Dimeric 2,2′-Bipyridylruthenium(II) Complexes Containing 2,2′-Bis(1,2,4-triazin-3-yl)-4,4′-bipyridine-Like Bridging Ligands: Syntheses, Characterization and DNA Binding

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Three new bridging ligands 2,2′-bis(1,2,4-triazin-3-yl)-4,4′-bipyridine (btb), 2,2′-bis(1,2,4-triazino[5,6-f]acenaphthylen-3-yl)-4,4′-bipyridine (btapb), 2,2′-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-4,4′-bipyridine (bdptb) and their dimeric 2,2′-bipyridylruthenium(II) complexes $[Ru(bpy)_2(btb)Ru(bpy)_2]^{4+}$ (**1**), $[Ru(bpy)_2(btapb)Ru(bpy)_2]^{4+}$ (**2**), $[Ru(bpy)_2(bdptb)Ru(bpy)_2]^{4+}$ (**3**) have been synthesized and characterized by elemental analysis, fast atom bombardment (FAB) mass spectrometry or electrospray mass spectrometry (ES-MS), ^1H NMR and UV/Visible spectroscopy. The binding behavior of these dimeric complexes with calf thymus DNA (CT-DNA) was investigated by electronic absorption spectroscopy, viscosity measurements, and equilibrium dialysis experiments. The hypochromism of the metal-ligand charge transfer (MLCT) band in the electronic absorption spectra of the dinuclear complexes **1**, **2**, and **3** is 8.7%, 19% and 33%, respectively, with bathochromic shifts of 5, 5 and 14 nm, respectively. The binding constants are 7.5×10^4 M^{-1}, 4.8×10^5 M^{-1} and 7.6×10^5 M^{-1}, respectively. Increasing the size of the plane of the bridging ligand increases the hydrophobicity of their complexes, leading to stronger binding by the complexes to calf thymus DNA. The effect of increasing concentrations of these novel dimeric ruthenium(II) complexes on the relative viscosities of CT-DNA is less notable than that of well-known intercalators such as $[Ru(bpy)_2(dppz)]^{2+}$. The equilibrium experiments showed that ΛΛ–**3** binding is stronger than ΔΔ–**3** binding to CT-DNA. This is the first example of a dinuclear complex binding enantioselectively to CT-DNA measured by equilibrium dialysis. The experiments suggest that the three complexes may be DNA groove binders.

Introduction

The design of molecules that target particular DNA sequences is one of the major challenges in the field of molecular recognition. The potential application of ruthenium complexes with polypyridyl ligands in the design and development of photophysical and stereoselective probes of nucleic acid structure has been explored extensively in recent years.[1−6] However, this work has focused primarily on mononuclear complexes, with di- or polynuclear complexes attracting limited attention. Dimeric ruthenium(II) complexes have some advantages over other complexes as photo- and stereochemical probes for nucleic acids, such as greater variations in size and shape. Additionally, the incorporation of two chiral centers into a single dimeric complex may enable amplification of the chiral discrimination. More recently, non-intercalating dinuclear ruthenium(II) complexes have been synthesized as probes of DNA structure.[7−10]

In a previous communication, we reported a novel dimeric ruthenium(II) complex $[Ru(bpy)_2(bdptb)Ru(bpy)_2]^{4+}$ [**3**; bdptb = 2,2′-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-4,4′-bipyridine] that displays enantiopreferential DNA-binding behavior after equilibrium dialysis.[10] We describe here the synthesis of the three new bridging ligands 2,2′-bis(1,2,4-triazin-3-yl)-4,4′-bipyridine (btb), 2,2′-bis(1,2,4-triazino[5,6-*f*]acenaphthylen-3-yl)-4,4′-bipyridine (btapb), bdptb and their dimeric 2,2′-bipyridylruthenium(II) complexes $[Ru(bpy)_2(btb)Ru(bpy)_2]^{4+}$ (**1**), $[Ru(bpy)_2(btapb)Ru(bpy)_2]^{4+}$ (**2**) and **3**. The binding behavior of these compounds with calf thymus DNA (CT-DNA) is also presented.

