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Excited-State Triplet Equilibria in a Series of Re(I)-Naphthalimide Bichromophores

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ABSTRACT

We present the synthesis, structural characterization, electronic structure calculations, and the ultrafast and supra-nanosecond photophysical properties of a series of five bichromophores of the general structural formula [Re(5-R-phen)(CO)₃(dmap)](PF₆), where R is a naphthalimide (NI), phen = 1,10-phenanthroline, and dmap is 4-dimethylaminopyridine. The NI chromophore was systematically modified at their 4-positions with -H (NI), -Br (BrNI), phenoxy (PONI), thiobenzene (PSNI), and piperidine (PNI), rendering a series of metal-organic bichromophores (Re1-Re5, respectively) featuring variability in the singlet and triplet energies in the pendant NI subunit. Five closely related organic chromophores as well as [Re(phen)(CO)₃(dmap)](PF₆) (Re6) were investigated in parallel to appropriately model the photophysical properties exhibited in the bichromophores. The excited state processes of all molecules in this study were elucidated using

a combination of transient absorption spectroscopy and time-resolved photoluminescence (PL) spectroscopy, revealing the kinetics of the energy transfer processes occurring between the appended chromophores. The spectroscopic analysis was further supported by electronic structure calculations which identified the origin of many of the experimentally observed electronic transitions.

INTRODUCTION

Rhenium(I) carbonyl-diimine (Re-CDI) complexes have been studied for many decades because of their desirable photophysical and redox properties, chemical robustness, and synthetic flexibility;¹ making them useful in fields such as photochemical molecular devices,^{2,3} solar energy conversion,^{4,5} luminescence sensing,⁶⁻¹⁴ and biotechnology,^{15,16} among others.¹⁷⁻¹⁹ More recently, these types of molecules have garnered interest as photocatalysts in carbon dioxide reduction, ¹⁹⁻²⁴ as the increase of atmospheric CO₂ has steadily risen across the world with no tangible solutions in sight.^{25, 26} In these systems, the Re-CDI is used in conjunction with a sacrificial electron donor and light to catalytically drive the reduction of CO_2 to CO. The most efficient photocatalyst to date, [Re(bpy)(CO)₃(P(OEt)₃)]⁺, was found to have a photocatalytic CO₂ reduction quantum yield of 0.38,²⁷ demonstrating the utility of these types of complexes in atmospheric CO₂ mitigation. Unfortunately, the drawback to many Re-CDI complexes used in CO₂ reduction is their inability to absorb strongly in the visible region. To counter this, highly absorbing ruthenium(II) complexes have been covalently linked to the Re-CDI CO₂ reduction catalyst, resulting in greatly improved photocatalytic activity attributed to intermolecular electron transfer between the Ru(II) and Re(I) species.²⁸⁻³⁰

In many Re-CDI complexes, the observed photoluminescence (PL) originates from the triplet metal-to-ligand charge transfer (MLCT) excited state.³¹⁻³³ Since these molecules have the general molecular formulae Re(L-L)(CO)₃X or [Re(L-L)(CO)₃L]⁺, the MLCT excited state can be energetically tuned through modification of the ancillary ligands (X or L) which coarsely modulates the Re(I) d-orbital energies, and thus the HOMO energy.³⁴ Additionally, the π^* energies of the chromophoric ligand (L-L), can also be modified, resulting in predictable changes to the LUMO energy.³⁵ Other types of excited states, such as ligand-centered (LC) excited states, can also be observed in the triplet manifold of Re-CDI complexes if conjugated aryl systems or organic chromophores are appended to either the ancillary or chromophoric ligands.³⁶⁻⁴⁰ Many of the synergistic benefits of polychromophoric systems (i.e. excited state lifetime extension, increase in absorption cross section, etc.) have been documented by our research group,^{33, 41-48} in addition to many others.⁴⁹⁻⁶⁰

The attachment of the organic chromophore 4-piperidinyl-naphthalenimide (**PNI**) to a Re-CDI complex was previously investigated, revealing profound changes in the resultant photophysical properties with respect to the two isolated molecules.³³ The Re(I) and **PNI** chromophores were purposefully selected in that study for their characteristic spectroscopic infrared handles that enabled transient vibrational spectroscopic interrogation of the energy transfer processes occurring between these moieties. The comprehensive utilization of time-resolved PL emission, transient absorption, and time-resolved infrared spectroscopies from the femtosecond to microsecond time regimes, revealed "ping-pong" energy transfer occurring between the **PNI** and Re-CDI complex. The initial ligand-centered singlet excited state was localized on the **PNI** chromophore (¹PNI) and underwent Förster-type resonance energy transfer (FRET) to the Re-CDI chromophore ($\tau_{FRET} = 43.5$ ps) forming the ³MLCT excited state. After approximately 20 ns, the excited state returned to

the PNI chromophore through a Dexter-like triplet-triplet energy transfer (TTET) process, finally populating the long-lived triplet excited state localized on the **PNI** chromophore (³**PNI**). Due to the energetic proximity between the ³MLCT and ³PNI excited states ($\Delta E = 1680 \text{ cm}^{-1}$) and rapid forward and reverse triplet-triplet energy transfer (rTTET) reactions with respect to the other deactivation pathways, a thermal excited state equilibrium became established between these two triplets resulting in a 3000-fold increase in the observed ³MLCT lifetime; this radiative process is termed thermally-activated delayed PL. At the conclusion of that study, two questions remained unanswered. First, if weakly emissive organic chromophores were used instead of PNI whose quantum yield for fluorescence approaches unity,⁶¹⁻⁶⁴ would singlet energy transfer to the Re-CDI moiety still take place? Second, what ³MLCT/³NI energy gap is sufficient for sustaining the equilibrium between these two excited states at room temperature. To address these questions, a series of five Re(I) bichromophores (Re1-Re5) were synthesized by substituting the 4-position of the NI subunit pendant to the 5-position of the phenanthroline ligand with various substituents: -H (NI, Re1), -Br (BrNI, Re2), phenoxy (PONI, Re3), thiobenzene (PSNI, Re4), or piperidine (PNI, Re5) (see Figure 1) while conserving the Re-CDI complex's ³MLCT excited state energetics across all molecules. The naphthalimide substitutions modulated many of the observed photophysical properties, including the energies of the associated NI excited states and fluorescence quantum yields, as observed in the appropriate model chromophores.



Figure 1. Naphthalimide chromophores evaluated in this study.

One objective was to investigate how the substitution of the naphthalimide subunit modulated the efficiency of the energy transfer processes that occurs in the bichromophore. Ultrafast transient absorption spectroscopy was used to compare the bichromophore to the appropriate model systems to assign the observed excited state features. Despite being weakly fluorescent, there was still energy transfer observed to the Re-CDI chromophore in the **NI** and **BrNI** containing bichromophores **Re1** and **Re2**. Of the five bichromophores interrogated, four were shown to exhibit "ping-pong" energy transfer characteristics, whereas the **PSNI** containing molecule (**Re4**) had photophysical properties echoing those of its model compound.

Another objective was to determine the energy gap between the low-lying triplet states on the Re-CDI complex (³MLCT) and the naphthalimide chromophore (³NI) where the excited state equilibrium would no longer be established at room temperature. To increase the energy gap with respect to that observed in the Re-PNI complex, the new molecules here replaced the chloride ligand with dimethylaminopyridine (dmap), resulting in a higher energy ³MLCT excited state. Additionally, this generated an ionic complex that was more soluble in spectroscopic friendly solvents including acetonitrile. Structural modification of the naphthalimides resulted in a 0.25 eV (2000 cm⁻¹) variation of the ³NI excited state energy across the series, with the **NI** being the highest

and the **PNI** being the lowest in energy. The change in ³NI excited state energies resulted in triplet excited state equilibrium and characteristic ³MLCT delayed PL being observed in the three naphthalimides with the highest energy ³NI excited states (**NI**, **BrNI**, and **PONI**), whereas **PSNI** and **PNI** exclusively featured ligand-localized photophysics with no observed ³MLCT emission.

