PAPER

Photoinduced intercomponent excited-state decays in a molecular dyad made of a dinuclear rhenium(I) chromophore and a fullerene electron acceptor unit†

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A novel molecular dyad, **1**, made of a dinuclear $\{[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-pyridazine})]\}$ component covalently-linked to a fullerene unit by a carbocyclic molecular bridge has been prepared and its redox, spectroscopic, and photophysical properties – including pump–probe transient absorption spectroscopy in the visible and near-infrared region – have been investigated, along with those of its model species. Photoinduced, inter-component electron transfer occurs in **1** from the thermally-equilibrated, triplet metal/ligand-to-ligand charge-transfer (^{3}MLLCT) state of the dinuclear rhenium(I) subunit to the fullerene acceptor, with a time constant of about 100 ps. The so-formed triplet charge-separated state recombines in a few nanoseconds by a spin-selective process yielding, rather than the ground state, the locally-excited, triplet fullerene state, which finally decays to the ground state by intersystem crossing in about 290 ns.

Introduction

Rhenium(I) compounds containing N-heterocyclic aromatics, like polypyridine ligands, have played key roles in the development of several fields of chemistry, such as photophysics and photochemistry,[1] photoinduced electron and energy transfer,[2] and photocatalysis (including CO_2 photoreduction).[3] In particular, some experimental techniques, like time-resolved infrared spectroscopy, have also largely benefitted from the excited-state properties of Re(I) polypyridine complexes for their diffusion.[4] Most of the attraction of Re(I) polypyridine compounds has indeed derived from the properties of their lowest-energy level, a relatively long-lived metal-to-ligand charge transfer triplet (^{3}MLCT) state, which (partly) deactivates by the radiative process, leading to moderately intense luminescence.[1–5]

In the last few years, a new family of luminescent rhenium(I) complexes have been discovered: the members of such a family are made of two $\{Re(CO)_3\}^+$ units joined by a bridging pyridazine ligand and two ancillary anionic ligands (typically, halogens), so they can be indicated as $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-L})]$ (X is an ancillary anionic ligand and L is a bridging pyridazine).[6] Like the mononuclear $Re(CO)_3(LL)X$ complexes (where LL is a bidentate polypyridine ligand), these dinuclear species emit from ^{3}MLCT excited states, but differently from their mononuclear counterparts, which are usually weak emitters, some of these complexes exhibit very high photoluminescence quantum yields (up to 0.5), both in deaerated solutions[7] and in the solid state.[8] Noteworthily, such high emission quantum yields allowed some compounds of this new family of lumino-phores to play the role of emissive components in OLED[7,8b] and of luminescent probes in biologically-relevant systems.[9] However, detailed investigations on photoinduced electron and/or energy transfer processes involving $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-L})]$ species – including covalently-linked molecular dyads based on $\{[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-L})]\}$ subunits – which are at the basis of any solar energy conversion scheme, have not been reported, although quite recently a member of this new family of dinuclear Re(I) complexes has been used as a photocatalyst for CO_2 reduction.[10] Also, fs pump–probe transient absorption spectra of $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-L})]$ species have not been studied.

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†Electronic supplementary information (ESI) available: General procedures, equipments and methods; synthesis and characterization details; ns flash photolysis of **1** and **2**; near-infrared fs transient spectrum of **2**; global kinetic analysis of **1**, comments on the possible presence of diastereoisomers in **1**, spectro-electrochemistry of **3**. See DOI: 10.1039/c4pp00301b
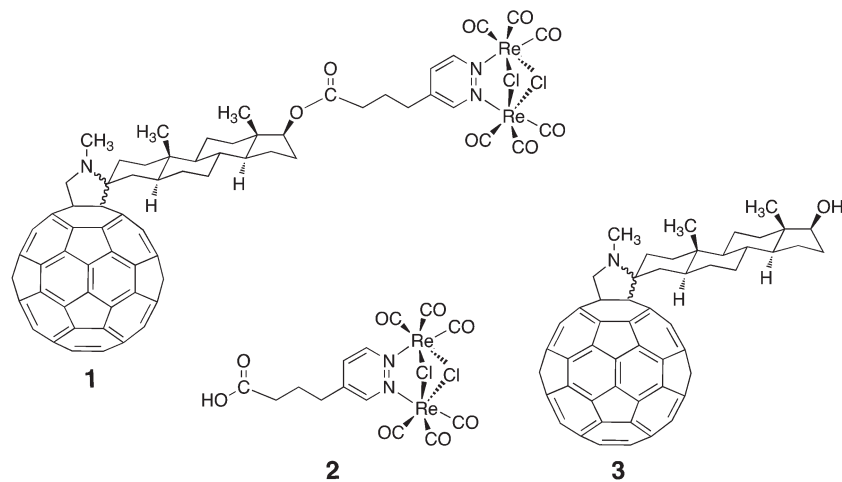
Fig. 1 Structural formulae of compounds **1–3**.

Here, we report on the first molecular dyad made of a $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}L)]$ unit covalently-linked to a fulleropyrrolidine electron acceptor (**1**, see Fig. 1), whose synthesis is reported in the ESI.† The molecular connection between the dinuclear rhenium(I) and fullerene units is provided by a short butanoate group and a rigid, non-conjugated androstane system. The absorption spectra and photophysical properties (including photoinduced intercomponent processes), studied using UV-Vis and NIR pump–probe femtosecond transient absorption spectroscopy, of **1** and of its molecular components **2** and **3** are shown and discussed. It is the first time that ultrafast transient absorption spectroscopy has been used to investigate the excited-state properties of a dirhenium compound of this new family of chromophores.

