CHCl_3/CH_3CN$ (2/3) by absorption spectroscopy (Figure 2). As the poor solvent (CH_3CN) was added to the

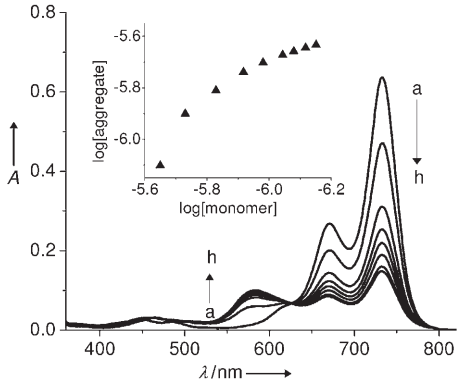


Figure 2. Absorption spectra of dye **1** (3.3 μM) recorded in $CHCl_3/CH_3CN$ (2/3) with increasing time: a) 0, b) 5, c) 7, d) 9, e) 12, f) 15, g) 18, h) 20, and i) 23 min. Inset: plot of log[monomer] versus log[aggregate] under similar conditions.

dye solution in $CHCl_3$, the absorption corresponding to the monomer at 740 nm decreased with a concomitant increase of the absorption corresponding to the aggregate at 578 nm. Formation of the aggregate was found to reach equilibrium at around 15 min, while for higher fractions of CH_3CN the equilibration time was shorter. Once equilibrium was reached in a particular mixture, we observed negligible changes in the intensity and sign of the Cotton effect even after 24 h (see Figure S2 in the Supporting Information). The inset of Figure 2 shows a plot of log[monomer] versus log[aggregate] for **1** in $CHCl_3/CH_3CN$ (2/3) with increasing time. The plot becomes nonlinear as aggregation proceeds and it reaches saturation after a particular time interval. This indicates that **1** has a tendency to form higher order aggregates, especially when the fraction of CH_3CN in the mixture is increased.

Aggregation experiments at different solvent compositions were also carried out with model compound **2**, which lacks the cholesterol moiety (Figure 3). Model squaraine dye **2** in $CHCl_3$ exhibited an absorption maximum at 729 nm corresponding to the monomer. However, with increasing fraction of CH_3CN, a new peak at around 840 nm corresponding to the aggregate was observed. Observation of a hypsochromically shifted absorption maximum indicates formation of J-type aggregates in **2**, wherein the individual dye molecules prefer to undergo end-to-end association, in contrast to the H-type aggregates formed in **1**. Circular dichroism studies under identical conditions showed that the aggregates formed from **2** were CD-inactive, which could be attributed to the absence of a chiral handle.

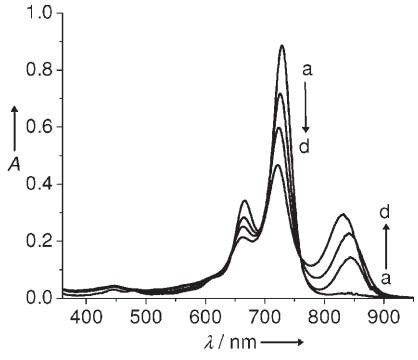


Figure 3. Absorption spectra of dye **2** (6.8 μM) recorded in $CHCl_3/CH_3CN$ with increasing fractions of CH_3CN: a) 1/0, b) 9/1, c) 7/3, and d) 1/9.

