

Controlling substrate selectivity in cross coupling with light

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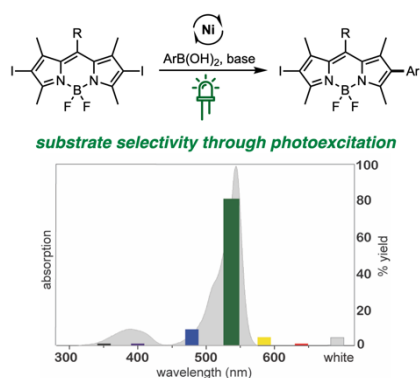
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Abstract: Substrate-selective reactions typically rely on differences in the ground-state reactivity of substrates or their interactions with supramolecular catalyst scaffolds. Here, we show that a photoinduced cross-coupling reaction provides high substrate selectivity that cannot be achieved under thermal conditions. We report a visible-light-promoted, Ni-catalyzed Suzuki–Miyaura cross-coupling of diiodo-boron-dipyrrromethene (BODIPY) chromophores displaying high selectivity for mono-arylation, enabling the efficient sequential synthesis of unsymmetrically substituted BODIPYs. Substrate selectivity is maintained in mixtures containing non-absorbing aryl iodides or halogenated BODIPYs with similar absorption. This work demonstrates the potential of substrate photoexcitation-based reaction mechanisms for the selective functionalization of organic chromophores with desirable excited-state properties.

Introduction

The selective activation of C–X bonds in polyhalogenated aromatic and heteroaromatic substrates enables the efficient synthesis of unsymmetrically substituted poly(hetero)aromatics, including pharmaceuticals,¹ sequence-defined oligo(phenylenes),^{2–4} and push-pull chromophores.^{5–8} Selectivity is most often based on intrinsic reactivity differences between sites on the (hetero)aromatic scaffold

(Figure 1a)^{9–12} or between C–X bonds.^{13,14} In Pd and Ni-catalyzed cross-coupling reactions of substrates with multiple types of (pseudo)halide, the identity of the ligand can be used to direct chemoselectivity (Figure 1b).^{15–19}

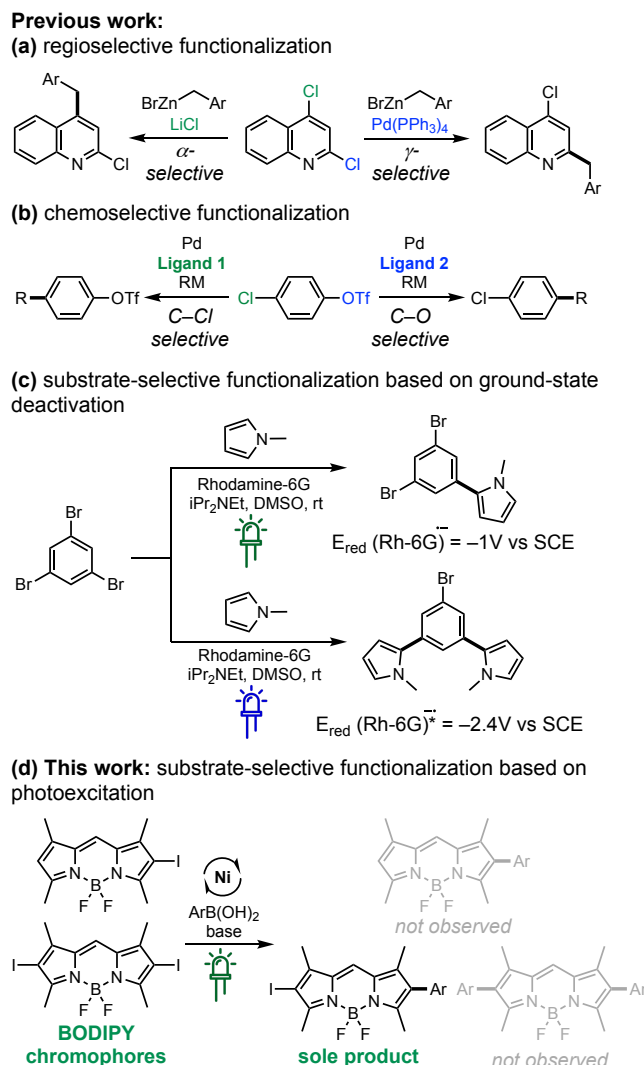


Figure 1. Previous work has demonstrated conditions for (a) regioselective (ref. 9) and (b) chemoselective (refs. 15–19) coupling. (c) Monoselective coupling (ref. 28) is an example of substrate selectivity based on ground-state deactivation of the product. (d) In this work, we show that a photoinduced reaction displays unique substrate selectivity, which can be tuned by the photophysical properties of the substrate.

