

Cross-linked Polymers with Exceptionally High $\text{Ru}(\text{bpy})_3^{2+}$ Loadings for Efficient Heterogeneous Photocatalysis

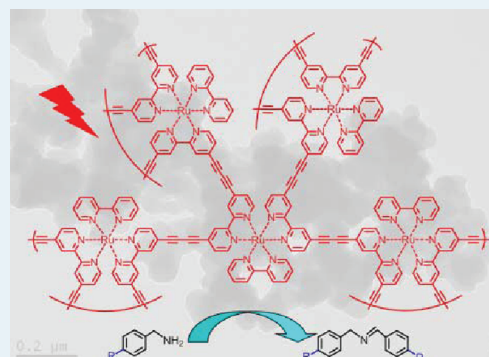
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Supporting Information

ABSTRACT: Phosphorescent cross-linked polymers **1** and **2** were synthesized via oxidative homocoupling reactions of tetra(ethynyl) derivatives of $\text{Ru}(\text{bpy})_3^{2+}$ (with the alkyne groups located at 4,4'- or 5,5'- positions of two substituted bipyridines). These cross-linked polymer particles contain exceptionally high $\text{Ru}(\text{bpy})_3^{2+}$ loadings and serve as highly efficient and reusable heterogeneous photocatalysts for a range of organic transformations, presumably owing to the ability of the $\text{Ru}(\text{bpy})_3^{2+}$ moieties in the polymer network to transport triplet excited states to particle surfaces to initiate the organic reactions. This work illustrates the potential of developing photocatalytic cross-linked polymers from photoactive molecular building blocks for solar energy utilization.

KEYWORDS: light-harvesting, cross-linked polymer, energy transfer, photocatalysis, heterogeneous catalysis, excited state migration



INTRODUCTION

The natural photosynthetic process of harvesting and converting solar energy to chemical energy has inspired scientists to develop various artificial photosynthetic systems.^{1–4} Particularly, utilizing visible light to photochemically activate organic substrates for synthetic transformations has gained significant interest because of the potential to develop chemical processes with minimum environmental impact and energy consumption.^{5–7} Metal complexes of phthalocyanines, porphyrins, and polypyridines have recently been used as photosensitizers to overcome the limited visible light absorption by organic substrates.^{8–15} $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) and its derivatives are among the most extensively investigated photocatalysts because of their relatively high quantum efficiency and long lifetime of photoexcited states.^{16–23} Moreover, the excited states can readily undergo redox reactions to initiate catalytic cycles.^{7,23,24} However, concerns have arisen about the contamination of products by toxic metals and the inability to recycle and reuse expensive photocatalysts.²⁴ It is therefore an important objective to develop heterogeneous photocatalysts based on precious metal complexes which can be easily recovered from the products and reused in photocatalytic reactions.

Over the past decade, new families of microporous molecular materials, including metal–organic frameworks (MOFs)^{25–31} and cross-linked polymers (CPs),^{32–40} have received considerable attention because of their potential applications in gas storage, separation, catalysis, and light-harvesting.^{41,42} Compared to the relatively labile MOFs, porous CPs have a distinct advantage as photocatalysts because of high thermal, chemical, and photochemical stabilities.^{43,44} Along this line, our group has recently reported the incorporation of Ru and Ir photo-

sensitizers into robust CPs through $\text{Co}_2(\text{CO})_8$ -mediated cotrimerization of linear ethynyl-substituted Ru or Ir complexes with tetrakis(4-ethynyl-phenyl)methane. The porous CPs were shown to serve as recyclable heterogeneous photocatalysts in light-driven organic transformations.⁴⁵ However, the loadings of Ru and Ir photosensitizers in these CPs were low (2.2 and 4.5 wt %, respectively) because of the competing homotrimerization of tetrakis(4-ethynyl-phenyl)methane. It is highly desirable to increase the loadings of $\text{Ru}(\text{bpy})_3^{2+}$ derivatives in CPs for more efficient light absorption and higher photocatalytic activity. In this paper, we report the synthesis of new butadiyne-type CPs **1** and **2** with very high $\text{Ru}(\text{bpy})_3^{2+}$ loadings via Eglinton homocoupling of tetra(ethynyl) derivatives of $\text{Ru}(\text{bpy})_3^{2+}$ (Scheme 1). The resultant CPs with diamondoid network as the ideal structure prototype are highly active and recyclable photocatalysts for a range of organic transformations including aza-Henry reactions, aerobic oxidative coupling of amine, and reductive dehalogenation reactions.

