

Supporting Information

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Supramolecular Architectures from Bent-Core Dendritic Molecules**

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SUPPORTING INFORMATION

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S1. Experimental Section.

- Materials and Techniques.

All chemical reagents were purchased from Aldrich and were used as received. PPI-(NH₂)₄ (G1) was purchased from SyMO-Chem BV (Eindhoven, The Netherlands). Solvents were purified and rigorously dried over appropriate drying agents and distilled prior to use. All atmosphere-sensitive reactions were carried out under dry argon using standard Schlenk techniques.

Analytical TLC was performed on 60F 254, 60A-15 mm silica gel polyester plates (SDS). Column chromatography was carried out under flash conditions using 60 Å silica gel (SDS). Silica gel type 7749 (with gypsum, Merck) was used for centrifugal force mediated preparative thin layer chromatography in conjunction with a Chromatotron from Harrison Research Europe (model 8924).

In order to confirm the molecular structures of the synthesized compounds the following analytical methods were applied.

The compositions of the synthesized compounds were determined by elemental analysis performed on a PERKIN-ELMER 24C CHNS elemental analyzer. FT-IR spectra were recorded on a THERMONICOLET Avatar 360 using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240 Analyzer. Mass spectrometry studies (FAB+, MALDI+) were performed on VG AutoSpec EBE and Microflex (MALDI-ToF) systems. The UV-spectra were obtained on a UV-spectrophotometer (UV4-2000 of ATI-UNICAM) using HELMA quartz cells (10 mm width).

¹H NMR spectra were recorded on spectrometers operating at 300.13 (Bruker ARX-300), 400.13 (Bruker AV-400) or 500.13 (Bruker AV-500) MHz, whereas ¹³C NMR spectra were recorded at 75.47, 100.5 and 125.7 MHz, respectively. Chemical shifts are given in ppm relative to TMS. NMR experiments in solution were carried out using standard pulse sequences on Bruker spectrometers. ¹H-¹³C HSQC experiments were used in conjunction with ¹H-¹³C HMBC, ¹H-¹H COSY and ¹H-¹H NOESY to complete the assignments of the resonances. Mixing time (between 0.6 and 1 s) was optimized by ¹H T₁ measurements and the relaxation delay was 3 s. ¹H NMR diffusion measurements (DOSY) were performed using a stimulated echo sequence with bipolar gradient pulses (BPLED). Diffusion time (Δ) was set to 140–180 ms. Pulsed gradients were incremented from 2 to 95% of the maximum strength in sixteen spaced steps with a duration (δ/2) between 1.4 and 1.8 ms.

The mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. NIKON and OLYMPUS BH-2 polarizing microscopes equipped with a LINKAM THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements performed with DSC TA Instrument Q-20 and Q-2000 systems. Thermogravimetric analysis (TGA) was performed using a TA Q5000IR instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. Molecular dimensions were estimated by molecular modeling (ChemSketch3D).

The X-ray investigations on non-oriented mesomorphic samples were carried out in Lindemann capillary tubes (diameter: 0.9 or 1 mm) using a PINHOLE (ANTON-PAAR) film camera.

Simultaneous small and wide-angle X-ray scattering (SAXS and WAXS, respectively) experiments for aggregates were performed using a Rigaku MicroMax-002+ microfocused beam (4 kW, 45 kV, 0.88 mA) in order to obtain direct information on the SAXS and WAXS reflections. CuK α radiation ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$) was collimated by three pinhole (0.4, 0.3, and 0.8 mm) collimators. The incident beam was normal to the surface of the sample. The scattered X-ray intensity was detected with a Fujifilm BAS-MS 2025 imaging plate system (15.2 x 15.2 cm², 50 μm resolution) and a two-dimensional Triton-200 X-ray detector (20 cm diameter, 200 μm resolution). An effective scattering vector range of $0.05 \text{ nm}^{-1} < q < 25 \text{ nm}^{-1}$ was obtained, where q is the scattering wavevector defined as $q = 4\pi \sin \theta / \lambda_{\text{CuK}\alpha}$, with a scattering angle of 2θ .

The TEM measurements were recorded on a TECNAI G² 20 (FEI COMPANY) microscope using a working voltage of 200 kV. The SEM measurements were performed on a QUANTA FEG 250 microscope. Advanced Microscopy Laboratory (LMA) of the Instituto de Nanociencia de Aragón (INA) owns both of the aforementioned systems.

- Synthesis of ionic dendrimers.

The synthesis of the ionic dendrimers was carried out according to the synthetic routes shown in Schemes S1, S2, S3 and S4.

Compounds **1a-d**, **2a-b**, **3**, **4a-b**, **5a-b**, **6e-f**, **7e-f**, **8e-f**, **9a.e**, **9a.f**, **9b.e**, **9b.f**, **10a.e**, **10a.f**, **10b.e**, **10b.f** and **PPI1-B1-10-14** have been described previously by different authors.¹⁻⁴

Chiral compounds **2c-d**, **4c-d**, **5c-d**, **9c.e**, **9d.e**, **10c.e**, **10d.e** were synthesized following synthetic methods adapted from those reported previously by some of us. Characterization data are given below.^{1, 2}

Synthetic methods used in the synthesis of compounds **11**, **12**, **13** and **14** and their characterization data are given below.

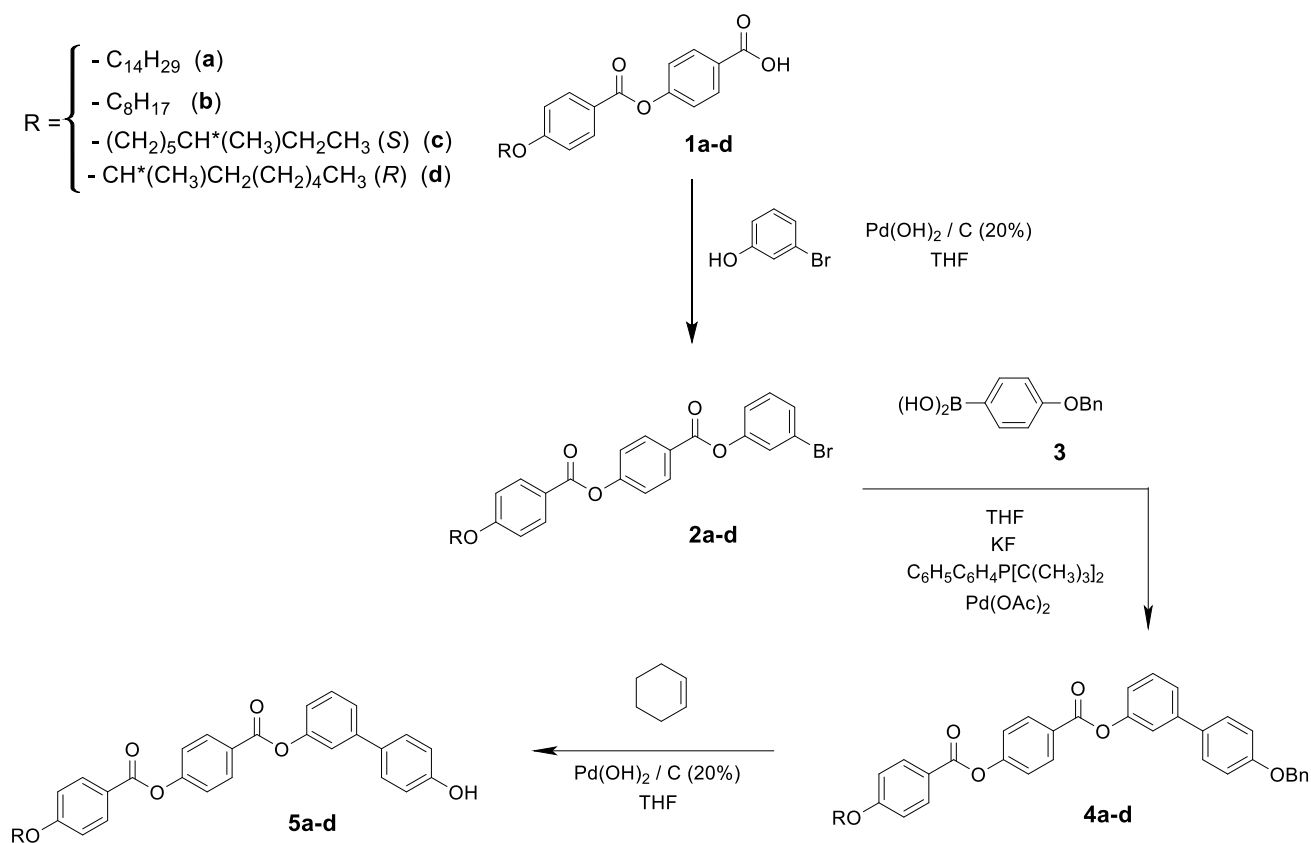
All new ionic dendrimers were prepared according to synthetic methodologies reported by us.² Characterization data are given below.

¹ N. Gimeno, J. Barberá, J. L. Serrano, M. B. Ros, M. R. de la Fuente, I. Alonso, C. L. Folcia, *Chem. Mater.* **2009**, 21, 4620.

