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Energy Transfer to Ni-amine Complexes in Dual Catalytic, Light-driven C–N Cross-Coupling Reactions

Max Kudisch[†], Chern-Hooi Lim^{†‡}, Pall Thordarson^{§*}, and Garret M. Miyake^{†*}

[†]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States.

[‡]New Iridium LLC, Boulder, Colorado 80303, United States.

[§]School of Chemistry, The Australian Centre for Nanomedicine and the ARC Centre of Excellence in Convergent Bio-Nano Science & Technology, The University of New South Wales, Sydney, NSW 2052, Australia.

Supporting Information Placeholder

ABSTRACT: Dual catalytic light-driven cross coupling methodologies utilizing a Ni(II) salt with a photocatalyst (PC) have emerged as promising methodologies to forge aryl C–N bonds under mild conditions. The recent discovery that the PC can be omitted and the Ni(II) complex directly photoexcited suggests that the PC may perform energy transfer (EnT) to the Ni(II) complex, a mechanistic possibility that has recently been proposed in other systems across dual Ni photocatalysis. Here, we report the first studies in this field capable of distinguishing EnT from electron transfer (ET), and the results are consistent with Förster type EnT from the excited state [Ru(bpy)₃]Cl₂ PC to Ni-amine complexes. The structure and speciation of Ni-amine complexes that are the proposed EnT acceptors were elucidated by crystallography and spectroscopic binding studies. With the acceptors known, quantitative Förster theory was utilized to predict the ratio of quenching rate constants upon changing the PC, enabling selection of an organic phenoxazine PC that proved to be more effective in catalyzing C–N cross coupling reactions with a diverse selection of amines and aryl halides.

INTRODUCTION

Dual catalytic, light-driven C–N,¹⁻² C–O,³ C–C,⁴ C–P,⁵ and C–S⁶ cross-coupling methodologies utilizing a Ni(II) catalyst along with a photocatalyst (PC) have recently emerged as promising systems for synthetic chemistry with advantages over traditional Pd catalysis in terms of sustainability, cost, and mildness of reaction conditions.⁷ As such, mechanistic understanding of these reactions is essential in order to rationally design effective catalysts and unlock new reactivity.

In 2016, two dual catalytic, C-N cross-coupling systems were independently developed. In both cases, a wide range of amines and aryl halides were coupled under blue light irradiation employing the same Ni(II) precatalyst (i.e. NiBr₂·glyme) and Ir(III) PC (Fig 1A).¹⁻² The Ir(III) PC used was $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ which is a strong photo-oxidant. In contrast, our group recently found that organic PCs (e.g. dihydrophenazines⁸ and phenoxazines⁹) that are strong photo-reductants also functioned efficiently for dual catalytic C-N cross-coupling under similar conditions (Fig. 1B).¹⁰ These results suggest two potential scenarios. In one case, the Ni(II) precatalyst is sufficiently robust that C-N cross-coupling can occur through both reductive and oxidative electron transfer (ET) cycles utilizing a photo-oxidant and a photo-reductant, respectively. Alternatively, the Ni(II) precatalyst might be activated via energy transfer (EnT) from the PC; notably, the possibility of an EnT cycle has seldom been considered to date in C-N cross coupling, with only one reported example describing the coupling of sulfonamides with aryl halides.¹¹

Furthermore, we recently discovered that a PC can be omitted from the dual catalytic C–N cross-coupling system. Specifically, upon amine addition to a solution containing Ni(II) and aryl halide, we observed *in situ* formation of Ni-amine ACS Paragon Plus

complexes that can be directly photoexcited with 365 nm LEDs for the formation of the desired aryl C–N product (Fig. **1C**).¹² The existence of a direct Ni(II) irradiation route supports the



Figure 1. Reported C–N cross coupling systems utilizing (A) a photo-oxidant, (B) photo-reductants, or (C) no added PC. This work (D) on C–N bond formation promoted by energy transfer from a PC to the Ni-amine complex. In (A), the Ir PC used was $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, where $dF(CF_3)ppy = 2-(2,4-difluor-ophenyl)-5-(trifluoromethyl)pyridine and dtbbpy = 4,4'-ditertbutyl-2,2'-bipyridine. The organic PCs used in (B) were 3,7-di([1,1'-biphenyl]-4-yl)-10-(naphthalen-1-yl)-10H-phenoxazine and 5,10-di(naphthalen-2-yl)-5,10-dihydrophenazine. PC = photocatalyst; DMAc =$ *N*.*N*-dimethylacetamide. ArBr = aryl bromide.

