



Organic Photocatalysis

Organic Photocatalysis: Carbon Nitride Semiconductors vs. Molecular Catalysts

Yevheniia Markushyna,^[a] Christene A. Smith,^[a] and Aleksandr Savateev^{*[a]}

Abstract: The development of novel chemical transformations calls for environmentally friendly synthetic methods. Visible light photoredox catalysis has gained attention as a versatile tool to address these challenges. Due to the well-defined structure of homogeneous transition metal-based catalysts and organic dyes, they have been widely used to drive a wide variety of organic transformations. On the other hand, due to low cost, simple preparation procedure, and chemical stability of carbon nitride semiconductors, they have been known almost exclu-

sively in environmental applications and water splitting. Until recently the applicability of carbon nitride semiconductors in organic synthesis has remained hidden from the broad community of organic chemists. In this review, we summarize reactions mediated by heterogeneous carbon nitride photocatalysts and common homogeneous photocatalysts in the same organic reactions, such as carbon-carbon or carbon-heteroatom bond formation reactions. We compare performance of both groups of catalysts in the discussed organic reactions.

1. Introduction

The intensification of problems caused by the wide use of fossil fuels and the ever rising demand for energy, as well as the level of pollution by coal and oil industries, has forced scientist to look for new clean and renewable sources of energy.^[1] As a result, in the last several decades, green solar energy has entered the scientists' horizon in many fields.^[2] Solar energy is already used to power solar cells,^[3] and has high potential in the generation of hydrogen from water splitting,^[4] reduction of carbon dioxide,^[5] and degradation of organic pollutants,^[6] as well as several other areas.

Light energy, typically from artificial light rather than natural sunlight, may also be used to drive synthesis of fine organic compounds. In fact the progress of the last few decades shows that many chemical transformations in chemists' everyday life can be successfully driven by light.^[2b,7]

In general, photochemical reactions are well-known today and have been commonly used in the synthesis of organic molecules.^[8] However, ultraviolet (UV) light is usually needed to drive photochemical reactions. As a consequence special laboratory equipment is required. Most of the reactants are molecules transparent in visible light. Therefore visible light by itself cannot directly excite the reagents to trigger the reaction. For

such cases, a photocatalyst serves as a bridge to convert the energy of visible light into energy for the formation of a chemical bond. As an example, the $\text{CF}_3\cdot$ radical can be generated by the reaction of $\text{Ph}_2\text{SCF}_3^+ \text{ TfO}^-$ with sodium dithionite.^[9] The same $\text{CF}_3\cdot$ radical can be generated from $\text{CF}_3\text{SO}_2\text{Cl}$ upon single electron transfer from the photocatalyst excited state.^[10] On the whole in the photocatalytic approach the energy of a photon is used to generate a reactive $\text{CF}_3\cdot$ radical for subsequent bond-forming reactions. In the photocatalytic approach we also achieve higher atom efficiency by using a reagent with lower molecular weight.

In the last several years increased interest in visible light photocatalysis by chemists has produced a wide variety of photocatalytic organic reactions. Most are mediated by homogeneous transition metal molecular catalysts, which are soluble in common organic solvents, and often contain ruthenium or iridium.^[15]

Alternatively, metal-free organic dyes, e.g. acridinium salts, riboflavins, chromones, have also been studied. Nevertheless, homogeneous catalysts, in general, possess a few drawbacks, for instance difficulties in separation from the product and its recovery. That is why the development of heterogeneous catalysts free from these problems is highly desired. These heterogeneous catalysts include semiconductors,^[16] organic porous polymers,^[17] plasmonic-metal nanoparticles^[18] and other novel materials.^[19]

Among different heterogeneous catalysts, an important role is played by polymeric carbon nitrides (CNs).^[20] These materials consist mostly of C, N and partially H atoms that terminate the fringe of the material (Figure 1). The advantages of these materials are that they are suitable for oxidation and reduction of organic compounds as demonstrated by the potentials of their valence and conduction band in comparison to common substrates for these reactions (Figure 1).

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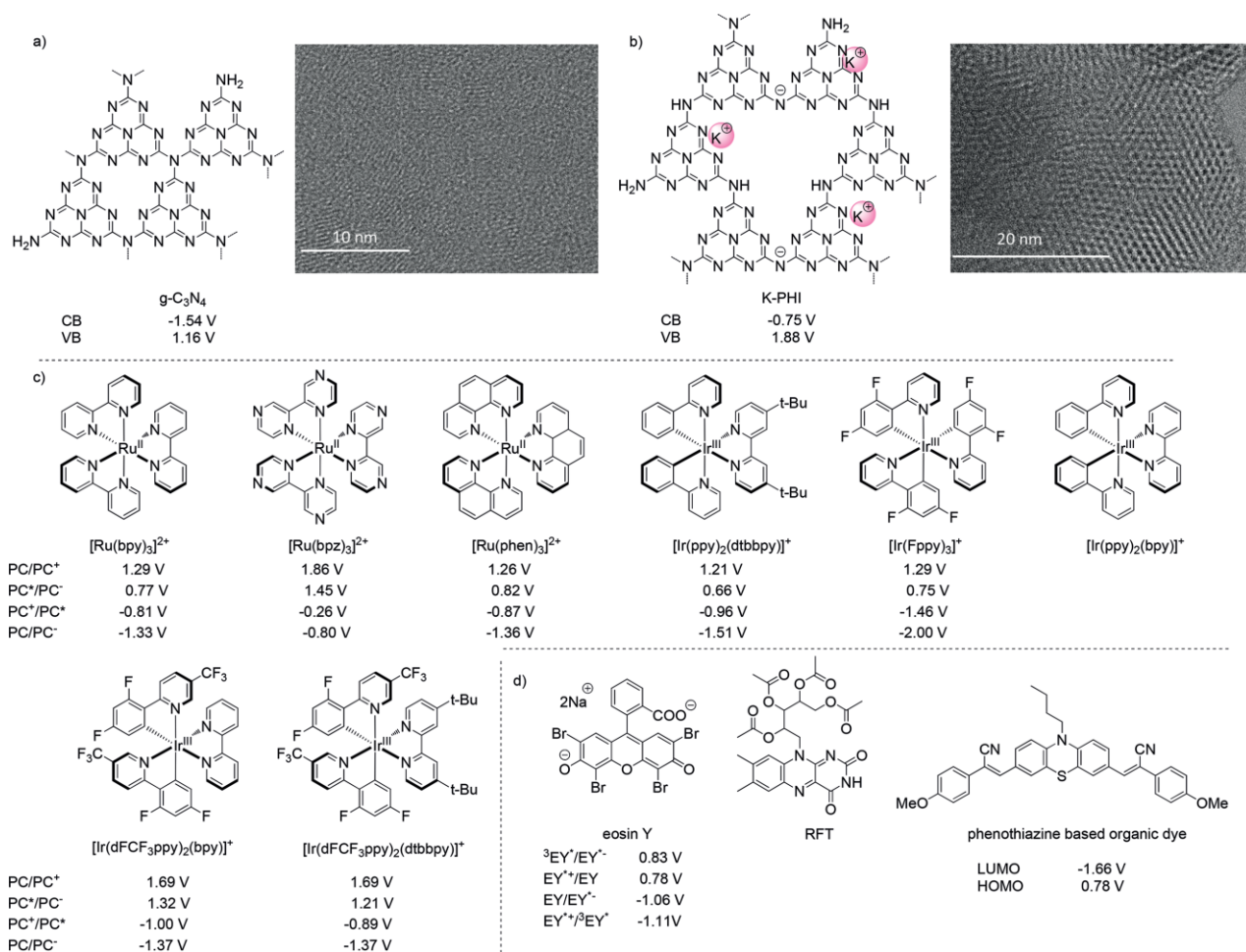


Figure 1. Overview of the heterogeneous carbon nitride photocatalysts and molecular photocatalysts. Catalyst structures: a) structure and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) image of g-C₃N₄, b) structure and AC-HRTEM image of K-PHI, c) transition metal-based complexes, d) organic dyes. The redox potentials of eosin Y,^[11] phenothiazine dye,^[12] and of metal-based complexes were taken from literature.^[13] The band gap potentials of carbon nitrides were taken from Savateev et al.^[14] The potentials are given vs. SCE.

Carbon nitrides possess a band gap of ca. 2.7 eV (460 nm), which allows for the use of visible light and therefore results in milder conditions compared to the photochemical reaction un-

der UV light. Thus a larger scope of functional groups is tolerated in these conditions since photolysis is minimized. Carbon nitrides may vary in repeating units, condensation degree, mo-



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Aleksandr Savateev obtained his PhD degree in organic chemistry in 2016. Starting from 2017 he has been leading a research group "Innovative Heterogeneous Photocatalysis" at the Max Planck Institute of Colloids and Interfaces in Potsdam, Germany. His group is focused on design of carbon nitride materials and application of these materials in photocatalysis to enable novel chemical reactions.

tifs and symmetry of intermolecular packing. A previously identified framework of CNs is a defect-rich *N*-bridged poly(tri-s-triazine),^[21] that was found to be the most stable allotrope of carbon nitride. The tri-s-triazine ring is aromatic in nature and allows for the formation of π -conjugated planar layers like that of graphite, which is often seen in carbon nitrides.^[22] In g-C₃N₄ (Figure 1a), heptazine rings are bonded through N-atoms, while in potassium poly(heptazine imide) (K-PHI) (Figure 1b), six tri-s-triazine rings form a hexagon, building a more ordered porous structure.^[23] Structural details can be observed in AC-HRTEM images in Figure 1.

