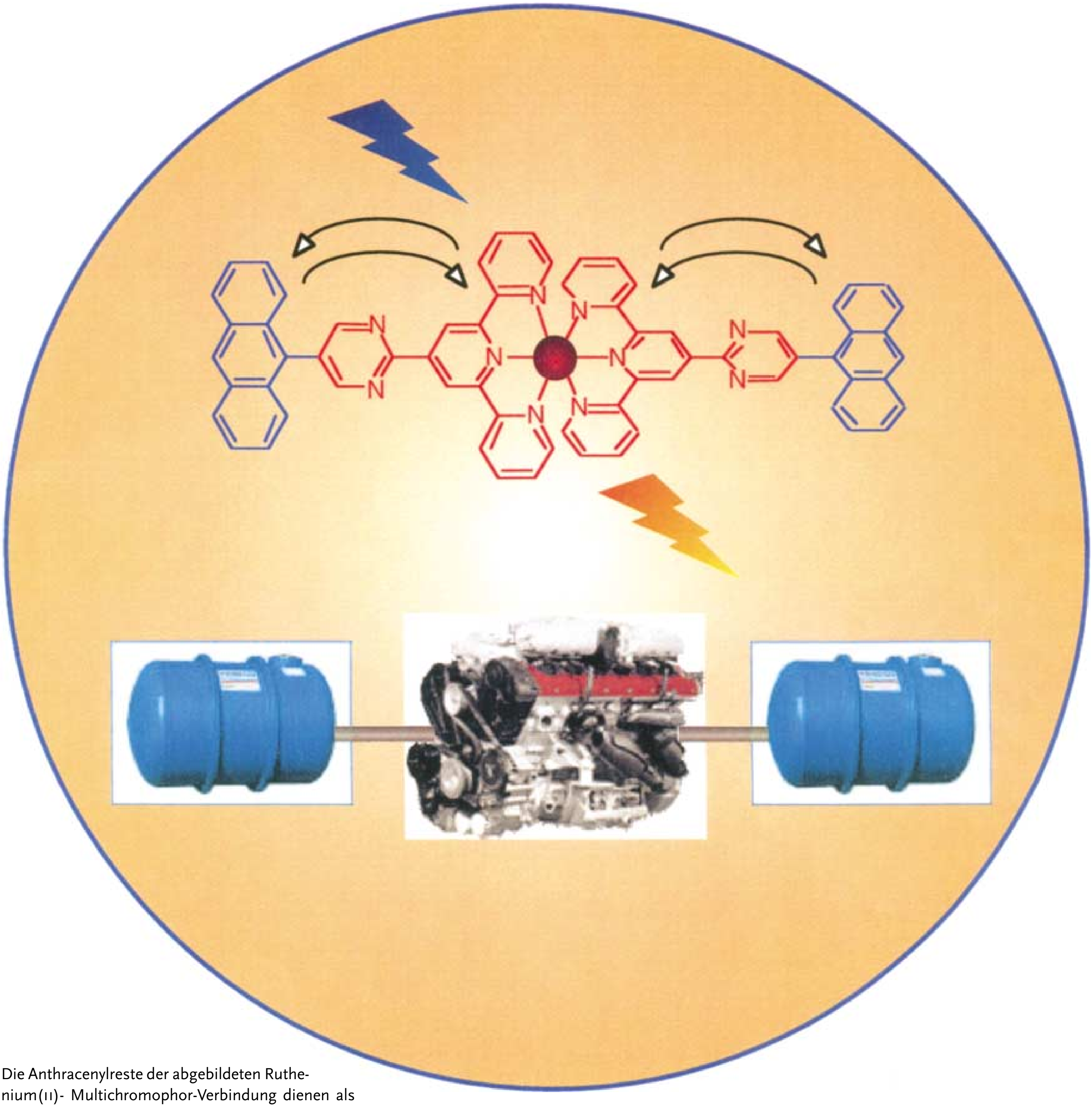
Zuschriften



Die Anthracenylreste der abgebildeten Ruthenium(II)- Multichromophor-Verbindung dienen als eine Art Angeregter-Zustand-Reservoirtank, der Metallchromophor ist als Motor versinnbildlicht. Die nur geringe Wechselwirkung der einzelnen Chromophore bewirkt Metall-zu-Ligand-Charge-Transfer mit besonders langer Lebensdauer. Mehr hierzu erfahren Sie auf den nächsten Seiten in der Zuschrift von Campagna, Hanan und Mitarbeitern.