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possibility of an EnT quenching mechanism as elucidated herein (Fig. **1D**). In the absence of an added PC, the Ni excited state is accessed directly through photo-excitation. Similarly, in a dual catalytic system, an analogous (but possibly distinct) Ni excited state can be accessed through EnT from a PC.

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This discovery is complemented by the finding that a PC can be omitted for dual catalytic C–O¹³ or C–C¹⁴ systems as the Ni complex can similarly be directly photoexcited, suggesting the possibility of an EnT pathway. More broadly, methods across photocatalysis which involve the direct excitation of transition metal complexes¹⁵⁻¹⁹ suggest systems which may be conducive to EnT upon addition of a PC. Importantly, EnT pathways have been proposed to be operative with Ni(II) or Cu(I) complexes serving as the acceptor in several systems across light-driven dual catalysis.²⁰⁻²³ However, to date, no study has utilized timeresolved techniques capable of distinguishing between electron and energy transfer to support that the excited state PC does indeed react via energy transfer in these systems.

Notably, obtaining spectroscopic evidence of an EnT pathway can unlock pivotal practical advances for a methodology as illustrated by the C–S cross coupling of alkenes/alkynes with disulfides in which replacement of the precious metal Ir(III) PC with an organic PC of higher triplet energy both accelerated the rate of product formation and alleviated sustainability concerns.²⁴ Furthermore, dual catalysis enables mild visible light irradiation while 365 nm light was required previously to directly excite the Ni complex. Thus, addition of a PC can enable use of UV-sensitive substrates.

Herein, we provide spectroscopic evidence in support of EnT from an excited state PC to Ni-amine complexes under conditions relevant for dual catalytic C-N cross-coupling driven by visible light (Fig. 1D). In particular, using nanosecond transient absorption (TA) spectroscopy, we observed the excited state of $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine) reacting with Ni-amine complexes formed in situ in C-N cross coupling reaction mixtures. The spectral data is consistent with an EnT pathway proceeding primarily through a Förster type mechanism, a result that is notably distinct from the Dexter type pathway typically invoked in the literature in catalytic cycles involving EnT that results in substrate sensitization.²⁵ Next, speciation studies elucidated the Ni-amine complexes that serve as EnT acceptors (or as light absorbers in the direct excitation method).¹² Finally, these mechanistic insights were utilized in conjunction with quantitative Förster theory to select an organic phenoxazine PC (the same shown in Fig 1C) that proved to be more effective than [Ru(bpy)₃]Cl₂ in the C–N coupling of 13 substrate pairs.

RESULTS AND DISCUSSION

[Ru(bpy)₃]Cl₂ was chosen as the PC for spectroscopic studies due to the extensive body of photophysical literature describing its spectral changes upon EnT or ET²⁶⁻²⁷ and the precedence for its use as a PC in related dual catalytic C–N cross coupling systems.^{1,28} Here, we initially confirmed that [Ru(bpy)₃]Cl₂ (PC 1) is an effective PC for C–N cross coupling involving 4-bromobenzotrifluoride and morpholine, achieving 88% conversion as measured by ¹⁹F NMR after 22 hours irradiation with a green (i.e. $\lambda_{max} = 523$ nm) LED (Fig. 2A). Importantly, no product was observed either in the absence of light or PC under these conditions, indicating that the direct excitation of the Ni complex was not a valid pathway, and thus the observed reactivity can be completely ascribed to the role of PC 1. The bimolecular quenching step (Fig. **2B**) between the excited state of PC **1** and the Ni-amine complex was further elucidated via nanosecond TA experiments. We note that the speciation of the Ni-amine complexes formed *in situ* is detailed later in this work. Laser irradiation at $\lambda_{pump} = 532$ nm in *N*,*N*-dimethylacetamide (DMAc) solvent containing PC **1** produced the long-lived (i.e. 870 ± 40 ns in DMAc, Fig. **S4**) metal-to-ligand charge-transfer (MLCT) triplet excited state characterized by an excited state absorption (ESA) feature at $\lambda = 370$ nm and a prominent ground state bleach (GSB) at $\lambda = 450$ nm (See SI, Fig. **S3**). The MLCT excited state lifetime measured here is consistent with previous reported values ranging from 800-1000 ns in polar, aprotic solvents.²⁹

