Supporting information: First-principles modeling of polysilazane derived SiCNH ceramics: insights into the organization of the free carbon phase

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Experimental Procedures

Materials

The manipulation of the polymer is carried out in an argon-filled glovebox (Jacomex, Campus-type; O_2 and H_2O concentrations kept at ≤ 0.1 ppm and ≤ 0.8 ppm, respectively) and through a vacuum/argon line by means of standard Schlenk techniques. Argon is purified by passing through a column of phosphorus pentoxide linked to the vacuum/argon line before being in contact with the different compounds. The cleaned glassware is stored in an oven at 95 °C overnight before being connected to the vacuum/argon line, assembled and pumped under vacuum for 30 min and then filled with argon. The polysilazane, the Durazane™ 1800, is provided in a 1 L container by durXtreme GmbH, Ulm (Germany) and then stored in a fridge and used as-received. It comes in the form of a very slightly yellowish transparent viscous liquid. Its elemental analysis gave the following element contents: Si, 41.3; C, 27.3; N, 22.7; H, 8.3; O, 0.4. $[Si_{1.0}C_{1.5}N_{1.1}H_{5.5}]_n$ (Normalized to total 100 wt.% (totals of wt.% was 98.9 wt.%) and reference to $Si_{1.0}$. Oxygen content (below 2 wt.%) omitted in the empirical formulae).

Attenuated total reflectance (ATR)-Fourier Transform Infrared (FTIR) spectroscopy allowed to characterize the bond features involved with Durazane™ 1800: FTIR (ATR/cm^{-1}): ν(N–H) = 3381 (s), ν (C–H in vinyl) = 3058 (m), ν (C–H in methyl) = 2954 (s), 2902 (m) and 2848 (w), ν (Si–H) = 2123 (s), δ (C=C) = 1594 (w), δ (=C–H) = 1405 (w), δ (Si–CH_3) = 1251 (m), δ(N–H): 1169 (s), δ (C=C/=CH_2) = 947 (w), ν (N–Si–N) = 897 (vs), δ (Si–CH_3) = 787 (m).

Polysilazane pyrolysis

In the glove-box, a controlled quantity of the Durazane®1800 is introduced in an alumina boat to be then put in a sealed tube in order to prevent any oxygen contamination of the sample during the transfer from the glove-box to the furnace. The sealed tube is introduced and then open into a silica tube from a horizontal furnace (Thermoconcept® ROK70/500/11) in flowing argon and the alumina boat containing the precursor powders is pushed to the heat zone of the furnace. The tube is then evacuated (0.1 mbar) for 30 min and refilled with nitrogen (99.99%) to atmospheric pressure. Subsequently, the sample is subjected to a cycle of ramping of 5 °C·min^{-1} to 1000 °C in flowing argon (dwelling time of 2 h). A constant flow (120 mL·min^{-1}) of nitrogen is passed through the tube during the pyrolysis cycle. After cooling in flowing argon, the SiCNH compound is recovered in the sealed tube under flowing argon in order to prevent any oxygen contamination during the transfer from the furnace to the glove-box.

PDF measurements

The atomic pair distribution functions $G(r)$ of the sample was obtained by X-ray total scattering. Measurements were performed at room temperature with a dedicated laboratory setup based on a Bruker D8 advance diffractometer equipped with a silver sealed tube ($\lambda = 0.559422$ Å) and a rapid LynxEye XE-T detector. This setup was modified to maximize collected intensities, minimize spurious signals from the empty environment and to obtain good counting statistics up to a large scattering vector length of 21.8 $Å^{-1}$. Fifty milligrams of powder were placed in a thin-walled (0.01 mm) borosilicate glass capillary with an inner diameter of 1.16 mm. The value of μR (where R is the radius of the capillary and μ is the linear attenuation coefficient of the sample) was estimated, based on precise measurements of the mass and dimensions of the samples, to be approximately 0.1, resulting in a very limited effect of absorption corrections. Once sealed, the capillary was mounted on a goniometric head and adjusted so that its axis coincides with the goniometer axis of the diffractometer. The data acquisition consisted of several scans in the 0–152, 50–152, and 100–152 °2θ ranges with a step size of 0.01°. The scans were subsequently merged, leading to a total equivalent acquisition time of about 50 hours. Raw data were

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corrected, normalized, and Fourier transformed using a homemade software[?] to obtain the reduced atomic pair distribution functions $G(r)$. The corrections included capillary, empty environment, Compton and multiple scatterings, absorption, and polarization effects. The x-ray mass attenuation coefficients, atomic scattering factors, and Compton scattering functions needed for data correction and normalization were calculated from tabulated data provided by the DABAX database[?] . The absorption correction was evaluated using a numerical midpoint integration method where the cross section of the sample is divided into a set of small subdomains following a method similar to that proposed by Soper and Egelstaf[?] . The normalization constant was determined using the high-angle method so that the coherently scattered intensity oscillates weakly around the sample's average atomic scattering factor at high values of the scattering vector length (from $k_{\max}/2$ to $k_{\max}$).

Supplementary figures and tables

Table S 1 Faber-Ziman coefficients for for different atom pairs.

Bond Type	**Value**
Si-Si	0.3790
Si-C	0.1080
Si-N	0.1242
Si-H	0.003079
C-C	0.03159
C-N	0.03642
C-H	0.0008717
N-N	0.04213
N-H	0.001017
H-H	0.00007783

Table S 2 Cutoff distances (Å) used to determine the coordination numbers and the atomic local environments.

