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Liquid-Crystal Molecular Design

Ionic Quaterrylenebis(dicarboximide): A Novel Mesogen and Long-Wavelength Polarizing Material**

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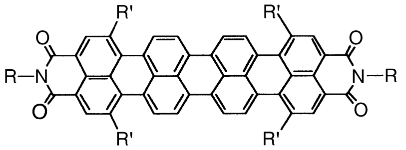
Within the broad scope of supramolecular chemistry,[1,2] the construction of materials and devices through self-assembly and self-organization processes is becoming one of the premier frontiers.[3–11] In the last decade, there has been extensive research on the interplay between molecular architecture, molecular order, and macroscopic properties.[12] In this paper, we report the aggregation and liquid-crystalline properties of a novel ionic quaterrylenebis(dicarboximide) **1** in aqueous solution. More importantly, by exploiting the self-organizing properties of **1**, unprecedented control of the molecular orientation of the quaterrylenebis(dicarboximide) in thin solid films was achieved, which produces a novel linear polarizer of light at long wavelengths.



1, R' = H, R = $(CH_2)_2NEt_2H^+$ $HCOO^-$
2a, R' = H, R = $C_{12}H_{25}$,
2b, R' = H, R = C_6H_3-2,6-*i*Pr$_2$,
2c, R' = OC_6H_4-4-*t*Bu, R = C_6H_3-2,6-*i*Pr$_2$

Nonionic quaterrylenebis(dicarboximide)s **2a–c** are known to absorb light at long wavelengths. In chlorinated organic solvents, the absorption maxima of **2b** and **2c** are at 764 nm and 781 nm, respectively.[13,14] These thermally and photochemically stable dyes can potentially be used in optical applications in conjunction with commercially available GaAlAs lasers that emit at 780 nm. Near-infrared (NIR) absorbing and emitting dyes have potential use in high-technology applications such as optical recording, thermally written displays, laser printers, laser filters, infrared photography, and fiber-optic communications.[15,16] However, the solubility of **2a–c** in chlorinated solvents is only about 10^{-2} M.[13,14] The design and synthesis of more-soluble quaterrylenebis(dicarboximide) derivatives will allow greater convenience in the processing of such materials. In addition, because of the intrinsic anisotropy in the molecular optical properties of quaterrylenebis(dicarboximide)s, the development of techniques for controlling their orientation on a macroscopic scale in the solid state will lead to novel anisotropic materials and broaden their utility. For instance, NIR polarizers have applications as optical isolators that are used in conjunction with semiconductor lasers and fiber optics.[17]

In the structural design of **1**, we anticipated that the functionalization of the hydrophobic quaterrylenebis(dicarboximide) core with cationic pendant groups would impart amphiphilicity, which would render it soluble in aqueous solution. Aggregation of these molecules in an aqueous medium is expected because of π-stacking among the "plank-shaped" aromatic molecules and the entropy-driven hydrophobic interactions. Furthermore, it was expected that the introduction of flexible alkyl chains would enhance the formation of lyotropic (solvent-dependent) liquid-crystalline phases by hindering regular close-packing of the molecules into a crystalline phase. Although liquid-crystalline phases are only of short-range structural regularity, induced alignment of the self-organized ensembles under an external force can increase the degree of orientational order over a substantially longer range in thin liquid films.[18] By preserving this long-range anisotropic order during the transition from the liquid to the solid state, desirable structural regularity and aniso-

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tropic properties persisting to the macroscopic scale can be obtained in thin solid films.[19,20]

The formate salt **1**[21] was only sparingly soluble in water (less than 10^{-7} M). However, it dissolved readily in 1.2 N $HCOOH_{(aq)}$ to give a 0.01 M solution, and its solubility increased at higher concentrations of formic acid. For instance, solutions with concentrations of **1** as high as 0.15 M could be prepared using 16.5 N $HCOOH_{(aq)}$ as the solvent.

