Supporting Information

Self-Assembly Modulation in Ionic PAMAM Derivatives

Silvia Hernández-Ainsa*[a,b], Elisabetta Fedeli[a], Joaquín Barberá[a], Mercedes Marcos[a], Teresa Sierra[a], José Luis Serrano*[c]

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1. General Techniques

The infrared spectra of all the complexes were obtained with a Mattson Genesis II FTIR and Nicolet Avatar 380 spectrophotometers in the 400-4000 cm^{-1} spectral range using KBr pellets or directly over NaCl cells. Nuclear magnetic resonance (NMR) experiments were recorded using standard pulse sequences on AVANCE 400 spectrometer operating at 400 MHz for ^{1}H. The spectra were measured in $CDCl_3$.

The optical textures of the mesophases were studied with a Olympus BH-2 polarizing microscope equipped with a Linkan THMS hot-stage, a central processor and a CS196 cooling system. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a DSC 2910 from TA Instruments operated at a scanning rate of 10°C min^{-1} on both heating and cooling cycles. The apparatus was calibrated with indium (156.6°C; 28.4 Jg^{-1}) as the standard. The temperatures were read at the maximun of the transition peaks and the glass transition temperature was read at the midpoint of the heat capacity increase. Thermogravimetric analysis (TGA) was performed using a TA instrument STD 2960 simultaneous TGA-DTA at a rate of 10ºC·min^{-1} under argon atmosphere. TGA data are given as the onset of the descomposition curve. The XRD patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The sample was held in Lindemann glass capillaries (0.9 mm diameter) and heated, when necessary, with a variable-temperature oven. The capillary axis is perpendicular to the X-ray beam and the pattern is collected on flat photographic film perpendicular to the X-ray beam. Spacing were obtained via Bragg's law.

TEM was measured using JEOL-2000 FXIII and TECNAI T20 (FEI COMPANY) electron microscopes. The sample were prepared in holey carbon film 300 mash coppered grids (Agar Scientific) and negative stained with a water solution of uranyl acetate (0.1N).

Particle Size Analysis was carried out in a Nanosizer ZS (Malvern Instruments) with a He-Ne laser (4mW) operating at a wavelength of 633nm. All experiments were performed at a scattering angle of 173º using a non-invasive Back-Scatter technology.

2. Characterization of the ionic dendrimers

$G2(C_{14})_4$

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.51-8.02 ($CON\underline{H}$), 4.50-4.00 ($NHCH_2CH_2N\underline{H}_3^+$, $NHCH_2CH_2N\underline{H}_2$), 3.39-3.25 ($NHC\underline{H}_2CH_2NH_3^+$, $NHC\underline{H}_2CH_2NH_2$), 3.25-3.15 ($NHC\underline{H}_2CH_2N$), 2.98-2.83 ($NHCH_2C\underline{H}_2NH_3^+$), 2.75-2.65 ($NC\underline{H}_2CH_2CONH$, $NHCH_2C\underline{H}_2NH_2$), 2.58-2.48 ($NHCH_2C\underline{H}_2N$), 2.45-2.25 (m, $NCH_2C\underline{H}_2CONH$), 2.18-2.15 ($CH_2C\underline{H}_2COO^-$), 1.60-1.50 ($C\underline{H}_2CH_2COO^-$), 1.35-1.20 ($CH_3(C\underline{H}_2)_{10}$), 0.89-0.86 ($C\underline{H}_3CH_2$). IR (KBr): ν = 3279 (w), 2924, 2853, 1644, 1554, 1464, 1393 cm^{-1}

$G2(C_{14})_8$

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.60-8.10 ($CON\underline{H}$), 4.90-4.70 ($NHCH_2CH_2N\underline{H}_3^+$, $NHCH_2CH_2N\underline{H}_2$), 3.45-3.32 ($NHC\underline{H}_2CH_2NH_3^+$, $NHC\underline{H}_2CH_2NH_2$), 3.30-3.15 ($NHC\underline{H}_2CH_2N$), 3.00-2.85 ($NHCH_2C\underline{H}_2NH_3^+$), 2.80-2.62 ($NC\underline{H}_2CH_2CONH$, $NHCH_2C\underline{H}_2NH_2$), 2.58-2.42 ($NHCH_2C\underline{H}_2N$), 2.40-2.30 ($NCH_2C\underline{H}_2CONH$), 2.16-2.11 ($CH_2C\underline{H}_2COO^-$), 1.60-1.48 ($C\underline{H}_2CH_2COO^-$), 1.31-1.18 ($CH_3(C\underline{H}_2)_{10}$), 0.90-0.85($C\underline{H}_3CH_2$). IR (KBr): ν = 3280 (w), 2924, 2852, 1641, 1556, 1462, 1396 cm^{-1}

