

A windmill-Shaped Discotic Columnar Liquid Crystal with Fast Ambipolar Charge Carrier Transport

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Materials and Methods

1. Materials.

Unless otherwise noted, all the reagents and solvents were used as received from Aldrich Chemical, Tokyo Chemical Industry, and Wako Pure Chemical Industries. Dry solvents, like dry THF, were dehydrated in a home-made equipment.

2. General.

Column chromatography was carried out with Wako gel silica (particle size: 200 μm). High-purity truxene samples were obtained by repetitive recrystallization from hexane. Through repeated recrystallization in ethanol and *n*-hexane, we are trying to remove the ionic and neutral impurities. In the last time, distilled *n*-hexane is required to remove the remained polar solvent and few impurities. ^1H spectra were recorded at 25 $^\circ\text{C}$ on a JEOL model JNM-ECA500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as an internal reference. HRMS were obtained on a double-focusing magnetic sector mass spectrometer JEOL JMS-700. In this research, DSC 220C system, Seiko Elec., was used. The polarized light microscope of Optiphot2-pol, Nikon, the hot-stage of FP900 thermo-system was employed for taking optical graphs. X-ray diffraction equipment (Rigaku RAD-2B) was used to determine the phase structure.

In the θ -2 θ scan, the spacing is estimated from Braggs equation.

$$d = \frac{\lambda}{2\sin\theta}$$

λ is the wavelength of X-ray radiation source $\text{CuK}\alpha$, 1.54 \AA .

3. Synthesis

4-hydroxyindan-1-one (2)

A mixture of dihydrocoumarin 1 (3 g, 34 mmol) and anhydrous AlCl_3 (13 g, 95 mmol) was fused at 210 °C for 1 hour. After the reaction mixture was cooled to room temperature, ice and cold hydrochloric acid (30 mL) were added to the mixture. The precipitate was collected and washed with EtOH. Recrystallization from absolute EtOH gave 2 (2.1g, 70%) as colorless crystal. Mp 240 °C.

Oxoinden-4-yltrifluoromethanesulfonate (3)

N-phenyltrifluoromethanesulphonimide (2.50 g, 7.00 mmol) was added to a solution of 4-hydroxyindan-1-one 2 (1.00 g, 6.75 mmol) and triethylamine (1.05 mL, 7.50 mmol) in dichloromethane (30 mL). The resulting mixture was stirred 24 h at ambient temperature. The mixture was washed with water (30 mL) and brine (30 mL), and extracted with dichloromethane (2 x 50 mL). The organic phase was dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure followed by flash column chromatography (eluent: $\text{CHCl}_3/\text{Hexane} = 1 : 4$) afforded the 3-oxoinden-4-yltrifluoromethanesulfonate (1.85 g, 6.61 mmol, 95 %) as colorless solid. $^1\text{HNMR}$ (500 MHz, CDCl_3) δ 7.80 (t, J= 6.0 Hz, 1H, Ar-H), 7.50 (d, J = 6.0 Hz, 1H, Ar-H), 7.17 (d, J = 8.0 Hz, 1H, Ar-H), 3.20 (t, J = 6.0 Hz, 2H, $\text{CH}_2\text{-CH}_2\text{CO}$), 2.77 (t, J = 6.0 Hz, 2H, CH_2CO);

7 - 7 - Alkylindan - 1 - one (4a and 4b)

A suspension of compound 2 (1mmol), Alkyl boronic acid (3 equiv.), $\text{Pd}(\text{dppf})\text{Cl}_2$ (10%mol), powdered K_2CO_3 (3 equiv.), and Ag_2O (2.5 equiv.) in THF (75ml) was stirred under argon at 80°C in a sealed tube. After 48 h, the mixture was cooled to room temperature. The dark solid was filtered, and water was added into the solution. The solution was extracted with CHCl_3 . After evaporation, chromatography column was carried out to purify the crude product to provide white crystal.

3a: yield 76% $^1\text{HNMR}$ (500 MHz, CDCl_3) δ 7.60(d, J=7.5Hz, 1H, Ar-H), 7.40(d, J=7.5Hz, 1H, Ar-H), 7.30(d, J=7.5Hz, 1H, Ar-H), 3.06(t, J = 6.0 Hz, 2H, $\text{CH}_2\text{-CH}_2\text{CO}$), 2.70(t, J=6.0Hz, 2H, Ar- CH_2 -), 1.62(m, 2H, - CH_2 -), 1.31-1.40(m, 6H, - CH_2 -), 0.88(t, J=7.0Hz, 3H)

