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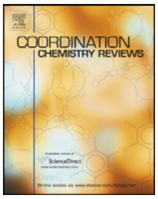

Review

Long-range electron transfer in artificial systems with d^6 and d^8 metal photosensitizers

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Contents

1. Introduction 1440
2. d^6 metal systems 1442
    2.1. Ruthenium(II) polypyridines 1442
        2.1.1. Swedish dyads and triads 1442
        2.1.2. Reductive excited-state quenching with tetrathiafulvalene donors 1443
        2.1.3. Systems with long helicoidal and rigid rod-like bridges 1444
        2.1.4. Supramolecular systems involving charge transfer across noncovalent bonds 1444
        2.1.5. Intervalence long-range electron transfer in ruthenium dimers 1445
    2.2. Rhenium(I) tricarbonyl diimines 1446
        2.2.1. Studies using transient infrared spectroscopy 1446
        2.2.2. Towards electron transfer-triggered cation release from an azacrown 1447
        2.2.3. Supramolecular dyads formed by hydrogen bonding or hydrophobic interactions 1447
        2.2.4. Distance-dependence studies of charge tunneling 1448
    2.3. Osmium(II) polypyridines 1449
        2.3.1. French-Italian bis-tolylterpyridine systems 1449
        2.3.2. Conformational switching between long-range charge and energy transfer 1449
        2.3.3. Interligand electron transfer 1450
    2.4. Iridium(III) 1450
        2.4.1. Iridium bis(terpyridine)–porphyrin systems 1450
        2.4.2. Iridium bis(terpyridine)-non-porphyrin systems 1451
        2.4.3. Cyclometalated iridium(III) 1452
3. d^8 metal systems 1452
    3.1. Iridium(I) dimers 1452
    3.2. Platinum(II) acetylides 1453
        3.2.1. The Rochester work 1453
        3.2.2. A platinum(II) acetylide–porphyrin dyad 1455
4. Summary 1455
    Acknowledgments 1456
    References 1456

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ABSTRACT

This review article summarizes the research progress made since the year 2000 in the field of long-range electron transfer with synthetic systems that use d^6 or d^8 metal complexes as photosensitizers. This includes charge transfer over distances greater than 10 Å in both covalent and noncovalent donor–bridge–acceptor systems. Metal complexes of Ru(II), Os(II), Re(I), Ir(III), Ir(I), and Pt(II) are considered.

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1. Introduction

Long-range electron transfer plays a key role in chemistry and biology. Two particularly important processes that involve charge transfer over long distances are photosynthesis and respiration [1–3]. This has stimulated much research on both biological and artificial long-range electron transfer systems [4–15]. After all, it is unusual for chemical reactions to occur between two reactants that are separated spatially by 10 Å or more. A common approach to experimental investigations in this field has been to study redox reactions that can be triggered by light, whereby the progress of a long-range electron transfer can often be resolved temporally. Such kinetic information is of particular interest for the construction of artificial systems that emulate natural photosynthesis since to an important extent, solar energy conversion is a matter of speeding-up desired energy-storing (long-range) electron transfer and slowing-down undesired energy-wasting reactions [16]. The experimental approach of photoinducing the electron transfer between distant redox partners has been applied to both biological and synthetic systems. For instance, redox-active proteins have been equipped with transition metal complexes that serve as phototriggers for long-range electron transfer involving the protein active sites [17]. On the other hand, purely artificial donor–bridge–acceptor systems have been investigated in large numbers, for example porphyrin–quinone molecules that seek a close chemical analogy to the redox partners involved in the primary light-induced reactions of photosynthesis [18,19]. Many other systems considered functional mimics of the photosynthetic reaction center are based on transition metal complexes whereby d^6 and d^8 metal diimines play a prominent role [20]. It is on recent progress in this particular sub-area of the long-range electron transfer field that this review article will focus. More precisely this includes studies on artificial systems that make use of d^6 or d^8 metal complexes for investigation of light-triggered electron transfer proceeding over distances of at least 10 Å. Work published since the year 2000 will be reviewed. In a sense, the current article could therefore be considered an update of previously published reviews, either on long-range electron transfer in general [18,20–25], or on charge transfer over long distances involving metal complexes of ruthenium(II) [26–34], rhenium(I) [14], osmium(II) [26,30], iridium(III) [28,35], iridium(I) [36], and platinum(II) [37]. Indeed, these are the most popular inorganic sensitizers. We begin with a short introductory tutorial on basic concepts used in this review. It is kept brief intentionally since there exist already several excellent publications that give detailed surveys of fundamental aspects of photoinduced electron transfer [18,20,21,38,39].

