

## Electronic supplementary information (ESI)

### Ringlike Molecule: Large Second-Order Nonlinear Optical Performance, Good Temporal Stability, Excellent Thermal Stability and Ideal Spherical Structure Conforming The “Site Isolation” Principle

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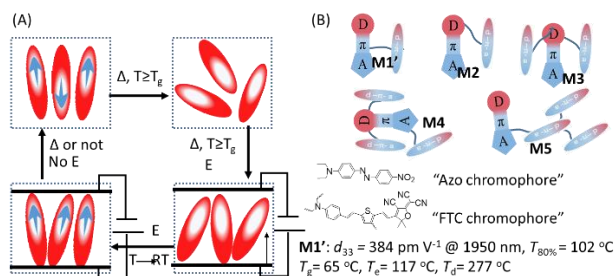
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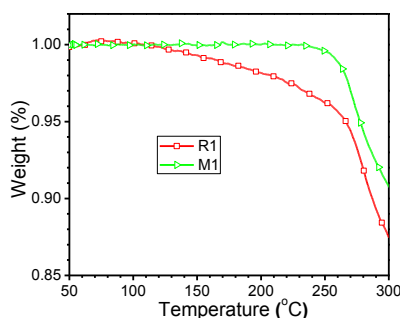
#### 3. Reference

## 1. Additional data and analysis

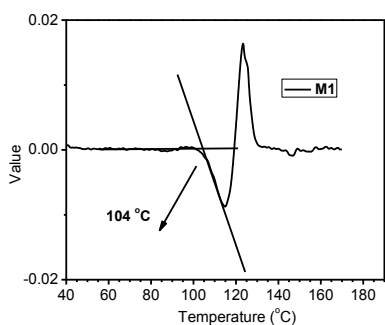


**Fig. S1** (A) Poling and depoling diagrammatic; (B) Our previous work.

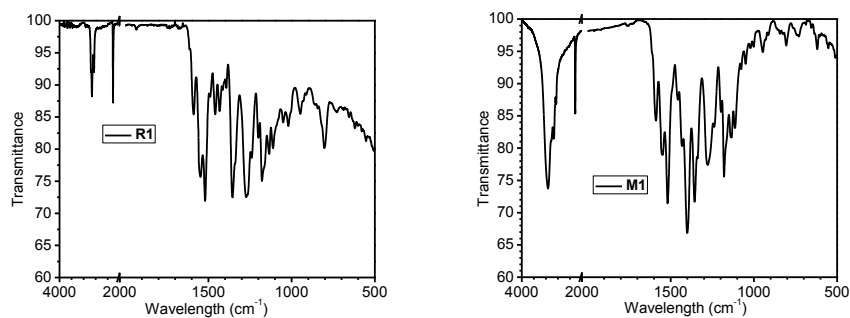
As shown in Figure S1A, under the applied electric field and high temperature, chromophore moieties would trend to arranging in non-centrosymmetry. After the electric field was turned off, chromophore moieties would recover the centrosymmetry arrangement due to the molecular thermodynamic movement and heating could accelerate this process. As shown in Figure S1B, the "isolation chromophore" concept was used in our previous work and five molecules were designed and synthesized. Among five of them, M1' obtained the best NLO performance, with its  $d_{33}$  value up to 384 pm/V @ 1950 nm ( $T_{80\%} = 102 \text{ }^\circ\text{C}$ ,  $T_g = 65 \text{ }^\circ\text{C}$ ,  $T_e = 117 \text{ }^\circ\text{C}$ ,  $T_d = 277 \text{ }^\circ\text{C}$ ).



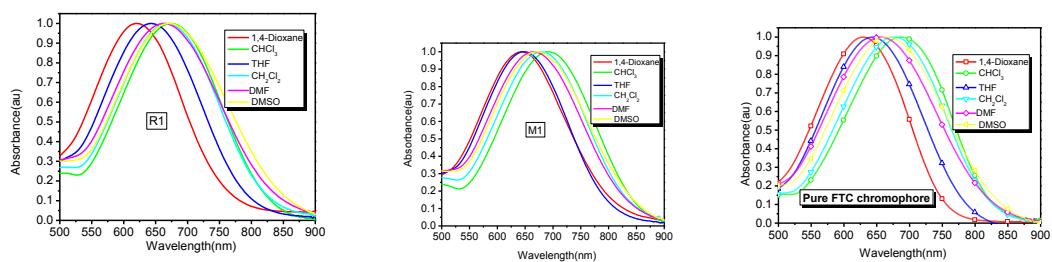
**Fig. S2** TGA curves of **R1** and **M1**.