EXPERIMENTAL

Reagents and Chemicals. All synthetic manipulations were performed under an inert and dry nitrogen atmosphere using standard techniques. All reagents were purchased from VWR and used as received. The precursors NNI, NNI-phen, PNI-phen, and Re(PNI-phen)(CO)₃Cl, as well as **PNI**, were synthesized according to their published procedures.^{33, 44, 46} The synthetic procedures used to make all the chromophores are outlined in Scheme 1. The identity and purity of all compounds studied were confirmed using ¹H NMR, ATR-FTIR, high-resolution mass spectrometry, and elemental analysis. Synthetic details for all precursors and products in this study are included in the Supporting Information. Spectroscopic samples were prepared using spectroscopic grade tetrahydrofuran or acetonitrile and were degassed using the freeze-pump-thaw technique.⁶⁵

Characterization data for the studied complexes:

2-(*p*-tolyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (*NI*). ¹H NMR (400 MHz, CD₂Cl₂), δ 8.60 (dd, J = 7.2, 1.1 Hz, 2H), 8.31 (dd, J = 8.1, 1.2 Hz, 2H), 7.81 (dd, J = 8.3, 7.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 288.1027 [M+H]⁺, calcd (C₁₉H₁₄NO₂) 288.1025. Anal. Calcd (found) for C₁₉H₁₃NO₂: C, 79.43 (79.14); H, 4.56 (4.81); N, 4.88 (4.87). ATR-FTIR: 490, 516, 538, 781, 812, 1185, 1234, 1352, 1373, 1514, 1587, 1656, 1673, 1699 cm⁻¹.

[$Re(NI-phen)(CO)_3(dmap)$](PF_6) (Re1). ¹H NMR (400 MHz, CD₂Cl₂), δ 9.58 (ddd, J = 12.8, 5.2, 1.4 Hz, 2H), 8.82 (dd, J = 8.4, 1.4 Hz, 1H), 8.66 (ddd, J = 16.2, 7.3, 1.2 Hz, 2H), 8.51 (dd, J = 8.5, 1.4 Hz, 1H), 8.48 – 8.43 (m, 2H), 8.25 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.04 (dd, J = 8.5, 5.1 Hz, 1H), 7.90 (ddd, J = 8.3, 7.3, 4.6 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 6.27 (d, J = 7.4 Hz, 2H), 2.91 (s, 6H). MS [HR-ESI (CH₂Cl₂) m/z] 766.1224 [M–PF₆]⁺, calcd (C₃₄H₂₃N₅O₅¹⁸⁵Re) 766.1229. Anal. Calcd (found) for C₃₄H₂₃F₆N₅O₅PRe·0.5H₂O: C, 44.30 (44.15); H, 2.62 (2.40); N, 7.60 (7.46). ATR-FTIR: 557, 730, 779, 838, 1234, 1350, 1587, 1626, 1673, 1709, 1903, 2058 cm⁻¹.

6-bromo-2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**BrNI**). ¹H NMR (400 MHz, CD₂Cl₂), δ 8.69 – 8.62 (m, 2H), 8.42 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 8.5, 7.3 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 366.0134 [M+H]⁺, calcd (C₁₉H₁₃NO₂⁷⁹Br) 366.0130. Anal. Calcd (found) for C₁₉H₁₂BrNO₂: C, 62.32 (62.04); H, 3.30 (3.27); N, 3.82 (3.81). ATR-FTIR: 422, 500, 518, 730, 781, 814, 1193, 1238, 1344, 1365, 1589, 1656, 1707 cm⁻¹.

[$Re(BrNI-phen)(CO)_3(dmap)$](PF_6) (Re2). ¹H NMR (400 MHz, CD₂Cl₂), δ 9.58 (ddd, J = 12.1, 5.1, 1.3 Hz, 2H), 8.81 (ddd, J = 9.3, 8.6, 1.2 Hz, 2H), 8.72 (ddd, J = 15.2, 7.3, 1.2 Hz, 1H), 8.52 – 8.43 (m, 2H), 8.26 (s, 1H), 8.23 – 8.13 (m, 2H), 8.08 – 7.96 (m, 2H), 7.65 (d, J = 7.4 Hz, 2H), 6.27 (d, J = 7.4 Hz, 2H), 2.91 (d, J = 0.5 Hz, 6H). MS [HR-ESI (CH₂Cl₂) m/z] 844.0316 [M–PF₆]⁺, calcd (C₃₄H₂₂N₅Os¹⁸⁵Re⁷⁹Br) 844.0334. Anal. Calcd (found) for C₃₄H₂₂BrF₆N₅OsPRe·0.5H₂O: C, 40.81 (40.58); H, 2.32 (2.17); N, 7.00 (6.72). ATR-FTIR: 418, 477, 514, 543, 557, 726, 781, 838, 1234, 1364, 1363, 1589, 1626, 1673, 1713, 1905, 2028 cm⁻¹.

6-*phenoxy*-2-(*p*-*tolyl*)-1*H*-*benzo*[*de*]*isoquinoline*-1,3(2*H*)-*dione* (*PONI*). ¹H NMR (400 MHz, CD₂Cl₂), δ 8.78 (dd, J = 8.4, 1.2 Hz, 1H), 8.66 (dd, J = 7.3, 1.2 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H),

7.84 (dd, J = 8.4, 7.3 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.39 – 7.30 (m, 3H), 7.27 – 7.22 (m, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.3 Hz, 1H), 2.46 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 380.1289 [M+H]⁺, calcd (C₂₅H₁₈NO₃) 380.1287. Anal. Calcd (found) for C₂₅H₁₇NO₃·0.1H₂O: C, 78.77 (78.84); H, 4.55 (4.73); N, 3.67 (3.67). ATR-FTIR: 485, 696, 753, 779, 804, 1136, 1177, 1201, 1236, 1356, 1575, 1660, 1699 cm⁻¹.

[*Re*(*PONI-phen*)(*CO*)₃(*dmap*)](*PF*₆) (*Re3*). ¹H NMR (400 MHz, CD₂Cl₂), 9.58 (ddd, *J* = 11.6, 5.2, 1.4 Hz, 2H), 8.94 (dd, J = 8.5, 1.2 Hz, 1H), 8.82 (dd, J = 8.4, 1.4 Hz, 1H), 8.71 (ddd, J = 15.9, 7.3, 1.2 Hz, 1H), 8.56 – 8.44 (m, 2H), 8.24 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.08 – 8.01 (m, 1H), 7.93 (ddd, J = 8.4, 7.3, 4.5 Hz, 1H), 7.65 (dd, J = 7.4, 2.2 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.38 (td, J = 7.4, 1.2 Hz, 1H), 7.29 (dd, J = 7.5, 1.2 Hz, 2H), 7.01 (dd, J = 8.3, 4.4 Hz, 1H), 6.26 (dd, J = 7.3, 5.2 Hz, 2H), 2.91 (s, 3H), 2.90 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 858.1478 [M–PF₆]⁺, calcd (C₄₀H₂₇N₅O₆¹⁸⁵Re) 858.1491. Anal. Calcd (found) for C₄₀H₂₇F₆N₅O₆PRe·H₂O: C, 46.97 (47.06); H, 2.86 (2.68); N, 6.85 (6.79). ATR-FTIR: 557, 781, 840, 1206, 1236, 1254, 1356, 1579, 1626, 1671, 1707, 1907, 2028 cm⁻¹.

6-(phenylthio)-2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**PSNI**). ¹H NMR (400 MHz, CD₂Cl₂), δ 8.73 (dd, J = 8.5, 1.1 Hz, 1H), 8.64 (dd, J = 7.3, 1.1 Hz, 1H), 8.35 (d, J = 7.9 Hz, 1H), 7.84 (dd, J = 8.5, 7.3 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.51 – 7.45 (m, 3H), 7.39 – 7.32 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 396.1058 [M+H]⁺, calcd (C₂₅H₁₈NO₂S) 396.1058. Anal. Calcd (found) for C₂₅H₁₇NO₂S: C, 75.93 (75.66); H, 4.33 (4.56); N, 3.54 (3.54). ATR-FTIR: 445, 516, 685, 747, 777, 810, 904, 1134, 1175, 1185, 1230, 1346, 1361, 1507, 1562, 1581, 1656, 1697 cm⁻¹.

[Re(PSNI-phen)(CO)₃(dmap)](PF₆) (*Re4*). ¹H NMR (400 MHz, CD₂Cl₂), δ 9.57 (ddd, J = 12.6, 5.1, 1.4 Hz, 2H), 8.84 (ddd, J = 24.3, 8.5, 1.3 Hz, 2H), 8.70 (ddd, J = 16.3, 7.3, 1.1 Hz, 1H), 8.48

(dd, J = 8.5, 1.3 Hz, 1H), 8.36 (dd, J = 15.7, 8.0 Hz, 1H), 8.23 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.04 (dd, J = 8.5, 5.1 Hz, 1H), 7.93 (ddd, J = 8.5, 7.4, 4.7 Hz, 1H), 7.67 – 7.62 (m, 4H), 7.56 – 7.52 (m, 3H), 7.31 (dd, J = 8.0, 5.0 Hz, 1H), 6.26 (td, J = 5.5, 1.6 Hz, 2H), 2.91 (s, 3H), 2.89 (s, 3H). MS [HR-ESI (CH₂Cl₂) m/z] 874.1242 [M–PF₆]⁺, calcd (C₄₀H₂₇N₅O₅S¹⁸⁵Re) 874.1262. Anal. Calcd (found) for C₄₀H₂₇F₆N₅O₅PReS: C, 47.06 (46.98); H, 2.67 (2.68); N, 6.86 (6.78). ATR-FTIR: 557, 728, 751, 779, 838, 1234, 1363, 1585, 1626, 1671, 1709, 1905, 2028 cm⁻¹.

