Supporting information

α-Cyanostilbene and fluorene based bolaamphiphiles: synthesis, self-assembly, AIEE properties with potentials as white-light emissive materials and light-emitting liquid crystal displays

Deling Zhang, Yuantao Liu, Hongfei Gao, Qing Chang, Xiaohong Cheng*

Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education; Yunnan Research & Development Center for Natural Products; School of Chemical Science and Technology, Yunnan University, Kunming, 650091, P. R. China E-mail: xhcheng@ynu.edu.cn

Content

1. Additional Experimental Data

1.1 Experimental techniques

A Mettler heating stage (FP 82 HT) was used for polarizing optical microscopy (POM, Optiphot 2, Nikon) and DSC were recorded with a DSC 200 F3 Maia calorimeter (NETZSCH) at 5 K min^{-1}.

SEM experiments were carried out on a ZEISS SIGMA 300 scanning electron microscopy (SEM, GER). All pictures were taken digitally. For the sample preparation, the gel was placed on an aluminium foil for some time until the gel became dry gel, then the sample was gold plated, finally the sample was put into the scanning electron microscopy for observation. XRD measurement of xerogels was used the X-ray powder diffraction (XRD, Rigaku Co., Tokyo, Japan)，analysis was conducted on a D/max-3B spectrometer with Cu Kα radiation.

Small-angle powder diffraction (SAXS) experiments were performed in transmission mode with synchrotron radiation at the 1W2A SAXS beamline at Beijing Accelerator Laboratory.[S1] A modified Linkam hot stage with a thermal stability within 0.2 °C was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. Samples were held in the poly(imide) (Kapton) film. A MarCCD 165 detector was used. *q* calibration and linearization were verified using several orders of layer reflections from silver behemate. Positions and intensities of the diffraction peaks were measured using PeakSolve^{TM} (Galactic).

For Electron density reconstruction. Fourier reconstruction of the electron density was carried out using the general formula for 2D periodic systems:

$$E(xy) = \Sigma_{hk}\ \mathrm{sqrt}[I(hk)]\ \exp[i2\pi(hx+ky) + \phi_{hk}]$$

For the centro-symmetric structures considered in this work the phase angle ϕ can take up the values of 0 or π. The choice of a phase combination was initially made on the merit of each reconstructed electron density map obtained using the most intense reflections, combined with the additional knowledge of the molecules (molecular shape, length, volume of each part and the distribution of electron density among the different moieties).

TEB300 (Δn = 0.166 (589 nm, 20 ℃), $\Delta\varepsilon$ = 29.3 (1 kHz, 20 ℃), $T_{\text{N-I}}$ = 63 ℃)) and SLC9023 (Δn = 0.251 (589 nm, 20 ℃), $\Delta\varepsilon$ = 1.517 (1 kHz, 20 ℃)) were purchased from Slichem Co., Ltd, China, The planar oriented LC cells (cell gap: 4.8 μm) with a homogeneously rubbed polyimide (PI) alignment layer were purchased from SOOBOO INTL SHARES LIMETED (China). The LC mixtures were prepared by combining solutions of the TEB300 or SLC9023 and 0.5 wt% of **FT/16** in dichloromethane. The resulting solutions were then sonicated for about 1 min in order to achieve good solution, and thereafter, dichloromethane was evaporated off completely. Then the LC mixture was filled into the empty cell by capillary action. The polarized emission spectra of the mixture in LC cell were measured by Hitachi F-7000 fluorescence spectrometer (Hitachi, Japan) with a polarization unit (P/N 250-2420). The rubbing direction of the LC cell must be made sure to be parallel to the analyzer. After we get the fluorescence intensity for parallel irradiation ($F_{//}$) and the fluorescence intensity for perpendicular irradiation ($F\perp$), the dichroic ratio (NF) was determined from the formula: NF = $F_{//}/F\perp$". For preparation of the LE-LCD device, commercially available LC cell coated with both ITO and the polyimide (PI) alignment layer was etched firstly. Thus such LC-cell was splitted into half. The surface coated with ITO and PI was covered with a mask with the hollow letters “LC”. The ITO and PI in the exposed area of the letters were rubbed off with cotton which has been soaked with 50% hydrochloric acid and dipped some zinc powder, so that the letters were imprinted on the glass. The exposed area was cleared with water; then the mask was removed off. The edge of the glass was coated with B-7000 glue, and pressed with another unetched half piece of glass into one LC cell again for LC mixture filling.

1.2 Additional textures of LC phases、Mass spectrum data and XRD data

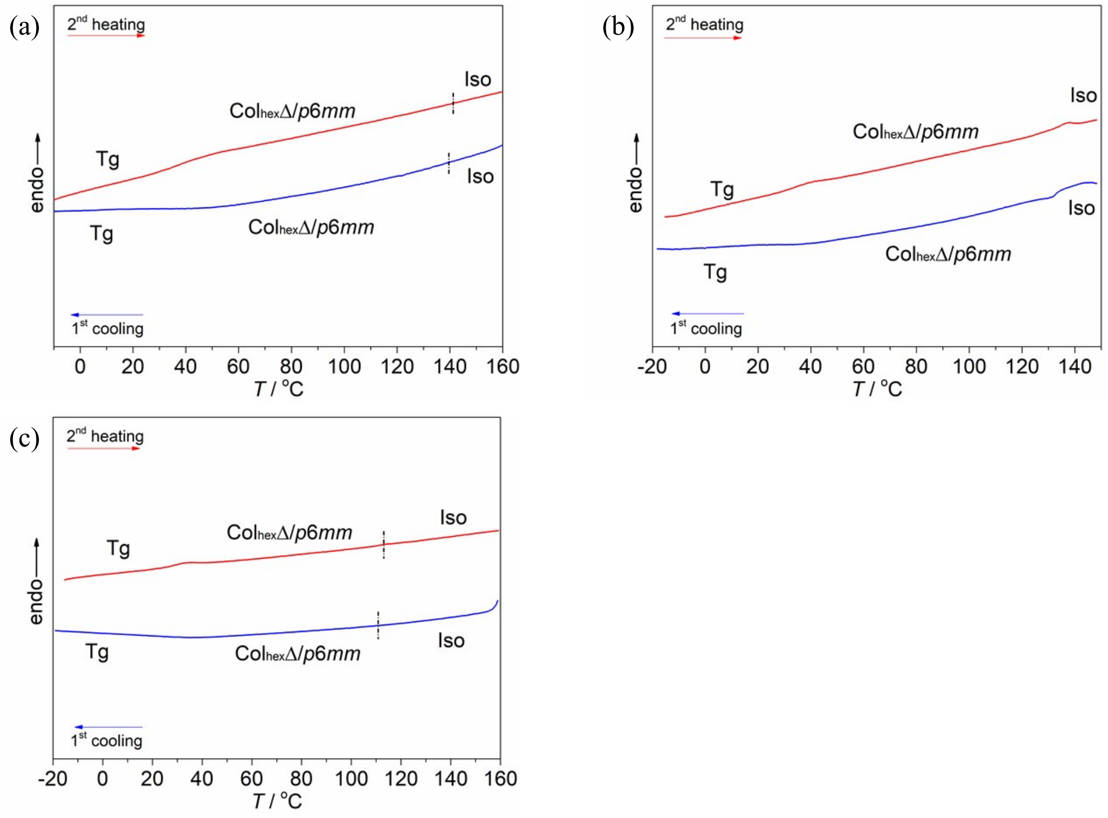


Fig. S1 The second DSC heating (green lines) and cooling (red lines) cycles of compounds **FT/n** at 10 K min^{-1}: (a) **FT/12**; (b) **FT/14**; (c) **FT/16**.

