

Supporting Information

Supramolecular Dendrimers Based on the Self-Assembly of Carbazole-Derived Dendrons and Triazine Rings. Liquid Crystal, Photophysical and Electrochemical Properties

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Experimental Section

Materials and Methods

Reagents were purchased from Aldrich and were used as received. Anhydrous THF and CH₂Cl₂ were purchased from Scharlau and dried using a solvent purification system.

The infrared spectra of all the compounds were obtained with a Nicolet Avatar 360 FTIR spectrophotometer in the 400–4000 cm⁻¹ spectral range using KBr pellets and NaCl cells. NMR data were obtained on Bruker AVANCE spectrometers operating at 500, 400 and 300 MHz for ¹H and 125, 100 and 75 MHz for ¹³C. Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer. Mass spectrometry studies (FAB+, MALDI+) were performed with a VG AutoSpec EBE and a Microflex (MALDI-ToF) instrument.

Mesogenic behavior and transition temperatures were determined using an Olympus DP12 polarizing optical microscope equipped with a Linkam TMS91 hot stage and a CS196 central processor.

Differential scanning calorimetry (DSC) experiments were performed on DSC TA Instruments Q-20 and Q-2000 systems. Samples were sealed in aluminum pans and a scanning rate of 10 °C•min⁻¹ under a nitrogen atmosphere was used. The systems were calibrated with indium (156.6 °C; 28.4 J•g⁻¹) as the standard. Three thermal cycles were carried out. The mesophase transition temperatures were read at the maximum of the corresponding peaks. Thermogravimetric analysis (TGA) was performed using a TA instruments TGA Q5000 at a rate of 10 °C•min⁻¹ under an argon atmosphere.

The XRD experiments were performed on a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-K α beam. Lindemann glass capillaries with 0.9 mm diameter were used to contain the sample and, where necessary, a variable-temperature attachment was used to heat the sample. The patterns were collected on flat photographic film perpendicular to the X-ray beam. Bragg's law was used to obtain the spacing.

UV-vis absorption spectra were measured with a UV4-200 from ATI-Unicam using 10⁻⁵–10⁻⁶ M solutions in CHCl₃ (HPLC Grade). Fluorescence spectra were measured with a Perkin Elmer LS50B fluorescence spectrometer using solutions in CHCl₃ of ca. 0.01

absorbance (about 10^{-8} – 10^{-9} M) under excitation at the absorption maximum. Films were prepared by casting of a solution of ~ 1 mg/mL in CHCl_3 onto a quartz plate.

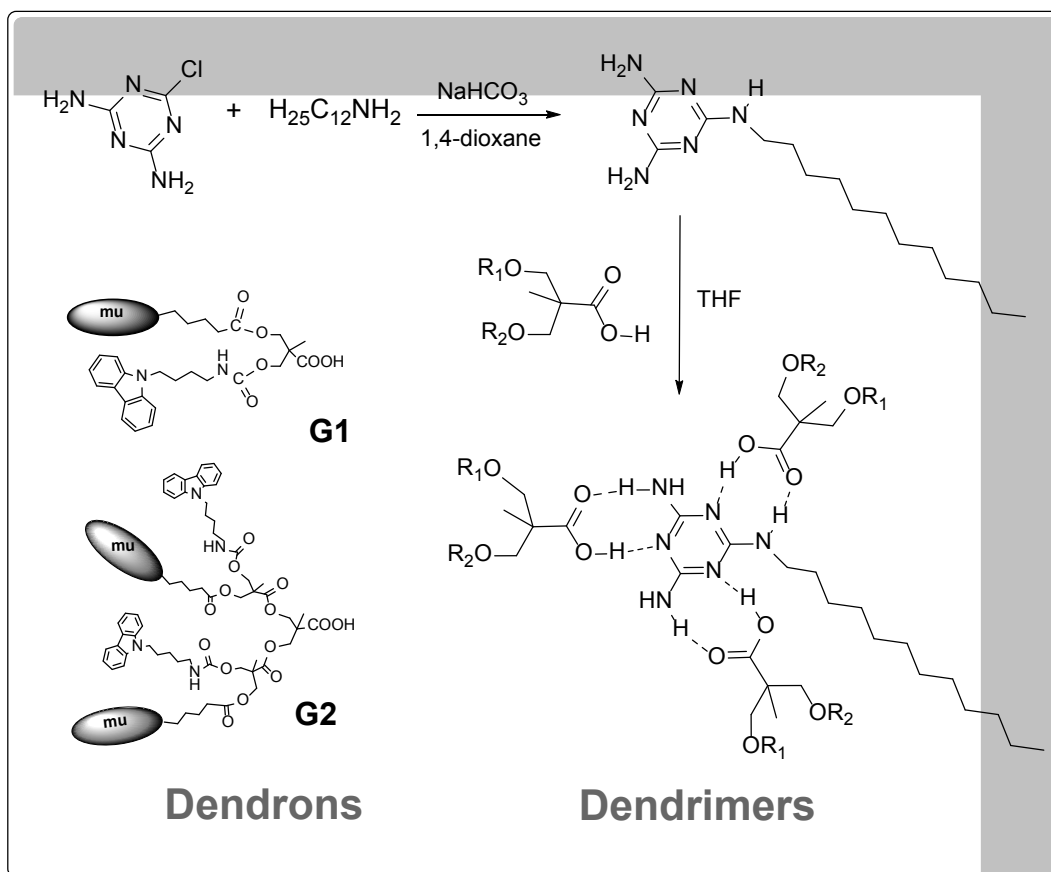
Cyclic voltammetry measurements were performed with a μ -Autolab ECO-Chemiepotentiostat, using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH_2Cl_2 , with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}); the scan rate was 100 mV s^{-1} .

Photoconductivity experiments were performed with light obtained from a Xe-Lamp/Monochromator system, with the light intensity changed using a set of neutral density filters with different transmittance values. The photocurrent was obtained from the difference between the steady state dark and light currents, measured using an electrometer (6517A from Keithley), which was also used to apply the electric field.

Cells for photoconductivity measurements were prepared in a clean-room by overlapping two glass slides covered with indium-tin oxide (ITO) electrodes, with the thickness controlled using $1.5 \mu\text{m}$ glass spacers. Interferometry was used to measure the actual cell thickness and values between 3 mm and 5 mm were obtained. The cells were then filled by capillary action by heating the material above the melting temperature and waiting until cells were completely filled. Samples were then cooled to room temperature.

Synthetic procedures and chemical compound information

1. Synthesis and characterization of the compounds



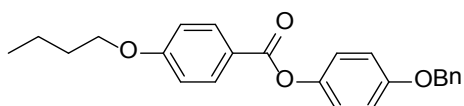
Scheme S1. Synthetic route to melamine and the complexes

1.1 Synthesis and characterization of dendrimer core: 2,4-diamino-6-dodecylamino-1,3,5-triazine (*M*)

The synthesis of this compound was described in: J. Barberá, L. Puig, P. Romero, J. L. Serrano, T. Sierra, *J. Am. Chem. Soc.*, **2006**, *128*, 4487.

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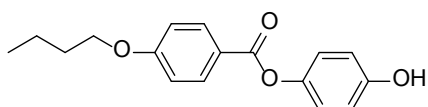
4-(benzyloxy)phenyl 4-butoxybenzoate



Dicyclohexylcarbodiimide (DCC) (61.8 mmol) was added dropwise to a cooled (0 °C) mixture of 4-butoxybenzoic acid (51.5 mmol), 4-benzyloxyphenol (56.7 mmol) and dimethylaminopyridine (DMAP) (6.5 mmol) in dry dichloromethane (200 mL) under argon. The mixture was stirred for 24 h. The crude product was purified by flash chromatography on silica gel, eluting with a hexane/ethyl acetate 8:2 mixture. Yield: 65%.

¹H NMR (400 MHz, CDCl₃, δ): 8.14-8.12 (m, AA'BB', 2H), 7.46-7.34 (m, 5H), 7.13-7.11 (m, AA'BB', 2H), 7.02-7.00 (m, AA'BB', 2H), 6.98-6.95 (m, AA'BB', 2H), 5.08 (s, 2H), 4.05 (t, J = 6.5 Hz, 2H), 1.85-1.78 (m, 2H), 1.56-1.49 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 164.95, 163.12, 156.06, 144.39, 136.54, 131.88, 128.27, 127.67, 127.15, 122.23, 121.28, 115.14, 113.91, 70.10, 67.65, 30.80, 18.86, 13.50. IR (KBr) (cm⁻¹): 2922 (C-H), 1728 (C=O), 1267 (C-O), 1073.

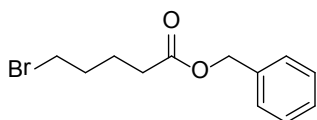
4-hydroxyphenyl 4-butoxybenzoate



A mixture of 4-(benzyloxy)phenyl 4-butoxybenzoate (13.3 mmol), THF (35 mL) and cyclohexene (90 mL) was heated under reflux and a teaspoon of Pd(OH)₂/C was added. The mixture was stirred for 2 h and then filtered through Celite[®]. The filtrate was evaporated to give pure 4-hydroxyphenyl 4-butoxybenzoate. Yield 90%.

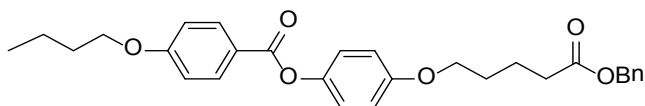
$^1\text{H NMR}$ (400 MHz, CDCl_3, δ): 8.14-8.12 (m, AA'BB', 2H), 7.04-7.02 (m, AA'BB', 2H), 6.98-6.95 (m, AA'BB', 2H), 6.82-6.80 (m, AA'BB', 2H), 5.23 (s, 1H), 4.05 (t, $J = 6.5$ Hz, 2H), 1.87-1.74 (m, 2H), 1.59-1.46 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3, δ): 165.31, 163.20, 152.99, 144.10, 131.93, 122.32, 121.16, 115.74, 113.94, 67.68, 30.80, 18.87, 13.50. **IR** (KBr) (cm^{-1}): 3454 (O-H), 3257 (O-H), 1720 (C=O), 1282, 1171 (C-O)

benzyl 5-bromopentanoate



5-Bromopentanoic acid (72.97 mmol), benzyl alcohol (66.34 mmol) and *N,N*-dimethyl-4-aminopyridine (DMAP) (10.04 mmol) were dissolved in dry CH_2Cl_2 (200 mL). A solution of *N,N'*-dicyclohexylcarbodiimide (DCC) (79.66 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise and the mixture was stirred at room temperature for 24 h. The white precipitate (*N,N'*-dicyclohexylurea) was filtered off from the solution. The solvent was evaporated and the resulting product was purified by column chromatography (silica gel, hexane 9: ethyl acetate 1) to give a colorless oil. Yield 84%. $^1\text{H NMR}$ (400 MHz, CDCl_3, δ): 7.40-7.31 (m, 5H), 5.13 (s, 2H), 3.40 (t, $J = 6.5$ Hz, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 1.94-1.86 (m, 2H), 1.85-1.77 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3, δ): 172.85, 135.86, 128.52, 128.21, 128.17, 66.23, 33.23, 32.94, 31.90, 23.44. **IR** (NaCl) (cm^{-1}): 2958 (C-H), 1738 (C=O), 1455, 1168.

4-[(5-(benzyloxy)-5-oxopentyl)oxy]phenyl 4-butoxybenzoate.

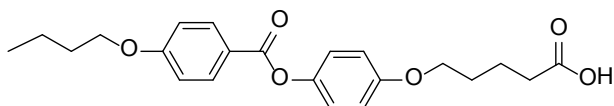


A mixture of 4-hydroxyphenyl 4-butoxybenzoate (11.7 mmol), anhydrous K_2CO_3 (70.4 mmol) and a teaspoon of KI in ethyl methyl ketone (150 mL) was stirred and heated under reflux. Benzyl 5-bromopentanoate (11.73 mmol) was added to the resulting solution and the mixture was stirred and heated under reflux for 72 h. The mixture was allowed to cool to room temperature and the solvent was evaporated. The residue was

dissolved in dichloromethane and washed with water and brine. The organic phase was dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2 and gradually increasing to CH_2Cl_2 /ethyl acetate to give a white powder. Yield 60%.

^1H NMR (400 MHz, CDCl_3 , δ): 8.14-8.12 (m, AA'BB', 2H), 7.40-7.31 (m, 5H), 7.11-7.08 (m, AA'BB', 2H), 6.98-6.95 (m, AA'BB', 2H), 6.91-6.89 (m, AA'BB', 2H), 5.13 (s, 2H), 4.05 (t, $J = 6.5$ Hz, 2H), 3.97 (t, $J = 5.8$ Hz, 2H), 2.46 (t, $J = 7.1$ Hz, 2H), 1.87-1.78 (m, 6H), 1.60-1.47 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H). **^{13}C NMR** (100 MHz, CDCl_3 , δ): 173.21, 165.28, 163.41, 156.51, 144.46, 135.98, 132.17, 128.54, 128.19, 122.48, 121.62, 115.01, 114.21, 67.95, 67.71, 66.19, 33.89, 31.11, 28.64, 21.62, 19.17, 13.81. **IR** (Nujol, NaCl) (cm^{-1}): 2922 (C-H), 1724 (C=O), 1251, 1165 (C-O).

5-[4-(4-butoxybenzoyloxy)phenoxy]pentanoic acid

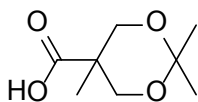


A teaspoon of $\text{Pd}(\text{OH})_2/\text{C}$ (20%) was added to a solution of 8.4 mmol of 4-(5-benzyloxy-5-oxopentyloxy)phenyl 4-butoxybenzoate in THF (64 mL) and cyclohexene (165 mL) under reflux. The reaction mixture was stirred and heated under reflux for 3 h. The catalyst was filtered off on a glass sinter through Celite[®] and carefully washed with THF. The filtrate was evaporated to give *5-[4-(4-butoxybenzoyloxy)phenoxy]pentanoic acid*. Yield 94%.

