Coordination Chemistry Reviews, 111 (1991) 261–266
Elsevier Science Publishers B.V., Amsterdam

Photoinduced intramolecular energy transfer processes in polynuclear ruthenium(II) polypyridine complexes. Design of long chain cyanobridged polynuclear species featuring vectorial energy transfer

C. A. Bignozzi[a], R. Argazzi[a], C. Chiorboli[a], S. Roffia[b], F. Scandola[a]

[a]Dipartimento di Chimica dell'Universitá, Centro di Fotochimica CNR,
via L. Borsari 46 I-44100 Ferrara, Italy

[b]Dipartimento di Chimica G. Ciamician, Universitá di Bologna,
via Selmi 2 I-40100 Bologna, Italy

Abstract

In polychromophoric complexes of the type: $[\mathrm{NC\text{-}Ru(L)_2\text{-}CN\text{-}Ru(L')_2\text{-}CN}]^{+}$, $[\mathrm{NC\text{-}Ru(L)_2\text{-}CN\text{-}Ru(L'')_2\text{-}NC\text{-}Ru(L)_2}]^{2+}$ (L = 2,2'bipyridine, L' = 2,2' bipyridine or 1-10 phenantroline, L''= 2,2' bipyridine or 4,4'dicarboxy-2,2'bipyridine) photoinduced energy transfer from C- to N- bonded Ru-units takes place. Photocurrent spectra on TiO_2 obtained with the trinuclear $[\mathrm{NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(bpy(COOH)_2)_2\text{-}NC\text{-}Ru(bpy)_2\text{-}CN}]^{2+}$ complex suggest that the light energy absorbed by the external moieties is efficiently funneled to the central fragment and used for the sensitization of the semiconductor. Towards the building of more extended antenna units, polychromophoric Re-Ru complexes of general formula: $[\mathrm{(phen)(CO)_3Re\text{-}CN\text{-}[Ru(bpy)_2\text{-}CN]_n\text{-}Ru(bpy)_2\text{-}CN}]^{(n+1)}$ (n = 0 - 3) have been synthesized and studied.

1. INTRODUCTION

A continuing theme of our research has been the development of polynuclear transition metal complexes in which photoinduced intramolecular energy and electron transfer processes can be controlled by an appropriate choice of the component subunits [1].

In the last years, a number of cyano-bridged adducts containing the $\mathrm{\text{-}Ru(bpy)_2\text{-}}^{2+}$ chromophoric unit and various metal-containing moieties (M) have been studied [1-3]. In this class of compounds, which can be schematized by the formula

$$[\mathrm{M\text{-}NC\text{-}Ru(bpy)_2\text{-}CN\text{-}M}]^{n+}$$

the properties of the Ru-bpy MLCT excited states can be differently perturbed by the covalently linked M unit. Thus, while with d^{10} metal ions or Pt(II) complexes the useful photophysical properties of the Ru-bpy excited state (emission energy and lifetime) can be tuned producing new photosensitizer molecules, with subunits such as $\mathrm{\text{-}Ru(NH_3)_5}^{2+/3+}$, excited state quenching occurs presumably via intramolecular electron transfer processes [4,5].

Given the relatively strong electronic coupling which is provided by the bridging cyanide, efficient intramolecular energy transfer processes from the ruthenium chromophore to the M molecular unit can also take place. A rather clear example of the occurrence of such process is given by a series of bi- and trinuclear complexes in which a Ru-bpy chromopore is bound to an emitting Cr(III) complex [6]. Selective excitation of the Ru-chromophore results in emission from the Cr-luminophore.

Another series of compounds exhibiting intercomponent energy transfer (IET) processes is represented by polychromophoric systems of the type:

$[NC\text{-}Ru(L)_2\text{-}CN\text{-}Ru(L')_2\text{-}CN]^+$, $[NC\text{-}Ru(L)_2\text{-}CN\text{-}Ru(L'')_2\text{-}NC\text{-}Ru(L)_2]^{2+}$ and

$[(L')(CO)_3Re\text{-}CN\text{-}[Ru(L)_2\text{-}CN]_n\text{-}Ru(L)_2\text{-}CN]^{(n+1)}$ (n = 0 - 3)

(L = 2,2'bipyridine, bpy; L'= bpy or 1,10 phenantroline, phen; L"= bpy or 4,4'dicarboxy-2,2'bipyridine, dcbpy) [7]. The spectroscopic, redox and photophysical properties of discrete oligomeric species are reported.

