

# Triazine-based Carbon Nitrides for Visible-Light-Driven Hydrogen Evolution

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The efficient conversion of solar energy into chemical energy is a major challenge of modern materials chemistry and energy research. One solution to the future's energy demands will be the generation of hydrogen by photochemical water splitting as an environmentally clean energy carrier with a high energy density. So far the majority of photocatalysts are of an inorganic nature containing heavy metals which increase cost, impede scalability, and add complexity. Therefore, the development of efficient, stable, economically feasible, and environmentally friendly catalysts is required.

For many years carbon nitrides ( $C_xN_yH_z$ ) were famed for their structural variety and potential as precursors for ultra-hard materials. The thermal condensation of simple carbon nitrides (CNs) can form several denser chemical species that differ with respect to their degree of condensation, hydrogen content, crystallinity and morphology. The discovery of extended carbon nitrides with semiconducting properties and band gaps  $< 3$  eV makes them an attractive alternative to metal-rich semiconductors for photocatalysis. In 2009, Wang et al. investigated and determined for the first time the photocatalytic activity of polymeric melon-type CNs based on imide-bridged heptazine units (Fig. 1a).<sup>[1]</sup> Further publications focused on the modifications of those heptazine based carbon nitrides to improve their photocatalytic activity, e.g. by expanding their surface area, as well as by doping with heteroatoms and organic compounds, which gives rise to an enhanced absorption in the visible light range of the electromagnetic spectrum.

Recently, a new class of CNs was discovered by Bojdy and Wirnhier et al.<sup>[2,3]</sup> This novel compound called poly(triazine imide) (PTI/ $Li^+Cl^-$ ) is the only structurally characterized, crystalline 2D CN network intercalated with lithium and chlorine ions, featuring imide-linked triazine units (Fig. 1b). Due to its crystallinity and its well-defined structure, PTI can serve as an excellent model to investigate photocatalytic activity towards water splitting as a function of the composition, the level of condensation, and the degree of structural perfection of the system. Initial photocatalytic studies of crystalline PTI showed photocatalytic activity comparable to that of heptazine-based melon. Moreover, we show that the performance of PTI can be amplified by increasing the structural imperfection with simple small-molecule doping, thus rendering amorphous PTI-type materials the most active nonmetal photocatalysts for the hydrogen evolution reaction that have been reported to date.<sup>[3]</sup>

Firstly, we synthesized crystalline PTI/ $Li^+Cl^-$  as a model structure for triazine-based CNs in a two-step ionothermal synthesis according to the procedure of Wirnhier et al.<sup>[3]</sup> As a starting material dicyandiamide and an eutectic mixture of 59.2 mol% lithium chloride and 40.8 mol% potassium chloride was heated at 400°C for 12 hours under atmospheric argon pressure. The precondensed CN was ground, filled in a quartz ampoule, sealed under vacuum and heated for 24 hours at 600°C. Crystalline PTI/ $Li^+Cl^-$  was obtained after several washing steps with water. To study the effect of crystallinity on the photocatalytic activity, we also synthesized an amorphous variant of PTI (aPTI), through a one-step ionothermal process. Here, the initial reaction mixture was heated in a muffle furnace for 6 hours at 500°C. In a third approach we added 4-amino-2,6-dihydropyrimidine (4AP, Fig. 1c) as an organic dopant to investigate its effect on the photocatalytic activity. 4AP was used because of its structural similarity to the basic repetitive unit of PTI, while having a higher carbon and oxygen content. The as-synthesized CNs were compared with that of crystalline PTI/ $Li^+Cl^-$  and heptazine-based amorphous melon towards their photocatalytic activity, optical absorption ability and structural differences.<sup>[4]</sup>

