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Highly efficient and selective photocatalytic hydrogenation of functionalized nitrobenzenes†

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We report a simple but efficient photocatalytic nitrobenzene reduction method employing eosin Y as the photocatalyst and TEOA as the reducing agent. With green LED light irradiation, the nitro group in the nitrobenzenes containing other reducible groups was chemoselectively reduced into an amino group, and the corresponding anilines were isolated in quantitative yields. The photoinduced electron transfer mechanism suggests that the high chemoselectivity originates from the better electron-withdrawing ability of the nitro group.

Functionalized anilines are important intermediates for the manufacture of agrochemicals, pharmaceuticals, dyes and pigments.[1] Most functionalized anilines are produced by hydrogenation of the corresponding aromatic nitro compounds. The key problem in such hydrogenation is the chemoselectivity when other reducible groups are present in the same molecule. A variety of methods for reducing the nitro group in a selective manner, involving noncatalytic[2] and catalytic[3] methods, and different reducing agents[3,4] have been developed. The noncatalytic processes use either Béchamp (with Fe/HCl as a reducing system)[2b] or sulfide reduction (with H_2S or NaSH as a reducing agent)[2a] technology. Although there are still certain selectivity problems that can only be solved by using these stoichiometric methods, these processes create large amounts of environmentally toxic waste.[5] In catalytic methods, the most frequently used catalysts are noble metals, Pt[6] and Au[7] supported on active carbon,[3a,4b,8] TiO_2,[6,7] SiO_2 [9] or Fe_2O_3,[3a] and Ni-based systems.[10] Whereas such conventional catalysts can adequately solve some selectivity problems, more demanding processes often require modified or tailored catalysts.[6] Furthermore, when H_2 is used as the reducing agent, high temperature and high pressure are usually needed which raise a high requirement for the equipment and may cause potential safety problems. Evidently, it is highly desirable to develop methods for the hydrogenation of aromatic nitro compounds that are economically feasible without toxic waste production, and are performed with high chemoselectivity under mild conditions.

Over the past few years, the use of visible-light photoredox catalysis to initiate organic transformations has made great progress and has become a powerful tool in synthetic organic chemistry,[11] because such catalytic reactions are environmentally benign, easy to handle, and carried out under mild conditions.[11b,12] A wide range of chemical reactions promoted by such catalysis have been elegantly devised and developed into practical synthetic methods.[11,12] Furthermore, several convenient photocatalysts such as organometallic complexes of ruthenium(II)[12a,d,13] and iridium(III),[12b,c] and purely organic dyes[14] have been successfully adopted in visible-light induced organic transformations. Among these, eosin Y (EY)[14c,15] is a widely used photocatalyst because it is structurally simple, inexpensive and effective. In addition, several metal-free heterogeneous organophotocatalysis systems for organic functional group transformations under visible light irradiation have also been reported.[16]

In the present study, we examined the visible-light photocatalytic reduction of nitrobenzenes containing other reducible groups (carbon–carbon or carbon–nitrogen triple bonds, carbonyl, Cl or Br substituents) by using EY as the photocatalyst and triethanolamine (TEOA) as the reducing agent. We found that only the nitro group was chemoselectively reduced to an amino group at full conversion for the examined nitrobenzene derivatives and that the aminobenzenes were isolated in almost quantitative yields. The photocatalytic reduction was carried out in oxygen-free ethanol–water (3 : 2, v/v) solution at room temperature and atmospheric pressure. Typically, 5 mL of a solution of the substrate (0.2 mmol), the photocatalyst (EY, 1 mol%) and the reducing agent (TEOA, 3–6 equiv.) in a Pyrex reactor was irradiated with a 3 W green LED light (525 nm). The progress of the reaction was followed by UV-Vis absorption spectra of the sample. For example, in the

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† Electronic supplementary information (ESI) available: Experimental details, control experiment, transient absorption spectra, ^1H NMR and ^{13}C NMR spectra. See DOI: 10.1039/c3gc42042f

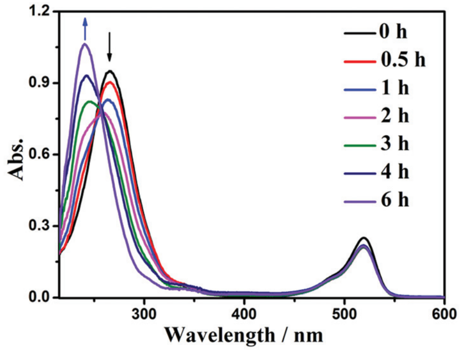
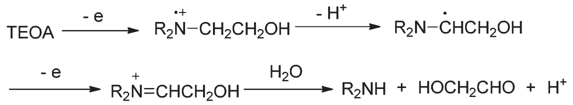


