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Strongly Reducing Visible Light Organic Photoredox Catalysts as Sustainable Alternatives to Precious Metals

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Abstract: Photoredox catalysis is a versatile approach for the construction of challenging covalent bonds under mild reaction conditions, commonly using photoredox catalysts (PCs) derived from precious metals. As such, there is need to develop organic analogues as sustainable replacements. Although several organic PCs have been introduced, there remains a lack of strongly reducing visible light organic PCs. Herein, we establish the critical photophysical and electrochemical characteristics of both a dihydrophenazine and a phenoxazine system that enables them success as strongly reducing visible light PCs for trifluoromethylations and dual photoredox/nickel catalyzed C-N and C-S cross-couplings, reactions which have been historically exclusive to precious metal PCs.

Visible light photoredox catalysis has gained prominence orchestrating challenging chemical transformations under mild reaction conditions.[1] A large majority of this work has employed precious metal polypyridyl iridium and ruthenium photoredox catalysts (PCs). The rapid establishment of these metal complexes as practical PCs leveraged their well-studied photophysical and photoredox properties, that in turn have enabled their incorporation in a range of applications including photovoltaics,[2] light emitting diodes,[3] imaging and sensing in biological systems,[4] therapeutics,[5] and redox active antibiotics.[6]

In regards to photoredox catalysis, these metal complexes exhibit essential characteristics, including strong absorption of visible light via spin-allowed metal-to-ligand charge transfer (MLCT), efficient conversion to long-lived triplet MLCT excited states (^{3}MLCT),[7] and redox reversibility.[7a, 8] Furthermore, ligand and metal modifications tailor the redox properties of the ground and excited states.[9] For example, *fac*-Ir(ppy)$_3$ (tris[2-phenylpyridinato-C^2,N]iridium(III), **1**, ppy = 2-phenylpyridine) is amongst the strongest reducing PCs, while [Ru(bpy)$_3$]$^{2+}$ (tris(2,2'-bipyridine)ruthenium(II), **2**, bpy = 2,2'-bipyridine) possesses redox properties that enable it to function either as a reductant or as an oxidant from the ^{3}MLCT state.

However, iridium and ruthenium are precious metals and amongst the rarest elements on earth, escalating their costs and presenting concerns related to sustainability and scalability, driving the need to realize new PCs incorporating non-precious metals[10] or to develop entirely organic replacements.[11] Several organic molecules have proven successful as visible light PCs for small molecule and polymeric transformations.[12] The majority of these organic PCs, such as Eosin Y,[13] rhodamine dyes,[14] acridinium salts,[15] perylene diimides,[16] and carbazolyls[17] are excited state oxidants and operate through a reductive quenching cycle. Although a few strongly reducing organic PCs exist,[18] many do not absorb visible light. PCs that operate using mild visible light and do not require sacrificial reductants are desired to minimize side reactions.

Our interest in organic PCs[19] initiated with the development of organocatalyzed atom transfer radical polymerization (O-ATRP).[20] ATRP has historically been mediated by transition metal catalysts, most commonly copper or ruthenium complexes, which can contaminate the polymer product and restrict applications.[21] A primary challenge in developing a photoredox mediated O-ATRP is presented by the strong reducing power that is required of the PC to activate a dormant alkyl halide.[22] In general, PCs that possess such strong excited state reducing powers are rare, and this is particularly true for organic systems (*vide supra*).

To address this challenge, we have introduced visible light organic PCs including perylene,[19a] *N,N*-diaryl dihydrophenazines,[19b, 23] and *N*-aryl phenoxazines[24] as organic PCs to mediate O-ATRP via an oxidative quenching pathway.[25] Dihydrophenazine and phenoxazine contain electron rich chromophore motifs that form rather stable radical cations upon oxidation and enable them to be strong excited state reductants.[26] However, a detailed comprehension of the characteristics of these molecules in regards to catalysis or their ability to catalyze other transformations has not been established. Herein, through investigation of their photophysical and electrochemical properties, we report the critical characteristics of *N,N*-5,10-di(2-naphthalene)-5,10-dihydrophenazine (**3**) and 3,7-(4-biphenyl)-1-naphthalene-10-phenoxazine (**4**) that enable them to serve as successful PCs. We further establish **3** and **4** as PCs through their employment in atom transfer radical additions or substitutions with CF$_3$I to alkenes and heterocycles as well as dual photoredox/nickel catalyzed C-N and C-S cross-couplings.

