Supporting information

Self-assembled Binary Multichromophore Dendrimers with Enhanced electro-optic coefficients and alignment stability

Huajun Xu, ^b* Jianpeng Liu, ^a Jun Liu, ^c* Canwen Yu, ^a Zhaofen Zhai, ^a Gangzhi Qin ^a and Fenggang Liu, ^a*

^a School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China. E-mail: liufg6@gzhu.edu.cn

^b Department of Chemistry, University of Washington, Seattle, WA, 98195, USA. E-mail: fromhjx@foxmail.com

^c Sichuan Key Laboratory of Imaging & Department of Chemistry, School of Preclinical Medicine, North Sichuan Medical College, Nanchong, 637000, China. E-mail: ustbliujun@iccas.ac.cn

1 Syntheses

1.1

Preparation

of

(E)-3-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethyl-2-(2-((tetrahydro-2H-pyr an-2-yl)oxy)ethyl)cyclohex-2-en-1-one (Compound 2).

Under a nitrogen atmosphere, a freshly prepared sodium ethoxide (22.50 mmol) was added to a solution of compound 1a (2.69 g, 15.00 mmol) and 1b (3.99 g, 15.00 mmol) in 30ml dry ethanol. The mixture was allowed to reflux overnight. Then DI water was added to quench the reaction. After removal of the solvent by roto-evaporator, the crude product was purified by silica chromatography, eluting with ethyl acetate/hexane (1:3 to 1:2, v/v) to give compound 2 as an orange-red oil with 59.6% yield (3.82g, 8.94 mmol). MS (EI) (M+,): calcd: 427.27; found: 450.3 [M+Na]⁺. ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 16.0 Hz, 1H), 6.95 – 6.87 (d, J = 16.0 Hz, 1H), 6.74 (d, J = 8.7 Hz, 2H), 4.61 (s, 1H), 3.85 – 3.81 (m, 4H), 3.54 (t, J = 5.8 Hz, 2H), 3.50 – 3.40 (m, 2H) 3.04 (s, 3H), 2.88 (t, J = 7.0 Hz, 2H), 2.51 (s, 2H), 2.30 (s, 2H), 1.53 (m, 6H), 1.06 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 199.14, 171.16, 150.13, 135.11, 128.47, 122.54, 112.30, 98.73, 66.71, 62.14, 60.39, 60.02, 54.79, 51.35, 40.09, 38.91, 32.41, 30.79, 28.43, 25.50, 21.02, 19.46, 14.19.

1.2Preparationof(E)-3-(4-((2-((tert-butyldiphenylsilyl)oxy)ethyl)(methyl)amino)styryl)-5,5-dimethyl-2-(2-((tet
rahydro-2H-pyran-2-yl)oxy)ethyl)cyclohex-2-en-1-one
(compound 3).

At room temperature, tert-butylchlorodiphenylsilane (4.11 g, 15.00 mmol) was added to a solution of compound 2 (2.14 g, 5.00 mmol) and imidazole (1.02 g, 15.00 mmol) in dry 20ml DMF under nitrogen atmosphere. After vigorously stirring for 3 h, the mixture was then poured into 100 mL H_2O . The crude product was extracted with ethyl acetate and concentrated at reduced pressure.

The crude product was purified by column chromatography using ethyl hexanes/ethyl acetate (v/v: 10/1 to 8/1) as the eluent to afford orange solid 3 in 87.6% yield (2.68 g, 4.38 mmol). MS (EI) (M+,): calcd: 614.85; found: 614.7 [M]⁺. ¹H NMR (300 MHz, CDCl₃) δ 7.40 (m, 10H), 7.30 (d, J = 16.1 Hz, 1H), 6.95 (d, J = 16.0 Hz, 1H), 6.59 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.6 Hz, 2H), 4.63 (s, 1H), 3.90 – 3.81 (m, 4H), 3.61 – 3.43 (m, 4H), 3.02 (s, 3H), 2.96 (t, J = 5.9 Hz, 2H), 2.55 (s, 2H), 2.35 (s, 2H), 2.31 (s, 2H), 1.64 – 1.42 (m, 6H), 1.08 (s, 9H), 1.07 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 199.00, 150.08, 135.61, 135.30, 133.36, 130.22, 129.79, 128.76, 127.78, 111.80, 98.74, 66.76, 65.91, 62.11, 61.07, 54.33, 51.44, 40.14, 39.21, 32.47, 32.47, 30.74, 26.91, 25.56, 19.54.

