

## Supplementary data

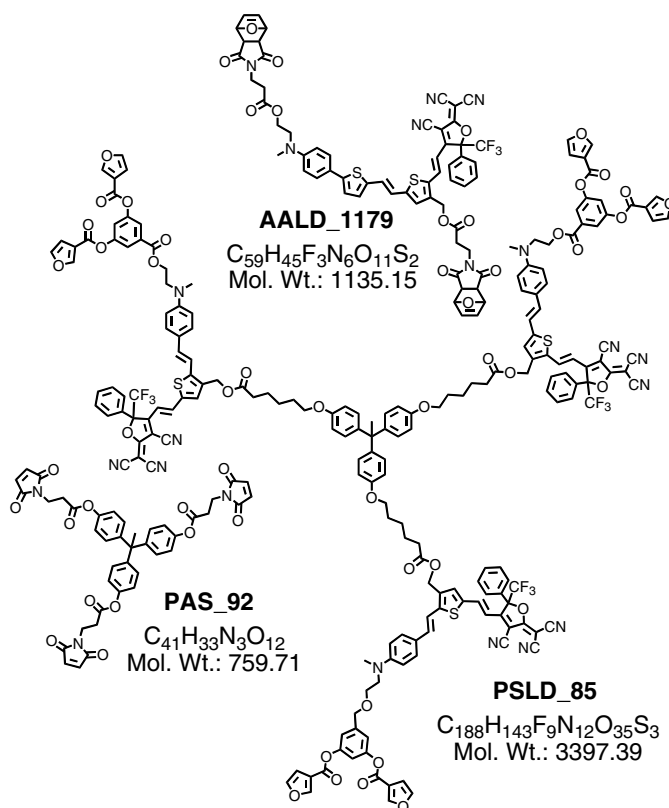
# Tri-component Diels-Alder Polymerized Dendrimer Glass Exhibiting Large, Thermally Stable, Electro-optic Activity

*Philip A. Sullivan,\* Benjamin C. Olbricht, Andrew J.P. Akelaitis, Alok A. Mistry, Yi Liao,*

Larry R. Dalton<sup>a</sup>

Department of Chemistry, University of Washington, 109 Bagley Hall Box 351700, Seattle, WA 98195-1700,

E-mail; Philip A. Sullivan: [psull76@u.washington.edu](mailto:psull76@u.washington.edu); Larry Dalton: [dalton@chem.washington.edu](mailto:dalton@chem.washington.edu)



**Fig. 1** Crosslinkable dendrimer PSLD\_85, chromophore AALD\_1179, and optically inert pre-crosslinker PAS\_92

## General procedures and materials

All commercially available starting materials were purchased from Aldrich, or ACROS Co. and used without further purification unless otherwise stated. HPLC grade tetrahydrofuran (THF), and dichloromethane (DCM) were purchased from Fisher chemical co., degassed by purging with high purity argon, and purified by passing through alumina columns using a Grubbs-type apparatus. Anhydrous N,N-dimethyl formamide (DMF) was purchased from Sigma Aldrich. Glassware was base-washed and either flame or oven dried prior to use. All reactions were performed under an argon atmosphere unless otherwise stated.

Melting temperatures and glass transition behavior were measured using a Shimadzu DSC-60 differential scanning calorimeter under nitrogen flow at a temperature ramp rate of 10 °C per minute. NMR spectra were recorded using a 300 MHz Bruker Avance NMR spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed by Prevalere Life Sciences, Inc., Whitesboro NY.

**6,7-furan (N-carboxyethylmaleimide) (6).**<sup>16</sup> An oven-dried, 100 mL, 1-neck, mag.-stirred RBF equipped with a reflux condenser was charged with N-carboxyethyl maleimide (1.01 g, 6.0 mmol) and furan (4.08 g, 60 mmol). To the reaction mixture was added 20 mL of benzene at RT. The mixture was heated to 75 °C where it refluxed for 12 hours. The solution was cooled to RT to produce a white precipitate, where the solvent was removed *in vacuo*. The solid was then dissolved in freshly distilled THF, dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. A white powder (1.4 g, 5.9 mmol) was obtained at 99% and was used without further purification.