	Si	C	N	H
Si	2.50	2.25	2.15	1.70
C	2.25	1.80	1.75	1.30
N	2.15	1.75	1.80	1.25
H	1.70	1.30	1.25	1.00

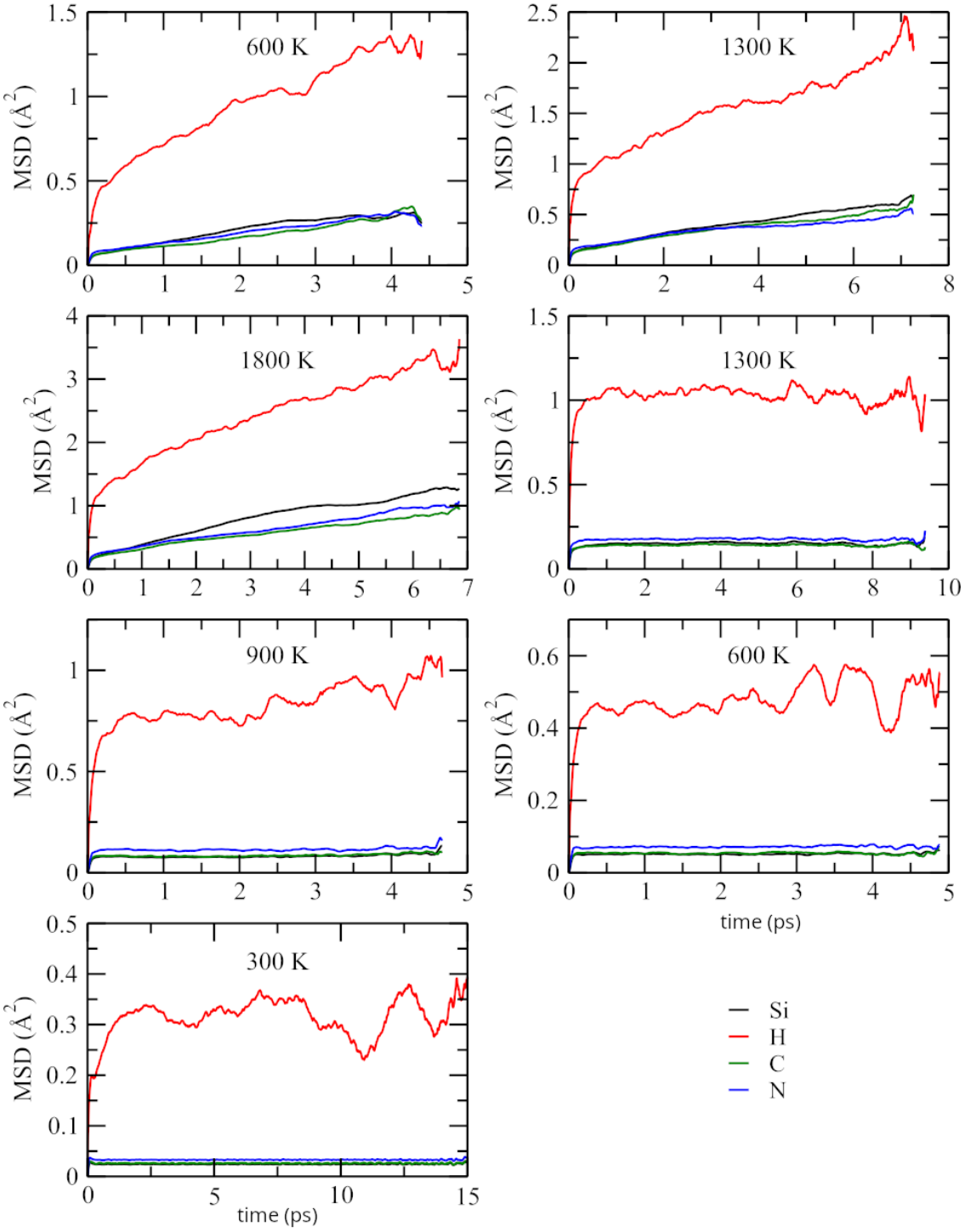

Fig. S 1 Atomic mean square displacement at various temperatures for the SiCNH200 model.

