Direct C−F Bond Formation Using Photoredox Catalysis

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S *Supporting Information*

ABSTRACT: We have developed the first example of a photoredox catalytic method for the formation of carbon−fluorine (C−F) bonds. The mechanism has been studied using transient absorption spectroscopy and involves a key single-electron transfer from the ^{3}MLCT (triplet metal-to-ligand charge transfer) state of Ru(bpy)$_3$$^{2+}$ to Selectfluor. Not only does this represent a new reaction for photoredox catalysis, but the mild reaction conditions and use of visible light also make it a practical improvement over previously developed UV-mediated decarboxylative fluorinations.
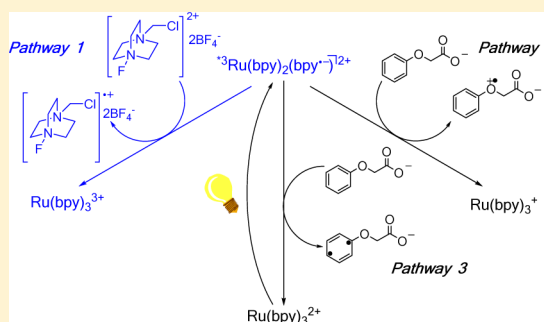
INTRODUCTION

Photoredox catalytic transformations have a rich history in organic synthesis starting with early work by Kellogg in the 1970s.[1,2] The reports of MacMillan[3] and Yoon[4] in 2008 have led to a dramatic increase in the number of outstanding contributions in this field.[5] All of this work has culminated in the development of numerous effective synthetic methodologies, particularly for the formation of carbon−carbon (C−C), carbon−hydrogen (C−H), and various carbon−heteroatom (C−Het) bonds.[5] Despite both the significant interest in photoredox catalysis and the pharmaceutical, agrochemical, and radiochemical importance of incorporating fluorine into molecules,[6] there have been no reports to date of the direct photoredox catalytic formation of carbon−fluorine (C−F) bonds (Figure 1). The only reports of fluorine incorporation[7] using photoredox catalysis focus on adding trifluoromethyl groups via C−C bond formation.[8]

The absence of photoredox catalytic methods for C−F bond formation is likely due to the paucity of known fluorine atom transfer reagents. For years, the few reagents that were available either required specialized handling protocols, such as F$_2$ or hypofluorites,[9] or are powerful oxidants, such as XeF$_2$.[10]
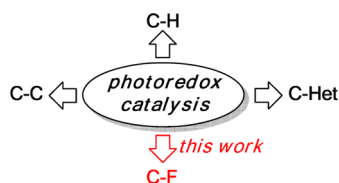
We recently reported that stable electrophilic fluorine sources, such as Selectfluor, can transfer fluorine to alkyl radicals.[11,12] Selectfluor may complicate photocatalytic transformations because it is an oxidant and has the potential to interfere with the redox catalytic cycle.

To test whether Selectfluor is compatible with common photoredox catalysts, we first needed to identify an appropriate substrate that has a suitably high oxidation potential such that it cannot be directly oxidized by Selectfluor[13] but can be oxidized with the assistance of a photocatalyst. We decided to investigate the photofluorodecarboxylation of aryloxyacetic derivatives (1, Scheme 1).[14] These substrates are ideal because they cannot be oxidized with Selectfluor unless they are first excited with 300 nm light. In the visible region needed to access the photoexcited catalyst (400−500 nm), neither the aryloxyacetic derivatives, such as 1a, nor Selectfluor absorbs light (Figure 2).

