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The Structural and Functional Roles of Rhodium(II)–Rhodium(II) Dimers in Multinuclear Ruthenium(II) Complexes**

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Polypyridylruthenium(II) complexes have received much attention as a result of their long-lived luminescent metal-to-ligand charge-transfer (MLCT) excited state, which is a useful property for intercomponent energy and electron-transfer processes in supramolecular systems.[1] In particular the characteristically rich electrochemistry of multinuclear Ru^{II}–polypyridyl assemblies make them excellent models for multicomponent systems capable of performing photo- and/or redox-active supramolecular functions, such as those occurring in light-harvesting antenna systems[2] and photo-activated molecular machines.[3]

Among the Ru^{II} chromophores employed in photoactive devices, particularly attractive are those based upon 2,2′:6′2″-terpyridine (tpy), as the $\{Ru(tpy)_2\}^{2+}$ unit is achiral when substituted in the 4′-position,[4] and appropriate substitution can render the complex emissive from an otherwise quasi-non-emissive excited state.[5,6] However, synthesis and purification becomes increasingly tedious as a function of the nuclearity of the photoactive complexes, particularly when the formation of covalent bonds and protection/deprotection sequences are relied upon to create the linkages.[7] As earlier work had shown that molecular squares and polymers can be built up using metal tetracarboxylato dimers,[8,9] we decided that a more facile strategy toward multinuclear systems could rely upon the coordination chemistry of metal dimers. Their well-known paddlewheel-like motif offers a robust template from which to attach appropriately functionalized Ru^{II}–polypyridyl units by using ligand exchange reactions. We selected the Rh^{II} dimer to assemble these chromophores as it is typically air stable, diamagnetic, and inert to scrambling of the carboxylate groups.[10]

The Ru^{II} chromophores are based on the readily available $[Ru(tpy)\{4'\text{-(4-carboxyphenyl)tpy}\}]^{2+}$ complex (**4**).[11] The methanol adduct of (tetra-μ-acetato)dirhodium(II,II) (**5**) can be substituted under relatively mild conditions to yield substitution products **1**–**3** in 63% yield in refluxing acetonitrile (Scheme 1).[12] The product distribution can be shifted to the higher substituted Ru complexes by increasing the ratio of **4** to **5**, the reaction time, and the temperature. However, no tetra-substituted ($n=4$) product was detected in any of the cases. The structural formulas of the new multinuclear complexes are shown in Scheme 2.

The substitution products, including the *cis/trans* isomers of **2**, can be separated by column chromatography. Crystals suitable for X-ray diffraction of *trans*-**2** were grown by vapor diffusion of diisopropyl ether into a dilute solution of *trans*-**2** in acetonitrile containing $NaBF_4$ and NH_4BPh_4 (Figure 1).[13] The solid-state structure shows a familiar paddlewheel motif about the rhodium(II) dimer, with a tip-to-tip distance of 36 Å and a nearly eclipsed relative disposition of the ligands. The metal–metal bond length of 2.367(2) Å is typical of dirhodium carboxylates,[10] as are the Rh−O(acetate) and Rh−N-(CH_3CN) bond lengths of 1.936(11) and 2.200(15) Å, respectively. However, the Rh−O(carboxylate-tpy) bond length in *trans*-**2** is markedly elongated at 2.052(7) Å and is, to our knowledge, the longest such bond known for dirhodium(II,II) carboxylates.

Complex **4** and the products **1**–**3** have been characterized by ^1H NMR spectroscopic analysis in CD_3CN. All of the complexes display a marked electronic effect on the phenyl protons that is dependent on the number of substituted ruthenium units. The identity of each complex is readily verified through integration of the methyl singlets corresponding to equatorially coordinated acetate groups, and this is also supported by electrospray mass spectrometry data.

Although the absorption spectra of multinuclear species **1**–**3** (Figure 2) are the sum of the spectra of the individual components, their luminescence properties are significantly different from those of model species **4** (Table 1). Indeed, the MLCT emission of **4** is totally quenched at room temperature in **1**–**3**, and greatly reduced, as evidenced by lifetime measurements, in a rigid matrix at 77 K (see Table 1 and inset of Figure 2).

