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## Energy Transfer from CdS QDs to a Photogenerated Pd Complex Enhances the Rate and Selectivity of a Pd-Photocatalyzed Heck Reaction

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### Abstract

This paper describes the design of a colloidal quantum dot (QD) photosensitizer for the Pdphotocatalyzed Heck coupling of styrene and iodocyclohexane to form 2-cyclohexylstyrene. In the presence of 0.05 mol% CdS QDs, which have an emission spectrum that overlaps the absorption spectrum of a key Pd(II)alkyliodide intermediate, the reaction proceeds with 82% yield for the Heck product at 0.5 mol% loading of Pd catalyst; no product forms at this loading without a sensitizer. A radical trapping experiment and steady-state and transient optical spectroscopies indicate that the QDs transfer energy to a Pd(II)alkyliodide intermediate, pushing the reaction toward a Pd(I) alkyl radical species that leads to the Heck coupled product, and suppressing undesired  $\beta$ -hydride elimination directly from the Pd(II)alkyliodide. Functionalization of the surfaces of the QDs with isonicotinic acid increases the rate constant of this reaction by a factor of 2.4 by co-localizing the QD and the Pd-complex. The modularity and tunability of the QD core and surface make it a convenient and effective chromophore for this alternative mode of cooperative photocatalysis.

Catalytic transformations involving the photoexcited state of a transition metal (TM) complex afford access to challenging substrates and unusual patterns of reactivity, but methods to controllably generate TM species with excited states that can participate directly in bond-breaking or bond-forming reactions are drastically less well-explored than ground state TM-catalyzed reactions.<sup>1</sup> Previously reported excited state TM-catalyzed reactions operate either by direct photoexcitation of the TM catalyst (Scheme 1A) or by cooperative photocatalysis, in which the TM catalyst is instead excited through energy transfer (EnT) from a photosensitizer (PS) (Scheme **1B**).<sup>2</sup> Among the class of excited state TM complex-catalyzed transformations, Pd-catalyzed Heck-type reactions of alkyl halides with alkenes are fundamentally interesting because they proceed through TM intermediates with radical character,<sup>3</sup> and are particularly useful because they achieve cross-couplings of un-activated sp<sup>3</sup> alkyl halides.<sup>4</sup> These photocatalytic reactions proceed through direct excitation of the starting Pd(0) complex (Scheme 1A), followed by single electron transfer (SET) to an alkyl substrate to generate a Pd(I) alkyl radical,<sup>5</sup> which can then participate in radical addition to an alkene. The photogenerated Pd(I) radical compounds rapidly relax to Pd(II) alkyl species, and can subsequently undergo classical Pd(II) chemistry, including undesirable  $\beta$ hydride elimination. Recent investigations by Fu and co-workers however suggest a second photoexcitation of the Pd(II) intermediate can re-form the Pd(I) alkyl excited state, analogous to known bond-breaking photoexcitations used to generate reactive radicals from transition metalalkyl or -acyl compounds.<sup>3g</sup> This result suggests a third model of TM-catalyzed excited state chemistry (Scheme 1C), in which a sensitizer designed to selectively excite a photogenerated TM intermediate dictates the reaction's rate and selectivity. Here, we demonstrate this alternative mode of cooperative photocatalysis by designing a colloidal quantum dot (QD) photosensitizer to efficiently promote Pd(I) radical chemistry while suppressing  $\beta$ -hydride elimination from the Pd(II) alkyl state in a Heck reaction between cyclohexyl iodide and styrene, Table 1 (top) and Scheme 2.

Dedicated photosensitizers are frequently employed to improve challenging photochemical transformations, especially when competing processes make direct excitation strategies inefficient.<sup>6</sup> This is especially relevant to the system we describe above, in which we propose to sensitize a transient, rather than ground state, species. Illuminating a dedicated photosensitizer with a finite exciton lifetime produces a steady-state concentration available excitons in solution. When sensitizing a ground-state species, having this supply is unimportant, but a transient species

is not certain to undergo direct excitation during its brief lifetime; the presence of excited photosensitizers guarantees a larger fraction of these intermediates will successfully be excited per unit time. We therefore hypothesized that transformations of the sort detailed above would proceed much more efficiently with the use of a dedicated photosensitizer than when relying on direct illumination.

