Supporting Information

Pressure-induced polymerization of 1,4-difluorobenzene towards fluorinated diamond nanothreads

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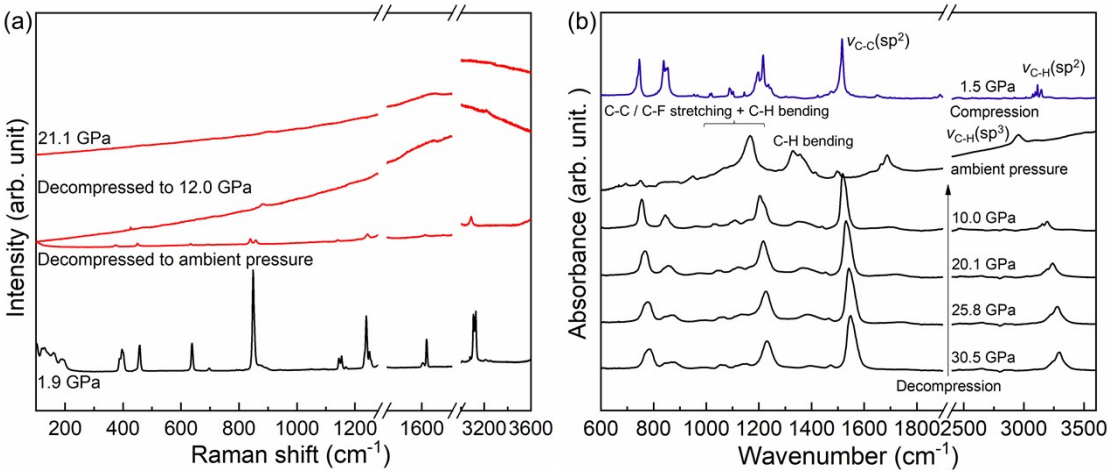

Fig. S1 (a) Raman spectra of 1,4-DFB upon decompression. (b) IR spectra of 1,4-DFB upon decompression.

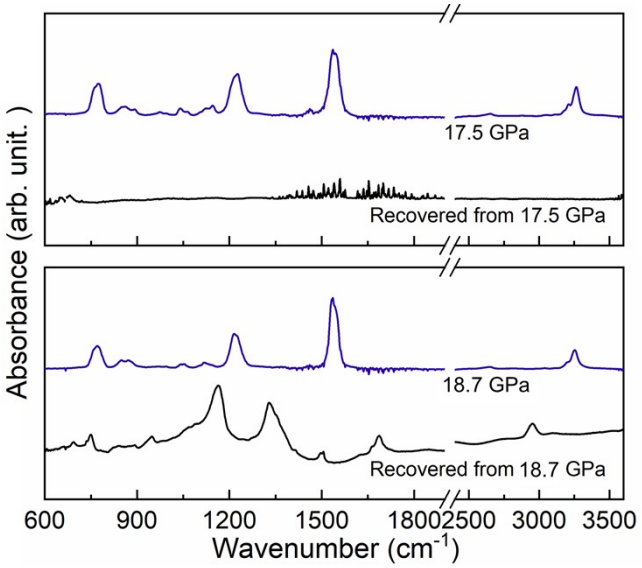

Fig. S2 IR spectra of samples recovered from 17.5 and 18.7 GPa. At ambient pressure, the raw material (1,4-DFB) was volatilized.

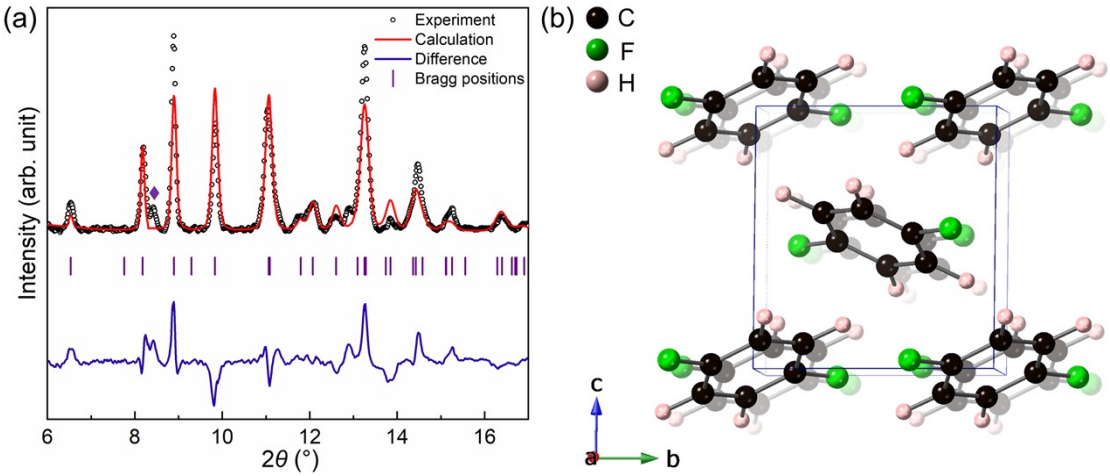

Fig. S3 (a) Rietveld refinement plot of 1,4-DFB at 4.3 GPa with R_{wp} at 13.49 %. To construct the complete 1,4-DFB molecule as a rigid body, we changed the space group to $P2_1$ during the refinement process. The peak marked with purple diamond originates from an unknown impurity. (b) Structure of 1,4-DFB along the $[100]$ axis at 4.3 GPa and room temperature.

