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Building photoactive molecular-scale wires

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Contents

Abstract

Polyalkynylene groups are known to function as excellent electronic conductors at the molecular level. Such moieties have now been used to interconnect redox and photoactive transition metal oligopyridine complexes so that the efficiency of light-induced energy or electron transfer along the molecular axis can be monitored. The important issues that control the effectiveness of electronic coupling through the alkyne are discussed. In particular, attention is given to separating the effects of electron delocalization within the triplet manifold from the more general decoupling of metal-centered and charge-transfer excited states that occurs upon lowering the triplet energy. The role of the auxiliary ligands is considered, as is the effect of nuclearity. Similarly, the size of the nuclear reorganization energy has to be taken into account in a proper discussion of the photophysical properties of such systems. A second issue of importance to the design of photoelectronic devices concerns the use of interspersed groups to modulate the electronic coupling properties of the alkyne spacer. Such electron relays may be aryl hydrocarbons or platinum *bis*-acetylides, both groups being able to curtail electron flow along the molecular axis. © 1998 Elsevier Science S.A.

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1. Introduction

The advent of molecular-scale electronic devices requires the ready availability of miniaturized components able to perform useful functions at the supramolecular

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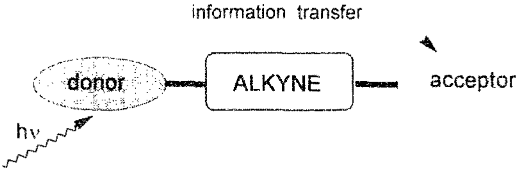
level, presumably after incorporation into a solid-state array. One of the more important needs in this area is to identify convenient ways by which to interconnect redox and/or photoactive subunits so as to promote unidirectional electron or energy flow along the molecular axis. Potential bridging units are subject to many requisites, including such diverse demands as synthetic accessibility, excellent thermal or photostability, and good electronic conductivity. As a starting point to the design of viable systems, specifically engineered towards photoactive devices, we have introduced the concept of using polyalkynylenes to span the gap between preselected transition metal complexes [1–3]. These bridges have to be kept short, so as to avoid complications from their direct participation in the photoprocesses that occur under visible light illumination, ensuring that electronic coupling between subunits will be restricted to short-range communication and [presumably] will be relatively strong [4,5].

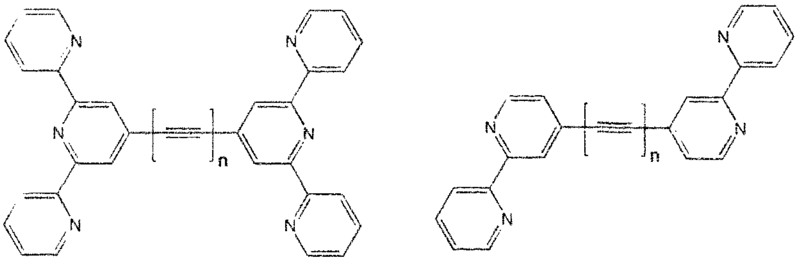


In order to extend the length of the molecular wire and to provide for unidirectionality, it becomes necessary to consider the use of electronic relays as intermediary carriers of information or energy [6,7].

In this regard, the so-called relay could be used as a "real" intermediate in a cascade of electron- or energy-transfer steps along the molecule [8] or simply as a means by which to modulate the rate of through-bond electron transfer [9]. Here, the relay would be expected to modify the energy of LUMOs or HOMOs resident on the bridge [10]. In other cases, the relay might serve as a "circuit breaker" that minimizes electronic communication between the terminal subunits [11].

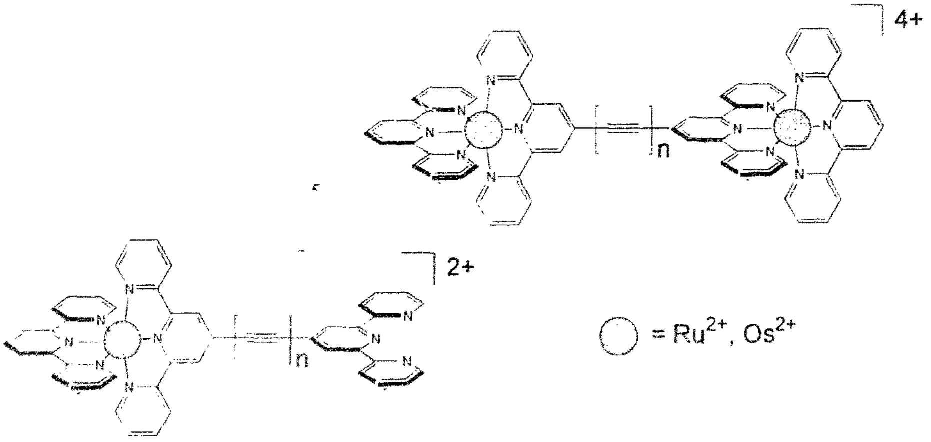
2. Electron delocalization in alkynylene-bridged multinuclear complexes

