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Photophysics of supercomplexes. A laser-induced optoacoustic study of the adducts between $Ru(bpy)(CN)_4^{2-}$ and polyaza macrocycles

Claudio D. Borsarelli [a,1], Silvia E. Braslavsky [a,*], María Teresa Indelli [b], Franco Scandola [b]

[a] *Max-Planck-Institut für Strahlenchemie, Postfach 10 13 65, D-45413 Mülheim an der Ruhr, Germany*
[b] *Dipartimento di Chimica dell'Università, Centro di Fotoreattività e Catalisi CNR, I-44100 Ferrara, Italy*

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Abstract

In aqueous solution, the energy content of the triplet metal-to-ligand charge transfer (^{3}MLCT) state, as determined by laser-induced optoacoustic spectroscopy, for both 1:1 supercomplexes $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$ and $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ are similar to that for free $Ru(bpy)(CN)_4^{2-}$ (223 ± 8 kJ/mol). The reduction of the structural volume change upon formation of the ^{3}MLCT state in the order $Ru(bpy)(CN)_4^{2-}$ (14.9 ml/mol), $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ (5.2 ml/mol) and $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$ (2.5 ml/mol) is attributed to the rigidity of the macrocycle cavity. The ^{3}MLCT state lifetime increase from 104 ns for $Ru(bpy)(CN)_4^{2-}$ to 150 ns for $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$ and 182 ns for $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ is due to the decrease in the number of CN groups free to form hydrogen bonds with water: four, one, and none, respectively.

1. Introduction

The photophysical and photochemical behavior of supramolecular structures is a subject of current interest [1]. In particular, the structures formed upon noncovalent interactions between a transition-metal coordination complex and a polyammonium macrocycle (a *supercomplex*) present interesting features, such as control of the reactivity of the complex [2,3], spectral shifts, and quenching protection [4].

In water and in acetonitrile, $Ru(bpy)(CN)_4^{2-}$ and the polyammonium macrocycle $[32]ane\text{-}N_8H_8^{8+}$ form a stable supercomplex [stability constant $> 1 \times 10^6$ M^{-1}, also stable in its metal-to-ligand charge transfer (MLCT) state] with stoichiometry 1:1 when equimolar concentrations of the two components are reached. Strong hydrogen-bond interactions between the complex CN ligands and the macrocycle ammonium groups are responsible for the binding [4]. These interactions are *second-sphere donor–acceptor* (SSDA) interactions [5].

SSDA interactions of $Ru(bpy)(CN)_4^{2-}$ in aqueous media have already been studied by laser-induced

* Corresponding author. Fax: +49-208-306-3951; e-mail: braslavskys@mpi-muelheim.mpg.de

[1] Permanent address: Departamento de Química y Física, Universidad Nacional de Rio Cuarto, RA-5800, Rio Cuarto, Argentina. Fax: +54-58-676233; e-mail: cbosarelli@exa.unrc.edu.ar.

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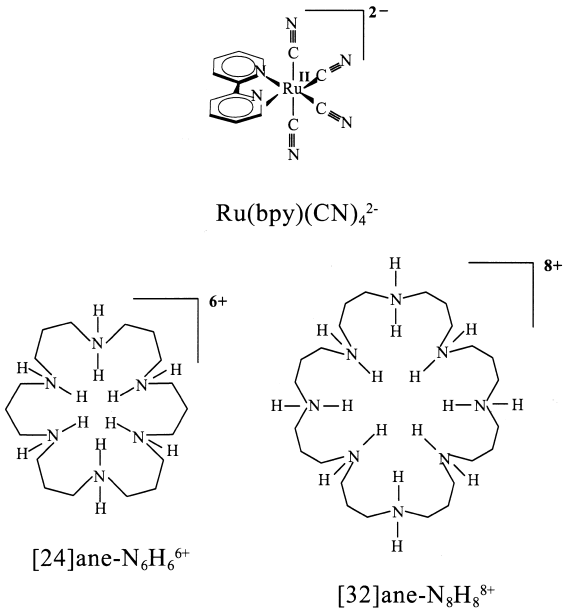


