

Photocatalytic (Het)Arylation of C(sp³)-H Bonds with Carbon Nitride

Saikat Das,^a Kathiravan Murugesan,^a Gonzalo J. Villegas Rodríguez,^a Jaspreet Kaur,^a Joshua. P. Barham,^a Aleksandr Savateev,^b Markus Antonietti,^b and Burkhard König*^a

^aFakultät für Chemie und Pharmazie, Universität Regensburg, 93040 Regensburg, Germany

^bDepartment of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces, Research Campus Golm, 14424 Potsdam, Germany

Supporting Information Placeholder

ABSTRACT: Graphitic carbon nitride materials have attracted significant interest in recent years and found applications in diverse light-to-energy conversions such as artificial photosynthesis, CO₂ reduction or degradation of organic pollutants. However, their utilization in synthetic photocatalysis especially in the direct functionalization of C(sp³)-H bonds remains underexplored. Herein, we report mesoporous graphitic carbon nitride (mpg-CN) as a heterogeneous organic semiconductor photocatalyst for direct arylation of sp³ C-H bonds in combination with nickel catalysis. Our protocol has a broad synthetic scope (>70 examples including late-stage functionalization of drugs and agrochemicals), is operationally simple, and shows high chemo- and regioselectivity. Facile separation and recycling of the mpg-CN catalyst in combination with its low preparation cost, innate photochemical stability and low toxicity are beneficial features overcoming typical shortcomings of homogeneous photocatalysis. Detailed mechanistic investigations and kinetic studies indicate that an unprecedented energy transfer process (EnT) from the organic semiconductor to the nickel complex is operating.

Keywords: heterogeneous photocatalysis, carbon nitride, hydrogen atom transfer, C(sp³)-H arylation, dual photo nickel, drug molecule functionalization

Over the last decade, the use of visible light has had a resurgence as an ideal reagent for catalytic synthetic transformations.^{1,2} A recent application of visible light photocatalysis is the direct functionalization of C(sp³)-H bonds. Since such bonds are the most abundant moiety in organic molecules, their direct activation allows for efficient chemical diversification avoiding pre-functionalization steps.^{3,4} Specially designed homogeneous catalysts such as transition metal based polypyridine complexes⁵ or organic dyes⁶ and in some cases inorganic semiconductors⁷ have been used for C-H bond functionalization. However, in practice, most solution-phase catalysts show limited durability; they are prone to deactivation in the presence of reactive radical intermediates^{6, 8-10} or suffer from drastic changes to their photophysical properties upon changes in the pH of the reaction medium¹¹. The selection of a photocatalyst for a given transformation therefore remains a challenge. In addition to catalyst instability, the non-recyclability limits the practical use of many well-known homogeneous catalysts for direct functionalization of C-H bonds, particularly on a larger scale. Herein, we report the use of a heterogeneous organic semiconductor, mesoporous graphitic carbon nitride (mpg-CN), as a robust photocatalyst for direct arylations of C(sp³)-H bonds.

Graphitic carbon nitride, the most stable allotrope of carbon nitride, is a purely organic semiconductor material composed of the earth-abundant light elements carbon and nitrogen.^{12,13} One of its morphology-wise modified analogues, called mesoporous graphitic carbon nitride (mpg-CN), is especially attractive as a heterogeneous catalyst due to its larger surface area.^{14,15} This

polymeric material possesses suitable valence band maxima (VBM) and conduction band minima (CBM), spanning a band gap of approximately 2.7 eV upon visible light photoexcitation. Although mpg-CN is yet to be commercialized, the cost of its synthesis falls within the range of a few euros/kg due to its inexpensive synthetic precursors (*e.g.*, urea and melamine) and easy synthetic procedures (see the Supporting Methods).¹⁶ Owing to its outstanding thermal, chemical and photostability, mpg-CN has found applications in various fields such as hydrogen production by overall water splitting¹², carbon dioxide reduction^{17,18} as well as in several synthetic transformations.¹⁵ Surprisingly, mpg-CN has rarely been used as a photocatalyst for direct C(sp³)-H functionalization by hydrogen atom transfer (HAT) chemistry.^{19,20} The synergistic combination of homogeneous photocatalysis, HAT and transition metal catalysis has provided several methods for selective C-H bond functionalization,²¹⁻²³ most of which remain restricted to either the use of i) activated Michael acceptors (electron-deficient olefins)²⁴⁻²⁶ or ii) stoichiometric amount of HAT agents.²⁷ Recently, halogen radicals are shown to act as effective HAT agents for C-H functionalizations. (**Figure 1a**).²⁸ Inspired by the pioneering works of Doyle,^{28b} Murakami^{28f} and Wu,²¹ we anticipated that the catalytically formed halogen radicals on the mpg-CN surface might involve in a HAT event for the generation of carbon radicals, which in combination with transition metal catalysis would enable arylation of C(sp³)-H bonds with aryl halides in a redox-neutral fashion.²⁹

