

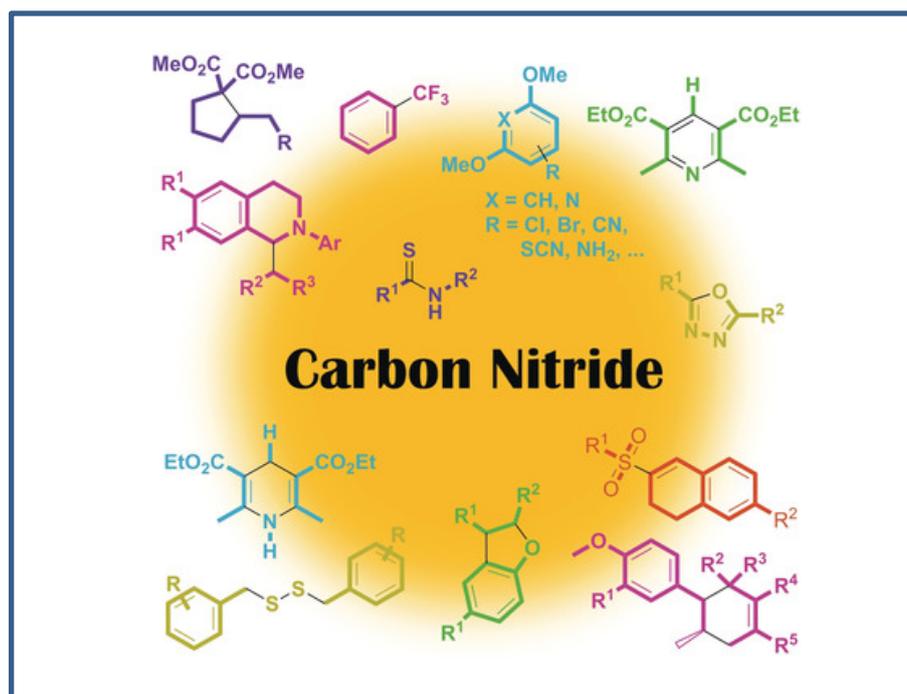


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# Photoredox catalytic organic transformations using heterogeneous carbon nitrides

Aleksandr Savateev, Indrajit Ghosh, Burkhard König, and Markus Antonietti



Carbon nitride a visible light heterogeneous photocatalyst enables different types of chemical reactions that yield diverse classes of organic compounds. The graphical abstract shows selected examples of organic molecules, which were prepared using carbon nitride as photocatalyst.

# Photoredox catalytic organic transformations using heterogeneous carbon nitrides

Aleksandr Savateev,<sup>[a]\*</sup> Indrajit Ghosh,<sup>[a,b]</sup> Burkhard König,<sup>[b]</sup> and Markus Antonietti<sup>[a]\*</sup>



**Abstract:** Photoredox catalysis that comprises homogeneous transition metal-based systems, organic dyes, and semiconductors, has now become a universal tool to catalyse a wide variety of chemical reactions with high selectivity under mild conditions using visible light irradiation. In this review, we summarize recent progress in photoredox catalysis mediated by heterogeneous carbon nitride materials, e.g., *mesoporous graphitic carbon nitride (mpg-CN)*, *polymeric carbon nitride*, and *potassium poly(heptazine imides) (K-PHI)*. Due to the high thermal, chemical, and photo stability, as well as favourable conduction and valence band positions, carbon nitrides expand the reaction range to many novel reactions, such as photocatalytic activation of elemental sulfur offering a convenient chemical route to organosulfur compounds.

## Introduction

Recently, visible light photoredox catalysis has gained enormous attention as an energy-efficient and versatile method for chemical synthesis.<sup>[1]</sup> However, the main contributions are based on homogeneous photoredox catalysts, such as ruthenium or iridium based transition metal complexes<sup>[1b]</sup> or organic dyes<sup>[2]</sup>, for example, eosin Y,<sup>[3]</sup> acridinium salts,<sup>[4]</sup> perylene,<sup>[5]</sup> Rhodamine 6G,<sup>[6]</sup> whose photo and redox properties are well known in the literature. Metal-organic frameworks, organic porous polymers and crystalline covalent organic frameworks are also represented in heterogeneous photocatalysis.<sup>[7]</sup> Despite some obvious advantages – ease of separation from the reaction mixtures, thermal, photo, and chemical stability, and most importantly "reusability" – heterogeneous semiconducting materials are less explored for photoredox catalytic transformations. Nevertheless, application of semiconductor photocatalysis in nitrogen fixation, C–H bond activation, and C–C bond forming reactions was surveyed.<sup>[1d]</sup>

Carbon nitride based semiconductors are well known in material chemistry as photocatalysts,<sup>[8]</sup> as a support to stabilize single metal atoms<sup>[9]</sup> or metal nanoparticles,<sup>[10]</sup> and as electrocatalysts.<sup>[11]</sup> Among others,<sup>[12]</sup> there are five main features that allow carbon nitrides (CNs) to stand out in those applications: (1) CNs are semiconductor materials, comprise of only light elements, and possess suitable valence band maxima (VBM) and conduction band minima (CBM) for controlled oxidation and reduction of substrates. Additionally, they can possess different functional groups (see the synthetic examples below) for the generation of reactive intermediates.<sup>[13]</sup> (2) The

band gap of ca. 2.7 eV ( $\lambda_{\text{ex}} \sim 460 \text{ nm}$ ) allows CNs to be used as visible light photoredox catalysts bypassing the use of UV light. (3) CNs have excellent chemical, and thermal stability up to 600 °C,<sup>[14]</sup> are easy to prepare and separate from the reaction mixtures, and most importantly, can be reused multiple times as photocatalysts. It is worth mentioning here that although not commercialized yet, the cost of synthesis of CNs is relatively low (within a few euros/kg range, taking both the cost of starting materials and the efforts require for synthesis into account) in comparison to the well-known commercialized Ru- or Ir- based photocatalysts. (4) The use of CNs as photoredox catalysts allows transition metal free reaction conditions, which are inevitable for the synthesis of medicinally important or biologically active compounds (c.f., late stage functionalization reactions). (5) Last but not the least, organophosphorus or organosulfur compounds that are commonly considered as poisons<sup>[15]</sup> in many metal based catalytic methods could readily be used as reaction partners or additives for synthetic transformations. More generally, carbon nitrides are tolerant against most, if not all, types of chemical functionalities and can therefore help to avoid the requirements of protecting groups in chemical synthesis.

