Soluble Ruthenium(II) Coordination Polymers Bearing Bulky Side Groups

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ABSTRACT: Ruthenium(II) coordination polymers bearing lateral methyl and adamantylmethylene substituents, respectively, have been prepared via reaction of equimolar amounts of tetrapyridophenazine **2** and the novel metal monomers $[Ru(R_2bpy)Cl_3]_x$ (**3a,b**) (R: **a**, methyl; **b**, adamantylmethylene). Moreover, the bulky adamantylmethylene substituents are shown to cause a significantly more extended chain conformation of the intrinsically rigid, ribbon-like coordination polymers **1** than is found for other polymers of this kind available so far.

Introduction

Coordination polymers, that is, polymers whose main chains are held together by coordinative bonds, are of considerable current interest not only in supramolecular science but also because of their potential use as magnetic, electronic or photooptical materials.[1−11] Recently, we reported the reaction of tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (**2**) with equimolar amounts of $[Ru(R_2bpy)Cl_3]_x$ (**3c,d**) (R: **c**, H; **d**, C_6H_5) to give readily soluble ruthenium(II) coordination polymers **1c,d** of homogeneous constitution and high molecular weights ($M_w \approx 45\,000$ g·mol^{-1}; small-angle X-ray scattering (SAXS)) according to Scheme 1.[12−14] Moreover, SAXS studies and viscosimetric investigations showed that these conformationally rigid, ribbon-like polymers **1c,d** assume compact, coiled chain conformations, as is visualized in Figure 2A for a pentameric sequence of polymer **1c**: even high-molecular-weight samples of **1c,d** gave intrinsic viscosities of only $[\eta] \approx 12$ mL·g^{-1}, and the largest radius of gyration found was $R_G = 8.4$ nm.

Now, we were interested in broadening the scope of the above synthetic strategy to polymers **1**, which have aliphatic side groups R: On one hand, such substituents should open up efficient access to further coordination polymers **1** via macromolecular substitution routes. On the other hand, we wanted to answer the question whether polymers **1** can be forced to assume less densely coiled conformations by the attachment of bulky substituents to the 2,2′-bipyridine ligands of **1** and thus by steric hindrance.

Results and Discussion

Methyl- and adamantyl-substituted polymers **1a,b** were selected as target polymers for this study, since these side groups should not affect the homogeneity of the conversion $\mathbf{4} + \mathbf{5} \rightarrow \mathbf{3}$ (Scheme 2), the most critical step in the whole synthesis of coordination polymers **1**. Moreover, adamantylmethylene substituents were expected to be bulky enough to influence the chain conformation of the resulting polymer **1b** and thus to cause more elongated backbones.

The required metal monomers **3a,b** were obtained according to Scheme 2: starting from 4,4′-dimethyl-2,2′-bipyridine (**4a**), 4,4′-bis(adamantylmethylene)-2,2′-bipyridine (**4b**) was synthesized in 20% yield via (i) lithiation of **4a** followed by (ii) conversion of the lithiated intermediate with adamantyl bromide. Subsequently, solutions of bipyridine derivatives **4a,b** were added slowly to $RuCl_3 \cdot 3H_2O$ (**5**), dissolved in mixtures of dilute aqueous HCl and acetone. The purity of the obtained solids **3a,b** was checked using NMR spectroscopy by means of model complexes **6a,b** which were prepared via conversion of representative samples of **3a,b** with 2,2′-bipyridine (**4c**). It was shown that under the optimum reaction conditions metal monomers are available with purities > 98%. When, on the other hand, the best conditions are not strictly adhered to, less homogeneous monomers **3** are formed which give low-molecular-weight and/or branched products **1** if polymerized according to Scheme 1.

The first aim of the subsequent polymerization experiments was to show that these new alkyl-substituted metal monomers **3a,b** also lead to soluble, high-molecular-weight coordination polymers **1a,b** when treated with exactly equimolar amounts of ligand monomer **2** in ethanol/water (Scheme 1). After a 24 h reaction time, a small volume of neutralized H_3PO_2 was added to the resulting homogeneous mixture in order to reduce all ruthenium centers to the diamagnetic ruthenium(II). Polymers **1a,b** were precipitated quantitatively either as hexafluorophosphates by adding aqueous NH_4PF_6 solution or as chlorides by adding acetone. The obtained brown solids indeed readily redissolved in acetonitrile, ethanol, or dimethylacetamide (DMA), and their constitution could thus be proved using ^1H (Figure 1) and ^{13}C NMR spectroscopy. Throughout, all detected absorptions could be assigned unambiguously to inner-chain repeat units of constitutionally homogeneous polymers **1a,b**.

