Synthesis of 2-Substituted Benzothiazoles by Visible Light-Driven Photoredox Catalysis

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Abstract: An efficient method for synthesis of the widely applicable 2-substituted benzothiazoles has been developed. The process requires only 0.1 mol% [Ru(bpy)₃Cl₂], O₂, and visible light irradiation with substrates: 2-aminothiophenol and a variety of aldehydes. We established an oxidative quenching of the photoredox catalyst as being the key process in this photoelectrocatalytic cycle.

Keywords: benzothiazoles; benzothiazolines; C–H oxidation; radical reaction; visible light

The benzothiazole structural motif has been of great importance in many applications (Figure 1).^[1,2] It is widely used in pharmaceuticals with a diverse range of biological properties, and currently the use of benzothiazole in the preparation of organic optoelectronic materials is gaining in importance^[3].

Consequently, great effort has been made to develop efficient processes for the preparation of benzothiazole derivatives.^[4,5] Since many of currently available synthetic methods rely on hazardous materials requiring costly containment and disposal (e.g., concentrated acids and high loadings of metal catalysts), the development of more efficient and convenient methods is still desired. Herein we present an alternative, environmentally benign method for benzothiazole synthesis from 2-aminothiophenol and aldehydes with molecular oxygen as oxidant by visible lightdriven photoredox catalysis.^[6,7] Mechanistic studies were further performed to establish the key action of the photoredox catalyst.

We envisioned that a 2-substituted benzothiazole 5 could be obtained *via* photoredox radical reactions between 2-aminothiophenol 1 and an aldehyde 2



Figure 1. Molecules containing the benzothiazole structural motif.

through an imine **3** or a benzothiazoline **4** as key intermediate (Scheme 1). It is assumed that the intermediates **3** and **4** are in equilibrium and their conversion to **5** proceeds by either or both of the following two possible pathways; radical thiol-ene type reaction of imine **3** (pathway A)^[8] or α -amino C–H oxidation of benzothiazoline **4** (pathway B)^[9].

We began by examining the benzothiazole synthesis from aminothiophenol **1** and octanal **2a** under visible light-induced photoredox catalysis. To our delight, the desired benzothiazole product **5a** was obtained in a 80% yield using 0.5 mol% of $[Ru(bpy)_3Cl_2]$ (bpy = 2,2'-bipyridine) as the photoredox catalyst in an airequilibrated MeCN solution under photoirradiation by blue LEDs (Scheme 2).

We investigated the reaction mechanism to confirm that the reaction proceeds by photoredox catalysis and to determine the reaction pathway. For this pur-

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Scheme 1. Hypothesis for the visible light-induced synthesis of benzothiazoles.



Scheme 2. Benzothiazole synthesis by the photoredox catalysis.

pose we originally planned to isolate possible intermediates and run reactions using them to produce 5a. Although we expected to isolate the imine **3a**, which has been predicted as the intermediate in most previous studies, in a mixture with benzothiazoline 4a, we could only isolate benzothiazoline 4a without even detecting 3a by ¹H NMR spectroscopy.^[10] Thus, we pursued the mechanistic studies using the isolated 4a only.^[11] Both blue LEDs as the visible light source and oxygen were essential for the reaction to proceed (Table 1, entries 2 and 3). Although a range of Ru and Ir photoredox catalysts were found to give the desired benzothiazole **5a** in good yields, $[Ru(bpy)_3Cl_2]$ was chosen for further studies because of its low cost. (Table 1, entries 1 and 5-7). The reaction showed better efficiency with blue LEDs than with a fluorescent light bulb (Table 1, entries 1 and 4).

To verify the catalytic activity of $[Ru(bpy)_3Cl_2]$, conversion yields (Y_{1h}) were measured by GC-MS for the air-equilibrated MeCN solutions containing **4a** and 0.5 mol% $[Ru(bpy)_3Cl_2]$, after 1 h photoirradiation at varying wavelengths ($\lambda_{ex} = 300-450$ nm). As shown in Figure 2 (a), a significant improvement in Y_{1h} was observed at wavelength > 380 nm which corresponded to the metal-to-ligand charge-transfer (MLCT) transition band of $[Ru(bpy)_3]^{2+,[12]}$ The coincidence between the photoaction profile (i.e, Y_{1h}) and the MLCT absorption band strongly suggests the key role of the photoinduced intramolecular charge separation in $[Ru(bpy)_3]^{2+}$. On the contrary, Y_{1h} remained below 20% at $\lambda_{ex} < 380$ nm. This result can be explained by the fact that the region (i.e., $\lambda_{ex} < 380$ nm), where the absorption by **4a** and the bpy ligand of

