Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information:

Pressure-driven electronic phase transition in the high-pressure phase of Nitrogen-rich 1-H Tetrazoles

Ying Liu,[†a,b] Huifang Du,[†c] Leiming Fang,[†d] Fei Sun,[e] Haipeng Su,[a] Zhongxue Ge,[*a] Wei Guo,[*c] and Jinlong Zhu[*b,e]

[a]*Xi'an Modern Chemistry Research Institute, Xi'an, 710065, China*
[b]*Department of Physics, Shenzhen Engineering Research Center for Frontier Materials Synthesis at High Pressures, Southern University of Science and Technology, Shenzhen 518055, China*
[c]*Beijing Key Laboratory of Nanophotonics and Ultrafine Optoelectronic Systems, School of Physics, Beijing Institute of Technology, Beijing 100081, China*
[d]*Key Laboratory for Neutron Physics, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China*[d]
[e]*Center for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing, 100094, China*

[†]Y. L., H. D. and L. F. contributed equally to this work.
*To whom correspondence may be addressed. Email: gzx204@sina.com; weiguo7@bit.edu.cn, zhujl@sustech.edu.cn.

In this study, we investigated the phase transition of 1H-tetrazole under high pressure at room temperature using in situ Raman, IR spectra, synchrotron X-ray diffraction (XRD) and Neutron diffraction techniques. Combined with first-principles calculations, we propose a possible hydrogen-bond-assisted phase transition in the high-pressure counterpart, which has not been reported in previous studies. We uncover the novel electronic and stereo-chemical evolution of 1H-tetrazole (CN_4H_2), providing a fundamental understanding of the nitrogen-rich system and a potential pathway to find a targeted system for new-generation high-energy materials.

Table S1 Lattice parameters of 1H-tetrazole in Run I of XRD

Pressure (GPa)	a (Å)	Error	b (Å)	Error	c (Å)	Error	α (°)	Error	β (°)	Error	γ (°)	Error	V (Å^3)	Error
0.24	3.6077	0.0028	4.7098	0.004	4.9285	0.007	107.97	0.011	106.92	0.011	100.27	0.008	72.82	0.008
4.1	5.2359	0.07058	6.4303	0.07747	4.8361	0.01801	84.02	0.19041	73.19	0.15667	134.99	0.02089	98.12	0.0583
5.5	5.1298	0.0567	6.3174	0.06903	4.8005	0.01843	84.48	0.15798	72.63	0.13449	134.28	0.01926	96.82	0.05359
7.3	5.1629	0.06872	6.1958	0.06975	4.7521	0.02001	85.03	0.18071	72.10	0.15173	134.04	0.01841	93.44	0.04937
9.2	4.8642	0.05912	6.0935	0.06694	4.6554	0.01563	83.85	0.17323	73.86	0.13618	133.94	0.02536	86.00	0.04065
10.5	5.2573	0.10042	6.1150	0.08325	4.7023	0.02885	86.21	0.24399	71.35	0.20401	134.14	0.0377	93.06	0.10322
12.2	4.8609	0.06241	6.0330	0.06521	4.6523	0.01871	84.66	0.17498	73.09	0.14059	134.13	0.0259	84.56	0.06148
15.3	4.7788	0.08437	5.9054	0.07591	4.6202	0.02906	85.10	0.2081	72.29	0.16811	133.87	0.05329	80.78	0.13271
17.4	4.5434	0.08961	5.8264	0.08828	4.5745	0.03584	83.90	0.22232	73.47	0.18627	133.41	0.05975	76.00	0.09804

Table S2 Atomic coordinates of 1H-tetrazole at representative pressure points in Run I of X-ray and neutron diffraction