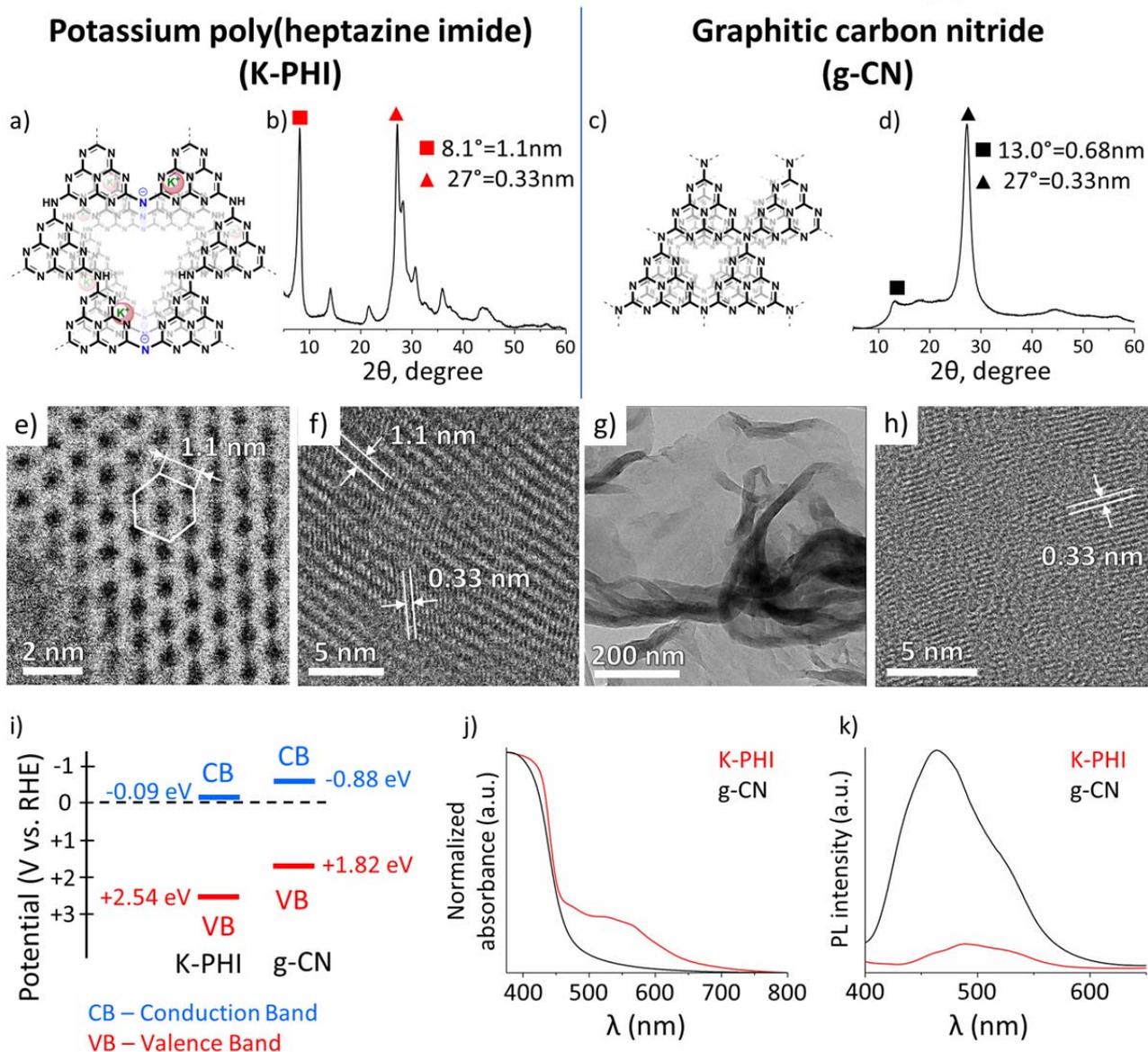
A literature survey confirmed that articles tagged with "carbon nitride" and "photocatalysis" mostly deal with either photocatalytic water splitting or degradation of pollutants. Although these reactions are important to materials chemists in order to assess the performance of newly developed materials/photocatalysts,<sup>[16]</sup> their numerous presence somehow overshadows the reports that deal with the potential of carbon nitrides in visible light mediated organic transformations.

In order to emphasize mainly the potential of carbon nitrides in organic photoredox transformations, we restrict this review to the recent advances in the field of organic synthesis assisted by "pure" carbon nitrides. Notably, the term "carbon nitride" as used by most chemists worldwide is rather broadly defined and involves several different materials (for example, salts of poly(triazine imide), or heteroelement-doped carbon nitrides).<sup>[17]</sup> Reactions catalyzed by *graphitic carbon nitride (g-CN)*<sup>[13]</sup> and its modified analogue *mesoporous graphitic carbon nitride (mpg-CN)* possessing much larger surface area,<sup>[18]</sup> and *potassium poly(heptazine imide) (K-PHI)*<sup>[19]</sup> that is extremely efficient in performing photooxidation of organic molecules, are among the other special structures covered in this review article. For illustration of the structural diversity, a brief overview on the synthesis, structures, and photo and redox properties of g-CN and K-PHI are summarized in Figure 1.<sup>[note 1]</sup> Photoredox synthetic applications based on more complex systems, such as carbon nitride photocatalysts in heterojunction with other semiconductors,<sup>[20]</sup> or carbon nitride nanocomposites with metal nanoparticles,<sup>[21]</sup> though not numerous, are not covered in this review and could be found elsewhere.<sup>[22]</sup>

Before we move on to the photosynthetic applications of CNs and K-PHI, we highlight some of their photo and redox properties, which are important in the context of photo-assisted redox interactions (i.e., electron transfer, see Figure 2).

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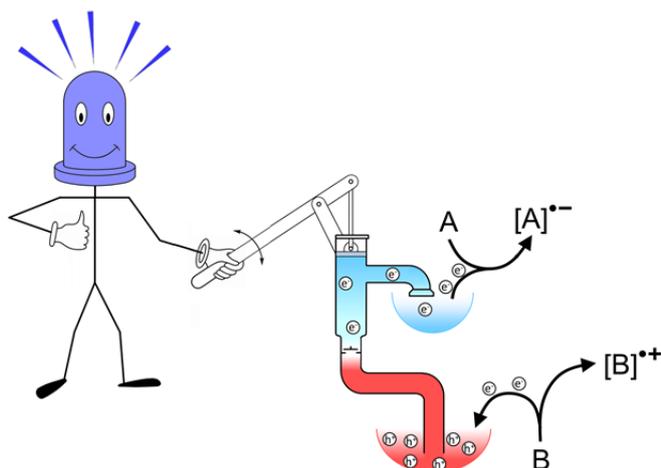


**Figure 1.** Overview of g-CN and K-PHI chemical structures and photo and redox properties: Schematic chemical structures (a and c), X-Ray diffraction patterns (b and d), AC-HRTEM images (e–h), band structure (i), absorption (j) and photoluminescence (k) spectra of K-PHI and g-CN are shown.

### 1.1. Synthesis

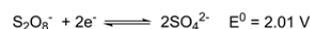
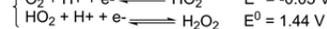
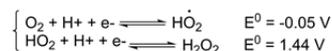
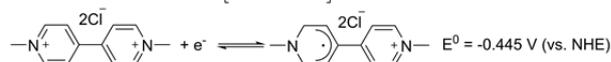
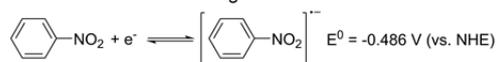
g-CN is prepared by thermolysis of melamine or other nitrogen rich precursors at 550–600 °C.<sup>[23]</sup> Whereas, K-PHI is synthesized by heat treatment of 5-aminotetrazole or triazole in LiCl/KCl eutectics at similar temperatures.<sup>[19, 24]</sup> The salt melt serves as a highly polar solvent and structural template. Both g-CN and K-PHI are built of tri-*s*-triazine rings<sup>[25]</sup> that are thermodynamically most stable at the synthesis temperature. Notably, g-CN is a covalent structure in which the heptazine rings are

interconnected through a nitrogen atom, whereas, in poly(heptazine imides), six tri-*s*-triazine molecules arranged as a hexagon with a metal cation in the core.<sup>[26]</sup> It is worth mentioning here that similar to zeolites and ion exchange resins, potassium cations in K-PHI can be easily and reversibly replaced with other metal cations.<sup>[27]</sup> The structural peculiarities of these materials are also reflected in their X-ray diffraction patterns. Both g-CN and K-PHI exhibit a strong diffraction peak at ~27° corresponding to a covalent layered structure, as in graphite, with the distance between neighbouring layers being between 0.31 nm – 0.33 nm. This repeating motif can be clearly observed

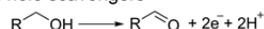


**Figure 2.** A general scheme illustrating the working principle of semiconductor-based photocatalysis upon photoexcitation. Standard reduction potentials are given for aqueous species.<sup>[26]</sup>

#### A. Common electron scavengers



#### B. Common hole scavengers



in high resolution transmission electron microscopy (HRTEM) images.<sup>[29]</sup> In addition, K-PHI possesses a characteristic peak at  $\sim 8^\circ$ , which is assigned to the holey structure. Both materials possess absorption spectra with an absorption edge at ca. 460 nm – typical for semiconductors, whereas K-PHI exhibits an additional absorption feature that covers the spectral range towards red although with relatively low extinction coefficients.

