Inorganic Chemistry

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Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX

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Spectroscopic and $^1O_2$ Sensitization Characteristics of a Series of Isomeric Re(bpy)$(CO)_3$Cl Complexes Bearing Pendant BODIPY Chromophores

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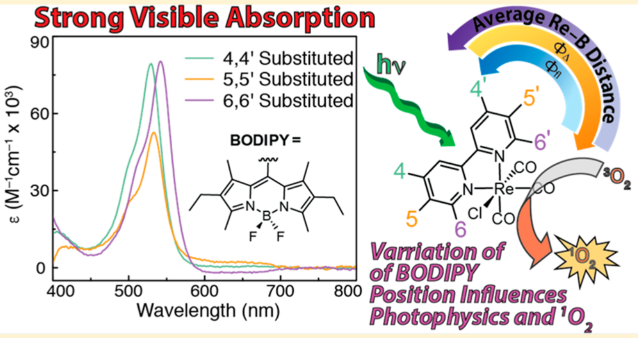
Supporting Information



ABSTRACT: Two new Re(I)bipyridyltricarbonyl chloride complexes, Re(BB3)$(CO)_3$Cl and Re(BB4)$(CO)_3$Cl, featuring BODIPY groups appended to the 5,5′- or 6,6′-positions of the bipyridine ligand, respectively, were synthesized as structurally isomeric compliments to a previously reported 4,4′-substituted homologue, Re(BB2)$(CO)_3$Cl. X-ray crystal structures of the compounds show that the 4,4′-, 5,5′-, and 6,6′-substitution patterns place the BODIPY groups at progressively shorter distances of 9.43, 8.39, and 5.56 Å, respectively, from the complexes' Re centers. The photophysical properties of the isomeric complexes were investigated to ascertain the manner in which the heavy rhenium atom might induce intersystem crossing of the pendant BODIPY moieties positioned at progressively shorter through-space distances. Electronic absorption spectroscopy revealed that the three metal complexes retain the strong visible absorption features characteristic of the bpyBODIPY (BB2−BB4) ligands; however, the fluorescence of the parent borondipyrromethane appended ligands is attenuated by more than an order of magnitude in Re(BB2)$(CO)_3$Cl and Re(BB3)$(CO)_3$Cl and by more than two orders of magnitude in Re(BB4)$(CO)_3$Cl. Furthermore, phosphorescence from Re(BB4)$(CO)_3$Cl is observed under a nitrogen atmosphere, consistent with highly efficient ISC to the triplet-excited state. Singlet oxygen sensitization studies confirm that all three complexes produce singlet oxygen with quantum yields that increase as the distance of the BODIPY groups to the heavy rhenium center is decreased. The trends observed across the series of rhenium complexes with respect to emission and $^1O_2$ sensitization properties can be rationalized in terms of the varied distal separation between the metal center and BODIPY groups in each system.

■ INTRODUCTION

Boron dipyrromethenes (BODIPYs) are well-known for their strong absorption of visible light, fluorescence quantum yields that can approach unity, and good photostability.[1,2] These characteristics have inspired studies of BODIPY-based compounds for applications as light harvesters in dye-sensitized solar cells,[3] as laser dyes,[4] and as fluorescent probes for biomolecules, pH, certain cations, anions, or gases, reactive oxygen or nitrogen species, redox potential, and viscosity, among other stimuli.[5−7] While population of the triplet excited-state manifold of traditional BODIPY compounds is typically negligible, other photosensitizers that support a more extensive triplet photochemistry have found uses in triplet−triplet annihilation upconversion,[8,9] photocatalysis,[10] and photodynamic therapy.[11] The ease with which the BODIPY framework can be synthetically modified[12−14] has buoyed efforts aimed at enabling the use of this popular class of luminophore for applications that require the photochemical generation of reactive triplet intermediates.[15]

A common strategy for transforming conventional fluorophores into triplet photosensitizers exploits the heavy atom effect to promote intersystem crossing (ISC) through enhanced spin orbit coupling.[11] Accordingly, numerous halogenated BODIPY derivatives featuring bromine or iodine substituents directly attached to, or in π-conjugation with the pyrrolic backbone, have been synthesized and reported to efficiently access the triplet state.[16−21] Ligands bearing BODIPY moieties have also been complexed with heavy transition metals such as Ru(II),[22−24] Pt(II),[25−29] Ir(III),[30−32] and Re(I)[33−35] to deliver systems that exhibit lower fluorescence quantum yields and, in some cases, detectable phosphorescence from the BODIPY triplet state following photoexcitation. Along these lines, we reported a 2,2′-bipyridine ligand functionalized with two BODIPY substituents at the 4- and 4′-positions (BB2)[36] and subsequently incorporated this ligand into a rhenium(I)tricarbonyl chloride complex to form Re(BB2)$(CO)_3$Cl (Scheme 1).[37] In related work, we synthesized the analogous 5,5′-substituted 2,2′-bpyBODIPY ligand (BB3), which had been introduced