3b: yield 70% $^1\text{HNMR}$ (500 MHz, CDCl_3) δ 7.65(d, J=7.5Hz, 1H, Ar-H), 7.43(d, J=7.5Hz, 1H, Ar-H), 7.32(d, J=7.5Hz, 1H, Ar-H), 3.13(t, J = 6.0 Hz, 2H, $\text{CH}_2\text{-CH}_2\text{CO}$), 2.85(t, J=6.0Hz, 2H, Ar- CH_2 -), 1.88(m, 2H, - CH_2 -), 1.40(m, 2H, - CH_2 -), 0.92(t, J=7.0Hz, -Me)

1, 5, 9-trialkyltruxene (Tru6 and Tru4)

A suspension of 3a/3b (1 mmol) in the mixture of HOAc and HCl (0.7 mL/0.7 mL) was refluxed at 125 °C for 2 days in a sealed tub. The mixture was poured into a mixture of ice and water. After filtration, the solid was washed with water and acetone to afford the desired product:

Tru6

Yield: 63%. Clear point: 172 °C

$^1\text{HNMR}$ (500 MHz, CDCl_3) δ 7.79(d, J=7.0Hz, H, Ar-H), 7.44(d, J=7.0Hz, H, Ar-H), 7.21(d,

J=7.0Hz, H, Ar-H), 4.11(s, 2H, Ar-CH₂-Ar), 2.83(t, J=7.0Hz, Ar-CH₂-), 1.51(m, 2H, -CH₂-), 1.25(m, 2H, -CH₂-), 0.91(t, J=7.0Hz, -Me). HRMS: Calcd. For C₄₅H₅₄ [M]⁺: 594.4226; Found: 594.4224.

Tru4

Yield: 52%. Clear point: 254°C

¹HNMR (500 MHz, CDCl₃) δ7.69(d, J=8.0Hz, H, Ar-H), 7.41(d, J=7.5Hz, H, Ar-H), 7.19(d, J=7.0Hz, H, Ar-H), 4.96(s, 2H, Ar-CH₂-Ar), 2.78(t, J=8.0Hz, Ar-CH₂-), 1.72-1.78(m, 2H, -CH₂-), 1.42-1.54(m, 2H, -CH₂-), 1.00(t, J=7.5Hz, -Me). HRMS: Calcd. For C₃₉H₄₂ [M]⁺: 510.3365; Found: 510.3363.

4. Thermal properties

4.1 DSC

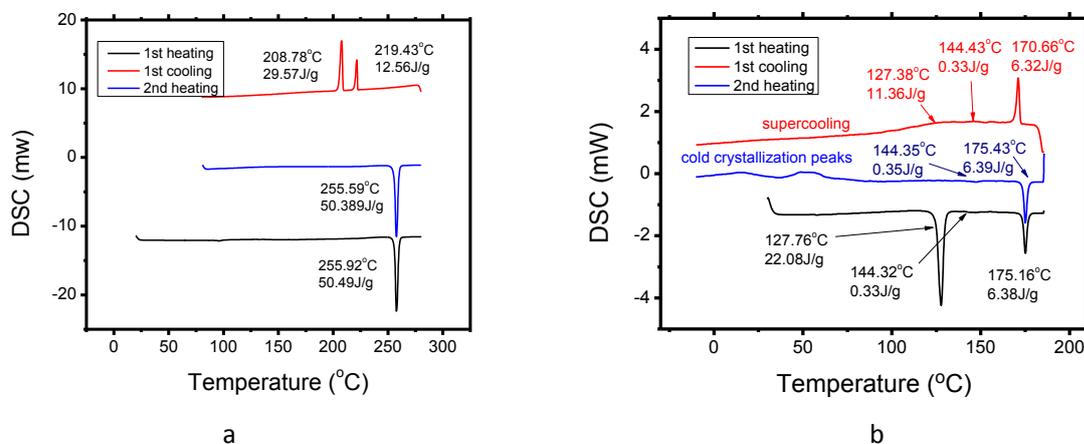


Figure S1 DSC curves of **Tru4** (a) and **Tru6** (b). The heating and cooling rates were 10Kmin^{-1} . The sample weight was 3.5mg. In the figure b, the peak appearing at 144°C is so small that we couldn't see it clearly, which just was confirmed by POM texture change and variable temperature XRD measurement.

4.2 POM

POM images were taken when the samples were sandwiched by two glass substrates. All of images were observed upon cooling after heating to isotropic phase.

