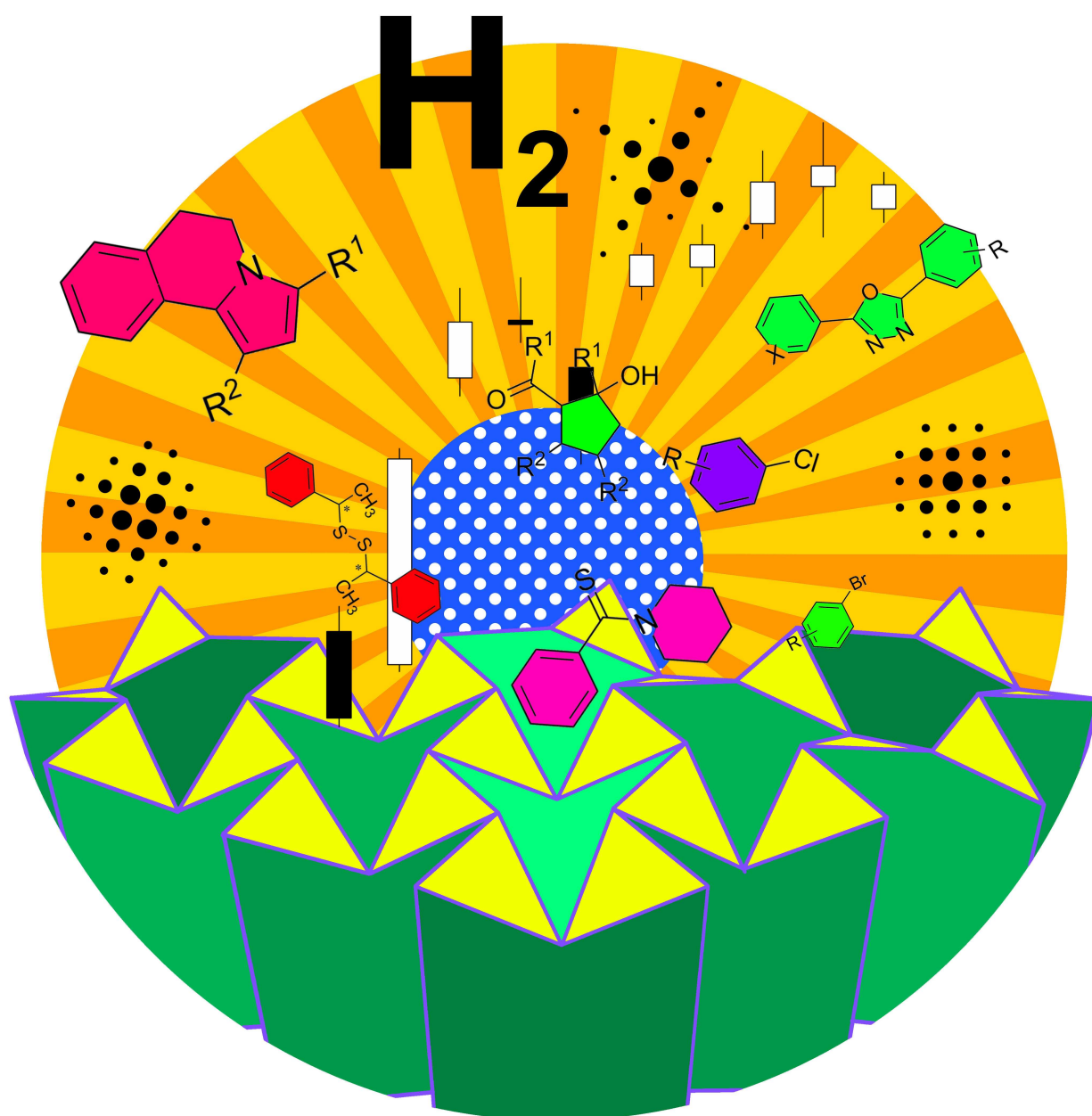




# Ionic Carbon Nitrides in Solar Hydrogen Production and Organic Synthesis: Exciting Chemistry and Economic Advantages

Aleksandr Savateev<sup>\*[a]</sup> and Markus Antonietti<sup>\*[a]</sup>



Molecular photoredox complexes from the platinum group paved the way of organic photocatalysis. However, high price and difficulties related to removal and recycling hamper application of such complexes on the larger scale. Carbon nitride semiconductor photocatalysts are deprived at large extent of such limitations. Herein, we summarize application of *ionic carbon nitrides* in photocatalysis. A salt-like structure of ionic carbon nitrides comprising negatively charged poly (heptazine imide) anion and positively charged alkali metal

cations gives rise to a number of unique properties and high activity in photocatalysis. The performance of ionic carbon nitrides in H<sub>2</sub> generation is up to 100 times higher compared with the covalent graphitic carbon nitrides. Eleven photocatalytic reactions mediated by ionic carbon nitrides and their long-lived radicals are reviewed. Economy of using carbon nitride photocatalysts in comparison with the photoredox complexes from the platinum group has been analyzed.

## 1. Introduction

The beginning of 21<sup>st</sup> century experienced the renaissance of photocatalysis.<sup>[1]</sup> High expectations are set on the development of photocatalytic methods for environmental remediation,<sup>[2]</sup> photo-fuel production<sup>[3]</sup> and synthesis of organic molecules.<sup>[4,5]</sup> Homogeneous systems, *i.e.* molecular catalysts, currently dominate the area of organic photocatalysis. Homogeneous photocatalysts are represented mostly by metal photoredox complexes largely based on Ir and Ru.<sup>[6]</sup> As considering sustainability is a central point of our society today, it is allowed to take up the question: "How sustainable is the use of two the rarest elements on Earth"?

Ru and Ir, the core of the photoredox complexes, gained 7.6 points out of 10 on the scale of the 'relative supply risk' by the Royal Society of Chemistry.<sup>[7,8]</sup> These high indices are the products of low abundance of the platinum group elements and localization of the production sites (60%) only in few countries, Russia, USA and South Africa. The platinum-elements economy, related to the photocatalysis, can to our opinion only be justified in niche applications, *e.g.* in reactions leading to high-end pharmaceutical drugs.<sup>[9]</sup> If we aim not only for momentary success by demonstrating breath-taking photocatalytic reactions, but to create a truly flexible chemical technology that will serve for decades, it is essential to develop synthetic protocols free of rare elements.

Earth abundant substitutes, Cu- and Fe-based sensitizers, are already known. Many research groups share the aspiration to create more sustainable versions of photocatalysts, and extensive work is conducted on synthesis and application of earth-abundant substitutes – copper<sup>[10,11,12]</sup> iron,<sup>[13,14,15]</sup> nickel,<sup>[16]</sup> vanadium<sup>[17]</sup> complexes, just to name a few.


On the organic side, acridinium salts,<sup>[18,19]</sup> flavines<sup>[20]</sup> and chromone derivatives<sup>[21,22,23]</sup> are totally metal free and therefore allow for 'fully-organic' photocatalysis. The structure of these dyes and therefore their redox properties may be well-tuned. Even though these catalysts are apparently much more sustainable, the synthesis of some of their representatives is a complicated, multistep process,<sup>[24]</sup> and the price of custom-made dyes can be eventually higher than that of Ru- and Ir-complexes.


A third class of materials with high sustainability and availability are heterogeneous, nanoscopic, semiconducting materials. TiO<sub>2</sub>, an industrial white pigment, is available on larger ton scale and an effective photocatalyst for environmental remediation. Although water splitting over TiO<sub>2</sub> was reported back in 1970ties,<sup>[25]</sup> the community working in the area of organic synthesis seems to hesitate using heterogeneous photocatalysis for preparative needs. The reason, in our opinion, partially lies in the wide band gap of this classical photocatalyst and the challenges associated with the use of UV light. In order to enable photochemistry under longer wavelength, dye-sensitized versions of TiO<sub>2</sub> have been developed.<sup>[26,27]</sup> Alternatively, medium band gap metal chalcogenides have been studied as well.<sup>[28]</sup>

Both economic and functionality requirements of heterogeneous photocatalysis are met in medium band gap organic semiconductors, such as covalent organic frameworks and carbon nitrides.<sup>[29,30]</sup> Carbon nitrides are metal free and essentially comprise of carbon and nitrogen, only, while precursors for their synthesis, *e.g.* urea or melamine, are megaton commodities. To improve the initially reported rather low efficiencies, a number of works report altering the intrinsic C,N-framework with one, two and even multiple organoelements.<sup>[31,32]</sup> Shalom and Antonietti developed an elegant approach for carbon nitrides structure design by supramolecular preorganization of the organic precursors.<sup>[33,34,35]</sup> Topotactic-like phase transition of triazole oligomer to carbon nitride has been reported by Dontsova et al.<sup>[36]</sup> The structural modifications have a profound impact on the band structure of carbon nitrides, mobility of the charge carriers and their lifetime.<sup>[37]</sup> Tailoring band gap of carbon nitrides has been summarized in several reviews, and we point to this work.<sup>[38]</sup> As a result, synthesis of CN-based photocatalysts with desirable redox properties and band gaps for many target applications can be achieved.