Results and discussion

Redox behavior

The redox behavior of the family of compounds with a general formula $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}L)]$, to which the model species **2** belongs, has been extensively investigated.[6–8,10] Such studies, also supported by theoretical analyses,[6a] have demonstrated that first reduction is monoelectronic, reversible and centered on the L ligand, whereas first oxidation is usually reversible and bielectronic in nature, and involves partly delocalized orbi-

tals receiving contributions from rhenium-centered and X-centered orbitals. Partial irreversibility of the oxidation process is found when X is a chloride, probably as a consequence of the highly positive potential value induced by the presence of the strongly electron withdrawing chlorides. On the basis of this well-established framework, the already reported[6a] redox behavior of $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}(4\text{-methyl})pyridazine)]$ can be taken as a model for the redox behavior of **2**.

$Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}(4\text{-methyl})pyridazine)]$ undergoes a quasi-reversible bielectronic oxidation at +1.67 V vs. SCE in acetonitrile.[6] The process is assigned to electron removal from an orbital which receives contributions mainly from both rhenium(I) centers and the bridging chloride ions,[6b] so it can be named as a metal/ligand-centered orbital. The bielectronic nature of such a redox process, expected on the basis of formerly studied species of the same family, is supported by internal comparison of the intensity of the cyclic voltammetry peak corresponding to this process with that of the reduction process. Indeed, a reversible, monoelectronic reduction process takes place for $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}(4\text{-methyl})pyridazine)]$ at −1.06 V, and is assigned to a pyridazine-centered orbital, in complete agreement with literature data of similar compounds.[6]

The cyclic voltammogram of the fullerene model compound **3**[11] shows a series of reversible one-electron reduction processes, the one at lower negative potential being at −0.62 V (Table 1). The cyclic voltammogram of **1** appears to be a com-

Table 1 Absorption spectra, redox and luminescence data[a]

	Absorption	Redox data		Luminescence				
	λ_{max} [nm] (ε [M^{-1} cm^{-1}])	$E_{1/2}$(ox) V vs. SCE	$E_{1/2}$(red) V vs. SCE	λ_{max} [nm] 298 K	τ [ns] 298 K	Φ 298 K	λ_{max} [nm] 77 K	τ [μs] 77 K
1	325 (42 400)	+1.67	−0.63	—	—	—	—	—
2	370 (8800)	+1.67[b]	−1.06[b]	575	1300 (480)[c]	0.11	503	27.6
3	325 (37 000)		−0.62	715	1.3	0.001	714	0.002

[a] Absorption and luminescence data are in de-aerated toluene, unless otherwise stated; redox data of **1** are in 1,2-dichloroethane; only the potentials of first oxidation or reduction processes are reported. [b] Data refers to $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}(4\text{-methyl})pyridazine)]$, taken as a model, in acetonitrile, see ref. 6a. [c] In parenthesis, the emission lifetime in aerated toluene solution is given.
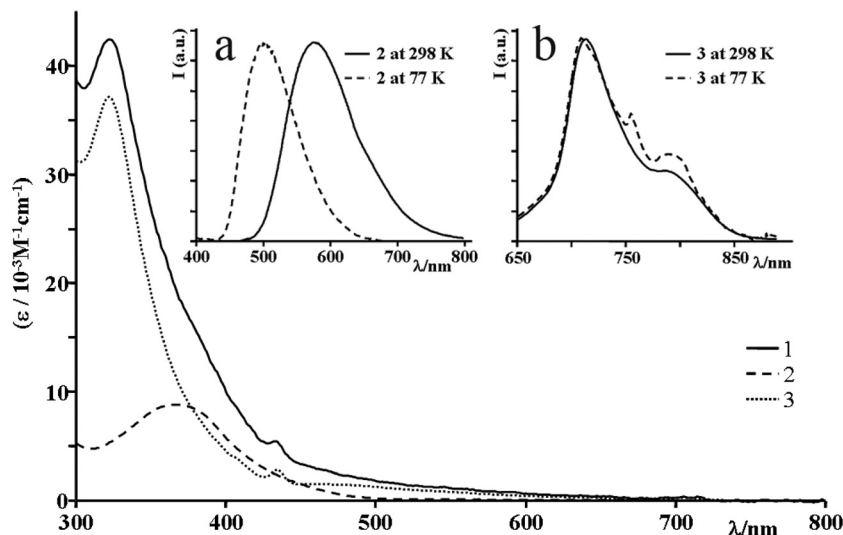
Fig. 2 Absorption spectra of **1** (solid), **2** (dashed), and **3** (dotted). Inset a shows the emission spectra of **2** at 298 K (solid) and at 77 K (dashed). Inset b shows phosphorescence of **3** at 298 K (solid) and at 77 K (dashed). All spectra are in toluene; emission spectra are normalized.

bination of those of its components (see Table 1): in particular, oxidation involves the dinuclear "Re(μ-Cl)$_2$Re" moiety, and the first reduction process involves the fullerene subunit. The very close redox potentials of the various subunits of **1** compared to the potential values of the corresponding redox processes of their isolated units indicate that the electronic coupling between the dinuclear rhenium and fullerene subunits is weak, as expected because of the rigidity (and lack of conjugation) provided by the aliphatic molecular bridge.

