Electronic Supplementary Information

Phase-Dependent Photoluminescent Discotic Liquid Crystal Bearing Graphdiyne Substructure

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1. Materials

All the starting reagents were purchased from commercial sources and used as received without further purification except where noted. Dichloromethane (CH_2Cl_2) were distilled from calcium hydride under N_2 atmosphere. All the experiments were carried out in oven-dried glassware using the standard Schlenk line technique under the protection of N_2 atmosphere.

2. Characterizations

All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker HW600 MHz spectrometer (AVANCE AV-600), or a Bruker HW300 MHz spectrometer (AVANCE AV-300), referenced to $CHCl_3$, DMSO-d_6 or $(CD_3)_2CO$. A liquid chromatography quadrupole time-of-flight mass (LC-QTOF-MS) instrument was adopted to obtain high-resolution mass spectra (HRMS) data. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on an ultrafleXtreme MALDI TOF/TOF spectrometry (Bruker Instruments) with HPLC grade THF as the solvent. Elemental analyses were performed using an elementar vario EL cube.

Thermogravimetric analysis (TGA) was carried out by using Perkin-Elmer TGA7 under nitrogen atmosphere at a heating rate of 10 °C/min from 25 to 800 °C. The mesomorphic properties of dodecadehydrotribenzo[18]annulene-core liquid crystal (LC) monomer were investigated by variable-temperature polarized optical microscope (POM) and differential scanning calorimetry (DSC). POM observations of the liquid

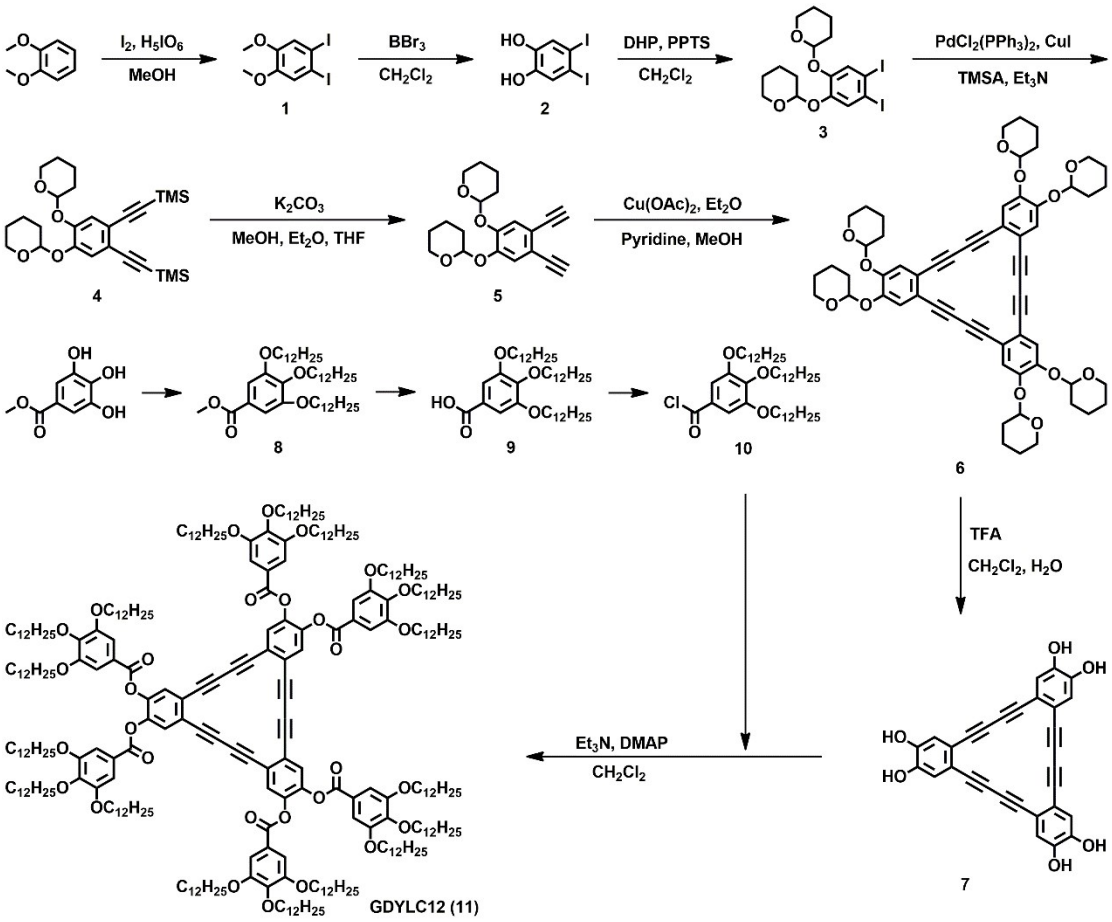
crystalline textures of dodecadehydrotribenzo[18]annulene-core LC monomer were performed on a Leica DM2700P microscope equipped with a THMS600 hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software. DSC spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) from −50 °C to 100 °C at a rate of 10 °C/min under a nitrogen atmosphere. X-ray scattering experiments were performed on Anton Paar SAXS point 2.0 with a TCStage 300 temperature controller. The specimen (in a TCS sample holder) was placed in the sample chamber, which was evacuated to a pressure below 3 Mbar in order to minimize the atmospheric scattering of the X-ray beam. All XRD Data were collected at a sample-to-detector distance (SDD) of 79 mm using an incident X-ray beam (50.047 keV, 0.999 mA, 1.542 Å wavelength).

Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu UV-2700 spectrophotometer equipped with a PTC-348WI temperature controller with the wavelength ranging from 190 nm to 800 nm. Steady-state fluorescence spectra were recorded on a Hitachi F-4700 fluorescence spectrophotometer equipped with TC 1 temperature controller. Time-resolved fluorescence measurements were carried out on the Fluorolog spectrophotometer using 340 nm nano-LED source.

Cyclic voltammetry (CV) experiments were conducted by using a CHI620E (Shanghai Chenhua Corporation) electrochemical workstation at room temperature. Following the literature protocol, compound **7** and GDYLC12 were completely dissolved in anhydrous chloroform (conc. = 10 mg/mL) respectively. The two uniform solutions were spin-coated on clean ITO substrates to form two films, which were

allowed to evaporate chloroform completely to give dry compound **7** and GDYLC12 films. The CV system used the sample-coated ITO film as a working electrode, platinum plate as a counter electrode and Ag/Ag^{+} as a reference electrode. Meanwhile, an acetonitrile solution of tetrabutylammonium hexafluorophosphate (0.1 M) was used as an electrolyte solution, and ferrocenium/ferrocene (Fc/Fc^{+}) was used as an internal standard compound ($E_{Fc/Fc+}$ = 0.11 V).

3. Synthetic procedures



Scheme S1. Synthetic route of the dodecadehydrotribenzo[18]annulene-core discotic liquid crystal monomer.

Preparation of 1,2-diiodo-4,5-dimethoxybenzene (1).[1]

In a 500 mL three-neck round-bottom flask, to a well-stirred solution of H_5IO_6 (11.40 g, 50.0 mmol) in MeOH (75 mL) was added iodine (25.38 g, 100.0 mmol). The reaction mixture was stirred vigorously for 10 min. 1,2-Dimethoxybenzene (17.27 g, 125.0 mmol) was then added into above solution. After stirring at 70 ℃ for 5 h, the hot reaction solution was poured into a saturated aqueous $Na_2S_2O_3$. The obtained precipitate was collected by filtration and washed with MeOH to give 1,2-diiodo-4,5-dimethoxybenzene (**1**) as a white solid (41.42 g, 85 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.24 (s, 2H), 3.83 (s, 6H).

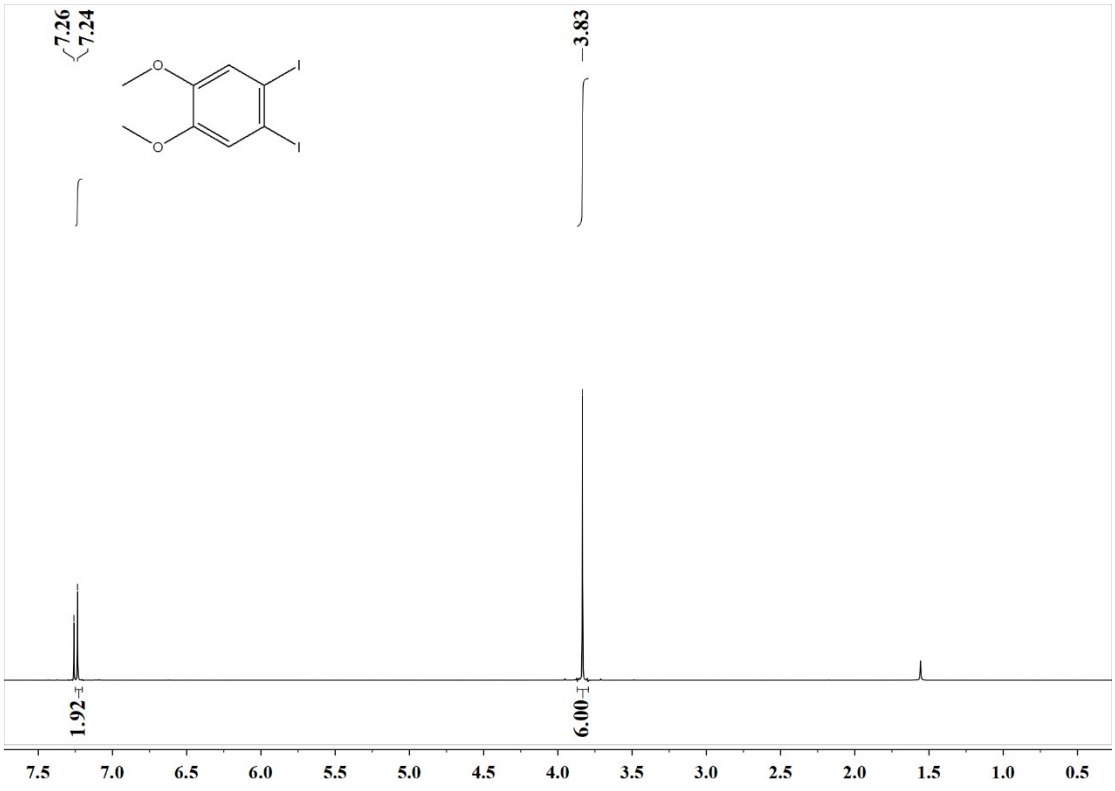


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

Preparation of 1,2-dihydroxy-4,5-diiodobenzene (2).[2]

In a 1000 mL three-neck round-bottom flask, 1,2-diiodo-4,5-dimethoxybenzene (**1**) (23.98 g, 61.5 mmol) was dissolved in anhydrous CH_2Cl_2 (450 mL). The resulting solution was cooled to −78 °C. Boron tribromide (1.0 M in CH_2Cl_2, 154 mL, 153.8 mmol) was slowly added into the above solution. After stirring at −78 °C for 2 h, the reaction mixture was heated to 0 °C and stirred for another 3 h. The reaction mixture was then cooled back to −78 °C again and quenched by methanol (450 mL). After heating to room temperature, the reaction solution was stirred for another 5 h. The resulting mixture was concentrated and purified by column chromatography using hexane/EtOAc as the eluent to give 1,2-dihydroxy-4,5-diiodobenzene (**2**) as a white solid (21.81 g, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.35 (s, 2H), 5.43 (s, 2H).

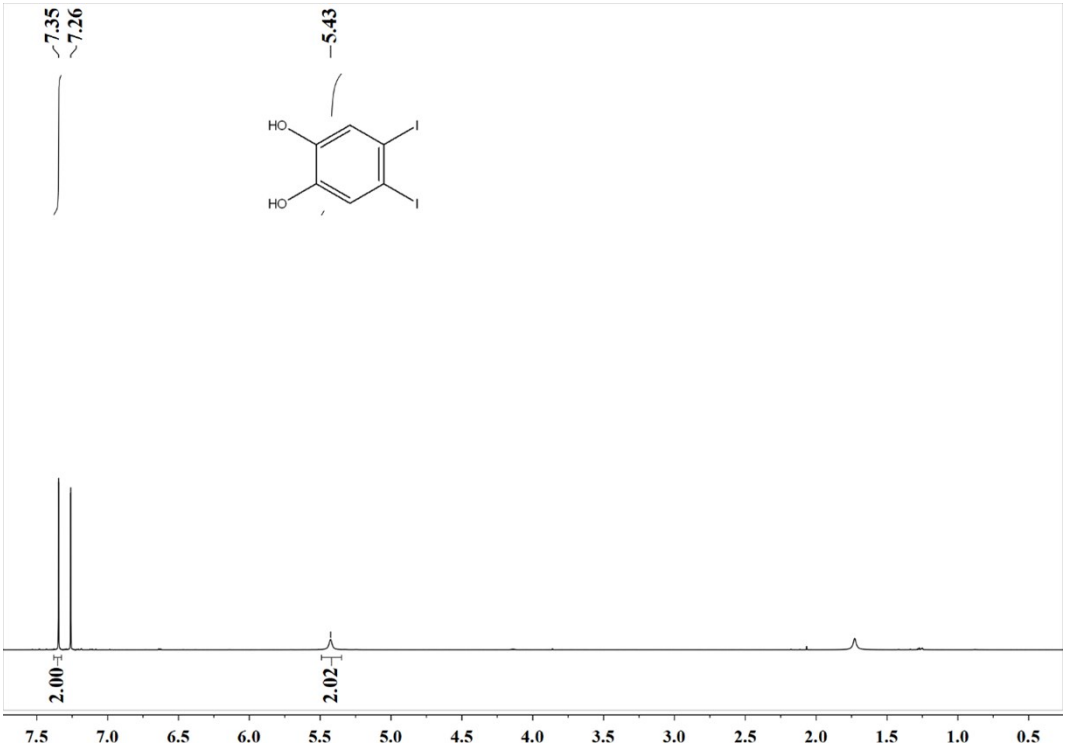


Figure S2. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

Preparation of compound 3.

