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Properties and structural coloured film preparation of some chiral dopants derived from D-Isosorbide

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ABSTRACT

A series of chiral dopants derived from D-isosorbide were synthesized. Some of them exhibita monotropicsmecticA phase. Comparison of the melting points of these chiral dopants, the decrease of them is mainly driven by the large entropy change. The helical twisting power (HTP) values of these chiral dopants with branched alkyl chains, lateral fluoro-substituents and double bonds are lower than those of the chiral dopants with hexyloxy chains. Structural colored polymer films with a right-handed helix are prepared using these chiral dopants.

KEYWORDS

Chiral dopant; fluorinated; isosorbide; liquid crystal

Introduction

Due to their helical structure, cholesteric liquid crystals (CLCs) exhibit unusual physical properties, such as the selective reflection of circularly polarized light based on the Bragg's law [1,2]. Up to now, they have been applied in low energy consumption displays and tunable optical or laser devices [3–7]. For the preparation of CLCs, chiral dopants (CDs) are usually added into achiral nematic liquid crystal (NLC) hosts. The helical pitches of CLCs can be adjusted by changing the concentrations the helical twisting powers (HTPs) of the CDs [8]. The HTP value is the ability of a CD to produce a helical structure in a given NLC host, which is calculated as HTP = $(Pc_w)^{-1}$, where *P* is the pitch of the chiral nematic phase, and c_w is the weight percentage concentration of the CD. The HTP values of some CDs are tunable underlight and electric field [9,10].

Excessive CDs will affect the clearing point and the viscosity of the LC mixture. Moreover, due to the limited solubility of CDs in the LC host, undesirable precipitation may occur [11–13]. Therefore, to avoid interfering with the original properties of LC matrix materials, CDs shall possess both high HTP value and high solubility. To date, many CDs with high HTP and high solubility have been developed, and the relationship between the molecular structure and the HTP value of CDs has been studied [14–17]. D-Isosorbide (1,4:3,6-dianhy-dro-D-sorbitol) is a good candidate for the synthesis of CDs due to its chirality and inherent

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rigidity. In general, isosorbide-based CDs can generate large HTPs, but their poor solubility in the LC hosts limits their applications [18–20]. In this paper, isosorbide-based dopants with carbon-carbon double bond, branched alkyl chain and fluorine atom are synthesized according to the literature [21]. The HTP values and phase transition behavior of the CDs were studied. These dopants can be used for the preparation of structural colored polymeric films.

Results and discussion

Nine isosorbide-based CDs, CD-6, CD-6-2F, CD-6-3F, CD-6D, CD-6D-2F, CD-6D-3F, CD-6E, CD-6E-2F and CD-6E-3F, were synthesized according to the literature (Scheme 1) [21]. Taking into account the economic and environmental issues, the method of esterification using acyl chloride in the literature was replaced with the *p*-toluenesulfonic acid catalysis or DCC/DMAP methods. The compounds, CD-6, CD-6-2F, CD-6-3F, CD-6D and CD-6D-2F, were obtained by recrystallization using a acetone/methanol mixture, while the others were firstly purified by chromatography using petroleum ether/ethyl acetate/dichloromethane at the volume ratio of 6/0.8/3 and then recrystallization from a acetone/methanol mixture.

The phase transition temperatures and the corresponding enthalpies of the compounds are summarized in Table 1. Differential scanning calorimetry (DSC) was used to determine the phase transition temperatures, and polarizing optical microscope (POM) was used to determine the liquid crystalline phases. Compounds, CD-6, CD-6-2F, CD-6D, CD-6D-2F and CD-6D-3F, exhibit a monotropic SmA phase (Fig. 1). The small angle X-ray scattering (SAXS) patterns of CD-6D-2F were taken at different temperatures during the cooling process (Fig. 2). A broad peak is found at about 0.46 nm at 100 °C, indicating a fluid smectic phase without in-plane order. The peak at 1.85 nm should originate from the layer spacing of the SmA phase, which is about half of the molecular length, indicating that the SmA phase has an intercalation structure [22,23]. Two crystalline states are identified at 75 and 60 °C. The *q* values at 12–15 nm⁻¹ indicate that the lateral molecular packing structures of these two crystals are different.

