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A chiral nickel DBFOX complex as a bifunctional catalyst for visible-light-promoted asymmetric photoredox reactions†

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The enantioselective photoredox reaction of α,β -unsaturated carbonyl compounds and tertiary/secondary α -silylamines was enabled by a readily available single Ni^{II}-DBFOX catalyst (DBFOX = 4,6-bis((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)dibenzo[*b,d*]furan) under visible light conditions. The non-precious chiral catalyst is involved in the photochemical process to initiate single electron transfer and at the same time provides a well-organized chiral environment for the subsequent radical transformations. Good to excellent enantioselectivities (80–99% ee) were obtained for the formation of chiral γ -amino carboxylic acid derivatives and γ -lactams.

Introduction

Visible light photoredox catalysis has emerged as a powerful strategy for organic synthesis.¹ However, the development of catalytic asymmetric photoredox reactions is still highly desirable and remains a formidable challenge owing to the difficulties in controlling the stereochemistry of highly reactive intermediates such as radicals and radical ions.^{2,3} Pioneering work by Sibi, Porter, and others has demonstrated that transition-metal-based chiral Lewis acids are capable of governing the enantioselective conjugate addition of radicals produced by stoichiometric reduction of organic halides (Fig. 1a, left).⁴ These studies inspired chemists to develop cooperative chiral Lewis acid/photoredox catalytic systems for light-induced stereoselective radical transformations, providing a high level of asymmetric induction at mild and convenient reaction conditions (Fig. 1a, right).^{5–11} For instance, Yoon's group reported the first highly enantioselective intermolecular conjugate addition of α -aminoalkyl radicals to α,β -unsaturated carbonyl compounds by utilizing the combination of a chiral Sc^{III} Lewis acid and Ru^{II} tris-bipyridine photocatalyst.⁶ Meggers *et al.* developed several chiral-at-metal rhodium complexes as chiral Lewis acids together with additional photocatalysts for highly enantioselective conjugate radical additions.^{7,8} The Kang group utilized a chiral-at-rhodium complex as a single catalyst for a catalytic asymmetric conjugate radical addition.⁹

Despite the impressive advances, typically two catalysts are required for this type of transformation: one photocatalyst for

the radical generation and an additional chiral Lewis acid for controlling the stereoselective radical addition. Furthermore, the photocatalyst and the chiral Lewis acid often contain a precious metal.^{11,12} Using earth-abundant, first-row transition metal complexes instead as bifunctional single catalysts for asymmetric photoredox reactions opens a new avenue for cheap and green synthesis of chiral molecules, but this has been investigated much less.¹³ As the only established example, Fu's group demonstrated that a chiral copper complex can catalyze light-induced enantioselective C–N cross-couplings, not only as the asymmetric catalyst but also as the precursor of the

a) Previous strategies for enantioselective radical conjugated additions



Fig. 1 Previous strategies for enantioselective radical conjugate additions and that developed in this study.

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photocatalyst.¹⁴ Although they are inexpensive and well-compatible in photochemical reactions,¹⁵ nickel complexes themselves have only been reported as potential photoredox catalysts very recently.^{16,17} Herein, we wish to reveal our discovery on using a readily available Ni^{II}-DBFOX complex as a bifunctional catalyst for visible-light-promoted enantioselective reactions between α,β -unsaturated carbonyl compounds and α -silylamines (Fig. 1b).

Results and discussion

Chiral Ni^{II}-DBFOX complexes have been used extensively in catalytic asymmetric nucleophilic additions, halogenation, cycloadditions and other transformations.¹⁸ Interestingly, we

observed that one member of this class of complexes, Ni-L1, generated *in situ* by mixing Ni(ClO₄)₂·6H₂O and chiral DBFOX ligand L1 in a 1 : 1 ratio, exhibited obvious blue-green luminescence in THF (Fig. S5 in the ESI[†]). In combination with its highly organized chiral environment and redox-active metal center, we envisioned that such a complex might be a potential candidate for asymmetric/photoredox bifunctional catalysis.¹⁹ With these considerations in mind, we commenced our study with α,β -unsaturated crotonyl oxazolidinone **1a** and tertiary α -silylamine **2a** as the model substrates. We here chose tertiary α -silylalkylamines as the target substrate because they have low oxidation potentials (for example, E_{ox} (**2a**^{•+}/**2a**) = +0.60 in CH₃CN, Fig. S6 in the ESI[†]) and are well-established to undergo single-electron oxidation followed by rapid desilylation to

