A Study in Red: The Overlooked Role of Azo-Moieties in Polymeric Carbon Nitride Photocatalysts with Strongly Extended Optical Absorption

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Abstract

The unique optical and photoredox properties of heptazine-based polymeric carbon nitride (PCN) materials make them promising semiconductors for driving various productive photocatalytic conversions. However, their typical absorption onset at ca. 430-450 nm is still far from optimum for efficient sunlight harvesting. Despite many reports of successful attempts to extend the light absorption range of PCNs, the determination of the structural features responsible for the red shift of the light absorption edge beyond 450 nm has often been obstructed by the highly disordered structure of PCNs and/or low content of the moieties responsible for changes in optical and electronic properties. In this work, we implement a high-temperature (900 °C) treatment procedure for turning the conventional melamine-derived yellow PCN into a red carbon nitride. This approach preserves the typical PCN structure but incorporates a new functionality that promotes visible light absorption. A detailed characterization of the prepared material reveals that partial heptazine fragmentation accompanied by de-ammonification leads to the formation of azo-groups in the red PCN, a chromophore moiety whose role in shifting the optical absorption edge of PCNs has been overlooked so far. These azo moieties can be activated under visible-light (470 nm) for H₂ evolution even without any additional co-catalyst, but are also responsible for enhanced charge-trapping and radiative recombination, as shown by spectroscopic studies. Our work thus highlights the importance of careful determination of structural features governing the complex interplay between the light absorption, charge separation and catalytic turnover in PCN-based polymers tailored for visible light-driven photocatalysis.
Introduction

Heptazine-based polymeric carbon nitride (PCN) materials[1] stand out from a range of other typical, mostly metal oxide-based photocatalysts mainly by their unique optical (i.e., bandgap and intra-gap states)[2] and photoredox (i.e., quasi-Fermi levels of electrons and holes) properties.[3] Nevertheless, the typical absorption onset of PCN is around 430-450 nm, which is far from making it an ideal absorber of solar radiation. This motivated significant research efforts directed towards shifting the optical absorption and the corresponding photocatalytic activity to the red. In general, one can distinguish two basic strategies for achieving this goal. Firstly, modified synthetic protocols aim at incorporating additional light absorbing moieties already during the synthesis of PCN, for example, by introducing sulfur species[4], aromatic carbon moieties,[5] creating copolymeric precursors with other N-containing molecules,[6] or by varying the condensation conditions, especially the temperature[7] or reaction medium composition.[8]

Secondly, post-synthetic approaches comprise chemical surface modification of conventional PCN, for instance, by hydrogenation or oxidation,[9] sensitization with light harvesting compounds such as organic dyes[10], carbon dots or fullerenes,[11] or various forms of post-synthetic thermal treatment.[12]

Although the condensation of PCN precursors at high temperatures (above 600 °C)[7] and the post-synthetic annealing of PCNs under similar conditions[12] might seem very similar, the essential difference lies in the lower ammonia gas evolution from the material in the latter case. While the two approaches have somewhat similar effects on the material’s optical properties if carried out under inert or reductive (NH₃, H₂) conditions[7, 13] or under vacuum,[14] the reports on the performance of the resulting photocatalysts in terms of activity or visible-light response are contradictory and show little consensus regarding the optimal thermal treatment conditions. For example, Wang et al. reported a continuous increase of the photocatalytic H₂ evolution rate with increasing temperature of PCN condensation up to 700 °C.[12] In accord with this result, P. Niu et al.
demonstrated an activity enhancement of PCN post-treated at 750 °C.\textsuperscript{[15]} Nevertheless, other authors observed a maximum activity at intermediate heat-treatment (condensation or post-treatment) temperatures of 500 °C,\textsuperscript{[14]} 550 °C,\textsuperscript{[7]} and 580 °C,\textsuperscript{[16]} 600 °C\textsuperscript{[10]} or 680 °C,\textsuperscript{[17]} followed by a significant drop in photocatalytic activity. These discrepancies in the reported photocatalytic performance of PCNs with extended visible-light absorption are clearly due to the lack of our knowledge on the nature of the colour centers that are responsible for the activation beyond wavelengths of \(\sim 450\) nm in various PCNs. A number of plausible suggestions have been made to explain the red shift of the optical absorption edge, including increased condensation degree due to a partial residual NH\textsubscript{2}-groups removal,\textsuperscript{[7]} improved stacking allowing normally forbidden n-\(\pi^*\) transitions,\textsuperscript{[12]} and creation of N-\textsuperscript{[17-18]} or C-vacancies.\textsuperscript{[13a, 19]} Nonetheless, given the disordered nature of PCN polymers, it is difficult to unambiguously prove the distinct type of colour centers in the material, so that they often remain rather hypothesised than proven. However, the determination of the moieties or structural features responsible for the red shift is crucial for developing an appropriate synthetic or post-synthetic technique for the preparation of efficient visible-light active PCNs.

Herein, we report a post-synthetic approach involving a brief (3 min) high-temperature (above 900 °C) treatment under vacuum that effectively turns the typically yellow PCN into a red PCN by significantly extending its visible light absorption down to \(>600\) nm. Interestingly, we demonstrate that the dramatic shift of the absorption edge is due to the formation of azo-linkages in the PCN structure, an aspect that has been largely overlooked so far. Finally, we elucidate and discuss the effects of the azo moieties on the charge transfer dynamics and photocatalytic activity of the obtained photocatalysts. This sheds some critical light on the general applicability of PCN photocatalysts with drastically extended visible-light absorption prepared by methods comprising a high-temperature treatment.
Materials and Methods

Synthesis of polymeric carbon nitride: The sample of conventional yellow PCN (Y-CNₙ) was prepared by thermal polycondensation of 30 g melamine at 530 ºC for 4h in a lid-covered crucible. The red PCN materials (R-CNₙ) were prepared by a heat treatment of Y-CNₙ in a quartz tube initially having a reduced pressure of 1.8 × 10⁻² mbar using a tube furnace operating at 900 ºC for 3 min. After the treatment the samples were cooled down, brought to ambient pressure and powdered.

