ARTICLE

Photocatalyst-free, visible-light-mediated nickel catalyzed carbon–heteroatom cross-couplings

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Abstract

Metallaphotocatalysis typically requires a photocatalyst to harness the energy of visible-light and transfer it to a transition metal catalyst to trigger chemical reactions. The most prominent example is the merger of photo- and nickel catalysis that unlocked various cross-couplings. However, the high reactivity of excited photocatalyst can lead to unwanted side reactions thus limiting this approach. Here we show that a bipyridine ligand that is subtly decorated with two carbazole groups forms a nickel complex that absorbs visible-light and promotes several carbon–heteroatom cross-couplings in the absence of an exogenous photocatalysts. The ligand can be polymerized in a simple one-step procedure to afford a porous organic polymer that can be used for heterogeneous nickel catalysis in the same reactions. The material can be easily recovered and reused multiple times maintaining high catalytic activity and selectivity.

MAIN

Introduction

Strategic carbon–carbon and carbon–heteroatom bond formations are key to the synthesis of fine chemicals.[1,2] Nickel catalysts are an abundant alternative to palladium catalysts, but reductive elimination is limiting this approach.[3,4] This problem was successfully tackled by combining nickel- and photocatalysis (Fig. 1a).[5-7] Suitable photocatalysts for dual photo/nickel catalytic carbon–heteroatom cross-couplings range from ruthenium and iridium polypyridyl complexes and organic dyes to heterogeneous semiconductors.[6] Moreover, nickel complexes and visible-light photocatalysts were combined in bifunctional heterogeneous materials, such as metal-organic frameworks,[8,9] organic polymers,[10] or functionalized semiconductors.[11-14] Although dual photo/nickel catalysis is attractive, the need for a photocatalyst is a drawback. Commonly applied homogeneous noble-metal based photocatalysts that are mainly applied are expensive, not easily recyclable and unsustainable. Moreover, their high reactivity upon excitation can trigger unwanted side-reactions[15] and deactivation of the nickel catalyst[16] results in low selectivities and often poor reproducibility.

The first mechanistic hypothesis for dual photo/nickel catalyzed carbon–heteroatom cross-couplings suggested that energy- or electron transfer between the photocatalyst and a thermodynamically stable Ni^{II} intermediate triggers reductive elimination of the desired product.[6,17] Recent studies provided evidence that these reactions proceed through Ni^{I}/Ni^{III} cycles without a Ni^{II} resting state.[18-21] Doyle and colleagues showed that upon absorption of light, Ni^{II}(dtbbpy) aryl halide complexes (dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) undergo Ni–aryl hemolysis to form a catalytically active Ni^{I} catalyst.[22,23] This observation was expanded to a synthetic protocol for C–O and C–N cross-couplings using UV-light irradiation.[24,25] More recently, pulse radiolysis together with spectroelectrochemistry indicated that Ni^{0}/Ni^{II} comproportonation generates a Ni^{I} bipyridyl species that rapidly undergoes oxidative addition with iodobenzene.[21] Moreover, Nocera and coworkers showed that sub-stoichiometric amounts of zinc can be used instead of a photocatalyst and light for C–N and C–O cross-couplings.[26] Here, the metal reductant was proposed to generate the active Ni^{I} catalyst from a Ni^{II} pre-catalyst that engages in a thermally sustained Ni^{I}/Ni^{III} cycle.

Based on these mechanistic findings, we questioned whether a visible-light-mediated approach to nickel-catalyzed carbon–heteroatom cross-couplings without an exogenous photocatalyst or reductant is feasible. The development of a benchstable Ni^{II} pre-catalyst that can be directly activated by visible-light would overcome the drawbacks associated with the price and reactivity of many photocatalysts without using highly energetic UV-light. We hypothesized that this can be realized via the modification of a bipyridyl ligand with a structural motif that extends the absorption of an *in situ* formed Ni^{II} pre-catalyst to visible-light. We speculated that such a complex might form the key Ni^{I} species upon irradiation through, for example, homolytic fission of a Ni-halogen bond, or intramolecular charge transfer.

Here we show that this can be indeed achieved by decorating 2-2'-bipyridine with two carbazole units (Fig. 1b). This ligand enables visible-light-mediated cross-couplings of several nucleophiles with aryl halides. Moreover, we demonstrate that the ligand can be polymerized to yield a conjugated microporous polymer that serves as a recyclable heterogeneous macroligand for metallaphotocatalytic carbon–heteroatom couplings.

