ACS Catalysis

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Modular, Self-Assembling Metallaphotocatalyst for Cross-Couplings Using the Full Visible-Light Spectrum

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Cite This: *ACS Catal.* 2020, 10, 13269−13274 Read Online

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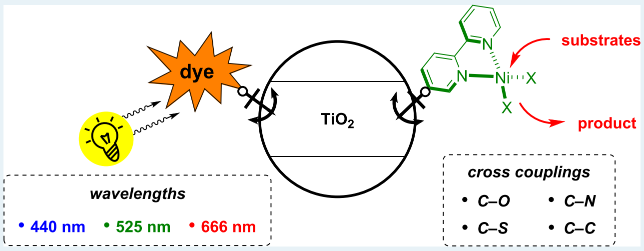


ABSTRACT: The combination of nickel and photocatalysis has unlocked a variety of cross-couplings. These protocols rely on a few photocatalysts that can only convert a small portion of visible light (<500 nm) into chemical energy. The high-energy photons that excite the photocatalyst can result in unwanted side reactions. Dyes that absorb a much broader spectrum of light are not applicable because of their short-lived singlet excited states. Here, we describe a self-assembling catalyst system that overcomes this limitation. Immobilization of a nickel catalyst on dye-sensitized titanium dioxide results in a material that catalyzes carbon−heteroatom and carbon−carbon bond formations. The modular approach of dye-sensitized metallaphotocatalysts accesses the entire visible light spectrum and allows tackling selectivity issues resulting from low wavelengths strategically. The concept overcomes current limitations of metallaphotocatalysis by unlocking the potential of dyes that were previously unsuitable.

KEYWORDS: *metallaphotocatalysis, dual catalysis, nickel catalysis, photoredox catalysis, dye-sensitized semiconductor*

The combination of photo and nickel catalysis (metallaphotocatalysis) has emerged as a powerful strategy for carbon−carbon and carbon−heteroatom cross-couplings (Figure 1A).[1−3] Key to the success is redox or photosensitization events between a nickel catalyst and a photocatalyst (PC). Applicable PCs are iridium and ruthenium polypyridyl complexes,[2] or carbazolyl dicyanobenzenes,[4] with tailored redox potentials or triplet energies, and long-lived excited triplet states (Figure 1B). These PCs are limited to short excitation wavelengths.[5] Current approaches toward photocatalysis with low photon energies require complex catalytic cocktails that enable photon upconversion,[6] osmium complexes as PCs,[7] or multiphoton excitation processes.[5]

The use of abundant dyes that absorb broadly across the visible-light spectrum is highly desirable. The redox potentials and excited state energies of many commodity chemicals, such as fluorescein, rose bengal, or coumarins are in theory suitable for metallaphotocatalysis,[8] but only their singlet exited states are available for photocatalysis because of slow intersystem crossing. The short excited state lifetime of S1 renders a diffusion-limited interaction with a nickel catalyst in a homogeneous solution unlikely (Figure 1B). These dyes are, however, able to sensitize metal oxide (MO) semiconductors, such as TiO$_2$, in dye-sensitized solar cells,[9] or dye-sensitized photocatalysts (DSPs) for light-driven H$_2$ production.[10] The carboxylic acid groups of the dyes bind to the surface hydroxyl groups of TiO$_2$. This facilitates electron injection into the conduction band of the semiconductor upon photoexcitation. This results in a charge-separated species that is sustained for several microseconds.[11]

We wondered whether immobilization of a suitable nickel complex on dye-sensitized TiO$_2$ accesses a bifunctional material that serves as the metallaphotocatalyst (Figure 1C). We hypothesized that such a system overcomes limitations related to short excited state lifetimes and diffusion-controlled energy or single-electron transfer (SET) events because of the close spatial proximity between the PC and the nickel catalyst. The proposed, modular design of dye-sensitized metallaphotocatalysts (DSMPs) allows selecting dyes/wavelengths and nickel complexes depending on the respective application.

