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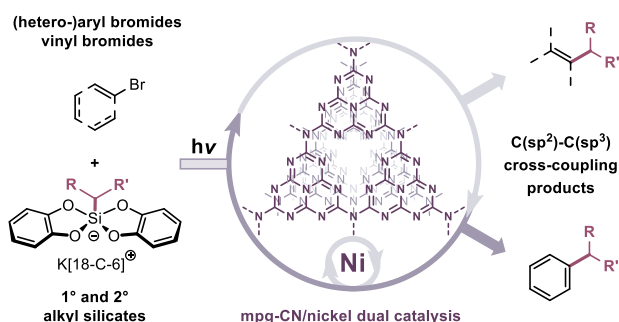
Mesoporous Graphitic Carbon Nitride as Heterogeneous Organic Photocatalyst in the Dual Catalytic Arylation of Alkyl Bis(catecholato)silicates

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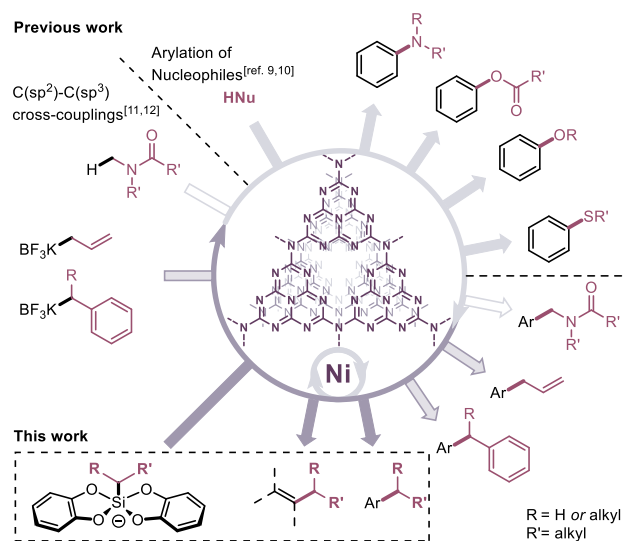
ABSTRACT: Mesoporous Graphitic Carbon Nitride is introduced as a heterogeneous photocatalyst to perform dual photoredox and nickel-catalysed cross-coupling reactions between alkyl bis(catecholato)silicates as radical precursors and aryl/alkenyl bromides. The synergy between this recyclable photocatalyst and the broadly applied homogenous nickel complex [Ni(dtbbpy)Br₂] gives access to C(sp²)-C(sp³) cross-coupling products in a sustainable fashion. Recycled mpg-CN photocatalyst was analyzed by time-resolved emission, and EPR spectroscopy.

Since MacMillan's, Doyle's¹, and Molander's² seminal reports, photoredox/nickel dual catalysis has attracted broad interest in the scientific community, in turn leading to the development of a multitude of new single-electron transmetalation based transformations.³ The number of compatible radical precursors, such as carboxylates, trifluoroborates, bis(catecholato)silicates, amides, and dihydropyridines increased rapidly,³⁻⁴ followed by the discovery of alternative photocatalysts that can promote such a transformation.⁵ This development went hand in hand with the quest for more sustainable alternatives to the common iridium- and ruthenium-based catalysts.⁶

In this context, mesoporous graphitic carbon nitride (mpg-CN) and derivatives thereof⁷ emerged as a viable alternative to metal-based photocatalysts, not only in photoredox chemistry itself,⁸ but also in photoredox/nickel dual catalytic applications. Initially, mpg-CN/nickel dual catalysis was employed to couple aryl halides with N-,⁹ O-¹⁰ and S-nucleophiles^{10d} in a more sustainable manner (Scheme 1). More recently, our group demonstrated that mpg-CN can also be employed to initiate α -arylation of amides by

