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Nickel(II) Tetraphenylporphyrin as an Efficient Photocatalyst Featuring Visible Light Promoted Dual Redox Activities

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Abstract. Nickel(II) tetraphenylporphyrin (NiTPP) is presented as a robust, cost-effective and efficient visible light induced photoredox catalyst. The ground state electrochemical data (CV) and electronic absorption (UV-Vis) spectra reveal the excited state redox potentials for $[NiTPP]^*/[NiTPP]^-$ and $NiTPP]^{.+}/[NiTPP]^*$ couples as +1.17 V and -1.57 V vs SCE respectively. The potential values represent NiTPP as a more potent photocatalyst compare to the well-explored $[Ru(bpy)_3]^{2+}$. The non-precious photocatalyst exhibits excited state redox reactions in dual fashions, i.e., it is capable of undergoing both oxidative as well as reductive quenching pathways. Such versatility of a photocatalyst based on first-row transition metals is very scarce.
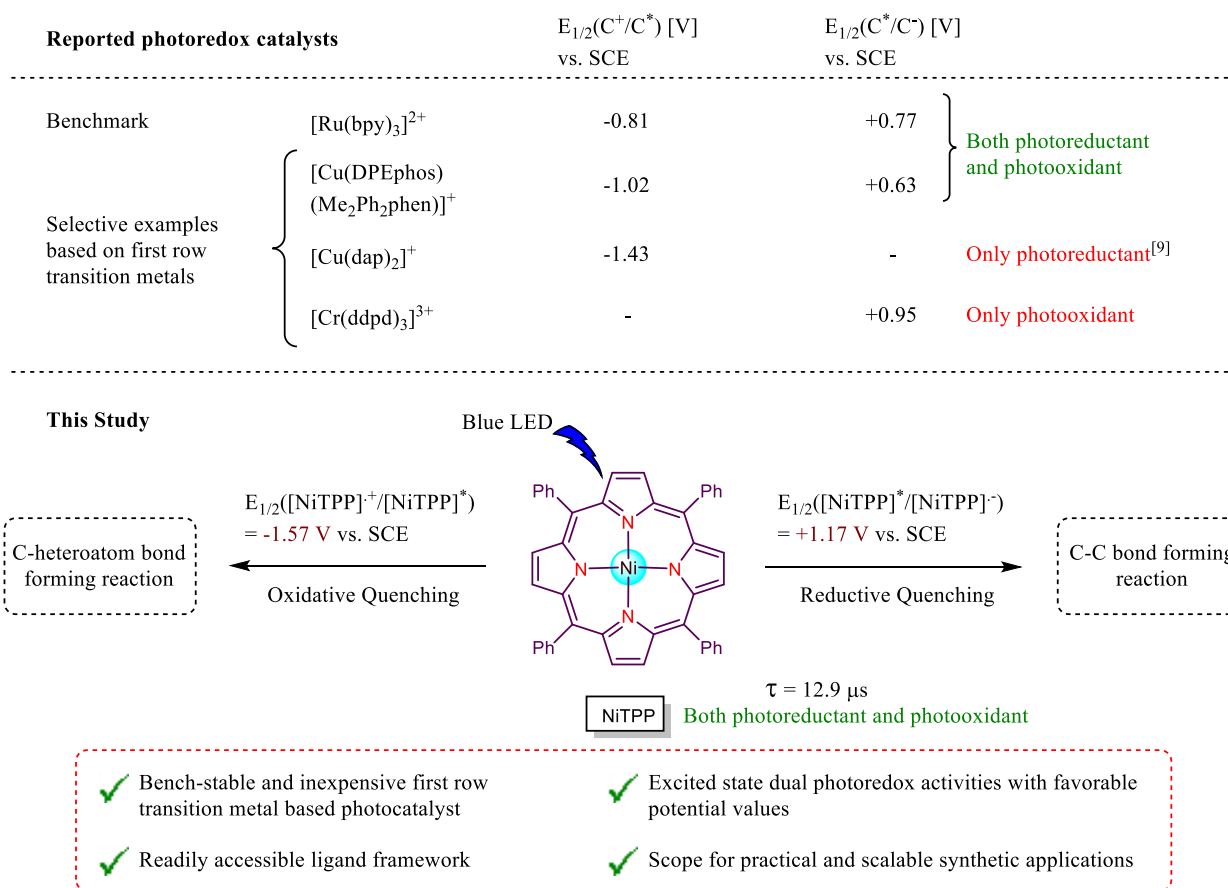
This unique phenomenon allows one to perform diverse types of redox reactions by employing a single catalyst. Two different sets of chemical reactions have been performed to represent the synthetic utility. The catalyst showed superior efficiency in both carbon-carbon and carbon-heteroatom bond-forming reactions. Thus, we believe that NiTPP is a valuable addition to the photocatalyst library and this study will lead to more practical synthetic applications of earth-abundant-metal-based photoredox catalysts.

Keywords: photoredox, homogeneous catalysis, nickel catalyst, tetrahydroquinoline, earth-abundant metal, maleimide, chalcogenation

Introduction

Light is the most abundant, inexpensive, everlasting and unpolluted energy source in nature and has been utilized in copious synthetic applications.[1] Apart from less discriminating and high energetic UV sources, visible light mediated photoredox catalysis has become a trustable and influential synthetic tool in organic synthesis over the last few years.[2] In search of some advantageous protocols, it is comprehended that photoinduced electron transfer (PET) could be a reliable transformative alternative to construct simple as well as complicated molecular architectures through the radical pathways. Apart from the environmentally benign nature and mild reaction conditions, this particular field also offers an ever-increasing number of generic activation modes where photonic energy can activate the targeted specially designed visible light sensing agents in a highly selective manner.[3] Upon irradiation, the photocatalyst excites the accompanying substrate which participates in further organic transformations.[4] Thus, by converting the

photo energy to chemical energy, visible light photoredox catalysis has opened up the door for some new bond-forming protocols under mild conditions that were elusive with traditional methods.[2b, 5]

