

Core Cross-Linked Micelle-Based Nanoreactors for Efficient Photocatalysis

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Abstract: Stable nanoscale cross-linked polymer micelles containing Ru complexes (Ru-CMs) were prepared from monomethoxy[poly(ethylene glycol)]-*block*-poly(L-lysine) (MPEG-PLys) and [(bpy)₂Ru(fmbpy)](PF₆)₂ (bpy = bipyridine, fmbpy = 5-formyl-5'-methyl-2,2'-bipyridine). To stabilize the micelles, bifunctional glutaraldehyde was used as a cross-linker to react with the free amino groups of the PLys block. After that, the Ru-CMs showed very good

stability in common solvents. The Ru-CMs showed photocatalytic activity and selectivity in the oxidation of sulfides that were as high as those of the well-known [Ru(bpy)₃(PF₆)₂] complex, because the micelles were swollen in the methanol-sulfide mixture. More-

over, because of the nanoscale size of the particles and their high stability, the Ru-CM photocatalysts can be readily recovered by ultrafiltration and reused without loss of photocatalytic activity. This work highlights the potential of using cross-linked micelles as a platform for developing highly efficient heterogeneous photocatalysts for a number of important organic transformations.

Keywords: micelles • nanoreactors • oxidation • photocatalysts • ruthenium

Introduction

Sunlight can be considered as a sustainable and renewable energy source for thermal and electrical energy (photovoltaic cells). Besides that, photocatalytic organic reactions driven by visible light are gaining interest from organic chemists, because of their mild conditions for substrate activation and the potential to mediate thermodynamically uphill reactions by harvesting energy from sunlight.^[1] Several metal complexes, including Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) and [Ir(ppy)₂(dtb-bpy)]⁺ (ppy = 2-phenylpyridine, dtb-bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), have been used as photocatalysts for a number of organic transforms.^[2] These photocatalysts display high catalytic activity and selectivity for many organic reactions as a result of the homogeneous reaction environment. However, the catalysts are prepared from precious metals, and as such, the recovery and reuse of the catalysts are essential and critical for their wide use in chemical industries. Great effort has been made to develop reusable heterogeneous photocatalytic systems based on Ru complexes. The reuse of such heterogeneous photocatalysts not only eliminates contamination of the organic products

by trace amounts of heavy metals but also reduces processing and waste disposal costs in large-scale production.^[3] Organometallic catalysts loaded on hard frameworks such as mesoporous silica and zeolites are extensively employed.^[4] However, the low dispersibility of inorganic catalysts in an organic reaction mixture often causes a low conversion rate of the reaction owing to the heterogeneous interface between the reactant and the catalyst.

Block copolymers (BCPs) can self-assemble into various kinds of nanoscale aggregates such as spheres, cylinders, and vesicles by varying the BCP composition, solvent, concentration, and temperature.^[5] Of the aggregates, BCP micelles have great potential for use in targeted drug delivery,^[6] nanoreactors for inorganic materials,^[7] mesoporous nanostructured templates,^[8] and hybrid composite materials.^[9] However, the dynamic instability of BCP micelles can hinder their use in such applications. Although the critical micelle concentration (CMC) of polymer micelles is much lower than that of small-molecule surfactants, BCP micelles are still susceptible to disassembly under high dilution conditions.^[5b] A change in the solvent, an increase in temperature, mechanical stress, and shear force can also lead to rapid disassembly of BCP micelles. These considerations have motivated important breakthroughs in the stabilization of BCP micelles through cross-linking of either their corona or cores.^[10] By interchain bonding, cross-linked micelles (CMs) are stable, self-assembled nanostructures that can be used under harsh conditions. A wide variety of micelle cross-linking methodologies have been developed, including radical-induced bond formation,^[11] photoinduced cycloadditions,^[12] siloxane condensation,^[13] the use of bifunctional cross-linking agents,^[14] and many others.^[10] CMs can serve as ideal nanoreactors to incorporate molecular catalytic modules into highly stable, recyclable, and reusable heterogene-