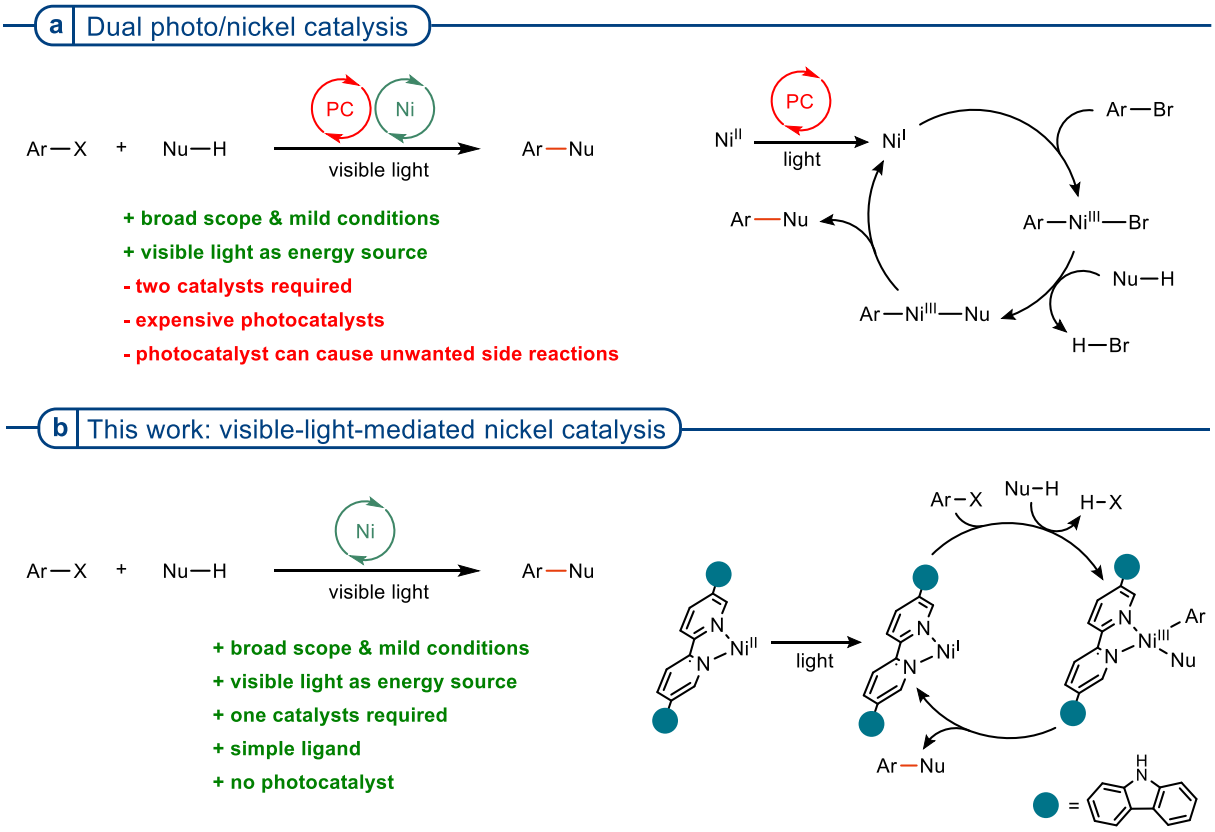


Figure 1 | Strategies for visible-light mediated nickel catalyzed carbon–heteroatom cross-couplings. a, Dual photo/nickel catalysis requires a nickel catalyst and an exogenous photocatalyst. **b,** Visible-light-mediated nickel catalysis through ligand modification requires only one molecular catalyst (this work).

Ligand design and evaluation

Ni^{II}(dtbbpy) aryl halide complexes catalyze cross-couplings using UV-light (390 nm LEDs).[22,23] These catalysts are synthesized from $Ni(COD)_2$ using glove-box or Schlenk techniques,[22,23] which, together with the constraint to high energy photons, limits their practicability. In dual photo/nickel catalysis, on the contrary, Ni(2,2'-bipyridyl)X_2 (X = Cl, Br) complexes that form *in situ* from cheap, benchstable Ni^{II} salts and the corresponding ligand can be used. [5-7] The UV-Vis absorption spectrum of a mixture of $NiCl_2$·glyme (glyme = 1,2-dimethoxyethane) and dtbbpy in DMAc (*N*,*N*-dimethylacetamide) shows that the resulting complex only absorbs light below 320 nm (Fig. S5). To shift the absorption towards the visible-light spectrum, we synthesized 5,5'-dicarbazolyl-2,2'-bipyridyl (czbpy) via a copper-catalyzed Ullmann coupling between 5,5'-dibromo-bipyridine and 9*H*-carbazole (Fig. 2a).[27] The UV-Vis spectrum of czbpy shows a strong absorption band centered at ~350 nm (Fig. S5). More importantly,

dissolving $NiCl_2$·glyme and czbpy in DMAc resulted in a complex that absorbs visible-light up to 450 nm (Fig. S5).

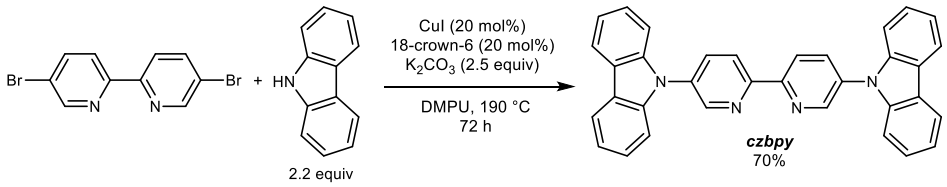
This single, high yielding modification of a commercially available bypridine derivative resulted in an in situ formed nickel catalyst that mitigates the necessity of exogeneous photocatalysts (Fig. 2b). The ligand was suitable for the coupling of aryl halides with sulfinates, carboxylic acids, and sulfonamides. The coupling of 4-iodobenzotrifluoride and a sodium sulfinate salt (C–S coupling), which was previously reported using combinations of a nickel catalyst with iridium[28] or ruthenium[29,30] polypyridyl complexes as photocatalyst, afforded sulfone ***1*** in excellent yield after 22 h irradiation with blue light (440 nm, entry 1). No conversion was detected when the reaction was carried out in the dark (entry 2). Sodium sulfinates and aryl halides can assemble in electron-donor acceptor (EDA) complexes and afford sulfones upon UV light irradiation.[31] Accordingly, even in absence of $NiCl_2$·glyme small amounts of ***1*** were formed (entry 3), due to partial emission in the UV region of the light source. When 2,2'-bipyridine (bpy), 9*H*-carbazole or a combination of bpy and 9*H*-carbazole were used, the desired product was also formed, although with significantly lower selectivity (entry 4-6).

