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Coordination Environment Prevents Access to Intraligand Charge-Transfer States through Remote Substitution in Rhenium(I) Terpyridinedicarbonyl Complexes

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ABSTRACT: Six (4-substituted ph	t rhenium(I) $\kappa^3 N$ -dicarbonyl c enyl)terpyridine ligands were	omplexes with 4'- evaluated in their		Three RINGS FOR The

(4-substituted phenyl)terpyridine ligands were evaluated in their ground and excited states. These complexes, bearing substituents of different electron-donating strengths—from CN to NMe₂—were studied by a combination of transient IR (TRIR), electrochemistry, and IR spectroelectrochemistry, as well as time-dependent density functional theory (TD-DFT). They exhibit panchromatic absorption and can act as stronger photoreductants than their tricarbonyl counterparts. The ground- and excited-state potentials, absorption maxima, and lifetimes (250–750 ps) of these complexes correlate well with the Hammett σ_p substituent constants, showing the systematic effect of remote substitution in the ligand framework. TRIR spectroscopy allowed us to assign the



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lowest singlet and triplet excited states to a metal-to-ligand charge-transfer (MLCT) character. This result contrasts our previous report on analogous $\kappa^2 N$ -tricarbonyl complexes, where remote substitution switched the character from MLCT to intraligand charge transfer. With the help of TD-DFT calculations, we dissect the geometric and electronic effects of coordination of the third pyridine, local symmetries, and increasing conjugation length. These results give valuable insights for the design of complexes with long-lived triplet excited states and enhanced absorption throughout the visible spectrum, while showcasing the boundaries of the excited-state switching strategy via remote substitution.

INTRODUCTION

Rhenium(I) carbonyl complexes have found widespread applications in chemistry, ranging from their ubiquitous role as photosensitizers in diverse photocatalytic transformations¹⁻¹² to their use as CO₂ reduction catalysts.^{13–18} Complexes of the type *fac*-[Re(N^N)(CO)₃L]⁺ (where N^N is a bidentate diimine ligand) have been studied to a great extent since the pioneering work by Wrighton and coworkers.^{19–21} as well as Lehn and co-workers.²²

While the photochemical and photophysical properties of fac-tricarbonylrhenium(I) complexes have been studied extensively, $1^{19,23-31}$ those of mononuclear *cis*-dicarbonylrhenium(I) complexes, in contrast, remain to date relatively unexplored.³² The groups of Castellano³³ and Sullivan³⁴ have recently reported on the substituent effects in rhenium(I) bis(diimine)dicarbonyl complexes with the general formula $[\text{Re}(\text{N^N})_2(\text{CO})_2]^+$ (Figure 1A). In addition, Morimoto and Ishitani³⁵ have reported on supramolecular assemblies of rhenium(I) dicarbonyl complexes with phosphine ligands. Furthermore, Dempsey and co-workers³⁶ have reported on a series of rhenium(I) bipyridinedicarbonyl complexes with axial ligands of different donating strengths (Figure 1B), exhibiting broadband visible absorption and



Figure 1. Different strategies for tuning the properties of rhenium(I) carbonyl complexes: (A) by substitution on the diimine ligands, (B) by tuning of the axial ligands, (C) by remote substitution in tricarbonyl complexes and (D) in their dicarbonyl analogues with a terpy framework.

acting as stronger photoreductants than conventional rhenium-(I) tricarbonyl complexes. Hightower and co-workers^{37,38} as well as Richeson and co-workers³⁹ have shown that *cis*-dicarbonylrhenium(I) complexes of nitrogen-donor ligands

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Scheme 1. Synthetic Route and Structures of the Compounds Studied in the Present Work

bearing a κ^3 N-coordination motif exhibit enhanced absorption properties throughout the entire visible spectrum—a common feature of these complexes that makes them attractive candidates for applications in photochemical energy conversion.