1.3

Preparation

of

(E)-2-(3-((E)-4-((2-((tert-butyldiphenylsilyl)oxy)ethyl)(methyl)amino)styryl)-5,5-dimethy l-2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethyl)cyclohex-2-en-1-ylidene)acetonitrile (compound 4).

Diethyl(cyanomethyl)phosphonate (2.58 mL, 2.84g, 16.00 mmol) was slowly introduced to a solution of NaH (0.39 g, 16.00mmol) in dry THF (20 mL) under nitrogen atmosphere at 0 °C . After the solution became clear, compound 3 (2.66 g, 4.00 mmol) in THF (10 mL) was added to the mixture which was then refluxed for 24 h. After the removal of THF in vacuo, the residue was directly purified by the column chromatography on silica gel using hexanes/ethyl acetate (v/v: 12/1 to 9/1) as the eluent to afford an orange solid 4 in 59.1% yield (1.26 g, 2.36 mmol). MS MS (EI) (M+,): calcd: 637.88; found: 650.8 [M+Na]⁺.¹H NMR (300 MHz, CDCl₃) δ 7.51 – 7.37 (m, 10H), 7.34 (d, J = 15.9 Hz, 2H), 7.11 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 15.9 Hz, 1H), 6.59 (d, J = 8.7 Hz, 1H), 5.48 (s, 1H), 4.65 (s, 1H), 3.97 – 3.73 (m, 4H), 3.63 – 3.46 (m, 4H), 3.03 (s, 3H), 3.00 (s, 2H), 2.89 (t, J = 7.3 Hz, 2H), 2.57 (s, 2H), 2.42 (s, 2H), 1.69 – 1.48 (m, 6H), 1.09 (d, J = 2.4 Hz, 2H), 1.07 – 1.02 (m, 15H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 159.12, 149.42, 141.26, 135.62, 133.43, 129.68, 128.38, 127.78, 119.37, 111.87, 98.95, 90.71, 66.51, 62.36, 61.13, 54.37, 43.61, 40.69, 39.19, 30.71, 28.19, 26.88, 25.58, 19.12.

1.4 Preparation of (E)-2-(3-((E)-4-((2-((tert-butyldiphenylsilyl)oxy)ethyl)(methyl)amino)styryl)-5,5-dimethy l-2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethyl)cyclohex-2-en-1-ylidene)acetaldehyde (compound 5) .

The solution of Diisobutylaluminum hydride in hexanes (1.5 M, 2.72 mL, 4.00 mmol) was added dropwise to the solution of compound 4 (1.38 g, 2.00 mmol) in 20.0 mL of dry toluene after it was cooled to -78 °C under a nitrogen atmosphere. The mixture was stirred at -78 °C for 2 h before wet silica gel (1.0 g) with 10.0 mL of H₂O was added and the reaction mixture was stirred at 0 °C for another 1 h. The organic products were extracted in ethyl acetate, washed with H₂O, and the solvent evaporated by roto-evaporator. The residue was purified by the column chromatography on silica gel using hexanes/ethyl acetate (v/v: 10/2 to 8/2) as the eluent to afford a red solid 5 in 71.1% yield (0.98 g, 1.42 mmol). MS (EI) (M+,): calcd: 640.33; found: 663.4 [M+Na]⁺. ¹H NMR (300 MHz, CDCl₃) δ 10.06 (d, J = 7.9 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.38 – 7.19 (m, 10H), 6.72 (d, J = 15.9 Hz, 1H), 6.47 (d, J = 8.6 Hz, 2H), 6.20 (d, J = 7.9 Hz, 1H), 4.54 (t, 1H), 3.83 – 3.65 (m, 4H), 3.42 (m, 4H), 2.91 (s, 3H), 2.84 (t, J = 7.6 Hz, 2H), 2.62 (s, 2H), 2.33 (s, 2H), 1.55 – 1.34 (m, 6H), 0.95 (d, 15H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 191.62, 157.52, 149.43, 135.61, 133.44,

129.77, 127.57, 111.85, 99.01, 66.59, 62.20, 61.13, 54.35, 40.67, 39.17, 30.69, 28.35, 26.86, 25.51, 19.11.

