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INTRAMOLECULAR ENERGY TRANSFER IN Ru(II)-Ru(II) and Ru(II)-Cr(III) POLYNUCLEAR COMPLEXES

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SUMMARY

Ligand-bridged polynuclear complexes made up of metal-containing subunits with long-lived excited states are suited for the study of intramolecular electronic energy transfer. Using Ru(II) and Cr(III) complex units as building blocks and cyanide as bridging ligand, a number of Ru(II)-Ru(II), Ru(II)-Cr(III) polynuclear complexes have been synthesized. Efficient intramolecular energy transfer between adjacent metal centers occurs in these systems, as shown by quenching and photosensitization of the appropriate emissions. When the behavior of the polynuclear complex is compared with that of the component subunits, a number of interesting effects are observed including spectral sensitization, antenna effect, luminescence shift, enhanced population of the emitting state, photoprotection, excited-state intervalence transfer, chemiluminescent charge recombination. Possible developments of the results towards the design of photonic molecular devices are discussed.

INTRODUCTION

The photochemistry and photophysics of simple coordination compounds has made substantial progress in the last two decades (ref. 1-3). By now, the fundamental factors governing the excited-state behavior of several classes of coordination compounds are relatively well understood. Particularly for many d^3 and d^6 metal complexes, synthetic control and tuning of important properties such as excited-state energy and lifetime, emission yields, photoreactivity, excited-state redox potentials is now feasible. Following the current "supramolecular" tendency of chemical research, inorganic photochemistry is evolving from the study of simple coordination compounds to that of more complex systems. Particularly interesting from this point of view are molecular systems that contain two or more metal centers connected by bridging ligands. These compounds are

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conveniently called polynuclear complexes.

To obtain a photochemically interesting polynuclear complex, an "assembling" procedure is usually followed, i.e., one starts with mononuclear species having well-defined individual properties (excited-state energies, redox potentials, photophysical parameters) and then makes the appropriate chemical connections between these units (usually by the strategy of "complexes as ligands" or by making chemical bonds between ligands on different metal centers). The first obvious question concerns the extent to which the energetics of the constituent metal-containing fragments is changed in this process. The answer depends on the degree of electronic interaction between the units, which in turn depends on a combination of metal fragment and bridge properties. In the limit of strong interaction, a delocalized description of the polynuclear complex would be needed, leading to energy levels (and to photochemical and photophysical properties) that are mostly unrelated to those of the individual subunits. This limit may be encountered in other polymetallic systems (e.g., clusters with direct metal-metal bonds) but is relatively rare in ligand-bridged polynuclear complexes. For these species the interaction is generally sufficiently small that, although the energy levels of the subunits can be somewhat perturbed by mutual interaction, a localized description is appropriate.* In other words, in most cases the known photophysical and photochemical properties of the individual subunits can still be used as a basis to analyze the behavior of the polynuclear complex.

If the behavior of a polynuclear complex were simply a superposition of those of the subunits, however, there would be little interest in this type of photochemical systems. The interest comes indeed from the fact that, besides (or in competition with) the characteristic processes of the single subunits (intracomponent processes), new processes involving different subunits (intercomponent processes) are possible in a polynuclear complex. The most important intercomponent processes

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*The relationship between the strength of interaction and the degree of localization has been worked out in particular detail in the case of "mixed-valence" polynuclear complexes (ref. 4), where the weak-interaction case of interest to this work is usually labelled as Class II behavior.

are photoinduced electron transfer and electronic energy transfer. In the photochemistry of coordination compounds energy and electron transfer are well known as bimolecular phenomena occurring upon collisional encounters between excited and ground-state reactants in solution. In principle, such processes should occur at least as rapidly and efficiently when, as in a polynuclear complex, the "reactant" units are covalently attached by a bridging ligand. The synthesis of polynuclear systems suitable for the study of intercomponent photoinduced energy or electron transfer processes has been undertaken in recent years in various laboratories (refs. 5-12). In this article, we will briefly summarize and discuss some of our work in this area, with particular regard to the study of intercomponent electronic energy transfer.