As a main asset, carbon nitrides possess secondary features that potentially will facilitate the transition of the photocatalytic

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technology from the laboratory to the industrial scale: easiness of preparation, availability and low cost of precursors, high thermal and chemical stability, and full recyclability of a heterogeneous system. A final property relates purely to efficient energy management – excitation of medium band gap semiconductor naturally requires photons with lower energy, which are now in the low cost LED range.

The class of carbon nitride materials is very large. In general it is not possible to separate a certain structure, as it can be done for molecular catalysts. A continuum of materials with gradual, but controllable chemical composition and structure does exist. Carbon nitride structure offers multiple ways to classify these materials. In this review we divide carbon nitrides into covalent and ionic structures. We will use the term 'ionic carbon nitrides' as a general name for materials possessing metal–nitrogen ionic bonds, but provide original label when refer to application of such materials in photocatalysis.

We need to emphasize that there are examples of metal intercalated carbon nitrides that do not contain metal–nitrogen bonds.<sup>[39,40,41,42]</sup> Layered LiCl•poly(triazine imide)<sup>[43,44]</sup> or LiBr•poly(triazine imide)<sup>[45]</sup> may be also regarded to this class. Synthesis, properties and application of metal intercalated carbon nitrides may be found in the review.<sup>[46]</sup>

Figure 1a shows a simplified chemical structure of potassium poly(heptazine imide) (K-PHI) possessing negatively charged poly(anion), while charge is compensated by potassium cations.<sup>[47]</sup> Poly(heptazine imide)s (PHIs) in general are prepared from *N*-rich heterocycles, *e.g.* triazoles, tetrazoles or melamine, in alkali metal chlorides eutectic melts or in solid state reactions with alkali metal chlorides.<sup>[47,48,49]</sup> Alternatively they can be made from precondensed covalent carbon nitrides by post-treatment in alkali metal salts.<sup>[50,51]</sup>

Precursors and composition of the reaction medium for ionothermal synthesis do affect the structure of carbon nitrides. Using the same organic precursor, but selecting different salts or salts mixtures, alkali metal doped covalent carbon nitrides, PHI and PTI may be synthesized. Thus Na, K and Cs based salts give metal PHIs,<sup>[48]</sup> while using Li salts results in formation of intercalation compound – crystalline layered poly(triazine imide) (PTI).<sup>[52,53,54]</sup> Secondly, excess of alkali metal salt is prerequisite for PHI formation, while heating of graphitic carbon nitride or cyanamide with only few weight percent of alkali metal hydroxide gives alkali metal doped covalent carbon nitride.<sup>[55,56]</sup> Finally, precursors and conditions should be carefully selected in order to obtain crystalline PHIs rather than

alkali metal modified carbon nitrides,<sup>[57]</sup> *N*-deficient  $g\text{-C}_3\text{N}_4$ ,<sup>[58]</sup>  $\text{K}^+$  decorated  $g\text{-C}_3\text{N}_4$ ,<sup>[59]</sup> or alkali metal doped  $g\text{-C}_3\text{N}_4$ <sup>[60]</sup> or simply change morphology of covalent  $g\text{-C}_3\text{N}_4$ .<sup>[61]</sup>

Division on ionic and covalent carbon nitrides is justified also by other reasons. Not only are the synthesis conditions different, but also chemical structure and the accompanying X-Ray patterns are. Taking K-PHI as an example, in addition to the typical for graphite-like materials peak at  $\sim 27^\circ$ , an intense peak at  $8.1^\circ$  together with several peaks of lower intensity appear in powder X-Ray (Figure 1b). Lotsch et al. solved the structure of K-PHI using transmission electron microscopy, while  $^{13}\text{C}$ - $^{15}\text{N}$  2D HETCOR spectrum confirmed that negative charge is localized at the deprotonated imide bridge between neighboring heptazine units.<sup>[62]</sup> Furthermore, X-Ray photoelectron spectroscopy (XPS) can be used to confirm the presence of deprotonated nitrogen atoms in the structure of K-PHI as a signal at 396.6 eV in N 1s spectrum.<sup>[47,63]</sup> Combination of these techniques can differentiate between metal intercalated carbon nitrides, resembling crown ether like supramolecular assemblies, from materials with defined K–N ionic bonds. Similarly HR-TEM image shows well organized structure of this material (Figure 1c). These changes are the result of potassium cation incorporation that alters drastically the crystal structure of carbon nitride. Therefore, we do not deal with a random elemental doping of the semiconductor in the ppm range, but with the formation of a new phase.<sup>[48]</sup>  $\text{K}^+$  cations in the K-PHI matrix do not only compensate negative charge of the poly(anion), but they also mediate interactions to further distant layers and therefore contribute to the formation of more ordered structure compared to the protonated PHI.<sup>[62]</sup>

Potassium cations can be exchanged by immersing K-PHI into solutions of other salts.<sup>[64]</sup> Optical and electronic properties of the materials depend only slightly on the nature of the introduced metal cation, but activity, for example, in photocatalytic  $\text{H}_2$  generation, depends on the metal cation (also explained down below).<sup>[64]</sup>

Probably the most spectacular and applied feature of ionic carbon nitrides is the ability for photocharging (Figure 1f) that we will discuss down below in detail.<sup>[65,66,67]</sup>

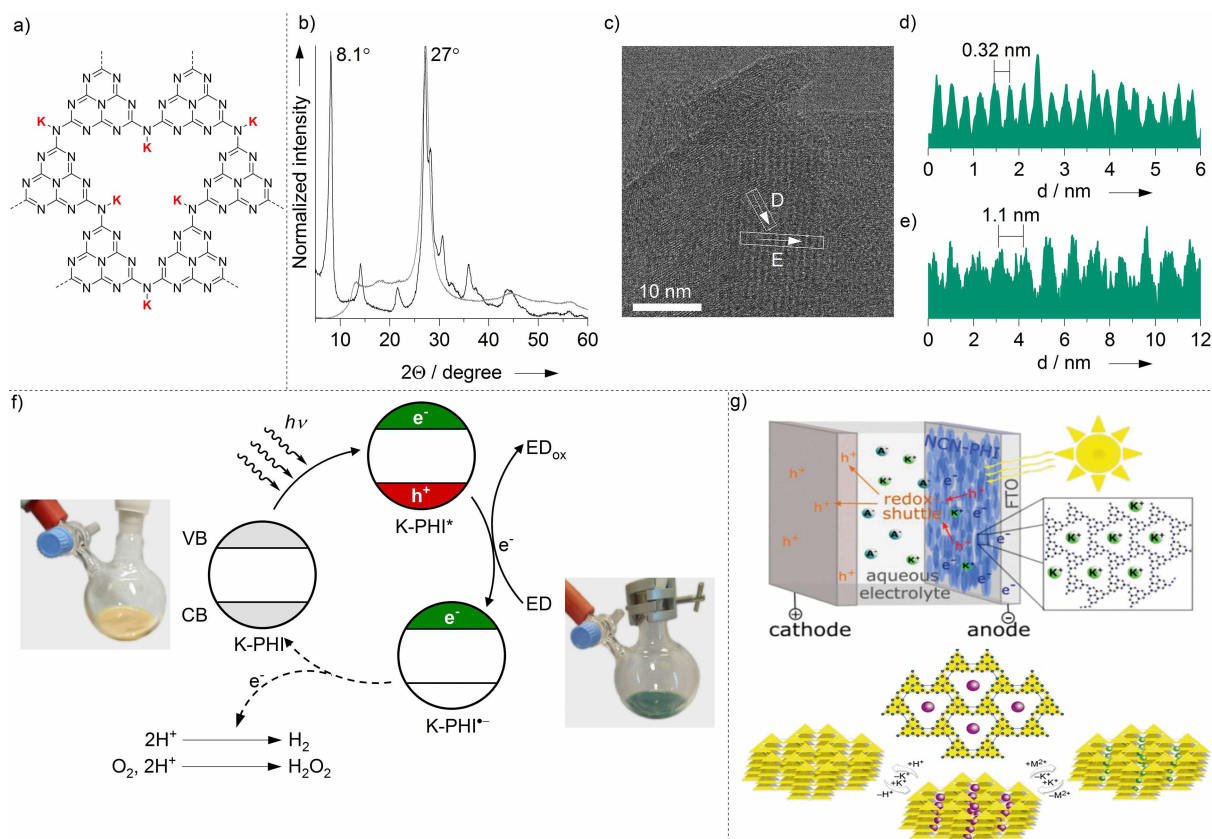
Despite ionic carbon nitrides were developed few years ago, they have been already validated in a number of fields. Taking into account such a rapid progress, this review will summarize available up to date literature on application of ionic carbon nitrides in photocatalysis and related areas. The discussed



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Markus Antonietti is director of Colloid Chemistry of the Max Planck Institute of Colloids and Interfaces. Starting from polymer science, he now works on modern materials chemistry, with sustainable processes and materials are a central theme. Carbon and Carbon–Nitrogen Materials exert a special fascination to him. Besides being a devoted scientist and an academic teacher, he is a passionate chef specialized in fusion cuisine and plays in a Rock'n'Roll band.