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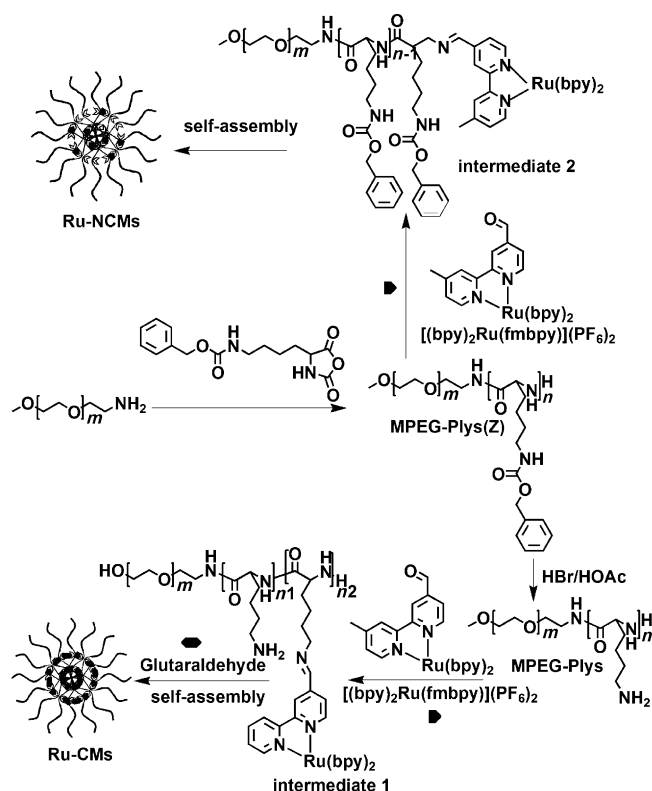
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/asia.201300668>.

ous catalysts by taking advantage of their nanoscale size and their good dispersity in the reaction solution owing to their outer corona.^[15] In addition, CMs could provide external shielding against micelle dissociation and catalyst leaching, which can benefit catalyst recovery and recycling.

In this work, we tried to incorporate Ru complexes into nanoscale BCP micelles simply through a Schiff base reaction. Further, the cores of the micelles were cross-linked by bifunctional glutaraldehyde to form cross-linked micelles loaded with Ru complexes (i.e., Ru-CMs). The resulting Ru-CMs are highly stable and active in catalyzing the visible-light-driven oxidation of sulfides. Owing to the existence of the outer corona of the CMs, the Ru-CMs can disperse into and swell in the reaction solution very well, so that the substrate can diffuse into the core and the reaction product can escape from the catalytic center. Therefore, the Ru-CMs exhibit a conversion rate and selectivity that are comparable to those of homogeneous Ru photocatalysts. Moreover, because of the nanoscale size of the particles and their high stability, the Ru-CMs photocatalysts can be readily recovered by ultrafiltration and reused without a decrease in catalytic efficiency.

Results and Discussion

The synthetic routes to Ru-CMs and non-cross-linked micelles loaded with Ru complexes (Ru-NCMs) are shown in the Scheme 1. There are free amino groups in



Scheme 1. Synthesis routes to the Ru-CMs and Ru-NCMs.

