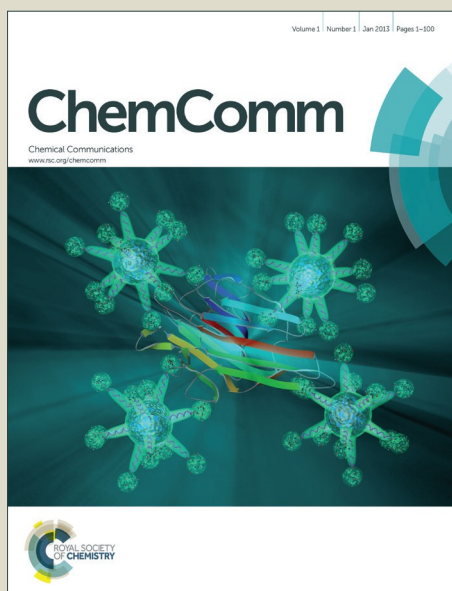


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## Ruthenium Bipyridyl Tethered Porous Organosilica: A Versatile, Durable and Reusable Heterogeneous Photocatalyst

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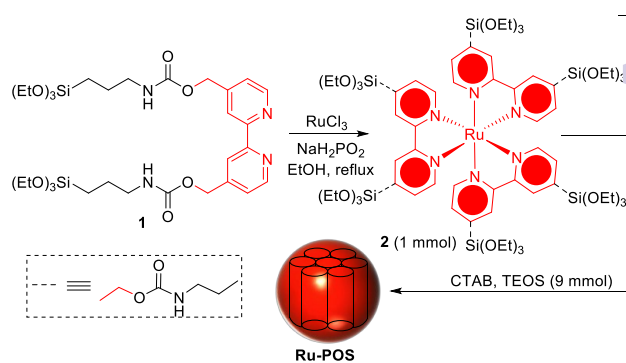
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**A versatile heterogeneous photocatalysis protocol was developed by using ruthenium bipyridyl tethered porous organosilica (Ru-POS). The versatility of the Ru-POS catalyst in organo-photocatalysis was explored by (i) oxidative aromatization of Hantzsch ester, (ii) reductive dehalogenation of alkyl halides, and (iii) functional group interconversion (FGI) of alcohols to alkyl halides.**

Visible light induced organic transformation was found to be an attractive way to initiate organic reactions,<sup>1</sup> since low absorbance of organic compounds in visible region could minimize the possibility of unwanted side reactions often associated with the use of high-energy UV light.<sup>2</sup> Recent advances in single electron transfer photoredox catalysis by employing catalytic amount of metal complexes such as [Ru(bpy)<sub>3</sub>Cl<sub>2</sub>] (bpy = bipyridine) has been proven to be an efficient tool in organic transformation over conventional organic synthesis.<sup>3</sup> The use of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex in photoredox catalysis is advantageous because of its high stability in the reaction medium such as in acidic and basic conditions, strong absorption in visible region ( $\lambda_{\text{max}} \approx 452$  nm in water), long lived triplet excited state, and most importantly its capability of readily undergoing oxidative and reductive quenching cycle in accordance with the reaction demand.<sup>4</sup> Therefore, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> mediated photosynthetic organic transformations have been found to be an rapidly growing field.<sup>3,5</sup> Apart from abovementioned advantages, however, there is a serious discrepancy associated with the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex, *i.e.*, its solubility in common organic solvents along with water makes the complex an excellent homogeneous catalyst, but the catalyst recovery is a demanding task. To address the issue associated with the catalyst recovery, various physicochemical immobilization techniques have been adopted using different types of matrices.<sup>6</sup> Such a physicochemical immobilization sometimes results in an uneven distribution of the catalyst as well as the catalyst leaching, which are major drawbacks to ultimately reduce the catalytic

activity of designed heterogeneous catalyst with respect to its homogeneous analogue.

