

Light-Harvesting Cross-Linked Polymers for Efficient Heterogeneous Photocatalysis

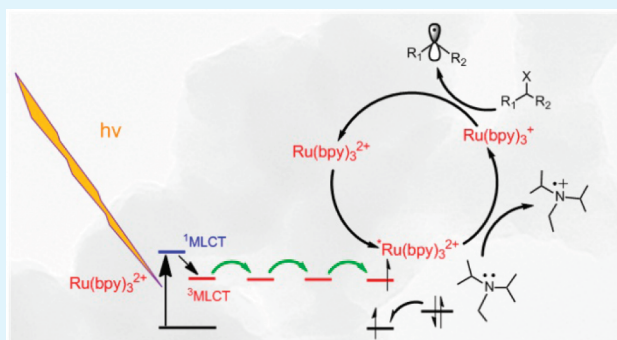
Cheng Wang,[†] Zhigang Xie,^{†,‡} Kathryn E. deKrafft, and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599, United States

Supporting Information

ABSTRACT: Nonporous, phosphorescent cross-linked polymers (**Ru-CP** and **Ir-CP**) were synthesized via Pd-catalyzed Sonogashira cross-coupling reactions between tetra(*p*-ethynylphenyl)methane and dibrominated $\text{Ru}(\text{bpy})_3^{2+}$ or $\text{Ir}(\text{ppy})_2(\text{bpy})^+$, respectively. The resultant particulate cross-linked polymer (CP) materials have very high catalyst loadings (76.3 wt % for **Ru-CP** and 71.6 wt % for **Ir-CP**), and are nonporous with negligibly small surface areas (2.9 m²/g for **Ru-CP** and 2.7 m²/g for **Ir-CP**). Despite their nonporous nature, the insoluble CP materials serve as highly active and recyclable heterogeneous photocatalysts for a range of organic transformations such as aza-Henry reaction, aerobic amine coupling, and dehalogenation of benzyl bromoacetate. An efficient light-harvesting mechanism, which involves collection of photons by exciting the ³MLCT states of the phosphors and migration of the excited states to the particle surface, is proposed to account for the very high catalytic activities of these nonporous CPs. Steady-state and time-resolved emission data, as well as the reduced catalytic activity of $\text{Os}(\text{bpy})_3^{2+}$ -doped **Ru-CPs** supports efficient excited state migration for the CP frameworks. This work uncovers a new strategy in designing highly efficient photocatalysts based on light-harvesting cross-linked polymers.

KEYWORDS: light-harvesting, cross-linked polymer, energy transfer, photocatalysis, excited-state migration, artificial photosynthesis



INTRODUCTION

The advancement of artificial photosynthesis heralds a promising and revolutionary approach toward green chemical transformations.¹ Several molecular chromophores, such as porphyrins and $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) have been created to absorb and convert solar energy to chemical potentials in molecular excited states or charge-separated pairs.² In parallel, many molecular systems have been developed to catalyze thermodynamically uphill reactions with the input of photo, chemical, or electrochemical energies, including water oxidation,³ proton reduction,⁴ CO_2 reduction,⁵ and general organic transformations.⁶ In order to achieve artificial photosynthesis, it is important to design molecular systems that can not only act as antenna for photon capture but also are able to transfer the energies to the reaction centers to drive desired chemical transformations.^{1b,c,2a,7} Natural photosynthesis takes advantage of a wired network of chromophores and functional centers to facilitate energy and electron transfer within the system, leading to efficient conversion of sunlight energy to chemical potential stored in reactive chemical bonds.^{1b,8} Chemists have created a variety of macromolecular and supramolecular systems, including arrays of porphyrins and other chromophores,⁹ linear polymers,¹⁰ dendrimers,¹¹ metal–organic frameworks,¹² bridged semiconducting nanoparticles,¹³ organogels and hybrid hydrogels,¹⁴ vesicles,¹⁵ and biomolecule-based assemblies,¹⁶ in order to mimic the energy and electron transfer processes in natural photosynthesis.

