An “Attachment Through Coordination” Approach to Side Chain Dendritic Polymers

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This paper reports the synthesis of side chain dendritic polymers by a newly developed "attachment through coordination" methodology. Initially, aromatic/aliphatic polyethers bearing two uncomplexed terpyridine (tpy) groups per repeating unit are prepared, and dendritic fragments core-functionalized with tpy-Ru^{III}Cl$_3$ moieties are afterwards attached onto these free tpy side groups. The two second-generation alkoxy-decorated side dendrons employed here provided solubility in the final polymeric system and potential for the development of ordered structures. Selective complexation between terpyridines and ruthenium ions proved to be an efficient tool for the complete coverage of all initial polymeric-tpy groups. Perfectly substituted dendronized polymers carrying two (dendritic)tpy-Ru^{II}-tpy side moieties per repeating unit were thus synthesized, as demonstrated by their ^{1}H NMR characterization. A polymerizable macromonomer diol already carrying the side (dendritic)tpy-Ru^{II}-tpy moieties was synthesized at the same time, enabling subsequent polymerization through the "macromonomer" growth approach.

Introduction

The syntheses and characterization of dendrons, dendrimers and side chain dendritic polymers (SCDPs) has been the target of intense scientific research over the past decades and has now reached a point where it is aiming in even more complicated directions, such as the development of supramolecular, self-assembling structures. Many such molecules, polymeric or monomeric, elegantly organized into multicomponent structures through various interactions, are the newest trend in the general field of dendrimers, and so efforts are currently being devoted towards the combination of different inter- or intramolecular forces that may give rise to well formed, well defined materials possessing controllable properties arising from, or depending on, the final material’s organizational patterns.[1] One fascinating approach for the fabrication of such architectural systems is the employment of metal to ligand bonding between different molecular entities or parts of the same molecule.[2] This kind of connectivity offers the opportunity to incorporate a large number of metals, each one providing its own unique properties (e.g., optical, electrochemical, catalytic and so on) to the final dendritic system.[3]

As far as SCDPs are concerned, the concept of side dendritic moieties attached in regular fashion onto linear polymeric main chain backbones through metal to ligand bonding has not, to the best of our knowledge, appeared in the literature up until now. For the preparation of dendronized polymers the well established “macromonomer” growth approach[4] requires the preparation of polymerizable macromonomers carrying the side dendrons prior to polymerization. On the other hand, the “divergent” or “attach to” methodology for SCDPs[4] proceeds either through construction of the side dendrons at appropriate side functionalities of the main polymeric chains or by attachment of prefabricated dendrons onto preexisting polymeric main chains. To extend these methodologies for the fabrication of SCDPs in which the side dendrons were held on the main polymeric backbones through metal to ligand coordination bonding, one would have either to prepare macromonomers carrying the side dendritic wedges connected through metal-ligand bonds or to attach the desired dendrons onto functional main polymeric chains by employing such coordination connectivity.

The latter pathway, an “attachment through coordination” approach, has been employed in this contribution. More particularly, dendronized aromatic/aliphatic polyethers, in which two side-dendritic moieties are held onto each main polymeric repeating unit through terpyridine-Ru^{II}-terpyridine (tpy-Ru^{II}-tpy) connecting points, have been developed. Through this “attachment through coordination” methodology, we were able to fulfil the prerequisite for dendronized polymers: that is, perfectly substituted polymers bearing side dendrons at every single repeating unit. At their peripheries the side dendrons used in this study bear alkoxy groups that have in the past offered the potential for the preparation of dendronized polymers forming ordered layered structures.[5] The defined distance

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of the two Ru^{II} ions attached on the same monomeric unit, the distances along the polymeric main chain determined by the spacer length, and finally the interchain distances dictated by the generation and the type of substitution of the alkoxy-decorated dendrons should result in regular positioning of the Ru^{II} ions with distances on nanometer scales (2–4 nm).

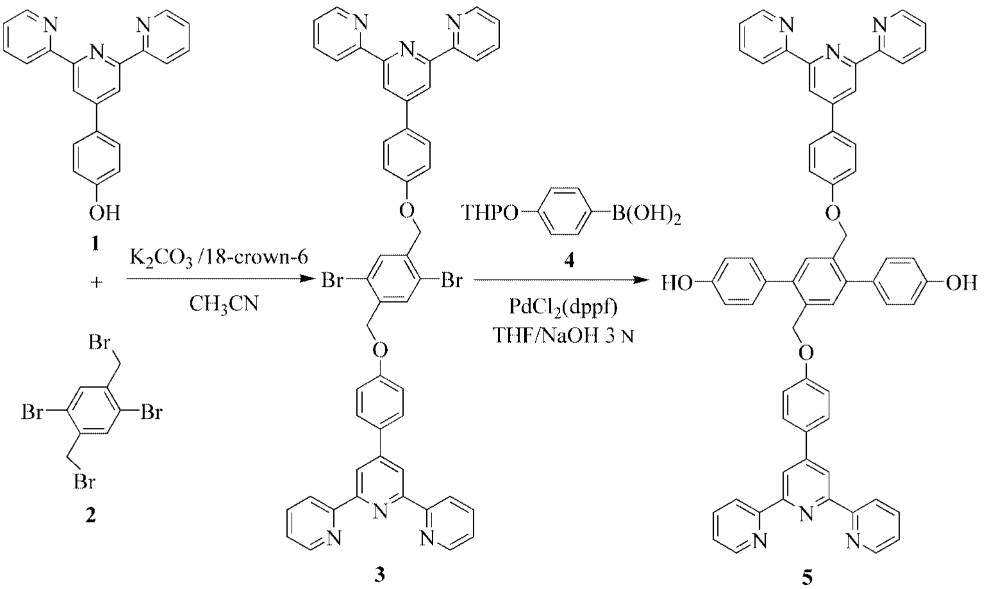
In addition to the dendronized polymeric complexes described above, a macromonomer already bearing the side (dendritic)tpy-Ru^{II}-tpy moieties has also been synthesized, showing that such dendronized systems may also be prepared by the "macromonomer" route. All the initial monomers and polymers, as well as the final dendronized polymeric complexes and the macromonomer dendronized complex, have been characterized and their structural perfection has been demonstrated by NMR spectroscopy and UV/Vis experiments.

Results and Discussion

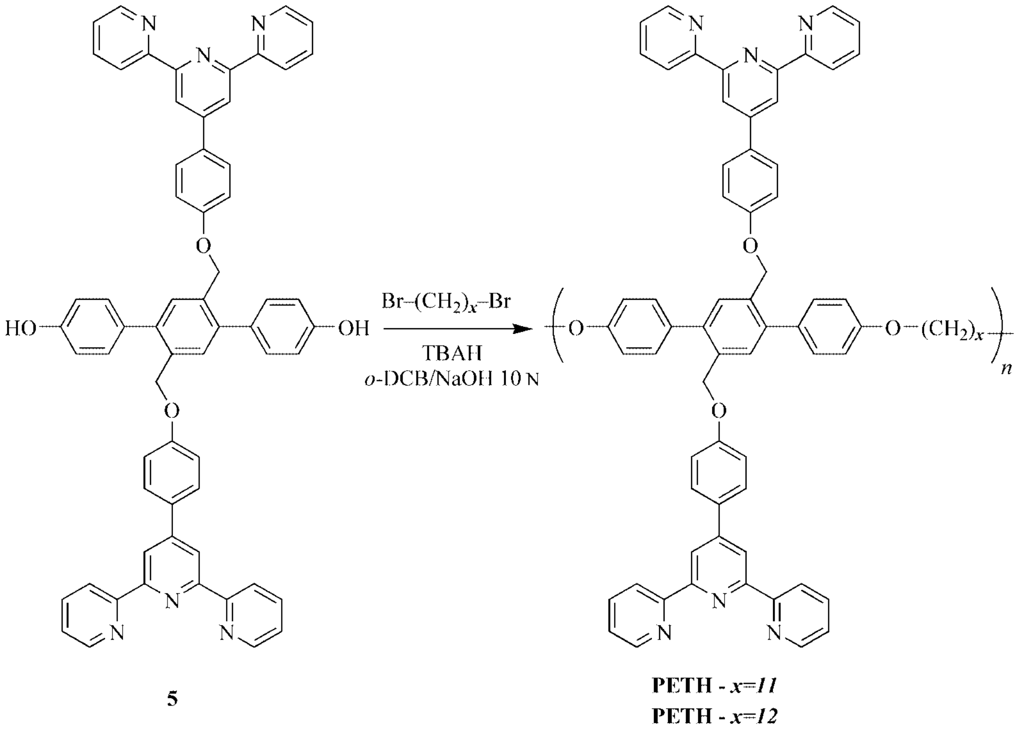
In order to accomplish this "attachment through coordination" strategy for the preparation of side chain dendritic polymers we first had to synthesize the desired main chain polymeric backbones. These had to bear side functionalities, in particular terpyridine (tpy) moieties, onto which the side dendritic fragments would later on be attached through metal to ligand bonding. For that reason we designed and synthesized aromatic/aliphatic polyethers with two side tpy groups per repeating unit, as depicted in Schemes 1 and 2.