We note that the MLCT state can be approximated as a formal reduction of one bpy ligand to the radical anion along with formal oxidation of the Ru center to Ru(III). As such, the ESA at $\lambda = 370$ nm has been previously assigned to a transition involving the radical anion of one bpy ligand on the basis of comparison to spectroelectrochemical measurement of the radical anion of free bpy and is thus diagnostic of MLCT state formation.²⁶ In addition, the GSB at $\lambda = 450$ nm was attributed to the presence of Ru(III) in the MLCT state which lacks a transition in this region. As such, quenching through ET is characterized by persistence of the ESA at $\lambda = 370$ nm in the case of reductive quenching since [Ru(bpy)₃]Cl₂ is formally reduced, while oxidative quenching leads to persistence of the GSB at λ = 450 nm.²⁷ However, in the case of EnT, both signals fully return to baseline since the ground state is recovered, and a decrease in the excited state lifetime is observed.²⁷

In a C–N cross-coupling reaction mixture consisting of the same molar ratio of components detailed in Fig. **2A**, we monitored excited state quenching of PC **1** using $\lambda_{pump} = 532$ nm, consistent with the green LED used in cross coupling reactions. We note that under these conditions, Ni-morpholine complexes are formed *in situ* (vide infra) and are active in quenching PC **1**'s excited state. Importantly, consistent with an EnT pathway, signals corresponding to PC **1**'s excited state return fully to the baseline at all wavelengths from $\lambda = 300-800$ nm (See SI, Fig. **S11**), indicative of recovery of the ground state of PC **1**. In particular, kinetic traces of PC **1** at both $\lambda_{probe} = 370$ nm and $\lambda_{probe} = 450$ nm returned fully to baseline (Fig. **2D**) and thus neither oxidized nor reduced PC **1** indicative of an ET mechanism was observed.

We further note that cyclic voltammetry experiments suggest that an ET quenching mechanism (either oxidative or reductive) is unlikely to occur (See SI, Section 4). Specifically, E^{0*} ([Ru(bpy)₃]*²⁺/[Ru(bpy)₃]³⁺) = -1.19 V vs. Fc/Fc⁺ (-0.74 V vs. SCE) as measured in this work in DMAc, while the first reduction of a Ni-morpholine complex occurs at $E_p = -1.71$ V vs. Fc/Fc⁺ (-1.26 V vs. SCE); thus, an oxidative quenching pathway is thermodynamically unfavorable. Similarly, reductive quenching is unlikely as E^{0*} ([Ru(bpy)₃]*²⁺/[Ru(bpy)₃]*) = 0.27 V vs. Fc/Fc⁺ (0.72 V vs. SCE), and the first oxidation of a Ni-morpholine complex occurs at $E_{p/2} \approx 0.48$ V vs. Fc/Fc⁺ (0.93 V vs. SCE).

Furthermore, the presence of Ni-morpholine complexes led to significant reduction in the excited state lifetime of PC 1 from 870 ± 40 ns to 360 ± 20 ns, while free morpholine did not lead to quenching (See SI, Fig. **S5-6**). Further control experiments showed that electron transfer products were not observed even under high laser power (See SI, Fig. **S9-10**). We note that subtraction of spectra did not yield any signals that could be

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Figure 2. (A) Dual catalytic C–N cross coupling control reactions. Reaction details: 0.4 mmol in aryl bromide in DMAc, 22 h reaction time. (B) Simplified catalytic cycle highlighting the focus of this work: the PC quenching step probed by transient absorption (TA) experiments and the speciation of the Ni catalyst. For the full proposed cycle, see Fig. S71. (C) Förster EnT efficiency approximated by overlap between PC 1 emission and Ni-amine complex absorption. (D) TA single wavelength kinetic traces acquired with $\lambda_{pump} = 532$ nm and $\lambda_{probe} = 450$ or 370 nm for PC 1 and a mixture (80:1 molar ratio of Ni:PC) containing PC 1 (0.1 mM) with Ni-morpholine complexes. (E) Stern-Volmer plot and extracted quenching rate constants. Quenchers are mixtures of Ni-amine complexes formed *in situ*. The species formed are determined later in this work. [‡]We note that debromination was not observed (See SI, Fig. S72); only unreacted aryl bromide was detected by ¹⁹F NMR. EnT = energy transfer. ET = electron transfer. k_q = quenching rate constant. k_0 = decay rate constant of PC 1. k_{obs} = observed decay rate constant in the presence of quencher. K_n = equilibrium binding constant. See SI, Section 2 for TA experimental details and spectra.

assigned to an excited state Ni complex, likely due to the excited state lifetime being too short to measure (See SI, Fig. **S12**); for example, a square planar Ni(II) aryl halide complex was observed to have a 4.2 ns lifetime,¹³ too short to be detectable with our setup. Overall, these results suggest that C–N cross-coupling reactivity is derived from excited Ni-amine complexes, which can be accessed through either EnT from a PC as in this work or through direct photo-excitation as in our previous work.¹² As such, we propose that mechanistic steps following the EnT step will mirror those we proposed previously (See SI, Fig. **S71** for the catalytic cycle).

