Electronic Supplementary Information of

Janus Molecule: Large Second-Order Nonlinear Optical Performance, Good Temporal Stability, Excellent Thermal Stability and Spherical Structure with Optimized Dendrimer structure

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1. Additional data and analysis

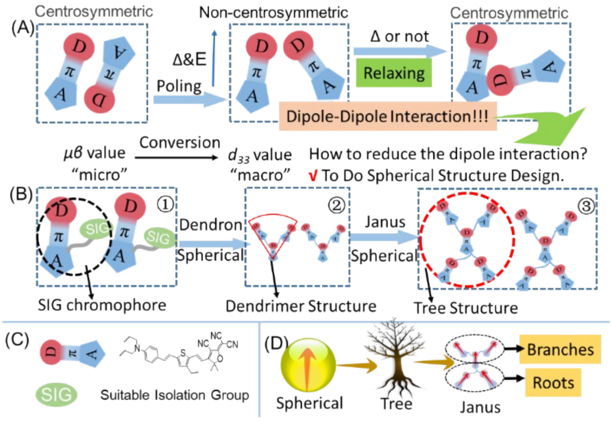
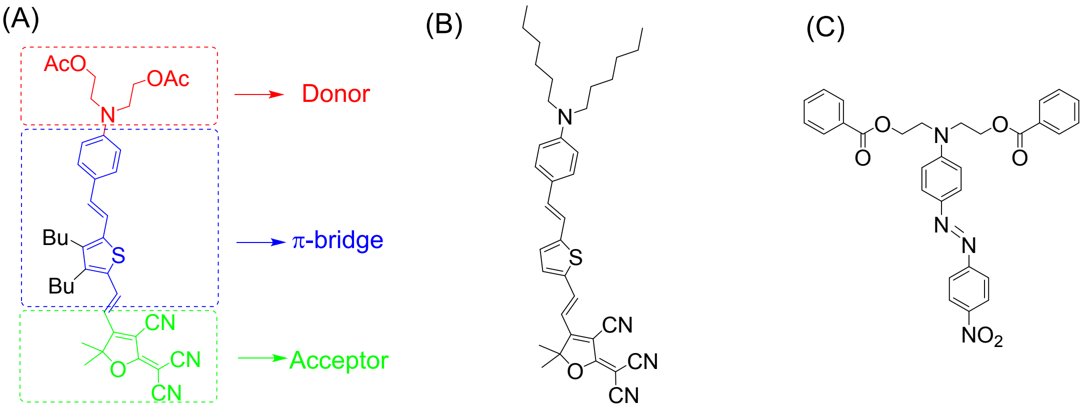


Fig. S1 (A) Poling and relaxing diagram: the most important thing is to overcome dipole-dipole interaction; (B) Spherical structure design: SIG chromophore, dendrimer structure and tree structure; (C) The meaning of two picture; (D) Diagram of the tree structure design: the tree structure was consisted of branches and roots, and chromophores in the two parts are all in similar direction.



FTC chromophore
"FTC" means
"Fang's Thermally-stable Chromophore"

The FTC-type chromophore
used in this paper

Azo chromophore

Fig. S2 (A) The earliest FTC (Fang's Thermally-Stable Chromophore) chromophore molecular structure; (B) The molecular structure of FTC chromophore which was used as comparison in this paper; (C) The molecular structure of Azo chromophore.

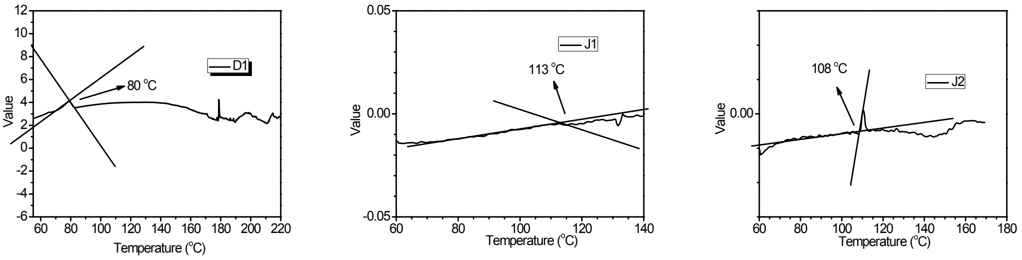


Fig. S3 DSC curves of **D1**, **J1** and **J2**.

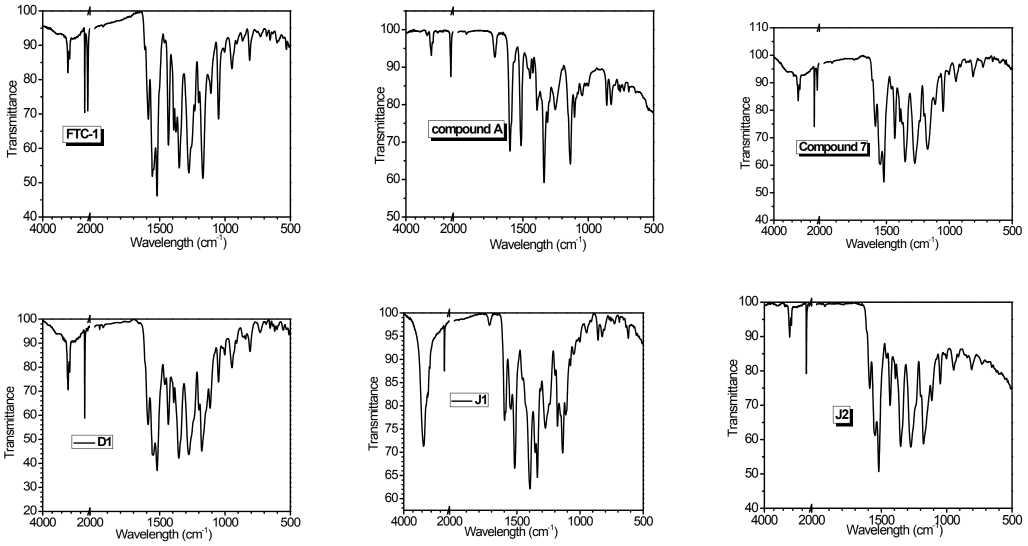


Fig. S4 FT-IR spectra of FTC-1, Compound A, Compound **7**, and **D1**, **J1** and **J2**.