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The photophysical properties of **3** and **4** were investigated and compared to that of transition metal complexes **1** and **2** (Figure 1). As photoexcitation is the first step in photoredox catalysis, PCs should be strong light absorbers. In *N,N*-dimethylacetamide (DMA), the molar absorptivities (ε) for transition metal complexes **1** and **2** are 13,100 and 12,500 $M^{-1}cm^{-1}$ at their maximum peak wavelengths of absorption ($\lambda_{max,abs}$) of 377 nm and 454 nm, respectively (Figure 1A). Dihydrophenazine **3** has a lower molar extinction ($\varepsilon_{max,abs}$ = 5,950 $M^{-1}cm^{-1}$; $\lambda_{max,abs}$ = 343 nm) in comparison to **1** and **2**, while phenoxazine **4** is an excellent light absorber and superior to the other three PCs ($\varepsilon_{max,abs}$ = 26,600 $M^{-1}cm^{-1}$; $\lambda_{max,abs}$ = 388 nm). In a similar fashion to **1**, although the $\lambda_{max,abs}$ values are < 400 nm, the absorption profiles of organic PCs **3** and **4** extend into the visible region and enable them to function as visible light PCs.

1 is known to be one of the strongest excited state transition metal PC reductants available, with an excited state reduction potential (E^{0*}) of $E^0(Ir(IV)/{}^3Ir(III)^*)$ = -1.73 V vs. SCE (Figure 1C). Excitingly, organic PCs **3** and **4** are equally reducing with E^{0*} = $E^0({}^2PC^{\bullet+}/{}^3PC^*)$ values of -1.69 and -1.80 V vs. SCE, respectively. Although **2** is not as reducing in the excited state [E^{0*} = $E^0(Ru(III)/{}^3Ru(II)^*)$ = -0.81 V vs. SCE], the Ru(III) generated after participating in a photoreduction event is strongly oxidizing, with an oxidation potential [E^0_{ox} = $E^0(Ru(III)/Ru(II))$] of 1.29 V vs. SCE. Notably, **1** and the organic PC **4** have similar E^0_{ox} values [$E^0(Ir(IV)/Ir(III))$ = 0.77 and $E^0({}^2PC^{\bullet+}/{}^1PC)$ = 0.65 V vs. SCE, respectively], while **3** forms a rather stable radical cation [E^0_{ox} = $E^0({}^2PC^{\bullet+}/{}^1PC)$ = 0.21 V vs. SCE]. In regards to triplet energy ($E_{triplet}$), both **1** and **4** have energetic triplets with $E_{triplet}$ of 2.50 and 2.45 V, respectively. Meanwhile, $E_{triplet}$ of **2** and **3** are lower, with respective values of 2.10 and 1.90 V.

