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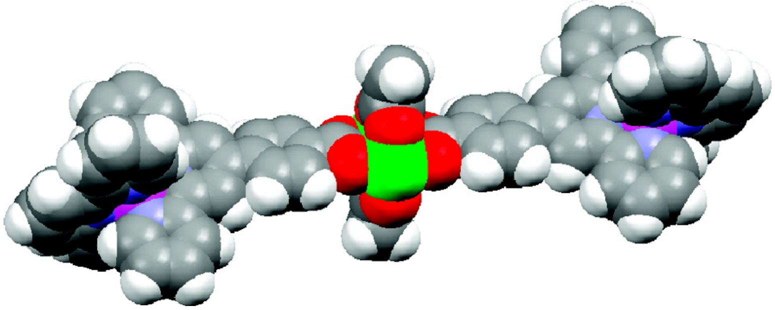

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Self-Assembled Light-Harvesting Systems: Ru(II) Complexes Assembled about Rh−Rh Cores

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Abstract: Ru(II) polypyridine species have been assembled about dirhodium(II, II) tetracarboxylate cores. The complexes prepared have general formulas $[\{(\mathrm{terpy})\mathrm{Ru}(\mathrm{La})\}_n\{\mathrm{Rh_2(CH_3COO)}_{4-n}\mathrm{(CH_3CN)_2}\}]^{2n+}$ (**a**-type compounds: terpy = 2,2′:6′,2″-terpyridine; **La** = 4′-(*p*-carboxyphenyl)-2,2′:6′,2″-terpyridine; $n = 1$, **1a**; $n = 2$, *cis*-**2a** and *trans*-**2a**-*cis* and *trans* refer to the arrangement of the Ru(II) species around the dirhodium core; $n = 3$, **3a**), $[\{(\mathrm{Lb})\mathrm{Ru}(\mathrm{La})\}_n\{\mathrm{Rh_2(CH_3COO)}_{4-n}\mathrm{(CH_3CN)_2}\}]^{2n+}$ (**b**-type compounds: **Lb** = 6-phenyl-2,4-di(2-pyridyl)-s-triazine; $n = 1$, **1b**; $n = 2$, an inseparable mixture of *cis*-**2b** and *trans*-**2b**; $n = 3$, **3b**; $n = 4$, **4b**), and $[\{(\mathrm{terpy})\mathrm{Ru}(\mathbf{Lc})\}\{\mathrm{Rh_2(CH_3COO)_3(CH_3CN)_2}\}]^{2+}$ (**1c**; **Lc** = 6-(*p*-carboxyphenyl)-2,4-di(2-pyridyl)-s-triazine). As model species, also the mononuclear $[(\mathrm{terpy})\mathrm{Ru}(\mathbf{La})]^{2+}$ (**5a**), $[(\mathbf{La})\mathrm{Ru}(\mathbf{Lb})]^{2+}$ (**5b**), and $[(\mathrm{terpy})\mathrm{Ru}(\mathbf{Lc})]^{2+}$ (**5c**) have been prepared. All of the complexes have been characterized by several techniques, including NMR and mass spectra, and the stability of the various species is discussed. The absorption spectra of all of the compounds are dominated by the Ru(II) polypyridine moieties, showing intense ligand-centered (LC) bands in the UV region and intense metal-to-ligand charge-transfer (MLCT) bands in the visible. The compounds exhibit several metal-centered oxidation and ligand-centered reduction processes, which have been assigned to specific subunits. Both absorption and redox data indicate a supramolecular nature of the assembled systems. Efficient energy transfer from the MLCT triplet state of the Ru-based components to the lowest-energy excited state of the dirhodium core takes place for the **a**-type compounds at 298 K in acetonitrile solution, whereas such a process is inefficient for the **b**-type and **c**-type species, which exhibit the typical MLCT emission. At 77 K in butyronitrile matrix, Ru-to-$\mathrm{Rh_2}$ energy transfer is partly efficient for both the **a**-type and the **b**-type compounds and is inefficient for **1c**. The reasons for such behavior are discussed by taking into account arguments concerning the driving force and reorganization energy of the complexes.

Introduction

Natural light-harvesting systems (LHSs) serve as inspiration for the development of artificial LHSs, which, when integrated into larger systems, are designed to perform valuable functions such as conversion of light energy into fuels and electricity.[1] The design of such artificial LHSs presents numerous challenges, with the efficient connection of multiple photoactive units by means that are still conducive to energy and electron transfer being one of the most challenging. In natural LHSs, many weak supramolecular interactions are used to obtain the appropriate structural organization and functionality, and the reversibility of such supramolecular interactions is instrumental to the self-assembly process.[2]

Synthetic self-assembled LHSs have been reported recently;[3] however, constructing artificial LHSs via self-assembly may not be suitable to the photoactive unit employed and/or to the conditions of operation of the device. On the other hand, covalently assembled LHSs have focused on utilizing elaborate ligand design and/or performing many iterative chemical

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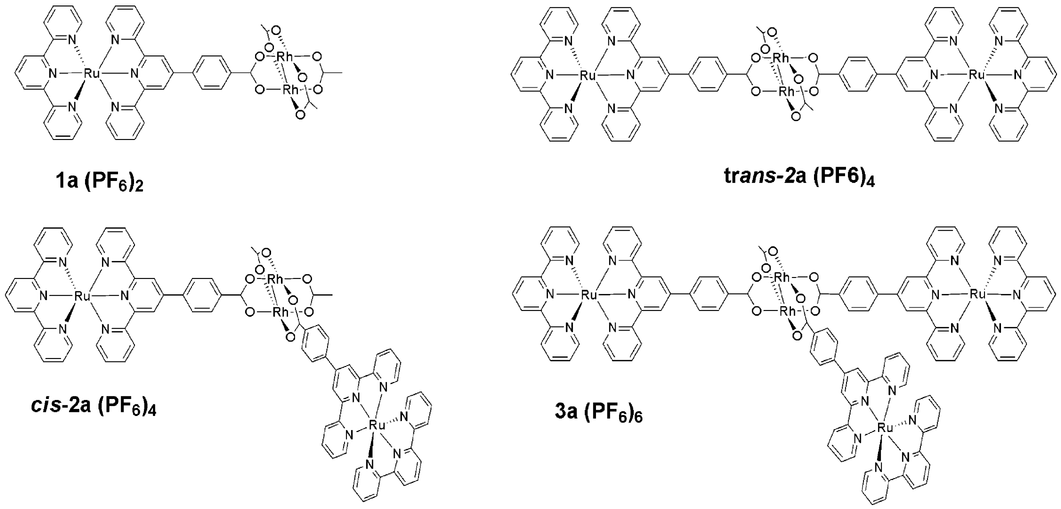
Chart 1. Complexes **1a**−**3a**



transformations with compromised efficiency and demanding purification sequences.[4] Although approaches to (partly) overcome these problems have been proposed, the synthesis of covalently assembled LHSs remains difficult, and structures of high nuclearity often possess a large degree of freedom that can preclude structural elucidation and frustrate energy transfer processes.[5]

An alternative strategy for building up artificial LHSs, coupling the precise structural organization of self-assembled systems with the robustness of covalent bonding, relies on a careful selection of building blocks. This approach may lead to bonding whose inherent reversibility allows for self-assembly while offering bond strengths suitable to afford robust systems. In this regard, dimetallic tetracarboxylates have shown enormous promise in the self-assembly of robust structures,[6] yet they possess intriguing functions depending on the building blocks incorporated into the final structure.

