

Supporting Information

Dependence of the Liquid Crystalline Properties on the Exactly Controlled Single-Site Functionalized Density of Mesogens focused on the Alternating Copolymer Model

Ruixue Zhang, Xuwen Li, Hongwei Ma, Li Han, Chao Li, Songbo Zhang, Hongyuan
Bai and Yang Li*

State Key Laboratory of Fine Chemicals, Department of Polymer Science and
Engineering, Liaoning key Laboratory of Polymer Science and Engineering, School of
Chemical Engineering, Dalian University of Technology, Dalian 116024, China.

Corresponding authors:

***E-mail: hanli@dlut.edu.cn (L. Han)**

1. Experimental Section

(1) Materials and Methods

Materials: The synthesis of 4-(allyloxy) benzoic acid (Vinyl-COOH), *alt*-P(D-S/Ip) and *alt*-P(D-2S/Ip) consulted prior work.^{1,2,3} A brief description for the purification and use of reagents is given below: 6-chlorohexanol, 4,4'-dihydroxydiphenyl and 4-(trifluoromethyl)phenol were purchased from Sinopharm Chemical Reagent and used directly. K₂CO₃, KI, NaOH, NaHCO₃, N,N-dimethylformamide (DMF), sulfone chloride, ethanol, dichloromethane, HCl, tetrahydrofuran (THF), pyridine were purchased from Tianjin Bodi Chemical Co., Ltd., analytical reagent and used without any purification. Pt (0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex (Karstedt catalyst, Pt~2% (mass fraction) solution in xylene, Sigma-Aldrich), toluene purchased from Sinopharm Chemical Reagent and refer to our previous report for specific refined steps.^{2,3} Toluene for hydrosilylation need to add sodium and benzophenone under the protection of high-purity argon, refluxed to blue-purple and distilled under reduced pressure and saved with wax seal. High-purity argon need to remove traces amount of water and oxygen through an activated manganese column.

Methods

FT-IR: Nicolet 6700 Flex spectrometer, using KBr sampling.

¹H-NMR: 400MHz NMR spectrometer from Germany's Advance Bruker Company, used to determine molecular structure.

Gel permeation chromatography (GPC): Malvern Corporation of the United States, Viscotek TDA-305 and Waters 1515 equipped with tetra detectors [Refractive index (RI), UV, viscosity (VISC), and laser light scattering (7° and 90°, wavelength of $\lambda=670$ nm)] and two separation columns (Malvern, T6000 M \times 2), calibrated with polystyrene (PS) standards ($M_w=104.071$ kg/mol, $M_n=100.967$ kg/mol, Viscotek Corp.). The data depending on the precise concentration was analyzed using OmniSEC software version 4.7.0 (Viscotek Corp.). Waters 1515 GPC (USA) equipped with one 2414 RI detectors and two separation columns (Waters, HT4 and HT5 columns), calibrated with PS standards. Mobile phase: THF (1.0 ml/min at 35 °C), used to test the number-average Molecular

Weight (M_n), mass average molar mass (M_w) and polymer dispersity index (PDI, M_w/M_n) of polymer backbones and FLCs.

Liquid chromatograph-mass spectrometer (LC-MS): Agilent Technologies Co. Ltd. of the United States, 1260 Infinity II Prime equipped with diode array detector, single quadrupole mass spectrometry, mass range: 10-3000 μ ; spectral range: 190-950 nm, used to determine molecular structure.

Matrix-assisted laser desorption (MALDI-TOF MS): Waters MALDI micro MX mass spectrometer with linear mode, the 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malonitrile (DCTB) (Aldrich, 99.0%) and sodium trifluoroacetate (Aldrich, 98.0%) used as assisted matrix, used to determine the sequence structure of backbones.

Polarized optical morphologies (POM) [500 μ m, 200 μ m, 50 μ m]: Leica DM4500P, conFigd with Linkam THMS420 program-controlled temperature heating station, for qualitative analysis of liquid crystal molecular texture.