^1H NMR (400 MHz, CDCl_3 , δ): 8.14-8.11 (m, AA'BB', 2H), 7.11-7.09 (m, AA'BB', 2H), 6.97-6.95 (m, AA'BB', 2H), 6.92-6.90 (m, AA'BB', 2H), 4.05 (t, $J = 6.5$ Hz, 2H), 3.99 (t, $J = 5.8$ Hz, 2H), 2.46 (t, $J = 7.0$ Hz, 2H), 1.87-1.77 (m, 6H), 1.56-1.47 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H). **^{13}C NMR** (100 MHz, CDCl_3 , δ): 178.56, 165.32, 163.43, 156.49, 144.50, 132.19, 122.50, 121.62, 115.04, 114.23, 67.97, 67.71, 33.43, 31.13, 28.56, 21.39, 19.19, 13.82. **IR** (Nujol, NaCl) (cm^{-1}): 2960 (O-H), 1726 (C=O), 1692 (C=O), 1254, 1085 (C-O).

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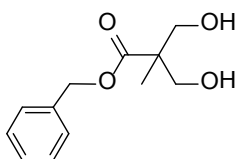
2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid



2,2-Di(hydroxymethyl)propionic acid (bis-MPA) (219.9 mmol), 2,2-dimethoxypropane (329.9 mmol) and p-toluenesulfonic acid monohydrate (11.9 mmol) were dissolved in acetone (150 mL). The reaction mixture was stirred for 5 h at room temperature. The catalyst was neutralized by adding approximately 4 mL of NH₃/EtOH (1:1) solution and the solvent was evaporated at room temperature. The residue was dissolved in CH₂Cl₂ (500 mL) and extracted with two portions of water (200 mL). The organic phase was dried over MgSO₄ and evaporated to give white crystals. Yield 70%.

¹H NMR (400 MHz, CDCl₃, δ): 4.19 (d, J = 12.0 Hz, 2H), 3.64 (d, J = 12.0 Hz, 2H), 1.43 (s, 3H), 1.39 (s, 3H), 1.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 180.01, 98.32, 65.86, 41.70, 25.31, 21.82, 18.38. IR (Nujol, NaCl) (cm⁻¹): 3300 (broad) (COO-H), 2854, 1722 (C=O). Pm (C₈H₁₄O₄): 174.19 g/mol.

benzyl 2,2'-bis(hydroxymethyl)propanoate



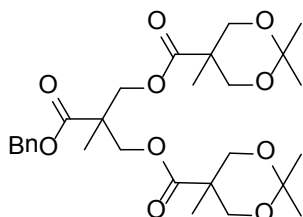
Bis-MPA (186.4 mmol) and KOH (195.3 mmol) were dissolved in DMF (140 mL). The potassium salt was allowed to form at 100 °C for 1 h and benzyl bromide (224 mmol) was added. After 24 h of stirring at 100 °C, the DMF was evaporated off. The residue was dissolved in CH₂Cl₂ (300 mL) and extracted with water (3 × 150 mL). The crude product was recrystallized from toluene. Yield 60%.

¹H NMR (400 MHz, CDCl₃, δ): 7.38-7.31 (m, 5H), 5.20 (s, 2H), 3.90 (d, J = 11.4 Hz, 2H), 3.73 (d, J = 11.4 Hz, 2H), 1.09 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 175.91,

135.65, 128.65, 128.33, 127.87, 68.41, 66.71, 49.24, 17.12. **IR** (Nujol, NaCl) (cm^{-1}): 3364 (broad) (O-H), 1705 (C=O), 1606, 1546, 1230.

DENDRON G2:

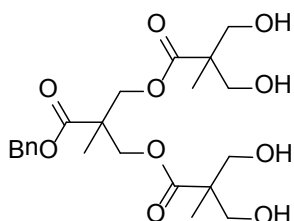
$[G\#2]-\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$



2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (12 mmol), benzyl-2,2-bis(hydroxymethyl)propionate (5 mmol) and DPTS (4.8 mmol) were mixed in CH_2Cl_2 (20 mL). The reaction flask was flushed with argon at $0\text{ }^\circ\text{C}$ and DCC (13 mmol) was added dropwise. Stirring was continued for 2 h at $0\text{ }^\circ\text{C}$ and for 24 h at room temperature under argon. Once the reaction was complete, the DCU was filtered off on a glass sinter and washed with a small volume of CH_2Cl_2 . The crude product was purified by column chromatography on silica gel, eluting with 1:1 ethyl acetate/hexane to give a colorless viscous oil. Yield 65%.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , δ) 7.55-7.29 (m, 5H), 5.16 (s, 2H), 4.51-4.27 (m, 4H), 4.10 (d, $J = 11.9\text{ Hz}$, 4H), 3.58 (d, $J = 11.6\text{ Hz}$, 4H), 1.41 (s, 6H), 1.34 (s, 6H), 1.30 (s, 3H), 1.09 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , δ) 173.51, 172.39, 135.43, 128.60, 128.40, 128.20, 98.07, 66.94, 65.93, 65.88, 65.32, 46.80, 41.99, 31.28, 24.98, 22.20, 18.43, 17.70. **IR** (NaCl) (cm^{-1}): 2855, 1711 (C=O).

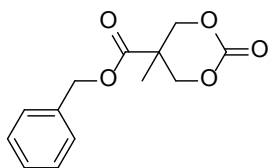
$(\text{OH})_4-[G\#2]-\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$.



[G#2]-CO₂CH₂C₆H₅ (19 mmol) was dissolved in methanol (150 mL). One teaspoon of a Dowex 50-X2 H⁺ resin was added and the reaction mixture was stirred for 5 h at room temperature. When the reaction was complete the Dowex H⁺ resin was filtered off on a glass sinter and carefully washed with methanol. The methanol was evaporated to give white crystals. Yield 90%.

¹H NMR (400 MHz, CDCl₃, δ) 7.40-7.32 (m, 5H), 5.18 (s, 2H), 4.45 (d, *J* = 11.1 Hz, 2H), 4.29 (d, *J* = 11.1 Hz, 2H), 3.81-3.78 (m, 4H), 3.69-3.63 (m, 4H), 3.14 (s, 2H), 1.69 (s, 2H), 1.32 (s, 3H), 0.97 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 175.11, 172.78, 128.67, 128.56, 128.36, 68.18, 68.15, 67.12, 64.81, 49.58, 46.42, 18.10, 17.01. IR (NaCl) (cm⁻¹): 3365 (broad) (O-H), 1705 (C=O), 1606, 1546, 1230.

benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate

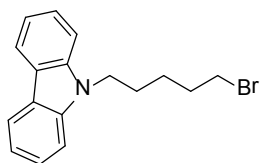


Triethylamine (173.4 mol) was added dropwise over a period of 30 min to a mixture of benzyl 2,2-bis(hydroxymethyl)propionate (33.4 mol) and ethyl chloroformate (164.2 mmol) in tetrahydrofuran (THF) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure. The residue was recrystallized from THF/ether (1:1) to give white crystals. Yield 80%.

¹H NMR (400 MHz, CDCl₃, δ): 7.41-7.32 (m, 5H), 5.22 (s, 2H), 4.71 (d, *J* = 10.8 Hz, 2H), 4.20 (d, *J* = 10.8 Hz, 2H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 170.88, 134.72, 128.76, 128.21, 72.92, 67.91, 40.21, 17.58. IR (Nujol, NaCl) (cm⁻¹): 1735 (C=O), 1230, 1172.

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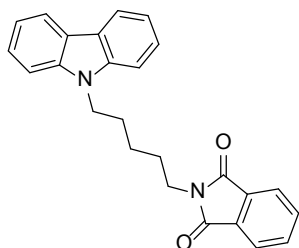
9-(5-bromopentyl)-9H-carbazole.



A mixture of 1,5-dibromopentane (18 mmol), tetrabutylammonium iodide (0.2 mmol), carbazole (6 mmol), 50% aqueous sodium hydroxide (50 mL) and toluene (50 mL) was stirred for 2 d. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 100 mL). The combined organic layers were washed with water (3 x 100 mL) and with sat aqueous NaCl (100 mL), dried over Mg₂SO₄ and evaporated. The crude product was purified by column chromatography on silica gel, eluting with 40:1 hexane:ethyl acetate. Yield 58%.

¹H NMR (400 MHz, CDCl₃, δ): 8.12-8.10 (m, 2H), 7.50-7.45 (m, 2H), 7.41 (d, *J* = 8.2 Hz), 7.26-7.22 (m, 2H), 4.33 (t, *J* = 7.2 Hz, 2H), 3.36 (t, *J* = 6.7 Hz, 2H), 1.95-1.85 (m, 4H), 1.58-1.50 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 140.34, 125.68, 122.87, 120.43, 118.57, 42.85, 33.38, 32.50, 28.23, 25.95. IR (Nujol, NaCl) (cm⁻¹): 2924 (C-H), 1692, 1458, 1325 (C-N). MS (MALDI-TOF) calcd for C₁₇H₁₈BrN (*m/z*) 316.2, found 316.2 [M+H]⁺

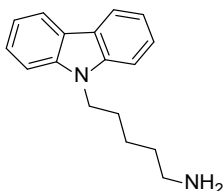
2-[5-(9H-carbazol-9-yl)pentyl]isoindoline-1,3-dione



Potassium phthalimide (5.2 mmol) was added to a mixture of (5-bromopentyl)-9H-carbazole (3.5 mmol) in DMF and the reaction mixture was stirred at 80 °C for 6 h. After the reaction was complete, sat. aqueous NH₄Cl and ethyl acetate were added. The organic layer was separated and was extracted with water (2 x 50 mL) and with sat. aqueous NaCl (2 x 50 mL), dried over Mg₂SO₄ and evaporated. The crude product was purified by column chromatography on silica gel, eluting with 7:1 hexane/ethyl acetate. Yield 85%.

¹H NMR (400 MHz, DMSO, δ): 8.13-8.11 (m, 2H), 7.87-7.82 (m, 4H), 7.58 (d, $J = 8.2$ Hz), 7.43-7.39 (m, 2H), 7.18-7.14 (m, 2H), 4.35 (t, $J = 7.2$ Hz, 2H), 3.53 (t, $J = 7.0$ Hz, 2H), 1.82-1.74 (m, 2H), 1.67-1.59 (m, 2H), 1.38-1.30 (m, 2H). **¹³C NMR** (100 MHz, DMSO, δ): 168.43, 155.19, 133.93, 132.11, 125.65, 123.25, 122.82, 120.36, 118.78, 108.60, 105.10, 100.01, 42.79, 37.69, 28.47, 28.36, 24.55. **IR** (KBr) (cm^{-1}): 2924 (C-H), 1707 (C=O), 1457, 1374 (C-N). **MS (MALDI-TOF)** calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$ (m/z) 382.5, found 383.3 $[\text{M}+\text{H}]^+$

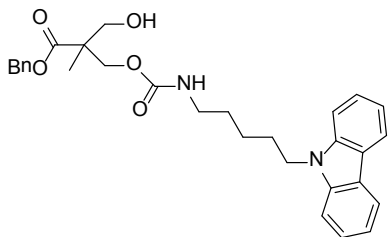
5-(9H-carbazol-9-yl)pentan-1-amine



Hydrazine monohydrate (6.5 mmol) was added to a mixture of 2-[5-(9H-carbazol-9-yl)pentyl]isoindoline-1,3-dione (2.6 mmol) in EtOH (50 mL) and the reaction mixture was stirred and heated under reflux for 2 h. The reaction mixture was allowed to cool down and the precipitate was filtered off. The filtrate was concentrated under reduced pressure. The crude product was redissolved in CHCl_3 and the solid residue was filtered off. The filtrate was reconcentrated under reduced pressure without purification. Yield 84%.

¹H NMR (400 MHz, CDCl_3 , δ): 8.12-8.10 (m, 2H), 7.49-7.45 (m, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.25-7.21 (m, 2H), 4.31 (t, $J = 7.2$ Hz, 2H), 2.65 (t, $J = 6.8$ Hz, 2H), 1.94-1.87 (m, 2H), 1.52-1.38 (m, 4H). **¹³C NMR** (100 MHz, CDCl_3 , δ): 140.36, 125.64, 125.57, 122.79, 120.34, 118.72, 108.58, 42.96, 41.97, 33.47, 28.87, 24.59. **IR** (NaCl) (cm^{-1}): 3358 (NH_2), 3280 (NH_2), 2926 (C-H), 1624 (NH_2), 1452, 1325 (C-N). **MS (MALDI-TOF)** calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2$ (m/z) 252.5, found 252.3 $[\text{M}+\text{H}]^+$

MONOFUNCTIONAL DENDRON:



In an oven-dried 50 mL vial containing a stirrer bar, 5-methyl-5-benzoyloxycarbonyl-1,3-dioxan-2-one (2.7 mmol) was dissolved in dry pyridine (5 mL). The solution was diluted with dry THF (5 mL), which caused the solution to become cloudy. 9-(5-Aminopentyl)-9H-carbazole (3.3 mmol) was added and the mixture became clear within a few min. The solution was stirred overnight under argon and then diluted with ethyl acetate. The organic solution was washed twice with 1 M aqueous NaHSO₄ solution and once with sat. aqueous NaCl. The ethyl acetate solution was dried over MgSO₄, filtered and concentrated *in vacuo* to give a colorless residue. The crude product was purified by column chromatography on silica gel, eluting with 1:1 hexane/ethyl acetate. Yield 45%. ¹H NMR (400 MHz, CDCl₃, δ): 8.11-8.09 (m, 2H), 7.49-7.45 (m, 2H), 7.41-7.38 (m, 2H), 7.36-7.29 (m, 5H), 7.25-7.21 (m, 2H), 5.16 (s, 2H), 4.60 (t, *J* = 5.5 Hz, 1H), 4.33-4.30 (m, 2H), 4.22-4.19 (m, 2H), 3.70-3.59 (m, 2H), 3.12-3.03 (m, 2H), 1.94-1.87 (m, 2H), 1.53-1.45 (m, 2H), 1.41-1.35 (m, 2H), 1.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 174.37, 156.88, 140.38, 135.80, 128.59, 128.28, 127.96, 125.70, 122.85, 120.42, 118.86, 108.64, 66.55, 65.84, 64.26, 48.81, 42.85, 40.88, 29.73, 28.66, 24.41, 17.58. IR (Nujol, NaCl) (cm⁻¹): 3406 (O-H), 2938 (C-H), 1728 (C=O), 1454, 1238 (C-N). MS (MALDI-TOF) calcd for C₃₀H₃₄N₂O₅ (*m/z*) 502.6, found 502.3 [M+H]⁺.