Absorption spectra and photophysical properties

The absorption spectrum of **2** in toluene (Fig. 2) is dominated by an intense absorption band with a maximum at about 380 nm, assigned to a spin-allowed metal/ligand-to-ligand charge-transfer (MLLCT) transition, in agreement with the absorption spectra of other compounds of the same class of
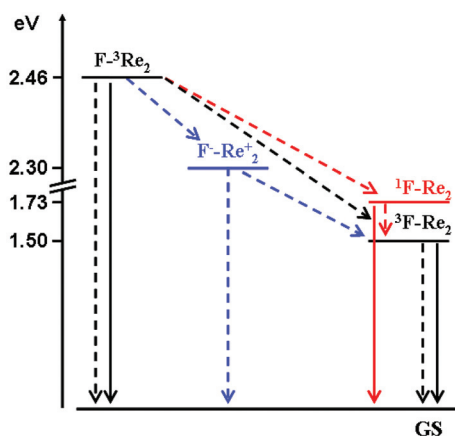

Fig. 3 Excited-state energy level diagram and possible decays of **1**, indicated as F-Re$_2$ to evidence its bicomponent nature. Solid lines are (possible) radiative decays, and dashed ones are (possible) radiationless decays. For further details, see text.

dinuclear, pyridazine-bridged Re(I) species.[6] The band is broad, with a tail extending to 500 nm, probably containing the corresponding (less intense) spin-forbidden ^{3}MLLCT band. The absorption band of **3** shows the usual intense absorption of fullerene species at about 320 nm. At longer wavelengths, also a small peak, typical of substituted fullerene, at about 435 nm, is present (Fig. 2).[12] In the absorption spectrum of **1** the MLLCT band is obscured by the more intense fullerene absorption, but is clearly visible as a shoulder in the range 350–440 nm.

Compound **2** is emissive in toluene, both at 77 K and at 298 K (Table 1 and Fig. 2, inset (a)), from its ^{3}MLLCT state, as indicated by its emission spectra, lifetimes and quantum yield, in agreement with data of similar compounds.[6a,9a] This emission is totally absent in **1**, indicating that new radiationless decay channels are available to the ^{3}MLLCT state in this latter species. The energy level diagram in Fig. 3, obtained on the basis of redox and luminescence data,‡ [13] shows the possible, intercomponent excited-state decay routes that are introduced in **1** by the presence of the fullerene unit: (i) electronic energy transfer to the fullerene singlet state, ^{1}F-Re$_2$ (driving force, $\Delta G = -0.73$ eV); (ii) electronic energy transfer to the fullerene triplet state, ^{3}F-Re$_2$ ($\Delta G = -0.96$ eV); (iii) oxidative electron transfer to the Re$_2^+$-F$^-$ charge-separated state ($\Delta G = -0.16$ eV).

‡The energy of the states indicated as F-^{3}Re$_2$ and ^{1}F-Re$_2$ in Fig. 3 are approximated to the 77 K emission of **2** and **3**, respectively. The energy of the ^{3}F-Re$_2$ state is approximated to the triplet state energy of C$_{60}$, and finally the energy of the charge-separated state, F$^-$-Re$_2^+$, is obtained by calculating the driving force for the photoinduced oxidative electron transfer process from *Re$_2$ to the fullerene unit, ΔG, using the simplified equation $\Delta G = e(E_{ox} - E_{red}) - E^{00}$, where E_{ox} is the ground state oxidation potential of the donor chromophore, E_{red} is the reduction potential of the acceptor (both expressed in V), E^{00} is the excited state energy of the donor (in eV), assumed as the emission maximum of its model **2** at 77 K. The term e is the electron charge.[13] In this equation, the work term is neglected. It can be noted, anyway, that spectroscopic and redox data have been obtained in different solvents because of technical problems (see Table 1), so the calculated values should be considered with some care.

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Route (i) is less probable, however, since it would be spin forbidden (though the formal spin-forbidden nature of the process could be alleviated by the presence of the heavy rhenium atom). We avoid any hypothesis of the favored quenching route based on estimation of electron or energy transfer rate constants in the light of theoretical approaches, and prefer to analyze the experimental data first, in particular the pump–probe transient absorption (TA) spectra.

To study the excited-state decay route of **1**, pump–probe transient absorption spectra were performed, starting with the component **2**, whose time-resolved TA spectra in toluene are shown in Fig. 4: the initial spectrum (160 fs after laser pulse; excitation wavelength, 400 nm) exhibits two clearly discernible absorption bands in the visible region and suggests that a bleach, assigned to disappearance of the MLLCT band, appears at shorter wavelengths than 460 nm (not shown; for technical reasons, we cannot obtain TA spectra with acceptable signal-to-noise ratio at wavelengths shorter than 450 nm). Within a few ps (time constant of the process, measured at 590 nm, $4(\pm 1)$ ps; see Fig. 4a) the absorption around 490 nm decreases and the one in the 540–670 nm range increases. On a longer timescale, the spectrum continues to evolve, until a stronger absorption, peaking at about 580 nm, is fully developed (Fig. 4b; time constant of this process, $70(\pm 7)$ ps). Successively, the TA spectrum monotonically decays to zero. This process, not accessible to our fs apparatus, has been checked on the ns timescale by following the recovery of the MLLCT bleach at 400 nm (excitation, 355 nm) with a ns flash photolysis equipment, see Fig. S1 in ESI.† The time constant of this latter process, 461 ns, very well agrees with the emission decay