Upon photoexcitation, transition metal complexes **1** and **2** form a MLCT excited state, which is suggested to facilitate electron transfer mechanisms in photocatalytic cycles.[8b, 9a] Recently, we reported that the lowest energy excited state of dihydrophenazine **3** is also CT in nature.[23] Specifically, intramolecular CT occurs from the electron rich phenazine core (donor) to one of the 2-naphthyl *N*-substituents (acceptor). Here we show that phenoxazine PC **4** similarly undergoes photoinduced intramolecular CT, as evidenced by a significant solvatochromic effect in the emission (Figure 2A). Additionally, the broad and featureless emission peaks are characteristic of emission from a CT state (Figure 2B).[27]
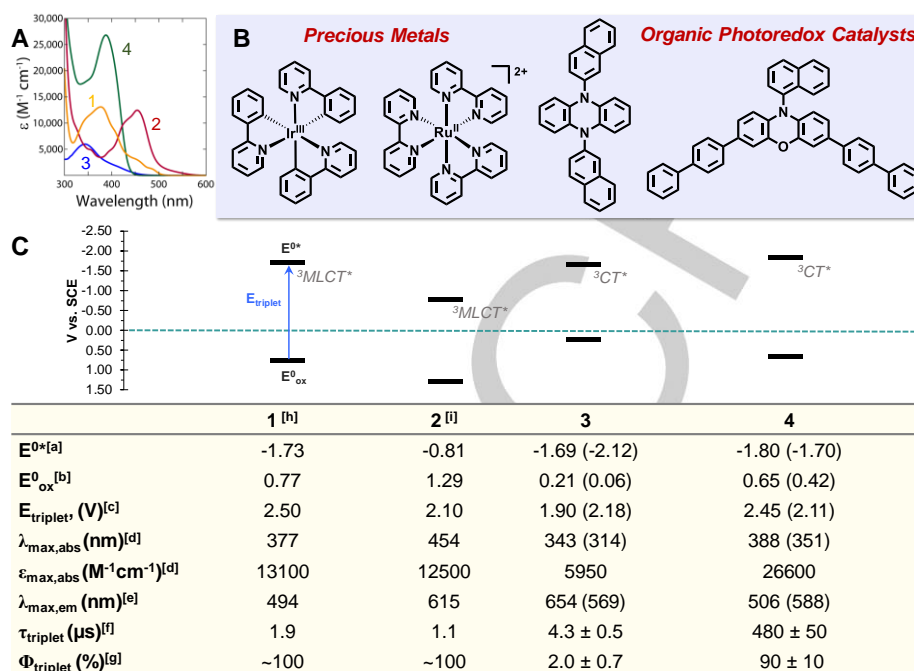

	1 [h]	**2** [i]	**3**	**4**
E^{0*}[a]	-1.73	-0.81	-1.69 (-2.12)	-1.80 (-1.70)
E^0_{ox}[b]	0.77	1.29	0.21 (0.06)	0.65 (0.42)
$E_{triplet}$, (V)[c]	2.50	2.10	1.90 (2.18)	2.45 (2.11)
$\lambda_{max,abs}$ (nm)[d]	377	454	343 (314)	388 (351)
$\varepsilon_{max,abs}$ ($M^{-1}cm^{-1}$)[d]	13100	12500	5950	26600
$\lambda_{max,em}$ (nm)[e]	494	615	654 (569)	506 (588)
$\tau_{triplet}$ (μs)[f]	1.9	1.1	4.3 ± 0.5	480 ± 50
$\Phi_{triplet}$ (%)[g]	~100	~100	2.0 ± 0.7	90 ± 10

Figure 1: Photophysical and electrochemical properties of precious metal and organic photoredox catalysts. (**A**) UV-vis absorption spectra of PCs **1-4** in *N,N*-dimethylacetamide (DMA). (**B**) Structures of precious metal and organic PCs. (**C**) Values enclosed in parentheses are from density functional theory (DFT) calculations. All experimental values for PCs **3** and **4** were measured in DMA at room temperature. [a] Triplet excited state reduction potential, E^{0*}, in units of V vs. SCE. [b] Ground state oxidation potential [c] Triplet energy ($E_{triplet}$), estimated from the fluorescence wavelength of the charge transfer singlet state. [d] Maximum absorption wavelength ($\lambda_{max,abs}$); molar absorptivity ($\varepsilon_{max,abs}$) at $\lambda_{max,abs}$. [e] Emission maximum wavelength ($\lambda_{max,em}$). [f] Triplet excited state lifetime ($\tau_{triplet}$). [g] Quantum yield ($\Phi_{triplet}$) of charge transfer triplet excited state (${}^3CT^*$), and metal-ligand charge transfer triplet excited state (${}^3MLCT^*$). [h] $\lambda_{max,abs}$ and $\varepsilon_{max,abs}$ were measured in this work in DMA. All other values were obtained from ref. [8a,9b], and were measured in acetonitrile, except for the $\lambda_{max,em}$, which was measured in alcoholic solvent at 77K. [i] $\lambda_{max,abs}$ and $\varepsilon_{max,abs}$ were measured in this work in DMA solvent for [Ru(bpy)$_3$](PF$_6$)$_2$. All other values were obtained from ref. [8b,9a], and were measured in acetonitrile. See Supporting Information for details.