Received: January 11, 2019

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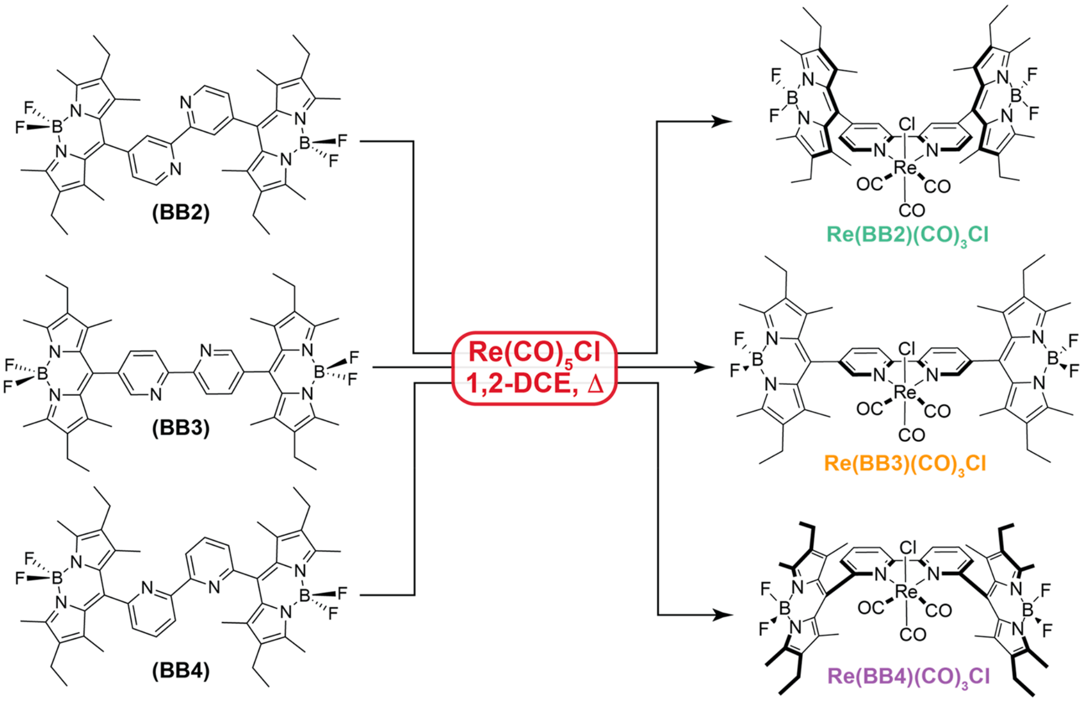
DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Metallation of bpyBODIPY Ligands to Generate an Isomeric Series of *fac*-Re(bpy)$(CO)_3$Cl Complexes



previously in the literature using a slightly different synthetic strategy,[38] as well as the homologous 6,6′-substituted 2,2′-bpyBODIPY ligand (BB4).[39] In this study, BB3 and BB4 have also been incorporated into rhenium(I)tricarbonyl chloride complexes (Re(BB3)$(CO)_3$Cl and Re(BB4)$(CO)_3$Cl, respectively) to complete the set of three homologous complexes shown in Scheme 1.

For each of the isomeric Re complexes of Scheme 1, the positions at which the BODIPY units are attached to the bipyridine scaffolds ultimately dictates the chromophores' proximities (∼5−10 Å) to the rhenium center. Accordingly, we anticipated that the photophysics of the pendant BODIPY units might be perturbed by varying degrees for each Re complex, and conducted steady state absorption and emission studies to probe how altering the (Re···BODIPY) separation influences the photophysical properties of the three isomers. The absorption profiles of the complexes are dominated by the strong BODIPY features in the visible region, while the emission spectra reveal evidence of greater spin−orbit coupling when the BODIPY groups are positioned closer to the metal center. Additionally, Re(BB2)$(CO)_3$Cl, Re(BB3)$(CO)_3$Cl, and Re(BB4)$(CO)_3$Cl all show the ability to sensitize $^1O_2$, but Re(BB4)$(CO)_3$Cl, which has the shortest average Re···BODIPY separation, photosensitizes the formation of $^1O_2$ with the highest quantum yield across the series. These constructs are notable as they form a structurally characterized set of isomeric homologues that add to the small number of BODIPY compounds tethered to a rhenium heavy atom to induce a triplet photochemistry[33−35] and as new examples of rhenium(I) complexes capable of generating $^1O_2$ upon irradiation with wavelengths of light longer than 500 nm.[11,33,40,41]

■ EXPERIMENTAL SECTION

General Materials and Methods. Reactions requiring an inert atmosphere were carried out under positive pressure of N_2 using flasks fitted with Suba-Seal rubber septa and standard Schlenk techniques. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were purchased from Sigma-Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Re(BB2)$(CO)_3$Cl and the BB3 and BB4 ligands were prepared according to published procedures.[36,37,39] Solvents used for synthesis were of reagent grade or better. Anhydrous solvents were dried by passage through activated alumina and stored over 4 Å molecular sieves prior to use. Column chromatography was performed with 40−63 μm silica gel from Silicycle.

Compound Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer with a cryogenic QNP probe. Proton spectra are referenced to the residual proton resonance of the deuterated solvent ($CDCl_3$ = δ 7.26), and carbon spectra are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16).[42] All chemical shifts are reported using the standard δ notation in parts per million, and positive chemical shifts are to higher frequency from the given reference. High-resolution mass spectrometry analyses were performed by the University of Delaware Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry.

Rhenium[5,5′-bis(BODIPY)-2,2′-bipyridine](CO)$_3$Cl (Re(BB3)(CO)$_3$Cl). 5,5′-bis(BODIPY)-2,2′-bipyridine (BB3) (84 mg, 0.11 mmol) and rhenium(I) pentacarbonylchloride (40 mg, 0.11 mmol) were combined in 50 mL of 1,2-dichloroethane. The resulting solution was heated to reflux while being stirred for 20 h under nitrogen and underwent a change in color from orange to dark red. The solvent was removed under reduced pressure, and the crude product was purified on silica by eluting with 5% hexanes in CH_2Cl_2 followed by straight CH_2Cl_2. The product was obtained as the second band immediately following a band of unreacted ligand. The desired product was obtained as 41 mg of a dark red powder (yield = 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ /ppm: 9.04 (d, *J* = 1.7 Hz, 2H), 8.42 (d, *J* = 8.2 Hz, 2H), 8.11 (dd, *J* = 8.2, 1.9 Hz, 2H), 2.57 (s, 12H), 2.39−2.28 (m, 8H), 1.47 (s, 6H), 1.46 (s, 6H), 1.02 (dt, *J* = 10.8, 7.6 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 196.02, 156.88, 155.35, 154.99, 152.40, 139.30, 138.18, 136.22, 134.44, 133.80, 130.64, 130.50, 129.89, 123.13, 29.50, 16.92, 16.89, 14.41, 14.29, 13.45, 13.01, 12.63, 12.51. HR-ESI-MS: $[M + H]^+$ *m*/*z*: calcd for $C_{47}H_{51}B_2ClN_6F_4O_3Re$, 1067.3391; found, 1067.3428.

