# Ruthenium-Phenothiazine Electron Transfer Dyad with a Photoswitchable Dithienylethene Bridge: Flash-Quench Studies with Methylviologen

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Ⓢ Supporting Information

ABSTRACT: A molecular ensemble composed of a phenothiazine (PTZ) electron donor, a photoisomerizable dithienylethene (DTE) bridge, and a $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) electron acceptor was synthesized and investigated by optical spectroscopic and electrochemical means. Our initial intention was to perform flash-quench transient absorption studies in which the $Ru(bpy)_3^{2+}$ unit is excited selectively ("flash") and its ^{3}MLCT excited state is quenched oxidatively ("quench") by excess methylviologen prior to intramolecular electron transfer from phenothiazine to Ru(III) across the dithienylethene bridge. However, after selective $Ru(bpy)_3^{2+}$ ^{1}MLCT excitation of the dyad with the DTE bridge in its open form, ^{1}MLCT → ^{3}MLCT intersystem crossing on the metal complex is followed by triplet–triplet energy transfer to a $^3\pi-\pi^*$ state localized on the DTE unit. This energy transfer process is faster than bimolecular oxidative quenching with methylviologen at the ruthenium site (Ru(III) is not observed); only the triplet-excited DTE then undergoes rapid (10 ns, instrumentally limited) bimolecular electron transfer with methylviologen. Subsequently, there is intramolecular electron transfer with PTZ. The time constant for formation of the phenothiazine radical cation via intramolecular electron transfer occurring over two p-xylene units is 41 ns. When the DTE bridge is photoisomerized to the closed form, PTZ$^+$ cannot be observed any more. Irrespective of the wavelength at which the closed isomer is irradiated, most of the excitation energy appears to be funneled rapidly into a DTE-localized singlet excited state from which photoisomerization to the open form occurs within picoseconds.
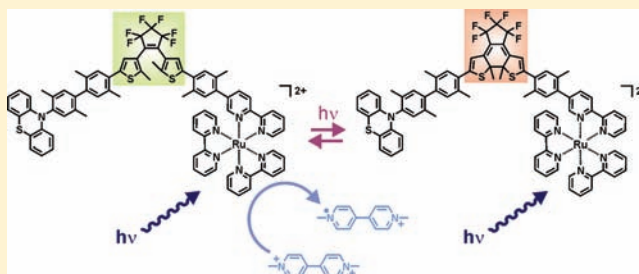
INTRODUCTION

Aside from azobenzene and its derivatives, dithienylethenes (DTEs) represent one of the most popular classes of molecules that can be switched by light between two stable isomeric forms.[1] Two important assets of DTEs are their fatigue resistance and the high reversibility of their photoisomerization reactions.[2] DTE switching units can easily be incorporated into purely organic molecular ensembles as well as into molecular constructs with metal centers.[3–11] A particularly intriguing aspect of DTE research is the question of how the two isomeric forms mediate long-range charge and energy transfer processes: In general, the photocyclized form exhibits a greater extent of π-conjugation than the open isomer,[12] and hence, there might be a possibility to control the efficiency of charge or energy transfer between distant donors and acceptors by photoswitching of a DTE bridging unit or "wire". There have been direct investigations of light-induced conductance switching in DTE molecules by integrating them into a break junction circuit, and it was found that the resistance of the DTE unit decreases from 526 ± 90 to 4 ± 1 MΩ upon photochemical ring-closure.[13] Already prior to these STM investigations, there had been work on donor-bridge-acceptor molecules in which the possibility of photonic switching of photoinduced intramolecular electron transfer was investigated, but such research

was not always crowned with success.[3,4,14–17] A common problem in this context is that phototriggering of the electron transfer event can in many cases also induce photochemical isomerization of the DTE unit.[18] Additional complications may arise from competing energy transfer processes because the closed isomer with its extended π-conjugation may act as an efficient trap for the excitation energy.[15,19–24]

For investigations of photoinduced electron transfer, porphyrins and d^6 metal diimine complexes are very attractive photosensitizers. Prior work on DTE systems with appended $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) units has shown that photoexcitation of these metal complexes ultimately populates an energetically low-lying triplet excited state of the DTE unit from where photoisomerization occurs on a nanosecond time scale.[15] Because of this quenching of the emissive ^{3}MLCT excited state of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ by DTEs, investigation of excited-state electron transfer is difficult in such systems. In this research project, we aimed to explore whether it would instead be possible to investigate ground-state electron transfer reactions involving photogenerated $Ru(bpy)_3^{3+}$ attached to a DTE unit and a suitable electron

donor. For this purpose, we synthesized a molecule composed of a phenothiazine (PTZ) electron donor, a photoswitchable DTE bridge, and a $Ru(bpy)_3^{2+}$ photosensitizer (Ru) as shown in Scheme 1. The plan was to use nanosecond laser pulses to

