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Conjugated polymers as photoredox catalysts: a new catalytic system using visible light to promote aryl aldehyde pinacol couplings

William D. Rouch, Miao Zhang, Ryan D. McCulla*

Department of Chemistry, Saint Louis University, 3501 Laclede Avenue, Saint Louis, Missouri 63104, USA

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ABSTRACT

The conjugated polymer poly-(*p*)-phenylene (PPP) was synthesized and used as a photoredox catalyst to promote pinacol coupling of aryl-aldehydes with visible light. The reaction required the use of a sacrificial electron donor (Et₃N), and was accelerated by the addition of Lewis and Brønsted acids. A distinct advantage of this photocatalytic system is the robust nature of the system, which is not overly sensitive to impurities, oxygen, or temperature, and proceeds cleanly with few side reactions. As a comparison with the PPP system, the reactivity of $Ru(bpy)_3Cl_2$, a popular photoredox catalyst was compared. The PPP system was superior to the $Ru(bpy)_3Cl_2$ for the pinacol couplings in both rate and yield.

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Since most organic molecules lack the ability to absorb visible light, photochemical reactions require the use of higher energy UV light to induce the desired transformations. Since many compounds absorb UV light, side-reactions and difficult product purifications are common for direct photolysis reactions. Photoredox catalysts have been developed that can become 'active' in the visible spectrum and then facilitate charge-transfer to the organic in question. The recent interest in the use of visible light photocatalytic systems for hydrogen production and waste water remediation are current examples of photoredox catalysis.

The use of photocatalysts in chemical synthesis has a venerable history, and recently, the conjoining of photoredox catalysts and visible light for applications in organic synthesis has been an expanding area of research.¹ Notably, organometallic ruthenium(II) and iridium(III) polypyridine complexes have been used for [2+2] cycloadditions, reductive dehalogenations, enantioselective trifluoromethylations, radical additions, and C–H bond activation.² Additionally, small organic photosensitizers have been used to promote electron transfer initiated radical additions into C=C and C=O.³ While the aforementioned homogenous photoredox catalysts have proven utility, heterogeneous catalysts can be desirable for certain applications.

Heterogeneous photocatalysts are often semiconductors.⁴ Irradiation of a semiconductor promotes electrons from the valence band to the conduction band, and the resulting charge carriers $(h^+_{VB} \text{ and } e^-_{CB})$ can be used to oxidize or reduce adsorbed species with the proper redox potentials. To catalyze organic reactions, photocatalytic systems are designed to take advantage of the reactivity of the nascent radical anion (A^{•-}) or radical cation (D^{•+}) to generate new products through unimolecular rearrangements or reactions with other species at the surface or in bulk solution as shown in Scheme 1. The majority of semiconductor photocatalysts are inorganic materials. An extremely active area of research is the use of titanium dioxide (TiO₂) as a means of pollution remediation.^{3b,3c} To a lesser extent, inorganic semiconductors have been used in synthetic organic reactions.^{1a} Compared to TiO₂, which only has a moderate conduction band potential (-0.7 V vs SCE),⁵ poly-(*p*)-phenylene (PPP) has a much higher conduction band potential of (-1.7 V vs SCE).⁶ Electron transfer to an acceptor can



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Scheme 1. Semiconductor photocatalysis.





^{*} Corresponding author. Tel.: +1 314 977 2838; fax: +1 314 977 2521. *E-mail addresses:* rmcculla@slu.edu, rmccull2@slu.edu (R.D. McCulla).

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Scheme 2. General reaction of benzaldehyde with PPP.

only occur easily if the reduction potential of the acceptor is below the conduction band potential of the photocatalyst. Thus, PPP is expected to behave as a strong reducing photocatalyst.

In initial work by Yanagida and co-workers, benzaldehyde (1) exclusively underwent a pinacol coupling reaction to form hydrobenzoin (2) when PPP was irradiated with visible light in the presence of triethylamine (Et₃N) as the sacrificial electron donor as shown in Scheme 2.^{6a} Upon repeating Yanagida's experiments with our PPP, the results showed that the reaction was very slow (<0.05 mM/h). Formation of the ketyl (I_k) was proposed as the key intermediate in the mechanism. Thus, we hypothesized the addition of Brønsted or Lewis acids would increase the observed rate of product formation.

