



Green-light-driven thioxanthylum-based organophotoredox catalysts: Organophotoredox promoted radical cation Diels–Alder reaction

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ARTICLE INFO

Article history:

Received 2 April 2018

Revised 24 July 2018

Accepted 27 July 2018

Available online 27 July 2018

Keywords:

Organophotoredox catalyst

Green light

Thioxanthylum

Radical cation Diels–Alder reaction

ABSTRACT

Thioxanthylum-based organophotoredox catalysts that operate under irradiation with green light have been developed. These catalysts present high excited-state reduction potentials ($E_0'(C^*/C^-) = +1.79$ – 1.94 V vs SCE). They are able to efficiently activate dienophiles under green or blue light irradiation afforded the targeted radical cation Diels–Alder cycloadducts in good yields. The present thioxanthylum-based catalysts provide a new green-light-driven photoredox catalysis system.

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1. Introduction

Chemical transformations mediated by visible light have attracted much attention due to their potential in sustainable energy-conversion systems. The current global situation with regard to the balance between the demand and supply of energy and its associated environmental implications could be ameliorated by developing clean systems for the chemical conversion of solar energy [1]. In organic synthesis, photoredox catalysts can be used to carry out a wide variety of organic transformations (Fig. 1) [2]. Polypyridyl complexes of ruthenium and iridium are among the most widely used photoredox catalysts, as they usually exhibit high activity and versatility [3]. However, such iridium and ruthenium catalysts are usually toxic and expensive. In light of the disadvantages associated with noble-metal-based catalysts, the recent focus of interest has shifted toward the development of metal-free photoredox catalysts, which represent a more cost-effective and sustainable approach [4]. Despite the promising properties of recently reported catalysts, including metal-based and metal-free photoredox catalysts, these normally suffer from narrow absorption windows and require the use of high-energy light sources. On the other hand, green light is of lower energy (500–600 nm) than blue and ultraviolet, thus efficiently reducing the risk of retinal damage and stress [5]. Eosin Y is the most widely used organic photoredox catalyst using green light as the irradiation source, and it can be employed in a wide variety of organic

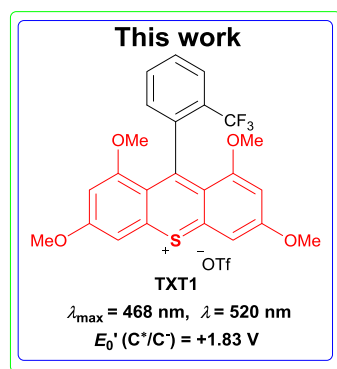
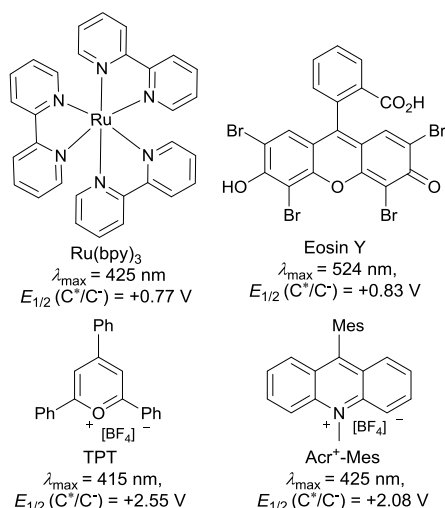
transformations [6]. However, despite its utility, it suffers from a low excited-state reduction potential, which narrows the scope of substrates, and from poor solubility in common organic solvents. Moreover, to the best of our knowledge, only a few green-light-activated photoredox catalysts have been reported, despite the desirability of this approach [7].

Thioxanthylum is a useful compound in the material and biological fields [8]. It is known that thioxanthylum has absorption in green region [9]. However, 1-, 3-, 6- and 8-positions of thioxanthylum are amenable to be attacked by nucleophiles, and benzene group at the 9-position is a key substituent group for stabilizing thioxanthylum core [10]. Then, in order to expand the utility of photoredox catalysts, we report herein thioxanthylum-based organophotoredox catalysts that operate under irradiation with green or blue light. These organophotoredox catalysts afford radical cation Diels–Alder cycloadducts in high yields.

We initially synthesized a series of thioxanthylum salts to probe the relationship between the structure and physical properties of these novel catalysts (Table 1). Their synthesis was accomplished through the reaction of a thioether that was treated in chlorobenzene at 120 °C for 1 h with benzoyl chloride in the presence of TfOH. These catalysts exhibit high excited-state reduction potentials ($E_0'(C^*/C^-) = +1.79$ – 1.94 V vs SCE). The substrate scope of such catalysts should therefore be larger than that of eosin Y ($E_{1/2}(C^*/C^-) = +0.83$ V vs SCE) [6]. Importantly, these thioxanthylum salts exhibit an absorption band in the blue/green region of the visible spectrum (~400–600 nm), which indicates that these catalysts may be activated by visible light. As shown in Table 1, almost the same physical properties were observed in spite of having different substituent groups on benzene ring at the 9-position.