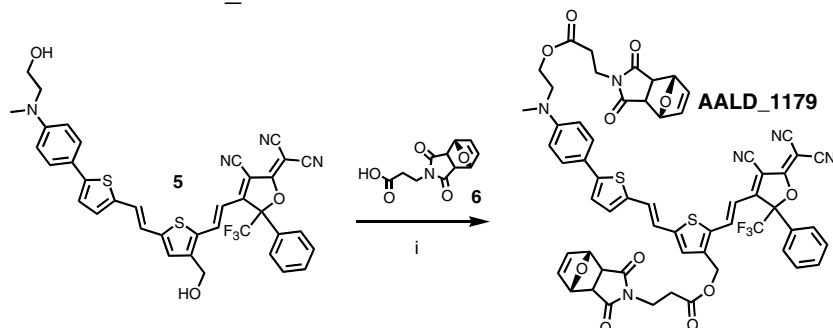
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 6.55 (s, 2H), 5.12 (s, 2H), 3.55 (t, 7.8Hz, 2H), 2.92 (s, 2H), 2.42 (t, 7.8Hz, 2H) ppm.

**PAS-92; 1,1,1-Tris [4-{6,7-furan(N-carboxyethylmaleimide)}phenyl]ethane.** An oven-dried, 100 mL, 1-neck, mag.-stirred RBF was charged with 1,1,1-Tris (4-hydroxyphenyl)ethane (1.00 g, 3.30 mmol), maleimide propanoic acid (3.10 g, 13.06 mmol), 1,3-dicyclohexylcarbodiimide (3.10 g, 14.85 mmol), and DPTS (0.29 g, 0.99 mmol). After 30 min of drying *in vacuo*, the mixture was dissolved in dry DMF (1 mL) and freshly distilled DCM (20 mL) and stirred overnight at 50 °C. The reaction was then diluted with DCM washed with brine. The organics were separated and the aqueous phase was extracted with DCM. The combined organics were washed with distilled water, dried over MgSO<sub>4</sub>, filtered, and the solvent removed *in vacuo*. The crude product was purified via silica gel column chromatography (5% EtOAc/DCM) to yield 0.58 g, 0.76 mmol (23%) of a white powder.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.08 (d, J = 8.7 Hz, 6H), 6.99 (d, J = 9 Hz, 6H), 6.74 (s, 6H), 3.97 (t, J = 6.9 Hz, 6H), 2.89 (t, J = 6.9 Hz, 6H), 2.14 (s, 3H) ppm.

M<sub>p</sub> = 205 °C

**Scheme 1.** General synthesis of AALD\_1179 active crosslinker



<sup>a</sup> Conditions: DCC / DPTS, DCM : DMF, reflux 48 hrs, 66%

**AALD-1179** An oven-dried, 100 mL, 1-neck, mag.-stirred RBF was charged with di-hydroxy precursor chromophore 5 (1.04 g, 1.46 mmol), furan-protected maleimide propanoic acid (0.98 g, 4.10 mmol), 1,3-dicyclohexylcarbodiimide (0.90 g, 4.38 mmol), and DPTS (0.430 g, 1.46 mmol). After 30 min of drying *in vacuo*, the mixture was dissolved in dry DMF (2 mL) and freshly distilled DCM (40 mL) and stirred for 20 min at 40 °C. Freshly distilled THF (5 mL) was added for solubility, and then the reaction proceeded overnight at 40-50 °C. The reaction was then diluted with DCM and neutralized with brine. The organics were separated and the aqueous phase was extracted with DCM. The combined organics were washed with distilled water, dried over MgSO<sub>4</sub>, filtered, and the solvent removed *in vacuo*. The crude product was purified via silica gel column chromatography (5% THF/DCM ramped to 10% THF/DCM) and then recrystallized from DCM in ethanol to afford 1.11 g (66%) of a dark blue flaky solid.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.91 (d, J = 15 Hz, 1H), 7.52 (m, 7H), 7.28 (s, 1H), 7.24 (d, 15.9 Hz, 1H), 7.12 (s, 2H), 7.06 (s, 1H), 6.87 (d, J = 15.3, 1H), 6.73 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 15 Hz, 1H), 6.52 (d, J = 2.1 Hz, 3H), 3.61 (s, 4H), 1.94 (s, 2H), 4.26 (t, J = 5.1 Hz, 2H), 3.78 (m, 4H), 3.59 (t, J = 6 Hz, 2H), 3.45 (dd, J<sub>1</sub> = 6 Hz, J<sub>2</sub> = 7.2 Hz, 2H), 2.86 (d, J = 12.6 Hz, 4H), 2.63 (t, J = 7.2 Hz, 4H), 1.68 (s, 1H), 1.21 (t, J = 6.9 Hz, 3H) ppm.

