

# Modulating the Surface and Photophysical Properties of Carbon Dots to Access Colloidal Photocatalysts for Cross-Couplings

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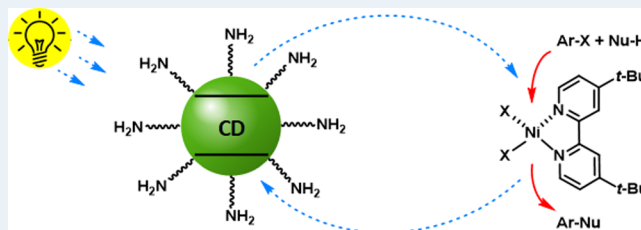
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Supporting Information

**ABSTRACT:** Photoredox-mediated Ni-catalyzed cross-couplings are powerful transformations to form carbon–heteroatom bonds and are generally photocatalyzed by noble metal complexes. Low-cost and easy-to-prepare carbon dots (CDs) are attractive quasi-homogeneous photocatalyst alternatives, but their applicability is limited by their short photoluminescence (PL) lifetimes. By tuning the surface and PL properties of CDs, we designed colloidal CD nano-photocatalysts for a broad range of Ni-mediated cross-couplings between aryl halides and nucleophiles. In particular, a CD decorated with amino groups permitted coupling to a wide range of aryl halides and thiols under mild, base-free conditions. Mechanistic studies suggested dynamic quenching of the CD excited state by the Ni co-catalyst and identified that pyridinium iodide (pyHI), a previously used additive in metallaphotocatalyzed cross-couplings, can also act as a photocatalyst in such transformations.

**KEYWORDS:** carbon dots, nano-photocatalyst, nickel catalysis, cross-coupling, pyridinium iodide



## 1. INTRODUCTION

Carbon dots (CDs) are a new class of carbon-based photoluminescent nanomaterials.<sup>1,2</sup> These low-cost, environmentally friendly nanoparticles can be easily prepared following simple carbonization methods from a variety of earth-abundant carbon sources, including waste products.<sup>3,4</sup> Owing to their excellent light absorption, electron-transfer ability, and photostability, CDs have shown high potential as photocatalysts for water splitting and pollutant degradation.<sup>5–7</sup> Thus, CDs also seem to be ideal sustainable alternatives to common photocatalysts in organic synthesis,<sup>8</sup> such as ruthenium and iridium polypyridyl complexes, organic dyes, and heterogeneous semiconductors.<sup>9–11</sup> However, their short photoluminescence (PL) lifetime limits their applications to simple organic transformations (Figure 1A).<sup>12–14</sup>

In our previous study, we overcame this drawback by immobilizing CDs on titanium dioxide (TiO<sub>2</sub>) to create a heterogeneous system that absorbs visible light and generates long-lived charge-separated species.<sup>15</sup> By combining these recyclable and photostable composite materials with an acid-functionalized Ni bipyridine complex, we could perform several visible-light-mediated carbon–heteroatom cross-couplings (Figure 1B). Efficient electronic communication between the Ni catalyst and our CD/TiO<sub>2</sub> nanocomposite required (i) pre-immobilization of the CDs on TiO<sub>2</sub> aided by carboxylic acid groups on the CD surface and (ii) Ni ligands containing carboxylic acid functionalities that, in return, decreased the electron density on the catalytic metal center, which limits the applicability to certain cross-couplings.<sup>16,17</sup>

The possibility of using CDs as quasi-homogeneous colloidal nanocatalysts is attractive<sup>14,18</sup> in allowing for a much more flexible catalytic system. The lack of a requirement for immobilization on TiO<sub>2</sub> would expand the portfolio of CDs to analogues with different surface functionalities and photophysical properties (i.e., not strictly matching the TiO<sub>2</sub> energy levels).<sup>19–21</sup> Similarly, more efficient Ni complexes could be implemented. In this scenario, the CDs act as visible-light-absorbing nanocatalysts, offering a higher surface area for catalysis and better light penetration.<sup>14,18</sup>