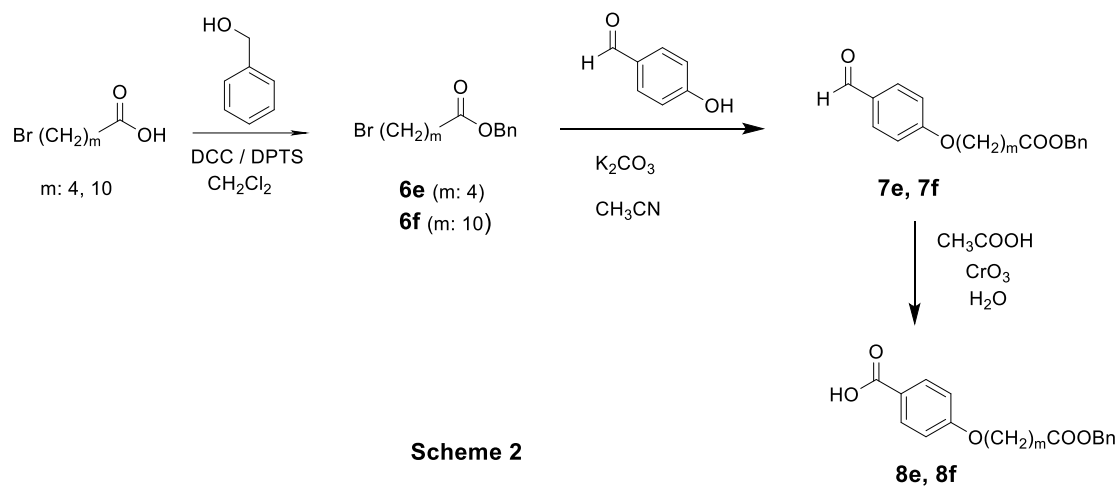
² J. Vergara, N. Gimeno, M. Cano, J. Barberá, P. Romero, J. L. Serrano, M. B. Ros, *Chem. Mater.* **2011**, 23, 4931

³ S.-C. Lin, R.-M. Ho, C.-Y. Chang, C.S. Hsu, *Chem.–Eur. J.* **2012**, 18, 9091.

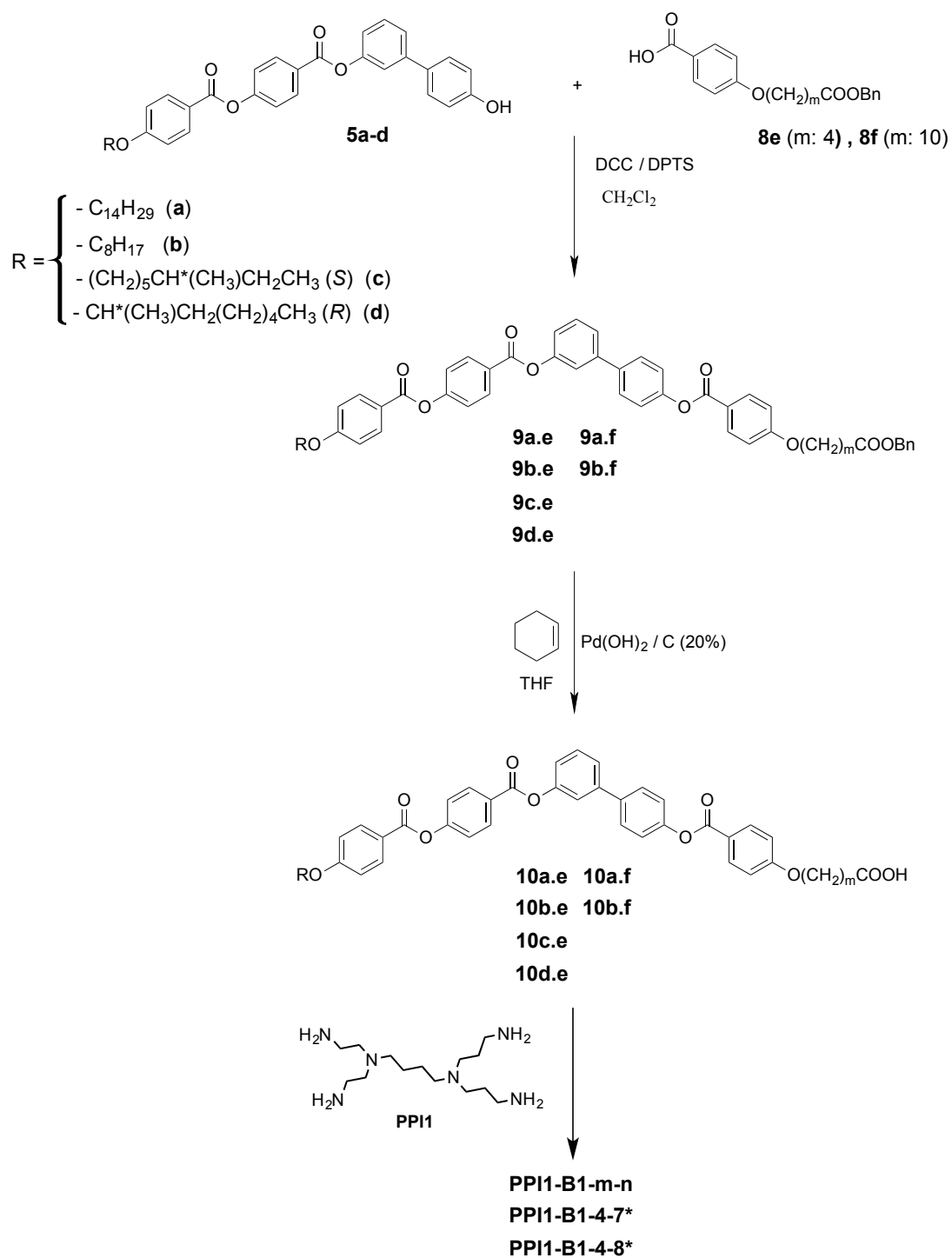
⁴ S. M. Kelly, R. Buchecker, *Helv. Chim. Acta*, **1988**, 71, 451.



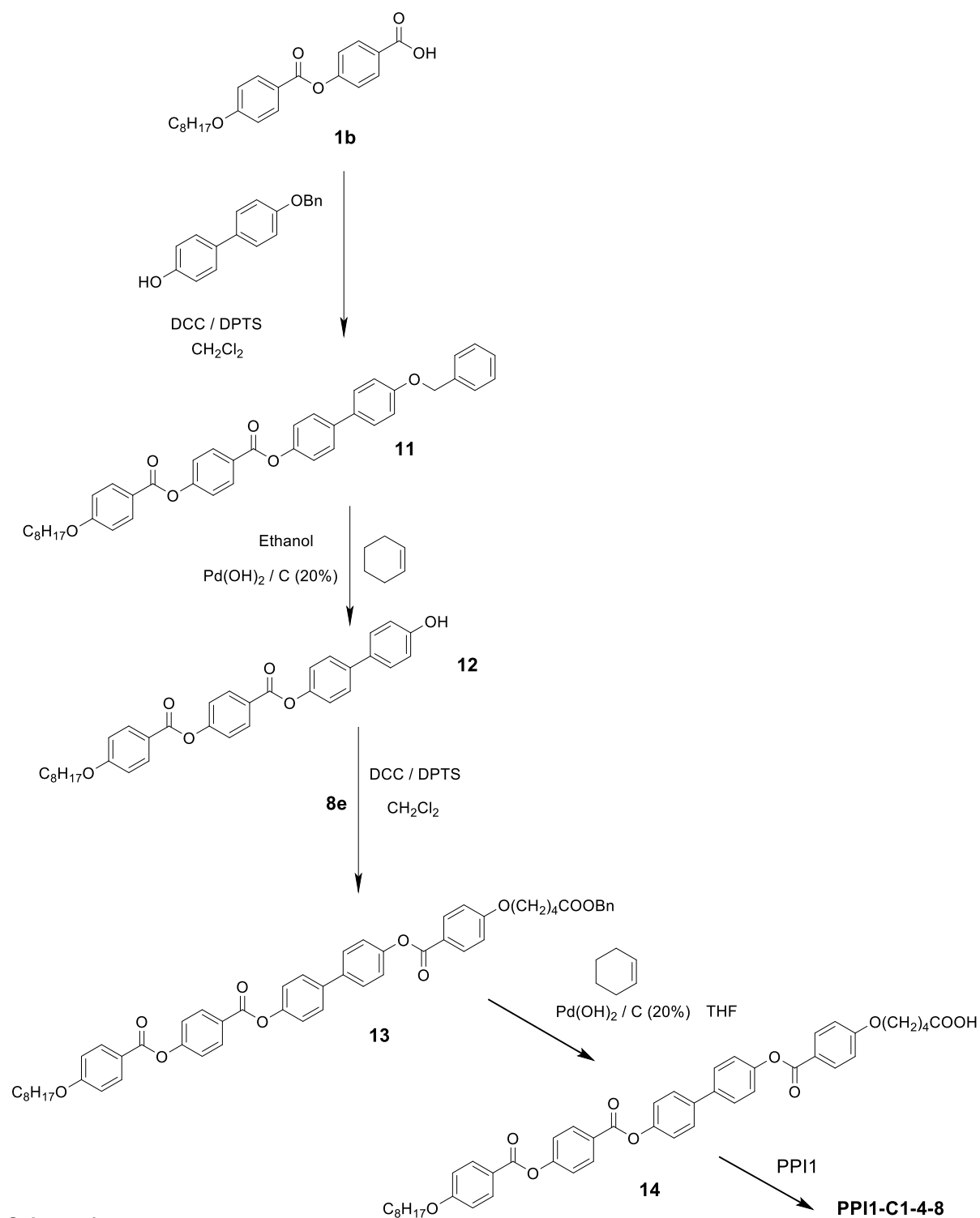
Scheme 1



Scheme 2



Scheme 3



Compound 2d. A mixture of compound **1d** (2.00 g, 5.4 mmol), 3-bromophenol (0.92 g, 5.4 mmol) and DMAP (0.07 g, 0.5 mmol) was dissolved in dry CH_2Cl_2 (50 mL). A solution of DCC (1.23 g, 5.9 mmol) in dry CH_2Cl_2 was added dropwise and the mixture was stirred at room temperature for 24 h. The white precipitate of *N,N'*-dicyclohexylurea was filtered off. The solvent was evaporated and the resulting product was purified by column chromatography (silica gel, eluent CH_2Cl_2) to give the product as a white

powder. Yield: 70%. **M.p.** 67 °C. **¹H NMR (400 MHz, CDCl₃):** δ, ppm = 0.91 (t, J = 6.9 Hz, 3H), 1.25-1.81 (m, 13H), 4.49-4.53 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 7.20-7.23 (m, 1H), 7.28-7.33 (m, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.43-7.49 (m, 2H), 8.17 (d, J = 8.9 Hz, 2H), 8.28 (d, J = 8.7 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ, ppm = 14.1, 19.6, 22.6, 25.4, 29.2, 31.8, 36.3, 74.2, 115.3, 120.6, 120.7, 122.2, 122.5, 125.3, 126.4, 129.2, 130.6, 131.9, 132.5, 151.4, 155.6, 163.1, 164.1, 164.3. **FTIR (KBr, ν: cm⁻¹):** 2914, 2857, 1735, 1608, 1589, 1270.

