Strongly Reducing Helical Phenothiazines as Recyclable Organophotoredox Catalysts

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ABSTRACT

Photocatalysts have recently attracted significant interest due to their potential applications in sustainable energy-conversion systems. In organic chemistry, recyclability of photocatalysts are important characteristics with respect to environmental concerns and economic benefits. Metal-based polypyridyl complexes of ruthenium and iridium have been widely used as recyclable homogeneous photoredox catalysts, whereas organophotoredox catalysts are less explored and usually limited to the use of polymer methods. Herein, we report the design and synthesis of recyclable phenothiazine organophotoredox catalysts (**PTHS 1–3**). These catalysts exhibit relatively high excited-state oxidation potentials ($E_{1/2}^{ox*}$ = −2.34 to −2.40 V vs. SCE) that can efficiently promote photoredox reactions via the one-electron reduction of 1,3-bis(trifluoromethyl)benzene and 4-trifluoromethyliodobenzene, which have high reduction potentials ($E_{p/2}$ = −2.07 to −2.16 V vs. SCE). Notably, when the recycling performance was evaluated in the cross-coupling reaction between an aryl halide and triethylphosphite, **PTHS-1** can be recovered at least four times without loss of its catalytic activity. The present recyclable and reusable organophotoredox catalysts thus represent a promising tool for sustainable organic synthesis.
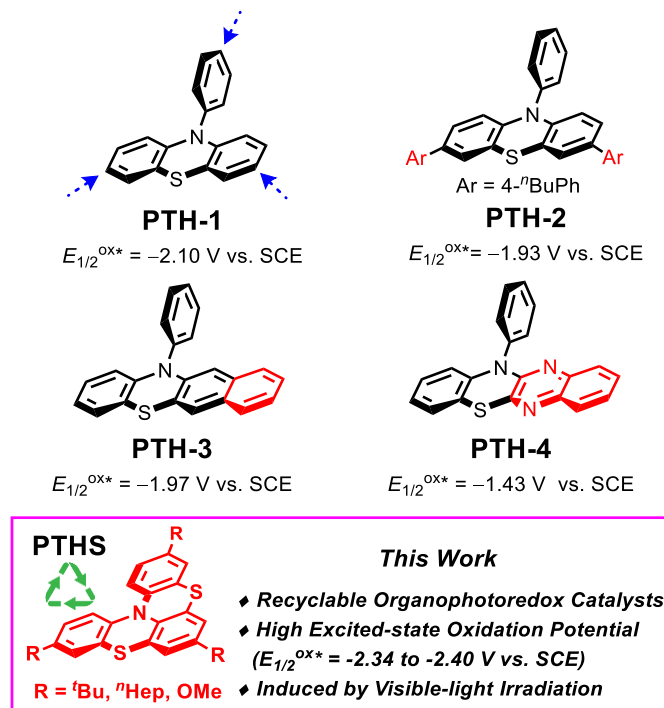
Introduction

Recycling photocatalysts has attracted much attention as a critical factor in emerging chemical technologies in terms of environmental concerns and economic benefits. Homogeneous photocatalysts such as metal-based polypyridyl complexes of ruthenium and iridium as well as organic dyes have been widely used in photoredox catalysis.[1,2] Although recycling metal-based polypyridyl complexes is common, that of organophotoredox catalysts remains much less explored and usually limited to the use of polymer methods.[3,4] Considering that organophotoredox catalysts are cost-effective and of low toxicity, the development of an approach for their recycling is essential in sustainable organic synthesis.

10-Aryl phenothiazines are widely used as photocatalysts for photoredox reactions and atom-transfer-radical-addition polymerizations in organic chemistry (Figure 1; e.g., **PTH-1**).[5] Due to their high excited-state oxidation potentials ($E_{1/2}^{ox*} \approx -2.10$ V vs. SCE), a number of 10-aryl-phenothiazine-catalyzed photoredox reactions that proceed via oxidative quenching cycles have been developed.[6] However, the high reactivity of the *p*-position relative to the nitrogen atom on 10-aryl phenothiazines renders these prone to react with electrophiles.[7] Thus, several modified 10-aryl phenothiazine catalysts have recently been explored (Figure 1; **PTH 2–4**).[8] Despite these advances, the development of more stable and sustainable photoredox catalysts remains highly desirable.