Efficient collection of photons in artificial systems can lead to the formation of charge-separated redox pairs or light-harvesting species such as singlet oxygen.¹⁷ However, few of the reported antenna systems can effectively use the harvested energy to drive productive chemical reactions.^{17d,18} We have recently become interested in designing multifunctional framework materials, including metal–organic frameworks and cross-linked polymers, as a potential platform to integrate light-harvesting and catalytic centers for solar energy utilization.^{12,19} Cross-linked polymers have recently emerged as a new class of highly stable functional solid-state materials that can be fine-tuned at the molecular level.²⁰ Because of their ease of functionalization and high chemical stability, cross-linked polymers have shown great promise in many applications, such as gas storage,^{19a} catalysis,^{19f,20} and light-harvesting.²¹ In this work, we synthesized nonporous cross-linked polymers based on tetra(*p*-ethynylphenyl)methane tetrahedral nodes and a stoichiometric amount of $[\text{Ru}(\text{bpy})_2(\text{dbbpy})]^{2+}$ (dbbpy is 5,5'-dibromo-2,2'-bipyridine) or $[\text{Ir}(\text{bpy})_2(\text{dbbpy})]^+$ linear linkers, with the diamondoid network as the ideal structure prototype. We discovered efficient core-to-surface excited state transport in cross-linked polymers (CPs) built from $[\text{Ru}(\text{bpy})_3]^{2+}$ - and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ -derived phosphors (ppy is 2-phenylpyridine).

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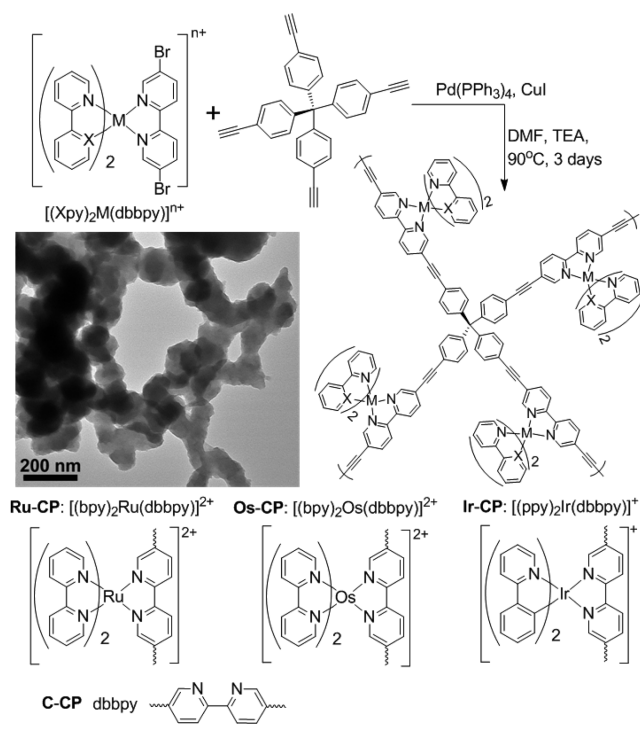
Importantly, the harvested energy can be used to drive chemical reactions on the polymer particle surface, leading to highly active heterogeneous photocatalysts.

RESULTS AND DISCUSSIONS

Cross-Linked Polymer Synthesis and Characterization.

The polymerization between the tetrahedral tetra(*p*-ethynylphenyl)methane and the linear dibromo compound, [Ru(bpy)₂(dbbpy)]²⁺ or Ir[(bpy)₂(dbbpy)]⁺, was realized through a Pd/CuI-catalyzed Sonogashira cross-coupling reaction (see Scheme 1). Based on the inductively coupled plasma mass

Scheme 1. Synthesis of Ru-CP, Os-CP, and Ir-CP (a TEM Image of Ru-CP is Also Shown)



spectrometry (ICP-MS) results, the resultant [Ru(bpy)₃]²⁺- and Ir[(bpy)₂(bpy)]⁺-based polymers (**Ru-CP** and **Ir-CP**) possess exceptionally high Ru and Ir catalyst loadings (76.3 and 71.6 wt %, respectively), which are very close to that of the stoichiometric polymer formulas (78.3 wt % for **Ru-CP** and 79.1 wt % for **Ir-CP**). These phosphor loadings are exceptionally high, when compared to recently reported [Ru(bpy)₃]²⁺- and Ir[(bpy)₂(bpy)]⁺-containing porous cross-linked polymers (2.2 and 4.5 wt %, respectively).^{19a}

Similar Sonogashira coupling reactions were recently used by Cooper et al. to synthesize conjugated microporous polymers with metallo-complexes in the backbones.^{19f} In their work, linear 1,4-dibromobenzene was added to the feed to achieve microporosity. It was found that increasing the amounts of the metallo-complexes drastically decreases the surface areas of the CPs, because of channel blocking by the bulky metallo-complexes. Since the **Ru-CP** and **Ir-CP** in our work contain stoichiometric amounts of the Ru and Ir complexes, they are nonporous with negligibly small BET surface areas of 2.9 m²/g and 2.7 m²/g, respectively (see Figure 1a).²² In comparison, the control polymer (**C-CP**) made by cross-coupling between

