

Supportting information

Asymmetric dendrimers with improved electro-optic performance:
synthesis and characterization.

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1. Experimental Details

1.1 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 MgSO₄, 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 DESD was synthesized according to the previous report.⁴ 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). ¹H and ¹³C NMR spectra were determined by Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). 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 °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.

1.2.2 Synthesis of compound 4.

To a stirred solution of compound **3** (3.38 g, 10 mmol), and methyl 1,1,1-Tris(4-hydroxyphenyl)ethane (3.06g, 10 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 (5.29g, 87.1%). ¹H NMR (400 MHz, DMSO) δ: 9.23 (s, 2H, -OH), 7.42 (d, 4H, Ar-H), 7.37 (t, 4H, Ar-H), 7.31 (d, 2H, Ar-H), 6.92 (d, 2H, Ar-H), 6.86 (d, 2H, Ar-H), 6.81 (d, 4H, Ar-H), 6.69 (s, 2H, Ar-H) 6.66 (d, 4H, Ar-H) 6.62 (s, 1H, Ar-H), 5.06 (s, 4H, -CH₂), 4.96 (s, 2H, -CH₂), 1.97 (s, 3H, -CH₃). ¹³C NMR (101 MHz, CDCl₃) δ: 156.15, 151.78, 144.25, 141.58, 140.54, 137.57, 129.36, 125.65, 114.67, 112.83, 107.10, 102.00, 78.46, 75.69, 69.89, 56.12, 50.78, 30.83. MALDI-TOF (M⁺): calcd: 608.72; found: 608.69.

1.2.3 Synthesis of dendrimer 5.

The procedure for dendrimer **5** was followed to prepare compound **4** as colorless solid (91.3%). ¹H NMR (400 MHz, CDCl₃) δ: 7.36 (m, 10H, Ar-H), 6.98 (dd, *J* = 8.9, 2.3 Hz, 6H, Ar-H), 6.86 – 6.81 (m, 6H, Ar-H), 6.68 (t, *J* = 2.6 Hz, 6H, Ar-H), 6.56 (d, *J* = 2.1 Hz, 3H, Ar-H), 5.03 (s, 4H, -CH₂), 4.97 (d, *J* = 6.7 Hz, 6H, -CH₂), 4.67 (d, *J* = 2.4 Hz, 8H, -CH₂), 2.50 (t, *J* = 2.4 Hz, 4H, Alkyne-H), 2.10 (s, 3H, -CH₃). ¹³C NMR (101 MHz, CDCl₃) δ: 160.29, 158.99, 156.80, 142.26, 139.94, 136.93, 129.77, 128.71, 128.13, 127.67, 114.18,

107.00, 106.54, 101.85, 78.45, 75.85, 56.08, 30.95. MALDI-TOF (M⁺): calcd: 1005.16; found: 1005.14.

1.2.4 Synthesis of compound 6

To a stirred solution of compound **3** (3.38 g, 10 mmol), and methyl 1,1,1-Tris(4-hydroxyphenyl)ethane (1.52g, 5 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 **6** as colorless solid (4.03g, 88.6%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.34 (m, 16H, Ar-H), 7.31 (t, J = 7.0 Hz, 4H, Ar-H), 6.98 (d, J = 8.8 Hz, 4H, Ar-H), 6.94 (d, J = 8.6 Hz, 2H, Ar-H), 6.82 (d, J = 8.8Hz, 4H, Ar-H), 6.70 (d, J = 8.6 Hz, 2H, Ar-H), 6.68 (s, 4H, Ar-H), 6.56 (s, 2H, Ar-H), 5.03 (s, 8H, CH₂), 4.96 (s, 4H, CH₂-H), 2.10 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃, ppm):δ=157.03, 152.83, 146.41, 142.38, 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: 910.39; found: 910.37.

