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Graphene oxide and Rose Bengal: oxidative C–H functionalisation of tertiary amines using visible light†

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Visible light induced oxidative C–H functionalisation of tertiary amines catalysed by the combination of graphene oxide and Rose Bengal was developed. This reaction avoids the use of stoichiometric amounts of peroxy compounds as terminal oxidants. This reaction is useful for tri-alkyl amines including chiral tertiary amines. Both cyanide and trifluoromethyl nucleophiles were shown to participate in this reaction, providing α-cyano- and α-trifluoromethylated tertiary amines.

Graphene oxide (GO), a two-dimensional carbon sheet, is traditionally used as a precursor to prepare graphene. Its unique physical and chemical properties have attracted the attention of chemists due to potential applications in plastic electronics, optical materials, solar cells and biosensors,[1] but its potential as a catalyst in organic transformation remains relatively unexplored.[2,3] The feasibility and potential of GO as catalyst were demonstrated by the seminal work of Bielawski and co-workers on the use of GO for the oxidation of alcohols and hydration of alkynes.[3a] Subsequently, RGO was reported to catalyse the hydrogenation of nitrobenzene at room temperature.[3b] The use of GO and reduced graphene oxide (RGO) as "carbocatalyst" in organic transformations is a nascent area and should lead to exciting discoveries.

On a different note, the use of visible light in organic synthesis has attracted the attention of various synthetic organic chemists recently.[4] The groups of MacMillan,[5] Yoon,[6] and Stephenson[7] have showed the ability of metal-based photosensitizers, such as Ru(bpy)$_3$Cl$_2$ (tris(2,2′-bipyridine)-ruthenium(II) chloride) (Fig. 1), as photoredox catalysts for organic transformations under visible light irradiation.[8] Organic dyes, which are often used in dye-sensitized solar cells, are considered to be cheaper and easier to modify relative to metal-based photosensitizers,[9] thus they are attractive alternatives as photoredox catalysts. The viability of organic dyes as photoredox catalysts has been demonstrated by several groups.[10] For example, Zeitler *et al.* reported eosin Y catalysed dehalogenation and enantioselective α-alkylation using a combination of photoredox catalyst and organocatalyst.[10a] Fukuzumi reported a selective aerobic bromination catalysed by 9-mesityl-10-methylacridinium perchlorate (Acr$^+$–Mes).[10b] We have also demonstrated that Rose Bengal (RB, Fig. 1) was able to photocatalyse α-oxyamination of 1,3-dicarbonyl compounds and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) using visible light.[10c]

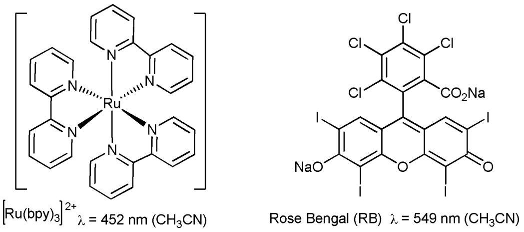

Fig. 1 Ruthenium bipyridyl complex and Rose Bengal.

Although GO has been reported as a photocatalyst for hydrogen production from water under UV irradiation,[11] the potential application of GO in synthetic photochemistry has not been explored. Therefore we wish to report the combination of GO and RB which works in synergy to efficiently catalyse the α-functionalisation of tertiary amines in the presence of visible light. The oxidative α-functionalisation of tertiary amines through highly reactive iminium intermediates has been reported with transition metals as catalysts and peroxo-compounds as terminal oxidants.[12] Recently, the groups of Stephenson,[7c] Rueping[13] and König[14] shown that this type reaction can be photocatalysed with Ru(bpy)$_3$Cl$_2$ or Eosin Y using various nucleophiles. We embark on our investigation with α-cyanation of tertiary amines (Table 1),[15] an important reaction which can lead to a mild synthetic approach towards amino acids and provide an alternative method to the Strecker reaction.‡

We chose green Light Emitting Diodes (LEDs) as the light source for this study, as RB has a strong absorption wavelength at around 549 nm; α-cyanation product **2a** was observed with