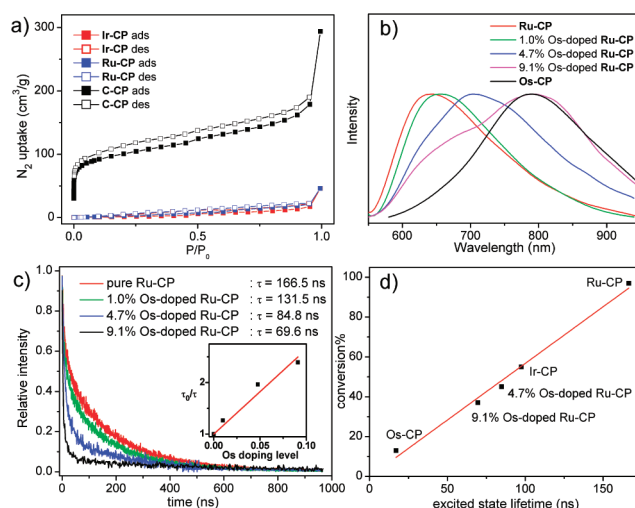


Figure 1. (a) Nitrogen sorption isotherms of **Ru-CP** (blue), **Ir-CP** (red), and **C-CP** (black) at 77 K. (b) Smoothed steady-state emission spectra of **Ru-CP** (red), 1.0 mol % Os-doped **Ru-CP** (green), 4.7 mol % Os-doped **Ru-CP** (blue), 9.1 mol % Os-doped **Ru-CP** (purple) and pure **Os-CP** (black); all of the spectra were taken while excited at 485 nm. (c) Decay transients measured at 630 nm (with 445-nm excitation) for **Ru-CP** (red), 1.0 mol % Os-doped **Ru-CP** (green), 4.7 mol % Os-doped **Ru-CP** (blue), and 9.1 mol % Os-doped **Ru-CP** (black); inset shows a plot of τ_0/τ vs Os doping levels. The emission decays in panel (c) were fit to the biexponential expression $A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The reported lifetime τ is the weighted lifetime $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. (d) Conversion percentage for the reactions between **1a** and nitromethane catalyzed by different CP catalysts, versus the phosphorescent lifetimes of these catalysts. Reactions were run at room temperature (rt) for 8 h, with 0.2 mol % catalyst loadings, ~5 cm in front of a 26-W fluorescent lamp.

dbbpy and tetra(*p*-ethynylphenyl)methane gave a BET surface area of 333.6 m²/g (Figure 1a).

Transmission electron microscopy (TEM) images (see Scheme 1 and Figure S1 in the Supporting Information) showed that **Ru-CP** and **Ir-CP** are composed of interconnected nanoparticles with dimensions of 100–200 nm. The particles are stable up to 300 °C in air, as revealed by thermogravimetric analysis (TGA) (see Figure 2d). The cross-linked polymers are insoluble in water and all of the organic solvents tested. The high degree of polymerization is indicated by the IR spectra. The absence of the carbon–hydrogen stretching peak of the C≡C–H group at ~3300 cm⁻¹ suggested that most of the alkyne groups in the starting materials have been consumed in the coupling reaction (see Figure 2c).

Light Harvesting by Cross-Linked Polymers: Photon Capture and Excited-State Dynamics. With such nonporous cross-linked polymer nanoparticles that contain stoichiometric amounts of Ru and Ir dye molecules, we hypothesized that the nanoparticles can serve as light-harvesting antenna to collect energy and drive chemical reactions on the polymer surfaces. The phosphor molecules in the interior of the nonporous CP materials can readily absorb visible light to form ³MLCT excited states, which can efficiently migrate to the particle surface. Based on the molar extinction coefficient of **Ru-CP** at 485 nm (Figure 2a), 90% of the light can reach the interior chromophoric centers for a nanoparticle with a size of 100 nm (with only ~10% of the photons absorbed by the Ru(bpy)₃²⁺ at the particle surface). The surface Ru and Ir phosphor molecules, which can either be excited directly by