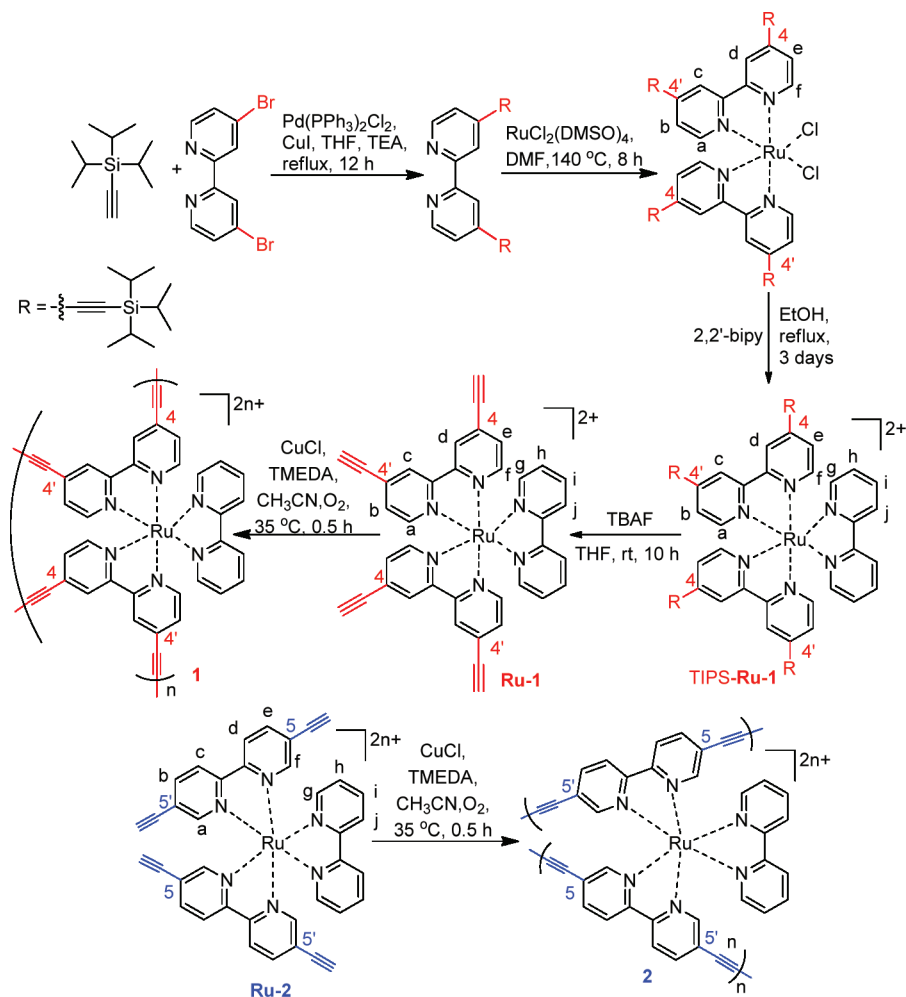
RESULTS AND DISCUSSION

4,4'-Bis[tri(isopropyl)silylethynyl]-2,2'-bipyridine was prepared by a Pd-catalyzed Sonogashira reaction between 4,4'-dibromo-2,2'-bipy⁴⁶ and [tri(isopropyl)silyl]acetylene in 93% yield. 4,4'-Bis[tri(isopropyl)silylethynyl]-2,2'-bipy was treated with $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ in dimethylformamide (DMF) at 140 °C for 8 h to give bis{[4,4'-bis(triisopropyl)silylethynyl]-2,2'-bipy}-ruthenium dichloride in 83% isolated yield,⁴⁷ which was

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Scheme 1. Synthesis of Ru(bpy)₃²⁺-Based Cross-linked Polymers 1 and 2

converted to Ru{[4,4'-bis(triisopropyl)silylethynyl]-2,2'-bipy}₂(2,2'-bipy)Cl₂ (TIPS-Ru-1) in 73% yield by treating with 2,2'-bipy. Removal of the tri(isopropyl)silyl (TIPS) groups with tetrabutylammonium fluoride (TBAF) followed by column chromatography with a solution of KNO₃ in acetonitrile and water gave Ru[4,4'-bis(ethynyl)-2,2'-bipy]₂(2,2'-bipy)(NO₃)₂ (Ru-1) in 60% isolated yield. The regioisomers with ethynyl groups in the 5,5'-positions of the bipy ligands, Ru{[5,5'-bis(triisopropyl)silylethynyl]-2,2'-bipy}₂(2,2'-bipy)Cl₂ (TIPS-Ru-2) and Ru[5,5'-bis(ethynyl)-2,2'-bipy]₂(2,2'-bipy)(NO₃)₂ (Ru-2) were similarly synthesized starting from 5,5'-dibromo-2,2'-bipy⁴⁸ in 58% and 23% overall yield, respectively (Scheme 1). All of the compounds were purified by silica gel chromatography and characterized by ¹H and ¹³C NMR spectroscopy and electrospray ionization-mass spectrometry. The ¹H NMR spectra of Ru-1 and Ru-2 both showed a pair of closely spaced singlets at approximately δ 4.35 ppm and 4.07 ppm for the terminal alkynyl protons, respectively. These chemical shifts have moved downfield as a result of coordination to the Ru centers when compared with the chemical shift of ~δ 3.2 ppm for the alkynyl protons of free bipy derivatives (See Supporting Information).⁴⁹ The monomers Ru-1 and Ru-2 are readily soluble in polar solvents such as MeOH, CH₃CN, and H₂O.

Oxidative Eglinton coupling reactions of the two regioisomeric tetra(ethynyl) derivatives of Ru(bpy)₃²⁺ were carried out

with the CuCl/*N,N,N',N'*-tetramethylethylenediamine catalyst under an oxygen atmosphere in acetonitrile at 35 °C for 0.5 h.⁵⁰ The resulting solids were washed with pyridine, methanol, water, and dried in vacuo to afford CPs 1 and 2 in 95% and 91% yield, respectively. Both 1 and 2 are black-red amorphous powders that are insoluble in common organic solvents such as DMF, H₂O, CH₃CN, and resistant toward acids and bases. 1 and 2 were characterized by inductively coupled plasma-mass spectroscopy (ICP-MS), Fourier transform-infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), nitrogen adsorption, and transmission electron microscopy (TEM).