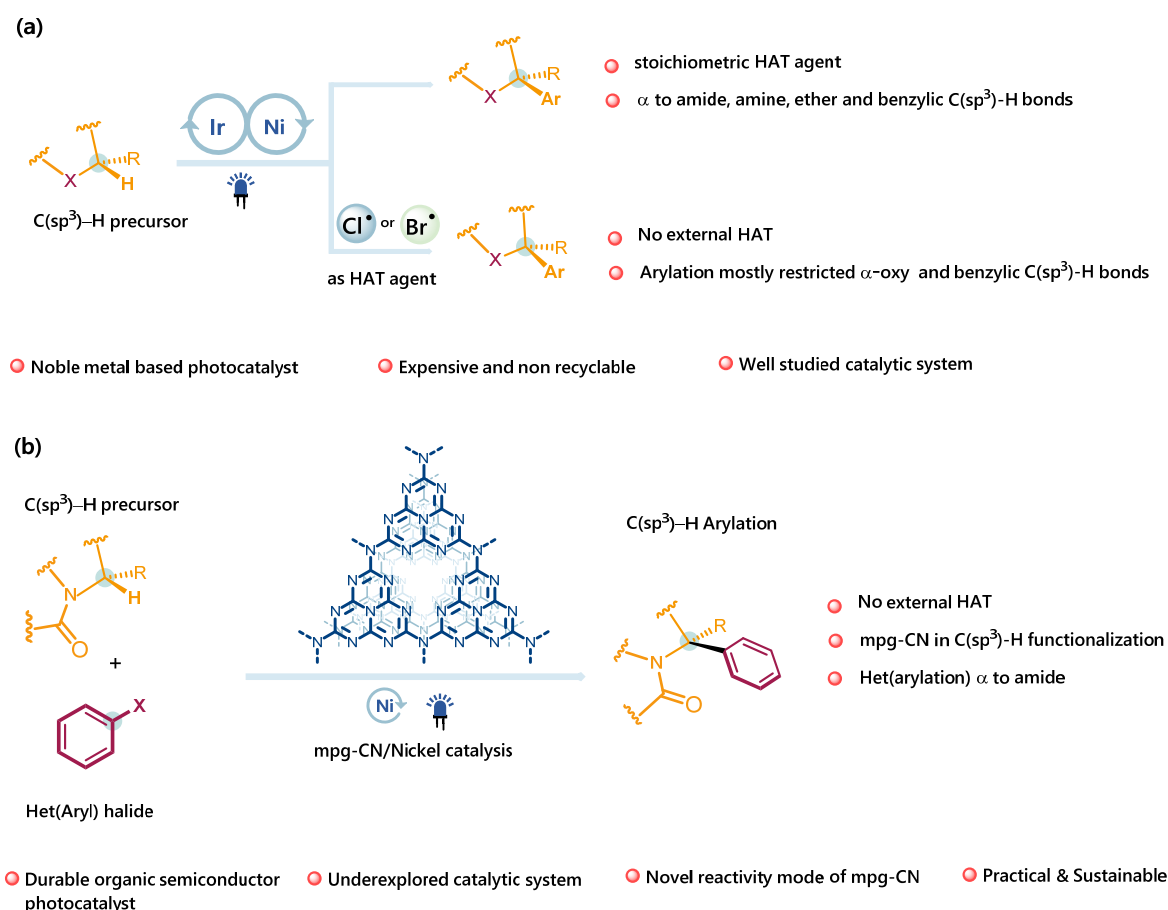
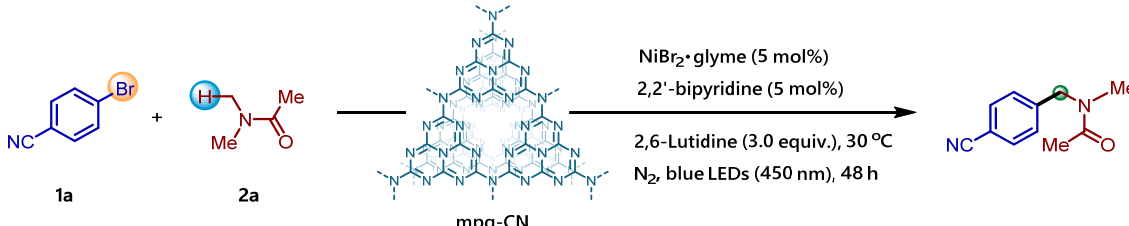


Figure 1. Schematic representation of different photocatalytic systems for C(sp³)-H arylations. (a) Homogeneous photocatalytic system for C(sp³)-H arylations with aryl halides. (b) The present study: mpg-CN photocatalytic C(sp³)-H arylations of amides.

Herein, we describe mpg-CN photocatalytic arylation of C(sp³)-H bonds in combination with nickel as metal catalyst,³⁰ as a robust, practical and tolerant protocol even suitable for late-stage functionalization of bio-active molecules (**Figure 1b**). The reaction is selective for C-H activations α -to amide groups. Mechanistic investigations and kinetic studies suggest energy transfer (EnT) from the organic semiconductor to the nickel metal centre as a new reaction mode distinguishing this reaction from typical semiconductor single electron transfer (SET). The synergistic use of HAT and EnT³¹ as mediated *via* a heterogeneous semiconductor photocatalyst is a concept expected to greatly expand the boundaries of synthetic photocatalysis.

We focused our investigation on the activation of C(sp³)-H bond adjacent to the nitrogen atom of amides due to the importance of this functional group. Particularly, benzyl amines with *N*-electron withdrawing groups are a prominent substructure in drugs, such as compounds for the treatment of plaque psoriasis, seizures or diabetes.³² In a typical synthesis, they are prepared through alkylation of amides with benzyl halides, but the chemical diversity of commercially available benzyl halides is limited. In contrast, the direct C-H arylation α -to amide *N*-atom constitutes a potentially better approach considering the available large number of aryl halides in chemical feedstocks, drug molecules and natural products. As a model system, 4-bro-

mobenzonitrile was employed towards the C(sp³)-H bond arylation of *N,N*-dimethyl acetamide (DMA) as both C-H precursor and solvent. **Table 1** summarizes the optimization of the reaction parameters and control experiments (see the Supporting Information for additional data). After systematic evaluation of various nickel(II) salts, ligands and bases, we found that a mixture consisting of NiBr₂·glyme, 2,2'-bipyridine, 2,6-lutidine and mpg-CN under blue LED (450±15 nm) irradiation at ambient temperature furnished the best result for our desired transformation, obtaining **1a** in 85% isolated yield after 48 h (**Table 1**, entry 1). The dehalogenation of starting material (benzonitrile) was the only detectable side product of the reaction. The reaction only required simple mixing of all the components in a vial followed by photoillumination. Control experiments which are either performed without mpg-CN, [Ni] catalyst, light or ligand revealed the necessity of each component for this novel C-C bond forming reaction (entries 2-5). Curiously, even in the absence of 2,6-lutidine, the reaction proceeded to some extent, possibly due to the basic nature of the bipyridine ligand (entry 6). The employment of recycled mpg-CN, without the renewed addition of [Ni] catalyst failed to afford the reaction product, corroborating the absence of active nickel catalyst remaining on the surface of the heterogeneous photocatalyst (entry 7). Unsubstituted bipyridine (bpy) served as the optimal ligand system; which is cheaper than dtbbpy(4,4'-di-*tert*-butyl 2,2'-bi

Table 1. Selected optimization and control experiments for mpg-CN photocatalyzed C(sp³)-H bond arylation

Entry	Deviation from standard conditions ^a	Yield (%) ^b
1.	None	90(85) ^c
2.	no mpg-CN	ND
3.	no NiBr ₂ ·glyme	ND
4.	no light	ND
5.	no ligand	<5
6.	no 2,6-lutidine	11
7.	no [Ni] catalyst & recovered mpg-CN	ND
8.	dtbbpy instead of bpy	52
9.	K ₃ PO ₄ instead of 2,6-lutidine	13
10.	no degassing and under N ₂	74
11.	under air	59
12.	NiBr ₂ ·3H ₂ O instead of NiBr ₂ ·glyme	72

^aReaction Conditions: 4-bromobenzonitrile (36.4 mg, 0.2 mmol), mpg-CN (10 mg), NiBr₂·glyme (3.2 mg, 5.0 mol%), 2,2'-bipyridine (1.6 mg, 5.0 mol%), 2,6-lutidine (70 μL, 3.0 equiv.) in 1 mL DMA under blue light irradiation (450±15 nm) at 30 °C for 48 h. ^bYields were determined by GC-FID using 1,4-dimethoxybenzene as an internal standard. ^cYield of the isolated product. ND, not detected.