Rhenium[6,6′-bis(BODIPY)-2,2′-bipyridine](CO)$_3$Cl (Re(BB4)(CO)$_3$Cl). 6,6′-bis(BODIPY)-2,2′-bipyridine (BB4)(84 mg, 0.11

DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX

mmol) and rhenium(I) pentacarbonylchloride (40 mg, 0.11 mmol) were combined in 50 mL of 1,2-dichloroethane. The resulting solution was heated to reflux while being stirred for 20 h under nitrogen and underwent a change in color from orange to dark red. The solvent was removed under reduced pressure, and the crude product was purified on silica by eluting 25% hexanes in CH_2Cl_2 followed by 1% methanol in CH_2Cl_2. The desired product was obtained as 75 mg of a dark red powder (yield = 64%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.46 (d, J = 8.2 Hz, 2H), 8.20 (t, J = 7.9 Hz, 2H), 7.72 (d, J = 7.7 Hz, 2H), 2.52 (s, 12H), 2.28 (q, J = 7.5 Hz, 4H), 2.20 (q, J = 7.6 Hz, 4H), 1.65 (s, 6H), 1.07 (s, 6H), 0.95 (t, J = 7.5 Hz, 6H), 0.87 (t, J = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ /ppm: 192.04, 187.33, 158.68, 158.09, 158.04, 155.29, 139.29, 138.93, 135.70, 134.50, 133.86, 133.13, 131.18, 129.94, 128.16, 124.26, 17.26, 17.12, 14.65, 14.25, 13.53, 13.09, 12.83, 11.36. HR-ESI-MS: $[M + H]^+$ m/z: calcd for $C_{47}H_{51}B_2ClN_6F_4O_3Re$, 1067.3391; found, 1067.3435.

X-ray Structural Analysis. Crystals of $Re(BB3)(CO)_3Cl$ and $Re(BB4)(CO)_3Cl$ were obtained via slow evaporation of saturated solutions of the respective complexes in 1,2-dichloroethane. Crystals were mounted on a glass fiber using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with $Pmn2_1/n$ for $Re(BB4)(CO)_3Cl$ with the Flack parameter refined to virtually nil, indicating the true hand of the data had been determined. For $Re(BB3)(CO)_3Cl$, no symmetry higher than triclinic was observed, and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data sets were treated with SADABS absorption corrections based on redundant multiscan data (Sheldrick, G., Bruker-AXS Inc., Madison, WI, 2001). For $Re(BB4)(CO)_3Cl$, the compound molecule was located on a mirror plane. Molecules of 1,2-dichloroethane solvent were located cocrystallized in a 1:1 ratio with the $Re(BB4)(CO)_3Cl$ complex with the solvent disordered at a mirror plane. For $Re(BB3)(CO)_3Cl$, the pyrrole(C)−ethyl(C) bonds were restrained to be similar with one ethyl group found disordered in two positions having a refined site occupancy of 60/40 with the disordered chemically equivalent atoms constrained with equal atomic displacement parameters and treated with three-dimensional rigid-bond displacement restraints. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2.[43] All nonhydrogen atoms were refined with anisotropic displacement parameters. All other hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL program library.[44] CIFs are deposited under CCDC depositary numbers 1879091 and 1879092.

Steady-State Spectroscopy Experiments. UV−visible absorbance spectra were collected at room temperature on a StellarNet Silver-NoVA CCD array UV−vis spectrometer using quartz cuvettes (6Q) with a 1.0 cm path length from Firefly Scientific. Absorption spectra of BB2, BB4, $Re(BB2)(CO)_3Cl$, $Re(BB3)(CO)_3Cl$, and $Re(BB4)(CO)_3Cl$ were collected in N,N-dimethylformamide at concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 μM. Absorption spectra of BB3 were collected in 10% CH_2Cl_2 in N,N-dimethylformamide at concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 μM.

Emission and excitation spectra were recorded on an automated Photon Technology International (PTI) QuantaMaster 40 fluorometer equipped with a 75-W Xenon arc lamp, an LPS-220B lamp power supply and a Hamamatsu R2658 photomultiplier tube. All samples were prepared in screw cap quartz cuvettes of 1.0 cm path length from Starna Cells, Inc. Solutions of BB2 (7.0 μM), BB4(6.0 μM), $Re(BB2)(CO)_3Cl$ (8.0 μM), $Re(BB3)(CO)_3Cl$ (9.0 μM) and $Re(BB4)(CO)_3Cl$ (10.0 μM) in N,N-dimethylformamide, and a solution of BB3(6.0 μM) in 10% CH_2Cl_2 in N,N-dimethylformamide were prepared in a nitrogen-filled glovebox such that the absorbance values of all samples at λ = 500 nm ranged between 2.60×10^{-1} and 3.15×10^{-1} (1 cm path length). Samples for emission experiments were excited at λ_{ex} = 500 nm, and emission was monitored from λ_{em} = 515−950 nm using a step size of 1 nm and an integration time of 0.25 s. Emission spectra were also measured following exposure of each of the samples to air. All reported spectra are the average of five individual acquisitions. Excitation spectra recorded for $Re(BB4)(CO)_3Cl$ were monitored at either 575 or 828 nm while varying the excitation wavelength from 420−650 nm.