Compound 2c. Synthesis as for **2d**. Yield 81%. **M.p.** 73 °C. **¹H-NMR (100 MHz, CDCl₃) [δ, ppm]:** 0.85-0.89 (m, 6H), 1.13-1.17 (m, 2H), 1.31-1.46 (m, 7H), 1.80-1.88 (m, 2H), 4.06 (t, J = 6.5 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 7.18-7.23 (m, 1H), 7.31 (t, J = 8.3 Hz, 1H), 7.38 (d, J = 8.7 Hz, 2H), 7.41-7.44 (m, 2H), 8.15 (d, J = 8.9 Hz, 2H), 8.26 (d, J = 8.7 Hz, 2H). **¹³C-NMR (100 MHz, CDCl₃) [δ, ppm]:** 11.4, 19.2, 26.3, 26.9, 29.1, 29.5, 34.4, 36.5, 68.4, 114.4, 120.6, 120.9, 122.2, 122.5, 125.3, 126.4, 129.2, 130.6, 131.9, 132.4, 151.4, 155.6, 163.9, 164.1, 164.3. **FTIR (KBr, ν: cm⁻¹):** 2923, 2859, 1738, 1725, 1602, 1584, 1460, 1264, 1193, 1167.

Compound 4d. A mixture of compound **2d** (1.50 g, 2.8 mmol), compound **3** (0.91 g, 4.0 mmol), DCC (0.33 g, 5.60 mmol), 2-biphenyl-di-tert-butylphosphine (0.04 g) and Pd(OAc)₂ (0.02 g, 0.06 mmol) was dissolved in dry THF (30 mL) in a Schlenk tube. The mixture was stirred overnight. The reaction mixture was filtered, the solvent evaporated and the resulting solid was dissolved in dichloromethane. The solution was washed with NaOH (1M solution) and brine, dried with CaCl₂ and evaporated. The product was purified by column chromatography (silica gel, eluent CH₂Cl₂). Yield: 69%. **M.p.** 105 °C. **¹H NMR (300 MHz, CDCl₃):** δ = 0.91 (t, J = 6.9 Hz, 3H), 1.25-1.81 (m, 13H), 4.49-4.53 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 7.08 (d, J = 8.7 Hz, 1H), 7.20-7.23 (m, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.36-7.51 (m, 10H), 7.57 (d, J = 8.7 Hz, 1H), 8.17 (d, J = 8.9 Hz, 2H), 8.32 (d, J = 8.7 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ, ppm = 14.2, 19.7, 22.7, 25.6, 29.4, 31.9, 36.5, 70.3, 74.4, 115.4, 115.5, 120.0, 120.1, 120.8, 122.3, 124.4, 127.1, 127.6, 128.2, 128.4, 128.8, 129.9, 132.0, 132.6, 133.1, 137.1, 142.7, 143.8, 151.5, 155.6, 158.8, 163.2, 164.5, 164.7. **FTIR (KBr, ν: cm⁻¹):** 2945, 2866, 1726, 1603, 1504, 1280.

Compound 4c. Synthesis as for **4d**. Yield 83%. **M.p.** 112 °C. **¹H-NMR (100 MHz, CDCl₃) [δ, ppm]:** 0.85-0.89 (m, 6H), 1.13-1.17 (m, 2H), 1.31-1.46 (m, 7H) 1.80-1.88 (m, 2H), 4.06 (t, J = 6.5 Hz, 2H), 5.12 (s, 2H), 6.98 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 7.17-7.28 (m, 1H), 7.36-7.48 (m, 10H), 7.55 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H). **¹³C-NMR (100 MHz, CDCl₃) [δ, ppm]:** 11.4, 19.2, 26.3, 26.4, 26.9, 29.1, 29.5, 34.4, 36.5, 68.4, 70.1, 114.4, 115.2, 119.9, 120.0, 121.0, 122.1, 124.3, 127.0, 127.5, 128.0, 128.3, 128.6, 129.7, 131.8, 132.4, 133.0, 136.9, 142.5, 151.3, 155.4, 158.7, 163.9, 164.4, 164.5. **FTIR (KBr, ν: cm⁻¹):** 2924, 2854, 1732, 1603, 1510, 1258, 1161.

Compound 5d. Compound **4d** (1.0 g, 1.6 mmol) and cyclohexene (20 mL) were dissolved in ethanol (30 mL) under an Ar atmosphere. Pd(OH)₂/C(20%) (0.1 g) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was purified by column chromatography (silica gel, eluent CH₂Cl₂). Yield: 93%. **M.p.** 125 °C. **¹H NMR (300 MHz, CDCl₃):** δ = 0.91 (t, J = 6.9 Hz, 3H), 1.25-1.81 (m, 13H), 4.52 (q, J = 6.1 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.16-7.20 (m, 1H), 7.39-7.50 (m, 7H), 8.18 (d, J = 8.9 Hz, 2H), 8.32 (d, J = 8.7 Hz, 2H). **¹³C NMR (75 MHz, CDCl₃):** δ, ppm = 14.1,

19.6, 22.6, 25.4, 29.2, 31.8, 36.3, 74.2, 115.3, 115.7, 119.8, 119.9, 120.6, 122.1, 124.3, 126.8, 128.4, 129.7, 131.8, 132.5, 132.8, 142.5, 151.3, 155.4, 155.5, 163.1, 164.4, 164.7. FTIR (KBr, ν : cm^{-1}): 3420, 2988, 2802, 1724, 1605, 1545, 1250.

Compound 5c. Synthesis as for compound **5d**. Yield 93%. **M.p.** 131 °C. $^1\text{H-NMR}$ (100 MHz, CDCl_3) [δ , ppm]: 0.86-0.89 (m, 6H), 1.13-1.17 (m, 2H), 1.31-1.46 (m, 7H) 1.82-1.86 (m, 2H), 4.06 (t, $J = 6.5$ Hz, 2H), 5.46 (s, 1H), 6.88 (d, $J = 8.1$ Hz, 2H), 7.00 (d, $J = 8.9$ Hz, 2H), 7.14-7.16 (m, 1H), 7.37-7.46 (m, 7H), 8.17 (d, $J = 8.8$ Hz, 2H), 8.31 (d, $J = 8.7$ Hz, 2H) $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [δ , ppm]: 11.4, 19.2, 26.3, 26.4, 26.9, 29.1, 29.5, 34.4, 68.4, 114.5, 115.7, 119.8, 119.9, 122.2, 124.3, 128.4, 129.8, 131.9, 132.5, 132.6, 142.6, 151.2, 155.4, 155.7, 163.9, 164.5, 164.8. FTIR (KBr, ν : cm^{-1}): 3422, 2924, 2854, 1722, 1604, 1462, 1259, 1201, 1159.

Compound 9d.e. A mixture of compound **5d** (0.8 g, 1.5 mmol), compound **8e** (0.54 g, 1.6 mmol) and DMAP (0.02 g, 0.15 mmol) was dissolved in dry CH_2Cl_2 (40 mL). A solution of DCC (0.37 g, 1.8 mmol) in dry CH_2Cl_2 was added dropwise and the mixture was stirred at room temperature for 24 h. The white precipitate of *N,N'*-dicyclohexylurea was filtered off. The solvent was evaporated and the resulting product was purified by column chromatography (silica gel, eluent CH_2Cl_2) to give the product as a white powder. Yield: 79%. **M.p.** 72 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ , ppm = 0.89 (t, $J = 6.9$ Hz, 3H), 1.25-1.81 (m, 13H), 1.70-1.95 (m, 4H), 2.46-2.49 (m, 2H), 3.19-3.22 (m, 2H), 4.05-4.07 (m, 2H), 4.49-4.53 (m, 1H), 6.96 (d, $J = 8.9$ Hz, 2H), 6.98 (d, $J = 8.9$ Hz, 2H), 7.20-7.23 (m, 1H), 7.30 (d, $J = 8.7$ Hz, 2H), 7.33-7.40 (m, 7H), 7.46-7.48 (m, 1H), 7.50-7.52 (m, 2H), 7.66 (d, $J = 8.7$ Hz, 2H), 8.16 (dd, $J_1 = 8.9$ Hz, $J_2 = 1.7$ Hz, 4H), 8.31 (d, $J = 8.7$ Hz, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ , ppm = 14.1, 14.2, 19.6, 21.6, 22.6, 24.7, 25.5, 28.5, 29.3, 29.7, 31.8, 33.9, 35.0, 36.3, 55.8, 66.3, 67.9, 74.2, 114.3, 115.3, 120.4, 120.6, 120.7, 121.6, 122.1, 122.2, 124.7, 128.3, 128.6, 129.9, 131.9, 132.3, 132.5, 136.0, 137.8, 142.1, 150.8, 151.3, 155.5, 163.1, 163.3, 164.5, 164.9, 173.1. FTIR (KBr, ν : cm^{-1}): 2922, 2851, 1730, 1605, 1510, 1254.