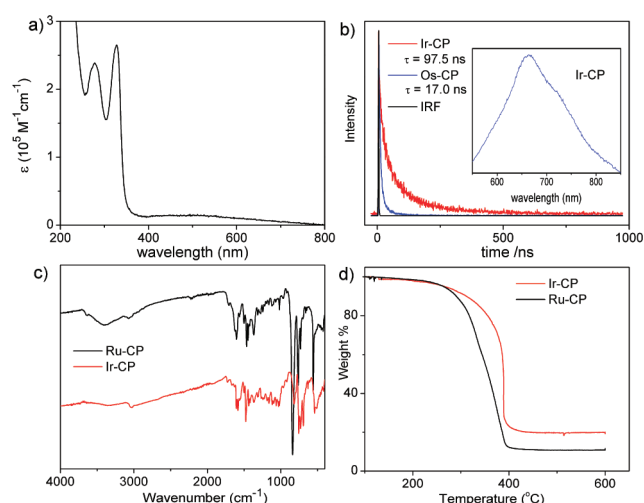


Figure 2. (a) UV-vis absorption spectrum of Ru-CP particles suspended in MeCN. (b) Decay transient measured at 650 nm for Ir-CP with excitation at 350 nm (red) and decay transient measured at 830 nm for Os-CP with excitation at 444.2 nm (blue). [IRF = Instrument Response Function for excitation at 444.2 nm (black).] The emission decay was fit to the biexponential expression $A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The reported lifetimes are the weighted lifetimes $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. Inset shows a steady-state emission spectrum of Ir-CP (excited at 440 nm). (c) FT-IR spectra of Ru-CP (black) and Ir-CP (red). (d) TGA curves of Ru-CP (black) and Ir-CP (red).

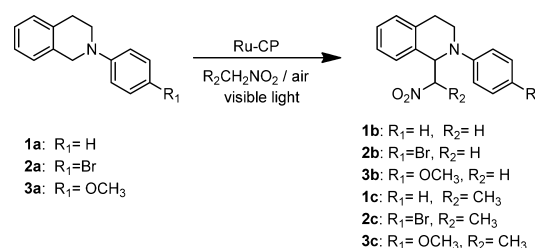
light or accept excited-state energy from the phosphors in the interior of the polymer particle, will undergo photoredox reactions and initiate a cascade of chemical transformations in a catalytic cycle. Such a core-to-surface excited-state transport process, followed by a redox catalytic reaction on the surface, renders all of the phosphors in the nonporous solid photoactive, akin to the light-harvesting processes in natural photosynthesis. A high chromophore concentration in the framework is essential for such effective light harvesting, since the probability of Dexter-type energy migration between adjacent chromophores decays exponentially with the increased distance between them.

To test the hypothesis of efficient excited state migration through the CP framework, we doped different amounts of $[\text{Os}(\text{bpy})_3]^{2+}$ entities into Ru-CP by copolymerization, and detected energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+*}$ to $[\text{Os}(\text{bpy})_3]^{2+}$ by luminescence measurements. If efficient energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+*}$ to $[\text{Os}(\text{bpy})_3]^{2+}$ can occur at relatively low $[\text{Os}(\text{bpy})_3]^{2+}$ loadings, the $[\text{Ru}(\text{bpy})_3]^{2+*}$ excited states must have hopped from site to site before reaching the $[\text{Os}(\text{bpy})_3]^{2+}$ traps. Steady-state luminescence measurements indicated a dramatic increase of the $[\text{Os}(\text{bpy})_3]^{2+}$ -based emission at ~ 800 nm as the Os doping level increased from 0 to 9.1 mol % (see Figure 1b). Deconvolution of the emission spectrum of the 9.1 mol % Os-doped Ru-CP gave a value of 2.46 for the ratio of $[\text{Os}(\text{bpy})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_3]^{2+}$ emission (see Figure S10 in the Supporting Information). Considering the different quantum yields and extinction coefficients of $[\text{Os}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ moieties in the framework $[\text{QY}(\text{Os})/\text{QY}(\text{Ru}) = 0.116$ and $\epsilon(\text{Os})_{485 \text{ nm}}/\epsilon(\text{Ru})_{485 \text{ nm}} = 0.538$ were experimentally determined with the polymer built from 100% Os (Os-CP) and 100% Ru (Ru-CP), we concluded that 95% of the excited state energy on $[\text{Ru}(\text{bpy})_3]^{2+}$ had migrated to the 9.1 mol % $[\text{Os}(\text{bpy})_3]^{2+}$ in the CP (see the Supporting Information for a

detailed analysis). This analysis indicates efficient excited-state migration, which was also evident in the steady-state emission spectra of 1.0 and 4.7 mol % Os-doped Ru-CPs. Quantitative analyses were less reliable for these systems due to incompatibly disparate Os and Ru emission intensities. The efficient energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+*}$ to $[\text{Os}(\text{bpy})_3]^{2+}$ was confirmed by time-resolved emission measurements of Os-doped Ru-CPs taken at 630 nm [λ_{max} for the $[\text{Ru}(\text{bpy})_3]^{2+}$ emission]. The averaged lifetime of the 630 nm emission steadily decreased as the Os doping level increased (Figure 1c), consistent with an increasing level of energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+*}$ to $[\text{Os}(\text{bpy})_3]^{2+}$.