Our investigations started with the O-arylation of carboxylic acids that was reported using the PC Ir(ppy)$_3$ (ppy = 2-phenylpyridine) and a nickel bipyridine complex. The cross-coupling proceeds via an energy transfer mechanism,[12,13] and is feasible using semiconductors that absorb blue light,[14−16] but does not work using simple organic dyes.[4] We first tested if anchoring of a nickel complex on TiO$_2$ P25 results (i) in an active, heterogeneous metallaphotocatalyst, and (ii) improves the reaction yield because of spatial proximity of the PC and the nickel catalyst using near-UV light. A ligand equipped with carboxylic acid groups (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid) indeed gave a higher yield of the C−O cross-

Received: September 9, 2020
Revised: October 20, 2020

https://dx.doi.org/10.1021/acscatal.0c03950

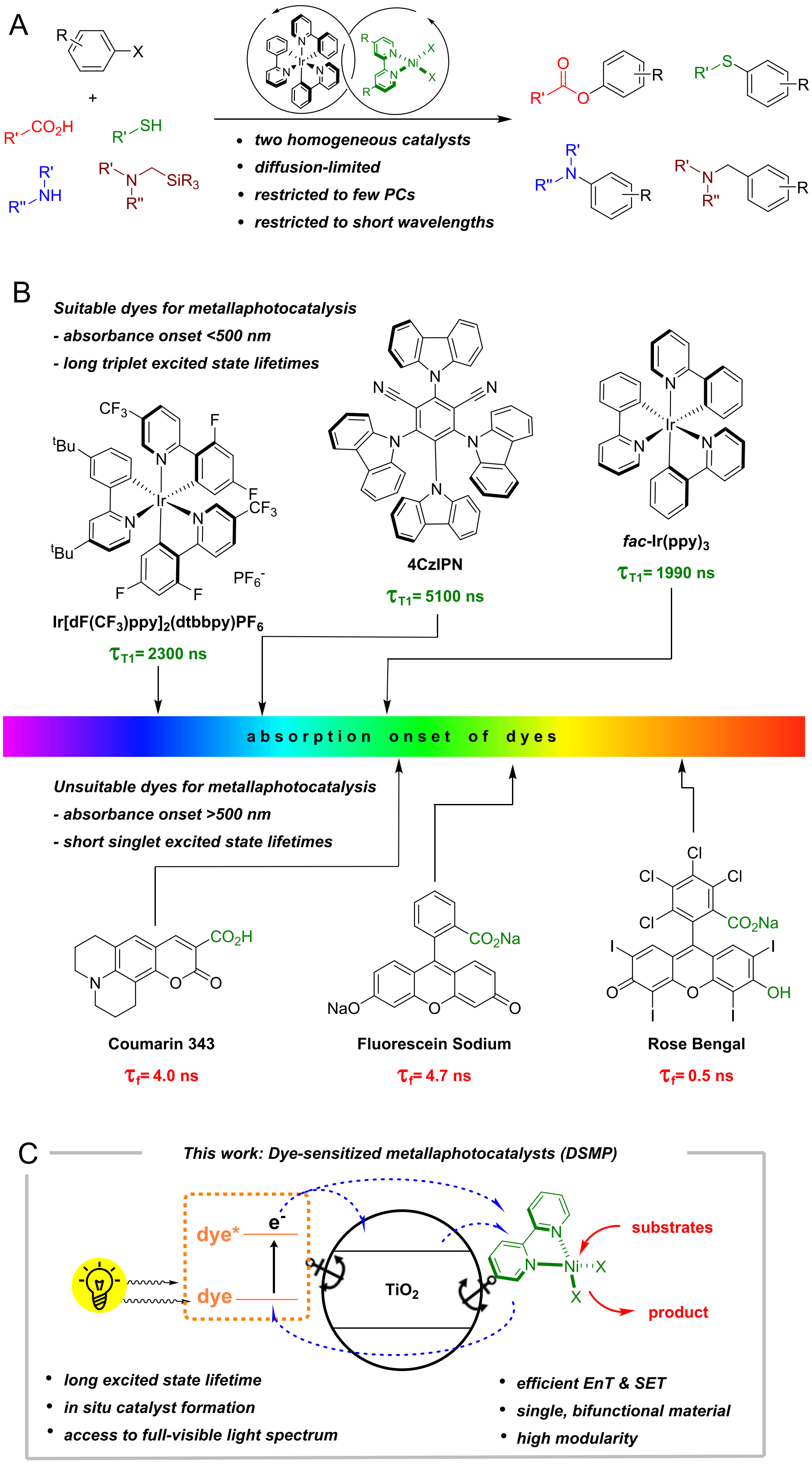
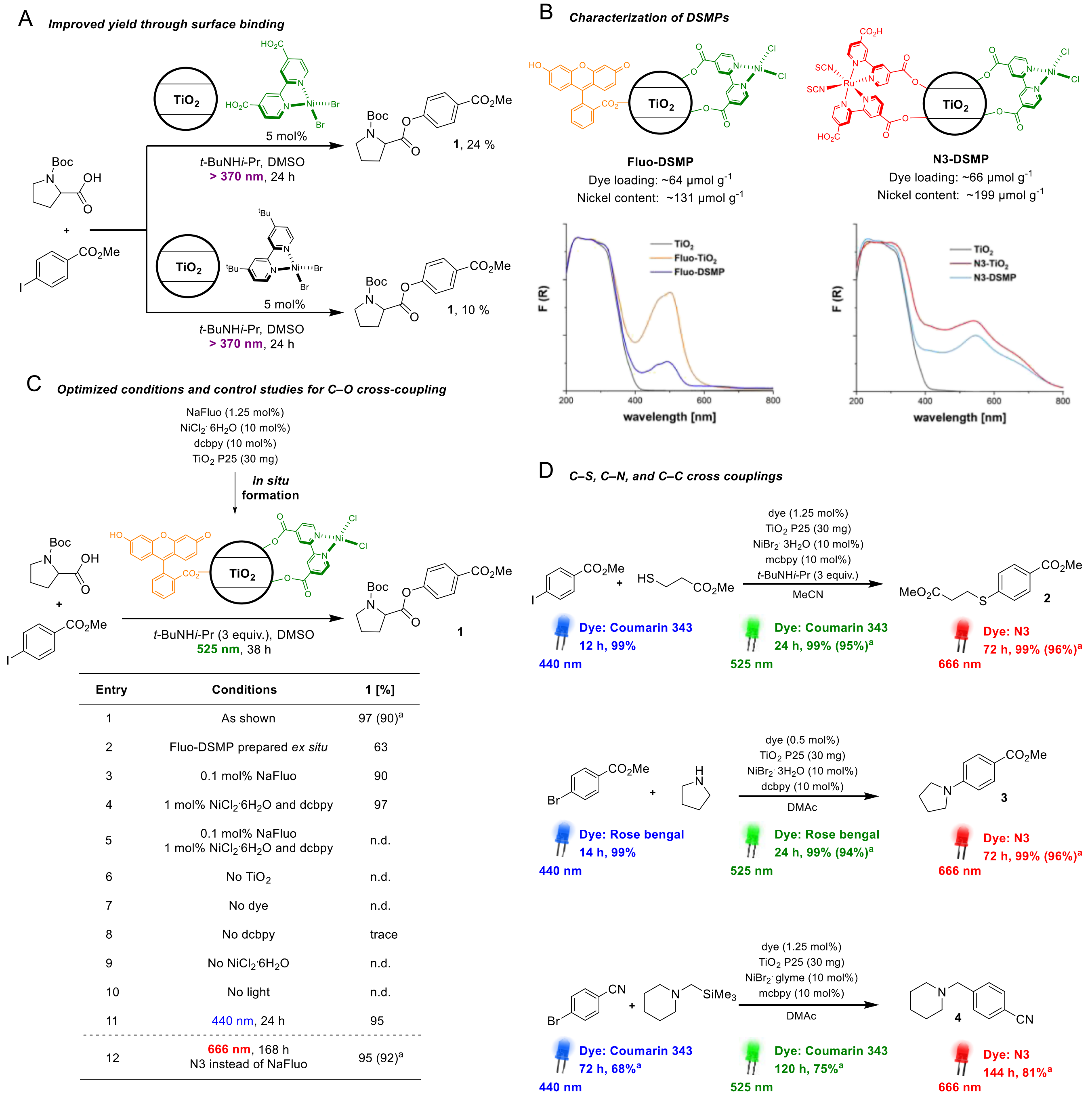


Figure 1. Working hypothesis toward a modular, heterogeneous metallaphotocatalyst. Cross-coupling reactions using homogeneous metallaphotocatalysis (A). Onset of absorption of PCs. The suitability for homogeneous metallaphotocatalysis depends on the excited state lifetime (B). DSMPs are proposed to overcome excited state lifetime limitations (C).