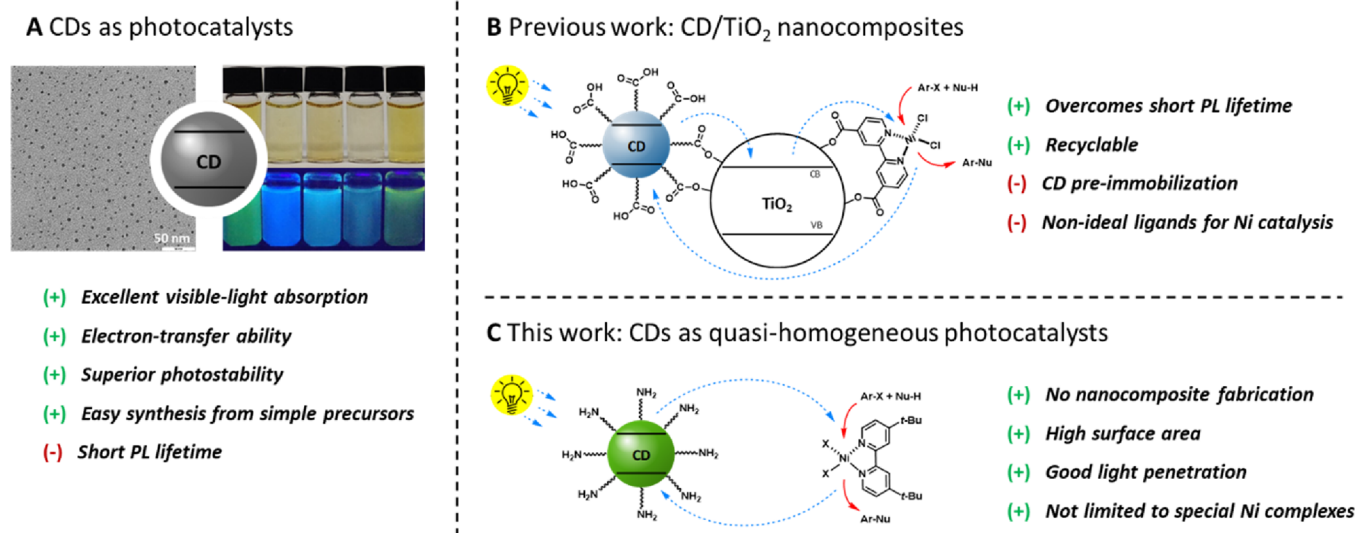
Here, we demonstrate that CDs can be designed to generate colloidal nano-photocatalysts for visible-light-mediated Ni-catalyzed cross-couplings. By tuning the surface and PL properties of CDs, we have discovered that a CD decorated with amino groups photocatalyzes a broad range of carbon–heteroatom cross-couplings between aryl halides and nucleophiles in the presence of a molecular Ni complex (Figure 1C). Moreover, this CD permitted the development of a base-free protocol that allowed for expanding the scope of C–S cross-couplings to aryl bromides. Mechanistic studies shined light on the process of sensitization and identified that pyridinium iodide (pyHI), which was previously used as an additive in metal-

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**Figure 1.** (A) Schematic representation of CDs as metal-free photocatalysts. (B) CD/TiO<sub>2</sub> nanocomposites as photocatalysts for dual Ni-mediated cross-couplings. (C) Colloidal CDs as photocatalysts for dual Ni-mediated cross-couplings (this work).

laphotocatalyzed cross-couplings,<sup>22</sup> also can act as a photocatalyst in such transformations.

## 2. RESULTS AND DISCUSSION

Two CDs (CD1 and CD2) were prepared from glucosamine hydrochloride (GlcN·HCl) using  $\beta$ -alanine ( $\beta$ -Ala) and 1,3-diaminobenzene as doping agents following established procedures (Figure 2A).<sup>23,24</sup> Both dots presented a spherical shape and an amorphous core (Figures S2 and S7). Due to the different dopants, the surface of CD1 mainly consisted of carboxylic acid groups,<sup>23</sup> whereas CD2 was predominantly stabilized by amino functionalities and deoxyfructosazine derivatives,<sup>24</sup> as indicated by NMR analysis (Figure S5) and the zeta potentials (Figure S4). Spectroscopic analysis of the colloidal carbon nanodots revealed that the aromatic doping agent led to significantly improved absorption in the visible part of the electromagnetic spectrum. Excitation of CD1 resulted in a blue luminescence, whereas CD2 emitted green light.

The surface carboxylic acid groups of CD1 enabled immobilization on TiO<sub>2</sub>, which was essential for the use of these CDs in heterogeneous metallaphotocatalytic C–O arylations of carboxylic acids (Figure 2B, entry 1).<sup>15</sup> No product was formed using CD1 in the absence of TiO<sub>2</sub> (Figure 2B, entry 2). Lower yields were obtained with the CD2/TiO<sub>2</sub> nanocomposite (Figure 2B, entry 3), but the reaction could be performed even in the absence of the semiconducting material. CD2 enabled homogeneously catalyzed metallaphotocatalysis, providing 23% of the target molecule under similar conditions (Figure 2B, entry 4). We assumed that the photocatalytic activity of CD2 is a result of the stronger absorption at 440 nm in combination with the amino surface groups that led to coordination to the Ni complex, thereby overcoming the short PL lifetime.<sup>25–27</sup> Optimization studies showed that 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbbpy), which is commonly used as a Ni ligand in homogeneous metallaphotocatalysis, gave improved results (Figure 2B, entry 5). Further screenings of all reaction parameters resulted in conditions that afforded the desired product in an 80% yield within 24 h (Figure 2B, entry 6, and Table S4). Control studies confirmed the necessity of all

