

Radical-Triggered Chemiluminescence of Phenanthroline Derivatives: An Insight into Radical–Aromatic Interaction

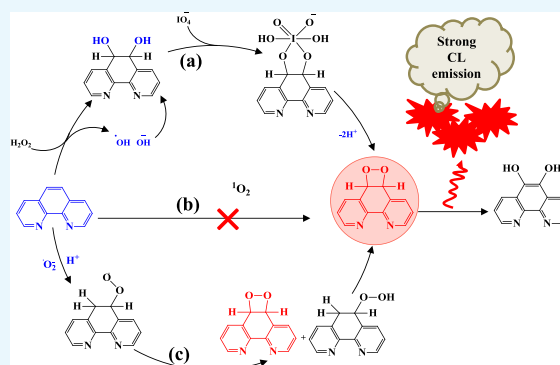
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Supporting Information

ABSTRACT: The hitherto unknown influence of 1,10-phenanthroline (1,10-phen) and its derivatives on the weak chemiluminescence (CL) of periodate–peroxide has been investigated, and a novel method for CL catalysis is described. Herein, we have deconvoluted the variation in CL intensity arising from the addition of various derivatives of 1,10-phen. Interestingly, similar derivatives of 1,10-phen show interesting differences in their reactivity toward CL. Electron-withdrawing substituents on 1,10-phen boosted the CL signals, indicating a negative charge buildup on 1,10-phen in the rate-determining step. The 1,10-phen derivatives having substitution at the C⁵=C⁶ position resulted in no CL signals due to the blockage of the reactive site. Mechanistic investigations are interpreted in terms of free radical (H₂O₂ reaction), followed by the oxygen atom transfer via an electrophilic attack of IO₄[−] (IO₄[−] reaction) on 1,10-phen resulting in dioxetane with enhanced CL emission. Additionally, the relationship between electronic structures and photophysical properties was investigated using density functional theory. Our results are expected to open up promising application of 1,10-phen as a molecular catalyst, providing a new strategy for metal-free catalytic CL enhancement reaction. We believe that this would foster in gleaning more detailed information on the nature of these reactions, thereby leading to a deeper understanding of the CL mechanism.



1. INTRODUCTION

The chemistry of 1,10-phenanthroline (1,10-phen) has got considerable attention due to its interesting nature and numerous applications.^{1,2} 1,10-Phen is an important chelating agent that can form coordination compounds with a multitude of metal ions.³ Despite the rich chemistry, the oxidation product of 1,10-phen has been challenging due to the competing reaction of the most reactive C^{5th} and C^{6th} centers with N atoms present in the ring. Its oxidation usually leads to the opening of the middle ring or dearomatization. The unique behavior was due to the rigid structure and limited space in the bay area of the 1,10-phen that cannot accommodate two O atoms.² Nevertheless, peroxy compounds have been reported to typically results in the oxidation of one N atom.² This may be due to the involvement of different poles of 1,10-phen in different reactions. The 1,10-phen derivatives are dipolar organic molecules with strong electron-withdrawing N atoms⁴ and low lying lowest unoccupied molecular orbital (LUMO), which act as single-electron-transfer mediators.⁵ The cis-locked nature of the 1,10-phen core provides several distinct structural and chemical benefits.^{2,6} Phenanthroline-based compounds show high electron mobility⁷ and have been used as energy-transfer reagents.^{8,9}

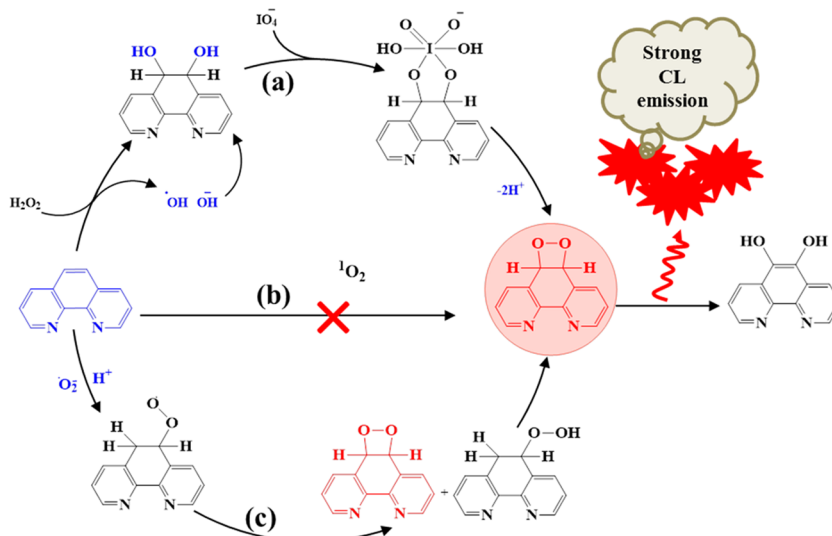
Enhanced chemiluminescence (CL) is a significant analytical technique in biological, environmental, and forensic analyses due to its sensitivity, simple instrumentation,^{10,11} forgo excitation source,^{10,12} and higher signal-to-noise ratio.^{12,13} However, most of the important CL systems suffer from challenges of weak CL intensity, which limits their applications.¹¹ Over the last few years, we have been interested in the enhancement of weak CL using nanomaterials.^{14–17} Among the weak CL systems, peroxide-induced systems are most important, widely investigated, and extensively used.^{18,19} Despite the great progress, the assignment of CL properties to structural features is often uncertain, and the understanding of the structural and functional variations in a compound with their corresponding CL behavior remains elusive. Nonetheless, to the best of our knowledge, the interesting trends of 1,10-phen with varying degrees and patterns of substitution on the CL study have not been thoroughly investigated.

