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Synthesis of Organoplatinum Poly(dendrimer)s: Pronounced Effect of Size and Geometry of Small Organoplatinum Linkers on the Copolymerization Efficiency with Bifunctional Dendritic Macromonomers

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Abstract: The copolymerizations of two series of surface functionalized bis(acetylene) G1–G3 dendrimers, one (S-Gn) having a structural rigid skeleton and the other (L-Gn) a relatively more flexible architecture, with two platinum linkers, *cis*- $[(Et_2PCH_2CH_2PEt_2)PtCl_2]$ (2) and [Cl- $(Et_3P)_2Pt-C\equiv C-p-C_6H_4-]_2$ (3) were investigated. For both series of dendrimers, only linear and/or cyclic oligomers were formed when the *cis*-platinum linker 2 was used. However, high mo-

Introduction

The synthesis of nanoscopic architectures with controllable size and shape from dendritic building blocks has become a subject of topic interest due to their potential catalysis, biological, and diagnostic applications.^[1] One inherent advantage of using dendrimers as the basic structural motif is because of their high structural homogeneity and well-defined three-dimensional topology, which enable one to exert better control on the final dimension and shape of, and functional group location in the target architecture. Many covalently-linked structures based on dendritic building blocks such as dendrimer–linear polymer hybrids,^[2] dendronized

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lier findings (S.-Y. Cheung, H.-F. Chow, T. Ngai, X. Wei, *Chem. Eur. J.* **2009**, *15*, 2278–2288) obtained by using a shorter linear platinum linker *trans*-[Pt-(PEt₃)₂Cl₂] (1), where a larger amount of cyclic oligomers was formed from the structural flexible **L**-**Gn** dendrimers. A model was proposed to rationalize how the geometry and size of the platinum linker could control the copolymerization behaviours of these dendritic macromonomers.

polymers,^[3] poly(dendrimer)s,^[4] poly(dendrimer) networks^[5] have already been reported. While there have been extensive studies on dendrimer–linear polymer hybrids and dendronized polymers, there are only a handful of examples on poly(dendrimer)s.^[4,5] One unique feature in the synthesis of poly(dendrimer)-based molecules is that dendrimer connection is formed via the two functionalities located on the dendrimer surface (outer-sphere–outer-sphere connection) (Scheme 1). This synthetic approach is therefore anticipated to experience less steric retardation than the graft to-, graftfrom, or macromonomer polymerization strategies used for the synthesis of dendronized polymers,^[3] in which dendrimer connection is realized via functional group(s) anchored near the sterically more hindered focal point position (inner-sphere–inner-sphere connection).

We reported earlier that poly(dendrimer)s with a high degree of polymerization (DP) value (30–1000 based on laser light scattering data) could be obtained from the copolymerization of surface functionalized bis(acetylene) dendritic macromonomers and *trans*-[Pt(PEt₃)₂Cl₂] (1).^[4b] To further elaborate on the general efficiency of this synthetic strategy, we later modified the backbone structure of the dendritic macromonomers and found that structurally more rigid Fréchet type oligo(benzyl ether) dendrimers **S-Gn** (n =1–3) tended to give organoplatinum poly(dendrimer)s *trans*-



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Scheme 1. a) Synthesis of dendronized polymer via focal point functional group connection and b) poly(dendrimer) via surface functional group connection.



Pt-S-Gn with higher DP values than structurally more flexible oligo(3-phenylpropyl ether) dendrimers **L-Gn** (n=1-3).^[4c] The main problem associated with the latter class of dendritic monomers was their relatively higher propensity to form cyclic oligomers due to the presence of the more flexible and elongated branches (Scheme 2). The DP values of the poly(dendrimer)s obtained from this study ranged from 20–60 (based on SEC data). However, the weight% of the cyclic oligomers (calculated up to the pentamer) obtained could be as high as 14%.