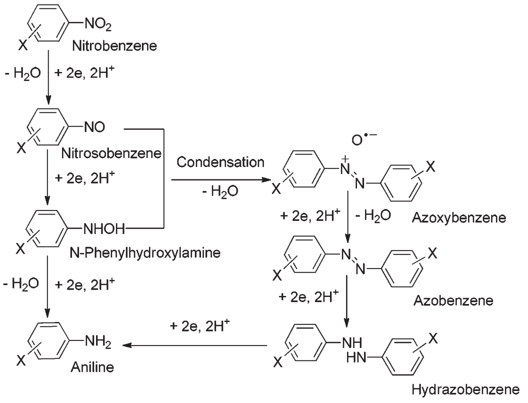
Fig. 1 UV-Vis absorption spectral change in the course of irradiation of the solution containing nitrobenzene (0.2 mmol), TEOA (20 equiv.) and EY (1 mol%) in 5 mL of EtOH–H_2O (3 : 2) at pH 8.50 with 525 nm LED (measured after a dilution of 150 times).



$$\mathrm{TEOA}\xrightarrow{-\,e}\mathrm{R_2\overset{\bullet+}{N}{-}CH_2CH_2OH}\xrightarrow{-\,H^+}\mathrm{R_2N{-}\overset{\bullet}{C}HCH_2OH}$$

$$\xrightarrow{-\,e}\mathrm{R_2\overset{+}{N}{=}CHCH_2OH}\xrightarrow{H_2O}\mathrm{R_2NH + HOCH_2CHO + H^+}$$

Scheme 1 Oxidation of triethanolamine.



Scheme 2 Possible reaction pathways for the reduction of an aromatic nitro compound to the corresponding aniline.

reduction of nitrobenzene, upon irradiation the absorption of the substrate with $\lambda_{\max}$ at 265 nm gradually decreased in intensity accompanying the appearance of a new absorption with $\lambda_{\max}$ at 240 nm ascribable to aniline, and an isobestic point at 256 nm was observed (Fig. 1). After irradiation, the product was isolated and identified by ^1H NMR spectroscopy, MS spectrometry and on the basis of a known retention time of an authentic compound on GC. Control experiments showed that the photocatalyst (EY), the reducing agent (TEOA) and light were all essential for the effective reduction of nitrobenzene (Table S1,† entries 1–4).

Two factors could affect the efficiency of the photocatalytic reduction of nitrobenzene. First, the photocatalytic reduction is very dependent on the pH value of the sample, and the optimal pH value is 8.50 (Table S1,† entries 4–8). In this photocatalytic system, TEOA acts as a sacrificial electron donor.[17] As shown in Scheme 1, in the course of the photocatalytic reaction, TEOA will provide electrons and protons for the reduction. In acidic solution, TEOA will be protonated which would reduce its electron donating ability. On the other hand, in strong basic solution, the reduction efficiency is also low as protons are involved in the reduction process.[15a] Secondly, the amount of TEOA used is crucial for efficient reduction (Table S1†). According to Scheme 1, each TEOA molecule with one H_2O molecule can provide two electrons and two protons for the reduction.[18] The reduction of one molecule of nitrobenzene to aniline requires 6 electrons and 6 protons. Thus, one can expect that full conversion could be achieved when 3 equivalents of TEOA are used. As shown in Table S1† (entries 12, 13), this is indeed the case. In such conditions by prolonging irradiation, the conversion of the starting material can reach above 90%. Employing excess TEOA can greatly shorten the irradiation time. Upon performing the photocatalytic reaction in a solution pH of 8.50 and using 3–6 equivalent of TEOA, full conversion and excellent chemoselectivity can be achieved in reasonable irradiation time. When using 1 mol% EY, the catalytic turnover number of the photocatalyst EY is close to 100, with the isolated yield of aniline 93%. As shown in Fig. 1, during the photocatalytic reduction the absorption of EY with $\lambda_{\max}$ at 520 nm remained unchanged, suggesting that this photocatalyst is stable. The high stability might be ascribed to the formation of EY cation radical ($EY^{+\bullet}$), and the electron transfer from TEOA to $EY^{+\bullet}$ can quickly regenerate EY.[19] Indeed, after the conversion of nitrobenzene is completed, we syringed additional nitrobenzene and TEOA to the reactor and irradiated the sample. We observed that the added nitrobenzene was reduced at a similar rate.

