A TiO₂ immobilized Ru(II) polyazine complex: a visible-light active photoredox catalyst for oxidative cyanation of tertiary amines†Cite this: *J. Mater. Chem. A*, 2014, 2, 4514Received 20th November 2013
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A chemically functionalized nanocrystalline TiO₂ grafted ruthenium(II) polyazine complex was found to be an efficient visible light photoredox catalyst for the oxidative cyanation of tertiary amines to the corresponding α -aminonitriles in high to excellent yields, using molecular oxygen as an oxidant and sodium cyanide in acetic acid as a cyanide source. The developed photoredox catalyst could be easily recovered by simple filtration and reused for several runs with consistent catalytic activity.

The use of visible light sensitization as a means to initiate organic reactions is an attractive tool as visible light is ubiquitous, renewable and a clean source of energy.¹ Furthermore, lack of visible light absorbance by organic compounds reduces the possibility of side reactions often associated with photochemical reactions conducted with high energy UV light. Among these, the use of photoredox catalysts, in particular Ru(II)polypyridine complexes, for organic transformations are of notable importance due to their ease of synthesis, stability at room temperature, and excellent photoredox properties.² However, similar to homogeneous catalysis, these complexes also suffer from the drawbacks of difficult recovery and an inability to reuse the catalyst. One of the elegant approaches for making these catalysts recyclable is to fix the homogeneous metal complexes to a solid matrix. In recent decades, modification of titanium dioxide *via* immobilization or functionalization with metal complexes has become an appealing approach. These immobilized metal complexes can harvest visible light and inject photogenerated electrons into the conduction band of the titania.³

α -Aminonitriles are highly useful and versatile intermediates for a wide range of natural products and nitrogen-containing bioactive compounds such as alkaloids.⁴ Also, these compounds show dual reactivity as nucleophilic addition

provides easy access to various compounds such as α -amino aldehydes, ketones and β -amino alcohols. On the other hand, these compounds can be easily hydrogenated to useful compounds such as 1,2-diamines.⁵ The most common method for their synthesis, also known as Strecker reaction, is well documented in the literature, though it is normally a multistep synthesis.⁶ An alternative and more convenient approach for the preparation of these structural motifs is the catalytic oxidative cyanation of sp³ C–H bonds adjacent to the nitrogen atoms in tertiary amines. In this context, a number of metal catalysts including Ru, Fe, V *etc.* in the presence of stoichiometric oxidants such as *m*-chloroperbenzoic acid, *tert*-butyl hydroperoxide, O₂, H₂O₂ has been reported.⁷ However, few reports are known on the use of photoredox catalysts for this transformation. In this regard, Rueping *et al.* reported [Ir(ppy)₂bpy] PF₆ as a visible light photoredox catalyst for aerobic oxidative cyanation of tertiary amines.⁸ However, difficult recovery and non-recyclability of the catalyst makes this method of limited synthetic utility.

In continuation of our recent research programme on photocatalysis, we herein report an efficient, heterogeneous, easily recoverable and recyclable visible light active TiO₂ immobilized ruthenium polyazine photoredox catalyst for the oxidative cyanation of tertiary amines using molecular oxygen as oxidant and NaCN in acetic acid as a cyanide source (Scheme 1).†

Scheme 1 Visible light active photoredox catalyst for the oxidative cyanation of tertiary amines.

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Synthesis and characterization of the catalyst 2

During the present investigation, nanocrystalline TiO_2 was prepared by following the literature procedure.⁹ Hydroxyl groups placed on TiO_2 were targeted for grafting of ruthenium polyazine complex using 3-chloropropyltrimethoxysilane (CPTS) as a coupler. The strategy used to synthesize the TiO_2 immobilized ruthenium-polyazine photocatalyst is shown in Scheme 2.

The successful synthesis of nanocrystalline TiO_2 and TiO_2 grafted ruthenium polyazine complex **2** was confirmed by various techniques including XRD, SEM, TEM, ICP-AES, CHNS, UV-Vis, NMR, ^{13}C NMR and FTIR spectroscopy. Characterization data of the catalyst are given in the ESI.[†] The values of BET surface area and BJH pore volume of **2**, as determined by nitrogen adsorption, were found to be $26.50 \text{ m}^2 \text{ g}^{-1}$ and $0.0622 \text{ cm}^3 \text{ g}^{-1}$, respectively (ESI, Fig S3[†]).

