Electronic Supplementary Information (ESI)

Low-energy 3D sp^2 carbons with versatile properties beyond graphite and graphene

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Table S1. Space group, lattice parameters (*a*, *b*, *c*, Å), atomic Wyckoff positions, and bond length (Å) of graphite, diamond, and 3D GNR polymers at ground state.

Structure	Space group	Lattice parameters	Atomic positions	Bond length (mean)
Graphite	*P*63/*mmc* (194)	2.442, 6.702	2*b* (0, 0, 1/4) 2*c* (1/3, 2/3, 1/4)	1.410
Diamond	*Fd*-3*m* (227)	3.528	8*a* (0, 0, 0)	1.528
(3,5)	*Imma* (74)	9.492, 8.143, 3.211	16*j* (-0.130, -0.580, -0.085) 8*h* (0, -0.163, 0.119) 8*g* (-1/4, -0.664, -1/4)	1.393–1.436 (1.417)
(5,7)	*Imma* (74)	14.222, 8.308, 3.272	16*j* (-0.414, -0.165, 0.437) 16*j* (-0.328, 0.419, 0.573) 8*g* (-1/4, 0.335, 3/4) 8*h* (-1/2, 0.417, 0.522)	1.391–1.435 (1.414)
(7,9)	*Imma* (74)	19.050, 8.360, 3.312	16*j* (0.372, 0.166, -0.551) 16*j* (0.308, -0.419, -0.430) 16*j* (0.436, -0.417, -0.491) 8*g* (1/4, -0.335, -1/4) 8*h* (1/2, 1/3, -0.509)	1.397–1.435 (1.411)
(9,11)	*Imma* (74)	23.918, 8.378, 3.356	16*j* (0.847, 0.666, -0.050) 16*j* (0.796, 1.081, -0.931) 16*j* (0.898, 1.083, -0.992) 16*j* (0.949, 1.167, -0.997) 8*g* (1/4, 0.665, -1/4) 8*h* (0, 1.084, -1.000)	1.399–1.437 (1.412)
(11,13)	*Imma* (74)	28.783, 8.393, 3.382	16*j* (-0.170, -0.834, 0.452) 16*j* (-0.212, -0.419, 0.569) 16*j* (-0.127, -0.417, 0.507) 16*j* (-0.085, -0.334, 0.502) 16*j* (-0.542, -0.916, -0.001) 8*h* (-1/2, -2/3, -0.002) 8*g* (1/4, -0.835, 1/4)	1.399–1.437 (1.412)
(13,15)	*Imma* (74)	33.678, 8.417, 3.511	16*j* (0.818, 1.166, 0.954) 16*j* (0.782, 0.581, 0.068) 16*j* (0.855, 0.583, 0.006) 16*j* (0.891, 0.666, 0.001) 16*j* (0.464, 1.333, 0.497) 16*j* (0.427, 1.083, 0.498) 8*g* (1/4, 1.165, 3/4) *8h* (0, 0.917, 0)	1.397–1.445 (1.415)

(15,17)	*Imma* (74)	38.574, 8.424, 3.509	16*j* (0.190, 1.166, 0.546) 16*j* (0.222, 0.581, 0.432) 16*j* (0.159, 0.583, 0.494) 16*j* (0.127, 0.667, 0.499) 16*j* (0.563, 1.333, 0.004) 16*j* (0.595, 1.083, 0.002) 16*j* (0.468, 1.083, 0.002) 8*h* (1/2, 1.167, 0.004) *8g* (3/4, 1.165, 3/4)	1.405–1.444 (1.415)
(3,3)	*Pmma* (51)	8.015, 7.177, 3.187	8*l* (-0.080, 0.172, 0.910) 8*l* (-0.163, 0.334, 0.755) 4*j* (-0.573, 1/2, 0.382) 4*i* (-0.662, 0, 0.130)	1.391–1.461 (1.417)
(5,5)	*Pmma* (51)	8.250, 11.847, 3.244	8*l* (0.080, 0.396, 0.421) 8*l* (0.165, 0.896, 0.068) 8*l* (-0.419, 0.793, 0.924) 8*l* (0.165, 0.300, 0.254) 4*j* (-0.163, 1/2, 0.609) 4*i* (-0.417, 0, 0.975)	1.386–1.441 (1.414)
(7,7)	*Pmma* (51)	8.342, 16.636, 3.282	8*l* (0.665, 0.426, 0.558) 8*l* (1.081, 0.353, 0.429) 8*l* (1.165, -0.147, 1.053) 8*l* (0.581, -0.220, 0.929) 8*l* (0.584, -0.073, 0.990) 8*l* (1.165, 0.287, 0.249) 4*j* (1.083, 1/2, 0.482) 4*i* (1/3, 0, 1.011)	1.395–1.435 (1.412)
(9,9)	*Pmma* (51)	8.373, 21.490, 3.319	8*l* (-0.334, 0.386, 0.549) 8*l* (0.081, 0.330, 0.431) 8*l* (0.165, 0.829, 0.051) 8*l* (-0.419, 0.773, 0.930) 8*l* (0.165, 0.278, 0.251) 8*l* (0.083, 0.443, 0.493) 8*l* (-0.417, 0.886, 0.992) 8*l* (-0.334, 0.943, 0.996) 4*j* (-1/6, 1/2, 0.506) 4*i* (-0.416, 0, 1.000)	1.399–1.436 (1.412)