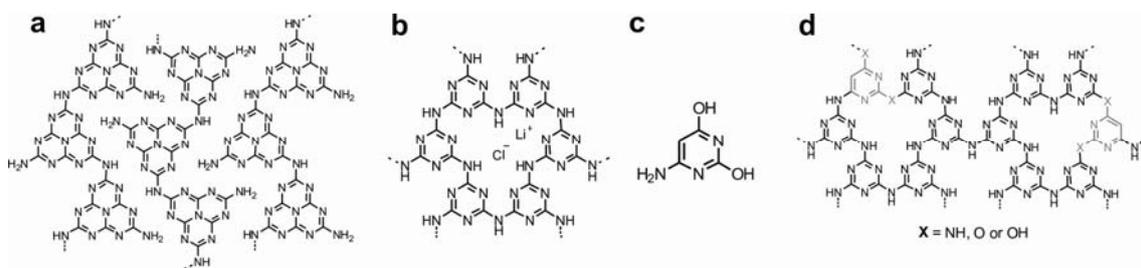


Figure 1: Chemical structures of a) melon, b) PTI/Li<sup>+</sup>Cl<sup>-</sup> (idealized structure), c) the dopant 4AP and d) proposed structure of aPTI<sub>4AP</sub>16%.

The XRD diagram of the PTI/Li<sup>+</sup>Cl<sup>-</sup> matches well with the pattern from the literature.<sup>[3]</sup> The amorphous character of the aPTI samples (doped or unmodified) is confirmed by the absence of sharp reflections in the XRD patterns. However, the FTIR spectra of the synthesized aPTI CNs are still largely reminiscent of crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup> (Fig. 2d). However, doping with 4AP leads to less resolved FTIR spectra, thereby indicating a lowering of structural order. Interestingly, the spectra of 16% and 32% doped aPTI feature another band at 914 cm<sup>-1</sup> that can be assigned to aromatic C-H bending vibrations of the dopant.<sup>[4]</sup>

Elemental analysis results in an atomic C/N ratio of 0.68 for crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup>. The amorphous samples show a slightly increased C/N ratio, which might indicate either more significant incorporation of oxygen or a higher degree of condensation. A higher amount of heteroatoms can play an essential role in the activity of CN photocatalysts. Apparently, synthesis in an open system leads to a lower incorporation of lithium and chloride ions in the structure. As expected, the C/N ratio gradually increases with increasing amount of incorporated 4AP, from 0.69 to 1.13 for 2% to 64% doped PTI, respectively. In summary, IR and EA results suggest that both oxygen and carbon atoms are incorporated into the amorphous CN structure, most likely through replacement of one of the bridging or ring nitrogen atoms, as proposed in Figure 1d.

Additional information on the structure of a 16% 4AP doped aPTI (aPTI<sub>4AP</sub>16%) was obtained by <sup>13</sup>C, and <sup>15</sup>N CP-MAS and <sup>15</sup>N CPPI NMR measurements (Fig. 2a-b). The investigated CN shows similar NMR spectra compared to crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup>, although with a broadened line width, which is due to the amorphous character of the sample. The <sup>15</sup>N CP-MAS spectrum contains two stronger signals at -175 and -245 ppm, the first assigned to the tertiary ring nitrogens (N<sub>tert</sub> assigned to the outer ring nitrogen atoms of triazine or heptazine rings) and the latter to bridging NH groups, and a very weak signal at -280 ppm which indicates that only a small amount of terminal NH<sub>2</sub> groups is present, hence a melon-type structure seems very unlikely. Small intensity ratio differences may indicate partial incorporation of the dopant into the PTI framework. An additional <sup>15</sup>N CPPI-MAS spectrum was recorded to ascertain if any central nitrogen atoms (N<sub>c</sub>) of heptazine rings are present, which only appear for melon-type structures. The absence of any signals in the region between -200 and -300 ppm therefore strongly supports the absence of heptazine units within the detection limit of roughly 10 – 15%.

