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Photophysics and Ultrafast Processes in Rhenium(I) Diimine Dicarbonyls

Hala Atallah, Chelsea M. Taliaferro, Kaylee A. Wells and Felix N. Castellano*

In this work, a series of nine Re(I) diimine dicarbonyl complexes of the general molecular formula *cis*-[Re(N^N)₂(CO)₂]⁺ (N^N are various 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) derivatives) were prepared and spectroscopically investigated to systematically evaluate the photophysical consequences of various substituents resident on the diimine ligands. These panchromatic absorbing chromophores were structurally characterized, evaluated for their electrochemical and spectrocelectrochemical properties, and investigated using static and dynamic electronic absorption, photoluminescence (PL), and infrared spectroscopy from ultrafast to supra-nanosecond time scales. The ultrafast time-resolved infrared (TRIR) analysis was further supported by electronic structure calculations which characterized the changes within the two C \equiv O vibrational modes upon formation of the metal-to-ligand charge transfer (MLCT) excited state. The MLCT excited state decay of this series of dicarbonyl molecules appears completely consistent with energy-gap law behavior, where the nonradiative decay rate constants increase logarithmically with decreasing excited state – ground state energy separation, expect in anticipated cases where the substituents were phenyl or *tert*-butyl.

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Introduction

The popularity of Re(I) diimine tricarbonyl complexes¹⁻⁶ of the general formula [fac-Re(N^N)(CO)₃L]⁺, revolves around their low-lying, tunable, metal-to-ligand charge transfer ((MLCT) $(d\pi(M)$ to diimine $\pi^*(L)$) excited states.⁷⁻⁹ Photonic applications such as biological labeling,^{10, 11} sensor development,¹²⁻¹⁴ photochemical molecular devices,^{15, 16} and solar energy conversion schemes¹⁷⁻²¹ have come to rely on this versatile class of chromophores. Extensive research has been conducted on these molecules to both enhance and tune the excited state photophysical properties through ligand modification^{3, 5, 22-25} as well as taking advantage of solvatochromic²⁶⁻²⁸ and rigidichromic^{1, 22, 29} effects on their charge-transfer character. Although all of the strategies to date have led to the improvement of the Re(I) diimine tricarbonyl's photophysical properties, the presence of high frequency C=O stretching modes (> 2000 cm⁻¹) results in rapid nonradiative decay from the lowest lying MLCT manifold to the ground state.^{7, 30, 31} To that end, rapid nonradiative decay channels, largely governed by the presence of the three high frequency vibrating Re-C≡O ligands, needs to be overcome. $^{\rm 30,\;32}$

A few reports have emerged on Re(I) dicarbonyl complexes, having the form *cis*-[Re(N^N)(L^L)(CO)₂]⁺ and *trans,cis*-[Re(N^N)(P)₂(CO)₂]⁺ (where L^L is either a chelating diphosphine or another diimine ligand and P is a monodentate

phosphine ligand), to attenuate nonradiative decay processes.⁷, ^{31, 33-36} Re(I) dicarbonyl complexes are potentially advantageous as they reduce the overall number of Re-C=O while lowering the frequencies of the two remaining Re-C=O vibrations. Lowering the energy of the two remaining Re-C=O stretching modes arises from π -backbonding being distributed across two C=O ligands instead of three. For example, the replacement of one high-energy Re-C=O mode in Re(I) dicarbonyl complexes of the form *trans,cis*-[Re(bpy)(P)₂(CO)₂]⁺ and *cis*-[Re(bpy)(P^P)(CO)₂]⁺ resulted in significant reduction in the associated nonradiative decay rate constant, k_{nr} ,³⁷⁻³⁹ with respect to those measured in the *fac*-Re(bpy)(CO)₃Lⁿ⁺ series.³¹

Based on the aforementioned advantages of Re(I) dicarbonyl complexes, several modifications can be executed in regard to the L^L ligand. Thus, our interest in the cis-[Re(N^N)₂(CO)₂]⁺ motif was inspired by the promising properties of cis-[Re(N^N)(P^P)(CO)₂]⁺ photophysical chromophores, to provide alternative molecular topologies with respect to Re(I) diimine tricarbonyl complexes.^{40, 41} While variations on the substituents of the N^N ligand framework has only been examined for Re(I) tricarbonyls, 1, 3-5, 8, 9, 12, 26 related systematic investigations for the Re(I) dicarbonyls remains largely unexplored. In this contribution, we evaluate the photophysical properties that result from modifications on the substituents on the 1,10-phenanthroline (phen) and 2,2'bipyridine (bpy) ligands contained in the cis-[Re(N^N)₂(CO)₂]⁺ structural motif, Fig. 1. All nine molecules investigated here display panchromatic ¹MLCT absorption bands across the visible and feature photoluminescence (PL) above 680 nm at room temperature with quantum yields as high as 1.6% and excited-

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⁺Electronic Supplementary Information (ESI) available: Additional synthetic details, structural characterization, and time-resolved spectra. See DOI: 10.1039/x0xx00000x





Fig. 1 Molecular structures of the Re(I) phenanthroline dicarbonyl panchromatic chromophores 1–9.

state lifetimes reaching 512 ns. The energy-gap law was successfully applied to each series of cis-[Re(N^N)₂(CO)₂]⁺ complexes in this manuscript, illustrating that the energy contained in the ³MLCT excited state is readily altered by both the nature of the diimine ligand and the location(s)/nature of the substituents.