Electronic absorption characteristics of **1** change significantly in different solvents (Figure 1). In concentrated sulfuric acid (98 %) at 25 °C, the electronic absorption spectrum of **1** (1×10^{-5} M) showed an intense sharp band with an absorption maximum (λ_{max}) at 856 nm and two weaker peaks at 800 and 772 nm. An intense absorption peak at 907 nm was reported for **2b** in concentrated H_2SO_4, which was attributed to the protonation of the carboximide function of **2b**.[14] In concentrated formic acid (in water, 23.4 N), the position of λ_{max} for **1** (3×10^{-7} M) shifted to 740 nm and a shoulder at 830 nm was observed. At lower concentrations of HCOOH, the shoulder at 830 nm disappeared and further shifts in λ_{max} to lower wavelengths were observed. The λ_{max} wavelengths of **1** in 16.7 N and 1.2 N $HCOOH_{(aq)}$ were 694 and 675 nm, respectively.

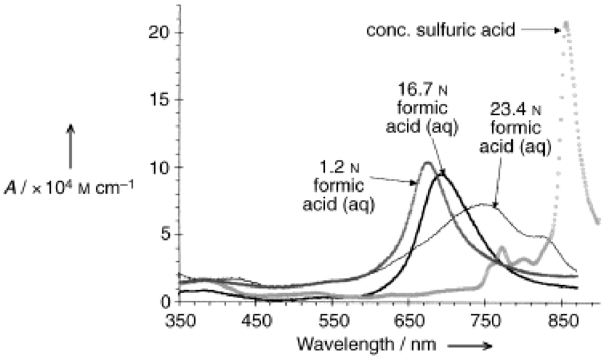

Figure 1. Effect of solvent on the electronic absorption of **1**. The concentration of **1** was approximately 3×10^{-7} M in the formic acid solutions, and 1×10^{-5} M in the concentrated sulfuric acid solution. A = molar absorptivity.

Furthermore, the absorption spectra of **1** in 23.4 N $HCOOH_{(aq)}$ varied with temperature (Figure 2) and the concentration of **1**. The absorption spectrum of **1** ($5\text{x}10^{-7}$ M) in 23.4 N $HCOOH_{(aq)}$ showed a broad absorption band with λ_{max} at 740 nm and a shoulder at 830 nm at 25 °C. As the temperature of this solution was raised slowly to 85 °C, the λ_{max} wavelength shifted to 765 nm and the intensity of the shoulder at 830 nm increased gradually. At 85 °C, the peak at 830 nm became more prominent when lower concentrations of **1** were used.

These changes in the electronic absorption spectrum of **1** may be attributed to H-aggregate formation. Strong π stacking and hydrophobic interactions among the molecules of **1** in aqueous solution were expected because of the presence of the large conjugated ring structure. In a strongly acidic solution such as 23.4 N $HCOOH_{(aq)}$, and at high temperatures (85 °C), the extent of aggregation decreased, which allows the absorption spectrum of the monomer at 830 nm to be observed. The extent of aggregation increased in dilute $HCOOH_{(aq)}$ (1.2 N), and only the broad absorption spectrum of the higher aggregates at 675 nm was observed at 25 °C. Since the wavelengths of the absorption maxima of the dimer and higher aggregates in $HCOOH_{(aq)}$ are blue-shifted from the monomer peaks, H-aggregates (in which the molecules are stacked in a ladder-like fashion)[22,23] are presumably formed.

