Supporting Information

Tuning of gallery heights in a crystalline 2D carbon nitride network

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1. Experimental (continued).

Materials. Dicyandiamide (DCDA), lithium bromide, potassium bromide, and ammonium fluoride were purchased in their highest-purity form from Sigma-Aldrich and used as received.

2. Characterisation methods.

Infrared spectroscopy: Fourier transform infrared (FT-IR) measurements were carried out on a Bio-Rad FTS-6000 system in attenuated total reflection (ATR) setup. FT-IR spectra of bulk samples were recorded at ambient temperature in a range from 4000 to 400 cm⁻¹.

Solid-state NMR: Solid-state NMR spectra were recorded on a Bruker DSX400 spectrometer at room temperature using zirconia MAS rotors. ${}^{1}\text{H}{}^{-13}\text{C}$ CP/MAS data were recorded using a 4mm H/X/Y probe head using a MAS rate of 10 kHz. The ${}^{1}\text{H}{}\pi/2$ pulse length was 3.1 µs with a recycle delay of 10 s. Two pulse phase modulation (TPPM) heteronuclear dipolar decoupling was used during acquisition. The Hartman-Hahn matching condition was set using hexamethylbenzene (HMB) and contact time in the range of 0.05 - 16 ms were used. ${}^{13}\text{C}{}^{1}\text{H}$ MAS were recorded using the same probe head and MAS frequency. A ${}^{13}\text{C}{}\pi/3$ pulse length of 2.6 µs, recycle delay of 20 s and TPPM decoupling were used in acquisition. All ${}^{13}\text{C}{}$ spectra are referenced to external TMS at 0 ppm. ${}^{1}\text{H}{}^{-15}\text{N}$ CP/MAS spectra were recorded using either a 4 mm H/X/Y or 7 mm H/X probe head using a MAS rate of 5 and 4 kHz, respectively. The ${}^{1}\text{H}{}\pi/2$ pulse length was 3.1 µs (4.2 µs, 7 mm probe) with a recycle delay of 10 s. Two pulse phase modulation (TPPM) heteronuclear dipolar decoupling was used during acquisition. The Hartman-Hahn matching condition was set using 95 % ${}^{15}\text{N}$ -Glyciene and contact time of 5 ms was used. All ${}^{15}\text{N}$ spectra were referenced to the -NH₂ signal of glyciene at 32.5 ppm with respect to NH_{3(liq)}. The analysis of the spectra (deconvolution) was carried out using Bruker TOPSPIN software.

Powder X-ray diffraction: Powder X-ray diffraction data was collected in two different set-ups for reproducibility, and diffraction pattern were selected by optimal resolution and signal-to-noise ratio. In one case, a PANalytical X'pert pro multi-purpose diffractometer (MPD) in transmission geometry operating with a Cu anode at 40 kV 40 mA was used. Samples were ground and mounted as loose powders onto a transparent film in a Al sample holder. PXRD patterns were collected in four 1 hour scans with a step size of 0.013 ° 20 and scan time of 115 s/step over 5 – 50 ° 20. The incident X-ray beam was conditioned with 0.02 rad Soller slits and an anti-scatter slit of 1/2 °. The diffracted beam passed through 0.02 rad Soller slits and Ni filter before processing by the PIXcel detector operating in scanning mode. High resolution synchrotron PXRD data were collected for a total exposure time of 100 s using the Mythen-II position sensitive detector at beamline I11 ($\lambda = 0.826157$ Å), Diamond Light Source on spinning samples held in 1 mm diameter special glass capillaries. Structural refinement and Le Bail fitting was carried out using the *TOPAS-Academic* software.¹

Transmission electron microscopy: TEM images were recorded on a GATAN MS794 P CCDcamera using a FEI Tecnai G² 20 S-TWIN transmission electron microscope with LaB₆-cathode and 200 keV acceleration voltage.

Scanning electron microscopy: SEM imaging of the platelet morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). The dry samples were prepared on 15 mm Hitachi M4 aluminum stubs using either silver dag or an adhesive high purity carbon tab. The FE-SEM measurement scale bar was calibrated using certified SIRA calibration standards. Imaging was conducted at a working distance of 8 mm and a working voltage of 5 kV using a mix of upper and lower secondary electron detectors.

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3. Elemental microanalysis and ICP.

Table S1. Elemental microanalysis and ICP for PTI/Br and for PTI/Br treated with conc. ammonium fluoride, PTI/F (mix).

wt %	PTI/Br	PTI/F (mix)		
С	32.6	32.2		
N	56.4	51.4		
Н	0.97	1.39		
0	4.7	5.2		
Li	1.51	0.78		
Br	3.82	1.77		
F	-	7.32		

4. ¹H-¹³C CP/MAS NMR kinetics data.

Table S2. ¹H-¹³C CP/MAS kinetics data for PTI/Br obtained from curve fitting using simple I-S model.²

Chemical shift /ppm	Signal Intensity / a.u.	T _{IS} / ms	${T_{1\rho}}^{H}/ms$	\mathbf{R}^2
157.8	$7.89 \text{ x}10^6 \pm 2.4 \text{ x}10^5$	1.17 ±0.07	28.3 ±3.11	0.994
162.6	$2.66 \text{ x} 10^7 \pm 4.7 \text{ x} 10^5$	0.99 ± 0.04	24.8 ±1.44	0.997
167.9	$9.96 \text{ x}10^6 \pm 3.5 \text{ x}10^5$	4.63 ±0.42	> 50	0.988

5. References.

- 1. P. A. Wright, *Microporous Framework Solids*, Royal Society of Chemistry, Cambridge, UK, 2008.
- 2. J. T. A. Jones, C. D. Wood, C. Dickinson and Y. Z. Khimyak, *Chem. Mat.*, 2008, **20**, 3385-3397.