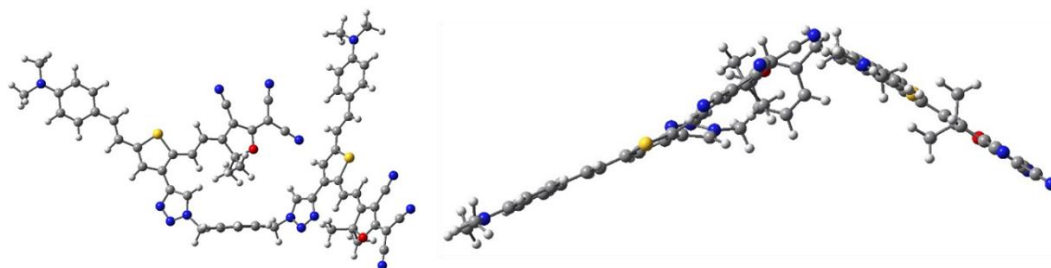
**Fig. S3** DSC curves of **M1**. (The  $T_g$  of **R1** could not be measured.)



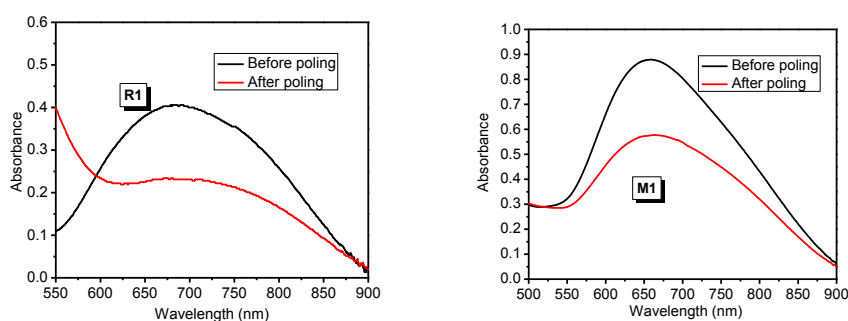
**Fig. S4** FT-IR spectra of **R1** and **M1**.