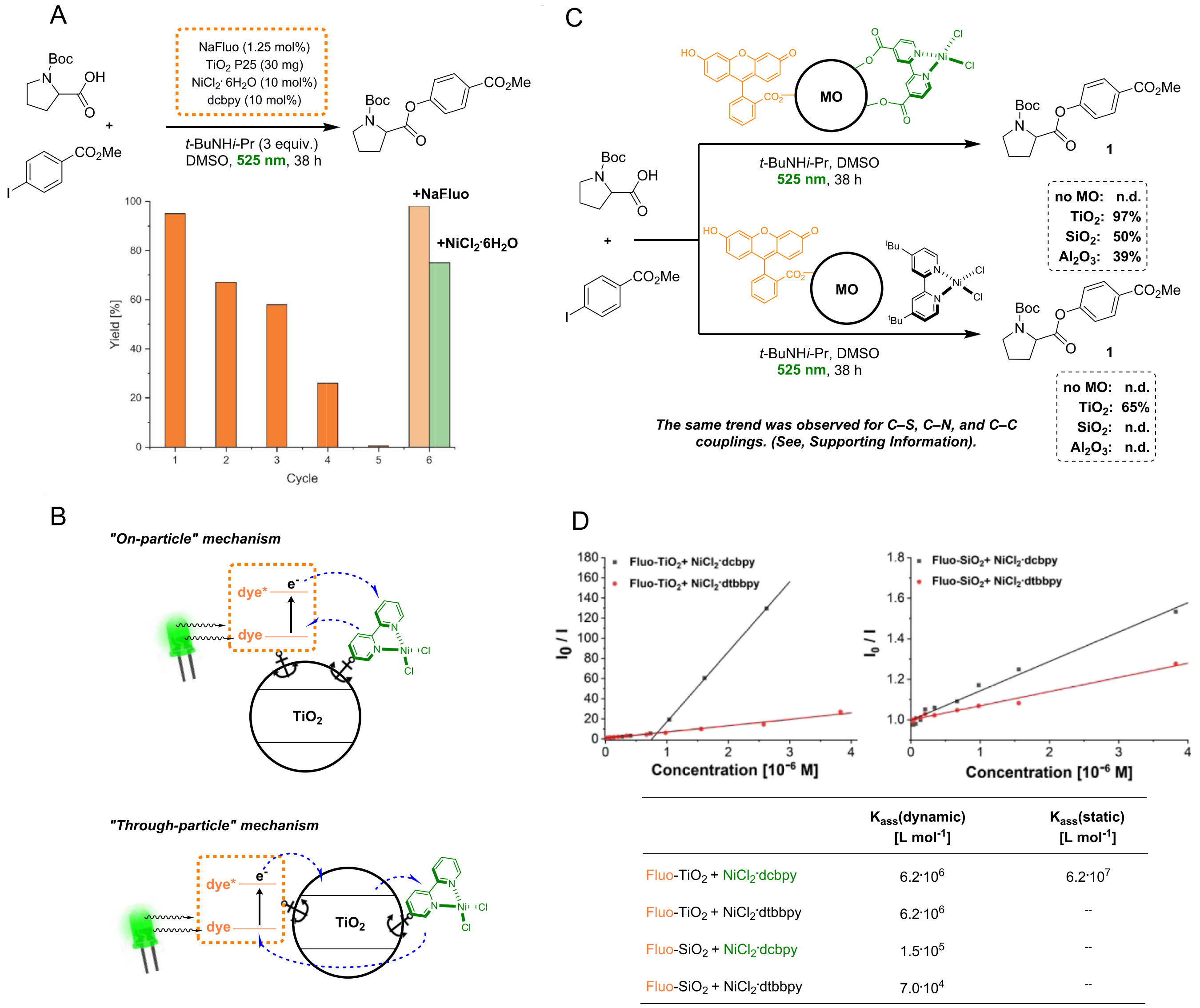


Entry	Conditions	1 [%]
1	As shown	97 (90)^a
2	Fluo-DSMP prepared *ex situ*	63
3	0.1 mol% NaFluo	90
4	1 mol% NiCl$_2$·6H$_2$O and dcbpy	97
5	0.1 mol% NaFluo 1 mol% NiCl$_2$·6H$_2$O and dcbpy	n.d.
6	No TiO$_2$	n.d.
7	No dye	n.d.
8	No dcbpy	trace
9	No NiCl$_2$·6H$_2$O	n.d.
10	No light	n.d.
11	440 nm, 24 h	95
12	666 nm, 168 h N3 instead of NaFluo	95 (92)^a

Figure 2. Self-assembling, modular metallaphotocatalysts enable cross-couplings using the entire visible-light spectrum. Anchoring of nickel complexes on TiO$_2$ P25 improves yield because of spatial proximity (A). UV−vis spectra and nickel/dye loadings of two representative DSMPs (B). Optimized conditions and control experiments for the O-arylation of carboxylic acids using DSMPs (C). C−S, C−N, and C−C cross-coupling catalyzed by DSMPs using blue, green, or red light (D). Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard if not stated otherwise. ^{a}Isolated yields. DSMP = dye-sensitized metallaphotocatalyst, n.d. = not detected, dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid, mcbpy = 4′-methyl-2,2′-bipyridine-4-carboxylic acid, glyme = 1,2-dimethoxyethane, and NaFluo = fluorescein sodium.

coupling product **1** than a ligand that lacks functionalities capable of binding to the semiconductor's surface (dtbbpy = 4,4′-di*tert*-butyl-2,2′-dipyridyl) (Figure 2A). Next, dyes that contain a suitable anchoring group were studied as sensitizers using green light (525 nm). Fluorescein sodium (NaFluo) showed the best results (see Supporting Information). The C−O coupling was also feasible at higher wavelengths (666 nm) using the ruthenium dye N3 that has an excited state lifetime of 20 ns.