monomethoxy[poly(ethylene glycol)]-*block*-poly(L-lysine) (MPEG-PLys) after deprotection from MPEG-PLys(Z) (Z = carbobenzyloxy). These amino groups can react with aldehyde groups to form C=N bonds through a Schiff base reaction. Given that the number of amino groups (1.00 equiv) is higher than the number of Ru complexes (0.016 equiv) in the reaction solution, the Ru complexes are covalently linked to only a portion of the amino groups on the PLys block. Then, glutaraldehyde is introduced into the reaction. Bifunctional glutaraldehyde (0.99 equiv) provides the excess amount of aldehyde groups for the Schiff base reaction and causes cross-linking in the PLys block. Because the cross-linking reaction lowers the hydrophilicity of the PLys block, the block copolymer self-assembles into nanoscale micelles with the cross-linked PLys as the core and MPEG as the corona. The Ru content of the micelles prepared through this route was determined by inductively coupled plasma mass spectrometry (ICP-MS) to be 0.67 wt % in the final product. Covalent attachment of the Ru complex on the PLys block results in a high local catalyst concentration inside the hydrophobic core of the polymeric micelles upon aggregation in a hydrophilic or aqueous environment, and this is beneficial to increase the reaction rates of catalytic reactions. Moreover, the cross-linked core layer provides a shield against metal leaching and catalyst poisoning, which could facilitate catalyst recovery and recycling. Furthermore, cross-linking of the core improves the stability of the catalyst, but the permeability of the micelles is retained, which allows the diffusion of small molecules in and out of the nanoreactors. As there are many amino groups in intermediate **1**, both blocks are hydrophilic. Intermediate **1** cannot form micelles in the water/THF mixture, which was determined by dynamic light scattering (DLS; Figure S1a, Supporting Information). To compare the stabilities of the CMs with BCP micelles, Ru-NCMs were designed and synthesized starting from MPEG-PLys(Z). Because the amine groups on the side chain of lysine were protected by benzyloxycarbonyl groups, the [(bpy)₂Ru(fmbpy)](PF₆)₂ (fmbpy = 5-formyl-5'-methyl-2,2'-bipyridine) photocatalyst was only linked at the end of the main chain. Intermediate **2** can self-assemble into micelles (i.e., Ru-NCMs) in H₂O/THF because of the weak hydrophilicity of the PLys(Z) block.

Figure 1a shows the FTIR spectra of the pure block copolymer MPEG-PLys, [(bpy)₂Ru(fmbpy)](PF₆)₂, and the Ru-CMs. For MPEG-PLys, the absorption peaks at 3270 and 1625 cm⁻¹ are assigned to stretching and bending vibrations of the N-H group of the amine, whereas the band at 1350 cm⁻¹ is attributed to the stretching vibration of C-NH. For [(bpy)₂Ru(fmbpy)](PF₆)₂, the peak at 1710 cm⁻¹ corresponds to the stretching vibration of the C=O moiety of the aldehyde group. After the Schiff base reaction, for the Ru-CMs, the characteristic bands for the vibrations of the N-H group disappeared, and at the same time, another new band appeared at 1650 cm⁻¹, which indicates that all of the amine groups have reacted with the aldehyde groups and that C=N bonds are formed as the product of the Schiff base reaction. The emission spectra of [(bpy)₂Ru(fmbpy)](PF₆)₂ and the

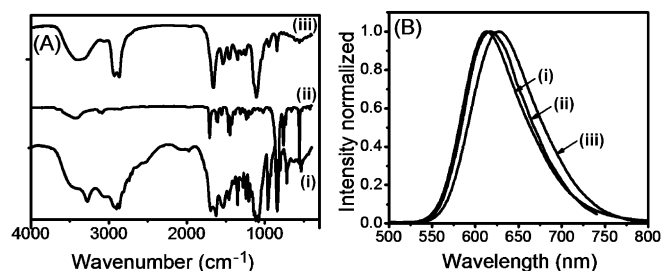


Figure 1. A) FTIR spectra of MPEG-PLys (i), $[(bpy)_2Ru(fmbpy)](PF_6)_2$ (ii), and the Ru-CMs (iii); B) emission spectra of $[(bpy)_2Ru(fmbpy)](PF_6)_2$ in MeOH (i) the Ru-CMs in MeOH (ii), and the Ru-NCMs in H_2O (iii) with excitation at 450 nm.

