Inorg. Chem. **1996,** *35,* 3355−3361 **3355**

Photophysics of Supercomplexes. Adduct between Ru(bpy)(CN)$_4^{2-}$ and the [32]ane-N$_8$H$_8^{8+}$ Polyaza Macrocycle

Maria Anita Rampi, Maria Teresa Indelli, and Franco Scandola*

Dipartimento di Chimica dell'Università, Centro di Fotoreattività e Catalisi CNR, 44100 Ferrara, Italy

Fernando Pina* and A. Jorge Parola

Departamento de Quimica (CQFB), Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal

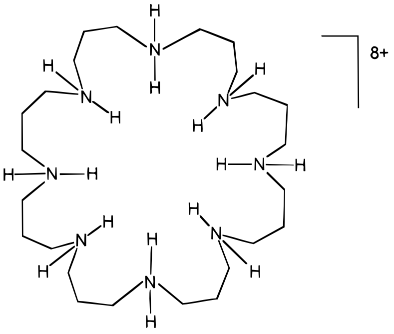
Received December 13, 1995⊗

The formation of a supercomplex between the Ru(bpy)(CN)$_4^{2-}$ (bpy = 2,2′-bipyridine) complex and the [32]-ane-N$_8$H$_8^{8+}$ macrocycle (**1**) has been studied in water and in acetonitrile. In acetonitrile, supercomplex formation is accompanied by (i) large hypsochromic shifts in the absorption spectrum (color changes from deep violet to yellow) and in the emission spectrum, (ii) large anodic shifts in standard oxidation (0.73 V) and reduction (0.37 V) potentials, (iii) typical shifts of ^{1}H-NMR signals for the macrocycle N-bound protons and the complex bipyridine protons, and (iv) a large increase in the MLCT excited-state lifetime of the complex. In water, the spectral shifts and the changes in standard potential are much less pronounced, but supercomplex formation is evidenced by ^{13}C-NMR (and ^{1}H-NMR) and by emission lifetime changes. In both solvents, supercomplex formation is complete in 1:1, 1.0×10^{-4} M solutions, indicating very large stability constant values. A structure of the supercomplex with the macrocycle bound in a "boat" conformation to the four cyanide ligands of the complex, plausible in terms of molecular models, is consistent with all the experimental data. In water, the supercomplex further associates with added negative species containing carboxylate functions, as shown by partial reversal of the lifetime changes. When the added species is also a potential electron transfer quencher (such as, e.g., Rh(dcb)$_3^{3-}$, dcb = 4,4′-dicarboxy-2,2′-bipyridine), however, association is not accompanied by quenching. This behavior is attributed to the structure of the supercomplex−quencher adduct, in which the macrocycle acts as an insulating spacer between the excited complex and the quencher.

Introduction

Supercomplexes ("complexes of complexes")[1] are supramolecular species in which a macrocyclic receptor is bound by noncovalent interactions to a transition-metal coordination compound. The name emphasizes the role of the macrocyclic species as a second-sphere ligand[2] on the metal complex. Notable examples of such species are the supercomplexes formed between hexacyanometalate ions and polyaza macrocycles[3,4] and between ammine metal complexes and crown ethers.[5−7]

As for most host−guest systems, two aspects are interesting in the chemistry of supercomplexes: (i) formation from individual molecular components (stability constants, structural complementarity, and chemical forces involved in the binding)[1−7] and (ii) specific properties of the adduct arising to the mutual *perturbation* of the two molecular components.[2] Taking the second viewpoint, of particular relevance is the possibility to modify *redox*, *spectroscopic*, *photochemical*, *and photophysical* properties of a metal complex by supercomplex formation with an appropriate macrocycle.[8] Within the class of supercomplexes involving polyaza macrocycles and metal cyanides, clear examples of changes in *redox* properties have been reported, e.g., for the adducts between [32]ane-N$_8$H$_8^{8+}$ (**1**) and Fe(CN)$_6^{4-}$ or Ru(CN)$_6^{4-}$.[9] These metal complexes, however, lack interesting and/or conveniently measurable spectroscopic, photochemical and photophysical properties. An interesting case of a



1

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Lehn, J. M. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 29.

(2) Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319.

(3) Dietrich, B.; Hosseini, M. W.; Lehn, J.-M.; Sessions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282.

(4) (a) Bencini, A.; Bianchi, A.; Garcia-Espanña, E.; Giusti, M.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 3902. (b) Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-España; Micheloni, M.; Ramirez, A.; Paoletti, P.; Paoli, P. *Inorg. Chem.* **1992**, *31*, 1902.

(5) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487.

(6) Todd, M. D.; Dong, Y.; Horney, G.; Yoon, D. I.; Hupp, J. T. *Inorg. Chem.* **1993**, *32*, 2001, and references therein.

(7) Ando, I.; Fujimoto, H.; Nakayama, K.; Ujimoto, K.; Kurihara, H. *Polyhedron* **1991**, *10*, 1139.

(8) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, England, 1991; Chapter 10.

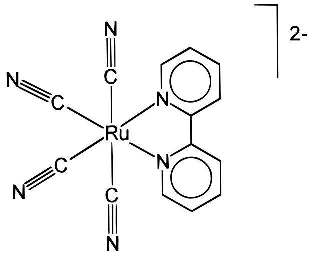
(9) (a) Peter, F.; Gross, M.; Hosseini, M. W.; Lehn, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 729. (b) Hosseini, M. W. In *Perspectives in Coordination Chemistry*; Williams, A.; Floriani, C., Merbach, A. E., Eds.; VCH: Weinheim, Germany, 1992; p 333.