### 1.2. Photo and redox properties

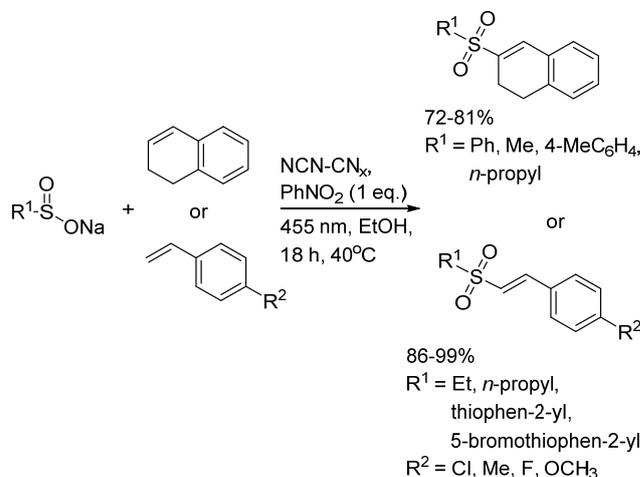
Semiconductors could be considered as visible light driven "pumps", where electrons are lifted from the VB to CB upon visible light photoexcitation, as schematically shown in Figure 2, creating a positive hole in the CB. For carbon nitrides, the photon energy is equal or greater than 2.7 eV (typical band gaps of CNs) is required. With respect to redox properties, g-CN has a VBM located at  $-0.88 \text{ V}$  (vs. RHE) and CBM at  $+1.82 \text{ V}$  (vs. RHE).<sup>[19]</sup> K-PHI, on the other hand, has a much more positive VBM at  $+2.54 \text{ V}$  (vs. RHE), while the CBM is shifted to  $-0.09 \text{ V}$  (vs. RHE).<sup>[24]</sup> Notably, the higher oxidation power of K-PHI is a direct consequence of its highly positive VBM position, and therefore, could successively be used for numerous photoredox reactions where substrate oxidation is the rate-determining step.<sup>[note 2]</sup>

With respect to photoluminescence lifetimes, which play an important role in photocatalysis, the average photoluminescence lifetime of g-CN and K-PHI are  $\sim 2 \text{ ns}$  and  $\sim 0.6 \text{ ns}$  respectively.<sup>[24], Note 3</sup> This lifetime can be tuned to some extent.<sup>[30]</sup> Notably, a major fraction of photogenerated charge carriers do not recombine and can participate in photocatalysis. Substrate oxidation at the VB site, and substrate reduction at the CB site, therefore could take place.

## 2. Photoredox catalytic applications of g-CN and mpg-CN

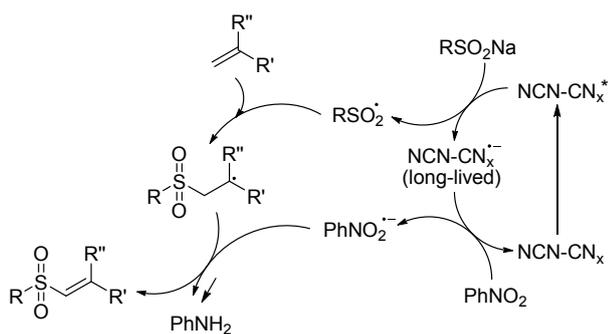
g-CN based photocatalysis was invented about ten years ago, and so far applied mainly for solar hydrogen production and dye degradation.<sup>[31]</sup> The following sections depict the reported applications of g-CN and mpg-CN in photoredox catalytic synthetic transformations.

In a joint effort, König and Lotsch developed the oxidative sulfonylation of alkenes using cyanamide-functionalized carbon nitride as a photocatalyst under visible light photoirradiation (Scheme 1) at  $40^\circ \text{C}$ .<sup>[32]</sup> Ethanol was used as a solvent and



**Scheme 1.** Photoredox catalytic sulfonylation of alkenes. Reaction was performed on 0.5 mmol scale. Isolated yields are shown.

nitrobenzene as a sacrificial oxidant. The reaction proceeds via the reductive quenching of carbon nitride; the long-lived radical anion (CN-CN<sub>x</sub><sup>•-</sup>) is reoxidized by nitrobenzene regenerating the photocatalyst (Scheme 2).

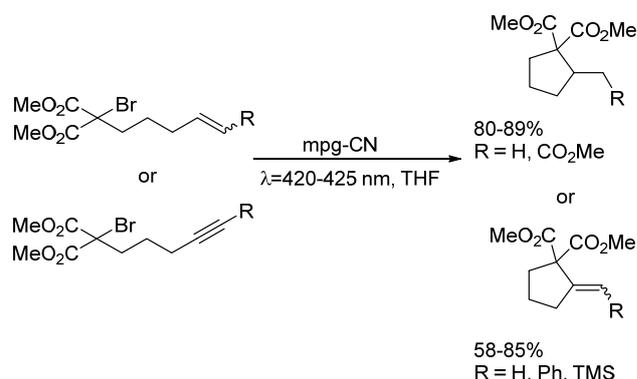


**Scheme 2.** A photocatalytic mechanism of sulfonates oxidation to vinyl sulfones.

In the same reaction surface CN-functionalized g-CN also showed high activity even under green (520 nm) light irradiation.<sup>[33]</sup>

Blechert and co-workers reported the synthesis of substituted cyclopentanes via radical cyclization of 2-bromo-1,3-dicarbonyl compounds using a fluorinated ethylene propylene (FEP) tube filled with mpg-CN (Scheme 3).<sup>[34]</sup> According to the proposed mechanism, bromomalonate is reduced to the free radical followed by cyclization to the cyclopentane (Scheme 4). Interestingly, tetrahydrofuran (THF) was used both as a solvent and as an electron donor. When traces of nucleophiles (e.g.

MeOH or EtOH) were introduced into the reactor, 2-alkoxytetrahydrofuranes were detected by GC-MS.



**Scheme 3.** Synthesis of substituted cyclopentanes using mpg-CN as a photoredox catalyst and visible light. Reaction was performed on 0.04 mmol scale. Isolated yields are shown.

Aleksandr Savateev studied organic chemistry in Kyiv, Ukraine and gained his PhD degree in 2016 with Prof. A. Kostyuk. Then he joined Prof. Markus Antonietti's department of the Max-Planck Institute of Colloids and Interfaces in Potsdam as a group leader. His group works on applications of carbon nitride based photocatalysts in organic synthesis.



Burkhard König received his Ph.D. from the University of Hamburg and continued his scientific education as a post-doctoral fellow with Prof. M. A. Bennett, Australian National University, Canberra, and Prof. B. M. Trost, Stanford University. Since 17 years, he is a full professor of organic chemistry at the University of Regensburg. His current research interest is the development of synthetic methods in photoredox catalysis.

