Macromolecules **1997,** *30,* 6185−6193

High-Molecular-Weight Ruthenium(II) Coordination Polymers: Synthesis and Solution Properties

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Received February 28, 1997; Revised Manuscript Received July 2, 1997[⊗]

ABSTRACT: A synthetic strategy is presented that allows the preparation of high-molecular-weight ruthenium(II) coordination polymers **1a,b** of homogeneous molecular constitution. The key to this success was the development of an efficient procedure leading to highly pure "metal monomers" $[Ru(R_2bpy)Cl_3]_x$ (**3a,b**) with (**b**: $R = C_6H_5$) and without (**a**: R = H) lateral phenyl substituents. Their conversion with equimolar quantities of "ligand monomer" tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (**2**) gave excellently soluble ruthenium(II) coordination polymers **1a** and **1b**, respectively, the molecular constitution of which was proven with high-resolution ^{1}H and ^{13}C NMR spectroscopy. The degrees of polymerization were estimated to be $P_n \geq 30$ because of the complete lack of end group absorptions in the NMR spectra. This estimate could be verified by small-angle X-ray scattering (SAXS) for the phenyl-substituted polymer **1b**: according to these investigations, the molecular weight reaches $M_w \approx 47\,000$, and the radius of gyration was found to be $R_G = 8.4$ nm. The intrinsic viscosities of high-molecular-weight polymers **1a** and **1b** were found to be $[\eta] \approx 12$ mL·g^{-1} for both polymers (0.01 M NaCl/DMA). At low ionic strengths, on the other hand, the unsubstituted polymer **1a** displays a much more pronounced polyelectrolyte effect in solvents like ethanol/water than the phenyl-substituted polymer **1b** of similar P_n. Considering all these results, the surprisingly high solubility of the conformationally rigid, ribbonlike polyelectrolytes **1a** and **1b** can be considered to be the result of (i) the coiled shape of the polymers, (ii) the intermolecular Coulomb repulsion and, in the case of the phenyl-substituted polymer **1b**, (iii) the laterally-attached phenyl substituents.

Introduction

Multinuclear transition metal complexes interconnected by rigid bridging ligands to give supramolecular assemblies of well-defined architecture represent key compounds for the profound understanding of energy- and electron-transfer processes occurring in organometallic compounds.[1] Moreover, such macromolecules are objects of increasing interest because of, for example, their liquid-crystalline phase behavior[2] and their solution properties.[3] Also, these systems might develop into materials of considerable practical importance because of their magnetic, electronic, and photooptical properties.[1] Concerning most of these aspects, ruthenium(II) complexes could play a key role since they combine considerable thermal, chemical, and photochemical stability with advantageous electronic properties. Therefore, an enormous variety of monomeric and oligomeric ruthenium complexes has been synthesized and analyzed during recent years.[1,4] Nevertheless, soluble, constitutionally well-defined and really high-molecular-weight ruthenium(II) coordination polymers are not available so far. This is rather surprising because it is these multinuclear complexes that might have an immense value for some of the above purposes like the elucidation of the solution properties of polyelectrolytes:[5−7] ruthenium(II) coordination polymers designed in a way that they represent rigid rods, helices, or coils might enable studies unaffected by conformative effects. Hence, in order to take advantage of their potential it is essential to develop efficient synthetic routes for the preparation of high-molecular-weight ruthenium(II) coordination polymers of homogeneous constitution. In addition to that, the full characterization of the obtained polymers is necessary to reliably determine all the molecular parameters like chain constitution, average molecular weight, conformation, and stability of these macromolecules held together only by coordinative bonds. While the proof of constitution and stability should easily be possible for these diamagnetic polymers with established methods like high-resolution NMR spectroscopy, the direct determination of molecular weights and chain conformation might be more complicated: osmotic measurements, for example, are aggravated because these polymers represent polyelectrolytes, and light scattering might be difficult because of the strong metal-to-ligand charge transfer (MLCT) bands absorbing in the visible range. Small-angle X-ray scattering (SAXS), on the other hand, might be the method of choice for this purpose because of the considerable difference in electron density between organometallic polymer and organic solvent. However, to the best knowledge of the authors, it has never been applied before to the molecular characterization of coordination polymers.

Recently, we were able to show that the conversion of tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (tppz) (**2**) with the ruthenium monomer $[Ru(bpy)Cl_3]_x$ (**3a**) (bpy = 2,2′-bipyridine) gives constitutionally homogeneous coordination polymers **1a** (eq 1).[8] Their excellent solubility in polar solvents permitted proof of their constitution and estimation of the degree of polymerization (P_n) achieved using NMR spectroscopy. While the constitution of **1a** could be shown to be highly regular, the P_n was still rather low ($P_n \approx 10-15$) and thus insufficient for a profound analysis of chain conformation or solution properties. To find out the reason for the limited P_n, model experiments were carried out that finally led to the conclusion that an impurity in the metal monomer **3a** was responsible for the rather low values of P_n achieved so far: when prepared according to the literature,[9] **3a** contains 5−10% ruthenium ions coordinated by two bpy ligands instead of only one. These latter ruthenium centers act as monofunctional species and

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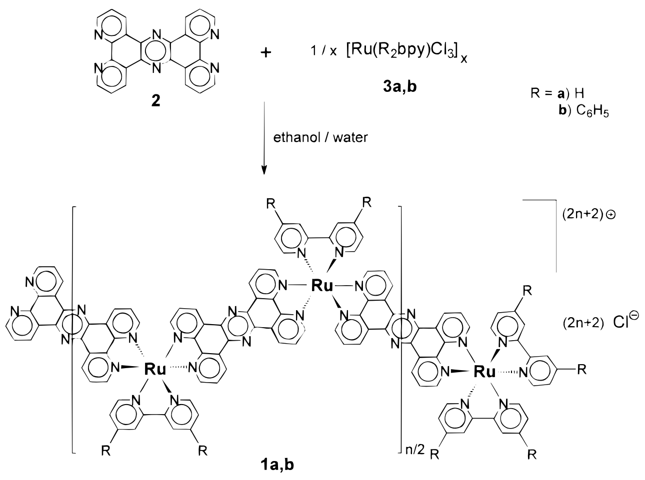
[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S0024-9297(97)00281-7 CCC: $14.00



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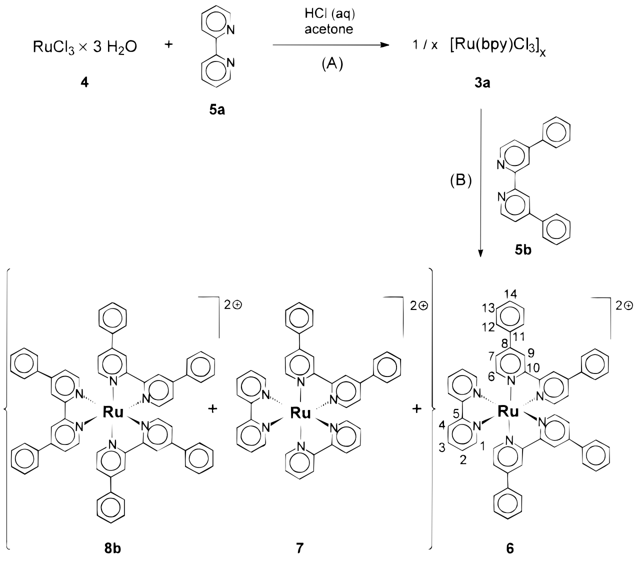
thus as end groups, in the subsequent polymerization, causing the observed limitation of the P_n. Unfortunately, purification of **3a** proved to be impossible due to the fact that $[Ru(bpy)Cl_3]_x$ (**3a**) itself exhibits a polymeric constitution, containing $[Ru(bpy)_2]^{z+}$ complexes ($z = 2$ or 3) as either end groups or defects. The only way to further increase the P_n of polymers **1** was thus to already minimize the formation of these latter defects in the course of the monomer synthesis.

In the present paper, we now describe an optimized procedure for the synthesis of highly homogeneous ruthenium monomer **3a**. Additionally, we show that coordination polymers **1a** of appreciable P_n are available through polymerization of this pure monomer **3a**. Moreover, we broadened the scope of the presented synthetic strategy as we developed appropriate conditions for the preparation of the corresponding phenyl-substituted metal monomer **3b**. By its polymerization we showed that the additional phenyl substitutents attached to the 4,4′-position of the bpy ligands dramatically increase the solubility of the coordination polymer **1b** in organic solvents without simultaneously affecting the reactivity of monomer **3b** for steric or electronic reasons. Finally, we describe the first studies concerning the solution properties of the novel coordination polymers **1a** and **1b**, performed by viscosimetry in salt-free and salt-containing solutions.