1.2. Synthesis and characterization data of the bifunctional dendrons

General experimental esterification procedure for the monofunctional dendrons:

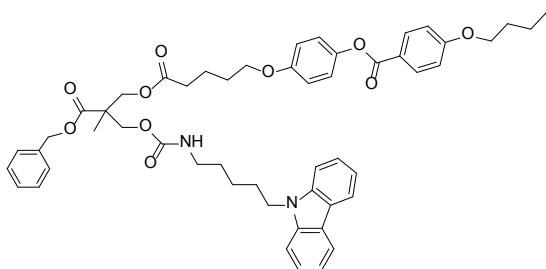
The promesogenic carboxylic acid (2 mmol), the monofunctional dendron (1.8 mmol) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (0.9 mmol) were dissolved in dichloromethane (40 mL). The reaction flask was flushed with argon and *N,N*-dicyclohexylcarbodiimide (DCC) (2.3 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for 24 h under an argon atmosphere. The white

precipitate (N,N-dicyclohexylurea) was filtered off and the solvent was evaporated. The crude product was purified by column chromatography on silica gel and eluted with dichloromethane, gradually increasing to ethyl acetate/dichloromethane depending on the case.

General experimental procedure for removal of the benzyl ester group:

A teaspoon of Pd(OH)₂/C (20%) was added to a solution of bifunctional Dendron with the benzyl ester group (1.04 mmol) in a mixture of THF (8 mL) and cyclohexene (20 mL) under reflux. The reaction mixture was stirred and heated under reflux for 5 h. The catalyst was filtered off on a glass sinter through Celite[®] and carefully washed with THF. The filtrate was evaporated to give the bifunctional dendron as the carboxylic acid. In some cases it was necessary to purify the product by column chromatography on silica gel, eluting with dichloromethane, gradually increasing to ethyl acetate.

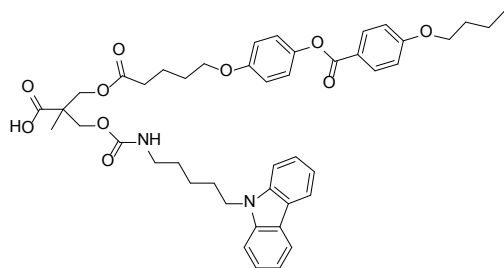
Dendron Bz-CzA1 (G = 1)



Yield 68%.

¹H NMR (400 MHz, CDCl₃, δ): 8.18-8.15 (m, AA'BB', 2H), 8.14-8.12 (m, 2H), 7.54-7.46 (m, 2H), 7.43-7.41 (m, 2H), 7.37-7.32 (m, 5H), 7.28-7.24 (m, 2H), 7.14-7.12 (m, AA'BB', 2H), 7.00-6.98 (m, AA'BB', 2H), 6.93-6.91 (m, AA'BB', 2H), 5.20 (s, 2H), 4.75 (t, *J* = 5.8 Hz, 1H), 4.32-4.28 (m, 6H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.93-3.92 (m, 2H), 3.12-3.07 (m, 2H), 2.38-2.35 (m, 2H), 1.91-1.80 (m, 8H), 1.60-1.45 (m, 4H), 1.43-1.34 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃, δ): 172.94, 172.82, 165.31, 163.47, 156.55, 155.83, 144.51, 140.36, 132.23, 128.79, 128.56, 128.30, 128.10, 126.05, 125.67, 122.82, 122.55, 121.65, 120.39, 118.83, 115.04, 114.27, 108.63, 106.61, 68.01, 67.71, 66.73, 65.51, 65.01, 46.66, 42.86, 40.83, 40.14, 33.69, 31.17, 29.75, 28.65, 24.43, 21.54, 19.24, 17.61, 13.82. **IR** (NaCl) (cm⁻¹): 3404 (N-H), 2938 (C-H), 1732 (C=O), 1250 (C-N). **MS (MALDI-TOF)** calcd for C₅₂H₅₈N₂O₁₀ (*m/z*) 871.0, found 871.0 [M+H]⁺, 894.1 [M+Na]⁺

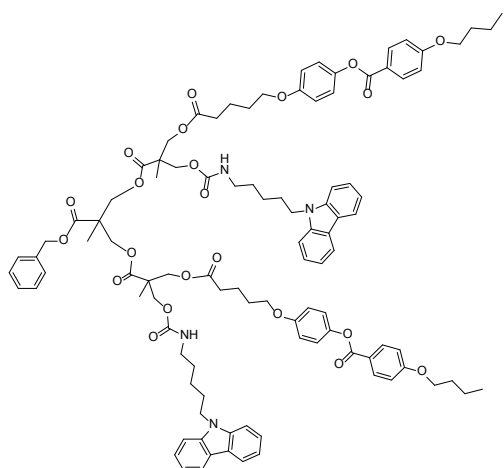
Dendron CzA1 (G = 1)



Yield 86%.

¹H NMR (400 MHz, CDCl₃, δ): 8.13-8.11 (m, AA'BB', 2H), 8.10-8.08 (m, 2H), 7.51-7.42 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 2H), 7.09-7.06 (m, AA'BB', 2H), 6.96-6.94 (m, AA'BB', 2H), 6.89-6.87 (m, AA'BB', 2H), 5.95-4.81 (broad band, 1H), 4.71 (t, *J* = 5.8 Hz, 1H), 4.28 (t, *J* = 7.1 Hz, 2H), 4.22 (d, *J* = 4.7 Hz, 4H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.94-3.92 (m, 2H), 3.09-3.04 (m, 2H), 2.41-2.39 (m, 2H), 1.92-1.81 (m, 4H), 1.80-1.77 (m, 4H), 1.59-1.45 (m, 4H), 1.36-1.34 (m, 2H), 1.25 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃, δ): 177.49, 172.95, 165.39, 163.44, 156.46, 155.85, 144.43, 140.29, 132.19, 125.61, 122.75, 122.50, 121.53, 120.32, 118.76, 115.03, 114.21, 108.58, 67.95, 67.68, 65.71, 65.21, 64.90, 46.28, 42.77, 40.80, 33.68, 31.10, 28.56, 28.52, 24.33, 21.53, 19.17, 17.61, 13.81. **IR** (Nujol, NaCl) (cm⁻¹): 3395 (N-H), 2937 (C-H), 2840 (O-H), 1729 (C=O), 1682 (C=O), 1250 (C-N). **MS (MALDI-TOF)** calcd for C₄₅H₅₂N₂O₁₀ (*m/z*) 780.5, found 803.5 [M+Na]⁺, 825.5 [M+2Na-H]⁺. **Anal.** Calcd for C₄₅H₅₂N₂O₁₀: C, 69.71; H, 7.65; N, 3.22. Found: C, 69.02; H, 7.51; N, 3.40.

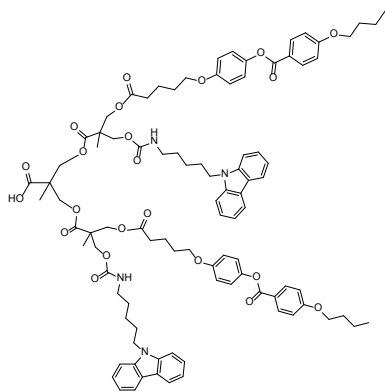
Dendron Bz-CzA2 (G = 2)



Yield 50%.

¹H NMR (400 MHz, CDCl₃, δ): 8.14-8.09 (m, AA'BB', 4H), 8.08-8.06 (m, 4H), 7.46-7.40 (m, 4H), 7.39-7.36 (m, 4H), 7.34-7.28 (m, 5H), 7.24-7.16 (m, 4H), 7.11-7.03 (m, AA'BB', 4H), 6.96-6.93 (m, AA'BB', 4H), 6.87-6.84 (m, AA'BB', 4H), 5.21 (m, 2H), 5.14 (s, 2H), 4.29-4.24 (m, 8H), 4.15-4.13 (m, 8H), 4.03 (t, *J* = 6.5 Hz, 4H), 3.92-3.86 (m, 4H), 3.09-3.03 (m, 4H), 2.37-2.35 (m, 4H), 1.94-1.68 (m, 16H), 1.58-1.33 (m, 12H), 1.28 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 6H), 0.99 (t, *J* = 7.4 Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃, δ): 172.93, 172.81, 165.31, 163.47, 156.55, 155.83, 144.51, 140.36, 132.23, 128.79, 128.56, 128.30, 128.10, 126.05, 125.67, 122.82, 122.55, 121.65, 120.39, 118.83, 115.04, 114.27, 108.63, 106.61, 68.01, 67.71, 66.73, 65.99, 65.51, 65.01, 46.66, 42.86, 40.83, 40.14, 33.69, 31.17, 29.75, 29.33, 28.65, 24.43, 21.54, 19.24, 17.97, 17.61, 13.82. **IR** (NaCl) (cm⁻¹): 3385 (N-H), 2934 (C-H), 1733 (C=O), 1239 (C-N). **MS (MALDI-TOF)** calcd for C₁₀₂H₁₁₆N₄O₂₂ (*m/z*) 1750.0, found 1772.8 [M+Na]⁺).

Dendron Cza2 (G = 2)

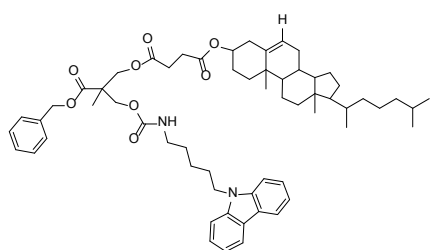


Yield 90%.

¹H NMR (300 MHz, CDCl₃, δ): 8.16-8.09 (m, AA'BB', 4H), 8.09-8.05 (m, 4H), 7.47-7.41 (m, 4H), 7.39-7.36 (m, 4H), 7.23-7.17 (m, 4H), 7.09-7.03 (m, AA'BB', 4H), 6.99-6.91 (m, AA'BB', 4H), 6.88-6.85 (m, AA'BB', 4H), 5.22 (t, *J* = 5.1 Hz, 2H), 4.35-4.05 (broad band, 1H), 4.27 (t, *J* = 7.2 Hz, 4H), 4.23-4.09 (m, 12H), 4.03 (t, *J* = 6.5 Hz, 4H), 3.92-3.90 (m, 4H), 3.10-3.04 (m, 4H), 2.38-2.36 (m, 4H), 1.94-1.72 (m, 16H), 1.60-1.32 (m, 12H), 1.23 (d, *J* = 3.2 Hz, 3H), 1.20 (s, 6H), 0.99 (t, *J* = 7.4 Hz, 6H). **¹³C NMR** (75

MHz, CDCl₃, δ): 176.00, 172.90, 165.40, 163.48, 156.49, 156.00, 144.43, 140.31, 132.21, 125.61, 122.78, 122.51, 120.31, 118.73, 115.05, 114.24, 108.61, 67.93, 67.65, 65.99, 65.76, 65.60, 65.26, 65.08, 46.84, 46.79, 46.17, 42.81, 40.83, 33.64, 31.11, 29.58, 29.33, 28.57, 24.36, 21.51, 19.18, 17.97, 17.60, 13.80. **IR** (NaCl) (cm⁻¹): 3389 (N-H), 2936 (C-H), 2930 (O-H), 1731 (C=O), 1703 (C=O), 1249 (C-N). **MS (MALDI+)** calcd for C₉₅H₁₁₀N₄O₂₂ (*m/z*) 1659.9, found 1682.8 [M+Na]⁺. **Anal.** Calcd for C₉₅H₁₁₀N₄O₂₂: C, 68.74; H, 6.68; N, 3.38. Found: C, 68.42; H, 6.81; N, 3.26.

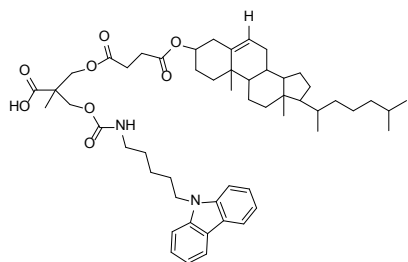
Dendron Bz-CzBI (G = 1)



Yield 70%.

¹H NMR (400 MHz, CDCl₃, δ): 8.11-8.09 (m, 2H), 7.49-7.45 (m, 2H), 7.41-7.39 (m, 2H), 7.37-7.30 (m, 5H), 7.25-7.21 (m, 2H), 5.36 (d, *J* = 4.2 Hz, 1H), 5.16 (s, 1H), 4.67-4.56 (m, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 4.24 (d, *J* = 16.8 Hz, 4H), 3.10-3.05 (m, 2H), 2.57-2.53 (m, 4H), 2.31 (d, *J* = 7.8 Hz, 2H), 2.02-1.04 (m, 32H), 1.24 (s, 3H), 1.01 (s, 3H), 0.95-0.85 (m, 9H), 0.68 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃, δ): 172.65, 171.81, 171.45, 155.73, 140.27, 139.47, 135.64, 128.47, 128.21, 128.06, 125.58, 122.75, 122.65, 120.31, 118.75, 108.53, 74.35, 66.66, 65.89, 65.67, 56.59, 56.05, 49.92, 46.58, 42.78, 42.23, 40.75, 39.64, 39.47, 37.99, 36.88, 36.50, 36.13, 35.74, 31.82, 31.77, 29.66, 29.25, 28.93, 28.59, 28.18, 27.97, 27.67, 24.36, 24.22, 23.78, 22.80, 22.54, 20.96, 19.25, 18.67, 17.62, 11.80. **IR** (Nujol, NaCl) (cm⁻¹): 3404 (N-H), 2928 (C-H), 1735 (C=O), 1238 (C-N). **MS (MALDI+)** calcd for C₆₁H₈₂N₂O₈ (*m/z*) 971.3, found 971.5 [M+H]⁺, 973.5 [M+Na]⁺.