Scheme 1. Two Isomers of the Ruthenium-Diethienylethene-Phenothiazine Molecule Investigated in This Work
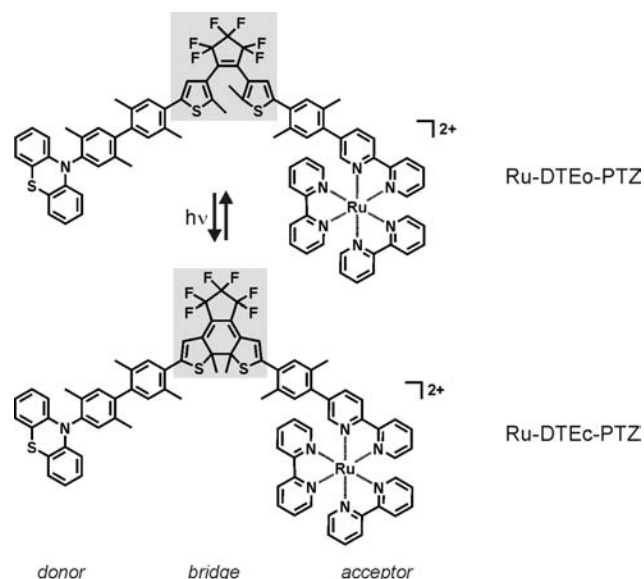
excite selectively the ruthenium moiety of this molecule while it is dissolved in acetonitrile in the presence of a large excess of the electron acceptor methylviologen. From research on numerous biological and artificial donor-bridge-acceptor systems with $Ru(bpy)_3^{2+}$ photosensitizers, it is known that this will generate $Ru(bpy)_3^{3+}$ and methylviologen radical monocation on a nanosecond time scale.[25−27] Subsequently, intramolecular electron transfer from PTZ to Ru(III) may occur, and this is a ground-state process which is no longer in competition with photoisomerization reactions associated with the DTE bridge. Our initial goal was to determine the difference in reaction kinetics for intramolecular PTZ-to-Ru(III) electron transfer in the open (DTEo) and closed (DTEc) form of the molecular bridge in order to assess to what extent long-range charge transfer rates can be controlled by photoswitchable DTE spacers. However, our efforts have been only partially successful: While it is possible to measure the kinetics of PTZ⁺ formation in the Ru-DTEo-PTZ molecule (Scheme 1, top), this turned out to be impossible for the Ru-DTEc-PTZ isomer (Scheme 1, bottom). Nevertheless, the results obtained on the open isomer are interesting in their own right because they provide new insight into charge and energy transfer processes in DTE systems with appended transition metal complexes. To the best of our knowledge, we report here on the first study of flash-quench triggered electron transfer in photoswitchable DTE systems.

RESULTS AND DISCUSSION

Synthesis. The synthesis of PTZ-DTEo-Ru is described in detail in the Supporting Information. The closed isomer Ru-DTEc-PTZ is obtained in nearly quantitative yield by irradiating solutions of the open isomer Ru-DTEo-PTZ with a portable UV lamp giving 254 nm light output. According to ¹H NMR spectroscopy, the photostationary state obtained in

CD_3CN solution under these irradiation conditions contains more than 90% of the closed isomer.

Photophysical and Electrochemical Properties. Figure 1 shows UV−vis spectra of the two isomers from Scheme 1 in
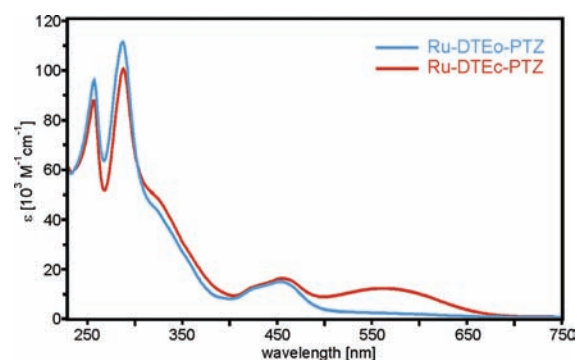

Figure 1. UV−vis spectra of the two isomers of the Ru-DTE-PTZ molecule in acetonitrile solution.

acetonitrile solution. One observes the metal-to-ligand charge transfer (MLCT) absorption associated with the $Ru(bpy)_3^{2+}$ unit centered around 450 nm, predominantly bpy-localized $\pi−\pi^*$ absorptions at 290 nm,[28] and a PTZ-localized excitation near 250 nm.[29,30] In both isomeric forms, the DTE unit contributes significantly to the absorption between 300 and 370 nm, and in the closed isomer, the absorption band extending from ∼460 to ∼750 nm is caused by the DTEc unit. At least with respect to singlet excited states, one may thus conclude that the energetically lowest lying excited state is $Ru(bpy)_3^{2+}$-localized in Ru-DTEo-PTZ and DTE-localized in Ru-DTEc-PTZ. To what extent this is also true for triplet excited states is a separate question that will be addressed below.

Figure 2 shows cyclic voltammograms of the two isomers from Scheme 1 measured in acetonitrile solution in the
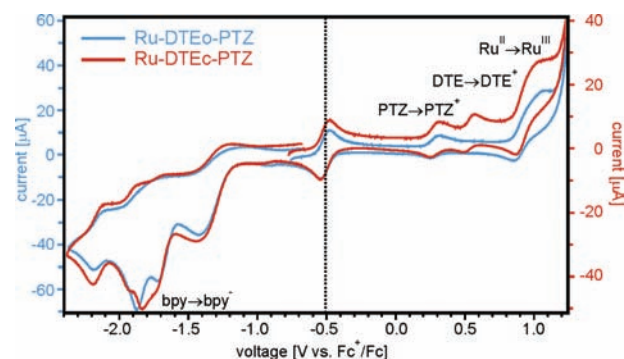

