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Highly Stable and Porous Cross-Linked Polymers for Efficient Photocatalysis

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S *Supporting Information*

ABSTRACT: Porous cross-linked polymers (PCPs) with phosphorescent $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ building blocks were obtained via octacarbonyldicobalt ($Co_2(CO)_8$)-catalyzed alkyne trimerization reactions. The resultant Ru- and Ir-PCPs exhibited high porosity with specific surface areas of 1348 and 1547 m^2/g, respectively. They are thermally stable at up to 350 °C in air and do not dissolve or decompose in all solvents tested, including concentrated hydrochloric acid. The photoactive PCPs were shown to be highly effective, recyclable, and reusable heterogeneous photocatalysts for aza-Henry reactions, α-arylation of bromomalonate, and oxyamination of an aldehyde, with catalytic activities comparable to those of the homogeneous $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ photocatalysts. This work highlights the potential of developing photoactive PCPs as highly stable, molecularly tunable, and recyclable and reusable heterogeneous photocatalysts for a variety of important organic transformations.

Organic transformations driven by visible light are gaining increasing interest from synthetic chemists because of their generally mild conditions for substrate activation, the ability to afford desired products without generating unwanted byproducts, and the potential to mediate thermodynamically uphill reactions by harvesting energy from the sunlight in these reactions.[1] Photocatalysts are often required in visible light driven organic reactions since the majority of organic substrates in these reactions do not readily absorb photons in the visible region. $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) is undoubtedly one of the most extensively studied photocatalysts since the pioneering work of Meyer and Whitten in the 1970s.[2] Taking advantage of the long lifetime of the ^{3}MLCT state of this Ru-based phosphor and its propensity to undergo redox quenching, a variety of new photocatalytic organic reactions, ranging from [2+2] cycloaddition to radical chemistry, have been developed recently.[3] Stephenson et al. and MacMillan et al. also reported the use of an Ir complex, $Ir(ppy)_2(dtbbpy)PF_6$ (ppy = 2-phenylpyridine; dtbbpy =4,4'-di-*tert*-butyl-2,2'-bipyridine), as a photoredox catalyst in tin-free dehalogenation, aza-Henry reactions, and α-trifluoromethylation of aldehydes.[4] Like other precious metal catalyzed reactions, it is highly desirable to develop recyclable and reusable heterogeneous photocatalytic systems based on the Ir and Ru phosphors. The ability to recover and reuse such heterogeneous photocatalysts can not only eliminate the contamination of organic products by trace amounts of heavy metals but also reduce processing and waste disposal costs in large-scale reactions.