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Long-Lived Luminescence

In Search of Ruthenium(II) Complexes Based on Tridentate Polypyridine Ligands that Feature Long-lived Room-Temperature Luminescence: The Multichromophore Approach**

*Rosalba Passalacqua, Frédérique Loiseau,
Sebastiano Campagna,* Yuan-Qing Fang, and
Garry S. Hanan**

*Dedicated to Professor Manfred T. Reetz
on the occasion of his 60th birthday*

Within the field of inorganic photochemistry, there is considerable interest in the design of ruthenium(II) complexes based on tridentate ligands that exhibit long-lived metal-to-ligand charge-transfer (MLCT) excited states.[1] Indeed, ruthenium(II) polypyridyl complexes play outstanding roles in fields connected to solar-energy conversion and the storage of light and/or electronic information at the molecular level.[2] The prototype of this class of compounds, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), has been one of the most studied metal-containing species in the last two decades.[2a,3] However, its homologous compound $[Ru(tpy)_2]^{2+}$, based on the tridentate polypyridine ligand 2,2′:6′,2′′-terpyridine (tpy), is structurally more appealing than $[Ru(bpy)_3]^{2+}$ for several reasons: 1) $[Ru(bpy)_3]^{2+}$ is a mixture of Δ and Λ enantiomers; 2) monosubstitution of bpy ligands introduces *fac* and *mer* isomerism, so that polynuclear arrays based on the $[Ru(bpy)_3]^{2+}$ motif are rarely pure species; 3) a linear arrangement of such $[Ru(bpy)_3]^{2+}$ chromophores, useful for the design of molecular wires and consequently vectorial energy and electron migration, is difficult to obtain. These problems can indeed be overcome by the use of tridentate, tpy-type polypyridine ligands. However, the photophysical properties of the $[Ru(tpy)_2]^{2+}$ ion and its derivatives are much less useful than those of the $[Ru(bpy)_3]^{2+}$ ion, essentially because the $[Ru(tpy)_2]^{2+}$ ion has a short excited-state lifetime at room temperature.[4]

Several strategies have been employed to prolong the room-temperature excited-state lifetime of ruthenium complexes with tridentate polypyridine ligands, these include the use of 1) cyclometalating ligands,[1e] 2) electron withdrawing and/or donor substituents,[1d] and 3) ligands with extended π* orbitals, to increase delocalization in the acceptor ligand of the MLCT state.[1c,5] The aim of the first two strategies is to increase the energy gap between the MLCT and the MC excited state, thereby minimizing the thermally activated surface crossing which dominates the MLCT deactivation processes,[4] while the third strategy is based on modification of the Frank–Condon factors for nonradiative decay.

Another approach has emerged as a very efficient tool to increase the excited-state lifetime of metal polypyridine complexes: the combination of metal complexes and organic chromophores which have triplet excited states (very long-lived, since their deactivation processes are strongly forbidden ones) at energies close to the triplet MLCT state of the metal chromophore.[6] This requires the synthesis of multichromophoric species (therefore this approach can be termed as "the multichromophore approach"), in which the various metal- and organic-based chromophores are only weakly interacting, so that their individual properties are essentially maintained.[7] However, if the electronic interaction is large enough, equilibration between the ^{3}MLCT and the lowest-lying organic triplet can occur, and the organic triplet may play the role of an energy-storage site, with the overall effect of extending the MLCT luminescence lifetime.[6]

Herein, we present a new strategy based on the fusion of two approaches: the coupling of ligands with extended π* orbitals and organic chromophores with suitable triplet states (the multichromophore approach). For the ligands containing extended π* orbitals, we chose pyrimidine-substituted tpy ligands, which recently have proved to be effective in achieving this aim,[5d] whereas anthracene derivatives have been selected to act as the suitable energy storage site(s). By applying this strategy, two novel, multichromophoric species have been prepared: $[(an\text{-}pym\text{-}tpy)Ru(tpy)](PF_6)_2$ (**1**, an-pym-tpy = 2′′′-(2,2′:6′,2′′-terpyrid-4′-yl)-5′′′-(9-anthryl)pyrimidine) and $[(an\text{-}pym\text{-}tpy)Ru(tpy\text{-}pym\text{-}an)](PF_6)_2$ (**2**). The results are extraordinary: compound **2** exhibits a MLCT luminescence lifetime of 1.8 μs at room temperature which, to our knowledge, is the longest-lived room-temperature emission reported for a ruthenium polypyridyl species based on tridentate ligands.

