Supporting Information for

Efficient Synthesis of Discrete Oligo(fluorenediacetylene)s Toward Chain-Length Dependent Optical and Structural Properties

Xianheng Shi,[1] Min Liu,[1] Lisan Li,[1] Jiandong Zhang,[1] Haiyan Li,[2] Zhihao Huang,[1] Wei Zhang,[1] Zhengbiao Zhang,[1*] Nianchen Zhou,[1*] and Xiulin Zhu[1]

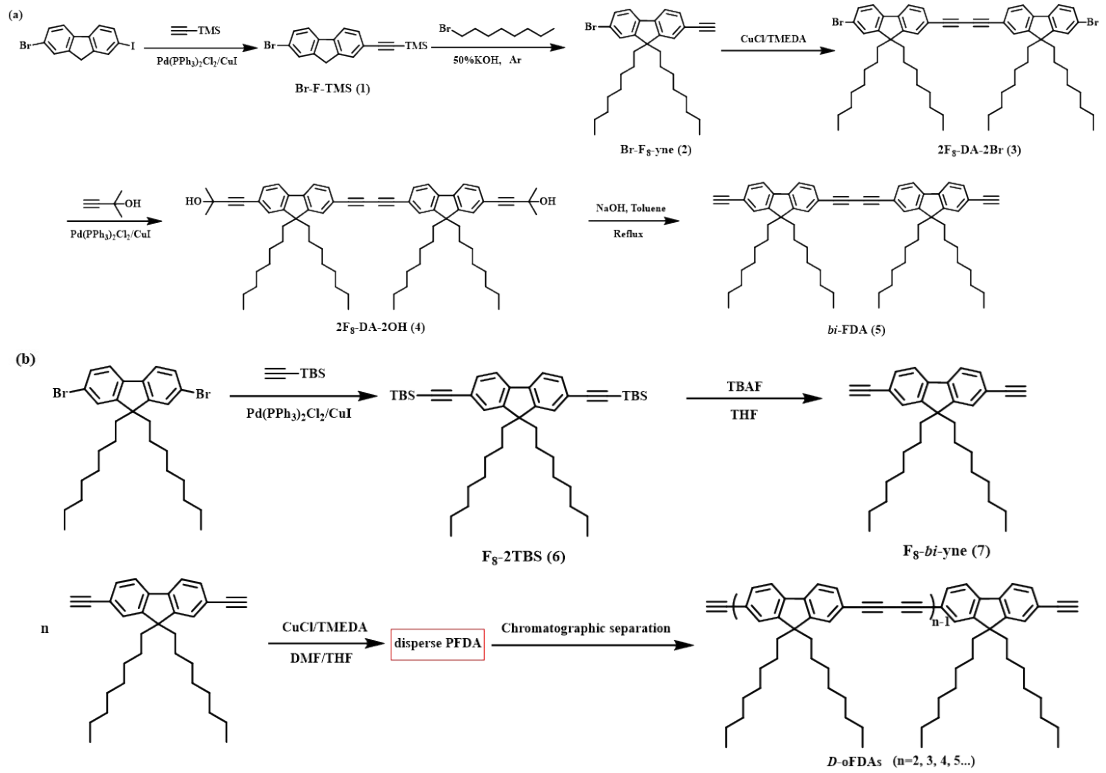
[1] Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou Industrial Park, Suzhou 215123, China.

[2] Analysis and Testing Center, Soochow University, Suzhou 215123, China.

* Email: nczhou@suda.edu.cn; zhangzhengbiao@suda.edu.cn

Experimental Section

Synthesis



Scheme S1. (a) Synthetic routes of 1,4-bis(7-ethynyl-9,9-dioctyl-9H-fluoren-2-yl)buta-1,3-diyne (*bi*-FDA). (b) Synthetic routes of *D*-oFDAs (DP=2,3,4,5) *via* chromatographic separation of disperse PFDA prepared *via* the Glaser coupling polycondensation using F_8-*bi*-yne as monomer.

Synthesis of ((7-bromo-9H-fluoren-2-yl)ethynyl)trimethylsilane (Br-F-TMS, 1)

2-Bromo-7-iodifluorene was first converted to ((7-bromo-9H-fluoren-2-yl)ethynyl)(tert-butyl) dimethylsilane via typical Sonogashira Reaction. 2-bromo-7-iodo-9H-fluorene 1 (1.0 g, 2.70 mmol, 1 eq.), copper iodide (41 mg, 0.22 mmol, 0.08 eq.), triphenylphosphine (57 mg, 0.22 mmol, 0.08 eq.) and $Pd(PPh_3)_2Cl_2$ (151 mg, 0.44 mmol, 0.08 eq.) were placed in a 50 mL three-necked flask with a stir bar and sealed with a rubber septum under argon. THF (15 mL) and diisopropylamine (10 mL) were injected via syringe. The yellow solution was sparged with argon for 30 minutes and began darkening to a brown/black. Ethynyltrimethylsilane (570 μL，4.05 mmol, 1.5 eq.) was injected via syringe and the solution returned to yellow after ~ 3 min., and

finally darkened to brown with a light ppt forming after about 5 minutes. The reaction was stirred at room temperature for 6 hours, filtered through a celite pad, concentrated by rotary evaporator, and purified via column chromatography (silica gel, petroleum ether eluent) to yield white solid. (0.82 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm):7.69 – 7.58 (m, 4H), 7.53 – 7.47 (m, 2H), 3.86 (s, 2H), 0.27 (s, 9H).

