

## Electronic Supporting Information

# Highly ordered smectic structures of disc-rod luminescent liquid crystals: the role of tolane group

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## 1. Experimental section

### Materials

All commercial reagents for chemical synthesis from J&K, Sigma-Aldrich, and TCI were used as received without further purification unless otherwise stated. The solvents used for the synthesis were of analytical grade. All synthetic reactions were monitored by silica gel thin-layer chromatography (TCL) with pre-coated aluminum plates from Merck. The purity and identity of products were confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy. Samples were recrystallized with methyl alcohol before all the measurements.

### Physical characterization

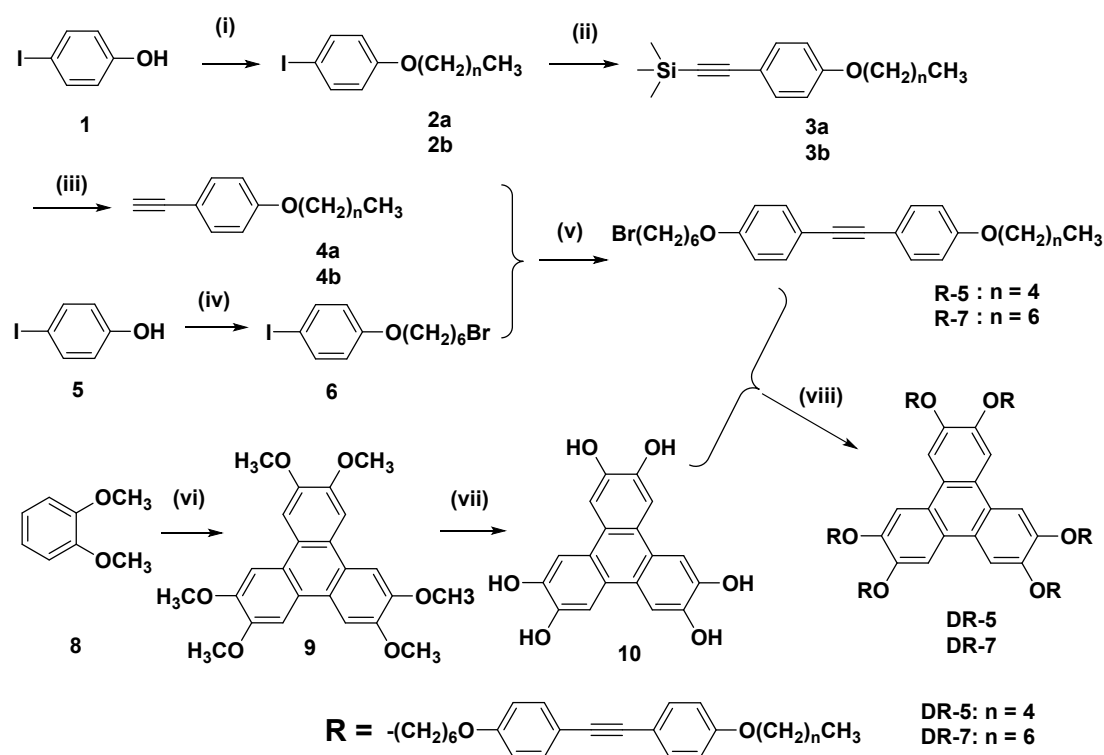
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured in deuterated solvents  $\text{CDCl}_3$  on a Varian INOVA 400M / Bruker AVANCE spectrometer with chemical shifts ( $\delta$  in ppm) quoted with tetramethylsilane as the internal standard. Mass spectrometry was carried out on a Bruker Autoflex matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). DSC results were collected by NETZSCH DSC 200 F3 while the POM images were recorded by Leica Dm1p. WAXD was performed on a Bruker D8 Advance X-ray diffractometer, with  $\text{Cu K}\alpha 1$  (45 kV, 100 mA). SEM was performed using FE-SEM (JSM-7800F & TEAM Octane Plus). UV-Vis absorption spectra were collected by Shimadzu UV-2500 while photoluminescence (PL) spectra were recorded by ThermoFisher Scientific Lumina fluorescence spectrometer. Thin films were prepared by evaporation of  $\text{CH}_2\text{Cl}_2$  solution of samples on quartz substrates. The photoluminescence quantum yields (QY) of these films were obtained by spectrofluorometer (FluoroMax-P, Horiba Jobin Yvon Inc.) equipped with a calibrated integrating sphere. Pure and dry nitrogen was used to purge the integrating sphere to give an inert environment during the measurements. The samples placed in the calibrated integrating sphere were excited by the selected monochromatic excitation light (the wavelength is 295 nm). The PL quantum yields were obtained by comparing the spectral intensities of the monochromatic excitation light and the PL emission.

To test the AIE activity of samples, solutions were prepared at first by dissolving recrystallized samples into anhydrous THF solvent. Filtration with microfilter was conducted before spectroscopy measurements. According to the different water fractions, deionized water was proportionally and

carefully added into the THF solution avoiding the generation of air bubbles in the mixture. Then the spectroscopy measurements for the fresh mixtures were performed.

To take photographs of samples under different illustration conditions, the recrystallized samples were placed above clear microscopy glass slides and heated to isotropic liquid state with a TH-II type TLC plate heater (Shanghai Kezhe Biochemical Technology co., ltd) at ambient temperature. Then the temperature of the heating stage was controlled and the photographs of the samples in different phase stages under sunlight and UV irradiation were respectively recorded by CAMAG Reprostar 3 recording system (CAMAG co. ltd).