[*Re*(*PNI-phen*)(*CO*)₃(*dmap*)](*PF*₆) (**Re5**). ¹H NMR (400 MHz, CD₂Cl₂), δ 9.56 (ddd, J = 13.1, 5.1, 1.4 Hz, 2H), 8.80 (dd, J = 8.3, 1.4 Hz, 1H), 8.66 – 8.44 (m, 4H), 8.22 (s, 1H), 8.14 (dd, J = 8.3, 5.2 Hz, 1H), 8.02 (dd, J = 8.5, 5.1 Hz, 1H), 7.79 (ddd, J = 8.5, 7.3, 5.3 Hz, 1H), 7.64 (d, J = 7.4 Hz, 2H), 7.27 (dd, J = 8.2, 6.1 Hz, 1H), 6.26 (d, J = 7.4 Hz, 2H), 3.36 (m, J = 5.4 Hz, 4H), 2.91 (s, 6H), 1.92 (m, J = 10.7 Hz, 4H), 1.78 (m, 2H). MS [HR-ESI (CH₂Cl₂) m/z] 849.1945 [M–PF₆]⁺, calcd (C₃₉H₃₂N₆O₅¹⁸⁵Re) 849.1964. Anal. Calcd (found) for C₃₉H₃₂F₆N₆O₅PRe·H₂O: C, 46.20 (46.17); H, 3.38 (3.16); N, 8.29 (8.10). ATR-FTIR: 557, 781, 840, 1232, 1365, 1583, 1626, 1664, 1701, 1909, 2028 cm⁻¹.

 $[Re(phen)(CO)_3(dmap)](PF_6)$ (**Re6**). ¹H NMR (400 MHz, CD₂Cl₂), δ 9.51 (dd, J = 5.1, 1.4 Hz, 2H), 8.79 (dd, J = 8.3, 1.4 Hz, 2H), 8.17 (s, 2H), 8.10 (dd, J = 8.3, 5.1 Hz, 2H), 7.53 (d, J = 7.4 Hz, 2H), 6.19 (d, J = 7.4 Hz, 2H), 2.86 (s, 6H). MS [HR-ESI (CH₂Cl₂) m/z] 571.0909 [M–PF₆]⁺, calcd (C₂₂H₁₈N₄O₃¹⁸⁵Re) 571.0908. Anal. Calcd (found) for C₂₂H₁₈F₆N₄O₃PRe·0.5H₂O: C, 36.37 (36.52); H, 2.64 (2.42); N, 7.71 (7.59). ATR-FTIR: 557, 724, 836, 1626, 1897, 1919, 2025 cm⁻¹.

General Techniques. ¹H and ¹³C NMR spectra were recorded on a Varian Inova 400 NMR operating at a working frequency of 400 MHz for ¹H. All chemical shifts were referenced to residual solvent signals. High-resolution electron spray ionization mass spectrometry (ESI-MS) were performed at Michigan State University Mass Spectrometry Facility. Elemental analysis data

was measured by Atlantic Microlab, Inc., Norcross, GA. Attenuated total reflectance fouriertransform infrared (ATR-FTIR) spectroscopy was performed using the Bruker Alpha Platinum ATR. Optical absorption spectra were measured on a Shimadzu UV-3600 spectrometer. Steadystate luminescence spectra were obtained from an Edinburgh FS 920. Quantum yield measurements were performed on **NI** and **BrNI** using anthracene in aerated ethanol as the standard ($\Phi_{PL} = 0.28$),⁶⁶ **PONI** using 9,10-diphenylanthracene in aerated cyclohexane as the standard ($\Phi_{PL} = 0.97$),⁶⁶ **PSNI** and **Re1-Re6** using [Ru(bpy)₃](PF₆)₂ in aerated acetonitrile as the standard ($\Phi_{PL} = 0.018$),⁶⁶ and **PNI** in acetonitrile using **PNI** in aerated toluene as the standard ($\Phi_{PL} = 0.91$).⁶⁴

Nanosecond Transient Absorption Spectroscopy. Transient absorption measurements were collected using a LP920 laser flash photolysis system (Edinburgh Instruments) described previously.⁶⁷ Samples were prepared to have a 25 μ M concentration (3.0 mJ/pulse) in a 1 cm path length quartz optical cell and degassed using the freeze-pump-thaw technique. All transient absorption experiments were performed at room temperature. The reported difference spectra and kinetic data are the average of 50 laser shots. The ground state absorption spectra were taken before and after each experiment to ensure there was no sample degradation. The transient kinetic data was evaluated using the fitting routines available in OriginPro 2016.

Ultrafast Transient Absorption Spectroscopy. The transient absorption measurements were performed at the NCSU Imaging and Kinetic Spectroscopy (IMAKS) Laboratory using a mode-locked Ti:sapphire laser (Coherent Libra) as described previously.⁶⁸ The pump beam was directed into a parametric amplifier (Coherent OPerA Solo) to generate the 350 and 400 nm excitation. The probe beam was focused onto a calcium fluoride crystal to generate a white light continuum between 350 to 775 nm. The pump beam was focused and overlapped with the probe beam through a 2 mm path length cuvette. The ground-state absorption spectra were taken before and after each

experiment to ensure there was no sample photo-degradation during the experiment. The transient kinetic data at specific wavelengths was evaluated using the fitting routines available in OriginPro 2016. The global fit analysis was performed using Surface Xplorer available from Ultrafast Systems.

Time-Resolved Emission Intensity Decay Measurements. Single wavelength emission intensity decays at 77 K and room temperature were acquired with an LP920 laser flash photolysis system (Edinburgh Instruments) using the Vibrant 355 LD Nd:YAG/OPO system (OPOTEK) as the excitation source ($\lambda_{ex} = 355/410$ nm, ~3.0 mJ/pulse). Spectroscopic samples were prepared to have a 25 μ M concentration and PL transients were collected at emission maximums for most experiments, with all exceptions noted in text. Time-gated emission spectra were collected using the same system. Emission spectra and PL transients were collected with an iStar ICCD camera (Andor Technology), which was controlled by the L900 software program (Edinburgh Instruments). Reported time-gated emission spectra are the average of 50 laser flashes.

Density Functional Theory (DFT) Calculations. The calculations utilized in this study were performed using the Gaussian 09 software package (revision D.01)⁶⁹ and the computation resources of the North Carolina State University High Performance Computing Center. Ground state and triplet state geometry optimizations were performed using the B3LYP,^{70, 71} M06,⁷² and CAM-B3LYP functionals,⁷³ along with the def2-SVP basis set of the Alrichs group as implemented in Gaussian 09.⁷⁴ The Stuttgart–Dresden effective core potentials (ECPs)⁷⁵ were used to replace the core electrons in rhenium for all calculations. The polarizable continuum model was used to simulate the acetonitrile solvent environment for all calculations.⁷⁶ 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 described for the geometry

optimizations.⁷⁷⁻⁷⁹ The energy and oscillator strengths were computed for each of the 50 lowest singlet excitations. The natural transition orbitals of the low-lying singlet and triplet transitions were generated using GaussView 5.0.⁸⁰

RESULTS AND DISCUSSION

Syntheses. The schemes used to synthesize all the chromophores in this study are collected in Scheme 1. Briefly, the naphthalimide chromophores were prepared by departing from the corresponding naphthalene anhydride (either unsubstituted or substituted with Br or NO₂ in the 4position) and reacting with a primary amine (*p*-toluidine or 5-amino-1,10-phenanthronline) using published protocols to generate the NI and BrNI model chromophores and ligands (NI-phen and BrNI-phen), along with the nitronaphthalimide intermediates (**NNI** and NNI-phen).⁴⁶ The nitro group was substituted by refluxing the nitronaphthalimide in DMF with a phenol or thiolbenzene under basic conditions or piperidine to yield the other three naphthalimide chromophores and ligands (PONI, PSNI, PNI, PONI-phen, PSNI-phen, and PNI-phen).^{33, 44, 81, 82} The 5-substituted phenanthroline ligands were coordinated to Re(CO)₅Cl using published protocols.³⁴ The chloride ligand was subsequently removed by refluxing fac-Re(L-L)(CO)₃Cl with silver triflate in ethanol, forming the solvato-complex. The silver chloride precipitate was removed by filtration over Celite. The dmap ligand was finally added to the isolated solvato-complex and refluxed in ethanol to yield the desired product (Re1-Re6). The final isolated products (facial isomers) were structurally characterized using ¹H NMR spectroscopy, high resolution mass spectroscopy, elemental analysis, and FT-IR spectroscopy. Furthermore, the molecular structures of the bichromophores **Re1** to **Re5** were confirmed using ¹H-¹H COSY NMR spectroscopy.