$G2(C_{14})_{12}$

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50-8.20 ($CON\underline{H}$), 6.05-5.80 ($NHCH_2CH_2N\underline{H}_3^+$, $NHCH_2CH_2N\underline{H}_2$), 3.48-3.40 ($NHC\underline{H}_2CH_2NH_3^+$, $NHC\underline{H}_2CH_2NH_2$), 3.30-3.15 ($NHC\underline{H}_2CH_2N$), 3.05-2.90 ($NHCH_2C\underline{H}_2NH_3^+$), 2.80-2.60 ($NC\underline{H}_2CH_2CONH$, $NHCH_2C\underline{H}_2NH_2$), 2.52-2.48 ($NHCH_2C\underline{H}_2N$), 2.40-2.28 ($NCH_2C\underline{H}_2CONH$), 2.17-2.12 ($CH_2C\underline{H}_2COO^-$), 1.60-1.50 ($C\underline{H}_2CH_2COO^-$), 1.30-1.15 ($CH_3(C\underline{H}_2)_{10}$), 0.90-0.81 (m, $C\underline{H}_3CH_2$). IR (KBr): ν = 3270 (w), 2923, 2852, 1648, 1557, 1464, 1398 cm^{-1}

$G2(C_{14})_{16}$

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.70-8.10 ($CON\underline{H}$), 6.50-6.20 ($NHCH_2CH_2N\underline{H}_3^+$), 3.49-3.38 ($NHC\underline{H}_2CH_2NH_3^+$), 3.29-3.12 ($NHC\underline{H}_2CH_2N$), 3.10-2.95 ($NHCH_2C\underline{H}_2NH_3^+$), 2.78-2.62

(NC$\underline{H}_2$CH$_2$CONH), 2.58-2.45 (NHCH$_2$C$\underline{H}_2$N), 2.40-2.29 (NCH$_2$C$\underline{H}_2$CONH), 2.18-2.10 (CH$_2$C$\underline{H}_2$COO$^-$), 1.60-1.48 (C$\underline{H}_2$CH$_2$COO$^-$), 1.30-1.18 (CH$_3$(C$\underline{H}_2$)$_{10}$), 0.90-0.87 (C$\underline{H}_3$CH$_2$). IR (KBr): v =3274 (w), 2924, 2853, 1643, 1553, 1464, 1399 cm^{-1}

G2(C$_{14}$)$_{20}$

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.80-8.10 (CON$\underline{H}$), 5.61-6.20 (NHCH$_2$CH$_2$N$\underline{H}_3^+$, NHCH$_2$CH$_2$N$\underline{H}^+$, NCH$_2$CH$_2$N$\underline{H}^+$ N$\underline{H}^+$CH$_2$CH$_2$CONH), 3.40-3.40 (NHC$\underline{H}_2$CH$_2$NH$_3^+$, NHC$\underline{H}_2$CH$_2$NH$^+$), 3.28-3.18 (NHC$\underline{H}_2$CH$_2$N, NHCH$_2$C$\underline{H}_2$NH$^+$, NH$^+$C$\underline{H}_2$CH$_2$CONH), 3.15-3.00 (NHCH$_2$C$\underline{H}_2$NH$_3^+$, NCH$_2$C$\underline{H}_2$NH$^+$), 2.79-2.61 (NC$\underline{H}_2$CH$_2$CONH, NH$^+$CH$_2$C$\underline{H}_2$CONH), 2.60-2.49 (NHCH$_2$C$\underline{H}_2$N, NC$\underline{H}_2$CH$_2$NH$^+$), 2.39-2.28 (NCH$_2$C$\underline{H}_2$CONH), 2.20-2.15 (CH$_2$C$\underline{H}_2$COO$^-$), 1.60-1.50 (C$\underline{H}_2$CH$_2$COO$^-$), 1.30-1.15 (CH$_3$(C$\underline{H}_2$)$_{10}$), 0.89-0.85 (C$\underline{H}_3$CH$_2$). IR (KBr): v =3260 (w), 2923, 2853, 1645, 1554, 1464, 1397 cm^{-1}

