Supporting Information

Multifunctional Ionic Hybrid Poly(propyleneimine) Dendrimers surrounded by Carbazole Dendrons: Liquid Crystals, Optical and Electrochemical Properties.

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EXPERIMENTAL SECTION

1. Materials and Methods

The poly(propyleneimine) dendrimer (PPI-$(NH_2)_n$) generations 1-5 were commercially available from SyMO-Chem BV (Eindhoven, The Netherlands), The rest of the reagents were purchased from Sigma-Aldrich Chemical Company and were used as received. Anhydrous THF used for dendrimer preparation was purchased from Scharlau Chemie s.a. and was dried using a solvent purification system.

The infrared spectra of all the compounds were obtained on a Nicolet Avatar 360 FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range using KBr pellets and NaCl cells. ^{1}H-NMR spectroscopy was performed on a Bruker AVANCE 400 spectrometer and on a Bruker AVANCE 300 spectrometer. ^{13}C-NMR spectroscopy was performed on a Bruker AVANCE 400 spectrometer operating at 100 MHz and on a Bruker AVANCE 300 spectrometer operating at 75 MHz. Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer.

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 calorimeters 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 10ºC•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-Kα beam. Lindemann glass capillaries with 0.9 mm diameter were used to contain the sample and, when 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.

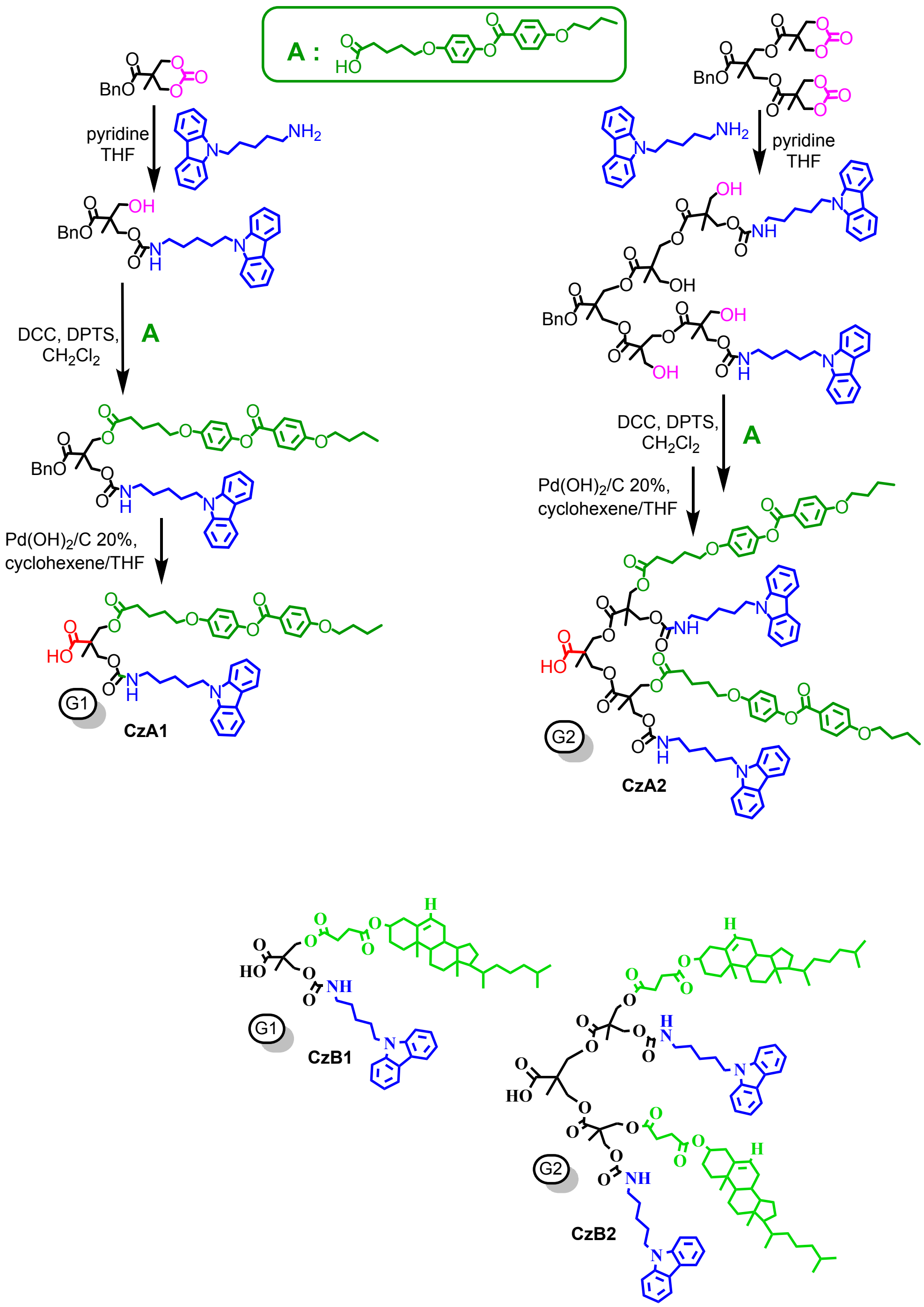
UV-vis absorption spectra were measured with a UV4-200 spectrophotometer from ATI-Unicam using 10-5-10-6 M solutions in $CHCl_3$ (HPLC Grade). Fluorescence spectra were measured with a Perkin-Elmer LS50B fluorescence spectrometer using solutions in $CHCl_3$ of ca. 0.01 absorbance (about 10-8-10-9 M) under excitation at the absorption maximum. Films were prepared by casting of a solution of ~1 mg/mL in $CHCl_3$ on a quartz plate.

Cyclic voltammetry measurements were performed on 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 can rate was 100 mV s^{-1}.

2. Synthetic procedures and chemical compound information

2.1 Synthesis and characterization of the compounds

Synthetic route to dendrons CzAm and CzBm

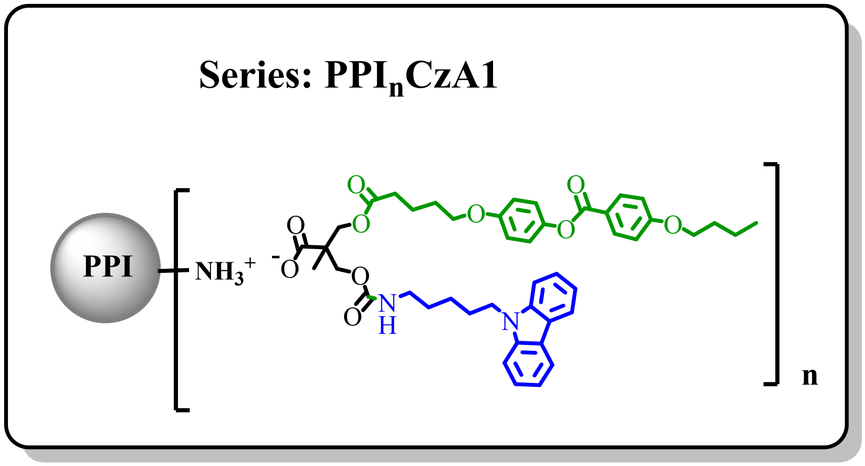


Scheme S1. a) Synthetic route to bifunctionalized dendrons CzAm (G1 and G2). b) Structure of dendrons CzBm (G1 and G2)

3. General procedure for the synthesis of the ionic hybrid dendrimers

Scheme S2. Synthetic route for ionic hybrid dendrimers derived from PPI dendrimers (G=1-5) and bis-(MPA) bifunctionalized dendrons (D=1,2). PPI is represented in pink. In the carboxylic acid dendrons the carbazole-containing moiety is represented in blue and the mesogenic unit in green.

The ionic hybrid dendrimers were prepared by addition of the PPI dendrimer of appropriate generation (G=1-5) dissolved in dry THF to a solution of the corresponding carboxylic acid dendrons in THF, with the appropriate stoichiometry to functionalize all amine groups of the periphery. The mixture was ultrasonicated for 5 min and the solvent was slowly evaporated at RT and the product dried in vacuum at 40 ºC until the weight remained constant.



PPI$_4$CzA1:

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.14-8.12 (m, AA’BB’, 8H), 8.09-8.08 (m, 8H), 7.53-7.42 (m, 8H), 7.40-7.39 (m, 8H), 7.26-7.18 (m, 8H), 7.08-7.07 (m, AA’BB’, 8H), 6.97-6.96 (m, AA’BB’, 8H), 6.88-6.86 (m, AA’BB’, 8H), 5.82 (s, 4H), 4.27 (t, *J* = 7.2 Hz, 8H), 4.20-4.10 (m, 16H), 4.05 (t, *J* = 6.5 Hz, 8H), 3.91-3.89 (m, 8H), 3.10-3.04 (m, 8H), 2.92-2.90 (m, 4H), 2.48-2.46 (m, 8H), 2.38-2.36 (m, 16H), 1.88-1.80 (m, 48H), 1.56-1.50 (m, 16H), 1.42-1.34 (m, 8H), 1.14 (s, 12H), 1.02 (t, *J* = 7.4 Hz, 12H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 178.98, 173.39, 165.34, 163.46, 156.64, 156.52, 144.46, 140.34, 132.19, 125.63, 122.75, 122.50, 121.59, 120.30, 118.76, 115.01, 114.24, 108.66, 67.97, 67.73, 66.96, 66.28, 46.78, 42.85, 40.82, 39.01, 33.85, 31.13, 29.79, 28.63, 24.46, 21.57, 19.18, 18.50, 13.81.

IR (Nujol) (cm^{-1}): 3368 (N-H), 2925 (C-H), 1728 (C=O), 1580 (COO^-_{asym}), 1400 (COO^-_{sym}).

PPI$_8$CzA1:

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.12-8.06 (m, AA'BB', 16H), 8.05-8.03 (m, 16H), 7.43-7.38 (m, 16H), 7.36-7.34 (m, 16H), 7.20-7.13 (m, 16H), 7.07-7.00 (m, AA'BB', 16H), 6.96-6.90 (m, AA'BB', 16H), 6.83-6.81 (m, AA'BB', 16H), 5.89 (s, 8H), 4.21 (t, *J* = 7.1 Hz, 16H), 4.15-4.10 (m, 32H), 4.01 (t, *J* = 6.5 Hz, 16H), 3.84-3.82 (m, 16H), 3.04-2.99 (m, 16H), 2.86 (s, 16H), 2.37 (s, 20H), 2.33 (s, 16H), 1.82-1.75 (m, 64H), 1.76-1.52 (m, 16H), 1.57-1.42 (m, 32H), 1.36-1.28 (m, 16H), 1.10 (s, 24H), 0.98 (t, *J* = 7.4 Hz, 24H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.97, 173.41, 165.31, 163.45, 156.51, 144.45, 140.32, 132.18, 125.62, 122.74, 122.50, 121.59, 120.29, 118.75, 114.98, 114.24, 108.65, 67.97, 67.71, 66.39, 52.67, 49.61, 46.73, 42.81, 40.82, 38.61, 33.85, 31.13, 29.82, 28.64, 26.85, 24.44, 21.58, 19.18, 18.69, 13.82.

