Primary charge separation in photoinduced multielectron storage systems. A dinuclear ruthenium(II) species featuring a charge-separated state with a lifetime of 1.3 μs†

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The primary photoinduced charge separation and recombination processes occurring in a dinuclear Ru(II) complex capable to perform multielectron storage upon light excitation have been studied in different solvents: the charge-separated state obtained in dichloromethane is, to the best of our knowledge, the longest-lived ever reported for a ruthenium polypyridine complex.

Multielectron transfer photocatalysts are expected to be essential components for the design of efficient artificial photosynthetic systems.[1] The various redox processes which have to be involved in the photoinduced production of high-energy content chemical species (including water splitting to generate hydrogen or reduction of carbon dioxide to more convenient carbon-containing species) are indeed multielectron processes.[2] Compared with the large efforts devoted to the design of artificial antenna systems and charge separation molecular devices,[3] the search for multielectron transfer photocatalysts,[4,5] is still in its infancy.

Quite recently, two dinuclear Ru(II) complexes capable of reversibly storing two or four electrons (and protons) per molecule upon visible light irradiation in deoxygenated acetonitrile and in the presence of sacrificial reductant agents, have been reported.[5] One such system (**P**) is shown in Scheme 1. In this species, it has been proposed that the central part of the bridging ligand plays at the same time the role of the electron acceptor subunit for the photoinduced charge-separation process and of the electron storage element.[5] However, the mechanistic aspects of the processes were not investigated in detail. We report here the first results obtained in the characterization by fast and ultrafast spectroscopy of the charge separation and recombination processes in **P**.

The absorption spectrum of **P** (see ESI†) is typical of Ru(II) polypyridine complexes: it is dominated by intense ligand-centered bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region.
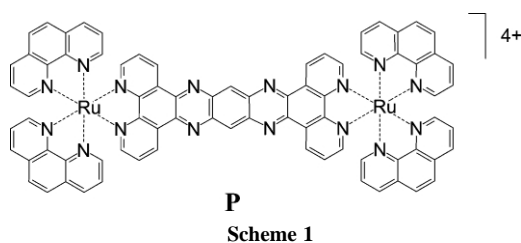
As for other similar Ru(II) complexes with extended aromatic bridging ligands containing N-heterocycles,[6,7] the main visible absorption band is due to spin-allowed MLCT transitions in which the electron is promoted to the peripheral ligands and/or to the bpy part of the bridge (from hereafter called bpy′), while a MLCT band to the central part of the bridge, which is the subunit easier to be reduced of the whole molecule, does not have appreciable intensity.[7,8] Reasons for such behaviour have been extensively discussed,[5–7] and reside in a weak coupling between the metal center and the central subunit (benzene-pyrazine-benzene-pyrazine-benzene, bz-pz-bz-pz-bz) of the bridge. Therefore, it is reasonable to assume that the excited state initially formed after excitation[9] is a triplet Ru → bpy′ CT. In the absence of intercomponent processes, such a state is expected to exhibit the characteristic MLCT emission and deactivate in about 1 μs to the ground state, analogously to [Ru(bpy)$_3$]$^{2+}$. In fact, **P** is non-luminescent in both fluid solution and 77 K rigid glasses[7] indicating efficient intramolecular quenching of the MLCT state.

Ultrafast absorption spectroscopy in acetonitrile (Fig. 1) clearly indicates that the initially formed excited state evolves in a very short time scale (apparently bi-exponential, with lifetimes of 1 and 35 ps) with the formation of an intense transient absorption with maximum at 590 nm. By analogy to what happens in related binuclear complexes of the [(bpy)$_2$M(tpphz)M(bpy)$_2$]$^{4+}$ type (M = Ru, Os),[10] this transient can be assigned to a species where the promoted electron is localized in the phenazine-like central part of the bridge.[11] In other words, in **P** charge separation (cs) takes place by electron transfer from the bpy′-centered orbital to an orbital located in the central part of the bridge (Scheme 2), in picosecond timescale. This charge-separated state starts to decay in the time scale of the experiment (Fig. 1, inset). The apparent lifetime for charge recombination (cr) is 4.8 ns. Indeed, no appreciable
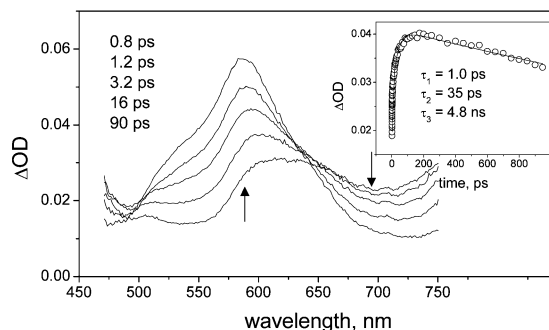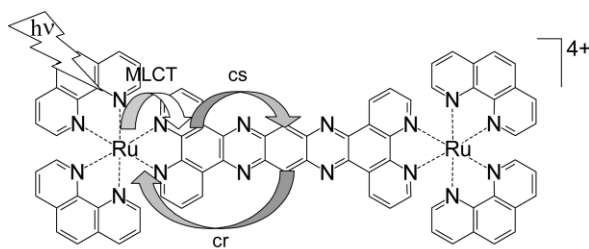

