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Trifluoroethoxy-Coated Subphthalocyanine affects Trifluoromethylation of Alkenes and Alkynes even under Low-Energy Red-Light Irradiation

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Photoredox chemical reactions induced by visible light have undergone a renaissance in recent years. Polypyridyl dyes such as Ir(ppy)$_3$ and Ru(bpy)$_3$ are key catalysts in this event, and blue- or white-light irradiation is required for the chemical transformations. However, it remains a challenge to achieve reactions under the lower energy of red light. We disclose, herein, that trifluoroethoxy-coated subphthalocyanine realizes the red-light-driven trifluoromethylation of alkenes and alkynes with trifluoromethyl iodide in good-to-high yields. Perfluoroalkylations were also achieved under red light. The reaction mechanism is discussed with the support of UV/Vis spectroscopy and cyclic voltammetry of trifluoroethoxy-coated subphthalocyanine. Light irradiation/dark study also supports the proposed mechanism.

Visible-light-mediated chemical transformations of organic molecules under photoredox catalysis has dramatically changed the realm of photochemical reactions in organic synthesis. Classical photochemical reactions under ultraviolet (UV)-light irradiation often damage substrates/products, resulting in undesired complex mixtures.[1] Owing to the high energy of UV irradiation (290–366 nm), control of the reaction is problematic, and thus careful and strict design of substrates/reactions is required.[1] More importantly, UV light is toxic. On the other hand, visible light is a longer wavelength light with lower energy (380–780 nm), and chemical transformations proceed efficiently under mild conditions in the presence of photoredox catalysts.[2] Polypyridyl dyes complexed with transition metals, such as Ir(ppy)$_3$ and Ru(bpy)$_3$, are the most powerful catalysts when irradiated by visible light. Although these photoredox systems are mild, high-energy photon sources such as blue light (400–500 nm) are still necessary for the chemical transformations.[2] In addition, there is a risk of photo-oxidative damage to eyes (retina) by the blue light.[3] Green light (500 nm), however, is one-tenth as hazardous to the retina as blue light.[4]

The move towards an “all-green” process by using lower power light for chemical reactions remains a challenge to achieve non-toxic, eco-friendly, mild, and selective transformations. In this context, red light has gained attention for its application in “greener” visible-light photoredox reactions.[5] Red light has the benefits of low power (600–700 nm), no risk of light hazard, and cheap lamps. More interestingly, it penetrates even bulk turbid media. Although versatile photocatalytic systems have been well researched to date, there are very few examples of the application of red light for organic synthesis, owing to a poor range of absorption windows for general photocatalysts [5] (e.g. maximum excitation wavelengths of $\lambda_{em}=$ 452 nm for Ru(bpy)$_3$,[6] 375 nm for *fac*-Ir(ppy)$_3$,[7] and 539 nm for eosin Y).[8] To expand the utilizable wavelength range of visible light for photochemical reactions, an Os^{II}/Re^{I} supramolecular complexed photosensitizer was designed for red-light-driven photocatalytic reactions.[9] This system is limited to the reduction of CO$_2$ and the catalyst requires a multi-step synthesis.

Phthalocyanines **1** are dyes with the most potential to be red-light-driven photocatalysts, owing to their absorption bands at around 600–700 nm,[10] followed closely by subphthalocyanines **2** at 500–600 nm.[11] However, the poor solubility of **1** and the instability of **2** strictly limit their utility in organic reactions.[12] Our group has researched a series of trifluoroethoxy-coated phthalocyanines and subphthalocyanines for the photodynamic therapy of cancer and electronic materials (Figure 1 a).[13] Drawing motivation form this background, we decided to develop a new utility of **1** and **2** for the photoredox catalytic system, especially under the low energy of red light. Trifluoromethylation is an attractive target reaction under a photoredox system.[14] Indeed, trifluoromethylation reactions induced by visible light constitute a recent breakthrough in organic chemistry.[15] However, all of the reported methods for trifluoromethylation reactions strictly require high-energy photon sources such as blue light-emitting diode (LED) photoirradiation (Figure 1 b). Before the completion of our research, You and co-workers reported the first attempt at the photoredox catalytic generation of trifluoromethyl radicals under low-energy photoirradiation.[16] Metal–porphyrins were selected for the trifluoromethylation of alkenes with trifluoromethyl iodide (CF$_3$I) by using LEDs. In the presence of oxalate, Pt–porphyrin was best for this transformation under green LEDs, but the substrate scope was narrow and limited, yields were low to