### Synthesis and molecular characterization



**Scheme S1.** Synthetic route to target compounds. Reagents: (i) bromoalkane, KOH; (ii) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, trimethylsilylne, CuI; (iii) TBAF; (iv) dibromoalkane, KOH; (v) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI; (vi) FeCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>; (vii) HBr in acetic acid; (viii) KOH.

### Synthesis of 2

*p*-Iodophenol (8.3 g, 37 mmol) was heated under reflux with 1-bromopentane (4.68 g, 31 mmol), KOH (3.52 g, 62 mmol) in acetone (200 mL) for 24 h. After cooling to room temperature, the reaction

mixture was filtered, and the solvent was removed. Subsequent column chromatography afforded the product **2a** with a yield of 91%.  $^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 7.56 (d,  $J = 8.0$  Hz, 2H), 6.68 (d,  $J = 8.0$  Hz, 2H), 3.91 (t,  $J = 4.0$  Hz, 2H), 1.82-1.75 (m, 2H), 1.47-1.36 (m, 4H), 0.96 (t,  $J = 4.0$  Hz, 3H).

To synthesize **2b**, 1-bromoheptane (5.56 g, 31 mmol) was used and a colorless liquid was obtained with a yield of 94%.  $^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 7.56 (d,  $J = 8.0$  Hz, 2H), 6.68 (d,  $J = 8.0$  Hz, 2H), 3.91 (t,  $J = 4.0$  Hz, 2H), 1.81-1.75 (m, 2H), 1.47-1.34 (m, 8H), 0.95 (t,  $J = 4.0$  Hz, 3H).

### *Synthesis of 3*

After removing the oxygen, compound **2a** (6.4 g, 22 mmol), CuI (71 mg, 373.2  $\mu\text{mol}$ ), and  $\text{PdCl}_2(\text{PPh}_3)_2$  (112 mg, 158.0  $\mu\text{mol}$ ) were added into an oven dried schlenk tube and then 30 mL anhydrous THF and 120 mL triethylamine were injected into the mixture which degassed with  $\text{N}_2$ . After the slow addition of 2.84 g (29 mmol) ethynyltrimethylsilane, the system was degassed again. After stirring at  $60^\circ\text{C}$  overnight, the reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted with DCM. The organic layer was combined, washed with 1 M aqueous HCl and saturated aqueous NaCl solution in sequence, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removing the solvent under vacuum, the residue was purified with silica column eluting with hexane to afford **3a**, a liquid in yield of 95%.  $^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 7.40 (d,  $J = 8.0$  Hz, 2H), 6.81 (d,  $J = 8.0$  Hz, 2H), 3.94 (t,  $J = 8.0$  Hz, 2H), 1.79-1.74 (m, 2H), 1.49-1.36 (m, 4H), 0.95 (t,  $J = 8.0$  Hz, 3H), 0.24 (s, 9H).

To synthesize **3b**, compound **2b** (7.1 g, 22 mmol) was used and a liquid was obtained with a yield of 96.8%.  $^1\text{H NMR}$ (400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 7.42 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 3.98 (t,  $J = 8.0$  Hz, 2H), 1.79-1.73 (m, 2H), 1.45-1.25 (m, 8H), 0.95 (t,  $J = 8.0$  Hz, 3H), 0.25 (s, 9H).

### *Synthesis of 4*

Compound **4a** was prepared based on following procedure: compound **3a** (4.4 g, 17 mmol) was dissolved into 30 mL THF before adding 15 mL 1 M THF solution of tetrabutylammonium fluoride (TBAF). The system was bubble purged with  $\text{N}_2$  and stirred at r.t for 2 h. Then the solvent was

vaporized under vacuum, the residue was extracted with DCM, and the sediment was filtered off. After that, the solvent was removed through reduced pressure to obtain a crude product, which was further purified with silica column eluting to afford a yellow liquid in 93.2% yield.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.45 (d,  $J = 8.0$  Hz, 2H), 6.86 (d,  $J = 8.0$  Hz, 2H), 3.97 (t,  $J = 4.0$  Hz, 2H), 3.01 (s, 1H), 1.83-1.79 (m, 2H), 1.50-1.38 (m, 4H), 0.96 (t,  $J = 4.0$  Hz, 3H).

To synthesize **4b**, compound **3b** (5 g, 17 mmol) was used and a liquid was obtained with a yield of 96.2.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 7.43 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 3.99 (t,  $J = 4.0$  Hz, 2H), 2.99 (s, 1H), 1.80-1.74 (m, 2H), 1.47-1.25 (m, 8H), 0.90 (t,  $J = 8.0$  Hz, 3H).

### Synthesis of **6**

*p*-Iodophenol (2.2 g, 10 mmol) was dissolved in acetonitrile (50 mL) and through dropping funnel, the mixture was slowly added into the 100 mL acetone solution containing 12-dibromohexane (2.93 g, 12 mmol) and KOH (1.12 g, 20 mmol). The system was heated under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the solvent was removed. Subsequent column chromatography afforded the product **6** with a yield of 82%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.56 (d,  $J = 8.0$  Hz, 2H), 6.69 (d,  $J = 8.0$  Hz, 2H), 3.92 (t,  $J = 8.0$  Hz, 2H), 3.43 (t,  $J = 8.0$  Hz, 2H), 1.94-1.87 (m, 4H), 1.52-1.47 (m, 4H).

