A Hole Delocalization Strategy: Photoinduced Mixed-Valence MLCT States Featuring Extended Lifetimes

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Supporting Information

ABSTRACT: Bimetallic trans-[RuII(tpm)(bpy)(μNC)-RuII(L)2(CN)]2+, where bpy is 2,2'-bipyridine, tpm is tris(1- pyrazolyl)methane and L = 4-methoxypyridine (MeOpy) or pyridine (py), was examined using ultrafast vis-NIR transient absorption spectroscopy. Of great relevance are the longest-lived excited states in the form of strongly coupled photoinduced mixed-valence systems, which exhibit intense photoinduced absorptions in the NIR and are freely tunable by the judicious choice of the coordination spheres of the metal ions. Using the latter strategy, we succeeded in tailoring the excited state lifetimes of bimetallic complexes and, in turn, achieving significantly longer values relative to related monometallic complexes. Notable is the success in extending the lifetimes, when considering the higher density of vibrational states, as they are expected to facilitate nonradiative ground-state recovery.

INTRODUCTION

Artificial photosynthesis, a multifaceted approach to foster the conversion of solar energy into chemical energy, is a promising alternative to the widespread use of fossil fuels. Success in artificial photosynthesis requires, however, the synergy of three key steps: light absorption, charge separation, and multicharge catalysis. All three steps have been unified in integrated systems by means of designing photocatalytically active electron donor–acceptor ensembles; they evolved as gold standards in the mimicking of natural photosynthesis. Implicit is a structural modification that targets at the optimization of the individual components as well as the integrated ensembles. An important consideration is that a unidirectional, high quantum-yield funneling of the excited state energy from the Franck-Condon excited states to the charge separated states should commence with the initial photoexcitation. Lifetimes of the correspondingly formed charge separated states are critical, as they determine the time window for the desired redox reactivity at the catalytic sites. A common denominator is the manipulation of electron donor–acceptor interactions in the excited state, that is, the electronic coupling element. For example, low-energy barriers are desirable for a fast excited-state transformation to afford the charge-separated state, while high-energy barriers are required to slow down the charge recombination.

As far as the ground state is concerned, electrochemical and spectroscopic assays provide an easy access to unravel electron donor–acceptor interactions. In stark contrast, insights into interactions in the excited state are much harder to gather; measuring, for example, excited-state electrochemical properties renders rather difficult. This leads to the grand challenge in the field of electron donor–acceptor systems: a direct comparison between ground and excited states. To this end, multimetallic chromophores, such as multimetallic ruthenium polypyridines, are ideally suited. Ground-state mixed-valence (GSVM) systems, which are generated by means of their one-electron oxidation and feature a metal–metal mixed-valence (MV) core, have been extensively studied, including mixed organic–inorganic approaches and supramolecular systems for...

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solar energy conversion in dye-sensitized solar cells (DSSCs)\textsuperscript{11−16} GSMV moieties are fully comparable with their excited state analogues, that is, photoinduced mixed-valence (PIMV) excited states. PIMV systems bear the same metal–metal MV core as GSMV but carry, in addition, an electron accepting ligand in its one-electron reduced form. For example, we have recently reported on a PIMV state with a \{tppRu\}\textsuperscript{II} configuration upon photoexcitation of trans-\{Ru\}\textsuperscript{II}(tpp)(bpy)(μCN)Ru\textsuperscript{II}(py)\textsubscript{2}Cl\textsuperscript{2−}\textsuperscript{+} (RuRuCl\textsuperscript{2+}). The PIMV lifetime was around 1 ns, while a localized \{(tppRu)\textsuperscript{II}Ru\textsuperscript{III}\} excited state persists in that complex for 6 ns.\textsuperscript{17}

In the current work, we turn to bimetallic trans-\{Ru\}\textsuperscript{II}(tpm)-(bpy)(μNC)Ru\textsuperscript{II}(L)\textsubscript{4}(CN)\textsuperscript{2−}\textsuperscript{+} (RuRuCl\textsuperscript{2+}). The tpm is tris(1-pyrazolyl)methane and L = 4-methoxypyridine (MeOpy) or pyridine (py) (Figure 1), and characterize their photoexcited states using vis-NIR transient absorption spectroscopy. We demonstrate that the longest-lived (trans-\{Ru\}\textsuperscript{II}(tpm)-(bpy)(μNC)Ru\textsuperscript{II}(L)\textsubscript{4}(CN)\textsuperscript{2−}\textsuperscript{+})\sp{2} excited state is a strongly coupled PIMV, whose MV properties rule the overall lifetimes. Our results are groundbreaking, as they corroborate that a judicious choice of the coordination spheres of the metallic ions allows tuning the electronic communication in the ground state and in the excited state. Notable is, for example, the significantly longer excited state lifetimes, which were realized for the bimetallic complexes in comparison with the related monometallic complexes.

