Research paper

Solvent-control of photoinduced electron transfer via hydrogen bonding in a molecular triad made of a dinuclear chromophore subunit

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ABSTRACT

We have prepared a molecular triad containing a triphenylamine as the electron donor D subunit, an anthraquinone derivative as the acceptor A group, and a dinuclear Ru(II) species (P-P) based on terpyridine-like ligands as light-harvesting subunit, so that a linearly arranged D-(P-P)-A molecular triad is obtained. In acetonitrile solution containing 1% (in volume) of methanol, photoinduced oxidative electron transfer occurs in 380 ps, with formation of the D-(P-P)$^{+}$-A^{-} charge-separated (CS) state. However, although formation of the fully-developed D^{+}-(P-P)-A^{-} state is favored by about 0.23 eV, such species is not formed since charge recombination within D-(P-P)$^{+}$-A^{-} appears to be faster.

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1. Introduction

In search of long-lived charge-separated state obtained by photoinduced electron transfer processes, the role of spacers, driving force, and electron transfer pathways have been extensively investigated [1–8]. Among various molecular assemblies, the so-called molecular triads have been explored. Such molecular triads can be made of a chromophoric subunit (P) to which an electron acceptor (A) and an electron donor (D) are linked, so producing a D-P-A (supra)molecular system, with the final aim to obtain a long-lived D^{+}-P-A^{-} species by a series of electron transfer steps from the initially formed D-*P-A excited state [9–16]. Species based on {M(terpy)$_2$}$^{n+}$ chromophoric unit (M = Ru(II), Ir(III); terpy = 2,2′:6′,2″-terpyridine) have been used, because they allow to have well-separated donor and acceptor units, by taking advantage of substitution on the 4′ position of the terpy ligands [9,16], which guarantees for a larger donor-acceptor separation.

Recently, focus has been directed to proton-coupled electron transfer processes, particularly for their importance in photosynthesis [17–25]. In particular, Wenger and coworkers have quite recently explored the photoinduced electron transfer processes of

molecular triads based on {Ru(bpy)$_3$}$^{2+}$-type chromophores and tri-arylamine donors and anthraquinone electron acceptors [26–29]. In some cases, also molecular pentads have been investigated, containing more than a single metal-based chromophore [27,28].

However, the presence of two metal-based chromophores interposed between the electron donor and acceptor subunits have never been explored. In principle this molecular arrangement, D-P-P-A, would allow to further separate the positive and negative charges, particularly when linear geometry is maintained by the use of terpyridine ligands, so increasing the lifetime of the charge-separated state. Here, we report the synthesis of such a system (**1**, whose structural formula is shown in Fig. 1; please note that **1** could be considered a molecular tetrad; however, when the two dinuclear chromophores are considered as a single unit, we can refer to it as a triad) and the study of its absorption spectrum, photophysical properties - including photoinduced electron transfer processes studied by pump-probe transient absorption spectroscopy - and redox behavior. The absorption spectra, photophysical properties and redox behavior of model species are also reported. The model species, whose structural formulae are also shown in Fig. 1, are (i) the dinuclear chromophore **Ru2**, composed by two Ru(II)-(terpy)$_2$ units connected together by a phenyl ring; (ii) the electron donor-containing complex **D-Ru-terpy**, based on a Ru(II)-(terpy)$_2$ subunit with a triphenylamine fragment linked to a terpyridine; and (iii) the electron acceptor-containing complex
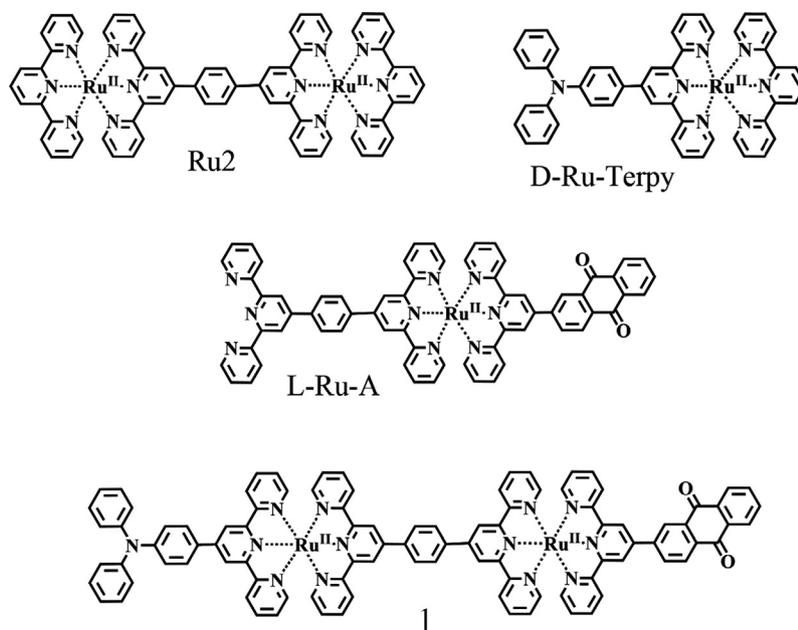
Fig. 1. Structural formulae of **1** and its model species.

