Cyano-Ambivalence: Spectroscopy and Photophysics of $[Ru(diimine)(CN\text{-}BR_3)_4]^{2-}$ Complexes

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Abstract:

The UV-visible absorption and luminescence spectra of $[Ru(diimine)(CN)_4]^{2-}$ derivatives have been tuned over wide ranges through variations in solvent, substituents on the diimine ligand, and boronation of the cyanide ligands. Trifluoromethyl substitution at the 4 and 4′ positions of the diimine induces red shifts in metal-to-ligand charge-transfer (MLCT) absorption and luminescence bands. Boronation of the cyanide ligands produces substantial blue shifts in MLCT energies. The combination of diimine trifluoromethylation and cyanide boronation produces MLCT blue shifts that are about 75% as large as those produced by boronation alone.

Keywords: cyanometalate; boronation; absorption spectra; luminescence spectra; solvatochromism

1. Introduction

The electronic, spectroscopic, and redox properties of cyanometalates are uniquely sensitive to outer-sphere effects. The reduction potential of $[Fe(CN)_6]^{3-}$, for example, shifts anodically 1.3 V when N-methylpyrolidinone replaces water as a solvent [1], and the metal-to-ligand charge-transfer (MLCT) absorption band of $[Fe(bpy)(CN)_4]^{2-}$ (bpy = 2,2′-bipyridine) red shifts by 0.86 eV upon changing the solvent from water to acetone [2]. Cyanometalate interactions with Lewis acids produce even greater perturbations: coordination of six $B(C_6F_5)_3$ groups to $[Fe(CN)_6]^{3-}$ produces a 2.1 V anodic shift in the Fe(III/II) reduction potential [3].

Outer-sphere effects also appear in the luminescence and photophysical properties of cyanometalates. The luminescence spectra and decay kinetics of $[Ru(diimine)(CN)_4]^{2-}$ complexes are tuned over wide ranges by the polarity, the presence of protons, and the isotopic composition of the surrounding solvent [4-8]. Electron-withdrawing substituents on the diimine, and adduct formation with boranes induce similar perturbations. We report here the luminescence properties of borane adducts of $[Ru(bpy)(CN)_4]^{2-}$ and $[Ru(^{CF3}bpy)(CN)_4]^{2-}$ (^{CF3}bpy = 4,4′-bis(trifluoromethyl)-2,2′-bipyridine).

2. Experimental

2.1. Syntheses

Tetrabutylammonium hydroxide (Sigma-Aldrich), bis(triphenylphosphine)iminium chloride (SigmaAldrich), tris(pentafluorophenyl)borane (Sigma-Aldrich), triphenylborane (Sigma-Aldrich), 2,2′-bipyridine (bpy) (Sigma-Aldrich), 4,4′-bis(trifluoromethyl)-2,2′-bipyridine (^{CF3}bpy) (Strem) were used as received. $K_2[Ru(^{CF3}bpy)(CN)_4]$, $(PPN)_2[Ru(^{CF3}bpy)(CN)_4]$, $(TBA)_2[Ru(bpy)(CN\text{-}B(C_6H_5)_3)_4]$, $(TBA)_2[Ru(bpy)(CN\text{-}B(C_6H_5)_3)_4]$, and $(PPN)_2[Ru(^{CF3}bpy)(CN\text{-}B(C_6F_5)_3)_4]$ (TBA^+ = tetra-*n*-butylammonium; PPN^+ = bis(triphenylphosphine)iminium) were prepared and characterized according to published procedures [9].

2.2. Methods

Absorption spectra were recorded on Cary 50 or Cary 500 spectrophotometers. Luminescence spectra were recorded using a Fluorolog-3 (Jobin-Yvon Horiba) instrument modified to use two overlapping (300-684 nm, 550-928 nm) QE Pro High Performance Spectrometers (Ocean Optics) with back-thinned, TE-cooled CCD detectors. The instrument is controlled using software developed in MATLAB (Mathworks, Inc). Luminescence from solid-state $K_2[Ru(^{CF3}bpy)(CN)_4]$ was recorded using an Andor spectrometer (Kymera 193i spectrograph; iDus CCD detector). Luminescence decay kinetics were recorded using 355-nm 8-ns excitation pulses from the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray Pro). Luminescence was collected using reflective optics, focused onto the entrance slit of a DH-10 double 100-mm spectrophotometer (Jobin Yvon), and detected using an R928 photomultiplier tube (Hamamatsu). The photomultiplier current was amplified and recorded using a Compuscope 85G transient digitizer (Gage Applied Inc) controlled with Labview software (National Instruments).