The C–O arylation of 4-iodobenzotrifluoride with *N*-Boc-proline under optimized conditions resulted in 88% of the desired product (***2***). No product formation was observed in the dark, without $NiCl_2$·glyme, or when 9*H*-carbazole was used as ligand (entry 8-10). While optimized conditions resulted in 88% of the desired product (***2***), only small amounts (<10 %) of **2** were formed using bpy, or bpy together with 9*H*-carbazole (entry 9, 11). These findings support our hypothesis that czbpy enables activation of nickel catalysts with wavelengths above 400 nm, which are not accessible to bpy complexes.

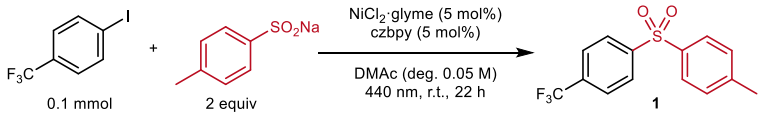
Under optimized conditions, the light-mediated, nickel-catalyzed *N*-arylation of sulfonamides afforded ***3*** in 75% yield (entry 13). Light and the nickel salt were crucial for product formation (entry 13-14). Partial consumption of the starting material in the absence of a nickel salt (entry 15) might be a result of a photocatalytic activation of aryl iodides.[15] Product formation was not detected using bpy as ligand (entry 17), but significant amounts of ***3*** were obtained in presence of 9*H*-carbazole (entry 16) or a combination of 9*H*-carbazole and bpy (entry 16, 18). Although such reactivity was not observed in the other coupling protocols, this effect might result from formation of photoactive Ni-carbazole complexes. It was recently shown that carbazole acts as a strong σ-donating ligand that reduces the energy difference in MLCT transitions that account for light absorption of nickel complexes.[32,33]

Electron paramagnetic resonance (EPR) spectroscopy was carried out to shed some light on the reaction mechanism. Up to two signals were found depending on the solution composition in frozen solution (Fig. S8 & S9). The first signal with a linewidth of approx. 20 G was found in all solutions and appeared to be light-independent. We assign this signal to a Cu^{II}·czbpy complex, owing to a residual Cu contamination from the ligand preparation process (~ 1 mg g^{-1} as measured by ICP-OES analysis). A second, narrow signal occurred upon illumination and rapid freezing to <25 K, when at least Ni·czbpy and an aryl iodide (4-iodobenzotriflouride) were present. A kinetic analysis of a related protocol using exogenous photocatalysts showed a rate dependence on the aryl halide, which was assigned to a direct

a Ligand synthesis

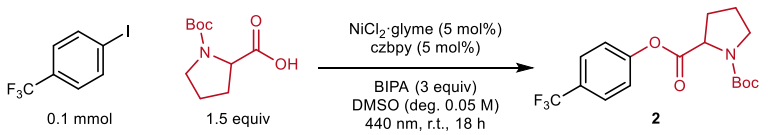


b Ligand evaluation



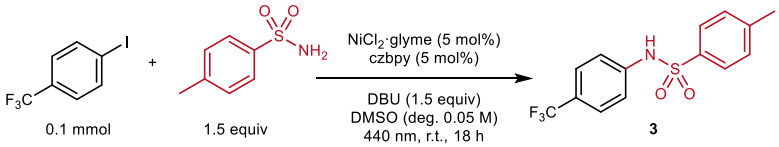
Entry	Variation	Conversion [%][a]	Yield [%][b]
1	none	>99	92
2	no light	n.d.	n.d.
3	no $NiCl_2$·glyme	86	17
4	9*H*-carbazole (10 mol%) instead of czbpy	20	6
5	bpy (5 mol%) instead of czbpy	57	34
6	bpy (5 mol%) & 9*H*-carbazole (10 mol%) instead of czbpy	>99	62

[a]Conversion of 4-iodobenzotrifluoride determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. n.d. = not detected



Entry	Variation	Conversion [%][a]	Yield [%][b]
7	none	>99	88
8	no light	n.d.	n.d.
9	no $NiCl_2$·glyme	n.d.	n.d.
10	9*H*-carbazole (10 mol%) instead of czbpy	n.d.	n.d.
11	bpy (5 mol%) instead of czbpy	8	4
12	bpy (5 mol%) & 9*H*-carbazole (10 mol%) instead of czbpy	14	8

[a]Conversion of 4-iodobenzotrifluoride determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. BIPA = *N*-*tert*-butylisopropylamine; n.d. = not detected;



Entry	Variation	Conversion [%][a]	Yield [%][b]
13	none	87	75
14	no light	n.d.	n.d.
15	no $NiCl_2$·glyme	18	n.d.
16	9*H*-carbazole (10 mol%) instead of czbpy	42	32
17	bpy (5 mol%) instead of czbpy	3	n.d.
18	bpy (5 mol%) & 9*H*-carbazole (10 mol%) instead of czbpy	61	51

[a]Conversion of 4-iodobenzotrifluoride determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene; n.d. = not detected

Figure 2 | Ligand synthesis, optimized reaction conditions and control experiments. a, The ligand for photocatalyst-free, visible-light-mediated nickel catalysis was synthesized via an Ullmann C–N coupling. **b**, Optimized Conditions and control experiments for the coupling of 4-iodobenzotrifluoride with sodium *p*-toluensulfinate, *N*-Boc-proline and *p*-toluensulfonamide.