Compound 9c.e. Synthesis as for compound **9d.e**. Yield 79%. **M.p.** 92 °C. $^1\text{H-NMR}$ (100 MHz, CDCl_3) [δ , ppm]: 0.86-0.89 (m, 6H), 1.25-1.81 (m, 11H), 1.82-1.90 (m, 6H), 2.46-2.49 (m, 2H), 4.06 (t, $J = 6.5$ Hz, 2H), 5.14 (s, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.20-7.23 (m, 1H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.33-7.40 (m, 7H), 7.46-7.48 (m, 1H), 7.50-7.52 (m, 2H), 7.66 (d, $J = 8.7$ Hz, 2H), 8.16 (dd, $J_1 = 8.9$ Hz, $J_2 = 1.7$ Hz, 4H), 8.31 (d, $J = 8.7$ Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [δ , ppm]: 11.4, 19.2, 21.5, 21.6, 26.3, 26.4, 26.9, 28.4, 28.5, 29.1, 29.5, 29.7, 33.8, 34.4, 66.3, 67.7, 68.4, 114.3, 114.4, 114.7, 115.7, 120.4, 122.1, 122.2, 128.3, 128.6, 131.9, 132.0, 132.3, 132.4, 137.8, 142.2, 150.9, 151.3, 155.4, 163.3, 164.5, 164.9 FTIR (KBr, ν : cm^{-1}): 2924, 2854, 1728, 1602, 1510, 1462, 1251, 1159.

Compound 10d.e. Compound **9d.e** (1.0 g, 1.2 mmol) and cyclohexene (20 mL) were dissolved in ethanol (30 mL) under an Ar atmosphere. $\text{Pd}(\text{OH})_2/\text{C}(20\%)$ (0.1 g) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was purified by column chromatography (silica gel, eluent CH_2Cl_2). Yield: 69%. **M.p.** 106 °C $^1\text{H NMR}$ (400 MHz, CDCl_3): δ , ppm = 0.89 (t, $J = 6.7$ Hz, 3H), 1.30-1.36 (m, 13H), 1.52-1.89 (m, 8H), 2.48 (t, $J = 6.7$ Hz, 2H), 4.09 (t, $J = 6.0$ Hz, 2H), 4.50 (q, $J = 6.1$ Hz, 1H), 6.97 (dd, $J_1 = 8.9$ Hz, $J_2 = 2.8$ Hz, 2H), 7.19-7.23 (m, 1H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.38 (d, $J = 8.7$ Hz, 2H),

7.45 (s, 1H), 7.51 (d, J = 4.7 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 8.16 (dd, J₁ = 8.9 Hz, J₂ = 4.7 Hz, 4H), 8.31 (d, J = 8.7 Hz, 2H) ¹³C NMR (75 MHz, CDCl₃): δ, ppm = 14.1, 19.6, 21.4, 22.6, 25.3, 25.4, 28.5, 29.2, 30.1, 31.8, 36.3, 67.7, 74.2, 114.3, 115.3, 120.4, 120.6, 121.7, 122.1, 122.2, 124.7, 126.8, 128.3, 129.9, 131.8, 132.3, 132.5, 137.8, 142.1, 150.8, 151.3, 155.5, 163.1, 163.3, 164.3, 164.5, 164.9. FTIR (KBr, ν: cm⁻¹): 3035, 2913, 2850, 1730, 1696, 1605, 1512, 1254.

Compound 10c.e. Synthesis as for compound **10d.e.** Yield 67%. **M.p.** 106 °C. ¹H-NMR (400 MHz, CDCl₃) [δ, ppm]: 0.86-0.89 (m, 6H), 1.25-1.81 (m, 11H), 1.82-1.90 (m, 6H), 2.46-2.49 (m, 2H), 4.06 (t, J = 6.5 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 7.12-7.25 (m, 3H), 7.29 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.45 (s, 1H), 7.50 (d, J = 4.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.9 Hz, 2H), 8.24 (d, J = 8.7 Hz, 2H) ¹³C-NMR (400 MHz, CDCl₃) [δ, ppm]: 11.4, 19.2, 21.6, 26.3, 26.9, 27.5, 29.2, 29.5, 33.9, 34.4, 36.5, 66.3, 67.7, 68.4, 114.2, 114.4, 115.3, 120.4, 120.6, 121.7, 122.1, 122.2, 124.6, 126.8, 128.1, 128.3, 129.9, 131.8, 132.3, 132.5, 137.8, 142.9, 150.8, 151.3, 155.5, 163.1, 163.7, 164.3, 164.5, 164.7.

Compound 11. A mixture of compound **1b** (2.1 g, 5.7 mmol), 4'-(benzyloxy)biphenyl-4-ol (1.6 g, 5.7 mmoles) and DPTS (1.7 g, 5.7 mmol) was dissolved in dry CH₂Cl₂ (100 mL). A solution of DCC (1.8 g, 8.5 mmoles) in dry CH₂Cl₂ (20 mL) was added dropwise and the mixture was stirred at room temperature for 24 h. The white precipitate of N,N'-dicyclohexylurea was filtered off. The solvent was evaporated and the resulting product was purified by chromatography column (silica gel, eluent CH₂Cl₂). Yield: 39%. **M.p.** 186 °C. ¹H NMR (400 MHz, CDCl₃): δ, ppm = 0.90 (t, J = 7.0 Hz, 3H), 1.22-1.39 (m, 8H), 1.39-1.52 (m, 2H), 1.83 (q, J = 7 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 5.12 (s, 2H), 6.99 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 7.33-7.43 (m, 5H), 7.47 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ, ppm = 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 60.6, 68.2, 70.1, 114.0, 114.4, 115.1, 115.2, 121.9, 122.1, 127.5, 127.7, 127.8, 128.0, 128.2, 128.6, 128.6, 131.5, 132.4, 137.0, 157.9, 170.5. FTIR (KBr, ν: cm⁻¹): 2920, 2851, 1727, 1604, 1509, 1256.

Compound 12. Compound **11** (1.4 g, 2.2 mmol) and cyclohexene (80 mL) were dissolved in ethanol (80 mL) under an Ar atmosphere. Pd(OH)₂/C(20%) (0.2 g) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The resulting product was purified by recrystallization from ethanol to give a pure white powder. Yield: 70%. **M.p.** 201 °C. ¹H NMR (400 MHz, DMSO-d₆): δ, ppm = 0.87 (t, J = 7.0 Hz, 3H), 1.23-1.35 (m, 8H), 1.36-1.46 (m, 2H), 1.76 (q, J = 7.0 Hz, 2H), 4.10 (t, J = 6.5 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.53 (dd, J = 8.8 Hz, J = 4.5 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ, ppm = 14.0, 22.1, 25.4, 28.6, 28.7, 30.4, 114.8, 115.6, 115.8, 122.2, 122.7, 127.0, 127.2, 127.8, 128.4, 131.2, 131.5, 132.2, 156.2, 170.7. FTIR (KBr, ν: cm⁻¹): 3300-3000, 2920, 2851, 1727, 1604, 1509, 1256.

Compound 13. A mixture of **12** (0.8 g, 1.5 mmol), compound **8e** (0.5 g, 1.5 mmol) and DPTS (0.4 g, 1.5 mmol) was dissolved in dry CH₂Cl₂ (150 mL). A solution of DCC (0.5 g, 2.2 mmol) in dry CH₂Cl₂ (10 mL) was added dropwise and the mixture was stirred at room temperature for 24 h. The white precipitate of

N,N'-dicyclohexylurea was filtered off. The solvent was evaporated and the resulting product was purified by column chromatography (silica gel, eluent CH₂Cl₂) to give the pure product as a white solid. Yield: 64%. **M.p.**: 161 °C. **¹H NMR (400 MHz, CDCl₃)**: δ, ppm = 0.90 (t, J = 7.1 Hz, 3H), 1.22-1.52 (m, 10H), 1.80-1.92 (m, 4H), 2.46-2.50 (m, 4H), 4.06 (t, J = 7.0 Hz, 4H), 5.14 (s, 2H), 6.98 (dd, J = 9.0 Hz, J = 4.2 Hz, 4H), 7.27-7.33 (m, 4H), 7.33-7.42 (m, 7H), 7.47 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.61-7.67 (m, 2H), 8.16 (d, J = 8.9 Hz, 4H), 8.30 (dd, J = 8.8 Hz, J = 4.2 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ, ppm = 14.1, 21.6, 22.7, 26.0, 28.5, 29.1, 29.2, 29.3, 31.8, 33.8, 66.3, 67.6, 68.4, 100.0, 114.3, 114.4, 120.4, 120.5, 120.9, 122.1, 122.2, 124.7, 126.8, 128.2, 128.6, 129.8, 131.8, 132.3, 132.4, 142.1, 149.6, 150.8, 151.3, 155.4, 163.3, 163.8, 164.3. **FTIR (KBr, ν: cm⁻¹)**: 2924, 2856, 1728, 1604, 1579, 1250.

Compound 14. Compound **13** (0.70 g, 0.8 mmol) and cyclohexene (60 mL) were dissolved in dry THF (60 mL) under an Ar atmosphere. Pd(OH)₂/C(20%) (0.1 g) was added and the reaction mixture stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The crude product was purified by crystallization from ethyl acetate to give a white solid. Yield: 50%. **M.p.** 189 °C. **¹H NMR (400 MHz, CDCl₃)**: δ, ppm = 0.92 (t, J = 7.0 Hz, 3H), 1.21-1.60 (m, 12H), 1.78-1.90 (m, 4H), 2.35 (t, J = 7.2 Hz, 2H), 4.05-4.15 (m, 4H), 6.83 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 7.28-7.38 (m, 4H), 7.44-7.48 (m, 4H), 7.68-7.76 (m, 2H), 8.12-8.18 (m, 4H), 8.25-8.32 (m, 2H), 10.85 (s, 1H). **¹³C NMR (100 MHz, CDCl₃)**: δ, ppm = 14.1, 21.4, 22.7, 26.0, 28.4, 29.1, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 33.4, 67.7, 68.4, 114.3, 120.4, 120.5, 121.0, 121.8, 122.1, 122.1, 124.7, 126.9, 128.2, 129.8, 131.8, 132.3, 132.4, 137.8, 142.2, 150.9, 151.4, 155.5, 163.3, 163.9, 164.3, 164.5, 178.2, 178.2. **FTIR (KBr, ν: cm⁻¹)**: 3040, 2920, 2851, 1729, 1604, 1512, 1250.

