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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Naturally occurring perylenequinonoid pigments (PQPs) have attracted considerable attention owing to their excellent properties of photosensitization. They have been widely investigated at aspect of photophysics and photobiology. However, their applications in photocatalysis are yet to be explored. We report here that sunlight along with 1 mol % cercosporin, which is one of perylenequinonoid pigments, catalyzes the direct C–H bond arylation of (het)arenes by a photoredox process with good regioselectivity and broad functional group compatibility. Furthermore, a gram-scale reaction with great conversions of substrates was achieved even by cercosporin-containing supernatant without organic solvent extraction and purification after liquid fermentation. Thus we set up a bridge between microbial fermentation and organic photocatalysis for chemical reactions in a sustainable, environmentally friendly manner.

Introduction

Visible light-driven photocatalysis is the cutting-edge of organic synthesis and has emerged into a green and mild mean to achieve unique chemical reactivity, as sunlight provides the most sustainable and redundant energy source.¹ Transition metal-based photocatalysis, especially driven by ruthenium and iridium polypyridyl complexes,² has been widely investigated in organic synthesis. Alternatively, metal-free organocatalysis has also been studied using organic dyes or large organic molecules,³ owing to their ability to absorbing the visible or near-visible light to participate in photoinduced electron transfer process, but their applications of catalytic reactivity in organic synthesis is somewhat less familiar.

Naturally occurring perylenequinonoid pigments (PQPs, Figure 1), such as cercosporin,⁴ hypocrellins A,⁵ elsinochrome C⁶ and phleichrome⁷ produced by endophytic fungi have aroused considerable attention owing to their excellent properties of photosensitization, which function as new potential compounds in photodynamic therapy and photophysical diagnosis.^{4c-f,6d-f,5} Particularly, cercosporin (CP), a phytotoxin produced by members of the genus Cercospora, exhibits the most active compound of PQPs against different cancer cell lines with its excellent properties of photosensitization.⁴ These photosensitizers can be activated to the excited state by visible light absorption and then undergo energy transfer (EnT) and electron transfer (ET),^{4c-f,6d-f,5} implying that these natural products PQPs may be used as "metal-free" photoredox catalysts for organic synthesis, but have never been investigated.

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Figure 1. Representatives of the naturally occurring mold perylenequinones.

Arylated (het)arenes are widely used in materials science because of their interesting optical and electronic properties, as well as biomedical applications including peptide mimetics or drugs.8 A variety of cross-coupling methods for the synthesis of arylated (het)arenes have been well established, mainly transition metal-mediated reactions between utilizing prefunctionalized substrates and arenes or C–H arylations with functionalization in only one coupling partner.⁹ Recent progress in arylation reactions was accomplished with photoredox catalysis,¹⁰ with notable contributions by Sanford,^{10c} König,^{10j,} ^{10m} Xiao^{10h} and Ackermann,^{10g} among others. The reported methodologies are most efficient with electron-rich heteroarenes (Scheme 1a), 10j-n or by merging transition-metal and photoredox catalysis (Scheme 1b)^{10c-e} with low regioselectivities (Scheme 1c).^{10f, 10h} However, the photoinduced C-H arylation of arenes and heteroarenes, especially for electron-deficient N-heteroarenes, with

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DOI:

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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regioselectivity under mild conditions only by organic photoredox catalysis has thus far proven elusive. Thus the development of more general and efficient organic photoredoxcatalyzed direct arylations of (het)aromatic bases is still a major challenge.

a Organic photoredox catalyst for arylation of (hetero)arenes



- X = O, S, N-Boc Only electron-rich heteroarenes!
- ${\bf b}$ Dual catalysis transition metal/ photoredox catalyst for arylation of benzenes



broad substrate scope good regioselectivity gram-scale synthesis with fermentation supernatant

perylenequinonoid as organic photoredox catalyst

biosynthesis of cercosporin sunlight-induced C-H arylation

Scheme 1. Photo-catalyzed C–H arylation with aryl diazonium salt.

