A Chain of Dendrimers

Synthesis and Characterization of Dendritic Necklaces: A Class of Outer-Sphere–Outer-Sphere Connected Dendronized Organoplatinum Polymers**

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Some years ago Newkome and Vögtle proposed the concept of dendritic networks[1] whereby simple dendrimer/dendron subunits could be connected together to form macromolecular assemblies with nanoscopic dimensions.[2] At about the same time, Schlüter and co-workers began to report their pioneering works on the synthesis and characterization of a special kind of dendritic networks, also known as cylindrical dendronized polymers,[3,4] based on an inner-sphere–inner-sphere connection[2] approach, that is, the resulting dendronized polymers may be viewed as constructed from the connection of individual dendrons through their internal focal-point functional groups. A large number of such inner-sphere–inner-sphere connected dendronized polymers were reported. Some of them were shown to have cylindrical geometry[4] while some were known to self-assemble into spherical nanostructures.[5] To our surprise, examples of dendritic networks created by the alternative outer-sphere–outer-sphere connection strategy[2] are less studied. A few examples were already reported but invariably they all involve a random polymerization of dendrimer subunits that have a large number of reactive functional groups on the dendrimer surface.[6] We report herein a new variant of the outer-sphere–outer-sphere connection strategy that allows us to prepare a novel class of nanoscopic dendritic networks (hereafter called dendritic necklaces because of their structural resemblance to untied necklaces) by the controlled polymerization of dendrimer subunits containing only two reactive surface functional moieties (Figure 1).[7] We also show that the resulting dendritic necklaces, in contrast to randomly connected dendritic networks, can be fully characterized by solution techniques such as NMR, MS, GPC and laser light scattering (LLS) to enable a thorough assessment of their structural identity and purity. Employing organoplatinum coordination chemistry as a method for the polymerization of bis(ethynyl) surface-functionalized G1–G3 dendritic beads **1–3**, we demonstrate that higher-order 1D dendritic necklaces with high degree-of-polymerization values (DP, from 30–880) could be prepared in high yields. We also describe a general synthetic protocol for the construction of dendrimers that contain a limited number of functional groups on the surface sector.

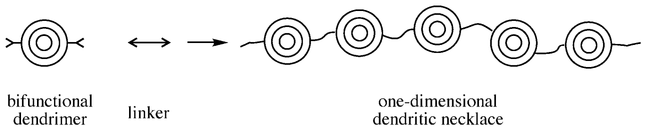
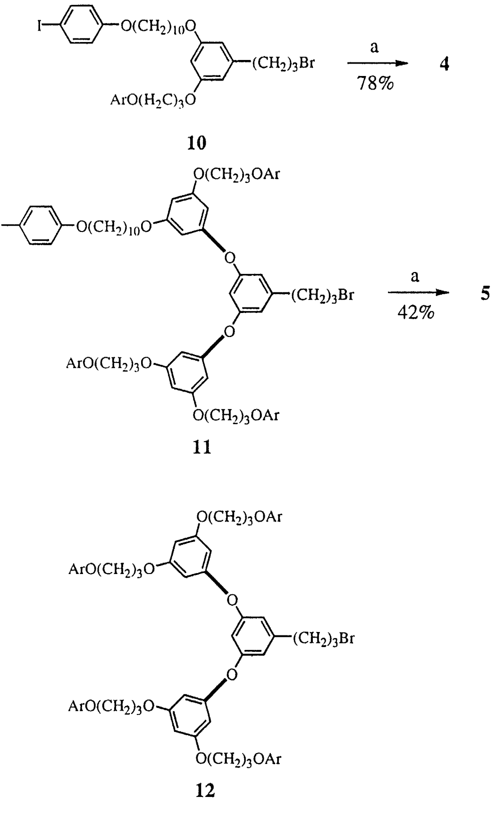


Figure 1. Synthesis of dendritic necklaces by outer-sphere–outer-sphere connection of bifunctional dendrimers.

Because bis(ethynyl) polyether-based dendrimers readily form *trans*-dialkynyl organoplatinum(II) complexes upon treatment with *trans*-$[(Et_3P)_2PtCl_2]$, this reaction was chosen to link the dendrimers **1–3** together.[8] To avoid random polymerization of the dendritic beads, only two of the surface moieties were functionalized with "reactive" long chain 10-(4-ethynylphenoxy)decyloxyl residues while the rest were decorated with "inert" 3-(4-*tert*-butylphenoxy)propoxy groups.