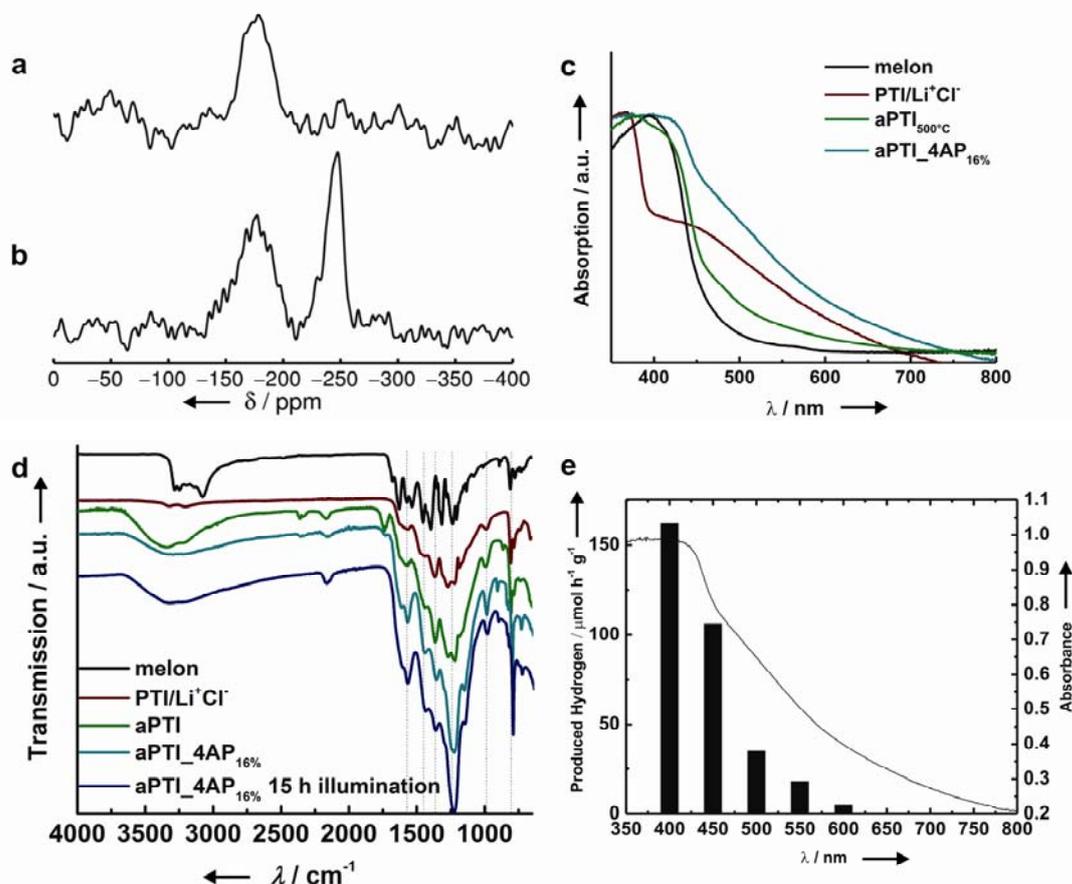


Figure 2: a)  $^{15}\text{N}$  CPPI-MAS NMR spectrum (6 Hz, inversion time = 400  $\mu\text{s}$ ) and b)  $^{15}\text{N}$  CP-MAS NMR spectrum (10 kHz) of aPTI\_4AP<sub>16%</sub>. c) UV/Vis spectra and d) FTIR spectra of aPTI\_4AP<sub>16%</sub> synthesized at 550°C before and after 15 h illumination, compared to crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup>, aPTI<sub>1500°C</sub>, and melon. e) Overlay of UV/Vis spectrum and wavelength-specific H<sub>2</sub> production (black bars) of aPTI\_4AP<sub>16%</sub> using 40 nm FWHM band-pass filters.