Recent advancements have demonstrated that developing organically functionalized porous silica materials<sup>7</sup> for the immobilization of metal complexes is a promising approach to solve the abovementioned problems, since the ligands of the metal complexes remain covalently linked to the silica matrices. High surface area, tunable pore size distribution, as well as high thermal, hydrothermal, and mechanical stability of porous materials make them an appropriate host matrix for grafting a wide range of catalytically active species. Keeping all these points in mind, herein we report a versatile, durable and reusable heterogeneous photocatalyst based on ruthenium bipyridyl tethered porous organosilica (Ru-POS), where the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex was grafted *in situ* with porous silica matrices to obtain highly uniform distribution of the complex with high surface area of 620 m<sup>2</sup>/g.



**Scheme 1.** Schematic representation for the synthesis of Ru-POS.

The silane modified bipyridyl ligand **1** was synthesized by the condensation of triethoxy(3-isocyanatopropyl)silane with [2',2''-bipyridine]-4,4'-diyl dimethanol. The complex **2** was then synthesized according to the standard procedure by using 1 equivalent of ligand **1** and 1 equivalent of ruthenium trichloride (RuCl<sub>3</sub>) in the presence of sodium hypophosphite (1.5 equivalent) in ethanol (EtOH) under refluxing condition for 3h. Finally, Ru-POS was synthesized by the co-condensation of complex **2** with tetraethoxysilane as the silica source and cetyltrimethylammonium bromide (CTAB) as the structure-directing template (Scheme 1).

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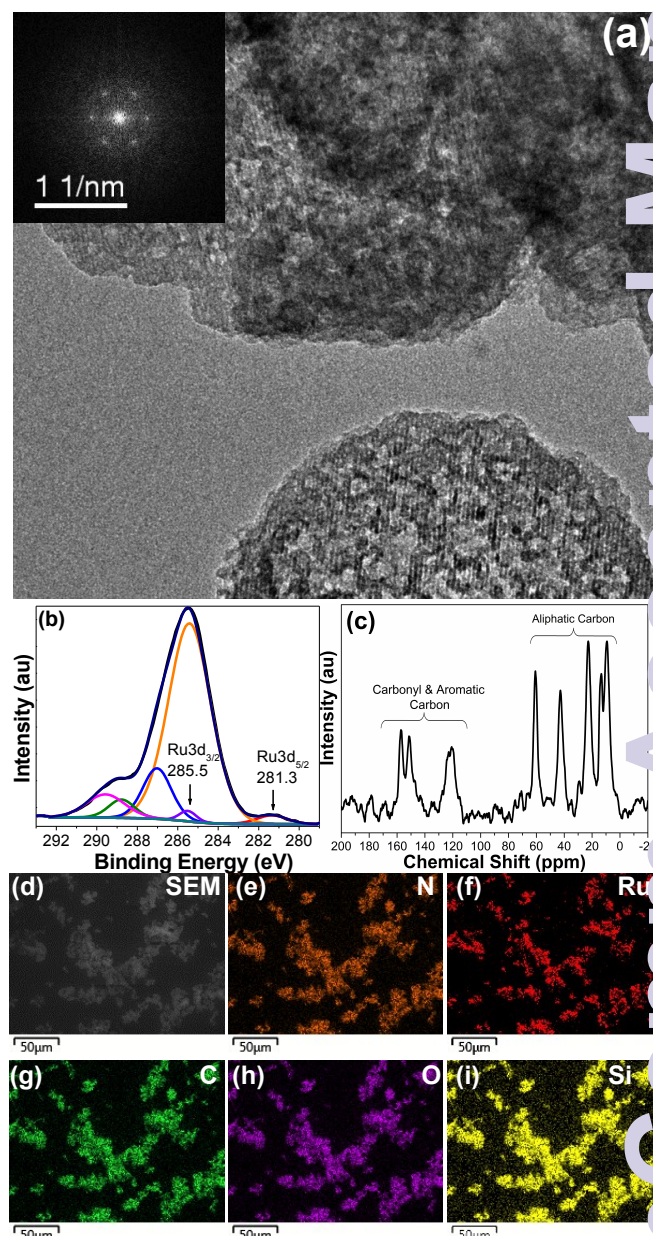
Electronic Supplementary Information (ESI) available: Additional synthesis and characterization data. See DOI: 10.1039/x0xx00000x