Next, we observed that when using different types of amines and the Ni:amine ratio is held at 1:70, the same molar ratio used in C-N reactions, PC 1 was quenched to different degrees. To explore this relationship, a Stern-Volmer quenching study was performed with ratios of Ni:PC 1 increasing from 10:1 to 80:1. Notably, use of morpholine gives $k_q = (2.3 \pm 0.1)^* 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at $\lambda_{\text{probe}} = 450$ nm while propylamine quenched with a significantly reduced rate constant of $k_q = (3.5 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 2E), consistent with the lower cross-coupling performance of primary amines relative to secondary amines observed herein and previously under direct excitation with 365 nm irradiation.¹² Since the same PC was used throughout and none of the other reaction components were suitable ET or EnT quenchers (See SI, Fig. S5-8), this variation in k_q must arise from changes in electronic structure of the Ni-amine complex, and thus the speciation of the complexes formed must be determined.

Unlike typical organic substrates for which the contribution of Förster type EnT can be deduced to be minimal *a priori* on account of lacking significant spectral overlap with the excited PC,²⁷ Ni-amine complexes absorb significantly in the wavelength range of PC **1** phosphorescence (Fig. **2C**). Further, the overlap area for absorption of Ni-morpholine and Ni-propylamine mixtures appears correlated with the rate of quenching, supporting the hypothesis of Förster type EnT. However, the components of the quenching mixture must be elucidated in order to determine the identity and molar absorptivity of the EnT acceptor(s) to utilize Förster theory quantitatively in examining this hypothesis. Turning to classic reports³⁰⁻³⁵ describing monodentate primary and secondary amine ligands binding to Ni(II),



Figure 3. (A) Crystal structures of [NiBr₂(propylamine)₄], [NiBr₂(morpholine)₃], and [NiBr₂(quinuclidine)₂] shown at 50% thermal ellipsoids with hydrogens omitted for clarity. (B) Left axis: molar absorptivity of Ni-amine complexes in DMAc solution. Right axis: solid-state UV-visible absorption spectra of single crystals of complexes shown in (A). Inset: photographs of crystals of each complex at 40X magnification. (C) Selected bond distances and angles. See SI, Section 4 for further experimental details.

the available information is insufficient due to the lack of both crystallographic characterization and speciation studies in DMAc solution.

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To address this challenge, we first grew single crystals from concentrated Ni-amine mixtures, and analysis by single crystal X-ray diffraction (XRD) revealed for the first time that propylamine, morpholine, and quinuclidine form 6-, 5-, and 4-coordinate Ni(II) bromide complexes, respectively (Fig. 3A). Importantly, these complexes are likely the EnT acceptors, but it must be confirmed that the structures obtained in solid-state can serve as reasonable approximations of the geometry of complexes formed in situ in DMAc solution. To confirm that this assumption is reasonable, single crystals were examined through solid state UV-visible absorption spectroscopy (Fig. 3B; see SI, Section 8 for details). Qualitatively, similar absorption features are observed in solution as are found in the single crystals for all complexes, suggesting that structures obtained from XRD are not changed significantly upon DMAc solvation. Further, a control UV-vis experiment supports that the same complexes also exist in the full C-N coupling reaction mixtures (i.e. with aryl halide and PC added; See SI, Fig. S58). As such, some bands in the UV-vis spectra of the quenching mixtures used in TA experiments can now be assigned to specific complexes, namely [NiBr₂(morpholine)₃] (i.e. $\lambda_{max,1} = 427$ nm, $\lambda_{max,2}$ = ~740 nm) and [NiBr₂(propylamine)₄] ($\lambda_{max,1}$ = 379 nm, $\lambda_{max,2}$ $= \sim 620 \text{ nm}$).

