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Optically Controlled Electron Transfer in a Re(I) Complex

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Abstract: We demonstrate ultrafast optical control of intramolecular charge flow which paves the way for photocurrent modulation and switching with a highly wavelength-selective ON/OFF ratio. The system we explore is a *fac*-[Re(CO)$_3$(TTF-DPPZ)Cl] complex, where TTF-DPPZ = 4',5'-bis(propylthio)tetrathiafulvenyl[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine. DFT calculations and AC-Stark spectroscopy confirm the presence of two distinct optically active charge-transfer processes, namely a metal-to-ligand charge transfer (MLCT) and an intra-ligand charge transfer (ILCT). Ultrafast transient absorption measurements show that the ILCT state decays in the ps regime. Upon excitation to the MLCT state, only a long-lived ^{3}MLCT state is observed after 80 ps. Remarkably, however, the bleaching of the ILCT absorption band remains as a result of the effective inhibition of the HOMO-LUMO transition.

A good understanding of how to control the charge transfer (CT) in multichromophore ensembles is essential for mimicking nature to capture and convert solar energy and eventually realizing high performance photocatalysis, photovoltaics, spintronics and optoelectronics.[1] Taking directed electron transfer as an example, if there is an increase in electron density on one part of the molecule upon excitation, then putting an acceptor near that part of the molecule will lower electrostatic barriers to photo-induced charge transfer. This rationale was reported to understand the placement of tryptophan donors used to reduce photoexcited flavins in DNA photolyase.[2] A variety of strategies have been developed particularly for facilitation of charge separation and inhibition of charge recombination in electron donor-bridge-acceptor (D-B-A) systems. Within the context of optical switches, gating of an intramolecular charge transfer (ICT) has been reported by incorporating a photochromic unit between D and A moieties.[3] In most cases, a photochromic Förster resonance energy transfer results in an ICT fluorescence quenching. In 2010, a state-selective electron transfer in an unsymmetric acceptor-Zn(II)porphyrin-acceptor triad was reported, however, the issue of repopulation of different states after photoexcitation still remains to be solved.[4] Although an example of excitation-wavelength-dependent photoinduced electron transfer in a fully π-conjugated oligomer was very recently reported,[5] optical control over multiple CT pathways in D-A systems remains a big challenge, and to the best of our knowledge, it has not been reported so far.

Here, we describe preparation, electronic properties, photocycle and ultrafast optical control of CT in a *fac*-[Re(CO)$_3$(TTF-DPPZ)Cl] complex. The interest in *fac*-[Re(L)(CO)$_3$(α-diimine)]$^{n+}$ complexes stems from their dynamic and exceptionally rich excited states properties that are dramatically altered by structural variations in ancillary ligand L and α-diimine as well as solvents.[6] Specifically, the DPPZ ligand shows LUMO and LUMO+1 localized on phenazine (phz, blue in Figure 1) and phenanthroline (phen, purple in Figure 1) units, respectively, which are energetically close to each other (#171 and #172 in Supporting Information, Table S2). As a consequence, the interplay of two close-lying ^{3}MLCT states of different nature in *fac*-[Re(L)(CO)$_3$(DPPZ)]$^{n+}$ complexes renders them promising for development of phosphorescent labels and probes of biomolecules such as DNA and proteins.[8] To modulate the energy levels of these two molecular orbitals, electron-donating or withdrawing substituents have been appended to the DPPZ core, leading to the formation of ^{3}ILπ-π* or ^{3}ILCT along with two ^{3}MLCT excited states in the corresponding Re(I) complexes.[6d,8]

To facilitate population of ILCT states that are well-separated from higher lying MLCT states, our strategy involves the coordination of a planar TTF-annulated DPPZ to the Re(CO)$_3$Cl chromophore. Our previous work has demonstrated that TTF-DPPZ exhibits a strong ILCT transition with the TTF as an electron donor and the DPPZ as an electron acceptor.[9] As illustrated in Figure 1, the excitation of two distinct CT states results in a charge flow either from the peripheral TTF (red) or the Re(CO)$_3$Cl chromophore to the central phz core, these being in opposite directions. This allows for optically gating the charge flow in D-A ensembles. In the present work, the involved CT states are identified *via* DFT calculations and AC-field Stark spectroscopy, and their ultrafast dynamics are investigated by femtosecond transient absorption spectroscopy (fs-TAS).