IR (Nujol) (cm^{-1}): 3400 (N-H), 2927 (C-H), 1727 (C=O), 1580 (COO^-_{asym}), 1401 (COO^-_{sym}).

PPI$_{16}$CzA1:

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.08-8.06 (m, *AA'BB', 32H*), 8.02-8.00 (m, 32H), 7.39-7.36 (m, 32H), 7.33-7.31 (m, 32H), 7.16-7.12 (m, 32H), 7.01-6.99 (m, AA'BB', 32H), 6.91-6.89 (m, AA'BB', 32H), 6.79-6.76 (m, AA'BB', 32H), 6.06 (s, 16H), 4.22-4.07 (m, 96H), 3.98 (t, *J* = 6.5 Hz, 32H), 3.76 (s, 32H), 3.05-2.95 (m, 32H), 2.89-2.79 (m, 32H), 2.48-2.34 (m, 44H), 2.32-2.21 (m, 32H), 1.78-1.73 (m, 128H), 1.68-1.61 (m, 32H), 1.51-1.42 (m, 64H), 1.31-1.22 (m, 32H), 1.08 (s, 48H), 0.97 (t, *J* = 7.4 Hz, 48H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.91, 173.21, 165.23, 163.45, 156.52, 144.44, 140.31, 132.18, 125.61, 122.75, 122.50, 121.56, 120.30, 118.75, 114.99, 114.23, 108.64, 67.97, 67.70, 66.12, 52.51, 46.53, 42.81, 40.82, 38.60, 33.65, 31.12, 29.62, 28.63, 26.95, 24.34, 21.56, 19.18, 18.59, 13.82.

IR (Nujol) (cm^{-1}): 3384 (N-H), 2937 (C-H), 1729 (C=O), 1578 (COO^-_{asym}), 1401 (COO^-_{sym}).

<u>PPI$_{32}$CzA1:</u>

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.06-8.04 (m, AA'BB', 64H), 8.00-7.98 (m, 64H), 7.37-7.33 (m, 64H), 7.30-7.28 (m, 64H), 7.14-7.10 (m, 64H), 6.99-6.96 (m, AA'BB', 64H), 6.89-6.87 (m, AA'BB', 64H), 6.76-6.73 (m, AA'BB', 64H), 6.03 (s, 32H), 4.22-4.08 (m, 192H), 3.95 (t, *J* = 6.5 Hz, 64H), 3.76 (s, 64H), 3.02-2.92 (m, 64H), 2.90-2.81 (m, 64H), 2.47-2.32 (m, 100H), 2.25-2.29 (m, 64H), 1.77-1.71 (m, 256H), 1.67-1.60 (m, 64H), 1.51-1.36 (m, 128H), 1.26-1.23 (m, 64H), 1.09 (s, 96H), 0.96 (t, *J* = 7.4 Hz, 96H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 178.95, 173.46, 165.29, 163.44, 156.74, 156.46, 144.38, 140.25, 132.14, 125.61, 122.66, 122.47, 121.51, 120.25, 118.72, 114.91, 114.19, 108.65, 67.92, 67.64, 46.64, 42.73, 40.73, 33.81, 31.08, 30.28, 29.69, 28.59, 28.55, 24.87, 24.34, 21.52, 19.15, 18.62, 13.80.

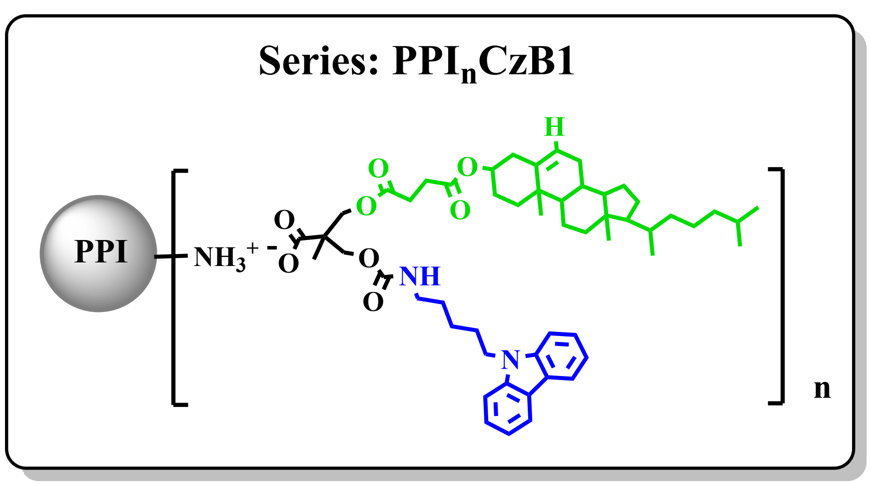
IR (Nujol) (cm^{-1}): 3386 (N-H), 2937 (C-H), 1729 (C=O), 1578 (COO^-_{asym}), 1401 (COO^-_{sym}).

<u>PPI$_{64}$CzA1:</u>

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.04-8.02 (m, AA’BB’, 128H), 7.98-7.96 (m, 128H), 7.33-7.31 (m, 128H), 7.28-7.26 (m, 128H), 7.11-7.09 (m, 128H), 6.96-6.94 (m, AA’BB’, 128H), 6.86-6.84 (m, AA’BB’, 128H), 6.73-6.71 (m, AA’BB’, 128H), 5.96 (s, 64H), 4.19-4.05 (m, 384H), 3.93 (t, J = 5.9 Hz, 128H), 3.69 (s, 128H), 3.02-2.88 (m, 128H), 2.88-2.74 (m, 128H), 2.45-2.13 (m, 364H), 2.25 (s, 128H), 1.77-1.66 (m, 512H), 1.66-1.55 (m, 252H), 1.52-1.33 (m, 256H), 1.27-1.17 (m, 128H), 1.10 (s, 192H), 0.95 (t, J = 7.4 Hz, 192H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 178.52, 173.39, 165.30, 163.44, 156.67, 156.49, 144.43, 140.29, 132.16, 125.63, 122.70, 122.49, 121.55, 120.27, 118.75, 114.96, 114.22, 108.66, 67.95, 67.69, 67.05, 66.35, 49.26, 46.61, 42.76, 40.76, 33.82, 31.11, 29.69, 28.61, 25.56, 24.88, 24.36, 21.55, 19.16, 18.56, 13.80.

IR (Nujol) (cm^{-1}): 3386 (N-H), 2935 (C-H), 1729 (C=O), 1578 (COO^{-}_{asym}), 1401 (COO^{-}_{sym}).



PPI$_4$CzB1:

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.07-8.05 (m, 8H), 7.45-7.41 (m, 8H), 7.39 - 7.36 (m, 8H), 7.22-7.17 (m, 8H), 5.68 (s, 4H), 5.31 (d, *J* = 4.2 Hz, 4H), 4.58-4.49 (m, 4H), 4.28-4.23 (m, 8H), 4.18-4.12 (m, 16H), 3.01 (s, 8H), 2.92-2.82 (m, 8H), 2.62-2.50 (m, 16H), 2.27 (m, 20H), 2.08-1.21 (m, 140H), 1.11 (s, 12H), 0.97 (s, 12H), 0.96-0.83 (m, 36H), 0.65 (s, 12H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 178.62, 172.67, 172.32, 171.78, 156.70, 140.32, 139.52, 129.53, 125.63, 122.75, 122.65, 120.28, 118.75, 115.40, 108.64, 77.20, 74.38, 67.07, 66.76, 56.60, 56.12, 49.95, 46.72, 42.85, 42.26, 40.79, 39.67, 39.50, 38.03, 36.90, 36.51, 36.18, 35.77, 31.83, 31.78, 29.72, 29.35, 29.12, 28.64, 28.20, 28.00, 27.69, 24.44, 24.24, 23.85, 22.80, 22.55, 20.98, 19.26, 18.70, 18.36, 11.82.

IR (Nujol) (cm^{-1}): 3400 (N-H), 2938 (C-H), 1729 (C=O), 1577 (COO^-_{asym}), 1408 (COO^-_{sym}).

PPI$_8$CzB1:

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.07-8.04 (m, 16H), 7.45-7.40 (m, 16H), 7.38-7.36 (m, 16H), 7.21-7.16 (m, 16H), 5.73 (s, 8H), 5.30 (d, *J* = 2.8 Hz, 8H), 4.60-4.53 (m, 8H), 4.28-4.22 (m, 16H), 4.15 (d, *J* = 16.1 Hz, 32H), 3.01 (s, 16H), 2.56 (s, 40H), 2.26 (m, 28H), 2.02-0.99 (m, 268H), 1.11 (s, 24H), 0.96 (s, 24H), 0.92-0.83 (m, 72H), 0.65 (s, 24H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 178.61, 172.33, 171.76, 156.73, 140.32, 139.52, 130.04, 125.64, 122.75, 122.65, 120.29, 118.77, 115.40, 108.65, 77.20, 74.37, 66.89, 56.60, 56.13, 49.94, 46.71, 42.85, 42.26, 40.78, 39.68, 39.51, 38.04, 36.90, 36.51, 36.18, 35.78, 31.78, 29.74, 29.37, 28.64, 28.20, 28.01, 27.70, 24.44, 24.24, 23.87, 22.81, 22.56, 20.98, 19.26, 18.71, 18.47, 11.83.

IR (Nujol) (cm^{-1}): 3373 (N-H), 2937 (C-H), 1728 (C=O), 1573 (COO^-_{asym}), 1406 (COO^-_{sym}).

<u>PPI₁₆CzB1:</u>

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.04-8.02 (m, 32H), 7.41-7.39 (m, 32H), 7.36-7.34 (m, 32H), 7.18-7.16 (m, 32H), 6.04 (s, 16H), 5.27 (s, 16H), 4.58-4.48 (s, 16H), 4.22-4.20 (m, 32H), 4.22-4.11 (m, 64H), 3.08-2.94 (m, 32H), 2.94-2.86 (m, 32H), 2.62-2.54 (m, 64H), 2.47-2.33 (m, 44H), 2.32-2.22 (m, 32H), 1.96-0.99 (m, 544H), 1.08 (s, 48H), 0.93 (s, 48H), 0.90-0.86 (m, 144H), 0.63 (s, 48H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.46, 172.36, 171.73, 156.81, 140.30, 139.46, 125.61, 122.74, 122.63, 120.28, 118.74, 108.64, 74.31, 67.96, 67.24, 66.86, 56.55, 56.13, 52.47, 52.07, 51.38, 49.89, 46.83, 42.84, 42.24, 40.84, 39.64, 39.51, 38.85, 38.01, 36.86, 36.48, 36.19, 35.79, 31.75, 30.31, 29.80, 29.32, 29.13, 28.65, 28.21, 28.01, 27.69, 27.07, 25.60, 24.47, 24.24, 23.91, 22.82, 22.57, 20.96, 19.24, 18.78, 18.72, 11.81.