Scheme 1. Photodecarboxylation of Aryloxyacetic Acid Derivatives and a Proposed Photoredox Catalyzed Variant

Figure 1. Bonds that can be formed using ruthenium and iridium-based photoredox catalysts.
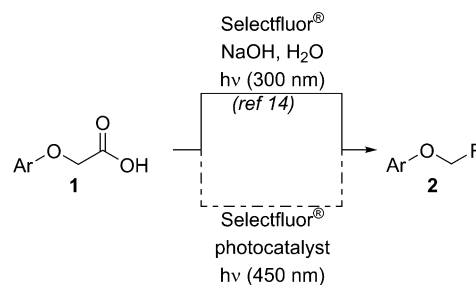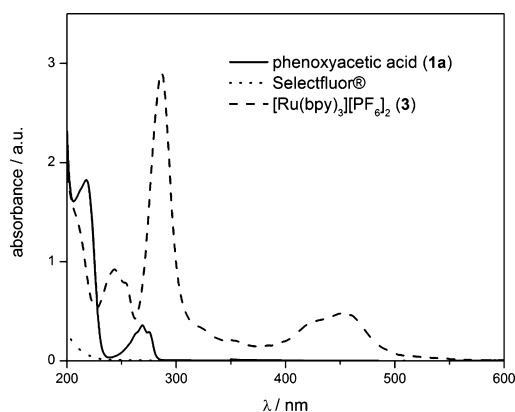
Figure 2. Absorption spectra of phenoxyacetic acid **1a** (H_2O), Selectfluor (H_2O), and $[Ru(bpy)_3][PF_6]_2$ (1:1 CH_3CN/H_2O).

An investigation of C–F bond formation using photoredox catalysis not only is an excellent opportunity to study the compatibility of Selectfluor with metal-based photoredox catalysts but also may provide a practical new method that represents an improvement over our recently reported light-mediated fluorination methodology (Scheme 1).[14] The presence of a photocatalyst that can be activated using visible light allows for the use of a lower energy light rather than near-UV light. Furthermore, our previous methodology relies on direct excitation of the substrate and any significant structural change necessitates changing the light source. A photoredox catalytic system has the significant advantage of requiring only one light source.

■ RESULTS AND DISCUSSION

We began our investigations with phenoxyacetic acid (**1a**, Table 1). In the absence of a photoredox catalyst, **1a** is unreactive when

Table 1. Control Experiments for Catalytic Photoredox Decarboxylative Fluorinations
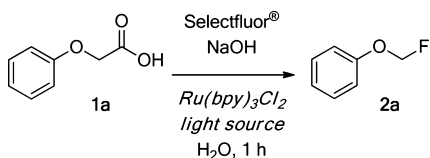
entry[a]	light source[b]	catalyst (mol %)	NMR yield (%)[c]
1	500 W lamp	0	0
2	none[d]	1	0
3	500 W lamp	1	84

[a]Conditions: 0.1 mmol phenoxyacetic acid, 3.5 equiv of Selectfluor, 1.5 equiv of NaOH, 0.1 M H_2O. [b]The lamp was positioned 30 cm from the reaction flask. See Supporting Information for details about the lamp. [c]The NMR yield was determined using 1,3,5-trimethoxybenzene as the internal standard. [d]The reaction was covered in aluminum foil. All other conditions were the same, including the proximity from the active light source to maintain a comparable reaction temperature.

visible light is used (entry 1). Furthermore, when a catalytic amount of $Ru(bpy)_3Cl_2$ is added to the reaction mixture, there is no reaction in the absence of light (entry 2). Gratifyingly, exposure of phenoxyacetic acid and a catalytic amount of $Ru(bpy)_3Cl_2$ to light leads to a high conversion to fluorodecarboxylated product **2a** in only 1 h (entry 3).