Temperature-dependent aggregation properties of 1: With a view to understanding the effect of temperature on the aggregate formation and handedness, assemblies were prepared at different temperatures. When the solutions were made below 15 °C, we observed formation of the aggregates with positive Cotton effect in $CHCl_3/CH_3CN$ (1/1). The temperature dependence of the Cotton effect was examined for this composition. With increasing temperature, the peak corresponding to the aggregate at 578 nm decreased with a concomitant increase of the peak corresponding to the monomer at 740 nm (Figure 4 A). Correspondingly, the CD spectra showed a decrease in intensity with increasing temperature (Figure 4 B). However, at 60 °C, the absence of any CD signal indicated complete transformation of the aggregate into monomers. In the cooling cycle, the aggregate with negative Cotton effect started to form and reached saturation at room temperature. Interestingly, the chirality of the aggregates thus formed showed no changes on further heating

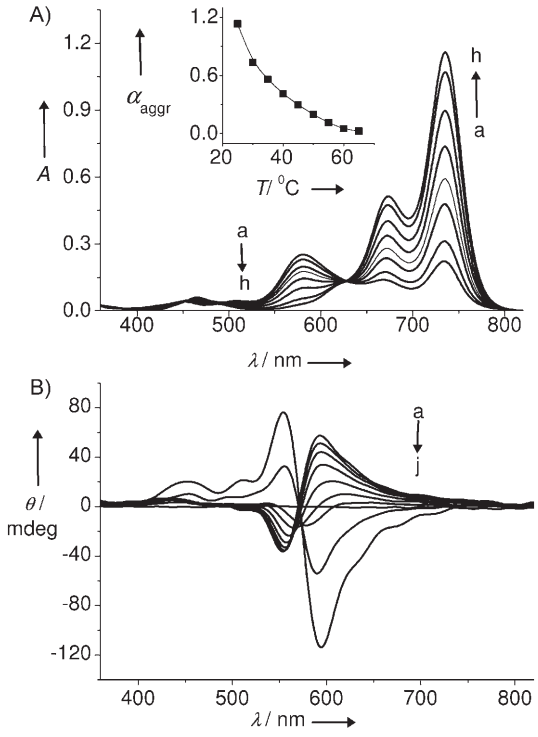


Figure 4. A) Absorption spectra of dye **1** (7.2 μM) recorded in $CHCl_3/CH_3CN$ (1/1) with increasing temperature: a) 25, b) 30, c) 35, d) 40, e) 45, f) 50, g) 55, and h) 60 °C. Inset: plot of aggregate/monomer ratio versus temperature. B) Corresponding CD spectra of dye **1** under similar conditions and after slow cooling at room temperature (26 °C) for i) 10 and j) 20 min.

and cooling the solution several times, and this indicates thermodynamic stability of these supramolecular assemblies.

The formation of the supramolecular assemblies was found to obey second-order kinetics in $CHCl_3/CH_3CN$ (1/1), with a rate constant of $k=3.8\times10^5\ dm^3\,mol^{-1}\,s^{-1}$. The non-sigmoidal nature of the plot of the ratio of the aggregate to monomer versus temperature shows that solvophobic interactions are the driving force for the formation of the aggregates (inset of Figure 4A). This was further supported by the rate of formation of the aggregate, monitored at three different temperatures (20, 30, and 40 °C; Figure 5A). With

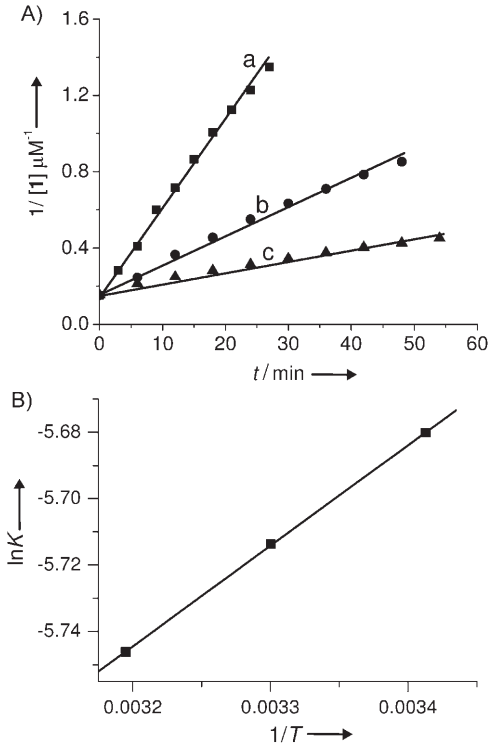


Figure 5. A) Second-order linear fit for the rate of formation of the aggregate from dye **1** in $CHCl_3/CH_3CN$ (1/1) at three different temperatures: a) 20 °C, b) 30 °C, and c) 40 °C. B) Corresponding Arrhenius plot for the formation the aggregates of **1** in $CHCl_3/CH_3CN$ (1/1).

