Supportting information

Synthesis of asymmetric dendrimers with controllable chromophore concentration and improved electro-optical performance via Cu-(I) catalyzed Huisgen-Reaction

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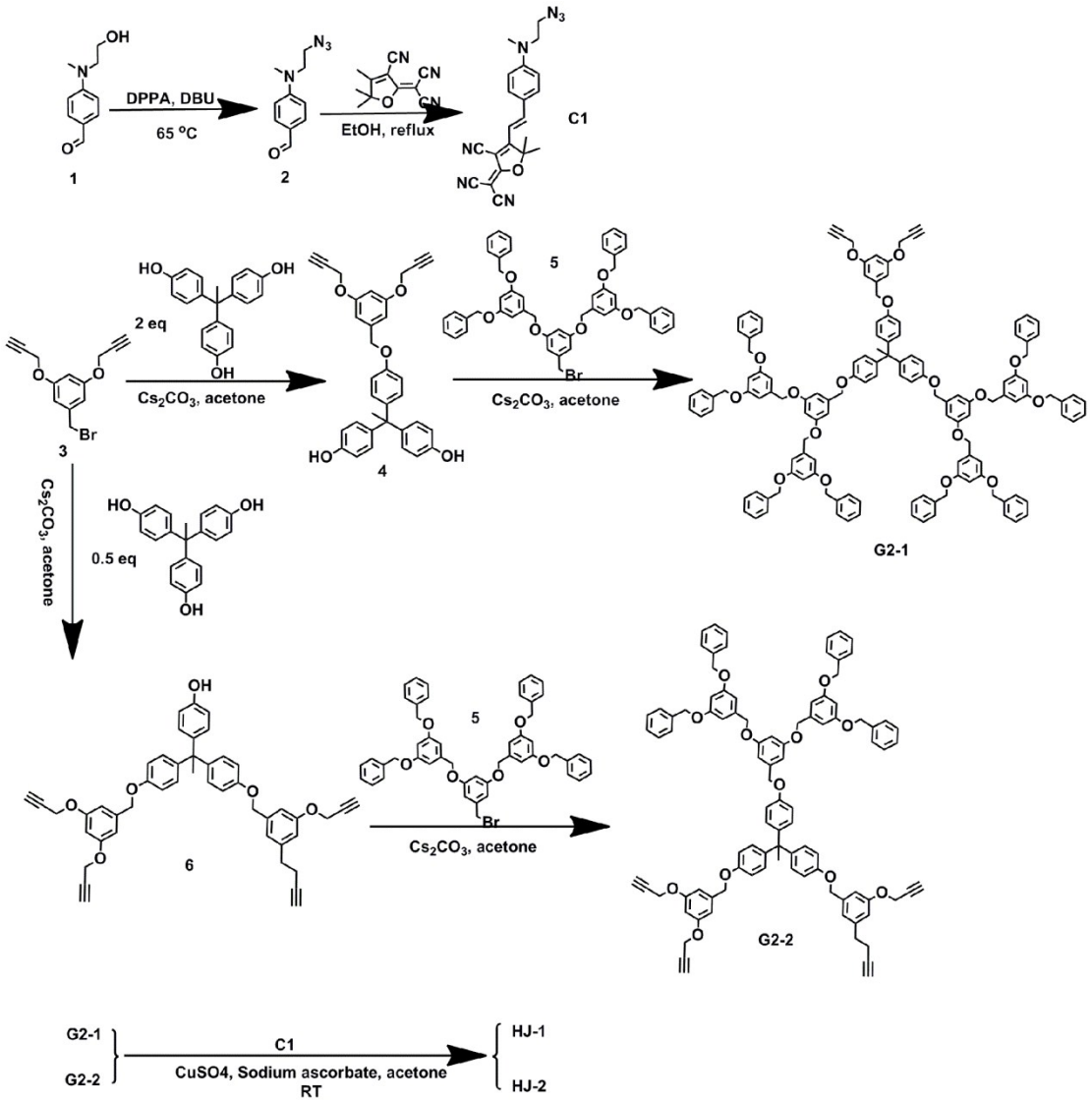
Content