### Synthesis of **Rs**

After removing the oxygen, compound **4a** (866 mg, 4.6 mmol), CuI (10 mg, 52  $\mu\text{mol}$ ), and **6** (2.1 g, 5.5 mmol) were placed into an oven vacuum-dried schlenk tube before 30 mL anhydrous THF and 120 mL triethylamine were added. The mixture was bubbled with  $\text{N}_2$ . After the slow addition of  $\text{PdCl}_2(\text{PPh}_3)_4$  (60 mg, 52  $\mu\text{mol}$ ), the system was degassed again. After stirring at 50°C for 20 h, the mixture was concentrated and extracted with DCM. The organic layer was combined, washed with water and saturated aqueous NaCl solution in sequence, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removing the solvent through reduced pressure, the residue was purified with silica column eluting with hexane/DCM (5:1) to afford a white solid **R-5** in 80% yield.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.45 (d,  $J = 12.0$  Hz, 4H), 6.87 (d,  $J = 12.0$ , 4H), 3.96 (td,  $J = 6.0$  Hz, 4.0 Hz, 4H), 3.43 (t,  $J = 8.0$  Hz, 2H), 1.95-1.76 (m, 6H), 1.53-1.46 (m, 8H), 0.94 (t,  $J = 8.0$  Hz, 3H).  $^{13}\text{C}$  NMR (400MHz,

CDCl<sub>3</sub>)  $\delta$ : 159.11, 133.03, 115.73, 114.68, 88.16, 68.24, 67.96, 33.98, 32.87, 29.17, 28.38, 28.12, 25.48, 22.66, 14.23.

**R-7** was synthesized by similar procedures while compound **4b** (995 mg, 4.6 mmol) was used to get a solid in yield of 83%. <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>),  $\delta$ (TMS, ppm): 7.45 (d,  $J$  = 8.0 Hz, 4H), 6.87 (d,  $J$  = 8.0, 4H), 3.96 (td,  $J$  = 8.0Hz, 4.0 Hz, 4H), 3.44 (t,  $J$  = 8.0 Hz, 2H), 1.94-1.78 (m, 6H), 1.58-1.33 (m, 12H), 0.91 (t,  $J$  = 8.0 Hz, 3H). <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ : 159.11, 133.03, 115.74, 114.68, 88.16, 68.26, 67.96, 33.97, 32.79, 31.98, 29.52, 28.12, 26.84, 26.19, 25.48, 22.81, 14.29.

### Synthesis of **9**

FeCl<sub>3</sub> (12.5 g, 76.9 mmol) was added in a CH<sub>2</sub>Cl<sub>2</sub> (100 mL) solution of compound **8** (15 g, 60 mmol) and 5 mL concentrated H<sub>2</sub>SO<sub>4</sub> was slowly dropped into the solution at 0 °C. The reaction mixture was stirred for 2 h at room temperature and then poured onto MeOH (100 mL). The precipitated product was collected by filtration and recrystallized by EtOH to get a solid with 70% yield. <sup>1</sup>H NMR (400MHz, DMSO),  $\delta$  (TMS, ppm): 7.79 (s, 6H), 4.13 (s, 18H).

### Synthesis of **10**

Under the protection of N<sub>2</sub>, 60 mL HBr in acetic acid (45% w/w) was slowly added into the system containing compound **9** (1 g, 2.4 mmol). The mixture was heated to 95°C to react for 24 h. After cooling to room temperature, the crude product was washed with plenty of water and then recrystallized in water to obtain a dark purple solid in yield of 55%. <sup>1</sup>H NMR (400MHz, DMSO)  $\delta$ : 9.32 (s, 6H), 7.62 (s, 6H).

### Synthesis of **DR-5**

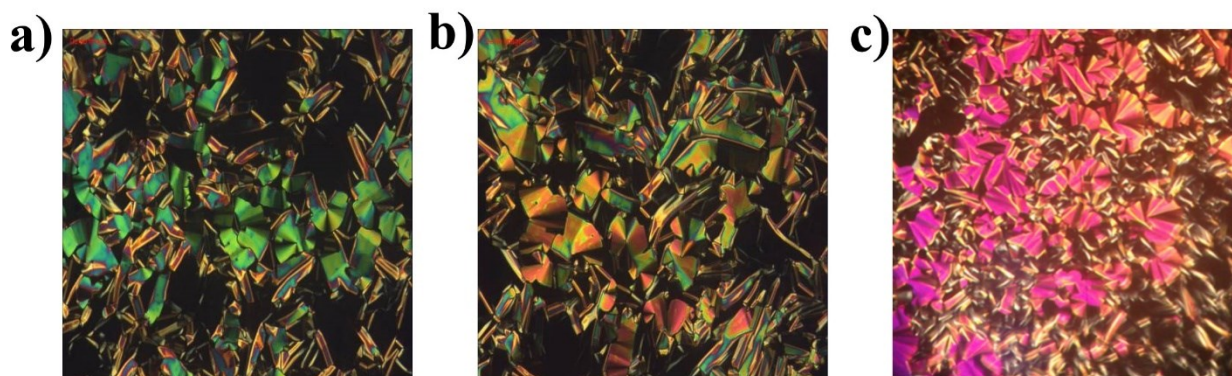
Hexahydroxytriphenylene (0.16 g, 0.4 mmol) and dried KOH (0.25 g, 3.6 mmol) were placed in an oven-dried flask. After three times of pumping and purging with N<sub>2</sub>, compound **R-5** (1.42 g, 3.2 mmol) dissolved in 15 mL anhydrous DMF was slowly injected into the mixture. The mixture was heated to 100 °C and allowed to react for 72 h. The mixture was poured into 50 mL water and the crude product was filtered and purified by column chromatography afforded the product with a yield of 20%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.06 (s, 6H), 7.44 (d,  $J$  = 8.0 Hz, 24H), 6.86 (d,  $J$  = 8.0

Hz, 24H), 4.19 (t,  $J = 4.0$  Hz, 12H), 3.98 (td,  $J = 8.0$ Hz, 4.0 Hz, 24H), 1.82-1.69 (m, 36H), 1.48-1.35 (m, 48H), 0.93 (t, 18H).  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.38, 159.13, 133.05, 115.76, 115.42, 114.70, 88.16, 68.27, 67.98, 64.13, 29.20, 28.94, 28.66, 28.39, 25.88, 22.57, 14.28; MALDI-TOF-MS (m/z):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{168}\text{H}_{193}\text{O}_{18}$ , 2499.4142. found, 2499.4120.