IR (Nujol) (cm^{-1}): 3384 (N-H), 2938 (C-H), 1726 (C=O), 1576 (COO^-_{asym}), 1405 (COO^-_{sym}).

<u>PPI$_{32}$CzB1:</u>

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.02-8.01 (m, 64H), 7.40-7.37 (m, 64H), 7.34-7.32 (m, 64H), 7.17-7.14 (m, 64H), 6.01 (s, 32H), 5.24 (s, 32H), 4.57-4.47 (s, 32H), 4.19-4.17 (m, 64H), 4.23-4.11 (m, 128H), 3.07-2.93 (m, 64H), 2.93-2.82 (m, 64H), 2.63-2.48 (m, 128H), 2.45-2.30 (m, 100H), 2.22-2.21 (m, 64H), 1.95-0.96 (m, 1024H), 1.08 (s, 96H), 0.90 (s, 96H), 0.88-0.86 (m, 288H), 0.62 (s, 96H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.34, 172.37, 171.72, 156.81, 140.31, 139.45, 125.60, 122.73, 122.62, 120.28, 118.75, 108.63, 74.32, 67.96, 67.24, 66.84, 56.55, 56.12, 52.50, 52.07, 51.50, 49.89, 46.82, 42.82, 42.24, 40.84, 39.64, 39.51, 38.83, 38.01, 36.86, 36.47, 36.18, 35.78, 31.75, 30.31, 29.80, 29.32, 29.13, 28.64, 28.21, 28.02, 27.69, 27.07, 25.60, 24.47, 24.24, 23.91, 22.82, 22.57, 20.96, 19.24, 18.75, 18.72, 11.81.

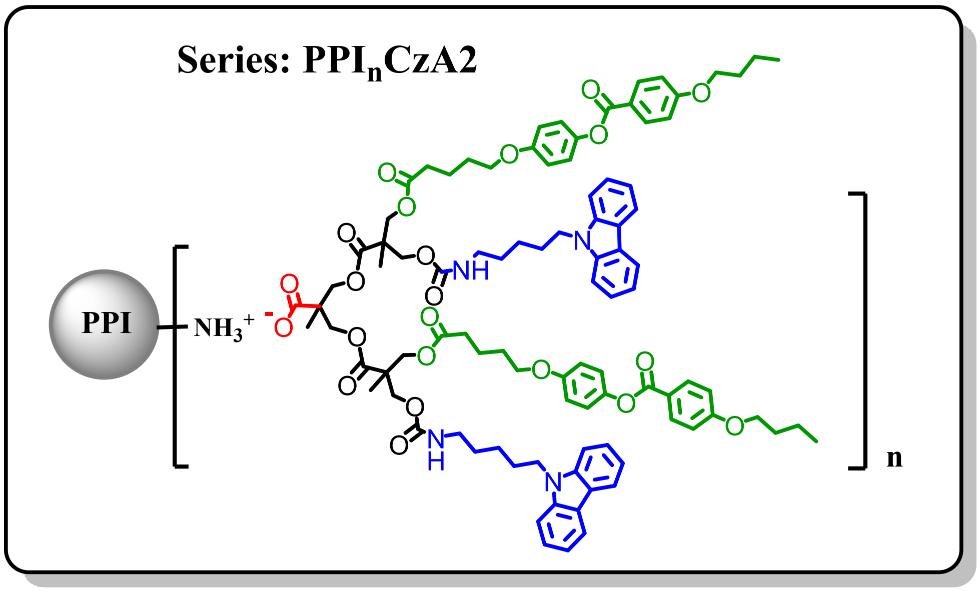
IR (Nujol) (cm^{-1}): 3385 (N-H), 2938 (C-H), 1729 (C=O), 1576 (COO^-_{asym}), 1404 (COO^-_{sym}).

PPI$_{64}$CzB1:

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.01-7.99 (m, 128H), 7.38-7.35 (m, 128H), 7.32-7.30 (m, 128H), 7.15-7.12 (m, 128H), 6.00 (s, 64H), 5.22 (s, 64H), 4.55-4.46 (s, 64H), 4.20-4.18 (m, 64H), 4.23-4.03 (m, 256H), 3.07-2.91 (m, 128H), 2.91-2.79 (m, 128H), 2.60-2.49 (m, 256H), 2.45-2.29 (m, 364H), 2.24-2.17 (m, 128H), 1.93-0.96 (m, 2048H), 1.08 (s, 192H), 0.89 (s, 192H), 0.88-0.86 (m, 576H), 0.61 (s, 192H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.29, 172.34, 171.66, 156.78, 140.28, 139.40, 125.62, 122.72, 120.26, 118.74, 108.65, 74.28, 67.96, 67.11, 66.76, 56.49, 56.14, 52.06, 51.78, 49.82, 46.81, 42.79, 42.21, 40.86, 39.61, 39.52, 38.02, 36.82, 36.42, 36.20, 35.80, 31.70, 30.31, 29.71, 29.32, 29.12, 28.61, 28.21, 28.02, 27.67, 25.60, 24.43, 24.22, 23.96, 22.84, 22.58, 20.94, 19.21, 18.72, 11.81.

IR (Nujol) (cm^{-1}): 3385 (N-H), 2938 (C-H), 1729 (C=O), 1573 (COO^{-}_{asym}), 1404 (COO^{-}_{sym}).



PPI$_4$CzA2:

^{1}H-NMR (500 MHz, $CDCl_3$, δ) 8.11-8.10 (m, AA’BB’, 16H), 8.07-8.06 (m, 16H), 7.45-7.41 (m, 16H),7.39-7.37 (m, 16H), 7.21-7.18 (m, 16H), 7.07-7.05 (m, AA’BB’, 16H), 6.95-6.93 (m, AA’BB’, 16H), 6.87-6.85 (m, AA’BB’, 16H), 5.43 (m, 8H), 4.26 (t, *J* = 7.2 Hz, 16H), 4.35-4.09 (m,48H), 4.03 (t, *J* = 6.5 Hz, 16H), 3.92-3.86 (m, 16H), 3.20-2.95 (m, 8H), 3.07-3.04 (m, 16H), 2.40-2.25 (m, 12H), 2.37-2.35 (m, 16H), 1.95–1.70 (m, 76H), 1.54-1.46 (m, 32H), 1.39-1.34 (m, 16H), 1.20 (s, 36H), 0.99 (t, *J* = 7.4 Hz, 24H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.58, 172.96, 165.48, 163.50, 156.48, 156.02, 144.47, 140.33, 132.22, 125.62, 122.76, 122.53, 121.52, 120.31, 118.75, 115.03, 114.24, 108.63, 67.98, 67.69, 65.96, 65.28, 52.13, 46.81, 46.32, 42.82, 40.83, 36.86, 33.68, 31.12, 29.58, 28.58, 24.37, 21.54, 19.18, 18.27, 17.68, 13.81.

IR (Nujol) (cm^{-1}): 3398 (N-H), 2938 (C-H), 1730 (C=O), 1579 (COO^{-}_{asym}), 1400 (COO^{-}_{sym}).

PPI$_8$CzA2:

^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.11-8.09 (m, AA'BB', 32H), 8.07-8.06 (m, 32H), 7.44-7.41 (m, 32H),7.38-7.37 (m, 32H), 7.21-7.18 (m, 32H), 7.06-7.05 (m, AA'BB', 32H), 6.95-6.93 (m, AA'BB', 32H), 6.86-6.85 (m, AA'BB', 32H), 5.41 (m, 16H), 4.26 (t, J = 7.2 Hz, 32H), 4.30-4.10 (m,96H), 4.03 (t, J = 6.5 Hz, 32H), 3.92-3.87 (m, 32H), 3.60-2.95 (m, 16H), 3.06-3.04 (m, 32H), 2.60-2.24 (m, 20H), 2.37-2.35 (m, 32H), 1.94–1.69 (m, 144H), 1.55-1.45 (m, 64H), 1.41-1.34 (m, 32H), 1.19 (s, 72H), 0.99 (t, J = 7.4 Hz, 48H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 179.30, 172.97, 165.46, 163.50, 156.48, 156.03, 144.49, 140.33, 132.22, 125.62, 122.77, 122.53, 121.53, 120.31, 118.76, 115.04, 114.25, 108.64, 67.98, 67.70, 65.97, 65.28, 50.30, 46.81, 46.32, 42.82, 40.83, 38.08, 33.68, 31.12, 29.58, 28.58, 24.37, 21.54, 19.18, 18.24, 17.67, 13.81.

IR (Nujol) (cm^{-1}): 3397 (N-H), 2936 (C-H), 1730 (C=O), 1579 (COO^{-}_{asym}), 1400 (COO^{-}_{sym}).

PPI$_{16}$CzA2:

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.09-8.07 (m, AA'BB', 64H), 8.04-8.02 (m, 64H), 7.42-7.38 (m, 64H),7.35-7.33 (m, 64H), 7.18-7.15 (m, 64H), 7.04-7.01 (m, AA'BB', 64H), 6.92-6.90 (m, AA'BB', 64H), 6.82-6.80 (m, AA'BB', 64H), 5.41 (m, 32H), 4.29-4.08 (m,256H), 4.00 (t, J = 6.5 Hz, 64H), 3.86-3.83 (m, 64H), 3.60-2.83 (m, 32H), 3.01-2.81 (m, 64H), 2.60-2.24 (m, 44H), 2.34-2.32 (m, 64H), 1.88–1.65 (m, 288H), 1.55-1.38 (m, 128H), 1.34-1.24 (m, 64H), 1.17 (s, 144H), 0.98 (t, *J* = 7.4 Hz, 96H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.94, 172.55, 165.07, 163.44, 156.44, 156.14, 144.42, 140.28, 132.18, 125.60, 122.71, 122.49, 121.51, 120.29, 118.74, 114.96, 114.21, 108.62, 67.95, 67.63, 65.91, 65.44, 51.47, 46.35, 42.75, 40.79, 38.05, 33.63, 31.11, 29.53, 28.55, 24.32, 21.48, 19.17, 18.52, 17.28, 13.82.

IR (Nujol) (cm^{-1}): 3394 (N-H), 2933 (C-H), 1729 (C=O), 1576 (COO^-_{asym}), 1401 (COO^-_{sym}).