On the basis of the ICP-MS results, 1 and 2 possess exceptionally high [Ru(bpy)₃]²⁺ loadings of 91.0 ± 5.0 wt % and 89.6 ± 5.0 wt %, respectively, close to that of the stoichiometric polymer formulas (87.0 wt %). Compared to previously reported [Ru(bpy)₃]²⁺-containing porous CPs (2.2–4.5 wt %),⁴⁵ the phosphor loadings in 1 and 2 have drastically increased as a result of support-less single component homocoupling reactions. The high concentrations of [Ru(bpy)₃]²⁺ dyes in the structures can not only enhance visible light absorption but also facilitate excited state migration in the CP networks through Dexter triplet to triplet energy transfer. The degree of polymerization is indicated by the IR spectra. IR spectra of monomers Ru-1 and Ru-2 showed a diagnostic absorption of carbon–hydrogen stretching peak of the C≡C–H group at about 3180 cm⁻¹ and 3200 cm⁻¹, respectively

(Figure 1). These peaks are mostly absent in the IR spectra of the CPs, indicating that most of the terminal alkyne groups in

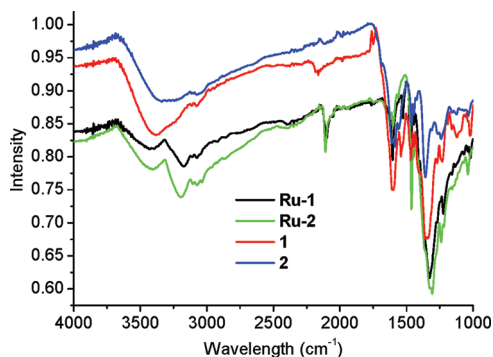


Figure 1. FT-IR spectra of Ru-1, Ru-2, 1, and 2.

the monomers have been consumed in the oxidative Eglinton coupling reactions. The particles are stable up to 200 °C in air, as revealed by TGA, which is consistent with previously reported CPs polymers based on butadiyne linkages.^{51–53}

The porosity of the CPs was investigated by nitrogen sorption measurements at 77 K. **1** exhibits a Brunauer–Emmett–Teller (BET) surface area of 198 m²/g whereas **2** shows a negligible BET surface area of 15 m²/g (Figure 2).

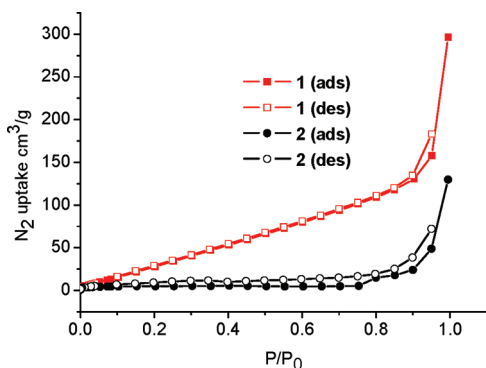


Figure 2. Nitrogen sorption isotherms of **1** and **2** in at 77 K.

These surface areas are significantly lower than those of the CPs based on tetrakis(4-ethynyl-phenyl)methane.^{51,54} We attributed the low porosity of **1** and **2** to the bulky groups of

the [Ru(bpy)₃]²⁺ complexes in the polymer networks, which is known to reduce the porosity of CPs.⁵⁵ The TEM sample was prepared by first dispersing the CPs in methanol, and then placing them on carbon-coated Cu/Ni grids. TEM images of both **1** and **2** showed that they are aggregates of spherical nanoparticles of ~100 nm in diameter (Figure 3).

CPs built from [Ru(bpy)₃]²⁺ complexes act as insoluble but dispersible photosensitizers by taking advantage of redox-active ³MLCT excited states of the chromophores. Steady-state UV–vis absorption and emission spectra and time-resolved phosphorescence spectra were recorded with a stirred suspension of **1** or **2** in CH₃CN and dilute solutions of Ru-**1** and Ru-**2** monomers in CH₃CN (2 × 10^{−5} M). They all showed a broad absorption between 300 and 800 nm with two or three additional discernible absorption bands (Figure 4). For

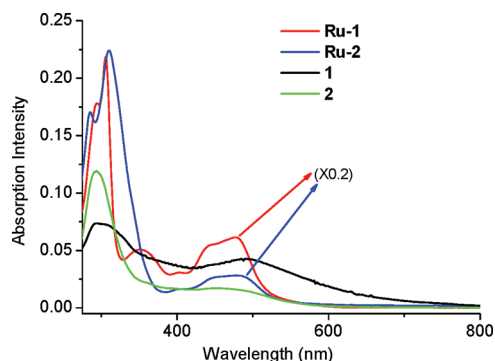


Figure 4. Steady-state absorption spectra of stirred suspensions of **1** and **2** in CH₃CN (2 × 10^{−5} M) and dilute solutions of Ru-**1** and Ru-**2** in CH₃CN (2 × 10^{−5} M). Absorption spectra of Ru-**1** and Ru-**2** are on a reduced scale (×0.2).

