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Photophysical Processes in Rhenium(I) Diiminetricarbonyl Arylisocyanides Featuring Three Interacting Triplet Excited States

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Supporting Information

ABSTRACT: We present a series of four transition-metal complexes based on the rhenium(I) tricarbonyl 1,10phenanthroline (phen) template, with a lone ancillary arylisocyanide (CNAr) ligand to yield metal-organic chromophores of the generic molecular formula [Re(phen)- $(CO)_3(CNAr)$]⁺ [CNAr = 2,6-diisopropylphenyl isocyanide (1), 4-phenyl-2,6-diisopropylphenyl isocyanide (2), 4-phenylethynyl-2,6-diisopropylphenyl isocyanide (3), and 4-biphenyl-2,6-diisopropylphenyl isocyanide (4)]. This particular series features varied degrees of π -conjugation length in the CNAr moiety, resulting in significant modulation in the resultant photophysical properties. All molecules possess long-lived [8-700 μ s at room temperature (RT)], strongly blue-green



photoluminescent and highly energetic excited states ($\lambda_{max,em} = 500-518$ nm; $\Phi = 14-64\%$). Each of these chromophores has been photophysically investigated using static and dynamic spectroscopic techniques, the latter probed from ultrafast to suprananosecond time scales using transient absorption and photoluminescence (PL). Time-resolved PL intensity decays recorded as a function of the temperature were consistent with the presence of at least two emissive states lying closely spaced in energy with a third nonemissive state lying much higher in energy and likely ligand-field in character. The combined experimental evidence, along with the aid of electronic structure calculations (density functional theory and time-dependent density functional theory performed at the M06/Def2-SVP/SDD level), illustrates that the CNAr ligand is actively engaged in manipulating the excited-state decay in three of these molecules (2-4), wherein the triplet metal-to-ligand charge-transfer (³MLCT) state along with two distinct triplet ligand-centered (³LC) excited-state configurations (phen and CNAr) conspire to produce the resultant photophysical properties. Because the π conjugation within the CNAr ligand was extended, an interesting shift in the dominant photophysical processes was observed. When the CNAr conjugation length is short, as in 1, the phenanthroline ³LC state dominates, resulting in a configurationally mixed triplet excited state of both LC and MLCT character. With more extended π conjugation in the CNAr subunit (2–4), the initially generated ${}^{3}LC(phen)/{}^{3}MLCT$ excited state ultimately migrates to the CNAr ³LC state on the order of tens of picoseconds. Molecules 3 and 4 in this series also feature unique examples of inorganic excimer formation, as evidenced by dynamic self-quenching in the corresponding PL intensity decays accompanied by the observation of a short-lived low-energy emission feature.

INTRODUCTION

For approximately 4 decades, fac-rhenium(I) diiminetricarbonyl complexes have drawn considerable attention and experimental investigation.¹⁻¹⁵ These chromophores have potential applications in a variety of photonics-relevant technologies including solar energy conversion, photochemical transformations, photocatalytic carbon dioxide and proton reduction, photoluminescent molecular devices, and photoluminescence (PL) sensing of numerous analytes.¹⁶⁻²⁹ These attributes result from their low-energy visible-light absorption properties with corresponding long excited-state lifetimes suitable for sensitizing myriad intramolecular and bimolecular electron- and energy-transfer reactions.

Prior investigations have concluded that the vast majority of chromophores in the particular rhenium(I) tricarbonyl family possess lowest-lying excited states, which are predominantly

metal-to-ligand charge transfer (MLCT) in nature. This manifests in broad, featureless emission spectra that are highly dependent on environmental factors such as the solvent polarity. It is also possible for low-energy ligand-centered (LC) excited states to be present in these molecules lying in close energetic proximity to the MLCT states. Any possible thermal equilibrium or activation between these closely lying states may lead to beneficial consequences, including dramatic extension of the original MLCT excited-state lifetime. The vast majority of previous studies have focused on tuning of the MLCT states through manipulation of the lowest unoccupied molecular orbital (LUMO) energetics directly resulting from structural modifications in the appended diimine ligand. It is

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Scheme 1. General Synthetic Pathway and Molecular Structures of the fac-Rhenium(I) Complexes 1-4



important to note that through temperature-dependent investigations, the proximity and ordering of multiple excited states resident in these chromophores can be readily elucidated.^{2,6-8,11,12,14,30}

To date, a variety of ancillary ligands have been incorporated in these rhenium(I) diiminetricarbonyl frameworks to systematically modulate excited-state decay properties, leveraging deterministic energy gap law behavior.^{31,32} These ancillary substitutions include the incorporation of halides,^{1,3,4} pyridine and piperidine,^{2,6,7,11,12} and, of particular significance to the present work, isocyanides.^{8,13,33–36} Isocyanide ligands, featuring both alkyl and aryl substituents, serve as strong σ donors and good π acceptors, similar to that imposed by carbon monoxide (CO).^{37–39} Therefore, isocyanides impart a strong ligand field to the rhenium(I) center while offering the opportunity for deliberately installing organic subunits with meaningful variation in their singlet and triplet excited-state energies. Extensive work into perturbation of the photophysical properties of rhenium(I) isocyano complexes has been performed, via substituent modification on simple arylisocyanide (CNAr) ligands and the number of isocyano versus carbonyl ligands on the complex.³³ These studies have found that the photophysical behavior of such complexes is dependent on the $d\pi(\text{Re}) - \pi\pi^*(\text{diimine})$ MLCT, with the electronic influence of the isocyanide playing an ancilliary role in the energetics of this excited state. It is noted that further functionalization of the isocyanide provides a route to a more drastic modification of the properties of these rhenium(I) complexes. Such molecules are potentially valuable for driving catalytic transformations initiated through triplet-triplet energy transfer, as has been recently discovered.^{40,41} Beyond rhenium(I) complexes, isocyanide ligands have been employed as ancillary ligands in other photophysically active systems. Most of these are derived from iridium(III) cyclometalate archetypes, and all feature bright phosphorescence across the visible spectrum from a predominantly ³LC state, depending on the cyclometalate chosen.⁴²⁻⁴⁶ Further utilization of isocyanides has come in the form of homoleptic complexes of group VI metals, where the isocyanide is the chromophoric ligand and the photophysics are dominated by pure ³MLCT.^{47–49} because of their utilization primarily as an ancillary ligand, the photophysical properties of lower-energy CNAr moieties have rarely been explored in rhenium(I).