Only when polymerizations were carried out in the presence of a small amount of the monofunctional complex $[Ru(R_2bpy)_2Cl_2]$ or when a slight excess of ligand monomer **2** was used were oligomers **1a,b** obtained, whose NMR spectra clearly showed absorptions of $[Ru(R_2bpy)_2]^{2+}$ end groups or terminal ligands **2**. Hence, because end group absorptions can be excluded within the limit of accuracy of the ^1H NMR

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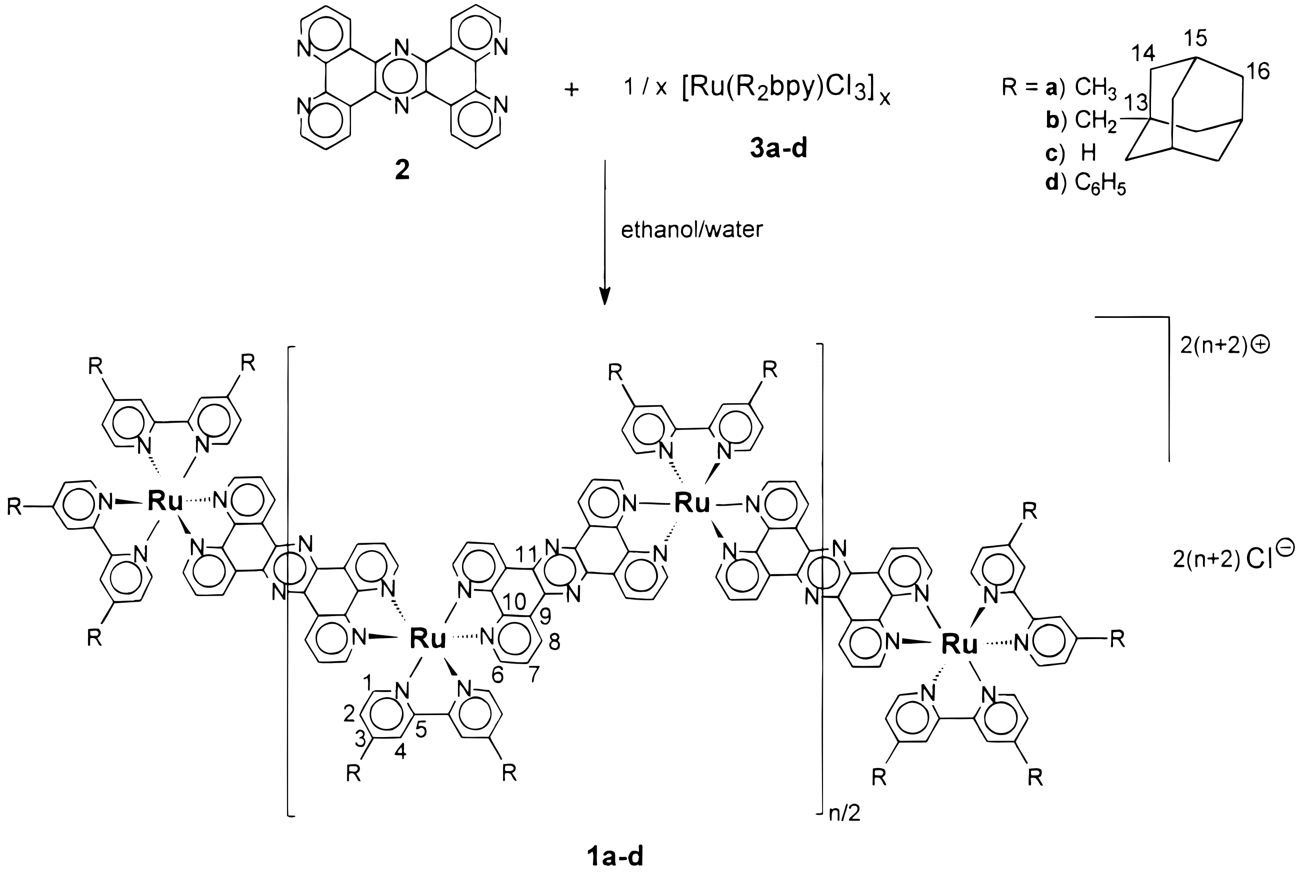
Scheme 1