The polynuclear complexes described in this article were specifically designed and synthesized. They have the general structures schematically shown in Fig. 1, where A, B, and X are metal-containing subunits bound together by bridging cyanide ligands. Various Ru(II) and Cr(III) complex fragments have been used as A, B, and X (A, B = cis-$Ru(bpy)_2CN^+$, $Ru(bpy)(CN)_3^-$, $Cr(CN)_5^{2-}$, trans-$Cr(cyclam)CN^{2+}$, $Cr(NH_3)_5^{3+}$; X = cis-$Ru(bpy)_2^{2+}$,

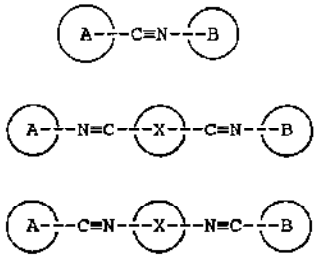


Fig. 1. Schematic structures of the polynuclear complexes investigated, consisting of various metal containing complex units (A, B, and X, see text) connected by bridging cyanide ligands.

cis-$Ru[bpy(COO)_2]_2^{2-}$, trans-$Ru(CN)_4^{2-}$). The results obtained are summarized and briefly discussed in the following sections.

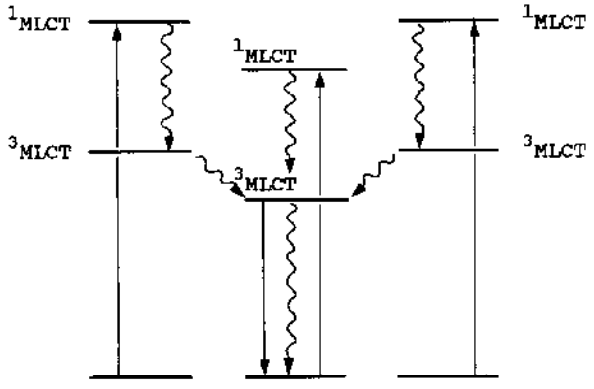
Ru(II) BIPYRIDINE POLYCHROMOPHORIC COMPLEXES.

These complexes (ref. 13) contain two or three cis-$Ru(bpy)_2^{2+}$ units, and cyanides as bridging and terminal ligands:

$$NC\text{-}Ru(bpy)_2\text{-}CN\text{-}Ru(bpy)_2\text{-}CN^{+}$$

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

They can be classified as polychromophoric systems, but the chromophoric units are not all identical, as they differ in the C- or N-bonded nature of the bridging cyanides. This affects to some extent the energies of the metal-to-ligand charge transfer (MLCT) states of the various $Ru(bpy)_2^{2+}$ chromophores, that decrease (by ca. 0.1 μm^{-1} for each step) in the order NC-Ru-CN > CN-Ru-CN > CN-Ru-NC . In these systems, a single emission is observed that can be attributed to the lowest energy chromophore. Although no selective population of the MLCT excited states of the various chromophores is possible in these systems due to overlapping absorption bands, the exact correspondence between excitation and absorption spectra in



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

Fig. 2. Schematic representation of the energy transfer mechanism for the trichromophoric complex. The efficiency of conversion to the emitting state is unitary.

these complexes points towards a very efficient intramolecular energy transfer process from the higher-energy chromophores to the lowest emitting one. The energy transfer process is likely of the triplet-triplet Dexter type (although a coulombic singlet mechanism cannot be ruled out). The photophysical behavior of these polychromophoric species (ref. 13) is schematically represented in Fig. 2, using the trinuclear complex as an example.

A related polychromophoric system that has been recently synthesized and studied (ref. 14) is the trinuclear complex

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

in which the carboxylic groups on the bipyridines of the central chromophoric unit have the effect of further lowering the MLCT energy of this unit relative to that of the terminal ones. This leads to sizeable shifts in MLCT absorption and thus to the possibility to address the individual chromophores with light of different wavelengths. Also in this case, emission from the central chromophore is observed with constant efficiency, independent on chromophore that undergoes light excitation.

The results show that in these polychromophoric systems fast (subnanosecond) intramolecular energy transfer between adjacent $Ru(bpy)_2^{2+}$ chromophores always leads to 100% efficient population of the lowest energy chromophore. It can be noticed that polychromophoric systems of this type exhibit an "antenna effect" similar (though probably different in mechanism) to that by which the antenna pigments increase the effective absorption cross-section of the special pair in natural photosynthetic reaction centers. It is conceivable that artificial antennas similar to the above-discussed ones but of larger size can be constructed by replacing the terminal units with polymeric polychromophoric chains.

