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Ruthenium Complex Fragments as Constituents of Trinuclear Photoactive Supramolecular Assemblies Based on Hydrogen Bond Association

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The reaction of the octahedral complexes *cis*- or *trans*-$[Ru(C{\equiv}N\text{-}tBu)_4(CN)_2]$, ($Ru(CN)_2$), with the photochemically active [bis(bipyridyl)bibenzimidazole-ruthenium(II)], ($RubiH_2$), component via hydrogen bond association results in the formation of supramolecular aggregates with modified photophysical properties. The first structural characterization of a supramolecular adduct is reported, in which the N–H functions of the ruthenium bound bibenzimidazole ligand via hydrogen bonds serve as an interface directly toward a cyanide ligand acting as a bridge to another transition metal. In addition, the maximum stoichiometry of the supramolecular associates is estimated by NMR titration experiments and association constants of the hydrogen bonded adducts are determined by the decay of the emission intensity during the titration experiments.

Introduction

One of the most challenging goals in chemistry is the conversion of sunlight into electrical, chemical or even mechanical energy. In order to achieve this goal a detailed understanding of suitable chromophore–quencher complexes is a crucial prerequisite for the construction of e.g. photovoltaic cells. Chromophore systems based on transition metals have been widely investigated for polypyridyl complexes[1] or on the basis of porphyrin complexes[2] closely resembling the natural chlorophyll chromophore used in photosynthetic organisms. In general, these efforts may be subdivided into systems in which the chromophore and the quencher are linked via strong interactions like covalent bonds or coordinative bonds on one side and aggregates that are interconnected via weak interactions like hydrogen bonds, hydrophobic interactions or π-stacking effects on the other side.[3]

The construction of multicentred supramolecular assemblies using complementary hydrogen-bond donor and acceptor sites is very appealing due to its synthetic advantages and intrinsic modular approach. In most examples that have been described in the literature up to now metal hybrid assemblies or organic assemblies have been investigated and hydrogen bonds between carboxylic acids (which by definition are self-complementary), nucleobases or protonated cyclam units were used to construct supramolecular assemblies of two different coordination complexes.[3] Campagna as well as Ward and co-workers have shown that Ru^{II} complexes may act as quencher components if they are assembled to suitable chromophore systems via hydrogen bonds realized by cyanide ligands.[3a,3c] Nevertheless, it has to be pointed out that the syntheses of bipy, terpy or porphyrin ligands with pendant nucleobase or cyclam units still are complex multi-step procedures and the distance between the photochemically active metal center and the additional coordination complex subunit is quite large.

We herein report the synthesis and characterisation of supramolecular assemblies between different Ru^{II} complexes where it is possible to control not only the photophysical properties of the chromophore but also the geometry and nuclearity of the aggregates formed. The control over the geometry can be exercised by variation of the H-bond acceptor utilised whereas the nuclearity can be influenced by simple stoichiometry.

Results and Discussion

Recently, some of us reported the synthesis of complexes of the type $[Ru(bipy^*)_2(biH_2)]^{2+}$ (biH_2 = 5,5′,6,6′-tetramethyl-2,2′-bibenzimidazole, bipy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine) which show photophysical properties that are comparable to those of the well-known $[Ru(bipy)_3]^{2+}$ compounds.[4] One of the most important features of the biH_2 ligand is the fact that the N–H functions are very efficient hydrogen-bond donor sites leading to the coordination of anions or solvent molecules in almost all structurally

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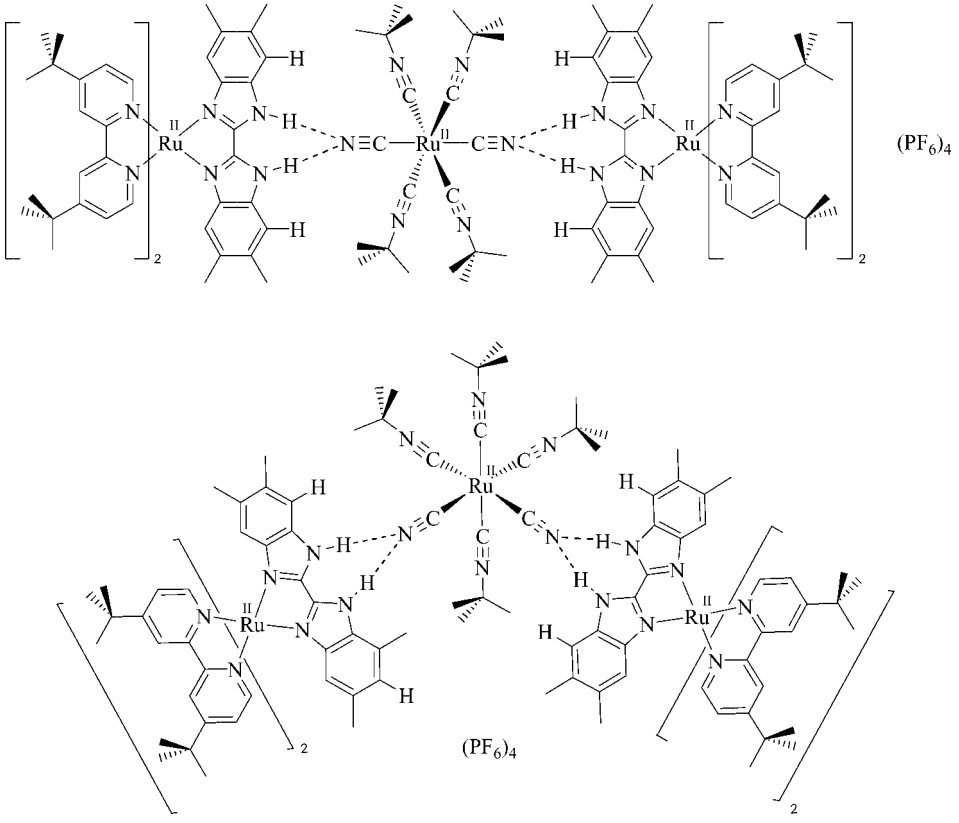
characterized derivatives.[5] It has already been demonstrated that a hydrogen-bonded adduct of this ruthenium complex together with an osmium compound containing a carboxylated bipy ligand exhibits an effective energy transfer from Ru to Os upon irradiation.[3c] So we decided to combine a $[Ru(bipy^*)_2(biH_2)]^{2+}$ complex with compounds of the type $[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$, which are easily accessible as a 1:1 mixture of the *cis*- and *trans*-isomers from the reaction of $Ru_3(CO)_{12}$ with *tert*-butyl isocyanide in the presence of of carbon monoxide (p = 10 atm).[6]