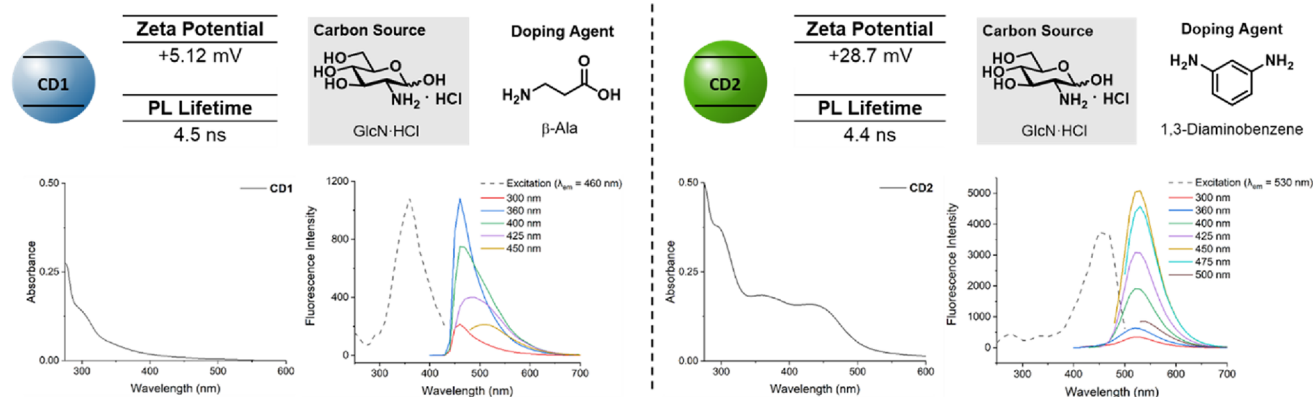
ingredients of the catalytic cocktail as well as blue light irradiation (Table S4).

Next, we studied if the combination of CD2, a Ni(II) salt, and dtbbpy could be used for other metallaphotocatalytic carbon–heteroatom cross-couplings (Figure 2C). To our delight, we found that CD2 was a suitable photocatalyst for the metallaphotocatalytic coupling of aryl halides with carboxylic acids, thiols, sodium sulfonates, sulfonamides, and amines. The optimized conditions also resulted in product formation using CD1, but yields were generally lower.

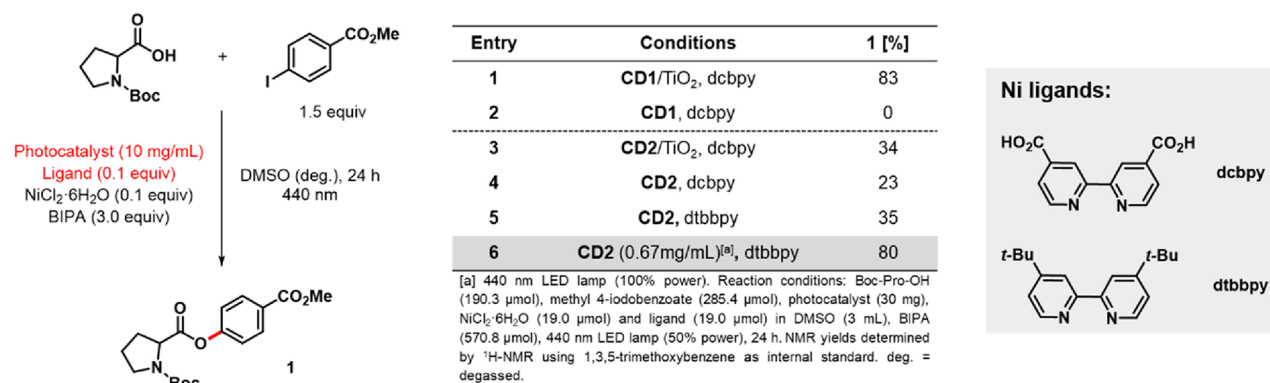
In particular, the use of CD2 in combination with NiBr<sub>2</sub>·3H<sub>2</sub>O, dtbbpy, and *N*-*tert*-butylisopropylamine (BIPA) in dimethylacetamide (DMAc) resulted in an excellent yield for the C–S cross-coupling of methyl 3-mercaptopropionate with methyl 4-iodobenzoate (Figure 3A, entry 1). No product formation was observed when the reaction was carried out using the corresponding aryl bromide under identical conditions (Figure 3A, entry 2). A literature survey revealed conflicting outcomes for this type of reaction. Aryl bromides were successfully coupled with thiols using metallaphotocatalysis when 3,7-(4-biphenyl)-1-naphthalene-10-phenoxazine was applied as a photocatalyst.<sup>28</sup> On the contrary, carbon nitride and dye-sensitized TiO<sub>2</sub> photocatalysts were limited to aryl iodides.<sup>29,30</sup> Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> in combination with a Ni(II) salt and dtbbpy was originally reported to only couple aryl iodides,<sup>31</sup> but a more recent report showed that the scope of this reaction could be extended to aryl bromides following the addition of pyHI to the reaction mixture.<sup>22</sup> This additive and its downstream products were proposed to serve as a quencher for the photocatalyst and as an electron shuttle between the photocatalyst and the Ni complex and to prevent the formation of Ni–thiolate complexes that act as inner filters.