A solution of $[Ru(bpy)_3](PF_6)_2$ in air-saturated acetonitrile was prepared at a concentration of ~120 μM such that its absorbance at λ = 500 nm fell between 2.60×10^{-1} and 3.15×10^{-1} for use as a luminescence reference (Φ_{ref} = 0.018).[45] Emission quantum yields were calculated using the expression below:

$$\Phi_s = \Phi_{ref}\left(\frac{I_s}{I_{ref}}\right)\left(\frac{A_{ref}}{A_s}\right)\left(\frac{n_s}{n_{ref}}\right)^2$$

where Φ_s and Φ_{ref} are the emission quantum yield of the sample and the reference, respectively, I_s and I_{ref} are the integrated emission intensities of the sample and reference, respectively, A_s and A_{ref} are the measured absorbances of the sample and reference at the excitation wavelength, respectively, and η_s and η_{ref} are the refractive indices of the solvents used for the sample and reference, respectively.

Determination of Singlet Oxygen Sensitization Quantum Yields. $^1O_2$ production was quantified by monitoring the fluorescence quenching of the $^1O_2$ trapping agent, 1,3-diphenylisobenzofuran (DPBF).[46,47] Measurements were carried out on an automated Photon Technology International (PTI) QuantaMaster 40 fluorometer equipped with a 75-W Xenon arc lamp, an LPS-220B lamp power supply, and a Hammamatsu R2658 photomultiplier tube using quartz cuvettes (6Q) of 1.0 cm path length. Each cuvette contained 2.0 mL of N,N-dimethylformamide solution that was 10.0 μM in $Re(BB2)(CO)_3Cl$, $Re(BB3)(CO)_3Cl$, $Re(BB4)(CO)_3Cl$, or $[Ru(bpy)_3](PF_6)_2$ (used as a reference, Φ_Δ = 0.57)[48] and 1.0 μM in DPBF. An additional cuvette containing only N,N-dimethlyformamide and 1.0 μM DPBF was used as a control. Consumption of DPBF was monitored by observing the change in its integrated emission intensity following irradiation with light from an Intralux 9000 light source (Volpi) fitted with a 10 nm (fwhm) bandpass filter centered at 500 nm (Thor Laboratories, FB500−10). During the studies of $Re(BB2)(CO)_3Cl$ and $Re(BB3)(CO)_3Cl$, the cuvettes were irradiated for 10 s intervals for a total of 40 s. Due to its greater $^1O_2$ generating efficiency, $Re(BB4)(CO)_3Cl$ was studied separately and irradiated for 5 s intervals for a total of 20 s. DPBF emission spectra were obtained by exciting at λ_{ex} = 405 nm and scanning from λ_{em} = 400−600 nm using a step size of 1 nm and an integration time of 0.25 s.

As has been reported previously,[49−52] calibration curves of the integrated emission intensity versus the concentration of unreacted DPBF remaining in solution were generated to correct for absorption of the photosensitizers and standard between 400−600 nm. Emission spectra were collected from 10.0 μM solutions of $Re(BB2)(CO)_3Cl$, $Re(BB3)(CO)_3Cl$, $Re(BB4)(CO)_3Cl$, and $[Ru(bpy)_3](PF_6)_2$ containing DPBF concentrations of 0, 0.25, 0.50, 0.75, 1.00, 1.25, or 1.50 μM. Linear regression lines fit to the calibration data from each solution enabled the integrated emission intensity values obtained from the $^1O_2$ sensitization experiments to be converted into the corresponding concentrations of unreacted DPBF. A final plot of the concentration of unreacted DPBF versus irradiation time formed a straight line of slope m, which allowed for calculation of the $^1O_2$ quantum yields via the following expression:

$$\Phi_s = \Phi_{ref}\left(\frac{m_s}{m_{ref}}\right)\left(\frac{\varepsilon_{ref}}{n_s}\right)$$

where Φ_s and Φ_{ref} are the $^1O_2$ sensitization quantum yields for the sample and $[Ru(bpy)_3](PF_6)_2$ reference, respectively, m_s and m_{ref} are the slopes of the concentration of unreacted DPBF vs irradiation time plots for the sample and reference, respectively, and ε_s and ε_{ref} are the extinction coefficients at the wavelength of irradiation (500 nm) for the sample and reference, respectively. All reported $^1O_2$ quantum yields were obtained from an average of three trials.

DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX

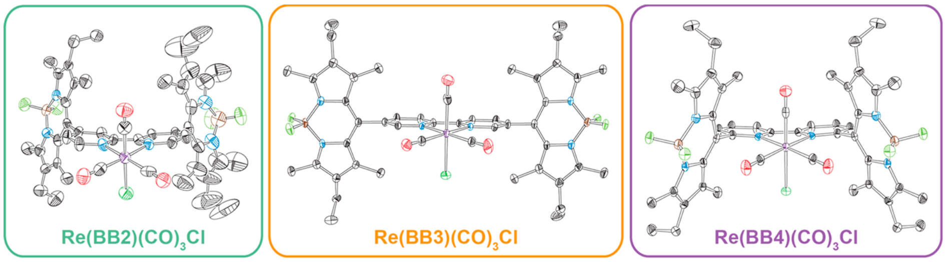


Figure 1. Solid state structures of Re(BB2)(CO)$_3$Cl,[37] Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl. Thermal ellipsoids are shown at the 30% probability level (C, black; O, red; N, blue; Cl, dark green; Re, purple; B, brown; F, light green). Hydrogen atoms and cocrystallized solvent molecules were omitted for clarity.

RESULTS

BB2, BB3, and BB4 were synthesized according to published procedures,[39] and metalation of these derivatives was achieved by heating solutions of the ligands with Re(CO)$_5$Cl in 1,2-dichloroethane at reflux for 20 h (Scheme 1). As reported previously for Re(BB2)(CO)$_3$Cl,[37] both Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl can be obtained in four steps from commercially available materials, as illustrated by Scheme S1 in the Supporting Information.