**Fig. S5** Solvatochromism spectra of **R1**, **M1** and pure FTC.

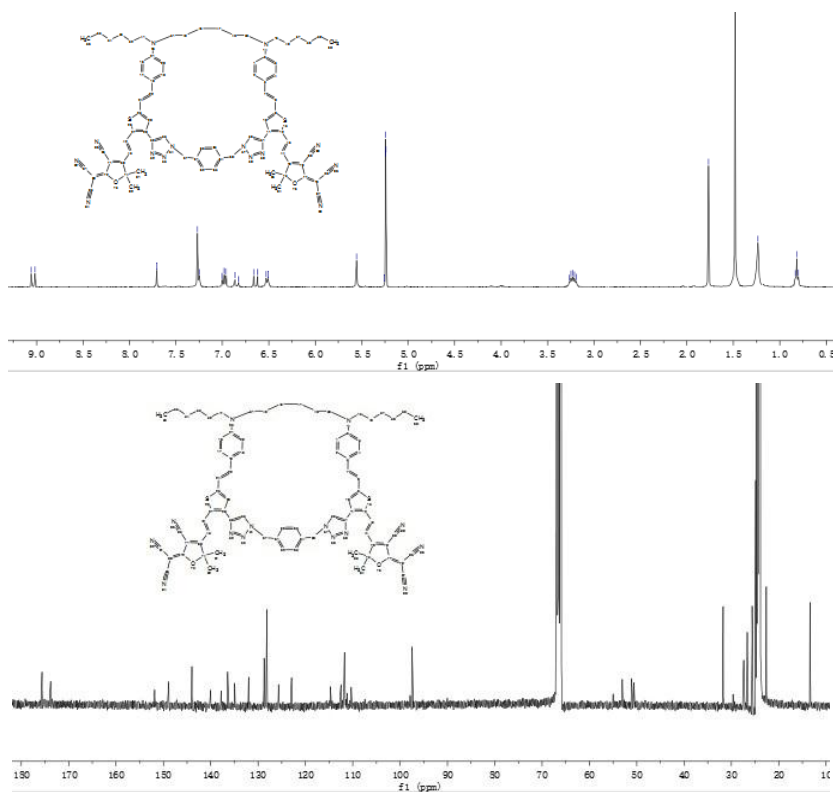


**Fig. S6** Optimized chemical structures of **M1**.

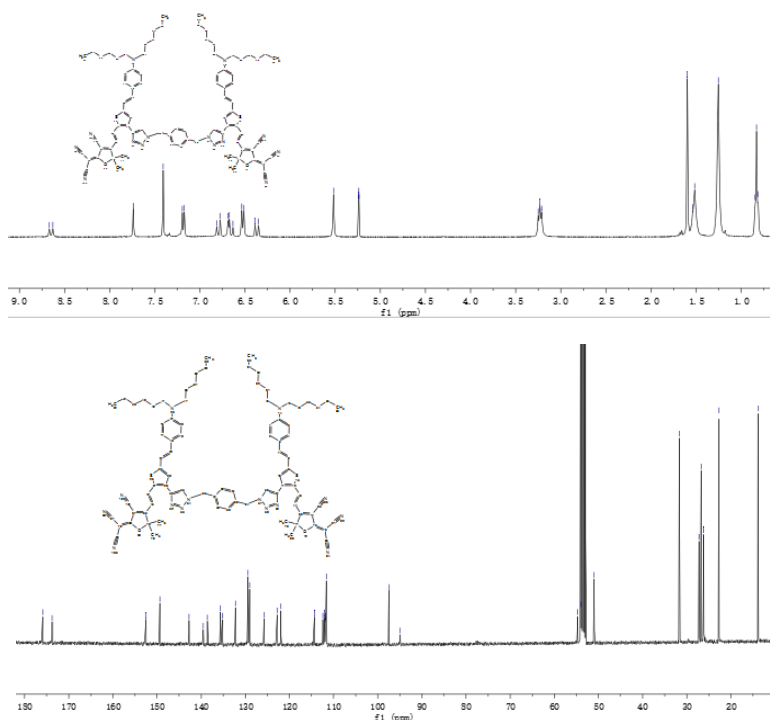


**Fig. S7** UV-Vis spectrum of films of **R1** and **M1**.

Order parameter  $\Phi = 1 - A_1/A_0$ , where  $A_1$  and  $A_0$  are the absorbance of the film after and before corona poling, respectively. So  $\Phi(R1)$  was 0.43 and  $\Phi(R1)$  was 0.34.



