

Synthesis and Supramolecular Association of Immobilized NCN-Pincer Platinum(II) Complexes on Hyperbranched Polyglycerol Supports

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Abstract: Pertosylation of hyperbranched polyglycerol ($M_n=2000$; $M_w/M_n=1.3$) followed by partial displacement of the tosyl groups with carboxylic acid functionalized NCN-pincer platinum(II) complexes [PtI-2,6-(NMe₂CH₂)₂C₆H₂-4-COOH], resulted in covalent attachment of the NCN-pincer complexes to the polyglycerol. These functionalized hyperbranched macromolecules have been character-

ized by ¹H, ¹³C, and ¹⁹⁵Pt NMR, UV-visible, and IR spectroscopy. The presence of Pt and I atoms renders them

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directly visible by transmission electron microscopy (TEM) without staining procedures, which offers images of associated hyperbranched macromolecules. TEM micrographs show disk-shaped structures with a small size-distribution (15–20 nm), and characteristic core-shell ring structures. The thickness of the corona observed in TEM could be correlated with the substitution degree with pincer platinum moieties.

Introduction

Immobilization of functional molecules on dendritic scaffolds in either a covalent or non-covalent fashion, and the control of their supramolecular architectures have been a subject of intense research in the last decade.^[1] This is important to tailor the properties of the supramolecular mate-

rial. Supramolecular association based on dendritic architecture can be useful to provide nanoscale dimensions. The investigation and elucidation of the shape of dendritic building blocks in both solution and in bulk is a crucial prerequisite to control their design, and to then fine-tune their properties. In this context, the application of transition-metal complexes in dendrimer chemistry as building blocks or functional moieties has attracted specific interest.^[2] Both dendrimers and hyperbranched polymers functionalized with catalytically active transition-metal complexes are promising scaffolds with respect to catalyst recovery.^[3] To this end, it is essential to analyse the possible macro-architecture that results from aggregation of the dendritic blocks bearing transition-metal complexes. In addition, dendrimers and hyperbranched macromolecules are interesting for the design of new materials with intriguing optical or electrochemical properties, and for diagnostic applications in medicine.^[4] Since dendrimers have to be prepared in tedious multistep syntheses, which is a limiting parameter for most (large scale) applications, hyperbranched polymers offer a promising alternative.^[5] These hyperbranched polymers are obtained in one-pot syntheses from branched AB_m-type monomers, which results in a randomly branched globular polymeric structure with a broad molecular-weight distribution.^[5a-e] Important recent progress in this field has been made with the development of slow monomer-addition strategies, which results in pseudo chain-growth and thus controlled molecular weights of the polymers, which is deter-

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mined by the monomer to initiator ratio. In this regard, anionic ring-opening multibranching polymerization (ROMBP) of glycidol results in a well-defined hyperbranched polyglycerol, which can be tailored in terms of core functionality and molecular weight.^[6] The narrow polydispersity of these materials ($1.3 < M_w/M_n < 1.5$), and the flexibility of the chemically inert polyether structure, allows further specific functionalization.^[7] To date, there are only few reports on the attachment of catalytically active transition-metal complexes to hyperbranched polymers.^[1c] In previous work, an approach to hyperbranched polycarbosilanes functionalized with aryldiamine palladium(II) complexes has been established by our group.^[8] The soluble macromolecular multisite catalyst obtained was as catalytically active as its carbosilane dendrimer analogue, and was suitable for continuous membrane applications.

Apart from being catalytically active compounds or sensor materials, organometallic NCN-pincer complexes (NCN-pincer = 2,6-bis[(dimethylamino)methyl]phenyl anion) are attractive building blocks, since they can be prepared with various *para*-substituents as anchoring moieties for immobilization purposes.^[9,10] Covalent introduction of these transition-metal complexes is also of interest in view of visualization and imaging of dendritic polymers by transmission electron microscopy (TEM). The electron-rich metal ions in the polymer structure create enhanced contrast and should permit direct visualization of isolated polymer molecules or supramolecular structures.^[11]