The current work focuses on varying the π -conjugation length in the ancillary CNAr ligand fused to the rhenium(I) tricarbonyl 1,10-phenanthroline (phen) template to yield metal-organic chromophores of the generic molecular formula $[Re(phen)(CO)_3(CNAr)]^+$ (1-4 in Scheme 1) featuring longlived and highly energetic excited-state properties. All of these molecules have been photophysically investigated using static and dynamic spectroscopic techniques, the latter probed from ultrafast to suprananosecond time scales using transient absorption (TA) and PL. Electronic structure calculations utilizing density functional theory (DFT) and time-dependent DFT (TD-DFT) methods have been performed on this series of chromophores to support the experimental spectroscopic assignments. The combined experimental and computational evidence illustrates that the CNAr subunit in 2-4 was actively engaged in manipulating the excited-state decay in these molecules, wherein the ³MLCT and two distinct ³LC excitedstate configurations (phen and CNAr) conspire to produce the resultant photophysical properties.

RESULTS AND DISCUSSION

Syntheses. The rhenium(I) complexes 1–4 were synthesized using the general procedure outlined in Scheme 1. Each of the isocyanide ligands was prepared following the general synthetic procedure outlined in Figures S1–S3. Each of the target compounds was purified through multiple precipitations by dissolving the isolated product in methanol, followed by treatment with aqueous NH_4PF_6 . The final rhenium(I) complexes were structurally characterized using ¹H and ¹³C NMR spectroscopy, high-resolution time-of-flight electrospray ionization mass spectrometry (ESI-MS), and Fourier transform infrared (FTIR) spectroscopy. The purified molecules were determined to be both thermally and photochemically stable in nonhalogenated solvents, with a minor degree of photodegradation observed in halogenated solvents upon extended



Figure 1. Frontier molecular orbitals for 1-4. Calculations were performed at the DFT//M06/Def2-SVP/SDD level of theory.



Figure 2. Electronic UV-vis absorption (red) and normalized static PL (blue) spectra of 1-4 in THF at RT. The PL spectra were recorded with samples having an o.d. = 0.1 at 355 nm excitation in deoxygenated THF.

light exposure. The new molecules are soluble in a variety of polar organic solvents, and tetrahydrofuran (THF) was selected as the solvent medium for all spectroscopic measurements in this contribution.

Electronic Structure Calculations. Prior to the discussion of the photophysical properties of complexes 1–4, a brief DFT-based analysis is presented. The DFT and TD-DFT calculations were performed at the M06/Def2-SVP/SDD level of theory using the polarizable continuum model (PCM) to simulate the THF solvent environment. The ground-state structures for 1–4 were optimized, and the frontier molecular orbitals are presented in Figure 1 and the resulting energies collected in Table S1. In all four molecules, LUMO and LUMO+1 are the in-phase and out-of-phase π^* -orbital combinations, respectively, localized on the phen ligand. The energies of LUMO (-3.080 to -3.089 eV) and LUMO+1 (-2.865 to -2.872 eV) are also consistent across the series,

demonstrating that modification of the ancillary isocyanide ligand does not significantly impact the electronic structure of the phen ligand. The highest occupied molecular orbital (HOMO) for these complexes is largely localized on the CNAr ligand, but there is a significant contribution from the Re d orbitals that decreases upon going from 1 to 4. The increase in the electronic localization on the isocyanide ligand also correlates with the change in the energy where the HOMO energy increases from -7.274 eV (in 1) to -6.676 eV (in 4). HOMO-1 consists largely of Re d orbital contributions with some contribution localized on the phen ligand (1 and 2) or the CNAr ligand (3 and 4).

Static Absorption and PL Measurements. The UV-vis electronic absorption and PL spectra of 1–4 measured in THF are presented in Figure 2, with additional information collected in Table 1. In all of the complexes in this study, the red edges of the absorption bands greater than 350 nm have been

Table 1. Static UV–Vis Absorption and PL Data for 1–4 at RT and 77 K^a

complex	Abs λ_{max} nm (ε , M ⁻¹ cm ⁻¹)	RT PL λ_{max} , nm	77 K Em λ _{max} , nm
1	273 (45700), 305 (16400), 365 (3000)	505	456
2	278 (57900), 315 (30200), 339 (15800), 367 (3600)	507	457
3	278 (40400), 300 (35900), 322 (40900), 341 (33000), 370 (4000)	503, 535 (sh)	492
4	277 (40600), 298 (38800), 319 (40500), 340 (29400), 370 (3800)	518	495
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^aAll RT spectra measured in THF (absorption), deoxygenated THF (PL), and 77 K PL data recorded in Me-THF frozen glasses. All wavelengths measured to ± 2 nm.

assigned as charge transfer in character. A previous study by Rillema and co-workers demonstrated that the lowest-energy absorption band on a rhenium(I) complex bearing a 2,6dimethylphenyl isocyanide was a metal-ligand-to-ligand charge-transfer singlet.¹³ The TD-DFT calculations performed here confirm this assignment as the lowest-energy transition in 1-4 consisting of a rhenium/isocyanide (metal/ligand)-tophen ligand charge-transfer transition (Figures S10-S13). However, the oscillator strength of this transition is low, so it likely contributes very little to the experimentally observed red shoulder in the corresponding absorption spectra (Figure 2). When the higher-lying transitions $S_0 \rightarrow S_2$ through $S_0 \rightarrow S_4$ in complexes 1 and 2 are examined, the transition type changes to a $\operatorname{Re}(d\pi) \to \operatorname{phen}(\pi^*)$ MLCT transition with higher oscillator strength, contributing to the observed shoulder in the measured spectra.