1, the absorption peak at ~294 nm is assigned to the π→π* bipy ligands in the [Ru(bpy)₃]²⁺ whereas the peak at ~493 nm is attributed to the metal-to-ligand charge transfer (¹MLCT) transition.⁵ Compared with Ru-**1** and Ru-**2**, the ¹MLCT peaks in CPs **1** and **2** became broadened and showed a slight red-shift, which is beneficial to absorbing the solar radiation. In the steady-state phosphorescence spectra, the emission maximum λ_{max} centered at 705 nm for **1** and at 696 nm for **2** (Figure 5). Interestingly, the phosphorescence maximum λ_{max} of **1** exhibited obvious red shift in comparison with that of monomer Ru-**1** owing to the increased effective conjugation

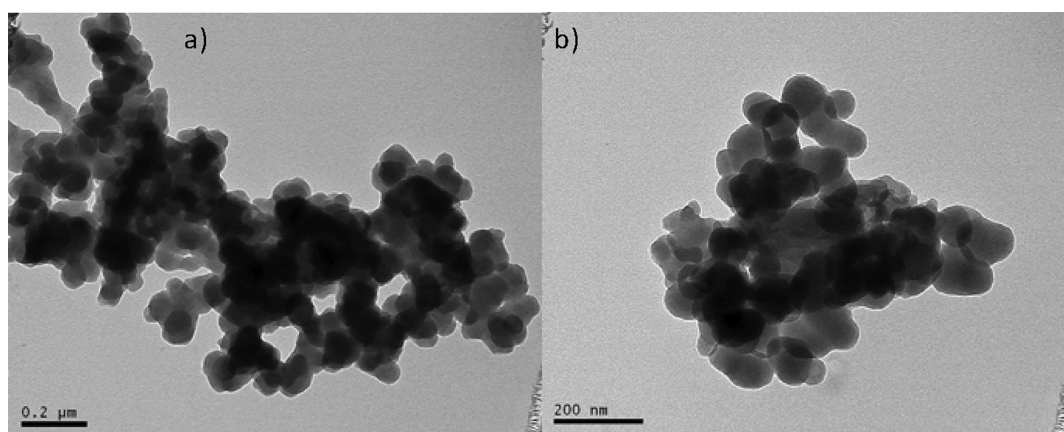


Figure 3. TEM images of **1** (a) and **2** (b) on a carbon-coated Cu/Ni grid.

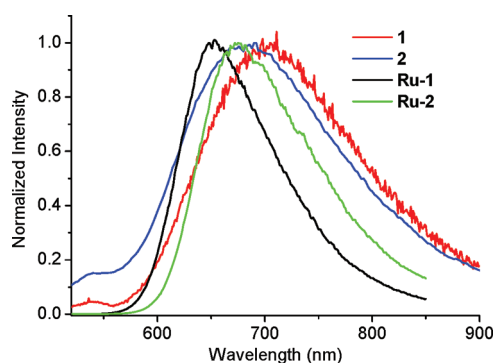


Figure 5. Steady-state phosphorescence spectra of stirred suspensions of **1** and **2** in CH_3CN (2×10^{-5} M) and dilute solutions of **Ru-1** and **Ru-2** in CH_3CN (2×10^{-5} M).

length of ligands in CP-1 and aggregation of **1** in the particle. The phosphorescence lifetimes of the CPs were measured using an Edinburgh FLS 920 in the time-correlated photon counting mode. When excited at ~ 440 nm, the decays of monomers **Ru-1** and **Ru-2** and CP-1 were well fitted with a monoexponential model, leading to emission lifetimes of 962 ns, 574 ns, and 423 ns, respectively (Figure 6). The emission decay of **2** was fitted

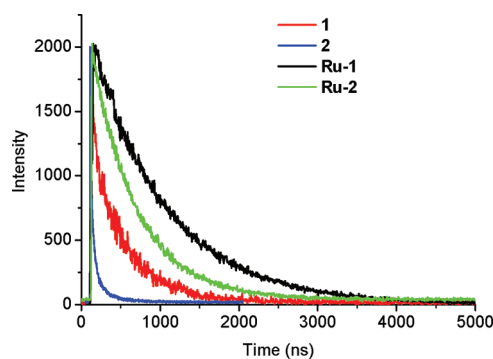


Figure 6. Time-resolved phosphorescence decays of **1** and **2** and monomers **Ru-1** and **Ru-2** (excitation: 440 nm; emission: 660 nm).

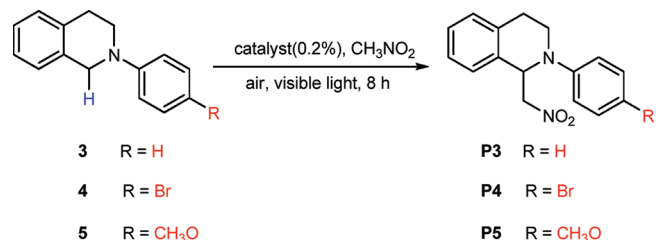
with a double-exponential model to give an averaged lifetime of 112 ns, indicating a much shorter-lived $^3\text{MLCT}$ phosphorescence. The broad absorption bands together with relatively long excited state lifetimes of the CPs make them good candidates as heterogeneous photocatalysts.