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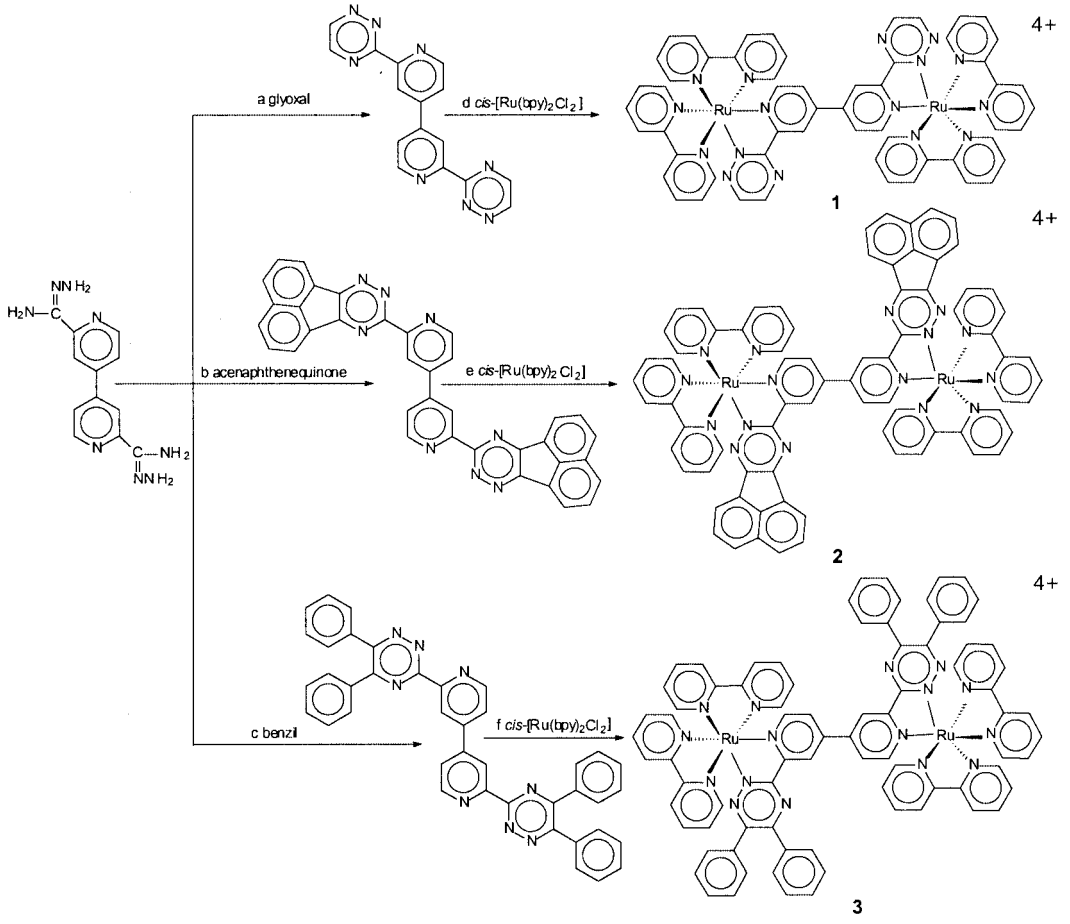
Results and Discussion

1. Syntheses and Characterization

The synthetic routes to the bidentate bridging ligands and their complexes with bpy diruthenium(II) are summarized in Scheme 1. The synthesis of the bridging ligands was based on the method for the 1,2,4-triazine ring preparation established by Case.[11,12] The condensation of bahmb with glyoxal, acenaphthenequinone or benzil produced btb, btapb and bdptb, respectively, in 78%, 72% and 75% yields. Their identities were confirmed by elemental analysis, fast atom bombardment (FAB) mass spectrometry and NMR



Scheme 1. The synthetic routes to the bidentate bridging ligands and bpy diruthenium(II) complexes

spectroscopy. Their complexes were also synthesized and characterized by elemental analysis and spectroscopic methods. The bridging ligands and their dimeric complexes give highly resolved ^{1}H NMR spectra in [D$_6$]DMSO and all proton resonance signals could be assigned by ^{1}H-^{1}H COSY experiments. The ^{1}H NMR spectral data of the dimeric complexes are listed in the Exp. Sect. The ^{1}H-^{1}H COSY NMR spectrum of the dimeric complex **2** is given in Figure 1 as an example.