In this paper we wish to report that changing the small organoplatinum linker and hence its geometry, size and rigidity also has a profound effect on the polymerization efficiency. Hence, no poly(dendrimer)s, but only oligomers were formed from using the *cis*-[(Et₂PCH₂CH₂PEt₂)PtCl₂] (2) linker. On the other hand, formation of cyclic oligomers was greatly suppressed if an elongated linear rigid rod organoplatinum complex [Cl(Et₃P)₂Pt-C=C-*p*-C₆H₄-]₂ (3) was used as the linker. By using this elongated linker, we showed that



Scheme 2. Cyclization vs polymerization for **S-G***n* and **L-G***n* with *trans*- $[Pt(PEt_3)_2Cl_2]$ **1**.

even the sterically bulky G3 macromonomers could be copolymerized to form poly(dendrimer)s of high molecular weight ($M_w \sim 150-190$ kD based on SEC calculations). This present study reveals that there are intrigue factors that control the cyclization versus propagation pathways during the copolymerization process, and that one can control the formation of the oligomers versus poly(dendrimer)s by careful design of the macromonomer and linker group. It was noted that formation of cyclic oligomers involving structurally flexible small monomers^[6] and macromonomers^[7] had been reported before.



Results and Discussion

The syntheses of the surface functionalized bis(acetylene) dendrimers S-Gn or L-Gn had been reported earlier,^[4c] while the organoplatinum complexes $2^{[8]}$ and $3^{[5]}$ were prepared according to literature methods. The copolymerization of S-Gn/L-Gn with organoplatinum complexes 2 or 3 is a step-growth reaction and involves the polycondensation of the terminal acetylene moiety on the dendrimer surface with the platinum-chlorine bond. The reactions were conducted under reaction conditions (8.7 mm; CuI, iPr₂NH, CHCl₃, 40°C, 48 h) that were identical to those involving *trans*- $[Pt(PEt_3)_2Cl_2]$ (1)^[4b] in order to evaluate the structural effect of the platinum linkers on the formation of the poly-(dendrimer)s (Scheme 3). After polymerization, the yellow products, cis-Pt-S-Gn, cis-Pt-L-Gn, long-trans-Pt-S-Gn and long-trans-Pt-L-Gn were isolated by passing them through a short column of alumina and washing with CHCl3 to remove the copper salt, followed by precipitation in MeOH. The resulting polymers were subjected to ¹H, ¹³C, and ³¹P NMR spectroscopic characterizations. On the other hand, size-exclusion chromatographic (SEC) analyses were performed on samples obtained prior to precipitation to ensure the SEC

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Scheme 3. 1: 1 Copolymerizations of **S-Gn** and **L-Gn** with *cis*- $[(Et_2PCH_2CH_2PEt_2)PtCl_2]$ **2** and elongated *trans*-platinum linker **3**. a) CuI, *i*Pr₂NH, CHCl₃, 40 °C, 48 h.

results reflected the full molecular weight distribution and not just that of the precipitated fractions.

Copolymerizations with *cis*-platinum linker 2: Examination of the ¹H NMR spectra of the various *cis*-Pt-L-Gn and *cis*-Pt-S-Gn revealed the presence of both the dendritic and the *cis*-platinum linker moieties (see Supporting Information for details). However, their ³¹P{¹H} NMR spectra showed that presence of many peaks (Figure 1), suggesting the product



Figure 1. ³¹P[¹H] NMR spectra (122 MHz, CDCl₃) of a) *cis*-**Pt-L-G2** and b) *cis*-**Pt-S-G2**, showing sets of ³¹P signals together with the corresponding ¹⁹⁵Pt satellite peaks.

had a very high degree of heterogeneity. More strikingly, the SEC chromatograms of the products showed the presence of mainly oligomeric species (Figure 2). The degree of polymerization (DP) values, as calculated based on polystyrene standards, were around 2-3 (Table 1) and the polydispersity indexes (PDI) ranged from 1.3-2.1. Mass spectral analyses of the slowest running SEC fraction from the various cis-Pt-L-Gn and cis-Pt-S-Gn samples confirmed that they were unreacted dendritic macromonomer, 1:1 Pt-dendritic monomer adduct, cyclic monomer, and/or their fragmentation products (Figure 3). The preferential formation of cyclic metallooligomers from non-linear platinum linkers and preorganized dendritic ligands had been reported before.^[8] The results obtained here suggested that the geometry of the small platinum linker played an important role in controlling the outcome of the polymerization process. The placement of two dendritic macromonomers at a 90° relationship at the