increasing temperature, the rate of formation of the aggregate decreased (3.79, 1.24, and $0.42\times10^5\ dm^3\,mol^{-1}\,s^{-1}$ at 20, 30, and 40 °C, respectively). From the rate of formation of the aggregate at different temperatures, the activation energy E_a for formation of aggregates of dye **1** was determined to be 2.5 kJ (Figure 5B).

Concentration-dependent aggregation properties of dye 1 To gain more insight into the chirality inversion, concentration-dependent aggregation experiments were carried out with dye **1** in $CHCl_3/CH_3CN$ (2/3); see Figure 6. At lower concentrations of **1**, only the monomer exists, but with increasing concentration, the absorption corresponding to the aggregate increases at 578 nm, with a concomitant decrease of the absorption corresponding to the monomer. In the CD

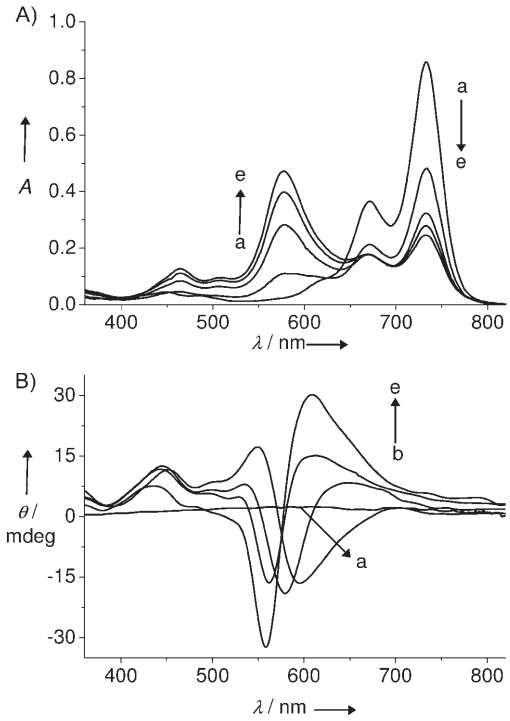


Figure 6. A) Absorption and B) corresponding CD spectra recorded in $CHCl_3/CH_3CN$ (2/3) with increasing concentration of **1**: a) 2.1, b) 3.84, c) 5.72, d) 7.3, and e) 8.8 μM.

spectra, on formation of the aggregate, a negative Cotton effect was observed, and its intensity increased with increasing concentration of **1** up to 3.8 μM. However, with further increase in concentration, the zero crossing of the CD signal undergoes a shift, as was observed in the experiments on solvent composition, and aggregates with a positive Cotton effect are formed.

Aggregation of squaraine dyes 1 and 2 in thin films: To correlate the chiral aggregation of squaraine dyes **1** and **2** in solution and under solvent-free conditions, thin films of the dye aggregates were made on glass surface and investigated by CD spectroscopy. When an aggregate-free solution of **1** (40 μM) in $CHCl_3$ was drop cast into a thin film, a negative Cotton effect was observed (Figure 7). However, in $CHCl_3/CH_3CN$, the sign of the Cotton effect varied with solvent composition. In relatively nonpolar ≥50 $CHCl_3/\leq50$ CH_3CN mixtures, we observed no aggregation of dye **1** in solution, but in thin films a positive CD signal corresponding to the supramolecular assembly was observed (Figure 7A). However, these aggregates exhibited different shape and nonbisignate CD signals when compared to the aggregates observed in solution and in the thin films made from polar ≤50 $CHCl_3/\geq50$ CH_3CN mixtures (Figure 7B).