3. Results and Discussion

3.1. $[Ru(^{CF3}bpy)(CN)_4]^{2-}$

The absorption and luminescence spectra of $[Ru(bpy)(CN)_4]^{2-}$ are extremely sensitive to the polarity and presence of protons in the solvent (Table 1) [8, 10]. Substituents on the diimine ligand further perturb the spectra: electron-donating groups ($-CH_3$) produce a blue shift; electron-withdrawing groups ($-C_6H_5$, $-COO^-$) produce red shifts [7]. The trifluoromethyl group is a much more effective electron withdrawing group than the substituents examined previously and consequently the absorption and luminescence maxima of $[Ru(^{CF3}bpy)(CN)_4]^{2-}$ are dramatically red-shifted relative to those of the parent dianion (Figure 1, Table 1). Although the trifluoromethyl groups should render the cyanide ligands somewhat less basic, removal of solvent protons nevertheless induces a 0.70-eV red-shift of the $[Ru(^{CF3}bpy)(CN)_4]^{2-}$ MLCT absorption maximum from its value in aqueous solution. This red-shift is only

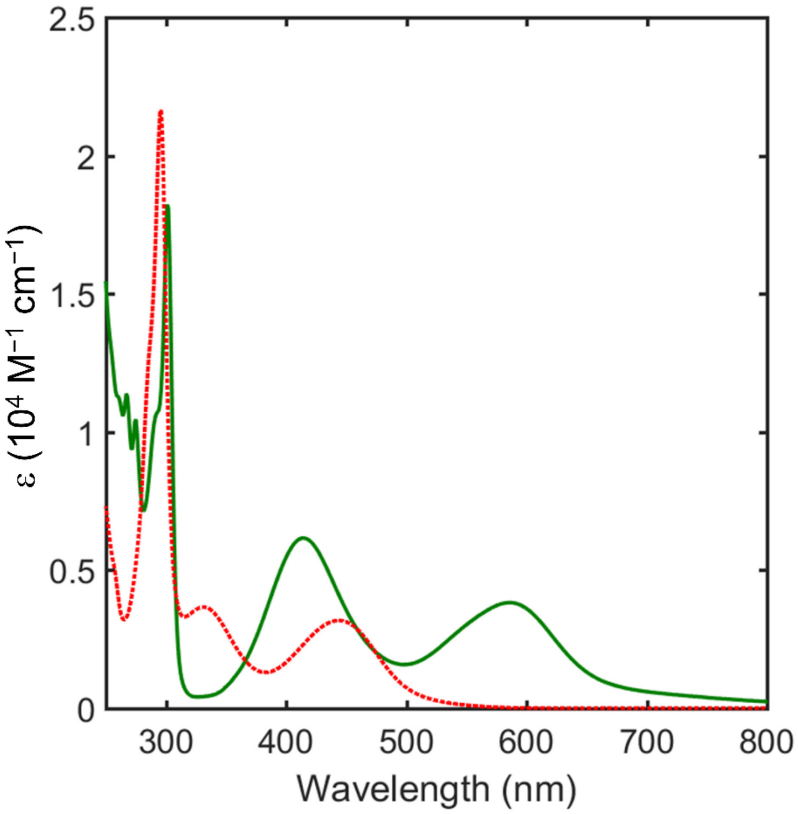

Figure 1. Absorption spectra of $K_2[Ru(^{CF3}bpy)(CN)_4]$ in water (red broken trace) and $(PPN)_2[Ru(^{CF3}bpy)(CN)_4]$ in acetonitrile (green solid trace) at room temperature.

slightly smaller than that found with $[Ru(bpy)(CN)_4]^{2-}$ (0.75 eV) [10, 11] and $[Ru(^{CH3}bpy)(CN)_4]^{2-}$ (0.82 eV) [12]. Luminescence from $[Ru(^{CF3}bpy)(CN)_4]^{2-}$ in aqueous solution exhibits a maximum at 706 nm. In the solid state, $K_2[Ru(^{CF3}bpy)(CN)_4]$ displays a luminescence maximum at 880 nm.