For substrates with multiple identical C–X bonds, however, distinguishing between the starting material and the product requires *substrate* selectivity rather than regio- or chemoselectivity (Figure 1c).²⁰ Typically, monoselectivity can only be achieved if the first substitution significantly deactivates the remaining C–X bonds through steric or electronic effects,^{21–28} changes in solubility,²⁹ or selective crystallization of the product.³⁰ Substrate selectivity thus originates in differences between ground-state physical and chemical properties. In principle, however, it should be possible to observe distinct selectivity based on the *excited*-state properties of substrates in light-controlled reactions. Here, we

report a visible-light-promoted cross coupling of halogenated boron-dipyrromethene (BODIPY) chromophores displaying high substrate selectivity that cannot be achieved under thermal conditions (**Figure 1d**).

BODIPYs are ubiquitous fluorophores in materials science and bioimaging due to large absorption coefficients, narrow emission profiles, high photoluminescence quantum yields, and good photostability.³¹ Derivatives that access the triplet state are additionally useful for photodynamic therapy³² and triplet-triplet annihilation upconversion.^{33,34} The photophysical and chemical properties of BODIPYs are highly tunable using modifications to the core.^{31,35–37} Furthermore, BODIPY derivatives have been used as photosensitizers and photocatalysts for transformations including oxidations,^{38,39} oxidative couplings,^{40–42} cross coupling,^{43–45} atom transfer radical addition,⁴⁶ and photopolymerization.^{47,48}

We envisioned that the same excited-state properties that make halogenated BODIPY chromophores effective photoredox catalysts—high triplet yields, long excited-state lifetimes, and high excited-state redox potentials—could be used to engage a ground-state transition-metal catalyst in a photoinduced cross-coupling. This approach is inspired by metallaphotoredox catalysis but exploits the excited state of the substrate rather than that of a photocatalyst.⁴⁹ Such a photoinduced cross-coupling reaction could exhibit selectivity in the presence of multiple substrates with similar sterics and electronics but distinct excited-state properties. While reactions are typically developed with the goal of broad scope, substrate-selective catalysis mimics enzymatic catalysis, which can occur selectively in the presence of many potential substrates. Light provides an alternative discrimination mechanism to the supramolecular recognition used in other substrate-selective catalysis.^{20,50–53}

We have developed a mild and selective photoinduced Ni-catalyzed cross-coupling of diiodo-BODIPY chromophores. These conditions are not only selective for the BODIPY substrate in the presence of aryl halides that do not absorb visible light, but are also highly selective for mono *vs.* bis addition. Mono-substituted products may be further elaborated by thermal cross-coupling reactions to yield donor-acceptor BODIPYs. Preliminary mechanistic studies to uncover the origin of substrate selectivity are described. We show that a mixture of halogenated BODIPYs with similar absorption spectra undergo selective photoinduced cross-coupling, in contrast to a thermal reaction that delivers a complex mixture of products. These results suggest that substrate photoexcitation can confer unique selectivity on cross-coupling reactions.

Results and Discussion

Reaction development

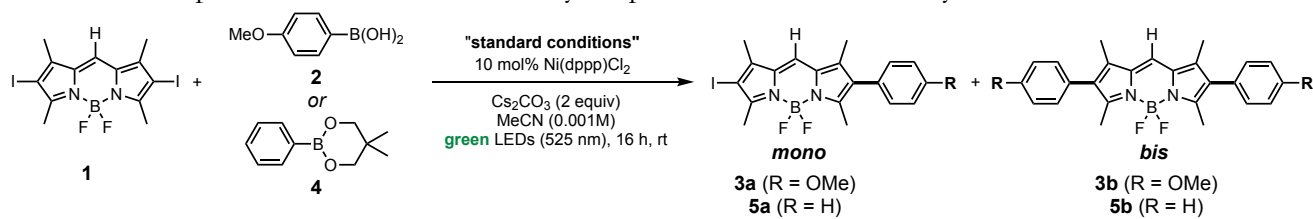
We turned our initial focus to halogenated BODIPY chromophores as substrates for the photoinduced cross-coupling reaction. We hypothesized that the identity of the halogen would strongly affect cross-coupling reactivity by virtue of its effect on C–X bond strength, redox potential, and internal heavy-atom effect.^{54–58} Therefore, we began our reaction development with diiodo-BODIPY chromophore **1**, a known photosensitizer⁵⁶ and photocatalyst⁵⁹ that absorbs green light.

We found promising reactivity with Ni catalysts, which are commonly employed in metallophotoredox reactions due to their propensity for single-electron chemistry.⁶⁰ Multiple mechanisms have been proposed for the role of light in these reactions, including oxidation-state modulation by a photoredox catalyst,^{61–64} direct photoexcitation of Ni(II) complexes,⁶⁵ and recovery of inactive off-cycle Ni(II) species by photoreduction.^{66,67}

Under the optimized conditions, **1** underwent Suzuki–Miyaura cross-coupling at room temperature under irradiation with green light in the presence of Ni(dppp)Cl₂ precatalyst. Even though a vast excess 4-methoxyphenyl boronic acid (**2**) was used (10 equivalents), mono-substituted BODIPY **3a** was selectively formed in 82% yield (**Table 1**, entry 1). No bis-substituted product **3b** could be detected in the crude reaction mixture by LCMS or ¹H NMR. This result was surprising given the precedent for diiodoarenes to favor bis-substitution under thermal cross-coupling conditions.^{21,25} Other monoarylation methods based on ground-state selectivity typically use 1–1.5 equiv of the coupling partner to discourage further reaction. Consistent with the absence of ground-state selectivity, traditional thermal Pd-catalyzed conditions (entry 2) favor bis-substituted product **3b**.

