

Eosin Y Catalyzed Photochemical Synthesis of Arylated Phenothiazones

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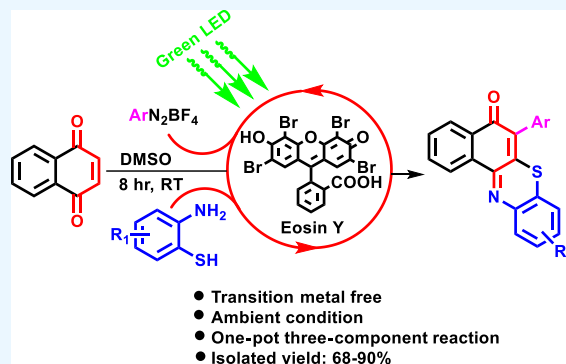


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Supporting Information

ABSTRACT: In the presence of Eosin Y (EY), the synthesis of substituted phenothiazones was carried out efficiently using various substituted 2-aminothiophenol, diazonium salts, and 1,4-naphthaquinones (1,4-NQ) at room temperature (RT) (condition: green LED of 525 nm, 44 W; reaction time: 8 h, isolated yield: 68–90%). A fluorescence quenching experiment and density functional theory (DFT) calculations suggested that the triplet photoexcited state of EY (EY^* ; $\tau_T = 320 \pm 10$ ns) converts to EY^{+*} via oxidative quenching by ArN_2^+ (-1.11 V vs SCE for EY^* to EY^{+*}) initially. Thiyl and aryl radicals were captured as TEMPO adducts in high-resolution mass spectroscopy (HRMS). The reaction was not inhibited by the addition of a singlet oxygen quencher such as 1,4-diazabicyclo [2.2.2] octane (DABCO), which suggests that singlet oxygen is not participated.



1. INTRODUCTION

Sulfur-containing heterocycles, such as phenothiazine and phenothiazone, belong to an important class of biologically active compounds, and their derivatives are well-known for their antipsychotic, antimalarial, anticancer, antimicrobial, antitumor, and antioxidant properties.^{1a–e,2} Phenothiazine-based first-generation antipsychotic medications (e.g., chlorpromazine, thioridazine, etc.) display antagonistic activity toward dopamine receptors and are used mostly to treat psychosis including schizophrenia; violent, agitated, disturbed behavior; and mania secondary to bipolar disorder. Moreover, phenothiazine has been used extensively as an insecticide, fungicide, antibacterial, and anthelmintic agent. Both phenothiazine and phenothiazone scaffolds exhibit photophysical properties and have tremendous applications in fluorescent imaging and sensing.^{2b,c}

In recent years, some new methods for the synthesis of phenothiazines using transition metals and metal-free conditions have been reported.³ For example, Jørgensen et al. reported an elegant method for the synthesis of substituted phenothiazines via palladium-catalyzed three-component coupling reaction of substituted 1-bromo-2-iodobenzenes with primary amines and 2-bromobenzenethiol in 2008.^{3a} In 2010, Ma et al. reported a CuI/l-proline-catalyzed C–S/C–N bond formation of 2-iodoanilines and 2-bromobenzenethiols (90 °C for 24–48 h, followed by 110 °C for 48–96 h).^{3b} Hu et al. developed an efficient method for the synthesis of phenothiazines via a tandem iron-catalyzed C–S/C–N cross-coupling reaction.^{3c} However, the development of a general and sustainable method to access the phenothiazone scaffolds continues to be a challenging task.⁴ Recently, the synthesis of arylated phenothiazine-5-one derivatives were reported using

palladium-catalyzed Suzuki-Miyaura cross-coupling reaction.^{4a} In 2016, the biocatalytic synthesis of phenothiazones and related compounds was also achieved in an aqueous system using Cu(I)-containing laccase enzyme, and the product yield was 9–53%.^{4b} However, less stability, limited substrate scope, poor tolerance to high temperature, expensive stimulators, and purification processes restrict the commercial application of laccase. In 2023, Wang et al. reported TEMPO-mediated electrochemical method to access a variety of phenothiazinones from 2-aminothiophenols and quinones (yield: 27–91%).^{2b} Using this method also, it was not possible to synthesize arylated phenothiazine at the C-6 position in a single step. Therefore, reasonable yield of substituted phenothiazone via a metal-free catalyst is highly desirable.

