Graphamine: Amine Functionalized Graphane for Intrinsic Anhydrous Proton Conduction Supporting Information

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Bonding & Lattice Parameters

The optimal lattice constant (a_0=1.545) was determined by fitting first-principles $E(V)$ energy(volume) data to the third-order Birch-Murnaghan equation of state shown in Figure S1. A list of all appropriate bonding parameters for the graphamine is listed in Table S1.

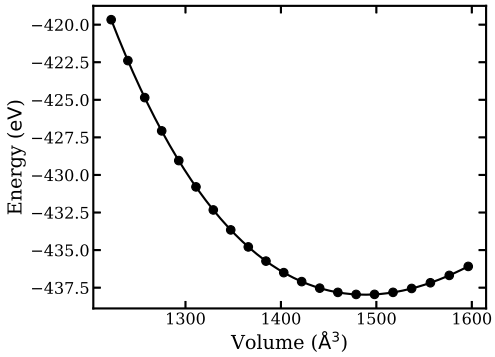

Figure S1: Total energy as a function of volume for the fit of the Birch-Murnaghan equation of state.

Table S1: Average bond lengths (Å) for the topology of graphamine

Bond type	Bond length
C—C	1.62
C—H	1.10
C—N	1.48
N—H	1.02

DDEC6 Partial Atomic Charges

The indistinguishable nature of the protons of the amine groups participating in the PC process (for the configuration in Figure S2) was tested by computing the partial atomic charges from the Density Derived Electrostatic and Chemical (DDEC6) charge analysis approach.[1] Table S2 presents the statistics of partial atomic charges and the actual charges of the protons are given in Table S3. The net atomic DDEC6 charges reported are computed by analyzing the charge densities obtained from VASP.

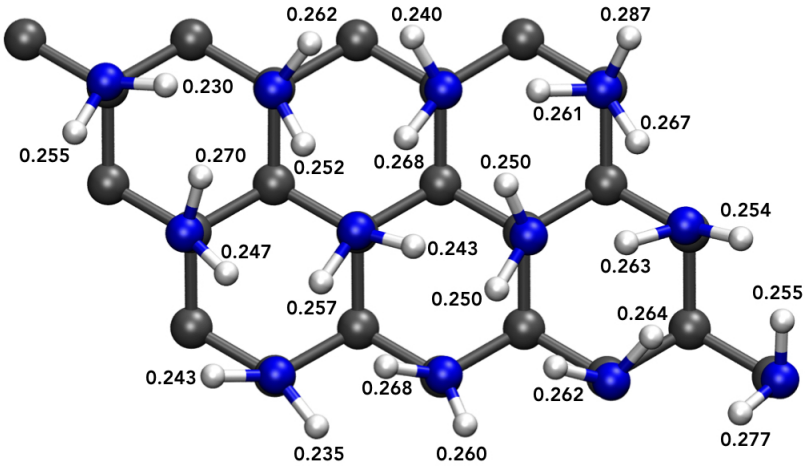

Figure S2: Schematic representation of top view, graphamine (4×3) supercell with an excess proton (carbons in gray, nitrogens in blue, hydrogens in white). DDEC6 atomic partial charges of the protons are noted.

Table S2: Statistics (mean, maximum, minimum and standard deviation) of DDEC6 atomic partial charges of protonated graphamine in comparison to the protonated 1-D hydroxylated graphane[2]

Quantity	Graphamine (this work)	1-D hydroxylated graphane[2]
$\overline{q}$	0.257	0.380
$q_{\max}$	0.287	0.404
$q_{\min}$	0.229	0.3527
q_{σ}	0.013	0.02

Table S3: DDEC6 partial charges for protons of amine groups (coordinates in Cartesian format) of protonated graphamine shown in Figure S2

x	y	z	q
0.089106	3.190138	4.418300	0.269171
-3.741856	6.902757	4.294100	0.243256
0.432799	1.610127	4.418560	0.246854
1.718076	3.723220	4.305420	0.252748
1.812217	5.348050	4.385620	0.262284
-2.205284	6.075514	4.271940	0.235236
1.978178	1.530945	4.298580	0.256931
3.039425	0.158753	4.403280	0.268328
3.368613	3.836946	4.308640	0.268068
3.449020	5.460538	4.281160	0.240221
3.475827	2.076492	4.349740	0.242828
0.263792	6.079977	4.377560	0.259875
4.831578	1.416657	4.303540	0.250217
4.975458	3.084845	4.440540	0.250497
5.528588	4.578911	4.218520	0.261013
5.776081	0.169570	4.419540	0.261804
6.945028	2.129403	4.339520	0.262915
6.987971	5.425487	4.329960	0.287465
7.115103	3.745863	4.222740	0.267854
7.341340	0.601628	4.356020	0.264667
4.757761	6.243540	4.449460	0.277082
8.804862	2.243281	4.409720	0.253956
9.319486	0.857380	4.404520	0.255595
-0.494370	4.674680	4.323420	0.229054
-1.957060	3.923983	4.356400	0.255776