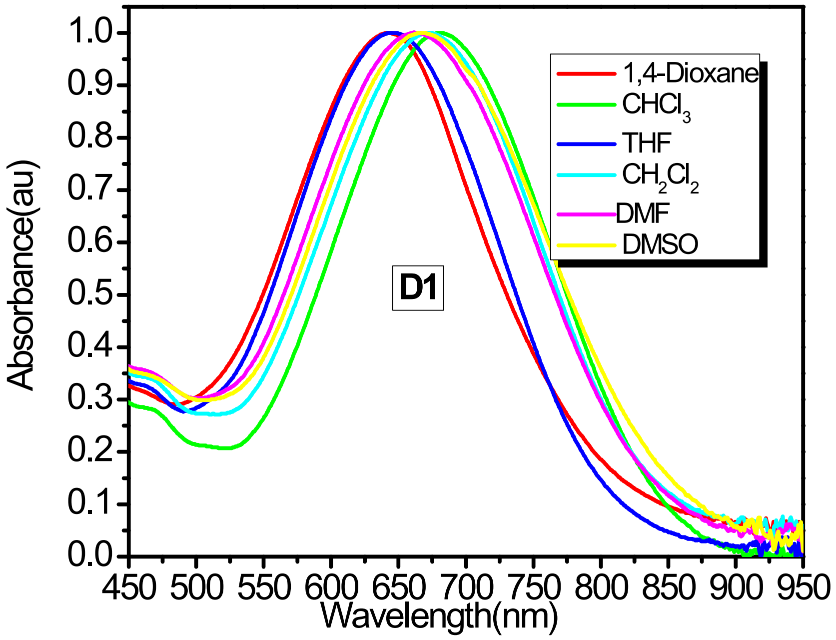
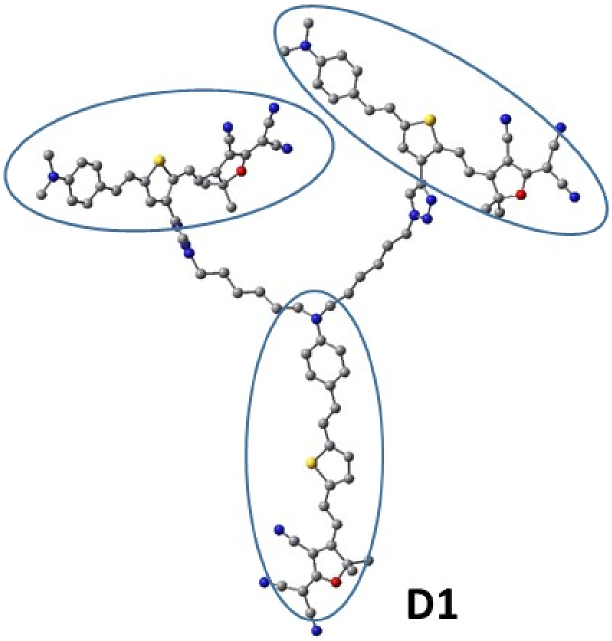
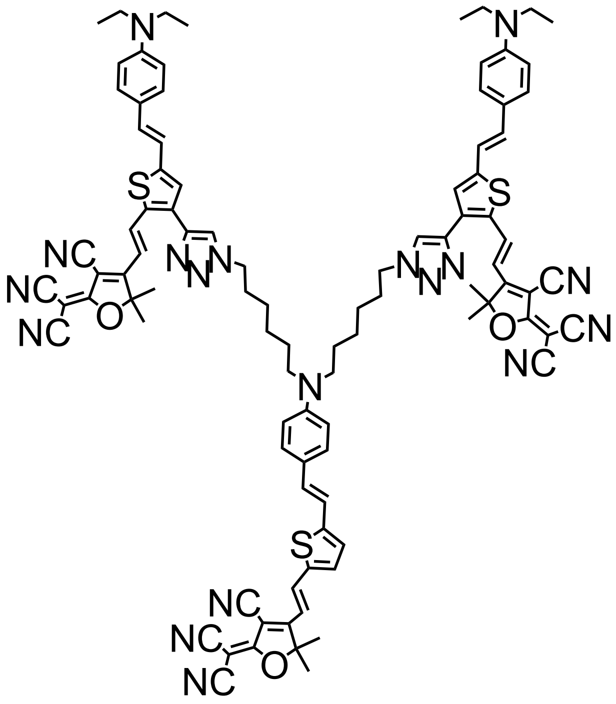
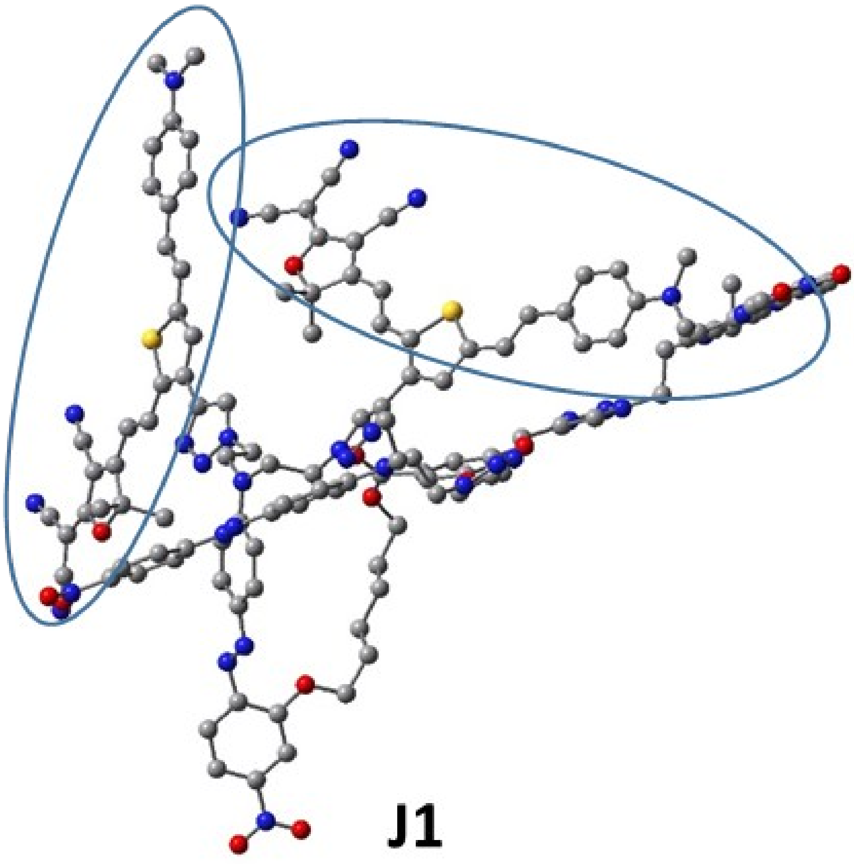