To understand the nature of the aggregates formed in the thin films under various conditions, the effects of concentration, temperature, and slow and fast evaporation of the solvent were investigated (see Figures S3–S5 in the Supporting Information). Although the time and rate of solvent evapo-

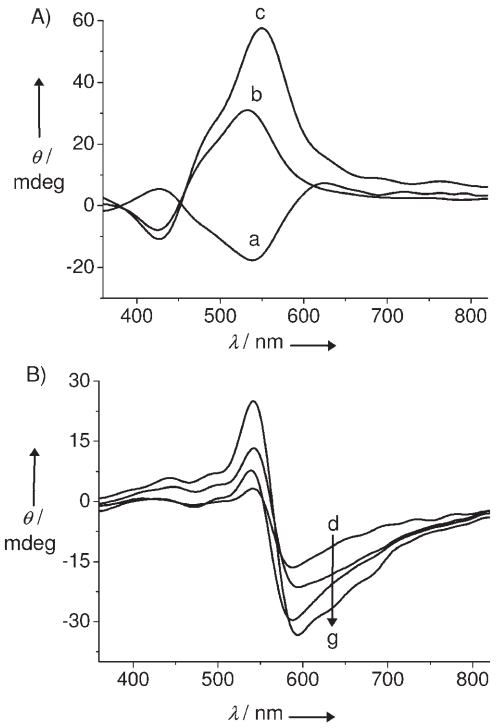


Figure 7. CD spectra of drop-cast films of **1** (40 μM) on a glass surface, made from $CHCl_3/CH_3CN$: a) 1/0, b) 9/1, c) 7/3, d) 1/1, e) 3/7, f) 1/4, and g) 1/9. The observed magnitude of the molecular ellipticity θ depends on the amount of dye deposited as thin film.

ration have negligible influence on the shape and sign of the Cotton effect of the aggregates formed in thin films, significant effects of dye concentration and solvent composition were observed. For example, when thin films of **1** (40 μM) were made from an aggregate-free $CHCl_3/CH_3CN$ mixture (7/3), we observed positive, nonbisignate CD signals. In contrast, negative, bisignate CD signals were observed when the thin films were prepared from the same solvent composition but under pre-aggregated conditions (>120 μM, see Figure S6 in the Supporting Information). Similarly, we observed significant effects of heating and freezing of the solutions followed by drop casting the thin films at room temperature. Dye **1** (40 μM) was found to exist in the pre-aggregated form in $CHCl_3$ and CH_3CN (3/2), and when this solution was drop cast the aggregates gave a left-handed, bisignate CD signal. However, when the same solution was refluxed at 60 °C for 10 min to completely convert the pre-aggregated form to the monomer followed by sudden freezing, the drop-cast film gave a positive, nonbisignate CD signal (see Figure S7 in the Supporting Information). This indicates a significant role of pre-aggregates in solution on the sign of the Cotton effect in the thin films. To further understand the nature of the aggregates, we carried out the CD measurements at different orientations of the thin films made from different solvent compositions. We observed negligible changes in the intensity of the CD signals, which indicated thereby the inherent helical arrangement of the dye aggregates. As observed under solution conditions, the supramolecular assemblies of model compound **2** obtained under identical conditions were found to be CD-inactive in thin films.

Atomic force microscopic (AFM) studies of the dye aggregates: AFM images of dye **1** prepared from $CHCl_3$ solution showed a layerlike structure with a height of less than 3 nm. However, when samples were prepared from $CHCl_3/CH_3CN$ (3/2), we observed an entangled network of chiral fibers with an average height of 8 nm (Figure 8A; see Figure S8 in the Supporting Information, for AFM images obtained under different conditions). Analysis of these chiral supramolecular assemblies indicates the presence of both M and P helical structures with a pitch length of (29±1) nm (Fig-