Colloidal QDs, wet chemistry-synthesized semiconductor nanocrystals with size- and materialdependent bandgaps and redox potentials, are ideal photosensitizers because of their large extinction coefficients,<sup>7</sup> stability upon photo-illumination with visible light (particularly when serving as energy donors as opposed to charge donors),<sup>8</sup> tunable surface chemistry,<sup>9</sup> and tunable, narrow-linewidth emission spectra,<sup>10</sup> which facilitates energy-selective photosensitization of species within a mixture.<sup>11</sup> Our group has reported the first example of chemical catalysis triggered by triplet-triplet EnT from a QD,<sup>12</sup> and the first use of energy relays (analogous to those operational within the natural photosynthetic system) to enhance the quantum efficiency of the photocatalytic reduction of H<sub>2</sub>.<sup>13</sup>



Scheme 1. General mechanisms for TM photocatalysis with (A) direct excitation of a TM photocatalyst, (B) EnT to a TM catalyst from a photosensitizer, and (C) direct excitation of a TM photocatalyst plus photosensitization (through EnT) of an intermediate of the TM catalyst.

In the current work, we identify the visible spectrum absorption feature of a photogenerated Pd complex intermediate – compound 7 in **Scheme 2** – and synthesize a QD photosensitizer of appropriate emission energy to efficiently promote re-excitation of this transient intermediate and drive the formation of the Heck intermediate (alkyl radical species) **6**. This second photoexcitation

step – in addition to direct photoexcitation of the initial Pd(0) catalyst – leads to a dramatic increase in reactivity and selectivity of the Heck coupling (**Table 1**, top) from that achieved without photosensitizer, or using a photosensitizer that cannot perform EnT to 7.

**Table 1.** Yield and Selectivity of the Pictured Photo-Heck Reaction upon Addition of Photosensitizers to the Reaction Mixture.<sup>a</sup>



<sup>*a*</sup>Standard conditions: 25 µmol of styrene, 37.5 µmol of iodocyclohexane, 75 µmol of Cs<sub>2</sub>CO<sub>3</sub>, 0.125 µmol of Pd(dba)<sub>2</sub>, 0.375 µmol of Xantphos, and 0.0125 µmol of CdS QDs in 1 mL of benzene were illuminated with 390 nm blue LED under Ar(g) atmosphere at room temperature for 24 h. The yields shown are the combined yield of E and Z isomers; significant yields of the Z isomer were only observed when using Ir photosensitizers. <sup>*b*</sup>NMR yields, reported with respect to their limiting reagent: styrene for Heck product **3** and iodocyclohexane for cyclohexene. <sup>*c*</sup> "Spectral overlap" refers to the extent of overlap between the emission spectra of a sensitizer and the absorbance spectra of intermediate **6**, see the SI for the calculation.



Scheme 2. Mechanism of Pd-photocatalyzed reaction between styrene and iodocyclohexane, illustrating the desired radical-Heck pathway (right) and the competing elimination pathway (left). The photoexcitation of 7 to re-form the Pd(I) alkyl radical species 6 is highlighted in blue. SET = single electron transfer.

Scheme 2 describes the mechanism of the Heck reaction between cyclohexyl iodide and styrene shown in Table 1.<sup>3d</sup> Upon absorption of a photon with minimum energy 2.8 eV, the first excited state of the Pd(0) photocatalyst 5 – which, for our reaction mixture is putatively Pd(0)(Xantphos)<sub>2</sub> – donates an electron to iodocyclohexane 1 (E<sub>0</sub> = -0.85 V *vs.* SCE) to form intermediate 6.<sup>14</sup> 6 then either (i) undergoes radical addition to styrene 2 to form intermediate 8, which forms 9 and the Heck product 3 following  $\beta$ -hydride elimination, or (ii) rapidly decays to the "oxidative addition product" 7, which undergoes  $\beta$ -hydride elimination to form 9 and the cyclohexene byproduct 4. Following either pathway, the starting Pd(0) catalyst is regenerated from 9 in the presence of base (here, Cs<sub>2</sub>CO<sub>3</sub>).