Photocatalysis. We then examined the photocatalytic activity of the Ru-CP particles, using the aza-Henry reaction²³ as a test reaction. The reaction between tetrahydroisoquinoline derivatives **1a–3a** (see Table 1) and nitromethane or nitroethane

Table 1. Photocatalytic aza-Henry Reactions^a



entry	amine substrate	product	Conversion (%) with Different Catalysts ^b	
			Ru-CP	Ru-M
1 ^c	1a	1b	97	85
2 ^c	2a	2b	>99	84
3 ^c	3a	3b	>99	90
4 ^d	1a	1c	94	81
5 ^d	2a	2c	88	57
6 ^d	3a	3c	>99	62

^aAll the reactions were run at room temperature (rt) for 8 h with 0.2 mol % catalyst. ^bConversions were determined by integrating the ¹H NMR peaks. Ru-M is $[(\text{bpy})_2\text{Ru}(\text{deppy})]\text{Cl}_2$ (deppy = 5,5'-diethynyl-2,2'-bipyridine), which models the Ru phosphor in the CP. ^cWith nitromethane as solvent. ^dWith nitroethane as solvent.

were carried out in air with a common fluorescent lamp (26 W) as the light source. As shown by the ¹H NMR-determined reaction conversions in Table 1, the Ru-CP is a highly effective photocatalyst for all the six reactions with 88% to >99% conversions at 0.2 mol % Ru-CP loadings. These conversions are higher than those of the homogeneous counterparts (Table 1). The efficient photocatalytic aza-Henry reactions are supported by high isolated yields of 77% and 74% for **1b** and **2b**, respectively. Control experiments were carefully carried out to demonstrate the photocatalytic and heterogeneous nature of the reactions (Table 2). Reactions in the absence of either light or the catalysts showed zero or simply background conversions. The reaction supernatant after removing the CP was also proved to be inactive by a substrate crossover experiment. Substrate **3a** was used in the Ru-CP-catalyzed aza-Henry reaction, and a complete conversion was achieved in 8 h. The Ru-CP catalyst was then removed by filtering through Celite, and the second substrate **1a** was added to the filtrate. After stirring the solution under light for 8 h, only 11% conversion was observed for **1a**. This low conversion, comparable to that of the background

Table 2. Control Experiments and Catalyst Reuse for Photocatalytic aza-Henry Reactions^a

entry	condition	substrate	conversion ^b (%)
1	no light, Ru-CP	1a	<5
2	no catalyst	1a	10
3	no catalyst	2a	11
4	no catalyst	3a	19
5	C-CP	1a	36
6	C-CP	2a	29
7	Ru-CP (first reuse)	1a	97
8	Ru-CP (second reuse)	1a	94
9	Ru-CP (third reuse)	1a	96
10	Ru-CP (fourth reuse)	1a	92

^aReactions were run at room temperature for 8 h, with 0.2 mol % catalyst loadings, ~5 cm in front of a 26 W fluorescent lamp.

^bConversions were determined by ¹H NMR.

reaction, proved that the supernatant of the reaction mixture is inactive in photocatalysis. In addition, ICP-MS studies showed very little Ru leaching (<0.3%) to the solution during the reaction. The Ru-CP was also easily recovered from the reaction mixture by centrifugation, and reused four times without any loss of activity (Table 2).

We also demonstrated the applicability of nonporous Ru-CP in other light-driven reactions. At 1 mol % loading, Ru-CP efficiently catalyzed aerobic oxidative coupling of a series of primary amines²⁴ with 84%–99% conversions in 1 h (Table 3,

Table 3. Photocatalytic Aerobic Oxidative Coupling of Amines^a

entry	catalyst	substrate	conversion ^b (%)
1	Ru-CP	4	99
2	Ru-CP (first reuse)	4	99
3	Ru-CP (second reuse)	4	99
4	Ru-CP	5	95
5	Ru-CP	6	84
6	Ru(bpy) ₃ Cl ₂	4	97
7	C-CP	4	8
8 ^c	no catalyst	4	<5
9 ^d	Ru-CP	4	<5
10 ^d	Ru(bpy) ₃ Cl ₂	4	<5

4: R = H 4a: R = H
5: R = CH₃ 5a: R = CH₃
6: R = OCH₃ 6a: R = OCH₃

^aAll the reactions were run at 60 °C for 1 h with 1 mol % Ru-CP at a distance of ~10 cm from a 450-W Xe lamp. ^bConversions were determined by integrating the ¹H NMR peaks. ^cWithout photocatalyst.