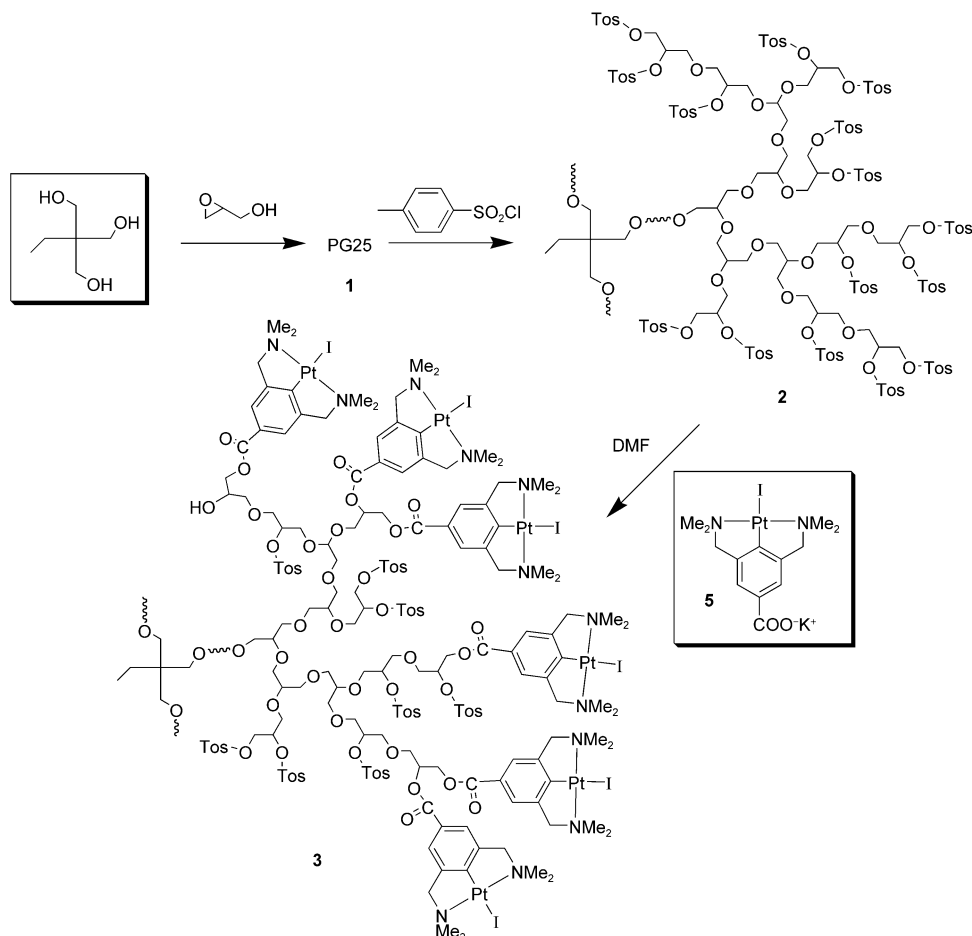
To date, only few molecular images of dendritic macromolecules have been published, because their size range (2–10 nm for dendrimers) and noncontrasting organic composition renders resolution by TEM to be very difficult. Moreover, the application of staining techniques to such small structures is not trivial.^[12] Here, we report a synthetic approach, in two steps for NCN-pincer platinum(II)-substituted polyglycerols obtained by nucleophilic displacement of a tosylated polyglycerol by the potassium carboxylate of a platinated NCN-pincer precursor, in order to prepare platinated hyperbranched polyglycerols. The platinated hyperbranched polyglycerols have been directly visualized by TEM, and compared to shape-persistent multi NCN-pincer platinum complexes with respect to size and structure.

Results

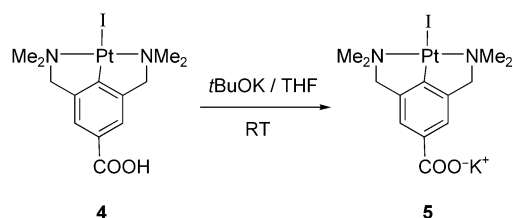
Synthesis: Tosylation of the hydroxyl groups of PG₂₅ (**1**) ($M_n=2000$; $M_w/M_n=1.3$) was carried out by using two equivalents of *para*-tosyl chloride for each hydroxyl group at 80 °C, which resulted in the pertosylated polyglycerol P(G₂₅Tos₁) (**2**) (Scheme 1).^[13] This compound was further purified by dialysis in chloroform. The purity and molecular weight were confirmed by ¹H and ¹³C{¹H} NMR, IR, UV-visible spectroscopy, and elemental analysis. The tosylated material was completely and homogeneously soluble in apolar solvents, in contrast to the hydrophilic starting material.

