1832 *Chem. Mater.* **2004,** *16,* 1832−1834

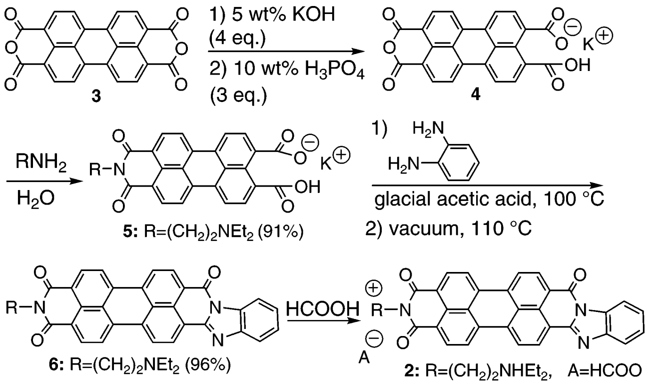
Molecularly Designed Chromonic Liquid Crystals for the Fabrication of Broad Spectrum Polarizing Materials

Suk-Wah Tam-Chang,* Wonewoo Seo,
Kyle Rove, and Sean M. Casey

Department of Chemistry, University of Nevada,
Reno, Nevada 89557

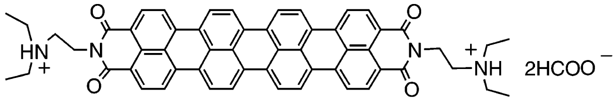
Received October 28, 2003
Revised Manuscript Received February 13, 2004

Scheme 1

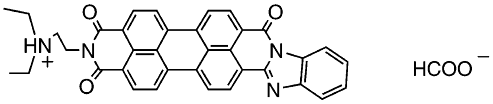


Organic materials have a wide range of uses including applications in the optical and electronic fields. Supramolecular assembly and self-organization strategies provide important approaches to control properties of organic materials both in solution[1−3] and in the solid state.[4−10] In addition to the manipulation of the properties of individual molecules and intermolecular interactions, the molecular level control of solid-state properties often requires the control of molecular order.[11−13] In a recent publication, we reported the design of compound **1**, which exhibits dichroic (direction-dependent absorption of light) and liquid-crystalline properties.[14] Mesogen **1** self-organizes in aqueous solutions to generate a chromonic liquid-crystalline phase[15−17] in which the molecules stack into columns possessing short-range structural regularity and liquidlike mobility. Induced orientation of the liquid-crystalline columns under a mechanical shearing force followed by the evaporation of solvent under ambient conditions resulted in anisotropically (direction-dependent) oriented solid films of **1**.[14] These films linearly polarize light at long wavelengths (from about 600 to 800 nm) and have potential uses in optical isolators and applications in conjunction with commercially available GaAlAs lasers that emit at 780 nm.[18,19] In this manuscript, we describe the extension of this control of molecular orientation and anisotropic properties to solid films that are composed of a mixture of chromonic mesogens, demonstrating the versatility of this approach. The employment of multicomponent liquid-crystalline materials allows the generation of anisotropic films that linearly polarize light over a much wider spectrum of wavelengths and broadens their potential utility. For example, films that polarize visible light are essential components of liquid-crystal displays.

1



2



The criteria for the structural design of the molecules used to fabricate broad spectrum polarizers are illustrated using compounds **1** and **2** and include the following: (1) The difference in the surface areas of the aromatic regions of **1** and **2** is not too large to preclude the formation of mixed aggregates of these compounds by solvophobic interactions and π-stacking. The formation of mixed aggregates (instead of self-aggregates) minimizes large regions of inhomogeneous color in the polarizing films. (2) Compounds **1** and **2** possess different aromatic ring systems that absorb at different wavelengths so that their mixtures absorb over a large wavelength range. (3) Both compounds are dichroic and the principle electronic transition axes align with the long molecular axes to ensure that their mixed aggregates and the anisotropic films produced subsequently exhibit direction-dependent optical properties. (4) Both components display chromonic liquid-crystalline properties in a common aqueous solvent permitting shear-induced alignment. The control of solubilities and chromonic liquid-crystalline properties of **1** and **2** were achieved by adjusting the number of bulky ionic groups attached to their aromatic rings.