Phonon Properties

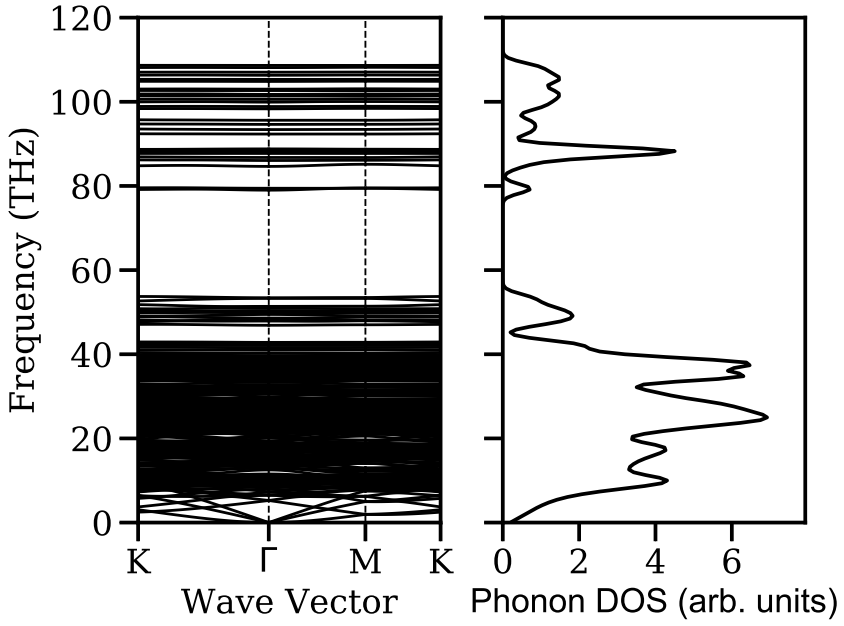

Figure S3: Phonon dispersion curves (left) and phonon density of states (right) computed with the PBE functional for a 3×3 supercell of the graphamine system shown in Figure 1 of the main text.

All the phonon bands for a 3×3 supercell of the configuration of graphamine shown in Figure 1 of the main text (total of 648 atoms) are shown in Figure S3. The phonon modes can be categorized into three regions: high, middle and low frequencies, which corresponds to the ranges ≈ 80—110 THz, ≈ 45—55 THz, ≈ 0 —40 THz, respectively. A feature of degeneracy for the optical modes can be found at several frequency ranges along the principle directions. We have also calculated the total phonon density of states (PDOS) (shown on the right of Figure S3). An analysis of the PDOS suggests that the sharp peaks at ≈ 2950 cm^{-1} (88.44 THz) corresponds to C—H stretching and the region between ≈ 3000 and 3500 cm^{-1} (90 and 105 THz) is related to the N —H stretching modes. Convergence of the size of the supercell was tested by comparing results from 2×2×1 and 3×3×1 calculations. We did not find any significant differences in the computed phonon frequencies between the supercell dimensions. Hence, a 3×3×1 supercell was used to assure accuracy of the calculations.

The phonon density of states calculations were used to generate thermodynamic properties of graphamine, specifically the Helmholtz free energy, the entropy, and the specific heat capacity, as a function of temperature. The results of these calculations are plotted in Figure S4.

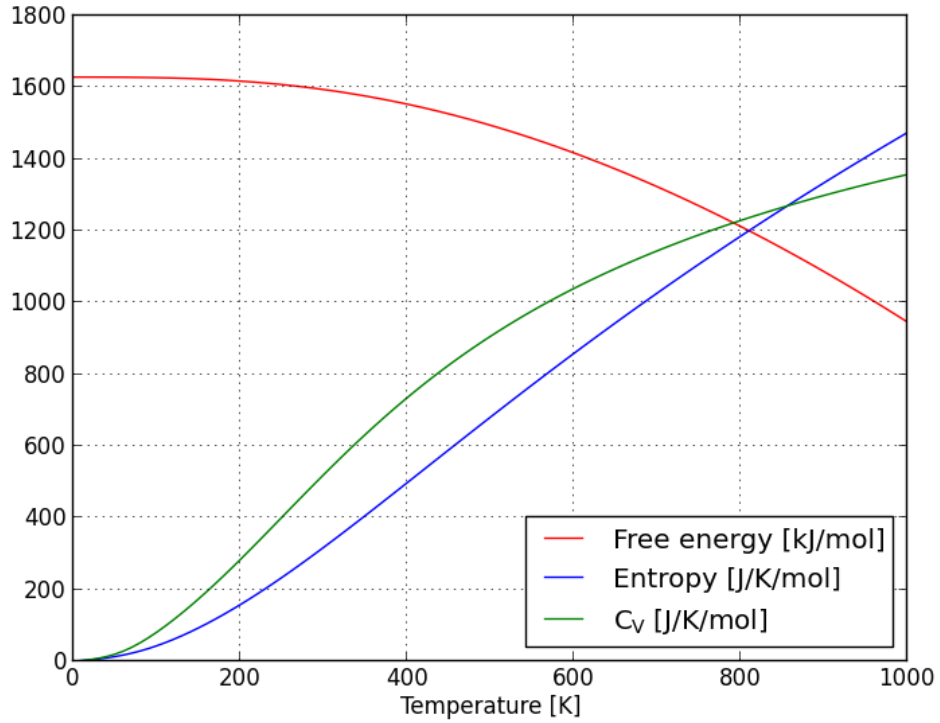

Figure S4: Thermodynamic properties for graphamine computed from the phonon density of states.