Preparation

1.5

(E)-2-(3-((E)-4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethyl-2-(2-((phosphanyl-t)oxy)ethyl)cyclohex-2-en-1-ylidene)acetaldehyde (compound 6).

of

Under a nitrogen atmosphere, tetrabutylammonium fluoride solution (1.0 M in THF, 10.00 mL, 10.00 mmol) was added dropwise to the solution of compound 5 (1.60 g, 2.50 mmol) in 40 mL dry THF. The mixture was stirred at RT for 1 h, then the solvent was evaporated by roto-evaporator, the residue was washed with 40 mL of NH₄Cl/water and 40 mL of ethyl acetate. Then the aqueous layer was extracted with ethyl acetate. After the removal of ethyl acetate in vacuo, the residue was directly purified by the column chromatography on silica gel using dichloromethane:ethyl acetate (v/v: 2/1 to 1/1) as the eluent to afford an dark red solid 6 in 82.1% yield (0.83 g, 2.05 mmol). MS (ESI) (M+,): calcd: 402.22; found: 426.1 [M+Na]⁺. ¹H NMR (300 MHz, CDCl₃) δ 10.05 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 15.9 Hz, 1H), 6.75 (d, J = 15.9 Hz, 1H), 6.68 (d, J = 8.8 Hz, 2H), 6.20 (d, J = 7.9 Hz, 1H), 4.57 – 4.49 (m, 1H), 3.85 – 3.70 (m, 4H), 3.50 – 3.37 (m, 4H), 2.96 (s, 3H), 2.83 (t, J = 7.6 Hz, 2H), 2.62 (s, 2H), 2.33 (s, 2H), 1.56 – 1.35 (m, 6H), 0.95 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 191.75, 157.63, 149.93, 142.59, 133.21, 129.23, 128.43, 125.76, 123.76, 122.98, 112.48, 98.95, 66.56, 62.23, 60.13, 54.90, 40.62, 39.49, 38.91, 30.64, 28.31, 25.46, 19.44, 14.21

1.6Preparationof2-((4-((E)-2-((E)-5,5-dimethyl-3-(2-oxoethylidene)-2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethyl)cyclohex-1-en-1-yl)vinyl)phenyl)(methyl)amino)ethyl3,5-bis(benzyloxy)benzoate(compound 7).

Under a nitrogen atmosphere, 3,5-bis(benzyloxy)benzoic acid (0.80 g, 2.40 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.96 g, 0.012 mmol) and EDCI (0.46 g, 2.40 mmol) was added to a solution of compound 6 (0.81 g, 2.00 mmol) in 30 mL of dry dichloromethane. The mixture was stirred at RT overnight. The mixture was then quenched with saturated ammonium chloride, extracted with ethyl acetate, dried over MgSO₄. After the removal of solvent in vacuo, the residue was directly purified by the column chromatography on silica gel using ethyl acetate: DCM (v/v: 8/1 to 6/1) as the eluent to afford a dark red solid 7 in 87.3% yield (1.34g, 1.75 mmol). MS (ESI) (M+,): calcd: 768.40; found: 791.3 [M+Na]⁺. ¹H NMR (500 MHz, CDCl₃) δ 10.14 (d, J = 7.8 Hz, 1H), 7.39-7.42 (m, 9H), 7.35 - 7.30 (m, 2H), 7.27 - 7.18 (m, 3H), 6.75 (m, 5H), 6.28 (d, J = 7.9 Hz, 1H), 5.01 (s, 4H), 4.59 (t, J = 3.3 Hz, 1H), 4.50 – 4.46 (m, 2H), 3.85 – 3.71 (m, 4H), 3.50 – 3.46 (m, 2H), 3.06 (s, 3H), 2.88 (t, J = 7.5 Hz, 2H), 2.69 (s, 2H), 2.35 (s, 2H), 1.84 – 1.75 (m, 1H), 1.73-1.66 (m, 1H), 1.59-1.48 (m, 4H), 1.01 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.81, 169.84, 164.08, 157.65, 151.17, 144.41, 143.44, 134.59, 133.96, 127.16, 126.54, 125.91, 123.83, 122.24, 121.46, 117.36, 114.24, 112.17, 111.27, 109.36, 107.78, 106.41, 104.44, 70.36, 63.76, 62.73, 63.13, 57.84, 54.48, 43.38, 42.36, 32.73, 30.73, 30.05, 28.32, 28.25, 27.46, 25.40, 22.59, 19.79.