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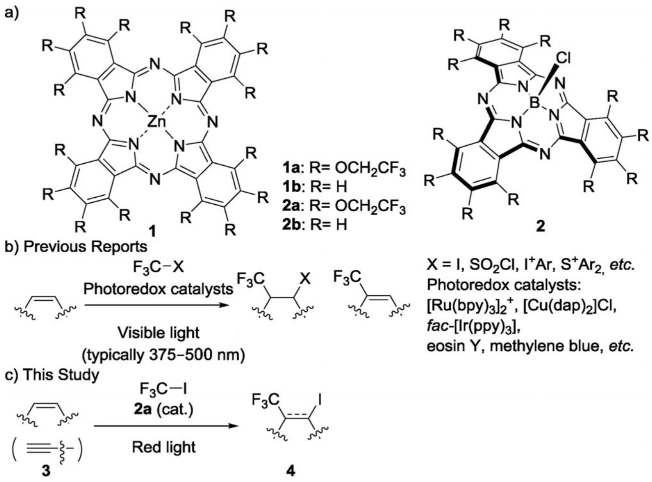
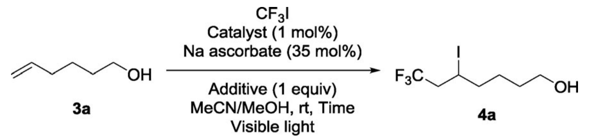


Figure 1. a) Structures of phthalocyanines **1** and subphthalocyanines **2**. b) Photoredox trifluoromethylation under visible light (previous reports). c) This work of photoredox trifluoromethylation under red light.

Table 1. Optimization of trifluoromethylation of alkene 3a with CF_3I under visible-light irradiation mediated by photoredox catalysts.[a]



Run	Catalyst	LED	Additive	Time [h]	Yield [%][b]
1	$[Ru(bpy)_3](PF_6)_2$	red	–	6	<5
2	Eosin Y	red	–	6	<5
3	Methylene blue	red	–	6	<5
4	**1a**	red	–	6	12
5	**1b**	red	–	6	<5
6	**2a**	red	–	6	92
7[c]	**2a**	red	–	3	62
8[c]	**2a**	red	–	1	35
9	**2b**	red	–	6	<5
10[c]	**2a**	red	LiBr	1	65
11[c]	**2a**	red	NaOAc	1	99
12[c]	**2a**	red	LiOAc	1	99
13[c]	**2a**	red	CsOAc	1	99
14[c]	**2a**	red	NaOAc[d]	1	96
15[c]	–	red	NaOAc	3	<5
16[e]	**2a**	red	NaOAc	3	<5
17[c]	**2a**	–[f]	NaOAc	3	<5
18	**2a**	white	–	0.5	90

[a] The reaction of alkene **3a** (0.25 mmol) with CF_3I (excess) was carried out in the presence of **1** or **2** (0.0025 mmol) and sodium L-ascorbate (0.0875 mmol) in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature. [b] Yields were determined by using ^{19}F NMR spectra of the crude product with $PhCF_3$ as an internal standard. [c] 5 mol% of Na ascorbate was used. [d] 20 mol% of NaOAc was used. [e] In the absence of Na ascorbate. [f] The reaction was carried out in the dark.

moderate, and products were mixtures of trifluoromethyl alkenes and trifluoromethylethyl iodides. Moreover, red LEDs were not as efficient as green LEDs when using metal–porphyrins.[16] We, herein, disclose that trifluoroethoxy-coated subphthalocyanine **2a** dramatically catalyzes the trifluoromethylation of alkenes **3**, including alkynes with CF_3I, under red-light-driven photoredox conditions to provide the corresponding trifluoromethylethyl iodides **4** in a short space of time and with very high yields (Figure 1c). The reaction mechanism is discussed based on cyclic voltammetry and the absorption spectra of **2a**.

