Exciton-like energy collection in an oligothiophene wire end-capped by Ru- and Os-polypyridine chromophores

Raymond Ziessel,*[a] Peter Bäuerle,[b] Martin Ammann,[b] Andrea Barbieri[c] and Francesco Barigelletti*[c]

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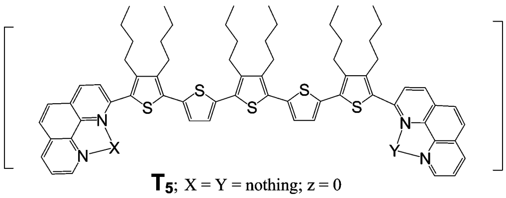
Ru(II)- and Os(II)-polypyridine *termini* are linked by a quinquethiophene bridge (the inter-metal separation is *ca.* 1.9 nm) wherein excitation energy flows into the luminescent Os-based unit by way of a conductive level.

Transfer of excitation energy between terminal chromophores of wire-like molecular arrays is well documented.[1] Typical systems are arranged as dyads and feature photoactive donor (D) and acceptor (A) units linked by a suitable bridge (B), which frequently includes a variable number of organic modular subunits.[1] In most D–B–A systems studied up to now, where D and A are Ru(II)-, Re(I)- or Os(II)-polypyridine chromophores,[2–5] the electronic coupling between D and A is weak and strongly distance-dependent over distances larger than their van der Waals separation. In these cases, non-adiabatic treatments apply because (i) B only plays a structural role (*i.e.*, excitation transfer is due to dipole–dipole interactions between electronic transitions localized at D and A) or (ii) B promotes superexchange paths ultimately resulting in double electron exchange between D and A (in this case, bridge-localized orbitals and states only provide a virtual mediation, *i.e.*, during the transfer, the excitation does not step on B).[1,2,5]

For cases where the modular subunits within B are strongly coupled, injection of excitation at B is expected to yield rapidly diffusing excitonic states,[6] until trapping at appended units may occur. Such cases of adiabatic transmission of excitation along molecular wires are less common than those due to non-adiabatic (weak) interactions. One reason relies on the required energetic matching of involved excited levels. Actually, for B to act as an efficient excitation conductor, the implied excitonic levels must lie between those for the D and A units (this is reminiscent of conceptually similar cases of efficient electron injection in molecular wires[7]). We report here one such case for the **RuT$_5$** and **RuT$_5$Os** molecular arrays depicted in Chart 1 (**T$_5$** is 2,2′-(3,4,3″,4″,3⁗,4⁗-hexabutyl-[2,2′ : 5′,2″ : 5″,2‴ : 5‴,2⁗]quinquethien-5,5⁗-diyl)bis-[1,10]phenanthroline), **RuT$_5$** is [(bpy)$_2$-Ru(**T$_5$**)]$^{2+}$, and **RuT$_5$Os** is [(bpy)$_2$Ru(**T$_5$**)Os(bpy)$_2$]$^{4+}$ (bpy is 2,2′-bipyridine). For the latter complex, molecular modelling provides an inter-metal separation of *ca.* 1.9 nm. In these molecules, excitation at the bridging component leads to excitonic states spread over the entire species; for **RuT$_5$Os**, Ru-based and Os-based energy levels located at the *termini* of the wire happen to be connected through an energetically interposed level.



T$_5$; X = Y = nothing; z = 0
RuT$_5$; X = [Ru(bpy)$_2$]$^{2+}$; Y = nothing; z = 2
RuT$_5$Os; X = [Ru(bpy)$_2$]$^{2+}$, Y = [Os(bpy)$_2$]$^{2+}$; z = 4

Chart 1

Ligand **T$_5$** was prepared in 27% yield by Negishi-type coupling between 2 equiv. of 2-iodo-1,10-phenanthroline and biszincated hexabutyl quinquethiophene under Pd° catalysis. A stepwise protocol was applied to complex the metals. First, [Ru(bpy)$_2$Cl$_2$] was added portionwise (by 0.2 equiv. up to 1 equiv.) to an EtOH solution of **T$_5$**, and **RuT$_5$** was isolated by chromatography (70%). The target **RuT$_5$Os** complex was synthesized in 65%, using [Os(bpy)$_2$Cl$_2$] (1.2 equiv.) and **RuT$_5$** in refluxing EtOH.†

