Electronic Supplementary Information

Self-Assembly of Poly(propylene imine) Glycodendrimers. Role of Aromatic Interactions in the Formation of Necklace- and Donut-like Nanostructures.

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Content of Electronic Supplemental Information

1 Experimental section.

1.1 Materials.

3rd and 5th generation poly(propylene imine) dendrimer (DAB-Am16 (Mw = 1686.79 g/mol) and DAB-Am-64 (Mw = 7167.96 g/mol) were used as purchased from SyMO-Chem (Eindhoven, The Netherlands). Sodium borohydride, phenyl isocyanate, 1-adamantyl isocyanate, and borane-pyridine complex were used as purchased from Aldrich. Chloroform was used as purchased from Acros. Maltose was used as purchased from Fluka. Membrane tubes (ZelluTransRoth VSerie with 1000 MWCO, Carl Roth GmbH&Co, Karlsruhe/Germany) for dialysis were used after washing with deionized water.

$CHCl_3$ (Chloroform), BH_3*Pyr (borane-pyridine complex), $NaBH_4$ (sodium borohydride), and PPI (poly(propylene imine)) are used as abbreviations.

1.2 Methods.

NMR Spectroscopy

The NMR measurements were performed using a Bruker Avance III 500 NMR spectrometer operating at 500.13 MHz for ^1H and at 125.75 MHz for ^{13}C. The solvent was used as lock and internal standard ($CDCl_3$: $\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.0 ppm; DMSO-d_6: $\delta(^1H)$ = 2.50 ppm, $\delta(^{13}C)$ = 39.6 ppm). Spectra recorded from D_2O solutions were referenced on external sodium 3-(trimethylsilyl)-3,3,2,2 tetradeuteropropionate in D_2O ($\delta(^1H)$ = 0 ppm, $\delta(^{13}C)$ = 0 ppm). The signal assignments were confirmed by ^1H-^1H COSY, ^1H-^1H TOCSY, ^1H-^{13}C HMQC, and ^1H-^{13}C HMBC 2D NMR experiments using the standard pulse sequences provided by Bruker.

Mass spectrometry

Laser-**i**nduced **l**iquid **b**ead **i**onization/**d**esorption mass spectrometry (LILBID-MS) is a recently developed method for the soft mass spectrometric investigation of biomolecules and biomolecular complexes.[S1] Liquid micro droplets of the aqueous sample fluid (ϕ ~50 µm) are irradiated by synchronized IR laser pulses produced by a Nd/ Yag pumped optic parametric oscillator (OPO) working at 2.9 µm. The energy is transferred by resonant excitation of a vibration of the water molecules, which led to the superexcitation and subsequent explosive disruption of the droplet. The biomolecules thus exjected into vacuum were then analyzed by a TOF mass spectrometer. The dendrimer samples were prepared in aqueous solution with concentrations of 4 x 10^{-6} M. All measurements were performed in anionic mode.

IR Spectroscopy

The IR investigations were carried out with a Bruker IFS66 spectrometer equipped with a heatable Golden Gate Diamond ATR-Unit (SPECAC). Each spectrum was the summation of 100 scans added at a spectroscopic resolution of 4 cm^{-1}.

Dynamic Light Scattering (DLS)

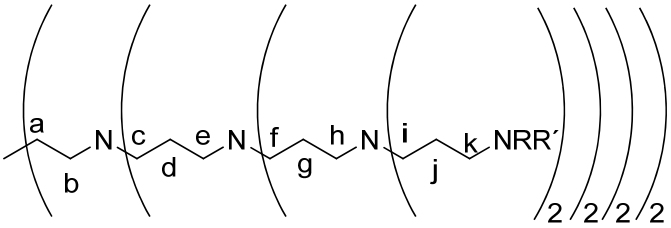
To characterize the glycodendrimer and aggregated glycodendrimer size and size distribution, dynamic light scattering (DLS) measurements were carried out at 25 °C at a fixed angle of 173° using the Nano Zetasizer (Malvern), equipped with a He–Ne laser (4 mW) and a digital autocorrelator. The observed data was analyzed very carefully. Thus only measurements with a good fit and an exponential graphic representation were considered here. The particle size distribution was determined by using a multimodal peak analysis by intensity, volume and number, respectively. The DLS measurements were made at concentrations of about 1 mg/mL. The investigated solutions were filtered directly through 0.8 mm filters and analyzed immediately.

Transmission Electronic Microscopy (TEM)

The morphology and size of the particles were determined by transmission electron microscopy with Libra 120 (Carl Zeiss AG, Oberkochen, Germany). The samples were prepared by dropping 5 µL of the sample solutions with a concentration of 1.0 mg/mL on carbon coated gold grids. The air dried samples were examined in the transmission electron microscope at an acceleration voltage of 120 kV. Final size measurements were carried out with imaging software Scandium (Olympus) Version 5.2. 1 mg/ml solution from glycodendrimer was used of (i) freezed-dried glycodendrimers, (ii) freezed-dried glycodendrimer sonicated for 5 minutes and immediately used for TEM study, and (iii) freezed-dried glycodendrimer sonicated for 5 minutes and used after 24h for TEM study. All glycodendrimer solutions were filtered directly through 0.8 mm filters before depositing on carbon coated gold grids. (i) – (iii) correspond to the description of the Figure 1 in the main text and Figure-ESI9 in the supporting information.

1.3 Synthesis of the dendrimers.

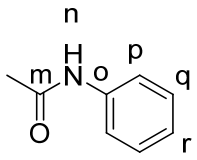
G3-Ph - Phenyl-substituted 3rd generation PPI dendrimer



G3-Ph

surface species I: R, R´ = H

surface species IIa: R = H (I), R´ =



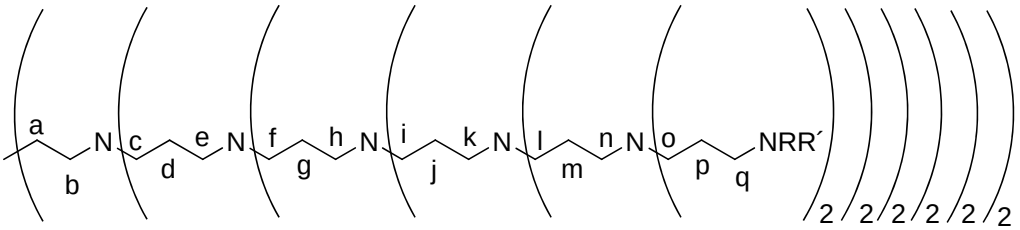
DAB-Am16 (0.30 g, 0.178 mmol) was solubilized in 30 mL of chloroform and the solution was degassed in argon atmosphere for 1 hour. A solution of phenyl isocyanate (0.17 g, 1.42 mmol, 0.155 mL) in 10 mL of chloroform was added dropwise and the resulting mixture was stirred at room temperature in argon atmosphere for 24 hours. Then, the solvent was removed under reduce pressure and the residual oil was washed with *n*-hexane to obtain **G3-Ph** (0.40 g, yield 89%) as a colorless oil. The number of phenyl urea groups per **G3-Ph** molecule was calculated from ^{1}H NMR spectrum from the intensity of all aromatic protons and the intensity of the 1.7–1.5 ppm region representing 60 protons (a, d, g, j) of the PPI scaffold. A value of 7.4 was determined (46% conversion).

The ^{1}H NMR spectrum is depicted in Figure ESI-1a.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.35 (n), 7.35 (p), 7.15 (q), 6.84 (r), 6.19 and 6.10 (l), 3.09 (k of IIa), 2.55 (k of I), 2.4–2.2 (b, c, e, f, h, i), 1.52 (j of IIa), 1.45 (d, g, j of I), 1.35 ppm (a).

IR: 3325 (NH_2), 2938, 2860, 2802 (CH_2), 1656 (C=O), 1596 (C=C), 1550 cm^{-1} (N-H, NH_2).