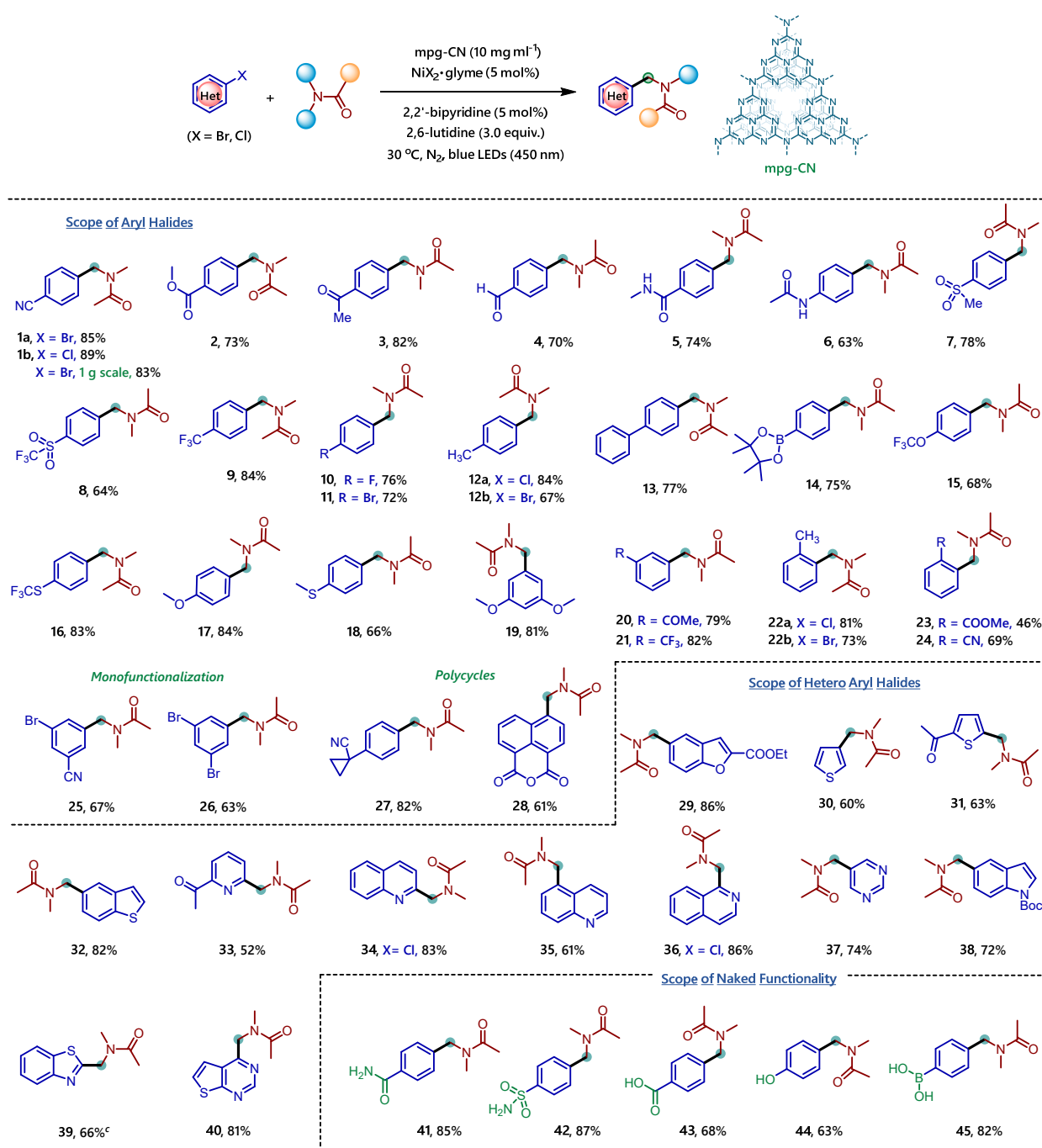
pyridine) the most commonly employed ligand in metallaphotoredox chemistry (entry 8). The choice of base is a crucial parameter, since most of the commonly employed inorganic or organic bases were ineffective in the reaction (entry 9 and Table S3). Ultimately, the use of 2,6-lutidine as a base proved to be optimal for this transformation. Comparable yields were also obtained without degassed solvents or under air (entries 10 and 11) or with inexpensive NiBr₂·3H₂O as nickel source (entry 12), thus showcasing the robustness of the mpg-CN photocatalytic C(sp³)-H bond arylation method.

With the optimized reaction conditions in hand, we next explored the scope of the mpg-CN/nickel catalyzed arylation process. Initially we examined, the generality of aryl halides as partners. As evident from the examples listed in **Table 2**, a diverse multitude of aryl halides bearing either electron-donating or electron-withdrawing substituents underwent C(sp³)-H arylation with DMA. Notably, mpg-CN photocatalytic C-H arylation displayed an excellent chemo-selectivity profile. For example, nitrile (**1a**), ester (**2**), ketone (**3**), aldehyde (**4**), amides (**5,6**), sulfone (**7**), trifluoromethyl sulfone (**8**) were tolerated. In addition, aryl boronic acid pinacol ester (**14**), and electrophilic sites that are sensitive to Ni-catalyzed cross coupling reactions such as aryl halides (**10, 11**) were also accommodated, thus providing handles for further functionalization. Aryl bromides, containing -CF₃ (**9**), -OCF₃ (**15**) or -SCF₃ (**16**) groups which are privileged functionalities in pharmaceuticals and agrochemicals, underwent arylation in good to excellent yields (68-84%). Moderately electron donating (**12b**) or electronically neutral (**13**) groups on the aryl moiety were well tolerated despite the propensity for homolytic C-H bond cleavage in the benzylic

position of **12b**. In terms of the arene partner, the efficacy of the reaction was hardly impacted by either i) a change in electronic properties from *meta*- substitution (**20, 21**) or ii) sterically encumbrance from *ortho*- substitution (**22b, 23, 24**). The reaction was very good compatible with highly electron rich aryl bromides among which the sulfide (**18**) or dimethoxy (**19**) containing moieties are particularly worth mentioning as they are generally considered to be labile towards oxidation by molecular photocatalysts. Gratifyingly, our method could be extended to aryl chlorides and **1b, 12a** and **22a** were obtained in excellent yields (81-89%). Aryl moieties having more than one reactive site (**25, 26**) are selectively mono-functionalized, thus allowing room for additional functionalization. The mpg-CN photochemical protocol was even effectively employed to polycyclic aryl bromides (**27, 28**) in spite of their tendency for ring opening reaction in the presence of a nickel catalyst.

