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Synthesis and Properties of the Elusive Ruthenium(II) Complexes of 4′-Cyano-2,2′:6′,2″-terpyridine

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The heteroleptic and homoleptic ruthenium(II) complexes of 4′-cyano-2,2′:6′,2″-terpyridine are synthesized by palladium catalyzed cyanation of the corresponding Ru(II) complexes of 4′-chloro-2,2′:6′,2″-terpyridine. The introduction of the strongly electron-withdrawing cyano group into the $Ru(tpy)_2^{2+}$ moiety dramatically changes its photophysical and redox properties as well as prolongs its room temperature excited-state lifetime.

In the last two decades, ruthenium(II) complexes have become widely studied within the field of inorganic chemistry.[1] Indeed, Ru(II) polypyridine 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.[2a,3] However, compared with achiral $Ru(tpy)_2^{2+}$ complexes based on the tridentate polypyridyl ligand 2,2′:6′,2″-terpyridine (tpy), $[Ru(bpy)_3]^{2+}$ has two main structural disadvantages: the Δ and Λ enantiomers of $[Ru(bpy)_3]^{2+}$ give rise to many diastereomers in polynuclear complexes and Ru(II) complexes of monosubstituted bpy ligands are mixtures of *fac* and *mer* isomers. These problems, inherent to the $[Ru(bpy)_3]^{2+}$ structural motif, can be overcome by the use of tridentate, tpy-type polypyridyl ligands. However, $[Ru(tpy)_2]^{2+}$ and its derivatives have far less useful photophysical properties as compared to $[Ru(bpy)_3]^{2+}$. This is essentially due to a shorter excited-state lifetime (<250 ps) at room temperature (rt) resulting from the population of a nonemissive metal-centered triplet (^{3}MC) state from the potentially emissive metal-to-ligand charge transfer (^{3}MLCT) state.[4] Nevertheless, this shortcoming may be overcome if new ligands are designed which enhance the rt luminescence lifetimes of Ru(II) complexes of tridentate ligands.[5]

Several strategies have been employed to prolong the rt excited-state lifetime of ruthenium(II) complexes with tridentate polypyridyl ligands, including the use of (a) electron withdrawing and/or donor substituents on tpy,[1d] (b) cyclometalating ligands,[1e] (c) ligands with extended acceptor orbitals,[1c] and (d) bichromophoric complexes.[6]

The first strategy was based on the introduction of electron-withdrawing and/or donor substituents into the 4′-position

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(4) These unfavorable photophysical properties are due to proximity (in energy) between the lowest-lying MLCT and metal-centered (MC) states, with the latter governing the excited-state decay dynamics by thermally activated surface crossing. This topic has been definitely clarified and is reported in detail in several reviews [refs 1e, 2a, 3a,b].

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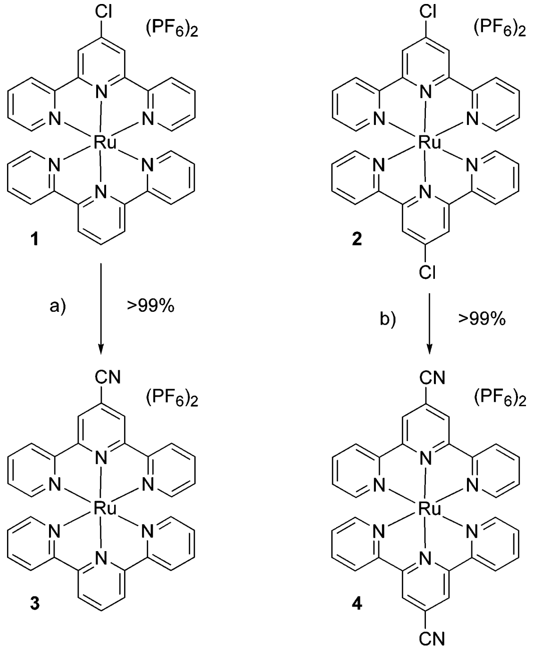
of tpy. The electron-withdrawing substituents stabilize the LUMO π^* ligand orbital more than the HOMO $\pi(t_{2g})$ metal orbital, thereby increasing the energy gap between ^{3}MLCT and ^{3}MC excited state and minimizing the thermally activated surface crossing which dominates the MLCT deactivation process.[4] It has been shown that 4′-(methyl-sulfonyl)-tpy based complexes have prolonged rt luminescence lifetimes ([(MeSO$_2$-tpy)$_2$Ru](PF$_6$)$_2$, 25.0 ns; [(MeSO$_2$-tpy)Ru(tpy-OH)](PF$_6$)$_2$, 50.0 ns) due to the strong electron-withdrawing ability of the methyl-sulfonyl group.[1d] One of the advantages of this strategy is the facile synthesis of the ligands and their complexes; thus, the synthetic procedure for building up the polynuclear arrays based on 4′-substituted tpy should be simplified. In addition, monoexponential decay of the excited state renders these complexes relatively easy to study as compared to bichromophoric systems based on an equilibrium between a nonemissive triplet organic state and the ^{3}MLCT state of the metal complex, which on the other side does not allow an increase in luminescence quantum yields.[5] In this context, we envisioned that coordination of 4′-cyano-tpy with a Ru(II) center should provide a very large effect on the ligand-based LUMO and increase the energy gap between the ^{3}MLCT and ^{3}MC states, thereby prolonging the rt luminescence lifetime (and increasing quantum yields) of the complexes. Moreover, cyano-complexes can act as building blocks to build up linear polymetallic units due to the strong coordination capacity of the cyano group.[7] However, until now no successful synthesis of the 4′-cyano-tpy Ru(II) complexes has been reported. Herein we report the synthesis of the heteroleptic and homoleptic Ru(II) complexes of 4′-cyano-tpy and the effect that the cyano group has on their photophysical and redox properties.