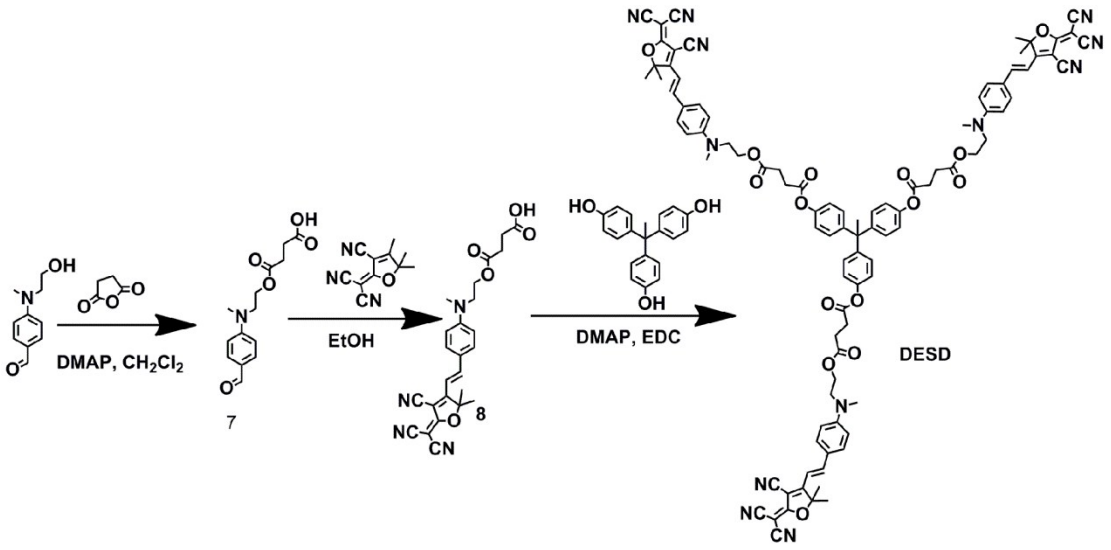
1. Experimental Details

General procedures.

All chemicals are commercially available and are used without further purification unless otherwise stated. N, N-dimethyl formamide (DMF) was distilled over calcium hydride and stored over molecular sieves (pore size 3Å). Acetone was dried with anhydrous $MgSO_4$, then distilled and stored over molecular sieves (pore size 3Å). The 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran(TCF) acceptor was prepared according to the literature.[1] Compound **2** and **C1** were prepared according to the literature.[2] Compounds **3** and **5** were prepared according to the literature.[3] TLC analyses were carried out on 0.25 mm thick precoated silica plates and spots were visualized under UV light. Chromatography on silica gel was carried out on Kieselgel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were determined by Advance Bruker 400M (400 MHZ) NMR spectrometer (tetramethylsilane as internalreference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-Vis experiments were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 ^{o}C min-1 under the protection of nitrogen. Atomic Force Microscope (AFM) was characterized by multimode 8 Bruker. DFT calculations using Gaussian 09 were carried out on three dendrimers at the PM3 level, employing the split valence 3-21 basis set. All calculations converged to a RMS error in the density matrix of $< 10^{-11}$ au.[4]



Scheme 1. Synthesis of dendrimers **HJ-1** and **HJ-2**.



Scheme 2. Synthesis of dendrimer **DESD**.

Synthesis of compound 4

To a stirred solution of compound **3** (2.79 g, 10 mmol), and methyl 1,1,1-Tris(4-hydroxyphenyl)ethane (6.12g, 20 mmol) in acetone (300 mL) were added cesium carbonate (3.26 g, 10 mmol) and 18-crown-6 (0.1 g, 0.4 mmol). The reaction mixture was heated at reflux under nitrogen for 24 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2x100 mL), and the combined extracts were dried and evaporated to dryness. The crude material was then purified by column chromatography using dichloromethane and methanol as the eluent to give compound **4** as colorless solid (2.92g, 58.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.99 (d, J = 2.0 Hz, 2H, Ar-**H**), 6.94 (d, J = 1.8 Hz, 4H, Ar-**H**), 6.84 (d, J = 2.0 Hz, 2H, Ar-**H**), 6.72 (d, J = 1.8 Hz, 4H, Ar-**H**), 6.69 (d, J = 2.3 Hz, 2H, Ar-**H**), 6.56 (t, J = 2.3 Hz, 1H, Ar-**H**), 4.98 (s, 2H, C**H**$_2$), 4.67 (s, 4H, C**H**$_2$), 2.51 (t, 2H, alkyne-**H**), 2.08 (s, 3H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, ppm):δ=159.03, 156.83, 153.81, 142.30, 141.87, 139.97, 129.86, 129.71, 114.69, 114.23, 107.10, 102.00, 78.46, 75.69, 69.89, 56.12, 50.78, 30.83. MALDI-TOF (M+,): calcd: 504.19; found: 504.17.

Synthesis of compound G2-1

The procedure for **G2-1** was followed to prepare compound **4** as colorless solid (91.3%). ^{1}H NMR (400 MHz, $CDCl_3$):δ=7.33 (m, 40H, Ar-**H**), 7.00 – 6.95 (d, J=11.0Hz, 6H, Ar-**H**), 6.82 (d, J = 11.0Hz, 6H, Ar-**H**), 7.25(d, 14H, Ar-**H**) 6.58 – 6.51 (m, 7H, Ar-**H**), 5.00 (s, 16H, C**H**$_2$), 4.94 (s, 14H, C**H**$_2$), 4.64 – 4.59 (m, 4H, C**H**$_2$), 2.49 – 2.43 (t, 2H, alkyne-**H**), 2.08 (s, 3H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=160.29, 160.18, 158.99, 156.93, 156.80, 142.22, 139.93, 139.75, 139.40, 136.94, 129.69, 128.57, 127.96, 127.51, 114.20, 107.06, 106.59, 101.87, 78.46, 75.68, 70.23, 70.11, 69.81, 56.05, 50.78, 30.83. MALDI-TOF (M+,): calcd: 1957.79; found: 1957.72.

