Supporting Information for

Aggregation Induced Enhanced Emission of Conjugated Dendrimers with Large Intrinsic Two-Photon Absorption Cross Section

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1. Synthesis and characterization of compounds:

The compounds of 1, 2, 3 and 4 were readily obtained according to the literature procedures.[18]

Synthesis of 5: A round-bottomed flask (50 ML) was oven dried and cooled under N_2 atmosphere. 4-(4-(diphenylamino) styryl)-N-(4-(4-(diphenylamino)styryl)phenyl)-N-(4-vinylphenyl)-aniline **4** (1.6g, 2 mmol), 4-(bis(4-iodophenyl)amino) benzaldehyde **2** (0.48 g, 0.9 mmol), K_3PO_4 (0.58 g, 2.7 mmol) and 5mg $Pd(OAc)_2$ were dissolved in dry DMAc (20 ml). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24h at this temperature. After being cooled to room temperature, the reaction mixture was poured into the water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=1:1) to give second generation aldehyde-focused dendron as a yellow solid. Then, in an oven-dried flask, second generation aldehyde-focused dendron (2 g, 1.06 mmol) and methyltriphenyl -phosphonium bromide (0.54 g, 1.5 mmol) were dissolved in 100 ml of dry THF. t-BuOK (0.20 mg, 1.8 mmol) in 50 ml of dry THF was added dropwise slowly to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 atmosphere for 10h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/ CH_2Cl_2=3:1) to give second generation alkene-focused dendron **5** as a yellow solid. ^{1}H NMR (500 MHz $CDCl_3$): 7.31-7.39 (m, 12H, Ar), 7.10-7.27 (m, 12H, Ar), 7.01-7.09 (m, 20H, Ar), 6.65-6.71 (m, 1H, CH), 6.70 (d, J = 17.5Hz, 1H, CH=CH2), 5.18(d, J =11.0Hz, 1H, CH=CH2), MALDI/TOF MS: Calcd for $C_{140}H_{107}N_7$: 1885.9, Found: 1887.2. Anal. Calcd for $C_{140}H_{107}N_7$: C, 89.09; H, 5.71; N, 5.19; Found: C, 88.57; H, 5.52; N, 5.08.

General reaction procedure for entries AnG0, AnG1 and AnG2: In an oven-dried flask with stirbar, corresponding dendrons with alkene, 9,10-dibromoanthracene, K_3PO_4 and $Pd(OAc)_2$ were dissolved in dry DMAc. The reaction mixture was heated to 110 °C in an oil bath and stirred for 24h at this temperature under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was poured into the water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography to obtain a yellow powdery product.

Synthesis of compound AnG0: 0.76 g (2.8 mmol) compound **3**, 0.336 g (1 mmol) 9,10-dibromoanthracene, 0.636 g (3 mmol) K_3PO_4, **5** mg $Pd(OAc)_2$, and 10 ml DMAc were reacted according to the general procedure to obtain compound **AnG0** as a yellow solid (0.45 g, yield: 63 %). ^{1}H NMR (500 MHz $CDCl_3$): 6.87 (d, J = 16.0 Hz, 2H, CH=CH), 7.05 (t, *J* = 6.5 Hz, 4H, Ar), 7.14–7.17 (m, 12 H, Ar), 7.29 (d, *J* = 7.0 Hz, 8H, Ar), 7.46–7.47 (m, 4H, An), 7.56 (d, *J* = 7.0 Hz, 4H, Ar), 7.82 (d, *J* = 16.0 Hz, 2H, CH=CH), 8.40–8.41 (m, 4H, Ar). ^{13}C NMR (125 MHz $CDCl_3$): 148.15, 147.98, 137.29, 133.19, 131.94, 130.04, 129.75, 127.86, 126.95, 125.54, 124.93, 124.15, 123.77, 123.51. MALDI/TOF MS: Calcd for $C_{54}H_{40}N_2$: 716.3, Found: 716.9. Anal. Calcd for $C_{54}H_{40}N_2$: C, 90.47; H, 5.62; N, 3.91; Found: C, 90.39; H, 5.65; N, 3.86.

Synthesis of compound AnG1: 1.13 g (1.4 mmol) compound **4**, 0.168 g (0.5 mmol) 9,10–dibromoanthracene, 0.318 g (1.5 mmol) K_3PO_4, 5 mg $Pd(OAc)_2$, and 15 ml DMAc were reacted according to the general procedure to obtain compound **AnG1** as a yellow solid (0.445 g, yield: 50%). ^{1}H NMR (500 MHz $CDCl_3$): 6.90 (d, *J* =