**Fig.S8A** <sup>1</sup>H and <sup>13</sup>C NMR spectra of R1



**Fig.S8B** <sup>1</sup>H and <sup>13</sup>C NMR spectra of M1

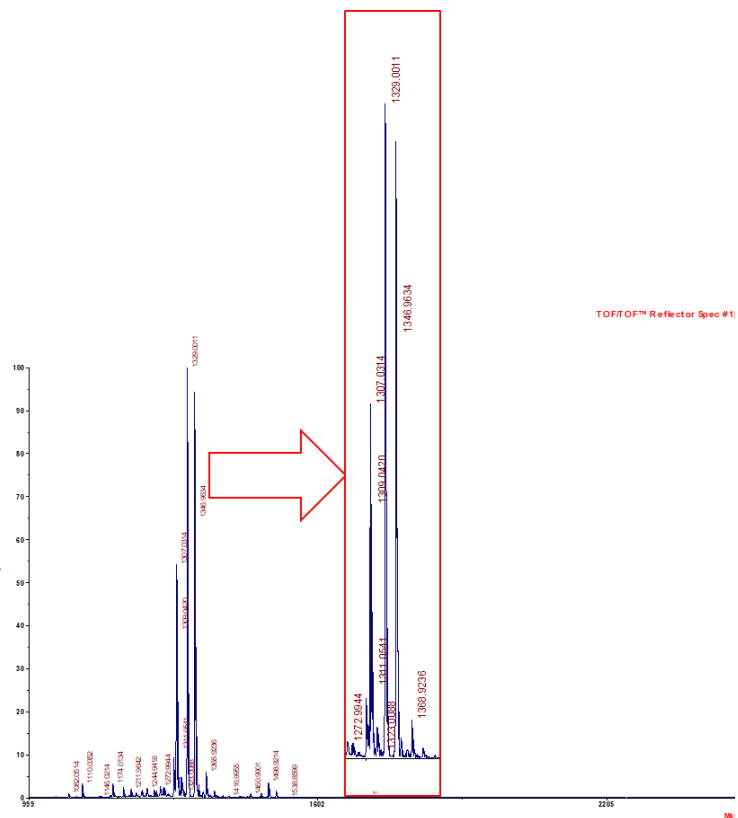


Fig. S9A TOF spectrum of R1.

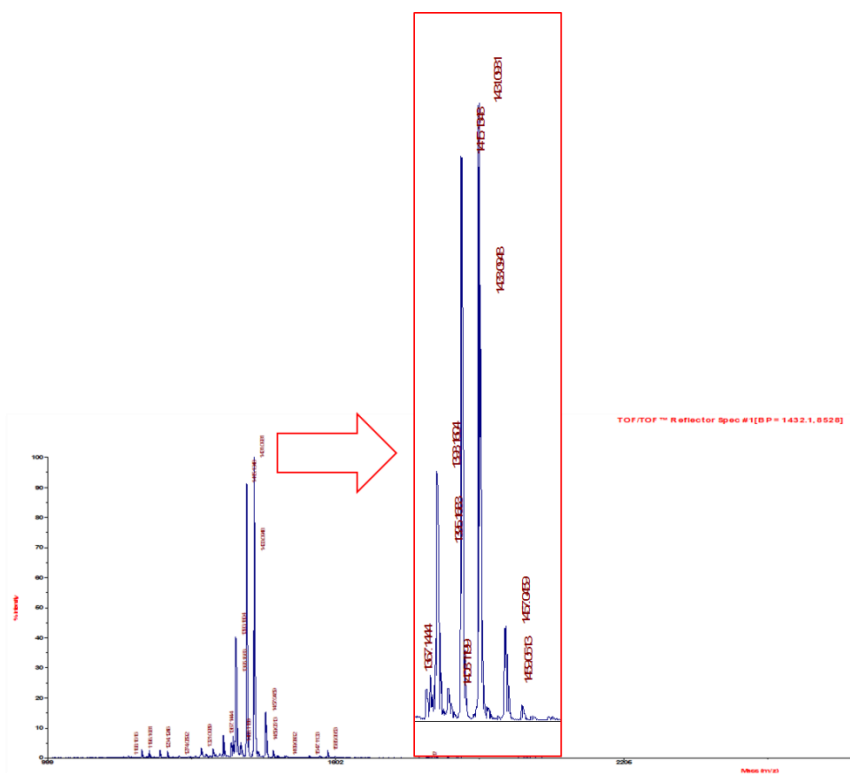
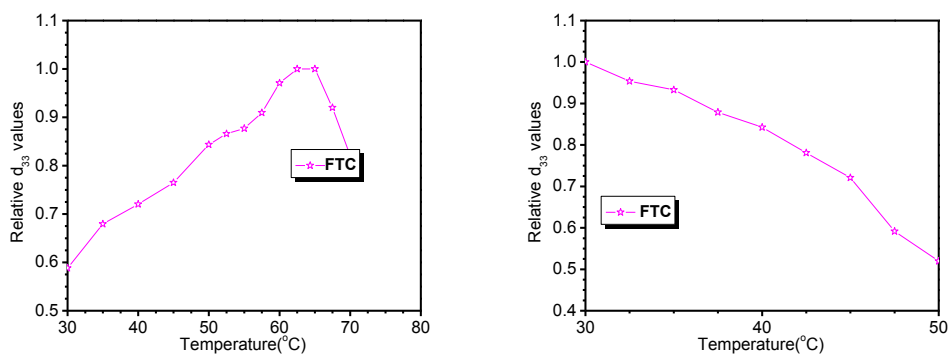


Fig. S9B TOF spectrum of M1.



**Fig. 10** Poling and decay curves of pure FTC.

Table S1 Thermal properties and NLO performance of pure FTC.