Figure 2. SEC chromatograms of a) *cis*-**Pt-S-G1**, b) *cis*-**Pt-L-G1**, c) *cis*-**Pt-S-G2**, d) *cis*-**Pt-L-G2**, e) *cis*-**Pt-S-G3**, and f) *cis*-**Pt-L-G3** (solid lines). The dotted lines are SEC traces of the corresponding dendritic macromonomers (data taken from reference [4c]).

Table 1. SEC data of cis-Pt-S-Gn and cis-Pt-L-Gn oligomers.^[a]

-	
DP ^[b]	PDI ^[b]
3	1.6
3	1.5
2	1.3
3	2.1
3	1.6
3	1.6
	DP ^[b] 3 3 2 3 3 3 3 3 3

[a] SEC conditions: Waters Styragel columns (HR1, HR2, HR3 and HR4; 7.8×300 mm in serial) at 40 °C using THF as eluent (flow rate = 1.0 mLmin-1) on a Waters HPLC 515 pump with a Waters 2489 tunable UV absorbance detector. [b] Values calculated from SEC data based on polystyrene standards.

platinum metal center would create severe steric congestion and angle strain of the resulting complex. As a result, the polymerization process was strongly disfavored and only oligomers/cyclic oligomers were formed from using the 90° *cis*-platinum complex 2.

Copolymerizations with long-*trans***-platinum linker 3**: The ¹H and ¹³C NMR spectra of long-*trans***-Pt-S-G***n* and long*trans***-Pt-L-G***n* again showed the presence of both the dendritic and platinum components. In sharp contrast to those of the *cis***-Pt-L-G***n* and *cis***-Pt-S-G***n*, the ³¹P{¹H} spectra of these poly(dendrimer)s consisted mainly of one major peak (see Supporting Information for details), suggesting the

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Figure 3. MALDI-TOF spectrum of the slowest running SEC fraction from *cis*-**Pt-S-G2**.

polymerization reactions proceeded smoothly to give poly-(dendrimer)s of high DP values. The appearance of the SEC chromatograms was even more astonishing (Figure 4). First,



Figure 4. SEC chromatograms of a) long-*trans*-**Pt-S-G1**, b) long-*trans*-**Pt**-**L-G1**, c) long-*trans*-**Pt-S-G2**, d) long-*trans*-**Pt-L-G2**, e) long-*trans*-**Pt-S-G3**, and f) long-*trans*-**Pt-L-G3**. The dotted lines are plots of the corresponding *trans*-**Pt-L-Gn** or *trans*-**Pt-S-Gn** taken from reference [4c].

peaks due to the cyclic oligomers that were so prominent in the SEC chromatographs of the poly(dendrimer)s obtained from the copolymerization of the same dendritic macromonomers with the shorter platinum linker *trans*-[Pt(PEt₃)₂Cl₂] (1), were greatly suppressed. Since the individual oligomeric peaks could not be clearly picked out, we were unable to calculate the weight% of the low molecular weight (LMW) oligomers in the present study. Nonetheless, it could be clearly seen that the amount of LMW oligomers was greatly suppressed by switching the platinum linker from the shorter linker 1 to the longer one 3. Second, both the S-Gn and L-Gn macromonomers copolymerized well with the longer platinum linker 3 to form poly(dendrimer)s with high DP values (Table 2). It was noted that the DP values obtained

Table 2. SEC data of *long-trans*-**Pt-S-G***n* and *long-trans*-**Pt-L-G***n* poly-(dendrimer)s.^[a]

