A Simple Poly(pyridine)ruthenium(II) Photosensitizer: (2,2′-Bipyridine)tetracyanoruthenate(II)

C. A. Bignozzi, C. Chiorboli, M. T. Indelli,
M. A. Rampi Scandola, G. Varani, and F. Scandola*

Dipartimento di Chimica dell'Università
Centro di Fotochimica C.N.R., 44100 Ferrara, Italy

Received June 4, 1986

The outstanding properties of the tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, photosensitizer[1-7] come from the presence of a long-lived, strongly reducing d–π^* metal-to-ligand charge-transfer triplet excited state. In recent years, compelling evidence has been accumulating for the fact that in the d–π^* state of $Ru(bpy)_3^{2+}$ the excited electron is localized on a single bpy ligand.[8-14] In principle, therefore, complexes containing a single Ru–bpy unit and four ancillary ligands could exhibit most of the interesting properties of the parent $Ru(bpy)_3^{2+}$. In practice, very little photophysical information is available[15] on mono-bpy complexes of the $Ru(bpy)X_4$ type (except for the cases in which the X_4 set is made by other polypyridine-type ligands[16]).[17-19] Aside from specific synthetic problems, this may be due to the fact that, unless very strong-field ancillary ligands are used, ligand field states provide a low-energy pathway for efficient radiationless decay of the useful d–π^* excited state.[20] In this paper, we report on the synthesis and basic photophysical properties of (2,2′-bipyridine)tetracyanoruthenate(II), $Ru(bpy)(CN)_4^{2-}$. Owing to its simplicity ("minimal" chromophoric unit, truly nonchromophoric ancillary ligands, full C_{2v} symmetry), this complex may be considered as a prototype for the class of Ru(II) polypyridine photosensitizers.

In order to arrive at $Ru(bpy)(CN)_4^{2-}$, we found it convenient to use a *photochemical* method, based on a photosubstitution reaction of hexacyanoruthenate(II) (eq 1).[21,22] With an appropriate choice of experimental conditions and purification procedures,[23] the method yields pure $K_2[Ru(bpy)(CN)_4]\cdot 2H_2O$.

$$\mathrm{Ru(CN)_6^{4-} + bpy \xrightarrow{h\nu,\ 254\ nm} Ru(bpy)(CN)_4^{2-} + 2CN^-} \qquad (1)$$

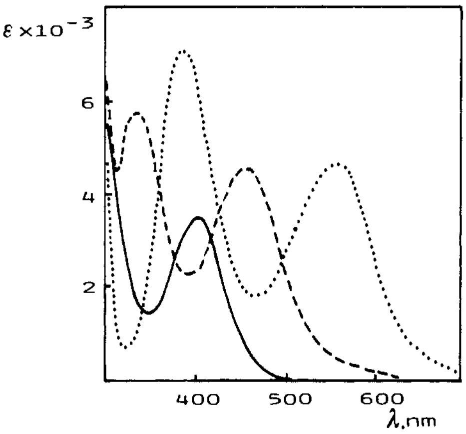

Figure 1. Absorption spectra of $Ru(bpy)(CN)_4^{2-}$ in water (continuous line), absolute ethanol (broken line), and DMF (dotted line) at room temperature (298 K).

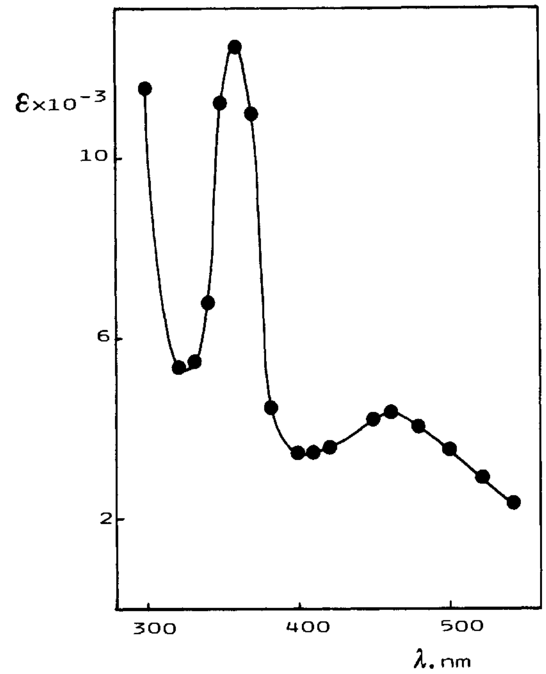

Figure 2. Excited-state absorption spectrum of $Ru(bpy)(CN)_4^{2-}$ in water.