(10) Manfrin, F.; Moggi, L.; Castelvetro, V.; Balzani, V.; Hosseini, M. W.; Lehn, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 6888.

S0020-1669(95)01590-4 CCC: $12.00

change in *photochemical* properties[10] is noted in the supercomplex between [32]ane-$N_8H_8^{8+}$ and the $Co(CN)_6^{3-}$ complex ion, for which the quantum yield for photochemical CN^- release (followed by solvation) is 70% smaller relative to that for the free complex. The effect was attributed[10] to the mechanical constraining effect of the macrocycle which can bind effectively four of the six cyanide ligands of the complex, most probably in an equatorial geometry.[11] With this metal complex, however, redox properties and photophysical parameters are not experimentally accessible and, in addition, effects on spectroscopic properties were almost negligible.

We would like to present here a case in which supercomplex formation with a polyazamacrocycle induces wide changes in the redox, spectroscopic, and photophysical properties of the complex. In designing the system, the following lines were followed. As the metal complex, the ideal candidate would be a Ru(II) polypyridine system. These complexes are the prototypal "photosensitizers" of inorganic photochemistry, and have well characterized redox, spectroscopic, and photophysical properties.[12,13] To provide binding sites for a polyaza macrocycle, however, cyanides should be present as ancillary ligands in the complex (possibly to the extent to give an overall negative charge to the complex). Therefore, attention was focussed on the $Ru(bpy)(CN)_4^{2-}$ complex ion (**2**),whose redox, spectroscopic, and photophysical properties have already been studied.[14−17] As to the macrocycle, [32]ane-$N_8H_8^{8+}$ was chosen on the basis of its optimal size for binding octahedral metal cyanides.[3,9−11] With such complexes, the binding probably involves four cyanide ligands in the equatorial plane ("belt" arrangement), but the flexible nature of the macrocycle was expected to allow a meridianal coordination ("boat" arrangement) as well.[11]



2

Experimental Section

Materials. $K_2[Ru(bpy)(CN)_4]$,[14] $[Rh(Me_2bpy)_3]Cl_3$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine),[19] and $K_3[Rh(dcb)_3]$ (dcb = 4,4′-dicarboxy-2,2′-bipyridine)[19] complexes were available from previous studies. The macrocycle [32]ane-N_8, 1,5,9,13,17,21,25,29-octaazacyclodotriaeicontane, was synthesized following a literature procedure[18] using 1,3-propanediamine as the starting material. The macrocycle was prepared and used as either the chloride ([32]ane-N_8·8HCl) or the perchlorate ([32]ane-N_8·$8HClO_4$) salt. Spectrograde organic solvents (Merck Uvasol) and triply distilled water were used. Other chemicals were all of reagent grade quality.

Apparatus and Procedures. The instruments and procedures used to obtain UV−vis absorption, emission, and excitation spectra were as described in a previous paper.[20]

Emission lifetimes were measured using a previously described time-correlated single-photon counting apparatus.[20] All measurements were carried out on deaerated solutions.

Cyclic voltammetry measurements were carried out on Ar-purged solutions containing 0.1 M $[TBA]PF_6$ using a previously described apparatus[21] and a conventional three-electrode cell assembly (platinum, working, saturated calomel electrode (SCE), reference; sweep rate, 100 mV s^{-1}).

^1H- and ^{13}C-NMR spectra were measured using a Bruker AM200 spectrometer (200 MHz). Chemical shifts (δ) are reported referenced to Me_4Si as the internal standard.

In water, the chloride salt of [32]ane-$N_8H_8^{8+}$ and the potassium salt of $Ru(bpy)(CN)_4^{2-}$ were used. The experiments were always performed on aqueous solutions containing 1.0×10^{-4} M HCl. In these conditions, $Ru(bpy)(CN)_4^{2-}$ is completely unprotonated both in the ground and in the excited state,[16] while [32]ane-$N_8H_8^{8+}$ is present in the fully protonated form.[3]

For solubility reasons, the perchlorate salt of [32]ane-$N_8H_8^{8+}$ and the tetrabutylammonium salt of $Ru(bpy)(CN)_4^{2-}$ were used in acetonitrile. In this solvent, there is no need for added acid to ensure full protonation of the macrocycle.

Unless otherwise noted, all the experiments refer to room temperature (298 K) solutions.

Results

The spectroscopic, redox, and photophysical properties of $Ru(bpy)(CN)_4^{2-}$ are known to be extremely dependent on solvent.[14,17] To keep track of these effects, which depend on second-sphere donor−acceptor interactions[15] between the solvent and the cyanide ligands, two solvents of widely different acceptor properties were chosen for this study: water and acetonitrile.

Absorption Spectra. The absorption spectrum of $Ru(bpy)(CN)_4^{2-}$ (1.0×10^{-4} M) in aqueous solution exhibits a maximum at 400 nm.[14] Addition of an equivalent amount of [32]ane-$N_8H_8^{8+}$ (nonabsorbing in the whole spectral range) resulted in a slight but reproducible blue shift (ca. 2 nm) in the absorption spectrum of the complex. Further addition of [32]ane-$N_8H_8^{8+}$ did not bring about any further changes.

The absorption spectrum of $Ru(bpy)(CN)_4^{2-}$ (1.0×10^{-4} M) in acetonitrile is shown in Figure 1 (curve 1). Addition of increasing amounts of [32]ane-$N_8H_8^{8+}$ resulted in a strong blue shift in the absorption spectrum of the complex (Figure 1, curves 2−6). No further spectral changes were observed after addition of 1 equiv of [32]ane-$N_8H_8^{8+}$ (curve 6). It should be noted that isosbestic points are maintained in the early stages of this spectrophotometric titration (curves 1−4, [[32]ane-$N_8H_8^{8+}$]/[$Ru(bpy)(CN)_4^{2-}$] ratios from 0 to ca. 0.2).