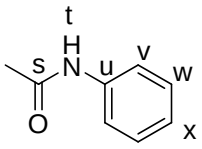
G5-Ph - Phenyl-substituted 5th generation PPI dendrimer**.**



G5-Ph

surface species I: R, R´ = H

surface species IIa: R = H (r), R´ =



DAB-Am64 (0.20 g, 0.28 mmol) was solubilized in 30 mL of chloroform and the solution was degassed in argon atmosphere for 1 hour. A solution of phenyl isocyanate (0.106 g, 0.89 mmol, 0.097 mL) in 10 mL of chloroform was added dropwise and the resulting mixture was stirred at room temperature in argon atmosphere for 24 hours. Then, the solvent was removed under reduce pressure and the residual oil was washed with *n*-hexane to obtain **G5-Ph** (0.31, yield 95%) as a colorless oil. 38 phenyl groups per **G5-Ph** molecule were calculated from the ^{1}H NMR spectrum according to the procedure reported for **G3-Ph** (59% conversion). 256 protons are used for the internal protons (a, d, g, j, m, p) of the 5th generation PPI scaffold to determine the degree of coupled phenyl groups.

The ^{1}H NMR and ^{13}C NMR spectra are depicted in Figure ESI-1b and Figure ESI-2, respectively.

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.2-8.3 (t), 7.35 (v), 7.12 (w), 6.82 (x), 6.7-6.0 (r), 3.08 (q of IIa), 2.57 (q of I), 2.45-2.1 (b, c, e, f, h, i, k, l, n, o), 1.7-1.3 ppm (a, d, g, j, m, p). ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.3 (s), 140.4 (u), 128.2 (w), 120.7 (x), 117.8 and 117.6 (v), 53 – 51 (b, c, e, f, h, i, k, l, n, o), 39.5 (q of I; identified in HSQC spectrum), 37.5 (q of IIa), 29.4 (p of I), 27.4 (a, p of IIa), 24.3 (d, g, j, m). IR: 3314 (NH_2), 2936, 2862, 2808 (CH_2), 1653 (C=O), 1596 (C=C), 1550 cm^{-1} (N-H, NH_2).

NMR spectra of G3-Ph and G5-Ph

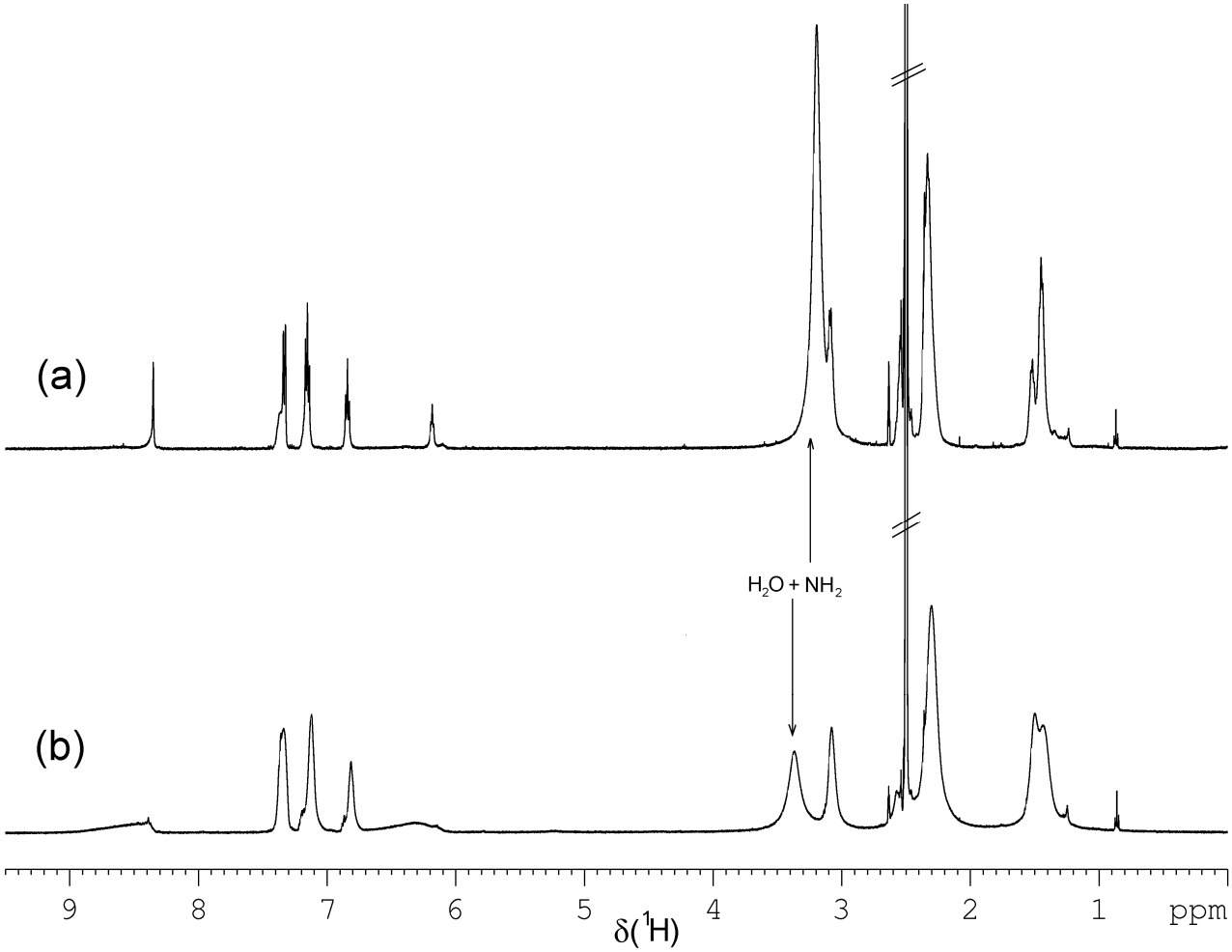


Figure ESI-1. ^{1}H NMR spectra of (a) **G3-Ph** and (b) **G5-Ph** in DMSO-d_6 at 303 K.

The signals of the aromatic protons p, q and r are a superposition of narrow signals (6.8 – 7.5 ppm) showing the J-coupling pattern and broadened signals (see Figure ESI-1a). Also at 373 K this effect does not disappear, that is, no exchange broadening due to different urea conformations is observed. Most probably this effect is caused by the substitution pattern of terminal $–N(CH_2CH_2CH_2NRR')_2$ moieties. If only one of the two terminal units is a phenyl urea group and the other a still non-reacted amino group (IIa/I combination; see surface species for **G3-Ph**) the urea moiety is mobile and results in narrow signals. If both end groups are phenyl urea groups (IIa/IIa combination) probably hindered mobility (hydrogen bonding, π–stacking) results in signal broadening. The NH signals of **G5-Ph** (see surface species) cover broad ppm ranges low-field shifted to the signals observed for **G3-Ph**. This is attributed to intramolecular hydrogen bonds between the urea groups involving several units. Such long-range hydrogen bonding seems possible because **G5-Ph** has a higher degree of substitution

and a denser packing of the terminal groups in the outer sphere. π-stacking can further reduce mobility. Narrow signals due to IIa/I combination are only of low intensity.