We have recently reported on a complementary remote substitution strategy to tune the photophysical and photochemical properties of rhenium(I) tricarbonyl complexes, using a ligand framework based on bidentate 4'-(4-R¹-phenyl)-2,2':6',2"-terpyridine (terpy) ligands (Figure 1C), decorated with electron-withdrawing and -donating substituents (ranging from CN to NMe₂).⁴⁰ In the present work, we extend our approach to their rhenium(I) *cis*-dicarbonyl analogues (Figure 1D).

We report herein the synthesis, spectroscopic, crystallographic, and electrochemical characterization of a series of rhenium(I) $\kappa^3 N$ -dicarbonyl complexes (3a-3f; Scheme 1) with substituted terpy ligands (L_a-L_f). The present study brings new insights into the photophysical and photochemical properties of this family of complexes. By combining experimental and computational methods, including UV pump–IR probe, Fourier transform infrared (FT-IR) spectroelectrochemistry, and time-dependent density functional theory calculations (TD-DFT), we establish herein the key differences between the photophysics of the $\kappa^2 N$ -tricarbonyl and $\kappa^3 N$ -dicarbonyl terpy frameworks.

We assess the impact of the different coordination geometries and local symmetries around the Re(I) center and correlate the observed properties with the electronic density on the terpy ligand. These two complementary approaches (i.e., remote substitution and coordination geometry) provide full control over the absorption properties of these complexes, while allowing us to look at their excitedstate structure and dynamics.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic route to the $\kappa^3 N$ -dicarbonyl complexes is shown in Scheme 1. In our previous report,⁴⁰ we have described the synthesis of the ligands ($L_a - L_b$ based on a modified Kröhnke strategy with 4-acetylpyridine and a 4-substituted benzaldehyde derivative)^{41,42} as well as the synthesis of the $\kappa^2 N$ -tricarbonyl

complexes (2a-2f), obtained from $Re^{I}(CO)_{5}Cl$ and the corresponding ligand).

The $\kappa^3 N$ -dicarbonyl complexes studied in this work (3a-3f) were obtained as air-stable black solids in quantitative yields by thermal decarbonylation of 2a-2f under vacuum (Scheme 1), an improved protocol with respect to previous literature reports.^{37–39} The key aspect to quantitative conversion is heating the complexes under vacuum (instead of under an inert atmosphere) because this is expected to promote CO loss. Complete experimental details are provided in the Supporting Information (SI).

It is worth mentioning that both the $\kappa^2 N$ -tricarbonyl and $\kappa^3 N$ -dicarbonyl complexes show remarkable photochemical and thermal stability. In comparison, manganese(I) tricarbonyl complexes with terpy ligands readily release CO upon photoexcitation, forming the corresponding $\kappa^3 N$ -dicarbonyl complex.⁴³

The crystal structures of these complexes (illustrated by that of **3f** in Figure 2) confirm the *mer,cis*-coordination geometry



Figure 2. Displacement ellipsoid representation (at the 50% probability level) of the crystal structure of complex 3f. H atoms and disordered solvent molecules are omitted for clarity.

around the Re(I) center. In the complexes studied in the present work, the plane of the $\{\text{Re}(\text{CO})_2\}^+$ moiety is almost perpendicular to the plane of the terpy ligand, in contrast to other reports of rhenium(I) dicarbonyl complexes, where the two CO groups are coplanar with the bis(diimine) ligand.³⁶ The N5–Re1–N15 angles close to 150° indicate a slight

distortion from the ideal octahedral geometry. In general, bond lengths and angles are in line with those previously reported for similar complexes.^{34,44–47} Additional crystallographic details are given in the SI.

The ¹H NMR spectra of all κ^3 N complexes (**3a**-**3f**) show a single set of seven signals for the terpy ligand framework, also in agreement with the crystallographically observed *mer,cis*- $(\kappa^3 N$ -terpy) coordination geometry and an apparent C_s symmetry around the Re(I) center. The chemical shifts of the 3' and 5' protons of the terpy ligand show a linear correlation with the Hammett σ_p substituent constants, suggesting good electronic communication between the ligand subunits. A similar correlation was also observed for the ¹³C NMR shifts of the equatorial carbonyl ligands of the κ^3 N complexes. The NMR spectra of all complexes are given in the SI.