Redox Behavior. Cyclic voltammograms of $Ru(bpy)(CN)_4^{2-}$ in aqueous solution show a reversible oxidation wave at +0.80 V vs SCE. The wave was not appreciably shifted on addition of 1 equiv of [32]ane-$N_8H_8^{8+}$.

In acetonitrile, a reversible oxidation wave at +0.27 V vs SCE ($\Delta E_p = 60$ mV) and a reversible reduction wave a −1.95 V vs SCE ($\Delta E_p = 100$ mV) are observed for $Ru(bpy)(CN)_4^{2-}$. When 1 equiv of [32]ane-$N_8H_8^{8+}$ is added, the waves shift to

---

(11) Parola, A. J.; Pina, F. *J. Photochem. Photobiol. A*: *Chem.* **1992**, *66*, 337.

(12) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *27*, 4587.

(13) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic: New York, 1992.

(14) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872.

(15) Scandola, F.; Indelli, M. T. *Pure Appl. Chem.* **1988**, *60*, 973.

(16) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. In *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, 1987; p 159.

(17) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381.

(18) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *Helv. Chim. Acta* **1983**, *66*, 1262.

(19) Indelli, M. T.; Bignozzi, C. A.; Pavanin, L.; Scandola, F. Manuscript in preparation.

(20) Indelli, M. T.; Bignozzi, C. A.; Harriman, T.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3768.

(21) Bignozzi, C. A.; Roffia, S.; Chiorboli, C.; Davila, J.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1989**, *28*, 4350.

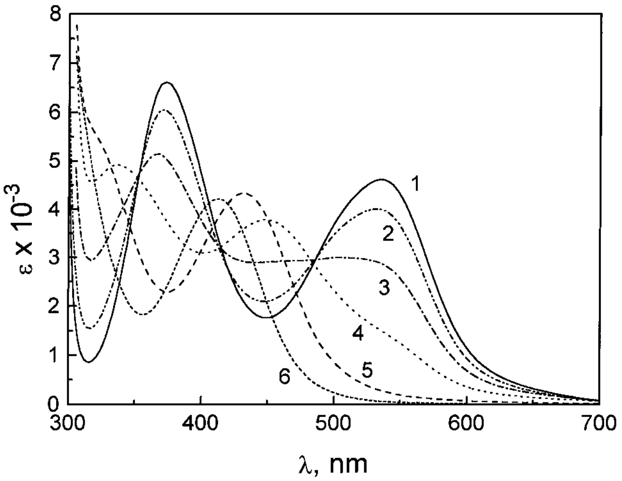


Figure 1. Absorption spectra in acetonitrile solutions: $Ru(bpy)(CN)_4^{2-}$ (1); $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$ in molar ratios 1:0.047 (2), 1:0.125 (3), 1:0.205 (4), 1:0.44 (5), and 1:1 (6). Molar absorptivity scale based on $Ru(bpy)(CN)_4^{2-}$. Concentration of $Ru(bpy)(CN)_4^{2-}$: 1.0×10^{-4} M.

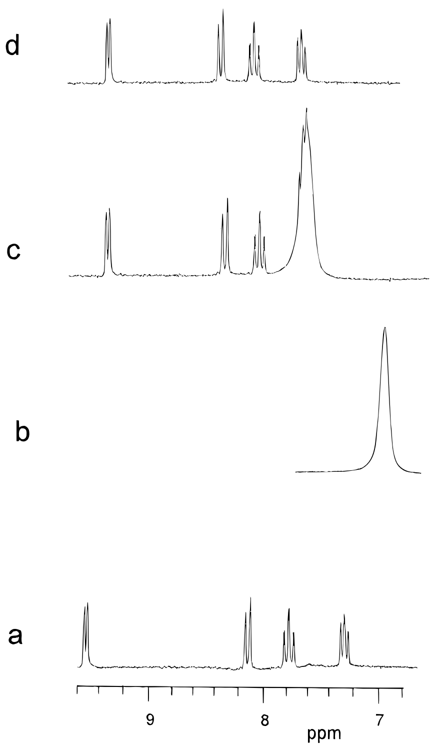


Figure 2. ^{1}H-NMR spectra in deuterated acetonitrile: (a) $Ru(bpy)(CN)_4^{2-}$; (b) [32]ane-$N_8H_8^{8+}$; (c) 1:1 $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$; (d) 1:1 $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$ with added D_2O.

+1.0 V vs SCE ($\Delta E_p = 80$ mV) and −1.58 V vs SCE (cathodic peak, poorly reversible). The [32]ane-$N_8H_8^{8+}$ macrocycle is electrochemically inert in acetonitrile in the +1.5 to −1.6 V vs SCE range.