Electrospray mass spectrometry (ES-MS) has recently been shown to be a powerful tool for measuring the molecular mass of nonvolatile, thermally unstable compounds.[13] In the ES-MS spectra for the diruthenium(II) complexes, intense signals for $[M - 2ClO_4]^{2+}$, $[M - 3ClO_4]^{3+}$ and $[M - 4ClO_4]^{4+}$ were observed. The ES-MS results are given in the Exp. Sect. The observed molecular weights are consistent with the expected values.

The electronic absorption spectra of the new bridging ligands and their dimeric complexes were recorded in chloroform and acetonitrile, respectively. The absorption data are shown in Table 1. The lowest energy absorption bands at 502, 532 and 506 nm for the dimeric complexes are assigned to the metal-ligand charge transfer (MLCT) transition. The high energy absorption bands are attributed to the intense intraligand π-π* transition by comparison with the spectra of the uncoordinated bridging ligand.[14]

2. DNA-Binding Studies

Electronic Absorption Titrations

The interaction of the diruthenium(II) complexes with DNA was investigated by electronic absorption spectroscopy. The absorption spectra of complexes **1**, **2** and **3** in the absence and presence of CT-DNA (with the same concentrations of the complexes) are given in Figure 2. The absorption spectrum of complex **3** has been reported previously.[10] These results are summarized in Table 2.

As the concentration of DNA is increased, the MLCT transition bands of the complexes **1**, **2** and **3** at 483, 523 and 492 nm, respectively, exhibit hypsochromic shifts of about 8.7%, 19% and 33%, and a bathochromism of 5, 5 and 14 nm, respectively. These spectral characteristics suggest that the complexes exhibit a high affinity for DNA.

In order to compare quantitatively the binding strength of the diruthenium(II) complexes, the intrinsic binding constants K_b of the complexes **1**, **2** and **3** with calf thymus DNA were determined from the decrease of the absorbance

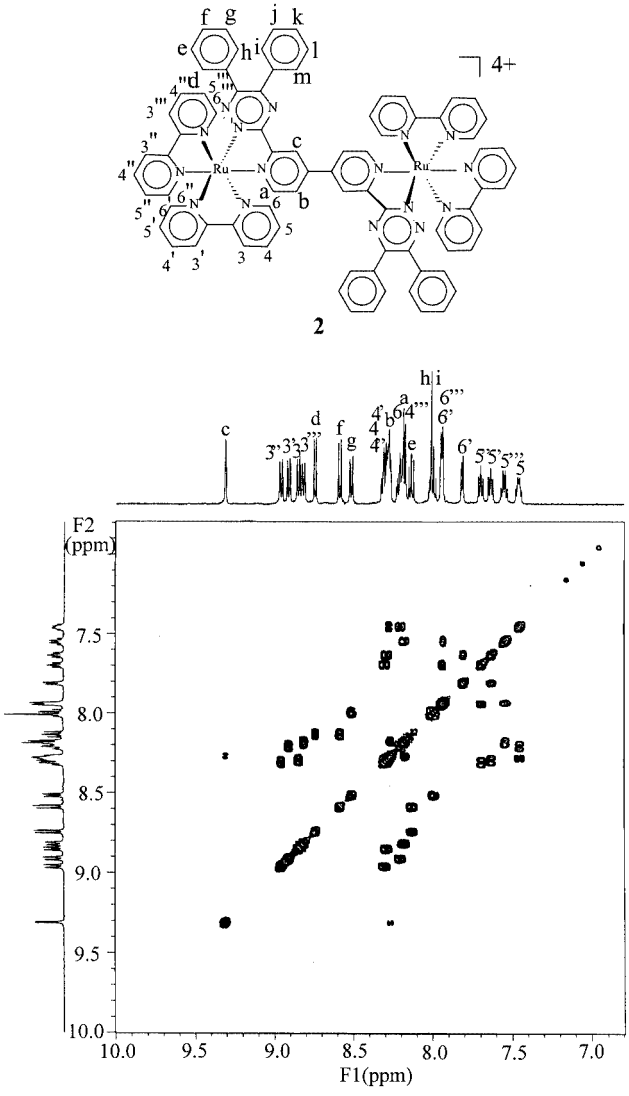


Figure 1. ^{1}H-^{1}H COSY spectra of $[Ru(bpy)_2(btapb)Ru(bpy)_2]]^{4+}$

Table 1. Electronic absorption spectroscopic data of the ligands and complexes

Compound	λ_{max}/nm(ε_{max}/M^{-1}·cm^{-1})
btb[a]	284.6(6540) 242(9630)
btapb[a]	316.6(11031) 235.8(10901)
bdptb[a]	304.4(7733) 240.8(10898)
1 [b]	502(23847) 421(27100) 284(109494) 244(69100)
2 [b]	532(24553) 434(26883) 386(41176) 284(101211)
3 [b]	506(32406) 425(32964) 284(119788) 245(64400)