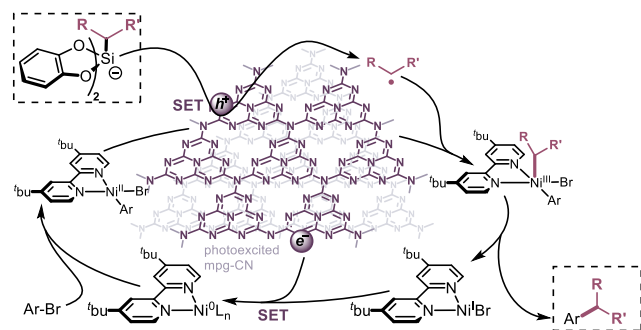
C(sp³)-H activation.¹¹ Further, single-electron transmetalation of organotrifluoroborates is achievable through mpg-CN and nickel catalysis. However, the latter methodology remains limited to benzylic and allylic radicals.¹² To broaden the scope of mpg-CN/nickel catalyzed C(sp²)-C(sp³) cross-couplings, we envisioned the use of alkyl bis(catecholato)silicates as radical precursors. Since their introduction as radical sources,¹³ bis(catecholato)silicates have proven to be reliable reagents in cross-coupling applications.¹⁴ In fact, both their low oxidation potential (< 0.9 V vs. SCE for alkyl bis(catecholato)silicates)^{13a} and their accessibility from commercial starting materials grant access to a variety of primary, secondary, and tertiary radicals.

Scheme 1: (A) mpg-CN/nickel dual catalytic transformations.



The combination with mpg-CN, its low price, its robustness, and facile recycling would offer a valuable extension to the current C(sp²)-C(sp³) cross-coupling toolbox. According to the general metalphotoredox mechanism proposed by MacMillan, Doyle¹, and Molander², such a transformation would start with the photoexcitation of the semiconductor material, generating an electron-hole pair (e⁻ and h⁺) on its surface (Scheme 2) with an oxidation potential of (+1.2 V vs. SCE) and a reduction potential of (-1.5 V vs. SCE).^{9a} The first potential is sufficient to oxidize alkyl bis(catecholato)silicates (< 0.9 V vs. SCE) and thereby induce the fragmentation to the alkyl radicals, while the latter potential can easily reduce the nickel(II) precatalyst and the nickel(I) intermediate to its active nickel(0) oxidation state, which would readily undergo oxidative addition with aryl bromides to furnish respective nickel(II) complex. It serves as a radical trap for the previously generated alkyl radical. Reductive elimination from the nickel(III) species to the C(sp²)-C(sp³) cross-coupling product and subsequent single-electron-reduction of the resulting nickel(I) complex by mpg-CN are closing the cycle.

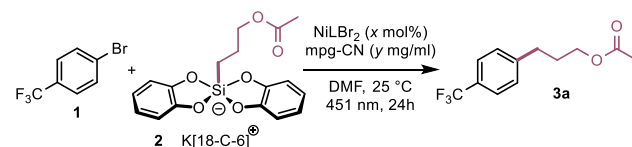
Scheme 2: A mechanistic hypothesis.



We began our investigation with 4-bromobenzotrifluoride and potassium[18-C-6] acetoxypropyl bis(catecholato)silicate as model substrates. The initial conditions were chosen according to our previous works, which repeatedly found a substrate concentration of 0.2 M and an mpg-CN loading of 10 mg/ml to be optimal,¹¹⁻¹² while DMF is the preferred solvent for most mpg-CN catalyzed reactions as well as for

photo-nickel catalyzed cross-couplings of bis(catecholato)silicates. The optimization began with a screening of different bipyridyl ligands (Table 1, entry 1-4) on the nickel(II) bromide precatalyst. With unsubstituted bipyridyl (bpy) a yield of 58% was achieved (entry 1), which could be improved to 63% by using 4,4'-dimethyl bipyridyl as a ligand (entry 2). The yield decreased to 44% when the position of the methyl groups was changed to 5,5'-position of the ligand (entry 3). However, upon using 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbbpy) as ligand, the product was obtained in 70% NMR-yield (entry 4). The increase of either the photocatalyst or the nickel salt loading slightly improved the yield to 71% and 72%, respectively (entries 5 and 6). Finally, increasing the equivalents of alkyl bis(catecholato)silicate furnished the desired product **3a** in 71% isolated yield (entry 7). Most economical conditions with slightly decreased yield are found in entry 4. Control reactions confirmed the essential role of both catalysts and light (entry 8-10).