NMR Spectra. ^{1}H-NMR spectra in the region 7−9.5 ppm, measured in deuterated acetonitrile, are shown in Figure 2. In the spectrum of $Ru(bpy)(CN)_4^{2-}$ (Figure 2a) resonance signals are assigned to the bipyridine protons[22] as follows: 9.55 ppm, 6,6′ protons; 8.13 ppm, 3,3′ protons; 7.75 ppm, 4,4′ protons; 7.32 ppm, 5.5′ protons. The spectrum of [32]ane-$N_8H_8^{8+}$ (Figure 2b) shows the resonances of the N-bound protons as a single broad band centered at 6.87 ppm. The 1:1 mixture of $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$ (Figure 2d) exhibits a superposition of the resonances of parts a and b of Figure 2, but with substantial shifts: the 6,6′ protons shift upfield to 9.30 ppm; the 3,3′, 4,4′, and 5,5′ protons shift downfield to 8.32, 8.05, and 7.76 ppm, respectively; the macrocyclie N-bound protons move downfield to 7.58 ppm. In Figure 2c, the bipyridine 5,5′ proton resonance signals and the broad band of the macrocycle overlap considerably. A clean spectrum of the bipyridine protons in the 1:1 mixture, free from such an overlap, is obtained in the presence of D_2O (Figure 2d), in which the N-bound protons of the macrocycle are exchanged, leading to the disappearance of the corresponding signals.

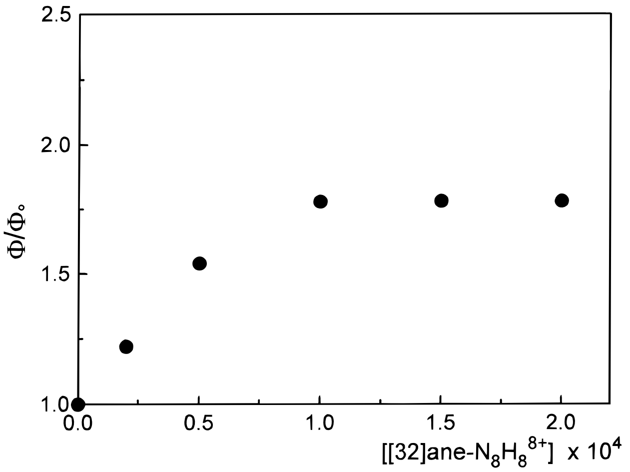


Figure 3. Relative change in emission quantum yields (Φ) in aqueous solutions of $Ru(bpy)(CN)_4^{2-}$ (1×10^{-4} M) as a function of the concentration of added [32]ane-$N_8H_8^{8+}$ (Φ_0 is the quantum yield in the absence of macrocycle).

The effect of temperature on the ^{1}H-NMR spectrum of a 1:1 mixture of $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$ was examined in a deuterated methanol solution. In this solvent, the spectrum at room temperature (22 °C) was almost identical to that in D_2O-containing acetonitrile (Figure 2d), with the same resonance pattern of the bipyridine protons, but slightly shifted owing to the solvent change (9.42, 8.41, 8.02, and 7.64 ppm). Upon lowering the temperature to −60 °C, no change in the ^{1}H-NMR spectrum was observed, except for a general very small downfield shift (0.03−0.08 ppm) of all the bands.

^{13}C-NMR spectra were measured in D_2O at room temperature. The spectra were assigned on the basis of ^{1}H−^{13}C HETCOR experiments. The spectrum of $Ru(bpy)(CN)_4^{2-}$ shows two resonances at 165.98 and 164.20 ppm corresponding to the cyanide carbons and bipyridine carbon resonances at 155.74 (2,2′), 152.80 (6,6′), 137.06 (4,4′), 126.05 (5,5′), and 122.63 ppm (3,3′). The ^{13}C-NMR spectrum of the 1:1 mixture of $Ru(bpy)(CN)_4^{2-}$ and [32]ane-$N_8H_8^{8+}$ displays cyanide carbon resonances at 165.69 and 163.77 ppm, shifted upfield with respect to those of free $Ru(bpy)(CN)_4^{2-}$. The bipyridine carbon resonances were shifted downfield (155.92 ppm, 2,2′; 137.59 ppm, 4,4′; 126.39 ppm, 5,5′; 123.06 ppm, 3,3′) except for the 6,6′ carbons (152.60 ppm).

Photophysical Behavior. In aqueous solution, $Ru(bpy)(CN)_4^{2-}$ emits at $\lambda_{max} = 610$ nm, with a quantum yield of 0.0068 and an emission lifetime of 101 ns.[14] Addition of [32]ane-$N_8H_8^{8+}$ caused negligible shifts in the emission maximum but sizable changes in the emission intensity and lifetime. The intensity of the emission increased with the concentration of [32]ane-$N_8H_8^{8+}$ (Figure 3); an upper limiting quantum yield value of 0.012 was obtained after addition of 1 equiv of the macrocycle. In solutions with [[32]ane-$N_8H_8^{8+}$]/[$Ru(bpy)(CN)_4^{2-}$] ≥ 1, the emission decay was monoexponential with a

---

(22) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239.

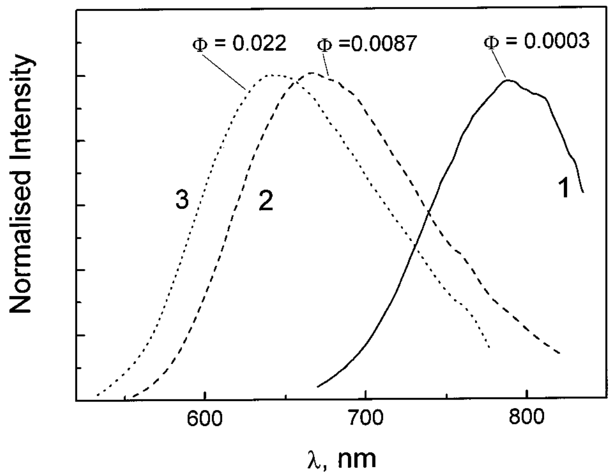


Figure 4. Emission spectra of acetonitrile solutions: Ru(bpy)(CN)$_4^{2-}$ (1); Ru(bpy)(CN)$_4^{2-}$ and [32]ane-N$_8$H$_8^{8+}$ in molar ratios 1:0.205 (2) and 1:1 (3).

constant lifetime of 180 ns. In contrast, complex nonexponential decays were observed in the intermediate concentration range $0 < [[32]\text{ane-N}_8\text{H}_8^{8+}]/[\text{Ru(bpy)(CN)}_4^{2-}] \leq 1$.