One of the most studied dimetallic tetracarboxylates is dirhodium(II, II) tetraacetate, which has found extensive application in catalysis, including cyclopropanation,[7] alkyne cyclopropenation,[8] C−H insertion,[9] and carbenoid initiated C−C bond formation.[10] Complementary to these applications was the report that some dirhodium(II, II) tetraacetate species can exhibit a long-lived, non-emissive lowest excited state, which was shown to lie between 1.34 and 1.77 eV with a lifetime of up to 5 μs depending on the solvent used.[11] Dirhodium(II, II) tetracarboxylates, and other paddlewheel metal dimers, have received much attention of late as building blocks for the creation of electrochemically rich supramolecular architectures.[12] More recently, we have identified this motif as a suitable template for growth of polynuclear Ru(II) polypyridine systems, capable to act as light-harvesting supramolecular species in virtue of their absorption and excited-state properties, based upon carboxylate-functionalized photoactive units (Chart 1, **1a**, **2a**-*cis*/*trans*, **3a**. In all charts and figures, except Figure 3, the axial acetonitrile ligands of the dirhodium core have been omitted for clarity).[13] We have shown that the dirhodium(II, II) subunit not only plays the role of a scaffold for multichromophore assembly, but can also have a functional role (i.e., energy trap) in that it can quench the Ru-based MLCT excited state by energy transfer.

Herein we extend our preliminary study through the preparation and characterization of a complete family of related, electron-deficient triazine-based analogues (Chart 2, **1b**−**4b** and **1c**) and by the study of the factors affecting the overall stability of such multi-metallic systems. Futhermore, the absorption spectra, redox bevahior, and photophysical properties (both at 77 K in rigid matrix and at 298 K in fluid solution) of all of the supramolecular arrays assembled on the dirhodium(II, II) cores are studied and discussed, along with those of suitable model mononuclear building blocks **5a**−**c** (Chart 3). All of the compounds under study are shown in Charts 1−3. These new systems can be viewed as promising synthetic self-assembled light-harvesting systems, because they are made of multiple chromophores (the Ru(II) subunits) arranged around a scaffold (the dirhodium core) by a simple ligand exchange reaction, which promotes chemical stability of the final structures, which

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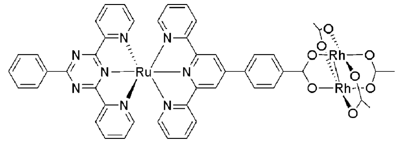
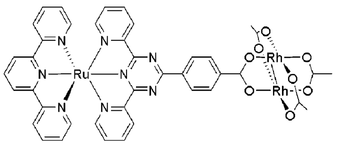
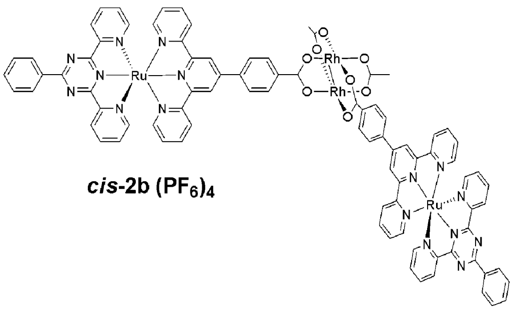
Chart 2. Complexes **1b**−**4b** and **1c**



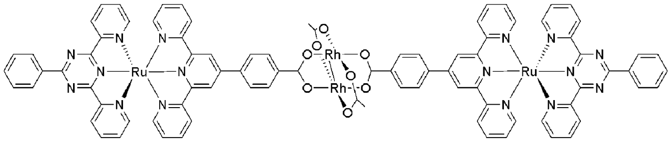
1b (PF$_6$)$_2$



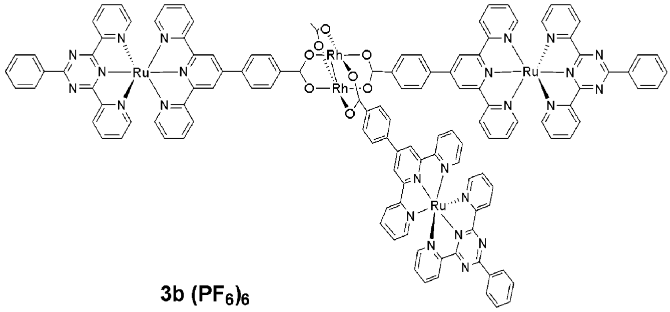
1c (PF$_6$)$_2$



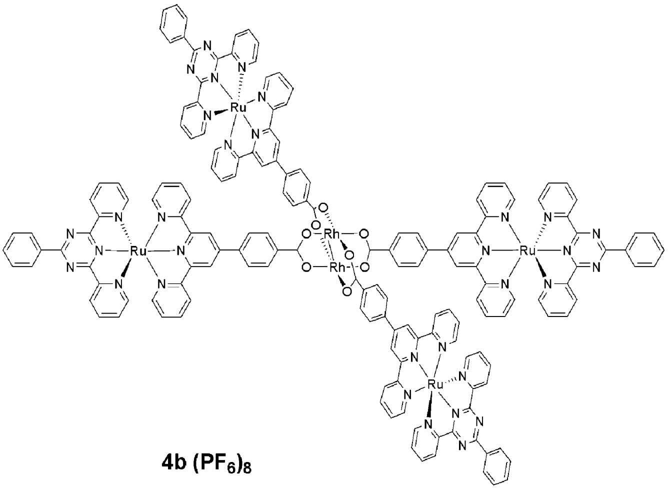
***cis*-2b (PF$_6$)$_4$**



***trans*-2b (PF$_6$)$_4$**



3b (PF$_6$)$_6$



4b (PF$_6$)$_8$

are comparable to covalent systems. Moreover, the core can also have an active role, acting as an excited-state energy trap.