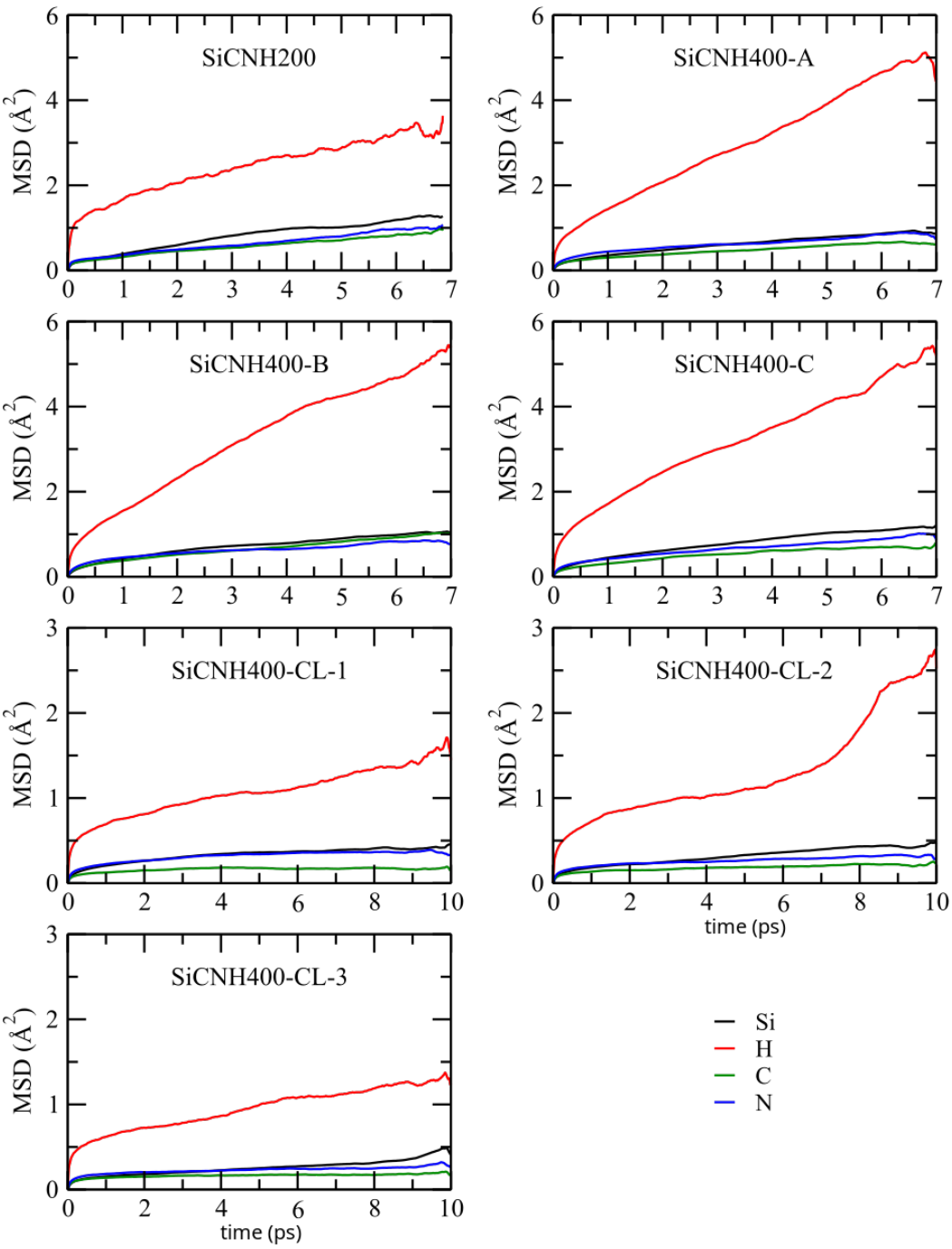

Fig. S 2 Atomic mean square displacement during the T = 1800 K stage of the thermal cycle for models SiCNH200, SiCNH400-A, SiCNH400-B and SiCNH400-C and during T = 1100 K step for models SiCNH400-CL-1, SiCNH400-CL-2 and SiCNH400-CL-3. The MSD increase at 8 ps for SiCNH400-CL-2 is attributed to the jump of an hydrogen atom crossing a small pore to stabilize an undercoordinated silicon atom.

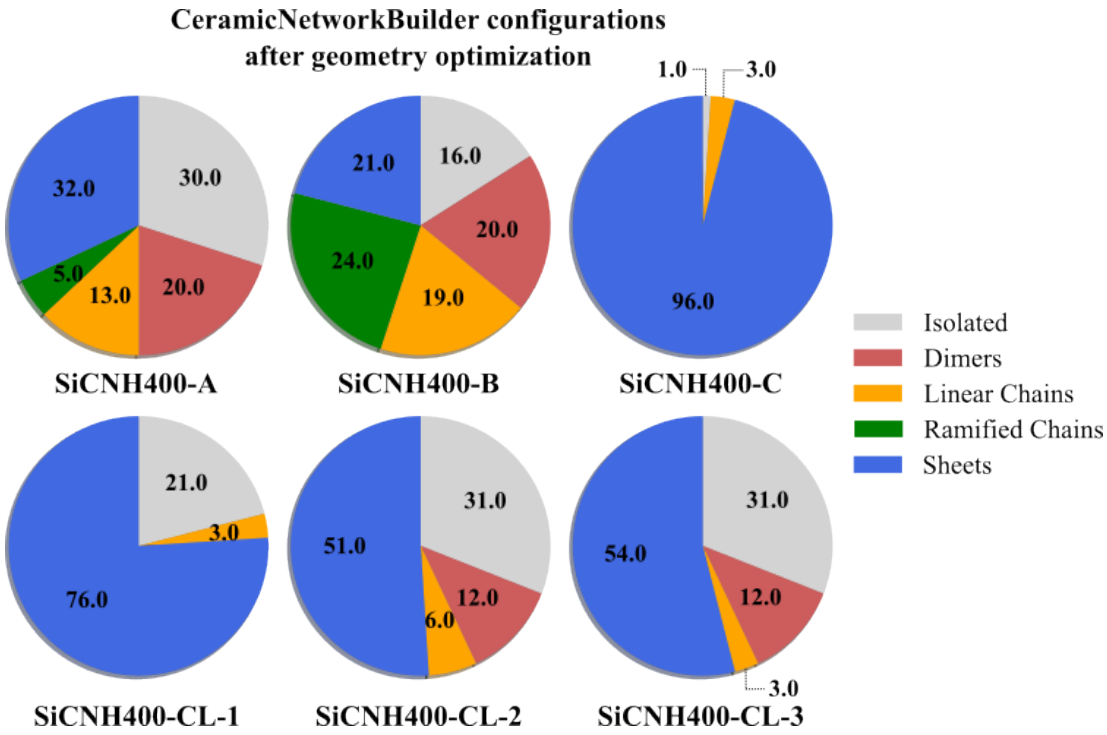

Fig. S 3 Distribution of carbon atoms in the 400-atoms models depending on their local environment after DFT geometry optimization of the atomic configurations generated by CeramicNetworkBuilder. 5 categories are drawn: atoms isolated in the amorphous ceramic network (only bonded to Si, N or H), carbon dimers, linear chains of more than 3 atoms, ramified chains and graphitic sheets. We consider a carbon cluster as a graphitic sheet if it contains at least 1 carbon cycle of more than three atoms.