photocatalytic activation.[15] Due to its nature (microwave power saturation and linewidth), the light-dependent EPR-signal is of organic origin without involvement of Ni. Therefore, we tentatively assign this signal to an elusive paramagnetic species that results from a light-induced reaction between a Ni·czbpy species and the aryl iodide, suggesting that the aryl iodide may play a role in the activation of the pre-catalyst. No signal for the proposed Ni^{I} intermediate was detected, which can be rationalized by the instability of such three-coordinate Ni halide complexes, or rapid oxidative addition.[21]

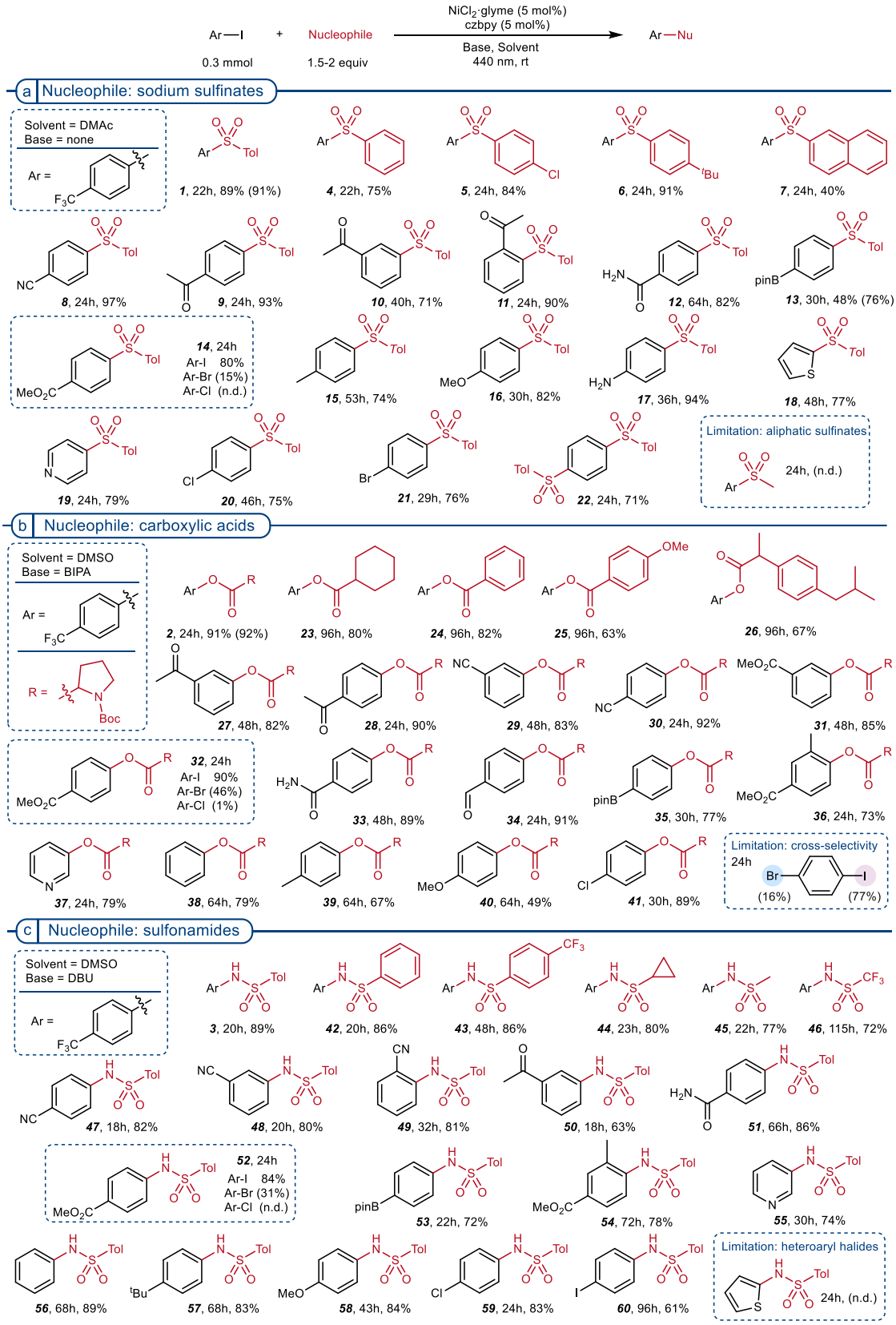
Scope and Limitations

Next, we explored the scope and limitations of photocatalyst-free, visible-light-mediated carbon–heteroatom cross-couplings (Table 1). Several aromatic sulfinate salts were successfully coupled with 4-iodobenzotrifluoride (Table 1a, ***1***, ***4-7***). Optimized reaction conditions did not result in the desired product using sodium methane sulfinate. It is noteworthy that this substrate was earlier reported as a successful coupling partner when $NiCl_2$·bpy was used in combination with tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate as exogenous photocatalyst.[30] With regard to the aryl iodide, the reaction affords the corresponding sulfones in presence of electron withdrawing groups such as trifluoromethyl (***1***), nitrile (***8***), ketone (***9-11***), amide (***12***), boron pinacolate ester (***13***), and methyl ester (***14***). Para- (***9***) and ortho- (***11***) substitution showed similar reactivity, whereas meta-substitution (***10)*** required a longer reaction time for full conversion. Electron-rich aryl iodides, such as 4-iodotoluene (***15***) and 4-iodoanisole (***16***), were suitable substrates and the presence of an unprotected amine group (***17***) was tolerated. Coupling of 2-iodothiophene (***18***) and 4-iodopyridine (***19***) showed that heteroaryl iodides are suitable substrates.

