



Review

Transition metal functionalized photo- and redox-switchable diarylethene based molecular switches



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ABSTRACT

In this review recent progress in combining metal carbonyl and bipyridyl transition metal complexes with dithienylethene photochromic switches is discussed. A key challenge in designing such systems is to allow for interaction between the various components, but without loss in photochemical activity, *i.e.* the cyclization/cycloreversion of the dithienylethene unit. Examples of where the properties of the switching unit can be fine-tuned either photochemically or electrochemically by the addition of either bipyridyl transition metals or organometallic moieties to the switch will be highlighted.

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1. Introduction

Photochromic molecular switches have continued to attract substantial scientific interest for over a century [1] for a wide range of applications from materials science to biological applications [2]. The number of distinct classes of photoswitches is

surprisingly limited, in large part due to relatively stringent demands that reversible photochemistry demands – *i.e.* reversible changes between distinct structures upon irradiation with light and sufficiently distinct absorption spectra and photochemical quantum yields to enable as complete as possible the switching between each state. Although the core structural motif of a photochromic switch must be conserved, there is extensive scope with regard to fine tuning the switches properties through variation in the substituents around the core (Fig. 1).

Attaching transition metal containing fragments to photochromic molecular switches opens the possibility of perturbing

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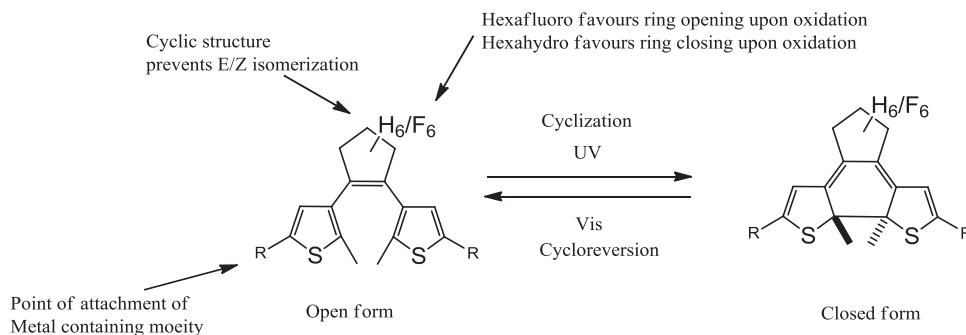


Fig. 1. Open and closed form of dithienylcyclopentene based photochromic molecular switches.

the excited-state properties of both components and generating new reactivity and photochemical properties, *e.g.*, photochemical on/off switching of luminescence in a stilbene-Re(I) dyad [3]. Since most of the photochromic molecular switches known undergo isomerization *via* singlet excited states within several picoseconds [4], perhaps the most basic effect that can be expected is that the presence of a heavy atom facilitates intersystem crossing and accesses triplet excited states and thereby distinct photostationary states [5], excited state lifetimes, emission and photochemical quantum efficiencies, as well as enabling electron and energy transfer to take place [6].

Diarylethenes, and in particular the dithienyl ethenes, have seen widespread application due to their excellent thermal stability in both the colorless open and colored closed forms [7] and, in certain cases, the ability to switch between states by oxidation or reduction [8]. Combining diaryl ethenes with transition metal complexes opens up the possibility therefore of both additional photochemical and electrochemical properties. The large differences in color between the open and closed forms are a manifestation of the changes in the extent of the π -conjugated system. Hence, using a dithienyl ethene photochromic switch as a bridging unit between two metal complexes can allow for the interaction between the metal centers to be changed between two states, *e.g.*, an “On” and an “Off” state, reversibly using light as a stimulus [9]. Such functionality would open up possibilities for molecular light responsive elements in electronic devices, *e.g.*, as wires, switches, diodes, transistors, and light-absorbing/emitting centers. The advantage of using metal centers in such applications is the ability to tune the energy levels, excited state lifetimes and the redox properties of the system by changing the metal used.

In this review, the various approaches taken in combining metal containing units with dithienyl ethenes and the effects such combinations have on both the dithienyl ethenes, photochromic and electrochemical properties will be discussed.

2. Photochromism of metal containing dithienyl ethene compounds

2.1. Dithienyl cyclopentene bipyridyl metal complexes

De Cola and coworkers [10–12] have reported the synthesis and characterization of a series of dithienyl ethenes connected covalently to Ru(II) and Os(II) polypyridyl complexes *via* a phenyl linker (Fig. 2). Irradiation of the Ru(II) complex **1** with UV light resulted in excitation of a singlet state (1IL) that was localized on the dithienyl perfluorocyclopentene unit and lead to cyclization of the dithienyl ethene unit, manifested in a change in color from yellow to green and the appearance of an absorption at 614 nm. Irradiation at 458 nm, and hence excitation of a singlet metal-to-ligand charge transfer (1MLCT) state localized on the Ru(II)(bpy)₃ moiety, did not result in population of the higher energy 1IL state. Instead intersystem crossing to the triplet MLCT state (3MLCT) occurs followed by energy transfer to a triplet state (3IL) and cyclisation (Scheme 1). The quantum yield for cyclisation *via* the 3IL state decreased significantly in the presence of dioxygen, in contrast to direct population of the 1IL state of the dithienyl ethene unit, which is insensitive to dioxygen. As the 3MLCT and 3IL states are close in energy, an equilibrium exists, thereby resulting in a competition between the emissive and reactive processes. Therefore, cyclisation from the triplet state takes a few nanoseconds, in contrast to the reaction from the 1IL state which proceeds on the picosecond timescale. Cycloreversion occurred upon irradiation with red light (600–750 nm), *i.e.* at longer wavelength than the 3MLCT absorption bands of the Ru(II) polypyridyl units.

Upon excitation into the 1IL and 1MLCT states of the open form of the Ru(II) complex, efficient energy transfer occurred to the 3MLCT state manifested in emission at 619 nm, albeit with a much lower emission quantum yield than for [Ru(bpy)₃]²⁺. The

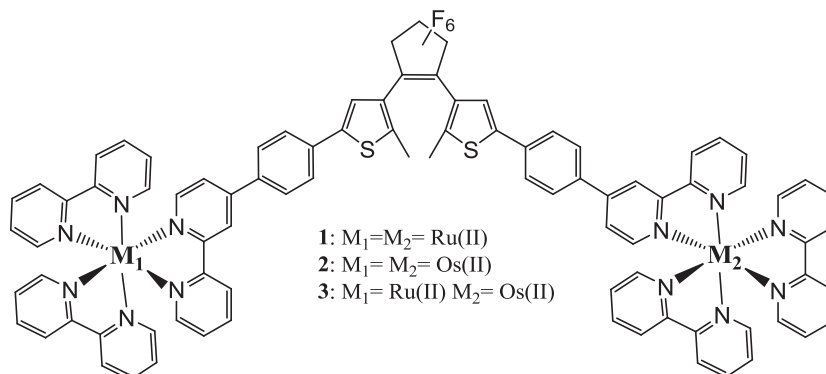


Fig. 2. Metallated tris(bipyridine) substituents attached to a 1,2-bis(2-methylthiophene)-perfluorocyclopentene unit *via* a phenyl linker. The metal centers were substituted with bis-ruthenium (**1**), bis-osmium (**2**), and ruthenium and osmium (**3**) [10–12].

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