Ru-CMs were recorded with excitation at 450 nm (Figure 1b). The characteristic band of $[(bpy)_2Ru(fmbpy)](PF_6)_2$ at 613 nm could be attributed to 3MLCT (metal-to-ligand charge transfer) transitions to the GS (ground state). The bands for the Ru-CMs and Ru-NCMs are at 617 and 627 nm, respectively, which are slightly redshifted relative to that of $[(bpy)_2Ru(fmbpy)](PF_6)_2$. These results confirmed that the conjugation of $[(bpy)_2Ru(fmbpy)](PF_6)_2$ with MPEG-PLys does not affect the luminescent properties of the Ru complexes.

The morphology of the micelles was characterized by using scanning electron microscopy (SEM). Figure 2a shows the SEM image of the Ru-CMs, which were cast from the MeOH solution onto a Si wafer. It clearly shows isolated spherical particles with an average diameter of $(72.9 \pm$

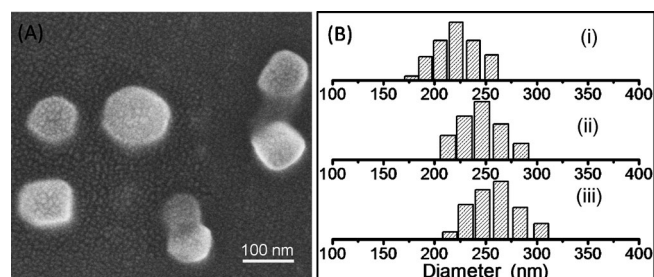


Figure 2. A) Scanning electron microscopy images of the Ru-CMs prepared from MeOH dispersion. SEM samples were sputter coated with gold; B) particle size of the Ru-CMs in MeOH (i), H_2O (ii), and THF (iii) determined by DLS.

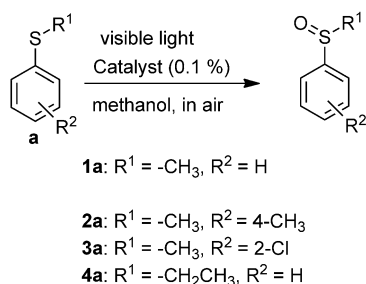
12.8) nm. Figure S2 (Supporting Information) shows the SEM image of a dispersion of the Ru-NCMs in water, and it also reveals isolated micelle particles with an average diameter of (50.0 ± 12.5) nm, because water is a poor solvent for the PLys(Z) block. To investigate the stability of the Ru-CMs, the hydrodynamic particle size of the micelles was characterized by DLS. In water, MeOH, and THF, the Ru-CMs show clear peaks at approximately 200 nm, and this indicates that the Ru-CMs can survive in polar solvents as a result of the cross-linked core. However, there are no clear peaks for MPEG-PLys and MPEG-PLys(Z) in the THF solution. Consequently, the non-cross-linked block co-

polymer was completely dissolved in THF. Thus, cross-linking plays a critical role in the formation of the micelles in addition to maintaining their stability. The particle size of the Ru-CMs in MeOH, H_2O , and THF solution determined by DLS (Figure 2b) is 221, 246, and 265 nm, respectively, and these values are more than two times larger than those determined by SEM. Because SEM characterizes the samples in the solid state, shrinkage while the micelles are dried results in a small particle size, whereas the diameter of the micelles determined by DLS represents the hydrodynamic diameter. The much larger apparent size of the particles in water, methanol, and THF implies that not only the corona MPEG block but also the core cross-linked PLys block of the Ru-CMs are in an extended state in the solution. Thus, the Ru-CMs can be swollen by the solvent. In that case, the Ru species have enough opportunity to come in contact with the reactant molecules in solution, and the reaction product can escape from the catalytic center with ease.