In a 250 mL three-neck round-bottom flask, to a solution of 1,2-dihydroxy-4,5-diiodobenzene (**2**) (20.01 g, 55.3 mmol) in CH_2Cl_2 (100 mL) was added pyridinium *p*-toluenesulfonate (3.47 g, 13.8 mmol) and 3,4-dihydro-*2H*-pyran (27.68 g, 329.0 mmol). The reaction solution was stirred at room temperature for 2 h. The resulting mixture was concentrated and purified by column chromatography using hexane/EtOAc (v/v = 10/1) as the eluent to give compound **3** as a white solid (21.11 g, 72 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.56 (d, *J* = 4.44 Hz, 2H), 5.59 (t, *J* = 2.64 Hz, 2H), 3.92-3.88 (m, 2H), 3.63-3.61 (m, 2H), 1.97-1.84 (m, 6H), 1.71-1.59 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 148.19, 147.98, 98.37, 98.19, 97.77, 97.39, 62.03, 61.90, 30.26, 30.23, 25.26, 25.25, 18.49, 18.39. HRMS (ESI) m/z calcd for $C_{16}H_{20}I_2O_4$ $[M+Na]^+$: 552.93486, found 552.93582.

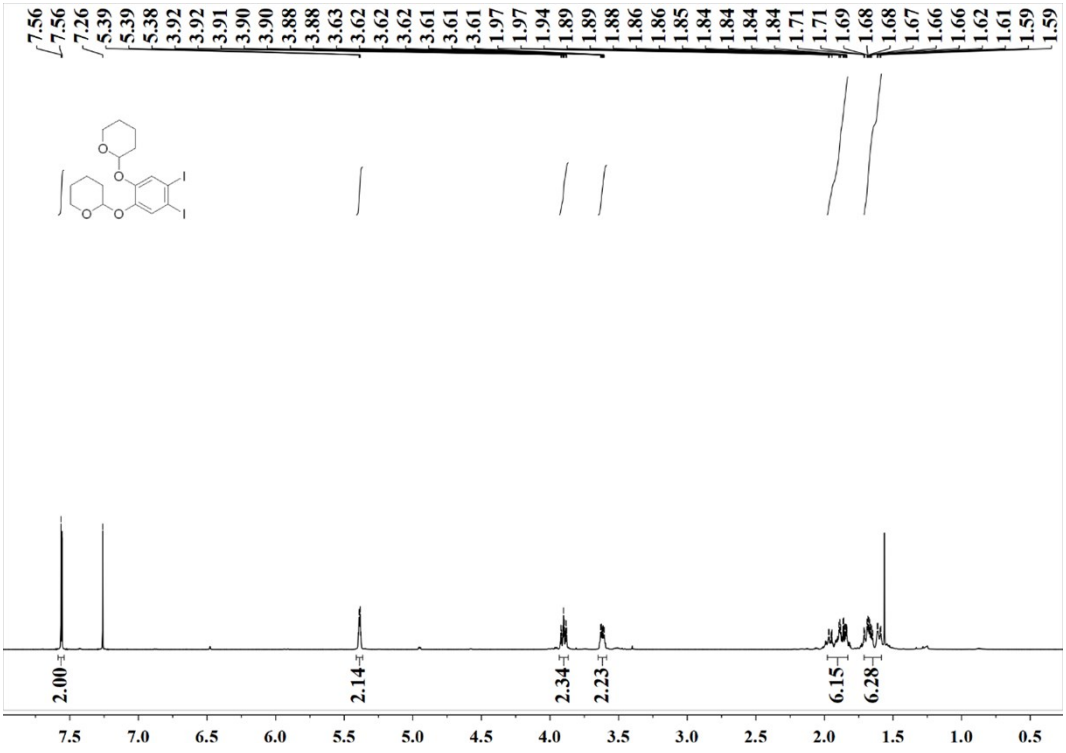


Figure S3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

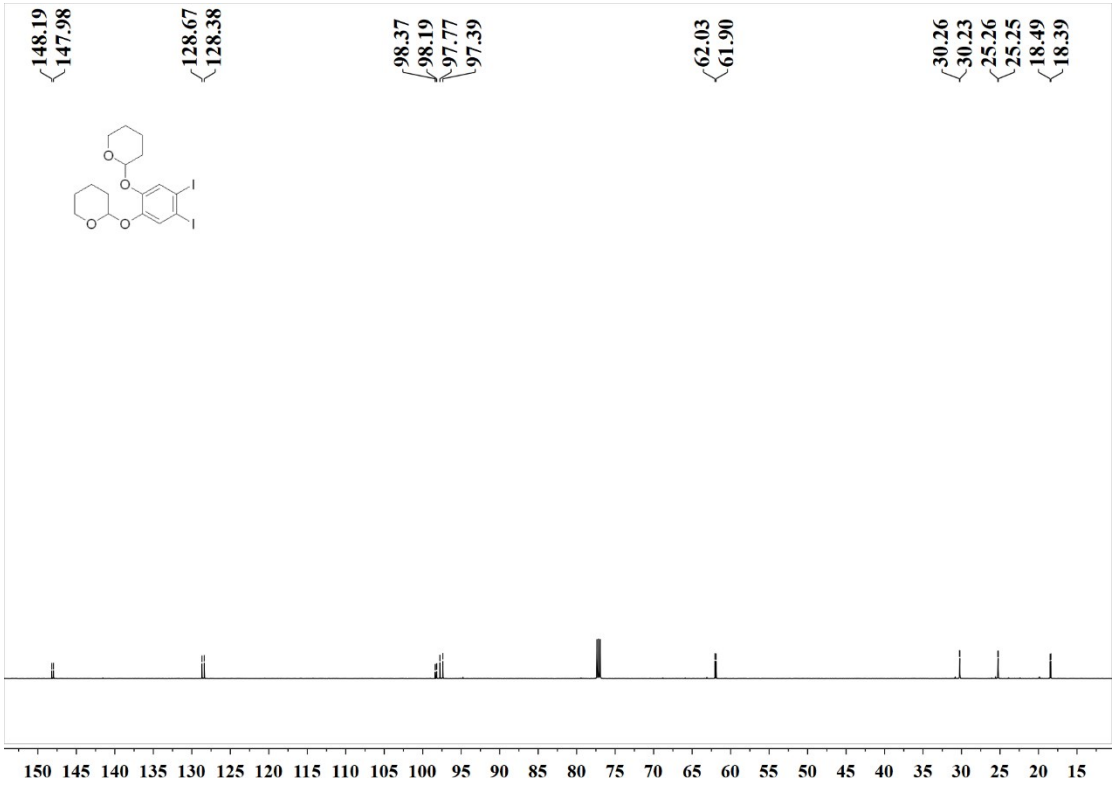


Figure S4. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

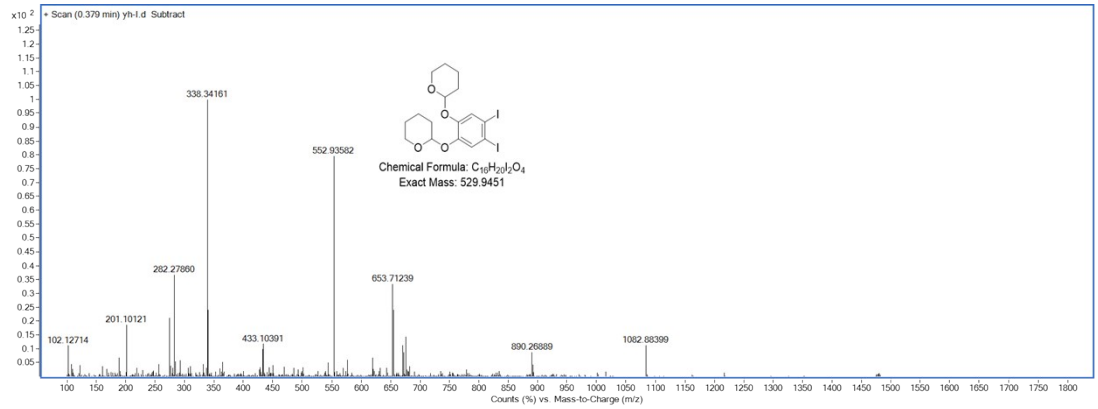


Figure S5. HRMS spectrum of compound **3**.

Preparation of compound 4.

In a 250 mL three-neck round-bottom flask, to a solution of compound **3** (18.40 g, 34.7 mmol) in triethylamine (100 mL) was added $PdCl_2(PPh_3)_2$ (487 mg, 0.7 mmol), CuI (267 mg, 1.4 mmol) and trimethylsilylacetylene (11.2 mL, 79.1 mmol). The

reaction mixture was stirred at 50 ^{0}C for 18 h. The resulting solution was extracted with H_2O/EtOAc (v/v = 1/1) for three times (3 × 100 mL). The combined organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated and purified by column chromatography using hexane/CH_2Cl_2 (v/v = 10/1) as the eluent to give compound **4** as a white solid (15.52 g, 95 % yield). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ ppm 7.20 (d, *J* = 1.80 Hz, 2H), 5.56-5.55 (m, 2H), 3.88-3.84 (m, 2H), 3.59-3.58 (m, 2H), 2.02-1.96 (m, 2H), 1.90-1.83 (m, 4H), 1.70-1.66 (m, 4H), 1.61-1.58 (m, 2H), 0.24(s, 18H). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ ppm 148.82, 148.63, 121.88, 121.60, 120.77, 120.64, 104.49, 104.44, 97.99, 97.65, 97.27, 97.21, 62.35, 62.23, 31.02, 30.98, 26.08, 26.06, 19.23, 19.17, 0.35. HRMS (ESI) m/z calcd for $C_{26}H_{38}O_4Si_2$ $[M+Na]^+$: 493.22063, found 493.22156.

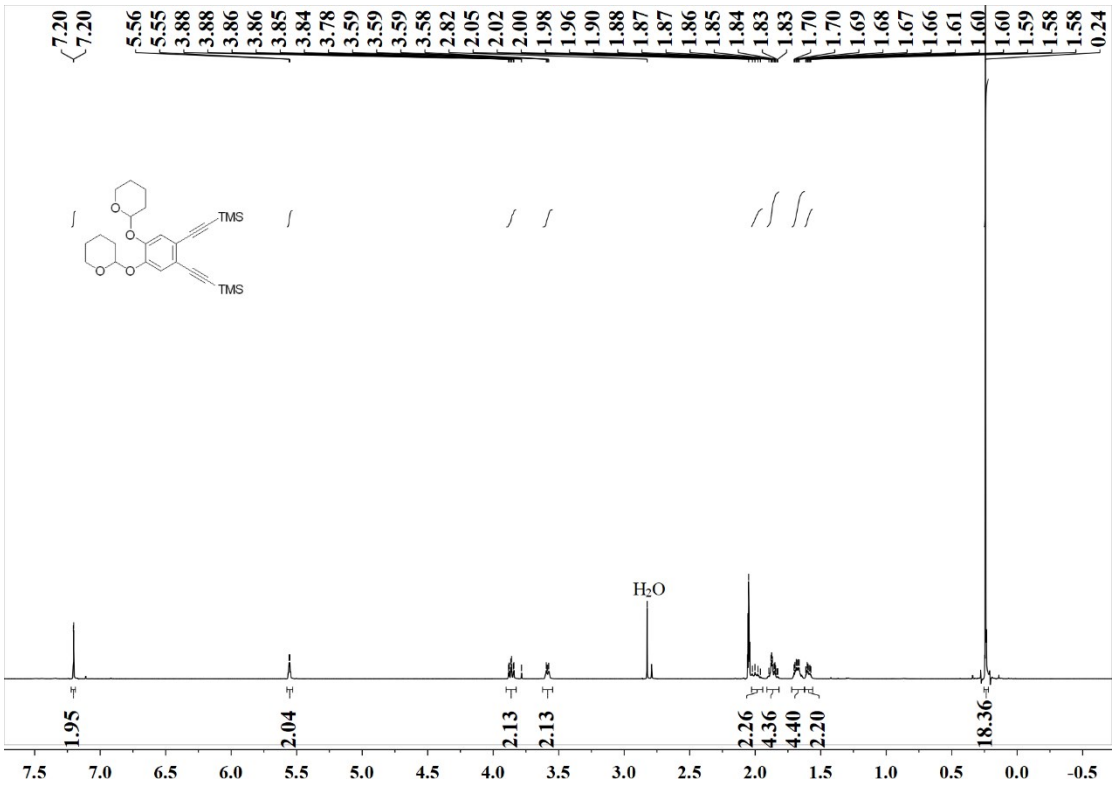


Figure S6. ^{1}H NMR spectrum of compound **4** in $(CD_3)_2CO$.

