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Visible light photoredox catalysis: conversion of a mixture of thiophenols and nitriles into 2-substituted benzothiazoles *via* consecutive C–S and C–N bond formation reactions†

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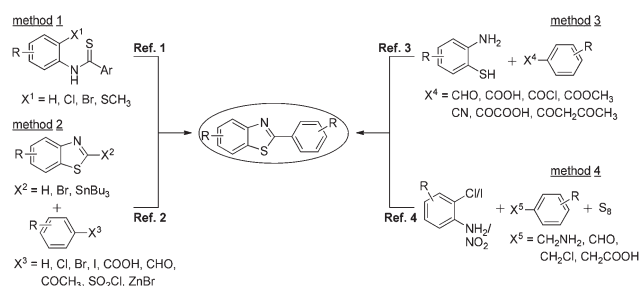
A novel, visible-light-mediated method for the construction of 2-substituted benzothiazoles from easily available thiophenols (2.0 equiv.) and alkyl/aryl nitriles (1.0 equiv.) in the presence of eosin Y (0.02 equiv.) under air atmosphere has been developed. The reaction proceeded smoothly, for a wide range of derivatives of thiophenols and nitriles, to give the expected products in moderate to good yields. A reaction mechanism involves the direct oxidative radical coupling of thiophenols with nitriles to afford iminyl radical intermediates giving the expected product by an intramolecular cyclization followed by hydrogen radical loss. To the best of our knowledge, this is the first example of the synthesis of 2-substituted benzothiazoles through sequential C–S and C–N bond formation reactions under photoredox catalysis.

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2-Substituted benzothiazoles have been of particular interest due to their diverse biological and pharmacological activities.¹ Moreover, the 2-arylbenzothiazole building block has largely been utilized for the development of advanced materials² showing applications in fluorescent sensors, liquid crystal display, nonlinear optics, organic light-emitting diodes, *etc.*^{1,2} Consequently, for their synthesis, several protocols³ (Scheme 1) including (i) the typical condensation–dehydration reactions of 2-aminothiophenols with aldehydes or carboxylic acids or β -diketones or acyl chlorides or esters (Method 3, Scheme 1),⁴ (ii) intramolecular cyclization of thiobenzanilide derivatives (Method 1, Scheme 1),⁵ (iii) one-pot three-component reaction of 2-haloanilines, aldehydes or benzylamine and elemental sulfur (Method 4, Scheme 1)⁶ and (iv) the direct oxidative coupling *via* C–H activation and subsequent C–C bond formation between benzothiazoles and various aryl coupling partners have been disclosed (Method 2, Scheme 1).⁷ Despite the significant advances with respect to the substrate scope and numerous options for the synthetic community, these methods largely suffer from several disadvantages such as harsh reaction conditions, inaccessible starting materials, cumbersome work-up procedures, metallic wastes, long reaction time and the use of toxic reagents.³ As a result, the evolution of mild and green methods to overcome these limitations

is still an important experimental challenge for researchers.^{1–3}

From the viewpoint of energy efficiency, mild reaction conditions, synthetic simplicity, step and cost economy and the environment, the chemical transformations initiated by visible light ($\lambda = 400\text{--}700\text{ nm}$) sources have attracted considerable attention over a decade.⁸ This protocol has found numerous applications in both industries and academics for the preparations of drugs, functional materials and natural products.^{8,9} Moreover, using visible-light photoredox catalysis, in 2012, Li's group has for the first time reported a protocol for the formation of 2-aryl benzothiazoles through the radical cyclization of thiobenzanilides under aerobic conditions (Method 1, Scheme 1).^{5,10} Subsequently, a few other research groups also reported methods for the synthesis of 2-aryl benzothiazole derivatives from mixtures of 2-aminothiophenol and aldehydes



Scheme 1 Literature reported methods for the synthesis of 2-aryl benzothiazoles through conventional and visible-light-promoted pathways.

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†Electronic supplementary information (ESI) available: Experimental procedures, characterization data, and copies of ¹H and ¹³C NMR spectra of products (PDF). See DOI: 10.1039/c8qo00219c

(Method 3, Scheme 1)^{4,11} or thiobenzanilides using different catalysts and irradiation sources (Method 1, Scheme 1).^{3,5} In all of these synthetic protocols, the products, *i.e.*, 2-aryl benzothiazoles, have been formed through either C-S or C-C bond formation reactions. Nevertheless, we hypothesized the preparation of 2-substituted benzothiazoles *via* sequential C-S and C-N bond formation reactions because a radical reaction of thiophenols and nitriles has been known to provide iminyl radicals that readily afford the benzothiazole scaffold by intramolecular cyclization and hydrogen radical loss.¹² In addition, both thiophenols and nitriles are biocompatible, relatively cheap, can be stored for longer periods of time under ambient conditions and a wide variety of derivatives are commercially available.