Herein, the weak CL from the periodate–peroxide reaction was greatly enhanced by the application of 1,10-phen and its derivatives. The possible CL enhancement mechanism was

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Scheme 1. Mechanism of Enhancement of Periodate–Peroxide CL System in the Presence of 1,10-phen^a

^a(a) CL enhancement in the presence of 1,10-phen proceeded through the $\cdot\text{OH}$ radical pathway, followed by the complexation of IO_4^- resulting in dioxetane with enhanced CL emission. (b) $^1\text{O}_2$ reaction with 1,10-phen. (c) $\cdot\text{O}_2^-$ radical pathway for the CL enhancement reaction of 1,10-phen.

discussed based on the electrochemical/optical results, including electron paramagnetic resonance (EPR), UV–vis absorption, photoluminescence (PL), and CL spectra, as well as the effect of radical scavengers on the 1,10-phen-catalyzed periodate–peroxide CL system, suggesting that CL might originate from the catalytic activity of 1,10-phen derivatives to decompose H_2O_2 to hydroxyl radicals ($\cdot\text{OH}$) and the reaction of these radicals with the 1,10-phen derivatives to form dioxetane in the excited state. This is the first example of 1,10-phen as a catalyst and unique compared with the previously reported catalyst in CL. It is noteworthy that the present system requires neither the participation of a metal catalyst nor the use of complicated reagents. Furthermore, the catalytic process that does not require a transition metal as a catalyst is important because of its cost-effectiveness and metal-free nature.²⁰ Moreover, the development of nanomaterial- and metal-free processes is expected to significantly change the strategies for CL enhancement.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Analytical grade chemicals, HCl (Tianjin Kaitong Chemical Co. Tianjin, China), NaIO_4 (Tianjin Damao Chemical Reagent Company, Tianjin, China), NaOH, 1,10-phen, NaN_3 , ascorbic acid, thiourea, H_2O_2 (Beijing Chemical Reagents Co. Beijing, China), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) (Tokyo Kasei Kogyo Co. Ltd. Tokyo, Japan), nitrotetrazolium blue (NBT) (Nacalai Tesque Inc. Tokyo, Japan), neocuproine, 5-nitro-1,10-phen, 3,4,7,8-tetramethyl-1,10-phen, 1,10-phen-5,6-dione, 4,7-phen (J & K Co. Ltd. Beijing, China), 1,10-phen-5-amine, 5,6-epoxy-5,6-dihydro-[1,10]phen, 1,7-phen,4,7-dihydroxy-1,10-phen, 5,6-dimethyl-1,10-phen, 2,2,6,6-tetramethyl-4-piperidine, tetradecahydro-4,7-phen, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB), and phenanthrene (Sigma-Aldrich) were purchased and used as such. All solutions were prepared in distilled water.

2.2. CL Analysis. The CL kinetic curves were obtained by batch experiments, which were carried out in a glass cuvette. The CL profiles were displayed at 1300 V negative voltage of

the photomultiplier tube and integrated at 0.1 s intervals. For the CL study, 50 μL of H_2O_2 and 50 μL of 1,10-phen were premixed and then 50 μL of IO_4^- was injected by a microliter syringe from the injector port, or otherwise specified. The CL studies of all compounds were carried out in the same experimental conditions. Various parameters influencing the CL signals, including the order of mixing reagent, pH, and concentration, were optimized.

2.3. EPR Analysis. Electron paramagnetic resonance (EPR) spectroscopy was carried out using a JEOL JES-FA200 spectrometer (conditions: microwave power, 1.0 mW; modulation amplitude, 1.0 G; and receiver gain, 1.00e^{+05}) by mixing H_2O_2 , IO_4^- , DMPO, and 1,10-phen derivatives in different mixing orders. The sample tube was filled with the reaction mixture and the analysis carried out at room temperature or otherwise specified temperature.

2.4. Cyclic Voltammetry (CV) Study. CV was carried out using a three-electrode system, i.e., a glassy carbon electrode as a working, a saturated calomel electrode (3 M KCl) as a reference, and a platinum electrode as a counter electrode at a scan rate of 100 mV/s and a potential window of -1.5 to 1.5 V. The measurement was carried out by dropwise addition of IO_4^- to the 1,10-phen-mixed H_2O_2 solution or otherwise specified with constant stirring. All potentials are mentioned versus SCE.

2.5. DFT Calculation. Computational calculations were performed using Gaussian 3.0 package. The energy of the molecules was calculated by reactions at different positions of the ring at a hybrid Becke three-parameter Lee–Yang–Parr exchange correlation function (B3LYP) level using a standard 6-31G basis set.