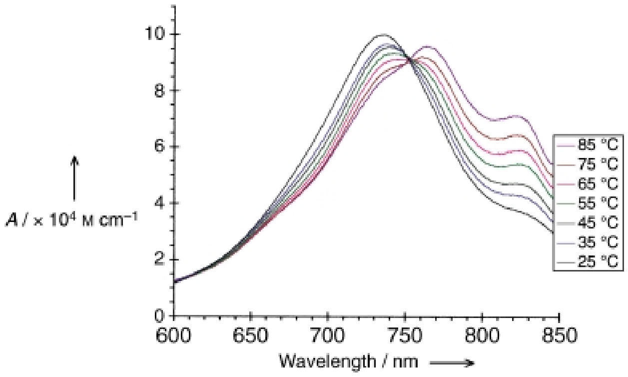

Figure 2. Effect of temperature (25 °C to 85 °C) on the absorption spectrum of **1** (5×10^{-7} M) in aqueous 23.4 N HCOOH. A = molar absorptivity.

When examined under a polarizing microscope, solutions of **1** (in 16.5 N $HCOOH_{(aq)}$) were birefringent at concentrations of 4 wt % and greater, which is indicative of the formation of a lyotropic liquid-crystalline phase.[18] The optical textures observed are consistent with a chromonic,[24] nematic liquid-crystalline phase (Figure 3).[25–27] In this type of phase, the mesogens typically stack to form columns (not necessarily simple one-molecule-wide columns), but there is no positional order among the columns. Similar optical textures were observed in 23.4 N $HCOOH_{(aq)}$ when the concentration of **1** was 15.7 wt % or greater.

Oriented thin solid films of **1** were prepared by simultaneously coating and aligning the solution of **1** (in the

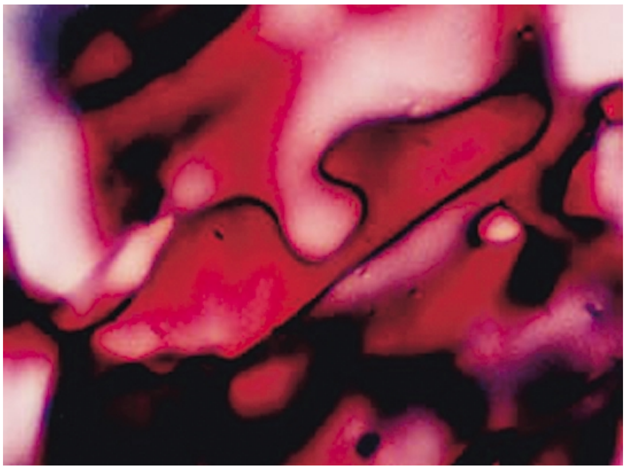

Figure 3. Optical photomicrograph of a solution of **1** (8.0 wt %) in aqueous 16.5 N HCOOH (200×, crossed polarizers).

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chromonic nematic phase) onto glass substrates using a mechanical shearing force. Solid films were obtained upon evaporation of solvent under ambient conditions. The anisotropic optical properties of the films were examined by polarized microscopy. The films were colorless and transparent (Figure 4, top) when the polarization axis of the incident light was parallel to the shearing direction. In contrast, only blue light was transmitted (green and red light was absorbed) when the polarization axis of the incident light was orthogonal to the shearing direction (Figure 4, bottom). When a liquid-crystalline solution of **1** was allowed to dry on a glass slide without alignment with the shearing force, no bulk anisotropic orientation or light polarization on a macroscopic scale was observed. In addition, no bulk orientation resulted if an isotropic solution of **1** was used. These results indicate that the self-organization of **1** into a liquid-crystalline phase and its induced orientation by shearing are both requirements for the fabrication of highly anisotropic films of **1**.

The optical properties of these films were quantified using polarized visible spectroscopy. As shown in Figure 5, the films exhibited very low transmittance (high absorbance) of green and red light when the shearing direction of the film was perpendicular to the polarization axis of the incident light. In contrast, when the film was rotated through 90°, such that the shearing direction was aligned with the polarization axis of the incident light, high transmittance was observed. The polarization efficiency of this film was greater than 98% in the range from 600 to 733 nm. These results suggest that the molecules on the glass substrate are oriented with their electronic transition moments preferentially aligned orthogonal to the shearing direction.