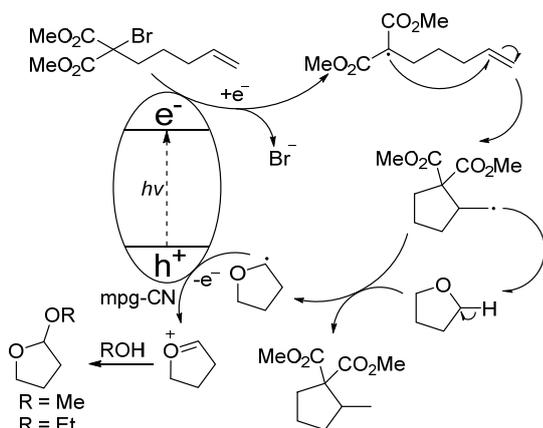


Indrajit Ghosh received his Ph.D. in 2013 from the group of Prof. Werner Nau at the Jacobs University Bremen. He then continued his scientific education as a post-doctoral researcher with Prof. Burkhard König, Regensburg University, Germany. Currently, he works as a post-doctoral researcher under the joint supervision of Prof. Burkhard König and Prof. Markus Antonietti at the University of Regensburg and Max Planck Institute of Colloids and Interfaces respectively. His current research interests include the application of visible light mediated photoredox processes in organic synthesis.



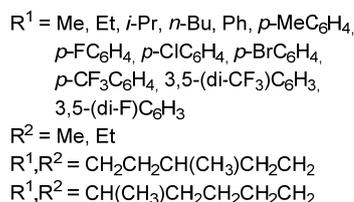
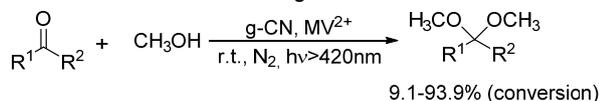
Markus Antonietti is Director of the Max Planck Institute of Colloids and Interfaces and works on the chemistry of carbon nitrides for now about 15 years. His work focusses on artificial photosynthesis, chemistry under extreme conditions (as prebiotic chemistry or unusual oxidation stresses), but also on special sorption properties and catalytic effects of heterogeneous solids.





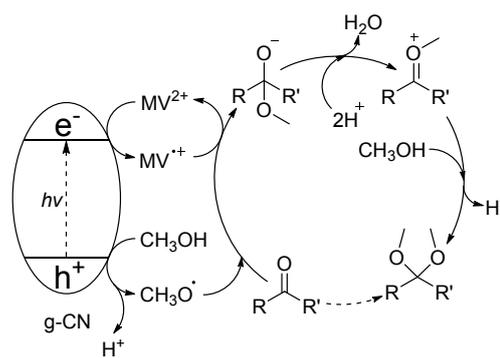
**Scheme 4.** A photocatalytic mechanism of radical cyclization catalysed by mpg-CN.

Zhao and Antonietti reported the photoredox catalytic ketalization of different aliphatic and aromatic ketones under very mild reaction conditions using catalytic amounts of methylviologen ( $MV^{2+}$ ) as an electron shuttle (Scheme 3).<sup>[35]</sup> In this example polymeric carbon nitride was synthesized from urea. Notably, high conversions of the ketones leading to highly selective formation of the corresponding products were observed along with relatively high apparent quantum yields (above 0.5). The turn over number (TON) of the involved  $MV^{2+}$  shuttle reached a remarkable high value of 31201  $h^{-1}$ . According



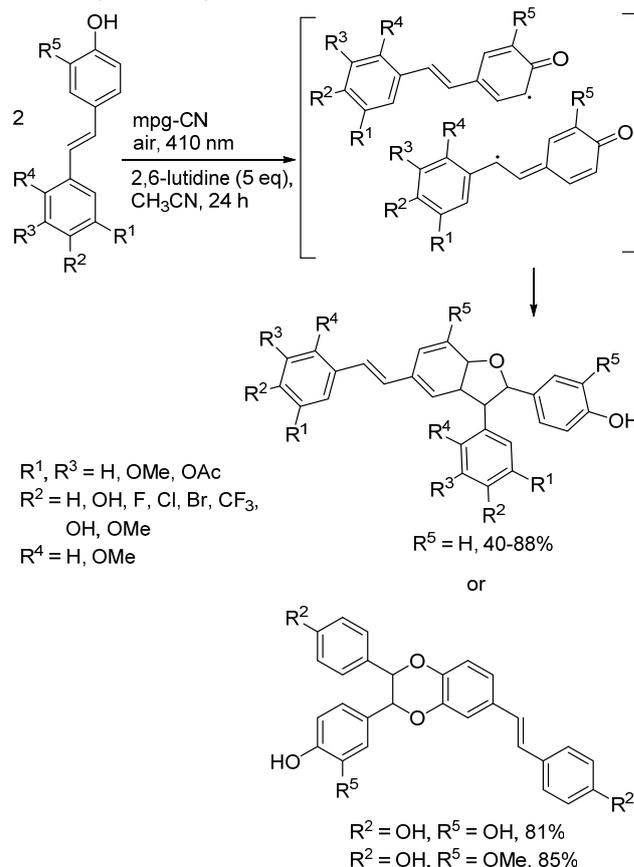
**Scheme 5.** Photoredox catalytic ketalization of different ketones using g-CN as a photocatalyst. Reaction was performed on 8.6–10 mmol scale. Conversions of ketones are shown.

to the postulated mechanism, the photogenerated holes oxidize methanol to generate a methoxy radical, while  $MV^{2+}$  receives electrons from the conduction band of g-CN generating a reduced  $MV^{+}$  species (Scheme 6). The methoxy radical reacts with the carbonyl group of the ketone to form the corresponding radical adduct, which then takes an electron from  $MV^{+}$  regenerating  $MV^{2+}$ .



**Scheme 6.** A photocatalytic mechanism of ketones ketalization using  $MV^{2+}$  as a redox shuttle.

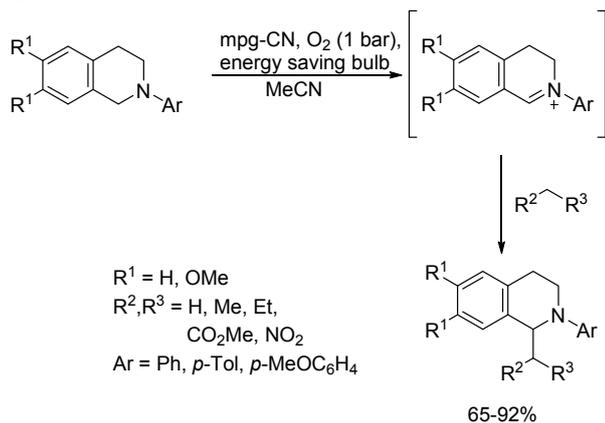
The synthesis of substituted 2,3-dihydrobenzofuranes and 1,2-dihydrobenzodioxines was reported by Liu and Wang employing an interesting radical–radical coupling reaction. The radicals are generated photocatalytically from resveratrol and its analogues, using mpg-CN in the presence of air- $O_2$  as a cheap electron mediator (Scheme 7).<sup>[36]</sup> 2,6-Lutidine was used as a base as



**Scheme 7.** g-CN-catalysed aerobic oxidative coupling of resveratrol and its analogues under visible light irradiation. Reaction was performed on 0.1 mmol scale. Isolated yields of 2,3-dihydrobenzofuranes and 1,2-dihydrobenzodioxines are shown.