Here we report an unprecedented photoinduced direct C-H arylations of arenes and heteroarenes catalyzed by one of naturally occurring PQPs, cercosporin. Notable features of our finding include (a) natural product cercosporin as an organic photoredox catalyst for C-H functionalization, (b) good regioselectivity and broad substrate scope, and (c) great conversions of substrates in the gram-scale reaction using cercosporin-containing supernatant in a sustainable, environmentally friendly manner (Scheme 1d).

Results and discussion

Cercosporin was produced by a new isolated endophytic fungus *Cercospora sp. JNU001* strain with high yield through liquid fermentation (see ESI). The photochemical and electrochemical properties were characterized (see ESI), which imply that cercosporin can undergo photoinduced electron transfer (PET) to facilitate chemical reactions through an oxidative or reductive quenching cycle.

To test its photocatalysis activity, cercosporin, was used as a photoredox catalyst to investigate the direct C-19/appation of arene (1a) with aryl diazonium salt (2a). The reaction condition was conducted by irradiating a mixture of 1a, 2a, and cercosporin (1 mol%) with sunlight at room temperature under nitrogen atmosphere (Table 1, entry 1). It gave the corresponding arylated product, showing that cercosporin indeed facilitated this direct arylation. Next, this reaction condition was optimized with various solvents, additives and the amount of 2a. The arylated product was obtained with a best yield at 58% when using an excess of 10 equiv of 1a (Table 1, entries 1-4) with dimethyl sulfoxide (DMSO) as solvent (entries 5-9), of which the yield were comparable with previous studies. The use of Cs₂CO₃ or K₂HPO₄ as an additional base had no effect on the yield (entries 10-11). We also tested other commercially available perylenequinonoid pigments. hypocrellin A and hypocrellin B, giving comparable catalytic activity (entries 12-13). But the use of common transition metal photocatalysts [Ru(bpy)₃]Cl₂ or another organic photocatalyst Eosin Y with sunlight resulted in lower yields (entries 14-15). Besides sunlight, blue LED light slightly promoted the reaction to a 63% yield (entry 16). However, irradiation of the reaction mixture with either green LED light or CFL (compact fluorescent lamp) delivered slightly low yields of the desired product (entries 17-18). Control experiments confirmed that both of light irradiation and cercosporin were necessary for significant conversion to the product (entries 19-20).

 Table 1
 Optimization
 of
 the
 carbamoylation
 reaction

 conditions^a

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	.н +	N ₂ BF ₄	2BF₄ Cercosporin (1 mol%) Sunlight, solvent room temperature, N ₂		EtO ₂ C		
1a		2a				3a	
Entry	Cond	itions			Yield ^b	(%)	
1	1a (5	equiv), C	OMSO		45		
2	1a (10	0 equiv),	DMSO		58		
3	1 a (1	5 equiv),	DMSO		50		
4	1a (20	0 equiv),	DMSO		51		
5	1a (10	0 equiv),	DMF		38		
6	1a (10	0 equiv),	THF		25		
7	1a (10	0 equiv),	EtOH		41		
8	1a (10	0 equiv),	CH₃CN		50		
9	1a (10	0 equiv),	EtOAc		29		
10	1a (10	0 equiv),	DMSO, Cs ₂	CO ₃	50		
11	1 a (10	0 equiv),	DMSO, KH	₂ PO ₄	48		
12 ^c	1 a (10	0 equiv),	DMSO		53		
13 ^d	1 a (10	0 equiv),	DMSO		50		
14 ^e	1 a (10	0 equiv),	DMSO		43		
15 ^f	1 a (10	0 equiv),	DMSO		40		
16 ^{<i>g</i>}	1 a (10	0 equiv),	DMSO, blu	e LED	63		
17 ^{<i>h</i>}	1 a (10	0 equiv),	DMSO, gre	en LED	51		
18 ⁱ	1 a (10	0 equiv),	DMSO, CFI	-	45		
19	1a (10	0 equiv),	DMSO, no	catalyst,	20		
20	1 a (10	0 equiv),	DMSO, no	light	trace		
^a All reactions were carried out on a scale of 2 mmol of 1a and 0.							
of 2a in 2 ml	of 2a in 2 mL of solvent with sunlight for 16h under nitrogen atmosphere.						

