

A Melt-Processable Squaraine-Based Organic Glass for Nonlinear Optics

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Supporting Information

Methods and General Remarks. 2,3,3-Trimethylindolenine (98%), 2-ethylhexyliodide, anhydrous acetonitrile, and 3,4-dihydroxy-3-cyclobutene-1,2-dione (99%) were obtained from Sigma Aldrich and used as received. All other solvents were of highest commercial quality and obtained from Fisher Scientific. Linear absorption, two-photon absorption, and photoluminescence (PL) measurements were carried out in anhydrous toluene which was purchased from Burdick & Jackson. Reagent grade chloroform (Sigma Aldrich) was used for the concentration-dependent PL measurements. ¹H NMR spectroscopic data were measured in CDCl₃, and chemical shifts are expressed in ppm relative to the CDCl₃ peak at 7.26 ppm. The ¹H NMR spectrum of **2** was obtained on a Varian 300 MHz NMR spectrometer and the spectrum of **3** was obtained on a Bruker 360 MHz NMR spectrometer. Elemental analysis was provided by the School of Engineering at the University of Fribourg, Switzerland.

Synthesis of 1-(2-ethylhexyl)-2,3,3-trimethyl-3H-indol-1-ium iodide (2). 2-Ethylhexyl iodide (14.15 g, 62.5 mmol) was combined with 2,3,3-trimethylindolenine (**1**) (3.99 g, 25 mmol) and anhydrous acetonitrile (38 mL) and the reaction mixture was heated under reflux for 8 days. The reaction mixture was cooled to room temperature and reduced *in vacuo*. A solution of concentrated hydrochloric acid (4 mL) in methanol (60 mL) was added to the residue and the mixture was stirred for 105 min. The volatiles were evaporated *in vacuo*, the organic residue was dissolved in CHCl₃, and the organic phase was

washed with distilled water (3 x 100 mL). The organic layer was separated off, and the solvent was evaporated. Drying *in vacuo* overnight yielded **2** as a viscous dark red oil (6.2 g, 62 %). ^1H NMR (300 MHz, CDCl_3): δ 7.61 (m, 4H), 4.59 (d, 2H), 3.05 (s, 3H), 2.11-2.00 (m, 1H), 1.69 (s, 3H), 1.57-1.25 (m, 8H), 1.01 (t, 3H), 0.91 (t, 3H).

Synthesis of 2,4-Bis[(1-(2-ethylhexyl)-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl]cyclobutene-diylum-1,3-diolate (3). Compound **2** (3.06 g, 7.6 mmol) and squaric acid (0.416 g, 3.7 mmol) were dissolved in a mixture of toluene (39 mL) and 1-butanol (39 mL) and the reaction mixture was heated under reflux for 42 h in a 250 mL round bottom flask using a Dean Stark trap for the azeotropic removal of water. The reaction mixture was cooled to room temperature and reduced *in vacuo* at 75 °C. The remaining residue was dissolved in a minimal amount of dichloromethane and purified by column chromatography (silica gel, eluent 6:4 ethyl acetate:hexanes). The resulting product was dried at 40 °C *in vacuo* to yield **3** in the form of green crystals with a metallic luster (0.91 g, 40%). ^1H NMR (360 MHz, CDCl_3): δ 7.37-7.26 (m, 4H), 7.16 (m, 2H), 6.99 (d, 2H), 5.99 (s, 2H), 3.89 (d, 4H), 2.20-2.01 (m, 2H), 1.80 (s, 12H), 1.50-1.21 (m, 16H), 0.97 (t, 6H), 0.88 (t, 6H). Anal. Calcd. for $\text{C}_{42}\text{H}_{56}\text{N}_2\text{O}_2$: C, 81.24; H, 9.09; N, 4.51. Found: C, 81.11; H, 9.34; N, 4.36. Extinction coefficient $\epsilon(\text{toluene}) = 250,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

UV-VIS Spectroscopy. Absorbance spectra were recorded on a Perkin Elmer Instruments Lambda 800 UV-VIS spectrophotometer. Solution experiments were carried out in toluene at a concentration of $1.6 \times 10^{-6} \text{ M}$ against toluene as a reference. A spin-cast sample was also measured. In this case, **3** was dissolved at a concentration of $1.3 \times 10^{-3} \text{ M}$ in toluene and spin-cast at 500 rpm onto a glass substrate. The melt-processed film was prepared by melting the dye at 235 °C on a Gel Instrumente AG hotstage with a TC2 temperature controller, placing a coverslip on top, turning off the hot stage and letting cool

to room temperature under ambient conditions. A glass microslide was used as a reference for the spin and melt-casted films.