The high-energy portion ($\lambda < 300$ nm) of the electronic spectrum of **1** is dominated by phen-based $\pi - \pi^*$ transitions with some $\pi - \pi^*$ contribution from the isocyanide ligand. The increased oscillator strength of the spectral features observed

between 300 and 350 nm when moving across the series is attributed to the presence of additional aromatic rings on the isocyanide ligands because extension of the π system lowers the energy while raising the oscillator strength of the LC π – π * transitions localized on the isocyanide ligand. Experimentally, this results in the red shift and broadening of the main absorption band in the electronic spectra.

The static PL spectra for **1** and **2** measured in THF are broad and featureless and are also highly quenched by dissolved oxygen, suggesting significant triplet excited-state character in the PL emission; all of these observations are consistent with some degree of charge-transfer character. We note that simple visual inspection of the RT PL spectra in these molecules can be misleading because multiple closely lying excited states each contribute PL intensity proportional to their respective radiative rate constant.⁸ Therefore, unambiguous identification of the lowest excited state requires more sophisticated spectroscopic examination as described below.

The structured PL spectra exhibited by 3 and 4 (Figure 2) at room temperature (RT) in THF immediately suggest interactions between multiple excited states in close energetic proximity. Here, 3 exhibits the most obvious vibronic components, whereas 4 features much more subtle broadening and shouldering toward lower emission energies. All PL spectral features in both 3 and 4 are strongly quenched by dissolved oxygen in THF solutions. This oxygen quenching was found to be asymmetric over the entire emission envelope, with the higher-energy emission more strongly quenched than the lower-energy region. Given these initial steady-state spectroscopic observations, the main PL emission features of 3 and 4 are tentatively assigned to a mixture of ³LC and ³MLCT excited states. In addition, the optimized triplet-state spin densities obtained from DFT support this as the localization of the unpaired spins to be localized on the rhenium, the isocyanide, and the phen ligand (Figures S16 and



Figure 3. Normalized static PL spectra of 1–4 measured in 2-MeTHF frozen glasses at 77 K (λ_{ex} = 355 nm). The vertical dashed lines are drawn as a guide for the eye to illustrate the marked differences in the PL spectral profiles in 1 and 2 with respect to 3 and 4.

S17). Additional static and dynamic experiments described below will help to elucidate the true nature of these excited manifolds and their respective interactions.

The static PL spectra for 1-4 were recorded at 77 K in 2methyltetrahydrofuran (2-MeTHF) glasses following 355 nm excitation (Figure 3). In 1 and 2, the 77 K PL emission spectra are significantly blue-shifted relative to their corresponding RT spectra recorded in THF and a high degree of vibronic structure also becomes evident. The thermally induced Stokes shifts $[\Delta E_s = E_{00}(77 \text{ K}) - E_{00}(298 \text{ K})]$ observed in 1 and 2 are quite large and quantitatively identical in magnitude given the 1 nm bandpass of the PL experiments, $\Delta E_{e} = 2128$ and 2158 cm⁻¹, respectively. By comparison, the ΔE_s measured for the rhenium(I) diiminetricarbonyl ³MLCT model complex Re- $(phen)(CO)_3Cl$ is 2381 cm⁻¹ in the same solvent measured under identical experimental conditions (Figure S18). In all of these instances, the magnitude of the ΔE_s values remained consistent with that anticipated for strongly polar chargetransfer excited states. However, the measured 77 K PL spectra of 1 and 2 quantitatively align with the ³LC phosphorescence measured for phen,² indicative of ³MLCT/³LC state crossover occurring between RT and 77 K. In essence, the lack of solvent reorganization in the vitrified medium renders the ³MLCT state slightly higher in energy with respect to the lower-lying 1,10-phenantholine-centered ³LC state. This behavior is analogous to previous work on rhenium(I) diimine complexes containing alkylisocyanide ancillary ligands, in addition to being observed in various MLCT excited states featuring other transition metals.^{2,50,51} Of particular relevance to the current observations, the 77 K emission spectrum of [Ir(phen)₂Cl₂]Cl is quantitatively similar to the PL spectrum recorded for 1, which is also similar to the phosphorescence of free phen.⁵

In 3 and 4, the static PL emission spectra exhibit substantially smaller thermally induced Stokes shifts (ΔE_{e} = 444 and 897 cm⁻¹, respectively) in comparison to 1 and 2, concomitant with the observation of distinct vibronic progressions becoming revealed at 77 K in these molecules (Figure 3). Because the MLCT states are expected to blue shift over 2000 cm⁻¹ in these chromophores while the phen-based ³LC states remain at much higher energy, this lower-energy phosphorescence emission measured in 3 and 4 must be emanating from a lower-energy triplet excited state. Because molecules 3 and 4 feature aryl-based isocyanide substituents possessing extended π conjugation (phenylacetylene and biphenyl, respectively), it immediately becomes apparent that these 77 K PL spectra are most appropriately assigned as the ³LC states localized on the CNAr substituents in 3 and 4. These particular molecules now emerge as quite interesting because they likely feature RT electronic interactions occurring between three distinct triplet excited states, namely, the lowest MLCT state and two low-lying ³LC states resident on two distinct chromophoric ligands (phen and CNAr) installed on the same rhenium(I) center. To the best of our knowledge, 3 and 4 represent the first examples of rhenium(I) tricarbonyl chromophores, with three distinct triplet excited states being thermally accessible simultaneously. These interactions will be further elucidated below through temperature-dependent excited-state dynamics.