Synthesis of compound 6

The procedure for **6** was followed to prepare compound **4** as colorless solid (68.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.99 (d, J = 2.1 Hz, 4H, Ar-**H**), 6.94 (d, J = 2.0 Hz, 2H, Ar-**H**), 6.85 (d, J = 2.1 Hz, 4H, Ar-**H**), 6.72 (d, J = 2.0 Hz, 2H, Ar-**H**), 6.68 (d, J = 2.2 Hz, 4H, Ar-**H**), 6.56 (t, J = 2.3 Hz, 2H, Ar-**H**), 4.98 (s, 4H, C**H**$_2$), 4.67 (d, J = 2.4 Hz, 8H, C**H**$_2$), 2.50 (t, J = 2.4 Hz, 4H, alkyne-**H**), 2.09 (s, 3H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=159.00, 156.77, 153.80, 142.40, 141.85, 139.94, 129.84, 129.71, 114.70, 114.23, 107.13, 102.04, 78.46, 75.73, 69.91, 56.12, 50.74, 30.85. MALDI-TOF (M+,): calcd: 702.26; found: 702.25.

Synthesis of compound G2-2

The procedure for **G2-2** was followed to prepare compound **4** as colorless solid (72.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 20H, Ar-**H**), 6.98 (d, J = 8.8 Hz, 6H, Ar-**H**), 6.87 – 6.81 (m, 6H, Ar-**H**), 6.69 – 6.64 (m, 10H, Ar-**H**), 6.56 (d, J = 4.4Hz, 5H, Ar-**H**), 5.02 (s, 8H, C**H**$_2$), 4.98 – 4.94 (m, 10H, C**H**$_2$), 4.65 (d, J = 2.4 Hz, 8H, C**H**$_2$), 2.49 (t, J = 2.4 Hz, 4H, alkyne-**H**), 2.08 (s, 3H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=160.27, 158.97, 156.78, 142.18, 139.91, 139.38, 136.92, 129.67, 128.57, 127.96, 127.51, 114.18, 107.02, 106.56, 102.02, 78.44, 75.70, 70.15, 56.04, 29.34. MALDI-TOF (M+,): calcd: 1429.56; found:

1429.50.

Synthesis of dendrimer HJ-1

A solution of the asymmetric dendrimer **G2-1** (0.196g, 0.1 mmol), chromophore **C1** (0.093g, 0.12 mmol), sodium ascorbate (2 mg, 12 μmol), and $CuSO_4$(1 mg, 6 μmol) in acetone (25 mL) was stirred at room temperature for ca. 48 h. After evaporation of the solvents, the crude product was purified by column chromatography, eluting with a 9:1 mixture of dichloromethane and methanol, to give **HJ-1** as a dark red solid (94.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, 18.2 Hz, 2H, C**H**=CN), 7.61 – 7.50 (d, J=16.3 Hz, 2H, C**H**=CH), 7.46 (t, J = 7.6 Hz, 4H, Ar-**H**), 7.33 (m, 40H, Ar-**H**), 6.97 (t, J = 8.2 Hz, 6H, Ar-**H**), 6.85 – 6.79 (t, J=8.2 Hz, 6H, Ar-**H**), 6.76 (d, J = 16.3 Hz, 2H, CH=C**H**), 6.70 (d, J = 7.6 Hz, 4H, Ar-**H**), 6.66 (s, 14H, Ar-**H**), 6.54 (d, J = 10.4 Hz, 7H, Ar-**H**), 5.13 (d, J = 18.2 Hz, 4H, C**H**$_2$), 5.01 (s, 16H, C**H**$_2$), 4.94 (d, J = 6.9 Hz, 14H, C**H**$_2$), 4.57 (s, 4H, C**H**$_2$), 3.93 (s, 4H, C**H**$_2$), 2.85 (s, 6H, C**H**$_3$), 2.07 (s, 3H, C**H**$_3$), 1.69 (s, 12H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=206.78, 176.27, 174.52, 174.41, 174.73, 160.32, 160.20, 156.96, 152.64, 148.52, 142.52, 139.40, 136.94, 132.22, 129.75, 128.61, 128.01, 127.54, 123.67, 114.22, 112.35, 110.27, 106.62, 101.85, 97.58, 70.27, 51.21, 30.83, 26.64. MALDI-TOF (M+,): calcd: 2728.12; found: 2728.15.