### Synthesis of **DR-7**

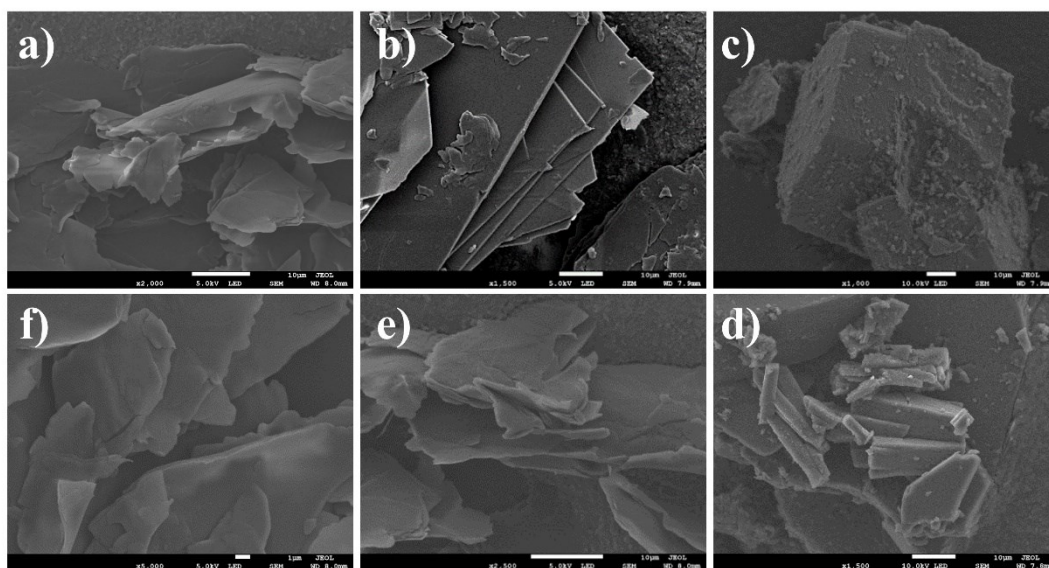
**DR-7** was synthesized by similar procedures to **DR-5** while compound **R-7** (1.51 g, 3.2 mmol) was used to get a white solid in yield of 22%.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ ),  $\delta$ (TMS, ppm): 8.05 (d, 6H), 7.43 (d,  $J = 8.0$  Hz, 24H), 6.83 (d,  $J = 8.0$  Hz, 24H), 4.16 (t,  $J = 4.0$  Hz, 12H), 3.94 (td,  $J = 8.0$ , 4.0 Hz, 24H), 1.81-1.72 (m, 24H), 1.46-1.30 (m, 72H), 0.89 (t,  $J = 8.0$  Hz, 18H).  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.33, 159.09, 133.01, 115.72, 115.70, 114.65, 88.15, 68.23, 67.93, 64.07, 31.97, 29.90, 29.33, 29.30, 28.63, 26.18, 25.85, 22.80, 14.28. MALDI-TOF-MS (m/z):  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{180}\text{H}_{217}\text{O}_{18}$ , 2667.6020; found, 2667.6101.

## 2. POM textures



**Fig. S1.** The magnification of POM textures of **DR-5** observed at a) 63 °C, b) 55 °C and c) that of **DR-7** at 75 °C upon cooling from isotropic melts with a cooling speed of  $1^\circ\text{C}\cdot\text{min}^{-1}$ .