Complexes **1** and **2** were synthesized using the "chemistry-on-the-complex" methodology,[8] in which the an-pym-tpy ligands were synthesized while directly attached to the metal ions. Thus, ruthenium complexes **5** and **6** were allowed to react with 9-anthrylboronic acid under Suzuki coupling conditions to afford complexes **1** (83% yield) and **2** (60% yield), respectively (full details are given in the Supporting Information).[9] Although previous work has shown that a chloro substituent in the 5-position of a pyrimidine group is relatively inert to heterocoupling reactions, the ruthenium cation effectively activates the 5-chloro group by an inductive effect.[10,11]

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[*] Prof. S. Campagna, R. Passalacqua, Dr. F. Loiseau
Dipartimento di Chimica Inorganica
Chimica Analitica e Chimica Fisica
Università di Messina, 98166 Messina (Italy)
Fax: (39) 090-393756
E-mail: photochem@chem.unime.it

Prof. G. S. Hanan,[+] Y.-Q. Fang
Department of Chemistry, University of Waterloo (Canada)
E-mail: garry.hanan@umontreal.ca

[+] Present address:
Département de chimie, Université de Montréal
2900 Edouard-Montpetit, Montréal, QC, H3T 1J4 (Canada)
Fax: (+1) 514-343-7586

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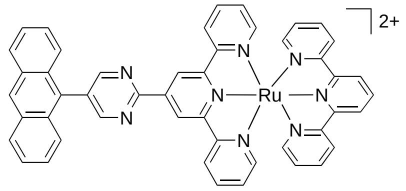

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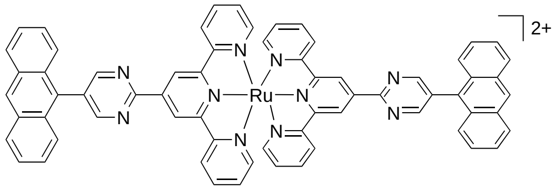

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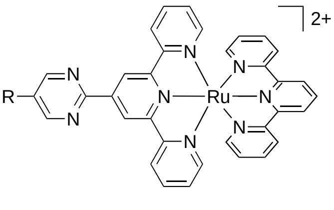
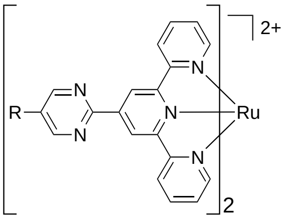


3; R = phenyl
5; R = Cl



4; R = phenyl
6; R = Cl

The absorption spectra of the new species (Figure 1) are dominated by spin-allowed MLCT bands in the visible and by spin-allowed polypyridine ligand-centered (LC) bands in the UV region. Moreover, typical anthracene absorption signatures appear in the 350–400 nm region (because of population of the ^1L_a state) and at about 254 nm (because of population of the ^1B_a state). As expected, the molar absorptivities of the anthracene-based absorption bands are larger in **2** than **1**. The absorption features indicate that in **1** and **2** the metal-based and organic chromophores are at best weakly interacting with one another.

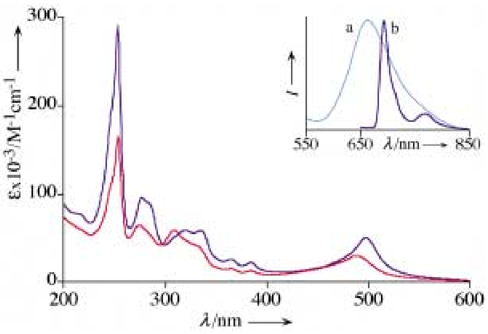


Figure 1. Absorption spectra of **1** (red) and **2** (blue) in acetonitrile solution and inset: uncorrected emission spectra of **2** in acetonitrile solution at room temperature (a) and in butyronitrile at 77 K (b). Corrected values for emission maxima are given in Table 1.

The luminescence data of **1** and **2** and of the reference compounds $[(tpy)Ru(tpy\text{-}pym\text{-}ph)]^{2+}$ (**3**, tpy-pym-ph = 2‴-(2,2′:6′,2″-terpyrid-4′-yl)-5‴-(phenyl)pyrimidine) and $[Ru(tpy\text{-}pym\text{-}ph)_2]^{2+}$ (**4**), are collected in Table 1, while the emission spectra of **2** are shown in Figure 1, inset. The experimental results at 77 K (in particular, lifetimes and emission spectra) clearly allow the low temperature emission to be attributed to the anthracene triplet.[12] At room temperature, the emission spectra of **1** and **2** are typical of MLCT emitters.[3] However, their luminescence decays are biexponential (Table 1, Figure 2), and in both cases one of the decay components is long-lived when compared to the emission lifetimes of similar species,[1,2,5] including **3** and **4**. Indeed, compounds **3** and **4** have emission spectra which are practically coincident with those of **1** and **2**, respectively. As the effect of the extended π* orbital(s) in **3** and **4** is already present in **1** and **2**,[13] the additional increase in the luminescence lifetimes of the anthracene-containing species is related to the presence of the anthracene triplet. It can be assumed that the ^{3}MLCT state(s) initially formed in **1** and **2** deactivate by energy transfer to the anthracene-based triplet states, which are lower in energy.[14] The fastest component of the luminescence decays of **1** and **2** can be assigned to decay of the initially formed ^{3}MLCT state, shortened in comparison with the luminescence lifetimes of the model species **3** and **4** (Table 1) because of the occurrence of the above mentioned energy-transfer to the anthracene-based triplet states. Equi-

Table 1: Luminescence data.