NO.	$T_g^a$ (°C)	$T_d^b$ (°C)	$T_e^c$ (°C)	$T_{80\%}^d$ (°C)	$d_{33}^e$ (pm/V)
FTC	-	263	62.5	41	119

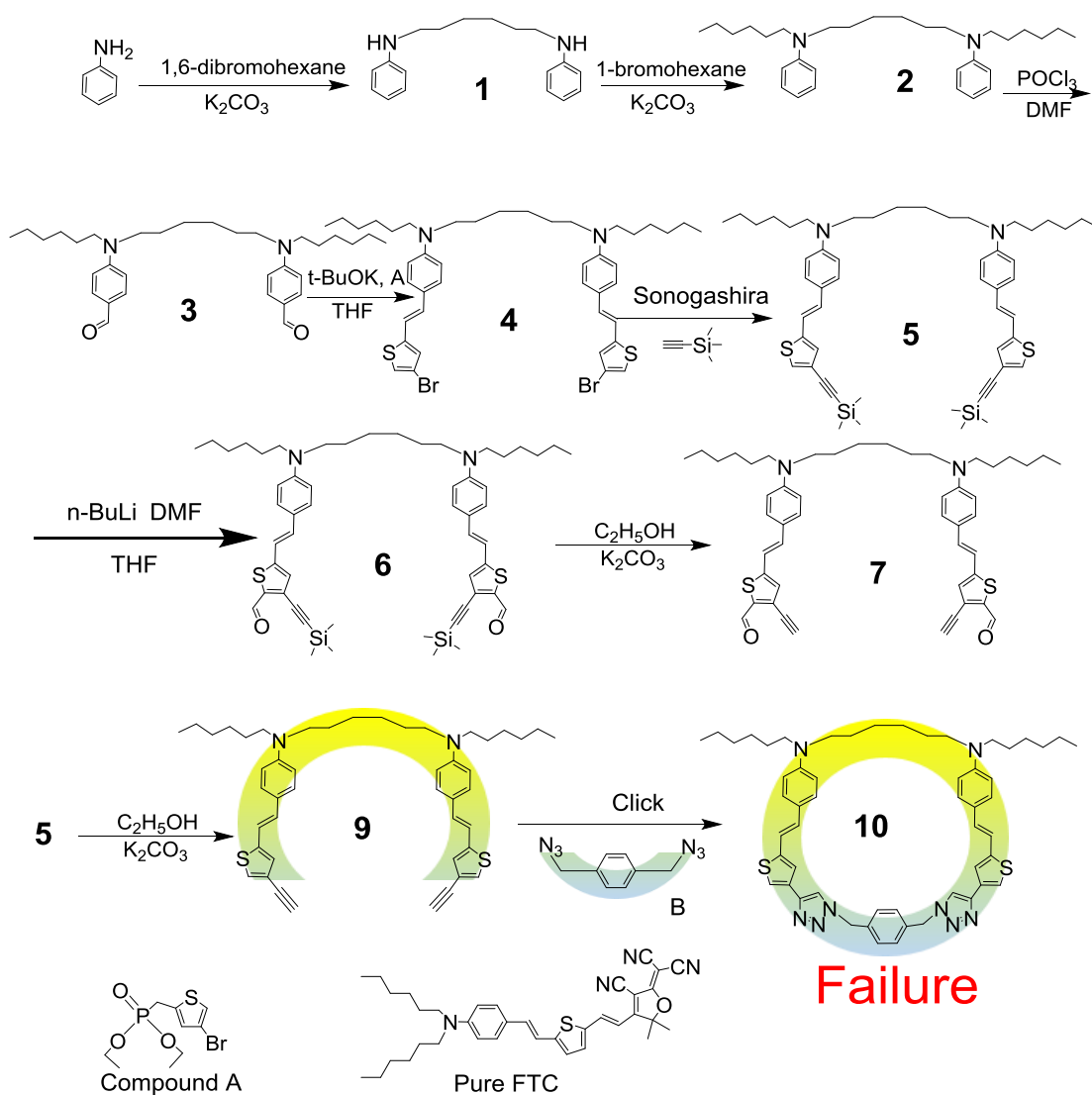
<sup>a</sup>Glass transition temperature. <sup>b</sup>The 5% weight loss temperature. <sup>c</sup>The best poling temperature.

<sup>d</sup>The temperature at which  $d_{33}$  values decreased to its 80%. <sup>e</sup>The  $d_{33}$  values (NLO performance).