Pressure	0.24 GPa			4 GPa			8 GPa		
Space-group	*P*1 (one molecule in unit cell) X-ray			*P*1 (two molecules in unit cell) Neutron			*P*1 (two molecules in unit cell) Neutron		
label	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
C5	0.757(30)	0.999(27)	0.789(21)	0.52(19)	0.61(12)	0.67(8)	0.52(12)	0.61(11)	0.68(5)
N1	0.740(26)	0.025(31)	0.631(23)	0.81(7)	0.875(31)	0.40(7)	0.82(9)	0.879(29)	0.41(4)
N2	0.894(19)	0.267(17)	0.622(20)	0.63(9)	0.88(7)	0.24(8)	0.65(13)	0.88(10)	0.24(7)
N3	0.824(15)	0.265(12)	0.304(18)	0.23(6)	0.61(10)	0.42(7)	0.24(11)	0.62(8)	0.42(4)
N4	0.436(14)	0.650(13)	0.335(23)	0.15(4)	0.44(5)	0.70(8)	0.15(5)	0.44(5)	0.70(7)
H5	0.801(fixed)	0.759(fixed)	0.439(fixed)	0.5(4)	0.55(27)	0.82(24)	0.6(3)	0.55(23)	0.83(18)
H1	0.078(fixed)	0.064(fixed)	0.958(fixed)	0.94(29)	0.98(20)	0.65(20)	0.9(3)	0.98(24)	0.64(23)
C25				0.50(12)	0.38(10)	0.33(5)	0.50(13)	0.38(8)	0.32(5)
N21				0.18(8)	0.11(3)	0.60(7)	0.17(8)	0.108(29)	0.59(4)
N22				0.33(8)	0.09(7)	0.78(8)	0.31(13)	0.08(9)	0.77(6)
N23				0.73(6)	0.34(8)	0.61(7)	0.72(7)	0.34(7)	0.61(5)
N24				0.85(4)	0.53(4)	0.33(7)	0.85(4)	0.53(4)	0.32(5)
H25				0.49(20)	0.45(14)	0.17(11)	0.49(25)	0.45(21)	0.16(12)

H21	0.06(19)	0.02(15)	0.33(14)	0.07(20)	0.02(18)	0.34(12)

Table S3 Frequencies and assignments of crystal vibration modes

Our work		Ref 1		Ref 2	Ref 3	
Raman	IR	Raman	IR	Raman	Raman	
659	663	663.7	663.1	663.9	665	γ(ring)
905	905.9	905.4	907.2	907	908	γ(C5-H5)
	937.6		937.1		938	δ(N-N=N)
947	951.5	947.2	951	947.6		δ(N-C=N)
1012.7	1011.2	1013.7	999.2 1015.1	1015	1012	ν(N1-N2)
1049.6	1050.3	1048.6	1049.6	1049	1048	ν(N3-N4)
1085.4	1085.5	1086.1	1085.3	1086.1	1082	δ(C5-H5)
1145.3	1144.5	1144.5	1145.1	1144.8	1140	δ(N1-H1)+ν(C5=N4)
1260.6	1256.4	1259.9	1259.3	1259.9	1259	ν(C5-N1)
	1331					
	1387					
1445.7 1353.3	1445 1452	1448.9	1444.8 1451.6	1445.3 1451.9	1440 1450	ν(N2=N3)
1528	1524	1530.3	1524.6	1526.3	1518	ν(C5=N4)+δ(N-H)
3154.7	3157	3158.5	3158.3	3157.1	3150	ν(C5-H5)

Table S4 Band centers of the conduction band and valence band of 1H-Tetrazole at different pressures

Pressure	Conduction band (eV)	Valence band (eV)
8 GPa	5.29	-1.45
9 GPa	5.14	-1.60
10 GPa	5.23	-1.53

Table S5 Band centers of different atoms in 1H-Tetrazole at different pressures

Pressure	C (eV)	N (eV)	H (eV)
8 GPa	-2.51	-0.23	-1.05
9 GPa	-2.58	-0.14	-1.07
10 GPa	-2.52	-0.14	-1.05