Steady-State Photoluminescence Spectroscopy. Photoluminescence (PL) measurements on dye-solutions in toluene, spin-cast and melt-processed films, prepared as described above, were acquired using a Photon Technology International C720 spectrophotometer with excitation at 615 nm. All spectra were corrected for the spectral dispersion of the Xe lamp, the instrument throughput, and the detector response. A reference detector accounted for fluctuation in lamp intensity. A series of **3** solutions in chloroform with concentrations between 8.3×10^{-6} and 1.3×10^{-4} M was also measured under the same conditions.

Thermal Characterization. The differential scanning calorimetry (DSC) traces were recorded using a Mettler-Toledo DSC-1 equipped with a Huber TC-100 cooling regulation system. All traces were recorded in a nitrogen atmosphere and were recorded with the heating and cooling rates indicated. The polarized optical microscopy images were taken on an Olympus BX51 Polarized Optical Microscope equipped with an Instec STC200 temperature controller and an Instec HCS402 hot stage. Here, the heating rate was 10K/min and cooling was done by allowing the sample reach room temperature after switching off the hot stage, leading to an average cooling rate of 10-15K/min. The nucleation experiments (both the mechanical scratching with the spatula and the nucleation via addition of crystals) were performed on a Gel Instrumente AG hotstage with a TC2 temperature controller.

Wide-Angle X-Ray Scattering. The 1D wide angle X-ray scattering (WAXS) experiments of **3** were carried out at ambient temperature in the reflection mode in a Rigaku diffractometer with a sealed-tube source

of CuK α radiation ($\lambda = 0.154$ nm) operated at 40 kV and 40 mA at ambient temperature. The scanning was performed at 0.3 °/min rate.

Two-Photon Absorption Measurements. Two photon absorption spectra were measured using the open-aperture Z-scan technique. A Ti:Sapphire regenerative amplifier (CPA-2010, from Clark-MXR) with 200 fs pulse duration and 1 mJ pulse energy pumped a traveling-wave optical parametric amplifier of superfluorescence (TOPAS, Light Conversion Ltd.). The second harmonic of the signal was passed through a spatial filter to isolate the lowest-order transverse mode of the beam. The beam was then split into a signal and reference arm which was used to divide by shot-to-shot noise. The beam waist and confocal parameter were determined through measurements of the beam size using a rotating slit beam profiler (BP104-VIS, Thorlabs Inc.) at several z-positions and then fitting these points to the well-known gaussian beam propagation equation.

Data was acquired from photodiodes in combination with a gated boxcar integrator (SR200 series, Stanford Research Systems) while the sample was translated through the focus by a computer-controlled translation stage. The accuracy of the Z-scan measurement was probed by measuring as standards the TPA cross-section of Rhodamine 6G (standard dye for visible region) and Styryl-9m (purchased from Exciton, standard dye for infrared region). The TPA cross-section was measured in spectroscopic grade toluene in a 1 mm path-length fused quartz cuvette.

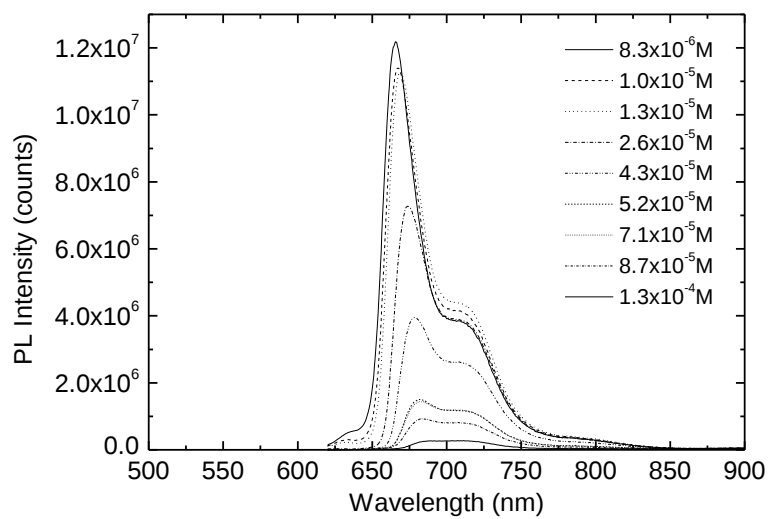


Figure S1. Photoluminescence spectra of **3** in chloroform as a function of dye concentration (excitation 615 nm).