The crystallinity of the as-synthesized TiO_2 and $\text{TiO}_2\text{-Ru(II)}$ polyazine photocatalyst **2** was examined by XRD¹⁰ analysis (Fig. 1). As shown in Fig 1a, the well resolved peaks and their intensities revealed good crystallinity of the TiO_2 , mainly in the anatase phase, and that the rutile form was only present in a small quantity. The peaks at 2θ values of 24.86, 37.41, 47.68, 54.23, 54.51, 63.33, 69.48, and 73.69 were identified by comparison with literature data which confirmed the successful synthesis of TiO_2 nanoparticles with an anatase structure. The as-synthesized TiO_2 was combined with phenanthroline-5-amine ligands followed by its reaction with a ruthenium pyridyl complex (Scheme 2). The XRD pattern of the TiO_2 immobilized ruthenium polyazine complex **2** is shown in Fig 1b. For comparison, we also prepared a homogeneous ruthenium polyazine complex by combining the ruthenium pyridyl complex with a phenanthroline-5-amine ligand. The XRD

Fig. 1 XRD pattern of (a) TiO_2 ; (b) TiO_2 grafted Ru-polyazine photocatalyst **2**; (c) Ru-polyazine complex.

pattern of the homogeneous ruthenium complex is shown in Fig. 1c. As shown, the XRD pattern of the TiO_2 immobilized ruthenium photocatalyst (Fig 1b) exhibits a combination of peaks from TiO_2 (Fig. 1a) and the ruthenium polyazine complex (Fig. 1c). Importantly, no impurity peaks appeared in the diffractogram of the synthesized photocatalyst **2** except for those of anatase TiO_2 and ruthenium polyazine complex. Furthermore, appearance of ruthenium polyazine complex peaks in the XRD pattern of **2** confirmed the successful attachment of the ruthenium complex to TiO_2 . Additionally, deposition of Ru(II) -polyazine onto the TiO_2 did not affect the morphology of the TiO_2 support (Fig 1b).

The size and morphology of the samples were analyzed by SEM and TEM measurements. The SEM image of the TiO_2 and photocatalyst **1** are given in ESI.[†]

The TEM image (Fig. 2) revealed that the product consisted of the homogeneous distribution of ruthenium over the TiO_2 support and showed that the particle size was 10–20 nm. The black particles visible in the TEM image (Fig. 2a) were attributed to the presence of ruthenium, which was further confirmed by EDX. Furthermore, selected area electron diffraction (SAED) analysis was carried out to identify the crystalline phases of TiO_2 (Fig. 2b).

The catalytic efficiency of the as-synthesized photocatalyst **2** was examined for the oxidative cyanation of tertiary amines **1** to α -aminonitriles **3**. The reaction used with molecular oxygen in the presence of NaCN and acetic acid with methanol as the solvent under visible light irradiation, using a household white LED (20 W) at room temperature (Scheme 1). We initiated our studies by selecting the photochemical oxidation of *N,N*-dimethylaniline in order to optimize the reaction conditions (Table 1). To our delight, we could isolate the desired α -aminonitrile at a very high yield (96%) in 4 h using only 1 mol% of the TiO_2 -grafted ruthenium photocatalyst **2** (Table 1, entry 2). In a controlled blank experiment, no reaction occurred in the absence of photocatalyst **2** (Table 1, entry 1). Similarly, there was no reaction observed by using nanocrystalline TiO_2 as a catalyst (Table 1, entry 3), proving that the ruthenium-polyazine was

Scheme 2 Synthesis of nanocrystalline TiO_2 immobilized ruthenium polyazine complex **2**.