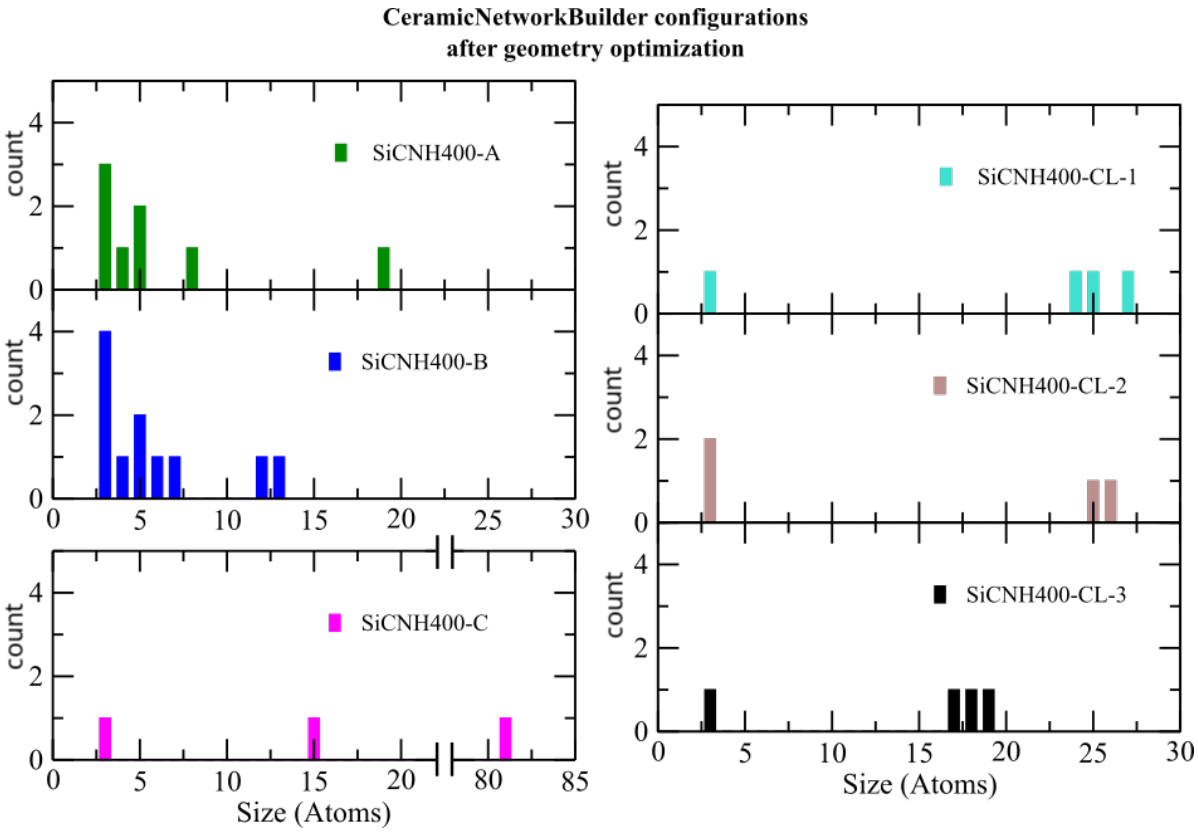

Fig. S 4 Carbon clusters sizes histogram after DFT geometry optimization of the atomic configurations generated by CeramicNetworkBuilder for the 400-atoms models of this study. Only cluster containing more than 3 atoms are shown.

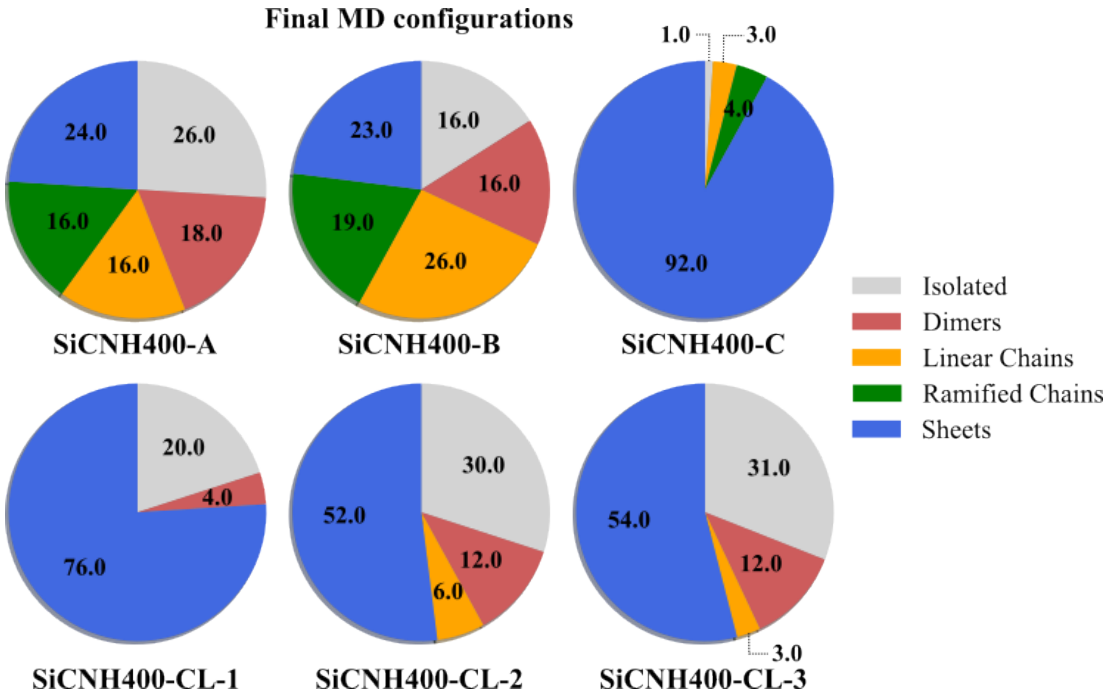

Fig. S 5 Distribution of carbon atoms in the 400-atoms models depending on their local environment after the molecular dynamics annealing thermal cycles. 5 categories are drawn: atoms isolated in the amorphous ceramic network (only bonded to Si, N or H), carbon dimers, linear chains of more than 3 atoms, ramified chains and graphitic sheets. We consider a carbon cluster as a graphitic sheet if it contains at least 1 carbon cycle of more than three atoms.