16.5 Hz, 4H, CH=CH), 6.99-7.06 (m, 28H, Ar), 7.12 (d, *J* = 7.5 Hz, 16H, Ar), 7.13-7.16 (m, 8H, Ar), 7.20–7.22 (m, 4H, Ar), 7.25–7.28 (m, 10H, Ar), 7.38 (d, *J* = 8.5 Hz, 8H, Ar), 7.42 (d, *J* = 8.5 Hz, 8H, Ar), 7.46–7.49 (m, 4H, Ar), 7.59 (d, J = 9.0Hz, 4H, Ar), 7.85 (d, *J* = 16.5 Hz, 2H, CH=CH), 8.41–8.43 (m, 4H, An). ^{13}C NMR (125 MHz $CDCl_3$): 147.57, 147.14, 146.41, 136.82, 132.75, 132.60, 132.02, 131.77, 129.63, 129.27, 127.54, 127.27, 127.19, 126.97, 126.54, 126.44, 125.30, 125.17, 124.44, 124.36, 124.23, 123.68, 123.26, 122.97. MALDI/TOF MS: Calcd for $C_{134}H_{100}N_6$： 1792.8, Found: 1794.1. Anal. Calcd for $C_{134}H_{100}N_6$: C, 89.70; H, 5.62; N, 4.68; Found: C, 89.62; H, 5.70; N, 4.62.

Synthesis of compound AnG2: 1.32 g (0.7 mmol) compound **5**, 0.084 g (0.25 mmol) 9,10-dibromoanthracene, 0.159 g (0.75 mmol) K_3PO_4, 5mg $Pd(OAc)_2$, and **5** ml DMAc were reacted according to the general procedure to obtain compound **AnG2** as a yellow solid (0.26 g, yield: 26%). ^{1}H NMR (500 MHz $CDCl_3$): 6.87–7.06 (m, 68H, Ar), 7.08–7.15 (m, 64H, Ar), 7.19–7.27 (m, 26H, Ar), 7.33-7.46(m, 48H, Ar), 7.46-7.48(m, 4H, An), 7.58 (d, *J* = 8.5 Hz, 4H, Ar), 7.84 (d, *J* = 16.5 Hz, 2H, CH=CH), 8.40-8.42 (m, 4H, An). ^{13}C NMR (125 MHz CDCl3): 147.5, 147.1, 146.5, 146.4, 136.8, 132.7, 132.4, 132.3, 132.1, 131.8, 129.6, 129.5, 129.3, 129.0, 127.6, 127.2, 126.9, 126.7, 126.4, 125.2, 124.4, 124.3, 124.2, 123.9, 123.7, 123.2, 123.0. MALDI/TOF MS: Calcd for $C_{294}H_{220}N_{14}$： 3945.7, Found: 3947.7. Anal. Calcd for $C_{294}H_{220}N_{14}$: C, 89.42; H, 5.61; N, 4.97; Found: C, 89.35; H, 5.67; N, 4.95.

2. TEM images of microstructure of dendrimers and Dynamic Light Scattering (DLS) measurements

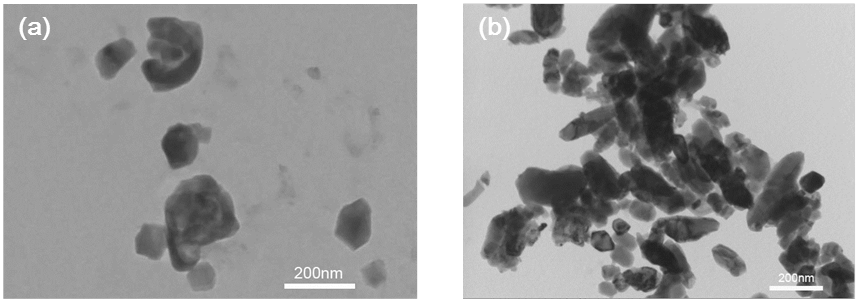
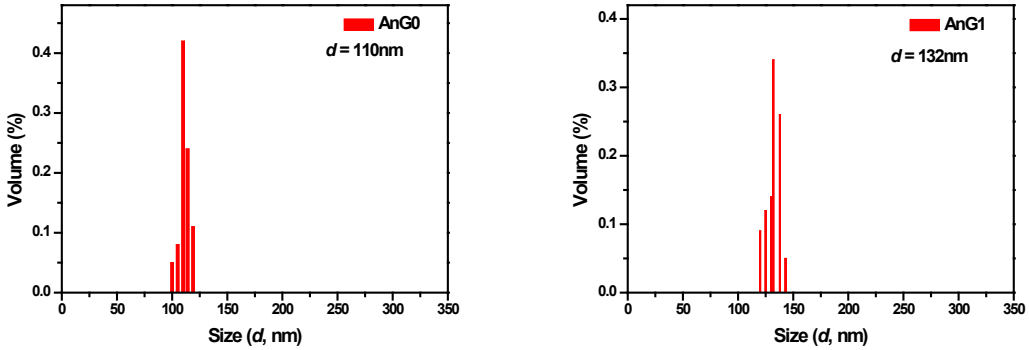


Figure S1. TEM image of the **AnG0** (a) and **AnG1** (b) nanoaggregates prepared in THF/ Water mixture (80% water volume fraction) at 5 μm.



