

# Synthesis of cross-linked polymers *via* multi-component Passerini reaction and their application as efficient photocatalysts†

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One-step synthesis of cross-linked polymers containing Ru complexes (Ru-CPs) is demonstrated *via* multi-component Passerini reaction. Ru-CPs were shown to be highly effective and recyclable heterogeneous photocatalysts for oxidation of thioanisole and benzyl amine.

The development of photocatalysts for organic reactions driven by visible light is gaining increasing 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.<sup>1–5</sup> Metal complexes such as [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine) and organic dyes have been used as photocatalysts for a number of organic transformations.<sup>6,7</sup> These photocatalysts display high catalytic activity and selectivity for many organic reactions as a result of the homogeneous reaction environment. Like other precious metal catalyzed reactions, it is highly desirable to develop recyclable heterogeneous photocatalytic systems.<sup>8</sup> The reuse of such heterogeneous photocatalyst 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.

Cross-linked polymers (CPs) represent a new class of robust and porous materials and have shown great promise in gas storage and chemical sensing.<sup>9–14</sup> Our previous work has demonstrated that CPs could serve as a platform for incorporating molecular catalytic modules into stable and reusable heterogeneous catalyst systems.<sup>15,16</sup> However, synthesis of CPs

usually needs harsh reaction conditions, like high temperature and pressure, or even a large amount of catalysts.<sup>17,18</sup> Therefore, developing of simple and mild reactions for preparing CPs is still a big challenge in this field.

Passerini three-component reaction could combine isocyanides, aldehydes, and carboxylic acids into the ester and amide linkages *via* an atom-economic way. This reaction has been employed to synthesize diverse monomers and functional polymers due to the mild conditions without catalysts and tolerance to many functional groups.<sup>19–22</sup> For example, Li *et al.* used this reaction to make various linear functional poly(ester-amide).<sup>23–26</sup> Up to now, no report using Passerini reaction to make branched or cross-linked polymers was found. In this work, we successfully incorporated Ru complexes into CPs simply through multi-component Passerini reaction. The resulting Ru-CPs are highly stable and exhibit a high conversion rate and selectivity that are comparable to those of homogeneous counterparts in catalyzing the visible-light-driven oxidation of sulfides and benzyl amine. Moreover, the Ru-CPs photocatalysts can be readily recovered by filtration and reused without a decrease in catalytic efficiency.

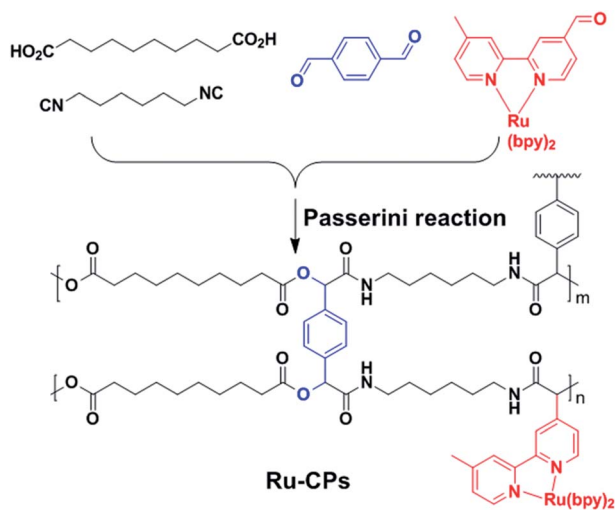
The synthetic route to Ru-CPs is shown in Scheme 1. The [(bpy)<sub>2</sub>Ru(fmbpy)] (PF<sub>6</sub>)<sub>2</sub> complex was prepared by the reaction of formyl-5'-methyl-2,2'-bipyridine (fmbpy) with Ru(bpy)<sub>2</sub>Cl<sub>2</sub> at 90 °C overnight according to literature methods.<sup>27,28</sup> Copolymerization of the [(bpy)<sub>2</sub>Ru(fmbpy)] (PF<sub>6</sub>)<sub>2</sub>, 1,6-di-isocyanohexane, sebacic acid and terephthalaldehyde was achieved through Passerini reaction in dichloromethane at room temperature for 4 days (ESI†). The resulting yellow solids were washed with various solvents to afford the Ru-CPs in 90% yield. The Ru-CPs were characterized by thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry (ICP-MS), infrared spectroscopy (IR), transmission electron microscopy (TEM), and solid-state <sup>13</sup>C cross polarization/magic angle spinning nuclear magnetic resonance (CP/MAS/NMR) spectroscopy. A control experiment was run in the absence of Ru complexes to afford the cross-linked polymers (CPs) without catalytic modules.

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Scheme 1 Synthesis of Ru-CPs.