of **2** (480 ns, see Table 1). Because it is the first time that time-resolved TA spectroscopy of a member of the family of $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}L)]$ luminophores is disclosed, it cannot be compared to existing cases, but the interpretation of the reported time-resolved processes can however be made on the basis of literature data accumulated on mononuclear Re(I) polypyridine compounds: the "initial" spectrum of **2** here recorded (after 160 fs from pump pulse) is attributed to the triplet MLLCT manifold, since intersystem crossing in MLCT states of tricarbonyl Re(I) polypyridine compounds have been reported to occur in times shorter than 150 fs,[14] therefore we assume that it occurs on a similar timescale in the present dirhenium chromophores. In mononuclear $[Re(CO)_3(LL)Y]^n$ species (Y = Cl, $n = 0$; Y = pyridine derivatives, $n = 1+$), however, time-resolved infrared spectroscopy indicates that two triplet states are populated simultaneously from the initially prepared singlet state, which successively equilibrate within a few picoseconds.[14] By analogy, the 7 ps process shown in Fig. 4a is tentatively assigned to equilibration between slightly different MLLCT triplets. Solvent relaxation would be involved in the 70 ps process (Fig. 4b), which finally leads to the thermally-equilibrated, long-lived and emissive ^{3}MLLCT level.§[14b] Scheme 1 schematizes the excited states and decays occurring in **2**. An important information that can therefore be derived by the present results is that the early events of excited state decay of the dirhenium(I) compounds, here represented by **2**, are qualitatively very similar to the early events occurring in mononuclear Re(I) polypyridine compounds.

With the information gained from the TA spectroscopy of **2**, we can analyze the time-resolved TA spectra of **1**, shown in Fig. 5. Four successive processes can be identified, starting from the initially-recorded spectrum. The first two processes (see Fig. 5a), are qualitatively similar to those of **2**, with (i) the first one showing a decrease in the absorption at about 490 nm and an increase of the transient absorption in the 550–640 nm region (time constant, 4 ± 1 ps) and (ii) the second one in which the transient absorption in the 460–670 nm range increases (time constant, 20 ± 2 ps). Comparison between spectral changes and time constants of TA data of **1** and **2** suggests that (i) and (ii) processes in **1** have the same origin compared with the first two processes in **2**, that is
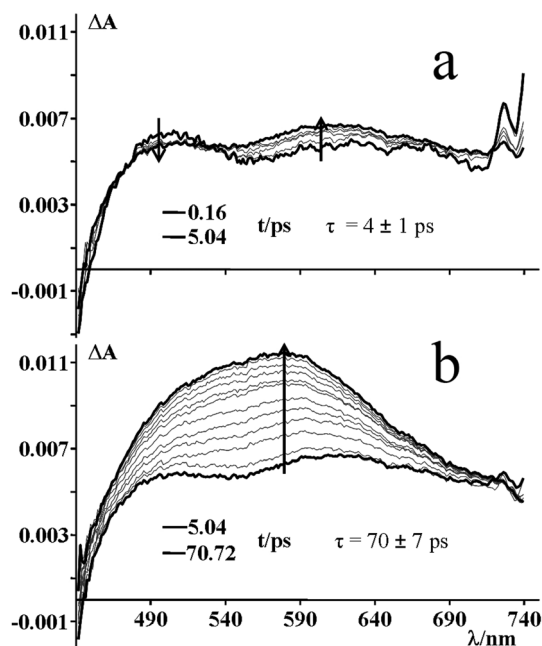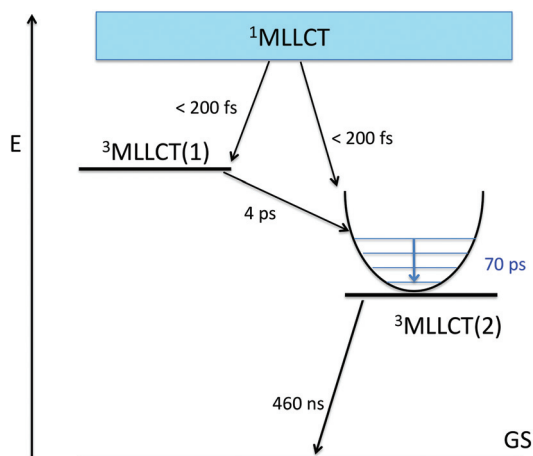

Fig. 4 Transient absorption spectra of **2** in toluene (excitation wavelength, 400 nm). Time delays from pump pulse are shown in figures (first and last delays are reported for each panel). For more details, see text.

§ The assignment of the 70 ps component in the excited-state decay of **2** to solvent relaxation could seem surprising, since vibrational cooling, including solvent relaxation, in metal polypyridine complexes commonly takes place with time constants smaller than 10 ps. However, slow local solvent-restructuring processes (in the range 15–40 ps, with a compound also exhibiting an excited-state decay with a component longer than 70 ps) have been recently assumed to explain excited-state decay components in some mononuclear Re(I) compounds containing polypyridine and carbonyl ligands.[14] Our interpretation here is presented to fit into the suggested figure. To discuss the origin of the slowness of the solvent relaxation process in such compounds is speculative at this stage, we can only offer the hypothesis that the fact that carbonyls are strongly involved in the excited-state of **2** (and probably of the mononuclear compounds discussed in ref. 14b), coupled with the fact that carbonyls can strongly interact with solvent, may have a role.

