Supplementary Information

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

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Results

Herein, 1,10-phen apparently catalyze the release of energy and direct it toward the formation of excited state. Various intermediate derivatives of 1,10-phen can be formed in the course of these reactions. Many interesting results concerning interconversion of electronic states during reaction can be observed. The reduction of IO_4^- (electron transfer, deoxygenation of IO_4^-) proceed by an inner sphere mechanism (Scheme S1c).[1] Alternatively, other mechanisms (free radical pathways/outer-sphere electron transfer) less related to the glycol oxidation process might operate (Scheme S1d).[2]

CL Study

The effect of acid base on the CL intensity of IO_4^--H_2O_2 (Figure S1a) and 1,10-phen enhanced IO_4^--H_2O_2 (Figure S1b) was the same. On the other hand, the effects of acid base on the order of reagents have different results (Figure S1c,d). Injection of IO_4^- to H_2O_2-1,10-phen mixture resulted in high CL signals in neutral as well as in basic mediums. Conversely, the injection of H_2O_2 to IOs_4^--1,10-phen mixture in neutral medium results in relatively high CL signals but have very poor CL signals in basic medium. The reduction of IO_4^- in basic medium was the cause of this low CL signals. The injection of 1,10-phen to H_2O_2-IO_4^- mixture in neutral and basic mediums have very poor CL signals. This was due to the injection of 1,10-phen after the manifestation of CL reaction.

MALDI-TOF-MS

In an attempt to validate this mechanistic hypothesis, we carried out MALDI-TOF mass spectrometry to identify the final products of the oxidation. The MALDI-TOF-MS spectrum of the reaction mixture of 1,10-phen with H_2O_2 and IO_4^- in neutral medium features two new peaks at m/z 215.06 and 235.04 that belong to H.1,10-phen$(OH)_2^+$ and Na.1,10-phen$(O)_2^+$, respectively (Figure S2).[3]

CV study

The semi in situ cyclic voltammetry (CV) was performed to investigate the redox process of 1,10-phen. Multiple CV cycles were started and the difference in voltammetric response on addition of reagents was observed (Figure 2d). 1,10-phen itself gives no redox reaction in the given potential window. The addition of H_2O_2 changes the onset of the current values but no significant change in peak was observed. However, when IO_4^- was added in the 1,10-phen solution, the significant changes in the redox behavior was observed. The two small reduction peaks at -0.6 and -1 V was observed. These peaks corresponds to the reduction of IO_4^- (Figure S3) but no oxidation peak were observed in any sample alone. However, upon addition of H_2O_2 and IO_4^- in 1,10-phen solution, the higher oxidation current and a clear oxidation peak at 0.6 V was observed. This oxidation peak corresponds to the product formed after addition of IO_4^- to H_2O_2 and 1,10-phen. Our proposed mechanism suggests the oxidation of 1,10-phen after mixing the three reagents altogether. Furthermore, the enhancement in oxidation current upon addition of IO_4^- to H_2O_2 and 1,10-phen solution as compared to 1,10-phen, 1,10-phen+H_2O_2 and 1,10phen+IO_4^- confirms that H_2O_2 and IO_4^- promotes the oxidation of 1,10-phen. The voltammetric study provides an additional support to our proposed mechanism of the CL of 1,10-phen (Scheme 2). The CV study of the reagents shows that there was no peak pointing the formation of the oxidized products in individuals reagents (Figure S3) contrast to voltammograms of the IO_4^- addition with H_2O_2-1,10-phen.

Free Radical Study

5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was utilized to trace the free radicals through EPR.[4] Free radicals in enhanced CL system were also recorded at different time (Figure S6a) and in freeze state (Figure S6b). The EPR spectra at different times show that the free radicals generation increases with time, and after certain time decreases. The EPR spectra in the freeze

state confirms the generation of free radicals in the system but the due to anisotropic effect the peak nature is different (Figure S6).

Subsequent experiments were conducted for the free radicals generated in presence and absence of 1,10-phen by the radical scavengers on the CL intensity (Table S1). Radical scavenger studies suggested that radicals are important in the CL system, and the results support free radical mechanism. The high CL signals in presence of NaN_3 ($^1O_2$ scavenger) pointed that the final emission is from 1,10-phen rather than from $^1O_2$.