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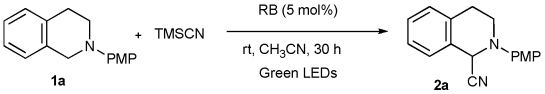
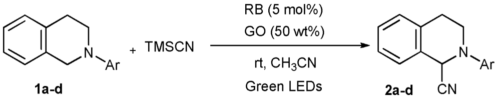
Table 1 α-Cyanation of tertiary amine in the presence of RB and GO[a]

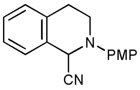
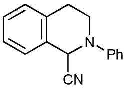
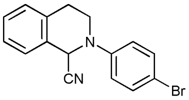
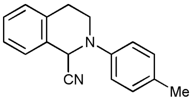


Entry	Carbon catalyst	Yield (%)[b]
1	none	60
2	50 wt% GO[c]	97
3	50 wt% graphite	65
4	50 wt% activated carbon	56
5	200 wt% GO	96
6[d]	50 wt% GO	94 (63)
7[e]	50 wt% GO	10
8[f]	50 wt% GO	0
9[g]	50 wt% GO	94

[a] Reaction was performed using 0.05 mmol of **1** and 0.125 mmol of TMSCN in 0.5 ml of CH_3CN. [b] Isolated yield. [c] GO was prepared according to the reported method.[16] [d] $Ru(bpy)_3Cl_2$ was used instead of RB. Number in bracket is the yield without GO. [e] Reaction was performed without RB. [f] Reaction was performed in dark. [g] Recycled GO was used.

Table 2 α-Cyanation of a series of cyclic tertiary amines[a]

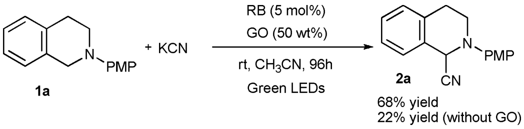


Entry	2	*t* (h)	Yield (%)[b]	Initial rate (10^{-4} mmol min^{-1})[c]
1	 **2a**	30	97 (60)	6.3 (3.2)
2	 **2b**	72	99 (45)	5.4 (4.1)
3	 **2c**	80	90 (63)	2.2 (0.4)
4	 **2d**	30	97 (62)	8.0 (4.2)

[a] Reaction was performed using 0.1 mmol of **1** and 0.25 mmol of TMSCN in 1.0 ml of CH_3CN [b] Isolated yield; number in bracket is the yield without GO. [c] Initial rate was determined by ^1H NMR analysis during the first 45 min using pentachlorobenzene as internal standard.

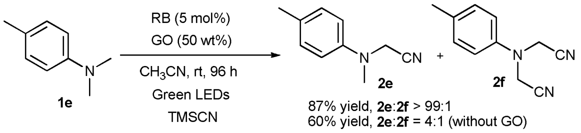
60% yield when *N*-aryl-tetrahydroisoquinoline **1a** and TMSCN were subjected to green LEDs irradiation using 5 mol% of RB (Table 1, entry 1). Following the report of Bielawski and co-workers,[3a] 200 wt% of GO was added to the reaction system and full conversion with 96% yield was observed within the same reaction time (Table 1, entry 5). To our delight, when the amount of GO was reduced to 50 wt%, the yield was not affected to any observable extent (Table, entry 2). Natural graphite and activated carbon showed no effect on the reaction (Table 1, entries 3 and 4). The addition of GO to $Ru(bpy)_3Cl_2$ catalysed reaction also resulted in an increased in reaction rate and yield of the reaction (Table 1, entry 6). Interestingly, GO can be recycled without the loss of the activity (Table 1, entry 9). Both light and photoredox catalyst were proved to be essential for this reaction. No desired product was observed when the reaction was conducted in the dark and only trace amount of product was detected when the reaction was performed without RB (Table 1, entries 7 and 8).

With the established conditions, we evaluated the performance of different *N*-aryl-tetrahydroisoquinolines with TMSCN in the presence of 5 mol% RB and 50 wt% GO (Table 2). Similar observations were made; the presence of GO increase the reaction rate and also improve the overall yield of the reactions. Electron donating *N*-protecting groups allow the reaction to be completed in a shorter time (Table 2, entries 1 and 4). This is ascribed to the increased stabilization of the iminium intermediate in these substrates. Moderate yield was achieved when KCN was used, which improved significantly when GO was added (Scheme 1).