The fundamental working method of a general metal based photoredox catalyst is the initiation via photon mediated excitation of the catalyst molecule and thereby transferring one t_{2g} electron to the π^* orbital of a highly conjugated ligand system to obtain its most stable triplet photo-excited state. This excited state ultimately returns to the relaxed state by single electron transfer process with the accompanying substrate molecule either by oxidation or reduction to promote the molecule for desirable organic reactions.[3] Various precious metal complexes of Ru(II), Re(I), Os(II) and Ir(III) with the d^6 electronic configuration exhibit reasonably long-lived electronic excited states, which possess entirely different redox behavior compared to the corresponding electronic ground states. This phenomenon is the foundation for their application as photoredox catalysts in several organic transformations.[3, 5-6]

Reported photoredox catalysts		$E_{1/2}(C^+/C^*)$ [V] vs. SCE	$E_{1/2}(C^*/C^-)$ [V] vs. SCE	
Benchmark	$[Ru(bpy)_3]^{2+}$	-0.81	+0.77	Both photoreductant and photooxidant
Selective examples based on first row transition metals	$[Cu(DPEphos)(Me_2Ph_2phen)]^+$	-1.02	+0.63	
	$[Cu(dap)_2]^+$	-1.43	-	Only photoreductant[9]
	$[Cr(ddpd)_3]^{3+}$	-	+0.95	Only photooxidant

This Study

Blue LED

$E_{1/2}([NiTPP]^{·+}/[NiTPP]^*)$ = -1.57 V vs. SCE

C-heteroatom bond forming reaction

Oxidative Quenching

$E_{1/2}([NiTPP]^*/[NiTPP]^-)$ = +1.17 V vs. SCE

C-C bond forming reaction

Reductive Quenching

τ = 12.9 µs

NiTPP   Both photoreductant and photooxidant

✓ Bench-stable and inexpensive first row transition metal based photocatalyst

✓ Excited state dual photoredox activities with favorable potential values

✓ Readily accessible ligand framework

✓ Scope for practical and scalable synthetic applications

Scheme 1. Comparison of NiTPP with selective photocatalysts and applications as both photoreductant and photooxidant

Since a long time chemists have tried to substitute the noble metals in photoactive coordination complexes by organic dyes[7] or with cost-effective more earth-abundant elements.[8] But this is extremely challenging, since, first-row transition metal complexes, in general, suffer from short-excited state lifetime. Several Cu(I) complexes[9] were thoroughly investigated as photoredox catalysts along with few reports of other photoactive Cr(III), Fe(II), Zn(II) compounds consisting of complex ligand systems are documented as well.[10] On the other hand, nickel catalysts have been utilized in cross-coupling reactions in the presence of additional photocatalytic systems.[11] A library of Ni(II) ligand-to-ligand charge transfer complexes recently was shown to possess beneficial properties as photosensitizers, but their application in typical photoredox catalysis is still underexplored.[11a, 12] Another important feature of a photoredox catalyst is the feasibility to undergo both oxidative and reductive quenching from the excited state which allows its application as both photoreductant and photooxidant.[3] Only a few catalysts are known to date (eg. $[Ru(bpy)_3]^{2+}$, $[Ir(ppy)_3]$ etc.) which possess these properties and examples of photo redox catalysts based on first-row transition metals are extremely scarce.[10a] Twigging the requirement for economically viable, more abundant first row transition metal photoactive catalysts, we explored the use of macrocyclic *meso*-tetraphenylporphyrin ligand coordinated Ni(II) complex [NiTPP] as a photoredox catalyst and disclosed its dual excited state redox properties, i.e., oxidative quenching as well as reductive quenching representing two different sets of chemical reactions under visible light promoted condition (Scheme 1). To the best of our knowledge, this is the first report to involve NiTPP as the sole catalyst in visible light mediated organic synthesis.[13]

Results and Discussion

Standard synthesis of the purple colored NiTPP was developed by Adler[14] and the physicochemical properties were examined.[15] However, the catalytic efficiency of such readily accessible, cheap and bench stable complex in organic synthesis has never been explored. The catalyst exhibits an absorption maxima at 417 nm followed by a small hump at 445 nm (Fig. 1). The latter arises probably on account of the internal π-π^* transition of the TPP ligand system.[15a] Different concentration of the catalyst was used to perform the luminescence experiment which was capable of providing the Lambert-Beer linear correlation between absorbance and concentration at λ_{max} = 417 nm. The emission maxima was found to be observed at 650 nm. The excited state lifetime of NiTPP was counted to be 12.9 µs from the decay/delay calculation (see SI).[16]