The phase transition behavior of CD-6 has been reported previously [21]. Herein, a narrow SmA phase (0.5 K) was identified using POM (Fig. 1a). Due to the steric effect of the carbon-carbon double bond, the temperature range of the SmA phase of CD-6D is increased to 1.3 K [24] (Fig. 1d). CD-6D-2F shows the widest SmA phase (34.9 K) (Fig. 1e). However, the olefination decreases the melting points of the compounds (Table 1) [25]. The compounds with branched ethyl chains are not liquid crystals and the melting points of them are lower than the corresponding compounds with straight alkyl chains. Since the enthalpies of them at the melting points are ultra-high, the low melting points should be caused by the large entropy changes.

To understand the effect of lateral fluoro-substitution, both enthalpy and entropy change at the melting point were taken into account. Since enthalpies of CD-6, CD-6-2F, CD-6D and CD-6D-2F are 35.76, 47.45, 39.81 and 40.69 KJ mol⁻¹, respectively, the intermolecular attractions are enhanced with the lateral fluoro-substitution. It was found that the melting points of CD-6-2F and CD-6D-2F were lower than those of CD-6 and CD-6D, respectively. The entropy changes ($\Delta S/R$) of CD-6 and CD-6-2F at the melting points are 10.35 and 14.40, respectively. Moreover, the entropy changes ($\Delta S/R$) of CD-6



Scheme 1. Synthetic routes for the CDs and the molecular structures of C_6M , RM105 and IRG651.

6D and CD-6D-2F at the melting points are 11.56 and 12.54, respectively. Therefore, the decrease of the melting points should be driven by the larger entropy changes [26]. It was also found that the phase transition temperature ranges of CD-6-2F and CD-6D-2F were wider than those of CD-6 and CD-6D, respectively. The lateral fluoro-substitution decreased the recrystallization temperature.

The HTP values of the CDs were studied in the commercially available NLC host (E7) using the Grandjean-Cano method [27]. A certain amount of a CD was added into

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Compound	Transition temperature (°C)/ [ΔH] (KJ mol $^{-1}$)	HTP (μm^{-1})
CD-6	Cr ₁ 102.4 [-5.52]Cr ₂ 111.9 [-1.76] Cr ₃ 142.3 [-35.76] 138.5 [#] SmA 138.0 Cr ₃ 107.3 Cr ₂ 96.3 Cr ₁	70.1
CD-6-2F	Cr ₁ 106.1 [-8.63] 109.6 [7.74] Cr ₂ 123.1 [-47.45] 120.4 SmA 104.8 Cr ₂ 104.2 Cr ₁	59.2
CD-6-3F	Cr ₁ 87.7 [-16.11] Cr ₂ 94.7 [-29.97] I 84.3 Cr ₂ 78.2 Cr ₁	59.5
CD-6D	Cr ₁ 115.9 [-6.70]Cr ₂ 141.2 [-39.81] 131.7 SmA 130.4 Cr ₂ 113.5 Cr ₁	64.2
CD-6D-2F	Cr ₁ 73.56 [-5.78] Cr ₂ 117.0 [-40.69] I 110.6 SmA 75.7 Cr ₂ 69.9 Cr ₁	56.5
CD-6D-3F	Cr ₁ 93.1 [-18.56] Cr ₂ 98.8 [-4.55] I 82.0 SmA 81.0 Recr	56.5
CD-6E	Cr ₁ 53.3 [9.10] Cr ₂ 93.9 [-114.12] 40.9Recr	54.7
CD-6E-2F	Cr 82.1 [-142.80] 41.5 Recr	49.4
CD-6E-3F	Cr 88.2 ⁺ [-137.84] I	50.0

Table 1. Transition temperatures, the corresponding enthalpiesand HTP values of the compounds.

Cr = crystal; SmA = smectic A; I = isotropic liquid and the corresponding enthalpies, ΔH in kJ mol⁻¹ detected on the second temperature run at a rate of 1.0 °C min⁻¹; [#]: the data are obtained from POM characterization; [†]the data are obtained from the first temperature run at a rate of 1.0 °C min⁻¹.