Table S6 The frequencies of 1-H Tetrazole at Gamma at 8 GPa, 9 GPa, 10GPa

Pressure(GPa)		8	9	10
Frequency(cm^{-1})	1 f	3239.691	3226.538	3243.629
	2 f	3235.231	3221.935	3238.693
	3 f	2656.292	2683.459	2610.393
	4 f	2654.338	2676.247	2605.261
	5 f	1501.029	1502.430	1503.179
	6 f	1499.620	1501.371	1502.128
	7 f	1445.809	1446.871	1449.578
	8 f	1436.909	1438.336	1440.227
	9 f	1312.865	1312.244	1319.422
	10 f	1304.011	1303.651	1309.648
	11 f	1276.154	1275.822	1282.014
	12 f	1274.719	1273.231	1280.364
	13 f	1198.843	1195.260	1206.905
	14 f	1187.458	1183.242	1194.837
	15 f	1131.800	1132.065	1140.266
	16 f	1126.522	1124.972	1134.556
	17 f	1116.592	1116.983	1122.495
	18 f	1109.091	1110.198	1111.565
	19 f	1050.392	1050.185	1057.715
	20 f	1050.060	1048.386	1055.397
	21 f	1026.487	1025.841	1032.735
	22 f	1010.137	1011.628	1014.480
	23 f	961.613	962.569	960.790
	24 f	948.276	950.450	945.027
	25 f	883.172	891.675	886.845
	26 f	882.294	889.380	885.180
	27 f	722.755	724.491	722.910
	28 f	720.512	721.420	720.398
	29 f	683.084	686.567	685.771
	30 f	679.850	683.185	682.590
	31 f	246.453	274.926	265.735
	32 f	231.503	251.633	245.791
	33 f	228.850	247.856	242.517
	34 f	212.865	238.290	228.540
	35 f	200.330	207.782	212.986
	36 f	196.068	199.146	204.382
	37 f	168.424	175.641	173.200
	38 f	152.166	159.941	159.501
	39 f	96.994	95.678	100.723
	40 f/i	0.279	0.209	0.230
	41 f/i	0.355	0.315	0.417

	$42\,f/i$	0.643	0.671	0.439

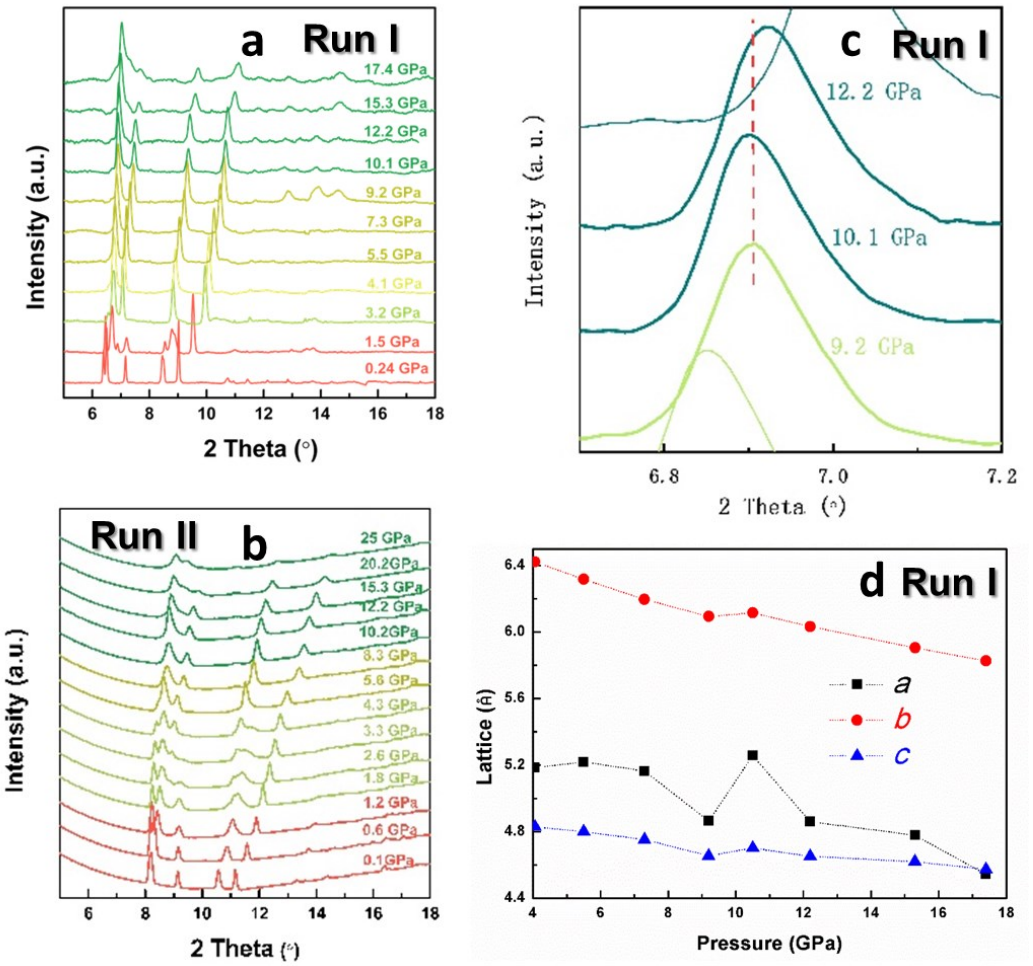

Figure S1 Diffraction patterns of X-ray and refined lattice parameters under pressure