[a] The solvent is chloroform for the ligands. [b] The solvent is acetonitrile for the complexes.

monitored, for the complexes **1**, **2** and **3**, at 483, 523 and 492 nm, respectively. The intrinsic binding constant K_b of the complex with CT-DNA was determined from the equation:[14] $[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b \cdot (\varepsilon_b - \varepsilon_f)$ by a plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA], where [DNA] is the concentration of DNA as base pairs. The ap-

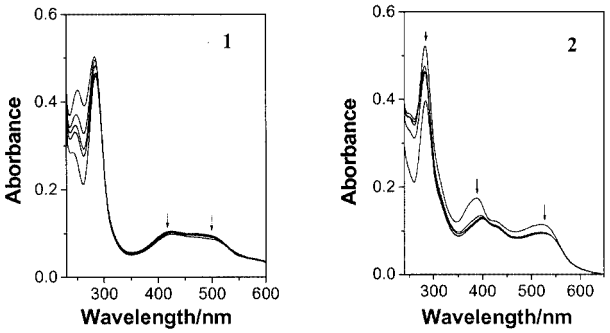


Figure 2. Absorption spectra of complexes **1** and **2** in Tris-HCl buffer upon addition of calf thymus DNA; [Ru] = 4 μM, [DNA] = (0−60) μM; the arrow shows the absorbance change upon increasing DNA concentrations

Table 2. Electronic absorption spectral changes upon addition of CT-DNA

Complexes	λ_{max}/nm free	bound	Bathochromism $\Delta\lambda$/ nm	Hypochromism %	K_b/M^{-1}
1	483	488	5	8.7	7.5×10^4
	422	426	4	8.2	
	284	274	−10	12	
2	523	528	5	19	4.8×10^5
	388	402	4	28.2	
	283	285	2	24	
3	492	506	14	33	7.6×10^5
	426	427	1	26	
	280	282	2	31	

parent absorption coefficients ε_a, ε_f and ε_b correspond to A_{obsd}/[Ru], the extinction coefficient for the free ruthenium complex and the extinction coefficient for the ruthenium complex in the fully bound form, respectively. The slope and *y* intercept of the linear fit of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA] give $1/(\varepsilon_b - \varepsilon_f)$ and $1/K_b \cdot (\varepsilon_b - \varepsilon_f)$, respectively. The intrinsic binding constant K_b can be obtained from the ratio of the slope and the *y* intercept. The intrinsic binding constants K_b of complexes **1**, **2** and **3** were calculated from the decrease of the absorbance to be 7.5×10^4, 4.8×10^5 and 7.6×10^5 M^{-1}, respectively. The K_b's of complexes **1**, **2** and **3** are smaller than that observed for $[Ru(bpy)_2(dppz)]^{2+}$ ($>10^6$ M^{-1}),[15] but larger than that observed for Δ-$[Ru(phen)_3]^{2+}$ (6.2×10^3 M^{-1}).[15] The experiments suggest that the three complexes may be bound to DNA by groove binding and that increasing the size of the plane of the bridging ligand increases the hydrophobicity of their complexes, leading to stronger binding by the complexes to calf thymus DNA.