Scheme 1 shows two possible 2:1 adducts of $[Ru(bipy^*)_2(biH_2)]^{2+}$ and $[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$ in *cis*- and *trans*-conformation. The assumption of 2:1 adducts under stoichiometric conditions seems to be reasonable from a thermodynamic point of view because it provides the formation of a maximum number of hydrogen bonds. This assumption is additionally confirmed by NMR titration experiments which show that the signal representing the protons in 4,4′-position of the biH_2 ligand is significantly influenced by the stepwise addition of *cis*-$[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$ (Figure 1). Compared to solutions of pure $RubiH_2$ the addition of *cis*-$Ru(CN)_2$ leads to a downfield shift of the corresponding signal. The effect is much less pronounced if the *trans*-isomer of the cyano complex is used presumably due to less steric interaction with the protons in 4,4′-position of the bibenzimidazole ligand in this case. In Figure 2 the product ($m_f \times \Delta\delta$) is plotted against the molar fraction itself. It can be seen that up to a m_f value of app. 0.66 representing a ratio $Ru(CN)_2$:$RubiH_2$ = 2:1 an increase of ($m_f \times \Delta\delta$) is observed whereas for higher m_f values a decrease of ($m_f \times \Delta\delta$) becomes evident. From this behaviour we can conclude that the maximum stoichiometry of hydrogen bonded associates consisting of $Ru(CN)_2$ and $RubiH_2$ in solution is 2:1.[7] Similar NMR titration experiments have also been used to determine the association constants of hydrogen bonded adducts.[3e,8] Nevertheless, this approach is only successful for associates of a 1:1 composition meaning that for the estimation of association constants of the aggregates that are present in our solutions we had to employ another method.

The fact that hydrogen bonds are readily formed in solution and that the so formed associates are quite stable is verified by the IR spectra of the corresponding mixtures which show a shift in the stretching frequencies of the cyanide and isocyanide ligands (cf. Experimental Part). For all molar fractions higher than 0.33 ($Ru(CN)_2$:$RubiH_2$ = 1:2) no bands corresponding to the free cyano complexes are visible in the IR spectra. So e.g. for mixtures of *trans*-$[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$ and $[Ru(bipy^*)_2(biH_2)]^{2+}$ in a 1:2 ratio, the corresponding bands are observed at 2164 and 2101 cm^{-1} compared to 2150 and 2108 cm^{-1} for pure *trans*-$[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$.[6] In the ESI-MS spectra of both compounds, peaks corresponding to the cationic 1:1 supramolecular assemblies $\{[Ru(bipy^*)_2(biH_2)][Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]\}(PF_6)$ are observed (cf. Experimental Part).

Recrystallization of a mixture of $[Ru(bipy^*)_2(biH_2)](PF_6)_2$ and *trans*-$[Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]$ in a 2:1 ratio from dichloromethane yielded crystals suitable for X-ray diffraction.[9] The supramolecular structure of the hydrogen-



Scheme 1. Hydrogen bonded 2:1 adducts produced by the interaction of N–H functions and cyanide ligands.