The aromatic dibromide **3** was prepared by etherification of 4′-(*p*-hydroxyphenyl)-2,2′:6′,2′′-terpyridine (OH-Ph-tpy; **1**)[6] with 1,4-dibromo-2,5-bis(bromomethyl)benzene (**2**)[7] (Scheme 1). Palladium mediated-cross coupling[8] of **3** with the THP-protected (THP = tetrahydropyranyl) hydroxyphenyl boronic acid **4**[9] produced the THP-end-protected terphenyl diol with two tpy side groups in its middle phenylene ring. Removal of the THP groups was performed by treatment with camphorsulfonic acid, while its complexation with the tpy units was reversed by stirring the crude material in aqueous Na_2CO_3 solution. The desired terphenyl diol **5** was obtained in gram scale quantities and was fully characterized by ^1H and ^{13}C NMR spectroscopy (see inset in Figure 1).

Afterwards, diol **5** was polymerized with aliphatic dibromides containing 11 or 12 methylene units under phase-transfer polymerization conditions[10] (Scheme 2). It is worth mentioning that the resulting aromatic-aliphatic polyethers are readily soluble in common chlorinated solvents such as $CHCl_3$, *o*-DCB, and TCE, unlike the initial diol **5**, which was only slightly soluble in *o*-DCB, forcing us to perform the polymerizations over long periods of time to ensure complete monomer consumption. Polyethers **PETH-*x=11*** and **PETH-*x=12*** were fully characterized by ^1H and ^{13}C NMR techniques (Figure 1), while their molecular characteristics were evaluated by GPC vs. PS standards with $CHCl_3$ as eluent (Table 1). It is reasonable to assume that their true molecular weights differ from those estimated by GPC not only because of the semi-rigid nature of the polymeric backbones but also because of possible interactions between the free tpy ligands and the chromatographic stationary phase. In cases in which low molecular weight materials were obtained (e.g., **PETH-*x=12(iii)***; see Table 1), the true number average molecular weight was calculated from the ^1H NMR spectrum by the end-group analysis technique. More particularly, peaks corresponding to aromatic protons of the diol could be found at δ = 7.1, and these, together with the tpy proton peaks at δ = 8.7, gave the actual degree of polymerization of the **PETH-*x=12(iii)*** sample [DPn = 3 Mn(NMR) = 3280]. Comparison of the DPn obtained from the NMR end-group analysis



Scheme 1. Synthesis of monomer diol **5**.



Scheme 2. Synthesis of polymers **PETH-*x=11*** and **PETH-*x=12***.

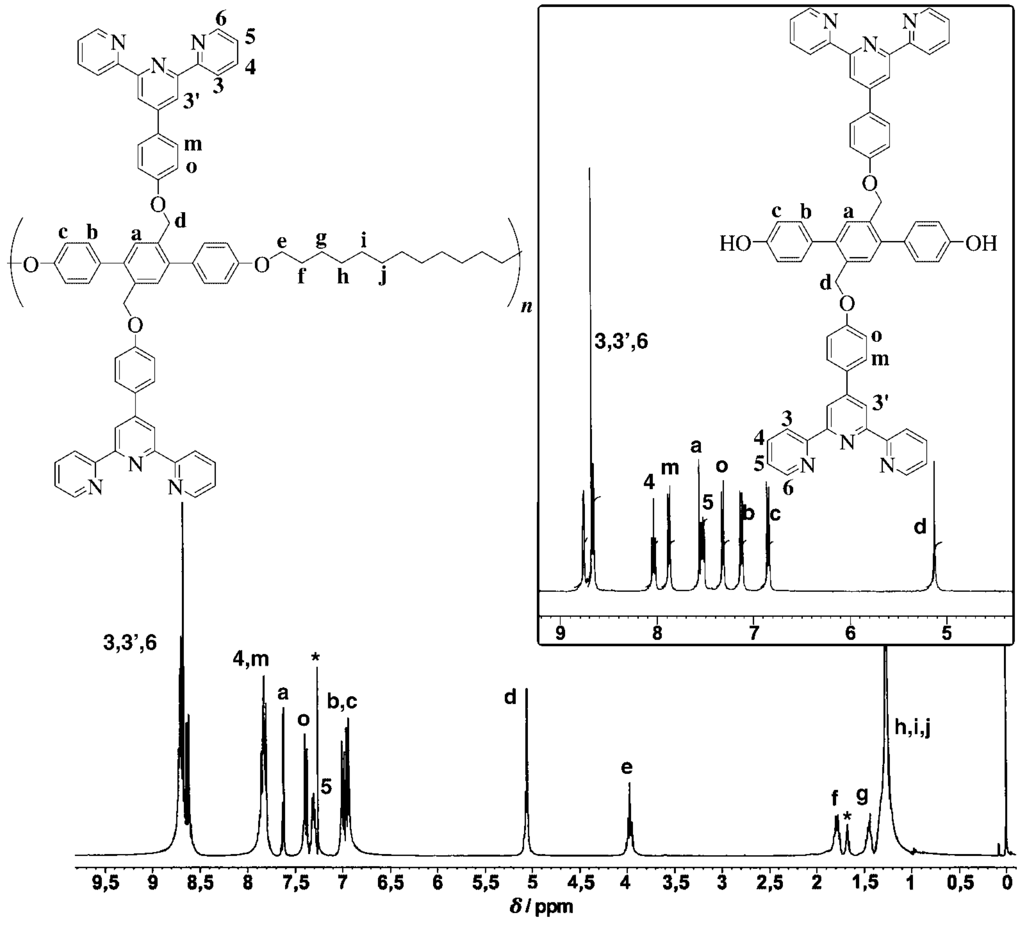


Figure 1. ^{1}H NMR of **PETH-*x=12(i)*** in $CDCl_3$ and of diol **5** in [D$_6$]DMSO (see inset).

Table 1. Molecular weight characteristics of the initial polyethers **PETH-*x=11*** and **PETH-*x=12***.[a]

Polymer	*Mn*	*Mw*	*Mw*/*Mn*
PETH-*x=11(i)*	8800	21900	2.5
PETH-*x=11(ii)*	2520	4110	1.6
PETH-*x=12(i)*	7160	13030	1.8
PETH-*x=12(ii)*	9710	26130	2.7
PETH-*x=12(iii)*[b]	1070	1680	1.6

[a] By size exclusion chromatography (GPC) with $CHCl_3$ as eluent, at room temperature, vs. PS standards. [b] For **PETH-*x=12(iii)*** the *Mn* was calculated from its ^1H NMR spectrum by end-group analyses and was found to be equal to 3280, DPn = 3.

for **PETH-*x=12(iii)*** with that provided by GPC demonstrates an underestimation of the true molecular characteristics of the synthesized polymers.