Sample	SEC $M_{\rm w} \times 10^{-3[b]}$	DP ^[b]	PDI ^[b]
long-trans-Pt-S-G1	107	59 (34) ^[c]	2.5
long-trans-Pt-S-G2	191	72 (60) ^[c]	2.3
long-trans-Pt-S-G3	148	$34(21)^{[c]}$	2.2
long-trans-Pt-L-G1	91	46 (39) ^[c]	2.0
long-trans-Pt-L-G2	127	41 (22) ^[c]	2.0
long-trans-Pt-L-G3	188	36 (19) ^[c]	1.9

[a] SEC conditions: Waters Styragel columns (HR1, HR2, HR3 and HR4; $7.8 \times 300 \text{ mm}$ in serial) at 40 °C using THF as eluent (flow rate = 1.0 mLmin^{-1}) on a Waters HPLC 515 pump with a Waters 2489 tunable UV absorbance detector. [b] Values calculated from SEC data based on polystyrene standards. [c] Number in parenthesis referred to the corresponding value obtained from using the shorter *trans*-[Pt(PEt₃)₂Cl₂] linker. The data were extracted from reference [4c].

from the structurally rigid S series were still larger than that of the structurally flexible L series of the same generation, indicating the structural flexibility of the macromonomers still exerted the same role in controlling the polymerization process. Third, a major peak with a shorter retention time as compared to the corresponding trans-Pt-S/L-Gn was found in all cases. SEC calculations also confirmed that the DP values of the long-trans-Pt-S/L-Gn poly(dendrimer)s were consistently higher than those of the trans-Pt-S/L-Gn poly-(dendrimer)s. Fourth, both third-generation macromonomers S-G3 and L-G3, previously found to have problems to undergo copolymerization, could form organoplatinum poly-(dendrimer)s with good DP values with the longer rod-liked linker 3. It should be pointed out here that although the SEC calculated DP values are in the order of 10^2 , the actual DP values can be 1.5–14 times higher as the hyperbranched poly(dendrimer)s have a much larger mass per unit length than the polystyrene standards.^[4b] Unfortunately, we were unable to obtain their absolute molecular weights by laser light-scattering studies as they tended to form large aggregates in relatively concentrated solutions.^[4c] On the other hand, the SEC experiments were conducted in highly diluted THF solutions at elevated temperature (40°C), under which conditions aggregate formation was greatly suppressed.

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Based on the experimental results obtained from this and our previous studies,^[4c] a model was proposed to rationalize the various observations in the copolymerizations between the different platinum linkers and the dendritic macromonomers (Scheme 4). The addition of the first dendritic macro-



Scheme 4. Polymerization vs cyclization of dendritic macromonomers with Pt-linkers.

monomer to the platinum linker should be a relatively facile process. However, addition of the second macromonomer is subjected to stronger steric inhibition due to the anchorage of the first macromonomer. Among the three platinum linkers, the steric environment around the long-trans-Pt-linker 3 is the least congested due to the larger spatial separation of the two Pt-Cl bonds. As a result, addition of the second macromonomer should be more facile and both the rigid S and flexible L series of macromonomers can undergo copolymerization efficiently (path A), and cyclization is greatly suppressed (path B). On the other hand, the steric environment around the *cis*-Pt-linker **2** is the most congested, as the remaining Pt-Cl bond is located cis to the first macromonomer with a 90° bonding angle. In this case, addition of the second macromonomer to the same Pt center is strongly prohibited (path C) and therefore only LMW oligomers (DP ~2-3) are formed (path D), regardless of the structural rigidity of the macromonomer. For the trans-Pt-linker 1, steric congestion around the Pt center must be less than that in 2, but stronger than that in 3. In this case, addition of the second macromonomer is not strictly prohibitive. As a result, poly(dendrimer)s formation is plausible (path E) but

this process must be slower as compared to the corresponding step in **3**. In this situation, the second acetylenic functionality of the first macromonomer may have enough opportunity and time to react with the Pt metal center to form cyclic monomers/oligomers (path F). This then creates a unique situation where the structural rigidity of the macromonomer can exert its control on the extent of propagation versus cyclic oligomerization. The **L** series, having a flexible structure and hence a high degree of freedom to orient the second acetylenic group to the Pt center, will have a higher opportunity than the rigid **S** series to form cyclic oligomers. This is also the reason why a clear difference in the polymerization behaviour can only be observed between the two series of dendritic macromonomers with platinum linker **1**.