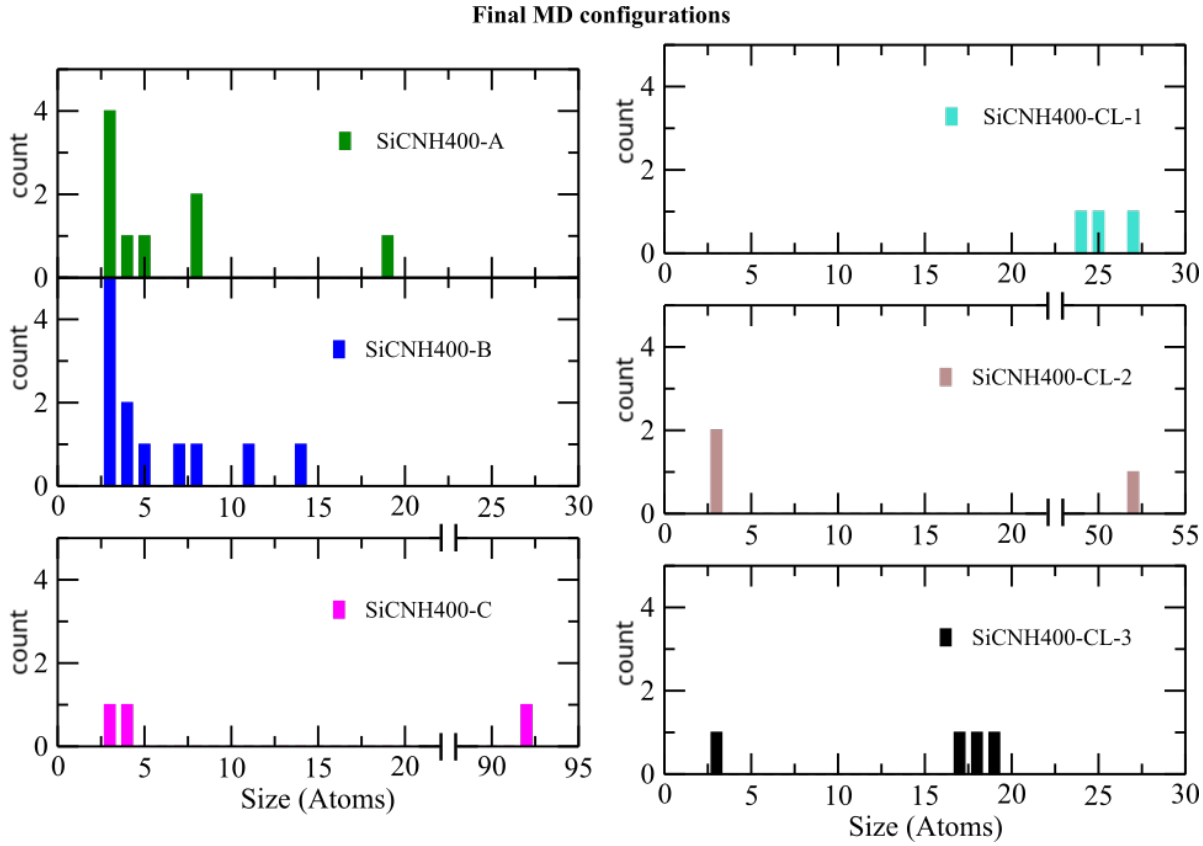

Fig. S 6 Carbon clusters sizes histogram after molecular dynamics thermal annealing cycle for the 400-atoms models of this study. Only cluster containing more than 3 atoms are shown.

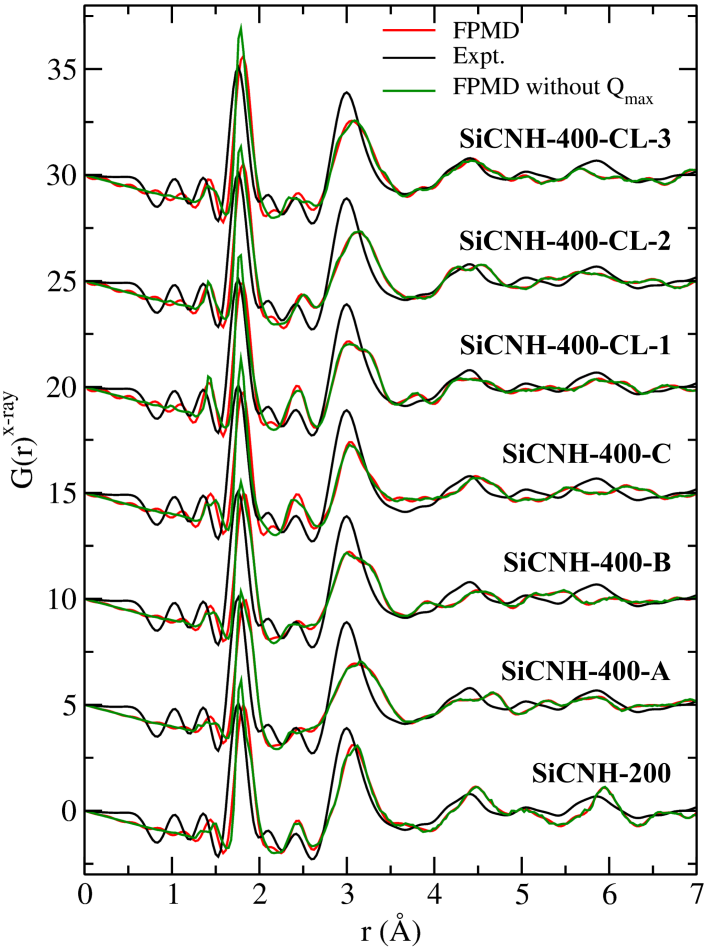

Fig. S 7 Experimental total pair distribution function compared to that computed on SiCNH200, SiCNH400-A, SiCNH400-B, SiCNH400-C, SiCNH400-CL-1, SiCNH400-CL-2 and SiCNH400-CL-3 with and without Q_{max} truncation.