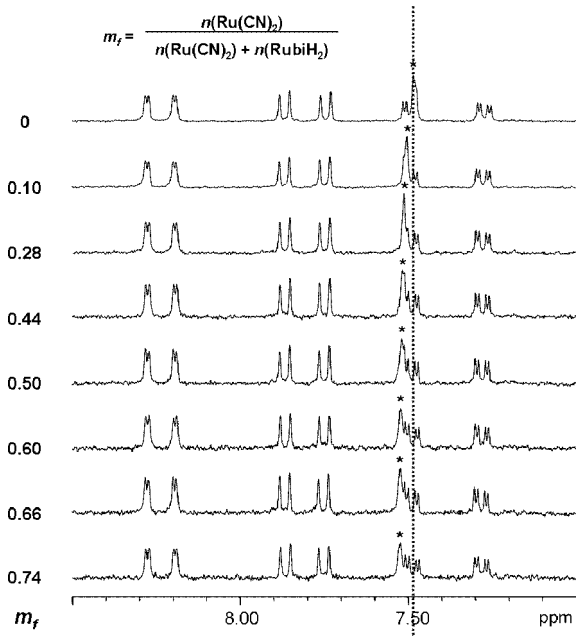


Figure 1. Section of the ^{1}H-NMR spectra of [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ and [*cis*-Ru(C≡N-*t*Bu)$_4$(CN)$_2$] at various molar fractions (m_f = n(Ru(CN)$_2$)/[n(Ru(CN)$_2$) + n(RubiH$_2$)]; signal of the 4,4′-position marked with an asterisk).

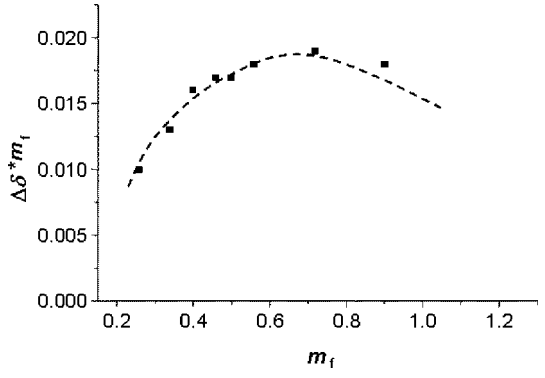


Figure 2. ($\Delta\delta^* \times m_f$) vs. m_f plot showing the maximum stoichiometry of hydrogen bonded adducts in solution to be of the composition Ru(CN)$_2$:RubiH$_2$ = 2:1 (m_f = 0.66).

bonded adduct is depicted in Figure 3. It is obvious that indeed a 2:1 assembly has been formed. All ruthenium atoms show a virtually perfect octahedral coordination sphere and bond lengths and angles of the ligands are as expected (Table 1). The observed monoclinic space group $P2_1/c$ shows Ru2 to be situated at the crystallographic center of inversion. Both N–H functions of the bibenzimidazole ligand are engaged in hydrogen bonds. N2–H2 acts as a hydrogen-bond donor site towards the cyanide nitrogen atom N9 with an N–N distance of 278(2) pm and a N2–H2···N9 bond angle of 166(1) deg. The second N–H group N4–H4 shows a hydrogen bond towards a water molecule (N4–O1w 282(2) pm, N4–H4···O1w 159(1) deg). The distance of 301(2) pm between O1w and N9 is indicative of another weak hydrogen bond between a proton of the water molecule and the cyanide nitrogen atom. The hydrogen bond lengths and angles fit very well to numerous examples of weak hydrogen bonding described in the literature.[10] Figure 3 also shows a view of the hydrogen-bonded adduct down the plane of the bibenzimidazole ligands. All carbon and hydrogen atoms of the bipy*, biH$_2$ (except C1 and C8) and *tert*-butyl groups have been omitted. The angle between the bibenzimidazole plane and the Ru2(CN)$_2$ plane measures to 131(2) deg.

It should be pointed out that from the same recrystallization another crystal has been investigated by means of X-ray crystallography (cf. Supporting Information). Although the quality of this crystal was inferior compared to the structure determination shown in Figure 3, the structural motif in this crystal structure unequivocally reveals a hydrogen bond network with the cyanide ligands being situated symmetrically between the two N–H groups of the bibenzimidazole ligands like it is depicted in Scheme 1. These different supramolecular assemblies clearly demonstrate that polar solvents compete for the hydrogen-bond donor sites with the cyanide ligands.

To the best of our knowledge these compounds are the first structurally characterized adducts of a photochemically active [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ complex in which the N–H functions are connected via hydrogen bonds directly to a cyanide ligand acting as a bridge to another transition metal. We therefore explored the influence of the binding of the cyano compound to the photochemically active ruthenium bibenzimidazole complex on the photophysical properties of the latter. Solutions of pure [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ typically exhibit a strong emission at app. 650 nm. Figure 4 illustrates the emission spectra of mixtures of [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ and *trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$] depending on the molar fraction of the cyano complex. It clearly demonstrates that there is a decay in emission intensity with increasing amount of *trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$] until the emission is almost completely quenched. In addition, the emission is shifted to app. 675 nm. Since the formation of hydrogen bonds may be understood in terms of an acid base reaction this bathochromic shift corresponds to observations reported in the literature, that deprotonation of the N–H functions in [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ complexes leads to quenching or at least a strong bathochromic shift of the emission band.[11] The emission intensities of solutions of the same concentrations of [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ are considerably higher than those of mixtures of [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ and *trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$]. The corresponding plot for *cis*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$], which may be found in the Supporting Information, is virtually identical. We therefore conclude that in both cases 1:1 and 2:1 adducts are readily formed in the quite diluted solutions that are used for the spectroscopic investigations (c(*cis*/*trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$]) + c([Ru(bipy*)$_2$(biH$_2$)]$^{2+}$) = 2.573×10^{-6} mol L^{-1}). In addition, a dilution experiment of a 2:1 mixture of *trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$] and [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ shows that the emission intensities for the mixtures are significantly lower than the emission intensity of [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ alone in a blank experiment down