 1.7
 Preparation
 of

 2-((4-((E)-2-((E)-2-(2-hydroxyethyl)-5,5-dimethyl-3-(2-oxoethylidene)cyclohex-1-en-1-yl)
 0

vinyl)phenyl)(methyl)amino)ethyl 3,5-bis(benzyloxy)benzoate (compound 8).

HCl (1 N, 4.0 mL) was added to a solution of compound 7 (1.54 g, 2.00 mmol) in 20 mL of methanol. The mixture was stirred at RT for 2 h. The mixture was then neutralized with NaHCO₃, extracted with ethyl acetate. After the removal of solvent in vacuo, the residue was directly purified by the column chromatography on silica gel using dichloromethane:ethyl acetate (v/v: 4/1 to 3/1) as the eluent to afford a dark red solid 8 in 73.1% yield (1.00g, 1.46 mmol). MS (ESI) (M+,): calcd: 684.34; found: 707.3 [M+Na]⁺. ¹H NMR (500 MHz, CDCl₃) δ 10.12 (d, *J* = 7.8 Hz, 1H), 7.44 –7.35 (m, 9H), 7.34 – 7.30 (m, 2H), 7.27 – 7.22 (m, 3H), 7.08 – 6.96 (m, 5H), 6.38 (d, *J* = 7.9 Hz, 1H), 5.03 (s, 4H), 4.50-4.46 (m, 2H), 3.76 – 3.68 (m, 2H), 3.50 – 3.46 (m, 2H), 3.36 (s, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.66 (s, 2H), 2.31(s, 2H), 1.09 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 192.03, 169.30, 164.27, 158.70, 155.63, 148.17, 147.38, 136.25, 132.32, 127.84, 127.48, 127.14, 126.48, 125.24, 124.46, 118.06, 115.20, 113.15, 112.25, 107.37, 106.76, 103.47, 70.24, 62.84, 61.53, 56.83, 52.43, 42.48, 41.26, 33.74, 30.95, 30.19, 28.62, 27.25, 26.76, 19.77.

1.8

Preparation

of

4-(2-((E)-2-((E)-4-((2-((3,5-bis(benzyloxy)benzoyl)oxy)ethyl)(methyl)amino)styryl)-4,4-di methyl-6-(2-oxoethylidene)cyclohex-1-en-1-yl)ethoxy)-4-oxobutanoic acid (compound 9). Under atmosphere, succinic anhydride 4.00 а nitrogen (0.47)g, mmol), 4-(dimethylamino)-pyridine (DMAP) (0.001 g, 0.01 mmol) and EDCI (0.38 g, 2.00 mmol), was added to a solution of compound 8 (0.68 g, 1.00 mmol) in 10 mL of dry dichloromethane. The mixture was stirred at RT overnight. The mixture was then quenched with saturated ammonium chloride, extracted with ethyl acetate, dried over MgSO₄. After the removal of solvent in vacuo, the residue was directly purified by the column chromatography on silica gel using ethyl acetate: DCM (v/v: 4/1 to 3/1) as the eluent to afford a dark red solid 9 in 87.3% yield (0.68g, 0.87 mmol). MS (ESI) (M+,): calcd: 784.36; found: 807.4 [M+Na]⁺. ¹H NMR (500 MHz, CDCl₃) δ 10.11 (d, J = 7.8 Hz, 1H), 7.45 - 7.38 (m, 9H), 7.31 - 7.29 (m, 2H), 7.27 - 7.14 (m, 3H), 6.85 - 6.74 (m, 5H), 6.24 (d, J = 7.8 Hz, 1H), 5.05 (s, 4H), 4.48 (t, J = 5.7 Hz, 2H), 4.17 - 4.09 (m, 2H), 3.75 (t, J = 5.6Hz, 2H), 3.04 (s, 3H), 2.94 – 2.83 (m, 2H), 2.69 – 2.62 (m, 2H), 2.58 – 2.56 (m, 2H), 2.36 (s, 2H), 2.12 (s, 2H), 1.01 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 194.03, 172.23, 169.10, 165.37, 159.80, 156.68, 149.18, 148.38, 136.35, 133.82, 128.74, 128.58, 128.14, 127.58, 126.14, 125.43, 119.06, 114.20, 112.16, 111.15, 108.47, 107.56, 103.41, 70.30, 63.84, 63.54, 58.81, 52.03, 44.58, 41.21, 35.71, 31.95, 30.19, 28.92, 28.68, 28.68, 28.25, 26.57, 19.73.