In acetonitrile, Ru(bpy)(CN)$_4^{2-}$ emits at $\lambda_{max} = 790$ nm, with an emission lifetime of 7 ns and a quantum yield of 3×10^{-4}.[17] Addition of [32]ane-N$_8$H$_8^{8+}$ led to spectral changes (Figure 4) similar to those observed in absorption: strong blue shifts up to the addition of 1 equiv of the macrocycle (curve 3, $\lambda_{max} = 640$ nm); no changes upon further addition. The effects of added macrocycle on the emission intensity were also very pronounced, as shown by the very different quantum yields for the three emissions reported in Figure 4. The behavior with respect to the emission decay was relatively complex. In the early stages of the spectrofluorimentric titration (for [[32]ane-N$_8$H$_8^{8+}$]/[Ru(bpy)(CN)$_4^{2-}$] ratios from 0 to ca. 0.2, i.e. for emission spectral changes from curve 1 to curve 2), the 790-nm emission is replaced[23] by an emission at $\lambda_{max} = 665$ nm, which is of increasing intensity. In this concentration ratio range, the emission at $\lambda_{max} = 665$ nm has a constant excitation spectrum peaking at 450 nm and exhibits a single-exponential decay with a lifetime of 130 ns. On the other hand, in the portion of the spectrofluorimetric titration going from spectrum 2 to spectrum 3 (i.e. for [[32]ane-N$_8$H$_8^{8+}$]/[Ru(bpy)(CN)$_4^{2-}$] ratios from ca. 0.2 to 1), the emission maximum and emission intensity continuously shift and the emission decay is complex. For [[32]ane-N$_8$H$_8^{8+}$/[Ru(bpy)(CN)$_4^{2-}$] = 1, the decay is again single-exponential with a lifetime of 330 ns, which remains unchanged upon further addition of the macrocycle.

The behavior of the 1:1 mixture of Ru(bpy)(CN)$_4^{2-}$ and [32]ane-N$_8$H$_8^{8+}$ was also investigated in aqueous solution in the presence of added species. Addition of EDTA to the 1:1 mixture of Ru(bpy)(CN)$_4^{2-}$ and [32]ane-N$_8$H$_8^{8+}$ caused a decrease in the emission lifetime. With 1 equiv of EDTA, a lifetime of 142 ns was observed. Further addition of EDTA caused no further decrease in the lifetime. Similar results were observed by addition of the tris(4,4′-dicarboxy-2,2′-bipyridine)-rhodium(III) complex, Rh(dcb)$_3^{3-}$, to the mixture. A decrease in the emission lifetime was also observed, that saturated sharply at a concentration of Rh(dcb)$_3^{3-}$ equivalent to that of the 1:1 Ru(bpy)(CN)$_4^{2-}$: [32]ane-N$_8$H$_8^{8+}$ mixture. The limiting lifetime was 120 ns. In contrast, fast bimolecular quenching (Stern-Volmer kinetics) was observed for the 1:1 mixture of Ru(bpy)(CN)$_4^{2-}$ and [32]ane-N$_8$H$_8^{8+}$ in the presence of methylviologen (N,N′-dimethyl-4,4′-bipyridinium dication); the quenching constant is 7×10^8 M^{-1} s^{-1} at 0.02 M ionic strength. Finally, a control experiment was carried out with Ru(bpy)(CN)$_4^{2-}$, in the absence of the macrocycle, using Rh(Me$_2$bpy)$_3^{3+}$ as an electron acceptor. Under these conditions, fast quenching of the excited state of Ru(bpy)(CN$_4$)$^{2-}$ occurred with a bimolecular quenching constant value of 2×10^{10} M^{-1} s^{-1} (0.001M ionic strength).

Discussion

Formation, Structure, and Properties of the Supercomplex. In acetonitrile, the interaction of Ru(bpy)(CN)$_4^{2-}$ with the macrocycle shows up visually as a sharp change in color, from deep violet to yellow. Indeed, huge blue shifts are noticeable in the absorption (Figure 1) and emission (Figure 4) spectra upon addition of [32]ane-N$_8$H$_8^{8+}$ to the complex. The excited states responsible for these spectral features have metal-to-ligand charge transfer (MLCT) character;[14] blue shifts in MLCT transitions are expected when the charge density at the Ru(II) center is decreased. Direct proof of the electron-withdrawing effect of the macrocycle is provided by the electrochemical experiments, which show that upon interaction with [32]ane-N$_8$H$_8^{8+}$ the Ru(III)/Ru(II) redox potential of the complex becomes more positive by as much as 0.77 V. This is indicative of an interaction predominantly made of hydrogen bonding between the azamacrocycle and the N-end of the cyanide ligands of the complex. Qualitatively similar effects were observed previously by protonation of Ru(bpy)(CN)$_4^{2-}$ with HClO$_4$[16] and by substitution of the CN$^-$ ligands with CNCH$_3$.[17] The interaction in this system is thus of the same type as that hypothesized in the formation of other supercomplexes between metal cyanides and azamacrocycles.[3,4]

The spectral effects are much less marked in water, where only very small blue shifts are noted. This is not unexpected, as the Ru(bpy)(CN)$_4^{2-}$ is extremely solvatochromic. The mechanism of solvatochromism is similar to that of supercomplex formation, being based on second-sphere donor−acceptor interactions at the cyanides.[2,15] Thus, in water strong hydrogen bonding to the cyanides already withdraws charge from the metal, shifting the Ru(III)/Ru(II) potential to substantially positive values and bringing the MLCT absorption and emission features to higher energy. Thus, any further blue shifts are not expected to be significant upon interaction of the complex with the macrocycle. It should be pointed out, however, that, despite the negligible spectral shifts, evidence for supercomplex formation in water comes from emission intensity (Figure 3) and lifetime measurements.