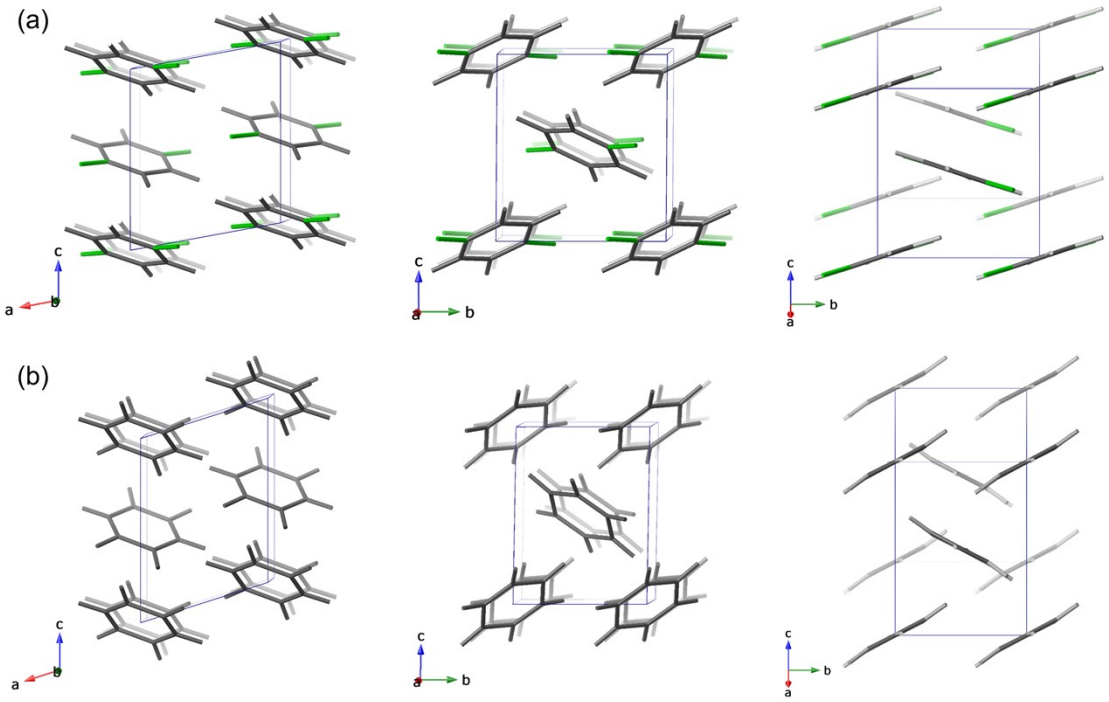

Fig. S4 (a) Crystal structures of 1,4-DFB at 9.4 GPa along the [010], [100] and [803] axes, respectively. (b) Crystal structures of d_6-benzene at 9.2 GPa along the [010], [100] and [803] axes, respectively.

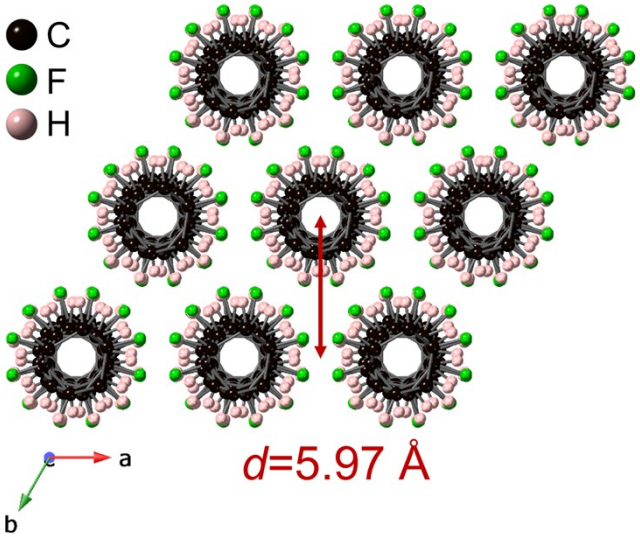

Fig. S5 A schematic diagram of the proposed packing of product, including a hypothetical intrathread structure (polytwistane model, based on the benzene-derived DNTh model by X. Li et al.[1]) for simulating the shape of the thread. After theoretical optimization, the *d*-spacing (the interplanar distance between the layers formed by DNThs) is 5.97 Å, which shows good agreement with our SAED results.