Table 1: Optimization and control reactions^a



entry	L	x (mol%)	y (mg/ml)	2 (equiv)	yield ^b (%)
1	bpy	5.0	10	1.5	58
2	4,4'-Me ₂ bpy	5.0	10	1.5	63
3	5,5'-Me ₂ bpy	5.0	10	1.5	44
4	dtbbpy	5.0	10	1.5	70
5	dtbbpy	10	10	1.5	71
6	dtbbpy	5.0	20	1.5	72
7	dtbbpy	5.0	20	2.0	76, (71)^c
8	-	-	20	2.0	n.d. ^d
9	dtbbpy	5.0	-	2.0	n.d. ^d
10 ^e	dtbbpy	5.0	20	2.0	n.d. ^d

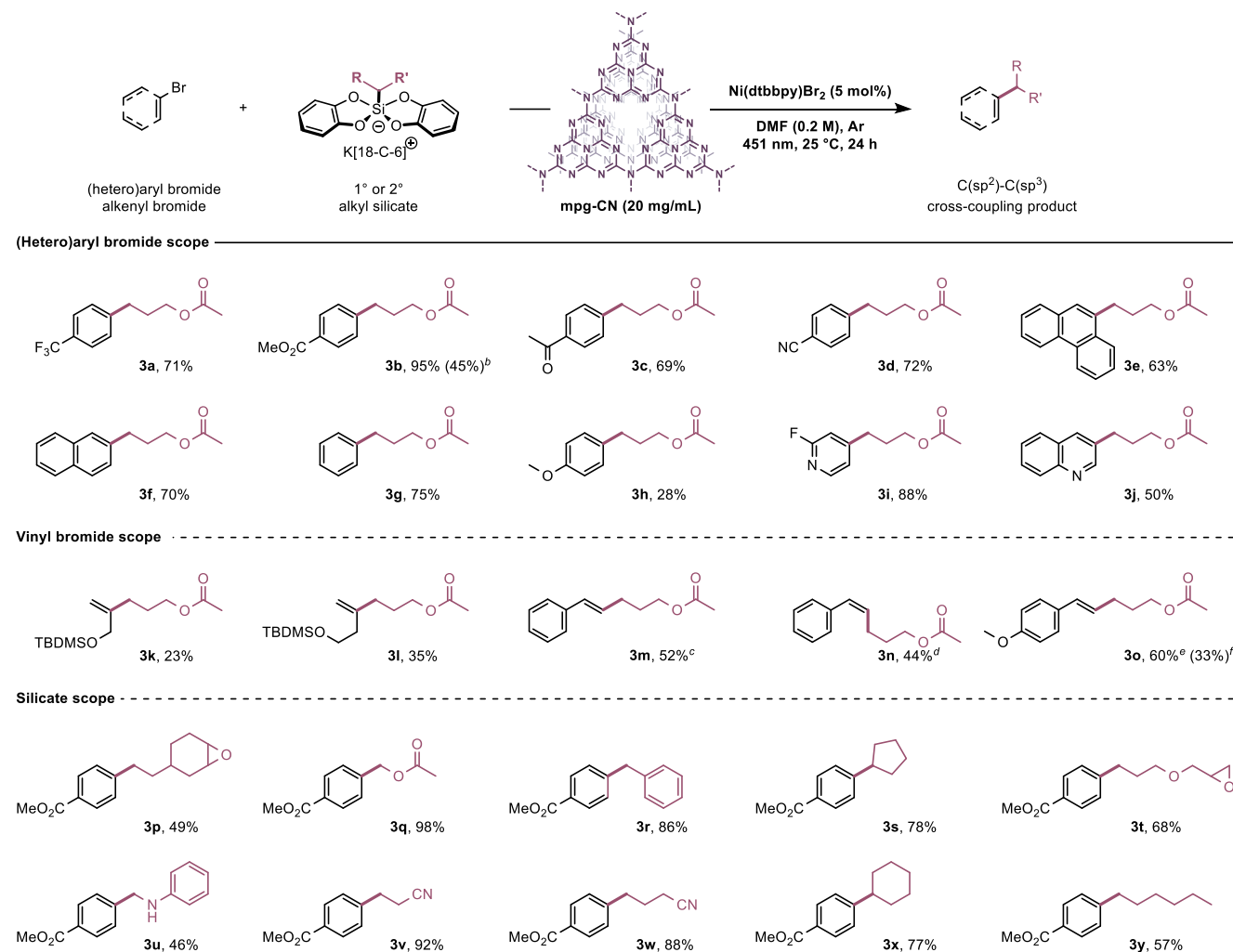
^a Reactions were run in anhydrous DMF (0.2 M) under irradiation with blue LEDs (451 nm) and under an Ar-atmosphere for 24 h at 25 °C. ^b Yield determined by ¹⁹F-crude NMR analysis with 4-fluoroanisole as internal standard. ^c Isolated yield. ^d n.d. = not detected. ^e No light.