Results and Discussion

Monomer Synthesis. The development of appropriate conditions for the preparation of $[Ru(bpy)Cl_3]_x$ (**3a**), and thus of a procedure that allows the efficient suppression of the formation of $[Ru(bpy)_2]^{z+}$ defects, was the central task of the present work. In systematic studies, therefore, the conversion **4** + **5a** → **3a** was investigated (eq 2, step A). All accessible reaction parameters were varied such as solvent, temperature, concentration, and reaction time to improve the homogeneity of the reaction. As the complexes **3a** cannot be analyzed directly with NMR spectroscopy, the purity of the products obtained under the respective conditions was determined by following their conversion with 4,4′-diphenyl-2,2′-bipyridine (**5b**) according to step B in eq 2. ^1H NMR spectra were recorded of representative samples of the complexes thus formed, which now permitted clear distinction of the absorptions of the main product **6** from those of side products like **7** or **8b**, caused by the $[Ru(bpy)_2]^{z+}$ defects and unreacted $RuCl_3{\cdot}3H_2O$, respectively, in monomer **3a**.

These studies finally led to the conclusion that highly pure $[Ru(bpy)Cl_3]_x$ (**3a**) is available when, in contrast



(2)

to the literature,[9] only 0.35 M hydrochloric acid is used as the reaction medium, together with acetone as the cosolvent. The highest purities were achieved when the solution of **5a** was added extremely slowly (within about 10 h; syringe pump) to the solution of $RuCl_3{\cdot}3H_2O$ (**4**) in aqueous 0.35 M hydrochloric acid. Under these conditions, formation of $[Ru(bpy)_2]^{z+}$ centers can be suppressed almost completely. Figure 1A displays the ^1H NMR spectrum of a representative product mixture obtained according to eq 2B, using monomer **3a** prepared under optimized conditions. For comparison purposes, the insert (Figure 1B) shows the 9 ppm region of a corresponding spectrum characteristic for monomers **3a** that were prepared without a syringe pump (ligand addition to $RuCl_3{\cdot}3H_2O$ within about 1 h).

In spectrum A, no evidence is found for the presence of $[Ru(bpy)_2]^{z+}$ defects or unreacted $RuCl_3{\cdot}3H_2O$ (**4**) in monomer **3a**, as is shown by the complete lack of absorptions at, for example, $\delta = 8.92$ and 8.98 ppm: only the intensive absorptions of model complex **6** are observed. On the other hand, when **3a** was prepared in the same reaction system but without using a syringe pump, a less homogeneous material **3a** was formed: in Figure 1B, small additional absorptions can be detected at $\delta = 8.92$ $\{[Ru(bpy)_2((C_6H_5)_2bpy)]^{2+}$ (**7**)$\}$ and 8.98 ppm $\{[Ru((C_6H_5)_2bpy)_3]^{2+}$ (**8b**)$\}$, in addition to the strong absorption of $[Ru(bpy)((C_6H_5)_2bpy)_2]^{2+}$ (**6**) at $\delta = 8.95$ ppm. Thus, $[Ru(bpy)_2]^{z+}$ defects and traces of unreacted $RuCl_3{\cdot}3H_2O$ (**4**) were present in this latter monomer **3a**. Since both impurities must be avoided—$[Ru(bpy)_2]^{z+}$ forms end groups, and $RuCl_3{\cdot}3H_2O$ (**4**) represents a trivalent monomer in the present system, causing branches and/or cross-links—the syringe pump technique was applied in all subsequent monomer syntheses. The purity of the best monomers **3a** obtained so far was estimated to be higher than 98% because no evidence can be found any more of complexes like **7** or **8b** in the NMR spectra recorded after model conversion according to step B of eq 2.

After the development of reaction conditions appropriate to the preparation of the highly pure unsubstituted monomer **3a**, the synthesis of the corresponding phenyl-substituted complex $[Ru((C_6H_5)_2bpy)Cl_3]$ (**3b**) from $RuCl_3{\cdot}3H_2O$ (**4**) and 4,4′-diphenyl-2,2′-bipyridine (**5b**) was studied as well to make available this monomer in adequate purities for the preparation of high-molecular-weight coordination polymers **1b**. We succeeded in this by application of reaction conditions nearly

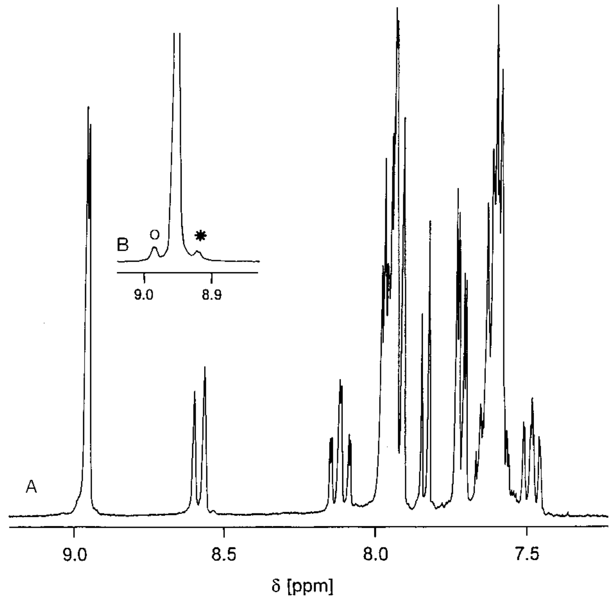
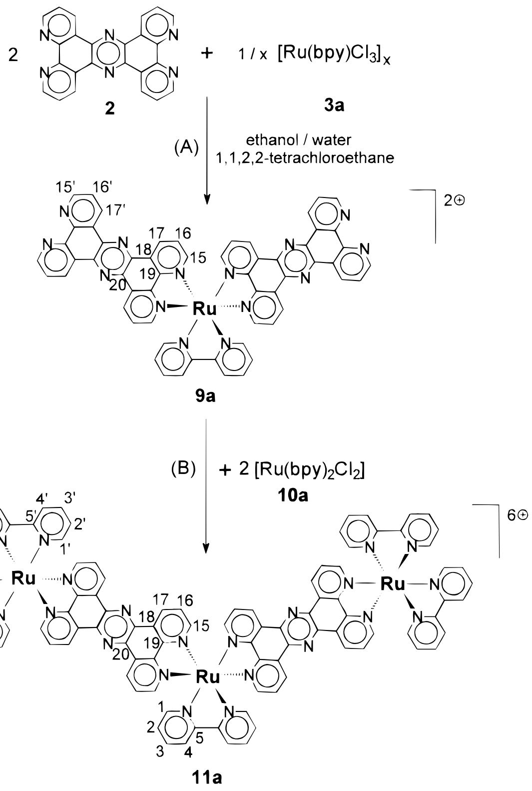


Figure 1. Aromatic regions of the ^{1}H NMR spectra of representative product mixtures obtained from model conversions of **3a** according to eq 2, step B, recorded in CD_3CN at room temperature. All intensive absorptions correspond to complex $[Ru(bpy)(dphbpy)_2]Cl_2$ (**6**). Other signals correspond to the side products $[Ru(bpy)_2(dphbpy)]Cl_2$ (**7**) (*) and $[Ru(dphbpy)_3]Cl_2$ (**8b**) (○). For details, see text.



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identical to those applied to monomer **3a**. Only a slight modification of the solvent mixture used was required to meet the lower solubility of 4,4′-diphenyl-2,2′-bipyridine **5b** in dilute hydrochloric acid (for details, see: Experimental Section). The purity of **3b** thus obtained was determined again with NMR spectroscopy after model conversion with 2,2′-bipyridine (**5a**) in analogy to eq 2. These model experiments led to $[Ru(C_6H_5)_2\text{-}bpy)(bpy)_2]^{2+}$ (**7**) as the main product and showed **3b** to have purities of >98%.

Model Studies. Prior to polymerization experiments, a number of model investigations were performed in order (i) to make available NMR spectra of ruthenium complexes required for the full assignment of all the end group absorptions that might be observable in the spectra of polymers **1a** and **1b** and (ii) to gain a more profound knowledge of the thermal and photochemical stability of the ruthenium complexes used here. Mononuclear and trinuclear complexes **9** and **11**, respectively, were selected as the model compounds for the first aim (see eq 3 for **a**: R = H). While complexes **9** represented the reference systems for terminal tppz ligands (left end group of polymer **1** in eq 1), the trinuclear complexes **11** were required for the $[Ru(bpy)_2]^{2+}$-terminated chain ends (right end group of polymer **1** in eq 1).