G2(C$_{14}$)$_{24}$

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.65-8.15 (CON$\underline{H}$), 4.50-4.00 (NHCH$_2$CH$_2$N$\underline{H}_3^+$, NHCH$_2$CH$_2$N$\underline{H}^+$, NCH$_2$CH$_2$N$\underline{H}^+$ N$\underline{H}^+$CH$_2$CH$_2$CONH), 3.48-3.42 (NHC$\underline{H}_2$CH$_2$NH$_3^+$, NHC$\underline{H}_2$CH$_2$NH$^+$), 3.28-3.15 (NHC$\underline{H}_2$CH$_2$N, NHCH$_2$C$\underline{H}_2$NH$^+$, NH$^+$C$\underline{H}_2$CH$_2$CONH,), 3.15-2.96 (NHCH$_2$C$\underline{H}_2$NH$_3^+$, NCH$_2$C$\underline{H}_2$NH$^+$), 2.78-2.65 (NC$\underline{H}_2$CH$_2$CONH, NH$^+$CH$_2$C$\underline{H}_2$CONH), 2.58-2.46 (NHCH$_2$C$\underline{H}_2$N, NC$\underline{H}_2$CH$_2$NH$^+$), 2.41-2.30 (NCH$_2$C$\underline{H}_2$CONH), 2.20-2.16 (CH$_2$C$\underline{H}_2$COO$^-$), 1.56-1.50 (C$\underline{H}_2$CH$_2$COO$^-$), 1.27-1.12 (CH$_3$(C$\underline{H}_2$)$_{10}$), 0.90-0.85 (C$\underline{H}_3$CH$_2$). IR (KBr): v = 3264 (w), 2923, 2853, 1644, 1550, 1464, 1397 cm^{-1}

G2(C$_{14}$)$_{28}$

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.90-8.10 (CON$\underline{H}$), 6.10-5.80 (NHCH$_2$CH$_2$N$\underline{H}_3^+$, NHCH$_2$CH$_2$N$\underline{H}^+$, NCH$_2$CH$_2$N$\underline{H}^+$ N$\underline{H}^+$CH$_2$CH$_2$CONH), 3.51-3.45 (NHC$\underline{H}_2$CH$_2$NH$_3^+$, NHC$\underline{H}_2$CH$_2$NH$^+$), 3.28-3.10 (NHC$\underline{H}_2$CH$_2$N, NHCH$_2$C$\underline{H}_2$NH$^+$, NH$^+$C$\underline{H}_2$CH$_2$CONH), 3.12-2.90 (NHCH$_2$C$\underline{H}_2$NH$_3^+$, NCH$_2$C$\underline{H}_2$NH$^+$), 2.72-2.61 (NC$\underline{H}_2$CH$_2$CONH, NH$^+$CH$_2$C$\underline{H}_2$CONH), 2.56-2.48 (NHCH$_2$C$\underline{H}_2$N, NC$\underline{H}_2$CH$_2$NH$^+$), 2.47-2.39 (NCH$_2$C$\underline{H}_2$CONH), 2.25-2.19

($\mathrm{CH_2C}\underline{H}_2\mathrm{COO^-}$), 1.60-1.50 ($\mathrm{C}\underline{H}_2\mathrm{CH_2COO^-}$), 1.30-1.10 ($\mathrm{CH_3(C}\underline{H}_2)_{10}$), 0.84-0.80 ($\mathrm{C}\underline{H}_3\mathrm{CH_2}$). IR (KBr): ν =3260 (w), 2923, 2853, 1645, 1547, 1464, 1398 $\mathrm{cm^{-1}}$

G2(C$_{14}$)$_{30}$

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 8.80-8.10 ($\mathrm{CON}\underline{H}$), 6.15-5.90 ($\mathrm{NHCH_2CH_2N}\underline{H}_3^+$, $\mathrm{NHCH_2CH_2N}\underline{H}^+$, $\mathrm{NCH_2CH_2N}\underline{H}^+$, $\mathrm{N}\underline{H}^+\mathrm{CH_2CH_2CONH}$), 3.58-3.40 ($\mathrm{NHC}\underline{H}_2\mathrm{CH_2NH_3^+}$, $\mathrm{NHC}\underline{H}_2\mathrm{CH_2NH^+}$), 3.25-3.10 ($\mathrm{NHC}\underline{H}_2\mathrm{CH_2N}$, $\mathrm{NHCH_2C}\underline{H}_2\mathrm{NH^+}$, $\mathrm{NH^+C}\underline{H}_2\mathrm{CH_2CONH}$), 3.10-2.95 ($\mathrm{NHCH_2C}\underline{H}_2\mathrm{NH_3^+}$, $\mathrm{NCH_2C}\underline{H}_2\mathrm{NH^+}$), 2.80-2.55 ($\mathrm{NC}\underline{H}_2\mathrm{CH_2CONH}$, $\mathrm{NH^+CH_2C}\underline{H}_2\mathrm{CONH}$), 2.55-2.45 ($\mathrm{NHCH_2C}\underline{H}_2\mathrm{N}$, $\mathrm{NC}\underline{H}_2\mathrm{CH_2NH^+}$), 2.37-2.25 ($\mathrm{NCH_2C}\underline{H}_2\mathrm{CONH}$), 2.25-2.20 ($\mathrm{CH_2C}\underline{H}_2\mathrm{COO^-}$), 1.60-1.50 ($\mathrm{C}\underline{H}_2\mathrm{CH_2COO^-}$), 1.30-1.10 ($\mathrm{CH_3(C}\underline{H}_2)_{10}$), 0.89-0.82 ($\mathrm{C}\underline{H}_3\mathrm{CH_2}$). IR (KBr): ν =3294 (w), 2926, 2851, 1643, 1549, 1459, 1375 $\mathrm{cm^{-1}}$