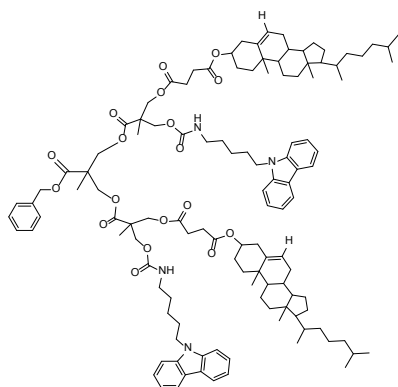
Dendron CzBI (G = 1)



Yield 82%.

¹H NMR (400 MHz, CDCl₃, δ): 8.09 (d, *J* = 7.7 Hz, 2H), 7.46 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.22 (ddd, *J* = 7.9, 7.1, 1.0 Hz, 2H), 6.26-4.51 (broad band, 1H), 5.34 (d, *J* = 4.0 Hz, 1H), 4.77 (t, *J* = 5.7 Hz, 1H), 4.66-4.54 (m, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 4.21 (dd, *J* = 15.4, 12.2 Hz, 4H), 3.09 (dd, *J* = 13.2, 6.7 Hz, 2H), 2.61 (dd, *J* = 13.6, 5.4 Hz, 4H), 2.29 (d, *J* = 7.7 Hz, 2H), 2.00-1.06 (m, 32H), 1.25 (s, 3H), 0.99 (s, 3H), 0.94-0.82 (m, 9H), 0.66 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃, δ): 177.50, 171.90, 171.64, 155.87, 140.29, 139.46, 125.61, 122.75, 122.70, 120.34, 118.76, 108.57, 74.47, 65.76, 65.48, 56.59, 56.06, 49.92, 46.34, 42.79, 42.24, 40.80, 39.64, 39.49, 37.98, 36.88, 36.51, 36.15, 35.76, 31.83, 31.77, 30.31, 29.62, 29.28, 28.99, 28.59, 28.20, 28.00, 27.66, 24.36, 24.24, 23.81, 22.82, 22.55, 20.97, 19.27, 18.69, 17.60, 14.18, 11.82. **IR** (Nujol, NaCl) (cm⁻¹): 3381 (N-H), 2944 (C-H), 2928 (O-H), 1732 (C=O), 1704 (C=O), 1237 (C-N). **MS (MALDI+)** calcd for C₅₄H₇₆N₂O₈ (*m/z*) 881.2, found 903.6 [M+Na]⁺, 925.6 [M+2Na-H]⁺. **Anal.** Calcd for C₅₄H₇₆N₂O₈: C, 72.60; H, 8.69; N, 3.18. Found: C, 72.72; H, 8.60; N, 3.09.

Dendron Bz-CzB2 (G = 2)

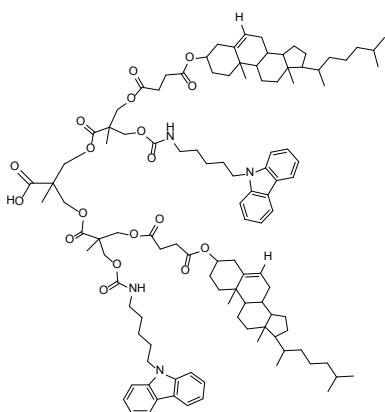


Yield 54%.

¹H NMR (300 MHz, CDCl₃, δ): 8.09-8.07 (m, 4H), 7.52-7.41 (m, 4H), 7.39-7.37 (m, 4H), 7.33-7.30 (m, 5H), 7.23-7.18 (m, 4H), 5.37-5.31 (m, 2H), 5.23-5.20 (m, 2H), 5.14 (s, 2H), 4.68-4.50 (m, 2H), 4.30-4.26 (m, 4H), 4.19-4.03 (m, 8H), 3.12-3.01 (m, 4H),

2.59-2.55 (m, 8H), 2.28 (d, $J = 8.1$ Hz, 4H), 2.11-1.13 (m, 64H), 0.98 (s, 9H), 0.92-0.85 (m, 24 H), 0.66 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 172.90, 172.76, 172.43, 172.38, 171.48, 170.63, 155.88, 140.23, 139.43, 128.71, 128.35, 125.64, 122.73, 120.36, 118.79, 108.64, 74.43, 56.66, 56.13, 49.99, 42.89, 39.74, 39.72, 39.55, 38.07, 36.94, 36.21, 35.82, 31.83, 29.64, 28.65, 28.26, 28.05, 27.74, 25.63, 24.96, 23.87, 22.86, 22.60, 21.04, 19.32, 18.75, 11.88. IR (Nujol, NaCl) (cm^{-1}): 3385 (N-H), 2950 (C-H), 1734 (C=O), 1239 (C-N). MS (MALDI+) calcd for $\text{C}_{120}\text{H}_{164}\text{N}_4\text{O}_{18}$ (m/z) 1950.6, found 1873.2 $[\text{M}+\text{Na}]^+$.

Dendron CzB2 (G = 2)



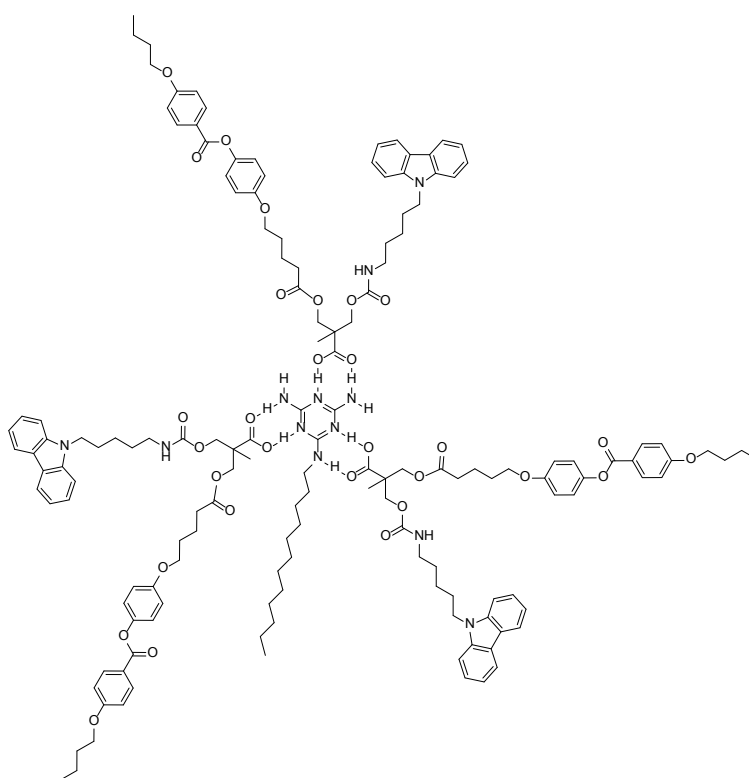
Yield 95%.

^1H NMR (400 MHz, CDCl_3 , δ): 8.09-8.07 (m, 4H), 7.45-7.43 (m, 4H), 7.40-7.37 (m, 4H), 7.23-7.19 (m, 4H), 5.34 (s, 2H), 4.62-4.60 (m, 2H), 4.53-3.79 (broad band, 1H), 4.30-4.26 (m, 4H), 4.23-4.15 (m, 8H), 3.16-3.04 (m, 4H), 2.72-2.51 (m, 8H), 2.30 (d, $J = 8.0$ Hz, 4H), 2.02-1.01 (m, 64H), 1.20 (s, 6H), 0.99 (s, 6H), 0.94-0.83 (m, 21H), 0.66 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 172.92, 172.73, 172.47, 172.34, 172.02, 171.90, 155.91, 140.30, 139.43, 125.64, 122.73, 120.36, 118.79, 108.64, 74.43, 67.95, 66.12, 65.98, 65.71, 65.61, 56.66, 56.13, 49.99, 46.74, 46.67, 46.06, 42.89, 39.74, 39.72, 39.55, 38.07, 36.94, 36.21, 35.82, 31.83, 29.64, 28.65, 28.26, 28.05, 27.74, 25.63, 24.96, 23.87, 22.86, 22.60, 21.04, 19.32, 17.60, 11.88. IR (Nujol, NaCl) (cm^{-1}): 3393 (N-H), 2938 (C-H), 2928 (O-H), 1732 (C=O), 1705 (C=O), 1239 (C-N). MS (MALDI+) calcd for $\text{C}_{113}\text{H}_{158}\text{N}_4\text{O}_{18}$ (m/z) 1860.5, found 1883.2 $[\text{M}+\text{Na}]^+$. Anal. Calcd for $\text{C}_{113}\text{H}_{158}\text{N}_4\text{O}_{18}$: C, 72.95; H, 8.56; N, 3.01. Found: C, 72.72; H, 8.60; N, 3.04.

1.3. General procedure to prepare the hydrogen-bonded dendrimers

Complexes between the melamine **M** and the appropriate carboxylic acid dendron, in a 1:3 ratio, were prepared by mixing CH_2Cl_2 solutions of the two components and slowly removing the solvent under mechanical stirring at room temperature. The samples of the complexes were heated above the clearing temperature and subsequent cooling yielded homogenous materials in all four cases.

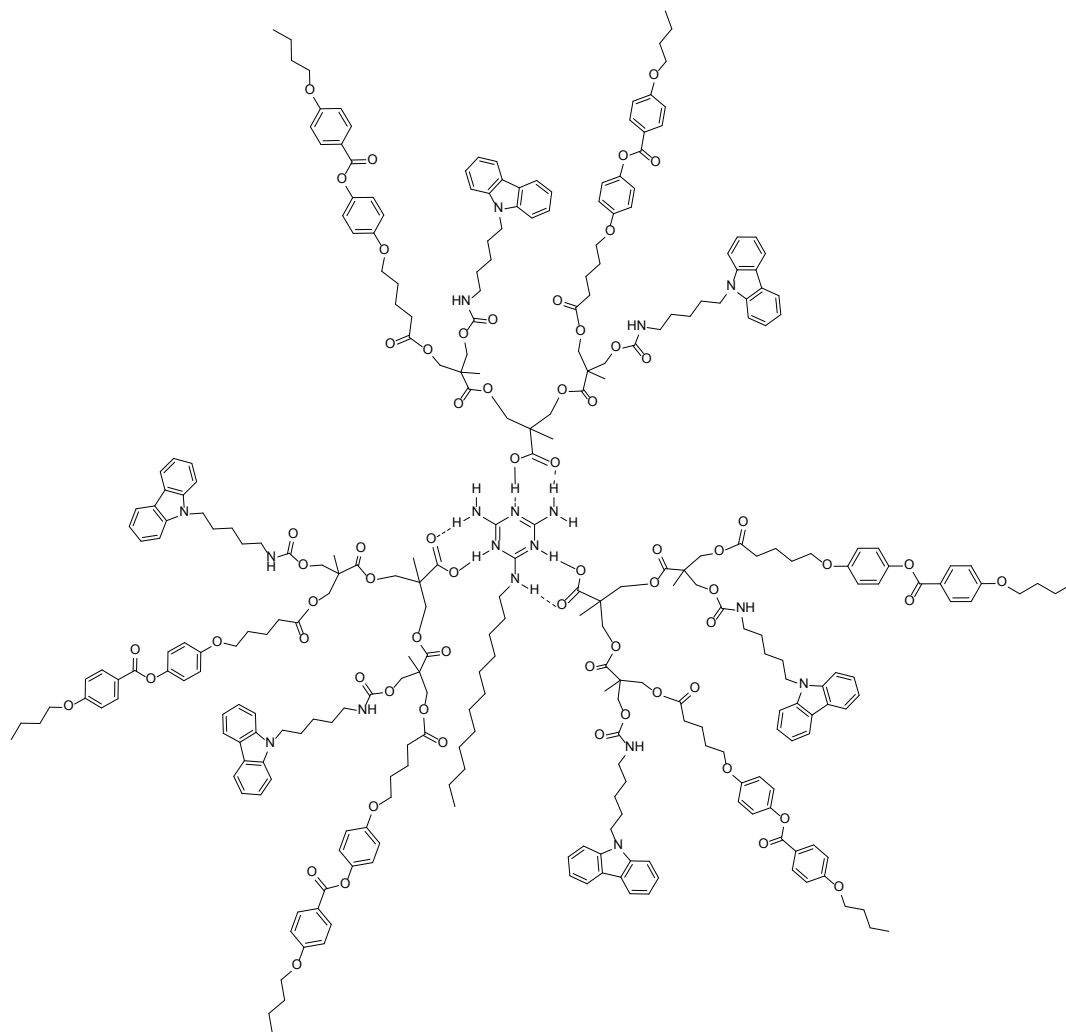
Dendrimer M-CzAI (G = 1)



¹H NMR (500 MHz, CDCl_3 , δ) 8.14-8.10 (m, AA'BB', 6H), 8.10-8.08 (m, 6H), 7.45-7.43 (m, 6H), 7.38 (d, $J = 8.2$ Hz, 6H), 7.24-7.19 (m, 6H), 7.10-7.05 (m, AA'BB', 6H), 6.97-6.93 (m, AA'BB', 6H), 6.89-6.87 (m, AA'BB', 6H), 6.24 (t, $J = 5.5$ Hz, 1H), 6.13 (s, 2H), 4.72 (t, $J = 5.9$ Hz, 3H), 4.28 (t, $J = 7.2$ Hz, 6H), 4.26-4.19 (m, 12H), 4.04 (t, $J = 6.5$ Hz, 6H), 3.94-3.92 (m, 6H), 3.28 (dd, $J = 13.9, 6.4$ Hz, 2H), 3.10-3.06 (m, 6H), 2.42-2.39 (m, 6H), 1.92-1.83 (m, 6H), 1.82-1.78 (m, 12H), 1.56-1.43 (m, 14H), 1.39-1.33 (m, 6H), 1.26 (m, 33H), 0.99 (t, $J = 7.4$ Hz, 9H), 0.87 (t, $J = 7.0$ Hz, 3H). **¹³C NMR** (125 MHz, CDCl_3 , δ) 177.68, 173.20, 165.69, 163.50, 162.6, 156.61, 155.92, 144.31, 140.33, 132.17, 125.70, 122.82, 122.55, 121.59, 120.39, 118.87, 115.15,

114.26, 108.67, 67.97, 67.80, 66.03, 65.52, 64.97, 46.34, 42.83, 40.78, 40.61, 33.88, 31.01, 29.93, 29.36, 28.62, 26.63, 24.11, 21.20, 19.02, 17.79, 14.24, 13.94. **IR** (NaCl) (cm^{-1}): 3379 (N-H), 3050 (N-H), 2930 (C-H), 2871 (O-H), 1736 (C=O), 1679 (C=O), 1251 (C-N).