Concentration-Dependent Self-Quenching. Another interesting phenomenon consistently observed in 3 and 4 was a concentration dependence of their excited-state lifetimes in THF. The combined photophysical data measured for 1-4 under optically dilute conditions are presented in Table 2. At

Table 2. Summary of the Photophysical Parameters of 1–4 Measured in THF at RT

complex	Φ^{a}	$ au_{ m em}~(\mu { m s})$	$ au_{\mathrm{TA}} \ (\mu \mathrm{s})$	$k_{\rm r} (\times 10^3 {\rm s}^{-1})^{b}$	$k_{\rm nr} (\times 10^3 \ {\rm s}^{-1})^b$
1	0.64	8.1	8.9	72.0	40.5
2	0.48	14.2	15.5	31.0	33.6
3	0.14	d	710 ^c	0.20	1.2
4	0.15	d	663 ^c	0.22	1.3

"Measured relative to a 9,10-diphenylanthracene standard quantum counter, $\pm 10\%$.⁵⁶ ^bValues calculated from the PL quantum yield and TA decay lifetime values, $\pm 5\%$. "Excited-state lifetime extrapolated to infinite dilution, $\pm 5\%$." Values could not be accurately determined because of the lower quantum yields and longer lifetimes. Higher concentrations were necessary for an accurate kinetic fit, which ultimately manifested quenched excited-state best fits using biexponential kinetics.

higher concentrations (> 10^{-5} M), the excited-state decay was best fit with a biexponential function in 3 and 4 because there was now clear evidence of an additional emissive species being present in these samples as visualized in static and dynamic PL experiments (Figure 4). Note that no aggregation was



Figure 4. Time-gated PL emission spectra recorded for 3 (bottom) and 4 (top) measured in THF using nanosecond laser pulses ($\lambda_{ex} = 355$ nm; 7 ns fwhm) and ICCD detection. Spectra at 250 ns delay (red), relative to the excitation pulse, recorded with a 50 ns gate width. Spectra at 50 μ s delay (blue) recorded with a 1 μ s gate width. Normalized steady-state PL spectra (black) are shown for comparison along with the static PL spectrum that subtracts the normalized time-resolved PL spectrum recorded at 50 μ s delay.

observed in the ground states of 3 and 4, as evidenced by the corresponding electronic absorption spectra being consistent with the Beer-Lambert law over all chromophore concentrations investigated. The static PL emission spectra measured in concentrated samples of 3 and 4 contained a lowenergy shoulder; see the solid black lines in Figure 4. In addition, time-resolved PL experiments revealed that both molecules possessed shorter lifetimes than those recorded in the corresponding diluted samples. Therefore, time-gated PL emission spectra were recorded for concentrated samples of 3 and 4 at both short (250 ns) and long (50 μ s) delay times in order differentiate the high- and low-energy features observed in the static PL spectra (Figure 4). The time-gated spectrum recorded for 3 at the 250 ns delay time (solid red line) was very broad in nature, spanning most of the visible region, and featured rather intense emission toward the red region of the



Figure 5. Ultrafast TA difference spectra of 1-4 recorded in THF. The ultrafast TA difference spectrum of the model chromophore Re(phen)(CO)₃Cl (red dashed line) at 2.12 ps delay is included with 1 for a direct comparison. All difference spectra were obtained using 352 nm excitation (0.4–0.8 mJ pulse⁻¹; 90 fs fwhm) with sample o.d.'s of ~0.45.

spectrum. The 50 μ s delay spectrum in 3 (solid blue line) almost quantitatively reproduced the static PL spectrum at this concentration, which possessed most of the spectral characteristics of the diluted chromophore, as seen in Figure 2. Similar results were obtained in analogous experiments, where 4 was examined under identical experimental conditions.

In both instances, the PL decay at earlier times was dominated by emission emanating from a characteristically distinct species decaying in parallel with the longer-lived bluer species corresponding to the photophysical response from the diluted molecule. Because the shorter-lived PL emission in 3 and 4 was red-shifted, in addition to being broad and featureless, we propose that an excimer-type interaction was responsible for this behavior. The excited-state lifetimes in 3 and 4 are so long-lived (710 and 663 μ s, respectively) that this readily enables bimolecular reactions with ground-state molecules, ultimately leading to low-energy excimer formation in a portion of the decaying excited-state population. Although rare, a handful of examples of inorganic triplet excimers have been reported, almost exclusively based on square-planar platinum(II) complexes.^{53–55} However, in the current molecules, it is the ³LC excited states resident on the CNAr ligands that are deemed responsible for producing the proposed excimers in 3 and 4. In an attempt to generate the true emission spectral profile of the proposed excimers, the normalized time-gated spectrum at 50 μ s was subtracted from the corresponding static spectrum in both 3 and 4 (Figure 4, dashed green lines). It is clear that these difference spectra produce profiles that are substantially red-shifted and distinct of those measured in the diluted molecules, indeed qualitatively consistent with excimer formation. This excimer interaction was also manifested in the static PL emission spectra measured in concentrated solutions of 3 and 4, where

significant amplification of the PL intensity on the red side of the static spectral envelope was clearly observed (Figure S19).

The excited-state decay kinetics was measured as a function of the chromophore concentration in order to use the Stern-Volmer equation to quantify the rate of self-quenching (k_a) in 3 and 4 as well as give an estimate of the excited-state lifetime at infinite dilution (τ_0). Figure S20 presents these Stern-Volmer plots, where the $k_{\rm q}$ values were found to be 8.8×10^8 and 5.80×10^8 M⁻¹ s⁻¹ for 3 and 4, respectively. Because the extent of orbital overlap in an excimer is related to the relative red shift observed between monomer and excimer emission, 3 is clearly red-shifted with respect to 4. To rationalize this result, we postulate that the isocyanide ligand in 3 has the potential for greater π overlap between distinct molecules due to the more planar nature of the ethynyl linker used in this instance. In 3, the red shift was approximately 2766 cm^{-1} , while that in 4 was found to be ~1511 cm⁻¹. Overall, the π conjugated CNAr subunits appear to facilitate intermolecular π stacking during excited-state decay, and it is this interaction that is most likely responsible for excimer formation in 3 and 4. Moving forward, this suggests a general design strategy in metal-organic chromophores wherein the efficient generation of a long-lived triplet intraligand excited state can lead to entirely new classes of excimer-based PL projecting from the red into the near-IR.

Excited-State Dynamics. In order to comprehend the photophysical processes leading to formation of the lowest excited-state configurations in 1-4, ultrafast TA experiments were performed in THF solutions. The TA difference spectra are shown in Figure 5, with the time constants fit to the most prominent signals summarized in Table 3, with kinetic data given in Figures S21 and S22. What becomes immediately apparent is the difference in dynamics between 1 and 2-4. In

Table 3. Summary of the Time Constants from Ultrafast TA Kinetic Modeling a

complex	$\lambda_{\mathrm{fit}} \; (\mathrm{nm})$	$ au_1$ (fs)	τ_2 (ps)	τ_3 (ps)
1	400, 417, 552, 649	200 (±50)	25 (±10)	
2	398, 536	190 (±50)	5 (±1)	50 (±8)
3	523, 537, 580	130 (±60)	3.0 (±0.2)	13.5 (±0.4)
4	572, 603	220 (±20)	3.4 (±0.3)	26 (±1)
^a Eite and kinetic data from which these time constants were obtained				

^aFits and kinetic data from which these time constants were obtained can be found in Figures S20 and S21.