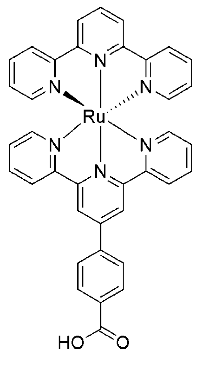
Experimental Section

Detailed synthetic procedures for **1a**−**3a**, **5a**, **1b**−**5b**, **1c**, and **5c** can be found in the Supporting Information. Details about the equipment and methods used for the photophysical and redox investigation have already been reported.[4b,13]

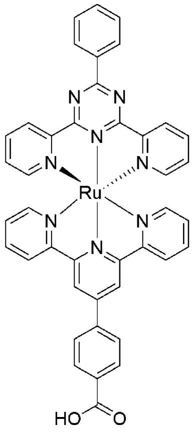
Results and Discussion

Synthesis. The mixed-metal polynuclear complexes are assembled following a classical ligand exchange process according to Scheme 1, in which acetic acid is removed by distillation from the reaction mixture. Considerable influence can be exerted on both the rate and the extent to which substitution proceeds simply by varying temperature, concentration, stoichiometry, and rate of acetic acid distillation. Because these products are strongly colored and stable to chromatographic separation, the reaction process may be monitored by TLC, and the products of different nuclearity are easily separated by column chromatography. The precursor complex **5b** can be synthesized as was **5a**,[13] by heating to reflux 4′-(*p*-carboxyphenyl)-2,2′:6′,2″-terpyridine (**La**) and Ru(**Lb**)Cl$_3$ (**Lb** = 6-phenyl-2,4-di(2-pyridyl)-s-triazine) in EtOH/H$_2$O in the presence of the dechlorinating agent AgNO$_3$, which affords **5b** in modest yield (41%) after column purification. In a typical preparation of the oligonuclear complexes of the **b** series, **1b**−**4b** can be prepared in modest overall yield (69%) after column chromatography, based on recovered **5b**, which is very similar to that obtained for the series **1a**−**3a**.[13] Solvents other than acetonitrile were used (e.g., DMF, benzonitrile); however, in all cases acetonitrile was found to be optimal with regard to controlling the reaction and minimizing the number of unidentified decomposition side-products. However, *trans*-**2b** and *cis*-**2b** were inseparable using the same technique as that used to separate *trans*-**2a** and *cis*-**2a**, and therefore the spectroscopic, luminescence, and redox properties of the **2b** complexes were not studied.

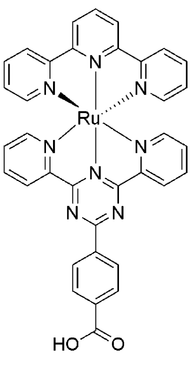
Chart 3. Mononuclear Ru(II) Building Blocks **5a**−**c**



5a (PF$_6$)$_2$



5b (PF$_6$)$_2$



5c (PF$_6$)$_2$

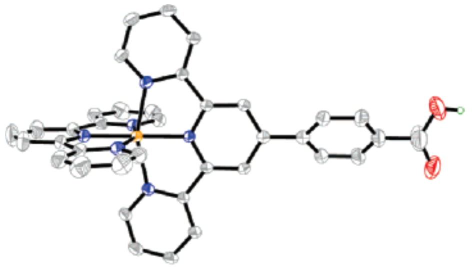
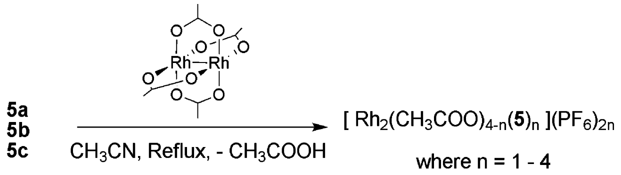


Figure 1. Ball and stick representation of the X-ray crystal structure of **5a**. Anions and solvent of crystallization have been removed for clarity.

Scheme 1. Synthesis of Oligonuclear Species in Refluxing Acetonitrile



To complete the family, it was desired to move the ligand component responsible for the emissive ^{3}MLCT state closer to the dirhodium(II, II) core, which was afforded by 6-(*p*-carboxyphenyl)-2,4-di(2-pyridyl)triazine (**Lc**).[14] Preparation of the precursor complex **5c** proceeded as with complexes **5a**,[13] involving simple reflux of **Lc** with Ru(tpy)Cl$_3$ in EtOH/H$_2$O in the presence of the dechlorinating agent AgNO$_3$, giving **5c** in modest yield (36%) after column purification. The application of **5c** in the same manner as depicted in Scheme 1 leads to a product distribution analogous to that for the series **1a**−**3a**, **1b**−**4b**. However, insignificant quantities of higher substitution products, as determined by high-resolution mass spectrometry, were found. The monosubstitution product **1c** could be produced in sufficient yield (57%), although this required longer reaction times (∼7 days) than that needed to produce **1a** and **1b** (∼1 day) using the same proportion of Rh$_2$(OAc)$_4$. These observations were not unexpected, because placement of the triazine moiety nearer the carboxylate group would be expected to reduce its dative bonding capacity to some degree. Nevertheless, **1c** was stable to chromatographic separation and isolated cleanly for further electrochemical and photophysical analysis.

Crystal Structure Determination of 5a-(BPh$_4$)$_2$, 5b-(BPh$_4$)-(PF$_6$), and *trans*-2a-(BPh$_4$)$_2$(BF$_4$)$_2$. For all crystal structures reported herein, the addition of a small amount of NH$_4$BPh$_4$ to an acetonitrile solution containing the complex (as either a PF$_6^-$ or a BF$_4^-$ salt) was essential to the expedient growth of single crystals of quality sufficient for diffraction studies. Although complex **5a** has been reported by several other groups, no X-ray structural data have been given until now (Figure 1). Similar to Ru(tpy)$_2^{2+}$,[15] **5a** contains mutually orthogonal ligands with a pseudo-octahedral geometry about the ruthenium atom. The phenyl ring bearing the carboxylic acid group is twisted with respect to the central pyridyl ring by 44°. Each oxygen atom of the carboxylic acid group, and hence the acidic proton as well, is located in two unique dispositions throughout the crystal lattice as indicated by site occupancy factors of 0.5 for each. As expected, the C−O bond lengths of this carboxylic acid group are 1.405(4) and 1.280(4) Å, corresponding to C−O single and double bonds, respectively. No hydrogen bonding is observed in the extended lattice structure.

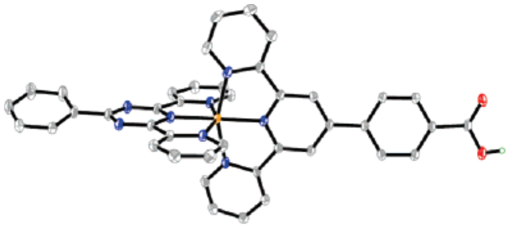


Figure 2. Ball and stick representation of the X-ray crystal structure of **5b**. Anions and solvent of crystallization have been removed for clarity.