Grafting of the NCN-pincer platinum(II) complexes was achieved by nucleophilic displacement of the tosylate groups by carboxylated NCN-platinum(II) complexes. The platinated NCN-pincer carboxylic acid (**4**)^[10] was deprotonated for this purpose by treatment with potassium *tert*-butoxide (*t*BuOK) in THF. The potassium carboxylate **5** immediately precipitated from the solution (Scheme 2). Based on the number of tosylate groups per polyglycerol, which is approximately equal to its DP_n (degree of polymerization) ($n=25$), we treated **2** with an excess of **5** in DMF at 80 °C (Scheme 1).

Irrespective of the excess of **5** (10–100%) employed in the substitution reactions, only 50% of the available tosylate



Scheme 1. Synthesis of the pertosylated hyperbranched polyglycerol **2** followed by partial substitution of tosyl groups with NCN-pincer platinum(II) carboxylates to afford **3**.



Scheme 2. Synthesis of the potassium carboxylate NCN-pincer platinum complex **5**.

groups could be replaced by the organometallic carboxylate, which afforded the modified hyperbranched polymer **3** (Scheme 1). Organometallic polymer **3** is constructed from 25 monomer units, with 50% of its hydroxyl groups substituted by NCN-pincer platinum iodide units, and 50% remaining tosyl groups. Thus, each modified polyglycerol molecule contains on average 12.5 platinum sites and 12.5 tosylate groups. Unreacted compound **5** was removed from **3** by repeated liquid–liquid extractions with water, and subsequent dialysis, MWCO (molecular weight cut off) = 1000 D, by using chloroform. Finally, separation by preparative SEC (size exclusion chromatography) equipped with a UV-visible detector was performed in order to study the fractions of different molecular weight with respect to their degree of NCN-pincer platinum substitution, and supramolecular-structure formation. The corresponding SEC diagram with the fractions sampled is shown in Figure 1. Apparently, both aqueous extractions, and dialysis of the crude coupling product were not sufficient enough to completely remove unreacted **5**.

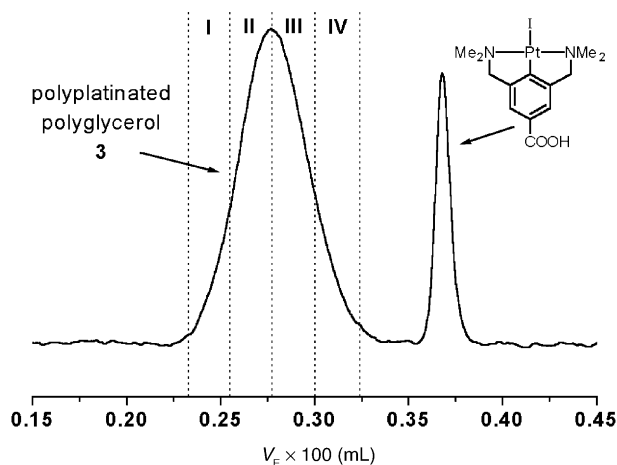


Figure 1. Preparative SEC traces of the separation and fractionation of **3**.

The immobilized platinum (II) iodide complexes could be converted in their cationic aqua complexes by dehalogenation upon treatment with AgBF_4 . The activity of dehalogenated **3**^[14] in the double Michael addition of two equivalents of methyl vinylketone to ethyl cyanoacetate as a model reaction has been tested. The observed reaction-rate for macromolecule **3** ($191 \times 10^{-3} \text{ h}^{-1}$) was relative to that of a nonimmobilized pincer-complex $[\text{Pt}(\text{OH}_2)\text{NCN}]^+\text{BF}_4^-$ ($280 \times 10^{-3} \text{ h}^{-1}$). Separation of products and catalyst **3** after full conversion was achieved conveniently by dialysis against neat dichloromethane. The catalytic material (7.3 mg, $0.65 \mu\text{mol}$) was recovered in near quantitative yields (92%).