Fig. 1. Structure of the Ru(bpy)$(CN)_4^{2-}$ and of the macrocyclic polyammonium ions.

optoacoustic spectroscopy (LIOAS) which allows the simultaneous determination of enthalpy and structural changes associated with light triggered processes [6,7]. The structural volume changes, ΔV_{MLCT}, for the formation (and decay) of the triplet ^{3}MLCT state of the complex were attributed to photoinduced changes in the hydrogen-bond strength between the CN ligands and the water molecules of the first solvation shell [6]. LIOAS served to study several effects affecting the hydrogen-bond interactions of Ru(bpy)$(CN)_4^{2-}$, such as water structure inside reverse micelles [8], proton concentration [9], and structure-making and -disrupting salts [10].

We present now a LIOAS study of the supercomplexes of Ru(bpy)$(CN)_4^{2-}$ and the polyammonium macrocycles [24]ane-$N_6H_6^{6+}$ and [32]ane-$N_8H_8^{8+}$ (Fig. 1).

2. Experimental

2.1. Materials

K_2[Ru(bpy)$(CN)_4$] (bpy = 2,2′-bipyridine) complex [11] and the macrocycle [32]ane-$N_8 \cdot 8HCl$[4] were available from previous studies. [24]ane-$N_6 \cdot 6HCl$ was supplied by Professor Vincenzo Balzani (Bologna) [2].

The experiments were performed with Ar-purged 10^{-4} M HCl (Merck) aqueous solutions. Water was triply distilled. The calorimetric reference was $Ni(ClO_4)_2$ (Fluka), which has similar absorption spectrum as Ru(bpy)$(CN)_4^{2-}$. The concentration of the ruthenium complex was $\sim 10^{-4}$ M, and the molar ratio complex/macrocycle was < 1. Under these conditions the binding of Ru(bpy)$(CN)_4^{2-}$ in the supercomplex is assured to occur with a 1:1 stoichiometry.

2.2. Methods

The equipment for emission lifetime measurements was as previously described [4]. The matched ($\pm 3\%$ at 400 nm) absorbances of reference and sample solutions were recorded with a Shimadzu UV-2102PC spectrophotometer. Our LIOAS set-up has been previously described [8–10]. The laser beam was shaped with a rectangular slit (0.2 w $\times$ 6 h) mm, so that the effective acoustic transient time was $\sim$ 130 ns. This allowed lifetimes resolution between $\sim$ 15 and 1000 ns with deconvolution procedures. Temperature-dependent measurements were performed in the range 15–35 (± 0.1°C). To avoid multiphotonic processes, the laser-pulse total energy was < 30 μJ.

The thermoelastic parameters ratio ($c_p \rho/\beta$) (c_p: heat capacity, ρ: mass density, β: cubic expansion coefficient of the solvent) of 10^{-4} M HCl aqueous solutions were identical to those of pure water at each temperature [12], as determined by comparing the fluence-normalized LIOAS signal amplitude for the calorimetric reference in water and in acid solutions.

In all cases, the LIOAS signals for the sample were fitted by deconvolution using the Sound Analysis 3000 1.13 computational program (Quantum Northwest, Spokane, WA). The signal of the calorimetric reference was used as the instrumental response. The principles of the deconvolution procedure in LIOAS affording the preexponential term (φ_i) for each of the steps (formation and decay of the ^{3}MLCT state) and the respective rate constants (k_i) have been described [13].