The spectroscopic properties of the **T$_5$** ligand, and of the derived mononuclear **RuT$_5$** and dinuclear **RuT$_5$Os** complexes are collected in Table 1.‡ Fig. 1 compares electronic absorption spectra and emission bands for the investigated compounds. From the absorption profiles of Fig. 1, one sees that the ligand and the complexes feature a qualitatively similar absorption envelop (peaking in the range 410–418 nm, $\varepsilon \sim 6 \times 10^4$ M^{-1} cm^{-1}). For **T$_5$**, $^1\pi$–π^* transitions are responsible for the absorption features that likely include intraligand charge transfer contributions (ILCT, of an oligothiophene-to-phenanthroline nature[8]). As found in several oligothiophene and other π-conjugated assemblies, the $^1\pi$–π^* state responsible for the intense, broad absorption band exhibited by the **T$_5$** ligand in the visible region, is due to highly mobile $^1\pi$–π^* excitons delocalised over the entire backbone of the oligomeric fragment;[6,9–14] excitation transfer through such oligothiophene bridges can take place with rate constants as high as $k_{\text{en}} \sim 10^{11}$ s^{-1}.[15] For the complexes, the lowest-energy absorption band is due to overlapping between strong $^1\pi$–π^* oligothiophene-centred transitions and weaker ^{1}MLCT transitions on the red side of the band, see Fig. 1. These latter transitions should involve the metal center(s) and the coordinated ligands, phen or bpy. Regarding **RuT$_5$Os**, an additional absorption tail extending to *ca.* 700 nm (ε = 3200 M^{-1} cm^{-1} at 615 nm, see Fig. 1) is due to direct singlet–triplet absorption leading to population of Os-centred ^{3}MLCT states, a well known effect due to the strong spin–orbit coupling of the heavy Os centre.[16]

The luminescence properties of the ligand and the complexes, as observed after excitation at 420 nm, are as follows. (i) The ligand **T$_5$** exhibits a strong emission ($\lambda_{\max}$ = 546 nm, ϕ = 0.11 and

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*ziessel@chimie.u-strasbg.fr (Raymond Ziessel)
franz@isof.cnr.it (Francesco Barigelletti)

Table 1 Photophysical properties[a]

	Absorption	Emission		
	λ_{max}/nm, ε/M^{-1} cm^{-1}	λ_{max}/nm[b]	ϕ[b]	τ/ns
T$_5$	411 (61 700)	546	0.11	0.8
RuT$_5$	418 (57 500), 285 (79 500)	[c]	[c]	[c]
RuT$_5$Os	615 (3200), 418 (60 100), 287 (118 700)	718[d]	1.3×10^{-3},[d]	140[d]

[a] In air-equilibrated CH_2Cl_2 and CH_3CN solutions for the ligand and complexes, respectively. [b] Excitation performed at 420 nm in all cases (at 375 nm for the lifetimes). [c] A weak emission band (λ_{max} = 546 nm, intensity <0.3%, τ = 0.8 ns) is ascribed to impurity traces from **T$_5$**. [d] Irradiation at 420 nm (375 nm for the lifetimes) or 560 nm (whereby the ^{3}Os-to-L CT level is directly excited, see Fig. 1), yields identical luminescence properties. The Os-based luminescence decay does not show rise time components , consistent with $k_{en} \geqslant 5 \times 10^9$ s^{-1}.