The dissolution of the synthesized samples was carried out by a modified method proposed by Horvarth-Bordon et al.[20] 1.0 g of the Y-CNₙ or R-CNₙ samples was suspended in 50 mL of 1M aqueous KOH solution and transferred into a Teflon-lined stainless steel autoclave with a total volume of 100 mL. The autoclaves were heated at 100 ºC for 16 h, then the obtained solution was filtered first through a paper filter and then through a 0.25 µm PTFE syringe filter. Tri-potassium cyamelurate crystals were produced from the above-mentioned solutions by evaporation and precipitation. The needle shaped tri-potassium cyamelurate crystals formed in both cases were filtered, washed with ethanol and dried. In order to analyse the presence of minor products of dissolution in KOH of Y-CNₙ (Y-CNₙ-K) and R-CNₙ (R-CNₙ-K), the solutions were subjected to several cycles of evaporation, tri-potassium cyamelurate crystals separation and subsequent concentration of the supernatant. The supernatant was subsequently analyzed. The solid crystalline powder was obtained from the R-CNₙ-K solution (R-CNₙ-KS) by slow evaporation of water from the R-CNₙ-K solution, then it was washed with deionized water and dried overnight at 70 ºC.

Deposition of co-catalysts for photocatalytic H₂ reactions. The preparation of photocatalysts modified with Pt nanoparticles or [Mo₃S₁₃]²⁻ (=Mo₃)[²b] clusters was described in details in our previous work.[21] Briefly, the platinized Y-CNₙ and R-CNₙ samples were prepared using photodeposition method. For this, the Y/R-CNₙ powder
(0.2 g) was suspended in 20 mL H₂O:MeOH (9:1, v:v) containing hexachloroplatinic acid (4 mg), ultrasonicated for 1 h, bubbled with argon gas and irradiated for 30 min with a 150 W Xe-lamp equipped with a KG3 (Schott) heat filter (intensity ca. 1 sun). Subsequently, the powder was washed by centrifugation and dried overnight at 60 °C. The {Mo₃} clusters were synthesized using (NH₄)₂[Mo₃S₁₃] × 2H₂O produced by the method described by Müller et al. [21-22] Then Na₂[Mo₃S₁₃] × 5H₂O (={Mo₃}) was obtained from (NH₄)₂[Mo₃S₁₃] ×2H₂O by its reaction in aqueous NaOH solution under reduced pressure (20 mbar) for 2 h. The resulting dark red solution was filtered into an aqueous NaCl solution, the precipitated product was isolated by filtration, washed with 2-propanol and diethyl ether, and dried in vacuo at room temperature to give red-brown {Mo₃}. The Y-CNₓ-{Mo₃} and R-CNₓ-{Mo₃} hybrids were synthesized through a two-step deposition process at room temperature. In a typical procedure, 20 mg of as-prepared Y/R-CNₓ was dispersed in 20 mL of methanol by ultrasonication for 3 h to prepare a homogenous suspension. Then, a measured amount of {Mo₃} (soluble in methanol) was added and stirred for 24 h. The solid was collected by centrifugation and three times washed with methanol to remove the excess of {Mo₃}. Finally, the obtained precipitates were dried at room temperature under ambient conditions yielding Y-CNₓ-{Mo₃} and R-CNₓ-{Mo₃}.

Characterization

FT-IR spectroscopy was performed on a Shimadzu FT-IR-8400S spectrometer. Samples were prepared as KBr pellets. X-ray powder diffraction (XRD) data were collected on a Rigaku XRD-6000 and a Pananalytical X’pert PRO diffractometers using Cu Kα radiation (λ = 0.154 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed from the samples deposited on a gold support using a UHV Multiprobe system (Scienta Omicron, Germany) with a monochromatic X-ray source (Al Kα) and an electron analyzer (Argus CU) with 0.6 eV energy resolution. Charge compensation during data acquisition was realized by an electron flood gun (NEK 150, Staib, Germany) at 6 eV and 50 μA. The background was subtracted and
spectra were calibrated using the Au 4f\textsubscript{7/2} peak (84.0 eV) before undergoing fitting using Voigt functions (30:70).

**UV Raman spectroscopy** was performed on a custom modified (to allow UV excitation) LabRAM HR 800 Raman System (Horiba Jobin Yvon, Bensheim, Germany) with an excitation wavelength of 244 nm provided by frequency doubling the 488 nm line of an Ar-Ion-Laser (Innova 300C Moto-FRED, Coherent Inc., Santa Clara, CA, United States of America). The laser power was attenuated from 13 mW to 5 mW or 10 mW via a neutral density filter depending on the photothermal stability of the samples. The samples were illuminated through a microscope (BX 41, Olympus Corporation, Tokyo, Japan) through a 15x/0.2NA UV objective (LMU UVB, Thorlabs Inc., Newton, NJ, United States of America) with UV optimized antireflection coating. The scattered light is collected in 180° geometry via the same objective, filtered through two long-pass filters to remove the Rayleigh scattered light, passed through an entrance slit (width = 300 µm) and diffracted by a 2400 lines/mm blazed grating to a liquid N\textsubscript{2}-cooled CCD (T\textsubscript{op} = 160 K). All spectra were recorded with an integration time of 300 s and 12 averaged accumulations (i.e., 1 hour of summed integration time). All samples were measured as manually compacted powders in a small stainless-steel mold. The Raman spectra were processed using R 3.5.1 by applying SNIP based baseline correction (100 iterations) and normalizing the spectra using Euclidean vector norm.[23]

**FT Raman spectroscopy** was performed on a Multispec FT-Raman spectrometer (Bruker Inc., Billerica, Massachusetts, United States of America). The excitation light at 1064 nm was provided by a Nd:YAG laser (Klastech DeniCAFC-LC-3/40, Dortmund, Germany). The spectra were recorded up to 4000 cm\textsuperscript{-1} with a spectral resolution of 4 cm\textsuperscript{-1}. The laser power at the samples was set to 200 mW for R-CN\textsubscript{x} and 500 mW for Y-CN\textsubscript{x}. R-CN\textsubscript{x}-KS could not be measured using FT-Raman spectroscopy due to excessive photoluminescence.
The Raman spectra were processed using R 3.5.1 by applying SNIP based baseline correction (60 iterations) and normalizing the spectra to the ring-breathing mode at 980 cm$^{-1}$ for visualization.