Conclusions

The synthesis of organoplatinum poly(dendrimer)s by the copolymerizations of surface-bifunctional dendritic macromonomers with two small platinum linker molecules 2 and 3 were reported. It was found that the geometry and the size of the platinum linker could exert a profound effect on the polymerization efficiency. The cis-Pt linker 2 produced mainly oligomers with both the structural rigid S series and structural flexible L series of macromonomers. On the other hand, poly(dendrimer)s with high DP values were obtained from the long-trans-Pt linker 3. The formation of cyclic oligomers, and the differential behaviour of the S and L series observed during copolymerizations with the shorter trans-[Pt(PEt₃)₂Cl₂], was not found with the long-*trans*-Pt linker **3**. A model was formulated to rationalize the various observations. We believe this working model can also be used to predict the cyclization versus propagation pathways of other polymerization reactions involving macromonomers. More importantly, we demonstrated that even the G3 dendritic macromonomers could copolymerize efficiently to give poly(dendrimer)s of M_w values of 150–190 kD (based on SEC data), suggesting the outer-sphere-outer-sphere connection^[1] is a viable strategy to construct nanoscopic-sized materials with controlled architecture.

Experimental Section

General information: The *cis*-Pt linker $2^{[9]}$ and the elongated *trans*-Pt linker $3^{[5]}$ were prepared according to literature procedure. For the *cis*-**Pt-S-Gn** and *cis*-**Pt-L-Gn** poly(dendrimer)s (n = 1, 2 and 3), they are mixture of oligomers and cyclic oligomers even after precipitation, therefore the NMR data were just taken for recording purpose. Details of which are given in the Supporting Information.

General procedure for the synthesis of long-trans-poly(dendrimer)s: A mixture of the S-Gn or L-Gn dendrimers (1.0 equiv, 8.7 mM), the elongated trans-Pt linker 3 (1.0 equiv) in CHCl₃/iPr₂NH (v/v 1:1) was frozen in a sealed tube under liquid N₂ and degassed with N₂ (3×). The mixture was allowed to warm to 25 °C followed by the addition of CuI (0.5 equiv). The mixture was then heated at 40 °C for 48 h. The solvent was concentrated in vacuo and the residue dissolved in minimum amount of CHCl₃, filtered through a short pad of alumina. A sample of the aliquot was then

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taken out for GPC analysis. The residue compounds was purified by precipitation in MeOH to obtain the target poly(dendrimer)s.

long-*trans***-Pt-S-G1**: Starting from **S-G1** dendrimer (100 mg, 0.131 mmol), Pt-linker **3** (148 mg, 0.131 mmol) and CuI (12.5 mg, 0.066 mmol) in CHCl₃/*i*Pr₂NH (v/v 1:1, 15 mL), the polymer (220 mg, 92%; 182 mg, 76% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): δ = 7.58–7.16 (m, 26H; Ar*H* + biphenyl-Ar*H*), 6.88 (s, 4H; core-Ar*H*), 6.67 (s, 4H; Ar*H*), 6.54 (s, 2H; Ar*H*), 5.12–4.86 (m, 12H; Ar*CH*₂O), 2.32–2.00 (m, 24H; PCH₂), 1.36–1.10 ppm (m, 36H; PCH₂C*H*₃); ¹³C NMR (75 MHz, CDCl₃): δ = 160.3, 160.2, 153.2, 139.8, 137.6, 136.9, 133.4, 131.1, 128.7, 128.1, 127.7, 127.5, 126.4, 115.9, 109.4 (*C*=CPt), 108.4 (*C*=CPt), 106.4, 101.6, 70.7, 70.2, 16.5 (quintet like, ¹/(C,P) = 17.5 Hz; PCH₂), 8.5 ppm; ³¹P NMR (122 MHz, CDCl₃): δ = (major peak): 11.1 (¹*J*(Pt,P)=2370 Hz); (minor peak): 14.9 ppm (¹*J*-(Pt,P)=2390 Hz).