As part of our ongoing research into the development of new and ecofriendly chemical transformations,¹³ herein we describe a method for the synthesis of 2-substituted benzothiazoles from thiophenols and nitriles under visible-light (green LEDs: λ_{\max} = 535 nm) photocatalyzed conditions, *cf.* Scheme 2. In addition, a tentative mechanism is described for the reaction, *vide infra*. To the best of our knowledge, using visible-light photocatalysis, this is the first example of the conversion of readily available thiophenols and nitriles into valuable benzothiazole derivatives *via* consecutive C-S and C-N bond formation reactions.

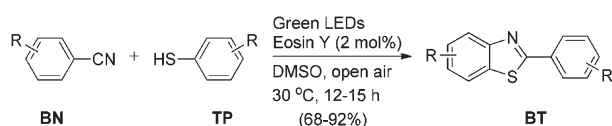
Cheap, environmentally friendly and commercially available eosin Y and 4-methylbenzenethiol (TP1) and benzonitrile (BN1), respectively, were chosen as photocatalyst and model substrates to optimize the reaction conditions. When a hexane solution containing TP1 (2.0 equiv.), BN1 (1.0 equiv.) and a catalytic amount of eosin Y (2.0 mol%) was irradiated by blue LEDs (λ_{\max} = 450 nm) in an open vessel under ambient conditions for 12 hours, the desired 5-methyl-2-phenylbenzo[d]thiazole (BT1, ESI[†]) was obtained in 38% yield, *cf.* Table 1 and entry 1. Encouraged by these initial results, a series of experiments were carried out to study the influences of various reaction parameters such as catalyst and its quantity, wavelength of radiation source, solvents and atmosphere for the reaction (Scheme 2). Interestingly, the yield of BT1 enhanced to 52% when the reaction was performed with green LEDs [λ_{\max} = 535 nm, Table 1 and entry 2]. In contrast, the yield of BT1 was lowered to 20–30% when the reaction was irradiated with either a xenon lamp or white LEDs (Table 1, entries 3 and 4). However, no product was detected in a dark environment (Table 1 and entry 5). Afterwards, the influence of solvents on the formation of BT1 was explored. The investigation revealed that DMSO was the most effective medium to promote the

Table 1 Selected results of screening the optimal conditions for the photocatalytic synthesis of 2-substituted benzothiazoles from thiophenols and nitriles^a

Entry	Catalyst ^b (mol%)	Solvent ^c	Time (h)	Yield ^d (%)
1	Eosin Y (2)	Hexane	12	38 ^e
2	Eosin Y (2)	Hexane	12	52
3	Eosin Y (2)	Hexane	24	23 ^f
4	Eosin Y (2)	Hexane	24	29 ^g
5	Eosin Y (2)	Hexane	24	NR ^h
6	Eosin Y (2)	DMSO	12	91
7	Eosin Y (2)	CH ₂ Cl ₂	12–24	32
8	Eosin Y (2)	C ₂ H ₄ Cl ₂	12–24	36
9	Eosin Y (2)	CH ₃ OH	12–24	17
10	Eosin Y (2)	DMF	12–24	49
11	Eosin Y (2)	Dioxane	12–24	22
12	Eosin Y (2)	Glyme	12–24	33
13	[Ru(bpy) ₃] ²⁺ (2)	DMSO	12	41
14	Ir(ppy) ₃ (2)	DMSO	12	35
15	Rose bengal (2)	DMSO	12	17
16	Fluorescein (2)	DMSO	12	29
17	Rhodamine (2)	DMSO	12	<5
18	Eosin B (2)	DMSO	12	39
19	Eosin Y (3)	DMSO	10	90
20	Eosin Y (5)	DMSO	9	92
21	Nil	DMSO	24	NR
22	Eosin Y (2)	DMSO	12	18 ⁱ

^a Unless stated otherwise all reactions were performed in a round bottom flask equipped with 1.0 equiv. of BN1, 2.0 equiv. of TP1 and 2.0 mol% of photocatalyst in dry solvent under an open air atmosphere at 30 °C using high power green LEDs. ^b Commercially available high purity catalyst were purchased and utilized as such. ^c Solvents were rigorously purified before use. ^d Isolated yield of the product. ^e Blue LEDs used. ^f Xenon lamp used. ^g White LEDs used. ^h Reaction was carried out in the dark. ⁱ Reaction performed under a N₂ atmosphere. N.R. No reaction.