**Neutron total scattering measurements:** Time-of-flight powder neutron diffraction experiments were conducted using the GEM diffractometer at the ISIS pulsed neutron and muon source, Rutherford Appleton Laboratory, UK\cite{24}. Powder samples of Y-CN$_x$ and R-CN$_x$ were loaded into 6 mm diameter cylindrical vanadium sample holders. Data collection consisted of ~ 6 h duration (1000 µA h) data sets, acquired at 300 K for total scattering analysis. MantidPlot software\cite{25} was used for data reduction and normalisation. Total scattering data (covering a scattering range 0.5 < $Q$ < 50 Å$^{-1}$ when using the final processed files from the six GEM detector banks) were corrected and the pair distribution function was generated using the GUDRUN software.\cite{26}

**Transmission Electron Microscopy (TEM):** The samples were dispersed in ethanol (supersonic bath) and drop-cast on holey carbon TEM grids. The TEM investigations were carried out using the chromatic (Cc) and spherical (Cs) aberration – corrected Sub-Ångström Low-Voltage Electron (SALVE) microscope operating at 80 kV. Values for Cc and Cs were in the range of -10 µm to -20 µm. Imaging included diffraction pattern from selected areas and high resolution (HR) TEM, recorded on a Ceta 16M camera. Energy-filtered imaging exploiting absorption edges for elemental mapping was acquired on an Ultrascan 1000 XP camera using a Quantum ERS low-voltage Gatan imaging filter (GIF), attached to the SALVE microscope.

**Diffuse reflectance spectroscopy (DRS) UV-vis spectra** of solids were taken by a Shimadzu UV2600 UV-vis spectrophotometer. **UV-vis spectra** of the dissolved in KOH carbon nitride samples were recorded using a Cary 60 (Agilent Technologies) spectrophotometer.

**Thermal decomposition** of the carbon nitride samples was studied using a Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C min$^{-1}$ in O$_2$ flow (50 mL min$^{-1}$) from 30 °C to 850 °C.
CHN analysis was performed using an Elementar Vario MICRO cube. The EDX analysis was carried out using a Scanning electron microscope (Supra 55VP, SmartSEMTM, Zeiss) equipped with an Oxford Instruments EDX detector.

The solid-state $^1$H, $^{13}$C, MAS NMR, $^1$H–$^{13}$C and $^1$H–$^{15}$N CPMAS NMR spectra were registered at the spinning rates of 12 kHz for $^1$H and 5 kHz for all other measurements using a Bruker Avance III 400WB spectrometer. $^1$H, $^{13}$C and $^{15}$N chemical shifts are quoted in ppm from: TMS (0 ppm) and α-glycine (secondary reference, C=O at 176.0 ppm and NH$_3^+$ at 347.6 ppm on the nitromethane scale, respectively).

Liquid state $^{13}$C NMR characterization of the products of the dissolution of carbon nitride samples in aqueous KOH (1.0 M) was carried out in a Bruker Avance II 400 MHz spectrometer at a 100 MHz frequency using TMS (0 ppm) standard. The samples were diluted in D$_2$O prior to analysis.

Gas chromatography: Gas-chromatography was performed on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve 5A 75 m × 0.53 mm, oven temperature 70 °C, flow rate 25 ml min$^{-1}$, detector temperature 200 °C) with Argon as carrier gas. The GC was calibrated by direct injection of known amounts of H$_2$ gas.

Emission spectroscopy: Polymeric carbon nitride suspensions for spectroscopic study were prepared by sonicating the carbon nitrides in deionized water (2mg/mL) for 15 min. The supernatant liquid was collected after centrifugation (10 min, 7500 rpm) and used for steady-state emission and fs-transient absorption spectroscopy. Steady-state emission spectra ($\lambda_{ex}$ = 380 nm) were recorded with a FLS980 spectrometer (Edinburgh Instruments) in a 1 cm quartz cell. Time resolved emission data were recorded using a Hamamatsu HPDTA streak camera. A Ti:sapphire laser (Tsunami, Newport Spectra-Physics GmbH) was used as the light source and a pulse selector (model 3980, Newport Spectra-Physics GmbH) was used to reduce the repetition rate of the fundamental to 400 kHz. The emission was collected from a 1 cm cuvette in a 90° angle between the pump beam and a CHROMEX spectrograph detector. Analysis of the time-resolved emission data was performed using DecayFit software.
Photocatalytic studies

The photocatalytic hydrogen production experiments were carried out using a custom-built air-cooling apparatus for maintaining room temperature (22°C) and constant irradiation of the sample. Experiments were carried out in 21 mL Schlenk tubes capped with rubber septa. 10 mg of the CN$_x$-based catalysts, which had been found to be the optimal loading determined in our previous study$^{[21]}$, was added to the Schlenk tube equipped with magnetic stirrer. The tube was evacuated and filled with argon. An H$_2$O : MeOH (9 : 1, v/v) solution, with or without addition of additional sacrificial electron donor, was purged with argon. 10 mL of the degassed solution was added to the photocatalyst in the Schlenk tube under inert conditions and kept under constant irradiation from an LED source ($\lambda = 420$ nm; 51.3 mW cm$^{-2}$ or $\lambda = 470$ nm; ca. 40 mW cm$^{-2}$) in air-cooled photoreactors. The gas phase above the solution was probed by inserting a gas-tight GC syringe through the septum and the amount of hydrogen in the gas phase was quantified using headspace gas chromatography.

Computational studies

All periodic density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP 5.4.4),$^{[27]}$ utilizing the projector-augmented wave (PAW) method to describe the core electrons, while valence states were expanded by plane waves up to an energy cut-off of 400 eV. Geometries were pre-optimized (up to a force criterion of 5·10$^{-2}$ eV·Å$^{-1}$) with the Perdew–Burke–Ernzerhof (PBE)$^{[28]}$ generalized-gradient-approximation (GGA) exchange—correlation functional, followed by a fine-optimization using the Heyd–Scuseria–Ernzerhof (HSE06)$^{[29]}$ hybrid functional (with the range separation parameter of 0.2 Å$^{-1}$) and 25% exact exchange. Van der Waals interactions were treated with Grimme’s D3 dispersion correction scheme$^{[30]}$. Self-consistency in the electronic structures were set to a limit of 10$^{-6}$ eV, utilizing a Gaussian smearing of 0.01 eV. Periodic images of the two-dimensional systems were separated by a vacuum layer of at least 20 Å, together with dipole corrections. Integrations in the reciprocal space were evaluated on a Monkhorst–Pack$^{[31]}$ grid of 5x5x1 $k$-points.
Results and Discussion

Materials characterization

A schematic representation of the synthetic procedures implemented in this work is depicted in Figure 1a. The change of colour from yellow to nearly red is observed if Y-CN\textsubscript{x} is heated at temperatures above 900 °C for a brief time interval (3 min) and under reduced pressure. The increase of the thermal treatment temperature or prolongation of this procedure do not lead to any further observable changes of the material’s appearance and only result in lower yields (Fig. 1a). The Y-CN\textsubscript{x} sample has a typical UV-vis diffuse reflectance spectrum (Fig. 1b) with an absorption edge of around 2.9 eV (Fig. 1c), while R-CN\textsubscript{x} shows another visible-light absorption band centred at ca. 483 nm (Fig. 1b). Apparently, the new absorption peak in the visible region observed for the R-CN\textsubscript{x} sample (Fig. 1b) is an additional feature and can hardly be considered as shifted Y-CN\textsubscript{x} absorption edge, which remains visible and manifests itself at an electronic transition energy of 2.9 eV, while the new contribution has an onset at ca. 2.2 eV (Fig. 1d).