To confirm the role of light and catalyst for the photoinduced conditions, we performed several control reactions. No product was observed in the absence of Ni catalyst (entry 3), and 10% yield was obtained when the reaction was conducted in the dark (entry 4). Under thermal conditions (78 °C) in the dark, both **3a** and **3b** were observed in low yield and in nearly equal quantities (entry 5), suggesting that the photoinduced reaction achieves selectivity through a distinct mechanism. Intriguingly, substituting Ni(dppp)Cl₂ with Pd(OAc)₂/dppp under the optimal photoinduced conditions also delivered **3a** as the major product, albeit with lower yield and selectivity, suggesting that the mechanism governing monoselectivity could be general for different transition-metal catalysts (SI, Table S3).

Table 1. Optimization of the nickel-catalyzed photoinduced Suzuki–Miyaura reaction.



Entry	Nucleophile	Deviation from “standard conditions” ^[a]	Conversion (%)	Yield (%) ^[b]	mono:bis
1	2	None (Condition A)	100	82	>15:1
2	2	10% Pd(PPh ₃) ₄ , Na ₂ CO ₃ , dioxane-H ₂ O, 100 °C, no light	89	57	1:8
3	2	no Ni(dppp)Cl ₂	12	<5	-
4	2	no light	26	10	>15:1
5	2	78 °C, no light ^c	49	14	1:1.3
6	2	10 mol% Ni(COD) ₂ , 12 mol% of (PCy ₂) ₂ ethane, toluene-dioxane (Condition B)	97	61	12:1
7	Phenylboronic acid	none (Condition A)	36	17	>15:1
8	4	Condition B	78	63	>15:1
9	4	no Ni(COD) ₂ or no ligand	15–20	<5	-
10	4	no light	26	11	>15:1

[a] All data represent the average of two experiments. Under the standard conditions, the reaction was performed on a 0.004 mmol scale. Irradiation was provided by green LEDs using fan cooling to maintain a

temperature of <30 °C. See SI for details. [b] Conversion, yield, and ratio of mono to bis products were determined by LCMS using Erythrosine-B as external standard. See SI for details. [c] Reaction was performed in a hood isolated from light exposure with blackout curtains, using a stir plate enclosed in an opaque cardboard box.

When we sought to expand the nucleophile scope to electron-neutral boronic acids, disappointingly, the standard conditions (A) delivered low yields of cross-coupled product (entry 7). Therefore, the catalyst, ligand, solvent, and nucleophile were re-evaluated. We found that a combination of Ni(COD)₂ and (PCy₂)₂ethane ligand in a mixed solvent of toluene and dioxane, using the neopentyl glycol ester **4**, yields the desired phenyl-substituted BODIPY chromophore **5a** in 63% yield with high chemoselectivity (entry 8, Condition B). Other bisphosphine ligands such as dppe and dppp also provide good yields (SI, Table S6). We repeated the key control reactions using these modified conditions and again saw no product in the absence of catalyst and 11% yield in the absence of light (entries 9 and 10), consistent with a Ni-catalyzed, light-promoted reaction. Condition B is also applicable to electron-rich boronic acids, albeit with slightly lower yield and selectivity (entry 6).

Green LEDs (centered at 525 nm, FWHM 30 nm; SI, Figures S9-S13) correspond to the substrate's maximum absorbance at 531 nm. To test wavelength dependence, we performed the reaction with LEDs ranging from UV (350 nm) to red (626 nm). As expected based on the absorption spectrum of **1**, under both Condition A and B, green LEDs yielded the desired product in the highest yield. Identical reactions with UV, violet, and red LEDs resulted in low conversions with no desired product, and blue, yellow, and white⁶⁸ LEDs provided low yields of product (**Figure 2**). The sensitivity of this reaction to the color of light further suggests that a thermal reaction is not responsible for catalysis. Other components of the reaction, such as the boronic acid/ester and the Ni precatalyst, do not absorb green light, also supporting the hypothesis that the BODIPY substrate or derivative thereof is involved in the light-dependent step.

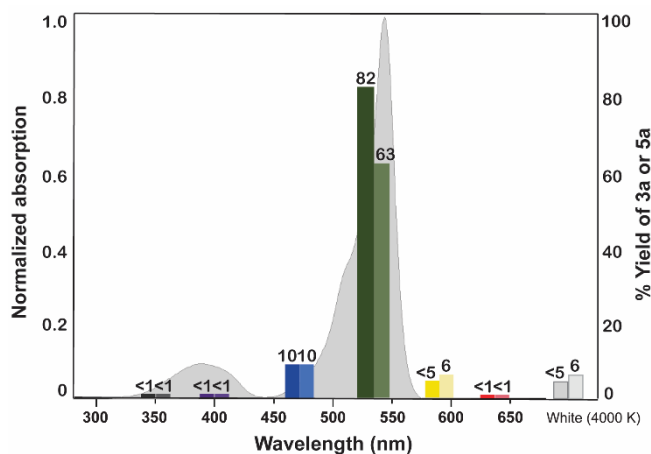


Figure 2. Wavelength screen for the reaction between BODIPY **1** and boronic acid **2** under Condition A (dark bars), or boronic ester **4** under Condition B (faded bars). The normalized UV-Vis absorption spectrum of **1** is superimposed in the background. See SI for details.