One of the most important factors to be considered in photocatalytic reactions is the redox potential of catalytic species and reactants. In the photocatalytic cycle, reduced species of the catalyst mediate substrate reduction, while oxidized species mediate oxidation of the substrate. Tuning of redox potentials is regarded as one of the key strategies for improving efficiency of the catalysts. Redox potentials of the catalysts discussed in this review are presented in Figure 1.

Potential of the valence and conduction band determine redox properties of semiconducting materials. Band potentials of carbon nitrides may significantly vary depending on the structure and method of synthesis. For example, g-C₃N₄ has more negative conduction band (CB) potential (−1.54 V) than that of K-PHI (−0.75 V), whereas valence band (VB) potential of K-PHI (1.88 V) is noticeably more positive than of g-C₃N₄ (1.16 V). Different strategies for modifying electronic properties of carbon nitrides will be discussed later. As we can see from Figure 1 carbon nitrides show comparable redox potentials to that of common transition metal-based homogeneous catalysts and organic dyes and therefore can be used for both oxidation and reduction reactions.

Chemical and thermal stability, reusability, and relatively low cost of production are crucial for potential industrial scale-up of photocatalytic methods. CNs fulfil all of these requirements. Finally, ease of CN separation from the reaction mixture by filtration or centrifugation is also of great advantage for scale-up.

A survey of the current literature suggests that up to date a colossal amount of photocatalytic organic reactions have been developed and summarized in several comprehensive reviews dedicated to transition metal complexes,^[15] organic dyes,^[24] and carbon nitrides.^[16a,25]

As we have been working on the design and application of carbon nitride materials, in particular in organic photocatalysis, we actively follow the progress in this area. In our opinion, a “critical mass” of publications on carbon nitrides in organic photocatalysis has been reported within past few years to initiate a new area of heterogeneous photocatalysis. Therefore, it is timely to make preliminary conclusions about the performance of this class of photocatalysts and to outline future paths for development.

In this review, we critically evaluate the performance of homogeneous molecular photocatalysts and heterogeneous carbon nitride photocatalysts in specific reactions under similar conditions. Namely we will consider carbon-carbon bond formation, carbon-carbon radical cyclizations, and carbon-heteroatom bond formation reactions. By this we will show the molec-

ular catalysis community the capabilities of carbon nitride photocatalysts in comparison to rather common homogeneous systems. On the other hand, the review will be useful for semiconductor catalysis community in order to expand the scope of intriguing and useful photocatalytic reactions where semiconductors may be potentially applied. The objective of the review is to build a bridge between the homogeneous and heterogeneous catalysis communities to solve the existing challenges in the most efficient way.

2. Synthesis and Properties of Carbon Nitrides

In general, carbon nitrides consist only of two earth-abundant elements – carbon and nitrogen in a variable ratio close to 3 to 4. Therefore carbon nitrides can be easily prepared at low cost from a variety of nitrogen-rich materials. It also means that their properties can be easily tuned by modification of the synthetic strategies, precursors, and polymerization conditions. Control of the valence and conduction band positions by simple tuning of the nitrogen/carbon ratio in the carbon nitride structure is one of the exciting and challenging research areas in recent years. Nitrogen content in the resulting carbon nitride polymer can also be controlled by using precursors with different nitrogen content.^[26]

Optical and redox properties of CN-materials also depend on the synthesis strategy and can be further tuned through some band engineering techniques, such as elemental or molecular doping.^[27]

One of the synthesis methods that allow for the tuning of the band gap of CNs is a salt-melt (or ionothermal) method of synthesis. It has been shown as a suitable technique for controlling the polymerization process and therefore for modifying optical and electronic properties of materials.^[28] For example, by simply changing the molten salts from a LiCl/KCl eutectic mixture to NaCl/KCl, the band gap of a CN-material changed from 1.87 to 2.2 V and the conduction band from −0.66 V to −0.2 V (vs. RHE).^[29] Even by modifying polymerization conditions by altering this one method, it is possible to slightly influence the band gap of the material.^[30]

Researchers recently found that the ionothermal method of synthesizing triazine-heptazine-based polymers in NaCl/KCl molten salts influences the electronic properties of the material. This resulted in a change in the activity of the catalyst in a water-splitting reaction. An apparent quantum yield of up to 60 % was achieved in the hydrogen evolution reaction by the most active photocatalyst synthesized.^[31]

Another simple approach to control chemical and photo-physical properties of CN-materials is supramolecular preorganization of monomers before calcination. This technique allows for the formation of specific morphologies and ordered structures before calcination by adjusting supramolecular interactions (hydrogen bonding, π - π interactions, etc.) of the CN monomer.^[32] The polymeric CN can be also synthesized from already preordered materials. For example, the *N*-rich semiconductor (3-amino-1,2,4-triazole oligomer) was recently used as a precursor for CN polymer.^[33] This approach allowed for the

preservation of the starting morphology of the semiconductor, while also changing the electronic and optical properties of the final polymeric material.

Molecular doping is another unique technique for modifying the band gap of CN-based materials, which is usually not suitable for inorganic materials. Molecular doping can be performed by copolymerization of CN precursors with appropriate structure-matching organic additives. Anchoring organic groups to CN-materials can significantly change their light-harvesting properties and sufficiently narrow the band gap. Not only small functional groups but also large functional units can be introduced into the CN-framework. One example of this is when a hexaazatriphenylene unit was installed in a CN-structure, which significantly narrowed the band gap.^[34] Doping the CN-material with carbon-rich molecules showed not only narrowing of the band gap, but also enhances the conductivity of the semiconductor.^[35] When CNs are modified with organic additives, a remarkable redshift of optical absorption is observed. This allows for the harvesting of photons more efficiently from the visible part of the optical spectrum.

A facile method for the functionalization of a CN was recently reported by Vinu et al. Inspired by natural enzymes, a CN with both basic and acidic sites in one structure was synthesized.^[36] By treatment of mesoporous g-C₃N₄ with oxygen under UV light irradiation, acid groups were introduced. Both introduced acidic sites and inherent basic sites of the CN were shown to catalyze cooperatively a one-pot deacetalization-Knoevenagel reaction, which requires both acidic and basic function.

Perhaps the most important technique for modifying the electronic structure of carbon nitrides is elemental doping. CNs can be modified with both non-metal and metal elements. In the case of doping with non-metals, such as fluorine, sulfur, phosphorus or boron, substitution of C or N atoms in the structure occurs. This affects the corresponding CB or VB. Doping by metals instead occurs by insertion of the metal into the carbon nitride framework. This important technique allows for versatile band gap engineering of CN materials by varying specific doping elements and their loadings in order to achieve the desired band gap positions. In most cases doping of the material results in a narrowing of the band gap and enhancement of the charge separation and transfer. An increase in the photocatalytic activity is achieved as a result.^[37]

Exploring structural and textural properties of carbon nitrides has been one area of intense scientific research in the past decade. CNs polymeric structure has made it possible to apply common surface engineering techniques to control surface properties of the material, which is especially important in photocatalysis. Significant effort has been put into the development of CNs with an ordered structure, extremely high surface areas, narrow pore size distribution, tunable pore size, uniform particle size, controllable shape, and morphology, as well as their crystallinity and semiconducting features.

Carbon nitrides can be simply synthesized by condensation of organic precursors. Directly after condensation, these materials have a small surface area of less than 10 m² g⁻¹^[38] and thus their practical application is limited. This is especially true for their application in catalysis, where the amount of reactive sites

in material is paramount. Therefore the development of CNs with a high surface area is desirable. To overcome the problem of low surface area, various techniques were developed for introduction of porosity in the CN matrix. Additionally, porous structures can be considered as effective channels to improve interactions between CN and reactants.

Templating strategies allow for the control of the porosity of the material, while at the same time retaining the chemical structure of the bulk g-C₃N₄. Hard and soft templating techniques are often considered as methods for creating a high surface area and an ordered porous structure.^[39]

Mesoporous g-C₃N₄ was successfully obtained from different precursors using mesoporous silica matrices as a template.^[22a,40] The resulting pore size was consistent with the size of the silica nanoparticles in the template. Recently, controlled synthesis of 3D mesoporous carbon nitride was proposed using the environmentally benign precursor guanidine and colloid silica nanoparticles as a hard template.^[41] Modification of this material with Pd(OAc)₂ produced an active and stable catalyst for room temperature Suzuki couplings.^[42]

The "hard template" method allows for the control of surface properties of CNs to a certain extent. Depending on the fraction of silica it is possible to achieve surface areas of 86–439 m² g⁻¹.^[43] Despite the effectiveness and diversity of this approach, it is considered to be a time consuming and hazardous process as the removal of the template involves toxic HF or ammonium bifluorides.

Due to the mentioned problems of the "hard template" strategy, the development of new strategies for the production of mesoporous materials using "soft templates" has obtained significant interest.^[44] The soft templating strategy was realized by Antonietti et al. using different surfactants or amphiphilic block polymers as structure-directing agents for polymerization of dicyandiamide.^[45] A stepwise heating program determined by decomposition temperature of the surfactants was used in order to avoid the destruction of the mesoporous structure in the CNs. A nicely developed pore system was found only for some selected templates, such as Triton X-100 (Brunauer-Emmett-Teller (BET) surface area of 76 m² g⁻¹) and several ionic liquids (BET surface area of 81 m² g⁻¹). The ionic liquids were found to have unique physical and chemical properties for high-temperature templating and gave good nanoporous structures.^[45] Using a "soft template" of butylmethylimidazolium tetrafluoroborate provided CNs doped with boron and fluorine.^[46] These materials showed excellent mesoporous morphology with a BET surface area of 444 m² g⁻¹ and total pore volume of 0.32 cm³ g⁻¹. Soft template synthesis of CNs with bimodal pore size distribution was proposed by Shen et al. using Triton X-100 as the soft template and melamine and glutaraldehyde as precursors.^[47] A BET surface area of these materials was reported as 221 m² g⁻¹.