With the optimized conditions in hand, we explored the scope of our methodology. Differently substituted aryl bromide acceptors were readily alkylated in between 69% and 95% yields (**3a-3d**), demonstrating that esters, ketones, and nitriles are well tolerated under these conditions. Bromobenzene as an electron neutral example was coupled in 75% yield (**3g**). Upon increasing the aromatic system from benzene to naphthalene, the yield slightly decreased to 70% (**3f**). The trend continued with 9-bromophenanthrene, which yielded the respective product **3e** in 63% yield. The

same tendency was observed for heteroarenes. While 2-fluoro-4-bromopyridine could be converted to the product **3i** in 88% yield, 3-bromoquinoline merely furnished half of the theoretical yield possible (**3j**). Electron-rich 4-bromoanisole, previously reported to be a rather challenging substrate for mpg-CN nickel dual catalysis,^{9b} yielded only

28% of the corresponding product **3h**. Next, we expanded the scope of our mpg-CN/nickel cross-coupling to alkenyl bromides, which were previously shown to undergo cross-coupling under dual catalytic conditions.^{14b,15} Starting from geminal substituted vinyl bromides, the products **3k** and **3l** were obtained in 23% and

Scheme 3: Substrate scope.^a



^a Reactions were run at a 0.2 mmol scale in anhydrous DMF (0.2 M) under irradiation with blue LEDs (451 nm) and under an Argon atmosphere for 24 h at 25 °C. Isolated yields are given. ^b 1.0 mmol scale (see the supporting information for details). ^c Received as an isomeric mixture (*E/Z* = 92/8) from the commercial starting material (*E/Z* = 90/10). ^d Received as an isomeric mixture (*E/Z* = 22/78) from the (*Z*)-vinyl bromide (*E/Z* = 2/98). ^e Received as an isomeric mixture (*E/Z* = 93/7) from the (*E*)-vinyl bromide (*E/Z* = 98/2). ^f Vinyl chloride was used as starting material.

35% yield, respectively. A commercial mixture of β -bromostyrene (*E/Z* = 90/10) was cross-coupled in 52% yield (**3m**, *E/Z* = 92/8). (*Z*)- β -bromostyrene (*E/Z* = 2/98) yielded product **3n** in 44% yield with an increased amount of the thermodynamically favored *E*-isomer (*E/Z* = 22/78).¹⁶ An improved yield of 60% was observed when 4-methoxybromostyrene was subjected to our cross-coupling protocol (**3o**, *E/Z* = 93/7). Further, its alkenyl chloride derivative could be employed in the reaction, albeit furnishing **3o** with around half the yield compared to the bromide.

Last, we explored the scope of the silicate radical precursors. Both primary and secondary silicates could be employed in this transformation. As examples, cyclopropyl and cyclohexyl bis(catecholato)silicates were transformed into respective products **3s** and **3x** in 78% and 77% yields. We then turned our attention to the more abundant primary silicates. Radicals derived from benzyl bis(catecholato)silicate and acetoxymethyl bis(catecholato)silicate were coupled in 86% and 98% yield (**3r** and **3q**), while methylanilino bis(catecholato)silicate was converted in only 46% yield to product **3u**. Both cyanoethyl and cyanopropyl bis(catecholato)silicate were competent coupling partners that reacted to the products **3v** and **3w** in 92% and 88% yields,

respectively. A significantly lower amount of product was formed when the parent silicate contained an epoxide, leading to 68% and 49% of product **3t** and **3p**. Lastly, from n-hexyl bis(catecholato)silicate, **3y** was synthesized in 57% yield.