Porous cross-linked polymers (PCPs), including crystalline covalent−organic frameworks, can be built from well-designed organic precursors and represent a new class of robust, nanoporous materials.[5] Like their porous metal−organic framework (MOF) counterparts,[6] PCPs have shown great promise in gas storage and separation and light harvesting.[7] Just like recently developed catalytic MOFs,[8] PCPs can serve as an ideal platform for incorporating molecular catalytic modules into highly stable, recyclable, and reusable heterogeneous catalyst systems by taking advantage of their permanent porosity and the ability to tune their compositions and properties at the molecular level.[9] PCPs are advantageous over MOFs as photocatalysts since many MOFs are constructed from metal connecting points with unfilled d orbitals which can readily quench the photoexcited states of the photocatalytic building units.[10] In this work, we report successful incorporation of the Ru and Ir phosphors into robust PCPs by cobalt carbonyl-mediated trimerization of the end alkyne groups on the monomers.[11] The resulting PCPs are highly active in catalyzing visible light driven aza-Henry reactions between nitromethane or nitroethane and tertiary aromatic amines, α-arylation of bromomalonate via intermolecular C−H functionalization, and oxyamination of an aldehyde with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). The PCP photocatalysts can be readily recycled and reused for these reactions without a decrease in catalytic efficiency.
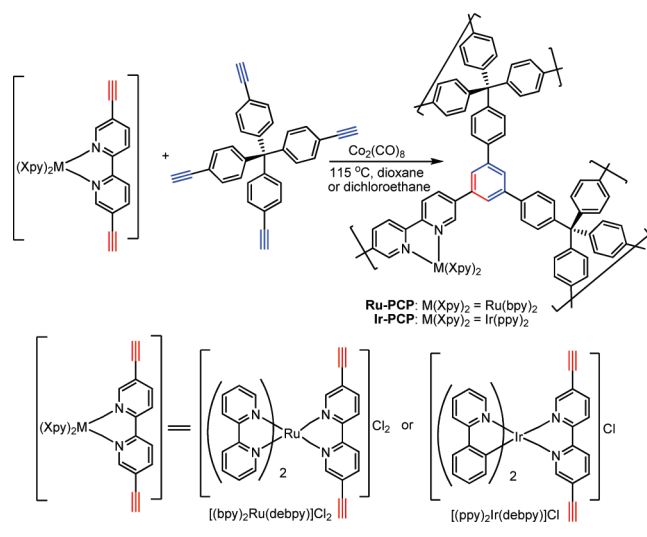
Phosphorescent Ir monomer $[(ppy)_2Ir(debpy)]Cl$ (debpy =5,5'-diethynyl-2,2'-bipyridine) and Ru monomer $[(bpy)_2Ru(debpy)]Cl_2$ were synthesized by allowing debpy to react with $[Ir(ppy)_2Cl_2]_2$ and $Ru(bpy)_2Cl_2$ at 90 °C overnight, respectively. Copolymerization of the monomer $[(ppy)_2Ir(debpy)]Cl$ or $[(bpy)_2Ru(debpy)]Cl_2$ with tetra(4-ethynylphenyl)methane was achieved through $Co_2(CO)_8$-mediated trimerization of the end alkyne groups of the monomers in dioxane or dichloroethane at 115 °C for 10 min (Scheme 1). The resulting brown solids were stirred in concentrated hydrochloric acid at room temperature for 2 h to remove all the Co species and then washed with various solvents to afford Ir-PCP and Ru-PCP in 97% yields. The Ir- and Ru-PCPs were characterized by thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry (ICP-MS), infrared spectroscopy (IR), nitrogen adsorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD).

Morphology of the PCPs was examined by SEM and TEM (Figure 1a,b). Particles on the order of several micrometers in size displayed rather rough surfaces and appear to be aggregates of much smaller particles with dimensions of around 10 nm. The

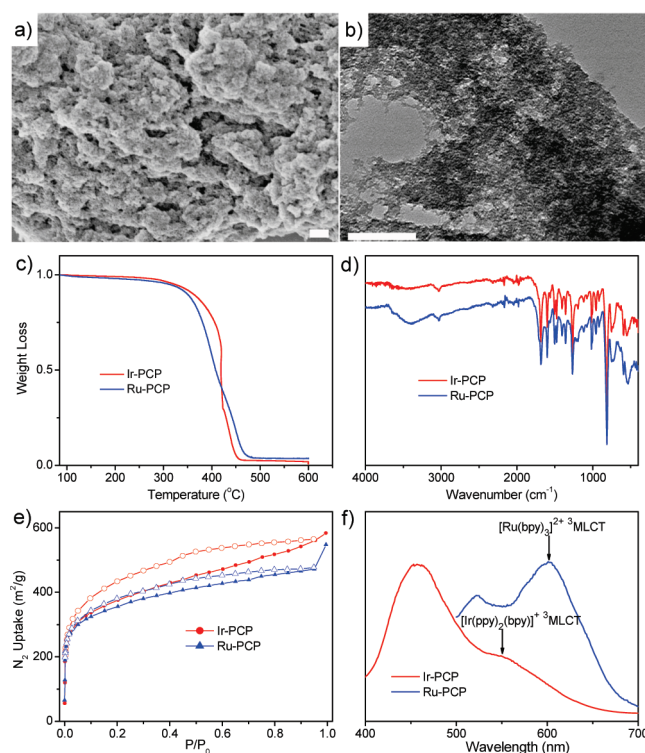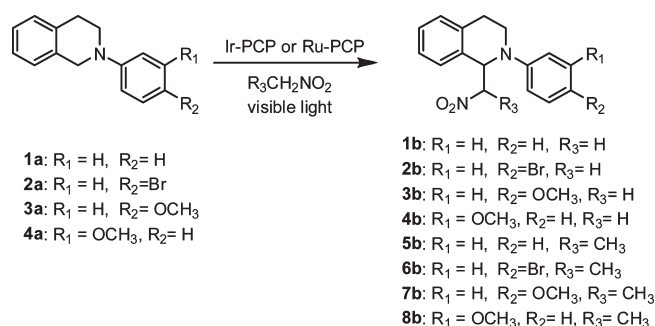**Scheme 1. Synthesis of Ir-PCP and Ru-PCP**