Effect of different analogues of 1,10-phen

A broad range of 1,10-phen derivatives, including those bearing high degree of functionality, are tolerated in the reaction. Particularly notable is the reaction tolerance of steric hindrance (2,9-dimethyl, 3,4,7,8-tetramethyl, 4,7-phen, 1,7-phen, 4,7-dihydoxy), common protecting groups (5-nitro, 5,6-dione, 5,6-epoxy-5,6-dihydro, 5,6-dimethyl, 5-amine), aromatic halides (2-chloro) and various analogues (tetradecahydro-4,7-phen, phenanthrene). The oxidation of 1,10-phen derivatives are governed by electronic and steric effects of the attached substituents. The stability of IO_4^- complex is subject to electric and steric influences.[5] The insight may provide O-O activation and CL chemistry in general. Similarly, phenanthrene, a tricyclic analogue of 1,10-phen with two C-atoms in place of the two N atoms,[6] also have very low CL signals. The lower CL signals of neocuproine put forward the role of two methyl groups at ortho positions to N-atoms which donate electron density.

DFT calculations

DFT calculations were performed to further support the experimental outcomes. The lowest energy optimized molecules were considered as stable molecules and hence more dominant product. The energy of the optimized reactants, intermediates and the products was calculated. The lowest energy optimized molecules were considered as stable molecules and hence dominant product. The OH groups were substituted at different positions in the 1,10-phen and the most stable configuration was found when the OH group is attached to C^{5th} and C^{6th} positions. Similarly, the OH-substituted 1,10-phen was further treated with IO_4^- and the consequent structures were optimized. The results support that the C^{5th} and C^{6th} gives the most stable product. The HOMO and LUMO of 1,10-phen derivatives was found (Figure S7). The figure shows that the HOMO and LUMO of compound i-v are not able to give the reaction that why there were no CL signals in

presence of these compounds. The methyl group present in compound vii cover the HOMO and LUMO, thus have low probability of CL reaction and consequently, low CL signal. The rest of the compounds (viii-xiv) have exposed HOMO and LUMO which is available for CL reaction and also resulted in high CL signals.

