SUPPORTING INFORMATION

Biaxial Negative Thermal Expansion in Carbon Nets – Graphyne and Derivatives

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1. Fig. S1. Hybridized carbon atoms visualization in 2D nets.

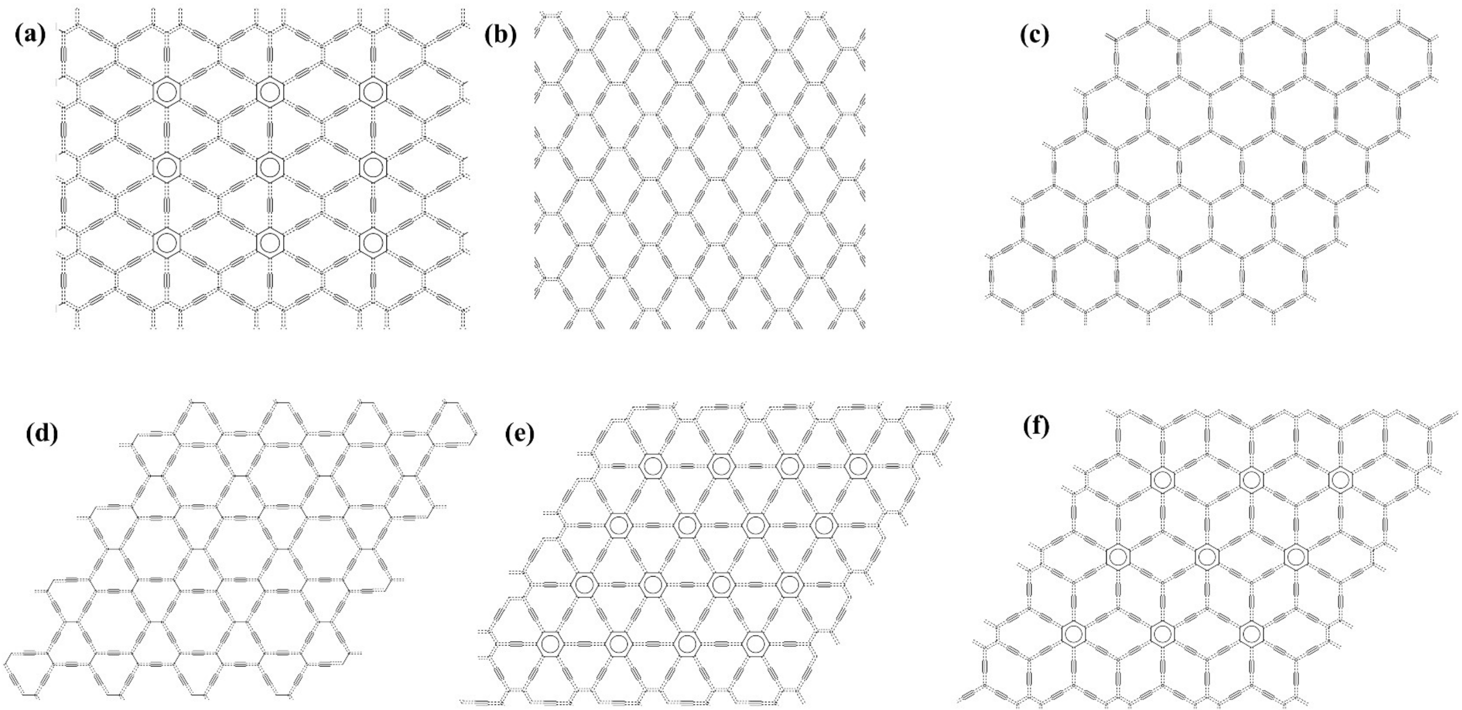


Figure S1. *Hybridized carbon atoms visualization in **(a)** (6,6,12-), **(b)** (14,14,14-), **(c)** α (18,18,18-), **(d)** β (12,12,12-), **(e)** γ (6,6,6-) and **(f)** δ (6,6,14-).*

2. **Table ST1**. Table for different graphyne systems showing a negative TEC.