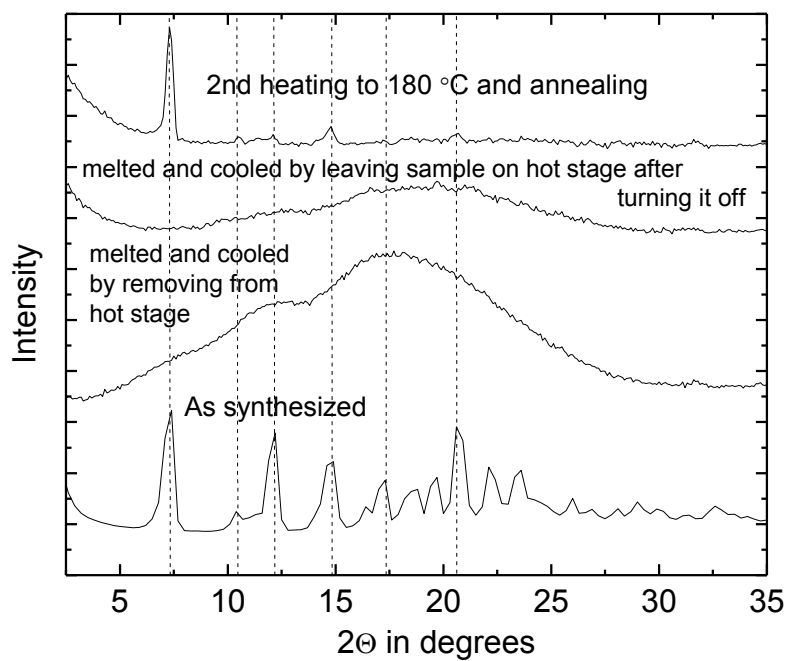


Figure S2. Wide-angle X-ray scattering data of **3** as a function of thermal history (as described in the figure).

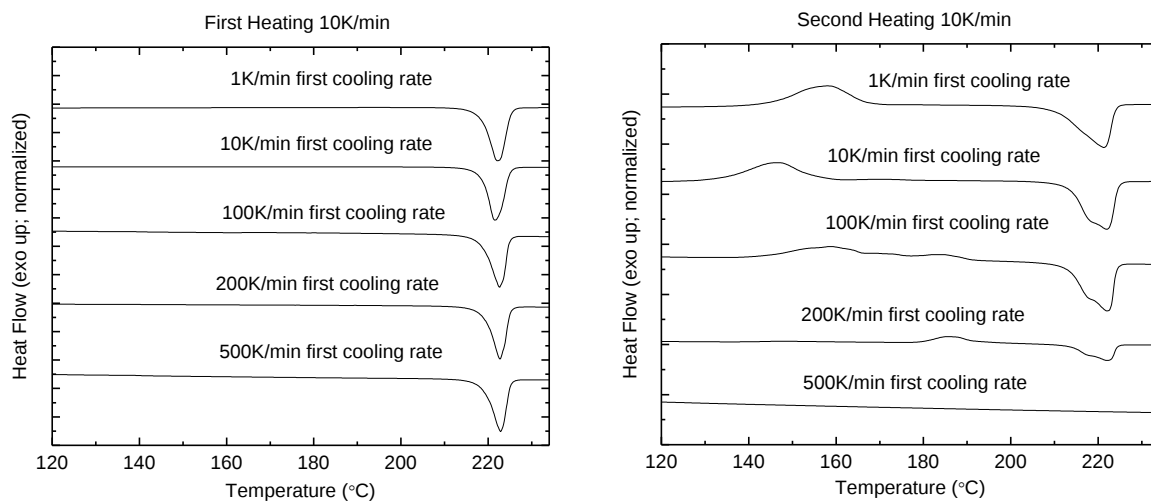


Figure S3. DSC traces of **3**. Left: First heating scans. The samples were subsequently cooled at the cooling rates indicated in the figure. Right: Subsequent second heating scans, conducted with a heating rate of 10K/min; the rate of the preceding cooling scan is indicated and the samples correspond to those shown on the left. To enable a comparison of the data in the right, the heat flow of the two graphs was normalized on the basis of equal melting enthalpies in the first heating scan.

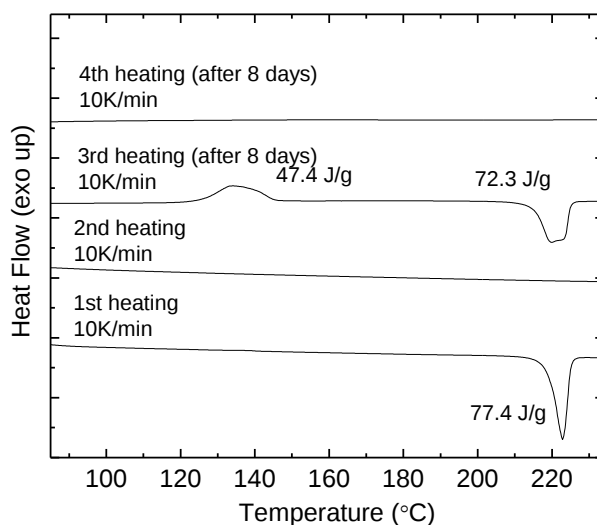


Figure S4. DSC traces of **3** as a function of thermal history. Shown are the 1st heating trace of an as-prepared sample (1st heating), and the heating trace of that same sample immediately after quenching it with a cooling rate of 500 K/min (2nd heating). The heating trace of the same sample was observed after storing under ambient conditions for 8 days (3rd heating) and immediately after quenching it with a cooling rate of 500 °K/min (4th heating).