The morphology of the Ru-CPs was examined by TEM. As shown in Fig. 1a and b, particles on the order of several micrometers in size displayed rather rough surfaces and appeared to be the aggregates of much smaller particles with dimensions of around 60 nm. CP/MAS/NMR spectroscopy in Fig. 1c gave all the carbon signals from 20 to 180 ppm. For example, the signals from 120 to 145 ppm and at 75 ppm are assigned to the  $^{13}\text{C}$  atoms of the phenyl and methine, respectively. More important, the signals for carbon atoms of carbonyl appeared around 175 ppm, indicating that the cross-coupling reaction had happened. The absence of the carbon-hydrogen

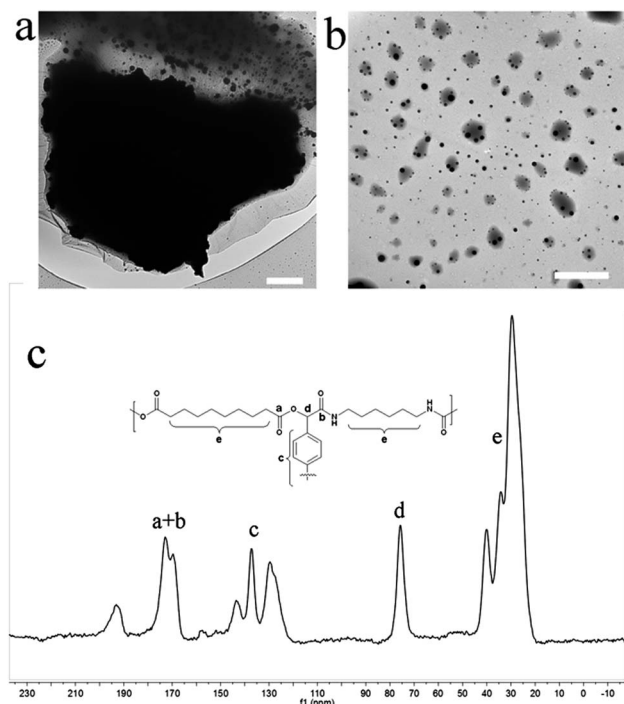


Fig. 1 TEM image (a) and (b), scale bars are 2  $\mu\text{m}$ ; and the solid-state  $^{13}\text{C}$  NMR spectrum (c) of Ru-CPs.

stretching peak of the  $-\text{CHO}$  around 2820 and 2720  $\text{cm}^{-1}$  in the IR spectra of the Ru-CPs and CPs suggested that most of the aldehyde groups in the starting materials have been consumed in the cross-linked polymers, and a high degree of polymerization was achieved (Fig. 2a).

The Ru-CPs are insoluble in water and all of the organic solvents we tested. Both Ru-CPs and CPs are thermal stable in air up to 300  $^{\circ}\text{C}$ , as revealed by TGA (Fig. 2b). Ru catalyst loading for Ru-CPs was determined by ICP-MS to be 3.9 wt%. As shown in Fig. S1,<sup>†</sup> there is no  $\text{N}_2$  uptake for Ru-CPs, indicating the nonporous nature. The UV-Vis spectra of Ru-CPs suspension of methanol is shown in Fig. 2c, a typical absorbance band of Ru complexes was observed at 452 nm, indicating that the catalytic Ru complexes were incorporated into the polymers.

With the Ru complexes covalently integrated into the cross-linked polymers, we believed Ru-CPs could act as solid-state photosensitizer by using the  $^3\text{MLST}$  states of the Ru complexes. Fluorescence measurements were performed on a suspension of the Ru-CPs in methanol. As shown in Fig. 2d (red solid line), one broad band centered at 603 nm was observed which is originated from  $^3\text{MLST}$  to MS transitions, which could be quenched by oxygen. A quenching experiment was carried out to confirm that the  $^3\text{MLST}$  state of the phosphors in the Ru-CPs can be quenched by oxygen. As shown in Fig. 2d, the intensity of phosphorescence increased after degassing using nitrogen for 5 min. The quenching results suggested that good photocatalytic performance of Ru-CPs should be expected.

Catalytic activities of the Ru-CPs were evaluated with thioanisole as the substrate and methanol as the solvent. The reaction was carried out in the presence of air with a 24 W household fluorescent lamp as the visible light source. The concentration of the substrates was 12.4% (v/v). The molar ratio of the catalyst (Ru) to substrates was 0.001. The reaction was stopped after 24 h by filtering off the Ru-CPs catalyst, and then the precipitate was washed with methanol three times and dried under vacuum. Conversions of the thioanisole were determined