General procedure for the synthesis of ionic dendrimers (PPI1-B1-m-n, PPI1-B1-4-7*, PPI1-B1-4-8* and PPI1-C1-4-8)

The amine-terminated first generation PPI dendrimer (PPI1) was dissolved in dry THF and was added to a solution of the corresponding acid in the same solvent, using a 1:1 stoichiometry between the acid and each of the N-terminal amine groups present in the dendrimer. The mixture was sonicated for 15 min and the solvent was evaporated. The dendrimers were further dried under vacuum.

Dendrimer PPI1-B1-4-14. **M.p.** Cr 90 °C SmCP 142 °C l. **¹H NMR (400 MHz, CDCl₃)**: δ, ppm = 0.88 (t, J = 7.0 Hz, 12H), 1.20-1.51 (m, 96H), 1.75-1.90 (m, 28H), 2.38 (t, J = 7.0 Hz, 8H), 2.40-2.65 (m, 8H), 2.90-3.15 (m, 8H), 3.30-3.60 (m, 4H), 4.04 (m, 16H), 4.4-5.6 (m, 12H), 6.95 (d, J = 8.9 Hz, 8H), 6.98 (d, J = 9.0 Hz, 8H), 7.19-7.23 (m, 4H), 7.27 (d, J = 8.8 Hz, 8H), 7.37 (dd, J = 8.8 Hz, J = 1.9 Hz, 8H), 7.42-7.45 (m, 4H), 7.49 (d, J = 4.9 Hz, 8H), 7.63 (d, J = 8.7 Hz, 8H), 8.13 (d, J = 8.0 Hz, 8H), 8.15 (d, J = 8.8 Hz, 8H), 8.29 (dd, J = 8.8 Hz, J = 1.9 Hz, 8H). **¹³C NMR (100 MHz, CDCl₃)**: δ, ppm = 14.1, 22.1, 22.7, 26.0, 28.7, 29.1, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 35.1, 67.8, 68.4, 114.3, 114.4, 120.4, 120.5, 120.9, 121.6, 122.1, 122.2, 124.7, 126.8, 128.2, 129.9, 131.8, 132.3, 132.4, 137.7, 142.1, 150.8, 151.3, 155.4, 163.4, 163.8, 164.3, 164.5, 178.2. **FTIR (KBr, ν = cm⁻¹)**: 3400-2800, 2918, 2850, 1733, 1606, 1578, 1510, 1474, 1256, 1207, 1163. **Elemental Analysis:** Calcd. for C₂₂₄H₂₇₂N₆O₄₀: C 72.94, H 7.43, N 2.28; found C 71.71, H 7.32, N 2.04.

Dendrimer PPI1-B1-4-8. M.p. Cr 86 °C Col_r 146 °C I. ¹H NMR (400 MHz, CDCl₃): δ, ppm = 0.90 (t, J = 7.1 Hz, 12H), 1.21-1.55 (m, 48H), 1.70-1.98 (m, 28H), 2.41 (t, J = 6.8 Hz, 8H), 2.43-2.70 (m, 8H), 3.05-3.15 (m, 8H), 3.35-3.55 (m, 4H), 4.05 (m, 16H), 6.96 (d, J = 9.0 Hz, 8H), 6.9 (dd, J = 9.0 Hz, J = 2.0 Hz, 8H), 7.20-7.23 (m, 4H), 7.27 (dd, J = 8.8 Hz, J = 2.0 Hz, 8H), 7.38 (dd, J = 8.8 Hz, J = 2.5 Hz, 8H), 7.43-7.45 (m, 4H), 7.49 (d, J = 5.2 Hz, 8H), 7.64 (dd, J = 8.7 Hz, J = 2.0 Hz, 8H), 8.15 (d, J = 8.9 Hz, 8H), 8.16 (dd, J = 9.0 Hz, J = 2.0 Hz, 8H), 8.30 (dd, J = 8.8 Hz, J = 2.0 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃): δ, ppm = 14.1, 22.5, 22.6, 26.0, 28.9, 29.1, 29.2, 29.3, 31.8, 36.3, 68.0, 68.4, 114.3, 114.4, 120.4, 121.0, 121.0, 121.6, 121.6, 122.1, 122.1, 126.8, 126.8, 128.2, 129.8, 131.8, 132.3, 132.4, 137.7, 137.7, 142.1, 150.8, 151.3, 155.4, 163.4, 163.4, 163.8, 163.8, 164.8, 179.2. FTIR (KBr, ν: cm⁻¹): 3400-2800, 2921, 2856, 1737, 1606, 1579, 1512, 1478, 1257, 1209, 1163, 1065. **Elemental Analysis:** Calcd. for C₂₀₀H₂₂₄N₆O₄₀: C 71.66, H 6.74, N 2.51; found C 70.20, H 6.75, N 2.44.

Dendrimer PPI1-B1-10-8. M.p. Cr 82 °C Cr' 102 °C SmCP 136 °C I. ¹H NMR (400 MHz, CDCl₃): δ, ppm = 0.90 (t, J = 7.0 Hz, 12H), 1.20-1.40 (m, 72H), 1.41-1.53 (m, 16H), 1.55-1.64 (m, 8H), 1.75-1.87 (m, 20H), 2.29 (t, J = 7.5 Hz, 8H), 2.35-2.67 (m, 8H), 2.92-3.12 (m, 8H), 3.35-3.55 (m, 8H), 3.75 (t, J = 6.6 Hz, 4H), 4.04 (q, J = 7.2 Hz, 16H), 6.98 (dd, J = 8.9 Hz, J = 8.9 Hz, 16H), 7.19-7.25 (m, 4H), 7.28 (dd, J = 8.6 Hz, J = 1.9 Hz, 8H), 7.38 (dd, J = 8.8 Hz, J = 2.0 Hz, 8H), 7.45 (s, 4H), 7.50 (d, J = 5.1 Hz, 8H), 7.64 (dd, J = 8.6 Hz, J = 1.9 Hz, 8H), 8.15 (dd, J = 9.0 Hz, J = 2.2 Hz, 16H), 8.30 (dd, J = 8.7 Hz, J = 1.9 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃): δ, ppm = 14.2, 22.7, 22.8, 26.1, 29.0, 29.2, 29.4, 29.5, 32.0, 36.5, 68.2, 68.5, 114.4, 114.6, 120.5, 121.1, 121.1, 121.7, 121.7, 122.3, 122.3, 127.0, 127.0, 128.4, 130.0, 132.0, 132.5, 132.6, 137.9, 137.9, 142.3, 150.9, 151.5, 155.6, 163.6, 163.6, 164.0, 164.0, 165.0, 179.3. FTIR (KBr, ν: cm⁻¹): 3300-2800, 2930, 2871, 1735, 1605, 1579, 1510, 1476, 1256, 1209, 1065. **Elemental Analysis:** Calcd. for C₂₂₄H₂₇₂N₆O₄₀: C 72.94, H 7.43, N 2.28; found C 72.04, H 7.69, N 2.01.

Dendrimer PPI1-B1-4-8*. M.p. Cr 127 °C M 169 °C I. ¹H NMR (500 MHz, CDCl₃): δ, ppm = 0.86 (m, 24H), 1.05-1.20 (m, 8H), 1.22-1.55 (m, 40H), 1.66-1.86 (m, 24H), 2.25-2.60 (m, 16H), 2.85-3.10 (m, 8H), 3.42-3.47 (m, 4H), 3.88-3.98 (m, 8H), 4.04 (t, J = 6.7 Hz, 8H), 6.82-6.90 (m, 10H), 6.96 (d, J = 8.7 Hz, 8H), 7.10-7.23 (m, 10H), 7.33 (d, J = 8.2 Hz, 8H), 7.34-7.45 (m, 12H), 7.48-7.60 (m, 8H), 8.00-8.10 (m, 8H), 8.13 (d, J = 8.6 Hz, 8H), 8.25 (d, J = 8.3 Hz, 8H). ¹³C NMR (125 MHz, CDCl₃): δ, ppm = 11.4, 19.2, 22.7, 26.3, 26.8, 29.1, 29.2, 29.5, 34.3, 36.5, 68.1, 68.2, 68.4, 114.1, 114.2, 114.4, 120.3, 120.5, 120.9, 121.5, 122.1, 122.1, 124.6, 126.8, 128.1, 128.8, 129.8, 131.8, 132.3, 132.4, 137.6, 142.0, 150.7, 151.3, 155.3, 163.4, 163.8, 164.3, 164.4, 164.7. FTIR (KBr, ν: cm⁻¹): 3400-2800, 2930, 2871, 1732, 1606, 1578, 1511, 1476, 1256, 1208, 1161, 1065. **Elemental Analysis:** Calcd. for C₂₀₄H₂₃₂N₆O₄₀: C 71.89, H 6.86, N 2.47; found C 70.54, H 6.27, N 2.33.