Even though the Pd(0)(Xantphos)<sub>2</sub> compound directly absorbs the 390-nm light of our illumination source, the Heck coupling between styrene and cyclohexyl iodide does not proceed at 0.5 mol% catalyst loading after 24 h illumination with a 390-nm LED without a photosensitizer, **Table 1**. The unsensitized reaction does however produce a 26% yield (with respect to cyclohexyl iodide) of cyclohexene as the only product; we therefore conclude that the photoexcitation and single electron transfer (SET) steps to form the Pd(I) alkyl radical **6** still occur without a

photosensitizer present, but that the relaxation of **6** to the Pd(II)-alkyliodide **7** and subsequent  $\beta$ hydride elimination outcompetes the addition of radical **6** to styrene. We hypothesized that, if we could form the excited state of **7** by EnT from a photosensitizer, we could push the Pd(I)-Pd(II) equilibrium toward the Pd(I) radical intermediate **6** (blue arrow in **Scheme 2**) and promote the corresponding radical pathway.

The proposed photosensitizer for Förster-type EnT to 7 needs to have an emission spectrum that overlaps energetically with the absorption spectrum of the intermediate.<sup>15</sup> Facile  $\beta$ -hydride elimination however makes isolating the absorption spectrum of the Pd(II)-alkyl species challenging (see the SI, Figure S1A); we therefore performed a model reaction where (iodomethyl)trimethylsilane (TMS-CH<sub>2</sub>I), which lacks eliminable protons, was substituted for cyclohexyl iodide. As shown by <sup>31</sup>P-NMR spectra of the reaction mixture after 30 minutes of illumination, Figure S1B of the SI, use of TMS-CH<sub>2</sub>I in place of cyclohexyl iodide leads to a comparatively long-lived intermediate, Pd(II)(Xantphos)alkyliodide, without formation of HPd(II)(Xantphos)I.<sup>16</sup> We could then study this intermediate with steady-state optical spectroscopy to determine an appropriate FRET donor for this species.



**Figure 1. (A)** Ground-state absorption spectra of  $Pd(dba)_2$  with 3 eq. of Xantphos (black), and the same sample plus 300 eq. of TMS-CH<sub>2</sub>I at 0 (red), 10 min. (blue), 20 min. (pink), and 30 min. (green) illumination with the blue LED. The samples were prepared in benzene and were purged with Ar for 10 min before illumination. The main text describes the assignment of the absorbance features. (B) Normalized absorbance (abs) of the  $Pd(II)CH_2TMS(Xantphos)I$  (solid black), obtained from Figure 1A through a procedure described in the text, overlaid with the emission (em) spectra of CdS QDs (R = 2.4 nm), CdS QDs (R= 2.7 nm), CdSe QDs (R = 1.3 nm and 1.4 nm), Ir(ppy)<sub>3</sub>, Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub>, Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, and with the output spectrum of the LED. The emission spectra were collected with an excitation wavelength of 390 nm.

**Figure 1A** shows absorbance spectra of the reaction mixtures following illumination of Pd/Xantphos and TMS-CH<sub>2</sub>I. With increasing time of illumination, the absorbance of Pd(Xantphos)<sub>2</sub> (arrow *1*) decreases and the absorbance of Pd(Xantphos) (arrow *2*) increases. In addition, we observe the formation of a new absorbance feature at ~450 nm (arrow *3*), which we attribute to the Pd(II)CH<sub>2</sub>TMS(Xantphos)I, since NMR indicates there are only three Pd-species present in the mixture: Pd(0)(Xantphos)<sub>2</sub>, Pd(0)Xantphos, and Pd(II)CH<sub>2</sub>TMS(Xantphos)I, see Figure S1B of the SI. To isolate the absorption spectrum of this intermediate, we subtracted the absorbance of the Pd(0) species and Xantphos from the mixture using a titration curve of Pd(dba)<sub>2</sub> with different equivalents of Xantphos (see the SI, Figure S2). The absorbance feature at ~450 nm is independent of the concentration of Pd(0)-species in the system or the equivalents of Xantphos added (see the SI, Figure S3), consistent with our attribution of this feature to Pd(II)CH<sub>2</sub>TMS(Xantphos)I. We did not observe this absorbance feature when performing the same experiment using cyclohexyl iodide, because its eliminable proton makes the corresponding intermediate short-lived (see the SI, Figure S4).