Figure 1. (a) Schematic representation of the synthetic procedures for conventional yellow Y-CN\textsubscript{x} and low-bandgap reddish R-CN\textsubscript{x}; diffuse reflectance spectra (b) and corresponding Tauc plots (assuming direct nature of the optical transition) for Y-CN\textsubscript{x} (c) and R-CN\textsubscript{x} (d).
Notably, R-CNₓ and Y-CNₓ possess very similar elemental composition of \( \text{C}_{2.88}\text{N}_{4.19}\text{H}_{1.69} \) and \( \text{C}_{2.89}\text{N}_{4.28}\text{H}_{1.84} \), respectively, with only a small reduction of N and H content in the red materials as compared to the yellow one. The thermal behaviour of the both samples is also alike, the R-CNₓ sample, though showing slightly lower degradation onset, reaches the maximum decomposition rate ca. 30 °C higher than Y-CNₓ (see Supplementary Information Fig. S1). As evidenced by TEM, the microstructure and morphology of the Y-CNₓ and R-CNₓ samples are also practically identical, thus not allowing to draw any definite conclusions regarding the high-temperature induced modifications (see Supplementary Information Fig. S7).

XRD data manifest that the typical PCN structure persists in the R-CNₓ material also after the high temperature treatment (Fig. 2a). The reflections corresponding to the typical for PCN (100), (002) and even the less intense (300) and (004) planes\(^{[32]}\) are clearly distinguishable in the R-CNₓ diffractogram, although having somewhat lower intensity owing to partial amorphization of PCN under thermal treatment at 900 °C (Fig. 2a). FTIR data also point to similar structure of Y-CNₓ and R-CNₓ as all the typical bands characteristic of PCN are also found in the spectrum of R-CNₓ (Fig. 2b), which is not the case, for instance, when PCN is treated in NaCl melt at high temperatures.\(^{[8]}\) Although no definite conclusion can be made from it, the appearance of another band at around 3400 cm\(^{-1}\) in the spectrum of R-CNₓ suggests the modification of H-bonding in the treated material (Fig. 2b). The FT-Raman spectra of these two materials confirm the observations obtained by the IR- and XRD-measurements. According to the Raman spectra, the structure of Y-CNₓ and R-CNₓ are practically the same with only minor changes in intensity ratios in the fingerprint region (Fig. 2c). The most noticeable difference between the two spectra is the stark decrease of intensity of the broad band between 2300 and 2500 cm\(^{-1}\) in R-CNₓ. This band can be assigned to a second-order vibration of graphite-like carbon nitride and can only be observed in ordered structures, which supports the XRD-observed amorphization of the PCN.\(^{[33]}\) The band at 980 cm\(^{-1}\)
can be assigned to the ring-breathing mode of the triazines present in the CN\textsubscript{x} structure while the band at 1235 cm\textsuperscript{-1} is specific to the \textnu{}(C-N) stretching vibration of the bridging amine moieties in the heptazine structure.\cite{34} FT-Raman spectroscopy shows that the ratio of bridging amine to the sym-triazine breathing mode decreases in R-CN\textsubscript{x} when comparing to Y-CN\textsubscript{x}. This could indicate a replacement of the bridging amine moieties by some other bridging functionality, which is further supported by the intensity increase of the shoulder located at 1662 cm\textsuperscript{-1} relative to the main band at 1618 cm\textsuperscript{-1} (aromatic ring stretching). This increase in intensity could indicate an increase in exo unsaturated functionalities. Due to the complicated spectra and the possible loss of unpolymerized triazine impurities during the heat-treatment, the Raman spectra do not allow for definitive conclusions regarding the precise chemical structure, but can at least confirm changes to the binding conditions and offer a hint that amine bridges are replaced by unsaturated functionalities. Neutron diffraction, possibly the most adequate tool for structural characterization of carbon nitrides composed of low electron density atoms,\cite{32} was further employed as a sensitive technique to detect the structural changes in PCN caused by the thermal treatment. The structure function F(Q) (Fig. S3) as well as the calculated pair distribution function (PDF) data (Fig. 2d) obtained from the neutron diffraction, however, show no significant differences in the analysed samples. This suggests that the PCN structure is mostly preserved in the R-CN\textsubscript{x} material and no significant changes of the interlayer distances corresponding to the corrugation or planarization can be evidenced, which were previously suggested to be responsible for the colour change.\cite{7,12}
Figure 2. (a) powder XRD, (b) FTIR, (c) Raman and (d) neutron diffraction PDF calculated data obtained for Y-CN$_x$ and R-CN$_x$

The C 1s XP spectra for both materials are dominated by the peak at 283.8 eV attributed to adventitious carbon, while the maxima at 285.7, 287.3 and 290.1 eV are assigned to C-NH$_x$, N=C-N, and COOH species respectively (Fig. S4). The N 1s spectrum of Y-CN$_x$ can be fitted with four peaks having their maxima at binding energy values typical of PCN 397.8, 399.7, 401.5 and 404.1 eV, the latter one being ascribed to $\pi$-$\pi$ excitation in the aromatic polyheptazine system (Fig. S5a). The peak at 401.5 eV corresponds to the nitrogen in C-NH$_x$ groups$^{[35]}$ and the maximum 397.8 eV is attributed to the C-N=C aromatic species. The contribution centred at 399.7 eV, usually assigned to N-C$_3$ groups,$^{[36]}$ should be rather assigned to the sum of these species and the triazine impurities, since the ratio between the maxima at 397.8 and 399.7 eV is far below 6, the
value one might expect to obtain for the heptazine structure. We assume that the Y-CNx sample contains certain amount of non-condensed impurities, which is in agreement with the XPS data obtained for melamine, which shows equal contributions at 398.4 and 399.7 eV in its XP N 1s spectrum.\textsuperscript{[37]} The respective spectrum of the R-CNx sample has, on the other hand, a more conventional profile, where the peaks corresponding to C-N=C, N-C$_3$ and C-NH$_x$ are clearly distinguished at 398.1, 399.5 and 400.5 eV respectively (Fig. S5b).