P

Scheme 1

† Electronic supplementary information (ESI) available: absorption spectrum of **P** in acetonitrile solution. See http://www.rsc.org/suppdata/cc/b3/b302962j/

Fig. 1 Transient absorption spectra and (inset) decay of **P** in acetonitrile.

Scheme 2

transient can be observed in acetonitrile by nanosecond laser photolysis (time resolution > 10 ns).

Interestingly, the behavior is strongly solvent-dependent. In DCM, the ultrafast behavior is similar to that observed in acetonitrile (fast formation of the transient with maximum at 590 nm, with $\tau_1 = 1$ ps and $\tau_2 = 20$ ps). The transient then stays constant, however, over the entire time scale of the experiment ($t < 1$ ns). Indeed, in DCM the transient is easily observed in nanosecond laser photolysis (Fig. 2). In this experiment, the charge-separated state is seen to decay to the ground with a (mono-exponential) lifetime of 1.3 μs (Fig. 2, inset).
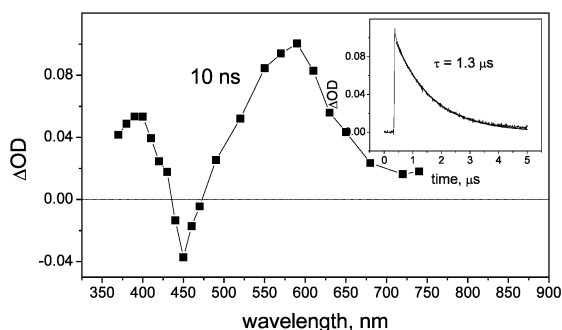

Fig. 2 Transient absorption spectrum and (inset) decay of **P** in DCM solution.

Thus, in DCM, the rate constant of charge recombination is 7.7×10^5 s^{-1}. To the best of our knowledge, this value is the slowest back electron transfer ever reported for a charge-separated state involving a Ru(II) chromophore. The reasons for such a result probably lie in a favorable combination of the electronic and nuclear factors that control electron transfer rates.[12] Certainly an important role is played by the very weak coupling of the involved orbitals, as suggested by ground state absorption spectra and also supported by theoretical calculations.[5,7] In terms of nuclear factors, on the other hand, charge recombination can be slow if it lies in the Marcus inverted region. To this purpose, given the relatively low energy of the charge-separated state (≤ 1.54 eV from electrochemistry),[7] a solvent of low-dielectric constant is required (so as to have a small outer-sphere contribution to the reorganizational energy). This explains why long-lived charge separation is obtained in DCM, whereas a 500-fold reduction in lifetime is observed in acetonitrile.[13]

In conclusion, the primary photoinduced processes operating in **P**, a species which is able to feature photoinduced multielectron storage — a key requisite for efficient artificial photosynthesis — have been investigated. Interestingly, the charge-separated (CS) state obtained exhibits in DCM the longest lifetime ever reported for a multicomponent system based on Ru(II) chromophores. In the sacrificial photochemical cycle that leads to multiple storage of electrons within the central bridge moiety,[5] two main scavenging processes are believed to occur on the charge-separated state: (i) competitive

reduction of the Ru(III) center by sacrificial agents, which restores the chromophore for successive photoinduced electron transfer; (ii) proton addition to the central subunit of the bridge, which stabilizes the reduced species. The direct observation of the charge-separated state and the study of the factors governing its lifetime constitute an essential step towards the rational design of multielectron storage systems of this type.

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