A comparison of different aryl halides showed that an aryl iodide reacts significantly faster than the corresponding bromide (***14***). This is in contrast to dual nickel/photocatalytic protocols, where iodides and bromides exhibit similar reactivity.[28,29] Aryl chlorides undergo nickel/photocatalytic reactions when the more electron donating ligand 4,4'-dimethoxy-bpy is used,[28] but czbpy was not suitable for aryl chloride. These observations were applied for selective couplings of aryl iodides that contain a chloride (***20***) or a bromide substituent (***21***). Moreover, diarylated product ***22*** was synthesized from 1,4-diiodobenzene using three equivalents of sodium *p*-toluensulfinate.

Good to excellent isolated yields were obtained for the C–O arylation of 4-iodobenzotrifluoride with aliphatic and aromatic carboxylic acids (Table 1b, ***2***, ***23-26***). Further, a range of aryl iodides containing electron-withdrawing groups afforded the corresponding products (***2***, ***27-35***). The influence of the substituents on the reactivity is highlighted by the longer reaction times required for the coupling of meta-substituted (***27***, ***29***, ***31***) aryl iodides, compared to their para-substituted analogues (***28***, ***30***, ***32***). The coupling of ortho-substituted aryl iodides was not possible in case of 2-iodoacetophenone, 2-iodobenzonitrile, but ***36*** was successfully synthesized from methyl 3-methyl-4-iodobenzoate. A heteroaryl iodide was also susceptible to the optimized reaction conditions (***38***). High electron densities on the aryl iodide decreased their reactivity towards the C–O coupling, as showcased for the series 4-

Table 1 | Visible-light-mediated nickel-catalyzed C–S, C–O and C–N cross-couplings.[a]



[a]Reaction conditions: aryl halide (300 µmol), nucleophile (a, sodium sulfinate, 600 µmol; b, carboxylic acid, 450 µmol; c, sulfonamide, 450 µmol), $NiCl_2$·glyme (15 µmol), czbpy (15 µmol), base (b, *N*-*tert*-butylisopropylamine, 900 µmol; c, 1,8-diazabicyclo[5.4.0]undec-7-ene, 450 µmol), solvent (a, DMAc, 6 mL; b, DMSO, 3 or 6 mL; c, DMSO, 6 mL), 440 nm LED (2 lamps at full power) at room temperature. Isolated yields are reported. NMR yields are in parantheses and were calculated via ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene or maleic acid as internal standard. n.d. = not detected. Bpin = boronic acid pinacolate ester.

iodobenzene (***38***), 4-iodotoluene (***39***) and 4-iodoanisole (***40***). Similar to the C–S coupling described above, aryl iodides work best in the reaction (***32***, 90% from Ar-I). The reaction is rather slow using the corresponding bromide (46% NMR yield from Ar-Br), and a chloride afforded only traces of the desired product. As a result, 1-chloro-4-iodobenzene (***41***) coupled selectively on the iodo-position, but 1-bromo-4-iodobenzene reacted unselectively. All of these results are in agreement with previous reports on the dual nickel/photocatalytic cross-coupling of carboxylic acids with aryl halides, indicating that the photocatalyst-free strategy follows a similar mechanism.[11,15,26,34,35]

Aromatic as well as aliphatic sulfonamides (***3***, ***42***-***46***) gave selective C–N cross-couplings with 4-iodobenzotrifluoride (Table 2c), even though long reaction times were necessary in case of electron-withdrawing groups (***43***, ***46***). In contrast to the previous C–S and C–O coupling, reactivity is not affected by the substitution pattern of the aryl iodide (***47***-***49***, ***54***) or by the presence of either electron-withdrawing or electron-donating functional groups (***3***, ***47***-***53***, ***56***-***58***). Heteroaryl halides are problematic substrates in dual nickel/photocatalytic sulfonamidation protocols and require a ligand-free approach at elevated temperature.[36] Under our optimized conditions 3-iodopyridine gave ***55*** in good yield, but no product was observed for 2-iodothipohene. Previously, aryl bromides were coupled with sulfonamides using combinations of nickel and iridium catalysts.[36] Screening of different halides revealed that bromides are suitable substrates but iodide reactivity is superior (***52***, 84% from Ar-I, 31% NMR yield from Ar-Br within 24h). Aryl chlorides are not reactive and ***59*** was obtained with good selectivity from 1-chloro-4-iodobenzene.

Unfortunately, this ligand was not suitable for coupling of aryl halides with amines, thiols or alcohols that were previously reported using dual nickel/photocatalysis.[6] Attempts to form carbon–carbon bonds through coupling of aryl halides with borontrifluorides[37] or α-silylamines[38] ,also did not meet with success or suffered from low selectivity (Table S30).