reaction with 91% yield (Table 1 and entry 6) while the use of other solvents resulted in lower yields (Table 1 and entries 7–12) even after 24 h of irradiation. Several other photocatalysts including [Ru(bpy)₃]²⁺, Ir(ppy)₃, rose bengal, fluorescein, rhodamine and eosin B were then examined. Compared to eosin Y (Table 1 and entries 13–18), these catalysts display much less efficiency towards the reaction. The influence of the quantity of eosin Y on the product yield was also investigated. With an increase in the catalyst amount from 2.0 mol% to 3.0–5.0 mol%, the reaction time was obviously shortened with 90–92% yield of BT1 (Table 1 and entries 19–20). However, no product was observed in the absence of photocatalyst (Table 1 and entry 21). Subsequently, we investigated the influence of atmosphere on the reaction. On switching the reaction atmosphere from open air/O₂ (balloon) to N₂, inferior yields of BT1 were obtained (Table 1 and entry 22). Thus, the optimized conditions for the synthesis of 2-substituted benzothiazoles from thiophenols (2.0 equiv.) and nitriles (1.0 equiv.) are 2.0 mol% of eosin Y, green LED lights as source in DMSO at 30 °C for about 12–15 h.



Scheme 2 Visible-light-induced synthesis of 2-substituted benzothiazoles from the mixture of thiophenols and nitriles reported in this work.

Under the optimized conditions (Table 1), the substrate scope of the transformation (Scheme 2) was investigated. The reaction between thiophenol (**TP2**) and various nitriles was looked at first and the results are summarized in Table 2. Unsurprisingly, both electron-rich and electron-deficient aryl nitriles reacted with **TP2** producing the desired products **BT2–BT16** (ESI[†]) in moderate to good yields. However, a strong dependence on the position of the substituents was observed, cf. Table 2 and **BT5**, **BT8** and **BT10**. For example, a reaction with *para*-methyl substituted aryl nitrile (**BT6**) afforded higher yield than *ortho*-methyl substituted aryl nitrile (Table 2 and **BT8**). This is likely attributed to the steric hindrance of the *ortho*-functionalized aryl nitriles as similar findings have been well documented in the literature.¹ To expand the scope of this methodology, we also examined a couple of aliphatic nitriles, i.e., **BT15–BT16**. As summarized in Table 2, the aliphatic nitriles are also favorable substrates for this reaction process, which represent an advantage of the present methodology. Thus, a wide range of electronically and structurally diverse nitriles and thiophenols can be cross-coupled efficiently with moderate to good yields of desired products, cf. Table 2.

Next, the scope of thiophenols was examined. As shown in Table 3, thiophenols bearing electron-donating or withdrawing groups were applicable to the coupling with moderate to good yields (**BT17–BT22**, Table 3). Nevertheless, alkyl thiophenols such as benzyl thiol and butyl thiol failed to react with **BN6** owing to the less stability of their corresponding radicals while

Table 2 Substrate scope for the transformation of a mixture of thiophenol and various nitriles into 2-substituted benzothiazoles^a

TP2	BN	BT2-BT16
BT2 , 89%	BT3 , 86%	BT4 , 87%
BT5 , 77%	BT6 , 90%	BT7 , 85%
BT8 , 79%	BT9 , 92%	BT10 , 76%
BT11 , 83%	BT12 , 78%	BT13 , 76%
BT14 , 68%	BT15 , 71%	BT16 , 69%

^a Unless stated otherwise all reactions were performed in a round bottom flask with 1.0 equiv. of **BN**, 2.0 equiv. of **TP2** and 2 mol% of eosin Y in DMSO under an open air atmosphere at 30 °C using high power green LEDs ($\lambda_{\text{max}} = 535 \text{ nm}$) as a visible-light source for 12–15 h.

Table 3 Substrate scope for the transformation of a mixture of various thiophenols and aryl nitriles (BN) into 2-substituted benzothiazoles^a

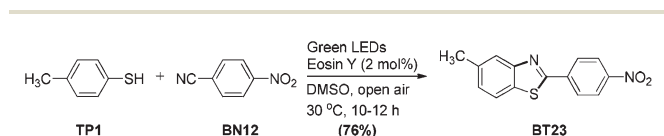
TP	BN	BT17-BT22
BT17 , 77%	BT18 , 69%	BT19 , 74%
BT20 , 74%	BT21 , 77%	BT22 , 71%

^a Unless stated otherwise all reactions were performed in a round bottom flask with 1.0 equiv. of **BN**, 2.0 equiv. of **TP** and 2 mol% of eosin Y in DMSO under an open air atmosphere at 30 °C using high power green LEDs ($\lambda_{\text{max}} = 535 \text{ nm}$) as a visible-light source for 12–15 h.

comparing with aromatic ones. Thus, a series of 2-substituted benzothiazoles (**BT1–BT22**) can be readily synthesized from the mixture of nitriles and thiophenols under photocatalyzed conditions. Moreover, this transformation has shown satisfactory tolerance to various functional groups including chloro, nitro and methoxy groups, which are generally advantageous for further functionalization.