Cyclic and differential pulse voltammetry studies showed that the new compounds all exhibit a single reversible

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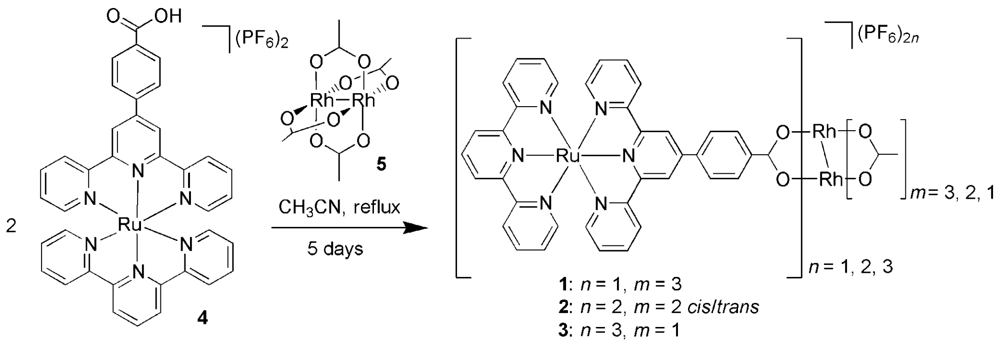
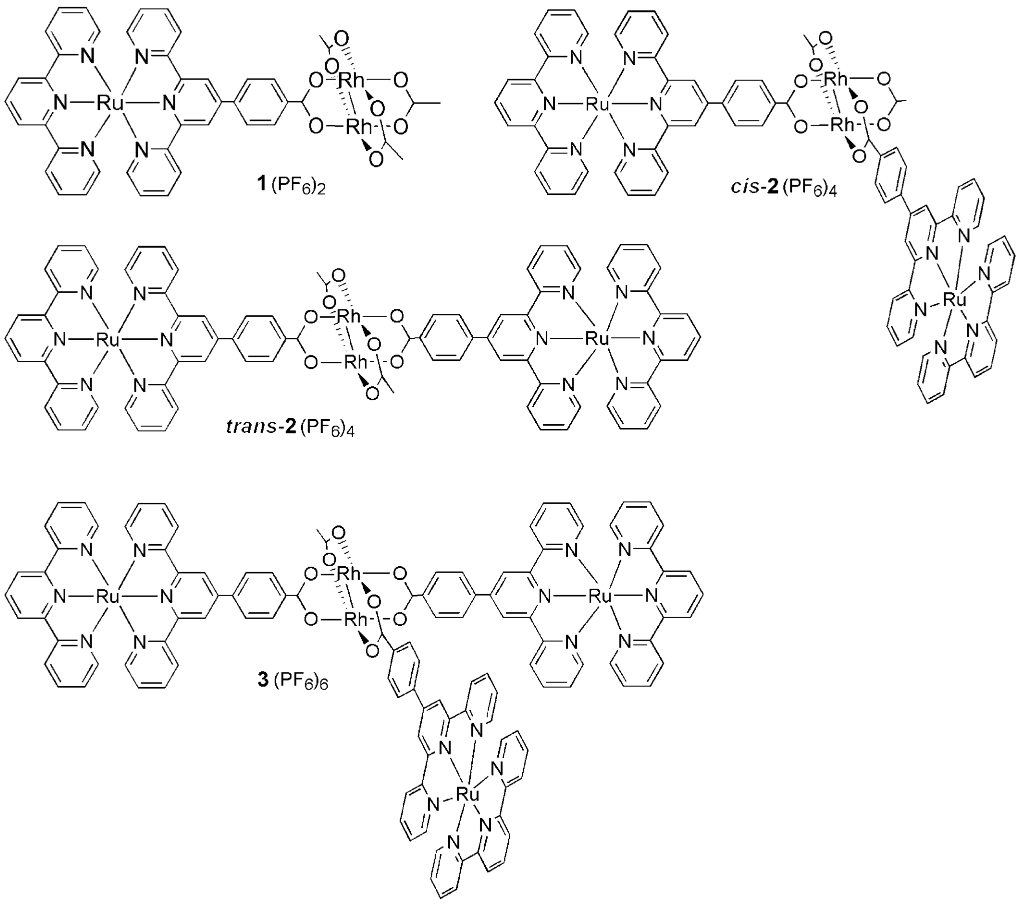
Supporting information for this article (^1H NMR spectra for complexes **1**–**3**, electrochemical studies of some representative compounds, details on the preparation and chromatographic separation of the compounds, elemental analysis, ESI-MS, and crystallographic data) is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of mulitinuclear complexes **1**, *cis*-**2**, *trans*-**2**, and **3**.