Fig. S5 Solvatochromism spectra of **D1**

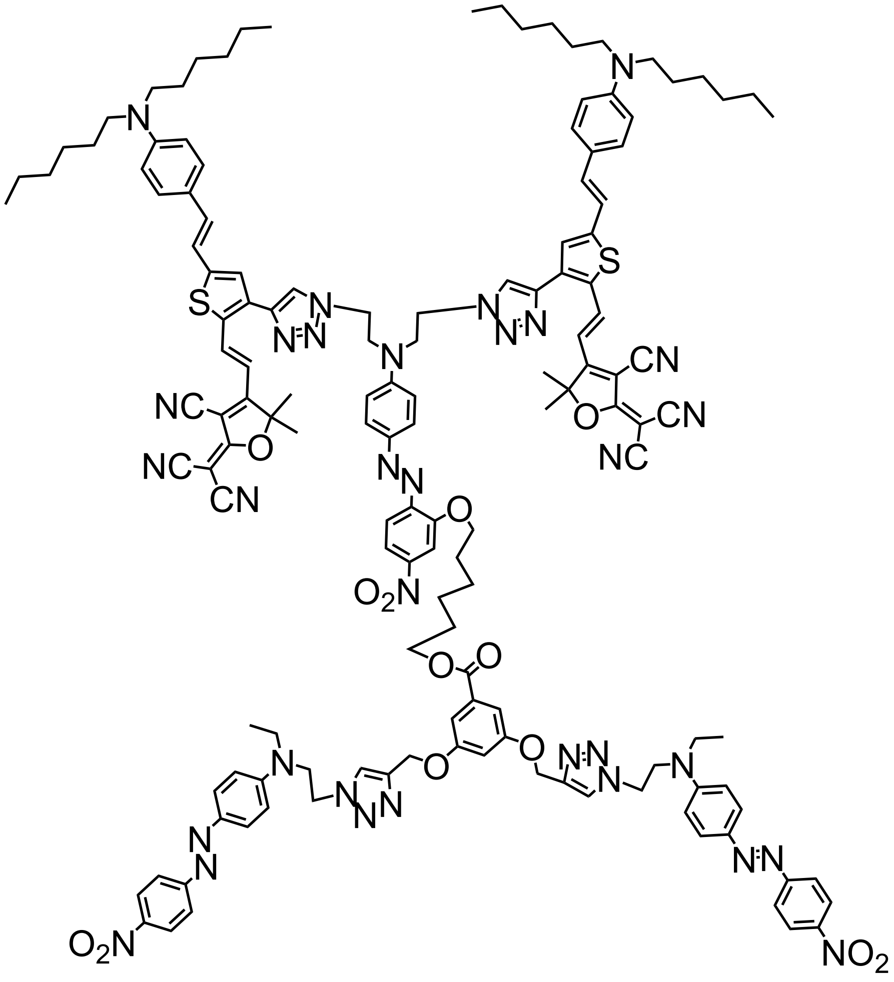


D1





J1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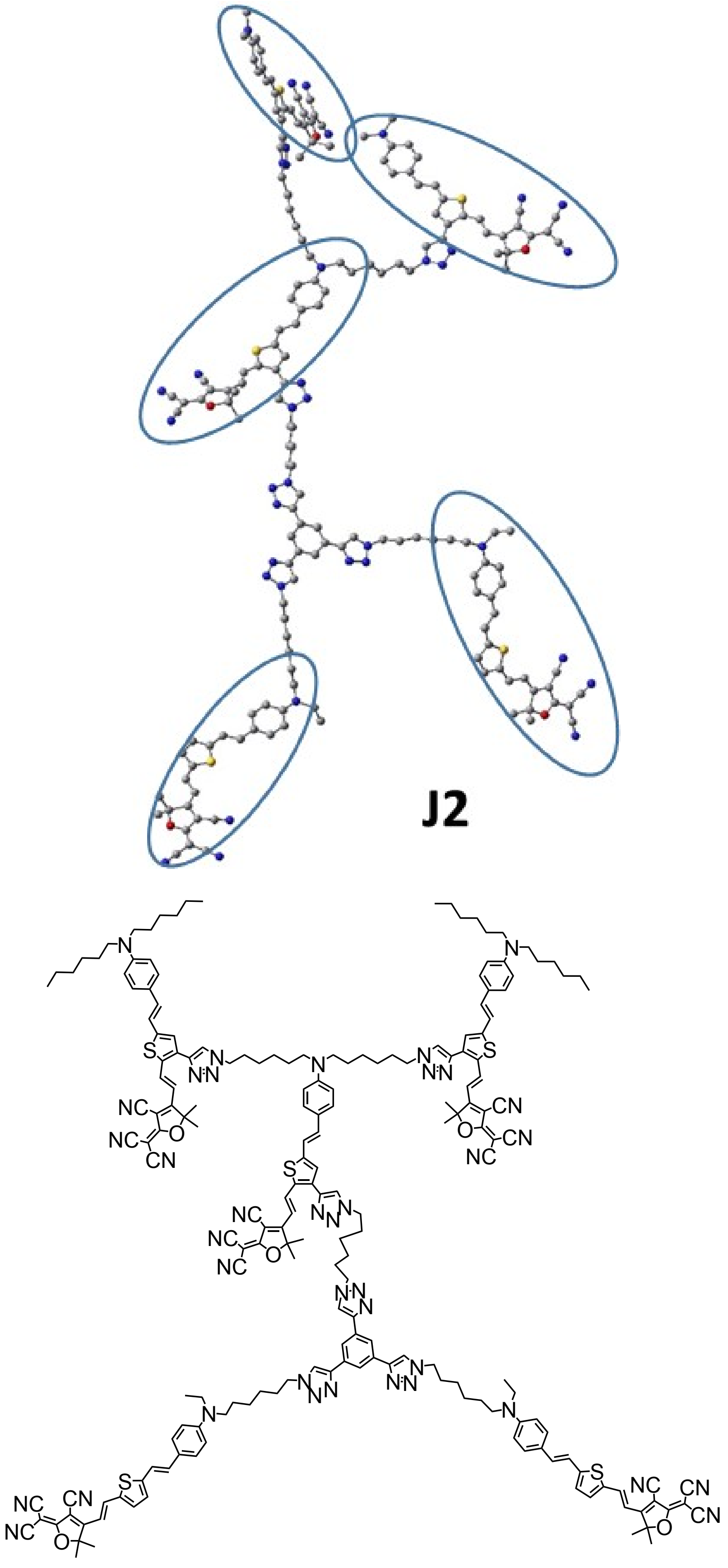


J2

Fig. S6 Optimized chemical structures of **D1**, **J1** and **J2** with FTC parts labelled in circle.

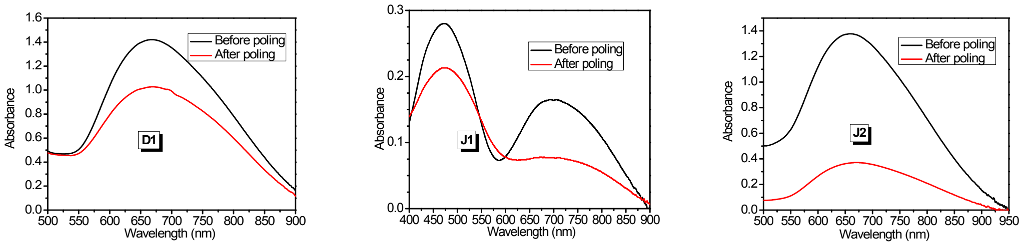


Fig. S7 UV-Vis spectrum of films of **D1**, **J1** and **J2**.

The order parameter at the λ_{max} $\Phi = 1-A_1/A_0$, where A_1 and A_0 were the absorbance of the film after and before corona poling, respectively. Φ of **D1**, **J1** and **J2** were 0.27, 0.23 (azo chromophore) & 0.52 (FTC chromophore) and 0.73, respectively.

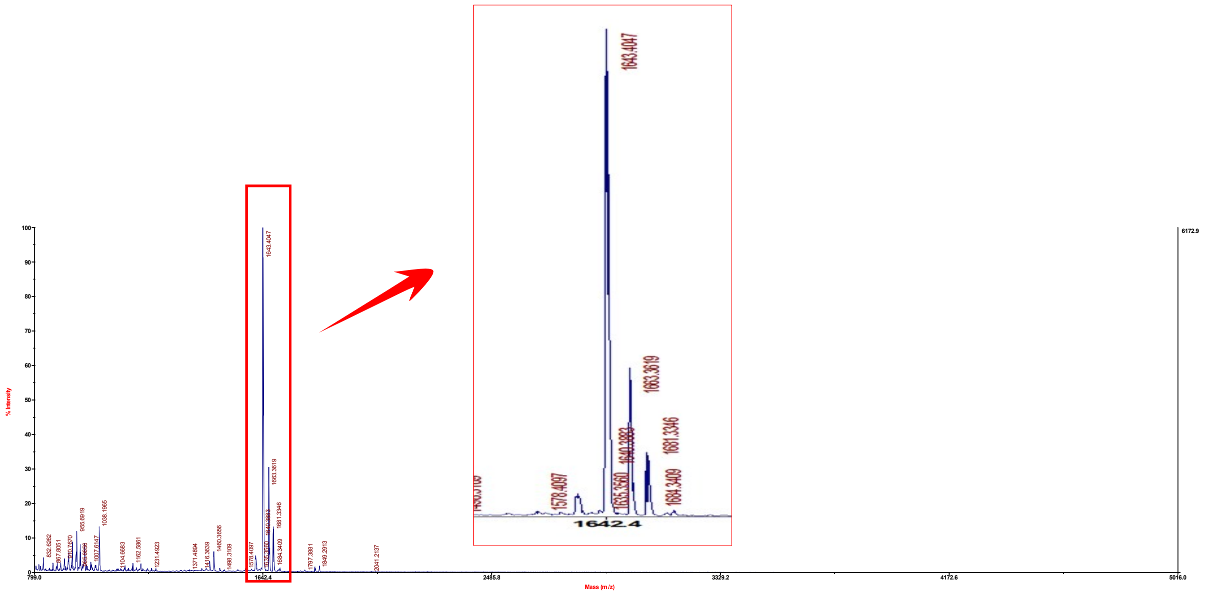


Fig. S8A. TOF spectrum **D1**.

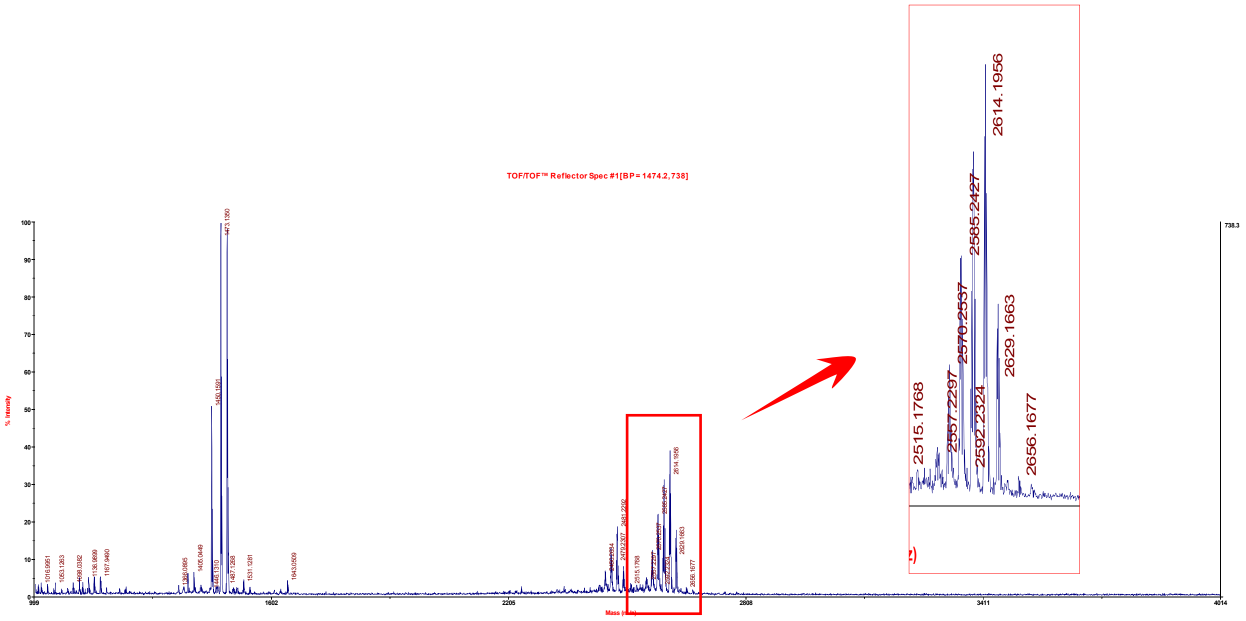


Fig. S8B. TOF spectrum of **J1**.