2. RESULTS AND DISCUSSION

2.1. Polynuclear ruthenium polypyridine complexes.

Relevant electrochemical and photophysical properties of a series of polynuclear Ru(II) complexes are reported in table 1. For the purpose of comparisons are also reported the properties of model mononuclear complexes. Abbreviations are related to the following complexes: (2), $Ru(bpy)_2(CN)_2$;
(2'), $Ru(phen)_2(CN)_2$; (2"), $Ru(dcbpy)_2(CN)_2{}^{4-}$;
(2,2), $[NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(bpy)_2\text{-}CN]^+$; (2,2'), $[NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(phen)_2\text{-}CN]^+$;
(2,2,2), $[NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Ru(bpy)_2\text{-}CN]^{2+}$;
(2,2",2), $[NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(dcbpy)_2\text{-}NC\text{-}Ru(bpy)_2\text{-}CN]^{2-}$.

Table 1
Redox and Photophysical Properties of Mononuclear and Polynuclear Ruthenium Complexes.[a]

	$E1/2^{ox}$,[b] V	$E1/2^{red}$,[b] V	$E_{0\text{-}0}$,[c] kK	λ max em. (298 K), kK	τ,[d] (298 K) ns	τ,[c] (77 K) μs
2	0.86	-1.62	17.0	14.5	240	4.0
2'	0.88	-1.62	17.6	14.9	950	12.5
2"	0.72	-1.72		14.2	557	3.5
2,2	0.74	-1.54	15.9	14.0	90	1.6
2,2'	0.75	-1.54	16.1	14.3	400	4.6
2,2,2	0.66	-1.53	14.6	13.6	50	1.3
2,2",2	0.54	-1.61		13.9	133	

[a] Data in CH_3CN unless otherwise noted. [b] vs SCE. [c] C_2H_5OH abs. [d] Deaerated solutions

Inspection of this table reveals regularities which reflect the influence of the redox asymmetry of the bridge. The comparison between the oxidation potentials of mononuclear vs polynuclear species shows that, in all cases, the ease of oxidation of the ruthenium atoms increases in the order NC-Ru-CN, NC-Ru-NC, CN-Ru-NC. As a consequence, in each complex the ^{3}MLCT state localized on the chromophore with the larger number of N-bonded cyanides is the lowest in energy. The fact that this trend is maintained for the 77 K emissions allows to rule out that conformational changes about the bridging cyanide may have a role in determining the red shift of the emission along the series. Worth of attention is also the trend of the lifetimes along the series (2), (2,2), (2,2,2) and the fact that where a different N-bonded chromophore, such as Ru-dcbpy or Ru-phen, is present in the polynuclear species, the emission lifetimes change proportionally to those of the model mononuclear species (see (2,2",2) vs (2"); (2,2') vs (2') and (2,2) vs (2)), a feature that labels the emitting state as belonging to the N-bonded chromophore. Since the corrected excitation spectra of the polychromophoric species matched the UV-Vis absorptions and monoexponential decays of the emission intensity were in all cases observed, it was concluded that efficient energy transfer processes from C- to N-bonded units take place in these molecules.

The ground state electronic spectra of the polynuclear species are due to overlapping contributions of π-π^* and MLCT transitions originating in the different component subunits. The increases in the absorption intensity in the UV-Vis region are in fact nearly proportional to the number of Ru units. The difference in energy between the various chromophores as estimated from electrochemistry (ca. 1000 cm^{-1}) is too small to give appreciable splitting of the lowest MLCT absorption bands of these polynuclear complexes. The order of magnitude of this energy difference is further confirmed by the properties of the two linkage isomeric species:

$[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re\text{-}CN\text{-}Ru(bpy)_2\text{-}CN}]^+$ $[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re\text{-}NC\text{-}Ru(bpy)_2\text{-}CN}]^+$