UV-Vis Electronic Spectra. The electronic spectra for the model compounds and bichromophores measured in acetonitrile are presented in Figure 2, with additional spectroscopic data collected in Table 1. The NI and BrNI chromophores both have structured lowest energy electronic transitions with a maximum absorbance corresponding to a $\pi \rightarrow \pi^*$ transition at 332 and 340 nm, respectively (Figure 2a). In PONI, PSNI, and PNI, the low energy transition, which is now broad and featureless, red shifts progressively (359, 384, and 407 nm, respectively) and is consistent with possessing significant charge transfer character as demonstrated in prior work, Figure 2a.^{33, 44, 46} All five naphthalimide model chromophores possess relatively intense low energy transitions with molar extinction coefficients ranging from 11300 to 17100 M⁻¹cm⁻¹, Figure 2a. The model Re(I) compound (**Re6**) has a broad and featureless absorption band centered at 368 nm which is assigned to the $d\pi(\text{Re}) \rightarrow \pi^*(\text{phen})$ MLCT transitions and a higher energy band at 276 nm which corresponds to the $\pi \rightarrow \pi^*$ transitions localized on the phen ligand, Figure 2b. As also illustrated in Figure 2b, the low energy electronic transitions observed in each of the bichromophores (**Re1-Re5**) emulates that expected for a simple mixture of the composing molecules. This is illustrated in Figures S40-S41, where the absorption spectrum of **Re6** is added to that of the appropriate NI model compound's absorption spectrum. In all cases, the additive and measured spectra of the five bichromophores were found to be in good quantitative agreement, illustrating that there is no significant electronic communication between the respective subunits.



Figure 2. (A) Electronic spectra of **NI**, **BrNI**, **PONI**, **PSNI**, and **PNI** recorded in acetonitrile. (B) Electronic spectra of **Re1-Re6** recorded in acetonitrile.

Electronic Structure Calculations. Time-dependent density functional theory (TD-DFT) calculations were performed on all the molecules to glean insight into the nature of the lowest energy electronic transitions observed experimentally. The B3LYP, M06, and CAM-B3LYP functionals were used to perform the ground state geometric optimization and the corresponding TD-DFT calculations, Table S2. Across the series of naphthalimide model chromophores, the M06 functional yielded the best quantitative modeling of the transition energies, whereas the B3LYP functional was consistently lower in energy and the CAM-B3LYP functional was consistently

higher in energy. Unfortunately, both the B3LYP and M06 functionals did not adequately model the **PSNI** chromophore, as both predicted a low energy transition with significant oscillator strength that was not observed experimentally. By using the long-range corrected functional, CAM-B3LYP, the energies of the calculated low energy transitions were all overcorrected (rendered too high in energy), however the trend in relative energies observed in the experimental data were revealed in the low energy transitions using this functional. Natural transition orbital analysis for the S₀ \rightarrow S₁ and S₀ \rightarrow S₂ transitions using the M06 and CAM-B3LYP functionals was performed on the naphthalimide chromophores, Figures S82-S86. The S₀ \rightarrow S₁ transition across the series can be best described as being $\pi \rightarrow \pi^*$ in character, with a small amount of charge transfer observed in **PONI** and a significant amount observed in both **PSNI** and **PNI**. The S₀ \rightarrow S₂ transition varied a greater amount across the series and its value was functional dependent. This transition is considerably weaker than the S₀ \rightarrow S₁ transition (**PSNI** is the only exception) and was not observed experimentally.

The same TD-DFT analysis was performed on the rhenium chromophores (**Re1-Re6**) with the calculated transitions available in the Supporting Information, Table S4. Using both the B3LYP and M06 functionals, the calculated charge transfer transition for the Re(I) model (**Re6**) was predicted as too low in energy when compared to the experimental data (0.54 and 0.31 eV lower in energy for the B3LYP and M06 functionals, respectively). Moreover, many new charge transfer transitions in the bichromophores were calculated that were simply not observed experimentally. As with the naphthalimide model compounds, the CAM-B3LYP functional gave the best quantitative match to experimental data based on the trends observed experimentally. Natural transition orbital analysis for the S₀ \rightarrow S₁, S₀ \rightarrow S₂, and S₀ \rightarrow S_n transitions using the M06 and CAM-

B3LYP functionals were performed on **Re1-Re6**, see Figures S87-S92. In the model MLCT chromophore **Re6**, the $S_0 \rightarrow S_1$ transition can best be described as charge transfer with electronic density originating from the metal and dmap ligands and transitioning to the phenanthroline ligand. This type of transition was observed in all the bichromophores near 3.66 eV (using the CAM-B3LYP functional) and represents the $S_0 \rightarrow S_1$ transition in **Re1-Re3** and the $S_0 \rightarrow S_2$ transition in **Re4-Re5**. The ligand-centered transition localized on the naphthalimide chromophore was also clearly observed in all instances (based on energy and oscillator strength). Using the CAM-B3LYP functional, the NI-localized LC transition is the $S_0 \rightarrow S_4$ transition in **Re1**, the $S_0 \rightarrow S_3$ transition in **Re2** and **Re3**, and the $S_0 \rightarrow S_1$ transition in **Re4** and **Re5**.

 Table 1. Static photophysical properties of the NI, BrNI, PONI, PSNI, PNI model compounds

 and Re1-Re6 measured in acetonitrile (black) and THF (blue).

Molecule	$\lambda_{abs max}/nm$	λ_{emmax}/nm	λ_{emmax}/nm	$\Phi_{\rm em}$	$\Phi_{\rm em}$
Molecule	$(\epsilon/M^{-1}cm^{-1})^{[a]}$	(RT) ^[a]	(77 K) ^[b,c]	in air ^[a]	deaerated ^[a,d]
NI	332 (14200)	374, 506	538	0.0005 ^[e]	
	330 (12500)	375, 486		$0.0004^{[e]}$	
BrNI	340 (17100)	387, 537	553	0.0005 ^[e]	
	339 (16300)	379, 514		0.0005 ^[e]	
PONI	359 (15601)	431	416, ^[f] 547	0.18 ^[g]	
	357 (14300)	422		0.038 ^[g]	
PSNI	384 (14700)	518	450, ^[f] 579	0.004 ^[h]	
	382 (13900)	500		0.006 ^[h]	
PNI	407 (11300)	539	492, ^[f] 605	$0.084^{[i]}$	
	398 (11300)	516		0.81 ^[i]	
Re1	334 (20400)	630 ^[d]	536, 512	0.0030 ^[h]	0.014 ^[h]
	334 (20200)	614 ^[d]		0.0028 ^[h]	0.020 ^[h]
Re2	343 (23200)	626 ^[d]	555, 516	0.0014 ^[h]	0.011 ^[h]
	343 (23900)	617 ^[d]		0.0014 ^[h]	0.015 ^[h]
Re3	364 (21600)	435, 628 ^[d]	546, 514	0.0023 ^[h]	0.014 ^[h]
	363 (24000)	611 ^[d]		0.0014 ^[h]	0.018 ^[h]
Re4	392 (20700)	613 ^[d]	577, 516	0.0011 ^[h]	0.0035 ^[h]
	393 (20700)	613, 645 ^[d]		0.0010 ^[h]	0.0082 ^[h]
Re5	415 (15800)	548 ^[d]	595, 512	0.0032 ^[h]	0.0031 ^[h]
	410 (15400)	523 ^[d]		0.0087 ^[h]	0.011 ^[h]
Re6	368 (3160)	602 ^[d]	507	0.011 ^[h]	0.024 ^[h]
	372 (3600)	601 ^[d]		$0.016^{[h]}$	0.029 ^[h]

^[a] Room temperature measurements were made with ACN or THF as a solvent. ^[b] 77 K measurements were made with 2-methyl-THF. ^[c] Emission maximum determined from timegated PL spectra using the LP 920. ^[d] Samples deaerated using freeze-pump-thaw method. ^[e] Quantum yields were measured using anthracene in aerated ethanol as the standard ($\Phi_{PL} = 0.28$).⁶⁶ ^[f] Emission maximum determined from steady-state PL spectra using the FS 920. ^[g] Quantum yields were measured using 9,10-diphenylanthracene in aerated cyclohexane as the standard ($\Phi_{PL} = 0.97$).⁶⁶ ^[h] Quantum yields were measured using [Ru(bpy)₃](PF₆)₂ in aerated acetonitrile as the standard ($\Phi_{PL} = 0.018$).⁶⁶ ^[i] Quantum yields were measured using PNI in aerated toluene as the standard ($\Phi_{PL} = 0.91$).⁶⁴