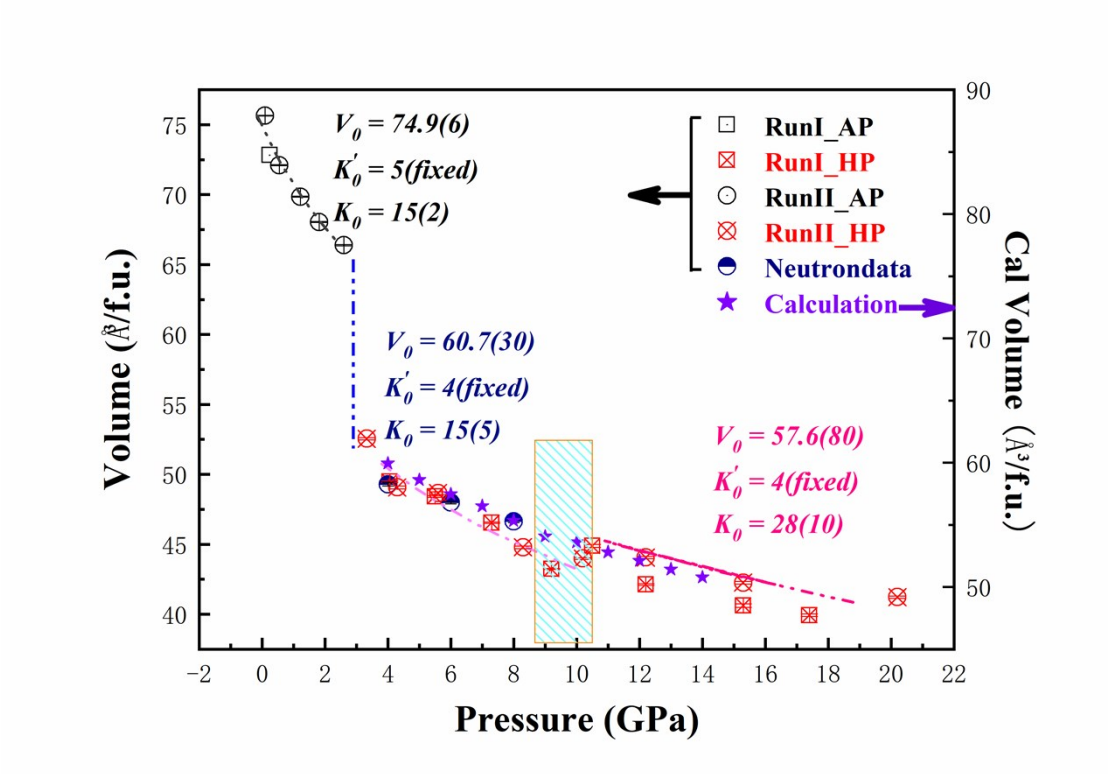

Figure S2 Refined volume of X-ray and neutron diffraction.