Steady-State Spectroscopic Properties. Compared to their $\kappa^2 N$ -tricarbonyl counterparts, the $\kappa^3 N$ -dicarbonyl complexes show panchromatic absorption (throughout the entire visible spectrum), manifested in three strong metal-to-ligand charge transfer (MLCT) bands around ca. 720, 480, and 410 nm (denoted herein as ν_1 , ν_2 , and ν_3 , respectively), accompanied by a shoulder around 575 nm (Figure 3A).



Figure 3. (A) UV–vis and (B) FT-IR absorption spectra in DMF of the unsubstituted $\kappa^2 N$ -tricarbonyl (2d, blue) and $\kappa^3 N$ -dicarbonyl (3d, red) complexes.

In the IR, the change from the fac-{Re(CO)₃}⁺ moiety to the cis-{Re(CO)₂}⁺ moiety leads to an average red shift of ca. 85 cm⁻¹ in the CO frequencies (i.e., average of all CO stretching frequencies). The two ν_{CO} absorption bands expected for the *cis*-dicarbonyl complexes are observed around ca. 1820 and 1895 cm⁻¹ (Figure 3B).

These two vibrations have antisymmetric and symmetric character (formally both of A' symmetry in the C_s point group)—consisting of out-of-phase and in-phase stretching of the two CO groups, respectively. They preserve the large

delocalization of the C \equiv O stretching modes observed in their tricarbonyl counterparts.⁴⁸ The red shift in the absorption frequencies can be explained by a significant increase in the electron density around the metal center due to replacement of an electron-accepting CO group by a donating imine group (from the now meridionally coordinated terpy ligand).

Complexes **3a-3e** show consistent hypsochromic (blue) shifts in all UV-vis absorption maxima as the electrondonating character of the substituent is increased—shifting by 614 (ν_1), 390 (ν_2), and 700 cm⁻¹ (ν_3), respectively, upon going from CN to OMe—accompanied by a slight increase in the extinction coefficients. These shifts are similar to those observed for **2a-2e**. Complete UV-vis and IR spectra are provided in Figures S1 and S2.

In contrast to its tricarbonyl counterpart, the NMe₂-substituted complex (**3f**) does not show any significant new bands in its UV–vis absorption spectrum. The positions (cm⁻¹) of the lowest-energy band (ν_1) of the UV–vis spectra show an excellent linear correlation with the Hammett σ_p substituent constants ($R^2 = 0.9983$; Figure S3), while those of ν_2 and ν_3 deviate from linearity for the extremely donating or withdrawing substituents.

Complexes 3a-3f are nonemissive—neither at room temperature nor at 77 K, in contrast to their $\kappa^2 N$ -tricarbonyl analogues (2a-2f). We attribute this to a faster nonradiative deactivation due to the significantly red-shifted absorption (as expected from the energy gap law).

Ground- and Excited-State Redox Properties. Electrochemical studies of these complexes were carried out in 0.1 M $[Bu_4N][PF_6]$ in *N*,*N*-dimethylformamide (DMF; Figure 4).



Figure 4. Cyclic voltammograms of selected dicarbonyl complexes in 0.1 M $[Bu_4N][PF_6]$ in DMF. Scan rate: 100 mV s⁻¹.

The $\kappa^3 N$ -dicarbonyl complexes show a one-electron chemically reversible oxidation around ~0 V versus ferrocenium/ ferrocene (Fc^{+/0}) and a stepwise two-electron reduction below -1.5 V versus Fc^{+/0}, analogous to that observed in their $\kappa^2 N$ -tricarbonyl analogues.⁴⁰ The dicarbonyl complexes show, however, a more evident separation of the two overlapping consecutive reduction waves, especially on the more electron-rich complex **3f**.

The partial irreversibility of the second reduction is attributed to loss of the chloride ligand. This was well reproduced in the DFT calculations, performed in *Gaussian 16*, revision B.01,⁴⁹ and in agreement with previous reports of related complexes.^{50–52} The redox potentials of the oxidative and reductive events shift to more negative values with more electron-donating substituents. Peak shifts of -160 and -60 mV were recorded for the reduction and oxidation waves, respectively, between CN and NMe₂ as substituents (Figure

S4). The ground- and excited-state redox properties of these complexes are summarized in Table 1 and discussed below.