We examined the photocatalytic activities of the CP particles, using the aza-Henry reaction,^{18,55} aerobic oxidative coupling of amine,⁵⁶ and dehalogenation of benzyl bromoacetate^{17c} as representative reactions. CPs **1** and **2** exhibited high photocatalytic activities in these reactions. aza-Henry reactions between tetrahydroisoquinoline derivatives **3**–**5** and nitromethane were carried out in air for 8 h with 0.2 mol % of CPs as the catalysts and a common fluorescent lamp (26 W) as the light source, in a similar fashion as those reported previously.⁴⁵ As shown in Table 1, the conversions of the reactions were calculated based on the ^1H NMR peak integrations of the crude products. After filtering off the CP catalysts, the solvents were removed, and the crude products were analyzed by ^1H NMR. The integrations of peaks of the featured protons in the products (about δ 5.5 ppm) and those of the corresponding starting materials (about δ 4.4 ppm) were used in the calculation (See Supporting Information). CP-1 gave a slightly higher conversion (94% for **3** with the phenyl substituent, 96%

for **5** with the *para*-methoxyphenyl substituent, and 99% for **4** with the *para*-bromophenyl substituent) than CP-2 (92% for **3**, 96% for **5**, and 94% for **4**). Notably, these conversions are slightly higher than those catalyzed by other Ru- or Ir-based cross-linked polymers we reported previously.⁴⁵ Moreover, aza-Henry products were isolated in very high yields after purification by chromatography (Table 1). We found that the isolated yields for these CP-catalyzed reactions are comparable to those of the homogeneous systems even though we reduced the reaction time (avg. 16 h to 8 h) and catalyst loading (1 mol % to 0.2 mol %) in these heterogeneous photocatalytic reactions. We have also carried out several control experiments to further investigate the details of these heterogeneous photocatalytic reactions. For example, the conversions and isolated yields afforded by **1** and **2** are higher than those of the monomer homogeneous catalysts (TIPS-**Ru-1** and TIPS-**Ru-2**). **Ru-1** and **Ru-2** are unstable and will polymerize under the photocatalytic reaction conditions and could not be used as control homogeneous catalysts. Moreover, low conversions (<20%) were detected in the absence of either light or the catalyst, indicating the photocatalytic nature of these reactions. We have also recycled and reused the CP catalysts. **1** was easily recovered from the reaction mixture by filtration, and could be reused for at least three times. ICP-MS studies showed very little Ru leaching (<0.5%) to the supernatant after these photocatalytic reactions. The recovered solid CP catalysts showed only slight decrease in conversions and isolated yields of aza-Henry products.

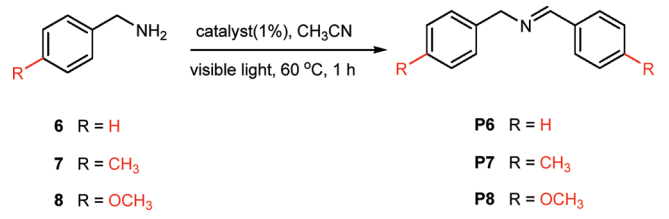
We further examined the scope of reactions catalyzed by the CPs. As shown in Table 2, aerobic oxidative coupling of a series of primary amines was also efficiently catalyzed at 1 mol % CP catalyst loadings with a 450 W Xe lamp. The conversions of various substrates catalyzed by the CPs were calculated based on the integration of the ^1H NMR peaks of the featured protons in the products and those of the corresponding starting materials (See Supporting Information). Nearly complete conversions (99%) of all the three substrates were observed with **1** as photocatalyst, which compare favorably with the monomer control catalyst. In contrast, the conversions for **2** were highly dependent on the substrates (99% for benzylamine, 76% for *p*-methylbenzylamine, 67% for *p*-methoxybenzylamine). Moreover, low conversions (<5%) were obtained in the absence of either light or the catalysts, confirming the photocatalytic role of the CPs. We have also determined the yields of oxidative coupling products by gas chromatography (GC) with *n*-undecane as the internal standard. The GC yields were slightly lower than the ^1H NMR conversions, but they both showed the same trends. We believe that some of the starting materials were consumed to form other byproducts that were not detected by GC. We also demonstrated that the photocatalyst **1** could be readily recovered and reused twice for all these three substrates with only slight decrease of the conversions and yields.

The photocatalyzed reductive dehalogenation reaction was also examined using the CP photocatalysts (Scheme 2). Benzyl bromoacetate was chosen as the substrate and a 26 W fluorescent lamp was used as the light source. Benzyl bromoacetate was completely converted to benzyl acetate with 1 mol % loadings of photocatalyst **1** or **2** based on ^1H NMR spectra (See Supporting Information). These results have been corroborated with high isolated yields of the benzyl acetate (92% for **1** and 86% for **2**). A control reaction in the absence of the CPs gave <10% conversion. The CP

Table 1. Photocatalytic aza-Henry Reactions Using CPs 1 and 2 as Catalysts^a


comps	catalyst	conversion% ^b	isolated yield% ^c
3	1	94	85
3	TIPS-Ru-1	91	76
4	1	99	89
4	1 (2 nd -use)	91	85
4	1 (3 rd -use)	90	80
4	1 (4 th -use)	87	76
5	1	96	90
3	2	92	81
3	TIPS-Ru-2	90	77
4	2	94	83
5	2	96	82

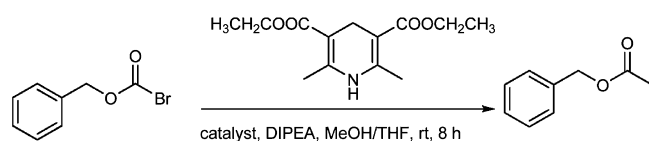
^aAll of the reactions were carried out at room temperature with 0.2 mol % ratio catalyst for 8 h with a 26 W fluorescent lamp. ^bConversions were determined by integrating the ¹H NMR peaks. ^cIsolated yields were calculated based on pure products after column chromatography.