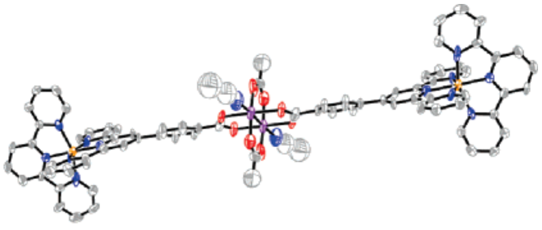


Figure 3. Ball and stick representation of the X-ray crystal structure of *trans*-**2a**. Anions and solvent of crystallization have been removed for clarity.

The structure of **5b** possesses a characteristic distorted octahedral geometry about the ruthenium atom with no relevant discrepancy in Ru−N bond lengths associated with the two electronically distinct ligands (e.g., Ru−N = 1.975(3) Å (central triazine ring) and Ru−N = 1.980(2) Å (central tpy ring)) (Figure 2). However, the phenyl ring of the tpy ligand is twisted out of the plane of the central pyridyl ring by only 17°. Hydrogen bonding of the phenyl protons to the triazine nitrogen lone-pair electrons has been found to yield a near coplanar orientation in some instances,[13] but here the phenyl ring is twisted by 20° with respect to the central triazine ring.

For adduct *trans*-**2a**,[13] the two appended ruthenium complexes possess structural features similar to that for **5a** with the exception that the phenyl ring is twisted out of the plane of the tpy ligand to a lesser extent (26°) (Figure 3). With respect to dirhodium(II, II) tetracarboxylates in general, the metal−metal bond length has been found to vary inversely with the basicity of the axially coordinated ligand and, to a lesser degree, the electronic influence of the carboxylate bridging ligand.[16] The Rh−O$_{\text{(caboxylate)}}$ bond lengths are largely invariant among dirhodium carboxylates, with an average length of 2.04 Å. Here, the Rh−Rh bond is 2.367(2) Å and the Rh−N$_{\text{(CH}_3\text{CN)}}$ axial bond is 2.200(15) Å, while the Rh−O bond length associated with the ruthenium complex is 2.051(2) and 2.052(5) Å. These distances are quite consistent with those found in other tetracarboxylate complexes of (bis)acetonitrile adducts.[17] However, the Rh−O bond length associated with the acetates is considerably shorter with bond lengths of 1.86(1) and 1.936(11) Å. The discrepancy between these two values is due to problems resolving one of these oxygen atoms, as evidenced by a larger isotropic displacement parameter. Regardless, the

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(14) See Supporting Information.

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Rh−O bond of 1.936(11) Å is about 0.1 Å shorter than expected, which suggests that the acetates are bound more strongly than the ruthenium complexes. This is supported by solution behavior in d_5-pyridine at room temperature, which shows gradual displacement of the coordinated ruthenium complex. Any strong electron-donating/-withdrawing affect exerted by the equatorially coordinated carboxylate should have ramifications on the strength of coordination by the axial ligand, which in turn will affect the metal−metal bond length.[15a,18] Because these lengths are in good agreement with related dirhodium tetracarboxylates, we are led to believe that the effect is not inductive but rather electrostatic in nature. In essence, we have appended multiply charged cations to a cationic dirhodium core, which draws the anionic acetates closer to the core to offset unfavorable electrostatic repulsions. The complete nonreactivity of dirhodium(II, II) tetrakis-trifluoroacetate toward ligand displacement utilizing the same reaction conditions employed with the acetate dimer supports this postulate, because a greater effective positive charge on the dirhodium core will arise as a consequence of the more electronegative trifluoracetate ligand.

NMR and Solution Behavior. In general, the ^{1}H NMR spectra of the parent chromophores **5a**, **5b**, and **5c** are similar to those of their substitution products with $Rh_2(OAc)_4$, although the methyl singlets from the acetates bound to the Rh−Rh dimer, located between 1.7 and 2.0 ppm, provide important information concerning product distribution (see Supporting Information). The presence of two methyl singlets in a ratio of 2:1 clearly indicates a monosubstitution product (**1a**, **1b**, **1c**), while the presence of one methyl singlet suggests either bis- or tris-adducts and its absence points to the tetrakis adduct. With increased substitution, the position of this singlet shifts slightly downfield, and, interestingly, spectra of the resolved isomers *trans*-**2a** and *cis*-**2a** show distinct methyl singlets (1.85 and 1.88 ppm, respectively). These singlets were located at almost the exact same position for the unresolved isomeric mix *cis*/*trans*-**2b**, and their relative integration points to a 3.3:1 *cis*/*trans* distribution. This is significantly greater than the statistical 2:1 *cis*/*trans* ratio expected in the absence of differences in donor capacities between acetate and ligand **Lb**. The labilizing *trans*-effect, well documented in mononuclear square planar and octahedral complexes, applies also to dimeric paddlewheel complexes.[19] One would expect a greater proportion of the *trans* isomer if ligand **Lb** is significantly more basic than acetate. That this is not the case suggests the opposite scenario due to the electrostatic factors.

Although complexes **1a**−**3a**, **1b**−**4b**, and **1c** are stable in acetonitrile solutions and to chromatographic separation on silica, higher substitution adducts based on **1c** were found to decompose significantly under the chromatographic conditions used, giving a mix of the desired product and the starting complex **1c**. The dissociation of these higher substitution adducts is no doubt linked to the more forcing conditions required to form even the monosubstituted adduct **1c** as compared to the conditions used to form the analogues **1a** and **1b**. Relative to tpy, the triazine-based ligand **Lc** is electron deficient, and so one expects a lower dative capacity for the carboxylate group. That this is also a function of the overall nuclear charge of the adduct points to an electrostatic origin of this instability, made more problematic upon compromising the basicity of the ligand employed. To further support this argument, the preparation of complexes **1a**−**3a** was attempted using the dirhodium(II, II) tetrafluoroacetate starting material. Ligand substitution reactions using the tetrafluoroacetate dimer typically proceed much faster as compared to those using the tetraacetate dimer,[20] due to the greatly reduced basicity of the tetrafluoroacetates.[21] These substitution reactions have, until now, exclusively involved neutral or anionic chelates. In this case, however, no substitution whatsoever was observed under the same reaction conditions using $Rh_2(O_2C_2F_3)_4$. It is unlikely that the dative capacity of **5a** is lower than that of tetrafluoroacetate; therefore, the installation of cationic complexes onto the already electron-deficient dirhodium core of $Rh_2(O_2C_2F_3)_4$ should be highly unfavorable due to Coulombic repulsion. This sort of decomposition is not unprecedented for highly charged polynuclear coordination systems,[22] but it is with regard to dirhodium(II, II) solution behavior.