Dendrimer PPI1-B1-4-7*. M.p. Cr 42 °C Col_r 104 °C I. ¹H NMR (400 MHz, CDCl₃): δ, ppm = 0.89 (t, J = 6.7 Hz, 12H), 1.30-1.36 (m, 52H), 1.52-1.89 (m, 40H), 2.48-2.70 (m, 16H), 2.95-3.15 (m, 8H), 3.30-3.55 (m, 4H), 4.09 (t, J = 6.0, 8H), 4.50 (q, J = 6.1 Hz, 4H), 7.00 (m, 16H), 7.21-7.24 (m, 4H), 7.28 (d, J = 8.6 Hz, 8H), 7.37 (d, J = 8.6 Hz, 8H), 7.42 (s, 4H), 7.49 (d, J = 4.8 Hz, 8H), 7.63 (d, J = 8.5 Hz, 8H), 8.12 (d, J = 8.9 Hz, 8H), 8.15 (d, J = 8.9 Hz, 8H), 8.33 (d, J = 8.5 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃): δ, ppm = 14.1, 19.6, 22.0, 22.2, 22.6, 24.7, 25.3, 25.4, 26.4, 28.6, 28.8, 29.2, 31.0, 31.8, 32.8, 35.3, 35.5, 36.3, 67.9, 74.0, 74.2, 114.3, 115.2, 115.3, 115.7, 120.4, 120.6, 120.7, 121.6, 122.1, 122.2, 124.7, 126.8, 128.9, 129.9, 137.8, 142.1, 150.8, 151.3, 151.5, 155.5, 162.1, 163.1, 163.4, 164.4, 164.5, 164.9, 178.7. FTIR (KBr, ν: cm⁻¹):

3100-3400, 2931, 2856, 1734, 1605, 1576, 1518, 1477, 1256, 1208, 1161, 106.3 **Elemental Analysis:** Calcd. for C₂₀₄H₂₃₂N₆O₄₀: C 71.66, H 6.74, N 2.51; Found: C 71.13, H 6.88, N 2.94.

Dendrimer PPI1-C1-4-8. M.p. Cr 112 °C SmC 137 °C l. **¹H NMR (400 MHz, CDCl₃):** δ, ppm = 0.90 (t, J = 7.0 Hz, 12H), 1.24-1.53 (m, 48H), 1.77-1.90 (m, 28H), 2.41-2.70 (m, 16H), 3.10-3.25 (m, 8H), 3.71-3.75 (m, 4H), 4.06 (t, J = 6.5 Hz, 16H), 6.92 (dd, J = 8.7 Hz, J = 2.1 Hz, 8H), 6.99 (dd, J = 9.0 Hz, J = 2.0 Hz, 8H), 7.24-7.34 (m, 20H), 7.38 (dd, J = 8.9 Hz, J = 2.1 Hz, 8H), 7.48 (dd, J = 8.7 Hz, J = 2.2 Hz, 8H), 7.58 (dd, J = 8.8 Hz, J = 2.1 Hz, 8H), 7.61-7.68 (m, 4H), 8.15 (dd, J = 9.0 Hz, J = 2.0 Hz, 8H), 8.30 (dd, J = 8.9 Hz, J = 2.1 Hz, 8H). **¹³C NMR (100 MHz, CDCl₃):** δ, ppm = 14.2, 22.7, 22.8, 26.1, 29.0, 29.2, 29.4, 29.5, 31.9, 36.5, 68.2, 68.5, 114.4, 114.6, 120.5, 121.1, 121.1, 121.7, 121.8, 122.3, 122.3, 127.0, 127.1, 12.4, 130.0, 132.0, 132.6, 137.9, 138.0, 142.2, 150.9, 151.5, 155.6, 163.6, 163.8, 163.9, 164.0, 165.0, 179.3. **FTIR (KBr, ν: cm⁻¹):** 3300-2800, 2857, 1736, 1606, 1578, 1511, 1478, 1256, 1210. **Elemental Analysis:** Calcd. for C₂₀₀H₂₂₄N₆O₄₀: C 71.66, H 6.74, N 2.51; found C 71.32, H 6.35, N 2.54.

- Additional experimental procedures:

Preparation of the aggregates in water.

The preparation of nanoobjects and turbidity measurements were performed according to published procedures (S. Hernandez-Ainsa, J. Barbera, M. Marcos, J.L. Serrano, *Soft Matter*. **2011**, 7, 2560).

The ionic dendrimer was dissolved in THF (an organic solvent that is miscible with water) at a concentration of 0.5 wt%. To perform the turbidity measurements, Milli-Q water was added to the solution very slowly (5–10 mL of water per minute to 1.5 mL of dendrimer solution) with gentle shaking. The optical density (turbidity) of the solution was measured after every addition of water at a wavelength of 650 nm using a quartz cell (path length 1 cm) with a Unicam UV/vis spectrophotometer. The solution was left to equilibrate until the turbidity value remained constant. The cycle of water addition, equilibration and turbidity measurement was continued until the increase in turbidity upon water addition was very small and a plateau was reached. The solution was then dialyzed against water for 3 days to remove THF using a Spectra/Por regenerated cellulose membrane with a molecular weight cutoff of 1000.

Preparation of samples for TEM and SEM studies.

Samples for TEM were prepared as follows. A droplet of the dialyzed aqueous dendrimer solution was deposited onto carbon-coated copper grids (previously treated in a UV-ozone chamber for 5 min). The samples were allowed to dry under ambient conditions after wicking away most of the solution. A droplet of an aqueous uranyl acetate solution was applied to the grid. After 1 min, the excess staining solution was removed with filter paper.

The samples for SEM were prepared by deposition of the dialyzed aqueous dendrimer solution onto quartz. The samples were allowed to dry under ambient conditions. The samples were then covered with gold.

S2. Representative FT-IR spectra of ionic dendrimers.

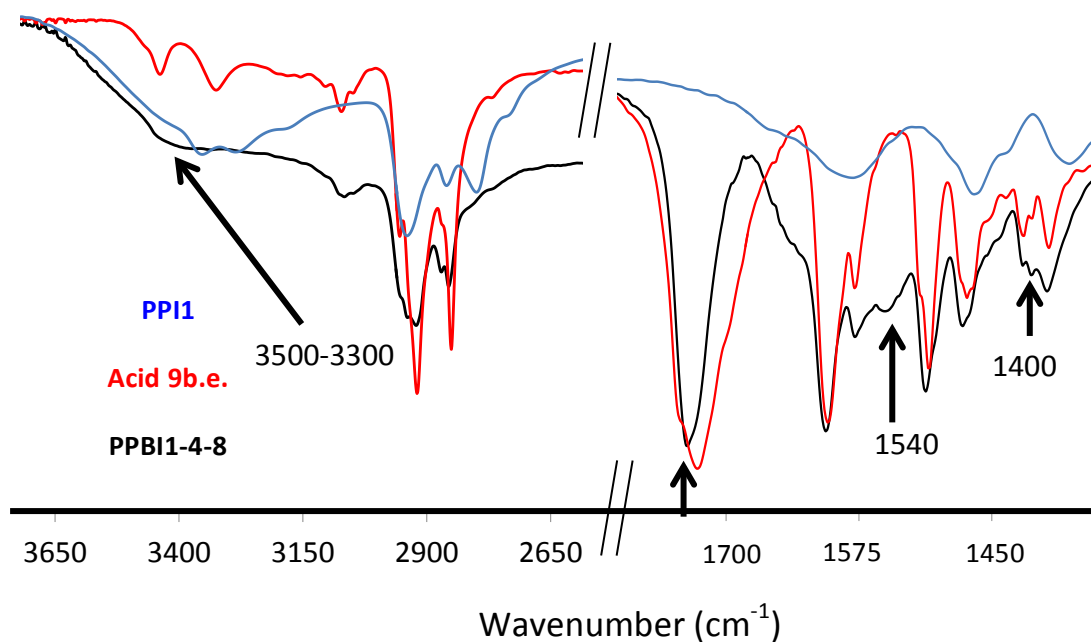


Figure S1. FTIR spectra (KBr) of the dendrimer **PPI1-B1-4-8** (black), the first generation PPI (blue) and the corresponding bent-core carboxylic acid (red).

S3. Representative DSC thermograms of mesogenic ionic dendrimers.

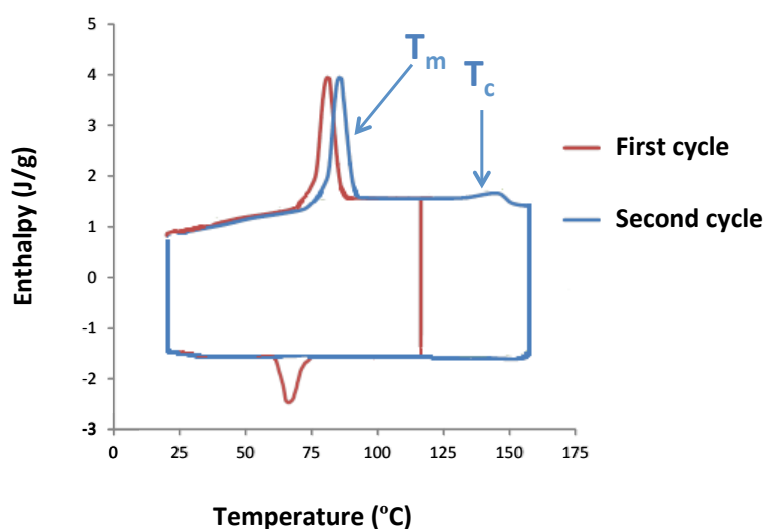


Figure S2. DSC thermograms of the dendrimer **PPI1-B1-4-8** corresponding to successive heating and cooling scans obtained at 10 °C/min [T_m : melting point temperature, T_c : clearing temperature]. In the first cycle (red) the clearing temperature was not exceeded as the sample decomposed in the isotropic liquid, as reported for numerous ionic dendromesogens. Thus, the compounds showed reproducible melting transitions if temperatures of 20-40 °C above the melting point were reached in all cycles.

S4. Representative POM textures of mesogenic ionic dendrimers.