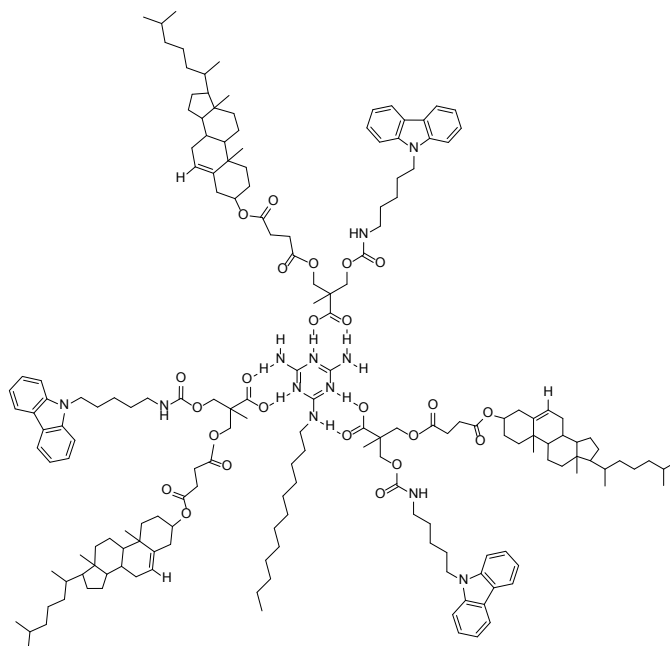
Dendrimer M-CzA2 ($G = 2$)



^1H NMR (500 MHz, CDCl_3 , δ) 8.12-8.10 (m, AA'BB', 12H), 8.08-8.06 (m, 12H), 7.45-7.42 (m, 12H), 7.39-7.37 (m, 12H), 7.21-7.18 (m, 12H), 7.07-7.05 (m, AA'BB', 12H), 6.95-6.94 (m, AA'BB', 12H), 6.87-6.85 (m, AA'BB', 12H), 6.45-6.39 (m, 3H), 5.31 (s, 6H), 4.29-4.25 (m, 12H), 4.24-4.08 (m, 36H), 4.03 (t, $J = 6.5$ Hz, 12H), 3.90 (s, 12H), 3.30 (dd, $J = 13.3, 6.8$ Hz, 2H), 3.13-3.05 (m, 12H), 2.37 (s, 12H), 1.90-1.70 (m, 36H), 1.54-1.48 (m, 26H), 1.38-1.36 (m, 12H), 1.25-1.23 (m, 32H), 1.20 (s, 18H), 0.99 (t, $J = 7.4$ Hz, 18H), 0.87 (t, $J = 6.9$ Hz, 3H). **^{13}C NMR** (125 MHz, CDCl_3 , δ) 176.06, 172.92, 165.39, 163.47, 162.62, 160.96, 156.48, 155.99, 144.47, 140.32, 132.19, 125.59, 122.76, 122.50, 121.56, 120.30, 118.74, 115.02, 114.23, 108.60, 67.96, 67.68,

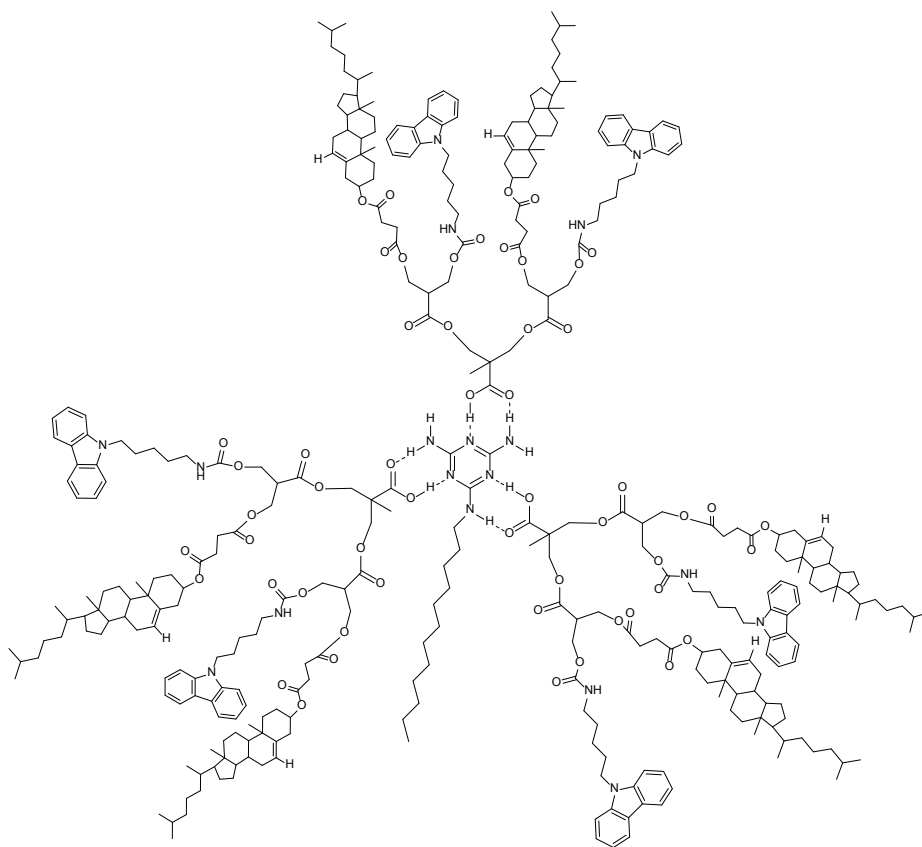
66.00, 65.63, 65.28, 58.41, 46.83, 46.78, 46.27, 42.80, 40.90, 40.82, 33.63, 31.89, 31.11, 29.57, 29.32, 28.56, 26.79, 24.35, 22.66, 21.50, 19.16, 18.35, 17.96, 17.64, 14.09, 13.79. **IR** (NaCl) (cm^{-1}): 3380 (N-H), 3050 (N-H), 2931 (C-H), 2873 (O-H), 1736 (C=O), 1680 (C=O), 1253 (C-N).

Dendrimer M-CzBI (G = 1)



^1H NMR (500 MHz, CDCl_3 , δ) 8.10-8.08 (m, AA'BB', 6H), 7.47-7.44 (m, AA'BB' 6H), 7.40-7.38 (m, AA'BB', 6H), 7.24-7.19 (m, AA'BB', 6H), 6.32-6.29 (t, $J = 5.7$ Hz, 1H), 6.19 (s, 2H), 5.34 (d, $J = 4.8$ Hz, 3H), 4.78 (t, $J = 5.5$ Hz, 3H), 4.66-4.54 (m, 3H), 4.31-4.18 (m, 21H), 3.29 (dd, $J = 14.0, 6.3$ Hz, 2H), 3.11-3.07 (m, 6H), 2.63-2.58 (m, 12H), 2.29 (d, $J = 7.4$ Hz, 6H), 2.03-1.02 (m, 116H), 0.99-0.85 (m, 30H), 0.66 (s, 9H).
 ^{13}C NMR (125 MHz, CDCl_3 , δ) 177.71, 171.96, 171.62, 162.32, 156.03, 140.33, 139.54, 125.62, 122.80, 122.68, 120.35, 118.78, 108.58, 74.45, 67.96, 66.11, 65.81, 56.64, 56.12, 49.98, 46.36, 42.83, 42.28, 40.92, 40.82, 39.70, 39.51, 38.02, 36.92, 36.54, 36.18, 35.78, 31.92, 31.86, 31.81, 29.69, 29.67, 29.64, 29.62, 29.59, 29.36, 29.30, 29.11, 28.61, 28.21, 28.01, 27.70, 26.82, 25.60, 24.41, 24.26, 23.84, 22.81, 22.69, 22.56, 21.00, 19.28, 18.71, 17.81, 14.12, 11.84. **IR** (NaCl) (cm^{-1}): 3396 (N-H), 3053 (N-H), 2931 (C-H), 2867 (O-H), 1736 (C=O), 1686 (C=O), 1249 (C-N).

Dendrimer M-CzB2 (G = 2)



¹H NMR (500 MHz, CDCl₃, δ) 8.09-8.07 (m, 12H), 7.45-7.43 (m, 12H), 7.40-7.38 (m, 12H), 7.22-7.19 (m, 12H), 6.18-6.16 (m, 3H), 5.36-5.33 (m, 6H), 4.63-4.57 (m, 6H), 4.44-4.02 (m, 36H), 3.29 (dd, *J* = 13.6, 6.6 Hz, 2H), 3.08-3.06 (m, 12H), 2.59 (dd, *J* = 23.0, 9.6 Hz, 24H), 2.29 (d, *J* = 8.0 Hz, 12H), 2.04-1.03 (m, 230H), 0.98 (s, 18H), 0.92-0.86 (m, 63H), 0.66 (s, 18H). **¹³C NMR** (125 MHz, CDCl₃, δ) 172.93, 172.74, 172.48, 172.35, 172.03, 171.91, 162.95, 155.90, 140.31, 139.45, 125.59, 122.76, 120.31, 118.73, 108.61, 74.75, 74.60, 67.95, 66.22, 66.00, 65.83, 65.61, 56.60, 56.08, 49.92, 46.74, 46.67, 46.10, 42.82, 42.25, 40.82, 39.66, 39.49, 37.95, 36.86, 36.50, 36.15, 35.76, 31.90, 31.82, 31.77, 30.92, 29.58, 29.34, 29.29, 29.18, 29.14, 28.78, 28.60, 28.19, 27.99, 27.64, 26.81, 25.58, 24.37, 24.23, 23.81, 22.80, 22.67, 22.54, 20.97, 19.25, 18.68, 17.93, 17.64, 14.11, 11.81. **IR** (NaCl) (cm⁻¹): 3394 (N-H), 3053 (N-H), 2931 (C-H), 2867 (O-H), 1736 (C=O), 1684 (C=O), 1249 (C-N).

Supporting Tables

Table S1. Molecular Weights of Carboxylic Acid Dendrons

Dendron	m/z (calculated)	m/z (found)
CzA1	780.4	780.5[M], 803.5[M+Na ⁺], 825.5[M+2Na-H]

CzA2	1659.8	1682.8[M-Na ⁺]
CzB1	880.6	903.6[M+Na ⁺], 925.6[M+2Na-H]
CzB2	1860.2	1883.2[M-Na ⁺]

Table S2. Main IR data (cm⁻¹) for the Melamine, Dendrons and Dendrimers

Compound	v(N-H)	v(N-H) carbamate	v(COOH)	v(C=O) ^a (H-bond)	v(C=O) (ester)	v(C=O) (acid)
M	3450, 3323, 3189					
CzA1		3395	2840		1729	1682

CzA2	3389	2930	1731	1703
CzB1	3381	2928	1732	1704
CzB2	3393	2928	1732	1705
M-CzA1	3379		1679	1736
M-CzA2	3380		1680	1736
M-CzB1	3396		1686	1736
M-CzB2	3394		1684	1736

^a shoulder

Table S3. Spectroscopic and Photophysical data of Dendrons and Dendrimers

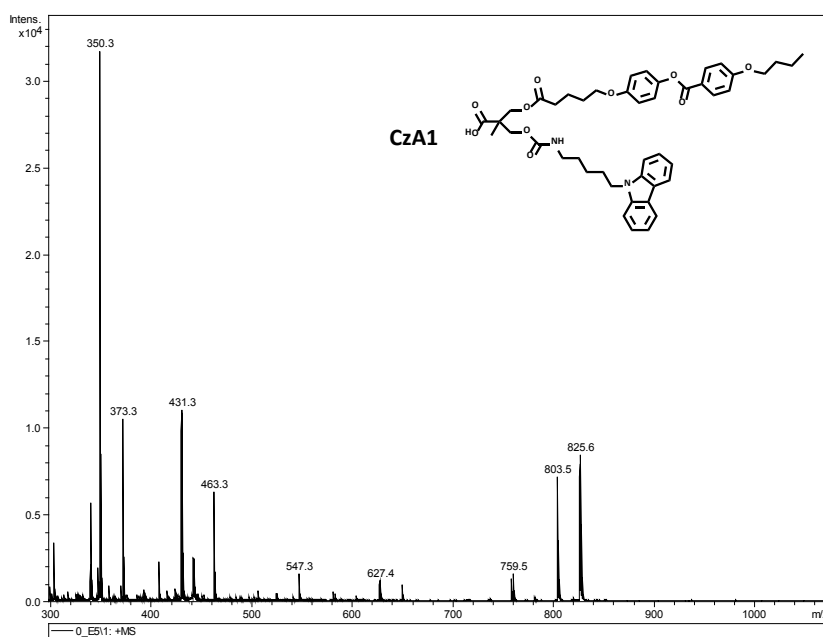
Compound	Abs (nm)	Abs (nm)	PL (nm)	PL (nm)
	Solution ^a ($\epsilon/10^4$) ^b	film	Solution ^a	film
CzA1	239 (4.3), 265 (4.4), 295 (1.8), 332 (0.4), 347 (0.4)	235, 266, 296, 335, 352	352, 369, 389 ^c	355, 371, 389 ^c