Slow evaporation of concentrated solutions of Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl dissolved in 1,2-dichloroethane yielded single crystals of both complexes. Figure 1 displays the solid-state structures obtained for Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl along with a reproduction of the structure obtained previously for Re(BB2)(CO)$_3$Cl.[37] Crystallographic parameters for Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl are summarized in Table 1, and fully labeled thermal ellipsoid plots for both complexes are available in the Supporting Information (Figure S1 and S2). The crystal structures of all three isomeric Re complexes reveal that the BODIPY units are nearly orthogonal to the bipyridine backbone. Table 2 summarizes the dihedral angles between each BODIPY moiety and the pyridine ring to which it is directly appended for each Re complex. For all three complexes, the bpy−BODIPY dihedral angles range from ∼74°−88°. Additionally, the ^{1}H NMR spectra of Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl show a desymmetrization of the aliphatic resonances attributable to the BODIPY alkyl substituents that is not seen in the ^{1}H NMR spectra of the free BB3 or BB4 ligands (Supporting Information Figure S3 and S4). Similar observations from the ^{1}H NMR spectra of BB2 and Re(BB2)(CO)$_3$Cl were attributed to a lack of free rotation about the indacene−bipyridine bonds, which places opposite sides of each BODIPY group in distinct environments as a result of being in closer proximity to either the axial chloride or the axial carbonyl ligand on each complex's Re center (Figure 1).[37] Given that dimethyl substitution at the 1- and 7-positions of the BODIPY framework has been reported to hinder rotation of *meso* substituents,[53−55] the rigid, nearly perpendicular orientation of the BODIPY groups with respect to the 2,2′-bipyridine backbone observed in all three rhenium complexes is not surprising.

Table 1. Crystallographic Parameters for Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl

	Re(BB3)(CO)$_3$Cl	Re(BB4)(CO)$_3$Cl
empirical formula	$C_{49}H_{54}B_2C_{13}F_4N_6O_3Re$	$C_{49}H_{54}B_2C_{13}F_4N_6O_3Re$
formula weight	1165.15	1165.15
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	$Pmn2(1)$
a	13.383(3) Å	27.663(4) Å
b	14.555(3) Å	11.5474(15) Å
c	14.563(3) Å	8.0100(10) Å
α	88.305(4)°	90°
β	81.330(4)°	90°
γ	62.646(4)°	90°
volume	2488.1(9) Å^3	2558.7(6) Å^3
Z	2	2
temperature	200(2) K	200(2) K
D_{calcd}	1.555 g/cm^{-3}	1.512 g/cm^{-3}
2θ range	1.725−28.302°	1.91−28.49°
μ	2.666 mm^{-1} (Mo Kα)	2.592 mm^{-1} (Mo Kα)
reflections	27,813	29,089
unique	12,249	6513
R(int)	0.0482	0.0716
R_1	0.0588	0.0390
wR_2	0.1297	0.0772

Table 2. Dihedral Angles and Average Re···BODIPY Distal Separation of Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl

	bpy−BODPIY dihedral angles[a] (°)	average Re···BODIPY separation (Å)
Re(BB2)(CO)$_3$Cl	73.8, 83.2	9.43
Re(BB3)(CO)$_3$Cl	83.9, 87.5	8.39
Re(BB4)(CO)$_3$Cl	79.5[b]	5.56[b]

[a]Dihedral angles measured between planes defined by each BODIPY unit and the directly appended pyridine ring. [b]Due to the presence of a mirror plane, the dihedral angles and Re···BODIPY distances measured for each BODIPY unit in Re(BB4)(CO)$_3$Cl are identical.

The solid-state structures of Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl also allow for the comparison of the proximity of the BODIPY luminophores to each of the complexes rhenium centers to be assessed across the series of isomeric compounds. The average through-space distance from the boron atoms of the two appended BODIPY groups to the central rhenium atom was determined to be 9.43 Å for Re(BB2)(CO)$_3$Cl, 8.39 Å for Re(BB3)(CO)$_3$Cl, and 5.56 Å for Re(BB4)(CO)$_3$Cl, as summarized in Table 2. Accordingly, the BODIPY substituents are positioned increasingly closer to the heavy metal as their points of attachment are changed from the 4,4′- to the 5,5′- to the 6,6′-positions on the 2,2′-bipyridine ligand.

The steady state photophysical properties of Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl were

DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX

studied and compared to those of the corresponding bpyBODIPY ligands in DMF. As shown in Figure 2 and summarized in Table 3, the absorption spectrum of each of the three rhenium complexes is dominated by a strong feature in the visible region with a maximum extinction coefficient of 79,400 M^{-1} cm^{-1} at 530 nm for Re(BB2)$(CO)_3$Cl, 52,700 M^{-1} cm^{-1} at 533 nm for Re(BB3)$(CO)_3$Cl and 88,500 M^{-1} cm^{-1} at 542 nm for Re(BB4)$(CO)_3$Cl. These absorption bands are attributed to the BODIPY-based $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition,[38] and similar features with maximum extinction coefficients of 86,000 M^{-1} cm^{-1} at 526 nm, 95,100 M^{-1} cm^{-1} at 528 nm, and 100,800 M^{-1} cm^{-1} at 526 nm are evident in the absorption profiles of the BB2, BB3, and BB4 ligands, respectively (Figure 2). While metalation weakly attenuates the characteristic BODIPY absorption features and shifts them toward slightly longer wavelengths, overall, the electronic spectra of the metal complexes are very similar to those of the corresponding bpyBODIPY ligands. This observation is notable, as Re(bpy)$(CO)_3$Cl complexes lacking additional pendant chromophores usually absorb poorly at wavelengths longer that ~450 nm.[56,57] We note that the BODIPY based adsorption observed for Re(BB3)$(CO)_3$Cl is reduced as compared to the other two isomeric complexes considered. This difference in absorptivity is presumably due to the differences in coupling between the BODIPY units when attached to the 5,5′-positions of the bipyridine ligand.