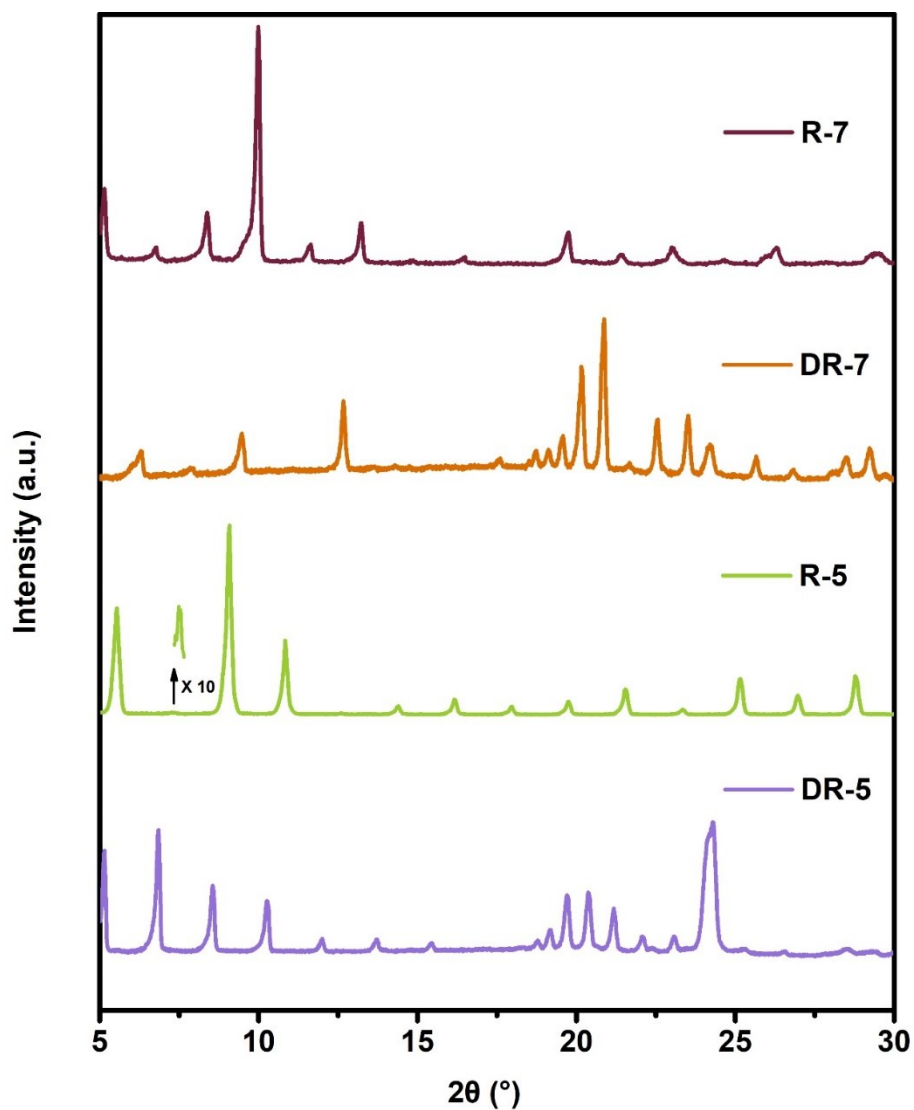
### 3. SEM images



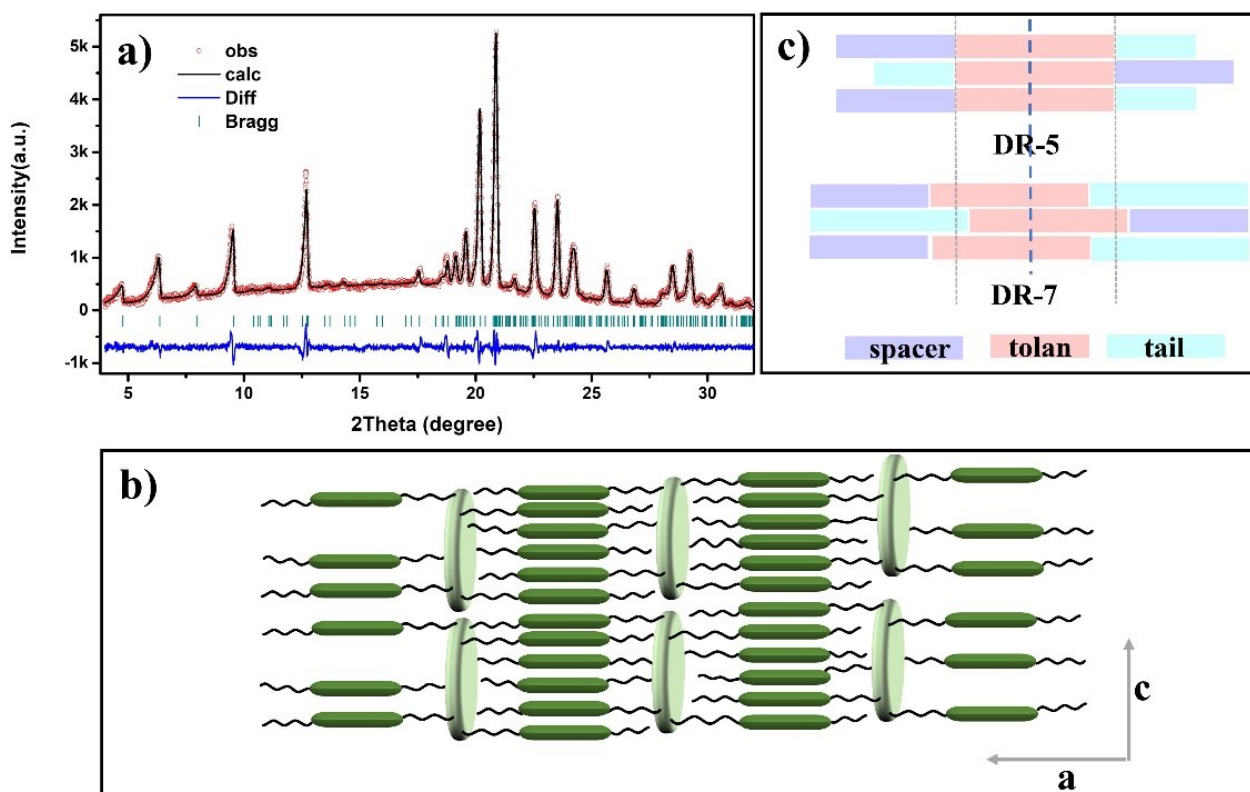
**Fig. S2.** The SEM images of a) R-5; b) DR-5; c) compound 9; d) R-7; e) DR-7 and f) compound 10. Scale bar: 10  $\mu\text{m}$  for a) to d) except 1  $\mu\text{m}$  for f).