3. Results and discussion

The supercomplexes formed quantitatively in 1×10^{-4} M solutions of $Ru(bpy)(CN)_4^{2-}$ and macrocycle in 1:1 ratio. This was previously established for [32]ane-$N_8 \cdot 8HCl$ by means of emission lifetime titrations [4]. Analogous experiments lead to the same conclusion for [24]ane-$N_6 \cdot 6HCl$, with a limiting lifetime for the ^{3}MLCT state of the 1:1 adduct of 140 ns (the shortest lifetime obtained upon adding the macrocycle to a $Ru(bpy)(CN)_4^{2-}$ solution). The absorption spectra of both supercomplexes are only slightly blue-shifted ($\sim$ 2 nm) with respect to that of $Ru(bpy)(CN)_4^{2-}$ ($\lambda_{max} = 400$ nm) [11]. A blue-shift in the transitions is expected when the charge density at the central metal is reduced. In the present case, the blue-shift is indicative of the hydrogen-bond interaction between the azamacrocycle ammonia groups and the N-end of complex CN groups, as reported earlier [4].

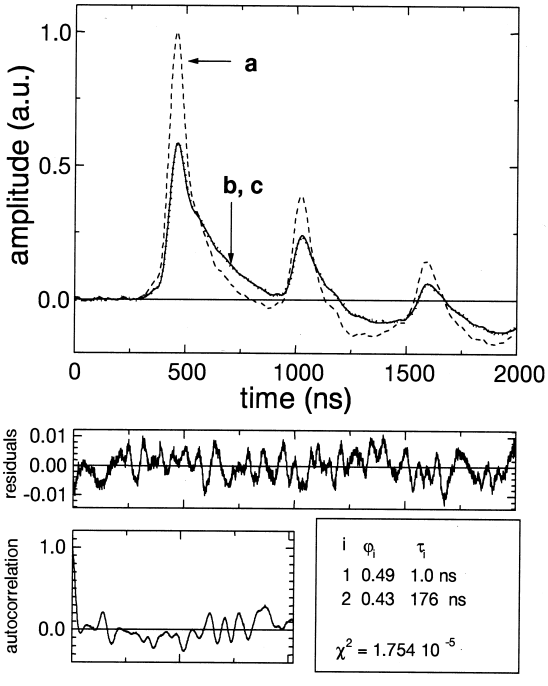


Fig. 2. LIOAS signals for $Ni(ClO_4)_2$ (curve a) and for $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ (curve b) in 10^{-4} M HCl aq. solutions at 25°C together with the fit (curve c), residuals distribution, and autocorrelation waveform, after deconvolution of the sample and reference signals.

Table 1
Lifetimes, τ_2 (ns), associated with the decay of the ^{3}MLCT state of free $Ru(bpy)(CN)_4^{2-}$ and forming 1:1 supercomplexes with polyammonium macrocycles, in aqueous 10^{-4} M HCl solutions as a function of temperature

T (°C)	$Ru(bpy)(CN)_4^{2-}$	$\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$	$\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$
15		168 ± 10	170 ± 10
17	98 ± 7	152 ± 5	184 ± 10
20	105 ± 5	146 ± 5	187 ± 10
22		149 ± 5	185 ± 10
25	102 ± 5	141 ± 5	176 ± 10
30	107 ± 5	145 ± 5	189 ± 10
35	110 ± 5		

The temporal shape of the LIOAS signal for the sample (Fig. 2) was different to that for the reference (the temporal shape of an instantaneous deactivation process).

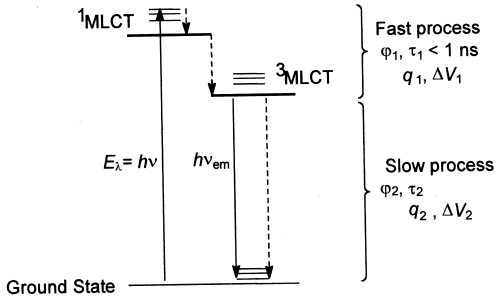
Similar to our previous reports [8–10], satisfactory fits of the LIOAS sample signal were obtained using a biexponential function (two lifetimes, τ_i, and two preexponential factors, φ_i) (Fig. 2). The same procedure gave good results for $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$.