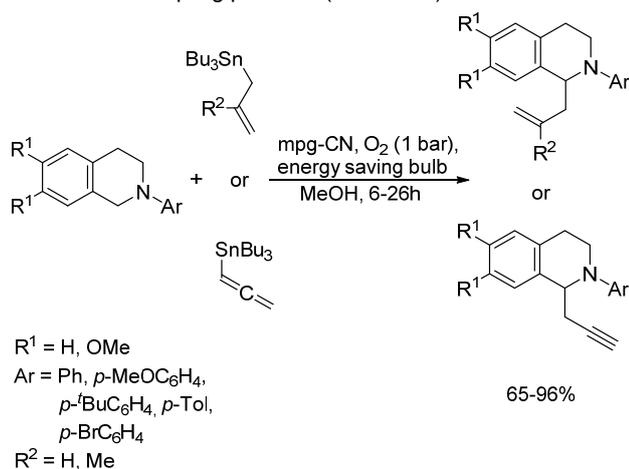
depicted in Scheme 7.

Blechert in 2012 reported the oxidation of *N*-aryltetrahydroisoquinolines using mpg-CN as a photocatalyst under O<sub>2</sub> in order to generate their radical cations.<sup>[37]</sup> They eventually form the corresponding iminium ions *via* loss of a hydrogen atom under the reaction conditions.<sup>[38]</sup> The generated iminium ions then reacted with different nucleophiles, for example, nitroalkanes and malonates, present in the reaction media to generate cross-dehydrogenative coupling products (Scheme 8). Furthermore, coupling of ketones to iminium ions was achieved through the combination of photocatalytic oxidation and proline-organocatalysis.



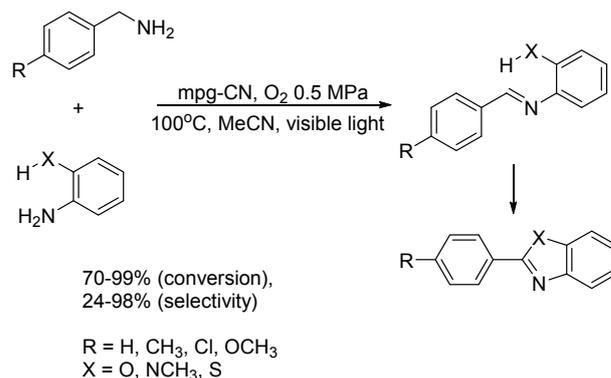
**Scheme 8.** The cross-dehydrogenative coupling reaction between *in situ* generated *N*-aryliminium ions and different nucleophiles. Reaction was performed on 0.25 mmol scale. Isolated yields are shown.

Similarly, Blechert also reported a photoredox catalytic Sakurai reaction<sup>[39]</sup> using mpg-CN as a photoredox catalyst. In this case, methanol was used as a solvent and the weak nucleophiles, such as allyl- or allenyl-stannanes, reacted selectively with the photoredox chemically generated iminium ions to furnish the desired cross-coupling products (Scheme 9).<sup>[40]</sup>



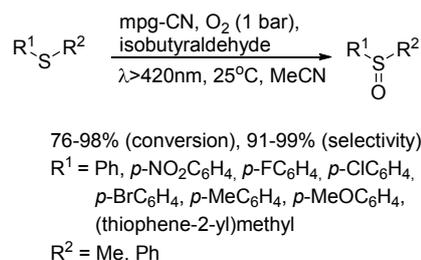
**Scheme 9.** mpg-CN assisted photoredox catalytic oxidation of *N*-aryltetrahydroisoquinolines coupled with the Sakurai reaction. Reaction was performed on 0.25 mmol scale. Isolated yields are shown.

Blechert and Wang reported the photoredox catalytic aerobic oxidation of benzylamines for the synthesis of benzoxazole, benzimidazole or benzothiazoles using excess amount of 2-aminophenol, 2-aminothiophenol or *o*-phenylenediamine respectively.<sup>[41]</sup> Notable, in this reaction, the oxidation of benzylamines leads to the formation of an imine species (*via* successive oxidation and a proton loss), which then react with the  $\alpha$ -substituted anilines to generate another intermediate imine, which *via* intramolecular nucleophilic attack of the heteroatom onto the imine's C=N bond is converted into benzoxazole, benzimidazole or benzothiazoles respectively (Scheme 10).

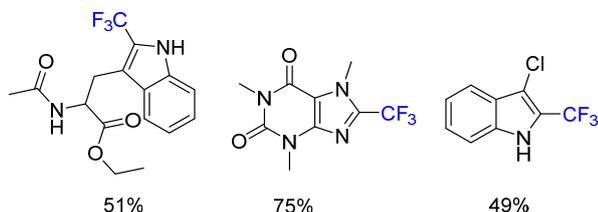
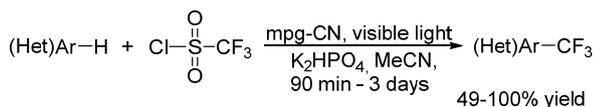


**Scheme 10.** mpg-CN catalyzed aerobic oxidation of benzylamines for the synthesis of benzoxazoles, benzimidazoles and benzothiazoles. Reaction was performed on 1 mmol scale.

Among other oxidative transformations using mpg-CN, the synthesis of sulfoxides from the respective sulphides (Scheme 11)<sup>[42]</sup> and trifluoromethylation of (hetero)arenes (using trifluoromethanesulfonyl chloride as a source of CF<sub>3</sub>-group, Scheme 12)<sup>[43]</sup> have been reported. Photoredox catalytic synthesis of esters from benzaldehyde and different alcohols using g-CN has also been reported.<sup>[44]</sup>

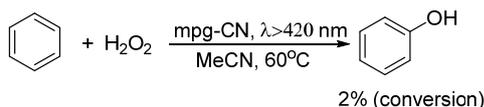


**Scheme 11.** Photoredox catalytic oxidation of sulfides to sulfoxides using mpg-CN and visible light.<sup>[42a]</sup> Reaction was performed on 1.0 mmol scale. Conversions of sulfides and selectivity with respect to sulfoxide formation are shown.



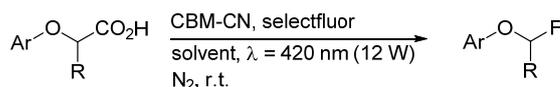
**Scheme 12.** Photoredox catalytic trifluoromethylation of arenes and heteroarenes using mpg-CN as a photocatalyst. Reaction was performed on 0.25 mmol scale. Yields determined by GC-FID,  $^1\text{H}$ , or  $^{19}\text{F}$  NMR. Some selected examples along with their isolated yields are shown.

Wang and Antonietti reported the thermodynamically challenging transformation of benzene to phenol<sup>[45]</sup> using mpg-CN as a photocatalyst and  $\text{H}_2\text{O}_2$  as a green oxidant (Scheme 13).<sup>[46]</sup> Although the conversion was rather low (conversion 2%) to be used synthetically, the conversion of benzene to phenol in a single run could be increased up to 12% by the introduction of an iron species and a porous support.



**Scheme 13.** Photoredox catalytic transformation of benzene to phenol using mpg-CN and visible light. Reaction was performed on 9.0 mmol scale. Conversion of benzene is shown.