In both water and acetonitrile, the changes in absorption spectra (Figure 1), emission spectra (Figure 4), emission quantum yields (Figures 3 and 4), and emission lifetimes observed upon addition of [[32]ane-N$_8$H$_8^{8+}$] to Ru(bpy)(CN)$_4^{2-}$ reach a limit at a 1:1 ratio, and subsequently undergo no further change. This is strong indication that a definite species having the stoichiometry

$$\{[\text{Ru(bpy)(CN)}_4]\cdot[[32]\text{ane-N}_8\text{H}_8]\}^{6+}$$

is formed. Formation of this species is practically quantitative in 1×10^{-4} M solution of the reactants, implying that the stability constant of this adduct is larger than 10^6 M^{-1} in both solvents. Large stability constants have been estimated from pH-metric titrations for supercomplex formation between [32]ane-N$_8$H$_8^{8+}$ and Co(CN)$_6^{3-}$ (log $K = 6.0$) and Fe(CN)$_6^{4-}$ (log

---

[23] A gradual decrease in the intensity of the 790-nm emission is likely to take place, although, because of its much smaller intensity, such emission is barely detectable after addition of very small amounts of the macrocycle.

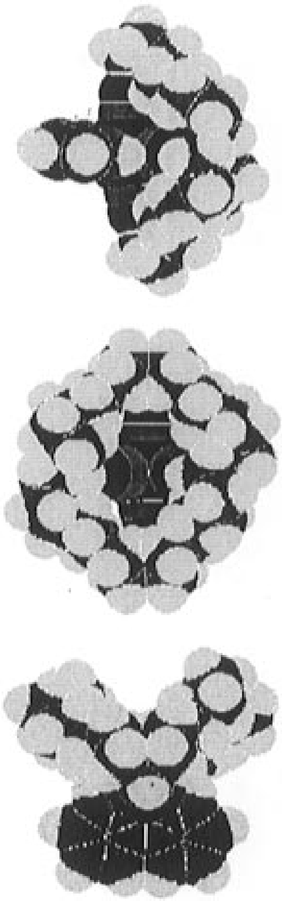


Figure 5. Computer generated (Alchemy II) space-filling model of the proposed supercomplex structure: side (top), front (middle), and top (bottom) views.

$K = 8.9$) in aqueous solution.[3] For systems of this type, stability constants are expected to increase in going from water to acetonitrile, on the basis of both electrostatic and hydrogen-bonding arguments. The spectral changes in acetonitrile, in which an isobestic point is first maintained (up to [32]ane-$N_8H_8^{8+}$/Ru(bpy)$(CN)_4^{2-}$ molar ratios of ca. 0.2) and then lost, indicate that the formation of the 1:1 supercomplex takes place through various intermediate species. In the initial steps, the formation of a neutral species with 1:4 stoichiometry is plausible.

In the absence of structural data, the geometry of the {[Ru(bpy)$(CN)_4$]•[[ane-N_8H_8]}$^{6+}$ supercomplex can only be presumed on the basis of the following considerations. The high stability constant tends to indicate binding interactions similar to those with the hexacyano complexes, i.e., four strong hydrogen bonds between the cyanide ligands and the macrocycle.[10] In the hexacyano complexes, the cyanides involved are equatorial, with the macrocycle in a "belt" arrangement.[10] For the present *cis*-tetracyano complex, this type of coordination is not available but, as shown by space-filling models, a structure of the type shown in Figure 5 with the macrocycle in a "boat" arrangement is entirely plausible.

The changes noted in the ^{1}H-NMR spectra of the complex and the macrocycle when the supercomplex formed are consistent with the above structural hypothesis. The marked downfield shift (0.5 ppm) of the broad signal corresponding to the NH protons of the macrocycle (Figure 2b,c) is indicative of hydrogen bond formation. The supercomplex formation is also clearly associated with shifts in the signals of the bipyridine protons (Figure 2a,d). The downfield shift of the 5,5′, 4,4′, and 3,3′ protons is as expected on the basis of the electron-withdrawing effect of the macrocycle on the metal. This enhances σ-donation from bipyridine and decreases π back-bonding from the metal, leading to decreased electron density on the bipyridine ligand and to deshielding of its protons. At variance with observations for the other protons of bipyridine, the shift is slightly upfield for the 6,6′ protons. These protons, however, are unique in their close proximity (Figure 5) to the equatorial cyanides and to the macrocycle which may provide additional shielding effects.

The equivalence of the *n,n′* positions in the bipyridine ^{1}H-NMR spectrum is retained in the spectrum of the supercomplex. This is as expected for a symmetric structure such as that illustrated in Figure 5; however, the presence of other less symmetric structures averaging rapidly on the NMR time scale is not precluded by our observations. A fast association−dissociation equilibrium is inferred by the retention of the equivalence of all the N−H protons of the macrocycle in the supercomplex (Figure 2c). In favor of the symmetrical structure is the observation that the ^{1}H-NMR spectrum of the supercomplex in the bipyridine region does not change appreciably by lowering the temperature, at least down to −80 °C (unfortunately, the N−H protons of the macrocycle cannot be looked at under the same conditions, because of their exchange with the deuterated methanol solvent).