Figure 1. POM images of six compoundstaken during the cooling process. (a) CD-6, the fan-shaped SmA texture taken at 139.6 °C; (b) CD-6-2F, the fan-shaped SmA texture taken at 119.2 °C; (c) CD-6-3F, the crystalline texture taken at 86.5 °C;(d) CD-6D, the fan-shaped SmA texture taken at 131.0 °C;(e) CD-6D-2F, the fan-shaped SmA texture taken at 105.5 °C;(f) CD-6D-3F, the fan-shaped SmA texture taken at 83.4 °C.

E7 and then heated to the isotropic state. After cooling down to 25 °C, the mixtures were injected into a wedge-shaped cell. Thirty minutes later, the distance (R) of the neighboring Cano lines was measured using POM at 25 °C (Fig. 3). The helical pitch can be obtained from the equation of $P = 2 \text{ R} \tan \theta$. $\theta(\theta = 2.219)$ is the wedge angle of the cell. The calculated HTP ($(Pc_w)^{-1}$) values are in the range of 49.4–70.1 μ m⁻¹ (Table 1). CD-6 has the highest HTP value. The HTP values of the CDs decreased by the substitution of ethyl group and olefination. The mismatch between the branched alkyl chain (or the alkenyl chain) and straight alkyl chain of E7 was proposed to decrease the



Figure 2. SAXS patterns of CD-6D-2F taken at different temperatures during the cooling process.



Figure 3. POM images of the mixtures of a CD and E7 in a wedge-shaped cell: CD-6, 0.54 wt%; CD-6-2F, 0.50 wt%; CD-6-3F, 0.54 wt%; CD-6D, 0.53 wt%; CD-6D-2F, 0.60 wt%; CD-6D-3F, 0.56 wt%; CD-6E, 0.51 wt%; CD-6E-2F, 0.51 wt%; CD-8-3F, 0.53 wt%.

HTP values. The fluoro-substitution can affect the conformations of the CDs and then affect the HTP values [28]. However, the position of the fluoro-substituent has almost no effect on the HTP value. For example, the HTP values of CD-6-2F and CD-6-3F are 59.2 and 59.5 μ m⁻¹, respectively.

LC polymer films were prepared using a CD, C6M, RM105 and IRG651 at the weight ratio of 4.3%, 75.8%, 19.0% and 0.9%, respectively, under a 365 nm-UV light [29,30]. The diffuse reflection UV-Vis (DRUV-Vis) and diffuse reflection circular dichroism (DRCD) spectra are shown in Fig. 4. The wavelengths of the DRUV-vis bands are consistent with those of the DRCD signals, indicating that the reflection bands originate from the Bragg reflections of the polymer films. Since the DRCD signals are all positive, the polymer films have a right-handed helix structure (Fig. 4b) [31]. Due to the difference of the HTP values, the wavelengths of the reflection bands are not same. The DRCD signals of the polymer films prepared using CD-6, CD-6D and CD-6E appear at 433, 453 and 531 nm, respectively, indicating that the HTP value of CD-6 is the largest. Although the difference of the LC host will lead to the change of the HTP value, the CDs



Figure 4. (a) DRUV-vis and (b) DRCD spectra of the films prepared using different CDs.

with different terminal carbon chains maintain the same changing trend in the acrylate liquid crystal mixtures. For the polymer films prepared using fluorinated CDs, the reflection wavelengths show red-shifts. Therefore, the fluoro-substitution also causes the decrease of the HTP value. It was found that the position of the fluoro-substituent also affected the HTP value. For CD-6 and CD-6D, the HTP values of the derivatives with a fluoro-substituent at 2-positionwere higher than those of the derivatives with a fluoro-substituent at 3-position. However, the HTP value of CD-6E-2F is lower than that of CD-6E-3F.

Conclusion

A series of CDs based on isosorbide for liquid crystals were synthesized. Some of them exhibit a monotropic SmA phase. The HTP values are tunable by changing the structures of the terminal chains and fluoro-substitution. Comparison of the melting points of them, the decrease of them is mainly driven by the large entropy change. Structural colored polymer films were prepared using these CDs, which were potentially applied as polarizers and sensors.