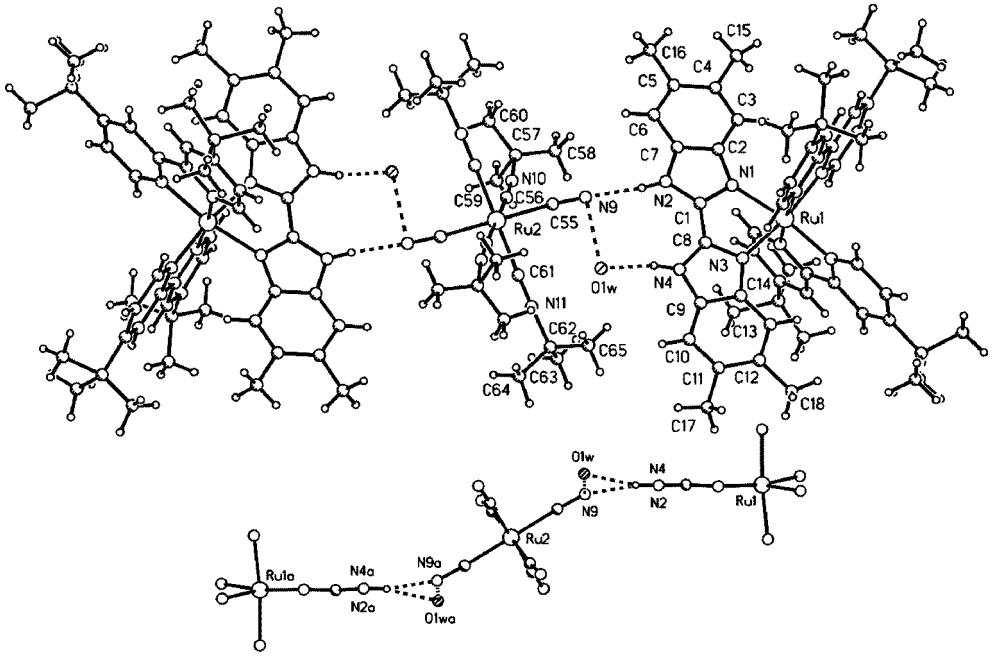


Figure 3. Molecular Structure of $\{[Ru(bipy^*)_2(biH_2)]_2[trans\text{-}Ru(C{\equiv}N\text{-}t\text{Bu})_4(CN)_2]\}^{4+} \times 2H_2O$; anions and additional solvent molecules have been omitted for the sake of clarity.

Table 1. Selected bond lengths [pm] and angles [°] of $\{(trans\text{-}Ru(CN)_2)(RubiH_2)_2\}(PF_6)_4 \times 8\ CH_2Cl_2 \times 6\ H_2O \times 2\ CH_3OH$.

Ru1–N1	210.0(6)	Ru1–N3	210.1(6)	Ru1–N5	206.7(7)
Ru1–N6	204.6(6)	Ru1–N7	204.7(6)	Ru1–N8	204.4(7)
N1–C1	133(1)	C1–N2	139(1)	N2–C7	139(1)
C7–C2	139(1)	C2–N1	141(1)	C1–C8	143(1)
N3–C8	135(1)	C8–N4	136(1)	N4–C9	136(1)
C9–C14	142(1)	C14–N3	138(1)	Ru2–C55	202.6(9)
Ru2–C56	200(1)	Ru2–C61	202.3(9)	C55–N9	116(1)
C56–N10	115(1)	C61–N11	115(1)	N2–N9	278(2)
N4–O1w	282(2)	N9–O1w	301(2)		
N1–Ru1–N3	77.5(3)	N1–Ru1–N5	88.2(3)	N1–Ru1–N6	95.4(2)
N1–Ru1–N7	170.6(3)	N1–Ru1–N8	95.7(3)	N3–Ru1–N5	93.6(3)
N3–Ru1–N6	169.5(3)	N3–Ru1–N7	95.9(2)	N3–Ru1–N8	91.9(3)
N5–Ru1–N6	78.4(3)	N5–Ru1–N7	98.9(3)	N5–Ru1–N8	173.9(2)
N6–Ru1–N7	92.0(2)	N6–Ru1–N8	96.5(3)	N7–Ru1–N8	77.8(3)
N1–C1–N2	113.3(7)	C2–N1–C1	105.9(6)	N1–C2–C7	107.2(7)
C2–C7–N2	108.2(7)	C7–N2–C1	105.3(7)	N1–C1–C8	117.0(7)
N2–C1–C8	129.6(7)	N3–C8–N4	111.5(7)	C8–N4–C9	107.8(7)
N4–C9–C14	106.5(7)	C9–C14–N3	108.2(7)	C14–N3–C8	105.9(6)
N3–C8–C1	116.4(7)	N4–C8–C1	132.1(8)	C55–Ru2–C56	89.1(4)
C55–Ru2–C61	88.0(4)	C56–Ru2–C61	95.1(4)	Ru2–C55–N9	175.8(9)
Ru2–C56–N10	173.1(9)	Ru2–C61–N11	172.0(9)		

to a concentration of app. 5×10^{-7} mol L^{-1} demonstrating the stability of the hydrogen bonded adducts.