Polymerization of czbpy for heterogeneous, visible-light-mediated nickel catalysis

Having shown that czbpy serves as a versatile ligand for visible-light-mediated cross-couplings via homogeneous nickel-catalysis without an exogenous photocatalyst, we aimed to extend this approach to develop a heterogeneous, recyclable catalytic system.[39] Defined porous materials are ideal candidates for immobilization of metal catalysts, as they enable optimal access to the catalytic sites. The microporous organic polymer network poly-czbpy was synthesized from czbpy via oxidative polymerization with iron(III) chloride and exhibits a Brunauer-Emmett-Teller surface area (S_{BET}) of 853 $m^2\ g^{-1}$ (Fig. 3a).[27] In accordance with the literature,[27] the chemical structure of poly-czbpy was confirmed by ^{13}C CPMAS NMR spectroscopy (Fig. S1) showing signals between 130 and 152 ppm, which verify the existence of bipyridine moieties within the structure. Additionally, at 137 ppm a signal corresponding to carbons in vicinity to carbazolyl nitrogen C_{Ar}-N was detected. Ni@poly-czbpy was subsequently prepared by refluxing a suspension of poly-czbpy and $NiCl_2$ in methanol. Investigation of the porosity by nitrogen sorption measurements after the metalation showed a decreased BET surface

of 470 m^2 g^{-1} due to the immobilization of the Ni(II) complex. Presence of nickel shifts the absorption of the material up to 650 nm (Fig. 3b), while the metal-free ligand framework poly-czbpy absorbs until 550 nm. Characterization of Ni@poly-czbpy by X-ray photoelectron spectroscopy (XPS) confirmed successful immobilization of Ni(II) species on the polymeric material. The N 1s core spectrum (Fig. 3c) contains three signals for nitrogen: i) an intense peak at 400.4 eV corresponding to polymerized carbazole moieties, ii) a signal at 399.7 eV which is assigned to N-Ni coordination of the Ni(II)-complex and iii) a low-intensity peak at 400.2 eV deriving from bipyridine nitrogen species which are not coordinated to nickel. The Ni 2p spectrum (Fig. 3d) shows a doublet and its corresponding satellites. Peaks located at 855.6 eV and 873.3 eV are assigned to $2p_{3/2}$ and $2p_{1/2}$ signals for Ni(II) species, respectively. ICP-OES analysis indicated presence of 3.7% w/w of nickel on the material Ni@poly-czbpy, corresponding to an occupation of 40% of bipyridine functionalities. Furthermore, scanning electron microscopy (SEM) images of Ni@poly-czbpy show the morphology of the amorphous polymeric particles analyzed by elemental mapping (Fig. S2). The images depict a homogeneous distribution of nickel, nitrogen and chlorine within the material.

After confirming that poly-czbpy is suitable to coordinate and immobilize nickel atoms, its use in the previously optimized coupling reactions was studied (Fig. 3e). The desired C-S, C-O and C-N coupling products were obtained by irradiation at 440 nm of mixtures of $NiCl_2$·glyme (5 mol%) and poly-czbpy (5 mol%), but the selectivity of the reactions was lower than using homogeneous conditions.

Next, we studied whether the heterogeneous catalytic system based on poly-czbpy can be recycled. Poly-czbpy was recovered after the C–S coupling reaction by centrifugation and was, after washing, reused for the same reaction (Fig. 3f). Initial results confirmed that poly-czbpy can be recycled ten times without significant loss in reactivity (orange bars). The addition of the nickel salt at each reaction cycle was not necessary in a second set of experiments (green bars) and the selectivity of the reaction improved upon washing and reusing the material without addition of fresh nickel salt (1^{st} cycle: 78% yield, 2^{nd} cycle: 90% yield). According to ICP-OES analysis, 40% of the pyridine sites in poly-czbpy coordinate to nickel. Therefore, equimolar amounts of nickel and poly-czbpy lead to an excess of unligated nickel in solution that presumably has a detrimental effect on the selectivity. This was confirmed during a series of experiments using lower nickel salt/macroligand ratio (2.5 mol% of $NiCl_2$·glyme, 5 mol% poly-czbpy) that improved selectivity for all transformations (Table S22-S24). A final recycling experiment where 2.5 mol% of $NiCl_2$·glyme was loaded only for the first reaction (Fig. 3f, blue bars) resulted in excellent yields for the C–S coupling reaction without significant loss in activity during ten recycling experiments.

The 2p Ni XPS spectra (Fig. S6) of the recycled catalyst confirm that the Ni(II) species remained intact within the polymer network demonstrating the recyclability of the material. The signals for the doublet were detected at 856.6 eV ($2p_{3/2}$) and 874.6 eV ($2p_{1/2}$), respectively. Furthermore, 1s N XPS core-level spectra (Fig. S7) show that by single addition of Ni(II) precursor predominantly the pyridinic nitrogen

signal at 399.2 eV was detected due to relatively low amount of Ni(II) coordinated to bipyridine, while addition of Ni(II) after each cycle result mainly in Ni-N coordination signals at 399.7 eV.