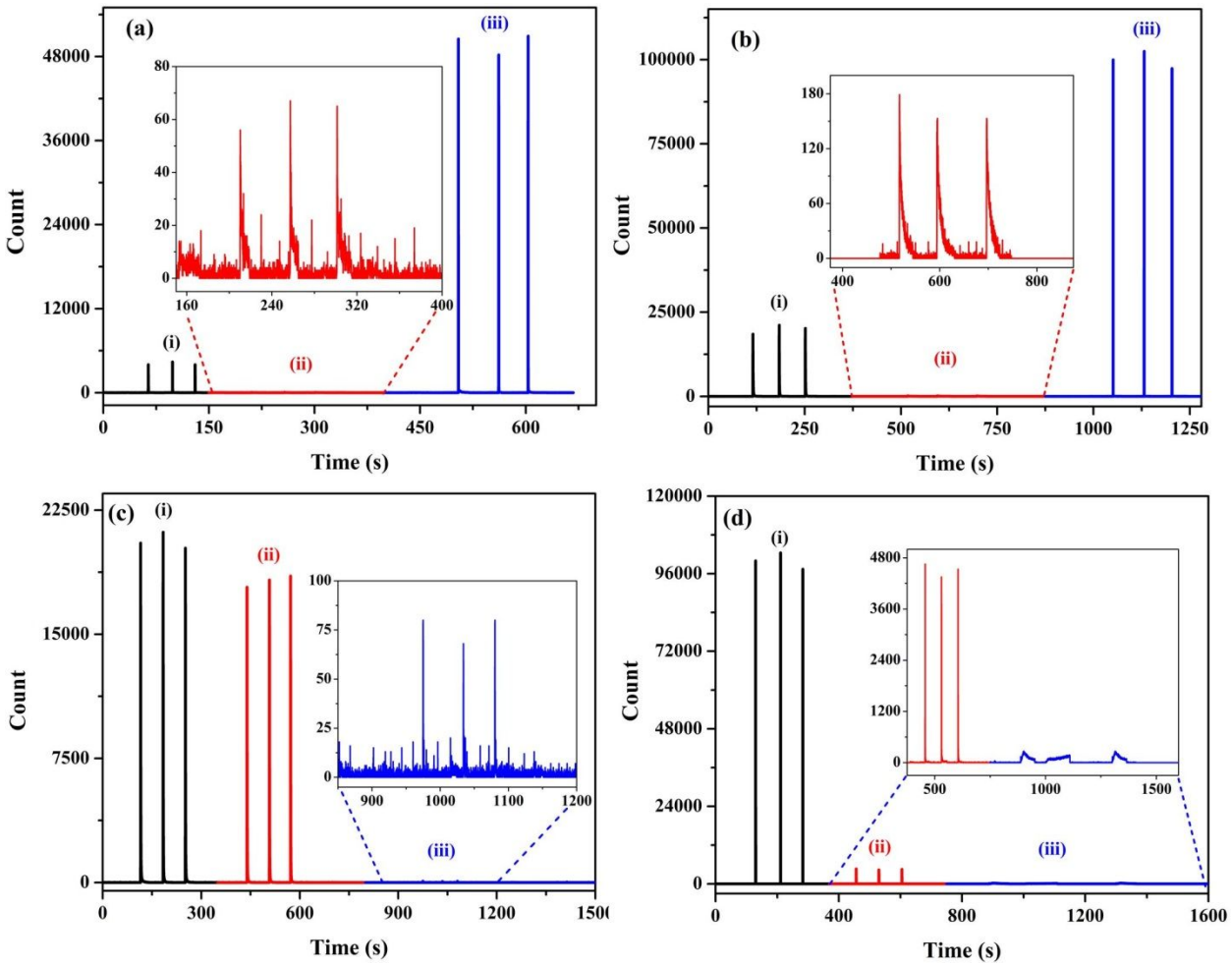


Figure S1. (a) Effect of acid base on CL intensity of IO_4^--H_2O_2 system (i) IO_4^- injected to H_2O_2 (ii) IO_4^- injected to H_2O_2+HCl (iii) IO_4^- injected to H_2O_2+NaOH. **(b)** Effect of acid base on CL intensity of 1,10-phen enhanced IO_4^--H_2O_2 system. (i) IO_4^- injected to H_2O_2+1,10-phen (ii) IO_4^- injected to H_2O_2+1,10-phen+HCl (iii) IO_4^- injected to H_2O_2+1,10-phen+NaOH. **(c)** Effect of order of addition of reagents on the CL intensity of 1,10-phen enhanced IO_4^--H_2O_2 system. (i) IO_4^- injected to H_2O_2+1,10-phen (ii) H_2O_2 injected to IO_4^-+1,10-phen (iii) 1,10-phen injected to H_2O_2+IO_4^-. **(d)** Effect of order of addition of reagents in basic medium on CL intensity of the system. (i) IO_4^- injected to H_2O_2+1,10-phen+NaOH (ii) H_2O_2 injected to IO_4^-+1,10-phen+NaOH (iii) 1,10-phen injected to H_2O_2+IO_4^-+NaOH. The concentration of IO_4^- was 0.01 M, 1,10-phen was 0.005 M while H_2O_2, HCl and NaOH were 0.1 M. The volume of each reagent was 50 µL.