The synthesis of the target dendritic monomers **1–3** required the availability of three bromo-dendrons **10**, **11**, and **12**[9] (Scheme 1). Hence, the G1-dendrimer **4** and G2-



Scheme 1. Reagents and conditions: a) hydroquinone (0.45 equiv), Cs_2CO_3, dibenzo-24-crown-8, DMF, 110 °C, 2 h.

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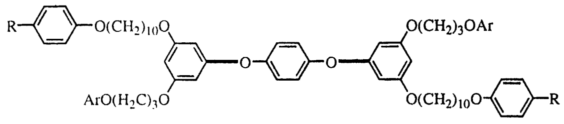
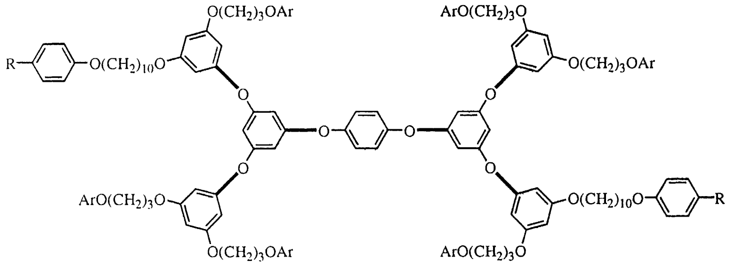
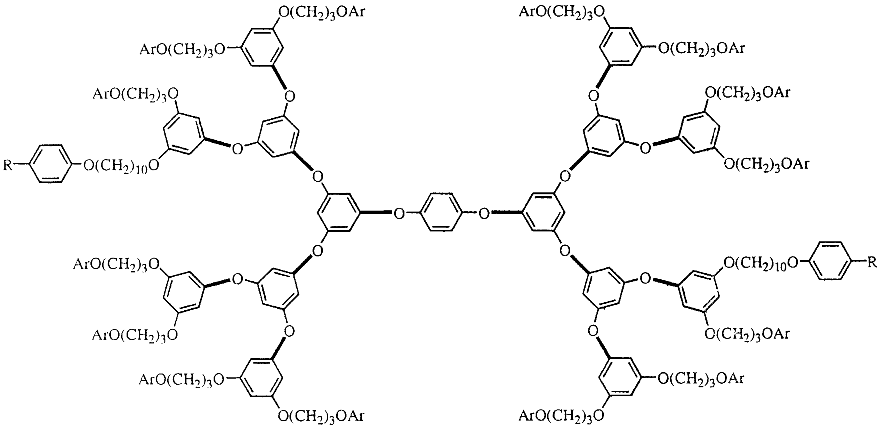


1 R = CCH
4 R = I
7 R = CCSiMe$_3$



2 R = CCH
5 R = I
8 R = CCSiMe$_3$



3 R = CCH
6 R = I
9 R = CCSiMe$_3$

dendrimer **5** containing two aryl iodide surface moieties were constructed by anchoring the mono-iodo surface-functionalized[10] G1-bromide **10** (2.2 equiv) and G2-bromide **11** (2.2 equiv), respectively, to a hydroquinone core in the presence of Cs$_2$CO$_3$ in reasonable yields. Conversely, a differentially (methoxymethyl (MOM) and benzyl) protected hypercore **13**[9] was used in the synthesis of the diiodo surface-functionalized G3-dendrimer **6** (see Scheme 2). Hence, the two MOM groups were cleaved under acidic conditions to afford a bis(phenol) intermediate **14**, which was then treated first with 2.2 equivalents of the symmetrical G2-bromide **12** to give a partially constructed G3-dendrimer **15**. The benzyl groups were then removed and the product **16** was reacted with 2.2 equivalents of the unsymmetrical G2-bromide **11** to give the G3-dendrimer **6**.