Experimental

Reagents and Chemicals

All reagents were purchased from VWR or Aldrich Chemical Company and used as received except for tetrabutylammonium hexafluorophosphate (TBAPF₆), which was recrystallized in ethanol and dried prior to use in all electrochemical and spectroelectrochemical measurements. The synthetic procedures used to make all of the complexes are outlined in Scheme 1. Synthetic procedures for the *cis*-[Re(N^N)₂(CO)₂]⁺ complexes in this study are included in the Electronic Supplementary Information. Spectroscopic samples were prepared using spectroscopic grade dichloromethane (CH₂Cl₂) and were degassed using freeze-pump-thaw technique.⁴²

cis-[Re(3,4,7,8-Me₄phen)₂(CO)₂](CF₃SO₃) (1). ¹H NMR (400 MHz, methylene chloride- d_2) δ 9.66 (s, 2H), 8.32 (d, J = 9.5 Hz, 2H), 8.21 (d, J = 9.4 Hz, 2H), 7.23 (s, 2H), 2.93 (s, 6H), 2.73 (s, 6H), 2.66 (s, 6H), 2.13 (s, 6H). ¹³C NMR (100 MHz, methylene chloride- d_2) δ 201.7, 156.3, 148.5, 146.7, 146.3, 146.0, 144.9, 135.6, 134.3, 130.1, 129.6, 124.5, 124.1, 18.1, 18.0, 15.3, 15.2. ESI-HRMS. Found: m/z 713.2069. Calcd for C₃₄H₃₂N₄O₂¹⁸⁵Re: m/z

713.2055. ATR-FTIR: 557, 636, 722, 816, 1030, 1146, 1220, 1263, 1426, 1824, 1891 cm⁻¹.

cis-[Re(4,7-Me₂phen)₂(CO)₂]PF₆ (2). ¹H NMR (400 MHz, acetonitrile-*d*₃) δ 9.74 (d, J = 5.4 Hz, 2 Hz), 8.36 (d, J = 9.3 Hz, 2H), 8.24 (d, J = 9.3 Hz, 2H), 7.85 (d, J = 5.4 Hz, 2H), 7.41 (d, J = 5.3 Hz, 2H), 7.27 (d, J = 5.3 Hz, 2H), 3.02 (s, 6H), 2.73 (s, 6H). ¹³C NMR (100 MHz, acetonitrile-*d*₃) δ 202.4, 156.4, 150.1, 148.8, 148.4, 147.7, 147.3, 131.9, 131.0, 128.3, 126.8, 125.4, 124.9, 19.1, 19.0. ESI-HRMS. Found: m/z 657.1432. Calcd for C₃₀H₂₄N₄O₂¹⁸⁵Re: m/z 657.1429. ATR-FTIR: 518, 555, 636, 828, 1030, 1265, 1420, 1448, 1520, 1571, 1603, 1624, 1828, 1899 cm⁻¹.

cis-[Re(5,6-Me₂phen)₂(CO)₂]PF₆ (3). ¹H NMR (400 MHz, acetonitrile- d_3) δ 9.87 (d, J = 5.2 Hz, 2H), 8.89 (d, J = 8.8 Hz, 2H), 8.61 (d, J = 8.3 Hz, 2H), 8.01 (dd, J = 8.4, 5.3 Hz, 2H), 7.45 (m, 2H), 2.84 (s, 6H), 2.70 (s, 6H). ¹³C NMR (100 MHz, acetonitrile-d3) δ 201.5, 155.7, 148.1, 147.1, 146.7, 136.3, 134.8, 133.5, 133.0, 132.9, 132.0, 127.4, 126.0, 15.7, 15.5. ESI-HRMS. Found: m/z 657.1439. Calcd for C₃₀H₂₄N₄O₂¹⁸⁵Re: m/z 657.1429. ATR-FTIR: 557, 714, 787, 806, 840, 1428, 1828, 1907 cm⁻¹.

cis-[Re(phen)₂(CO)₂](CF₃SO₃) (4).⁷ ¹H NMR (400 MHz, acetonitrile- d_3) δ 9.93 (dd, J = 5.3, 1.3 Hz, 2H), 8.77 (dd, J = 8.2, 1.3 Hz, 2H), 8.50 (dd, J = 8.2, 1.4 Hz, 2H), 8.23 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 8.03 (dd, J = 8.2, 5.3 Hz, 2H), 7.58 (dd, J = 5.2, 1.4 Hz, 2H), 7.46 (dd, J = 8.2, 5.1 Hz, 2H). The ¹H NMR spectrum quantitatively matched that reported in the literature.⁷ ATR-FTIR: 514, 551, 571, 634, 720, 842, 1030, 1095, 1136, 1220, 1263, 1428, 1828, 1905 cm⁻¹.

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Scheme 1 Generalized synthetic scheme for the preparation of the Re(I) bis-diimine dicarbonyl chromophores 1–9.

cis-[Re(4,7-Ph₂phen)₂(CO)₂]PF₆ (5).⁷ ¹H NMR (400 MHz, acetonitrile- d_3) δ 10.02 (d, J = 5.6 Hz, 2H), 8.19 (d, J = 9.5 Hz, 2H), 8.06 (d, J = 9.4 Hz, 2H), 8.00 (d, J = 5.5 Hz, 2H), 7.82 (d, J = 5.4 Hz, 2H), 7.79 – 7.75 (m, 4H), 7.74 – 7.64 (m, 6H), 7.56 (t, J = 3.3 Hz, 6H), 7.50 – 7.43 (m, 6H). The ¹H NMR spectrum quantitatively matches the spectrum reported in the literature.⁷ ATR-FTIR: 702, 765, 832, 849, 1226, 1393, 1593, 1622, 1828, 1899 cm⁻¹.

cis-[Re(5,5'-Me₂bpy)₂(CO)₂]PF₆ (6). ¹H NMR (400 MHz, methylene chloride- d_2) δ 9.27 (s, 2H), 8.51 (dd, J = 11.7, 8.6 Hz, 4H), 7.92 (dd, J = 8.3, 1.3 Hz, 2H), 7.83 (dd, J = 8.4, 1.3 Hz, 2H), 7.06 (s, 2H), 2.55 (s, 6H), 2.17 (s, 6H). ¹³C NMR (100 MHz, methylene chloride- d_2) δ 200.9, 155.5, 154.0, 153.9, 147.3, 140.4, 138.6, 137.9, 124.5, 124.0, 18.7, 18.6. ESI-HRMS. Found: m/z 609.1438. Calcd for C₃₀H₂₄N₄O₂¹⁸⁵Re: m/z 609.1429. ATR-FTIR: 553, 616, 822, 836, 1042, 1146, 1242, 1382, 1473, 1603, 1828, 1893 cm⁻¹.