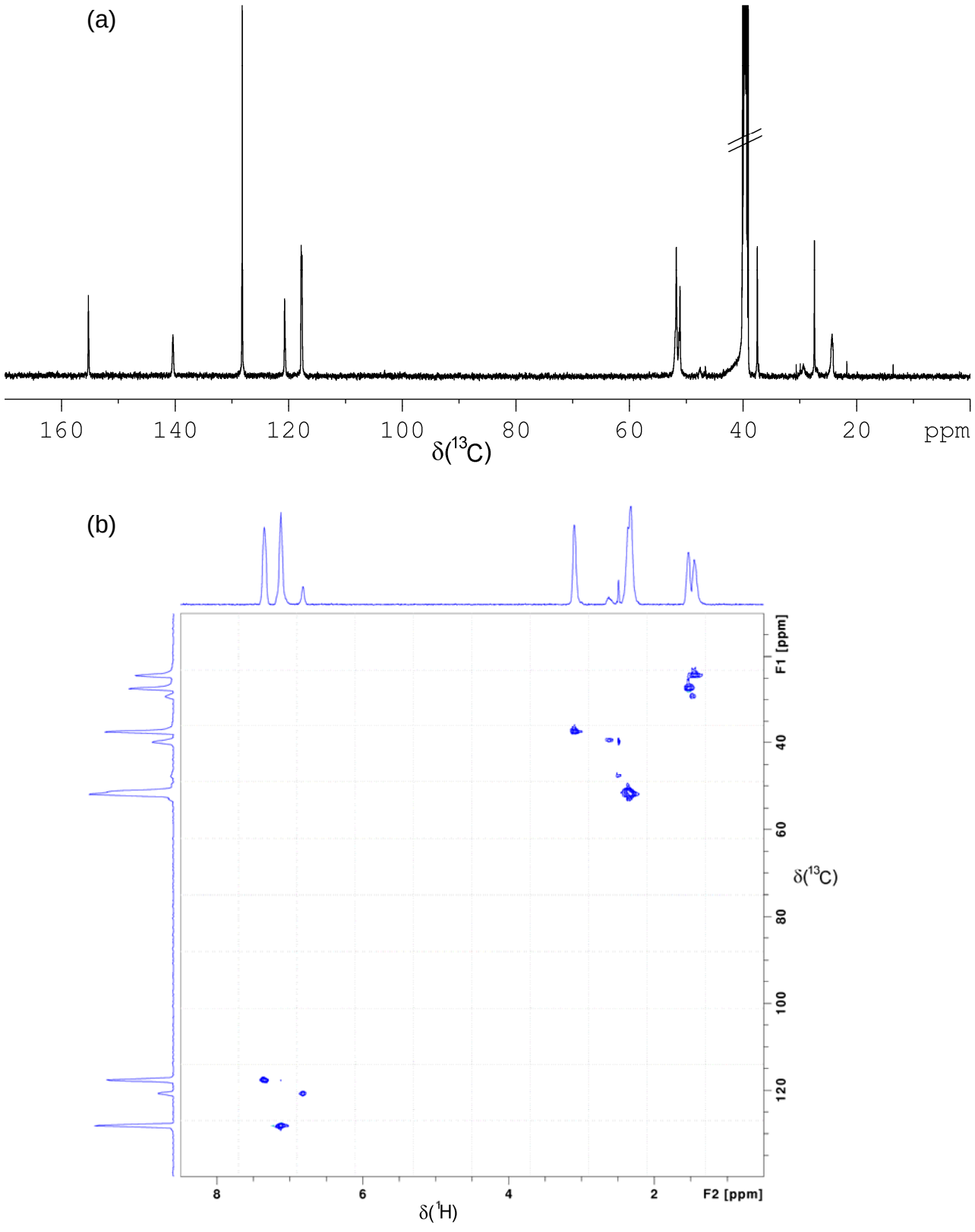
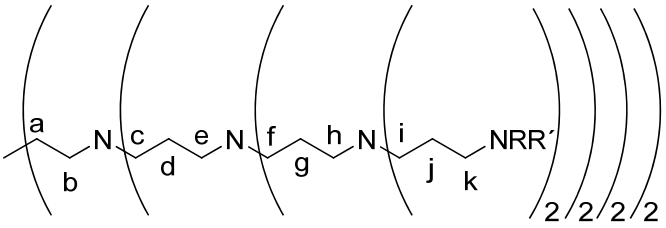
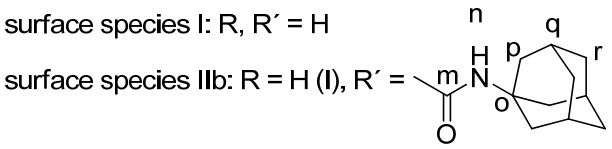


Figure ESI-2. ^{13}C NMR (a) and HSQC spectrum (b) of **G5-Ph** in DMSO-d_6 at 333 K.

G3-Ada - Adamantyl-substituted 3rd generation PPI dendrimer



G3-Ada

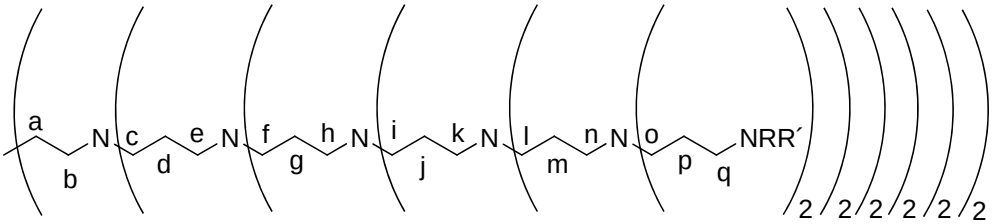


DAB-Am16 (0.20 g, 0.119 mmol) was solubilized in 30 mL of chloroform and the solution was degassed in argon atmosphere for 1 hour. Then, 1-adamantyl isocyanate (0.17 g, 0.95 mmol) in 10 mL of chloroform was added dropwise and the resulting mixture was stirred at room temperature in argon atmosphere for 24 hours. The solvent was removed under reduce pressure to obtain a desired materials **G3-Ada** as colorless oil (yield >95%). The number of adamantyl groups per **G3-Ada** molecule was calculated from the intensities of the k group signals resulting from surface species I (2.73 ppm) and IIb (3.12 ppm) taking into account 16 terminal groups. A value of 8.8 was determined (55% conversion).

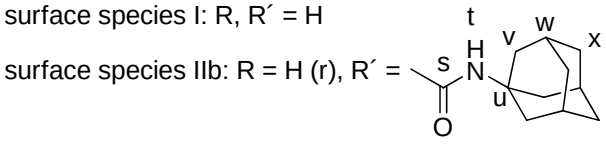
The ^{1}H NMR spectrum is depicted in Figure ESI-3a.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.2-5.4 (l), 5.4-4.7 (n), 3.12 (k of IIb), 2.73 (k of I), 2.44 (i of I), 2.39 (b, c, e, f, h, i of IIb), 2.03 (q), 1.96 (p), 1.65 (r), 1.65-1.45 (d, g, j), 1.39 ppm (a). IR: 3310 (NH_2), 2903, 2848, 2800 (CH, CH_2), 1635 (C=O), 1558 cm^{-1} (N-H, NH_2). MALDI-TOF: ms m/z calculated for $C_{176}H_{328}N_{38}O_8$ = 3104.74 (related to 8 adamantyl urea connect to PPI-G3), found (main peaks) 3104.42 (M)

G5-Ada - Adamantyl-substituted 5th generation PPI dendrimer



G5-Ada



DAB-Am64 (0.20 g, 0.028 mmol) was solubilized in 30 mL of chloroform and the solution was degassed in argon atmosphere for 1 hour. Then, 1-adamantyl isocyanate (0.16 g, 0.89 mmol) in 10 mL of chloroform was added dropwise and the resulting mixture was stirred at room temperature in argon atmosphere for 24 hours. The solvent was removed under reduce pressure to obtain the desired material **G5-Ada** as colorless oil (yield >95%). 34 adamantyl groups per **G5-Ada** molecule were calculated from the ^{1}H NMR spectrum according the procedure reported for **G3-Ada** (54% conversion).

The ^{1}H NMR and ^{13}C NMR spectra are depicted in Figure ESI-3b and Figure ESI-4 respectively.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.3-5.6 (r), 5.6-5.0 (t), 3.11 (q of IIb), 2.73 (q of I), 2.5–2.3 (b, c, e, f, h, i, k, l, n, o), 2.03 (w), 1.96 (v), 1.65 (x), 1.65-1.45 (d, g, j, m, p), 1.36 ppm (a). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6 (s), 53 – 51 (b, c, e, f, h, i, k, l, n, o), 50.4 (u), 42.7 and 42.6 (v), 40.7 (q of I), 38.2 and 38.0 (q of IIb), 36.6 (x), 30.6 (p of I), 29.6 (w), 27.9 (a, p of IIb), 24.6 (d, g, j, m). NMR data of fully adamantine-substituted G5 were reported by D. Banerjee et al. in the reference S2. IR: 3306 (NH_2), 2904, 2848, 2800 (CH, CH_2), 1636 (C=O), 1558 cm^{-1} (N-H, NH_2).