PPI_{32}CzA2:

^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.09-8.07 (m, AA’BB’, 128H), 8.04-8.02 (m, 128H), 7.42-7.38 (m, 128H),7.35-7.33 (m, 128H), 7.18-7.14 (m, 128H), 7.03-7.01 (m, AA’BB’, 128H), 6.92-6.90 (m, AA’BB’, 128H), 6.82-6.80 (m, AA’BB’, 128H), 5.43 (m, 64H), 4.33-4.08 (m,512H), 3.99 (t, *J* = 6.5 Hz, 128H), 3.86-3.83 (m, 128H), 3.06-2.53 (m, 64H), 3.00-2.98 (m, 128H), 2.60-2.24 (m, 100H), 2.34-2.32 (m, 128H), 1.80–1.65 (m, 576H), 1.54-1.37 (m, 256H), 1.36-1.24 (m, 128H), 1.17 (s, 288H), 0.97 (t, *J* = 7.4 Hz, 192H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.92, 172.55, 165.07, 163.44, 156.44, 156.14, 144.42, 140.28, 132.18, 125.60, 122.50, 122.49, 121.51, 120.29, 118.74, 114.96, 114.22, 108.63, 67.95, 67.63, 65.91, 65.44, 58.59, 51.47, 46.35, 42.75, 40.79, 38.05, 33.63, 31.11, 29.53, 28.57, 24.33, 21.48, 19.17, 18.52, 17.28, 13.82.

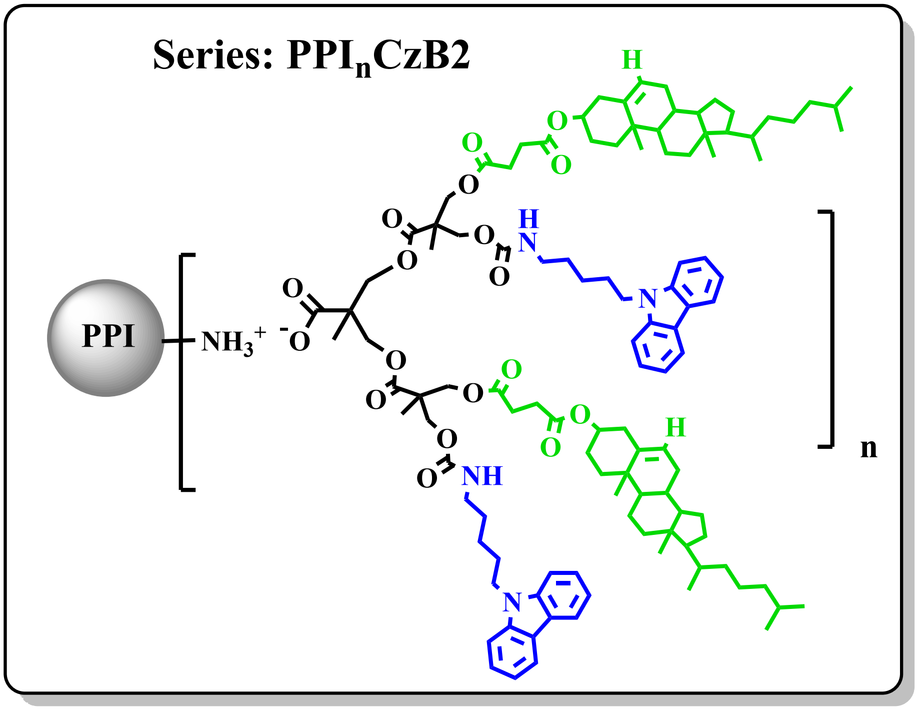
IR (Nujol) (cm^{-1}): 3396 (N-H), 2936 (C-H), 1730 (C=O), 1578 (COO^-_{asym}), 1401 (COO^-_{sym}).

PPI$_{64}$CzA2:

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.09-8.07 (m, AA'BB', 256H), 8.04-8.02 (m, 256H), 7.42-7.38 (m, 256H),7.35-7.33 (m, 256H), 7.18-7.15 (m, 256H), 7.04-7.02 (m, AA'BB', 256H), 6.93-6.90 (m, AA'BB', 256H), 6.83-6.81 (m, AA'BB', 256H), 5.40 (m, 128H), 4.30-4.10 (m,1024H), 4.00 (t, J = 6.5 Hz, 256H), 3.85-3.83 (m, 256H), 3.06-2.66 (m, 128H), 3.01-2.99 (m, 256H), 2.60-2.24 (m, 364H), 2.34-2.32 (m, 256H), 1.83–1.66 (m, 1276H), 1.55-1.38 (m, 512H), 1.36-1.24 (m, 256H), 1.18 (s, 576H), 0.98 (t, J = 7.4 Hz, 384H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.90, 172.53, 165.09, 163.43, 156.45, 156.14, 144.42, 140.31, 132.21, 125.62, 122.74, 122.53, 121.51, 120.31, 118.76, 114.99, 114.24, 108.64, 67.98, 67.61, 65.93, 65.45, 58.57, 51.45, 46.35, 42.75, 40.78, 38.05, 33.63, 31.13, 29.53, 28.58, 24.31, 21.49, 19.20, 18.52, 17.28, 13.84.

IR (Nujol) (cm^{-1}): 3397 (N-H), 2935 (C-H), 1730 (C=O), 1579 (COO^-_{asym}), 1400 (COO^-_{sym}).



PPI$_4$CzB2:

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.11-8.09 (m, 16H), 7.49-7.45 (m, 16H), 7.44-7.40 (m, 16H), 7.24-7.22 (m, 16H), 5.35 (s, 8H), 5.42-5.25 (m, 8H), 4.67-4.57 (m, 8H), 4.39-4.10 (m, 64H), 3.95-3.61 (m, 8H), 3.14 –3.06 (m, 16H), 2.72-2.52 (m, 44H), 2.37-2.27 (m, 16H), 2.02-1.05 (m, 268H), 1.22 (s, 24H), 1.01 (s, 24H), 0.94-0.88 (m, 84H), 0.68 (s, 24H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.15, 172.96, 172.81, 172.73, 172.43, 172.21, 171.89, 155.89, 140.31, 139.41, 125.62, 122.72, 120.30, 118.75, 108.60, 76.71, 74.85, 74.67, 66.36, 66.21, 66.12, 65.98, 65.70, 56.62, 56.10, 49.93, 46.78, 46.70, 42.84, 42.27, 40.75, 39.65, 39.50, 38.04, 37.90, 36.88, 36.52, 36.17, 35.78, 31.85, 31.79, 29.59, 29.20, 29.15, 28.75, 28.62, 28.21, 28.01, 27.65, 24.40, 24.24, 23.82, 22.81, 22.56, 20.98, 19.26, 18.70, 18.05, 17.66, 11.82.

IR (Nujol) (cm^{-1}): 3385 (N-H), 2942 (C-H), 1733 (C=O), 1557 (COO^-_{asym}), 1438 (COO^-_{sym}).

PPI_8CzB2:

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.11-8.09 (m, 32H), 7.48-7.45 (m, 32H), 7.43-7.40 (m, 32H), 7.25-7.22 (m, 32H), 5.36 (s, 16H), 5.42-5.25 (m, 16H), 4.67-4.57 (m, 16H), 4.39-4.10 (m, 128H), 3.95-3.61 (m, 16H), 3.14 –3.06 (m, 32H), 2.72-2.52 (m, 84H), 2.37-2.27 (m, 32H), 2.02-1.05 (m, 528H), 1.22 (s, 48H), 1.01 (s, 48H), 0.94-0.88 (m, 168H), 0.68 (s, 48H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 179.13, 172.98, 172.89, 172.75, 172.49, 172.23, 171.92, 155.92, 140.34, 139.45, 125.62, 122.78, 120.32, 118.76, 108.63, 76.75, 74.86, 74.68, 66.38, 66.24, 66.13, 65.99, 65.71, 56.63, 56.11, 49.95, 46.77, 46.71, 42.85, 42.28, 40.85, 39.68, 39.51, 38.07, 37.97, 36.88, 36.52, 36.17, 35.78, 31.85, 31.79, 29.59, 29.20, 29.15, 28.75, 28.62, 28.21, 28.01, 27.66, 24.40, 24.25, 23.83, 22.81, 22.56, 20.99, 19.26, 18.70, 18.06, 17.68, 11.83.

IR (Nujol) (cm^{-1}): 3388 (N-H), 2943 (C-H), 1733 (C=O), 1557 (COO^-_{asym}), 1436 (COO^-_{sym}).

PPI_{16}CzB2:

^{1}H-NMR (300 MHz, $CDCl_3$, δ) 8.08-8.06 (m, 64H), 7.46-7.41 (m, 64H), 7.39-7.37 (m, 64H), 7.22-7.18 (m, 64H), 5.32 (s, 32H), 5.44-5.13 (32H), 4.66-4.51 (m, 32H), 4.35-4.04 (m, 256H), 3.13-2.88 (m, 64H), 2.64-2.52 (m, 160H), 2.35-2.25 (m, 108H), 2.04-1.05 (m, 1056H), 1.18 (s, 96H), 0.98 (s, 96H), 0.92-0.86 (m, 336H), 0.66 (s, 96H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 179.15, 172.86, 172.83, 172.71, 172.52, 172.21, 171.90, 155.62, 140.14, 139.43, 125.63, 122.73, 120.30, 118.67, 108.66, 76.74, 74.83, 74.68, 66.41, 66.25, 66.10, 65.90, 65.73, 56.65, 56.08, 49.93, 46.87, 46.72, 42.83, 42.28, 40.84, 39.62, 39.49, 38.07, 37.97, 36.82, 36.51, 36.18, 35.79, 31.82, 31.73, 29.56, 29.21, 29.11, 28.75, 28.62, 28.21, 28.03, 27.66, 24.40, 24.23, 23.83, 22.81, 22.56, 20.97, 19.26, 18.70, 18.06, 17.68, 11.83.

IR (Nujol) (cm^{-1}): 3389 (N-H), 2936 (C-H), 1729 (C=O), 1548 (COO^-_{asym}), 1439 (COO^-_{sym})

<u>PPI$_{32}$CzB2:</u>

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.09-8.07 (m, 128H), 7.45-7.41 (m, 128H), 7.39-7.37 (m, 128H), 7.21-7.18 (m, 128H), 5.33 (s, 64H), 5.45-5.15 (64H), 4.65-4.50 (m, 64H), 4.32-4.01 (m, 512H), 3.12-3.01 (m, 128H), 2.62-2.54 (m, 320H), 2.33-2.23 (m, 228H), 2.03-1.01 (m, 2112H), 1.19 (s, 192H), 0.99 (s, 192H), 0.91-0.84 (m, 672H), 0.65 (s, 192H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 179.14, 172.96, 172.87, 172.73, 172.45, 172.22, 171.92, 155.92, 140.34, 139.44, 125.62, 122.78, 120.32, 118.75, 108.63, 76.75, 74.86, 74.68, 66.38, 66.24, 66.13, 65.92, 65.71, 56.63, 56.11, 49.95, 46.78, 46.73, 42.85, 42.28, 40.85, 39.68, 39.51, 38.07, 37.97, 36.88, 36.52, 36.30, 35.78, 31.83, 31.79, 29.59, 29.21, 29.15, 28.75, 28.62, 28.21, 28.01, 27.68, 24.40, 24.25, 23.83, 22.80, 22.56, 20.99, 19.26, 18.70, 18.08, 17.68, 11.82.