**Figure 1B** shows the isolated absorption spectrum of the Pd(II)CH<sub>2</sub>TMS(Xantphos)I obtained from **Figure 1A** using the procedure described above, overlaid with both the emission spectra of several molecular and QD photosensitizers and the spectrum of the LED used to drive the reaction. The spectral overlap with the emission of CdS QDs with a radius of 2.4 nm suggests that these QDs will best sensitize the Pd(II)cyclohexyl(Xantphos)I intermediate **7**, assuming it has a similar absorbance spectrum to that of the structurally analogous test species formed using TMS-CH<sub>2</sub>I.

As shown in **Table 1**, we do observe dramatically improved yields of Heck product when including 0.05 mol% 2.4 nm CdS QDs in the reaction mixture, compared with the yields of the unsensitized case or when using photosensitizers having weaker spectral overlap with the identified absorption feature. **Figure 2A** illustrates the marked change in the rates of reagent conversion and product formation when the QD photosensitizer is included. The yield of the desired Heck product is reasonably well predicted by the degree of spectral overlap with the identified absorption feature of **7**; note that although the emission of  $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$  is a closer energetic match than that of  $Ir(ppy)_3$ , poorer absorptivity at the excitation wavelength results in a lower magnitude of spectral overlap, as shown in **Table 1**.

Both Ir sensitizers give the Heck product **3** predominantly as its Z isomer, suggesting that each participates in a competing process of triplet-triplet energy transfer with the formed product,

potentially lowering the efficiency of the reaction. We tested additional organic and inorganic sensitizers having emission energies more similar to that of 2.4-nm CdS QDs, but we found that the limited set of very well-matched sensitizers performed poorly due to poor solubility or short fluorescence lifetime (**Table S1**). This result highlights an important advantage of using QDs as photosensitizers: the facile ability to synthetically select a narrow emission spectrum at any desired wavelength, while utilizing tunable surface chemistry to ensure good solubility and stability across a range of reaction conditions.

We performed a set of experiments employing a 467 nm LED as an additional light source, chosen to match the identified absorption of 7, to test our hypothesis that a dedicated photosensitizer would prove superior to direct illumination for exciting a transient species. (**Table S2**) We observe that, as would be expected, addition of the second light source with 0.5 mol% Pd and without QDs increases the production of Heck product from 0% to 5% yield with a product/byproduct ratio of 0.1 after 24 h of illumination. Addition of the second light source with 10 mol% Pd and without QDs increases the production of Heck product from 33% to 55% with a product/byproduct ratio of 0.6 after 24h illumination, in keeping with the reasonable yields observed previously for this reaction when using high Pd loadings and broad excitation. Each of our two-color direct excitation reactions was outperformed by the CdS QD-sensitized reactions shown in **Table 1**, which featured only 0.5 mol% loadings of Pd. These results indicate that (i) direct excitation of the identified Pd(II) intermediate 7 to reform **6** is possible, consistent with the proposed mechanism and the identified absorption feature, and (ii) direct excitation is significantly less effective for sensitizing the transient Pd(II)-alkyl species than including an energetically well-matched photosensitizer.