Figure 2. Cyclic voltammograms of the two isomers of the Ru-DTE-PTZ molecule in CH_3CN in the presence of 0.1 M TBAPF₆ electrolyte. The reversible wave at −0.51 V vs Fc⁺/Fc (dashed vertical line) is due to decamethylferrocene which was added to the solutions for internal voltage referencing.

presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte. Traces of decamethylferrocene (Me₁₀Fc) were added to the solutions for internal voltage referencing, and the reversible signals at −0.51 V vs Fc⁺/Fc (Fc = ferrocene) are due to the Me₁₀Fc⁺/Me₁₀Fc couple (dashed vertical line).[31] The PTZ unit exhibits a reversible oxidation at a potential of 0.27 V vs Fc⁺/Fc (Table 1), in line with prior investigations.[32] The $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$ couple appears as a quasi-

Table 1. Second and Third Column: Electrochemical Potentials (in V vs. Fc⁺/Fc) for the Individual Redox-Active Components of the Open and Closed Isomer of the Ru-DTE-PTZ Molecule. Last Column: Reduction Potentials for the Isolated Components of the Ru-DTE-PTZ Molecule in Reference Compounds or in the Free Ru(bpy)₃²⁺ Complex

| | in molecular ensemble | | |
	Ru-DTEo-PTZ	Ru-DTEc-PTZ	in reference compound from the literature
PTZ⁺/⁰	0.27	0.28	0.37[a]
DTE⁺/⁰		0.54	DTEo: 1.3[b] DTEc: 0.63[b]
Ru(III/II)	0.97	0.94	0.89[c]
bpy⁻/⁰	−1.7	−1.7	−1.68[d]
bpy⁻/⁰	−1.9	−1.9	−1.88[d]
bpy⁻/⁰	−2.1	−2.1	−2.15[d]

[a]From ref 38. [b]Measured on the DTE-ref molecule from Scheme 4.[35] [c]From ref 28. [d]From ref 39.

reversible wave at 0.97 V vs Fc⁺/Fc, consistent with previous studies.[28] In the closed isomer, a DTE-localized oxidation process is observed as a reversible wave centered at 0.54 V vs Fc⁺/Fc. Indeed, the closed forms of DTEs are known to exhibit oxidations below 1 V vs Fc⁺/Fc while the open isomers are usually oxidized at higher potentials;[33,34] in our case, the oxidation of the DTEo unit falls out of the investigated potential range. At an electrochemical potential of about −1.4 V vs Fc⁺/Fc, one observes a reduction wave that is most likely due to a reduction process involving the bridging DTE moiety.[35] At potentials of ca. −1.7, −1.9, and −2.2 V vs Fc⁺/Fc, the common bpy-reductions of the Ru(bpy)₃²⁺ complex occur.[28] All electrochemical potentials are summarized in Table 1.

The Ru-DTEo-PTZ isomer is emissive after excitation into the MLCT absorption band at 450 or 532 nm (data not shown). The luminescence band coincides spectrally with that of the isolated Ru(bpy)₃²⁺ complex in acetonitrile solution, and therefore, the emission of Ru-DTEo-PTZ is assigned to the common ³MLCT luminescence of Ru(bpy)₃²⁺. In contrast, the closed isomer is nonluminescent in acetonitrile solution, which is no surprise given the absorption data discussed above: In Ru-DTEc-PTZ, the lowest singlet excited state is DTEc-localized (Figure 1); hence, it is plausible that the lowest triplet excited state is localized on the DTEc unit as well. Indeed, prior work has demonstrated that a triplet state of DTE can be populated efficiently from the Ru(bpy)₃²⁺ ³MLCT state by triplet−triplet energy transfer; in some selected systems with emissive d⁶ metal diimine complexes, this phenomenon even served as a basis for obtaining photoswitchable luminescence properties.[36,37]

When irradiating a CH₃CN solution of Ru-DTEo-PTZ with visible or UV light, the ³MLCT emission intensity rapidly decreases, which we interpret as a manifestation of photochemical isomerization of the DTE spacer from the open to the closed form. Direct evidence for this phenomenon comes from the transient absorption data in Figure 3.

The blue trace in Figure 3a shows a transient absorption spectrum detected in a 200 ns time window starting immediately after exciting the Ru-DTEo-PTZ compound in CH₃CN at 532 nm with 10 ns laser pulses.[40] The detected spectrum is markedly different from the spectral signature of ³MLCT-excited Ru(bpy)₃²⁺ for which one commonly observes a bleach around 450 nm (due to Ru(III)) and a positive
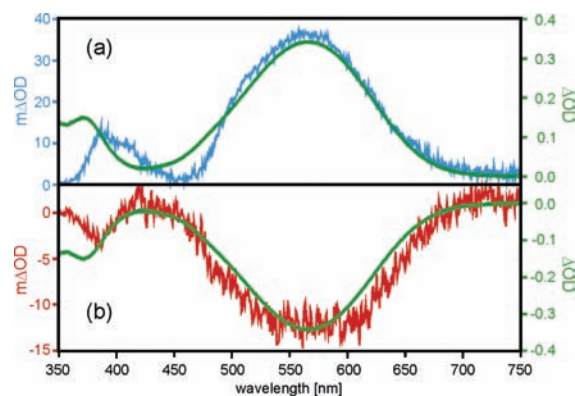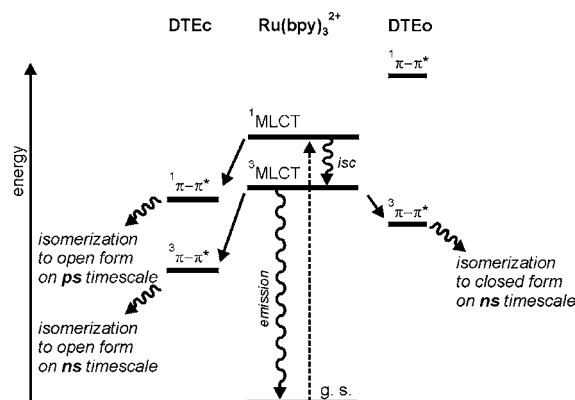