Differential scanning calorimeter (DSC): TA Q2000 and TA Q20 instruments, used under the nitrogen (N_2) environment at a heating and cooling rate of 10 $^{\circ}$ C/min to determine different phase transition temperature.

Wide angle X-ray scattering (WAXS): performed for the samples on a long-slit collimating ANTON PAAR SAXSESS MC² instrument (wavelength $\lambda_{CuK\alpha}=1.54$ \AA) operated at 40 kV, 40 mA in vacuum. The periodicity was calculated from the first order Bragg peak by $2\theta=2\times 57.3\times \arcsin(0.01226q)$; $2d\sin\theta=n\lambda$, $n=1$.

2. Synthesis and characterizations

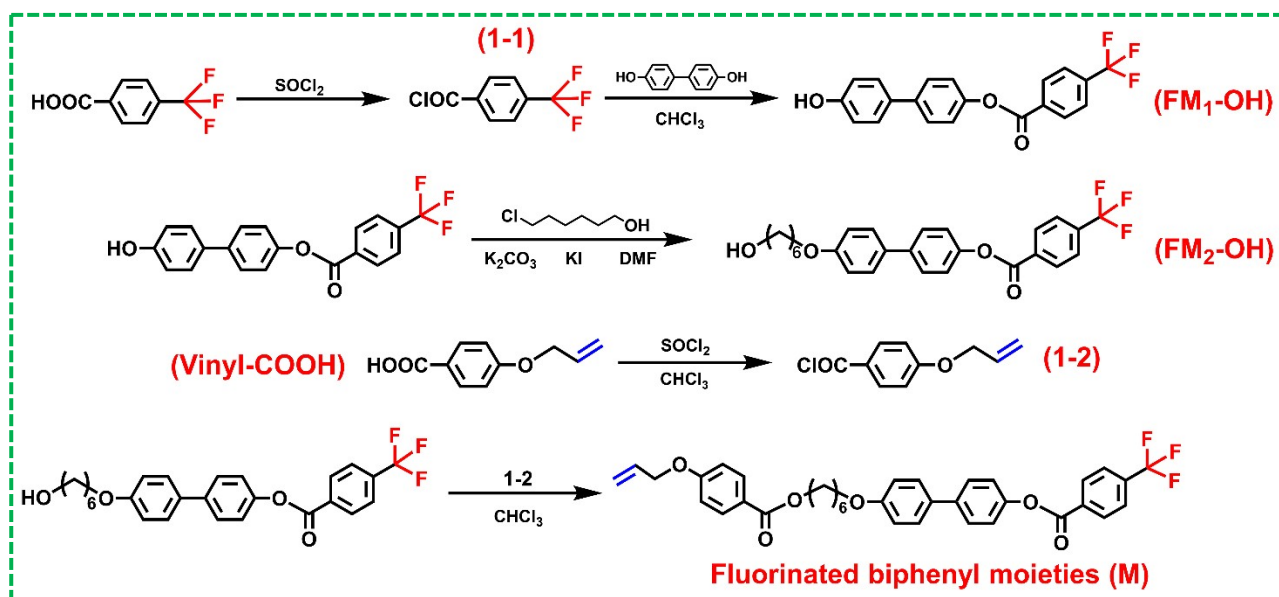


Fig. S1. The synthetic route of fluorinated biphenyl moiety (FM).