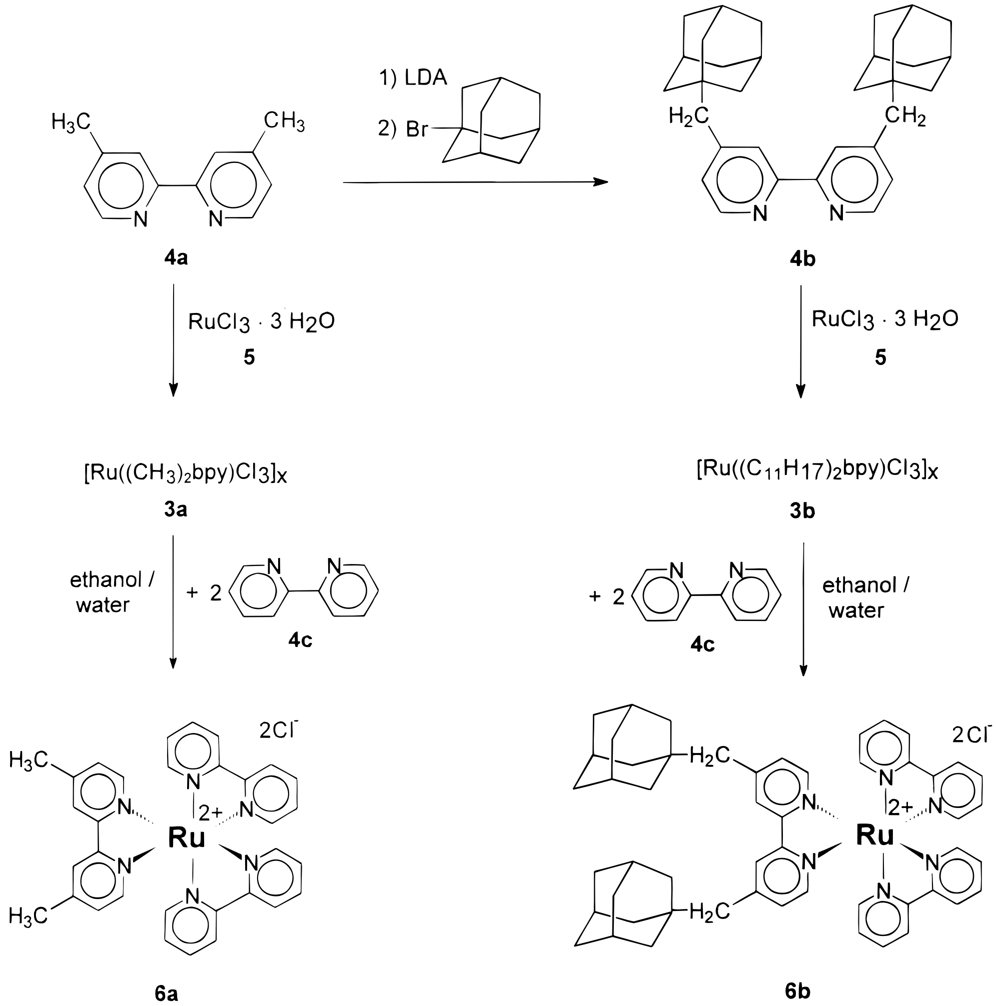


method for all products **1a,b** prepared by using exactly equimolar amounts of monomers **2** and **3a,b**, the average degrees of polymerization of these polymers were estimated to be $P_{n(NMR)} \geq 30$ ($M_n \geq 30\,000$ g·mol^{-1}), in agreement with the results found in our previous investigations.[13,14]