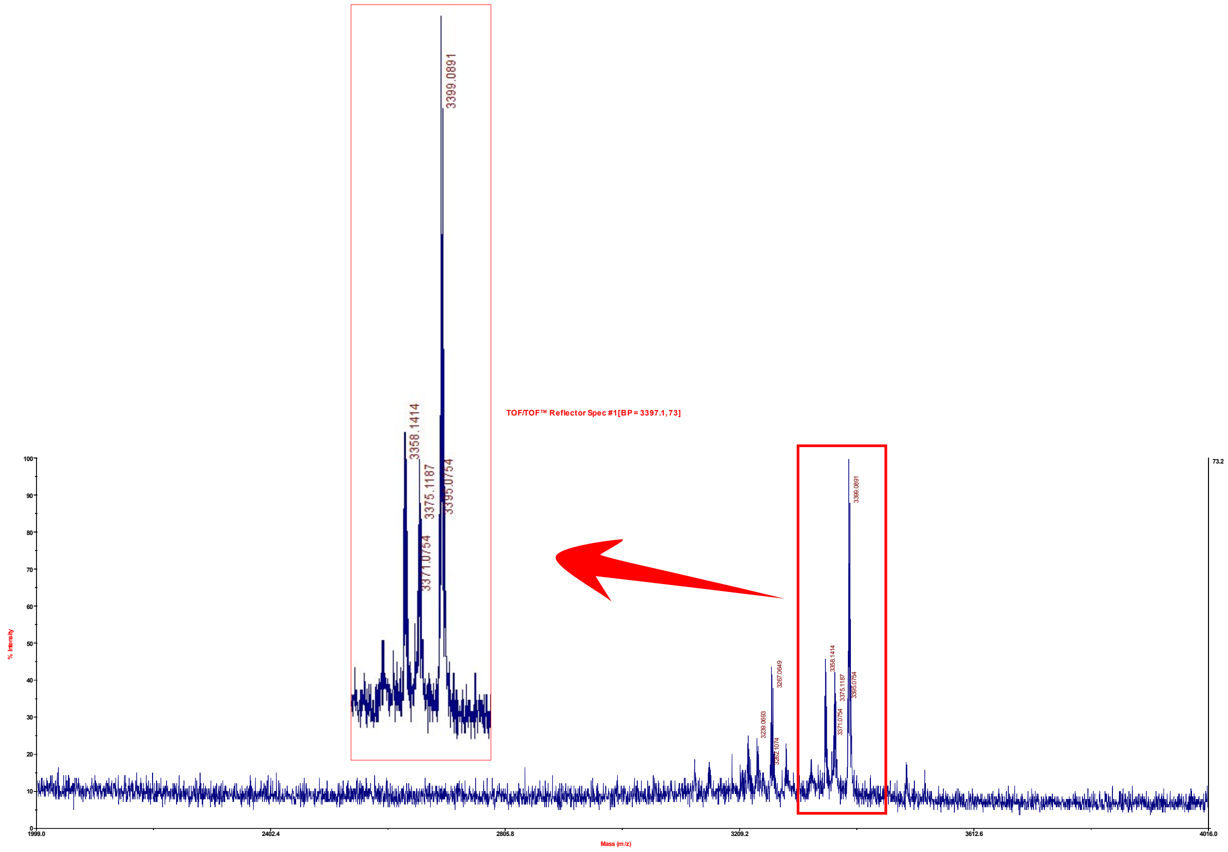
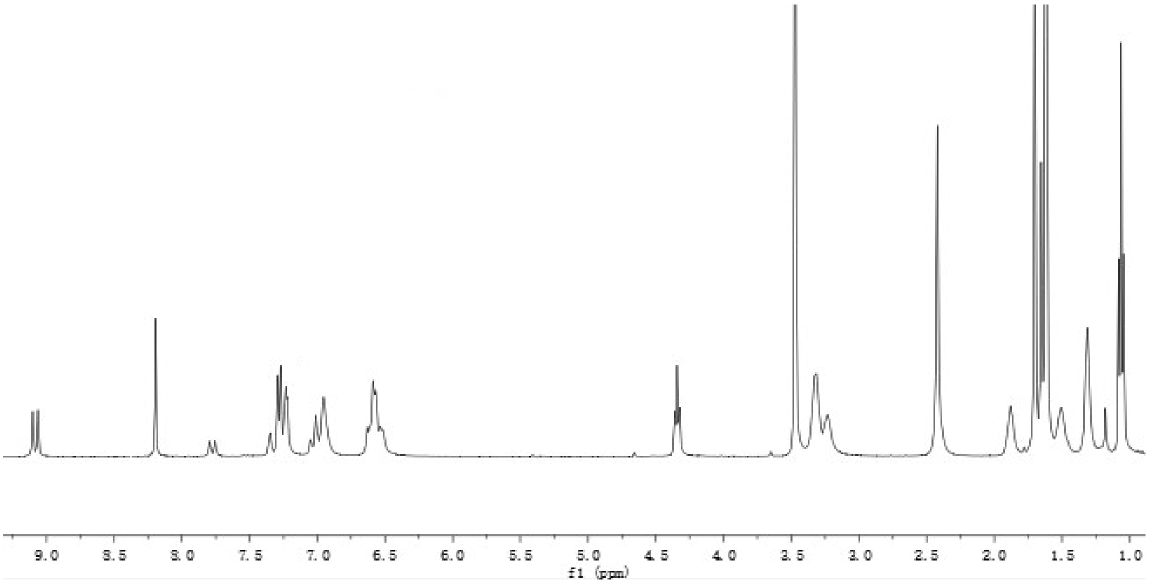


Fig. S8C. TOF spectrum of **J2**.