Table I. Spectroscopic and Photophysical Properties of $Ru(bpy)(CN)_4^{2-}$

	H_2O	EtOH	DMF
$\bar{\nu}_{max}^{abs}$(298 K), μm^{-1}	2.50	2.19	1.78
$\bar{\nu}_{max}^{em}$(298 K),[a] μm^{-1}	1.64	1.49	1.23
$\bar{\nu}_{max}^{em}$(77 K),[a] μm^{-1}	1.92[b]	1.76	1.64[c]
τ(298 K),[d] ns	101	25	~4
τ(77 K), μs	6.8	2.2	2.0

[a] Uncorrected emission maxima. [b] 9 M aqueous LiCl glass. [c] 9:1 DMF/CH_2Cl_2 glass. [d] Deaerated solution.

The absorption spectrum of $Ru(bpy)(CN)_4^{2-}$ in various solvents[24] is shown in Figure 1. As expected, the visible spectrum

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(21) Photosubstitution reactions of this type have been studied in some detail for Fe(II) complexes and to a lesser extent for Ru(II) complexes.[22] An alternative route to $Ru(bpy)(CN)_4^{2-}$ is via photosubstitution of bpy by CN^- in $Ru(bpy)_2(CN)_2$. This reaction has also been accomplished but, owing to the use of large excess amounts of cyanide, it is less practical than the proposed one.

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(23) In a typical preparation, 0.5 g of $K_4[Ru(CN)_6]\cdot 3H_2O$ and 0.16 g of 2,2′-bipyridine in 40 mL of 1:3 methanol/water were irradiated for 16 h with a 254-nm immersion lamp. The irradiated solution was evaporated to dryness and the solid was dissolved with 3 mL of cold water, leaving as a residue the unreacted 2,2′-bipyridine. Excess methanol (100 mL) was added to the aqueous solution in order to precipitate the unreacted $K_4Ru(CN)_6$ and the solution evaporated to dryness. The solid was redissolved in water (3 mL) and treated with excess (100 mL) acetone, giving $K_2Ru(bpy)(CN)_4$ as a yellow precipitate and leaving some $Ru(bpy)_2(CN)_2$ in solution. The complex was further freed from trace impurities by ion-exchange chromatography (anionic DEAE Sephadex A-25 resin, eluant 0.05 M KOH), precipitation as $H_2Ru(bpy)(CN)_4$ (1 M HCl), redissolution in dilute KOH, and precipitation with excess acetone as $K_2[Ru(bpy)(CN)_4]\cdot 2H_2O$ (Anal. Calcd: C, 35.36; H, 2.54; N, 17.67. Found: C, 34.96; H, 2.45; N, 17.44). Yield, 30%.

0002-7863/86/1508-7872$01.50/0

is quite similar to those of $Ru(bpy)_3^{2+}$[1-3] and $Ru(bpy)_2(CN)_2$[25] except for a smaller integrated intensity of the d–π^* transition. The spectrum exhibits an extremely pronounced solvatochromic behavior, with solvent shifts that are twice as large as observed for $Ru(bpy)_2(CN)_2$.[25,26] This strengthens previous proposals[26-28] that in this class of complexes the relevant interactions with the solvent involve the cyanides, being presumably of the donor–acceptor type.[29]

The complex emits in fluid solution at room temperature with solvent-dependent energy and lifetime (Table I). In deaerated water, the emission quantum yield[30] is 0.0068, corresponding to a radiative rate constant of 7.1×10^4 s^{-1}, practically coincident with the values found for $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CN)_2$.[31] The smaller solvent dependence of emission relative to absorption is consistent with the expected lower basicity of the cyanides in the d–π^* excited state. In low-temperature glasses, the emission is substantially blue shifted with respect to room temperature and depends to a smaller extent on the matrix (Table I). The minor dependence of the lifetime observed in these conditions probably arises from energy-gap-law effects.[20,32] The comparison between the low-temperature and room-temperature lifetimes indicates that the solvent has a large influence on the rate of the main thermally activated excited-state decay process, most probably the conversion between the d–π^* state and a d–d state.[20,32,33]

The excited-state absorption (ESA) spectrum[34,35] of $Ru(bpy)(CN)_4^{2-}$ is shown in Figure 2. It is quite similar to that reported for $Ru(bpy)_3^{2+}$[9,35-38] except for a greater sharpness and lower intensity of most bands, consistent with the greater simplicity of the chromophoric unit of the mono-bpy complex.