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Scheme 1 Excited state diagram (not scaled) and kinetics involved in the deactivation of the model species **2**. [1]MLLCT identifies the upper-energy excited states initially populated by light excitation and eventually decayed to the lowest-energy singlet state. [3]MLLCT(1) and [3]MLLCT(2) states are the two different triplet CT states populated *via* intersystem crossing (see text and also ref. 14). Vibrational cooling within the [3]MLLCT state is indicated by the blue arrow, for simplicity, also vibrational levels within this state are indicated in blue, to differentiate them from the electronic states, indicated in black. The energy potential curve is only showed for the lowest-energy CT state, where vibrational cooling is comparatively slow with respect to decays among higher-energy electronic states. GS is the ground state. This interpretation is inspired by a similar interpretation used for the excited-state decay of mononuclear Re(I) compounds.[14]

reorganization processes within the dirhenium-based, triplet manifold(s), leading to the thermally-equilibrated [3]MLLCT state. Successively, the TA of **1** decays without any significant change (process (iii), time constant 120 ± 27 ps, see Fig. 5b), then process (iv) occurs, revealed by a spectral profile change, with a strong decrease of the absorption in the region 450–650 nm and a concomitant appearance of an absorption maximum at about 695 nm (Fig. 5c); the process is too slow for our fs apparatus, which only allows to estimate a limit for the time constant (*i.e.*, longer than 3 ns). To analyze the slow process we performed ns flash photolysis, which indicated that the final TA spectrum recorded by the fs apparatus corresponds to that recorded after 50 ns (Fig. S2 in ESI†), and is quite similar to that reported for triplet states of other fullerene compounds,[12,15] so it is assigned to the triplet state of the fullerene unit, which finally decays to the ground state with a time constant of 286 ns (Fig. S2†).¶ Such a decay is short for a fullerene intersystem crossing, usually occurring in the micro-
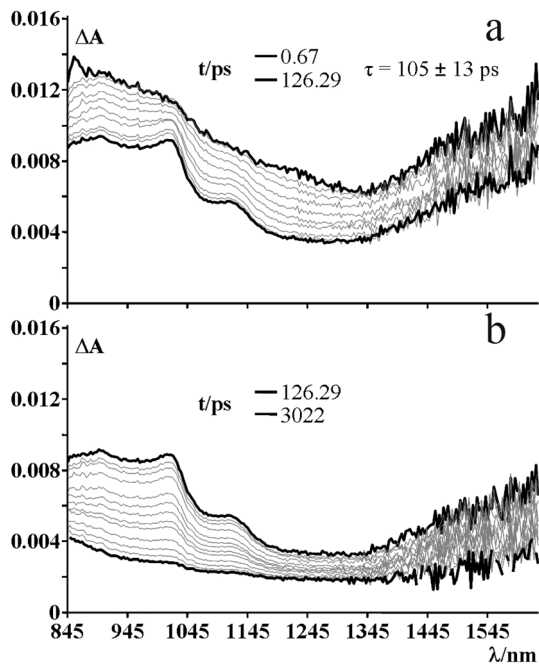
¶A risetime is present in the ns flash photolysis experiment (see ESI,† Fig. S2). This risetime, which should include process (iv) cited above as the rate limiting step, is too fast to be fitted by our flash photolysis apparatus. This, however, allows one to identify a time limit for process (iv), that together with the limit identified by fs spectroscopy, indicates that the process leading to the triplet state of the fullerene subunit in **1** occurs with a time constant between 3 and 10 ns.
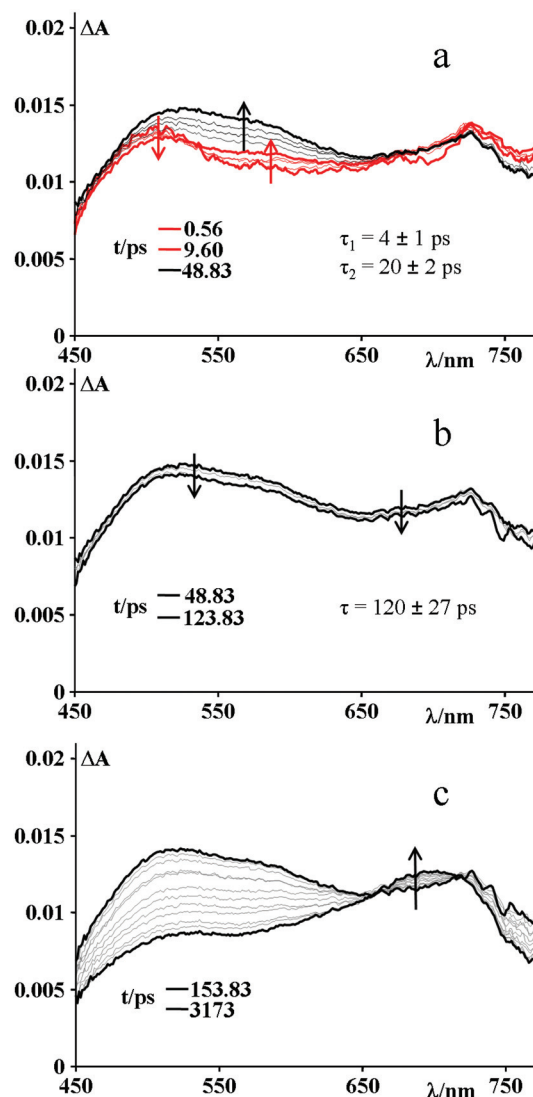
Fig. 5 Transient absorption spectra of **1** in toluene (excitation wavelength, 400 nm). Time delays from pump pulse are shown in figures (first and last for each panel, except for b, which shows three spectra, identified by colors and arrows). For details, see text.

second timescale, however is probably accelerated by an enhanced spin–orbit coupling induced by the presence of the two rhenium atoms.