Compound **2** was synthesized according to the procedure outlined in Scheme 1. When compounds **1** and **2** were dissolved separately in 16.5 N HCOOH(aq), the visible absorption spectra of their solutions (Figure 1a and 1b, respectively) showed a blue shift in the λ_{max}

---

(1) Fyfe, M. C.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393.
(2) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(3) Wu, A.; Chakraborty, A.; Fettinger, J. C.; Flowers, R. A., II.; Isaacs, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 4028.
(4) Clark, S. L.; Hammond, P. T. *Adv. Mater.* **1998**, *10*, 1515.
(5) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science (Washington, D.C.)* **1997**, *276*, 384.
(6) Gin, D. L.; Gu, W.; Pindzola, B. A.; Zhou, W.-J. *Acc. Chem. Res.* **2001**, *34*, 973.
(7) MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6931.
(8) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.
(9) Ward, M. D.; Pivovar, A. M. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 581.
(10) Shenhar, R.; Rotello, V. M. *Acc. Chem. Res.* **2003**, *36*, 549.
(11) Garcia-Garibay, M. A. *Acc. Chem. Res.* **2003**, *36*, 491.
(12) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209.
(13) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402.
(14) Tam-Chang, S. W.; Seo, W.; Iverson, I. K.; Casey, S. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 897.
(15) Lydon, J. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, p 981.
(16) Ruslim, C.; Matsunaga, D.; Hashimoto, M.; Tamaki, T.; Ichimura, K. *Langmuir* **2003**, *19*, 3686.
(17) Lydon, J. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 458.
(18) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449.
(19) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445.

10.1021/cm030128q CCC: $27.50

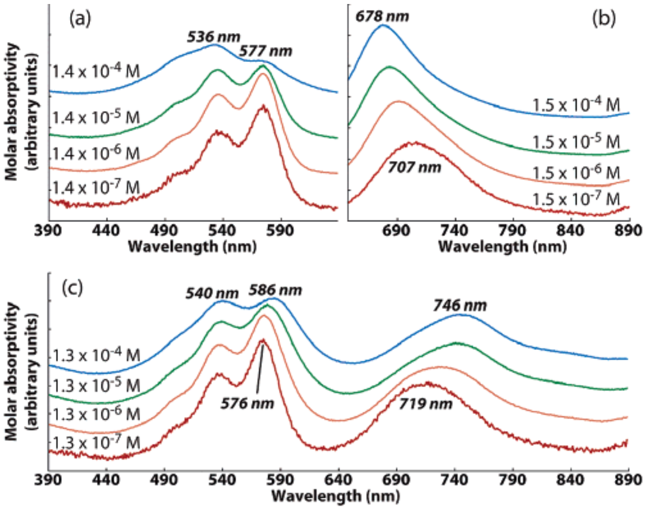


Figure 1. Series of offset visible spectra of 16.5 N HCOOH(aq) solutions that contained (a) **2** only, (b) **1** only, and (c) a mixture of **1** and **2** (~1:1 molar ratio).

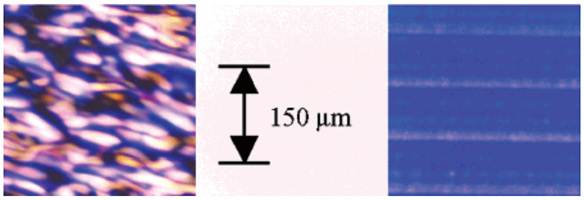


Figure 2. (Left) Optical photomicrograph of a liquid-crystalline solution of both **1** and **2** (~1:1 molar ratio, 10 wt % total in 16.5 N HCOOH(aq)) when viewed between crossed polarizers. (Middle and right) Photomicrographs of an oriented film prepared from the liquid-crystalline solution when viewed using a single polarizer. The polarization axis of incident light was (middle) parallel to the shearing direction and (right) perpendicular to the shearing direction. The light color strips in the film occur during the shearing and are a result of the 3-mil wire that is coiled around the coating rod.