Enantioselectivity of DNA-Binding

Equilibrium dialysis experiments offer the opportunity to examine the enantioselectivities of DNA-binding by the complexes. Figure 3 shows the UV region of the CD spectra for the dimeric ruthenium complexes **1**, **2** and **3** after their

racemic solutions had been dialyzed against calf thymus DNA with stirring for 48 h. An interesting phenomenon was observed in the equilibrium dialysis of the complexes. After dialysis against calf thymus DNA with stirring for 48 h, the dialyzate of complex **3** shows two strong CD signals, with a positive peak at 263 nm and a negative peak at 289.5 nm, which are the CD signals of the ΔΔ-enantiomer of complex **3** assigned by comparison with the CD spectrum of the chiral complex **3.**[16] The presence of these signals indicates enrichment of the isomer which is less likely to bind DNA, indicating that the ΛΛ-enantiomer binds DNA more strongly than the ΔΔ-enantiomer. The other complexes, **1** and **2**, don't show strong CD signals for their enantiomers indicating that complexes **1** and **2** do not bind DNA stereoselectively. The results indicate that complex **3** is an enantioselective binder of DNA while complexes **1** and **2** are not, which may be explained by the differences in the bridging ligand of the complexes: the plane of the bridging ligand for **3** is the largest of the three complexes. To the best of our knowledge, complex **3** is the first example of a dinuclear ruthenium(II) complex binding enantioselectively to CT-DNA measured by equilibrium dialysis. Furthermore, it is interesting to observe that the ΛΛ-bpy complex was found to bind DNA more strongly than the ΔΔ-bpy complex, as indicated by the presence of CD signals. This contrasts with previous reports in which the ΔΔ-diruthenium(II) complexes show preferential DNA binding.[10]

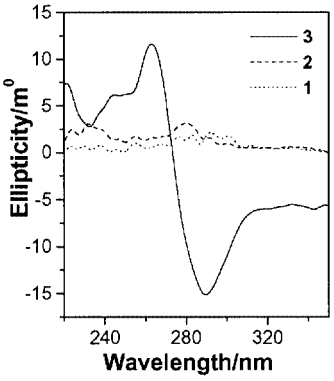


Figure 3. CD spectrum of complexes **1**, **2**,and **3** after 48 h of dialysis against calf thymus DNA with stirring of the solution

The equilibrium dialysis results indicate that complex **3** is a good candidate as an enantioselective binder of DNA.

Viscosity Measurements

In order to further clarify the interaction of the complexes **1**, **2** and **3** with DNA, viscosity measurements were carried out. Optical probes provide essential, but insufficient, evidence to support a binding model. Hydrodynamic measurements, which are sensitive to changes in molecular length (i.e. viscosity and sedimentation), are regarded as the least ambiguous and the most critical tests of a binding model in solution in the absence of crystallographic data.[17] A classical intercalation model demands that the DNA helix must lengthen as base pairs are separated to accommodate the binding ligand, leading to an increase in DNA viscosity. In contrast, a partial and/or non-classical intercalating ligand could bend (or kink) the DNA helix, reducing its effective length and, concomitantly, its viscosity.[18] The effects of complexes **1**, **2** and **3** on the viscosity of rod-like DNA are shown in Figure 4 together with the corresponding data for ethidium bromide (EB) and $[Ru(bpy)_3]^{2+}$.

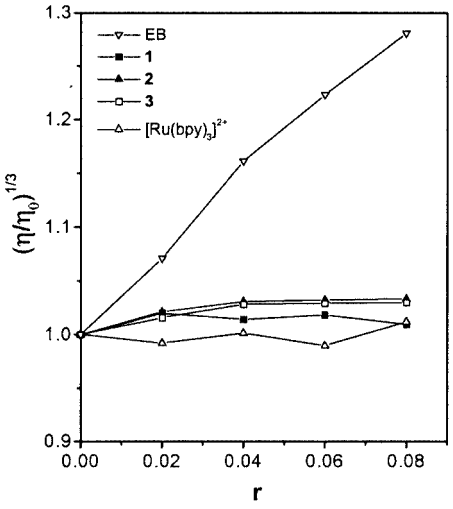


Figure 4. Effect of increasing amounts of complexes **1**, **2**, **3**, ethidium bromide (EB) and the parent complex $[Ru(bpy)_3]^{2+}$ on the relative viscosities of CT-DNA at 28.0 (± 0.1) °C, [DNA]= 0.5 mM and r = [Ru]/[DNA]

The experiments suggest that the dimeric ruthenium(II) complexes bind to the polyanionic DNA via a non-intercalating mode and may be bound to DNA by groove binding.