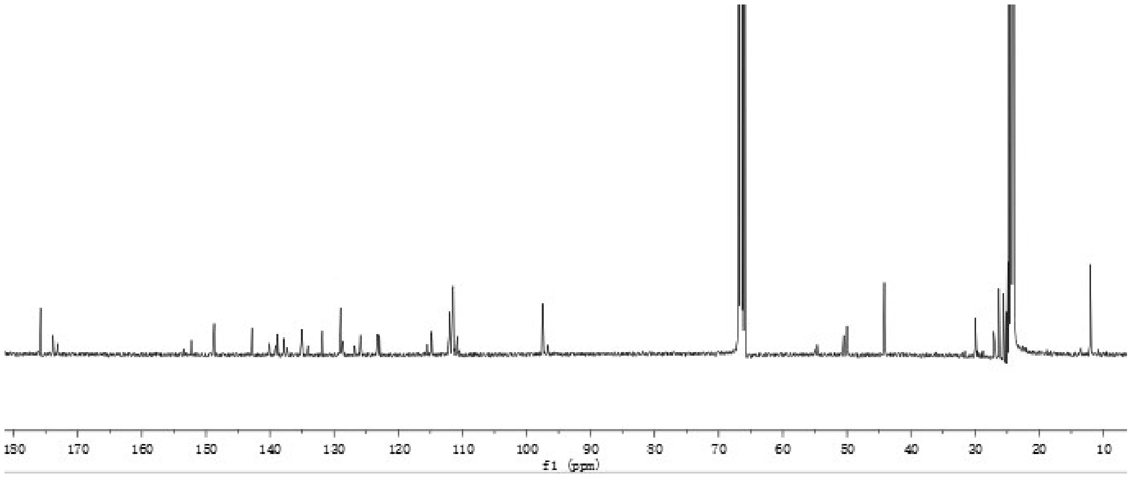


Fig.S9A ^{1}H and ^{13}C spectra of **D1**

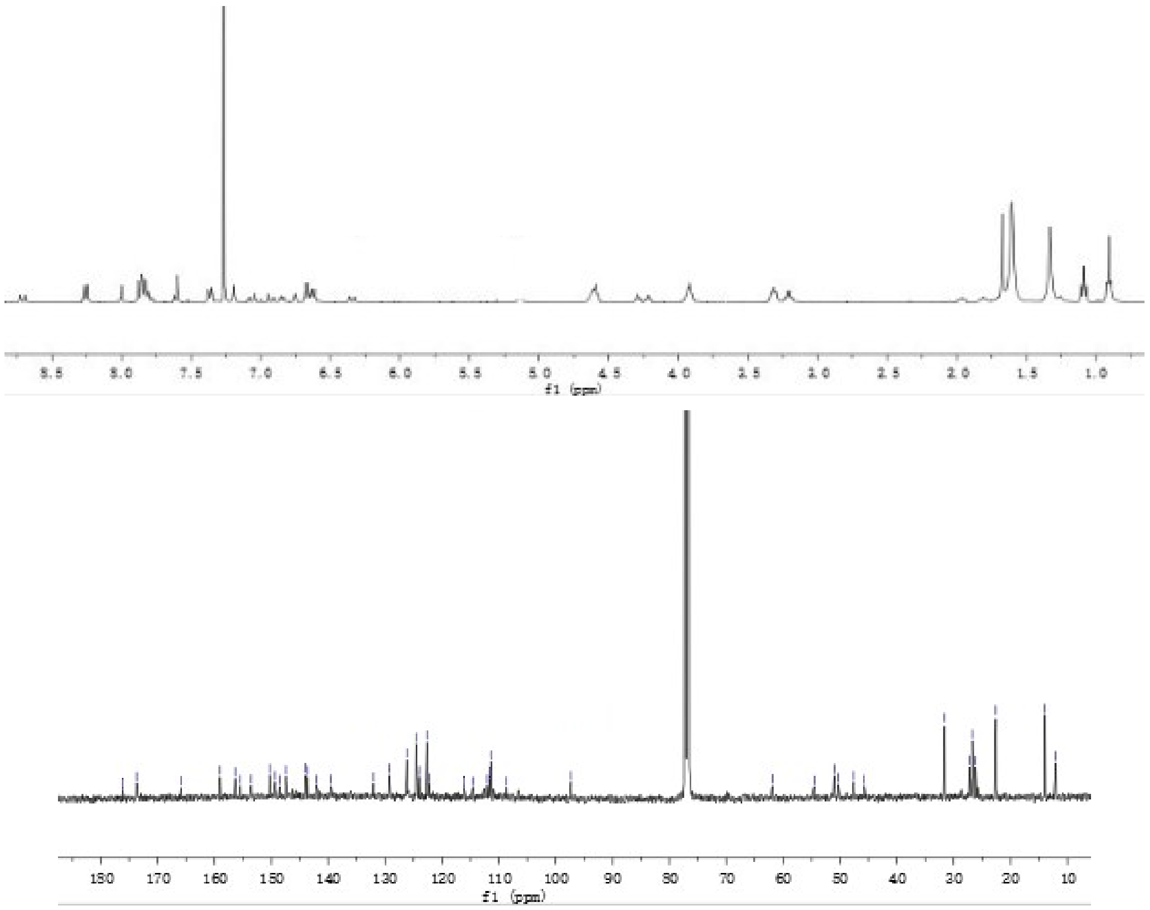


Fig.S9B ^{1}H and ^{13}C spectra of **J1**

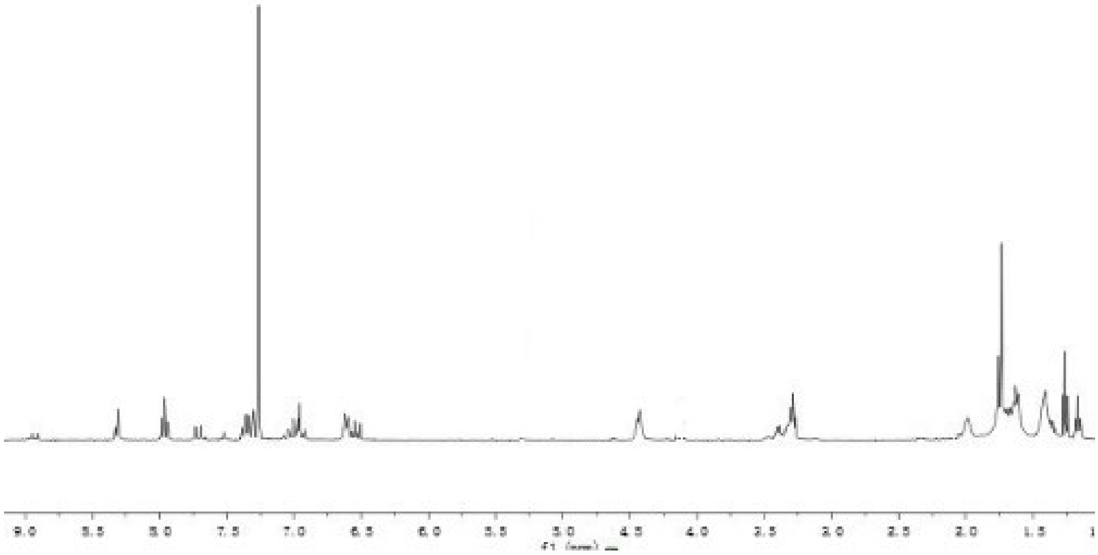


Fig.S9C ^{1}H spectrum of Compound **7**

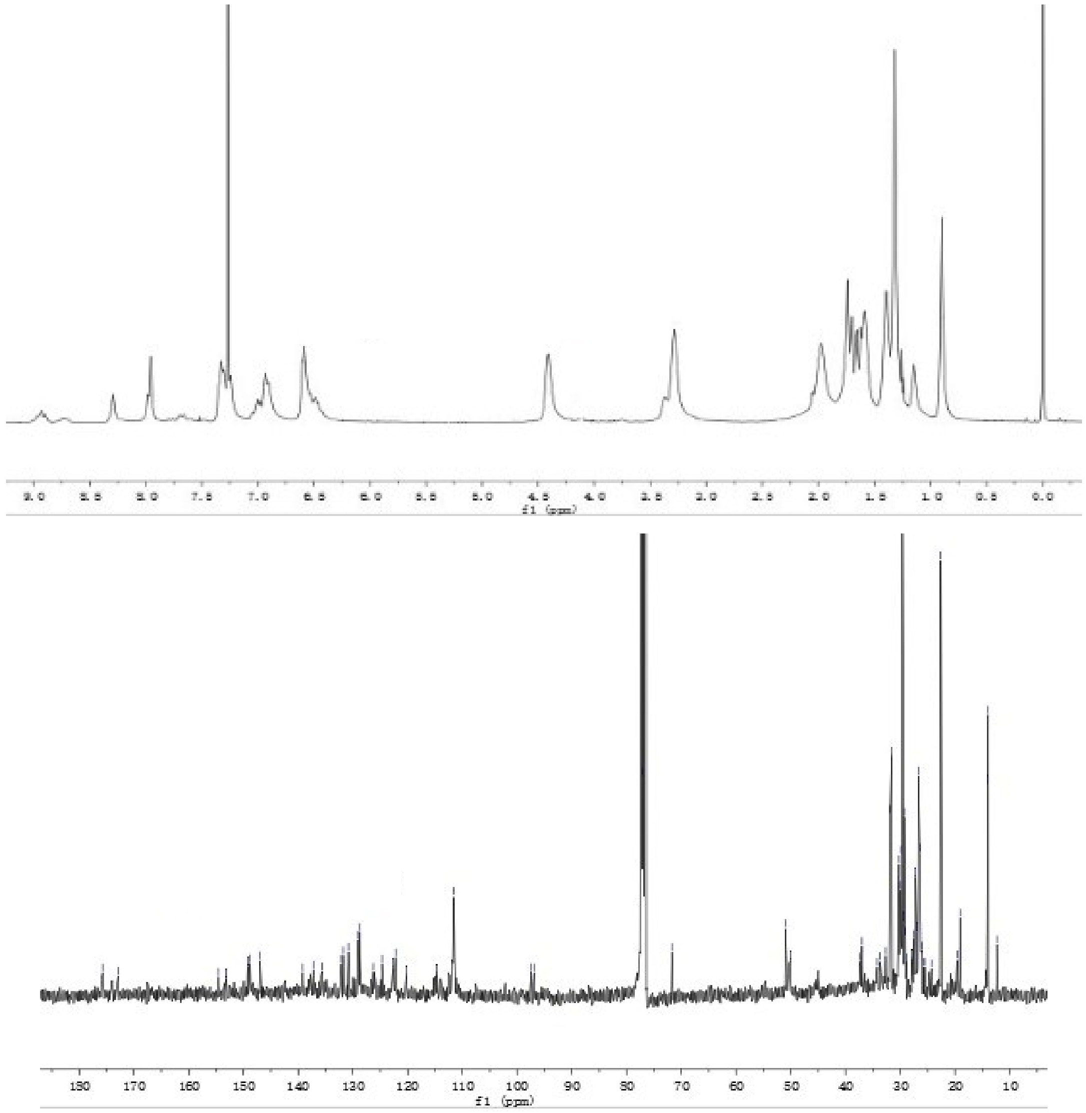


Fig.S9D ^{1}H and ^{13}C spectra of **J2.**

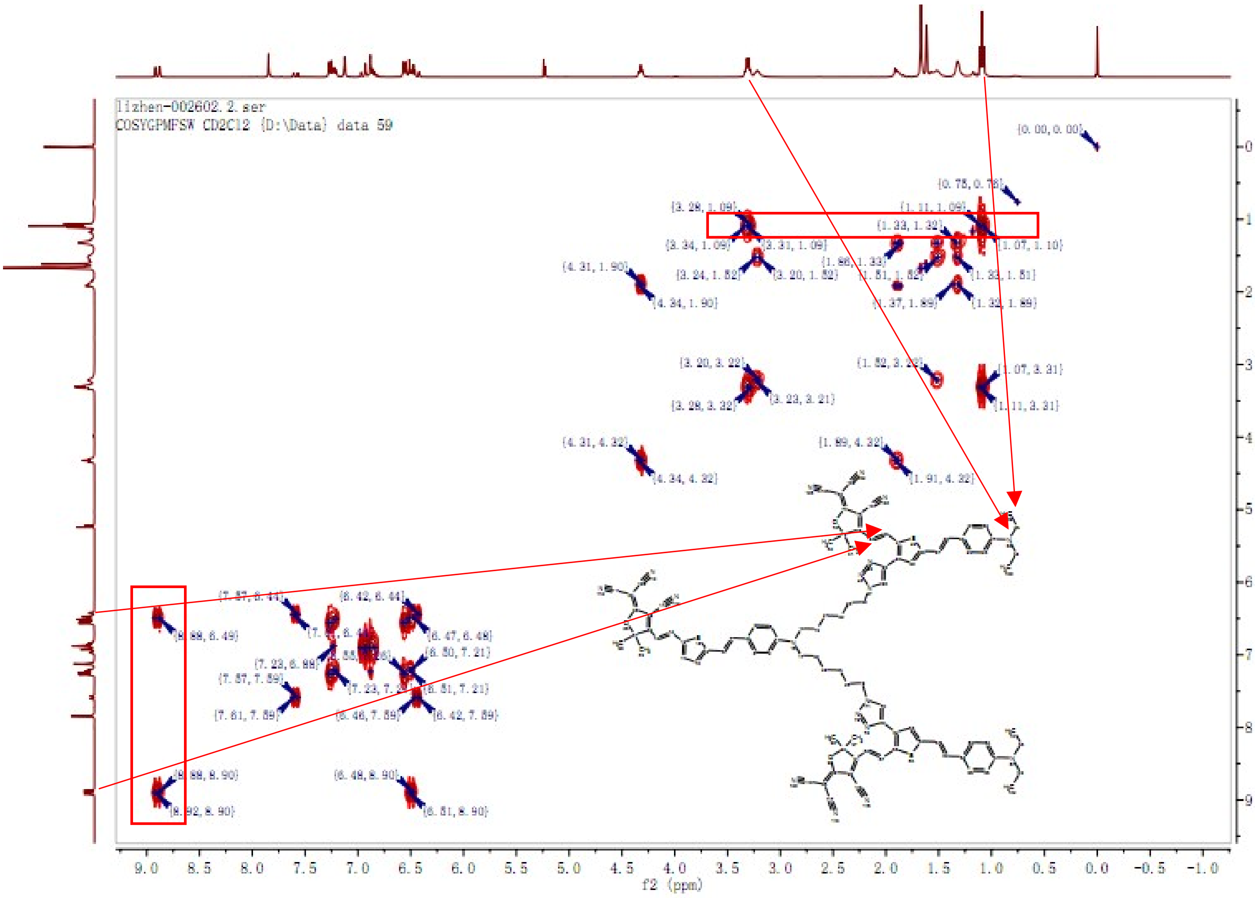


Fig. S10A COSY NMR of D1

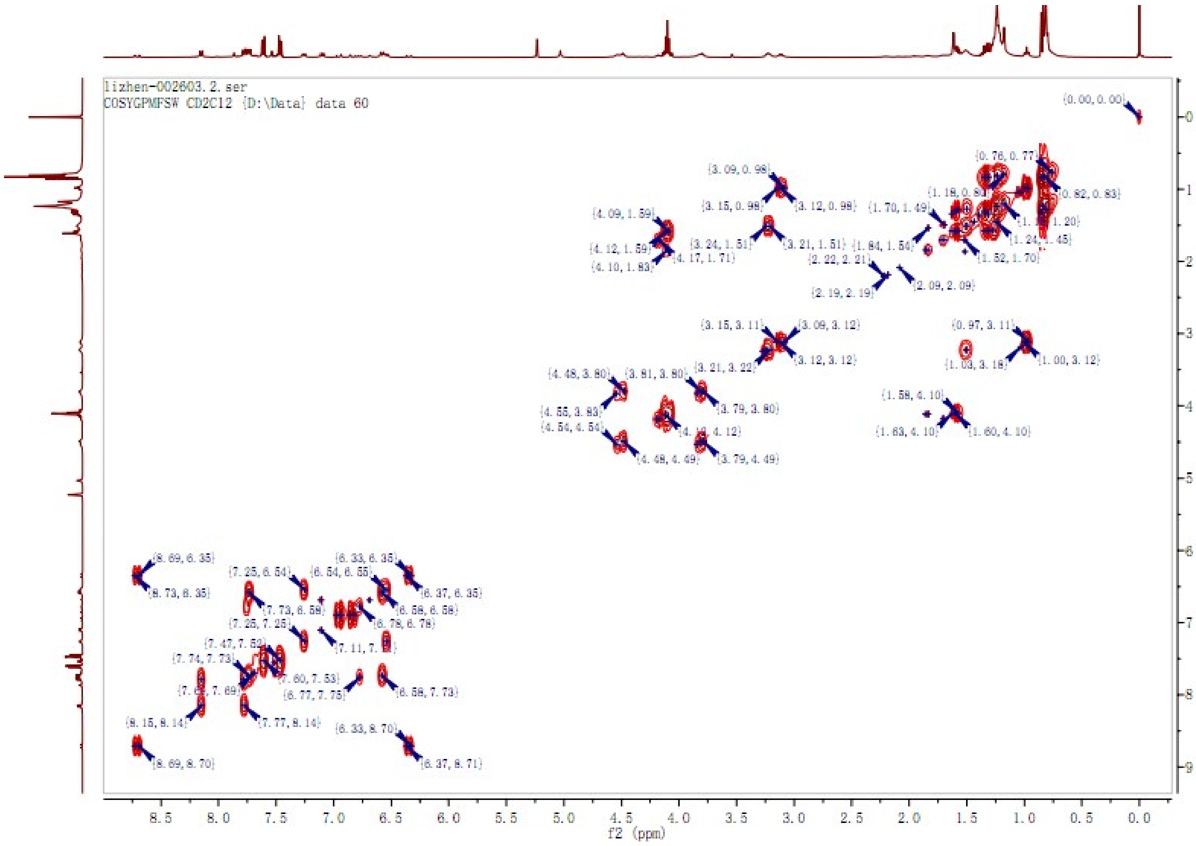


Fig. S10B COSY NMR of J1