Table 2. Photocatalytic Aerobic Oxidative Coupling Reactions Using CPs 1 and 2 as Catalysts^a


comps	catalyst	conversion % ^b	GC yield %
6	1	99	93
7	1	99	88
7	1 (2 nd -use)	99	85
7	1 (3 rd -use)	97	84
8	1	99	87
6	2	99	88
7	2	76	52
8	2	67	51
6	TIPS-Ru-2	99	89
7	TIPS-Ru-2	97	87
8	TIPS-Ru-2	90	79

^aAll of the reactions were done at 60 °C for 1 h with 1 mol % catalyst under a 450 W Xe lamp. ^bConversions were determined by integrating the ¹H NMR peaks.

Scheme 2. Photocatalytic Dehalogenation of Benzyl Bromoacetate Using 1 and 2 as Catalysts



photocatalyst could also be recovered and reused without significant decrease in conversions and yields.

The almost nonporous nature of Ru-based CPs indicates that only a small fraction of [Ru(bpy)₃]²⁺ chromophores is at or near the surface and is accessible to the organic substrates. The

reason why such nonporous heterogeneous cross-linked polymers still exhibit extremely high photocatalytic activity can be explained by efficient excited state migration among the chromophore framework. The interior [Ru(bpy)₃]²⁺ chromophores of the cross-linked polymers can be excited by light, and the generated excited states can migrate among the chromophore networks through Dexter triplet to triplet energy transfer, finally reaching the reactive sites of the polymer surface to drive redox reactions.⁵⁸ We suggested that Ru chromophores in the interior of the polymers can effectively serve as light harvesting antenna to collect photon energy and transfer them to the reactive sites, which is dominant and much faster compared to the reversed process of excited state

migration from the surface to the interior of the polymers. The Ru chromophores on the surface can either be directly excited by light or accept excited state energy from the interior of the polymer particle to form the ³MLCT states and then undergo redox reactions to initiate the photocatalytic cycle.⁵⁹ Such a light-harvesting phenomenon was recently unambiguously demonstrated by Lin et al. in [Ru(bpy)₃]²⁺-derived MOFs.⁶⁰

CONCLUSIONS

Two different cross-linked polymers based on Ru(bpy)₃²⁺ chromophores with tetra-alkynyl substituents at 4,4',- or 5,5',- position of two bipyridine moieties were synthesized through Eglinton alkyne homocoupling with high yields and extremely high chromophore loadings (~90%). The CPs are almost nonporous with small surface areas based on the nitrogen adsorption experiments at 77 K, but efficiently catalyze a range of organic transformations (aza-Henry reaction, aerobic oxidative coupling of amine, and reductive dehalogenation reaction) in the presence of visible light. The excellent photocatalytic activities are attributed to high content of light-absorbing Ru(bpy)₃²⁺ chromophores as well as excited state energy migration from the chromophores in the interior of the polymer particle to the reactive sites on the surface of the polymer particle.

EXPERIMENTAL SECTION

General Procedures. Chemicals were purchased from commercial sources and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker NMR 400 DRX Spectrometer at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform (δ 7.27) except where noted. A Varian 820-MS Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine Ru content. TEM was used to image the particles, using a JEM 100CX-II Transmission Electron Microscope. TGA was performed using a Shimadzu TGA-50 equipped with a platinum pan, and all samples were heated at a rate of 5 °C per minute under air. Nitrogen adsorption experiments were performed with a Quantachrome Autosorb-1C 77K after activating under vacuum at 60 °C for 10 h. UV-vis spectra were recorded on a Perkin-Elmer Lambda 35 UV-vis spectrometer. Steady-state and time-resolved emission spectra were recorded on an Edinburgh FLS 920.

Ru{4,4'-bis[(tri(isopropyl)silylethynyl]-2,2'-bipy)}₂(2,2'-bipy)Cl₂ (TIPS-Ru-1). 2,2'-Bipyridine (17.2 mg, 0.11 mmol) and bis{4,4'-bis[(tri(isopropyl)silylethynyl]-2,2'-bipy}ruthenium dichloride⁴⁷ (120 mg, 0.1 mmol) were dissolved in a mixture of chloroform (20 mL) and EtOH (20 mL) and refluxed for 3 days. The solvent was evaporated, and the residue was purified by silica gel chromatography using dichloromethane/methanol (20:1) as an eluent to afford a red solid (100 mg, 73%). ¹H NMR (CD₂Cl₂, 400 MHz, ppm): δ 8.95 (d, J = 8.0 Hz, 2H, Py-*H*^f), 8.28 (m, 4H, Py-*H*^{c,d}), 8.13–8.17 (m, 2H, Py-*H*^f), 7.99 (d, J = 5.6 Hz, 2H, Py-*H*^f), 7.94 (d, J = 5.6 Hz, 2H, Py-*H*^a), 7.86 (d, J = 5.6 Hz, 2H, Py-*H*^g), 7.53–7.57 (m, 2H, Py-*H*^h), 7.48 (dd, J = 5.6, 1.6 Hz, 2H, Py-*H*^{b,e}), 1.13–1.17 (m, 84H, CH₃, CH); ¹³C NMR (CD₂Cl₂, 100 MHz, ppm): δ 156.8, 156.5, 156.2, 152.7, 152.5, 151.9, 139.2, 133.30, 133.25, 130.7, 130.5, 128.7, 126.0, 125.6, 104.1, 104.0, 102.4, 102.3, 18.7, 11.5; ESI MS (m/z): Calcd. for [C₇₄H₁₀₄Cl₂N₆RuSi₄]⁺: 1360.6. Found: 1325.5 [M-Cl]⁺, 645.3[M-2Cl]²⁺.