Table S2. 3D *sp*^{2} carbons listed in Fig. 2. $\Delta E=E_{carbon}-E_{diamond}$ is calculated energy of 3D *sp*^{2} carbon relative to diamond, and $\Delta E'$ is relative energy from references for comparisons.

3D *sp*^{2} carbon	No.	Name in Ref.	Name in SACADA	ΔE (eV/atom)	$\Delta E'$ (eV/atom)
Schwarzites	18	6.8^{2}P	pbp	0.463	0.491[1], 0.488[2]
	19	6.8^{2}D	pbz	0.232	0.227[1], 0.208[2]
	20	G688	pbg	0.424	0.447[1]
	23	P8	mct	0.209	0.201[1]
	26	P7par	3^{6}T5	0.228	0.237[1]
	28	fcc-$(C_{28})_2$	kgz	0.742	0.70[3], 0.771[4]
	29	fcc-$(C_{36})_2$	—	0.710	0.65[3]
	30	fcc-$(C_{40})_2$	—	0.512	0.44[3]
	31	G8	3^{4}T13	0.301	0.234[1]
	34	D8	pbz-m	0.244	0.244[1]
	36	fcc-$(C_{64})_2$	3^{5}T6	0.388	0.42[4]

Table S3. Space group, lattice parameters (a, b, c, Å), and atomic Wyckoff positions of some 3D sp^2 carbons at ground state. The crystal structure information of other 3D sp^2 carbons are in SACADA (http://sacada.sctms.ru).

Structure	Space group	Lattice parameters	Atomic positions
C_{168}D (Model H)	*Fd*-3*m* (227)	23.820	192*i* (0.708, 0.624, 0.834) 192*i* (0.494, 0.661, 0.422) 192*i* (0.292, 0.626, 0.415) 96*j* (0.521, 0.675, 0.521)
C_{192}D	*Fd*-3*m* (227)	23.163	192*i* (-0.177, 0.409, 0.366) 192*i* (-0.379, 0.038, -0.207) 192*i* (-0.530, 0.427, -0.234) 192*i* (-0.569, 0.238, 0.026)
C_{216}D (Model K)	*Fd*-3*m* (227)	24.556	192*i* (0.927, 2.114, -0.345) 192*i* (0.781, 1.632, -0.448) 192*i* (0.493, 1.709, -0.332) 192*i* (1.074, 1.505, -0.223) 96*g* (0.981, 1.520, 0.215)
C_{216}G (Model O)	*Ia*-3 (206)	19.255	48*e* (0.898, 0.355, 0.810) 48*e* (0.788, 0.309, 0.730) 48*e* (0.224, 0.871, 0.975) 48*e* (0.347, 0.615, 0.506) 48*e* (0.475, 0.559, 0.466) 48*e* (0.372, 0.787, 0.320) 48*e* (0.099, 0.236, 0.367) 48*e* (0.118, 0.067, 0.550) 48*e* (0.118, 0.141, 0.448)
fcc-$(C_{36})_2$	*Fd*-3*m* (227)	17.299	96*g* (0.105, 0.199, 0.605) 96*g* (0.358, 0.142, 0.744) 96*g* (0.279, 0.221, 0.623)
fcc-$(C_{40})_2$	*Fd*-3*m* (227)	15.706	192*i* (0.703, 1.417, 0.479) 96*g* (0.937, 0.563, 0.174) 32*e* (0.892, 0.608, 0.108)