**Figure 1.** Introduction to ionic carbon nitrides. a) Structure of potassium poly(heptazine imide) (K-PHI); b) PXRD pattern of K-PHI (black) and covalent graphitic carbon nitride (grey); c) HR-TEM image with the profiles of the selected areas (d, e); f) Generation of long lived green radical of K-PHI ( $\text{K-PHI}^{\bullet-}$ ) and role of  $\text{K-PHI}^{\bullet-}$  in substrate reduction.  $\text{K-PHI}^*$  denotes excited state of K-PHI, ED – electron donor,  $\text{ED}_{\text{ox}}$  – a product of electron donor oxidation. Dashed arrow shows recovery of the K-PHI ground state (closure of the photocatalytic cycle) and reduction of electron acceptors; g) Application of the ionic carbon nitrides in “solar batteries” and schematic representation of ion exchange in metal PHIs. Reproduced with a permission from the references [68] and [64].

reactions are evaluated in the view of sustainable chemical production by mean of photocatalysis.

## 2. Charge Storage in Ionic Carbon Nitrides

Long-lived radicals have been a topic of research for several decades. Every chemist either prepared in the laboratory or at least is aware about the ketyl radical (common desiccant of aprotic solvents) and the methylviologen radical cation (a redox indicator). Moreover, long-lived radicals are the base of the living radical polymerization.<sup>[69]</sup> Due to the large conjugated structure and optical band gap of ca. 2.7 eV, carbon nitrides are a convenient framework for electron delocalization and storage. Although persistent radicals typically are generated by the aid of reactive reagents, carbon nitride can be converted to long-lived radical species employing only light to drive exciton separation and a simple sacrificial electron donor to quench the photogenerated hole.

Physico-chemical characterization of long-lived radical species of carbon nitrides is scarce, partially due to necessity to keep the samples strictly under air free conditions. Albeit,

cyanamide surface functionalized melon-type carbon nitride ( $^{\text{N}}\text{CN}^{\text{N}}\text{CN}_x$ ) have been characterized by transient spectroscopy.<sup>[70]</sup> Taking into account significance of charge storage in carbon nitrides for light energy conversion, we anticipate growth of research interest to long-lived carbon nitride radicals in the nearest future. For now we provide a simple model that is useful for explaining the mechanism of photocatalytic reaction mediated by ionic carbon nitrides, exemplified on K-PHI, that comprise long-lived tinted radicals (Figure 1f).

In a typical experiment of long-lived radical generation, K-PHI is dispersed in a polar solvent, e.g. acetonitrile, ethanol or water, followed by addition of a sacrificial electron donor (ED). Upon light irradiation under air free conditions, K-PHI is converted to the excited state ( $\text{K-PHI}^*$ ). Followed by reductive quenching of the hole in the VB by sacrificial electron donor,  $\text{K-PHI}^{\bullet-}$  radical anion ( $\text{K-PHI}^{\bullet-}$ ) is formed (Figure 1f). The formation of the radical is accompanied by distinct color change from yellow to green or dark-blue and may be detected by EPR.<sup>[67,71]</sup> In the presence of electron acceptors radical species can transfer electrons to such molecules. The photocatalytic cycle is closed in this way. However, in the absence of the appropriate electron acceptor the radical species ‘live’ for hours, which



means that the kinetics of photooxidation and photoreduction are successfully decoupled. The color on the other hand under air free conditions persists for months! It implies that a considerable fraction of radical sites remains in the material. Charge storage in ionic carbon nitrides has already been acknowledged by the scientific community, and several keywords for this effect have been coined – dark photocatalysis<sup>[67]</sup> and memory catalysis.<sup>[72]</sup>

Electrochemical measurements and measurements of the methylviologen radical cation absorption spectrum produced upon the long-lived radical quenching with methylviologen dichloride have been proposed to quantify the capacity of ionic carbon nitrides.<sup>[68,66]</sup> Both methods suggest that the capacity can reach 1000  $\mu\text{mol}$  per g of the material. Until now it is known that ionic carbon nitrides can stabilize a high electron density metastable state, while the capacity of covalent carbon nitrides is orders of magnitude lower.<sup>[73]</sup>

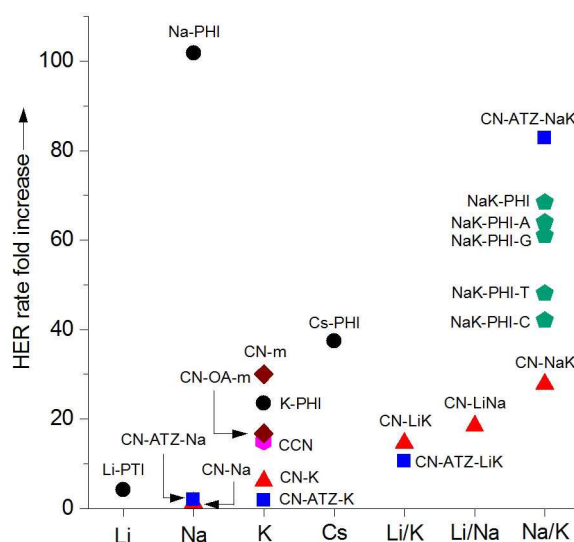
Durrant reported that the rate of the excited state quenching of cyanamide surface-functionalized melon-type carbon nitride is  $< 3 \mu\text{s}$ , while the rate of the respective radical anion quenching is  $> 2 \text{ s}$ .<sup>[74]</sup> In other words, the long-lived radical is formed much faster compared to the recovery of the carbon nitride ground state. Considering very different time-scales of these processes separation of oxidation and reduction reaction may be achieved. Using this concept, Lotsch and Reisner proposed a combination of light harvesting cycle, leading to the formation of the long-lived radical, and the dark cycle accompanied by  $\text{H}_2$  release upon proton reduction.<sup>[67]</sup> Zheng and Quan generated a long-lived radical of  $\text{g-C}_3\text{N}_4$  modified with cyano-groups (CCN) and followed by the addition of  $\text{O}_2$  producing  $\text{H}_2\text{O}_2$  in the dark.<sup>[75]</sup> Ou and Wang applied this feature of carbon nitrides for simultaneous alcohols dehydrogenation and  $\text{H}_2\text{O}_2$  production.<sup>[76]</sup> Finally, Lotsch et al. developed solar batteries with chargeable FTO-electrode made from cyanamide-functionalized polyheptazine imide (NCN-PHI) (Figure 1g).<sup>[68]</sup>

### 3. Application of Ionic Carbon Nitrides in Photocatalysis

#### 3.1. Hydrogen Production

Hydrogen is considered as a green and highly energetic fuel. In order to provide a steady supply of such commodity in the future from dilute solar light, the photocatalytic systems must consist of durable and highly-performing materials. With few exceptions semiconductor photocatalysis require Pt as a co-catalyst for HER.<sup>[77]</sup>

The rate of  $\text{H}_2$  production over ionic carbon nitrides is 10–100 times higher compared to the reference covalent carbon nitrides under the same conditions (Figure 2). Note that activity of reference carbon nitrides was measured under the identical conditions and taken from the same sources. Therefore, variance to differences in setup, light source, Pt co-catalyst content, etc. can be excluded. More careful analysis of the