Recycling experiments demonstrate the reusability of recovered mpg-CN in this reaction – the yield of **3a** remained at around 76% after using the photocatalyst for three consecutive cycles but decreased to 43% after our cycles (See the supporting information). To gain insights into possible deactivation modes of the catalyst, a sample of photocatalyst from the large-scale reaction has been recovered and analyzed. Time-correlated single-photon counting time-resolved emission spectroscopy (TCSPC-TRES) of the recovered material in comparison to freshly prepared one show a decrease in fluorescence lifetime from 0.143 ± 0.012 ns to 0.0338 ± 0.0037 ns (Figure 1a). This observation is consistent with the results of an electron paramagnetic resonance (EPR) spectroscopy experiment: the EPR signal, attributed to the electrons trapped in the mpg-CN structure, was found to decrease after the recovery of the catalyst (see figure 1b).

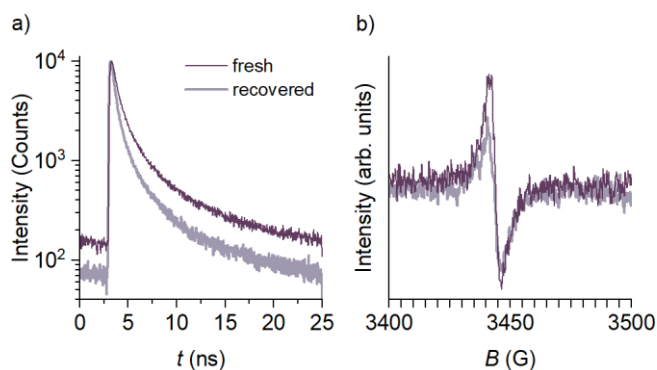


Figure 1: a) Fluorescence decay curves in semi-logarithmic scale. b) EPR spectra of fresh mpg-CN and recovered after the photocatalytic experiment

We invoked inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the nickel content of the recovered material to be 0.146 ± 0.002 wt.%. This value corresponds to roughly 5% of the nickel atoms that were originally added as the catalyst and were not removed during the recovery process. Given recent works on carbon nitride materials with atomically dispersed metals that retain their photocatalytic activity up to at least five cycles without the necessity of adding fresh portions of Ni-precatalyst, it is not clear, whether the nickel deposits are the reason for the decrease of the yield after only four cycles.^{10a, 10f} Additionally, similar methodologies report no loss of activity after up to six reaction cycles.^{11-12, 17} The explanation of the reduced activity, especially compared to other mpg-CN/nickel catalyzed C(sp²)-C(sp³) cross-couplings (scheme 1), might originate from the formation of bis(catecholato) silane side products.^{13b} In fact, the low solubility attributed to these compounds has been rationalized only very recently as originating from the rapid formation of oligomers.¹⁸ This property might be problematic for our heterogeneous system, as those species would be recovered together with the catalyst at the centrifugation step. Additionally, organic solvents would hardly remove this side product from the recovered semiconductor. The bis(catecholato)silanes, potentially accumulating with each cycle, might obstruct the accessibility of the

substrate to the surface of the mpg-CN in a new cycle or inhibit redox events of the catalysts.

In conclusion, we developed a new mpg-CN/nickel-based protocol to cross-couple alkyl bis(catecholato)silicates with aryl bromides in generally good yields and vinyl bromides in low to moderate yields. We demonstrated the reusability of the catalyst for four consecutive cycles. Analysis of recovered material shows a decrease in fluorescence lifetime and EPR signal strength, indicating partial deactivation of the catalyst by either deposits of nickel or (bis)catecholato silane side products. Engineering of atomically dispersed transition metal sites at carbon nitride surface might be a viable strategy to further improve the recyclability of the photocatalyst.¹⁹

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the internet at <http://pubs.acs.org>.

Experimental details, characterization data, spectra (PDF)

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Author Contributions

All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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