HRMS (ESI) (M+, $C_{40}H_{51}N_5OS$): calcd: 2727.12017; found: 2727.12021.

Synthesis of dendrimer HJ-2

The procedure for **HJ-2** was followed to prepare compound **4** as colorless solid (88.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.66 (dd, J = 6.7 Hz, 4H, C**H**=CN), 7.63 (d, J = 9.3 Hz, 4H, C**H**=CH), 7.48 (d, J = 5.7 Hz, 8H, Ar-**H**), 7.34 (m, 20H, Ar-**H**), 6.94 (d, J = 8.2 Hz, 6H, Ar-**H**), 6.82 (d, J = 9.3 Hz, 4H, CH=C**H**), 6.76 (d, J = 8.2 Hz, 6H, Ar-**H**), 6.66 (s, 10H, Ar-**H**), 6.62 (d, J=5.7 Hz, 8H, Ar-**H**), 6.56 (s, 5H, Ar-**H**), 5.09 (s, 8H, C**H**$_2$), 5.01 (s, 8H, C**H**$_2$), 4.97 – 4.83 (m, 10H, C**H**$_2$), 4.57 (s, 8H, C**H**$_2$), 3.94 (s, 8H, C**H**$_2$), 2.84 (s, 12H, C**H**$_3$), 2.06 (s, 3H, C**H**$_3$), 1.69 (s, 24H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=177.09, 175.38, 161.01, 160.28, 153.05, 149.08, 143.03, 140.72, 137.61, 133.07, 130.49, 129.45, 128.89, 128.40, 123.72, 114.87, 113.47, 110.52, 107.40, 98.09, 95.80, 70.89, 62.71, 55.75, 53.17, 39.59, 31.76.

HRMS (ESI) (M+, $C_{179}H_{156}N_{28}O_{17}$): calcd: 2969.22033; found: 2969.22030.

Synthesis of compound 7

To a stirred solution of N-Methyl-N-hydroxyethyl-4-amino-2-methyl benzaldehyde (1.79 g, 10 mmol), and succinic anhydride (2.00g, 20 mmol) in THF (25 mL) were added DMAP (1.22 g, 10 mmol). The reaction mixture was stirred under nitrogen for 24 h, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2x100 mL), and the combined extracts were dried and evaporated to dryness. The crude material was then purified by column chromatography using hexane/acetone=2/1 as the eluent to give compound **7** as yellowish solid (2.68g, 96.1%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (s, 1H, C**H**O), 7.78 – 7.71 (d, J = 9.0 Hz, 2H, Ar-**H**), 6.76 (d, J = 9.0 Hz, 2H, Ar-**H**), 4.33 (t, J = 5.9 Hz, 2H, C**H**$_2$), 3.71 (t, J = 5.9 Hz, 2H, C**H**$_2$), 3.09 (s, 3H, C**H**$_3$), 2.70 – 2.53 (m, 4H, COC**H**$_2$C**H**$_2$CO). ^{13}C NMR (101 MHz, $CDCl_3$) δ=190.55, 177.73, 171.82, 153.29, 132.24, 125.55, 110.92, 61.49, 50.64, 38.86, 29.06. MALDI-TOF (M+,): calcd: 279.11; found: 279.08.

Synthesis of compound 8.

To a 50 mL round bottle flask were added compound **7** (0.38g, 10 mmol) and TCF acceptor in 20 mL ethanol. The reaction mixture was heated to reflux under nitrogen for 2 h, then evaporated to dryness. The crude material was then purified by column chromatography using dichloromethane and methanol as the eluent to give compound **8** as dark purple solid (0.44g, 95.6%). ^{1}H NMR (400 MHz, Acetone-d6) δ=8.00 (d, J = 16.0 Hz, 1H, C**H**=CH), 7.81 (d, J = 9.1 Hz, 2H, Ar-**H**), 7.02 (d, J = 16.0 Hz, 1H, Ar-**H**), 6.96 (d, J = 9.1 Hz, 2H, CH=C**H**), 4.35 (t, J = 5.6 Hz, 2H, C**H**$_2$), 3.87 (t, J = 5.6 Hz, 2H, C**H**$_2$), 3.20 (s, 3H, C**H**$_3$), 2.29 (m, 4H, C**H**$_2$), 1.86 (s, 6H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=194.1, 174.7, 173.1, 162.8, 148.8, 134.5, 129.7, 127.3, 124.7, 113.6, 111.7, 100.8, 99.8 61.4, 60.6, 45.0, 41.4, 29.2, 24.5. MALDI-TOF (M+,): calcd: 460.48; found: 460.43.

Synthesis of dendrimer DESD.