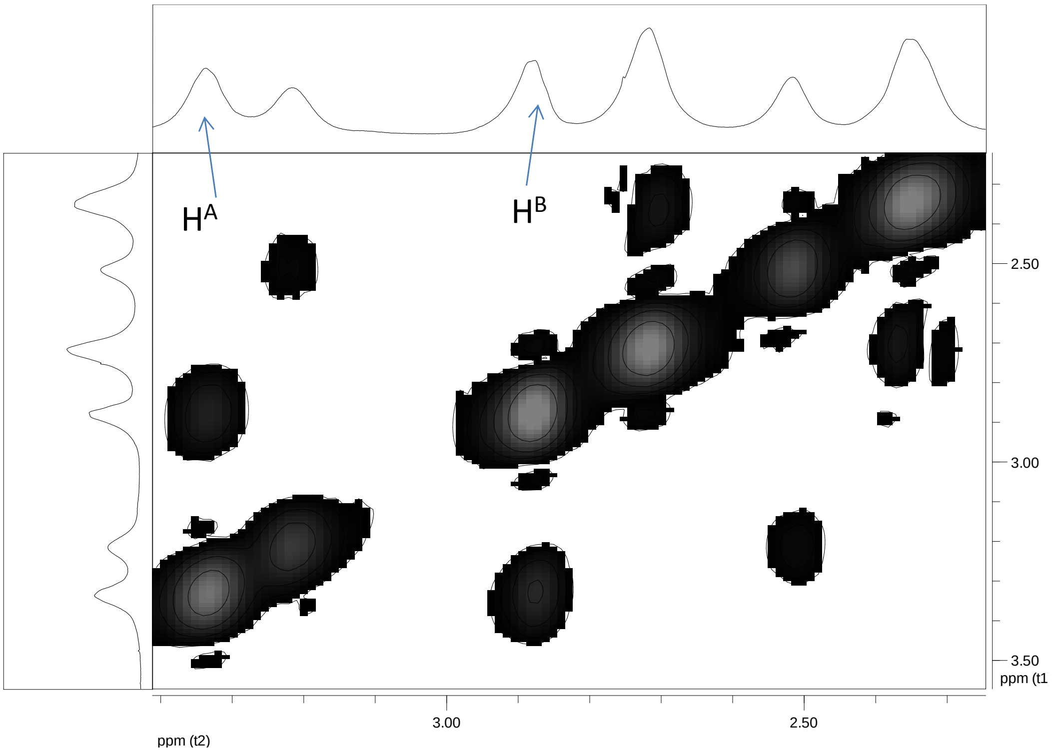
3. ^{1}H-^{1}H COSY spectra

Identification of the protonated amines was done using two-dimensional ^{1}H-^{1}HCOSY experiments and guided by the identification of similar compounds previously described [RefS1, RefS2]

Some examples are shown here (Figure S1, S2 and S3)