2

The cyclic voltammetry experiment was conducted to recognize the ground-state redox properties of NiTPP. The values empowered us to compute the reduction potentials of redox couples as -1.44 V for [NiTPP]/[NiTPP]⁻ and +1.04 V for [NiTPP]⁻⁺/[NiTPP] vs SCE (Fig. 1). Consequently, the excited state redox potentials for [NiTPP]*/[NiTPP]⁻ and NiTPP]⁻⁺/[NiTPP]* couples were evaluated as +1.17 V and -1.57 V respectively using the Rehm–Weller formalism (see SI).[17] Conspicuously, the estimated redox behavior in the excited state of NiTPP photocatalyst is analogous to that of other reported Ni(II)-complexes which were recently explored as potential photoredox catalysts.[12]
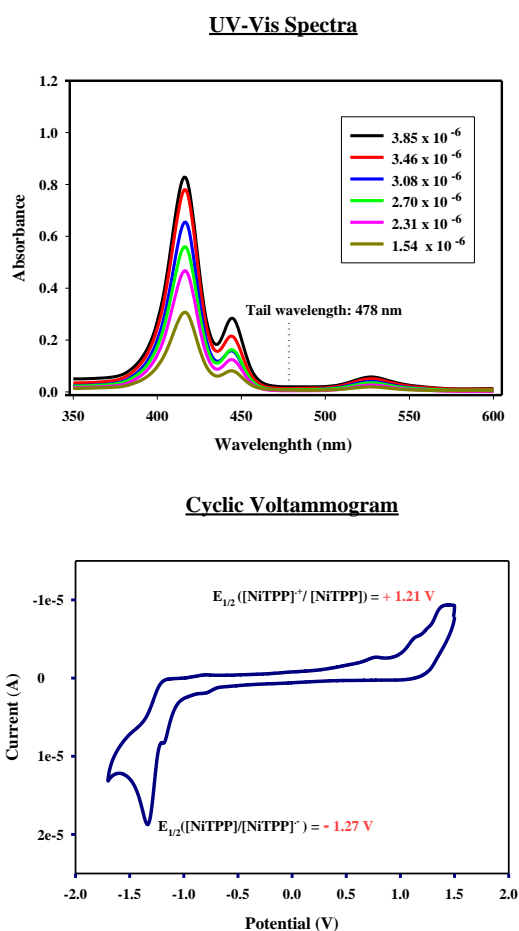
UV-Vis Spectra

Cyclic Voltammogram

Figure 1. UV-Vis Spectra and Cyclic Voltammogram of NiTPP

Next, we examined applications of this first-row transition metal centered photocatalyst in various synthetic transformations. Prior spectrochemical and electrochemical findings indicate that single electron transfer (SET) from *N,N*-dimethylaniline[18] (**1a**) to NiTPP under visible light irradiation is thermodynamically favorable. Thus, we began our investigation by choosing **1a** and *N*-phenylmaleimide **2a** in DMF as a prototypical condition and irradiated the reaction mixture with 30W CFL bulb under an oxygen atmosphere for 36 hours in presence of 3 mol% of NiTPP catalyst (Table 1). To our delight, the

successful formation of the desired annulated product was observed in 62% isolated yield (entry 1).

Table 1. Optimization Studies for Reductive Quenching Pathway[a]

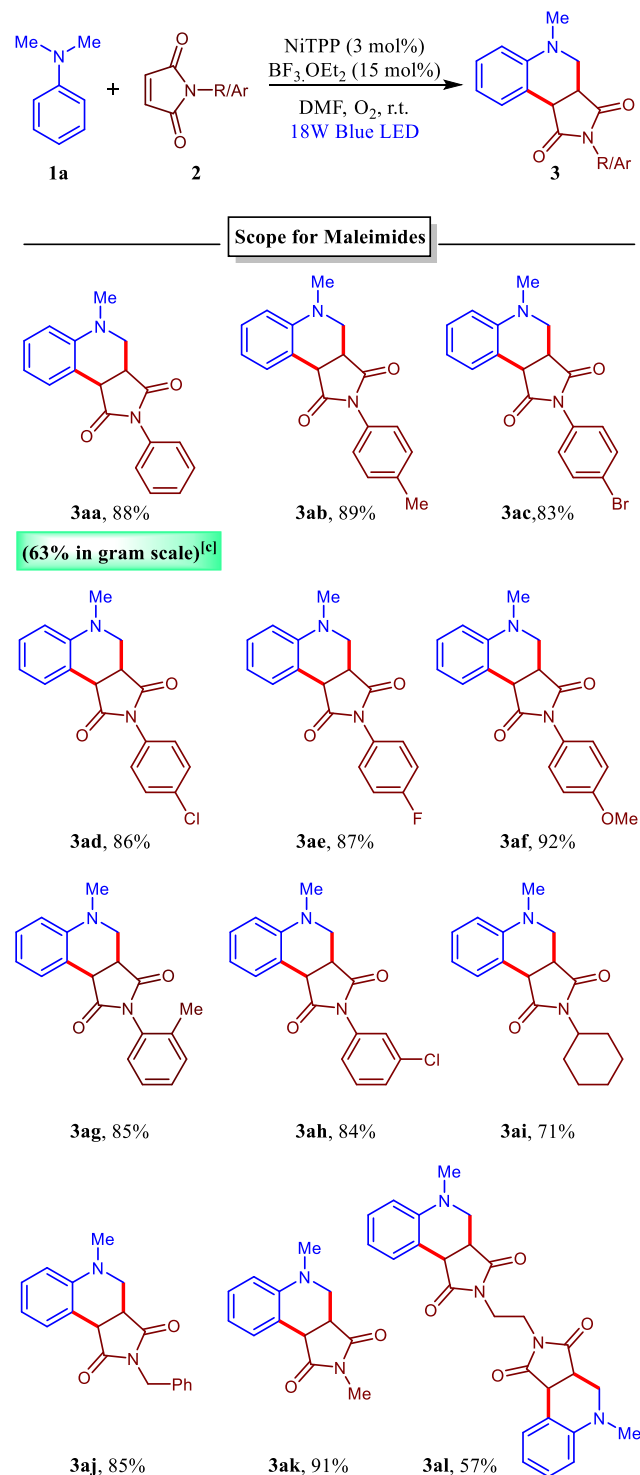| SL No.	Light Source	Additive	Solvent	Time	Yield [%][b]
1	30W CFL	-	DMF	36 h	62
2[c]	30W CFL	-	DMF	36 h	0
3[d]	-	-	DMF	36 h	0
4[e]	30W CFL	-	DMF	36 h	0
5[f]	30W CFL	-	DMF	36 h	43
6	30W CFL	-	DCE	36 h	24
7	30W CFL	-	MeCN	36 h	47
8	30W CFL	TFA	DMF	20 h	67
9	30W CFL	BF₃.OEt₂	DMF	20 h	76
10	30W CFL	Sc(OTf)₃	DMF	20 h	59
11	**18W Blue LED**	**BF₃.OEt₂**	**DMF**	**20 h**	**88**
12	3W Blue LED	BF₃.OEt₂	DMF	20 h	71

[a] **Reaction conditions: 1a** (0.5 mmol), **2a** (0.25 mmol), NiTPP (3 mol%), solvent (1.5 mL), under O₂. [b] Isolated yield. [c] Without photocatalyst. [d] Reaction performed without irradiation. [e] Under Ar atmosphere. [f] Open atmosphere.