The poly-(p)-phenylene polymers that were prepared by Yanagida and co-workers in this study, were prepared according to procedures described by Yamamoto and co-workers.^{7,8} After preparation of the Grignard reagent of 1,4-dibromobenzene, the polymerization was catalyzed by nickel(II) dichloride bipyridine to afford a yellow slurry. Soxhlet extraction of the solids for 30 h with toluene yielded a yellow powder of lower molecular weight polymer, PPP-1. Elemental analysis of several batches showed that the extracted PPP consisted of 77.5% carbon, 5.2% hydrogen, and 13.5% bromine on average.⁹ Using GPC analysis, the Mw and Mn were determined to be 500 Da and 363 Da, respectively corresponding to a poly-dispersity of 1.38.9 If it is assumed that the polymerization was terminated by the reaction by a protic impurity, these values correspond with an average chain length of 5-6 phenyl units for PPP-1 with one end terminated by bromine. The insoluble material remaining after Soxhlet extraction consisted of higher molecular weight polymer, PPP-2, which was supported by elemental analysis. The insoluble PPP-2 consisted on average 84.5% carbon, 5.0% hydrogen, and 7.6% bromine, which was consistent with a PPP chain of 12 phenylene units for PPP-2. Since PPP-2 was completely insoluble in all examined organic solvents, the molecular weight could not be determined by GPC. The UV Spectrum of PPP-1, which is available in the supporting information, dissolved in chloroform shows a weak single absorption band that extends past 400 nm with a maximum absorbance at 300 nm. As shown in the supporting information, PPP-2 suspended in chloroform shows an absorbance band that extends past 400 nm with a maximum absorbance at 364 nm.⁹

The FT-IR spectrum of the PPP-2 showed an out-of-plane vibration of the C–H bonds in the *p*-phenylene units at $807 \pm 3 \text{ cm}^{-1}$ $(\delta(para))$ and two out-of-plane C–H vibrations due to a terminal phenyl group at $766 \pm 3 \text{ cm}^{-1}$ ($\delta(\text{mono}_1)$ and $692 \pm 3 \text{ cm}^{-1}$ $(\delta(\text{mono}_2)$ respectively. There was a medium to weak signal at $1075 \pm 3 \text{ cm}^{-1}$ corresponding to the terminal *p*-bromophenyl group v(C-Br). This suggests that the PPP-2 has both terminal phenyl and terminal bromophenyl groups as part of the chain. Since the intensity of the v(C-Br) band is still significant versus the intensity of the combined ($\delta(mono)$ bands suggests that there is a significant amount of the terminal bromophenyl present. Yamamoto and Kovacic have shown that the degree of polymerization in PPP can be approximated by taking the relative intensity ratio (R) of $(\delta(\text{para}))/(\delta(\text{mono}_1) + (\delta(\text{mono}_2))^{10})$ The R ratio of PPP-2 prepared in this study was 2.4–2.6, which shows a relatively high degree of polymerization as comparable to PPP polymers prepared by Yamamoto (*R* = 1.9–3.9) and Kovacic (*R* = 0.6–8.4).

The photoreduction of **1** (5–6 mM) was performed in acetonitrile with 10 mg of either PPP-1 or PPP-2, 1 M Et₃N, and a 0.75 M protic equivalent of a Brønsted acid.¹¹ Initially, the concentration of the hydrogen donor from the Brønsted acid was kept at 75% of the Et₃N concentration so as to maintain excess of the sacrificial electron donor. The basic environment also reduced the possibility of pinacol rearrangement. The photolysis was carried out with eight fluorescent bulbs with an emission range of 400-440 nm in borosilicate test tubes. Prior to irradiation, the heterogeneous mixture was sonicated to break-up the PPP into smaller, more uniform particles followed by argon (Ar) sparging to remove oxygen. The photolysis products were analyzed using GC, GC-MS, and HPLC, and identified as **2** and **3** by comparison with authentic standards.⁵ Rates of product formation and reactant consumption were determined by sampling the photolysis reaction at four or five time points. The reactions were zero-order with respect to 1 and 2 over nearly the entire photolysis, which indicates the reaction is limited by the photon flux. Photoreactions used for the comparison of reactivity were carried out simultaneously. The reactivity of the PPP-1 was compared to PPP-2 using formic acid as the added acid. This revealed that the PPP-2 was 13 times more active than the PPP-1 under these conditions. For the remaining studies, only virgin PPP-2 was used in the model system to compare reactivity rates. PPP can be easily recovered and reused from the reaction by simple centrifugation or filtration. In general, the addition of a Brønsted acid to the photocatalytic system made a dramatic increase in the reaction rate; up to 39.5 times faster for oxalic acid versus no acid. The reaction underwent almost exclusive pinacol coupling with only a trace amount of benzyl alcohol observed. The overall yield of 2 was determined by HPLC analysis and was normally greater than 80%. It should be noted that the formation of **2** always resulted in nearly equal concentrations of the meso and d/l products. The results for our model system with a series of Brønsted acids are presented in Table 1.