We noticed that, in our protocol, addition of BIPA to the reaction mixture promoted the formation of a highly absorbing Ni–thiolate complex, acting as an inner filter (Figure 3A). Considering the abundant amino groups on the surface of CD2 (9303  $\mu$ mol/g; Section S3.3), we hypothesized that the reaction could be performed under “base-free” conditions to limit the formation of these highly absorbing species. In the absence of the base (BIPA), aryl bromides (and iodides) reacted efficiently

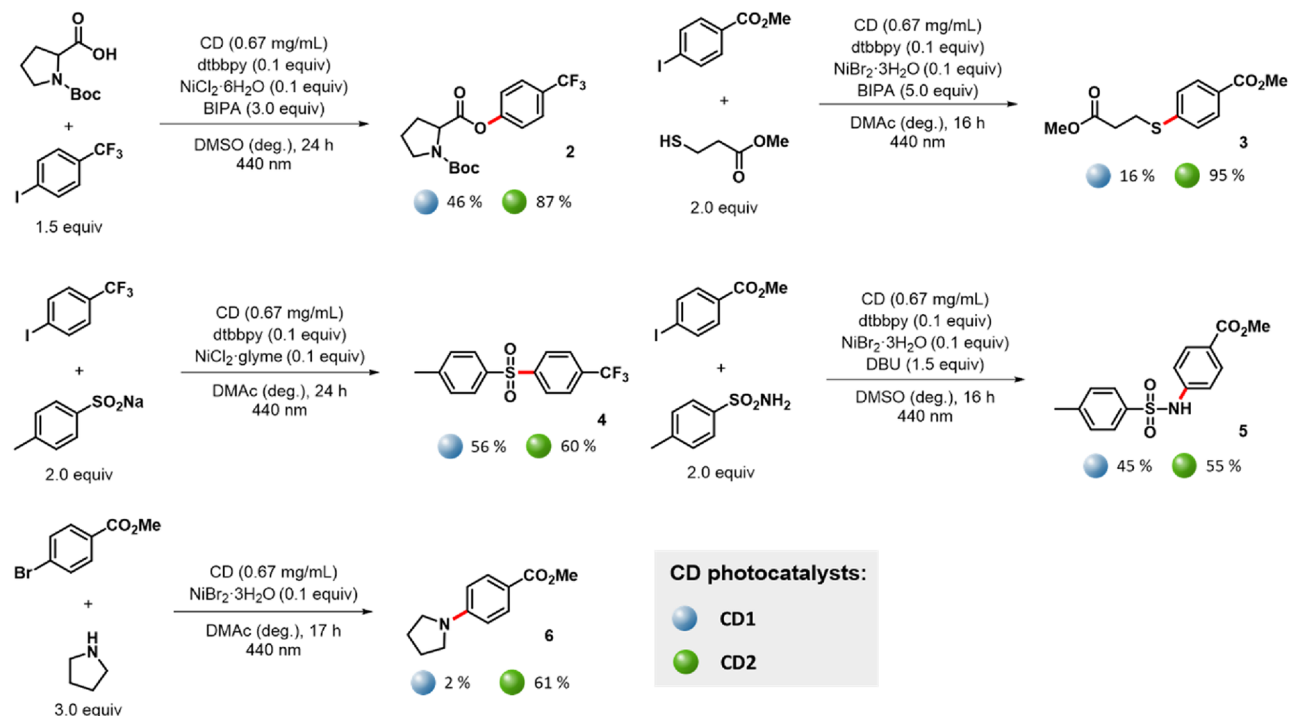
## A CDs used in this study



## B From a heterogeneous to a quasi-homogeneous system



## C Metallaphotocatalytic carbon–heteroatom cross-couplings catalyzed by CDs

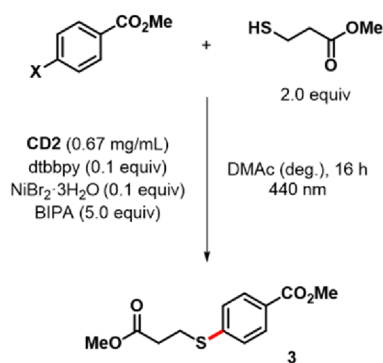