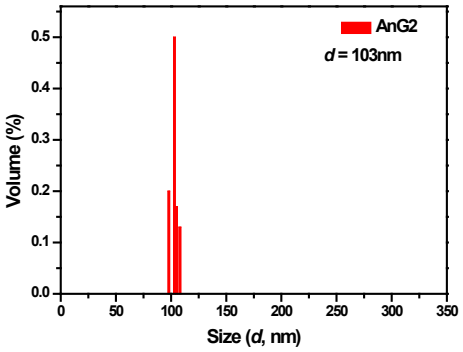


Figure S2. Dynamic light scattering image of dendrimers **AnG0**, **AnG1** and **AnG2** nanoaggregates dispersion in THF/Water mixture (80% water volume fraction) at 10 μm.

3. Photophysical properties of dendrimers

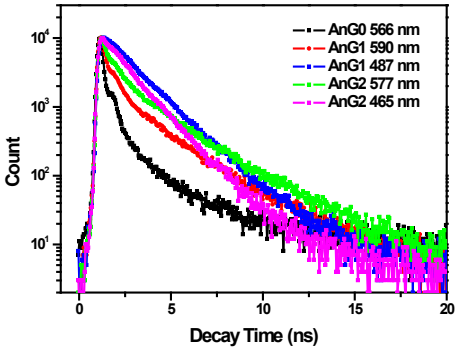


Figure S3. Time-resolved fluorescence of the dendrimers in THF solution, monitoring with different emission wavelength.

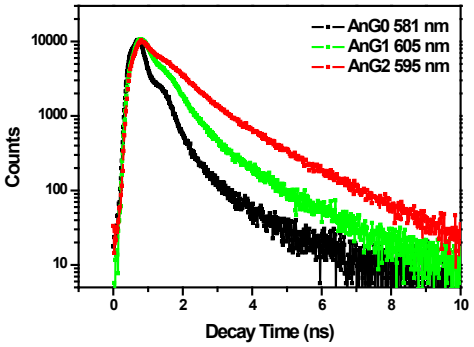


Figure S4. Time-resolved fluorescence of the dendrimers in thin film.

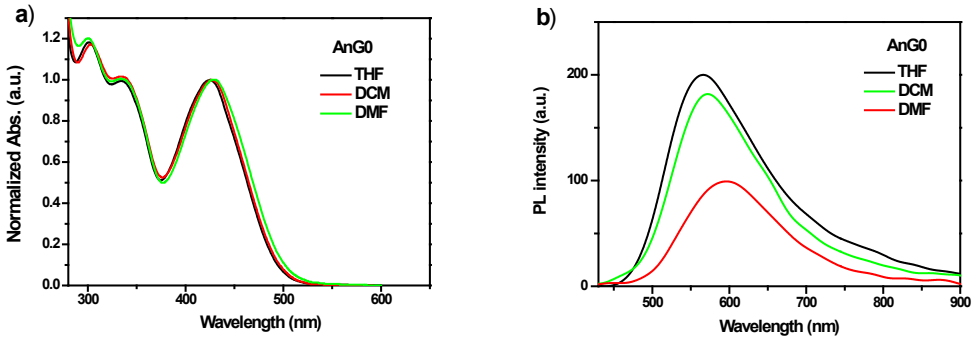


Figure S5. Solvatochromic behavior of **AnG0** in different solvents (a) normalized absorption and (b) PL spectra.

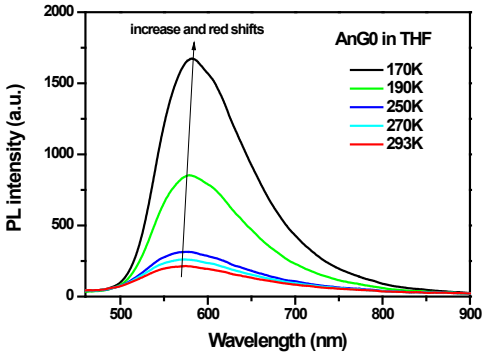


Figure S6. Temperature dependence of the emission spectra of AnG0 in THF solution (10^{-5}M)

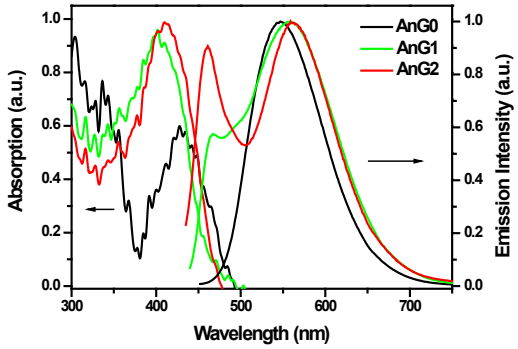


Figure S7. Normalized absorption and PL spectra of An-TPA dendrimer molecular dispersion in PMMA film (2% wt, monomer state)

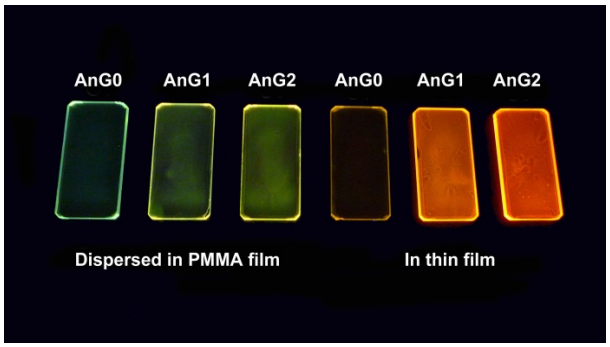


Figure S8. Fluorescence emission of all three dendrimers dispersed in PMMA film and in thin film under 365 nm illumination.