3.2. $[Ru(bpy)(CN\text{-}BR_3)_4]^{2-}$

Boronation produces a dramatic change in the electronic properties of cyanide ligands: they become weaker σ donors and stronger π acceptors [3]. Notably, boronation of $[Ru(bpy)(CN)_4]^{2-}$ greatly blue shifts the MLCT absorption (CN-B(C_6H_5)$_3$, 0.85 eV; CN-B(C_6F_5)$_3$, 1.15 eV) and luminescence (0.74, 0.91 eV) bands (Figure 2, Table 1). These large blue shifts are accompanied by substantial increases in excited-state lifetimes. Part of this increase may be attributed to energy-gap effects [13], but protection of the cyanide ligands from solvent interactions likely is the main contributor. It is interesting to compare the

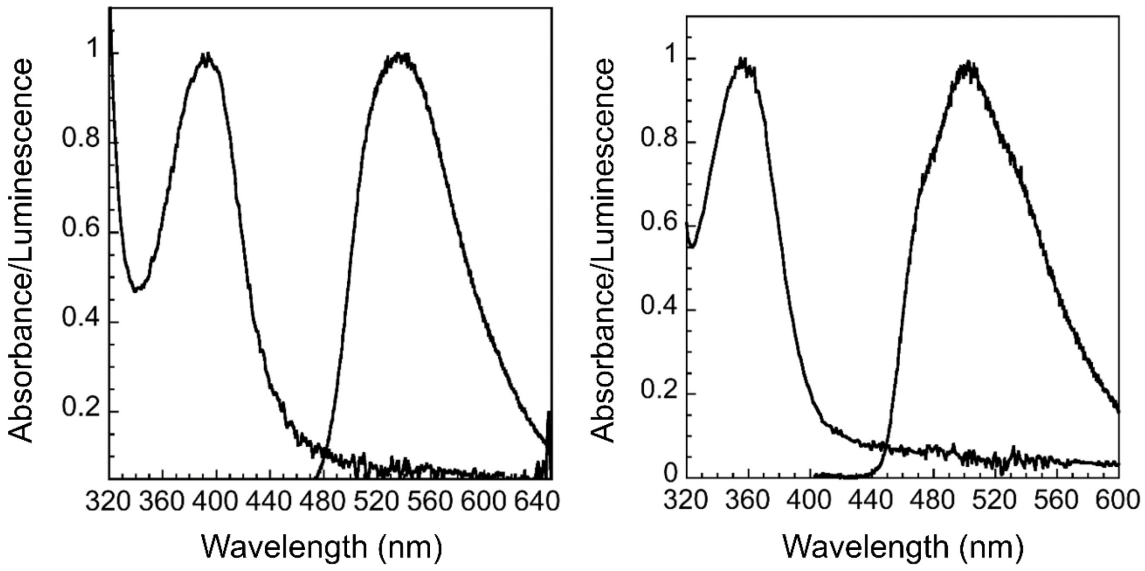

Figure 2. UV-visible absorption and luminescence spectra of $(TBA)_2[Ru(bpy)(CN\text{-}B(C_6H_5)_3)_4]$ (left) and $(TBA)_2[Ru(bpy)(CN\text{-}B(C_6F_5)_3)_4]$ (right) in CH_3CN at room temperature.

effects of boronation and methylation in $[Ru(bpy)(CN)_4]^{2-}$. The lowest energy MLCT absorption maximum in $[Ru(bpy)(CNCH_3)_4]^{2+}$ is blue shifted so far that it is obscured by bpy ligand centered absorptions. Moreover, the luminescence observed in this complex appears to be ligand centered [14].

3.3. $[Ru(^{CF3}bpy)(CN\text{-}B(C_6F_5)_3)_4]^{2-}$

The foregoing data demonstrate that trifluoromethyl substituents on bpy and cyanide boronation have countervailing effects on the absorption and luminescence spectra of $[Ru(bpy)(CN)_4]^{2-}$. When both

Table 1. UV-vis absorption and luminescence properties of $[Ru(diimine)(CN)_4]^{2-}$ and $[Ru(diimine)(CN\text{-}BR_3)_4]^{2-}$ complexes.