Fig. 2 (a) TEM image of TiO_2 -grafted photocatalyst 2; (b) SAED image; (c) EDX.

truly required for this transformation. When the reaction was performed using the homogeneous ruthenium(II) polyazine complex as the catalyst (1 mol%) under the described experimental conditions, the reaction did occur but afforded a poor yield of the desired product, indicating the promoting effect of TiO_2 on the photocatalytic activity of the catalyst (Table 1, entry 4). However, the reaction of *N,N*-dimethylaniline with TiO_2 immobilized photocatalyst 2 in the dark was found to be very slow and afforded a poor yield of the desired product (Table 1, entry 5). Furthermore, the use of air in place of molecular oxygen afforded the desired product in comparatively lower yield (Table 1, entry 6). Acetic acid was found to be crucial in this transformation and no reaction took place in its absence (Table 1, entry 7). The role of acetic acid can be attributed to the liberation of HCN in the presence of AcOH. Hence, acetic acid

acts as a co-catalyst in this transformation. To evaluate the effect of solvent, the photochemical oxidative cyanation of *N,N*-dimethylaniline was studied in various solvents such as dichloroethane, acetonitrile, toluene, methanol and ethanol. The results of these experiments are summarized in Table 1 (entries 8–11). Among the various solvents studied, polar and protic solvents such as methanol and ethanol were found to be the best reaction media for this transformation.

To further investigate the substrate scope, the oxidative cyanation of a variety of aromatic and cyclic tertiary amines was studied under similar experimental conditions. The results of these experiments are presented in Table 2. The conversion and selectivity of the product was confirmed by GCMS and identity was confirmed by comparing the physical and spectral data with those of authentic samples. Among various substrates, aromatic substrates with electron donating groups (Table 2, entries 2 and 3) were found to be more reactive compared to substrates bearing electron withdrawing groups (Table 2, entries 4 and 5). Cyclic amines such as *N*-phenyl piperidine, *N*-phenylpyrrolidine and *N*-phenyltetrahydro-isoquinoline gave high yields of α -aminonitriles (Table 2, entries 7–9). Under the described experimental conditions, aliphatic tertiary amine such as *tert*-butyl amine did not produce any product (Table 2, entry 10). However, the reaction of tertiary amine containing benzyl groups was found to be slow and provided the corresponding α -aminonitriles in moderate yields (Table 2, entries 11 and 12).

We then tested the recycling of the photocatalyst by selecting the photochemical oxidation of the *N,N*-dimethylaniline as a representative example. After completion of the reaction, the photocatalyst was easily separated by filtration, washed with acetone, dried and reused for subsequent experiments (for eight runs). The results of the recycling experiments are depicted in Fig. 3. In all cases, the yield of the desired product was found to be similar, establishing the efficient recycling of the catalyst. Furthermore, the selected filtrate samples were subjected to ICP-AES analysis to check the leaching of the metal/ligand. No

Table 1 Results of the optimization experiments^a

Entry	Catalyst (1 mol%)	Solvent	Yield ^b (%)	TOF (h^{-1})
1	—	MeOH	—	—
2	2	MeOH	96	24
3	TiO_2	MeOH	—	—
4	Ru(II)polyazine	MeOH	90	22.5
5	2	MeOH	40 ^c	10
6	2	MeOH	92 ^d	23
7	2	MeOH	20 ^e	5
8	2	$\text{ClCH}_2\text{CH}_2\text{Cl}$	Trace	—
9	2	Toluene	25	6.3
10	2	CH_3CN	40	10
11	2	EtOH	92	23

^a Reaction conditions: substrate (1 mmol), photocatalyst (1 mol%), NaCN (1.2 mmol), solvent (4 mL) in the presence of molecular oxygen; reaction time 4 h. ^b Isolated yield. ^c Reaction was performed in the dark. ^d By using air in place of oxygen. ^e In the absence of acetic acid.

Table 2 TiO₂-immobilized ruthenium polyazine complex 2-catalyzed oxidative cyanation of tertiary amines^a

Entry	Reactant 1	Product 3	Time (h)	Yield ^b (%)	TOF (h ⁻¹)
1			4	96	24
2			4	91	23
3			3.5	84	24
4			5	75	15
5			4	85	21.2
6			4	90	22.5
7			4.5	88	19.5
8			4.5	89	20
9			5	92	18.4
10	(<i>n</i> -Bu) ₃ N	—	48	—	—
11			30	48	1.6
12			24	55	2.3

^a Reaction conditions: substrate 1 (1 mmol), catalyst 2 (1 mol%), NaCN (1.2 mmol), AcOH (1 mL), MeOH (4 mL) in the presence of O₂ at room temperature. ^b Isolated yield.

metal/ligand was observed during these experiments, proving that the reaction was truly heterogeneous in nature and no leaching had occurred during the photochemical reaction.