It is generally accepted that the reduction of nitrobenzene to aniline proceeds either through the direct route *via* nitrosobenzene and *N*-phenylhydroxylamine intermediates, or a condensation route *via* azoxybenzene, azobenzene and hydrazobenzene (Scheme 2).[20] We applied ^1H NMR spectroscopy to follow the photocatalytic reduction and indeed detected nitrosobenzene and *N*-phenylhydroxylamine in the initial stage of the reaction (Fig. S1†). No azoxybenzene, azobenzene and hydrazobenzene were observed. Furthermore, we carried out the photocatalytic reduction of azobenzene under similar conditions, and only isolated hydrazobenzene. No aniline was detected (Table S2†). These results suggest that the photocatalytic reduction of nitrobenzene to aniline proceeds *via* the direct route.

A visible-light photoredox catalytic reaction has been proposed to originate from single electron transfer.[14b,d] To elucidate the mechanism for the photocatalytic reduction of nitrobenzene, we examined the quenching of EY excited states by nitrobenzene and TEOA. EY in a water–ethanol mixed solution shows fluorescence with $\lambda_{\max}$ at 543 nm. Experiments revealed that nitrobenzene or TEOA only slightly quenched fluorescence of EY even at high concentrations, suggesting that neither electron transfer between the EY singlet excited state ($^1EY^*$) and nitrobenzene, nor that between $^1EY^*$ and

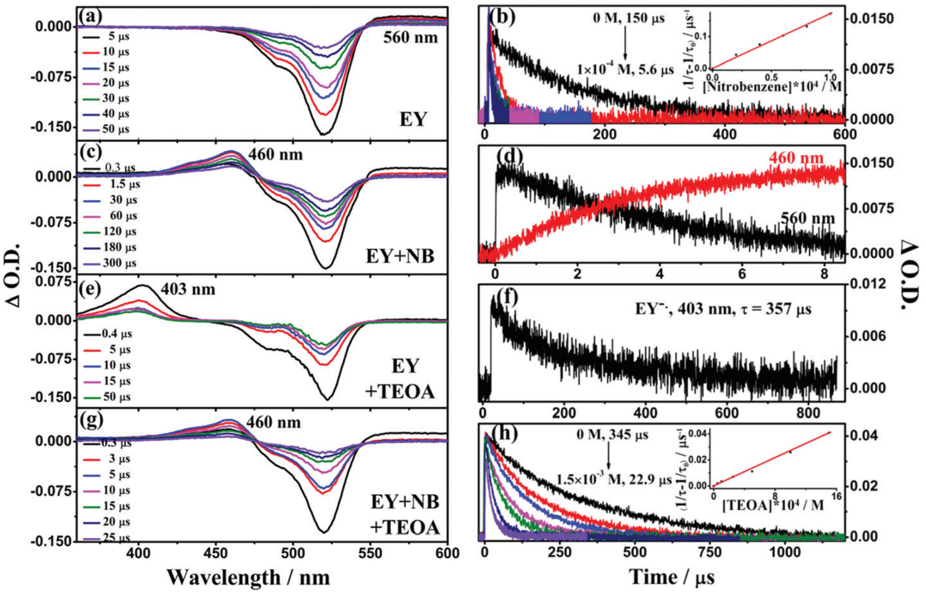
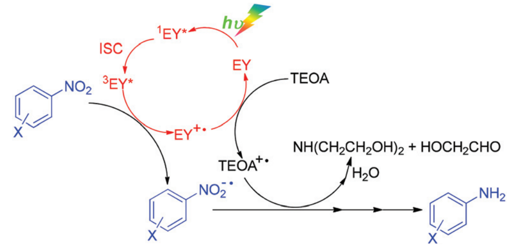