Ru{4,4'-bis(ethynyl)-2,2'-bipy}₂(2,2'-bipy)(NO₃)₂ (Ru-1). To a solution of Ru{4,4'-bis[(tri(isopropyl)silylethynyl]-2,2'-bipy}₂(2,2'-bipy)Cl₂ (160 mg, 0.12 mmol) in THF (20 mL) was added dropwise a solution of TBAF (0.5 mmol, 0.5 mL) in THF. The reaction was stirred at room temperature (RT) for 10 h. The reaction was quenched with water, and all of solvents were evaporated in vacuo. The crude product was purified by flash chromatography (silica gel, CH₃CN/KNO_{3(aq.)} 5/1) to afford a red solid (45 mg, 60%). ¹H NMR (400 MHz, ppm): δ 8.82 (m, 4H, Py-*H*^{c,d}), 8.69–8.71 (d, J = 8.0 Hz, 2H, Py-*H*^f), 8.12–8.16 (m, 2H, Py-*H*^f), 7.78–7.85 (d, d, d, J = 5.6 Hz, J = 5.6 Hz, J = 5.6 Hz, 6H, Py-*H*^{a,b,g}), 7.49–7.53 (m, 6H, Py-*H*^{b,e,i}), 4.329 (s, 2H, CCH). 4.322 (s, 2H, CCH). ¹³C NMR (100 MHz, ppm): δ 156.34, 156.31, 151.0, 150.9, 150.8, 137.8, 131.89, 131.86, 129.24, 129.18, 127.2, 126.42, 126.40, 123.9, 86.8, 78.69, 78.65; ESI MS (m/z): Calcd. (found) for [M-NO₃]⁺: 728.1 (728.1); Calcd. (found) for [M-2NO₃]²⁺: 333.1 (333.1).

5,5'-Bis[(tri(isopropyl)silylethynyl)-2,2'-bipyridine. To a solution of 5,5'-dibromo-2,2'-bipyridine (0.76 g, 2.4 mmol), Pd(PPh₃)₂Cl₂ (45 mg) and CuI (24 mg) in 40 mL of triethylamine were added under argon. Tri(isopropyl)silylacetylene (1.78 g, 9.6 mmol) was then added to the solution. The mixture was refluxed for 12 h under argon. After removal of the solvent, the crude product was purified by silica gel chromatography eluting with CH₂Cl₂ to afford a white solid (0.9 g, 90%). ¹H NMR (400 MHz, ppm): δ 8.74 (d, J = 0.8 Hz, 2H, Py-*H*^{6,6'}), 8.37 (d, J = 8.4 Hz, 2H, Py-*H*^{3,3'}), 7.85–7.88 (dd, J = 8.4, 0.8 Hz, 2H, Py-*H*^{4,4'}), 1.16 (m, 42H, TIPS-*H*). ¹³C NMR (100 MHz): δ 154.3, 152.4, 139.9, 120.9, 120.6, 104.0, 96.3, 18.9, 11.5; MALDI-ToF MS (m/z): Calcd. for [C₃₂H₄₈N₂Si₂+H]⁺: 517.3. Found: 517.4 [M+H]⁺.

Bis{5,5'-bis[(tri(isopropyl)silylethynyl)-2,2'-bipy]}ruthenium Dichloride. Ru(DMSO)₄Cl₂ (460 mg, 0.96 mmol) and 5,5'-bis[(tri(isopropyl)silylethynyl)-2,2'-bipy] (1.0 g, 1.92 mmol) were dissolved in dry DMF (30 mL), and the mixture was heated to 140 °C for 8 h. DMF was removed in vacuo, and the crude dark solid was purified by silica gel chromatography using dichloromethane/methanol = 20/1 to afford a dark green solid (1.1 g, 87%). ¹H NMR (CD₂Cl₂, 400 MHz, ppm): δ 10.15 (d, J = 1.2 Hz, 2H, Py-*H*^f), 8.10 (d, J = 8.4 Hz, 2H, Py-*H*^d), 8.91–8.97 (m, 4H, Py-*H*^{c,e}), 7.55–7.58 (m, 4H, Py-*H*^{a,b}), 1.16–1.20 (m, 21H, CH₃, CH), 1.02–1.04 (m, 21H, CH₃, CH); ¹³C NMR (CD₂Cl₂, 100 MHz, ppm): δ 159.3, 156.9, 156.3, 155.7, 137.7, 135.3, 123.1, 122.4, 122.3, 121.9, 102.5, 102.1, 99.7, 99.6, 18.8, 18.7, 11.7, 11.5; ESI MS (m/z): Calcd. for [C₆₄H₉₆Cl₂N₄RuSi₄]⁺: 1204.5. Found: 1169.5 [M-Cl]⁺.