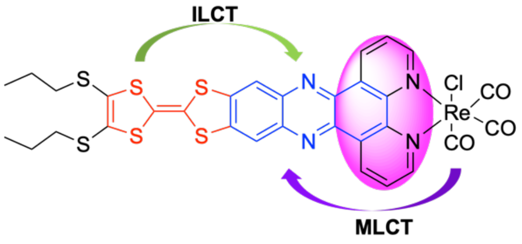

Figure 1. Chemical structure of the target complex.

The TTF-DPPZ ligand was synthesized according to published procedures.[9a] Reaction of [Re(CO)$_5$Cl] with TTF-DPPZ in EtOH afforded the target complex *fac*-[Re(CO)$_3$(TTF-DPPZ)Cl]. It is unambiguously characterized by elemental analysis, ^{1}H NMR, UV-Vis and IR spectroscopy. Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of its solution in cyclohexane. The single-crystal structure (Figure 2) shows that the Re(I) ion is coordinated by three CO molecules, one chloride and one phen chelating unit from TTF-DPPZ in a distorted octahedral fashion. Two CO molecules and the phen subunit of TTF-DPPZ occupy the equatorial positions around the Re(I) ion. The skeleton of TTF-DPPZ is almost planar and the Re(I) ion is displaced out of a least-squares plane through all ligand atoms, except two propyl groups, by only 0.133(9) Å. The crystal and refinement data as well as a crystal packing diagram are given in Table S1 and Figure S1, respectively.

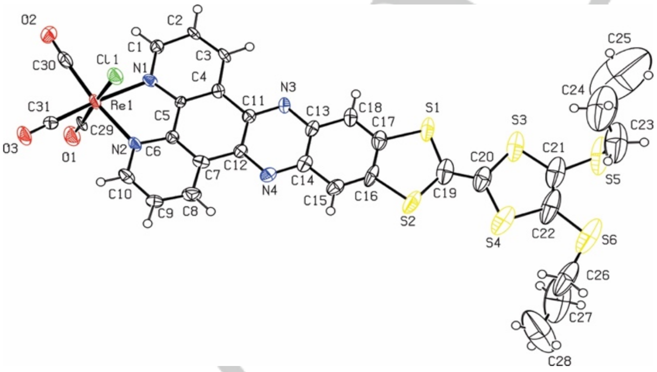

Figure 2. ORTEP structure of the Re(I) complex drawn with 50% ellipsoid probability and with atom numbering scheme; H-atoms given arbitrary displacement parameters for clarity.

The electrochemical properties of the Re(I) complex in CH$_2$Cl$_2$ were investigated by cyclic voltammetry (Figure S2). It displays two reversible single electron oxidation waves ($E_{1/2}^{ox1}$ = 0.28 V, $E_{1/2}^{ox2}$ = 0.62 V) for successive oxidation of the TTF subunit to the radical cation and dication states and one reversible reduction wave at -1.41 V for the reduction of the phz component of the DPPZ subunit. The UV-vis spectrum of the complex in CH$_2$Cl$_2$ (Figure S3) shows a strong and broad absorption band centered at 580 nm. Akin to Ru(II) and Fe(II) complexes with TTF-DPPZ,[10] this lowest energy absorption band is attributed to a spin-allowed π-π* ILCT transition from the HOMO localized on the electron donor TTF to the LUMO localized on the phz component of the DPPZ subunit. As expected, the MLCT transition peaks appear at 375 nm. Importantly, the ILCT transition is well separated from the MLCT transition. Moreover, an intense absorption band approaching the UV edge of the spectrum is characteristic of several overlapping π-π* transitions of the TTF and DPPZ moieties.