2.6. Matrix-Assisted Laser Desorption/Ionization–Time-of-Flight–Mass Spectrometry (MALDI-TOF-MS). Mass spectra were recorded to know the final product of the reaction mixture. The sample was uniformly mixed with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as a matrix. For MALDI analysis, the sample and matrix were mixed in a 1:1 ratio. One microliter of the sample was spotted directly onto a stainless steel plate and

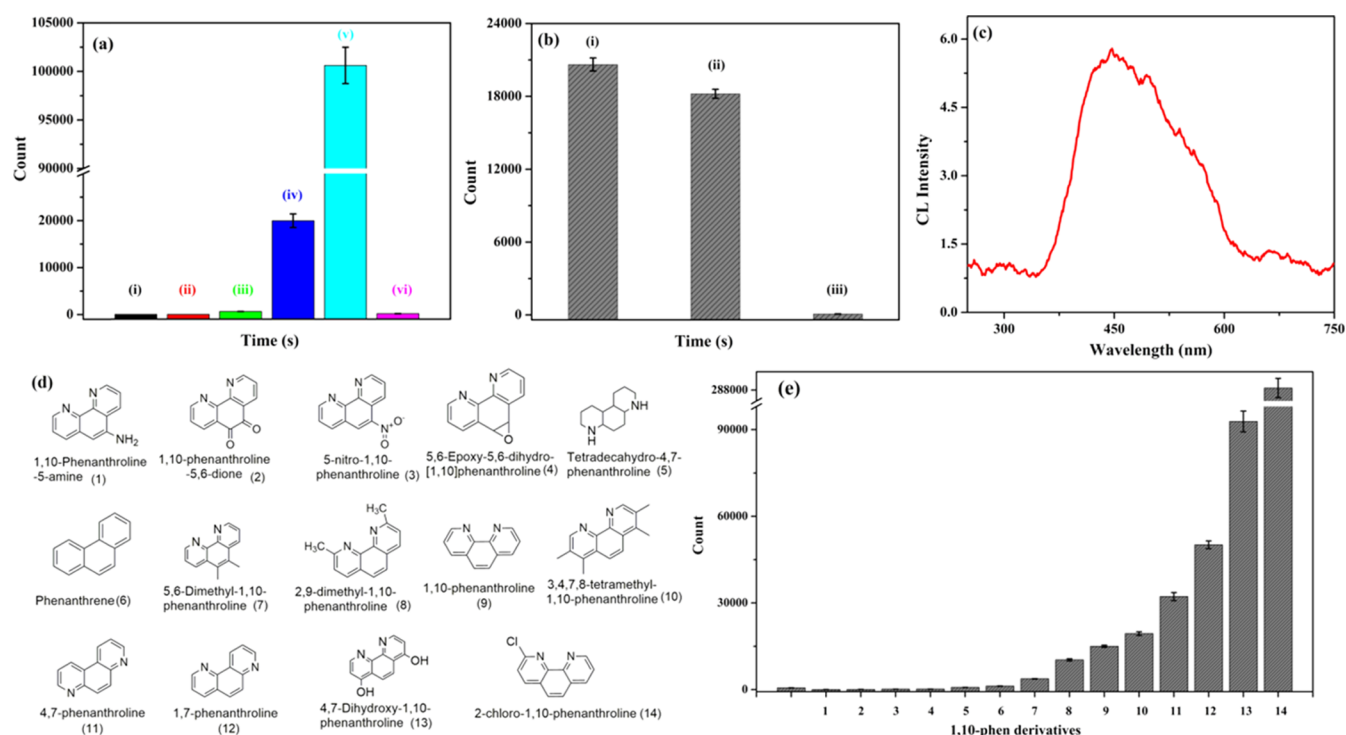


Figure 1. Enhancement of CL signals from the IO_4^- – H_2O_2 reaction with 1,10-phen and its derivatives (a): (i) IO_4^- injected into 1,10-phen (no CL), (ii) H_2O_2 injected into 1,10-phen (no CL), (iii) IO_4^- injected into H_2O_2 (weak CL), (iv) IO_4^- injected into H_2O_2 + 1,10-phen (~ 30 times), (v) IO_4^- injected into H_2O_2 + 1,10-phen + NaOH (~ 160 times), and (vi) IO_4^- injected into H_2O_2 + 1,10-phen + HCl (suppressed CL). Conditions: 0.01 M IO_4^- ; 0.1 M H_2O_2 , HCl, and NaOH; and 0.005 M 1,10-phen. The volume of each reagent was 50 μL . (b) The order of the addition of reagents: (i) IO_4^- injected into H_2O_2 + 1,10-phen, (ii) H_2O_2 injected into IO_4^- + 1,10-phen, and (iii) 1,10-phen injected into H_2O_2 + IO_4^- . (c) CL spectra of the IO_4^- – H_2O_2 system in the presence of 1,10-phen in a basic medium. The flow rate of each reagent was 3 mL/min. (d) Molecular structures of 1,10-phen, substituted derivatives, and its analogues. (e) Effect of various analogues of 1,10-phen (given in d) on the CL intensity of the IO_4^- – H_2O_2 system.

allowed to dry in air at room temperature. Individual spectra of all reagents were recorded and compared with those of the reaction mixtures.

2.7. Instrumentations. CL aptitudes were measured with a BPCL luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). A F-7000 fluorescence spectrophotometer (Hitachi, Japan) was used for the photoluminescence (PL) study, and absorption spectra were recorded by a UV-3900s spectrophotometer (Hitachi, Japan). Electron spin resonance (ESR) analysis was performed on a JEOL JES-FA200 ESR spectrometer (ESP-300E, Bruker, Japan). Mass spectrometry was performed on MALDI-TOF-MS (Shimadzu Biotech Axima, Japan). Electrochemical measurements were carried out using a Zahner IM6 potentiostat (Zahner Elektrik GmbH & Co. KG-Kronach, Germany). The CL spectra were recorded by a F-7000 fluorescence spectrophotometer (Hitachi, Japan) at a closed light source in a flow cell connected to peristaltic pumps.