Since oxalic acid was the most effective in our standard reaction conditions, the amount of oxalic acid was optimized. The optimum molar ratio of Et_3N /oxalic acid was found to be 5.7. The molar ratio of Et_3N -oxalic acid:**1** showed no significant improvement in rate at a ratio beyond 120. Semi-preparatory scale reactions, (100 mg of **1**), were successful as well.¹² The product could be isolated with a simple work-up followed by silica gel purification (7:3 hexanes/EtOAc, 82 mg, 81% yield).¹²

The addition of an acid has the potential to increase the rate in several ways. First, the pK_a of the ketyl radical in aqueous solution is 8.4–10.5,¹³ and thus, the addition of an acid (HA) would be expected to favor the formation of the ketyl radical ($I_k(H^*)$) versus the ketal anion (I_k), which is expected to disfavor non-productive

Table 1				
Photoredox system	with	Brønsted	acids	

Brønsted acid	Acid ^a (mM)	Rel. rate ^b	2 ^c (% Yield)	3 ^c (% Yield)
None	0	1.0	76 ± 7 ^d	n.d. ^e
HCl	750	9.3	89 ± 7	2 ± 1
Sulfuric	375	17.8	83 ± 1	3 ± 1
Nitric	750	7.4	77 ± 4	3 ± 1
Formic	750	14.4	91 ± 1	n.d. ^e
Acetic	750	14.2	83 ± 11	n.d.
Trifluoroacetic	750	5.8	56 ± 10	3 ± 2
Methanesulfonic	750	4.7	64 ± 10	3 ± 2
Oxalic	375	39.5	90 ± 5	n.d.
Trimesic	250	18.3	91 ± 5	n.d.

^a Theoretical H⁺ concentration available 750 mM.

Relative rates for at least 80% consumption of 1.

 $^{\rm c}\,$ % Yield determined by HPLC relative to consumption of 1 at 80–99% conversion

of **1**.

^d 95% Confidence level.

e not detected.



Scheme 3. Proposed mechanism for acid photocatalytic system.

Table 2

Photoredox system with Lewis acids

Lewis Acid	Acid (mM)	Rel. Rate ^a	2 ^b (% yield)	3 ^b (% yield)
None	0	1.0	76 ± 7 ^c	n.d. ^d
NiCl ₂	6	1.0	n.d.	n.d.
FeCl ₃	6	1.2	50 ± 10	6 ± 3
AlCl ₃	6	7.8	53 ± 10	4 ± 2
$MgCl_2$	6	2.3	57 ± 10	10 ± 8

^a Relative rates for at least 70% consumption of **1** (Ni no reaction).

 $^{\rm c}$ % Yield determined by HPLC or GC relative to consumption of **1** at 70–90% conversion of **1**.

^b 95% Confidence level.

^d Not detected.

oxidations that regenerate **1**. Secondly, the ability of an acid to increase the rate of reaction could occur as a result of electron transfer from the acid anion (A⁻) to either the Et_3N^+or h^+_{VB} . This electron transfer would decrease the amount of non-productive e^-_{CB}/h^+_{VB} recombinations. Examples of this have been shown using a dual electron donor system of ascorbic acid and 1,5-dimethoxy-naphthalene.^{2k} To test this second possibility, an experiment was performed to determine the effect of oxalate on the reaction system in the presence of a non-electron donating base (pyridine). Other bases were tried such as tetramethyl and tetrabutyl ammonium hydroxide but the solubilities of the resulting salts were low. The photoreduction of **1** (5–6 mM) was performed in 9:1 methanol-water with 10 mg of PPP-2, 1 M pyridine, and a 0.75 M protic equivalent of oxalic acid. It was found that this did result in the

Table	3			
PPP-2	versus	$Ru(bpy)_3Cl_2$	in 50 mM	1

Catalyst/Polymer PPP/cat. (mg) Et₃N (mM) Pinacol^a (% yield) Alcohol (% yield) Oxalic acid (mM) PPP-2^b 25 1000 175 81 ± 5 n.d. 7 Ru(bpy)₃Cl₂^d 95 0 Trace n.d. 25 1000 0 Trace Ru(bpy)₃Cl₂ n.d. $Ru(bpy)_3Cl_2^d$ 25 1000 175 Trace n.d. Ru(bpy)₃Cl₂e 7 1000 175 Trace n.d.