CzA2	239 (8.0), 265 (8.2), 295 (3.8), 332 (0.5), 347 (0.7)	240, 264, 296, 332, 348	352, 370, 388 ^c	355, 370, 389 ^c
CzB1	238 (2.1), 265 (1.1), 295 (0.8), 332 (0.1), 348 (0.1)	238, 265, 297, 334, 348	353, 369, 389 ^c	352, 368, 390 ^c
CzB2	237 (1.9), 265 (0.9), 295 (0.1), 332 (0.05), 347 (0.05)	240, 264, 296, 332, 348	352, 369, 388 ^c	355, 370, 389 ^c
M-CzA1	239 (43.0), 264 (42.1), 295 (16.5), 332 (3.9), 347 (4.4)	238, 263.5, 296, 331, 347	353, 370, 389	356, 372, 390 ^c
M-CzA2	239 (61.0), 265 (62.8), 295 (24.4), 332 (5.6), 347 (6.4), 353 (1.9)	238, 264, 296, 331, 348	353, 370, 388 ^c	356, 372, 390 ^c
M-CzB1	238 (15.5), 265 (8.9), 295 (6.0), 332 (1.7), 347 (1.8), 353 (0.6)	238, 265, 296, 332, 348	353, 370, 389 ^c	356, 375, 396 ^c
M-CzB2	239 (35.5), 265 (21.1), 296 (13.9), 332 (3.8), 347 (4.2), 353 (1.5)	238, 262, 296, 331, 347	353, 365, 389 ^c	354, 374, 392 ^c

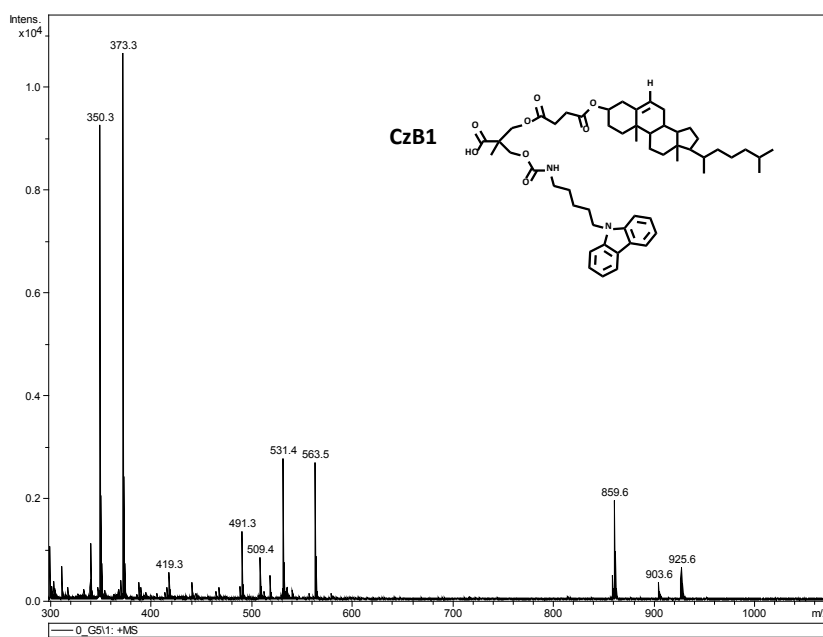
^aMeasured in CH₂Cl₂ solution, ^b Molar absorption coefficient (ϵ): M⁻¹ cm⁻¹, ^c shoulder
(h)

Supporting Figures

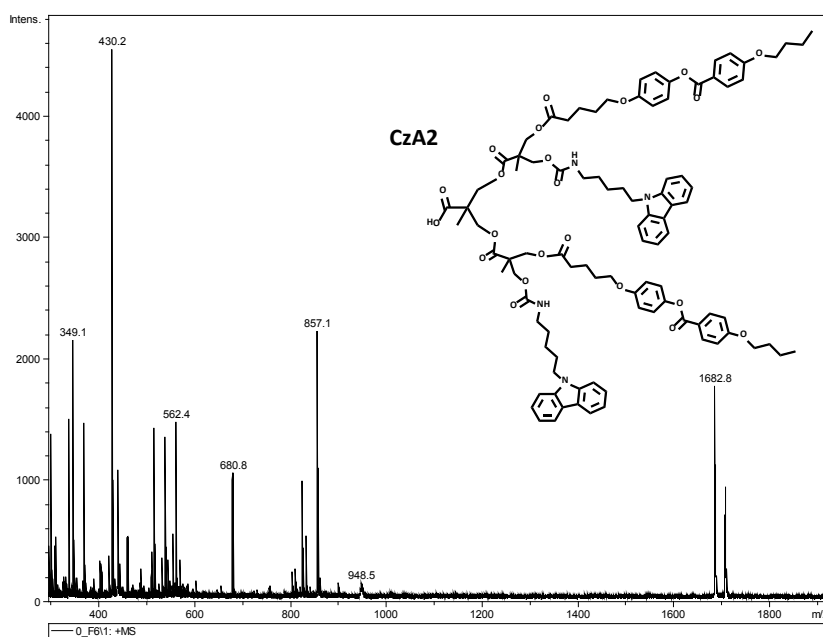
MALDI-TOF-MS Spectra



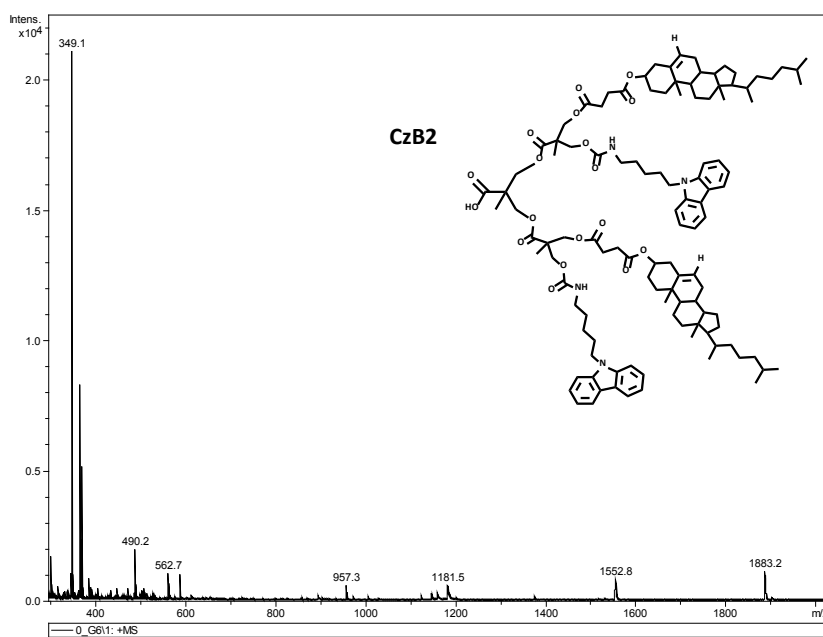
(a)



(b)



(c)



(d)

Figure S1. MS MALDI⁺ dendrons (a) CzA1, (b) CzB1, (c) CzA2, (d) CzB2

NMR Spectra of dendrons

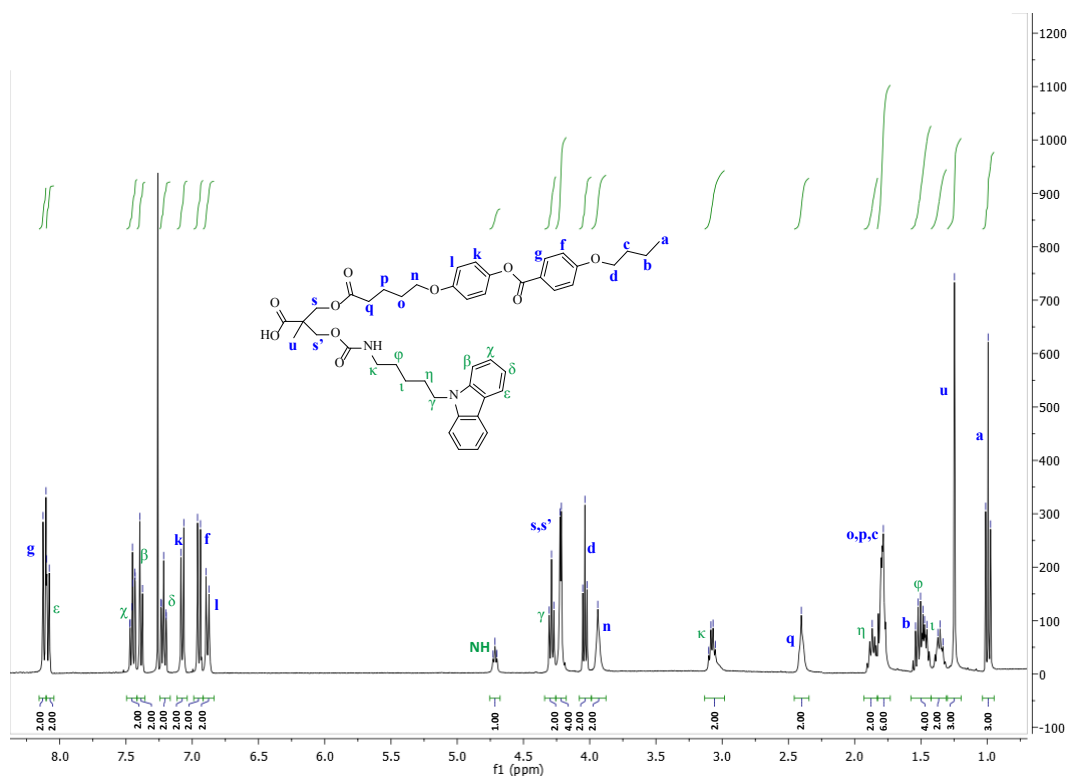


Figure S2. ¹H NMR spectrum of Dendron CzA1.

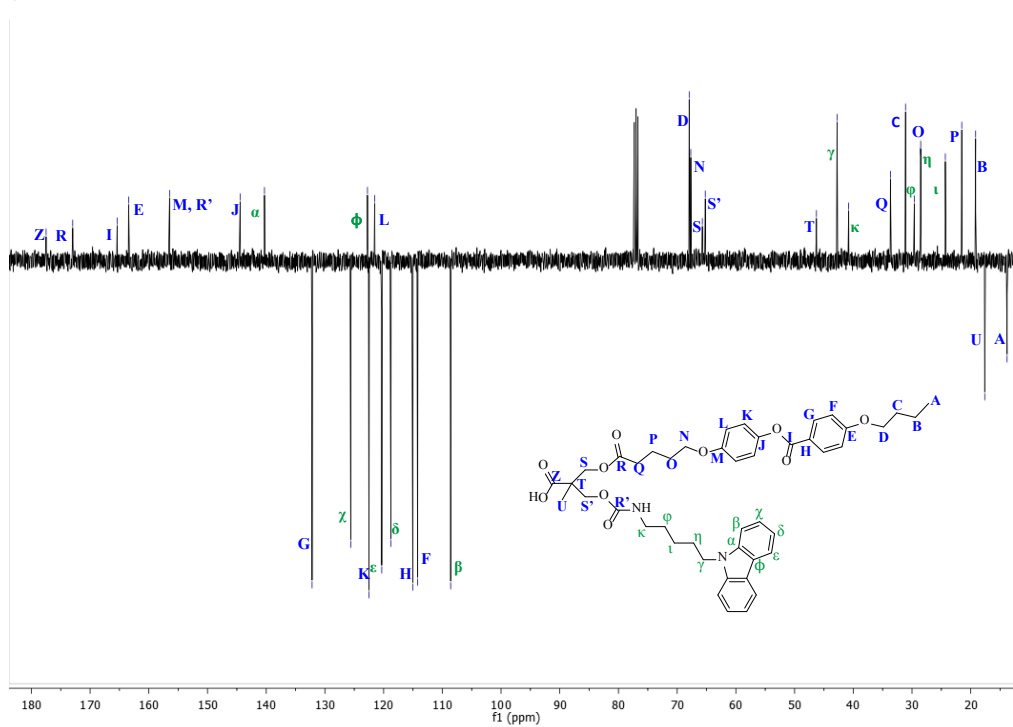


Figure S3. ¹³C NMR spectrum of Dendron CzA1

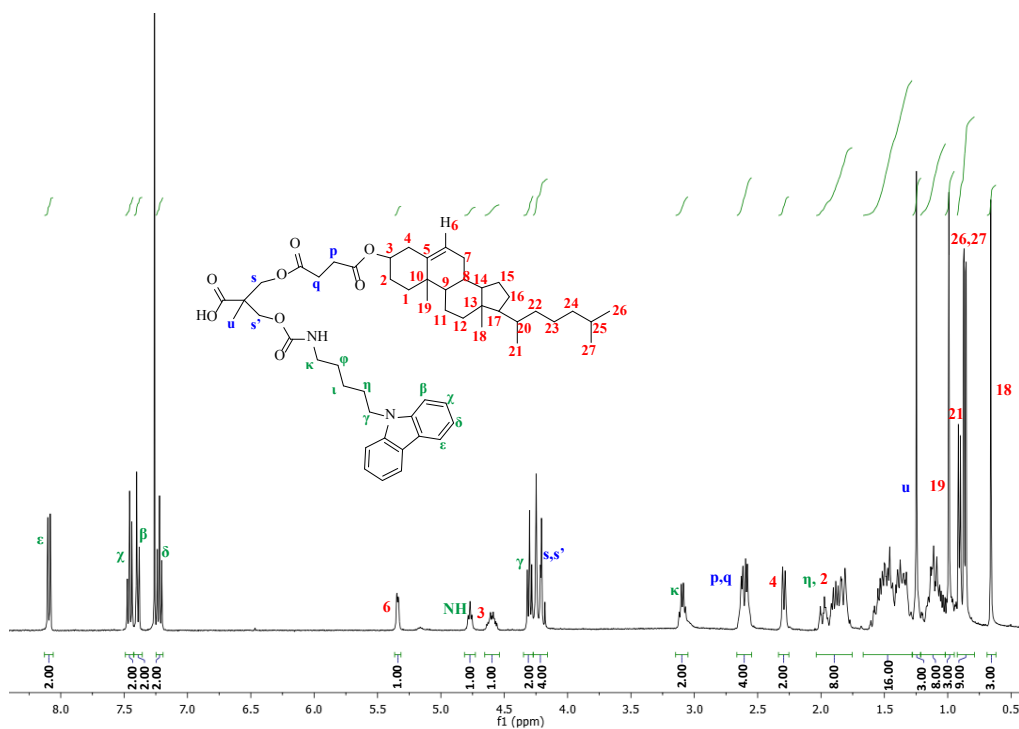


Figure S4. ¹H NMR spectrum of Dendron CzB1

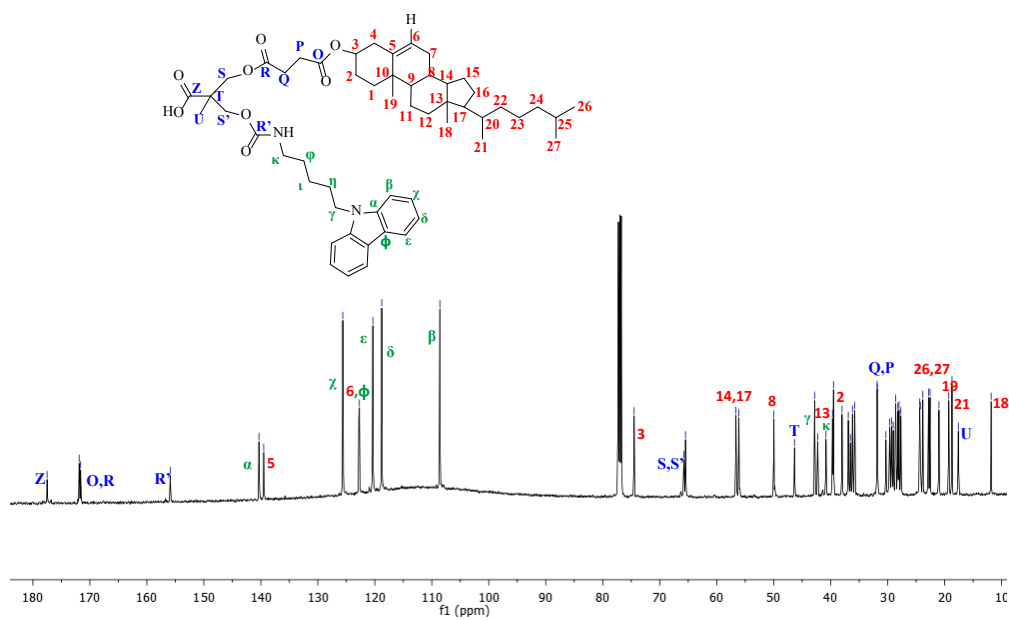


Figure S5. ¹³C NMR spectrum of Dendron CzB1.