Redox Behavior. Cyclic voltammetry of complexes **1a**−**3a** revealed little difference as compared to that of the parent complex **5a** (Table 1). Apparently, no redox process corresponding to processes occurring in the $Rh_2(OAc)_4$ species, considered as a model for the core of the multicomponent systems, was observed. The original assignment was that the $Rh_2^{4+/5+}$couple,[13] observed at ∼1.02 V vs SCE in $Rh_2(OAc)_4$,[23] was shifted outside the potential window investigated (+2.0 to −2.0 V), due to the presence of the highly charged Ru(II) units, which behave as electron-withdrawing groups for the dirhodium core. However, the cyclic voltammetry of complexes **1b** and **1c** (see Figure 4) reveals two distinct and reversible redox couples corresponding to one-electron oxidations, which, on the basis of the oxidation behavior of the model compounds $Rh_2(OAc)_4$, **5b**, and **5c** (Table 1), are assigned to the Rh_2(II, II) and the Ru(II) centers (see Table 1 and Figure 4). In **1b** and **1c**, the $Rh_2^{4+/5+}$couple is shifted to higher potential by ∼0.2 V relative to the parent $Rh_2(OAc)_4$, as expected based on the fact that the species is no longer neutral. It is therefore more likely that the $Rh_2^{4+/5+}$ couple is simply superimposed with the Ru(III)/Ru(II) couple in **1a**, and becomes resolved in **1b** and **1c** because of the more positive oxidation potential for the Ru(III)/Ru(II) couple in these latter species due to the presence of the more electron-deficient triazine-based ligands, as confirmed by square-wave voltammetry. However, for the higher substitution products **3b** and **4b**, only one oxidation process is observed, and it is assigned as the Ru(III)/Ru(II) couple, based upon similarity to that for the parent complex **5b**.

The absence of the Rh_2(II, II)/(II, III) couple for the higher nuclearity systems can be rationalized assuming that the 0.2 V positive shift of Rh_2 core oxidation in the presence of a Ru(II) moiety, as evidenced for **1b** and **1c**, is applied as more Ru(II) units are connected to the dirhodium unit. With this assumption, in **3b** and **4b** the expected dirhodium oxidation should occur at about 1.60 and 1.80 V, respectively. Obviously, there is no

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Table 1. Redox Potential Data for Complexes **1**−**5**[a,b]

cpd	potential [V] vs SCE ΔE_p (mV)[a]		I_c/I_a[c] ($Ru^{2+/3+}$)	I_c/I_a[c] ($Rh_2^{4+/5+}$)
1a	1.27 (100)	−1.21 (ir), −1.55 (ir)	0.70	
1b	1.43 (80), 1.23 (70)	−0.76 (60), −1.33 (ir), −1.64[d]	0.72	0.95
1c	1.46 (70), 1.25 (80)	−0.74 (50), −1.37 (ir), −1.62[d]	0.95	1.14
cis-**2a**	1.29 (80)	−1.18 (ir), −1.53 (ir)	0.95	
trans-**2a**	1.29 (80)	−1.20 (ir), −1.48 (ir)	1.06	
3a	1.29 (80)	−1.18 (ir), −1.53 (ir)	0.94	
3b	1.44 (80)	−0.71 (ir), −1.33 (ir), −1.61[d]	0.25	
4b	1.46 (90)	−0.73 (ir), −1.35 (ir), −1.48[d]	0.19	
5a	1.28 (67)	−1.24 (ir), −1.49 (ir)	0.73	
5b	1.43 (80)	−0.78 (60), −1.43 (ir), −1.64[d]	0.67	
5c	1.46 (70)	−0.74 (60), −1.41 (ir), −1.64[d]	0.88	
$Rh_2(OAc)_4$[e]	1.02	−1.08 (ir)		
$Ru(tpy)_2^{2+}$[f]	1.30	−1.24, −1.49		

[a] Scan rate 100 mV s^{-1}. $E_{1/2} = {}^1/_2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potential, respectively. $\Delta E_p = E_{pa} - E_{pc}$. Reported values for irreversible processes, labeled ir, are peak potentials. Potentials are corrected by internal reference, ferrocene (395 mV vs SCE). [b] The *cis* and *trans* isomers of **2b** could not be separated, and complex **4a** was not obtained. [c] I_c = cathodic peak current, I_a = anodic peak current. [d] From square-wave voltammetry. [e] Reference 23. [f] Reference 24.

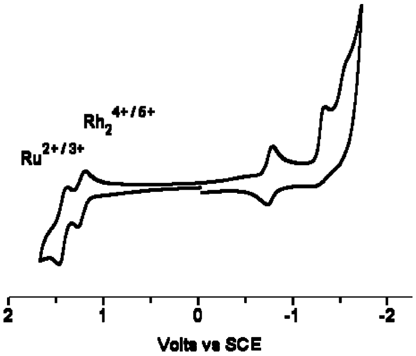

Figure 4. Cyclic voltammogram of complex **1b**.

reason why the positive shift of dirhodium oxidation is linear with the number of Ru(II) linked; on the contrary, smaller effects are expected for successive Ru(II) addition. Anyway, it has also to take into account that when a Ru(II) unit is oxidized, the positive shift of dirhodium core oxidation increases further. These considerations are enough to justify the redox data.

Ligand-based reductions are found for all species at negatively applied potentials. It is noteworthy that the Ru(II) bis(pyridyl)-triazine complexes are reduced at less negative potentials than analogous Ru(II) terpyridine-like complexes.[25] Moreover, the former species also possess one more reduction process than the latter ones. The first reduction processes of the **b** and **c** complexes here studied are significantly less negative than those of the **a** series, which allows their assignment to the bis(2-pyridyl)triazine ligand(s). For adducts **3b** and **4b**, this reduction process becomes chemically irreversible as indicated by their respective cyclic voltammograms, while their square-wave voltammograms show an anodic shift of 0.07 V (**3b**) and 0.15 V (**4b**) relative to the parent complex **5b**. Such a shift can be rationalized by the high positive charge of these complexes, making reduction more facile. The second reduction process of all of the **b** and **c** complexes is tpy-based and is reversible for parent complexes **5b** and **5c**, but becomes irreversible for higher nuclearity systems (Table 1). The third reduction process is triazine-based and is either not observed or chemically irreversible by cyclic voltammetry (Table 1), with the exception of **1c**, which shows a reversible process but with diminished current response relative to the two preceding one-electron reductions. Enhanced resolution inherent to the square wave experiment clearly shows this third reduction process in all cases.