Substrate scope

Based on our optimization studies in **Table 1**, we next explored the scope of the photoinduced cross-coupling reaction with respect to boronic acid/ester coupling partner. On preparative scale, it was possible to increase the concentration to 0.01 M without sacrificing yield or selectivity (see SI,

Tables S2 and S5 for details). Using Condition A, electron-rich aromatic, heteroaromatic, and vinyl boronic acids provided the mono-functionalized products in 30–80% isolated yield (**Figure 3**). Minor bis-substituted products were only observed in the crude reaction mixture when using 5-membered heteroaromatic boronic acids (**13** and **14**, ~6-8:1). Azide- and alkyne-substituted boronic acids furnished BODIPYs **16** and **17** with handles for conjugation by Cu-catalyzed click chemistry. Under Condition B, electron-neutral and -poor boronic esters provided mono-substituted products in 32–63% isolated yield, accompanied by unreacted starting material (8–25%); the modest reactivity of electron-poor nucleophiles remains a limitation of this method.

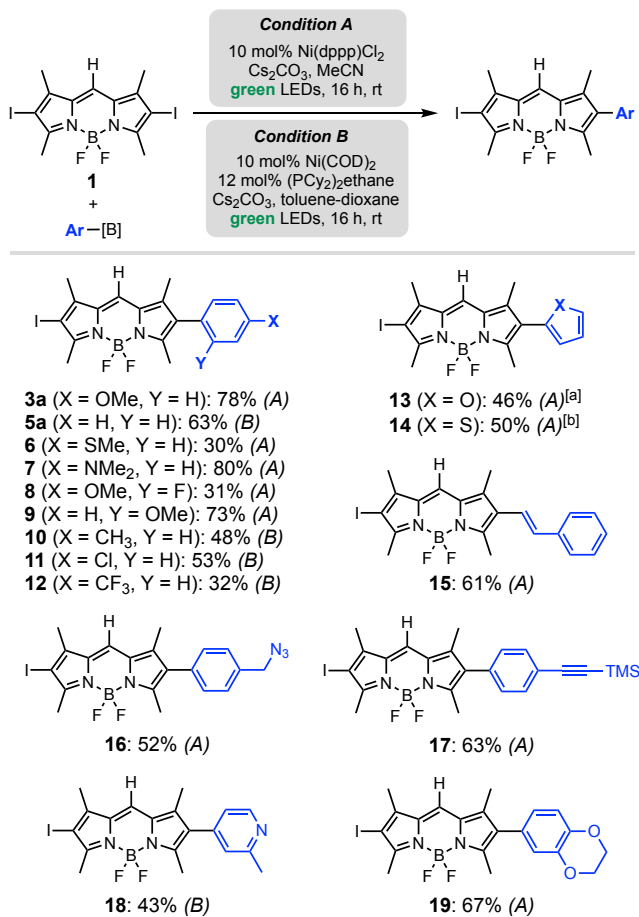
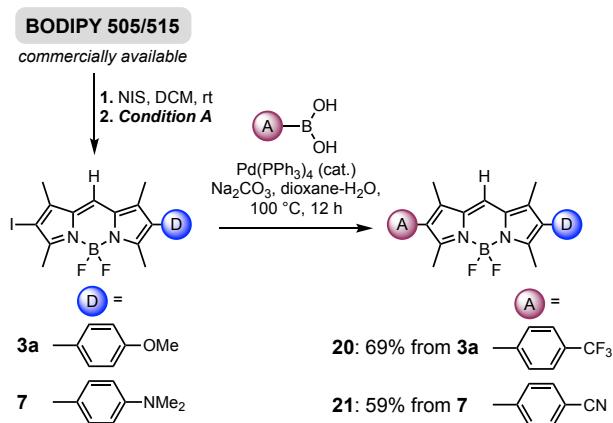


Figure 3. Nucleophile scope for the photoinduced Suzuki–Miyaura reaction. Reactions were performed on a 0.024 mmol scale at 0.01 M using Condition A or B. Products were purified by flash column chromatography. [a] The crude reaction mixture was a 6.7:1 ratio of mono:bis products. [b] The crude reaction mixture was a 8.2:1 ratio of mono:bis products.