To a stirred solution of compound **8** (0.46g, 1mmol) and 1,1,1-Tris(4-hydroxyphenyl)ethane (0.085g, 0.28mmol) were added EDCI (0.23g, 1.2 mmol) and DMAP (0.012g, 0.1mmol). The reaction mixture was stirred under nitrogen for 24 h, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2x100 mL), and the combined extracts were dried and evaporated to dryness. The crude material was then purified by column chromatography using hexane/acetone=3/1 as the eluent to give **DESD** as dark purple solid (0.396g, 87.3%). ^{1}H NMR (400 MHz, CDCl3) δ=7.63 (d, J = 16.0 Hz, 3H, C**H**=CH), 7.56 (d, J = 8.9 Hz, 6H, Ar-**H**), 7.09 (d, J = 8.7 Hz, 6H, Ar-**H**), 6.97 (d, J = 8.7 Hz, 6H, Ar-**H**), 6.80 (d, J = 8.9 Hz, 6H, Ar-**H**), 6.76 (d, J = 16.0 Hz, 3H, CH=C**H**), 4.34 (t, J = 5.6 Hz, 6H, C**H**$_2$), 3.77 (t, J = 5.6 Hz, 6H, C**H**$_2$), 3.15 (s, 9H, C**H**$_3$), 2.54 (t, J = 6.6 Hz, 6H, C**H**$_2$), 2.33 (t, J = 6.6 Hz, 6H, C**H**$_2$), 1.73 (s, 18H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ=195.9, 172.3, 173.1, 164.4, 153.6.8, 133.7, 129.7, 127.3, 125.7, 113.6, 111.5, 108.8, 93.7 61.4, 60.6, 45.0, 41.4, 29.2, 24.5. MALDI-TOF (M+,): calcd: 1633.75; found: 1633.71.

HRMS (ESI) (M+, $C_{95}H_{84}N_{12}O_{15}$): calcd: 1632.61791; found: 1632.61787.

2. The general procedure for preparing films.

In order to evaluate their EO activities, the dendritic and polymeric films using 1,1,2-trichloroethane (TCE) as the solvent were prepared to investigate the translating of the microscopic hyperpolarizability into macroscopic EO response (r_{33}). The solution was filtered using a 0.2-μm syringe filter to remove large particulates. And then the solution was spin-coated on indium-tin oxide (ITO) glass substrates. The films were dried in vacuo for 12 h to remove the residual solvent. The thickness of the films was measured with an Ambios Technology XP-1 profilometer. The thickness of films were about 2.1μm-2.6μm, which should be thicker than the films poled in contact poling to prevent the possible film damage (in contact poling, films thickness will be about 1.3μm-2.0μm).

3. DSC curves of three dendrimers

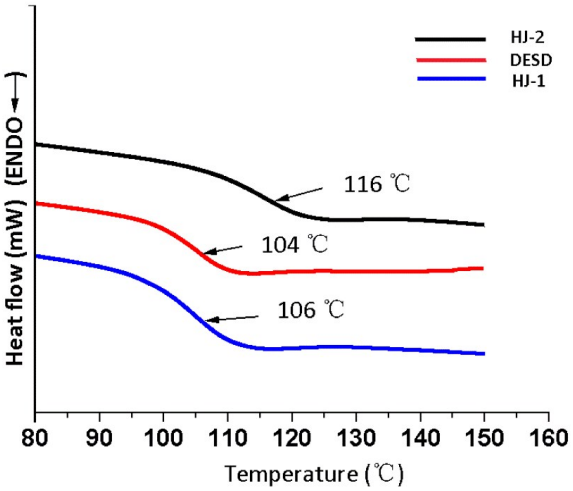


Figure 1. DSC curves and glass transition temperatures for three dendrimers.

4. UV-Vis spectra for solutions.

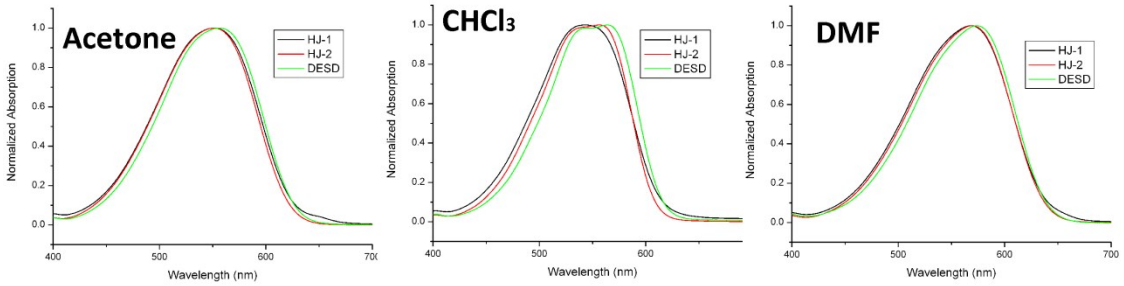


Figure 2. UV-Vis absorptions in acetone and chloroform.