**Figure 2.** Increase of  $\text{H}_2$  production (folds) by ionic carbon nitrides in comparison with the covalent (graphitic) carbon nitride measured under identical conditions. Alkali metal cation incorporated into the structure is shown on abscissa. Pt was used as a co-catalyst. Calculated from the references: circles – Li-PTI, Na-PHI, K-PHI, Cs-PHI;<sup>[48]</sup> squares – CN-ATZ-Na, CN-ATZ-K, CN-ATZ-LiK, CN-ATZ-NaK;<sup>[79]</sup> triangles pointing upward – CN-Na, CN-K, CN-LiK, CN-LiNa, CN-NaK;<sup>[78]</sup> diamonds – CN-m, CN-OA-m;<sup>[50]</sup> hexagons – CCN;<sup>[75]</sup> pentagons (NaK poly(heptazine imide) modified with nucleobases) – NaK-PHI, NaK-PHI-A, NaK-PHI-G, NaK-PHI-T, NaK-PHI-C.<sup>[80]</sup>

literature suggests that variation of the precursors, salt source, nature of the cation and synthesis conditions are decisive for the high photocatalytic activity in hydrogen evolution reaction (HER). Zhang and Antonietti optimized the properties of ionic carbon nitrides by condensation of urea with oxamide followed by calcination in molten salts (diamonds on the Figure 2).<sup>[50]</sup> In particular they achieved compression of the interlayer distance to 0.292 nm that improves lateral charge transport and interlayer excitons dissociation. Already high rates of  $\text{H}_2$  production are explained by extremely high apparent quantum yield (AQY) of 57% at 420 nm. Furthermore, the AQY was increased to 60% at 420 nm by preparing triazine–heptazine copolymer by calcination of polymeric carbon nitride in NaCl/KCl eutectic mixture (triangles pointing upwards on the Figure 2).<sup>[78]</sup> It has been also shown that the AQY can be further increased to 65% if reaction is performed in the presence of  $\text{K}_2\text{HPO}_4$ .<sup>[79]</sup>

As mentioned above, performance of metal PHIs in hydrogen production is different, while higher  $\text{H}_2$  evolution rate is explained by improved charge separation and localization efficiency.<sup>[64]</sup> Interesting the activity of Mg-PHI was the highest in the row of alkali and alkaline earth metal PHI illustrating remote resemblance of this polymeric photocatalyst with chlorophyll. Metal free PHI (*i.e.* acid treated K-PHI, H-PHI) on the other hand showed ca. 38 times higher activity in HER compared to K-PHI.<sup>[62]</sup>

### 3.2. Organic Synthesis

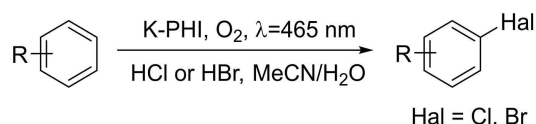
#### 3.2.1. Transition Metal-Free Heterogeneous Catalysis

Recently we have summarized the results on using carbon nitrides, in particular K-PHI, in photocatalytic synthesis of organic molecules.<sup>[5,4]</sup> Therefore, we highlight only more recent progress of using ionic carbon nitrides in organic synthesis. It must be pointed out that most of the reactions highlighted below can be successfully accomplished at room temperature (20–25 °C). However, elevated temperature may have a positive effect by reducing reaction time.

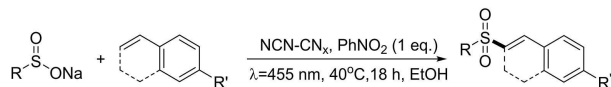
Markushyna and Savateev developed oxidative halogenation of electron rich aromatic compounds using HCl and O<sub>2</sub> as reagents (Scheme 1).<sup>[81]</sup> By using K-PHI the reaction conditions were much simplified not only compared to the classical Friedel-Crafts reaction, but also in comparison with the homogeneous photocatalysis.<sup>[82]</sup> Catalysts screening revealed that K-PHI is also more active compared to the covalent graphitic carbon nitride. Reaction works also with NaCl as Cl<sup>−</sup> source. Therefore, potentially sea water may be used as a chlorination agent.

König and Lotsch used cyanamide-functionalized carbon nitride (NCN-CN<sub>x</sub>) to drive C–S coupling between alkyl/aryl sulfinates and styrenes/dihydronaphthalenes (Scheme 2).<sup>[83]</sup>

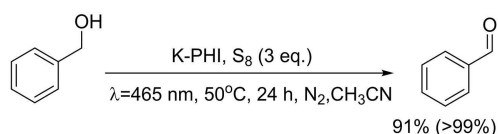
Despite relative simplicity of alcohols oxidation to the carbonyl compound, the reaction has high applicability in organic synthesis. In the laboratory practice this reaction is accomplished by stoichiometric quantities of pyridinium chlorochromate. Photocatalytically, this reaction is realized by the heterogeneous carbon nitride photocatalyst using O<sub>2</sub> as electron acceptor.<sup>[84]</sup> The O<sub>2</sub>-based approach quite often suffers



**Scheme 1.** Photocatalytic oxidative halogenation of electron rich aromatic compounds.



**Scheme 2.** Synthesis of vinylsulfones using heterogeneous NCN-CN<sub>x</sub> photocatalyst.



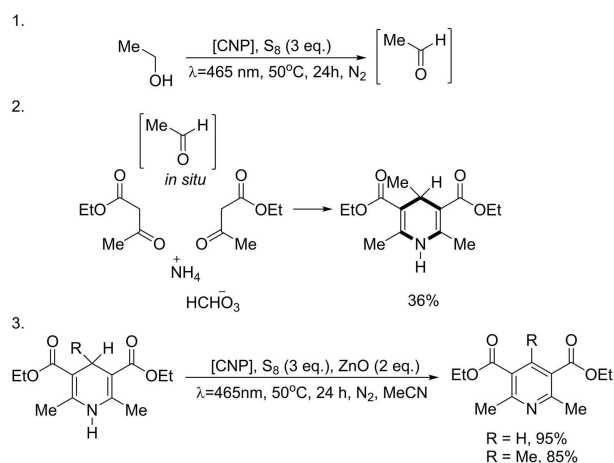
**Scheme 3.** Oxidation of benzyl alcohol by K-PHI and S<sub>8</sub> as electron acceptor. Conversion and selectivity (in parentheses) are shown.

from low selectivity due to overoxidation of the aldehyde to the carboxylic acid.<sup>[85]</sup> The selectivity of the process can thereby be significantly enhanced by replacing O<sub>2</sub> with elemental sulfur (S<sub>8</sub>) (Scheme 3).<sup>[86]</sup>

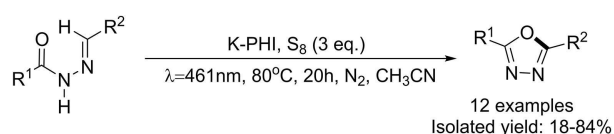
Photo-Hantzsch synthesis of pyridines has been developed using K-PHI (Scheme 4).<sup>[86]</sup> Herein, instead of handling the aliphatic aldehyde under air free conditions, it is produced right before consumption from the respective alcohol in a first step. In the second step, 1,4-dihydropyridine is synthesized *via* classical Hantzsch reaction. In a possible third step, after replacing ethanol by the solvent more stable against oxidation, *i.e.* acetonitrile, 1,4-dihydropyridine can be converted to the corresponding pyridine derivative.

K-PHI is a convenient photocatalyst to trigger dehydrogenation reactions. This feature has been employed in oxidative cyclization of *N*-alkylidene hydrazones to 1,3,4-oxadiazoles (Scheme 5).<sup>[87]</sup> The method works excellent when S<sub>8</sub> was used as electron acceptor. The selectivity was significantly lower when O<sub>2</sub> has been employed, apparently due to formation of the reactive oxygen species. In this example, elevated temperature is required to enable disfavored 5-*endo*-trig cyclization process.<sup>[88]</sup>

The reactions presented on the Schemes 3–5 illustrate the versatility of the system consisting of K-PHI/S<sub>8</sub> to enable various photocatalytic reactions with high selectivity. In the dehydrogenation reactions S<sub>8</sub> is converted into H<sub>2</sub>S. On the other hand, photocatalytic decomposition of H<sub>2</sub>S to H<sub>2</sub> and sulfur has been reported.<sup>[89]</sup> Therefore, potentially sulfur can be envisioned as a redox shuttle in photocatalysis according to the S<sub>8</sub>-H<sub>2</sub>S-S<sub>8</sub> scheme, resembling that in metal sulfide batteries.



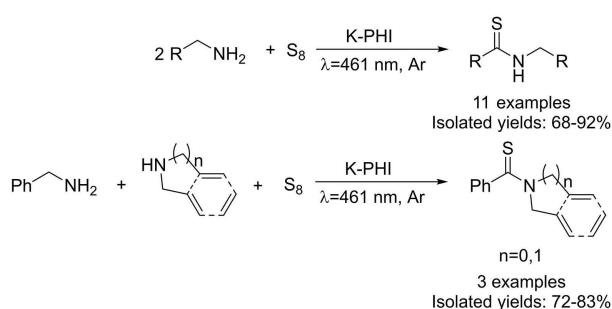
**Scheme 4.** Photo-Hantzsch synthesis.