To explore the recyclability of organophotoredox photocatalysts, we have designed and synthesized recyclable phenothiazine organophotoredox catalysts (Figure 1; **PTHS**). The catalyst design is based on the following considerations: i) to increase the stability and reducing properties, bulky and electron-donating groups such as the *t*Bu group are introduced at the *p*-position relative to the nitrogen atom on the phenothiazine catalysts; ii) to absorb visible light and increase the stability, the phenothiazine catalysts are endowed with a thia-bridged helically shaped structure.
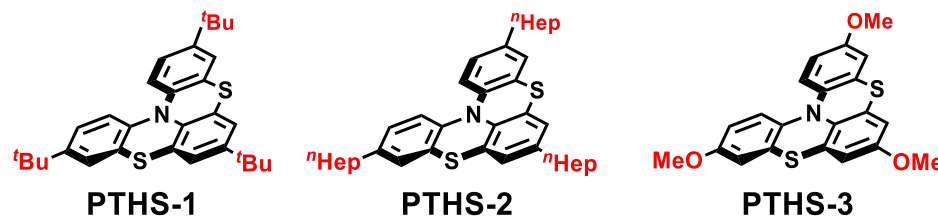
Figure 1. Representative Phenothiazine Catalysts

PTH-1
$E_{1/2}^{ox*} = -2.10$ V vs. SCE

Ar = 4-^{n}BuPh
PTH-2
$E_{1/2}^{ox*} = -1.93$ V vs. SCE

PTH-3
$E_{1/2}^{ox*} = -1.97$ V vs. SCE

PTH-4
$E_{1/2}^{ox*} = -1.43$ V vs. SCE

PTHS

This Work
- *Recyclable Organophotoredox Catalysts*
- *High Excited-state Oxidation Potential ($E_{1/2}^{ox*} = $ -2.34 to -2.40 V vs. SCE)*
- *Induced by Visible-light Irradiation*

R = ^{t}Bu, ^{n}Hep, OMe

Results and Discussion

We initially synthesized a series of phenothiazine catalysts (**PTHS 1–3**) in short steps and moderate yield using commercially available starting materials to probe the relationship between their structure and physical properties (Table 1).[9,10] Interestingly, we found that these catalysts have high excited-state oxidation potentials ($E_{1/2}^{ox*} = -2.34$ to -2.40 V vs. SCE) compared to other phenothiazine catalysts such as **PTH 1–4**. Therefore, **PTHS 1–3** were expected to reduce various substrates via oxidative quenching cycles. In addition, the **PTHS** catalysts exhibit an absorption band in the visible spectrum, which indicates that they can be activated by visible light.

With these promising results in hand, we applied the **PTHS** catalysts to various types of photoredox reactions. First, we examined the three-component oxytrifluoromethylation of 1,1-diphenylethylene (**2**; Table 2).[11] The reactions proceeded smoothly in the presence of a catalytic amount of **PTHS 1–3** (1.0 mol%) to give the desired product (**3**) in good yield. Blank experiments in the absence of a catalyst or light confirmed that the reaction requires a **PTHS** catalyst and irradiation with blue LED to proceed.[9] Since the **PTHS** catalysts have high excited-state oxidation potentials, the CF$_3$ radical was smoothly generated from Umemoto's reagent (**1**; $E_{p/2} = -0.25$ V vs. SCE)[12] and then reacted with **2** to give the desired product (**3**). This organophotocatalytic reaction is significantly more cost-effective and sustainable compared to previously reported methods based on transition-metal catalysts.[11]

