



# Recyclable alkylated Ru(bpy)<sub>3</sub><sup>2+</sup> complex as a visible-light photoredox catalyst for perfluoroalkylation

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## ABSTRACT

A recyclable Ruthenium tris [4,4'-bis (dinonylmethyl)-2,2'-bipyridine] (Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup>) photocatalyst (PC) was synthesized. Hexane-phase-selective solubility allowed its simple and efficient separation from reaction products via solvent extraction. The excellent catalytic activity and recoverability were demonstrated in batch and flow perfluoroalkylation reactions of coumarin under visible-light irradiation. High reaction rates and easy reusability of the catalyst make this approach attractive for large-scale applications.

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## 1. Introduction

Visible light can serve as an attractive, sustainable, non-toxic, easy to use and universally available energy source. Photocatalysis involving visible light to trigger reactions is an alternative type of catalysis and a variety of photoredox catalysts have been used for a broad range of synthetic transformations including trifluoromethylation of arenes and heteroarenes, which are the fundamental building blocks of many top-selling pharmaceuticals and agrochemicals.<sup>1</sup> MacMillan reported on a strategy for the direct trifluoromethylation of unactivated arenes and heteroarenes using a Ru complex photocatalyst (PC) and a household light bulb.<sup>2–4</sup> Following this report, more intensive research on visible light photocatalyzed trifluoromethylation has been pursued in recent years. In 2015, Stephenson<sup>5</sup> reported a strategy for the use of trifluoroacetic anhydride in a scalable and operationally simple trifluoromethylation reaction using pyridine *N*-oxide, via photoredox catalysis, to realize facile decarboxylation to the CF<sub>3</sub> radical.

Several transition-metal complexes such as [Ru(phen)]<sub>3</sub><sup>2+</sup>, [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, Ir(I) complexes, [Ir(ppy)<sub>2</sub>(dtbpy)]<sup>+</sup>, and neutral *fac*-Ir(ppy)<sub>3</sub> are the most versatile PC for a broad range of reactions owing to their long excited state lifetime and good chemical

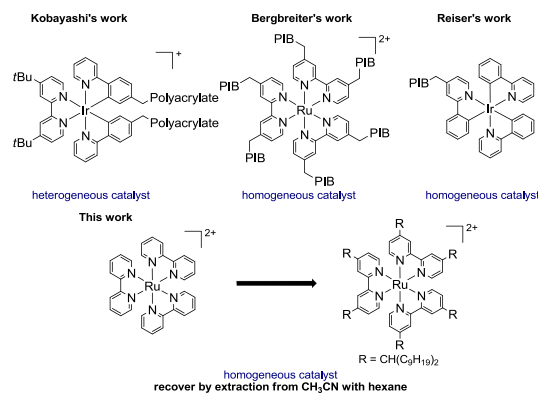
stability.<sup>6</sup> Unfortunately, large-scale applications in industrial area with these Ru or Ir complexes PCs are currently limited.<sup>7</sup> Issues including catalyst cost, catalyst toxicity or contamination, make catalyst recycling desirable. Hence, chemists have focused on the modification of PC ligands (Scheme 1). In 2014, Kobayashi<sup>8</sup> reported an Ir-based heterogeneous complex immobilized by polyacrylate, which was used to catalyze the aerobic phosphorylation of *N*-aryl tetrahydroisoquinolines under visible light. Bergbreiter separately carried out the polymeric reaction, oxidative C–C bond cleavage of aldehydes and [2 + 2] cycloaddition of *bis*(enone)s in 2013<sup>9a</sup> and 2016<sup>9b</sup> catalyzed by polyisobutylene (PIB)-polymer-tagged Ru complexes, which could be recycled by extraction with heptane.

A common problem encountered with the mentioned heterogeneous catalysts is poor mass transport. Moreover, heterogeneous supported PCs were impenetrable by visible light, which greatly reduces the quantum yield for a given reaction. In 2016, Reiser<sup>7</sup> developed a (PIB-polymer-tagged) *fac*-Ir(ppy)<sub>3</sub> PC, which catalyzed deiodination, deiodination/cyclization, and *E/Z* isomerization, and showed high activity due to its homogeneous nature in solution. However, since the molecular weight distribution of (PIB-polymer-tagged) *fac*-Ir(ppy)<sub>3</sub>, solubility limitations (activity) and catalyst leaching problems occurred. We aimed to develop a recyclable and homogeneous Ru complex PC with an accurate structure. Our initial strategy was to design a long alkyl-chain-bound bipyridine Ru complex as a phase-selectively soluble homogeneous PC that could be extracted by hexane and reused.

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**Scheme 1.** Reported recoverable Ru and Ir complex PCs immobilized by polymers.

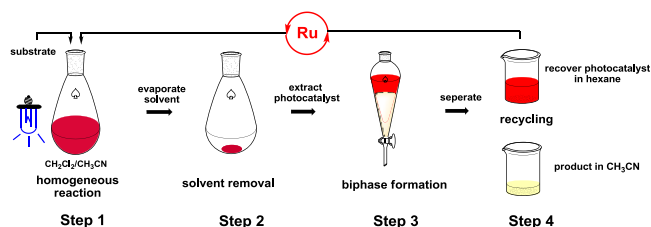
With particular interest in photochemistry and fluorine chemistry, we describe herein an alkyl-bound bipyridine Ru complex, which serves as a recoverable, reusable and hexane-soluble PC. This PC showed good catalytic activity for the perfluoroalkylation of coumarin under visible light, in the presence of trifluoroacetic and pentafluoropropionic anhydride as the CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub> sources, respectively. The reaction proceeded on a range of substrates and had been demonstrated on a significant scale in both batch and flow reactor.