	$\sim S$ $\sim N_{6}$ $\sim Conditions$ $\sim Conditions$ $\sim Conditions$ $\sim Conditions$	S N
	4a	5a
Entry	Conditions	Product yield [%] ^[b]
1	blue LED, O_2 , $Ru(bpy)_3Cl_2$	89
2	blue LED, Ru(bpy) $_3Cl_2$, (without O_2)	trace
3	$O_{2,} Ru(bpy)_3 Cl_2$, (no light)	trace
4	14 W fluorescent lamp, O_{2_1} Ru(bpy) $_3Cl_2$	65
5	blue LED, O_2 , $Ru(phen)_3Cl_2$	86
6	blue LED, O ₂ , <i>fac</i> -lr(ppy) ₃	85
7	blue LED, O ₂ , Ir(ppy) ₂ (dtb-bpy)PF ₆	86
8	blue LED, O ₂ , (no photocatalyst)	21

Table 1. Radical α -amino C-H oxidation of benzothiazoline **4a**.^[a]

[a] Reaction conditions: 4a (0.2 mmol), photoredox catalyst (0.5 mol%), MeCN (2 mL), room temperature, 3 h. phen=1,10-phenanthroline, ppy=2-phenylpyridinate, dtb-bpy=4,4'-di-*tert*-butyl-2,2'-bipyridine.

^[b] The yield was determined by GC-MS with dodecane as an internal standard.

 $[Ru(bpy)_3]^{2+}$ predominated, barely contributes to the charge separation.

Photon absorption by the MLCT transition in $[Ru(II)(bpy)_3]^{2+}$ produced an intramolecular chargeseparated species, $[Ru(III)(bpy)_2(bpy)^{-}]^{2+}$. The excited-state oxidation (E^*_{ox}) and reduction (E^*_{red}) potentials of $[Ru(III)(bpy)_2(bpy)^{-}]^{2+}$ are -1.21 V and 1.08 V, respectively (vs. SCE), as determined by cyclic voltammetry and steady-state optical measurements (see the Supporting Information, Figures S1 and S2). Judging from these potential values and the oxidation potential of **4a** (0.61 V, vs. SCE), two photoredox routes to the radical α -amino C–H oxidation of **4a** can be suggested. The first route is the direct oxidation of **4a**:

$[Ru(III)(bpy)_2(bpy)^{\bullet-}]^{2+} + 4a \rightarrow [Ru(II)(bpy)_2(bpy)^{\bullet-}]^+ + 4a^{\bullet+}$

The driving force for the electron transfer $(-\Delta G_{eT})$ from **4a** to $[\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_2(\operatorname{bpy})^{-}]^{2+}$ is 0.47 eV, as estimated by $-\Delta G_{eT} = e \cdot [E^{\circ}_{ox}(\mathbf{4a}) - E^*_{red}(\operatorname{Ru}\operatorname{complex})]$. The other route is the two-step process that involves the reduction of O₂ by $[\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_2(\operatorname{bpy})^{-}]^{2+}$ to form superoxide (O_2^{-}) and $[\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_3]^{3+}$, followed by the oxidation of **4a** by $[\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_3]^{3+}$:

 $[\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_2(\operatorname{bpy})^{\bullet-}]^{2+} + \operatorname{O}_2 \rightarrow [\operatorname{Ru}(\operatorname{III})(\operatorname{bpy})_3]^{3+} + \operatorname{O}_2^{\bullet-}$

 $[\mathsf{Ru}(\mathsf{III})(\mathsf{bpy})_3]^{3^+} + \mathbf{4a} \rightarrow [\mathsf{Ru}(\mathsf{II})(\mathsf{bpy})_3]^{2^+} + \mathbf{4a^{\bullet^+}}$

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Figure 2. (a) UV-Vis absorption spectra of **4a** and $[Ru(bpy)_3Cl_2]$ (10 μ M in deaerated MeCN). Filled circles are conversion yields obtained after 1 h photoirradiation at different photoirradiation wavelengths in the region of 300–450 nm. (b) Photoluminescence decay traces of 50 μ M [Ru(bpy)₃Cl₂] in argon-saturated MeCN (filled circles), O₂-equilibrated MeCN (empty circles), and argon-saturated MeCN containing 50 μ M **4a** (triangles) after nanosecond photoexcitation at 377 nm.