Scheme 2. Multinuclear complexes **1**, *cis*-**2**, *trans*-**2**, and **3**. Charges are omitted for simplicity.

oxidation process in the potential window investigated (−1.70/+1.50 V versus the saturated calomel electrode (SCE)). The process is assigned to the oxidation of the Ru^{II} subunit(s) on the basis of the oxidation potential of **4** and of the constancy of the potential within the **1**–**3** series (Table 2). Oxidation of the Rh dimer apparently does not take place within the potential window, most likely because of the coordination of the positively charged Ru^{II} moieties. The new compounds all exhibit irreversible reduction processes, probably involving overlapping reduction of the Rh dimer and the Ru^{II} chromophores, namely the tpy ligands. The irreversibility of the reduction processes make their detailed discussion difficult.

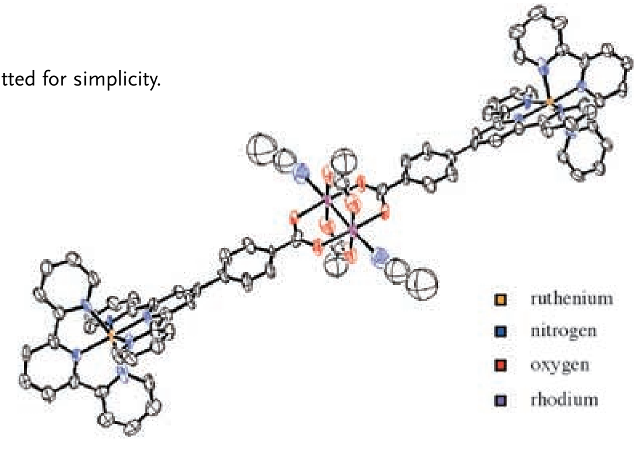


Figure 1. ORTEP diagram with 30% probability ellipsoids of *trans*-**2**. H atoms, solvent, and counterions have been omitted for clarity. The atoms are color coded as indicated.

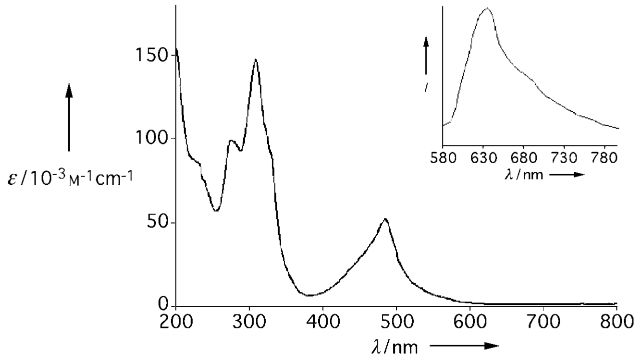


Figure 2. Absorption (298 K) and emission (inset, 77 K) spectra of *trans*-**2**.

Table 1: Luminescence data in a deoxygenated solution of acetonitrile (298 K) and in butyronitrile glass (77 K).

	298 K			77 K	
	λ_{max} [nm]	τ [ns]	Φ	λ_{max} [nm]	τ [μs]
1	–	–	–	639	2.5
cis-**2**	–	–	–	636	0.8
trans-**2**	–	–	–	634	1.2
3	–	–	–	635	0.8
4	666	9.5	8.4×10^{-5}	635	13.2

Table 2: Redox potentials for complexes **1**–**4** and models in argon-purged solutions of acetonitrile.[a]

	Potential [V] versus SCE			
	oxidation		reduction	
1	1.27		−1.21 (irr)	−1.55 (irr)
cis-**2**	1.29		−1.18 (irr)	−1.53 (irr)
trans-**2**	1.29		−1.20 (irr)	−1.48 (irr)
3	1.29		−1.18 (irr)	−1.53 (irr)
4	1.28		−1.24 (irr)	−1.49 (irr)
$Rh_2(OAc)_4$[b]	1.02	−1.08 (irr)		
$[Ru(tpy)_2]^{2+}$[c]	1.30		−1.24	−1.49

[a] $E_{1/2}$ values are given for reversible processes. The reported values for irreversible processes, labeled irr, are peak potentials. [b] Ref. [14]. [c] Ref. [15].