^{1}H NMR spectra of G3-Ada and G5-Ada

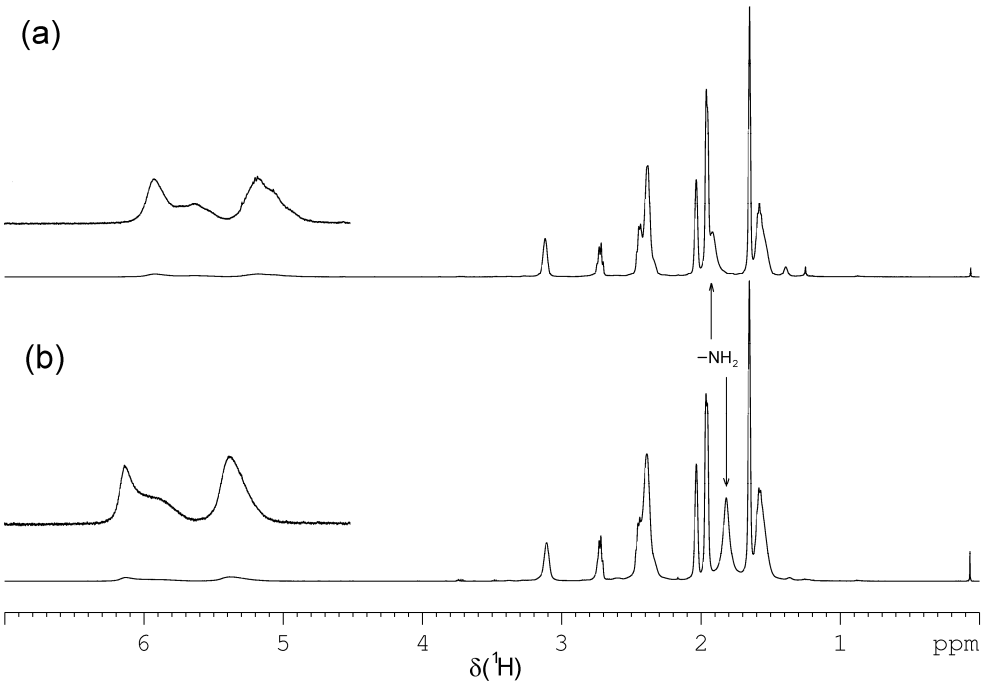


Figure ESI-3. ^{1}H NMR spectra of (a) **G3-Ada** and (b) **G5-Ada** in $CDCl_3$ at 303 K.

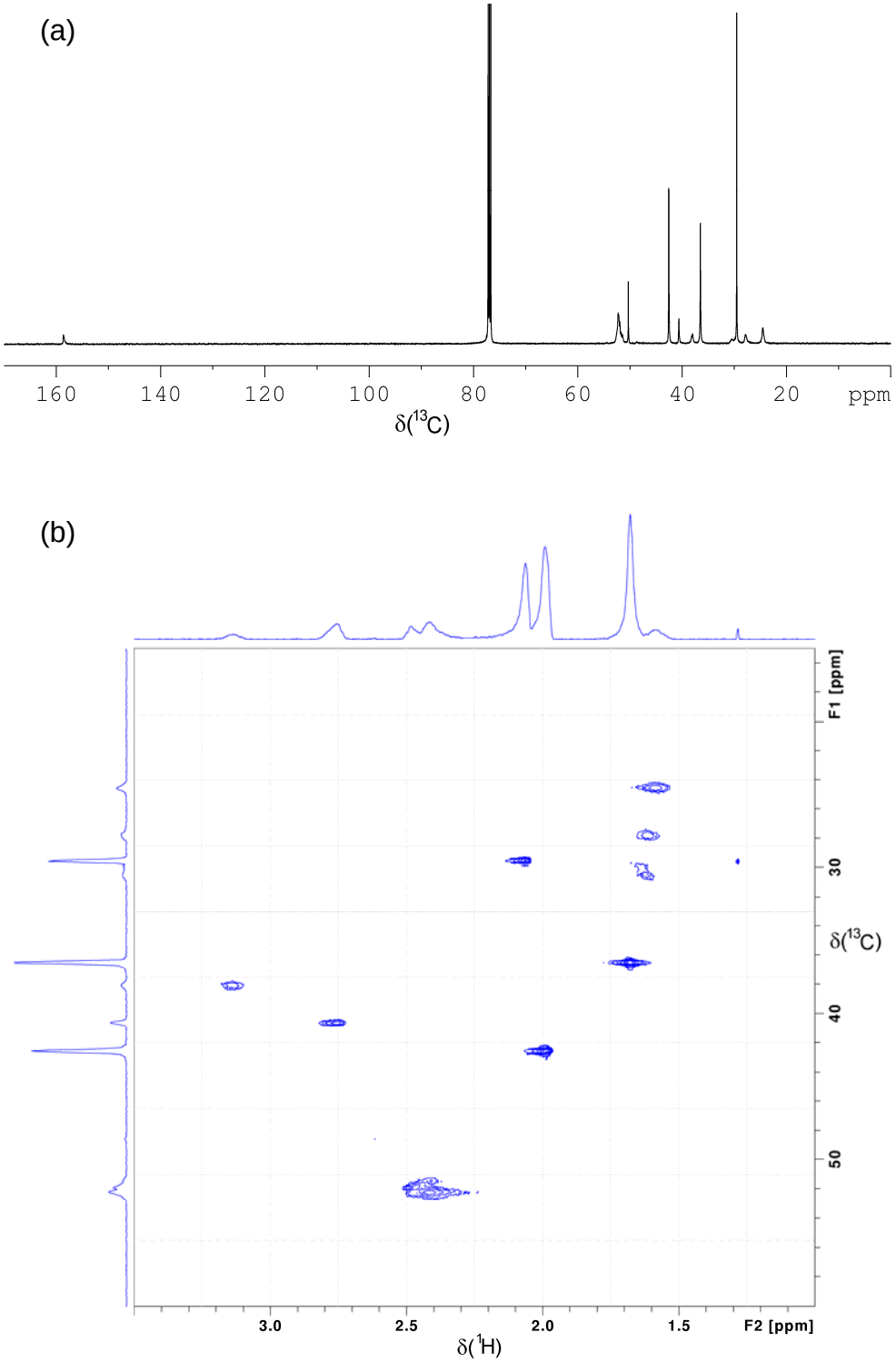
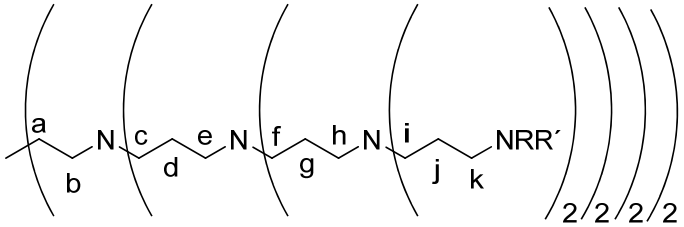


Figure ESI-4. ^{13}C NMR (a) and HSQC spectrum (b) of **G5-Ada** in $CDCl_3$ at 303 K.

General procedure for the synthesis of PPI glycodendrimers.

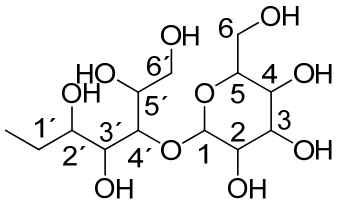
The appropriate dendrimeric material (**G3-Ph**, **G5-Ph**, **G3-Ada**, or **G5-Ada**), D(+)-maltose monohydrate (20 eq. in free amino groups), and borane–pyridine complex (solution 8 M, 40 eq. in free amino groups), were taken up in a sodium borate buffer (30 mL, 0.1 M). The reaction solution was stirred at 50 °C for 7 d. Then, the resulting crude solutions, containing all substance soluble in the reaction condition, were purified by dialysis towards deionised water for 3 d. Then, the water was eliminated by freeze-drying to obtain the desired products.