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^b Yields of isolated product. ^c 1 mol% of hypocrellin A as photocatalyst. ^d 1 mol% of hypocrellin B as photocatalyst. ^e 1 mol% of [Ru(bpy)₃] Cl₂ as photocatalyst. ^f 1 mol% of Eosin Y as photocatalyst. ^g 5 W blue LED was used. ^h 5 W green LED was used. ⁱ 5 W CFL bulb was used.

Using the optimized conditions, the reaction scope of the sunlight-enabled C–H arylation of arenes **1** was explored (Scheme 2) with electron-acceptor- (CO₂Et, CN, NO₂, COCH₃), electron donor-and neutral substituted (Me, OMe) diazonium salts. All gave the corresponding products in moderate to good yields. Notably, it was also observed that halogen-substituted aryl diazonium salts successfully underwent C–H bond arylation and kept the C–halogen bond intact (**3ad** and **3am**), which is useful for further synthetic elaboration. Furthermore, we also found that this kind of C–H arylation were efficiently functionalized with electron-rich heteroarenes **4** (Schemes 3), such as furan (**5aa-5ao**), thiophene (**5ba-5bn**) and pyrrole (**5ca-5cl**), in moderate to good yields and all arylations selectively happened in 2-position of heteroarenes.



Scheme 2. Cercosporin-catalyzed C–H arylation of arenes with sunlight.







Scheme 3. Cercosporin-catalyzed C–H arylation of electron-rich heteroarenes with sunlight.

Normally the direct derivatization of electron-deficient Nheteroarenes, such as pyridines, pyrimidines, oxazoles, thiazoles and quinolines, are difficult to be achieved. In particular, it has not been reported by commercial available organic photoredox catalysts,^{10j-n} such as Eosin Y, Acr⁺-Mes and Rhodamine B. Surprisingly, we clearly showed that cercosporindriven photocatalysis was proved to be compatible with this challenging arylation approach (Scheme 4) with an array of pyridines (7aa-7ai), pyrimidines (7ba-7bb), benzothiazoles (7ca-7cb), benzoxazoles (7da-7db) and guinolines (7ea-7ec). They afforded the corresponding arylated derivatives in good to excellent yields. Additional benefits of this arylation approach are the tolerance of halides, multiple substitution, steric bulk, and diversity in the electronic properties of the N-heteroarenes. Next, we also explored the scope of aryldiazonium salts, showing that they all afforded good yields irrespective of

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whether they were electron-poor or electron-rich (Scheme 4). Increasing steric bulk of the diazonium salts had negative effect the yields (7ai). Compared with the reported on photocatalysts,^{10f, 10h} cercosporin showed good regioselectivity in this direct C-H arylation of pyridine derivatives. With pyridine, only 2-arylated products were isolated (7aa-7ae). With 2-substituted pyridines, only 6-arylated products were obtained (7af-7ai). With 2-substituted pyrimidines, 4-arylated products were obtained (7ba and 7bb). Benzothiazole (7ca and 7cb) and benzoxazole (7da and 7db) were also proved to produce the 2-arylated products in good yields. For guinolines, both of 2-arylated and 5-arylated products were obtained in ratio 5:1 (7ec). Only 5-arylated quinolines were obtained when 2-substituted quinolines were used as substrates (7ea, 7eb). The reason that the excellent photocatalysis activity of cercosporin may correlated with its structural similarity to the odd alternant hydrocarbon phenalenyl (PLY), which is wellknown to stabilize the radical state due to the presence of a nonbonding molecular orbital (NBMO).¹¹ Thus it shows the advantage of cercosporin as an organic photocatalyst with broad substrate scope in this C-H arylation as compared with other commercial available Eosin Y and Rhodamine B.