TEM characterization: TEM images of the platinum(II), that contained macromolecule **5** were obtained by depositing a dilute solution on carbon-coated electron microscopy grids, followed by evaporation of the solvent. The presence of the platinum and iodine atoms in the hyperbranched materials renders them directly visible by TEM, and leads to the possibility to study their aggregation behavior and supramolecular structures in more detail. Figure 2 represents the TEM

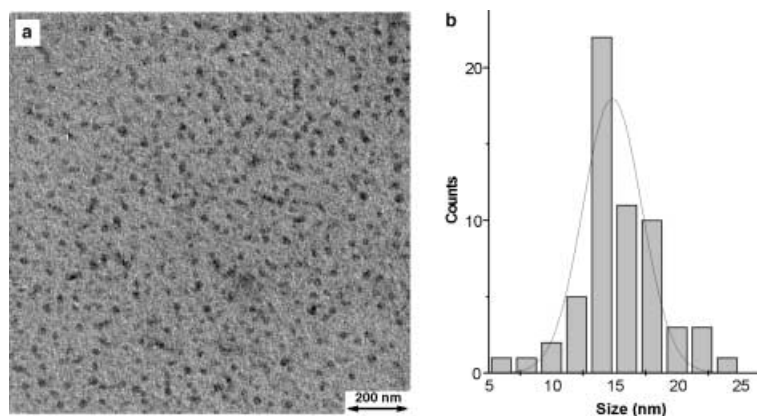


Figure 2. a) TEM image of **3** before SEC fractionation and b) histogram of the particle size distribution.

image obtained for a sample of **5** prior to fractionation, and shows the presence of particles in the size range of 10–25 nm.

In order to obtain a more detailed insight, fractions obtained from preparative SEC were employed in the TEM studies.^[15] Figure 3a and b show the noncontrasted images of two typical hyper fractions (fraction II and fraction IV) of the Pt-loaded hyperbranched polymers. For these, and all other samples studied, a remarkable narrow size distribution of the nanostructures was observed.

For comparison we also studied the earlier reported^[16] rigid dodeca-platinated NCN-pincer complex **6** as depicted. This complex has a calculated diameter of 3.2 nm (from MM2 calculations) and is a monodisperse compound, in contrast to the hyperbranched polymers that possess quite narrow, yet non-negligible molecular-weight distributions. A TEM-image of **6**, together with the corresponding histogram is shown in Figure 4.

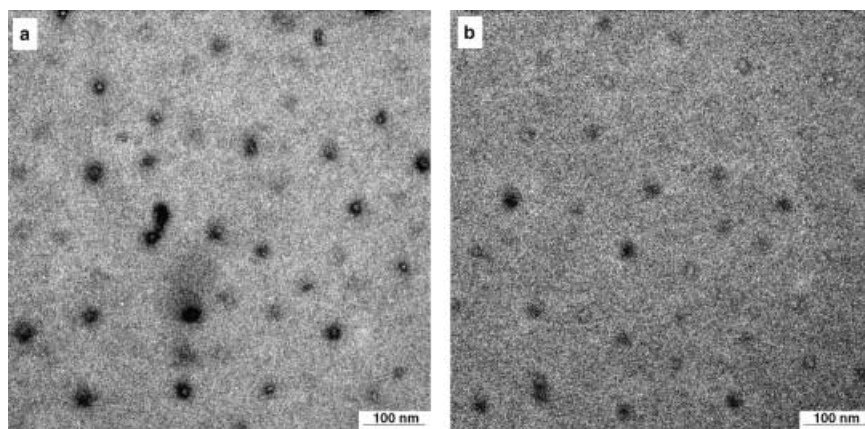


Figure 3. a) TEM image of fraction II after SEC separation and b) TEM image of fraction IV after SEC separation.