The "soft-templating" approach mostly affords disordered porous structures with low surface areas and specific pore volumes as compared to CNs synthesized using the "hard-templating" method. However, the "soft-templating" technique is a more eco-friendly and environmentally benign method.

This reveals that development of new methods to achieve carbon nitrides with a high surface area is still a challenging

task. Synthesis strategy mainly determines the final physico-chemical properties of the material. The nature of the precursors, degree of polymerization, and experimental conditions regulate crystallinity and carbon/nitrogen content of the material.

Recently theoretical studies predicted the structure of carbon nitride with C/N stoichiometric ratio of 0.75 as the most stable allotrope at ambient conditions.^[48] Saturated, sp³-hybridized, crystalline g-C₃N₄ was predicted to have outstanding physical properties, hardness and low compressibility comparable or exceeding that of diamond.^[49] However, it has been revealed to be difficult to prepare the desired single-phase sp³-hybridized carbon nitride. This is mainly considered to be a kinetic problem with the reaction.^[43a] Polymerization of carbon nitrides is a combination of polyaddition and polycondensation processes in a stepwise manner at different temperatures. These transformations are hard to control during the heating program, which results in different levels of condensation and therefore structural defects in the final material.

Therefore, smaller or higher C/N molar ratios than the ideal g-C₃N₄ are attributed to the presence of these structural defects resulted from the degree of condensation. The average C/N ratio of bulk carbon nitrides is around 0.72, and a small amount of hydrogen (2 %) is also usually found. When a smaller C/N ratio than one of the ideal g-C₃N₄ is obtained it is due to incomplete condensation of the precursors, which leads to the presence of uncondensed amino groups. These amino groups can partially reduce the inert nature of the material and promote its interactions with reactants. Furthermore, excessive defects due to incomplete condensation may also negatively affect charge migration and separation. Incomplete polymerization results in the formation of amorphous or semi-crystalline phases. However, a few approaches have been found to synthesize highly crystalline CNs. Schnick and co-workers isolated and identified the crystal structures of heptazine derivatives, such as melem C₆N₇(NH₂)₃^[50] and melam [(NH₂)₂(C₃N₃)₂NH]^[51] This work appeared as an argument in the discussion of possible building units of CNs as well as it shows that high local crystal packing in carbon nitrides is possible. The McMillan group later reported the synthesis of a crystalline carbon nitride imide phase C₂N₂(NH) with high-pressure, high-temperature (HP-HT) reaction conditions.^[52] The synthesis of a highly crystalline carbon nitride by a simple condensation in a salt melt of LiCl/KCl has been reported by Antonietti and co-workers.^[28a,30,53]

On the other hand, a trace amount of defects can improve catalytic properties of the carbon nitride. Moreover, introduction of "catalytically useful" defects enhances the activity of the catalyst. A carbon nitride photocatalyst modified with cyanamide groups was reported to have 12 and 16 times the hydrogen evolution rate and apparent quantum yield efficiency compared to an unmodified catalyst.^[54] The authors suggested that cyanamide moieties improve coordination to the platinum co-catalyst and therefore enhance charge transfer kinetics and charge separation. Recently, a protonic acid-assisted synthesis of carbon nitride with abundant nitrogen and oxygen-containing defects was published.^[55] This catalyst showed high efficiency in hydrogen evolution reaction and selectivity of 92.4 %

in photocatalytic CO₂ reduction as well as sufficient improvement in photocatalytic NO removal.

Generally, the photocatalytic activity of the material benefits from a certain level of defects. Stacking defects, grain boundaries, surface terminations, and structural defects seem to serve as active sites for reactions. While crystalline perfection largely affects the bulk properties of the material, such as graphitic structure, thermal and chemical stability, and semiconductor electronic structure.^[43a]

3. Organic Photocatalytic Reactions

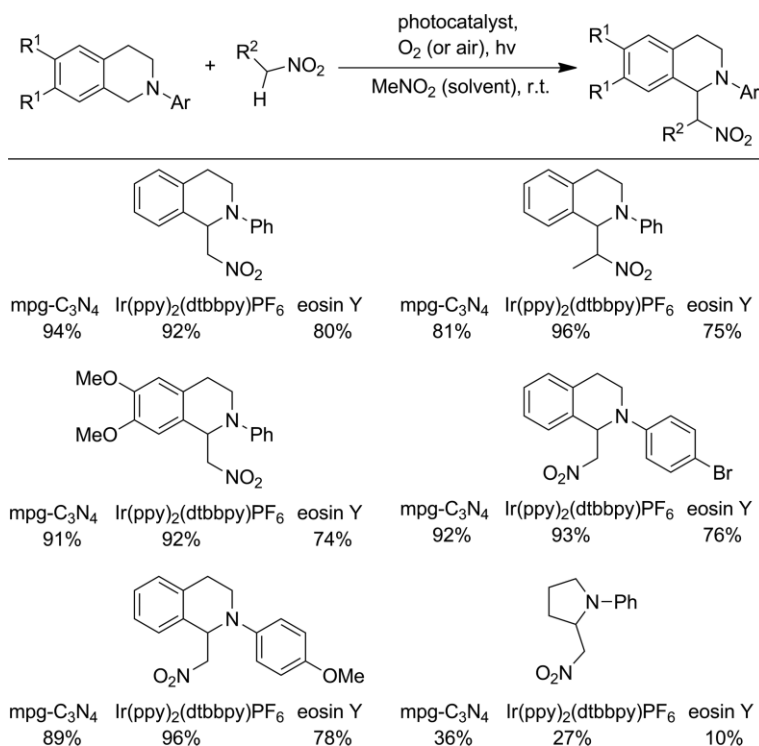
3.1. Carbon-Carbon Bond Formation Reactions

Direct formation of C–C bonds is a challenging research area in organic synthesis, especially when done in an environmentally friendly manner. In recent years photoredox catalysis, as a green synthetic method, has been successfully applied to cross-coupling reactions. Traditionally, this approach is largely represented by transition-metal catalysis. However, examples mediated by organic dyes and carbon nitrides have also been reported.

The tetrahydroisoquinoline (THIQ) framework is a common element in a number of natural bioactive compounds.^[56] Therefore, many techniques have been developed in order to functionalize tetrahydroisoquinoline fragment,^[57] including photochemical approaches.

In general, amines are known to be very good electron donors, which easily undergo single-electron oxidation to give an aminium radical cation, and two-electron oxidation followed by proton abstraction to give an iminium ion. Catalytically generated iminium ion intermediates can be subsequently trapped by the nucleophilic compounds to form a new bond at α -position. In 2010, Stephenson et al. published the photocatalyzed *aza*-Henry reaction with nitroalkanes and *N*-aryltetrahydroisoquinolines under visible light irradiation with an iridium catalyst (Scheme 1).^[58] After this, König and Hari developed a transition metal-free version of this reaction with eosin Y, a common organic dye.^[59] Despite the high yields of the products by both methods, the drawback of these systems is the difficulty in recycling of the catalyst. Among heterogeneous catalysts, metal-free carbon nitride has been used by Blechert's group.^[60] Mesoporous graphitic carbon nitride (mpg-C₃N₄) showed comparable activity to the homogeneous systems. In all approaches the reaction conditions were almost the same, except of course the catalyst used. In the more complicated reaction with *N*-phenylpyrrolidine, however, mpg-C₃N₄ gave higher yield than both homogeneous catalysts.

The Mannich-type reaction shown in Scheme 2 was accomplished on tetrahydroisoquinoline substrates using proline as a co-catalyst with both mpg-C₃N₄ and Ru(bpy)₃(PF₆)₂. The reaction proceeds through the formation of a nucleophilic enamine from the proline and ketone, followed by subsequent addition to the iminium ion (Scheme 2).^[60,61] This reaction catalyzed by Ru(bpy)₃(PF₆)₂ has been published by Rueping and co-authors,^[61] and with mpg-C₃N₄ as published by Blechert et al. Similar product yields were achieved by catalysis with heteroge-