Last, to demonstrate the synthetic utility and e othis regioselective cercosporin-catalyzed Dophotored 600 diffect arylation of (het) arenes, the gram-scale reaction was carried out using cercosporin-containing fermentation supernatant. Direct use of fermentation supernatant as a catalyst avoids the solvent-involved extraction and purification process of cercosporin. In fact, it also gave the desired products with comparable yields as purified cercosporin did (Table 2). Notably, only a very small proportion of chemical solvents (\leq 10%) were used in this direct C-H arylation, thus providing a possibility for large scale synthesis of arylated (het) arenes in a sustainable, environmentally friendly manner.

Table 2 Gram-scale synthesis with fermentation supernatant ^a



^{*a*}All reactions were carried out on a scale of 50 mmol of (het)arene and 5 mmol of **2** with 5 W blue LED under nitrogen atmosphere catalyzed by fermentation supernatant, details see Experimental. ^{*b*}Yields of isolated product.

Subsequently, we conducted mechanistic studies to gain insights into the mode of action of cercosporin as a photoredox catalyst in the direct arylation of (het)arenes (Scheme 5 and ESI). First, the addition of the radical inhibitors TEMPO, or hydroquinone, or the electron-transfer scavenger 1,4dinitrobenzene significantly inhibits the transformation, and the TEMPO trapped intermediates 8 and 9 were detected by MS analysis (Scheme 5-1 and ESI). This finding implies a radical pathway that proceeds through a single-electron transfer (SET) process should be involved. Next, intermolecular competition experiments indicated that electron-poor aryl diazonium salts 2 can preferentially react with benzene when compared with electron-rich one (Scheme 5-2 and ESI), which correlated with their reduction potential. A notable intermolecular kinetic isotope effect (KIE, $k_H/k_D = 1.13$) was not observed (Scheme 5-3 and ESI), indicating a non-kinetically relevant C-H cleavage. Last, the interaction between aryl diazonium salt 2a and cercosporin has also been studied by means of UV-vis and fluorescence spectroscopy (see ESI). It showed 2a has no obvious interaction with ground state CP according to UV-vis titration. It was found that the fluorescence intensity diminished upon the gradual addition of 2a and the decrease fitted well with Stern–Volmer plots. These results indicated the electron transfer (ET) process between cercosporin and arryl diazonium salt 2.

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Scheme 5. Mechanistic experiments.

Based on the above observations and literature reports, ^{10a-} ⁿ a plausible mechanism for this photoreaction is proposed (Scheme 6). Initially, cercosporin was activated to excited state after irradiation with sunlight and then aryl radical **10** was formed by SET from the cercosporin to aryl diazonium salt **2**. Addition of aryl radical **10** to (het)arene **1** or **4** or **6** gave radical intermediate **11**, which was further oxidized by the cercosporin radical cation or the aryl diazonium salt **2** and transformed to carbocation intermediate **12**. Finally, intermediate **12** is deprotonated to regenerate the aromatic system and lead to the desired coupling product **3** or **5** or **7**.



Scheme 6. Proposed mechanism for cercosporin-catalyzed C–H arylation of (het)arenes.

Conclusions

DOI: 10.1039/C9OB00659A In summary, we reported a new class of organic photoredox catalyst, natural occurring perylenequinonoid pigment, for photoinduced C–H direct arylations of (het)arenes with sunlight under mild conditions. This C–H direct arylation is compatible with a wide array of functional groups with excellent regioselectivity and broad substrate scope. Mechanistic studies provided strong support for an efficient SET process. The use of this new class of photoredox catalyst for other chemical reactions awaits further investigation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank for the National Natural Science Foundation of China (21703036), Natural Science Foundation of Jiangsu Province (Grants No BK20160167), the Thousand Talents Plan (Young Professionals), Jiangsu Specially-Appointed Professor Program (1016010241160390) and the Fundamental Research Funds for the Central Universities (JUSRP51712B), the National First-class Discipline Program of Light Industry Technology and Engineering (LITE2018-14) for funding support.

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