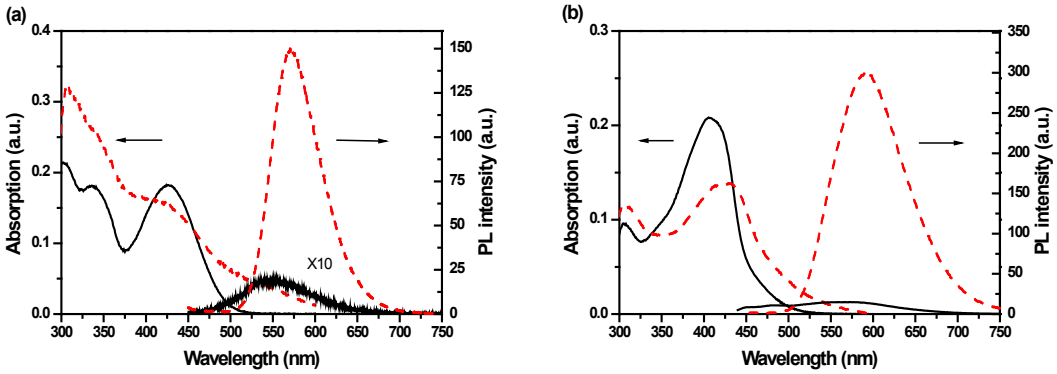


Figure S9. Absorption and photoluminescence spectra of G0 and G1 in the dilute THF solution (solid line) and in dispersion of the nanoaggregation form (THF/Water =1:8 v/v) at 10 μM (dash line)

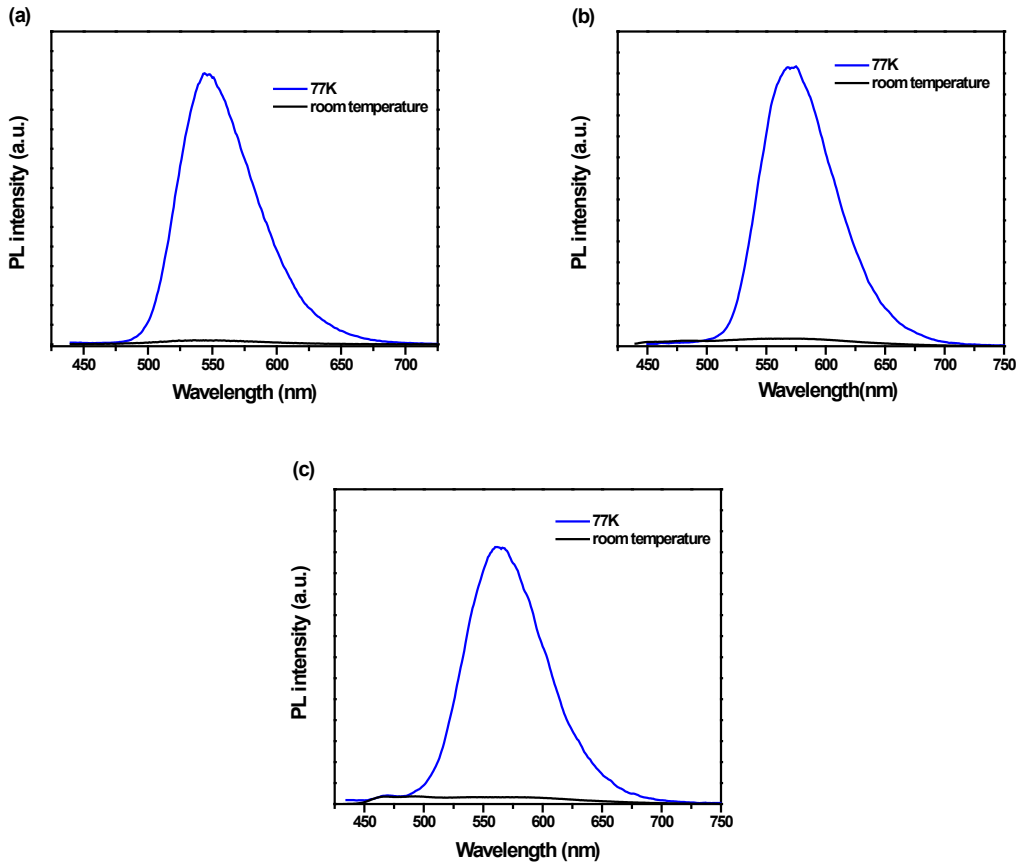


Figure S10. PL spectra of dendrimers **AnG0** (a), **AnG1** (b) and **AnG2** (c) at room temperature (free state) and 77 K (frozen state) in dilute THF solution (1×10^{-5} mol)

Table S1. Fluorescence lifetime of the dendrimers in various conditions.