Static and Dynamic PL Spectroscopy. The static PL spectra recorded for the model chromophores and Re(I) bichromophores in acetonitrile are presented in Figure 3, with additional

spectroscopic data collected in Table 1. The NI and BrNI molecules have two observable emission bands in aerated acetonitrile at room temperature, Figure 3a. The high energy band in both molecules was structured with emission maxima at 374 and 387 nm, respectively, consistent with fluorescence from the S₁ $\pi \rightarrow \pi^*$ excited state. The low energy PL observed was broad, featureless, and sensitive to solvent polarity, with emission maxima at 506 and 537 nm, respectively. Additionally, excitation spectra were measured in acetonitrile at the high and low energy emission maxima for both dual-emitting chromophores. Regardless of the monitored wavelength, the recorded spectra mimic the low energy transition observed in the electronic spectra of NI and **BrNI**, supporting the assignment as dual emission (Figures S43-44). The low-energy emission bands likely originate from a conformational change of the molecule and the formation of planarintramolecular charge transfer (PICT) excited states. This dual emission phenomenon has been documented by multiple research groups and demonstrated to occur when the N-aryl group of the 1,8-napthalimide is substituted with an electronically donating substituent.^{63, 83-85} First documented by Bérces and coworkers, a series of 1,8-napthalimides were prepared using an unsubstituted phenyl ring as the model and adding electron donating or withdrawing substituents to the para position of the N-aryl group (among many other NI derivatives). In their model system, only the short-wave fluorescence emission (386 nm in ACN) originating from the S₁ $\pi \rightarrow \pi^*$ excited state was observed. By adding an electron donating group (p-MeO) to the N-aryl group, the two lowlying excited states undergo pseudo-Jahn-Teller coupling which allows the excited state to cross to the nearly isoenergetic S_2 potential energy surface. Once on this surface, the N-aryl group rotates to nearly a coplanar geometry with the naphthalimide and stabilizes the charge transfer excited state. In the p-MeO substituted molecule, the long-wave fluorescence (603 nm in ACN) originating from the S₂ CT excited state is observed almost exclusively.⁸⁵ In the case of NI and BrNI, the *p*- methyl on the *N*-aryl group is electronically more donating than hydrogen but less so than a *p*-MeO so it is probable that some degree of pseudo-Jahn-Teller coupling takes place, therefore supporting the observation of both short-wave and long-wave fluorescence bands in **NI** and **BrNI**.

The **PONI**, **PSNI**, and **PNI** molecules all have broad and featureless fluorescence spectra, with maxima at 431, 518, and 539 nm, respectively, Figure 3a. When PONI, PSNI, and PNI are dissolved in lower polarity solvents such as THF or toluene, they experience positive solvatochromism whereas the corresponding PL spectra shift to lower energy with increasing medium polarity. The combination of the broad featureless emission spectra and solvatochromic nature of this PL are both indicative of charge transfer character in the emissive state of these three molecules. In acetonitrile, the emission quantum yield of **PONI** is substantial ($\Phi_F = 0.18$), followed by **PNI** and **PSNI** ($\Phi_F = 0.084$ and 0.004, respectively). When dissolved in a lower polarity solvent, such as THF, the **PNI** becomes the most emissive ($\Phi_F = 0.81$), followed by **PONI** and PSNI ($\Phi_F = 0.038$ and 0.006, respectively). In the case of NI, BrNI, PSNI, the low fluorescence quantum yields are likely due to efficient intersystem crossing (ISC) from the S₁ excited state to the triplet manifold.⁶¹ The **PONI** chromophore has a substantially larger fluorescence quantum yield and likely has less efficient ISC. The emission intensity of PNI is extremely solvent dependent where fluorescence quantum yields greater than 90% persist in nonpolar solvents such as toluene. In this case, the fluorescence is likely quenched through another mechanism, such as twisted intermolecular charge transfer (TICT) states as the solvent polarity plays a large role in TICT excited state decay.⁸⁶⁻⁸⁸



Figure 3. Room temperature emission spectra of (A) **NI** ($\lambda_{ex} = 325 \text{ nm}$), **BrNI** ($\lambda_{ex} = 325 \text{ nm}$), **PONI** ($\lambda_{ex} = 355 \text{ nm}$), **PSNI** ($\lambda_{ex} = 395$), and **PNI** ($\lambda_{ex} = 395$) recorded in aerated acetonitrile and of (B) **Re1-Re6** ($\lambda_{ex} = 385$) recorded in deaerated acetonitrile.

The Re(I) model complex (**Re6**) displays a broad, featureless PL emission band centered at 602 nm, which originates from the ³MLCT excited state, Figure 3b. The light emission of **Re6** is quenched by molecular oxygen and possesses a lifetime of 176 ns in deaerated acetonitrile (Figure S48), consistent with the lowest excited state being triplet in origin. Similarly, ³MLCT PL was observed in **Re1-Re4**, however the spectral profiles are slightly red-shifted to 628 nm in these

molecules, Figure 3b. Furthermore, the naphthalimide fluorescence is quantitatively quenched in **Re1** and **Re2** (not shown), predominantly quenched in **Re3**, appears as a shoulder in **Re4**, and is the PL spectrum primarily observed in **Re5**, Figure 3b. Since prior studies have demonstrated that Förster-like energy transfer is the primary quenching pathway of the naphthalimide fluorescence in related metal-organic chromophores,^{33, 44} this implies that the energy transfer efficiency is decreasing as the fluorescence of the appended naphthalimide red-shifts. The fact that there is less spectral overlap between the singlet fluorescence donor emission (naphthalimide) and the acceptor absorbance (Re-CDI) as the naphthalimide red-shifts supports these experimental observations being consistent with resonance energy transfer quenching across the series. The PL quantum yields of the bichromophores are smaller than that of **Re6** with **Re1-Re3** having about half the efficiency when compared to the model chromophore ($\Phi_{PL} = 0.013, 0.009,$ and 0.011, respectively). The other two bichromophores (**Re4** and **Re5**) have substantially less MLCT-based PL and in the case of **Re5**, the observed spectrum is composed of predominately unquenched fluorescence from the PNI moiety. As demonstrated in our previous study, the MLCT phosphorescence in the bichromophores is mostly derived from the triplet excited state equilibrium formed between the ³MLCT and ³LC states, with the population of the higher energy ³MLCT excited state based on a Boltzmann distribution.³³ Therefore, the lower the energy of the ³NI excited state (as in **Re4** and **Re5**), the lower the relative population of the ³MLCT excited state and therefore less PL emanating from that state.

PL intensity decays of the metal-organic bichromophores were collected at 600 nm to investigate the population decay kinetics of the ³MLCT state whose data are collected in Table 2. In **Re1-Re3**, the emission intensity decays were adequately fit to biexponential functions whose average

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lifetimes were much longer lived with respect to the Re-CDI model complex, suggesting that equilibrium is indeed operative between the ³MLCT and ³NI excited states.^{33, 44} The biexponential nature of these decays have been previously observed and attributed to concentration-dependent self-quenching.^{33, 44, 46, 61} To simplify comparisons between molecules, average lifetimes were used and it was determined that **Re1** possessed the shortest lifetime when compared to **Re2** and **Re3** measured at matched concentrations under identical experimental conditions. Furthermore, time-gated PL spectra acquired at numerous delay times confirmed that the emission originated from the ³MLCT excited state in all instances, Figure S49. There was no evidence of any delayed ³MLCT PL in **Re4** and **Re5**, instead only prompt emission from a combination of the naphthalimide fluorescence and strongly quenched MLCT PL was observed. Time-gated PL spectra confirmed these findings as there was little delayed emission observed beyond those prompt signals seen in **Re4** and **Re5**. Since these molecules have the lowest ³NI energies, it is likely that the energy gap is too large to enable thermal population of the higher lying ³MLCT excited state at room temperature and therefore no delayed PL could be observed.

Since phosphorescence was not observed from the ${}^{3}LC$ excited state in any of the metal-organic bichromophores at room temperature, each molecule was dissolved in 2-methyltetrahydrofuran (2-MeTHF) and frozen at 77 K by immersion in liquid N₂. At this temperature, the distinct phosphorescence from the ${}^{3}NI$ excited states in each instance (**Re1-Re5**) was experimentally distinguished from the ${}^{1}NI$ and ${}^{3}MLCT$ states using time-gated PL, Figure 4. The PL spectra measured at 1 µs was broad and featureless, with a maximum near 515 nm for all bichromophores (**Re1-Re5**), very closely matching that of the model MLCT complex **Re6**. We conclude that the origin of the emission observed at this time delay emanates from the ${}^{3}MLCT$ state resident on the Re-CDI complex. Extending the observation onset to 25 ms after the laser pulse, the observed PL was red-shifted with respect to the ³MLCT PL spectrum, and is vibronically structured, suggesting that the emission now originates from the ³NI excited state. To confirm these assignments, the naphthalimide models were also measured at 77 K under identical conditions, revealing emission spectra that were very close in energy and spectral features to those of the bichromophores measured at 25 ms delay, Figure S50. The PL decays at 77 K were well modeled using biexponential kinetics for the bichromophores where the first component corresponded to the decay of the ³MLCT excited state ($\tau \sim 11 \ \mu$ s) and the second component corresponded to the decay of the extremely long-lived ³NI excited state ($\tau \geq 10 \ ms$). Since both the ³MLCT and ³NI excited states decay independently at 77 K, the excited state equilibrium observed at room temperature in **Re1-Re3** no longer takes place, thereby eliminating any observation of delayed ³MLCT PL.