The ^{13}C-NMR spectra also confirm hydrogen bonding at the cyanide ligands as the main interaction responsible for the binding. Upon supercomplex formation, the cyanide carbon signals shift upfield, whereas the bipyridine carbon signals (except for the 6,6′) shift downfield, with the same trend as seen previously for the protons. The increased shielding of the cyanide carbon is as expected on the basis of the increase in their π-acceptor character and consequent shift of electron density from the metal. Charge withdrawal from the metal then reflects on the bipyridine ligand, where a general deshielding (except, again, for the 6,6′ carbons) is observed.

The photophysical results indicate a general tendency to increases in lifetimes and in emission quantum yields upon supercomplex formation. This observation is common for complexes derived from Ru(bpy)$(CN)_4^{2-}$, in which an increase in the MLCT excited-state energy caused by second-sphere donor−acceptor interactions at the cyanides (solvent effects, protonation, substitution of cyanide with methyl isocyanide) is always accompanied by an increase in excited-state lifetime.[14,15,17] This effect has been attributed mainly to the energy-gap law.[14] Of interest is the fact that the increase in lifetime observed on going from free Ru(bpy)$(CN)_4^{2-}$ to the 1:1 supercomplex takes place through an intermediate regime of nonexponential behavior. This shows that the various species existing in this intermediate regime (free Ru(bpy)$(CN)_4^{2-}$, the 1:1 supercomplex, and species of intermediate molar ratios) do not undergo rapid exchange on the time scale of the excited-state decay. This is largely as expected in acetonitrile, where such related processes (e.g., proton transfer) are known to be slow,[24] but is also true in water, where such processes are potentially much faster.

Behavior of the Supercomplex in Oxidative Quenching. As shown by the electrochemical and photophysical results, both the ground-state redox properties and the excited-state energies change upon supercomplex formation (substantially in acetonitrile and much less in water). As a consequence, the excited-state redox properties[12] are also expected to change. Owing to the parallel shift in the ground-state redox potential and excited-state energy, however, such changes are relatively small. The MLCT excited state, which is a very powerful reductant for

---

(24) Davila, J.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.*, **1989**, *93*, 1373.

$Ru(bpy)(CN)_4^{2-}$ ($E°(Ru(III)/{}^*Ru(II)) = -1.60$ V in water and -1.57 V in acetonitrile, vs SCE[25]), remains so also in the supercomplex ($E°(Ru(III)/{}^*Ru(II)) = -1.60$ V in water and -1.29 in acetonitrile, vs SCE[25]). It should be stressed that, although the thermodynamics for photoinduced electron transfer do not change substantially upon supercomplex formation, the kinetics may change. First of all, the large change in electric charge (from 2− in the complex to 6+ in the supercomplex) is expected to bring about drastic changes in the bimolecular reaction rates with charged quenchers, with a reversal in the kinetic discrimination between cations and anions. It should also be noted that the attached macrocycle, which in the proposed structure (Figure 5) is shaped as a cavity, retains residual hydrogen-bonding capability. The possibility that negatively charged, hydrogen-bonding substrates undergo specific host−guest interactions at this cavity should also be considered as a possible factor affecting electron transfer quenching.

The ability of the $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]]\}^{6+}$ supercomplex to further associate with highly charged anions is witnessed by the effects observed with polycarboxylate ions. For instance, addition of EDTA to aqueous solutions of $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\}^{6+}$ causes a decrease in emission lifetime. The decrease saturates sharply at a 1:1 EDTA: supercomplex molar ratio. The limiting lifetime, 142 ns, is distinctly lower than that of the supercomplex (180 ns) and higher than that of free $Ru(bpy)(CN)_4^{2-}$ (101 ns). The results indicate that a three-component supramolecular species, $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]]\cdot[EDTA]\}^{2+}$,[26] is formed under these conditions. As EDTA has no ability to quench the excited state by either energy or electron transfer, the decrease in the excited-state lifetime must be viewed as a perturbation effect. This is likely caused by the competition between EDTA and $Ru(bpy)(CN)_4^{2-}$ for the macrocycle in the three-component species. Binding with EDTA weakens the interaction between the macrocycle and $Ru(bpy)(CN)_4^{2-}$, thus partially reversing the lifetime changes observed upon supercomplex formation.

By analogy, one would expect that negatively charged *electron acceptors* upon association with the supercomplex induce efficient oxidative quenching of the $Ru(bpy)(CN)_4^{2-}$ excited state. This possibility has been verified using the $Rh(dcb)_3^{3-}$ complex.[27] Electron transfer from excited $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\}^{6+}$ to this rhodium(III) complex is exergonic by ca. 0.70 eV,[28] and is thus expected to be very fast.[29,30] Quite unexpectedly, however, the results obtained by adding $Rh(dcb)_3^{3-}$ to aqueous solutions of the supercomplex are very similar to those obtained with EDTA: the lifetime undergoes a moderate decrease, saturating sharply at a 1:1 $Rh(dcb)_3^{3-}$: supercomplex molar ratio, with a limiting lifetime of 120 ns. Thus, a $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\cdot[Rh(dcb)_3]\}^{3+}$ species *is* formed, but intramolecular electron transfer quenching does *not* take place in this species. It should be noted that related processes taking place in the absence of the macrocyclic component look as expected: e.g. bimolecular quenching of $Ru(bpy)(CN)_4^{2-}$ by $Rh(Me_2bpy)_3^{3+}$ is diffusion controlled (implying[31,32] a unimolecular rate constant in the encounter complex greater than 2×10^8 s^{-1}). On the other hand, processes taking place in the presence of the macrocyclic component but with positively charged quenchers also behave normally: e.g., quenching of the $[\{Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\}^{6+}$ supercomplex by methylviologen is diffusion controlled (implying[31,32] a unimolecular rate constant in the encounter complex greater than 10^{10} s^{-1}). Clearly, there must be some peculiar effect unfavorable to photoinduced electron transfer, related to the *structure* of the $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\cdot[Rh(dcb)_3]\}^{3+}$ species.