## 2. Results and discussion

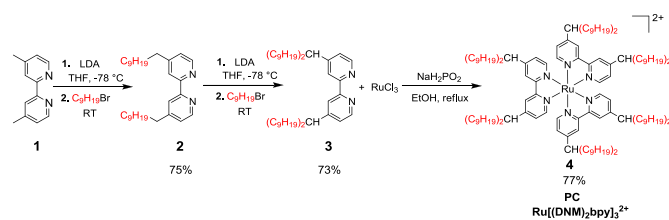
As shown in **Scheme 2**, the substrate for the photochemical reaction and the Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> PC were dissolved in an CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent to form a homogeneous solution (**step 1**). After the completion of reaction, the solvent was removed by vacuum evaporation (**step 2**). Then, two immiscible solvents, hexane and CH<sub>3</sub>CN, were added to dissolve the residue, leading to organic biphasic formation. The less polar PC was extracted by hexane based on the huge solubility gap between the nonpolar and polar solvents (**step 3**). The recovered PC in hexane could be separated and reused for use in the next reaction (**step 4**).

The synthesis of the Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> PC is shown in **Scheme 3**. Commercially available 4,4'-dimethyl-2,2'-dipyridine (**1**) first reacted with 1-bromononane and converted to the alkyl-bound bipyridine ligand, 4,4'-bis (dinonylmethyl)-2,2'-bipyridine, which was then allowed to react with RuCl<sub>3</sub> to generate the alkyl-bound bipyridine Ru complex (**4**) (for detailed synthetic procedures, see experimental section and **Supplementary Information**).

To demonstrate the feasibility of the phase-selectively soluble homogeneous PC, trifluoromethylation of coumarin catalyzed by Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> (**4**) was applied as the model reaction (**Table 1**). The reaction conditions were optimized for the trifluoromethylation of coumarin with trifluoroacetic anhydride/pyridine *N*-oxide under irradiation from a blue light emitting diode (LED) for 12 h. When using 1 mol% traditional Ru(bpy)<sub>3</sub>Cl<sub>2</sub> PC and



**Scheme 2.** Recoverable alkyl-bound Ru complex photocatalyst and recovery process.



**Scheme 3.** Synthesis of Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup>.

**Table 1**

Optimization of the trifluoromethylation reaction conditions<sup>a</sup>.

Entry <sup>a</sup>	Photocatalyst (PC)	Solvent	7a	Time	Yield (%)
1	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	12	63	
2	Ru[(DNM) <sub>2</sub> bpy] <sub>3</sub> <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (5/5)	12	55	
3	Ru[(DNM) <sub>2</sub> bpy] <sub>3</sub> <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (5/5)	24	66	
4	Ru[(DNM) <sub>2</sub> bpy] <sub>3</sub> <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (5/5)	36	64	
5 <sup>b</sup>	Ru[(DNM) <sub>2</sub> bpy] <sub>3</sub> <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (5/5)	24	48	

<sup>a</sup> Reaction conditions: coumarin (0.4 mmol), PC (1 mol %), pyridine *N*-oxide (0.82 mmol), trifluoroacetic anhydride (0.8 mmol), and solvent (1 mL), irradiation with 15 W blue LED at room temperature; isolated yields.

<sup>b</sup> PC (0.5 mol %).

CH<sub>3</sub>CN solvent, 3-trifluoromethyl coumarin (**7a**) was obtained in 63% yield (**entry 1**). Next Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> (**4**) was used as PC. Considering the poor solubility of Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> in CH<sub>3</sub>CN, we chose a CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent system. After 12 h irradiation, **7a** was obtained in a slightly low yield of 55% (**entry 2**). Increasing the reaction time to 24 h increased the yield of **7a** to 66% (**entry 3**), which was comparable to that obtained when using the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> PC. Upon further extension of the reaction time to 36 h, the product yield remained unchanged. Finally, when reducing the amount of catalyst to 0.5 mol%, the yield of **7a** decreased to 48% (**entry 5**).

A recyclability test on the Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> PC in the trifluoromethylation of coumarin was further investigated (**Table 2**). After completion of the 1st run reaction, the CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent was evaporated under reduced pressure, and the residue was redissolved in CH<sub>3</sub>CN. The recycled Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> was extracted 5 times with hexane and collected for the next run. The product 3-trifluoromethyl coumarin (**7a**) remained in the CH<sub>3</sub>CN phase, which was desolventized by rotary evaporation and purified by silica gel column chromatography.

As shown in **Table 2**, a new trifluoromethyl reaction (2nd run) was then performed using fresh reactants under the same conditions. The recycled Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> was collected and reused without significant loss of catalytic activity (yield 64%). After the 6th run, only a slight decrease in the yield (51%) of 3-trifluoromethyl coumarin (**7a**) was observed. The approximate yield (0.3%) of the residual **7a** in the hexane phase was determined

**Table 2**

Yields of 3-trifluoromethyl coumarin (**7a**) obtained using the Ru[(DNM)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup> <sup>a</sup>.

Run	1	2	3	4	5	6
Yield (%)	66	64	64	61	57	51

<sup>a</sup> Reaction conditions: coumarin (0.4 mmol), PC (1 mol %), pyridine *N*-oxide (0.82 mmol), anhydride (0.8 mmol), and CH<sub>3</sub>CN (0.5 mL), CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), irradiation with 15 W blue LED at room temperature; isolated yields.

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