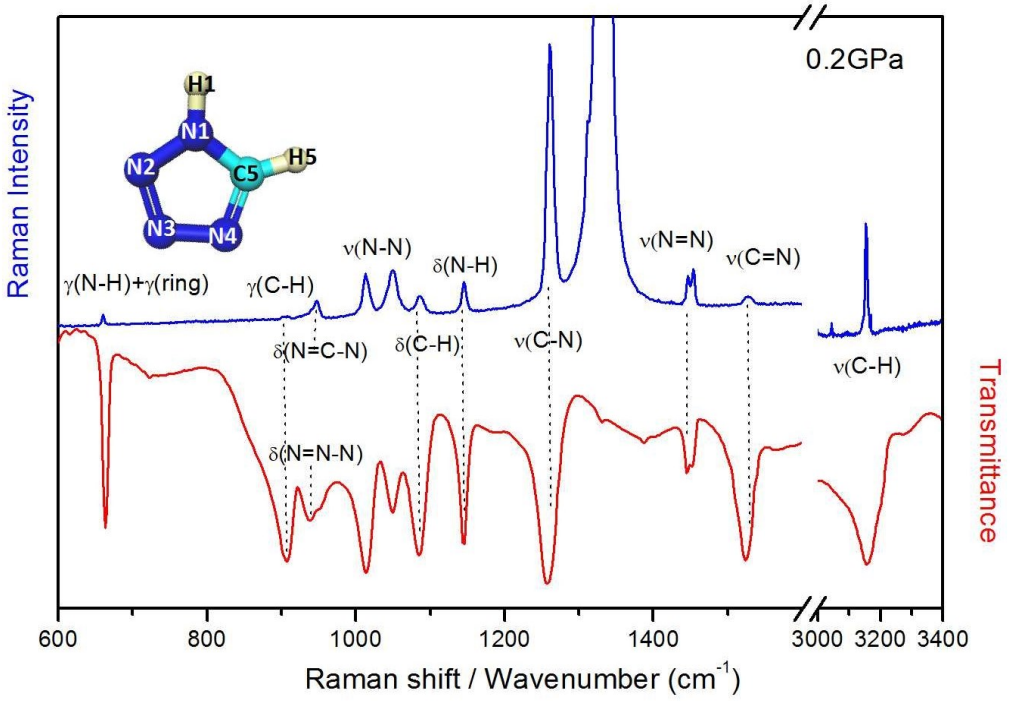

Figure S3 the Raman and IR spectra at near ambient pressure in the 600-3400 cm^{-1} region. The corresponding vibration modes were donated.

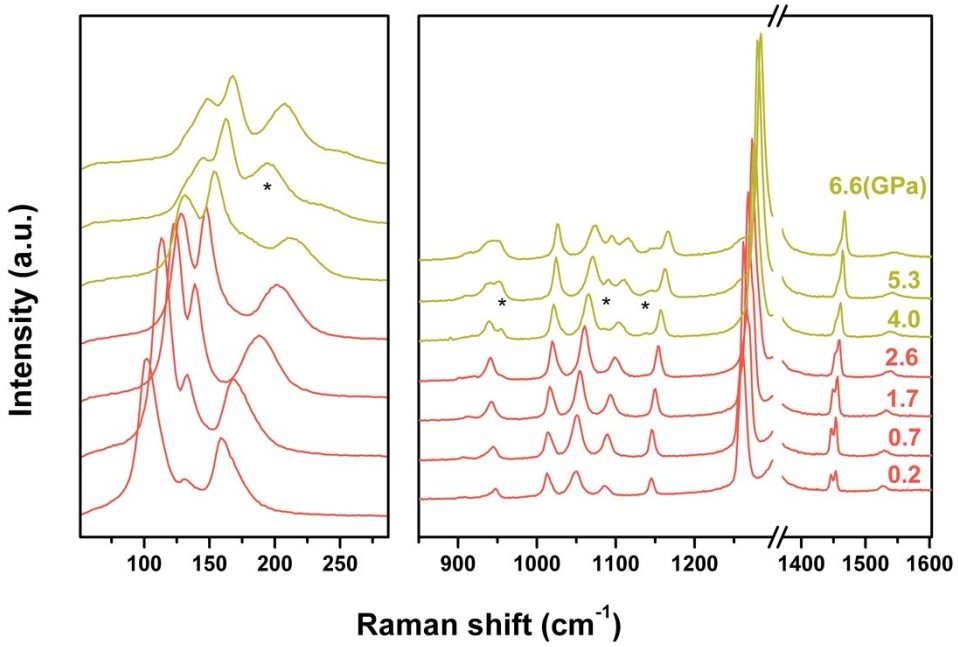

Figure S4 Raman spectra in a particular spectral region and pressure, indicating the first structural transition as reported in Ref. [2]