Very recently, Pieber, Gilmore and Seeberger have developed a flow photoreactor that combines the principles of batch and continuous flow photoreactors.<sup>[47]</sup> In their report, CBM-CN (a polymeric carbon nitride derived from cyanuric acid/barbituric acid/melamine complex)<sup>[48]</sup> was suspended in "Serial Micro-Batch Reactors" (SMBR) that were passed through the FEP tubing under visible light irradiation. The developed technology provides much more efficient delivery of the light energy to the photocatalyst particles. It was elegantly applied for decarboxylative fluorination of carboxylic acids (Scheme 14). Notably, the heterogeneous g-CN was found to clearly outperform the known homogeneous  $[\text{Ru}(\text{bpy})_3]^{2+}$  photocatalyst, which is also supported by the photocatalyst stability and practicality of handling.



Ar = Ph, R = H, 14 min, 60%  
 Ar = *p*- $^t\text{BuC}_6\text{H}_4$ , R = H, 14 min, 79%  
 Ar = *o*- $\text{MeC}_6\text{H}_4$ , R = H, 24 min, 64%  
 Ar = 2,4-di- $\text{ClC}_6\text{H}_3$ , R = H, 24 min, 80%  
 Ar = *p*- $\text{BrC}_6\text{H}_4$ , R = H, 48 min, 52%  
 Ar = *p*-formyl- $\text{C}_6\text{H}_4$ , R = H, 48 min, 62%  
 Ar = *p*- $\text{FC}_6\text{H}_4$ , R = H, 24 min, 71%  
 Ar = Ph, R = Me, 14 min, 31%  
 Ar = 3-pyridyl, R = H, 24 min, 40%

**Scheme 14.** g-CN assisted decarboxylative fluorination of carboxylic acids performed in a SMBR. Reaction was performed on 0.3 mmol scale. Retention times and isolated yields are shown.

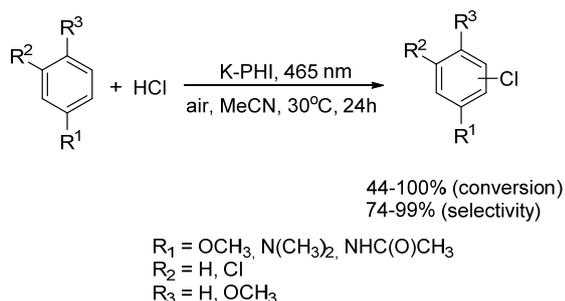
As exemplified, CNs are commonly used to generate reactive radical intermediates for synthetic applications. However, carbon nitride assisted Diels-Alder cycloaddition reaction was also reported (Scheme 15).<sup>[49]</sup> In this example polymeric carbon nitride was synthesized from a cyanuric acid-melamine complex.<sup>[50]</sup>  $\text{O}_2$  was used as a cheap electron mediator. Surprisingly, the apparent quantum yield (AQY) reached 48%, suggesting that the developed photocatalytic system is extremely efficient in converting light energy to chemical energy. The reaction proceeds *via* 4-membered ring as shown in Scheme 15.



**Scheme 15.** Selected structures of the products obtained by g-CN catalysed Diels-Alder reactions. Reactions were performed on 0.5 or 6.7 mmol scale.  $^1\text{H}$  NMR yields determined with respect to appropriate internal standards are given. The intermediary species observed in GC-MS analysis is shown on the right.

### 3. Applications of K-PHI

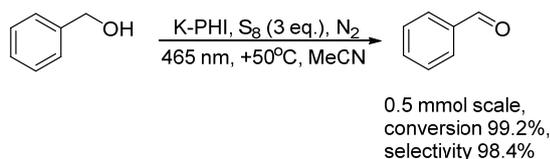
Although the synthesis of K-PHI has been reported relatively recently,<sup>[19]</sup> due to its suitable photo and redox properties (especially suitable for photo-induced oxidative transformations, see below) a large number of useful synthetic transformations have been reported under visible light photoirradiation. For example, our preliminary results suggest that oxidative chlorination of electron rich arenes can be catalysed by K-PHI using  $\text{HCl}$  as a chlorinating reagent and  $\text{O}_2$  as an electron scavenger (Scheme 16).<sup>[51]</sup> Note that the syntheses of bench-stable halogenated arenes are important as they are used extensively in cross-coupling reactions.



**Scheme 16.** K-PHI photocatalyzed chlorination of electron rich aromatic compounds. Reaction was performed on 0.02 mmol scale. Conversion of aromatic hydrocarbon and selectivity with respect to arylchloride determined from GC-MS or <sup>1</sup>H NMR spectra.

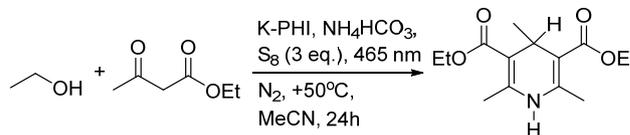
In other applications, K-PHI has been shown to be highly effective to provide heterogeneous alternatives to many known reactions.<sup>[52]</sup> Recently, Savateev et al. have reported various oxidative transformations by using K-PHI as a photocatalyst in the presence of elemental sulphur, which is either employed as a sacrificial oxidant, or as a reaction partner, or both. Most compelling, the combination of K-PHI/elemental sulfur/visible light could be used for the synthesis of disulfanes and thioamides (see below). It is worth mentioning here that every year more than seven billion tons of elemental sulfur are produced as a side product of petroleum and natural gas desulfurization process worldwide, but only limited methods are known to use it as a value-added organic substance and materials.<sup>[53]</sup>

Selective oxidation of alcohols to aldehydes is one of the most studied model reactions in photocatalysis.<sup>[54],[55]</sup> Savateev and Antonietti reported selective conversion of benzyl alcohol to benzaldehyde in high yield using K-PHI as a photoredox catalyst and elemental sulfur (S<sub>8</sub>) as a very selective sacrificial electron acceptor under relatively mild reaction conditions (*i.e.*, at 50 °C under inert atmosphere, Scheme 17).<sup>[52]</sup> Note that photooxidation of benzyl alcohols by carbon nitrides classically relies on temperature 60–150 °C, O<sub>2</sub> pressure up to 8 bar relatively.<sup>[56]</sup> The choice of K-PHI can be justified by milder conditions compared to earlier carbon nitride photocatalysts that makes the process more energy efficient. In this photoredox catalytic transformation, the choice of electron acceptor is crucial in order to achieve high selectivity and reaction rates. In comparison, when O<sub>2</sub> was used as an oxidant, both the conversion and selectivity were dropped to 29.0% and 70.5% respectively which could be a direct consequence of the in-situ formation of H<sub>2</sub>O<sub>2</sub><sup>[57]</sup> promoting further aldehyde oxidation.<sup>[42a]</sup>



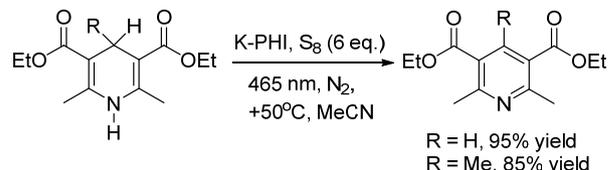
**Scheme 17.** Selective photocatalytic oxidation of benzyl alcohol to benzaldehyde using K-PHI as a photocatalyst and elemental sulfur (S<sub>8</sub>) as a sacrificial electron acceptor.

The developed photocatalytic system was shown to be useful for the generation of acetaldehyde *via* ethanol oxidation. The generated acetaldehyde further reacted with ethyl 3-aminocrotonate – the product of ammonia with ethyl acetoacetate interaction, to furnish substituted Hantzsch ester (Scheme 18).<sup>[52]</sup>



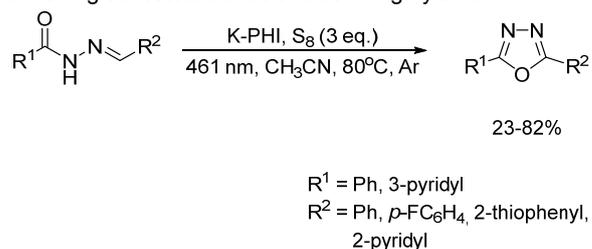
**Scheme 18.** Synthesis of Hantzsch 1,4-dihydropyridine using K-PHI as a photocatalyst.