1, there is the prompt (\sim 200 fs) formation of a broad excitedstate absorbance feature traversing most of the visible spectrum. This is followed by very subtle shifts in the signal maximum around 400-450 nm with a corresponding formation time constant of 25 ps (Figure S22). These dynamics differ significantly from those found in the ³MLCT model compound Re(phen)(CO)₃Cl, whose difference spectrum is presented in Figure 5 at 2.12 ps delay. In our experiments (Figure S23) and previous literature results, 57,58 100 fs pulsed-laser excitation of Re(phen)(CO)₃Cl results in the nearly prompt formation of its ³MLCT excited-state absorption with a maximum near 475 nm, consistent with that shown in Figure 5. This was followed by the growth of a shoulder at 575 nm taking place on the order of tens of picoseconds. The prompt signal has been assigned to rapid dynamics associated with the formation of the phen radical anion along with intersystem crossing to the ³MLCT manifold. The longer-time-scale (picosecond) dynamics was assigned to vibrational relaxation occurring within the ³MLCT manifold that ultimately produces a transient signal that persists into the nanoseconds time scale, which is the lowest-energy ³MLCT excited state. By comparison, the prompt TA signatures measured in 1 on femtosecond-to-nanosecond time scales are clearly inconsistent with the expected salient features of the phen radical anion. Instead, there is a prompt formation of a broad transient absorbance (across most of the visible region) with a discernible peak at 400 nm, which decays away only slightly over the entire length of the delay line (5.5 ns). Because the molecular photophysics from the lowest excited state in 1 and related molecules based on iridium(III) and platinum(II) is considered to be configurationally mixed because of energetically proximate ³MLCT and ³LC (phen) manifolds, 50,59-63 we assign the TAs observed in 1 to the ³phen moiety because the phen radical anion does not contribute significant oscillator strength. In the available published examples of TA studies executed on configurationally mixed excited states, the dominating absorbing species is unequivocally the ³LC state in all instances. Similar results have also been echoed in metal-organic molecules featuring triplet excited-state equilibria.58,64-70

For 2–4, it is clear that the ultimate triplet excited state formed is significantly different with respect to that measured in 1, as evidenced by the continued growth in the TA signals on the order of tens of picoseconds. These molecules also possess a similar prompt (130-220 fs) formation of the broad visible absorption signal observed in 1 at both short and long delay times. Combined together, we assign this initial absorption feature in 2–4 as resulting from intersystem crossing from the singlet manifold to the configurationally mixed triplet state (³MLCT/³LC) analogous to that assigned



Figure 6. Normalized nanosecond sensitized triplet absorption difference spectra (red spectra) of the free isocyanide ligands corresponding to those in molecules 2–4 compared to the normalized absorption difference spectra for 2–4 measured promptly in nanosecond TA experiments (blue spectra). Excitation was performed at 355 nm (~1.0 mJ pulse⁻¹; 7 ns fwhm), and spectra were recorded with 5 μ s delay relative to excitation and 50 ns gate width. The triplet sensitizers were benzophenone for 2 and thioxanthen-9-one for 3 and 4.



Figure 7. Qualitative energy-level diagrams summarizing the photophysical behavior of 1-4.

in 1. This is followed by vibrational relaxation within this configurationally mixed triplet excited state that is similar to 1, now with a slightly faster time constant ranging between 3 and 5 ps. However, after the prompt formation and vibrational cooling of this initially populated state, there is a significantly slower process (ranging from 13 to 50 ps) believed to be triplet migration to an excited state with a significantly higher extinction coefficient, which is also responsible for the substantial absorption growth observed for 2-4 in the visible region over this time range.

Because these data are quite distinguishing, we assign the long-lived excited-state absorptions in 2-4 to the pure ³LC excited states corresponding to the respective isocyanide ligand residents in the structure. Further evidence for these assignments emerges from the sensitized triplet spectra of the free isocyanide ligands resulting from sensitization of 2 with benzophenone and sensitization of 3 and 4 with thioxanthen-9-one (Figure 6). In order to best mimic the Lewis acidic character of the rhenium(I) center, trifluoroacetic acid (TFA) was added to the respective sensitization experiments to singly protonate the relevant isocyanide ligand. Although the positions of the resultant triplet absorbances in the free ligands are somewhat shifted with respect to the TAs observed in the analogous rhenium(I) chromophores, their bandshapes are qualitatively similar and therefore consistent with formation of the ³LC excited state on the respective isocyanide moiety. Overall, the combined ultrafast TA data and the nanosecond triplet sensitization experiments suggest triplet energy migration from the initially populated ³MLCT/³LC state to the ³LC state of the respective isocyanide ligand occurring with time constants of 50, 13.5, and 26 ps in 2-4, respectively. An extensive literature search revealed no related reports of excited-state dynamics occurring between configurationally mixed ${}^{3}MLCT/{}^{3}LC$ excited states, with a second ${}^{3}LC$ excited state located on an ancillary ligand. Clearly, there is ample space for additional investigations in this general area, and many combinations of metal centers and ligands can be conceived to glean further insight into such intramolecular triplet-energy migration processes.