One major question arising in the investigation of the supramolecular adducts described herein is the question concerning the association constants of these associates. In the literature either NMR titration experiments or Stern–Volmer plots have frequently been employed in similar cases. Nevertheless, these approaches have almost exclusively been applied to 1:1 adducts. From NMR experiments (vide supra) and from the fact that a distinct decrase of the emission intensity is observed up to a $m_f = 0.66$ (and a much less pronounced decrase for higher concentrations of $Ru(CN)_2$) we conclude that in solution adducts of the general formula $\{(RubiH_2)(Ru(CN)_2)_2\}$ are formed. We therefore have to address the question of the equilibrium constant of the following reaction

$$\{(RubiH_2)(Ru(CN)_2)_2\} \rightleftharpoons RubiH_2 + 2\ Ru(CN)_2$$

with the mass-action law

$$K_D = \frac{c(RubiH_2) \cdot c(Ru(CN)_2)^2}{c\{(RubiH_2)(Ru(CN)_2)_2\}}$$

providing us with the dissociation constant K_D. From the mass-action law we can conclude

$$\log\left(\frac{c(\mathrm{RubiH_2})}{c\{(\mathrm{RubiH_2})(\mathrm{Ru(CN)_2})_2\}}\right) = -2\log(c(\mathrm{Ru(CN)_2})) - \mathrm{p}K_D$$

Applying a methodology that has been used to elucidate the pK_a values of bibenzimidazole ligands in ruthenium complexes from absorption intensities depending on the amount of base present in the solution[12] we are now able to calculate the pK_D value from the emission intensity of pure $RubiH_2$ (I($RubiH_2$)), the emission intensities of mixtures with an excess of *cis*/*trans*-$Ru(CN)_2$ (I\{($RubiH_2$)($Ru(CN)_2$)$_2$\}) and the emission intensity of the mixtures with different concentrations of *cis*/*trans*-$Ru(CN)_2$ (I(M)).

$$\log\left(\frac{I\{(\mathrm{RubiH_2})(\mathrm{Ru(CN)_2})_2\} - I(\mathrm{M})}{I(\mathrm{M}) - I(\mathrm{RubiH_2})}\right) = -2\log(c(\mathrm{Ru(CN)_2})) - \mathrm{p}K_D$$

This means that a plot of the logarithmic term on the left side of the equation vs. –2 log(c($Ru(CN)_2$)) should give a linear function with the axis intercept representing the pK_D value of the corresponding supramolecular adduct. In Figure 5 a plot of the emission intensity vs. log(c(*trans*-$Ru(CN)_2$)) showing a sigmoidal shape typical for titration curves and another plot of the logarithmic term of the latter equation vs. –2 log(c(*trans*-$Ru(CN)_2$)) of linear shape are depicted. The titration of $RubiH_2$ with *cis*-$Ru(CN)_2$ leads to very similar plots although the sigmoidal shape of the titration curve is less pronounced (cf. Supporting Information). From the linear functions we can estimate a pK_D value for \{($Ru(biH_2)$(*cis*-$Ru(CN)_2$)$_2$\} of 7.1 and for

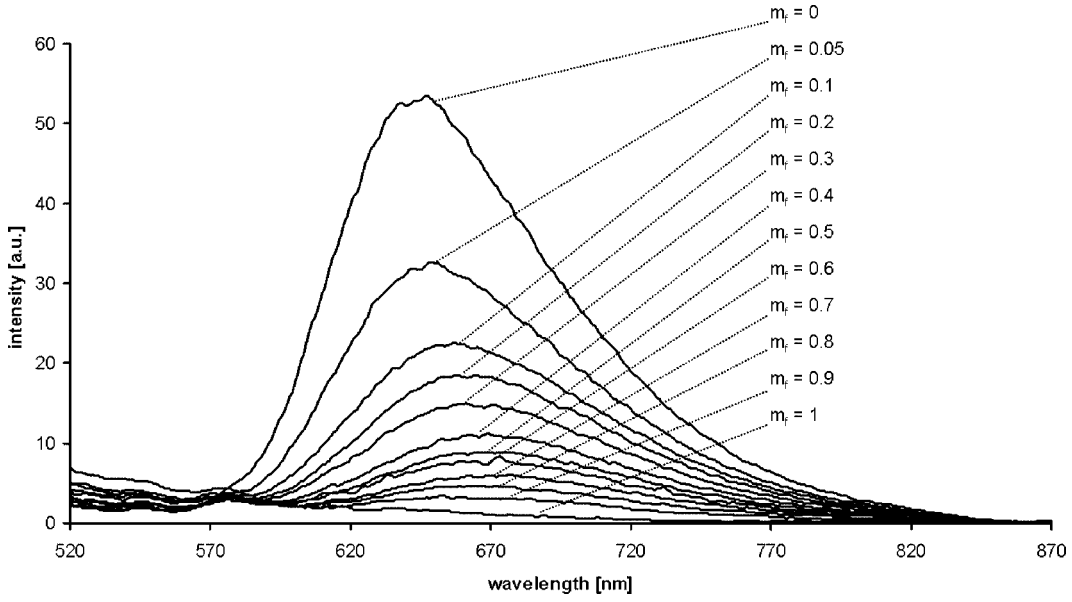


Figure 4. Emission spectra of the mixtures of [$Ru(bipy^*)_2(biH_2)$](PF_6)$_2$ and [*trans*-$Ru(C{\equiv}N\text{-}tBu)_4(CN)_2$] at various molar fractions.