The direct $^{13}$C NMR excitation spectra show a typical profile for heptazine based PCN materials with maxima in the range of 157-156 ppm and 165-164 ppm corresponding to the carbon atoms in N-C=N and -C-NH$_x$ groups, respectively (Fig. 3a). The reduction of

\textbf{Figure 3.} SS NMR (a) $^{13}$C MAS, (b) $^1$H-$^{13}$C CPMAS, (c) $^1$H-$^{15}$N CPMAS and (d) $^1$H MAS spectra of Y-CNx and R-CNx.
the peak intensity and its slight shift from 156.7 to 157.4 ppm with respect to that of Y-CN, is evident in the spectrum of R-CN, (Fig. 3a). This shift might be attributed either to
a higher degree of disorder due to heptazine fragmentation in R-CN, caused by the
thermal treatment or to the formation of some new species in the material. According
to the tabulated data of $^{13}$C NMR chemical shifts,[38] the appearance of imine-like or
azomethine groups (>C=N-) formed as the result of heptazine fragmentation is one of
the conceivable possibilities. Another possibility is the formation of -C-N=N-C- azo
functions that are known to promote visible-light absorption of tuned carbon nitrides.[39]
The ratio between the peaks assigned to N-C=N to that of C-NH, in the $^{13}$C spectra is
around 1.1 for Y-CN, and 0.8 for R-CN,. We assume that this might be attributed to a
partial fragmentation of the heptazine structure in the thermally treated material, hence
the loss of aromatic carbon-species. The $^1$H-$^{13}$C CPMAS spectra show the enhancement
of the peak intensity at 165-164 ppm confirming its assignment to the C-NH, moieties
(Fig. 3b). The intensity of the peak at around 157.4 ppm in the spectrum of R-CN, is not
increased significantly, suggesting that the new species formed after the treatment is not
in the immediate proximity to any H atoms. This leads us to the conclusion that the
formation of -C-N=N-C- azo linkages is more likely (Fig. 3b). The $^1$H-$^{15}$N CPMAS spectra
show the same set of peaks at -191, -224, -245 and -265 ppm for both samples, which
can be assigned to the peripheral heptazine N atoms, central heptazine nitrogen,
nitrogen of NH- groups and of NH, species, respectively (Fig. 3c).[35] A reduction of the
FWHM and the intensity of the peak ascribed to the NH, functions can be observed for
R-CN, compared to Y-CN, (Fig. 3c). The peak fitting shows that the contribution centred
at about -274 ppm is significantly reduced in the case of the R-CN, sample (Fig. S6).
The amino-groups can manifest themselves in a large range of chemical shifts from -267
to -291[40] depending on their environment. Thus, we assume that the reduction of the
NH, peak contribution at -274 ppm might be due to the elimination of more volatile carbon
nitride constituents or impurities during the thermal treatment. The $^1$H spectra are
composed of two main contributions at 9.7 and 4.1 ppm which correspond to the
hydrogens of hydrogen-bonded amino-groups and adsorbed water molecules, respectively (Fig. 3d).\(^4\)

The comparative analysis of R-CN\(_x\) and Y-CN\(_x\) presented above shows that the structural modifications produced by the high-temperature treatment are not easily detectable by conventional solid-state characterization approaches, although they clearly have a great impact on the light absorption properties of the materials (Figure 1). Therefore, further attempts to characterize the R-CN\(_x\) material were carried out starting by its dissolution in an appropriate solvent. The dissolution of PCN in KOH proceeds via hydroxyl attack on amino-groups of the polymer replacing them and forming water-soluble tri-potassium cyamelurate. Crucially, this approach enabling us to dissolve melon polymer has a potential to spectroscopically separate the contribution from species which possibly endow R-CN\(_x\) with extended light-absorption in the visible range. Notably, the dissolution of the Y-CN\(_x\) and R-CN\(_x\) samples resulted in colourless and yellow-green coloured solutions, respectively (Fig. 4a). The evaporation and slow cooling of these solutions lead in both cases to the formation of needle-shaped single-crystals of different colour (Fig.4a). In spite of that, the \(^{13}\)C NMR analysis of the crystals dissolved in D\(_2\)O shows identical signals at 158.2 and 168.7 ppm for both samples with the integrated areas ratio of ca. 1:1 and assigned to CN\(_3\) of the heptazine and N-C-O\(^-\) species, respectively, which is typical for potassium salts of cyameluric acid (Fig. 4b,c).\(^2\) In order to evaluate the presence of minor components in the solutions, which might be responsible for the R-CN\(_x\) coloration, the obtained solutes of the PCN samples in KOH were concentrated by evaporation, while the formed tri-potassium cyamelurate crystals were removed from the system. The solution of Y-CN\(_x\) sample still showed the presence of a nearly pure potassium salt of cyameluric acid (Fig.4d), having only one additional peak at 171.6 ppm, which we attribute to the C of potassium carbonate. In the \(^{13}\)C NMR spectrum of the solution of R-CN\(_x\) in KOH, on the other hand, the signal ascribed to carbon atoms in CN\(_3\) environment of the heptazine is absent, instead the intense peaks at the chemical shifts of 168.6-168.4 ppm suggest the presence of triazine species bearing fully deprotonated
N-C-O$^-$ groups\cite{42} (Fig. 4e). Additionally, a peak at 173.5 ppm is observed, which can be ascribed to the presence of C-N=N-C inter-triazine linkages (Fig. 4e).\cite{43}

Figure 4. (a) The products of the Y-CN$_x$ and R-CN$_x$ dissolution in KOH and their UV-vis spectra; $^{13}$C NMR spectra in D$_2$O of the crystals obtained from the dissolved in KOH (b) Y-CN$_x$ and (c) R-CN$_x$ samples; $^{13}$C NMR spectra of the minor products of the (d) Y-CN$_x$ and (e) R-CN$_x$ samples dissolution in KOH with addition of D$_2$O.