Fig. 2 Transient absorption spectra of (a) EY (1×10^{-5} M); (c) EY (1×10^{-5} M) and nitrobenzene (NB, 4×10^{-4} M); (e) EY (1×10^{-5} M) and TEOA (2.4×10^{-3} M); (g) EY (1×10^{-5} M), nitrobenzene (4×10^{-4} M) and TEOA (2.4×10^{-3} M) with 532 nm light in de-aerated EtOH–H_2O (3 : 2); (b) kinetic traces at 560 nm obtained on laser photolysis of EY (1×10^{-5} M) and nitrobenzene at different concentrations ranging from 0 M to 1×10^{-4} M at intervals of 2×10^{-5} M and Stern–Volmer plots (inset); (d) decay and rise-time profiles at 560 nm and 460 nm respectively upon excitation of the solution of EY (1×10^{-5} M) and nitrobenzene (4×10^{-4} M); (f) kinetic traces at 403 nm obtained on laser photolysis of EY (1×10^{-5} M) and TEOA (2.4×10^{-3} M) with 532 nm light; (h) kinetic traces at 460 nm obtained on laser photolysis of the solution of EY (1×10^{-5} M), nitrobenzene (4×10^{-4}) and TEOA at different concentrations ranging from 0 M to 1.5×10^{-3} M and Stern–Volmer plots (inset).

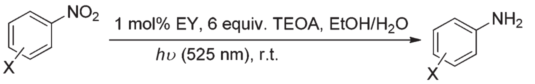
TEOA is important in the photocatalytic reduction. Thus, we carried out the flash-photolysis study in degassed water–ethanol solutions. Upon laser excitation at 532 nm, the solution of EY alone exhibited a strong bleaching of the ground state around 520 nm and the triplet state (^{3}EY*) absorption with $\lambda_{\max}$ at 560 nm (Fig. 2a).[21] The decay throughout the absorption region and the recovery of the bleach occurs simultaneously and can be described by a monoexponential function with a lifetime of *ca.* 150 μs (Fig. 2b, curve 1). Upon addition of nitrobenzene into the solution of EY, the absorption at 560 nm was gradually replaced by a new absorption centered at 460 nm (Fig. 2c). The new absorption is assigned to the absorption of $EY^{+\bullet}$ based on the literature.[21] The decay of the triplet absorption and the rise of the radical cation occur in the same time scale, suggesting occurrence of the electron transfer from the triplet EY to nitrobenzene (Fig. 2d). As the concentration of nitrobenzene increases from 0 to 1×10^{-4} M, the lifetime of ^{3}EY* decreases from 150 μs to 5.6 μs (Fig. 2b). From the Stern–Volmer plots, the electron transfer rate constant from ^{3}EY* to nitrobenzene (k_1) was calculated to be 1.72×10^9 M^{-1} s^{-1} (Fig. 2b). The triplet EY can also be quenched by TEOA. When the solution of EY and TEOA was excited with a 532 nm laser pulse, the absorption of ^{3}EY* around 560 nm was immediately observed and gradually replaced by an absorption at 403 nm (Fig. 2e). The later absorption has a lifetime of 357 μs (Fig. 2f) and is ascribed to the absorption of the EY radical anion ($EY^{-\bullet}$).[21] Again the decay of ^{3}EY* and the rise of $EY^{-\bullet}$ occurred in the same time scale (Fig. S2†), indicating electron transfer from TEOA to ^{3}EY*. The Stern–Volmer plots give the electron transfer rate constant (k_2) to be 1.96×10^7 M^{-1} s^{-1} (Fig. S3†). This rate constant is two orders of magnitude smaller than that of electron transfer from ^{3}EY* to nitrobenzene (k_1, 1.72×10^9 M^{-1} s^{-1}). Although the amount of TEOA used was 3–6 equivalents of nitrobenzene in our photocatalytic reduction, the quenching rate of ^{3}EY* by nitrobenzene would be *ca.* 30–15 times that by TEOA. Thus, we infer that the triplet excited state of EY is quenched mainly by nitrobenzene *via* electron transfer.