Table 1 Initial experiments^a



Entry	Substrate	Ligand	Light source	Additives	<i>t</i> (h)	Product	Conv. ^b (%)	ee ^c (%)
1	1a	L1	White CFL	None	12	3a	0	n.a.
2	1b	L1	White CFL	None	12	3b	22	78
3	1c	L1	White CFL	None	6	3c	95	91
4	1d	L1	White CFL	None	12	3d	0	n.a.
5	1c	L2	White CFL	None	12	3c	23	0
6	1c	L3	White CFL	None	12	3c	21	n.d.
7	1c	L4	White CFL	None	12	3c	0	n.a.
8	1c	L1	Blue LEDs	None	3	3c	95	91
9	1c	L1	Red LEDs	None	12	3c	<5	n.d.
10	1c	L1	Yellow LEDs	None	12	3c	0	n.a.
11	1c	L1	UV (365 nm)	None	6	3c	90	91
12 ^d	1c	L1	Blue LEDs	None	12	3c	0	n.a.
13 ^e	1c	L1	Blue LEDs	None	12	3c	0	n.a.
14 ^f	1c	L1	Blue LEDs	None	12	3c	0	n.a.
15	1c	None	Blue LEDs	None	12	3c	0	n.a.
16	1c	L1	None	None	12	3c	<5	n.a.
17 ^g	1c	L1	Blue LEDs	None	12	3c	0	n.a.
18	1c	L1	Blue LEDs	1 eq. TEMPO	12	3c	0	n.a.
19	1c	L1	Blue LEDs	3 eq. BHT	12	3c	0	n.a.

^a Reaction conditions: **1a-d** (0.10 mmol), **2a** (0.30 mmol), Ni(ClO₄)₂·6H₂O (10 mol%), ligand **L1-4** (12 mol%), THF (0.50 mL), indicated light source, 25 °C, under argon; see more details of the screening of metal salts and solvents in the ESI. ^b Conversion determined by ¹H-NMR. ^c ee value determined by chiral HPLC. ^d Reaction performed in the absence of nickel salt. ^e Reaction performed by replacing Ni(ClO₄)₂·6H₂O with Mg(OTf)₂. ^f Reaction performed by replacing Ni(ClO₄)₂·6H₂O with Ni(COD)₂. ^g Reaction performed in air. n.d. = not determined; n.a. = not applicable.



generate nucleophilic α -aminoalkyl radicals.^{6,9} However, under irradiation with a 23 W white CFL lamp at 25 °C in the presence of premixed 10 mol% Ni(ClO₄)₂·6H₂O and 12 mol% **L1** in THF, no desired product **3a** was observed (Table 1, entry 1). Next, we screened α,β -unsaturated carbonyl compounds **1b–d** bearing different moieties adjacent to the carbonyl group (entries 2–4). To our delight, the reaction of α,β -unsaturated imidazole **1b** led to the formation of **3b** in 22% conversion and with 78% ee (entry 2). Most interestingly, α,β -unsaturated *N*-acyl pyrazole **1c** provided significantly improved catalytic outcomes. Adduct **3c** was afforded in 95% conversion and with 91% ee within only 6 h (entry 3). Other bisoxazoline ligands, **L2–4**, were also tested in the reaction, which, however, resulted in a much worse reaction rate and enantioselectivity (entries 5–7). The reaction was further improved by using a 24 W blue LED lamp, providing **3c** in 95% conversion and with 91% ee in only 3 h (entry 8). Notably, when we replaced the blue LEDs with 30 W red or yellow LEDs, we failed to obtain the product (entries 9 and 10), while irradiation with a 15 W UV lamp (365 nm) still resulted in the production of **3c** in good conversion and with high enantioselectivity (entry 11). These results indicate that the appropriate wavelength range of the light source is very critical for the transformation.

To obtain a better understanding of the system, several control experiments were conducted. As revealed by entries 12–16, the nickel salt, DBFOX ligand **L1**, and visible light are all essential for the product formation. For example, after

removing Ni(ClO₄)₂·6H₂O (entry 12) or replacing Ni(ClO₄)₂·6H₂O with Mg(OTf)₂ (entry 13), the reaction did not produce any desired product. Interestingly, the replacement of Ni^{II} by Ni⁰ such as when using Ni(COD)₂ as the metal source also led to failure in obtaining **3c**, which indicates the possibility of nickel being involved in the redox process (entry 14). Moreover, air (entry 17), radical quencher TEMPO (entry 18) and BHT (entry 19) completely inhibited the transformation of **1c** + **2a** → **3c**. These observations are consistent with a radical pathway.

Next, UV-Vis spectra were recorded to evaluate the light absorptions of the reaction components. The individual substrates **1c** and **2a** and the chiral ligand **L1** do not feature any absorption in the visible light region, while a 1 : 1 mixture of [Ni(ClO₄)·6H₂O + **L1**] and 1 : 1 : 1 mixture of [Ni(ClO₄)·6H₂O + **L1** + **1c**], leading to the *in situ* generation of the chiral nickel catalyst Ni–**L1** and potential intermediate Ni–**L1**–**1c** respectively, exhibit significant absorption enhancement in the range of 400–450 nm (Fig. 2a). The broad peak at ~600 nm is probably attributed to the nickel center. The spectroscopic analysis indicates that both Ni–**L1** and Ni–**L1**–**1c** could be the potential photocatalysts. This conjecture was further strengthened by luminescence quenching experiments and Stern–Volmer quenching plots, which revealed obvious intermolecular interactions between Ni–**L1** (or Ni–**L1**–**1c**) and **2a** (Fig. S12–S15 in the ESI†).