Experimental

Characterization

FT-IR spectra were performed on a Nicolet 6700 spectrometer at 2 cm^{-1} resolution by averaging over 32 scans. The ¹H NMR spectra were taken on a Varian NMR (400 MHz)

spectrometer in DMSO- d_6 solutions using tetramethylsilane (TMS) as an internal standard at room temperature. Elemental analysis was measured on an EA-1106 instrument. Mass spectra (MS) were measured with Ultraflextreme MALDI TOF/TOF spectroscope. The specific rotation measurement was performed using Autopol IV polarimeter. DSC measurements were conducted on a TA-Q200 under nitrogen at $1.0 \,^{\circ}\text{C} \, \text{min}^{-1}$. The POM images of the target compounds were taken using a CPV-900C polarization microscope fitted with a Linkam LTS420 hot stage. The transition temperatures reported in this paper were the peak values of the transition on DSC traces. Few of them were the values obtained using POM. SAXS patterns were taken using an X-ray scattering instrument (SAXSess mc2, Anton Paar) equipped with line collimation and a 2200 W sealed-tube X-ray generator (Cu-K α , $\lambda = 0.154$ nm). Diffuse reflectance circular dichroism (DRCD) spectra were measured using a JASCO 815 spectrometer (Tokyo, Japan). UV-Vis diffuse reflection spectra were measured by UV-VIS-NIR spectrophotometer (UV3600).

Synthesis

Isosorbide was purchased from AccelaChemBio Co., Ltd. 4-Toluenesulfonic acid monohydrate (TsOH·H₂O), bromohexane, 6-bromo-1-hexene and 1-bromo-iso-octanewas purchased from AladdinCo., Ltd.4-Hydroxybenzoic acid, 2-fluoro-4-hydroxybenzoic acid and 3-fluoro-4-hydroxybenzoic acid was purchased from MeryerCo., Ltd. *N,N*-Dicyclohexylcarbodiimide (DCC) was purchased from Suzhou Highfine Biotech Co., Ltd. 4-Dimethylaminopyridine (DMAP) was obtained from J&K Scientific Ltd. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in an atmosphere of nitrogen. All other chemicals including ethanol (EtOH), dichloromethane (DCM), petroleum ether (PE) and ethyl acetate (EA) were purchased from Sinopharm Group Chemical Reagent Co., Ltd and used as received without further purification. The wedge-shaped cell comes from Zhiya Display Technology (Shenzhen) Co., Ltd. IRG651, C6M and RM105 were given by Suzhou SoochiralChem. &Tech. Co., Ltd. 4-*n*-Hexyloxybenzoic acid, 4-(2-ethyl) hexyloxybenzoic acid and 4-(5-hexenyloxy) benzoic acid were synthesized according to the literature [32]. Compound 1 was synthesized according to the literature [33].

D-Isosorbide2,5-bis(2-fluoro-4-hydroxybenzoate) (2)

2-Fluoro-4-hydroxybenzoic acid (18.1 g, 115.9 mmol), isosorbide (8 g, 54.8 mmol) and TsOH·H₂O (0.44 g, 2.3 mmol) were added into a 500 mL three-necked flask. Xylene was used as solvent and stirred at 175 °C for 7 h. The water generated in the reaction was removed through a water separator. TsOH·H₂O (0.22 g, 1.1 mmol) was added, and the reaction continued for 3 h, followed by cooling. The black solid was dissolved in ethyl acetate and extracted $2 \sim 3$ times in saturated sodium bicarbonate solution. Activated carbon adsorbs impurities and recrystallizes in methanol to purify crude products. A light yellow solid was obtained in 67.1% (15.5 g). FT-IR (cm⁻¹): 3556, 3159 (ν_{O-H}), 1724 ($\nu_{C=O}$), 1619, 1592, 1508 and 1458 (ν_{Ph}).¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 3.80–4.03 (m, 4H; -OC*HCH₂O-), 4.56 (d, J=4.8 Hz, 1H; -C*HC*H-), 4.91 (t, J=5.2 Hz, 1H; -C*HC*H-), 5.23–5.37 (m, 2H; -COOC*HCH₂O-), 6.48–6.85 (m,

