Synthesis and Luminescence Properties of Ru_2/Cu, Ru_2/Ni, and Ru_2/Os Mixed Metal Polypyridine Complexes Bound by 1,3,5-Triethynylenebenzene

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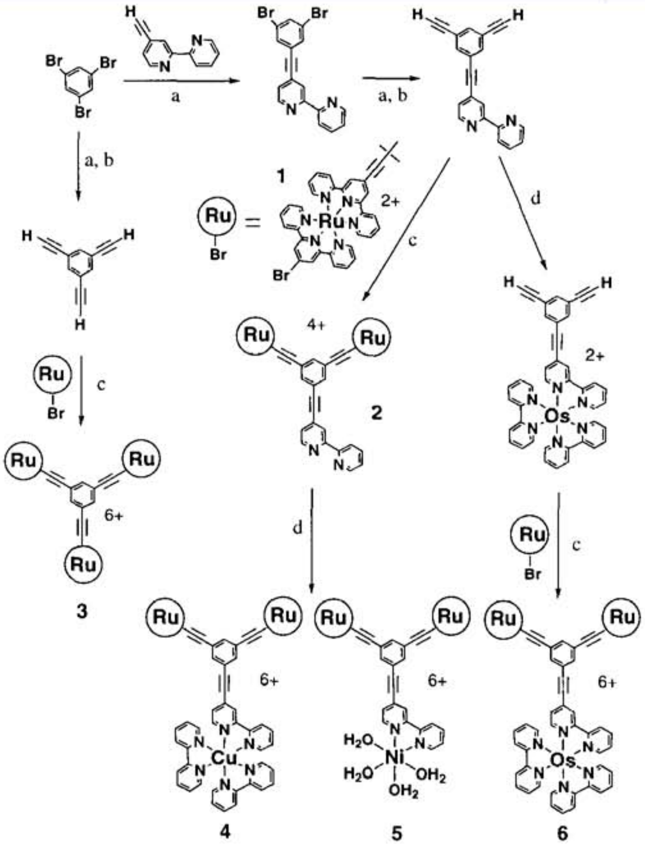
(Received July 28, 1998; CL-980571)

Novel polypyridine metal complexes have been prepared, wherein two $(terpy)_2Ru$ units and one $(bipy)_3M$ (M=Cu, Os) or $(bipy)Ni(H_2O)_4$ unit (terpy= 2,2':6,6'-terpyridine, bipy= 2,2'-bipyridine) are bonded to 1,3,5-positions of a benzene ring via ethynylene bridges. Photophysical study of these hetero trinuclear complexes has indicated effective electronic energy transfer between the metal components can take place.

In our project to construct dendritic molecules containing photoactive metal units, we have been interested in rigid rod spacers, such as ethynylene and *p*-phenylene, to connect such metallo components because practical light-harvesting devices would require vectorial energy or electron transfer over long distances.[1] In the chemistry of metal-containing one-dimensional molecular rods, efficient transfer of electronic energy from an excited $(terpy)_2Ru$ terminal towards a $(terpy)_2Os$ moiety at the other end through a *p*-phenylene or ethynylene bridge has been observed.[2,3] For the construction of three-dimensional rigid dendritic networks, 1,3,5-triethynylenebenzene is an important candidate of a branching unit.[4] We therefore decided to examine if the photoexcited electronic energy can transfer between polypyridine metal units bound to the 1,3,5-positions, i.e. mutually *m*-oriented position, of a benzene ring and if this type of metal-containing branching species is potentially useful in photoactive metallodendrimers. Tzalis and Tor have recently reported the synthesis of 1,3,5-tris[$(bipy)_2Ru$(3-ethynylene-phenanthroline)]benzene and, based on UV-VIS spectra, concluded that each of the metal unit is electronically isolated and not involved in π-conjugation.[5]



Scheme 1. a) $Pd(PPh_3)_2Cl_2$, CuI, in Et_3N. b) K_2CO_3, in THF and MeOH. c) $Pd(PPh_3)_4$, CuI, Et_3N, in CH_2Cl_2. d) $(bpy)_2OsCl_2$, $(bpy)_2Cu$, or $NiSO_4 \bullet 4H_2O$; $HOCH_2CH_2OH$ for **6**, MeOH for **4** and **5**.