^dWithout light.

entries 1–3), again comparable to that of the homogeneous catalyst. The isolated yield for 4a was 88%. The recyclability and reusability of the Ru-CP catalyst was also evaluated for this reaction. The recovered catalyst after simple filtration was reused three times, showing no deterioration in conversion percentage (Table 3; see the Supporting Information for more details). Similarly, a visible-light-driven dehalogenation of benzyl bromoacetate²⁵ catalyzed by 1 mol % Ru-CP catalyst also gave complete substrate transformation in 8 h, with an

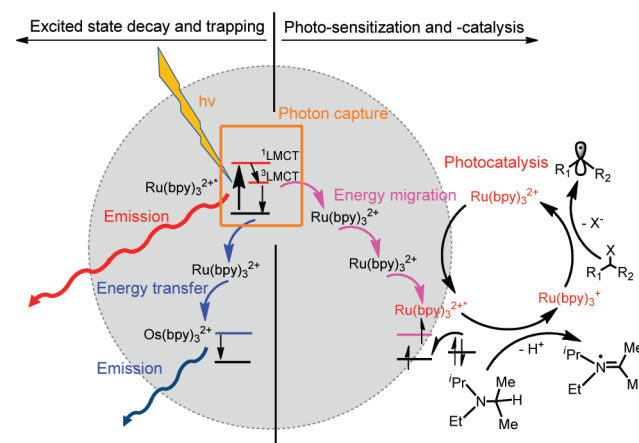
Table 4. Photocatalytic Dehalogenation of Benzyl Bromoacetate^a

entry	catalyst	conversion ^b (%)
1	Ru-CP	>99
2	Ru(bpy) ₃ Cl ₂	>99
3	no catalyst	8
4	C-CP	27

^aReactions were run at room temperature (rt) for 8 h with 1 mol % Ru-based catalyst. ^bConversions were determined by ¹H NMR.

isolated yield of 84% (Table 4; see the Supporting Information for more details).

The nonporous nature of Ru-CP indicates that only a very small fraction of [Ru(bpy)₃]²⁺ phosphors are at or near the surface and accessible to the organic substrates. The reason why Ru-CP still exhibits extremely high photocatalytic activity can only be explained by the fact that Ru phosphors embedded in the core of Ru-CP can serve as antenna to harvest light energy and the excited states generated at the interior of the material can easily migrate through the framework and reach the surface active sites (see Scheme 2).

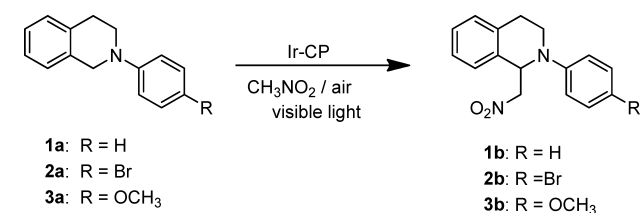
Scheme 2. Schematic Representation of Core-to-Surface Excited State Transport in Ru-CP-Catalyzed Photoreactions

Catalysis results using Os-doped Ru-CP and Os-CP support the light-harvesting nature of these photocatalytic reactions. Aza-Henry reaction between 1a and CH₃NO₂ was employed to probe the photocatalytic activity of Os-doped Ru-CPs. The 4.7 mol % Os-doped Ru-CP gave only 45% conversion of the substrate after reactions of 8 h, compared to 97% conversion catalyzed by the Ru-CP under identical conditions. The 9.1 mol % Os-doped Ru-CP catalyst further decreased the conversion to 37%. Interestingly, although the homogeneous Os(bpy)₃(PF₆)₂ catalyst gave a complete conversion of 1a under the same reaction conditions, the Os-CP gave 13% conversion, which is only slightly above that of the background reaction (10%). The drastically different behavior of Os-CP, compared to its Ru-CP counterpart, indicates that the [Os(bpy)₂(dbbpy)]^{2+*} excited state cannot effectively migrate

in the **Os-CP** framework. This is consistent with the much shorter lifetime of **Os-CP** ($\tau = 17$ ns; see Figure 2b), which translates to less time and a shorter distance that the $[\text{Os}(\text{bpy})_3]^{2+*}$ excited state can travel. In the **Os-doped Ru-CP**-catalyzed reactions, the $[\text{Ru}(\text{bpy})_3]^{2+*}$ excited states generated in the interior of the solid may transfer energy to the $[\text{Os}(\text{bpy})_3]^{2+}$ traps before migrating to the solid surface to drive redox reactions. In both cases, the low activities of the **Os-CP** and the **Os-doped Ru-CPs** can be explained by the inability of the excited states to reach the polymer surface, supporting the role of core-to-surface excited-state migration in the **CP** photocatalysis.