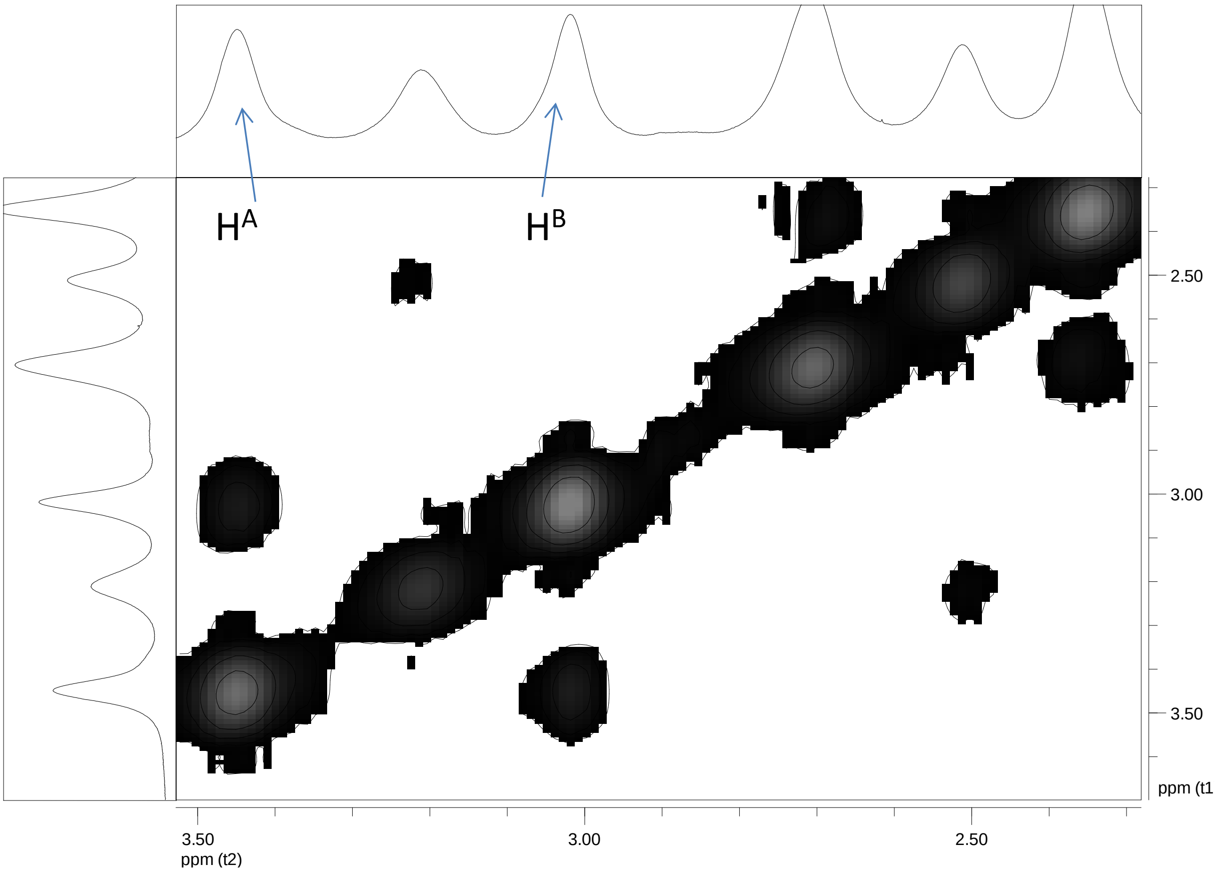
G2(C$_{14}$)$_4$(figure S1)

The protonated primary amine groups are detected by the presence of the signal at 3.39-3.30 ($NHC\underline{H^A}_2CH_2NH_3^+$) that correlates by COSY with the signal at 2.98-2.83 ($NHCH_2C\underline{H^B}_2NH_3^+$).



G2(C$_{14}$)$_{16}$(figure S2)

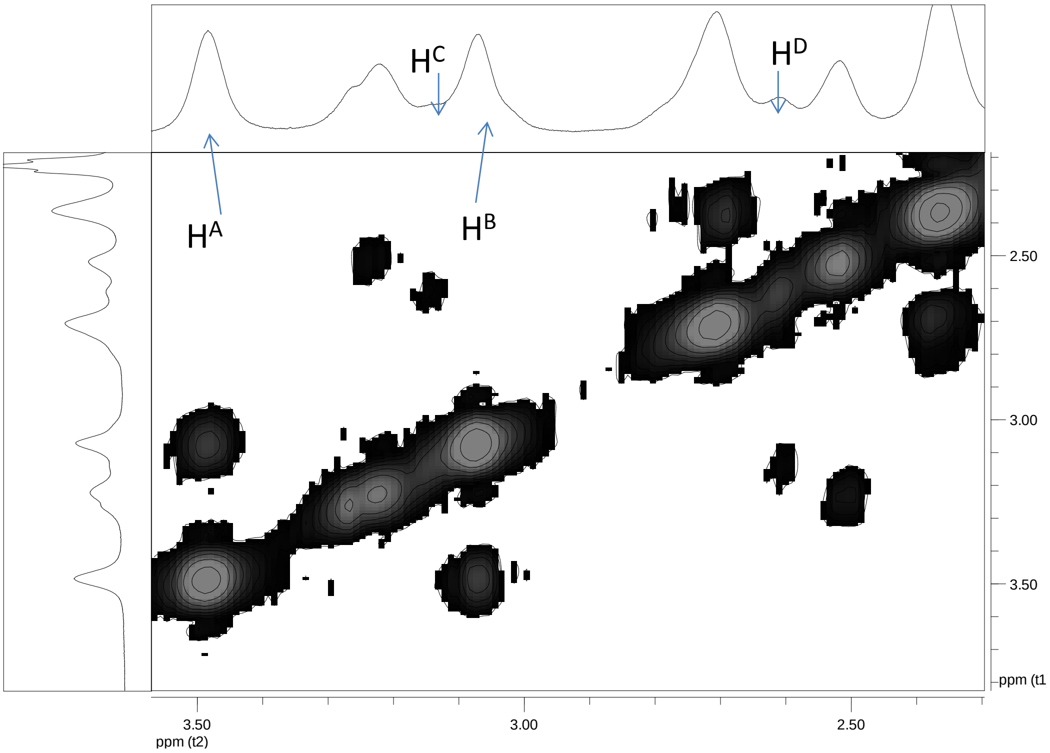
The protonated primary amine groups are detected by the presence of the signal at 3.49-3.38 (NHC$H^{\underline{A}}_2$CH$_2$NH$_3^+$) that correlates by COSY with the signal at 3.10-2.95 (NHCH$_2$C$H^{\underline{B}}_2$NH$_3^+$).