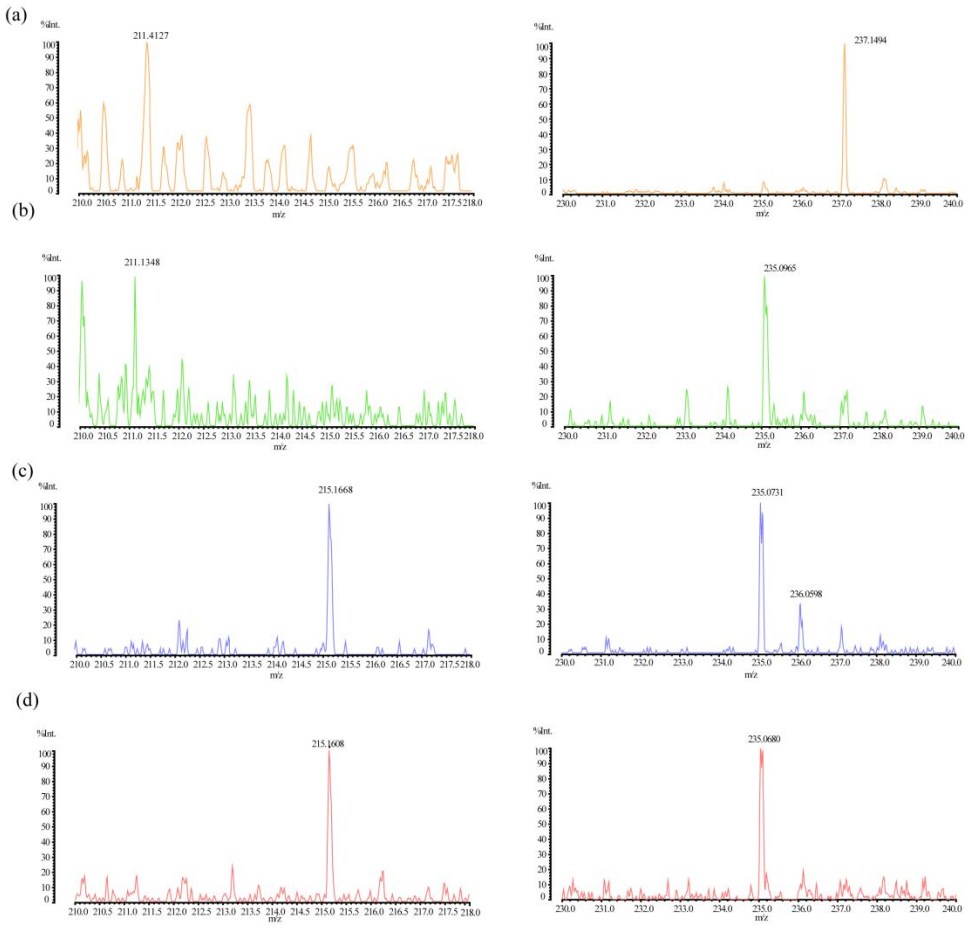


Figure S2. MALDI-TOF MS analysis of the different combination of CL system. Mass spectrum of (a) 1,10-phen (b) 1,10-phen+H_2O_2 (c) 1,10-phen+$NaIO_4$ (d) 1,10-phen+ H_2O_2+$NaIO_4$.

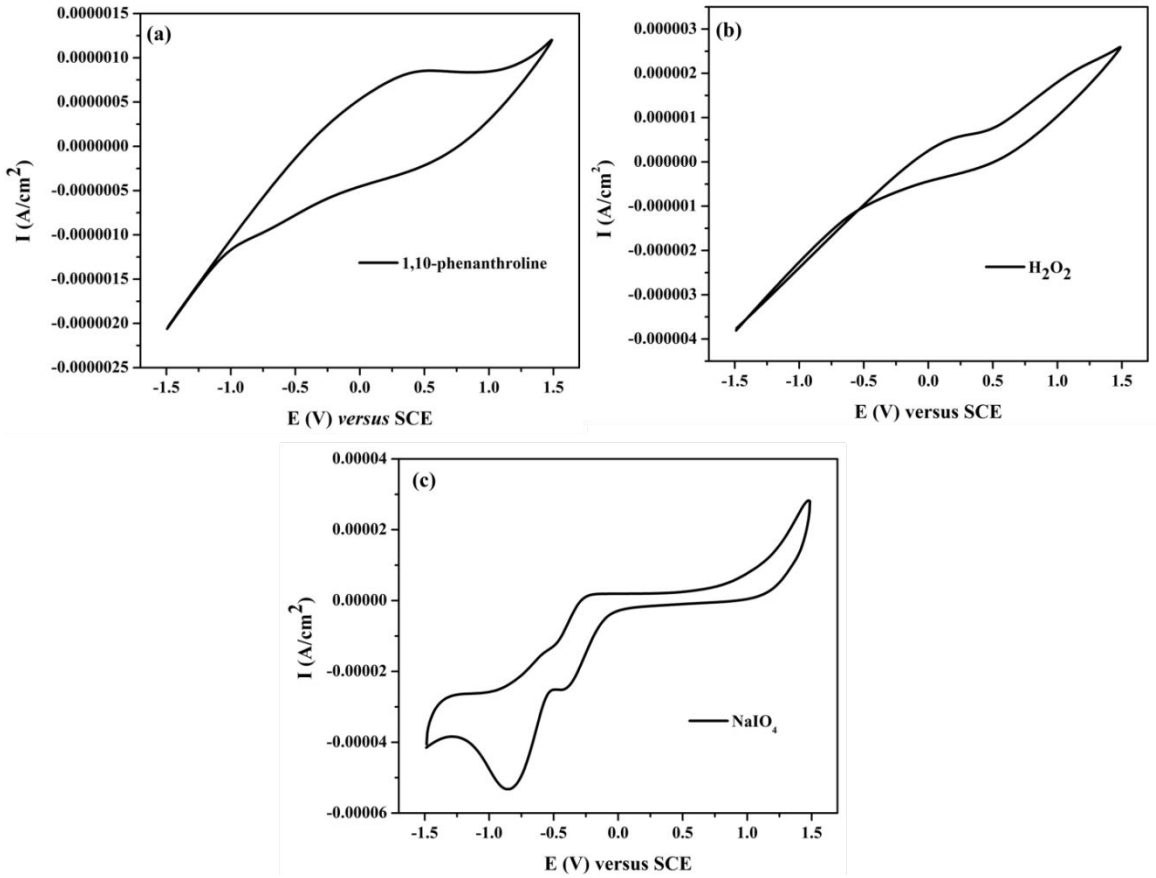


Figure S3. Cyclic voltammetry of **(a)** 1,10-phen **(b)** H_2O_2 **(c)** IO_4^-.