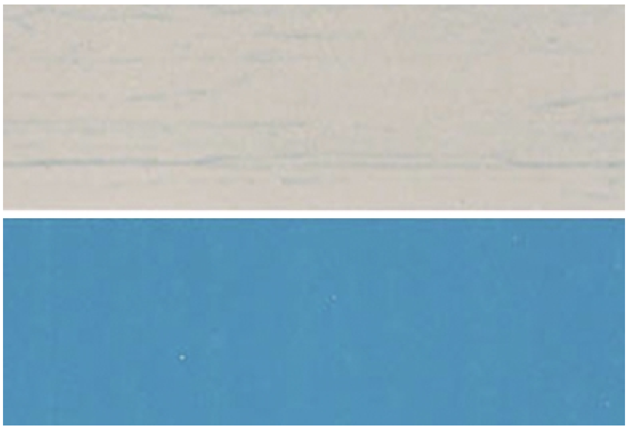

Figure 4. Optical photomicrograph of an air-dried oriented film prepared from a solution of **1** (11 wt%) in aqueous 16.5 N HCOOH: (top) polarization axis of incident light parallel to the shearing direction, and (bottom) polarization axis of incident light perpendicular to the shearing direction (200×, single polarizer).

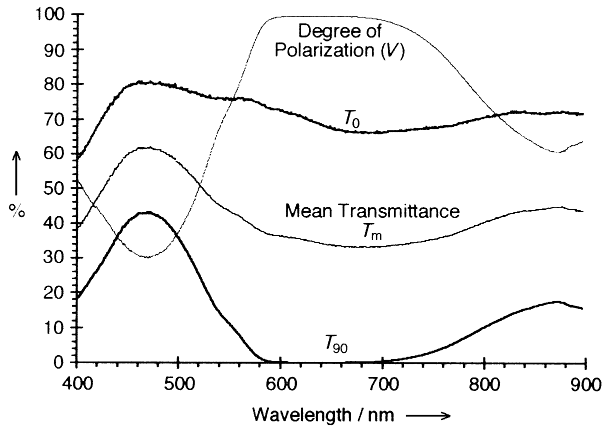

Figure 5. Optical properties of a solid film of **1** on glass prepared from a solution of **1** (11 wt%) in aqueous 16.5 N HCOOH. T_{90} is the transmittance when the shearing axis of the aligned film is perpendicular to the polarization of the incident light; T_0 is the transmittance when it is parallel. The mean transmittance (T_m) is calculated as $[T_0+T_{90}]/2$ and is a measure of the transmittance of unpolarized incident light. The degree of polarization (V) is calculated as $100\% \times [T_0-T_{90}]/[T_0+T_{90}]$.

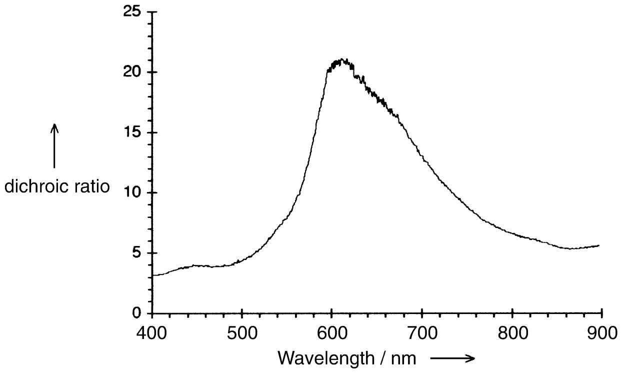

Figure 6. The change in the dichroic ratio of an oriented solid film of **1** with wavelength.