The mononuclear complexes $[Ru(R_2bpy)(tppz)_2]Cl_2$ (**9a,b**) (R = (**a**) H, (**b**) C_6H_5) were prepared via the conversion of 1 equiv of $[Ru(R_2bpy)Cl_3]_x$ (**3a,b**) with 2 equiv of tppz **2**. As tppz **2** is insoluble in ethanol/water, it was predissolved in a small volume of 1,1,2,2-tetrachloroethane and the solution of complex **3a** or **3b** in ethanol/water was then added with a syringe pump. Under these conditions, the competitive oligomerization could be suppressed, and pure mononuclear complexes **9a** and **9b** were obtained. Unfortunately, the products proved to be nearly insoluble in all solvents tested, and well-resolved NMR spectra could not be obtained. Only broad absorptions were found in the ^{1}H NMR spectra even when recorded at a very high dilution. Nevertheless, the obtained spectra were of significance because they showed that the protons H15′ of complexes **9**—and thus also tppz termini of coordination polymers **1a** or **1b**, if present in a substantial amount—absorb at δ = 9.6 and 9.7 ppm (Figure 2B) and thus at chemical shifts where no signal of the inner-chain repeat units of coordination polymers **1** appears.[8] Therefore, such end groups of **1** were now recognized to be readily detectable by ^{1}H NMR spectroscopy.

For the preparation of **11**, complexes **9** were treated with 2 equiv of $[Ru(R_2bpy)_2Cl_2]$ (**10**) in ethanol/water (eq 3, step B for **a**, R = H). Readily soluble, trinuclear complexes **11** were obtained, which, on the one hand, subsequently proved the correct molecular constitution of the nearly insoluble mononuclear complexes **9** not fully characterized before: chemical shifts as well as signal intensities were in full agreement with the constitution of **11**. On the other hand, complexes **11** proved to be appropriate model compounds for $[Ru(R_2\text{-}bpy)_2]^{z+}$ termini of polymers **1a** and **1b**. Absorptions at δ = 7.2, 7.5, and 7.8 ppm were found to be characteristic for polymers **1a** with a substantial amount of terminal $[Ru(bpy)_2]^{2+}$ complexes, while the corresponding $[Ru((C_6H_5)_2bpy)_2]^{2+}$ termini of the phenyl-substituted polymer **1b** could now be expected to appear at δ = 7.8 and 7.9 ppm. Figure 2A shows the ^{1}H NMR spectrum of product **11a** as a representative example.

The second aim of the model investigations was to reconfirm the exceptional stability of the ruthenium complexes under consideration here toward competitive ligands, thermal load, or irradiation. Despite the fact that the excellent stability of ruthenium(II)–polyimine complexes is well-known,[1,4] additional proof of complex stability was considered to be necessary with regard to the planned synthesis of very high-molecular-weight coordination polymers **1**: even if side reactions like ligand exchange occurred to a very small extent, they would destroy an originally homogeneous constitution of a coordination polymer **1** and thus considerably affect its properties. Therefore, mononuclear complexes like

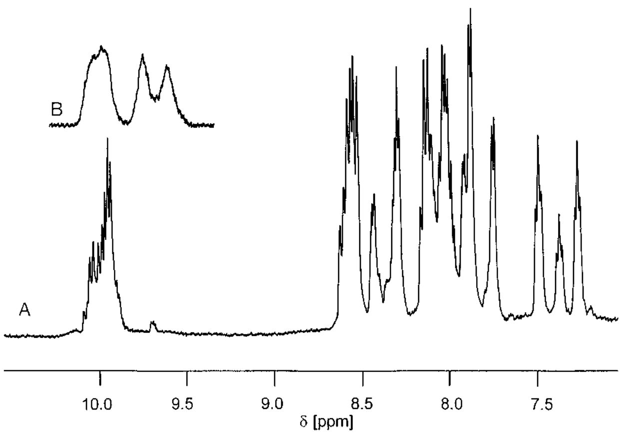
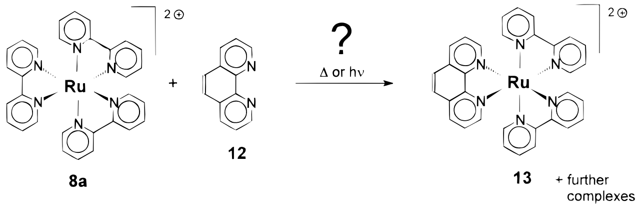


Figure 2. Aromatic regions of the ^{1}H NMR spectra of model complexes **11a** (A) and **9a** (B) prepared according to eq 3, recorded in CD_3CN at room temperature.

$[Ru(bpy)_3]Cl_2$ (**8a**) were dissolved together with the 10-fold excess of a free chelating ligand like *o*-phenanthroline (**12**) in different solvents and solvent mixtures and then heated or irradiated for 24 h. The resulting solutions were analyzed using NMR spectroscopy. If a ligand exchange occurred according to eq 4, it should be easily detectable by this technique. However, it was clearly evident that a thermally induced ligand exchange occurred in none of the solvents and solvent mixtures tested. In ethanol/water, for example, which is the reaction medium for the subsequent polymerizations, not even traces of complexes like **13** were found. Exposure to daylight, even over weeks, forced neither a detectable ligand exchange nor other side reactions. Only irradiation with a mercury lamp caused ligand exchange and further unidentified side reactions (10–20%, depending on the solvent). Identical results were obtained when the model experiments were repeated with mixtures of two different ruthenium complexes like **8a** and **14** (eq 5). Here, as well, only the irradiation with a mercury lamp caused decomposition. These experiments thus clearly proved the exceptional stability of the ruthenium complexes under all possible conditions the coordination polymers **1** might be subjected to during their synthesis and characterization.



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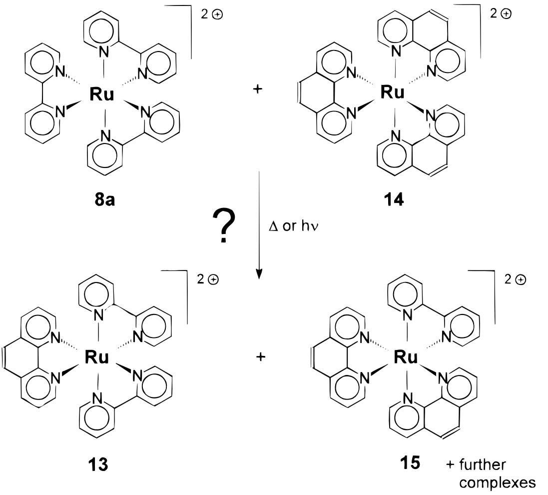

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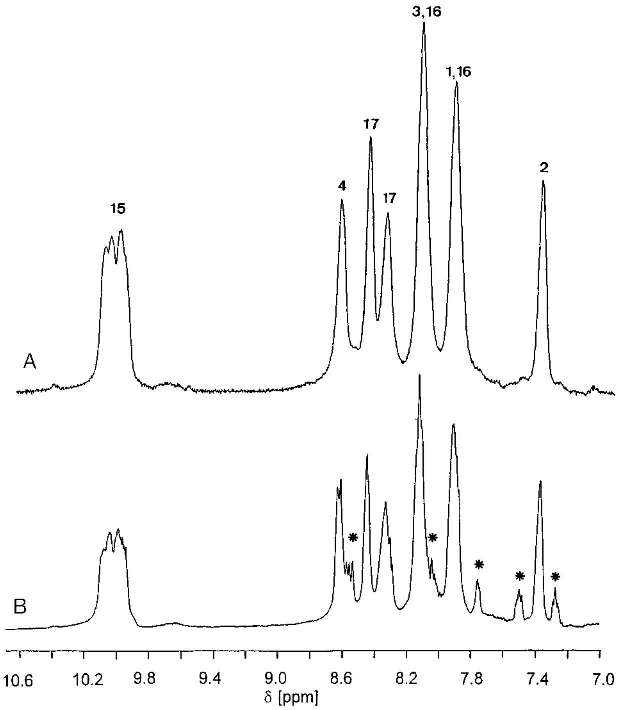

Figure 3. Aromatic regions of the ^{1}H NMR spectra of (A) high-molecular-weight polymer **1a** and (B) the corresponding oligomer **1a**, having $[Ru(bpy)_2]^{2+}$ end groups (*), recorded in CD_3CN at room temperature. For details, see text.