Ru(II)-Cr(III) CHROMOPHORE-LUMINOPHORE COMPLEXES

Selective excitation of the energy donor and unambiguous identification of the excited state of the acceptor are ideal requisites to be sought in the design of a polynuclear complex for intramolecular energy transfer studies. In order to meet

these conditions, one should choose as components (i) an energy donor unit (chromophore) with good light-absorbing properties in a spectral region in which the acceptor is transparent and (ii) a transparent energy acceptor unit with very specific light-emitting properties (luminophore). The strong visible absorption makes Ru(II) polypyridine complexes good candidates as chromophoric units. Among possible luminophores, Cr(III) complexes have been selected because of their week visible ligand field absorption and their very characteristic doublet emission.

Using cis-$Ru(bpy)_2^{2+}$ as chromophoric and $Cr(CN)_6^{3-}$ as luminophoric unit, the cyano-bridged trinuclear complex

$$Cr(CN)_5\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5^{4-}$$

has been synthesized (ref. 15). The visible absorption spectrum is dominated by the MLCT bands of the chromophoric unit, the contribution by the luminophoric units in this region being absolutely negligible. In DMF, visible excitation of the complex gives rise to the long-lived sharp phosphorescence typical of the $Cr(CN)_6^{3-}$ ^2E_g state, while the MLCT phosphorescence expected from the -CN-Ru(bpy)-NC- unit (see, e.g. the trinuclear complex of the previous section as a model molecule) is completely quenched. The excitation spectrum of the luminophore-based emission coincides with the chromophore-based absorption spectrum. This is clear indication for the occurrence of an efficient intramolecular chromophore-to-luminophore energy transfer process. The detailed mechanism inferred from quantitative measurents (ref. 15) is shown in Fig. 3, where the behavior of the chromophore-luminophore complex is compared with that (ref. 16) of the isolated luminophore. The key step is an exchange energy transfer process leading from the chromophore triplet ($Ru(T_1)$) to the luminophore doublet state ($Cr(D_0)$). In the isolated luminophore, the doublet state can only be reached (following ultraviolet light absorption) through the excited quartet ($Cr(Q_1)$), resulting in photolability (because of a quartet photosubstitution reaction) and low doublet yield (because of inefficient quartet-->doublet intersystem crossing)

(ref. 16). Because of the direct access to the doublet, on the contrary, the chromophore-luminophore complex has a unitary doublet yield and is photostable.

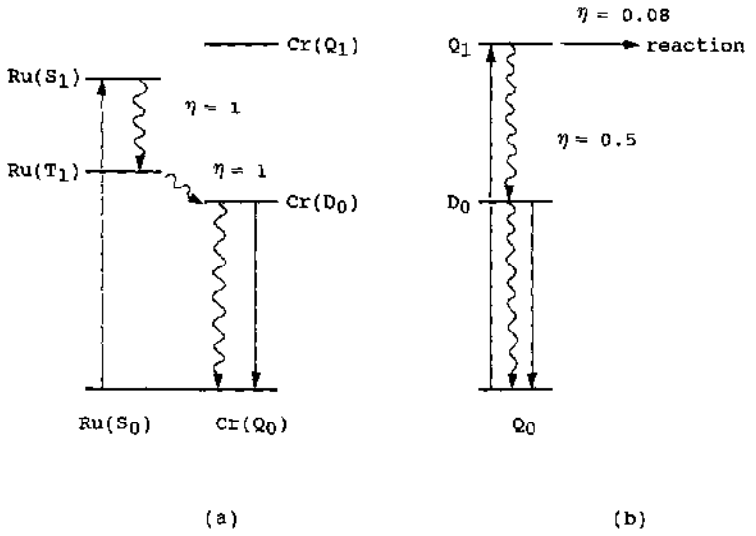


Fig. 3. Photophysical mechanisms for the chromophore-luminophore complex (a) and luminophore (b) in DMF.

The behavior of this complex illustrates some of the ways in which the performance of a luminophore can be improved by covalent coupling to a chromophoric unit: (i) spectral sensitization; (ii) antenna effect; (iii) enhancement of luminescence yields; (iv) photoprotection.

There are other interesting ways in which the chromophore-luminophore complex differs from the bare luminophore (ref. 15). One of these is that the absorption spectrum of the long-lived doublet state of the chromophore luminophore complex (excited-state absorption spectrum, ESA) exhibits a broad visible band that is completely absent in the ESA spectrum of the

luminophore. This corresponds to an "intervalence transfer" (IT) transition in which ruthenium is oxidized and excited chromium is reduced, i.e.,

$$Cr(III)\text{-}Ru(II)\text{-}{}^{*}Cr(III) \xrightarrow{h\nu} Cr(III)\text{-}Ru(III)\text{-}Cr(II)$$

The presence of this IT excited state is probably responsible for the failure to obtain doubly excited species of the *Cr(III)-Ru(II)-*Cr(III) type upon two-photon excitation of the trinuclear complex. The IT excited state is not seen in the ground-state absorption spectrum as it is hidden by the intense MLCT bands of the chromophore.