IR (Nujol) (cm^{-1}): 3388 (N-H), 2944 (C-H), 1729 (C=O), 1549 (COO^-_{asym}), 1436 (COO^-_{sym}).

$PPI_{64}CzB2$:

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.08-8.06 (m, 256H), 7.45-7.41 (m, 256H), 7.40-7.38 (m, 256H), 7.21-7.18 (m, 256H), 5.33 (s, 128H), 5.45-5.12 (128H), 4.65-4.51 (m, 128H), 4.37-4.04 (m, 1024H), 3.13-3.03 (m, 256H), 2.65-2.51 (m, 640H), 2.33-2.25 (m, 620H), 2.05-1.05 (m, 4348H), 1.19 (s, 384H), 0.99 (s, 384H), 0.94-0.86 (m, 1344H), 0.65 (s, 384H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ): 179.15, 172.97, 172.88, 172.74, 172.45, 172.21, 171.95, 155.98, 140.34, 139.45, 125.65, 122.78, 120.32, 118.74, 108.63, 76.75, 74.89, 74.68, 66.38, 66.24, 66.13, 65.94, 65.71, 56.63, 56.11, 49.91, 46.77, 46.73, 42.85, 42.28, 40.85, 39.65, 39.51, 38.03, 37.97, 36.88, 36.52, 36.17, 35.75, 31.85, 31.75, 29.59, 29.20, 29.14, 28.73, 28.62, 28.21, 28.02, 27.66, 24.40, 24.26, 23.83, 22.82, 22.56, 20.95, 19.26, 18.70, 18.09, 17.68, 11.82.

IR (Nujol) (cm^{-1}): 3389 (N-H), 2943 (C-H), 1730 (C=O), 1550 (COO^{-}_{asym}), 1436 (COO^{-}_{sym}).

3. Supporting Tables

Table S1. Main IR data (cm^{-1}) for ionic hybrid dendrimers

Compound	N-H (carbamate)	COO^-_{asym} (carboxylate)	COO^-_{sym} (carboxylate)	C=O (ester and carbamate)
PPI_4CzA1	3368 cm^{-1}	1580 cm^{-1}	1400 cm^{-1}	1728 cm^{-1}
PPI_8CzA1	3400 cm^{-1}	1580 cm^{-1}	1401 cm^{-1}	1727 cm^{-1}
$PPI_{16}CzA1$	3384 cm^{-1}	1578 cm^{-1}	1401 cm^{-1}	1729 cm^{-1}
$PPI_{32}CzA1$	3386 cm^{-1}	1578 cm^{-1}	1401 cm^{-1}	1729 cm^{-1}
$PPI_{64}CzA1$	3386 cm^{-1}	1578 cm^{-1}	1401 cm^{-1}	1729 cm^{-1}
PPI_4CzA2	3398 cm^{-1}	1579 cm^{-1}	1400 cm^{-1}	1730 cm^{-1}
PPI_8CzA2	3397 cm^{-1}	1579 cm^{-1}	1400 cm^{-1}	1730 cm^{-1}
$PPI_{16}CzA2$	3394 cm^{-1}	1576 cm^{-1}	1401 cm^{-1}	1729 cm^{-1}
$PPI_{32}CzA2$	3396 cm^{-1}	1578 cm^{-1}	1401 cm^{-1}	1730 cm^{-1}
$PPI_{64}CzA2$	3397 cm^{-1}	1579 cm^{-1}	1400 cm^{-1}	1730 cm^{-1}
PPI_4CzB1	3400 cm^{-1}	1577 cm^{-1}	1408 cm^{-1}	1729 cm^{-1}
PPI_8CzB1	3373 cm^{-1}	1573 cm^{-1}	1406 cm^{-1}	1728 cm^{-1}
$PPI_{16}CzB1$	3384 cm^{-1}	1576 cm^{-1}	1405 cm^{-1}	1726 cm^{-1}
$PPI_{32}CzB1$	3385 cm^{-1}	1576 cm^{-1}	1404 cm^{-1}	1729 cm^{-1}
$PPI_{64}CzB1$	3385 cm^{-1}	1573 cm^{-1}	1404 cm^{-1}	1729 cm^{-1}
PPI_4CzB2	3385 cm^{-1}	1557 cm^{-1}	1438 cm^{-1}	1733 cm^{-1}
PPI_8CzB2	3388 cm^{-1}	1557 cm^{-1}	1436 cm^{-1}	1733 cm^{-1}
$PPI_{16}CzB2$	3389 cm^{-1}	1548 cm^{-1}	1439 cm^{-1}	1729 cm^{-1}
$PPI_{32}CzB2$	3388 cm^{-1}	1549 cm^{-1}	1436 cm^{-1}	1729 cm^{-1}
$PPI_{64}CzB2$	3389 cm^{-1}	1550 cm^{-1}	1436 cm^{-1}	1730 cm^{-1}

Table S2. Main shifts in the ^{1}H NMR spectra of dendrons and ionic hybrid dendrimers for G3 complexes.

Compound	$-C\underline{H}_2-NH_2$	$C\underline{H}_2-CH_2-NH_2$	$N\underline{H}COO$	$C\underline{H}_3CCOOH$	$-CC\underline{H}_2O-$
$PPI_{16}-NH_2$	2.56	1.43			
CzA1			4.71/5.30	1.25	4.22/4.21
CzA2			5.22	1.20	4.19/4.14
CzB1			4.79/5.46	1.24	4.25/4.20
CzB2			4.61/5.04	1.20	4.20/4.16
PPI_{16}CzA1	2.85	1.65	6.06	1.08	4.19/4.15
PPI_{16}CzA2	2.86	1.70	5.41	1.17	4.17/4.16
PPI_{16}CzB1	2.88	1.68	6.04/5.76	1.08	4.22/4.11
PPI_{16}CzB2	2.90	1.65	5.42/5.28	1.08	4.31/4.22

Table S3. Thermal stability of dendrimers under study.

Ionic hybrid dendrimer	$T_{5\%}$	T^{a}_{onset} (ºC)
PPI_4CzA1	145	237
PPI_8CzA1	151	215
$PPI_{16}CzA1$	129	237
$PPI_{32}CzA1$	135	235
$PPI_{64}CzA1$	172	234
PPI_4CzB1	182	258
PPI_8CzB1	168	246
$PPI_{16}CzB1$	191	260
$PPI_{32}CzB1$	202	242
$PPI_{64}CzB1$	205	241
PPI_4CzA2	169	229
PPI_8CzA2	159	221
$PPI_{16}CzA2$	234	247
$PPI_{32}CzA2$	234	248
$PPI_{64}CzA2$	239	246
PPI_4CzB2	151	244
PPI_8CzB2	135	235
$PPI_{16}CzB2$	224	273
$PPI_{32}CzB2$	228	276
$PPI_{64}CzB2$	230	279

Table S4. Photophysical data for hybrid dendrimers derived from CzA1 and CzA2 dendrons.

Compound	λabs [nm] (CH_2Cl_2)	λabs [nm] (film)	λem [nm] (CH_2Cl_2)	λem [nm] (film)	Compound	λabs [nm] (CH_2Cl_2)	λabs [nm] (film)	λem [nm] (CH_2Cl_2)	λem [nm] (film)
PPI_4CzA1	230	236	352	355(h)	PPI_4CzA2	238	240	352,5	355
	265	265	368,5	372		265	264	369	372,5
	295	296	388(h)	389,5(h)		295	296	388(h)	389,5(h)
	332	332				332	332		
	347	347				347	348		
PPI_8CzA1	238	236	352	359	PPI_8CzA2	238	240	352,5	356
	264	265	369,5	372,5		265	266	369	371
	295	295	389(h)	392(h)		295	296	388(h)	389,5(h)
	332	332				332	332		
	347	348				347	348		
PPI_{16}CzA1	238,5	239	352,5	353,5	PPI_{16}CzA2	238,5	240	352,5	355,5
	264	267	369,5	371		263,5	268	369	370,5
	295	297	388(h)	389(h)		295	296	388,5(h)	389(h)
	332	335				332,5	332		
	347	350				347	348		
PPI_{32}CzA1	238	244	352,5	354,5	PPI_{32}CzA2	238	240	352	356
	265	268	367	369		265	264	369	371,5
	295	296	390(h)	391,5(h)		295	296	388(h)	389(h)
	332,5	332				332	336		
	348	348				347	348		
PPI_{64}CzA1	238,5	232	352,5	354	PPI_{64}CzA2	238,5	240	352,5	355
	263,5	264	368,5	370		264	264	368,5	370,5
	295	296	388(h)	389,5(h)		295	296	388(h)	389,5(h)
	332,5	332				331,5	332		
	347	348				347	348		

[a] Measured in CH_2Cl_2 solution, [b] shoulder (h)

Table S5. Photophysical data for hybrid dendrimers derived from CzB1 and CzB2 dendrons.

Compound	λabs [nm] (CH_2Cl_2)	λabs [nm] (film)	λem [nm] (CH_2Cl_2)	λem [nm] (film)	Compound	λabs [nm] (CH_2Cl_2)	λabs [nm] (film)	λem [nm] (CH_2Cl_2)	λem [nm] (film)
PPI_4CzB1	238	236	352,5	355,5	PPI_4CzB2	238	240	352,5	354
	265	265	368,5	370,5		265	266	368,5	370,5
	295	295	388(h)	389,5(h)		295	296	388(h)	389(h)
	332	332				332	332		
	347	348				347	348		
PPI_8CzB1	238	236	352	354,5	PPI_8CzB2	238	240	352,5	354,5
	265	266	368	370		265	268	369	370
	295	296	388(h)	389,5(h)		295	296	389(h)	389,5(h)
	332	333				332	332		
	347	348				347	348		
$PPI_{16}CzB1$	240	236,5	352	353,5	$PPI_{16}CzB2$	239	240	352	354
	264	266	369	369,5		265	268	370	370,5
	296	297	388(h)	389,5(h)		295	296	388(h)	389(h)
	332	333,5				333	332		
	348	348				346	348		
$PPI_{32}CzB1$	236	244	352	354,5	$PPI_{32}CzB2$	238	240	352	354,5
	264	268	369	370		265	264	369	371
	296	296	388,5(h)	391(h)		295	296	389(h)	389,5(h)
	332	336				333	336		
	348	348				347	348		
$PPI_{64}CzB1$	236	232	352,5	353	$PPI_{64}CzB2$	238	240	352	354
	264	264	368,5	369,5		264	264	369	370
	296	296	388,5(h)	390,5(h)		295	296	388(h)	389(h)
	332	336				332	332		
	348	348				347	348		

[a] Measured in CH_2Cl_2 solution, [b] shoulder (h)

Table S6. Molar absorptivity parameters for ionic derivatives CzA1 dendrimers and calculated numbers of carbazoles.

