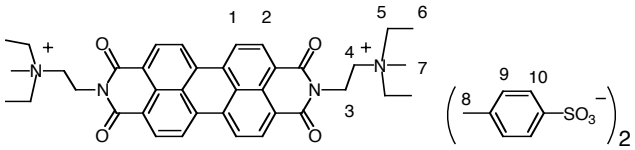
Template-Guided Organization of Chromonic Liquid Crystals into Micropatterned Anisotropic Organic Solids

Suk-Wah Tam-Chang,* Jennifer Helbley, Travis D. Carson, Wonewoo Seo, and Isaac K. Iverson

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

Compound **1** was synthesized in 85% yield by the reaction of **3** with methyl *p*-toluene sulfonate. A mixture of 4.56 g (11.6 mmol) of 3,4:9,10-perylenetetracarboxylic dianhydride and 25 mL of *N,N*-diethylethylenediamine was stirred approximately 15 hours at 100 °C and allowed to cool. The mixture was filtered and the isolated solid rinsed with ethanol and diethyl ether. This solid was then mixed with 18 mL of methyl *p*-toluene sulfonate for 15 hours at 50 °C. The cooled solution was then added to methanol and filtered. The filtrate volume was reduced with a rotary evaporator and ethyl ether was used to precipitate impure **1**. The mixture was filtered and rinsed with diethyl ether. Purification was achieved by suspending **1** in ethanol and the undissolved solid was filtered. The solid was rinsed with diethyl ether and dried under vacuum to yield 9.5 g of **1** (9.9 mmol, 85 %). ^{1}H NMR (300 MHz, CF_3COOD): δ = 8.85, (overlapping doublets, 8H, H-1,2), 7.65 (d, 4H, *J* = 8 Hz, H-10), 7.20 (d, 4H, *J* = 8 Hz, H-9), 4.77 (m, 4H, H–3), 3.70 (m, 4H, H–4), 3.55 (q, 8H, *J* = 6.8 Hz, H-5), 3.22 (s, 6H, H-7), 2.27 (s, 6H, H-8), 1.53 (t, 12H, *J* = 6.8 Hz, H-6) ppm; ^{13}C NMR (75 MHz, CD_3OD) δ=163.49, 144.31, 141.85, 133.74, 131.52, 131.48, 130.14, 128.11, 127.24, 124.57, 122.09, 58.64, 57.06, 34.68, 21.57, 9.41, 8.55 ppm; UV (H_2O, 1.7 x 10^{-5} M) λ_{max} = 465 (ε=17600), 500 (ε=36700), 540 (ε=19900) nm. UV (H_2O, 1.7 x 10^{-7} M) λ_{max} = 469 (ε=13400), 500 (ε=31000), 533 (ε=34500) nm. IR (KBr): ν = 1695 (sharp, C=O stretch), 1656 (sharp, C=O stretch), 1593 (sharp, C=C stretch), 1440 (w), 1401 (w), 1362 (sharp, C-N stretch), 1195 (br, s, Ar-SO_3^- stretch), 1119 (m), 1032 (m), 1010 (m), 810 (m, perylene C-H wag), 747 (w, perylene C-H wag), 680 (m), 566 (m) cm^{-1}; HRMS (FAB, *m/z*) Calcd for $C_{20}H_{42}N_4O_4$ [M^+]: 618.3201; found: 618.3206; mp 280 °C.



Aqueous solutions of **1** were prepared by dissolving **1** in double distilled water. Concentrated solutions (~20 wt %) **1** in double distilled water were shaken overnight at 45 °C in a vial sealed with Teflon tape on the threads and Parafilm sealing film on the outside of the cap.

Deuterated trifluoroacetic acid (TFA-*d*, D-99.5%) used for ^{1}H and ^{13}C NMR measurements was purchased from Cambridge Isotopes. ^{1}H and ^{13}C NMR spectra were acquired on a GE QE 300 MHz spectrometer. Electronic spectra were obtained with a dual-beam Cary-14 spectrophotometer fitted with an A/D converter and software by OLIS, Inc. Visible spectra of aqueous solutions were taken in cuvettes of the desired path length (1-mm or 1-cm). Infrared spectrum was recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. IR spectrum of **1** was obtained in the form of KBr pellets prepared with dried KBr using a mini-press from SpectraTech, Inc.