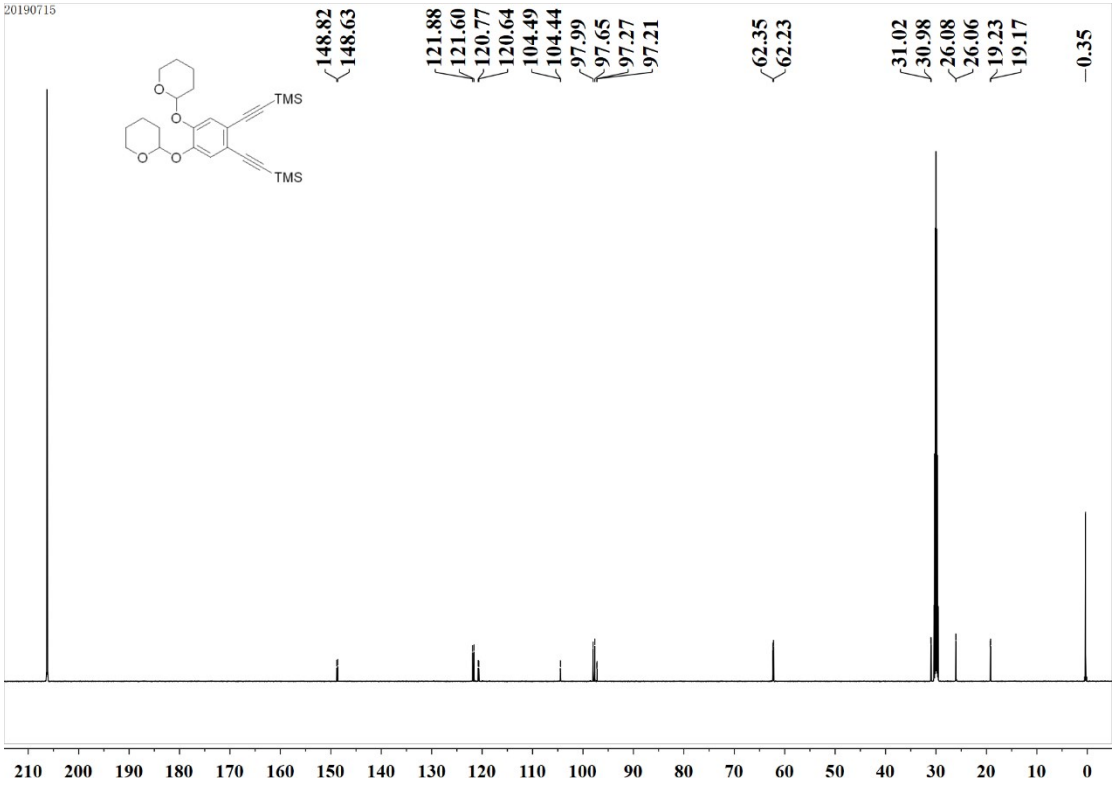


Figure S7. ^{13}C NMR spectrum of compound **4** in $(CD_3)_2CO$.

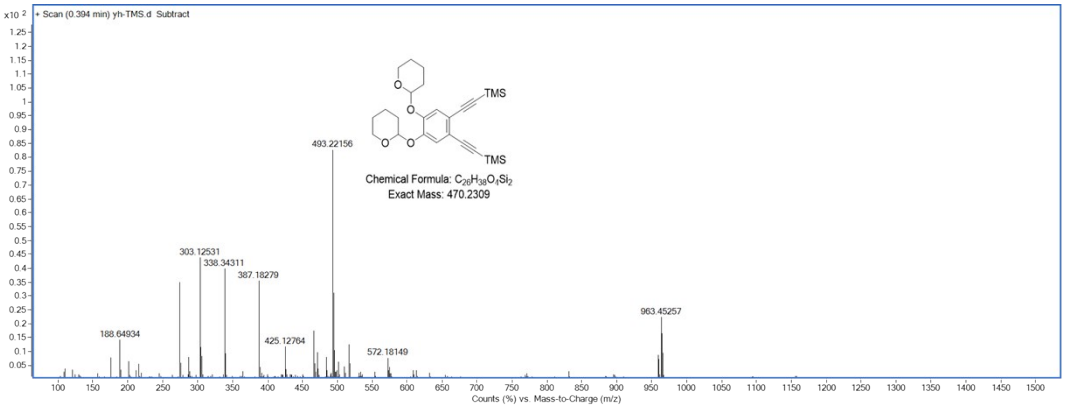


Figure S8. HRMS spectrum of compound **4**.

Preparation of compound 5.

In a 250 mL three-neck round-bottom flask, to a solution of compound **4** (14.31 g, 30.4 mmol) in MeOH/Et_2O/THF (v/v/v = 2/1/1, 160 mL) was added K_2CO_3 (13.4 g, 97.3 mmol). The reaction mixture was stirred at room temperature for 3 h. The resulting

mixture was concentrated and extracted with H_2O/Et_2O (v/v = 1/1) for three times (3 × 200 mL). The organic phase was dried over Na_2SO_4 and then filtered. The filtrate was concentrated and purified by column chromatography using hexane/CH_2Cl_2 (v/v = 10/1) as the eluent to give compound **5** as a brown solid (8.04 g, 81 % yield). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ ppm 7.26 (d, *J* = 1.44 Hz, 2H), 5.56-5.55 (m, 2H), 3.90-3.86 (m, 2H), 3.77 (d, *J* = 2.64, 2H), 3.60-3.58 (m, 2H), 2.05-1.96 (m, 2H), 1.89-1.85 (m, 4H), 1.71-1.66 (m, 4H), 1.61-1.58 (m, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ ppm 148.90, 148.73, 122.39, 122.14, 120.11, 119.98, 98.10, 97.81, 82.67, 82.64, 81.84, 81.79, 62.45, 62.33, 31.00, 30.97, 26.04, 26.03, 19.30, 19.23. HRMS (ESI) m/z calcd for $C_{20}H_{22}O_4$ $[M+Na]^+$: 349.14158, found 349.13964.

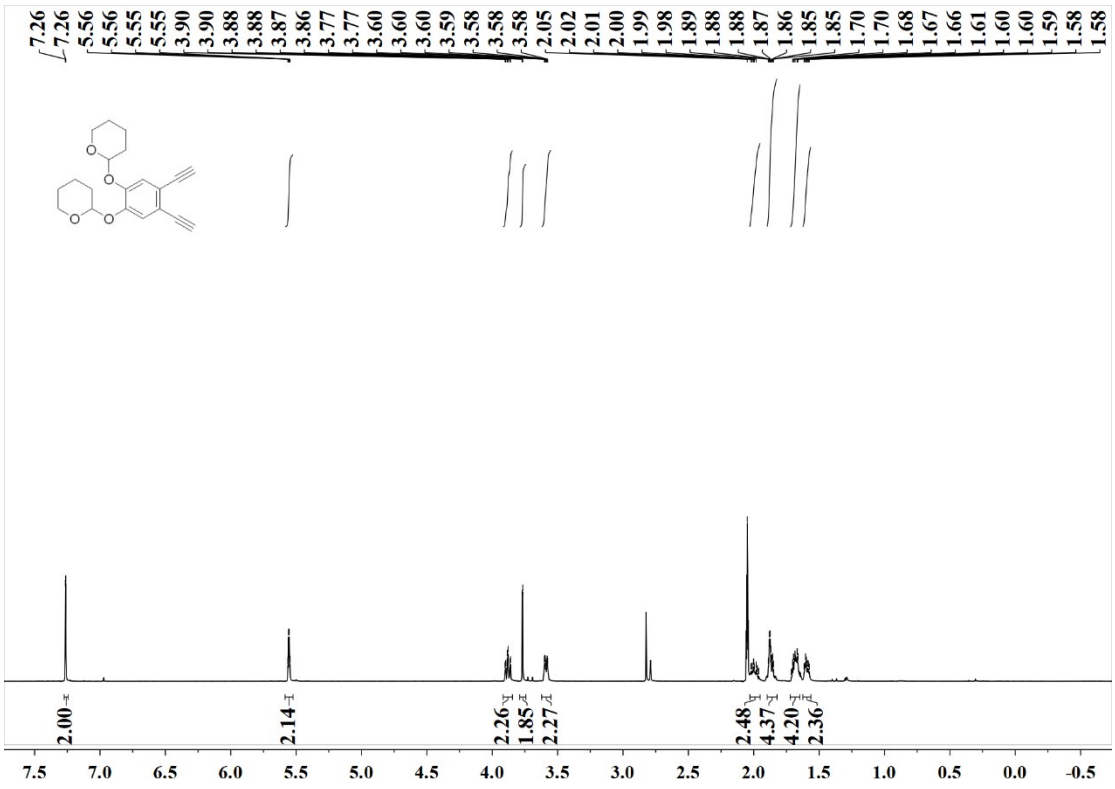


Figure S9. ^{1}H NMR spectrum of compound **5** in $(CD_3)_2CO$.

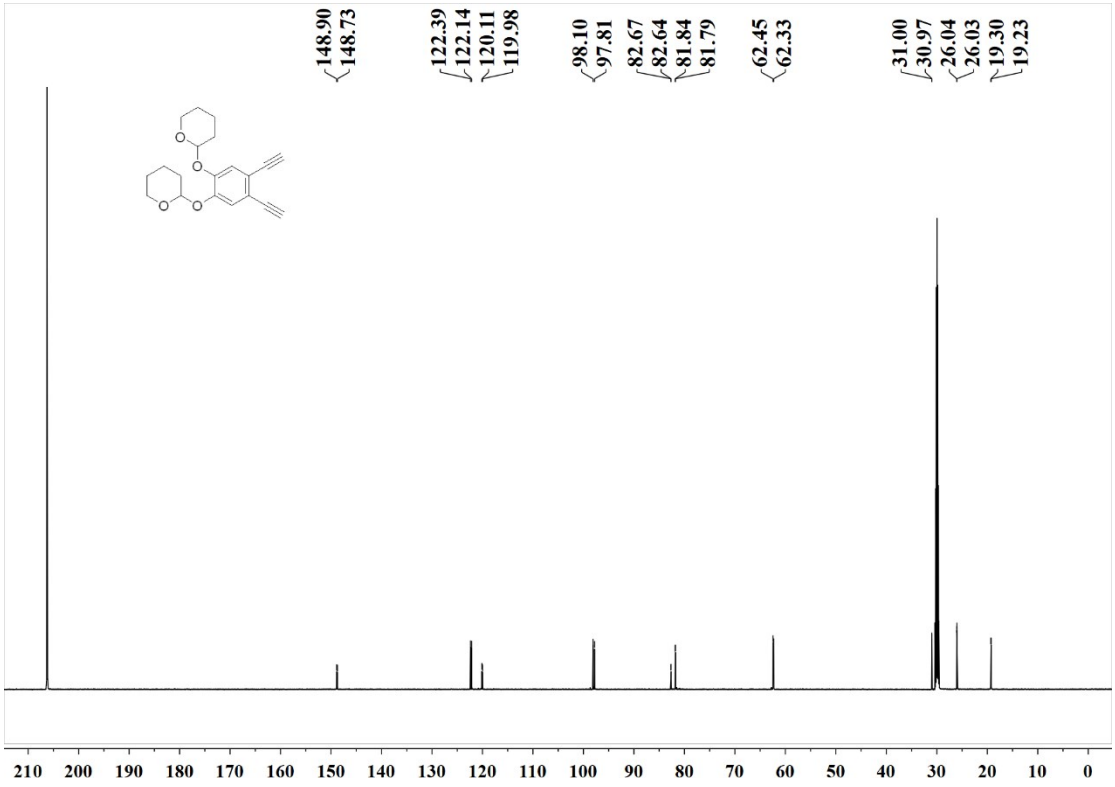


Figure S10. ^{13}C NMR spectrum of compound **5** in $(CD_3)_2CO$.

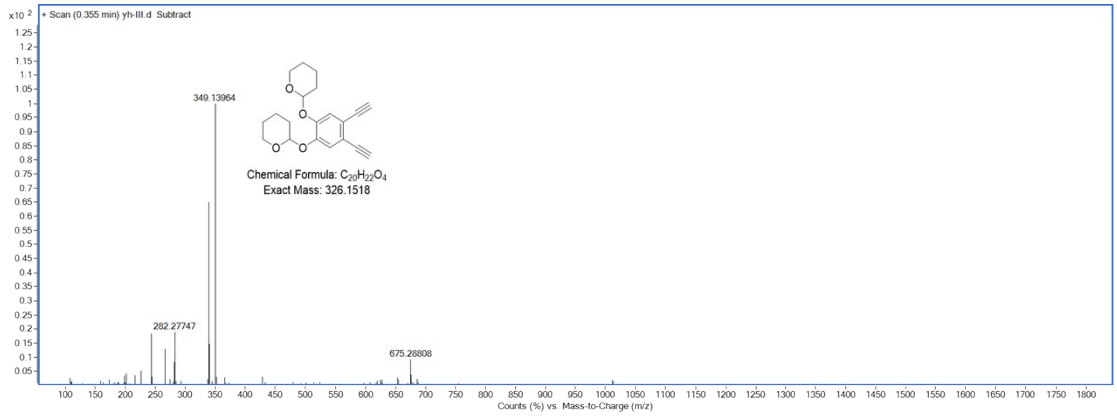


Figure S11. HRMS spectrum of compound **5**.

Preparation of compound 6.

In a 1000 mL three-neck round-bottom flask, to a solution of $Cu(OAc)_2$ (8.18 g, 41.0 mmol) in MeOH/Et_2O/THF (v/v/v = 1/5/5, 550 mL) was added dropwise a solution of compound **5** (3.43 g, 10.5 mmol) in MeOH/pyridine (v/v = 1/1, 120 mL). The

reaction mixture was stirred at 60 °C for 48 h. The resulting solution was concentrated and purified by column chromatography using hexane/CH_2Cl_2 (v/v = 1/1) as the eluent to give compound **6** as a yellow solid (2.25 g, 22 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.26 (dd, *J* = 2.76 Hz, 6H), 5.49-5.47 (m, 6H), 3.93 (t, *J* = 10.38 Hz, 6H), 3.66-3.63 (m, 6H), 2.01-1.88 (m, 18H), 1.74-1.60 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 148.21, 147.96, 121.30, 120.97, 119.83, 119.68, 97.69, 97.65, 97.26, 97.22, 94.58, 80.78, 64.01, 62.20, 62.04, 32.03, 30.30, 30.27, 29.84, 25.34, 25.25, 20.36, 18.63, 18.52. MS (MODLI-TOF) m/z calcd for $C_{60}H_{60}O_{12}$ $[M+H_2O+H]^+$: 991.427, found 991.652.