**RESULTS**

The absorption spectra of RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+} and their electrochemistry have been previously reported.\textsuperscript{18,19} Their one-electron oxidized species, namely, mixed-valence RuRu(MeOpy)\textsuperscript{3+} and RuRu(py)\textsuperscript{3+}, have also been characterized.\textsuperscript{19} Figure 2 shows the differential absorption spectra following the one-electron oxidation process of the two complexes, corresponding to \{Ru(L)\textsubscript{4}\} oxidation. In the visible region, bleaching of the MLCT absorptions is attenuated by the presence of broad bands relating to ground-state and in the excited state. Notable is, for example, the significantly longer excited state lifetimes, which were realized for the bimetallic complexes in comparison with the related monometallic complexes.

![Figure 1. Structure of the bimetallic RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+} complexes and monometallic Ru(NCS)\textsuperscript{2−} reference.](image)

which were recorded upon excitations at different wavelengths, are displayed in Figures S1 and S2. Quite interesting is the dependence of the emission maxima—715 versus 739 nm—upon the excitation wavelength—387 versus 505 nm. This leads us to postulate the presence of more than one emissive state. In complementary emission lifetime measurements (Figure S3), we derive biexponential decays. This is per se consistent with the involvement of two states, that is, a short-lived and a long-lived, in the emissive cascade of RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+}. Overall, the emission energies as well as the emission lifetimes (Table 1) are in a range typical of MLCT excited states.\textsuperscript{20} In contrast, the emission in the monometallic Ru(NCS)\textsuperscript{2−} reference stems from a single state regardless of the excitation wavelength.\textsuperscript{21} In other words, the presence of a second metal center seems responsible for an additional emitting state in bimetallic RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+}. Despite the higher density of vibrational states that are present in bimetallic RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+}, their emission lifetimes are, however, longer than those in monometallic Ru(NCS)\textsuperscript{2−}. It is worth noting that linked Ru polypyridines exhibiting dual emission phenomena have been reported, but in those cases, each of the linked fragments is itself emissive.\textsuperscript{20−27} In contrast, the bimetallic complexes presented in this work bear a nonemitting \{Ru(L)\textsubscript{4}\} site,\textsuperscript{28} which highlights the impact of metal–metal interactions in the excited state properties.

To unveil the nature of the emitting excited states and their dynamics, we performed nanosecond transient absorption spectroscopic (ns-TAS) measurements with RuRu(py)\textsuperscript{2+} and RuRu(MeOpy)\textsuperscript{2+} using 387 and 505 nm excitation. Following time delays of 15 ns, only single exponential decay kinetics are observed independently of the excitation wavelength. Figure 3 shows representative spectra at 15 ns time delays. Common to both of them are a total of four features: On one hand, two identical photoinduced transitions evolve at around 19,000 and 13,000 cm\textsuperscript{−1}. On the other hand, two nonidentical photoinduced transitions are noted at around 23,000 and 8500 cm\textsuperscript{−1}. The earlier differs in terms of intensity; the intensity is higher for RuRu(MeOpy)\textsuperscript{2+} than for RuRu(py)\textsuperscript{2+} due to contributions from PILMCT absorptions from the MeOpy ligands.\textsuperscript{28} The latter differs in terms of energy and depends on the nature of the complex. For example, it is absent in the monometallic
DMSO at Room Temperature

Regarding the long-lived excited states, whose lifetimes are 15 ns and longer, the holes located in d-orbitals parallel to the main molecular z-axis that contains the cyanide bridge. Thus, we label them 3MLCTz. In the corresponding spectra, the MLCT(bpy)-centered GS bleaching is absent, in contrast with the vast majority of {Ru(pollypyridine)} complexes. Here, the negative signal is masked by much stronger photoinduced LMCT (PILMCT) transitions in the same spectral region, in sound agreement with observations on the {Ru(tpm)(bpy)} fragment. We assign a similar, bpy-centered configuration of the electron for 3MLCTxy (blue) and 3MLCTz (green). Bottom right: concentration evolution over time of the 3MLCT excited states.