The radical cation $EY^{+\bullet}$ generated through electron transfer from ^{3}EY* to nitrobenzene can undergo electron transfer with TEOA producing $TEOA^{+\bullet}$ and ground state EY. As evidenced in Fig. 2g, photolysis of the solution of EY, nitrobenzene and TEOA immediately results in the triplet EY absorption at 560 nm. This absorption was gradually replaced by the transient absorption of $EY^{+\bullet}$ around 460 nm owing to electron transfer from ^{3}EY* to nitrobenzene. The $EY^{+\bullet}$ absorption is greatly quenched by TEOA. In the absence of TEOA, the lifetime of $EY^{+\bullet}$ is *ca.* 345 μs (Fig. 2h, curve 1), while in the presence of 1.5×10^{-3} M TEOA the lifetime of $EY^{+\bullet}$ is shortened to 22.9 μs. The Stern–Volmer plots in Fig. 2h give the electron transfer rate constant (k_3) from TEOA to $EY^{+\bullet}$ to be 2.7×10^7 M^{-1} s^{-1}. On the basis of the above-mentioned results, the photocatalytic reduction mechanism is summarized in Scheme 3. The photoinduced electron transfer from the triplet EY to nitrobenzene (oxidative quenching) results in the formation of $EY^{+\bullet}$ and the nitrobenzene radical anion. Subsequent electron transfer from TEOA to $EY^{+\bullet}$ regenerates EY and yields $TEOA^{+\bullet}$. Reaction of the nitrobenzene radical anion with the TEOA



Scheme 3 Possible mechanism for the photocatalytic reduction of nitrobenzenes.

Table 1 Photocatalytic reduction of nitrobenzenes[a]



Entry	Position	Reducible group : X	Conversion[b] [%]	Selectivity[c] [%]
1	—	–H	99	99
2	*p*-	–Cl	99	98
3	*p*-	–Br	98	100
4	*p*-	–CH$_3$	100	95
5	*p*-	–OCH$_3$	100	96
6	*p*-	–CHO	100	100
7	*p*-	–COCH$_3$	>99	93
8	*p*-	–C≡CH	>99	90
9	*p*-	–C≡N	>99	100
10	*m*-	–C≡N	>99	100
11	*o*-	–C≡N	99[d]	100[d]

[a] Light source: LED (green light, 525 nm); room temperature; substrate amount: 0.2 mmol; EY: 1 mol%; TEOA: 6 equiv.; EtOH–H$_2$O (3 : 2), 5 mL; pH = 8.50; irradiation time: 24 h. [b] Determined by ^{1}H NMR (CDCl$_3$). [c] Selectivity = yield/conversion. [d] 2-Aminobenzamide was yielded as the product.

radical cation in the presence of H$_2$O gives glycolaldehyde and diethanolamine (Scheme 1), and produces the intermediates shown in Scheme 2. The intermediates further undergo photocatalytic reduction in a similar manner and eventually yield aniline.

With the understanding of the reaction mechanism, the photocatalytic reduction was further extended to the nitrobenzene derivatives with reducible groups, and the chemoselectivity was particularly examined. Table 1 summarizes the results for a variety of substrates. The nitro group in the substrates bearing either an electron-donating (entries 4 and 5) or an electron-withdrawing (entries 6–11) substituent could be reduced to the corresponding amino group. The reducible groups other than nitro existing in the substrates involve carbonyl (aldehyde and ketone), carbon–carbon triple bond, carbon–nitrogen triple bond, Cl and Br. For all the substrates examined except *ortho* cyanonitrobenzene[22] only the nitro group was reduced, and the isolated yields for the corresponding anilines were close to 100% at full conversion. We note that the factors governing the chemoselectivity in such photocatalytic reduction are different from the classical heterogeneous catalytic reduction. In classical heterogeneous catalytic reduction, the adsorption–reaction–desorption mechanism[7b] suggests that the chemoselectivity will depend on the strength of the adsorption of the respective reducible groups on the catalyst surface. Here, in the photocatalytic reduction the chemoselectivity will be determined by the ability of accepting electrons of the respective reducible groups, as suggested by Scheme 3. The nitro group has much greater ability of accepting electrons than the other reducible groups in the substrates shown in Table 1. Thus, it is not difficult to understand why the nitro group in the substrates is selectively reduced in the photocatalytic reduction.

In summary, we have developed an efficient green light driven catalytic reduction of nitrobenzenes into industrially important anilines by using a pure organic photocatalyst. This reaction shows excellent chemoselectivity when other reducible groups are present in the same nitrobenzene molecule. Flash-photolysis investigation revealed that the reaction was initiated by single electron transfer from the photocatalyst triplet excited state to the nitrobenzenes. The photocatalyst was regenerated by receiving an electron from the reducing agent. Reaction of the nitrobenzene radical anion with the reducing agent radical cation produced the anilines.

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22 The reduction of *ortho* cyanonitrobenzene yields 2-aminobenzamide. This reaction has been reported. The nitrile moiety in this case is not reduced but rather its hydrolysis to an amide group. See ref. 1*b*.