We first investigated the trifluoromethylation of hex-5-en-1-ol (**3a**) with CF_3I by using various photocatalysts under red-light irradiation (Table 1). Following an earlier report by Stephenson and co-workers, a catalytic amount of sodium L-ascorbate (35 mol%) was used as the initial reductant in a MeCN/MeOH system.[15b,17] Apparently, in the red-light-driven system, powerful photocatalysts such as $[Ru(bpy)_3](PF_6)_2$, eosin Y, and methylene blue were completely useless (runs 1–3). We next examined the reaction using trifluoroethoxy-coated phthalocyanine **1a**. To our disappointment, the desired 6-trifluoromethyl-5-iodohexan-1-ol (**4a**) was obtained only in 12% yield (run 4). The performance of non-substituted phthalocyanine **1b** was even worse (run 5). We, thus, reverted to our second choice of catalyst, subphthalocyanines **2**. We were excited to observe that trifluoroethoxy-coated subphthalocyanine **2a** was very effective for the transformation of **3a** with CF_3I under red LED irradiation for 6 h, furnishing **4a** in a high yield of 92% (run 6). The yields decreased to 35% with 5 mol% of sodium L-ascorbate in a shorter reaction time (runs 7 and 8). The reaction was not catalyzed by non-substituted subphthalocyanine **2b** (run 9); thus, the effect of the trifluoroethoxy coating on **2** is obvious. The trifluoroethoxy effect should increase the solubility and stability of subphthalocyanine.[13b] We next examined the effect of additives on the reaction. Stephenson and co-workers reported that LiBr affects the atom-transfer radical addition (ATRA) of CF_3I to alkenes as Lewis acid.[15b,f] Indeed, an improvement was observed to 65% within 1 h (run 10). It should be noted that the yield and reaction time improved further in the presence of sodium acetate, even within 1 h (run 11, 99%). This phenomenon is in good agreement with the report by Sajiki and co-workers that sodium acetate is an efficient auxiliary agent for the radical pathway of ATRA of fluoroalkyl iodine to olefins in thermal conditions.[18] The same effect was observed by using lithium acetate and cesium acetate (runs 12 and 13). The amount of sodium acetate could also be reduced (run 14, 96%). In the control experiment, the reaction did not take place without **2a**, sodium ascorbate or red light (runs 15–17). Additional optimization of reaction conditions, including screening of additives and solvents, are shown in Table S1. We also attempted the transformation of **3a** under the stronger energy light of white LED irradiation in the presence of **2a**. The reaction proceeded very smoothly to provide **4a** in 90% yield (run 18). These results indicate that trifluoroethoxy **2a** catalyzes the photoredox reaction under the low energy of red LED, whereas non-fluorinated **2b**, phthalocyanines **1a**, and **1b** are entirely useless.

Although the effect of light was clear (Table 1, run 17), a further investigation was attempted to confirm the necessity of light to maintain the transformation or whether it was only required to initiate a reaction, according to a light irradiation/dark study (Scheme S1). These results clearly indicate that the light must be maintained during the transformation as well.

The effectiveness of **2a** rather than **1a**, **1b**, or **2b**, can be explained by the UV/Vis spectra of catalysts and LED lights. The UV/Vis spectra of **1** and **2** were recorded in MeCN/MeOH and/or 1,4-dioxane at a concentration of 1×10^{-5} M, depending on the solubility (Figure 2, also see Figure S1). Their Q bands were slightly blue shifted in MeCN/MeOH compared to 1,4-dioxane, but the differences were small. These spectra indicate that all phthalocyanines **1** and subphthalocyanines **2** were present solely as monomers and were characterized by sharp absorption bands in the Q-band region. Strong absorption peaks were observed at 710 or 703 nm for **1a**, 666 nm for **1b**, 603 and 598 nm for **2a**, and 563 nm for **2b**. On the other hand, white LEDs showed broad spectrum of 430–700 nm with two peaks, and red LEDs displayed a sharp absorption at 600–650 nm. These results suggest that the absorption of **2a** shows a suitable overlap with red LEDs, resulting in a 99 % yield of **4a**, whereas catalysts **1b** and **2b** were useless, owing to the lack of overlapping spectra. The 12 % formation of **4a** from **1a** is reasonable, as **1a** has an overlapping shoulder peak at 638 or 632 nm. White LEDs are effective enough for the activation of **2a** with a wide range of overlapping spectra.