While this initial study clearly demonstrates that $Ru(bpy)_3Cl_2$ effectively promotes the decarboxylative fluorination of phenoxyacetic acid (**1a**), there are still several important mechanistic questions that need to be addressed to determine if this new C–F bond forming methodology is a catalytic photoredox process as proposed. The reaction begins with the excitation of $Ru(bpy)_3^{2+}$ to afford a singlet excited state that rapidly undergoes an intersystem crossing to the key triplet excited state, $*^3[Ru(bpy)_2(bpy^{•-})]^{2+}$ (Figure 3). At this stage, there are three
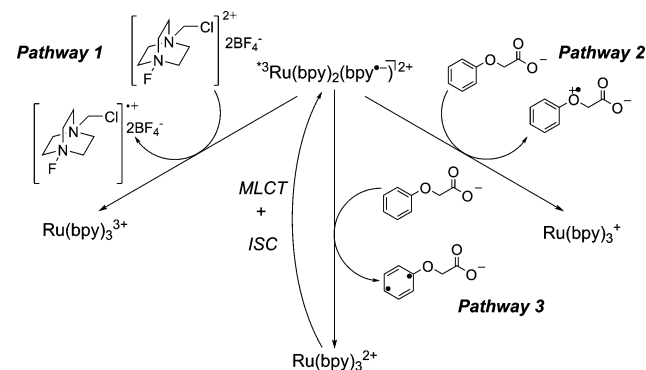

Figure 3. Oxidative, reductive, and energy transfer pathways from excited intermediate $*^3Ru(bpy)_2(bpy^{•-})^{2+}$.

possible mechanistic pathways.[15] The first option is that $*^3[Ru(bpy)_2(bpy^{•-})]^{2+}$ undergoes a SET to reduce Selectfluor and form $Ru(bpy)_3^{3+}$ (pathway 1). Alternatively, $*^3[Ru(bpy)_2(bpy^{•-})]^{2+}$ may oxidize phenoxyacetic acid to initiate the decarboxylation and concomitantly form reduced $Ru(bpy)_3^+$ (pathway 2). The third mechanistic possibility is that the catalyst may simply act as a photosensitizer by transferring energy from $*^3[Ru(bpy)_2(bpy^{•-})]^{2+}$ to phenoxyacetic acid (pathway 3), which would then intersect with the mechanism previously proposed.[14]

To differentiate between the three mechanistic possibilities, we utilized transient absorption (TA) spectroscopy. TA spectroscopy provides a direct method to monitor the excitation and oxidation states of the ruthenium catalyst, including $Ru(bpy)_3^{2+}$ and $*^3[Ru(bpy)_2(bpy^{•-})]^{2+}$.[16] If a difference is observed in the TA spectrum when phenoxyacetic acid is added, then the catalyst likely undergoes either reduction (Figure 3, pathway 2) or energy transfer (pathway 3). Similarly, if a difference occurs with the addition of Selectfluor, the catalyst likely undergoes oxidation (pathway 1).

During our initial TA spectroscopic experiments, it was observed that a small amount of precipitate was formed when the decarboxylative fluorination was carried out with $Ru(bpy)_3Cl_2$ in water. This led to light scattering and complicated data analysis. This problem was circumvented by using the PF_6^- salt of $Ru(bpy)_3^{2+}$ in a 1:1 mixture of H_2O/CH_3CN. The yield of the decarboxylative fluorination of **1a** in 1:1 H_2O/CH_3CN was the same regardless of which catalyst was utilized (Scheme 2).