In order to provide for vectorial transfer of stored information along the molecular axis under external stimulation, it is necessary to provide an appropriate pathway for electronic conduction. This is most easily achieved by coupling together the photoactive subunits via highly-conjugated spacer groups (or conduits) that promote electron transfer without direct participation in the process. After comparing several different types of molecular conduits [12–15], we conclude that polyalkynes provide the best opportunities for constructing large-scale unidirectional networks having addressable terminals [16–18]. Consequently, a detailed synthetic strategy has evolved [1] that permits functionalization of heterocyclic ligands with polyalkynes of predetermined length. This strategy allows coordination of redox-active metals to the vacant ligands in such a way that intricate multicomponent systems can be engineered via a layered procedure.



The effect of incorporating a short polyalkyne substituent at the 4′-position of a ruthenium(II) *bis*-terpyridyl complex is dramatic in that luminescence is readily detected and there is a substantial (e.g. 300-fold) increase in triplet lifetime in deoxygenated solution at ambient temperature [16]. Such behavior is more pronounced for the binuclear metal complexes assembled around alkynylene bridges, where prolongation of the triplet lifetime can approach a factor of ca. 3000-fold. In part, these effects can be attributed to a lowering of the triplet energy without serious disruption to the energy of the metal-centered state, since this will curtail mixing within the triplet manifold [19]. Laser flash photolysis studies have shown that illumination with visible light causes selective charge injection from the ruthenium(II) center to the alkyne-substituted ligand [20]. The promoted electron is extensively delocalized over the ditopic ligand, resulting in a red-shifted luminescence spectrum. Since the electron now samples a larger number of nuclei [21–23], the average nuclear displacement for any given bond is reduced and, within the framework of the "energy-gap law" [24], this causes an increase in triplet lifetime.

We have now demonstrated such effects for a variety of alkynylene- and alkenylene-bridged metal complexes, comprising ruthenium(II), osmium(II) or rhenium(I) centers, of varying nuclearity [19]. The effect is general and readily explained in



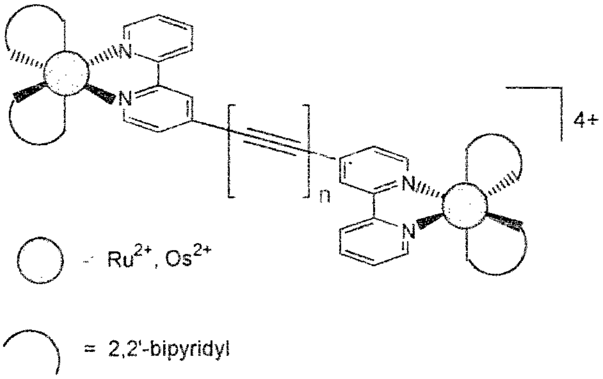
terms of current theories of non-radiative deactivation of excited states [24]. Several important questions remain unanswered, however, and some of these can be expressed as follows.

(1) How important is the effect of electron delocalization when isolated from the [dominant] effect of minimizing interaction with the higher-energy metal-centered state?
(2) What role, if any, is played by the auxiliary ligands?
(3) How symmetrical does the molecule have to be?
(4) What effect, if any, does electron delocalization have on the nuclear reorganization energy?
(5) How can we quantify the extent of electron delocalization?
(6) How can we exploit this effect to construct effective molecular-scale wires?

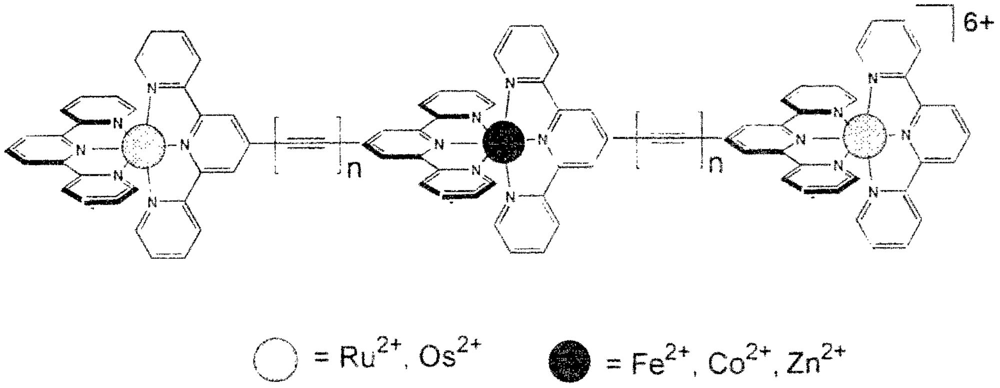
These questions can now be addressed by way of systematic investigation of appropriate binuclear metal complexes.