3. RESULTS AND DISCUSSION

3.1. CL Profile of 1,10-Phen-Mixed Periodate–Peroxide System. The weak CL from the periodate–peroxide reaction was enhanced by 1,10-phen and the mechanism analyzed (Scheme 1). No CL signals were observed in the mixture of 1,10-phen with IO_4^- or H_2O_2 . The weak CL intensity of the IO_4^- – H_2O_2 system was increased approximately 30 times by 1,10-phen, which was further boosted in a basic medium (~ 160 times). Conversely, the acidic medium caused a decrease in the CL signals (Figure

1a). The oxidation of 1,10-phen derivatives is associated with the acid–base equilibria.¹ Protonation of 1,10-phen is expected to hinder the oxidation, making it less reactive.² Presumably, the higher sluggishness of Hphen^+ compared to that of 1,10-phen in neutral and basic media is a consequence of the low CL intensity, which efficiently hinders the attack of oxidant on 1,10-phen.^{1,2} Second, a lower pH suppresses the production of free radicals and reduces IO_4^- .¹⁸ On the other hand, the high stability of free radicals in a basic medium boosted the CL signals. Likewise, the generation of free radicals in the base-mediated transformation of IO_4^- to IO_3^- ²¹ also contributed to the high CL signals.

To know the effect of different mixing orders on the CL intensity, different injection orders were analyzed (Figure 1b). The highest CL intensity was obtained when IO_4^- was injected into the H_2O_2 –1,10-phen mixture due to the decomposition of H_2O_2 on 1,10-phen. The injection of H_2O_2 into the IO_4^- –1,10-phen mixture resulted in the second highest CL intensity. Lastly, the injection of 1,10-phen into the H_2O_2 – IO_4^- solution resulted in very poor signals due to the addition of 1,10-phen after the manifestation of the reaction. However, the effect of an acid–base was very different in the case of the order of injections. The maximum CL intensity was observed when IO_4^- was injected into the 1,10-phen– H_2O_2 mixture in a basic medium, but very low signals were observed in the case of the injection of H_2O_2 due to the unavailability of IO_4^- in an alkaline medium (Figure S1). To better understand the CL properties of the 1,10-phen-enhanced periodate–peroxide system, the emitting species in the system were initially