Polymer Syntheses. The primary task of the subsequent polymerizations was to show (i) that the highly pure metal monomers **3a,b** now available indeed form constitutionally homogeneous coordination polymers **1a,b** of high molecular weight and (ii) that even polymers **1a,b** with a very high P_n remain soluble, and thus accessible to a full characterization. Starting with the unsubstituted coordination polymer **1a**, exactly equimolar amounts of pure metal monomer **3a** and ligand monomer tppz (**2**) were polymerized in the usual solvent mixture of ethanol and water (eq 1). After 12 h, a small volume of 4-ethylmorpholine was added to reduce all ruthenium centers to the diamagnetic ruthenium(II). Subsequently, polymers **1a** were precipitated quantitatively from the homogeneous reaction mixtures, either as hexafluorophosphates by adding aqueous NH_4PF_6 solutions or as chlorides by adding acetone. As hexafluorophosphates, the obtained brownish-black solids could be redissolved in acetonitrile, ethanol, or dimethylacetamide (DMA) easily and completely. The chlorides, on the other hand, were soluble even in pure water. Figure 3A displays a characteristic ^{1}H NMR spectrum of the polymers **1a** obtained under the above conditions. All observed absorptions can be assigned unambiguously to inner-chain repeat units of a constitutionally homogeneous product **1a**. In clear contrast to all spectra obtained so far, spectrum A does not contain any absorption of $[Ru(bpy)_2]^{2+}$ end groups (δ = 7.2, 7.5, and 7.8 ppm), only a very weak signal that might result from terminal tppz ligands (δ = 9.6 and 9.7 ppm). The same is valid for the ^{13}C NMR spectra: there, as well, only the characteristic absorptions of the inner-chain repeat units were found (Figure 4).

When, on the other hand, polymerizations were carried out in which either 10% of monomer **3a** was

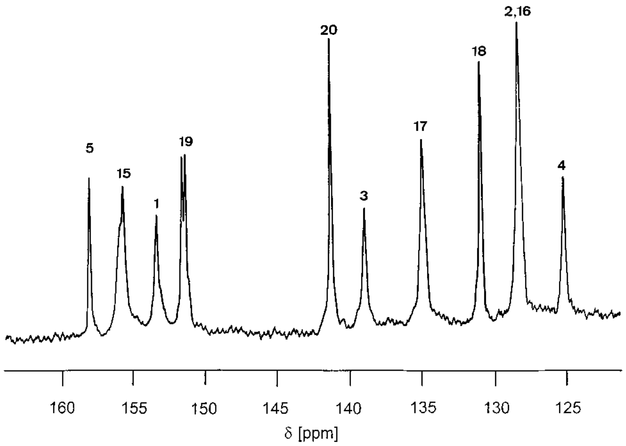

Figure 4. Aromatic region of the ^{13}C NMR spectrum of high-molecular-weight coordination polymer **1a**, recorded in CD_3CN at room temperature.

replaced by an equivalent quantity of $[Ru(bpy)_2Cl_2]$ (**10a**) or a 10% excess of ligand monomer **2** was used, oligomers **1a** were obtained whose NMR spectra clearly showed absorptions of $[Ru(bpy)_2]^{2+}$ (Figure 3B) and tppz (not shown) end groups, respectively. Moreover, Figure 3B is practically identical to those spectra recorded previously[8] from polymers **1a** synthesized using metal monomer **3a** prepared according to the literature.[9] Thus, the experiments performed here constitute further proof of the final conclusion of our foregoing paper[8] that $[Ru(bpy)_2]^{z+}$ defects in **3a** are responsible for the limitation of P_n, rather than another unidentified side reaction. Moreover, because end groups can be excluded now within the limits of accuracy of the NMR method for all polymers **1a** prepared from exactly equimolar amounts of monomers **2** and **3a**, their average degrees of polymerization were estimated to be higher than $P_{n(NMR)} \approx 30$ ($M_n \approx 30\,000$). This estimate corresponds to more than triple the values of P_n achieved hitherto using conventionally prepared ruthenium monomer **3a**. The present experiments also show that the unsubstituted polymers **1a** remain excellently soluble even if their molecular weights are increased significantly.

Now, we also tried to prepare the phenyl-substituted coordination polymer **1b**. According to eq 1, exactly equimolar amounts of $[Ru((C_6H_5)_2bpy)Cl_3]_x$ (**3b**) and tppz (**2**) were polymerized under the same conditions as used before for the unsubstituted parent polymer **1a**. Moreover, oligomers **1b** having either $[Ru((C_6H_5)_2bpy)_2]^{2+}$ or tppz termini were prepared in analogy to the procedures used for the synthesis of oligomers **1a** (see above). The formed polymers **1b** were finally precipitated from the homogeneous reaction mixtures either as hexafluorophosphates (by addition of NH_4PF_6) or as chlorides (by addition of water). The brownish-black solids could be redissolved in acetonitrile or DMA (as hexafluorophosphates) or, when chloride was the counterion, in solvents like ethanol or ethanol/water. Figure 5A displays the ^1H NMR spectrum of a coordination polymer **1b** prepared at precise 1:1 stoichiometry of **2** and **3b**; Figure 5B, the corresponding spectrum of an oligomer **1b** ($P_n \approx 10$) having $[Ru((C_6H_5)_2bpy)_2]^{2+}$ end groups.

In spectrum A, all absorptions can be assigned unambiguously to the inner-chain repeat units of a constitutionally homogeneous coordination polymer **1b**. No absorptions are detectable that point toward chain end groups or constitutional defects. In contrast to this, spectrum B as well as all spectra recorded from polymers **1b** with tppz termini (not shown) clearly exhibit absorptions of the respective chain termini. Since it was obvious (a) that both possible end groups are clearly detectable using NMR spectroscopy, also in the case of polymer **1b**, and (b) that such absorptions were absent in all spectra of polymers **1b** prepared at precise 1:1 stoichiometry of **2** and **3b**, it was clearly evident that the polymerizations using the phenyl-substituted monomer **3b** also occur highly selectively and quantitatively, leading to constitutionally homogeneous polymers **1b** of high molecular weights ($P_{n(NMR)} \geq 30$). This assumption was additionally verified by SAXS investigations (see below).

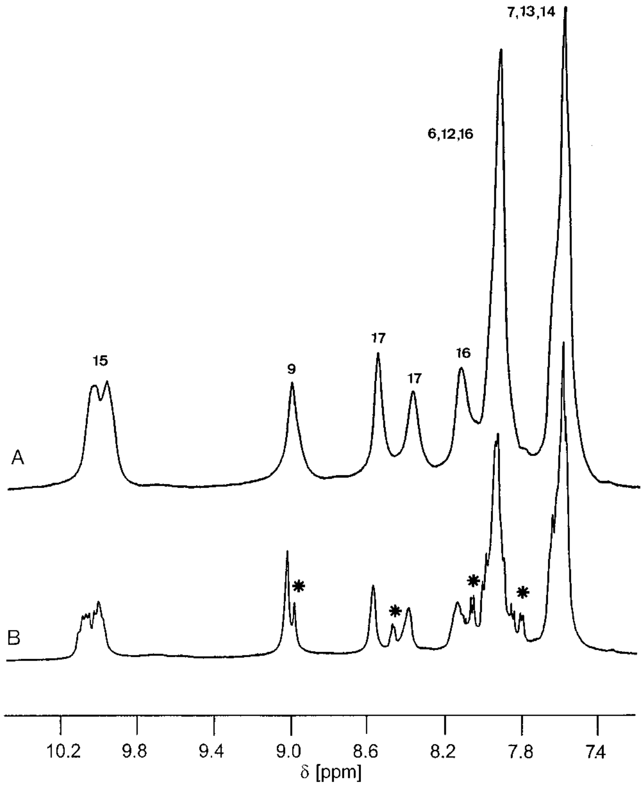

Figure 5. Aromatic regions of the ^1H NMR spectra of (A) high-molecular-weight polymer **1b** and (B) the corresponding oligomer **1b**, having $[Ru(dphbpy)_2]^{2+}$ end groups (*), recorded in CD_3CN at room temperature. For details, see text.

Finally, the above model studies concerning the thermal and photochemical stability of the ruthenium complexes were verified for the high-molecular-weight polymers **1**. As expected, no changes were found in the NMR spectra of these polymers neither after heating nor after exposing the polymer solutions to daylight over weeks. Also, no insoluble material was formed due to cross-linking.