cis-[Re(4,4'-dtbbpy)₂(CO)₂]PF₆ (7). ¹H NMR (400 MHz, acetonitrile-*d*₃) δ 9.29 (d, J = 6.0 Hz, 2H), 8.44 (s, 2H), 8.38 (s, 2H), 7.63 (d, J = 6.0 Hz, 2H), 7.35 (d, J = 6.0 Hz, 2H), 1.50 (s, 18H), 1.33 (s, 18H). ¹³C NMR (100 MHz, acetonitrile-*d*₃) δ 202.1, 165.2, 163.4, 156.9, 156.6, 156.2, 148.2, 126.3, 125.2, 122.9, 118.3, 36.4 (x2), 30.5, 30.3. ESI-HRMS. Found: m/z 777.3300. Calcd for C₃₈H₄₈N₄O₂¹⁸⁵Re: m/z 777.3307. ATR-FTIR: 559, 604, 749, 838, 897, 1024, 1134, 1203, 1252, 1367, 1412, 1481, 1613, 1668, 18286, 1899 cm⁻¹.

cis-[Re(bpy)₂(CO)₂]PF₆ (8).⁷ ¹H NMR (400 MHz, acetonitrile*d*₃) δ 9.45 (d, J = 5.8 Hz, 2H), 8.46 (d, J = 8.3 Hz, 2H), 8.38 (d, J = 8.2 Hz, 2H), 8.14 (t, J = 8.0 Hz, 2H), 8.02 (t, J = 7.5 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.41 (d, J = 5.6 Hz, 2H), 7.36 – 7.30 (m, 2H). The ¹H NMR spectrum matches that reported in the literature.⁷ ATR- FTIR: 557, 732, 765, 836, 879, 1275, 1316, 1420, 1444, 1467, 1603, 1834, 1907 cm⁻¹.

cis-[**Re(4,4'-Me₂bpy)**₂(**CO**)₂]**PF**₆ (9). ¹H NMR (400 MHz, acetonitrile-*d*₃) δ 9.23 (d, J = 5.9 Hz, 2H), 8.31 (s, 2H), 8.24 (s, 2H), 7.44 (dd, J = 5.8, 1.1 Hz, 2H), 7.22 (d, J = 5.7 Hz, 2H), 7.15 (d, J = 5.8 Hz, 2H), 2.61 (s, 6H), 2.42 (s, 6H). ¹³C NMR (100 MHz, acetonitrile-*d*₃) δ 202.0, 156.5, 156.3, 156.0, 153.0, 151.1, 147.9, 129.8, 128.8, 126.2, 125.3, 21.4, 21.3. ESI-HRMS. Found: m/z 609.1443. Calcd for C₃₀H₂₄N₄O₂¹⁸⁵Re: m/z 609.1429. ATR-FTIR: 510, 557, 834, 1240, 1412, 1448, 1479, 1620, 1797, 1901 cm⁻¹.

General

The coordination compounds fac-Re(N^N)(CO)₃Cl, fac- $[Re(N^N)(CO)_3(NCMe)]BF_4$ and $fac-[Re(N^N)(CO)_3(CF_3SO_3)]$ were prepared as described in the literature.^{23, 43, 44} The synthetic procedures used to prepare all of the molecules are outlined in Scheme 1. Synthetic procedures for the cis-[Re(N^N)₂(CO)₂]⁺ complexes in this study are included as Electronic Supplementary Information. ¹H NMR spectra were recorded on a Varian Innova 400 NMR spectrometer operating at 400 MHz or a Bruker Avance NEO spectrometer operating at 400 MHz. ¹³C NMR spectra were recorded on the Bruker Avance NEO spectrometer operating at 100 MHz. ¹H and ¹³C NMR spectra were processed using MestReNova and Topspin software packages and are provided for all Re(I) final products as Electronic Supplementary Information, Figs. S1-S15⁺. All chemical shifts were referenced to residual solvent signals, and the splitting patterns are listed as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet). Highresolution electrospray ionization mass spectrometry (ESI-HRMS) was performed at the Michigan State University Mass

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Spectrometry and Metabolomics Core and mass spectra are provided for all of the six newly synthesized Re(I) molecules in this study, along with comparisons to their respective calculated spectra, Figs. S16–S27⁺. Solid-state IR spectra for the nine powdered samples of the Re(I) complexes evaluated here were measured using an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer from Bruker (Alpha ATR-FTIR) equipped with a diamond anvil. The FTIR spectra of the powders for all nine Re(I) molecules, including stacked spectral comparisons in the carbonyl region, are provided as Electronic Supplementary Information, Figs. S28–S38⁺. Steadystate PL spectra were measured on an Edinburgh FS920 Photoluminescence spectrofluorimeter. quantum vield (Φ) measurements were performed using deaerated (freezepump-thaw degassed in a 1 cm path length quartz cuvette) samples measured relative to aerated [Ru(bpy)₃](PF₆)₂ standard in acetonitrile (CH₃CN) (λ_{exc} = 475 nm; Φ_{std} = 0.018).⁴⁵ The absorbance of the samples and the standard were maintained at 0.1 ± 0.005 OD at the excitation wavelength.

Nanosecond Transient Absorption (nsTA) Spectroscopy

Nanosecond transient absorption measurements were performed on a LP920 laser flash-photolysis system (Edinburgh Instruments). For nanosecond pulsed-laser excitation, a tunable Vibrant 355 Nd:YAG/OPO system (OPOTEK) was used. An iStar ICCD camera (Andor Technologies), controlled by the LP920 software program (Edinburgh Instruments) was used to collect the transient absorption difference spectra in the visible portion of the spectrum. The samples were freeze-pump-thaw degassed in 1 cm path-length quartz optical cells except for complex 4 which was bubble degassed with a stream of N₂ for 40 mins. The optical densities of the samples at the excitation wavelength (λ_{ex} = 500 nm; 2.0 mJ/pulse; 7 ns fwhm) were maintained between 0.4 and 0.5 OD. All nsTA experiments were conducted at room temperature. Ground state absorption spectra were recorded before and after each experiment to ensure sample stability using an Agilent 8453 UV-visible spectrophotometer. The single-wavelength transient kinetic data were fitted and analyzed using OriginPro 2016.