A high-molecular-weight sample of ruthenium(II) coordination polymer **1b** was subsequently studied by viscosimetry to find out whether the bulky adamantylmethylene substituents had influenced the chain conformation. Since in salt-free DMA solutions a pronounced polyelectrolyte effect prevented the determination of the intrinsic viscosity $[\eta]$, all experiments were carried out in the presence of foreign salt (0.02 M NH_4PF_6 in DMA) to screen out the intermolecular Coulomb interactions. Linear extrapolation of η_{sp}/c_P was now possible to $c_P = 0$, and intrinsic viscosities of $[\eta] \approx 23$ mL·g^{-1} were determined. This value of $[\eta]$ is nearly double the value determined for all other ruthenium(II) coordination polymers **1** investigated so far ($[\eta] \leq 12$ mL·g^{-1}). From this result it is obvious that the adamantylmethylene-substituted coordination polymer **1b** exhibits a significantly higher hydrodynamic volume than coordination polymers **1a,c,d**. Thus, under the realistic assumption that the maximum degrees of polymerization are very similar for all polymers **1** prepared according to Scheme 1, we conclude that polymer **1b** has indeed a less densely coiled chain conformation—visualized in Figure 2B—than all other coordination polymers **1a,c,d**.

Taking into account all available data, the strategy shown in Scheme 1 is indeed also applicable to metal monomers **3** which bear aliphatic side groups. The resulting high-molecular-weight polymers are excellently soluble in a variety of solvents, and moreover, there is strong evidence that the attachment of bulky side groups to polymer **1b** causes more elongated main chains. Nevertheless, the UV–vis spectrum of polymer **1b** is practically identical, in the 250–700 nm region, with that of the unsubstituted polymer **1c** (Figure 3): At wavelengths below 400 nm, the absorptions of the ligand-centered (LC) $\pi^* \leftarrow \pi$ transitions were observed as intense signals in both cases; absorptions at 280–310 nm were assigned to the 2,2′-bipyridine moieties, and absorptions at 350–370 nm, to the tetrapyridophenazine ligands. This latter assignment is further supported by the spectrum of model complex **6b** shown in Figure 3 as well, where the tetrapyridophenazine ligand is missing and thus all absorptions between 350 and 370 nm. Above 400 nm, finally, signals were observed which correspond to metal–ligand charge-transfer (MLCT) transitions. It is obvious from these spectra that the chain conformation of polymers **1** does not influence the absorption behavior of these macromolecules markedly. This is in harmony with earlier investigations[13] where we could show that the ruthenium centers of multinuclear complexes such as **1** can be considered to be nearly independent of one another: π-electron delocalization, metal–metal interactions, and conformational effects seem to be rather weak. Currently, we are analyzing the electronic and solution properties of polymers **1a,b** in more detail. Special emphasis is directed to the question whether the bulky substituents of **1b** not only cause a more expanded chain conformation but also lead to the preference of some specific diastereoisomeric sequences of Δ or Λ configurated chiral ruthenium(II) complexes along the polymer backbones.

Scheme 2



Experimental Section

$RuCl_3 \cdot 3H_2O$ (**5**) and $[Ru((CH_3)_2bpy)_2Cl_2]$ (**4a**) were purchased from Aldrich and Strem Chemical Co. Other chemicals and solvents were purchased from Aldrich, Fluka, and Lancaster Chemical Co. and used without further purification. 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 polymer **1** in Scheme 1. 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.

4,4′-Bis(adamantylmethylene)-2,2′-bipyridine (4b). Lithium diisopropylamide (2 M in THF, 11 mL, 22 mmol) is added to a solution of 4,4′-dimethyl-2,2′-bipyridine (0.5 g, 2.72 mmol) in THF (40 mL). To the resulting mixture, adamantyl bromide (1.2 g, 5.58 mmol) in THF (16 mL) is added within 12 h under reflux. A mixture of methanol (40 mL) and water (40 mL) is added, and the resulting mixture is evaporated to dryness. The raw material is purified chromatographically (silica gel; methylene chloride/acetone = 98/2). Yield: 0.230 g (0.51 mmol, 19%). ^1H NMR ($CDCl_3$): $\delta = 1.53$ (m, 12 H, H16), 1.56, 1.67 (2m, 12 H, H14), 1.95 (m, 6 H, H15), 2.48 (s, 4H, H12), 7.05 (d, 2 H, H2), 8.16 (s, 2 H, H4), 8.56 (d, 2 H, H1). ^{13}C NMR ($CDCl_3$): $\delta = 28.58$ (C15), 33.61 (C13), 36.80 (C16), 42.33 (C14), 50.71 (C12), 123.35 (C4), 126.02 (C2), 148.16 (C1), 148.51 (C3), 155.26 (C5). Elemental analysis ($C_{32}H_{40}N_2 \cdot H_2O$). Calcd: C, 81.66; H, 8.99; N, 5.95. Found: C, 82.22; H, 8.71; N, 5.56.