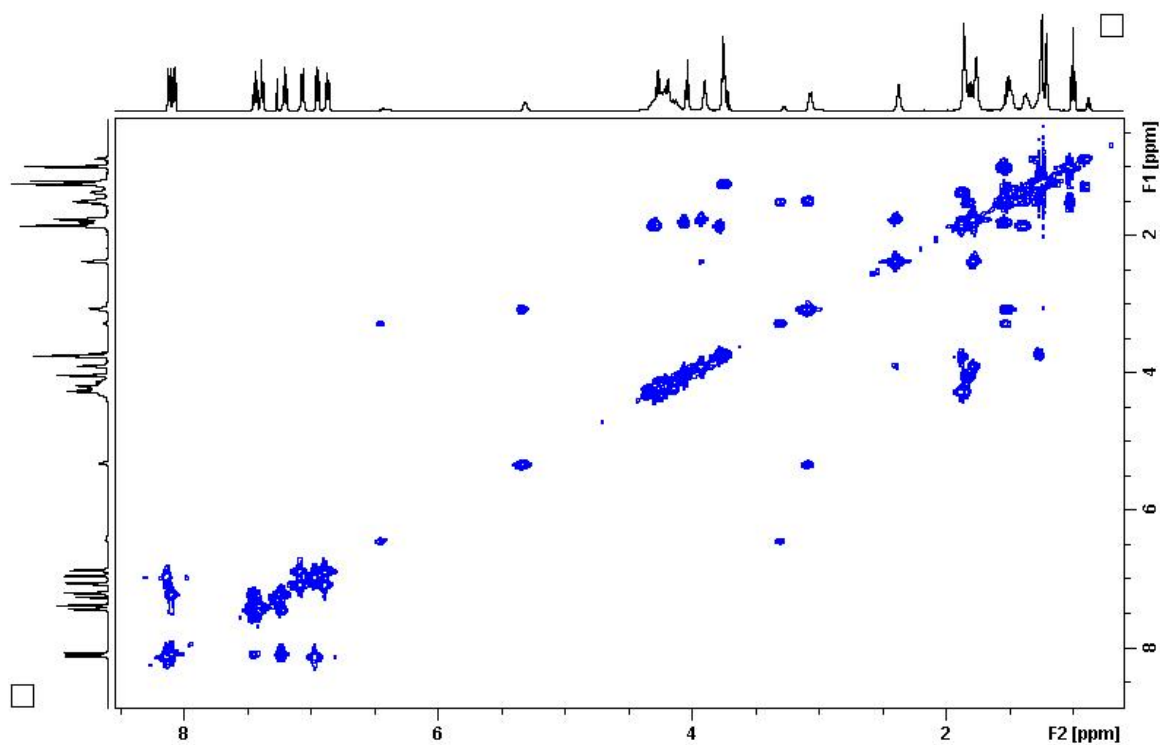


Figure S6. COSY spectrum of M-CzA2 (CDCl_3 , 500 MHz, 25 °C)

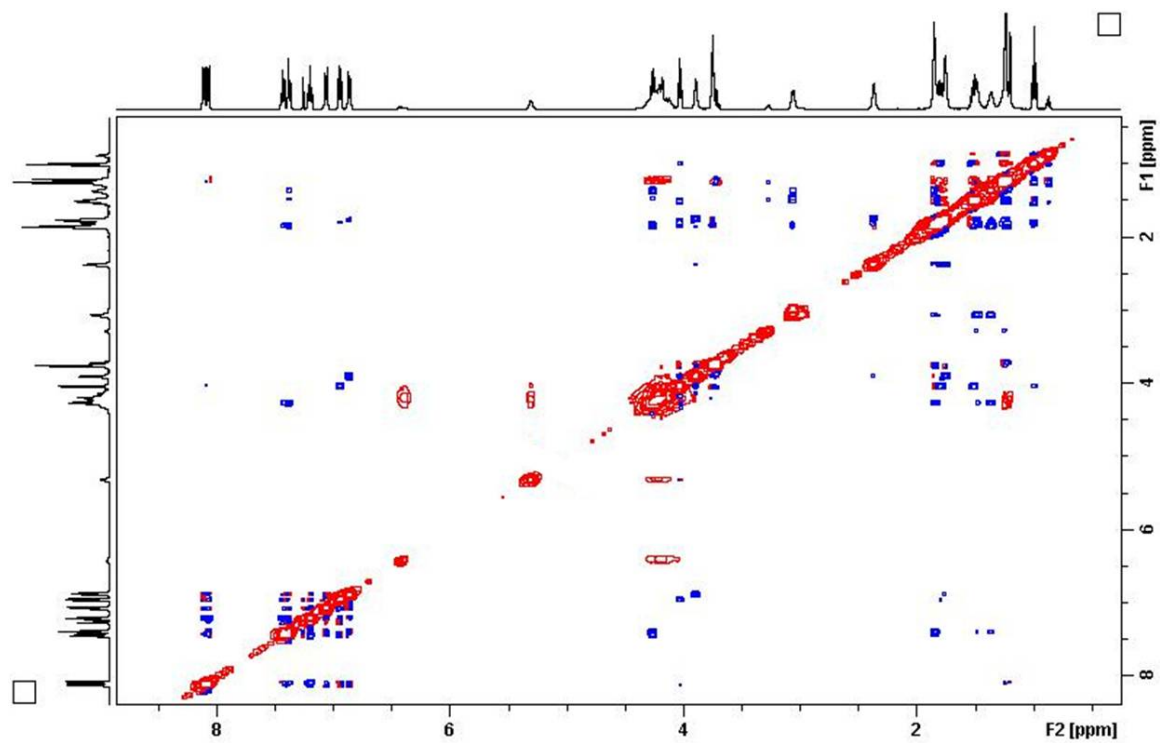


Figure S7. NOESY spectrum of M-CzA2 (CDCl_3 , 500 MHz, 25 °C) ($t_{\text{mix}} = 1\text{ s}$)

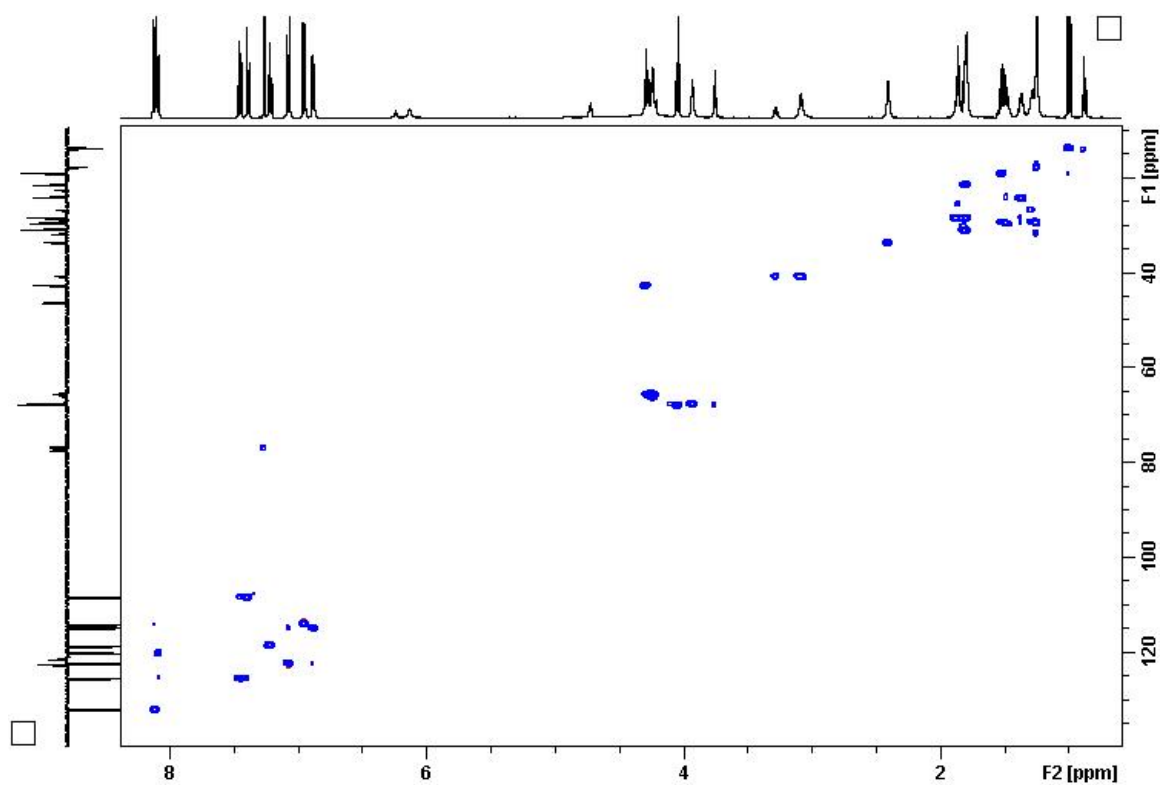


Figure S8. HSQC spectrum of M-CzA1 (CDCl₃, 500 MHz, 25 °C)

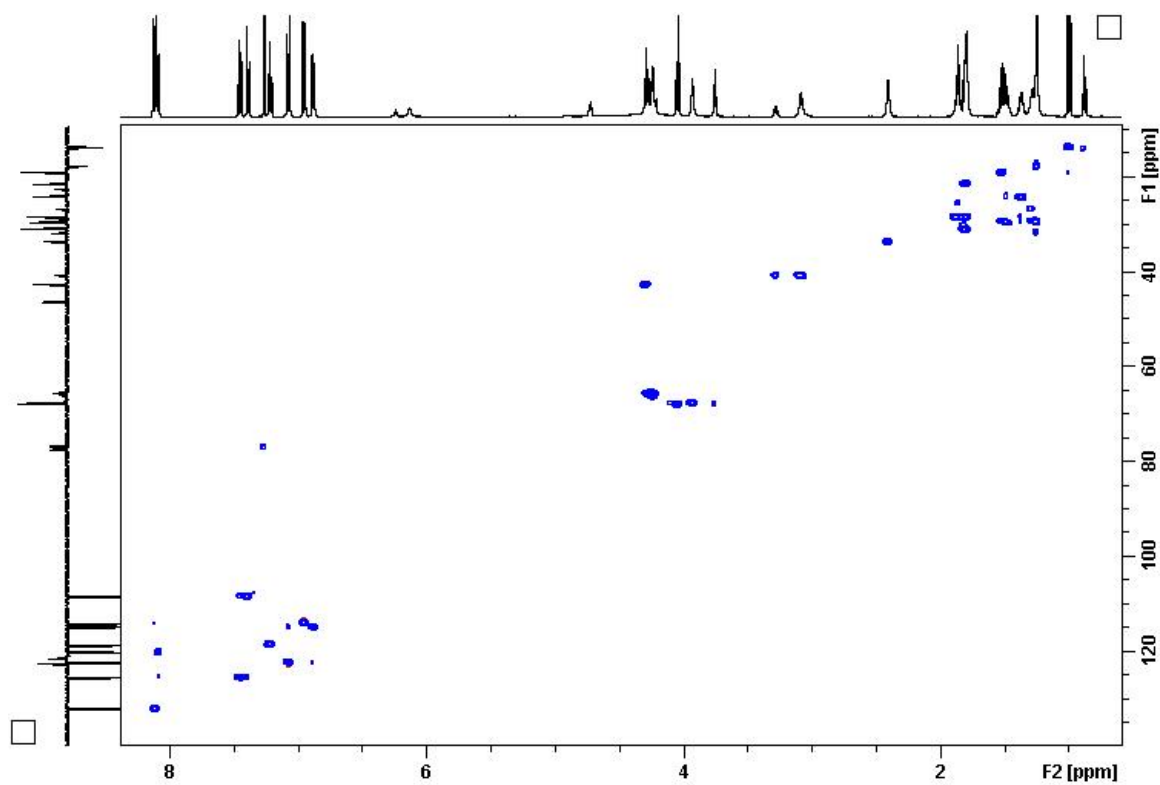


Figure S9. HSQC spectrum of M-CzB2 (CDCl₃, 500 MHz, 25 °C)