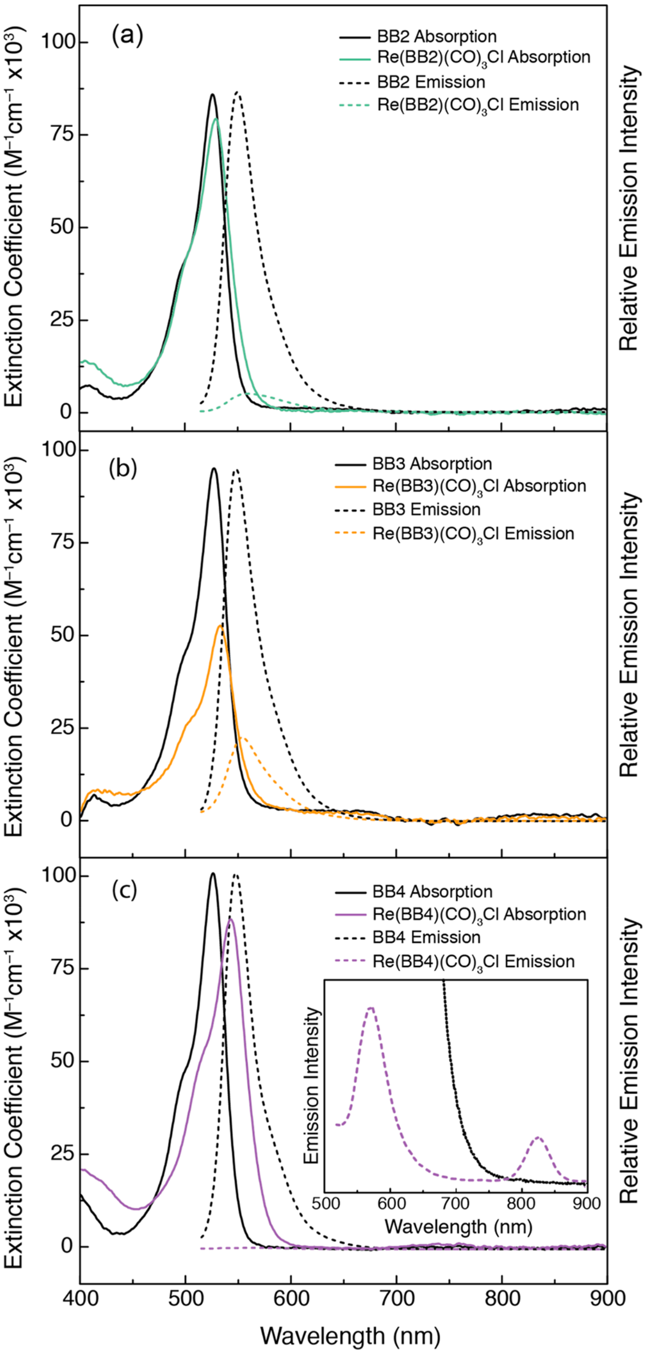


Figure 2. Electronic absorption spectra (solid lines) recorded under air and normalized emission spectra (dashed lines) recorded under a nitrogen atmosphere for (a) BB2 (black) and Re(BB2)$(CO)_3$Cl (green) in DMF, (b) BB3(black) in DMF containing 10% CH_2Cl_2 and Re(BB3)$(CO)_3$Cl(orange) in DMF, and (c) BB4 (black) and Re(BB4)$(CO)_3$Cl (purple) in DMF. All spectra were recorded at 298 K. Inset: Emission spectra of BB4 and Re(BB4)$(CO)_3$Cl rescaled to illustrate the weak emission features of the Re complex.

The room temperature emission spectra of BB2, BB3, BB4, Re(BB2)$(CO)_3$Cl, Re(BB3)$(CO)_3$Cl, and Re(BB4)$(CO)_3$Cl were collected from DMF solutions under a nitrogen atmosphere with λ_{exc} = 500 nm and are overlaid with the corresponding absorption spectra in Figure 2. In contrast to the minor differences observed in the absorption spectra between each free bpyBODPY ligand (i.e., BB2−BB4) and the corresponding Re complexes, incorporation of the BODIPY-based bpy ligands onto the rhenium tricarbonylchloride center results in dramatic changes to the indacenes' emission properties. For example, BB2 shows a single, intense emission feature centered at λ_{fl} = 550 nm, and similar features appear in the emission spectra of BB3 and BB4 centered at λ_{fl} = 548 nm. Table 3 lists the emission quantum yields determined for the bpyBODIPY ligands; BB2 and BB4 display Φ_{fl} values close to unity, and the quantum yield for BB3 ($\Phi_{fl} = 3.5 \times 10^{-1}$) is also relatively large. Accordingly, the three ligands exhibit the small Stokes shifts and high fluorescence quantum yields that are hallmarks of traditional BODIPY photophysics.[2,12] By contrast, each of the isomeric rhenium complexes emit at slightly longer wavelengths (λ_{fl} = 561 nm for Re(BB2)$(CO)_3$Cl; λ_{fl} = 553 nm for Re(BB3)$(CO)_3$Cl; and λ_{fl} = 564 nm for Re(BB4)$(CO)_3$Cl) and with considerably diminished intensity. The fluorescence quantum yields of Re(BB2)$(CO)_3$Cl and Re(BB3)$(CO)_3$Cl are $\Phi_{fl} = 1.4 \times 10^{-2}$ and $\Phi_{fl} = 1.3 \times 10^{-2}$, respectively, representing ~10−100 fold reductions in magnitude relative to the corresponding free bpyBODIPY ligands (i.e., BB2 and BB3). The fluorescence from Re(BB4)$(CO)_3$Cl, in which the BODIPY groups are held closest to the rhenium center is attenuated even further with $\Phi_{fl} = 1.3 \times 10^{-3}$. The decrease in fluorescence quantum yield observed when BB2 and BB3 are complexed to rhenium, which places the BODIPY fluorophores ~9.5 and 8.4 Å, respectively, from the metal center, coupled with the even lower Φ_{fl} obtained when the BODIPY units are brought within ~5.5 Å of the rhenium atom in Re(BB4)$(CO)_3$Cl, suggest that enhanced ISC to the triplet excited state is being promoted by the heavy rhenium atom. The rhenium mediated ISC to the triplet provides a competing process to the facile radiative relaxation of the BODIPY singlet excited states in each of the isomeric Re complexes.