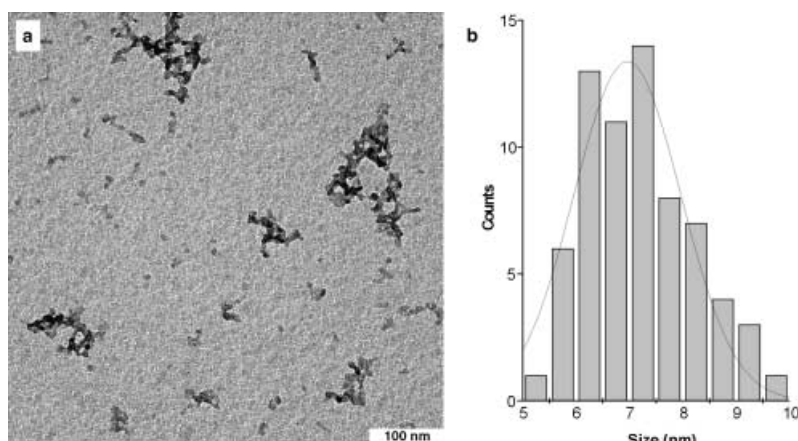
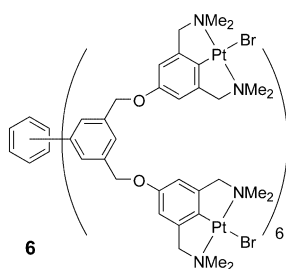


Figure 4. a) TEM image of the dodecaplatin(II) pincer **6** and b) histogram of particle size distribution.

Discussion

Synthesis: Hyperbranched polyglycerols possess terminal and internal hydroxyl groups, which can be functionalized through several routes.^[7] Esterification with acyl chlorides in a mixture of pyridine/toluene affords partially esterified polyglycerols that have been demonstrated to form compact “nanocapsule” structures in apolar media.^[7a,e,1h] This direct substitution route turned out to be impractical for the introduction of the pincer complexes, since the corresponding acyl chloride of **4** was prepared in low yields, and had to be reacted with polyglycerol under harsh reaction conditions. We therefore turned to an alternative strategy, that is, the

preparation of an activated polyglycerol derivative with easily displaceable tosyl groups. Full tosylation was confirmed both by NMR spectroscopy, and the disappearance of the OH-band in the IR spectra. Surprisingly, substitution of the tosylate groups on **2** with **5** did not result in the formation of a fully platinated polyglycerol polymer. No evidence was found for preferential substitution of either primary or secondary tosylate groups of the tosylated hyperbranched polyglycerols. We tentatively explain the incomplete substitution by excessive steric crowding of the bulky pincer system, which disabled complete substitution.

¹H-, and ¹⁹⁵Pt NMR spectroscopy, and UV-visible analysis:

¹H NMR spectra of **3** clearly show partial replacement of the tosylate groups by NCN-pincer platinum groups. While the intensity of the signals originating from the tosylate groups, located at 7.78, 7.36 (ArH) and 2.45 ppm (CH₃) decreased, new signals appeared at 7.56 (ArH), 4.07 (CH₂N), and 3.19 ppm (NMe₂), which is typical of platinated NCN-pincer complexes. The degree of substitution was determined to be 50% by the relative intensity ratios of these signals. The ³J_{Pt-H} couplings of **4** with the NMe₂ (28.8 Hz) and CH₂N (39.0 Hz) protons in the ¹H NMR spectra were not fully resolved in spectra of **3**, due to broadening of the signals caused by the immobilization on a polymeric support. ¹⁹⁵Pt NMR spectroscopy clearly showed the presence of one discrete platinum(II) site, which originated from the immobilized NCN-pincer complexes as a single resonance at

−1914 ppm. For comparison, carboxylic acid **4** showed a singlet located at −1899 ppm in the ¹⁹⁵Pt NMR spectrum. UV-visible spectroscopic analysis of tosylated polyglycerol **2** in chloroform showed an absorption band at 262 nm ($\epsilon \approx 10^5 \text{ M}^{-1}$). In the spectra (UV/Vis) of **3** an additional band shows up at 324 nm ($\epsilon \approx 10^5 \text{ M}^{-1}$), which originates from the NCN-pincer platinum moieties covalently linked to the polymer. For comparison, the NCN-pincer platinum carboxylate **4** exhibits an absorption band located at 326 nm ($\epsilon \approx 10^4 \text{ M}^{-1}$). Furthermore, in the spectra (UV/Vis) of **2** and the polyplatinated polymer **3**, the shoulder of an additional absorption band with its maximum located below 225 nm was visible.