Synthesis of 2-bromo-7-ethynyl-9,9-dioctyl-9H-fluorene (Br-F_8-yne, 2)

Octyl group was introduced to the C-9 position of the fluorene, and then the protected-TMS group was removed. In a 100 mL two-neck round-bottom flask fitted with a mechanical stirrer, the compound **1** (1.0 g, 2.62 mmol, 1 eq.) was added to 40 mL of dimethylsulfoxide under argon atmosphere. 50% aq. KOH (1 mL) was introduced dropwise with giving a bright red solution, darkening quickly with time to a maroon. The solution was stirred vigorously as 1- bromooctane (1.2 mL, 7.86 mmol, 3 equiv.) was added and the solution turned purple. After stirring for 6 h at room temperature, the reaction was poured into 100 mL water and then was extracted with ethyl acetate for three times. The organic layer was dried over Na_2SO_4 and the solvent was evaporated by rotary evaporator. The solution was concentrated by rotary evaporator and purified via column chromatography (silica gel, petroleum ether eluent) to yield a viscous yellow oil (0.77 g, 60%).^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm): 7.64 – 7.39 (m, Ar-H, 6H), 3.14 (s, -CCH, 1H), 1.92 (ddd, J = 10.3, 5.5, 1.3 Hz, 4H), 1.33 – 0.96 (m, 22H), 0.82 (t, J = 7.0 Hz, 6H), 0.57 (tt, J = 11.3, 5.8 Hz, 4H).

Synthesis of 1,4-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)buta-1,3-diyne (2F_8-DA-2Br, 3)

Two fluorene units were joined through Glaser coupling. To a 25 mL round-bottom flask, the compound **2** (2 g, 4.06 mmol, 1eq.) was dissolved in 10 mL chloroform and heated up to 30^{o}C. Cuprous chloride (210 mg, 2.03 mmol, 0.5 eq.) and tetramethylenediamine (300 μL, 2.03 mmol, 0.5 eq.) were added sequentially to the mixture. Three hours later, the reaction was poured into 50 mL water and extracted with equivalent ethyl acetate for three times. The organic phase was dried over Na_2SO_4, filtered, concentrated by rotary evaporation and purified via column chromatography (silica gel, hexanes eluent) to yield a yellow solid (1.9 g, 95 %).^{1}H NMR (300 MHz,

$CDCl_3$): δ_H (ppm): 7.67 – 7.43 (m, 12H), 2.00 – 1.84 (m, 8H), 1.25 – 0.99 (m, 41H), 0.83 (t, J = 7.0 Hz, 12H), 0.59 (s, 8H).

Synthesis of 4,4'-(buta-1,3-diyne-1,4-diylbis(9,9-dioctyl-9H-fluorene-7,2-diyl))bis(2-methylbut-3-yn-2-ol) ($2F_8$-DA-2OH, 4)

The compound **3** (1.0 g, 1.02 mmol, 1 eq.), copper iodide (21 mg, 0.08 mmol, 0.08 eq.), triphenylphosphine (28 mg, 0.08 mmol, 0.08 eq.) and $Pd(PPh_3)_2Cl_2$ (151 mg, 0.44 mmol, 0.16 eq.) were placed in a 50 mL three-necked flask with a stir bar and sealed with a rubber septum under argon. Diisopropylamine (30 mL) was injected via syringe. The yellow solution was sparged with argon for 30 minutes and began darkening to a brown/black. 2-methylbut-3-yn-2-ol (570 μL，3.06 mmol, 3 eq.) was injected via syringe and the solution returned to yellow after ~3 min., and finally darkened to black after about 5 minutes. The reaction was stirred at 80°C for 12 hours, filtered through a celite pad, concentrated by rotary evaporator, and purified via column chromatography (silica gel, petroleum ether/ethyl acetate = 4/1) to yield a yellow solid (0.91 g, 90%). ^{1}H NMR (300 MHz, DMSO): δ_H (ppm): 7.84 (dd, J = 9.5, 7.9 Hz, 4H), 7.65 (d, J = 1.4 Hz, 2H), 7.56 (dd, J = 7.9, 1.4 Hz, 2H), 7.45 (d, J = 1.4 Hz, 2H), 7.37 (dd, J = 7.9, 1.4 Hz, 2H), 5.32 (s, 2H), 1.99 (t, J = 8.2 Hz, 8H), 1.49 (s, 13H), 1.37 – 0.88 (m, 45H), 0.78 (t, J = 7.0 Hz, 13H), 0.47 (s, 8H).

Synthesis of 1,4-bis(7-ethynyl-9,9-dioctyl-9H-fluoren-2-yl)buta-1,3-diyne (*bi*-FDA, 5)

The bromide end groups were replaced by 2-methylbut-3-yn-2-ol. The compound 4 (1 g, 1.00 mmol, 1 eq.) was dissolved in 10 mL toluene and stirred in an oil bath at 120°C. Then, the protected bis(2-methylbut-3-yn-2-ol) group was removed in the presence of strong alkalinity of sodium hydroxide. Sodium hydroxide (0.12 g, 2.20 mmol, 2.2 eq.) was added to the above solution and stirred for 3h. After the reaction, the mixture was filtered through a celite pad, concentrated by rotary evaporation, purified via column chromatography (silica gel, hexanes eluent) to a pale yellow solid (0.57 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm): 7.65 (ddd, J = 7.8, 3.1, 0.8 Hz, 4H), 7.50 (td, J = 9.4, 1.7 Hz, 8H), 3.16 (s, 2H), 2.03 – 1.85 (m, 8H), 1.30 – 0.95 (m, 42H), 0.83 (t, J = 7.0 Hz, 13H), 0.58 (s, 8H).

Synthesis of ((9,9-dioctyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl))bis(tert-butyldimethylsilane) (F_8-2TBS, 6)

The synthesis method of compound 6 is similar to Br-F-TMS via Sonogashira Reaction. 2,7-dibromo-9,9-dioctyl-9H-fluorene (1.0 g, 1.82 mmol, 1 eq.), copper iodide (55 mg, 0.29 mmol, 0.16 eq.), triphenylphosphine (76 mg, 0.29 mmol, 0.16 eq.) and $Pd(PPh_3)_2Cl_2$ (205 mg, 0.29 mmol, 0.16 eq.) were placed in a 50 mL three-necked flask with a stir bar and sealed with a rubber septum under argon. THF (20 mL) and diisopropylamine (15 mL) were injected via syringe. The yellow solution was sparged with argon for 30 minutes and began darkening to a brown/black. Tert-butyl(ethynyl)dimethylsilane (1140 μL，9.27 mmol, 3.0 eq.) was injected via syringe and the solution returned to yellow after ~ 3 min., and finally darkened to brown with a light ppt forming after about 5 minutes. The reaction was stirred at room temperature for 8 hours, filtered through a celite pad, concentrated by rotary evaporator, and purified via column chromatography (silica gel, petroleum ether eluent) to yield white solid. (1.16 g, 85%).^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm): 7.37 (d, J = 7.9 Hz, 2H), 7.27 – 7.16 (m, 4H), 1.76 – 1.67 (m, 4H), 0.81 (s, 38H), 0.61 (t, J = 7.0 Hz, 6H), 0.33 (s, 4H).