In every case the fitting program found a fast process ($\tau_1 < 1$ ns) independent of the sample (complex or supercomplexes) and a slow decay with a sample-dependent lifetime (τ_2) (Table 1).

The value $\tau_1 < 1$ ns only means that the process is faster than the time resolution of our experimental set-up. Fixing this parameter at any value between 0.1 and 10 ns always resulted in the same value of φ_1. Therefore, φ_1 is associated with the prompt formation of the ^{3}MLCT state, which occurs in the subnanosecond times for Ru(II) bipyridine complexes [14].

The slow component is associated with the ^{3}MLCT state decay, since in Ar-purged solutions and in the absence of quenchers the excited species must totally return to the ground state within its lifetime (Scheme 1).

This is in line with the similarity of the τ_2 values and the emission lifetimes of the complex (100 ns)



Scheme 1. Term scheme for the deactivation of the ^{3}MLCT state of free Ru(bpy)$(CN)_4^{4-}$ and included in the polyaza macrocycles. Dash arrows represent non-radiative decay processes.

[11], $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ (180 ns) [4], and $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$ (140 ns).

In all cases $\varphi_1+\varphi_2=1.00\pm0.1$, which agrees with Scheme 1, since in all cases the energy lost by radiation ($E_{em}\Phi_{em}<5$ kJ/mol) is $\ll E_\lambda$ (the exciting molar energy, $\equiv 299$ kJ/mol at 400 nm).

The φ_i values were plotted vs. the respective $(c_p\rho/\beta)_T$ values, (Eq. (1), Fig. 3) in order to obtain q_i and ΔV_i, i.e., the total (and also the molar since the quantum yield for the formation of the ^{3}MLCT state is 1) [15] heat and structural volume change, respectively, associated with the formation ($i=1$) and decay ($i=2$) of the ^{3}MLCT state [6,8,10,13]

$$E_\lambda\varphi_i=q_i+\Delta V_i\left(\frac{c_p\rho}{\beta}\right)_T. \quad (1)$$

In all cases, good linear plots were obtained (Fig. 3, data collected in Table 2) confirming that the structural volume changes are invariant within the (relatively small) temperature range studied, or that there is an enthalpy–structural volume (entropy) compensation effect [10]. The linearity of the plots together with the invariability of the lifetimes of the supercomplexes with temperature (Table 1) indicate also that no important changes were produced in the stability constant for the formation of both supercomplexes (typically, $>1\times10^6$ M^{-1}) in the temperature range used [4].

The enthalpy content of the ^{3}MLCT state is $\Delta H_{MLCT}=E_\lambda-q_1$ or directly $=q_2$, inasmuch as the ^{3}MLCT state fully returns to the ground state with negligible energy loss by emission (see above). Thus, the average values of ΔH_{MLCT} for Ru(bpy)-$(CN)_4^{2-}$, $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$, and $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$ are 223 ± 8, 222 ± 8, and 228 ± 10 kJ/mol, respectively.

Therefore, supercomplex formation does not alter appreciably the energy level of the ^{3}MLCT state of the parent Ru(bpy)$(CN)_4^{2-}$. This is in agreement with the negligible shifts in the emission maximum of Ru(bpy)$(CN)_4^{2-}$ upon addition of [32]ane-$N_8H_8^{8+}$ [4]. However, the emission quantum yield of the ruthenium complex increases upon supercomplex formation (e.g., 0.0068 for the free complex and 0.012 for $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$) [4]. As expected, τ_2 undergoes a parallel increase (Table 1).