4H; 3,5-Ph*H*-), 7.70–7.85 (m, 8.8, 2H; 6-Ph*H*-), 10.88 (s, 2H; $-C_6H_4OH$). MS m/z (rel. int.): 445 (\overline{M}^+ +Na, 100). Elemental analysis (%): calcd for $C_{20}H_{16}F_2O_8$ (422.08): C: 56.88; H: 3.82. Found: C: 57.09; H: 3.95.

D-Isosorbide2,5-bis(3-fluoro-4-hydroxybenzoate) (3)

The yield is 63.6%. FT-IR (cm⁻¹): 3204 ($\nu_{\text{O-H}}$), 2886 ($\nu_{\text{C-H}}$), 1724 ($\nu_{\text{C=O}}$), 1622, 1599, 1528 and 1440 (ν_{Ph}). ¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 3.88–4.03 (m, 4H; -OC*HCH₂O-), 4.59 (d, J=4.8 Hz; -C*HC*H-), 4.96 (t, J=5.2 Hz, 1H; -C*HC*H-), 5.25–5.37 (m, 2H; -COOC*HCH₂O-), 7.07 (q, J=8.0 Hz, 2H; 5-PhH-), 7.67 (dd, J=11.6, 6.8 Hz, 4H; 2,6-PhH-), 10.95 (s, 2H; -C₆H₄OH). MS m/z (rel. int.): 445 (M⁺+Na, 100). Elemental analysis (%): calcd for C₂₀H₁₆F₂O₈ (422.08): C: 56.88; H: 3.82. Found: C: 56.49; H: 3.73.

D-Isosorbide2,5-bis(2-fluoro-4-(4-(hexyloxy)benzoyloxy)benzoate) (CD-6-2F)

Compound 2 (5.0 g, 11.8 mmol), 4-hexyloxybenzoic acid (6.0 g, 27.2 mmol), DCC (3.5 g, 16.8 mmol), DMAP (0.3 g, 2.6 mmol) were added into a 100 mL eggplant-shaped flask under nitrogen, and 70 mL THF was used as solvent for two days. After filtration, the product was purified by recrystallization in an acetone/methanol mixture. A white solid was obtained in 64.3% (6.3 g). Mp: 133.6 °C. $[\alpha]_D^{20} = -71.2^\circ$ (c = 1.0, CHCl₃). FT-IR (cm⁻¹): 2931, 2869 (ν_{C-H} , alkyl chain), 1725 ($\nu_{C=O}$), 1604, 1509 and 1468 (ν_{Ph}). ¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 0.80–0.95 (m, 6H; CH₃-), 1.22–1.51 (m, 12H; CH₃CH₂CH₂CH₂CH₂-), 1.66–1.82 (m, 4H; CH₃CH₂CH₂CH₂CH₂-), 3.91–4.15 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.65 (d, J = 4.0 Hz, 1H; -C*HC*H-), 4.94–5.03 (m, 1H; -C*HC*H-), 5.31–5.45 (m, 2H; -COOC*HCH₂O-), 7.13 (d, $\overline{J} = 8.0$ Hz, 4H; 3,5-PhHOCH₂CH₂CH₂-), 7.33 (t, J = 6.4 Hz, 2H; 5-PhHFCOOC*H-), 7.43–7.54 (m, 2H; 3-PhHFCOOC*H-), 7.94–8.13 (m, 6H; 2,6- PhHOCH₂CH₂-, 6-PhHFCOOC*H-). MS m/z (rel. int.): 853 (M⁺+Na, 100). Elemental analysis (%): calcd for C₄₆H₄₈F₂O₁₂ (830.31): C: 66.50; H: 5.82. Found: C: 66.50; H: 5.76.