Compound	Absorptivity molar (ε)*	No of carbazoles (actual)	No of carbazoles (calculated)
CzA1	44400	1	1
PPI_4CzA1	140800	4	3.2
PPI_8CzA1	421200	8	9.5
$PPI_{16}CzA1$	739500	16	16.6
$PPI_{32}CzA1$	1153000	32	26
$PPI_{64}CzA1$	2712000	64	61.1

*Data at 265 nm

Table S7. Molar absorptivity parameters for ionic CzB1 dendrimer derivatives and calculated numbers of carbazoles.

Compound	Absorptivity molar (ε)*	No of carbazoles (actual)	No of carbazoles (calculated)
CzB1	11320	1	1
PPI_4CzB1	89000	4	7.9
PPI_8CzB1	178000	8	15.7
$PPI_{16}CzB1$	776365	16	68.6
$PPI_{32}CzB1$	691887	32	61.1
$PPI_{64}CzB1$	1220000	64	107.8

*Data at 265 nm.

Table S8. Quantum yields for the PPI_nCzB1 family

Compound	Quantum yields (Φ)
Cz	0.101
$CzNH_2$	0.027
CzB1	0.093
PPI_4CzB1	0.098
PPI_8CzB1	0.123
$PPI_{16}CzB1$	0.149
$PPI_{32}CzB1$	0.107
$PPI_{64}CzB1$	0.100

[a] Onset oxidation and reduction potentials versus Ag/Ag^+,[b] Estimated from the onset oxidation and reduction potential by using HOMO = $-E_{onset(ox)}$ - 4.8 eV and LUMO = $-E_{onset(red)}$-4.8 eV., [c] Electrochemical band gaps determined using $Eg = E_{onset(ox)} - E_{onset(red)}$

Table S9. Cyclic voltammety data for ionic hybrid dendrimers

Compound	E_{ox} (V)	Compound	E_{ox} (V)
PPI_4CzA1	1.356; 1.766	PPI_4CzA2	1.295; 1.681
PPI_8CzA1	1.132; 1.395	PPI_8CzA2	1.326; 1.597
$PPI_{16}CzA1$	1.409; 1.719	$PPI_{16}CzA2$	1.412
$PPI_{32}CzA1$	1.326; 1.651	$PPI_{32}CzA2$	1.212; 1.648
$PPI_{64}CzA1$	1.283; 1.396	$PPI_{64}CzA2$	1.221; 1.781
PPI_4CzB1	1.284	PPI_4CzB2	1.294
PPI_8CzB1	1.301	PPI_8CzB2	1.353
$PPI_{16}CzB1$	0.945; 1.299	$PPI_{16}CzB2$	1.463
$PPI_{32}CzB1$	1.418	$PPI_{32}CzB2$	1.298; 1.516
$PPI_{64}CzB1$	1.362	$PPI_{64}CzB2$	1.223; 1.613

[a] Calculated from absorption spectrum λ onset.

4. Calculations based on the X-ray data

Smectic mesophases

The volume of a cylindrical molecule in the smectic phase can be calculated from its height d (measured experimentally) and its cross-section S:

$$V = d \times S = d \times \pi r^2 = d \times \pi \times \left(\text{Ø}/_2\right)^2 = d \times \pi/_4 \times \text{Ø}^2$$

and the cylinder diameter Ø is related to the density ρ by the following equation:

$$\rho = \frac{m}{V} = \frac{M/_{N_A}}{d \times \pi\text{Ø}^2/_{4 \times 10^{24}}} \approx 1$$

From the cylinder diameter it is possible to calculate the total cross-section S_t and the cross-section per dendron S_d:

$$S_t = \pi \times \left(\text{Ø}/_2\right)^2 \qquad\qquad S_d = \frac{S_t \times 2}{n}$$

m being the number of dendrons in each ionic hybrid dendrimer.

Columnar mesophases

The cross-sectional area S of each column in the two-dimensional rectangular lattice can be calculated as S = a x b/2, where a and b are the rectangular lattice constants (Table 3). The reason for dividing by 2 is the fact that the rectangular columnar mesophase usually contains two columns per elementary lattice. This assumption is supported by the fact that the S values obtained in this way are consistent with those deduced for the hexagonal columnar mesophase of $PPI_{64}CzA2$ and $PPI_{64}CzB2$. It must be pointed out that the gap between the rigid regions of neighboring columns is filled by the peripheral hydrocarbon chains and therefore the effective cross-section of the column corresponds to half the rectangular cell surface. The column cross-section S and the disc thickness h_d are related by the formula

$$h_d \times S = V_m$$

where is the molecule volume. In the absence of a scattering maximum related to the stacking distance, h_d cannot be measured experimentally but can be estimated from the above-mentioned formula taking into account that the molecule volume V_m is related to the density ρ and the molar mass M by the following equation:

$$\rho = (M \times 10^{24}/(N \times V_m)$$

where N is Avogadro's number. Making the density equal to 1 g cm^{-3}, the following equation is deduced:

$$h_d = M \times 10^{24}/(N \times S)$$

From this equation the values for h_d shown in Table 3 are deduced.

5. Supporting Figures

FT-IR spectra

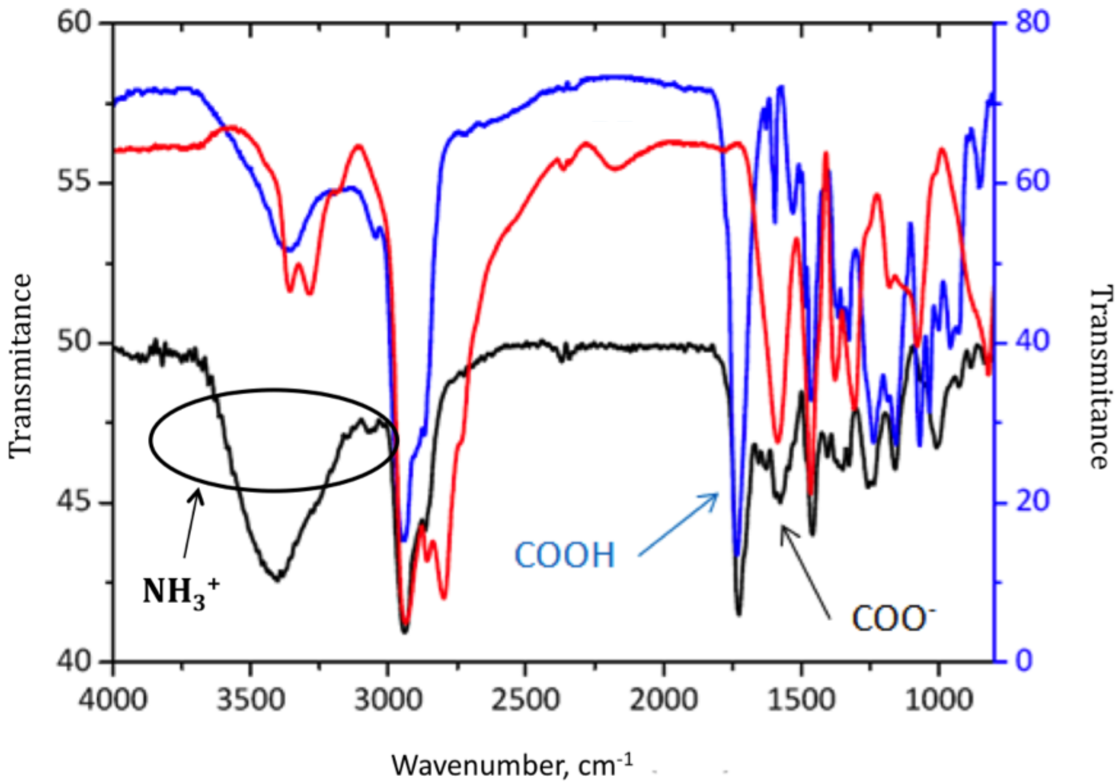


Figure S1. FT-IR spectra for $PPI_{16}CzB1$ (black), dendron CzB1 (blue) and dendrimer PPI_{16}-NH_2 (red)

NMR Spectra

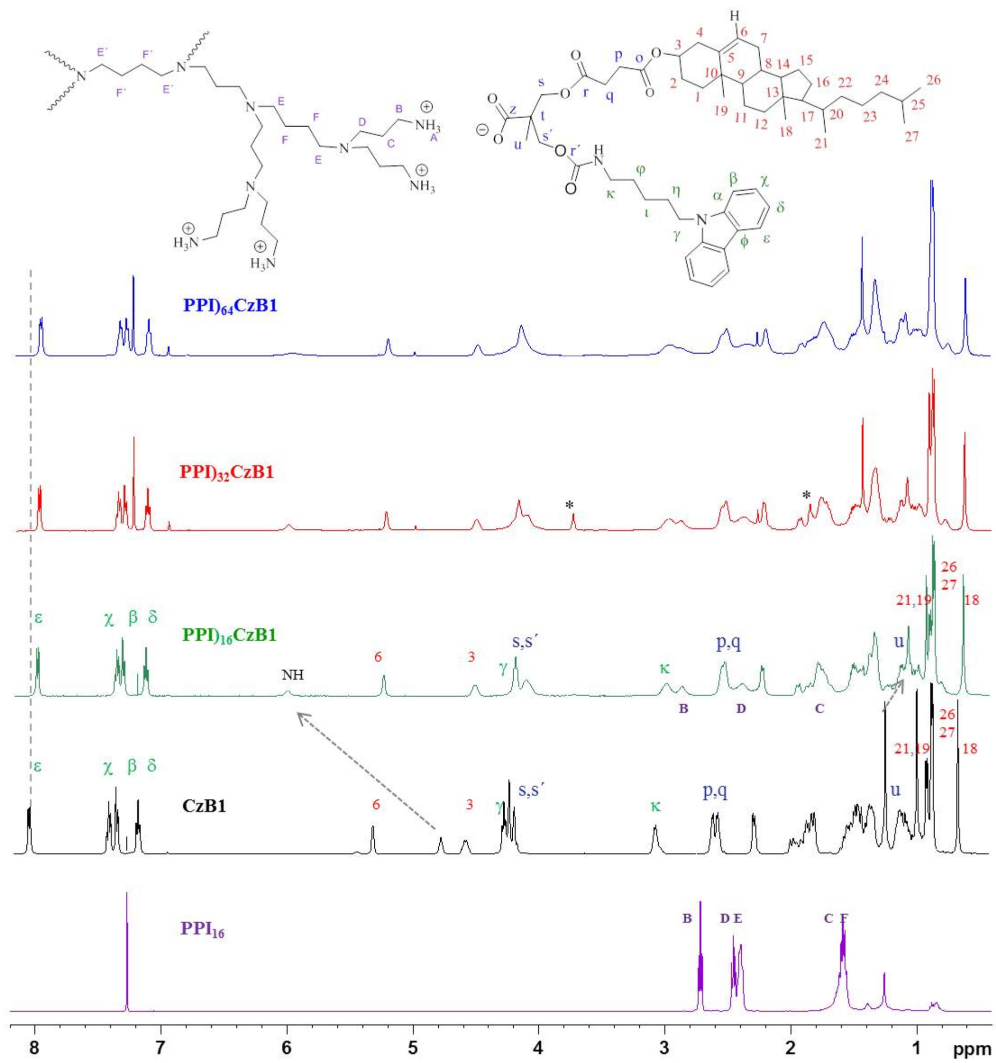


Fig. S2. Proton assignment for PPI_{16}CzB1 and comparative spectra of the dendron CzB1 dendrimer PPI_{16} (G=3) and its ionic hybrid dendrimers PPI_{16}CzB1, PPI_{32}CzB1, PPI_{64}CzB1. (500 MHz, $CDCl_3$, 25 °C). *Residual THF.