**Figure 2.** (A) Characterization of CD1 and CD2 (H<sub>2</sub>O, 298 K). (B) Optimization of the cross-coupling of Boc-Pro-OH with methyl 4-iodobenzoate. (C) Application of CD1 and CD2 as photocatalysts for C–O, C–S, and C–N cross-couplings.

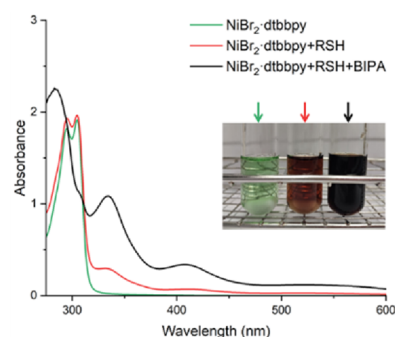
using our catalytic system (Figure 3A, entries 3,4). Spectroscopic investigations also identified dramatic changes in the

emission and absorbance for CD2 in the presence of BIPA, indicating a strong interaction between these two components

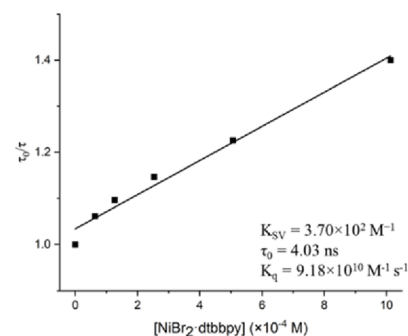
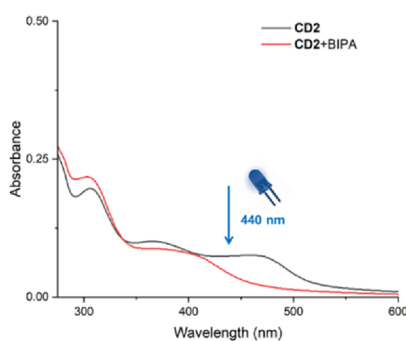
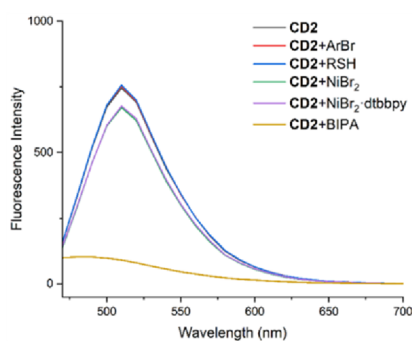
## A C-S cross-coupling catalyzed by CD2



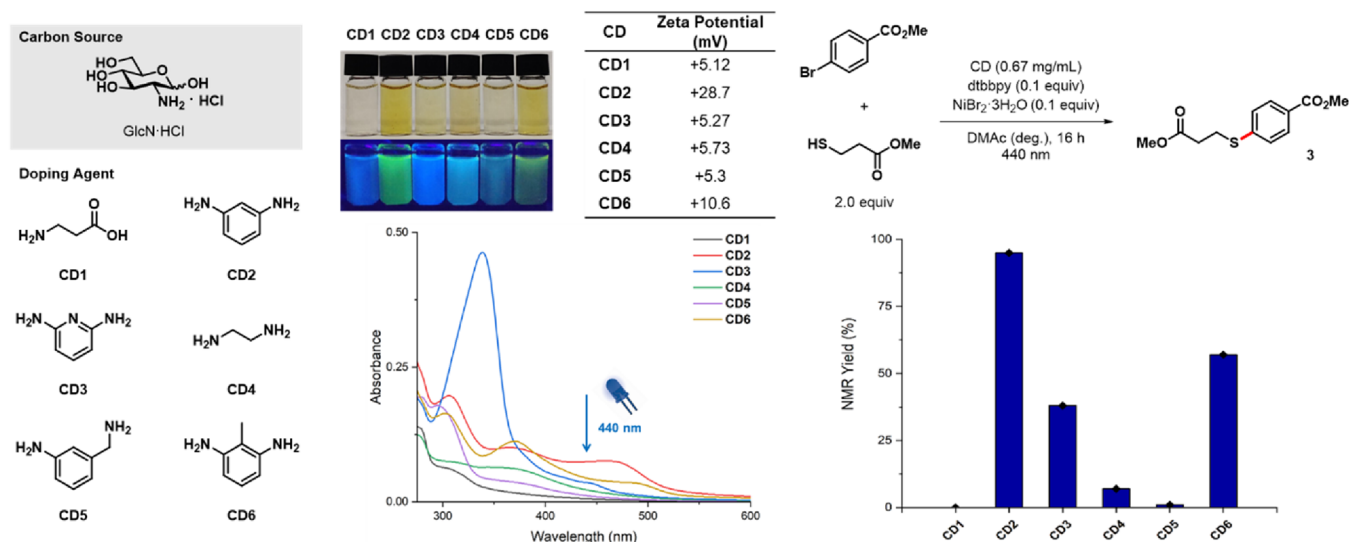
Entry	X	Conditions	3 [%]
1	I	As shown	95
2	Br	As shown	0
3	I	No BIPA	99
4	Br	No BIPA	95