1.2.5 Synthesis of dendrimer 8

The procedure for dendrimer **8** was followed to prepare compound **4** as colorless solid (91.3%). ¹H NMR (400 MHz, CDCl₃):δ= 7.45 – 7.31 (m, 20H, Ar-H), 7.02 (dd, J= 8.9, 2.2Hz, 6H, Ar-H), 6.86 (d, J = 8.9Hz, 6H, Ar-H), 6.71(d, J = 2.1, 6H, Ar-H) 6.59 (t, J = 2.1Hz, 3H, Ar-H), 5.05 (s, 8H, CH₂), 4.99 (d, J = 6.0 Hz, 6H, CH₂), 4.68 (d, J = 2.4Hz, 4H, CH₂), 2.52 (t, 2H, alkyne-H), 2.08 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ= 160.30, 159.00, 156.93, 142.24, 139.78 (s), 136.95, 129.78, 128.73, 128.14, 127.69, 114.18, 107.01, 106.56, 75.86, 70.26, 56.09. MALDI-TOF (M⁺): calcd: 1108.46; found: 1108.38.

1.2.6 Synthesis of dendrimer AD-1

A solution of the asymmetric dendrimer **8** (0.11g, 0.1 mmol), chromophore **C1** (0.093g, 0.24 mmol), sodium ascorbate (2 mg, 12 μmol), and CuSO₄(1 mg, 6 μmol) in acetone (25 mL) was stirred at room temperature for 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 **AD-1** as a dark red solid (94.0% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, 15.9 Hz, 2H, CH=CH), 7.48 (d, J=6.9 Hz, 2H, CH=CN), 7.44 – 7.28 (m, 20H, Ar-H), 7.03 – 6.94 (d, 6H, Ar-H), 6.80 (d, 6H, Ar-H), 6.72 (d, J = 15.9 Hz, 2H, CH=CH), 6.67 (d, J = 2.0 Hz, 6H, Ar-H), 6.60 – 6.53 (m, 6H, Ar-H), 5.11 (s, 4H, CH₂), 5.03 (s, 8H, CH₂), 4.94 (d, J = 13.5 Hz, 6H, CH₂), 4.62 (s, 4H, CH₂), 3.98 (s, 4H, CH₂), 2.88 (s, 6H, CH₃), 2.09 (s, 3H, CH₃), 1.72 (s, 12H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ=177.09, 175.38, 161.01, 160.28, 157.44, 153.05, 149.08, 143.03, 140.72, 137.61, 133.07, 130.49, 129.45, 128.89, 128.40, 123.72, 114.87, 113.10, 110.52, 107.40, 98.09, 70.99, 53.17, 39.59, 27.46. MALDI-TOF (M⁺): calcd: 1907.82; found: 1907.79.

HRMS (ESI) (M⁺, C₁₁₉H₁₀₆N₁₄O₁₁): calcd: 1906.81655; found: 1906.81648.

1.2.7 Synthesis of dendrimer AD-2.

A solution of the asymmetric dendrimer **5** (0.05g, 0.05 mmol), chromophore **C1** (0.093g, 0.24 mmol), sodium ascorbate (2 mg, 12 μ mol), and CuSO_4 (1 mg, 6 μ mol) in acetone (25 mL) was stirred at room temperature for 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 **AD-2** as a dark red solid (91.0% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.61 (d, 8H, $\text{CH}=\text{CH}+\text{CH}=\text{CN}$), 7.48 (d, 8H, Ar-H), 7.43 – 7.28 (m, 10H, Ar-H), 6.97 (t, 6H, Ar-H), 6.83 (t, 6H, Ar-H), 6.73 (d, 4H, $\text{CH}=\text{CH}$), 6.68 (d, 4H, Ar-H), 6.63 (s, 2H, Ar-H), 6.58 (d, 9H, Ar-H), 6.46 (s, 2H, Ar-H), 5.30 (s, 4H, $-\text{CH}_2$) 5.11 (s, 8H, $-\text{CH}_2$), 5.02 (s, 4H, $-\text{CH}_2$), 4.93 (d, 6H, $-\text{CH}_2$), 4.60 (s, 8H, $-\text{CH}_2$), 3.97 (s, 8H, $-\text{CH}_2$), 2.87 (s, 12H, $-\text{CH}_3$), 2.07 (s, 3H, $-\text{CH}_3$), 1.71 (s, 24H, $-\text{CH}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ : 177.09, 175.38, 161.01, 160.28, 153.05, 149.08, 137.61, 133.07, 130.49, 129.45 (s), 128.89, 128.40, 123.72, 114.87, 113.10, 110.52, 107.40, 98.09, 95.80, 70.99, 62.71, 39.59, 27.46. MALDI-TOF (M^+): calcd: 2546.84; found: 2546.81. HRMS (ESI) (M^+ , $\text{C}_{151}\text{H}_{132}\text{N}_{28}\text{O}_{13}$): calcd: 2545.05287; found: 2545.05285.