Surfactant extracted Ru-POS was fully characterized using inductive coupled plasma mass spectrometry (ICP-MS), nitrogen adsorption/desorption measurements, high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS),  $^{13}\text{C}$  solid state cross-polarization magic angle spinning (CPMAS) NMR and  $^{29}\text{Si}$  solid state NMR spectroscopy. HRTEM image (Figure 1a) of Ru-POS indicates that the pores having diameters of 3-4 nm are homogeneously distributed throughout the sample. In a similar manner, the pore channels can be observed in parallel direction to the 110 reflection plane of Ru-POS (Figure S1 in ESI). Furthermore, fast Fourier transform (FFT) diffractogram of Ru-POS (inset of Figure 1a) reveals a two-dimensional hexagonal porous channel pattern. The dark black spots (Figure 1a) could be attributed to the  $\text{Ru}(\text{bpy})_3$  complexes at the surface as well as in the porous channels, since the frameworks were formed based on the coordination of nitrogen atoms from bipyridine rings with Ru. Such uniformly distributed fine Ru complex nanoclusters are responsible for high catalytic activity of Ru-POS. The pore diameter observed from the HRTEM images was found to be in good agreement with the pore size obtained from the  $\text{N}_2$  adsorption/desorption data (Figure S2 in ESI). Pore size distribution was calculated by employing Barrett-Joyner-Halenda (BJH) method (inset of Figure S2 in ESI), which shows tetramodal porosity at 3.82 nm, 3.64 nm, 3.37, and 3.08 nm. The existence of pores with tetramodal distribution could be due to the large Ru-bipyridyl complex between the repeating units. Pore volume of this material is  $0.77 \text{ cc g}^{-1}$ , which is large enough for encapsulating a large number of organic molecules to carry out catalytic reactions. The calculated Brunauer–Emmett–Teller (BET) surface area of Ru-POS is  $620 \text{ m}^2 \text{ g}^{-1}$ . The large hysteresis in high pressure region is attributed to the existence of non-uniform mesopores throughout the materials. The ICP-MS analysis reveals that the Ru content of the catalyst is  $0.0495 \text{ mmol/g}$ .

XPS is an indispensable tool to evaluate the oxidation state of Ru related to the bipyridyl units in Ru-POS. The XPS spectrum of Ru-POS is displayed in Figure 1b and Figure S3 (ESI). The C1s-Ru3d core level XPS spectrum shows two binding energy (BE) peaks centered at 281.3 eV and 285.5 eV, respectively. The first peak is well resolved and can be assigned to the BE of Ru3d $_{5/2}$ . As the second peak is associated with the contribution by C1s as well as Ru3d $_{3/2}$ , the peak at 285.5 eV was deconvoluted and can be assigned to the existence of Ru in +2 oxidation state.<sup>8</sup> In addition, the intensity ratio of Ru3d $_{5/2}$  to Ru3d $_{3/2}$  was calculated to be 1.48. Solid state  $^{13}\text{C}$  CPMAS NMR spectrum (Figure 1c) of Ru-POS exhibits characteristic peaks for the organic ligands integrated within Ru-POS. The SEM elemental mapping images (Figure 1d-i) clearly validate the homogenous distribution of C, O, N, Si and Ru elements throughout the material. Energy dispersive X-Ray (EDX) pattern indicates the presence of Ru in Ru-POS (Figure S4 in ESI).