Further examination of the ns-TAS data reveals the nature of another ns-lived state, as suggested by TCSPC experiments. Global target analyses of the transient absorption data (Tables S1 and S2) were performed by means of the kinetic model shown in Figure S7: two coexisting species, which both decay to the GS, as one of them transforms into the other. [Evidence for the process connecting these excited states comes from picosecond experiments; please see below.] In the case of RuRu(MeOpy)2+, 387 nm photoexcitation leads to lifetimes of 0.9 and 513 ns. The species-associated difference spectra (SADS) are summarized in Figure 4. Regarding the long-lived species (513 ns), its SADS is virtually identical to the differential absorption spectrum at 15 ns time delay assigned as 3MLCTz. The short-lived species (0.9 ns) lacks any appreciable transition in the NIR region. This leads us to conclude that it must be an excited state without any sizable metal–metal electronic communication. Here, the hole resides in an orbital perpendicular to the main molecular z-axis. Consequently, metal–metal overlaps as well as electronic couplings are both insignificant. Its label is 3MLCTxy. 3MLCTxy and 3MLCTz feature similar fingerprints in the 450 nm region due to the one-electron reduction of the bpy ligand (Figure 4). Thus, we assign a similar, bpy-centered configuration of the electron for 3MLCTxy and 3MLCTz. We applied the same kinetic model for 387 nm excitation of RuRu(py)2+ (Figure S5) and for 505 nm excitation of RuRu(py)2+ and RuRu(MeOpy)2+ (Figures S4 and S6). The fitting parameters are put together in Table S3.

To shed light onto the population mechanisms of 3MLCTxy and 3MLCTz, femtosecond transient absorption spectroscopic (fs-TAS) measurements were carried out by using a 387 nm excitation wavelength. Of great value are the time-dependent absorption changes observed for RuRu(py)2+ and RuRu(MeOpy)2+ reference spectra in Table S1. Excitation at 405 nm. Excitation at 515 nm.

**Table 1. Photophysical Data for the Bimetallic RuRu(MeOpy)2+, RuRu(py)2+, and Monometallic Ru(NCS)+ Reference in DMSO at Room Temperature**

| compound | \(\lambda_{em}/\text{nm} \) | \(\phi_{int}/10^{-3} \) | \(\tau_{em}/\text{ns} \) |
|---|---|---|---|
| Ru(NCS)+ | 740 | 3.1 | 30.5 |
| RuRu(MeOpy)2+ | 715 | 2.5 | 47 (0.76), 51.5 (0.24) |
| RuRu(py)2+ | 712 | 1.3 | 4.5 (0.84), 49.4 (0.16) |
| RuRu(MeOpy)2+ | 740 | 3.0 | 31.5 |
| RuRu(py)2+ | 739 | 4.6 | 4.1 (0.41), 51.4 (0.59) |
| RuRuCl2+ | 738 | 4.0 | 3.8 (0.69), 54.4 (0.31) |

“Lifetime errors for the biexponential fits for RuRu(MeOpy)2+ and RuRu(py)2+ are indicated in Table S1. Excitation at 405 nm. Excitation at 515 nm.”

**Table 2. Electrochemical and Spectroscopic Information Regarding the Electronic Communication in Bimetallic RuRu(py)2+, RuRu(MeOpy)2+, and RuRuCl2+**

| compound | \(\Delta(\Delta E)/V \) | \(\nu(\text{GSIVCT})/\text{cm}^{-1} \) | \(\nu(\text{PIIVCT})/\text{cm}^{-1} \) |
|---|---|---|---|
| RuRu(py)2+ | 0.41 | 6200 | 8800 |
| RuRu(MeOpy)2+ | 0.50 | 6500 | 8100 |
| RuRuCl2+ | 0.87 | 10400 | 6900 |

“Differences between Ru(III/II) couples within each bimetallic complex, measured in ACN. Measured in ACN. Measured in DMSO. *From ref 19. **From ref 29. ***From ref 17.”

**Figure 3.** Normalized differential absorption spectra of RuRu-(MeOpy)2+, RuRu(py)2+, and Ru(NCS)+ at a 15 ns time delay, upon 387 nm excitation in DMSO at room temperature.