The G1–G3 diiodide surface-functionalized dendrimers **4**–**6** were then converted to the corresponding bis(trimethylsilylethynyl) dendrimers **7**–**9**, respectively, by the Sonogashira coupling reaction with 1-trimethylsilylethyne. The trimethylsilyl groups were then removed under basic conditions to afford the target bifunctional dendrimers **1**–**3**, respectively, from compounds **7**–**9**. The structures of the target monomers **7**–**9** were confirmed by ^{1}H and ^{13}C NMR and mass spectroscopic measurements,[9] and their purity and homogeneity (polydispersity index (PDI) = 1.04) were also evaluated by GPC analysis (Figure 2).

Copolymerization reactions of a 1:1 molar ratio (20–30 mM) of the bifunctional dendrimers **1**–**3** and *trans*-[(Et$_3$P)$_2$PtCl$_2$] were conducted in the presence of CuI, diisopropylamine in CH$_2$Cl$_2$ to afford G1–G3 dendritic necklaces **17**–**19**, respectively (Scheme 3). The light yellow organoplatinum products were isolated by successive precipitation from the addition of a CH$_2$Cl$_2$ solution to acetone and to methanol and their structures were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Figure 3 showed the ^{1}H NMR spectra of the G2-monomer **2** and the resulting G2-dendritic necklace **18**. Prior to Pt complexation, the terminal acetylenic proton gave a sharp singlet at $\delta = 3.0$ ppm and an AB system ($\delta = 7.4$ and 6.8 ppm) due to the aromatic protons of the 4-ethynylphenoxy surface groups. After complexation, the positions of the AB system were shifted upfield ($\delta = 7.2$ and 6.7 ppm) while the signal of the acetylenic proton due to the end group could hardly be observed because of the high degree of polymerization (DP ≈ 90, see below). The ^{31}P{^{1}H} NMR spectra of the G1-**17** and G2- **18** dendritic necklaces consisted of one ^{31}P signal located at about $\delta = 17.5$ ppm with two ^{195}Pt satellite signals [^1J(Pt,P) ≈ 2380 Hz] of

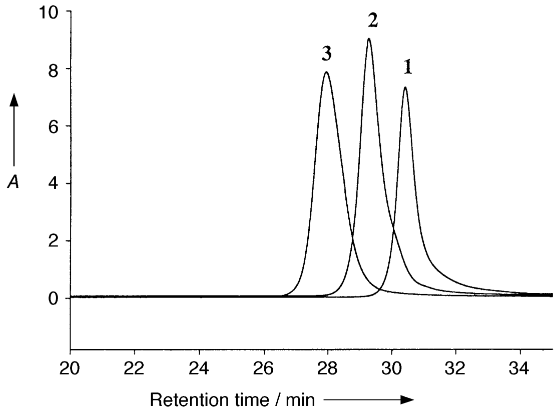
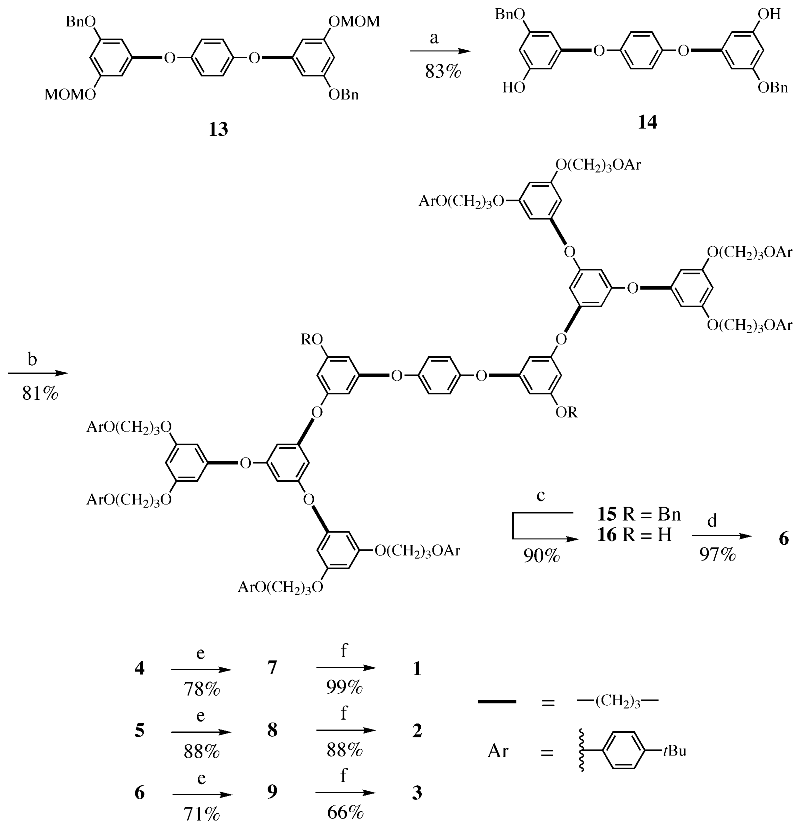