Solution Properties. The readily soluble, high-molecular-weight ruthenium(II) coordination polymers **1a** and **1b** now available allowed systematic studies of the solution properties of such macromolecules. All viscosity experiments performed so far were carried out in ethanol/water or dimethylacetamide (DMA) solution, with or without addition of foreign salt. Throughout, high-molecular-weight samples of coordination polymer **1a** gave a pronounced polyelectrolyte effect,[5-7] *i.e.*, a drastic increase of the reduced specific viscosity, η_{sp}/c_P, at decreasing polymer concentration, c_P, when measurements were performed without added salt and thus at low ionic strengths. The values of η_{sp}/c_P only decreased again at very low polymer concentrations. As an example, Figure 6 displays the Huggins plots of (a) the high-molecular-weight polymer **1a** (A; $P_n \geq 30$, ○), and (b) the low-molecular-weight polymer **1a** (B; $P_n \approx 12$,

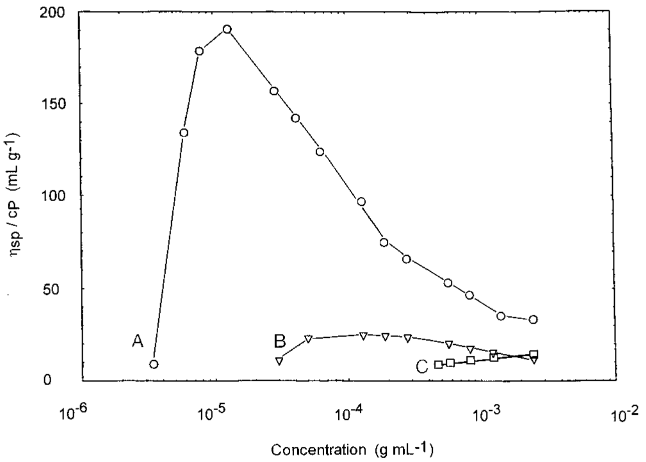

Figure 6. Huggins plots of coordination polymers **1a**: (A) $P_n \geq 30$, salt-free DMA; (B) $P_n \approx 12$, salt-free DMA; (C) $P_n \geq 30$, 0.01 N NaCl/DMA.

▽), both measured in salt-free DMA, and (c) the plot obtained from the high-molecular-weight polymer **1a** in the system 0.01 N NaCl/DMA (C; $P_n \geq 30$, □).

It is obvious that under otherwise identical conditions the high-molecular-weight polymer **1a** displays a much more pronounced polyelectrolyte effect than the low-molecular-weight material (A *vs* B). A maximum of $(\eta_{sp}/c_P)_{max} \approx 200$ mL·g^{-1} is found at $c_P \approx 10^{-5}$ g·mL^{-1} for the high-molecular-weight material (curve A), while in the case of the low-molecular-weight polymer **1a**, this maximum reaches only $(\eta_{sp}/c_P)_{max} \approx 30$ mL·g^{-1} and is found at a polymer concentration higher by 1 order of magnitude ($c_P \approx 1 \times 10^{-4}$ g·mL^{-1}).

In the case of the phenyl-substituted polymer **1b**, on the other hand, the polyelectrolyte effect was found to be much less pronounced than that of unsubstituted polymers **1a** of comparable P_n under the same conditions. Here, the maximum in the Huggins plot reaches only $(\eta_{sp}/c_P)_{max} \approx 60$ mL·g^{-1} and is found at a polymer concentration of about $c_P \approx 2 \times 10^{-4}$ g·mL^{-1} in salt-free DMA solution. Thus, the intermolecular Coulomb interactions are significantly weaker in the case of the phenyl-substituted polymer **1b**. The reason for this difference is not understood up to now.

In the presence of foreign salt, on the other hand, the polyelectrolyte effect disappears in the case of polymers **1a** as well as of polymers **1b** through screening out the intermolecular Coulomb interactions. Linear extrapolation of η_{sp}/c_P was thus possible to $c_P = 0$, and intrinsic viscosities of $[\eta] \approx 12$ mL·g^{-1} were determined for both the high-molecular-weight polymers **1a** and **1b** (Figure 6C). The nearly identical values of $[\eta]$ obtained for **1a** and **1b** prove that these two samples had indeed very similar hydrodynamic volumes, and thus comparable degrees of polymerization, despite their rather different behaviors in salt-free solutions.

Small-angle X-ray scattering was considered to be the method of choice for the direct determination of the molecular weights of the coordination polymers **1**.[10] Unfortunately, the experiments performed on high-molecular-weight coordination polymers **1a** led to the conclusion that their solubility was not sufficiently high in all solvents tested for a detailed SAXS analysis: throughout, the scattering intensities drastically increased at low values of the scattering vector q [$=(4\pi/\lambda)\sin(\theta/2)$], clearly pointing toward the formation of aggregates. Therefore, we tested polymer **1b** as well because we assumed that the phenyl substituents would further increase the solubility of a coordination polymer like **1** in organic media. Here, we succeeded in our efforts because DMA proved to be an excellent solvent for **1b** and no evidence was found any more for aggregation in this solvent, and all the following SAXS investigations performed to determine the molecular weights, M_w, and the radii of gyration, R_G, were performed in ca. 0.01 M NH_4PF_6/DMA solutions.[11] For the highest-molecular-weight polymer **1b** prepared so far, for example, an $M_w \approx 47\,000$ was calculated from the Zimm plot thus obtained. Considering the mass per repeat unit of 1083 g·mol^{-1} of this polymer, this result corresponds to an average degree of polymerization of $P_w \approx 43$. Combination of this result with the number-average degree of polymerization determined using NMR spectroscopy ($P_n \approx 30$) gives, as a first estimate, a polydispersity of $M_w/M_n \approx 1.5$. Finally, the radius of gyration was calculated to be $R_G \approx 8.4$ nm for the polymer sample **1b**.

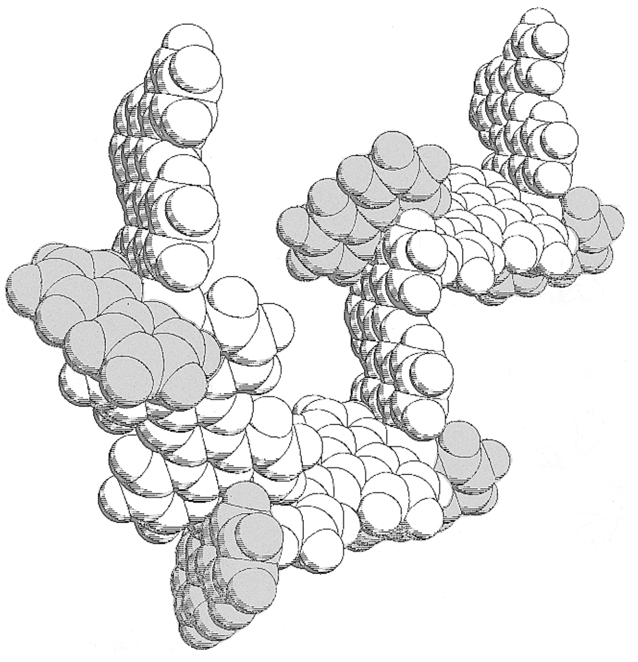

Figure 7. Space-filling molecular model of a chain segment (pentamer) of coordination polymer **1a**. 2,2′-Bipyridine ligands are colored.

Summarizing the information available on this particular polymer sample **1b**, *i.e.*, $M_w \approx 47\,000$, $R_G \approx 8.4$ nm, $[\eta] \approx 12$ mL·g^{-1}, and the length of the conformationally rigid repeat units of about 1.2 nm,[12] it becomes obvious that macromolecules **1** must have a coiled chain conformation with quite closely packed chain segments (Figure 7). This interpretation further supports the initial assumption of random occurrence of the differently configurated, chiral ruthenium(II) complexes (Δ or Λ configuration) along the polymer backbone: their irregular sequence was anticipated[8] because neither steric reasons[13] nor application of enantiomerically pure starting materials[14] could cause stereoselective polymerization and thus a regular and, in general, more elongated chain conformation.