Molecule	ι_{PL}	l _{PL} ave	ι_{TA}	1 _{TA ave}	τ_{PL}
Wolecule	(298 K) ^[a]	(298 K) ^[b]	(298 K) ^[c]	(298 K) ^[d]	(77 K) ^[e]
Re1	6.5 μs, 27.0 μs	14.5 µs	6.6 µs, 19.6 µs	11.9 µs	11.1 µs, 544 ms
Re2	9.5 µs, 60.7 µs	56.6 µs	21.9 µs, 81.3 µs	53.7 µs	10.6 µs, 8.6 ms
Re3	16 µs, 64.6 µs	54.7 μs	18.8 µs, 70.0 µs	42.2 µs	12.6 µs, 612 ms
Re4	< 15 ns		34.2 µs, 186 µs	116 µs	10.6 µs, 102 ms
Re5	< 15 ns		43.9 μs, 177 μs	136 µs	9.2 µs, 288 ms
Re6	176 ns		182 ns		13.6 µs

 Table 2. Time-resolved PL and TA data recorded for Re1-Re6 in acetonitrile.

^[a] PL decay of **Re1-Re6** ($25 \pm 2 \mu$ M) measured at 600 nm in deaerated acetonitrile at room temperature. ^[b] Average time constant determined from a weighted average of biexponential components measured in deaerated acetonitrile at room temperature. ^[c] Transient absorption intensity decay of **Re1-Re6** ($25 \pm 2 \mu$ M) measured at 470 nm (**Re1**), 480 nm (**Re2**), 480 nm (**Re3**), 670 nm (**Re4**), 480 nm (**Re5**), 475 nm (**Re6**) in deaerated acetonitrile at room temperature. ^[d] Average time constant determined from a weighted average of biexponential components measured in deaerated acetonitrile at room temperature. ^[e] PL decay of **Re1-Re6** measured at 535 nm (**Re1**), 555 nm (**Re2**), 550 nm (**Re3**), 575 nm (**Re4**), 600 nm (**Re5**), 500 nm (**Re6**) in 2-MeTHF at 77 K.



Figure 4. Time-resolved 77 K PL emission spectra of **Re1-Re6** at the specified delay times following a 7 ns fwhm, 350 nm (**Re1-Re3**) or 400 nm (**Re4-Re6**) laser pulse in 2-MeTHF.

Transient Absorption Spectroscopy. When attaching the **NI** or **BrNI** structural motif to the Re(I) chromophore, as in the case for **Re1** and **Re2**, the observed excited state processes are consistent with energy transfer occurring between the chromophores. As presented in Figure 5, following 350 nm excitation, a transient absorption feature near 475 nm is promptly observed and quantitatively matches that of the S_1 excited state absorptions observed in the **NI** moiety, Figure S51. Unlike the model chromophore, this transient feature in **Re1** decays rapidly ($\tau = 400$ fs) with a new absorption appearing at 370 nm ($\tau = 315$ fs) along with a broad feature near 525 nm that spans into the NIR region. This excited state transient is completely formed by 5 ps and is assigned as the ³MLCT state of the Re(I) chromophore as it matches the excited state features observed in the Re(I) model (**Re6**) measured under the same experimental conditions, Figure S68. The transition from the ¹LC, $\pi.\pi^*$ state localized on the NI chromophore to the ³MLCT state was found to have a time constant of 400 fs as this matches the decay of the 470 nm transient feature and the subsequent growth of the 370 nm feature, Figure S54. Going from 5 ps through the end of the delay stage on the nanosecond timescale, the broad excited state absorbance from 500 nm to the NIR decreases in intensity whereas the transient feature at 470 nm grows in; the latter has been previously assigned to the ${}^{3}LC$ triplet excited state localized on the NI chromophore. The kinetic transition from the ³MLCT excited state to the ³LC excited state was tracked by analyzing the growth of the 470 nm transient feature, which corresponded to a time constant of 4.1 ± 0.2 ns. Since NI has its major low energy absorption band positioned well into the UV, the MLCT state could be selectively excited in **Re1**, Figure S53. Using 400 nm as the excitation source, the initially observed features at 510 fs revealed the presence of the ³MLCT state with a concomitant growth of the ³LC feature (470 nm) occurring with a similar time constant as measured with 350 nm laser pulses, $\tau = 4.0$ ns. **Re2** displays similar excited state features and kinetics to that measured in **Re1**,

demonstrating that the addition of the bromo substituent to the naphthalimide does not drastically alter the cascade of excited states or their relative time constants, Figures S56-S58.



Figure 5. Excited-state absorption difference spectra of **Re1** in ACN during short delay times (A) and long delay times (B) following 350 nm pulsed excitation (105 fs fwhm).

When the **PONI** chromophore is attached to the Re(I) subunit, as in **Re3**, the effects of energy transfer between chromophores are also clearly delineated. When using 350 nm laser pulses, the excited state difference spectrum of **Re3** at 250 fs quantitatively matches that of the **PONI** model,

suggesting that the initial excited state is indeed localized on the **PONI** chromophore, Figure 6. The excited state absorbance at 450 nm undergoes a similar thermalization process observed with the **PONI** model, except now when the blue-shifted excited state absorbance at 425 nm decays, a new excited state feature at 360 nm grows in and matches that of the ³MLCT excited state of the Re(I) model **Re6**. The change in these absorption features suggests vibrational relaxation from the initially populated Franck-Condon state localized on the **PONI** moiety ($\tau = 170$ fs) is followed by resonance energy transfer to the Re(I) chromophore ($\tau = 1.5$ ps) with subsequent ultrafast intersystem crossing to the ³MLCT excited state. When examining the kinetics at 370 nm, the data is best fit to a sum of three exponentials yielding one time constant ($\tau = 26$ ps) matching that observed in **Re6** measured under the same conditions, Figure S69. Towards the end of the delay stage, the excited state absorbance at 360 nm and at 725 nm decrease in intensity as the excited state feature at 475 nm, assigned as the triplet localized on the **PONI**, gains intensity. The growth of this 475 nm feature is best fit to a single exponential function with a time constant of 4.4 ns, nearly matching what was observed in **Re1** and **Re2**, Figure S60. The change in these spectral features suggest a triplet-triplet energy transfer process returning the excited state density from the ³MLCT state back to the ³LC state on the **PONI** ligand.



Figure 6. Excited-state absorption difference spectra of **Re3** measured in acetonitrile across short (A) and long (B) delay times following 350 nm pulsed laser excitation (105 fs fwhm).

Unlike **Re1-Re3**, when coupling the **PSNI** subunit to the Re(I) complex to yield **Re4**, there were no significant changes in terms of the transient absorption difference spectra and kinetics in comparison to the **PSNI** model chromophore. As displayed in Figure 7, the excited state absorption features for the short and intermediate time ranges in **Re4** nearly match those observed in **PSNI**, suggesting that the ³LC formation does not proceed through the ³MLCT excited state as was observed in **Re1-Re3**. Following the first relaxation process at 450 nm, the kinetics in **Re4** are best

modeled using a biexponential function recovering time constants consistent to those of the **PSNI** model ($\tau_1 = 100$ fs; $\tau_2 = 3.3$ ps; see Figure S63). As stated earlier, the initial time constant is assigned to vibrational relaxation of the initially prepared "hot" excited state whereas the second component is associated with the rotation of the N-phenanthroline and/or thiobenzene groups leading to the relaxed geometry of the ¹PSNI charge transfer excited state. Since the fluorescence of the **PSNI** and the absorbance of the Re(I) complex have minimal spectral overlap, any possible FRET occurring between the two covalently linked molecules is likely inefficient and slow. To benchmark representative efficient and rapid FRET in a related molecule, a 45 ps time constant was observed for this process in a Re(I)-PNI bichromophore.³³ Since internal conversion to a nonfluorescent excited state on the **PSNI** moiety is markedly faster ($\tau = 3.3$ ps) with respect to an efficient FRET process, energy transfer to the Re(I) chromophore is no longer possible and excited state density remains fixed on the **PSNI** subunit in **Re4**. Following the decay of the excited state features in the intermediate time regime, subsequent formation of the long-lived ³NI excited state occurred with a time constant of 73 ps. The minor variation in the excited state difference spectra at long delay times are attributed to a minor fraction of ³MLCT excited state being generated as a result of non-selective sample excitation. When using 400 nm laser pulses in **Re4**, the ¹NI excited state is predominately populated, however there is a small fraction of the ¹MLCT excited state being generated in this experiment. Since population of the ¹MLCT excited state will almost immediately intersystem cross to the ³MLCT excited state, the observed changes at long delay times are likely due to triplet-triplet energy transfer from the minor ³MLCT excited state population converting into the long-lived ³LC **PSNI** excited state. The time constant for this process was determined to be 2.9 ns in acetonitrile using global fit analysis, Figure S64.



