Supporting Information

A Templated 2D Carbon Nitride Network: Structure Elucidation by Electron Diffraction

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Experimental Details

Synthesis: Templated polyheptazine imide was prepared by heating ^{15}N enriched melamine (200 mg) in a sealed quartz tube (length: 120 mm, $\varnothing_{ext}$:. 15 mm, $\varnothing_{int.}$: 11 mm) under dry argon at 630 °C (heating rate 1 K min^{-1}) for ≈ 12 h. ^{15}N melamine was obtained by fusing sodium tricyanomelaminate $Na_3[C_6N_9]$ (742.5 mg, 2.78 10^{-3} mol) with $^{15}NH_4Cl$ (183 mg, 3.36 10^{-3} mol, ≥ 98 %, Cambridge Isotopes) in a Duran tube (length: 160 mm, $\varnothing_{ext.}$: 26 mm, $\varnothing_{int.}$: 24 mm) at 470 °C (heating rate of 1 K min^{-1}) for 12 h. The melamine raw material obtained as a side product in the above synthesis was further purified by

sublimation (1 Pa, 220 °C).[1]

Electron Diffraction was carried out on a FEI Titan 80-300 equipped with a field emission gun operating at 300 kV. The images were recorded using a Gatan UltraScan 1000 (2k × 2k) camera. The carbon-coated copper grids were mounted on a double tilt holder with a maximum tilt angle of 30°. After removal of the diffuse background of the SAED patterns, reflection intensities were extracted using the ELD program package.[2] The diffraction patterns show 6*mm* symmetry with no systematic absences. After symmetry averaging a dataset of 55 independent reflections was obtained with an internal reliability factor[3] of R_{rim}= 12 %, reflecting the good quality of the obtained dataset. The most probable solution as found by SIR–97[4] had a figure of merit of 24.0 %.[5] A refinement of the electron diffraction data was attempted using ShelXL-97.[6] Assuming kinematical diffraction, but including a phenomenological factor accounting for dynamical effects, the refinement of the structure yields residuals of R1 = 9.19 % for 38 reflections stronger than 4σ (12.75 % for all 55 reflections) and *wR*2 = 25.5 %. Fixing hydrogen atoms at their corresponding sites, but without further constraints, the refinement delivers realistic distances and geometries involving all carbon and nitrogen atoms. The structure was verified by simulating a kinematical diffraction pattern using the JEMS software package.[7]

Theoretical calculations: The input structures were created from the ED structure solution with hydrogen atoms added to the N(H) and N(H_2) groups. Calculations under periodic boundary conditions were performed with the MS Modelling 4.0 package from Accelrys. The input cell was created in trigonal symmetry. For the CASTEP[8] calculations the PBE functional and ultrasoft pseudopotentials were used with sampling over 8 k-points. In the structure optimization of the input cell, an energy cutoff of 280 eV and a constrained slab of 6 Å along the c axis were used. For the CASTEP optimized cell, the Hirschfeld charges were determined with the $DMol^3$ program, the PBE functional and the DNP basis set.[9] These partial charges were used in flexible body structure optimizations of the input cell with the Dreiding force field.[10]

Figure S1. Original SAED image used for the structure solution prior to subtraction of the diffuse background.

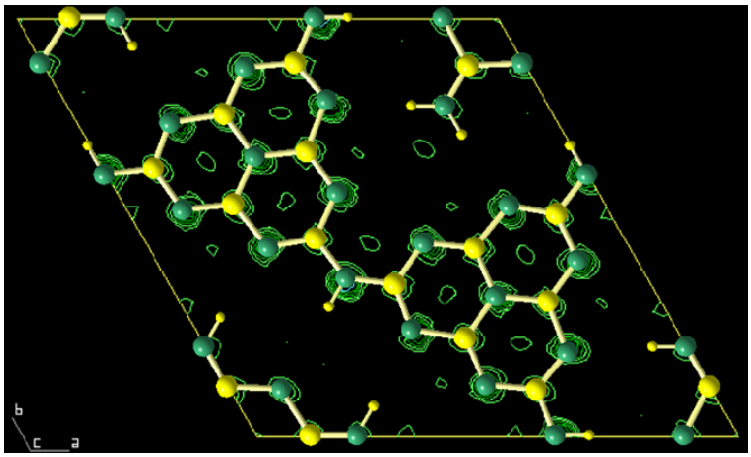

Figure S2. Electron density distribution as obtained after structure solution with SIR-97. The structural building blocks are indicated for clarity. Yellow: C and H, green: N.

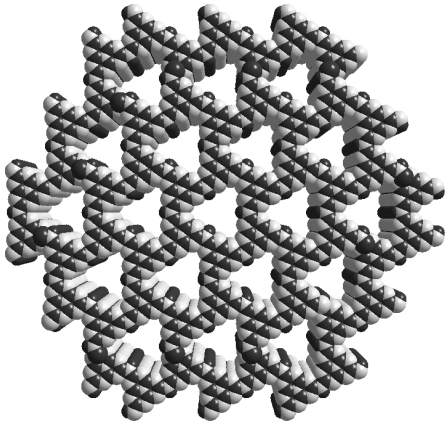

Figure S3. Representation of the hypothetical polyheptazine imide framework without melamine templates, view along [001]. Dark gray: C and H, light gray: N.

Table S1. Atomic positions, site occupation factors and isotropic thermal displacement parameters as obtained from the refinement of the ED structure solution of melamine templated polyheptazine imide. The z-parameters were fixed at 0.0 and the isotropic thermal displacement factors for the non-hydrogen atoms were refined using a common value.