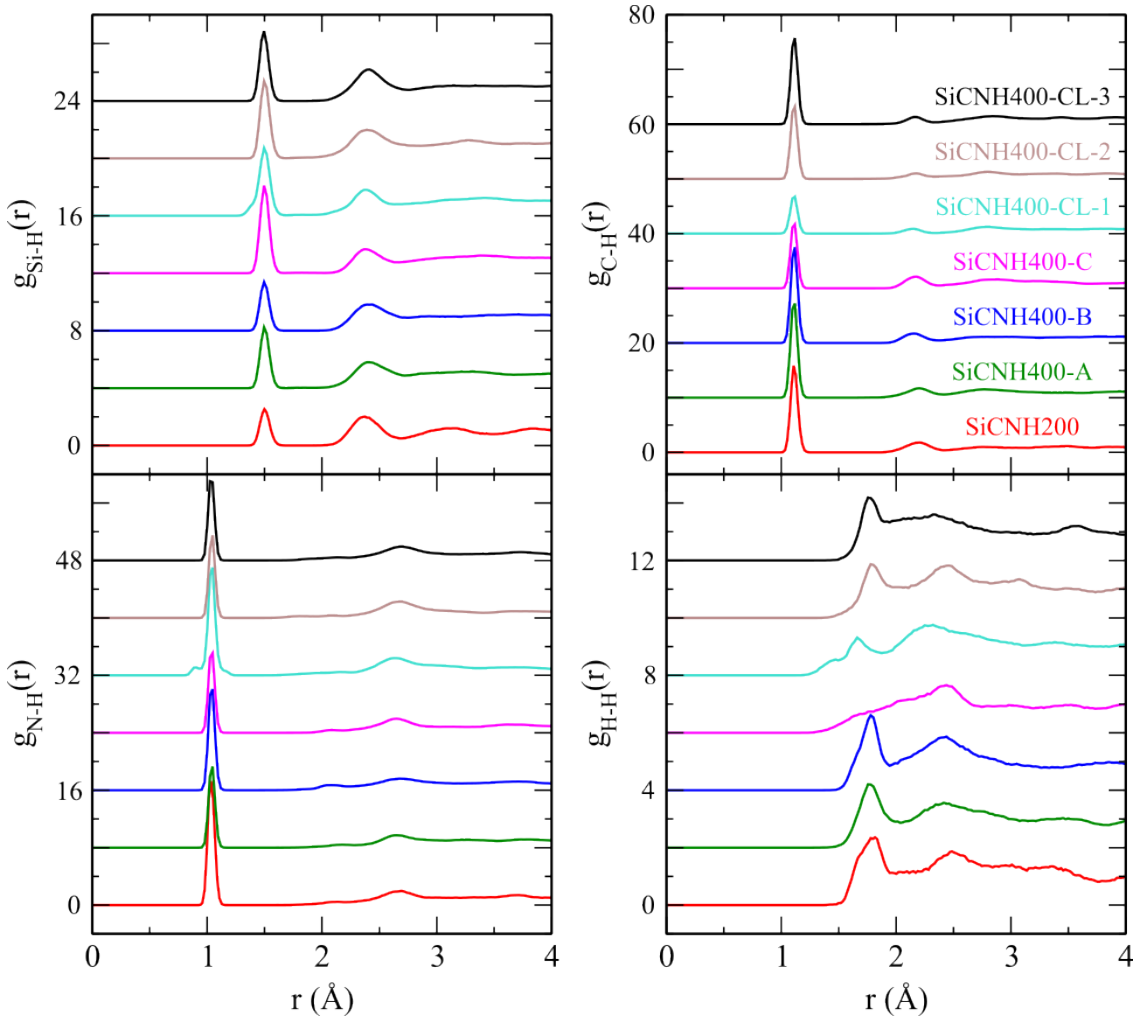

Fig. S 8 Partial pair distribution functions obtained for the seven models of this study on pair containing hydrogen.