Figure 7. Excited-state absorption difference spectra of **Re4** measured in acetonitrile during short (A) intermediate (B) and long (C) delay times following 400 nm pulsed laser excitation (105 fs fwhm).

The excited state difference spectra recorded for the **Re5** species is shown in Figure 8. At 300 fs, the excited state features quantitatively match those previously measured for the ¹NI excited state localized on **PNI**. By kinetically tracking the excited state absorbance at 430 nm, the decay can best be fit to two time constants where the fast component ($\tau = 900$ fs) is assigned to vibrational relaxation and the slower component ($\tau = 42$ ps) corresponds to energy transfer to the Re(I)

chromophore through the FRET mechanism as observed in the previous investigated Re(I)-PNI bichromophore.³³ Translating towards the end of the delay stage, the ground state bleach recovers as the excited state features at 470 and 750 nm increase, which are characteristic signatures of the ³NI excited state, indicating the final triplet-triplet energy transfer process from the ³MLCT to the ³NI excited state. Following the kinetics of the transient features at 415 or 475 nm reveal a single exponential time constant of 2.1 ns for this TTET process, Figure S66.



Figure 8. Excited-state absorption difference spectra of **Re5** measured in acetonitrile during short (A) and long (B) delay times following 400 nm pulsed laser excitation (105 fs fwhm).

The excited state absorption difference spectra measured in the microsecond time domain for the five **Re1-Re5** bichromophores are presented in Figure 9. In each case, the observed excited state difference spectra were consistent with the ultrafast excited state difference spectra obtained at 6.1 ns, implying that the identical excited state was observed throughout the time scales of these two experiments. These excited state features continue to persist for tens to hundreds of microseconds (Table 2), suggesting that the absorption features originate from a long-lived ³LC excited state in each instance. Since each naphthalimide model chromophore forms the corresponding triplet excited state independently (except in the case of **PNI**), the same transient absorption experiments were performed on the model molecules in order to compare the excited state difference spectra directly, Figure S70. The excited state difference spectra for NI and Re1, include two excited state absorptions at 370 and 475 nm, Figure 9a. The difference spectra for **BrNI** and **Re2** are very similar to that of **NI** and **Re1**, where the two characteristic excited state absorptions were red-shifted to 380 and 490 nm, Figure 9b. The excited state difference spectra for **PONI** and **Re3** have a broad excited state absorbance centered at 470 nm and a ground state bleach located at 365 nm (Figure 9c) while **PSNI** and **Re4** have a broad excited state absorbance centered at 675 nm and a ground state bleach located at 390 nm, Figure 9d. The excited state difference spectrum for **Re5** has a broad excited state absorbance with two peaks at 480 and 725 nm and a ground state bleach located at 410 nm, Figure 9e. Previous experiments using thioxanthone sensitized the triplet excited state in **PNI** which is in qualitatively good agreement to the excited state difference spectra presented for **Re5** in Figure 9e.⁴⁴ The transient absorption decay kinetics were also collected for each of the NI models and presented in the Supporting Information (Figures S71-74).



Figure 9. Excited-state absorption difference spectra of **Re1** (A), **Re2** (B), **Re3** (C), **Re4** (D), and **Re5** (E) measured in acetonitrile following 350 nm pulsed laser excitation (2.5 mJ/pulse, 7 ns fwhm) or 400 nm pulsed laser excitation (3.0 mJ/pulse, 7 ns fwhm). Samples were deaerated using the freeze-pump-thaw degas method.

Excited State Equilibrium. The decay kinetics of the delayed ³MLCT PL and the ³LC excited state absorptions measured in **Re1-Re3** at room temperature are very similar, suggesting that the two excited states in these molecules are indeed in thermal equilibrium. As observed previously, the time constant measured from both experiments was found to lie in between that of the anticipated ³MLCT decay (174 ns) and ³NI decay time constants (> 500 µs), indicative of a thermal equilibrium process occurring between the two triplet excited states.^{33, 44, 46} The excited state lifetime was shortest in **Re1** and this is likely due to the energy gap between the two triplet excited states being smallest and therefore more rapid population of the shorter-lived ³MLCT excited state. As the energy gap between the triplet excited states increase across the series (based on ^{3}LC phosphorescence data), the population of the higher energy ³MLCT excited state is anticipated to systematically decrease, resulting in excited state lifetime properties more characteristic of the organic chromophore. Once this energy gap becomes too large for sufficient population of the higher energy excited state at room temperature, the bichromophore photophysics in **Re4** and **Re5** then strongly resembles those of the **PSNI** and **PNI** models, respectively. The long-lived ³LC excited state absorption was also observed in Re4 and Re5, however, there was no significant evidence of delayed ³MLCT PL observed on similar time-scales and therefore no evidence for a triplet excited state equilibrium.

The triplet energy gap between the ³NI and ³MLCT excited states in **Re1-Re5** was estimated using several different experimental and electronic structure calculation-based methodologies as summarized in Table 3. The simplest method for estimating the energy gap between the two excited states is to compare the phosphorescence energies of the two emitting states using timegated PL spectroscopy. Since the phosphorescence of the ³NI excited state was not observed at

room temperature in any of the molecules under investigation, the 77 K PL spectra (Figure 4) originating from the two excited states were resolved. From this spectral information, the energy gap was found to range from 2430 to 3900 cm⁻¹ with **Re1** having the smallest energy gap and **Re5** having the largest energy gap. Unfortunately, this particular method cannot be considered reliable since the state energies of charge transfer states substantially shift when measured as 77 K glasses due to a combination of a pronounced thermally-induced Stokes shift and the rigidochromic effect. Since the naphthalimide chromophores have little to no charge character in their triplet excited states when compared to the parent Re(I) MLCT complex, the resulting phosphorescence of the naphthalimides shift insignificantly upon cooling to 77 K. Therefore, the calculated triplet energy gaps using this methodology are substantially overestimated with respect to room temperature. The ³MLCT/³NI energy gap for the five bichromophores were also estimated by taking the difference between the experimental room temperature MLCT PL tangent (using the highest energy side of the emission band and intersecting this with the x-axis) and the 77 K NI tangent to circumvent the temperature-dependent shift of the MLCT excited state energy. In this case, the energy gaps were determined to be much smaller, ranging from 600 to 2120 cm⁻¹ with the energetic ordering following the respective compound numbering scheme, **Re1** to **Re5**. The energy gaps calculated in this manner are likely more accurate to the true room temperature triplet separation but are believed to be slightly underestimated due to the $< 500 \text{ cm}^{-1}$ blue shift expected for the nonpolar naphthalimide triplet excited states resident in these metal-organic bichromophores.^{67, 89}

	Emission	Emission	Equilibrium	ΔSCF	TD-DF
Molecule	$\Delta E_{MLCT-NI}$	$\Delta E_{MLCT-NI}$	ΔE	ΔE_{Re6-NI}	ΔЕт2-т1
	$(cm^{-1})^{[a,b]}$	$(cm^{-1})^{[a,c]}$	$(cm^{-1})^{[d]}$	$(cm^{-1})^{[e]}$	$(cm^{-1})^{[f]}$
Re1	2430	600	880	1740	2860
Re2	2800	1070	1280	2430	3580
Re3	2680	860	1180	2140	2860
Re4	3650	1870	2000	2980	4060
Re5	3900	2120	1860 ^[g]	4020	4340

Table 3. Calculated triplet energy gap of Re1-Re5 using different methodologies.