After successful synthesis and characterization of Ru-POS, we intended to explore it as a versatile heterogeneous photoredox catalyst. Thus, catalytic activity of Ru-POS was tested for three different sets of organic transformations as described below. Dihydropyridine (DHP) derivatives commonly known as Hantzsch esters (HE) were found to be attractive candidates in medicinal chemistry owing to their uses in the treatment of cardiovascular diseases.<sup>9,10</sup> The DHP derivatives can be synthesized *via* three component Hantzsch reaction. There are several reports regarding the synthesis of DHP derivatives, mostly focusing on the optimization of the reaction conditions to obtain DHP derivatives in

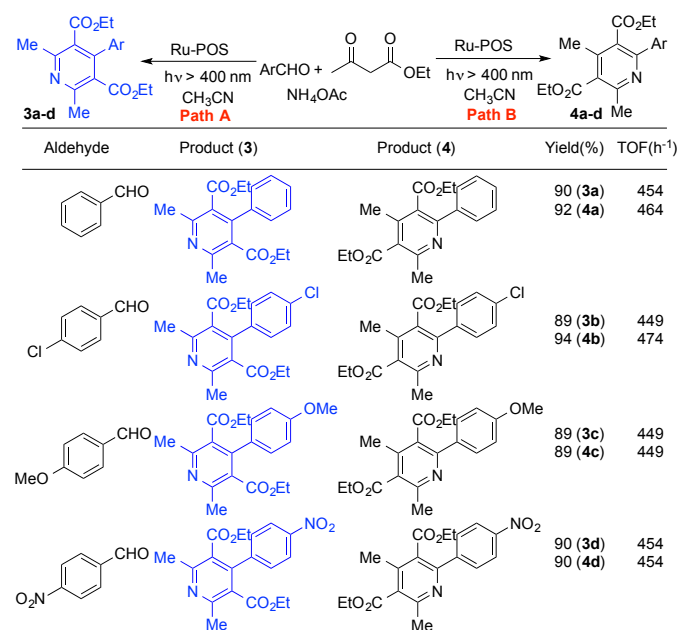
high yield and high purity. There are also some reports which investigated catalytic oxidation mediated dehydrogenation of DHP derivatives<sup>9c</sup> and the as-produced hydrogen was further employed in several organic transformations.<sup>3c,3e,11</sup> To explore the catalytic activity of the Ru-POS catalyst towards the reductive quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  mediated organic transformation as a flexible method, oxidative elimination of hydrogen from HE to obtain corresponding highly substituted pyridine derivatives was tested in this work. Both usual (path A)<sup>12</sup> and unusual (path B)<sup>10</sup> HEs were synthesized (Schemes S2-S5 in ESI) followed by dehydrogenation in the presence of Ru-POS in acetonitrile suspension under atmospheric oxygen (Table 1), leading to corresponding pyridine derivatives.



**Figure 1.** Characterization of Ru-POS: (a) HRTEM image of surfactant extracted Ru-POS, (b) XPS spectra of Ru-POS, (c) solid state  $^{13}\text{C}$  CPMAS NMR spectrum of Ru-POS, (d) SEM image of Ru-POS, (e-i) SEM X-ray elemental mapping of Ru-POS showing the presence of constituting elements: (e) nitrogen (N), (f) ruthenium (Ru), (g) carbon (C), (h) oxygen (O), and (i) silicon (Si).



**Table 1.** Synthesis of various 2-arylpyridines and 4-arylpyridines from their corresponding DHP derivatives by following the optimized photocatalytic conditions.<sup>a</sup>



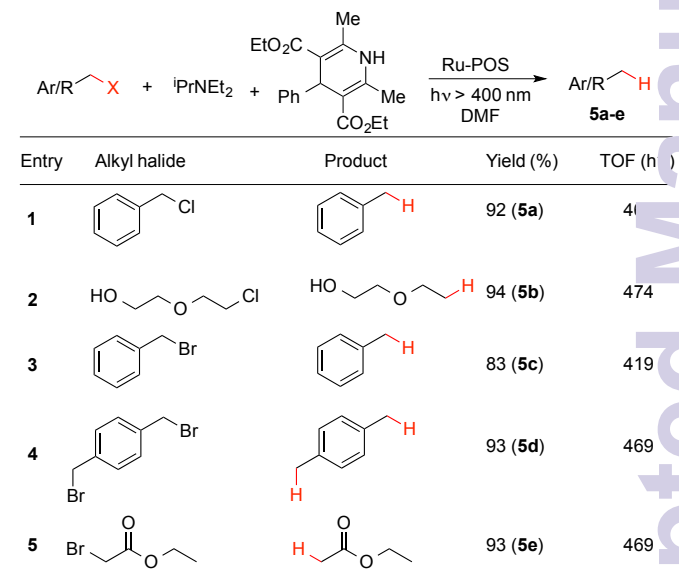
<sup>a</sup> DHP (1 mmol) and Ru-POS (20 mg) in 10 mL acetonitrile under light irradiation for 2h