Table S4. Calculated elastic constants C_{ij} (GPa) of 3D GNR polymers at ambient pressure. For a stable orthorhombic crystal, its independent elastic constants should satisfy the corresponding generalized Born stability criteria: $C_{11}>0$, $C_{22}>0$, $C_{33}>0$, $C_{44}>0$, $C_{55}>0$, $C_{66}>0$, $C_{11}+C_{22}-2C_{12}>0$, $C_{11}+C_{33}-2C_{13}>0$, $C_{22}+C_{33}-2C_{23}>0$, $C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23}>0$. Clearly, the calculated elastic constants C_{ij} of 3D GNR polymers meet the mechanical stability criteria, suggesting that they are mechanically stable at ambient pressure.

Structure	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
(3,5)	894.34	790.60	108.16	72.48	63.35	404.80	319.67	59.16	78.17
(5,7)	869.45	884.57	90.20	38.62	31.39	375.67	313.62	57.86	36.26
(7,9)	869.89	944.14	74.53	27.38	15.48	360.21	292.91	43.01	18.12
(9,11)	907.59	975.03	61.60	17.32	7.55	358.35	250.13	35.39	8.55
(3,3)	753.19	901.20	124.29	60.45	89.29	388.10	301.24	110.41	52.49
(5,5)	854.42	884.08	104.21	45.45	50.74	396.67	312.03	48.60	58.43
(7,7)	918.31	901.63	80.27	29.50	31.31	387.22	289.03	18.91	57.29
(9,9)	981.31	919.15	64.12	16.61	21.34	367.18	256.82	18.79	38.69

Table S5. Bulk moduli (B, GPa), shear moduli (G, GPa), Young's moduli along the *x*-, *y*- and *z*-axis (Y_x, Y_y, Y_z, GPa), and tensile strain and strength (GPa) of graphite, diamond, and 3D GNR polymers at ambient pressure. The lowest tensile strength listed below is along the [111] direction for diamond and [001] direction for 3D GNR polymers.

Structure	B	G	Y_x	Y_y	Y_z	Tensile	
						Strain	Strength
Graphite	16.3 14.0–16.9[5]	0.6 0.25–1.2[6]	1036.7	1036.7	29.7	–	–
Diamond	432.4 442[7]	527.1 544[7]	1021.7	1021.7	1021.7	0.13	93.9
(3,5)	203.0	147.1	757.5	645.1	99.4	1.66	51.9
(5,7)	191.1	123.2	735.4	768.7	86.0	1.52	29.0
(7,9)	179.8	111.1	760.2	845.3	72.4	1.38	19.3
(9,11)	170.0	104.7	825.5	906.1	60.2	1.35	15.1
(3,3)	209.7	148.4	581.4	780.1	108.0	1.12	41.0
(5,5)	198.8	136.4	736.5	753.8	99.3	1.58	36.7
(7,7)	184.3	123.5	825.7	777.7	76.6	1.41	22.7
(9,9)	175.0	114.0	908.5	834.0	62.4	1.33	16.8

Table S6. Calculated tensile strength (GPa) and corresponding strain along different crystal directions for selected 3D GNR polymers. The lowest tensile strength of diamond is along its [111] direction. For 3D GNR polymers, the crystal directions [100], [010], and [001] are corresponding to the *x*-, *y*-, and *z*-axis, respectively.

Structure	[hkl]	Strain	Strength
Diamond	[111]	0.13	93.9
		0.13	90.6[8]
		–	93[9]
		0.13	90[10]
(3,3)	[100]	0.21	114.3
	[010]	0.33	123.0
	[001]	1.12	41.0
(3,5)	[100]	0.35	122.2
	[010]	0.24	111.6
	[001]	1.66	51.9
(9,11)	[100]	0.25	118.1
	[010]	0.20	108.1
	[001]	1.35	15.1