Table 1. Ground- and Excited-State Redox Properties of the Studied Complexes in DMF

	\mathbb{R}^1	${E_{\rm red}}^{\circ\prime}_{\rm (V)}^{a}$	${{E_{ox}}^{\circ \prime}}{{\left(\mathrm{V} \right)}^{a}}$	${\Delta G_{\mathrm{ST}}^{\mathrm{theo}}\over (\mathrm{eV})^{b}}$	$(E_{\mathrm{red}}^{\circ \prime})^{e}$ (V) ^c	$(E_{ox}^{\circ'})^{*}$ $(V)^{c}$
3a	CN	-1.58	0.09	1.35	-0.19	-1.26
3b	CF ₃	-1.60	0.07	1.39	-0.20	-1.32
3c	Br	-1.62	0.06	1.42	-0.20	-1.36
3d	Н	-1.65	0.05	1.44	-0.21	-1.39
3e	OMe	-1.67	0.05	1.47	-0.19	-1.42
3f	$\rm NMe_2$	-1.71	0.03	1.51	-0.20	-1.48

"Electrochemical potential in volts versus $Fc^{+/0}$ in DMF. "Energy difference between the optimized S_0 and T_1 structures. "Excited-state potentials estimated from eqs 1 and 2.

Any potential application of these complexes for photoinduced electron-transfer reactions requires knowledge of their excited-state redox potentials, which can be estimated by eqs 1 and 2.

$$E_{\rm red}^{\circ\prime}({}^3[{\rm Re}^1]^*) = E_{\rm red}^{\circ\prime} + \Delta G_{\rm ST}$$
(1)

$$E_{\rm ox}^{\circ'}({}^3[{\rm Re}^1]^*) = E_{\rm ox}^{\circ'} - \Delta G_{\rm ST}$$
⁽²⁾

Because the $\kappa^3 N$ complexes are nonemissive, we estimated the $\Delta G_{\rm ST}$ values of these complexes directly from the energy differences between the optimized ground-state and lowest triplet excited-state structures (without further corrections). We base this approach on the excellent agreement between the experimental and calculated values obtained in our previous report for the $\kappa^2 N$ complexes (with a mean deviation of ± 0.02 eV for complexes $2\mathbf{a}-2\mathbf{e}$, operating from the lowest ³MLCT state).⁴⁰ Considering the reported $(E_{ox}^{\circ \prime})^*$ values for rhenium(I) tricarbonyl complexes (≈ 1 V vs Fc^{+/0} in acetonitrile),³⁶ we conclude that the $\kappa^3 N$ complexes are stronger photoreductants but weaker photooxidants than their $\kappa^2 N$ analogues.

Spectroelectrochemical studies in the IR (IR-SEC) revealed the absorption features of the singly oxidized, as well as the singly and doubly reduced species. The experimental and calculated IR-SEC difference spectra of **3d** (as a representative example) are shown in Figure 5.

Upon oxidation, the antisymmetric and symmetric CO stretches blue shift by ca. 95 and 120 cm⁻¹, respectively. Similarly, upon reduction, both carbonyl stretching bands exhibit red shifts of ~18 cm⁻¹ (first reduction) and ~55 cm⁻¹ (second reduction). Ishitani and co-workers reported red shifts of 27 and 33 cm⁻¹ for the first reduction and red shifts of 55 and 66 cm⁻¹ for the second (irreversible) reduction of *cis,trans*-[Re(CO)₂(bpy){P(OEt)₃}₂]^{+,51} In a similar fashion, Hartl and Vlček observed blue shifts of 78 and 92 cm⁻¹ (for the first reduction) and red shifts of 42 and 53 cm⁻¹ (for the first reduction) for a rhenium(I) diphosphinedicarbonyl complex with a quinone ligand.⁵⁰

We tentatively conclude that complexes 3a-3f undergo similar structural changes upon reduction as their tricarbonyl counterparts (2a-2f),^{40,53} leading to Cl⁻ dissociation after the second reduction. DFT optimization of the structure of the doubly reduced species also led to dissociation of the Cl ligand. In this case, the doubly reduced complexes were reoptimized after manually removing the Cl ligand.