TEM characterization: In contrast to dendrimers, molecular images of hyperbranched macromolecules have not yet been reported. The introduction of heavy atoms (Pt, I) on the polyglycerol backbone permits imaging of molecular or defined supramolecular structures of the materials by TEM without staining procedures. The platinum(II) atoms are covalently bonded to the aryl carbon atom in the stabilizing coordination environment of the NCN-pincer ligand. This in turn is covalently linked to the polyglycerol structure, thereby ensuring that the metal is attached to the hyperbranched polyglycerol support and cannot leach from the material without cleavage of the ester bond.

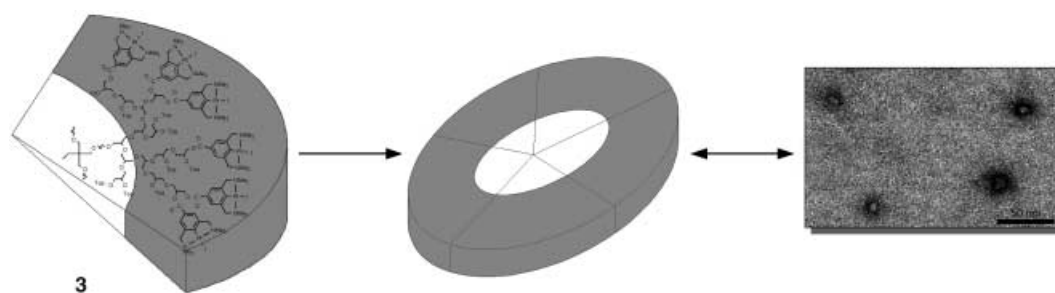
In the TEM image of **3** (Figure 2), prior to fractionation by SEC, the functionalized hyperbranched polymers appear as dark spots in the range of 10–25 nm. Since the size of single hyperbranched macromolecules is expected to be in the range of 5–10 nm based on the molecular modeling of their three dimensional structures, by considering surface interaction and consequent flattening of the structures, these metal-rich particles are due to the association of the macromolecules, not unimolecular species. SEC revealed that the sample still contained unreacted **5**, which is expected to be accommodated in the polyglycerol core of the hyperbranched polymeric aggregates, which resulted in the observed problems when attempting to remove this material by dialysis, and repeated washing with aqueous solution. The TEM-images of the SEC fractions II and IV (Figure 3a and b) show particles of rather narrow polydispersity. In many cases, an unusual core-shell-type substructure with lighter cores and darker corona is observed. In view of the smaller size of single hyperbranched macromolecules, we interpret the core-shell structures as collapsed micellar aggregates of the functionalized hyperbranched polymers. The observed core-shell separated structure can be attributed to differences in polarity between the polyglycerol backbone and the NCN-pincer platinum(II) moieties mainly located in the periphery. In the less contrasting core of the structures only the polyether scaffold is present, while in the dark corona of the core-shell assemblies the NCN-pincer platinum(II) complexes dominate. An intuitive two-dimensional projection that can account for the observed core-shell-separated structure is given in Scheme 3.

An additional feature shown in Figure 3a and b is an increase in the size of the dark corona for the higher molecular-weight fractions. The TEM image of fraction II (Figure 3a) shows dense coronas, while for the lower molecular-

weight fraction IV (Figure 3b) less contrasted coronas are observed. The molecular weight of the functionalized polyglycerol (molecular weight of **2** amounts to 5800 D) is highly dependent on the substitution degree with relatively heavy NCN-pincer complexes (molecular weight of **5** equals 557.3). The thickness of the corona can thus be correlated with the degree of polyglycerol substitution. With an increase in the degree of substitution, the size of the NCN-pincer platinum(II) rich corona increases. We tentatively conclude that the unusual aggregation of **3** is a consequence of the flexible polar structural core of the hyperbranched polyglycerols. In order to rationalize the behavior of NCN-pincer platinum species in TEM studies, a previously described NCN-pincer Pt-loaded dendrimer loaded scaffold **6** was also investigated. The TEM image of **6** (Figure 4a) shows this dodeca-platinated NCN-pincer species as roughly spherical dark spots, which in certain cases assemble to irregular-shaped aggregates. This irregular aggregation is most likely to be attributed to the TEM sample preparation. The particle size of the individual black dots, as can be deduced from the histogram (Figure 4b), is in the range of 5–10 nm. As shown in Figure 4, no core-shell-type supramolecular organization similar to **3** is observed. Both TEM studies clearly show that the attached NCN-pincer platinum species can be applied conveniently for the imaging of small (dendritic) molecules and their supramolecular structures by TEM, without the need for staining procedures. The broad range of available *para*-substituted NCN-pincer complexes^[10] makes their (covalent) attachment to virtually any (organic) scaffold feasible, which allows electron microscopic studies to be performed.