[9] The DSMPs self-assemble in situ. An ex situ preparation of the DSMPs was carried out to characterize the bifunctional materials (Figure 2B). The UV−vis spectra of the materials confirmed immobilization of the dyes on the MO, and inductively coupled plasma−optical emission spectrometry corroborated anchoring of the nickel complex.

The in situ DSMP approach resulted in a highly selective formation of **1** using blue (440 nm), green (525 nm), or red (666 nm) light (Figure 2C). The best catalytic activities were obtained when the amount of dye (1.25 mol %) and NiCl$_2$·



	K_{ass}(dynamic) [L mol^{-1}]	K_{ass}(static) [L mol^{-1}]
Fluo-TiO_2 + $NiCl_2$·dcbpy	$6.2 \cdot 10^6$	$6.2 \cdot 10^7$
Fluo-TiO_2 + $NiCl_2$·dtbbpy	$6.2 \cdot 10^6$	--
Fluo-SiO_2 + $NiCl_2$·dcbpy	$1.5 \cdot 10^5$	--
Fluo-SiO_2 + $NiCl_2$·dtbbpy	$7.0 \cdot 10^4$	--

Figure 3. Mechanistic investigations. Recycling experiments showed that catalytic inactive materials still contain nickel complexes and dye molecules (A). DSMPs might work via an "on-particle" and/or "through-particle" mechanism (B). Experiments using insulating MO and diffusion-controlled metallaphotocatalysis (C). Spectrophotometric titrations show static quenching for DSMPs, whereas solely dynamic quenching was observed in other systems (D). MO = metal oxide, dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid, dtbbpy = 4,4′-di*tert*-butyl-2,2′-bipyridine, and Fluo = fluorescein.