5. **UV-Vis spectra for films.**

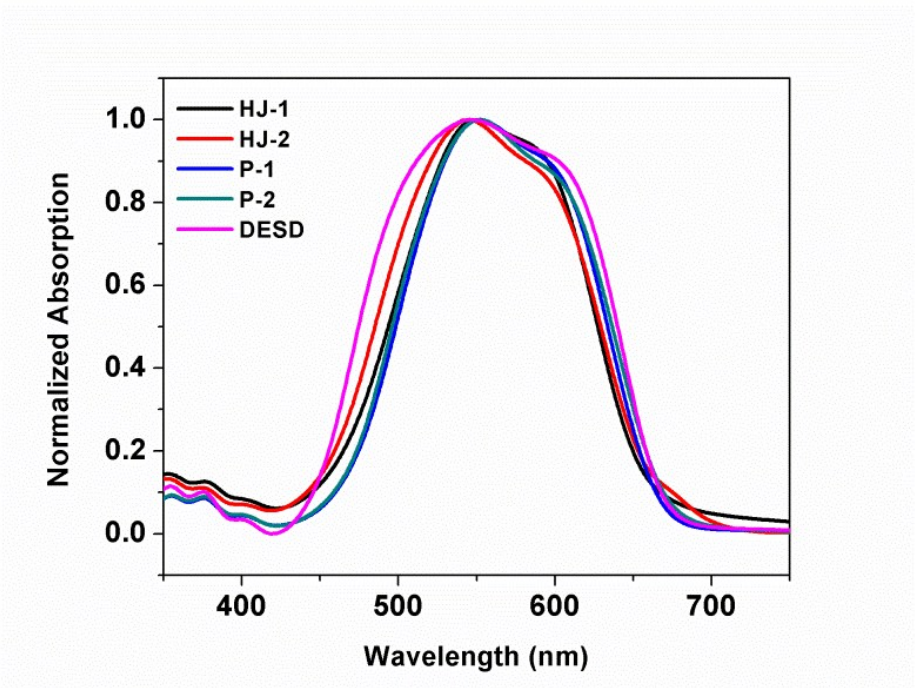


Figure 3. UV-Vis absorptions for five films.

6. **Infrared spectra.**

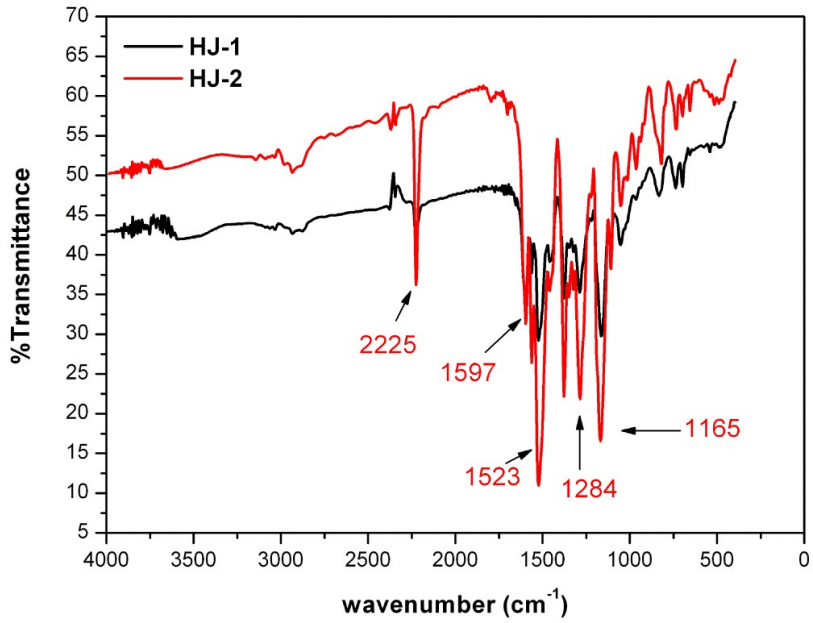


Figure 4. Infrared spectra for **HJ-1** and **HJ-2**.

7. Temporal stability of poled films at 75 °C for 300 h.

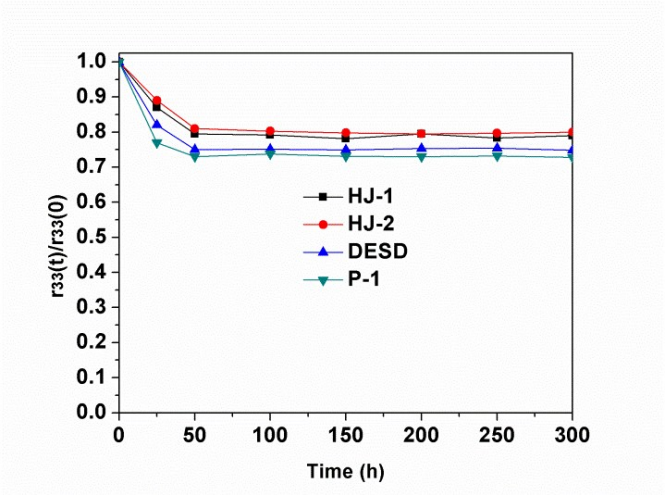


Figure 5. temporal stability for poled films.