Tentatively, one could envision the three-component species as having the $Rh(dcb)_3^{3-}$ anion partially inserted into the cavity of the $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\}^{6+}$ supercomplex, probably using carboxylate groups to form hydrogen bonds with the macrocycle. In any case, a structure in which the macrocyclic cation is simultaneously bound to, and interposed between, the two complex anions is likely. In this view, the reason for the observed lack of electron transfer quenching could be attributed to small electronic coupling between the centers involved in the process. Remembering that the excited state to be quenched is MLCT in character and that the site of reduction in Rh(III) polypyridine complexes is the metal,[20] the redox orbitals involved in the process are the lowest π^* MO of the bipyridine ligand on Ru(II) and an e_g^* d-orbital of Rh(III). In a structure of this type, the through-space overlap between such orbitals is certainly quite small. On the other hand, through-bond electronic coupling[33−37] is expected to be relatively inefficient owing (i) to the saturated nature of the macrocyclic “spacer” and (ii) to the noncovalent nature of the bonding between the “spacer” and the metal complex units.

Conclusions

This work provides a further example of how supercomplexation with an azamacrocycle can be used to substantially modify the properties of a transition metal cyano complex. The complex chosen for this study, $Ru(bpy)(CN)_4^{2-}$, couples chromophoric and luminophoric properties with macrocycle binding capability. Thus, at variance with previously reported cases, supercomplex formation shows up visually (in acetonitrile) as a sharp color change, and brings about large changes in the

---

(25) Values of the excited-state redox potentials are obtained using the ground-state redox potentials and excited-state energies estimated from the onset (5% relative intensity) of the room-temperature emission spectra.

(26) For simplicity, an overall charge corresponding to fully deprotonated EDTA is indicated. At the experimental pH, EDTA is present as a mixture of 2− and 3− species.

(27) Spectrophotometric titrations indicate that the complex is present as the fully deprotonated $Rh(dcb)_3^{3-}$ form at pH ≥ 4.

(28) $E°(Rh(dcb)_3^{3-}/Rh(dcb)_3^{4-}) = -0.90$ V vs SCE.[19] It could be said that the excited-state redox properties to be used in this estimate are is neither those of free $Ru(bpy)(CN)_4^{2-}$ nor those of the $\{[Ru(bpy)(CN)_4][[32]ane\text{-}N_8H_8]\}^{6+}$ supercomplex, but rather those of the $\{[Ru(bpy)(CN)_4]\cdot[[32]ane\text{-}N_8H_8]\cdot[Rh(dcb)_3]\}^{3+}$ species. However, since the properties of $\{[Ru(bpy)(CN)_4]\cdot[32]ane\text{-}N_8H_8]\cdot[Rh(dcb)_3]\}^{3+}$ are expected to be intermediate between those of $Ru(bpy)(CN)_4^{2-}$ and $\{[Ru(bpy)(CN)_4]\cdot[32]]ane\text{-}N_8H_8]\}^{6+}$, and these two species are only slightly different in this respect, the above procedure is deemed correct.

(29) With this driving force, photoinduced electron transfer processes between Ru(II) and Rh(III) complexes are likely to be nearly activationless[20] and have been found to be very fast in other systems: diffusion-controlled, as bimolecular processes between Ru(II) and Rh(III) complexes in solution;[30] in the picosecond time domain, as unimolecular processes in weakly coupled covalently-linked Ru(II)−Rh(III) systems.[20]

(30) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.

(31) The unimolecular rate constant in the encounter complex can be evaluated (as an actual or limiting value) from the bimolecular electron transfer rate constant, provided that accurate values of the rate constants for diffusion and cage escape are available.[32]

(32) Chiorboli, C.; Indelli, M. T.; Scandola, M. A.; Scandola, F. *J. Phys. Chem.* **1988**, *92*, 156.

(33) Mc Connell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

(34) Hoffmann, R.; Imamura, A.; Here, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

(35) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751.

(36) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(37) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, England, 1991; Chapter 5.

photophysical parameters (emission energy, lifetime, and quantum yield) of the complex. A structure of the supercomplex with the [32]ane-$N_8H_8^{8+}$ macrocycle hydrogen-bound in a "boat" conformation to the four cyanide ligands of $Ru(bpy)(CN)_4^{2-}$, plausible on the basis of molecular models, is consistent with all the experimental data. The supercomplex exhibits peculiar properties (relative to the naked metal complex) in excited-state quenching by added electron acceptors. This behavior seems to be related not only to the change in the overall charge but also to the detailed structure of the precursor for the quenching process. The perspectives for the use of systems of this type as excited-state reactants with built-in receptor capability are currently under scrutiny.

Acknowledgment. This work was triggered by a stimulating discussion with Professor J.-M. Lehn. The authors are grateful to P. Bergamini and M. Scoponi for the NMR measurements and to C. A. Bignozzi for the cyclic voltammetry experiments. Financial support from MURST and the CNR (Italy) and from the JNICT (Portugal) is gratefully acknowledged. A.J.P. and F.P. thank NATO for an NCR Grant (No. 920629).

IC951590I