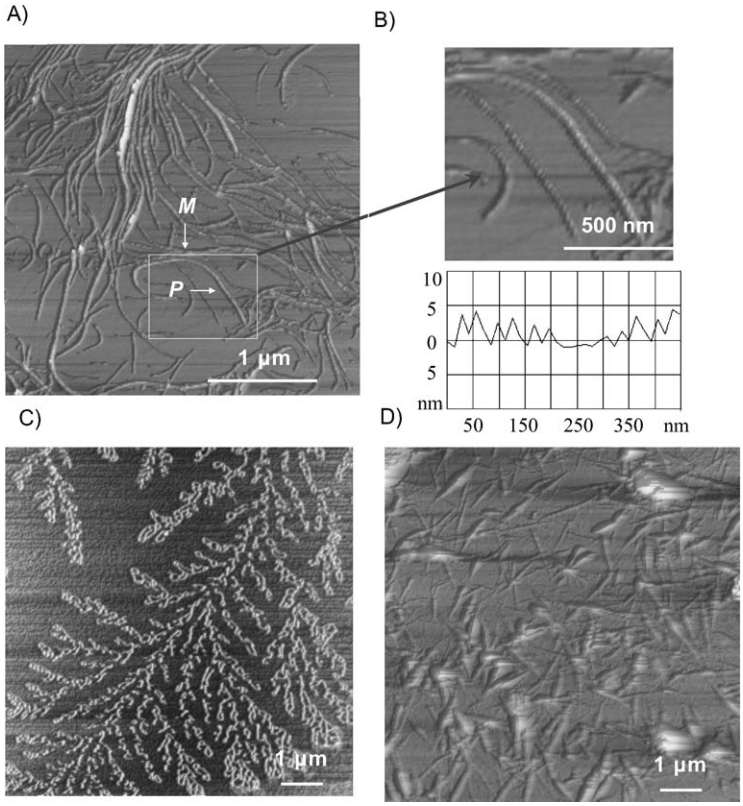


Figure 8. Tapping-mode AFM images of samples prepared by drop casting solutions of A) dye **1** (40 μM) in $CHCl_3/CH_3CN$ (3/2); B) zoomed region of A) with corresponding section analysis; C) dye **1** (40 μM) in $CHCl_3/CH_3CN$ 1/1); and D) dye **2** (40 μM) in CH_3CN.

ure 8B). On increasing the fraction of CH_3CN ($CHCl_3$/CH_3CN 1/1), the fibrous nature of the supramolecular assemblies decreased and the fibers without any helical twist predominated (Figure 8C). Interestingly, at different fractions of CH_3CN in $CHCl_3$ (3/2, 7/3, and 4/1), we observed both fibrous and disklike structures in AFM images (see Figure S9 in the Supporting Information). A complete transition from the fibrous structure to the disklike morphology was observed at the highest ratio of CH_3CN to $CHCl_3$ (4/1). These disklike structures showed a uniform diameter of (500 ± 50) nm and a height of (10 ± 2) nm. The AFM images of model compound **2** prepared from CH_3CN solution, on the other hand, showed less fibrous nature, that is, higher order packing is not favored in this case (Figure 8D).

Discussion

The observed chiral inversion of the supramolecular assemblies formed from dye **1** in solution can be explained in terms of the formation of novel kinetically and thermodynamically controlled H-type aggregates having different structures and opposite chirality. We assign the aggregate formed from **1** with negative Cotton effect to the thermodynamically controlled supramolecular assembly, and the aggregate with positive Cotton effect observed at higher fractions of CH_3CN to the kinetically controlled supramolecular assembly. Evidence for this assignment comes from the temperature- and concentration-dependent aggregation experiments. The kinetically controlled assembly (right-handed, P) was found to form in $CHCl_3/CH_3CN$ (1/1) below room temperature (ca. 15°C). However, when the temperature was increased, the chirality of the initial aggregate was lost; on cooling, the aggregate with opposite chirality (left-handed, *M*) was formed. Similar observations were made in the concentration-dependent aggregation experiments. At lower concentrations of dye **1**, the thermodynamically stable form exists (left handed, *M*); however, as the concentration increased, aggregation proceeded under kinetic control to give rise to the right-handed (*P*) supramolecular assembly.