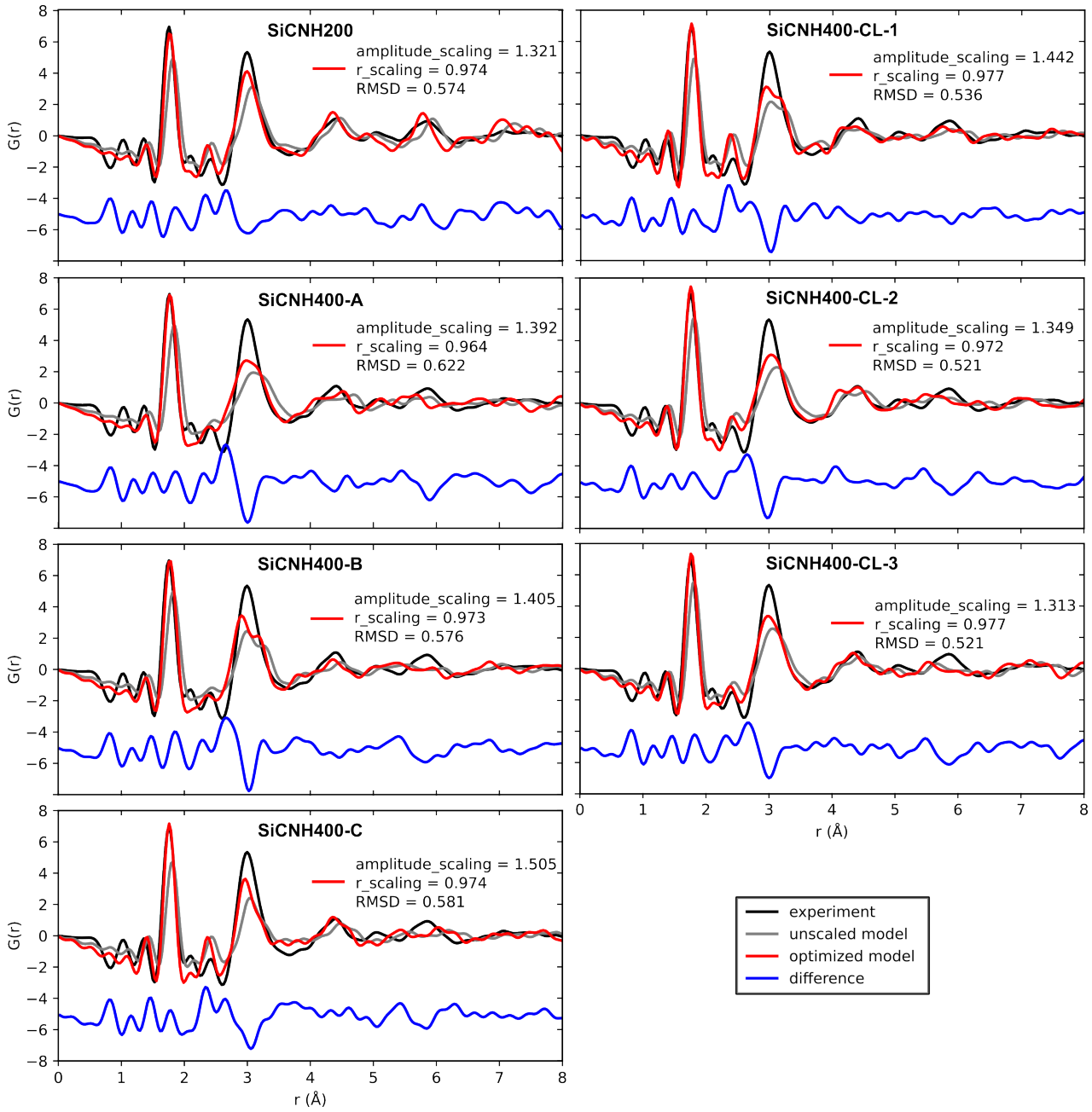

Fig. S 9 Total X-ray scattering PDF data simulated for all SiCNH PDC models studied in this work, and compared to experimental data (in black). Data in grey are the raw simulated PDFs. Data in red correspond to simulated PDFs wherein an amplitude scaling factor and a r-scaling factor have been optimized for best match to the experiment. The corresponding scaling factor and RMSE are indicated in the legend. Difference between scaled-optimized simulated and experimental PDF is shown below, in blue.

Table S 3 Local environment of atoms in SiCNH400-A. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0.0		1.8		9.1		75.7		13.4	
	Other	0.0	Other	1.8	Other	9.1	$Si-C_2N_2$	16.2	$Si-SiC_2N_2$	3.8
							$Si-CN_3$	15.5	Other	9.6
							$Si-C_3N$	8.8		
							$Si-SiCN_2$	5.6		
							$Si-CN_2H$	5.5		
							$Si-N_4$	4.4		
							Other	19.6		
C atom	0		1.1		43.5		55.4		0.1	
			Other	1.1	$C-SiC_2$	11.8	$C-Si_4$	14.0	Other	0.1
					$C-Si_2C$	8.2	$C-Si_3C$	8.7		
					$C-C_3$	6.0	$C-Si_2CH$	8.0		
					C-SiCN	3.8	$C-SiC_2H$	4.9		
					C-SiCH	3.0	$C-SiCH_2$	4.0		
					$C-C_2N$	3.0	$C-Si_3H$	3.6		
					Other	7.6	Other	12.2		
N atom	0		12.5		79.9		7.6		0	
			$N-Si_2$	5.2	$N-Si_3$	55.5	$N-Si_3H$	3.7		
			N-SiC	7.3	$N-Si_2C$	12.5	Other	3.9		
					$N-Si_2H$	9.9				
					Other	2.1				
H atom	100.0		0.0		0		0		0	
	H-C	44.7	Other	0.0						
	H-Si	32.9								
	H-N	22.4								

Table S 4 Local environment of atoms in SiCNH400-B. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0.6		0.9		11.1		71.7		15.7	
	Other	0.6	Other	0.9	Other	11.1	$Si\text{-}CN_3$	11.8	$Si\text{-}SiCN_3$	5.9
							$Si\text{-}C_2N_2$	11.5	Other	9.8
							$Si\text{-}SiCN_2$	10.5		
							$Si\text{-}SiC_2N$	6.9		
							$Si\text{-}N_4$	4.0		
							Si-SiCNH	3.4		
							$Si\text{-}C_3N$	3.1		
							$Si\text{-}CN_2H$	3.1		
							Other	17.4		
C atom	0		0.1		55.3		44.6		0.0	
			Other	0.1	$C\text{-}SiC_2$	17.9	$C\text{-}Si_2C_2$	9.0	Other	0.0
					$C\text{-}Si_2C$	16.9	$C\text{-}SiC_2H$	6.9		
					$C\text{-}C_3$	6.0	$C\text{-}Si_3C$	5.1		
					C-SiCH	4.0	$C\text{-}Si_4$	4.7		
					C-SiCN	3.1	$C\text{-}Si_3H$	4.0		
					Other	7.4	$C\text{-}Si_2CH$	3.0		
							$C\text{-}Si_2H_2$	3.0		
							Other	8.9		
N atom	0		6.6		84.6		8.8		0	
			$N\text{-}Si_2$	5.4	$N\text{-}Si_3$	58.4	Other	8.8		
			Other	1.2	$N\text{-}Si_2H$	13.0				
					$N\text{-}Si_2C$	8.3				
					Other	5.0				
H atom	100.0		0		0		0		0	
	H-C	44.7								
	H-N	28.9								
	H-Si	26.3								