G3-Ph-Mal - Phenyl-substituted 3rd generation PPI dendrimer with dense maltose shell

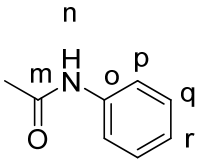


G3-Ph-Mal

surface species **III**: R, R´ =



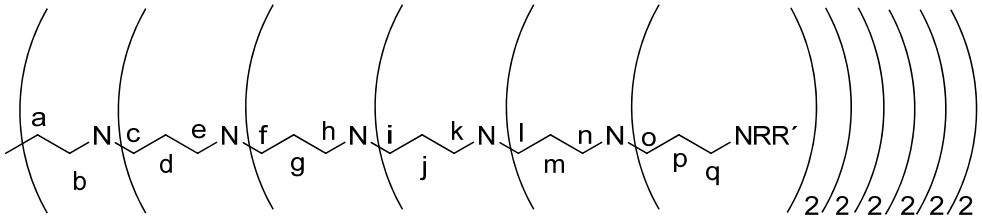
surface species **IIa**: R = H, R´ =



This glycodendrimer was obtained from material **G3-Ph** (0.25 g, 0.099 mmol) soluble in the reaction condition as white fluffy material (0.49 g, 44%). The lower yield of **G3-Ph-Mal** is explainable due to the presence of substantial amount of insoluble material in the reaction condition which was separated by centrifugation before the purification by dialysis and water elimination by freeze drying step. The ^{1}H NMR is depicted in Figure ESI-5a.

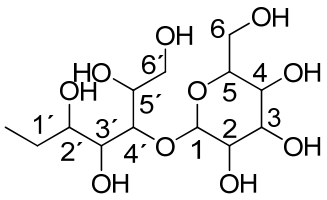
^{1}H NMR (500 MHz, D_2O): δ 7.37 (p, q), 7.14 (r), 5.11 (1), 4.4-3.3 (2-6, 2'-6'), 3.3–2.2 (1', b, c, e, f, h, i, k), 2.2-1.4 (a ,d, g, j). IR: 3276 (OH), 2932 (CH, CH_2), 1654 (C=O), 1597 (C=C), 1551 (N-H), 1021 cm^{-1} (C-O). LILBID MS: $C_{438}H_{834}N_{32}O_{282}$ (11055 g/mol relating to 28 maltose units and 2 phenyl urea moieties connected to DAB-Am16); m/z = top of the peak of about 11134 (M^-).

G5-Ph-Mal - Phenyl-substituted 5th generation PPI dendrimer with dense maltose shell

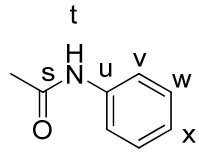


G5-Ph-Mal

surface species **III**: R, R´ =



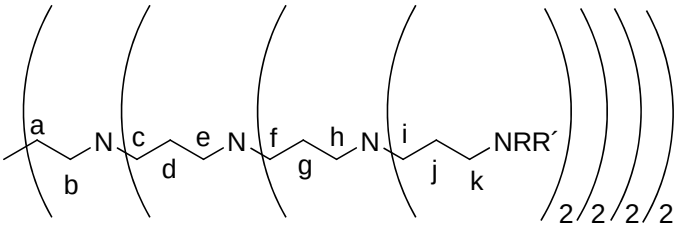
surface species **IIa**: R = H, R´ =



This glycodendrimer was obtained from material **G5-Ph** (0.29 g, 0.025 mmol) as white fluffy material soluble in the reaction condition (0.51 g, 74%). The ^{1}H NMR and ^{13}C NMR spectra are depicted in Figure ESI-5b and Figure ESI-6a, respectively.

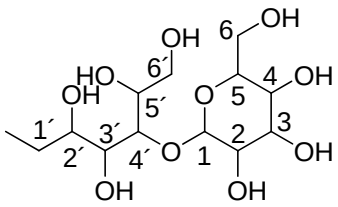
^{1}H NMR (500 MHz, D_2O): δ 7.5-6.8 (v, w, x), 5.10 (1), 4.4-3.3 (2-6, 2'-6'), 3.3–2.0 (1', b, c, e, f, h, i, k, l, n, o, q), 2.0-1.4 (a ,d, g, j, m, p). ^{13}C NMR (125 MHz, D_2O): δ 159.9 (s), 142.3 (u), 132.0 (w), 125.6 (x), 122.3 (v), 103.5 (1), 85.4 (4'), 75.8, 75.4 and 74.5 (2, 3, 3', 5, 5'), 72.3 (4), 71.2 (2'), 65.7 and 65.2 (6'), 63.3 (6), 59.8 (1'), 58-51 (b, c, e, f, h, i, k, l, n, o, q of III), 40.6 (q of IIa), 28.5 (p of IIa), 28-21 (a, d, g, j, m, p of III). IR: 3233 (OH), 2932 (CH, CH_2), 1658 (C=O), 1597 (C=C), 1551 (N-H), 1021 cm^{-1} (C-O). LILBID MS: $C_{1218}H_{2126}N_{164}O_{518}$ (27340 g/mol relating to 48 maltose units and 38 phenyl urea moieties connected to DAB-Am64); m/z = top of the peak of about 27391 (M^-).

G3-Ada-Mal - Adamantyl-substituted 3rd generation PPI dendrimer with dense maltose shell

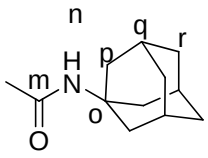


G3-Ada-Mal

surface species III: R, R´ =



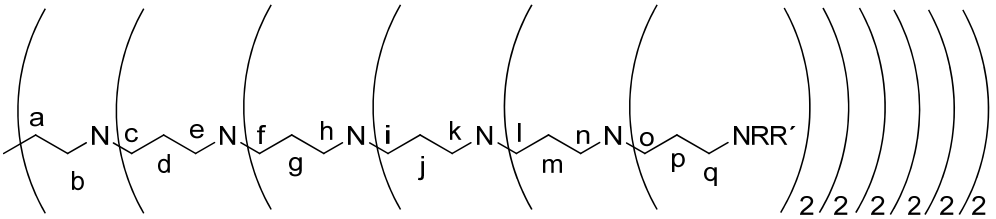
surface species IIb: R = H, R´ =



This glycodendrimer was obtained from material **G3-Ada** (0.29 g, 0.093 mmol) as white fluffy material soluble in the reaction condition (0.58 g, 78%). The ^{1}H NMR is depicted in Figure ESI-5c.

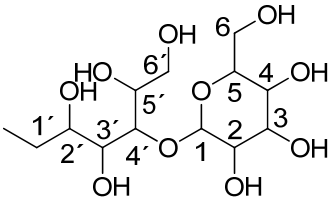
^{1}H NMR (500 MHz, D_2O): δ 5.11 (1), 4.4-3.3 (2-6, 2'-6'), 3.3–2.2 (1', b, c, e, f, h, i, k), 2.2-1.4 (a, d, g, j), 2.03 (q), 1.95 (p), 1.68 (r). IR: 3326 (OH), 2906, 2849 (CH, CH_2), 1639 (C=O), 1559 (NH), 1021 cm^{-1} (C-O). LILBID MS: $C_{346}H_{650}N_{36}O_{160}$ (7966 g/mol relating to 16 maltose units and 6 adamantyl urea moieties connected to DAB-Am16); m/z = top of the peak of about 7982 (M^-).

G5-Ada-Mal - Adamantyl-substituted 5th generation PPI dendrimer with dense maltose shell

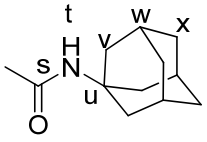


G5-Ada-Mal

surface species III: R, R´ =



surface species IIb: R = H, R´ =



This glycodendrimer was obtained from material **G5-Ada** (0.28 g, 0.021 mmol) as white fluffy material soluble in the reaction condition (0.60 g, 94%). The ^{1}H NMR and ^{13}C NMR spectra are depicted in Figure ESI-5d and Figure ESI-6b, respectively.