^[a] The E_{0,0} emission energies were estimated using highest energy side of the emission band and intersecting this with the x-axis. ^[b] The ³MLCT and ³NI emission measured at 77 K in 2-MeTHF. ^[c] The ³MLCT emission taken at room temperature (in THF) with the ³NI emission measured at 77 K in 2-MeTHF. ^[d] The energy gap was calculated using equations 1-3 based on prior studies.^{33, 44} ^[e] The energy gap was calculated by subtracting the Δ SCF (TS-GS) energy of NI models from the Δ SCF (TS-GS) energy of the **Re6** using DFT//CAM-B3LYP/Def2-SVP/SDD level of theory.^[f] The energy gap was calculated by subtracting the S₀ \rightarrow T₂ energy from the S₀ \rightarrow T₁ energy of **Re1-Re5** using TD-DFT//B3LYP/Def2-SVP/SDD level of theory.^[g] The ³NI rate constant was approximated to 6670 s⁻¹ ($\tau \approx 150 \ \mu$ s) since ³NI formation was not observed in **PNI**; estimated from previous triplet sensitization efforts using thioxanthone.

The third method for estimating the energy gap was identical to our prior studies,^{33, 44} where the energy separation between the two triplet excited states can be approximated using the measured rate constants in Eqs. 1-3. The bimolecular nature of the ³MLCT emission of the bichromophores were simplified using a weighted average of the two components. Using **Re1** as a representative example, the time constants obtained from transient absorption decays for **NI**, **Re1**, and **Re6** were converted to rate constants (5.80×10^3 s⁻¹, 8.40×10^4 s⁻¹ and 5.50×10^6 s⁻¹, respectively) and inserted into Eq. 1 to determine the relative population of each excited state. The relative population (α) is then used to determine the equilibrium constant (K_{eq}) in Eq. 2, which was determined to be 69.2 in this instance. Finally, the equilibrium constant was substituted into the

Arrhenius equation (Eq. 3) to determine the energy difference between the two excited states. Using this method, energy gaps of 880, 1280, 1180, 2000, and 1860 cm⁻¹ were determined for **Re1**, **Re2, Re3, Re4**, and **Re5** respectively. Please note that the model **PNI** chromophore does not populate a triplet excited state without being photosensitized by a triplet donor such as thioxanthone. The resulting kinetics from this sensitization process are complicated (in addition to being concentration dependent) so the time constant for the triplet excited state decay was estimated as $\tau \approx 150 \,\mu$ s. The energy gaps calculated in this manner agree well with the differences in the phosphorescence energies detailed above.

$$k_{obs} = \alpha[k_{LC}] + (1 - \alpha)[k_{MLCT}]$$
⁽¹⁾

$$K_{eq} = \frac{{}^{3}LC}{{}^{3}MLCT} = \frac{\alpha}{1-\alpha}$$
(2)

$$\Delta E = -RT ln(K_{eq}) \tag{3}$$

The remaining approaches for estimating the energy gap between the two triplet excited states in **Re1-Re5** was through DFT calculations. For the delta self-consistent field (Δ SCF) method, the optimized ground state and triplet state geometries of the model chromophores (**NI**, **BrNI**, **PONI**, **PSNI**, **PNI** and **Re6**) were used to estimate their energies. The estimated energy of the ³NI and ³MLCT excited states (depending on the functionals used) were calculated by taking the difference in the respective triplet state and ground state energies. Finally, the ³NI energy of the five naphthalimide model compounds were subtracted from the ³MLCT energy of **Re6** to determine the energy gap. Using this approach, the trend in energy gaps correlate well with the other three experimental methods with values ranging from 1740 to 4020 cm⁻¹. When comparing energy gaps obtained from the equilibrium method, there appears to be a systematic error of approximately 900 cm⁻¹ where the Δ SCF approach overestimates the triplet gap. The TD-DFT method calculates the energies of the S₀ \rightarrow T₁ and S₀ \rightarrow T₂ transitions from the optimized ground state and takes the difference in energy between the two states. Using natural transition orbital (NTO) analysis, the ³NI and ³MLCT excited states can be clearly delineated for the S₀ \rightarrow T₁ and S₀ \rightarrow T₂ transitions, respectively for **Re1-Re5**, Figures S87-S91. The same trend is observed here as was determined in the Δ SCF method, but now there appears to be a larger systematic error as the energy gaps using the NTOs range from 2860 to 4340 cm⁻¹.

Overall, the five approaches consistently varied with the anticipated trends in the energy gaps but had a larger variance when it came to the absolute values. The equilibrium method was likely the most accurate when estimating the energy gap but exact triplet excited state decay kinetics are needed for both model chromophores in order to be useful. The largest energy gaps previously reported for similar excited state equilibria between 2 triplet excited states in a metal-organic bichromophores were 1680 cm⁻¹ and 1740 cm⁻¹,^{33, 41} so the energy gap in **Re4** is sufficiently large for the ³NI decay kinetics to outcompete thermal activation of the ³MLCT excited state, thereby shunting the triplet equilibrium process.

Excited State Evolution and Decay Kinetics. The relevant energy level diagrams summarizing the observed photophysical processes of **Re1-Re5** are displayed in Figure 10. **Re1-Re3** follow the "ping-pong" energy transfer mechanism described previously,³³ where the initially populated ¹NI excited state localized on the naphthalimide subunit first transfers its energy to the ¹MLCT excited state localized on the Re(I) chromophore. These three bichromophores feature significantly faster singlet energy transfer time constants ($\tau = 360$ fs to $\tau = 1.5$ ps) compared to the previous

bichromophore containing PNI ($\tau = 45$ ps),³³ due to greater spectral overlaps between the naphthalimide emission and Re(I) MLCT absorption. The second energy transfer process takes place once the ³MLCT excited state is formed, this time returning the excited state energy back to the naphthalimide chromophore yielding its long-lived ³NI excited state. While the ³NI is the lowest energy excited state, in **Re1-Re3** the ³MLCT is in sufficient energetic proximity enabling thermally activated reverse TTET facilitating a triplet excited state equilibrium. This results in the generation of markedly extended lifetimes for the ³MLCT excited state, manifested through the observation of delayed MLCT-based PL.

Re4 breaks the trend observed in the first three bichromophores by maintaining the excited state density localized predominately on the naphthalimide chromophore, following near identical excited state decay as that observed in the **PSNI** model. This occurs since the singlet energy transfer efficiency to the Re(I) chromophore is extremely slow (poor spectral overlap) and efficient internal conversion/intersystem crossing rapidly takes place within the **PSNI** subunit. Once the long-lived ³NI excited state is formed, it is also too low in energy with respect to the ³MLCT excited state to yield any excited state equilibrium, so subsequently no delayed MLCT PL is observed. Since intersystem crossing was not observed in the **PNI** chromophore, **Re5** still relies on inefficient singlet energy transfer to the Re(I) chromophore in order to access the triplet manifold (despite the poor spectral overlap) resulting in another example of "ping-pong" energy transfer leading to the generation of the lowest excited state. However, unlike **Re1-Re3**, the energy gap between the ³MLCT and ³NI excited states in **Re5** is simply too large for excited state equilibrium to become established at room temperature so this excited state dissipates non-radiatively exclusively through the ³NI excited state.



Figure 10. Qualitative energy level diagrams of the photophysical processes occurring in **Re1**-**Re3** (A), **Re4** (B), and **Re5** (C) in acetonitrile at room temperature.

CONCLUSIONS

In this investigation, the excited state processes and the associated kinetics of a series of five distinct NI chromophores along with five Re(I)-NI bichromophores were elucidated using a combination of transient absorption spectroscopy and time-resolved PL spectroscopy. Additionally, the spectroscopic analysis was supported by electronic structure calculations to identify the origin of many of the observed electronic transitions. The series of naphthalimides were synthesized by substituting the 4-position of the naphthalimide with various substituents (hydrogen, bromine, phenoxy, thiobenzene, piperidine), resulting in changes to many of the requisite photophysical properties, including energies of the ¹NI and ³NI states and fluorescence quantum yields. By covalently attaching these newly synthesized naphthalimide ligands to a Re(I) MLCT complex, a series of bichromophores were created to evaluate the energy transfer processes occurring between the two chromophores and the subsequent excited state equilibrium formed between the low energy ³MLCT and ³NI excited states. Four of the five bichromophores demonstrated "ping-pong" energy transfer where the initially excited naphthalimide chromophore was found to rapidly transfer its energy to the Re(I) chromophore. Following fast intersystem crossing and the formation of the ³MLCT excited state localized on the Re(I) chromophore, the excited state energy was back transferred to the naphthalimide chromophore and the formation of the ³NI state was observed. Excited state triplet equilibrium was observed in the three bichromophores featuring the highest energy ³NI excited states (Re1-Re3), resulting in the observation of delayed ³MLCT PL with lifetimes extending well into the microsecond time regime. The two bichromophores with the lowest energy ³NI excited states (**Re4** and **Re5**) did not thermally populate the higher energy ³MLCT level. In these instances, ³NI ligand-centered

deactivation dominated the photophysical processes, decaying with lifetimes exceeding 100 μ s at room temperature.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, structural characterization data, additional static and time-resolved spectra, temperature dependent data, and density functional theory calculations for the molecules in this study are available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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