Additionally, as can be seen in the ^1H NMR spectrum of **PETH-*x=12(i)*** (Figure 1), no end groups at δ = 6.8 or 7.1 – corresponding to the aromatic protons of the initial diol **5** adjacent to the hydroxy functionalities – are evident in the case of the higher molecular weight materials, so we can conclude that those are indeed high molecular weight polymeric materials.

For the preparation of the tpy core-functionalized side dendritic wedges we etherified the dendritic benzyl bromide

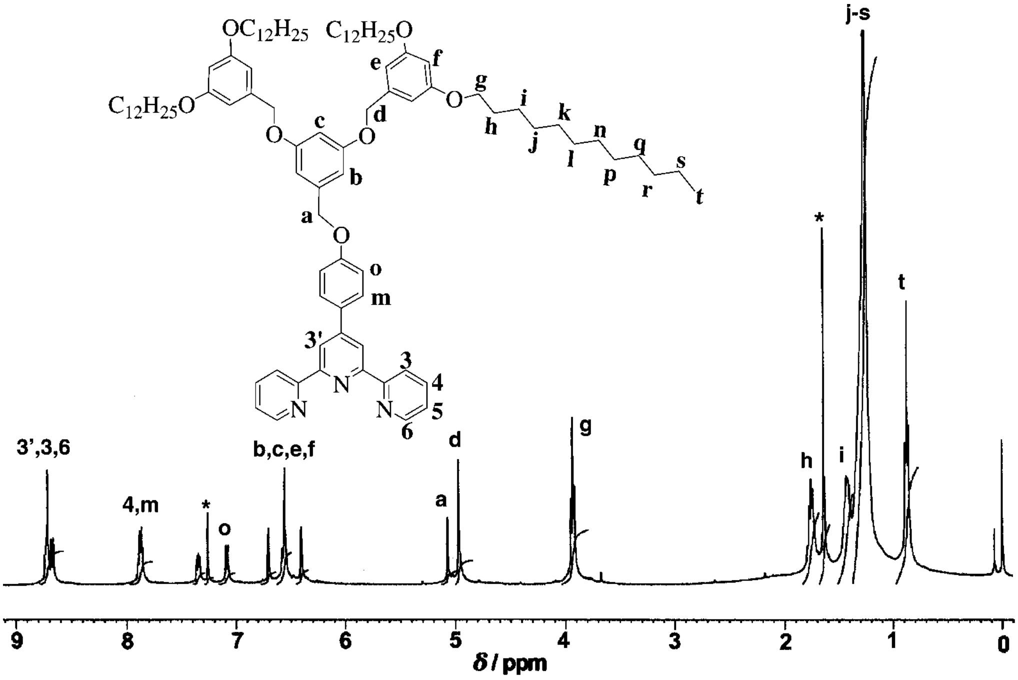
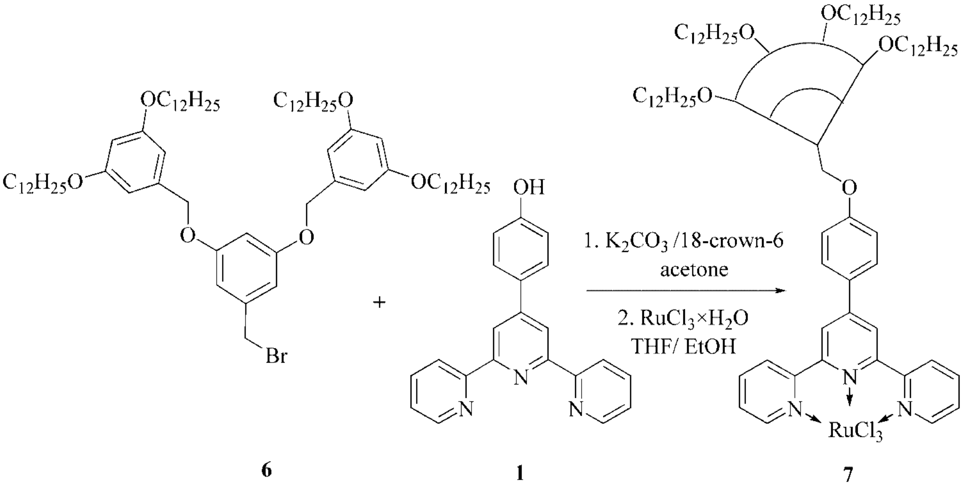


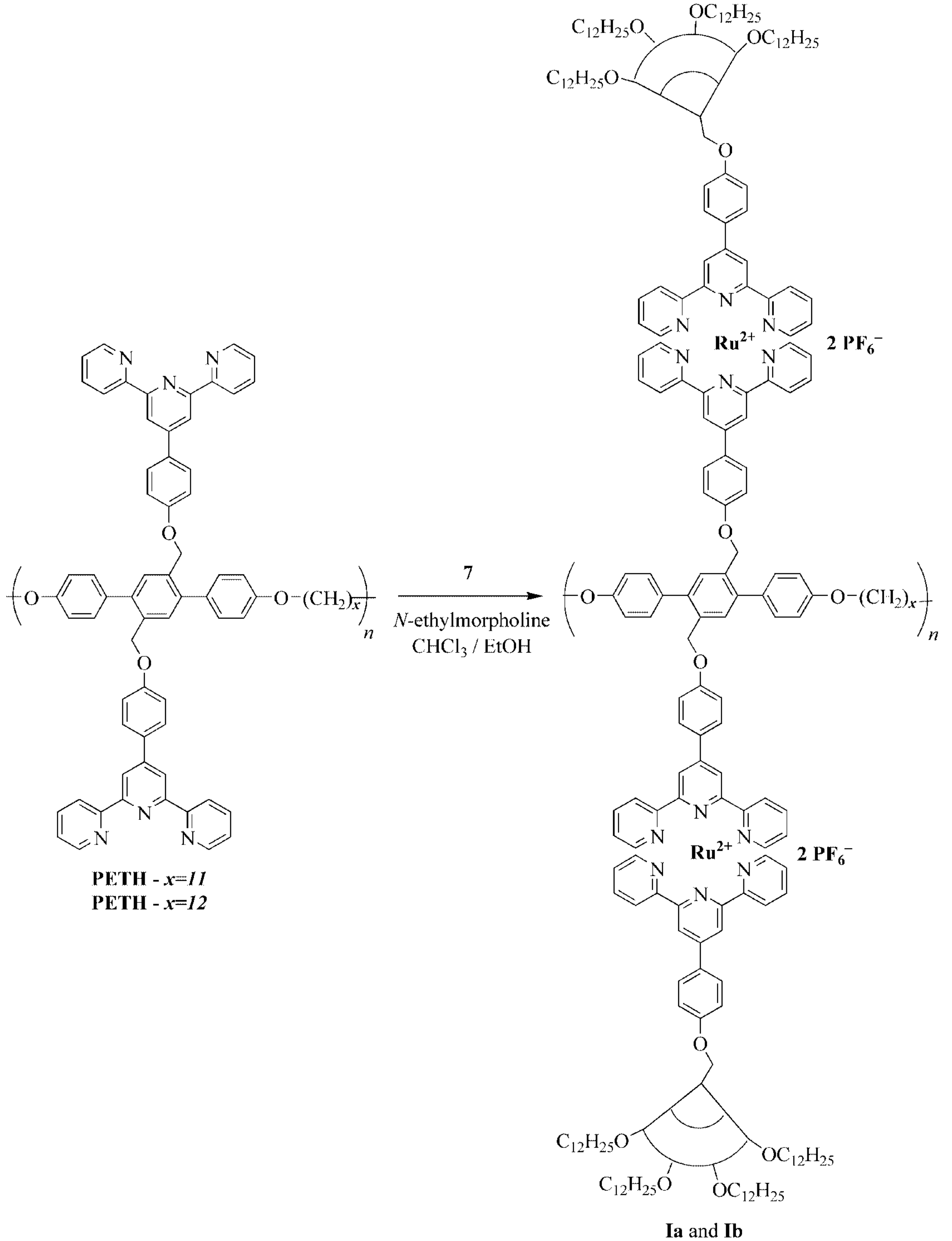
Figure 2. ^1H NMR of uncomplexed **G_2-tpy dendron** in $CDCl_3$.