Pleasingly, the developed conditions easily translated on a gram scale in batch-mode processing without noticeable erosion in yield (**1a**, 83%). Elsewhere, continuous flow chemistry is widely appreciated as an enabling technology for the scale-up of photochemical processes.³³ Scalability was evaluated³⁴ in two commercially-available suspension/slurry-handling continuous flow reactors (10-15 mL reactor sizes), one tubular reactor and one which used state-of-the-art oscillatory flow and pulsation technology together with hi-power LED modules (24-45 W radiant power). Surprisingly, preliminary results found conversion and productivity (mg h⁻¹) inferior to that obtained on gram-scale in a batch reactor (100 mL reactor size) and postulate that the mismatched time domains of a faster-flowing liquid phase and slower flowing solid particles in a continuously flowing

Table 2. Scope of (hetero)aryl halides.^{a,b}



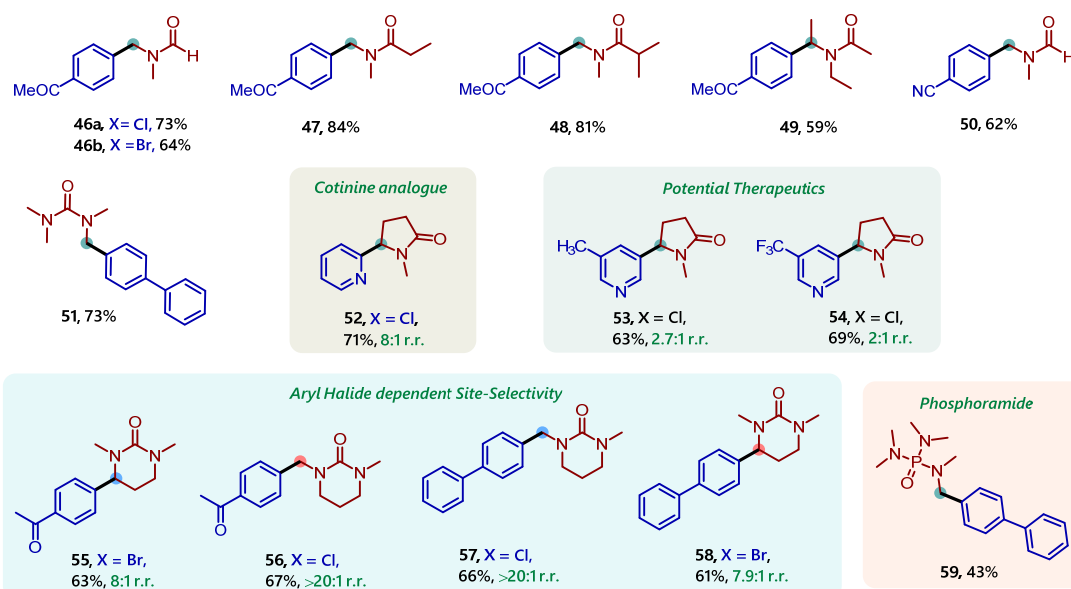
^aReaction conditions: as Table 1 (entry 1). ^bYields of the isolated products. ^c1.0 equivalent tetrabutylammonium chloride was used as an additive. Unless otherwise stated, products derive from their (hetero)aryl bromide precursors.

stream is counter-productive for adsorption of reactive species to the mpg-CN surface in context of the photocatalytic chemistry herein (see the Supporting Information for a detailed investigation).

Next, the amenability toward heteroaryl halides was assessed. Notably, our protocol displayed an exceptional level of tolerance towards a broad range of heteroaryl bromides as well as chlorides (Table 2). A wide variety of electron-poor nitrogen-containing heterocycles such as pyridine (33), quinolines (34,

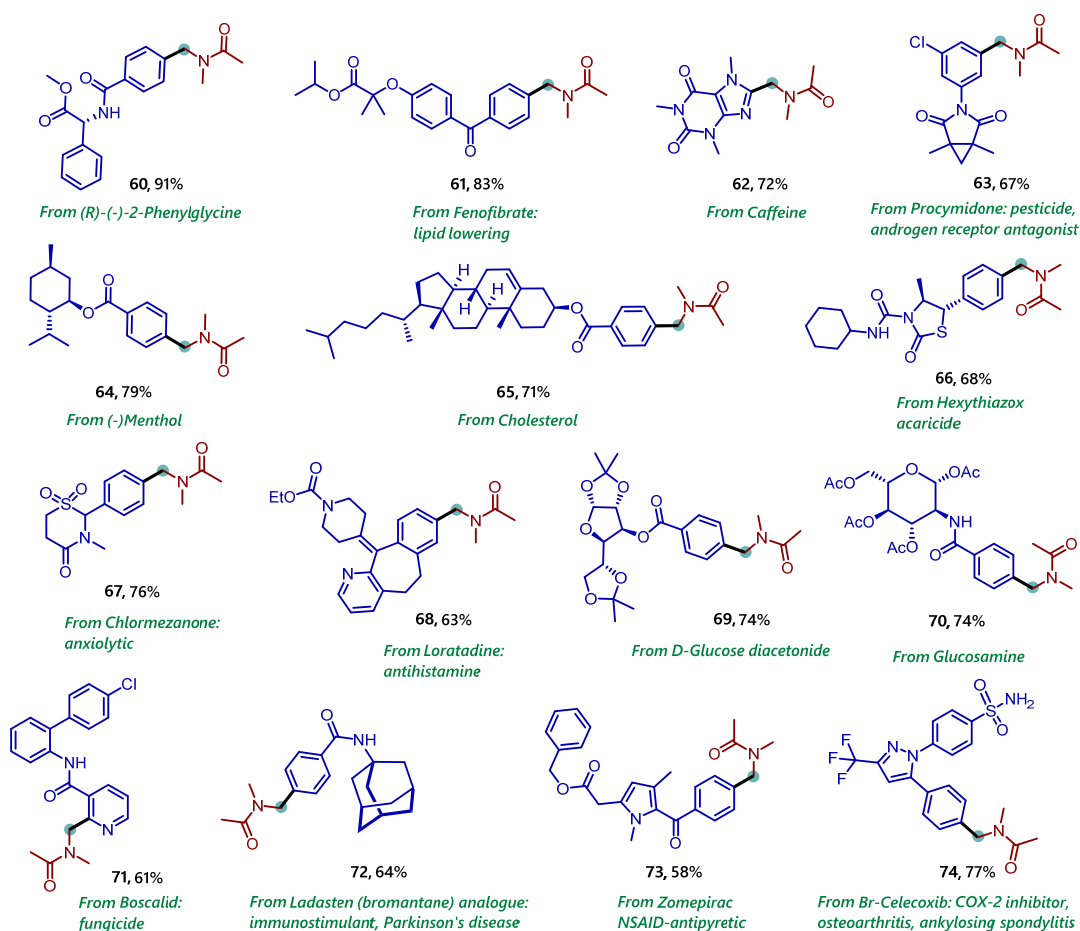
35), isoquinoline (36), pyrimidine (37), indole (38), benzothiazole (39), thieno[2,3-*d*]pyrimidine (40) could all be functionalized. We note that such nitrogen-containing heterocycles bearing an amide functionality are typical scaffolds in many active pharmaceutical ingredients. Moreover, electron-rich heterocycles such as benzofuran (29), thiophene (30, 31) and benzothiofene (32) were also well tolerated. The robustness of mpg-CN photocatalysis compared to metallaphotoredox reactions of iridium polypyridyl complexes is a potential advantage. The