Figure 2. GPC chromatograms of bis(ethynyl) surface-functionalized dendrimers **1**–**3**. *A* = UV absorbance, arbitrary units.



Scheme 2. Reagents and conditions: a) HCl, EtOH, THF, 0 °C, 1 h; b) **12** (2.2 equiv), Cs_2CO_3, dibenzo-24-crown-8, DMF, 60 °C, 3 h; c) H_2 (1 atm), 10% Pd/C, EtOH, EtOAc (1:1), 25 °C, 6 h; d) **11** (2.2 equiv), Cs_2CO_3, dibenzo-24-crown-8, DMF, 60 °C, 3 h; e) TMSC·CH, $[Pd(PPh_3)_2Cl_2]$, CuI, NEt_3, PPh_3, toluene, 60 °C, 24 h; f) K_2CO_3, MeOH, THF, 25 °C, 1.5 h.

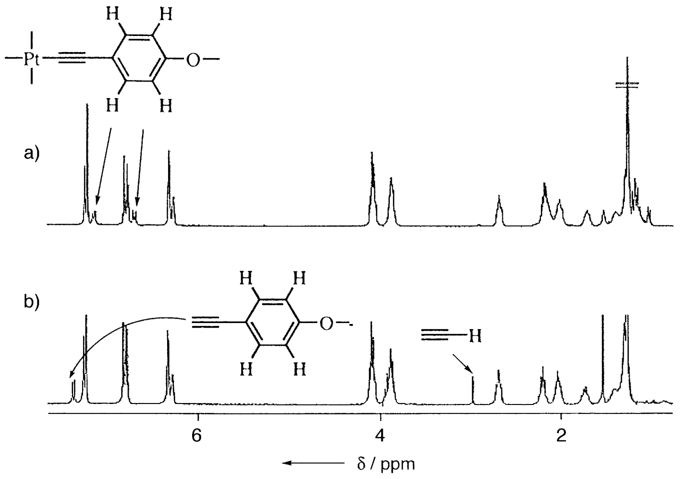
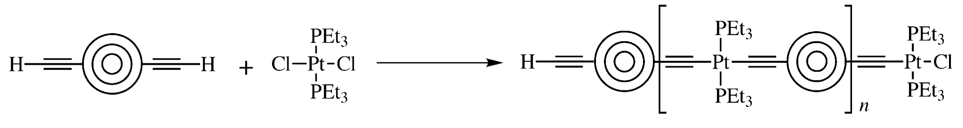


Figure 3. ^1H NMR (300 MHz, $CDCl_3$) spectra of a) G2-dendritic necklace **18** and b) G2-dendrimer **2**.

one sixth intensity (Figure 4). Conversely, the $^{31}P\{^1H\}$ NMR spectrum of the G3 dendritic necklace **19** consisted of one major ^{31}P signal at about the same position ($\delta = 16.3$ ppm). However, two additional ^{31}P signals ($\delta = 20.2$ and 14.0 ppm) of lower intensities were also noted. These signals probably arose from ^{31}P resonances of the end group, which became more evident due to the lower DP value (≈ 30) of the G3-dendritic necklace **19**.