Additional evidence of triplet state population in the isomeric rhenium complexes of Scheme 1 is garnered by observation of a second red-shifted feature in the emission spectrum recorded for Re(BB4)$(CO)_3$Cl. This long-wave-

DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX

Table 3. Photophysical Data Recorded for BB2, BB3, BB4, Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl[a]

	$\lambda_{\mathrm{max\ abs}}$/nm($\varepsilon \times 10^3$ M^{-1} cm^{-1})	λ_{fl}/nm(Φ_{fl})	λ_{ph}/nm(Φ_{ph})	Φ_Δ (%)
BB2	526 (86.0)	550 (~1)		
Re(BB2)(CO)$_3$Cl	530 (79.4)	561 (1.4×10^{-2})		1.7
BB3	528 (95.1)	548 (3.5×10^{-1})		
Re(BB3)(CO)$_3$Cl	533 (52.7)	553 (1.3×10^{-2})		1.6
BB4	526 (100.8)	548 (~1)		
Re(BB4)(CO)$_3$Cl	542 (88.5)	564 (1.3×10^{-3})	829 (1.6×10^{-4})	18.6

[a] Spectroscopic data for BB3 was recorded in 10% CH$_2$Cl$_2$ in DMF. All other data was recorded in DMF.

length band is centered at λ_{em} = 828 nm and has a quantum yield of $\Phi_{\mathrm{ph}} = 1.6 \times 10^{-4}$ (see Figure 2c, inset and Table 3). This long-wavelength signal was conspicuously absent when the emission spectrum of Re(BB4)(CO)$_3$Cl was measured under air, while the shorter-wavelength features observed for Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl at around 555−565 nm remain unperturbed (see Figure S5). Molecular oxygen in its triplet ground state (^{3}O$_2$) can engage in energy transfer with chromophores and metal complexes in triplet excited states to return the excited light-absorber to its ground state and is converted to singlet oxygen (^{1}O$_2$) in the process. Consequently, emission quenching as a result of exposure to air is often diagnostic of phosphorescence. Rhenium bipyridyltricarbonyl chloride complexes are often phosphorescent; however, emission from the ^{3}MLCT state is normally observed between 600−650 nm.[57,58] The spectral position of the emission feature of Re(BB4)(CO)$_3$Cl (~830 nm) is more consistent with emission from the BODIPY $^3\pi{-}\pi^*$ manifold, which has been previously observed at wavelengths longer than 700 nm.[15] Excitation spectra recorded for Re(BB4)(CO)$_3$Cl (Figure S6) while monitoring either the fluorescence (575 nm) or phosphorescence (828 nm) emission are consistent with the BODIPY absorbance profile (Figure 2), demonstrating that both the singlet and triplet emission of Re(BB4)(CO)$_3$Cl arise from the BODIPY moieties.

To confirm that the air-sensitivity of the long-wavelength emission feature of Re(BB4)(CO)$_3$Cl is a result of energy transfer to molecular oxygen and to investigate whether Re(BB2)(CO)$_3$Cl and Re(BB3)(CO)$_3$Cl also support triplet photochemistries and photosensitize the formation of ^{1}O$_2$, the three isomeric complexes of Scheme 1 were probed using the singlet oxygen trapping agent 1,3-diphenylisobenzofuran (DPBF)[46,47] in DMF and irradiated with λ_{ex} = 500 nm. Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl and Re(BB4)(CO)$_3$Cl all demonstrate an ability to produce ^{1}O$_2$, indicating that even the 4,4′- and 5,5′-substituted isomers undergo at least some ISC to the triplet excited state upon irradiation with 500 nm light. Furthermore, because most traditional *fac*-Re(bpy)(CO)$_3$Cl derivatives fail to absorb light longer than ~450 nm, Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl join a small group of such complexes capable of sensitizing the formation of ^{1}O$_2$ upon irradiation with light of $\lambda \geq 500$ nm.[11,33,40,41]

[Ru(bpy)$_3$]$^{2+}$ was used as an actinometer (Φ_Δ = 0.57 in DMF)[48] to determine the ^{1}O$_2$ quantum yields (Φ_Δ) for each of the isomeric Re complexes. The values of Φ_Δ for Re(BB2)(CO)$_3$Cl and Re(BB3)(CO)$_3$Cl (λ_{ex} = 500 nm) were found to be low and essentially equivalent (Φ_Δ = 1.7 and 1.6%, respectively). Re(BB4)(CO)$_3$Cl displayed a significantly higher quantum yield for ^{1}O$_2$ production of Φ_Δ = 18.6%. The enhanced efficiency with which Re(BB4)(CO)$_3$Cl acts as a ^{1}O$_2$ photosensitizer compared to the other two complexes of Scheme 1 is consistent with the spectroscopic observations/rationale presented above (vide supra); although the rhenium center promotes ISC due to enhanced spin−orbit coupling in all three Re complexes, the especially close proximities of the BODIPY moieties (~5.5 Å) to the heavy metal center as a result of their attachment at the 6,6′-positions of the bipyridyl backbone leads to much more effective population or longer lifetime of the triplet excited state for Re(BB4)(CO)$_3$Cl. As such, of the three isomeric Re complexes considered in this work, Re(BB4)(CO)$_3$Cl represents a platform that is most suitable for ^{1}O$_2$ sensitization and related triplet photochemical applications using visible excitation sources.