2.1 Synthesis of fluorinated biphenyl moieties (M)

Dry 4-(trifluoromethyl) phenol (5 g, 25 mmol) is added into the 250 ml flask connected with exhaust gas collecting plant at R.T. Sulfone chloride (21.45 g, 0.3 mol) and a small amount of DMF are carefully added into flask and reaction for 6 h at 60 °C. The excess sulfoxide chloride is removed and a yellow oily liquid **1-1** is obtained for use. Dry 4,4'-dihydroxydiphenyl (13.9 g, 75 mmol), 80 ml chloroform and 8 ml pyridine are added into a 250 ml flask, 20 ml chloroform is used to dissolve **1-1** and slowly drops into the flask. After reacts for 10 h at 65 °C, the system is concentrated and a large amount of HCl (2 mol/L) is added to acidify overnight. **The crude wash with a large amount of sodium hydroxide aqueous solution (3 mol/L) and deionized water, and recrystallized with ethanol for twice.** The white solid powder of **$\text{FM}_1\text{-OH}$** is obtained after dried under high vacuum, yield: 60%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) $\delta=9.58$ (s, 1H, **-OH**), 8.34 (d, $J=7.9$, 2H, **Ar-H**), 7.99 (d, $J=7.8$, 2H, **Ar-H**), 7.67 (d, $J=7.7$, 2H, **Ar-H**), 7.52 (d, $J=7.7$, 2H, **Ar-H**), 7.35 (d, $J=7.7$, 2H, **Ar-H**), 6.87 (d, $J=7.7$, 2H, **Ar-H**).

Under argon atmosphere, **$\text{FM}_1\text{-OH}$** (5 g, 14 mmol), potassium carbonate (5.78 g, 42 mmol), a trace of potassium iodide (0.1 g, 0.56 mmol) and 80 ml DMF are added into the 250 ml flask. After fully stirring for 1 h at R.T., 6-chlorohexanol (2.28 g, 17 mmol) dissolved in 15 ml DMF is slowly

dropped into the flask and reacts for 10 h at 80 °C. The system is cooled to R.T. and remove the salt by filtration. Ethyl acetate and saturated sodium bicarbonate solution are used for extraction, the organic phase is concentrated and separated by silica gel column chromatography (hexane/ethyl acetate=80:1 (v/v)) to obtain the white solid product **FM₂-OH**, Yield: 56%. ¹H-NMR (400 MHz, DMSO-*d*₆) δ=9.40 (s, 1 H, -OH), 8.15 (d, *J*=7.9 Hz, 2 H, Ar-H), 7.89 (d, *J*=8.0 Hz, 2 H, Ar-H), 7.42 (dd, *J*=24.0, 8.4 Hz, 4 H, Ar-H), 6.94 (d, *J*=8.4 Hz, 2 H, Ar-H), 6.80 (d, *J*=8.3 Hz, 2 H, Ar-H), 4.34 (d, *J*=6.3 Hz, 2 H, -O-CH₂-CH₂-), 3.99 (d, *J*=6.1 Hz, 2 H, -CH₂-OH), 1.75 (s, 4 H, -CH₂-CH₂-CH₂-CH₂-CH₂OH), 1.49 (s, 4 H, -CH₂-CH₂-CH₂-CH₂-CH₂OH).

Vinyl-COOH (3.125 g, 17 mmol) is added into the 250 ml flask connected with a exhaust gas collecting plant at R.T. Then, sulfone chloride (21.45 g, 0.3 mol) is carefully added into flask and reaction for 6 h at 60 °C. The excess sulfoxide chloride is removed by concentrate and a yellow oily liquid **1-2** is obtained for use. Dry 4,4'-dihydroxydiphenyl (13.9 g, 75 mmol), 60 ml chloroform and 6 ml pyridine are added into a 250 ml flask, **1-2** dissolved in 15 ml chloroform is slowly drops into the flask. After reacts for 10 h at 65 °C, the system is concentrated and a large amount of HCl (2 mol/L) is added to acidify overnight. The crude is recrystallized with ethyl acetate and dried under high vacuum to obtain creamy white crystal **fluorinated biphenyl moieties (M)**, yield: 62%. ¹H NMR (400 MHz, CDCl₃) δ=8.14 (s, 4H, Ar-H), 7.69 (s, 2H, Ar-H), 7.56 (d, *J*=5.5 Hz, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 7.23-7.17 (m, 2H, Ar-H), 7.04-6.90 (m, 4H, Ar-H), 6.05 (s, 1H, CH₂=CH-CH₂-O-), 5.38 (dd, *J*=44.5, 13.5 Hz, 2H, CH₂=CH-CH₂-O-), 4.63 (s, 2H, CH₂=CH-CH₂-O-), 4.37 (s, 2H, COOCH₂-CH₂-CH₂-CH₂-CH₂-CH₂-O-), 4.00 (s, 2H, COOCH₂-CH₂-CH₂-CH₂-CH₂-CH₂-O-), 1.83 (s, 4H, COOCH₂-CH₂-CH₂-CH₂-CH₂-O-), 1.55 (s, 4H, COOCH₂-CH₂-CH₂-CH₂-O-).