A trinuclear complex of similar structure has been recently synthesized (ref. 17) using the same chromophore and trans-$Cr(cyclam)(CN)_2^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) as luminophoric unit:

$$NC\text{-}Cr(cyclam)\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(cyclam)\text{-}CN^{2+}$$

The reasons for choosing this luminophore lie in its superior thermal and photochemical stability and in its ability to emit strongly in many solvents including water ($Cr(CN)_6^{3-}$ was limited to DMF as working solvent). Moreover, its trans dicyano structure seems to be ideally suited in view of developments towards more extended polynuclear systems (see later). This complex also exhibits efficient intramolecular chromophore-to-luminophore energy transfer, and its photophysical behavior (ref. 17) is, as a whole, quite similar to that described above for the analogous $Cr(CN)_5\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5^{4-}$.

In principle, an exchange mechanism permits energy transfer from the triplet state of the chromophore to both the doublet and the quartet states of the luminophore. In $Cr(CN)_5\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5^{4-}$, only the doublet pathway was energetically possible because of the large doublet-quartet separation in the luminophore and the relatively low triplet energy of the chromophore, but in other systems of this type competition with a quartet pathway ($Ru(T_1) \rightarrow Cr(Q_1) \rightarrow Cr(D_0)$) cannot be ruled out. To investigate this point, a particular

chromophore-luminophore complex, namely,

$$Ru(bpy)(CN)_3\text{-}CN\text{-}Cr(NH_3)_5^{+}$$

has been recently synthesized (ref. 18). This complex has the built-in property of a tunable chromophore triplet energy, as the three non-bridging cyanides are extremely sensitive to outer-sphere donor-acceptor interactions (refs. 19,20). Thus, the energy gap between the $Ru(T_1)$ state and the $Cr(D_0)$ and $Cr(Q_1)$ states can be easily changed by means of solvent effects or protonation. The results available indicate sensitization of the luminophore phosphorescence by the chromophore under a variety of experimental conditions (solvent composition and acid content). The doublet yield, however, appears to decrease with increasing donor triplet energy, consistent with competition between a low-energy, efficient doublet pathway and a high-energy, inefficient quartet pathway (ref. 18). Aside from the quartet complication, chromophore-luminophore complexes with tunable donor-acceptor energy gap should also be useful to investigate the driving force requirements of the energy transfer step, a point that may be relevant for future extensions of the work (see below). This question could be particularly important when, as in these cases, polar MLCT states are involved and some solvent reorganization should accompany the energy transfer process.

SENSITIZATION OF LUMINOPHORE EMISSION BY AN UNUSUAL MECHANISM

The trinuclear complex

$$NC\text{-}Cr(cyclam)\text{-}CN\text{-}Ru(CN)_4\text{-}NC\text{-}Cr(cyclam)\text{-}CN$$

has been recently synthesized and studied (ref. 21). Experimentally, the complex behaves in many respects like the previously described chromophore-luminophore complexes, but the mechanism underlying this behavior is quite different. The lowest energy feature in the absorption spectrum of the complex is an intense band in the near ultraviolet. Contrary to what happened in the previous complexes, however, the lowest energy band cannot be assigned to the Ru(II)-containing fragment (that absorbs farther in the ultraviolet and is therefore not a true

"chromophore" in this complex). This band actually corresponds to an IT transition of the type

$$Cr(III)\text{-}Ru(II)\text{-}Cr(III) \xrightarrow{h\nu} Cr(III)\text{-}Ru(III)\text{-}Cr(II)$$

Excitation into this band gives rise to very efficient phosphorescence from the $Cr(cyclam)(CN)_2^+$ luminophore. This result does not arise, as in the previous chromophore-luminophore complexes, from energy transfer but rather from a back electron transfer process that leaves the Cr(III) center in the excited doublet state

$$Cr(III)\text{-}Ru(III)\text{-}Cr(II) \longrightarrow Cr(III)\text{-}Ru(II)\text{-}{}^*Cr(III)$$

This process is interesting from several viewpoints. It can be noticed that this process is the intramolecular analog of a chemiluminescent electron transfer reaction. Bimolecular processes of this type have been extensively investigated with several reactant pairs, and a number of Ru(III)/Cr(II) cases, e.g.,

$$Ru(bpy)_3^{3+} + Cr(4,4'\text{-}Me_2bpy)_3^{2+} \longrightarrow Ru(bpy)_3^{2+} + {}^*Cr(4,4'\text{-}Me_2bpy)_3^{3+}$$

have been reported (ref 22). Therefore, the mechanism by which the luminophore emission is sensitized in this complex can be conveniently called "chemiluminescent charge recombination".