Conclusion

Three new asymmetric binuclear ligands 2,2′-bis(1,2,4-triazin-3-yl)-4,4′-bipyridine (btb), 2,2′-bis(1,2,4-triazino-[5,6-*f*]acenaphthylen-3-yl)-4,4′-bipyridine (btapb), 2,2′-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-4,4′-bipyridine (bdptb) and their binuclear bpy complexes $[Ru(bpy)_2(btb)Ru(bpy)_2](ClO_4)_4$ (**1**), $[Ru(bpy)_2(btapb)Ru(bpy)_2](ClO_4)_4$ (**2**), $[Ru(bpy)_2(bdptb)Ru(bpy)_2](ClO_4)_4$ (**3**) were synthesized and characterized. Binding behavior of these dimeric complexes with calf thymus DNA was investigated by electronic absorption spectroscopy, viscosity measurements and equilibrium dialysis experiments. The results indicate that the three complexes bind to polyanionic DNA in a non-intercalating mode and may be bound to DNA by groove binding, and that complex **3** is a good candidate as an enantioselective binder of DNA.

Experimental Section

Materials: All reagents and solvents were purchased commercially and used without further purification unless otherwise noted. Solutions of calf thymus DNA in 50 mM NaCl/5 mM Tris-HCl (pH 7.2) gave a ratio of UV absorbance at 260 and 280 nm of 1.8−1.9:1, indicating that the DNA was sufficiently free of protein.[19] The DNA concentration per nucleotide was determined by electronic absorption spectroscopy using the molar absorption coefficient (6600 $M^{-1}\cdot cm^{-1}$) at 260 nm.[20] Doubly distilled water was used to prepare buffers.

Physical Measurements: Microanalysis (C, H, and N) was carried out with a Perkin−Elmer 240Q elemental analyzer. Fast atom bombardment mass spectra were recorded on a VG ZAB-HS spectrometer using 3-nitrobenzyl alcohol as the matrix. Electrospray mass spectra were recorded on an LCQ system (Finnigan MAT, USA) using methanol as the mobile phase. The spray voltage, tube lens offset, capillary voltage and capillary temperature were set at 4.50 kV, 30.00 V, 23.00 V and 200 °C, respectively, and the quoted *m*/*z* values are for the major peak in the isotope distribution. ^{1}H NMR spectra were recorded on a Varian-500 spectrometer. All chemical shifts are relative to tetramethylsilane (TMS). UV/Vis spectra were recorded on a Shimadzu UV-3101PC or Agilent 8453 spectrophotometer. Emission spectra were recorded at room temperature on a Shimadzu RF-5000 luminescence spectrometer.

Viscosity measurements were carried out using an Ubbelodhe viscometer maintained at a constant temperature of 28.0 ± 0.1 °C in a thermostatted water bath. DNA samples of approximately 200 base pairs average length were prepared by sonication in order to minimize complexities arising from DNA flexibility.[21] Flow time was measured with a digital stopwatch. Each sample was measured three times and an average flow time was calculated. Data are presented as $(\eta/\eta^\circ)^{1/3}$ versus binding ratio,[22] where η is the viscosity of DNA in the presence of complex and η^0 is the viscosity of DNA alone.

Equilibrium dialyses were conducted at room temperature with 5 mL of CT-DNA (1.0 mM) sealed in a dialysis bag and 10 mL of the dinuclear rac complexes (10 μM) outside the bag. The solution containing the dialysis bag was stirred for 48 h.

Syntheses of Complexes

2,2′-Bis[amino(hydrazono)methyl]-4,4′-bipyridine (bahmb),[16] *cis*-$Ru(bpy)_2Cl_2$[23] were prepared as described previously.

2,2′-Bis(1,2,4-triazin-3-yl)-4,4′-bipyridine (btb): A mixture of bahmb (0.27 g, 1 mmol), 30% aqueous glyoxal (5 mL), and ethanol (20 mL) was refluxed with stirring for 2 h. After cooling to room temperature, the yellow precipitate was collected by filtration, washed with ethanol (3×5 cm^3), then dried at 50 °C in vacuo. Yield: 78%. $C_{16}H_{10}N_8$ (314.3): calcd. C 61.1, H 3.2, N 35.7; found C 59.8, H 2.9, N 36.2. FAB-MS: *m*/*z* = 315 ($C_{16}H_{10}N_8$ requires 314). ^{1}H NMR ([D$_6$]DMSO): 9.55 (d, *J* = 2.5 Hz, 2 H), 9.08 (d, *J* = 2.5 Hz, 2 H), 9.03 (dd, 2 H, *J* = 2.5, J_1 = 1, J_2 = 5.5 Hz), 8.90 (dd, J_1 = 0.5, J_2 = 1.5 Hz, 2 H), 8.19 (s, 2 H) ppm.