The efficient access of a long-lived excited species by the PC enables sufficient time for bimolecular electron transfer with the desired substrate(s). In the case of transition metal complexes **1** and **2**, ultrafast intersystem crossing produces the ^{3}MLCT and is useful by way of extending excited state lifetimes (τ). Photoexcitation quantitatively leads to a long-lived ^{3}MLCT which survives for 1.9 and 1.1 µs (in acetonitrile) for **1** and **2**, respectively (Figure 1C). Using nanosecond transient-absorption (TA) spectroscopy performed in DMA at room temperature, we identified long-lived excited states for the organic PCs **3** and **4**. The τ of **3** was determined to be 4.3 ± 0.5 µs (Figure 2C) whereas for **4**, it is a remarkable two orders of magnitude longer than that of **1**, **2** or **3**, with τ = 480 ± 50 µs (Figure 2D). By use of a triplet-triplet energy transfer method, we have determined the triplet quantum yield ($\Phi_{triplet}$) of **3** and **4** in DMA at ambient temperature: **3**'s $\Phi_{triplet}$ is relatively low at 2.0 ± 0.7% while **4** has an impressively high $\Phi_{triplet}$ of 90% ± 10%.

Another critical characteristic for successful PCs is radical stability following single electron transfer events. Transition metal complexes **1** and **2** exhibit reversible waves in cyclic voltammetry (CV), a property that indicates stability of the redox-altered catalyst.[7a, 8] Similarly, the CVs corresponding to the ${}^2PC^{\bullet+}/{}^1PC$ couple of **3** and **4** are reversible (Figure 2E and F). In particular, the difference between the anodic and cathodic peak

potential (ΔE_p) for **3** is 67 mV (compared to theoretical value of 59 mV),[28] while the ratio of the peak anodic current (i_{pa}) to the peak cathodic current (i_{pc}) is 0.97 (compared to theoretical value of 1) (Figure 2E). Redox reversibility of **3** is in part attributed to the stability of **3**'s $^2PC^{\bullet+}$, as indicated by low E^0_{ox} value of 0.21 V vs. SCE; this value is even lower than the redox couple producing ferrocenium (E^0_{ox} = ~ 0.4 V vs. SCE).[29] Likewise, the CV of **4** reveals ΔE_p = 68 mV and i_{pa}/i_{pc} = 1.28.[30] Additionally, a

Figure 2. Photophysical properties of organic PCs. (**A**) Photograph showing solvatochromic shifts in the emission of **4** when irradiated with 365 nm light in solvents of increasing polarity; from left to right: 1-hexene, benzene, dioxane, ethyl acetate, pyridine, and DMF. (**B**) Normalized emission spectra of **4** in solvents of varying polarity. Transient absorption spectra of **3** (**C**) and **4** (**D**) in DMA at room temperature. Cyclic voltammetry (CV) experiments with various scan rates for (**E**) **3** and (**F**) **4**. See Supporting Information for details.

linear relationship between i_{pa} and the square root of the scan rate ($v^{1/2}$) reveals that the CV of **3** and **4** are diffusion limited (Figure 2E and F, insets); this supports the idea that electron transfer between the PC and the electrode (for either **3** or **4**) is fast and likely facilitated by small structural reorganization[24] between ^1PC and $^2PC^{\bullet+}$.

With the confirmation that **3** and **4** possess key photophysical and electrochemical characteristics critical for photoredox catalysis, we set out to establish their broader catalytic ability and potential to replace precious metal PCs through performing challenging chemical transformations, particularly ones that have been previously directed by polypyridyl iridium and ruthenium PCs such as **1** and **2**.