Ru{5,5'-bis[(tri(isopropyl)silylethynyl)-2,2'-bipy]}₂(2,2'-bipy)Cl₂ (TIPS-Ru-2). 2,2'-Bipyridine (55.0 mg, 0.3 mmol) and bis{5,5'-bis[(tri(isopropyl)silylethynyl)-2,2'-bipy]}ruthenium dichloride (360 mg, 0.3 mmol) were dissolved in a mixture of chloroform (20 mL) and EtOH (20 mL) and refluxed for 3 days. The solvent was evaporated, and the residue was chromatographed on silica gel using dichloromethane/methanol (10:1) as an eluent to afford a red solid (300 mg, 73%). ¹H NMR (CD₂Cl₂, 400 MHz, ppm): δ 9.58 (d, J = 8.8 Hz, 2H, Py-*H*^c), 9.49 (d, J = 8.8 Hz, 2H, Py-*H*^d), 8.96 (d, J = 8.0 Hz, 2H, Py-*H*^f), 8.11–8.20 (m, 6H, Py-*H*^{b,e,i}), 7.72 (d, J = 4.2 Hz, 2H, Py-*H*^g), 7.50–7.54 (m, 6H, Py-*H*^{a,f,h}), 1.03–1.11 (m, 84H, CH₃, CH). ¹³C NMR (CD₂Cl₂, 100 MHz, ppm): δ 157.2, 155.9, 155.7, 152.9, 152.6, 151.5, 141.0, 138.9, 128.5, 126.8, 126.4, 125.6, 124.8, 124.8, 102.4, 101.0, 100.7, 18.5, 11.29, 11.28; ESI

MS (m/z): Calcd. for $[C_{74}H_{104}Cl_2N_6RuSi_4]^+$: 1360.6. Found: 1325.5 $[M-Cl]^-$, 645.3 $[M-2Cl]^{2+}$.

Ru[5,5'-bis(ethynyl)-2,2'-bipy]₂(2,2'-bipy)(NO₃)₂ (Ru-2). To a solution of Ru[5,5'-bis(tri(isopropyl)silylethynyl)-2,2'-bipy]₂(2,2'-bipy)Cl₂ (160 mg, 0.12 mmol) in THF (20 mL) was added dropwise a solution of TBAF (0.5 mmol, 0.5 mL) in THF. The reaction was stirred at RT for 10 h and then quenched with water. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (silica gel, CH₃CN/KNO₃(aq.), 5/1) to afford a red solid (35 mg, 40%). ¹H NMR (CD₃OD, 400 MHz, ppm): δ 8.73–8.75 (d, J = 8.0 Hz, 2H, Py- H^f), 8.69–8.71 (d, J = 8.0 Hz, 4H, Py- $H^{c,d}$), 8.15–8.21 (m, 6H, Py- $H^{b,e}$), 7.893–7.896 (d, J = 1.2 Hz, 2H, Py- H^f), 7.85–7.86 (d, J = 5.6 Hz, 2H, Py- H^g), 7.765–7.769 (d, J = 1.2 Hz, 2H, Py- H^a), 7.52–7.55 (m, 2H, Py- H^h), 4.079 (s, 2H, CCH). 4.072 (s, 2H, CCH). ¹³C NMR (CD₃OD, 100 MHz, ppm): δ 156.3, 155.5, 155.2, 153.2, 152.8, 151.3, 140.3, 140.2, 137.9, 127.4, 124.0, 123.94, 123.91, 123.1, 122.9, 85.7, 77.1, 76.9. ESI MS (m/z): Calcd. (found) for $[M-NO_3]^-$: 728.1 (728.1); Calcd. (found) for $[M-2NO_3]^{2+}$: 333.1 (333.1).

1 or 2. Ru-1 or Ru-2 (70 mg, 0.095 mmol) was added to a stirred mixture of CuCl (1 mg, 0.01 mmol) and *N,N,N',N'*-tetramethylethylenediamine (1 mL) in CH₃CN (40 mL). O₂ was bubbled through the mixture which was kept at 35 °C for 0.5 h. The solid was collected by filtration and washed with pyridine, methanol, water, and dried in vacuum. Further purification of the product was carried out by Soxhlet extraction with methanol for 24 h to afford the CP-1 (63 mg, 95%) or -2 (60 mg, 91%) as red-black powder, respectively.

Detailed Procedures for Photocatalytic Reactions with CPs. *aza-Henry Reactions.* To a flame-dried 10 mL vial was added catalyst (0.50 μmol, 0.002 equiv), tetrahydroisoquinoline derivative (0.25 mmol, 1.0 equiv), and the nitromethane (2.5 mL). The reaction mixture was stirred at room temperature in air and at a distance of ~5 cm from a 26 W fluorescent lamp. After the reaction was complete, the catalyst was removed by filtration. After removal of the solvents, the residue was directly used in the ¹H NMR spectrum. The conversion yields were calculated by integrating the peaks in the ¹H NMR spectrum. Isolated yields were obtained by silica gel column chromatography (CH₂Cl₂/hexane, 3/1 to 1/1).

Aerobic Oxidative Coupling of Amines. To a flame-dried 25 mL flask were added catalyst (0.01equiv), benzylamine (38 μL, 1.0 equiv) (or other benzylamine derivatives), and acetonitrile (10 mL). The reaction mixture was stirred at 60 °C at a distance of ~10 cm from a 450 W Xe lamp. The conversion was obtained by integration of the NMR peaks.

Dehalogenation of Benzyl Bromoacetate. To a flame-dried 25 mL flask was added catalyst (4 μmol, 0.01 equiv), benzyl bromoacetate (92 mg, 0.4 mmol, 1.0 equiv), DIPEA (140 μL), diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate ("Hantzsch ester", 112 mg), and MeOH/THF(10 mL,1/1). The mixture was degassed by three freeze–pump–thaw cycles and was stirred at room temperature at a distance of ~5 cm from a 26 W fluorescent lamp. After the reaction was complete, the catalyst was removed by filtration. After removal of the solvents, the residue was directly used in the ¹H NMR determination. The conversion was calculated by integrating the ¹H NMR spectrum. The benzyl acetate product was isolated by purification with silica gel chromatography with DCM as the eluent.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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