Figure S5. Optical microscopy images of an amorphous film of **3**, which was cooled from the melt under ambient conditions and stored at room temperature for 20 days. The same section (750 x 750 μm) was imaged without polarizer (left) and between crossed-polarizers (right).

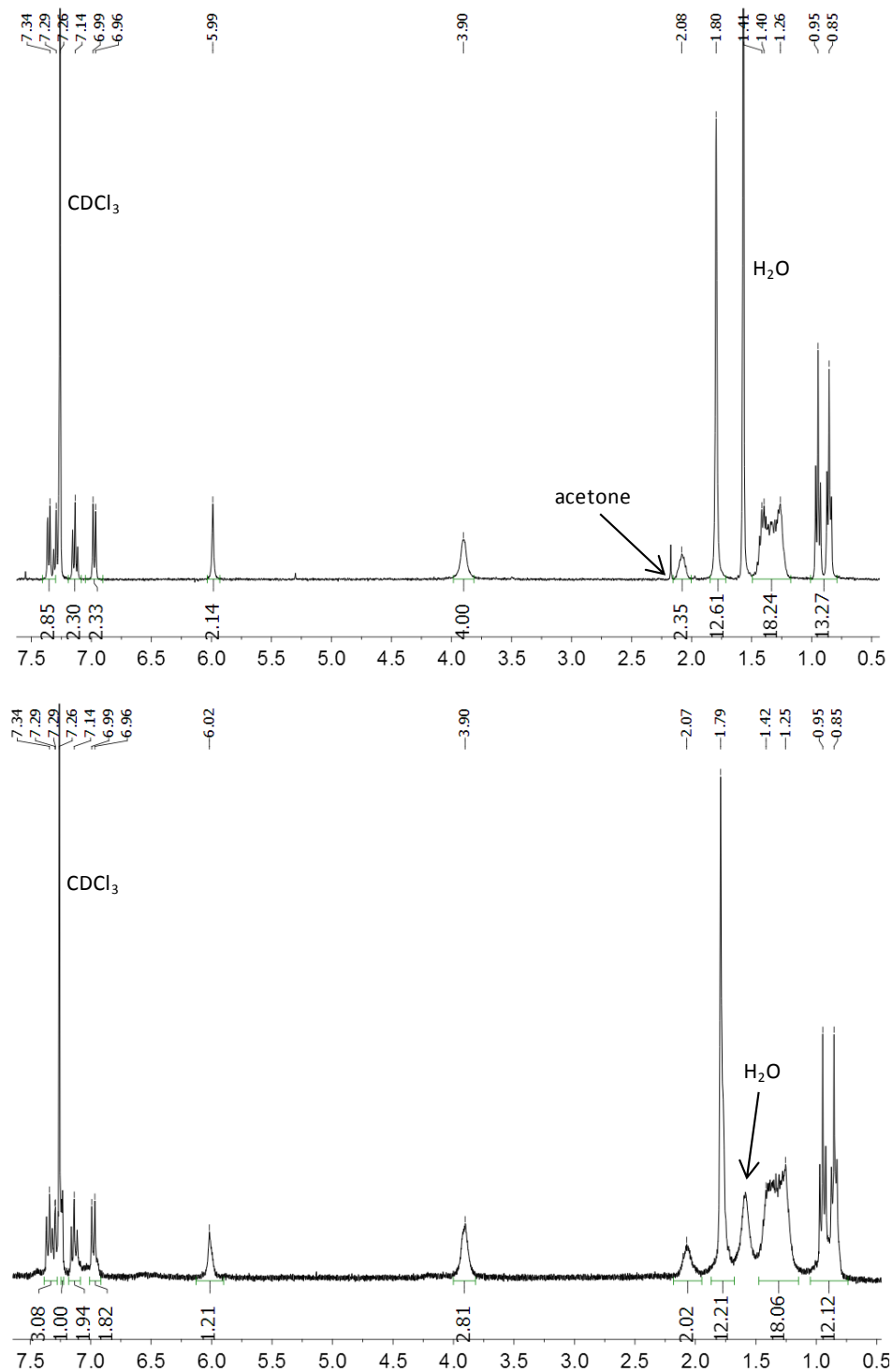


Figure S6. NMR spectra of **3** as-produced (top) and after melting and cooling back to room temp. under ambient conditions (bottom). Note that the acetone peak is a solvent impurity that was introduced in the NMR experiment.

Full author list for references (5) and (9):

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