	solution[a]					film[b]				
	λ_{em}[c]	A_1/A_2[d]	τ_1	τ_2	τ_{avg}	λ_{em}	A_1/A_2	τ_1	τ_2	τ_{avg}
AnG0	566	0.97/0.03	0.16	1.67	0.21	581	0.99/0.01	0.18	2.87	0.21
AnG1	487	0.47/0.53	0.56	1.39	1.00	605	0.96/0.04	0.33	2.00	0.40
	590	0.90/0.10	0.24	1.96	0.41					
AnG2	465	0.44/0.56	0.70	1.22	1.00	595	0.82/0.18	0.44	1.84	0.69
	577	0.82/0.18	0.41	1.82	0.67					

[a] In dilute THF solution at 10 μM. [b] in thin film. [c] monitor emission wavelength. [d] A_1 and A_2 are preexponential factors representing the functional contributions to the time-resolved decay of the compounds with a lifetime τ_1 and τ_2, respectively.

4. Semiempirical Calculation Methods

All semiempirical calculations were performed using the Gaussian 03 package program. The ground-state geometry of the model structure in the gas phase was optimized semiempirically using the pm3 formalism.

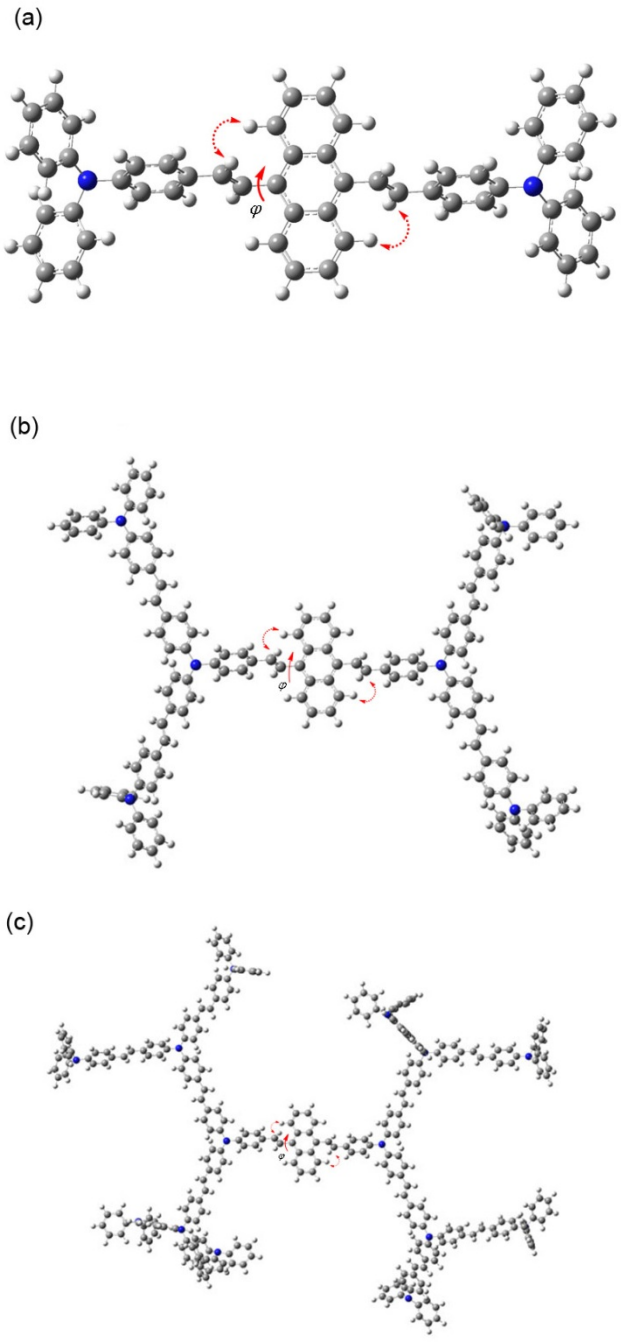


Figure S11. Semiempirical calculation (pm3 formalism) for G0 (a), G1 (b) and G2 (c) model structure Optimized geometries of the monomer from different viewpoints. The torsional angle is defined by four carbons and indicated by the solid arrows. Sterically hindered hydrogens are indicated by the dotted arrows.