Enthralled by this initial result, we first proved the necessity of light and photocatalyst for this reaction (entry 2 and 3). Further assessment revealed that complete oxygen atmosphere was essential for the better conversion of starting materials (entry 4 and 5). Excluding DMF, other solvents like DCE, MeCN were unable to promote the product formation to a good extent (entry 6-7). Addition of Brønsted and Lewis acids offered superior yields and the best yield was achieved with 15 mol% of BF₃.OEt₂ (entry 9) where the reaction was completed within 20 h. Afterwards, we optimized the light source, and 18 W blue LED strip proved to be superior over CFL lamps providing 88% isolated yield of tetrahydroquinoline derivative **3a** (entry 11).

With the optimized condition in hand, we surveyed the scope by reacting *N,N*-dimethylaniline **1a** with diversely substituted *N*-aryl or *N*-alkyl maleimides **2**. It was observed that *N,N*-dimethylaniline (**1a**) reacted successfully with electronically diverse *N*-aryl maleimides (Table 2) bearing halogens (**2c-e, 2h**),

3

alkyl (**2b**, **2g**) and alkoxy (**2f**) groups at the *ortho-, meta-*, and *para-* positions of the aryl ring. Additionally, several *N*-alkyl maleimides (**2i-l**) also offered good to excellent yields of the products **3**.

Table 2. Substrate Scope using *N,N*-Dimethylaniline and Various Maleimides[a,b]

3aa, 88%
(63% in gram scale)[c]

3ab, 89%

3ac, 83%

3ad, 86%

3ae, 87%

3af, 92%

3ag, 85%

3ah, 84%

3ai, 71%

3aj, 85%

3ak, 91%

3al, 57%

[a] **Reaction conditions: 1a** (1.0 mmol), **2** (0.5 mmol), NiTPP (3 mol%), BF$_3$.OEt$_2$ (15 mol%) in DMF (2.5 mL), under O$_2$ for 20 h. [b] Isolated yield. [c] **Reaction conditions: 1a** (12.0 mmol), **2** (6.0 mmol), NiTPP (3 mol%), BF$_3$.OEt$_2$ (15 mol%) in DMF (15 mL), under O$_2$ for 20 h.

High photocatalytic efficiency of NiTPP was demonstrated by the double annulation with the bis-maleimide system **2l** providing the desired product **3al** in moderate yield, which was usually not observed by others.[18a, 18e] The cheap NiTPP catalyst was employed in the gram scale synthesis of **3aa** in an acceptable yield (63%) which indicates its potential application in the large scale synthesis as a photocatalyst.

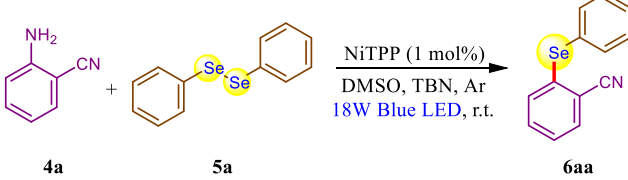**Table 3.** Substrate Scope Using Substituted *N,N*-Dimethylanilines and *N*-Aryl Maleimides[a,b]

3ba, 84%

3ca, 81%

3da, 94%

3ea, 86%

3bf, 97%

3cb, 78%

3eg, 91%

3fa:3'fa = 2:1, 58%
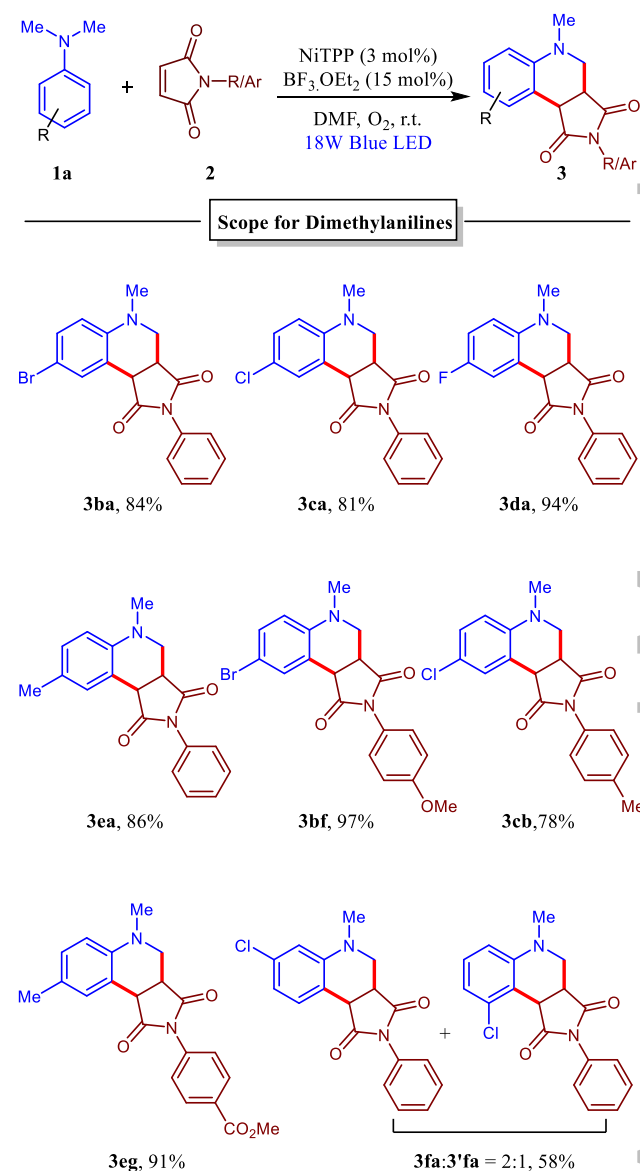
[a] **Reaction conditions: 1** (1.0 mmol), **2** (0.5 mmol), NiTPP (3 mol%), BF$_3$.OEt$_2$ (15 mol%) in DMF (2.5 mL), under O$_2$ for 20 h. [b] Isolated yield.