^a Yield determined by HPLC at 99% conversion of **1**.

^b Reaction complete (99% conversion of **1**) in 26 h. ^c not detected.

not detected.

^d Allowed to react 40.5 h.

^e Allowed to react 45.5 h.

The following mechanism is proposed for the use of Brønsted acids, which is shown in Scheme 3. The reaction involves the formation of a ketyl anion (I_k) which is converted to a ketyl radical ($I_k(H^*)$). The formation of 2 could be initiated from the coupling of two $I_k(H^*)$ or by coupling $I_k(H^*)$ with I_k or 1. The acid anion can assist the reaction by either electron transfer to the Et₃N⁻⁺ or h⁺_{VB} to regenerate Et₃N or fill h⁺_{VB} preventing charge recombination.

The addition of Lewis acids to the system was also investigated to determine their catalytic ability in the model system. An equimolar equivalent of a Lewis acid was first added to **1** in acetonitrile to form a metal–carbonyl complex, to which Et_3N (1 M) and PPP-2 (10 mg) were then added. Upon complexation of the Lewis acid with the carbonyl, the reactivity of the carbonyl carbon was expected to increase. The results for the addition of four different Lewis acids are shown in Table 2. The addition of Lewis acids to the model system did increase the reaction rates of **1** up to 7.8 times faster for aluminum chloride versus no acid. The reaction also underwent almost exclusive pinacol coupling; however, the overall yields were poor. Further investigation using Lewis acid catalysis was not pursued.

The reactivity of PPP-2 was compared to the photoredox catalyst Ru(bpy)₃Cl₂ to compare its reactivity in our model system. Upon excitation with visible light, Ru(bpy)₃Cl₂ populates a metal to ligand charge transfer state that is easily reductively quenched to form Ru(bpy)₃⁺. Since the reduction potential of Ru(bpy)₃⁺ (-1.3 V vs SCE)^{1b} is below that of **1** (-1.6 V vs SCE)⁶ it was hypothesized that the Ru-catalyst would not effectively reduce **1** (-1.6 V vs SCE). Using three different conditions: oxalic acid-Et₃N catalytic system, 1 M Et₃N, and two-fold excess of Et₃N, the reduction of **1** with 7–10 mg of Ru(bpy)₃Cl₂ was not successful as shown in Table 3. Degradation of **1** with Ru(bpy)₃Cl₂ did occur, but the by-products could not be identified as the mixture was complicated by HPLC. PPP-2 has a high reduction potential and therefore offers a broad scope as to potential compounds that can be reduced.

In summary, the conjugated polymer, poly-(p)-phenylene was synthesized and used to promote homolytic pinacol couplings of aryl-aldehydes with visible light. Analysis of the polymer showed that the PPP-2 had an average chain length of 12 benzene rings. The reaction requires the use of a sacrificial electron donor (Et₃N) and is catalyzed by the presence of certain Lewis or Brønsted acids, with Brønsted acids being the most effective. Yields of the pinacol were as high as 90%, with oxalic acid being the most effective acid tried in the study. The yields of the Lewis acid catalyzed reaction were low, 57% and reactivity was lower. As a comparison, the reactivity of a popular photoredox catalyst Ru(bpy)₃Cl₂ was compared to PPP-2. The Ru-catalyst did not reduce benzaldehyde as expected while PPP-2 reduced benzaldehyde efficiently. The explanation for the rate increases on the addition of acid to the reaction centers on the prevention of back-electron transfer from the ketyl intermediate by either stabilization or filling of the valence band hole in the polymer.