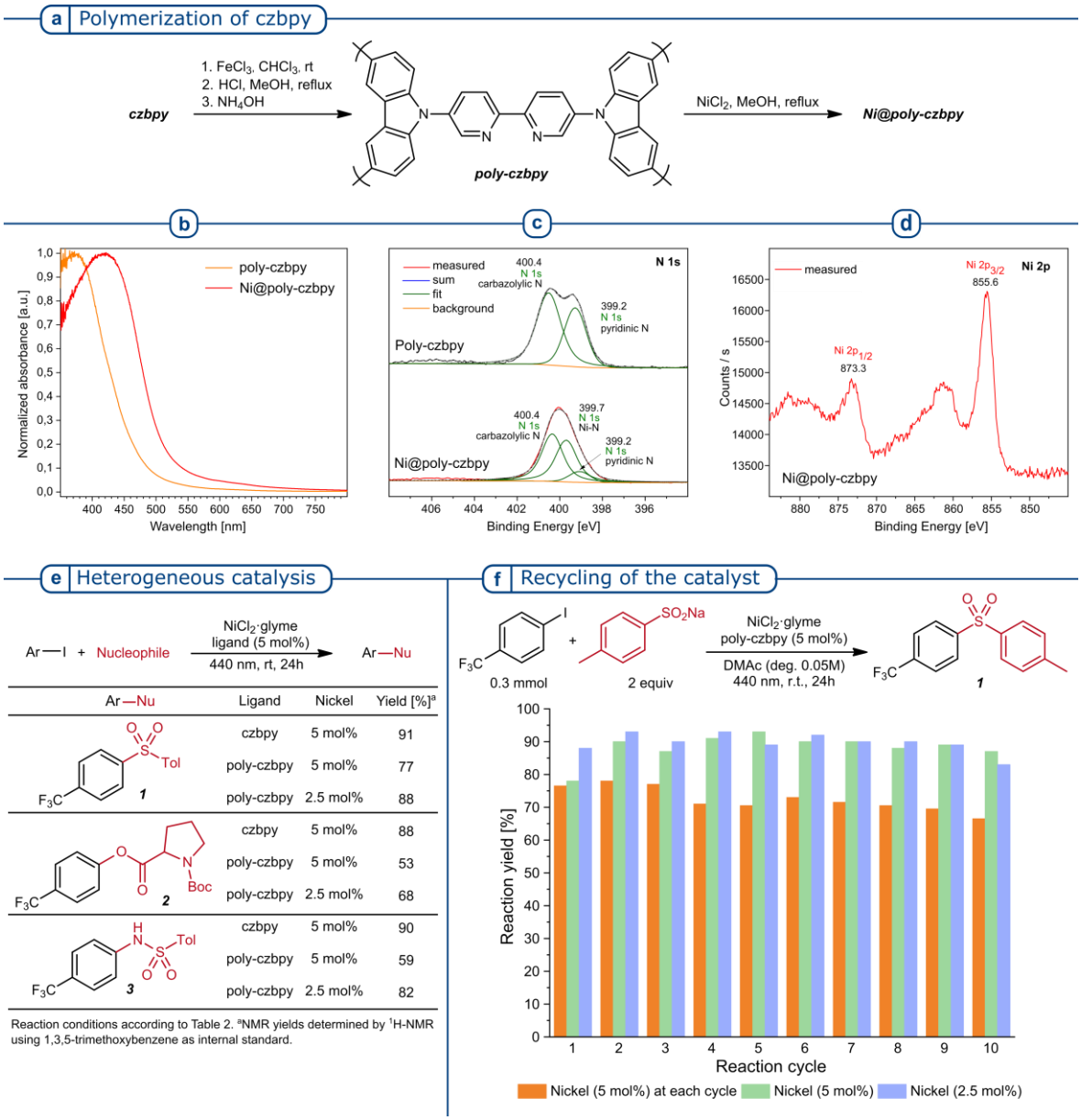


Figure 3 | Heterogeneous visible-light-mediated nickel catalysis with poly-czbpy. **a,** Preparation of the porous organic polymer poly-czbpy and metalation with nickel. **b**, Characterization of poly-czbpy and Ni@poly-czbpy by UV-visible spectroscopy. XPS analysis of Ni@czbpy: N 1s (**c**) and Ni 2p core-level spectra (**d**). **e**, Heterogeneous visible-light-mediated nickel catalysis using poly-czbpy. **f**, Catalyst recycling in the C–S coupling reaction. Reaction conditions: 4-iodobenzotrifluoride (300 µmol), sodium *p*-toluensulfinate (600 µmol), $NiCl_2$·glyme (7.5-15 µmol), poly-czbpy (7.43 mg), DMAc (6 mL), 440 nm LED (two lamps at full power) at room temperature. Yields were calculated via ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard. Orange: 5 mol% of $NiCl_2$·glyme at each reaction cycle; green: 5 mol% of $NiCl_2$·glyme only for the first cycle; blue: 2.5 mol% of $NiCl_2$·glyme only for the first cycle.

Conclusion

Combining a Ni(II) salt with czbpy results in a homogeneous complex that absorbs up to 450 nm and enables visible-light-mediated carbon–heteroatom cross-couplings without exogenous photocatalysts. Selective C–S, C–O and C–N bond formations were achieved by coupling aryl iodides with sodium sulfinates, carboxylic acids or sulfonamides, respectively. A porous organic polymer that was prepared by oxidative polymerization of czbpy, is suitable for immobilization of nickel and enables heterogeneous, visible-light-mediated nickel catalysis. The heterogeneous material recovered after the reaction can be reused, maintaining a high activity over ten reaction cycles. EPR experiments indicated an involvement of the aryl iodide for the light-mediated activation of the pre-catalyst. Further investigations to understand the mechanism of these reactions are currently underway in our laboratory.

Methods

Experimental procedure for the synthesis of 5,5'-Di(9H-carbazol-9-yl)-2,2'-bipyridine (czbpy).

Under Argon atmosphere, a mixture of 5,5'-dibromo-2,2'-bipyridine (500 mg, 1.59 mmol), carbazole (586 mg, 3.5 mmol), copper(I) iodide (61 mg, 0.32 mmol), 18-crown-6 (84 mg, 0.32 mmol), potassium carbonate (549 mg, 3.98 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 1.67 mL) were placed in a pre-heated 100 mL Schlenk flask. The flask was connected to a reflux condenser before the mixture was stirred for 24 h at 190 °C in an oil bath. At 190 °C the reaction mixture turned into a yellow solution, after 24 h a black viscous oil was obtained which was quenched with 2 M HCl solution (100 mL). The mixture was extracted with dichloromethane and washed with $NH_3 \cdot H_2O$ (25%, 60 mL) and water. The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by column chromatography on amino-functionalized silica gel from cyclohexane and dichloromethane. The obtained yellow solid was further purified by recrystallization from a mixture of cyclohexane and dichloromethane to afford the title compound as a light yellow crystalline solid (540 mg, 1.11 mmol, 70 %).