#### 4. WAXD analysis



**Fig. S3.** The comparison on WAXD patterns for DRs and referential compounds **R**s, which are obtained at room temperature. The diffractions in small-angle region of **R-5** shows a  $d$ -spacing ratio of 1/3:1/4:1/5:1/6; for **DR-5**, that ratio is 1/3:1/4:1/5:1/6:1/7:1/8; for **R-7**, that ratio is 1/3:1/4:1/5:1/6:1/7:1/8; for **DR-7**, that ratio is 1/4:1/5:1/6:1/7. ( $2\theta$  from 5° to 30°). These  $d$ -spacing ratios confirm their layered structures.



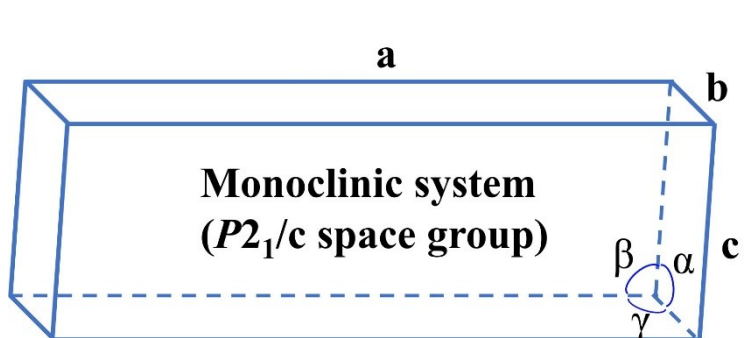
**Fig. S4.** a) The refinement of WAXD pattern for **DR-7**. b) The schematics of the proposed crystal packing of **DR-5**, viewing along the *b* axis. c) The schematics of the of tolan stacking for **DRs** with different length of tail. The tolan is assumed to be perfectly stacked. The lengths of tolan, spacer and alkyl tail are proportionally drawn.

**Table S1.** Structure refinement data for **DRs**.

	<b>DR-5</b>	<b>DR-7</b>
Crystal system	Monoclinic systems	Monoclinic systems
Space group	$P2_1/c$	$P2_1/c$
$a$ [Å]	51.89479_0.01064	55.56923_0.00719
$b$ [Å]	4.80360_0.00091	4.78209_0.00086
$c$ [Å]	17.28970_0.00368	17.03028_0.00747
$\alpha$ [Å]	90	90
$\beta$ [Å]	94.26744_0.00959	93.50626_0.03835
$\gamma$ [Å]	90	90
$2\theta$ [°]	1.50418 -34.98521	1.50418 - 34.98521
$R_p$ <sup>[a]</sup>	0.07980	0.07131
$R_{wp}$ <sup>[a]</sup>	0.11007	0.09771
$R_{exp}$ <sup>[a]</sup>	0.03201	0.04387
$R_{bragg}$	0.0576866581	0.0422025638
Goodness of fit	3.438	2.227

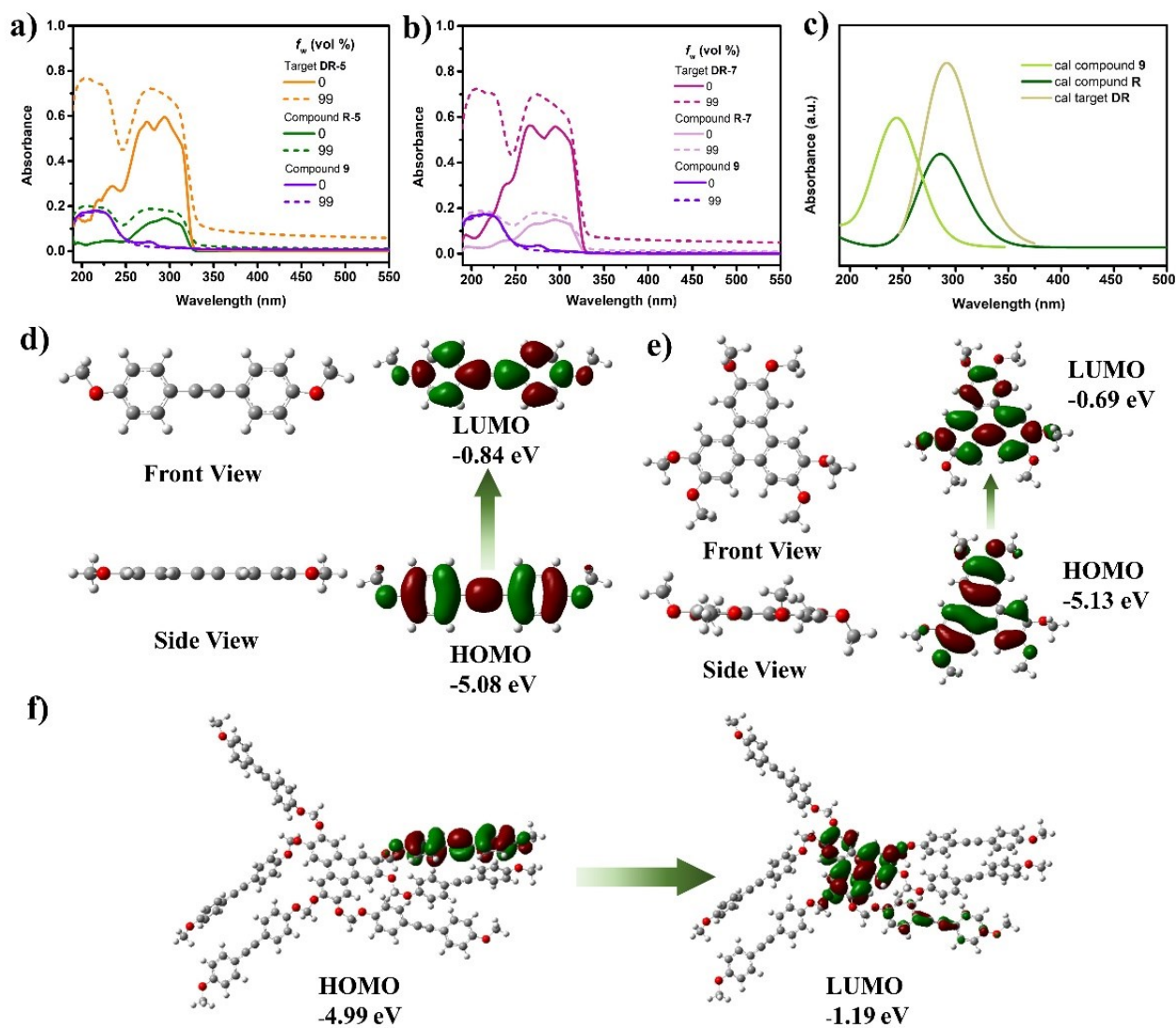
$$R_p = \sum_i |y_{i,o} - y_{i,c}| / \sum_i |y_{i,o}| \quad ; \quad R_{wp} = \left[ \frac{\sum_i w_i (y_{i,o} - y_{i,c})^2}{\sum_i w_i (y_{i,o})^2} \right]^{1/2} \quad ; \quad R_{exp} = R_{wp} / \chi^2 ;$$