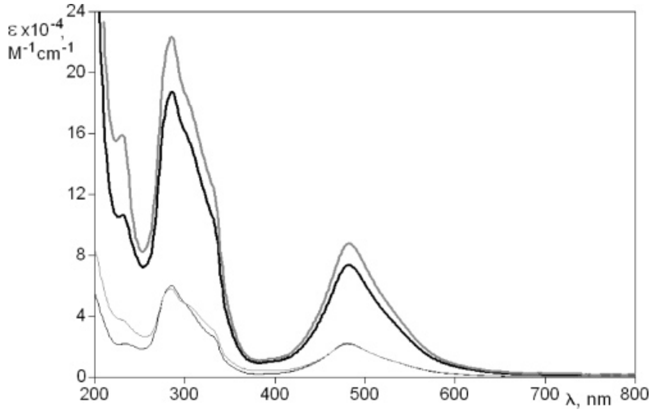

Figure 5. Absorption spectra of compounds **1b** (gray line), **3b** (bold black line), **4b** (bold gray line), and **5b** (black line) in acetonitrile solution.

From the above discussion, it is also clear that the redox processes of the species containing more than one Ru(II) subunit are multielectronic processes, each one corresponding to simultaneous one-electron processes related to virtually identical sites. This process demonstrates that the electronic coupling between the various Ru(II) moieties through the dirhodium core is weak. The high nuclearity assemblies therefore behave as supramolecular systems from an electrochemical viewpoint.

Absorption Spectra. The spectroscopic data for the complexes are gathered in Table 2, and Figure 5 shows the absorption spectra of some representative complexes. The absorption characteristics and profiles of all of the systems here studied are dominated by the appended ruthenium complexes, resembling strongly the absorption spectra of other ruthenium(II) polypyridyl complexes.[26] In fact, spin-allowed metal-to-ligand charge transfer (MLCT) bands of moderately high intensity (ϵ in the range 10^4−10^5 M^{-1} cm^{-1}) dominate the

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Table 2. Spectroscopic and Photophysical Data in Deaerated CH_3CN Solutions at 298 K, unless Otherwise Stated[a]

	absorption	luminescence, 298 K			luminescence, 77 K[b]	
compd	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	Φ ($\times 10^{-4}$)	λ_{max}, nm	τ, μs
1a	230 (49.4), 273 (46.8), 281 (45.4), 307 (63.8), 330 (34.7), 484 (19.2)				639	2.50
1b	285 (61.9), 307 (49.6), 481 (23.1)	731	4.3	1.2	690	0.75
1c	283 (40.3), 299 (38.4), 330 (24.4), 480 (17.8)	750	14.3	0.7	703	1.30
cis-**2a**	230 (98.4), 274 (103), 281 (101), 307 (136), 330 (76.1), 485 (39.4)				636	0.80
trans-**2a**	230 (88.9), 274 (96.2), 281 (93.9), 308 (139), 330 (83.6), 485 (43.1)				634	1.2
3a	230 (127), 274 (138), 281 (135), 307 (175), 330 (103), 485 (57.2)				635	0.80
3b	232 (107), 286 (190), 482 (73.6)	731	5.8	1.1	692	0.86
4b	231 (166), 285 (22.5), 482 (87.1)	733	5.3	1.3	692	0.77
5a	230 (39.2), 272 (34.5), 331 (15.0), 484 (10.8)	666	9.5	0.8	635	13.2
5b	232 (24.5), 286 (60.0), 481 (22.2)	735	5.3	1.2	689	1.37
5c	283 (59.1), 299 (57.6), 478 (22.1)	745	14.4	1.9	698	1.38
$Ru(tpy)_2^{2+}$[c]	474 (10.4)	629	0.25	≤0.05		
$Ru(Ph\text{-}tpy)_2^{2+}$[c]	487 (26.2)	715	1.0	0.4		

[a] The *cis* and *trans* isomers of **2b** could not be separated, and complex **4a** was not obtained. [b] In butyronitrile rigid matrix. [c] Reference 28.

visible region: these bands receive contributions from Ru-to-terpyridine and Ru-to-bis(pyridyl)triazine transitions, with the latter ones expected to be lower in energy.[25] The UV region is dominated by very intense (ϵ even higher than 10^5 M^{-1} cm^{-1}) ligand-centered (LC) spin-allowed $\pi \rightarrow \pi^*$ transitions.

The absence of sizable contributions from absorption of the dirhodium unit is easily explained. The absorption spectra of the parent $Rh_2(OAc)_4$ species are characterized by two absorption bands in the visible region. The lower energy band has been assigned to a $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition[27a] and is shifted strongly to higher energy as a function of the solvent basicity (it is at 552 nm in acetonitrile). The second, higher energy band has been attributed to a $\pi(Rh-O) \rightarrow \sigma^*(Rh-O)$ transition.[27b] Both bands are extremely weak ($\epsilon = 235$ M^{-1} cm^{-1} and $\epsilon = 112$ M^{-1} cm^{-1}, respectively) due to poor orbital overlap. A third band, observed in the UV region and assigned to a $\sigma(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition, is moderately strong (221 nm, $\epsilon = 18\,400$ M^{-1} cm^{-1}).[27b,c] By comparing the molar absorptivities of the dirhodium parent species with those of the (overlapping) bands of the Ru(II) chromophores, it is clear that in the assembled species studied here the dirhodium core bands cannot be observed. Thus, for the compounds of the **a** and **b** series, the absorption intensities of the bands at 480 and 285 nm are roughly integral values of those for the parent complex **5a** and **5b**, corresponding to the number of photoactive Ru(II) units appended to the dirhodium(II, II) unit (see Table 2, cf., spectra of **1b** and **5b** in Figure 5). The absorption band at 230 nm for both series does not follow this trend, likely due in part to overlap with the relatively strong $\sigma(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition. The additivity of the absorption spectra of the higher nuclearity species demonstrates that each Ru(II) chromophore carries in the assemblies its own, roughly unperturbed, absorption properties, further confirming the supramolecular nature of the assemblies, in agreement with the redox data.

Luminescence Properties. All of the complexes emit at 77 K in butyronitrile matrix, whereas only the complexes containing bis(2-pyridyl)triazine ligands (i.e., the **b** and **c** series) show room-temperature emission in fluid solution. Luminescence energies, lifetimes, and quantum yields, along with comparison with suitable model compounds, identify the emitting level as a triplet MLCT state in all cases.[25] Table 2 collects the luminescence data, and Figures 6 and 7 display the luminescence spectra of some representative species.