1.9

Preparation

of

tris (2-((E)-2-((E)-4-((2-((3,5-bis(benzyloxy)benzoyl)oxy)ethyl)(methyl)amino)styryl)-4, 4-dimethyl-6-(2-oxoethylidene)cyclohex-1-en-1-yl)ethyl)

O,O',O''-(ethane-1,1,1-triyltris(benzene-4,1-diyl)) trisuccinate (compound 10).

Under a nitrogen atmosphere, N,N-dimethylaminopyridine (DMAP) (0.0015 g, 0.012 mmol) and EDCI (0.17 g, 0.90 mmol) was added to a solution of compound 9 (0.12 g, 0.15 mmol) in 10 mL dry dichloromethane, the mixture was then cooled to 0 °C .The solution was cloudy initially, and became clear after 30 min. Then 4,4',4"-(ethane-1,1,1-triyl)triphenol (0.01 g, 0.05 mmol) was added to the mixture. The mixture was stirred at room temperature overnight after 2 hr at 0 °C. Then the solution was filtered, washed with 50 mL dichloromethane, extracted with dichloromethane, dried over MgSO₄. After the removal of solvent in vacuo, the residue was

directly purified by the column chromatography on silica gel using hexanes/ethyl acetate (v/v: 4/1 to 3/1) as the eluent to afford a dark red solid 10 in 77.3% yield (0.10g, 0.04 mmol). HRMS (ESI) (M+, C₁₆₄H₁₆₅N₃O₂₇): calcd: 2609.1709; found: 2609.1699. ¹H NMR (500 MHz, CDCl₃) δ 10.13 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.40 - 7.33 (m, 7H), 7.30 (ddd, J = 7.0, 3.7, 1.5 Hz), 7.40 - 7.33 (m, 7H), 7.30 (ddd, J = 7.0, 3.7, 1.5 Hz)1H), 7.23 (dd, J = 18.1, 2.6 Hz, 3H), 7.00 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.80 – 6.65 (m, 4H), 6.21 (d, J = 7.7 Hz, 1H), 4.99 (s, 5H), 4.44 (t, J = 5.7 Hz, 2H), 4.15 (t, J = 7.4 Hz, 2H), 3.70 (t, J = 5.6 Hz, 2H), 3.00 (d, J = 5.5 Hz, 3H), 2.88 (t, J = 7.4 Hz, 2H), 2.78 (t, J = 6.8 Hz, 2H), 2.65 (dd, J = 17.1, 10.1 Hz, 5H), 2.36 (d, J = 19.9 Hz, 2H), 2.16 (d, J = 5.0 Hz, 2H), 2.05 (s, 1H), 1.00 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 191.45, 171.90, 166.29, 162.52, 159.81, 157.12, 148.75, 146.09, 143.54, 138.16, 136.47, 131.88, 129.62, 128.69, 128.63, 128.14, 127.57, 123.51, 122.11, 120.92, 115.98, 112.28, 112.22, 108.43, 107.48, 100.04, 70.27, 63.45, 62.31, 56.07, 50.77, 45.73, 40.51, 38.64, 34.57, 30.94, 30.22, 29.28, 29.15, 28.30, 26.50, 19.28.