The photocatalytic behavior of the nickel complex was further explored by coupling differently substituted *N,N*-dimethylanilines **1** carrying electron withdrawing (**1b-d**) as well as electron donating groups (**1e**) with *N*-aryl maleimides (Table 3). Excellent yields were obtained with *para*-substituted derivatives and other *N*-aryl maleimides (**78%** to **97%**). When the reaction

4

was conducted using 3-chloroaniline and *N*-phenyl maleimide, a mixture of **3fa** and **3'fa** was obtained with the diastereomeric ratio of 2:1, similar to the previous reports.

To address the ability of the catalyst as a photoreductant we performed direct conversion of aryl/heteroaryl amines to diaryl selenides.[19] One of the major aspects of this methodology is that an aryl radical is generated through the diazotization of anilines when using tertiary butyl nitrite (TBN) and thereafter it is cleaved by electron donation from photoexcited NiTPP [20] to ultimately derivatize the aromatic ring, evading the "so-called powerful" transition-metal-mediated cross-coupling reaction.

**Table 4.** Optimization Studies for Oxidative Quenching Pathway[a]

Entry	Variation from standard conditions	Yield [%][b]
1	**No variation**	**94**
2	In absence of TBN	-
3	Reaction performed under dark	trace
4	No photocatalyst was used	13
5[c]	H$_2$TPP was used as a photocatalyst	47
6	DCE as solvent	51
7	Toluene as solvent	trace
8	3W Blue LED was used	79

[a] **Reaction conditions: 4** (0.5 mmol), **5a** (0.6 mmol), NiTPP (1 mol%), TBN (1.5 equiv) in DMSO (2.5 mL), under Ar for 6 h. [b] Isolated yield. [c] 5 mol% H$_2$TPP was used.

The combination of 2-cyano aniline (0.3 mmol), commercially available diphenyl diselenide (1.2 equiv) and *tert*-butyl nitrite (1.5 equiv) in DMSO solvent was exposed to blue LED under an argon atmosphere (Table 4). Gratifyingly, we were able to obtain the desired denitrogenated selenylation product in 94% of isolated yield. No reaction was observed in the absence of light and TBN, although a much lesser amount of product was formed when the reaction was executed in photocatalyst free condition. However, only H$_2$TPP was able to promote the reaction with reduced yield, and high catalyst loading was necessary in this case (entry 5). Non-polar solvent like toluene was completely incompetent, and chlorinated solvent like DCE showed a negative influence on the reaction outcome.

Table 5. Selenylation and Thiolation of Substituted Anilines[a,b]
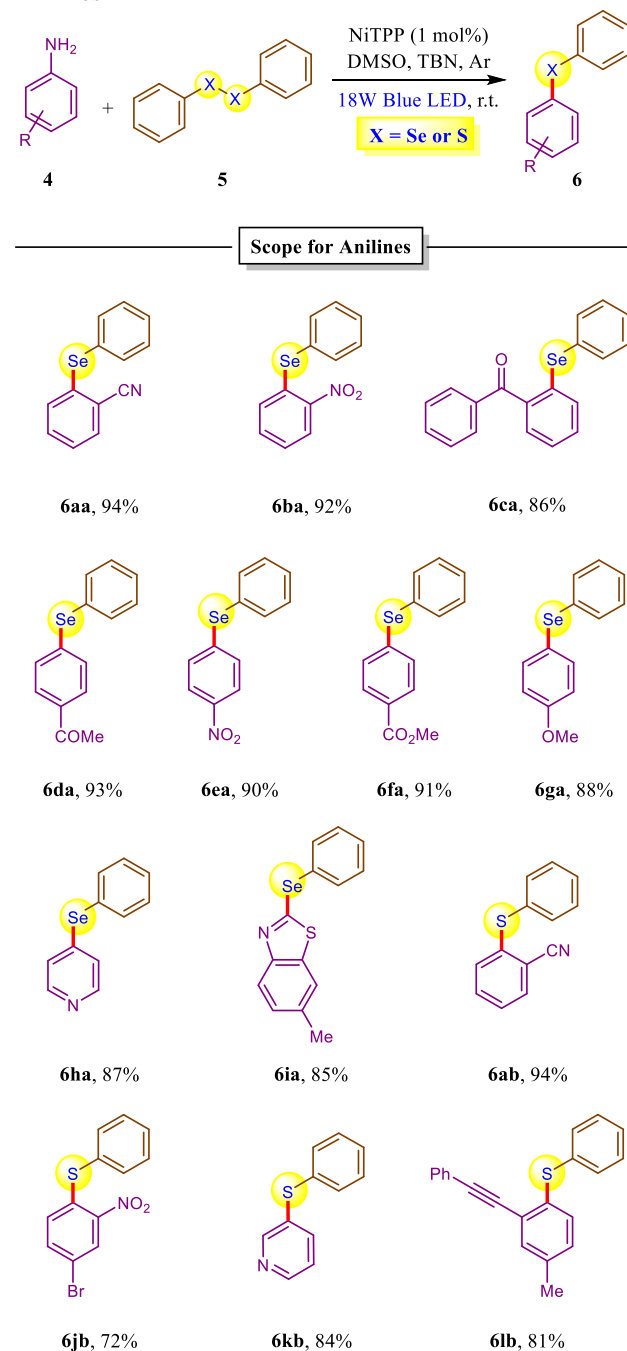
[a] **Reaction conditions: 4** (0.5 mmol), **5a** (0.6 mmol), NiTPP (1 mol%), TBN (1.5 equiv) in DMSO (2.5 mL), under Ar for 6 h. [b] Isolated yield.