Neglecting possible changes in electronic coupling (i.e., focussing on the Franck–Condon term of the transition probability) [16,17], differences in radiationless decay rates may be related to two factors, changes in: (1) the energy gap to the ground state or (2) the number and/or frequency of the accepting vibrational modes. Clear effects of the energy gap were obtained in other types of SSDA interactions of Ru(bpy)$(CN)_4^{2-}$ (such as protonation, solvent effects, substitution of cyanide with methyl isocyanide) where substantial increments of the ^{3}MLCT state energy

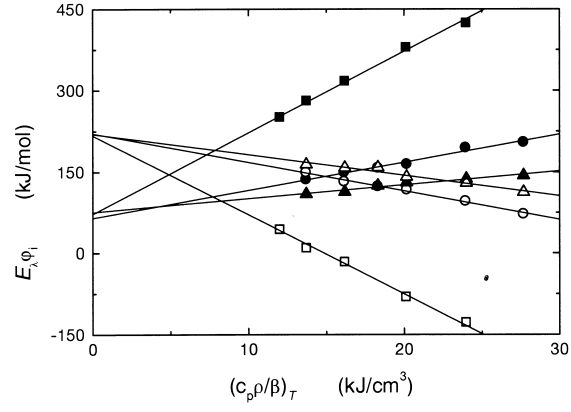


Fig. 3. $E_\lambda\varphi_1$ and $E_\lambda\varphi_2$ associated with the formation (filled symbols) and decay (open symbols), respectively, of the ^{3}MLCT state of (squares) Ru(bpy)$(CN)_4^{2-}$, (circles) $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}[N_8H_8]\}^{6+}$, and (triangles) $\{[Ru(bpy)(CN)_4]\cdot[24]ane\text{-}[N_6H_6]\}^{4+}$ vs. $(c_p\rho/\beta)$ of the medium. The temperatures for Ru(bpy)$(CN)_4^{2-}$ were from left to right 35, 30, 25, 20, and 17°C, whereas for both supercomplexes they were 30, 25, 22, 20, 17, and 15°C.

Table 2
Heat evolved, q_i, and structural volume changes, ΔV_i, associated with the photoinduced formation ($i = 1$) and decay ($i = 2$) of the ^{3}MLCT state of free Ru(bpy)$(CN)_4^{2-}$ and its 1:1 supercomplexes with polyammonium macrocycles, in aqueous 10^{-4} M HCl solutions

	Ru(bpy) $(CN)_4^{2-}$	$\{[Ru(bpy)(CN)_4]\cdot$ [24]ane-$[N_6H_6]\}^{4+}$	$\{[Ru(bpy)(CN)_4]\cdot$ [32]ane-$[N_8H_8]\}^{6+}$
q_1 (kJ/mol)	71 ± 9	75 ± 6	64 ± 7
ΔV_1 (cm^3/mol)	14.9 ± 0.5	2.5 ± 0.3	5.2 ± 0.3
q_2 (kJ/mol)	217 ± 10	220 ± 9	221 ± 7
ΔV_2 (cm^3/mol)	-14.6 ± 0.5	-3.7 ± 0.4	-5.3 ± 0.3

were observed [18]. The large lifetime increases observed upon supercomplex formation in solvents of low acceptor number (e.g., acetonitrile, where the supercomplex formation was accompanied by a blue-shift in emission of ~ 36 kJ/mol) [4] are certainly also dominated by energy-gap-law effects.

In water, on the other hand, the energy changes upon supercomplex formation were very small [2], and changes in the acceptor modes could also play an appreciable role. Such changes arise from the replacement of four independent water molecules by covalently-interconnected subunits of the aza macrocycle in the second sphere of the cyanides. This could result in a reduction in the number and/or frequency [3] of high-energy accepting modes, and thus in a decrease in the radiationless deactivation probability. The effect observed for Ru(bpy)$(CN)_4^{2-}$ inside the water pools of reverse micelles, when the rigidity of the water pool was increased, is probably of similar origin [8].