6. ^{1}H and ^{13}C NMR spectra, MALDI-TOF MS data for dendrimers

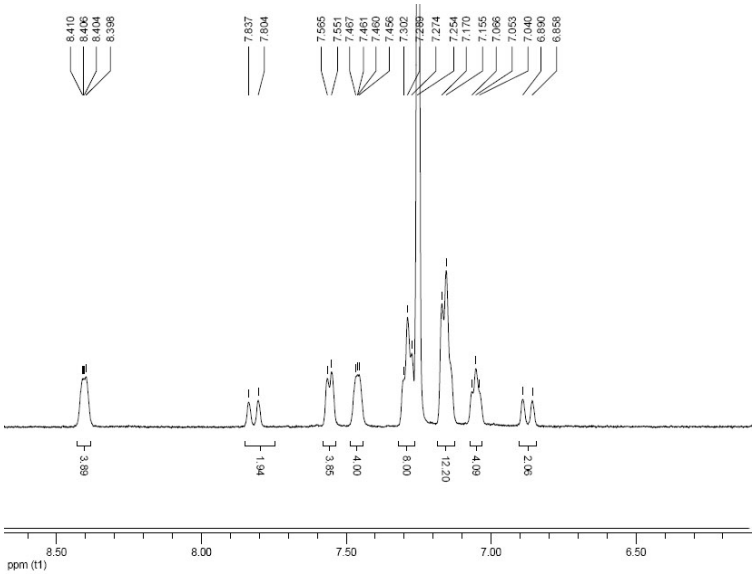


Figure S12. ^{1}H NMR spectrum of **AnG0**

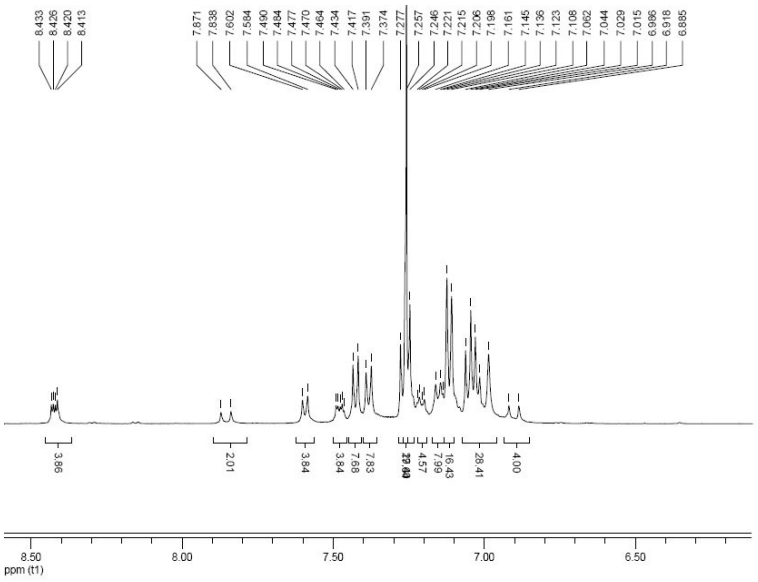


Figure S13. ^{1}H NMR spectrum of **AnG1**

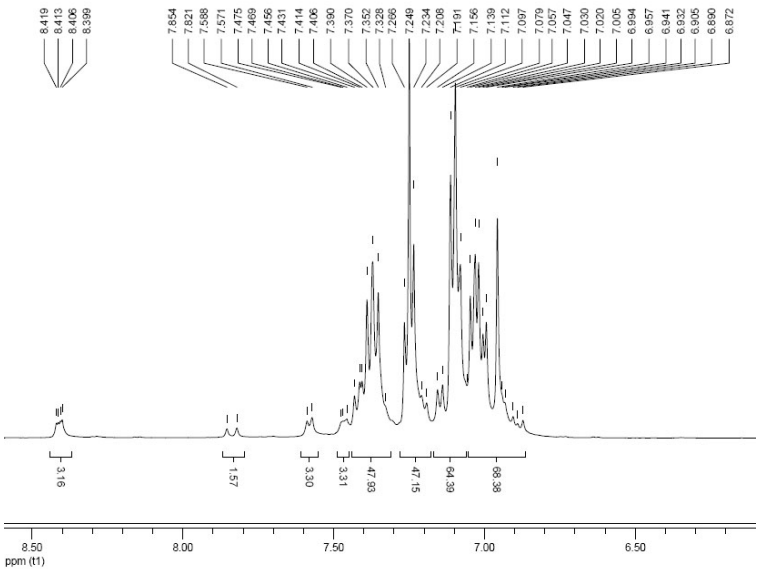


Figure S14. ^{1}H NMR spectrum of **AnG2**