$\chi^2 = \sum_i w_i (y_{i,o} - y_{i,c})^2 / (N_{obs} - N_{var})$  ;  $y_{i,o}$  and  $y_{i,c}$  are the observed and calculated intensities at point  $i$  of the profile, respectively,  $N_{obs}$  is the number of theoretical Bragg peaks in the  $2\theta$  range,  $N_{var}$  is number of the refined parameters. Statistical weights  $w_i$  are normally taken as  $1/y_{i,o}$ .



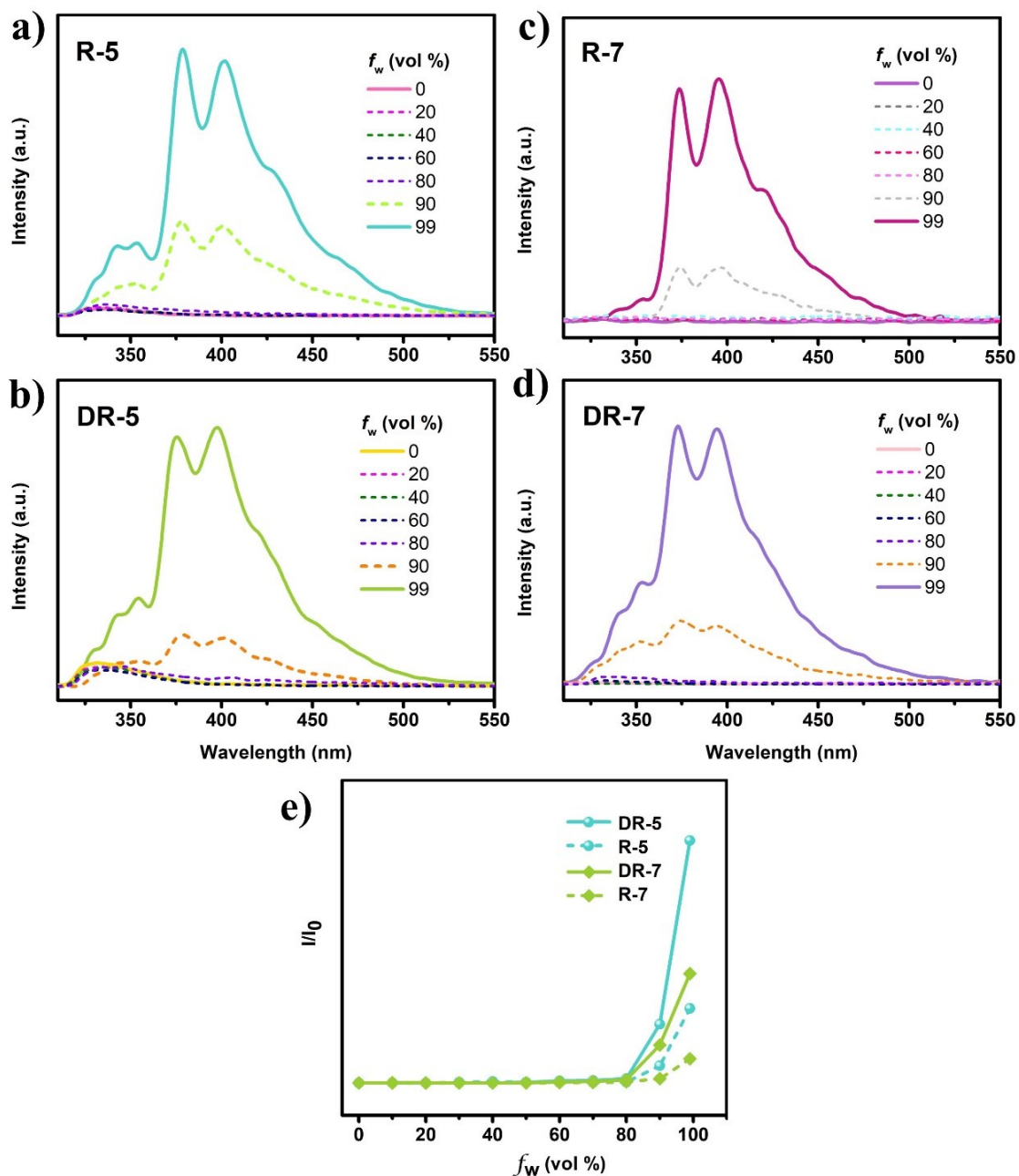
**Fig. S5.** The illustration of the crystal structures. The sizes of the cell are proportionally drawn. For **DR-5**,  $a = 51.8 \text{ \AA}$ ,  $b = 4.8 \text{ \AA}$ ,  $c = 17.3 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 94^\circ$ ; for **DR-7**,  $a = 55.6 \text{ \AA}$ ,  $b = 4.8 \text{ \AA}$ ,  $c = 17.0 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 94^\circ$ .