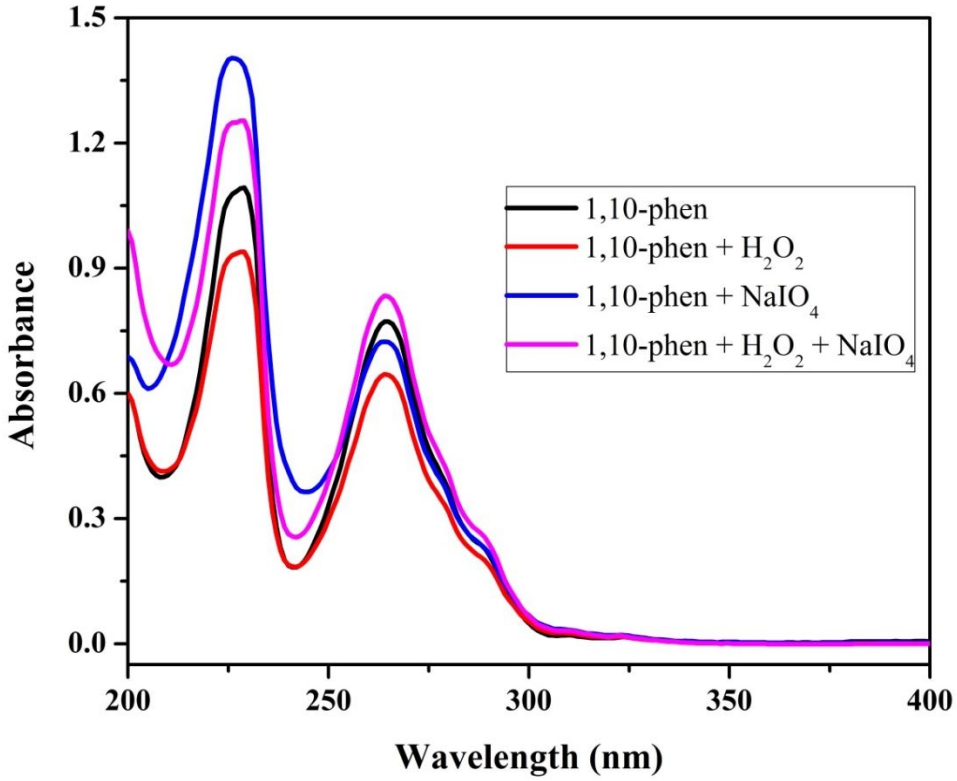


Figure S4. UV-visible spectroscopy of phenanthroline enhanced $NaIO_4$-H_2O_2 system in different combinations of the reaction mixture.