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Figure 5. Experimental (solid lines) and calculated (dashed lines) difference IR spectra of the redox states of **3d**. Experimental spectra measured in 0.1 M $[Bu_4N][PF_6]$ in DMF. Potentials versus $Fc^{+/0}$. Theoretical frequencies were scaled by 0.969 to better match the experimentally obtained values.

Overall, the shifts observed upon electrochemical oxidation and reduction of 3a-3f correlate well with those of similar complexes, being significantly higher for the one-electron oxidation. These shifts were almost quantitatively reproduced in DFT calculations of the different redox states, allowing us to safely assign them as described above.

Excited-State Dynamics. We now turn to the excitedstate dynamics of complexes 3a-3f. Transient absorption experiments were performed with a UV pump and ultrashort broadband mid-IR pulses derived from a home-built optical parametric amplifier as the probe (complete experimental details are given in section 1.3 of the SI).³⁴⁻⁵⁶ Transient IR (TRIR) spectra of complexes 3a-3f in air-saturated DMF were recorded upon excitation with 420 nm ultrashort pulses and are illustrated in Figure 6 by those of 3d as a representative



Figure 6. FT-IR spectrum (top) and magic-angle TRIR spectra (bottom) of **3d** (5 mM in DMF) at different pump-probe delays.

example. Overall, the TRIR spectra of all complexes show two excited-state absorption (ESA) bands, centered around 1871 and 1970 cm⁻¹, and the corresponding ground-state bleach signatures at 1820 and 1890 cm⁻¹.

(TD-)DFT calculations of the TRIR spectroscopic signatures for these complexes almost quantitatively matched the experimental TRIR spectra (Figure 7). On this basis, we assigned the observed spectroscopic signatures to population of the lowest ³MLCT state of the $\kappa^{3}N$ -dicarbonyl complexes after ultrafast intersystem crossing (ISC) and/or internal



Figure 7. Calculated (A) absolute and (B) difference spectra of the ground and lowest singlet and triplet excited states. (C) Experimental TRIR spectra at early and late population delays. All spectra correspond to **3d** in DMF. Calculated frequencies were scaled by 0.971 to better match the experiment. Vertical colored bars indicate the positions of the calculated (scaled) frequencies for each state.

conversion from an initially populated higher singlet excited state. Evidence for this assignment comes from the pronounced time-dependent blue shift of the two ESA bands (also reproduced in the DFT calculations; Figure 7A,B). This process, taking place on a time scale of ca. 10 ps, is attributed to a convolution of relaxation on the excited state(s) (internal conversion) and ISC, analogous to that observed for rhenium(I) tricarbonyl complexes.^{28,57,58}

It is important here to emphasize that excitation with 420 nm initially populates higher singlet excited states in the $\kappa^3 N$ -dicarbonyl complexes. According to TD-DFT calculations, all of these excited states (up to at least S₅) have MLCT character, irrespective of the substituent on the ligand scaffold. This sharply contrasts the excited-state character switching observed with the NMe₂ substituent in the $\kappa^2 N$ -tricarbonyl complexes from our previous report.⁴⁰

The excellent agreement between the experimental and calculated UV-vis absorption spectra (Figure S5) shows that our computational approach accurately reproduces the groundand excited-state properties.

Considering current and previous observations on rhenium-(I) $\kappa^2 N$ -tricarbonyl complexes, we conclude that the photophysics of $\kappa^3 N$ -dicarbonyl complexes follow a very similar pathway: excitation to one of the ¹MLCT states leads to ultrafast internal conversion and ISC to the lowest-lying ³MLCT state, independent of the substituent on the terpy ligand framework.