Table 3. Scope of C(sp³)-H precursors.^{a,b}



^aYields of the isolated products. ^bSee the supporting information for (hetero)aryl halide precursors. r.r. = regioisomeric ratio.

Table 4. Application of the mpg-CN photocatalytic C(sp³)-H arylation method to bio-active molecules.^{a,b}



^aYields of the isolated products. ^bSee the supporting information for (hetero)aryl halide precursors.

iridium complexes could lead to lower product yields of electron-rich heterocycles due to the competing SET processes.²⁸

We then tested the compatibility of our mpg-CN photocatalytic arylation method with unprotected polar functional groups, an important criterion for assessing a method's robustness and applicability towards drug discovery and the synthesis of bioactive molecules. Strikingly, aryl bromides containing unprotected amide, sulfonamide, carboxylic acid, phenol or boronic

acid functionalities all reacted smoothly and afforded the desired products (**41–45**) in excellent yields (**Table 2**). For instance, the free –OH group in **44** remains untouched even though phenolic compounds are typically sensitive towards oxidation under photochemical conditions. The presence of a boronic acid in **45** demonstrates i) the orthogonality of our protocol compared to classical metal-catalyzed cross-coupling reactions, and ii) our protocol's tolerance of a valuable handle for further synthetic transformations.

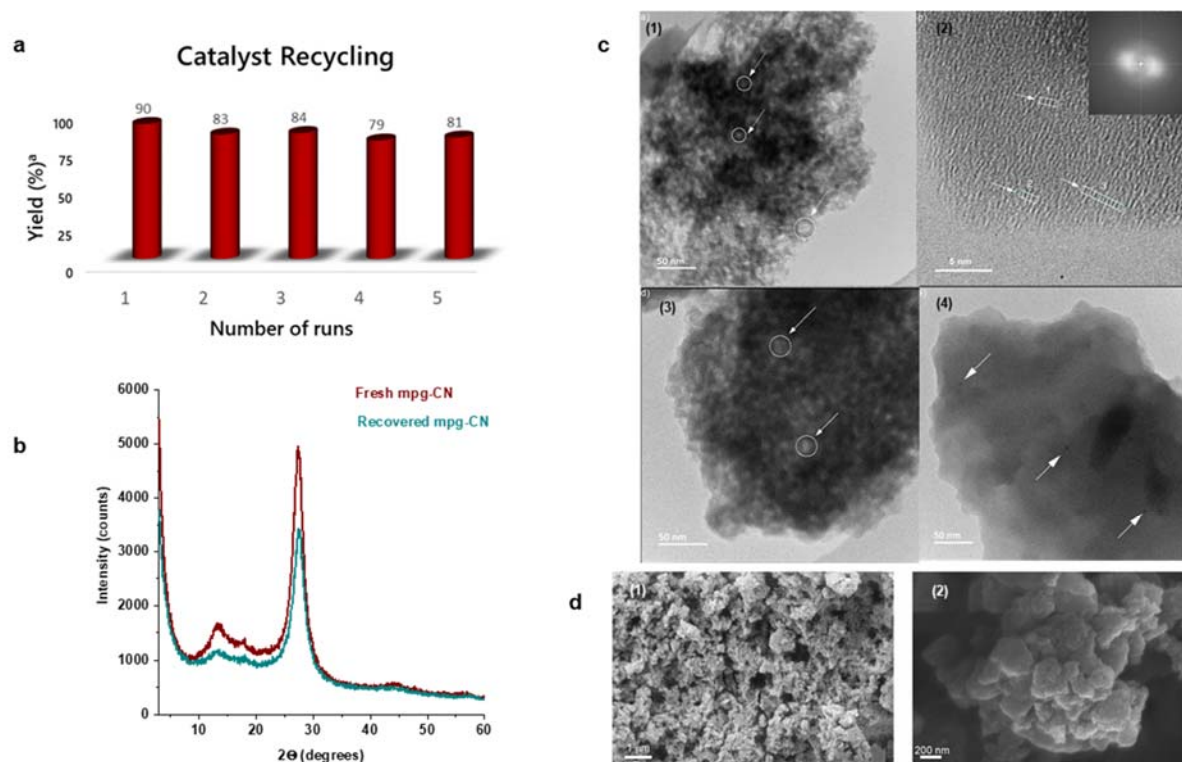


Figure 2. Characterization of fresh and recovered mpg-CN. (a) Evaluation of catalytic recycling. (b) PXRD pattern of fresh and recovered mpg-CN. (c) TEM images of mpg-CN (1) fresh mpg-CN, overview image, circles mark mesopores, (2) HR-TEM image of fresh mpg-CN with the corresponding FFT as inset, (3) TEM image of recovered mpg-CN, overview image, circles mark mesopores, (4) TEM image of recovered mpg-CN, arrows indicate Ni(0) nanoparticles. (d) SEM images of fresh mpg-CN (1) and recovered (2)

Encouraged by the aforementioned results, we expanded the mpg-CN semiconductor photocatalytic arylation method to C–H precursors other than DMA.³⁵ Gratifyingly, this was possible, and a variety of acyclic and cyclic amides could be employed as C(sp³)–H bond functional handles with similar results to DMA. *N,N*-Dimethyl-formamide, -propionamide, -isobutyramide all furnished their corresponding arylated products (**46–48**, **50**) in good to excellent yields (73–84%). Even a more sterically encumbered secondary C(sp³)–H position of *N,N*-diethyl acetamide (**49**) could be functionalized, albeit in slightly lower yields. Here it is worth mentioning that C–H arylation could also be performed in acetonitrile as solvent using 10 equivalents of amide C–H precursor and catalytic amounts of tetrabutylammonium chloride as an additive.³⁶ We were quite surprised to find that C(sp³)–H arylation of *N*-methyl pyrrolidone (NMP) with 2-chloropyridine rapidly afforded the corresponding Cotinine analogue (**52**) in very good yield and excellent regioselectivity. Although, 3-chloropyridine derivatives provided diminished regioselectivity, Cotinine **53**, the methyl analogue of a potential therapeutic agent against Alzheimer's