MALDI-TOF MS is utilized to verify the sequence of backbones and the spectrum of *alt*-P(D-S/Ip) and *alt*-P(D-2S/Ip) is shown in **Scheme 1**. Four series of peaks can be attributed in the partially enlarged Fig to [*Sec*-butyl·D_nI_(n-1)·Na⁺], [*Sec*-butyl·D_nI_n·Na⁺], [*Sec*-butyl·D_nI_(n+1)·Na⁺] and [*Sec*-butyl·D_nI_(n+2)·Na⁺] in **Scheme 1a**. Similarly, two series of peaks can be attributed to [*Sec*-butyl·D_nI_(n-1)·Na⁺], [*Sec*-butyl·D_nI_n·Na⁺] in **Scheme 1b**. The results further indicated that the backbones

composed of DPE-SiH/DPE-2SiH with Ip have alternating-sequenced structure as expected.²

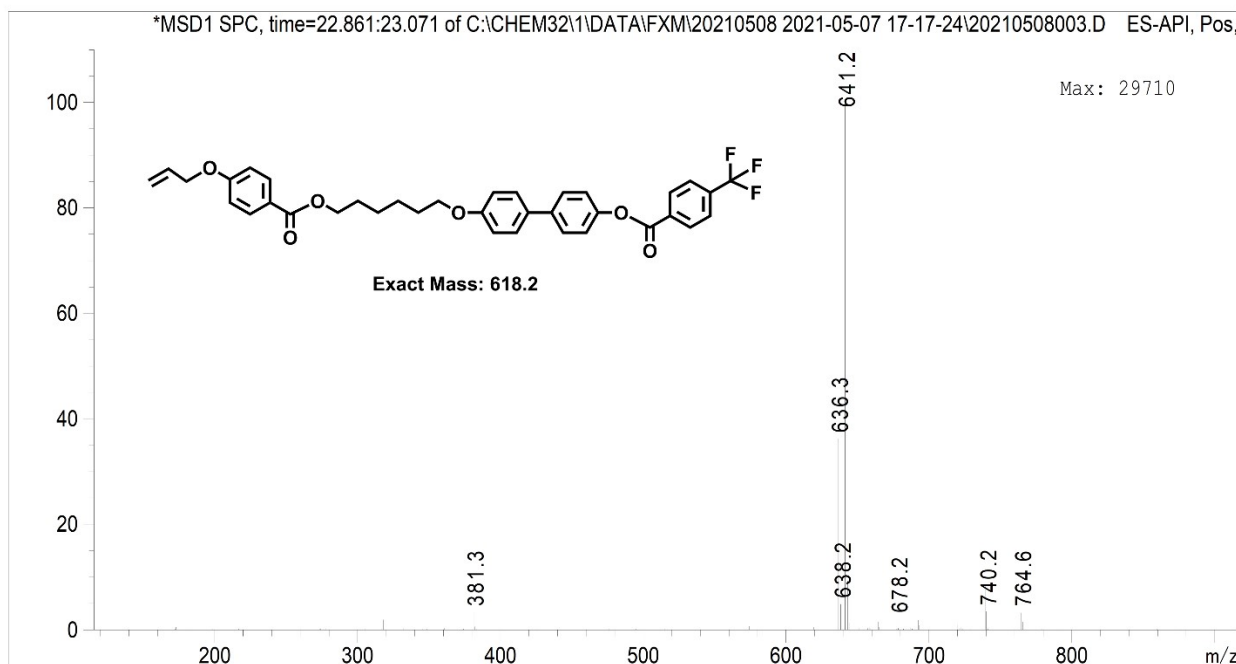


Fig. S2. LC-MS spectrum of fluorinated biphenyl moieties (M).