## 5. Computational simulation



**Fig. S6.** a) and b) The UV-Vis absorption spectra of **DRs**, compounds **R**s and **9** in the mixture with  $f_w$  of 0% and 99%, respectively. Concentration:  $5 \mu\text{M}$ . c) Absorption spectra of **DR**, **R** and **9** calculated by TD-DFT at D 01 at B3LYP/6-31G level.; d) Main molecular orbitals of **R** and **9** involved in the electron transitions of the corresponding absorption peaks in a). f) Main molecular orbitals of **DRs** involved in the electron transitions.

## 6. Photophysical properties



**Fig. S7.** Emission spectra of a) R-5, b) R-7, c) DR-5 and d) DR-7 in THF/water mixtures with different water fractions ( $f_w$ ). Concentration: 5  $\mu\text{M}$ . e) The plots of the relative emission intensities versus  $f_w$  in THF/water mixtures. Concentration: 5  $\mu\text{M}$ . Excitation wavelength: 290 nm.

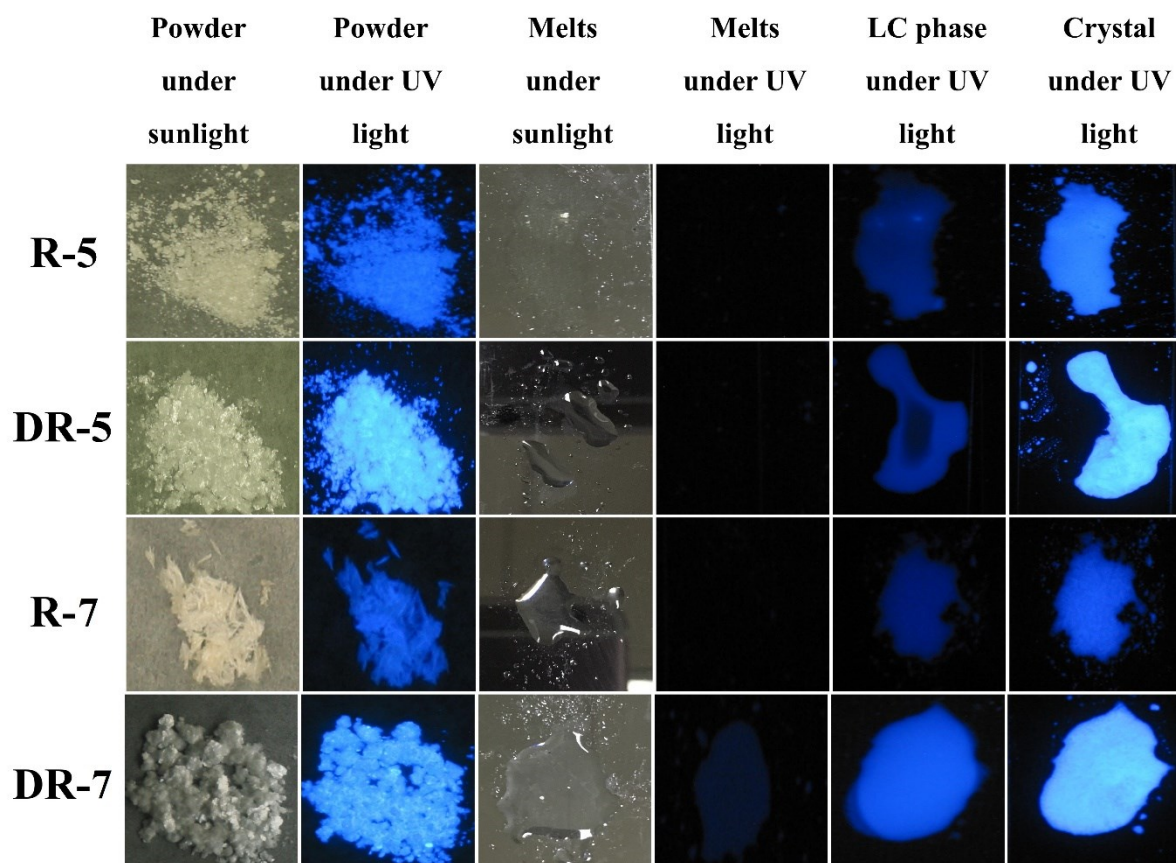


Fig. S8. The photographs of samples in different states and illumination conditions.

Table S2. Phase behaviors of DRs and Rs.

Compounds	Phase transition <sup>[a]</sup>
DR-5	Iso→SmB→SmE→Cr
DR-7	Iso→SmB→Cr
R-5	Iso→less ordered smectic phase→Cr
R-7	Iso→less ordered smectic phase→Cr

[a] Iso = isotropic liquid, SmB = smectic B phase, SmE = smectic E phase, Cr = crystal phase.