First, we investigated if the strongly reducing dihydrophenazine **3** could directly reduce CF$_3$I (peak reduction potential (E_p) of -1.52 V vs. SCE on glassy carbon),[31] thereby generating CF$_3^{\bullet}$ for the trifluoromethylation of unsaturated substrates (Figure 3A).[32] Using white LED irradiation of **3** (1 to 5 mol %) in the presence of 1.5 eq. of potassium formate (HCOOK), CF$_3$ was successfully installed onto five-membered heteroarenes (indoles, pyrroles), arenes, and alkenes at

moderate to excellent yields (42% to 98%). For alkenes, the presence of HCOOK base affords the substitution product while the absence of HCOOK favors the addition product. The reduction of CF$_3$CF$_2$I was also accomplished, generating CF$_3$CF$_2^{\bullet}$ for substitution onto indoles and alkenes. The trifluoromethylation of 3-methylindole was achieved with similar yield using natural sunlight. The substitution reaction between 10-undecene-1-ol and CF$_3$I could be performed using lower catalyst loading (0.25 mol %, 69 % yield) or on a larger 10 mmol scale (1.74 g product, 73% yield) while maintaining good yields.

Dual catalytic approaches integrating photoredox catalysis using iridium PCs and nickel-catalyzed cross-coupling reactions have enabled access to C-O,[33] C-S,[34] C-N[35] and various C-C[36] reactions. Incorporating the photoredox cycle introduces redox or energy transfer[37] mechanisms with the nickel complexes to complete otherwise demanding catalytic cycles. Cross-coupling reactions have traditionally been catalyzed by palladium complexes at elevated temperatures to construct such critical bonds.[38] Thus, to entirely remove precious metals out of cross-couplings through dual catalytic reactions, we sought to determine if organic PCs **3** and **4** could also enable such challenging reactions.

Previously, a dual photoredox/nickel catalytic approach employing 0.02 mol % of polypyridyl iridium PC Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ [dF(CF$_3$)ppy = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; dtbbpy = 4,4′-ditertbutyl-2,2′-bipyridine] in conjunction with NiBr$_2$•glyme could efficiently catalyze C-N bond formation under mild reaction conditions.[35a] At similar reaction conditions, albeit using a higher catalyst loading (0.4 mol %) PC **3** or PC **4** in combination with NiBr$_2$•glyme successfully catalyzed C-N coupling reactions at good to excellent yields (68% to 96%, Figure 3B). The scope of amines included both primary (aniline, furfurylamine, and propylamine) and secondary amines (pyrrolidine and morpholine) and were effectively coupled with electron rich, electron poor, and heterocyclic aryl bromides. For secondary amines, both PC **3** and **4** catalyzed C-N bond formations, although PC **3** generally gave slightly higher yields. Whilst PC **3** was unsuccessful in effecting C-N cross-coupling involving primary amines, PC **4** proved to be effective to couple primary amines in high yields.

In regards to C-S cross-coupling, the dual photoredox/nickel catalysis with 2 mol % Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ and NiCl$_2$•glyme produced C-S coupled products under mild conditions.[34] At analogous reaction conditions, phenoxazine PC **4** achieved C-S cross-couplings at good to excellent yields (64% to 98%, Figure 3C) but proved efficient at a much lower PC loading of 0.2 mol %. Aryl thiol (thiophenol), alkyl thiol (4-Methoxybenzyl mercaptan, 1-octanethiol and cyclohexanethiol) and cysteine (N-(tert-Butoxycarbonyl)-L-cysteine methyl ester) successfully coupled with a variety of aryl bromides. It is important to note that aryl
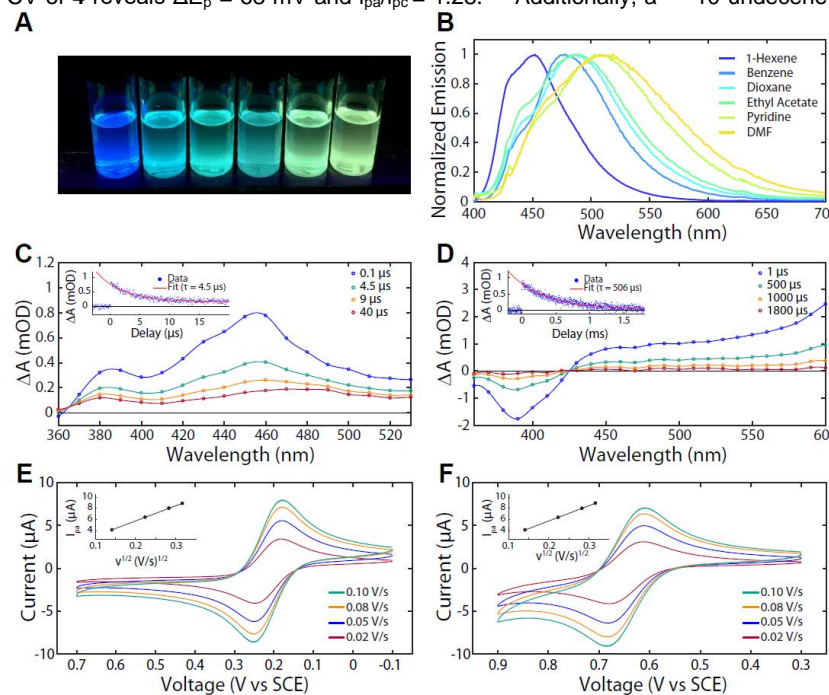
bromide coupling partners were successfully incorporated with organic PC **4**, which were shown to be inactive when using Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆.[34] PC **3** was unsuccessful in C-S coupling reactions, presumably due to its stable radical cation (E^0_{ox} = 0.21 V vs. SCE) being unable to generate a thiol radical involved in the coupling reaction.[34]