2,2′-Bis(1,2,4-triazino[5,6-*f*]acenaphthylen-3-yl)-4,4′-bipyridine (btapb): A mixture of bahmb (0.27 g, 1 mmol), acenaphthenequinone (0.346 g, 1.9 mmol) and ethanol (40 mL) was refluxed with stirring for 4 h. The resulting yellow precipitate was collected by filtration while hot, washed with ethanol (3×5 mL), then dried at 50 °C in vacuo. Yield: 72%. $C_{36}H_{18}N_8$ (562.6): calcd. C 76.9, H 3.2, N 19.9; found C 77.3, H 3.6, N 20.2. FAB-MS: *m*/*z* = 564 ($C_{36}H_{18}N_8$ requires 563). ^{1}H NMR ($CDCl_3$): 9.29 (d, *J* = 7.5 Hz, 2 H), 9.17 (d, *J* = 5 Hz, 2 H), 8.65 (dd, 2 H, J_1 = 5.5, J_2 =12 Hz), 8.31 (d, *J* = 8.5 Hz, 2 H), 8.24 (d, *J* = 8 Hz, 2 H), 8.18 (d, 2 H, J_1 = 2.5, J_2 = 9 Hz), 8.04 (d, *J* = 8 Hz, 2 H), 7.82 (t, *J* = 8 Hz, 2 H), 7.70 (t, *J* = 8 Hz, 2 H) ppm.

2,2′-Bis(5,6-diphenyl-1,2,4-triazin-3-yl)-4,4′-bipyridine (bdptb): A mixture of bahmb (0.27 g, 1.0 mmol), benzil (0.4 g, 1.9 mmol), and ethanol (40 cm^3) was refluxed with stirring for 4 h. The resulting yellow precipitate was collected by filtration while hot, washed with ethanol (3×5 mL), then dried at 50 °C in vacuo. Yield: 75%. $C_{40}H_{26}N_8$ (618.7): calcd. C 77.6, H 4.2, N 18.1; found C 78.0, H 3.9, N 18.2. FAB-MS: *m*/*z* = 619 ($C_{40}H_{26}N_8$ requires 618). ^{1}H NMR ($CDCl_3$): 9.13 (d, *J* = 2.5 Hz, 2 H), 9.11 (d, 2 H, *J* = 5 Hz), 7.9 (dd, 2 H, J_1 = 2, J_2 =5 Hz), 7.72 (dd, 4 H, J_1 = 1, J_2 = 8.5 Hz), 7.66 (dd, 4 H, J_1 = 1, J_2 = 8 Hz), 7.47 (t, *J* = 8 Hz, 4 H), 7.41 (t, *J* = 8 Hz, 4 H), 7.39 (t, *J* = 7 Hz, 4 H) ppm.

$[Ru(bpy)_2(btb)Ru(bpy)_2](ClO_4)_4$ (1): *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (1 mmol, 0.432 g), btb (0.5 mmol, 0.157 g) and ethylene glycol (20 cm^3) were refluxed under argon for 6 h. The solution was cooled to room temperature, and H_2O (50 cm^3) was added. After filtration, a dark red precipitate was obtained by dropwise addition of aqueous $NaClO_4$ solution. The product was purified by column chromatography on alumina using acetonitrile/ethanol, 2:1 (v/v) as eluent and then dried in vacuo. Yield: 66%. $C_{56}H_{42}N_{16}Cl_4O_{16}Ru_2\cdot 2H_2O$ (1570.0): calcd. C 42.7, H 2.9, N 14.2%; found C 42.3, H 3.3, N 14.1%. ES-MS [CH_3OH, *m*/*z*]: 670.6 $[M - 2ClO_4]^{2+}$, 413.4 $[M - 3ClO_4]^{3+}$, 285.6 $[M - 4ClO_4]^{4+}$. ^{1}H NMR ([D$_6$]DMSO): δ = 9.33 (d, *J* = 6 Hz, 2 H), 9.18 (s, *J* = 6 Hz, 2 H), 9.16 (d, *J* = 6 Hz, 2 H), 8.91 (d, *J* = 10.5 Hz, 2 H), 8.88 (d, *J* = 7.5 Hz, 2 H), 8.85 (d, *J* = 12.5 Hz, 2 H), 8.81 (d, *J* = 8 Hz, 2 H), 8.27 (t, *J* = 8 Hz, 2 H), 8.24−8.19 (m, 6 H), 8.17 (d, *J* = 4 Hz, 2 H), 8.12 (d, *J* = 8 Hz, 4 H), 7.85 (d, *J* = 8 Hz, 4 H), 7.64 (t, *J* = 1 Hz, 4 H), 7.35 (dd, 4 H, J_1 = 7.5, J_2 =12 Hz) ppm.