$[Ru((CH_3)_2bpy)Cl_3]_x$ (3a). A solution of 4,4′-dimethyl-2,2′-bipyridine (**4a**) (0.086 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 $RuCl_3 \cdot 3H_2O$ (**5**) (0.125 g, 0.48 mmol) in aqueous hydrochloric acid (0.6 M, 1.0 mL). The mixture is stirred for a further 24 h at room temperature. Then, it is allowed to stand at room temperature for 7 days. The formed solid is filtered off and washed successively with 0.6 M hydrochloric acid and water until the washing solution remains colorless. **3a** is finally dried in vacuo at room temperature (P_4O_{10}). Yield: 0.121 g (61%).

$[Ru((C_{11}H_{17})_2bpy)Cl_3]_x$ (3b). A solution of 4,4′-bis(adamantylmethylene)-2,2′-bipyridine (**4b**) (0.102 g, 0.22 mmol), dissolved in a mixture of aqueous hydrochloric acid (0.50 M, 4.0 mL) and acetone (12.0 mL), is added under an atmosphere of nitrogen with a syringe pump (10 h, 25 °C) to a solution of $RuCl_3 \cdot 3H_2O$ (**5**) (0.060 g, 0.23 mmol) in aqueous hydrochloric acid (0.50 M, 1 mL). The mixture is stirred for a further 24 h at room temperature. Then, it is allowed to stand at room temperature for 48 h. The formed solid is filtered off and washed successively with 0.50 M hydrochloric acid and water until the washing solution remains colorless. **3b** is finally dried in vacuo at room temperature (P_4O_{10}). Yield: 0.117 g (75%).

$[Ru((CH_3)_2bpy)(bpy)_2](PF_6)_2$ (6a). A mixture of $[Ru((CH_3)_2bpy)Cl_3]_x$ (**3a**) (0.011 g, 0.025 mmol), 2,2′-bipyridine (0.009 g, 0.050 mmol), ethanol (4 mL) and water (2 mL) is stirred and refluxed for 24 h. After the reaction mixture is cooled to 0 °C, a solution of NH_4PF_6 (0.06 g, 0.38 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_4O_{10}). Yield: 0.023 g (98%). ^1H NMR (CD_3CN): $\delta = 2.52$ (s, 6 H, CH_3), 7.21 (d, 2

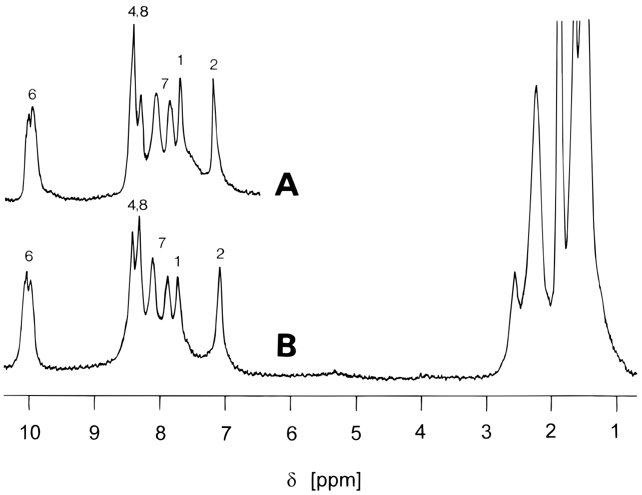


Figure 1. ^{1}H NMR spectra (400 MHz) of polymer **1a** (A, R = CH_3, aromatic region only) and of polymer **1b** (B, R = $C_{11}H_{17}$), recorded in CD_3CN at room temperature. The signal assignment is done according to the numbering given in Scheme 1.