Once the optimized condition was identified, we investigated the generality of our protocol with substituted anilines bearing different functional groups (Table 5). It was observed that electron-withdrawing (**4a-4f**), electron-donating (**4g**), halogen (**4j**) and alkyl (**4l**) groups at *ortho-*, *para-* and *meta-* positions of anilines were sustainable for our strategy, offering excellent yields in both cases for selenylation as well as thiolation. Furthermore, heteroarenes (**4h, 4i,** and **4k**) were also successfully reacted to deliver the desired product in significant yields.

5
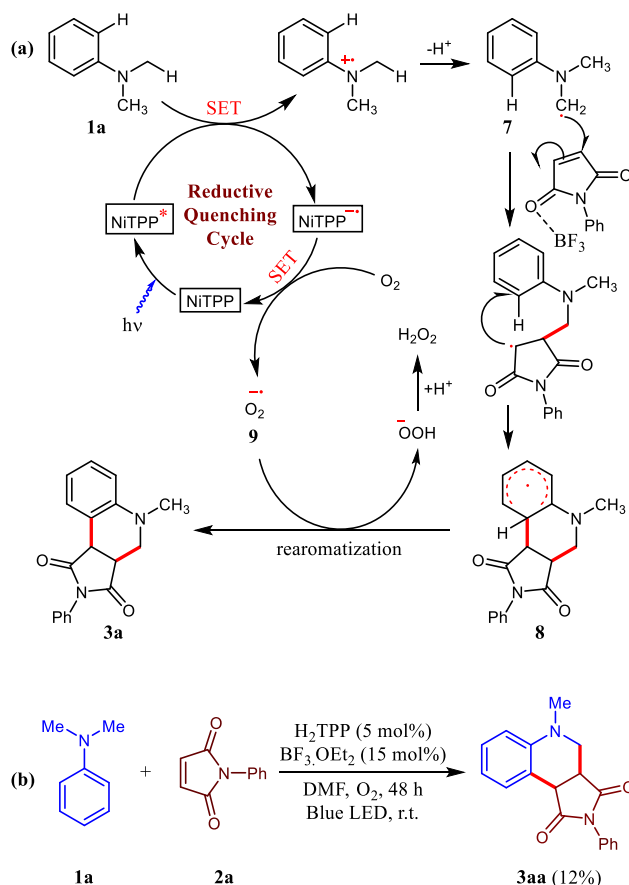
Scheme 2. Proposed Mechanism and Control Experiment for the Reductive Quenching Pathway

Mechanistically, it is proposed that the single electron transfer (SET) from the electron-rich amine system to photoexcited NiTPP* following reductive quenching pathway leads to the generation of α-aminoalkyl radical **7**, which undergoes addition to the olefinic double bond and subsequent free radical cyclization gives **8** (Scheme 2a). Most likely, the Lewis acidic additive BF_3 is accelerating this step by coordinating with the carbonyl group. The redox cycle of the photocatalyst is completed by the generation of per-oxy radical **9** by SET which also helps in the rearomatization to furnish highly substituted tetrahydroquinoline **3**. Generation of H_2O_2 as a byproduct was confirmed spectrophotometrically following the gradual development of the characteristic peak of I_3^- at λmax = 343 nm, upon reaction with KI (see SI). This per-oxy radical may compete in the generation of α-aminoalkyl radicals and thereby participate in the follow-up cyclisation process. To examine this possibility, we replicated the experiment reported by Yu and Bian using H_2TPP, which is a common photosensitizer (Scheme 2b).[18g] The reaction proceeded slowly with much inferior yield of the product, thus excluding the role of NiTPP only as photosensitizer instead of a photoredox catalyst. A significant decrease of absorption maxima was observed in the photo quenching experiment with **1a** as the quencher; whereas **2a** did not show any effect

(see SI). Furthermore, a time-dependent UV-Vis absorption quenching study was done using a particular concentration of the photocatalyst and amine (Fig. 2a). A considerable decrease in the absorption maxima was witnessed with increasing the excitation time, while the absorbance value became static when only NiTPP sample solution was irradiated under blue LED. Moreover, luminescence quenching experiments in the presence of different reactions components were recorded and the Stern-Volmer plot is depicted (Fig. 2b). The quenching effect of the amine **1a** was quite significant on the photocatalyst, however *N*-phenyl maleimide **2a** was found to be incompetent to impose any effect on the emission intensities of the catalyst. These observations indicate the interaction between NiTPP and **1a** under visible light irradiation. Finally, the involvement of radical pathway was verified by arresting of the reaction in the presence of TEMPO (see SI).

