

Structure elucidation of polyheptazine imide by electron diffraction—a templated 2D carbon nitride network†

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Structure elucidation of a condensed carbon(IV) nitride with a stoichiometry close to C₃N₄ by electron diffraction reveals a two-dimensional planar heptazine-based network containing isolated melamine molecules in the trigonal voids.

Owing to their exceptional chemical stability and hardness, nitrides of main group elements have entered the stage as ubiquitous light-weight, high-performance materials relevant to a multitude of technological applications. Although 3D phases of binary carbon nitride C₃N₄ hold promise as new ultra-hard materials,¹ the layered polymorph, graphitic carbon nitride (g-C₃N₄) has recently garnered attention for its versatile optical, electronic and tribological properties apt to being exploited in solar cell, sensor and transistor technologies.^{1–3} Moreover, hydrogen-rich graphitic carbon nitride materials are currently unfolding their potential as metal-free heterogeneous catalysts and hold promise as electron-rich organic semiconductors.^{4,5}

Recent reports on the structural characterization of crystalline pre-stages of carbon nitride have added momentum to the quest for the hydrogen-free prototype g-C₃N₄: although carbon nitride imide, C₂N₂(NH), with a defect wurtzite-type structure features a 3D carbon nitride framework,⁶ the literature on 2D carbon nitrides is still dominated by controversial speculations about the type of heterocycle—triazine or heptazine—constituting the carbon nitride backbone.^{2,4,5} Recently, Thomas *et al.* reported on an ionothermal approach to afford bulk amounts of crystalline g-C₃N₄. The proposed structure model based on PXRD corresponds to staggered sheets of 2D condensed heptazine building blocks,^{5f} which likewise have been found to be the structural motifs of the 1D polymer melon.⁷

The increasingly dense population of the previously uncharted map of possible carbon nitride structures calls for a deeper understanding of the mechanistic pathways governing the condensation of molecular precursors and the formation of side phases and intermediates, which may direct subsequent synthesis strategies. In addition, the majority of carbon nitride structures reported to date remain tentative

owing to the lack of single-crystal data. Electron diffraction is a powerful tool to deliver on both requirements by locally probing the real structure of nanocrystalline materials and minority phases not previously accessible to bulk structural analysis.

Here, we communicate the structure elucidation of a crystalline 2D carbon nitride network with the formula (C₆N₇)₂(NH)₃·C₃N₃(NH₂)₃ by electron diffraction. This novel member of the carbon nitride family, featuring an intermediate condensation stage halfway between melon and g-C₃N₄, may shed light on structural implications and stability considerations associated with graphitic carbon nitride.

Pyrolysis of melamine C₃N₃(NH₂)₃ under autogenous pressure of ammonia yields a material predominantly composed of melon. Owing to the high temperatures (630 °C) and peak pressures generated by the condensation of melamine and concomitant elimination of ammonia, judicious control over the course of the reaction remains a challenge. This in turn leads to the inevitable formation of side phases, among which polymorphs of melon and polymers exhibiting different degrees of condensation are likely present.⁸

The title compound was observed in a relatively hydrogen and carbon rich bulk sample of melon, obtained by pyrolysis of melamine,⁷ which is consistent with *in situ* pyrolysis temperatures in excess of 630 °C. Phase analysis revealed the coexistence of several layered phases, which we assume are structurally related to the majority phase melon. Close inspection of the crystalline domains by TEM gave evidence of the presence of trace amounts of a highly crystalline minority phase clearly distinct from melon by its high symmetry.⁷

Fig. 1 (left) presents the experimental diffraction pattern on the basis of which the structure solution and refinement was carried out. The kinematical simulation based on the refined structure model (Fig. 1, right) clearly maps the hexagonal

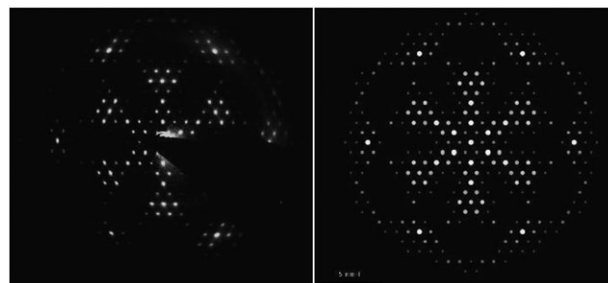


Fig. 1 Experimental (left) and simulated kinematical (right) ED pattern of the *hk0* plane (zone axis [001]).