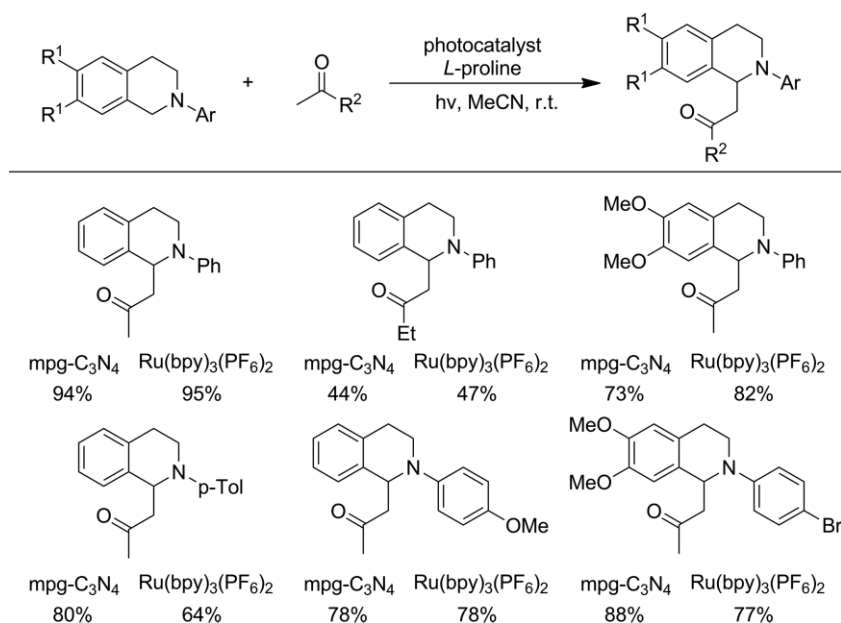


Scheme 1. Photocatalytic *aza*-Henry reaction with nitroalkanes and *N*-aryltetrahydroisoquinolines.

neous carbon nitride when compared to the homogeneous catalyst.^[60]

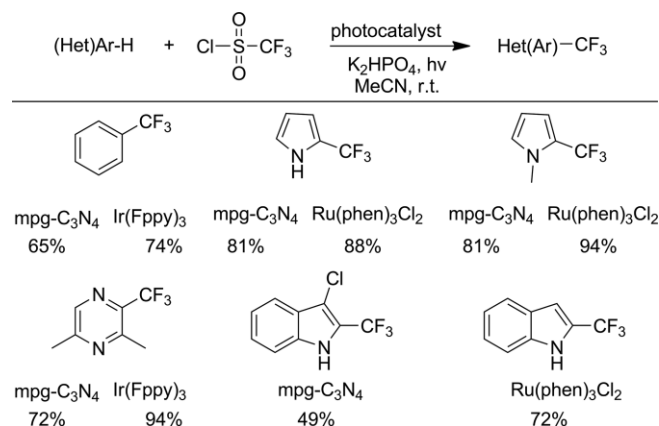
In drug discovery practice a common strategy to protect a drug candidate against *in vivo* metabolism is incorporation of electron-withdrawing groups, such as trifluoromethyl (CF₃).^[62] The CF₃ moiety is typically installed by transition metal-catalyzed cross-coupling reactions. However, several photochemical approaches have been recently introduced. Trifluoromethyl-

ation of arenes and heteroarenes by iridium and ruthenium photocatalysts has been reported by MacMillan et al. (Scheme 3).^[10a] A broad scope of products, benzene derivatives and CF₃-functionalized 5- and 6-membered heterocycles, were synthesized with moderate to excellent yields. A method with carbon nitride photocatalyst was published by Blechert et al., but the yields, in this case, were slightly lower.^[10b] Nevertheless, a large variety of heterocycles has been studied. In both cases



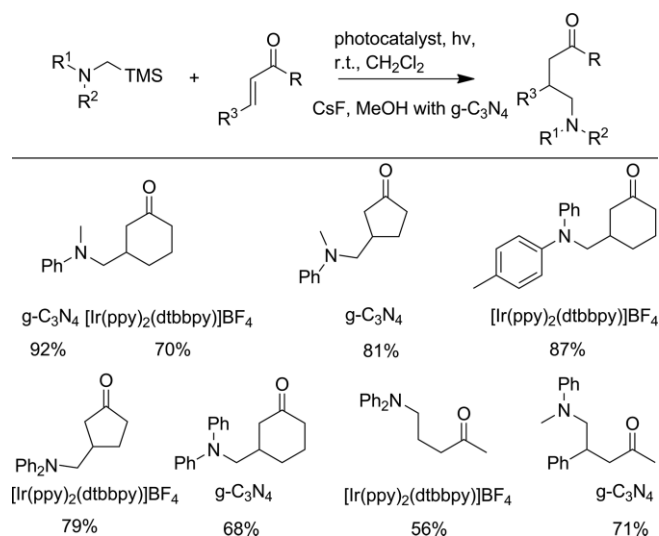
Scheme 2. Photocatalytic Mannich-type reaction with *N*-aryltetrahydro-isoquinolines and ketones.

a CF_3 radical was generated by single-electron reduction of trifluoromethanesulfonyl chloride. The value of this transformation has been shown by trifluoromethylation of biologically active molecules, e.g. caffeine.^[10b]



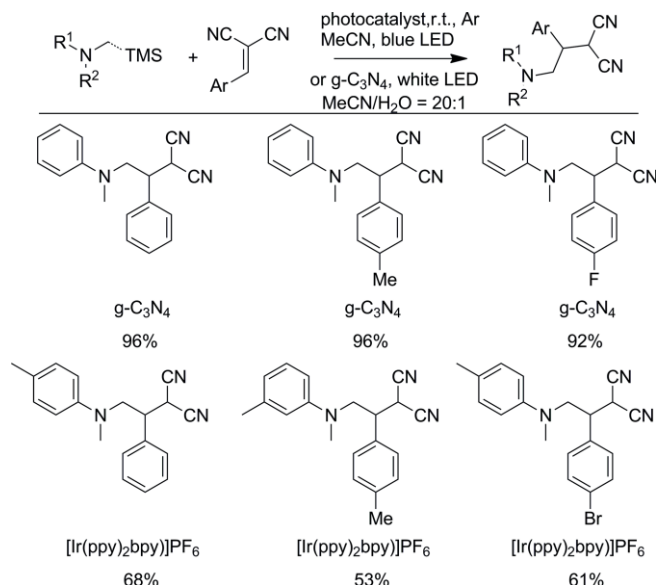
Scheme 3. Photocatalytic trifluoromethylation of arenes and heteroarenes.

Reactions such as α -aminoalkyl radical additions, allylation, and heteroarylations, are quite well represented by homogeneous catalysis. However, in 2018 Rueping et al. published several reactions involving the generation of reactive α -aminoalkyl radicals with heterogeneous $\text{g-C}_3\text{N}_4$.^[63] Desilylative addition of α -silylamine to activated alkenes, such as 2-cyclohexenone, other cyclic unsaturated ketones (Scheme 4), and dicyanostyrenes (Scheme 5) was performed.



Scheme 4. Photocatalytic alkylation of ketoalkenes via α -aminoalkyl radicals.

Silyl-substituted amines were chosen as substrates for the selective formation of α -aminoalkyl radicals at the desired position. This reaction catalyzed by $\text{g-C}_3\text{N}_4$ with enones required CsF as a base.^[63] Variety of substituents of different electronic properties were investigated and showed no effect on the reactivity of the substrate. Moreover, a study of the reaction pathway in case of catalysis by $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{BF}_4$ was done.

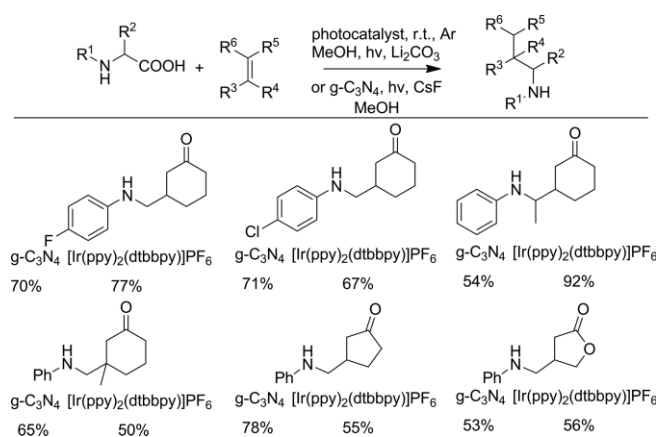


Scheme 5. Photocatalytic alkylation of dicyanoalkenes.

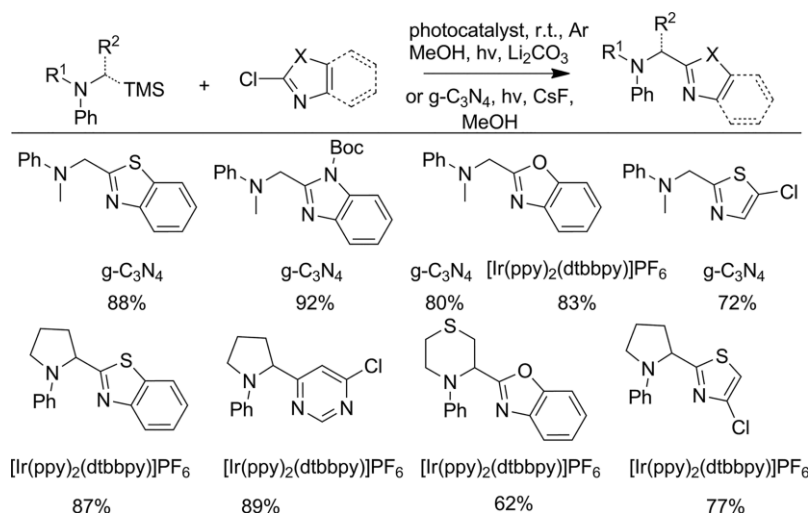
A primary product of the addition – silyl enol ether was isolated.^[64]

The reaction with dicyanoalkenes with the homogeneous catalyst $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ was performed with conventional amines without silyl substituent (Scheme 5).^[65] Based on this reaction the authors showed the principal role of oxygen in the synthesis. In the presence of oxygen, selective formation of cyclic products was observed. In the reaction catalyzed by $\text{g-C}_3\text{N}_4$, acrylonitrile derivatives showed excellent reactivity and higher yields in comparison to iridium-catalyzed approach.^[63] To illustrate the practicability of the heterogeneous process catalyst was recycled for 8 times without losing its activity.