^{1}H NMR (500 MHz, D_2O): 5.10 (1), 4.4-3.3 (2-6, 2'-6'), 3.3–2.0 (1', b, c, e, f, h, i, k, l, n, o, q), 2.2-1.3 (a ,d, g, j, m, p), 2.08 (w), 1.98 (v), 1.69 (x). ^{13}C NMR (125 MHz, D_2O): δ 162.0 (s), 103.5 (1), 85.3 (4'), 75.8, 75.4 and 74.5 (2, 3, 3', 5, 5'), 72.3 (4), 71.2 (2'), 65.7 and 65.2 (6'), 63.3 (6), 59.8 (1'), 58-51 (b, c, e, f, h, i, k, l, n, o, q of III), 53.1 (u), 45.0 (v), 40.4 (q of IIa), 39.4 (x), 32.4 (w), 28.5 (p of IIa), 28-21 (a, d, g, j, m, p of III). IR: 3328 (OH), 2906 (CH, CH_2), 2850 (C-C), 1640 (C=O), 1559 (N-H), 1021 cm^{-1}(C-O). LILBID MS: $C_{1375}H_{2541}N_{159}O_{563}$ (30292 g/mol relating to 53 maltose units and 33 adamantyl urea moieties connected to DAB-Am64); m/z = top of the peak of about 30333 (M^-).

NMR spectra of glycodendrimers

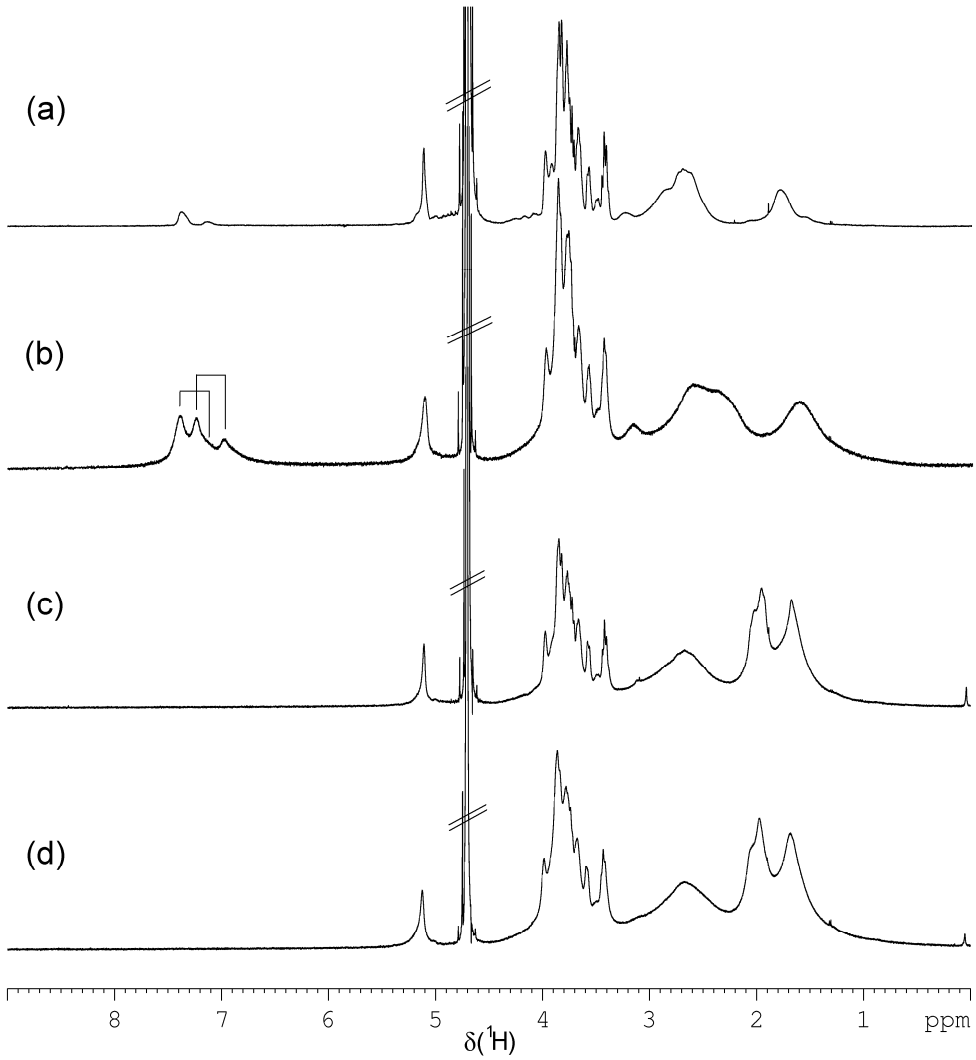


Figure ESI-5. ^{1}H NMR spectra of (a) **G3-Ph-Mal** (soluble part), (b) **G5-Ph-Mal**, (c) **G3-Ada-Mal**, and (d) **G5-Ada-Mal** in D_2O at 303 K.

The water soluble part of **G3-Ph-Mal** contains only 2.5 phenyl units per dendrimer molecule. Thus, it is most likely that the observed phenyl signals (4:1 intensity ratio assigned to signals of (p+q):r) are only due to terminal $-N(CH_2CH_2CH_2NRR')_2$ groups with one urea moiety (I/IIa combination). For **G5-Ph-Mal** an additional signal pattern of similar shape but high-field-shifted to the signals before observed for **G3-Ph** is obvious. These signals are attributed to terminal $-N(CH_2CH_2CH_2NRR')_2$ groups with two urea moieties (IIa/IIa combination). They are probable because here the soluble part is higher phenyl substituted.

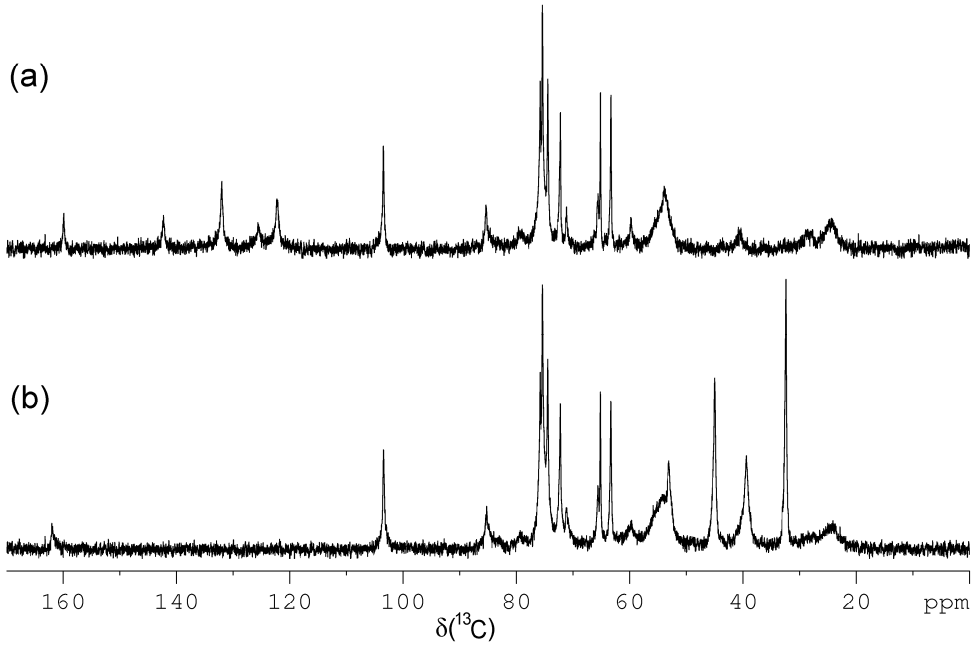


Figure ESI-6. ^{13}C NMR spectra of (a) **G5-Ph-Mal** and (b) **G5-Ada-Mal** in D_2O at 303 K.