Graphynes	Negative TEC range (K)
6,6,12-	Beyond 1000K
14,14,14-	800K
Alpha (α)	Beyond 1000K
Beta (β)	710K
Gamma (γ)	950K
Delta (δ)	Beyond 1000K

Calculations were done till T_{max} = 1000K.

3. **Table ST2.** Table for different graphynes showing different types of bonds

Graphynes	C(sp)–C(sp)	$C(sp^2)$–$C(sp^2)$ (Type 1)	$C(sp^2)$–$C(sp^2)$ (Type 2)	$C(sp^2)$–C(sp) (Type 1)	$C(sp^2)$–C(sp) (Type 2)
6,6,12	1.226	1.431	1.425	1.397	
14,14,14	1.229	1.448		1.390	
Alpha	1.229			1.394	
Beta	1.231	1.457		1.387	
Gamma	1.221	1.425		1.406	
Delta	1.228	1.437		1.388	1.394

4. Fig. S2. Energy vs volume plots required for thermal properties calculation.

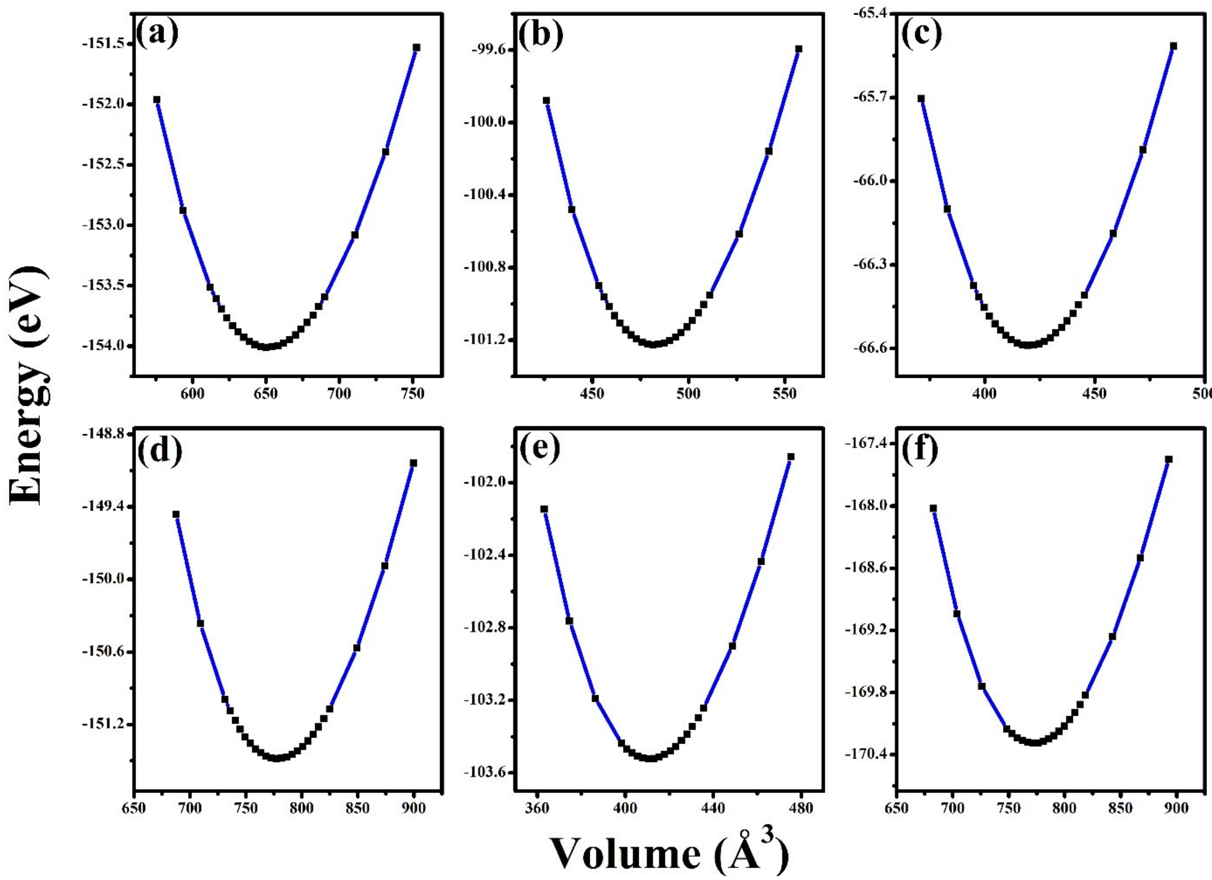


Figure S2: *Free-energy vs volume plots for* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-).*

5. **Fig. S3.** Phonon band structure shows stability of the 2D systems.