Sulfoxides are important intermediates for the synthesis of valuable compounds such as pharmaceuticals and other chemicals.^[16] The selective oxidation of sulfides to sulfoxides is one of the most fundamental processes from a synthetic point of view.^[17] Herein, we demonstrate the oxidation reaction of sulfides photocatalyzed by the Ru-CMs. The reactions were performed in methanol at room temperature without any additives. A 24 W household fluorescent lamp with a highpass filter ($\lambda = 395$ nm) was used as the visible-light source (400 to 700 nm). The concentration of the substrates was approximately 12.4% (v/v). The molar ratio of the catalyst (Ru) to substrates was 0.001. The reaction was stopped after 24 h by ultrafiltration of the mixture, and then the precipitate was washed with methanol (3 \times) and dried under vacuum. Conversions of the reactions were determined by 1H NMR spectroscopy by integrating the signals of the reactant ($\delta = 2.48$ ppm) and the product ($\delta = 2.74$ ppm) in the crude reaction mixtures.^[18]

As shown in Table 1 (entry 2), although the molar ratio of the Ru catalyst to thioanisole was only 0.001, the Ru-CMs were highly effective photocatalysts for the oxidation of thioanisole, as a conversion of 99% was obtained. No sulfone was detected by 1H NMR spectroscopy, which demonstrates the high degree of selectivity of this reaction (Figures S3 and S4, Supporting Information). These results are consistent with our previous report.^[18] The high conversion and selectivity are comparable to those obtained with the use of their homogeneous counterparts $[Ru(bpy)_3]^{2+}$; Table 1, entry 1]. To compare the catalytic reactivities of Ru-CMs and $[Ru(bpy)_3]^{2+}$, a kinetic study was performed at the same catalyst loading. Figure S5 (Supporting Information) shows the conversion yield as a function of reaction time. From this figure, it can be seen that $[Ru(bpy)_3]^{2+}$ showed higher catalytic activity in the oxidation of thioanisole and provided the product in 90% yield after 2 h; in contrast, the Ru-CMs afforded the sulfoxide in 49% yield in the same amount of time. For the Ru-CMs, the conversion increased from 49 to 89.3% as the time was increased from 2 to 8 h. At a longer reaction time (12 h), the conversion increased

Table 1. Photocatalytic aerobic oxidation of sulfides.^[a]



Entry	Catalyst	Substrate	Conv. [%] ^[b]
1	Ru(bpy) ₃ ²⁺	1a	98
2	Ru-CMs	1a	99
3	Ru-CMs, 1st reuse	1a	99
4	Ru-CMs, 2nd reuse	1a	98
5	Ru-CMs, 3rd reuse	1a	98
6	Ru(bpy) ₃ ²⁺	2a	94
7	Ru-CMs	2a	99
8	Ru(bpy) ₃ ²⁺	3a	60
9	Ru-CMs	3a	50
10	Ru(bpy) ₃ ²⁺	4a	53
11	Ru-CMs	4a	58
12	no catalyst with light	1a	0
13	no light with Ru-CMs	1a	0
14	Ru-CMs under N ₂	1a	6
15	Ru-NCMs with light	1a	98

[a] All of the reactions were run at room temperature for 24 h. [b] Conversions were determined by ¹H NMR spectroscopy.

slightly to 97.1%, which indicated the reaction was almost complete. These results show that the Ru-CMs have comparable catalytic activity to Ru(bpy)₃²⁺ at reaction times of 12 and 24 h. The possible reason for this result is due to the heterogeneous nature of the Ru-CMs, and the substrates have to diffuse into the hydrophobic core of the micelles and then react with the catalysts. Although the core of the Ru-CMs is cross-linked by glutaraldehyde, the substrates and the products are able to diffuse in and out of the micelles smoothly.

We examined the scope of the substrates for the oxidation reaction catalyzed by the Ru-CMs. Several sulfides were efficiently oxidized under ambient conditions, and the corresponding sulfoxides were produced with high conversions (Table 1, entries 6–11). The catalytic reactivity of the Ru-CMs toward these sulfides is comparable to that of the homogeneous Ru(bpy)₃²⁺ catalyst. Moreover, we also examined the recyclability of the Ru-CMs catalysts. The Ru-CMs were readily recovered from the reaction mixtures by simple ultrafiltration. The recovered catalysts showed no deterioration in conversion for the oxidation of thioanisole after recycling three times (Table 1, entries 3–5). Furthermore, photoluminescent analysis of the supernatant showed no sign of leaching of the Ru complexes into the solution (Figure S6, Supporting Information). This was further supported by the absence of Ru complexes in the supernatants of the Ru-CMs-catalyzed reaction mixtures, as determined by ICP-MS. Upon use of the Ru-NCMs as photocatalysts, high reactivity for the oxidation of thioanisole was observed; a conversion