We also tested the photocatalytic activity of **Ir-CP** using the aza-Henry reaction. As a result of the core-to-surface excited-state migration, the **Ir-CP** also serves as an active photocatalyst with 55%, 54%, and 99% conversions in 8 h for reactions between nitromethane and **1a**, **2a**, and **3a**, respectively. (See Table 5.) Except for substrate **3a**, the conversions of the

Table 5. Photocatalytic aza-Henry Reactions^a Using Ir-CP and Homogeneous Ir Complex (Ir-M) as Photocatalysts



entry	condition	substrate	conversion ^b (%)
1	Ir-CP	1a	55
2	Ir-CP	2a	54
3	Ir-CP	3a	>99
4	Ir-M	1a	99
5	Ir-M	2a	99
6	Ir-M	3a	81

^aReactions were run at room temperature (rt) for 8 h, with 0.2 mol % catalyst loadings, ~5 cm in front of a 26-W fluorescent lamp.

^bConversions were determined by ¹H NMR. Ir-M is [(ppy)₂Ir-(deppy)]Cl, which models the Ir phosphor in the CP.

reactions catalyzed by **Ir-CP** are significantly lower than that of the **Ru-CP**-catalyzed reactions, which is consistent with the shorter lifetime of the **Ir-CP** ($\tau = 97.5$ ns; see Figure 2a) than the **Ru-CP** counterpart ($\tau = 166.5$ ns). An empirical linear relationship was obtained by plotting the conversions of reactions between **1a** and nitromethane catalyzed by different CP catalysts against the phosphorescent lifetimes of those catalysts (the catalysts include **Ru-CP**, **Ir-CP**, 4.7% **Os-doped Ru-CP**, 9.1% **Os-doped Ru-CP**, **Os-CP**; see Figure 1d). Such correlation between the photochemical activity and the excited-state lifetime in CPs, which is absent in homogeneous molecular catalytic systems,²³ provides additional evidence for the core-to-surface excited-state transport mechanism of these highly active CP photocatalysts.

In an additional control experiment, we observed that photocatalytic reactions with **C-CP** (without the metallo-phosphor) gave slightly higher conversions than corresponding background reactions. For example, in the aza-Henry reactions with nitromethane, **C-CP** gave conversions of 36% and 29% for **1a** and **2a**, in comparison to the background conversions of 10% and 11% (see Table 1). In the aerobic oxidative coupling of **4**, **C-CP** gave a conversion of 8% in comparison to <5% for the

background reaction (see Table 4). **C-CP** gave a conversion of 27% for **7** in the dehalogenation reaction, as compared to the 8% conversion for the background reaction. Therefore, we believe that the antenna effect of the framework, through either sensitizing ³MLCT excitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ phosphor or directly activating the substrates, also contributes to the excellent photocatalytic activities of **Ru-CP**.²⁶

CONCLUSION

Nearly stoichiometric amounts of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{ppy})_2(\text{bpy})^+$ phosphors have been incorporated into cross-linked polymers **Ru-CP** and **Ir-CP** by Sonogashira cross-coupling reactions. Despite their nonporous nature, the **Ru-CP** and **Ir-CP** are highly active and recyclable heterogeneous photocatalysts for a range of organic transformations such as aza-Henry reaction, aerobic amine coupling, and dehalogenation of benzyl bromoacetate. The very high catalytic activities of these nonporous CPs result from their light-harvesting ability, which allows collection of photons by exciting the ³MLCT states of the excited states to the particle surface to drive the redox catalysis. This light-harvesting mechanism was supported by steady-state and time-resolved emission data as well as the reduced catalytic activities of **Os-CP** and **Os-doped Ru-CPs**. This work illustrates the potential for designing highly efficient photocatalysts based on light-harvesting cross-linked polymers.

EXPERIMENTAL SECTION

All starting materials were purchased from Aldrich and Fisher, unless otherwise noted, and used without further purification. ¹H NMR spectra were recorded on a Bruker Model NMR 400 DRX spectrometer at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform (δ 7.26). A Varian 820-MS inductively coupled plasma-mass spectrometer (ICP-MS) was used to determine the Ru and Ir content. Transmission electron microscopy (TEM) was used to image the particles, using a JEM Model 100CX-II TEM system. Thermogravimetric analysis (TGA) was performed using a Shimadzu Model TGA-50 system that was equipped with a platinum pan, and all samples were heated at a rate of 5 °C/min in air. Nitrogen adsorption experiments were performed with a Quantachrome Autosorb-1C system. Steady-state and time-resolved emission spectra were recorded on an Edinburgh FLS 920 system.