Notably, the structure obtained for [NiBr₂(morpholine)₃] closely matches the density functional theory (DFT) optimized ground state geometry in DMAc solution described in our previous work,¹² supporting this assignment as well as the accuracy of our reported DFT calculations. Further, the formation of [NiBr₂(propylamine)₄] suggests the general trend that primary amines form 6-coordinate NiBr₂ complexes as supported by the isolation of [NiBr₂(aniline)₄] and [NiBr₂(cyclohexylamine)₄] (see SI, Fig. S48-49). Ni-amine complexes of the type characterized here are proposed to form across Ni catalysis in systems lacking exogenous ligand and employing amines in conjunction with NiBr₂, regardless of the NiBr₂ source used (e.g. NiBr₂·glyme, NiBr₂·3H₂O, or anhydrous NiBr₂, See SI, Fig. **S57**). The same complexes also form in the presence of all PCs used in C-N coupling reactions (Ir(III), Ru(II), and phenoxazine; See SI, Fig. S54-56), suggesting they may more broadly serve as mechanistically relevant species in many dual catalytic Ni(II) cross coupling systems.

Reported magnetic moment measurements of identical³⁴ or related³⁶⁻³⁸ Ni(II) complexes, as well as our previous DFT calculations, are consistent with $[NiBr_2(propylamine)_4]$, [NiBr₂(morpholine)₃] possessing triplet ground states in DMAc solution, suggesting that the d-d absorptions in the region of Förster overlap are of triplet to triplet nature. As such, Förster EnT is allowed based on the conservation of spin angular momenta³⁹ from the triplet excited state of PC **1** as the donor to form a triplet excited state Ni-amine complex. In order to employ Förster theory in modeling this excited state reactivity, the molar absorptivity of each acceptor complex overlapping with PC 1 emission must be known. However, UV-vis absorption peaks are observed in the Ni-amine solutions which remain to be assigned (e.g. the feature at ~550 nm in the Ni-morpholine DMAc solution, Fig. 2C) that might be viable EnT acceptors. We hypothesized that these features must originate from other Ni-amine complexes with fewer amine ligands, since a stepwise series of amine additions is required in the formation of the observed complexes from the NiBr₂·3H₂O precatalyst. These binding equilibria were directly observed through UV-vis isothermal titrations in which mixtures were analyzed with increasing ratios of the amine ligand:Ni.

UV-vis of these mixtures shows the evolution and demise of species with increasing numbers of amine ligands in the Nimorpholine mixture (Fig. **4A**). Initially, we note that the DMAc solvent forms the salt [Ni(DMAc)₆][NiBr₄] prior to amine addition (See SI, Fig. **S51**) and that multiple pathways exist for the first two amine additions (See SI, Fig. **S69-70**). However, all pathways converge to form the tetrahedral [NiBr₂(morpholine)₂] as the product of K₂, which can be assigned to the signal with $\lambda_{max,1} = \sim 550$ nm and $\lambda_{max,2} = \sim 850$ nm. To precisely determine the ratio of these species in the Ni-morpholine quenching mixture, the titration data was fitted to four variants (flavors)⁴⁰ of a 1:3 (metal:ligand or host:guest) binding model. This analysis was performed using a Matlab code based on the analytical



Figure 4. (A) Selected UV-vis traces from one replicate titration experiment showing equilibria between Ni-morpholine complexes. Arrows indicate features that rise or fall in the forward direction of each equilibrium. 70 eq. of amine ligand added (relative to Ni) corresponds to the exact conditions used in C–N cross coupling reactions. (B) Calculated average molar absorptivity (n = 3 replicates) of Ni-morpholine complexes. (C) Scheme defining stepwise series of equilibria upon addition of amine ligands. Equilibrium constants and molar absorptivities were extracted from titration data via a global analysis fitting procedure (See SI, Fig. S62-65 for details). ^aWe note that the NiBr₂ precatalyst forms a tetrabromonickelate salt in DMAc solution from which multiple amine addition pathways are possible for K₁ and K₂. ^bValues in kcal mol⁻¹. See SI for details.

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solution to the system of equations for the 1:3 equilibria, similar to that described in a NMR study on a 3:1 complexation of a bis-antimony receptor with halide anions.⁴¹ In our work we performed a global analysis⁴² using the UV-vis binding isotherms from $\lambda = 395$ -1200 nm (See SI, Section **7**, for details). Comparing how the various flavors of the 1:3 binding model fitted the data^{40, 43} clearly showed that the "full" 1:3 model which assumes i) cooperativity and ii) that the 1:1, 1:2, and 1:3 stepwise complexes have distinct spectra, gave a significantly better fit to the data than the other binding model (flavors) considered.