These photoredox/nickel C-N and C-S cross-coupling reactions could be driven by natural sunlight to obtain similarly high yield. Furthermore, both the C-N and C-S couplings could be performed on a larger 10 mmol scale reaction for C-N (1.22g, 53% yield) and C-S (2.92g, 98% yield) couplings. In these scaled reactions, C-S coupling maintained the high yield while

C-N coupling suffered a 30% drop in yield. This lower yield was attributed to limited light penetration owing to the opaque solution mixture compounded by the lower molar absorptivity of PC **3**.

In sum, photophysical and electrochemical characterizations on dihydrophenazine and phenoxazine PCs **3** and **4** reveal that these molecules possess the key attributes vital to successful photoredox catalysis, including redox reversibility and strong visible light absorption to efficiently access a highly reducing triplet state through formation of CT excited state. The triplet excited state of these organic PCs are long-lived and accessed in 90% ± 10% quantum yield by PC **4**. Highlighting that **4** is an organic analogue of the iridium complex **1**, both PCs have almost identical E^{0*}, E^0_{ox} and $E_{triplet}$ values. The potential for replacement of polypyridyl iridium and ruthenium complexes by organic PCs **3** and **4** is demonstrated by the ability of these organic analogues to catalyze trifluoromethylations and dual photoredox/nickel C-N and C-S cross-coupling reactions using visible light, including natural sunlight.

†Y. Du, R.M.Pearson and C.-H. Lim contributed equally to this work.

Figure 3. Photoredox catalyzed transformations using organic PCs **3** and **4**. (**A**) Radical trifluoromethylations using PC **3** on alkenes, five-membered heteroarenes, arenes, and cross-addition on alkenes. (**B**) Dual organic photoredox and nickel catalyzed C-N cross-coupling reaction scope. (**C**) Dual organic photoredox and nickel catalyzed C-S cross-coupling scope. Data reported as isolated yields. Values in parentheses are the ratio of Z : E : β-hydride elimination product. ᵃReaction was also conducted using sunlight for 1 week (67% yield for trifluoromethylation, 83% yield for C-N coupling, 94% yield for C-S coupling). ᵇCF₃CF₂I was used instead of CF₃I. ᶜReaction time 6 hours. ᵈReaction was also conducted on a larger 10 mmol scale (73% yield for trifluoromethylation, 53% yield for C-N coupling, 98% yield for C-S coupling). ᵉReaction was also conducted at reduced catalyst loading of 0.25 mol %, instead of standard 1.0 mol % (69% yield for trifluoromethylation, 53% yield for C-N coupling, 98% yield for C-S coupling after 24 hours). ᶠPerformed without HCOOK. ᵍReaction performed with 10 mol % pyrrolidine as the ligand and reduced nickel loading to 1.0 mol %. ʰReaction catalyzed by PC **4**. ᵢReaction catalyzed by PC **3**.