In recent days, visiblelight-mediated photoredox catalysis using metal-free organic dyes has become a powerful strategy for activating small molecules via the single-electron transfer (SET) process. Compared to metal (Ru and Ir)-based photocatalysts, organic dyes are inexpensive, less harmful, easier to handle, and nonpolluting to initiate organic changes. Recently, various fluorescein dyes, such as eosin Y (EY), are successfully utilized as photoredox catalysts in various organic transformations.⁵ After photoexcitation, the triplet excited state of EY (EY^*) undergoes

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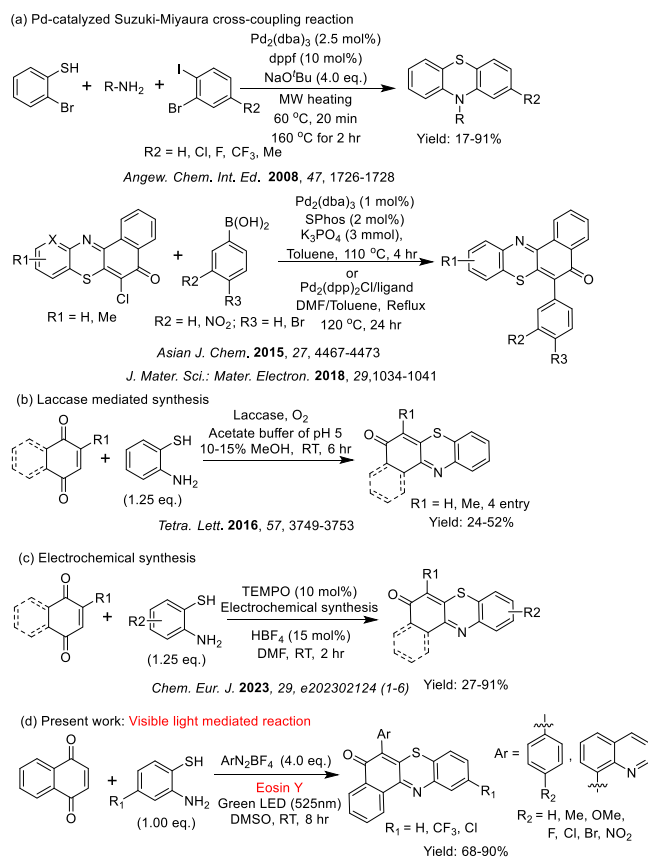
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reductive or oxidative quenching by accepting or donating an electron to produce a radical anion or radical cation, respectively. Herein, we would like to report an efficient, sustainable, one-step procedure for constructing arylated phenothiazine-5-one derivatives with 1,4-NQ, diazonium salts, and substituted 2-aminothiophenol using EY as a photoredox catalyst in the presence of green light (525 nm, 44W LED) at room temperature (RT) (Scheme 1).

Scheme 1. Synthesis of Phenothiazine and Arylated Phenothiazone^{2b,c,3,4}



2. RESULTS AND DISCUSSION

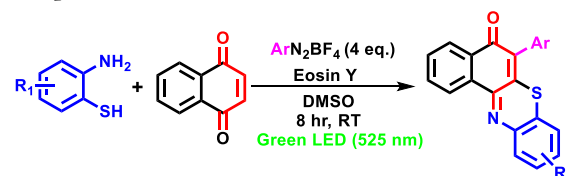
All the reactions were performed using Kessil lamp (PR160L, 525 nm, 44 W (W) inside PR160 Rig with a fan kit, which is a specifically designed mounting system for typical laboratory photocatalytic reactions. The reaction was carried out in an irradiated glass round-bottom flask containing a magnetic stir bar, and the photoreactor was placed on a magnetic stirrer (Figure S1). For optimizing the three-component reaction, 1,4-NQ, 2-amino thiophenol (1a), and *p*-fluorophenyl diazonium tetrafluoroborate salt (2c) were chosen (Table 1). The reaction was performed using various solvents (HPLC grade) such as dimethyl sulfoxide (DMSO), methanol (MeOH), acetonitrile (CH₃CN), tetrahydrofuran (THF), ethyl acetate (EtOAc), and dimethylformamide (DMF). All the three components and EY were soluble in these solvents. The solubility of 1a was found to be less in water compared to both DMSO and Me organic solvents. Using 2 mol % EY and irradiation with green light, 6-*p*-fluorophenyl-5H-benzo[*a*]phenothiazin-5-one (3c) was obtained in ~50% isolated yield at RT in DMSO after 8 h in the presence of air (entry 1). After increasing the amount of the