Scheme 3. Synthesis of **G_2-tpy$Ru^{III}Cl_3$** dendron **7**.

6[11] with OH-Ph-tpy **1** (Scheme 3, Figure 2). The particular alkoxy-decorated second-generation dendron **6** was employed in order to confer solubility to the final metal-containing polymeric systems and, more importantly, for future correlations with some analogous dendronized polyethers that had been found to present interesting self-organizational solid-state patterns.[5] The paramagnetic G_2-tpyRu^{III}Cl$_3$ dendron **7** was synthesized by heating of the uncomplexed dendron **6** at reflux with $RuCl_3 \cdot xH_2O$ in THF/EtOH solution, and was used without further purification.

Having prepared the main polymeric backbones and the ruthenium-functionalized side-dendrons we were able to proceed to their complexation, to afford the final dendronized ruthenium loaded polymers. As shown in Scheme 4, polyethers **PETH-*x=11(i)*** and **PETH-*x=12(i)*** were treated with the monocomplexed dendron **7** under reductive conditions in the presence of catalytic amounts of *N*-ethylmorpholine in $CHCl_3$/EtOH solutions. In order to ensure complete coverage of all free polymeric tpy units with the side dendrons, excesses of dendron **7** and long reaction



Scheme 4. Synthesis of dendronized polymeric complexes **Ia** and **Ib**.

times were employed. The final dendronized polymeric materials **Ia** and **Ib**, respectively, were precipitated from the reaction mixture after counterion exchange with addition of excess of methanolic NH_4PF_6 solution.[12] The red polymeric powders were collected and thoroughly washed with diethyl ether for the selective removal of the excess side dendritic monocomplex employed. We were thus able to obtain pure, perfectly dendronized aromatic-aliphatic polyethers bearing two side (dendritic)tpy-Ru^{II}-tpy moieties on every single polymeric unit (**Ia** and **Ib**).

These dendronized highly Ru-loaded polymers are soluble in common organic solvents such as $CHCl_3$, THF, and DMSO, allowing their characterization by ^{1}H and ^{13}C NMR techniques. A typical ^{1}H NMR spectrum, for the dendronized polymeric complex **Ib**, is presented in Figure 3. The spectrum of **Ib** possesses all the characteristic peaks corresponding to the aromatic protons of tpyRu^{II}tpy protons: both those arising from the main polymeric backbone and those arising from the side dendritic fragments. On comparison of the ^{1}H NMR spectra of the uncomplexed

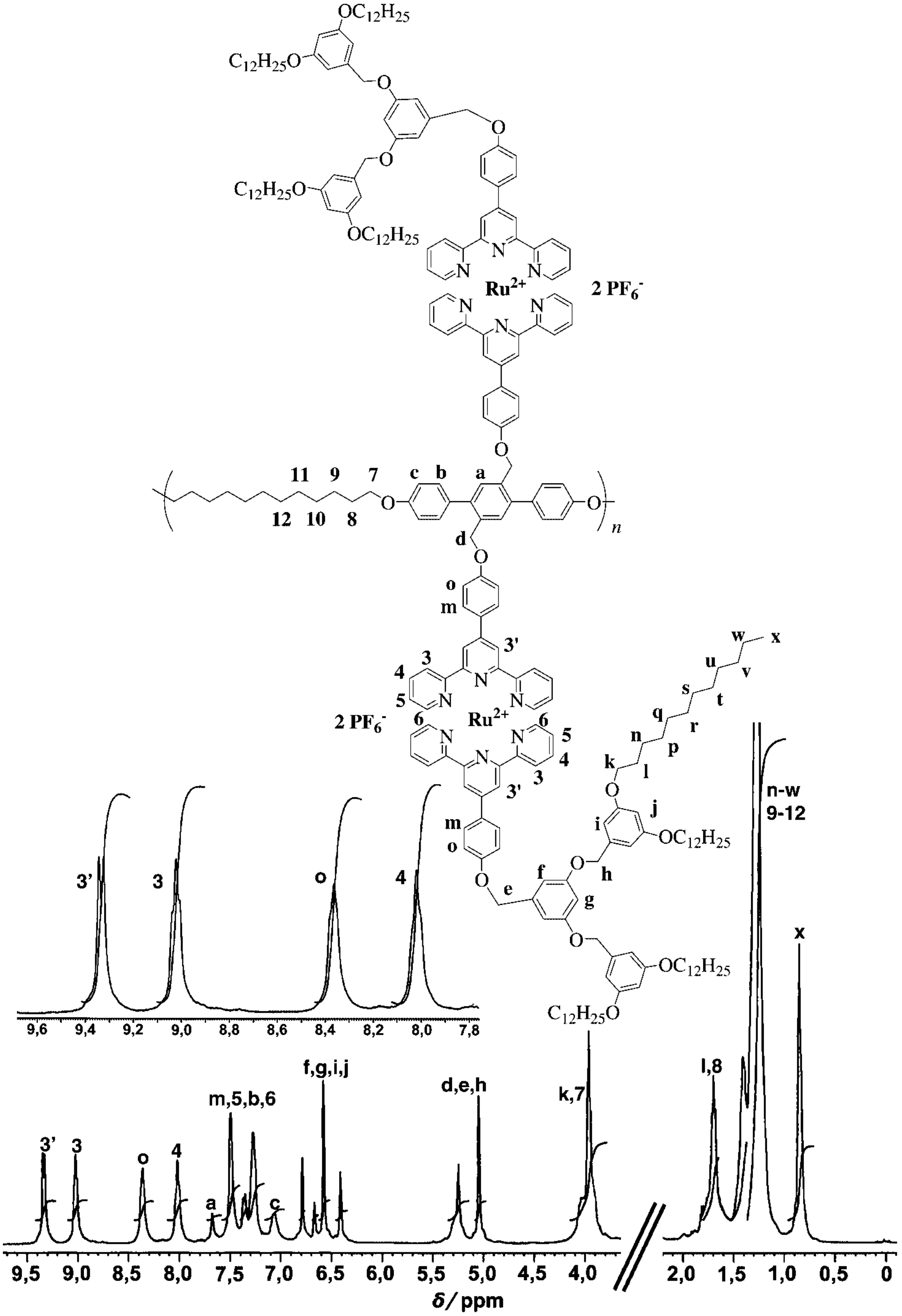


Figure 3. ^{1}H NMR of dendronized polymeric complex **Ib** in [D$_6$]DMSO.

polyether **PETH-*x=12(i)*** (Figure 1) and of the respective dendronized polymeric complex **Ib** (Figure 3) one can observe the expected downfield shift of the 3′ and 3 tpy protons after complexation – from δ = ca. 8.6 to 9 and 9.35, respectively – and the upfield shift of the 6 tpy protons, from δ = ca. 8.6 to ca. 7.3. Moreover, no differentiation between the dendritic tpy protons and the tpy protons of the main polymeric chain was seen, due to the similarity of their neighboring environment.