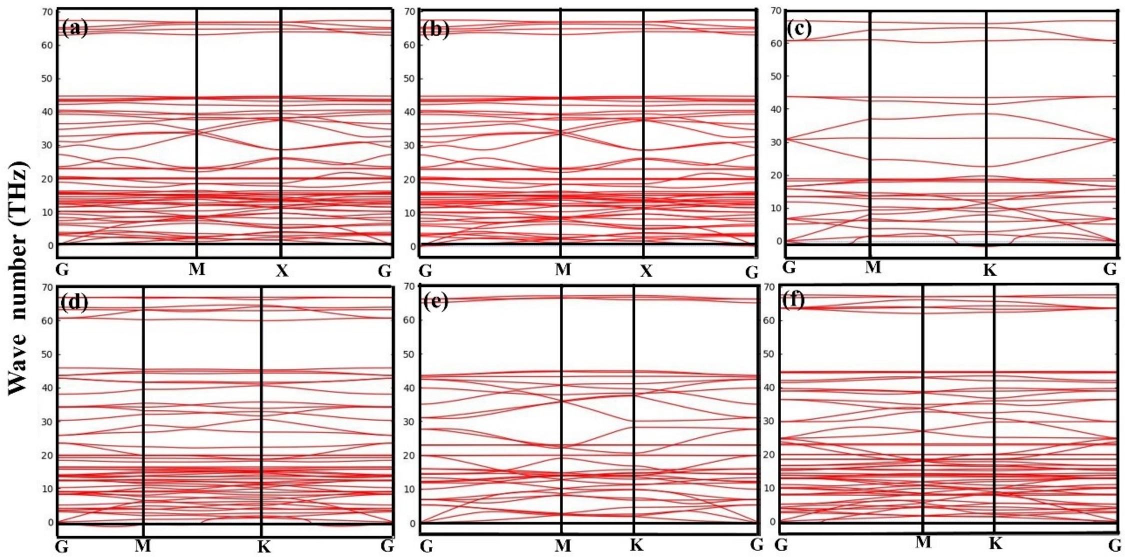


Figure S3: *Phonon dispersion bands show stability of the structure* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-).*

6. POSCARS of the 2D materials.

POSCARS

(a)

```
6,6,12
 1.000
    9.4271667524014706    0.0000000000000002    0.0000000000000000
   -0.0000000000000000    6.8981955867425802    0.0000000000000000
    0.0000000000000000    0.0000000000000000    10.000000000000000
  C
   18
Direct
  0.8690582460326451  0.8958567441619639  0.5000000000000000
  0.1309417539673544  0.1041432558380350  0.5000000000000000
  0.1309417539673544  0.8958567441619639  0.5000000000000000
  0.8690582460326451  0.1041432558380350  0.5000000000000000
  0.2592161817490509  0.2055606248952588  0.5000000000000000
  0.7407838182509487  0.7944393751047414  0.5000000000000000
  0.7407838182509487  0.2055606248952588  0.5000000000000000
  0.2592161817490509  0.7944393751047414  0.5000000000000000
  0.5000000000000000  0.6037338793575838  0.5000000000000000
  0.5000000000000000  0.3962661206424153  0.5000000000000000
  0.6278563803015278  0.2936757788500661  0.5000000000000000
  0.3721436196984722  0.7063242211499342  0.5000000000000000
  0.3721436196984722  0.2936757788500661  0.5000000000000000
  0.6278563803015278  0.7063242211499342  0.5000000000000000
```

```
0.0000000000000000  0.2074092193736203  0.5000000000000000
0.0000000000000000  0.7925907806263796  0.5000000000000000
0.0000000000000000  0.4114039429882726  0.5000000000000000
0.0000000000000000  0.5885960570117275  0.5000000000000000
```