Time-resolved investigations of mononuclear rhenium(I) dicarbonyl complexes are relatively scarce in the literature. Ishitani and co-workers have reported on the photophysical and photochemical properties of *cis,trans*- $[Re(CO)_2(bpy)]$

 $(OEt)_{3}_{2}]^{+.51}$ In their work, they showed that, upon photoexcitation, the ν_{CO} antisymmetric (lower energy) and symmetric (higher energy) bands of this complex blue shift by ca. 45 and 56 cm⁻¹. Similarly, Castellano and co-workers observed blue shifts of ca. 40 and 75 cm⁻¹ upon photoexcitation of rhenium(I) dicarbonyl complexes with substituted bis(diimine) ligands.³³ In the excited ³MLCT state, complexes **3a**–**3f** display a blue shift of the CO stretching bands of ca. 49 and 77 cm⁻¹, in line with previous reports for similar complexes.

We observe, across the series of complexes 3a-3f, a systematic modification of the lifetimes of the lowest triplet excited state (Figure 8), analogous to that observed for 2a-2e.



Figure 8. Linear correlations between the ³MLCT lifetimes (from TRIR) and the Hammett σ_p substituent constants for the $\kappa^2 N$ -tricarbonyl complexes (**2a**-**2e**, in blue; **2f** excluded for clarity) and $\kappa^3 N$ -dicarbonyl complexes (**3a**-**3f**, in red).

The lifetimes increase from 251 to 762 ps between the CNand OMe-substituted complexes, up to a maximum of 947 ps for the NMe₂-substituted complex (3f). The fitted lifetimes of all complexes can be found in Table S2 and the corresponding TRIR kinetic traces in Figure S6.

When comparing the slopes of the lifetimes and Hammett σ_p substituent constants, we observe that the change for $\kappa^2 N$ -tricarbonyl complexes (2a-2e) is more prominent than that for the $\kappa^3 N$ -dicarbonyl complexes (3a-3f). These results are intriguing, considering that both series show similar spectral shifts upon substitution (717 and 614 cm⁻¹, respectively, upon going from CN to OMe), excluding the NMe₂ complexes.

Computational Aspects. We now turn to TD-DFT calculations to rationalize the observed properties and the differences between the $\kappa^2 N$ -tricarbonyl complexes and their $\kappa^3 N$ -dicarbonyl counterparts.

Neither the energy levels of the lowest unoccupied molecular orbital (LUMO) nor those of the highest occupied molecular orbital (HOMO) of complexes 3a-3f correlate with the electron-donating/withdrawing properties of the substituents. This contrasts the trends observed for both HOMO and LUMO of their tricarbonyl analogues (2a-2f). On average, while the LUMO orbitals of 3a-3f remain at similar energies compared to those of 2a-2f, the HOMO orbitals are ~1 eV higher in energy (making the HOMO–LUMO gap correspondingly smaller). These results are in line with the similar reduction potentials observed on both series and the significantly lower oxidation potential of the dicarbonyl complexes. Orbital energy diagrams are shown in Figure S7.

Apart from the significant change in the electronic density around the Re(I) center introduced by replacing a C \equiv O ligand for a pyridine ligand (evidenced by the large red shift of all IR absorption bands), the local symmetry of the orbitals around the metal center is increased upon going from the $\kappa^2 N$ to $\kappa^3 N$ geometry. Planarization of the terpy ligand generates also a significant increase in conjugation, which now spans across the three aromatic rings of the terpy ligand (also evidenced in the crystal structures of these complexes). This change in the geometry suffices to introduce additional electronic transitions, as evidenced by inspection of the UV– vis absorption spectra (Figure 3A) and reproduced by TD-DFT calculations (Figure S5).

The charge density difference (CDD) isosurfaces of complexes 3d-3f further support the observed TRIR results: no significant character change of the excited states was observed upon going from the unsubstituted terpy ligand ($R^1 = H$, 3d) to the ligand substituted with the most electron-donating group ($R^1 = NMe_2$, 3f). This contrasts with the case of the tricarbonyl complex 2f. The CDD isosurfaces for the $S_1 \leftarrow S_0$ transitions of 2a-2f and 3d-3f, calculated with *MultiWfn*, version 3.7,⁵⁹ are shown in Figure 9 as representative examples.