The redox data indicate that reductive electron transfer cannot be considered as a viable route for quenching. In fact, oxidation of the Rh dimer unit in **1**–**3** does not occur until above +1.5 V, and since the first reduction of the Ru moieties is about −1.2 V in all the new species, reductive electron transfer would be endoergonic and not efficient. Similar arguments also apply to oxidative electron transfer. However, the lowest-lying excited state of Rh dimers similar to those used here as templating units has been reported to lie between 1.30 and 1.70 eV, as characterized by relatively long lifetimes in solution (up to 5 μs, depending on the solvent and substituents), although they were found to be nonluminescent.[14a] Despite the large uncertainty concerning the exact energy level of the Rh dimer subunits, there is a substantial driving force in **1**–**3** for energy transfer from the (potentially emitting) Ru-based MLCT states (whose energy is around 1.95 eV) to the excited state based on the Rh dimer. Even if it is assumed that the limiting value of the excited-state energy of the acceptor Rh dimers is 1.70 eV, a Δ*G* value of −0.25 eV is found (the excited-state energy of the donor Ru chromophores is approximately the same as the maximum value of the emission of **4** at 77 K), which is large enough to make the energy-transfer process efficient. As a consequence, we attribute the quenching of the Ru-based MLCT luminescence in **1**–**3** to energy transfer from the MLCT state(s) to the lowest-lying Rh dimer based level, which would play the role of the energy trap in the multinuclear systems. Therefore, **1**–**3** behave as efficient light-harvesting antennae, where the light energy collected by the Ru^{II}-appended chromophore(s) is conveyed to the Rh dimer subunit. Interestingly, the energy-transfer process appears to be partial at 77 K, thus indicating the presence of significant energy barriers and suggesting that the dominating energy-transfer mechanism of the fast room temperature process could be electron exchange. Ultrafast experiments are in progress to fully characterize the photophysical properties of the new species.

In conclusion, we have developed a novel approach to build-up multinuclear polypyridylruthenium systems by relying upon coordination to a tetracarboxylato metal dimer. Multinuclear complexes are readily available by attaching mononuclear functional subunits (namely, Ru^{II} chromophores) to structural subunits (namely, metal dimers). This "chemistry-on-the-complex" approach simplifies the synthesis of multinuclear assemblies by allowing independent preparation of the different subunits.[8c,16] Intercomponent energy transfer between subunits is efficient, thus indicating that the metal dimers may play a functional role and not only act as a template. The rich chemistry of tetracarboxylato metal dimers and metal–polypyridine complexes with useful photophysical properties should provide ready access to diverse structures with different cores and/or peripheral chromophores and lead to a large library of novel and easily accessible multicomponent species with made-to-order properties. For example, replacement of the Ru chromophores employed here with Ru^{II}–polypyridine species having lower MLCT excited states would make the energy-transfer quenching inefficient and restore peripheral subunit luminescence, whereas the reaction of the partially "uncompleted" species bearing available coordinating units such as **1** and **2** with other metal chromophores (namely, Os^{II} species) should lead to more elaborated mixed-chromophore architectures.

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[1] a) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, UK, **1991**; b) G. R. Newkome, K. S. Yoo, H. J. Kim, C. N. Moorefield, *Chem. Eur. J.* **2003**, *9*, 3367; c) H. Jiang, S. J. Lee, W. Lin, *J. Chem. Soc. Dalton Trans.* **2002**, 3429; d) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines. A Journey into the Nanoworld*, Wiley-VCH, Weinheim, **2003**.

[2] a) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26; b) J. Andersson, F. Puntoriero, S. Serroni, A. Yartsev, T. Pascher, T. Polivka, S. Campagna, V. Sundström, *Faraday Discuss.* **2004**, *127*, 295; c) J. Andersson, F. Puntoriero, S. Serroni, A. Yartsev, T. Pascher, T. Polivka, S. Campagna, V. Sundström, *Chem. Phys. Lett.* **2004**, *386*, 336.

[3] J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845, and references therein.

[4] a) E. C. Constable, P. Harverson, C. E. Housecroft, *J. Chem. Soc. Dalton Trans.* **1999**, 3693; b) J.-P. Sauvage, J.-P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993.

[5] a) R. Passalacqua, L. Loiseau, S. Campagna, Y.-Q. Fang, G. S. Hanan, *Angew. Chem.* **2003**, *115*, 1646; *Angew. Chem. Int. Ed.* **2003**, *42*, 1608; b) M. I. J. Polson, N. J. Taylor, G. S. Hanan, *Chem. Commun.* **2002**, 1356; c) Y. Q. Fang, N. J. Taylor, G. S. Hanan, F. Loiseau, R. Passalacqua, S. Campagna, H. Nierengarten, A. Van Dorsselaer, *J. Am. Chem. Soc.* **2002**, *124*, 7912; d) E. A. Medlycott, G. S. Hanan, *Chem. Soc. Rev.* **2005**, *34*, 133.