(b)

```
14,14,14
  1.00000000000000
    6.9646204389481561    0.0000000000000003    0.0000000000000000
   -0.0000000000000003    6.9139516066262923    0.0000000000000000
    0.0000000000000000    0.0000000000000000   10.0000000000000000
  C
   12
Direct
  0.5445714632838077  0.4232793896600577  0.5000000000000000
  0.4554285367161918  0.5767206103399419  0.5000000000000000
  0.9554285367161923  0.4232793896600577  0.5000000000000000
  0.0445714632838082  0.5767206103399419  0.5000000000000000
  0.3539678493014367  0.7500004960090529  0.5000000000000000
  0.6460321506985630  0.2499995039909462  0.5000000000000000
  0.1460321506985634  0.7500004960090529  0.5000000000000000
  0.8539678493014370  0.2499995039909462  0.5000000000000000
  0.0445768529185766  0.9232816320557032  0.5000000000000000
  0.9554231470814230  0.0767183679442976  0.5000000000000000
  0.4554231470814238  0.9232816320557032  0.5000000000000000
  0.5445768529185770  0.0767183679442976  0.5000000000000000
```

(c)

```
alpha
 1.
   -3.4806940398795039    6.0282976565876591    0.0000000000000000
   -6.9610047190400426    0.0002218122655804    0.0000000000000000
    0.0000000000000000    0.0000000000000000   10.0000000000000000
  C
    8
Direct
  0.6666594678622411  0.6666594679848559  0.5000000000000000
  0.3333405321377595  0.3333405320151435  0.5000000000000000
  0.4490179205247912  0.4490169204972826  0.5000000000000000
  0.5509715714013934  0.8980304038068082  0.5000000000000000
```

```
 0.1019695963048948  0.4490284285310064  0.5000000000000000
 0.5509820794752087  0.5509830795027172  0.5000000000000000
 0.4490284285986065  0.1019695961931918  0.5000000000000000
 0.8980304036951062  0.5509715714689936  0.5000000000000000
```

(d)

```
beta
 1.
    4.7360247716038053    8.2030333740699835   -0.0000000000000000
   -4.7360247716038053    8.2030333740699835   -0.0000000000000000
    0.0000000000000000    0.0000000000000000   10.0000000000000000
  C
   18
Direct
 0.7239027157887824  0.8539093663111416  0.5000000000000000
 0.1460906336920166  0.5778100820978254  0.5000000000000000
 0.4221899179032365  0.7239027157866865  0.5000000000000000
 0.2760972842112179  0.1460906336888588  0.5000000000000000
 0.8539093663079833  0.4221899179021745  0.5000000000000000
 0.5778100820967615  0.2760972842133134  0.5000000000000000
 0.8539093663111416  0.7239027157887824  0.5000000000000000
 0.2760972842133134  0.5778100820967615  0.5000000000000000
 0.4221899179021746  0.8539093663079833  0.5000000000000000
 0.1460906336888588  0.2760972842112179  0.5000000000000000
 0.7239027157866866  0.4221899179032365  0.5000000000000000
 0.5778100820978254  0.1460906336920166  0.5000000000000000
 0.4230544953802079  0.5769455046197917  0.5000000000000000
 0.4230544953770726 -0.0000000000031351  0.5000000000000000
-0.0000000000031351  0.4230544953770725  0.5000000000000000
 0.5769455046197914  0.4230544953802079  0.5000000000000000
 0.5769455046229277  0.0000000000031351  0.5000000000000000
 0.0000000000031351  0.5769455046229277  0.5000000000000000
```