HRMS (ESI): exact mass calcd for C<sub>60</sub>H<sub>49</sub>F<sub>3</sub>N<sub>6</sub>O<sub>11</sub>S<sub>2</sub> [M+H]<sup>+</sup>, 1150.29. Found, 1150.2879.

λ<sub>max</sub>(CHCl<sub>3</sub>) = 737 nm.

**Tri-acid dendrimer core (1).** was prepared according to literature method<sup>18</sup>

**PSLD\_33 tri-TBDMS dendrimer.** An oven dried, mag.- stirred, 100mL two-neck RBF was charged with tri-acid core 1 (0.221 g, 0.341 mmol), chromophore 2 (0.820 g, 1.13 mmol), 1,3-dicyclohexylcarbodiimide (0.260 g, 1.26 mmol), and DPTS (0.10 g, 0.341mmol). After 1hr of drying under a high vacuum, the mixture was dissolved in freshly distilled THF (10 mL) and DCM (15 mL). The reaction was stirred for 48 hr, washed with NaCl (sat.), and organic layer collected. The aqueous layer was extracted with DCM, and the combined

organics were washed with water, dried over  $\text{MgSO}_4$ , and condensed *in vacuo*. The dark blue crude solid was purified by silica gel column chromatography (5% THF/ DCM) to yield 0.182 g (25%) of a deep blue solid.

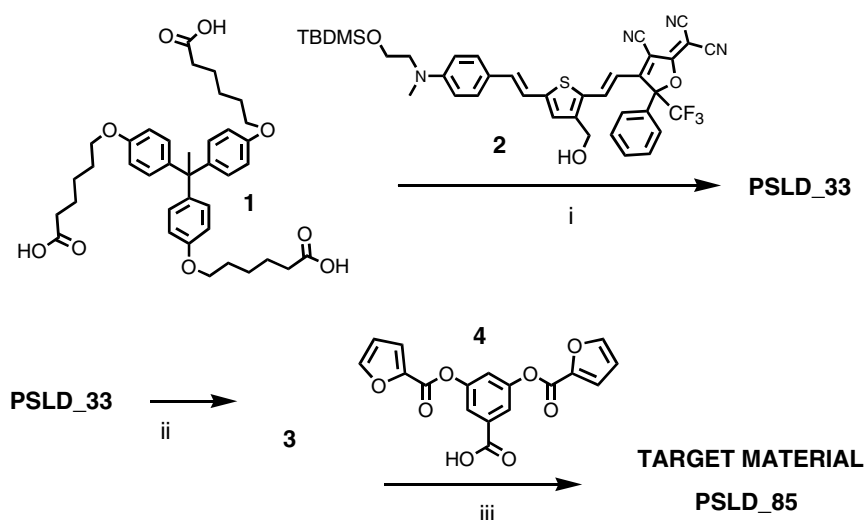
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J = 15.3$  Hz), 7.58-7.54 (m, 15H), 7.39 (d,  $J = 9$  Hz, 6H), 7.13 (d,  $J = 15.9$  Hz, 3H), 7.03 (s, 3H), 6.98, (d,  $J = 8.7$  Hz, 6H), 6.96 (d,  $J = 15.9$  Hz, 3H), 6.77 (d,  $J = 8.7$  Hz, 6H), 6.68 (d,  $J = 8.7$  Hz, 6H), 6.64 (d,  $J = 15.3$  Hz, 3H), 4.92 (d,  $J = 3$  Hz, 6H), 3.94 (t,  $J = 6.3$  Hz, 6H), 3.81 (t,  $J = 6$  Hz, 6H), 3.56 (t,  $J = 6$  Hz, 6H), 3.10 (s, 9H), 2.35 (t,  $J = 7.2$  Hz, 6H), 2.09 (br-s, 3H), 1.87-1.79 (m, 6H), 1.72-1.67(m, 6H), 1.55-1.49 (m, 6H), 0.89 (s, 27H), 0.03 (s, 18H), ppm.

MALDI-TOF:  $[\text{M}+\text{Na}]$ , 2804.476 (m/z).