dcbpy (10 mol %) exceeded the loading that was determined using ex situ DSMP preparation. This is rationalized by a dynamic equilibrium between immobilized and unbound $NiCl_2$·dcbpy as well as dye molecules, which also contribute to productive catalysis in the course of the bulk experiment.[10] Reducing the amount of dye (0.1 mol %) or $NiCl_2$·dcbpy (1 mol %) still resulted in almost quantitative yield of the desired ester. When the dye and the nickel complex are used in such low amounts, no product formation was observed. We assume that high loadings of either $NiCl_2$·dcbpy or the dye are sufficient for the formation of a monolayer on TiO_2 and the resulting close spatial proximity of Fluo and the nickel complex is responsible for the catalytic activity. It has to be noted that also the substrates and the base are likely to bind to the surface of TiO_2, which could contribute to the performance of the catalytic system. No product formation was observed in the absence of TiO_2 P25, the dye, dcbpy, nickel salt, or light. In agreement with previously reported protocols for metallaphotocatalyzed C−O arylation of carboxylic acids,[12−16] the substrate scope is limited to electron-poor aryl halides (see Supporting Information).

The DSMP approach also enabled metallaphotocatalyzed C−S,[17] C−N,[18] and C−C[19] bond formations that proceed via SET processes (Figure 2D). Because the C−S[17] and C−C[19] couplings proceed via a single-electron oxidation of the substrate and a single-electron reduction of a nickel complex, we assume that the affinity of the substrates to the semiconductors' surface has a positive effect on the catalytic activity.

The modular design principle and the self-assembling strategy facilitated a straightforward optimization of dyes, nickel salts, and ligands resulting in selective cross-couplings using blue (440 nm), green (525 nm), and red (666 nm) light. With regard to the C−C coupling, 68% of the desired product (**4**) were obtained using blue light, which is similar to the homogeneous metallaphotocatalysis system.[19] Reactions at

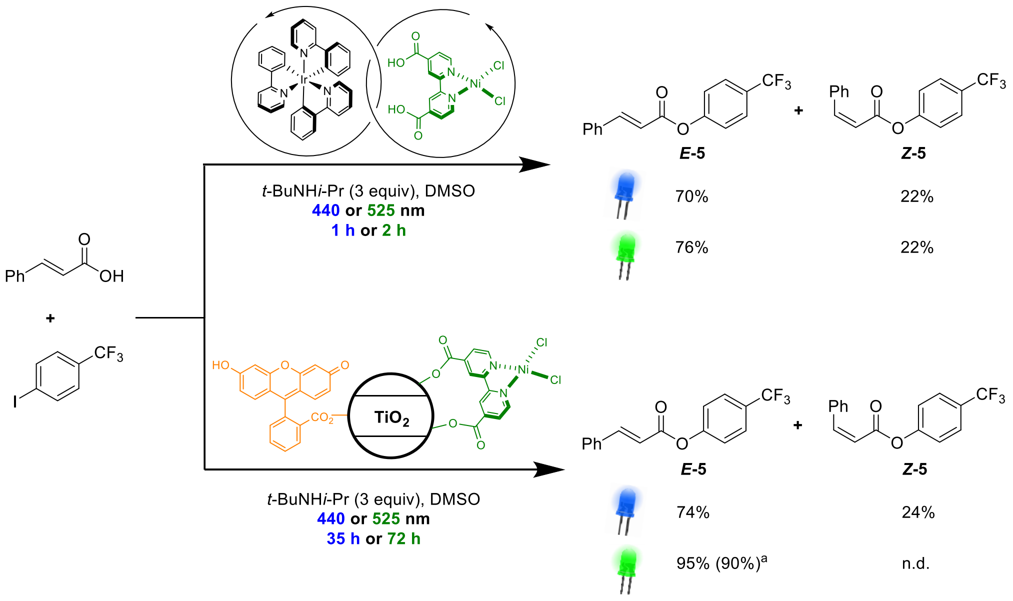


Figure 4. C−O arylation of (*E*)-cinnamic acid with 4-iodobenzotrifluoride with different metallaphotocatalyst systems. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard if not stated otherwise. [a]Isolated yield in parentheses.

higher wavelengths, not accessible with the original, homogeneous approach, resulted in a higher selectivity.