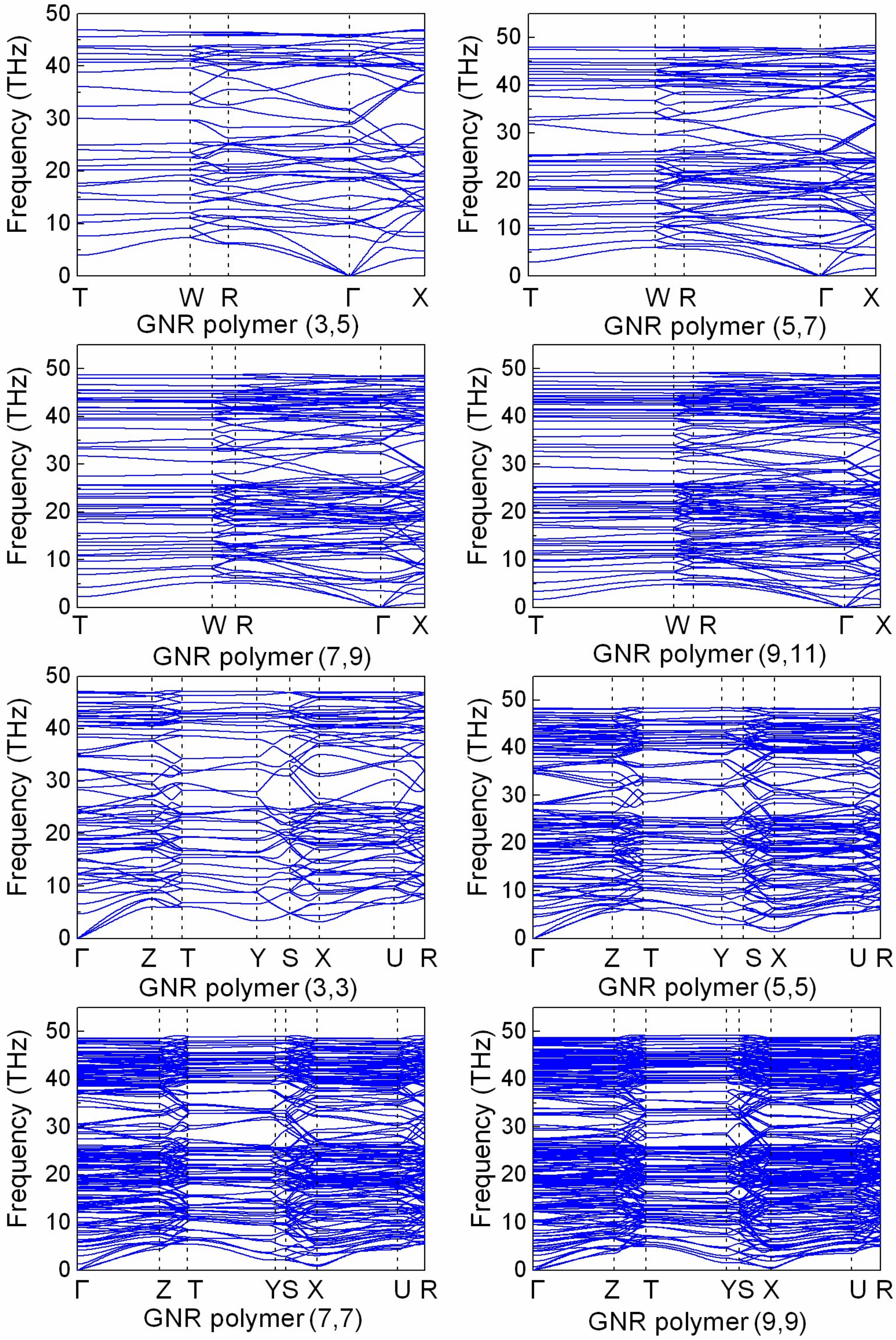

Fig. S1 Calculated phonon dispersion curves of 3D GNR polymers at ambient pressure. No imaginary phonon frequency was observed throughout the whole Brillouin zone, which demonstrates the dynamic stabilities of these carbon allotropes.