Figure 3. (a) Blue trace: Transient absorption spectrum measured in a 200 ns time window after excitation of a ∼2 × 10⁻⁵ M acetonitrile solution of Ru-DTEo-PTZ at 532 nm with laser pulses of 10 ns width.[40] Green trace: Result of a subtraction of the UV−vis spectrum of Ru-DTEo-PTZ in CH₃CN from that of Ru-DTEc-PTZ. (b) Red trace: Transient absorption spectrum measured in a 200 ns time window after excitation of a ∼2 × 10⁻⁵ M acetonitrile solution of Ru-DTEc-PTZ at 532 nm with laser pulses of 10 ns width.[40] Green trace: Result of a subtraction of the UV−vis spectrum of Ru-DTEc-PTZ in CH₃CN from that of Ru-DTEo-PTZ.

transient absorption signal around 380 nm (due to bpy⁻).[41] Here, there are two positive transient absorption signals: the more intense one maximizing near 560 nm and the weaker one centered around 400 nm. The green trace which is superimposed on the transient absorption data in Figure 3a is the result of a subtraction of the UV−vis spectrum of Ru-DTEo-PTZ from that of Ru-DTEc-PTZ.[42] This derived spectrum corresponds very well to the experimentally observed transient absorption spectrum, indicating that one essentially observes the accumulation of DTE ring-closure photoproducts in this transient absorption experiment.[43] Despite selective excitation of the ruthenium unit, ultimately, the excitation energy seems to arrive at the DTE unit where it induces photochemical isomerization. The most plausible explanation for this behavior is the presence of an energetically low lying triplet excited state on the DTE unit (even in the open isomer) which is fed from the ³MLCT state of Ru(bpy)₃²⁺ by triplet−triplet energy transfer as illustrated in the right part of Scheme 2.[15] From the ³π−π* state of DTEo, photochemical ring-closure can then occur.

Scheme 2. Qualitative Energy Level Scheme for the Ru-DTE-PTZ Molecule

When performing the exactly same transient absorption experiment with an acetonitrile solution of Ru-DTEc-PTZ, one obtains the spectrum represented by the red trace in Figure 3b. This spectrum is essentially a mirror image of that observed for the open isomer in Figure 3a (blue trace) and corresponds to the subtraction of the absorption spectrum of Ru-DTEc-PTZ from that of Ru-DTEo-PTZ (green trace in Figure 3b). We conclude that one essentially detects the accumulation of DTE ring-opening photoproducts in this experiment. In the case of the closed form of DTE, the excitation energy may arrive at the photochemically active unit either by singlet−singlet energy transfer directly from the ^{1}MLCT state or through a sequence of ^{1}MLCT to ^{3}MLCT intersystem crossing (isc) and triplet−triplet energy transfer. Depending on which pathway is taken, photoisomerization then either occurs from a $^1\pi-\pi^*$ or a $^3\pi-\pi^*$ state (left part of Scheme 2).[6,8] Photoisomerization of DTEs can occur within a few picoseconds from singlet excited states, while the lowest triplet state was previously found to react on a nanosecond time scale. When monitoring the transient absorption signals of Ru-DTEo-PTZ or Ru-DTEc-PTZ at 590 nm as a function of time (data not shown), the photoproducts are found to build up within the 10 ns duration of the laser excitation pulse. Thus, we cannot temporally resolve the photoisomerization reactions with our nanosecond equipment.

Scheme 2 illustrates why the photophysical and photochemical behavior of the Ru-DTEo-PTZ and Ru-DTEc-PTZ molecules is essentially independent of the excitation wavelength: Irrespective of whether the initial excitation occurs into the Ru(bpy)$_3^{2+}$ complex (e.g., at 450 or 532 nm) or directly into a DTE absorption (e.g., at 355 nm) and regardless of whether the DTE unit is in its open or in its closed form, the excitation energy always ends up on the DTE unit from where photoisomerization can occur. In a sense, the metal complex thus acts as a sensitizer for DTE isomerization.[6,8] One might expect different photoisomerization quantum yields depending on whether photoexcitation leads to population of a $^1\pi-\pi^*$ or a $^3\pi-\pi^*$ state on the DTE unit, but investigation of this aspect is beyond the scope of the current study.

Flash-Quench Studies of the Open Isomer with Methylviologen. Figure 4a shows the transient absorption spectrum obtained after a 532 nm excitation of a freshly prepared acetonitrile solution containing ∼2·10^{-5} M PTZ-DTEo-Ru and 50 mM methylviologen (MV^{2+}). The resulting spectrum, detected in a 200 ns time window starting immediately after the 10 ns laser pulse,[40] provides clear evidence for the formation of reduced methylviologen: Both the sharp and intense absorption at 397 nm as well as the majority of the broad band extending from 460 to 720 nm can readily be attributed to methylviologen monocation (MV$^+$).[26,32] Thus, the flash-quench method illustrated in Scheme 3 seems to work for the Ru-DTEo-PTZ compound: Following pulsed Ru(bpy)$_3^{2+}$ irradiation ("flash"), the excitation energy is used for a bimolecular electron transfer process from which MV$^+$ is the resulting reduction product.