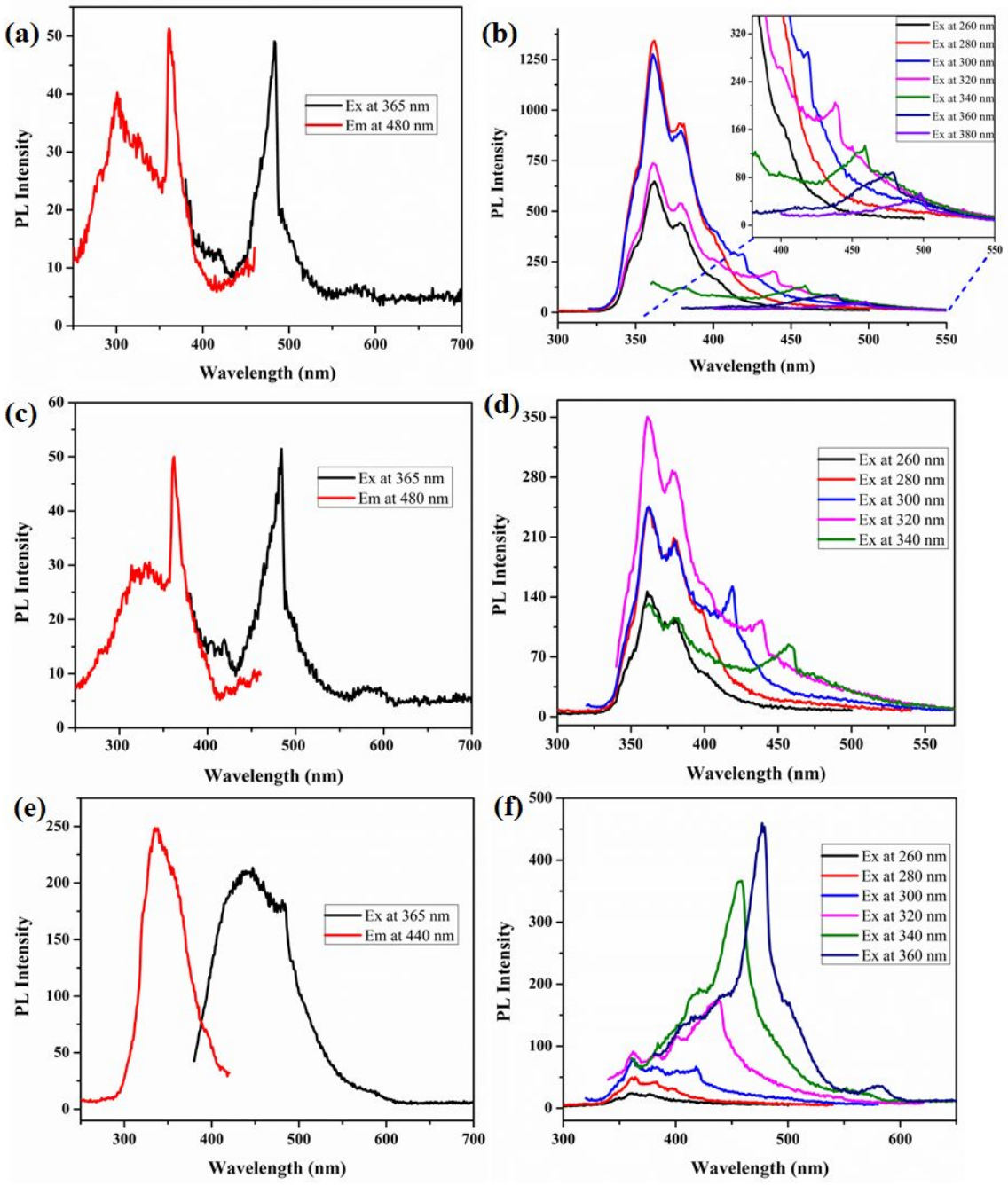


Figure S5. (a, b) PL spectra of 1,10-phen+H_2O_2. **(c, d)** PL spectra of 1,10-phen+$NaIO_4$. **(e, f)** PL spectra of 1,10-phen+$NaIO_4$+H_2O_2.

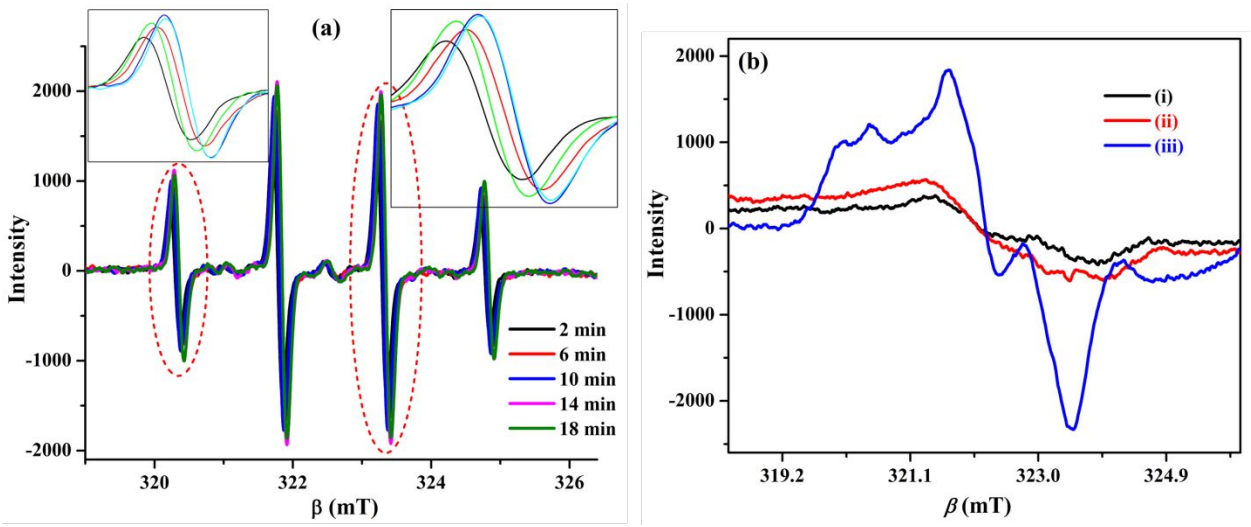


Figure S6. Free radical trapping study using EPR spectroscopy. DMPO/•OH adducts of IO_4^--H_2O_2 system in presence of 1,10-phen. **(a)** Spectra of IO_4^--H_2O_2-1,10-phen at different times. **(b)** EPR spectra of IO_4^--H_2O_2-1,10-phen in freeze state (i) -100 °C (ii) -150 °C (iii) -150 °C without sample tube. Conditions: In all experiments, the concentration of IO_4^- was 0.01 M, 1,10-phen was 0.005 M, H_2O_2, NaOH and DMPO were 0.1 M.