Table S 5 Local environment of atoms in SiCNH400-C. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0.0		2.4		10.3		77.0		10.3	
	Other	0.0	Other	2.4	Other	10.3	$Si\text{-}N_4$	12.3	Other	10.3
							$Si\text{-}SiCN_2$	8.6		
							$Si\text{-}SiN_3$	8.1		
							$Si\text{-}Si_2N_2$	6.9		
							$Si\text{-}N_3H$	4.9		
							$Si\text{-}CN_3$	4.7		
							$Si\text{-}SiN_2H$	3.6		
							$Si\text{-}C_2N_2$	3.3		
							Other	24.5		
C atom	0		0		63.6		36.4		0	
					$C\text{-}C_3$	26.1	$C\text{-}Si_2C_2$	5.7		
					$C\text{-}SiC_2$	22.3	$C\text{-}SiC_2H$	5.0		
					$C\text{-}C_2H$	5.0	$C\text{-}SiC_3$	4.9		
					$C\text{-}Si_2C$	4.2	$C\text{-}Si_3C$	4.9		
					C-SiCH	3.0	$C\text{-}Si_2CH$	4.0		
					Other	3.0	$C\text{-}C_3H$	4.0		
							$C\text{-}C_4$	4.0		
							Other	3.9		
N atom	0		2.2		93.8		4.0		0	
			Other	2.2	$N\text{-}Si_3$	72.9	Other	4.0		
					$N\text{-}Si_2H$	12.7				
					$N\text{-}Si_2C$	5.2				
					Other	3.1				
H atom	100.0		0.0		0		0		0	
	H-Si	47.3	Other	0.0						
	H-C	30.3								
	H-N	22.4								

Table S 6 Local environment of atoms in SiCNH400-CL-1. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0.0		4.0		7.2		79.7		8.8	
	Other	0.0	Other	4.0	Other	7.2	$Si\text{-}N_3C$	9.9	Other	8.8
							$Si\text{-}SiCN_2$	9.0		
							$Si\text{-}N_3H$	7.4		
							$Si\text{-}N_4$	7.4		
							$Si\text{-}SiN_3$	6.9		
							$Si\text{-}C_2N_2$	6.4		
							Si-SiCNH	4.5		
							$Si\text{-}Si_2C_2$	4.2		
							$Si\text{-}Si_2CN$	3.6		
							$Si\text{-}SiN_2H$	3.1		
							$Si\text{-}C_3N$	3.1		
							Other	14.1		
C atom	0		0.1		71.6		28.2		0	
			Other	0.1	$C\text{-}C_3$	40.0	$C\text{-}Si_3H$	8.9		
					$C\text{-}SiC_2$	21.0	$C\text{-}Si_4$	6.7		
					$C\text{-}C_2H$	3.0	$C\text{-}Si_2C_2$	5.0		
					Other	7.6	Other	7.7		
N atom	0		3.8		91.0		5.2		0	
			$N\text{-}Si_2$	3.8	$N\text{-}Si_3$	68.1	Other	5.2		
					$N\text{-}Si_2H$	15.6				
					$N\text{-}Si_2C$	4.2				
					Other	3.1				
H atom	100.0		0		0		0		0	
	H-Si	43.4								
	H-N	30.3								
	H-C	26.3								

Table S 7 Local environment of atoms in SiCNH400-CL-2. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0.1		4.0		9.1		71.0		15.7	
	Other	0.1	Other	4.0	Other	9.1	$Si-N_3C$	16.1	$Si-SiC_2N_2$	3.6
							$Si-C_2N_2$	8.5	$Si-SiCN_3$	3.5
							$Si-C_3N$	8.3	Other	8.6
							$Si-CN_2H$	7.2		
							$Si-N_4$	6.8		
							$Si-SiCN_2$	3.4		
							$Si-N_3H$	3.1		
							Other	17.6		
C atom	0		1.0		58.7		40.3		0	
			Other	1.0	$C-C_3$	27.5	$C-Si_4$	11.9		
					$C-SiC_2$	16.0	$C-Si_3H$	7.0		
					$C-Si_2C$	7.0	$C-Si_2CH$	7.0		
					$C-Si_3$	5.1	$C-Si_2H_2$	3.0		
					Other	3.0	Other	11.4		
N atom	0		3.4		87.5		7.3		0	
			$N-Si_2$	3.4	$N-Si_3$	70.9	$N-Si_4$	3.9		
					$N-Si_2H$	11.2	$N-Si_3H$	3.4		
					Other	5.4	Other	1.8		
H atom	100.0		0.0		0		0		0	
	H-Si	43.4								
	H-C	34.2								
	H-N	22.4								

Table S 8 Local environment of atoms in SiCNH400-CL-3. For each coordination number, the other sections gather all the configurations accounting for less than 3% of the local environments of the atoms.

	Fraction [%]									
Coord. number	l=1		l=2		l=3		l=4		l≥ 5	
Si atom	0		1.9		7.2		82.7		8.3	
			Other	1.9	Other	7.2	$Si-CN_3$	14.5	Other	8.3
							$Si-N_4$	11.2		
							$Si-C_2N_2$	8.8		
							$Si-SiC_2N$	8.1		
							$Si-SiCN_2$	5.4		
							$Si-CN_2H$	5.2		
							$Si-SiN_3$	4.6		
							Si-SiCNH	4.1		
							$Si-C_3N$	3.9		
							$Si-C_2NH$	3.1		
							Other	13.7		
C atom	0		2.0		56.1		41.9		0	
			Other	2.0	$C-C_3$	20.0	$C-Si_3H$	11.0		
					$C-SiC_2$	15.0	$C-Si_4$	8.0		
					$C-Si_2C$	12.0	$C-Si_2CH$	3.0		
					$C-Si_3$	5.0	$C-SiC_2H$	3.0		
					Other	4.1	$C-Si_2H_2$	3.0		
							$C-SiC_3$	3.0		
							Other	11.0		
N atom	1.0		4.4		91.2		3.3		0	
	Other	1.0	$N-Si_2$	3.3	$N-Si_3$	68.3	Other	3.3		
			Other	1.1	$N-Si_2H$	15.7				
					$N-Si_2C$	5.2				
					Other	2.1				
H atom	100.0		0		0		0		0	
	H-C	40.8								
	H-Si	36.8								
	H-N	22.4								