The DFT calculations of the Re(I) complex (Table S2) predict a separated $S_0 \rightarrow S_1$ transition in the low energy visible region (660 nm in vacuum) that consists of a pure HOMO-LUMO transition. The HOMO is localized on TTF, while the LUMO is localized on DPPZ weighted towards the phz part. The calculations predict an associated change in dipole moment of 20 D and a 10% increase in polarizability of 36 Å^3 over this ILCT transition. A transition with comparable oscillator strength is found at 384 nm and is attributed to the $S_0 \rightarrow S_{14}$ transition. The excitation is dominated (76%) by electron transfer from a molecular orbital spread broadly over TTF to the LUMO. Despite the ILCT nature of the transition, the associated dipole moment change is only 1.2 D according to DFT. The next largest oscillator strength belongs to the $S_0 \rightarrow S_7$ transition at 455 nm, which is dominated (93%) by electron transfer from a molecular orbital localized around the Re(I) ion, to the phen component of the DPPZ unit. This MLCT transition is characterized by a small dipole moment change of 1 D. Similar MLCT transitions but with weaker oscillator strengths can be found at 500 nm ($S_0 \rightarrow S_4$) and at 410 nm ($S_0 \rightarrow S_9$). The former is dominated by a charge migration (77%) from the same Re(I)-localized MO mentioned before to the phz-localized LUMO which in turn implies a larger dipole moment change of 9.5 D. The latter also entails charge migration from the Re(I) to DPPZ, however both molecular orbitals are more distributed across the Re(I) chromophore and entire DPPZ unit, respectively. The associated dipole moment change is correspondingly intermediate with a value of 3.8 D. We note that for all the aforementioned MLCT transitions, the change in polarizability is no longer marginal and at least one order of magnitude larger than for the HOMO-LUMO excitation. It is important to mention that higher energy ILCT transitions also absorb in this area albeit weakly, for example $S_0 \rightarrow S_6$ at 466 nm with associated charge migration from TTF (HOMO) to DPPZ (distributed). Furthermore, in the UV region (sub-400 nm) the remaining transitions with significant oscillator strengths are $S_0 \rightarrow S_{12}$ (395 nm) and $S_0 \rightarrow S_{16}$ (360 nm). The former has a mixed MLCT and ILCT nature with all contributing MO transitions concentrating charge on DPPZ and an associated 11 D dipole moment change and marginal change in polarizability. The latter seems to be a $\pi \rightarrow \pi^*$ transition on the TTF part with a dipole moment change of 2.6 D and large change in polarizability.

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To identify relevant transitions with large charge redistribution, the Re(I) complex was dissolved in toluene and studied with AC-Stark spectroscopy. The Stark spectrum shown in Figure 3 reveals three distinct Stark active transitions that correspond to peaks observed in the ground state absorption spectrum (Figure 3a). Liptay analysis[11] of the Stark spectra using simultaneous fitting of the ground state absorption spectrum and higher order derivative lineshapes therein allows us to extract the electronic properties of the three Stark-active transitions. They consist of a low energy absorption band attributed to the HOMO-LUMO transition, a mid-spectrum band and a UV band below 400 nm (above 25000 cm^{-1}). The parameters extracted by Liptay analysis are the change in dipole moment (Δμ), the trace of the change in polarizability tensor (Tr(Δα)), the component of change in polarizability along the transition dipole moment (m·Δα·m) and the angle between the change in dipole moment and the transition dipole moment (ζ). These parameters are listed in Table 1.

Table 1. Parameters extracted from Liptay analysis of the Stark spectra of the Re(I) complex relating to three observable transitions. See Supporting Information for details.

Transition	Δμ (D)	ζ	Tr(Δα) (Å^3)	m·Δα·m (Å^3)
HOMO-LUMO (~625 nm)	21 ± 1	22° ± 10	40 ± 20	90 ± 30
Mid spectrum (~400 nm)	9 ± 3	23° ± 8	170 ± 60	230 ± 80
UV (~320 nm)	7 ± 2	12° ± 7	N/A	N/A