Formation of α -aminoalkyl radicals was completed from more easily available α -amino acids (Scheme 6).^[63,66] Secondary amine alkyl radicals were formed through a decarboxylation process. The reactivity of substrates was proven by achieving formation of a quaternary center. The yield was higher for



Scheme 6. Photocatalytic decarboxylative addition of α -amino acids to activated alkenes.



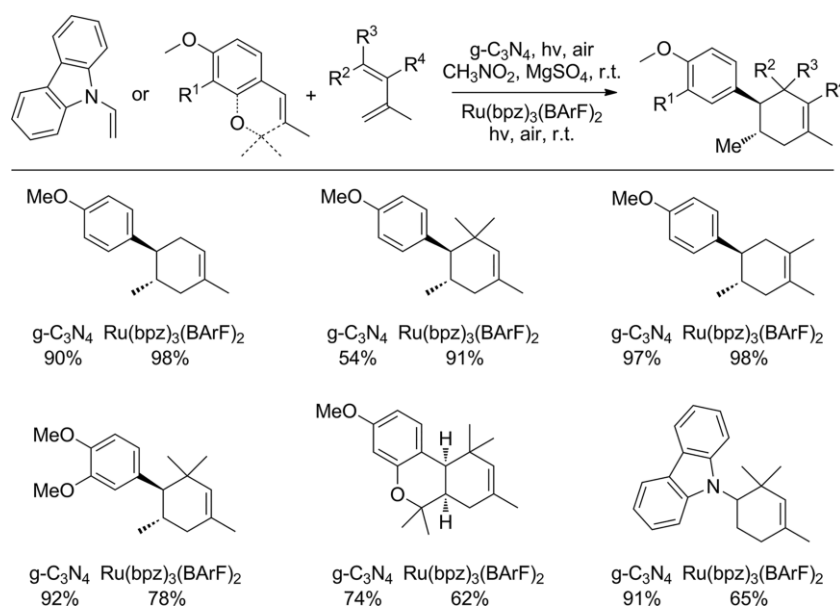
Scheme 7. Photocatalytic arylation through α -aminoalkyl radical addition.

carbon nitride catalyzed reactions rather than for the homogeneous catalyst $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (65 % and 50 % respectively). Five-membered rings were tolerated in this reaction as well, however, only moderate yields were reported due to unselective polymerization and cycloaddition processes.

Following the additions to activated double bonds, heteroarylation was explored with $\text{g-C}_3\text{N}_4$ as an alternative to the homogeneous catalyst $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$. As a result, photocatalytic amine α -arylation was achieved by the addition of an α -amino radical to a neutral arene (Scheme 7). Heteroarylation catalyzed by $\text{g-C}_3\text{N}_4$ was performed in a desilylative manner.^[63] Condensed five-membered heterocycles, as well as monocyclic thiasole, were tolerated under these conditions. The homogeneously catalyzed reaction showed great performance with six-membered heterocycles as well as five- and six-membered cyclic amines.^[67]

3.2. Carbon-Carbon Radical Cyclizations

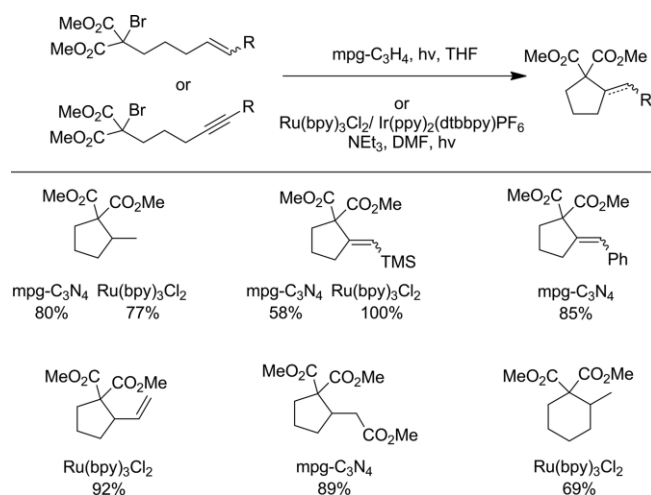
The Diels-Alder reaction is a common and powerful tool in organic synthesis for the formation of new cyclic compounds.^[68] It was found that radical cations generated from electron-rich alkenes by using photoredox catalysis react with dienes to give Diels-Alder adducts (Scheme 8). Yoon and co-authors have published a radical cation [4+2] cycloaddition with $\text{Ru}(\text{bpz})_3(\text{BARF})_2$ photocatalyst (Figure 1).^[69] They demonstrated the value of the proposed method by synthesis of natural regioisomer of heitzamide A. The similar method, but with metal-free $\text{g-C}_3\text{N}_4$ was proposed by Zhao and Antonietti, which gave comparable yields and in some cases outperformed the homogeneous catalyst.^[70] In one case, 9-vinyl-9H-carbazole, $\text{g-C}_3\text{N}_4$ catalyst showed 91 % product yield after only 1 h of irradiation compared to 65 % for $\text{Ru}(\text{bpz})_3(\text{BARF})_2$ after 24 h of irradiation.



Scheme 8. Photocatalytic Diels-Alder cyclization.

The apparent quantum yield for g-C₃N₄ in this reaction reached an outstanding value of 47 %. Aerobic conditions for this reaction were required, as O₂ plays the role of electron mediator in the reaction mechanism.

Photoredox catalysts are able to reduce carbon-halogen bond by a single-electron transfer to form alkyl radicals. The photogenerated radical then reacts with the unsaturated part of the molecule to cyclize. One example of this utilizing homogeneous catalysts was reported by Stephenson et al. (Scheme 9).^[71] Bromomalonate was reduced to the corresponding radical and subsequently cyclized to cyclopentane through reaction with the double bond. The reaction is mediated by ruthenium (Ru(bpy)₃Cl₂) and iridium (Ir(ppy)₂(dtbbpy)PF₆) catalysts under visible light conditions in the presence of Et₃N as a sacrificial electron donor.



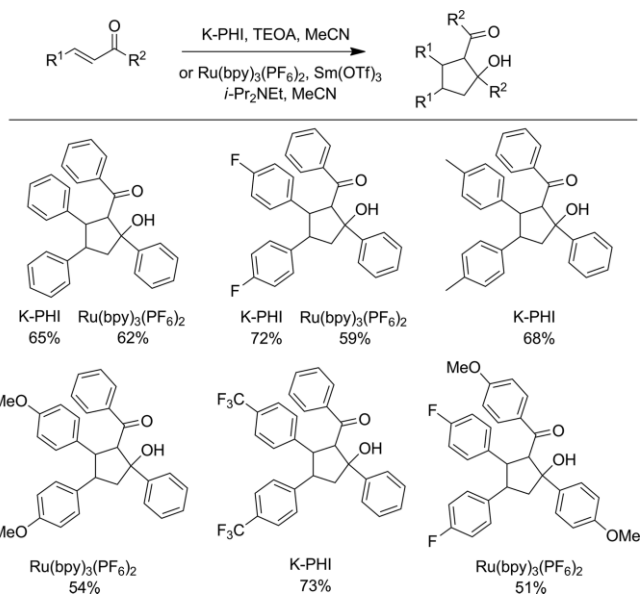
Scheme 9. Photocatalytic formation of cyclopentane by reduction of carbon-halogen bond.

Being insoluble in any organic solvent, Blechert et al. used mpq-C₃N₄ in a packed bed flow photoreactor in order to increase contact with the reaction media.^[72] This approach increased the selectivity and reduced the reaction time. Furthermore, THF (the solvent) also served as a sacrificial electron donor.

Reductive cyclodimerization of chalcones was recently catalyzed by homogeneous Ru(bpy)₃(PF₆)₂ catalyst (Scheme 10).^[73]

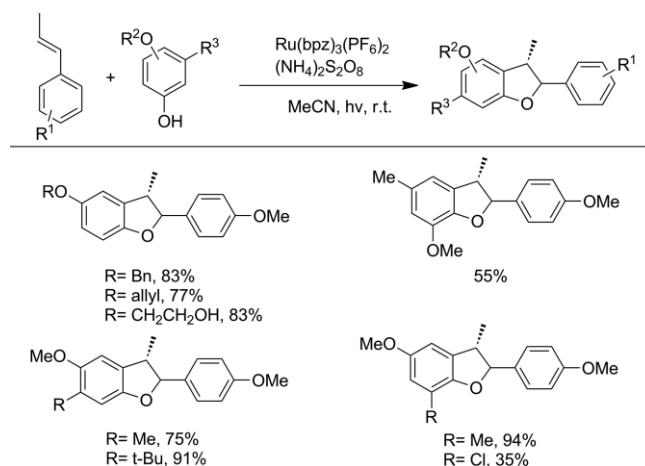
The reaction proceeds through a single-electron reduction of the chalcone with its subsequent dimerization and aldol-type cyclization. The regioselectivity plays an important role in this transformation, as the only one regioisomer can be cyclized. An additional reagent for coordination of the carbonyl and enol groups, e.g. Sm(OTf)₃, is necessary to achieve higher selectivity toward cyclopentanol. In the heterogeneous version of this reaction, developed by Kurpil and Savateev, with the heterogeneous K-PHI photocatalyst, a coordination additive is not required, as the catalyst itself plays a coordination role.^[14] This feature of the heterogeneous photocatalysis simplifies the conditions and allows for high regioselectivity. In both reactions schemes amine was used as a sacrificial electron donor.