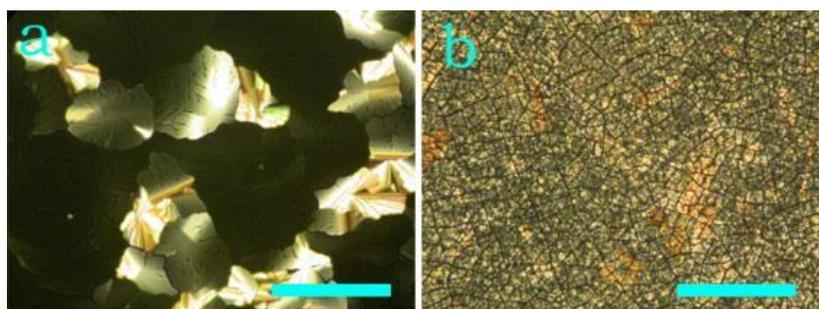


Figure S2 POM images of **Tru4**, a hexagonal columnar phase (210°C), b polycrystalline phase (room temperature, $2\text{k}/\text{min}$), the scale bars represent $100\ \mu\text{m}$. In the Fig a, the black region exhibits perfect homeotropic columnar alignment, while the birefringence region shows defective domains.

5. Time-of-flight experiments

The charged carrier mobility was obtained by a TOF technique under controlled temperatures. TOF equipment consists of a nitrogen gas laser ($\lambda = 337$ nm, pulse duration time = 600 ps, power per pulse = 13.6 μ J), digital oscilloscope, and hot stage whose temperature is controlled by PID thermocontroller. Carrier mobility μ was calculated through the equation: $\mu = d^2/V\tau_T$. Where d is the sample thickness, and V the applied Voltage, and τ_T the transit time of photo-generated carriers traversing the sample layer. The τ_T was determined from an inflection point in a double logarithmic plot of transient photocurrent as a function of time. In all measurements, the used resistance is 100 Ω .

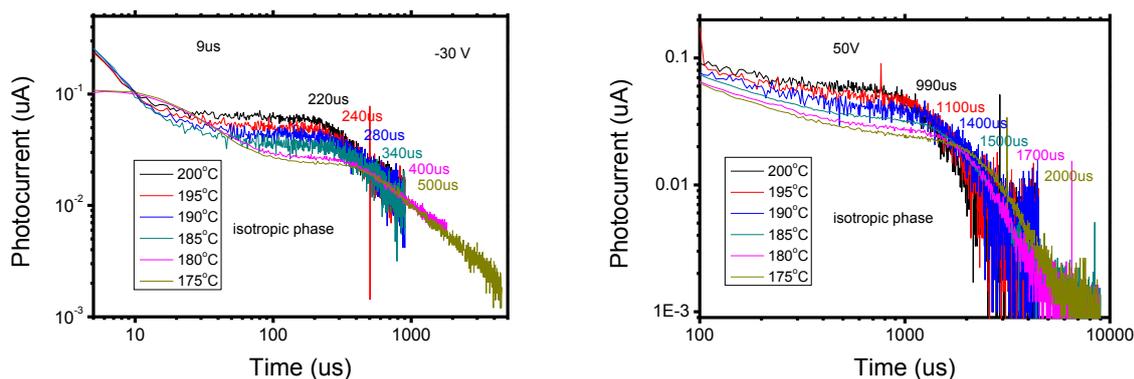


Figure S3 Transient photocurrents of **Tru6** in isotropic phase (left: for negative carriers; right: for positive carriers)

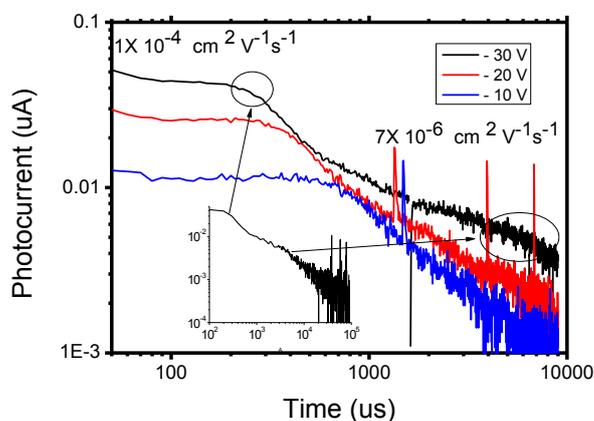


Figure S4 Negative transient photocurrents for **Tru6** in isotropic phase, the short transient time of 260 μ s was caused by electron transport, while another one appearing at long time region was by ionic transport.