**Table 1. Synthesis and Physical Properties of PTHS Organophotoredox Catalysts**

Catalyst	$E_{1/2}(C^{\bullet+}/C^*)^a$ (V)	$E_{1/2}(C^{\bullet+}/C)^b$ (V)	$E_{0,0}$ (eV)	Excitation λ_{max} (nm)	Emission λ_{max} (nm)
PTHS-1	−2.34	0.86	3.20	317	449
PTHS-2	−2.35	0.80	3.15	316	460
PTHS-3	−2.40	0.64	3.04	314	475

[a] Excited-state oxidation potentials were estimated on the basis of the ground-state redox potentials and the intersection of the absorption and emission bands. [b] Determined by cyclic voltammetry in CH_2Cl_2 vs. SCE.[9]

Next, we investigated a visible-light-mediated decarboxylative C(sp³)–O bond formation (Table 3). Nagao and Ohmiya have already reported that **PTH-3** catalyzes the decarboxylative coupling between aliphatic alcohol **5** and redox-active esters such as **4** ($E_{p/2}$ = −1.08 V vs. SCE).[8b] It thus seems feasible to speculate that the **PTHS** catalysts might also be applied to the decarboxylative C(sp³)–O bond formation from ester **4** to provide the corresponding ether (**6**) in moderate yield.

The results of the defluoroalkylation of 1,3-bis(trifluoromethyl)benzene (**7**) with unactivated alkenes are shown in Table 4.[13] When **7** ($E_{p/2}$ = −2.07 V vs. SCE) was treated with 3-buten-1-ol (**8**) in the presence of **PTHS-1** and **PTHS-2**, the reaction proceeded effectively to give **9** in moderate to good yields (Table 4, entries 1 and 2). In contrast, **PTHS-3** could not be applied to the reaction (Table 4, entry 3). Since the excited-state oxidation potential of **PTH-3** is lower than the reduction potential of **7**, the reaction with **PTH-3** was also inefficient (Table 4, entry 4).

Subsequently, we investigated the photoredox cross-coupling reaction between 4-trifluoromethyliodobenzene (**10**) and triethylphosphite in the presence of the **PTHS** catalysts, which afforded aromatic phosphonate **11** in good yield (Table 5).[14] Although **10** has a high reduction potential ($E_{p/2}$ = −2.16 V vs. SCE),[15] the single-electron transfer from the **PTHS** catalysts to **10** is energetically favorable due to the high excited-state oxidation potentials of the **PTHS** catalysts ($E_{1/2}^{ox}$* = −2.34 to −2.40 V vs. SCE). Accordingly, the **PTHS** catalysts are suitable for photoredox reactions via oxidation-quenching cycles.

**Table 2. Three-component Oxytrifluoromethylation of 1,1-Diphenylethylene[a]**
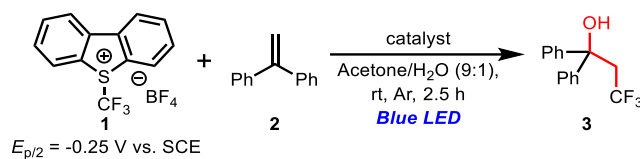
Entry	Catalyst	Yield (%)
1	**PTHS-1**	79
2	**PTHS-2**	72
3	**PTHS-3**	80

[a] All reactions were carried out with **1** (0.105 mmol), **2** (0.1 mmol), and catalyst (1.0 mol%) in acetone/H_2O (9:1, v/v) at room temperature under an Ar atmosphere and blue-light irradiation.