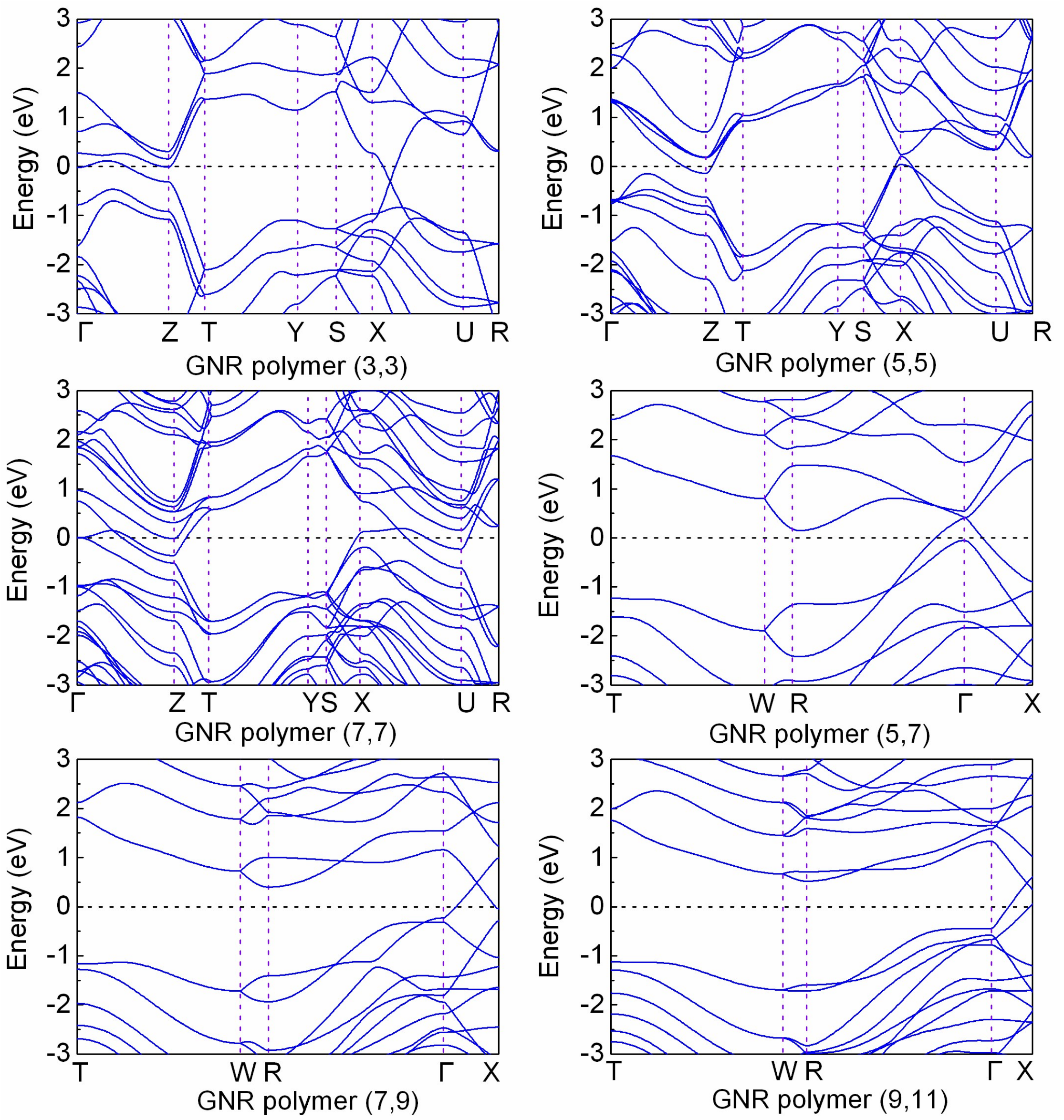

Fig. S2 Calculated electronic band structures of 3D GNR polymers at ambient pressure. 3D GNR polymers show metallic properties including certain characteristics of graphene-like linear dispersion.