2.2 Synthesis of fluorinated liquid crystalline polymers (FLCPs)

The synthesis of *alt*-P(D-S/Ip) and *alt*-P(D-2S/Ip) refers to our previous work, the structures and briefly synthetic route are shown in **Fig S3**.^{2,3}

To ensure the alternating sequence-controlled backbones shared the similar overall concentration of Si-H groups, the number of DPE-SiH/DPE-2SiH (N_D) in *alt*-P(D-S/Ip)/*alt*-P(D-2S/Ip) are calculated according to ¹H-NMR as shown in **Fig S4**, and the specific calculation principle have been explained in our previous work.² Herein, the 3 hydrogen atoms on *Sec*-butyl peaks at δ (ppm)=0.66-0.53 ppm (S_a) are set as 6 and the characteristic peaks at δ (ppm)=7.70-6.62 (9 H/8 H) on the DPE units are located at “b” area (S_b). According to the selection of standard peaks, the integral value of (S_b) in *alt*-P(D-S/Ip) and *alt*-P(D-2S/Ip) is 99.00 and 40.66, respectively, and the responding numbers of DPE units is 11 and 5, respectively. The results indicates that the molecular structures of backbones are consistent with design.

The treatment of *alt*-P(D-S/Ip)/*alt*-P(D-2S/Ip) with FM is performed via hydrosilylation under 60 °C, which exhibits high efficiency and convenience for the construction of sequence-defined

FLCPs. The *alt*-P(D-S/Ip)/*alt*-P(D-2S/Ip) (100 mg) and 10 mol% excess of FM were added into the 100 ml ampoules. Toluene (15-20 ml) and Karstedt catalyst (2-3 drops) are sequentially added into the mixtures. The system is stirred for 72 h at 60 °C under argon, after removal of toluene, the *alt*-P(D-S/Ip)-M and *alt*-P(D-2S/Ip)-M are purified by centrifugating with ethanol and a small amount of THF. All the products need to further drying under vacuum for more than 24 h.

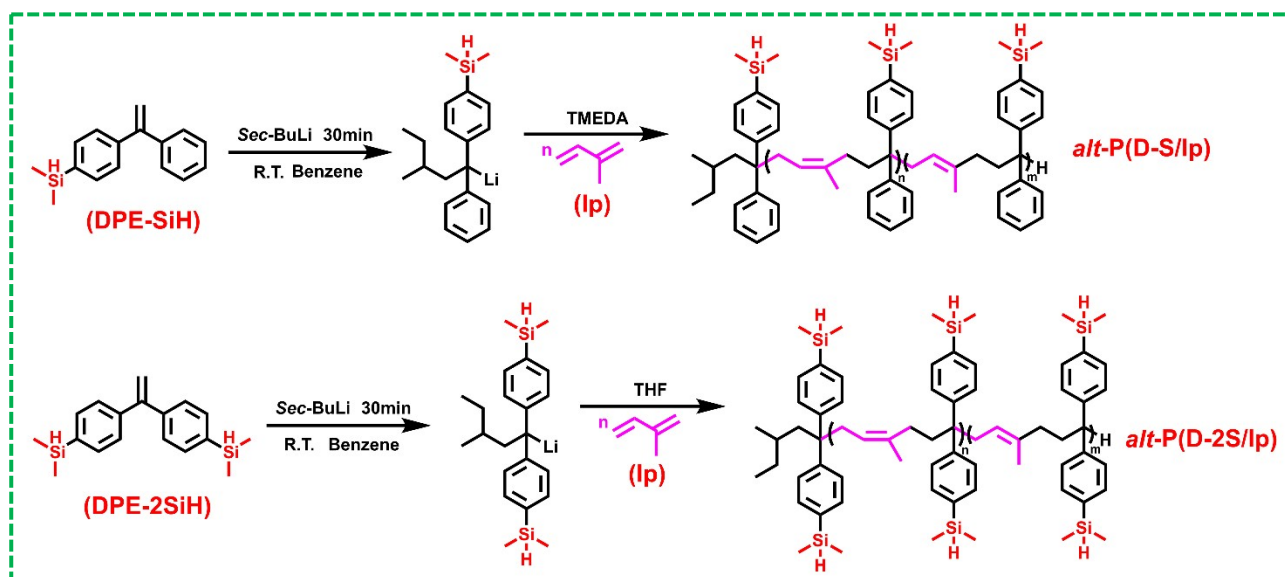


Fig. S3. The synthetic routes of the *alt*-P(D-S/Ip) and *alt*-P(D-2S/Ip).