$\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) = 759 nm ;  $\lambda_{\text{max}}$  (flm) = 734 nm

$T_g = 90$  °C

### Scheme 2. General synthesis PSLD\_85



<sup>a</sup>Conditions: i) DCC / DPTS, DCM : DMF, reflux 48 hrs, 50%; ii) 1N HCl (MeOH soln.), acetone, RT 2.5 hrs, quant.; iii) DCC / DPTS, DCM : DMF, reflux 48 hrs, 62%

**Deprotection of PSLD\_33 (3).** A 50mL RBF is charged with PSLD\_33 (0.19 g) and acetone was added to dissolve (4 mL). 1N HCl (0.5 mL) was then added. The reaction was allowed to proceed for 2.5 hr. The mixture was then neutralized with  $\text{NaHCO}_3$  and product collected by filtration. The blue solid was obtained in quantitative yield and used without further purification.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (d,  $J = 15$  Hz, 3H), 7.58-7.52 (m, 15H), 7.37 (d,  $J = 8.7$  Hz, 6H), 7.08 (d,  $J = 15.6$ Hz, 3H), 7.01 (s, 3H), 6.96 (d,  $J = 8.7$  Hz, 6H) 6.93 (d,  $J = 15.3$  Hz, 3H), 6.77-6.74 (m, 12H), 6.60 (d,  $J = 15.3$  Hz, 3H), 4.91 (s, 6H), 3.95 (t,  $J = 6.3$  Hz, 6H), 3.86 (t,  $J = 5.4$  Hz, 6H), 3.6 (t,  $J = 5.4$  Hz, 6H), 3.09 (s, 9H), 2.35 (t,  $J = 7.5$  Hz, 6H), 2.08 (s, 3H), 1.83-1.74 (m, 6H), 1.72-1.64 (m, 6H), 1.54-1.45 (m, 6H) ppm.

MALDI-TOF: m/z calc. 2437.78; found,  $[\text{M}+\text{H}]$ , 2438.1,  $[\text{M}+\text{Na}]$ , 2461.040 (m/z).

**PSLD\_85 Diels-Alder dendrimer.** An oven dried, mag.- stirred, 100mL two-neck RBF was charged with PSLD\_40 (0.10 g, 0.041 mmol), dendron 4 (0.164 mmol), 1,3-dicyclohexylcarbodiimide (0.038 g, 0.184 mmol), and DPTS (0.030 g, 0.20 mmol). After 1hr of drying under a high vacuum, the mixture was dissolved in freshly distilled THF (10 mL) and DCM (15 mL). The reaction was stirred for 48 hr, washed with NaCl (sat.),

and organic layer collected. The aqueous layer was extracted with DCM, and the combined organics were washed with water, dried over MgSO<sub>4</sub>, and condensed *in vacuo*. The dark blue crude solid was purified by silica gel column chromatography (2.5% THF/ DCM) to yield 0.1 g (0.025 mmol, 62%), of a deep blue solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.20 (q, J = 1 Hz, 4H), 7.89 (d, J = 15 Hz, 3H), 7.71 (d, J = 2.4 Hz, 6H), 7.56 (m, 15H), 7.52 (t, J = 1.5 Hz, 6H), 7.37 (d, J = 8.8 Hz, 6H), 7.34 (t, J = 2.1 Hz, 3H), 7.04 (d, J = 15.5 Hz, 3H), 7.01 (s, 3H), 6.97 (d, J = 8.8 Hz, 6H), 6.91 (d, 15 Hz), 6.87 (m, 6H), 6.78 (d, J = 8.8 Hz, 6H), 6.75 (d, J = 8.8 Hz, 6H), 6.65 (d, J = 15 Hz, 3H), 4.92 (d, J = 3.3 Hz, 6H), 4.51 (t, J = 5.4 Hz, 6H), 3.93 (t, J = 6.3 Hz, 6H), 3.82 (t, J = 5.4 Hz, 6H), 3.12 (s, 9H), 2.35 (t, J = 7.2 Hz, 6H), 2.09 (s, 3H), 1.87 (m, 6H), 1.82 (m, 6H), 1.65 (m, 6H) ppm.

HRMS (MALDI-TOF): found, 3413.969 (M+H)

EA (CHN) analysis calcd for C<sub>188</sub>H<sub>141</sub>F<sub>9</sub>N<sub>12</sub>O<sub>36</sub>S<sub>3</sub>, C; 66.19, H; 4.17, N; 4.93, Found, C; 65.68, H; 4.21, N; 4.15 %

$\lambda_{\max}$  = 725 nm (CHCl<sub>3</sub>)

T<sub>g</sub> = 85° C