Figure 4b shows the transient absorption spectrum measured on a reference compound called Ru-ref (Scheme 4) in the presence of 50 mM MV^{2+} in acetonitrile in the same spectral range. This compound was available from a recent study and, in a flash-quench experiment with methylviologen, exhibits rapid (τ_{ET} = 24 ns) intramolecular electron transfer from the attached tetramethoxybenzene unit to photogenerated Ru(bpy)$_3^{3+}$.[32] The oxidized tetramethoxybenzene unit has only very weak
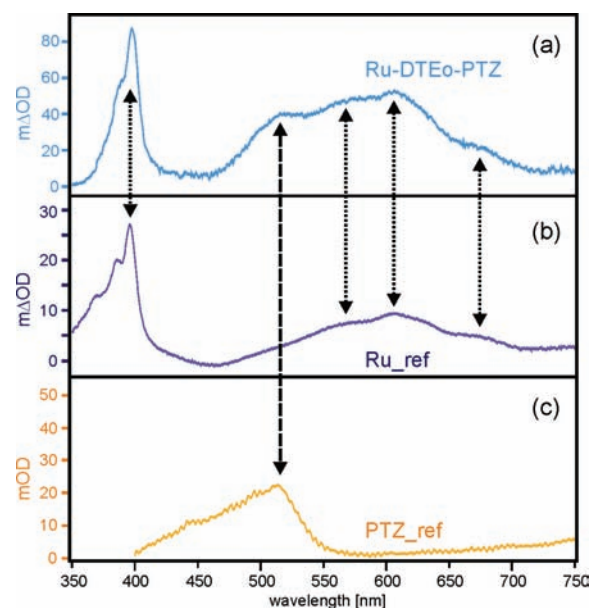

Figure 4. (a) Transient absorption spectrum obtained from an acetonitrile solution containing ∼2 × 10^{-5} M Ru-DTEo-PTZ and 50 mM methylviologen after excitation at 532 nm with 10 ns laser pulses. The data was acquired in a 200 ns time window.[40] (b) Transient absorption spectrum obtained from the reference molecule Ru-ref (Scheme 4) under analogous experimental conditions. (c) Result of a spectro-electrochemical investigation of reference molecule PTZ-ref (Scheme 4); the absorption spectrum was acquired after application of an electrochemical potential of 0.5 V vs Fc$^+$/Fc to a dichloromethane solution of PTZ-ref.

Scheme 3. Flash-Quench Method as Originally Envisioned for Investigation of Intramolecular PTZ-to-Ru(III) Electron Transfer in the Ru-DTE-PTZ Molecule
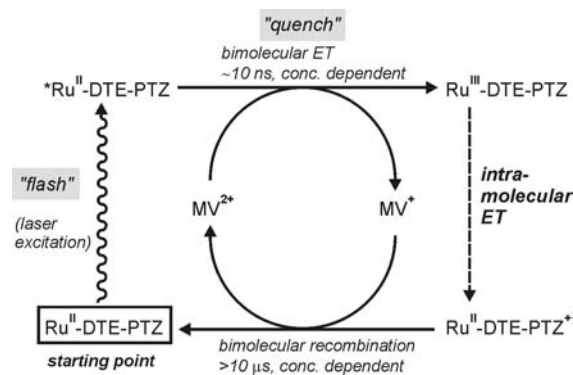
absorptions in the spectral range considered here, and therefore, the spectrum shown in Figure 4b essentially represents the spectral signature of MV$^+$ without significant interference from other absorbing species (including the ruthenium complex and attached organic moieties).[13] There is great similarity between the transient absorption spectra in Figure 4a,b: As marked by the vertical dotted arrows, there are common local absorption maxima at 397, 565, 608, and 677 nm. However, the spectrum of Figure 4a contains an additional sideband at 518 nm which is absent in the spectrum of Figure 4b and which can therefore not be attributed to MV$^+$. With the help of the spectrum in Figure 4c, the additional absorption at 518 nm is identified as a spectral fingerprint of PTZ$^+$: The spectrum in Figure 4c is the result of a spectro-electrochemical