Keywords: photocatalysis • photochemistry • organocatalysis • radicals • sustainable chemistry catalysis

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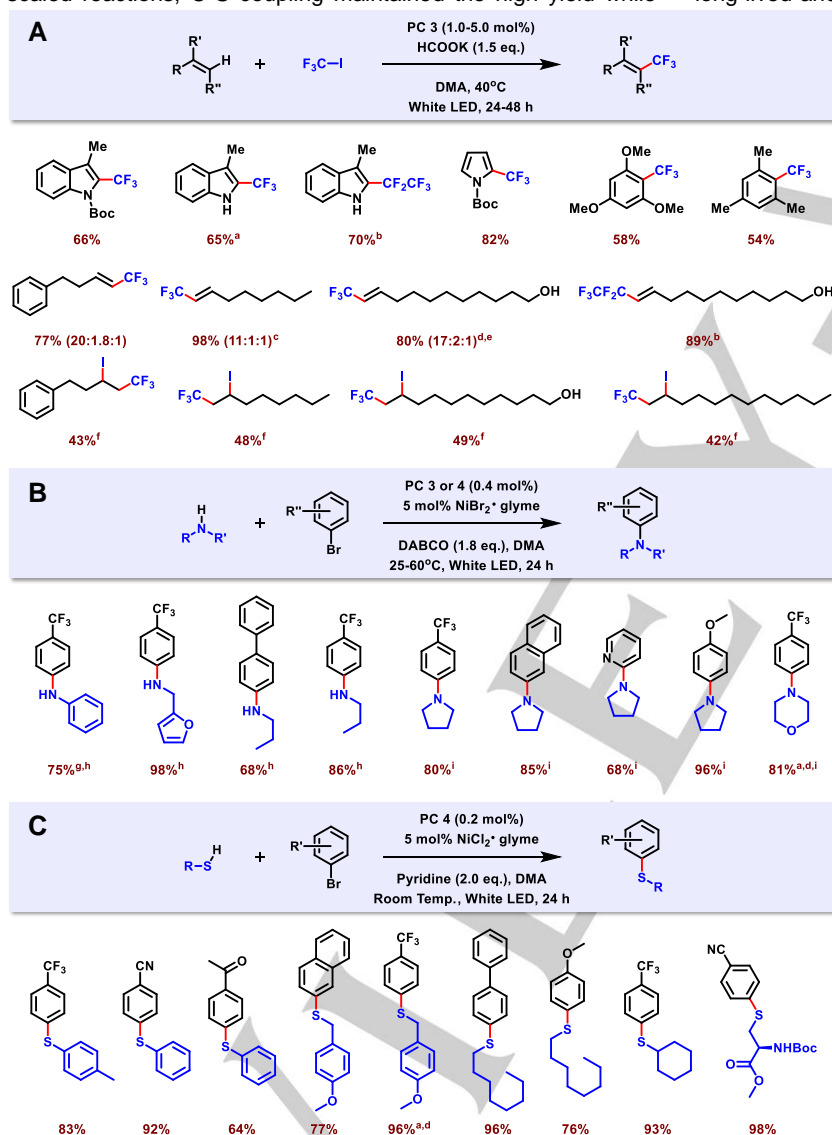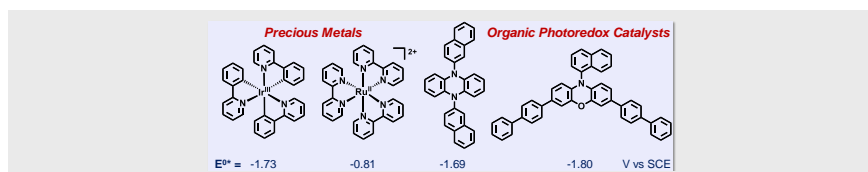
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Precious Metals   *Organic Photoredox Catalysts*

E^{0*} = -1.73   -0.81   -1.69   -1.80   V vs SCE

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Title

The new iridium. The photophysical and electrochemical properties of a strongly reducing phenazine and phenoxazine enable their application as visible light photoredox catalysts to catalyze reactions that were previously restricted to precious metals. These organic visible light photoredox catalysts not only present sustainable alternatives to precious metals, but can possess enhanced properties to their metal counterparts for catalysis.