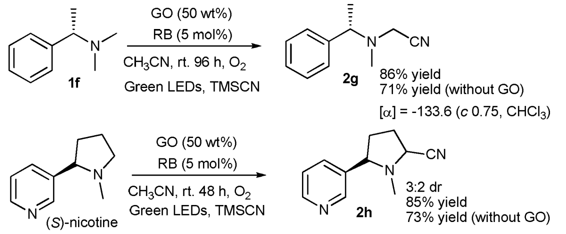
Scheme 1 α-Cyanation between tertiary amines and KCN.

Linear amines usually exhibit reduced reactivity due to the absence of stabilization provided by the benzylic position to the iminium intermediate.[17] However, when 4-methyl-*N*,*N*-dimethylaniline was subjected to the reaction condition that we have just developed, good yields were obtained (Scheme 2). The superiority of the combination of RB and GO was obvious; not only was the yield improved, chemoselectivity was also improved. While mono-cyanation product was observed as the only product when GO was used, a mixture of mono- and bis-cyanation products was observed in the absence of GO.



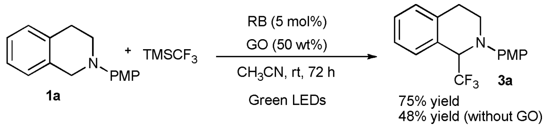
Scheme 2 α-Cyanation of 4-methyl-*N*,*N*-dimethylaniline in presence of RB and GO.

Tri-alkyl amines are more challenging substrates for α-CH functionalisation reactions. We were pleased to find that α-cyanation occurs with chiral amine **1f** under the optimized conditions to provide adduct **2g** selectively (Scheme 3). We observed that reaction rates increased when an oxygen atmosphere was introduced to the reaction *via* a balloon, as compared to just exposing the reaction to air. No bis-cyanation product was observed. The α-cyanation of (*S*)-nicotine was intriguing as it occurs selectively at the 5′-position rather than the *N*-methyl group to give adduct **2h**. The stereoelectronic preference of this reaction would require further investigation to be fully understood.



Scheme 3 α-Cyanation of tri-alkyl amines in presence of RB and GO.

There is a strong demand for versatile fluorine-containing building blocks.[18] The preparation of trifluoromethylated compounds is particularly important as this moiety is present in many pharmaceuticals.[19] Using **1a** as the iminium precursor and TMSCF$_3$, trifluoromethylated *N*-aryl-tetrahydroisoquinoline product **3a** was obtained using RB/GO catalytic system (Scheme 4).[20] A significant amount of a by-product, trifluoromethylated *N*-aryl-dihydroisoquinoline was obtained even with GO.



Scheme 4 α-Trifluoromethylation between **1a** and TMSCF$_3$ in presence of RB and GO.

Mechanistically, we proposed that the highly reactive iminium intermediate was formed by the oxidation of the C–H bond adjacent to the nitrogen (Fig. 2). RB accepts a photon from the visible light source to populate the excited state RB* and remove one electron from the nitrogen atom *via* a single electron transfer (SET) process.[7c,10a,13a] The photoredox cycle is accomplished by re-oxidizing the radical anion RB$^{\bullet-}$ to the ground state RB by molecular oxygen (pathway a). The relatively acidic tertiary amine radical cation is deprotonated by a strongly basic species, superoxide anion $O_2^{\bullet-}$. The strongly reductive species generated, the α-aminated carbon radical is further oxidized by a second SET process resulting in the highly reactive iminium intermediate, which could be easily trapped by nucleophile to release the final product under mild conditions. The nucleophiles investigated in this report were cyanide and trifluoromethyl anion.