The absorbance at different wavelengths of light polarized perpendicular (A_{90}) and parallel (A_0) to the shearing direction of this film were used to calculate the dichroic ratios (A_{90}/A_0). The highest dichroic ratio (greater than 20) of this film occurred at approximately 611 nm, and significant polarization of light was still observed at wavelengths above 700 nm (Figure 6). For more accurate determination of the maximum dichroic ratio of this film, the transmittance of the film as a function of the angle (θ) between the shearing direction and the polarization axis of the incident light (at 611 nm) was determined. The transmittance (T_θ) of the polarized incident light at an angle θ can be related to the transmittance at 90° (T_{90}) and 0° (T_0) by Equation (1)[28] as follows:

$$T_\theta = (T_0 - T_{90})\cos^2\theta + T_{90} \qquad (1)$$

Fitting the values of T_θ to Equation (1) allowed accurate determination of the values of T_{90} and T_0. These values were then converted to absorbance values (A_{90} and A_0) and their ratio yielded a dichroic ratio of 21.2 ± 0.2 at 611 nm. Since dichroic ratios are, in principle, independent of the thickness of the films, they serve as useful parameters for measuring anisotropic order in thin solid films.

This work has demonstrated, with quaterrylenebis(dicarboximide) **1** as an example, that large conjugated compounds can be imparted with lyotropic liquid-crystalline properties by molecular design. An important consequence of the self-organization of **1** into a liquid-crystalline phase is that it allows the unprecedented control of the molecular orientation of **1** in thin solid films. Induced orientation of the liquid-crystalline domains of **1** under a shearing force results in highly anisotropically ordered thin solid films that serve as dichroic polarizers of light at long wavelengths (greater than 600 nm). Future work will investigate the fluorescence, semiconducting, and photoconducting properties of **1**.

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Pentalene Bonding in Fullerenes

$Sc_3N@C_{68}$: Folded Pentalene Coordination in an Endohedral Fullerene that Does Not Obey the Isolated Pentagon Rule[**]

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The new family of endohedral metallofullerenes, $Sc_3N@C_{80}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{68}$, has been prepared by the Krätschmer–Huffman arc fullerene preparation with graphite rods doped with Sc_3O_2 in a dynamic atmosphere of helium and dinitrogen.[1–4] Crystallographic studies have shown that $Sc_3N@C_{80}$ contains a planar {Sc_3N} unit within a C_{80} cage with I_h symmetry,[1] while $Sc_3N@C_{78}$ consists of a similar {Sc_3N} unit contained within a fullerene cage of D_{3h} symmetry.[3] These endohedral structures, as well as most known empty-cage fullerenes, obey the isolated pentagon rule (IPR) which requires that each of the twelve pentagons in the carbon cage be surrounded by five hexagons. However, theoretical studies have suggested that some endohedral fullerenes (for example, $Ca@C_{72}$ and $La_2@C_{74}$) may not obey the IPR.[5] Additionally, two endohedral fullerenes, $Sc_3N@C_{68}$[4] and $Sc_2@C_{66}$,[6] and one empty-cage fullerene, C_{62},[7] have been recently reported, which cannot obey the IPR as no possible IPR cages exist for C_{62}, C_{64}, C_{66}, or C_{68}.[8]

Here we report the detailed structural characterization of $Sc_3N@C_{68}$. For a C_{68} cage whose surface consists solely of pentagons and hexagons, there are 6332 possible isomers, but the ^{13}C NMR spectrum of $Sc_3N@C_{68}$ restricts these possibilities to only 11 isomers that have either D_3 or S_6 symmetry.[4] On the basis of density functional calculations, two isomers (isomer 6140[4] and isomer 6275;[9] Figure 1) have emerged as the likely cage structures present in $Sc_3N@C_{68}$. As Figure 1 shows, these isomers have different shapes (6140 is rounded while 6275 is flattened), although both have D_3 symmetry.

Black crystals of $Sc_3N@C_{68}\cdot[Ni^{II}(OEP)]\cdot 2\,C_6H_6$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphinate) were obtained by the gradual diffusion of a solution of $Sc_3N@C_{68}$ (prepared

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