Scheme 4. Molecular Structures of Three Reference Molecules
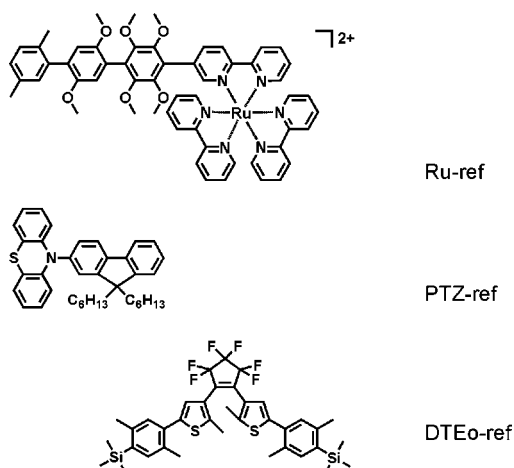
investigation of a molecule named PTZ-ref in Scheme 4.[32] Specifically, it is the UV−vis spectrum of a dichloromethane solution of PTZ-ref measured under application of an electrochemical potential of 0.5 V vs Fc$^+$/Fc.[32] Because charge-neutral PTZ is spectroscopically innocent in the relevant spectral range, the spectrum shown in Figure 4c corresponds essentially to the one-electron oxidation product PTZ$^+$. The dashed vertical double arrow in Figure 4 shows that the absorption maximum from Figure 4c coincides precisely with the additional absorption sideband in Figure 4a that is not caused by MV$^+$. We conclude that the transient absorption spectrum of Ru-DTEo-PTZ in Figure 4a is essentially a superposition of MV$^+$ and PTZ$^+$ photoproducts; in fact, it closely resembles previously reported transient absorption spectra of ruthenium-phenothiazine dyads investigated by the flash-quench technique with methylviologen.[27,30,32,44]

Figure 5a shows the temporal evolution of the transient absorption intensity from Figure 4a at 397 nm (purple trace)
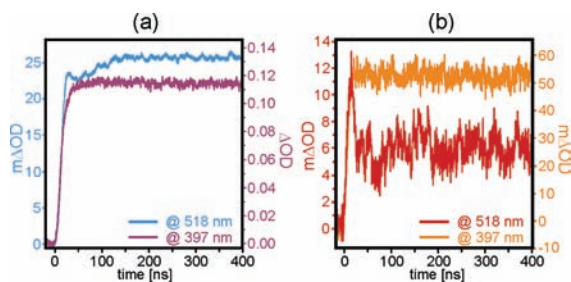

Figure 5. (a) Temporal evolution of the transient absorption signals at 397 and 518 nm from Figure 4a. (b) Temporal evolution of the transient absorption signals at 397 and 518 nm from Figure 6b.

and at 518 nm (blue trace). The optical density at 397 nm raises with an instrumentally limited rate constant of ∼8·10^7 s^{-1}; i. e., MV$^+$ is formed within the duration of the laser pulse. Such rapid kinetics at a concentration of 50 mM in MV^{2+} is consistent with the previously determined rate constant of 2.4·10^9 M^{-1} s^{-1} for the bimolecular electron transfer reaction between isolated Ru(bpy)$_3$$^{2+}$ complex and MV^{2+} in CH$_3$CN at 25 °C.[28] However, the blue trace in Figure 5a contains more important information: At 518 nm, there is an initial rapid increase of the optical density, followed by a significantly slower

rise which is only complete after ∼200 ns. The initial fast increase is attributed to the formation of MV$^+$; as seen from Figure 4b, this species has a non-negligible extinction at 518 nm. The subsequent slower rise is attributed to the formation of PTZ$^+$ by an intramolecular electron transfer event. The rate constant for this process is 2.4·10^7 s^{-1} which is clearly not an instrumentally limited value.

Our original hypothesis was that photogenerated Ru(bpy)$_3$$^{3+}$ would be the redox partner for intramolecular electron transfer with PTZ (Scheme 3). Therefore, we measured the temporal evolution of the transient absorption signal at 450 nm and were surprised to find that there are virtually no changes in optical density at this wavelength on a nanosecond time scale (data not shown). The Ru(III) oxidation product commonly displays an easily detectable bleach at 450 nm due to the disappearance of the ^{1}MLCT absorption of Ru(bpy)$_3$$^{2+}$. Intramolecular electron transfer with PTZ would be expected to lead to a bleach recovery with a rate constant of 2.4·10^7 s^{-1}, corresponding to the rate at which PTZ$^+$ is formed. The absence of any detectable MLCT bleach at 450 nm indicates that Ru(III) is either never produced or it reacts with a rate constant greater than 10^8 s^{-1}.

Prior work on DTE systems with covalently attached Ru(bpy)$_3$$^{2+}$ complexes has demonstrated that the lowest $^3\pi-\pi^*$ state of the DTE unit is populated from the ^{3}MLCT state within picoseconds.[3,4,15,23] In the flash-quench experiment, quenching of the Ru(bpy)$_3$$^{2+}$ ^{3}MLCT state by MV^{2+} is limited by diffusion and can only occur on the order of ∼1 ns when MV^{2+} is present at 50 mM concentration (this is near the solubility limit of ∼80 mM in CH$_3$CN at 25 °C). Thus, even in the presence of a large excess of MV^{2+}, intramolecular triplet−triplet energy transfer to the lowest $^3\pi-\pi^*$ state of DTEo is likely to be the most efficient ^{3}MLCT depopulation process. The question then is whether $^3\pi-\pi^*$-excited DTEo can be oxidized by MV^{2+}. The reference molecule DTEo-ref (Scheme 4) is oxidized at an electrochemical potential of 1.3 V vs Fc$^+$/Fc.[35] The precise energy of the DTEo $^3\pi-\pi^*$ state is not known, but an upper limit of 2.1 eV can be set because this is the energy of the lowest Ru(bpy)$_3$$^{2+}$ ^{3}MLCT state.[28] On this basis, we estimate an electrochemical potential for oxidation of $^3\pi-\pi^*$-excited DTEo of −0.8 V vs Fc$^+$/Fc. In acetonitrile, MV^{2+} is reduced to MV$^+$ at a potential of −0.84 V vs Fc$^+$/Fc.[28] Consequently, bimolecular electron transfer between $^3\pi-\pi^*$-excited DTEo and MV^{2+} appears thermodynamically feasible even though it may be slightly endergonic. Photoisomerization from the $^3\pi-\pi^*$ state is known to be relatively slow (nanosecond time scale; Scheme 2);[6,8] hence, bimolecular electron transfer with MV^{2+} followed by intramolecular PTZ-to-DTEo$^+$ electron transfer may indeed be a competitive reaction sequence.