Additionally, and most importantly, no peaks corresponding to uncomplexed, free tpy units along the polymeric main chains, at δ = 8.6–8.71, were detected. This can be clearly seen in the inset of Figure 3, where the region from δ = 9.6 to 7.8 is enlarged. We can thus safely draw the conclusion that this "attachment through coordination" methodology employed for the preparation of side dendritic polymers had proved efficient, producing perfectly substituted polymers with two side dendrons on every single repeating unit and, moreover, held onto the polymeric main backbones through metal to ligand (tpy-Ru^{II}-tpy) bonding. Unfortunately, the dendronized polymeric complexes **Ia** and **Ib** could not be characterized by GPC. Similar problems have also been reported in the literature and have been assigned to the strong interaction of ruthenium with the stationary phase used in the GPC columns.[13]

On the other hand, viscosity measurements were performed for a dendronized polymeric complex and its uncomplexed polymeric precursor. Figure 4 shows the viscosity values obtained for polymeric complex **Ia** in comparison with its precursor **PETH-*x=11(i)***. Polyether **PETH-*x=11(i)*** showed typical polymeric behavior with an intrinsic viscosity [n] = 0.13 in $CHCl_3$ at 30 °C. In the case of the polymeric complex **Ia** the viscosity measurements were performed in DMSO, also at 30 °C. An increase in the reduced viscosity is evident as the concentration decreases. Such behavior has been reported for various coordination polymers containing tpy-Ru^{II}-tpy groups and can be explained in terms of the polyelectrolytic nature of the polymers due to the presence of the Ru^{II} and their counterions.[14] Attempts to reduce the polyelectrolyte repulsion and obtain true viscosity values by means of intrinsic viscosity were also made, by addition of NH_4PF_6 to the DMSO solutions, but even a 10 mM salt concentration caused the polymeric complex to precipitate from the solution. In any case, these observations alone demonstrate the different nature of the dendronized polymeric complexes with respect to the uncomplexed polyether precursors. Unfortunately, $CHCl_3$ could not be used as solvent for **Ia**. Actually the polymeric complexes, even though macroscopically soluble in $CHCl_3$, gave irreproducible viscosity values, probably owing to the formation of aggregates. As an example, a 0.23 g dL^{-1} solution of the dendronized complex **Ia** in $CHCl_3$ gave an n_{red} = 0.08 dL g^{-1} at 30 °C, while the same polymeric complex in DMSO at C = 0.23 g dL^{-1} gave an n_{red} = 0.53 dL g^{-1}.

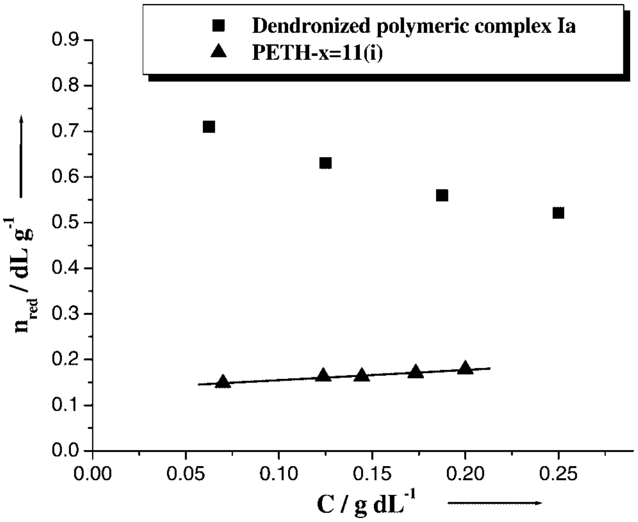
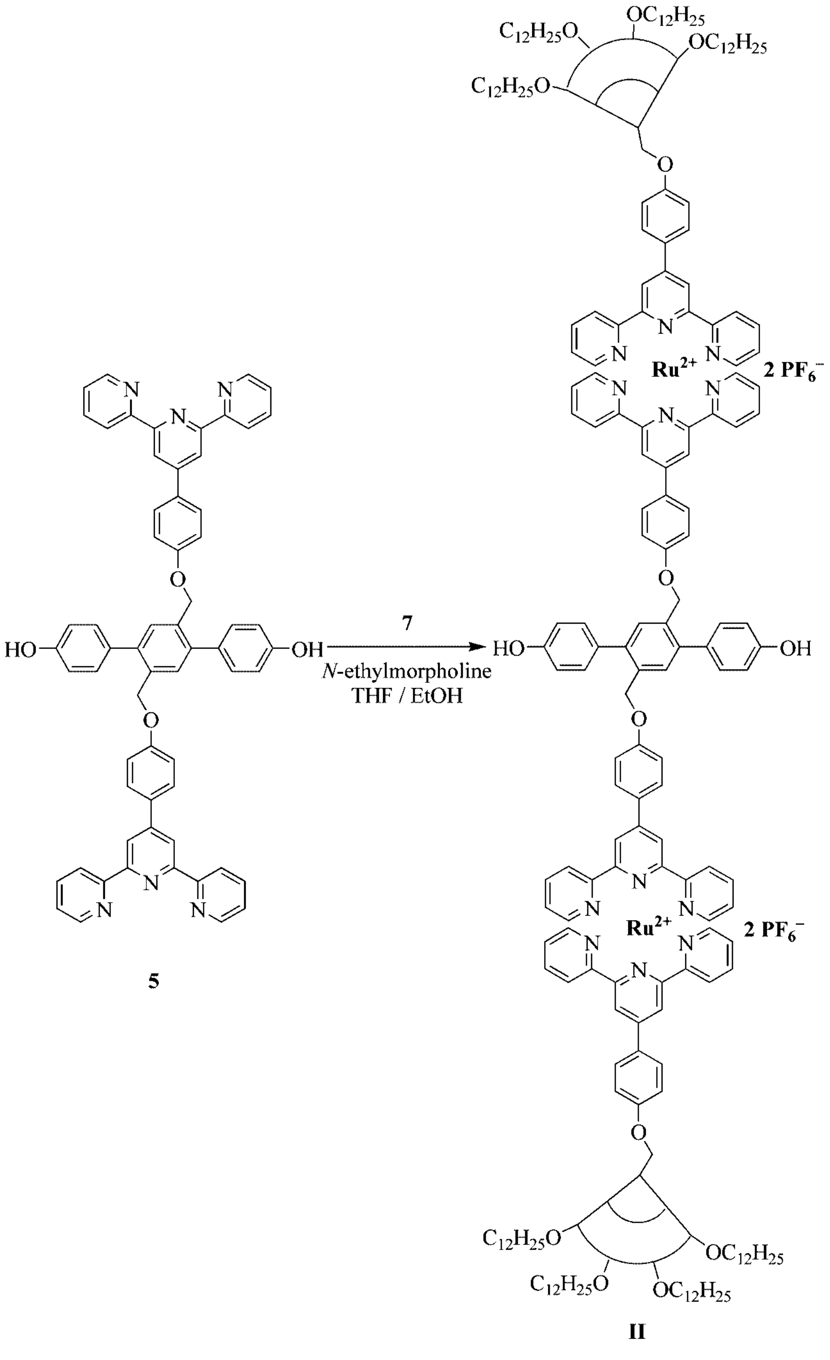


Figure 4. Concentration-dependence measurements of the reduced viscosities of **PETH-*x=11(i)*** in $CHCl_3$ and of **Ia** in DMSO, at 30 °C.