Conclusion

The activation of hyperbranched polyglycerols through tosylation was found to be an efficient method to produce suitable starting materials for further functionalization. The nucleophilic displacement of the tosyl groups by NCN-pincer platinum(II) carboxylate (**5**) gives access to a new polyorganometallic polyglycerol polymer **3** with discrete platinum(II) sites. The presence of the covalently bound heavy platinum and iodine atoms in this polyorganometallic material, allowed visualization of organized supramolecular structures by TEM without the need to use staining techniques; which shows core-shell type aggregates. To the best of our knowl-



Scheme 3. Two-dimensional projection model for the core-shell micelle structure of aggregation for **3**.

edge, this is the first time that transition-metal complexes have been linked to a hyperbranched polyether backbone, and TEM has been applied to study the size and shape of such species.

Experimental Section

All reactions were performed under an inert argon atmosphere. Polyglycerol **1** ($DP_n=25$, $M_n=2000$, $M_w/M_n=1.3$) was prepared as reported previously,^[6a] by using trimethylolpropane (TMP) as an initiator. NCN-pincer platinum complex **4**^[10] and the dodecaplatinum(II) pincer dendrimer **6**^[16] were prepared according to literature procedures. Pyridine was distilled from KOH, toluene, and DMF was distilled from calcium hydride; all other solvents were used without further purification. *p*-Tosyl chloride and *tert*-butoxide potassium were purchased from Aldrich. Benzoylated cellulose tubing for dialysis (MWCO=1000 D) was obtained from Sigma.

¹H NMR and ¹³C{¹H} NMR spectra were obtained from solutions in CDCl₃ on a Bruker ARX 300 spectrometer operating at 300 and 75.4 MHz, respectively. ¹⁵⁹Pt{¹H} NMR spectra were measured by using a Varian Inova 300 from solutions in CDCl₃. IR spectra were recorded on a Bruker Vector 22 spectrophotometer, by using thin polymer films on KBr disks. UV/Vis spectra were obtained by using a Perkin-Elmer Lambda 2 spectrophotometer. Preparative GPC (gel permeation chromatography) was carried out on an MZ-Gel Sdplus column (250×40 mm) by means of THF (p.a.) as eluent. The separation of the samples was monitored by using a variable wavelength monitor at 320 nm with a flow of 5 mL min⁻¹.

TEM measurements: TEM analyses were carried out on a LEO 912 Omega apparatus by using an acceleration voltage of 120 kV. Samples were prepared by applying a drop of the THF solvated organometallic macromolecule **3** to a carbon-coated grid, followed by drying the sample in air. Samples were generally not stained.