The routes to the trinuclear complexes Ru_2/Cu **4**, Ru_2/Ni **5**, and Ru_2/Os **6** are shown in Scheme 1. The mononuclear Ru unit $\mathbf{1}\cdot 2PF_6$ was prepared by the reaction of (4-tBu-CC-terpy)$RuCl_3$ with 4-Br-terpy followed by addition of KPF_6. The branching benzene unit with one ethynylene-bipy and two ethynyl groups was obtained by the Sonogashira-Hagiwara coupling reaction[6] starting from 1,3,5-tribromobenzene. The next coupling reaction of the branching benzene unit with two equiv $\mathbf{1}\cdot 2PF_6$ in CH_2Cl_2 gave $\mathbf{2}\cdot 4PF_6$ in 97% yield as an orange-red powder. Finally, on treatment of a MeOH solution of $\mathbf{2}\cdot 4PF_6$ with $(bpy)_2CuCl_2$ or $NiSO_4\cdot 4H_2O$ under a refluxing condition, the ligation reaction proceeded smoothly to give dark red powder of the trinuclear complexes $\mathbf{4}\cdot 6PF_6$[8] and $\mathbf{5}\cdot 6PF_6$[9] in excellent yields, 90% and 95%, respectively, based on **2** after re-crystallization from MeOH. A similar route to prepare Ru_2/Os **6** did not work because the high temperature (reflux in ethylene glycohol) condition to react $Os(bpy)_2Cl_3$ caused partial dissociation of the terpy ligand from Ru and the reaction resulted in scrambling of the metal-ligand combination. To avoid this problem, the $Os(bpy)_2$ unit was introduced to the benzene unit prior to the incorporation of the $(terpy)_2Ru$ component. The product $\mathbf{6}\cdot 6PF_6$[10] was obtained in 38% yield as a black powder after purification through a cellulose column chromatography. Homo trinuclear complex $\mathbf{3}\cdot 6PF_6$[7] was easily prepared *via* a route similar to that employed by Tzaris and Tor (Scheme 1).[5]

As listed in Table 1, the MLCT absorption bands for the Ru component in complexes **3**-**6** are red-shifted compared to that of the mononuclear (4-tBu-CC-terpy)(4-HCC-terpy)$Ru\cdot 2PF_6$ by 8-10 nm. This indicates that some π-conjugation, though small, with the central benzene unit is present and differs from the observation made in the Tor's trinuclear complex. The emission spectra exited at 355nm were recorded in n-butyronitrile solutions at 150 k (Figure 1). The concentration of all samples were adjusted so that the absorbance at 355nm is 0.2 (±10%). Under such conditions, the luminescence behavior of trinuclear complexes **3** and **4** are almost the same whereas **5** shows a large decrease in the emission intensity to about 25%. Since absorbance of the Ni(bipy) unit at 355 nm is negligible, this finding suggests that ca. 75% of photoenergy absorbed by the Ru

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units is transmitted to the Ni unit through the conjugated linker and ends up as radiationless decay. By comparison of the emission spectra for the 2:1 mixture of (4-tBuCC-terpy)(terpy)Ru^{2+} and $(bipy)_3Os^{2+}$ (see the insert in Figure 1), it is obvious that in complex **6** an intramolecular energy transfer process takes place, which quenches the luminescent excited state of the Ru-based unit by 90% efficiency and sensitizes the luminescent excited state of the Os-based unit by the same order.

Table 1. Absorption and emission data of trinuclear complexes **3-6**, $[Os(bipy)_3]\cdot 2PF_6$, and $[(4\text{-tBu-CC-terpy})(terpy)Ru]\cdot 2PF_6$

	Absorption [a] λ_{max}/nm(ε/$10^4 M^{-1} cm^{-1}$)	Emission [b] λ_{max}/nm	Lifetime µs
3·$6PF_6$	499 (6.5)	680	0.77
4·$6PF_6$	497 (4.7)	685	0.59
5·$6PF_6$	497 (5.1)	685	0.55
6·$6PF_6$	497 (5.6)	670(Ru) 755(Os)	0.42(Ru) 0.27(Os)
$[Os(bipy)_3]\cdot 2PF_6$	575(0.3),479(1.2) 436(1.1)	730	0.27
$[(4\text{-tBu-CC-terpy})(terpy)Ru]\cdot 2PF_6$	484(2.2)	650	0.59

[a] MLCT absorption measured in CH_3CN at room temperature.