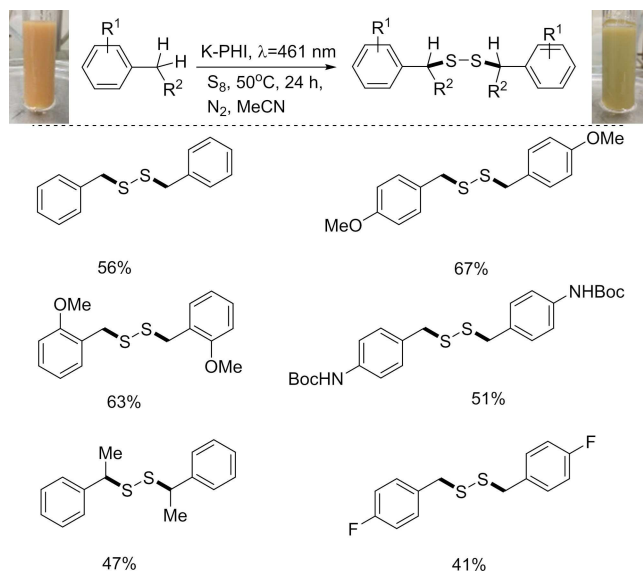
**Scheme 5.** Photocatalytic oxidative cyclization of *N*-alkylidene hydrazones by K-PHI.

A series of thioamides was assembled by means of K-PHI from amines and  $S_8$  (Scheme 6).<sup>[90]</sup> Important advantage of using heterogeneous carbon nitride here is that the reaction is performed under milder conditions, 70 °C or room temperature, compared to 100 °C reported for non-photocatalytic conditions.<sup>[91,92]</sup> Reactive linear aliphatic thioamides ( $R = C_5H_{11}$ ,  $C_3H_7$ , on the Scheme 6) have been obtained for the first time in 72–78% yields, while room temperature in this case is essential.

Savateev and Antonietti developed a photocatalytic reaction of disulfanes synthesis from methyl arenes, *e.g.* toluene is the simplest example, and elemental sulfur, a by-product of oil refinery (Scheme 7).<sup>[66]</sup> Color staining was observed once all sulfur is consumed indicating that the reaction proceeds via reductive quenching of the radical-anion of K-PHI (Figure 1f). It is also a handy feature of the photocatalytic system that as such



**Scheme 6.** Photo-Kindler reaction mediated by K-PHI photocatalyst.



**Scheme 7.** Oxidative thiolation of methylarenes using elemental sulfur as inexpensive S-source. Images of the reaction mixture before light irradiation (left) and after all sulfur is consumed (right) are adapted from the reference [66].

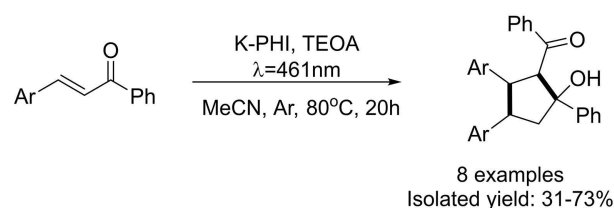
the photocatalysts has a ‘built-in indicator’ for reaching the end of reaction.

Due to the presence of  $C=C$  and  $C=O$  moieties  $\alpha,\beta$ -unsaturated enones, *i.e.* chalcones, are versatile reagents in organic synthesis and a privilege structures in medicinal chemistry.<sup>[93]</sup> Long-lived radicals of K-PHI generated under air free conditions trigger cyclodimerization of the chalcones *via* formal [3+2]-cycloaddition and yields cyclopentanoles (Scheme 8).<sup>[94]</sup> The advantage of using K-PHI is that the photocatalytic system is free of any metals. It is very unique considering that all reports on cyclopentanoles synthesis by chalcones dimerization strongly rely on rare-earth elements, *e.g.* ytterbium.<sup>[95]</sup>

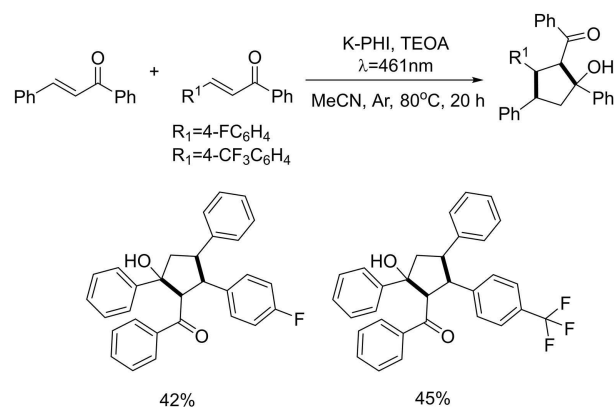
Moreover cross-reductive cyclodimerization between two chalcones is enabled by the heterogeneous K-PHI photocatalyst (Scheme 9). This reaction on the contrary does not proceed using homogeneous Ru-photocatalyst.<sup>[96]</sup> This suggests that K-PHI not only enables the photoredox process, but also serves as a support to direct the regioselectivity of the C–C coupling.

Ionic carbon nitrides also enable counter-intuitive chemical transformations. For example, *N*-aryltetrahydroisoquinolines are well studied in the Mannich and Aza-Henry reactions.<sup>[97]</sup> On the other hand, bare tetrahydroisoquinoline (THIQ) itself typically undergoes dehydrogenation.<sup>[98]</sup>

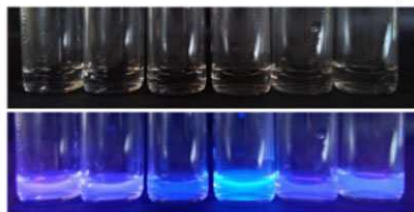
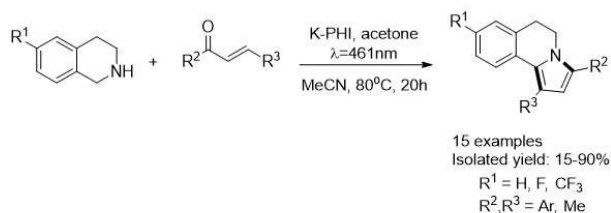
Kurpil and Savateev prepared highly-fluorescent conjugated polyaromatic heterocycles with quantum yield of fluorescence of up to 24% from tetrahydroisoquinoline and  $\alpha,\beta$ -unsaturated enones using K-PHI photocatalyst (Scheme 10).<sup>[71]</sup> Since oxida-



**Scheme 8.** Metal-free reductive cyclodimerization of  $\alpha,\beta$ -unsaturated ketones. TEOA stands for triethanolamine.



**Scheme 9.** Regioselective synthesis of polysubstituted cyclopentanoles via cross reductive cyclodimerization of  $\alpha,\beta$ -unsaturated ketones. TEOA stands for triethanolamine.



**Scheme 10.** Synthesis of fluorescent *N*-fused pyrroles *via* tandem photocatalytic reaction between THIQ and a chalcone. Appearance of the solutions of *N*-fused pyrroles in acetonitrile under ambient light and UV irradiation reproduced with permission from reference [71].

tion and reduction of the substrates on the K-PHI surface are separated in time and space, it allows for coupling a tentative radical cation of THIQ and the radical anion of enone in a regioselective fashion. Heating accelerates the reaction. Nevertheless, comparable yield was obtained performing the reaction at room temperature for 72 h.

The above-mentioned examples illustrate versatility of carbon nitride photocatalysis. The reactions proceed without toxic oxidants in stoichiometric quantities (*e.g.* synthesis of oxadiazole-1,2,4 and disulfanes), using simpler reaction conditions (*e.g.* synthesis of *N*-fused pyrroles and oxidative halogenation) and industrial by-products rather than expensive chemicals (*e.g.* elemental sulfur instead of Lawesson reagent in synthesis of disulfanes and thioamides).

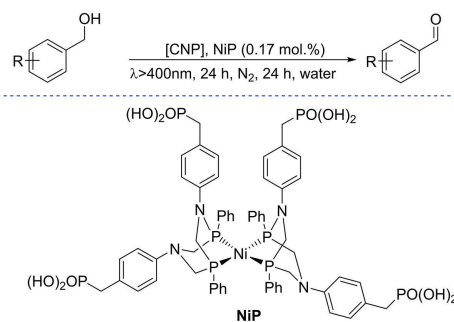
### 3.2.2. Hybrid Transition Metal and Semiconductor Catalysis

Until now we discussed only metal-free systems. Several examples in the literature are known where heterogeneous carbon nitride photocatalysis is coupled with earth-abundant metal catalysis.