The absorption spectra of these complexes are dominated, in the visible region, by Ru-bpy MLCT transitions with absorption maxima at 20.74 kK for Re-CN-Ru and 21.74 kK for Re-NC-Ru, in CH_3CN solutions. The emissions of the Re-NC-Ru and of the Re-CN-Ru complexes are red-shifted with respect to $(\mathrm{phen})(\mathrm{CO})_3\mathrm{ReCN}$ (17.12 kK) of 2000 and 2900 cm^{-1} respectively. These emissions are structureless at room temperature and show at 77 K the typical vibrational structure of the Ru-bpy chromophore with a vibrational progression of ca 1300 cm^{-1}. These emissions are independent of excitation wavelength and monoexponential, indicating efficient Re → Ru IET.

Due to the strong electronic coupling character of the bridge, the IET processes are very fast. From the lack of observation of the emission risetimes, in all the investigated polynuclear complexes, k_{IET} is expected to be higher than 10^9 sec^{-1}.

Evidence that the transfer processes can be thought to occur between excited states localized on the different units comes from the analysis of the transient absorbance spectra. Excited state absorption spectra (ESA) were measured in CH_3CN solutions. As an example, the ESA spectrum of the (2,2) complex is compared, in Figure 1, with the ground state spectrum and with the spectrum of the mixed valence (2,3) species.

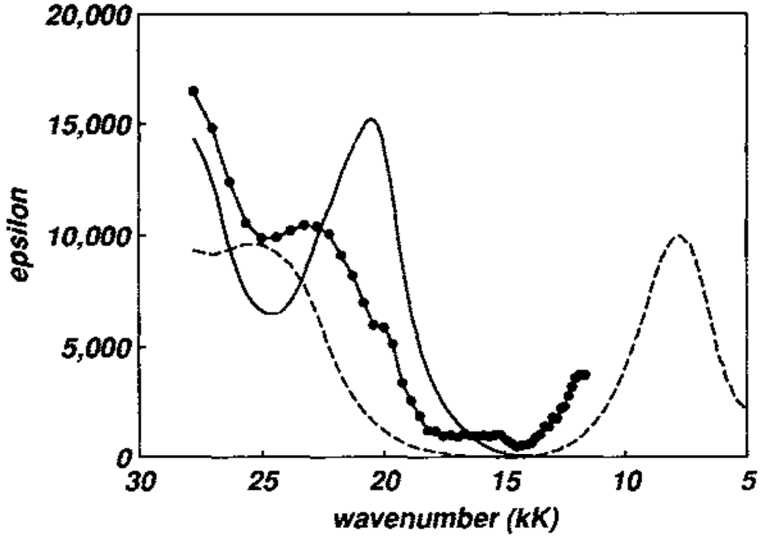


Figure 1. Absorption spectra of (2,2), (—); (2,3) (---); and (2,2*) (—•—) in CH_3CN solution.

The ESA spectrum of the (2,2*) complex, shows features that can be understood on the basis of the electronic transitions exhibited by (2,2) and (2,3). For the mixed valence (2,3) complex, the residual absorption in the visible is assigned to a Ru(II) → bpy MLCT transition on the basis of the electrochemistry and of comparisons with the absorption spectra of a series of related bi- and trinuclear species. LMCT $\pi \rightarrow t_{2g}$ (bpy → Ru(III) [8] or (CN → Ru(III) [9] transitions can also contribute to the total absorption in the same energy region. Such transitions are expected however to be overlapped to the MLCT and of a remarkably lower intensity. Localization of such transitions for the model $[Ru(III)(bpy)_2(CN)_2]^+$ complex is unfortunately not possible due to the high instability of this complex in all the polar and non polar solvents investigated. The band observed for (2,3) in the NIR region is assigned to an IT transition between Ru(II) → Ru(III) centers. The ESA spectrum can be therefore explained by considering a localized model for the excited complex. The visible absorption is mainly attributed to MLCT Ru(II) → bpy and $\pi \rightarrow \pi^*$ bpy$^-$ transitions. The high intensity of the red absorption is attributed to the presence of an IT transition between the Ru(II) and Ru(III)-(bpy$^-$) centers. Energy differences between ground- and excited-state CT transitions are in agreement with the different thermodynamic energy contribution to the optical energies [10].