2 Mass spectrometry

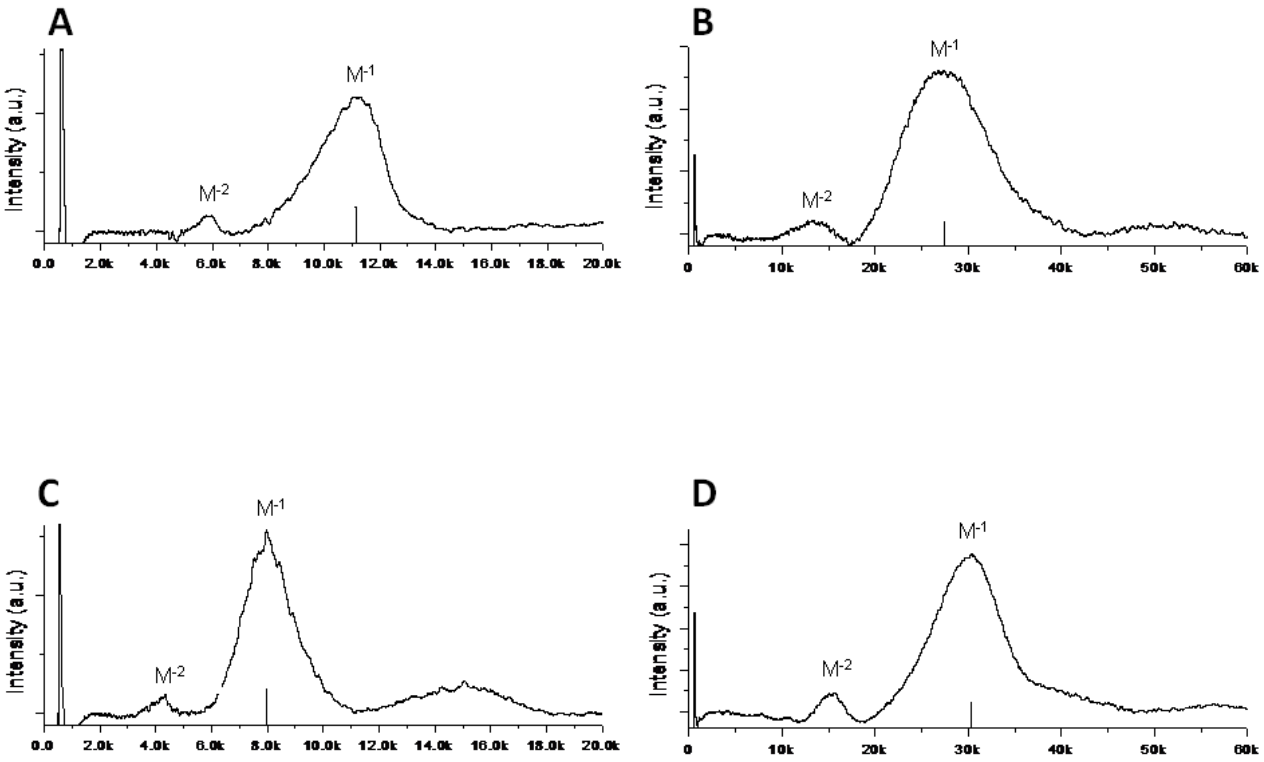


Figure ESI-7. LILBID-mass spectra: A) **G3-Ph-Mal**; B) **G5-Ph-Mal**; C) **G3-Ada-Mal**; D) **G5-Ada-Mal**. The mass scale is m/z.

3 Dynamic light scattering study on G3-Ph-Mal, G5-Ph-Mal, G3-Ada-Mal, G5-Ada-Mal

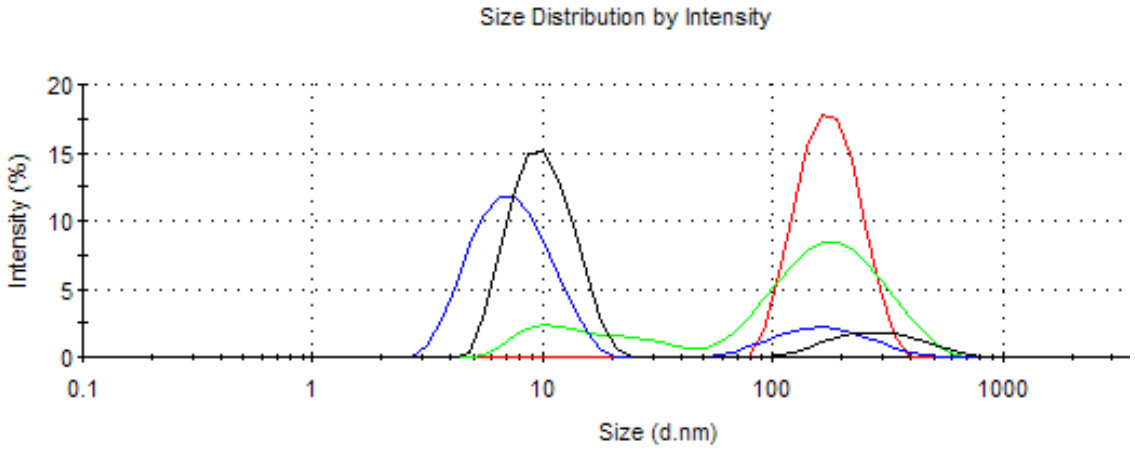


Figure ESI-8. DLS analysis of glycodendrimers **G3-Ph-Mal** (red), **G3-Ada-Mal** (blue), **G5-Ph-Mal** (green), **G5-Ada-Mal** (black).

Table ESI-1. PDI data from DLS study obtained from corresponding size dimensions of glycodendrimers

Dendrimer	PDI
G3-Ph-Mal	0.431
G5-Ph-Mal	0.631
G3-Ada-Mal	0.307
G5-Ada-Mal	0.284

4 TEM study on G3-Ph-Mal, G5-Ph-Mal, G3-Ph and G5-Ph

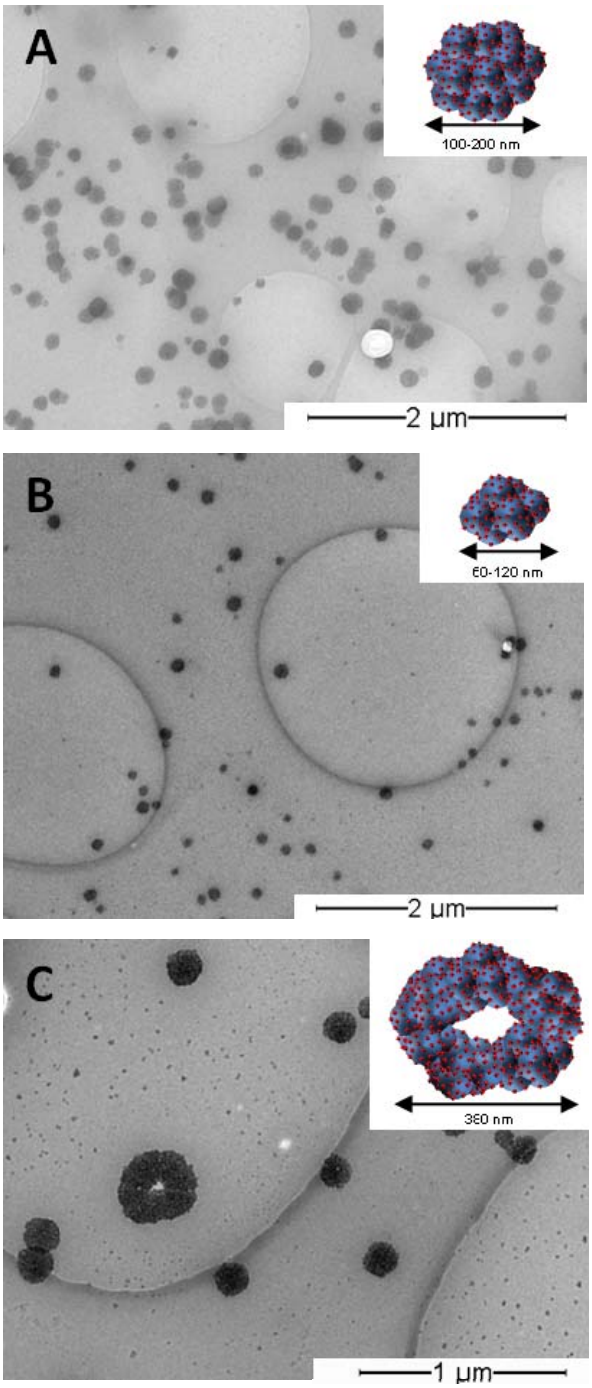


Figure ESI-9. TEM analysis of **G5-Ph-Mal** and cartoon representation of aggregate structures: (i = A) elimination of water by freeze drying and solubilisation in Millipore water; (ii = B) sonication for 5 min.; (iii = C) sonication for 5 min. and keeping the solution at room temperature for 1 day.