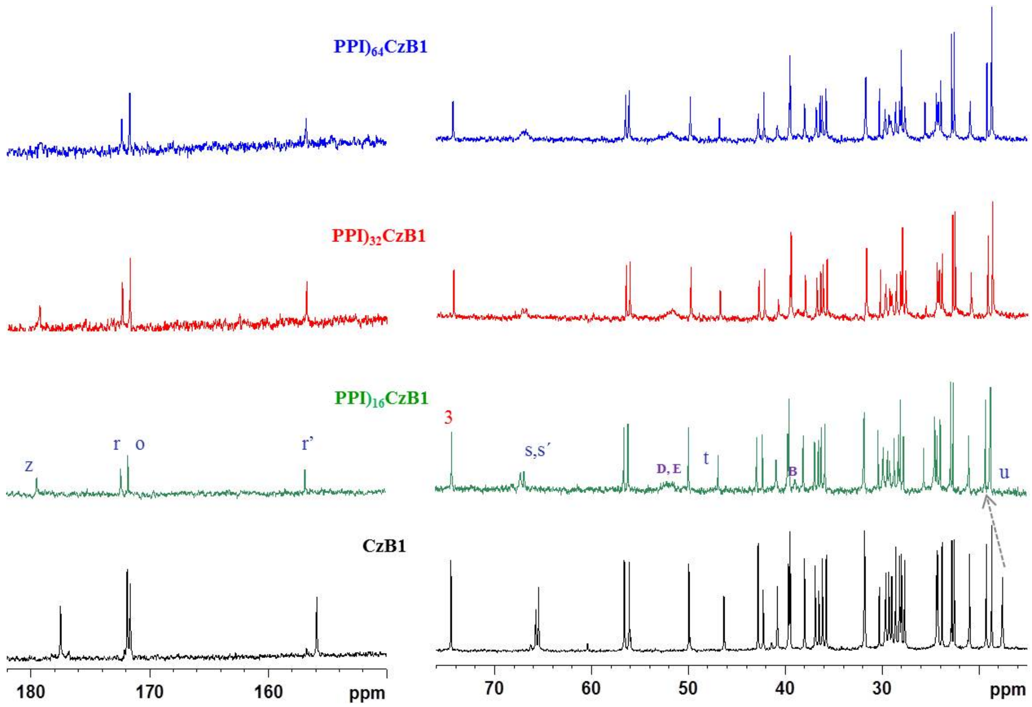


Fig. S3. Expansions of [13]C NMR spectra for dendron CzB1 and its ionic dendrimers: PPI_{16}CzB1, PPI_{32}CzB1, PPI_{64}CzB1. (125 MHz, $CDCl_3$, 25 ºC).

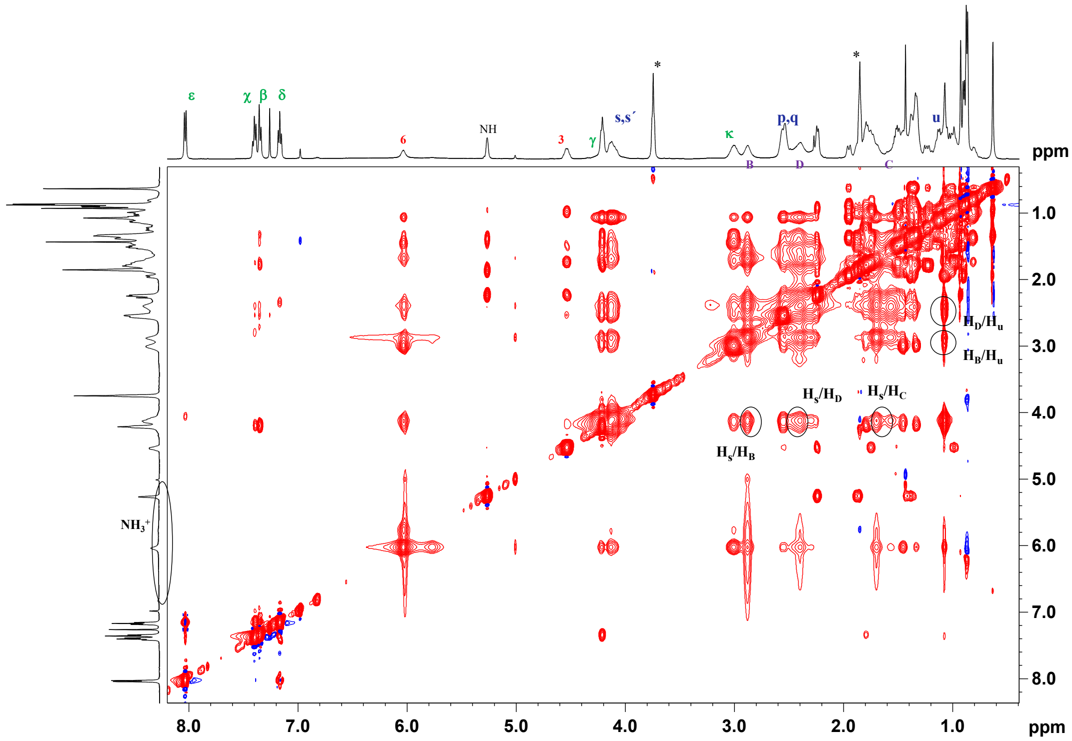


Figure S4. NOESY spectrum of $PPI_{16}CzB1$ ($CDCl_3$, 298 K, tmix = 200 ms).

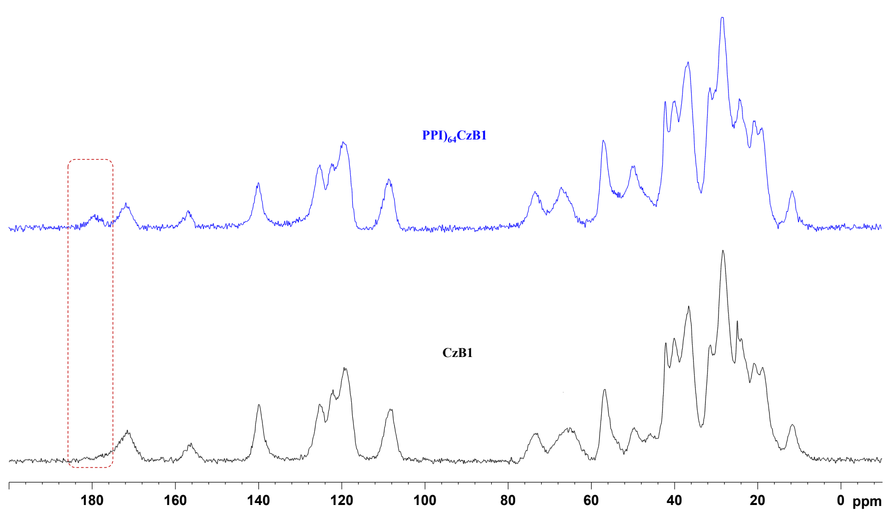


Figure S5. ^{13}C CPMAS NMR spectra of CzB1dendron and its ionic hybrid dendrimer $PPI_{64}CzB1$