D-Isosorbide2,5-bis(3-fluoro-4-(4-(hexyloxy)benzoyloxy)benzoate) (CD-6-3F)

The yield is 57.1%. Mp: 97.8 °C. $[\alpha]_D^{20} = -68.6^{\circ}$ (c = 1.0, CHCl₃). FT-IR (cm⁻¹): 2928, 2867 (ν_{C-H} , alkyl chain), 1719 ($\nu_{C=O}$), 1603, 1510 and 1469 (ν_{Ph}). ¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 0.79–0.97 (m, 6H; CH₃-), 1.21–1.53 (m, 12H; CH₃CH₂CH₂CH₂-), 1.69–1.82 (m, 4H; CH₃CH₂CH₂CH₂CH₂-), 3.91–4.18 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.68 (d, J = 4.8 Hz, 1H; -C*HC*H-), 5.04 (t, J = 5.2 Hz, 1H; -C*HC*H-), 5.35–5.45 (m, 2H; -COOC*HCH₂O-), 7.10–7.19 (m, 4H; 3,5-PhHOCH₂CH₂-), 7.66 (q, J = 7.6 Hz, 2H; 5-PhHFCOOC*H-), 7.85–8.00 (m, 4H; 2,6-PhHFCOOC*H-), 8.10 (dd, J = 8.4, 2.0 Hz, 4H; 2,6-PhHOCH₂CH₂-). MS m/z (rel. int.): 853 (M⁺+Na, 100). Elemental analysis (%): calcd for C₄₆H₄₈F₂O₁₂ (830.31): C: 66.50; H: 5.82. Found: C: 66.13; H: 5.78.

D-Isosorbide2,5-bis(4-(4-(5-hexenyloxy)benzoyloxy)benzoate) (CD-6D)

The yield is 68.9%. Mp: 144.8 °C. $[\alpha]_D^{20} = -86.0^{\circ} (c = 1.0, \text{CHCl}_3)$. FT-IR (cm⁻¹): 2938, 2872 ($\nu_{\text{C-H}}$, alkyl chain), 1720 ($\nu_{\text{C=O}}$), 1641 ($\nu_{\text{C=C}}$), 1603, 1510 and 1469 (ν_{Ph}).¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 1.41–1.55 (m, 4H; CH₂=CHCH₂CH₂-), 1.66–1.77 (m, 4H; -OCH₂CH₂-), 1.98–2.13 (m, 4H; CH₂=CHCH₂-), 3.84–4.16 (m, 8.4, 8H; -CH₂OC₆H₄CO-, -OC^{*}HCH₂O-), 4.61 (d, J=4.4 Hz, IH; -C^{*}HC^{*}H-), 4.87–5.05 (m, 5H; -C^{*}HC^{*}H-, CH₂=CH-), 5.29–5.42 (m, 2H; -COOC^{*}HCH₂O-), 5.70–5.85 (m, 2H; CH₂=CH-), 7.08 (d, J=8.0 Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.42 (t, J=7.2 Hz, 4H; 3,5-PhHCOOC^{*}H-), 7.94–8.14 (m, 8H; 2,6-PhH-). MS m/z (rel. int.): 813 (M⁺+Na, 100). Elemental analysis (%): calcd for C₄₆H₄₆O₁₂ (790.30): C: 69.86; H: 5.86. Found: C: 70.03; H: 6.16.

D-Isosorbide2,5-bis(2-fluoro-4-(4-(5-hexenyloxy)benzoyloxy)benzoate) (CD-6D-2F)

The yield is 72.7%. Mp: $123.5 \,^{\circ}$ C. $[\alpha]_{D}^{20} = -74.6^{\circ}$ (c = 1.0, CHCl₃). FT-IR (cm⁻¹): 2941, 2866 (ν_{C-H} , alkyl chain), 1724 ($\nu_{C=O}$), 1641($\nu_{C=C}$), 1604, 1510 and 1470 (ν_{Ph}).¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 1.41–1.56 (m, 4H; CH₂=CHCH₂CH₂-), 1.64–1.78 (m, 4H; -OCH₂CH₂-), 2.06 (q, J = 6.8 Hz, 4H; CH₂=CHCH₂-), 3.85–4.14 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.60 (d, J = 4.8 Hz, 1H; -C* $H\overline{C}^*$ H-), 4.87–5.10 (m, 5H; -C*HC*H-, CH₂=CH-), 5.28–5.43 (m, 2H; -COOC* $H\overline{CH}_2$ O-), 5.71–5.86 (m, 2H; CH₂= \overline{CH} -), 7.09 (d, J = 7.2 Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.23–7.33 (m, 2H; 5-PhHFCOOC*H-), 7.39–7.50 (m, 2H; 3-PhHFCOOC*H-), 7.89–8.12 (m, 6H; 2,6-PhHOCH₂CH₂-, 6-PhHFCOOC*H-). MS m/z (rel. int.): 849 (M⁺+Na, 100). Elemental analysis (%): calcd for C₄₆H₄₄F₂O₁₂ (826.28): C: 66.82; H: 5.36. Found: C: 67.27; H: 5.92.