The full model allowed us not only to extract the stepwise equilibrium binding constants but also the molar absorptivity (Fig **4B**) of each species, giving $K_1 = (6 \pm 3) \times 10^3 \text{ M}^{-1}$, $K_2 = 130 \pm 30 \text{ M}^{-1}$, and $K_3 = 2.6 \pm 0.5 \text{ M}^{-1}$ with the corresponding free energies (after correcting for statistical factors) $\Delta G_1 = -2.0 \pm 0.3 \text{ kcal mol}^{-1}$, $\Delta G_2 = -1.3 \pm 0.1 \text{ kcal mol}^{-1}$, and $\Delta G_3 = -0.5 \pm 0.1 \text{ kcal mol}^{-1}$, respectively (Fig. **4C**). The increasing ΔG values indicate negative binding cooperativity, or less favorable addition of morpholine to Ni with each successive association. Notably, $\Delta G_3 = -0.5 \text{ kcal mol}^{-1}$ is reasonably close to the value of $\Delta G_3 = -1.1 \text{ kcal mol}^{-1}$ calculated by DFT in our previous work.¹²

Furthermore, we calculate that under C–N coupling conditions (i.e. 70:1 amine:Ni molar ratio), the Ni-morpholine quenching mixture consists of 73 % [NiBr₂(morpholine)₃], 27 % [NiBr₂(morpholine)₂], and < 0.3 % other complexes. As shown in Fig. 2C, both [NiBr₂(morpholine)₂] and [NiBr₂(morpholine)₃] demonstrate absorptions that overlap significantly with PC 1's emission. While [NiBr₂(morpholine)₂] shows the largest overlap, it is present in lower concentration. Interestingly, [NiBr₂(morpholine)₃] contains a morpholine bound in the apical position (Fig. 3A) with a significantly shortened Ni-N bond of 2.050(4) Å compared the other morpholines (i.e. 2.099(4) and 2.101(4); thus, this morpholine is the strongest donor and may facilitate the subsequent proposed mechanistic step, intramolecular ET to generate a Ni(I) center and a morpholino radical cation (See SI, Fig. S71 for our proposed mechanism). As such, both [NiBr₂(morpholine)₂] and [NiBr₂(morpholine)₃] show positive features for EnT catalysis and we conclude that both are the EnT acceptors.

With the acceptors and their respective molar absorptivities known, we turned to classical Förster theory in which the theoretical energy transfer rate constant, k_{EnT} , can be calculated as follows:²⁷

$$k_{EnT} = k_{r,D} \left(\frac{R_0}{R}\right)^6 where$$
 (Eq. 1)

$$R_0^{\ 6} = \frac{8.79 \times 10^{-25} \kappa^2 J}{\eta^4} \text{ and }$$
(Eq. 2)

$$J = \int_0^\infty \frac{F_D(\nu)\varepsilon_A(\nu)}{\nu^4} d\nu$$
 (Eq. 3)

In these equations, R is the donor-acceptor distance, R₀ is the critical Förster distance defined in Eq. 2, $k_{r,D}$ is the radiative decay constant of the donor in absence of acceptor, κ is the dipolar orientation factor, η is the refractive index of the solvent, and J is the spectral overlap integral defined in Eq. 3 which involves F_D , the area-normalized emission spectrum of the donor, and ε_A , the molar absorptivity of the acceptor as a function of frequency. In order to apply this equation to the reaction between excited state PC 1 and a Ni-amine complex, we needed to eliminate variables R and κ which are difficult to measure in solution with freely tumbling donors and acceptors.

Utilizing an approach similar to that first demonstrated in the study of a system involving intramolecular EnT from a Re

donor to a transition metal acceptor,⁴⁴⁻⁴⁵ an expression was derived (see SI, section **3** for details) to evaluate the ratio of quenching rate constants ($k_{EnT,1}/k_{EnT,2}$) as the donor, PC **1**, was held constant but the acceptor was changed, from the Ni-morpholine quenching mixture to the Ni-propylamine quenching mixture, according to the following equation:

$$\frac{k_{EnT,A1}}{k_{EnT,A2}} = \frac{J_1}{J_2}$$
 (Eq. 4)

Using Equation 4, the ratio for PC **1** was calculated as $k_{EnT,AI}/k_{EnT,A2} = 4.6$, which compares favorably with the experimental value of 6.5 obtained from the TA experiments described above (See SI, Table **S5**, for *J* integrals used in the calculation). This level of agreement compares very well with that obtained for similar calculations in the literature,⁴⁴ supporting our assignment of the EnT quenching step as a Förster type EnT process. Thus, based on equations **1-3**, it can be seen that selection of a PC with higher radiative rate constant $k_{r,D}$ and higher overlap integral *J* will result in a higher EnT rate.