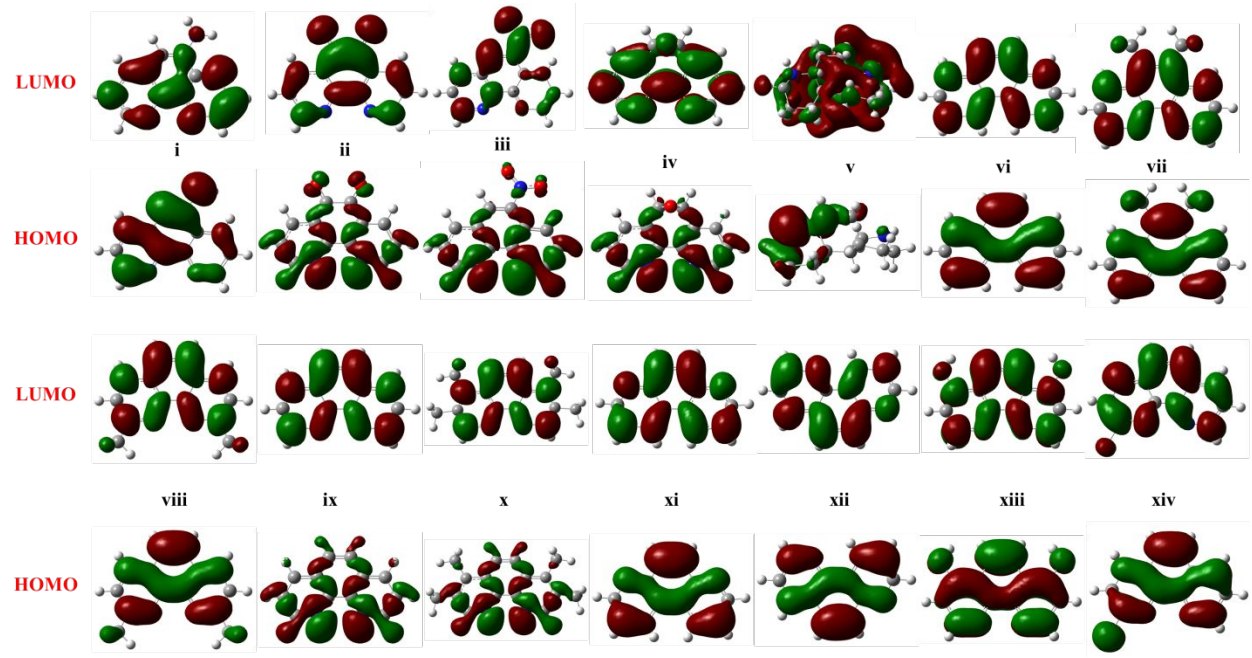
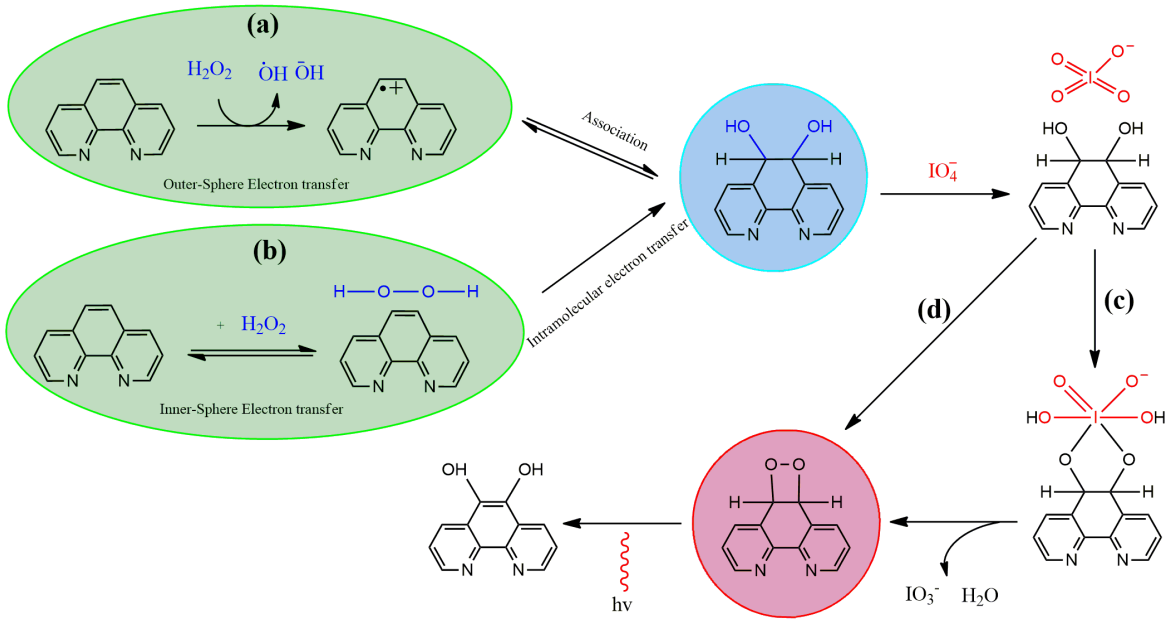


Figure S7. HOMO and LUMO of 1,10-phen derivatives.