## B Quenching studies



## C Screening of CDs

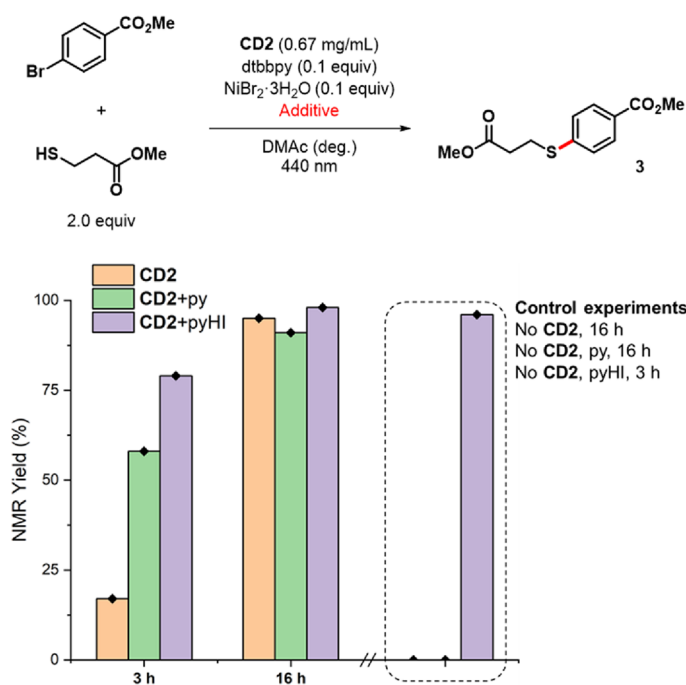


**Figure 3.** (A) Comparison of the applicability of aryl bromides and aryl iodides in the C–S cross-coupling under different reaction conditions and the formation of highly absorbing Ni-thiolate species in the presence of BIPA. (B) Spectroscopic investigations (DMAc, 298 K,  $\lambda_{\text{exc}} = 440$  nm) and dynamic Stern–Volmer quenching plot of CD2. (C) Chemical structures of the carbon source and doping agents used for CD synthesis, characterization of CDs (13.3  $\mu\text{g}/\text{mL}$ , DMAc, 298 K, for UV–vis absorption), and evaluation of different CDs as photocatalysts for C–S cross-coupling.

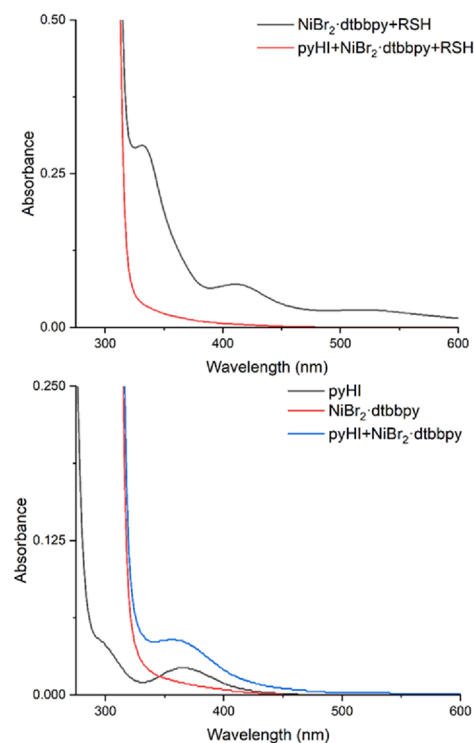
(Figure 3B). No changes in the emission of CD2 were observed in the presence of the starting materials, but the addition of NiBr<sub>2</sub> resulted in moderate quenching. This is in agreement with the accepted mechanistic hypothesis that these cross-couplings are initiated by a photocatalytic reduction of Ni<sup>II</sup> to Ni<sup>I</sup>.<sup>32–34</sup> No significant changes in the absorption of CD2 in the presence of the Ni complex implied negligible static interactions (Figures S28 and S31) but indicated a dynamic type of quenching. This