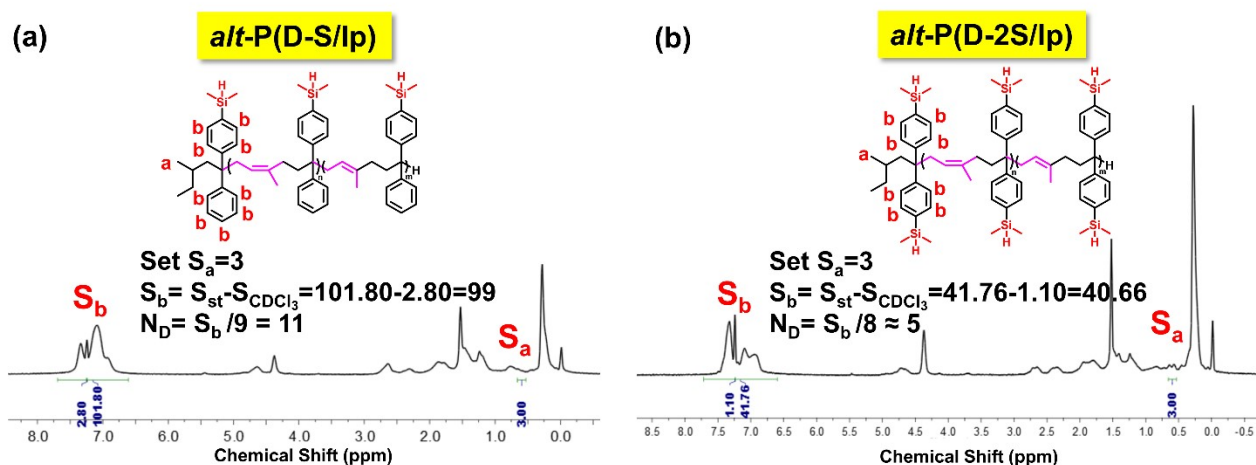


Fig. S4. The average number of DPE-SiH/DPE-2SiH (N_D) in alternating-sequence backbones, i.e., *alt*-P(D-S/Ip)/*alt*-P(D-2S/Ip) calculated from ^1H NMR.

Fig S5 shows the peak calibration and accurate addition efficiency (E_A) of the two FLCPs. The specific calculation method of E_A is: the integral area of the characteristic peak $\delta(\text{ppm})=8.20-8.02$ (4 H) on the benzene ring of the grafted side chain is located at 4 ($S_b=4$), and the integral area of the characteristic peak $\delta=0.27-0.15$ on the two silicomethyls of the

side chain is located at “a” area. According to the selection of standard peaks, the integral area of “a” (S_a) in **Fig S5a, b** is 6.15, 6.19, respectively. E_A =molar content of Si-H participating in the reaction/molar content of total Si-H, $S_b/4$ represents the silicon hydrogen group participating in the reaction and $(S_a-6)/6$ represents the unreacted silicon hydrogen group, the E_A values can be calculated from the equation in **Fig S5**.