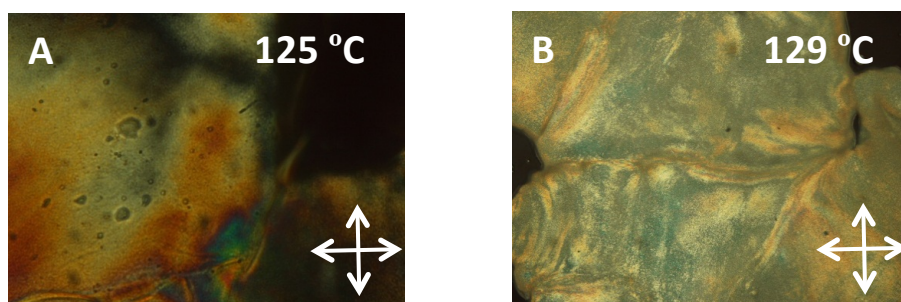


Figure S3. Mesophase textures observed by POM in the first heating cycle of the following dendrimers: A) PPI1-B1-4-14, B) PPI1-B1-4-8

S5. ^1H NMR studies in solution of PPI1-B1-4-8.

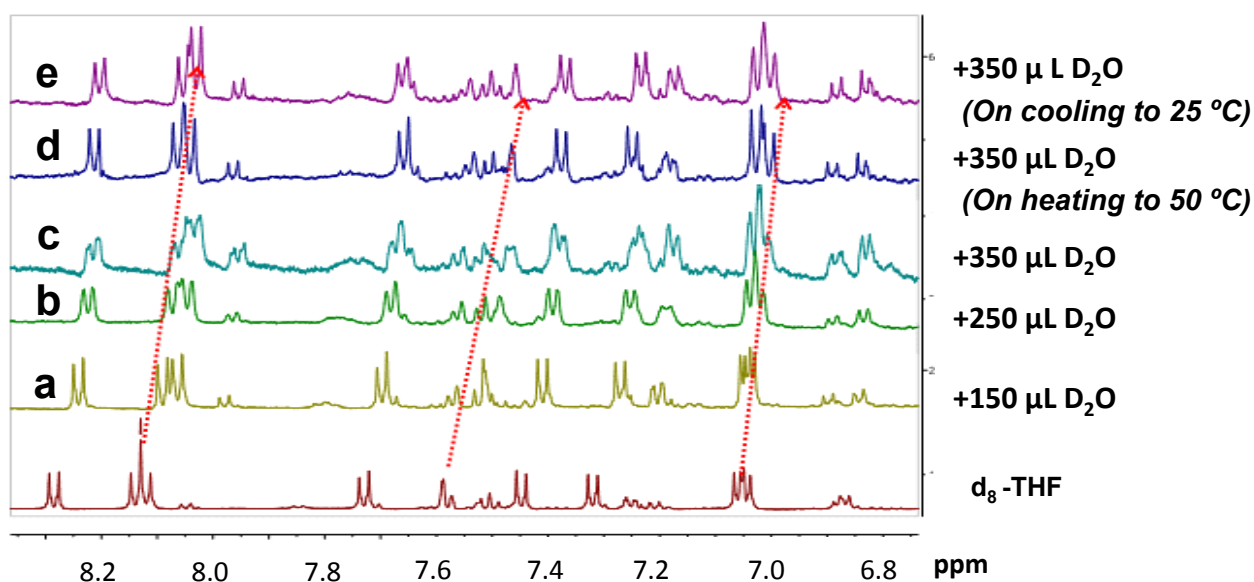


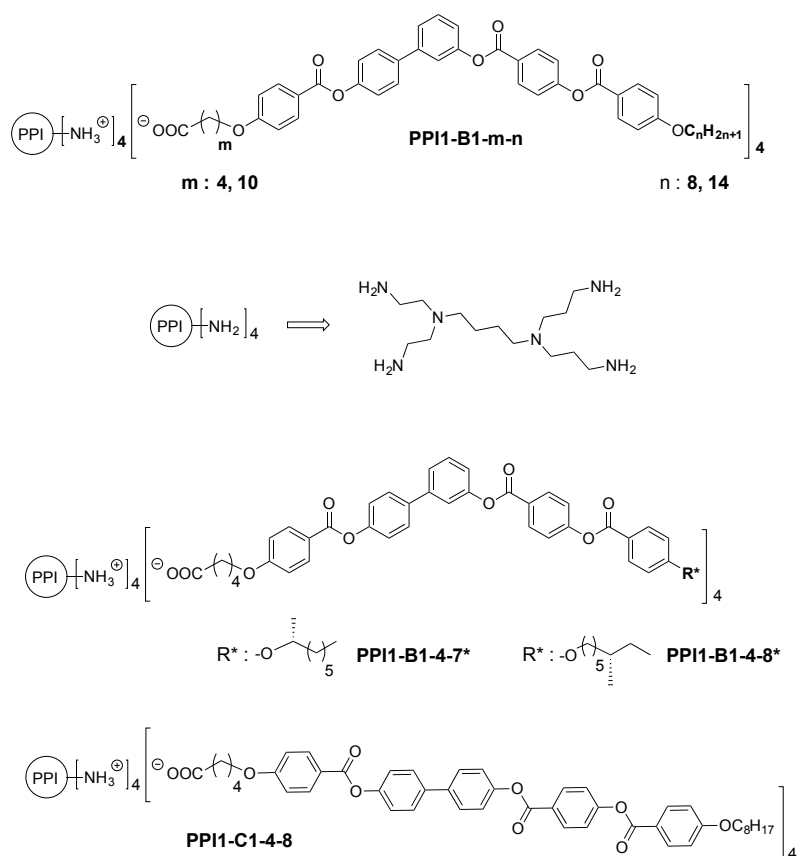
Figure S4. ^1H NMR studies for PPI1-B1-4-8. Starting from a d_8 -THF solution, the addition of D_2O induces (a-c) upfield shifts of the aromatic proton signals. On heating these solutions up to 50 °C, aggregates open and break (d) which grow back on cooling the solution to room temperature (e). [see also Fig. S7].

S6. Table S1.

Table S1. Transition temperatures as determined by DSC for the ionic bent-core based dendrimers and morphology of their aggregates formed in the presence of water.

	AC ^[a]	m ^[b]	n ^[c]	Phase transition temperatures ^{[d][e]} [°C]	Morphology of aggregates in water
PPI1-B1-10-14 ^[f]	B1	10	14	Cr 104 SmCP 156 I	rods
PPI1-B1-10-8	B1	10	8	Cr 102 SmCP 136 I	ribbons and spheres
PPI1-B1-4-14	B1	4	14	Cr 90 SmCP 142 I	twisted ribbons
PPI1-B1-4-8	B1	4	8	Cr 86 Col _r 146 I	helical ribbons and tubules
PPI1-B1-4-8*	B1	4	8*	Cr 127 M 169 I	ribbons and coils
PPI1-B1-4-7*	B1	4	7*	Cr 42 Col _r 104 I	precipitate (undefined) ^[g]
PPI1-C1-4-8	C1	4	8	Cr 112 SmC 137 I	ribbons

[a] AC: identification of the aromatic-core structure, B1: 3,4'-biphenylene-based bent-core structure with 5 aromatic rings, C1: 4,4'-biphenyl rod-core structure with 5 aromatic rings (linear isomeric structure of bent-core B1). [b] Number of -(CH₂)- units in the flexible linker connecting the dendritic- and the aromatic-rigid cores. [c] Number of -(CH₂)- units in the terminal tails of the dendrimer. [d] Data determined in the first scan at a scanning rate of 10 °C/min. [e] Cr: crystal; SmCP: polar smectic C mesophase; Col_r: rectangular columnar mesophase; M: unidentified mesophase; SmC: smectic C mesophase; I: isotropic liquid. [f] Compound reported previously in reference 9. [g] The aggregate precipitates with an undefined morphology by TEM.



S7. SEM images of the aggregation process of PPI1-B1-4-8 upon addition of water.

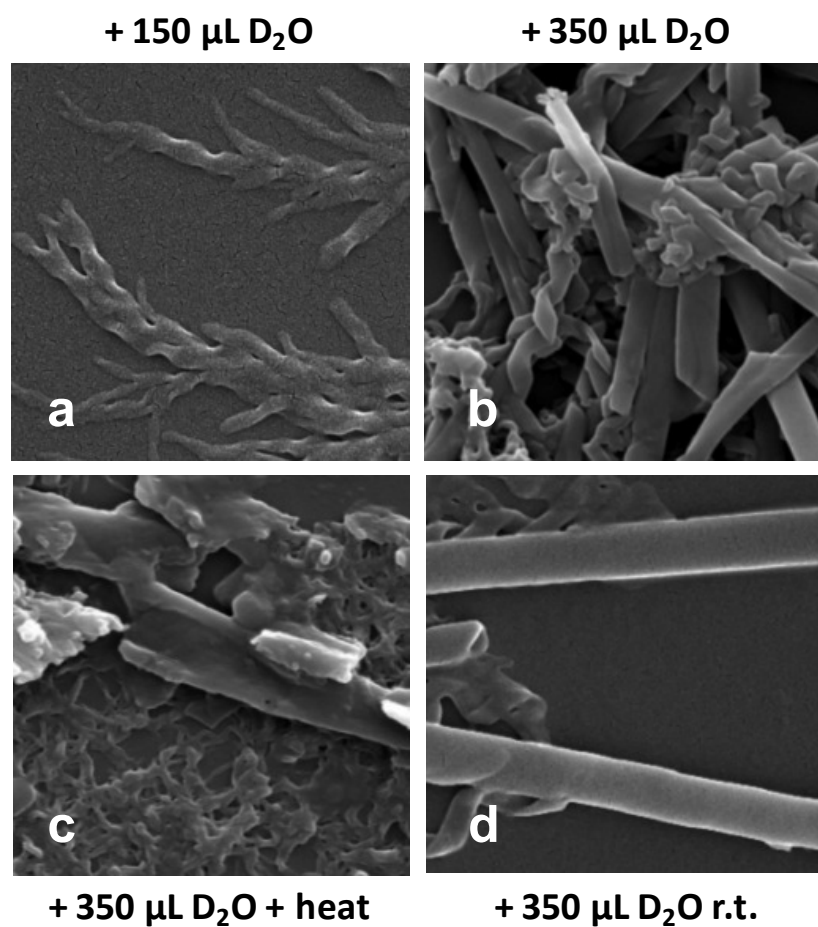


Figure S5. Aggregation process for **PPI1-B1-4-8** studied by SEM on cast samples: at low D₂O proportions, small twisted ribbons are formed, which finally render helical nanoribbons and nanotubes (tubules) (a-b). On heating these solutions up to 50 °C, tubular aggregates open and break to form ribbons (c), which grow back to the large tubules on cooling the solution to room temperature (d) in a self-healing process.