In particular, specific assignments of the emissive MLCT state can be made: for **1a**−**3a**, the emissive state is a MLCT level in which the ligand involved is the phenyl-terpy, that is, the ligand to which the Rh_2 core is directly linked (obviously, this statement is not applicable to **5a**, where the dirhodium unit is not present. In this case, it is the carboxylated ligand involved in the emissive MLCT state). For the **b** and **c** series of compounds, the ligand involved in the emitting MLCT level is the bis(pyridyl)triazine. However, an interesting difference exists between **1c** and **5c** and the other species, that is, **5b**, **1b**, *trans*-

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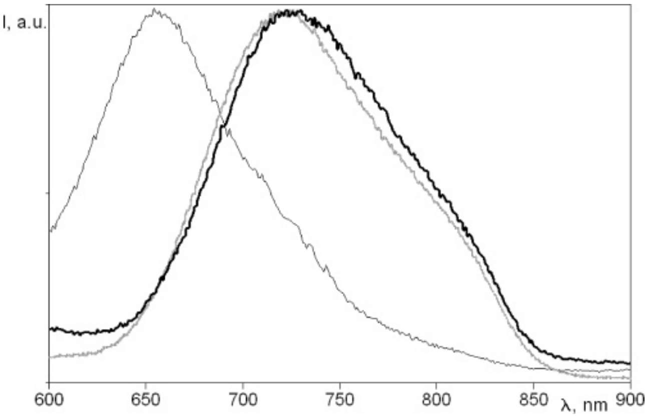

Figure 6. Uncorrected emission spectra of compounds **5a** (black line), **5b** (gray line), and **5c** (bold black line) in acetonitrile fluid solution at room temperature. For corrected values, see Table 2.

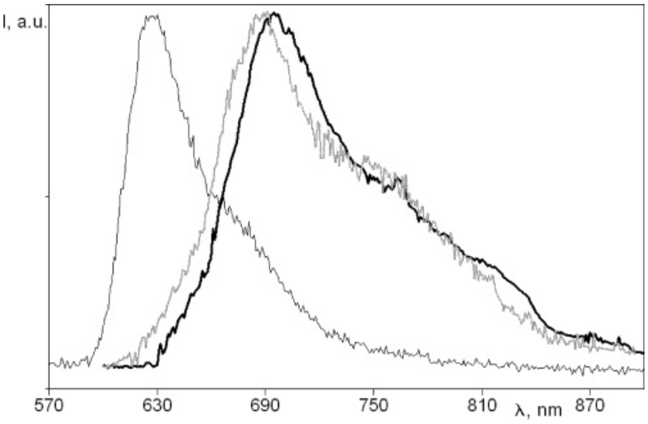

Figure 7. Uncorrected emission spectra of compounds **1c** (bold black line), **3a** (black line), and **4b** (gray line) in butyronitrile rigid matrix at 77 K. For corrected values, see Table 2.

2b, *cis*-**2b**, **3b**, and **4b**. In the latter species, the emitting level involves a peripheral ligand of the multicomponent assemblies, while in the former couple of complexes it involves the (triazine-based) carboxylate ligand connected directly to the Rh_2 core in **1c**. The differences in emission energy between the **b** and **c** series (see Table 2) agree with such a detailed assignment and can be explained in terms of the electron-withdrawing effect of the carboxylate subunit, which lowers the emitting level of **c**-type compounds as compared to **b**-type compounds.

It can also be noted that the room-temperature emission lifetimes of the **c** series are longer than room-temperature emission lifetimes of the **b** series (Table 2). This agrees with the circumstance that the room-temperature excited-state lifetimes of Ru(II) MLCT emitters containing tridentate ligands are mainly governed by the energy gap between the emitting MLCT triplet state and the upper-lying metal-centered (MC) triplet state.[25] By assuming that the MC level is constant in the compounds investigated herein, the above-mentioned decreased energy of the MLCT state in the **c** series in comparison to the **b** series (Table 2) fully accounts for this result.

The absence of luminescence of the **a** series complexes at room temperature was attributed to energy transfer to the dirhodium subunit.[13] The excited-state energy of the dirhodium carboxylate system indeed has been proposed to lie between 1.34 and 1.77 eV (the axial ligands of the published systems are different from the acetonitrile molecules, which play the role of axial ligands in our systems, but in the absence of more similar compounds no better model is available),[11] so energy transfer from the lowest-lying, potentially emitting MLCT triplet state of the **a** series complexes is thermodynamically allowed by at least 0.18 eV (for this calculation, the excited-state energy of the complexes is approximate to the 77 K emission maximum, that is, about 1.94 eV, Table 2). Electron-transfer quenching is ruled out because oxidative electron transfer is highly endoergonic (assuming $E_{red}(Rh_2) = -1.08$ V, $*E_{ox}(Ru) = -0.65$ V, $\Delta G = +0.43$ eV).[29] As far as reductive electron transfer is concerned, a similar result is obtained (assuming $*E_{red}(Ru) = +0.76$ V, $E_{ox}(Rh_2) = +1.20$ V, $\Delta G = +0.44$ eV). MLCT emission is partly recovered on passing to 77 K, suggesting a non-negligible nuclear barrier for the energy transfer process, and also implying a Dexter-type, electron exchange mechanism.[13]

On passing to the **b** and **c** series, the energy of the Ru-based MLCT states decreases significantly from the **a** series. For the **b** series (emitting MLCT states involving peripheral ligands) the triplet MLCT state lies at about 1.80 eV (from the 77 K emission maxima, Table 2), whereas for the **c** series (emitting MLCT states involving the carboxylate ligands connected to the dirhodium core) the triplet MLCT state lies at about 1.78 eV. It should be noted that the 77 K emission maximum represents an upper limit for the MLCT emission at room temperature, because solvent reorganization is not taken into account. From a recent paper where the 77 K emission maxima were compared to calculated (by emission spectral fittings) room-temperature MLCT energies for a series of Ru-terpy like complexes similar to the species studied here,[30] it can be inferred that solvent effects stabilize MLCT states by about 0.07 eV (averaged value of 11 compounds) in this type of complex. While such a stabilization does not change the discussion for the strongly exoergonic energy transfer involving Ru(II) chromophores and dirhodium subunits in the **a** series, it leads us to consider energy transfer from the MLCT levels of the Ru(II) chromophores to the excited state of the dirhodium units in the **b** and **c** series as roughly isoergonic. By taking into account the non-negligible nuclear barrier for the energy transfer process, as inferred by the 77 K emission properties of the **a** series (see above), and the relatively short lifetimes of the room-temperature MLCT states of the complexes, it is reasonable that energy transfer from Ru-based MLCT states to the dirhodium excited states does not take place at room temperature in the **b** and **c** series. As far as electron-transfer processes are concerned, both reductive and oxidative processes are endoergonic, so the absence of luminescence quenching for **b** and **c** complexes is fully reasonable.