of 98% was found, which is comparable to that obtained with the Ru-CMs. However, the Ru-NCMs catalysts did not survive the reaction conditions, and they could not be collected by ultrafiltration after a reaction time of 24 h. This was also proved by DLS measurements. As shown in Figure S7 (Supporting Information), although the Ru-NCMs with a diameter of 177 nm as determined by DLS (Figure S7a, Supporting Information) are stable in H₂O, the micelles collapse in the presence of a mixture of methanol and thioanisole, and no micelle particles were detected by DLS (Figure S7b, Supporting Information). The poor stability of the Ru-NCMs limits their use as heterogeneous photocatalysts. Therefore, the cross-linked core in the Ru-CMs provides extra shielding against metal leaching and catalyst poisoning, which benefit catalyst recovery and recycling.

A number of control experiments were performed to demonstrate the heterogeneous and photocatalytic nature of the reactions. Reactions performed in the dark and those performed under light in the absence of the Ru-CMs showed no conversion of thioanisole into methyl phenyl sulfoxide (Table 1, entries 12 and 13), and only 6% of thioanisole was converted if the reaction was performed under a protected atmosphere of N₂ (Table 1, entry 14). These results indicate that light, the catalyst, and oxygen are essential for this reaction. In addition, a crossover experiment was performed to prove the heterogeneity of the Ru-CMs catalysts. Thioanisole was used in the CMs-catalyzed reaction, and 99% conversion was achieved after 24 h. The Ru-CMs were then removed by ultrafiltration, and another substrate, methyl *p*-tolyl sulfide, was added to the supernatant solution. After the solution was stirred under light for 24 h, no conversion was observed for the second substrate. This proved that the supernatant of the Ru-CMs reaction mixture is inactive in photocatalysis and supports the heterogeneous nature of the Ru-CMs photocatalysts.

Conclusions

In summary, a Ru catalyst was successfully integrated into nanoscale block copolymer MPEG-PLys micelles. To stabilize the micelles used as nanoreactors, glutaraldehyde was added to cross-link the core of the micelles. Stable MPEG-PLys micelles loaded with the Ru catalyst were obtained and were readily dispersed into normal solvents such as water, methanol, and THF. The Ru-CMs were shown to be highly active, recyclable, and reusable heterogeneous photocatalysts in the oxidation of sulfides. This work highlights the potential of using cross-linked micelles as a platform to develop highly efficient heterogeneous photocatalysts for a number of important organic transformations.

Experimental Section

Materials and General Measurements

All reagents were purchased from commercial sources and used without further treatment, unless indicated otherwise. ^1H NMR spectra were recorded at 300 MHz with tetramethylsilane as an internal standard at 25 °C with a Bruker AV 300M spectrometer. The morphologies of the micelles were measured by scanning electron microscopy (SEM, model JEOL JXA-840). Size distribution of the micelles was determined by DLS with a vertically polarized He–Ne laser (DAWNEOS, Wyatt Technology, USA). Inductively coupled plasma mass spectrometry (ICP-MS, X series II, ThermoScientific, USA) was used for the quantitative determination of trace levels of ruthenium. Fluorescence emission spectra were recorded with a LS-55 fluorophotometer. IR spectra were recorded with a Vertex 70 FTIR spectrophotometer by using KBr pellets. A YM-3 ultrafiltration apparatus (cut-off $M_w=30$ kDa, Millipore Co., Bedford, MA, USA) was used to recover the Ru-CMs in the recycling experiment.