Scheme S1. Proposed pathways for the enhancement of periodate-peroxide CL system in presence of 1,10-phen. Pathway **(a)** was the most probable way for the insertion of H_2O_2 with 1,10-phen compared to the concerted path **(b)**. The reduction of IO_4^- most probably take place following outer-sphere mechanism **(c)**, and the chances of pathway **(d)** was very low.

Table S1. Effect of free radicals scavengers on the CL intensity of IO_4^--H_2O_2 in the presence of 1,10-phenathroline.

Free radical scavengers	Radicals	Concentration (M)	$NaIO_4$-H_2O_2-1,10-phen (% decrease)	$NaIO_4$-H_2O_2-1,10-phen-NaOH (% decrease)
-	-	-	32,000	300,000
Water	-	-	19,700 (38)	200,000 (33)
NaN_3	$^1O_2$	0.1	72,170 (-125)↑	232,000 (23)
Ascorbic acid	$^{\bullet}OH$	0.1	00 (100)	00 (100)
NBT	$^{\bullet}O_2^-$	0.01	2293 (93)	140,000 (53)
DMPO	$^{\bullet}O_2^-$	0.1	200 (99)	117,500 (61)
Thiourea	$^{\bullet}OH$	0.1	00 (100)	29,400 (90)

Each result is an average of triplicate readings. The concentration of NaN_3, ascorbic acid, DMPO, thiourea and H_2O_2 was 0.1 M. NBT and $NaIO_4$ was 0.01 M. 1,10-phen was 0.005 M. The volume of each reagent used was 50 μL.

Table S2 Effect of different derivatives of 1,10-phen on the CL intensity of IO_4^--H_2O_2 system in different pH.

S. No.	Reagents	$NaIO_4$-H_2O_2 (% effect)	$NaIO_4$-H_2O_2-HCl (% effect)	$NaIO_4$-H_2O_2-NaOH (% effect)
-	-	600	40	1500
1	1,10-phen-5-amine	30 (95)↓	20	50
2	1,10-phen-5,6-dione	70 (88) ↓	30	300
3	5-nitro-1,10-phen	165 (72) ↓	60	1460
4	5,6-epoxy-1,10-phen	181 (70) ↓	105	51000
5	Tetradecahydro-4,7-phenanthroline	783 (30)↑	355	440
6	Phenanthrene	1215 (102)↑	80	475
7	5,6-dimethyl-1,10-phen	3736 (522)↑	90	2070
8	2,9-dimethyl-1,10-phen	10300 (1616)↑	400	2444
9	1,10-phen	15000 (2400)↑	170	99300
10	3,4,7,8-tetramethyl-1,10-phen	19400 (3133)↑	850	101300
11	4,7-phen	32200 (5266)↑	47660	63300
12	1,7-phen	49900 (8216)↑	1740	1070
13	4,7-dihydroxy-1,10-phen	93900 (15550)↑	105	2735
14	2-chloro-1,10-phen	288556 (47991)↑	350	27900

Each result is an average of triplicate readings. The concentration of H_2O_2, HCl and NaOH was 0.1 M. $NaIO_4$ was 0.01 M while 1,10-phen and its derivatives were 0.005 M. The volume of each reagent used was 50 µL. The upward arrow shows the increase compare to original reaction, while the downward arrow shows the decrease.

Table S3 Theoretical parameters obtained from DFT calculations

Name	HOMO	LUMO	I.E	E.A	E.N
1	-0.19644	-0.04546	0.19644	0.04546	-3.24×10^3
2	-0.25693	-0.13375	0.25693	0.13375	-3.64×10^3
3	-0.24939	-0.12063	0.24939	0.12063	-4.00×10^3
4	-0.23754	-0.06202	0.23754	0.06202	-3.31×10^3
5	-0.18731	0.07770	0.18731	-0.07770	-3.33×10^3
6	-0.21204	-0.03654	0.21204	0.03654	-2.79×10^3
7	-0.22484	-0.04973	0.22484	0.04973	-3.52×10^3
8	-0.22366	-0.04653	0.22366	0.04653	-3.48×10^3
9	-0.23141	-0.05499	0.23141	0.05499	-2.89×10^3
10	-0.22077	-0.04989	0.22077	0.04989	-4.13×10^3
11	-0.23815	-0.06020	0.23815	0.06020	-2.88×10^3
12	-0.23750	-0.05638	0.23750	0.05638	-2.89×10^3
13	-0.22977	-0.05953	0.22977	0.05953	-3.69×10^3
14	-0.24263	-0.06534	0.24263	0.06534	-4.34×10^3

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