Supporting Information

**Bulk-Mediated *In-Situ* Homogeneous Photoalignment Induced by Reactive Mesogen Containing Diphenylacetylene Moiety**

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## 1. Synthesis of DAT

The synthetic route of the liquid crystalline monomer consisting of tolane moiety (DAT) is demonstrated in Scheme S1.



Scheme S1. Synthetic route for DAT.

#### *1.1 Synthesis of compound (5)*

To a 500 mL flask, we added 9.92 g (40.0 mmol) of p-iodobenzoic acid, 33.1 g (280.0 mmol) of 1,6-hexandiol and several drops of methanesulfonic acid. After stirring at 115 °C for 4h, the mixture was poured into 1 L of water and extracted with ethyl acetate for several times. The combined organic solution was washed with deionized water for several times and washed with saturated aqueous NaHCO3, and then, dried over anhydrous sodium sulfate. The solution was evaporated to obtain a crude product (5). The crude product (5) was purified by chromatography (dichloromethane: ethyl acetate = 1:1) to obtain the product (5) as a dark yellow oil. Yield: 88%.

#### *1.2 Synthesis of compound (6)*

To a 100 mL flask, we added 10.5 g (30.0 mmol) of compound (5), 80 ml of triethylamine, 114.3 mg (0.6 mmol) of copper (I) iodide and 693.3 mg (0.6 mmol) of tetrakis(triphenyphosphine) palladium (0). The mixture was flushed with nitrogen and 4.4 g (45.0 mmol) of trimethylsilylacetylene was added with magnetic stirring. After stirring at 40 °C for 24 h, 14.4 ml of a 75% (w/w) tetrabutylammonium fluoride solution in water was added to deprotect the silane moiety. After stirring for another 30 minutes, the solvent was evaporated under vacuum, and the residual mixture was dissolved in dichloromethane and filtered. The obtained organic phase was washed with a 0.5 M HCl aqueous solution for several times and dried over anhydrous magnesium sulfate. The solvent was evaporated to obtain a crude product (6), which was further purified by chromatography (dichloromethane: ethyl acetate = 2:1) to obtain the product (6) as a dark yellow liquid. Yield: 72%.

#### *1.3 Synthesis of compound (7)*

To a 100 mL flask, we added 4.93 g (20.0 mmol) of compound (6), 3.0 g (30.0 mmol) of triethylamine and 40mL of dichloromethane. The mixture was flushed with nitrogen, and 2.2 g (24.0 mmol) of acryloyl chloride was added slowly under magnetic stirring in ice-bath. After stirring at room temperature for 12 h, the solution was diluted with 40 mL of dichloromethane, and then, washed with 20 mL of 1.0 M HCl aqueous solution and deionized water, respectively. The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated to obtain a crude product (7). The crude product (7) was purified by chromatography (dichloromethane) to obtain the product (7) as a yellowish liquid. Yield: 41%.

#### *1.4 Synthesis of DAT*

The compound (4) was synthesized according to the reported procedure[1]. To a 50 ml flask, we added 1.98 g (4.0 mmol) of compound (4), 1.32 g (4.4 mmol) of compound (7), 25 ml of triethylamine, 25.4 mg (0.13 mmol) of copper(I) iodide and 154.1 mg (0.13 mmol) of tetrakis(triphenyphosphine)palladium (0). The flask was flushed with nitrogen and placed under magnetic stirring. After stirring at 45 °C for 24 h, the solvent was evaporated under vacuum, and the residual mixture was dissolved in dichloromethane and filtered. The obtained organic phase was washed with a 0.5 M HCl aqueous solution, dried over anhydrous magnesium sulfate, and the solvent was evaporated to obtain a crude product. The crude product was purified by chromatography (ethyl acetate: dichloromethane: petroleum ether = 1:10:10) and recrystallization from ethanol for several times to obtain the final product DAT as white crystals. Yield: 70%.