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 2.1 μm -2.6 μm , 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 1.3 μm -2.0 μm).

3. DSC curves of three dendrimers

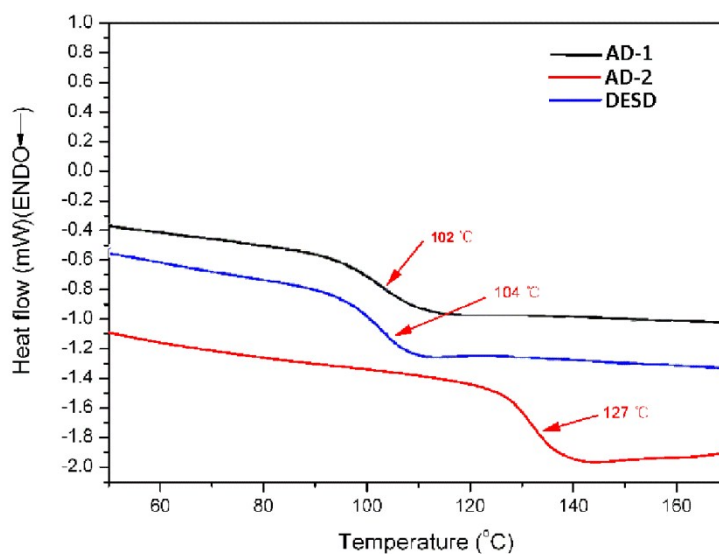


Figure 1. DSC curves and glass transition temperatures for three dendrimers.

4. UV-Vis spectra in chloroform

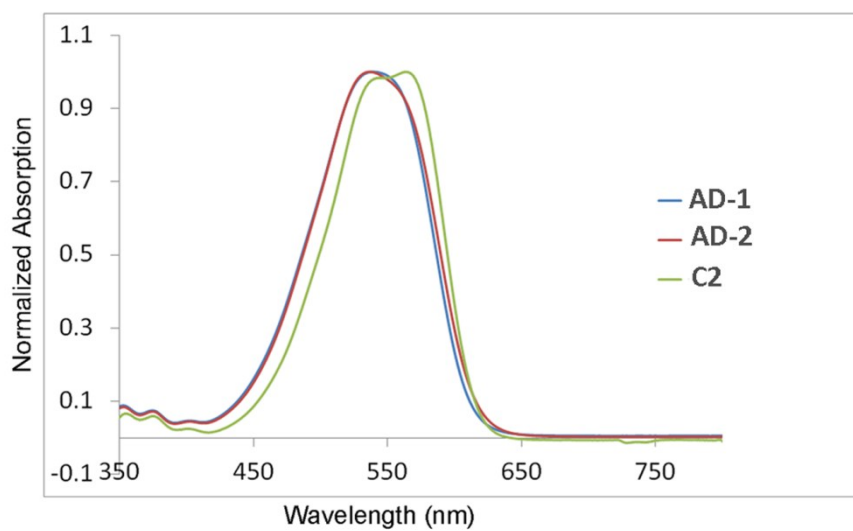


Figure 2. UV-Vis absorptions in chloroform.