In this case, the overall driving force is the sum of $e \cdot [E^*_{ox}(\text{Ru} \text{ complex}) - E^\circ_{red}(O_2)]$ and $e \cdot [E^\circ_{ox}(4a) - E^\circ_{redox}(\text{Ru}(\text{III})/(\text{II}))]$, which is 0.91 eV.^[13] Thus, the first and second routes characterized by the reductive and the oxidative quenching, respectively, are thermodynamically favourable.

To detect a preference between the two photoredox routes suggested above, we monitored the transient photoluminescence ($\lambda_{obs} = 620 \text{ nm}$) of [Ru(bpy)₃Cl₂] in the presence of either O₂ or **4a**. As shown in Figure 2 (b), the photoluminescence lifetime (τ_{obs}) of [Ru(bpy)₃Cl₂] was significantly shortened by O₂ from 1.02 µs to 0.174 µs, corresponding to an electron transfer rate of $k_{obs} = 4.77 \times 10^6 \text{ s}^{-1}$. In sharp contrast, the addition of 50 µM **4a** had no apparent influence on τ_{obs} . This result provides strong evidence for the absence of the direct photoinduced electron transfer between **4a** and [Ru(bpy)₃]²⁺ (the reductive quenching). In fact, dominance of the oxidative quenching (i.e., O₂ reduction followed by electron transfer from **4a**) over the reductive quenching is anticipated due to the larger driving force (i.e., 0.91 eV vs. 0.47 eV).

Based on these results, we propose a plausible mechanism for the α -amino C–H oxidation (Figure 3). The MLCT photoexcitation of $[Ru(II)(bpy)_3]^{2+}$ by visible light promotes the intra-



Figure 3. Proposed mechanism of the benzothiazole synthesis.

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SH		0.5 mol% Ru(bpy) ₃ Cl ₂ blue LEDs, O ₂ , 4 h, r.t	
1	1:1 2a		5a
Entry	Solvent (concentration)	Variations to standard conditions	Product yield [%] ^[a]
1	DMF (0.1 M)		82
2	$CH_2Cl_2 (0.1 \text{ M})$		60
3	MeOH (0.1 M)		72
4	MeCN (0.1 M)		83
5	MeCN (0.2 M)		90
6	MeCN (0.5 M)		91
7	MeCN (1.0 M)		91
8	MeCN (0.2 M)	with 3 Å MS	87
9	MeCN (0.2 M)	0.01 mol% Ru	79
10	MeCN (0.2 M)	0.1 mol% Ru	89
11	MeCN (0.2 M)	1.0 mol% Ru	90
12	MeCN (0.2 M)	1 : 2a = 1:1.1	85
13	MeCN (0.2 M)	1:2a = 1.1 :1	93

[a] The yield was determined by GC-MS with dodecane as an internal standard.

molecular charge separation to generate $[Ru(III)(bpy)_2(bpy)^{-}]^{2+}$. This charge-separated species is oxidatively quenched by O₂ to produce $[Ru(III)(bpy)_3]^{3+}$ and superoxide. The $[Ru(III)(bpy)_3]^{3+}$ subsequently oxidizes 4a into 4a⁺. returning to [Ru(II)(bpy)₃]²⁺. Deprotonation of 4a⁺⁺ by superoxide followed by hydrogen atom abstraction by hydroperoxyl radical (HOO[•]) yields the desired benzothiazole 5a. The H_2O_2 generated in the last step was detected by ¹H NMR spectroscopy ($\delta = 8.8$ ppm in CD₃CN)^[14] and an H₂O₂ indicator,^[15] which strongly supports our hypothesis.

Having understood the visible light-driven photoredox catalytic mechanism, we further explored optimal conditions for benzothiazole synthesis with 2-aminothiophenol 1 and octanal 2a in the presence of [Ru-(bpy)₃Cl₂] (Table 2). Although the reaction proceeded well in a variety of solvents including DMF, CH₂Cl₂, and methanol, it worked best in MeCN at a 0.2M concentration (Table 3, entries 1-7). The presence of molecular sieves did not influence the reactivity significantly (Table 3, entry 8). The result also suggested that the presence of water formed from the condensation between 1 and 2a does not affect the reactivity. The catalyst loading can be lowered down to 0.1 mol% without loss in yield (Table 3, entries 9–11). A slight excess of 1 gave a higher yield of 5a and made it easier to purify the product.