To better study processes (iii) and (iv), the near-infrared (NIR) spectral region (845–1600 nm) has been investigated. For compound **2**, TA spectroscopy in the NIR did not give any sizeable signal (see ESI,† Fig. S3). In contrast, a broad absorption appears in the initially-recorded (600 fs after laser pulse) TA spectrum of **1** in the 850–1250 nm region (Fig. 6). This TA decreases at many wavelengths, but spectral changes occur, with the appearance of a structure peaking at about 870, 1020 and 1130 nm (Fig. 6, panel a). Such a spectral evolution takes place with a time constant of 105(±13) ps, and therefore is attributed to process (iii), occurring in the same time range, shown in Fig. 5b. A spectroelectrochemical study indicates that

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Fig. 6 NIR transient absorption spectra of **1**. Time delays from pump pulse are shown in figures (first and last for each panel; transient absorption spectra intensity is decreasing with time at any wavelength). For more details, see text.

the reduced anion of **3** (that is, the fullerene anion) has similar signatures (see ESI,† Fig. S4),[16] so process (iii) is suggested to be photoinduced oxidative electron transfer from the thermally-equilibrated ^{3}MLLCT state of the dirhenium subunit to the fullerene acceptor, with the formation of the Re$_2$$^+$–F$^-$ charge-separated state (CS). Rate constant of the photoinduced charge separation process originating from the ^{3}MLLCT state is therefore about 9.5×10^9 s^{-1} in **1**. The successive disappearance of the structured absorption in the NIR (Fig. 6, panel b) takes place with a similar time constant of process (iv) in Fig. 5 (that is, in the range 3–10 ns, see also footnote ¶), so it can be attributed to population of the triplet fullerene-centered state from the CS state. In fact, triplet excited states of fullerene derivatives have been reported to exhibit an absorption peak in the range 675–705 nm,[15,17] similar to that shown in Fig. 5c, and formed by process (iv) described above.
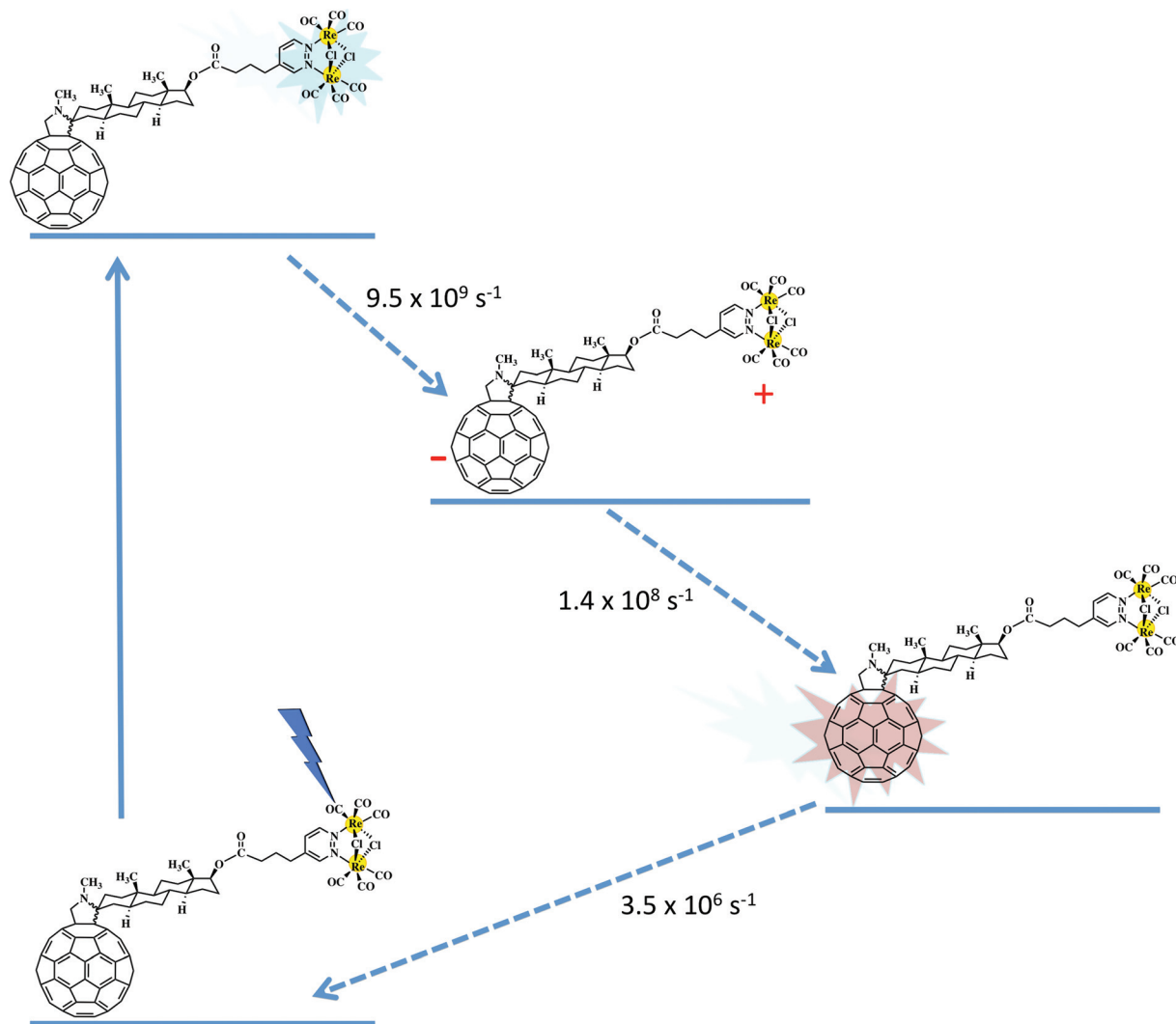
On the basis of the above discussion, the general main scheme for the excited state decay of **1** can be represented as in Fig. 7. Further comments can be added, based on the experimental data. First of all, part of the exciting light at 400 nm is directly absorbed by the fullerene subunit (see absorption spectra in Fig. 2). However, fluorescence of fullerene does not take place, indicating that fast radiationless decay processes also deactivate such fullerene-based singlet excited states. Most likely it is a fast intersystem crossing to the fullerene triplet state, accelerated by the presence of the heavy dirhenium subunit to be responsible for fullerene fluorescence quenching. Actually, the effect of the dirhenium