In 1–4, the persistent transient signals from the ultrafast TA experiments measured at long delay times quantitatively match the corresponding nanosecond TA difference spectra, indicating that no significant dynamics are taking place between the 5.5 ns delay time in the ultrafast experiment and 15 ns, the earliest prompt signal resolvable in the nanosecond TA apparatus. The nanosecond TA difference spectra of 1-4 as well as their associated transient decay kinetics are provided in

Figures S24–S27. The PL and TA decay kinetics measured for 1–4 using conventional time-resolved PL and laser flash photolysis experiments were all adequately modeled with single-exponential decays and featured quantitative agreement between both experiments in all instances (Table 2). Consistent with the ³MLCT/³LC (phen; in 1) and ³LC (isocyanide; in 2–4) excited-state assignments suggested above, the long-lived excited-state lifetimes recorded here, 8.9, 15.5, 710, and 663 μ s, respectively, are completely congruent with those assignments. Figure 7 presents qualitative Jablonski diagrams of 1–4, summarizing all of the photophysical processes and their corresponding assignments resulting from the current investigation.

Temperature-Dependent Time-Resolved PL and TA Experiments. In order to investigate the relative energies of the closely lying triplet excited states featured in this series of molecules, the excited-state decay rates of each chromophore were measured as a function of the temperature. To best fit the series dynamic temperature data, a three-state Boltzmann distribution model was invoked; Figure 8 and eqs 1–3 describe



Figure 8. Generalized energy-level diagram depicting the parameters of three-state Boltzmann model used to model temperature-dependent excited-state decay in molecules 1–4.

this three-state model.^{8,71} The three excited states involved here are defined as two emissive triplet states of charge-transfer and/or LC character and the third of a thermally deactivating metal-centered ligand-field state. This three-state model has been successfully applied to similar rhenium(I) diimine complexes.⁸ Consistent with these previous studies, a simple two-state model using one triplet excited state and one d–d state does not adequately fit our data without giving physically unreasonable results.

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$$k_{\rm d1} = A_1 \mathrm{e}^{-\Delta E_2/kT} \tag{1}$$

$$k_{\rm d2} = A_2 e^{-\Delta E_2 - \Delta E_1/kT} \tag{2}$$

$$\tau = \frac{1}{k_{\rm obs}} = \frac{1 + e^{-\Delta E_1/RT}}{k_1 + k_2 e^{-\Delta E_1/kT} + (A_1 + A_2)e^{-\Delta E_2/kT}}$$
(3)

A few assumptions accompany this particular model. The first is that the two lower excited states are photoluminescent. The second is that the upper d-d ligand-field states deactivate so efficiently that, once this state is populated, there are no viable radiative decay pathways. Third, the role of the selfquenching phenomenon noted for complexes 3 and 4 is negated by conducting experiments at low concentrations where self-quenching was not observed. Finally, it is also assumed that ΔE_2 is sufficiently greater than ΔE_1 such that the rates of thermal activation to the ligand-field state can be combined into a single preexponential factor $(A_1 + A_2)$. The most adequate fits taking into account all of the time-resolved temperature-dependent PL (1 and 2) or absorbance data (3 and 4) for all four complexes are presented in Figure S28, and the values for each relevant fitting parameter are summarized in Table 4.

Table 4. Summary of Fitting Values from the Three-StateBoltzmann Distribution Model^a

complex	$\Delta E_1^{\ b}$	ΔE_2^{b}	k_1^c	k_2^c
1	545	4042	9.3	53.0
2	496	4042	3.1	55.0
3	775	5622	0.55	22.5
4	806	5957	0.12	25.1

^{*a*}The preexponential factor $(A_1 + A_2)$ was fixed to 4×10^{12} for 1 and 2^8 and floated between 4×10^{14} and 8×10^{14} for 3 and 4. ^{*b*}Units of cm⁻¹ ^{*c*}Value $\times 10^4$ s⁻¹

From the extracted parameters, a number of conclusions can be drawn. In 1 and 2, the energy gap between the lowest triplet manifold and the d-d state is approximately 4000 cm^{-1} , in good agreement with similar molecules modeled in an identical fashion.⁸ According to the relative rates of decay from the two emissive excited states, the lower state is consistent with being ³LC in character, whereas the higher-lying excited state is more in line with the ³CT character. Additionally, the ordering of triplet states is consistent with the TD-DFT modeling of the transitions, where $S_0 \rightarrow T_1$ is LC on the phen ligand and $S_0 \rightarrow$ T_2 is the MLCT transition (Figure S14). From a combination of the kinetic and DFT modeling, 77 K PL emission spectra, and conclusions drawn from the TA dynamics, it can be concluded that the lower triplet excited state in 1 is ³LC (phen) and the upper excited state is likely ³MLCT. Definitive assignments of the lowest ³LC state in 2 are more difficult because this molecule likely features a mixed ³LC state resulting from the nearly isoenergetic combination of both the phen and the isocyanide triplets. TD-DFT modeling reveals that the energy difference between $S_0 \rightarrow T_1$ (phen) and $S_0 \rightarrow$ T₂ (isocyanide) is approximately 0.03 eV (Figure S15). Because these two states are relatively isoenergetic, they could not be distinguished with the use of an additional parameter in the Boltzmann fit, so their relative ordering simply cannot be determined using temperature-dependent PL decay data. However, the RT TA data suggest that the lowestenergy state is most likely ³LC (CNAr) in the case of 2.

Complexes 3 and 4 feature an entirely different series of molecular excited states that are in play. The first obvious difference is that a much larger energy gap between the lowest triplet and ligand-field states now exists, \sim 5600–6000 cm⁻¹. Additionally, the decay rate from that lowest triplet excited state is significantly slower in comparison to that observed in 1 and 2. If it is assumed that the differences in the ligand-field state energy between all four molecules are negligible, we can readily conclude that the lower triplet excited states in 3 and 4 are no longer ³LC (phen)/³MLCT-based but rather ³LC (CNAr)-localized. This is consistent with the combined PL, TA, and electronic structure calculations (Figures S16 and S17), therefore rendering the upper excited state in 3 and 4 using the model presented in Figure 8 as an admixture of nearly isoenergetic ³LC(phen)/³MLCT states.