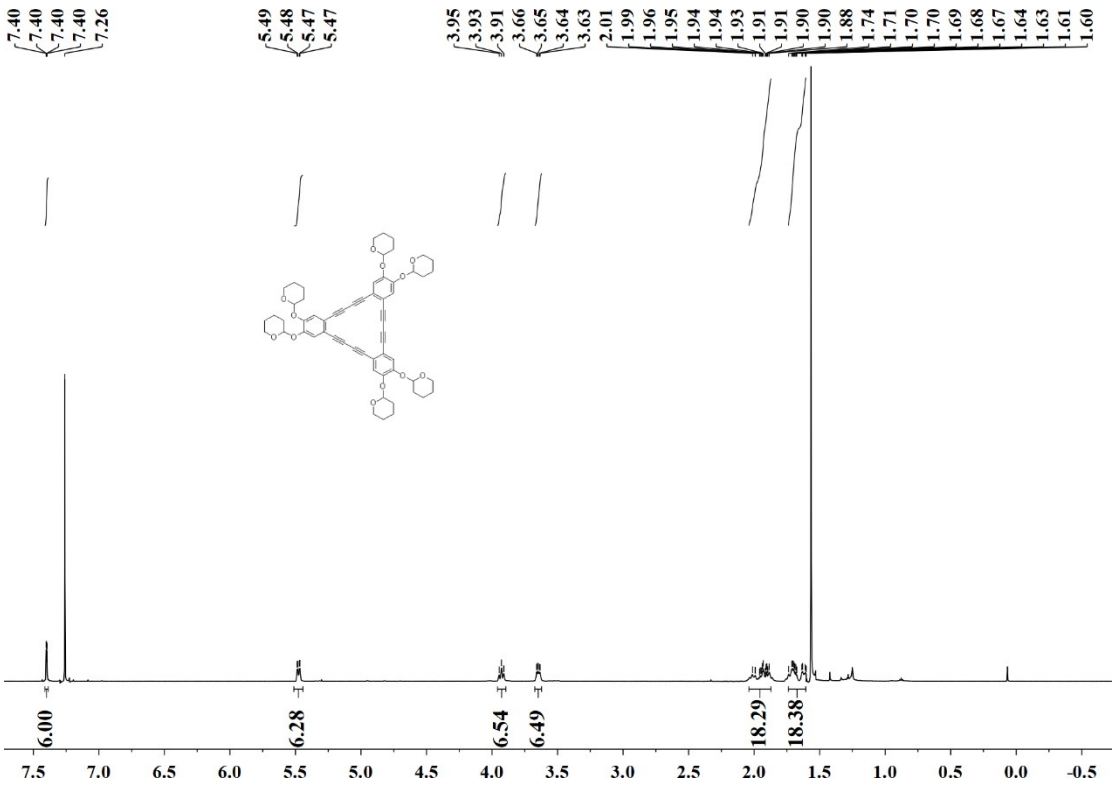


Figure S12. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

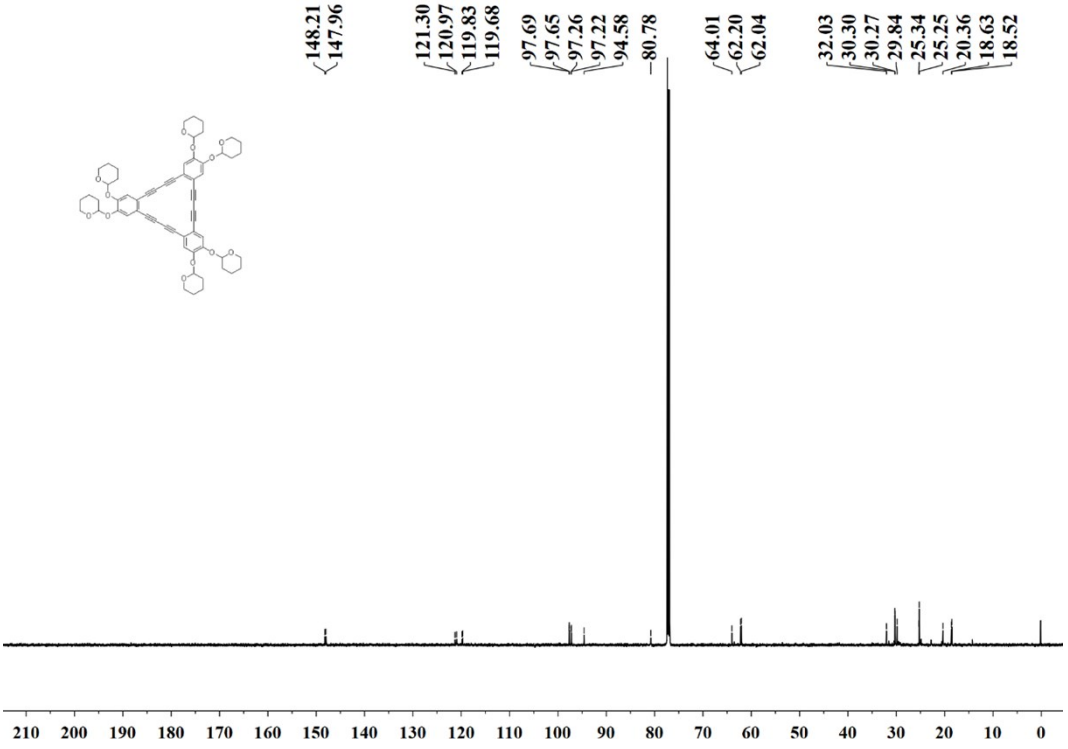


Figure S13. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

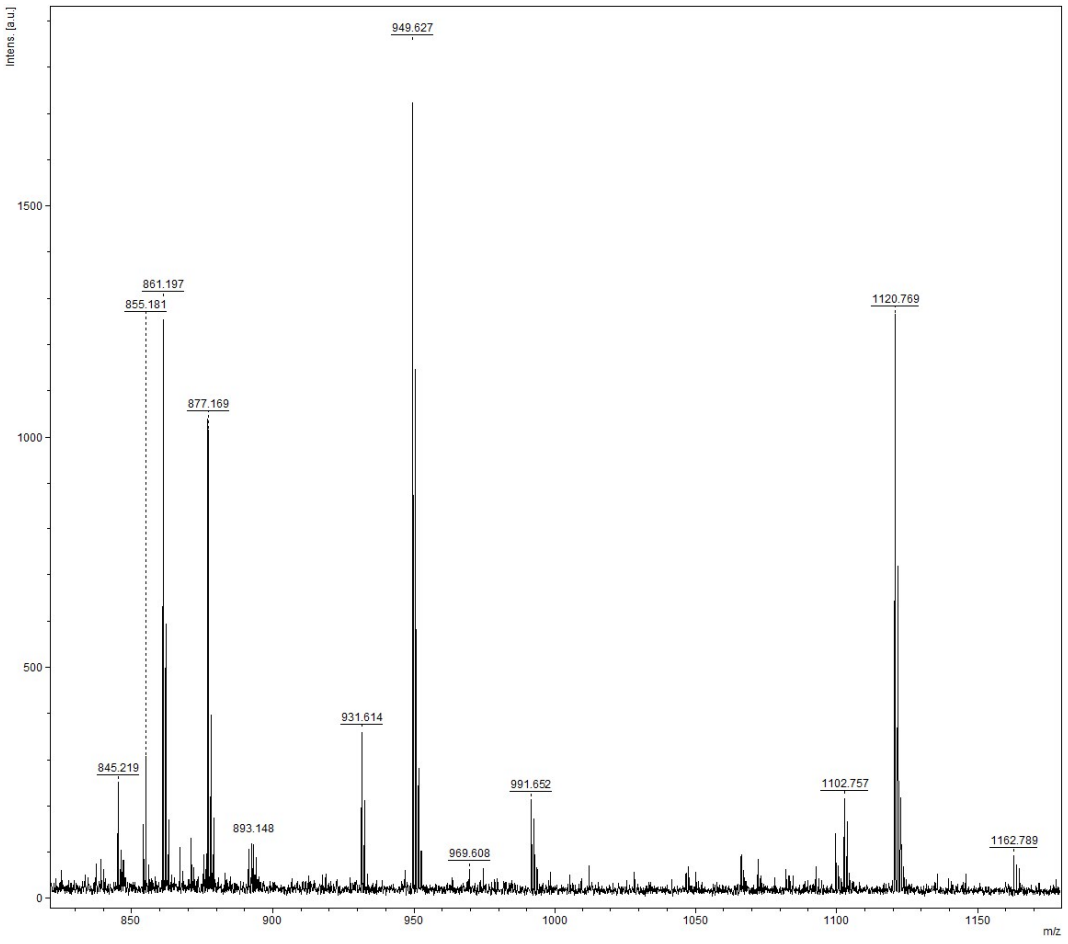


Figure S14. MS spectrum of compound **6**.

Preparation of compound 7.

In a 250 mL three-neck round-bottom flask, to a solution of compound **6** (0.97 g, 1.0 mmol) in CH_2Cl_2/H_2O (v/v = 10/1, 132 mL) was added dropwise trifluoroacetic acid (4 mL). The reaction mixture was stirred at room temperature for 2 h. The resulting solution was concentrated and then washed with H_2O (20 mL), hexane (20 mL) and ethanol (20 mL) in turn to give compound **7** as a green solid (0.37 g, 78 % yield). ^{1}H NMR (600 MHz, DMSO-d_6): δ ppm 10.20 (s, 6H), 7.09 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6): δ ppm 147.70, 118.86, 115.51, 81.02, 75.64. HRMS (ESI) m/z calcd for $C_{30}H_{12}O_6$ $[M-H]^-$: 467.05556, found 467.05783.

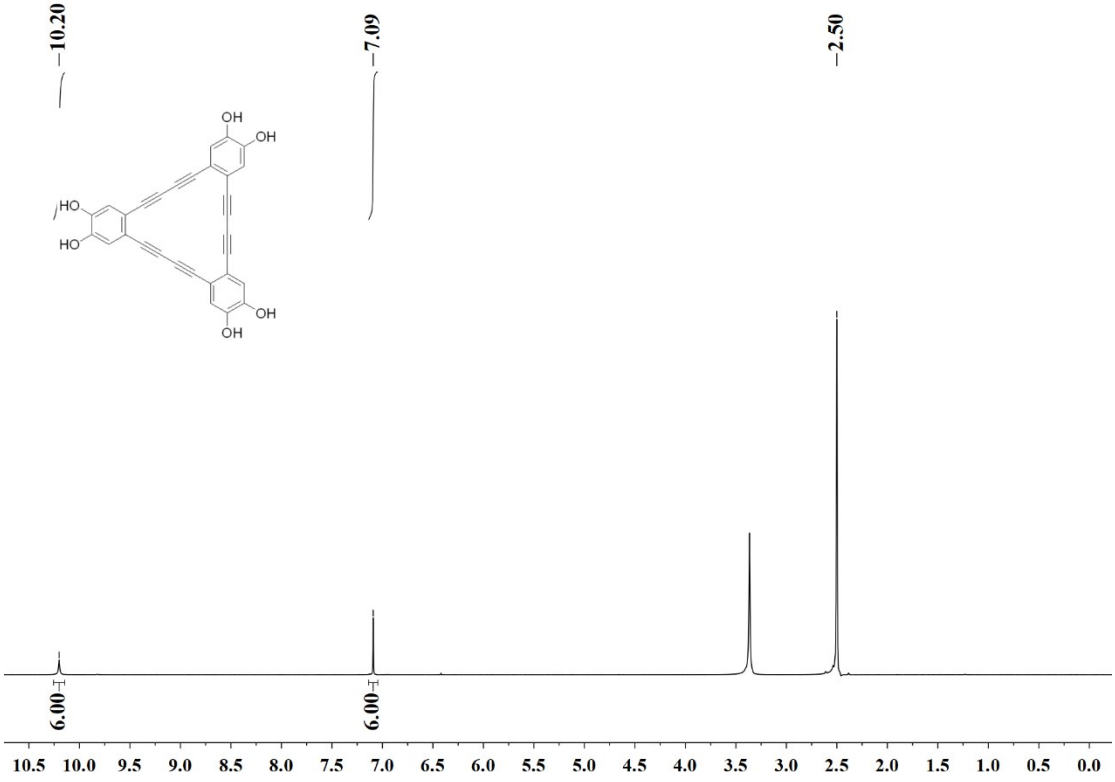


Figure S15. ^{1}H NMR spectrum of compound **7** in DMSO-d_6.