subunit in accelerating spin–orbit coupling in the fullerene subunit in **1** is also evident in the already-mentioned, relatively short fullerene triplet lifetime, 286 ns, see above. The spectroscopic signatures of the excited-state decay process emanating from the fullerene singlet state are probably buried within the larger spectroscopic changes derived from the dirhenium-based, MLLCT excitation (in particular, the broad transient absorption increasing in the visible region on the timescale of tens of ps, see Fig. 4b and 5a).

As a further confirmation of the occurrence of photo-induced electron transfer as the main decay of the MLLCT triplet state of **1** at room temperature, it can be noted that spin-forbidden energy transfer from the ^{3}MLLCT state to the fullerene singlet state via Coulombic mechanism can be estimated by the simplified Förster equation (see details in ESI†).[5a] Even for quite compact structural arrangements of **1**, with edge-to-edge donor–acceptor distance as close as 10 Å (smaller than the size of the steroid moiety of the spacer), time constant for Förster energy transfer is not smaller than 10 ns, therefore the Coulombic energy transfer cannot compete with the charge separation process, which is about two orders of magnitude faster (ca. 100 ps, from experimental data). Estimation of Dexter, electron-exchange energy transfer rate constant, which could contribute to the ^{3}MLLCT quenching and could also involve the fullerene triplet state as the acceptor, is not made in detail. The time-resolved TA spectroscopy experiments, anyway, indicate that charge separation dominates, at least at room temperature, although Dexter energy transfer to the fullerene triplet state would have a much higher driving force (−0.96 eV) than electron transfer (−0.16 eV; see above and also Fig. 3). Since ^{3}MLLCT quenching is also present at 77 K in the rigid matrix, where electron transfers are usually much slower, except in favored cases (i.e. for activationless electron transfer processes; Dexter energy transfer can also be slowed down on passing to lower temperature, but to a smaller extent than electron transfer processes), we cannot exclude that Dexter energy transfer becomes the dominant contribution to the ^{3}MLLCT decay on passing from room temperature fluid solution to rigid matrix at 77 K.

Comparison with molecular analogues

It is interesting to compare the results obtained here for the new molecular dyad **1** with the properties of similar molecular dyads containing fullerene units as the acceptor and other metal-based complexes as donors. Indeed, donor-fullerene dyads in which the donor is a Ru(ɪɪ) polypyridine unit,[11,17,18] an Ir(ɪɪɪ) cyclometalated chromophore,[19] a dinuclear Cu(ɪ) helicate chromophore,[20] or a mononuclear Re(ɪ) polypyridine unit[21] have been reported. In most cases, the ^{3}MLCT excited state is quenched by oxidative electron transfer processes similar to that found for **1**, thereby generating charge-separated states containing a reduced fullerene subunit. Probably the most relevant species, with respect to the system here studied, is compound **4**, whose molecular structure is shown in Fig. 8:[17] this latter D–A species contains a very similar spacer, differing from **1** only for the absence of a flexible alkyl chain connecting the steroid

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Fig. 7 Schematic representation of the main excited-state decay route following [3]MLLCT state formation of **1**, at room temperature in fluid solution. All the states (except the ground state) are triplets. State diagrams are not in scale. The rate constant for the formation of the triplet fullerene state from the CS state has been calculated by assuming an average value for the time constant limits of this processes (3 and 10 ns), as estimated by fs pump–probe and ns flash photolysis experiments. For details, see text.