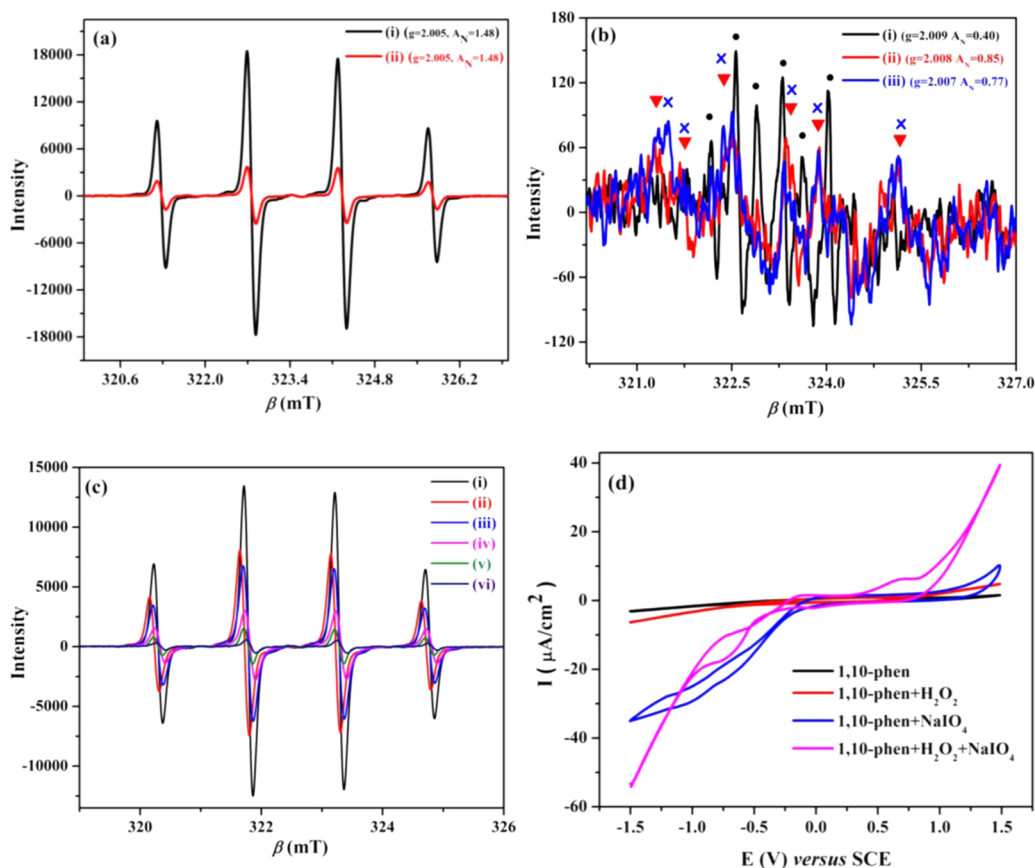


Figure 2. (a) Free radical study using EPR spectroscopy. DMPO/ \bullet OH adducts of the IO_4^- – H_2O_2 system in the presence of 1,10-phen: (i) $\text{IO}_4^- + \text{H}_2\text{O}_2$ and (ii) $\text{H}_2\text{O}_2 + 1,10\text{-phen} + \text{IO}_4^-$. (b) DMPO/ \bullet OOH/ \bullet OR adducts: (i) $\text{IO}_4^- + 1,10\text{-phen} + \text{H}_2\text{O}_2$, (ii) $\text{H}_2\text{O}_2 + 1,10\text{-phen} + \bullet\text{OH} + \text{IO}_4^-$, and (iii) $\text{IO}_4^- + 1,10\text{-phen} + \bullet\text{OH} + \text{H}_2\text{O}_2$. DMPO–OR peaks are depicted by circles and DMPO–OOH peaks are depicted by triangles and crosses, respectively. (c) DMPO/ \bullet OH adducts of the IO_4^- – H_2O_2 system in the presence of different derivatives of 1,10-phen: (i) 3,4,7,8-tetramethyl-1,10-phen, (ii) 5-nitro-1,10-phen, (iii) 4,7-phen, (iv) 2,9-dimethyl, (v) 1,10-phen, and (vi) 1,10-phen-5,6-dione. (d) Cyclic voltammetry of the CL system in different combinations.

studied by the CL spectrum by monitoring the CL intensity with respect to the wavelength by continuously flowing the reagent into a flow cell. The CL spectrum of the enhanced system has the same emission as that of 1,10-phen, pointing out that the final emission is from 1,10-phen (Figure 1c).

3.2. CL Mechanism. Before entering into the mechanistic interpretations of our results, we enumerate briefly the salient features observed in Result section. (1) The CL properties in the presence of a substituted 1,10-phen are different than those of the parent 1,10-phen. (2) Not only the substitution but also the position of N on 1,10-phen affects the CL intensity of the system. (3) There are no CL signals for the 1,10-phen derivatives in which substitutions are at the 5th and 6th C-atoms. (4) The CL signals decrease with electron-donating groups and vice versa. (5) pH has a different effect on the CL properties of different substituted 1,10-phen derivatives. The CL enhancement obtained here is expected to follow a completely different reaction route than the conventional metal- and nanomaterial-catalyzed systems.

It is well-known that the CL system usually requires the involvement of oxidants, such as H_2O_2 .¹¹ To confirm that the CL behavior was only due to H_2O_2 or IO_4^- , separate effect of each of these reagents with 1,10-phen was checked (Figure 1). No CL signals in the case of only H_2O_2 or IO_4^- with 1,10-phen suggested that the combined effect of H_2O_2 and IO_4^- resulted in an enhanced emission from the 1,10-phen-enhanced CL

system. It could be suggested that the role of H_2O_2 in the CL emission was possibly associated with the generation of reactive oxygen species (ROS). In the reaction of H_2O_2 , extensive oxidation of the aromatic ring occurs,²² involving the cleavage of the peroxy (O–O) bond of H_2O_2 and the C–O bond formation. 1,10-Phen facilitated the generation of radicals by electron transfer.²⁰ However, for small molecules in solution, which undergo electron transfer, Marcus theory is usually an effective model.²³ 1,10-phen derivatives are oxidized to radical cations by the transfer of an electron to H_2O_2 ,²² producing $\bullet\text{OH}$ and $\bullet\text{OH}$ radicals, which, in turn, cause the oxidative destruction of 1,10-phen at its most reactive $\text{C}^5=\text{C}^6$ bond to form 5,6-dihydro-1,10-phen-5,6-diol.

To thoroughly understand the CL mechanism, radicals that may be formed in the CL system, i.e., superoxide radicals ($\bullet\text{O}_2^-$), $\bullet\text{OH}$ radical, and singlet oxygen ($^1\text{O}_2$), which were identified by EPR spectroscopy and free radical scavenger studies.²⁴ The enhanced CL emission generally involves the increased production of free radicals, i.e., $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and substrate radicals.¹⁸ The confirmation was done by the addition of one equivalent ascorbic acid and thiourea ($\bullet\text{OH}$ radical scavengers), which completely inhibit the CL intensity (Table S1). Ascorbic acid and thiourea can be oxidized by radicals, utilizing the produced radicals, which resulted in inhibited CL signals.^{11,22} Similarly, the decrease in the CL signals in the presence of 5,5-dimethyl-1-pyrroline-N-oxide

(DMPO) and nitrotetrazolium blue (NBT) also confirmed the presence of free radicals in the system. The addition of 1,10-phen to $\text{IO}_4^-/\text{H}_2\text{O}_2/\text{DMPO}$ mixture results in much lower CL intensities, confirming the efficient utilization of the radicals by 1,10-phen.