K-PHI could also be used to convert substituted 1,4-dihydropyridines into their corresponding pyridines in high yields *via* an oxidative dehydrogenation step (Scheme 19).<sup>[52]</sup> Notably, despite the presence of elemental sulfur, K-PHI demonstrates excellent stability – no catalyst deactivation was observed even after four catalytic cycles.



**Scheme 19.** Photoredox catalytic oxidation of 1,4-dihydropyridines to pyridines using K-PHI. Reaction was performed on 0.25 mmol scale. Isolated yields are shown.

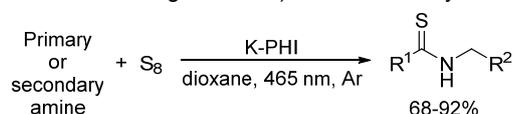
The same catalytic system was also shown to be highly efficient in synthesizing various substituted oxadiazoles from their corresponding hydrazones *via* a photoredox catalytic oxidative cyclization reaction (Scheme 20).<sup>[58]</sup> Here, elemental sulfur was used again as a more selective electron acceptor, compared to O<sub>2</sub>, furnishing substituted oxadiazoles in high yields.



**Scheme 20.** Highly efficient synthesis of oxadiazoles under oxidative photocatalysis. Reaction was performed on 0.06 mmol scale. Isolated yields are shown.

Savateev et al. also reported the synthesis of various thioamides using primary or secondary amines, elemental sulfur and K-PHI as a heterogeneous photocatalyst under visible light irradiation (Scheme 21).<sup>[59]</sup> Note that in these transformations elemental sulfur is used both as electron acceptor and as reagent. This

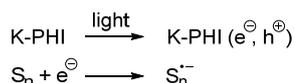
photoredox catalytic method allows synthesis of thioamides with aromatic, heteroaromatic, and aliphatic substituents in 68–92% isolated yields. Under the optimized reaction conditions, unsymmetrical thioamides and short chain thiopeptides (using diamines as starting materials) could also be synthesized.



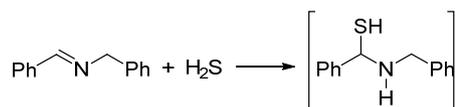
R<sup>1</sup> = Ph, *m*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, furan-2-yl, *n*-propyl, *n*-pentyl  
 R<sup>2</sup> = Ph, *m*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, furan-2-yl, *n*-propyl, *n*-pentyl, pyrrolidin-1-yl, piperidin-1-yl, 1,2,3,4-tetrahydroisoquinolin-2-yl

**Scheme 21.** Photoredox catalytic synthesis of thioamides from the respective amines and elemental sulfur using K-PHI as a photocatalyst under blue light irradiation. Reaction was performed on 0.5 mmol scale. Isolated yields are shown.

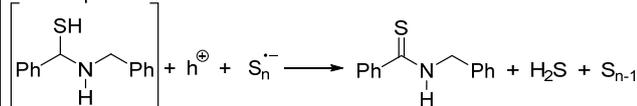
The photoredox catalytic reaction is believed to proceed via the formation of the corresponding imine as reported previously (Scheme 22).<sup>[41]</sup> Hydrogen sulphide is generated upon reduction



First photooxidation reaction



Second photooxidation reaction

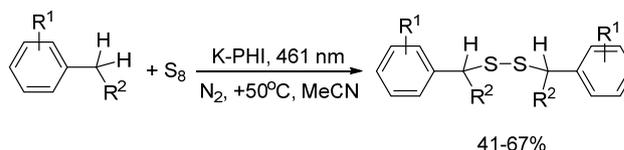


**Scheme 22.** The mechanism of photocatalytic thioamide synthesis incorporating one-pot, double photoredox catalytic oxidation.

of S<sub>8</sub> at the CBM of K-PHI, which then adds to the imine C=N bond leading to the intermediary  $\alpha$ -aminothiol. The latter species is then further oxidized under the photoredox catalytic conditions furnishing the targeted thioamide. Note that this reaction is one of the very first examples of a one-pot, double photoredox catalytic oxidations using carbon nitride (in this case, K-PHI) as a photocatalyst.

Notably, direct functionalization of hydrocarbons is an extremely important industrial process. It affords valuable chemicals from inexpensive feedstocks. The products of methylarenes

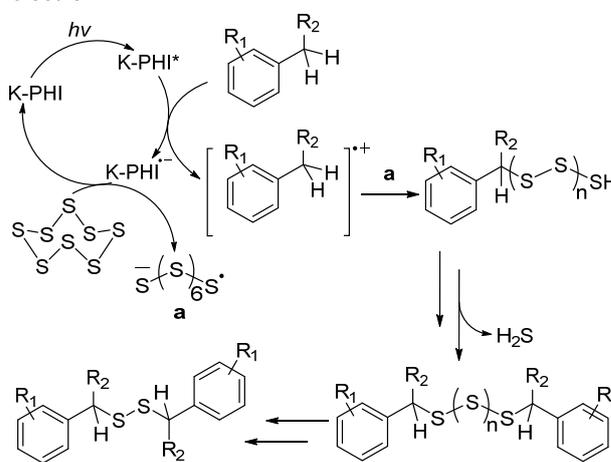
functionalization at the relatively reactive benzylic position are mostly presented by alcohols, aldehydes and carboxylic acids since O<sub>2</sub> is commonly used as electron scavenger.<sup>[60]</sup> Recently, Savateev et al. described the direct functionalization of substituted toluenes in order to access the corresponding disulphides using K-PHI and S<sub>8</sub>. Due to the high oxidation power of the holes generated upon K-PHI excitation, the oxidation of the methyl group in toluene can be easily accomplished under visible light photoirradiation and atmospheric pressure with moderate heating (Scheme 23).<sup>[61]</sup>



R<sup>1</sup> = H, *p*-Me, *o*-MeO, *p*-F, *p*-BocNH  
 R<sup>2</sup> = H, Me

**Scheme 23.** Metal free photocatalytic oxidation of methylarenes by K-PHI. Reaction was performed on 0.1–0.06 mmol scale. Isolated yields are shown.

Various disulfanes were isolated in moderate 41–67% yields. It has been shown (experimentally as well as by DFT calculations) that the reaction proceeds *via* reductive quenching of the radical anion, *i.e.* the oxidation of toluene precedes sulfur reduction (Scheme 24). The intermediary radical cation of benzylic type is intercepted by a polysulfide anion giving rise to disulfane, after extrusion of the extra sulfur atoms and evolution of H<sub>2</sub>S molecule.



**Scheme 24.** A photocatalytic mechanism of methylarenes photooxidation by K-PHI.

Noteworthy, when O<sub>2</sub> was employed instead of S<sub>8</sub>, the corresponding aldehydes were obtained.