Table 1. Optimization of Reaction Conditions for the Synthesis of Arylated Phenothiazone.^a

entry	eosin Y (mol %)	solvent	isolated yield (%)
1	2	DMSO	50
2	5	DMSO	72
3	7.5	DMSO	85
4	7.5	MeOH	45
5	7.5	CH ₃ CN	00 ^b
6	7.5	THF	00 ^b
7	7.5	DMF	37
8	7.5	EtOAc	15–20
9	7.5	H ₂ O	22
10 ^c	7.5	DMSO	83
11 ^d	7.5	DMSO	00
12 ^e	-	DMSO	00
13 ^f	7.5	DMSO	65

^aReaction conditions (unless otherwise specified): 1,4 NQ (0.64 mmol), 1a (0.64 mmol), 2c (2.56 mmol), solvent (5 mL), eosin Y: 7.5 mol %, irradiation under air atmosphere at room temperature (RT) using 44 W green LED; reaction completed within 8 h. ^bNegligible yield; not able to isolate the desired product. ^cIn an N₂ atmosphere. ^dIn the absence of green light. ^eIn the absence of EY. ^fIn the presence of blue LED.

photocatalyst EY from 2 to 7.5 mol %, we observed a significant increase in the product isolated yield from 50 to 85% (entry 3). Changing the solvent from DMSO to MeOH, a considerable decrease in the isolated yield (~45%) was observed (entry 4). In the case of MeCN and THF, a negligible amount of the product was formed (entries 5 and 6), and it was not possible to isolate the desired product from the reaction mixture. However, in the case of DMF and EtOAc, the isolated yields were 37% and 15–20%, respectively (entries 7 and 8). In water (entry 9), the isolated yield was 22%. The yield was not affected when the reaction was carried out in an N₂ atmosphere (entry 10) in DMSO. It suggested that oxygen has no role in the photoredox cycle. Meanwhile, without a photocatalyst or light, the desired product was not found (entries 11 and 12). In the presence of blue light (440 nm, 45 W LED, Kessil), the isolated yield was dropped to ~65% (entry 13). The reactions were also performed in the presence of green LED of 33 W (75% intensity), 22 W (50 intensity), and 11 W (25% intensity), keeping 7.5 mol % EY in DMSO, and the isolated yields were 63, 45, and 33%, respectively. Other than EY, reactions were also performed with [Ru(bipy)₃]²⁺ and Rose Bengal (condition was similar to entry 3 without EY). The reactivity of [Ru(bipy)₃]²⁺ was comparable to that of EY (~80% isolated yield); however, Rose Bengal had less efficiency (~65% isolated yield). Aryl hydrazine was used instead of diazonium salts in the reaction, but no desired product was observed.



After optimizing the reaction condition, the generality and substrate scope of the reaction over various substituted 2-aminothiophenol (1a–c) and diazonium salts (2a–i) with 1,4-NQ in the presence of 7.5 mol % EY were investigated (Figure 1). In all cases, moderate to good yields (isolated yield: 68–90%, Figure 1) were observed. A reaction was also carried out in 2