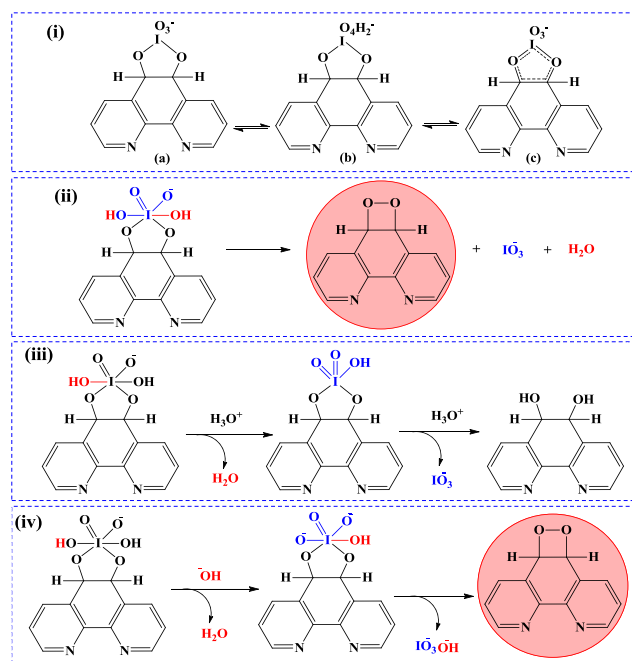
In the $\text{IO}_4^- - \text{H}_2\text{O}_2$ system, a four-line electron paramagnetic resonance (EPR) spectrum with $g = 2.0057$ and a hyperfine splitting $A_N = 14.8$ G with a 1:2:2:1 quartet peak (characteristic of $\text{DMPO} - \bullet\text{OH}$) was attributed to $\bullet\text{OH}$ radicals (Figure 2a).^{11,25} The addition of 1,10-phen to the $\text{IO}_4^- - \text{H}_2\text{O}_2$ mixture demonstrates a substantial decrease in radicals compared to the $\text{IO}_4^- - \text{H}_2\text{O}_2$ mixture, indicating that $\bullet\text{OH}$ radicals lead to the oxidation of 1,10-phen. In other combinations, $\bullet\text{OR}$ radicals were formed and the basic medium revealed a new signal with $g = 2.0058$ and $A_N = 8.5$ G corresponding to the $\text{DMPO}/\bullet\text{OOH}$ adduct (Figure 2b).²⁵ Free radicals were produced in the reaction of some 1,10-phen derivatives (Figure 2c), but the inability of these radicals to form emissive species, due to the blockage of the reactive site ($\text{C}^5 = \text{C}^6$), resulted in low CL signals. Therefore, not only the generation of free radicals but also the reaction of these radicals to form emissive species is critical for the enhanced CL emission. Therefore, pathway a in Scheme S1 is a prominent possibility. Conversely, there are chances of synchronous concerted or merged mechanism, involving simultaneous $\text{O}-\text{O}'$ and $\text{C}^5 = \text{C}^6$ bond extensions followed by rupture of the former to form products (Scheme S1b).²⁶ The free radical studies reject this mechanism to be following here.

As reported by Bokare et al., the oxidation of organic diol involves the formation of a cyclic diol–periodate monoester, which further undergoes a base-catalyzed rearrangement to form an unstable intermediate complex.²¹ The base-catalyzed cyclic rearrangement needs alkaline conditions, thus the CL intensity increases in basic conditions. The electrophilic attack of IO_4^- on the glycol oxygen of 5,6-dihydro-1,10-phen-5,6-diol (α -diol) forms a transient intermediate as a cyclic complex. This uninegatively charged complex undergoes a rearrangement to form dioxetane, which spontaneously decomposes into products. The trans- β -H elimination and reoxidation of 5,6-dihydroxy-1,10-phen-5,6-diol by IO_4^- coordination provide oxidation product (1,10-phen-5,6-diol). This was confirmed by MALDI-TOF-MS, and the two new peaks appearing at m/z 215.06 and 235.04 belong to $\text{H.1,10-phen}(\text{OH})_2^+$ and $\text{Na.1,10-phen}(\text{O})_2^+$, respectively, in the reaction mixture of 1,10-phen with H_2O_2 and IO_4^- (Figure S2). The chemiexcitation relies on electron transfer,¹³ and the large activation entropies are characteristic of $2e^-$ oxidation, i.e., O-atom transfer.^{1,2} The $2e^-$ oxidations require one molecule of IO_4^- in which an I atom is reduced from +7 to +5 (reduction to IO_3^-).

1,10-Phen itself gives no redox reaction in cyclic voltammetry (CV), but the addition of H_2O_2 changes the onset of the current values (Figure 2d). The addition of IO_4^- significantly changed the redox behavior of 1,10-phen with two reduction peaks at -0.6 and -1 V, which correspond to the reduction of IO_4^- (Figure S3). However, addition of IO_4^- to a premixed 1,10-phen– H_2O_2 solution resulted in a higher oxidation current and a clear oxidation peak at 0.6 V, which correspond to the new product formed. Furthermore, enhancement in the oxidation current upon addition of IO_4^- to the 1,10-phen– H_2O_2 solution confirms that H_2O_2 and IO_4^- promote the oxidation of 1,10-phen, which also supports our proposed mechanism.

The intermediate to be concluded as a cyclic diester of periodic acid or its hydrated form, if not so, a liable charge-transfer complex between IO_4^- and quinone, would conceivably be the intermediate (Scheme 2i). The decomposition

Scheme 2. Intermediates and Its Decomposition Pathways^a



Intermediates as (a) a cyclic diester of periodic acid and (b) hydrated form of cyclic diester and (c) liable charge-transfer complex. ^aDecomposition pathways of intermediates in (ii) neutral, (iii) acidic, and (iv) basic media.

of the intermediate is rather sensitive to acidity. Three paths of the decomposition of the diester intermediate based on H^+ and OH^- ion concentrations are proposed (Scheme 2ii–iv). The protonated form of the intermediate complex should decompose more readily than the unprotonated one because the former process does not correspond to dioxetane formation. The decrement of the CL intensity in acidic media and vice versa proves the validity of the OH^- -catalyzed decomposition of intermediates, hence a base-assisted H-bond cleavage was found to be the key step, which was reflected in general base catalysis of the overall reaction.