A structural model for the spatial arrangement of the chromophores in dye **1** is proposed in Figure 9. Formation of the kinetically controlled aggregate could be largely dependent on the bolamphiphilic nature of the molecule and the amount of the poor solvent. This argument is based on the fact that model squaraine dye **2** forms only J-type achiral assemblies under similar conditions. The CD data strongly suggest that solvent effects (solvation and solvent polarity) surrounding the aggregate may hold the key to determining the handedness of the resultant supramolecular assemblies. The squaraine dye aggregates formed under kinetically controlled conditions may shrink due to the minimum solvation and fold in excess poor solvent, as compared to the thermodynamically controlled aggregates.

In thin films, the sign of Cotton effect was found to vary with concentration and the solvent composition from which the films were made. However, in relatively nonpolar solvent mixtures, λ_{max} and nature of the CD signal observed is significantly different from the CD signals observed at higher fractions of CH_3CN (≤ 50 $CHCl_3$/≥ 50 CH_3CN). This indicates that the aggregates formed at these solvent compositions are different from both the kinetically and thermodynamically controlled assemblies formed under solution conditions. We assign these aggregates as kinetically trapped supramolecular assemblies,[14a,d,20] since they are formed from aggregate-free solutions and can be obtained from pre-aggregated solutions at higher temperatures. This assumption is supported by the CD spectra obtained with thin films made from mixtures of 1/1, 3/7, 1/4, and 1/9 $CHCl_3/CH_3CN$ mixtures. Under these conditions, the dye is in the aggregated form (right-handed, kinetically controlled) in solution, but on drop casting showed a left-handed CD signal which is structurally similar to that of thermodynamically controlled assembly in solution. Furthermore, we observed that pre-aggregated dye in solution can be converted to the monomer at higher temperatures, which on sudden freezing and drop casting gave a positive CD signal corresponding to the kinetically trapped molecular assembly. Moreover, thermal annealing (90–100°C) of thin films of dyes **1** and **2** under inert nitrogen atmosphere for several cycles showed no significant chiroptical changes, and this indicates the stability of the supramolecular assemblies under these conditions. The observation of both right- and left-handed fibers in the AFM images clearly indicates that the macroscopic helicity of the self-assemblies of **1** is not necessarily related to the microscopic helicity observed in CD studies, as reported earlier with crown-appended cholesterol derivatives.[21]

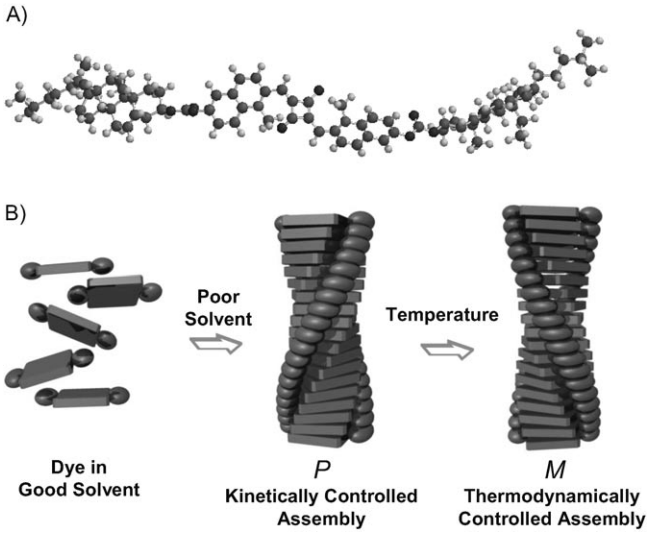


Figure 9. A) Geometry-optimized structure of cholesterol-linked squaraine dye **1** obtained by semiemperical calculations.[22] B) Schematic representation of kinetically and thermodynamically controlled self-assembly of dye **1**.