result was corroborated by a decrease in the excited state lifetime of CD2 in the presence of the Ni complex in a concentration-dependent manner (Figure S33). The dynamic Stern–Volmer plot permitted us to calculate a bimolecular quenching rate constant ( $K_q$ ) of  $9.18 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the Ni complex (Figure 3B). The steady-state quenching rate constant could not be accurately measured due to the broad absorption of Ni(dtbbpy)Br<sub>2</sub> that overlaps with CD2 (Figure S32).

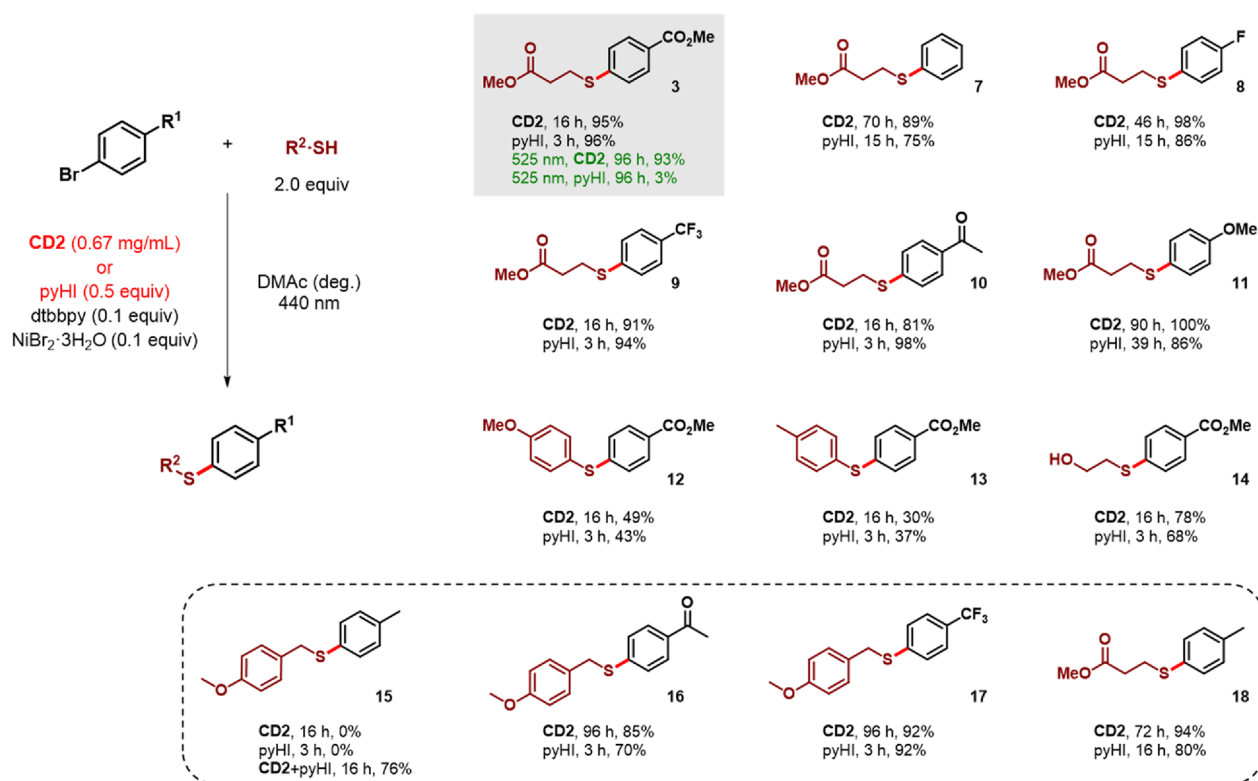
## A Improving the reaction rate



## B Photophysical characterization



## C pyHI in C-S cross-coupling



**Figure 4.** (A) Condition optimization and control experiments to accelerate the C–S cross-coupling using additives py or pyHI. (B) Photophysical characterization of pyHI in the C–S cross-coupling (DMAc, 298 K). (C) Comparison of the reaction scope for the CD2 and pyHI protocols.