We have shown that, whereas the built-in facility for electron delocalization within the triplet manifold exerts a tremendous effect on the photophysical properties of ruthenium(II) *bis*-terpyridine, the effect on the corresponding osmium(II) complexes is more modest [16] while the effect on the analogous ruthenium(II) and osmium(II) 2,2′-bipyridine complexes is hardly discernible. Similarly, the photophysical properties of ruthenium(II) *bis*-terpyridine and its alkynylated derivatives become comparable at low temperature. These findings suggest that the principal effect of extended electron delocalization in ruthenium(II) *bis*-terpyridyl complexes is to separate the MLCT and metal-centered states within the triplet manifold. For the 2,2′-bipyridyl complexes, the presence of a highly-conjugated alkynylene bridge prolongs the triplet lifetime by a factor of ca. three-fold in a frozen glass at 77 K [18]. The substituent also lowers the triplet energy, affects the half-wave potential for reduction of the coordinated ligands, and introduces directionality into the triplet state inasmuch as the promoted electron resides exclusively on the substituted ligand.

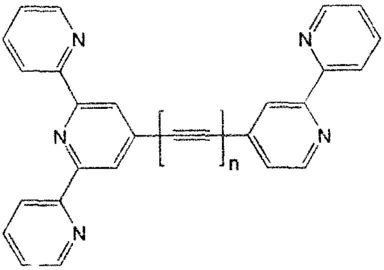
For the 2,2′-bipyridyl-based ruthenium(II) and osmium(II) complexes at low



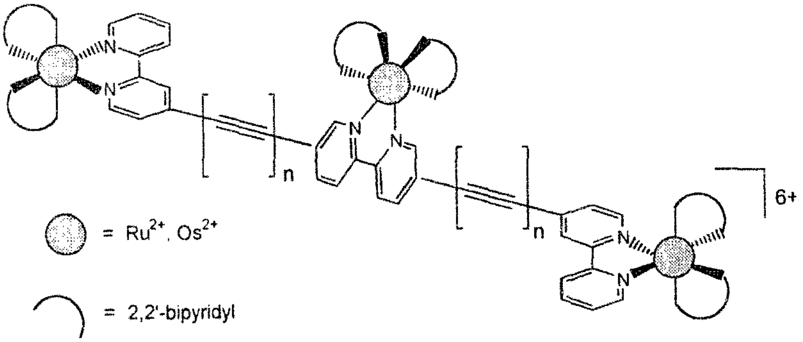
temperature, the actual extent of temporal stabilization of the triplet state against non-radiative deactivation depends on the amount of energy to be dissipated [18]. Contrary to the energy-gap law [24], decreasing the triplet energy results in a prolongation of the triplet lifetime. Since mixing with higher-energy metal-centered or ligand-centered excited states is unlikely under these conditions, we consider that the perturbing excited state is the MLCT triplet associated with the parent 2,2′-bipyridyl ligand. Indeed, changing the energy of the parent MLCT triplet state, by direct substitution of electron-withdrawing groups, has a marked effect on the photophysical properties of the supermolecule. It becomes clear, therefore, that the auxiliary ligands coordinated to the metal center play a significant role in the photophysical properties of these multicomponent complexes.



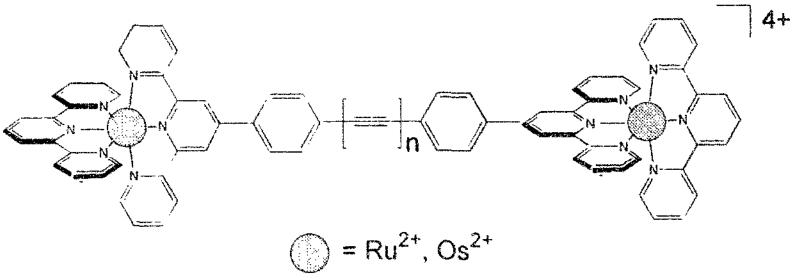
We have observed significant differences in the photophysical properties of mono- and binuclear complexes where the only structural variation concerns the nuclearity [1]. Mixed-metal complexes tend to exhibit photophysical properties somewhere between those of the mono- and binuclear complexes. Such behavior can be interpreted in terms of the extent of electron delocalization within the triplet state being determined, in part, by the internal energy distribution. For mononuclear complexes the vacant ligand at the other end of the alkyne will be at higher energy than the coordinated ligand, such that the promoted electron will not be fully delocalized over the entire ditopic ligand. For a symmetrical binuclear complex it is likely that complete electron delocalization occurs over the ditopic ligand within the triplet state [21–23], as is suggested by electrochemical studies. The degree of electron delocalization in mixed-metal complexes assembled around the same ditopic ligand depends on the difference in energy between the relevant metal complexes. In extreme cases, net energy or electron transfer will occur between the terminal complexes [17,19], but in other cases, where innocent cations like zinc(II) are used, there exists the capability to tune the extent of electron delocalization.