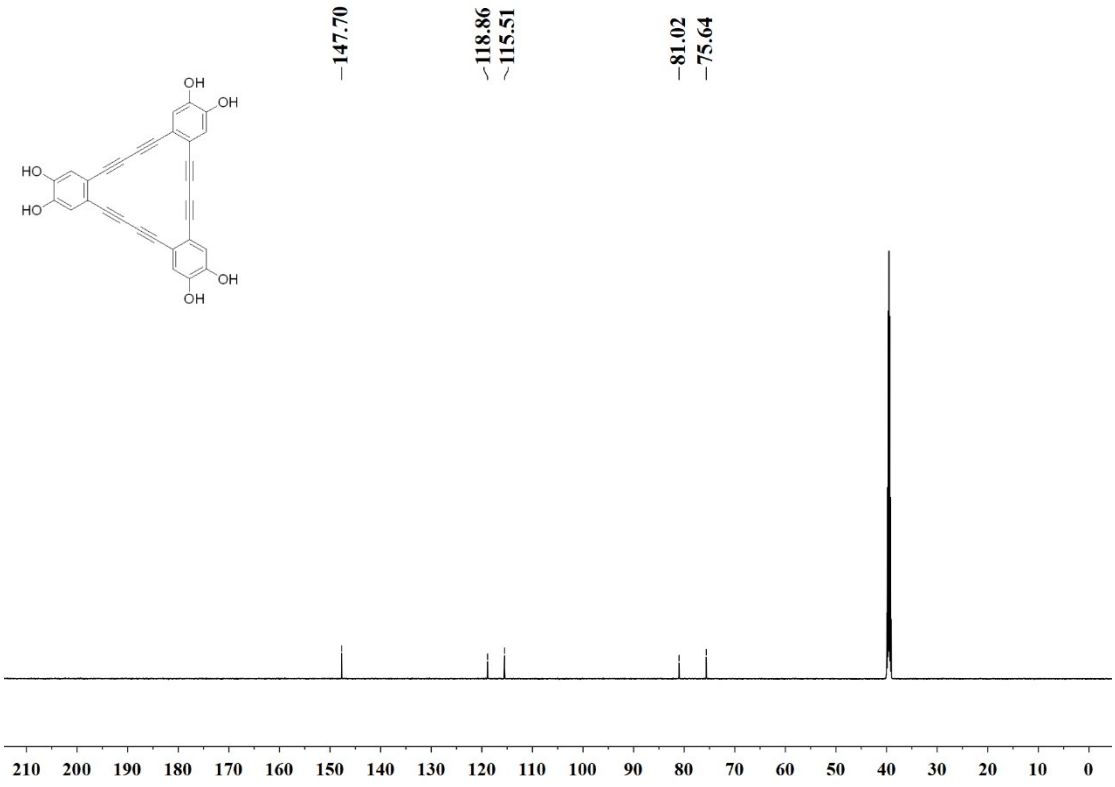


Figure S16. ^{13}C NMR spectrum of compound **7** in DMSO-d_6.

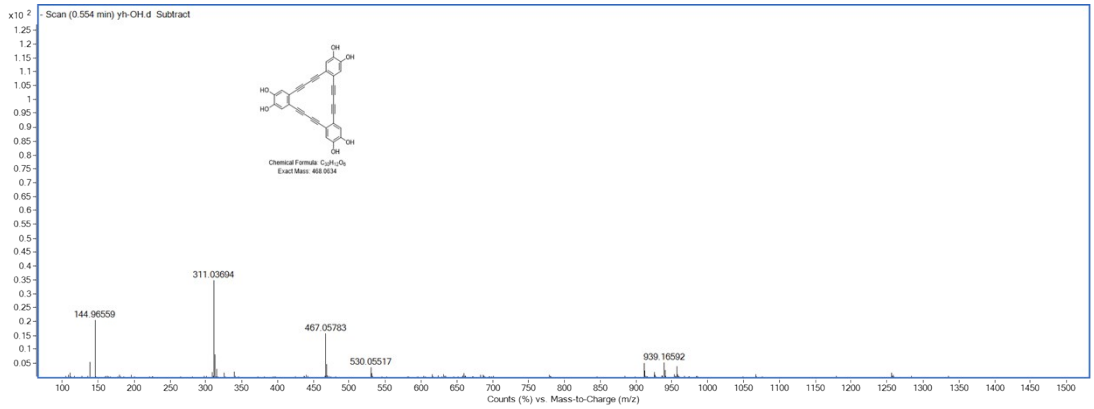


Figure S17. HRMS spectrum of compound **7**.

Preparation of 3,4,5-tris(dodecyloxy)methyl benzoate (8).

In a 1000 mL three-neck round-bottom flask, to a well-stirred solution of methyl gallate (20.00 g, 108.6 mmol) and potassium carbonate (90.06 g, 651.6 mmol) in DMF (500 mL) was slowly added 1-bromododecane (243.60 g, 977.4 mmol). The reaction

mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the resulting solution was extracted with H_2O/Et_2O (v/v = 1/1) for three times (3 × 300 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography using hexane/EtOAc (v/v = 10/1) as the eluent to give compound **8** as a light yellow oil (59.87 g, 80 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.25 (s, 2H), 4.02-3.99 (m, 6H), 3.89 (s, 3H), 1.83-1.72 (m, 4H), 1.49-1.44 (m, 4H), 1.29-1.26 (m, 52H), 0.88 (t, *J* = 6.78 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 167.09, 152.96, 142.47, 124.78, 108.09, 73.62, 69.29, 52.24, 32.09, 32.07, 30.47, 29.90, 29.88, 29.87, 29.85, 29.81, 29.78, 29.72, 29.54, 29.52, 29.44, 26.22, 26.20, 22.84, 14.26.

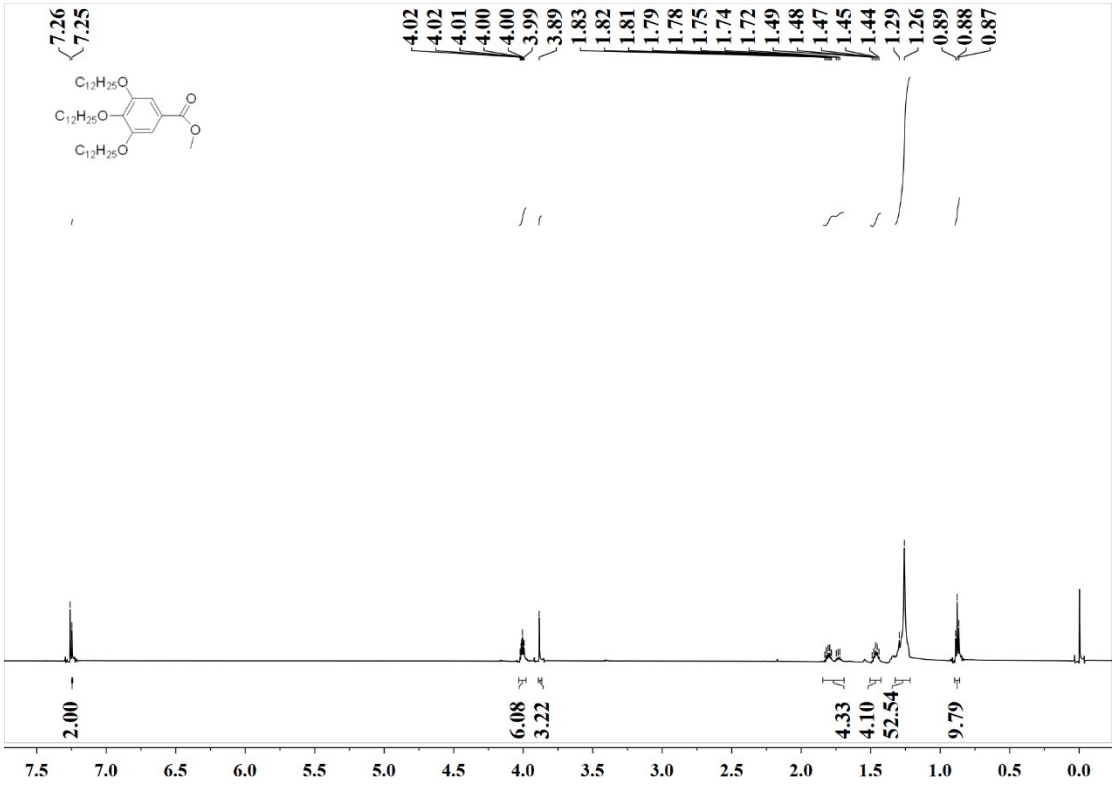


Figure S18. ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

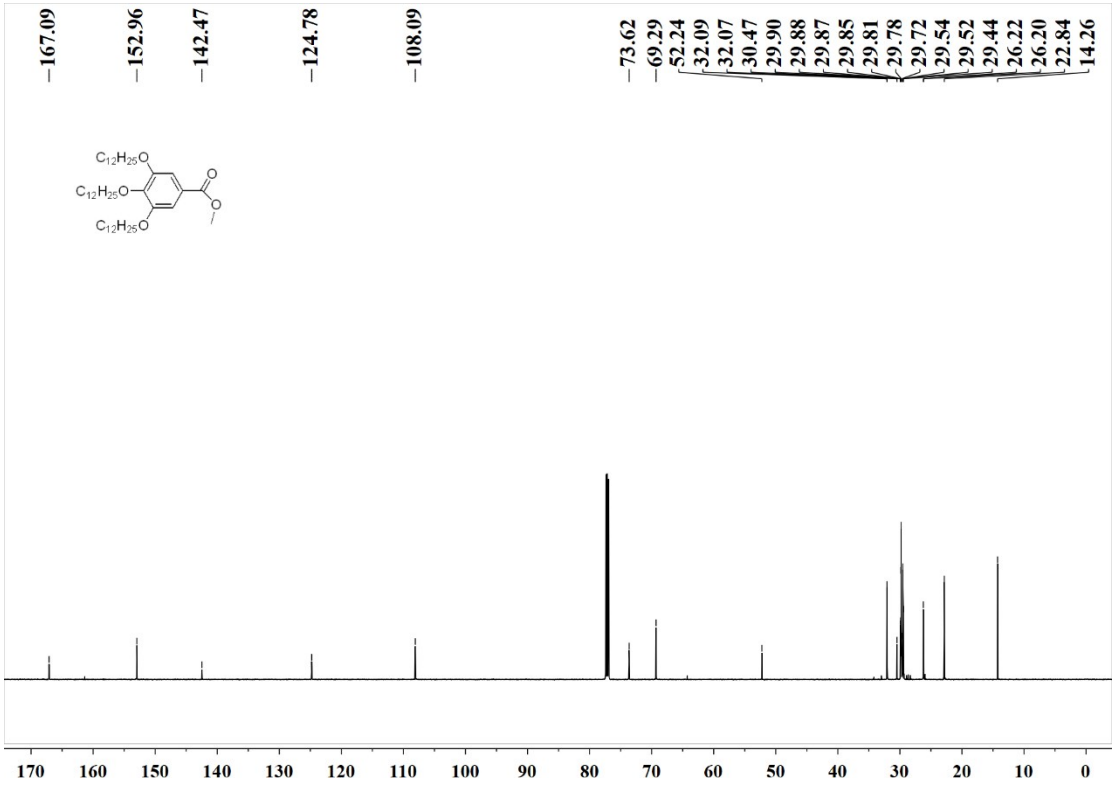


Figure S19. ^{13}C NMR spectrum of compound **8** in $CDCl_3$.

Preparation of 3,4,5-tris(dodecyloxy)benzoic acid (9).

In a 500 mL three-neck round-bottom flask, compound **8** (21.22 g, 30.8 mmol) and potassium hydroxide (13.82 g, 246.4 mmol) was dissolved in a mixed solvent of ethanol (150 mL) and H_2O (150 mL). The reaction mixture was stirred at 80 °C for 15 h. After cooling to room temperature, the resulting mixture was acidified to pH = 2 by diluted HCl solution and then the precipitate was collected by filtration. The precipitate was washed with H_2O (100 mL) and dried over $MgSO_4$. The crude compound was recrystallized from methanol for three times to give compound **9** as a white solid (17.41 g, 86.0 % yield). ^1H NMR (600 MHz, $CDCl_3$): δ ppm 7.32 (s, 2H), 4.04-4.01 (m, 6H), 1.84-1.80 (m, 4H), 1.77-1.72 (m, 2H), 1.50-1.45 (m, 4H), 1.36-1.26 (m, 48H), 0.88 (t, J = 6.90 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 172.16, 152.99, 143.27, 123.79,

108.67, 73.70, 69.32, 32.09, 32.08, 30.47, 29.90, 29.89, 29.88, 29.85, 29.82, 29.79, 29.71, 29.55, 29.52, 29.42, 26.23, 26.19, 22.84, 14.26.