^{1}H NMR (400 MHz, CDCl3) δ 9.03 (d, J = 1.8 Hz, 2H), 8.81 (d, J = 7.7 Hz, 2H), 8.19 (d, J = 7.7 Hz, 4H), 8.15 (dd, J = 8.4, 2.6 Hz, 2H), 7.55 – 7.44 (m, 8H), 7.36 (m, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 153.5, 147.5, 140.6, 135.5, 135.2, 126.6, 124.0, 122.5, 121.0, 120.8, 109.6. HRMS (ESI) m/z calcd for $C_{34}H_{23}N_4$ [$(M+H)^+$] 487.1923, found 487.1918. This data is in full agreement with the data previously published in the literature.[27,40]

Poly-czbpy was prepared by polymerization of czbpy according to literature.[27]

5,5'-Di(9*H*-carbazol-9-yl)-2,2'-bipyridine (200 mg, 0.41 mmol) was dissolved in anhydrous chloroform (30 mL) and added dropwise to a suspension of $FeCl_3$ (1.20 g, 7.40 mmol) in anhydrous chloroform (30 mL) under argon. The reaction mixture was stirred at room temperature for 24 h. Then methanol (50

mL) was added, and the mixture was stirred vigorously for 2 h. The insoluble solid was collected by filtration and washed with tetrahydrofuran and chloroform, respectively. The filtration cake was transferred into a solution of HCl in methanol (6 M, 50 mL) and heated for 48 h under agitation. The methanolic HCl solution was replaced by a fresh one every 24 h. The precipitate was filtered and subsequently washed with aqueous ammonia solution (10 wt %) and methanol, respectively. The resulting solid was finally purified through Soxhlet extraction in methanol and dried in vacuo at 80 °C for 12 h to afford poly-czbpy as a yellow powder (190 mg, 95%).

Experimental procedure for homogeneous visible-light-mediated nickel catalysis

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with $NiCl_2$·glyme (3.3 mg, 15 µmol, 5 mol%), czbpy (7.3 mg, 15 µmol, 5 mol%), the aryl iodide (300 µmol) and the nucleophile (C–S: sodium sulfinate, 600 µmol, equiv; C–O: carboxylic acid, 450 µmol, 1.5 equiv; C–N: sulfonamide, 450 µmol, 1.5 equiv). Solvent (C–S: DMAc, 6mL; C–O: DMSO, 3 mL; C–N: DMSO, 6 mL) and base (C–O: N-tert-butylisopropylamine, 900 µmol, 3 equiv; C–N: 1,8-diazabicyclo[5.4.0]undec-7-ene, 450 µmol, 1.5 equiv) were added, then the vessel was sealed with a septum and Parafilm. The mixture was stirred for 1 minute at high speed, followed by sonication for 5 minutes and degassing by bubbling argon for 10 minutes. The reaction mixture was stirred at high speed (800 rpm) while irradiating it with two LED lamps (440 nm) at full power. After the respective reaction time, an internal standard (maleic acid 34.9 mg, 300 µmol, 1 equiv or 1,3,5-trimethoxybenzene 50.5 mg, 300 µmol, 1 equiv) was added to the reaction vessel, the mixture was stirred and an aliquote (20 µL) was diluted in DMSO-*d6* and analyzed by ^{1}H-NMR. The NMR sample and the reaction mixture were combined together and diluted (C–S: 0.5M HCl, 60 mL; C–O: water, 40 mL; C–N: water, 60 mL). The aqueous phase was extracted (C–S and C–N: ethyl acetate, 3x40 mL; C–O: DCM, 3x40 mL). Collected organic layers were washed with brine (2 x 40 mL) and dried on Na_2SO_4 before removing solvents under reduced pressure. The residue was purified by flash chromatography on silica gel using mixtures of hexane/ethyl acetate to obtain the desired product.

Experimental procedure for heterogeneous visible-light-mediated nickel catalysis

An oven dried vial (13 x 80 mm) equipped with a stir bar was charged with poly-czbpy (7.3 mg), sodium *p*-toluensulfinate (106.9 mg, 0.6 mmol, 2 equiv.) and $NiCl_2$·glyme (3.3 mg, 15 µmol, 5 mol%). Subsequently, 4-iodobenzotrifluoride (81.6 mg, 0.3 mmol, 1 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was stirred at high speed (800 rpm) while irradiating it with two blue LED lamps (440 nm) at full power. After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) was added and the mixture was stirred for

5 min. The reaction mixture was centrifuged at 3500 rpm for 15 min and the liquid phase was carefully separated and analyzed by ^{1}H-NMR. The recovered poly-czbpy was washed two times with DMAc (anhydrous, 6 mL, followed by centrifugation at 3500 rpm for 15 min and separation of the liquid phase), lyophilized (overnight) and reused in the next reaction.

Data availability

All experimental procedures and analytical data are available in the Supplementary Information. All data is available from the authors on reasonable request.

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Author contributions

C.C., S.G. and N. R. performed all photocatalytic experiments. S.V. synthesized and characterized czbpy and poly-czbpy. S.S. and C.T carried out EPR studies. B.P., A.T. and P.H.S., directed all research efforts. B.P. and A.T. conceived the research study. C.C., S.G. and B.P. wrote the manuscript with contributions from all authors.

Competing interest statement

The authors declare no competing interests.

Additional information

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