(a) Time Dependent UV-Vis Absorption Quenching Study
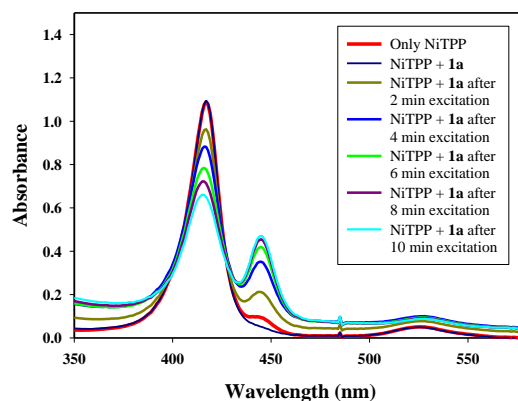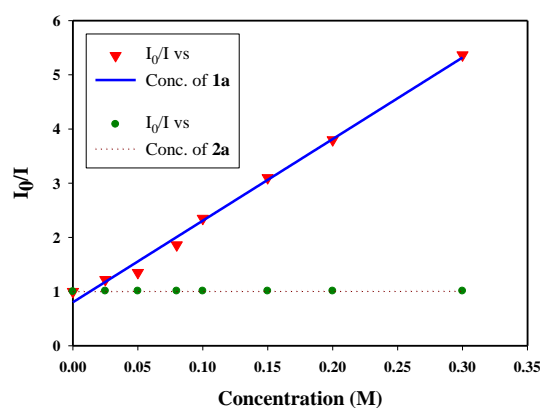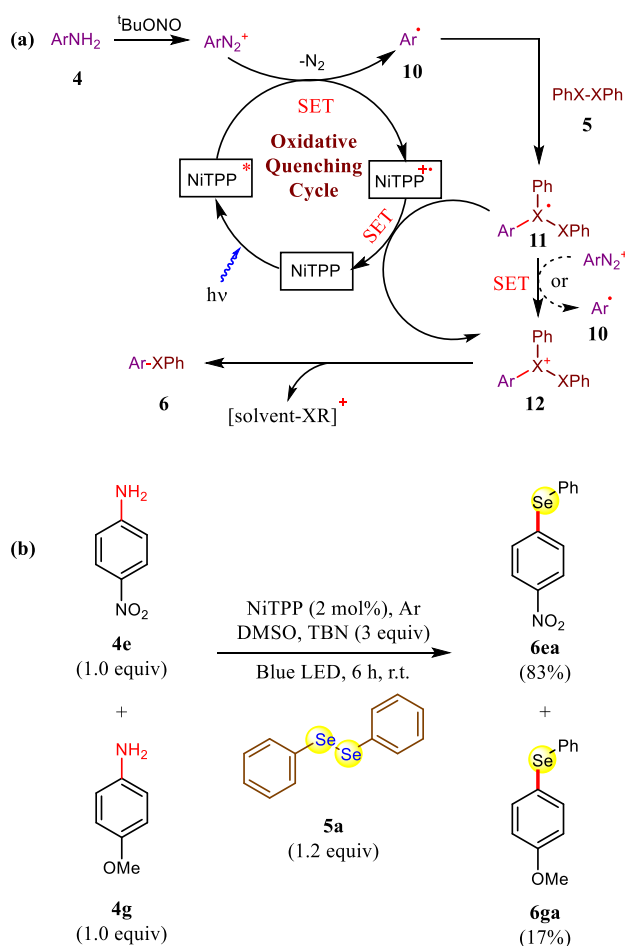

(b) Stern-Vlomer Plot

Figure 2. (a) Time-Dependent UV-Vis Absorption Quenching Study and (b) Stern-Volmer Plot

Scheme 3. Proposed Mechanism and Competitive Study for the Oxidative Quenching Pathway

In case of selenylation and thiolation, the aryl radical **10** is generated from the aryldiazonium ion by SET from the photo-excited catalyst through oxidative quenching process, which then interacts with phenyl dichalcogenide to produce a trivalent chalcogenide radical intermediate **11** (Scheme 3a). To complete the catalytic cycle, NiTPP radical-cation finally revokes its electron from **11** leading to the formation of chalcogenide cationic intermediate **12**, which cleaves to provide the desired product **6**. Alternatively, SET from **11** to aryldiazonium ion can also generate aryl radical **10**. Similar to the previous case this reaction was also completely shut down in the presence of TEMPO indicating the existence of radical intermediates (see SI). Competitive experiment between electron rich and electron poor anilines revealed that the latter undergoes almost five times faster reaction giving 83% of the corresponding selenylation product (Scheme 3b, see SI for details). This is most likely because of the rapid generation of the aryl radical by the faster SET process in electron-deficient aryl system. Luminescence quenching experiment was performed and a drastic change in the emission maxima of NiTPP was observed when diazotized aniline (**4e**) was used as the quencher (see SI).
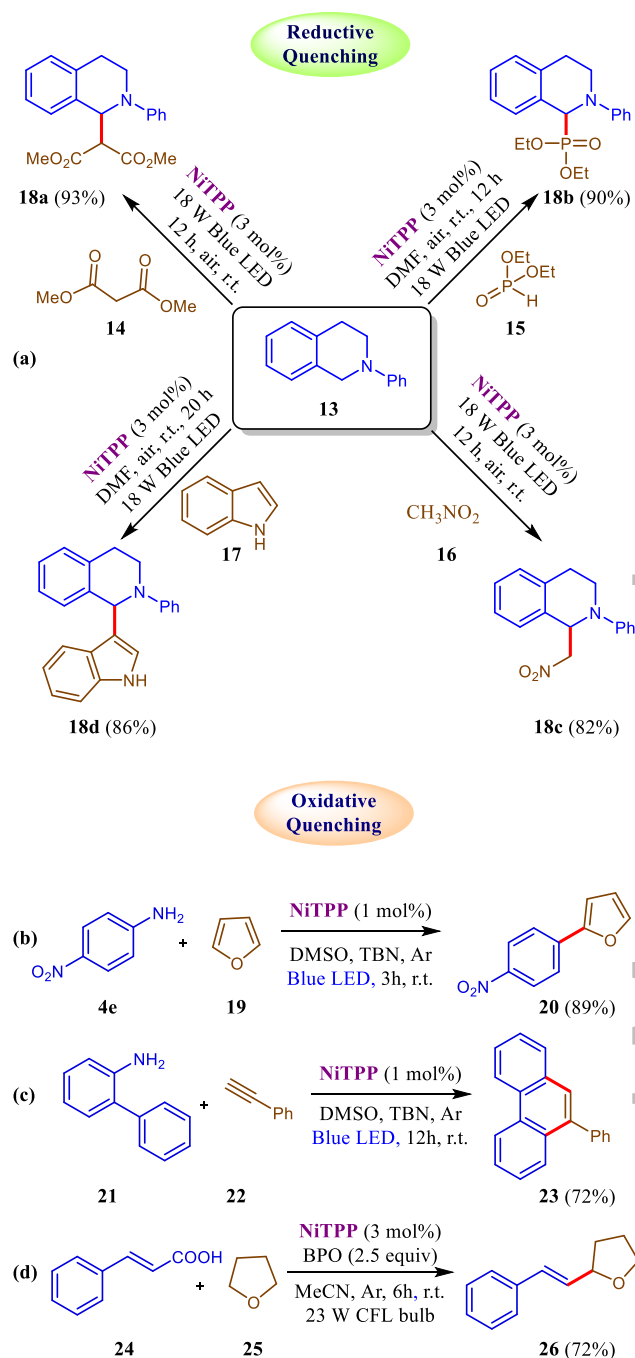
Scheme 4. Application of NiTPP Photocatalyst in C-C and C-Heteroatom Bond Forming Reactions