We emphasize that metal···BODIPY distance may not the only factor that ultimately controls ^{1}O$_2$ sensitization efficiency. While the series of isomeric rhenium complexes we present demonstrates how distal separation between the BODIPY light absorber and metal center can be correlated with intersystem crossing efficiency and ^{1}O$_2$ quantum yield, many other factors ultimately control the efficacy of these two processes. In particular, the strength of spin−orbit coupling, which promotes ISC to the triplet excited state is largely dependent on identity of the metal center.[31] Similarly, the manner by which the visible light absorber is attached to the metal center is also critical, as a rhenium bipyridine complex in which a BODIPY light absorber is tethered to a Re(bpy)(CO)$_3$Cl core via an alkyne linker shows Φ_Δ = 0.88.[59] Accordingly molecular topology is an important consideration in the construction of new complexes that support triplet photochemistry.

■ CONCLUSIONS AND FUTURE DIRECTIONS

Typical BODIPY chromophores strongly absorb visible light and are characterized by high photostability and large fluorescence quantum yields that can approach unity. Although these traits make them effective as fluorophores, standard BODIPYs are generally not suitable for applications requiring triplet photosensitizers due to their negligible rates of intersystem crossing. Conversely, *fac*-Re(bpy)(CO)$_3$Cl complexes readily populate the triplet excited state due to the presence of the heavy metal atom, but their utility as triplet photosensitizers is often limited by poor light absorption within the visible region (especially beyond 450 nm). In this study, we detailed an isomeric set of *fac*-Re(bpy)(CO)$_3$Cl homologues with pendant BODIPY chromophores attached at either the 4,4′-, 5,5′-, or 6,6′-positions of the 2,2-bipyridine ligand. We anticipated these complexes would combine the favorable photophysical properties of the two individual classes of light absorbers (i.e., BODIPY and *fac*-Re(bpy)(CO)$_3$Cl) to deliver robust and efficient triplet photosensitizers that strongly absorb visible light.

Re(BB2)(CO)$_3$Cl, Re(BB3)(CO)$_3$Cl, and Re(BB4)(CO)$_3$Cl form a series of three isomeric complexes in which the position of the BODIPY units is attached to the 2,2-bipyridine ligand at progressively shorter distances from the rhenium center. The Re(BB2)$(CO)_3$Cl complex (4,4′-BODIPY substituents), Re(BB3)$(CO)_3$Cl complex (5,5′-BODIPY substituents), and Re(BB4)$(CO)_3$Cl complex (6,6′-BODIPY substituents) position the light absorbing indacene moieties at ~9.4, 8.4, and 5.5 Å from the heavy Re center, respectively. Electronic absorption spectra recorded for each of these rhenium complexes show that the characteristic BODIPY absorption features are preserved and confirm that all three compounds are strong visible light absorbers. The high emission quantum yields typical of traditional BODIPY derivatives are not observed for any of the three rhenium complexes, however, and the decrease in fluorescence intensity becomes more extreme as the BODIPY moiety is placed closer to the rhenium center. Re(BB4)$(CO)_3$Cl, which has the shortest average through-space Re···BODIPY separation (~5.5 Å) of the three complexes studied, also exhibits weak phosphorescence. The quenched BODIPY fluorescence observed across the series of rhenium complexes and the phosphorescence of Re(BB4)$(CO)_3$Cl are consistent with the heavy rhenium atom enhancing the rate of ISC to deliver a triplet excited state using visible light excitation.

The ability of Re(BB2)$(CO)_3$Cl, Re(BB3)$(CO)_3$Cl, and Re(BB4)$(CO)_3$Cl to undergo ISC following excitation with light of λ = 450−550 nm makes these systems potentially suitable for triplet photochemistry applications. To this end, evaluation of these complexes' abilities to photosensitize the formation of $^1O_2$ upon irradiation with light of λ_{ex} = 500 nm demonstrates that each system can produce singlet oxygen using visible light. In keeping with the observed trends in singlet and triplet emission properties across the series of complexes, Re(BB4)$(CO)_3$Cl displays the highest quantum yield for $^1O_2$ production (Φ_Δ = 18.6%), consistent with this isomer presenting the shortest distal separation between the heavy Re center and ancillary BODIPY light absorbers.

When viewed in whole, the results presented herein demonstrate that appending chromophores at the 6,6′-positions of the 2,2′-bipyridine ligand of *fac*-Re(bpy)$(CO)_3$Cl complexes is an effective strategy to construct triplet photosensitizers that effectively harvest visible light. Additionally, the appreciable $^1O_2$ quantum yield realized with Re(BB4)$(CO)_3$Cl suggests that architectures that provide a similar topological arrangement of chromophore and heavy metal center may potentially be of use in photodynamic therapy or as photoCORMs[60−66] that can be used to administer CO inside cells upon visible light irradiation.[67,68] Although the absorbance profile of Re(BB4)$(CO)_3$Cl only extends out to about 585 nm, which falls just short of the therapeutic window (~600−900 nm) of red to near IR light that most deeply penetrates biological tissues, synthetic modification of the pendant BODIPY moieties or introduction of alternative chromophores that absorb longer wavelength light at the 6,6′-positions of the bipyridyl ligand of *fac*-Re(bpy)$(CO)_3$Cl may yield promising candidates for applications in photodynamic therapy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00102.

Crystallographic and spectroscopic data (PDF)

Accession Codes

CCDC 1879091−1879092 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by NSF CAREER Award CHE1352120 and NIH P20GM104316. NMR and other data were acquired at UD using instrumentation obtained with assistance from the NSF and NIH (NSF-MIR 0421224, NSF-MIR 1048367, NSF-CRIF MU CHE-0840401, and CHE-0541775, NIH P20 RR017716).

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DOI: 10.1021/acs.inorgchem.9b00102
Inorg. Chem. XXXX, XXX, XXX−XXX