Ultrafast Transient Absorption (UFTA) Spectroscopy

Sub-picosecond transient absorption (TA) measurements were performed using an amplified Ti:sapphire laser system described previously.47 Briefly, 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 pump beam was directed into an optical parametric amplifier (Coherent OPerA Solo) to generate the 500 nm pump pulse (100 fs fwhm, 0.5 µJ/pulse) while the probe beam was delayed in a 6.6 ns optical delay stage. The probe beam was focused into a CaF_2 crystal to generate the white light continuum spanning 340–750 nm. The two beams were focused and spatially and temporally overlapped into a spot on the sample, with the relative polarizations of the pump and probe beams set at the magic angle. All solvents were fresh and spectrophotometric grade, and ground-state absorption spectra were taken before and after each experiment using an Agilent 8453 UV-visible spectrophotometer to ensure there

was no sample decomposition. Samples were prepared in 2 mm path length quartz cuvettes to allow for a stir bar to prevent the photodegradation of the samples. The transient spectra and kinetics were obtained using a commercially available transient absorption spectrometer (Helios, Ultrafast Systems), averaging at least three complete time delay scans and using 2 s of averaging at each respective time delay. Transient kinetics were evaluated using Igor Pro 7.

Ultrafast Time-Resolved Mid-Infrared (TRIR) Absorption Spectroscopy

Sub-picosecond mid-infrared time-resolved measurements (TRIR) were performed using an in-house constructed pumpprobe transient infrared absorption spectrometer. 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 pump beam was directed into an optical parametric amplifier (Coherent OPerA Solo, UV-VIS) to generate tunable excitation (500 nm, 0.7 µJ/pulse), delayed in a 3.6 ns optical delay stage, and then focused into the sample. An optical chopper synchronized with the laser output at 500 Hz was placed in the pump beam for the delta OD calculation, and a wavelength-appropriate half-wave plate rotated polarization to ensure excitation at the magic angle. The probe beam was directed into a second optical parametric amplifier for difference frequency generation (DFG) (Coherent OPerA Solo) to generate the mid-IR probe beam. After entering the N2purged sample compartment, the probe beam was split 50/50 into probe and reference beams which were both focused into the sample sealed in a demountable flow cell with round 25 mm (diameter) x 1 mm BaF₂ windows and a variable spacer but only the probe was overlapped with the pump. Both probe and reference were re-focused onto the entrance slit of a Horiba Scientific iHR320 imaging spectrometer. The signal was collected using a 64x2 dual array MCT liquid N₂-cooled detector (FPAS integrator and electronics from Infrared Systems Development Corporation). The experiment was controlled by in-house coded LabVIEW software. Typically, 1600 laser pulses were averaged to generate sufficient kinetic transients. The sample solutions were prepared to maintain FTIR absorbance values of ~ 0.6 at the metal carbonyl stretching frequencies. Ground state IR absorption spectra were taken before and after each experiment using a Bruker Vertex 80V FTIR spectrophotometer operating with OPUS v.7.2 software to ensure there was no sample decomposition observable in the mid-IR fingerprint region.

Electrochemistry

Cyclic voltammetry (CV) measurements were carried out inside a dinitrogen filled glovebox (MBraun). Samples were dissolved in spectrophotometric grade acetonitrile containing recrystallized 0.1 M TBAPF₆ as the supporting electrolyte. The voltammograms were measured using a CH Instruments model 600E series electrochemical workstation. A platinum disk was used as the working electrode (1.6 mm), a platinum wire as the counter electrode, and Ag/AgNO₃ as the reference electrode. The scan rate for the measurements was 20 mV/s, and (Fc⁺/Fc) was used as an internal standard.⁴⁶ Fig. S39–S47⁺ present the

cyclic voltammograms for all of the Re(I) complexes investigated in this contribution.

Spectroelectrochemistry

UV-vis spectroelectrochemical oxidation and reduction experiments were carried out inside a dinitrogen filled glovebox (MBraun). A 0.1 M solution of TBAPF₆ in spectrophotometric grade CH₃CN was used as the supporting electrolyte. The Ag/AgNO₃ redox couple was used as an internal reference for all measurements. Experiments were performed using a Honeycomb Spectroelectrochemical Cell Kit (Pine Research Instrumentation). This kit uses a Pt counter electrode and Pt working electrode along with a Ag/AgNO₃ reference electrode. The measurements were acquired by using an Ocean Optics HR2000+ spectrometer equipped with deuterium and halogen light sources for UV-visible experiments. Spectra were collected continuously for 40 mins while under electrical bias. Oneelectron reduction or oxidation was performed through controlled potential electrolysis, with overpotentials of at least 100 mV to ensure complete electrolysis. The electronic absorption spectra taken prior to bulk electrolysis was used as the neutral reference spectrum.

Electronic Structure Calculations

The electronic structure calculations performed on molecules **1–9** in this study were performed using the Gaussian 09⁴⁸ software package and the computation resources of the North Carolina State University High Performance Computing Center (ESI, Fig. S73⁺). Ground state and triplet state geometry optimizations were performed at the B3LYP-D3/6-31G*/LANL2DZ level of theory for the Re(I) dicarbonyl series.⁴⁹⁻⁵⁶ The polarizable continuum model (PCM) was used to simulate the solvent environments for all calculations.⁵⁷ Frequency calculations were performed on all optimized structures and no imaginary frequencies were obtained in any instance.