Synthesis of the Ru-CMs

Monomethoxy[poly(ethylene glycol)]-*block*-poly[ϵ -(benzyloxycarbonyl)-L-lysine] [MPEG-PLys(Z)] and monomethoxy[poly(ethylene glycol)]-*block*-poly(L-lysine) (MPEG-PLys) were synthesized according to previous reports.^[19] The molecular weights of MPEG and PLys(Z) were determined by ^1H NMR spectroscopy to be 2000 and 3336 Da, respectively (Figure S8, Supporting Information). The [(bpy)₂Ru(fmbpy)](PF₆)₂ complex was prepared by the reaction of fmbpy with Ru(bpy)₂Cl₂ at 90 °C overnight according to literature methods.^[20] The structure was confirmed by ^1H NMR spectroscopy (Figure S9, Supporting Information), which was consistent with the literature. Typically, [(bpy)₂Ru(fmbpy)](PF₆)₂ (10 mg, 0.011 mmol) was added to a solution of MPEG-PLys (0.2 g, 0.69 mmol amino groups) in water/THF (1:1 v/v, 20 mL), and the mixture was then stirred at room temperature for 12 h. The Ru complex was partially linked on the lysine units of MPEG-PLys through covalent bonds through a Schiff base reaction. Then, glutaraldehyde (67 mg, 0.67 mmol) was added to the reaction mixture to cross-link the remaining amino groups on the lysine block. After stirring overnight, the mixture was dialyzed in water for 12 h (cut-off $M_w=3500$ Da) to remove any impurities and small molecules. The lyophilized powders of the cross-linked micelles loaded with Ru complexes (Ru-CMs) were obtained after freeze drying. The Ru content of the Ru-CMs was determined by ICP-MS to be 0.67 wt %, and therefore, it was concluded that the weight percent of the Ru complex in the Ru-CMs was 6.0 %.

Synthesis of the Ru-NCMs

[(bpy)₂Ru(fmbpy)](PF₆)₂ (35 mg, 0.039 mmol) was added to a solution of MPEG-PLys(Z) (0.2 g, 0.039 mmol amino groups) in water/THF (1:1 v/v, 20 mL; see Scheme 1). The mixture was stirred at room temperature for 12 h and then dialyzed for 12 h (cut-off $M_w=3500$ Da). The lyophilized powders of the Ru-NCMs were obtained after freeze drying. The Ru content of the Ru-NCMs was determined by ICP-MS to be 1.6 wt %, by which the weight percent of Ru complex in the Ru-NCMs was calculated to be 14.3 %.

Procedure for the Photo-oxidation of Sulfides

Oxidation of thioanisole as an example: A 10 mL vial equipped with a magnetic stir bar was charged with the Ru-CMs (10 mg, 0.66 μmol , 0.001 equiv.), thioanisole (62 μL , 0.5 mmol, 1.0 equiv.), and methanol (0.5 mL). A 24 W household fluorescent light bulb with a highpass filter ($\lambda=395$ nm) was used as the visible-light source. The reaction mixture was stirred at room temperature in air at a distance of approximately 5 cm from the lamp (the irradiance was ≈ 17.5 W m^{-2} for the distance). After 24 h, the reaction was complete, because of its nanoscale size, and the Ru-CMs could be recovered easily by passing the reaction solution through an ultrafiltration membrane with a molecular weight cutoff of 30000 Da. The ^1H NMR spectrum of the reaction mixture was recorded, and the integrated area ratio between the signals of the substrate and product was used to calculate the conversion yields.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 21201159, 61176016, and 21104075), the China Postdoctoral Science Foundation Grant (No. 2012M510892), the Science and Technology Department of Jilin Province (No. 20121801), and Returnee Startup Fund of Jilin is gratefully acknowledged. Z.S. thanks the support of the “Hundred Talent Program” of the Chinese Academy of Sciences (CAS) and the Innovation and Entrepreneurship Program of Jilin. Z.X. thanks the support of the Changchun Institute of Applied Chemistry (CIAC) through a startup fund.

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Received: May 15, 2013
Published online: August 12, 2013