After having a clear understanding of the photophysical properties as well as on the reactivity, we tested the generality of NiTPP catalyst on other C-C and C-heteroatom bond forming reactions (Scheme 4). For reductive quenching cycle, *N*-phenyl-tetrahydroisoquinoline **13** was taken as the model substrate, and iminium ion was generated by oxidation under photochemical conditions (Scheme 4a). Stabilized carbanion produced from dimethylmalonate or nitromethane smoothly reacted and delivered **18a** and **18c** respectively under the standard reaction condition.[21] Electron-rich aromatic system like indole also found to be a competent coupling partner and C3-

substituted indole **18d** was formed in good yield.[22] Lastly, phosphonate **15** was used as a nucleophile and desired C-P bond was formed in **18b**.[21, 23] Next, we tested the efficiency of the photocatalyst in the oxidative quenching pathway (Scheme 4b-d). In situ generated aryldiazonium ion upon reduction by photoexcited NiTPP formed the corresponding aryl radical which underwent coupling with furan or alkyne to deliver biaryl **20** and polyarene **23** respectively.[20a, 20c] The oxidative quenching pathway is not limited to reaction with aryldiazonium ions, it efficiently resulted in the formation of α-oxo radical from tetrahydrofuran via the initial generation of the benzoyloxy radical upon cleaving benzoyl peroxide (BPO) (Scheme 4d).[24] Follow up addition and decarboxylation yielded substituted styrene derivative **26**.

Conclusion

In summary, we have disclosed that a macrocyclic *meso*-tetraphenylporphyrin ligand coordinated Ni(II) complex (NiTPP) has great synthetic utility as a photoredox catalyst. This catalyst is superior compared to the known non-precious metal-based photocatalysts in terms of ready availability and excited state redox properties. NiTPP also exhibits the dual activity of both excited state photo-oxidant and photo-reductant as shown in maleimide annulation and chalcogenylation reactions respectively. Considering the earth-abundant, less-toxic core metal and readily accessible ligand framework, mild reaction conditions, and high catalytic efficiency, this system is anticipated to offer new scope to promote green and economical synthesis using visible light photoredox catalysis. Further research on unexplored synthetic transformations using this photocatalytic system is currently ongoing in our laboratory.

Experimental Section

General procedure for the photoredox mediated coupling of N,N-dimethylanilines, and N-aryl or N-alkyl maleimides: The *N,N*-dimethylanilines **1** (1.0 mmol, 2.0 equiv *N*-aryl or alkyl maleimides **2** (0.50 mmol, 1.0equiv), NiTPP (11 mg, 3 mol %) were placed in a pre-dried standard glass reaction tube. The tube was degassed and purged with oxygen three times. After that BF₃.Et₂O (0.045 mmol, 0.15 equiv) and DMF (2.5 mL) was added as solvent. The mixture was stirred at room temperature under oxygen atmosphere using a balloon and irradiated with blue LEDs for 20 h. EtOAc (20 mL) was added, and the reaction mixture was washed with brine (10 mL), dried over Na₂SO₄, concentrated under a vacuum, and purified by silica gel column chromatography using 20% ethyl acetate in hexanes to deliver the tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-diones **3**.

General procedure for the photoredox mediated coupling of anilines and diphenyl diselenides or diphenyl disulfides: In a pre-dried standard glass reaction tube respected aniline **4** (0.5 mmol, 1.0 equiv), diphenyl diselenide **5a** (188 mg, 0.6mmol, 1.2 equiv) or diphenyl disulfide **5b** (131 mg, 0.6mmol, 1.2 equiv) and NiTPP (4 mg, 0.005 mmol, 0.01 equiv) were placed. The tube was degassed and purged with argon three times. After that *tert*-butyl nitrite (0.12 mL, 0.75 mmol, 1.5 equiv) and DMSO (2.5 mL) was added as solvent. The mixture was stirred at room temperature under an argon atmosphere using a balloon and irradiated with blue LEDs for 6h. EtOAc (20 mL) was added, and the reaction mixture was washed with brine (10 mL), dried over sodium sulfate, concentrated under a vacuum, and purified by silica gel column chromatography using 1% ethyl acetate in hexane to deliver substituted-phenyl-selane or substituted-phenyl-sulfane.

Acknowledgements

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9

FULL PAPER

Nickel(II) Tetraphenylporphyrin as an Efficient Photocatalyst Featuring Visible Light Promoted Dual Redox Activities

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Blue LED

NiTPP Photocatalyst
Active as Both
Photoreductant
and Photooxidant

O$_2$ Atmosphere
Reductive
Quenching

Ar Atmosphere
Oxidative
Quenching

20 examples
up to 97% isolated yield

13 examples
up to 94% isolated yield

Accepted Manuscript

10