1.10 Preparation of HDSD

1.11

Under а nitrogen atmosphere, 2-(3-Cyano-4-methyl-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile (CF₃-Ph-TCF) (0.17 g, 0.56 mmol) was added to a solution of compound 10 (0.44g, 0.17 mmol) in 6 mL of dry ethanol, the mixture was then heated to 60 °C, the mixture was stirred for 2h, color changed from red to dark blue-green. TLC traces. After the removal of solvent in vacuo, the residue was directly purified by the column chromatography on silica gel using dichloromethane/ethyl acetate (v/v: 120/5 to 95/5) as the eluent to afford a dark solid HDSD in 66.1% yield (0.39g, 0.11 mmol). HRMS (ESI) (M+, C₂₁₂H₁₈₃F₉N₁₂O₂₇): calcd: 3500.3250; found: 3500.3281. ¹H NMR (300 MHz, CDCl₃) δ 7.64 – 7.42 (m, 6H), 7.40-7.26 (m, 11H), 7.26 (s, 1H), 7.20-7.09(m, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.96-6.85 (m, 4H), 6.79-6.72 (m, 3H), 6.67 (d, J = 14.4 Hz, 1H), 6.49 (d, J = 14.4 Hz, 1H), 4.98 (s, 4H), 4.46 (t, J = 5.3 Hz, 2H), 4.27 - 3.96 (m, 2H), 3.77-3.67 (m, 2H), 3.04 (s, 3H), 2.91-2.76 (m, J = 5.6 Hz, 2H), 2.71-2.56 (t, J = 5.6 Hz, 2H), 2.42 (d, J = 5.4 Hz, 2H), 2.16(s, 4H), 0.94 (s, 3H), 0.85 (s, 3H). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 175.86, 170.80, 166.11, 162.60, 159.81, 150.07, 148.64, 146.02, 136.48, 131.67, 131.31, 130.11, 129.76, 129.67, 129.61, 128.62, 128.15, 127.54, 126.76, 125.25, 124.91, 122.38 120.86, 116.55, 112.19, 111.55, 111.34, 110.88, 108.41, 107.49, 70.27, 63.44, 62.19, 51.32, 50.62, 40.54, 38.70, 34.68, 31.59, 30.92, 30.52, 28.51, 25.32, 22.66, 13.97.

Preparation 2-(4-((1E,3E)-3-(3-((E)-4-((2-((tert-butyldiphenylsilyl)oxy)ethyl)(methyl)amino)styryl)-2-((2-((tert-butyldiphenylsilyl)oxy)ethyl)thio)-5,5-dimethylcyclohex-2-en-1-ylidene)prop-1en-1-yl)-3-cyano-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile (HJD). HRMS (ESI) (M+, C₇₁H₇₃F₃N₄O₃SSi₂): calcd: 1175.4972; found: 1175.4984. ¹H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 15.9 Hz, 1H), 7.66 – 7.56 (m, 9H), 7.54 – 7.48 (m, 5H), 7.44 – 7.39 (m, 3H), 7.38 - 7.32 (m, 8H), 7.30 - 7.25 (m, 4H), 6.96 (d, J = 16.0 Hz, 1H), 6.50 (d, J = 8.6 Hz, 2H), 6.41(d, J = 14.6 Hz, 1H), 3.81 (t, J = 5.7 Hz, 2H), 3.71 (t, J = 6.5 Hz, 2H), 3.54 (t, J = 5.4 Hz, 2H),3.01 (s, 3H), 2.71 (t, J = 6.5 Hz, 2H), 2.46 (s, 2H), 2.33 (s, 2H), 1.03 (s, 9H), 1.00 (s, 9H), 0.93 (s, 3H), 0.85 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) & 175.66, 162.59, 158.21, 154.19, 150.47, 147.37, 138.20, 135.56, 135.46, 133.39, 133.22, 131.27, 130.17, 129.82, 129.78, 129.71, 129.63, 128.39, 127.75, 127.68, 126.73, 124.66, 116.80, 111.92, 111.33, 110.84, 62.99, 61.08, 54.24, 41.71,

of

2. Thermal property



Fig. S1 DSC curves of chromophores HDSD, FDSD, HJD and their blends with a heating rate of $10 \,^{\circ}$ C min⁻¹ in nitrogen atmosphere.



Fig. S2 TGA curves of chromophores HDSD, FDSD and HJD with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

3. ¹H and ¹³C{¹H} NMR spectra



Figure S3 ¹H NMR spectra of Chromophore HDSD



Figure S4 ¹³C{¹H} NMR spectra of Chromophore HDSD



Figure S5 ¹H NMR spectra of Chromophore HJD



Figure S6 ¹³C{¹H} NMR spectra of Chromophore HJD