long-*trans***-Pt-S-G2**: Starting from **S-G2** dendrimer (60.0 mg, 0.037 mmol), Pt-linker **3** (42.1 mg, 0.037 mmol), CuI (3.5 mg, 0.019 mmol) in CHCl₃/*i*Pr₂NH (v/v 1:1, 4.2 mL), the polymer (87 mg, 87%; 78 mg, 78% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): δ = 7.51–7.20 (m, 46H; Ar*H* + biphenyl-Ar*H*), 6.88 (s, 4H; core-Ar*H*), 6.67 (s, 12H; Ar*H*), 6.60–6.50 (m, 6H; Ar*H*), 5.07–4.88 (m, 28H; ArCH₂O), 2.32–2.01 (m, 24H; PCH₂), 1.36–1.09 ppm (m, 36H; PCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 160.2, 160.1, 153.1, 139.8, 139.3, 137.6, 136.8, 133.3, 131.3, 131.1, 128.6, 128.1, 127.6, 126.6, 126.3, 115.8, 109.3 (C≡CPt), 108.4 (C≡CPt), 106.4, 101.6, 70.5, 70.1, 16.4 (quintet like, ¹*J*(C,P)=17.7 Hz; PCH₂), 8.4 ppm; ³¹P NMR (122 MHz, CDCl₃): δ = (major peak): 11.2 (¹*J*(Pt,P)=2370 Hz); (minor peaks): 15.0 (¹*J*(Pt,P)=2390 Hz), 8.7 ppm (¹*J*(Pt,P)=2320 Hz).

long-*trans***-Pt-S-G3**: Starting from **S-G3** dendrimer (119 mg, 0.036 mmol), Pt-linker **3** (40.8 mg, 0.036 mmol), CuI (3.4 mg, 0.018 mmol) in CHCl₃/ *i*Pr₂NH (v/v 1:1, 4.1 mL), the product (115 mg, 73%; 79 mg, 50% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): δ =7.50–7.16 (m, 86H; Ar*H* + biphenyl-Ar*H*), 6.83 (s, 4H; core-Ar*H*), 6.66 (brs, 28H; Ar*H*), 6.55 (brs, 14H; Ar*H*), 5.06–4.79 (m, 60H; Ar*CH*₂O), 2.34–1.99 (m, 24H; PCH₂), 1.35–1.08 ppm (m, 36H; PCH₂C*H*₃); ¹³C NMR (75 MHz, CDCl₃) (*C*≡CPt signal was too weak to be observed): δ =160.2, 160.1, 153.1, 139.9, 139.3, 137.6, 136.8, 133.3, 131.3, 131.1, 128.7, 128.1, 127.7, 126.4, 115.8, 108.0 (C≡CPt), 106.4, 101.7, 70.6, 70.2, 70.1, 16.4 (quintet like, ¹*J*(C,P)=17.7 Hz; PCH₂), 8.5 ppm; ³¹P NMR (122 MHz, CDCl₃): δ =(major peak): 11.1 (¹*J*(Pt,P)=2370 Hz); (minor peaks): 14.9 (¹*J*(Pt,P)=2390 Hz), 8.6 ppm (¹*J*(Pt,P)=2320 Hz).