Table S1 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound **FT/12** at 110 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*
(10)	3.49	3.50	100.00
(11)	2.02	2.02	5.84
(20)	1.75	1.75	8.01
a_{hex} = 4.04 nm			

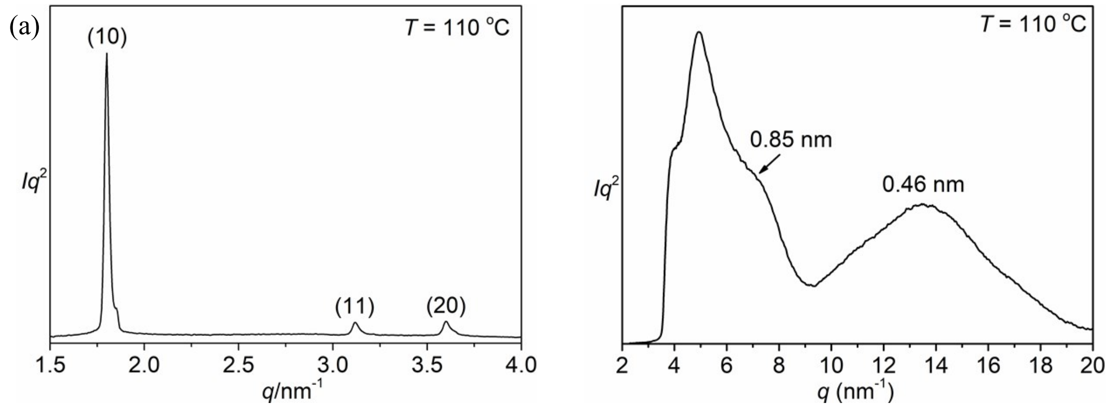


Fig. S2 a) SAXS diffraction patterns of hexagonal phase of compound **FT/12** recorded at 110 °C; b) WAXS diffraction patterns of hexagonal phase of compound **FT/12** recorded at 110 °C (the huge diffuse in the range of 4-6 nm^{-1} might be resulted by the beamstop, and should be ignored).

Table S2 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound **FT/14** at 110 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*
(10)	3.39	3.39	100.00
(11)	1.96	1.96	1.95
(20)	1.70	1.70	3.49
a_{hex} = 3.92 nm			

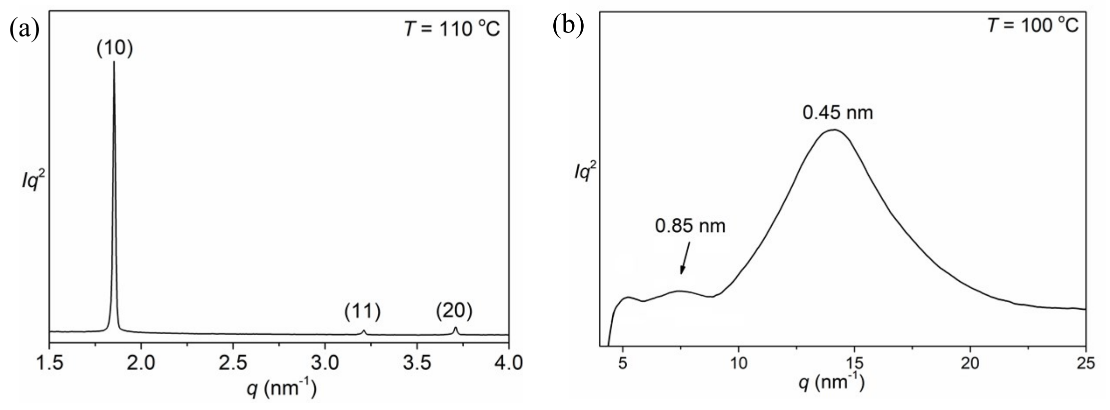


Fig. S3 SAXS diffraction patterns of hexagonal phase of compound **FT/14** recorded at 110 °C; b) WAXS diffraction patterns of hexagonal phase of compound **FT/14** recorded at 100 °C.

Table S3 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound **FT/16** at 100 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ –spacing (nm)	$d_{cal.}$ –spacing (nm)	*intensity*

(10)	3.45	3.45	100.00
(11)	1.99	1.99	3.02
(20)	1.73	1.72	4.16
a_{hex} = 3.98 nm			

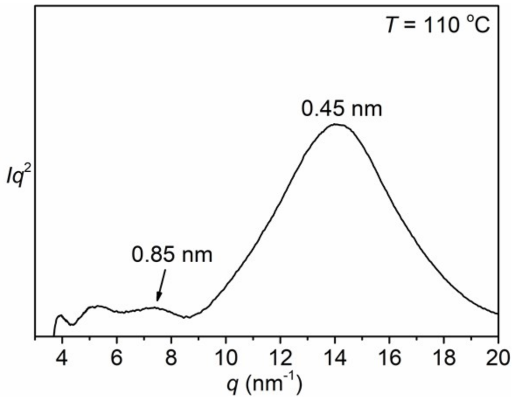


Fig. S4 WAXS diffraction patterns of hexagonal phase of compound **FT/16** recorded at 110 °C.

More details about the structure of the honeycomb LC phases were gained from the analysis of the molecular packing in the honeycombs based on the XRD data in Tables S1-S3 and the calculated parameters collated in Table S4. The number of molecules in a hypothetical 3D unit cell was calculated from the volume of this unit cell (V_{cell}) and the volume of a molecule (V_{mol}, calculated using crystal volume increments[S2]) according to $n_{cell} = V_{cell}/V_{mol}$. V_{cell} was estimated based on the experimental 2D lattice parameters and an assumed one-molecule thickness of h = 0.45-0.46 nm corresponding to the experimentally determined maxima of the diffuse wide angle scatterings as shown in Figs S2b and S4.

Table S4 Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells(V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Comp	phase	a/nm	(T/°C)	V_{cell}/nm³	V_{mol}/nm³	$n_{\mathrm{cell,cryst}}$	$n_{\mathrm{cell,liq}}$	n_{cell}	n_{wall}
FT/12	Col$_{\mathrm{hex}}\Delta$/*p*6*mm*	4.03	120	6.19	1.551	3.99	3.135	3.56	1.19
FT/14	Col$_{\mathrm{hex}}\Delta$/*p*6*mm*	3.92	110	5.86	1.650	3.55	2.79	3.17	1.06
FT/16	Col$_{\mathrm{hex}}\Delta$/*p*6*mm*	3.98	100	6.04	1.750	3.45	2.71	3.08	1.03

[a] V_{cell} = volume of the unit cell defined by $a^2 \times \sin(60°) \times h$ nm for hexagonal phases, assuming a height h = 0.45 nm; V_{mol} = volume for a single molecule as calculated using the crystal volume increments,[S2] $n_{\mathrm{cell,cryst}}$ = number of molecules in the unit cell, calculated according to $n_{\mathrm{cell,cryst}} = V_{\mathrm{cell}}/V_{\mathrm{mol}}$ (average packing coefficient in the crystal is k = 0.7;[S3] $n_{\mathrm{cell,liq}}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient k = 0.55, calculated according to $n_{\mathrm{cell,liq}} = 0.55/0.7 \times n_{\mathrm{cell,cryst}}$; n_{cell}(average) = number of molecules in the unit cell in the columnar phase estimated as the average of that in the $n_{\mathrm{cell,cryst}}$ and $n_{\mathrm{cell,liq}}$.

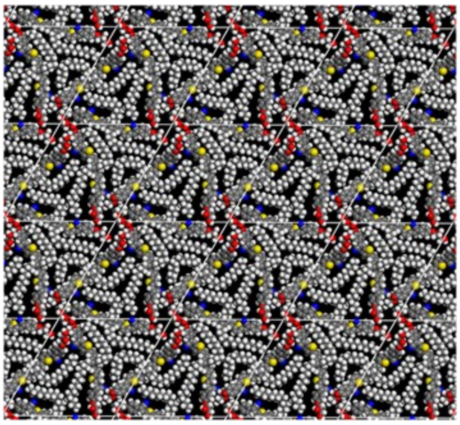


Fig. S5 Snapshot of the $\mathrm{Col_{hex}}\Delta/p6mm$ phase after molecular dynamics (MD) annealing.

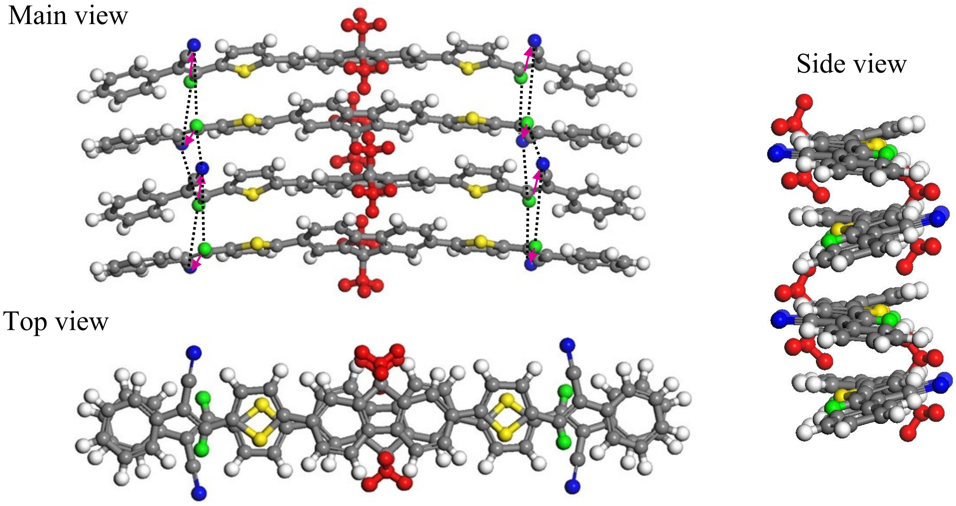


Fig. S6 The possible self-assembly model of triangular honeycomb phase; the enlarged cylinder wall area is illustrated by a molecular stick model, where the lateral chains are replaced by two methyl groups and the terminal glycerol groups are omitted.