**Figure 4.** Upper left: Differential absorption 3D map obtained from ns-TAS experiments \(\lambda_{em} = 387 \text{ nm} \) for RuRu(MeOpy)2+ in DMSO at room temperature. Upper right: Time absorption profiles (open circles) and corresponding fittings from target analysis (solid lines). Bottom left: Species-associated differential absorption spectra for 3MLCTxy (blue) and 3MLCTz (green). Bottom right: concentration evolution over time of the 3MLCT excited states. **Figure S5.**
revealed four consecutive processes (Table S4), target analysis using a four-species model (Figure 6) was used to fit the data.

Figure 6. Four-state kinetic model used to fit the picosecond pump–probe data recorded with bimetallic RuRu(MeOpy)2+ and RuRu(py)2+ upon 387 nm excitation.

It includes an initially populated state, which represents a combination of different vibrationally hot-3MLCT excited states, all of which are short-lived. [All of our attempts to individually resolve them failed.] During the first picoseconds, these hot-3MLCTs decay via three parallel branches. The result is the population of three different, coexisting excited states. Two of them, namely, 3MLCTxy and 3MLCTz, are long-lived, while a third one decays completely within a few tens of picoseconds. Analyses yield a lifetime of 72 ps for the short-lived excited states, while the lifetimes of 4.7 and 51.3 ns, respectively, in agreement with ns-TAS and TCSPC experiments.

First, the differential absorption spectrum of hot-3MLCT shows a combination of features stemming from the initially populated excited states. Second, the 72 ps lived species gives rise to very weak photoinduced absorbance in the NIR. Hence, we assign it as a state where the hole is, on one hand, perpendicular to the bridge and, on the other hand, centered on the Ru of the {Ru(L)4} moiety. Its label is 3MLCTr, that is, a \( \{Ru^{II}(tpm)(bpy^-)\}_{\mu NC}Ru^{II}(L)_4(CN)^- \) configuration. [This excited state is also involved, for example, as the final state in electronic transitions from the singlet ground state of these complexes calculated by TDDFT methods (transition nos. 4–6 for RuRu(MeOpy)2+ and 6 and 7 for RuRu(py)2+, Figures S17 and S18, Tables S8 and S9).] Importantly, the fact that the \( \{Ru(L)_4\} \) fragment is prone to nonradiative deactivation;20 it causes the overall short lifetime. We believe that 3MLCTr is originated from a fractional, initial population of \( \{Ru(L)_4\} \)-centered MLCT states, which are only accessible upon 387 nm but not 505 nm light absorption. This is consistent with our experiments using 505 nm excitation (Figure S8), which leads to similar results with the exception that a reasonable fitting is based on only three species: hot-3MLCT, 3MLCTxy, and 3MLCTz. [The behavior of RuRu(py)2+ under 387 and 505 nm excitation (Figures S9 and S10) is analogous to that of RuRu(MeOpy)2+.] Importantly, the mechanism, which we present in Figure 6, is virtually identical to the model employed to fit the decay of the related cyanide-bridged bimetallic complex RuRuCl2+.17 Please note the continuous growth of the PIIVCT throughout the entire fs-TAS time scale (trace at 7690 cm\(^{-1}\), Figure 5), which corroborates that 3MLCTr and 3MLCTxy transition into 3MLCTz. Third, the differential absorption spectra of the 4.7 and 51.3 ns lived species resemble those found in ns-TAS experiments and, as such, further support their assignment as 3MLCTxy and 3MLCTz. All kinetic parameters extracted from target analyses are collected in Table S5.

■ DISCUSSION

Excited State Differential Spectra and Hole Delocalization. The 3MLCTz differential absorption spectra for RuRu(py)2+ and RuRu(MeOpy)2+ are in sound agreement with the findings for the emissive MLCT state in Ru(NCS)2+. In Ru(NCS)2+, the emissive state corresponds to an electronic configuration with the hole in a d(Ru) orbital that points toward the NCS ligand. In other words, an orientation along the z-axis similar to that in RuRu(py)2+ and RuRu(MeOpy)2+. The spectroscopic signature is a strong photoinduced dπ( Ru) ← π(NCS) LMCT absorption at 16,500 cm\(^{-1}\) (600–610 nm) (Figure 3).22 For 3MLCTz in RuRu(py)2+ and RuRu(MeOpy)2+, the lowest energy photoinduced fingerprint is ascribed to a PIIVCT transition.17 The latter is centered at 8100 cm\(^{-1}\) (1230 nm) for RuRu(MeOpy)2+ and 8800 cm\(^{-1}\) (1150 nm) for RuRu(py)2+. As the donor strength of L increases, PIIVCT shifts to the red. This indicates that, in contrast to the GS, in the excited state \( \{Ru(bpy)\} \), dπ orbitals lie above those of the \( \{Ru(L)_4\} \) moiety. This is a consequence of the destabilizing effects of the bpy radical anion. As far as the PIIVCT transitions are concerned, the electron donor and acceptor roles are reversed relative to the GSIVCT transitions and now the Ru in \( \{Ru(tpm)(bpy)\} \) is the acceptor. This behavior has been recently observed in related ruthenium bimetallic complexes.33 Common to RuRu(py)2+ and RuRu(MeOpy)2+ is an additional 3MLCTz fingerprint at 12,500 cm\(^{-1}\) (800 nm), which is, however, independent of L. Its origin is similar to that for the PIVMLCT transition in Ru(NCS)2+ at 16,500 cm\(^{-1}\); it is ascribed to a photoinduced dπ(Ru) ←
π(CN) LMCT involving the cyanide bridge and \{Ru(bpy)\} with contributions from photoinduced dπ(Ru) → π(bpy) LMCT (Tables S7 and S8).