CONCLUSIONS

This study investigated a series of rhenium(I)-based diiminetricarbonyl arylisocyanide chromophores (1-4) featuring interactions between three closely lying triplet excited states. The combined experimental evidence illustrated that the CNAr ligand was actively engaged in manipulating excitedstate decay in three of these molecules (2-4), wherein the ³MLCT state along with two ³LC excited-state configurations (phen and CNAr) conspired to produce the resultant photophysical properties. As the π conjugation within the CNAr ligand was extended, the initially generated ³LC-(phen)/³MLCT excited state in 1 ultimately migrated to the CNAr ${}^{3}LC$ state on the order of tens of picoseconds in 2–4. It should be noted that previous literature has described $d\pi(\text{Re}) - \pi^*(\text{CNAr})$ ³MLCT transitions existing in a number of complexes not featuring a diimine moiety.^{35,36} The existence of this transition and any role it may play in the photophysics of the complexes in this current study was considered; however, no spectroscopic or computational evidence was found to support this consideration. Chromophores 3 and 4 with RT lifetimes near 700 μ s represent unique examples of excimer formation from inorganic molecules, albeit from interactions between the ³LC state and a corresponding ground-state molecule, as evidenced by dynamic selfquenching in the corresponding PL intensity decays, accompanied by the observation of a short-lived low-energy orange-to-red emission feature in both instances. In the quest for generating new classes of molecular-based charge-transfer excited states intended for driving high-energy chemical transformations, all excited configurations must be considered to achieve the proper chromophore design. While ³LC excited states on diimine and ancillary ligands are energetically out-ofreach in most visible-absorbing MLCT chromophores, they are quite relevant and can dominate excited-state decay in near-UV-absorbing MLCT molecules, as was observed in 2-4 in the present study.

EXPERIMENTAL SECTION

General Procedures. All reagents and solvents used in the synthetic procedures were obtained from commercial sources and used as received, unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on a Varian Innova 400 MHz spectrometer with working frequencies of 400 and 100 MHz for ¹H and ¹³C NMR, respectively. All NMR spectra were plotted and processed using the *MestReNova* software, version 10.0.2. High-resolution ESI-MS data were measured at the Michigan State University Mass Spectrometry and Metabolomics Core (Waters Xevo G2-XS QTOF). Electronic

absorption spectroscopic measurements were recorded on a Shimadzu UV-3600 spectrophotometer in 1 cm quartz cuvettes with spectrophotometric-grade THF as the solvent. Steady-state emission measurements were made on an FS-980 fluorimeter (Edinburgh Instruments) fitted with a 450 W xenon arc lamp and a PMT detector in sealable 1 cm quartz cuvettes designed for air-free handling.

Ultrafast TA Spectroscopy. Time-resolved TA measurements were performed at the NCSU Imaging and Kinetic Spectroscopy Laboratory in the Department of Chemistry. Subpicosecond absorption transients were detected using a Helios TA spectrometer from Ultrafast Systems. A portion of the output from a 1 kHz Ti:sapphire Coherent Libra regenerative amplifier (4 mJ; 100 fs fwhm at 800 nm) was split into the pump and probe beams. The probe beam was delayed in a 6 ns optical delay stage, while the pump beam was directed into an optical parametric amplifier (Coherent OPerA Solo) to generate tunable excitation. These measurements were performed according to previously published methods.^{58,72}

Nanosecond TA Spectroscopy, Time-Resolved PL, and Time-Gated PL Spectroscopic Measurements. Nanosecond TA measurements and time-gated PL spectra were collected with a LP920 laser flash photolysis system (Edinburgh Instruments) using, for excitation, a Minilite 355 Nd:YAG (Continuum). TA difference and PL spectra were collected using an iStar ICCD camera (Andor Technology), controlled by the LP900 software (Edinburgh Instruments). Emission decay kinetics were measured using Minilite 355 Nd:YAG (Continuum) excitation and collected using an apparatus described previously.⁶⁴ All samples were prepared air-free in a glovebox and sealed in sealable 1 cm quartz cuvettes.

Triplet Sensitization of Free Ligands. In order to obtain freeligand triplet TA spectra, a sensitizer was added (to achieve an o.d. at excitation of ~ 0.2) to saturated solutions of the free ligands is THF. All preparation was done air-free in a glovebox. For the phen and isocyanide ligands of 2, benzophenone was used as the sensitizer and excited at 355 nm. For the isocyanide ligands of 3 and 4, thioxanthone was used as the sensitizer and excited at 410 nm using the Vibrant 355 Nd:YAG/OPO (OPOTEK). For the spectra of all isocyanide ligands, TFA ($\sim 10\%$) was added to mimic the Lewis acid effect of complexation.

DFT Calculations. The calculations utilized in this study were performed using the Gaussian 09 software package (revision D.01)73 and the computation resources of the NCSU High Performance Computing Center. Ground- and triplet-state geometry optimizations were performed using the M06 functional,⁷⁴ along with the def2-SVP basis set of Aldrich's group, as implemented in Gaussian 09.75 The Stuttgart–Dresden effective core potentials⁷⁶ were used to replace the core electrons in rhenium for all calculations. The PCM was used to simulate the THF solvent environment for all calculations. Frequency calculations were performed on all optimized structures, and no imaginary frequencies were obtained. The TD-DFT calculations were performed using the same conditions as those described for the geometry optimizations.78-80 The energy and oscillator strengths were computed for each of the 50 lowest singlet excitations and 10 lowest triplet excitations. The natural transition orbitals of the low-lying singlet and triplet transitions were generated using GaussView 5.0.8

General Synthetic Procedure for the Re-CNAr Molecules. This general preparation was adapted from the previously reported synthesis.¹³ In a two-necked 100 mL round-bottom flask with a reflux condenser, solid Re(phen)(CO)₃Cl and silver triflate (slight excess) were purged with a heavy N₂ gas flow. To the solids was added absolute ethanol (25 mL), and the mixture was sealed under N₂. The mixture was protected from light and heated to 85 °C for 4 h. The mixture was then filtered hot over Celite. The filter solution was returned to reflux and the appropriate isocyanide ligand was dissolved in a minimal amount of absolute ethanol and added to the reflux reaction via a syringe. After another 4 h. the reaction mixture was cooled and the solvent concentrated to ~5 mL in vacuo. This concentrated solution was added dropwise to 150 mL of stirring diethyl ether, producing a solid slurry. These solids were filtered and dried to yield the crude product as triflate salt. This solid was

dissolved in minimal methanol and recrystallized by the addition of a saturated solution of $\rm NH_4PF_6$ in deionized water. The pure recrystallized solid was filtered, washed with excess deionized water and pentane, and then dried under vacuum.