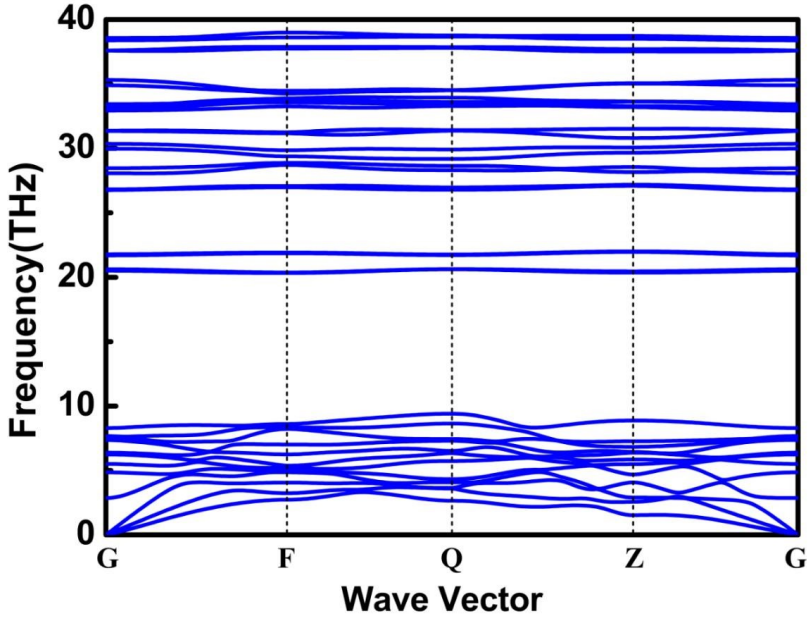

Figure S5 Phonon dispersion curves of 1-H Tetrazole at 8GPa.

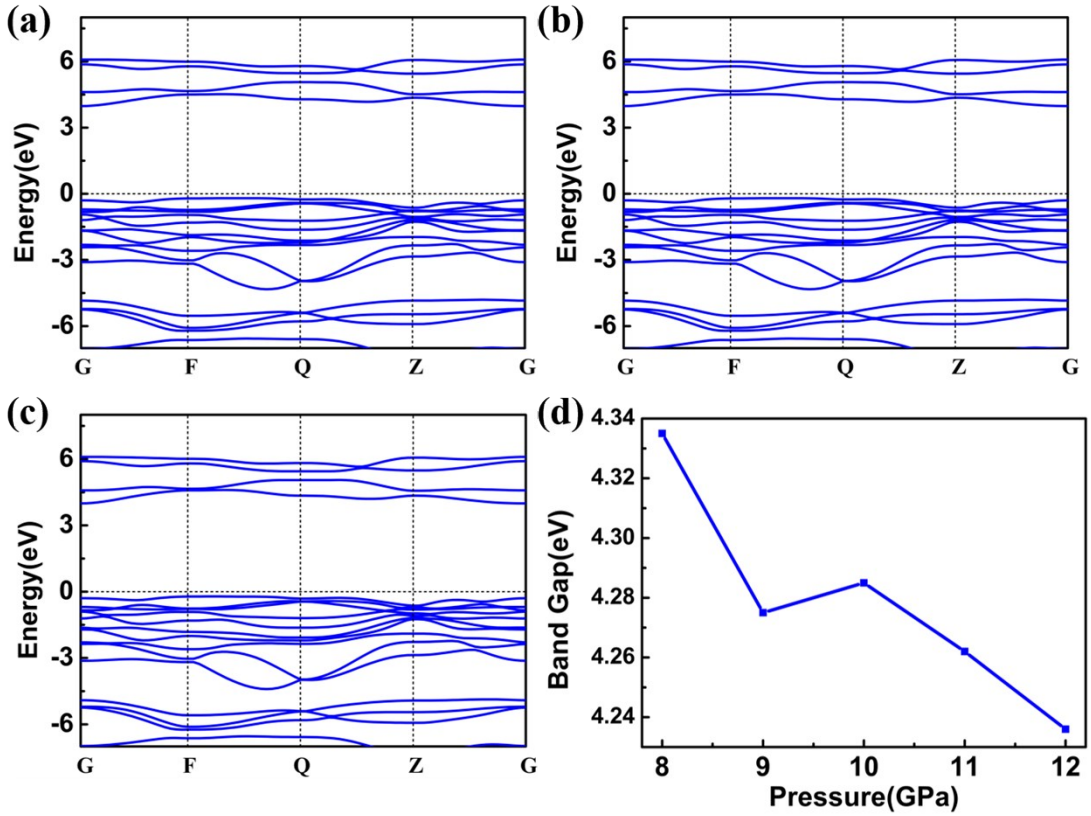

Figure S6 The electronic band structure at (a) 8 GPa, (b) 9 GPa, (c) 10 GPa and (d) the change of bandgap with pressure of 1-H Tetrazole.

References:

1 X. D. Wen, R. Hoffmann, N. W. Ashcroft, *J. Am. Chem. Soc.*, 2011, **133**, 9023-9035

2 W. B. Li, X. L. Huang, K. Bao, et al., *Scientific Reports*, 2017, **7**, 39249

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