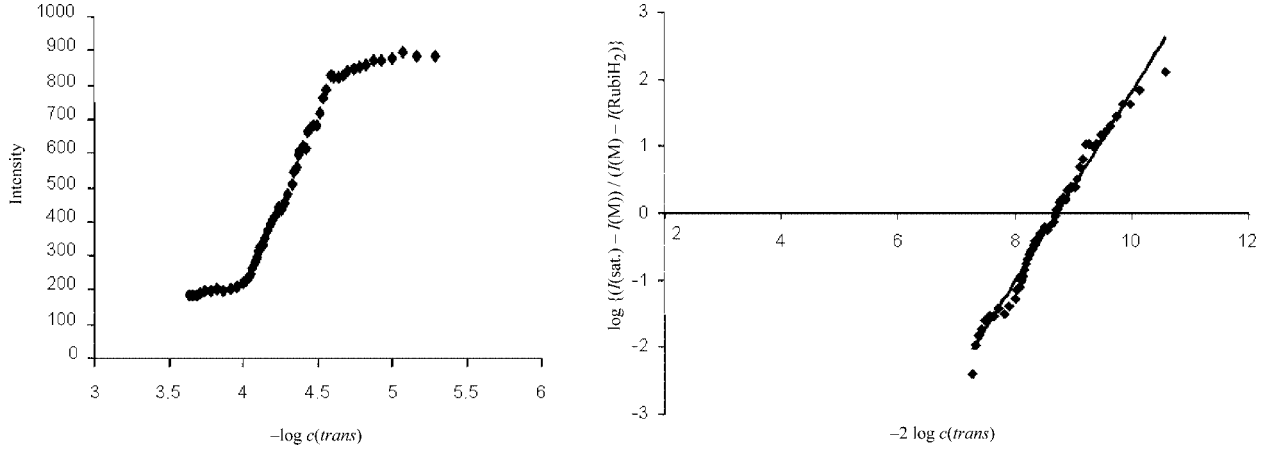


Figure 5. Emission intensity vs. log c(*trans*-$Ru(CN)_2$) plot (left) and log \{(I(sat.) – I(M))/(I(M) – (I($RubiH_2$)\} vs. –2 log c(*trans*-$Ru(CN)_2$).

{(Ru(biH$_2$)(*trans*-Ru(CN)$_2$)$_2$} a pK_D value of 12.3. The adduct of *trans*-Ru(CN)$_2$ thus is much more stable compared to the *cis* analogue which makes sense in terms of less steric interactions with the bibenzimidazole ligand leading to the much better pronounced saturation behaviour and titration curves.

The deactivation of the excited state of the [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ component may in principle be achieved by either electron or energy transfer from the [Ru(bipy*)$_2$(biH$_2$)]$^{2+}$ fragment to the cyano complex fragment. Taking into account the results described in the literature in connection with related systems[3] as well as cyclovoltammetric investigations of the cyano compounds showing that both isomers may be neither reduced nor oxidised makes the former possibility quite unlikely.

Experimental Section

All procedures were carried out in anhydrous, freshly distilled solvents. Infrared spectra were recorded on a Perkin–Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker DRX400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.62 MHz, $CDCl_3$ as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. Elemental analyses were carried out at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-Universität, Jena, Germany.

X-ray Crystallographic Studies: The structure determinations were carried out on a Enraf Nonius Kappa CCD diffractometer, the crystals being mounted in a stream of cold nitrogen, crystal detector distance 29 mm using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were dissolved by direct methods and refined by full-matrix least-squares techniques against F^2 using the programs SHELXS86 and SHELXL97.[13] All hydrogen atoms were constrained in idealized positions during the final stages of the refinement. The isotropic replacement parameters of all hydrogen atoms were fixed to 1.5 times the value of the corresponding carbon or nitrogen atom. The molecular illustrations were drawn using the program XP.[14]