It is also probable that excitation occurs directly through the interaction of 1,10-phen with $^1\text{O}_2$, possibly from the $\text{IO}_4^- - \text{H}_2\text{O}_2$ reaction to produce CL.²² Dioxetane could be formed from 1,10-phen by reaction with $^1\text{O}_2$, the latter readily forms a dioxetane adduct with most double-bond organic compounds.²² If so, the decrease in the rate of $^1\text{O}_2$ should decrease the CL intensity and vice versa. It was noted that the CL intensity increased by the addition of NaN_3 (Table S1), an inhibitor of $^1\text{O}_2$. This excluded the possibility that $^1\text{O}_2$ was involved in the CL reaction (Scheme 1b).

It seems to follow that the immediate radical, $\bullet\text{O}_2^-$, is an active reducing agent; however, it can also function as an oxidizing agent in oxidative destruction of aromatic compounds. The proof of the participation of $\bullet\text{O}_2^-$ in the concerned reaction here was obtained by studying the effect of NBT and DMPO, effective acceptors of $\bullet\text{O}_2^-$. Addition of NBT and DMPO to the system suppresses the CL intensity

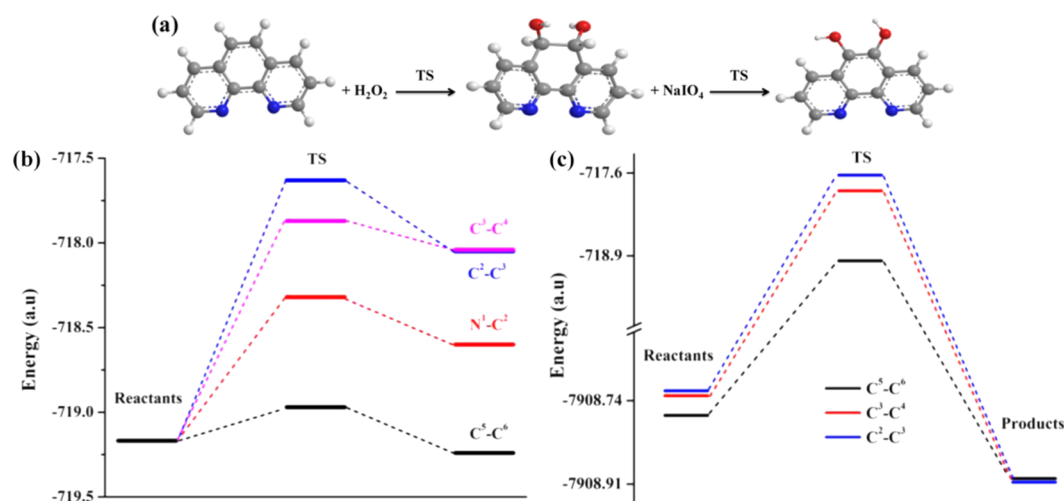


Figure 3. Theoretical calculations. (a) Possible mechanism of region selective H₂O₂ reaction with 1,10-phen and with IO₄⁻. (b) Theoretical calculations of insertion of H₂O₂ and (c) complexation of IO₄⁻ with 1,10-phen. Structures were optimized by density functional theory (DFT).

(Table S1), which strengthens the assumption that CL arises through the interaction of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ with 1,10-phen. The reaction of 1,10-phen and $\bullet\text{O}_2^-$, beginning with the addition at C⁵=C⁶ bond, proceeding reversibly to only a small fraction of 1,10-phen existing in radical adduct form at any time, followed by rearrangement of the adduct to peroxide. Subsequent disproportionation of two peroxide radicals leads to the unstable dioxetane, which then breakdowns to emit in a subsequent nonlimiting step (Scheme 1c).²² However, the very low EPR signals of the $\bullet\text{O}_2^-$ radical revealed that this pathway contributes very little and occurs concomitantly with the main $\bullet\text{OH}$ radical pathway (Scheme 1a).

Lastly, the N-heterocyclic aromatic compounds convert to N oxides by reaction with peracids.²² It was, therefore, possible that such oxides might be formed from 1,10-phen in our system. The high steric repulsion between the “bay-region” and the low CL intensity in the presence of 1,10-phen compounds with substitutions at the 5th or 6th C-atoms (entries 1–4, Figure 1d) excluded this possibility.

3.3. Effect of Various Derivatives of 1,10-Phen on CL.

A broad range of 1,10-phen derivatives, including those bearing high degree of functionality, are tried in the reaction to track the effectiveness of various substituents on the electronic and steric properties of the 1,10-phen derivatives with their oxidation and consequently on CL intensity (Figure 1d). The electronic features affect the reactivities of the 1,10-phen derivatives, and substitutions in different regions explain the selectivity of the reaction site and thereby drastically obvious CL signals. The presence of substituents at some critical positions (5th, 6th C-atoms, i.e., entries 1–4 in Figure 1d) on 1,10-phen covers the active site of oxidation, resulting in no CL signals, thus providing the evidence of a reaction at this site. McCann et al. suggested that increasing conjugation at 5- and 6-positions of 1,10-phen may not be a suitable strategy for its activity.²⁷ Likewise, the oxidation of phenanthrene exclusively occurs in the K-region due to the most olefinic and less aromatic character of this bond and the highest occupied molecular orbital (HOMO) and LUMO located in this region.^{28,29} Taking the olefinic nature of the C⁵=C⁶ position into account, attack of the $\bullet\text{OH}$ radical species across this region of 1,10-phen most likely occurs, and the subsequent

deprotonation processes (by IO₄⁻) would afford the oxidation product (Scheme 1a).