The dynamic equilibrium between immobilized and unbound molecules is responsible for leaching of nickel and fluorescein during catalyst recycling studies and caused a gradual decrease of the yield of **1** (Figure 3A). Addition of either NaFluo or the nickel salt restored the catalytic activity, which is in agreement with the experiments using low amounts of either the dye or the nickel complex (Figure 2C). This indicated that the amount of immobilized dye molecules and nickel complexes has to be above a certain limit to observe catalytic activity. We, therefore, questioned if only the close proximity of the dye molecules and the nickel complex is responsible for productive catalysis, and TiO_2 P25 only acts as the support. In other words, an "on-particle" rather than a "through-particle" mechanism could be responsible for overcoming the short excited state lifetime (Figure 3B). To test this hypothesis, we substituted TiO_2 P25 with the insulating MO SiO_2 and Al_2O_3 that only enable binding of the dye and the nickel complex and observed product formation for all cross-couplings, but with a significantly lower efficiency compared to TiO_2 P25 (Figure 3C). A second set of experiments was carried out using a nickel complex that is not able to bind to the surface of MO. Here, only experiments with the semiconductor TiO_2 P25 gave productive catalysis. This confirms that dye sensitization leads to a charge-separated species that is sufficiently long-lived to turn over a homogeneous nickel catalyst in a semiheterogeneous, diffusion-controlled reaction. Spectrophotometric titrations unveiled the electronic communication between the excited dye and the immobilized nickel complex "through" a semiconductor. Static fluorescence quenching of fluorescein-sensitized TiO_2 P25 was observed with a nickel complex that binds to the semiconductor's surface ($NiCl_2$·dcbpy). $NiCl_2$·dtbbpy showed solely dynamic quenching (Figure 3D). Titration experiments with fluorescein bound to SiO_2 instead of TiO_2 P25 displayed dynamic quenching behavior in the case of both nickel complexes, and significantly lower quenching rates. Taking all results together, we assume that a combination of "on-particle" and "through-particle" processes is responsible for the high catalytic activity of DSMPs with TiO_2 P25.

In addition, we sought to compare the selectivity of DSMPs with homogenous metallaphotocatalysis systems in the C−O arylation of (*E*)-cinnamic acid with 4-iodobenzotrifluoride (Figure 4). The resulting coupling product (***E*-5**) is prone to subsequent photocatalytic isomerization or cycloadditions that could lead to low selectivities.[20,21] We indeed observed significant amounts of the undesired *Z*-isomer (***Z*-5**) when $Ir(ppy_3)$ was used as PC using 440 nm irradiation. Other Ir complexes gave even worse results (see Supporting Information). Control experiments showed that ***E*-5** is also slowly converted to ***Z*-5** at 440 nm in the absence of a PC (see Supporting Information). The selectivity was, however, not improved using $Ir(ppy_3)$ and 525 nm irradiation, because the triplet energy of the PC is not wavelength-dependent. The *E*−*Z* isomerization was also observed when the reaction was catalyzed by a DSMP at 440 nm, but was totally suppressed by switching to higher wavelengths, resulting in the selective formation of ***E*-5**.

The DSMP concept overcomes the constraint of long excited triplet state lifetimes of PCs for metallaphotocatalysis and unlocks the potential of many dyes that were previously unsuitable because of their short-lived excited S1 states. Many cross-couplings can be carried out using the entire visible light spectrum and selectivity issues can be tackled strategically. The simplicity and modularity of DSMPs suggest that the present approach will complement the existing methods.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c03950.

Experimental procedures, characterization of products, and copies of the $^1H/^{13}C/^{19}F$ NMR spectra of the prepared compounds (PDF)

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Notes

An early version of this manuscript was previously deposited on ChemRxiv: Reischauer, S., Strauss, V., and Pieber, B. A Modular, Self-Assembling Metallaphotocatalyst for Cross-Couplings Using the Full Visible-Light Spectrum. https://doi.org/10.26434/chemrxiv.12444908.v1 (2020).

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the Max-Planck Society for generous financial support. S.R. and B.P. thank the German Chemical Industry Fund (Fonds der Chemischen Industrie, FCI) for funding through a Liebig Fellowship. B.P. thanks the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy—EXC 2008—390540038—UniSysCat for financial support. We thank our colleagues Prof. Peter H. Seeberger, Dr. Jamal Malik, Dr. Martina Delbianco, Dr. Kerry Gilmore, Dr. Lukas Zeininger, Cristian Cavedon, Silvia Fürstenberg, Jessica Brandt, and Katharina ten Brummelhuis (all MPIKG) for scientific, technical, and analytical support.

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