In our light-dependent reaction, the mono-substituted products are deactivated towards the photoinduced cross-coupling, but not to thermal conditions. Thus, the remaining C–I bond can be engaged in thermal cross-coupling reactions to deliver unsymmetrically substituted BODIPY chromophores, which are found in dyads and triads designed for light harvesting, nonlinear optics, and bioconjugation.^{6,36,69–72} To highlight the utility of this strategy, we applied our protocol to the construction of BODIPYs containing electron donors and acceptors at the 2 and 6 positions. The conventional route to prepare such donor-acceptor BODIPYs relies on sequential mono-

halogenation, cross-coupling, halogenation, and cross-coupling, rendering this stepwise sequence inefficient (10% overall yield, see SI). In contrast, the photoinduced cross-coupling of diiodo-BODIPY **1** with an electron-rich (donor) arylboronic acid selectively delivers the mono-substituted product (**3a** or **7**) in high yield. This intermediate can be directly elaborated with an electron-poor (acceptor) boronic acid using traditional thermal, Pd-catalyzed cross-coupling conditions (**Scheme 1**). This route was used to prepare donor-acceptor BODIPYs **20** and **21** in 39–46% overall yield over 3 steps from the commercial laser dye BODIPY 505/515 (CAS 21658-70-8). Thus, the photoinduced cross-coupling protocol improves synthetic access to unsymmetrically substituted BODIPYs for materials-science applications.



Scheme 1. Synthesis of unsymmetrical BODIPY chromophores by photoinduced cross-coupling.

Next, we explored the scope of this cross-coupling with respect to the BODIPY substrate (**Table 3**). Diiodo-BODIPYs containing methyl, phenyl, or *para*-substituted aryl groups at the *meso* position all provided the mono-substituted products in 34–72% yield, using Condition A for electron-rich boronic acids (**22**, **24**, **26**) and Condition B for electron-neutral and -poor boronic esters (**23**, **25**). Notably, placing a sterically hindered mesityl substituent at the *meso* position (BODIPY **28**) altered the selectivity of the photoinduced cross-coupling. Under the standard conditions (16 h), exclusively bis-substituted product **29b** was observed and isolated in 72% yield. By running the reaction to incomplete conversion (5 h), we could obtain a 1:2 ratio of mono- to bis-substituted products in high yield and isolate pure **29a** in 32% yield. Therefore, mesityl-BODIPY **28** continues to react after the initial mono-substitution, unlike the other chromophores studied. Bis-substitution was also observed for the reaction of **28** with other boronic acids and esters under Conditions A and B (**30**, **31**). Neither a dibromo-BODIPY (**32**) nor a monoiodo-BODIPY (**33**) substrate underwent cross-coupling under the photoinduced conditions.

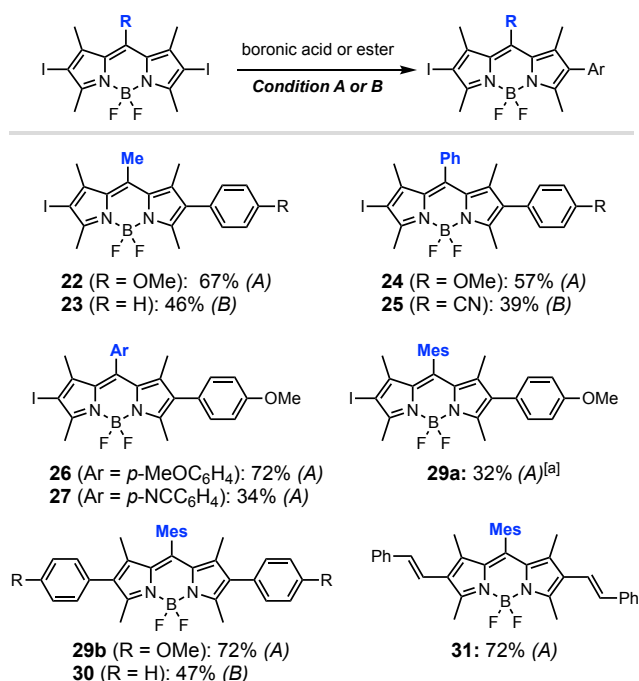
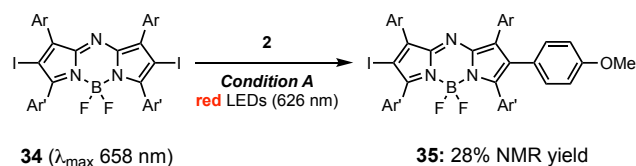


Figure 4. BODIPY scope for the photoinduced Suzuki–Miyaura reaction. Reactions were performed on a 0.024 mmol scale at 0.01 M using Condition A or B. Products were purified by flash column chromatography. ^[a]The reaction was stopped after 5 h.

Finally, we sought to determine whether chromophores with red-shifted absorption can undergo photoinduced cross-coupling with lower-energy light. Aza-BODIPYs are red-shifted relative to BODIPYs due to the electronegative N atom lowering the LUMO energy.⁷³ This effect, in combination with electron-rich aryl substituents, results in chromophores that absorb in the red to near-IR ranges.^{74,75} Halogenated aza-BODIPYs have been used as photosensitizers for singlet oxygen generation^{76,77} and photoredox catalysts for radical polymerization.⁴⁷ We found that aza-BODIPY **34** (λ_{\max} = 658 nm) underwent red-light-promoted Suzuki–Miyaura cross-coupling to deliver mono-substituted product **35** in 28% yield (**Scheme 2**). Future work will include the optimization of photoinduced cross-coupling conditions for these red-shifted substrates.