8. The optimized configuration of three dendrimers in vacuum.

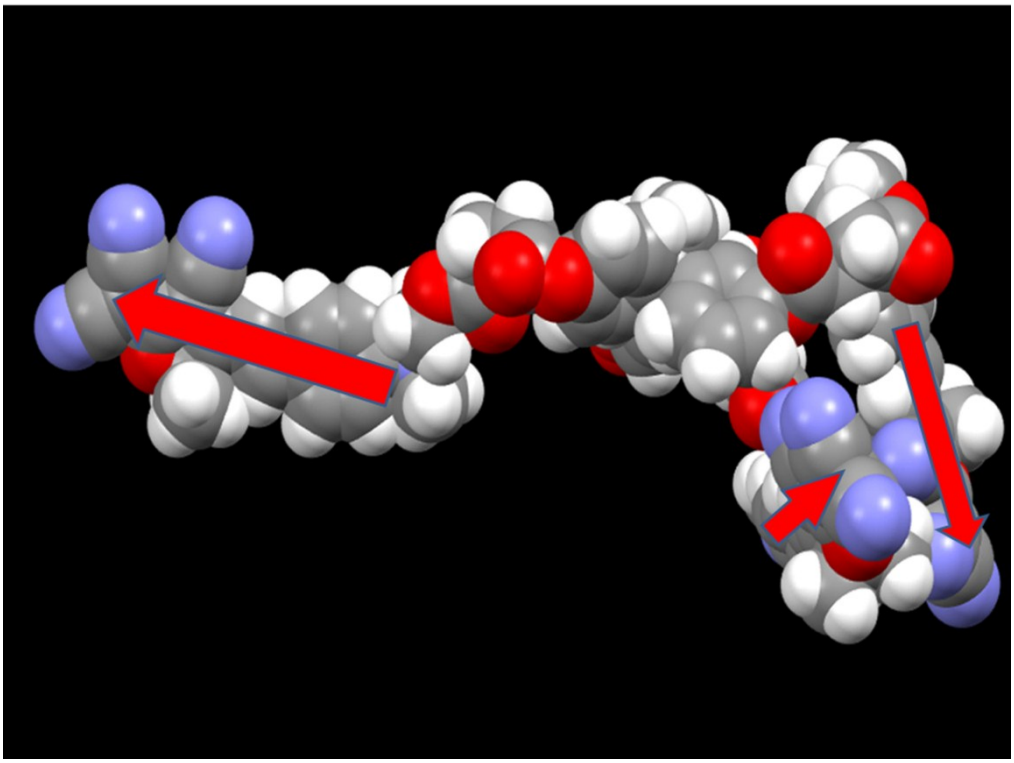


Figure 6. Optimized configuration of **DESD**.