On the other hand, random occurrence of the differently configured complexes along the polymer chain should lead to a much larger number of discrete absorptions in the NMR spectra of polymers **1**, resulting from the different diastereomeric sequences along the chains. However, this is not the case, and we suppose, therefore, that in this particular case, where the multinuclear ruthenium complexes contain tppz **2** as the bridging ligands, the distance between the individual stereo-

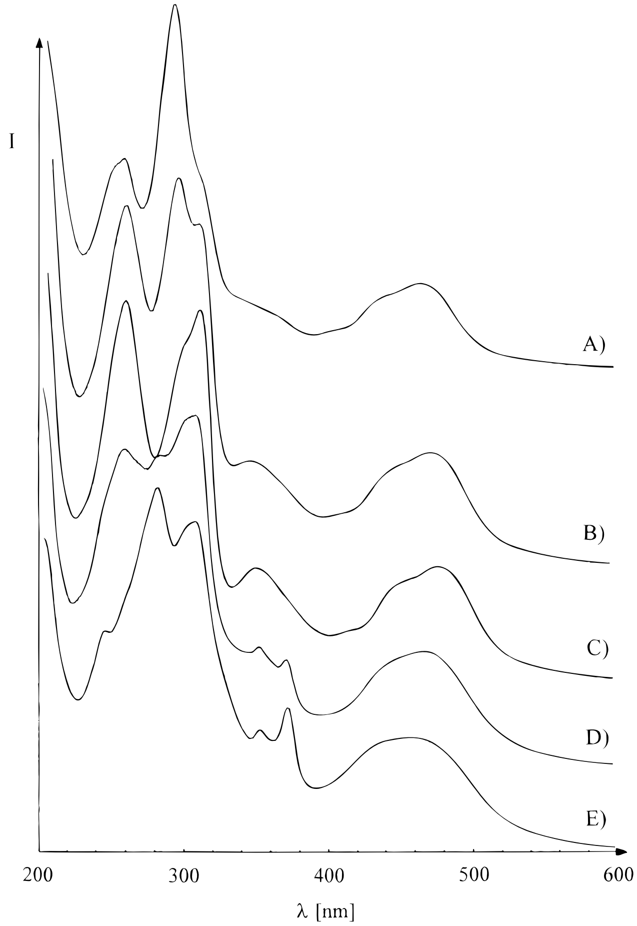

Figure 8. UV−vis absorption spectra of the monomeric complexes **7** (A), **6** (B), and **8b** (C), of the dinuclear model compound $[(C_6H_5bpy)_2Ru(tppz)Ru(C_6H_5)_2](PF_6)_2$ (D),[8] and of polymer **1b** (E), recorded in acetonitrile at room temperature.

centers is too long (>12 Å), not allowing mutual interactions efficiently enough to end up with detectable changes in the chemical shifts in the NMR spectra.

Figure 8 shows the UV−vis absorption spectra of the monomeric complexes **7** (A), **6** (B), and **8b** (C), of the dinuclear model compound $[(C_6H_5bpy)_2Ru(tppz)Ru(C_6H_5)_2](PF_6)_2$ (D),[8] and of polymer **1b** (E). At wavelengths below 400 nm, the absorptions of the ligand-centered (LC) $\pi^* \leftarrow \pi$ transitions were observed as intense signals: absorptions at 280−310 nm were assigned to the 2,2′-bipyridine and the 4,4′-diphenyl-2,2′-bipyridine ligands, and absorptions at 350−370 nm (spectra D and E) to the tetrapyridophenazine ligands. Above 400 nm, absorptions were observed that correspond to metal−ligand charge-transfer (MLCT) transitions. As could be shown earlier for other ruthenium complexes, the wavelengths of all these absorptions are mainly determined by the ligands that are grouped around an individual metal complex.[1,4,8] The same applies to the results of the electrochemical investigations, the detailed results of which will be reported in a subsequent paper and compared with those of related polymers. Thus, absorption spectra as well as electrochemical data show that the ruthenium centers of the multinuclear complexes described here can be considered to be nearly independent of one another: π-electron delocalization and metal−metal interactions seem to be rather weak. This finding is in agreement with observations made with many other coordination compounds of similar constitution.

Conclusions

In the present work it is shown that preparation of readily soluble, constitutionally homogeneous and high-molecular-weight ruthenium(II) coordination polymers **1a** and **1b** is possible through the polymerization of the highly pure metal monomers **3a** or **3b** with tppz **2** as the bridging ligand monomer. The polymers are shown to be very stable against thermal load and UV irradiation. Moreover, these macromolecules, held together only by coordinative bonds, have molecular weights of the order of M_w = 40 000−50 000, as determined by SAXS, and display a more (**1a**) or less (**1b**) pronounced polyelectrolyte effect in polar solvents at low ionic strength. The excellent solubility of the conformationally rigid, ribbonlike coordination polymers **1a** and **1b** is shown to be primarily due to their coillike shape. The latter is caused by the random sequence of Λ and Δ configurated complexes together with the 120° angles that alter the chain direction at each ruthenium center and efficiently prevent the chain segments from assuming an advantageous conformation for crystallization. Moreover, Coulomb interactions as well as the attached phenyl substituents further increase the solubility of polymers **1**. As the synthetic strategy developed here for the preparation of macromolecules like **1a** and **1b** proceeds highly selectively and nearly quantitatively, and because it is well-suited to the preparation of coordination polymers even on the gram scale, the present work is expected to stimulate further investigations of these, and related, coordination polymers regarding, for example, their solution properties or their energy- and electron-transfer characteristics.

Experimental Section

$RuCl_3{\cdot}3H_2O$ (**4**) and $[Ru(bpy)_2Cl_2]$ (**10a**) were purchased from Strem Chemical Co. Other chemicals and solvents were purchased from Aldrich, Fluka, and Lancaster Chemical Co. and used without further purification. 1,10-Phenanthroline-5,6-quinone was prepared according to the literature.[15] NMR spectra were recorded with a Bruker AM 400 NMR spectrometer at 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR). The signal assignment of the absorptions in the ^1H and ^{13}C NMR spectra was carried out according to the numbering given for complexes **6**, **9**, and **11** (eqs 2 and 3, respectively). Viscosity measurements were carried out at 30 °C (±0.1 °C) using Ubbelohde viscosimeters (type 0c, Schott). Flow times of the order of 200 s were measured with an accuracy of ±0.1 s. Every determination of the specific viscosity η_{sp} [$\eta_{sp} = (t - t_o)/t_o$; t and t_o, flow time of solution and solvent, respectively] was repeated at least six times to check the reproducibility. SAXS measurements were performed using a Kratky Kompakt camera with a position-sensitive detector. Details of SAXS measurements are given elsewhere.[16]

Tetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-*h*:2′′′,3′′′-*j*]phenazine (2). 1,10-Phenanthroline-5,6-quinone (5.0 g, 21.9 mmol) and dry ammonium acetate (100 g, 1.3 mol) are heated to 180 °C within 30 min. The dark brown melt is stirred for a further 2.5 h at 180 °C. After cooling to room temperature, ethanol (20 mL) is added, and the resulting solution is poured into acetone (900 mL). The yellow precipitate is filtered off, dried in vacuo (P_4O_{10}), and subsequently extracted in a Soxhlet apparatus (12 h, chloroform, 600 mL). The obtained yellow solution is concentrated to about 300 mL. At 0 °C, the product crystallizes within 2−3 days as a bright-yellow solid. Yield: 0.92 g (20%). Mp >340 °C. ^1H NMR ($C_2D_2Cl_4$, 363 K): $\delta = 7.89$ (dd; 4H, H^{16}), 9.31 (dd; $^3J = 4.4$ Hz, $^4J = 1.4$ Hz, 4H, H^{17}), 9.77 (dd; $^3J = 8.1$ Hz, 4H, H^{15}). ^{13}C NMR ($C_2D_2Cl_4$, 363 K): $\delta =$ 123.79 (d; C^{16}), 126.97 (s; C^{18}), 133.06 (d; C^{17}), 140.00 (s; C^{20}), 148.10 (s; C^{19}), 152.31 (d; C^{15}).

$[Ru(bpy)Cl_3]_x$ (3a). A solution of 2,2′-bipyridine (**5a**) (0.291 g, 1.86 mmol), dissolved in a mixture of aqueous hydrochloric acid (0.35 M, 3.0 mL) and acetone (3.0 mL), is added under an atmosphere of nitrogen with a syringe pump (10 h, 25 °C) to a solution of RuCl$_3$·3H$_2$O (**4**) (0.504 g, 1.93 mmol) in aqueous hydrochloric acid (0.35 M, 2 mL). The mixture is stirred for a further 24 h at room temperature. Then, it is allowed to stay at room temperature for 7 days. The formed solid is filtered off, washed successively with 0.35 M hydrochloric acid and water until the washing solution remains colorless. **3a** is finally dried in vacuo at room temperature (P$_4$O$_{10}$). Yield: 0.533 g (89%). The proof of the constitution of **3a**, and determination of its purity, were done after conversion of representative samples of **3a** into complex **6**. To identify impurities in the resulting product mixture, complexes **7** and **8b** were prepared additionally as described below.

[Ru((C$_6$H$_5$)$_2$bpy)Cl$_3$]$_x$ (3b). A solution of 4,4′-diphenyl-2,2′-bipyridine (**5b**) (0.144 g, 0.47 mmol), dissolved in a mixture of aqueous hydrochloric acid (0.6 M, 2.0 mL) and acetone (4.0 mL), is added under an atmosphere of nitrogen with a syringe pump (10 h, 25 °C) to a solution of RuCl$_3$·3H$_2$O (**4**) (0.125 g, 0.48 mmol) in aqueous hydrochloric acid (0.6 M, 1 mL). The mixture is stirred for a further 24 h at room temperature. Then, it is allowed to stay at room temperature for 7 days. The formed solid is filtered off, washed successively with 0.6 M hydrochloric acid and water until the washing solution remains colorless. **3b** is finally dried in vacuo at room temperature (P$_4$O$_{10}$). Yield: 0.202 g (77%). The proof of the constitution of **3b**, and determination of its purity, were done after conversion of representative samples of **3b** into complex **7**.