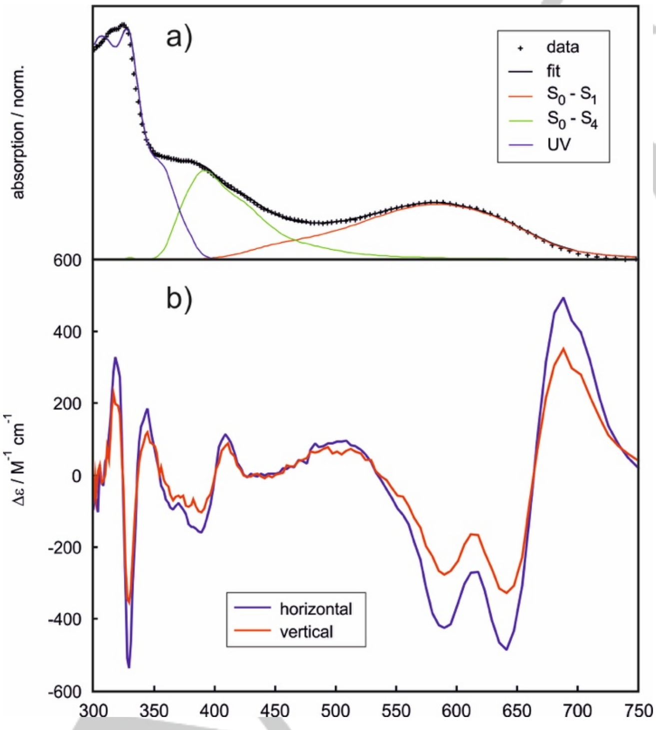

Figure 3. Ground state absorption at low temperature (a) used for Liptay analysis and Stark spectrum (b) of the Re(I) complex.

The spectrally isolated HOMO-LUMO transition in the low energy band shows a (21 ± 1) D change in dipole moment and a (40 ± 20) Å^3 change in polarizability, which is in perfect agreement with the DFT calculations for the $S_0 \rightarrow S_1$ transition predicting 20 D and 36 Å^3. The transition mid-spectrum has an associated dipole moment change of (9 ± 3) D and a change in polarizability of (170 ± 80) Å^3, which strongly suggests that this transition is dominated by $S_0 \rightarrow S_4$ with calculated values of 9.5 D and 300 Å^3. The size of the dipole moment change indicates that the charge reaches phz (DPPZ) and is not limited to the more proximate phen (DPPZ). The UV transition with a measured (7 ± 2) D dipole moment change and a negligible polarizability change appears to be a higher energy ILCT transition. A breakdown of contributions to the overall Stark spectrum is given in the SI. To get a good understanding of effect of changes in dipole moment and polarizability is vital for engineering the molecules for certain applications. We can imagine that a larger dipole moment, for example, could be advantageous for solar energy harvesting because of greater (and longer) charge separation in the photo-excited state. A sudden large increase in polarizability after photo-excitation may be interesting for molecular electronics/switching.

Femtosecond transient absorption spectroscopy (fs-TAS) of the Re(I) complex in DMF was performed with excitation of the HOMO-LUMO transition at 560 nm and of higher-lying transitions at 400 nm (Figure 4a and 4b, respectively).

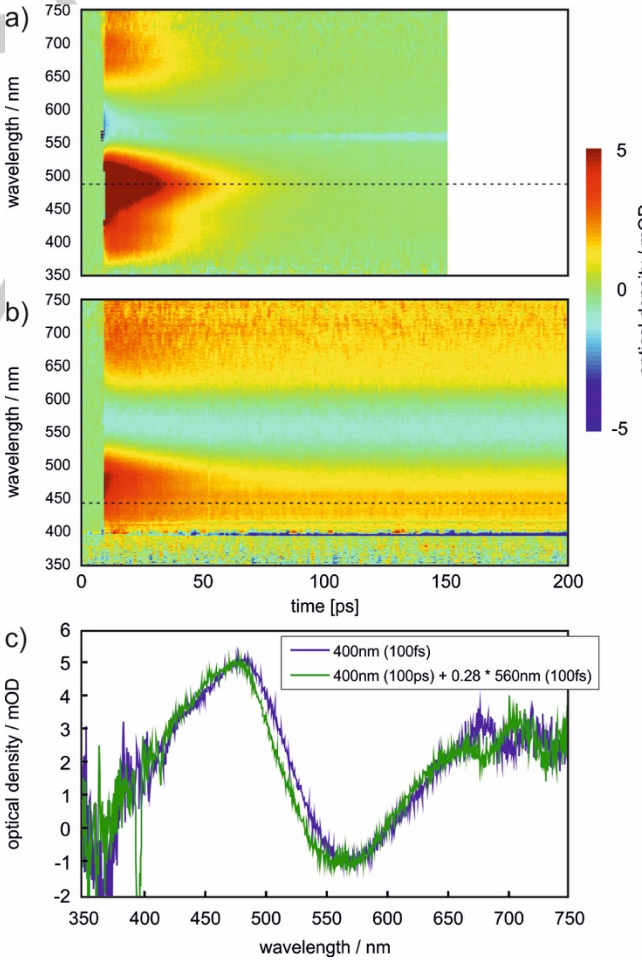

Figure 4. Femtosecond transient absorption spectra of the Re(I) complex in DMF a): λ_{ex} = 560 nm and b): λ_{ex} = 400 nm. In c) we compare the spectrum of b) at 100 fs to the sum of the spectra of b) at 100 ps plus 0.28 times the spectrum in a) at 100 fs.