$[Ru(bpy)_2(btapb)Ru(bpy)_2](ClO_4)_4$ (2): This complex (dark red) was synthesized in a similar manner to that described for complex **1**, with btapb (0.5 mmol, 0.286 g) in place of btb. Yield: 65%. $C_{76}H_{50}Cl_4N_{16}O_{16}Ru_2\cdot 3H_2O$ (840.0): calcd. C 49.6, H 3.1, N 12.2; found C 50.0, H 2.9, N 12.4. ES-MS [CH_3OH, *m*/*z*]: 793.4 $[M - 2ClO_4]^{2+}$, 496.5 $[M - 3ClO_4]^{3+}$, 347.7 $[M - 4ClO_4]^{4+}$. ^{1}H NMR ([D$_6$]DMSO): δ = 9.31 (s, 2 H), 8.98 (d, *J* = 8.5 Hz, 2 H), 8.93 (d, *J* = 8.5 Hz, 2 H), 8.87 (d, *J* = 7.5 Hz, 2 H), 8.83 (d, *J* = 8.5 Hz, 2 H), 8.75 (d, *J* = 7 Hz, 2 H), 8.59 (d, *J* = 8.5 Hz, 2 H), 8.52 (d, *J* = 8.5 Hz, 2 H), 8.33−8.27 (m, 8 H), 8.19 (dd, 6 H, J_1 = 7.5, J_2 = 19.5 Hz), 8.14 (t, *J* = 8 Hz, 2 H), 8.00 (dd, 4 H, J_1 = 6.5, J_2 =14 Hz), 7.94 (t, *J* = 5 Hz, 4 H), 7.82 (d, *J* = 5 Hz, 2 H), 7.70 (t, *J* = 7 Hz, 2 H), 7.64 (t, *J* = 7 Hz, 2 H), 7.56 (dd, 2 H, *J* = 7 Hz), 7.46 (dd, 2 H, J_1 = 6, J_2 = 11.5 Hz) ppm.

$[Ru(bpy)_2(bdptb)Ru(bpy)_2](ClO_4)_4$ (3): This complex (dark red) was synthesized in a similar manner to that described for complex **1**, with bdptb (0.5 mmol, 0.307 g) in place of btb. Yield: 68%. $C_{80}H_{58}Cl_4N_{16}O_{16}Ru_2\cdot H_2O$ (1856.1): calcd. C 51.6, H 3.3, N 12.0%; found C 51.8, H 3.6, N 12.3%. ES-MS [CH_3OH, *m*/*z*]: 821.6 $[M - 2ClO_4]^{2+}$, 516 $[M - 3ClO_4]^{3+}$, 361.7 $[M - 4ClO_4]^{4+}$. ^{1}H NMR ([D$_6$]DMSO): δ = 9.17 (s, *J* = 2 Hz, 2 H), 8.93 (d, *J* = 8 Hz, 2 H), 8.88 (d, *J* = 8 Hz, 2 H), 8.78 (t, *J* = 8 Hz, 4 H), 8.29 (dd, 6 H, J_1 = 7.5, J_2 = 9 Hz), 8.14 (dd, 2 H, J_1 = 1, J_2 = 5.5 Hz), 7.94 (t, *J* = 9 Hz, 2 H), 7.88 (d, *J* = 5.5 Hz, 2 H), 7.75 (t, *J* = 5.5 Hz, 6 H), 7.67 (t, *J* = 5.5 Hz, 2 H), 7.60−7.52 (m, 8 H), 7.48−7.40 (m, 6 H), 7.11 (d, *J* = 7.5 Hz, 4 H) ppm.

Acknowledgments

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