Synthesis of 2,7-diethynyl-9,9-dioctyl-9H-fluorene (F_8-*bi*-yne, 7)

The protected-TBS group was removed. In a 50 mL two-neck round-bottom flask fitted with a mechanical stirrer, the compound 6 (1.0 g, 1.50 mmol, 1 eq.) was added to 40 mL of tetrahydrofuran and then tetrabutylammonium fluoride (820 μL, 3.00, 2 eq.) was introduced drop-wise with giving a red solution, darkening quickly with time. The solution was stirred vigorously for 6 hours at room temperature. Then the solution was concentrated by rotary evaporator and was extracted with ethyl acetate for three times. The organic layer was dried over Na_2SO_4 and the solvent was evaporated by rotary evaporator to yield a viscous yellow powder (0.60 g, 92%).^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm): 7.63 (dd, J = 7.8, 0.8 Hz, 2H), 7.51 – 7.44 (m, 4H), 3.15 (s, 2H), 1.98 – 1.88 (m, 4H), 1.28 – 0.98 (m, 31H), 0.82 (t, J = 7.0 Hz, 8H), 0.57 (d, J = 8.5 Hz, 4H).

Glaser Polymerization of *bi*-FDA and F_8-*bi*-yne

The *bi*-FDA (1 g, 1.14 mmol, 1 eq.) was dissolved in 18 mL N,N-dimethylformamide

and 6 mL tetrahydrofuran and stirred in an oil bath at 30°C. Then, cuprous chloride (0.035 g, 0.34 mmol, 0.3 eq.) and N,N,N',N'-tetramethylethylenediamine (55 μL, 0.34 mmol, 0.3 eq.) were added to the above solution and stirred for 1.5 h in the presence of oxygen. As mentioned above, the polymerization of F_8-*bi*-yne was carried out in the same conditions.

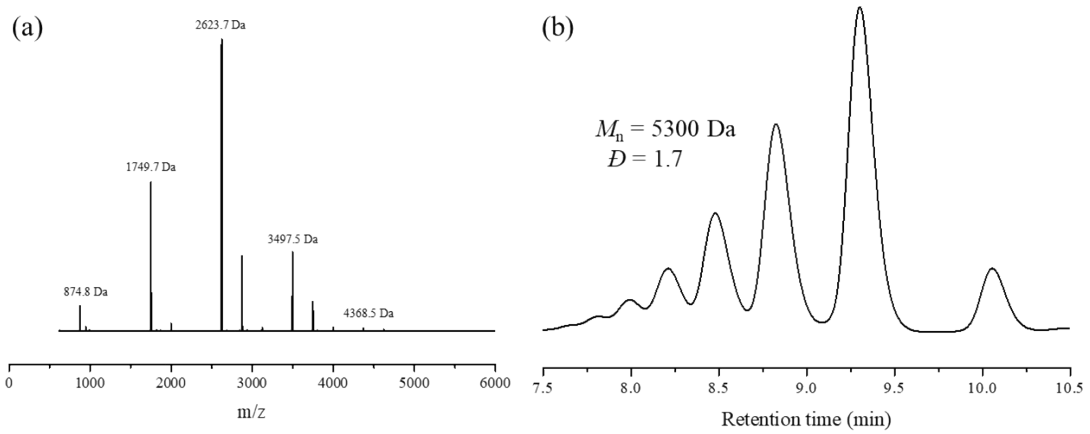


Fig. S1 (a) The MALDI-TOF spectrum and (b) SEC trace of the oligomer mixture obtained by the Glaser coupling polycondensation of *bi*-FDA.

Table S1 Gradient profile for *D*-oFDA separation (eluent: petroleum ether/chloroform)

%Petroleum ether	%Chloroform	Column Volume (CV)
100	0	2
90	10	3
86	14	4
82	18	6
80	20	6

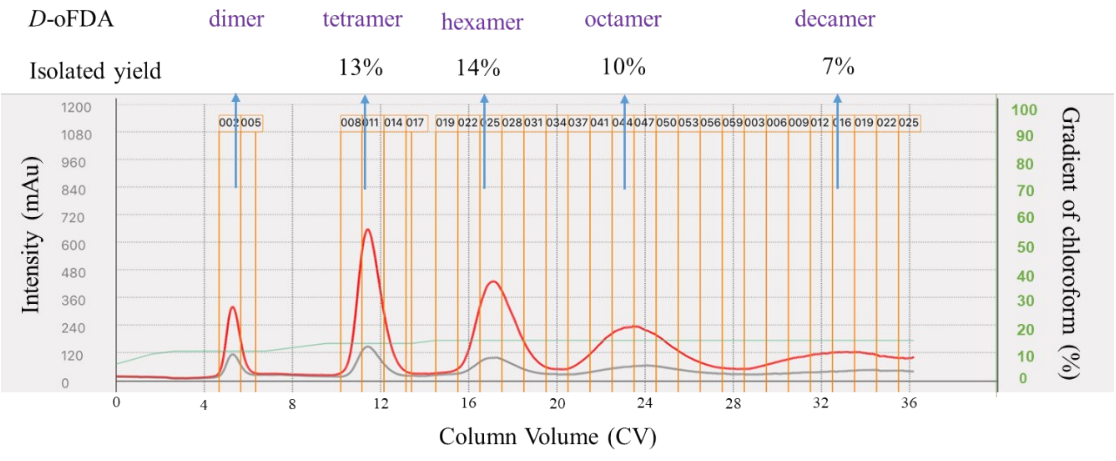


Fig. S2 The trace of SepaBean^{TM} automated column chromatography as function of column volume, which shows different *D*-oFDAs with DP from 4 to 10 separated at amounts of chloroform in petroleum ether/chloroform gradient. The isolated yield of each *D*-oFDA after separation is shown. Note that one column volume is 100 mL.