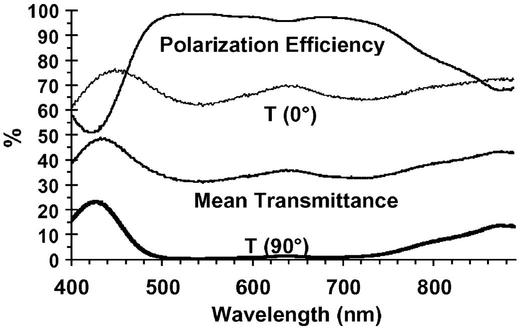


Figure 3. Optical properties of an oriented solid film on glass prepared from a 10 wt % solution of **1** and **2** (~1:1 molar ratio) in 16.5 N HCOOH(aq). $T(0°)$ is the transmittance when the aligned film's shearing axis is parallel to the polarization axis of the incident light. $T(90°)$ is the transmittance when it is perpendicular. The mean transmittance (T_0) is calculated as $[T(0°) + T(90°)]/2$ and is a measure of the transmittance of unpolarized incident light. The efficiency polarization is calculated as $100\% \times [T(0°) - T(90°)]/[T(0°) + T(90°)]$.[22]

values as the concentrations of the solutions were increased from $\sim 10^{-7}$ to $\sim 10^{-4}$ M. This indicates the formation of H-aggregates[20] by each compound when present alone in solution. However, when mixed in a mole ratio of ~1:1, red shifts in λ_{max} values of **1** and **2** were observed (Figure 1c), providing evidence for intermolecular interactions and the formation of mixed aggregates (probably J-aggregates)[21] of **1** and **2**. At a concentration of about 10^{-4} M, the λ_{max} value of **1** in the solution containing both **1** and **2** was almost 70-nm longer (to the red) than the solutions of **1** alone.

When a solution of both **1** and **2** at high concentration (e.g., 10 wt % total of **1** and **2**) in HCOOH (aq, 16.5 N) was viewed between crossed polarizers under an optical microscope, the optical textures observed were consistent with a chromonic, nematic liquid-crystalline phase (Figure 2, left).[15] 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. Under a mechanical shearing force that spreads the liquid-crystalline solution containing both **1** and **2** onto a glass substrate, the liquid-crystalline domains are aligned and the degree of orientational order of the molecules can be extended over a substantially longer range. This order can then be transferred to the solid state upon removal of the solvent. The anisotropic optical properties of the sheared films formed from a mixture of both **1** and **2** were apparent when the films were examined by polarized optical microscopy. The films were transparent and very light in color (Figure 2, middle) when the polarization axis of the incident light was parallel to the shearing direction of the films. In contrast, an intense blue color was observed when the polarization axis of the incident light was orthogonal to the shearing direction (Figure 2, right).

Figure 3 shows the polarized visible spectra (in transmission mode) of a sheared film formed from a mixture of **1** and **2**, with the incident radiation normal to the film surface. Significant broadening of the spectra of the solid films occurred compared to the spectra of the solutions, presumably because of intermolecular interactions in the solid phase. Furthermore, the oriented films exhibited intense absorption of light when the polarization axis of the incident light was perpendicular to the shearing direction, while only weak absorption occurred when the polarization axis of the incident light was parallel to the shearing direction (Figure 3). This indicates that the majority of the molecules on the glass substrate are oriented with their long axes orthogonal to the shearing direction since the electronic transition moments for these transitions of both **1** and **2** are aligned with the long axes of their molecular planes. The oriented films showed anisotropic optical properties over a broad range of wavelengths (~450−890 nm); the degree of polarization of these films was typically over 80% from about 470 to 800 nm (Figure 3).

Polarized transmission IR spectroscopy was used to further elucidate the molecular orientation in the sheared films of the mixture of **1** and **2**. With the substrate in the XY plane and the shearing direction and the polarized IR radiation parallel to the X-axis, the C−H perylene wagging resonance will be strongest when the molecular planes of **1** and **2** are in the YZ plane. This will be the case whether the long axes of the molecules are aligned with the Y-axis or the Z-axis

---

(20) Czikklely, V.; Forsterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 207.

(21) Harrison, W. J.; Mateer, D. L.; Tiddy, G. J. T. *Faraday Discuss.* **1996**, *104*, 139.

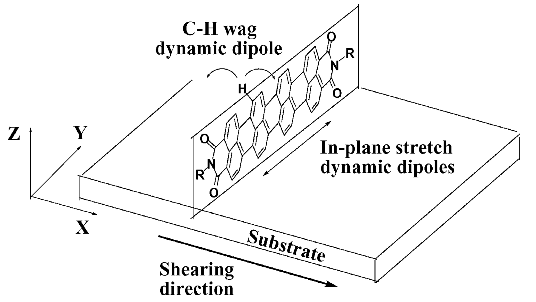


Figure 4. Schematic diagram showing a possible orientation of a molecule of **1** in a sheared film of both **1** and **2** on a substrate with defining axes labeled and the planes of the relevant IR dynamic dipoles of the molecule indicated. Compound **2** possesses similar IR dynamic dipoles, although **2** is not shown in the diagram for simplicity.