Recognizing that the well established "macromonomer" route towards dendronized polymers can guarantee the structural perfection of the final polymers in all cases, we decided to take a first step towards it and to prepare a macromonomer carrying the desired dendritic fragments prior to polymerization. The initial diol **5** was thus treated with excess G_2-tpyRu$^{III}Cl_3$ monocomplex **7** in THF/EtOH solution containing a catalytic amount of *N*-ethylmorpholine (Scheme 5). The dendronized macromonomer dicomplex was precipitated from the reaction mixture after counterion exchange with addition of excess methanolic NH_4PF_6 solution. All excess of G_2-dendritic monocomplex was selectively removed by washing with diethyl ether. This macromonomer dicomplex **II** also showed improved solubilities relative to the initial diol **5**, being soluble in $CHCl_3$, THF, DMSO, etc. The ^{1}H NMR spectrum of the second-generation macromonomer dicomplex **II** is presented in Figure 5, with an assignment of all peaks. Also in this case, no peaks corresponding to free tpy units were detected in the δ = 9.5 to 7.8 region. Moreover, the ^{1}H NMR spectrum of the dicomplex **II** is in perfect agreement with its counterpart for the dendronized polymeric complex **Ib** presented in Figure 3, providing additional evidence for the structural perfection of the dendronized polyether prepared through the "attachment through coordination" approach. This macromonomer dicomplex should also give us the opportunity to prepare the whole series of dendronized polymers with other generation side dendrons and two Ru^{II} ions on every repeating polymeric unit.

Examination of the prepared materials' optical properties was performed with the aid of UV/Vis absorption measurements in dilute $CHCl_3$ solutions (Figure 6). Since the uncomplexed diol **5** was insoluble in $CHCl_3$ we prepared the corresponding didodecyloxy-end-functionalized uncomplexed monomer (model compound **M**; see Experimental) in order to compare its absorption spectra safely with those of the other materials in the same solvent. For the uncomplexed samples, **PETH-*x=12*** and model compound **M**, characteristic bands attributable to the free tpy groups can be found at 284 nm. After the formation of the tpy-Ru^{II}-tpy complexes, materials **Ib** and **II**, another intense



Scheme 5. Synthesis of dendronized macromonomer **II**.

peak can be observed at 310 nm, originating from the ligand-centered (LC) π–π* transition of the tpy ligand. In addition, the characteristic band of tpy-Ru^{II}-tpy complexes, arising from the d–π* metal to ligand charge transfer (MLCT) transitions, is now obvious at 496 nm. Moreover the monocomplexed G$_2$-tpyRu^{III}Cl$_3$ dendron **7** presents a band at ca. 420 nm, as would be expected for a tpy-Ru^{III} monocomplex.

Conclusions

In conclusion we were able to prepare second-generation alkoxy-functionalized SCDPs by a newly developed "attachment through coordination" approach. The coordination chemistry of the tpy-Ru^{II}-tpy complexes has been used for the attachment of alkoxy(G$_2$)-tpy-functionalized dendrons onto polymeric backbones bearing two tpy side

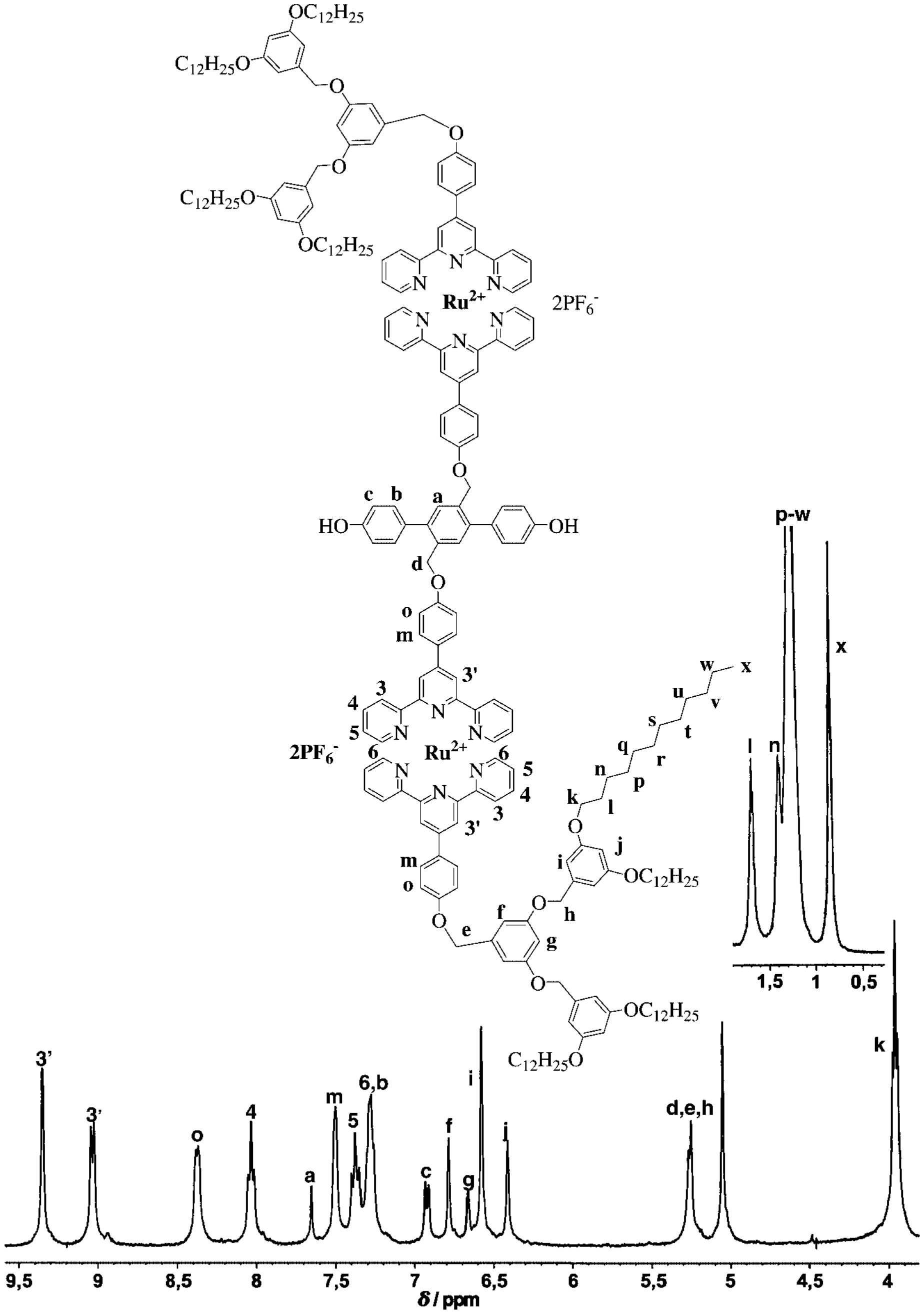


Figure 5. ^{1}H NMR of macromonomer dicomplex **II** in [D$_6$]DMSO.

groups per repeating unit. In addition, a macromonomer diol already carrying the side dendrons was synthesized, opening the pathway for the development of such dendronized polymers through the "macromonomer" route. Evidence for the dicomplexes' structural perfection came from their NMR characterization. Their UV/Vis absorption spectra are also in accordance with the incorporation of the tpy-Ru^{II}-tpy moieties. The developed methodology should give us the ability to arrange the Ru centers nicely in well defined, predictable positions along the polymeric chains and finally in the whole polymeric matrix and to explore the influence of the polymeric architectures on their final properties further.