TA spectroscopy of $Ru(bpy)_3(PF_6)_2$ (Figure 4a) is consistent with previous reports,[16] with a depletion of the band at 450 nm, which correlates to $Ru(bpy)_3^{2+}$ (Figure 2, $Ru(bpy)_3PF_6$), and an increase of the band at 375 nm, which correlates to the $^3[Ru(bpy)_2(bpy^{•-})]^{2+}$. In the presence of phenoxyacetic acid (**1a**), the excited state difference spectrum of $Ru(bpy)_3(PF_6)_2$ (Figure 4b) is identical to that of $Ru(bpy)_3(PF_6)_2$ (Figure 4a), which qualitatively suggests that there is no interaction between the catalyst and phenoxyacetic acid and is not consistent with
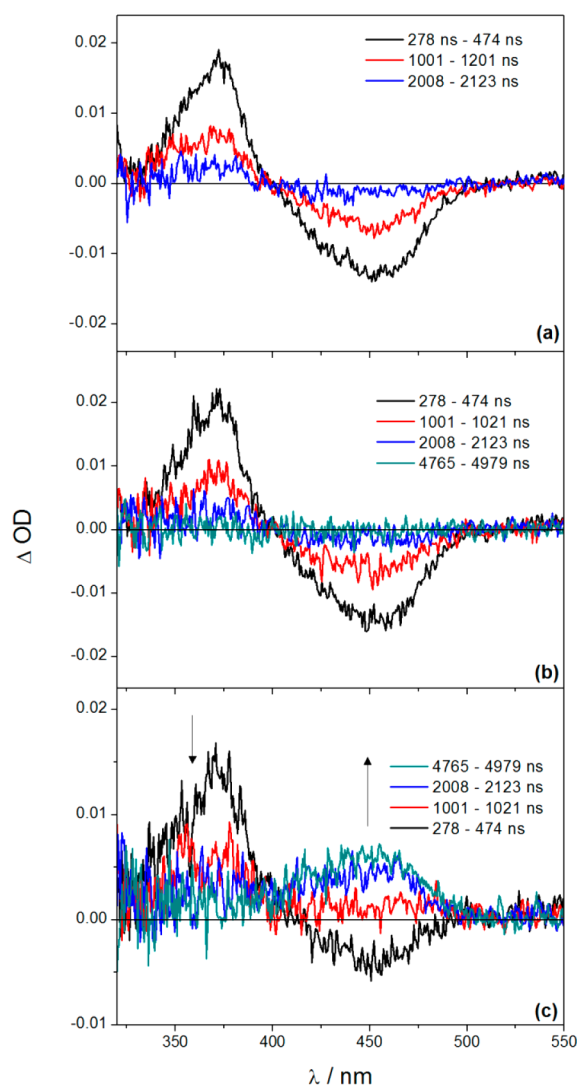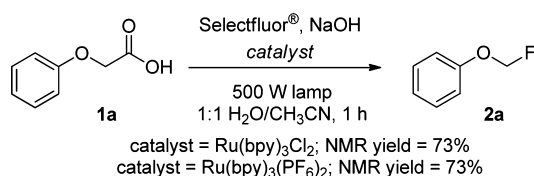
Scheme 2. Photodecarboxylative Fluorination with Ru(bpy)$_3$(PF$_6$)$_2$ and Ru(bpy)$_3$Cl$_2$

catalyst = Ru(bpy)$_3$Cl$_2$; NMR yield = 73%
catalyst = Ru(bpy)$_3$(PF$_6$)$_2$; NMR yield = 73%

Figure 4. Excited state difference spectra of (a) Ru(bpy)$_3$(PF$_6$)$_2$, (b) Ru(bpy)$_3$(PF$_6$)$_2$ (0.11 mM) in the presence of 2-phenoxyacetic acid (**1a**, 2.6 mM), and (c) Ru(bpy)$_3$(PF$_6$)$_2$ (0.11 mM) in the presence of Selectfluor (2.6 mM) in 1:1 H$_2$O/CH$_3$CN (λ_{ex} = 450 nm).

pathways 2 and 3 (Figure 3).[17] Conversely, the excited state difference spectrum of Ru(bpy)$_3$(PF$_6$)$_2$ in the presence of an excess of Selectfluor (Figure 4c) shows the growth of a new absorption band centered at 450 nm[18] concomitant with the decay of the band attributed to the bpy anion. This new band was not found to decay over the course of the time regimes studied ($t \leq 10\ \mu s$).[19] These findings are most consistent with pathway 1 (Figure 3), in which the catalyst is first oxidized by Selectfluor.