Conclusion

In conclusion, we demonstrate the formation of two novel chiral H-type supramolecular assemblies from the cholesterol-linked squaraine dye **1**, whereas J-type achiral assemblies were obtained from the model compound **2**. The chiral assemblies observed in **1** were found to exhibit switchable chiroptical characteristics in a mixture of good/poor solvents, controllable by the choice of the solvent ratio (solvent polarity), concentration, and temperature. The kinetically controlled aggregates were presumed to be formed in a rapid process and undergo a transformation in a much slower process to give the thermodynamically stable supramolecular assembly with opposite handedness. These results indicate that a nonpolar and chiral moiety like cholesterol can be effective for the formation of novel chiral assemblies and induce chirality reversal of the chromophore backbone in a polar environment. However, under solvent-free conditions, left-handed CD signals corresponding to the thermodynamically controlled assemblies were observed when drop cast from the pre-aggregated solutions, whereas assemblies that differ structurally from both the kinetically and thermodynamically controlled aggregates were observed when drop cast from the aggregation free solutions. These results provide valuable insights into the factors that control the chiral switching and indicate that these novel dyes which exhibit interesting supramolecular assemblies can have potential applications as chiroptical materials.

Experimental Section

Methods: All melting points are uncorrected and were determined on a Mel-Temp II melting point apparatus.[23] Solvents and reagents were purified and dried by usual methods prior to use. The IR spectra were recorded on a Perkin–Elmer Model 882 infrared spectrometer. UV/Vis and CD spectra were recorded in 1×1 cm quartz cuvettes at 25 °C. UV/Vis spectra were recorded on a Shimadzu UV-2401 PC UV/Vis scanning double-beam spectrophotometer. CD spectra were recorded on a Jasco J-810 spectropolarimeter equipped with Jasco PTC-423S Peltier-type temperature-control system. (1*S*)-(+)-10-Camphorsulfonic acid, ammonium salt (0.06% aqueous solution, 1 cm light path) was used for calibration of spectropolarimeter sensitivity and wavelength (CD = +190.4 mdeg at 291.0 nm). Aggregates were spontaneously formed on adding nonsolvent to the stock solution, without the need for ultrasonication or any other special treatment. Contribution from linear dichroism could be ruled out, since the aggregate solutions were optically clear at all temperatures studied, that is, there was no macroscopic anisotropy in solution.

Thin-film samples were made by drop casting the freshly prepared dye solution (40 μM) from a given $CHCl_3/CH_3CN$ mixture at room temperature onto fresh glass slides or mica surface for CD and AFM measurements, respectively. The drop-cast slides were then allowed to dry at room temperature for 30 min for complete evaporation of the solvent. The AFM images were recorded after 24 h under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in tapping mode. Microfabricated silicon cantilever tips (MPP-11100-10) with a resonance frequency of 299 kHz and a spring constant of 20–80 $N\,m^{-1}$ were used. The scan rate varied from 0.5 to 1 Hz.

Materials: *N*-Methyl-2-quinaldine (m.p. 278–280 °C), 6-hydroxy-2-quinaldine (m.p. 262–264 °C), and model squaraine dye **2** (m.p. 298 °C)[24] were prepared by modifying the reported procedures. Cholesteryl chloroformate was purchased from Aldrich and used as such, while squaric acid was a gift from Prof. Waldemar Adam, University of Würzburg, Germany.