5. UV-Vis spectra for films.

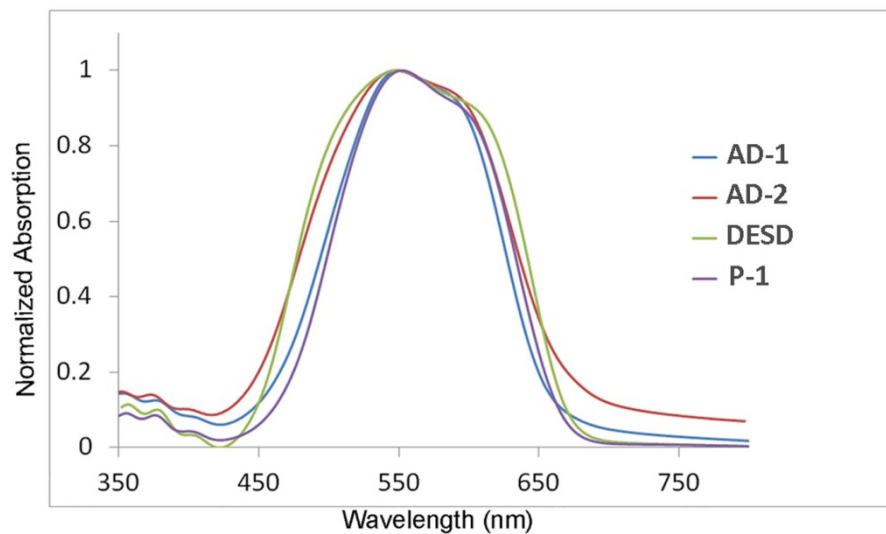


Figure 3. UV-Vis absorptions for films.

6. Infrared spectra.

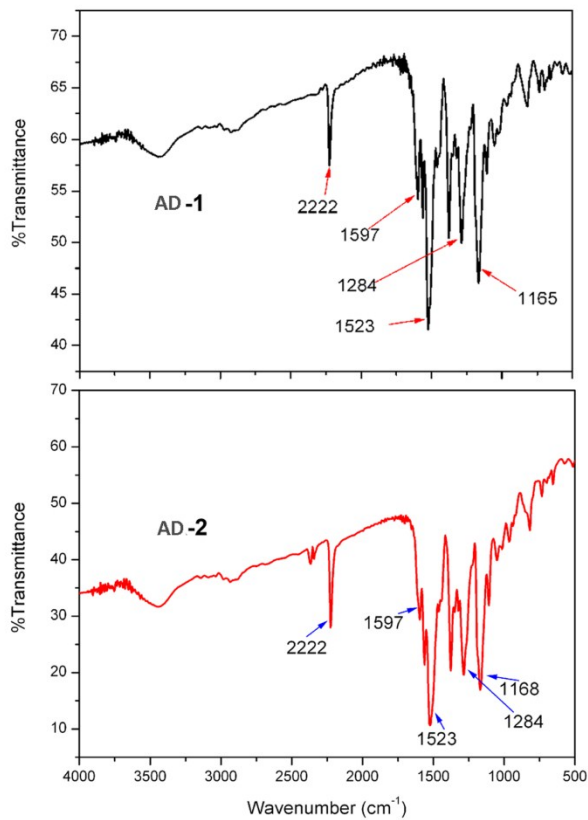


Figure 4. Infrared spectra for AD-1 and AD-2.

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

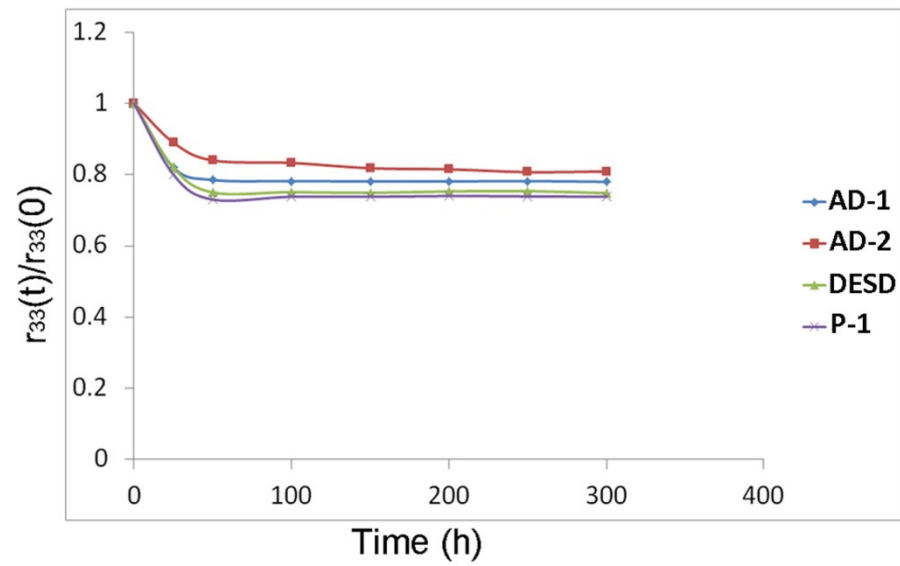


Figure 5. Temporal stability for poled films.