At variance with the enthalpy changes, the values of ΔV_i for the formation and decay of the ^{3}MLCT state of Ru(bpy)$(CN)_4^{2-}$ are strongly reduced upon supercomplex formation (Table 2).

The expansions for Ru(bpy)$(CN)_4^{2-}$ in aqueous solutions [6,9,10] and in the water pool of reverse micelles [7] have been rationalized in terms of changes in the strength of the CN $\cdots$ HOH bonds. Thus, the hydrogen bonds to the water molecules are expected to be weakened, resulting in an expansion of the solvation sphere. In turn, when the ^{3}MLCT state decays, the opposite effect occurs and a volume contraction of the same magnitude is observed.

The same explanation can be applied in the case of the supercomplexes, taking into account that the changes in strength refer to the CN $\cdots$ HN^+R_2H hydrogen bonds. Therefore, ^{3}MLCT formation is expected to yield an expansion of the whole macrocycle, and excited-state relaxation a contraction of the same magnitude. The values observed for the supercomplexes confirm this prediction (Table 2). They are definitely smaller, however, than the expansions for Ru(bpy)$(CN)_4^{2-}$ in aqueous solution. This can be readily related with the more rigid second-sphere provided by the macrocycles (vide supra).

The relative magnitude of the structural volume changes for the two macrocycles is not easy to analyze in detail, as two factors could play opposite roles: (1) the two macrocycles are expected to exhibit a different degree of rigidity, with the smaller [24]ane-$[N_6H_6]^{6+}$ being less flexible than the larger [32]ane-$[N_8H_8]^{8+}$ and (2) the two macrocycles are expected to exhibit different binding modes, with the smaller [24]ane-$[N_6H_6]^{6+}$ being hydrogen bound to three facial cyanides [2], and the larger [32]ane-$[N_8H_8]^{8+}$ being bound to all four cyanides in a 'boat' conformation [4]. The first factor predicts a smaller volume change for $\{[Ru(bpy)(CN)_4]\cdot$ [24]-ane-$[N_6H_6]\}^{4+}$. The second one, considering the

[2] A word of caution is required with respect to such a statement. Given the exponential form of the energy-gap law ($\ln k \propto \alpha\Delta E$), 'negligible' energy changes could have non-negligible consequences on the lifetime. For instance, using a standard value of $\alpha = 12$ kJ/mol^{-1} [16,17], an increase in lifetime from 100 to 180 ns could be accounted for by an increase in excited-state energy as small as 8 kJ/mol.

[3] One possible way of looking at this effect is to consider the macrocycle as introducing a large reduced mass into the new oscillators.

presence of one free cyanide hydrogen-bonded to water, would suggest a larger structural change for $\{[Ru(bpy)(CN)_4] \cdot [24]ane\text{-}[N_6H_6]\}^{4+}$. The observed behavior (i.e., a smaller value of ΔV_i for the smaller macrocycle, Table 2) seems to indicate a prevailing effect of the macrocycle flexibility factor over the free cyanide contribution [4].

The binding mode of the macrocycle, on the other hand, could be relevant to the observed trend in lifetimes, i.e., $\{[Ru(bpy)(CN)_4] \cdot [32]ane\text{-}[N_8H_8]^{6+} > [Ru(bpy)(CN)_4][24]ane\text{-}[N_6H_6]\}^{4+} > [Ru(bpy)(CN)_4]^{2-}$ (Table 1).This order parallels the number of free CN groups in these species (0, 1, and 4). Given the negligible changes in excited-state energy [16,17], the trend in τ_2 is explained on the basis of the water molecule oscillators bound to the free cyanides providing (vide supra) effective nonradiative deactivation pathways.

Acknowledgements

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[4] In this respect, it may be pointed out that not all of the four cyanides must respond to excitation to the same extent. In fact, for *trans* $Ru(bpy)(CN)_2(CNCH_3)_2$, where the only free cyanides are axial, little structural volume change was observed upon MLCT excitation [6].

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