Table S2 Gradient profile for *D*-oFDAs separation to obtain trimer (eluent: petroleum ether/chloroform)

%Petroleum ether	%Chloroform	Column Volume (CV)
100	0	2
90	10	3
86	14	4
82	18	6
80	20	6

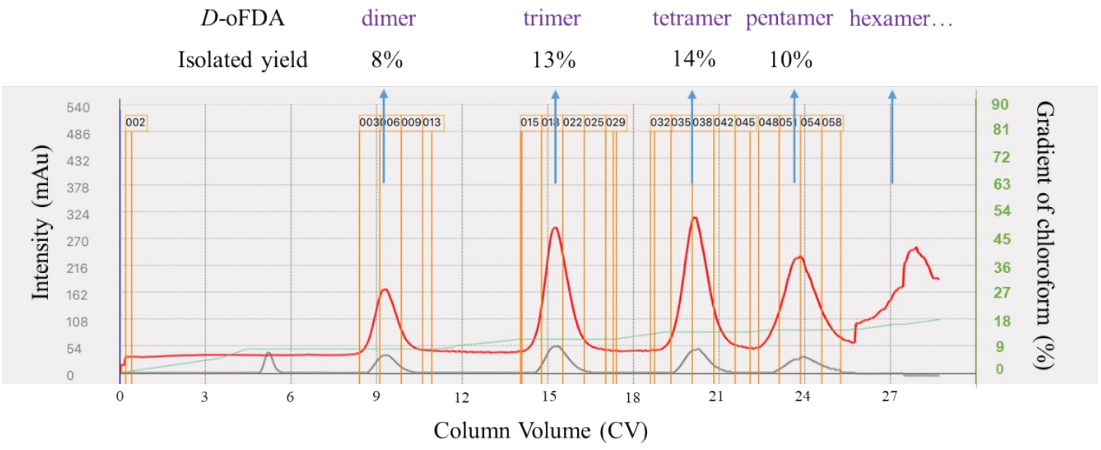


Fig. S3 The trace of SepaBean^{TM} automated column chromatography as function of column volume, which showed different *D*-oFDAs with DP from 2 to 6 separated at amounts of chloroform in petroleum ether/chloroform gradient. The isolated yield of each *D*-oFDA after separation is shown. Note that one column volume is 80 mL.