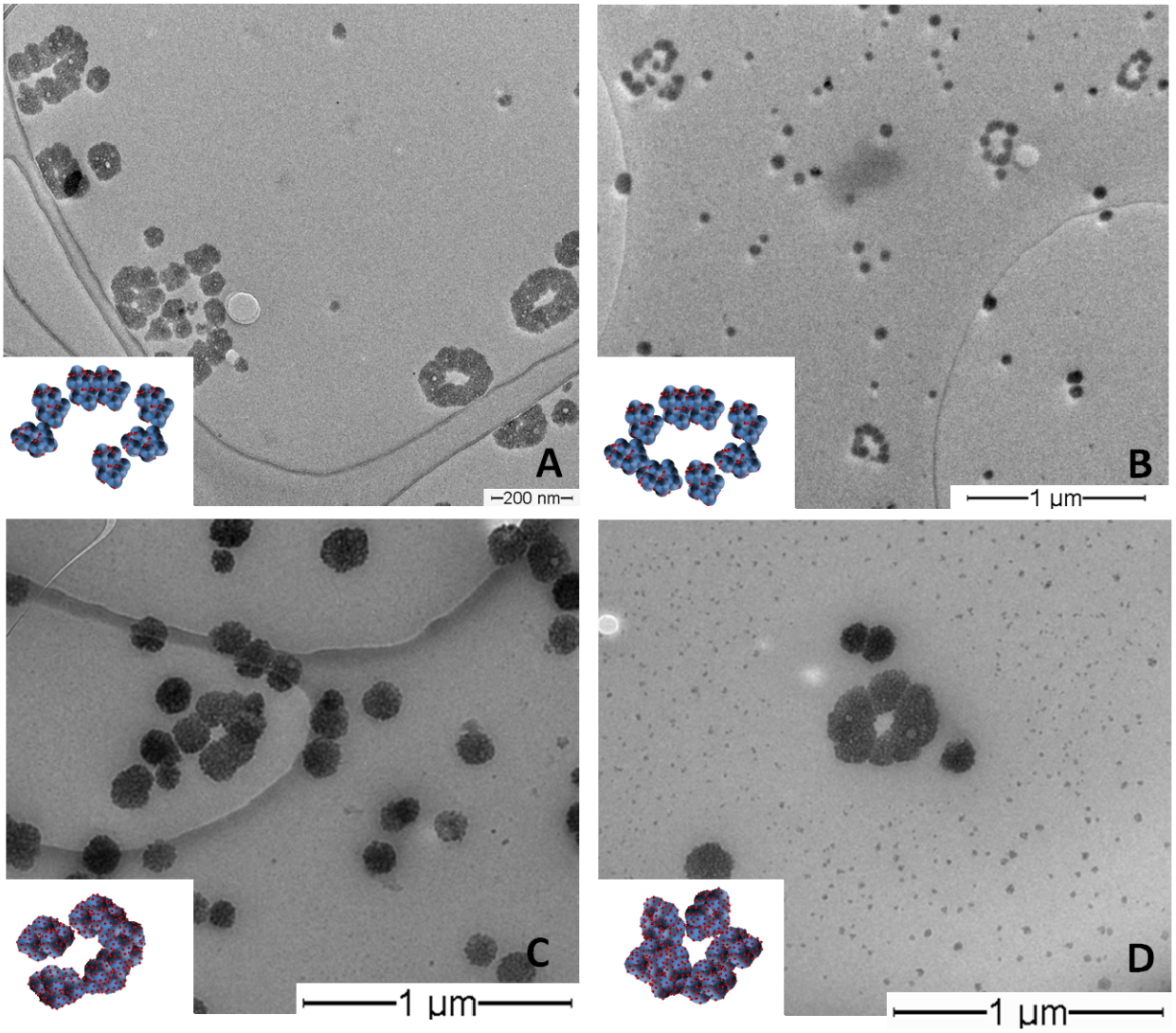


Figure ESI-10. TEM Analysis of PPI-glycodendrimers **G3-Ph-Mal** and **G5-Ph-Mal**. Panels A and B show the preassembling state of **G3-Ph-Mal** after 1 day**;** panels C and D show the pre-assembling state of **G5-Ph-Mal** after 1 day.

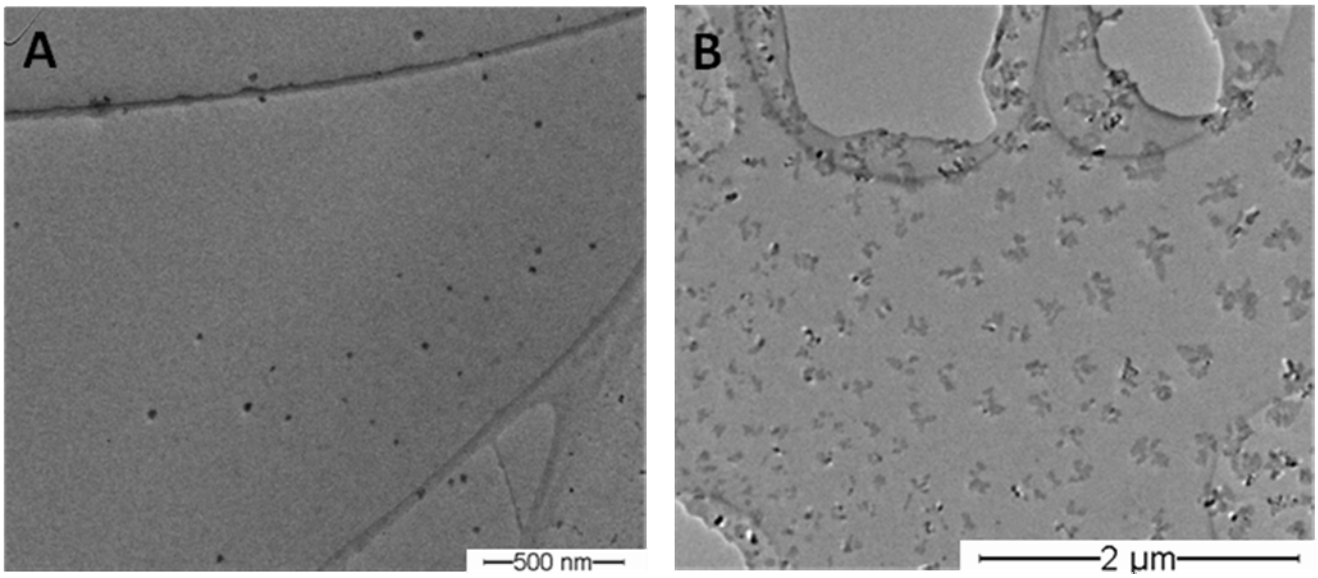


Figure ESI-11. TEM analysis of soluble portion of dendrimers **G3-Ph** (panel A) and **G5-Ph** (panel B).

The particular aggregation behavior of **G3-Ph-Mal** and **G5-Ph-Mal** was not observed in the case of the precursors **G3-Ph** and **G5-Ph**. **G3-Ph** and **G5-Ph** which do not show appreciable solubility in water. However, in small soluble portions of these dendrimers, obtained after sonication and filtration of the suspension, the presence of small aggregates for the dendrimer **G3-Ph** and aggregates of confused shapes for the dendrimer **G5-Ph** has been verified, totally different from the structures obtained with the corresponding glycodendrimers.

5 Reference

[S1] N. Morgner, H.-D. Barth, B. Brutschy, *Aust. J. Chem.* **2006**, *59*, 109.

[S2] D. Banerjee, M. A. C. Broeren, M. H. P. van Genderen, E. W. Meijer, P. L. Rinaldi, *Macromolecules* **2004**, *37*, 8313.