Synthesis of squaraine dye 1: A mixture of 6-hydroxyquinaldine (100 mg, 0.63 mmol), cholesteryl chloroformate (450 mg, 1 mmol), and pyridine (5 mL) was heated at 70 °C for 12 h. Removal of the solvent gave a residue, which was then subjected to column chromatography over silica gel. Elution of the column with ethyl acetate/petroleum ether (1/9) gave 85% of the corresponding cholesterol-linked quinaldine derivative. M.p. 100–102 °C, IR (KBr): $\tilde{\nu}_{max}=1753$, 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.02$ (m, 2H; ArH), 7.61 (s, 1H; ArH), 7.52 (d, $J=9.13$ Hz, 1H; ArH), 5.34 (s, 1H; cholesteryl-H), 4.61 (s, 1H; cholesteryl-H), 2.74 (s, 3H; ArMe), 2.04–0.67 ppm (m, 54H; cholesteryl-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=157.78$, 151.86, 147.48, 144.18, 139.82, 138.06, 135.44, 128.74, 125.64, 124.32, 122.28, 121.82, 121.63, 120.61, 116.64, 78.16, 70.69, 55.76, 55.69, 55.15, 48.99, 41.32, 38.71, 38.52, 35.84, 35.20, 34.78, 30.92, 30.84, 27.22, 27.00, 23.27, 22.84, 21.81, 21.55, 20.05, 18.27, 17.72, 10.85 ppm.

A mixture of 6-cholesteryl-2-quinaldine (1 mmol) and methyl iodide (4 mmol) was heated in a sealed tube at 90–100 °C for 4 h. The precipitate formed was collected by filtration, washed thoroughly with cold diethyl ether, and subjected to column chromatography over silica gel. Elution of the column with methanol/chloroform (1/4) gave 95% of the corresponding quinaldinium salt. M.p. 215–217 °C, IR (KBr): $\tilde{\nu}_{max}=1762$, 1612 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$: CD_3OD): $\delta=8.92$ (d, $J=8.4$ Hz, 1H; ArH), 8.57 (d, $J=9.9$ Hz, 1H; ArH), 8.17 (s, 1H; ArH), 8.05 (m, 2H; ArH), 7.47 (s, 1H; ArH), 5.45 (s, 1H; cholesteryl-H), 4.60 (s, 3H; ArNMe), 4.59 (s, 1H; cholesteryl-H), 3.35 (s, 3H; ArMe), 2.05–0.71 ppm (m, 48H; cholesteryl-H); ^{13}C NMR (75 Hz, $CDCl_3$): $\delta=160.33$, 151.84, 150.75, 145.56, 138.68, 130.02, 129.20, 126.01, 123.40, 120.51, 120.22, 80.08, 56.56, 56.04, 49.91, 49.10, 48.81, 48.53, 48.24, 47.96, 42.17, 40.62, 39.57, 39.34, 37.69, 36.65, 36.40, 36.02, 35.62, 31.73, 28.01, 27.79, 27.42, 24.07, 23.63, 22.45, 22.21, 21.10, 20.89, 18.98, 18.44 ppm.

A mixture of 6-cholesteryl-*N*-methyl-2-quinaldinium iodide (0.06 mmol), squaric acid (0.03 mmol), and quinoline (0.5 mL) was refluxed in *n*-butanol/benzene (12 mL, 1/1) with azeotropic distillation of water for 12 h. The solvent was distilled off under reduced pressure to obtain a residue, which was subjected to chromatography over silica gel. Elution of the column with methanol/chloroform (1/9) gave 85% of squaraine dye **1**, which was then purified by recrystallization from chloroform/ethyl acetate (1/1). M.p. 296–298 °C, IR (KBr): $\tilde{\nu}_{max}=2947$, 2943, 1757, 1613, 1566 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.31$ (d, $J=9.57$ Hz, 2H; ArH), 7.44–7.30 (m, 8H; ArH), 5.80 (s, 2H; olefinic), 5.43 (s, 2H; cholesteryl-H), 4.60 (s, 2H; cholesteryl-H), 3.79 (s, 6H; ArMe), 2.50 (s, 6H; cholesteryl-H), 2.04–0.69 ppm (m, 80H; cholesterol-H); MS (FAB) calcd for $C_{82}H_{108}N_2O_8$: 1248.842; found: 1248.846.

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