8. The optimized configuration of three dendrimers in vacuum.

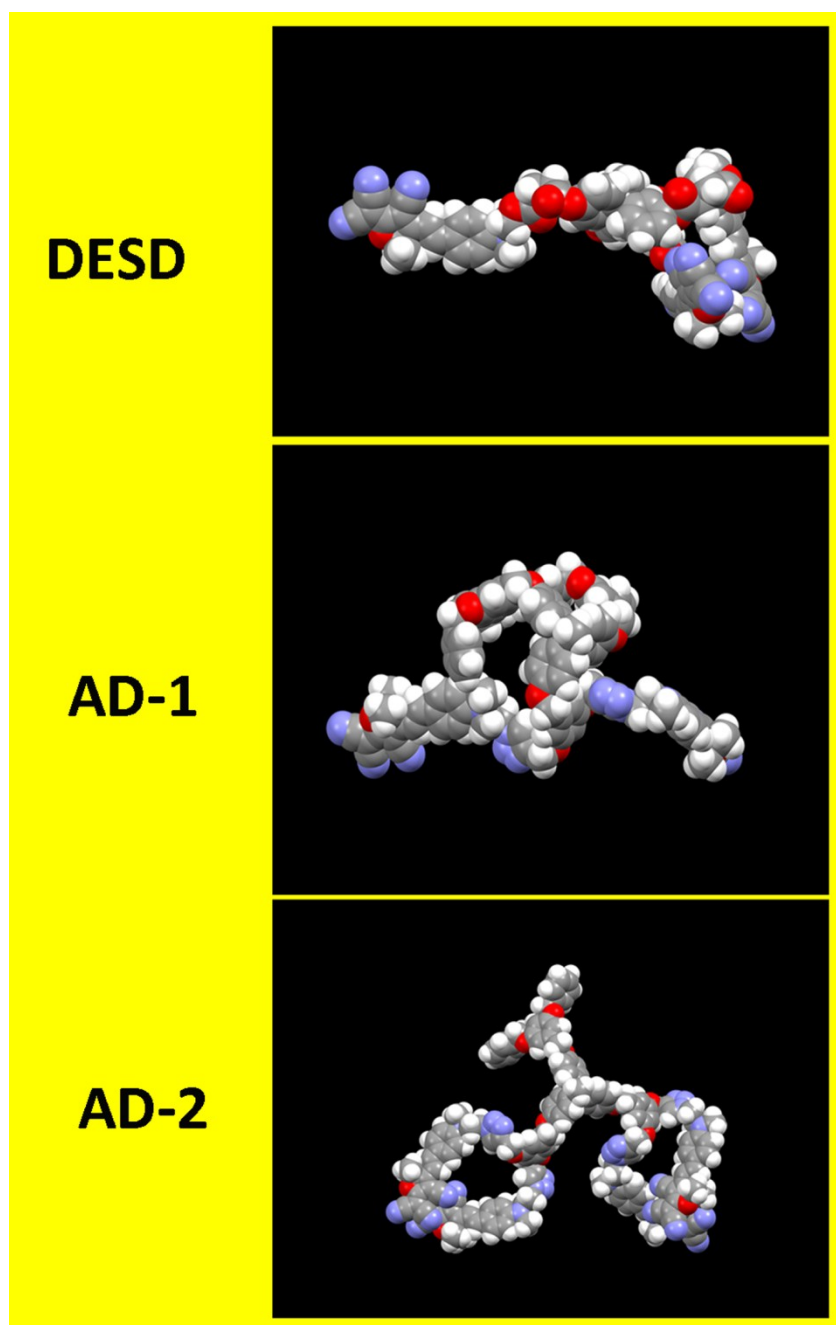


Figure 6. Optimized configuration of **DESD**.

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