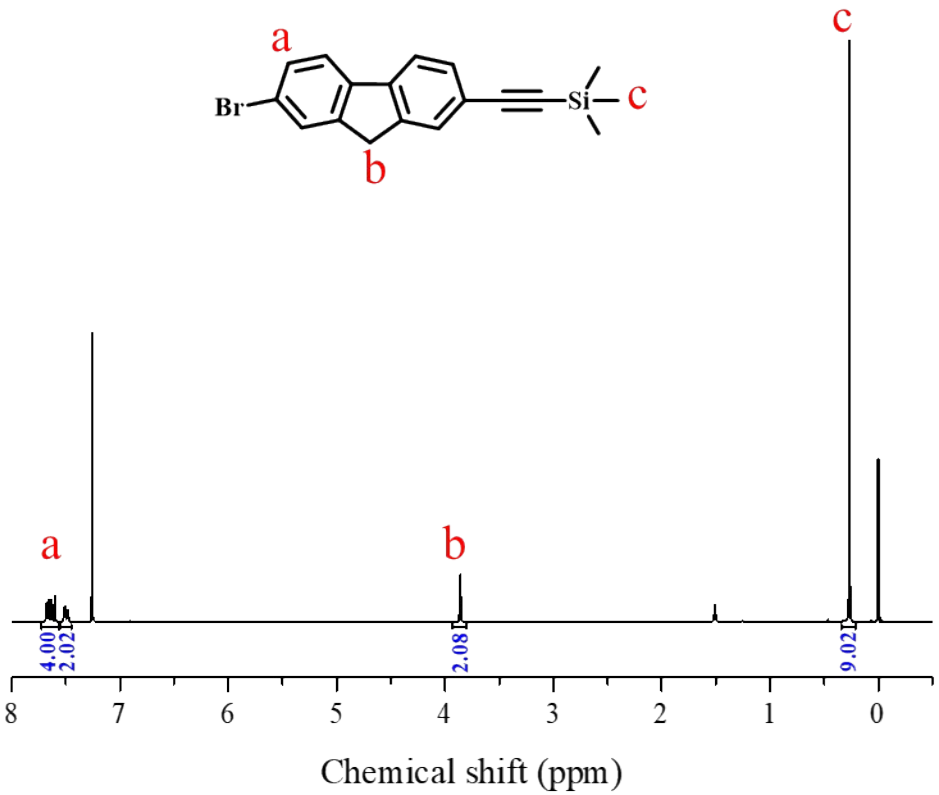


Fig. S4 ^{1}H NMR spectrum of Br-F-TMS in $CDCl_3$

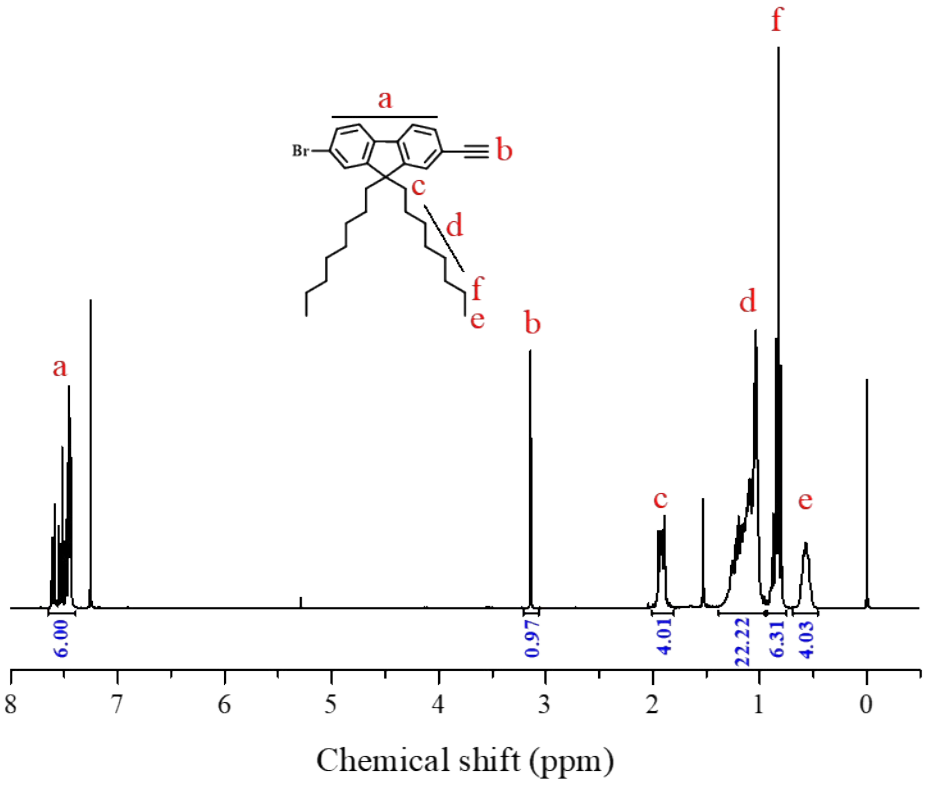


Fig. S5 ^{1}H NMR spectrum of Br-F_8-yne in $CDCl_3$

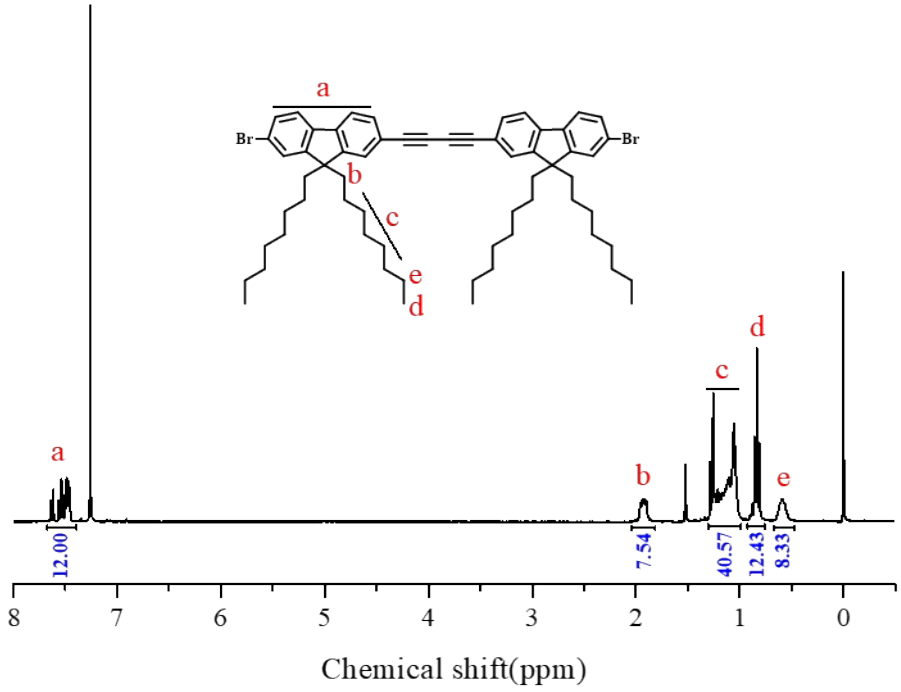


Fig. S6 ^{1}H NMR spectrum of 2F$_8$-DA-2Br in $CDCl_3$

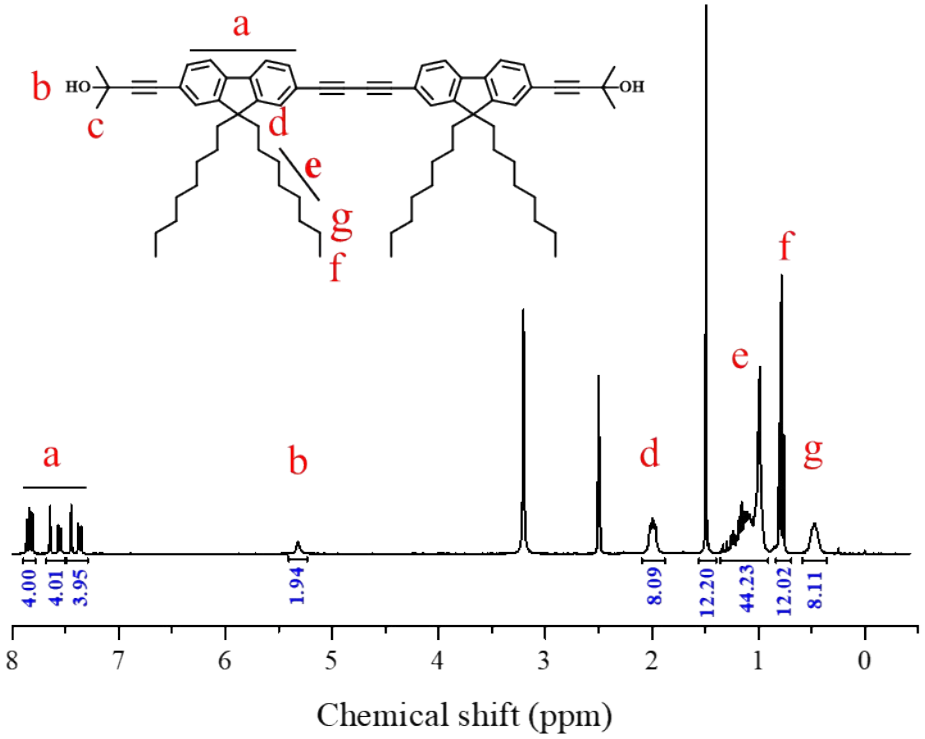


Fig. S7 ^{1}H NMR spectrum of 2F$_8$-DA-2OH in DMSO-d_6

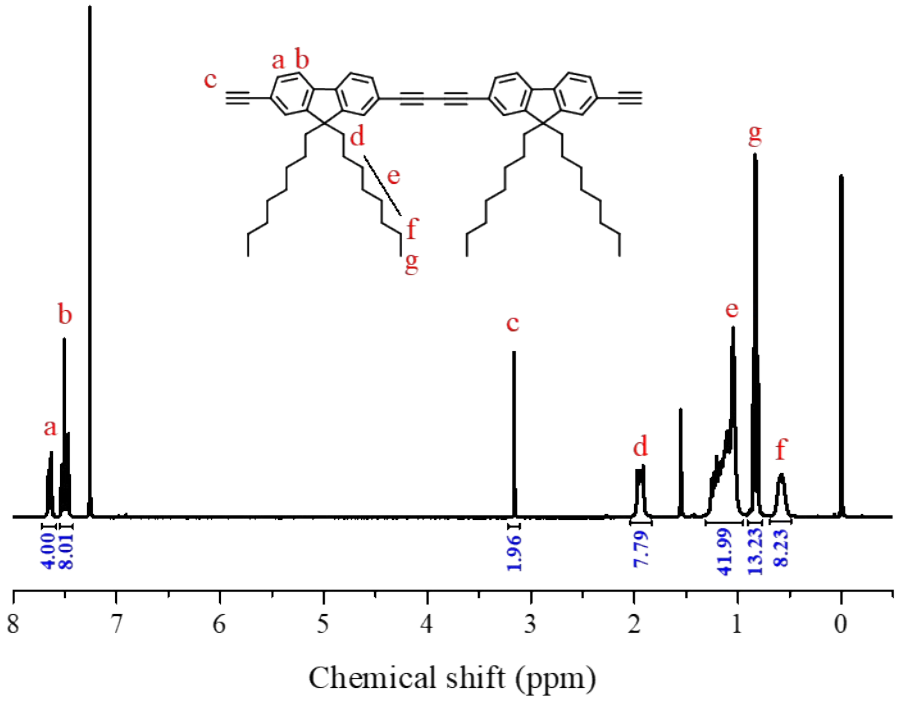