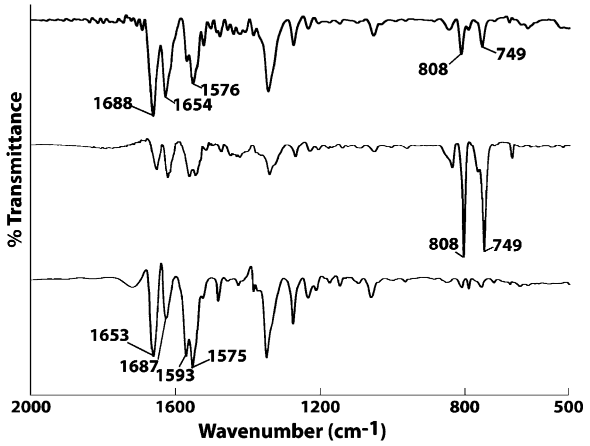


Figure 5. (Top) FTIR spectrum of a randomly oriented mixture of **1** and **2** in a KBr pellet. (Middle) Polarized FTIR spectrum of an oriented film of **1** and **2** on a KRS-5 substrate, with the incident light polarized parallel to the shearing direction. (Bottom) The same film and same incident polarization as (middle) with the sample rotated 90° about the *z*-axis.

or something between (Figure 4). This molecular orientation causes the dynamic dipole vector (μ) of the C−H perylene wagging mode to lie along the *X*-axis (the axis of polarized IR irradiation). If the average molecular planes of **1** and **2** were in the *XZ* plane or in the *XY* plane parallel to the substrate surface, the dipole vector of the C−H wagging mode would be perpendicular to the axis of polarized IR radiation, and the C−H wagging resonance would not be observed.

As shown in Figure 5 (middle), when the shearing direction of the film and the electric vector of IR polarization were parallel, the out-of-plane C−H wagging resonances of **1** and **2** at about 750−810 cm^{-1} were greatly enhanced in intensity relative to the normally dominant in-plane stretches at 1570−1690 cm^{-1}. Upon rotation of the sheared sample 90°, so that the shearing direction was perpendicular to the electronic vector of the incident IR radiation, the opposite effect was seen as all of the in-plane imide and aromatic stretches (1570−1690 cm^{-1}) of **1** and **2** increased in relative intensity while the peaks at 750−810 cm^{-1} almost disappeared (Figure 5, bottom). These results provide strong evidence that the molecular planes of **1** and **2** in these oriented films are aligned with the *YZ* plane. The studies by polarized visible spectroscopy discussed above show that the long molecular axes of **1** and **2** align with the *Y* axis, although the results cannot exclude the possibility that the long axis of some molecules in the films are aligned with the *Z* axis.

In summary, dichroic mesogens **1** and **2** were designed to absorb at very different wavelengths and yet display chromonic liquid-crystalline properties in a common aqueous solvent. These properties allowed the induced orientation of the mixed liquid crystals by a mechanical shearing force and subsequently produced solid films that exhibit anisotropic optical properties over a broad spectrum. In addition to the fabrication of polarizing films useful for display technologies, this work presents the design principles for mixed chromonic liquid crystals that should be broadly applicable to other mesogens and may benefit other alignment techniques such as the induced orientation of chromonic liquid crystals by photoaligned polymers.[23,24] Future research includes detailed studies of the aggregation properties of **1** and **2** in solution and determination of the molecular order in the anisotropic films by X-ray diffractometry.

Acknowledgment. S.W.T.C. is grateful for the NSF Career Award that supported this research (DMR-9876027). K.R. thanks NSF EPSCoR for an Undergraduate Summer Research Fellowship (EPS-0132556).

Supporting Information Available: Experimental conditions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM030128Q

---

(22) West, C. D.; Jones, R. C. *J. Opt. Soc. Am.* **1951**, *41*, 976.

(23) Matsunaga, D.; Tamaki, T.; Akiyama, H.; Ichimura, K. *Adv. Mater.* **2002**, *14*, 1477.

(24) Ichimura, K.; Fujiwara, T.; Momose, M.; Matsunaga, D. *J. Mater. Chem.* **2002**, *12*, 3380.