long-trans-Pt-L-G1: Starting from L-G1 dendrimer (111 mg, 0.119 mmol), Pt-linker 3 (134 mg, 0.119 mmol), CuI (11.3 mg, 0.059 mmol) in CHCl₃/iPr₂NH (v/v 1:1, 13.6 mL), the product (229 mg, 97%; 174 mg, 74% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.44$ (d, ³J(H,H) = 7.5 Hz, 4H; biphenyl-ArH), 7.38–7.12 (m, 18H; ArH + biphenyl-ArH), 7.05 (d, ${}^{3}J(H,H) =$ 8.1 Hz, 4H; ArH), 6.82 (s, 4H; core-ArH), 6.35 (s, 4H; ArH), 6.31-6.21 (m, 2H; ArH), 3.97–3.77 (m, 12H; ArOCH₂), 2.85–2.57 (m, 12H; ArCH₂ + PhCH₂), 2.32–2.11 (m, 24H; PCH₂), 2.11–1.91 (m, 12H; $ArCH_2CH_2$ + PhCH_2CH_2), 1.34–1.07 ppm (m, 36 H; PCH_2CH_3); ^{13}C NMR (75 MHz, CDCl₃): $\delta \!=\! 160.31,\, 160.28,\, 153.3,\, 144.0,\, 141.7,\, 138.4,$ 137.6, 131.3, 131.0, 128.6, 128.5, 128.3, 126.6, 126.4, 126.0, 115.5, 109.2 $(C{\equiv}CPt),\,107.3,\,106.8\,\,(C{\equiv}CPt),\,99.0,\,67.6,\,66.9,\,32.6,\,32.3,\,32.1,\,31.0,\,30.9,$ 16.4 (quintet like, ${}^{1}J(C,P) = 17.5 \text{ Hz}$; PCH₂), 8.5 ppm; ³¹P NMR (122 MHz, CDCl₃): $\delta = 11.1$ ppm (¹*J*(Pt,P) = 2370 Hz).

long-*trans***-Pt-L-G2**: Starting from **L-G2** dendrimer (131 mg, 0.066 mmol), Pt-linker **3** (74.2 mg, 0.066 mmol), CuI (6.2 mg, 0.033 mmol) in CHCl₃/*i*Pr₂NH (v/v 1:1, 7.5 mL), the product (175 mg, 87%; 174 mg, 86% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): δ =7.45 (d, ³*J*(H,H)=8.1 Hz, 4H; biphenyl-Ar*H*), 7.39–7.12 (m, 38H; Ar*H* + biphenyl-Ar*H*), 7.06 (d, ³*J*(H,H)=7.5 Hz, 4H; Ar*H*), 6.82 (s, 4H; core-Ar*H*), 6.45–6.24 (m, 18H; Ar*H*), 4.02–3.82

(m, 28H; ArOCH₂), 2.89–2.62 (m, 28H; ArCH₂ + PhCH₂), 2.34–1.92 (m, 52H; PCH₂ + ArCH₂CH₂ + PhCH₂CH₂), 1.44–1.09 ppm (m, 36H; PCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃): δ =160.3, 153.2, 144.0, 143.9, 141.6, 138.3, 137.5, 131.3, 130.9, 128.6, 128.5, 128.2, 126.6, 126.3, 126.0, 115.5, 109.2 (*C*=CPt), 107.2, 106.8 (C=CPt), 99.0, 67.6, 66.9, 32.5, 32.2, 32.0, 30.9, 30.7, 16.4 (quintet like, ¹J(C,P)=17.6 Hz; PCH₂), 8.5 ppm; ³¹P NMR (122 MHz, CDCl₃): δ =11.1 ppm (¹J(Pt,P)=2370 Hz).