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symmetry and intensity distribution of the experimental pattern, suggesting excellent agreement with the experimental data. The selected area electron diffraction (SAED) pattern was indexed on a hexagonal cell with lattice parameter $a = 12.4 \text{ \AA}$. Evaluation of the intensity data was carried out within the framework of kinematical scattering theory ($I_{hkl} \propto |F_{hkl}|^2$), as dynamical contributions and multiple scattering were assumed to be minimized owing to the small structure factors and sample thickness. The structure was solved in [001] projection in the plane group $p31m$. The non-hydrogen atom positions were refined without restraints, yielding final R values ($R1 = 9.19\%$, $wR2 = 25.50\%$) well below typical values obtained from structure refinements based solely on electron diffraction data.⁹ The positions of the hydrogen atoms was refined by quantum chemical calculations (see below).

Information on the third dimension may be introduced by taking the interplanar distance to be 3.2 \AA by analogy with the majority phase melon. This choice is supported by the X-ray powder pattern of melon-type phases, which are characterized by a single prominent $00l$ reflection corresponding to the above d -spacing.^{4–7} The hexagonal symmetry of the SAED patterns is in agreement with an eclipsed AAA-type stacking sequence of the layers; however, triclinic stacking ($\alpha, \beta \neq 90^\circ$), with deviations from the 90° angle not exceeding $\approx 10^\circ$, does not violate the hexagonal symmetry observed in [001] projection.⁷

The structure of the templated polyheptazine imide (PHI) is represented by a “holey,” yet continuous heptazine network, in which melamine (triamino-*s*-triazine) molecules are embedded, giving rise to a 2D planar array exclusively based on C(IV)–N linkages. The network forming heptazine units are connected along [100] in a zig-zag type fashion similar to melon and bridged *via* imide-bonds to three neighboring heptazine molecules each, such that all amide moieties present in melon are lost. Alternatively, the structure can be viewed as consisting of an infinite array of parallel melon strands connected to their mirror images *via* C–NH–C bridges (Fig. 2, top), thus yielding a degree of condensation higher (2D) than that in melon (1D). The above connectivity scheme introduces large triangular voids into the planar network, each hosting a single melamine molecule. The triazine units are tightly anchored to the surrounding heterocycles *via* a manifold of two symmetry equivalent NH \cdots N hydrogen bonds.

A similar open 2D topology with hexagonal symmetry was previously described by Kawaguchi *et al.*^{5e} and Zhang *et al.*^{5f} Although no single-crystal data were available at that time, both structure models are based on triazine building blocks containing smaller voids likely filled by chloride ions.^{5f} However, as there is increasing evidence that thermodynamic reaction control affords heptazine-based structures, PHI rather than triazine-derived models may represent a pre-stage of $g\text{-C}_3\text{N}_4$.⁴ Interestingly, DFT calculations predict fully condensed $g\text{-C}_3\text{N}_4$ sheets to be buckled to release strain introduced by close inter-ring N \cdots N contacts.^{4,8} In contrast, the reduction of the number of these contacts to three due to the presence of voids, and the hydrogen bonds between melamine and the framework favours a planar arrangement of the layers in PHI.

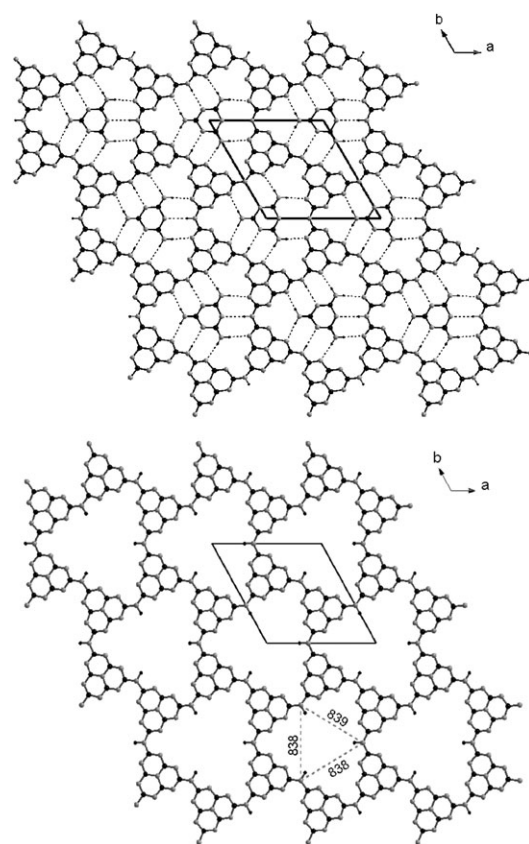


Fig. 2 Top: Supercell representation of the projected structure of PHI based on ED data, view along [001]. The hydrogen bonding network is indicated by dotted lines. Bottom: Polyheptazine imide framework without melamine templates, as calculated on the DFT level of theory. N \cdots N distances within a triangular void are given in pm. Dark gray: C and H, light gray: N.