S8. TEM images of different aggregates formed by PPI1-B1-m-n dendrimers.

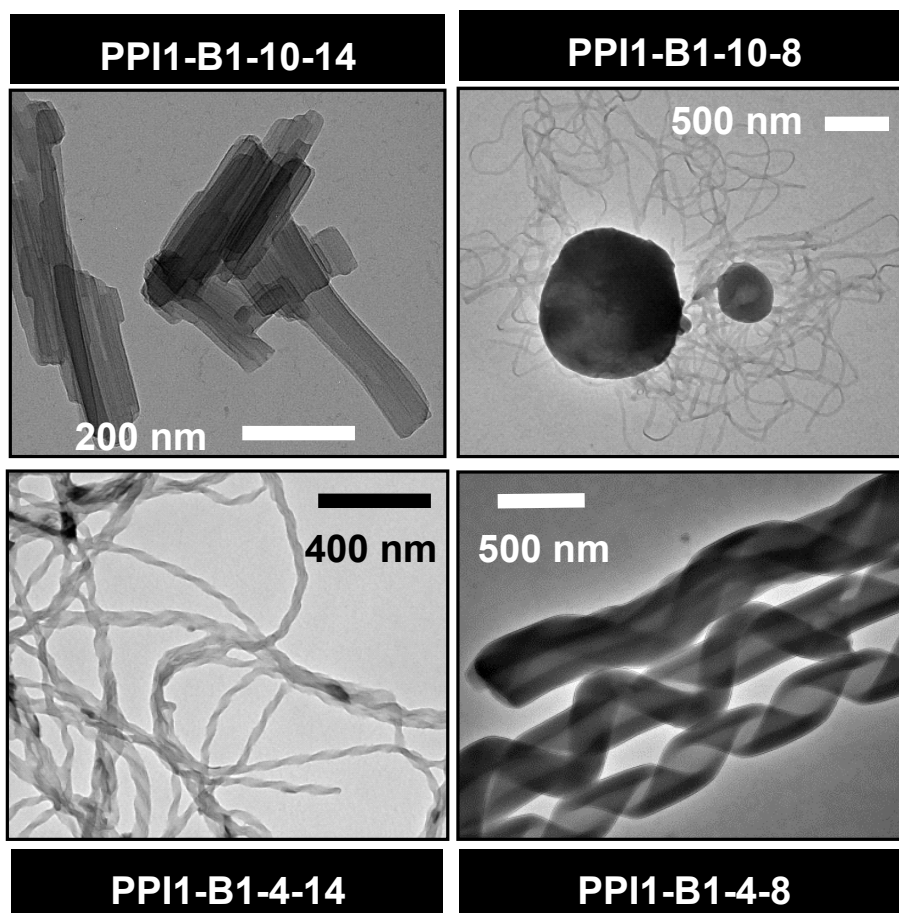


Figure S6. Comparative TEM images of different PPI1-B1-m-n dendrimers from dialyzed aqueous solutions. Aggregates with different morphologies, which depend on the molecular structure of the dendrimer, can be achieved.

S9. X-ray diffraction parameters and evaluation.

Table S2. X-ray diffraction data for mesophases formed by the new ionic dendrimers.

Dendrimer ^a	Mesophase	d [Å]	Miller indexes (hkl)	Parameters [Å]
PPI1-B1-10-8	SmCP	46.2	002	c = 92.6
		30.8	003	
		15.5	006	
PPI1-B1-4-14	SmCP	82.1	001	c = 82.2
		41.1	002	
		27.4	003	
		20.6	004	
PPI1-B1-4-8	Col _r	59.0	010	a = 59.8 b = 51.2
		29.9	020	
		26.0	120	
		19.8	220	
PPI1-B1-4-7*	Col _r	61.6	010	a = 61.6 b = 41.2
		34.2	110	
		30.8	020	
		24.7	120	
PPI1-C1-4-8	SmC	46.9	002	c = 93.8
		31.8	003	
		23.5	004	

^a The quality of diffractograms from **PPI1-B1-4-8*** did not allow characterization of its mesophase.

S9a. X-ray diffraction patterns for the mesophase formed by the ionic dendrimers.

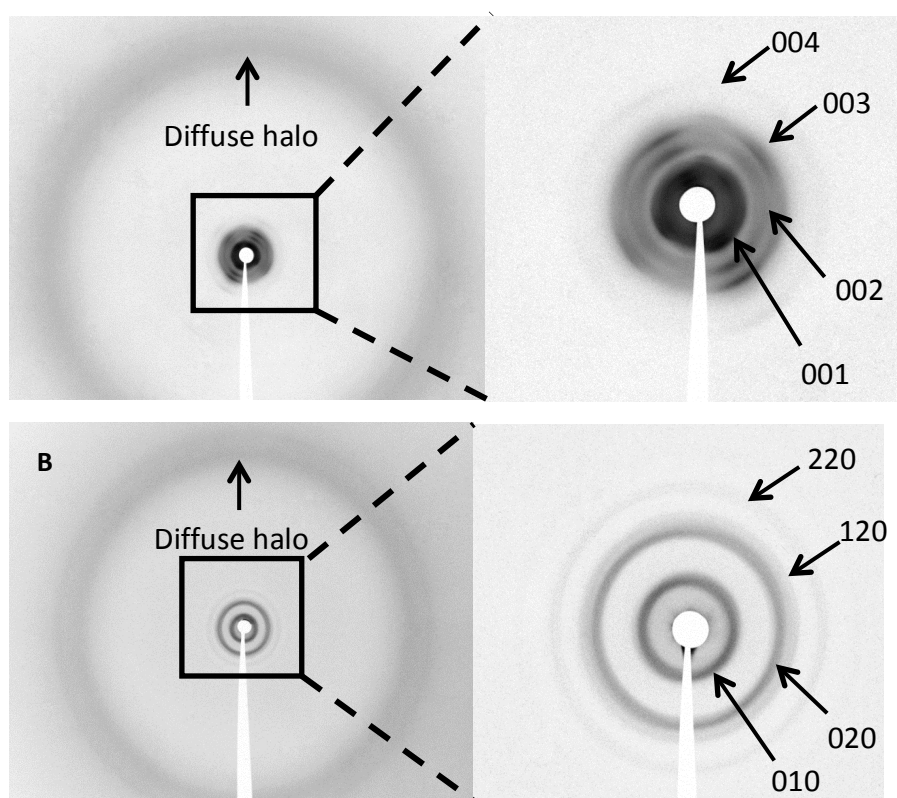


Figure S7. Diffractogram of (A) PPI1-B1-4-14 (mesophase $SmCP$) and (B) PPI1-B1-4-8 (mesophase Col_r) at ambient temperature.

S9b. SAXS and WAXS distribution for aggregates formed by the ionic dendrimers.

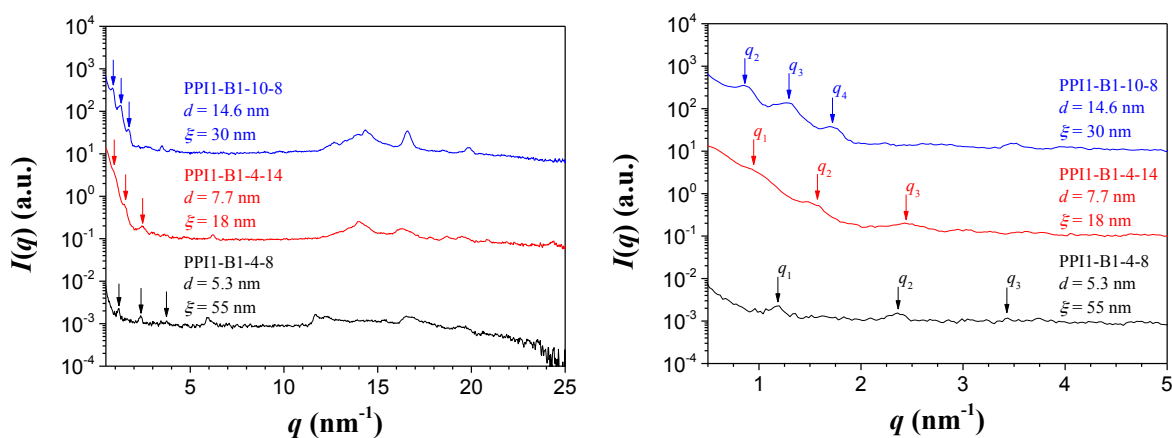


Figure S8. Wide and small angle X-ray scattering radial intensity distribution for the ionic dendrimers PPI1-B1-4-8 (black), PPI1-B1-4-14 (red) and PPI1-B1-10-8 (blue) after precipitation from water and drying. Data are consistent with lamellar structures ($q = 0.5$ to 5 nm^{-1}) and crystallinity from the hydrocarbon chains ($q = 12$ to 17 nm^{-1}).