CCDC-600734 and -600735 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***trans*-[Ru(C≡N-*t*Bu)$_4$(CN)$_2$] and [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ (1:1):** 20.1 mg (0.0165 mmol) [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ dissolved in dichloromethane were added to a solution of 8 mg (0.0165 mmol) *trans*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] in dichloromethane at room temperature. After 1 h the solvent was evaporated at room temperature resulting in the formation of a red powder (yield 28 mg). IR (CH_2Cl_2): $\tilde{\nu}$ = (CH) 3051 w, 2987 s, ν(-C≡N/-N≡C) 2163 vs, 2126 s, 2103 s, 1606 m, δ(CH) 1479 m, 1423 m, δ(–C(CH$_3$)$_3$) 1372 s, 1246 s, 1096 vs, 1015 vs, 846 vs cm^{-1}. MS (Micro-ESI in CH_2Cl_2/CH_3OH) *m*/*z*(%): 1559(2) [Ru(bipy*)$_2$(biH$_2$)(PF$_6$)Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$^+$, 994(10) [Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$_2$Na$^+$, 927(100) [Ru(bipy*)$_2$(biH$_2$)](-H)$^+$, 509(3) [Ru(CN)$_2$(C≡N-*t*Bu)$_4$]Na$^+$, 487 (3) [Ru(CN)$_2$(C≡N-*t*Bu)$_4$]H$^+$, 464(7) [Ru(bipy*)$_2$(biH$_2$)]$^{++}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.380 (s, 18 H, CH$_3$), 1.497 (s, 18 H, CH$_3$), 1.519 (s, 36 H, CH$_3$), 2.030 (s, 6 H, CH$_3$), 2.321 (s, 6 H, CH$_3$), 5.439 (s, 2 H, CH), 7.539 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.305 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.399 (s, 2 H, CH), 7.868 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.729 (d, $^3J_{HH}$ = 6.4 Hz, 2 H, CH), 8.295 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, CH), 8.221 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, CH) ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 20.649 (CH$_3$), 20.688 (CH$_3$), 30.384 (CH$_3$), 30.612 (CH$_3$), 30.758 (CH$_3$), 35.714 (C), 35.901 (C), 58.114 (C), 113.739 (CH), 115.978 (CH), 120.541 (CH), 124.855 (C), 125.560 (CH), 133.359 (C), 135.163 (C), 136.864 (C), 137.175 (-C≡N), 140.877 (C), 142.313 (-C≡N-*t*Bu), 143.449 (C), 151.859 (C), 152.668 (C), 157.521 (C), 159.180 (C), 161.938 (C), 162.664 (C) ppm.

***trans*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] and [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ (1:2):** 40.2 mg (0.033 mmol) [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ dissolved in dichloromethane were added to a solution of 8 mg (0.0165 mmol) *trans*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] in dichloromethane at room temperature. The solvent was evaporated at room temperature (yield 48 mg). Crystallisation from dichloromethane yielded red crystals which were suitable for X-ray diffraction studies. IR (CH_2Cl_2) [cm^{-1}]: ν(NH) 3379 m, ν(CH) 3072 w, 2968 s, ν(-C≡N/-N≡C) 2164 vs, 2101 s, 1613 m, δ(CH) 1480 m, 1414 m, δ(-C(CH$_3$)$_3$) 1371 s, 1203 s, 1097 vs, 1013 vs, 846 vs, 807 vs, 558 s. MS (Micro-ESI in CH_2Cl_2) *m*/*z*(%): 927(100) [Ru(bipy*)$_2$(biH$_2$)](-H)$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.384 (s, 36 H, CH$_3$), 1.500 (s, 36 H, CH$_3$), 1.520 (s, 36 H, CH$_3$), 2.041 (s, 12 H, CH$_3$), 2.320 (s, 12 H, CH$_3$), 5.438 (s, 4 H, CH), 7.540 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 6.2 Hz, 4 H, CH), 7.307 (d, $^3J_{HH}$ = 4.8 Hz, 4 H, CH), 7.410 (s, 4 H, CH), 7.870 (d, $^3J_{HH}$ = 6 Hz, 4 H, CH), 7.729 (d, $^3J_{HH}$ = 6 Hz, 4 H, CH), 8.299 (d, $^4J_{HH}$ = 1.6 Hz, 4 H, CH), 8.225 (d, $^4J_{HH}$ = 1.6 Hz, 4 H, CH) ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 20.632 (CH$_3$), 20.706 (CH$_3$), 30.429 (CH$_3$), 30.659 (CH$_3$), 30.802 (CH$_3$), 35.764 (C), 35.939 (C), 58.297 (C), 113.846 (CH), 115.997 (CH), 120.581 (CH), 124.895 (C), 125.609 (CH), 133.418 (C), 134.248 (C), 137.028 (C), 138.005 (-C≡N), 140.901 (C), 142.313 (-C≡N-*t*Bu), 143.305 (C), 151.891 (C), 152.687 (C), 157.574 (C), 159.245 (C), 162.040 (C), 162.757 (C) ppm.