From a retrosynthetic perspective, the formation of PHI bears a conceptual analogy with the synthesis of microporous ceramic materials based on sacrificial structure-directing agents. Moreover, it is noteworthy that this arrangement is reminiscent of crystalline covalent organic frameworks (boron oxide based COFs and covalent triazine frameworks, CTFs), which have been widely recognized in the recent literature as novel microporous materials with high total pore volumes and internal surface areas.^{10,11} In contrast to CTFs such as polytriazine networks obtained by the trimerization of dicyanobenzene,¹¹ the title compound possesses a “homogeneous” framework as opposed to the “heterogeneous” node + spacer topology encountered in COFs. However, the voids occupied by melamine in PHI resemble the periodicities typically found in covalent organic frameworks.¹⁰ In COFs, the pores are commonly occupied by solvents or reactant molecules, which may be removed at temperatures around $200 \text{ }^\circ\text{C}$ without collapse of the framework structure.^{10,11}

For an independent confirmation of the structure model and the localization of the hydrogen atoms, DFT calculations based on periodic boundary conditions were performed. The relaxation of the structure was carried out in space group $P1$. Since no information about the stacking disorder was available, the c -axis was fixed at 6 \AA to exclude interactions

between neighboring layers. The quantum chemically relaxed structure is virtually unchanged except for the positions of the hydrogen atoms. In particular, the trigonal symmetry and the planarity of the layers are retained with only a slight increase of the lattice parameters to 12.67 Å. This corresponds to a deviation of 2% from the ED data, which is well within the error of the experimental data.

It should be noted that even after removing the melamine units, the network structure represents a minimum on the energy hypersurface after geometry optimization in space group *P1* (Fig. 2, bottom). The surface of the voids in the network increases slightly ($\approx 2\%$). This corresponds to the larger lattice parameter of 12.77 Å. However, also in this case the trigonal symmetry and the planarity of the layers are retained.

To judge the influence of the incorporated melamine molecules as structure-directing agents, we performed force field calculations in space group *P1*. To this end, the Dreiding force field was chosen, since it is designed to derive the contribution of hydrogen bonding to the total of all dispersion forces separately.¹² The resulting lattice parameters amount to 12.74 Å, which is only slightly larger than the value derived from the DFT calculations. As for melon, when assuming an AAA-stacking the layer distance turns out to be 3.44 Å, which is significantly larger than the interlayer distance experimentally observed for graphite-like CN polymers (3.2 Å).⁷

In addition, we calculated the partial energy contribution of an isolated melamine molecule and of the network without melamine to the total structure. The calculations reveal a stabilization of the network by 136.36 kJ mol⁻¹ when melamine is incorporated (Table S2, ESI†). Furthermore, the Dreiding potential assigns roughly 90 kJ mol⁻¹ of the dispersion energy to the hydrogen bonding network. Since one melamine molecule takes part in nine hydrogen bonds, a mean value of ≈ 10 kJ mol⁻¹ is derived, which is small enough to render the “extraction” of melamine from the cavities a realistic scenario.

Expanding on the analogy with COFs, which is backed by the above theoretical calculations, the melamine molecules can be envisioned to function as templates in the framework condensation process, which may subsequently be removed by vacuum annealing at high temperatures (Fig. 2, bottom).

The dimensions of the trigonal void created by the triazine “porogen” provide exactly the space required to accommodate another heptazine nucleus, which highlights a hypothetical transformation pathway from PHI into heptazine-based

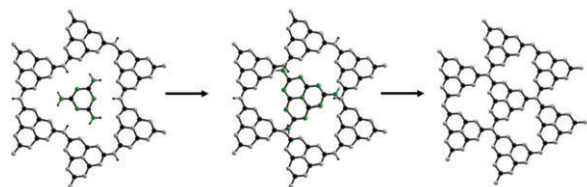


Fig. 3 Hypothetical reaction cascade featuring the removal of the triazine “template” and covalent anchoring of a melon unit to the trigonal void affording graphitic carbon nitride, g-C₃N₄. Although the actual chemical relationship between PHI and g-C₃N₄ is yet to be studied, the scheme highlights the topological similarities between the two structures.

g-C₃N₄ (Fig. 3). This close topological and compositional analogy with the hypothetical g-C₃N₄ suggests that by further exploring and fine-tuning the condensation conditions the synthesis of the binary prototype is within reach. Studies aiming at the directed synthesis of phase-pure PHI are currently underway.

In conclusion, we have presented the crystal structure of a 2D framework in which melamine is present as a template as well as potential “porogen.” This carbon(IV)nitride polymer, which bears some resemblance to COF-type networks, bridges the gap between the 1D topology of melon and the hypothetical, fully condensed network structure of graphitic carbon nitride.

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