As such, we hypothesized that changing the donor PC from PC 1 to the organic phenoxazine PC 2 would impart improved performance in C–N cross coupling reactions given that PC 2 covers increased spectral range in its emission compared to PC 1 (See SI, Fig. S33) and has a radiative rate constant reported⁴⁶ to be $4 \pm 1 \times 10^6$ s⁻¹ which is significantly higher than that of PC 1 (i.e. 7×10^4 s⁻¹).²⁹ First, we confirmed that PC 2 also reacts via EnT as opposed to ET through spectroscopic (See SI, Fig. S24-32) and electrochemical (See SI, Section 4) control experiments. To theoretically probe the hypothesis that PC 2 will increase the rate of EnT, a second equation was derived (See SI, Section 3) to predict the ratio of quenching rate constants as the PC is changed but the Ni-morpholine mixture is kept constant as the acceptor:

$$\frac{k_{EnT,D1}}{k_{EnT,D2}} = \frac{k_{r,D1}J_{D1}}{k_{r,D2}J_{D2}}$$
(Eq 5)

We note that the photophysics of PC 2 are more complicated than PC 1 in that both singlet and triplet excited states are populated. The triplet state is unlikely to react at a kinetically significant rate via a Förster type pathway given the extremely low phosphorescence radiative decay rates of organic PCs in solution, typically on the order of 10^{0} - 10^{3} s⁻¹.⁴⁷ Thus, the fluorescence spectrum and fluorescence radiative decay constant were used in conjunction with Eq. 5 to calculate the ratio of $k_{EnT,PC}$ $2:k_{EnT,PCI} = 20.4$, which is within a factor of 3 of the value of 12.7 determined experimentally from quenching studies (see above for PC 1 and SI, section 3 for PC 2). Agreement between these values suggests that the observed EnT occurs through primarily a Förster type pathway in the case of both PCs and with a much higher rate constant for PC 2 of $(2.9 \pm 0.2) * 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (See SI, Fig. S36) as compared to that for PC 1 of (2.3 ± 0.1) *10⁸ M⁻¹ s⁻¹.

With these results in hand, we compared the performance of PCs 1 and 2 in C–N cross coupling reactions (Fig. 5; see SI, section 9 for experimental details and product characterization). In order to directly compare the PCs, we chose to use the exact same conditions for all reactions. In particular, blue 457 nm light irradiation was chosen since PC 2 cannot absorb green light. Further, an irradiation time of 15 hours was chosen to allow for direct comparison with our previous work.¹² Control reactions confirmed that no product is formed in the absence of PC under blue irradiation (See SI, Table S9), and we further note that for PC 1 blue LED irradiation accesses the same



Figure 5. Scope of C-N coupling reactions using PC 1 and PC 2; PC 1 = [Ru(bpy)₃]Cl₂ and PC 2 = 3,7-di([1,1'-biphenyl]-4-yl)-10-(naphthalen-1-yl)-10*H*-phenoxazine. Yields were determined using ¹⁹F NMR for products containing fluorine. Isolated yields are reported in parentheses. X = Br unless otherwise indicated. ^a1 eq. KBr was used as an additive. ^b1.5 eq. of the amine was used with 1.5 eq. added quinuclidine. ^cAn aryl iodide was used. tr = trace product isolated. Reactions were performed with 0.4 mmol of aryl halide at room temperature. See SI, Section 9, for details and characterizations. The blue LED emission $\lambda_{max} = 457$ nm.

absorption band as green irradiation, forming the same lowest MLCT excited state that we propose reacts via EnT.

Under these conditions, the performance with PC **1** and morpholine is significantly worsened (e.g. 43% conversion vs. 88% in Fig. **2A**), and this can be attributed to a combination of factors, namely the lower catalyst loading which leads to a loss of 23% conversion (See SI, Table **S9**), the lower luminous flux of the blue LED as compared with the green LED (1:4.4, blue:green; See SI, Table **S1**), and the inner-filter effect resulting from increased unproductive absorption of blue vs. green excitation light by the Ni-morpholine complexes (3:1, blue:green; See SI, Fig. **S33**). Despite these worsened conditions, PC **1** is effective for coupling of secondary aliphatic amines with 4-bromobenzotrifluoride, highlighted by coupling of unprotected piperazine (51%) and indoline (73%), nitrogen heterocycles that are among those most frequently used in medicinal chemistry.⁴⁸