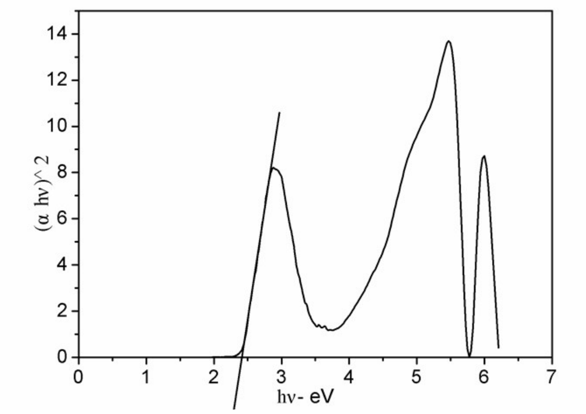


Fig. S7 Optical energy gap of **FT/12** in thin film

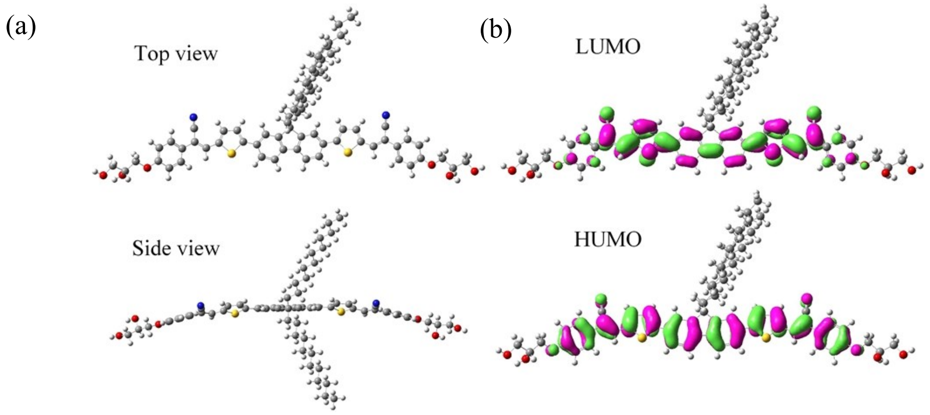


Fig. S8 a) Optimized structures and b) frontier molecular orbitals of **FT/12**.

Table S5 UV-vis, PL data and HOMO and LUMO obtained from CV measurements and DFT calculations for representative compound **FT/12**

THF	Film	Electrochemical potentials and energy levels		DFT data (eV)	
$\lambda^{abs}_{max}/\lambda^{em}_{max}$[a] (nm)	$\lambda^{abs}_{max}/\lambda^{em}_{max}$ (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	HOMO	LUMO
442/529	434/576	-6.18	-3.96	-6.09	-3.80

[a] Excited at the absorption maxima

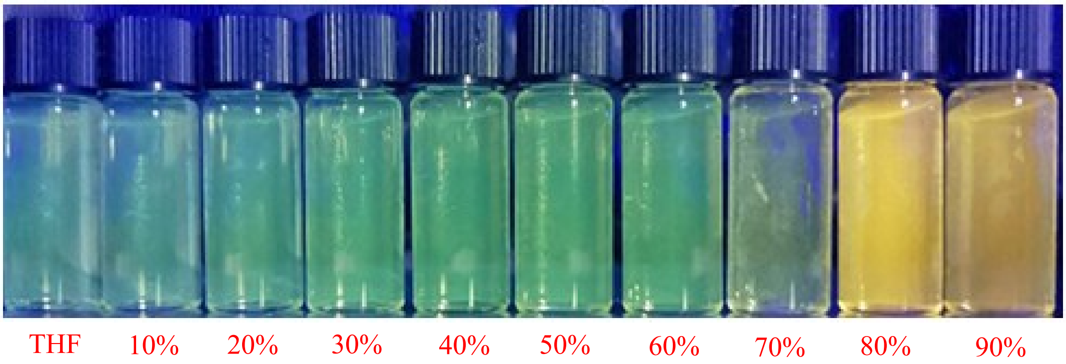


Fig. S9 Photographs of THF/water mixtures from 0 to 90% of **FT/12** with different f_w values under 365 nm UV light.

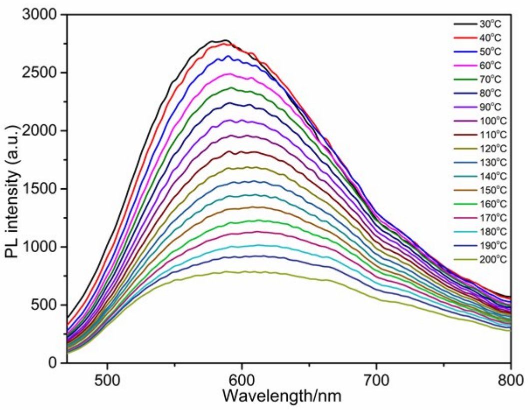


Fig. S10 Emission spectra of compound **FT/12** recorded during heating from solid to $Col_{hex}\Delta/p6mm$ to isotropic phase.

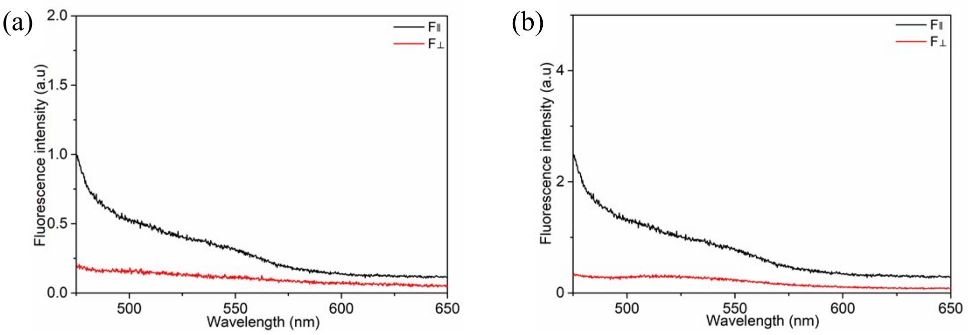
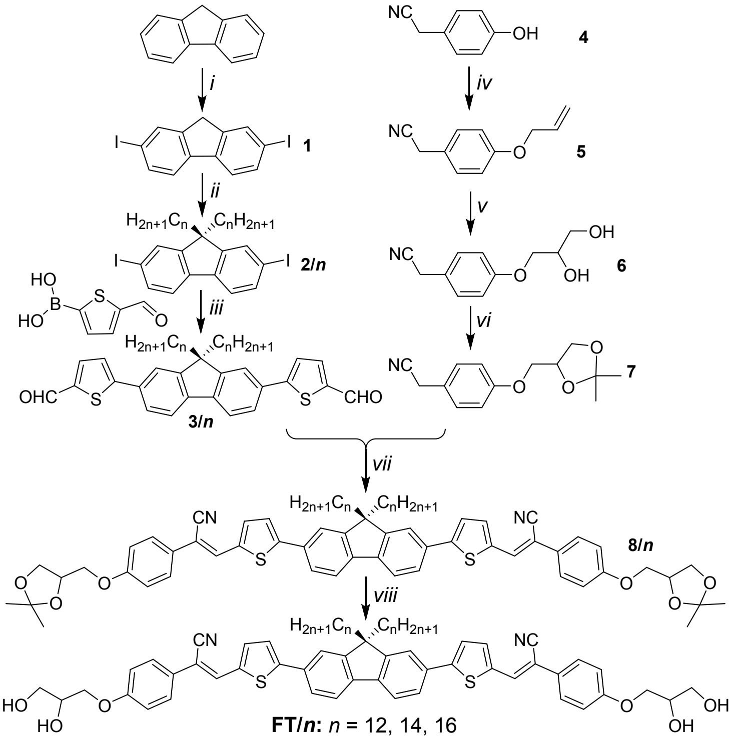


Fig. S11 Polarized fluorescence spectra of light-emitting LC cell in electric field-off status: a) SLC9023; b) TEB300.