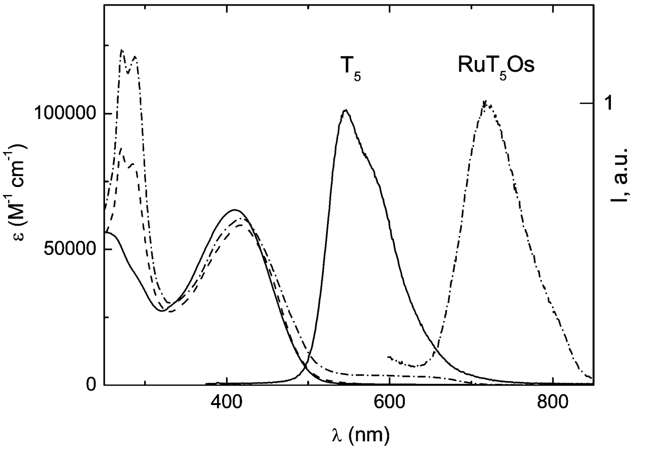
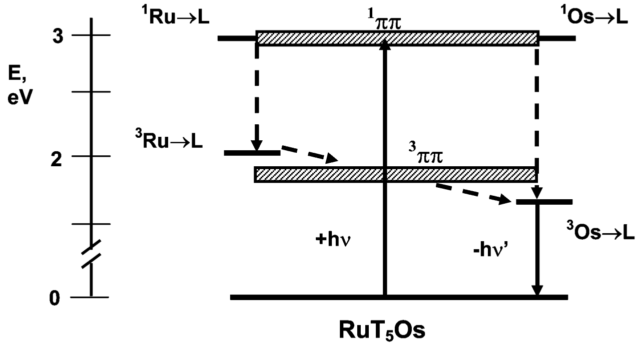


Fig. 1 Absorption and luminescence (uncorrected) spectra of the investigated ligand **T$_5$** (full line) in CH_2Cl_2, and complexes **RuT$_5$** (dashed, no emission registered), and **RuT$_5$Os** (dashed-dotted) in CH_3CN; excitation was at 420 nm in all cases.

τ = 0.8 ns) which is identified as $^1\pi\pi^*$ fluorescence.[9,10,17] Its $^1E_{00}$ energy level can be estimated by Franck–Condon analysis of the luminescence profile,[18] yielding $^1E_{00}$ = 2.43 eV. No phosphorescence is observed, as it happens for this class of oligomers,[17] however, the triplet level is estimated to lie 0.5–0.7 eV below the singlet,[10] and for **T$_5$**, $^3E_{00}$ = 1.83 ± 0.1 eV. (ii) For **RuT$_5$**, use of light at 420 nm predominantly yields $^1\pi\pi^*$ at the **T$_5$** bridge (besides small amounts of ^{1}MLCT states at the Ru-based unit). However neither ligand-centred fluorescence nor ^{3}MLCT phosphorescence are registered for **RuT$_5$** (Fig. 1 and Table 1), even if $[Ru(bpy)_2(phen)]^{2+}$ is known to be strongly phosphorescent.[19] An explanation for this finding relies on the energy layout of implied excited levels. For $[Ru(bpy)_2(phen)]^{2+}$, the lowest-lying ^{3}Ru-to-L CT level is at 2.1 eV[19] so that within **RuT$_5$** an effective two-step deactivation path is open, consistent with the energy sequence $^1\pi\pi^*$ ($^1E_{00}$ = 2.43 eV) > ^{3}Ru-to-L CT (2.1 eV) > $^3\pi\pi^*$ ($^3E_{00}$ = 1.83 eV). It consists of (ii-a) a $^1\pi\pi^* \rightarrow {}^3$Ru-to-L CT transition (whose occurrence causes complete quenching of the $^1\pi\pi^*$ fluorescence in **RuT$_5$** with respect to what happens in **T$_5$**), followed by (ii-b) a ^{3}Ru-to-L CT $\rightarrow {}^3\pi\pi^*$ transition (in turn, consistent with the lack of any Ru-based emission in **RuT$_5$**, with respect to what happens for $[Ru(bpy)_2(phen)]^{2+}$,[19]).§ (iii) For **RuT$_5$Os**, excitation at 420 nm (predominantly yielding $^1\pi\pi^*$ states at the **T$_5$** bridge but also ^{1}MLCT states at both Ru- and Os-based terminal units, Fig. 1) again does not result in $^1\pi\pi^*$ fluorescence; instead the registered luminescence properties λ_{max} = 718 nm (uncorrected, λ_{max} = 740 nm upon correction), $\phi = 1.3 \times 10^{-3}$, and τ = 140 ns, are as expected for typical ^{3}Os-to-L CT levels.[16] In addition, direct excitation to the ^{3}Os-to-L CT level by use of 560 nm light (see Fig. 1), yields the same values for the luminescence parameters. This indicates that upon excitation at 420 nm, conversion from the higher-lying $^1\pi\pi$ and ^{1}Ru-to-L CT levels to the ^{3}Os-to-L CT luminescent level (1.6–1.7 eV)[16] is complete. Thus for **RuT$_5$Os**, excitation energy is effectively drained from all locations of the molecular wire to the terminal $[Os(bpy)_2(phen)]^{2+}$ unit. In particular, also the excitation initially placed on the Ru-based terminal unit flows to the Os-based unit. The above observations allow us to draw the energetic diagram shown in Scheme 1. Here the $^3\pi\pi^*$ level from the parent $^1\pi\pi^*$ excitonic level of the **T$_5$** bridging fragment lies between the ^{3}MLCT levels of the Ru- and Os-based terminals.