Oxidation of phenols to the corresponding phenoxonium cations, followed by their coupling with alkenes is one method



Scheme 10. Photocatalytic reductive cyclodimerization of chalcones.

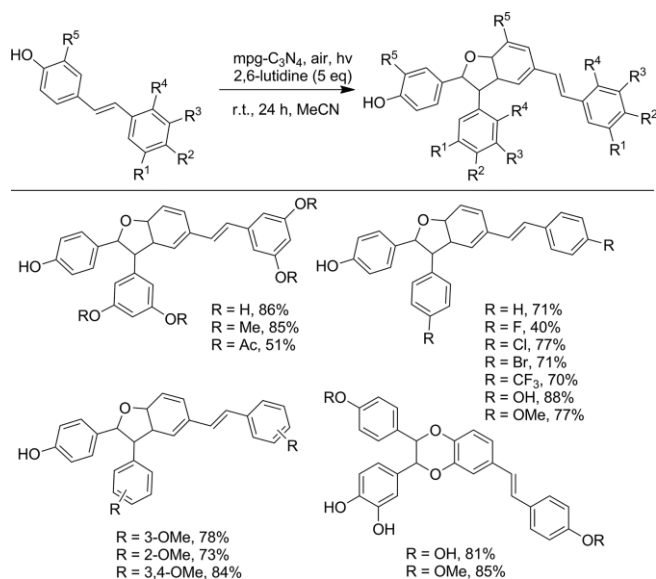
to build dihydrobenzofuran rings by [3+2] cycloaddition (Scheme 11). This reaction can be catalyzed by the relatively strong oxidation photocatalyst Ru(bpy)₃(PF₆)₂. When more popular photocatalyst Ru(bpy)₃(PF₆)₂ was used it was shown to be less efficient.^[74] In order for the reaction to proceed efficiently, the oxidation potential of the alkene must be outside of the working range of the photocatalyst. The phenols must bear alkoxy substituents in 2- or 4- position in order to stabilize the phenoxonium cation. The proposed method requires the use of (NH₄)₂S₂O₈ as an oxidant.



Scheme 11. Photocatalytic dihydrobenzofuran ring formation through [3+2] cycloaddition.

Another approach for building a dihydrobenzofuran fragment was shown by mpq-C₃N₄ photocatalyzed oxidative dimerization of resveratrol and its analogs (Scheme 12).^[75] Mimicking the biosynthesis of δ-viniferin, in the proposed method free oxygen was used as an oxidizing reagent instead of (NH₄)₂S₂O₈, while 2,6-lutidine was used as a base. Fifteen 4-hydroxy-*trans*-stilbenes, including resveratrol, were shown to be suitable sub-

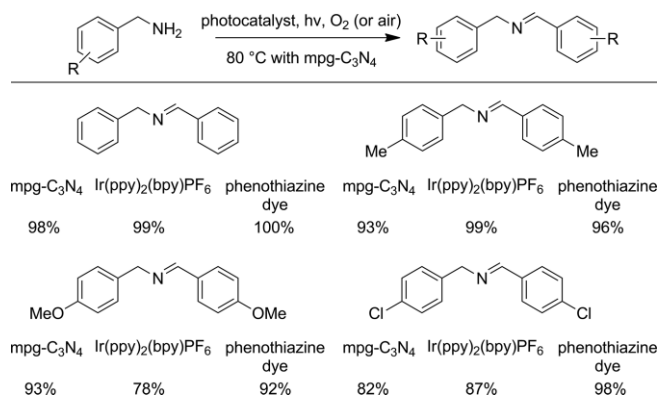
strates. Additionally 3,4-dihydroxy-*trans*-stilbenes under the same reaction conditions gave benzodioxane-based dimers.



Scheme 12. Photocatalytic synthesis of dihydrobenzofurans by oxidative dimerization of resveratrol and its analogs.

3.3. Carbon-Heteroatom Bond Formation Reactions

The oxidation of amines is an important chemical reaction, as it is one of the key steps in the synthesis of biologically active compounds in drug discovery and agrochemistry.^[76] Photoredox catalysis has been widely presented as a suitable technique for this transformation. Both heterogeneous and homogeneous catalysts can easily oxidize amines, especially primary amines (Scheme 13).



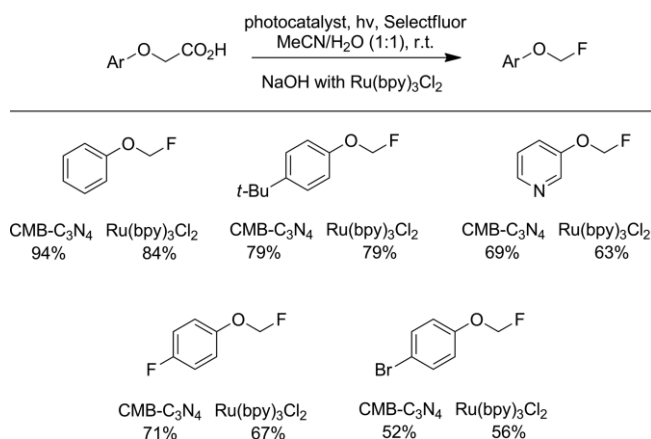
Scheme 13. Oxidative formation of imines by photocatalysis.

In the oxidation of amines, reactions where O_2 acts as an electron acceptor under visible light are common. This shows the advantages of the photocatalytic methods compared to the traditional purely chemical methods when stoichiometric quantities of strong oxidants are usually required as opposed to O_2 as an oxidant.^[77] The transition metal-free heterogeneous mpg- C_3N_4 was reported as a suitable photocatalyst for selective oxidation of amines to the corresponding imines.^[78] Despite the

high selectivity of this method, it requires a reaction temperature of 80 °C. Homogeneous version of this photocatalytic reaction mediated by Ir(ppy)₃(bpy)PF₆ was shown by Rueping et al.^[79] A metal-free homogeneous catalysis under visible light with phenothiazine dye (Figure 1) gave overall higher yields and selectivities under mild conditions.^[12]

The synthetic pathways for the incorporation of fluorine atoms into potential biologically active molecules has significant interest for pharmaceutical and agrochemical areas.^[80]

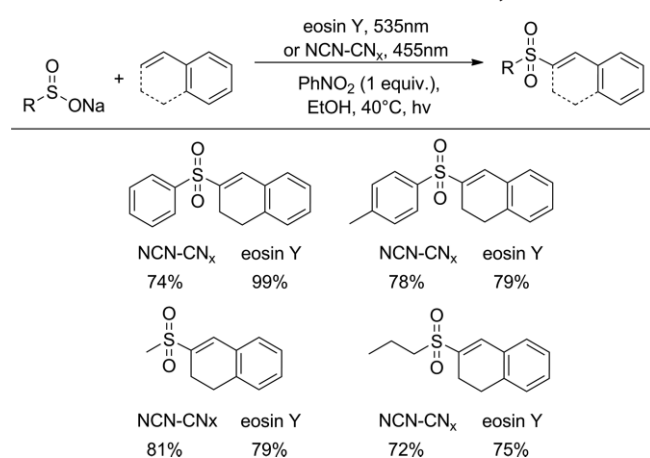
Until recently there were no methods for direct photocatalytic carbon-fluorine bond formation. Among different carbon-heteroatom couplings, C–F bond formation has remained one of the most challenging reactions for years, because it usually requires specific fluorinating reagents that are not tolerated in photocatalytic systems. Nevertheless, Selectfluor, one of the most common fluorinating reagents, was found to be suitable for this reaction in combination with the photocatalysts Ru(bpy)₃Cl₂ and CMB–C₃N₄ (carbon nitride prepared from cyanuric acid, melamine, and barbituric acid). The first example of photocatalytic fluorination with Selectfluor was reported in 2014 with a common homogeneous catalyst Ru(bpy)₃Cl₂ (Scheme 14).^[81] Aryloxyacetic acid derivatives as substrates were chosen. Under the reaction conditions, they release the CO₂ molecule and couple with F atom.



Scheme 14. Photocatalytic decarboxylative fluorination.

Flow reactor enhance mass and heat transfer in reactions, enables precise control over the reaction parameters, and increases the overall process efficiency and safety.^[82] Despite these advantages, flow chemistry is barely used together with heterogeneous photocatalysis due to poor light penetration and high back pressure (packed bed reactor), or clogging and poor reproducibility (pumping a suspension).^[83] In order to overcome these existing challenges, Pieber developed serial micro-batch photoreactors (SMBRs).^[84] Using this technology, decarboxylative fluorination was enabled by CMB-C₃N₄ photocatalyst (Scheme 14). This approach was extended to fluorination of three different types of substrates. The practical application of this method was shown by the direct fluorination of ibuprofen. The reaction with the homogeneous catalyst Ru(bpy)₃Cl₂ requires the use of NaOH in excess, while the procedure with CMB-C₃N₄ was performed without any additives.