Compound	298 K[a]			77 K[b]	
	λ_{max} [nm]	τ [ns]	Φ	λ_{max} [nm]	τ
1	680	5.5; 402	1.3×10^{-4}	692	3.5 ms
2	675	5.8; 1806	1.8×10^{-4}	694	3.5 ms
3	680	15	1.8×10^{-4}	654	15.0 µs
4	675	21	4.4×10^{-4}	651	13.8 µs

[a] In deaerated CH_3CN. [b] In butyronitrile.

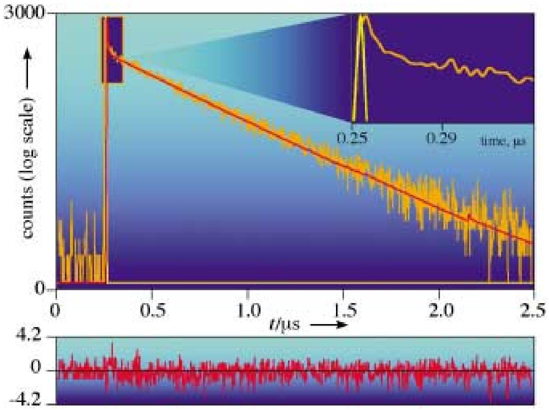


Figure 2. Luminescence decay (orange), lamp profile (yellow), and fitting (red) of the emission of **2** at room temperature in degassed acetonitrile.

libration between ^{3}MLCT and the triplet anthracene states is established by the Boltzmann distribution,[6] which results in a significant increase of the ^{3}MLCT luminescence lifetime. The extension of the ^{3}MLCT luminescence lifetime is particularly noticeable in **2**, as the slower component of its luminescence decay lasts up to 1.8 μs.

To further confirm our interpretation, we performed transient absorption spectroscopy experiments on **1**–**4** at room temperature. Whereas no transient spectrum was obtained for **3** and **4** 100 ns after the laser flash, transient spectra with typical features of anthracene triplet absorption[6e,12] were obtained for **1** and **2**, with decays in very good agreement with their respective long-lived luminescence lifetimes.

It has been reported that there is a linear dependence between the extension of lifetime of Ru$^{\mathrm{II}}$ polypyridine chromophores and the number of identical organic chromophores added.[6e] On looking at Table 1, it appears that the data for **1** and **2** do not agree with this statement: it should be considered that their ^{3}MLCT levels are slightly different to one another (as well as those of their respective model compounds **3** and **4**), since an-pym-tpy is a better electron-withdrawing ligand than tpy and is expected to leave less electron density on the metal center, thus increasing the energy of the MLCT state(s). This argument also agrees with emission maxima of **1**–**4** at room temperature (Table 1). As a consequence, the partitioning of the population between the MLCT and anthracene triplet levels changes on passing from **1** to **2** not only because of the change in the number of the organic chromophores, but also because of the difference in the energy gap between the relevant states. As such, **1** and **2** are not totally homologous, which translates into an extension of the luminescence lifetime in **2** by much more than twice that of **1**.

In conclusion, the fusion of two design strategies affords long-lived luminescence at room temperature in Ru$^{\mathrm{II}}$ complexes based on tridentate ligands. In particular, the multichromophore approach proved to be very efficient and allowed us to obtain novel species (**1** and **2**) which displayed impressive long-lived MLCT luminescence. Coupling of the novel chromophores with suitable acceptor/donor subunits to prepare multicomponent species for vectorial-energy and electron-transfer studies is under way.

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Keywords: chromophores · luminescence · N ligands · photochemistry · ruthenium

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[14] The energy of the triplet anthracene can be inferred by the highest-energy emission maximum of **1** and **2** at 77 K, and the energy of the ^{3}MLCT states can be approximatly equal to the highest-energy emission maximum of **3** and **4** at 77 K (Table 1). Based on these data, driving forces for the energy-transfer process are 840 and 960 cm^{-1} in **1** and **2**, respectively.