G2(C_{14})$_{30}$(figure S3)

The protonated primary amine groups are detected by the presence of the signal at 3.58-3.40 ($NHC\underline{H}^{A}{}_{2}CH_2NH_3^+$) that correlates by COSY with the signal at 3.10-2.95 ($NHCH_2C\underline{H}^{B}{}_{2}NH_3^+$).

The protonated tertiary amine groups are detected by the presence of the signal at 3.15-3.10 ($NH^+C\underline{H}^{C}{}_{2}CH_2CONH$), that correlates by COSY with 2.70-2.60 ($NH^+CH_2C\underline{H}^{D}{}_{2}CONH$).



4. POM textures of the compounds.

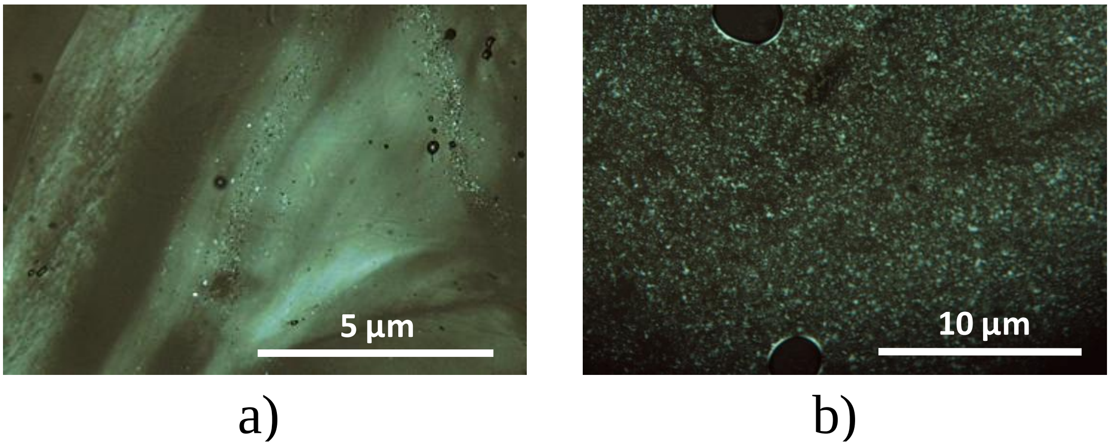


Figure S4. POM textures of a) G2(C_{14})$_8$ at room temperature (pristine sample), b) G2(C_{14})$_{20}$ at 117ºC in the first cooling process.

5. X-ray data of the compounds

Table S1. X-ray data of the compounds

Compounds	Phase [a)]	*T [ºC]*[b)]	d [Å] [c)]	Ø [Å] [d)]
G2(C_{14})$_8$	SmA	rt	42.9	15.8
G2(C_{14})$_{12}$	SmA	rt	41.0	17.6
G2(C_{14})$_{16}$	SmA	60	41.0	18.9
G2(C_{14})$_{20}$	SmA	60	39.6	20.4
G2(C_{14})$_{24}$	SmA	60	37.0	22.3
G2(C_{14})$_{28}$	SmA	60	36.5	23.6
G2(C_{14})$_{30}$	SmA	60	36.3	24.3

a) Mesophases exhibited by the compounds. b) Temperature of the X-ray study of these mesophases. c) Layer spacing "d" of the smectic phase determined by X-ray diffraction. d) Diameter of the molecule assuming a cylindrical shape (calculations have been performed following the method described in reference [RefS1]