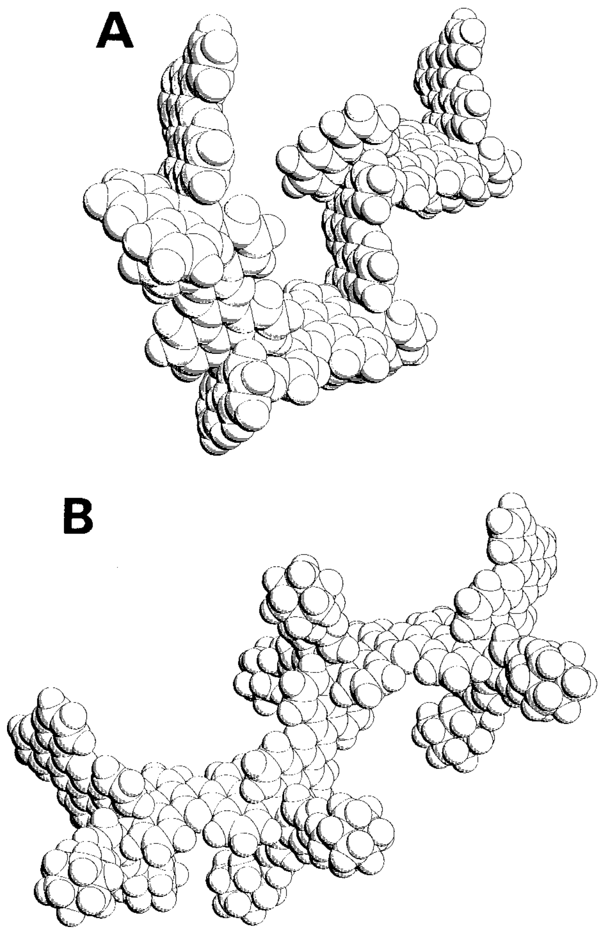


Figure 2. Idealized illustration of the densely coiled chains of polymer **1c** (A) and of the more extended chains of polymer **1b** (B) by means of space-filling molecular models of chain segments.

H, H2), 7.38 (m, 4 H, H7), 7.51 (d, 2 H, H1), 7.71 (m, 4 H, H6), 8.03 (m, 4 H, H8), 8.35 (s, 2 H, H4), 8.48 (d, 4 H, H9). ^{13}C NMR (CD_3CN): $\delta = 125.12$ (C9), 125.86 (C4), 128.43 (C7), 129.21 (C2), 138.53 (C8), 151.38 (C3), 151.68 (C1), 152.52 (C6), 157.38 (C5), 157.98 (C10). Elemental analysis ($C_{32}H_{28}N_6F_{12}P_2Ru\cdot 2H_2O$). Calcd: C, 41.61; H, 3.49; N, 9.10. Found: C, 42.05; H, 3.48; N, 9.09.

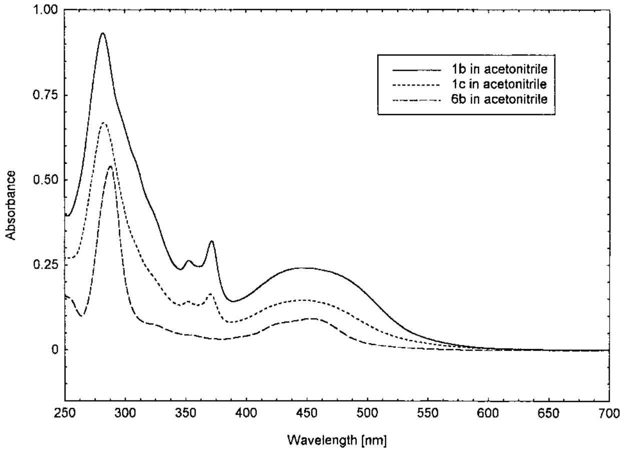


Figure 3. UV−vis absorption spectra of the monomeric complex **6b** and of the polymeric complexes **1b** and **1c** recorded in acetonitrile at room temperature.