A fascinating method for the synthesis of vinyl sulfones was discovered by König and co-authors (Scheme 15). First, they published the method for sulfonylation of alkenes with aryl sulfonates^[85] and later extended this method to alkyl sulfonates.^[86]

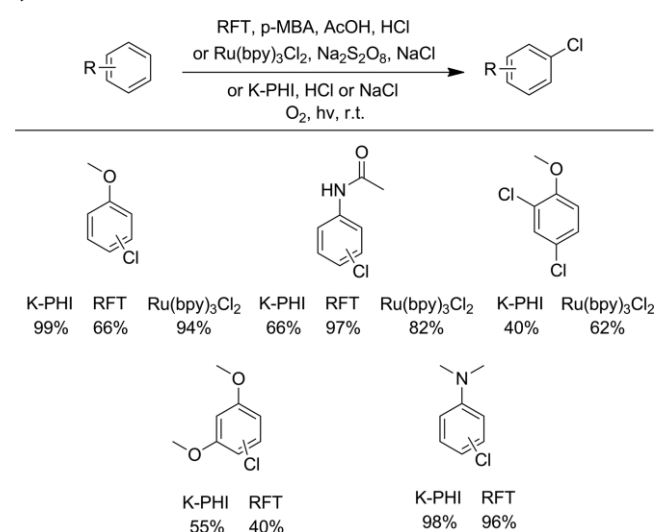


Scheme 15. Photocatalyzed oxidative sulfonylation of arylalkenes with sulfonates.

These reactions were enabled by the organic dye, eosin Y, under green light irradiation ($\lambda_{\text{max}}=535$ nm). A heterogeneous version of this reaction was performed with cyanamide- and urea-functionalized graphitic carbon nitrides (NCN-CN_x) under blue light irradiation ($\lambda_{\text{max}}=455$ nm).^[87] The performance of NCN-CN_x in general is similar to homogeneous eosin Y. The reaction between styrene and benzenesulfinate under green light irradiation was achieved with g-C₃N₄ modified with cyano groups.^[88] For this reaction PhNO₂ (1 equiv.) was required as electron acceptor, and without it the yields were significantly lower.

Halogenated products are versatile starting materials in organic synthesis, widely used for transition-metal catalyzed cross-couplings, as well as broadly presented in biologically active compounds.^[89] Among all methods of their synthesis, oxidative halogenation of hydrocarbons is probably one of the most environmentally benign.^[90] The photocatalytic version of this reaction was published by König et al. by mimicking the process in nature with the use of organic dye riboflavin tetraacetate (RFT) (Scheme 16).^[91] In this method they used *p*-methoxybenzyl alcohol as electron donor and acetic acid as a hydrogen peroxide stabilizer. Selective chlorination of aryl C–H bonds with Ru(bpy)₃Cl₂ photocatalyst was published as well.^[92] In this approach NaCl was used as a chlorinating reagent and Na₂S₂O₈ as an oxidant. Selective chlorination of the aromatic C–H bond was achieved only when the α -H in benzylic position was available. The utility of the method was shown by the synthesis of several drugs or their precursors. The heterogeneous oxidative halogenation was reported by Markushyna and Savateev using K-PHI photocatalyst (Figure 1, Scheme 16).^[93] The reaction was carried out under simplified conditions, using hydrochloric acid and oxygen as the only reagents. The reaction worked well for the chlorination and bromination of substituted benzenes. The possibility of using seawater as a chlorination reagent was shown by chlorination with NaCl solution. All methods are in agreement with the limitation for electrophilic halogenation

and substitution of substrates bearing electron-withdrawing groups was not achieved. Further improvement is needed to extend the scope of substrates to electron deficient aromatic systems.

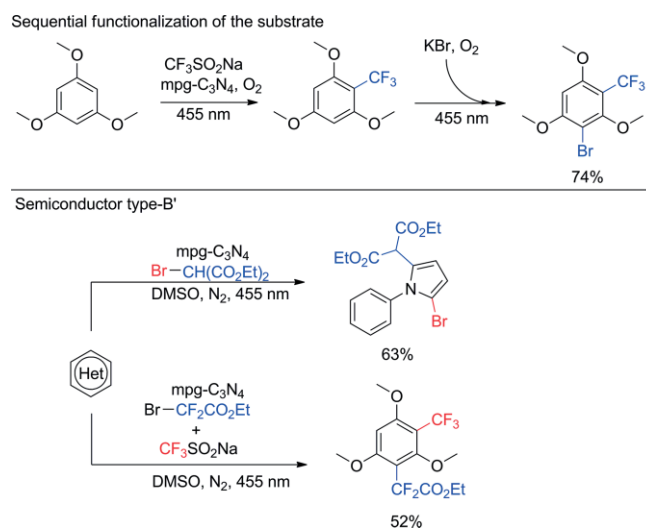


Scheme 16. Photocatalytic oxidative halogenation of electron-rich arenes.

Until now we have discussed photocatalytic mono-functionalization of substrates, i.e. installation of one functional group or formation of one chemical bond. In principle, photocatalysis can be used in sequential functionalizations of substrates.

Ghosh, König, and Antonietti implemented this idea in the sequential trifluoromethylation and bromination of trimethoxybenzene as a model compound using mpg-C₃N₄ (Scheme 17).^[94] Once all of the sodium trifluoromethylsulfinate was consumed, potassium bromide was added to the reaction mixture and the photocatalytic reaction was continued to obtain polyfunctionalized benzene derivatives.

Recently the intriguing and practical simultaneous installation of two or more functionalities at once, i.e. semiconductor photocatalysis of type B', was explored. This concept was vali-



Scheme 17. Sequential trifluoromethylation/bromination of trimethoxybenzene (top) and semiconductor photoredox catalytic reaction mode of type B' (bottom).

dated in the reaction of simultaneous trifluoromethylation/difluoromethylation or bromination/alkylation of the (hetero)-aromatic compounds (Scheme 17).^[94]

All in all, the photogenerated hole-electron pair on the carbon nitride surface activates the molecules for reactions. The carbon nitride photocatalyst is insensitive to the reaction type and solvents, and it enables practically any C(sp²)-C(sp³), C(sp²)-C(sp²), and C(sp²)-heteroatom bond forming reactions.

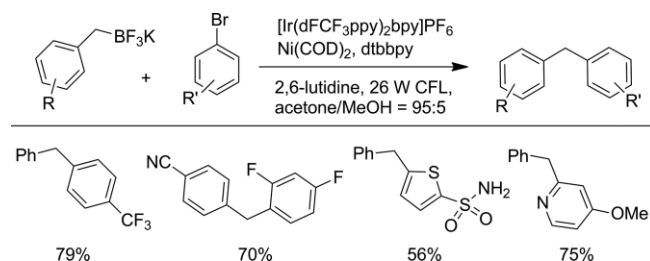
3.4. Dual Ni-Carbon Nitride Photocatalysis

Transition metal-catalyzed cross-coupling reactions became a classic technique for building carbon-carbon and carbon-heteroatom bonds in modern organic chemistry. However, these methods typically rely on rare transition metals, such as palladium, as transmetalating agents. The high economic and environmental cost of such catalysis makes these systems undesirable in the long-term. Therefore, nickel is considered as an attractive alternative to rare metal catalysts.^[95] Moreover, the union of nickel and photoredox catalysis has opened a new horizon in radical and cross-coupling chemistry.^[96]

Alkylborane, alkylzinc or alkyl Grignard reagents are common precursors for transmetalation reactions. However, traditionally they require high temperatures and strong base for activation, which can lead to the formation of side products due to protodeboronation, β -hydride elimination and subsequent isomerization.^[97] In recent years, dual nickel/photoredox catalysis has been employed in cross-coupling chemistry for a variety of carbon-carbon and carbon-heteroatom coupling reactions under exceptionally mild conditions.

The combination of nickel (Ni(COD)₂) and iridium [Ir(dFCF₃ppy)₂bpy]PF₆ organometallic complexes was implemented in a coupling reaction of electronically activated potassium alkyltrifluoroborates with a variety of aryl bromides.

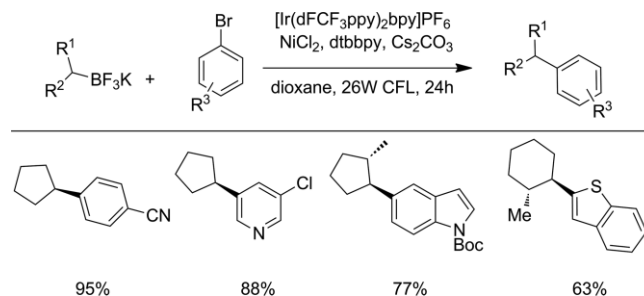
In 2014, Molander et al. reported a single-electron transfer-based (SET) strategy for the activation of organoboron reagents in the cross-coupling of primary benzyltrifluoroborates with substituted aryl bromides (Scheme 18).^[98] The extremely mild conditions (visible light, ambient temperature, and no strong base) resulted in the selective formation of the desired products with only unreacted arylhalide remaining. The reported approach also showed excellent functional group tolerance.



Scheme 18. Photocatalytic C-C coupling of primary potassium benzyltrifluoroborates with aryl bromides.

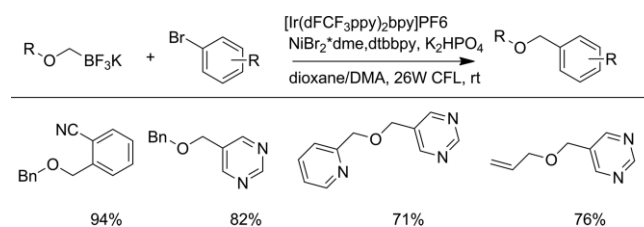
In the subsequent year, Molander and co-authors reported the use of the developed SET strategy to secondary alkyltrifluoroborates (Scheme 19).^[99] The reaction system was slightly

modified to avoid the formation of side products due to the higher reactivity of secondary borates. This reaction was shown to also be efficient on a gram scale as well.