Elastic Properties

A rectangular supercell (Figure S5) was used for these calculations. A set of 20 lattice parameters were obtained by perturbing the equilibrium lattice parameters accordingly to reflect compression and tension. The atomic positions were then scaled to accommodate the new lattice parameters and the atoms were allowed to fully relax until the energy convergence tolerance of 10^{-8} eV. The elastic strain energy (E_s) per unit area was determined as a difference between electronic energy under strain ($E_s(\epsilon)$) and system at equilibrium ($E_s(\epsilon = 0)$). Under uniaxial conditions, strain was applied only along x-direction ($\epsilon_{yy} = 0$) and strain energy was fitted to a parabolic expression $E_s(\epsilon_{xx}) = C_{11}\epsilon_{xx}^2/2$. Similarly, equi-biaxial ($\epsilon_{xx} = \epsilon_{yy}$) strain energy was fitted to an expression $E_s(\epsilon_{xx}) = (C_{11} + C_{12})\epsilon_{xx}^2$. Elastic strain energies under the conditions of uniaxial and equi-biaxial strain loading were fitted to a parabolic equation and the elastic constants (C_{11}=267.09, C_{12}=34.59) were determined. A plot of the fit is shown in Figure S6.

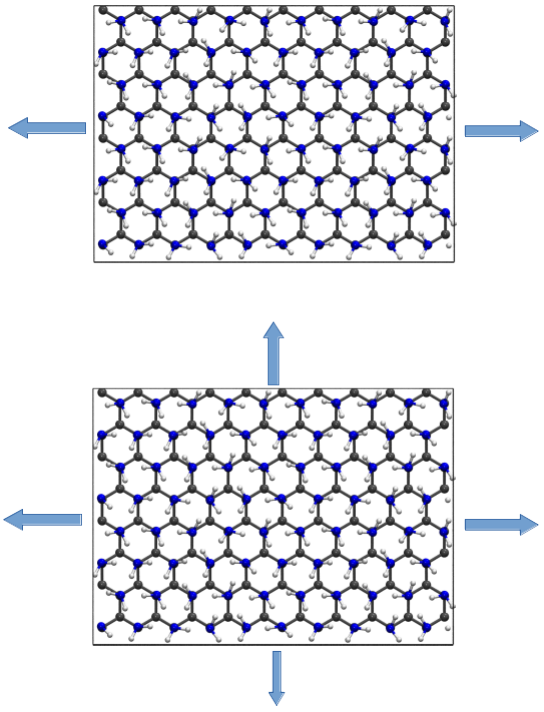

Figure S5: Equilibrium supercell used to compute elastic properties is shown under (top) uniaxial strain, (bottom) equi-biaxial strain.

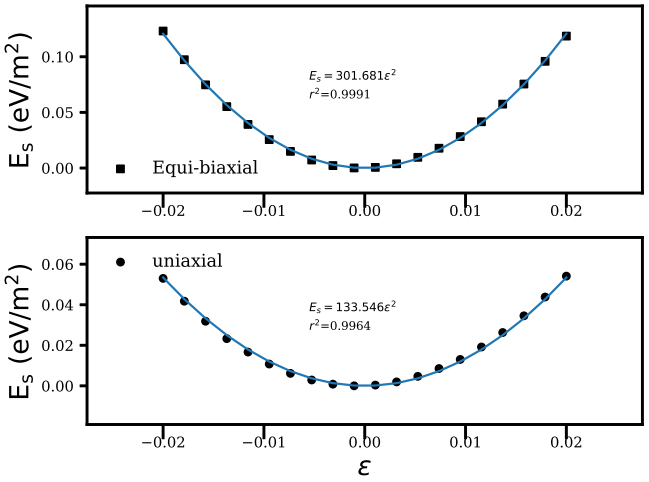

Figure S6: Parabolic fit of strain energy under uniaxial and equi-biaxial strain loading within the limits of ± 2%.

Atomic Coordinates

Fractional representation of positions for graphamine in Figure 1. of main text.

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     0.0000000000000000    0.0000000000000000   20.0000000000000000
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References

(1) Limas, N. G.; Manz, T. A. Introducing DDEC6 Atomic Population Analysis: Part 2. Computed Results for a Wide Range of Periodic and Nonperiodic Materials. *RSC Adv.* **2016**, *6*, 45727.

(2) Bagusetty, A.; Choudhury, P.; Saidi, W. A.; Derksen, B.; Gatto, E.; Johnson, J. K. Facile Anhydrous Proton Transport on Hydroxyl Functionalized Graphane. *Phys. Rev. Lett.* **2017**, *118*, 186101.