To further illustrate the preparative utility of this methodology, a scale-up synthesis of **BT23** was carried out (Scheme 3) in a round bottom flask. The reaction turned out to be scalable and practical as the gram-scale reaction was equally efficient. Viz., the reaction of **TP1** (50.0 mmol, 2.0 equiv.) and **BN12** (25.0 mmol, 1.0 equiv.) provided the desired product **BT23** in 76% yield under optimized reaction conditions (ESI[†]).

To gain mechanistic insights, some control experiments were carried out. First, 2,2,6,6-tetramethyl-1-piperidinyloxy and butylated hydroxytoluene were employed in the reaction as radical inhibitors. These reactions were completely inhibited. Likewise, when the reaction was carried out under a nitrogen atmosphere, the reaction was suppressed severely and only 18% yield of product was obtained (Table 1 and entry 22). Thus, the radical intermediates and oxygen were involved in the benzothiazoles formation.⁹ Later on we performed cyclic voltammetry experiments for a few substrates and determined their standard redox potentials in the ground state (ESI[†]). The oxidation potential of aryl thiols is +0.43–0.71 V vs. SCE and the reduction potential of aryl nitrile is –2.07–2.34 V vs. SCE, which are in good agreement with the literature reports.¹⁴ The redox potentials of the excited state of eosin Y are –1.60 V vs. SCE (EY^+/EY^*) and +0.83 V vs. SCE (EY^*/EY^-).¹⁵ Accordingly, a



Scheme 3 A scale-up synthesis of **BT23** from **TP1** and **BN12** using optimized reaction conditions.

plausible mechanism for the reaction was proposed in the Scheme 4.

Upon irradiation by green LEDs, eosin Y was converted to the excited state eosin Y*, which then underwent reductive single-electron transfer quenching by a thiophenol derivative to afford a radical cation (I) and an eosin Y radical anion. Afterwards, to complete the photoredox cycle, the eosin Y radical anion was oxidized to the ground state by aerobic oxygen. In this step, molecular oxygen was transformed into a superoxide radical anion ($O_2^{\cdot-}$). A deprotonation reaction between I and $O_2^{\cdot-}$ afforded the thiyl radical (II) and so reacted with the carbon atom of the nitrile group to generate the iminyl radical (III). Subsequently, III underwent intramolecular cyclization followed by hydrogen radical loss to afford the desired product, *i.e.*, 2-substituted benzothiazoles (ESI†).

As mentioned at the outset, photoredox catalyzed syntheses of 2-substituted benzothiazoles reported so far have been performed through either C–S or C–C bond formation protocols.^{3–7} Nevertheless, the method reported here is based on C–S and C–N bond formation reactions to construct 2-substituted benzothiazoles from inexpensive starting materials. Moreover, this protocol meets many of the requirements of green chemistry¹³ as: (i) the reaction is driven by visible-light and takes place at room temperature; (ii) the reaction uses O_2 from air as the oxidant; (iii) it is atom-economical and (iv) merely 2.0 mol% of organic dye is used as catalyst in the reaction. Thus, we believe that the present protocol may find a bright future, especially in the pharmaceutical industries.

In summary, a novel, visible-light photoredox catalysis for the conversion of a mixture of thiophenols and nitriles into 2-substituted benzothiazoles *via* sequential C–S and C–N bond formation reactions has been developed. This method is operationally simple, atom-economic, good functional group tolerant, ecofriendly and requires a very small quantity (2.0 mol%) of non-metal catalyst. Further studies on synthetic applications

of this transformation are ongoing in our laboratories and the results will be disclosed in due course.

Conflicts of interest

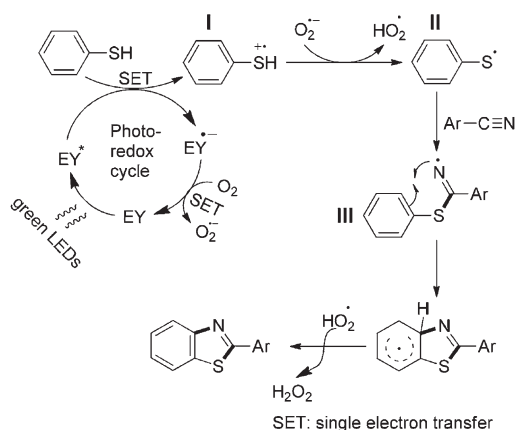
There are no conflicts to declare.

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Scheme 4 A plausible reaction mechanism for the visible-light-induced synthesis of 2-substituted benzothiazoles from the mixture of thiophenols and nitriles.

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