**Figure 2. (A)** Concentrations of cyclohexyl iodide (black), Heck coupling product (red), and cyclohexene (blue) over the course of this reaction without (open symbols, dashed), and with (solid symbols, solid) the presence of 0.05 mol% CdS QDs. The numbers above the points are the yields of Heck product. **(B)** Yield of the Heck coupling product, relative to styrene, *vs.* illumination time when the reaction mixture includes 0.05 mol% oleate (OA)-capped CdS QDs (black), 0.05 mol% OA-capped CdS QDs with 200 eq. iso-nicotinic acid (red), 0.05 mol% OA-capped CdS QDs with 200 eq. pyridine (green), and 0.05 mol% OA-capped CdS QDs with 200 eq. benzoic acid (blue), determined by <sup>1</sup>H-NMR using diglyme as the internal standard. The ratios between product **3** and byproduct **4** are 3.7 for OA-capped QDs, 2.7 for OA/iNA-capped QDs, 2.2 for OA/BA-capped QDs, and 1.9 for OA-capped QDs with pyridine. The samples were prepared with 25 μmol of styrene, 37.5 μmol of iodocyclohexane, 0.0125 μmol of CdS QDs, 75 μmol of Cs<sub>2</sub>CO<sub>3</sub>, 0.125 μmol of Pd(dba)<sub>2</sub>, and 0.375 μmol of Xantphos in 1 mL of benzene, and were illuminated with a blue LED under Ar(g) atmosphere at room temperature. The lines are guides to the eye.

When one equivalent of the stable radical TEMPO was added to the reaction system without QDs, no TEMPO products were detected and the reaction proceeded as before. In contrast, addition of TEMPO to the QD-sensitized system completely inhibited the reaction, and we observed the TEMPO adduct of the cyclohexyl radical (see the SI, Figure S6). These results indicate that the cyclohexyl radical is (i) a crucial intermediate in the photo-Heck pathway, (ii) not appreciably present in the absence of the photosensitizer, perhaps because of rapid relaxation to the Pd(II) alkyl species, and (iii) formed in the presence of CdS QD photosensitizer, consistent with the proposed cooperative sensitization mechanism (**Scheme 1C**).

It is possible, in principle, that the enhancement of Heck product yield in the presence of QDs is due to either (i) electron transfer (eT) from the QDs to cyclohexyl iodide or (ii) EnT from the QD to the Pd(Xantphos)<sub>2</sub> catalyst, rather than through our proposed mechanism, sensitization of intermediate 7. We have however eliminated these alternative mechanisms through steady-state and time-resolved optical measurements of QD-cyclohexyl iodide and QD-Pd/Xantphos mixtures, detailed in the SI, Figures S7, S8. A further proof that the QDs do not enhance the yield of Heck product by photosensitizing the initial catalyst Pd(Xantphos)<sub>2</sub> catalyst is that, when we attempt the reaction with 450-nm monochromatic excitation (which photoexcites the QDs but not Pd(Xantphos)<sub>2</sub>) in place of the blue LED, we observe no formation of Heck product. When we use 405-nm monochromatic excitation (which photoexcites both the QDs and Pd(Xantphos)<sub>2</sub>), we do form 5% Heck product with respect to styrene, see Figure S9 of the SI. This result indicates that direct excitation of the Pd(0) catalyst is necessary for the reaction to proceed, consistent with the proposed mechanism of QD involvement by selective sensitization of the photogenerated intermediate 7. In addition, we observe no change in the absorption features of the QDs during the course of the reaction, indicating the photosensitizer is highly stable (see Figure S10 of the SI). This is consistent with an energy transfer (as opposed to redox) mechanism of sensitization, which avoids the deleterious buildup of charge in the QDs by removing both charge carriers from the QD simultaneously.

We undertook a small exploration of substrate scope, to demonstrate the general applicability of our results. (**Table S3**) We observe reasonable yields for styrene substrates having both electron-withdrawing and electron-donating aryl substituents. We also tested a small scope of alkyl halides, and found the reaction to be considerably slower when using an alkyl bromide rather than an alkyl iodide (5% yield of desired Heck product), or when using a primary rather than secondary

alkyl iodide (38% yield), in both cases presumably because of a less favorable SET from the excited Pd(0) species to the substrate. This is reflected in the correspondingly low yield of the elimination side product and the low overall consumption of the substrate. In contrast, the reaction proceeds readily when using TMS-CH<sub>2</sub>I because the alpha silicon effect facilitates SET to the halide, and we observe a 77% yield when using this substrate, similar to that obtained with the original secondary alkyl iodide.