Table S1. The experimental Raman results (4.2 GPa, room temperature) and the calculated data (4.3 GPa, 0 K) with corresponding vibrational assignments. *ν*, *γ*, and *β* represent the stretching, out-of-plane bending, and in-plane bending vibration, respectively.

Experiment (cm^{-1})	Calculation (cm^{-1})	Assignments
391	396	$\gamma_{C\text{-}C\text{-}C}$
408	400	$\gamma_{C\text{-}C\text{-}C}$
458	457	$\beta_{C\text{-}C\text{-}C}$
639	631	$\beta_{C\text{-}C}$
701	701	$\gamma_{C\text{-}C\text{-}C}$
853	855	$\beta_{C\text{-}C\text{-}C}$
1164	1196	$\beta_{C\text{-}H}$
1243	1247	$\beta_{C\text{-}H}$
1259	1261	$\nu_{C\text{-}F}$

1610	1611	$\nu_{C\text{-}C}$
1628	1627	$\nu_{C\text{-}C}$
3114	3110	$\nu_{C\text{-}H}$
3133	3112	$\nu_{C\text{-}H}$

Table S2. The experimental IR results (4.3 GPa, room temperature) and the calculated data (4.3 GPa, 0 K) with the assignments. *ν*, *γ*, and *β* represent the stretching, out-of-plane bending, and in-plane bending vibration, respectively.

Experiment (cm^{-1})	Calculation (cm^{-1})	Assignments
736	736	$\beta_{C\text{-}C}$
834	816	$\gamma_{C\text{-}H}$
845	822	$\gamma_{C\text{-}H}$
948	933	$\gamma_{C\text{-}H}$
1012	1001	$\beta_{C\text{-}C}$
1085	1053	$\beta_{C\text{-}H}$
1183	1191	$\beta_{C\text{-}C}$
1203	1193	$\nu_{C\text{-}F}$
1418	1411	$\nu_{C\text{-}C}$
1494	1492	$\nu_{C\text{-}C}$
1508	1497	$\nu_{C\text{-}C}$
3077	3086	$\nu_{C\text{-}H}$
3100	3106	$\nu_{C\text{-}H}$
3136	3108	$\nu_{C\text{-}H}$

Table S3. Atomic coordinates of 1,4-DFB at 4.3 GPa. They were obtained by geometry optimization using DFT, based on the structure determined by Rietveld refinement.

atom	x	y	z
C1	0.6702	0.6656	0.7600
C2	0.7396	0.4590	0.8519
C3	0.5643	0.2892	0.8420
C4	0.3282	0.3345	0.7395
C5	0.2588	0.5409	0.6472
C6	0.4342	0.7108	0.6571
F1	0.8403	0.8319	0.7741
F4	0.1580	0.1684	0.7263
H2	0.9275	0.4319	0.9347
H3	0.6117	0.1225	0.9120
H5	0.0709	0.5679	0.5643
H6	0.3871	0.8774	0.5869

Table S4. Atomic coordinates of 1,4-DFB at 9.4 GPa. They were obtained by geometry optimization using DFT, based on the structure determined by Rietveld refinement.

atom	x	y	z
C1	1.1725	0.5377	0.2580
C2	1.2444	0.3258	0.3506
C3	1.0663	0.1520	0.3431
C4	0.8253	0.2002	0.2422
C5	0.7535	0.4119	0.1491
C6	0.9317	0.5857	0.1567
F1	1.3463	0.7075	0.2714
F4	0.6513	0.0305	0.2299
H2	1.4362	0.2984	0.4327
H3	1.1160	-0.0196	0.4120
H5	0.5618	0.4390	0.0666

H6	0.8822	0.7573	0.0879

Table S5. Atomic coordinates of d_6-benzene at 9.2 GPa. They were obtained by geometry optimization using DFT, based on the structure determined by Rietveld refinement.

atom	x	y	z
C1	-0.2754	-0.0121	-0.1218
C2	-0.0907	-0.2282	-0.1315
C3	-0.1902	0.2057	-0.0027
D1	-0.4822	-0.0457	-0.2140
D2	-0.1321	-0.3877	-0.2343
D3	-0.3504	0.3505	0.0119

References

1. X. Li, M. Baldini, T. Wang, B. Chen, E.S. Xu, B. Vermilyea, V. H. Crespi, R. Hoffmann, J. J. Molaison, C. A. Tulk, M. Guthrie, S. Sinogeikin and J. V. Badding, *J. Am. Chem. Soc.,* 2017, **139,** 16343-16349.