After the electron transfer in pathway 1 (Figure 3), the decarboxylative fluorination likely proceeds according to Figure 5. Instead of the previously proposed direct excitation and
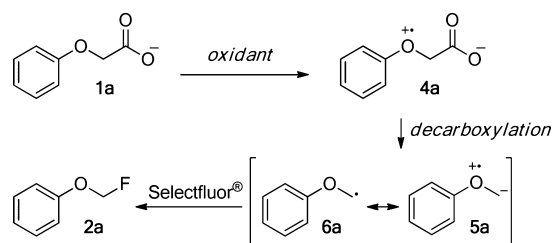

Figure 5. Oxidation and decarboxylative fluorination of phenoxyacetic acid.

oxidation of phenoxyacetic acid,[14] an oxidant in solution performs a direct oxidation of the substrate.[20−22] Once oxidized, **4a** undergoes decarboxylation to **5a/6a** and fluorination to afford the desired fluoromethoxy ether, **2a**.[14]

With proof-of-concept for the first use of photoredox catalysis for the direct formation of C−F bonds, we next investigated whether this is a practical improvement. Systematic optimization of the reaction conditions indicated that optimal yields could be obtained using 1 mol % of Ru(bpy)$_3$Cl$_2$, 3.5 equiv of Selectfluor, and 1.5 equiv of NaOH in either H$_2$O or H$_2$O/CH$_3$CN mixtures depending on substrate solubility. The reaction was typically irradiated with a visible-light-emitting 500 W lamp for 1 h.[23] The base is useful to increase the solubility of the substrate but was not required.[24]
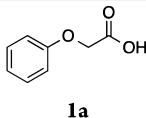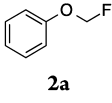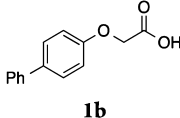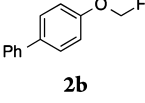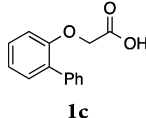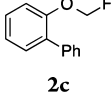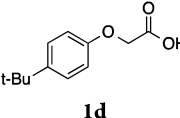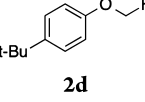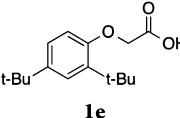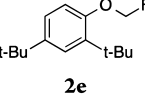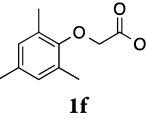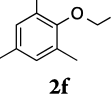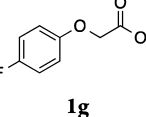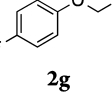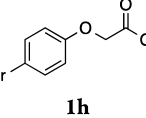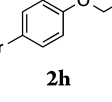
These optimized conditions led to the photoredox decarboxylative fluorination of a range of aryloxyacetic acid derivatives in good to excellent yields (Table 2). *p*-Phenylaryloxy rings performed comparably to *o*-phenyl derivatives (entries 2, 3). Increasing the alkyl substitution in the ortho-position of the aryloxy ring (entries 4−6) also did not significantly impact the yield of fluorinated product. Electron-withdrawing substituents on the aryloxy rings, such as fluorine (**1g**, entry 7) or bromine (**1h**, entry 8), led to a slight decrease in yield compared to phenoxyacetic acid (entry 1). Pyridyl derivative **1i** was successfully fluorinated in good yield (entry 9). This methodology is also applicable to double decarboxylative fluorinations, as illustrated by entry 10.

These new visible light decarboxylative fluorination conditions provide access to a broader scope of substrates compared to our previously developed UV light-promoted methodology.[14] Substrates that can successfully be fluorinated using UV light generally perform comparably under these new conditions. For exampl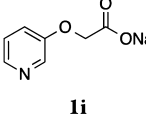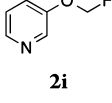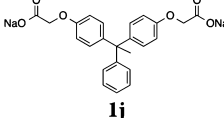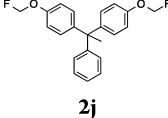e, under the UV light conditions, substrates **1a**, **1d**, **1g**, and **1h** afforded yields of 84%, 83%, 94%, and 60%, respectively. However, substrates that were not fluorinated in good yields using UV light, such as **1b** and **1f**,[25] can be accessed using these visible light conditions. We next explored the decarboxylative fluorination in a more complex substrate derived from the naturally occurring hormone estrone (**1k**), which has the potential to enolize under the basic reaction conditions (Scheme 3). Indeed, treatment of **1k** under either our UV[14] or visible light standard basic reaction conditions led to multiple fluorination products. Application of base-free conditions to substrate **1k** afforded the desired product (**2k**) in 51% yield (Scheme 4).