The optical absorption of a photocatalyst is important, since a high absorption in the visible light range is expected to increase photocatalytic performance. Brown, crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup> absorbs mostly in the UV region, yet interestingly, additional broad absorption takes place in the blue part of the visible spectrum (Fig. 2c). The amorphous, undoped, yellowish CN absorbs toward higher wavelengths, similar to melon. With increasing amount of dopant the color of the 4AP doped CNs gets darker, changing from yellow (2%) to red-brown (64%), which correlates well with the red-shift observed in the absorption spectra. The wavelength-specific H<sub>2</sub> evolution of aPTI\_4AP<sub>16%</sub> was measured and overlaid with its absorption graph (Fig. 3e). The measurements showed a fall-off of the H<sub>2</sub> production rate at 450 – 500 nm, which indicates that the majority of photons contributing to the H<sub>2</sub> evolution are at  $\lambda < 500$  nm.

Crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup> is expected to be a promising 2D photocatalyst due to its expanded conjugated  $\pi$ -electron system, suitable band gap ( $\approx 2.2$  eV) and enhanced absorption in the visible, which may even outperform heptazine-based semiconductors. Photocatalytic measurements of PTI/Li<sup>+</sup>Cl<sup>-</sup> showed a moderate H<sub>2</sub> evolution (864  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ; approximately 15% error) in the presence of 2.3 wt% platinum as a co-catalyst and triethanolamine (TEoA) as sacrificial electron donor (Fig. 3). In our studies, melon on the other hand produces 20% less H<sub>2</sub> (722  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) compared to PTI/Li<sup>+</sup>Cl<sup>-</sup>. The highest photocatalytic activity of the amorphous, undoped CNs was achieved at a reaction temperature of 500 °C (1080  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ; approximately 50% enhancement compared to melon). Doping with 16% 4AP of aPTI at a reaction temperature of 550°C (aPTI\_4AP<sub>16%</sub>; 4907  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) enhanced the photocatalytic activity by 5 – 6 times compared to crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup> and 6 - 7 times compared to melon. 4AP-doping of crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup> leads to no apparent photocatalytic activity. It is worth mentioning that pure and thermally treated 4AP is

photocatalytically inactive. Analyzing the sample morphology and porosity reveals only a weak correlation between surface area and photoactivity.

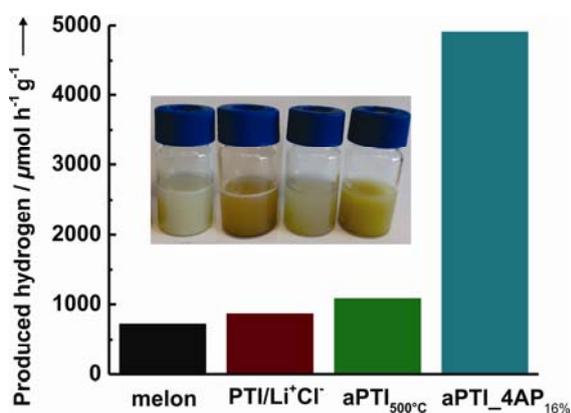


Figure 3: Comparison of triazine-based carbon nitrides for the photocatalytic activity towards H<sub>2</sub> production. The inset shows the color of the water/TEoA suspensions of aPTI<sub>4AP</sub><sub>16%</sub> synthesized at 550°C compared to crystalline PTI/Li<sup>+</sup>Cl<sup>-</sup>, aPTI synthesized at 500°C, and melon.

In conclusion, we have reported a new family of 2D triazine-based carbon nitride photocatalysts that shows high visible-light-induced H<sub>2</sub> evolution from water, which is superior to that observed for most heptazine-based carbon nitrides. The amorphous carbon- and oxygen-enriched poly(triazine imide) species, with an external quantum efficiency of 3.4%, does not only show a 6 - 7 times higher photocatalytic activity compared to melon-type photocatalysts, but also outperforms crystalline PTI about a factor of 5 - 6. The judicious modification of carbon nitride photocatalysts with different types of molecular dopants will allow for the rational design of a diverse set of triazine-based carbon nitride polymers with controlled functions, opening new avenues for the development of light-harvesting semiconductors for solar energy applications.

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