Reisner et al. used NCN-CN<sub>x</sub> in combination with hydrogen evolution molecular Ni complex (NiP) for oxidation of benzyl alcohols to aldehydes (Scheme 11).<sup>[74]</sup> Two value added products – benzaldehyde and H<sub>2</sub> – were prepared in one pot.

Pieber et al. have coupled Ni-catalyst with CN-OA-m photocatalyst for selective C–O coupling of carboxylic acids and arylhalides (Scheme 12).<sup>[99]</sup> The idea behind this intriguing combination of the catalysts is to use carbon nitride, with the advantages of heterogeneous approach discussed in the introduction, for reduction of the intermediary Ni(II)-molecular complex.<sup>[100]</sup>

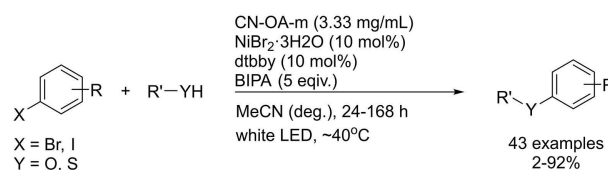
Furthermore, the method has been extended on Dual Nickel/Photocatalytic (Thio)etherification (Scheme 13).<sup>[101]</sup>



**Scheme 11.** Oxidation of alcohols by hybrid molecular Ni-catalyst and ionic carbon nitride.



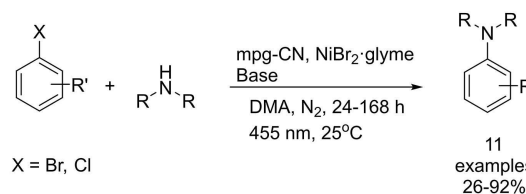
**Scheme 12.** C–O cross-coupling enabled by the semi-heterogeneous photocatalysis.



**Scheme 13.** Semi-heterogeneous (thio)esterification of arylbromides and aryl iodides with Ni(II) complex and carbon nitride photocatalyst.

Finally, mesoporous graphitic carbon nitride (mpg-CN) complements the dual photocatalysis with C–N cross-coupling reactions as demonstrated by Ghosh and König (Scheme 14).<sup>[102]</sup>

These examples demonstrate enormous opportunities offered for organic synthesis by coupling heterogeneous carbon nitride photocatalysis with molecular transition metal catalysis.



**Scheme 14.** C–N cross-coupling mediated by Ni complex and mpg-CN.



## 4. Conclusion and Outlook

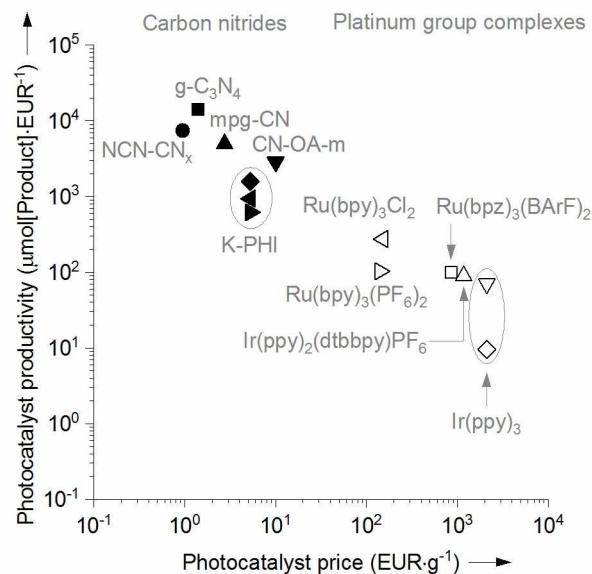
Research on ionic carbon nitrides is a fast-growing field that lies on the border between heterogeneous photocatalysis and material chemistry. Despite relatively short history, the utility of this class of materials has been already proven in different reactions and also in solar energy harvesting and storage. The achievements, even for researchers working in the area, are well beyond our expectations and we rise the following questions just to illustrate potential perspectives and further applications.

- In the long-lived radical of the ionic carbon nitrides one electron is delocalized over 5 heptazine units (as calculated from the capacity of  $\sim 1000 \mu\text{g}^{-1}$ ). Is this the maximum capacity? Until now, structure-capacity relationships of ionic carbon nitrides have not been derived yet. Considering the number of parameters of ionic carbon nitride, "degree of doping" with alkali metal, nature of alkali metal, crystallite size, etc., which can influence the capacity of ionic carbon nitride, the potential is broad.
- The scope of the reaction mediated by carbon nitrides still does not match that of the transition metal molecular catalysts. Chemists who used to work with soluble molecular photocatalysts apparently are very sceptic about the performance of heterogeneous systems. This review gives 11 examples where ionic carbon nitrides have advantages compared to non-photocatalytic methods or molecular photocatalysis, but: are we restricted by accepting previous limitations?

In order to take into account also the economy of the photocatalytic approach we analyzed available in the literature reactions mediated both by carbon nitrides and molecular catalysts from the platinum group. Figure 3 represents the amount of the product ( $\mu\text{mol}$ ) produced per 1 EUR spent for procurement or synthesis of the photocatalyst. Costs of chemicals needed for synthesis of non-commercialized systems were used to calculate the price. The results suggest that productivity of the carbon nitride photocatalysts is one to three orders of magnitude higher compared to that of photoredox complexes. This is especially true for Ir-based systems, due to high price of the precursor –  $\text{IrCl}_3$ . On the other hand,  $\text{RuCl}_3$  is cheaper when compared to Ir salts. However, Ru-complexes of sophisticated structure, e.g.  $\text{Ru}(\text{bpz})_2(\text{BArF})_2$  are expensive because of the ligands, the cost of which by far exceed the metal center.<sup>[103]</sup>

To conclude, we think that the results presented in the review suggest that ionic carbon nitride catalysis enables multiple organic reactions. Under similar conditions (substrate and catalyst loading, reaction time, etc.) their performance is comparable to that of molecular transition metals. In addition, several unique reactions were reported where molecular catalysts do show low or even no activity. The results reported until now suggest immense opportunities for academic research in the very near future.

Earlier we have pointed out that development of the sustainable technologies is only possible when the technology supports itself, but is not only due to gracious donations by the society.<sup>[107]</sup> For the first time, a very simple in preparation visible



**Figure 3.** Performance of the carbon nitride and redox photocatalysts in photocatalytic reactions versus price of the photocatalyst. The symbols of the same type denote the same photocatalytic reaction using the same reagents, i.e. squares – Diels-Alder cycloaddition;<sup>[104,103]</sup> triangles pointing upward – the Mannich reaction between THIQ and nitroethane;<sup>[97,105]</sup> triangles pointing downward – C–O coupling between *p*-iodobenzoic acid methylester and *N*-Bocproline;<sup>[99]</sup> diamonds – DHPIQ synthesis;<sup>[71]</sup> triangles pointing left – oxidative chlorination of anisole;<sup>[81,106]</sup> triangles pointing right – cyclodimerization of the chalcones;<sup>[94,96]</sup> circle – coupling of benzenesulfonate with 1,2-dihydronaphthalene.<sup>[83]</sup> Filled symbols correspond to the heterogeneous carbon nitride photocatalysts, hollow symbols correspond to the photoredox complexes of the group of platinum.

light active heterogeneous photocatalytic system has to offer not only exciting chemistry, but more than competitive price versus homogeneous systems. A very first example of using graphitic carbon nitride for production of diazo compounds on kg scale has been reported.<sup>[108]</sup>

These two factors, photocatalytic versatility and economic affordability at high sustainability, will in our opinion contribute to the establishment of carbon nitride photocatalysis, even in previously not expected industrial fields.

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## Conflict of Interest

The authors declare no conflict of interest.