Scheme 19. Photocatalytic C-C coupling of secondary potassium benzyltrifluoroborates with aryl bromides.

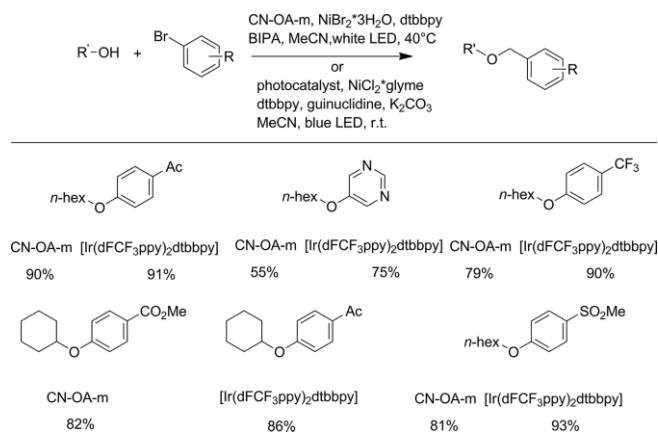
Molander and co-authors also reported a similar approach of single-electron transmetalation for the coupling of α -alkoxy-methyltrifluoroborates with aryl and heteroaryl bromides to form benzyl ethers (Scheme 20).^[100] The proposed method showed high tolerance to both heteroaryl and alkoxy-methyltrifluoroborate substrates. This approach was highly compatible with both alkenes and alkynes as demonstrated by their high yields in this reaction.



Scheme 20. Photocatalytic C-C coupling of primary potassium alkoxy-methyltrifluoroborates with aryl bromides.

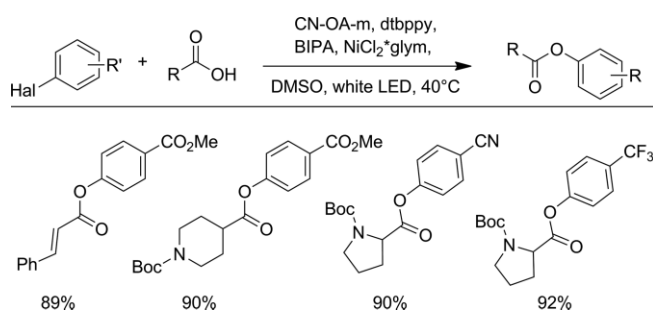
Synthesis of ethers through the coupling of alcohols with aryl bromides was reported by dual catalysis of nickel with both a transition metal-based catalyst as well as with a carbon nitride. MacMillan et al. developed a system that can modulate the preferred oxidation states of nickel alkoxides in an operative catalytic cycle, which provides access to Ni species that readily participate in reductive elimination.^[101] This development allowed the critical C-O bond formation step to proceed. The system was applied to a variety of aliphatic alcohols and aromatic and heteroaromatic bromides (Scheme 21). Recently, CN-OA-m (carbon nitride prepared through calcination in a molten salt of recondensed urea with oxamide) was found to be able to stimulate reductive elimination by SET modification of the oxidation state of Ni complexes in a similar system.^[102] This catalytic system was used for the selective coupling of a broad range of primary and secondary alcohols with electron-deficient aryl bromides.

Another variation of carbon-oxygen coupling by CN/Ni catalysis was showed by Pieber and co-authors (Scheme 22). Esterification of carboxylic acids with aryl halides was performed under mild conditions.^[103] The catalyst system was shown to harvest a broad range of visible-light spectrum (up to 600 nm), which was shown by in situ FT-IR analysis of the reaction



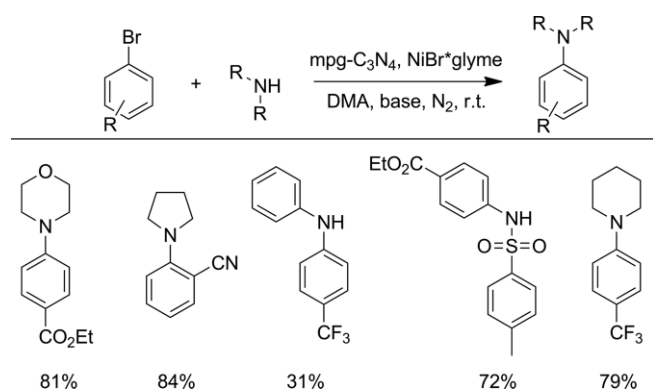
Scheme 21. Photocatalytic C–O coupling of alcohols and aryl bromides.

progress. The organic semiconductor was recycled 3 times without any loss of activity. No products of the decarboxylative C–C coupling were detected, which indicates selective photosensitization rather than the described above single-electron transfer.



Scheme 22. Photocatalytic C–O coupling of carboxylic acids and aryl bromides.

Recently an interesting variation of the dual catalyst system was reported by Ghosh et al.^[104] Through the activation of C–Br bonds in electron-poor aryl halides, regioselective coupling with amines was accomplished. The reaction conditions did not require additional ligands for nickel complexation. Generally, the reaction was performed in mild conditions at room temperature, and as a result different functional groups, such as halo-



Scheme 23. Photocatalytic C–N coupling of amines and aryl bromides.

gens, ester, aldehyde, and cyano group, were well tolerated providing products in good to excellent yields (Scheme 23).

4. Photocatalytic Productivity of Homogeneous and Heterogeneous Catalyst

Thus far we have presented the scope of organic reactions catalyzed by both homogeneous and heterogeneous catalysts under similar conditions. However, the yields presented on the schemes above, in general, depend on the amount of the substrate. Therefore certain photocatalysts can demonstrate virtually higher yields when lower substrate loadings are used. To solve this issue we present a graph that correlates the product yield and the substrate amount taken for the reactions discussed above (Figure 2).

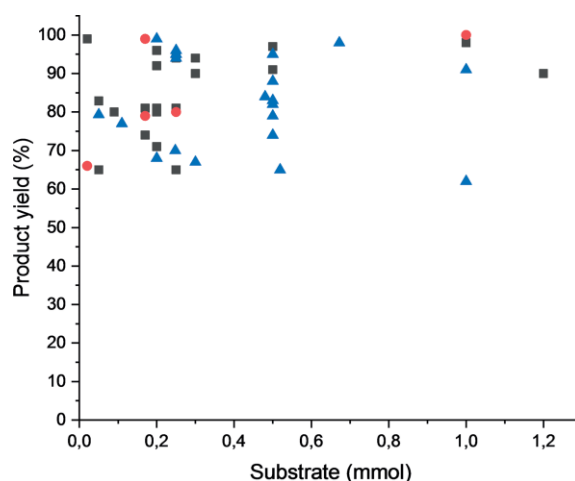


Figure 2. Comparison of productivities of homogeneous catalysts and carbon nitride catalysts. Squares – heterogeneous carbon nitride photocatalysts, triangles – transition metal-based photoredox complexes, circles – organic dyes.

All in all, the discussed photocatalytic reactions in this review have been studied on 20–1000 μmol reaction scales. Three classes of the photocatalysts, i.e. transition metal-based complexes, organic dyes, and heterogeneous carbon nitride materials, show nearly the same dispersion of yields regardless of the reaction type and substrate loading. This general tendency also shows that all photocatalysts show good performance and give good to excellent yields in these reactions. Therefore, a photocatalytic approach can serve as an effective replacement for common synthetic procedures. The heterogeneous carbon nitride based materials in this tendency show comparable to homogeneous catalysts productivities.

3. Summary and Outlook

We have compared the performance of heterogeneous carbon nitride semiconductors with homogeneous transition metal-based photocatalysts and metal-free organic dyes in 15 reactions. In all reported reactions discussed, the performance of these classes of photocatalysts was similar. Based on this data, we can anticipate that this is also true for practically any photocatalytic reaction.

However, carbon nitrides stand out from the series of photocatalysts due to the following features: low cost (few €/g on gram scale synthesis), simple preparation procedure (mix precursors and “bake”), high chemical and thermal stability and recyclability as the carbon nitride can be separated from the reaction mixture by filtration or centrifugation. As non-soluble materials, carbon nitrides offer wide possibilities for designing packed bed photoreactors in order to further simplify the photocatalytic experiment in a flow system. Carbon nitrides also offer enormous opportunities for structural modification, i.e. adjusting the morphology and the chemical and band structure. These changes have a profound impact on the activity of the heterogeneous photocatalysts in the model reaction of water splitting. It also implies that the activity of carbon nitrides in organic photocatalysis may be enhanced using the same principles of materials design.

Despite the already rich chemistry of carbon nitrides, herein we would like to outline potential routes for further development of the carbon nitride photocatalysis in the view of their properties and the needs of synthetic chemistry.

● Most of the reactions catalyzed by carbon nitrides are based on electron transfer. Energy transfer, on the other hand, has not been yet fully utilized, although several papers suggest existence of either triplet states or non-emitive charge states in carbon nitrides.^[105,106]

● The high chemical stability of carbon nitrides that has been already utilized several times in the literature may be further applied to run harsh photocatalytic reactions with highly-reactive intermediates, e.g. alkyl radicals, carbenes, etc.

All in all, successful implementation of carbon nitride photocatalysis in organic synthesis requires cooperation between two communities: material and organic chemists.

Acknowledgments

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Keywords: Carbon nitride · Heterogeneous catalysis · Homogeneous catalysis · Photocatalysis · Synthetic methods

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