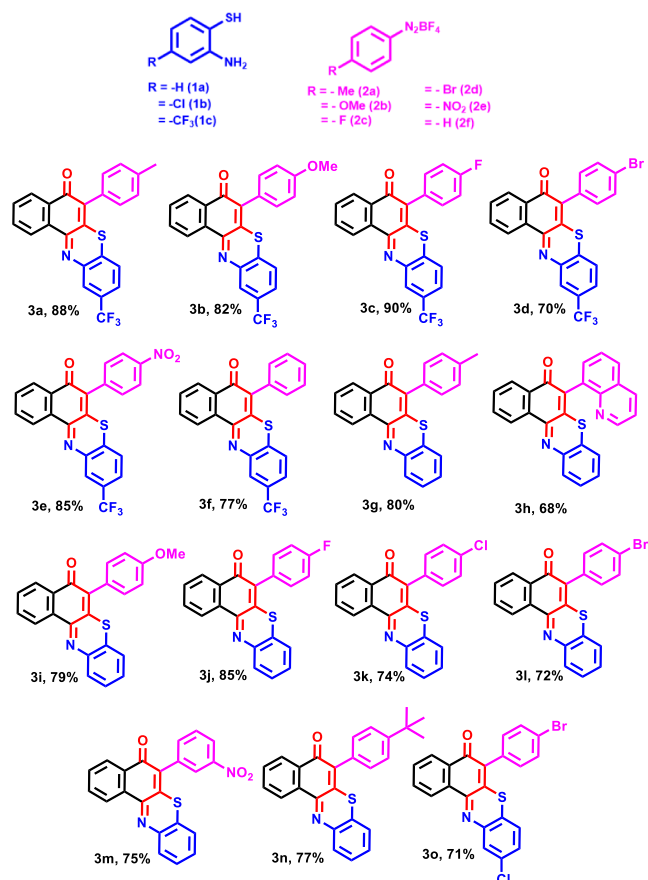


Figure 1. Chemical structure of the substituted 2-aminothiophenol (**1a–c**) and diazonium salts (**2a–f**) and arylated phenothiazone (**3a–p**) obtained using EY in the presence of green light. Isolated yields are mentioned.

mmol scale (condition: **1,4-NQ** (2 mmol), **1a** (2 mmol), and **2c** (10 mmol), total volume: 15 mL, 7.5 mol % EY, RT, 12 h), and ~68% yield (isolated) was observed.

A kinetic study revealed that the yield and rate of the reaction are unaffected if the reaction is conducted in an N_2 atmosphere. It confirms that O_2 is not involved in the photoredox catalytic cycle. In our previous study, we found that the catalytic cycle of thiolation for **1,4-NQ** was completed by involvement of O_2 as initially EY^{\bullet} formed due to electron transfer from thiol to EY (reductive quenching). However, here, we are expecting that the photoredox reaction is the combination of aryl and thiyl radical generations from ArN_2^+ (electron acceptor) and thiol (electron donor), respectively. Therefore, in photoredox catalytic cycle, oxygen is not involved as an electron acceptor. Furthermore, the reaction was quenched by the TEMPO, and an adduct product of TEMPO with aryl (Ar^{\bullet}) and thiyl ($Ar-S^{\bullet}$) was detected in HRMS technique (Figure S2).⁶ Very small amounts of organic disulfide were detected in HRMS, which were primarily generated by a combination of two thiyl radicals (Figure S2b).^{6a}

A fluorescence quenching experiment (Figure S3) revealed that the Stern–Volmer quenching constant value (K_{SV}) of **1a** (1.62) was lower in comparison to those of **2a** (2.2) and **1,4-NQ**.^{6b} This result suggested that the triplet photoexcited state (EY^*) ($\tau_T = 320 \pm 10$ ns) converts to $EY^{+\bullet}$ via oxidative quenching by ArN_2^+ to EY^* (−1.11 V vs SCE for EY^* to $EY^{+\bullet}$) initially.^{6,7} To support this experimental observation, we performed density functional theory (DFT) calculations to

understand the reactivity pattern of EY^* with ArN_2^+ and aryl amino thiol ($ArSH$). The Gibbs free-energy data show that the formation of aryl radical from the reaction of ArN_2^+ with EY^* is thermodynamically more favorable than the reaction of EY^* with aryl thiol. The reaction of EY^* with ArN_2^+ results in the formation of an aryl radical and $EY^{+\bullet}$, along with the release of a stable molecule, N_2 . The reaction-free energy is found to be exothermic in nature by around 30 kcal/mol, with respect to EY^* . However, the reaction of EY^* with aryl thiol is endothermic since, in this process, both the products ($ArSH^{+\bullet}$ and EY^{\bullet}) would be charged molecules. The potential energy diagram in Figure S4, in the Supporting Information, shows the relative stabilities of the reaction products and the reaction-free energy values.