[Ru(($C_{11}H_{17}$)$_2$bpy)(bpy)$_2$](PF$_6$)$_2$ (6b). A mixture of [Ru(($C_{11}H_{17}$)$_2$bpy)Cl_3]$_x$ (**3b**) (0.018 g, 0.025 mmol), 2,2′-bipyridine (0.009 g, 0.050 mmol), ethanol (4 mL), and water (2 mL) is stirred and refluxed for 24 h. After the reaction mixture is cooled to 0 °C, a solution of NH_4PF_6 (0.06 g, 0.38 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_4O_{10}). Yield: 0.030 g (97%). ^{1}H NMR (CD_3CN): $\delta = 1.52$ (m, 12 H, H16), 1.58, 1.70 (2m, 12 H, H14), 2.15 (m, 6 H, H15), 2.57 (s, 4 H, H12), 7.11 (d, 2 H, H2), 7.39 (d, 4 H, H7), 7.53 (d, 2 H, H1), 7.72 (d, 4 H, H6), 8.04 (m, 4 H, H8), 8.21 (s, 2 H, H4), 8.49 (d, 4 H, H9). ^{13}C NMR (CD_3CN): $\delta = 29.63$ (C15), 34.93 (C13), 37.36 (C16), 42.74 (C14), 50.50 (C12), 125.19 (C9), 126.84 (C4), 128.51 (C7), 130.31 (C2), 138.60 (C8), 151.22 (C3), 152.66 (C1,6), 157.50 (C5), 158.07 (C10). Elemental analysis ($C_{52}H_{56}N_6F_{12}P_2Ru\cdot 4H_2O$). Calcd: C, 50.86; H, 5.25; N, 6.84. Found: C, 50.40; H, 4.68; N, 6.44.

Poly{Ru[(CH_3)$_2$bpy](tppz)(PF$_6$)$_2$} (1a). A mixture of [Ru((CH_3)$_2$bpy)Cl_3]$_x$ (**3a**) (0.054 g, 0.13 mmol), tppz (**2**) (0.050 g, 0.13 mmol), ethanol (15 mL), and water (7 mL) is stirred and refluxed for 8 h. At room temperature, neutralized H_3PO_2 (1 mL) is added. Stirring and heating is continued for a further 12 h. At 0 °C, a solution of NH_4PF_6 (0.3 g, 1.88 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. Yield: 0.096 g (72%). ^{1}H NMR (CD_3CN): $\delta = 2.55$ (s, 6 H, CH_3), 7.20 (m, 2 H, H2), 7.72 (m, 2 H, H1), 7.87 (m, 2 H, H7b), 8.09 (m, 2 H, H7a), 8.33 (m, 2 H, H8b), 8.45 (m, 4 H, H4, H8a), 9.96 (m, 2 H, H6b), 10.02 (m, 2 H, H6a). ^{13}C NMR (CD_3CN): $\delta = 21.14$ (CH_3), 125.99 (C4), 128.32 (C7), 129.00 (C2), 130.96 (C9), 134.79 (C8), 141.42 (C11), 151.73 (C3, C10), 152.54 (C1), 155.56 (C6), 157.60 (C5). Elemental analysis [($C_{36}H_{24}N_8F_{12}P_2Ru\cdot 4H_2O$)$_n$]. Calcd: C, 41.91; H, 3.13; N, 10.86. Found: C, 40.78; H, 3.30; N, 10.64.

Poly{Ru[($C_{11}H_{17}$)$_2$bpy](tppz)(PF$_6$)$_2$} (1b). A mixture of [Ru(($C_{11}H_{17}$)$_2$bpy)Cl_3]$_x$ (**3b**) (0.80 g, 0.11 mmol), tppz (**2**) (0.045 g, 0.11 mmol), ethanol (8 mL), and water (4 mL) is stirred and refluxed for 24 h. At room temperature, neutralized H_3PO_2 (1 mL) and ethanol (1 mL) are added. Stirring and heating is continued for a further 12 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: 0.141 g (99%). ^{1}H NMR (CD_3CN): $\delta = 1.53$, 1.69 (2m, 24 H, H14, H16), 2.26 (m, 6 H, H15), 2.59 (s, 4 H, H12), 7.08 (d, 2 H, H2), 7.73 (d, 2 H, H1), 7.89 (d, 2 H, H7b), 8.12 (d, 2 H, H7a), 8.33 (m, 4 H, H4, H8b), 8.43 (d, 2 H, H8a), 9.67 (d, 2 H, H6b), 10.03 (d, 2 H, H6a). ^{13}C NMR (CD_3CN): $\delta = 29.64$ (C15), 35.02 (C13), 37.38 (C16), 42.75 (C14), 50.55 (C12), 127.08 (C4), 128.67 (C7), 129.85 (C2), 130.43 (C9), 135.01 (C8), 141.62 (C11), 151.80 (C1, C3, C10), 157.79 (C5), 157.55 (C6). Elemental analysis [$(C_{56}H_{52}N_8F_{12}P_2Ru{\cdot}4H_2O)_n$]. Calcd: C, 51.73; H, 4.65; N, 8.62. Found: C, 52.77; H, 4.67; N, 8.12.

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