(e)

```
gamma
 1.
    3.4421820432063441    5.9620358095904313    0.0000000000000000
   -6.8845582108901695    0.0001114159548589    0.0000000000000000
    0.0000000000000000    0.0000000000000000    10.000000000000000
  C
   12
Direct
```

```
  0.7930076869094723  0.0000029999965364  0.5000000000000000
  0.0000050262357737  0.7930130180561835  0.5000000000000000
  0.2069950081792522  0.2069929819416107  0.5000000000000000
  0.7930069918207500  0.7930130180583880  0.5000000000000000
  0.2069953130905271  0.0000030000034626  0.5000000000000000
 -0.0000020262357741  0.2069929819438154  0.5000000000000000
  0.4112803979674287  0.0000029999993803  0.5000000000000000
 -0.0000059883407783  0.4112787327096286  0.5000000000000000
  0.5887182789531307  0.5887262672961298  0.5000000000000000
  0.4112847210468684  0.4112787327038721  0.5000000000000000
  0.5887226020325712  0.0000030000006188  0.5000000000000000
  0.0000089883407779  0.5887262672903728  0.5000000000000000
```

(f)

```
 delta
 1.
    9.4379390822686720   -0.0002649031811799    0.0000000000000000
   -4.7191991039962060    8.1733627052312396    0.0000000000000000
    0.0000000000000000    0.0000000000000000    10.000000000000000
   C
    20
Direct
  0.2479694561395410  0.4960115373027623  0.5000000000000000
  0.5039895873323368  0.7519976927319558  0.5000000000000000
  0.2480035477221697  0.7520209268554863  0.5000000000000000
  0.7520209268551472  0.2480035477218417  0.5000000000000000
  0.7519966927317315  0.5039885873320820  0.5000000000000000
  0.4960115373024710  0.2479694561392838  0.5000000000000000
  0.1728325983050894  0.3456675271388799  0.5000000000000000
  0.6543325337001911  0.8271627190199241  0.5000000000000000
  0.1728253090523797  0.8271785095274382  0.5000000000000000
  0.8271805095271396  0.1728273090520701  0.5000000000000000
  0.8271627190202880  0.6543325337008460  0.5000000000000000
  0.3456685271395762  0.1728335983054705  0.5000000000000000
  0.0879037670601799  0.9120968562292792  0.5000000000000000
  0.0879156571764941  0.1758198948213042  0.5000000000000000
  0.8241822703896071  0.9120869262146953  0.5000000000000000
  0.9120869262147469  0.8241822703897435  0.5000000000000000
  0.1758198948214758  0.0879156571765707  0.5000000000000000
  0.9120988562292609  0.0879057670601676  0.5000000000000000
  0.3333198923220006  0.6666787909585861  0.5000000000000000
  0.6666787909581795  0.3333198923216016  0.5000000000000000
```

(g)

```
B-GY-Hex.
   1.00000000000000
     7.3985768927001310    0.0000058864104552    0.0000000000000000
     3.6992925599641975    6.4073541688052842    0.0000000000000000
     0.0000000000000000    0.0000000000000000    10.0000000000000000
   C    B
     6     2
Direct
  0.5480051837482589  0.9039797381042334  0.5000000000000000
  0.5480167961658137  0.5480056294028631  0.5000000000000000
  0.4519939647686109  0.4519868456339889  0.5000000000000000
  0.4519870622138260  0.0960215522336111  0.5000000000000000
  0.9039797215650441  0.5480164499593383  0.5000000000000000
  0.0960215707594674  0.4519941174178072  0.5000000000000000
  0.3333342484097408  0.3333342143072284  0.5000000000000000
  0.6666672793638893  0.6666673221597982  0.5000000000000000
```

(h)

```
Al-GY-Hex.
   1.00000000000000
     8.7292510320336536    0.0000399583282936    0.0000000000000000
     4.3647179555265385    7.5598209048815503    0.0000000000000000
     0.0000000000000000    0.0000000000000000    10.0000000000000000
   C    Al
     6     2
Direct
  0.4591962865857292  0.0816078486538355  0.5000000000000000
  0.4591898664767544  0.4591919082530335  0.5000000000000000
  0.5407974684911886  0.5408068509427233  0.5000000000000000
  0.5408028012315087  0.9183850125660149  0.5000000000000000
  0.0816089709949422  0.4591876019746850  0.5000000000000000
  0.9183841353760663  0.5407995058120216  0.5000000000000000
  0.3333330652406348  0.3333286985048345  0.5000000000000000
  0.6666603648335161  0.6666642778206753  0.5000000000000000
```

(i)