Differential Scanning Calorimetry

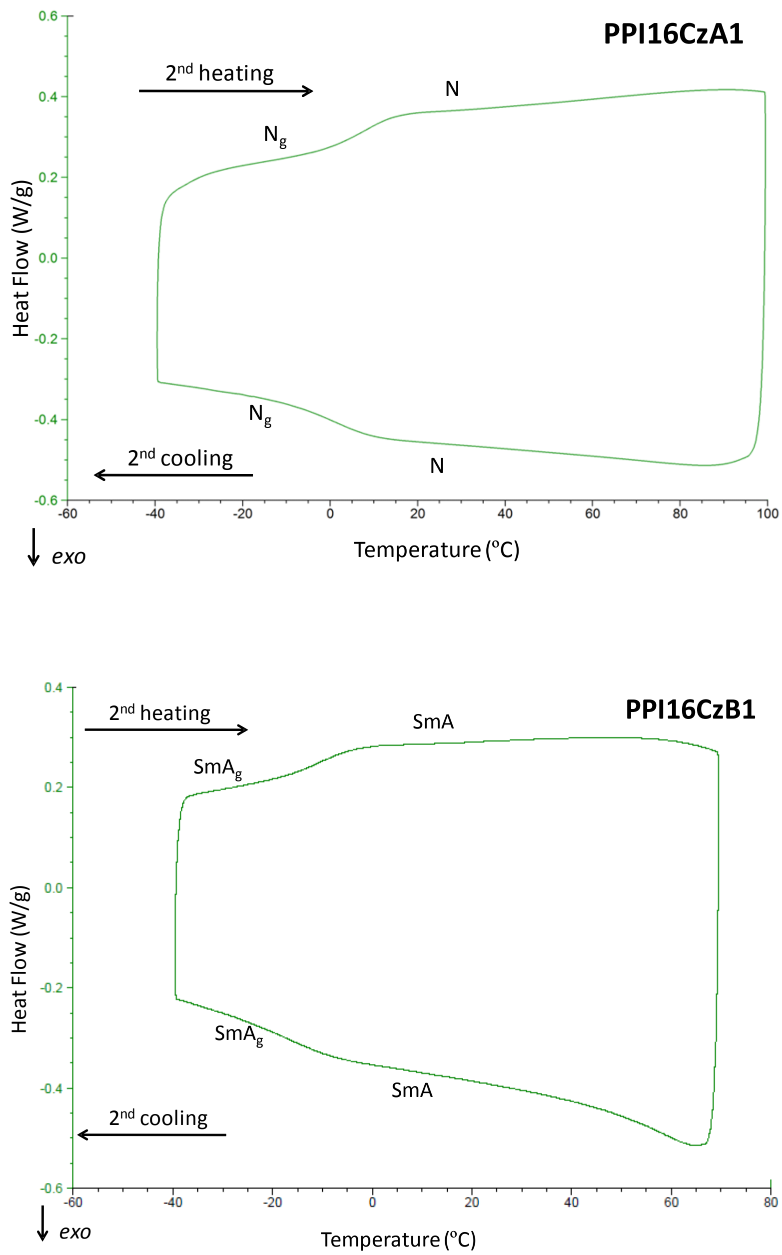
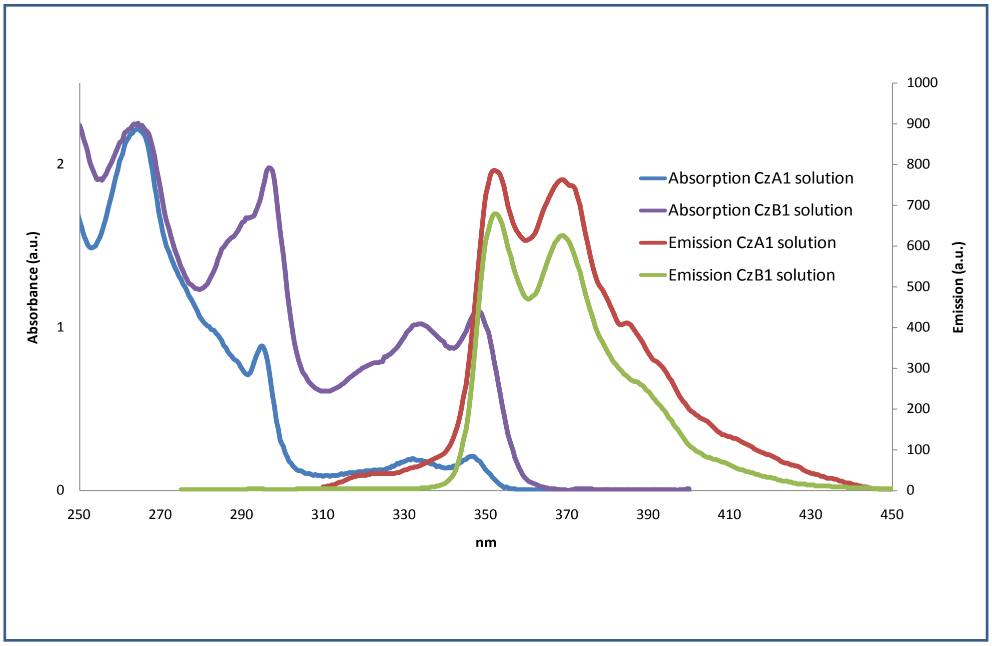
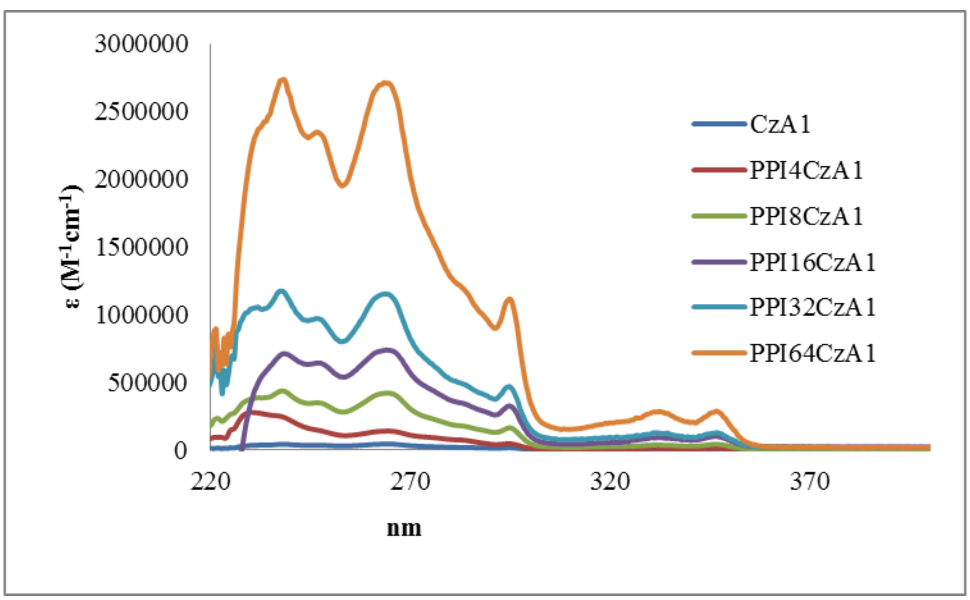


Figure S6. a) DSC scan at 10 ºC/min for ionic hybrid dendrimer $PPI_{16}CzA1$, **b)** DSC scan at 10 ºC/min for ionic hybrid dendrimer $PPI_{16}CzB1$

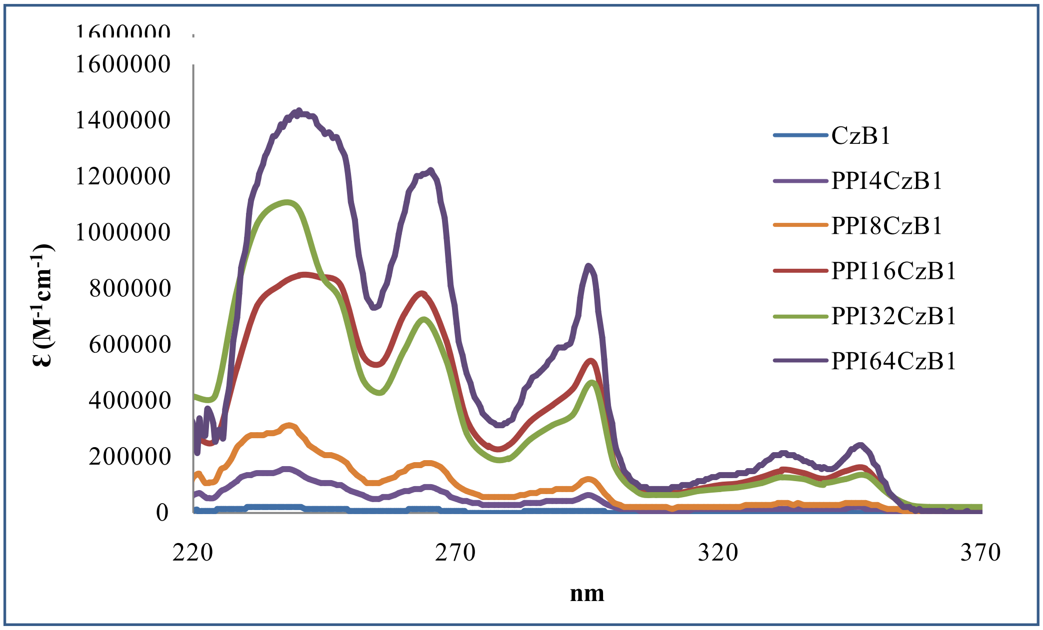
UV-Vis absorption and emission spectra



a)



b)



c)

Figure S7. Normalized UV-vis absorption spectra in CH_2Cl_2 solution of of a) dendrons, b) dendrimers PPI_nCzA1, c) dendrimer PPI_nCzB1

Cyclic voltammetry plots

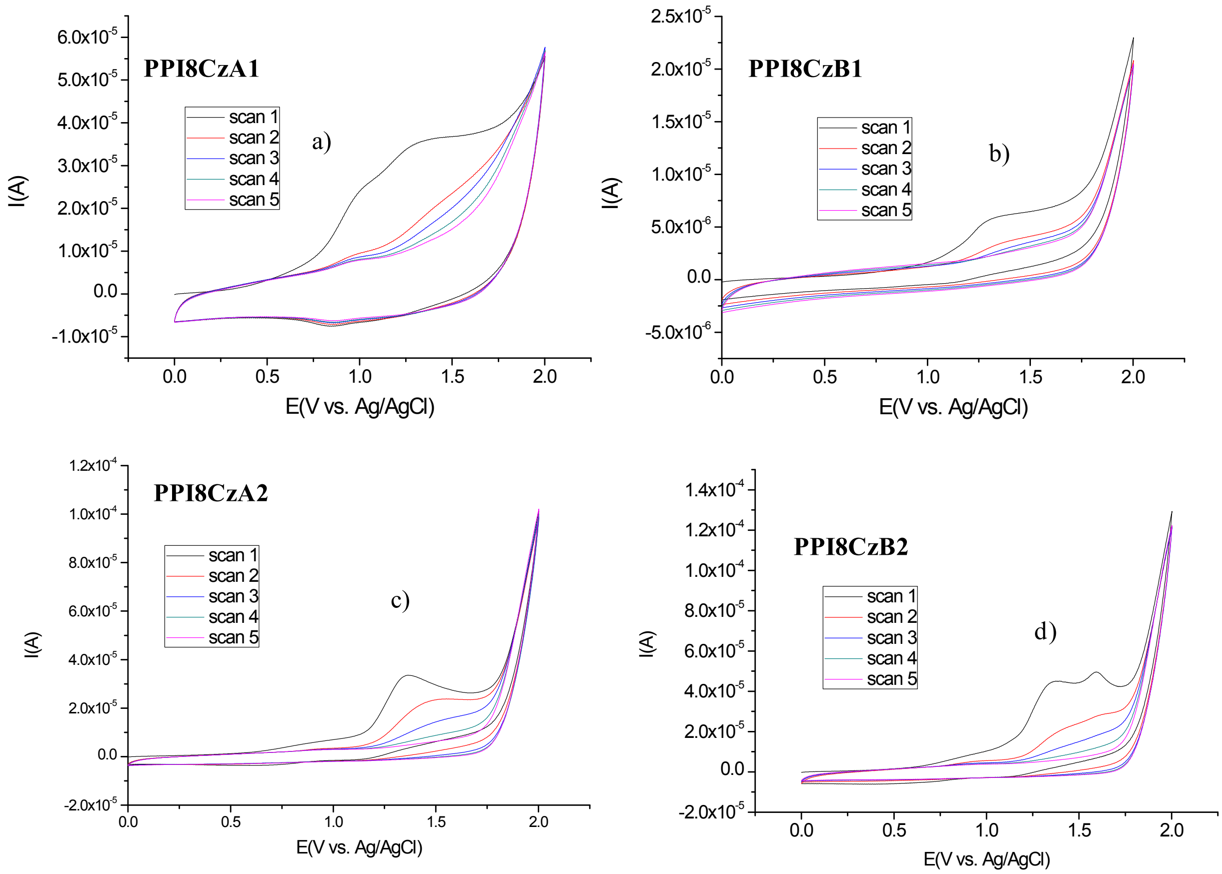


Figure S8. Cyclic voltammograms of the first five cycles of: a) PPI$_8$CzA1, b) PPI$_8$CzB1, c) PPI$_8$CzA2, d) PPI$_8$CzB2.