Figure 9. CDD isosurfaces of the $S_1 \leftarrow S_0$ transition of complexes 2d-2f (top row) and 3d-3f (bottom row), shown at $|\Delta \rho| = 0.002$ au.

Two parallel effects—increased electron density and local symmetry—explain the more complex UV–vis absorption spectrum of the dicarbonyls and the red shift of ca. 1.55 eV in the energy of the $S_1 \leftarrow S_0$ transition. We attribute ca. 1 eV of this shift to the increase in the HOMO relative energies and the remainder to the increased conjugation. Furthermore, we believe the increased electron density on the $\{\text{Re}(\text{CO})_2\}^+$ moiety compared to the $\{\text{Re}(\text{CO})_3\}^+$ core hinders charge transfer from the NMe₂ group because the former is a more potent donor in the excited state.

The impact of the increased local symmetry around the metal center in the dicarbonyl complexes 3a-3f can be further evidenced in the CDD isosurfaces of the higher excited states $(S_n \leftarrow S_0)$, shown in Figure 10.

The fact that the CDD isosurfaces bear strong similarities results from an increase in the local symmetry of the complexes and also serves to illustrate that these higher excited states all have MLCT character.



Figure 10. CDD isosurfaces of the $S_n \leftarrow S_0$ transitions for the first five singlet states of complex 3d, shown at $|\Delta \rho| = 0.001$ au.

The computational results presented herein serve to explain the observed changes in the electronic structure of these complexes upon going from the $\kappa^2 N$ -tricarbonyl to $\kappa^3 N$ dicarbonyl coordination geometry. In addition, the limitations of the excited-state switching strategy (to avoid the energy gap law), toward increasing the lifetime and red shifting the absorption, are dissected in terms of symmetry and conjugation.

CONCLUDING REMARKS

Herein we studied the ground- and excited-state properties of a series of rhenium(I) dicarbonyl complexes with substituted 4'- $(4-R^1-\text{phenyl})-2,2':6',2''$ -terpyridine ligands in a κ^3N coordination motif, by employing a combination of ultrafast and steady-state spectroscopic methods ranging from TRIR to IR spectroelectrochemistry and DFT calculations.

In contrast to our previous report on analogous $\kappa^2 N$ tricarbonyl complexes,⁴⁰ we did not observe excited-state character switching when increasing the electron-donating strength of the substituent from CN to NMe₂. In the present case, all excited states preserved their MLCT character, as evidenced by TRIR spectroscopy and supported by TD-DFT calculations. The photophysical and electrochemical properties of these complexes showed excellent linear correlations with the Hammett σ_p substituent constants, in line with the results observed for their $\kappa^2 N$ -tricarbonyl analogues operating from an MLCT excited state (2a-2e).

TD-DFT calculations revealed the fundamental differences in the electronic structure between complexes of the two series. We show that a combination of destabilization of the HOMO orbitals (by replacing one CO with a pyridine) and an increase in the conjugation length is responsible for the observed ca. 1.55 eV red shift in the absorption. This shift consequently lowers the excited-state lifetimes according to the energy gap law. We also show that, for the remote substitution strategy to switch the lowest excited state to intraligand charge-transfer (ILCT) character in the excited state, a third carbonyl is needed, since the electron-rich $\{Re(CO)_2\}^+$ moiety outcompetes the electron-donating power of the NMe_2 substituent, thus hindering access to the ILCT states in these complexes.

We believe that this work illustrates the boundaries of the MLCT-to-ILCT switching strategy to enhance the lifetimes and absorption properties of rhenium(I) carbonyl complexes. This brings fundamental insights into the rich photochemistry, photophysics, and electronic structure of rhenium(I) carbonyl complexes with substituted terpyridine ligands.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02914.

Full experimental details, including synthetic procedures, characterization details, crystallographic discussions, details about the transient absorption and electrochemistry experiments; UV–vis absorption, NMR and FT-IR spectra of all complexes; details of the computational calculations; and additional tables and figures (PDF)

Accession Codes

CCDC 2032841 and 2032842 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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