**Table 3. Decarboxylative C(sp^3)–O Bond Formation[a]**
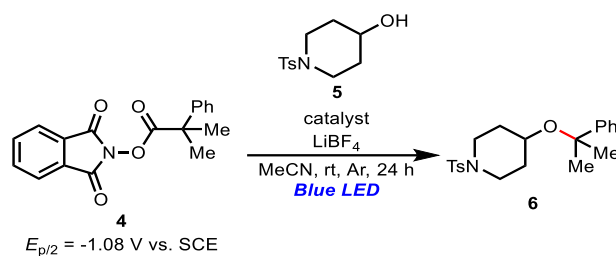
Entry	Catalyst	Yield (%)
1	**PTHS-1**	60
2	**PTHS-2**	48
3	**PTHS-3**	40

[a] All reactions were carried out with **4** (0.2 mmol), **5** (0.6 mmol), LiBF$_4$ (10 mol%), and catalyst (10 mol%) in MeCN at room temperature under an Ar atmosphere and blue-light irradiation.

Table 4. Defluoroalkylation of 1,3-Bis(trifluoromethyl)benzene[a]

$E_{p/2}$ = -2.07 V vs. SCE
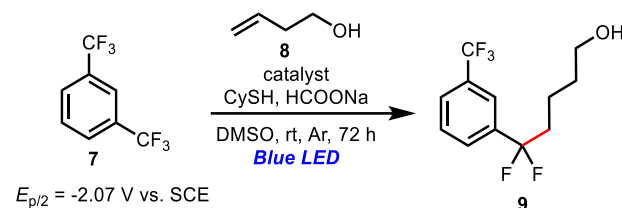
| Entry	Catalyst	Yield (%)
1	**PTHS-1**	83
2	**PTHS-2**	47
3	**PTHS-3**	trace
4	**PTH-3**	6

[a] All reactions were carried out with **7** (0.1 mmol), **8** (0.3 mmol), cyclohexane thiol (10 mol%), sodium formate (0.3 mmol), and catalyst (10 mol%) in DMSO at room temperature under an Ar atmosphere and blue-light irradiation.

Table 5. Photoredox Cross-coupling Reaction of 4-Trifluoromethyliodobenzene with Triethylphosphite[a]

$E_{p/2}$ = -2.16 V vs. SCE
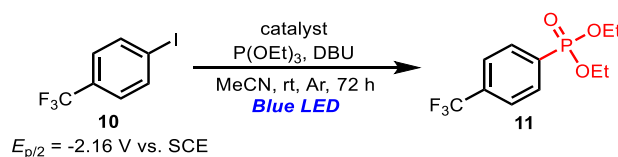
Entry	Catalyst	Yield (%)
1	**PTHS-1**	77
2	**PTHS-2**	78
3	**PTHS-3**	78

[a] All reactions were carried out with **10** (0.1 mmol), triethylphosphite (0.3 mmol), DBU (0.2 mmol), and catalyst (10 mol%) in MeCN at room temperature under an Ar atmosphere and blue-light irradiation.

**Scheme 1. Photochemical Sulfonylation of Phenothiazines[a]**
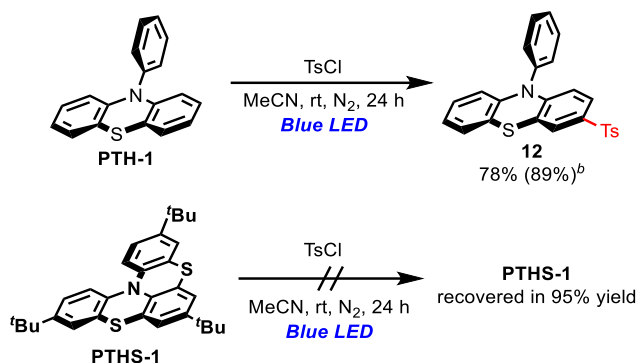
[a] All reactions were carried out with phenothiazines (0.2 mmol) and tosyl chloride (TsCl; 0.2 mmol) in MeCN at room temperature for 24 h under an N_2 atmosphere and blue-light irradiation. [b]Previously reported product yield.[7]

To examine the stability of the catalysts, we carried out the photochemical sulfonylation of **PTH-1** and **PTHS-1** (Scheme 1). When **PTH-1** was treated with tosyl chloride (TsCl) under irradiation from blue LEDs, monosulfonylated **12** was obtained in 78% yield due to the high reactivity of the *p*-position relative to the nitrogen atom in 10-aryl phenothiazines.[7a] In contrast, the **PTHS-1** catalyst was effectively recovered in 95% yield, proving that the presence of *t*Bu groups increases the catalyst stability. Therefore, the **PTHS-1** catalyst is applicable to various photoredox reactions, which cannot be effectively achieved by hitherto reported phenothiazine catalysts.