The molecular weights and distributions of the necklaces **17**–**19** in THF were determined by LLS and GPC studies (Table 1) and the measured values were not influenced by the monomer concentration used in the copolymerization. Furthermore, the molecular-weight values of the G1-dendritic necklace **17** obtained from GPC studies were also independent of the sample concentration used in the measurements,[11] which suggests the values in Table 1 reflect the molecular weights of individual dendritic necklaces and not those of the aggregates. The PDI values obtained were rather large (≈ 2.0) and were independent of dendrimer generation. Examination of the LLS data indicated that this new outer-sphere–outer-sphere connection strategy could produce large nanoscopic-sized ($R_g \approx$ 100 nm) dendritic necklaces of high molecular weights ($\bar{M}_w > 1.8 \times 10^5$). It was also noted that the copolymerization was sensitive to steric inhibition as the DP value dropped significantly from 880 to 30 on going from the first to the third generation. Nonetheless, the DP values were still comparable to the high-end values of dendronized polymers obtained from inner-sphere–inner-sphere connection strategy.[4c] Furthermore, GPC measurements tended to produce much smaller $\bar{M}_w$ values as polystyrenes were not good calibration standards for dendritic polymers. The ratio of the $\bar{M}_w$ values obtained from LLS and GPC, values that indicated how much the GPC results underestimated the real molar mass of the tested compounds, showed a gradual decrease (from 14.0 to 1.5) from the G1- to the G3-dendritic necklace. The ratios are much greater than unity as the hyperbranched dendritic necklaces are expected to have a much larger mass per unit length than polystyrene. However, as the size of the dendritic beads was getting larger for the G3-necklace, the long hydrocarbon linker groups were



1-3 (G1-G3)

17-19 dendritic necklaces G1-G3

Scheme 3. Reagents and conditions: $HN(iPr)_2$, CuI, CH_2Cl_2, 25 °C, 12 h.

Table 1: LLS and GPC data of G1-G3 dendritic necklaces **17**–**19**.

Dendritic necklaces	Yield % [a]	LLS[b]			GPC[c]		$\bar{M}_w$ (DLLS)/
		$\bar{M}_w\times10^3$	DP[d]	R_g [nm]	$\bar{M}_w\times10^3$	PDI	$\bar{M}_w$ (GPC)
G1 **17**	88	1500 (1.7)[e]	8.8×10^2	170	107[f]	1.9	14.0
G2 **18**	78	290 (3.1)	0.9×10^2	76	82[g]	1.7	3.5
G3 **19**	58	180 (5.8)	0.3×10^2	124	117[g]	2.0	1.5

[a] Yield after precipitation from solvents. [b] Solvent: THF. [c] Solvent: THF. Polystyrenes were used as calibration standards. [d] Calculated from $\bar{M}_w$ determined by LLS. [e] Values in brackets are the calculated molecular weights of the repeating unit. [f] Sample concentration = 2.7 mg mL^{-1}. [g] Sample concentration = 0.54 mg mL^{-1}.

expected to stiffen and result in an increase of hydrodynamic volume and hence a decrease of the ratio.

A scanning tunneling microscopic (STM) study on spin-casted (3000 rpm) samples of dendritic necklaces **17**–**19** from diluted THF solutions (≈10 μg mL^{-1}) on highly oriented pyrolytic graphite (HOPG) showed that the necklaces existed in aggregate form and adopted a coiled structure. An increase in the spin-casting speed to 5000 rpm facilitated the rate of solvent evaporation and prevented aggregate formation, and the dendritic necklaces were found across the steps of the freshly cleaved HOPG surface as thin threads (Figure 5). The mean cross-section diameter of the individual threads was found to increase from 1.1 to 1.6 and then to 2.0 nm on going from G1–G3, thus showing that the size of the dendritic beads also played a role in controlling the molecular dimensions of these dendritic necklaces.

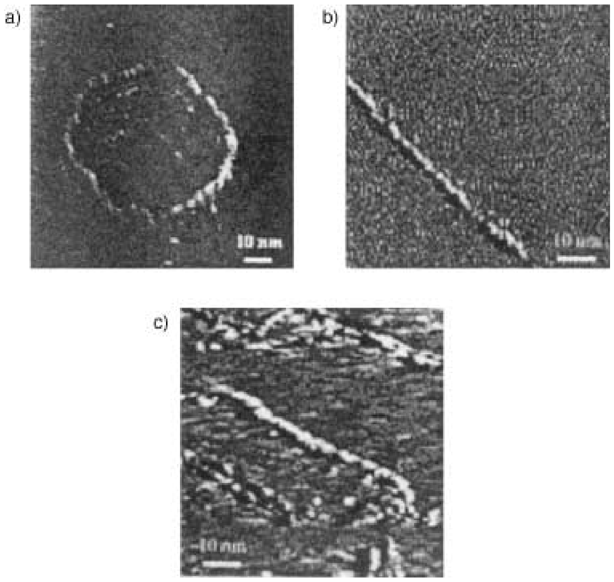


Figure 5. STM images of dendritic necklaces a) **17** b) **18** and c) **19** spin-casted (5000 rpm) on HOPG.