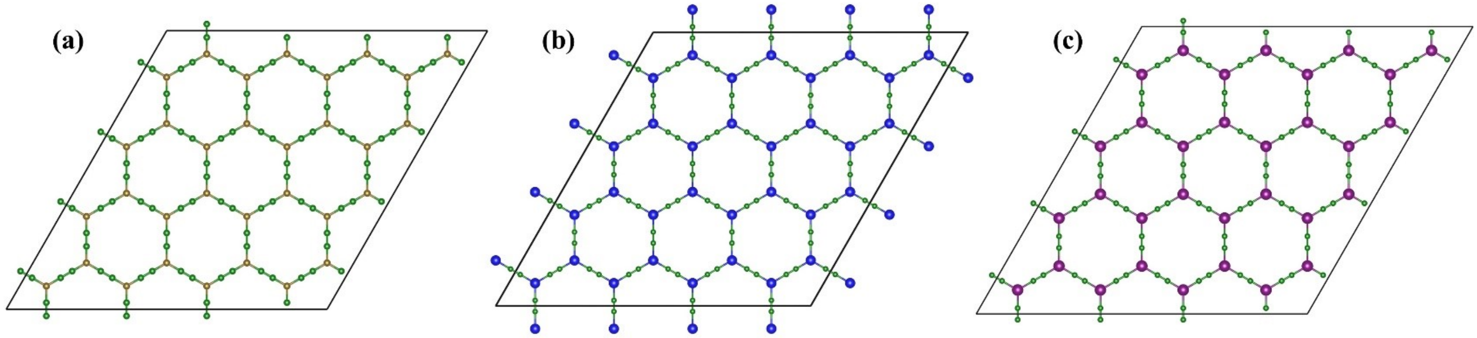
```
Ga-GY-Hex.
   1.00000000000000
     8.7876692321278949   -0.0000019610212960    0.0000000000000000
     4.3938341899755695    7.6103522914667696    0.0000000000000000
     0.0000000000000000    0.0000000000000000    10.0000000000000000
   C    Ga
```

6 2

Direct

0.4596041182239771	0.0807581226457835	0.5000000000000000
0.4596124596528161	0.4596053424620033	0.5000000000000000
0.5403754259025234	0.5403748192655542	0.5000000000000000
0.5403738607923467	0.9192257284507722	0.5000000000000000
0.0807582698624911	0.4596115767332606	0.5000000000000000
0.9192258758667919	0.5403741527713094	0.5000000000000000
0.3333252353095594	0.3333255382564111	0.5000000000000000
0.6666589394242616	0.6666583919345664	0.5000000000000000

7. **Figure S4.** **(a)** BGy-HEX **(b)** AlGy-HEX **(c)** GaGy-HEX. Analogues of α-Graphyne.



8. **Figure S5.** Normalized Area vs Temperature plot for **BGy-HEX**.