The high stability of **PTHS-1** also prompted us to investigate its recycling performance (Table 6). After completion of the cross-coupling reaction of **10** with triethylphosphite, **PTHS-1** was collected via extraction with EtOAc and column chromatography, and the ability of recycled **PTHS-1** to catalyze the reaction was examined. **PTHS-1** could be recovered at least four times without loss of its catalytic activity. Thus, **PTHS-1** is demonstrably a recyclable organophotocatalyst and suitable for sustainable synthetic methods.

Finally, when the reaction was performed on the gram scale, the desired product was obtained in 85% yield (1.20 g) with 96% recovery of **PTHS-1** (Scheme 2). Thus, **PTHS-1** is a highly active catalyst with high recoverability even when used on the gram scale.

Table 6. Recycling Performance of PTHS-1[a]

$E_{p/2}$ = -2.16 V vs. SCE
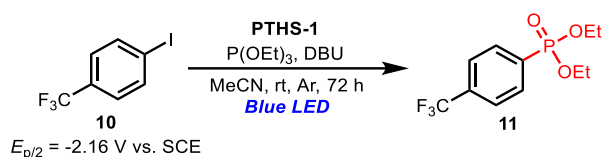
Run	1	2	3	4
Yield (%)	77	78	75	79

[a] All reactions were carried out with **10** (0.1 mmol), triethylphosphite (0.3 mmol), DBU (0.2 mmol), and **PTHS-1** (10 mol%) in MeCN at room temperature under an Ar atmosphere and blue-light irradiation.

Scheme 2. Gram-scale Photoredox Cross-coupling Reaction of 4-Trifluoromethylbenzene with Triethylphosphite[a]
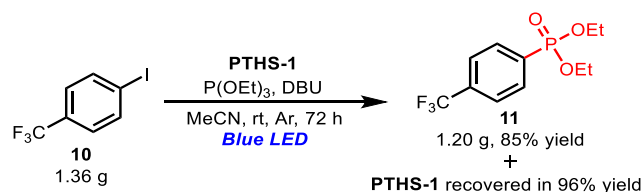
[a] The reaction was carried out with **10** (5.0 mmol), triethylphosphite (15.0 mmol), DBU (10.0 mmol), and **PTHS-1** (10 mol%) in MeCN at room temperature under an Ar atmosphere and blue-light irradiation.

In summary, we have developed strongly reducing and recyclable phenothiazine organophotoredox catalysts (**PTHS 1–3**) that can be activated by visible light. These catalysts exhibit relatively high excited-state oxidation potentials ($E_{1/2}^{ox}$* = −2.34 to −2.40 V vs. SCE), which can efficiently promote four photoredox reactions via oxidative-quenching cycles in good yields. The presence of *t*Bu groups in the **PTHS-1** catalyst increases its stability, thus enabling its recovery under photochemical sulfonylation conditions, outperforming previously reported phenothiazine catalysts for such photoredox reactions. In fact, **PTHS-1** can be recovered at least four times without loss of its catalytic activity in the cross-coupling reaction of 4-trifluoromethyliodobenzene ($E_{p/2}$ = −2.16 V vs. SCE), highlighting its potential for sustainable photocatalysis. Moreover, when the reaction was performed on a gram scale, the desired product was obtained in 85% yield (1.20 g) with 96% recovery of **PTHS-1**.

These recyclable organophotoredox catalysts thus represent a promising tool for sustainable organic synthesis.

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Note

The authors declare no competing financial interest.

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