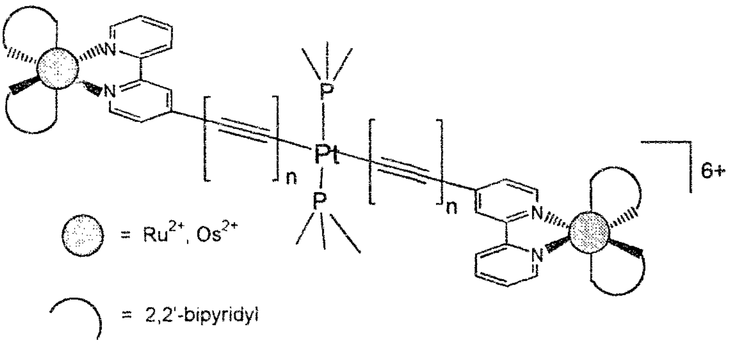
A more refined way in which to vary the spatial distribution of the promoted electron is to use different ligands at either end of the alkyne bridge. In such cases, it becomes possible to arrange for a gradient of electron distribution along the molecular axis by judicious selection of the coordination spheres. We have used this strategy to construct several types of linear trinuclear complexes where the internal energetics differ slightly around the metal centers. A single electron added to the LUMO of such trinuclear complexes is extensively delocalized over the multitopic ligand, but the photon is more localized at the lowest energy site.



Although there is little attenuation of electron (or hole) propagation along polyalkynylene bridges [17], it is possible to interrupt electron flow by incorporating adventitious groups into the chain. Thus, adding a phenyl ring between polypyridine ligand and polyalkyne spacer causes a dramatic reduction in the extent of electron delocalization [25].

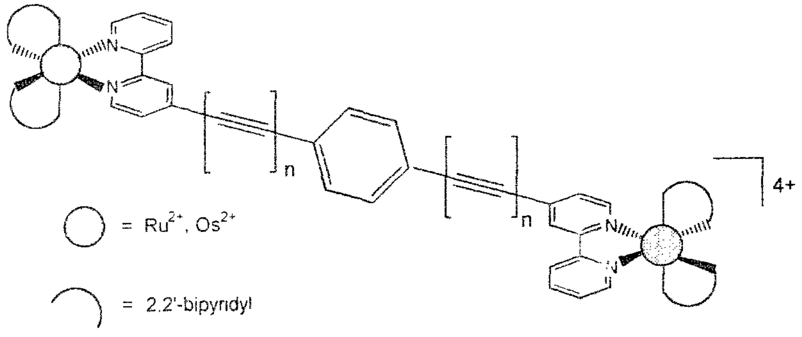


In such cases, the promoted electron seems not to reach the alkyne but to remain distributed over the coordinated ligand. Similarly, placing a platinium *bis*-phosphine in the polyalkyne bridge [20] causes localization of the electron at the unsubstituted parent ligands.



The behavior is more complicated when an aryl hydrocarbon is built into the polyalkyne spacer, as opposed to its being the first component in the bridge, and the photophysical properties of the terminal metal complexes depend markedly on the nature of the hydrocarbon [1].

A major factor of interest with respect to these alkynylene-bridged metal complexes concerns the magnitude of the reorganization energy accompanying electron delocalization. The total reorganization energy increases with increasing extent of electron delocalization but, because there are more skeletal modes to accommodate the structural change, there is a decrease in the distortion of individual vibrational modes [24].



An important and inherent aspect of these multinuclear metal complexes concerns the specific charge injection into the functionalized ligand that occurs under visible-light illumination. This provides the impetus for vectorial information flow along the molecular axis and, in many cases, accounts for the rapid rates of intramolecular energy and electron transfer. We have also found that the highly-conjugated multinuclear metal complexes are relatively poor sensitizers for the generation of singlet molecular oxygen when illuminated in aerated solution. This provides for self-protection of the system against oxidative damage and could be an important property of photoactive molecular-scale devices.

Acknowledgements

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