After tri-potassium cyamelurate crystals were extracted from the concentrated product of the R-CN$_x$ dissolution in KOH, the slow evaporation of the solution yields a yellow
powder (R-CNₓ-KS) with the composition C_{1.00}N_{1.90}O_{0.90}K_{0.01} according to EDX elemental analysis which is insoluble in water and DMSO. According to the XRD analysis (Fig.5a) and considering the presence of only triazine species in the initial solution, the crystalline phase of the separated compound might be ascribed to the poly(triazine imide) phase.\textsuperscript{[44]} FTIR and Raman spectra reveal a wide absorption region in 1400-1660 cm\textsuperscript{-1} ascribed to C=N stretching of the heterocycle and a very intense Raman band at 704 cm\textsuperscript{-1} accompanied by a weaker band at 989 cm\textsuperscript{-1} (Fig. S8a,b) attributed to triazine breathing modes,\textsuperscript{[45]} thus corroborating the polytriazine nature of the material. The intense absorption peak at 1736 cm\textsuperscript{-1} coincides with the C=O bond stretching vibrations in alkali isocyanurates (Fig. S8a,b), while the absorption in the 3145-3340 cm\textsuperscript{-1} range and at ca. 2850 cm\textsuperscript{-1} is attributed to free and H-bonded NHₓ-moieties, respectively.\textsuperscript{[46]} This suggests that the fully deprotonated cyanurate mono or oligomeric species in the solution undergo tautomeric transformation producing insoluble polymerized isocyanurate fragments. A comparative analysis of UV Raman and FTIR spectra shows multiple strongly Raman active modes that are not visible in the IR spectrum 1578, 1389, 1285 and 589 cm\textsuperscript{-1}. These can be attributed to N=N stretching,\textsuperscript{[47]} N=N in trans-aromatic azo compounds, azoxy groups\textsuperscript{[34a]} and C-N=N stretching combined with a C-N deformation vibrations,\textsuperscript{[48]} respectively. The observed bands at 1389 and 589 cm\textsuperscript{-1} are especially indicative of a trans-azo moiety inside the R-CNₓ-KS (i.e., in the solid obtained by slow evaporation of the R-CNₓ-K solution that was obtained after filtering off the tri-potassium cyamelurate crystals from the concentrated product solution of the R-CNₓ dissolution in KOH). Considering that it is very unlikely that azo groups are formed during KOH treatment of R-CNₓ, we conclude that they were a part of its structural units in the solid-state, linking the heptazine or triazine moieties and being responsible for the visible-light absorption. Indeed, the type of the linkage between the structural units of polymeric carbon nitride determines the materials optical properties to a greater extent than the substitutional doping of the heptazine itself, as it defines the symmetry, planarity or corrugation of the polymeric system.\textsuperscript{[49]} Notably, a band in the visible-light absorption
region is still present in the UV-vis spectrum of the R-CNₓ-KS, though blue-shifted with respect to that observed for R-CNₓ (Fig. S9).

To summarize, we suggest that the high-temperature treatment of Y-CNₓ induces partial heptazine fragmentation accompanied by NH₃ evolution which under the given conditions is decomposed into H₂ and N₂. The reductive atmosphere causes formation of C-NH-NH-C linkages in place of the opened heptazine, which – upon further de-ammonification – eventually produce the C-N=N-C azo moieties. In other words, a PCN material with strongly extended visible light absorption is obtained that contains, apart from typical PCN structural features, also poly(heptazine/triazine) azo-linked fragments that are chiefly responsible for the red shift of the optical absorption edge.

**Figure 5.** (a) XRD pattern and (b) comparative analysis of FTIR and Raman spectra of the insoluble R-CNₓ-KS powder obtained by slow evaporation of R-CNₓ-K solution.

In order to better understand the electronic structures and optical properties of the different systems, periodic density functional theory calculations have been performed on various systems. Figure 6a shows the most relevant systems that were obtained after an extensive screening for possible structures of R-CNₓ and Y-CNₓ. For the red carbon nitride system two different configurations were found (see Fig. 6), one in a planar configuration (planar-R-CNₓ), and a second one with an azo-linkage at the N=N group that leads to a step-like structure of the layer. Interestingly, the planar configuration is 0.42 eV less stable than the R-CNₓ system (Fig. S10). However, while the latter one has
a bandgap of 3.5 eV, which is in the expected range of carbon nitrides, the planar-R-CNₓ system has a direct bandgap of only 2.2 eV. Regarding the Y-CNₓ, a fully interconnected layer (E_gap = 2.8 eV) as well as a configuration with hydrogenated amino endgroups (E_gap = 3.6 eV), that leads to strand-like structures, were considered. All band structures and projected density of states of the different systems can be found in the Supplementary information (Fig. S10, S11), together with the charge density distributions at the corresponding valence band maxima (VBM) and conduction band minima (CBM) (Fig. S12). The Fig. 6b shows the calculated absorption spectra, which reveal the expected UV-absorbance for all CNₓ structures except for planar-R-CNₓ that shows absorption at longer wavelengths close to 400 nm.

Figure 6. (a) Most relevant systems used for the in-depth analysis. For the R-CNₓ systems both the top and side views are shown, while for the Y-CNₓ systems only top views are shown. (b) Calculated absorption spectra for the four different systems.

The question remains why the experimentally observed optical properties of red carbon nitride conforms with the calculated behavior of planar-R-CNₓ, though this structure is less stable than the step-like R-CNₓ configuration (see Figure 6). Our present hypothesis is that red carbon nitride is confined in a Y-CNₓ framework (as shown in Figure 7a), which stabilizes the planar configuration, leading to localized planar-R-CNₓ units. The azo-linkages in the planar-R-CNₓ units then lead to reduction of the overall bandgap as
depicted in the energy scheme shown in Figure 7b. Such confinement effects have also been observed for other two-dimensional systems (e.g., TaSe$_2$), where the embedding in a larger framework leads to a stabilization of the usually less preferred configuration$^{[50]}$.

![Diagram](image)

**Figure 7.** Proposed diagram of possible transitions for R-CN$_x$. The model (a) shows the confined localized planar-R-CN$_x$ unit in the Y-CN$_x$ framework, while the energy diagram (b) shows the corresponding energy states. Here the azo-linkage lowers the bandgap and leads to light absorption at wavelengths in the visible spectral range.

**Photoluminescence spectroscopy**

Photoluminescence (PL) spectra of drop-casted CN$_x$ films are shown in Figure 8a. The PL of R-CN$_x$ is spectrally broader and appears red-shifted compared to the benchmark material Y-CN$_x$. Fitting the steady-state PL spectra of both materials to a sum of two Gaussian peaks reveals that the apparent spectral broadening of the R-CN$_x$ spectrum is due to the increase of a low-energy emission component (sub-peak B) below 2.5 eV. When monitoring the low-energy emission of R-CN$_x$, a distinct new peak (centered at 540 nm) becomes apparent in the PL excitation spectrum. This suggests the presence of distinct emissive states below the band edge of R-CN$_x$$^{[16]}$ which are clearly visible also in the PL spectra recorded for different excitation wavelengths (Fig. 8b). The sub-bandgap emission observed in R-CN$_x$ is likely associated with an increased number of tail states due to the higher density of localized planar-R-CN$_x$ units in the Y-CN$_x$. 