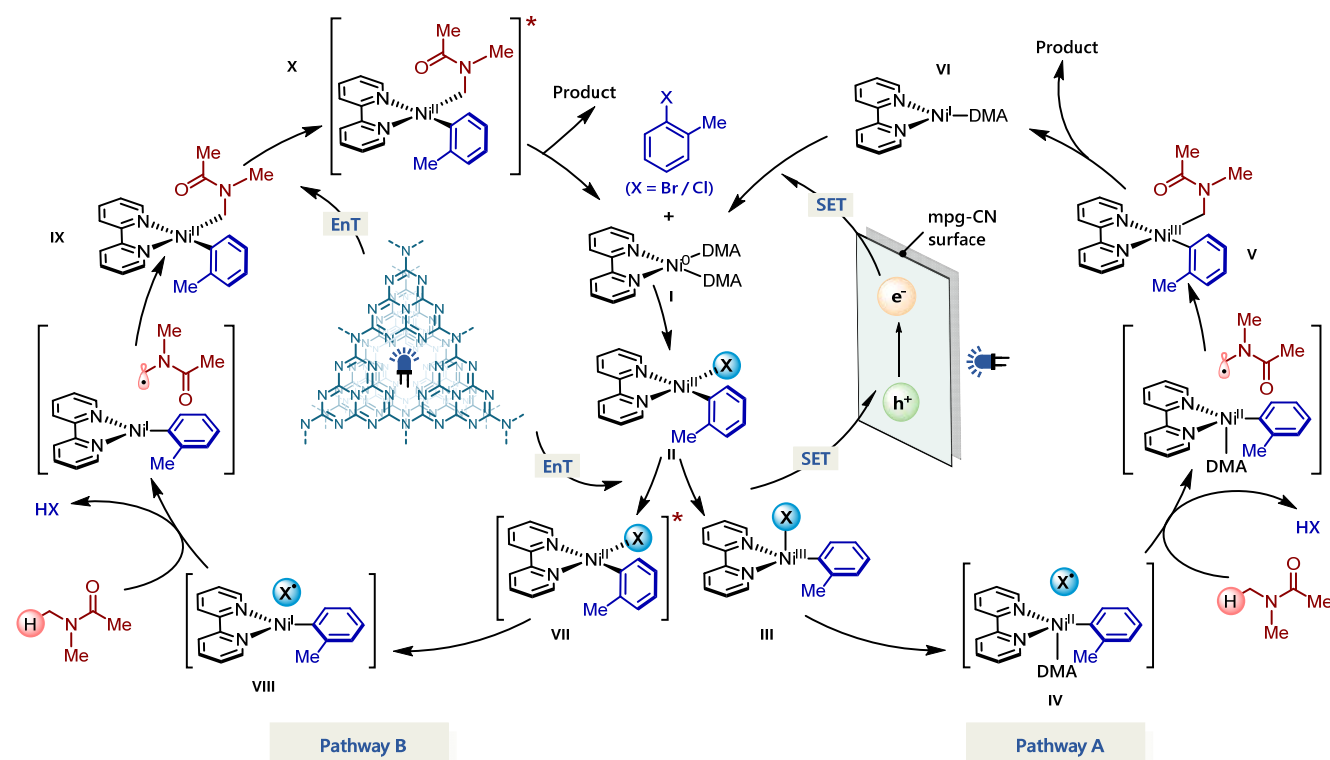
disease,³⁷ is not easily accessible by conventional synthetic methods and its –CF₃ derivative **54** has not been described. We observed high regioselectivity for methyl and methylene C–H bonds by choosing appropriate aryl halides. A cyclic urea derivative reacted preferentially at its *N*-CH₂ position in the presence of aryl bromides (**55**, **58**) whereas the same derivative reacted exclusively at its *N*-CH₃ position in the presence of aryl chlorides (**56**, **57**). This preference for activation of the least-substituted C–H bond by Cl radicals and activation of the most-substituted C–H bond by Br radicals reflects a previous report concerning C(sp³)–H functionalization of hydrocarbons.^{24,38} Interestingly, most of the compounds shown in **Table 3** have not been prepared before, illustrating the capability of our method to branch into new chemical space. For example, the successful arylation of hexamethylphosphoramide (**59**) as a C–H precursor provided rapid access to benzyl amine derivatives with potential physiological activity.

Finally, we demonstrated the application of our mpg-CN photocatalytic C(sp³)–H arylation method to the late-stage func-

tionalization of bio-active molecules including pharmaceuticals, hormones, agrochemicals (pesticide, fungicide) as aryl coupling components and were delighted to observe desired products (**60-74**) in good to excellent yields (**Table 4**). Our protocol therefore enlarges the palette of opportunities for modern applications in drug discovery and agrochemicals.

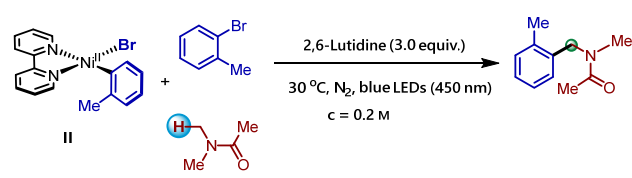
Apart from innate chemical and photostability, one of the prime advantages of mpg-CN is its heterogeneous nature that allows straightforward recovery of the catalyst from the reaction mixture and the recovered catalyst can be reused multiple times preserving its photocatalytic reactivity. As demonstrated in the **Figure 2a** mpg-CN photocatalyst can at least be recycled five times without appreciable loss in the product yield. The recovered material was characterized by a series of techniques used for the characterization of fresh mpg-CN (see the Supporting Information for details) such as Fourier-transform infrared spectroscopy (FT-IR), powder X-Ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), X-Ray Analysis (EDX), energy dispersive inductively coupled plasma optical emission spectrometry (ICP-OES) transmission electron microscopy (TEM) etc.. The position and intensity of all peaks in FT-IR and PXRD spectrum revealed that the bulk chemical structure of the recovered photocatalyst was unchanged (**Figure 2b, S14**), while EDX and XPS elemental analysis showed enhanced oxygen content on the surface of the recovered photocatalyst (Table S8 and S9). Additional, ICP-OES experiments identified 0.07 ± 0.013 wt% Ni contained on the mpg-CN (Table S10). Interestingly, nickel 2p XPS did not show any distinct signal of nickel (**Figure S24**). Considering that XPS is a surface-sensitive technique, such an apparently anomalous result confirmed that nickel in the sample is mainly located in the bulk of the