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- [1] B. König, *Eur. J. Org. Chem.* **2017**, 2017, 1979–1981.
- [2] W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* **2016**, *116*, 7159–7329.
- [3] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, *Energy Environ. Sci.* **2012**, *5*, 6717–6731.
- [4] A. Savateev, M. Antonietti, *ACS Catal.* **2018**, *8*, 9790–9808.
- [5] A. Savateev, I. Ghosh, B. König, M. Antonietti, *Angew. Chem. Int. Ed.* **2018**, *57*, 15936–15947.
- [6] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926.
- [7] <http://www.rsc.org/periodic-table/element/44/ruthenium>.
- [8] <http://www.rsc.org/periodic-table/element/77/iridium>.
- [9] T. P. Nicholls, D. Leonori, A. C. Bissember, *Nat. Prod. Rep.* **2016**, *33*, 1248–1254.
- [10] A. C. Hernandez-Perez, S. K. Collins, *Acc. Chem. Res.* **2016**, *49*, 1557–1565.
- [11] Y. Y. Ng, L. J. Tan, S. M. Ng, Y. T. Chai, R. Ganguly, Y. Du, E. K. L. Yeow, H. S. Soo, *ACS Catal.* **2018**, *8*, 11277–11286.
- [12] A. Rosas-Hernández, C. Steinlechner, H. Junge, M. Beller, *Green Chem.* **2017**, *19*, 2356–2360.
- [13] Y. Liu, P. Persson, V. Sundström, K. Wärnmark, *Acc. Chem. Res.* **2016**, *49*, 1477–1485.
- [14] S. Fischer, A. Rösel, A. Kammer, E. Barsch, R. Schoch, H. Junge, M. Bauer, M. Beller, R. Ludwig, *Chem. Eur. J.* **2018**, *24*, 16052–16065.
- [15] J. H. Lim, X. Engelmann, S. Corby, R. Ganguly, K. Ray, H. S. Soo, *Chem. Sci.* **2018**, *9*, 3992–4002.
- [16] X. L. Ho, H. Shao, Y. Y. Ng, R. Ganguly, Y. Lu, H. S. Soo, *Inorg. Chem.* **2019**, *58*, 1469–1480.
- [17] S. Gazi, W. K. Hung Ng, R. Ganguly, A. M. Putra Moeljadi, H. Hirao, H. S. Soo, *Chem. Sci.* **2015**, *6*, 7130–7142.
- [18] A. Joshi-Pangu, F. Lévesque, H. G. Roth, S. F. Oliver, L.-C. Campeau, D. Nicewicz, D. A. Di Rocco, *J. Org. Chem.* **2016**, *81*, 7244–7249.
- [19] S. Fukuzumi, K. Ohkubo, *Chem. Sci.* **2013**, *4*, 561–574.
- [20] I. K. Sideri, E. Voutyritsa, C. G. Kokotos, *Org. Biomol. Chem.* **2018**, *16*, 4596–4614.
- [21] D. P. Hari, B. König, *Chem. Commun.* **2014**, *50*, 6688–6699.
- [22] V. Srivastava, P. P. Singh, *RSC Adv.* **2017**, *7*, 31377–31392.
- [23] I. Ghosh, B. König, *Angew. Chem. Int. Ed.* **2016**, *55*, 7676–7679; *Angew. Chem.* **2016**, *128*, 7806–7810.
- [24] V. Mojr, E. Svobodová, K. Straková, T. Neveselý, J. Chudoba, H. Dvořáková, R. Cibulka, *Chem. Commun.* **2015**, *51*, 12036–12039.
- [25] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.
- [26] S. Földner, T. Mitkina, T. Trottmann, A. Frimberger, M. Gruber, B. König, *Photochem. Photobiol. Sci.* **2011**, *10*, 623–625.
- [27] B. Kükrer Kaletas, V. N. Kozhevnikov, M. Zimine, R. M. Williams, B. König, L. De Cola, *Eur. J. Org. Chem.* **2005**, 2005, 3443–3449.
- [28] A. Pal, I. Ghosh, S. Sapra, B. König, *Chem. Mater.* **2017**, *29*, 5225–5231.
- [29] M. E. Briggs, A. I. Cooper, *Chem. Mater.* **2017**, *29*, 149–157.
- [30] X. Wang, K. Maeda, A. Thomas, K. Takaneba, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2008**, *8*, 76.
- [31] J. Ran, T. Y. Ma, G. Gao, X.-W. Du, S. Z. Qiao, *Energy Environ. Sci.* **2015**, *8*, 3708–3717.
- [32] Q. Liu, J. Shen, X. Yu, X. Yang, W. Liu, J. Yang, H. Tang, H. Xu, H. Li, Y. Li, J. Xu, *Appl. Catal. B* **2019**, *248*, 84–94.
- [33] J. Barrio, L. Lin, X. Wang, M. Shalom, *ACS Sustainable Chem. Eng.* **2018**, *6*, 519–530.
- [34] M. Shalom, S. Inal, C. Fettkenhauer, D. Neher, M. Antonietti, *J. Am. Chem. Soc.* **2013**, *135*, 7118–7121.
- [35] L. Li, M. Shalom, Y. Zhao, J. Barrio, M. Antonietti, *J. Mater. Chem. A* **2017**, *5*, 18502–18508.
- [36] A. Savateev, S. Pronkin, J. D. Epping, M. G. Willinger, M. Antonietti, D. Dontsova, *J. Mater. Chem. A* **2017**, *5*, 8394–8401.
- [37] S. Dolai, J. Barrio, G. Peng, A. Grafmüller, M. Shalom, *Nanoscale* **2019**, *11*, 5564–5570.
- [38] L. Zhou, H. Zhang, H. Sun, S. Liu, M. O. Tade, S. Wang, W. Jin, *Catal. Sci. Technol.* **2016**, *6*, 7002–7023.
- [39] M. J. Bojdys, J.-O. Müller, M. Antonietti, A. Thomas, *Chem. Eur. J.* **2008**, *14*, 8177–8182.
- [40] C. Qiu, Y. Xu, X. Fan, D. Xu, R. Tandiana, X. Ling, Y. Jiang, C. Liu, L. Yu, W. Chen, C. Su, *Adv. Sci.* **2019**, *6*, 1801403.
- [41] Z. Wu, H. Gao, S. Yan, Z. Zou, *Dalton Trans.* **2014**, *43*, 12013–12017.
- [42] Z. Zhang, J. Huang, Q. Yuan, B. Dong, *Nanoscale* **2014**, *6*, 9250–9256.
- [43] E. Wirnhier, M. Döblinger, D. Gunzelmann, J. Senker, B. V. Lotsch, W. Schnick, *Chem. Eur. J.* **2011**, *17*, 3213–3221.
- [44] Y. Ham, K. Maeda, D. Cha, K. Takaneba, K. Domen, *Chem. Asian J.* **2013**, *8*, 218–224.
- [45] T. M. Suter, T. S. Miller, J. K. Cockcroft, A. E. Aliev, M. C. Wilding, A. Sella, F. Corà, C. A. Howard, P. F. McMillan, *Chem. Sci.* **2019**, *10*, 2519–2528.
- [46] F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nat. Rev. Mater.* **2017**, *2*, 17030.
- [47] D. Dontsova, S. Pronkin, M. Wehle, Z. Chen, C. Fettkenhauer, G. Clavel, M. Antonietti, *Chem. Mater.* **2015**, *27*, 5170–5179.
- [48] Z. Chen, A. Savateev, S. Pronkin, V. Papaefthimiou, C. Wolff, M. G. Willinger, E. Willinger, D. Neher, M. Antonietti, D. Dontsova, *Adv. Mater.* **2017**, *29*, 1700555.
- [49] A. Savateev, S. Pronkin, J. D. Epping, M. G. Willinger, C. Wolff, D. Neher, M. Antonietti, D. Dontsova, *ChemCatChem* **2017**, *9*, 167–174.
- [50] G. Zhang, G. Li, Z.-A. Lan, L. Lin, A. Savateev, T. Heil, S. Zafeiratos, X. Wang, M. Antonietti, *Angew. Chem. Int. Ed.* **2017**, *56*, 13445–13449; *Angew. Chem.* **2017**, *129*, 13630–13634.
- [51] V. W.-h. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum, B. V. Lotsch, *Nat. Commun.* **2016**, *7*, 12165.
- [52] F. K. Kessler, W. Schnick, *Z. Anorg. Allg. Chem.* **2019**, *645*, 857–862.
- [53] L. Lin, C. Wang, W. Ren, H. Ou, Y. Zhang, X. Wang, *Chem. Sci.* **2017**, *8*, 5506–5511.
- [54] L. Heymann, B. Schiller, H. Noei, A. Stierle, C. Klinke, *ACS Omega* **2018**, *3*, 3892–3900.
- [55] S. Hu, F. Li, Z. Fan, F. Wang, Y. Zhao, Z. Lv, *Dalton Trans.* **2015**, *44*, 1084–1092.
- [56] J. Jiang, S. Cao, C. Hu, C. Chen, *Chin. J. Catal.* **2017**, *38*, 1981–1989.
- [57] Y. Xu, Y. Gong, H. Ren, W. Liu, L. Niu, C. Li, X. Liu, *RSC Adv.* **2017**, *7*, 32592–32600.
- [58] J. Liu, W. Fang, Z. Wei, Z. Qin, Z. Jiang, W. Shangguan, *Appl. Catal. B* **2018**, *238*, 465–470.
- [59] J. Yang, Y. Liang, K. Li, G. Yang, K. Wang, R. Xu, X. Xie, *Catal. Sci. Technol.* **2019**, *9*, 3342–3346.
- [60] Z. Shu, Y. Wang, W. Wang, J. Zhou, T. Li, X. Liu, Y. Tan, Z. Zhao, *Int. J. Hydrogen Energy* **2019**, *44*, 748–756.
- [61] F. Yang, D. Liu, Y. Li, L. Cheng, J. Ye, *Appl. Catal. B* **2019**, *240*, 64–71.
- [62] H. Schlömerberg, J. Kröger, G. Savasci, M. W. Terban, S. Bette, I. Moudrakovski, V. Duppel, F. Podjaski, R. Siegel, J. Senker, R. E. Dinnebier, C. Ochsenfeld, B. V. Lotsch, *Chem. Mater.* **2019**, *31*, 7478–7486.
- [63] B. Kurpil, A. Savateev, V. Papaefthimiou, S. Zafeiratos, T. Heil, S. Özenler, D. Dontsova, M. Antonietti, *Appl. Catal. B* **2017**, *217*, 622–628.
- [64] A. Savateev, S. Pronkin, M. G. Willinger, M. Antonietti, D. Dontsova, *Chem. Asian J.* **2017**, *12*, 1517–1522.
- [65] N. A. Rodríguez, A. Savateev, M. A. Grela, D. Dontsova, *ACS Appl. Mater. Interfaces* **2017**, *9*, 22941–22949.
- [66] A. Savateev, B. Kurpil, A. Mishchenko, G. Zhang, M. Antonietti, *Chem. Sci.* **2018**, *9*, 3584–3591.
- [67] V. W.-h. Lau, D. Klose, H. Kasap, F. Podjaski, M.-C. Pignié, E. Reisner, G. Jeschke, B. V. Lotsch, *Angew. Chem. Int. Ed.* **2017**, *56*, 510–514; *Angew. Chem.* **2017**, *129*, 525–529.
- [68] F. Podjaski, J. Kröger, B. V. Lotsch, *Adv. Mater.* **2018**, *30*, 1705477.
- [69] M. Szwarc, *Nature* **1956**, *178*, 1168–1169.
- [70] W. Yang, R. Godin, H. Kasap, B. Moss, Y. Dong, S. A. J. Hillman, L. Steier, E. Reisner, J. R. Durrant, *J. Am. Chem. Soc.* **2019**, *141*, 11219–11229.
- [71] B. Kurpil, K. Otte, A. Mishchenko, P. Lamagni, W. Lipiński, N. Lock, M. Antonietti, A. Savateev, *Nat. Commun.* **2019**, *10*, 945.
- [72] T. Cai, Y. Liu, L. Wang, S. Zhang, J. Ma, W. Dong, Y. Zeng, J. Yuan, C. Liu, S. Luo, *ACS Appl. Mater. Interfaces* **2018**, *10*, 25350–25359.
- [73] H. Schlömerberg, F. Podjaski, J. Kroeger, B. Lotsch, *Nachr. Chem.* **2018**, *66*, 1157–1161.
- [74] H. Kasap, C. A. Caputo, B. C. M. Martindale, R. Godin, V. W.-h. Lau, B. V. Lotsch, J. R. Durrant, E. Reisner, *J. Am. Chem. Soc.* **2016**, *138*, 9183–9192.
- [75] Z. Zeng, X. Quan, H. Yu, S. Chen, Y. Zhang, H. Zhao, S. Zhang, *Appl. Catal. B* **2018**, *236*, 99–106.
- [76] H. Ou, C. Tang, X. Chen, M. Zhou, X. Wang, *ACS Catal.* **2019**, *9*, 2949–2955.
- [77] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong, Z. Kang, *Science* **2015**, *347*, 970–974.
- [78] G. Zhang, L. Lin, G. Li, Y. Zhang, A. Savateev, S. Zafeiratos, X. Wang, M. Antonietti, *Angew. Chem. Int. Ed.* **2018**, *57*, 9372–9376.