***cis*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] and [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ (1:1):** 20.1 mg (0.0165 mmol) [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ dissolved in dichloromethane were added to a solution of 8 mg (0.0165 mmol) *cis*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] in dichloromethane at room temperature. The solvent was evaporated at room temperature after stirring the solution for 1 h (yield: 28 mg). IR (CH_2Cl_2) [cm^{-1}]: ν(CH) 3071 w, 2971 s, ν(-C≡N/-N≡C) 2220 m, 2169 vs, 2117 s, 1613 m, δ(CH) 1480 m, 1414 m, δ(-C(CH$_3$)$_3$) 1371 s, 1236 m, 1204 s, 1097 s, 1013 d, 846 vs, 807 s, 558 s. MS (Micro-ESI in CH_2Cl_2) *m*/*z*(%): 1559([Ru(bipy*)$_2$Ru(biH$_2$)(PF$_6$)Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$^+$, 1413(1) [Ru(bipy*)$_2$(biH$_2$)Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$^{++}$, 927(100) [Ru(bipy*)$_2$(biH$_2$)](-H)$^{++}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.380 (s, 18 H, CH$_3$), 1.499 (s, 18 H, CH$_3$), 1.441 (s, 18 H, CH$_3$), 1.519 (s, 36 H, CH$_3$), 2.028 (s, 6 H, CH$_3$), 2.312 (s, 6 H, CH$_3$), 5.415 (s, 2 H, CH), 7.532 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.290 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.604 (s, 2 H, CH), 7.867 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH), 7.721 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH), 8.296 (d, $^4J_{HH}$ = 2 Hz, 2 H, CH), 8.219 (d, $^4J_{HH}$ = 1.2 Hz, 2 H, CH) ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 20.587 (CH$_3$), 20.698 (CH$_3$), 30.433 (CH$_3$), 30.664 (CH$_3$), 30.664 (CH$_3$), 30.918 (CH$_3$), 35.753 (C), 35.934 (C), 58.384 (C), 114.518 (CH), 115.734 (CH), 120.563 (CH), 124.872 (C), 125.529 (CH), 133.691 (C), 135.053 (C), 136.764 (C), 139.460 (-C≡N), 140.906 (C), 141.437 (-C≡N-*t*Bu), 141.637 (-C≡N-*t*Bu), 143.504 (C), 151.854 (C), 152.661 (C), 157.610 (C), 159.244 (C), 161.961 (C), 162.701 (C) ppm.

***cis*-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] and [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ (1:2):** 49.7 mg (0.0408 mmol) [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ dissolved in dichloromethane were added to a solution of 9.9 mg (0.0204 mmol)

cis-[Ru(CN)$_2$(C≡N-*t*Bu)$_4$] in dichloromethane at room temperature. After 1 h the solvent was evaporated at room temperature (yield 59 mg). IR (CH_2Cl_2) [cm^{-1}]: ν(CH) 3051 w, 2987 s, ν(-C≡N/–N≡C) 2163 m, 2123 m, 1675 m, δ(CH) 1440 s, 1423 s, δ(-C-(CH$_3$)$_3$) 1363 s, 1223 s, 1090 m, 1048 m, 1031 m, 846 vs. MS (Micro-ESI in CH_2Cl_2/CH_3OH) *m*/*z*(%): 1559(9) [Ru(bipy*)$_2$(biH$_2$)(PF$_6$)-Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$^+$, 994(2) [Ru(CN)$_2$(C≡N-*t*Bu)$_4$]$_2$Na$^+$, 927(100) [Ru(bipy*)$_2$(biH$_2$)](-H)$^+$, 509(3) [Ru(CN)$_2$(C≡N-*t*Bu)$_4$]-Na$^+$, 464(33) [Ru(bipy*)$_2$(biH$_2$)]$^{++}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.379 (s, 36 H, CH_3), 1.500 (s, 36 H, CH_3), 1.442 (s, 18 H, CH_3), 1.562 (s, 18 H, CH_3), 2.028 (s, 12 H, CH_3), 2.301 (s, 12 H, CH_3), 5.417 (s, 4 H, CH), 7.533 (dd, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 6 Hz, 4 H, CH), 7.282 (d, $^3J_{HH}$ = 5.2 Hz, 4 H, CH), 7.540 (s, 4 H, CH), 7.870 (d, $^3J_{HH}$ = 6.4 Hz, 4 H, CH), 7.730 (d, $^3J_{HH}$ = 6 Hz, 4 H, CH), 8.296 (d, $^4J_{HH}$ = 2 Hz, 4 H, CH), 8.219 (d, $^4J_{HH}$ = 2 Hz, 4 H, CH) ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 20.546 (CH_3), 20.685 (CH_3), 30.377 (CH_3), 30.602 (CH_3), 30.602 (CH_3), 30.846 (CH_3), 35.684 (C), 35.871 (C), 58.289 (C), 114.435 (CH), 115.636 (CH), 120.494 (CH), 124.762 (C), 125.467 (CH), 133.864 (C), 134.847 (C), 137.525 (C), 139.768 (-C≡N), 140.904 (C), 141.126 (-C≡N-*t*Bu), 141.362 (-C≡N-*t*Bu), 143.706 (C), 151.812 (C), 152.576 (C), 157.493 (C), 159.180 (C), 161.779 (C), 162.546 (C) ppm.

Supporting Information (see also the footnote on the first page of this article): Molecular structure of {[Ru(bipy*)$_2$(biH$_2$)]$_2$[*trans*-Ru(C≡N-*t*Bu)$_4$(CN)$_2$]}(PF$_6$)$_4$, emission spectra of the mixtures of [Ru(bipy*)$_2$(biH$_2$)](PF$_6$)$_2$ and [*cis*-Ru(C≡N-*t*Bu)$_4$(CN)$_2$], emission intensity vs. log *c*(*cis*-Ru(CN)$_2$) plot and log {(*I*(sat.) – *I*(M))/(*I*(M) – (*I*(RubiH$_2$)} vs. –2 log *c*(*cis*-Ru(CN)$_2$).

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