Atom	x	y	z	SOF	U_{iso}
N1	2/3	1/3	0	1/3	0.035(5)
N2	0	0.377(3)	0	0.5	0.035(5)
N3	0.879(2)	0.460(2)	0	1	0.035(5)
N4	0.788(3)	0	0	0.5	0.035(5)
N5	0.802(2)	0.252(3)	0	1	0.035(5)
N6	0	0.109(3)	0	0.5	0.035(5)
C1	0.891(3)	0.361(3)	0	1	0.035(5)
C2	0.884(4)	0	0	0.5	0.035(5)
C3	0.679(2)	0.232(2)	0	1	0.035(5)
H11	0	0.30724	0	0.5	0.29755
H4A	0.78831	0.06935	0	0.5	0.04258
H4B	0.71895	-0.06935	0	0.5	0.04258

Table S2. Energies obtained from the force field (Dreiding) calculations for the total structure model, isolated melamine molecules and the network without melamine. The lattice parameters were fixed at 12.74 Å.

Structure element	Energy (Dreiding) [kJ mol^{-1}]
A Total structure	-426.84
B Network	-166.74
C Melamine	-123.74
$\sum$ **B** + **C**	-290.48
Δ **A** – (**B** + **C**)[a]	-136.36

[a] Corresponds to the stabilization of the total structure when melamine is incorporated.

Table S3. Relevant structural parameters for the total structure as obtained by DFT calculations with periodic boundary conditions.

a = 12.67 Å, b = 12.67 Å, c = 6.0 Å (fix), α = 90.00°, β = 90.00°, γ = 120.03°, V = 834.1 Å^3

Element	**x**	**y**	**z**
H1	-0.209714	0.080229	0.533333
H2	-0.080533	-0.290154	0.533333
H3	0.290029	0.209713	0.533333
H4	0.080229	-0.209714	0.533333
H5	-0.290154	-0.080533	0.533333
H6	0.209713	0.290029	0.533333
H7	-0.000186	0.289768	0.533333
H8	0.710212	0.710212	0.533333
H9	0.289768	-0.000186	0.533333
C1	0.887394	0.363447	0.533333
C2	0.682185	0.231830	0.533333
C3	0.636676	0.524059	0.533333
C4	0.768314	0.450536	0.533333
C5	0.475964	0.112637	0.533333
C6	0.549621	0.317846	0.533333
C7	0.363447	0.887394	0.533333

C8	0.231830	0.682185	0.533333
C9	0.524059	0.636676	0.533333
C10	0.450536	0.768314	0.533333
C11	0.112637	0.475964	0.533333
C12	0.317846	0.549621	0.533333
C13	-0.103682	-0.000049	0.533333
C14	-0.000049	-0.103682	0.533333
C15	0.103621	0.103621	0.533333
N1	0.878408	0.463487	0.533333
N2	0.793994	0.248156	0.533333
N3	0.536621	0.414943	0.533333
N4	0.752001	0.546047	0.533333
N5	0.585016	0.121712	0.533333
N6	0.454054	0.205974	0.533333
N7	0.463487	0.878408	0.533333
N8	0.248156	0.793994	0.533333
N9	0.414943	0.536621	0.533333
N10	0.546047	0.752001	0.533333
N11	0.121712	0.585016	0.533333
N12	0.205974	0.454054	0.533333
N13	0.666701	0.333406	0.533333
N14	0.333406	0.666701	0.533333
N15	-0.000039	0.372408	0.533333
N16	-0.000001	0.109008	0.533333
N17	0.627607	0.627607	0.533333
N18	-0.109062	-0.109062	0.533333
N19	0.372408	-0.000039	0.533333
N20	0.109008	-0.000001	0.533333
N21	-0.209353	-0.000136	0.533333
N22	-0.000136	-0.209353	0.533333
N23	0.209285	0.209285	0.533333

Table S4. Relevant structural parameters for the network without melamine as obtained by DFT calculations with periodic boundary conditions.

a = 12.77 Å, b = 12.77 Å, c = 6.0 Å (fix), α = 90.00°, β = 90.00°, γ = 120.04°, V = 846.9 Å^3

Element	x	y	z
H1	-0.000145	0.298881	0.533333
H2	0.701134	0.701134	0.533333
H3	0.298881	-0.000145	0.533333
C1	0.886729	0.367351	0.533333
C2	0.684495	0.233645	0.533333
C3	0.632736	0.519492	0.533333
C4	0.766443	0.451008	0.533333
C5	0.480488	0.113243	0.533333
C6	0.549101	0.315495	0.533333
C7	0.367351	0.886729	0.533333
C8	0.233645	0.684495	0.533333
C9	0.519492	0.632736	0.533333
C10	0.451008	0.766443	0.533333
C11	0.113243	0.480488	0.533333
C12	0.315495	0.549101	0.533333
N1	0.876610	0.465751	0.533333
N2	0.796359	0.251978	0.533333
N3	0.534264	0.410837	0.533333
N4	0.748088	0.544533	0.533333
N5	0.589037	0.123454	0.533333
N6	0.455477	0.203532	0.533333
N7	0.465751	0.876610	0.533333
N8	0.251978	0.796359	0.533333
N9	0.410837	0.534264	0.533333
N10	0.544533	0.748088	0.533333

N11	0.123454	0.589037	0.533333
N12	0.203532	0.455477	0.533333
N13	0.666674	0.333382	0.533333
N14	0.333382	0.666674	0.533333
N15	-0.000070	0.379031	0.533333
N16	0.620965	0.620965	0.533333
N17	0.379031	-0.000070	0.533333

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