Results and discussion

Synthesis and characterization

The synthon chloride complexes of the general formula fac-Re(N^N)(CO)₃Cl were prepared using procedures reported in the literature.⁴³ This involves refluxing Re(CO)₅Cl in 1:1 eq. with the corresponding diimine ligand in toluene for two hours. The isolated product was then used to synthesize either fac- $[Re(N^N)(CO)_3(NCMe)]BF_4$ or fac- $[Re(N^N)(CO)_3(CF_3SO_3)]$. The synthesis of the fac-[Re(N^N)(CO)₃(NCMe)]BF₄ and fac- $[Re(N^N)(CO)_3(CF_3SO_3)]$ were also executed as adapted from the literature.^{23, 44} This involves refluxing fac-Re(N^N)(CO)₃Cl with AgOTF or AgBF₄ in ethanol or acetonitrile to obtain the desired triflate or acetonitrile coordinated product, respectively. The title compounds were synthesized under harsh forcing conditions that utilized a high temperature "melt" of the tricarbonyl-diimine precursor with excess diimine ligand, producing cis-[Re(N^N)₂(CO)₂]^{+,7} Scheme 1 presents the generalized synthetic procedure yielding the desired cis- $[Re(N^N)_2(CO)_2]^+$ species. The ¹H and ¹³C NMR spectra are

universally consistent with the *cis*-arrangement of ligands. The *cis*- $[Re(N^N)_2(CO)_2]^+$ complexes have C₂ symmetry which leads to an inequivalence in each half of the diimine ligand and therefore exhibits twice the number of the resonances in NMR spectroscopy with respect to that of the free diimine ligand.

Electronic absorption spectroscopy

The electronic absorption spectra of **1–5** are displayed in Fig. 2A. These molecules are orange-to-red in hue due to their panchromatic MLCT transitions that span the range of 350–650 nm. In the UV region of the spectra (250–350 nm), intraligand (IL) $\pi \rightarrow \pi^*$ transitions within the diimine ligands are observed. Molecules **6–9** (Fig. 2B) are also red in color and exhibit similar absorption spectral features and transitions in the visible (MLCT transitions) and UV (IL transitions) as seen in **1–5**. The assignment of MLCT character to the lower energy absorption features is based on literature precedence.^{7, 36, 58} Additional support for the charge transfer (assignment at the low energy transitions (350–650 nm) are its broad featureless absorption (Fig. 2) and the magnitude of the molar extinction coefficient (~10⁴ M⁻¹ cm⁻¹) as presented in Table 1.



Fig. 2 Static electronic spectra of the Re(I) bis-diimine dicarbonyl complexes (A) 1–5 and (B) 6-9 measured in CH₂Cl₂.

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| Table 1 | Solid-state ATR-FTIR alo | ng with absorption and | selected photophysical | I properties of 1-9 measur | ed in CH ₂ Cl ₂ . |
|---------|--------------------------|------------------------|------------------------|----------------------------|---|
|---------|--------------------------|------------------------|------------------------|----------------------------|---|

| Complexes | Uco (cm ⁻¹) ^a | λ _{abs} ((ε x 10 ³ (Ν π- π* | nm) <u>//¹cm⁻¹))^b</u> <u>MLCT</u> (dπ-π*) | - λ _{em max} (nm) ^b | $\Phi_{em}{}^{c}$ (%) | $k_r \ge 10^4 (s^{-1})^d$ | k _{nr} x 10 ⁶ (s ⁻¹) ^e |
|-----------|---|--|---|---|-----------------------|---------------------------|---|
| 1 | 1891 1824 | 271 (76.3) 300 (25.5) | 391 (9.06) 449 (8.13) 521 (5.38) | 681 | 1.60 | 3.12 | 1.92 |
| 2 | 1899 1828 | 265 (86.7) 286 (24.5) 305 (10.7) | 400 (9.15) 474 (7.79) 543 (5.12) | 698 | 0.49 | 2.33 | 4.69 |
| 3 | 1907 1828 | 272 (63.0) 317 (9.10) | 408 (8.20) 483 (6.27) 555 (5.12) | 703 | 0.43 | 3.39 | 7.78 |
| 4 | 1905 1828 | 266 (74.2) 293(21.4) | 410 (8.74) 485 (6.85) 554 (4.64) | 704 | 0.75 | 5.74 | 7.58 |
| 5 | 1899 1828 | 279 (95.1) 298 (62.4) 320 (26.5) | 429 (14.9) 493 (12.5) 572 (7.97) | 722 | 0.88 | 4.81 | 5.45 |
| 6 | 1893 1828 | 294 (54.9) | 364 (7.29) 394 (7.71) 475 (6.26) 545 (4.22) | 695 | 0.34 | 5.63 | 16.6 |
| 7 | 1899 1826 | 287 (57.7) | 362 (8.19) 400 (8.64) 483 (6.74) 552)4.80) | 706 | 0.14 | 5.42 | 38.4 |
| 8 | 1907 1834 | 289 (54.1) | 361 (7.01) 402 (7.55) 494 (6.11) 564 (4.27) | 714 | 0.11 | 4.42 | 40.0 |
| 9 | 1901 1797 | 286 (48.3) | 362 (6.67) 399 (7.12) 486 (5.41) 554 (3.84) | 715 | 0.09 | 4.02 | 43.4 |

^aError $\pm 4 \text{ cm}^{-1}$. ^bRoom temperature measurements were performed in CH₂Cl₂. ^cQuantum yield measurements were performed using aerated [Ru(bpy)₃](PF₆)₂] in acetonitrile as the standard λ_{exc} = 475 nm; Φ_{std} = 0.018)^{45,d} k_r = Φ/τ . ^ek_{nr} = (1 - Φ) / τ ; the excited state lifetimes used in these calculations are collected in Table 2.

The MLCT bands of 1–9 shift depending on the substituents and the positions of the substituents on the diimine ligand. Replacement of the hydrogen atoms on the phen and bpy ligands with methyl groups shifts the MLCT band to higher energies. For example, 1 exhibits the most apparent blue shift in the MLCT band as it features four methyl groups in the 4-, 5-, 6- and 7- positions on the phen ligand. On the other hand, phenyl groups (electron delocalizing substituents) in the 4- and 7- positions on the phen ligand (5) induce a red shift in the MLCT band. These results match well with the potential differences (Eox-Ered) measured from electrochemistry experiments (discussed below). Interestingly, 5 has the highest molar extinction coefficient (Table 1) in comparison to the other molecules. Molecules containing phenyl groups result in a smaller polarization difference between the ground and excited states causing the electrons in the excited state to disperse across both the phen ligand and phenyl substituents; i.e. greater

 π -conjugation leads to greater electron delocalization. This results in a decrease in the lateral displacement between the ground and the excited states. In the case of **5**, the absorption is observed at longer wavelengths and the electronic transitions are concentrated to lower vibrational levels of the excited state in comparison to the methyl substituted phen derivatives. This results in a higher intensity absorption band for phenyl substituted phenanthroline ligands.