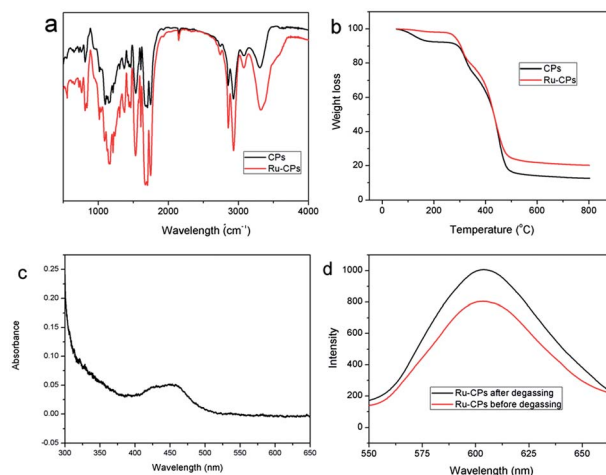
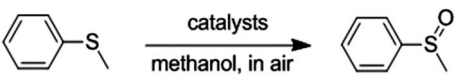


Fig. 2 Characterization of Ru-CPs and CPs: (a) IR, (b) TGA, (c) UV-Vis, (d) emission spectra. The Ru-CPs emission spectrum was collected when excited at 452 nm. The degassing was done using nitrogen for 5 min.

Table 1 Photocatalytic oxidation of sulfides<sup>a</sup>


Entry	Catalyst	Substrate	Conversion <sup>b</sup> (%)
1	Ru(bpy) <sub>3</sub> <sup>2+</sup>	Thioanisole	92
2	Ru-CPs	Thioanisole	92
3	Ru-CPs, reuse 1	Thioanisole	91
4	Ru-CPs, reuse 2	Thioanisole	92
5	Ru-CPs, reuse 3	Thioanisole	85
6	CPs	Thioanisole	<5
7	Ru-CPs	Phenyl ethyl sulfide	55
8	Ru(bpy) <sub>3</sub> <sup>2+</sup>	Phenyl ethyl sulfide	56
9	Ru-CPs	Methyl <i>p</i> -tolyl sulfide	90
10	Ru(bpy) <sub>3</sub> <sup>2+</sup>	Methyl <i>p</i> -tolyl sulfide	92

<sup>a</sup> All of the reactions were run at room temperature for 24 h.<sup>b</sup> Conversions were determined by <sup>1</sup>H 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 (Fig. S2†).<sup>29</sup>

As shown in Table 1, the Ru-CPs are highly effective photocatalysts for the oxidation of thioanisole, as a conversion of 92% was obtained. No sulfone was detected by <sup>1</sup>H NMR spectroscopy, which demonstrates the high degree of selectivity of this reaction. The high conversion and selectivity are comparable to those obtained with the use of their homogeneous counterparts Ru(bpy)<sub>3</sub><sup>2+</sup>. We also examined the scope of the substrates for the oxidation reaction using Ru-CPs. Several sulfides were efficiently oxidized under ambient condition, and the corresponding sulfoxides were produced with high conversions. We studied the recyclability and reusability of the Ru-CPs catalyst. Ru-CPs could be readily recovered from the reaction mixtures *via* simple filtration. The recovered Ru-CPs showed no decrease of conversion for oxidation of thioanisole after recycling three times (Table 1, entry 3–5). Furthermore, UV-Vis spectra of the supernatant showed no characteristic sign of Ru complexes leaching into the solution. This result supports the heterogeneous nature of the Ru-CPs photocatalysts.

We have also demonstrated the applicability of the Ru-CPs photocatalysts in oxidation of benzyl amine in chloroform. Oxidation of benzyl amine under visible light using homogeneous photocatalysts had been reported.<sup>30,31</sup> Here, we used this reaction to study the versatility of Ru-CPs in photocatalysis. As show in Fig. 3, Ru-CPs efficiently catalyzed the oxidation of

benzyl amine in chloroform with 90% conversion (Fig. S3†), which showed similar catalytic activity with Ru(bpy)<sub>3</sub><sup>2+</sup>. We also showed that Ru-CPs could be recovered and reused for oxidation of benzyl amine without drop in the conversion. These results indicate the generality of the phosphorescent Ru-CPs in catalyzing photodriven organic transformations.

In summary, Ru complexes have been integrated into cross-linked polymers *via* multi-component Passerini reaction. This facile reaction is convenient for the synthesis of various functional polymeric materials. The formed cross-linked polymeric materials are stable in various solvents and were shown to be highly active and recyclable heterogeneous photocatalyst in oxidation of thioanisole and benzyl amine. This work highlights the potential of using multi-component Passerini reaction as a mild method for developing highly efficient heterogeneous photocatalyst for a number of organic transformations.

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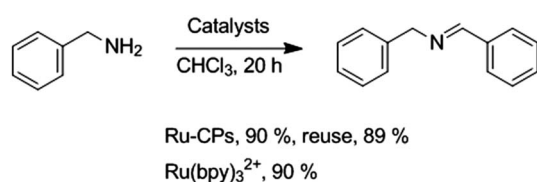


Fig. 3 Ru-CPs catalyzed oxidation of benzyl amine.

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