■ CONCLUSION

We have successfully developed the first example of direct C−F bond formation using a Ru(bpy)$_3$Cl$_2$ photocatalyst with Selectfluor. Mechanistically, the reaction proceeds through a photoredox pathway involving a SET from the ^{3}MLCT state of the ruthenium catalyst to Selectfluor. This forms the key oxidant

Table 2. Substrate Scope for the Catalytic Photoredox Decarboxylative Fluorination

entry	substrate	product	% yield[a]
1	1a	2a	(84)[b,c]
2	1b	2b	92[d]
3	1c	2c	89[e]
4	1d	2d	79[e]
5	1e	2e	74[c,d]
6	1f	2f	65[c,d]
7	1g	2g	(67)[b,c]
8	1h	2h	56[c,e]
9	1i	2i	(63)[e]
10	1j	2j	80[f]

[a]Isolated yield (NMR yield). NMR yields obtained by ^{1}H NMR spectroscopy using trimethoxybenzene as an internal standard. [b]Conditions: 3.5 equiv of Selectfluor, 1.5 equiv of NaOH, H_2O. [c]The product is volatile and is challenging to isolate in high yield. [d]Conditions: 3.5 equiv of Selectfluor, 1.5 equiv of NaOH, 1:1 H_2O/ CH_3CN. [e]Conditions: 2.1 equiv of Selectfluor, 1.0 equiv of NaOH, 3:1 H_2O/ CH_3CN. [f]Conditions: 3.5 equiv of Selectfluor, 1:1 H_2O/ CH_3CN.
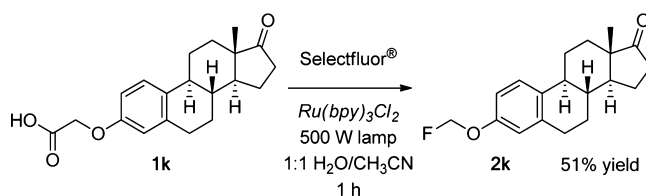
during the reaction, which enables a subsequent decarboxylative fluorination. Not only does this represent the first direct C—F

Scheme 3. Attempted Photodecarboxylative Fluorination with Estrone Derivative 1k

Selectfluor®
NaOH

$Ru(bpy)_3Cl_2$
500 W lamp
1:1 H_2O/ CH_3CN, 1 h

multiple fluorination products

1k
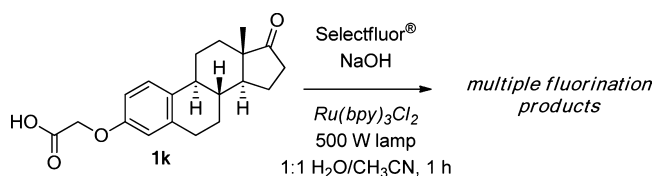
Scheme 4. Base-Free Photodecarboxylative Fluorination Conditions

Selectfluor®

$Ru(bpy)_3Cl_2$
500 W lamp
1:1 H_2O/ CH_3CN
1 h

1k   2k   51% yield

bond formation using photoredox catalysis, but the methodology also is applicable to a wide range of substrates and the use of visible light represents a practical improvement over UV light mediated alternatives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details and ^{1}H, ^{13}C, and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) This new band could correspond to the presence of a new ruthenium species, or it may be attributed to the formation of a reduced Selectfluor species.

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(25) See Supporting Information for details.