Expanding the Color Space in the Two-Color Heterogeneous Photocatalysis of Ullmann C-C Coupling Reactions

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*KEYWORDS Heterogeneous catalysis, Photocatalysis, Ullmann reaction, C-C cross-coupling.*

ABSTRACT: Ullmann reaction can be heterogeneously photocatalyzed by UV excitation of Pd@TiO$_2$. While a similar dose of visible light does not initiate the reaction, combination with UV light enhances activity and selectivity towards cross-combination products. The reaction involves photo-responsive intermediates, likely associated to the catalyst, where Pd nanostructures can absorb visible radiation and TiO$_2$ the UV component. Hence, a single hybrid-photo-responsive material can have different reactivity upon two-wavelength irradiation enabling direct tuning of yields and selectivity. This color-space expansion promises unprecedented uses in organic chemistry, where improvement in catalytic activity and selectivity will impact the development of catalytic processes with long-term multicycle performance.

The Ullmann reaction reported in 1901[1-2] described the formation of symmetrical biaryl compounds by C-C coupling of aryl halides catalyzed by Cu species. The classic mechanism is mediated by an aryl-cuprate, which after oxidative addition of a second aryl halide yields the final product.[2-3] Ullmann-type reactions produce biaryls with potential pharmacological properties.[4] The challenging formation of non-symmetrical biaryl compounds is specially desirable given their increased synthetic value.[5] Many examples have shown the versatility of C-C cross-coupling reactions that can furnish diverse heterocyclic systems, [6-8] although frequently involving special carbon nucleophiles (i.e. Suzuki, Stille, Hiyama, Negishi or Kumada coupling reagents), higher temperatures and longer reaction times.[9-10] Ullmann homogeneous reactions can also be favored by a combination of bi-metallic catalysts.[11] Studies on heterogeneous catalysis of this reaction were primarily performed utilizing coinage-metal substrates. Ullmann on-surface reactions are known to proceed on Cu, Ag, and Au, usually by the scission of the C-X bonds followed by the formation of C-metal coordination bonds.[12] Further, it is known that the de-halogenation of aryl halides can be performed at room temperature over different metals, including Pd, usually assisted by light or *in situ* H$_2$ sources.[12-14] Additionally, on-surface Ullmann reactions catalyzed by bimetallic nanoalloys show Pd-Au nanoclusters favor C-C couplings under mild conditions.[15-16]

Photoinitiated Ullmann couplings have been reported in homogeneous systems [17-18] and on surfaces where at least the initial dehalogenation step, can be photoactivated.[14] Heterogeneous photoresponsive materials is a growing field in catalysis, where easy separation, minimal product contamination, and reusability are major assets that can be combined with milder photoreaction conditions.[19-21] We have reported on heterogeneous photoresponsive palladium-doped titania (Pd@TiO$_2$), with wavelength-dependent reactivity with different outcomes for upon UV or visible irradiation.[10, 22-23] Here we show that this hybrid photoresponsive material can have different reactivity when irradiated simultaneously with two-color light sources. Briefly, we demonstrate that Pd@TiO$_2$ can catalyze Ullmann reactions under mild conditions, with short reaction times, and excellent yields and selectivity towards non-symmetrical biaryl products using UV-Visible two-color irradiation. Further, Pd@TiO$_2$ photocatalyst can be reused at least three times without significant loss of activity (TOF per PdNP ~5,000 h^{-1}) and excellent selectivity.