Fig. S8 ^{1}H NMR spectrum of *bi*-FDA in $CDCl_3$

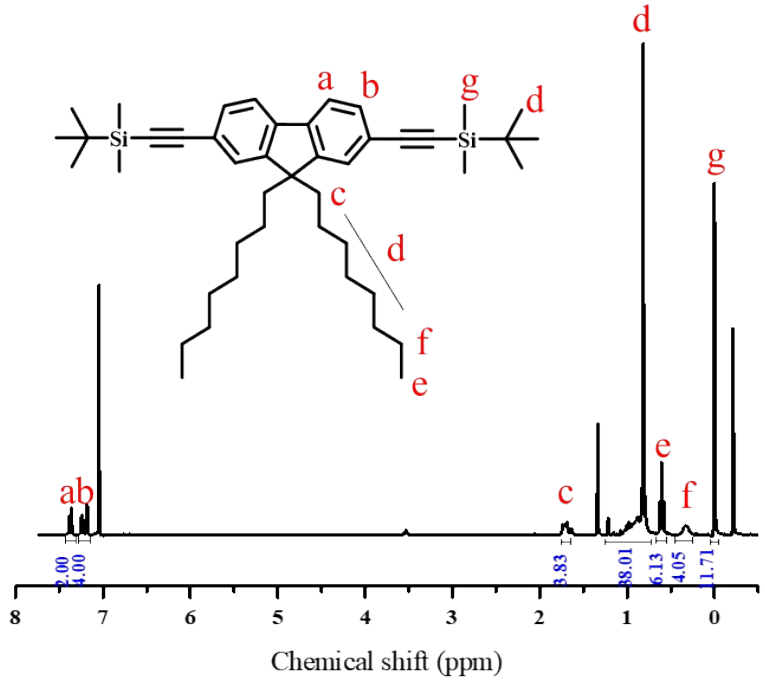


Fig. S9 ^{1}H NMR spectrum of F_8-2TBS in $CDCl_3$

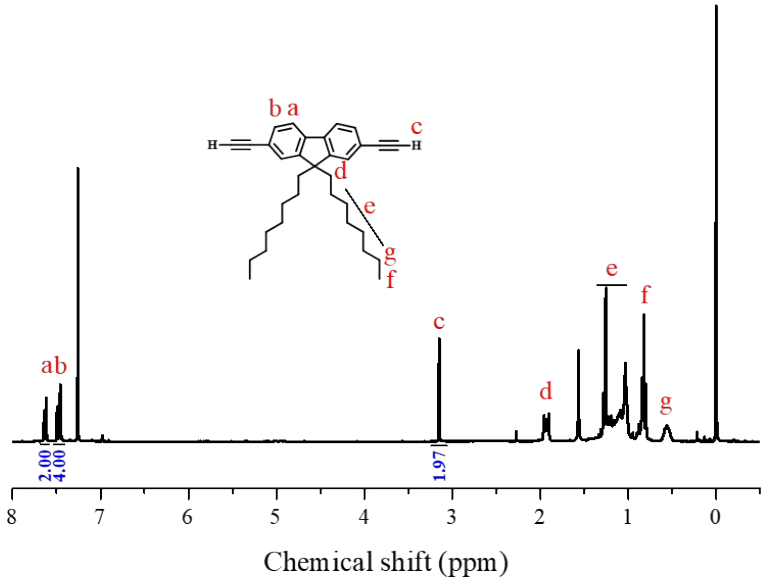


Fig. S10 ^{1}H NMR spectrum of F_8-*bi*-yne in $CDCl_3$

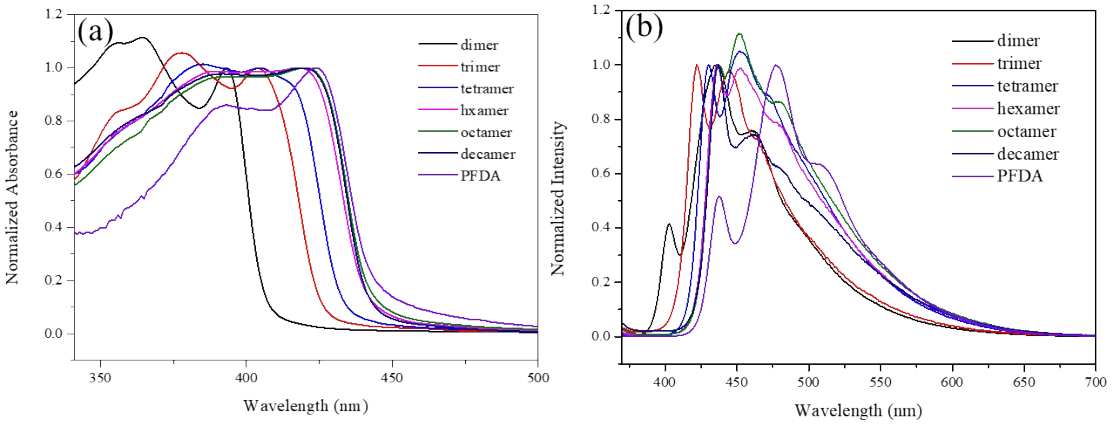


Fig. S11 (a) UV−vis spectra of *D*-oFDAs and disperse PFDA obtained by polycondensation of *bi*-FDA ($M_{n,SEC}$ = 12000, $Đ$ =1.7) in the film; (b) PL spectra of *D*-oFDAs and disperse PFDA measured in the film at excitation wavelength of 390 nm.