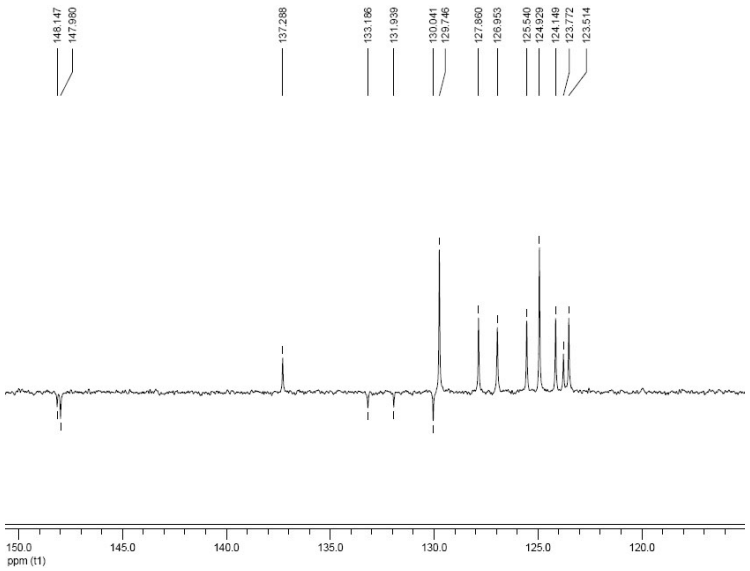


Figure S15. ^{13}C NMR spectrum of **AnG0**

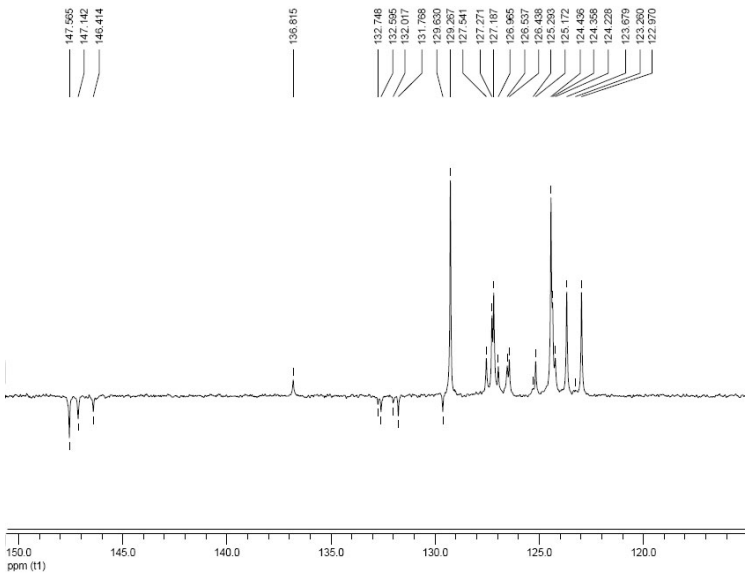


Figure S16. ^{13}C NMR spectrum of **AnG1**

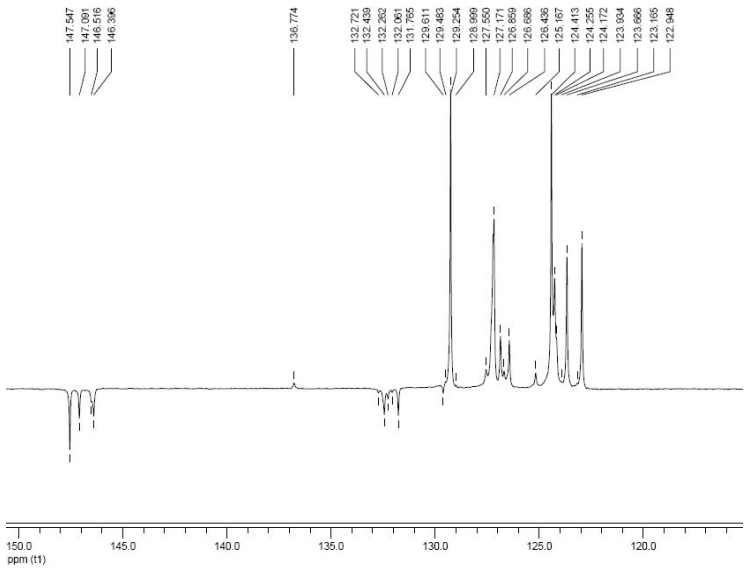


Figure S17. ^{13}C NMR spectrum of **AnG2**

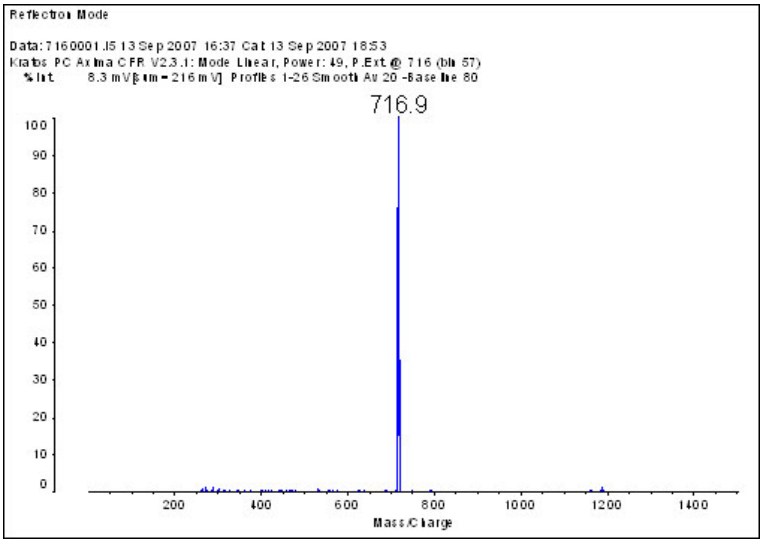