Photomicrographs were taken using a Nikon N70 single lens reflex camera mounted on a trinocular head of a Nikon E600pol microscope with strain free objectives. Photomicrographs were taken without any color filters in the light path. The samples were viewed between crossed polarizers or through a single polarizer that was placed between the incident light and the sample.

Digital images (gray scale only) were taken using a Qimaging Microimager II digital camera (Qimaging Quantitative Imaging Corp., Vancouver, B.C.) mounted on the trinocular head of the Nikon E600pol microscope. The samples were viewed through a single polarizer that

was placed between the incident light and the sample. In addition, a color filter that allowed light of 515-555 nm (green region) or 573-648 nm (red region) to pass through was placed between the sample and the digital camera. The digital images captured by the camera were analyzed in Adobe Photoshop version 7.

The following experiments were performed to provide evidence that the micropatterned solid of **1** transmits light at long wavelengths (orange and red region) with low anisotropy and absorbs light at shorter wavelengths (e.g., green region) with high anisotropy. The micro-patterns of solid **1** on glass were viewed under an optical microscope that was equipped with a single polarizer (between the incident light and the sample), a color filter (between the sample and a digital camera) that transmitted light in wavelength range of 515-555 nm, and a digital camera mounted on the trinocular head of the microscope. When the polarization axis of incident light of 515-555 nm was perpendicular to the direction of the lines, very low intensity of light was transmitted through the solid lines. On a grayscale of light levels 0-255 (from dark to bright) for the digital signals, the difference in the median values of the light levels between the regions of plain glass and the regions of solid lines was as high as about 160. In contrast, when the polarization axis of incident light of 515-555 nm was parallel to the direction of the solid lines, the intensity of light transmitted through the solid lines of **1** was close to that of the plain glass region. The difference in the median values of the light levels through the two regions was about 10. When the experiment was repeated using a color filter that transmitted that in the wavelength range of 573-648 nm, very high intensity of light was transmitted through the solid lines of **1** regardless the direction of the polarization axis of the incident light.

We were able to generate a pattern over 5 mm^2 in size, (Figure S1), although the patterns were not free from defects because the conditions for generating the patterns have not been optimized. Figure S1a shows the area without any magnification under ambient lighting. Looking at this sample under 40x magnification using a polarizing light microscope, Figure S1b and Figure S1c are observed. Increasing magnification of the area to 100x and 200x are also shown in Figure S1 (d)-(e) and (f)-(g), respectively.

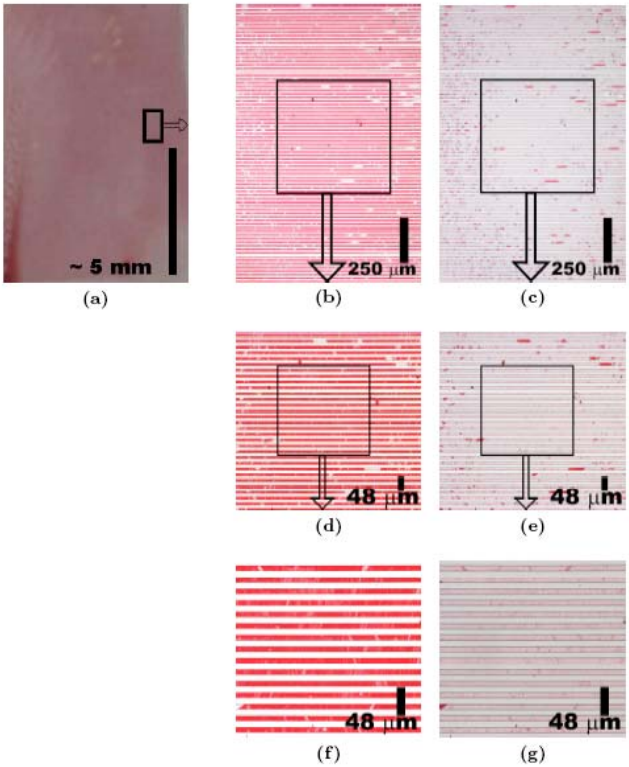


Figure S 1. A patterned sample of 10 μm lines showing a relatively large patterned area. (a) Shows the sample without any magnification or polarization. Each row on the right shows a magnification of the area above. (b), (d), and (f) show the sample with light polarized at 90°relative to the lines. (c), (e) and (g) show the sample with light polarized at 0°relative to the lines.