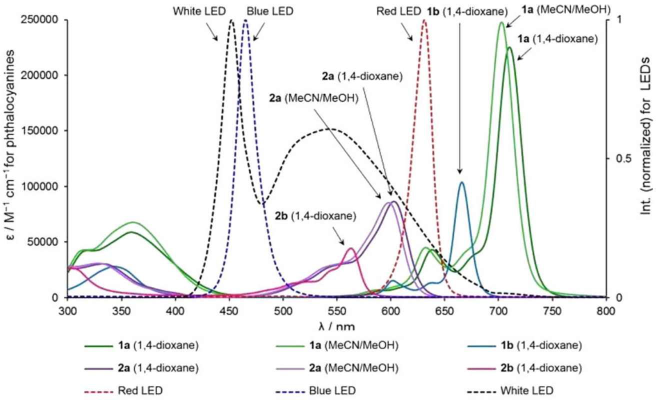
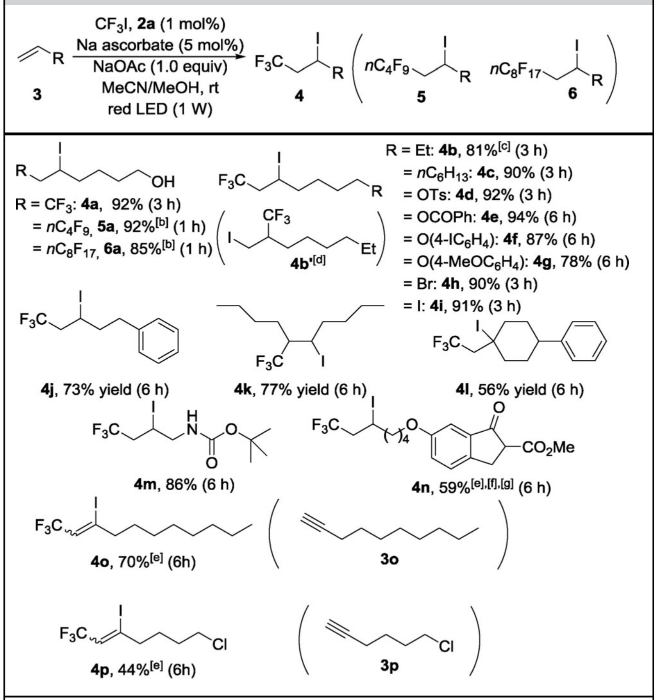


Figure 2. UV/Vis spectra of phthalocyanines **1** and subphthalocyanines **2** at 1×10^{-5} M and absorption of blue, white, and red LEDs.

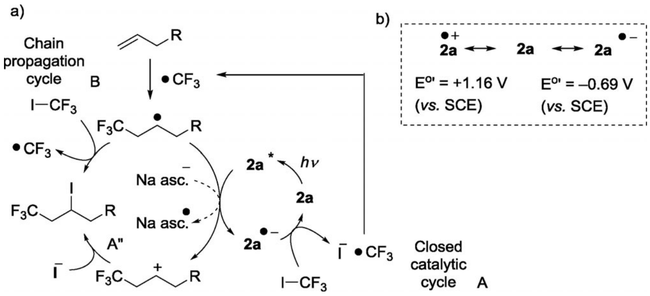
With the optimized conditions under red light in hand, the substrate scope of **3** was investigated (Table 2). Terminal olefin-like **3a**–**j** finely reacted with CF_3I to afford the desired adducts **4a**–**j** under the red-light-induced photocatalytic system by using **2a**. Common functional groups such as tosyl **3d**, ester **3e**, alkyl- and aryl-halide **3f**, **h**, **i**, carbamate **3m**, and electron-rich aromatic groups **3g** were tolerated under these conditions. Internal olefin **3k** and *exo*-olefin **3l** also gave good yields. The alkene **3n**, appending a β-keto ester functionality, reacted selectively with CF_3I at the olefinic moiety to provide **4n** (66 % ^{19}F NMR yield and 59 % isolated yield), whereas the active methylene of **3n** was touched with only 2 % ^{19}F NMR yield. The result is worth noting, because the β-keto esters reacted with CF_3I under white LEDs or radical conditions.[19] Not only alkenes **3**, but also alkynes **3o** and **3p**, were converted into the corresponding adducts **4o** and **4p** in 70 and 44 % yield, respectively. In all cases, the regioselectivity was almost perfect and only a trace amount of regioisomers, such as **4b′**, were observed in the ^{19}F NMR (< 4 % as a doublet at around δ-70 ppm in the ^{19}F NMR analysis). The red-light methodology was extended to the perfluoroalkylation of **2a** using nC_4F_9-I and nC_8F_{17}-I to give perfluoroalkylation adducts **5a** and **6a** in 92 and 85 %, respectively. Although the reaction has a wide scope, electron-deficient alkenes and styrene were not accepted.

Table 2. Substrate scope of trifluoromethylation of alkenes **3** with **2a** catalysis under red-light irradiation.[a]



[a] The reaction of alkenes **3** (0.25 mmol) with CF_3I (26–29 equiv) was carried out in the presence of **2a** (0.0025 mmol), sodium L-ascorbate (0.0125 mmol), and sodium acetate (0.25 mmol) in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature. [b] R_FI (1.5 equiv) was employed. [c] **4d**/**4d′** = > 25:1. [d] The minor isomer **4b′** was characterized through the total synthesis of **4b′** by using a different method (see the Supporting Information). [e] 35 mol % of sodium L-ascorbate was used without the addition of sodium acetate. [f] ^{19}F NMR yield of **4n** is 66 %. [g] 2 % of α-trifluoromethylated β-keto ester was observed in the crude ^{19}F NMR.