## 4. Perspectives and Challenges

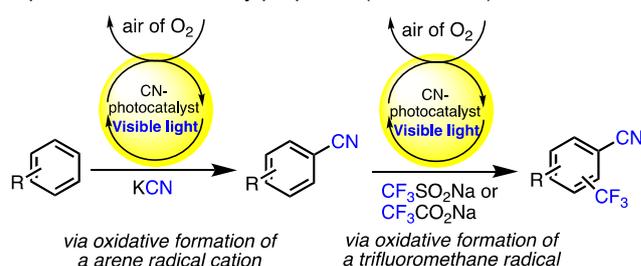
As can be seen from the discussed examples, the use of CNs as a visible light photoredox catalyst is rapidly expanding the toolbox of synthetic transformations. The reported photoredox CNs catalysts use the energy of visible light in order to execute chemical transformations, which are kinetically hindered or even endergonic. The catalytic system is purely based on lightweight elements, is thereby devoid of transition metals and tolerates various chemical functionalities. Additionally, for oxidation reactions, air oxygen or elemental sulfur are typically used as reagents to take up the electrons. Having discussed all these, in most of the synthetic applications – except for a few discrete examples – the main advantage of using CNs as photocatalysts is still discussed on the basis of the very low price and their reusability for a single chemical transformation. However, the above listed cases of the review indicate another fundamental advantage: we describe no less than 23 photochemical reactions, partly with highest selectivities and yields, all done with one catalytic system, and 4 of them even have not been described to work with alternative photocatalysts. This to our opinion underlines that CNs are indeed extremely versatile and flexible, a good first choice to make a reaction work.

CN materials combine several properties in a unique way: (i) Upon excitation, high redox potentials for oxidation and reduction, also in comparison to the well-established homogeneous photoredox catalysts, are reached. (ii) CN show exceptionally high chemical stability in the presence of nucleophiles, electrophiles, radicals, and are very photostable. (iii) Their selectivity in electron transfer to or from organic substrates are determined on one side by the difference in redox potentials, but in many cases specific interactions, e.g., between  $\pi$ -systems and the two-dimensional CNs, affect the reactivity and selectivity significantly. These individual properties are found in typical homogeneous photocatalysts or heterogeneous metal oxide semiconductor photocatalysts, but their combination is unique to CNs.

For all these reasons, this class of photocatalysts is also ideally set to perform "light driven chemical transformation sequences" that are otherwise difficult to realize.

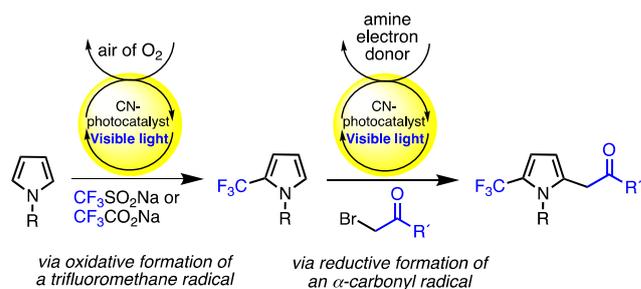
Several terminologies describe multi-step catalysed reactions that take place in one pot, including domino, cascade reaction, sequential or tandem reaction and combinations thereof.<sup>[62]</sup> Independent from the specific classification used, successive chemical transformations in just one reactor improve the efficiency of a chemical reaction. While the concept of one-pot sequential catalytic reactions is well established in homogeneous metal-, organo- or enzyme-catalysis, it remains largely unexplored in visible light photocatalysis.<sup>[6a, 63]</sup> The rather specific properties of common photocatalysts in terms of excited state redox potentials suitable for a given transformation and their reactivity towards nucleophiles, bases or acids in many cases, hamper the one-pot sequential operation of photocatalytic transformations with a single catalyst. The properties of CNs may overcome this limitation. We illustrate this potential of CNs photocatalysis with two proposed sequences that should be feasible based on the previously discussed literature reports.

A sequential twofold functionalization of an arene by oxidative CNs photocatalysis may be envisaged *via* the photooxidation of the arene to the corresponding radical cation and reaction with a nucleophile, such as cyanide. Successive chemical transformations (e.g., rearomatization) lead to the aryl nitrile. To initiate the subsequent second step, a precursor for the oxidative generation of trifluoromethyl radicals is added to the reaction mixture, e.g., trifluoroacetate, which is now photooxidized preferentially. The trifluoromethyl radical will react with the arene product from the first step yielding a two-fold functionalized product in one pot with a single photocatalyst. Many variations and extensions of such photocatalytic oxidative reaction sequences can be readily proposed (Scheme 25).



**Scheme 25.** Example of an oxidative reaction sequence that may be realized by CN-photocatalysts.

The ability of CNs to operate as robust photocatalysts under oxidative and reductive conditions may find use in combining photooxidations and photoreductions in one reaction sequence in one pot. An example could be the trifluoromethylation of an arene *via* oxidative formation of the trifluoromethyl radical followed by addition of an electron donor to the reaction mixture allowing now for the reductive activation of  $\alpha$ -bromo carbonyl compounds as the second reactant (Scheme 26).



**Scheme 26.** Example of combining an oxidative and a reductive photocatalytic reaction in a one-pot sequence that may be realized by CN-photocatalysts.

While determining the exact scope and the reaction conditions of such one-pot sequential photooxidative/reductive catalytic transformations will require further reaction optimization and the careful selection of the best-suited carbon nitride material, it can already be concluded that they will enhance the efficiency of synthetic photocatalysis and streamline the multistep synthesis of functionalized organic compounds.

In this regard, one must also recall that this review summarizes only the use of pure carbon nitrides as a proof-of-concept that this class of semiconductors are versatile photocatalysts, and occasionally exceed the best homogeneous photocatalysts in their performance. For example, K-PHI allows the synthesis of disulfanes and thioamides in a simple photoredox transformation, reactions which are possible only with metal-free catalysts. There is a plethora of carbon nitride related semiconductors, for instance, doped with different elements or synthesized in heterojunction with inorganic photocatalysts, TiO<sub>2</sub>, ZnO, CdS, etc. All these materials have photo and redox properties different from pure carbon nitrides, and therefore, we believe that using these materials will expand synthetic space towards novel chemical transformations in the near future.

How far can we go with new, even “stranger” oxidation and reduction reactions? In semiconductor photocatalysis, the oxidation and reduction power are given by the HOMO and LUMO position, respectively.

Using visible light puts restrictions on band gap width. Nevertheless, using the classical tools of band engineering, as known from organic photovoltaics, catalysts with stronger reduction or oxidation power may be developed. It is to be repeated that K-PHI with its VBM of + 2.54 V is already very oxidizing, e.g., it can oxidize even Pt or sulfate-anions.<sup>[64]</sup> We can envision however even more oxidizing organic solid state structures, and the design rules for this endeavour have been recently described.<sup>[65]</sup>

Additionally, more advanced engineering of the set-ups for photochemical reactions is currently emerging. For example, the concept of the serial micro-batch reactors<sup>[47]</sup> improves the general efficacy of heterogeneous photocatalysis due to better delivery of light energy to the photocatalyst particles, and pays off in larger product scales, and more importantly, shorter reaction times.

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**Keywords:** visible light • heterogeneous catalysis • metal-free • photoredox catalysis • organic synthesis

Note 1: The readers may wish to be referred to other reviews, which present a more comprehensive overview at the structural and morphological synthesis and other applications of carbon nitrides.<sup>[14, 66]</sup>

Note 2: When chemists are only interested in one kind of reaction, sacrificial agents are to be used. If substrate oxidation is required, an electron acceptor electron scavenger is to be employed, in order to enable oxidation process at the VB site. On the contrary, if substrate reduction is wanted, a hole scavenger is used to feed the wanted reactant with electrons.

Note 3: Generally K-PHI exhibits a lower photoluminescence compared to g-CN, which is beneficial for photocatalytic applications.

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