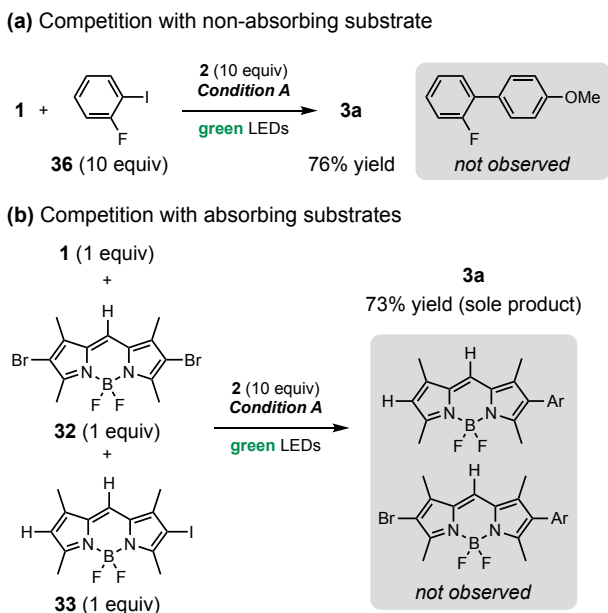


Scheme 2. Cross-coupling of aza-BODIPY with red light. Ar = 3,4,5-trimethoxybenzene; Ar' = 4-*t*BuPh.

Selectivity of the photoinduced reaction in competition experiments

The monoselectivity of the photoinduced reaction, with the exception of mesityl-BODIPY **28**, suggests that high substrate selectivity should also be observed for mixtures of substrates that would react similarly under thermal conditions. First, we examined the substrate selectivity of the photoinduced cross-coupling in the presence of a simple aryl halide, 2-fluoroiodobenzene (**36**), which does not absorb past 300 nm (SI, Figure S24). While **36** undergoes efficient Suzuki–Miyaura cross-coupling under thermal conditions with various Pd catalysts,⁷⁸ in a competition experiment between **1**

and **36** (1:10 molar ratio) under Condition A, we observed exclusive formation of **3a** arising from mono-arylation of **1** (**Scheme 3a**). By ^{19}F NMR, we observed neither conversion of **36** nor formation of the expected biphenyl product (SI, Figure S25).



Scheme 3. Competition experiments demonstrating substrate selectivity. (a) Competition between BODIPY **1** and 2-fluoriodobenzene (**36**). (b) Competition between BODIPYs with different halogenation. Conversions and yields were determined by ^1H NMR using dibromomethane as external standard; the absence of products was confirmed by ^1H NMR and HRMS with comparison to an authentic standard.

Next, we tested the substrate selectivity in the presence of multiple BODIPYs with similar absorption. A 1:1:1 mixture of **1**, **32**, and **33** was subjected to Condition A with excess arylboronic acid (**Scheme 3b**). Again, only the monosubstituted product **3a** derived from **1** could be observed by ^1H NMR and high-resolution mass spectrometry; **32** and **33** were recovered unreacted (SI, Figures S26-29). Under standard thermal Pd-catalyzed conditions, a complex mixture of products arising from **1**, **32**, and **33** is observed (SI, Figure S30).

These competition experiments demonstrate that selectivity is maintained in mixtures of competent substrates with other aryl halides, including chromophores with similar absorption characteristics. This substrate selectivity is not observed under thermal cross-coupling conditions and is therefore proposed to arise from the photoinduced cross-coupling mechanism. Furthermore, the selectivity suggests that **1** does not act as photoredox catalyst or photosensitizer to promote the reaction of other substrates. To better understand the selectivity of the photoinduced cross-coupling reaction, we probed the nature of the light dependence and the photophysical and photochemical properties of the substrates in greater detail.

Preliminary mechanistic studies

Figure 2 shows that the optimal wavelengths of the photoinduced cross-coupling correspond to the absorption of the BODIPY substrate. We sought to establish whether the reaction is photoinitiated or photocontrolled. If the reaction is photoinitiated, product formation should

continue in the dark after a period of initial irradiation. We monitored the conversion of **1** under Condition A as a function of time during alternating green irradiation and dark. During the periods with green irradiation, we saw significant conversion of **1** to mono-substituted product **3a**. During the dark periods, we continued to see conversion of **1** but minor formation of **3a** (<5% yield in 6 hours), consistent with the unproductive background decomposition that occurs in the dark (Table 1, entry 4). The difference in the rate of product formation between the irradiated and dark periods suggests that some thermal background reaction can occur in the dark, representing less than one catalyst turnover, but the productive reaction is significantly accelerated (and the decomposition suppressed) under irradiation.