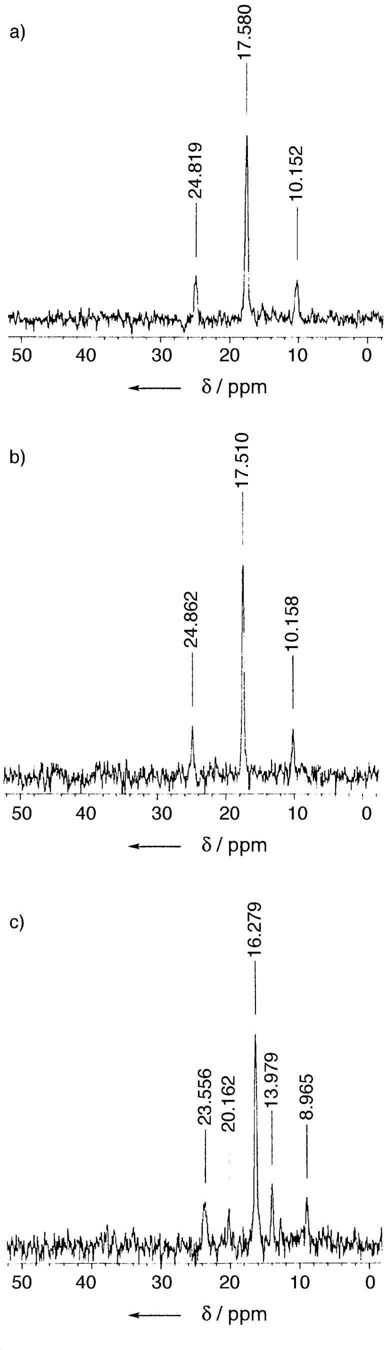


Figure 4. ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$) spectra of dendritic necklaces a) G1 **17**, b) G2 **18**, and c) G3 **19**.

In summary, we report here a general method for the synthesis of functional dendrimers that contain a limited number of reactive functional groups on the dendritic surface and also a new strategy for the construction of a novel class of structurally defined dendritic necklaces by using an outer-sphere–outer-sphere connection strategy. One notable feature of this method is that the dendritic necklaces thus obtained have a very high degree of polymerization. We believe this new method offers a new entry towards the construction of nanoscale shape-controlled polymers. Two important structural elements in this strategy are the length of the linker groups and the size of the dendrimer beads, which are expected to be the key variables that can be used to control the three dimensional morphology of the dendritic networks. Hence, dendritic necklaces that have tight packing dendrimer subunits may be realized by using shorter linker molecules and larger dendrimer beads. Furthermore, multiblock dendritic necklaces that have segregated regions can also be constructed from dendrimer beads and linker units that are of different physical properties.

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[1] The term "networks" coined by Newkome and Vögtle has a different conception from that used in polymer chemistry. In polymer chemistry, networks are generally referred to highly cross-linking systems while dendritic networks do not necessarily have a cross-linking architecture.

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[7] A recent paper describing the synthesis of G1- and G2-dendritic monomers that have bifunctional surface moieties for outer-sphere–outer-sphere connection had appeared. However, no polymerization study was disclosed, see R. N. Ganesh, J. Shraberg, P. G. Sheridan, S. Thayumanavan, *Tetrahedron Lett.* **2002**, *43*, 7217–7220.

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[9] See Supporting Information for details of synthetic procedures and physical data.

[10] The methodology used in the synthesis of the surface-functionalized G1-bromide **10** and G2-bromide dendrons **11** was similar to that described in the literature, see K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc. Perkin Trans. 1* **1991**, 1059–1076 for details.

[11] The estimated GPC mass-average molar mass ($\bar{M}_w$) of the G1-dendritic necklace **17** at concentrations 0.11, 0.54, and 2.70 $mg\,mL^{-1}$ were 1.05×10^5, 1.04×10^5 and, 1.07×10^5 respectively.