To confirm our spectral assignment of the electronic 3MLCTz configuration, we calculated the electronic absorption spectra of the lowest triplet states of \(\text{RuRu(py)}^{2+}\) and \(\text{RuRu(MeOpy)}^{2+}\) by (TD)DFT methods. Notably, the calculations show intense transitions with IVCT character, whose energies match those observed experimentally for both complexes (Figures S12 and S13, Table S6) and whose computed electronic configuration is an accurate description of the 3MLCTz excited state. The calculated density of unpaired spins is largely located on the \{Ru(tpm)(bpy)\} fragment (Figure S14), supporting our interpretation of a photoinduced acceptor and leading to a higher degree of delocalization for \(\text{RuRu(MeOpy)}^{2+}\). The Mulliken spin densities on the \{Ru(bpy)\} and \{Ru(L)4\} metallic ions are 0.71 and 0.18, respectively, in \(\text{RuRu(MeOpy)}^{2+}\), and 0.79 and 0.13, respectively in \(\text{RuRu(py)}^{2+}\). Interestingly, 3MLCTz is more localized in \(\text{RuRu(MeOpy)}^{2+}\) and \(\text{RuRu(py)}^{2+}\) than in \(\text{RuRuCl2}^{+}\). For \(\text{RuRuCl2}^{+}\), a delocalized configuration with Mulliken spin densities of 0.50 and 0.47 and a lower PIIVCT energy were calculated. As a matter of fact, the PIIVCT energy was much lower than the values obtained here. In other words, a shift to lower energies goes hand-in-hand with a higher delocalized character as, for example, in the GSIVCTs.

From the lack of photoinduced absorptions in the NIR for 3MLCTxy differential absorption spectra, we conclude that the metal–metal electronic coupling in these excited states is weak. Additionally, the 12,500 cm\(^{-1}\) fingerprint is absent. The visible range of this differential spectrum is governed by a bleaching at 22,200–20,000 cm\(^{-1}\) (450–500 nm), where the MLCT \{Ru(bpy)\} absorptions dominate the ground state. A very similar differential absorption spectrum was gathered for an excited state with the hole repelled from the z-axis in \(\text{Ru(NCS)}^{+}\). Together, these observations are in line with the proposed \{Ru\{tpm\}(bpy)\}(πNC)Ru\{L\}4(CN)\} configuration for this state.

**Kinetic Model and Excited State Lifetimes.** Notably, our kinetic model describes the excited state dynamics of \(\text{RuRu(py)}^{2+}\) and \(\text{RuRu(MeOpy)}^{2+}\) very well. A similar model was also employed to analyze the excited state decay of the closely related complex \(\text{RuRuCl2}^{+}\). Thus, it seems widely applicable in the field of multimetallic chromophoric coordination compounds.