[b] Emission spectra excited at 355nm are recorded in n-C_3H_7CN at 150 K. The concentration of all measured samples were adjusted to 0.2 in absorbance at 355nm.

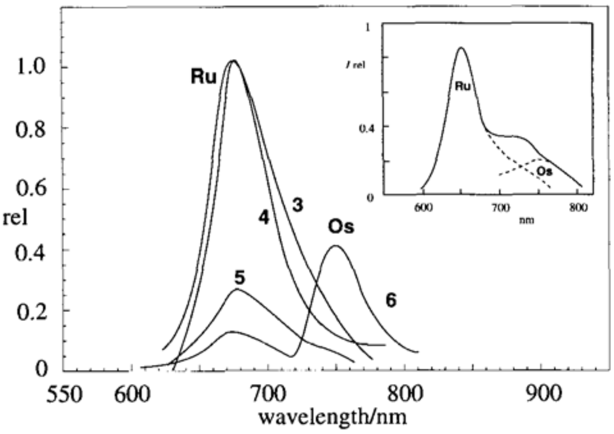

Figure 1. Emission spectra of **3-6** in n-C_4H_9CN at 150 K: (inset) 1:2 mixture of $[Os(bipy)_3]\cdot 2PF_6$ and $[(4\text{-tBu-CC-terpy})(terpy)Ru]\cdot 2PF_6$.

In summary, we have synthesized novel hetero trinuclear complexes based on tris(ethynylene)-substituted benzene in a stepwise fashion. The study of their photophysical properties has shown that an efficient electronic energy transfer from one metal to another across the 1,3,5-triethynylene benzene core is possible, suggesting that the unit may be useful as a branching component for photoactive metallodendritic compounds. The synthetic work along this line is now in progress.

This work has been partly supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation (JST).

References and Notes

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7 UV/Vis (CH_3CN, nm): λmax(ε), 499(65000). Anal. Found: C, 48.53%; H, 3.24%; N, 8.35%; Ru, 9.78%. Calcd for $C_{120}H_{90}N_{18}F_{36}P_6Ru_3$: C, 48.74%; H, 3.07%; N, 8.52%; Ru,10.26%. IR(DMF, cm^{-1}): ν(C≡C), 2218(br). FAB-MS (m/Z): 2816 (**3**·$5PF_6$), 2668 (**3**·$4PF_6$), 2523(**3**·$3PF_6$).

8 UV/Vis (CH_3CN, nm): λmax(ε), 497(47000). Anal. Found: C, 48.33%; H, 2.86%; N, 8.69%; Ru, 7.59%; Cu, 2.31%. Calcd for $C_{114}H_{84}N_{18}F_{36}P_6Cu_1Ru_2$: C, 48.18%; H, 2.98%; N, 8.87%; Ru, 7.12%; Cu, 2.24%. IR(DMF, cm^{-1}): ν(C≡C), 2218(br). FAB-MS (m/Z): 2406 (**4**·$3PF_6$), 2261 (**4**·$2PF_6$).

9 UV/Vis (CH_3CN, nm): λmax(ε), 497(51000). Anal. Found: C, 43.29%; H, 2.93%; N, 7.67%; Ru, 7.53%; Ni, 2.19%. Calcd for $C_{94}H_{76}N_{14}F_{36}P_6Ru_2Ni_1$: C, 43.48%; H, 2.95%; N, 7.55%; Ru, 7.79%; Ni, 2.26%. IR(KBr, cm^{-1}): ν(C≡C), 2216(br). FAB-MS (m/Z): 2090 (**5**·$3PF_6$-$4H_2O$), 1945 (**5**·$2PF_6$-$4H_2O$).

10 UV/Vis (CH_3CN, nm): λmax(ε), 497(56000). Anal. Found: C, 43.29%; H, 2.93%; N, 7.67%; Ru, 7.53%; Os, 6.38%. Calcd for $C_{114}H_{84}N_{18}F_{36}P_6Ru_2Os_1$: C, 46.13%; H, 2.85%; N, 8.49%; Ru, 6.82%; Os, 6.41%. IR(KBr, cm^{-1}): ν(C≡C), 2216(br). FAB-MS (m/Z): 2826 (**6**·$5PF_6$), 2679 (**6**·$4PF_6$), 2536 (**6**·$3PF_6$), 2389 (**6**·$2PF_6$).