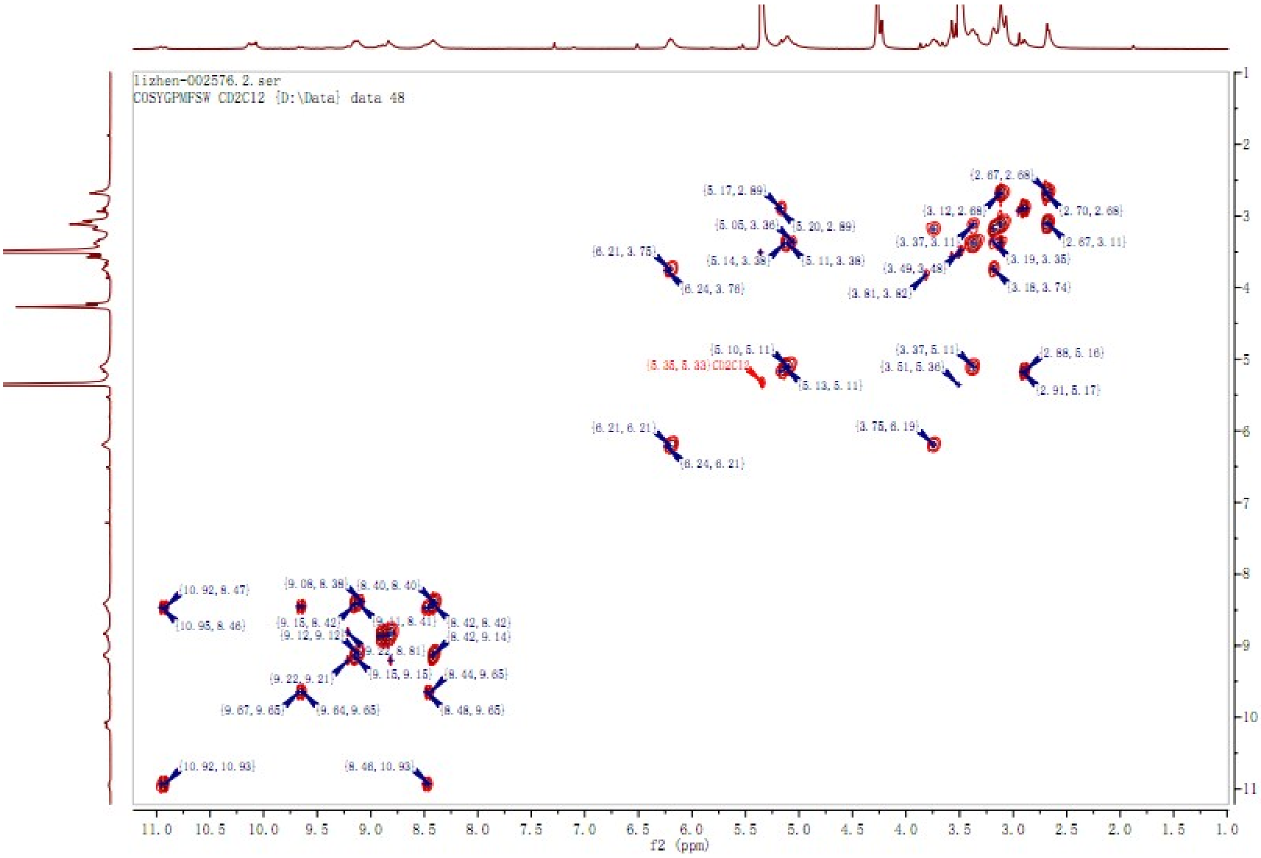
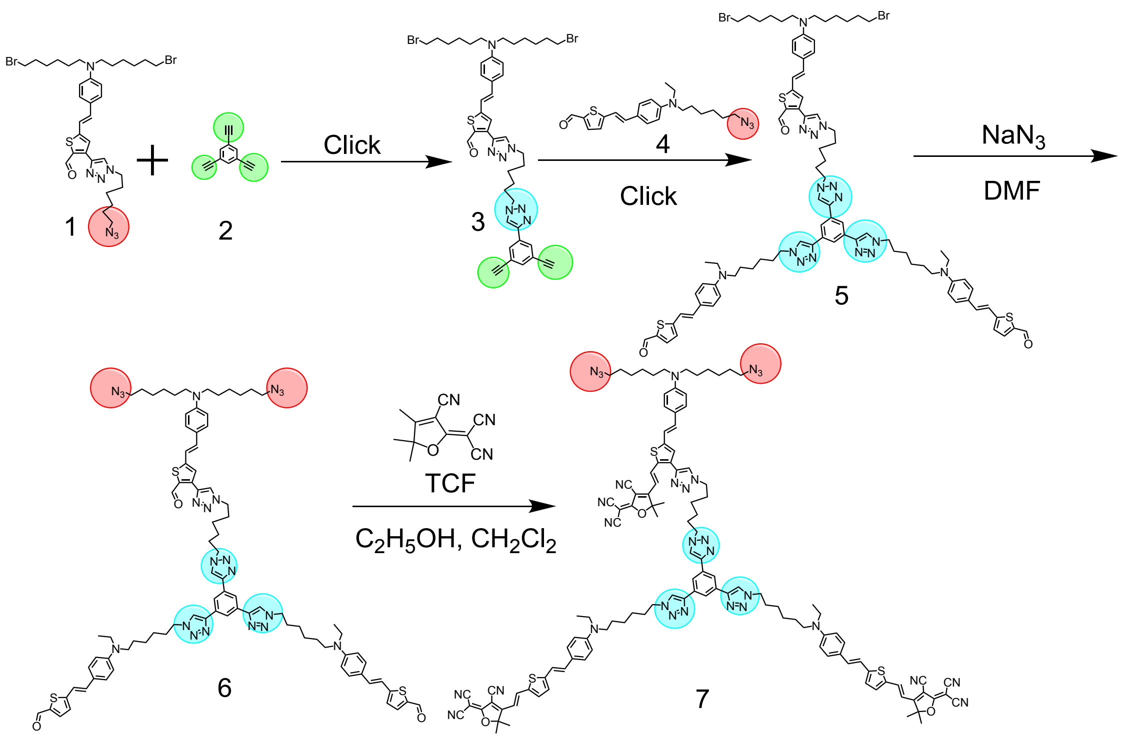


Fig. S10C COSY NMR of J2.

COSY NMR spectra were studied to further characterize **D1**, **J1** and **J2**. Figure S10 showed these two-dimensional NMR spectra. It was easy to identify the coupling between ^{1}H and ^{1}H, which was helpful for attribution and analysis of ^{1}H NMR spectra. For example, as shown in Figure S10A, the chemical shifts of two kinds of hydrogen atoms were confirmed easily according to the correlation peaks (in the red boxes).