Next, we sought to clarify if the catalytic performance of CD2 could be ascribed to surface effects, which eventually promotes a

dynamic interaction with the Ni catalyst overcoming diffusion/lifetime limitations. A collection of CDs was synthesized using

different amino-containing doping agents (Figure 3C). Within this library, two CDs (CD2 and CD6) have a highly positive zeta potential and show significantly better catalytic performances in a model C–S cross-coupling. However, CD2 and CD6 also show a stronger absorption at 440 nm than all other CDs and are the only examples that emit green light. These results suggest that the photocatalytic activity is a synergistic effect of the surface and photophysical properties of the dots.

We wondered whether the addition of pyHI could increase the rate of the C–S coupling protocol, shortening the long reaction time required for quantitative product formation (16 h; Figure 4A and Figure S21). Indeed, we observed a significant increase in the reaction rate. In agreement with the work of Nocera and co-workers,<sup>22</sup> we found that pyHI suppressed the formation of the Ni–thiolate complex in a concentration-dependent manner (Figure 4B and Figure S36). The addition of pyridine (py) as an additive also resulted in an increased reaction rate, albeit less significant, confirming the important role of the base (in form of pyH<sup>+</sup>) in connecting the photocatalyst and Ni cycle.<sup>22</sup> UV–vis spectroscopy confirmed that pyridine had, in contrast to BIPA, little effect on the spectral properties of CD2 (Figures S29 and S30).

To our surprise, control studies showed that the reaction could be performed even in the absence of the photocatalyst when pyHI was present (Figure 4A). This result might be explained with the formation a visible-light-induced ion pair charge transfer state derived from pyHI that could activate the Ni cycle. Indeed, heteroarenum iodides have been previously shown to act as photocatalysts in photoredox catalysis.<sup>35</sup> The pyHI protocol seemed specific to the C–S cross-coupling; little to no yields were obtained under those conditions for other carbon–heteroatom cross-couplings (Figure S27). Moreover, longer wavelengths (525 nm) did not enable cross-couplings using pyHI, but excellent yields were obtained using the CD2 protocol under green light irradiation (Figure 4C), offering an interesting alternative for light-sensitive substrates.

The fact that pyHI alone can induce cross-couplings contradicts the findings of Nocera and co-workers, who reported that both pyHI and a photocatalyst were required for productive catalysis.<sup>22</sup> By studying the scope and limitations of the C–S cross-coupling using either CD2 or pyHI as photocatalysts, we realized that the discrepancy between Nocera et al.'s and our findings is connected to the substrates used (Figure 4C). Moderate to excellent yields were achieved for a range of starting material combinations, including primary and aromatic thiols as well as electron-poor and electron-rich aryl bromides using either the CD2 or the pyHI protocol. The only exception was the reaction of 4-methoxybenzyl mercaptan with 4-bromotoluene to prepare 15 that did not result in any product formation, which is also the model reaction analyzed in the mechanistic study of the Ir/Ni/pyHI protocol by Nocera and co-workers. However, we synthesized compounds 16–18 in good yields, indicating that 4-methoxybenzyl mercaptan and 4-bromotoluene individually are not responsible for this discrepancy. Moreover, a protocol that included both CD2 and pyHI afforded compound 15 in a good yield, highlighting the applicability of CD2 as a sustainable alternative for Ir(III) photocatalysts. Although we have no satisfactory explanation for this phenomenon, these results stressed how small variations in the starting materials' combination apparently have dramatic effects on the reaction mechanism.

### 3. CONCLUSIONS

We demonstrated that CDs are efficient colloidal nano-catalysts for metallaphotocatalytic carbon–heteroatom cross-couplings in combination with a Ni(II) complex. Aryl halides were coupled with a carboxylic acid, a thiol, a sodium sulfonate, a sulfonamide, and an amine under blue light irradiation. In particular, the synergistic effect of the amino-rich surface and photophysical properties made CD2 a valuable alternative to precious Ir complexes for C–S cross-coupling reactions. Mild, base-free conditions were applied to couple a wide range of aryl halides and thiols. Mechanistic studies suggested dynamic quenching of the CD2 excited state by the Ni co-catalyst and identified that pyHI can also act as a photocatalyst in such transformations. A systematic comparison between the two protocols stressed how small variations in the starting materials' combination could have dramatic effects on the reaction mechanism.

### ■ ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.2c04025>.

General materials and methods, synthesis and characterization of CDs, experimental procedures, and photophysical characterization of cross-coupling reactions (PDF)

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#### Notes

The authors declare no competing financial interest.

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