It was observed that both usual and unusual HEs underwent efficient photocatalytic oxidative hydrogen elimination in the presence of atmospheric oxygen. The atmospheric oxygen forms superoxide radical ion ( $O_2^{\cdot-}$ ) under photolytic conditions, which is the active oxidizing agent responsible for the abstraction of proton from HEs to afford corresponding highly substituted pyridine derivatives<sup>10</sup> in high yields and high turnover frequency (TOF  $\geq 449$ ). By employing the optimized reaction conditions, the oxidative aromatization of HE to yield the pyridine derivative **4a** was carried out again to demonstrate the durability and recyclability of Ru-POS in ten successive catalytic cycles. The reused Ru-POS catalyst after 10th catalytic cycle was characterized employing HRTEM (Figure S1d in ESI), XPS (Figure S3d in ESI), <sup>13</sup>C CP MAS NMR (Figure S6 in ESI), and FT-IR (Figure S7 in ESI) techniques, indicating that the integrity of the Ru-POS catalyst was well preserved even after 10 catalytic cycles. The catalyst was recovered in a constant rate after each catalytic cycle without a significant loss of catalytic activity (Figure S9 in ESI). In addition, leaching test was performed to demonstrate heterogeneous nature of the catalyst. No leaching of Ru from Ru-POS took place during the course of the catalytic reaction. The Ru content in reused Ru-POS after 10th catalytic cycle was examined employing ICP-MS technique, showing a comparable amount of 0.0480 mmol/g.

To establish the versatility of the newly designed Ru-POS in organic synthesis, after successful demonstration of oxidative dehydrogenation induced aromatization of HE, we applied the same catalyst in reductive quenching mediated dehalogenation of alkyl halides to obtain corresponding alkanes, where HE was employed as the hydrogen source under photoredox catalytic reaction conditions. Stephenson and co-workers validated that Ru(bpy)<sub>3</sub><sup>2+</sup> could serve as a useful photoredox catalyst to carry out the abovementioned reductive dehalogenation of alkyl halides.<sup>3e</sup> By following the standard protocol from homogeneous catalysis, heterogeneous photoredox catalytic transformation of alkyl halides

to alkanes was carried out, where Ru-POS was used in *N,N*-dimethylformamide (DMF) suspension. Alkyl halides and diethylisopropylamine (<sup>i</sup>PrNEt<sub>2</sub>) were dissolved in DMF, and the reaction mixture was irradiated using 25W compact fluorescent lamp (CFL) for 2h to afford the corresponding alkanes in excellent yields with high TOF of  $\geq 419$  (Table 2) as quantified by gas chromatography (GC) analysis of the reaction mixture. The product identification was demonstrated by gas chromatography–mass spectrometry (GCMS).

**Table 2.** Reductive dehalogenation of various alkyl halides to produce corresponding alkanes under the optimized photocatalytic conditions.<sup>a</sup>



<sup>a</sup> Ar/RCH<sub>2</sub>X (1 mmol), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (1.2 mmol), <sup>i</sup>Pr<sub>2</sub>NEt (2 mmol), and Ru-POS (20 mg) in 10 mL dry DMF under light irradiation for 3h