material and completely removed from the surface. Similarly, no signal was observed in Br 3d XPS which could potentially be related to using NiBr₂ as metal precursor (**Figure S25**). HR-TEM images of the recovered mpg-CN i) indicated that its mesoporous structure was retained and ii) revealed the presence of dark spots with a diameter of 2-6 nm. These could be attributed to the formation of Ni(0) nanoparticles (**Figure 2c**) Indeed, deposition of Ni(0) nanoparticles, albeit significantly larger amounts (1.4-12.6 wt.%) of Ni black, compared to ~0.07 wt.% in this work, has been previously reported.^{39,40} Nitrogen 1s XPS indicated the di-coordinated nitrogen of C=N-C moieties in tri-s-triazine unit as observed in the fresh catalyst (**Figure S16**). The abundance of nitrogen atoms renders the material as an effective polydentate ligand to coordinate nickel atoms. Coordination with the covalent carbon nitride mpg-CN gives rise to a 16 electron Ni(II) chelate complex compared to a more reactive 14 electron Ni(II)-amide complex in the case of ionic carbon nitrides (**Figure S26**). These observations indicate that the problem of nickel black formation in dual nickel/photoredox catalysis (in addition to adjusting the rates of oxidative addition and reductive elimination by tuning the energy of incident light and the concentration of reagents)³⁹ could also be eliminated by using a robust carbon nitride photocatalyst stabilizes the low valent nickel species without altering the overall reaction rates. The recovered mpg-CN showed a slight shift of the absorption onset in the DRUV-vis spectrum and an expansion of the optical band gap by ~0.05 eV (**Figure S20**). In steady-state PL such surface modification of mpg-CN is observed as a blue shift in fluorescence by ~0.1 eV (**Figure S21**).



Scheme 1. Plausible mechanistic pathways for mpg-CN/nickel photocatalytic C(sp³)-H arylation.

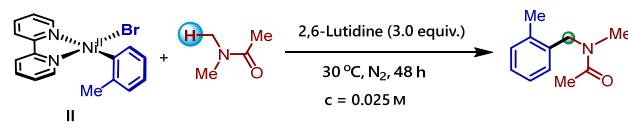
Table 5. Catalytic experiments with preformed [(bpy)Ni^{II}(*o*-tolyl)Br] complex **II^{a,b}**



Entry	Deviation from the above condition	Yield
1.	none	5%
2.	With mpg-CN (10 mg mL ⁻¹)	56%

^aWith 5 mol% **II**. ^bYields were determined by GC-FID using 1,4-dimethoxybenzene as an internal standard.

Table 6. Stoichiometric experiments with preformed [(bpy)Ni^{II}(*o*-tolyl)Br] complex **II^{a,b}**



Entry	Light source	Yield
1.	340 nm	17%
2.	450 nm	20%
3.	Dark	ND

^aSee supporting information for details. ^bYields were determined by GC-FID using 1,4-dimethoxybenzene as an internal standard.

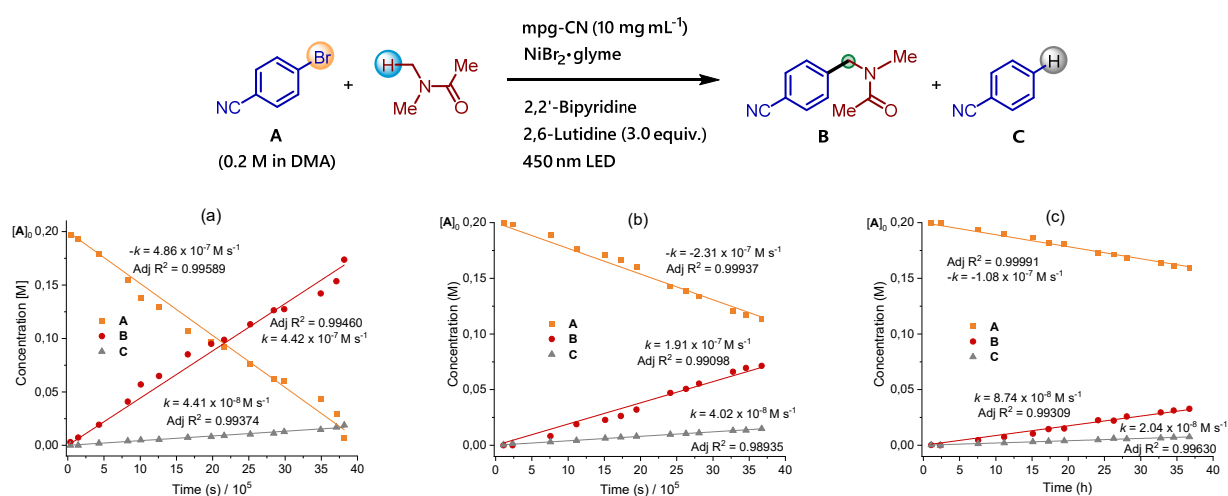


Figure 3. Reaction kinetic profile for Ni/mpg-CN photocatalytic arylation. Reaction conditions: 4-bromobenzonitrile (A) (0.2 mmol), mpg-CN (10 mg mL⁻¹), 2,6-lutidine (3.0 equiv.), DMA (0.2 M with respect to A) under 450 nm blue light irradiation at 25 °C. (a) with 5 mol% NiBr₂·glyme and 5 mol% 2,2'-bipyridine. (b) with 15 mol% NiBr₂·glyme and 2,2'-bipyridine. (c) with 0.6 M of A in DMA at 25 °C.

The recovered mpg-CN showed a slight shift of the absorption onset in the DRUV-vis spectrum and an expansion of the optical band gap by ~ 0.05 eV (Figure S20). In steady-state PL such surface modification of mpg-CN is observed as a blue shift in fluorescence by ~ 0.1 eV (Figure S21). The morphology of recovered mpg-CN particles adopted a more rounded shape compared to a rougher surface of freshly prepared mpg-CN (Figure 2d). Taken together, the post characterization data of recovered mpg-CN clearly shows robustness, stability and durability of this heterogeneous organic semiconductor as a photocatalyst.