Figure 1. Characterization of Ir-PCP and Ru-PCP: (a) SEM and (b) TEM images of Ir-PCP. The scale bars represent 200 nm. (c) TGA, (d) FT-IR, (e) nitrogen adsorption isotherms at 77 K, and (f) uncorrected emission spectra. The Ir-PCP emission spectrum (red line) was taken when excited at 380 nm. The broad emission around 458.5 nm comes from fluorescence of the framework. The Ru-PCP emission spectrum (blue line) was taken when excited at 450 nm. The broad emission around 522.5 nm comes from fluorescence of the framework.

PXRD patterns indicated that the Ir-PCP and Ru-PCP are amorphous in nature (Figure S1, Supporting Information (SI)).

The Ir-PCP and Ru-PCP are insoluble in water, concentrated hydrochloric acid and all of the organic solvents tested. The PCPs are stable in air up to 350 °C, as revealed by TGA (Figure 1c). The Ir and Ru catalyst loadings for Ir-PCP and Ru-PCP were determined by ICP-MS to be 4.5 and 2.2 wt %, respectively. The absence of the carbon−hydrogen stretching peak of the C≡C—H group around 3300 cm^{-1} in the IR spectra of the Ir-PCP and Ru-PCP suggested that most of the alkyne groups in the starting materials have been consumed to form benzene rings in the PCPs, consistent with a high degree of polymerization (Figure 1d).

Porosity of the PCPs was revealed by nitrogen sorption measurements at 77 K. The PCPs exhibit large reversible adsorptions at low pressure ($P/P_0 < 0.1$) and hysteresis loops at higher pressure, suggesting the coexistence of micro- and mesopores in the framework (Figure 1e).[12,13] The BET surface areas were determined to be 1547 and 1348 m^2/g for Ir-PCP and Ru-PCP in the $P/P_0 = 0.03−0.2$ range, respectively. Both of the PCPs have wide pore size distributions, with the pore widths centering around 7.5, 11.0, 13.5, and 16.5 Å, as calculated by the nonlocal density functional theory method (NLDFT) (Figure S2, SI).

With the Ir/Ru-based phosphors covalently integrated into the skeletons, we hypothesized that the synthesized PCPs can act as solid-state photosensitizers by utilizing the ^{3}MLCT states of the Ir/Ru complexes. Phosphorescence measurements were performed on a stirred suspension of the PCPs in CH$_3$NO$_2$, showing peaks originating from ^{3}MLCT → GS transitions around 550 nm for the Ir-PCP and 602 nm for the Ru-PCP (Figure 1f). We intended to explore the utility of the Ir-PCP and Ru-PCP in catalyzing visible light driven organic reactions such as the aza-Henry reaction between nitromethane or nitroethane and aromatic tertiary amines. Before the catalysis test of the materials, a preliminary quenching experiment was carried out to confirm that the ^{3}MLCT state of the phosphors in the PCPs can be reductively quenched by the amine substrate, which is the very first step of the photocatalytic cycle of homogeneous aza-Henry reactions as proposed by Stephenson and co-workers.[4b] A Stern−Volmer plot for the Ru-PCP was obtained by plotting the intensity ratio I_0/I at 602 nm vs the amine concentration, leading