A comparison of the catalytic performance of the developed photocatalyst 2 with previously reported heterogeneous catalysts is shown in Table 3. In comparison, the present photocatalyst 2 has the following significant advantages; (a) the use of visible light, (b) the use of molecular oxygen as a terminal oxidant, (c) ability to use lower catalyst concentration (1 mol%), (d) higher product yields, (e) mild experimental conditions, and (f) the reusability of the TiO₂ grafted ruthenium photocatalyst.

Fig. 3 Results of the recycling experiments.

Although the exact mechanism of the reaction is not known at this stage, a possible mechanistic pathway of the reaction is shown in Scheme 3. In accordance with existing reports, two important steps can be assumed for the photocatalytic oxidative cyanation of the tertiary amine. The first step of the reaction may involve the single electron transfer from the tertiary amine for reductive quenching of the excited triplet state of the complex (^{*}[Ru(bpy)₂]²⁺) to generate intermediate [Ru(bpy)₂]⁺ and a radical cation of the tertiary amine. The formation of transient species [Ru(bpy)₂]⁺ under visible light in the presence of a donor is well documented in the literature. The photoredox catalyst was regenerated by its reoxidation with molecular oxygen to give a superoxide radical anion (O₂^{•-}). The second step of the reaction possibly involves the abstraction of an hydrogen atom (H[•]) from the amine cation radical B, by the superoxide anion (O₂^{•-}) to give iminium ion intermediate C, as shown in Scheme 3. The iminium ion intermediate C subsequently reacts with hydrogen cyanide that is generated *in situ* from NaCN and acetic acid to yield the corresponding α-aminonitriles.

In summary, we have developed for the first time an efficient, recyclable and heterogeneous aerobic photocatalytic oxidative

Table 3 Comparison of various heterogeneous catalysts for oxidative cyanation of tertiary amines

Substrate	Catalyst	CN source/oxidant	Time/h	Yield (%)	Ref.
Ru/C (2 mol%)	Ethyl cyano-formate/TBHP	6.0	95	11
Fe _{0.64} H _{0.36} PMo ₁₂ O ₄₀ /Nb ₂ O ₅ (50 mg)	Ethyl cyano-formate/TBHP	7.0	96	12
RuCl ₄ [−] on starch (2 mol%)	NaCN/H ₂ O ₂	2.0	82	7j
Polymer supported Fe(II)Pc (2 mol%)	NaCN/H ₂ O ₂	2.5	95	7f
Iron@graphene oxide (2 mol%)	NaCN/(tBuO) ₂	2.5	90	7k
Iron oligopyridine/SBA-15 (5 mol%)	NaCN/O ₂	12	71	13
TiO ₂ (1 eq.) (11 W fluorescent)	KCN/O ₂	20	95	14
MnO ₂ -based catalyst (2 g)	TMSCN/O ₂	2	90	15
TiO ₂ supported ruthenium (II)polyazine (1 mol%)	NaCN/O ₂	4.0	96	—

Scheme 3 Possible mechanism of the photocatalytic oxidative cyanation.

cyanation of tertiary amines to valuable α -aminonitriles compounds in high yields. The reaction required molecular oxygen in presence of NaCN in acetic acid under visible light irradiation, using a household white LED (20 W). It is anticipated that the developed visible light photoredox catalyst can be further explored to develop a number of environmentally benign and cost effective methodologies for organic transformations.

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Notes and references

† General experimental procedure: a 25 mL round bottomed flask equipped with a magnetic stirrer bar was charged with tertiary amine (1 mmol), NaCN (1.2 mmol), MeOH (2 mL), catalyst (1 mol%) and AcOH (1 mL). The stirring was continued at room temperature under an oxygen atmosphere with visible light irradiation, using a household white LED (20 W). The progress of the reaction was monitored by TLC (SiO₂). After completion of the reaction, the catalyst was recovered by precipitation with diethyl ether followed by filtration. The obtained organic layer was washed with water, dried over anhydrous Na₂SO₄ and concentrated under vacuum to give the crude product, which was purified by flash chromatography to

afford pure α -aminonitrile. The conversion of tertiary amines into corresponding α -aminonitriles and their selectivity was determined by GC-MS (EI quadrupole mass analyzer, EM detector) and the identity of the selected products was established by comparing their spectral data with authentic samples.

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