2.2. Antenna-sensitizer complex.

From the whole of the above considerations, it appears that vectorial IET processes can be driven in homopolynuclear complexes, containing bridging cyanides, through synthetic control of the linkage. This has suggested the design of an antenna-sensitizer polynuclear complex:

$$[NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(H_2dcbpy)_2\text{-}NC\text{-}Ru(bpy)_2\text{-}CN]^{2+}$$

in which the two carboxylic functions of the central unit can bind to the surface of a TiO_2 semiconductor electrode. The photocurrent action spectrum obtained with this complex suggests that the light absorbed by the NC-Ru(bpy)$_2$-CN antenna units is efficiently funneled to the central -Ru(H_2dcbpy)$_2$- unit and used for sensitization of the semiconductor in the 400-600 nm spectral range [11].

2.3. Polynuclear rhenium-ruthenium polypyridine complexes.

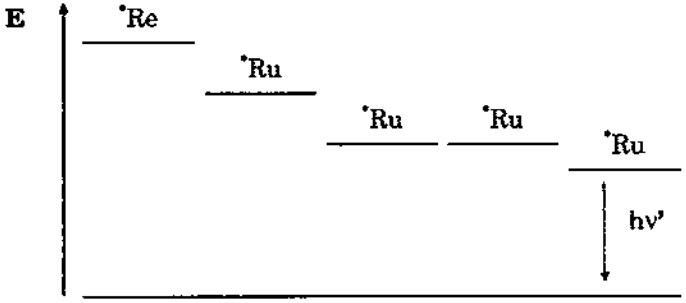
At monolayer coverage of the semiconductor surface with the antenna-sensitizer complex, conversion of light energy into electricity should be improved by increasing the light absorption efficiency of the antenna units. Towards this aim we have prepared and characterized a series of polynuclear complexes of general formula:

$$[(phen)(CO)_3Re\text{-}CN\text{-}[Ru(bpy)_2\text{-}CN]_n\text{-}Ru(bpy)_2\text{-}CN]^{(n+1)} \quad n = 0 - 3$$

Contrary to the binuclear case, in which the driving force for the Re-Ru IET process is rather high, for the more complex oligomeric species the driving force for Ru-Ru IET processes should decrease by increasing the number of bonded ruthenium moieties. The room temperature emission spectra show a red shift of 560 cm^{-1} in going from the binuclear Re-CN-Ru-CN complex to the trinuclear Re-CN-Ru-CN-Ru-CN complex and a smaller shift of 40 cm^{-1} from the trinuclear to the tetranuclear and pentanuclear species. These results are in qualitative agreement with the observed trend of the first oxidation potentials along the series.

By considering that specific solvent interactions are the main responsible of changes in redox and spectroscopic properties of cyanides complexes [12,13] and that solvent sensitivity of these properties is proportional to the number of terminal cyanides [13], emission solvent dependence measurements on the series of Re-Ru oligomers were undertaken. The slopes of the linear plots of ^{3}MLCT energies vs the solvent acceptor number were found to be of comparable magnitude with that of a [Ru(bpy)$_2$(py)CN]$^+$, one half with respect to Ru(bpy)$_2$(CN)$_2$ and twice that of [NC-Ru(bpy)$_2$-CN-Ru(bpy)$_2$-NC-Ru(bpy)$_2$-CN]$^{2+}$ in which the emitting central units is protected by a direct donor-acceptor iteraction with the solvent. This result suggests that the terminal unit is involved in the radiative process.

In the limit of a localized description, there is an energy cascade in the binuclear, trinuclear and tetranuclear complexes. In the pentanuclear species it seems reasonable to assume that one IET step occurs between isoenergetic MLCT excited states, as shown in the scheme.



It is worth to observe that one electron oxidation of these oligomeric species results in complete quenching of the emission, a feature suggesting that intramolecular electron transfer processes may have an important role in the deactivation of the excited mixed-valence complexes.

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