Our room-temperature results also contribute to better delineate the reported uncertainty on the excited-state energy of the dirhodium core unit.[11] In fact, the above considerations have been made by assuming the upper limit of the calculated excited-state energy, that is, 1.77 eV. If we consider the reported lower limit, 1.34 eV, it is hard to believe that the nuclear barrier for

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Table 3. Calculated Rate Constants of the Ru-to-Rh_2 Energy Transfer Processes at 77 K[a]

	compound						
	1a	*cis*-**2a**	*trans*-**2a**	**3a**	**1b**	**3b**	**4b**
k_{en} (10^5 s^{-1})	3.2	12.0	7.5	12.0	6.0	4.3	5.8

[a] Calculated values are based on the 77 K lifetimes given in Table 2. Reference species are **5a** for the **a** series and **5b** for the **b** series.

energy transfer could limit the energy transfer process in the **b** and **c** series, in the presence of driving forces of about 0.40 eV, even in the presence of a non-negligible nuclear barrier. In energy transfer processes, the nuclear barrier is usually limited to inner reorganization energies. For Ru(II) polypyridine complexes, inner reorganization energy for energy transfer is very small,[1a] as also confirmed by similarity of the ground- and excited-state X-ray structures.[31] Some exception could be considered in the presence of particular substituents on the acceptor ligand of the MLCT state, as for **c** compounds (the carboxylate moiety), but this is not the case for the **b** species. For the dirhodium unit, inner reorganization is expected to be of significantly higher energy,[32] but in any case it is hard to assume a total inner reorganization energy higher than 0.40 eV for the energy transfer process. Even in the case of relatively weak coupling (coupling cannot be negligible in our case, otherwise energy transfer in the **a** complexes would be impossible), nuclear barriers of 0.25 eV are easily bypassed at room temperature for exergonic processes, thus (on the basis of the absence of energy transfer in **1c**, for which a MLCT level at about 1.70 eV is estimated, taking into account solvent stabilization) the lower limit for the dirhodium excited state can be located at about 1.55 eV.

As previously mentioned, energy transfer is also effective in the **a** series at 77 K, although it is not effective enough to totally quench the luminescence in these conditions. On the basis of the luminescence lifetime of the model compound **5a**, energy transfer rate constants can be calculated by the equation $k_{en} = 1/\tau_i - 1/\tau_0$, where τ_i and τ_0 are the 77 K emission lifetimes of the compounds under study and of the model compound, respectively. From the data in Table 3, the rate constants of the compounds of the **a** series are close one another, as expected because of the roughly identical donor/acceptor pair involved. Small differences in rate are still appreciable, and they can be tentatively attributed to small modifications in the energy of the acceptor dirhodium-based excited state (with modification in the driving force) or to small changes in the reorganization energy within the acceptor unit as a function of different Ru chromophores arrangements.

Energy transfer is also partly effective at 77 K for the **b** series, on comparing emission lifetimes of these species with that of their model species **5b**. Energy transfer rate constants are also shown in Table 3, and interestingly they are close to one another and also to those of the **a** series. This latter finding is puzzling, considering the different driving forces for the intramolecular Ru(MLCT)-to-Rh_2 energy transfer processes in the **a**-type compounds (about 0.18 eV, in the upper limit of Rh_2 excited-state level) and in the **b**-type species (about 0.03 eV with the same assumption): in fact, a difference of 0.15 eV (which is independent of the effective energy level of the acceptor subunit) should lead to a substantial difference in rate constants, when all of the other parameters are constant. From these considerations, it can be inferred that at least another parameter governing energy transfer rate is different for the two series of complexes.

Electronic coupling cannot be held responsible for this effect: in fact, on looking at the structural formulas of **a** and **b** complexes, electronic coupling would be higher for the **a** series, because the donor/acceptor distance is smaller in this case (the MLCT state in **a** systems is directed toward the Rh_2 unit, while in the **b** series it is directed toward the periphery), and this would lead to the reverse effect. So the decisive effect has to be linked to nuclear factors. On a more careful examination, it should be considered that the acceptor ligand of the MLCT state of the **a** series also extends to the carboxylate moieties. Reorganization energy within the Ru(II) partner of the energy transfer process would therefore be larger for **a** compounds than for **b** compounds. Larger reorganization energy can compensate for larger driving forces in Dexter-type energy transfer processes and could explain the similarity in energy transfer rate constants between **a** and **b** complexes at 77 K.[33]

Compound **1c** does not exhibit luminescence quenching, even at 77 K. As compared to the **b** series, the MLCT excited state of **1c** is even further shifted to lower energy, so the driving force is less favorable, and, on the basis of the above discussion, also its reorganization energy is probably higher. Both such factors allow the inefficiency of the energy transfer process to be explained.

The 77 K data contribute to further limit the uncertainty on the dirhodium excited-state level. As mentioned above, the 1.77 eV upper limit for this latter state implies a 0.03 eV value for the driving force for energy transfer in the **b** series (the MLCT state in this condition would be 1.80 eV, from 77 K emission maxima in Table 2). At 77 K and in the presence of non-negligible reorganization energy, this driving force would make the process hardly efficient. It seems therefore reasonable to propose that the upper limit for the dirhodium core excited state is 1.70 eV.

Conclusion

We have demonstrated the utility of the dirhodium(II, II) tetracarboxylate motif toward convergent and controlled self-assembly of polynuclear photoactive compounds based upon suitable carboxy-functionalized $Ru(tpy)_2^{2+}$ photoactive units, due in part to inherent advantages of the dirhodium(II, II) tetracarboxylate unit regarding its relative inertness to ligand scrambling and its diamagnetic nature. In addition to this, it appears that there exists some difficulty to append such cationic complexes onto the Rh_2^{4+} core, the origins of which are likely electrostatic in nature, as evidenced by the crystal structure of *trans*-**2a** and nonreactivity to ligand displacement when employ-

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(33) An alternative explanation for the observed shortened luminescence lifetimes of the adducts at 77 K as compared to the model species would be an increased spin-orbit coupling for MLCT decay due to the presence of the dirhodium subunit. This explanation would account for the larger effect in lifetime reduction obtained for the **a** series (for which the MLCT state is closer to the dirhodium unit) as compared to the **b** series, but fails to explain the roughly constant values between **1c** and **5c**. Moreover, it would disagree with the room-temperature lifetime data of the **b** and **c** series, where luminescence lifetime of the MLCT states is not affected by the presence of the dirhodium units.

ing the relatively electron-deficient $Rh_2(O_2CCF_3)_4$. The net result is control over the extent of substitution en route to polynuclear species. Contributions of electron transfer to the efficient quenching observed in the series **1a**−**3a** are precluded on thermodynamic grounds and through the preparation of relatively electron-deficient triazine analogues **1b**, **2b**, **4b**, and **1c**, which have enabled direct observation of the $Rh_2^{4+/5+}$ couple (**1b** and **1c**) previously unobserved for **1a**. Moreover, the triazine analogues emit almost unperturbed relative to their respective parent complexes **5b** and **5c** subsequent to initial photoexcitation, which places the non-emissive state of the dirhodium(II, II) tetraacetate near the previously reported upper limit of 1.77 eV. Considering the recent elucidation of other long-lived dimeric photoexcited states,[34] more evolved examples of these systems should prove to be ideal models for study of energy and electron-transfer processes.

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Supporting Information Available: Crystallographic data in CIF format for **5a**, **5b**, and *trans*-**2a**. Synthetic procedures for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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