L-Ru-A, containing one Ru(II) chromophore coordinated by a terpyridine bearing an anthraquinone unit.

2. Results and discussion

2.1. Synthetic strategy

The D and A ligands, that is the terpyridine ligands carrying the donor and the acceptor subunits, 4-[4-(N,N-diphenylamino)phenyl]-2,2:6,2-terpyridine and 4′-[9,10-Dioxo-9,10-dihydroanthracen-2-yl]-2,2′:6′,2″-terpyridine, respectively, have been prepared by using modified procedures with respect to reported ones [30–32], details are given in the supplementary information. The synthetic approach adopted to prepare the triad and the model species is reported in Scheme 1 and the details of the synthesis are also reported as supplementary information.

The preparation of the new species have been made by using the 'complexes as ligands and complexes as metals' synthetic strategy [33,34], that is an example of modular synthetic chemistry, and is based on the use of complexes instead of metal ions and free ligands. In this strategy, metal complexes containing ligands that can be easily substituted, so that they are precursors of species with unsaturated metal coordination sites, are named 'complex metals', and metal complexes containing ligands with free chelating sites are named 'complex ligands'.

The first step of the synthesis is the preparation of the precursor complex metals. The two terpyridine ligands bearing the donor or the acceptor unit were reacted with $RuCl_3 \cdot 3H_2O$, to form the corresponding complexes **A-RuCl₃** and **D-RuCl₃**. The **A-RuCl₃** species was used as 'complex metal' to prepare the **L-Ru-A** species (see scheme 1). The "complex ligand" so obtained was used to synthesize **1**, by reaction with the "complex metal" **D-RuCl₃**.

All the new species, except the metal complexes trichlorides, have been isolated and studied as PF_6^- salts.

2.2. Redox properties

All the investigated species show several processes in the investigated redox potentials window (see Table 1). Compound **1** shows two reversible anodic oxidation waves at +1.06 and +1.29 V vs SCE

(Fig. 2). The oxidation process occurring at less positive potential, by comparison with the data registered for the mononuclear **D-Ru-tpy** and **Ru2** species, is attributed to the oxidation of the triarylamine moiety (see also redox data in Refs. [9,27,28]). The oxidation process occurring at more positive potential is at a potential similar to that registered for **Ru2** species. The oxidation process of **Ru2** involves two electrons, and can straightforwardly be attributed to the simultaneous one-electron oxidation of the two metal centers. The analogous process of **1** also involves two electrons, by comparison with first oxidation process (see cyclic voltammetry in Fig. 2), so the attribution is identical to that of **Ru2**. This suggests that, both in **Ru2** and **1**, the interaction between the two metal units is negligible at the ground state from a redox point of view. The second oxidation of **D-Ru-terpy** is straightforwardly assigned to metal oxidation.

On reduction, it can be noted the first reduction of **L-Ru-A** and **1** occurs for both species at −0.68 V vs SCE, a much less negative potential than for the other species, including **Ru2**. This suggests that for both **L-Ru-A** and **1** the first reduction can be assigned to the anthraquinone subunit. At more negative potentials, **1** exhibits another reduction process, that is assigned to reduction of the bridging ligand. These results are in fair agreement with the redox data of the model species **Ru2** (Table 1). Indeed, the reduction behavior of **Ru2** (bielectronic in nature) warrants some comments: in this species, the bridging ligand and the two peripheral ligands are not expected to be reduced at quite different potentials [35], so three roughly equivalent reduction-active sites (or even four, when the bridge is considered to be made by two weakly-interacting terpy moieties) are present. Most likely, the first electron is added to the bridging ligand, and at a very close potential a second electron could be added to a peripheral terpy ligand. So, the bielectronic process of **Ru2** can be assigned to almost simultaneous one-electron reduction of the bridge and of one peripheral ligand. However, the second electron addition could have the effect of shifting the first added electron from the bridge to the other peripheral ligand, to minimize electron interaction. The final result would be that at a specific potential two electrons are added to **Ru2**, with electrons localized on the two peripheral ligands. It is not possible to distinguish between these two cases, although examples of electron shifting between orbitals upon successive