The film-forming property of pure FTC chromophore was not very good. The films based on it were inhomogeneous. Related data of them may be not very reliable.

## 2. Experimental details

Dichloromethane and *N,N*-dimethylform amide (DMF) were dried over and distilled from calcium hydride. Anhydrous ethanol were dried over and distilled from sodium metallic. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Compound A and pure FTC were synthesized according to our previous literature method.<sup>1</sup> All other reagents were used as received.



**Fig. S11** Synthetic route of intermediate product compound **7** and the molecular structure of pure FTC.

**Compound 1.** A solution of aniline (18.6 g, 200 mmol), 1,6-dibromohexane (12.1 g, 50 mmol), potassium carbonate (6.9 g, 50 mmol) and potassium iodide (0.83 g, 5 mmol) was stirred at 80 °C for 12 hrs. Then the solid residue was removed through filtration, and rest aniline and 1,6-dibromohexane was removed through distillation. The residue was purified by column spectroscopy on silica gel using  $CH_2Cl_2/PE$  (3:1) as eluent to yield a white solid (9.0 g, 67.0%).  $^1H$  NMR (300 MHz,  $CDCl_3$ , 298 K),  $\delta$  (TMS, ppm): 7.19-7.14 (m, 4H, ArH), 6.71-6.85 (m, 2H, ArH), 6.61-6.58 (m, 4H, ArH), 3.58 (m, 2H, -NH-), 3.13-3.08 (m, 4H, - $CH_2$ -), 1.63-1.61 (m, 4H, - $CH_2$ -), 1.44 (m, 4H, - $CH_2$ -).

**Compound 2.** A solution of Compound **1** (5.4 g, 20 mmol), 1-bromohexane (8.5 g, 50 mmol), potassium carbonate (6.9 g, 50 mmol) and potassium iodide (0.83 g, 5 mmol) was stirred at 80 °C for 12 hrs. Then the reaction mixture was poured into water. After separation of the organic layer,

the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  2). The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation and reduced pressure distillation. The residue was purified by column spectroscopy on silica gel using  $\text{CH}_2\text{Cl}_2/\text{PE}$  (1:5) as eluent to give a yellow oil (7.6 g, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K),  $\delta$  (TMS, ppm): 7.22-7.18 (m, 4H, ArH), 6.64-6.60 (m, 6H, ArH), 3.27-3.22 (m, 8H,  $-\text{CH}_2-$ ), 1.58 (m, 4H), 1.37 (m, 4H,  $-\text{CH}_2-$ ), 1.31 (m, 12H,  $-\text{CH}_2-$ ), 0.91-0.88 (m, 6H,  $-\text{CH}_3$ ).

Compound **3**. DMF (10 mL) was cooled to 0 °C and phosphorus oxychloride (1.26 mL, 13.7 mmol) was added dropwise. The solution was kept stirred at 0 °C for 3 h and the temperature was kept constant during the dropwise addition of a solution of Compound **2** (2.0 g, 4.58 mmol) into DMF (10 mL). The solution was stirred for 2 h and gradually warmed to room temperature and stirred for 12 hrs at 80 °C before being poured into a 100 mL solution of potassium carbonate (10%) for quenching. The reaction mixture was extracted by dichloromethane (50 mL $\times$ 3), washed with brine. The organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The resultant crude product was purified by column chromatography with pure DCM as an eluent to give the product as a yellow oil (2.26 g, 100%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K),  $\delta$  (TMS, ppm): 9.70 (s, 2H,  $-\text{CHO}$ ), 7.71-7.69 (d,  $J=8$  Hz, 4H, ArH), 6.64-6.62 (d,  $J=8$  Hz, 4H, ArH), 3.37-3.31 (m, 8H,  $-\text{CH}_2-$ ), 1.64-1.61 (m, 4H,  $-\text{CH}_2-$ ), 1.40 (m, 4H,  $-\text{CH}_2-$ ), 1.33-1.32 (m, 12H,  $-\text{CH}_2-$ ), 0.92-0.89 (m, 6H,  $-\text{CH}_3$ ).