subunit of the spacer to the metal-based chromophore. In **4**, the [3]MLCT state is quenched by electron transfer to fullerene with time constants of about 1.4 ns in a toluene–CH_2Cl_2 mixture, 470 ps in CH_2Cl_2, and 196 ps in acetonitrile.[17] Differences in electron transfer rates have been attributed to the solvent polarity effect, in particular to the different stabilization of the CS state occurring in more polar solvents (*i.e.* acetonitrile), making the electron transfer more favorable from a thermodynamic viewpoint. Interestingly, in acetonitrile the charge-separated state formed in **4** decays to the ground state through the energetically lower-lying triplet excited state involving the fullerene subunit (the triplet fullerene level is estimated to be 0.23 eV lower than the CS state in this solvent), that is *via* a spin-selective recombination process, analogous to what happens in **1**, whereas in CH_2Cl_2 the CS state undergoes excited-state equilibration with the [3]MLCT Ru-based level, whose energy is very close to that of the CS state in such

solvent (energy difference between the two states has been calculated to be 0.02 eV, compatible with excited-state equilibration).[17] In the case of **1**, the photoinduced charge separation is formed with a time constant of about 110 ps. Considering the driving force of the same process of **4** calculated in acetonitrile (−0.24 eV),[17] the driving force estimated for **1** in toluene (−0.16 eV), and the different nature of the two solvents (driving force would favor **4**, but "costs" in terms of reorganization energy would favor **1**, since outer reorganization energy for CS is expected to be lower in less polar solvents), the difference in time constants of the photoinduced charge separation process in the two cases is acceptable. Excited-state equilibration is also fully excluded in **1** in toluene, since such a situation should allow for [3]MLLCT emission from the dirhenium-based chromophore to be detected, although with a reduced quantum yield with respect to the model species **2**, and this is not the case for **1**.
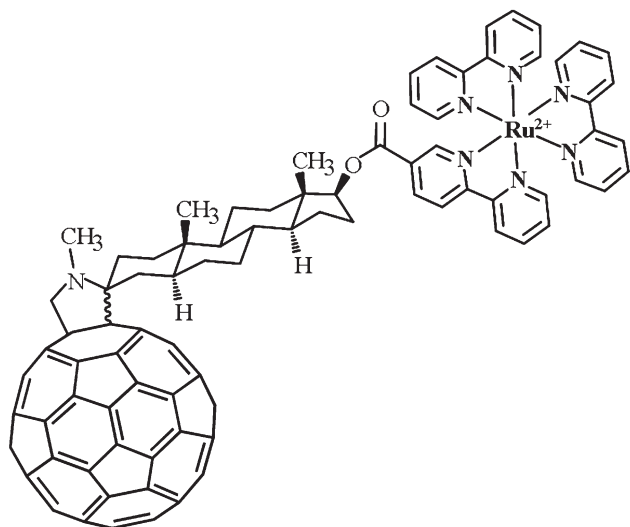
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Fig. 8 Structural formula of the molecular dyad **4**,[17] similar to compound **1**. Charge of the compound is omitted.

Noteworthily, photoinduced, oxidative charge separation followed by recombination *via* the fullerene triplet state analogous to the excited-state decay route found for **1** is also reported to occur for an Ir(III) cyclometalated/fullerene system, where phosphorescence of the fullerene triplet at 77 K also takes place.[19]

Conclusions

In conclusion, we have synthesized the first molecular dyad, **1**, containing the dinuclear rhenium(I) {[Re₂(μ-X)₂(CO)₆(μ-pyridazine)]} moiety as the chromophore subunit. Compound **1** does not exhibit any emission, since the strongly emissive metal/ligand-to-ligand charge-transfer (³MLLCT) state of its chromophoric subunit is efficiently quenched, *via* oxidative electron transfer, by the (covalently-linked) fullerene subunit. The intercomponent, photoinduced electron transfer processes occurring in **1** have been studied in some detail by pump–probe femtosecond absorption spectroscopy, both in the visible and in the near infrared region. By the way, it is also the first time that such a technique is employed to investigate the excited-state properties of a member of this dinuclear class of rhenium complexes. The charge-separated (CS) species Re_2^+–F^- is formed from the thermally-equilibrated ³MLLCT excited state of the dirhenium subunit by electron transfer to the fullerene acceptor unit, with a time constant of about 110 ps. Because of the triplet nature of the MLLCT state, the so-formed CS is also expected to be a triplet state. Such a CS species decays, with a time constant of few ns, to the fullerene triplet state. Successive charge recombination is spin selective, *i.e.* the triplet CS state recombines to yield, rather than the ground state, a locally-excited (fullerene-centered) triplet state. Besides spin reasons, even thermodynamics can favor charge recombination (CR) to the triplet fullerene state over CR to the

ground state. In fact, driving force for CR to the triplet fullerene state is about 0.80 eV, whereas CR to the ground state is about 2.30 eV, so this latter process could lie well within the Marcus inverted region and thus be definitely slower than the former one. The fullerene triplet excited state finally decays to the ground state by intersystem crossing on the hundreds of nanoseconds timescale.

Although the lifetime of the CS of **1** is limited owing to the presence of the triplet fullerene state, it is still much faster than the charge separation rate constant and promises to be long-lived enough to allow stepwise injection of the electron transiently stored on the fullerene framework into another, better electron acceptor substrate, for example other carbon nanostructures, eventually connected to the fullerene subunit. This would produce triads with long-lived fully-developed CS states. Work towards this direction is planned in our laboratories.

Acknowledgements

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