2.Material synthesis and analytical data

2.1 General remarks

For the structures of the compounds see Scheme 1 in the main text. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 ℃). Tetrahydrofuran (THF) was distilled from sodium prior to use. Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-DRX-400 spectrometer. **ESI-TOF-MS** were performed on an Agilen LC/Msd TOF instrument. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Thin-layer chromatography was performed on aluminum plates precoated with 5735 silica gel 60 PF254 (Merck). Column chromatography was performed on Merck silica gel 60 (230-400 mesh).



Scheme S1 Scheme 1 Synthesis of compounds **FT/*n***. Reagents and conditions: (*i*) I_2, H_2SO_4, CH_3COOH, KIO_3, H_2O, 80 °C, 12 h; (*ii*) $C_nH_{2n+1}Br$, NaOH, toluene, H_2O, TBAB, RT, 12 h; (*iii*) $Pd(PPh_3)_4$, K_2CO_3, H_2O, THF, 78 °C, 15 h; (*iv*) K_2CO_3, CH_3CN, allylbromide, reflux, 6 h; (*v*) OsO_4, N-Methylmorpholine N-oxide (NMMNO, 60% aqueous solution Aldrich), H_2O, acetone, 50 ºC, 5h; (*vi*) 2,2-dimethoxypropane, pyridiniump-toluenesulfonate, RT, 5h; (*vii*) ethanol, Sodium methoxide, reflux, 12 h; (*viii*) 10 % HCl, methanol, reflux, 12 h.

General procedure for the synthesis of 2,7-diiodo-9*H*-fluorene 1

Fluorene (3.0 g, 18 mmol) was dissolved in 220 mL of a mixed solvent (CH_3COOH: H_2O: H_2SO_4/ 50:4:1) at 80 °C, followed by addition of KIO_3 (1.54 g, 72 mmol) and I_2 (6 g, 23.6 mmol). Then the mixture was stirred at this temperature for 10 h. After the reaction was complete (TLC), the mixture was cooled to RT. The precipitate was collected by filtration and washed with 10% aqueous Na_2CO_3 (10 mL), 5% aqueous $NaHSO_3$ (10 mL) and water (20 mL). The crude material was recrystallized from dichloromethane.
Yield: 6.56 g, 87 %; white solid. m.p. 155-156 °C. ^1H NMR (400 MHz, $CDCl_3$): δ =7.86 (s, 2 H, 2Ar**H**), 7.71 (d, *J* = 8.06 Hz, 2 H, 2Ar**H**), 7.51 (d, *J*= 8.06 Hz, 2 H, 2Ar**H**), 3.85 (s, 2 H, 2Ar**H**).

General procedure for the synthesis of the compounds 2/n

Bromoalkane (7.2 mmol) and compounds **1** (1 g, 2.4 mmol) were added to a mixture of tetrabutylammonium bromide (TBAB) (48 mg, 0.144 mmol) and aqueous KOH (50% v/v, 10 mL) in a 150 mL round-bottom flask with a stir bar, and the reaction was allowed to proceed overnight at room temperature under stirring. After the reaction was complete (TLC), the residue was diluted with H_2O (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layer was washed successively with aqueous HCl (0.1 M, 10 mL) and water (20 mL), dried over anhydrous Na_2SO_4 and then the solvent was removed in vacuo. The residue was purified by column chromatography (petroleum ether).

2/12: Yield: 1.62 g, 90 %; colorless transparent liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4 H, 4Ar**H**), 7.40 (s, 2 H, 2Ar**H**), 1.94–1.82 (m, 4 H, 2ArC**H₂**), 1.36–0.95 (m, 40 H, 20 $CH_2C\mathbf{H_2}$), 0.87 (t, 6 H, *J* = 6.8 Hz, $2CH_2C\mathbf{H_3}$).

2/14: Yield: 1.76 g, 91 %; colorless transparent liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.63 (m, 4 H, 4Ar**H**), 7.41 (s, 2H, 2Ar**H**), 1.95–1.80 (m, 4 H, $2ArC\mathbf{H_2}$), 1.35–0.95 (m, 48 H, $24CH_2C\mathbf{H_2}$), 0.87 (t, 6 H, *J* = 6.8 Hz, $2CH_2C\mathbf{H_3}$).

2/16: Yield: 1.87 g, 90 %; colorless transparent liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4 H, 4Ar**H**), 7.40 (s, 2 H, 2ArH), 1.93–1.81 (m, 4 H, $2ArC\mathbf{H_2}$), 1.35–0.95 (m, 56 H, $28CH_2C\mathbf{H_2}$), 0.88 (t, 6 H, *J* = 6.9 Hz, $2CH_2C\mathbf{H_3}$).

General procedure for the synthesis of the compounds 3/n

(5-formylthiophen-2-yl) boronic acid (93.6mg, 0.60 mmol), compounds **2/n** (0.27 mmol), aqueous solution of K_2CO_3 (1 M, 10 mL) were dissolved in THF (10 ml), then $Pd(PPh_3)_4$ (12.0 mg) was added under N_2 atmosphere. The mixture was refluxed at 78 °C and stirred for 15 h. After the reaction was complete (TLC), the mixture was cooled to RT. The residue was diluted with H_2O

(20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined extract was washed with H_2O (3 × 25 ml), dried over anhydrous Na_2SO_4, then the solvent was removed in vacuo. The residue was purified by column chromatography (petroleum ether: ethyl acetate = 5 : 1).

3/12: yield: 145.6 mg, 76%; yellow solid. m.p. 51-53 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 9.91 (s, 2 H, 2ArC**H**), 7.78-7.75 (m, 4 H, 4Ar**H**), 7.71-7.68 (dd, 2 H, *J* = 8.0, 1.6 Hz, 2Ar**H**), 7.64 (s, 2 H, 2Ar**H**), 7.49-7.48 (d, 2 H, *J* = 3.92 Hz, 2Ar**H**), 2.05-2.01 (m, 4 H, 2ArC**H₂**), 1.25-1.05 (m, 40 H, 20$CH_2C\mathbf{H_2}$), 0.87-0.83 (t, 6 H, *J* = 7.0 Hz, 2$CH_2C\mathbf{H_3}$).

3/14: yield: 159.9 mg, 76%; yellow solid. m.p. 53-55 °C.^{1}H NMR (CDCl3; 400 MHz): δ = 9.91 (s, 2 H, 2ArC**H**), 7.78-7.75 (m, 4 H, 4Ar**H**), 7.70-7.66 (dd, 2 H, *J* = 8.1, 1.7 Hz, 2Ar**H**), 7.64 (s, 2 H, 2Ar**H**), 7.49-7.46 (d, 2 H, *J* = 3.90 Hz, 2Ar**H**), 2.04-2.00 (m, 4 H, 2Ar$C\mathbf{H_2}$), 1.23-1.06 (m, 48 H, 24$CH_2C\mathbf{H_2}$), 0.87-0.84 (t, 6 H, *J* = 7.0 Hz, 2$CH_2C\mathbf{H_3}$).

3/16: 173.7 mg, yield: 77%; yellow solid. m.p. 55-57 °C .^{1}H NMR (CDCl3; 400 MHz): δ = 9.90 (s, 2 H, ArC**H**), 7.80-7.74 (m, 4 H, 4Ar**H**), 7.72-7.67 (dd, 2 H, *J* = 7.9, 1.6 Hz, 2Ar**H**), 7.65 (s, 2 H, 2Ar**H**), 7.49-7.48 (d, 2 H, *J* = 3.91 Hz, 2Ar**H**), 2.05-2.00 (m, 4 H, Ar$C\mathbf{H_2}$), 1.26-1.05 (m, 56 H, 28$CH_2C\mathbf{H_2}$), 0.87-0.83 (t, 6 H, *J* = 7.1 Hz, 2$CH_2C\mathbf{H_3}$).