Experimental Section

Materials: Second-generation dendron **6**,[11] 4′-(*p*-hydroxyphenyl)-2,2′:6′,2′′-terpyridine (**1**),[6] 1,4-dibromo-2,5-bisbromomethyl benzene (**2**),[7] and catalyst PdCl$_2$(dppf)[15] were prepared by literature procedures. The synthesis of 2-tetrahydropyranyloxy-4-phenylboronic acid (**4**) was described in a previous publication.[9] Tetrahydrofuran (THF) was distilled from sodium prior to use. Reagents

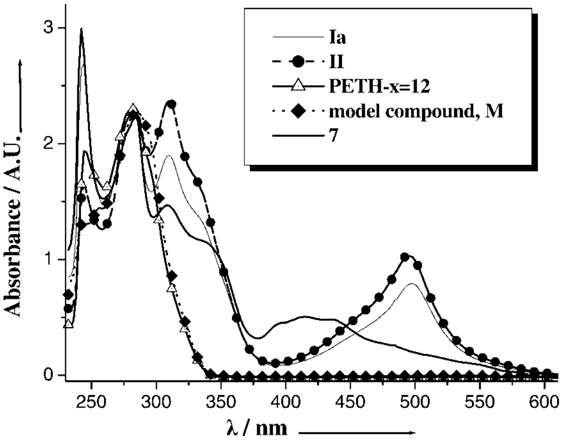


Figure 6. UV/Vis absorption spectra in $CHCl_3$ (≈ 10^{-5} M). All spectra were normalized to the 284 nm peak of dicomplex **II**.

and solvents of analytical grade purity were purchased from Aldrich or Merck and were used without further purification unless otherwise noted. Aliphatic dibromide $x = 12$ was recrystallized from methanol. All reactions were performed under argon. Degassing of reaction mixtures was performed by subsequent cycles of evacuation and filling with argon (three times).

Instrumentation: ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX (400 MHz and 100 MHz, respectively) spectrometer in $CDCl_3$ or [D$_6$]DMSO and with TMS as internal standard. Gel permeation chromatography (GPC) measurements for polyethers **PETH-*x=11*** and **PETH-*x=12*** were carried out with a Polymer Lab chromatograph with two Ultra Styragel linear columns with pore sizes of 10^4 and 500 Å, respectively, UV detector (254 nm), polystyrene standards, and $CHCl_3$ as eluent, at 25 °C with a flow rate of 1 mL min^{-1}. Viscosity measurements of polymers **PETH-*x=11(i)*** and **Ia** were conducted in $CHCl_3$ or DMSO with Ubbelohde- or Ostwald-type viscometers, respectively, at 30 °C in a Scott Gerate AVS. 310. The UV spectra were recorded on a Hewlett Packard 8452A Diode Array UV/Visible spectrophotometer, in dilute $CHCl_3$ (≈ 10^{-5} M) solutions.

Dibromide 3: A mixture of **1** (2.445 g, 7.523 mmol), **2** (1.270 g, 3.010 mmol), K_2CO_3 (8.306 g, 0.060 mol), and 18-crown-6 (0.159 g, 0.602 mmol) in CH_3CN (120 mL) was heated at reflux for 48 h. The solvent was evaporated under reduced pressure and the mixture was dispersed in H_2O, stirred, and filtered. Washing with H_2O, EtOH, and *n*-hexane afforded the desired monomer **3** as a yellowish powder, which was used without further purification. Yield 2.60 g (95%).

Diol 5: A degassed mixture of **3** (2.60 g, 2.86 mmol), **4** (2.54 g, 11.44 mmol), $PdCl_2$(dppf) (0.10 g, 0.14 mmol), THF (200 mL) and NaOH (3 M, 11.43 mL, 34.28 mmol) was heated under reflux with vigorous stirring for 96 h. Most of the organic solvent was afterwards removed under reduced pressure, MeOH was then added and, after filtration and washing with MeOH, H_2O, and *n*-hexane, the THP-end-protected diol was obtained as a grayish powder. Yield 2.00 g (63.5%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.5–2 (three m, 12 H), 3.63 (m, 2 H), 3.95 (m, 2 H), 5.08 (s, 4 H), 5.47 (t, 2 H), 7.02 (d, 4 H), 7.12 (d, 4 H), 7.33 (t, 4 H), 7.4 (d, 4 H), 7.64 (s, 2 H), 7.83–7.89 (d, 4H and m, 4 H), 8.66 (d, 4 H), 8.7 (s, 4 H), 8.73 (d, 4 H) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$, TMS): δ = 19.22, 25.60, 30.78, 62.57, 68.48, 96.82, 115.70, 116.74, 118.73, 121.74, 124.12, 128.90, 130.72, 131.39, 131.67, 133.51, 134.20, 137.21, 141.12, 149.51, 150.15, 156.24, 156.82, 157.12, 160.00 ppm.

Camphorsulfonic acid (CSA; 6.31 g, 27.17 mmol) was added to a solution of THP-protected diol (2.00 g, 1.81 mmol) in DMA (100 mL) and THF (100 mL) and the mixture was stirred at room temperature for 48 h. THF was then removed under reduced pressure, Na_2CO_3 (2 M, 120 mL) was then added, and the mixture was stirred for another 48 h. Filtration, washing with H_2O, MeOH, $CHCl_3$, and *n*-hexane, and drying under vacuum afforded the final monomeric diol **5** as a white solid. Yield 1.64 g (96.7%). ^1H NMR (400 MHz, 80 °C [D$_6$]DMSO, TMS): δ = 5.1 (s, 4 H), 6.83 (d, 4 H), 7.1 (d, 4 H), 7.3 (d, 4 H), 7.5 (t, 4 H), 7.53 (s, 2 H), 7.85 (d, 4 H), 8.01 (t, 4 H), 8.63–8.65 (s, 4H and d, 4 H), 8.74 (d, 4 H) ppm. ^{13}C NMR (100 MHz, 80 °C, [D$_6$]DMSO, TMS): δ = 68.15, 115.69, 116.01, 117.76, 121.38, 124.93, 128.69, 130.27, 130.40, 130.58, 131.65, 133.93, 137.93, 140.83, 149.40, 149.74, 155.46, 156.02, 157.37, 159.82 ppm. $C_{62}H_{44}N_6O_4$ (936): calcd. C 79.49, H 4.7, N 8.97; found C 79.61, H 5.09, N 8.6.

Uncomplexed G$_2$-Dendron-tpy: A mixture of **1** (0.50 g, 1.54 mmol), G$_2$-dendron **6** (1.90 g, 1.70 mmol), K_2CO_3 (0.43 g, 3.08 mmol), and 18-crown-6 (0.04 g, 0.15 mmol) in acetone (60 mL) was heated at reflux for 48 h. Filtration and rotary evaporation of the organic solvent afforded the crude product, which was stirred with MeOH for several hours. Drying under vacuum at 40 °C gave the final product as a viscous oil. Yield 2.01 g (96%). ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): δ = 0.86 (t, 12 H), 1.25–1.43 (two m, 72 H), 1.76 (m, 8 H), 3.93 (t, 8 H), 4.97 (s, 4 H), 5.07 (s, 2 H), 6.4 (d, 2 H), 6.56 (m, 3 H), 6.7 (d, 2 H), 7.08 (d, 2 H), 7.35 (t, 2 H), 7.86–7.88 (m, 4 H), 8.66 (d, 2 H), 8.71–8.75 (m, 4 H) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$, TMS): δ = 14.32, 22.97, 26.40, 29.64–29.93, 32.23, 68.56, 70.60, 70.70, 101.49, 102.32, 106.26, 106.88, 115.77, 118.73, 121.70, 123.99, 128.87, 131.25, 137.09, 139.41, 149.44, 152.30, 156.30, 156.89, 160.08, 160.68, 160.98 ppm.

Monocomplex 7: A solution of uncomplexed G$_2$-dendron-tpy (0.5233 g, 0.3840 mmol), $RuCl_3\cdot xH_2O$ (0.0836 g, 0.4031 mmol), THF (5 mL), and EtOH (15 mL) was heated at reflux for 24 h. After cooling to room temperature the solvent was reduced to almost half its volume and the resulting mixture was filtered, washed with EtOH and cold acetone, and dried under vacuum, affording monocomplex **7** as a brown powder, which was used without further purification. Yield 0.47 g (78.3%).