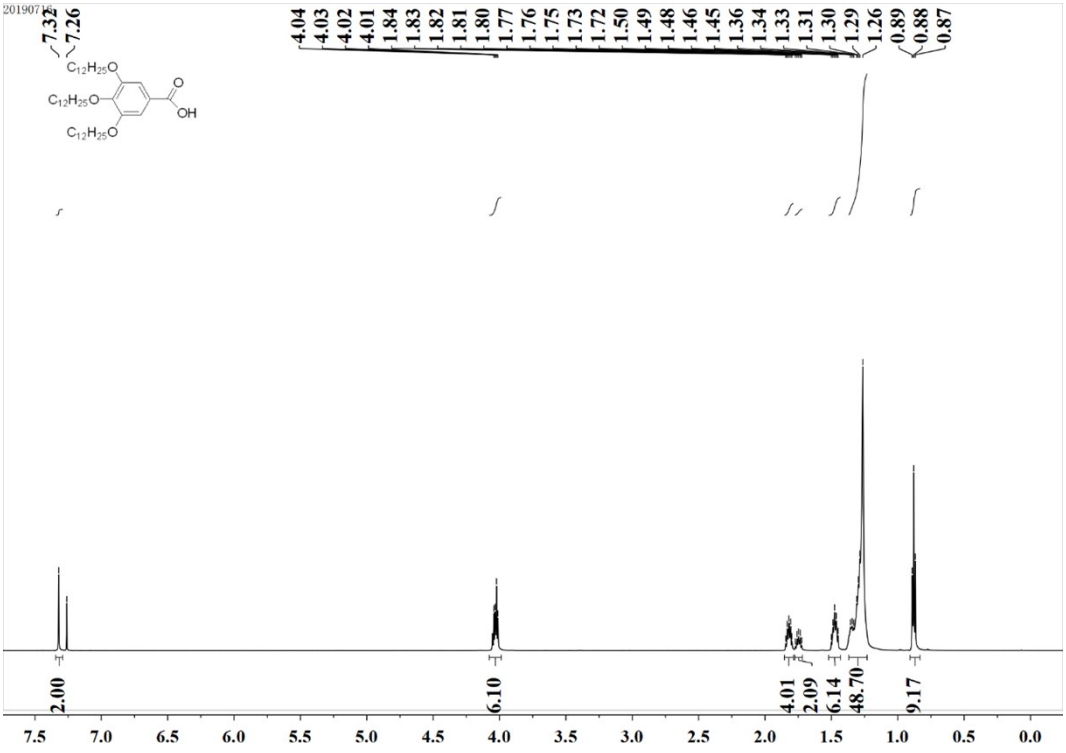


Figure S20. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

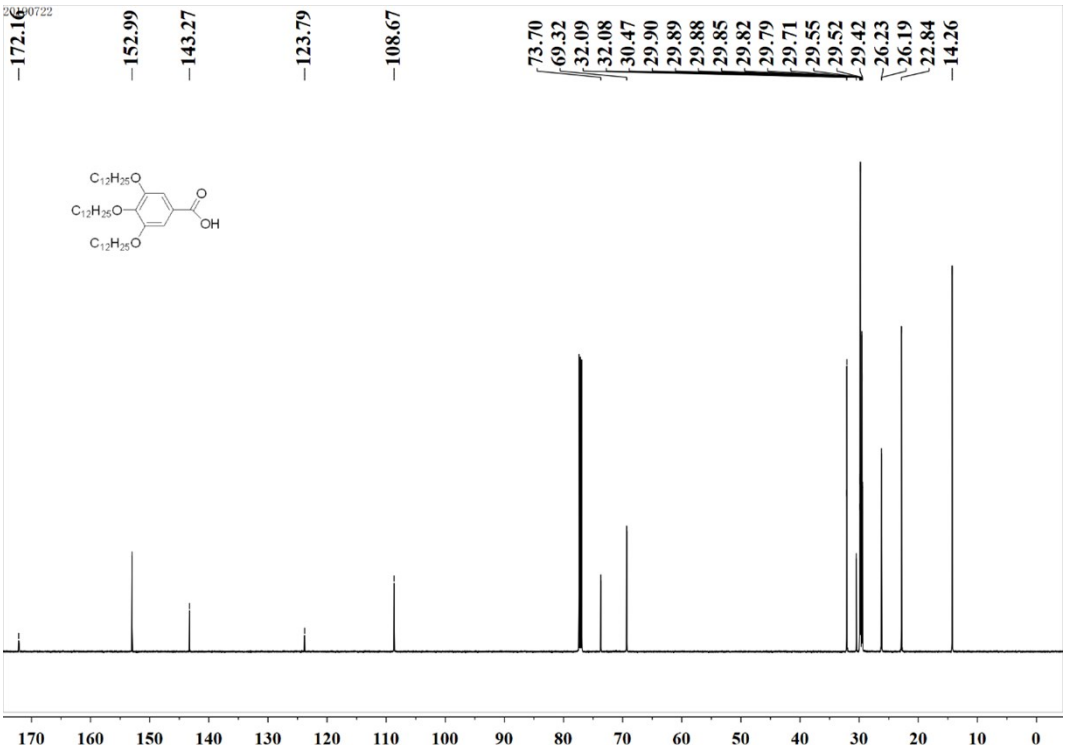


Figure S21. ^{13}C NMR spectrum of compound **9** in $CDCl_3$.

Preparation of 3,4,5-tris(dodecyloxy)benzoyl chloride (10).

In a 25 mL three-neck round-bottom flask, compound **9** (675 mg, 1.75 mmol) was dissolved in $SOCl_2$ (3.5 mL). The reaction mixture was stirred at 79 ℃ for 4 h. After cooling to room temperature, the reaction solution was dried under vacuum to removed solvent and excess $SOCl_2$ and give 3,4,5-tris(dodecyloxy)benzoyl chloride (**10**). The crude compound **10** was immediately used in the next reaction without further purification.

Preparation of GDYLC12.

In a 50 mL three-neck round-bottom flask, to a well-stirred solution of compound **7** (117 mg, 0.25 mmol) and 4-(N,N-dimethylamino)pyridine (31 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) was added triethylamine (304 mg, 3.00 mmol) and 3,4,5-tri(dodecyloxy)benzoyl chloride (**10**) (2.078 g, 3.00 mmol). The reaction mixture was stirred at 40 ℃ for 24 h. The resulting mixture was concentrated and purified by column chromatography using hexane/CH_2Cl_2 (v/v = 10/1) as the eluent to give the target compound GDYLC12 as a yellow oil (551 mg, yield: 50.0 %). ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.73 (s, 6H), 7.24 (s, 12H), 4.00 (m, 12H), 3.84 (m, 24H), 1.75-1.72 (m, 54H), 1.57-1.51 (m, 36H), 1.45-1.42 (m, 54 H), 1.33-1.26 (m, 216 H), 0.89-0.87 (m, 54H). ^{13}C NMR (151 MHz, $CDCl_3$): δ ppm 163.43, 152.95, 143.40, 143.30, 127.75, 123.65, 122.42, 108.47, 79.92, 78.70, 73.57, 69.13, 31.96, 30.42, 29.80, 29.79, 29.77, 29.72, 29.63, 29.51, 29.43, 29.42, 29.33, 26.16, 26.09, 22.72, 14.13. MS (MODLI-TOF) m/z calcd for $C_{288}H_{468}O_{30}$ $[M+Na]^+$: 4433.509, found 4433.832. Elemental

Analysis calcd (%) for $C_{288}H_{468}O_{30}$: C 78.42, H 10.69; found: C 78.09, H 10.74.

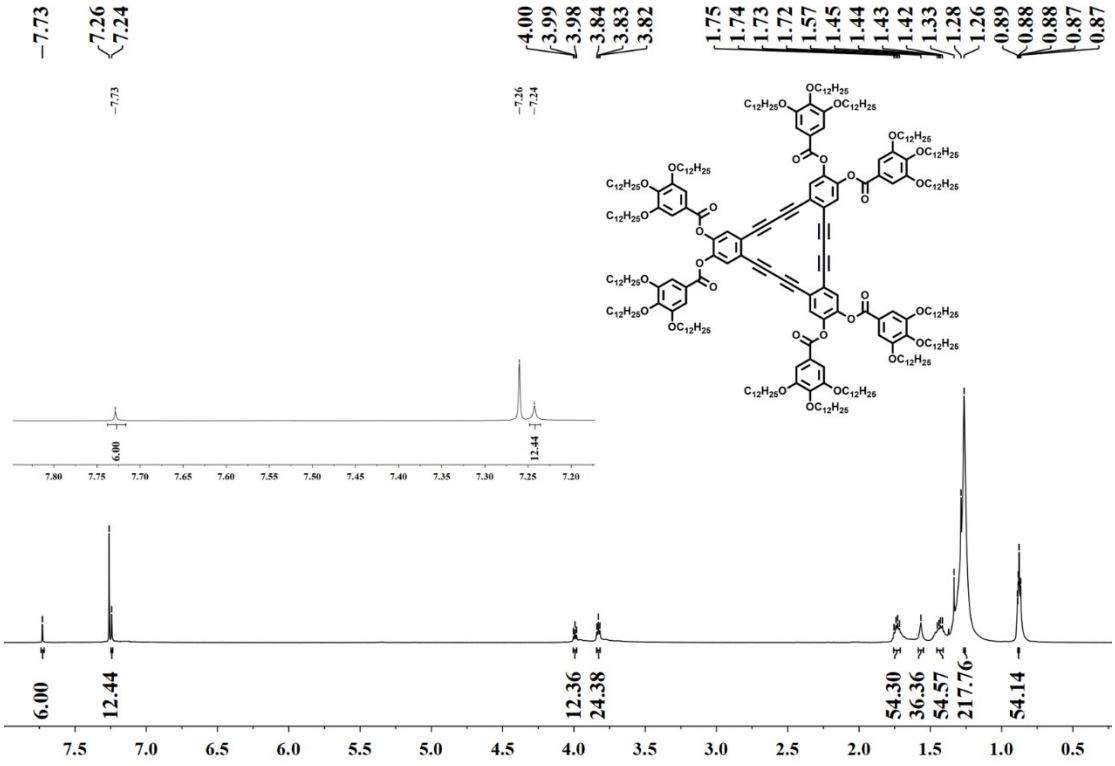


Figure S22. ^{1}H NMR spectrum of GDYLC12 in $CDCl_3$.

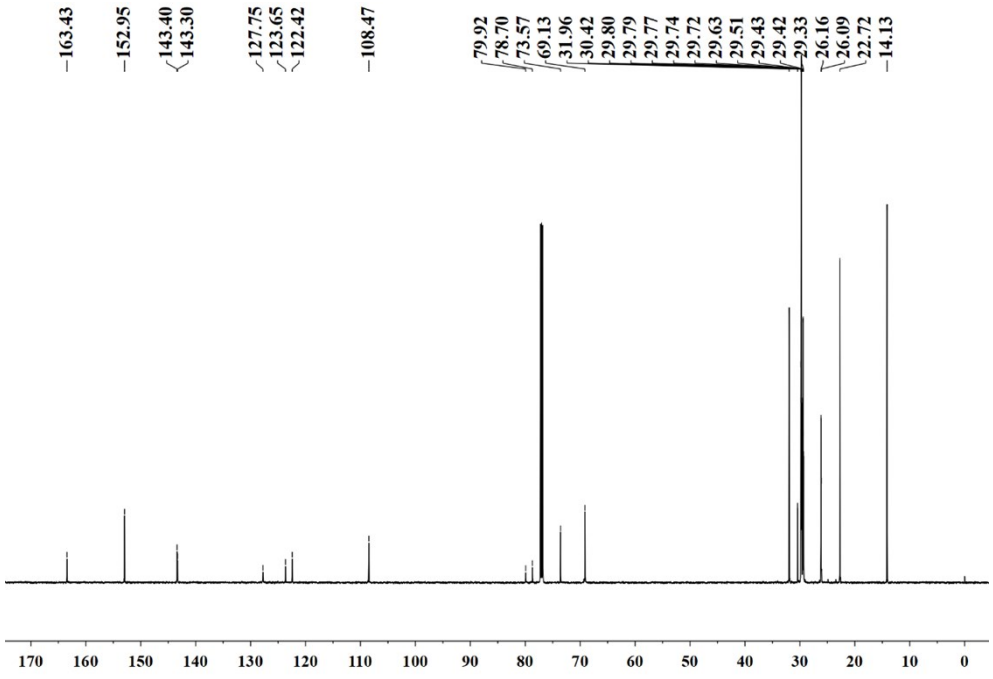


Figure S23. ^{13}C NMR spectrum of GDYLC12 in $CDCl_3$.

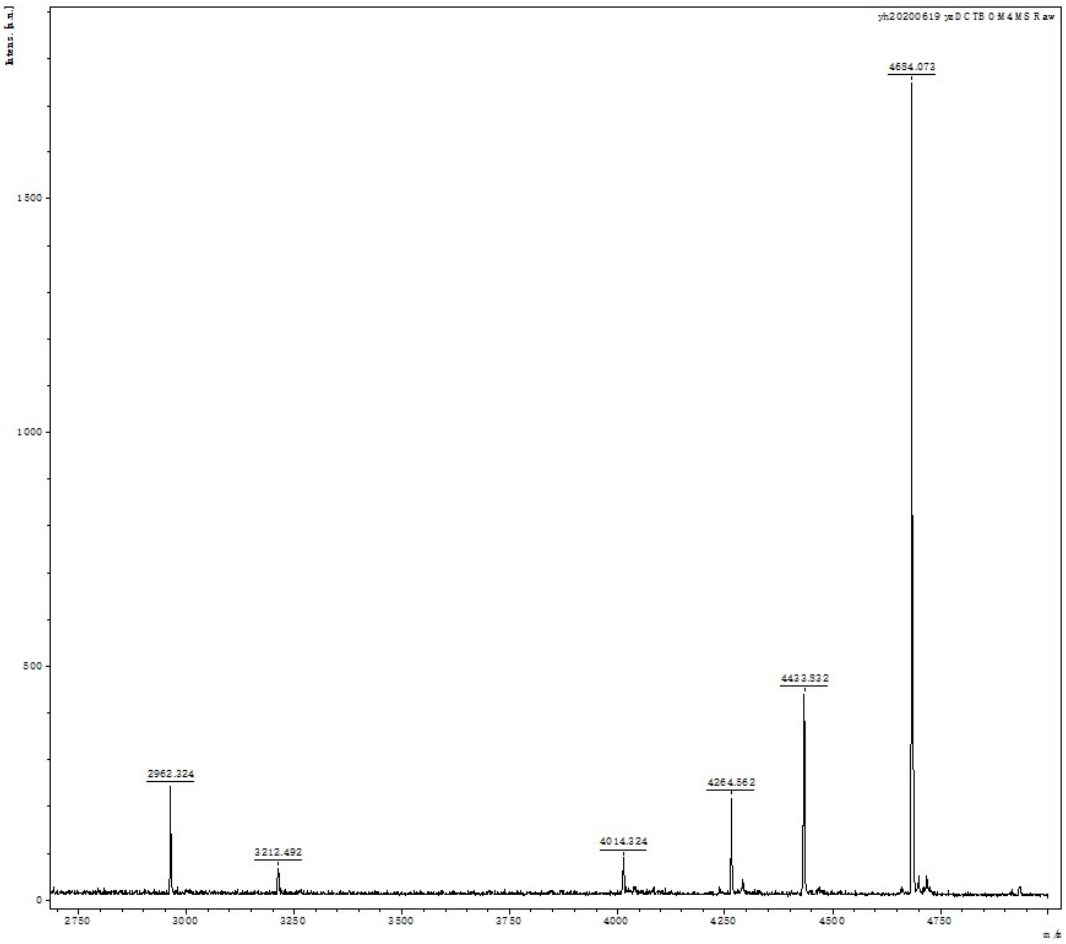


Figure S24. MS spectrum of GDYLC12.