[a] Reaction *conditions:* **1** (1.1 mmol), **2** (1.0 mmol), $[Ru(bpy)_3Cl_2]$ (1.0 µmol), MeCN (5.0 mL), blue LEDs, room temperature, 3-10 h.

[b] Isolated yields based on an average of two runs. Numbers in parentheses indicate yield obtained under the standard reaction conditions where [Ru(bpy)₃Cl₂] was excluded.

With the optimized conditions in hand, we evaluated the reactions of 2-aminothiophenol with a variety of aldehydes for the synthesis of 2-substituted benzothiazoles (Table 3). Both aliphatic and aromatic aldehydes are suitable substrates and provide benzothiazoles in good to excellent yields. In addition, reactions

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Scheme 3. Reactions of substituted 2-aminothiophenols.

of both electron-poor and electron-rich aromatic aldehydes gave high yields of products. The mild reaction conditions allowed for benzothiazole syntheses in the presence of a range of functional groups such as aryl halides (5g, 5h) and heteroaromatic (5k) systems. The current reaction conditions were amenable to a largescale reaction such that 5d was prepared on a 5 nmmol scale with the yield being similar to that of a 1 mmol scale reaction. Notably, reactions proceeded even in the absence of the photocatalyst, as expected from the large positive driving force for the photoinduced electron transfer from the benzothiazoline intermediate to O_2 (for example, $-\Delta G_{eT} = e \cdot [E^*_{ox}(\mathbf{4a}) - E^{o}_{red}(O_2)] = 2.23 \text{ eV}; \quad E^*_{ox}(\mathbf{4a}) = -3.12 \text{ V},$ vs. SCE). However, due to the very small absorbance in the visible region, the reaction took much longer $(>15 h)^{[16]}$ and resulted in much lower yields, which indicates the crucial role of $[Ru(bpy)_3Cl_2]$.

Reactions of substituted 2-aminothiophenols such as 2-amino-4-chlorobenzenethiol **6** and 2-amino-4-(trifluoromethyl)benzenethiol **8** also gave excellent yields of the desired benzothiazole products (Scheme 3).

To summarize, we have developed a protocol for the synthesis of 2-substituted benzothiazoles using visible light-induced photoredox catalysis. This protocol is noteworthy for the mild reaction conditions, enabling the preparation of a broad range of benzothiazoles, and for minimizing toxic waste by using $[Ru(bpy)_3Cl_2]$ at concentrations as low as 0.1 mol% as catalyst and O_2 as an oxidant in the photoreaction. We identified the key action of $[Ru(bpy)_3Cl_2]$ in the photoredox catalytic processes by performing mechanistic studies: the catalytic cycle of [Ru(bpy)₃Cl₂] involves O_2 reduction followed by electron transfer from benzothiazoline. We present our protocol mediated by visible light as a prudent and efficient alternative to current methods of benzothiazole derivatization.

Experimental Section

General Procedure

An open test tube equipped with a magnetic stir bar was charged with 2-aminothiophenol (1.1 mmol). Then were added MeCN (5.0 mL, 0.20 M), an aldehyde (1.0 mmol), and $[Ru(bpy)_3Cl_2]$ (0.10 mol%, 1.0 µmol). The open test tube was placed under blue LEDs and the mixture allowed to stir at room temperature for 3–10 h. Reaction progress was checked by thin layer chromatography (TLC)^[17] or gas chromatography (GC). The reaction mixture was concentrated under vacuum, and benzothiazole products were purified by flash column chromatography.

Acknowledgements

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- [15] A peroxide indicator, QUANTOFIX Peroxid 25, was used.
- [16] Most of the reactions did not go to completion even upon longer times in the absence of a photocatalyst and gave lower yields of the products as shown in Table 3.
- [17] We observed several unidentified compounds by TLC. Although these were easily seen by UV or a stain (*p*-anisaldehyde), the amount of each compound was less than 1% based on the weight.

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Synthesis of 2-Substituted Benzothiazoles by Visible Light-Driven Photoredox Catalysis

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