Complex	Solvent	${}^{abs}\overline{\nu}_{max}$, cm^{-1} (${}^{abs}\lambda_{max}$, nm)	${}^{lum}\overline{\nu}_{max}$, cm^{-1} (${}^{lum}\lambda_{max}$, nm)	Φ_{lum}	τ_{lum}, ns
$K_2[Ru(bpy)(CN)_4]$	H_2O	24,750 (404) [a]	16,030 (624) [a]	0.0076 [b]	120 [b]
$(TBA)_2[Ru(bpy)(CN)_4]$	CH_3CN	18,690 (535) [c]	12,660 (790) [c]	0.0003 [c]	7 [c]
$K_2[Ru(^{CF3}bpy)(CN)_4]$	H_2O	22,570 (443)	14,160 (706)		
$(PPN)_2[Ru(^{CF3}bpy)(CN)_4]$	CH_3CN	16,980 (589)			
$(TBA)_2[Ru(bpy)(CN\text{-}B(C_6H_5)_3)_4]$	CH_3CN	25,570 (391)	18,620 (537)		810
$(TBA)_2[Ru(bpy)(CN\text{-}B(C_6F_5)_3)_4]$	CH_3CN	28,010 (357)	19,960 (501)		210
$(PPN)_2[Ru(^{CF3}bpy)(CN\text{-}B(C_6F_5)_3)_4]$	CH_3CN	25,640 (390)	18,350 (545)	0.14	3400

[a] Reference 11.
[b] Reference 7.
[c] Reference 10.

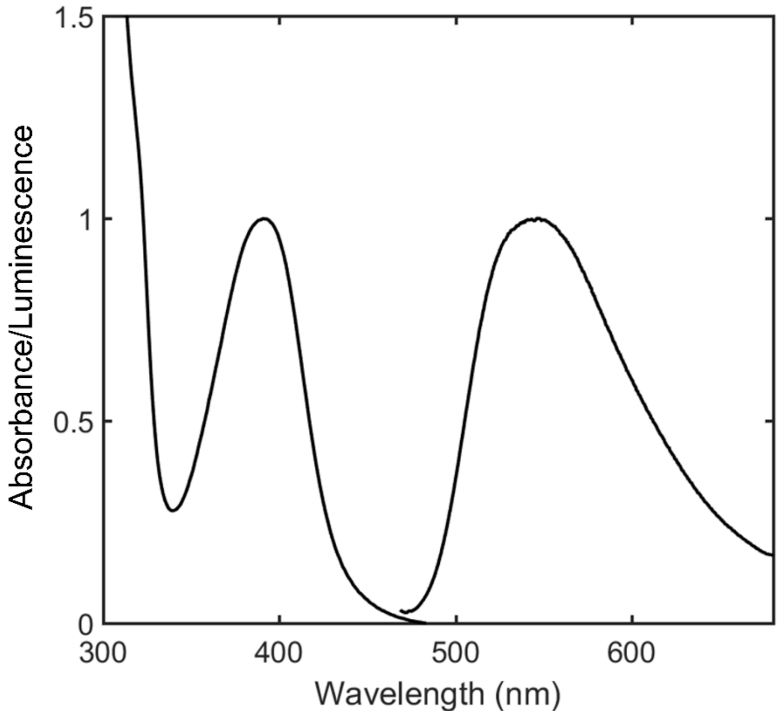

Figure 3. UV-visible absorption (left) and luminescence (right) spectra for $(PPN)_2[Ru(^{CF3}bpy)(CN\text{-}B(C_6F_5)_3)_4]$ in acetonitrile at room temperature.

modifications are introduced it is clear that boronation dominates: the absorption and luminescence maxima of $[Ru(^{CF3}bpy)(CN\text{-}B(C_6F_5)_3)_4]^{2-}$ are markedly blue-shifted (0.86 and 0.71 eV, respectively) from those of $[Ru(bpy)(CN)_4]^{2-}$ (Figure 3, Table 1). The effects on the excited-state lifetime and quantum yield are even more dramatic, with both quantities increasing by a factor of nearly 500.

4. Concluding Remarks

The 1.4-eV energy range over which MLCT absorption and luminescence can be modulated through solvent variations, diimine substitution, and cyanide boronation of the basic $[Ru(diimine)(CN)_4]^{2-}$ platform is remarkable. With relatively minor alterations in the complex and solvent, luminescence can be transformed from green to deep red. The relative ease of varying these spectroscopic properties enhances the utility of this class of molecules in applications ranging from photoredox chemistry to solar cell sensitizers to vapor sensors.

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