General procedure for the synthesis of the compounds 2-(4-(allyloxy)phenyl)acetonitrile 5 [S4]

Allyl bromide (2.18 g, 18 mmol) was added to a mixture of 4-hydroxyphenylacetonitrile (2.0 g, 15 mmol) and K_2CO_3 (4.15 g, 30 mmol) in dry CH_3CN (50 mL) under N_2 atmosphere. The mixture was refluxed for 6 hours. After the reaction was complete (TLC), CH_3CN was evaporated in vacuo. The residue was diluted with H_2O (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined extract was washed with H_2O (3 × 25 ml), dried over anhydrous Na_2SO_4, then the solvent was removed in vacuo. The crude product was purified by column chromatography (petroleum mether : ethyl acetate = 15 : 1).
Yield: 2.52 g, 97%; colorless transparent liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.23 (d, 2 H, *J* = 8.7 Hz, 2Ar**H**), 6.91 (d, 2 H, *J* = 8.6 Hz, 2Ar**H**), 6.11-6.00 (m, 1 H, C**H**=CH_2), 5.42 (m, 1 H, CH=$C\mathbf{H_a}H_b$), 5.31 (m, 1 H, CH=$CH_a\mathbf{H_b}$), 4.55 (m, 2 H, ArO$C\mathbf{H_2}$), 3.69 (s, 2 H, $C\mathbf{H_2}$CN).

General procedure for the synthesis of the compounds 2-(4-(2,3-dihydroxypro poxy)phenyl) acetonitrile 6

Compounds **5** (1.04 g, 6 mmol) and NMMNO (2.0 mL, 60% solution in water) were dissolved in acetone. Osmium tetroxide (2.8 mL, 0.004 M solution in tert-butanol) was added, and the solution was refluxed for 5 hours at 50 ºC. After the reaction was complete (TLC), saturated aqueous Na_2SO_3 (20 mL) was added, and the mixture was stirred for 30 min at room temperature. The mixture was filtered. Organic compounds were extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with $NaHCO_3$ aq. solution (3 × 25 mL) and H_2O (3 × 25 mL), dried over anhydrous Na_2SO_4, and then the solvent was removed in vacuo. The crude product was purified by column chromatography (dichloromethane : ethyl acetate = 15 : 1).

Yield: 1.14g, 92%; white solid. m.p. 75-77 °C. ^{1}H NMR (400 MHz, CDCl$_3$), ^{1}H NMR (400 MHz, CDCl$_3$), δ = 7.24-7.22 (d, 2 H, *J* = 8.68 Hz, 2Ar**H**), 6.93-6.89 (d, 2H, *J* = 8.68 Hz, 2Ar**H**), 4.14-4.09 (m, 1 H, C**H**), 4.07-4.00 (m, 2 H, C**H**$_2$), 3.86-3.82 (dd, 1H, *J* = 11.36 Hz, *J* = 3.72 Hz, OC**H**$_a$H$_b$), 3.77-3.72 (dd, 1H, *J* = 11.36 Hz, *J* = 5.44 Hz, OCH$_a$**H**$_b$), 3.68 (m, 2 **H**, C**H**$_2$CN).

General procedure for the synthesis of the compounds 2-(4-((2,2-dimethyl-1,3-dioxolan-4-yl) methoxy)phenyl)acetonitrile 7 [S5]

Compounds **6** (1.14 g, 5.5 mmol) and 2,2-dimethoxypropane (5 mL) were dissolved in dry THF (20 mL) under an N$_2$ atmosphere. After addition of pyridium p-toluene solfonate (50 mg), the mixture was stirred at RT for 5 hours. After the reaction was complete (TLC), the mixture was cooled to RT, and extracted with ethyl acetate (3 × 25 mL). The combined extract was washed with H$_2$O (3 × 25 mL), dried over anhydrous MgSO$_4$, then the solvent was removed in vacuo. The obtained product was used directly for the next step without further purification.
Yield: 1.23g, 96%; colorless liquid. ^{1} H NMR (400 MHz, CDCl$_3$), δ = 7.25-7.21 (d, 2 H, *J* = 8.80 Hz, 2Ar**H**), 6.92-6.90 (d, 2 H, *J* = 8.72 Hz, 2Ar**H**), 4.50-4.45 (m, 1 H, C**H**), 4.19-4.15 (m, 1H, OC**H**$_a$H$_b$), 4.07-4.03 (m, 1H, OCH$_a$**H**$_b$), 3.96-3.88 (m, 2 H, OC**H**$_2$), 3.69 (s, 2 H, C**H**$_2$CN), 1.46 (s, 3 H, C**H**$_3$), 1.40 (s, 3 H, C**H**$_3$).

General procedure for the synthesis of the compounds 8/n

Compounds **7** (108.8 mg, 0.44 mmol) and **3/n** (0.20 mmol) were dissolved in dry ethanol (20 mL). Sodium methoxide (0.8 mmol, 42.3 mg) was added, and the solution was refluxed for 12 hours. After the reaction was complete (TLC), the mixture was cooled to 0 °C, the precipitate was collected by filtration and washed with ethanol.

8/12: Yield: 160.7 mg, 68%. Orange yellow solid, m.p. 115-117 °C.. ^{1}H NMR (CDCl$_3$; 300 MHz): δ =7.72-7.53 (m, 10 H, 10Ar**H**), 7.45-7.39 (m, 4 H, 2Ar**H**, 2**ArCH**), 7.25-7.15 (m, 2 H, 2Ar**H**), 6.96-7.05 (m, 4 H, 4Ar**H**), 4.56-4.46 (m, 2 H, 2C**H**), 4.24-4.16 (m, 2 H, 2OC**H**$_a$H$_b$), 4.15-4.07 (m, 2 H, 2OCH$_a$**H**$_b$) 4.01-3.90 (m, 4 H, 2OC**H**$_2$), 2.06-1.99 (m, 4 H, 2 ArC**H**$_2$), 1.51-1.48 (d, 6 H, *J* = 8.68 Hz, 2OCC**H**$_3$), 1.44-1.42 (d, 6 H, J = 8.64 Hz, 2OCC**H**$_3$) 1.33-1.05 (m, 40 H, 20CH$_2$C**H**$_2$), 0.89-0.84 (m, 6 H, 2 C**H**$_3$);

8/14: Yield: 170.8 mg, 69%. Orange yellow solid, m.p. 120-122 °C. ^{1}H NMR (CDCl$_3$; 300 MHz): δ =7.73-7.54 (m, 10 H, 10Ar**H**), 7.46-7.39 (m, 4 H, 2Ar**H**, 2**ArCH**), 7.27-7.15 (m, 2 H, 2Ar**H**), 6.98-7.05 (m, 4 H, 4Ar**H**), 4.55-4.44 (m, 2 H, 2C**H**), 4.23-4.15 (m, 2 H, 2OC**H**$_a$H$_b$), 4.14-4.08 (m, 2 H, 2OCH$_a$**H**$_b$) 4.03-3.90 (m, 4 H, 2OC**H**$_2$), 2.05-1.99 (m, 4 H, 2 ArC**H**$_2$), 1.53-1.48 (d, 6 H, J = 8.68 Hz 2 OCC**H**$_3$), 1.45-1.42 (d, 6 H, J = 8.64 Hz, 2OCC**H**$_3$) 1.34-1.05 (m, 48 H, 24CH$_2$C**H**$_2$), 0.89-0.82 (m, 6 H, 2 C**H**$_3$);

8/16: Yield: 176.0 mg, 68%. Orange yellow solid, m.p. 124-126 °C. ^{1}H NMR (CDCl$_3$; 300 MHz): δ =7.74-7.53 (m, 10 H, 10Ar**H**), 7.44-7.38 (m, 4 H, 2Ar**H**, 2**ArCH**), 7.24-7.15 (m, 2 H, 2Ar**H**), 6.96-7.05 (m, 4 H, 4Ar**H**), 4.55-4.46 (m, 2 H, 2C**H**), 4.27-4.16 (m, 2 H, 2OC**H**$_a$H$_b$), 4.16-4.07 (m, 2 H, 2OCH$_a$**H**$_b$) 4.01-3.91 (m, 4 H, 2OC**H**$_2$), 2.06-1.97 (m, 4 H, 2 ArC**H**$_2$), 1.51-1.46 (d, 6 H, J =

8.69 Hz 2 OCC**H₃**), 1.48-1.42 (d, 6 H, J = 8.64 Hz, 2OCC**H₃**) 1.33-1.05 (m, 56 H, 28CH₂C**H**₂), 0.89-0.80 (m, 6 H, 2 C**H**₃).

General procedure for the synthesis of the compounds FT/n

A mixture of compounds **8/n** (0.13mmol) and 10% HCl (8 mL) in MeOH (30 mL) was refluxed for 12 hours and then cooled down to room temperature. After the reaction was complete (TLC), the solvent was evaporated and saturated aqueous $NaHCO_3$ (50 mL) was added. The crude product was filtered and washed with water (3 × 20 mL) and then the crude product was purified by column chromatography (dichloromethane : methanol = 10 : 1).