In addition to increasing the selectivity of the reaction for the Heck product over cyclohexene, inclusion of the QD photosensitizer increases the overall rate of consumption of the cyclohexyliodide starting material by a factor of three, **Figure 2A**. This result is not inconsistent with, although not necessarily implied by, the proposed mechanism of QD involvement in this reaction. The result could mean that the starting Pd(0) catalyst is re-formed directly from the Pd(II)-alkyl species 7 at an appreciable rate. This elimination is plausible, but we do not have direct evidence for it at this time.<sup>17</sup>

We note that, in contrast with the 0.5 mol% Pd case discussed above, higher loadings of Pd catalyst do produce some Heck product **3** even without inclusion of a photosensitizer. In each case, however, the yield improves dramatically when using 0.05 mol% CdS QDs photosensitizer, and the selectivity diminishes as the Pd loading increases (Table S4 of the SI). These results suggest that a mechanism other than that pictured in **Scheme 2** is active at these higher catalyst loadings.

Given our conclusion that the QD promotes Heck coupling by transferring energy to the Pd(II) intermediate **7** at low catalyst loading, we exploited the tunable surface chemistry of the QDs to further enhance the reaction rate.<sup>18</sup> We functionalized our CdS photosensitizer with iso-nicotinic acid (iNA, see NMR spectra in Figure S11 of the SI), which binds to the QD surface through its carboxylic acid, displacing some of the native oleate ligand, and is terminated with a pyridinic nitrogen that could potentially coordinate to Pd-complexes. We envisioned that this ligand would co-localize the QD and the Pd-catalyst and improve the yield of EnT to **7**. As shown in **Figure 2B**, the rate constant of Heck product formation is a factor of 1.4 times higher when using the iNA-functionalized QDs than for the original oleate-capped QD (see the SI, Figure S12). This enhancement does not occur when we instead add pyridine, which mimics the basicity of the iNA, or benzoic acid (BA), which mimics the structure of the iNA on the surface of the QD. iNA-functionalized QDs also however produce approximately 1.6 times the amount of the cyclohexene byproduct **4** than do OA-capped QDs at 24 h. In addition to increasing the rate of reaction, iNA-

capped QDs produce a better selectivity (ratio of desired Heck product **3** to byproduct **4** = 2.7) when compared to reaction systems featuring BA (2.2), pyridine (1.9), or BA and pyridine together (2.0) (Table S5 of the SI).

In summary, we have identified a mode of cooperative photocatalysis for transition metalcatalyzed excited state reactions in which a photosensitizer interacts selectively with a photogenerated transition metal intermediate. By choosing a CdS QD sensitizer with an emission spectrum that overlaps with the absorption of a Pd(II) intermediate, we drive the formation of a Pd(I) intermediate that promotes Heck coupling rather than to the direct  $\beta$ -hydride elimination byproduct, and improved both the rate and selectivity of a Pd(0)-Pd(I)-Pd(II) photocatalytic cycle. This strategy also drastically reduces the required Pd loading necessary for formation of the Heck product, and significantly outperforms unsensitized systems even when the intermediate is directly excited by a separate light source. Due to the electronically tunable colloidal QDs in this reaction, the ability to design the surfaces of the QDs to have a high affinity for TM complexes, and the versatile chemistry of the radical species the reaction generates, we view this strategy – selective photosensitization of transition metal radical intermediates by QDs – as a general and straightforward pathway to identify and promote reactive transition metal species with radical character, which could be deployed for a diverse set of catalytic transformations.

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**Supporting Information Available.** Experimental details, NMR spectra, additional control experiments, transient absorption and photoluminescence data, Tables S1-S5 and Figures S1-S12.

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