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framework (Fig. 7) produced by heptazine fragmentation and azo-linkages formation after elevated temperature processing.\textsuperscript{[51]}

**Figure 8.** (a) PL and PL excitation spectra of dropcasted Y-CN\textsubscript{x} and R-CN\textsubscript{x}. Emission upon excitation at 380 (solid lines) and PL excitation spectra recorded at 600 nm (dashed lines) spectra were taken at room temperature. Multi-peaks of the PL spectra for Y-CN\textsubscript{x} (A\textsubscript{y}, B\textsubscript{y}) and R-CN\textsubscript{x} (A\textsubscript{r}, B\textsubscript{r}) were fitted with a Gaussian function. (b) PL spectra of Y-CN\textsubscript{x} and R-CN\textsubscript{x} acquired at different excitation wavelengths. (c) Streak camera image showing the PL as a function of emission wavelength and time recorded for dropcasted R-CN\textsubscript{x} upon 385 nm excitation. The experimental time window was chosen to be 10 ns. (d) PL decay kinetics of R-CN\textsubscript{x} after excited at 385 nm (upper panel) and 520 nm (lower panel). To derive the kinetics, the streak camera data has been integrated in a spectral
range of ± 5 nm with respect to the probe wavelengths indicated in panel (d). For comparison the respective PL decay kinetics of Y-CNₓ are shown.

To obtain more insight into the distinct PL properties of R-CNₓ, time-resolved PL data were collected upon excitation at 380 and 520 nm. The choice of excitation wavelengths enables a comparison between bandgap excitation and direct excitation of the sub-band emission. Figure 8c exemplarily shows the streak camera data for R-CNₓ upon excitation at 385 nm. The transient PL spectra can be fitted to a sum of two Gaussian peaks centered at 2.32 and 2.76 eV (Fig. S13a). The corresponding time-resolved PL spectra for Y-CNₓ yield emission contributions at 2.55 and 2.80 eV (see Figure S13a). Upon excitation at 520 nm a long-wave PL emission centered at 2.20 eV is visible (Fig. S13b). To derive PL kinetics reflecting the lifetime of the emission upon excitation at 385 nm, the transient PL spectra are integrated in over 10 nm around the peak wavelength of the individual emission contributions (Fig. 8d). The transient PL kinetics of R-CNₓ (recorded both at about 2.8 and 2.5 eV) are fitted by a bi-exponential decay yielding the characteristic time constants τ₁ = 0.17 ns and τ₂ = 1.34 ns. For Y-CNₓ the equivalent data decay with slightly longer time constants, i.e. τ₁ = 0.39 ns and τ₂ = 1.91 ns. This comparison indicates somewhat faster exciton dissociation in R-CNₓ, likely associated with higher defect density and the more localized excited state in the planar R-CNₓ units (see Figure 7). The bi-exponential decay of the excitonic emission is related to different recombination centers in the material. If excitons are generated in proximity to such a recombination center, they decay more rapidly on a sub-ns timescale, while excitons generated distant from such recombination centers decay on a longer timescale. The decay of the sub-bandgap emission (recorded upon excitation at 520 nm and derived by integration over the entire PL band) is non-exponential decay, i.e. it follows a power law kinetic \( I_{PL}(t) \sim t^{-\alpha} \) commonly used to account for reaction kinetics in diffusive systems.\(^{[52]}\)

\[^{[53]}\] Comparing R-CNₓ to Y-CNₓ, the value of the characteristic exponent decreases from
\[ \alpha_{\text{RCN}_x} \approx 2.2 \text{ to } \alpha_{\text{YCN}_x} \approx 1.3. \] The more rapid decay in R-CN\(_x\) is attributed to an increased number of defect states serving as recombination centers.

**Photocatalytic hydrogen evolution**

Conventional Y-CN\(_x\) modified with appropriate co-catalysts is known for its ability to produce H\(_2\) in presence of a sacrificial reducing agent under visible light irradiation.\(^{[1a]}\) Pristine Y-CN\(_x\) is inactive for photocatalytic HER under monochromatic LED light irradiation at 420 nm (Fig. 9a). However, after deposition of the \{Mo\(_3\)\} clusters and especially Pt nanoparticles, it demonstrates a very good performance reaching a H\(_2\) production of around 0.04 mmol in 7 h (Fig. 9a). Although the experimental data exposed and discussed above indicate that the basic structure of conventional yellow PCN is preserved also in the R-CN\(_x\) material, its photocatalytic behaviour is very different. The activity of the red R-CN\(_x\) modified with \{Mo\(_3\)\} clusters or Pt nanoparticles is lower by an order of magnitude compared to Y-CN\(_x\), reaching only 0.005 mmol H\(_2\) after 7 h of irradiation (Fig. 9b). Similar to the conventional PCN counterpart, bare R-CN\(_x\) without a co-catalyst does not photocatalyze HER under 420 nm light irradiation (Fig. 9b). Contrary to the case of Y-CN\(_x\), R-CN\(_x\) shows higher photocatalytic activity if modified with the \{Mo\(_3\)\} clusters than with Pt nanoparticles (Fig. 9b). A similar observation was reported by Wang *et al.* for protonated mesoporous carbon nitride materials.\(^{[54]}\) These results suggest that the surface properties of the R-CN\(_x\) sample are different to a significant extent from those of Y-CN\(_x\), affecting the interaction of the former with co-catalysts.
Figure 9: Photocatalytic HER performed using (a) Y-CNₓ and (b) R-CNₓ based materials under monochromatic 420 nm LED irradiation. Conditions: [catalyst]: 10 mg, Solvent: H₂O:MeOH (9:1, v:v), in absence of any additional electron donor.