6. X-ray diffractogrammes of the compounds

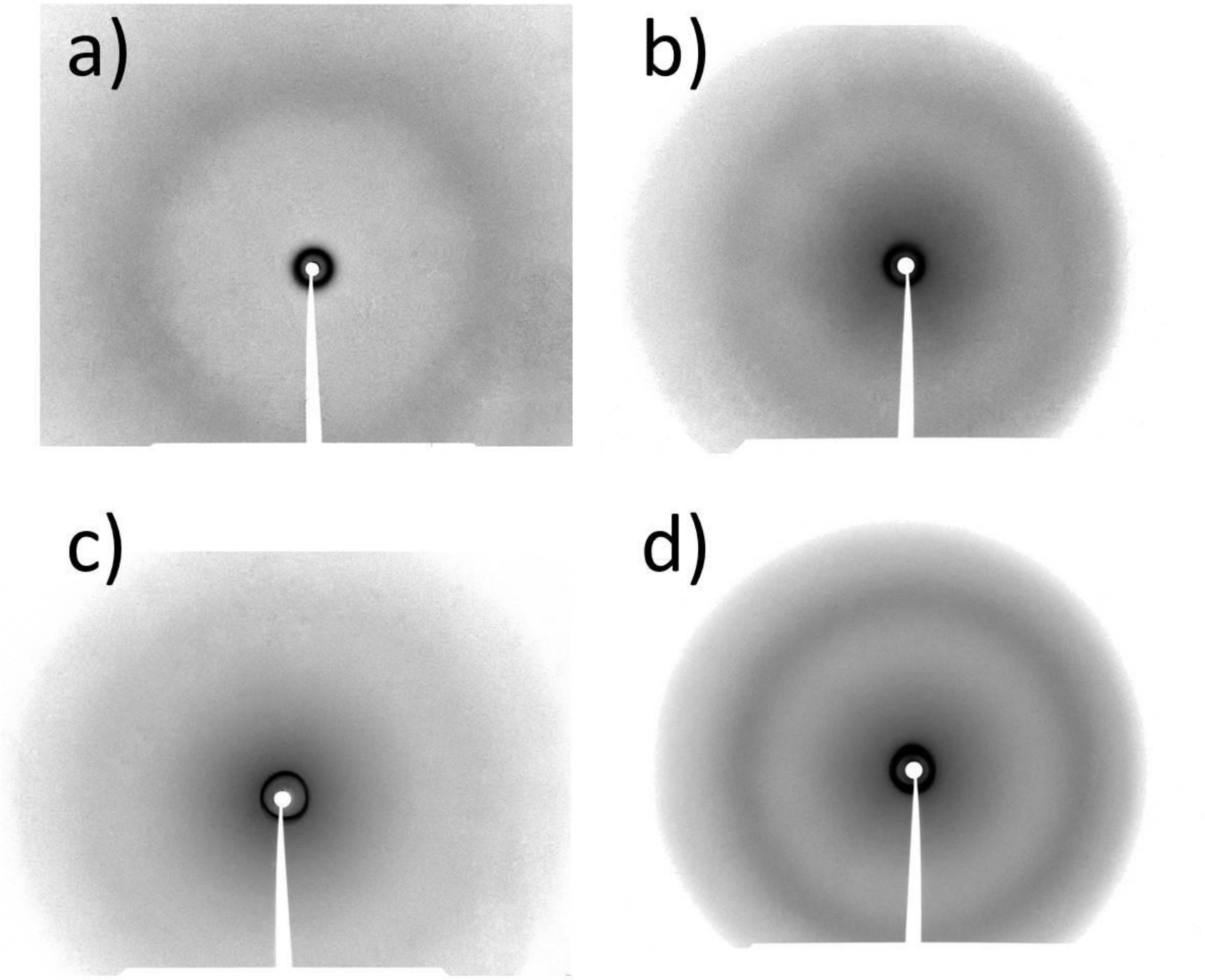


Figure S5. Small-angle XRD patterns of a) $G2(C_{14})_8$ in the SmA phase at room temperature, b) $G2(C_{14})_{16}$ in the SmA phase at 60ºC, c) $G2(C_{14})_{24}$ in the SmA phase at 60ºC and d) $G2(C_{14})_{28}$ in the SmA phase at 60ºC.

7. Nanoobjects preparation procedure

5-10 μl per minute of Milli-Q water was added to 1.5 ml of the dendrimer solution (0.5 wt% in DMSO) in a quartz cell (path length 1 cm). After each addition the cuvette is slightly shaken and then the optical density (turbidity) of the solution was taken when the value remains constant at a wavelength of 650 nm using a Unicam UV/vis spectrophotometer. This 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 DMSO using a Spectra/Por regenerated cellulose membrane with a molecular weight cut-off of 1000.

8. Procedure for the encapsulation of 9,10-diphenylanthracene

9,10-diphenylanthracene and the PAMAM ionic dendrimers were dissolved separately in 0.5 ml of DMSO each one. The two solutions were mixed together for few minutes in a closed vial. Then, 1 ml of Milli-Q water was added and the solution was slightly shaken. The quantities of both lipophilic guest and dendrimeric derivative were chosen in order to obtain a final water solution containing 0.5 μmol/ml of ionic PAMAM derivative and 0.25 μmol/ml of 9,10-diphenylanthracene. In order to remove the organic solvent, the solution was dialyzed against Milli-Q water for three days using a Spectra/Por regenerated cellulose membrane with a molecular weight cut-off of 1000. To remove the solid precipitate formed after the complete removal of DMSO, the solution was washed with dichloromethane and the organic fraction was removed and put in a new vial with known weight. This vial containing the organic fraction was dried under vacuum for 3 days at 50°C until its weight remained constant. The quantity of precipitate was calculated by weight difference, while its nature was confirmed by ^{1}H-NMR; with these two analyses, the composition of the host-guest systems in solution was evaluated.