The heterogeneous photocatalysis of Ullmann cross-coupling of aryl iodides is explored by using test reaction 1 under conditions described in SI. In brief, catalyst and reagents are mixed together in THF and purged with Ar. The products are obtained upon irradiation with 368 nm and 465 nm LEDs working at 0.4 Wcm^{-2} and 1.0 Wcm^{-2}, respectively, until complete conversion of limiting reagent, or up to 24 h.
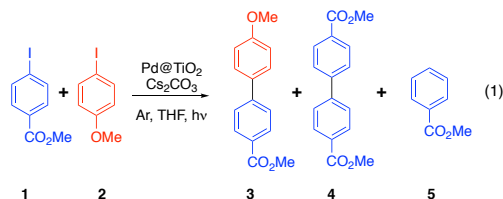
The reaction proceeds under mild conditions in short times (100 % conversion in 1h) when UV and visible light initiate the reaction. Whereas UVA light alone can initiate the reaction, both UV and visible light are required in order to maximize cross-coupling yields, with visible light being responsible for this selectivity (Figure 1). No reaction is observed when the same dose of blue light is used, in spite of the proposed plasmonic absorption of Pd in this region,[24] and only small yields are seen after 24 h. No reaction is detected in the dark.
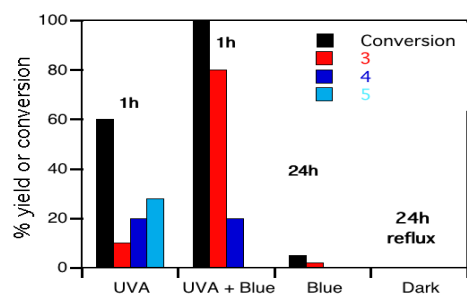
Figure 1. Photocatalytic Ullmann coupling between methyl 4-iodobenzoate and 4-iodoanisol (reaction 1) under different irradiation conditions: UVA (1 h, 368 nm working at 0.4 Wcm^{-2}), UVA + blue – dual-color irradiation – (1 h, 368 nm working at 0.4 Wcm^{-2} and 465 nm working at 1.0 Wcm^{-2}), blue (24 h, 465 nm working at 1.0 Wcm^{-2}) and dark (24 h, reflux). Conversion (black), Ullmann cross-coupling product **3** (red), Ullmann homo-coupling product **4** (blue) and dehalogenation product **5** (light-blue). See also Table S4.

An extensive screening of conditions – where the role of the solvent, base, and wavelength are evaluated – is shown in the SI. The solvent plays an important role in the reaction and deserves special attention (*vide infra*). Among the organic and inorganic bases evaluated (Table S3), Cs$_2$CO$_3$ favors the coupling products and shows negligible amounts of reduced product **5**. Importantly, **3** and **4** are not formed in the absence of base; only **5** is formed under base-free conditions. Figure 1 shows that UV-blue light combination is required to optimize cross-coupling product **3** (Table S4). Under dark conditions no reaction is detected, including no formation of dehalogenate products. This could be explained by the presence of base and the deactivation of Pd surface by iodide formed *in situ*, as recently suggested.[25] This combination of UV and visible light was selected after evaluation of the action spectrum of the system: yield of reaction versus irradiation wavelength (Table S5). The best results are obtained when UV and blue light are combined. Further, the reaction is intensity dependent (Figure 2): increasing UV-light intensity raises both conversion and yield (selectivity remains constant ~0.75); however, greater blue-light intensity favors the cross-coupling product (selectivity increases from ~0.17 up to ~0.75). In an attempt to generalize these observations, we examined a number of related systems, including Au or Cu-decorated TiO$_2$ catalysts, bimetallic materials and the use of Nb$_2$O$_5$ or nanodiamonds (CND) as supports. It is important to highlight that the presence of both TiO$_2$ and Pd are essential for the reaction to proceed (Table S6) and that under those conditions blue light can increase the cross-coupling product formation (Table S5). This is in agreement with dual-color catalytic activity where TiO$_2$ can absorb UV light whereas PdNP be responsible for the visible light absorption, as previously demonstrated.[23] Whereas Pd@TiO$_2$ can serve as catalyst for aryl iodide derivatives, bimetallic systems, such as Pd@Au@TiO$_2$, can extent the scope towards other aryl halides such as Br (not shown).
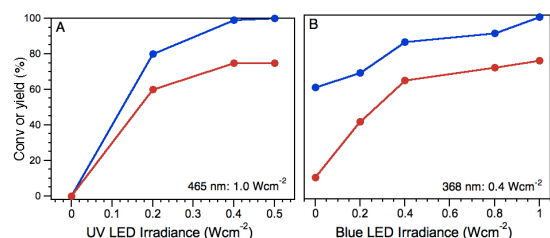