## 2. Synthesis and characterization of DAT monomer

The structure of DAT was characterized by 1H NMR spectrum, as shown in Figure S1. In the 1H NMR spectrum of DAT, all the protons in the structure matched well with the corresponding peaks in the spectrum as depicted in Figure S1. The peaks at 5.8-6.5 ppm were assigned to the protons of terminal acrylate groups, and the multiplet at 0.9-2.0 ppm was assigned to be the alky protons, indicating the existence of alkyl spacer. The four doublets at 7.2, 7.5, 7.6 and 8.0 ppm were attributed to the aromatic protons in the tolane structure, and the two doublets peaks at 7.0 and 8.1 ppm were attributed to the aromatic protons next to the tolane structure, indicating the existence of the DAT mesogenic core structure. The 1H NMR spectrum confirmed a successful synthesis of DAT monomer.

DAT: 1H NMR (400 MHz, chloroform-d) δ 8.20-8.10 (m, 2H), 8.02 (d, J = 8.2 Hz, 2H), 7.64-.56 (m, 4H), 7.27-7.20 (m, 2H), 7.06-6.94 (m, 2H), 6.41 (dt, J = 17.1, 2.0 Hz, 2H), 6.12 (ddd, J = 17.3, 10.4, 3.4 Hz, 2H), 5.82 (dt, J = 10.7, 2.3 Hz, 2H), 4.33 (t, J = 6.6 Hz, 2H), 4.18 (td, J = 6.6, 3.2 Hz, 4H), 4.05 (t, J = 6.4 Hz, 2H), 1.82 (ddt, J = 19.0, 14.1, 6.9 Hz, 4H), 1.72 (ddq, J = 10.7, 6.8, 3.8, 3.2 Hz, 4H), 1.61-1.40 (m, 8H).



Figure S1. 1H NMR spectrum of DAT.

## 3. Thermal property of DAT

The thermal stability of DAT was evaluated by TGA in nitrogen atmosphere with a heating rate of 10 oC min-1 as shown in Figure S2, and the results were summarized in Table S1. Thermal degradation of DAT occurred in a two-step manner. The first decomposition was around 293 oC corresponding to the cleavage of ester linkages present in DAT core. The second stage was around 396 ºC, at which the weight loss was attributed to the decomposition of aryl-alkyl-ether linkages.



Figure S2. TGA curve of DAT.

Table S1. Thermal properties of DAT

|  |  |
| --- | --- |
| **Phase transition temperature / oC** | |
| Heating cycle | Cr - 63.8 – SmA - 121.0 – N - 128.7 - I |
| Cooling cycle | I - 126.5 – N - 119.2 – SmA - 33.1 - Cr |
| **TGA decomposition temperature / oC** | |
| 1st decomposition | 293 |
| 2nd decomposition | 396 |

## 4. Photo-induced alignment of DAT-ITO cell

The POM images of the DAT-ITO samples with various LPUV exposure energy were examined under crossed polarizer, as shown in Figure S3. All the POM images showed perfect dark and bright states when the alignment direction is 0 o and 45 o to the polarizer, respectively, which confirms the LC molecules are uniaxially aligned on the ITO surface.



Figure S3. POM images of DAT-ITO cells under crossed polarizer with various LPUV exposure energy.



Figure S4. Light leakage of the DAT-ITO cell with respect to the LPUV exposure energy.

## 5. Electro-optic properties of DAT-IPS and PI-IPS cells

In Figure S5 (a) and (b), POM images of DAT-IPS and PI-IPS cells at various applied voltages are displayed. In both cases, the transmittance increased with increasing applied voltage from 0 to 7.7 V. The DAT-IPS cell and PI-IPS cell exhibited the gray scale images almost at the same level. Moreover, the voltage-dependent response time of DAT-IPS and PI-IPS cells were measured at various applied voltages as shown in Figure S6. The rise time (τr) of DAT-IPS and PI-IPS cells are 20.9 and 20.5 ms, and the decay time (τd) of DAT-IPS and PI-IPS cells are 22.3 and 21.8 ms, respectively. The results further confirmed that the DAT-IPS cell exhibited comparable electro-optic switching properties to the conventional PI-IPS cell.



Figure S5. POM gray-scale images of DAT-IPS and PI-IPS cells at various applied voltages. (a) DAT-IPS cell and (b) PI-IPS cell.



Figure S6. Voltage-dependent response time of DAT-IPS and PI-IPS cells.

**References**

[1] Broer DJ, Boven J, Mol GN, et al. In-situ photopolymerization of oriented liquid-crystalline acrylates, 3. Oriented polymer networks from a mesogenic diacrylate. Macromol Chem Phys. 1989;190(9):2255-2268.