In an effort to find additional experimental support for our proposed reaction sequence, we attempted to determine the spectral signature of the oxidized DTEo-ref molecule from Scheme 4 in an independent spectro-electrochemistry experiment, in order to be able to search for spectral signs of this species in transient absorption studies. However, as reported already in a recent publication, the first two oxidations of the respective DTEo unit occur at nearly the same potential, and hence, the one-electron oxidized form cannot be observed in spectro-electrochemistry.[35] Instead, one only detects the closed form of the 2-fold oxidized species, which is the result of an electrochemically induced ring-closure reaction as commonly observed for DTEs.[14]

One further piece of information supports the hypothesis of PTZ$^+$ formation via intramolecular electron transfer involving DTEo$^+$ as a redox partner, namely, the magnitude of the rate constant with which PTZ$^+$ is formed: In the Ru-DTEo-PTZ molecule, the PTZ and DTE units are connected to each other via two *p*-xylene spacers. Our own recent studies of phototriggered electron transfer with PTZ units demonstrated that rate constants on the order of 10^7 s^{-1} are typically observed for charge transfer events across two *p*-xylene, two *p*-phenylene, or one fluorene unit.[44−46] For electron transfer from PTZ to the ruthenium center in Ru-DTEo-PTZ, the observed rate constant of $2.4 \cdot 10^7$ s^{-1} is at least 3 orders of magnitude too large.

Flash-Quench Studies of the Closed Isomer with Methylviologen. Figure 6b (red trace) shows the transient
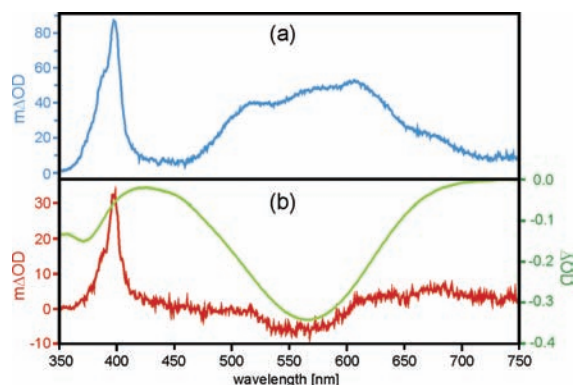

Figure 6. (a) Transient absorption spectrum obtained from an acetonitrile solution containing ∼2 × 10^{-5} M Ru-DTEo-PTZ and 50 mM methylviologen after excitation at 532 nm with 10 ns laser pulses. The data was acquired in a 200 ns time window.[40] (b) Red trace: Transient absorption spectrum obtained under identical conditions for Ru-DTEc-PTZ. Green trace: Result of a subtraction of the UV−vis spectrum of Ru-DTEc-PTZ in CH$_3$CN from that of Ru-DTEo-PTZ.

absorption spectrum obtained after a 532 nm excitation of a freshly prepared acetonitrile solution containing ∼2·10^{-5} M PTZ-DTEc-Ru and 50 mM methylviologen (MV^{2+}). The spectrum was detected in a 200 ns time window starting immediately after the 10 ns laser pulse,[40] i.e., under exactly the same conditions as the transient absorption spectrum of the open isomer from Figure 4a. For better comparison with the closed isomer, the spectrum obtained from Ru-DTEo-PTZ has been reproduced in Figure 6a (blue trace).

The sharp signal at 397 nm in Figure 6b is indicative of MV$^+$, but most of the absorbance expected for the MV$^+$ monocation between 460 and 720 nm is absent. It appears that the respective MV$^+$ absorptions are masked by a process that causes negative absorbance changes in the relevant spectral range; this is particularly evident between 520 and 600 nm where the ΔOD signal becomes negative. The green trace in Figure 6b is the result of a subtraction of the ground-state absorption spectrum of Ru-DTEc-PTZ from that of Ru-DTEo-PTZ. The superposition of the two traces in Figure 6b strongly suggests that the MV$^+$ absorptions between 460 and 720 nm cannot be observed because photoisomerization of DTEc to DTEo is a competitive process after photoexcitation of Ru-DTEc-PTZ. This makes sense because, in the case of the closed isomer, a DTE-localized $^1\pi-\pi^*$ state can be populated after Ru-(bpy)$_3^{2+1}$MLCT excitation (Scheme 2). Photoisomerization of DTEs from singlet excited states is known to be about 3

orders of magnitude more rapid than from triplet excited states.[3,4,15] Thus, a significant portion of the excitation energy seems to be funneled directly into rapid DTEc → DTEo isomerization, while another portion of the excitation is obviously used to generate MV$^+$ (Figure 6b). Specifically, we assume that another portion of the excitation energy ends up in a DTE-localized $^3\pi-\pi^*$ state which lives long enough to undergo bimolecular electron transfer with MV^{2+}. Scheme 2 shows that this is thermodynamically possible. There is no simple experimental way to support this hypothesis, but given the undisputable observation of reduced methylviologen and photochemical ring-opening, it is a very plausible reasoning. The primary oxidation product of bimolecular electron transfer between MV^{2+} and PTZ-DTEc-Ru is likely to be DTEc$^+$ because photoexcited DTEc is even easier to oxidize than photoexcited DTEo (see Figure 2 and Table 1 for ground-state potentials).