4. Thermal stability

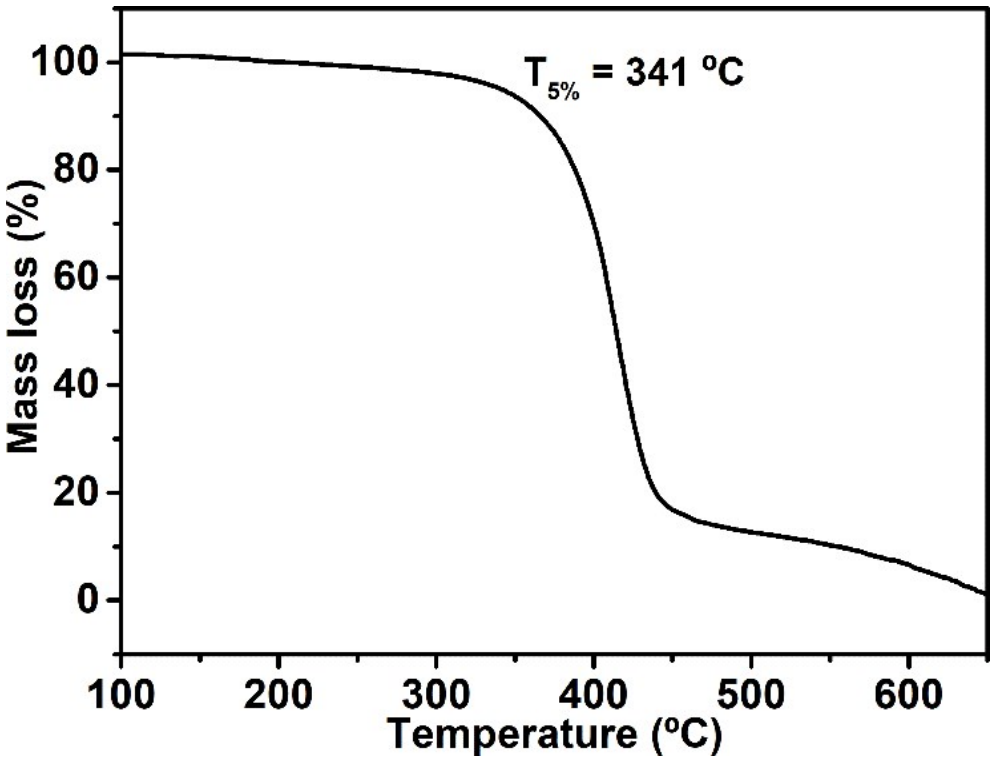


Figure S25. TGA graph of GDYLC12.

5. Mesomorphic Properties

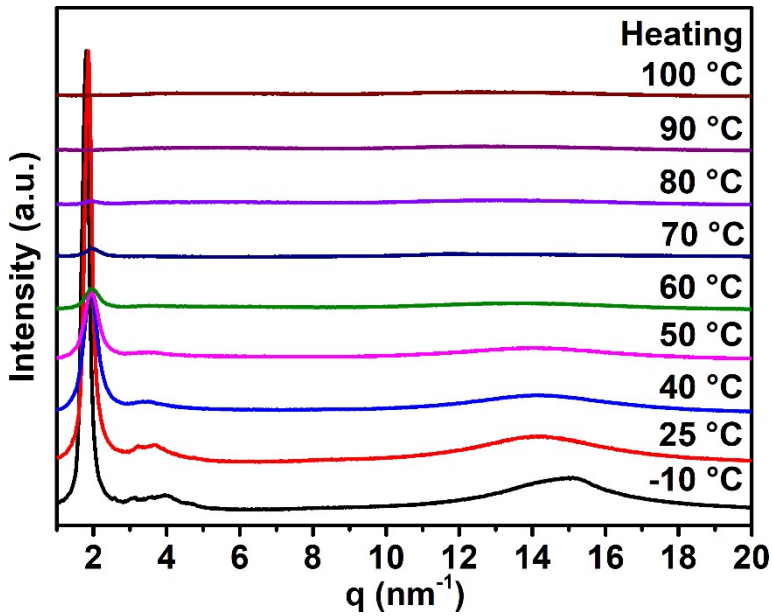


Figure S26. SAXS−WAXS patterns of GDYLC12 recorded on heating process.

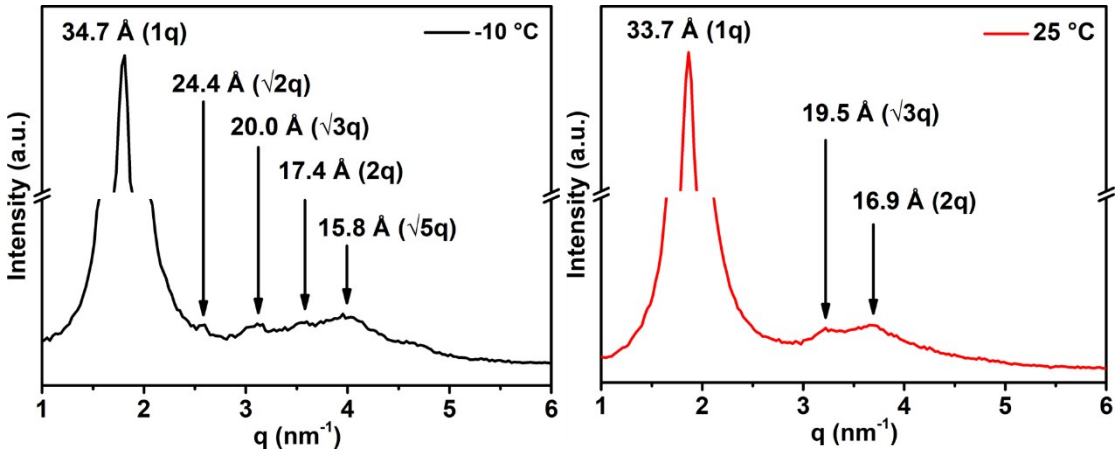


Figure S27. The enlarged small-angle diffraction patterns of GDYLC12 examined at −10 °C and 25 °C during the heating process.

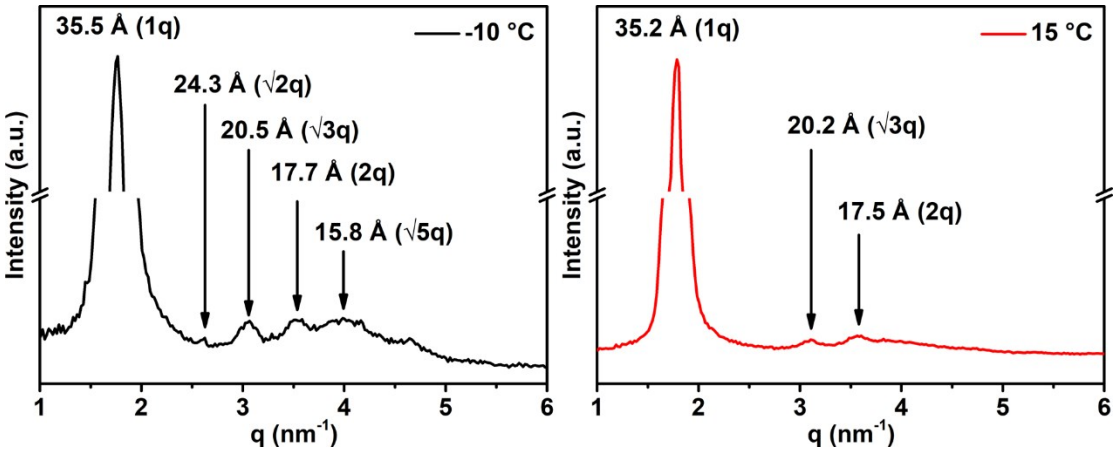


Figure S28. The enlarged small-angle diffraction patterns of GDYLC12 examined at −10 °C and 15 °C during the cooling process.

Table S1. Experimental and calculated *d*-spacing of the observed SAXS reflection of the Col_h phase in GDYLC12 at 15 ºC during the cooling process.

(*hkl*)	$d_{obs.}$-spacing(nm)	$d_{cal.}$-spacing(nm)
(100)	3.52	3.52
(110)	2.02	2.03
(200)	1.75	1.76
a_{hex} = 4.06 nm		

Table S2. Experimental and calculated *d*-spacing of the observed SAXS reflection of the Cub phase in GDYLC12 at −10 ºC during the cooling process.[a]

(*hkl*)	$d_{obs.}$-spacing(nm)	$d_{cal.}$-spacing(nm)
(100)	3.55	3.52
(110)	2.43	2.48
(111)	2.05	2.03
(200)	1.77	1.76
(210)	1.58	1.57
a_{cub} = 3.52 nm		

[a] $d_{hkl} = 2\pi/q_{hkl}$; $a_{hkl} = (h^2 + k^2 + l^2)^{1/2} d_{hkl}$; $a_{cub} = (a_{100} + a_{110} + a_{111} + a_{200} + a_{210})/5$.

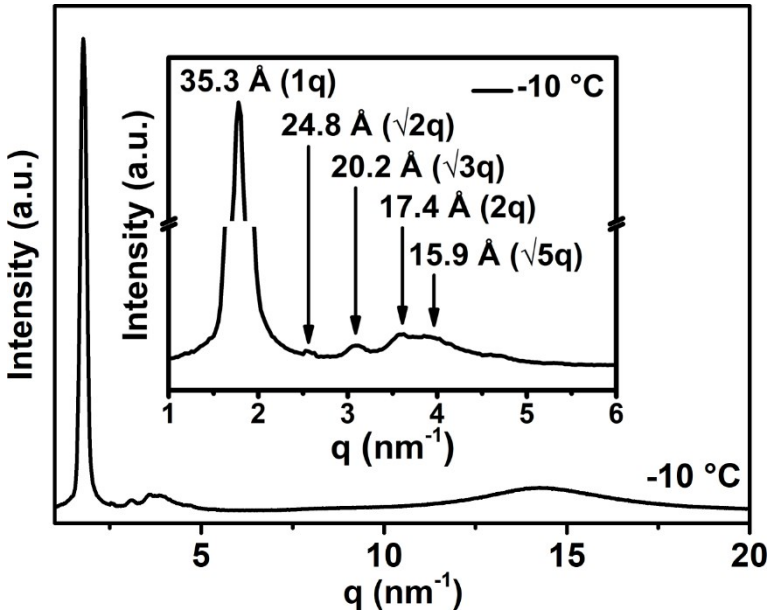


Figure S29. SAXS−WAXS patterns of GDYLC12 examined after being kept at −10 °C for 24 h.

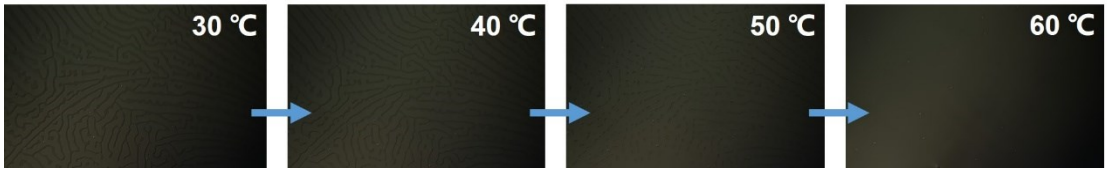


Figure S30. Textures of GDYLC12 from Col_h phase to the isotropic phase (from 30 to 60 °C) as observed under POM.

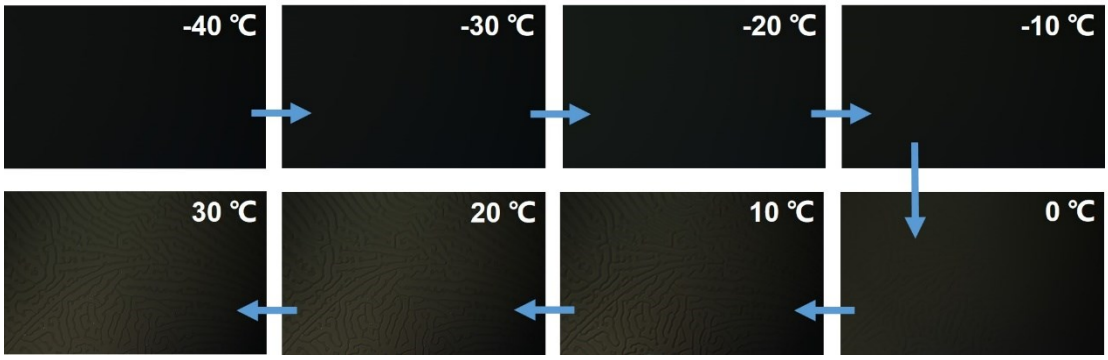


Figure S31. Textures of GDYLC12 from Cub phase to Col_h phase (from −40 to 30 °C) as observed under POM.