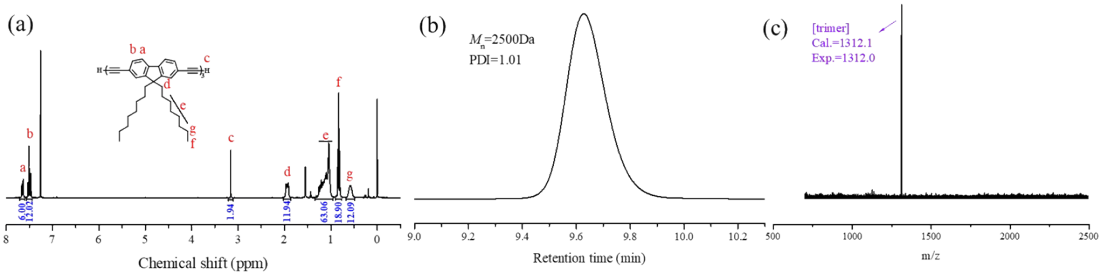


Fig. S12 (a) ^{1}H NMR spectra, (b) SEC traces and (c) MALDI-TOF of trimer.

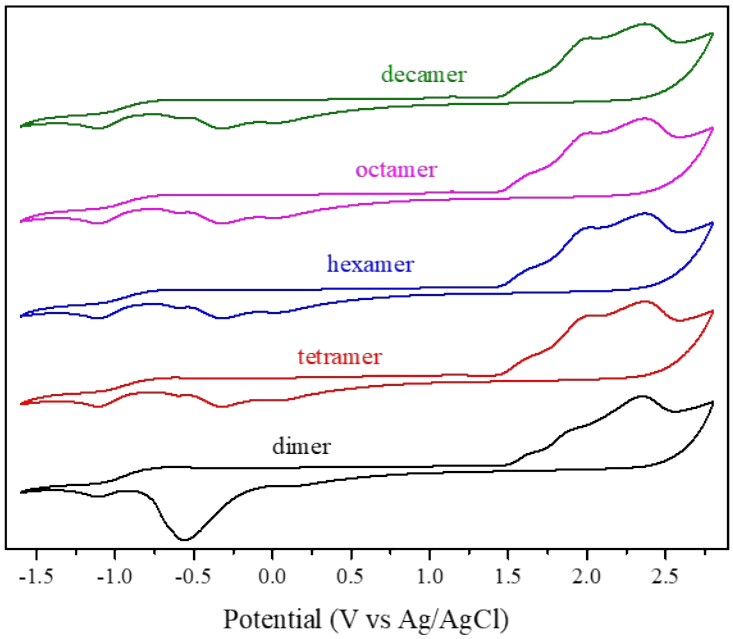


Fig. S13 CV curves of the dimer, tetramer, hexamer, octamer and decamer with concentration of 1 × 10^{-3} mol/L in anhydrous CH_2Cl_2 with 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte in at a scan rate of 100 mV · s^{-1}