Scheme 1 Excited levels for **RuT$_5$Os**.

In conclusion, the absorption and luminescence properties observed for **T$_5$**, **RuT$_5$**, and **RuT$_5$Os**, indicate that in the heterometallic species, the Ru- and Os-based metal units (at an inter-metal distance of 1.9 nm) are connected *via* electronic levels that allow physical (*i.e.*, not virtual) flow of excitonic energy to the Os-based trap.

Raymond Ziessel,*[a] Peter Bäuerle,[b] Martin Ammann,[b] Andrea Barbieri[c] and Francesco Barigelletti*[c]
[a]*Laboratoire de Chimie Moléculaire, Ecole de Chimie, Polymères, Matériaux (ECPM), Université Louis Pasteur (ULP), 25 rue Becquerel, 67087 Strasbourg Cedex 02, France.*
E-mail: ziessel@chimie.u-strasbg.fr
[b]*Department Organic Chemistry II, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany*
[c]*Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche (ISOF-CNR), Via P. Gobetti 101, 40129 Bologna, Italy.*
E-mail: franz@isof.cnr.it

Notes and references

† ES-MS in CH_3CN (V_c = 80 V): **RuT$_5$** 1663.2 $[M\text{-}PF_6]^+$, 759.2 $[M\text{-}2PF_6]^{2+}$; **RuT$_5$Os** 1156.2 $[M'\text{-}2PF_6]^{2+}$, 506.0 $[M'\text{-}4PF_6]^{4+}$.

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‡ Absorption and luminescence spectra were measured in the indicated air-equilibrated solvents with a Perkin-Elmer Lambda 5 UV–Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter (λ_{exc} was 420 nm in all cases), respectively. Luminescence quantum yields (ϕ) were evaluated with reference to air-equilibrated Ru(bpy)$_3$Cl$_2$ in water as a standard ($\phi = 0.028$). Luminescence lifetimes (τ) were obtained with IBH single photon counting equipment whose instrumental resolution is 0.2 ns, and by using nanoLED sources of excitation (λ_{exc} = 375 or 560 nm); single exponential decays were observed in all cases. The experimental uncertainty on the absorption and luminescence maxima is 2 nm, that for the ϕ and τ values is 10%.

§ An alternative explanation could be based on the formation of charge separated (CS) states. Actually, electrochemical data indicate that for **RuT$_5$**, the easier oxidation steps, at +0.87 and +1.01 V *vs.* SCE, are centred at the **T$_5$** bridge, while the oxidation step at the Ru(II) metal centre only occurs at +1.36 V and reduction, −1.31 V, is localized at the bpy or phen ligand. This suggests that CS states (lying at *ca.* 2.2 eV, *i.e.*, in between the $^1\pi\pi^*$ and $^3\pi\pi^*$ levels of the **T$_5$** bridge) may also be implicated in the deactivation of the $^1\pi\pi^*$ fluorescence of the **T$_5$** fragment.

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