The cyclic voltammogram of α -silylamine **2a** exhibited an irreversible oxidation at +0.60 V ($E_{ox}(2a^+/2a)$) in CH₃CN (Fig. S6 in the ESI†), while those of Ni–**L1** and Ni–**L1**–**1c** showed reductive peaks at –1.35 V and –0.65 V respectively (Fig. 2b),



Fig. 2 (a) Left: UV-Vis absorption spectra recorded on a Shimadzu UV-2550 in a 10.0 mm quartz cuvette. Middle: I. Substrate **1c** in THF (0.030 M). II. Substrate **2a** in THF (0.030 M). III. Ni–**L1** in THF (0.030 M). IV. Ni–**L1**–**1c** in THF (0.030 M). Right: A THF solution of nickel catalyst Ni–**L1** (0.030 M) in the dark and in the light. (b) Cyclic voltammogram of nickel catalyst Ni–**L1** (0.030 M) and potential intermediate complex Ni–**L1**–**1c** (0.030 M) in TBAPF₆ (0.10 M) in CH₃CN. Sweep rate: 20 mV s^{–1}. A Pt electrode was used as the working electrode, a SCE as the reference electrode, and Pt wire as the auxiliary electrode. E_p^A is the anodic peak potential. E_p^C is the cathodic peak potential. (c) Calculated reductive potentials of nickel catalyst Ni–**L1** and potential intermediate complex Ni–**L1**–**1c** in the excited states.



Fig. 3 Mechanistic investigation. (a) Intervals of irradiation and dark periods for the nickel-catalyzed reaction **1c** + **2a** → **3c**. (b) Radical trapping experiment in the nickel-catalyzed reaction **1c** + **2d** → **3r**.



Fig. 7 Substrate scope with respect to tertiary α -silylamines.

summarized in Fig. 6, a range of α,β -unsaturated *N*-acyl pyrazoles containing aliphatic (products **3c** and **e-h**), aromatic (products **3l-p**) or electron-donating (product **3i**) substituents at the β -position were well tolerated. The products were obtained in 47–81% yields and with 80–99% ee. However, a strong electron-withdrawing β -CF₃ or β -CO₂Me substituent led to the further cyclized product **3j** or **3k**. Although the yields and diastereoselectivities were good, the enantioselectivities were both



Fig. 8 Synthetic applications of the methodology.

close to zero, which is most likely attributed to uncatalyzed background radical additions.

The tertiary α -silylamines bearing more sterically demanding *N*-substituents (products **3q-t**), and electron donating (**3u-v**) or withdrawing groups on the aniline moiety (**3x-za**) were also compatible (Fig. 7) with respect to the yields (32–86%) and enantioselectivities (87–95% ee). However, a methyl substituent in the 2-position of the aniline ring failed to provide the desired product **3w**, perhaps due to steric hindrance.

The *N*-acyl pyrazole moiety can be readily converted to a range of functional groups under mild conditions.²⁴ As an example, the reaction of **3s** (95% ee) with sodium borohydride in a 1 : 1 mixture of THF and water afforded the corresponding alcohol (*S*)-5 in a yield of 94% and with 95% ee (Fig. 8a). Accordingly, the absolute configuration of **3s** was assigned as *S*.⁶ More interestingly, if the tertiary α -silylamines were replaced by secondary α -silylamines in the nickel-catalyzed enantioselective photoredox reaction, further lactamization occurred to afford chiral γ -lactams (**3zb-zg**, 63–80% yield, 91–93% ee), one class of important building blocks in synthetic chemistry (Fig. 8b).²⁵

Conclusions

In summary, we have revealed that a conventional Ni^{II}-DBFOX complex can effectively catalyze the asymmetric photoredox reaction between α,β -unsaturated carbonyl compounds and tertiary/secondary α -silylamines. As a bifunctional catalyst, the chiral nickel complex is not only involved in a photo-induced single electron transfer process to initiate the formation of the radical species, but also activates the α,β -unsaturated carbonyl substrates as a Lewis acid and governs the radical transformation in an enantioselective fashion. Good to excellent yields and enantioselectivities were achieved for the chiral γ -amino carboxylic acid derivatives and γ -lactam products. In view of the non-precious, low-toxic metal salt, readily available chiral ligand, mild reaction conditions and high asymmetric induction, this strategy might provide new opportunities to develop cheap and green synthesis of chiral molecules. Further investigations of reaction mechanisms and applications of the catalytic system in asymmetric photoredox catalysis are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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