The lower CL signals of neocuproine put forward the role of two methyl groups, which donate electrons. The electron-donating groups decrease the acid strength compared to unsubstituted 1,10-phen.¹ Moreover, the electron donor produces a multidirectional charge transfer, which results in a high degree of electron delocalization and the subsequent protonation of 1,10-phen.¹ Conversely, the electron-withdrawing groups (–Cl, –OH) on 1,10-phen resulted in high CL signals. The electron-withdrawing groups decrease the electron density,³ increasing the electron mobility and the nucleophilic nature⁷ of 1,10-phen to make it more acidic.³⁰ Strong electrophilic substituents enhance the acidity of the H atom on the C⁵=C⁶ position and lead to enhanced CL signals. This is also consistent with base-catalyzed reaction, i.e., a high pH increases the CL intensity and vice versa. The CL enhancement induced by electron-withdrawing substituents on 1,10-phen is in accordance with what would be expected if 1,10-phen acted as a nucleophile in the rate-determining step. The 4,7-Phen has a pendant proton in close proximity to N, which is close to the active site, generate an intramolecular H-bond and causes enlarged resonance. The H bond stabilizes the high-energy transition state and thus results in high CL signals. Likewise, in 4,7-dihydroxy-1,10-phen, two hydroxyl substituents are spatially suitable for H-bonding with the H of the reactive C atoms (C⁵=C⁶), which are prone to chemical reactions.

3.4. Spectral Studies. As a supplement to CL study, a series of spectral studies were performed to better understand the mechanism of the system. The absorption at ~285 nm for all compounds^{31–33} was attributed to the electronic transition from the ground state (π, S_0) to the excited state (π^*, S_1) of 1,10-phen.^{8,34} However, the absorption bands at 330 nm of 5-nitro-1,10-phen and 298 of 1,10-phen-5,6-dione can be attributed to the $n-\pi^*$ transition of the oxygen atom.³² A red shift from 1,10-phen to its electron-donating substituted compound implies that the introduction of an electron donor is beneficial to reducing the absorption energy.³² There was no peak in the visible region of all mixtures, implying that there are no charge-transfer bands (Figure S4). Thus, it is clear that

1,10-phen has no complexation, even at different combinations.

UV-vis spectra showed two independent absorbing species in the reaction (Figure S4), and these experimental results are consistent with photoluminescence (PL) spectra (Figure S5).² In the PL study, the emission spectra were obtained by monitoring the excitation wavelength from 260 to 500 nm with 20 nm increment. On variation of the excitation intensity, variable emission intensity was observed along with a bathochromic shift. In the PL spectra, upon excitation at $\lambda \geq 260$ nm, 1,10-phen produced luminescence, which decreased in intensity with increase in excitation wavelength. This emission was assigned to the $\pi-\pi^*$ luminescence, derived from 1,10-phen moiety.³⁵ Different emissions may be suggestive of different origins.³⁵

3.5. Theoretical Studies. DFT calculations were performed to further support the experimental outcomes (Figure 3). The complexation of IO_4^- with 1,10-phen-5,6-diol is highly exothermic and releases significant amount of energy, which provides energy for the formation of high-energy excited state. The electron densities in the HOMO are delocalized over the entire molecule, whereas the distributions in the LUMO appear to be at the $\text{C}^5=\text{C}^6$ positions. The OH groups when substituted at the $\text{C}^{5\text{th}}$ and $\text{C}^{6\text{th}}$ positions in the 1,10-phen give the most stable configuration. Similarly, the OH-substituted 1,10-phen was further treated with IO_4^- and the results support the fact that $\text{C}^{5\text{th}}$ and $\text{C}^{6\text{th}}$ give the most stable products (Figure 3).

4. CONCLUSIONS

A new reactivity pattern in the context of 1,10-phen as well as a novel approach for CL enhancement using 1,10-phen as a catalyst is described. The various derivatives of 1,10-phen led to enhanced CL signals from the IO_4^- - H_2O_2 reaction. The CL enhancement is due to the degradation of 1,10-phen by $\bullet\text{OH}$ radical through a radical-based mechanism. Importantly, the oxidation of 1,10-phen proceeds at a higher rate in a basic medium compared to that in neutral and acidic media. Consequently, the CL intensity increased in a basic medium and vice versa. In the course of these studies, we determined that the $\text{C}^5=\text{C}^6$ bond of 1,10-phen is mainly responsible for the CL reaction to results in the enhanced emission. The CL retardation when substituents are attached at specific position ($\text{C}^5=\text{C}^6$ bond), blocking up the reaction site, resulted in no CL signals. A reaction sequence initiated by single-electron transfer from 1,10-phen to H_2O_2 produces $\bullet\text{OH}$ radical and its reaction with 1,10-phen, followed by the reduction of the IO_4^- -bound 1,10-phen complex, which then undergoes a rapid reaction to give dioxetane with enhanced CL emission. The findings are a breakthrough in the CL catalysis using organic materials and will encourage further consideration to analyze certain chemical reactions, especially those involving organic molecules in excited states. We believe that this will aid in the development and search of more active catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01785.

Effect of acid-base on the CL intensity and order of injection of reagents (Figure S1), MALDI-TOF-MS

study (Figure S2), CV study (Figure S3), UV-vis (Figure S4), PL (Figure S5), EPR (Figure S6), and HOMO LUMO study (Figure S7); additionally, the detail of reaction mechanism (Scheme S1), effect of free radical scavengers (Table S1), CL study of different derivatives (Table S2), and theoretical parameters (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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