Ar^{\bullet} generated via photoredox process readily reacts with quinone moiety and produces $[1,4-SNQ-Ar]^{\bullet}$ adduct, and the photoredox cycle can be completed via electron transfer from $[1,4-SNQ-Ar]^{\bullet}$ to $EY^{+\bullet}$.^{6b} We also isolated (5–7%) arylated **1,4-NQ** (**1,4-SNQ-Ar**) after the reaction. Based on our previous report^{6a} and similar mechanisms reported in the literature, it might be possible for the photoredox cycle to also be completed via electron transfer from substituted 2-aminothiophenol (**1a–c**) to $EY^{+\bullet}$. After that, BF_4^- abstracted a proton from thiyl radical cation, resulting in the generation of a thiyl radical (Figure SI2a). Thiyl radical then reacts with **1,4-SNQ-Ar**. An H atom was abstracted from $[1,4-SNQ-Ar-S-Ar]^{\bullet}$ adduct in a stepwise manner. At the end, the amine group attacked the electron-deficient C4 carbonyl center, and the desired product was formed. Auto-oxidized product of **1a–c** was also trapped in HRMS (Figure S2b). The reaction was not inhibited by the addition of a singlet oxygen quencher such as 1,4-diazobicyclo [2.2.2] octane (DABCO), which suggests that singlet oxygen is not necessary. The reaction was performed in the absence of air or oxygen; however, it does not affect the isolated yield% of the product. Light on–off experiment was also performed, and results suggested that radical chain mechanism was absent (Figure S5). Plausible reaction mechanisms are described in Figure 2.

Arylated phenothiazones possess electron-rich “nitrogen” and “sulfur” in their core structure as donor moieties and therefore could be useful as photosensitizers in dye-sensitized solar cells (DSSC), bioimaging, and sensing the lipid droplet.^{2b,8} The routine optical and spectral properties of some phenothiazones (**3a–e**) were collected (Figures S6–S8), and the molar absorption coefficients are listed in Table S1.^{2b,4a,c} The application of arylated phenothiazones as sensors is under investigation in our laboratory.

3. EXPERIMENTAL SECTION

3.1. General Information. All commercially available compounds were supplied by Sigma-Aldrich and Alfa Aesar and used directly in the reaction. The PR160L LED lamps (525 nm, 44 W) from Kessil were used inside PR160 Rig with fan kit (Figure S1). Thin layer chromatography (TLC) was performed on an aluminum plate coated with SiO_2 (Merck 60, F-254 MS grade) to follow the progress of reactions. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature using tetramethylsilane (0.00 ppm) as an internal standard, with Bruker instruments at 400 and 100 MHz, respectively. Agilent 6540 UHD accurate-mass quadrupole time-of-flight (Q-TOF) mass spectrometer equipped with Agilent 1290 UPLC system was used for high-resolution mass spectroscopy (HRMS). Steady-state fluorescence quenching experiment was carried out