A plausible reaction mechanism involving both a closed catalytic cycle A and chain propagation cycle B was proposed (Scheme 1) with the support of cyclic voltammetry of **2a** (Figure S2). Earlier reports of CF_3-I ATRA reactions have shown that the reaction is based on an effective radical chain reaction that can be initiated through visible-light irradiation even without photocatalysts;[20] however, our system requires both photocatalyst **2a** (run 15, Table 1) and light (run 17, Table 1). Thus, in the initial step, photo-excited trifluoroethoxy subphthalocyanine **2a** receives one electron from sodium ascorbate to form an anion radical of **2a**.[15b,17] The anion radical [$E^{o\prime}(\mathbf{2a}/\mathbf{2a}^{\cdot-}) = -0.69$ V vs. SCE] should reduce CF_3I ($E^{o\prime} = -1.22$ V vs. SCE)[21] to generate the CF_3 radical ($\cdot CF_3$) (Scheme S3). Although this reduction process is a thermodynamically unfavorable electron transfer[22] from the reduced photocatalyst to CF_3I (about



Scheme 1. a) Plausible reaction mechanism for the trifluoromethylation of alkene **3**. b) Redox potential of **2 a** vs. SCE in MeCN at room temperature.

0.5 V), sodium ascorbate and/or sodium acetate presumably acts as a Lewis acid to support this step through the activation of the carbon–iodine (C–I) bond to overcome this conflict. This suggestion is partially supported by the result of the LiBr effect (run 10, Table 1), which is in good agreement with the report by Stephenson and co-workers.[15b,f] Next, the CF_3 radical attacks the double bond to furnish a radical intermediate. The radical species has enough reductive potential ($E^{o\prime} = +0.47$ V vs. SCE for secondary alkyl radical)[23] to regenerate an active radical anion species of the catalyst **2 a** to follow the closed catalytic cycle A. This is the reason for the usage of a catalytic amount of sodium ascorbate.[15b,17] Another possibility for the mechanism is that the addition of CF_3-I to alkenes may proceed through a self-propagating radical chain mechanism, in which the alkyl radical abstracts the iodine atom of CF_3I to generate the product and a CF_3 radical as the chain carrier (the classical ATRA manifold). The effect of sodium acetate (run 11, Table 1) strongly supports the contribution of the chain propagation mechanism B reported by Sajiki and co-workers.[18] As light irradiation is required not only for the initiation of the reaction (run 17, Table 1), but also to maintain the reaction (Scheme 1), both the closed catalytic cycle A and the chain propagation cycle B would be involved in this transformation.[24] Further mechanistic studies should be required to elucidate the mechanism.

In conclusion, we have disclosed that trifluoroethoxy-coated subphthalocyanine **2 a** is an efficient photoredox catalyst for the trifluoromethylation of alkenes and alkynes **3** under red light. Although a variety of photocatalysts have been reported, they require blue- or white-light irradiation for chemical transformation, and are unreactive under the low energy of red light. Trifluoroethoxy-subphthalocyanine **2 a** is activated under either red or white light. As red light is much "greener" than white or blue light, this strategy is likely to be increasingly used in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: photoredox catalysis · phthalocyanine · red light · subphthalocyanine · trifluoromethylation

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COMMUNICATIONS

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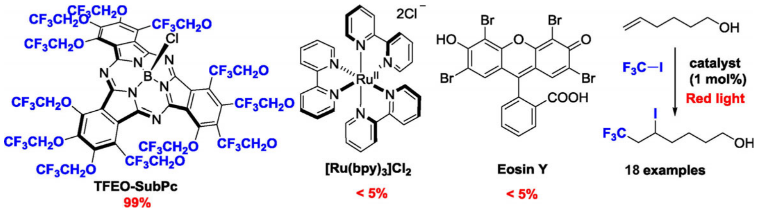
Trifluoroethoxy-Coated Subphthalocyanine affects Trifluoromethylation of Alkenes and Alkynes even under Low-Energy Red-Light Irradiation



Red is the new “green”! Trifluoroethoxy-coated subphthalocyanine (TFEO-SubPc) realizes red-light-driven trifluoromethylation of alkenes and alkynes with trifluoromethyl iodide in good-to-high yields. The reaction mechanism is discussed with the support of UV/Vis spectra and cyclic voltammetry of TFEO-SubPc.