Photoluminescence spectroscopy

The static photoluminescence spectra of the studied complexes are shown in Fig.3. The PL exhibited from all nine chromophores is broad and featureless with large apparent Stokes shifts consistent with PL emanating from a triplet MLCT (³MLCT) excited state. We therefore assigned the PL as ³MLCT phosphorescence as seen in previously published works.^{7, 36} As presented in Table 1, the PL λ_{max} of the

methyl derivatives are shifted to higher energies with respect to the unsubstituted diimine ligands, **4** (phen) and **8** (bpy) ($\Delta\lambda_{max}$ = 20–480 cm⁻¹ for the phen derivatives (1-3) and $\Delta\lambda_{max}$ = 159 and 382 cm⁻¹ for the bpy derivatives, 7 and 6 respectively relative to 8). On the other hand, the diphenyl-phen derivative (5) is lower in energy with respect to the unsubstituted phen, 4. These changes in λ_{max} mirrors the behaviour seen in the electronic absorption spectra and are caused by the same phenomenon as discussed in the previous section. In regard to the position of the methyl groups, the λ_{max} of $\boldsymbol{2}$ is lower than 3 (697 nm and 703 nm respectively). This illustrates that a greater shift is observed when the methyl groups occupy the 4- and 7- positions than when occupying the 5- and 6- positions of the phen ligand. This is also demonstrated in the bpy complexes were methyl groups occupy 5- and 5'- positions (695 nm for 6) result in a greater shift than when occupying 4- and 4'-positions (715 nm for 9). The position of the methyl substituents on the diimine ligand having significance in the tunability of the photophysics is highlighted here in their photoluminescent properties, Table 1. For example, when comparing the PL properties of 9 (and to a lesser extent 7) to the parent molecule 8, the methyl substituents have a negligible effect on the energy, quantum yield, and calculated k_r and k_{nr} values. However, **1** has the lowest λ_{max} and a drastically different quantum yield of all studied phen derivatives since it has the greatest number of methyl substituents on the phen ligand. The combined PL properties of these nine compounds are presented in Table 1 (static) and Table 2 (dynamic). Chromophores 1-5 exhibited photoluminescence lifetimes that ranged between 128 and 512 ns (Figs. S48–S52⁺) while 6–9 have lifetimes that ranged from 23-60 ns (Figs. S53-S56⁺) with each molecule following first-order decay kinetics. In general, as the λ_{max} of the PL emission decreased, the lifetime increased, with the notable exception of 5. Once again this is due to the different electronic effects exhibited by the phenyl substituents. These results, to a large extent, are in accordance with the energy-gap law which states that the excited state lifetimes should decrease with respect to decreasing PL emission energy;59 namely the ground and excited state energy gap. As seen with the PL lifetimes (Table 2), the quantum yields (Table 1) increase with increasing MLCT energy with the phenanthroline derivatives exhibiting overall higher quantum yields and longer excited state lifetimes. It is noteworthy to mention, the difference in the values of the quantum yields and excited state lifetimes for 1-5 in comparison to 6-9. Molecules 1-5 have higher frequency vibrational breathing modes relative to 6-9, resulting in higher values of Φ and τ for the former with respect to the latter.

From the excited state lifetimes and quantum yields, k_r and k_{nr} decay rate constants were calculated and are collected in Table 1. From the plot of $ln(k_{nr})$ vs E_{em} , consistent with the energy-gap law,⁶⁰ **1–4** (Fig. 4A) lie on the same trend line, whereas **5** exhibited a lower k_{nr} than predicted. Again, this is due to the phenyl groups having different polarizability between the ground and excited states from that of the methyl groups.³⁴ Similarly, **6**, **8** and **9** lie on the same trendline whereas **7**, containing *tert*-butyl groups, does not. Complex **7** most likely falls off of the trend line due to the free rotation of the *tert*-butyl groups which markedly increases its k_{nr} value (Fig. 4B) likely due to the "loose bolt" effect.⁶¹



Fig. 3 PL spectra of Re(I) bis-diimine dicarbonyl complexes (λ_{ex} = 475 nm) in CH₂Cl₂ at room temperature for (A) **1–5** and (B) **6–9**.

Table 2 Time-Resolved TA and PL data recorded for 1-9 in $CH_2Cl_2.$

| Complexes | τ _{υFTA} (ps) ^a | τ _{nsTA} (ns) ^b | τ _{PL} (ns) ^c |
|-----------|-------------------------------------|-------------------------------------|-----------------------------------|
| 1 | 62.95 ± 11.7 | 504 | 512 |
| 2 | 76.02 ± 9.45 | 210 | 212 |
| 3 | 80.04 ± 11.60 | 127 | 128 |
| 4 | 56.30 ± 9.98 | 56.30 ± 9.98 124 | |
| 5 | 148.41 ± 18.10 | 179 | 182 |
| 6 | 22.81 ± 1.93 | 59 | 60 |
| 7 | 13.42 ± 2.81 | 26 | 26 |
| 8 | 15.95 ± 2.68 | .68 24 25 | |
| 9 | 9.24 ± 2.05 | 22 | 23 |

^aUltrafast transient absorption determined time constants of the high energy transient feature measured at 360 nm for 1–9. ^bNanosecond transient absorption kinetic decay of 1–9 measured at 680 nm (1), 700 nm (2) 705 nm (3), 707 nm (4), 730 nm (5), 696 nm (6), 710 nm (7), 720 nm (8), and 718 nm (9). ^cPL decay of 1–9 measured at 470 nm (1, 2 and 4), 435 nm (3), 480 nm (5), 535 nm (6), 540 nm (7), and 550 nm (8 and 9).