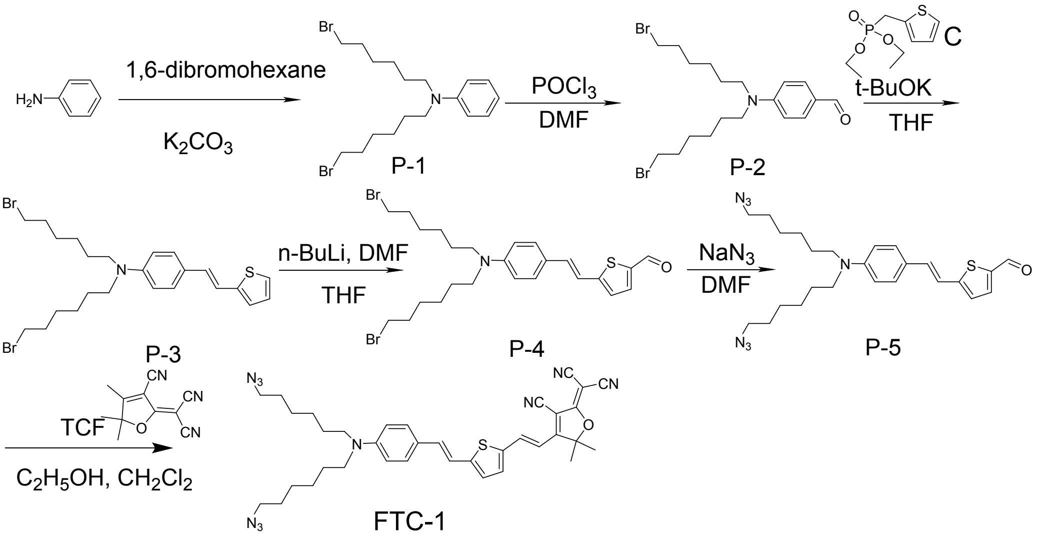
2. Experimental details

In this paper, we have synthesized 7 kinds of intermediate products. Compound 1, 2, 4, C, D, TCF, FTC-1, FTC-2 and FTC-3 were synthesized according to our previous work and other researchers' work.[1-4] Compound **3**, **5**, **6** and **7** were synthesized according to the synthesis route and procedures presented below.

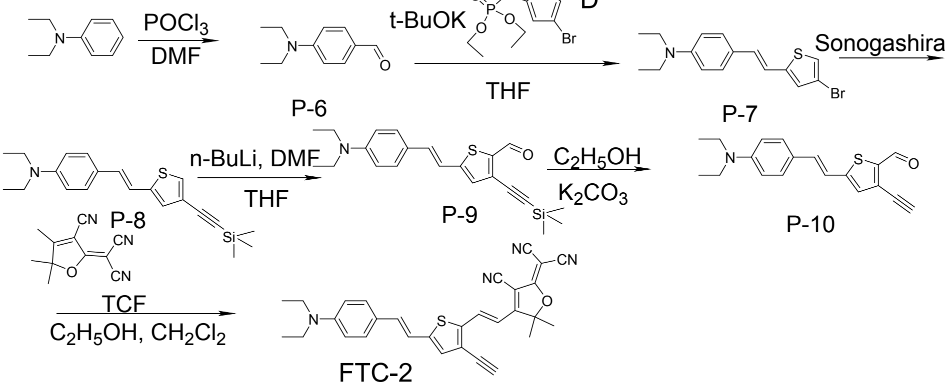


Our Previous Work:

Sythetic Route of FTC-1



Sythetic Route of FTC-2



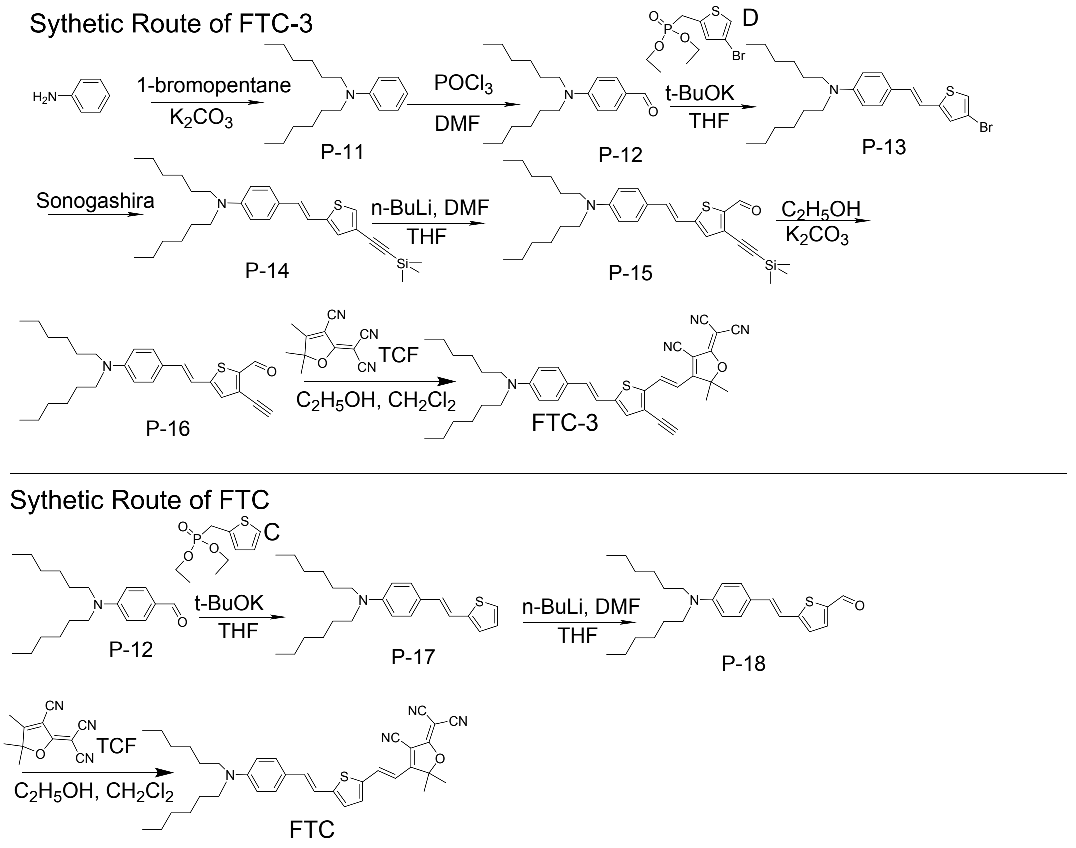


Fig.S11 Synthetic route of Compound **7** and Synthetic routes FTC, FTC-1-FTC-3 in our previous work.

Compound **3**. Under an atmosphere of dry nitrogen, a solution of compound **1** (160 mg, 0.214 mmol), compound **2** (160 mg, 1.07 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), sodium L-ascorbate (20% mmol) in 5/1 mL of THF/H_2O was stirred at 28 ^{o}C for 3 hrs. Then the reaction mixture was poured into water and extracted with CH_2Cl_2 for three times (50 mL×3). The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column spectroscopy on silica gel using CH_2Cl_2/PE (1:3) as eluent to give 162 mg of red solid (yield 84.3%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 10.33 (s, 1H, -CHO), 8.06 (s, H, ArH), 7.95 (m, 2H, ArH), 7.80 (s, H, -CH=), 7.56 (s, H, -CH=), 7.41 (s, H, ArH), 7.37-7.35 (d, *J*=8 Hz, 2H, ArH), 7.12-6.93 (m, 2H, -CH=), 6.61-6.59 (d, *J*=8 Hz, 2H, ArH), 4.44-4.38 (m, 4H, -CH_2-), 3.57-3.53 (m, 4H, -CH_2-), 3.32-3.29 (m, 4H, -CH_2-),3.12 (s, 2H, HC≡), 1.99-1.94 (m, 4H, -CH_2-), 1.81-1.78 (m, 4H, -CH_2-), 1.70 (m, 2H, -CH_2-), 1.61-1.60 (m, 4H, -CH_2-), 1.52-1.48 (m, 4H, -CH_2-), 1.43-1.36 (m, 6H, -CH_2-).

Compound **5**. Under an atmosphere of dry nitrogen, a solution of compound **3** (130 mg, 0.144 mmol), compound **4** (116 mg, 0.303 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), sodium L-ascorbate (20% mmol) in 5/1 mL of THF/H_2O was stirred at 28-30 ^{o}C for 3 hrs. Then the reaction mixture was poured into water and extracted with CH_2Cl_2 for three times (50 mL×3). The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column spectroscopy on silica gel using CH_2Cl_2/EA (1:5) as eluent to give 120 mg of red solid (yield 50.0%). ^{1}H NMR (400

MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 10.34 (s, 1H, -CHO), 9.79 (s, 2H, -CHO), 8.34-8.30 (m, 3H, ArH), 8.06 (s, 1H, ArH), 7.97 (s, 3H, ArH), 7.62-7.59 (m, 2H, ArH), 7.44-7.29 (m, 7H, ArH), 7.03-7,00 (m, 2H, ArH), 7.06-6.90 (m, 6H, -CH=), 6.63-6.56 (m, 6H, ArH), 4.45-4.39 (m, 8H, $-CH_2-$), 3.57-3.52 (m, 4H, $-CH_2-$), 3.42-3.34 (m, 4H, $-CH_2-$), 3.32-3.24 (m, 8H, $-CH_2-$), 2.03-1.93 (m, 8H, $-CH_2-$), 1.83-1.74 (m, 4H, $-CH_2-$), 1.66-1.54 (m, 8H, $-CH_2-$), 1.44-1.23 (m, 20H, $-CH_2-$), 1.18-1.11 (m, 6H, $-CH_3$).

Compound **6**. Under an atmosphere of nitrogen, a solution of compound **5** (120 mg, 0.072 mmol) and sodium azide (0.12 g, 1.84 mmol) in DMF (20 mL) was stirred at 80 ^{o}C for 6 h. Then the reaction mixture was poured into water. $CHCl_3$ (60 mL) was added. The DMF was removed by washing with water. After separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2 (50 mL × 2). The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column spectroscopy on silica gel using CH_2Cl_2/PE (1:1) as eluent to give a red solid (112 mg, 98.0%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 10.34 (s, 1H, -CHO), 9.79 (s, 2H, -CHO), 8.35-8.30 (m, 3H, ArH), 8.07 (s, 1H, ArH), 7.99 (s, 3H, ArH), 7.63-7.59 (m, 2H, ArH), 7.44-7.30 (m, 7H, ArH), 7.04-7,00 (m, 2H, ArH), 7.08-6.89 (m, 6H, -CH=), 6.63-6.54 (m, 6H, ArH), 4.46-4.35 (m, 8H, $-CH_2-$), 3.41-3.33 (m, 4H, $-CH_2-$), 3.33-3.21 (m, 12H, $-CH_2-$), 2.03-1.91 (m, 8H, $-CH_2-$), 1.71-1.51 (m, 12H, $-CH_2-$), 1.48-1.29 (m, 20H, $-CH_2-$), 1.18-1.11 (m, 6H, $-CH_3$).

Compound **7**. Under an atmosphere of nitrogen, a solution of compound **6** (93 mg, 0.058 mmol), TCF (46 mg, 0.229 mmol) and ammonium acetate in C_2H_5OH/DCM (3/0.6 mL) was stirred at room temperature for 12 h. Then the solution was condensed via rotary evaporation. The resultant crude product was purified by column chromatography with DCM/EA (3:1) as an eluent to give a blue powder (117 mg, 94.3%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.95-8.91 (d, J=8 Hz, 2H, -CH=), 8.34-8.29 (m, 3H, ArH), 8.00-7.92 (m, 3H, ArH), 7.73 (s, 1H, ArH), 7.69 (s, 1H, ArH), 7.40-7.29 (m, 8H, ArH), 7.05-6.90 (m, 7H, -CH=, ArH), 6.66-6.49 (m, 11H, ArH, -CH=), 4.48-4.38 (m, 8H, $-CH_2-$), 3.52-3.22 (m, 12H, $-CH_2-$), 2.04-1.92 (m, 8H, $-CH_2-$), 1.87-1.53 (m, 36H, $-CH_2-$), 1.48-1.31 (m, 18H, $-CH_3$), 1.18-1.11 (m, 6H, $-CH_3$).

Notes and references

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