[6] The parent $[Ru(tpy)_2]^{2+}$ has an excited-state lifetime at RT on the order of 250 ps, see: a) J. R. Winkler, T. L. Netzel, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1987**, *109*, 2381; b) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, A. M. W. Cargill Thompson, *Inorg. Chem.* **1995**, *34*, 2759.

[7] a) G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano, V. Balzani, *Inorg. Chem.* **1990**, *29*, 4750; b) G. Denti, S. Campagna, S. Serroni, M. Ciano, V. Balzani, *J. Am. Chem. Soc.* **1992**, *114*, 2944.

[8] a) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759; b) M. H. Chisholm, *J. Organomet. Chem.* **2002**, *641*, 15; c) J. K. Bera, B. W. Smucker, R. A. Walton, K. R. Dunbar, *Chem. Commun.* **2001**, 2562.

[9] S. Lo Schiavo, S. Serroni, F. Puntoriero, G. Tresoldi, P. Piraino, *Eur. J. Inorg. Chem.* **2002**, 79, and references therein.

[10] a) F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 3rd ed., Wiley, New York, **1994**; b) F. Basolo, R. G. Pearson, *Mechanisms of Inorganic Reactions: A Study of Metal Complexes in Solution*, 2nd ed., Wiley, New York, **1968**.

[11] E. Figgemeier, V. Aranyos, E. C. Constable, R. W. Handel, C. E. Housecroft, C. Risinger, A. Hagfeldt, E. Mukhtar, *Inorg. Chem. Commun.* **2004**, *7*, 117.

[12] Yield of 63 % based on 11 mg of recovered **4**. In the reaction of two equivalents of **4** with **5**, the yield based on recovered **4** is **1**: 10 %, *cis*-**2**:14 %, *trans*-**2**: 18 %, **3**: 21 %.

[13] Crystal data for *trans*-**2**: $C_{82}H_{62}N_{14}O_8Rh_2Ru_2\cdot 2(C_{24}H_{20}B)\cdot 2\,BF_4$ was collected on a Bruker APEX at 100 K using $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Full-matrix, least-squares refinements on F^2 using all data. 7673 reflections, $M_r = 2591.46$, triclinic, space group $P\bar{1}$, $a = 9.5166(7)$, $b = 13.4933(10)$, $c = 26.5103(17)$ Å, $\alpha = 89.659(4)$, $\beta = 82.213(4)$, $\gamma = 71.513(4)°$, $V = 3196.3(4)$ Å^3, $Z = 1$, $R1\ [I > 2\sigma(I)] = 0.0708$, $wR2 = 0.1905$.

[14] a) P. M. Bradley, B. E. Bursten, C. Turro, *Inorg. Chem.* **2001**, *40*, 1376; b) W. R. Tikkanen, E. Binamira-Soriaga, W. C. Kaska, P. C. Ford, *Inorg. Chem.* **1984**, *23*, 141.

[15] M. Beley, J.-P. Collin, J.-P. Sauvage, H. Sugihara, F. Heisel, A. Miehé, *J. Chem. Soc. Dalton Trans.* **1991**, 3157.

[16] a) F. M. MacDonnell, M.-J. Kim, K. L. Wouters, R. Konduri, *Coord. Chem. Rev.* **2003**, *242*, 47; b) Y.-Q. Fang, M. I. J. Polson, G. S. Hanan, *Inorg. Chem.* **2003**, *42*, 5; c) S.-S. Sun, A. J. Lees, *Coord. Chem. Rev.* **2002**, *230*, 171; d) S.-S. Sun, A. J. Lees, *Organometallics* **2002**, *21*, 39; e) S.-S. Sun, A. J. Lees, *Chem. Commun.* **2001**, 103; f) S.-S. Sun, A. J. Lees, *Inorg. Chem.* **2001**, *40*, 3154; g) O. Johansson, C. C. Tong, J. A. Lotoski, G. S. Hanan, *Chem. Commun.* **2000**, 819; h) S. Bodige, A. S. Torres, D. J. Maloney, D. Tate, G. Kinsel, A. Walker, F. M. MacDonnell, *J. Am. Chem. Soc.* **1997**, *119*, 10364.