Figure S18. MALDI-TOF mass spectrum of **AnG0**

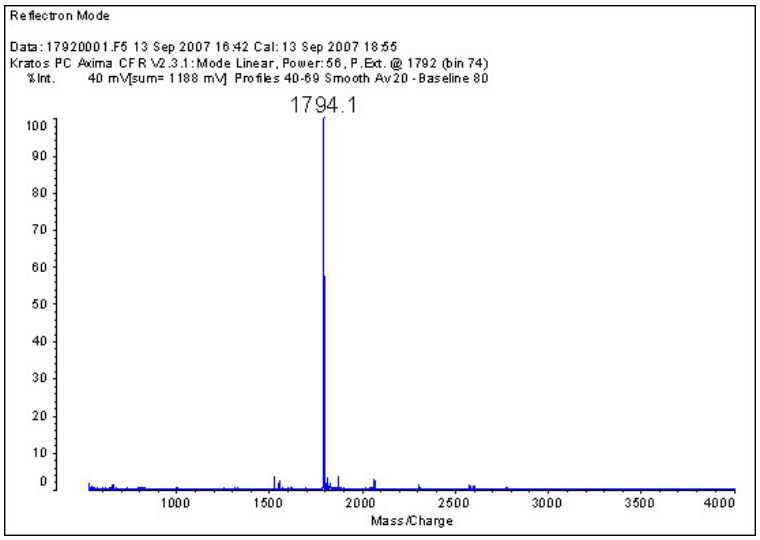


Figure S19. MALDI-TOF mass spectrum of **AnG1**

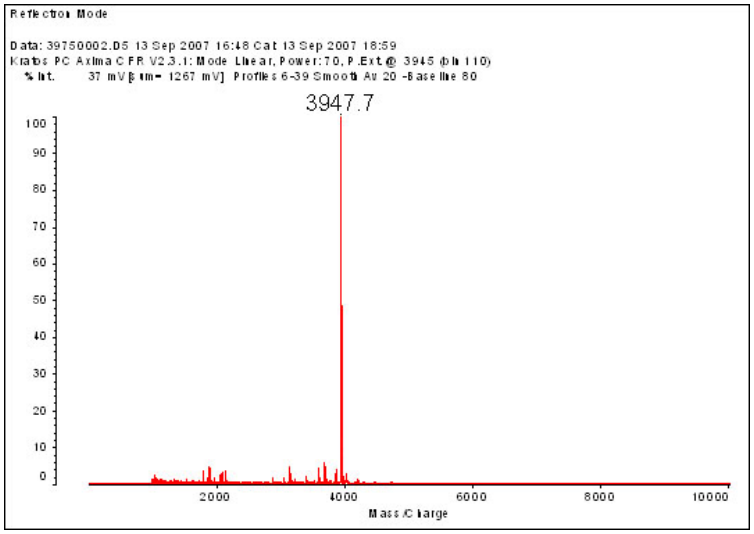


Figure S20. MALDI-TOF mass spectrum of **AnG2**

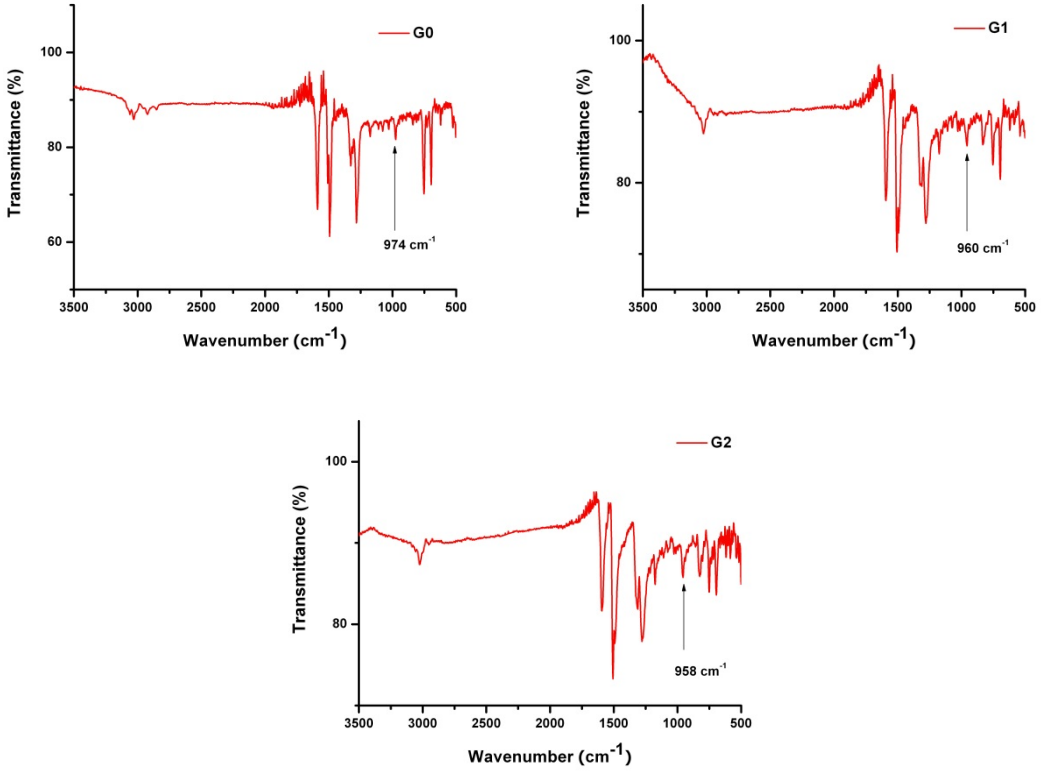


Figure S21. FR-IR spectra of dendrimers **AnG0**, **AnG1** and **AnG2**.