All d^6 metal photosensitizers considered in this review are hexacoordinate, and the metal ions are practically in octahedral microsymmetry. In strict O_h symmetry, the set of five d-orbitals that are degenerate in the free metal ion splits into three essentially nonbonding degenerate t_{2g} orbitals and two degenerate antibonding orbitals with e_g symmetry (Fig. 1). These three- and two-fold degeneracies are further lifted by deviations from O_h to lower point symmetries, but this effect is neglected here for simplicity. The energetic splitting between the t_{2g}- and the e_g-orbital sets is essentially a function of both the chemical nature of the metal and its ligands. The polypyridine ligands relevant to this review exert fairly strong ligand fields. As far as the metal is concerned, the 4d and 5d electrons of second- and third-row metals have a larger spatial distribution than the 3d electrons of first-row metals. These two facts lead to a situation for octahedral $4d^6$ and $5d^6$ polypyridine complexes in which the HOMO corresponds to the metal-localized t_{2g}-orbitals, and the LUMO is an antibonding π^*-orbital that is localized on a polypyridine ligand; the ligand field is sufficiently strong for the e_g metal orbitals to lie energetically above the ligand π^* orbitals. This particular electronic structure forms the basis for the unique photoredox properties of this class of compounds: upon photoexcitation with visible light, an electron is promoted from the t_{2g} to the π^* orbital, resulting in a metal-to-ligand charge transfer (MLCT) state (Fig. 1, right) that is long-lived (>100 ns) in many cases. During this excited-state lifetime, the redox potentials of the complex are dramatically altered: the metal complexes become both better oxidants and reductants than in their electronic ground states (their reduction can now occur by hosting the additional electron in a t_{2g}-orbital instead of a higher-energy π^* orbital; conversely their oxidation occurs by removal of the excited π^* electron which is more readily abstracted than a t_{2g} electron in the ground state). The excited-state oxidation and reduction potentials are generally estimated by subtracting and adding, respectively, the energy of the electronic origin of the emissive ^{3}MLCT state (E_{00}) from the ground-state potentials:

$$E(M^+/{}^*M) = E(M^+/M) - E_{00} \quad (1)$$

$$E({}^*M/M^-) = E(M/M^-) + E_{00} \quad (2)$$

Based on these photoinduced redox potential changes, electron transfer can be phototriggered: reactions that are thermodynamically uphill from the ground state become exergonic upon light excitation. This is the principle of photosensitizing in the vast majority of systems considered in this review. Depending on the exact values of ground-state potentials and MLCT energies, a specific d^6 polypyridine photosensitizer may either be used preferably as an excited-state reductant or oxidant. The Re(I) and most of the Ir(III) systems mentioned in this review behave as excited-state acceptors, whereas the Os(II) complexes are donors. Ru(II) sensitizers can be both.

The energy level diagram in Fig. 2 illustrates the photoinduced processes that may occur upon excitation of a photoreductant, i.e., an excited-state donor: from the MLCT-excited state, a so-called charge-separated state with an oxidized donor and a reduced acceptor is thermodynamically accessible via an electron transfer process that is referred to as photoinduced charge-separation.