to a Stern−Volmer constant of 23 M^{-1}, which is comparable to that of the monomeric [(bpy)$_2$Ru(debpy)]Cl$_2$ complex (20 M^{-1}). This result indicates effective quenching of the ^{3}MLCT phosphorescence of the Ru-PCP by the amine. In the case of Ir-PCP, the quenching effect was also observed but could not be quantified spectroscopically owing to the interference of the framework fluorescence (Figure 1f). The quenching result suggested that good photocatalytic performance of the PCPs should be expected.

Catalytic activities of the Ir-PCP and Ru-PCP toward photocatalytic aza-Henry reaction were evaluated with tetrahydroisoquinoline (1a) as the amine substrate and CH$_3$NO$_2$ as solvent. The reaction was carried out in the presence of air with a common fluorescent lamp (26 W) as the light source. The reaction was stopped after 8 h by filtering off the PCP catalysts. Conversions of the reactions were determined by integrating the peaks of ^{1}H NMR spectra of the crude reaction mixtures (Supporting Information). As shown in Table 1 (entry 1), both the Ir- and Ru-PCPs are highly effective photocatalysts for the aza-Henry reaction between 1a and nitromethane, with >90% conversions. These conversions are comparable to those of the homogeneous counterparts. We have also explored the scope of substrates for this photocatalytic reaction (Table 1). The Ir- and Ru-PCPs catalyzed aza-Henry reactions between nitromethane and a variety of tertiary aromatic amines with different functional groups (Table 1, entries 1−4). The PCPs also catalyzed aza-Henry reactions between nitroethane and tertiary aromatic amines (Table 1, entries 5−8).

Table 1. Photocatalytic Aza-Henry Reactions[a]

1a: R₁ = H, R₂= H
2a: R₁ = H, R₂=Br
3a: R₁ = H, R₂= OCH₃
4a: R₁ = OCH₃, R₂=H

1b: R₁ = H, R₂=H, R₃= H
2b: R₁ = H, R₂=Br, R₃= H
3b: R₁ = H, R₂= OCH₃, R₃= H
4b: R₁ = OCH₃, R₂=H, R₃= H
5b: R₁ = H, R₂=H, R₃= CH₃
6b: R₁ = H, R₂=Br, R₃= CH₃
7b: R₁ = H, R₂= OCH₃, R₃= CH₃
8b: R₁ = OCH₃, R₂=H, R₃= CH₃

entry	amine substrate	product	Ir-M	Ir-PCP	Ru-M	Ru-PCP
1[c]	1a	1b	99	94	85	90
2[c]	2a	2b	99	97	84	87
3[c]	3a	3b	81	91	90	>99
4[c]	4a	4b	79	98	65	85
5[d]	1a	5b	94	94	81	84
6[d]	2a	6b	73	75	57	78
7[d]	3a	7b	86	97	62	95
8[d]	4a	8b	66	86	76	91

conv (%) with different catalysts[b]

[a] All the reactions were run at room temperature for 8 h with 1 mol % Ir-based catalyst or 0.2 mol % Ru-based catalyst. [b] Conversions were determined by integrating the ¹H NMR spectra. Ir-M and Ru-M are Ir monomer [((ppy)₂Ir(debpy)]Cl and Ru monomer [(bpy)₂Ru(debpy)]Cl₂, respectively. [c] With nitromethane as solvent. [d] With nitroethane as solvent.

Interestingly, most of the PCP-catalyzed aza-Henry reactions have higher conversions than those catalyzed by their homogeneous counterparts.