Synthesis of Ru-CP. Bis(2,2'-bipyridine)(5,5'-dibromo-2,2'-bipyridine)ruthenium(II) dihexafluorophosphate ($[\text{Ru}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$) and tetra(4-ethynylphenyl)methane were synthesized by following the literature procedure.^{27,28} $[\text{Ru}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$ (50 mg, 0.05 mmol), tetra(4-ethynylphenyl)methane (15 mg, 0.037 mmol), tetrakis(triphenylphosphine)palladium (15 mg), and copper(I) iodide (10 mg) were dissolved in a mixture of DMF (2.5 mL) and triethylamine (2.5 mL). The reaction mixture was heated to 90 °C and stirred for 72 h under a nitrogen atmosphere. The mixture was cooled to room temperature, and the insoluble precipitated product was filtered and washed with acetonitrile, water, methanol, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the product was carried out by Soxhlet extraction with methanol for 24 h.²⁹ The product was dried under vacuum for 24 h at 50 °C to give brown powder (yield: 40 mg, 76%).

Synthesis of [Os(bpy)₃]²⁺-Doped Ru-CP and Os-CP. Bis(2,2'-bipyridine)(5,5'-dibromo-2,2'-bipyridine)osmium(II) dihexafluorophosphate ($[\text{Os}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$) was synthesized by following the literature procedure.³⁰ A procedure similar to the synthesis of **Ru-CP** was followed for the synthesis of $[\text{Os}(\text{bpy})_3]^{2+}$ -doped **Ru-CP** and **Os-CP**, except that mixtures of $[\text{Ru}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$ and $[\text{Os}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$ of appropriate molar ratios, or pure $[\text{Os}(\text{bpy})_2(\text{dbbpy})](\text{PF}_6)_2$ were added as the monomers.

Synthesis of Ir-CP. Bis(2-phenylpyridine)(5,5'-dibromo-2,2'-bipyridine)iridium(III) chloride ($[\text{Ir}(\text{ppy})_2(\text{dbbpy})]\text{Cl}$) was synthesized following the literature procedure.³¹ A procedure similar to the synthesis of Ru-CP was followed for the synthesis of Ir-CP, except that $[\text{Ir}(\text{ppy})_2(\text{dbbpy})]\text{Cl}$ was added as the monomer. Pd particles in the as-synthesized samples were further removed by dispersing the solids in a 0.4 M NaCN aqueous solution and bubbling air through the solution for 2 days. The obtained solids were then washed with water and acetone several times, followed by vacuum drying.

Synthesis of Control Cross-Linked Polymer (C-CP). A procedure similar to the synthesis of Ru-CP was followed for the synthesis of C-CP, by substituting $[\text{Ru}(\text{bpy})_2(\text{dbbpy})]^{2+}$ with dbbpy. Pd particles in the as-synthesized samples were further removed by dispersing the solids in a 0.4 M NaCN aqueous solution and bubbling air through the solution for 2 days. The solids were further purified by Soxhlet extraction with methanol for 24 h. The product was then washed with water and acetone several times, followed by drying under vacuum.

■ ASSOCIATED CONTENT

Supporting Information

Characterization of CPs, procedures for photocatalysis, and analysis of energy transfer efficiency. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: 1 919 962 6320. Fax: 1 919 962 2388. E-mail: wlin@unc.edu.

Present Address

‡Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PRC.

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

Ru-CP = cross-linked polymer built from tetra(*p*-ethynylphenyl)methane and bis(2,2'-bipyridine)(5,5'-dibromo-2,2'-bipyridine)-ruthenium(II) dihexafluorophosphate

Ir-CP = cross-linked polymer built from tetra(*p*-ethynylphenyl)methane and bis(2-phenylpyridine)(5,5'-dibromo-2,2'-bipyridine)iridium(III) chloride

Os-CP = cross-linked polymer built from tetra(*p*-ethynylphenyl)methane and bis(2,2'-bipyridine)(5,5'-dibromo-2,2'-bipyridine)osmium(II) dihexafluorophosphate

C-CP = cross-linked polymer built from tetra(*p*-ethynylphenyl)methane and 5,5'-dibromo-2,2'-bipyridine, serving as a control

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