Functional group interconversion (FGI) of alcohols to corresponding alkyl halides is one of the most widely explored reaction in synthetic organic chemistry, and thereby numerous methodologies have been developed using various harsh reagents like thionyl chloride and phosphorous halides. The Appel reaction, in which the combination of triphenylphosphine (PPh<sub>3</sub>) and an electrophilic halogen source such as CCl<sub>4</sub>, CBr<sub>4</sub> or I<sub>2</sub> is used to obtain the desired conversion of alcohols to corresponding alkyl halides, is so far the mildest reaction in this category, although the process is known for producing stoichiometric waste by-product of triphenylphosphine oxide. Recently, Stephenson and co-workers demonstrated a greener approach of converting alcohols to corresponding alkyl halides, where CBr<sub>4</sub> or CHI<sub>3</sub> was used as the halogen source and Ru[bpy]Cl<sub>2</sub> was employed as a homogeneous photoredox catalyst.<sup>13</sup> Herein, to test the versatile catalytic activity of the Ru-POS catalyst towards oxidative quenching mediated FGI of alcohols to alkyl halides, we introduced a heterogeneous photoredox catalytic protocol using Ru-POS as the catalyst, in which Ru(bpy)<sub>3</sub><sup>2+</sup> underwent an oxidative quenching cycle (oxidation potential<sup>13</sup> of [Ru(bpy)<sub>3</sub>]<sup>3+</sup> = 1.27 V vs saturated calomel electrode (SCE)) in the presence of polyhalomethane such as CBr<sub>4</sub> (E<sub>1/2</sub> = -0.30 V vs SCE) and CHI<sub>3</sub> (E<sub>1/2</sub> = -0.49 V vs SCE). To evaluate the catalytic activity of the newly designed Ru-POS in visible light induced oxidative FGI of alcohols to alkyl halides, we carried out heterogeneous photoredox catalytic reactions, where the alcohol and halogen (CBr<sub>4</sub> or CHI<sub>3</sub>) sources were dissolved in DMF followed by the addition of Ru-POS in DMF suspension. The reaction mixture

was irradiated using 25 W CFL for 5h to obtain the corresponding alkyl halides in 60-70% yields. When adding external halogen source such as NaBr and NaI for corresponding bromination and iodination, the reactions could be completed within 3h in high yield (Table 3), which are in accordance with the results obtained by Stephenson and co-workers.<sup>13</sup>

**Table 3.** Oxidative halogenation of alcohols to produce corresponding alkyl halides under the optimized photo-catalytic conditions.<sup>a</sup>

Entry	Alcohol	Product	Yield(%)	TOF (h <sup>-1</sup> )
1			89 (6a)	299
			92 (7a)	309
2			85 (6b)	286
			82 (7b)	276
3			90 (6c)	303
			91 (7c)	306
4			93 (6d)	313
			91 (7d)	306
5			88 (6e)	296
			76 (7e)	255

<sup>a</sup> Alcohol (1 mmol), CBr<sub>4</sub>/CHI<sub>3</sub> (2 mmol), NaBr/NaI (2 mmol), and Ru-POS (20 mg) in 10 mL dry DMF under light irradiation for 3h or 5h

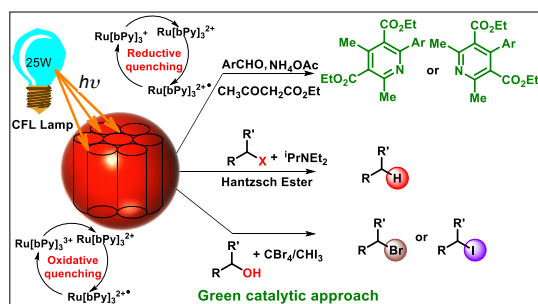
In summary, we have successfully incorporated [Ru(bpy)<sub>3</sub>]<sup>2+</sup> within porous organosilica as a versatile heterogeneous photoredox catalyst. The Ru-POS catalyst has been employed for three different catalytic organic transformations. The catalyst has been exploited both for reductive and oxidative quenching mediated catalytic reactions to afford desired products in excellent yields. The newly developed catalyst was found to be durable and reusable, and no pre-activation was required to recover its catalytic activities. The present work exhibits an approach for developing Ru-based heterogeneous catalysts.

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TOC Figure

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Ruthenium bipyridyl tethered mesoporous organosilica (Ru-POS) was developed as a versatile heterogeneous photoredox catalyst in several organic transformations.