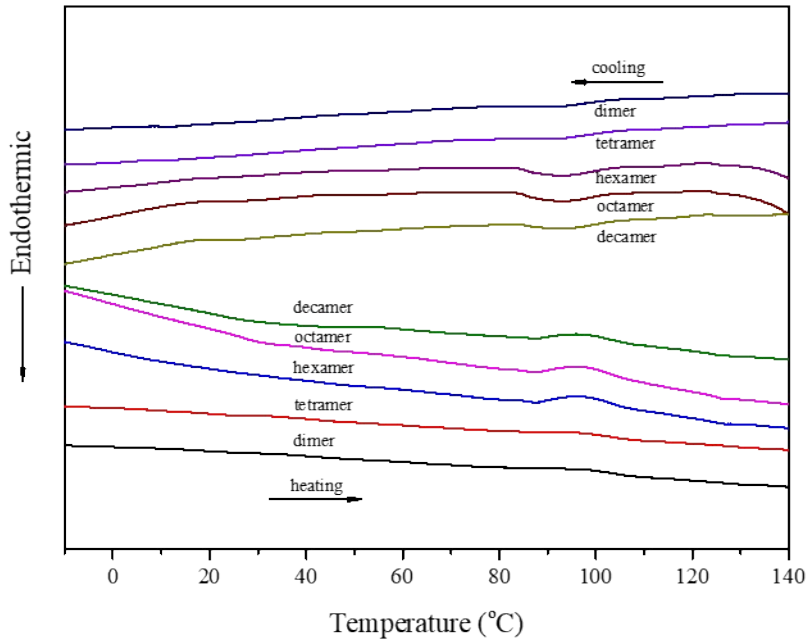


Fig. S14 The second DSC heating and cooling scans of *D*-oFDAs with a rate of 10 °C/min.

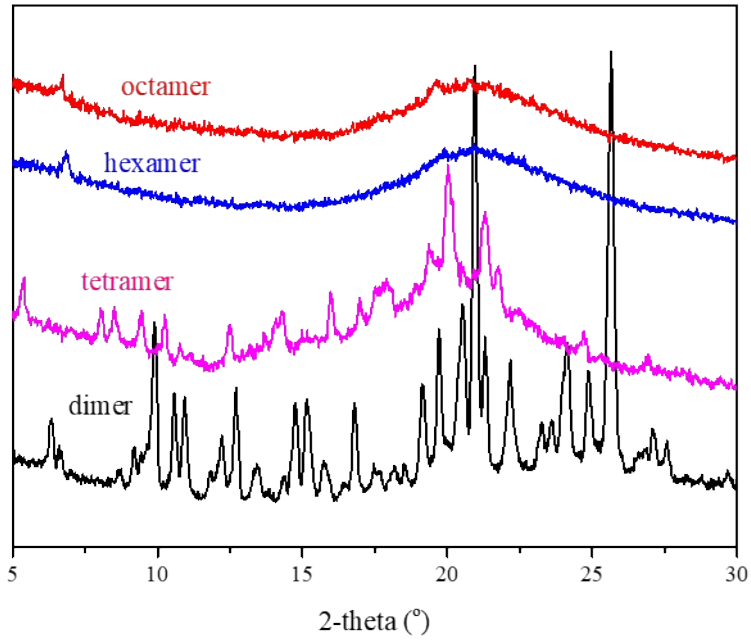


Fig. S15 XRD spectra of dimer, tetramer, hexamer and octamer.

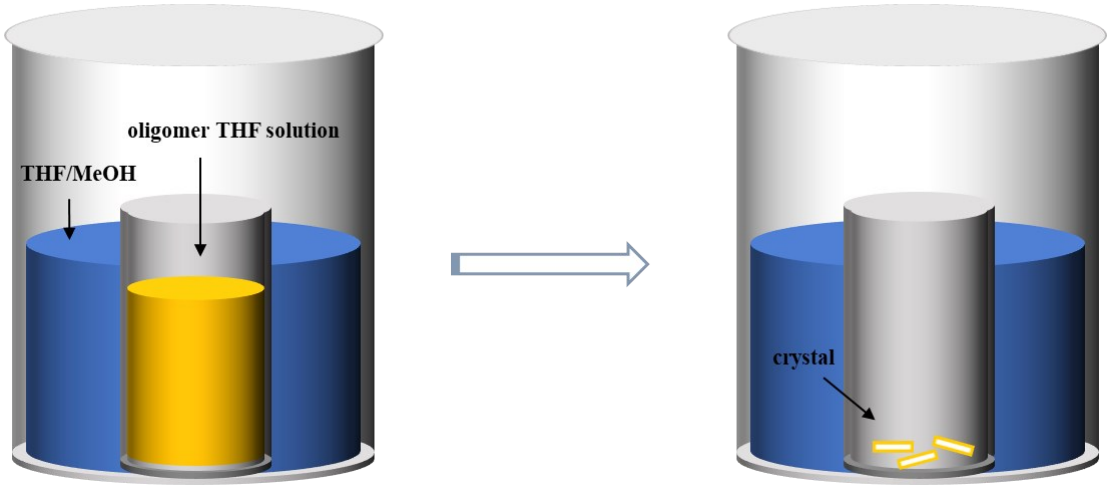


Fig. S16 Schematics of the device for preparing crystal of *D*-oFDAs and $2F_8$-DA-2Br. The concentration of oligomer solution in THF was 10 mg/mL.

It was worth noting that the external solvent is essential for the formation of lamellar crystal, by which the solvent was slowly evaporated within a sufficient period of time. In addition, the certain solvent pressure in the closed jar could ensure the free movement of the oligomer molecules and then induced them self-assemble and generate crystal leading to formation of well-organized lamellar crystal. If the solvent was replaced by poor solvent methanol, the crystal can be obtained in shorter time.

Table S3. Crystallographic data for $2F_8$-DA-2Br

	$2F_8$-DA-2Br
Empirical formula	$C_{31}H_{40}Br$
Formula weight	492.54
Temperature (K)	296.15
Crystal system	monoclinic
Space group	P 2_1/c
a (Å)	14.4463(7)
b (Å)	23.1330(11)
c (Å)	9.7793(5)
α (°)	90
β (°)	100.1500(10)
γ (°)	90
Volume ($Å^3$)	3217.0(3)
Z	4
Density (cal.) (g/cm^3)	1.017
Absorption coeff. (mm^{-1})	1.291
Crystal size (mm^3)	0.5 × 0.4 × 0.36
Reflections collected	30503
Independent reflections	7374 [R_{int} = 0.0761, R_{sigma} = 0.0792]
Data/restraints/parameters	7374 / 716 / 291
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0869, wR_2 = 0.1983
andR indexes [all data]	R_1 = 0.1497, wR_2 = 0.2327
Largest diff. peak and hole ($e.Å^{-3}$)	0.89 and -1.19