long-trans-Pt-L-G3: Starting from L-G3 dendrimer (154 mg, 0.037 mmol), Pt-linker 3 (41.9 mg, 0.037 mmol), CuI (3.5 mg, 0.019 mmol) in CHCl₃/iPr₂NH (v/v 1:1, 4.2 mL), the product (191 mg, 99%; 160 mg, 83% after precipitation) was obtained as a yellow powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.53-7.12$ (m, 82 H; ArH + biphenyl-ArH), 7.07 (d, ${}^{3}J(H,H) = 7.2$ Hz, 4H; ArH), 6.82 (s, 4H; core-ArH), 6.47–6.25 (m, 42 H; ArH), 4.04–3.79 (m, 60 H; ArOCH₂), 2.95–2.61 (m, 60 H; ArCH₂ + PhCH₂), 2.34–1.95 (m, 84H; PCH₂ + ArCH₂CH₂ + PhCH₂CH₂), 1.41– 1.08 ppm (m, 36 H; PCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) (C≡CPt signal was too weak to be observed): $\delta = 160.31$, 160.26, 153.2, 144.0, 143.94, 143.88, 141.6, 138.3, 137.5, 131.3, 130.9, 128.6, 128.5, 128.2, 126.3, 126.0, 115.4, 109.2 (C=CPt), 107.2, 99.0, 67.6, 66.92, 66.85, 32.5, 32.2, 32.0, 30.9, 30.8, 30.7, 16.4 (quintet like, ¹*J*(C,P)=17.7 Hz; PCH₂), 8.5 ppm; ³¹P NMR (122 MHz, CDCl₃): $\delta =$ (major peak): 11.1 (¹*J*(Pt,P)=2370 Hz); (minor peaks): 14.9 (${}^{1}J(Pt,P) = 2390 \text{ Hz}$), 8.7 ppm (${}^{1}J(Pt,P) = 2330 \text{ Hz}$).

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- G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons. Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, 2001, pp. 539–562.
- [2] For recent examples: a) S. J. Guillaudeu, M. E. Fox, Y. M. Haidar,
 E. E. Dy, F. C. Szoka, J. M. J. Fréchet, *Bioconjugate Chem.* 2008, 19, 461–469;
 b) L. A. Connal, R. Vestberg, C. J. Hawker, G. G. Qiao, *Macromolecules* 2007, 40, 7855–7863;
 c) C. Kojima, Y. Toi, A. Harada, K. Kono, *Bioconjugate Chem.* 2007, 18, 663–670.
- [3] For recent reviews: a) A. Zhang, L. Shu, Z. Bo, A. D. Schlüter, Macromol. Chem. Phys. 2003, 204, 328–339; b) A. D. Schlüter, C. R. Chim. 2003, 6, 843–851; c) A. D. Schlüter, Top. Curr. Chem. 2005, 245, 151–191; d) H. Frauenrath, Prog. Polym. Sci. 2005, 30, 325–384.
- [4] For examples: a) R. N. Ganesh, J. Shraberg, P. G. Sheridan, S. Thayumanavan, *Tetrahedron Lett.* 2002, 43, 7217–7220; b) H.-F. Chow, C.-F. Leung, W. Li, K.-W. Wong, L. Xi, *Angew. Chem.* 2003, 115, 5069–5073; *Angew. Chem. Int. Ed.* 2003, 42, 4919–4923; c) S.-Y. Cheung, H.-F. Chow, T. Ngai, X. Wei, *Chem. Eur. J.* 2009, 15, 2278–2288.
- [5] H.-F. Chow, C.-F. Leung, L. Xi, L. W. M. Lau, *Macromolecules* 2004, 37, 3595–3605.
- [6] a) N. V. Tsarevsky, B. S. Sumerlin, K. Matyjaszewski, *Macromolecules* 2005, *38*, 3558–3561; b) B. A. Laurent, S. M. Grayson, *J. Am. Chem. Soc.* 2006, *128*, 4238–4239.
- [7] K.-N. Lau, H.-F. Chow, M.-C. Chan, K.-W. Wong, Angew. Chem. 2008, 120, 7018–7022; Angew. Chem. Int. Ed. 2008, 47, 6912–6916.
- [8] a) H.-B. Yang, N. Das, F. Huang, A. M. Hawkridge, D. C. Muddiman,
 P. J. Stang, J. Am. Chem. Soc. 2006, 128, 10014–10015; b) H.-B. Yang,
 A. M. Hawkridge, S. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman,
 P. J. Stang, J. Am. Chem. Soc. 2007, 129, 2120–2129.
- [9] M. Ferrer, M. Mounir, O. Rossell, E. Ruiz, M. A. Maestro, *Inorg. Chem.* 2003, 42, 5890–5899.

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