Figure 2. Conversion (blue) and yield (red) of the Ullmann cross-coupling product **3** obtained after 1 h irradiation as a function of the A) UV LED irradiance and B) Blue LED irradiance

As already noted, THF plays an important role on this reaction; when solvents such as dichloromethane (DCM) or MeCN are used, no conversion is detected after 24 h (Table S2). Not surprisingly, MeOH yields **5**, mediated by the strongly reducing ·CH$_2$OH.[22, 26] Further, addition of 1 equivalent of THF to the reaction using an inert solvent (MeCN), is enough to reach reasonable yields in 4.5 h (Figure 3). Under these conditions, THF can easily form the tetrahydrofuranyl radical (THF·, *vide infra*),[27] which is confirmed by addition of TEMPO as a radical trapping agent (Table 1, Figure S11). Not surprisingly,[28] TEMPO inhibits the Ullmann reaction (Figure S12-S13) and only after several hours when TEMPO is depleted the Ullmann reaction occurs (entry iii). A preliminary rate calculation suggests the formation rate for THF· is around 4.4 10^{-5} M s^{-1} under our exposure conditions.
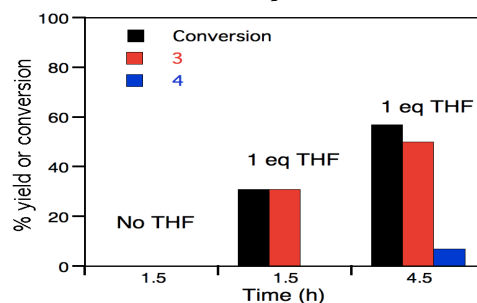

Figure 3. Conversion (black) and yields (Ullmann cross-coupling product **3** –red–, Ullmann homo-coupling product **4** –blue–) of the photocatalytic Ullmann coupling (reaction 1) obtained using MeCN in the absence and in the presence of 1 eq. of THF. Reaction conditions: 0.1 mmol **1**, 0.2 mmol **2**, 20 mg Pd@TiO$_2$, 2 eq. Cs$_2$CO$_3$, 5 mL MeCN and dual-color irradiation (368 nm working at 0.4 Wcm^{-2} and 465 nm working at 1.0 Wcm^{-2}).

Table 1. Ullmann reaction 1 in the presence of TEMPO
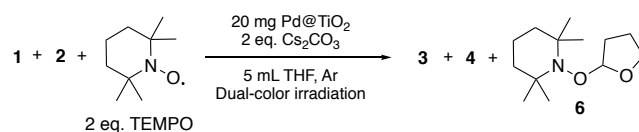
#	1 mmol	2 mmol	Time (h)	Yields% 3	Yields% 4	Yields% 6
i	0.1	0.2	1	ND	ND	39
ii	0.1	0.2	4	12	6	70
iii	0.1	0.2	7	73	29	>99
iv	0	0	7	--	--	>99

The reusability of the material retains 100 % conversion after the 4 cycles tested, preserving great selectivity towards cross-coupling product **3** for at least 3 cycles (Figure 4). Leaching tests suggest that the reaction occurs in the heterogeneous phase: the reaction stops after removal of the solid catalyst confirming the absence of catalytic species in the homogeneous phase (Figure S14). TON values depends on the number of cycles included and after 3 cycles TON ~15,000.
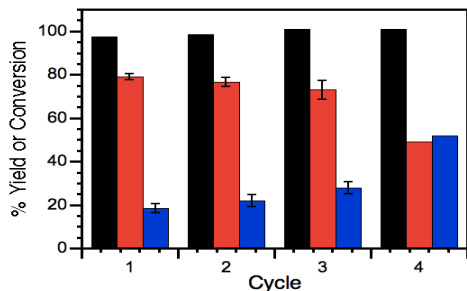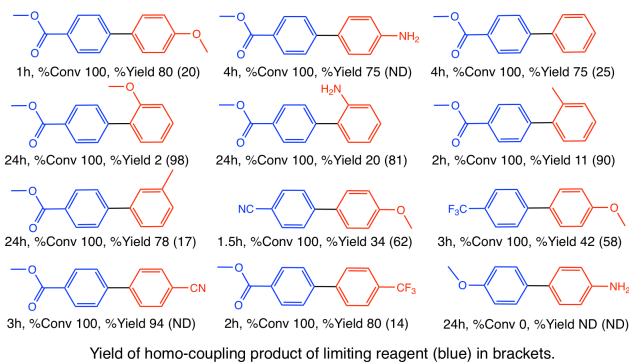
Figure 4. Conversion (black) and yields for **3** (red) and **4** (blue) after several catalytic cycles.