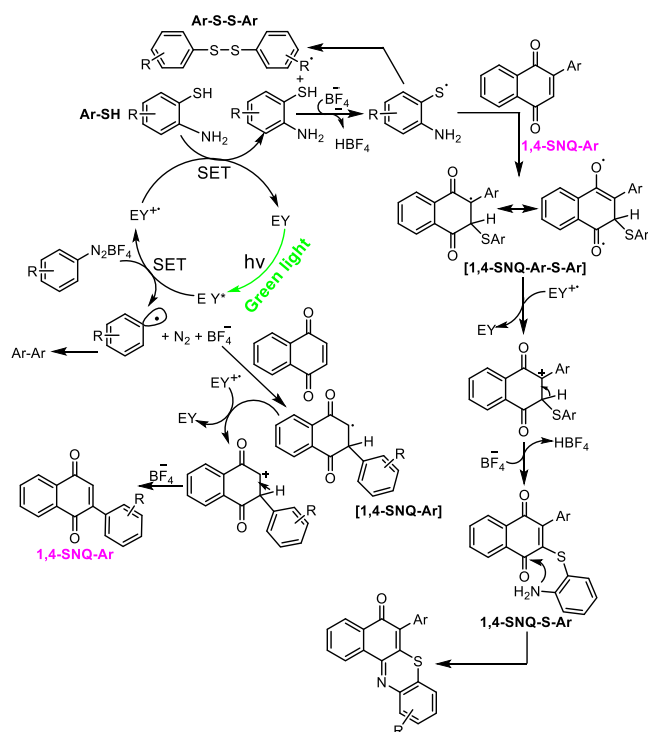


Figure 2. Plausible mechanism for the synthesis of arylated phenothiazone using EY as the photoredox catalyst.

in a spectrofluorometer (FS5, Edinburgh) at RT. UV–vis and FT-IR spectra were recorded using Cary 8454 diode array spectrophotometer (Agilent) and Nicolet iS20 FT-IR spectrophotometer (Thermo Scientific). Melting points were measured using a KRÜSS Optronic melting point meter. Single-crystal X-ray study was performed on a D8 Venture Bruker AXS single-crystal X-ray diffractometer equipped with CMOS PHOTON 100 detector having monochromatized microfocus sources (Mo- $K\alpha = 0.71073 \text{ \AA}$) at room temperature.

3.2. Eosin Y–Mediated Reaction. 1,4-NQ (0.64 mmol, 1 equiv weight (eq wt)), 2-aminothiophenol (0.64 mmol, 1 eq wt), *p*-fluorophenyl diazonium tetrafluoroborate salt (2.56 mmol, 4 eq wt), and EY (7.5 mol %, 0.048 mmol, 33 mg) were dissolved in 5 mL of DMSO and irradiated with a green LED (44 W, 530–535 nm) at RT for 8–12 h. The reactions were monitored using TLC. After complete consumption of the starting materials, chloroform and water were added to the reaction mixture, and the organic phase was separated. The extraction procedure was carried out two or three times with chloroform. The extracted organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated using a rotary evaporator. The residue was purified by column chromatography (silica gel mesh size of 200–300) with pet ether-ethyl acetate as the eluent.

3.3. DFT Calculations. All calculations were performed using the Gaussian 09 package.⁹ The hybrid DFT functional B3LYP^{10,11,12} and Gaussian basis set 6-311G+(d,p)^{13,14,15,16} were used to find the minimum energy structures. The implicit solvent environment modeled by the polarizable continuum medium (PCM) implemented in Gaussian 09 package with dielectric coefficient equivalent to DMSO was used to define the solvent interactions.¹⁷

4. CONCLUSION

We developed an efficient, inexpensive, metal-free photocatalytic method of synthesizing arylated phenothiazones in DMSO with very good yield (isolated yield: 68–90%) at RT. The method is an example of a one-pot, three-component reaction and could be a useful alternative to the transition metal (Fe, Cu, Pd, etc.)-catalyzed reaction. The reaction proceeds through the generation of aryl and thiyl radicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c02167>.

Photoreactor setup; mass spectrometry analysis; steady-state quenching study; DFT calculation; light on–off experiment; characterization data of arylated phenothiazine-5-one; UV–vis and fluorescence data; melting point data; FT-IR data; single-crystal diffraction; ^1H and ^{13}C {1H} NMR spectra (PDF)
Symmetry information (CIF)
Structure factors (PDF)

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Author Contributions

B.B.D. conceptualized and supervised the overall work. All the synthesis, characterization (^1H , ^{13}C NMR, HRMS, single crystal X-RD) and mechanistic experiments have been done by B.N. S.K.Y performed COSY, NOESY, FT-IR, UV–vis, fluorescence and melting point studies. N.K.M did the DFT study. The manuscript was written by B.B.D. with the help of other authors.

Notes

The authors declare no competing financial interest.

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