A number of control experiments were carried out to demonstrate the heterogeneous and photocatalytic nature of the reactions. The reaction of **1a** in the dark yielded negligible amounts of aza-Henry products (<5%, Table S1, SI), demonstrating the necessity of light in this reaction. On the other hand, the background reaction in the absence of the catalysts but in the presence of light showed only around 10% conversions after 8 h (Table S1), verifying that the PCPs played a catalytic role in the reactions. These observations are consistent with those for the homogeneous system reported by Stephenson and co-workers.[4b] In addition, a crossover experiment was carried out to prove the heterogeneity of the PCP catalyst. Substrate **1a** was used in the Ir-PCP-catalyzed aza-Henry reaction, and 94% conversion was achieved after 8 h. The PCP catalyst was then removed by filtering through Celite, and another substrate **3a** was added to the supernatant solution. After the solution was stirred under light for 8 h, only 12% conversion was observed for the second substrate (**3a**). This low conversion, comparable to that of the background reaction with visible light but without a photocatalyst, proved that the supernatant of the Ir-PCP reaction mixture is inactive in photocatalysis. This result supports the heterogeneous nature of the PCP photocatalysts.

We have examined recyclability and reusability of the PCP catalysts. Ir-PCP and Ru-PCP were readily recovered from the reaction mixtures via simple filtration. The recovered catalyst showed no deterioration of conversion for aza-Henry reactions after

Scheme 2. Ru-PCP-Catalyzed α-Arylation of Bromomalonate and Oxyamination of 3-Phenylpropanal[a]
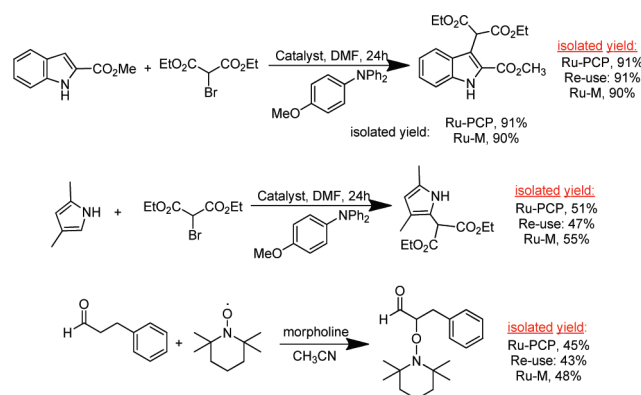
[a] The Ru-PCP catalyst was readily recovered and reused for these reactions.

recycling four times (Table S2, SI). Furthermore, UV−vis analysis of the supernatant showed no sign of Ir/Ru complex leaching into the solution. This is further supported by the absence of Ir or Ru in the supernatants of the PCP-catalyzed reaction mixtures by ICP-MS.

We have also demonstrated the applicability of the PCP photocatalysts in other visible light driven reactions. As shown in Scheme 2, Ru-PCP efficiently catalyzed the α-arylation of bromomalonate via direct intermolecular C−H functionalization[3e] as well as oxyamination of 3-phenylpropanal,[14] with isolated product yields comparable to those of the homogeneous control catalyst. We also showed that the Ru-PCP catalyst could be readily recovered and reused for all of these reactions with no or little drop in the product isolated yields (Scheme 2). These results illustrate the generality of the phosphorescent PCP materials in catalyzing photodriven organic transformations.

In conclusion, Ir and Ru phosphors have been successfully integrated into porous cross-linked polymers via cobalt-catalyzed alkyne trimerization. The resultant framework materials are stable in various solvents, including concentrated hydrochloric acid, and are thermally and oxidatively stable in air up to 350 °C. These phosphorescent Ir- and Ru-based PCPs were shown to be highly active, recyclable, and reusable heterogeneous photocatalysts in aza-Henry reactions of a variety of amine substrates. This work highlights the potential of using PCPs as a stable and molecularly tunable platform for developing highly efficient heterogeneous photocatalysts for a number of important organic transformations.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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