- [79] G. Zhang, G. Li, T. Heil, S. Zafeiratos, F. Lai, A. Savateev, M. Antonietti, X. Wang, *Angew. Chem. Int. Ed.* **2019**, *58*, 3433–3437.
- [80] G. Zhang, M. Liu, T. Heil, S. Zafeiratos, A. Savateev, M. Antonietti, X. Wang, *Angew. Chem. Int. Ed.* doi: 10.1002/anie.201908322.
- [81] Y. Markushyna, C. Teutloff, B. Kurpil, D. Cruz, I. Laueremann, Y. Zhao, M. Antonietti, A. Savateev, *Appl. Catal. B* **2019**, *248*, 211–217.
- [82] T. Hering, B. Mühlendorf, R. Wolf, B. König, *Angew. Chem. Int. Ed.* **2016**, *55*, 5342–5345; *Angew. Chem.* **2016**, *128*, 5428–5431.
- [83] A. U. Meyer, V. W.-h. Lau, B. König, B. V. Lotsch, *Eur. J. Org. Chem.* **2017**, *2017*, 2179–2185.
- [84] Y. Chen, J. Zhang, M. Zhang, X. Wang, *Chem. Sci.* **2013**, *4*, 3244–3248.
- [85] B. Long, Z. Ding, X. Wang, *ChemSusChem* **2013**, *6*, 2074–2078.
- [86] A. Savateev, D. Dontsova, B. Kurpil, M. Antonietti, *J. Catal.* **2017**, *350*, 203–211.
- [87] B. Kurpil, K. Otte, M. Antonietti, A. Savateev, *Appl. Catal. B* **2018**, *228*, 97–102.
- [88] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.
- [89] X. Zong, J. Han, B. Seger, H. Chen, G. Lu, C. Li, L. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4399–4403; *Angew. Chem.* **2014**, *126*, 4488–4492.
- [90] B. Kurpil, B. Kumru, T. Heil, M. Antonietti, A. Savateev, *Green Chem.* **2018**, *20*, 838–842.
- [91] J. Wei, Y. Li, X. Jiang, *Org. Lett.* **2016**, *18*, 340–343.
- [92] H.-Z. Li, W.-J. Xue, G.-D. Yin, A.-X. Wu, *Tetrahedron Lett.* **2015**, *56*, 5843–5846.
- [93] C. Zhuang, W. Zhang, C. Sheng, W. Zhang, C. Xing, Z. Miao, *Chem. Rev.* **2017**, *117*, 7762–7810.
- [94] B. Kurpil, Y. Markushyna, A. Savateev, *ACS Catal.* **2019**, *9*, 1531–1538.
- [95] K. Takaki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku, Y. Fujiwara, *J. Chem. Soc., Chem. Commun.* **1990**, 516–517.
- [96] G. Zhao, C. Yang, L. Guo, H. Sun, R. Lin, W. Xia, *J. Org. Chem.* **2012**, *77*, 6302–6306.
- [97] L. Möhlmann, M. Baar, J. Rieß, M. Antonietti, X. Wang, S. Blechert, *Adv. Synth. Catal.* **2012**, *354*, 1909–1913.
- [98] F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, *Angew. Chem. Int. Ed.* **2011**, *50*, 657–660; *Angew. Chem.* **2011**, *123*, 683–686.
- [99] B. Pieber, J. A. Malik, C. Cavedon, S. Gisbertz, A. Savateev, D. Cruz, T. Heil, G. Zhang, P. H. Seeberger, *Angew. Chem. Int. Ed.* **2019**, *58*, 9575–9580.
- [100] J. C. Tellis, D. N. Primer, G. A. Molander, *Science* **2014**, *345*, 433–436.
- [101] C. Cavedon, A. Madani, P. H. Seeberger, B. Pieber, *Org. Lett.* **2019**, *21*, 5331–5334.
- [102] I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti, B. König, *Science* **2019**, *365*, 360–366.
- [103] S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350–19353.
- [104] Y. Zhao, M. Antonietti, *Angew. Chem. Int. Ed.* **2017**, *56*, 9336–9340; *Angew. Chem.* **2017**, *129*, 9464–9468.
- [105] A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464–1465.
- [106] L. Zhang, X. Hu, *Chem. Sci.* **2017**, *8*, 7009–7013.
- [107] M. Antonietti, A. Savateev, *Chem. Rec.* **2018**, *18*, 969–972.
- [108] Y. Dai, C. Li, Y. Shen, T. Lim, J. Xu, Y. Li, H. Niemantsverdriet, F. Besenbacher, N. Lock, R. Su, *Nat. Commun.* **2018**, *9*, 60.

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