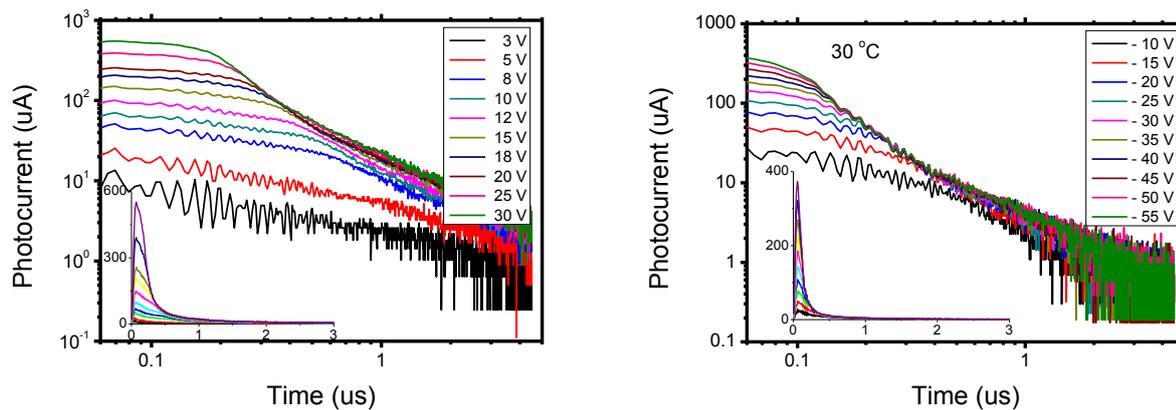


Figure S5. Typical transient photocurrent of **Tru6** by time of flight measurement in polycrystalline phase at 30°C, the mobility of hole and electron was determined to be 0.1 cm²/Vs.

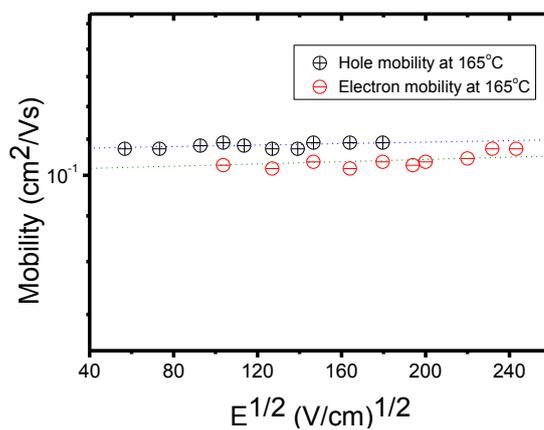


Figure S6. Electric field dependence of charge carrier mobility for hole and electron in hexagonal columnar phase of **Tru6** at 165°C

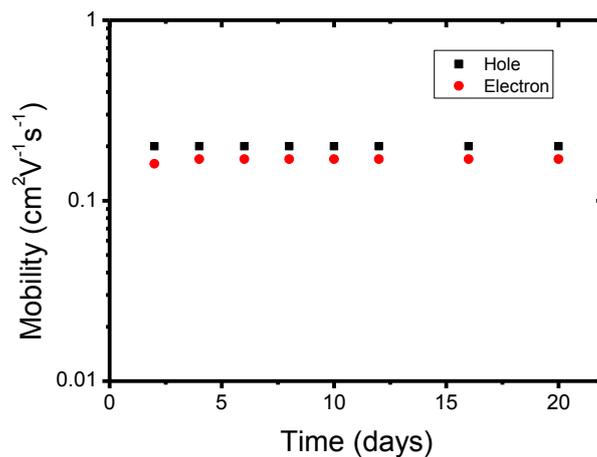


Figure S7 Stability of mobility in polycrystalline state of **Tru6**. This sample was quite stable in ambient atmosphere, so that the charge transport could be determined for long period, even several weeks.

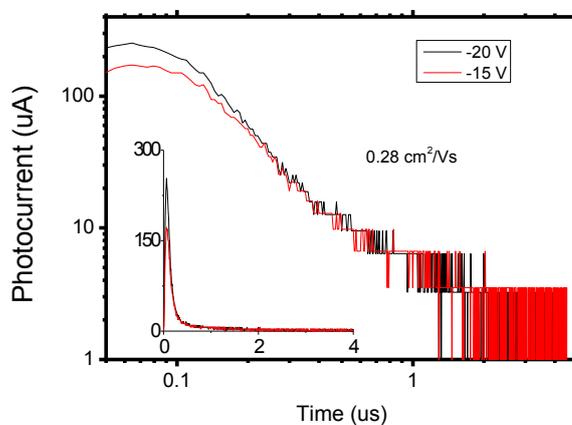
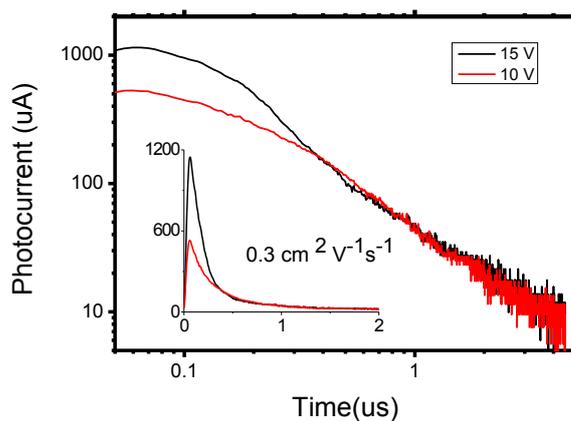


Figure S8 Transient photocurrent in polycrystalline phases of **Tru4**, the sample thickness was 9um.