Tosylated polyglycerol 2: *p*-Toluene sulfonic acid chloride (25.7 g, 135 mmol) in pyridine (150 mL) at 50°C was added dropwise to a solution of dried hyperbranched polyglycerol ($DP_n=25$) **1** (5 g, 67.5 mmol of OH groups) in pyridine (100 mL). The resulting mixture was stirred at 80°C for 3 h. After cooling to room temperature chloroform (200 mL) was added, and the solution was poured onto a mixture of ice and HCl solution (100 mL of 10 N). The organic layer was separated, washed three times with water, and dried over Na₂SO₄. The product was transferred to benzoylated cellulose tubing for dialysis in chloroform overnight. Chloroform was removed under vacuum pressure, and the product was dried under vacuum, yielding a yellowish oil (70%). ¹H NMR (300 MHz, CDCl₃): $\delta=1.19$ (t, 3H; CH₃, initiator TMP), 2.32 (s, 3H; CH₃, tosylate), 2.34 (s, 3H; CH₃, tosylate), 3.37–3.95 (m, br, polyether scaffold), 3.97–4.04 (q, 2H; CH₂, initiator TEM), 4.45–4.58 (br m, polyether scaffold), 7.23–7.26 (m, 4H; tosylate), 7.64–7.70 ppm (m, 4H, tosylate); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): $\delta=14.5$ (CH₃, TEM), 21.5 (CH₃, tosylate), 66.7, 67.1, 67.26, 68.0, 68.7, 69.7, 71.4, 77.2, 77.4, 127.6, 128.5, 129.8, 132.0, 132.5, 132.8, 132.9, 133.1, 133.6, 139.2, 143.4, 144.5, 144.8, 145.1 ppm; IR (KBr): $\nu=1595$ (C–H aromatic), 1494 (C–H aromatic), 1453 (C–H sat), 1420–1330 (S=O), 1200–1145 (S=O), 1170 cm⁻¹ (C–O). UV/Vis (CHCl₃): $\lambda_{max}(\epsilon)=334$ nm; elemental analysis calcd (%) C 52.38, H 5.71, S 13.98; found: C 52.33, H 5.15, S 12.85.

Synthesis of pincer complex 5: A stoichiometric amount of KOtBu (0.10 g, 0.90 mmol) in THF (20 mL) was added at once to a solution of **4** (0.50 g, 0.90 mmol) in THF (50 mL). A solid precipitated immediately upon addition. The product was isolated by centrifugation, and washed twice with THF (15 mL) to afford **5** as an off-white solid. The solid was used directly in the substitution reactions with tosylated polyglycerols.

Synthesis of polyorganometallic polyglycerols 3: Compound **5** (1.1–2.0 equivalents per DP_n) was added at once to a solution of tosylated polyglycerol (0.2–0.5 g) in DMF (20 mL). The solution was heated at 80°C for 16 h, followed by removal of all volatiles in vacuum. The brownish residue was redissolved in dichloromethane and washed twice with NaOH (1 M) and brine. The solution was dried over MgSO₄, concentrated to 5 mL, filtered over Celite, and dialyzed against neat dichloromethane

(250 mL) to afford a brownish solid. The product was then dissolved in THF and purified with preparative GPC by using THF as an eluent. A yellow fraction was first isolated which corresponded to compound **3** with 50% tosylated and 50% substituted with **5** (50%). The second fraction was discarded, since it corresponded to the free-platinum pincer complex **5**.

Compound 3: $M_n=10541$; ¹H NMR (300 MHz, CDCl₃) $\delta=2.41$ (3H; CH₃ tosylate), 3.19 (12H; NMe₂ pincer), 4.07 (4H; CH₂N pincer), 5.4–3.0 (m, PG), 7.32 (2H; ArH tosylate), 7.56 (2H; ArH pincer), 7.77 ppm (2H; ArH tosylate); ¹³C{¹H} NMR (75.4 MHz, CDCl₃) $\delta=130.2$, 155.0, 144.1, 127.9, 125.2, 120.1, 77.3, 81–78, 74–68, 55.1, 42.7 ppm; ¹⁵⁹Pt{¹H} NMR (64.4 MHz, CDCl₃) $\delta=-1914$; IR (KBr): $\nu=1720$ (C=O), 1420–1330 cm⁻¹ (S=O); UV/Vis (CHCl₃): $\lambda_{max}(\epsilon)=262$, 324 nm.

Conditions for double Michael addition: Ethyl cyanoacetate (1.6 mmol) was added at once to a solution of methyl vinyl ketone (4.8 mmol), Et₂Pr₂N₂O (16 mmol), and catalyst (1 mol%) based on its [Pt] content (12.5 sites for **3**) in 5 mL CH₂Cl₂. The mixture was stirred at room temperature, and 100 μ L aliquots for ¹H NMR spectroscopy analysis were taken in the course of the reaction. Full conversion of **3** was recovered from the product mixture by dialysis against neat dichloromethane (250 mL) for 48 h. The catalytic materials and products were recovered separately in near quantitative yields (92%).

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