The reaction scope includes i) push-pull systems – with one aryl group substituted with an electron donating group (EDG) and the other with an electron withdrawing group (EWG) – and ii) pull-pull or push-push systems where both substituents are either EWG or EDG. For push-pull systems with moderate EWG (*i.e.* methyl 4-iodobenzoate) the cross-coupling reaction is favored under the conditions studied. Interestingly, no condensation products are found when substituents such as –NH$_2$ are used.[29] EDGs in *ortho* positions usually favor the homo-coupling product of the *para*-substituted aryl iodide. Further, if a strong EWG is used the selectivity towards the homo-coupling product increases, Scheme 1. Although the pull-pull system considered seems to be inactive under the conditions studied, the push-push systems delivered great conversion and yields in 2-3 h (Table S7).

1h, %Conv 100, %Yield 80 (20)   4h, %Conv 100, %Yield 75 (ND)   4h, %Conv 100, %Yield 75 (25)

24h, %Conv 100, %Yield 2 (98)   24h, %Conv 100, %Yield 20 (81)   2h, %Conv 100, %Yield 11 (90)

24h, %Conv 100, %Yield 78 (17)   1.5h, %Conv 100, %Yield 34 (62)   3h, %Conv 100, %Yield 42 (58)

3h, %Conv 100, %Yield 94 (ND)   2h, %Conv 100, %Yield 80 (14)   24h, %Conv 0, %Yield ND (ND)

Yield of homo-coupling product of limiting reagent (blue) in brackets.

Scheme 1: Ullmann reaction scope under two-color heterogeneous photocatalysis.

Our results show that dual-color excitation of the catalytic system improves catalytic activity and selectivity. Thus, UV irradiation can initiate the Ullmann reaction favoring homocoupling (**4**); however, the addition of the second color, can increase the selectivity toward cross-coupling (**3**). Notably, the same visible light colors that controls the Ullmann kinetics and selectivity have no effect (or very little) when UV light is not present, that is, no reaction is observed under visible light only, unless high-power is applied during long-exposure times (Table S4). Based on these results, we propose the reaction mechanism in Scheme 2. The reaction is initiated by formation of the electron-hole pair on the TiO$_2$ surface upon UVA excitation.[22, 30] PdNP, similarly to other metal nanoparticles, serves to capture the electron from the conduction band (CB) increasing the lifetime of the electron-hole pair through energy and spatial separation.[31] The hole in the valence band (VB) is initially trapped by THF yielding THF$^{\bullet}$ (**A**)[27, 32] and a proton; the latter scavenged by the base (**B**). In the absence of base, the proton can be reduced

on the Pd surface yielding surface Pd-H species,[22] favoring the reduction of the aryl iodide whereas inhibiting the reaction of interest (Table S3). The formation of THF$^{\bullet}$ as a mobile radical is confirmed by addition of TEMPO that quantitatively traps the radical to produce **6** (Table 1). These reactions are known to occur with rate constants exceeding 10^8 M^{-1}s^{-1}.[33] The Ullmann reaction is effectively inhibited until the TEMPO scavenger runs out (Table 1 and Figures S12-S13).