From the data in Figure 5b, we learn that the absorption at 518 nm reaches a maximum within the laser pulse and then rapidly decreases to reach a ΔOD value that is essentially constant on a microsecond time scale. The fast rise within the laser pulse is likely to reflect formation of MV$^+$ (possibly including a fraction of PTZ$^+$) before a second process, presumably photoisomerization, leads to a reduction of the ΔOD value which is complete after 25 ns. Given the fact that the rate for bimolecular electron transfer with methylviologen is already limited by diffusion, there is no possibility to accelerate electron transfer with respect to the competing photo-isomerization reaction. Consequently, the spectrum from Figure 6b cannot be disentangled any further, and we are forced to conclude that we can observe neither PTZ$^+$ nor any other oxidized component of the Ru-DTEc-PTZ molecule in our flash-quench experiment.[47]

■ SUMMARY AND CONCLUSIONS

The main purpose of the current study was to assess to what extent flash-quench transient absorption studies are useful for investigation of phototriggered electron transfer in donor-bridge-acceptor systems containing photoisomerizable DTE units and d^6 metal diimine photosensitizers. To the best of our knowledge, our paper represents the first report of a photoswitchable donor−acceptor system investigated by the flash-quench method. The most important conclusion is that, regardless of what excitation wavelength is used and irrespective of which DTE isomer is considered, in the PTZ-DTE-Ru molecule the excitation energy always ends up on the DTE unit. In the case of the open isomer, the excitation energy is fed into a $^3\pi-\pi^*$ state of the DTE unit while in the closed isomer it is a $^1\pi-\pi^*$ state, only a small fraction of the excitation energy appears to end up in the $^3\pi-\pi^*$ state of the closed DTE. This is important because photoisomerization from the $^3\pi-\pi^*$ state occurs only on a nanosecond time scale while the $^1\pi-\pi^*$ state reacts within picoseconds.[6,8] Since bimolecular electron transfer with methylviologen can only occur on a nanosecond time scale, the flash-quench procedure can only be applied successfully to the open isomer, while for the closed form there is too much interference from photoisomerization side reactions.

In Ru-DTEo-PTZ, the ultimate oxidation product of the flash-quench sequence is PTZ$^+$. It appears plausible that the rate-determining step ($k = 2.4 \cdot 10^7$ s^{-1}) for the formation of this species is intramolecular electron transfer to flash-quench generated DTE$^+$. Without the use of the flash-quench method,

the Ru-DTEo-PTZ molecule simply photoisomerizes and intramolecular electron transfer cannot be observed. Thus, at least for the open isomer of our dyad, the applied method leads to (partial) success. The finding that DTE is directly involved as a redox partner in intramolecular electron transfer with PTZ (and not just as a bridge mediating electron transfer between PTZ and ruthenium) is noteworthy.

In agreement with prior investigations, we find that the $Ru(bpy)_3^{2+}$ complex acts as a sensitizer for DTE photoisomerization,[6,8] but for investigations of phototriggered intramolecular electron transfer in systems containing DTE units in their closed forms, it represents a rather poor choice. Thus, it appears much more promising to investigate the switching of electron transfer in DTE molecules by focusing on mixed-valence systems, where phototriggering of charge transfer is not required and where detection of intervalence absorption bands can occur in spectral ranges in which undesired photoisomerization reactions cannot be induced unintentionally.[35,48−53] However, as long as one is interested in charge transfer phenomena involving the open forms of DTEs, the flash-quench method can provide insight that cannot be obtained from simple photoexcitation.

EXPERIMENTAL SECTION

Commercially available chemicals were used as received without further purification. Solvents where dried by standard methods. Preparative column chromatography occurred on Silica Gel 60 from Machery-Nagel. For NMR spectroscopy, Bruker Avance DRX 300 and Bruker B-ACS-120 instruments were employed. Electron ionization mass spectrometry (EI-MS) was performed on a Finnigan MAT8200 instrument; for elemental analysis, a Vario EL III CHNS analyzer from Elementar was used. Cyclic voltammetry measurements were made using a Versastat 3-200 potentiostat from Princeton Applied Research equipped with a glassy carbon working electrode, a silver counter electrode, and a silver wire quasi-reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Decamethylferrocene (Me$_{10}$Fc) was added for internal voltage referencing. Nitrogen gas was bubbled through the dried solvent before starting voltage sweeps at 100 mV/s. UV−vis spectra were measured on a Cary 300 instrument from Varian. Steady-state luminescence spectra were measured on a Fluorolog-3 instrument (FL322) from Horiba Jobin-Yvon, equipped with a TBC-07C detection module from Hamamatsu. For transient absorption spectroscopy, we used an LP920-KS instrument from Edinburgh Instruments, equipped with an iCCD camera from Andor and an R928 photomultiplier. The excitation source was a Quantel Brilliant b laser equipped with an OPO from Opotek. All spectroscopic measurements occurred in aerated acetonitrile solution.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic protocols and characterization data for the Ru-DTEo-PTZ molecule and all intermediate reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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