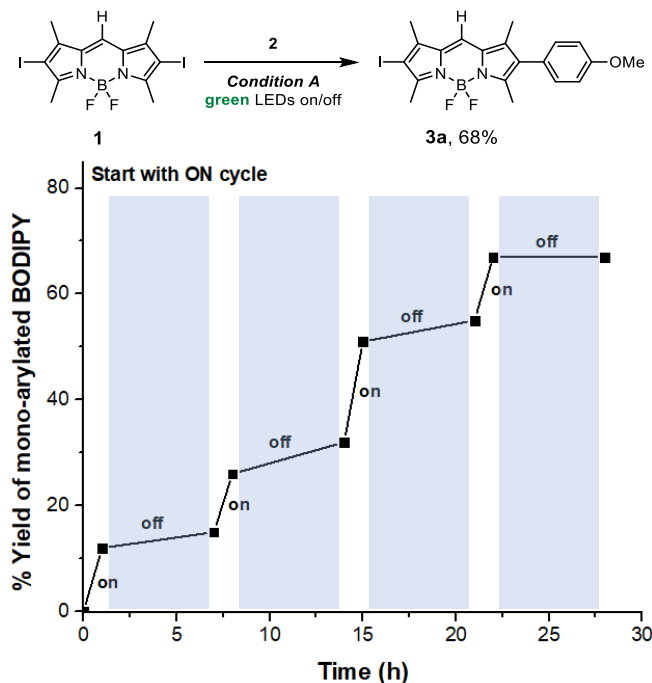


Figure 5. On/off experiment with BODIPY **1** under Condition A. Measurements were taken at an interval of 1 hr for the “on” cycles and 6 hrs for “off” cycles. See SI for details.

To rationalize the observed reactivity and selectivity under irradiation wavelengths corresponding to substrate absorption, we next turned our attention towards the excited-state properties of the BODIPY substrates. Since the identity and number of halogens is expected to significantly influence excited-state properties,⁵⁸ we included unreactive substrates **32** and **33** in our analysis (**Figure 6a**). While the inertness of **32** could be explained by the lower reactivity of C–Br bonds towards oxidative addition, the absence of reactivity for **33**, which only differs from substrate **1** by one iodine atom, suggests a photophysical or photochemical origin for selectivity.

We compared the unreactive substrates **32**, **33**, and **3a** to **1**, mesityl-BODIPY **28**, and its intermediate **29a**, which continues to react to form bis-substituted **29b**. We measured the ground-state absorption spectra, steady-state fluorescence spectra, fluorescence lifetimes (τ_s), fluorescence quantum yields (Φ_F), and intersystem crossing quantum yields (Φ_{ISC}). The collection of these data permitted the calculation of the radiative decay rate constant (k_r), the non-radiative decay rate constant (k_{nr}), and the intersystem crossing rate constant (k_{ISC}). The ground-state redox potentials determined by cyclic voltammetry and the triplet energies (E_T) determined by phosphorescence measurements in

a solvent glass at 77 K were used to calculate excited-state redox potentials. Photochemical and photophysical data are summarized in Tables S9-10 (SI).

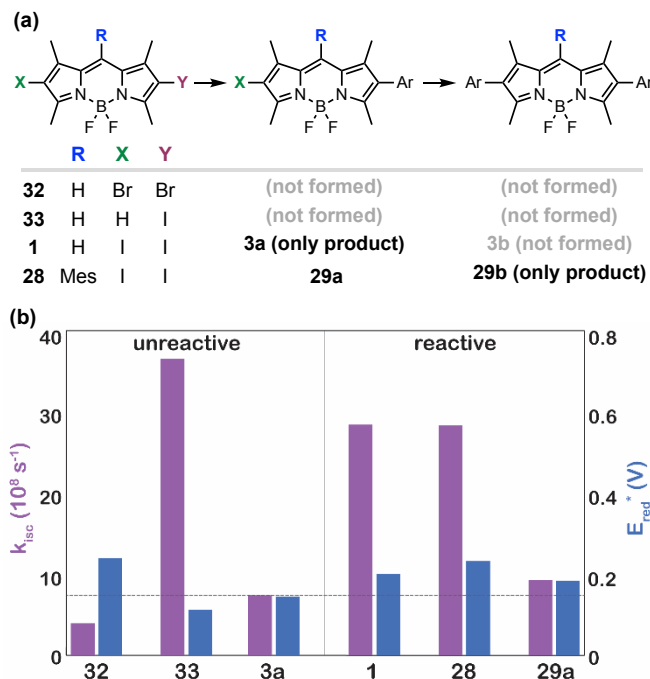


Figure 6. (a) Summary of reactivity for different BODIPY derivatives. (b) Summary of excited-state properties of reactive and unreactive BODIPY chromophores. The experimental cutoff for reactivity is shown as a dotted line. See SI for tabulated data and details of measurements.

These data revealed only subtle differences in the excited-state properties of reactive and unreactive substrates. The normalized ground-state absorption of chromophores **32**, **33**, **1**, **3a**, **28** and **29a** in acetonitrile all exhibit narrow absorption transitions with high extinction coefficients between 525 and 538 nm (**Figure S17**), suggesting that differences in the absorption are not responsible for the changes in reactivity. While the singlet excited-state dynamics in these molecules are influenced by their halogen content, arylation at the 6-position,^{79–81} and the size of the substituent at the *meso* position,^{82,83} clear correlations to reactivity were not identified. For example, unreactive product **3a** displays lower k_{ISC} and Φ_{\square} compared to reactive substrates **1**, **28**, and **29a**, while mono-iodo BODIPY **35** exhibits high ISC quantum yield and rate but does not undergo photoinduced coupling. Furthermore, all of the iodinated BODIPYs measured had triplet lifetimes 0.85 μs or greater, and we did not observe any trend between triplet lifetime and reactivity.