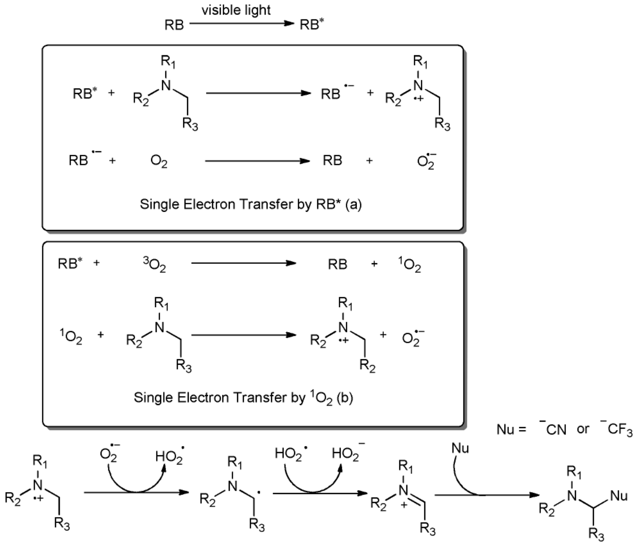


Fig. 2 Proposed mechanism of α-functionalisation of tertiary amines catalysed by Rose Bengal using visible light.

Alternatively, RB is well known for the generation of singlet oxygen in polar aprotic solvents by energy tranfer from the triplet RB* to ground-state triplet oxygen (pathway b). The resulting singlet oxygen is able to oxidize tertiary amines. This process is supported by Ferroud's report using the pre-synthesised singlet oxygen source.[21] However, 65% yield of **2a** was obtained when Fluorescin (a sensitizer that does not produce singlet oxygen) was used instead of RB in the optimized conditions without GO (see ESI†). On the other hand, TPP/DCM system, a well known singlet oxygen generation system was also tested in the reaction between *N*-aryl-tetrahydroisoquinolines **1a** and TMSCN. 100% conversion with only 19% yield of **2a** was obtained after 30 h.[22] Therefore, singlet oxygen is not crucial and thus reduction of RB* may occur predominantly on triplet oxygen.[23]

The role of GO in this reaction is not clear at this stage. Controlled experiment revealed that GO can be recycled without the loss of its activity (Table 1, entry 9) and itself alone does not catalyse this reaction (Table 1, entry 7). These observations ruled out the possibility that GO showed significant oxidation activity in these reactions. On the other hand, hydrophobic graphite and activated carbon had no effect on the reaction rate enhancement (Table 1, entries 3 and 4). The stabilization of iminium intermediate by slightly acidic GO and the intrinsic high surface area of GO may participate in the rate enhancement. UV/Vis absorption and fluorescence quenching study (see ESI†) revealed that there was no strong π–π interaction between RB and GO, which was reasonable due to the electrostatic repulsion between the RB anion and the negatively charged functional groups of GO.

In summary, we have developed a cooperative catalyst system based on an organic dye and GO, and applied them successfully in photocatalysing oxidative C–H functionalisation of tertiary amines. These reactions were found to proceed smoothly under mild conditions and afford the desired products in good to excellent yields. Adding of GO as co-catalyst typically resulted in an increased in reaction rate and also the yield of products obtained. Our methodology avoids the use of metal catalyst and stoichiometric amount of peroxy-compounds as terminal oxidant. Cheap and readily available organic dye is used and air is used as the oxidant. To the best of our knowledge, this is the first example of using GO to facilitate the synthesis of small molecular organic compounds under visible light irradiation. Detail mechanistic study and other applications of GO in synthetic organic chemistry are ongoing in our laboratory.

Acknowledgements

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Notes and references

‡ Representative procedure for α-cyanation between *N*-aryl-tetrahydroisoquinoline **1a** and TMSCN catalysed by the combination of Rose Bengal and GO: **1a** (23.9 mg, 0.1 mmol, 1.0 equiv.) and GO

(12.0 mg, 50 wt%) were added to a solution of RB (5.0 mg, 0.005 mmol, 5 mol%) in 1.0 ml CH_3CN followed by adding TMSCN (31.3 µl, 0.25 mmol, 2.5 equiv.) slowly. The reaction mixture was stirred under green LED irradiation at room temperature. After 30 hours, the solvent was removed *in vacuo* and the crude product was directly loaded onto a short silica gel column. Flash chromatography was performed using gradient elution with hexane/EA mixtures (40/1–10/1 ratio). After removing solvent, product **2a** (25.5 mg) was obtained as pale yellow solid in 97% yield.

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23 An insightful reviewer also suggested in the presence of very high concentration of solid surface, the rate of physical quenching of singlet oxygen will be very high. Its lifetime in acetonitrile is also not high. The reaction may occur predominantly on electron-transfer process rather than singlet oxygen process.