FT/12: Yield: 88.8 mg, 62%, Orange yellow soft solid, phase transistion: Tg 49°C Col 143 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ =7.65-7.53 (m, 12 H, 12Ar**H**), 7.45-7.39 (m, 2 H, 2**Ar**C**H**), 7.26-7.13 (m, 2 H, 2Ar**H**), 6.99-6.97 (d, 4 H, *J* = 8.4 Hz, 4Ar**H**), 4.15-4.09 (m, 6 H, 2OC**H₂**, 2OCH₂C**H**), 3.89-3.80 (m, 4 H, 2OC**H₂**), 2.00-1.99 (m, 4 H, 2ArC**H₂**), 1.25-1.03 (m, 40 H, 20 CH₂C**H**₂), 0.86-0.81 (m, 6 H, 2C**H₃**). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* =159.31 (2 C), 151.76 (2 C), 148.54 (2 C), 140.69 (2 C), 136.82 (2 C), 133.50 (2 C), 132.25 (2 C), 132.14 (2 C), 126.63 (4 C), 126.30 (2 C), 125.02 (2 C), 123.32 (2 C), 120.26 (2 C), 119.79 (2 C), 118.24 (2 C), 114.91 (4 C), 106.47 (2 C), 70.16 (2 C), 69.17 (2 C), 63.37(2 C), 55.24(1 C), 40.42-39.27, 31.57, 29.62-28.94, 23.45, 22.34, 13.85. Elemental analysis calcd (%) for $C_{69}H_{84}N_2O_6S_2$ (1101.56); C, 75.24; H, 7.69; N, 2.54; found: C, 75.03; H, 7.67; N, 2.54; **ESI-TOF-MS**: *m/z* 1123.5667 [**FT/12**+Na]$^+$, calcd. For $[C_{69}H_{84}N_2O_6S_2Na]^+$, 1123.5663.

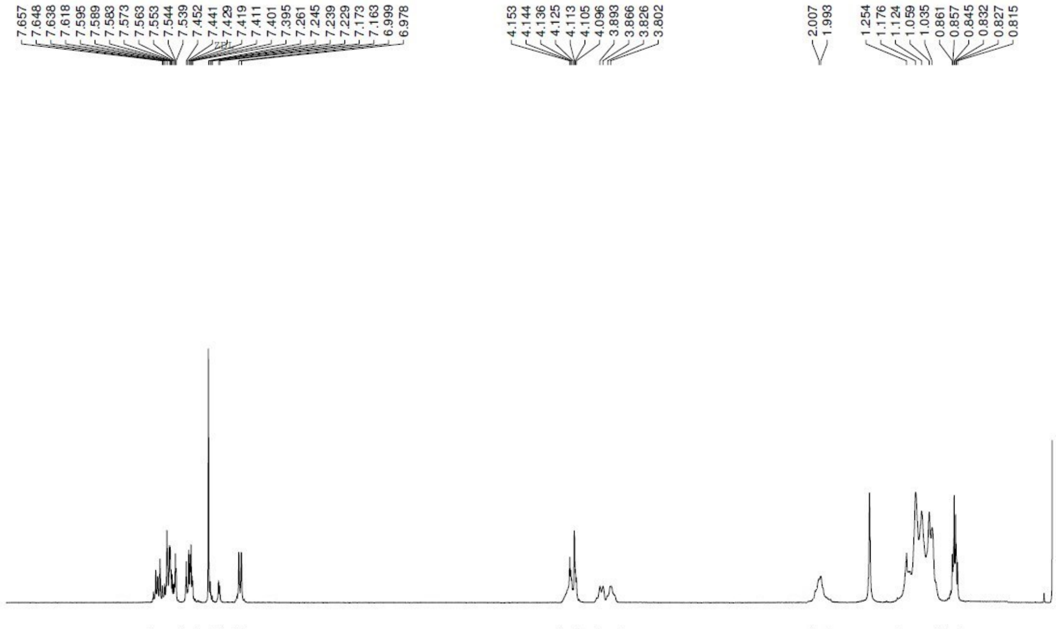


Fig. S12 ^{1}H NMR spectrum of **FT/12**.

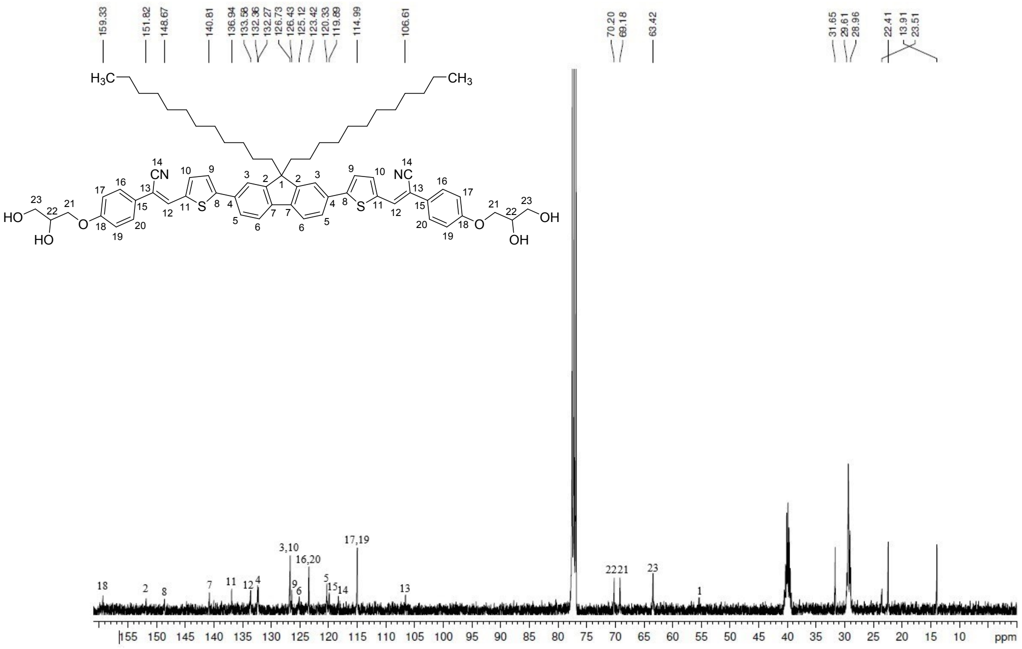


Fig. S13 ^{13}C NMR spectrum of **FT/12**.

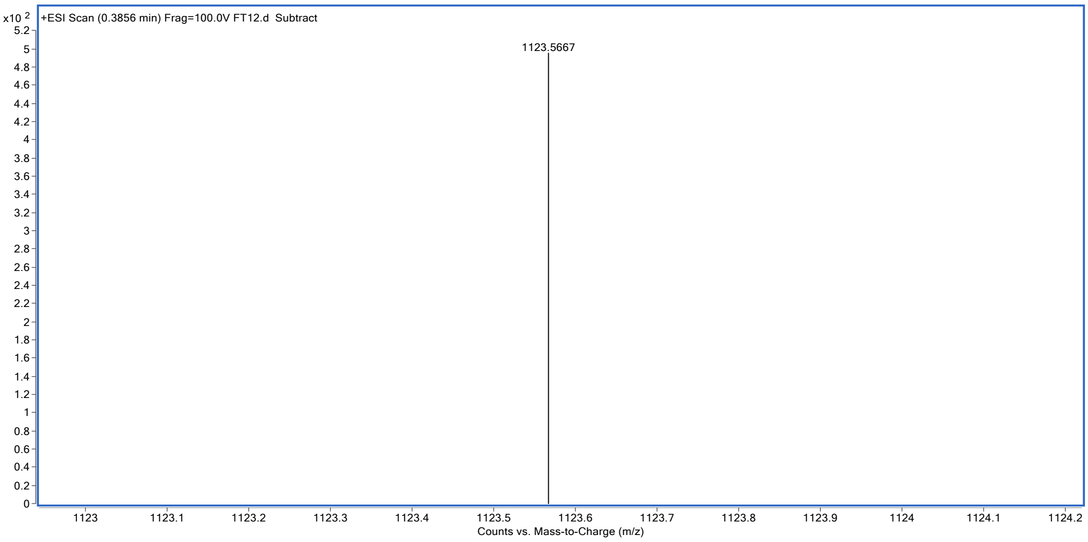


Fig. S14 ESI-TOF-MS spectrum of **FT/12**.