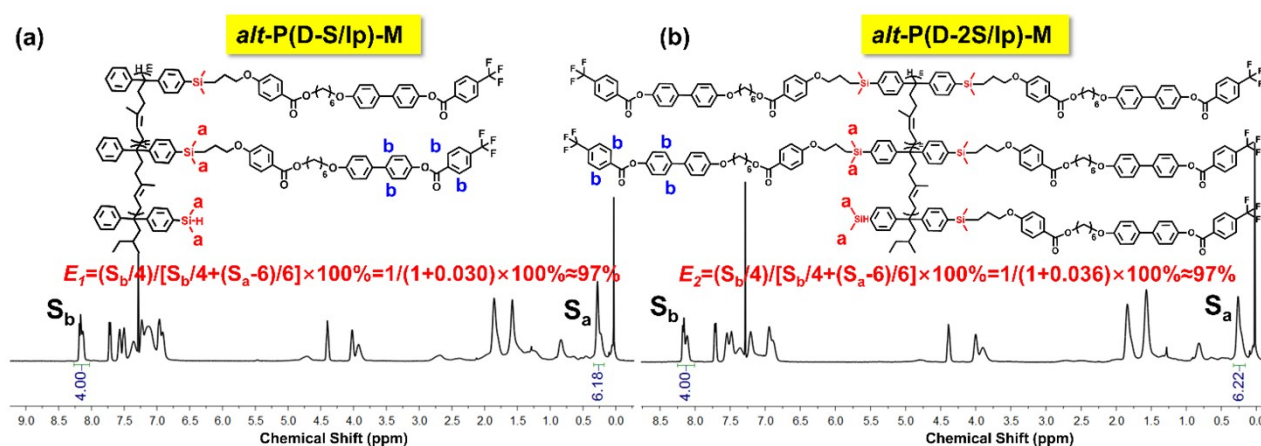


Fig. S5. The accurate addition efficiency (E_A) of fluorinated biphenyl moiety (FM) into alternating sequence backbones, i.e., *alt-P(D-S/Ip)* and *alt-P(D-2S/Ip)*.

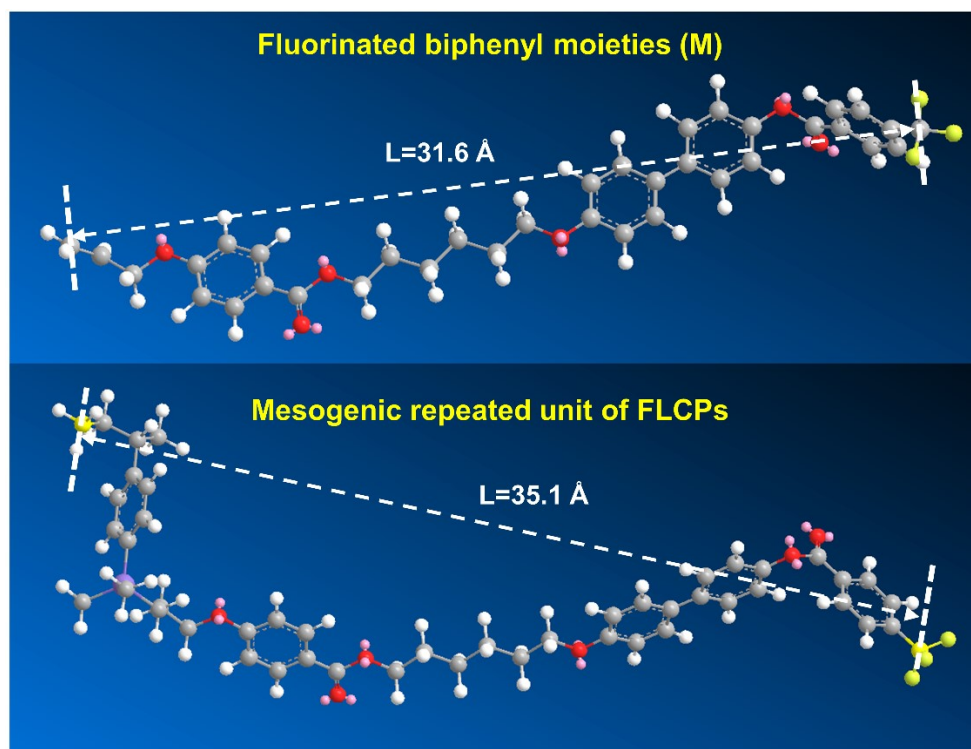


Fig. S6. Molecular models simulated by ChemBio3D and the theoretical coplanar molecular length (L) of FM and repeated unit of FLCPs.

References

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