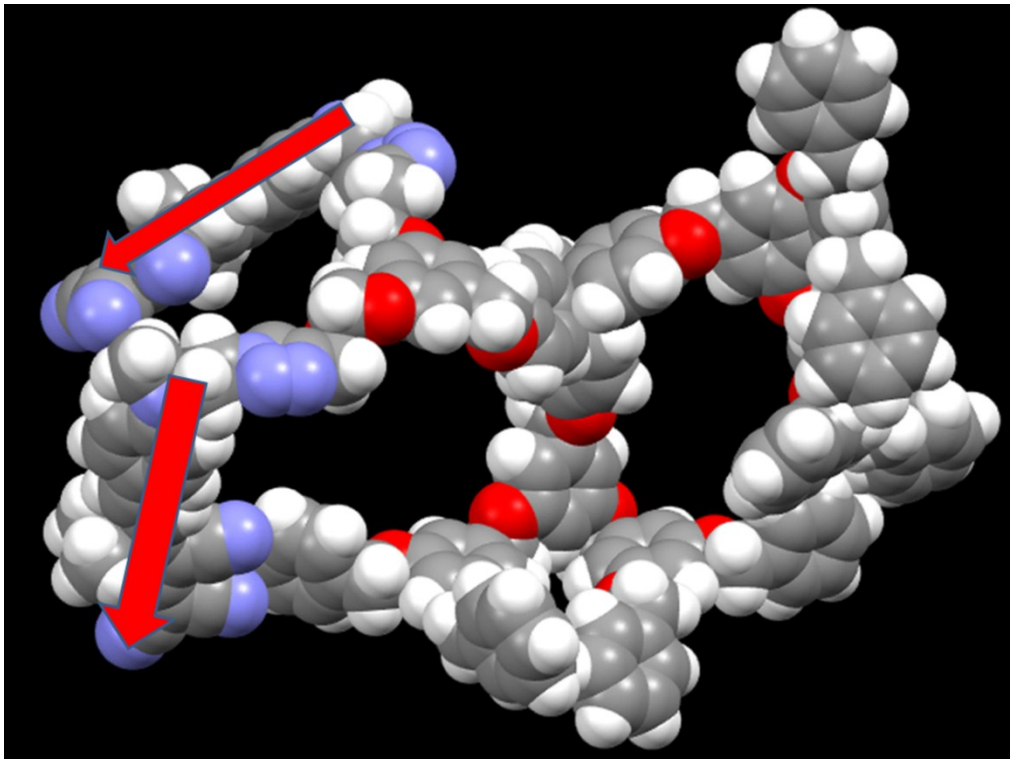


Figure 7. Optimized configuration of **HJ-1**.

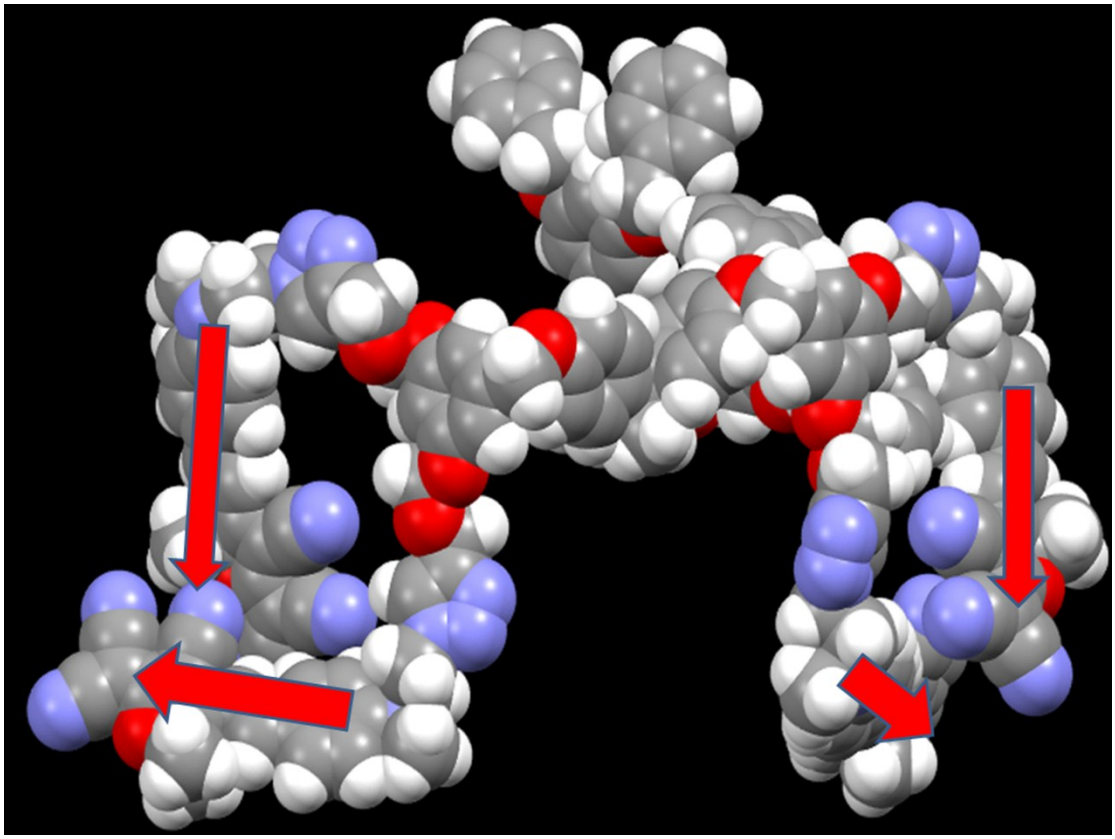


Figure 8. Optimized configuration of **HJ-2**.

References.

1. M. Q. He, T. M. Leslie and J. A. Sinicropi, *Chem. Mater.*, 2002, **14**, 2393-2400.
2. J. Liu, P. Si, X. Liu and Z. Zhen, *Opt. Mater.*, 2015, **47**, 256-262.
3. M. Malkoch, K. Schleicher, E. Drockenmuller, C. J. Hawker, T. P. Russell, P. Wu and V. V. Fokin, *Macromolecules*, 2005, **38**, 3663-3678.
4. M. Frisch, G. Trucks, H. B. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *Inc., Wallingford, CT*, 2009, **200**.