General Polymerization Procedure: A carefully degassed mixture of diol **5** (0.200 g, 0.210 mmol), α,ω-aliphatic dibromide (x = 11, 0.066 g, 0.210 mmol; x = 12: 0.070 g, 0.210 mmol), TBAH (0.029 g, 0.085 mmol), *o*-DCB (2 mL), and NaOH (10 N, 1 mL) was vigorously stirred at 120 °C under a continuous stream of argon for 5 days. The resulting mixture was diluted with $CHCl_3$ and precipitated from a tenfold amount of MeOH, filtered, redisolved in $CHCl_3$, filtered once more in order to remove any traces of salt, and precipitated in MeOH or film-cast to produce the final polymeric material in powder or film form. Elemental analyses for

PETH-*x=12(i)*: $C_{74}H_{66}O_4N_6$ (1102): calcd. C 80.58, H 5.99, N 7.62; found C 80.78, H 5.77, N 7.25.

PETH-*x=11(i)*: $C_{73}H_{64}N_6O_4$ (1088): calcd. C 80.51, H 5.88, N 7.72; found C 80.74, H 5.85, N 7.31.

PETH-*x=12(i)*: ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): δ = 1.26 (broad, 12 H), 1.43 (m, 4 H), 1.77 (m, 4 H), 3.97 (t, 4 H), 5.05 (m, 4 H), 6.93–7 (two d, 8 H), 7.31 (m, 4 H), 7.38 (d, 4 H), 7.63 (s, 2 H), 7.8–7.85 (m, 8 H), 8.6–8.71 (m, 12 H) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$, TMS): δ = 26.02, 29.31–29.55, 68.11, 68.30, 114.43, 115.29, 118.29, 121.32, 123.69, 128.48, 130.33, 131.00, 131.31, 132.01, 133.79, 136.76, 140.73, 149.07, 149.73, 155.82, 156.38, 158.75, 159.52 ppm.

Dendronized Polymeric Complexes Ia and Ib: A solution of polymeric material [**PETH-*x=11(i)***: 0.0200 g, 0.0184 mmol, or **PETH-*x=12(i)***: 0.0200 g, 0.0181 mmol], monocomplex **7** (0.1155 g, 0.0735 mmol or 0.1140 g, 0.0726 mmol, respectively), $CHCl_3$ (8 mL), EtOH (3 mL), and *N*-ethylmorpholine (10 drops) was heated at reflux for 5 days. The resulting deep red solution was filtered through celite and the desired polymeric complex **Ia** or **Ib** was obtained after precipitation with addition of excess saturated NH_4PF_6/MeOH solution, filtration, and washing with EtOH, H_2O, and diethyl ether. Yield 0.0420 g for **Ia** and 0.0376 g for **Ib** (50% and 45%, respectively). Dendronized polymeric complex **Ia**: ^{1}H NMR (400 MHz, 80 °C, [D$_6$]DMSO, TMS): δ = 0.84 (t, 24 H), 1.25 (broad, 158 H), 1.69 (m, 20 H), 3.96 (m, 20 H), 5.05 (s, 8 H), 5.25 (m, 8 H), 6.41 (s, 4 H), 6.58 (s, 10 H), 6.79 (s, 4 H), 7.1 (b, 4 H), 7.27–7.5 (broad, 28 H), 7.7 (s, 2 H), 8.02 (m, 8 H), 8.37 (m, 8 H), 9.03 (m, 8 H), 9.34 (s, 8 H) ppm. ^{13}C NMR (100 MHz, 80 °C, [D$_6$]DMSO, TMS): δ = 13.62, 21.96, 25.36, 28.59–28.9, 31.17, 67.26, 69.05, 100.01, 101.00, 105.52, 106.62, 114.28, 115.30, 120.14, 124.54, 127.52, 129.02, 130.09, 131.84, 137.76, 138.97, 146.50, 152.10, 154.8, 157.99, 159.37, 159.74, 160.02 ppm.

Dicomplex II: A mixture of diol **5** (20.0 mg), monocomplex **7** (100.7 mg), THF (15 mL), EtOH (5 mL), and *N*-ethylmorpholine (5 drops) was heated at reflux for 48 h. After cooling to room temperature the deep red solution was filtered from celite and the solvent was reduced to almost half its volume. Addition of excess saturated NH_4PF_6/MeOH solution caused the complex to precipitate as a red powder, which was filtered and washed with EtOH, H_2O, *n*-hexane, and cold diethyl ether. Yield 57 mg (60%). ^{1}H NMR (400 MHz, 80 °C, [D$_6$]DMSO, TMS): δ = 0.84 (t, 24 H), 1.24–1.4 (two m, 144 H), 1.70 (m, 16 H), 3.95 (t, 16 H), 5.05 (s, 8 H), 5.25 (two s, 8 H), 6.41 (s, 4 H), 6.58 (s, 8 H), 6.66 (s, 2 H), 6.78 (s, 4 H), 6.93 (d, 4 H), 7.27 (m, 12 H), 7.37 (t, 8 H), 7.5 (broad, 8 H), 7.65 (s, 2 H), 8.03 (t, 8 H), 8.37 (d, 8 H), 9.03 (d, 8 H), 9.35 (s, 8 H) ppm. ^{13}C NMR (100 MHz, 80 °C, [D$_6$]DMSO, TMS): δ = 13.78, 21.96, 25.37, 28.59–29.65, 31.16, 67.36, 67.90, 69.12, 69.20, 100.14, 101.09, 105.70, 106.69, 115.16, 115.37, 115.53, 120.25, 124.69, 127.55, 129.06, 129.10, 130.12, 131.37, 133.49, 137.84, 139.11, 146.52, 152.04 (broad), 154.87, 156.97, 158.03, 159.42, 159.81, 160.05 ppm. $C_{242}H_{302}F_{24}N_{12}O_{18}P_4Ru_2$ (4444): calcd. C 65.35, H 6.8, N 3.78; found C 65.70, H 6.11, N 3.43.

Model Compound M: A carefully degassed mixture of diol **5** (0.11 g, 0.12 mmol), dodecyl bromide $C_{12}H_{25}Br$ (0.117 g, 0.47 mmol), TBAH (0.016 g, 0.047 mmol), *o*-DCB (1.5 mL), and NaOH (10 N, 1 mL) was vigorously stirred at 120 °C under a continuous stream of argon for 24 h. The resulting mixture was diluted with $CHCl_3$ and precipitated from a tenfold amount of MeOH, filtered, redissolved in $CHCl_3$, filtered once more in order to remove any traces of salt, and precipitated from MeOH. The model didodecyloxy end-functionalized diol, **M**, was obtained as a yellowish powder. Yield 0.126 g (84.3%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): δ = 0.87 (t, 6 H), 1.25 (m, 32 H), 1.46 (m, 4 H), 1.8 (m, 4 H), 3.99 (t, 4 H), 6.96 (d, 4 H), 7.01 (d, 4 H), 7.35 (dd, 4 H), 7.39 (d, 4 H), 7.64 (s, 2 H), 7.84 (d, 4 H), 7.89 (m, 4 H), 8.66 (d, 4 H), 8.7 (s, 4 H), 8.74 (d, 4 H) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$, TMS): δ = 14.32, 22.96, 26.41, 29.62–29.9, 32.21, 68.55, 68.6, 114.86, 115.76, 118.72, 121.65, 123.95, 128.83, 130.67, 131.52, 131.53, 132.48, 132.51, 137.03, 141.2, 149.44, 150.16, 156.27, 156.89, 159.18, 159.97 ppm.

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