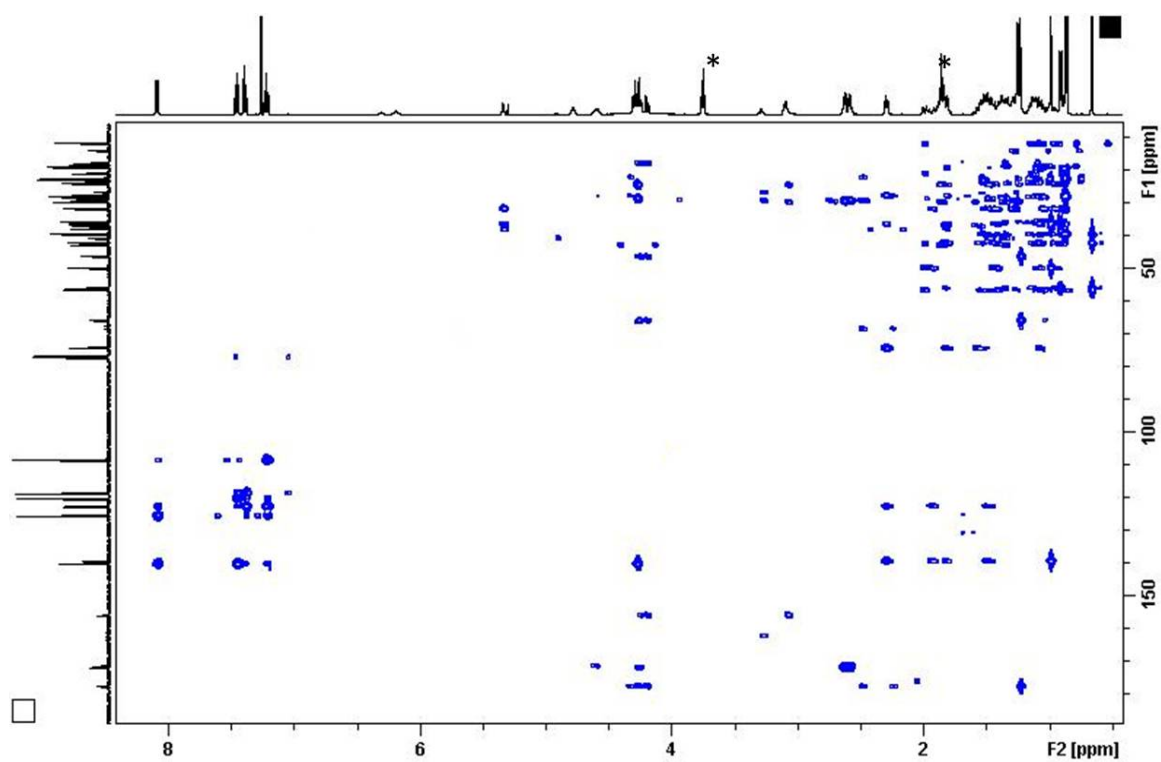


Figure S10. HMBC spectrum of M-CzB1 (CDCl₃, 500 MHz, 25 °C).

POM observations and X-Ray diffraction studies

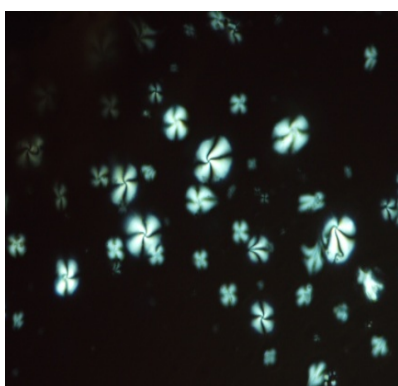


Figure S11. Microphotographs of (a) the droplet optical texture for CzA2 in the cooling process.

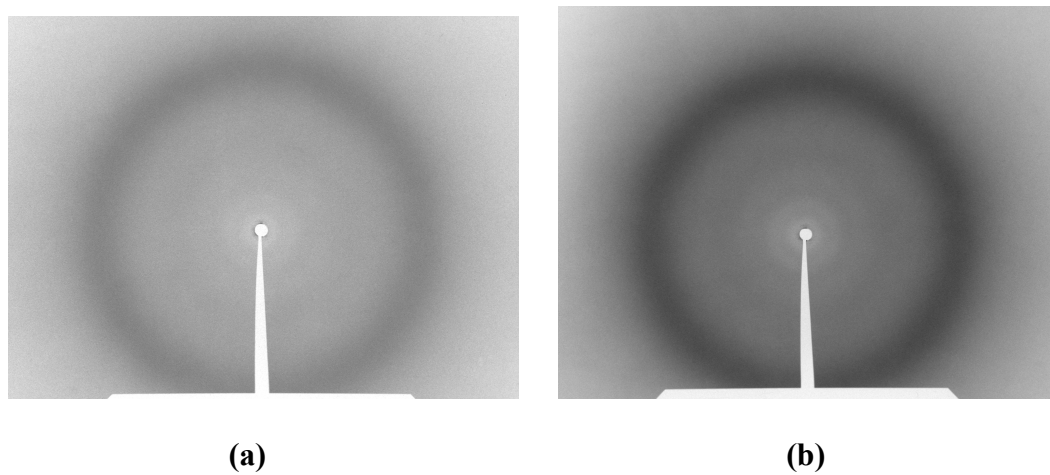


Figure S12. X-ray pattern of complex CzA2 (a) in its pristine state at rt (b) in nematic mesophase (cooled from the isotropic liquid).

Differential Scanning Calorimetry

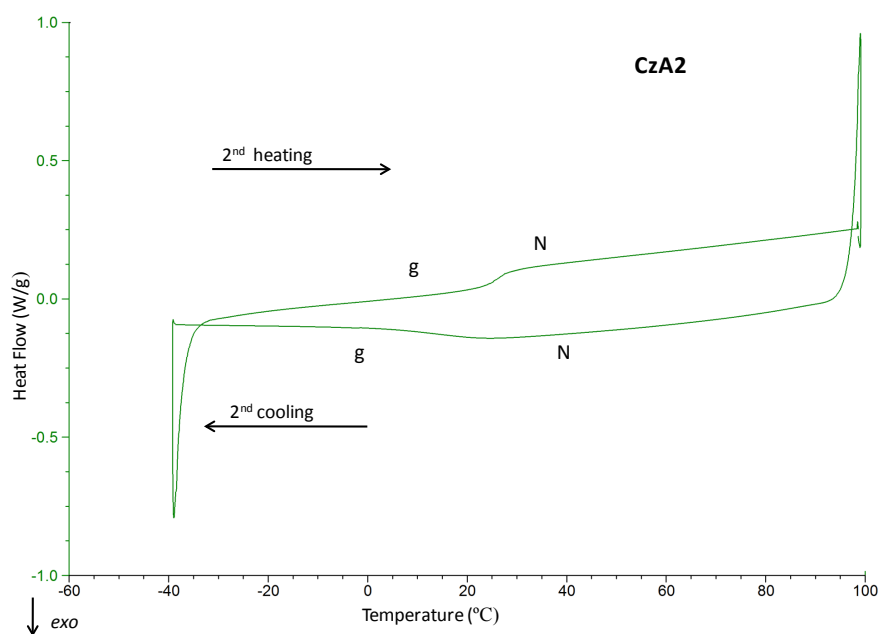


Figure S13. DSC scans at 10 °C/min for complex CzA2 second heating scan.

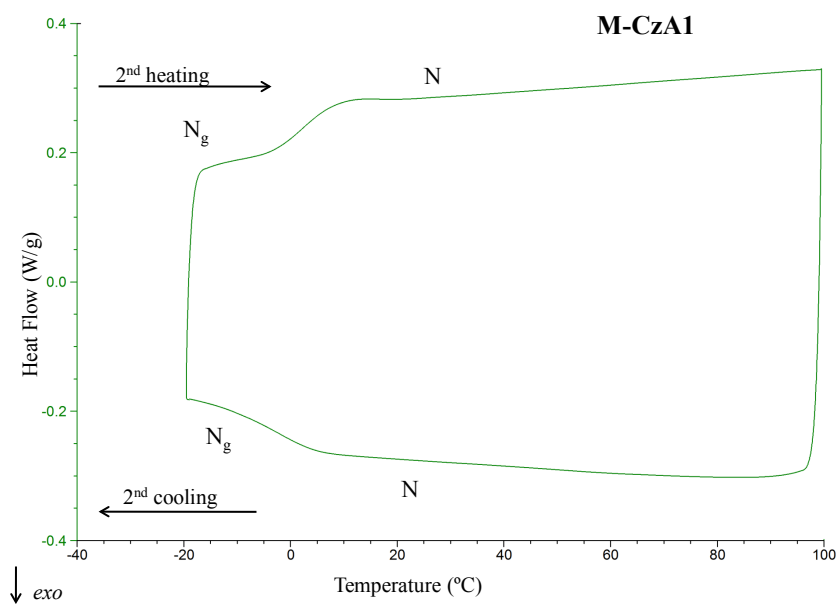


Figure S14. DSC scans at 10 °C/min for complex M-CzA1 second heating scan.

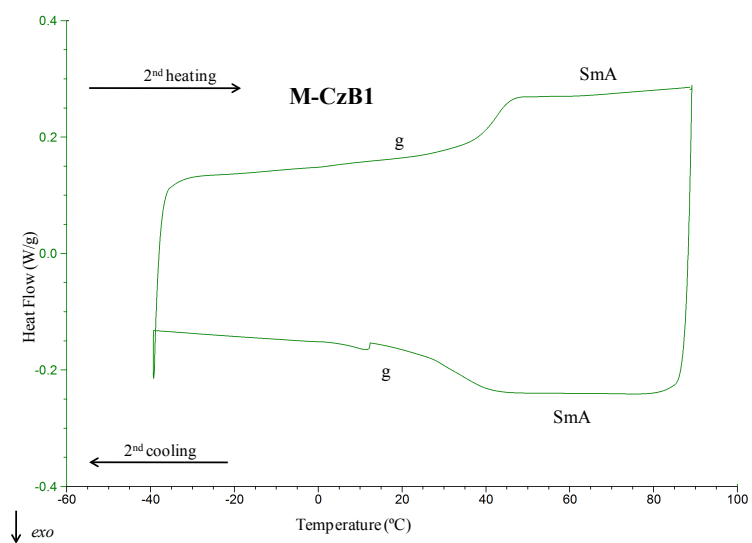
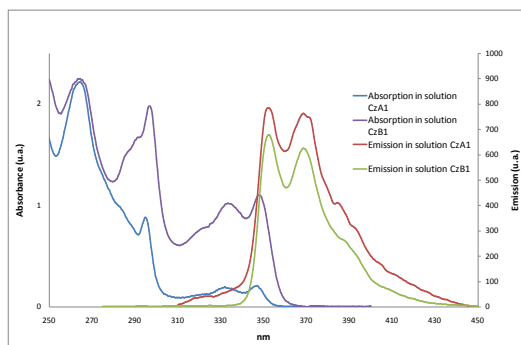
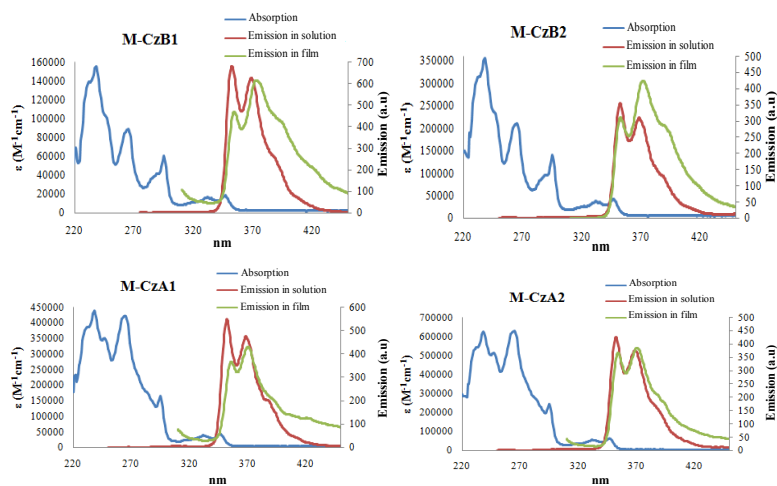


Figure S15. DSC scans at 10 °C/min for complex M-CzB1 second heating scan.

UV-Vis absorption and emission spectra



(a)



(b)

Figure S16. a) Normalized UV-vis absorption spectra and emission spectra in solution in CH_2Cl_2 of dendrons CzA1 and CzB1. b) Normalized UV-vis absorption spectra in CH_2Cl_2 and emission spectra in solution and in film of M-CzA1, M-CzB1 and M-CzB2 dendrimers

Cyclic voltammetry plots

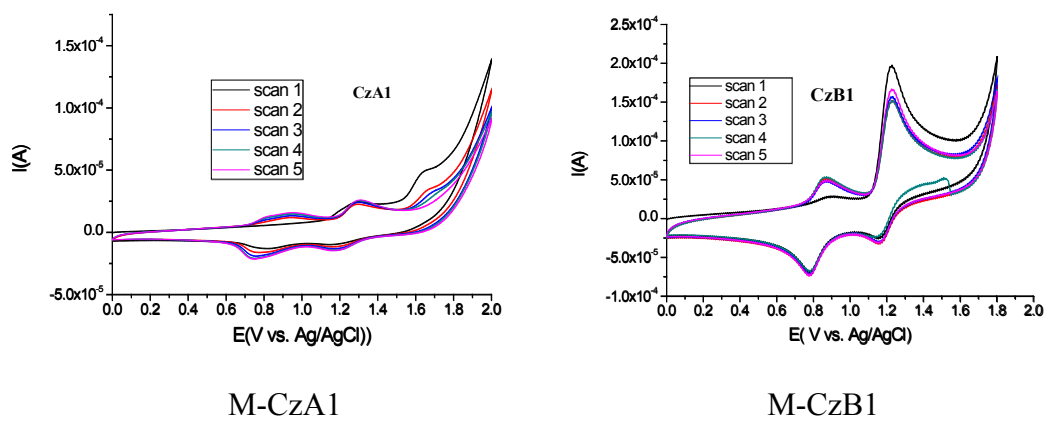


Figure S17. Cyclic voltammograms of dendrons: (a) CzA1 and (b) CzB1, in dichloromethane.