D-Isosorbide2,5-bis(3-fluoro-4-(4-(5-hexenyloxy)benzoyloxy)benzoate) (CD-6D-3F)

The product was purified by chromatography and further purified by recrystallization in an acetone/methanol mixture. The product was eluted by PE: EA: DCM = 6: 0.8: 3. A white solid was obtained in 84.4% (6.5 g). Mp: 102.3 °C. $[\alpha]_D^{20} = -70.0^\circ$ (c=1.0, CHCl₃). FT-IR (cm⁻¹): 2933, 2871 (ν_{C-H} , alkyl chain), 1719 ($\nu_{C=O}$), 1641 ($\nu_{C=C}$), 1605, 1511 and 1471(ν_{Ph}).¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 1.44–1.61 (m, 4H; CH₂=CHCH₂CH₂-), 1.66–1.86 (m, 4H; -OCH₂CH₂-), 2.11 (q, J=6.8 Hz, 4H; CH₂=CHCH₂-), 3.92–4.19 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.68 (d, J=4.4 Hz, 1H; -C*HC*H-), 4.90–5.15 (m, 5H; -C*HC*H-, CH₂=CH-), 5.32–5.50 (m, 2H; -COOC*HCH₂O-), 5.76–5.91 (m, 2H; CH₂=CH-), 7.15 (d, J=7.2 Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.66 (dd, J=15.2, 8.0 Hz, 2H; 5-PhHFCOOC*H-), 7.84–8.01 (m, 4H; 2,6-PhHFCOOC*H-), 8.10 (d, J=6.8 Hz, 4H; 2,6-PhHOCH₂CH₂-). MS m/z (rel. int.): 849 (M⁺+Na, 100). Elemental analysis (%): calcd for C₄₆H₄₄F₂O₁₂ (826.28): C: 66.82; H: 5.36. Found: C: 66.89; H: 5.80.

D-Isosorbide2,5-bis(-4-(4-(2-ethylhexyloxy)benzoyloxy)benzoate) (CD-6E)

The yield is 62.8%. Mp: 101.9 °C. $[\alpha]_D^{20} = -74.2^{\circ}$ (c = 1.0, CHCl₃). FT-IR (cm⁻¹): 2928, 2873 (ν_{C-H} , alkyl chain), 1717 ($\nu_{C=O}$), 1601, 1508 and 1462 (ν_{Ph}). ¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 0.76–1.03 (m, 12H; CH₃CH₂-), 1.17–1.57

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(m, 16H; $CH_3CH_2CH_2CH_2CH_2$, $-CH_2CH_3$), 1.63–1.82 (m, 2H; $-CH_2CH_2CH_2$), 3.90–4.12 (m, 8H; $-CH_2OC_6H_4CO$ -, $-OC^*HCH_2O$ -), 4.67 (d, J = 4.0 Hz, 1H; $-C^*HC^*H$ -), 5.02 (t, J = 5.2 Hz, 1H; $-C^*HC^*H$ -), 5.32–5.46 (m, 2H; $-COOC^*HCH_2O$ -), 7.14 (d, J = 7.2 Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.44 (dd, J = 7.6, 6.8 Hz, 4H; 3,5-PhHCOOC*H-), 7.97–8.18 (m, 8H; 2,6-PhH-). MS m/z (rel. int.): 873 (M⁺+Na, 100). Elemental analysis (%): calcd for $C_{50}H_{58}O_{12}$ (850.39): C: 70.57; H: 6.87. Found: C: 70.64; H: 6.90.