The complex is reversibly oxidized in cyclic voltammetry,[39] with potentials that are remarkably dependent on the solvent: $E_{1/2}$[Ru(III)/Ru(II)] = 0.78 V vs. SCE in H_2O, and $E_{1/2}$[Ru(III)/Ru(II)] = 0.20 V vs. SCE in DMF. The observed potential shift is comparable to the spectral shifts (Table I) and provides further, direct evidence for the importance of second-sphere donor–acceptor interactions[29] between the cyanide ligands and the solvent. In DMF, the complex is reversibly reduced in cyclic voltammetry[39] with $E_{1/2}$[Ru(II)/Ru(I)] = -1.95 V vs. SCE.

For systems, such as $Ru(bpy)(CN)_4^{2-}$, in which the emission energy is strongly dependent on solvent *and* physical state, the usual procedures[4,40] for estimating the excited-state redox potentials involve large uncertainties.[26] Taking 77 and 298 K emission maxima as upper and lower limits, respectively, for the zero-zero excited state energy, the following estimates can be made for the redox potential $^*E°$ (V vs. SCE) of the $Ru(bpy)(CN)_4^-/{}^*Ru(bpy)(CN)_4^{2-}$ couple: $-1.60 < {}^*E° < -1.28$ in water and $-1.83 < {}^*E° < -1.32$ in DMF. Within these uncertainties, the excited state of $Ru(bpy)(CN)_4^{2-}$ is expected to be a very strong reductant. In fact, in 3:1 water/acetonitrile the emission is quenched at diffusion-controlled rate ($k_q = 7.5 \times 10^9$ M^{-1} s^{-1}) by nitrobenzene (reduction potential, -1.15 V vs. SCE). For comparison purposes, it may be recalled that nitrobenzene does not quench $^*Ru(bpy)_3^{2+}$ ($k_q < 2 \times 10^5$ M^{-1} s^{-1}).[41]

Work is in progress toward a more complete characterization of $Ru(bpy)(CN)_4^{2-}$, with particular regard to solvent and temperature dependence of the photophysical behavior, ground- and excited-state acid–base equilibria, electron-transfer quenching, and metalation via cyanide bridges.

Acknowledgment. This work was supported by the Consiglio Nazionale delle Ricerche (P. S. "Dinamica Molecolare e Catalisi") and by the Ministero della Pubblica Istruzione. We are indebted to Professor V. Balzani for suggesting the photochemical synthetic route.

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(24) Measurements in nonaqueous solvents were carried out by using the tetrabutylammonium salt of the complex. This salt (deep violet when dry) was obtained from the potassium salt by ion exchange on a cationic CM Sephadex C-25 resin in aqueous solution, followed by evaporation to dryness. Notice that small amounts of water left in this step can substantially affect the results in nonaqueous solutions.

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π-Facially Controlled Nucleophilic Additions of Chiral Vinylorganometallics to Chiral β,γ-Unsaturated Ketones. 1. Double Diastereoselection Studies Involving 7,7-Dimethoxy-5-norbornen-2-one

Leo A. Paquette* and Keith S. Learn

Evans Chemical Laboratories
The Ohio State University, Columbus, Ohio 43210

Received July 8, 1986
Revised Manuscript Received October 1, 1986

A wealth of information exists concerning methods for achieving relative asymmetric induction in nucleophilic additions to optically active acyclic carbonyl compounds.[1] Transition state models based on steric considerations,[2] stereoelectronic factors,[3] and σ-orbital interactions involving the α-substituents[4] abound. Much less well understood is the extent to which stereochemistry can be controlled, both in a relative and absolute sense, when the carbonyl group is only remotely perturbed.[5]

To our mind, the oxy-Cope rearrangement holds considerable synthetic promise, much of which is yet untapped. Importantly,

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