[**R**e(phen)(**CO**)₃(**DippCN**)]**PF**₆ (1). Re(phen)(**CO**)₃Cl (340 mg, 0.699 mmol), AgCF₃SO₃ (185 mg, 0.720 mmol), and 2,6diisopropylphenyl isocyanide (132 mg, 0.705 mmol) were used. Yield: 443 mg, 81%. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.46 (dd, 2H, *J* = 5.2 and 1.4 Hz), 8.87 (dd, 2H, *J* = 8.3 and 1.4 Hz), 8.28 (s, 2H), 8.10 (dd, 2H, *J* = 8.3 and 5.2 Hz), 7.29 (t, 1H, *J* = 7.9 Hz), 7.03 (d, 2H, *J* = 7.9 Hz), 2.43 (sep, 2H, *J* = 6.9 Hz), 0.84 (d, 12H, *J* = 6.9 Hz). ¹³C NMR (100 MHz, CD₂Cl₂): δ 191.5 (2C), 188.3, 155.0 (2C), 147.5, 146.0, 140.1, 132.0, 131.6 (2C), 129.1, 127.6, 124.4, 131.2 (2C), 128.8, 128.6, 128.5, 127.9, 127.8, 126.9, 126.7, 126.1, 125.8, 125.7, 125.4, 30.6, 22.1. HR-MS ([M – PF₆]⁺). Calcd: *m*/*z* 636.1426. FTIR (ATR, cm⁻¹): 2172 (m), 2035 (s), 1961 (sh), 1925 (s).

[Re(phen)(CO)₃(PhDippCN)]PF₆ (2). Re(phen)(CO)₃Cl (340 mg, 0.699 mmol), AgCF₃SO₃ (185 mg, 0.720 mmol), and 4-phenyl-2,6-diisopropylphenyl isocyanide (187 mg, 0.710 mmol) were used. Yield: 444 mg, 74%. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.48 (dd, 2H, *J* = 5.2 and 1.4 Hz), 8.88 (dd, 2H, *J* = 8.3 and 1.4 Hz), 8.29 (s, 2H), 8.11 (dd, 2H, *J* = 8.3 and 5.2 Hz), 7.47–7.36 (m, 5H), 7.23 (s, 2H), 2.49 (sep, 2H, *J* = 6.9 Hz), 0.89 (d, 12H, *J* = 6.9 Hz). ¹³C NMR (100 MHz, CD₂Cl₂): δ 190.9 (2C), 187.8, 154.4 (3C), 146.9, 145.9, 143.8, 140.2, 139.6, 131.5, 128.9, 128.5, 128.3, 127.1, 127.0, 122.6, 30.2, 21.6. HR-MS ([M - PF₆]⁺). Calcd: *m/z* 712.1738. Found: *m/z* 712.1730. FTIR (ATR, cm⁻¹): 2174 (m), 2034 (s), 1965 (sh), 1938 (s).

[Re(phen)(CO)₃(PhEthDippCN)]PF₆ (3). Re(phen)(CO)₃Cl (340 mg, 0.699 mmol), AgCF₃SO₃ (185 mg, 0.720 mmol), and 4-phenylethynyl-2,6-diisopropylphenyl isocyanide (202 mg, 0.703 mmol) were used. Yield: 463 mg, 75%. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.47 (dd, 2H, *J* = 5.2 and 1.4 Hz), 8.88 (dd, 2H, *J* = 8.3 and 1.4 Hz), 8.29 (s, 2H), 8.11 (dd, 2H, *J* = 8.3 and 5.2 Hz), 7.48 (m, 2H), 7.35 (m, 3H), 7.20 (s, 2H), 2.43 (sep, 2H, *J* = 6.9 Hz), 0.87 (d, 12H, *J* = 6.9 Hz). ¹³C NMR (100 MHz, CD₂Cl₂): δ 191.3 (2C), 188.2, 155.0 (2C), 147.5, 146.2, 140.8, 132.2, 132.0, 129.6, 129.1, 127.6, 127.5, 126.7, 122.8, 93.0, 88.6, 30.6, 22.0. HR-MS ([M – PF₆]⁺). Calcd: *m/z* 736.1738. Found: *m/z* 736.1728. FTIR (ATR, cm⁻¹): 2172 (m), 2032 (s), 1959 (sh), 1947 (s).

[**Re(phen)**(**CO**)₃(**DiPhDippCN**)] **PF**₆ (4). Re(phen)(CO)₃Cl (340 mg, 0.699 mmol), AgCF₃SO₃ (185 mg, 0.720 mmol), and 4-biphenyl-2,6-diisopropylphenyl isocyanide (240 mg, 0.707 mmol) were used. Yield: 516 mg, 79%. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.48 (dd, 2H, *J* = 5.2 and 1.4 Hz), 8.88 (dd, 2H, *J* = 8.3 and 1.4 Hz), 8.29 (s, 2H), 8.12 (dd, 2H, *J* = 8.3 and 5.2 Hz), 7.66 (m, 2H), 7.62 (m, 2H), 7.56 (m, 2H), 7.45 (m, 2H), 7.36 (m, 1H), 7.29 (s, 2H), 2.43 (sep, 2H, *J* = 6.9 Hz), 0.84 (d, 12H, *J* = 6.9 Hz). ¹³C NMR (100 MHz, CD₂Cl₂): δ 191.5 (2C), 188.3, 155.0 (2C), 147.5, 146.5, 143.9, 141.7, 140.8, 140.6, 138.9, 132.0, 129.4, 129.1, 128.3, 128.1, 127.6, 127.5, 123.0 (2C), 30.8, 22.2. HR-MS ([M - PF₆]⁺). Calcd: *m/z* 788.2051. Found: *m/z* 788.2136. FTIR (ATR, cm⁻¹): 2169 (m), 2035 (s), 1965 (sh), 1932 (s).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01155.

Additional static and time-resolved spectra, temperaturedependent data, structural characterization data, and DFT calculations for 1–4 (PDF)

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Notes

The authors declare no competing financial interest.

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