The photocatalytic activity of R-CNₓ under 420 nm irradiation is inferior to that of its yellow counterpart, nonetheless the appearance of an additional absorption band in the visible-light range in the UV-vis spectrum of R-CNₓ (Fig. 1b,d) prompted us to study its performance also under excitation with lower energy light at the wavelength of 470 nm. Under these conditions, the Y-CNₓ sample is, as expected, completely inactive in photocatalytic HER both with and without co-catalysts (Fig. 10a), since it does not absorb in this spectral region (Fig. 1b,c). Intriguingly, the red R-CNₓ is not only capable of sacrificial H₂ evolution under irradiation at 470 nm when modified with {Mo₃} or Pt nanoparticles, but the pristine R-CNₓ without any co-catalysts even shows a superior photocatalytic activity (Fig. 10b). Therefore, the new functional groups in the red carbon nitride, the azo-linked poly(heptazine/triazines) formed as the result of the high-temperature treatment, are not only responsible for the strong red shift of the optical absorption edge of the material, but they also might possibly play an additional role of an active site for H₂ evolution. Despite the rather moderate activity of this material, its ability to absorb a significant portion of the visible light spectrum and the metal-free nature of its active site for photocatalytic HER represent intriguing aspects of R-CNₓ with
respect to solar light-driven photocatalysis. From the R-CN₉ catalyzed H₂ evolution plots one can observe an apparent deactivation trend (Fig. 10b).

![Graphs showing H₂ production over time for different conditions.](image)

**Figure 10:** Photocatalytic HER performed using (a) Y-CN₉ and R-CN₉ based materials under 470 nm irradiation (b) in absence of any electron donor, (c) in presence of ascorbic acid (0.1 M; pH 2.4) and (d) 10% of TEOA (pH 10.5). Conditions: [catalyst] : 10 mg, Solvent: H₂O:MeOH (9:1, v:v).

We hypothesized that this was due to the weak reductive power of methanol as a sacrificial reducing agent, hence some stronger reductants were added to the R-CN₉ suspensions. The addition of ascorbic acid improved the photocatalytic performance of R-CN₉ modified with {Mo₃} and Pt nanoparticles up to the level of the pristine catalyst, while leaving the activity of the co-catalyst modified samples unchanged (Fig. 10c). The introduction of another strong reductant, triethanolamine (TEOA), affected the activity of bare R-CN₉ only slightly, but had a strong impact on the activity of co-catalyst-modified R-CN₉ (Fig. 10d). Most notably, the strong deactivation trend could be reversed for the
\{\text{Mo}_3\}\text{-modified R-CN}_x\text{ photocatalyst in the presence of TEOA, leading to a stable rate of H}_2\text{ evolution (green trace in Fig. 10d). This might be attributed to a more effective oxidation of TEOA compared to ascorbic acid since positively charged TEOA at pH 10.5 (pK}_a = 7.9\text{) is expected to adsorb more effectively at the negatively charged R-CN}_x\text{, than non-dissociated ascorbic acid (pK}_a = 4.3\text{) at pH 2.4.}

**Conclusions**

We report a simple post-synthetic approach involving a brief high-temperature treatment under vacuum that effectively turns the typically yellow PCN into a red PCN by extending significantly its visible light absorption to >600 nm. Most importantly, we provide evidence that the extended optical absorption edge of PCNs subjected to high-temperature treatment is due to the formation of azo-moieties that act as linkages between the heptazine units inherent to PCN structure and/or between heptazine and triazine units formed upon partial fragmentation of PCN. Our present understanding is that the formation of planar-R-CN\(_x\) units comprising the azo-linkages and embedded in the yellow carbon nitride framework is responsible for the reduction of the overall bandgap and the red color of the material. Notably, the azo moieties effectively sensitize the red PCN for photocatalytic H\(_2\) evolution even under low energy (470 nm) light where conventional yellow PCN is inactive. Moreover, the red carbon nitride clearly contains moieties that can act as metal-free catalytic sites for H\(_2\) as evidenced by effective operation even without any additional co-catalyst. The downside of the high-temperature treatment of PCN is the partial fragmentation of the heptazine network creating large number of recombination centers and decreasing the overall photocatalytic activity of the resulting photocatalyst. We assume that our findings on the so far overlooked role of azo moieties in PCNs with strongly extended absorption edge might not only be valid only for this particular case, but also for other cases in which a strong shift of the PCN absorption edge has been observed upon thermal treatment procedures at temperatures exceeding the temperature of ammonia decomposition into N\(_2\) and H\(_2\), rendering thus the
atmosphere more reductive.\textsuperscript{[12, 15]} The present work thus highlights the importance of a careful determination of structural features governing the complex interplay between the light absorption, charge separation and catalytic turnover in PCN-based polymers tailored for visible light-driven photocatalysis.

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References


SUPPLEMENTARY INFORMATION

A Study in Red: The Overlooked Role of Azo-Moieties in Polymeric Carbon Nitride Photocatalysts with Strongly Extended Optical Absorption

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Figure S1. Thermogravimetric analysis of the Y-CNₓ and R-CNₓ samples
Figure S2. UV-Raman spectra of the Y-CN$_x$ and R-CN$_x$ samples

Figure S3. Neutron diffraction structure function obtained for Y-CN$_x$ and R-CN$_x$
Figure S4. XPS C 1s spectra of the Y-CNₓ (left) and R-CNₓ (right) samples.

Figure S5. Fitted XPS N 1s spectra of (a) Y-CNₓ and (b) R-CNₓ samples.

Figure S6. Deconvoluted °H-°N SS NMR spectra of the Y-CNₓ and R-CNₓ samples.
Figure S7. TEM data for Y-CN_x (a-d) and R-CN_x (e-h): Overview image (a) of the sample on amorphous carbon film with graphene as a support. The red marked area is further magnified in (b) showing agglomerated particles. Energy filtered TEM (EFTEM) mapping (c) of C- and N-K lines show homogeneous distribution of carbon and nitrogen in the particles. Electron diffraction pattern (d) shows amorphous rings in addition to the graphene spots. Overview image (e) for R-CNx shows similar agglomerations, further magnified from the red marked area in (f). EFTEM mapping (g) from the region shows homogeneous distribution of C and N. Diffraction pattern (h) shows amorphous rings.

Figure S8. (a) FTIR and (b) Raman spectra of the R-CN_x-KS sample

Figure S9. DRUV-vis spectrum of the R-CN_x-KS sample
Figure S10. Electronic band structures, projected density of states and the structural images of the R-CNₓ models.

Figure S11. Electronic band structures, projected density of states and the structural images of the Y-CNₓ models.
Figure S12. Charge densities at VBM (bottom) and CBM (top). The blue color is for nitrogen and the silver is for carbon.

Figure S13. Gaussian fit of time-resolved emission spectra of dropcasted Y-CNₓ and R-CNₓ under 385 nm (a) with the high energy (blue line) and low energy (red line) PL centers and under 520 nm excitation (b).