6. Cub and Col_h phase models

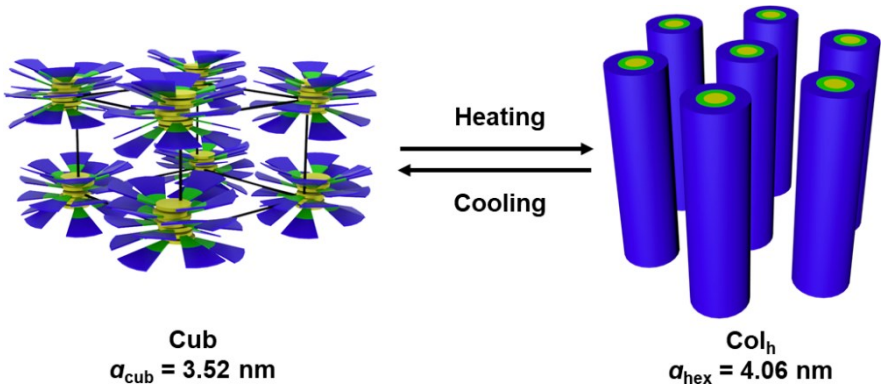


Figure S32. Schematic illustration of the proposed packing models for the Cub and Col_h phases.

The unit cell volume $V_{\text{unit cell}}(Col_h)$ in a hexagonal lattice is calculated as $a_{hex}^2 \times\sqrt{3}/2\times c$, where a_{hex} is the lattice constant and c is the mean stacking distance between the molecules deduced from the X-ray patterns (4.4 Å). In addition, the cubic cell volume $V_{\text{unit cell}}(\text{Cub})$ is calculated as a_{cub}^3, a_{cub} is the cubic lattice parameter. Thus, the values of $V_{\text{unit cell}}(Col_h)$ = 6281.1 Å^3 and $V_{\text{unit cell}}(\text{Cub})$ = 43614.2 Å^3 are obtained. The number of molecules inside the unit cell is directly given by the relation $Z = V_{\text{unit cell}}/V_m$ in which V_m is the molecular volume.[R3-5] Geometry optimization has been carried out by using MMFF94 force field and Chem3D package.[R6] Furthermore, Multiwfn 3.7 (dev) software has been used to perform wave function analyses to obtain the molecular volume.[R7] Overall, a value of V_m = 6324.451 Å^3 is obtained, the hexagonal unit cell contained 1 molecule and the cubic unit cell contained 7 molecules.

7. Optical Properties

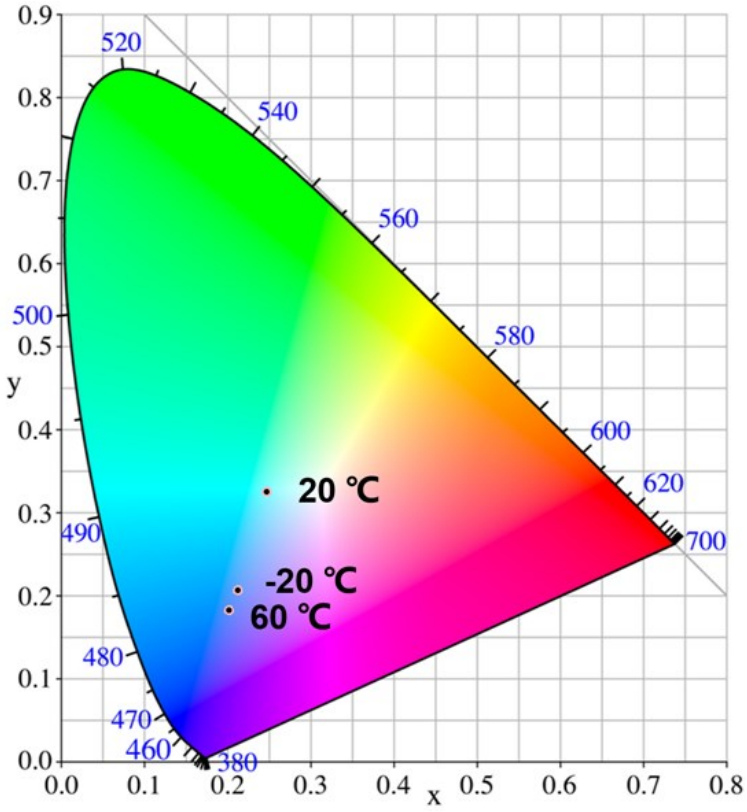


Figure S33. The CIE 1931 chromaticity diagram shows the luminescent color changes of GDYLC12 at indicated temperatures.

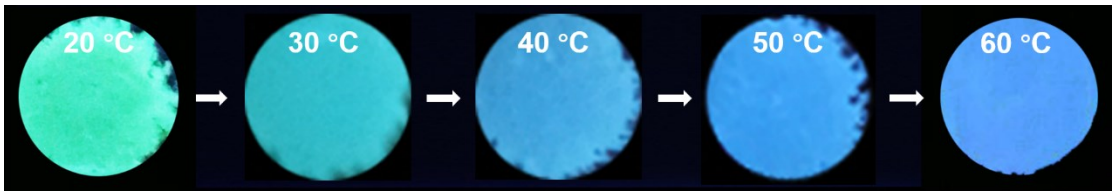


Figure S34. Fluorescence images of GDYLC12 thin film under 365 nm UV illumination from 20 ºC to 60 ºC.

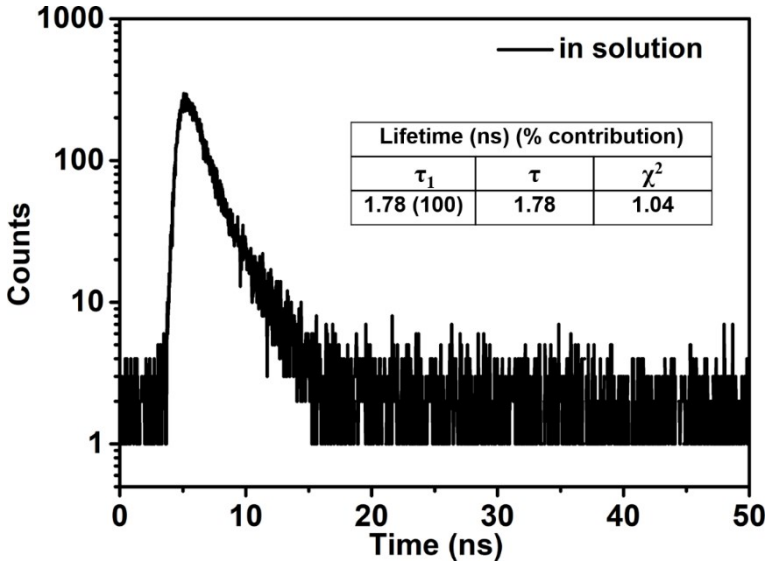


Figure S35. The fluorescence lifetime of GDYLC12 in aqueous $CHCl_3$ solution (ca. 10^{-5} mol/L) at room temperature.

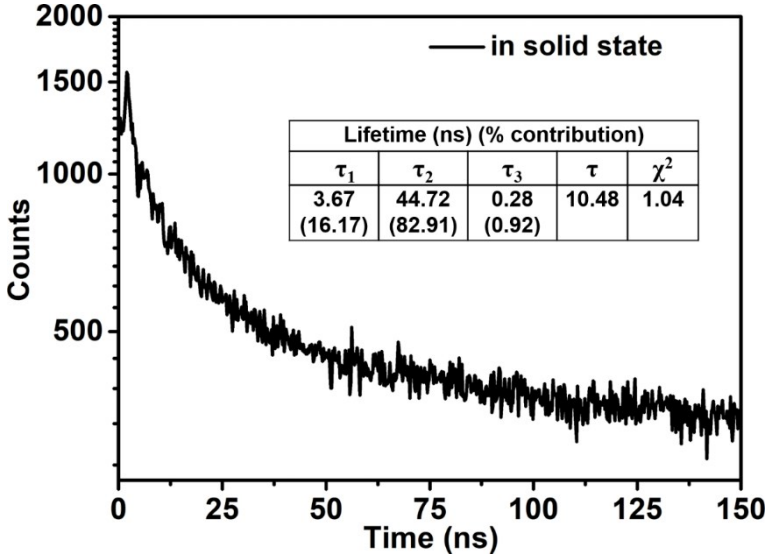


Figure S36. The fluorescence lifetime of GDYLC12 in solid state at room temperature.

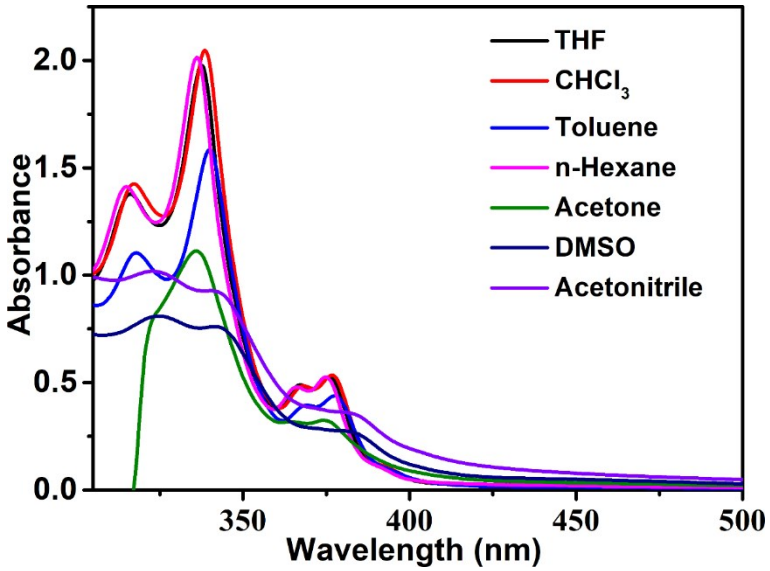


Figure S37. UV-Vis spectra of GDYLC12 (conc. = ca. 10^{-5} mol/L) in different solvents.

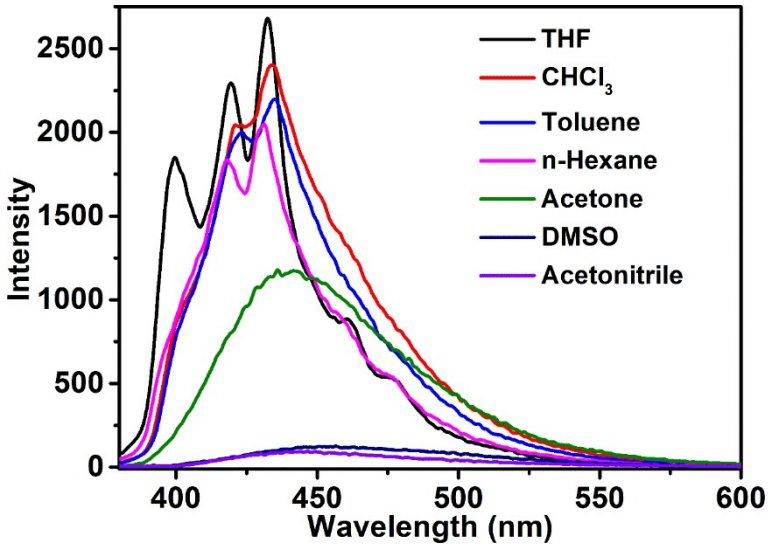


Figure S38. Fluorescence spectra (λ_{ex} = 350 nm) of GDYLC12 (conc. = ca. 10^{-5} mol/L) in different solvents.

For the spin-coated thin film of GDYLC12 at solid state, the molecular structure of the material itself has a decisive influence on the absorption spectrum, whereas the absorption intensity is related to many factors such as the wavelength of the incident light, temperature, etc.[8,9] Since the molecular structure of GDYLC12 film did not change at different temperatures, the valence electron transition did not change, thus we obtained the absorption curves (Figure 3b) with similar shapes. However, the

molecular packing plays a key role on the absorption intensity. When the temperature is decreased, the molecular packing becomes more and more ordered, which will lead to increased light-reflecting and decreased absorption intensity, as shown in Figure 3b.

8. Electrochemical property

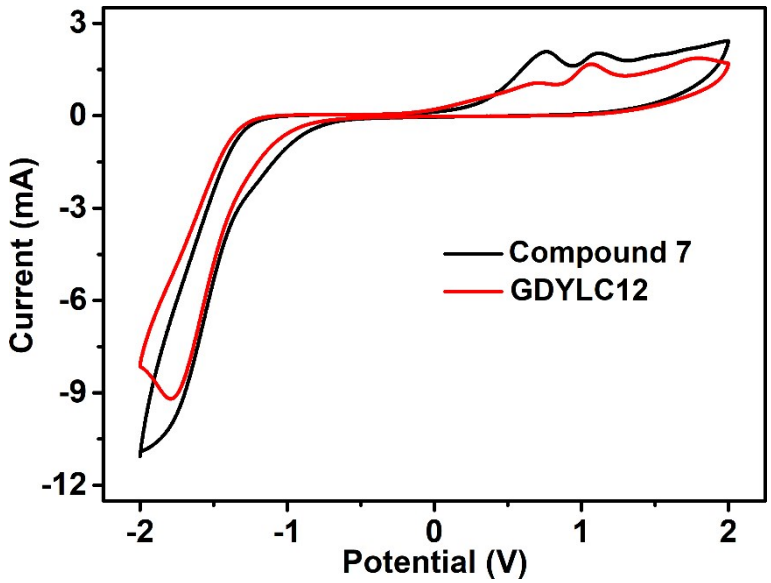


Figure S39. Cyclic voltammetry curves of compound **7** and GDYLC12 in anhydrous chloroform solution (conc. = ca. 10 mg/mL) with a scanning rate of 0.5 V/s at room temperature.

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