9. Turbidity curves by water addition.

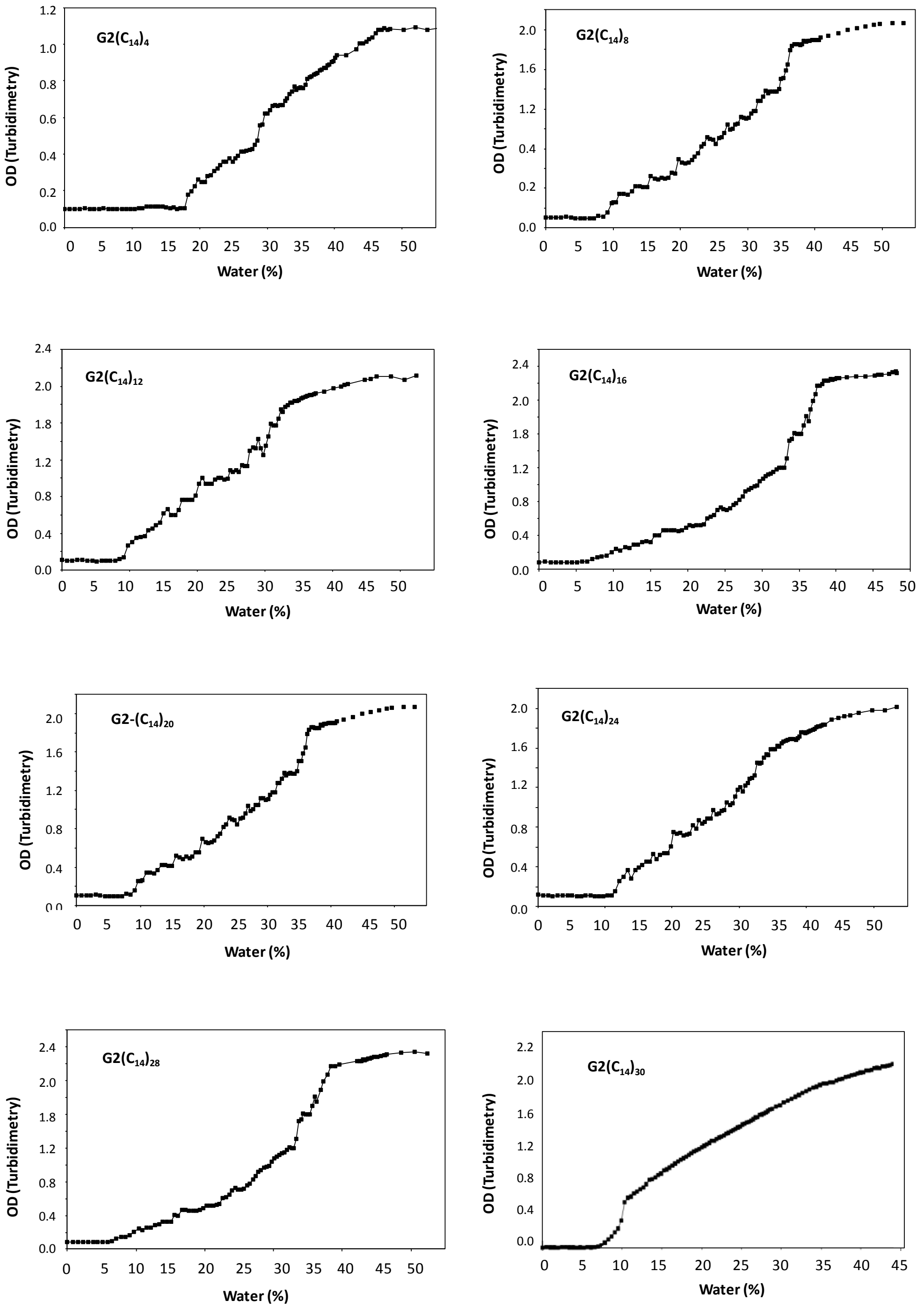


Figure S6. Turbidity (optical density) curves of the compounds in DMSO solution of (0.5%, w/w) as a function of the amount of water added to the solution

References

[refS1] R. Martín-Rapún, M. Marcos, A. Omenat, J. Barberá, P. Romero and J. L. Serrano, *J. Am. Chem. Soc.* 2005, **127**, 7397

[refS2] S. Hernández-Ainsa, J. Barberá, M. Marcos, and J. L. Serrano, *Soft Matter*, 2011, ***7***, 2560-2568