FT/14: Yield: 93.3 mg, 62%, Orange yellow soft solid, Tg 40°C Col 137 °C. ^{1}H NMR (CDCl$_3$; 400 MHz): δ =7.73-7.65 (m, 4 H, 4Ar**H**), 7.63-7.52 (m, 8 H, 8Ar**H**), 7.45-7.39 (m, 2 H, 2**Ar**C**H**), 7.26-7.16 (m, 2 H, 2Ar**H**), 7.00-6.97 (d, 4 H, *J* = 8.8 Hz, 4Ar**H**), 4.15-4.10 (m, 6 H, 2OC**H$_2$**, 2OCH$_2$C**H**), 3.90-3.79 (m, 4 H, 2OC**H$_2$**), 2.01-1.98 (m, 4 H, 2ArC**H$_2$**), 1.25-1.05 (m, 48 H, 24 CH$_2$C**H$_2$**), 0.86-0.82 (m, 6 H, 2C**H$_3$**). ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* =159.26 (2 C), 151.72 (2 C), 148.54 (2 C), 140.70 (2 C), 136.85 (2 C), 133.57 (2 C), 132.28 (2 C), 132.17 (2 C), 126.63 (4 C), 126.30 (2 C), 125.03 (2 C), 123.35 (2 C), 120.24 (2 C), 119.77 (2 C), 118.21 (2 C), 114.91 (4 C), 106.47 (2 C), 70.12 (2 C), 69.12 (2 C), 63.31(2 C), 55.24(1 C), 40.42-39.30, 31.57, 29.52-28.87, 23.45, 22.34, 13.85. Elemental analysis calcd (%) for $C_{73}H_{92}N_2O_6S_2$ (1157.67); C, 75.74; H, 8.01; N, 2.42; found: C, 75.93; H, 8.03; N, 2.42; **ESI-TOF-MS**: *m/z* 1179.6285 [**FT/14**+Na]$^+$, calcd. For $[C_{73}H_{92}N_2O_6S_2Na]^+$, 1179.6289

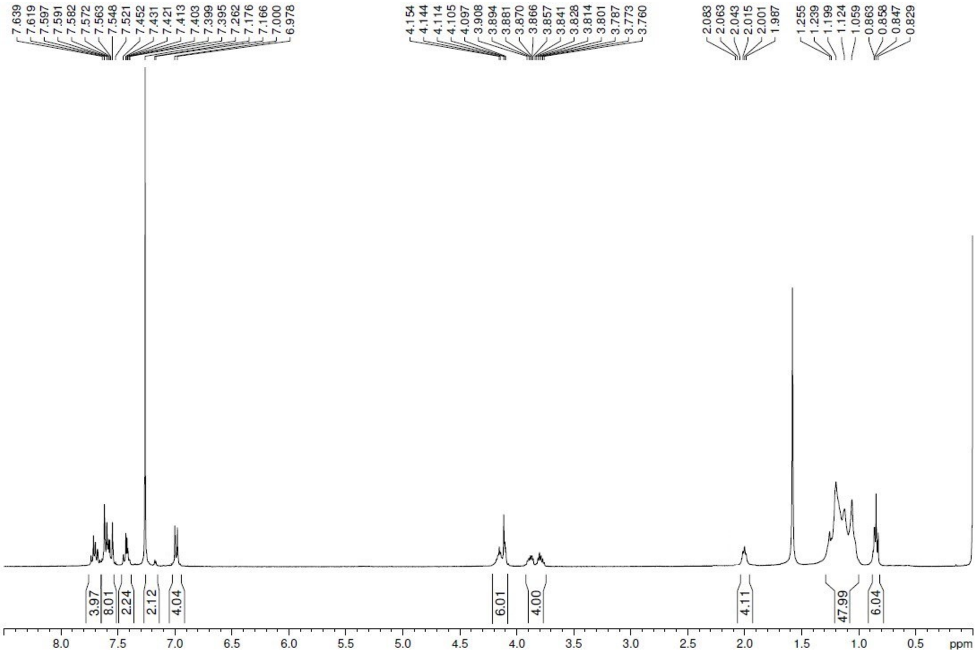


Fig. S15 ^{1}H NMR spectrum of **FT/14**.

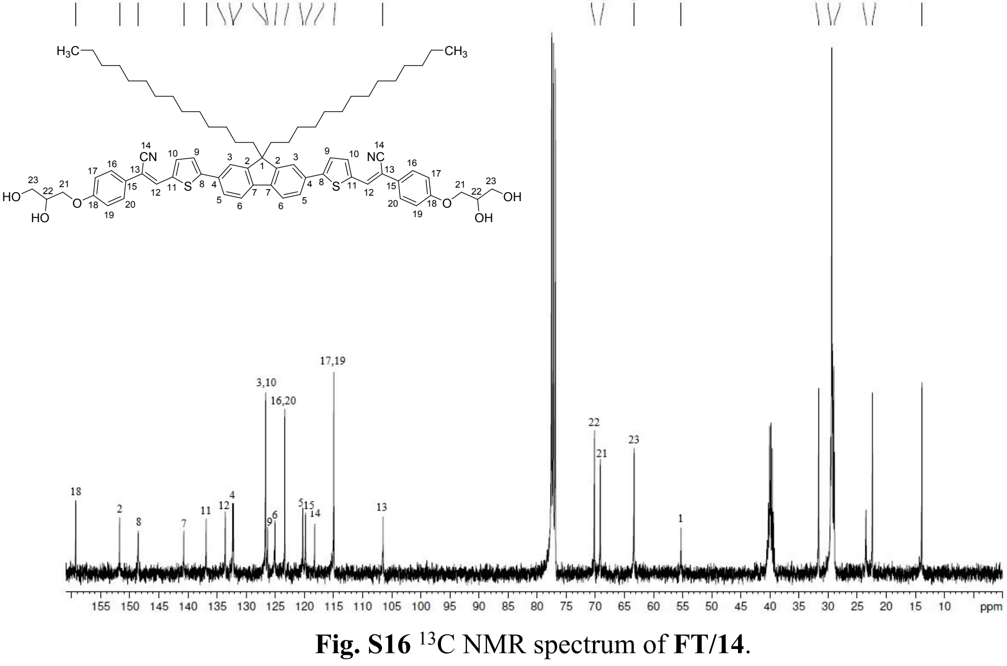


Fig. S16 ^{13}C NMR spectrum of **FT/14**.

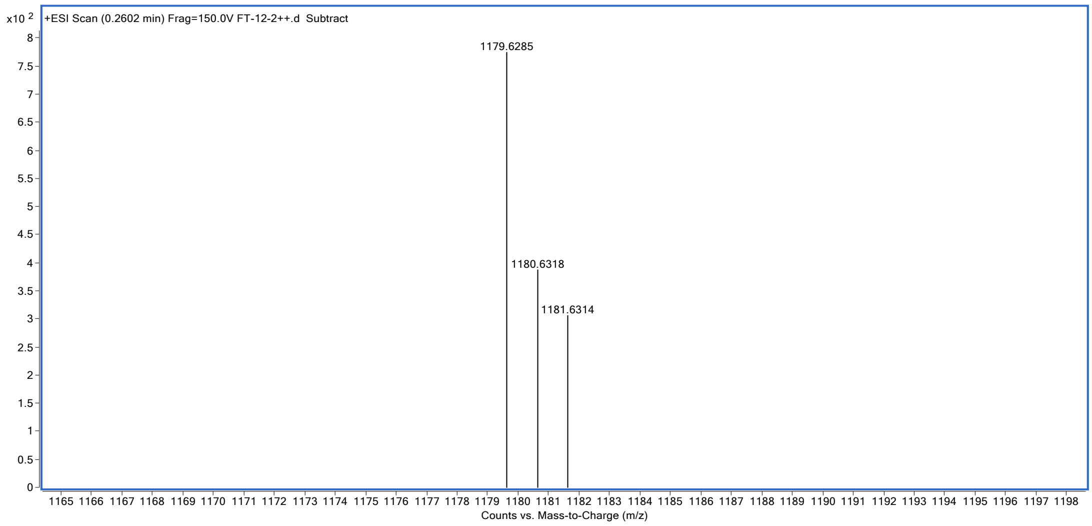


Fig. S17 ESI-TOF-MS spectrum of **FT/14**.