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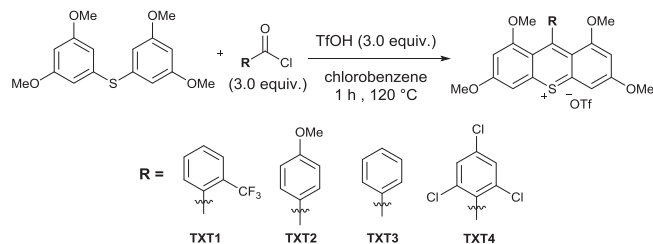
·green-light-driven organophotoredox catalysts
 ·high excited-state reduction potentials

Figure 1. Absorption and excited-state reduction potential of representative photoredox catalysts.

In addition, when the solvent effects were examined using MeCN, CH₃NO₂, DMSO and MeOH, no substantial shifts in both UV-vis and emission spectra were observed (see [Supporting Information](#)), which exhibit these catalysts would have π - π^* transition state. Importantly, it is expected that 9-aromatic substituent on thioxanthylum would be a key important group for stabilizing catalysts [10,11].

Table 1

Synthesis and physical properties of thioxanthylum-based photocatalysts.



Photocatalyst	$E_0'(\text{C}^+/\text{C}^-)^a$ (V)	$E_0(\text{C}^+/\text{C}^-)^b$ (V)	Absorption λ_{max} (nm)/ $\epsilon \times 10^{-3}$ (mol ⁻¹ dm ³ cm ⁻¹)	Absorption λ (nm)/ $\epsilon \times 10^{-3}$ (mol ⁻¹ dm ³ cm ⁻¹)	Excitation λ_{max} (nm)	Emission λ_{max} (nm)
TXT1	+1.83	−0.31	468/31.7	520/5.5	468	636
TXT2	+1.94	−0.27	461/28.3	520/6.7	461	659
TXT3	+1.86	−0.35	463/42.3	520/7.4	463	620
TXT4	+1.79	−0.35	478/32.8	520/6.9	478	666

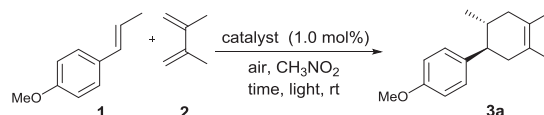
^a Excited-state reduction potentials were estimated from ground-state redox potentials and the intersection of the absorption and emission bands.^{4a}

^b Determined by cyclic voltammetry in acetonitrile vs SCE. See the Supporting Information.

Recently, visible-light-driven radical cation Diels–Alder reactions catalyzed by metal-based photoredox catalysts have been developed that employ ruthenium complexes under irradiation with visible light or chromium complexes under irradiation with NUV light [12]. From a fundamental perspective, as well as with respect to practical applications, the relatively low cost and the fact that these photocatalytic systems operate with visible light are highly desirable. Subsequently, the radical cation Diels–Alder reaction of *trans*-anethole (**1**) with 2,3-dimethylbutadiene (**2**) was screened in the presence of an organophotoredox catalyst (Table 2). First, all blank experiments, i.e., in the absence of a catalyst, light source, and air (degassed CH₃NO₂ was used under N₂), afforded trace amounts of the product **3a** (entries 1 and 2), and 4% yield of the product (entry 3). When the reaction was carried out with **1** (0.5 mmol), **2** (1.5 mmol), and **TXT1** (1.0 mol%) in CH₃NO₂ (0.0625 M) at room temperature under air and irradiation with blue light, excellent yield was obtained within 15 min (entries 4).

Table 2

Optimization of the reaction conditions.^a



Entry	Time (h)	Light	Catalyst	Yield (%)
1	0.25	Blue	No catalyst	0
2	0.25	No light	TXT1	0
3 ^{b,c}	0.25	Blue	TXT1	4
4	0.25	Blue	TXT1	92
5	15	Blue	TXT2	94
6	1.15	Blue	TXT3	89
7	0.75	Blue	TXT4	89
8	0.25	Blue	Eosin Y	0
9	0.25, (1.5)	Blue	Acr ⁺ -Mes	5 ^b , (91)
10	0.25, (1.5)	Blue	TPT	16 ^b , (91)
11	0.25	Green	TXT1	88
12	15	Green	TXT2	92
13	1.15	Green	TXT3	91
14	0.5	Green	TXT4	95
15	0.25, (15)	Green	Eosin Y	0, (0)
16	0.25, (15)	Green	Acr ⁺ -Mes	0, (11) ^b
17	0.25, (15)	Green	TPT	0, (0)

^a All reactions were carried out with **1** (0.5 mmol), **2** (1.5 mmol), and the catalyst (1.0 mol%) in the specified solvent (0.0625 M) at room temperature under air and irradiation with visible light. ^bNMR yield. ^cUnder N₂.

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