When pumping the HOMO-LUMO transition at 560 nm, a negative ground state bleaching (GSB) signal is observed between 540 nm and 600 nm, which is attenuated by its overlap with the more intense excited state absorption signals (ESA) as shown in Figure 4a. Positive ESA signals are observed between 370 nm and 540 nm and from 630 nm to the edge of the spectral observation window. The latter absorbs with considerably lower cross-section. The ESA features and their rapid decay in the tens of ps regime are similar to those observed in other TTF-fused donor-acceptor systems.[9a,10,12] Moreover, the spectro-electrochemical measurements show that the singly-oxidized TTF radical cation absorbs at 475 nm and 830 nm while the reduced DPPZ anion absorbs at 490 nm (Figure S4). Consequently, these ESA bands are tentatively assigned to a charge-separated state *fac*-$[Re(CO)_3(TTF^{\cdot +}\text{-}DPPZ^{\cdot -})Cl]$. The back electron transfer to the ground state configuration occurs on the same time scale as the ESA signal decay.

The most apparent difference when exciting at 400 nm, is the persistent transient signal after 200 ps (Figure 4b). The early time dynamics seems to be similar to that in Figure 4a. In fact, if we compare a spectral slice from Figure 4b at 100 fs to the weighted sum of spectral slices from Figure 4b at 100 ps and Figure 4a at 100 fs, as shown in Figure 4c, we find excellent agreement. The comparison suggests that 400 nm excitation results in a superposition of two ESA features resulting from an ILCT (21%) and a MLCT (79%) transitions. This agrees surprisingly well with the $S_0 \rightarrow S_4$ transition which according to DFT calculations has 77% MLCT and 19% ILCT character. The broadband ESA with peak at 450 nm seen at later times after excitation and subsequent ILCT dynamics, seems to be characteristic of a whole class of $[Re(CO)_3(\alpha\text{-diimine})Cl]$ complexes, which is associated with the formation of a long-lived triplet MLCT state *via* intersystem crossing as previously observed in Re(I) complexes.[6b,6c,6g,8a,8c,13]. Remarkably, the GSB signal in a range from 520 nm to 600 nm, which is assigned to the HOMO-LUMO transition with a charge flow from the TTF to DPPZ moieties, persists along with the triplet state ESA even after the back electron transfer following ILCT. This implies that the electron resides on the LUMO on the phz of DPPZ upon excitation to the MLCT state and therefore blocks the ILCT pathway.

In conclusion, using a combination of DFT calculations, AC-Stark spectroscopy and fs-TAS, we have characterized ILCT and MLCT in the complex $[Re(CO)_3(TTF\text{-}DPPZ)Cl]$, these being associated with CT from opposite ends of the molecule to the central DPPZ unit (Figure 1). The spectrally isolated ILCT transition from the TTF to the phz of the DPPZ unit occurs at 560 nm and is accompanied by a change in dipole moment of 20 D and a slight increase in polarizability. In contrast, various MLCT-dominated transitions appear at higher energies with up to 10 D change in dipole moment and significant polarizability change. The MLCT transitions with larger dipole moment change as shown by AC-Stark Spectroscopy and fs-TAS, even reach the phz subunit and block ILCT from the opposite end. This property provides an optical control of the direction of the photo-induced CT, which is of high importance to develop an optoelectronic molecular switch triggered by light of different wavelengths.

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Keywords: Re(I) complexes • charge-transfer transitions • fused tetrathiafulvalene ligand • femtosecond transient absorption spectroscopy • AC-Stark spectroscopy

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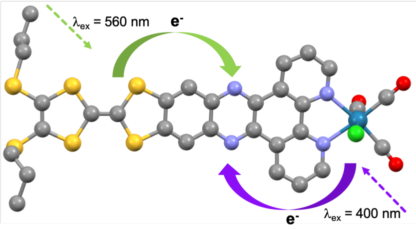

Optical control of photoinduced electron transfer *via* selective excitation wavelength is for the first time achieved by incorporation of a tetrathiafulvalene-fused dipyrido[3,2-*a*:2',3'-*c*]phenazine ligand to a Re(I) chromophore. Gating of charge flow over multiple charge-transfer pathways is a prerequisite to success in photodiodes.