The difficulty in the preparation of Ru(II) complexes of 4′-cyano-tpy results from the activation of the cyano group toward nucleophilic attack by the electron withdrawing Ru(II) metal center. In order to bypass the possible destruction of the cyano group, we shifted our focus toward a "chemistry-on-the-complex" approach,[8] that is, the transition-metal catalyzed cyanation of appropriately functionalized Ru(II) complexes.

In order to elucidate the methodology for cyanation on the complex, we chose two Ru(II) terpyridine complexes, **1** and **2**, as our starting materials (Scheme 1). After several unsuccessful attempts to perform Ni(0) catalyzed cyanation of **1** and **2** (1.0 equiv of KCN, 10 mol % Ni(PPh$_3$)$_2$Br, 10 mol % Zn, 20 mol % PPh$_3$, DMF, or acetonitrile, 60 °C),[9] we turned to the Pd(0)-catalyzed-cyanation of the complexes. Previously reported reaction conditions for purely organic systems seemed promising with very high yields.[10] We applied slightly modified conditions to complexes **1** and **2** in order to synthesize cyano complexes **3** and **4** (Scheme 1).

Scheme 1. Palladium-Catalyzed Cyanation of Ru(II) Complexes of 4′-Chloro-tpy[a]



[a] Reagents and conditions: (a) 0.6 equiv Zn(CN)$_2$, 5 mol % Pd$_2$(dba)$_3$, 10 mol % dppf, 30 mol % Zn dust (325 mesh), DMA, 120 °C, 6 h; (b) 1.2 equiv Zn(CN)$_2$, 10 mol % Pd$_2$(dba)$_3$, 20 mol % dppf, 60 mol % Zn dust (325 mesh), DMA, 120 °C, 12 h.

The reaction of heteroleptic complex **1** with 0.6 equiv of Zn(CN)$_2$, 5 mol % Pd$_2$(dba)$_3$, 10 mol % dppf, and 30 mol % Zn dust (325 mesh) in DMA at 120 °C for 6 h afforded cyano-complex **3** quantitatively. For homoleptic complex **2**, modification of the stoichiometry of the reagents and a longer reaction time afforded the same full conversion to homoleptic complex **4**. The full conversion of the 4′-chloro-tpy complexes to the cyano-complexes was secured by the strongly activating Ru(II) cations.

The electrochemical data indicates that the introduction of the cyano group into the Ru(tpy)$_2^{2+}$ moiety stabilizes the metal center as it is more difficult to oxidize (Table 1). The half-wave potentials of metal-centered oxidation of **3** and **4** have increased by more than 80 mV compared to Ru(tpy)$_2^{2+}$ (**5**). In addition, the ligand-centered reductions are facilitated as a result of the electron-withdrawing nature of the cyano group.