Similarly, the excited-state oxidation potentials of both reactive and unreactive BODIPYs fell between -0.68 and -0.82 vs. Fc/Fc^+ (SI, Table S9) and did not reveal any trends consistent with the reactivity (Table S10). The excited-state reduction potentials reveal a narrow cutoff between reactive substrates (**1**, **28**, **29a** ≥ 0.23 V) and unreactive substrates (**33**, **3a** ≤ 0.18 V), corresponding to a 1.61 kcal/mol difference in thermodynamic driving force for electron transfer.

Taken together, our data reveal apparent cutoffs for reactivity based on the combination of triplet formation and excited-state reduction potential (**Figure 6b**). However, the subtlety of these differences and the absence of clear trends prompted us to question whether excitation of the

substrate itself or an organometallic intermediate is relevant to the catalytic cycle. Therefore, we probed the mechanism in more detail using stoichiometric experiments.

Ni(dppp)(cod) was subjected to substrate **1** (0.9 equiv) in the dark and with green irradiation. Surprisingly, under both conditions we observed clean formation of the oxidative addition complex **37** (Figure 7). Therefore, we hypothesize that the light-dependent step of the catalytic cycle occurs after oxidative addition (see SI for further discussion).^{65,84} Such a mechanism, which relies on photoexcitation of an organometallic derivative of the substrate rather than the substrate itself, explains why the excited-state data in Figure 6b do not show clear distinctions between reactive and unreactive substrates. Further studies to study the photophysics and photoreactivity of Ni–BODIPY complexes and identify the light-dependent step are underway.

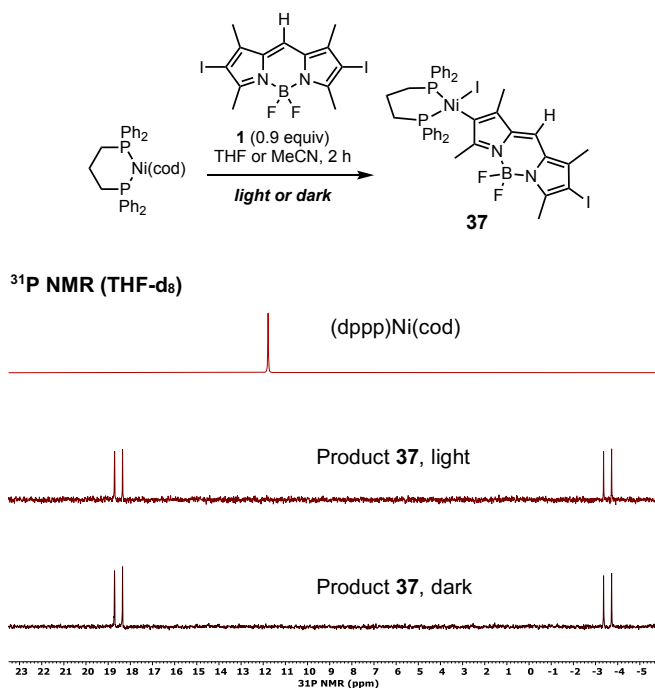


Figure 7. Stoichiometric oxidative addition and corresponding ³¹P NMR spectra in THF-d₈. Data shown are from reactions in THF; for MeCN data, see SI.

Conclusions

We have developed a photoinduced, Ni-catalyzed Suzuki–Miyaura cross-coupling of halogenated BODIPY chromophores. This reaction exhibits high substrate selectivity, distinguishing between compounds with similar absorption, sterics, and electronics. For diiodo-BODIPY substrates with small groups at the *meso* position, we observe selective formation of the mono-functionalized product, providing rapid synthetic access to unsymmetrically substituted BODIPYs. Preliminary results demonstrate that this reactivity can be extended to bathochromically-shifted chromophores such as aza-BODIPYs using red light. Substitution at the *meso* position of diiodo-BODIPY with a mesityl group does not perturb the C–I bonds sterically or electronically, but shifts the reactivity to favor bis-substitution. Comparison of the excited-state properties of reactive and unreactive substrates and preliminary mechanistic studies suggest that the cross-coupling mechanism involves photoexcitation of an organometallic intermediate derived from the chromophore substrate.

Selective photoreactions have been used to identify new photoswitches from a dynamic covalent library.⁸⁵ Analogously, we envision that the substrate-selective photoinduced cross-coupling will enable the discovery of new triplet sensitizers and photoredox catalysts from complex mixtures of chromophores. Such a goal will require us to broaden the scope of this reaction to classes beyond BODIPY and aza-BODIPY. Efforts to realize this reactivity-driven approach to materials discovery and detailed mechanistic investigations of the organometallic mechanism are underway in our lab.

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