A distinct advantage of this photocatalytic system is that it is robust and not overly sensitive to impurities and other factors. It is also very clean with few side reactions. All reagents were used as supplied from the vendors eliminating the need for elaborate purification or drying of reagents. No elaborate set-ups or equipment are needed to perform the reactions. The reactions will work using regular glass or borosilicate glass reactors. The reactions were not overly sensitive to oxygen as a simple Ar sparging of the reaction mixture was sufficient to remove oxygen.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012. 06.144.

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- 8. Poly-(p)-phenylene PPP; general procedure: 1,4-dibromobenzene (11.8 g) and magnesium turnings (1.22 g) were combined in dry THF (40 mL) under dry argon atmosphere and stirred at room temperature for 1 hour. 50.0 mg of Ni(bpy)Cl2 was added at room temperature, which turned the reaction to a dark red-brown color. The polymerization was highly exothermic, and the reaction was allowed to proceed at reflux for another 16–30 h before being cooled to room temperature. Reaction quenched into 600 mL of EtOH followed by filtration. The solids were then reconstituted with 100 mL 0.1 M HCl(aq), filtered, and washed with water and EtOH prior being dried under reduced pressure. The sample was then purified by Soxhlet extraction with toluene for 30 h. The extract was concentrated under reduced pressure to yield 300 mg of a yellow powder, PPP(1). The insoluble solids were dried under reduced pressure to yield 2.3 g of a yellow powder, PPP(2).
- 9. General Methods: Ultra-visible absorbance spectra of PPP-1 were collected with a shimadzu pharmaspec UV-1700. Ultra-visible absorbance spectra of PPP-2 were collected with a Olis RSM 1000UV/VIS spectrophotometer using an Olis Clarity sample holder. GPC analysis was performed using Agilent 1100 Series HPLC fitted with a UV-Vis diode array detector and Shodex LF-404 temperature controlled column using chloroform. FT-IR performed using a Shimadzu 8400S using KBr pellets. Bruker 400 MHz Broadband NMR with direct probe was used to collect proton signal for the isolated compounds. Shimadzu GC-MS QP2010S, was used to collect molecular fragmentation information for initial identification of possible photoproducts. For elemental analysis, compounds were sent to Atlantic Microlabs (Norcross, GA, USA) for C, H, and Br content.
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- 11. Photocatalytic reactions; general procedure: Carried out using a LZ4-X Luzchem Photoreactor with eight fluorescent bulbs generating approximately 70 W m-2 from 400 to 440 nm. Prior to photolysis, all of the samples were sparged with argon for at least 30 min and sonicated to break up the heterogeneous PPP powder. During the photoreaction, the samples were stirred and the temperature held constant at 25–30 °C. The product analysis was performed by periodic GC analysis using a Hewlett-Packard 5890 Series II GC fitted with a flame ionization detector and DB-5 column. The internal standard used for GC quantifying the aryl aldehydes and products was dodecane. For products not amenable to GC analysis, an Agilent 1100 Series HPLC fitted with a UV-Vis diode array detector and Phenomenex 4.6 × 150 mm C-4 column was used. For determining reaction rates, control reactions were performed where one variable (light, PPP, Et3 N, or the acid) was removed and as comparison to determine the effect of the change.
- 12. Photo-reduction (semi-prep scale) of benzaldehyde with Brønsted acid 2; general procedure: In a 25 mL glass vial, 1370 mg of Et3 N was added to 20 mL of ACN to which 213 mg of oxalic acid was added. 107 mg of 1 was added along with 25 mg of PPP-2. The vial was sealed and sonicated for 30 minutes and sparged with Ar for 30 min. Reaction was photolyzed for 24–36 h, until completed by HPLC. Reaction was filtered to remove catalyst and concentrated to dryness under reduced pressure. Residue dissolved in 5 mL ethyl acetate and 5 mL of water, layers cut, and organics washed with 5 mL sat. bicarbonate (aq) and dried over magnesium sulfate. Purified by silica gel column chromatography using 7:3 ethyl acetate/hexanes. Yield: 82 mg (81% yield). White solid; ¹H NMR (CDCl₃, 400 MHz) δ 2.16 (t, 1H), 2.80 (t, 1H), 4.63 (t, 1H), 4.75 (t, 1H), 7.01–7.18 (m, 10H); ¹³C NMR (CDCl₃, 400 MHz) δ 78.12, 79.13, 126.95(2), 127.10(2), 127.95(2), 128.15(2), 128.27(2), 139.82, 139.76); GC–EIMS *m*/*z* 214, 108, 107, 79, 77.
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