FT/16: Yield: 97.8mg, 62%, Orange yellow soft solid, Tg 39°C Col 113 °C. ^{1}H NMR (CDCl$_3$; 400 MHz): δ =7.73-7.54 (m, 12 H, 12Ar**H**),7.45-7.39 (m, 2 H, 2**ArCH**), 7.26-7.16 (m, 2 H, 2Ar**H**), 6.99-6.97 (d, 4 H, *J* = 8.8 Hz, 4Ar**H**), 4.15-4.09 (m, 6 H, 2OC**H$_2$**, 2OCH$_2$C**H**), 3.89-3.77 (m, 4 H, 2OC**H**$_2$), 2.08-1.99 (m, 4 H, 2ArC**H$_2$**), 1.25-1.05 (m, 56 H, 28 CH$_2$C**H**$_2$), 0.88-0.84 (m, 6 H, 2C**H$_3$**). ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* =159.19 (2 C), 151.70 (2 C), 148.55 (2 C), 140.70 (2 C), 136.82 (2 C), 133.53 (2 C), 132.25 (2 C), 132.12 (2 C), 126.61 (4 C), 126.31 (2 C), 125.01 (2 C), 123.30 (2 C), 120.22 (2 C), 119.73 (2 C), 118.19 (2 C), 114.89 (4 C), 106.43 (2 C), 70.06 (2 C), 69.12 (2 C), 63.31(2 C), 55.23(1 C), 40.35-39.31, 31.57, 29.53-28.89, 23.46, 22.35, 13.84. Elemental analysis calcd (%) for $C_{77}H_{100}N_2O_6S_2$ (1213.78); C, 76.20; H, 8.30; N, 2.31, 2.54; found: C, 76.00; H, 8.28; N, 2.31; **ESI-TOF-MS**: *m/z* 1235.6930 [**FT/16**+Na]$^+$, calcd. For [$C_{77}H_{100}N_2O_6S_2Na$]$^+$, 1235.6915

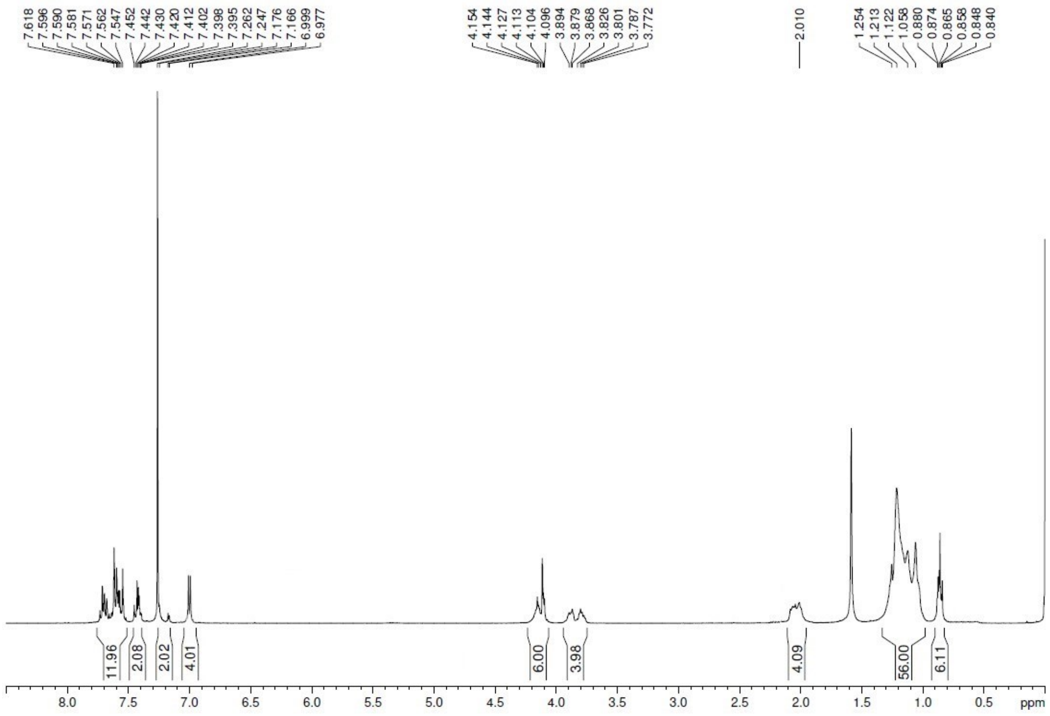


Fig. S18 ^{1}H NMR spectrum of **FT/16**.

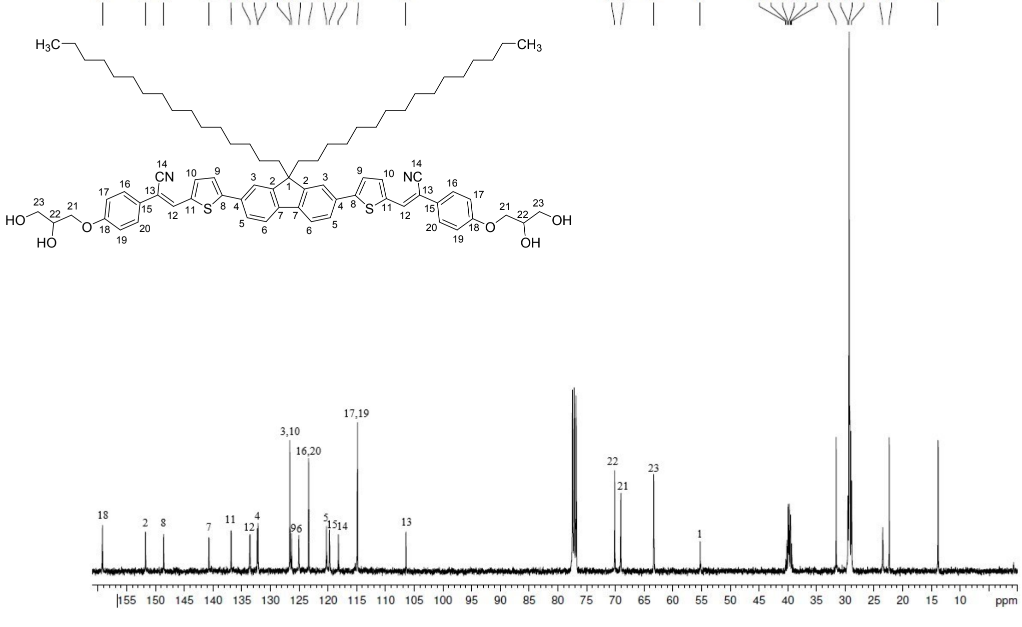


Fig. S19 ^{13}C NMR spectrum of **FT/16**.

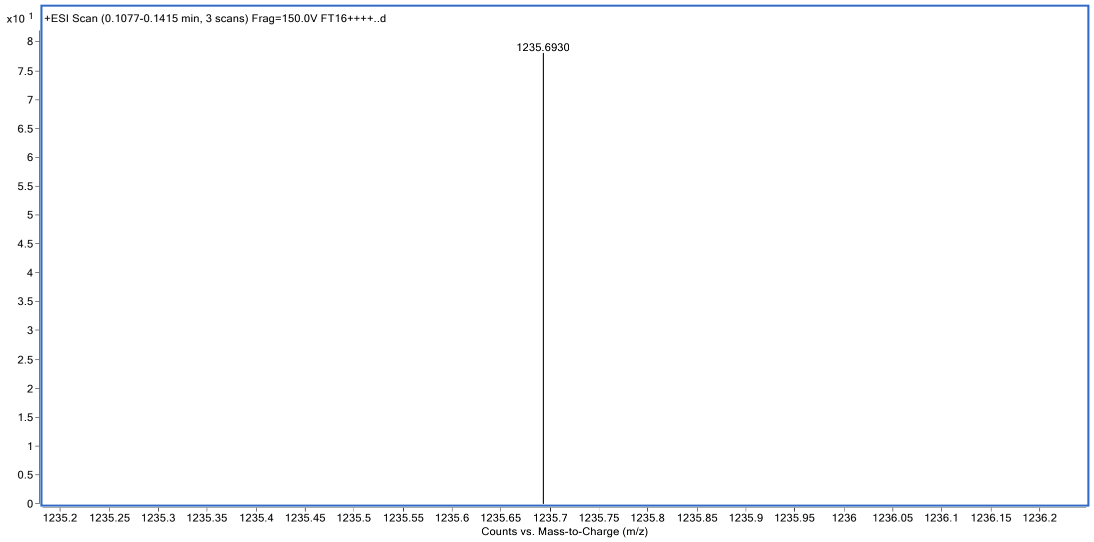


Fig. S20 ESI-TOF-MS spectrum of **FT/16**.

3. References

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