Transient Absorption Spectroscopy

The excited state difference spectra of 6 is presented in Fig. 5, again as a representative example of what is observed across the series of 9 molecules. The difference spectra feature two broad excited state features, one in the UV (300-450 nm) and one that spans from the visible to the NIR (600-800 nm). There is also a ground-state bleach that occurs in the visible region (451-583 nm). These difference spectra are representative for what was observed in 1-9 (Figs. S57 and S58⁺) as the similarity of the bidentate N-donor ligands of bpy and phen are shared throughout these molecules. In all cases, as depicted in Table 2, the kinetic decays of the transient features quantitatively match their respective PL intensity decays (Figs. S59-S67⁺ and Figs. S48-S56⁺). From this, one can infer that the excited state spectral features seen originate from the same emitting excited state observed in the steady-state PL spectra. Ergo, the transient absorption difference spectrum is illustrative of the decay of the ³MLCT excited state. The MLCT excited state is also supported from the spectroelectrochemical data. To that end, 6 was selected as a representative sample and its spectroelectrochemical data are presented in Fig. S68. To a large extent, the resultant spectrum from superposing the one electron oxidation with the one electron reduction contains









features that correspond to the nsTA difference spectrum which correlates to the proposed MLCT nature of their excited states.

The excited state absorption difference spectra in the ultrafast time domain for the nine complexes were also measured. Complex 6 was selected as a representative sample and its excited state absorption difference spectra are presented in Fig. 6. The transient absorption kinetics and the PL intensity decay measurements for the rhenium(I) bis-diimine dicarbonyl complexes indicate repopulation of the ground state from the lowest-energy MLCT excited state. In the ultrafast time regime (Table 2), a short-lived relaxation process precludes the long-lived decay of the ³MLCT excited state (Figs. S57–S58⁺ and Figs. S69–S70⁺) with time constants ranging from 60 to 150 ps for 1–5 and 10 to 20 ps for 6–9. These values are consistent with time constants expected for combinations of intramolecular vibrational relaxation and intersystem crossing (ISC) processes. The notable difference in rates implies less wavefunction overlap between the excited states in 1-5 compared to 6-9; unsurprisingly, when considering the increase in rigidity in phen compared to bpy. Although complexes 1-4 possess very similar ISC rates (~70 ps), the increased electronic delocalization and

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further steric rigidity in **5** reduces vibrational overlap further, leading to slower formation of the relaxed ³MLCT excited state (150 ps).

Electrochemical properties

The redox potentials (determined by CV, measured vs SCE) of 1-5 (Figs. S39–S43⁺) are summarized in Table 3. Each of these molecules exhibits ligand-centred reduction waves and a metalcentred oxidation wave (Re^{II/I}). The redox potentials for $E_{1/2}^{ox}$ and the first $E_{1/2}^{red}$ reveal the redox potentials of the HOMO and LUMO orbitals contained in all of these molecules. The HOMO consists of $d\pi$ character while the LUMO consists of π^* based on electronic absorption and steady state PL (discussed above). Accordingly, one-electron oxidation of the metal removes an electron from the $d\pi$ orbitals of the Re(I) moiety while oneelectron reduction adds an electron to the π^{\ast} orbitals of the diimine ligand. Thus, electron donating substituents such as methyl groups will shift the redox potentials in the negative direction while increasing π -conjugation with phenyl substituents, shifts the redox potential towards more positive bias. The first $E_{1/2}^{red}$ value measured in the methyl derivatives of 1,10-phenanthroline (1-3) are more negative than those of the parent complex 4 (between 40-240 mV), whereas that of the phenyl derivative (5) is slightly more positive with respect to 4 (40 mV). From Table 3, the $E_{1/2}{}^{\text{red}}$ is clearly more sensitive with respect to $E_{1/2}^{ox}$ in these molecules as a function of the degree of alkylation present in the diimine ligand. As phenyl groups are added to the 4- and 7- positions of the phenanthroline, the difference between the $d\pi$ - π^* orbitals (E_{ox}-E_{red}) decreases, as is the case for **5**. The first $E_{1/2}^{red}$ of **2** is more negative than **3** by approximately 120 mV. Therefore, a greater shift is observed when the methyl groups occupy the 4- and 7- positions of 1,10phen than when occupying the 5- and 6- positions. The $E_{1/2}^{red}$ of 1 is the hardest molecule to be reduced across the entire series investigated (-1.54 V), demonstrating that more electron donating substituents on the phen ligand shifts the measured $E_{1/2}^{red}$ to more negative electrochemical potentials. The corresponding redox potentials in 6-9 were also measured (Table 3 and Figs. S44–S47⁺) and were shown to echo the results as obtained for 1-5. Complex 6 has the widest separation between the between the $d\pi$ - π^* orbitals (E_{ox}-E_{red}) across the bpy series. Hence, a greater shift is observed when the methyl groups occupy the 5- and 5'- positions of bpy than when occupying the 4- and 4'- positions. For **7** and **9**, their $E_{1/2}^{ox}$ and E1/2^{red} potentials are similar, illustrating that tert-butyl groups have a similar electronic effect with respect to that of the methyl substituents. Similar trends have been previously reported for the Re(I) diimine tricarbonyls, 1, 12, 24, 62-64 suggesting that the nature and position of the substituents on the diimine ligands shift the reduction potentials to either more negative or positive potentials.