On the other hand, PC **2** is more broadly effective, achieving higher yields than PC **1** with almost all substrates (Fig. **5**). Notably, PC **2** is effective in coupling difficult aliphatic (e.g. propylamine, 50%) and aromatic primary amines such as 4fluoroaniline (55%) and 3-aminopyridine (33%) with 4-bromobenzotrifluoride while PC **1** is ineffective, achieving only trace product formation with primary aliphatic amines. PC **2**'s emission extends ~100 nm further into the blue than PC **1**, overlapping an absorption band of [NiBr₂(propylamine)₄] that PC **1** cannot access (See SI, Fig. **S33**). Since the efficiency of EnT has been shown to depend on specific electronic transitions,⁴⁵ we hypothesize that this blue-shifted band may facilitate EnT and thus might explain PC **2**'s increased performance.

With aromatic amines (e.g. 4-fluoroaniline), quinuclidine was employed as a base additive based on a beneficial effect on yield observed in our previous work.¹² The effect of quinuclidine is likely due at least in part to its role in controlling the speciation of the Ni catalyst; investigation by UV-vis revealed

that quinuclidine binds more strongly than aniline to NiBr₂ (See SI, Fig. S59), forming [NiBr₂(quinuclidine)₂] which has good overlap between its absorption and PC 2's emission (See SI, Fig. S33). In addition, the use of 1 equivalent of KBr as an additive improved the performance of some amines such as propylamine and unprotected piperazine (14% and 26% increase, respectively; see SI, table S10 and following supplemental discussion). With propylamine, we hypothesize that KBr improves reactivity by inhibiting the speciation equilibria as observed by UV-vis (See SI, Fig S60-61); this inhibition increases the concentration of [NiBr₂(propylamine)₄.

With regard to the aryl halide coupling partner, PC **2** successfully promotes coupling of morpholine with aryl halides containing electron-withdrawing groups (EWGs, e.g. 4-bromobenzotrifluoride, 92%) as well as electron-donating groups (EDGs, e.g. 4-bromoanisole, 31%). Notably, a heterocyclic aryl bromide, 3-bromopyridine, could be coupled in good yield (58%). In addition, the difficult *ortho*-substituted aryl halide, 2-iodotoluene could be coupled with morpholine in moderate yield (27%), constituting the first example of C–N bond formation with this substrate pair in light-driven Ni catalysis.

Trends in reactivity for both PCs mirror those observed in our previous work with secondary > primary > primary aromatic amines in terms of yield. Similarly, aryl halides containing EWGs gave greater yields than those containing EDGs. Overall, the similarity in these trends across both PCs to trends obtained in our previous work¹² support that a similar Ni-amine excited state intermediate forms in both cases that can be accessed either via EnT from a PC under visible light or via direct excitation under 365 nm irradiation.

CONCLUSION

In sum, spectroscopic evidence supports an EnT quenching mechanism in dual catalytic C-N cross coupling that proceeds via a Förster type pathway. In addition, the EnT acceptors have been identified via single crystal XRD and spectroscopic binding studies as a series of [Ni(II)Br₂(amine)_x] complexes formed in situ in C-N cross coupling reaction mixtures. These complexes are proposed to form more broadly across catalytic systems utilizing NiBr₂ and amines and thus constitute mechanistically-significant intermediates across Ni catalysis. Elucidating the speciation enabled the use of quantitative Förster theory to calculate EnT rate constant ratios that agreed with values determined experimentally from spectroscopic studies. Employment of this mechanistic knowledge through selection of phenoxazine PC 2 led to increased performance relative to [Ru(bpy)₃]Cl₂ PC 1 in catalyzing C–N bond formation between diverse amines and aryl halides under mild conditions. Ultimately, future work utilizing quantitative Förster theory has the potential to both predict and discover new reactivity in energy transfer systems across light-driven Ni catalysis.

ASSOCIATED CONTENT

Supporting Information. The supporting information consists of transient absorption spectroscopic data, cyclic voltammetry data, derivations of equations using Förster theory, emission spectroscopy, single crystal X-ray crystallography procedures (for details, see the attached .cif files), UV-visible spectroscopy and data analysis, a proposed catalytic cycle, and details regarding C–N cross coupling reaction procedures and product characterization. This

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material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*p.thordarson@unsw.edu.au

*garret.miyake@colostate.edu

Notes

The authors declare no competing financial interests.

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ABBREVIATIONS

PC, photocatalyst; TA, transient absorption; ET, electron transfer; EnT, energy transfer; k_q , quenching rate constant.

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