In the absence of TEMPO, THF$^{\bullet}$ can transfer its electron to either of the two aryl-iodides, present in the system in comparable concentrations. Thus, it is reasonable to assume that the one with EWG substitution will normally be favored in the competition illustrated in **C**. The aryl radical anion produced by electron capture (**C**) is anticipated to be very short lived[34] and loses iodide before, or concurrently, with the aryl radical associating with the Pd@TiO$_2$ surface (**D**). The kinetics of phenyl radical with THF are around 5 x 10^6 M^{-1}s^{-1}, or about 1000 times slower than diffusion control and thus, even a free aryl radical has a reasonable chance of finding the Pd@TiO$_2$ surface. Notice that in the absence of base the dominant pathway is the reduced product (**5**), emphasizing the importance of proton trapping by the base (Table S3). The EDG-substituted aryl iodide is more likely the favored species to associate with the Pd@TiO$_2$ surface, as other electron rich aromatics are known to do.[35] It is possible that this association occurs at both TiO$_2$ and Pd surface, being the latter more important from a mechanistic point of view (**E**). The oxidative addition of the second aryl halide (assisted by THF$^{\bullet}$) can furnish product through a photoreductive elimination.[36] Thus, visible light makes the final stage of electron transfer from the PdNP to the remaining iodide paving the way for cross-coupling product formation (**F**).

Recent work by Wu, Zhu and col. demonstrated that non-plasmonic NPs, such as PdNP, can induce photocatalysis in the visible region by hot-electron processes.[37-38] Also, the efficiency of visible light in those processes not only depends on the nature of the photocatalyst, but also in the orbital energy of the reagents involved in the reaction,[37] which for the same type of reaction can differ drastically depending on their electronic substitution.[39] Thus, among visible range, short and long wavelengths might have different efficiency to transfer hot electrons to the LUMO orbitals of different reagents. For Ullmann reaction, blue light proved to be the most efficient one when tested for reaction 1 (Table S5). From these seminal studies, the formation of C-C bonds in this system and the role of the visible irradiation fall in line with observations in a variety of other photoactive systems. Thus, visible light can catalyze the reductive elimination (**F**) favoring cross- or homo-coupling products according to the electronic substitution of the reagents.[39]

Finally, iodide can find its way to yield iodine (Figure S15), likely to occur by TiO$_2$ hole scavenging,[40] that may gain some importance as iodide accumulates towards the end of the reaction.
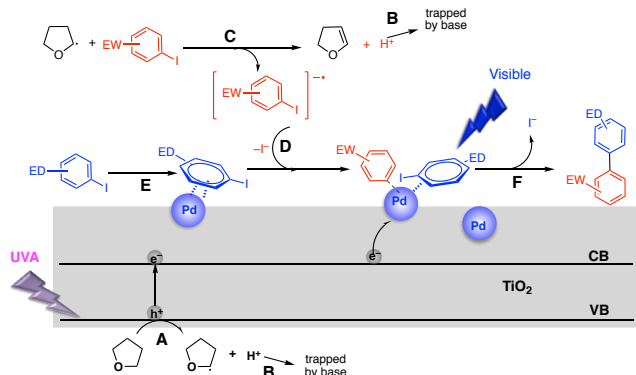
Scheme 2: Proposed mechanism of the photocatalytic Ullmann cross-coupling reaction.

In conclusion, the selective two-color irradiation of Pd@TiO$_2$ as a photocatalyst favors the preferential formation of cross-coupling products by using the corresponding aryl iodide derivatives. Pre-activation of the reagents is not needed as the reaction proceeds with excellent yields under mild conditions. The system is completely heterogeneous and reusable. We believe the expansion of the color-space is an unprecedented strategy that opens the path to complicated cross-coupling reactions by utilizing light as one more reagent that needs optimization. For the Ullmann reaction, two-color exposure enables cross-coupling product formation in a manner that monochromatic exposure cannot achieve.

ASSOCIATED CONTENT

Supporting Information

Details of the synthesis and characterization of catalysts and catalytic reactions procedures as well as other methodological information are reported in the Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

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ABBREVIATIONS

CCR2, CC chemokine receptor 2; CCL2, CC chemokine ligand 2; CCR5, CC chemokine receptor 5; TLC, thin layer chromatography.

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