FTIR and TRIR

Table 3 Electrochemical data for 1–9 in V ($\pm 5~mV)$ vs SCE measured in CH_3CN with 0.1 M TBAPF_6.

| Complexes | E _{1/2} ox | $E_{1/2}^{red}$ | E_{gap} |
|-----------|---------------------|-----------------|-----------|
| 1 | 0.79 | -1.54, -1.72 | 2.33 |
| 2 | 0.82 | -1.46, -1.63 | 2.28 |
| 3 | 0.90 | -1.34, -1.56 | 2.24 |
| 4 | 0.91 | -1.30, -1.50 | 2.21 |
| 5 | 0.90 | -1.26, -1.42 | 2.16 |
| 6 | 0.87 | -1.43, -1.66 | 2.30 |
| 7 | 0.84 | -1.40, -1.61 | 2.24 |
| 8 | 0.91 | -1.31, -1.53 | 2.22 |
| 9 | 0.84 | -1.39, -1.60 | 2.23 |

As can be inferred from Table 1, a pattern of two peaks for the carbonyl region of the infrared spectrum is observed which is typical of cis-[Re(N^N)₂(CO)₂]⁺ complexes (Figs. S28–S36⁺ and Fig. S37– S38⁺ corresponding to the CO stretching region for 1-**9**).⁷ The two $\upsilon_{\text{Re-C=0}}$ peaks shift to lower frequencies with respect to the rhenium(I) tricarbonyl complexes.^{1, 41} The higher energy Re-C≡O vibrational stretching modes in the tricarbonyl complexes largely result from significant π -backbonding distribution. In essence, the $d\pi$ electrons from the Re(I) tricarbonyl distribute across three ligand C≡O's whereas in the dicarbonyl molecules **1-9**, the $d\pi$ electrons can only π -backbond into two ligand C=O's. Therefore, more metal d-electron density comes to reside within the π^* orbitals of the two C=O ligands, manifesting as lower frequency with respect to the tricarbonyl analogs. When stronger electron donating substituents are resident on the diimine ligand, such as is the case for 1, there is a further energetic lowering of these C≡O stretching frequencies to 1891 and 1824 cm⁻¹ as shown in Table 1. Similar to the argument made for the decrease in stretching frequencies when moving from a tricarbonyl to a dicarbonyl species, an increased occupation of π^* antibonding orbitals (from the electron donating substituents) further weakens the C=O bonds within the ligands themselves. The excited state dynamics described in the ultrafast transient absorption experiments were mirrored in the ultrafast TRIR experiments. Upon selective MLCT excitation, the Re(I) metal center becomes transiently oxidized to Re(II), leading to a reduction in π backbonding and a concomitant increase of the C≡O bond order is observed in both the symmetric and antisymmetric Re-C≡O vibrational modes. This translates as an increase in energy of these vibrational modes in the TRIR difference spectra, exemplified by the TRIR difference spectrum of **6** shown in Fig. 7 as a representative example for the entire series of molecules. The excited state features are long-lived, with little decay occurring over the entire 4 ns delay line of these experiments (Fig. S71⁺), consistent with the exclusive formation of ³MLCT excited states in all instances. To garner additional evidence for this MLCT assignment, DFT calculations were performed in which the S₀ and T₁ state geometries were optimized and their calculated IR spectra subtracted to simulate the experimental TRIR difference spectra. The general spectral profiles of the DFTcalculated difference spectra agree well with the experimental data in which both the symmetric (at higher energy) and

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antisymmetric (lower energy) modes clearly shift to higher energy upon formation of the ${}^{3}MLCT$ excited state (ESI, Fig. S72⁺).



Fig. 7 Ultrafast TR-IR difference spectrum of 6 measured at 4.5 ps delay in CH₂Cl₂ (λ_{pump} = 500 nm, 0.7 µJ/pulse, and spacer *u*/dth = 750 um).

Conclusions

This report illustrates for the first time the combined experimental results on the UV-vis spectroelectrochemistry and on the ultrafast dynamics of Re(I) complexes featuring cisdicarbonyl molecular topologies using both electronic and vibrational spectroscopy. Additionally, the excited state spectral and kinetic processes were also investigated using a combination of nanosecond time scale transient absorption spectroscopy and time-resolved PL spectroscopy. The nine cis- $[Re(N^N)_2(CO)_2]^+$ complexes investigated were synthesized by the forced removal of one C≡O ligand which resulted in drastic absorption and PL property changes from their respective tricarbonyl and cis-[Re(bpy)(P^P)(CO)₂]⁺ analogues. The redshifted absorption and PL emission observed for the cis- $[Re(N^N)_2(CO)_2]^+$ chromophores relative to the *trans,cis*-[Re(bpy)(P)₂(CO)₂]⁺, cis-[Re(bpy)(P^P)(CO)₂]⁺ and fac-[Re(N^N)(CO)₃L]⁺ resulted from significant reduction of the ligand field strength upon removal of one carbonyl ligand. Although the cis-[Re(N^N)2(CO)2]⁺ molecules have different photophysical properties with respect to the tricarbonyls, both Re(I) dicarbonyls and tricarbonyls complexes abide by the energy-gap law to a large extent.^{3, 7} As can be gleaned from our data, electron donating groups, such as methyl substituents, induce a blue shift in both electronic absorption and PL emission energies with a concomitant decrease in the k_{nr} value with respect to the parent compounds. On the other hand, electron delocalizing substituents, such as phenyl groups, cause a red shift in electronic absorption and PL emission energy with a corresponding decrease in the k_{nr} value with respect to the parent compound. The discrepancy in the energy-gap law for the latter is due to the decrease in polarization differences between the MLCT ground and excited states. In addition, the

energy of the MLCT state is more sensitive to changes when the substituents are positioned closer to the chelating N of the phen or bpy ligands used. The MLCT assignment was based not only on the electronic absorption and photoluminescence spectroscopy but also on the correlation between spectroelectrochemistry and nsTA spectroscopy. The fact that the absorption of the ligand radical anion was observed in each nsTA experiment represents a diagnostic signal that can only be associated with the MLCT excited states.65 Regarding the excited state spectral features, identical spectral features observed at longer time delays in the ultrafast experiments were carried over into the nanosecond time regime. This indicates that subsequent to excitation, the formation of the relaxed ³MLCT excited state occurred on the tens of picoseconds time scales with no evidence that any other low energy excited states were present. Further support of ultrafast MLCT state formation was provided in the ultrafast TRIR difference spectra where the two Re-C≡O modes were bleached and two new blue shifted vibrations appeared, consistent with reduced π -backbonding. In summary, the panchromatic absorbing molecules 1-9 universally display spectroscopic, electrochemical, and excited state properties consistent with MICT character

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