The aforementioned results provide evidence for catalytic generation of HAT agent on the mpg-CN semiconductor surface, which operates in synergy with nickel catalysis to enable C(sp³)-H bond functionalization. However, the photoactivity of mpg-CN/nickel dual catalytic system for C-H bond cleavage at a molecular level remains to be elucidated. Based on prior mechanistic investigations of photo/Ni-dual catalyzed cross coupling reactions in homogeneous systems,⁴¹ we postulate two plausible mechanistic scenarios as depicted in Scheme 1. Initially, the Ni(0) complex **I** undergoes oxidative addition with an

aryl halide delivering Ni(II) oxidative addition complex **II**. Concurrently, light absorption by the mpg-CN semiconductor photocatalyst triggers the charge separation producing two-dimensional surface redox centres as electron-hole pairs. In pathway A, SET oxidation of complex **II** by the photogenerated hole (VBM located at +1.2 V vs SCE, $E_{1/2}(\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}) = +0.85$ V vs SCE) affords species **III**, which may undergo Ni(III)-X homolysis to give a halogen radical and Ni(II) species **IV**.²⁸ The resulting halogen radical can rapidly abstract a hydrogen atom from DMA (H-Br BDE ~ 88 kcal/mol, H-Cl BDE ~ 102 kcal/mol, α -amino C-H BDE ~ 89 to 94 kcal/mol)²⁷ which immediately recombines with species **IV** to form **V**. Subsequent reductive elimination of **V** results in the desired product and Ni(I) species **VI**. Finally, reduction of **VI** by the electron located on the semiconductor surface (CBM located at -1.5 V vs SCE, $E_{1/2}(\text{Ni}^{\text{I}}/\text{Ni}^{\text{0}}) = -1.42$ V vs SCE)⁴¹ regenerates Ni(0) and completes the catalytic cycle. In pathway B, mpg-CN serves as a light absorbing antenna undergoing an energy transfer process (EnT) (singlet-triplet band gap *ca.* 0.39 eV)⁴² to produce electronically excited Ni(II) species **VII**. Homolysis of the Ni(II)-X

bond and HAT followed by rebound of the resulting carbon centered radical with **VIII** generates Ni(II) species **IX**. Reductive elimination from the electronically excited species **X**, promoted by EnT with mpg-CN, provides the final product and regenerates Ni(0) species thus completing the catalytic cycle.

Control experiments with a catalytic amount of preformed [(bpy)Ni^{II}(*o*-tolyl)Br] complex **II** in our standard reaction conditions (Table 5) show that both complex **II** and mpg-CN are required in the productive reaction pathway. A major distinction between these two pathways as shown in Scheme 1 is that EnT process involves the excited state of Ni(II) species which should be directly accessible via visible light excitation in the absence of photocatalyst (Figure S27). Indeed, a stoichiometric experiment with [(bpy)Ni^{II}(*o*-tolyl)Br] complex **II** via direct photoexcitation at 450 nm (*i.e.* without mpg-CN) revealed the formation of the desired product in appreciable yield (Table 6). An additional control experiment performed under identical conditions in the absence of light failed to produce any detectable product. These experiments are indicative towards pathway B where the formation of an electronically excited Ni(II) complex is a prerequisite for bond formation.

The reaction kinetics were monitored at different concentrations of the nickel complex as well as aryl bromide. In all cases we observed a zero order kinetic profile (Figure 3) at room temperature (Table S14), which is a typical behaviour of heterogeneous catalytic reactions in which active sites are saturated by adsorbed reactant molecules. Similar observations have been reported previously for carbon nitride/nickel dual photocatalysis.⁴³ Interestingly, increasing the [Ni] loading by three times increased the relative amount of debrominated product and halved the reaction rate (Figure 3a vs. 3b). This could be ascribed to saturating the mpg-CN active sites while having more [Ni] complexes in solution. As a result the [Ni] complex, which is involved in the rate-determining step, has to compete with other off-cycle or non-rate-determining on-cycle [Ni] complexes for mpg-CN active sites leading to the overall decline in rate. Likewise, increasing the concentration of 4-bromobenzonitrile further decreased the reaction rate (Fig 3a vs. 3c). Such rate dependence on nickel and haloarene concentration may indicate that the rate-determining step occurs as a result of adsorption to the mpg-CN surface.⁴³ Given that EnT processes are only efficient over short distances, effective adsorption may be more critical to an EnT mechanism than a SET mechanism, which can occur over longer distances assisted by solvent molecules.⁴⁴ Nevertheless, we cannot rule out the possibility of a disproportionation reaction between photoexcited Ni(II)* and ground state Ni(II) to give Ni(I) and Ni(III) species followed by reductive elimination to afford the product. However, the low concentration as well as short lifetime of the Ni(II)* complex (*ca.* $\tau = 2.53$ ns for [(bpy)Ni^{II}(*o*-tolyl)Br]) make this mechanism very unlikely to be a major contributing pathway.⁴⁴

We have demonstrated the so far unrecognized potential of mesoporous graphitic carbon nitride (mpg-CN) in direct (hetero)arylations of C(sp³)-H bonds via a synergistic combination with nickel catalysis. Catalytically-generated halogen radicals act as hydrogen atom transfer agents for the functionalization of C(sp³)-H bonds, while tolerating a large number of functional groups. The protocol, based on a durable organic semiconductor mpg-CN photocatalyst and a simple nickel catalyst, provides a powerful alternative to conventional homogeneous photoredox catalysts. From a sustainable chemistry perspective, our protocol offers a distinct advantage over others. Namely, its

heterogeneous nature means that mpg-CN is readily recovered from the reaction media by simple centrifugation and can be re-used multiple times without appreciable loss in activity. Gram-scale reactions are possible in batch, where batch-processing surprisingly provided a more viable option for scale-up than continuous flow using a dedicated slurry-handling oscillatory flow reactors. Mechanistic investigations provide evidence of an energy transfer driven pathway generating an electronically excited nickel complex as a reactive intermediate. Lastly, the potentiality of mpg-CN as an attractive visible light absorbing organic semiconductor photocatalyst has been manifested by performing late-stage functionalization on complex molecules. Considering the use of bio-active (hetero)aromatic halides as potential coupling partners, the cost-effective technology may find applications in modern drug discovery. Finally, we believe that the distinct reactivity mode of mpg-CN described herein may lead novel designs in EnT catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental details, characterization data for the products, and supporting crystallographic data.

AUTHOR INFORMATION

Corresponding Author

*E-mail: burkhard.koenig@ur.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The German Science Foundation (DFG, KO 1537/18-1) supported this work. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme (grant agreement No. 741623). We thank Dr. Rudolf Vasold for GC-MS measurements and Regina Hoheisel for Cyclic Voltammetry measurements. We also thank Miss Jiamei Liu at Instrument Analysis Center of Xi'an Jiaotong University for her assistance with XPS analysis and Borlortuya Badamdorj for acquiring TEM images. We thank Dr. Hannes Gemoets for helpful discussions and CreaFlow for providing an oscillatory flow reactor (HANU reactor) and Peschl Ultraviolet GmbH for providing an appropriate hi-power LED module.

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