[Ru((C$_6$H$_5$)$_2$bpy)$_2$(bpy)](PF$_6$)$_2$ (6). A mixture of [Ru(bpy)Cl$_3$]$_x$ (**3a**) (0.09 mg, 0.225 mmol), 4,4′-diphenyl-2,2′-bipyridine (**5b**) (0.139 g, 0.450 mmol), ethanol (12 mL), and water (6 mL) is stirred and refluxed for 2 h. After cooling to room temperature, neutralized (NaOH concentrated) H$_3$PO$_2$ solution (2 mL, pH 7) is added. Subsequently, the mixture is stirred and refluxed for a further 4 h. At room temperature, a solution of NH$_4$PF$_6$ (0.4 g, 2.4 mmol) in water (4 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P$_4$O$_{10}$). Yield: practically quantitative; after recrystallization from a mixture of ethanol (40 mL) and water (10 mL), 0.121 g (43%). ^{1}H NMR (CD$_3$CN): $\delta =$ 7.45 (m; $^3J = 6.0$ Hz, 2 H, H^2), 7.59 (m; 12 H, H^{13,14}), 7.69 (m; $^3J = 6.0$ Hz, 4 H, H^7), 7.80 (d; $^3J = 6.0$ Hz, 2 H, H^1), 7.89 (d; $^3J = 6.0$ Hz, 4 H, H^6), 7.93 (m; 8 H, H^{12}), 8.09 (m; $^3J = 8.0$ Hz, 2 H, H^3), 8.55 (m; $^3J = 8.0$ Hz, 2 H; H^4), 8.95 (m; 4 H, H^9). ^{13}C-NMR (CD$_3$CN): $\delta =$ 123.05 (d; C^9), 125.25 (d; C^4), 125.94 (d; C^7), 128.47 (d; C^{2,12}), 130.41 (d; C^{13}), 131.47 (d; C^{14}), 136.69 (s; C^{11}), 138.80 (d; C^3), 150.53 (s; C^8), 152.62 (d; C^{1,6}), 158.00 (s; C^5), 158.39 (s; C^{10}).

[Ru((C$_6$H$_5$)$_2$bpy)(bpy)$_2$](PF$_6$)$_2$ (7). A mixture of [Ru(bpy)$_2$Cl$_2$] (**10a**) (0.15 g, 0.3 mmol), 4,4′-diphenyl-2,2′-bipyridine (**5b**) (0.096 g, 0.31 mmol), methanol (10 mL), and water (20 mL) is stirred and refluxed for 12 h. After cooling to 0 °C, a solution of NH$_4$PF$_6$ (0.4 g, 2.4 mmol) in water (4 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P$_4$O$_{10}$). Yield: practically quantitative; after recrystallization from a mixture of ethanol (40 mL) and water (10 mL), 0.107 g (40%). ^{1}H-NMR (CD$_3$CN): $\delta =$ 7.41 (m; $^3J = 6.0$ Hz, 4 H, H^2), 7.59 (m; 6 H, H^{13,14}), 7.66 (m; $^3J = 5.7$ Hz, 2 H, H^7), 7.75 (d; $^3J = 6.0$ Hz, 4 H, H^1), 7.83 (d; $^3J = 5.7$ Hz, 2 H, H^6), 7.91 (m; 4 H, H^{12}), 8.05 (m; $^3J = 8.1$ Hz, 4 H, H^3), 8.52 (m; $^3J = 8.1$ Hz, 4 H, H^4), 8.90 (m; 2 H, H^9). ^{13}C-NMR (CD$_3$CN): $\delta =$ 123.04 (d; C^9), 125.23 (d; C^4), 125.89 (d; C^7), 128.45 (d; C^{12}), 128.57 (d; C^2), 130.41 (d; C^{13}), 131.48 (d; C^{14}), 136.67 (s; C^{11}), 138.77 (d; C^3), 150.51 (s; C^8), 152.61 (d; C^{1,6}), 157.97 (s; C^5), 158.37 (s; C^{10}).

[Ru((C$_6$H$_5$)$_2$bpy)$_3$](PF$_6$)$_2$ (8b). A solution of 4,4′-diphenyl-2,2′-bipyridine (**5b**) (0.231 g, 0.75 mmol) in DMF (8 mL) is added to a heated (70 °C) and stirred solution of RuCl$_3$·3H$_2$O (**4**) (0.065 g, 0.25 mmol) in a mixture of water (10 mL) and concentrated hydrochloric acid (0.5 mL). The resulting mixture is refluxed for 2.5 h. After cooling to room temperature, neutralized (NaOH concentrated) H$_3$PO$_2$ solution (1.0 mL, pH 7) is added. The mixture is stirred and refluxed for a further 1 h. At room temperature, a solution of NH$_4$PF$_6$ (0.3 g, 1.9 mmol) in water (2 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P$_4$O$_{10}$). Yield: practically quantitative; after recrystallization from a mixture of ethanol (90 mL) and acetone (15 mL), 0.277 g (81%). ^{1}H-NMR (CD$_3$CN): $\delta = 7.60$ (m; 24 H, H^{7,13,14}), 7.72 (m; 6 H, H^6), 7.94 (m; 12 H, H^{12}), 8.97 (s; 6 H, H^9). ^{13}C-NMR (CD$_3$CN): $\delta =$ 123.08 (d; C^9), 125.95 (d; C^7), 128.48 (d; C^{12}), 130.40 (d; C^{13}), 131.48 (d; C^{14}), 136.70 (s; C^{11}), 150.58 (s; C^8), 152.62 (d; C^6), 158.45 (s; C^{10}).

[Ru(bpy)(tppz)$_2$](PF$_6$)$_2$ (9a). A solution of [Ru(bpy)Cl$_3$]$_x$ (**3a**) (0.02 g, 0.05 mmol) in a mixture of ethanol (4 mL) and water (2 mL) is added with a syringe pump (8 h) to a stirred and heated (120 °C) solution of tppz (**2**) (0.042 g, 0.10 mmol) in 1,1,2,2-tetrachloroethane (2 mL). Heating and stirring is continued for a further 4 h. At room temperature, 4-ethylmorpholine (0.05 mL) is added, and heating is continued for 12 h. For preparation of complex **11a**, this solution is treated as described below. To isolate complex **9a**, the resulting solution is allowed to cool to room temperature. A solution of NH$_4$PF$_6$ (0.4 g, 2.4 mmol) in water (4 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P$_4$O$_{10}$). Yield: practically quantitative. **9a** is nearly insoluble in all available solvents. Therefore, only the proton NMR spectrum was recorded. All absorptions were at least 10 Hz broad and unstructured. ^{1}H NMR (CD$_3$CN): $\delta = 7.39$ (2 H, H^2), 7.85 (6 H, H^{1,16}), 8.10 (6 H, H^{3,16}), 8.30 (4 H, H^{17}), 8.43 (4 H, H^{17}), 8.62 (2 H, H^4), 9.58 (2 H, H$^{15'}$), 9.73 (2 H, H$^{15'}$), 9.98 (2 H, H^{15}), 10.05 (2 H, H^{15}).

Pentakis(2,2′-bipyridine)(tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)ruthenium(II) Hexafluorophosphate (11a). First, a solution of [Ru(tppz)$_2$(bpy)]Cl$_2$ (**9a**) was prepared as described above. At room temperature, [Ru(bpy)$_2$Cl$_2$] (**10a**) (0.052 g, 0.10 mmol) is added, and stirring and refluxing is continued for a further 12 h. The solution is cooled (0 °C), and a solution of NH$_4$PF$_6$ (0.4 g, 2.4 mmol) in water (4 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P$_4$O$_{10}$). Yield: 0.142 g (96%). ^{1}H NMR (CD$_3$CN): $\delta = 7.27$ (m; 4 H, H$^{2'}$), 7.37 (m; 2 H, H^2), 7.50 (m; 4 H, H$^{2'}$), 7.75 (d; 4 H, H$^{1'}$), 7.88 (d; 4 H, H$^{1'}$), 7.92 (d; 2 H, H^1), 8.01 (m; 10 H, H$^{3,3'}$), 8.13 (2d; 4 H, H^{16}), 8.30 (m; 8 H, H^{16,17}), 8.44 (d; 4 H, H^{17}), 8.57 (m; 10 H, H$^{4,4'}$), 9.97 (m; 4 H, H^{15}), 10.05 (m; 4 H, H^{15}). ^{13}C-NMR (CD$_3$CN): δ = 125.35 (d; C^4), 128.52 (m; C^{2,16}), 131.06 (s; C^{18}), 134.90, 135.09 (d; C^{17}), 138.95, 139.04 (d; C^3), 141.51 (s; C^{20}), 151.51, 151.74 (2s; C^{19}), 153.09, 153.55 (2d; C^1), 155.51, 155.86 (2d; C^{15}), 157.96, 158.19 (2s; C^5). Anal. Calcd for C$_{98}$H$_{64}$N$_{22}$F$_{36}$P$_6$Ru$_3$·10H$_2$O: C, 40.49; H, 2.92; N, 10.61. Found: C, 40.09; H, 3.08; N, 10.15.