3MLCTxy and 3MLCTz coexist on the nanosecond time scale. However, in contrast to \(\text{RuRuCl2}^{+}\), 3MLCTz is the longest lived excited state for \(\text{RuRu(MeOpy)}^{2+}\) and \(\text{RuRu(py)}^{2+}\). We believe that three factors contribute to these findings: First, like electron delocalization in extended aromatic ligands,

\[\Delta \text{H}_{\text{c}} = 0.095 \text{ kcal mol}^{-1}\]

\[\Delta \text{H}_{\text{c}} = 387 \text{ and } 505 \text{ nm, } 70 \text{ pJ per pulse}\]

3MLCTz is more localized in \(\text{RuRu(MeOpy)}^{2+}\) and \(\text{RuRu(py)}^{2+}\) than in \(\text{RuRuCl2}^{+}\). For \(\text{RuRuCl2}^{+}\), a delocalized configuration with Mulliken spin densities of 0.50 and 0.47 and a lower PIIVCT energy were calculated. As a matter of fact, the PIIVCT energy was much lower than the values obtained here. In other words, a shift to lower energies goes hand-in-hand with a higher delocalized character as, for example, in the GSIVCTs.

Furthermore, experiments to investigate these barriers are being carried out in our laboratories.

**EXPERIMENTAL SECTION**

**Materials and Methods.** \(\text{RuRu(MeOpy)}^{2+}\) and \(\text{RuRu(py)}^{2+}\) were prepared according to published procedures. Anhydrous DMSO was provided by Sigma-Aldrich and used as supplied.

Excitation and emission spectra were recorded in a PTI-QuantaMaster or a Cary Eclipse spectrophotometer. Quantum yields were measured in argon-saturated solutions using \([\text{Ru(bpy)}]^{2+}\) (\(\phi = 0.095\) \text{ kcal mol}^{-1\	ext{ACN}}\text{ at } 25 \text{ °C})

Fluorescence lifetimes were determined through the time-correlated single photon counting (TCSPC) technique using a system of in-lab built laser LEDs (7 MHz, \(\phi = 50 \text{ps, } \Delta \text{H}_{\text{c}} = 405 \text{ and } 515 \text{ nm, } 70 \text{ pJ per pulse}\)) with a SPAD detection system from Micro Photon Devices controlled by a TimeHarp 260 board from PicoQuant. Photolysis studies were performed following a previously reported procedure. All measurements were conducted under an argon atmosphere. The time profiles were recorded at 700 nm. Ultrafast transient absorption (TA) experiments were conducted using an amplified Ti:sapphire fs laser system (Clark MXR CPA2101 and 2110, 1 kHz, \(\phi = 150 \text{fs, } \Delta \text{H}_{\text{c}} = 387 \text{ and } 505 \text{ nm, } 200–300 \text{ pJ per pulse}\)) with TA pump/probe Helios and EOS detection systems from Ultrafast Systems. For the picosecond to nanosecond experiments (Helios), white light was generated focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk (\(\sim 430–760 \text{ nm}\)) or a 1 cm sapphire disk (\(\sim 800–1600 \text{ nm}\)). A magic angle configuration was employed to avoid rotational dynamics. Excitation pulses of 387 and 505 nm wavelength were generated by a NOPA. Bandpass filters with \(\pm 5 \text{ or } \pm 10 \text{ nm were used to ensure a low spectral width and to exclude } 775 \text{ nm photons. For the nanosecond to microsecond experiments (EOS), white light (\(\sim 370 \text{ to } 1600 \text{ nm}\)) was generated by a built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and a pulse width of approximately 1 ns. All measurements were conducted in a 2 mm quartz cuvette under an argon atmosphere.

To analyze transient absorption data, we use a suggested procedure. Further experiments to investigate these barriers are being carried out in our laboratories.

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were treated by global and target analyses using the R- package TIMP and GloTarAn.$^\text{8–10}$

**Theoretical Calculations.** Density functional theory (DFT) computations were employed to fully optimize geometries of the compound in DMSO, without symmetry constraints. Geometries of the singlet ground state were optimized and serve as the starting point for the optimization of the lowest-lying triplet state species. The calculations were done with the Gaussian 09 package,$^\text{11}$ at the B3LYP level of theory using restricted and unrestricted approximations of the Kohn–Sham equations, depending on the system multiplicity.$^\text{12}$ In all cases, we employed the effective core potential basis set LanL2DZ, which proved to be suitable for geometry predictions in coordination compounds containing metals of the second row of the transition elements in the Periodic Table. All of the calculations were performed using an UltraFine grid. Solvation effects were accounted for using the most recent implementation of the implicit IEF-PCM solvation model.$^\text{13}$ We used tight convergence criteria in the geometry optimizations and default settings for IR calculations. All optimized structures were confirmed as minima by analyzing the harmonic vibrational frequencies.$^\text{14}$ Vertical electronic excitation energies and vibrational frequencies.$^\text{15}$ Vertical electronic excitation energies and vibrational frequencies.$^\text{16}$

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