Looking at the polynuclear complex as a single (albeit supermolecular) entity, inter-component photophysical processes are simply viewed as processes interconverting different excited states of the supermolecule. In intramolecular energy transfer, a locally excited state is converted into another one. In photoinduced intramolecular electron transfer (ref. 23) a locally excited state is converted into a charge transfer (IT) state. Chemiluminescent charge recombination is the conversion of a charge transfer (IT) state into a locally excited state, i.e, the reverse of photoinduced electron transfer. Its observation fills an empty place in the catalogue of the

possible inter-component processes of polynuclear complexes.

TOWARDS PHOTONIC MOLECULAR DEVICES

There is currently a growing interest in the possibility to extend the macroscopic concept of "device" at the molecular level (refs. 24-27). The idea of "molecular device" stands at the crossroads between molecular biology, where the relationship between molecular structure and function is an all-pervading concept, and microelectronics, where the possibility to start with molecules and go "small upward" is seen as the ultimate alternative to the "large downward" approach of lithographic techniques. A molecular device is an assembly of molecular components (i.e., a supramolecular structure) that, because of the specific arrangement of the components in the dimensions of space and energy, is able to perform a function. Molecular devices capable of performing light-induced functions (i.e., devices powered by light or capable of elaborating light signals) can be called photonic molecular devices (PMD). General requirements, action mechanisms, machinery, and possible applications of PMDs have been discussed (refs.28,29).

In the previous sections we have seen that (i) polynuclear complexes are made of components with individual photochemical and photophysical properties and (ii) the behavior of the polynuclear complex is determined by the spatial arrangement and relative energetics of the components. Polynuclear complexes clearly have some of the distinctive features of PMDs. Whether or not a given polynuclear complex is to be considered a PMD depends, of course, on the extent to which its behavior constitutes a useful light induced function. Some of the polynuclear complexes discussed in this article perform functions that could be interesting in the context of PMDs.

For example, polynuclear complexes featuring efficient antenna effects could serve as energy collecting subunits in various kinds of PMDs for energy conversion. In particular, complexes such as

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

(or more extended versions of it) could be profitably used to overcome the problem of insufficient light absorption in the

sensitization of semiconductor electrodes for wet photovoltaic cells (ref. 30). Polynuclear complexes featuring antenna effect and spectral sensitization may also find applications as luminescent labels or wavelength shifters.

The facile observation of exchange energy transfer in ligand-bridged polynuclear complexes suggests that multi-step energy migration through extended chains or networks of transition metal centers could be feasible, provided that the energy gradient required for each transfer step is small. As a first step in this direction, it has been recently verified (ref. 31) that energy transfer is fast and efficient in the binuclear Cr(III)/Cr(III) complex

$$NC\text{-}Cr(cyclam)\text{-}CN\text{-}Cr(CN)_5^-$$

that emits efficiently from the doublet state localized on the pentacyano unit irrespective of the initially excited unit. When this result is coupled with those described above for

$$NC\text{-}Cr(cyclam)\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(cyclam)\text{-}CN^{2+}$$

the possibility to fuse the two systems and obtain a two-step chromophore-relay-luminophore energy transfer is apparent. The synthetic feasibility of such an extended polynuclear complex is currently under examination.

In a perspective view, polynuclear complexes featuring chemiluminescent charge recombination also look as interesting building blocks for MPDs. In fact, if such systems could be connected by suitable "molecular wires" to electrodes, conversion of electricity into light at a molecular level could be achieved.

These are but a few hints at some of the roles that polynuclear complexes featuring intramolecular photosensitization could play in conceivable PMDs. It should be kept in mind, of course, that the development of practical PMDs is a formidable chemical problem, that will certainly require long times and largely interdisciplinary efforts. However, the basic idea that molecular systems can be engineered so as to perform specific light-induced functions is stimulating, and (as shown, e.g., by recent work on photoinduced charge separation (refs.

32-34)) important information concerning the structure-function relationships can be obtained from the study of relatively simple supramolecular systems. From this viewpoint, polynuclear complexes seem to be interesting versatile systems to work with.

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