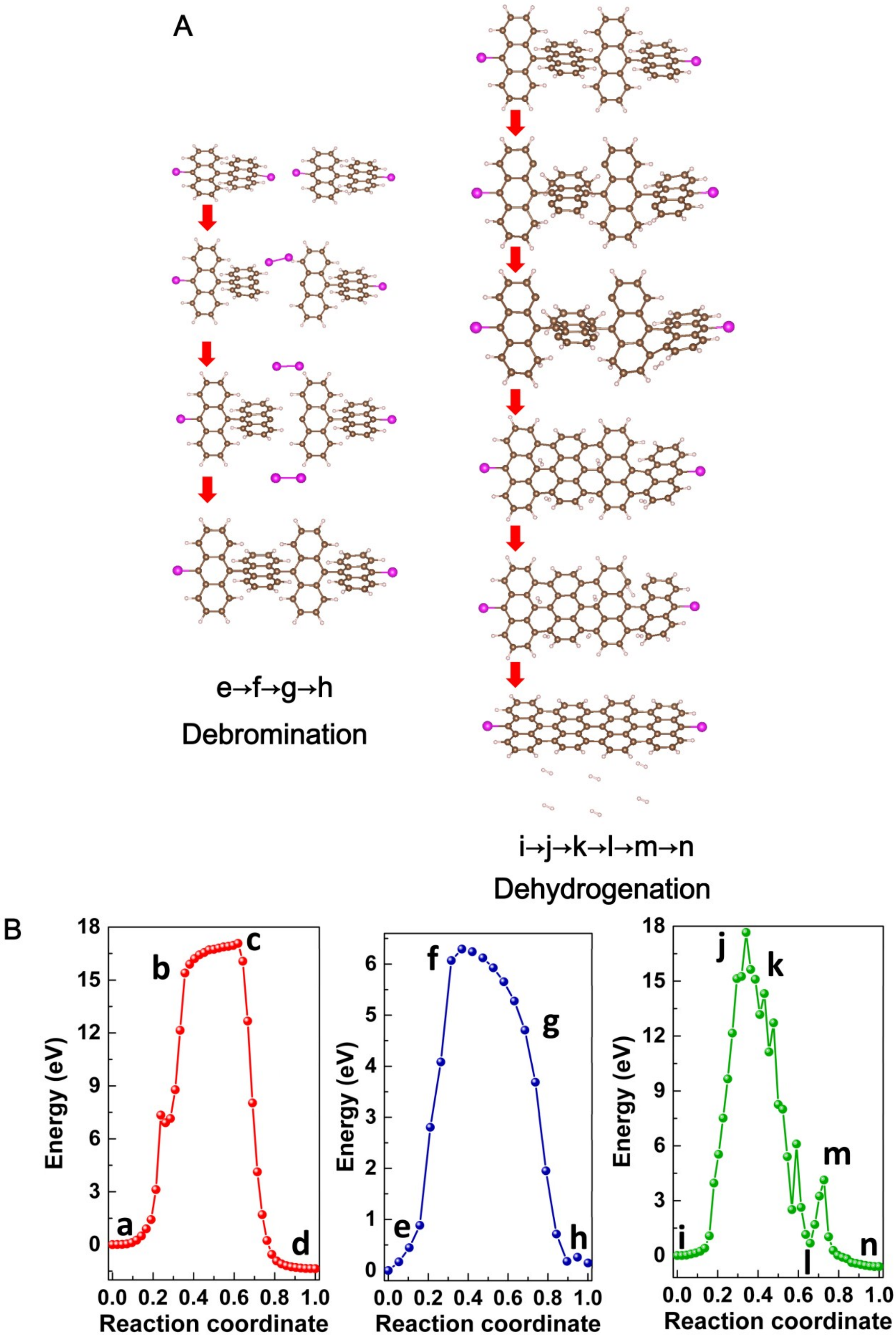

Fig. S3 (A) The reported bottom-up synthesis of atomically precise GNRs through debromination from 10,10’-dibromo-9,9’-bianthryl monomer precursors to non-coplanar intermediate of linear polymer (e–h), and dehydrogenation from the linear polymer to GNR (i–n).[11] The brown, magenta, and light pink spheres represent carbon, bromine, and hydrogen atoms, respectively. (B) Calculated energy change during reactions. The calculated energies are the total values of current considered systems, i.e. dehydrobromination of edge-functionalized GNRs to generate 4 HBr molecules (a-d), debromination of 10,10’-dibromo-9,9’-bianthryl monomer precursor to generate one Br_2 molecule (e–h), and dehydrogenation of intermediate of linear polymer to generate $5H_2$ molecules (i–n). Therefore, the average barrier is 4.41 eV to generate one HBr molecule during GNR polymerization. As a comparison, the calculated average barriers in the bottom-up fabrication of atomically precise GNRs[11] are 6.29 eV for debromination to generate one Br_2 molecule and3.41 eV for subsequent dehydrogenation to generate one H_2 molecule, respectively. The dehydrobromination progress to form 2D GNR polymer has a moderate energy barrier between those of debromination and dehydrogenation procedures both taking place in bottom-up GNR synthesis.[11]

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