Compound **4**. Under an atmosphere of nitrogen, a solution of potassium *tert*-butoxide (1.3 g, 11.45 mmol) in THF (20 mL) was added to a mixture of compound **3** (2.26 g, 4.58 mmol), compound A (3.01 g, 4.58 mmol) in THF (20 mL) over 10 min under magnetic stirring. Stirring was continued for 10 min after the addition, and the reaction mixture was poured into water. After separation of the organic layer, the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  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  $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$  (1:10) as eluent to give the product (3.05 g, 80.8%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K),  $\delta$  (TMS, ppm): 7.31-7.29 (d,  $J=8\text{Hz}$ , 4H, ArH), 6.98 (s, 2H, ArH), 6.87-6.80 (m, 6H, ArH,  $-\text{CH}=\text{}$ ), 6.60-6.58 (d,  $J=8$  Hz, 4H, ArH), 3.30-3.25 (m, 8H,  $-\text{CH}_2-$ ), 1.57 (m, 4H,  $-\text{CH}_2-$ ), 1.38 (m, 4H,  $-\text{CH}_2-$ ), 1.31 (m, 12H,  $-\text{CH}_2-$ ), 0.90-0.88 (m, 6H,  $-\text{CH}_3$ ).

Compound **5**. Under an atmosphere of nitrogen, a solution of compound **4** (2.75 g, 3.39 mmol), CuI (32 mg, 0.163 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (19 mg, 0.027 mmol),  $\text{PPh}_3$  (29 mg, 0.11 mmol) in  $\text{Et}_3\text{N}$  (30



mL) was cooled to 0 °C, and ethynyltrimethylsilane (1.5 mL, 10.17 mmol) was added dropwise. The solution was stirred for 2 hrs and gradually warmed to room temperature and stirred for 12 hrs at 80 °C. Then the solution was condensed via rotary evaporation. The resultant crude product was purified by column chromatography with DCM/PE (1:10) as an eluent to give a yellow powder (2.8 g, 100%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 7.31-7.29 (d, *J*=8Hz, 4H, ArH), 7.24 (s, 2H, ArH), 6.96 (s, 2H, ArH), 6.87-6.80 (m, 4H, -CH=), 6.60-6.58 (d, *J*=8 Hz, 4H, ArH), 3.28-3.25 (m, 8H, -CH<sub>2</sub>-), 1.58 (m, 4H, -CH<sub>2</sub>-), 1.37 (m, 4H, -CH<sub>2</sub>-), 1.31 (m, 12H, -CH<sub>2</sub>-), 0.91-0.86 (m, 6H, -CH<sub>3</sub>), 0.23 (s, 18H, -CH<sub>3</sub>).

**Compound 6.** Under an atmosphere of nitrogen, a solution of compound **5** (2.8 g, 3.35 mmol) in THF (30 mL) was cooled to -78 °C, and *N*-butyllithium (4 mL, 8.74 mol, 2.175 M in hexane) was added dropwise. Stirring was continued for another 1 h, then anhydrous DMF (0.68 mL) was added through syringe over 5 min. The mixture was heated to room temperature and stirred for 30 min. Then the reaction mixture was poured into water. After separation of the organic layer, the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2) as eluent to give a red solid (2.1 g, 69.3%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K), δ (TMS, ppm): 10.03 (s, 2H, -CHO), 7.39-7.37 (d, *J*=8Hz, 4H, ArH), 7.12-6.92 (m, 6H, -CH=, ArH), 6.66-6.64 (d, *J*=8 Hz, 4H, ArH), 3.33 (m, 8H, -CH<sub>2</sub>-), 1.62 (m, 4H, -CH<sub>2</sub>-), 1.42 (m, 4H, -CH<sub>2</sub>-), 1.35 (m, 12H, -CH<sub>2</sub>-), 0.93-0.92 (m, 6H, -CH<sub>3</sub>), 0.31 (s, 18H, -CH<sub>3</sub>).

**Compound 9.** Compound **9** was synthesized in a similar method to Compound **7** and the pure product was yellow solid (1.3 g, 85.0%). This compound was not very stable.

**Compound 10.** Compound **10** was synthesized in a similar method to Compound **8** and no target product was found.

## Notes and references

- 1 P. Chen, X. Yin, Y. Xie, S. Li, S. Luo, H. Zeng, G. Guo, Q. Li and Z. Li, *J. Mater. Chem. C*, 2016, **4**, 11474.