The absorption spectra of the new species (see Figure 1) are dominated by spin-allowed ^{1}MLCT bands in the visible region. We note that the cyano-substitution on the 4′-position of tpy has an strong electron-withdrawing effect on the tpy ligand, and, consequently, the metal center. The ^{1}MLCT

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Table 1. Electrochemical Potential Data[a]

complex	E_{ox}/V	E_{red}/V
1[b]	1.33	−1.16, −1.46
2[b]	1.40	−1.27, −1.46
3	1.42 (64)	−1.15 (70), −1.44 (70), −1.81 (60)
4	1.49 (65)	−0.88 (70), −1.15 (ir), −1.63 (ir)
5[b]	1.32	−1.27, −1.52

[a] V vs SCE. Data were collected in deaerated acetonitrile with 0.1 M supporting electrolyte, Bu_4NPF_6. Working electrode, platinum wire. Redox potentials were corrected by internal reference to ferrocene. [b] Data from ref 1f; **5** = $Ru(tpy)_2^{2+}$.

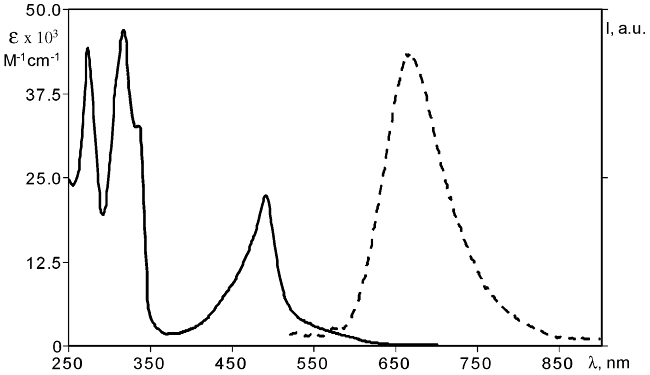

Figure 1. Absorption (—) and emission (- - -) spectra of **4** in acetonitrile solution.

bands of **3** and **4** have red-shifted (to 489 and 490 nm, respectively) as compared to their counterparts in **1** and **2** (Table 2). The introduction of the cyano group on the 4′-position of tpy lowers the energy of ^{1}MLCT state significantly as compared to **5**.

The rt emission spectra showed that the energy of the ^{3}MLCT state was also lowered with the introduction of cyano group. The corresponding emission maxima (λ_{max}) for **3** and **4** (see Figure 1) have red-shifted compared to **5** to 701 and 680 nm, respectively, due to the greater lowering of the ligand-based LUMO energy (π^*_L) over the metal-based HOMO energy (π_M). Since the introduction of the cyano group has less effect on the metal-based orbitals, the energy gap between ^{3}MC and ^{3}MLCT increases. As a consequence, the efficiency of the thermally activated surface crossing process from the ^{3}MLCT state to the ^{3}MC state decreases, thus prolonging the rt luminescence lifetime and significantly increasing quantum yields.

Table 2. Absorption Spectra and Luminescence Data[a]

	abs 298 K λ/nm	em 298 K		
compd	($\epsilon/10^3\,M^{-1}\,cm^{-1}$)	λ_{max}/nm	τ/ns	Φ
4′-cyano-tpy	336 (6.9)	353	1.2	3×10^{-4}
1	478 (14.5)	651	0.7	4×10^{-5}
2[b]	480 (16.0)	653	0.2	$\leq 1 \times 10^{-5}$
3	489 (15.7)	701	75	2×10^{-3}
4	490 (22.4)	680	50	2×10^{-3}
5[b]	474 (10.4)	629	<0.25	$\leq 1 \times 10^{-6}$

[a] Data were collected in deaerated acetonitrile. [b] Data from ref 1d; **5** = $Ru(tpy)_2^{2+}$.

In conclusion, we have introduced a cyano group onto the 4′-position of $Ru(tpy)_2^{2+}$ complexes via a palladium-catalyzed cyanation reaction. This approach enables the synthesis of Ru(II) complexes of 4′-cyano-tpy from the corresponding 4′-chloro-tpy complexes. The substitution of the cyano group on $Ru(tpy)_2^{2+}$ causes dramatic changes to its photophysical properties. Prolonged rt excited-state lifetimes and significantly higher luminescence quantum yields compared to the prototype $Ru(tpy)_2^{2+}$ species are achieved, due to the increased energy gap between ^{3}MLCT and ^{3}MC states induced by the electron-withdrawing cyano group. Intensive work on the generality of this cyanation methodology and full characterization of new Ru(II) species will be described at a later date.

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Supporting Information Available: Experimental details for the synthesis of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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