D-Isosorbide2,5-bis(2-fluoro-4-(4-(2-ethylhexyloxy)benzoyloxy)benzoate) (**CD-6E-2F**) The yield is 55.8%. Mp: 86.4 °C. $[\alpha]_D^{20} = -62.6^\circ$ (c = 1.0, CHCl₃). FT-IR (cm⁻¹): 2929, 2873 (ν_{C-H} , alkyl chain), 1728 ($\nu_{C=O}$), 1604, 1510 and 1463 (ν_{Ph}). ¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 0.78–0.98 (m, 12H; CH₃CH₂-), 1.17–1.56 (m, 16H; CH₃CH₂CH₂CH₂CH₂CH-, -CH₂CH₃), 1.63–1.80 (m, 2H; -CH₂CH₂CH-), 3.88–4.13 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.65 (d, J = 4.0 Hz, 1H; -C*HC*H-), 5.00 (t, J = 4.4 Hz, 1H; -C*HC*H-), 5.32–5.48 (m, 2H; -COOC*HCH₂O-), 7.14 (d, J = 8.0 Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.33 (t, J = 7.2 Hz, 2H; 5-PhHFCOOC*H-), 7.48 (dd, J = 11.2,6.8 Hz, 2H; 3-PhHFCOOC*H-), 7.94–8.15 (m, 6H; 2,6-PhHOCH₂CH₂-, 6-PhHFCOOC*H-). MS m/z (rel. int.): 909 (M⁺+Na, 100). Elemental analysis (%): calcd for C₅₀H₅₆F₂O₁₂ (886.37): C: 67.71; H: 6.36. Found: C: 67.56; H: 6.51.

D-Isosorbide2,5-bis(3-fluoro-4-(4-(2-ethylhexyloxy)benzoyloxy)benzoate) (CD-6E-3F) The solution of 2° (see the second se

The yield is 60.5%. Mp: 88.2 °C. $[\alpha]_D^{20} = -69.2^{\circ} (c = 1.0, \text{CHCl}_3)$. FT-IR (cm⁻¹): 2930, 2873 ($\nu_{\text{C-H}}$, alkyl chain), 1718 ($\nu_{\text{C=O}}$), 1604, 1511 and 1462 (ν_{Ph}).¹H NMR (400 MHz, DMSO- d_6 , 25 °C), δ (TMS, ppm): 0.74–1.01 (m, 12H; CH₃CH₂-), 1.17–1.55 (m, 16H; CH₃CH₂CH₂CH₂CH₂-CH, -CH₂CH₃), 1.66–1.79 (m, 2H; -CH₂CH₂CH₂-), 3.90–4.18 (m, 8H; -CH₂OC₆H₄CO-, -OC*HCH₂O-), 4.68 (d, J = 4.4 Hz, 1H; -C*HC*H-), 5.09 (t,J = 4.4 Hz, 1H; -C*HC*H-), 5.29–5.50 (m, 2H; -COOC*HCH₂O-), 7.16 (d, J = 8.4Hz, 4H; 3,5-PhHOCH₂CH₂-), 7.65 (q, J = 7.6 Hz, 2H; 5-PhHFCOOC*H-), 7.82–8.02 (m, 4H; 2,6-PhHFCOOC*H-), 8.10 (d, J = 8.0 Hz, 4H; 2,6-PhHOCH₂CH₂-). MS m/z (rel. int.): 909 (M⁺+Na, 100). Elemental analysis (%): calcd for C₅₀H₅₆F₂O₁₂ (886.37): C: 67.71; H: 6.36. Found: C: 67.52; H: 6.40.

Preparation of polymer films

160 mg of C₆M, 40 mg of RM105, 9 mg of a CD and 2 mg of IRG651 are dissolved in 2 mL of THF. After removing THF on the surface of a glass slide at 120 °C, another glass slide is covered. Then, the liquid crystal mixture is cooled down to 60 °C. The polymer film is obtained by photopolymerization using a 365-nm UV lamp.

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