[Ru((C$_6$H$_5$)$_2$bpy)$_2$Cl$_2$] (10b). A solution of 4,4′-diphenyl-2,2′-bipyridine (**5b**) (0.245 g, 0.79 mmol) in a mixture of dimethylformamide (DMF)/acetone (16 mL, 1:1) is added to a solution of RuCl$_3$·3H$_2$O (**4**) (0.107 g, 0.41 mmol) and LiCl (0.110 g, 2.6 mmol) in DMF (3.0 mL) over a period of 12 h (syringe pump). Subsequently, the resulting mixture is refluxed for a further 4 h and then concentrated to about 5 mL. Finally, acetone (25 mL) is added, and at −18 °C the complex **10b** precipitates within 7 days. The formed solid is filtered off and dried in vacuo at room temperature (P$_4$O$_{10}$). Yield: 0.211 g (65%).

[Ru((C$_6$H$_5$)$_2$bpy)(tppz)$_2$](PF$_6$)$_2$ (9b). A solution of [Ru((C$_6$H$_5$)$_2$bpy)Cl$_3$]$_x$ (**3b**) (0.03 g, 0.05 mmol) in a mixture of ethanol (4 mL) and water (2 mL) is added with a syringe pump (8 h) to a stirred and heated (120 °C) solution of tppz (**2**) (0.046 g, 0.11 mmol) in 1,1,2,2-tetrachloroethane (2 mL). Heating and stirring is continued for a further 4 h. At room temperature, 4-ethylmorpholine (0.05 mL) is added, and heating is continued for 12 h. Isolation is possible as described for **9a**. For preparation of complex **11b**, see below.

Pentakis(4,4′-diphenyl-2,2′-bipyridine)bis(tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)triruthenium(II) Hexafluorophosphate (11b). To a solution of [Ru(tppz)$_2$((C$_6$H$_5$)$_2$bpy)]Cl$_2$ (**9b**) is added [Ru((C$_6$H$_5$)$_2$bpy)$_2$Cl$_2$] (**10b**) (0.090 g, 0.11 mmol) at room temperature. Then, stirring and refluxing is continued for a further 12 h. The solution is cooled (0 °C), and a solution of NH$_4$PF$_6$ (0.08 g, 0.5 mmol) in water (4 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P_4O_{10}). Yield: 0.195 g (97%). ^{1}H NMR (CD_3CN): $\delta = 7.61$ (m; 36H, H^7, H^{7be}, H^{13}, H^{14}), 7.81 (d; 4H, H^{7ae}), 7.85 (d; 4H, H^{6be}), 7.90 (m; 10H, H^{12b}), 7.94 (m; 2H, H^6), 7.99 (m; 10H, H^{12a}), 8.09 (m; 12H, H6ae, H^{16}), 8.39 (d; 2H, H^{17b}), 8.47 (d; 4H, H^{17}), 8.57 (d; 2H, H^{17a}), 9.01 (d; 10H, H9), 10.01 (m; 4H, H^{15b}), 10.03 (m; 4H, H^{15a}). ^{13}C-NMR (CD_3CN): $\delta = 123.22$ (d; C^9), 125.86 (d; C^7), 128.53 (d, $C^{12,16}$), 130.44 (d; C^{13}), 131.12 (s; C^{18}), 131.57 (d; C^{14}), 134.93 (d; C^{17}), 136.61 (s; C^{11}), 141.56 (s; C^{20}), 150.82 (s; C^8), 151.60 (s; C^{19}), 153.10 (m; C^6), 155.47 (m; C^{15}), 158.45, 158.69 (2s; C^{10}). Anal. Calcd for $C_{158}H_{104}N_{22}F_{36}P_6Ru_3 \cdot 10H_2O$: C, 51.74; H, 3.41; N, 8.41. Found: C, 51.89; H, 3.66; N, 8.06.

Poly{(2,2′-bipyridine)(tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)ruthenium(II) hexafluorophosphate} (1a). A mixture of $[Ru(bpy)Cl_3]_x$ (**3a**) (0.156 g, 0.390 mmol), tppz (**2**) (0.164 g, 0.390 mmol), ethanol (16 mL), and water (8 mL) is stirred and refluxed for 12 h. At room temperature, 4-ethylmorpholine (0.04 mL) is added. Stirring and heating is continued for a further 6 h. At 0 °C, a solution of NH_4PF_6 (0.65 g, 4.0 mmol) in water (20 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P_4O_{10}). Yield: 0.361 g (99%). ^{1}H NMR (CD_3CN): $\delta =$ 7.38 (m; 2 H, H^2), 7.92 (m; 4 H, $H^{1,16}$), 8.12 (m; 4 H, $H^{3,16}$), 8.34 (m; 2 H, H^{17}), 8.45 (m; 2 H, H^{17}), 8.63 (m; 2 H, H^4), 9.98 (m; 2 H, H^{15}), 10.05 (m; 2 H, H^{15}). ^{13}C NMR (CD_3CN): $\delta = 125.42$ (d; C^4), 128.59 (2d; $C^{2,16}$), 131.14 (s; C^{18}), 135.14 (d; C^{17}), 139.21 (d; C^3), 141.54 (s; C^{20}), 151.55, 151.76 (2s; C^{19}), 153.54 (d; C^1), 155.86 (d; C^{15}), 158.23 (s; C^5). Anal. Calcd for $[C_{34}H_{20}N_8F_{12}P_2Ru \cdot 4H_2O]_n$: C, 40.69; H, 2.81; N, 11.16. Found: C, 40.17; H, 2.71; N, 10.88.

Poly{(4,4′-diphenyl-2,2′-bipyridine)(tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)ruthenium(II) hexafluorophosphate} (1b). A mixture of $[Ru((C_6H_5)_2bpy)Cl_3]_x$ (**3b**) (0.159 g, 0.290 mmol), tppz (**2**) (0.115 g, 0.290 mmol), ethanol (12 mL), and water (6 mL) is stirred and refluxed for 12 h. At room temperature, 4-ethylmorpholine (0.03 mL) is added. Stirring and heating are continued for a further 6 h. At 0 °C, a solution of NH_4PF_6 (0.49 g, 3.0 mmol) in water (15 mL) is added. The precipitation of the product is completed by stirring the mixture at 0 °C for 3 h. The solid is filtered off, washed with water, and dried in vacuo (P_4O_{10}). Yield: 0.361 g (99%). ^{1}H NMR (CD_3CN): $\delta = 7.59$ (m; 8H, $H^{7,13,14}$), 7.93 (m; 8H, $H^{6,13,16}$), 8.13 (m; 2H, H^{16}), 8.39 (m; 2H, H^{17}), 8.58 (m; 2H, H^{17}), 9.03 (m; 2H, H^9), 10.01 (m; 2H, H^{15}), 10.08 (m; 2H, H^{15}). ^{13}C NMR (CD_3CN): $\delta = 123.34$ (d; C^9), 126.00 (d; C^7), 128.60 (d; $C^{12,16}$), 130.54 (d; C^{13}), 131.28 (s; C^{18}), 131.70 (d; C^{14}), 135.28 (2d; C^{17}), 136.70 (s; C^{11}), 141.68 (s; C^{20}), 151.09 (s; C^8), 151.68, 151.94 (2s; C^{19}), 153.66 (d; C^6), 155.92 (2d; C^{15}), 158.77 (s; C^{10}). Anal. Calcd for $[C_{46}H_{28}N_8F_{12}P_2Ru \cdot 4H_2O]_n$: C, 47.80; H, 3.14; N, 9.69. Found: C, 49.56; H, 3.76; N, 9.64.

Acknowledgment. The authors are grateful to Professor M. Ballauff, Karlsruhe, for his support of this work. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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MA9702814