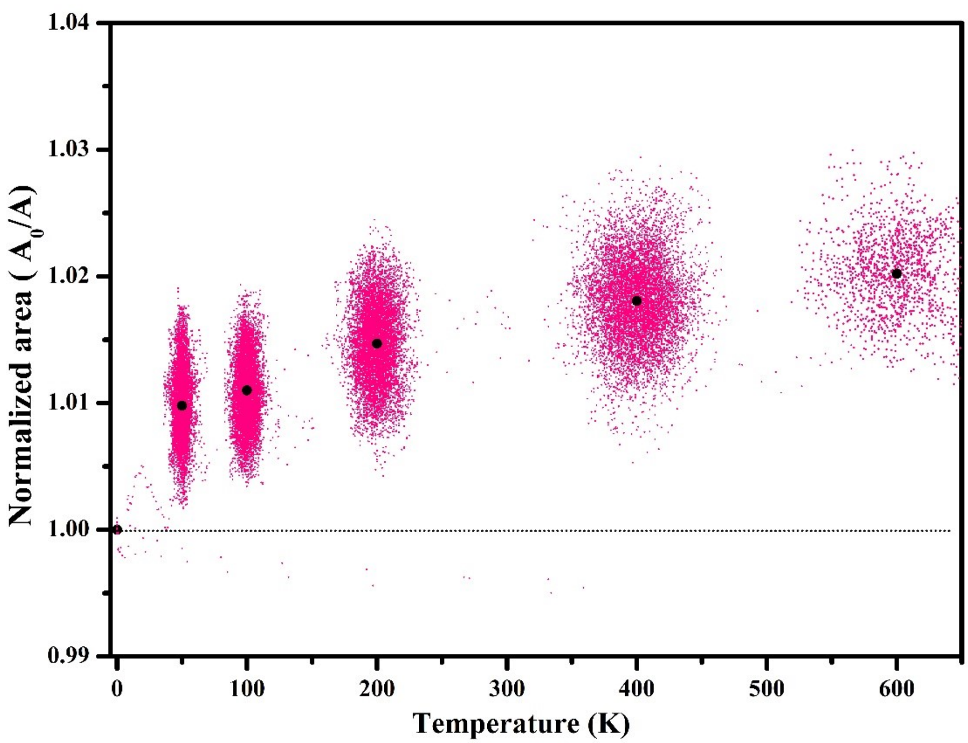


Figure S5. Normalized area for **BGy-HEX** (Boron substituted α-Gy) with pink and black dots represent the normalized and average normalized area.

Supercell with ~300 atoms couldn't capture NTE. We expect a bigger cell would give a perfect matchable result with that of the obtained result from *qha-approximation*.

9. **Figure S6.** TECs for **(a)** BGy-Hex **(b)** AlGy-Hex **(c)** GaGy-Hex.

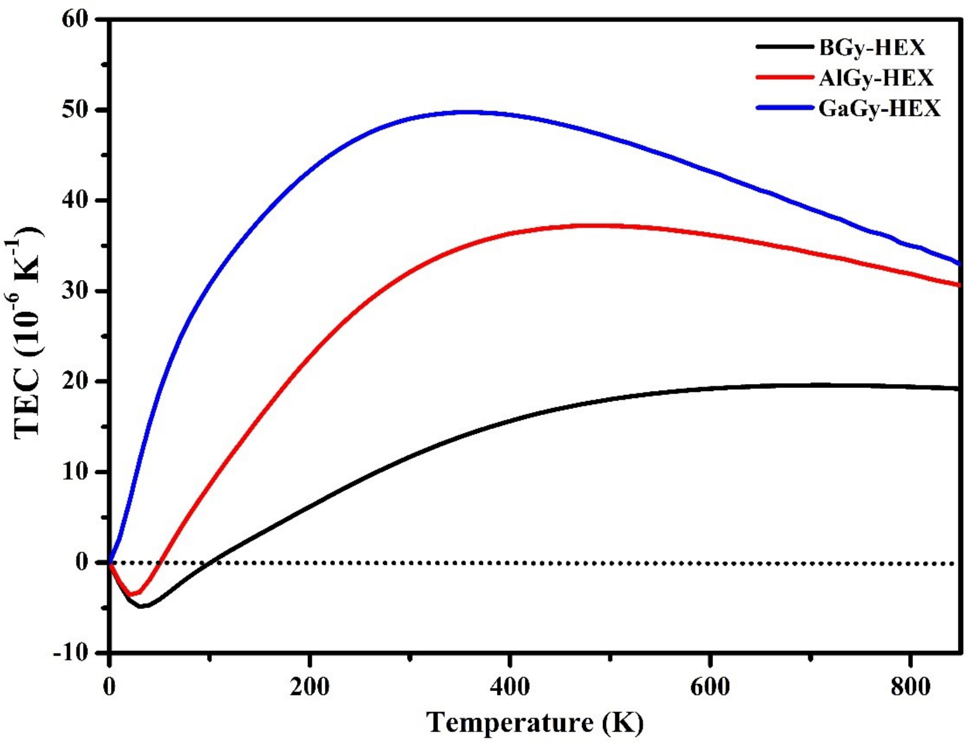


Figure S6. TEC upto our calculated temperature **(a)** BGy-HEX, **(b)** AlGy-HEX, **(c)** GaGy-HEX.

BGy-HEX, AlGy-HEX show NTE upto 100K and 50K respectively. GaGy-HEX doesn't show negative TEC at all.

10. Fig. S7. RMSD vs MD time frame plots

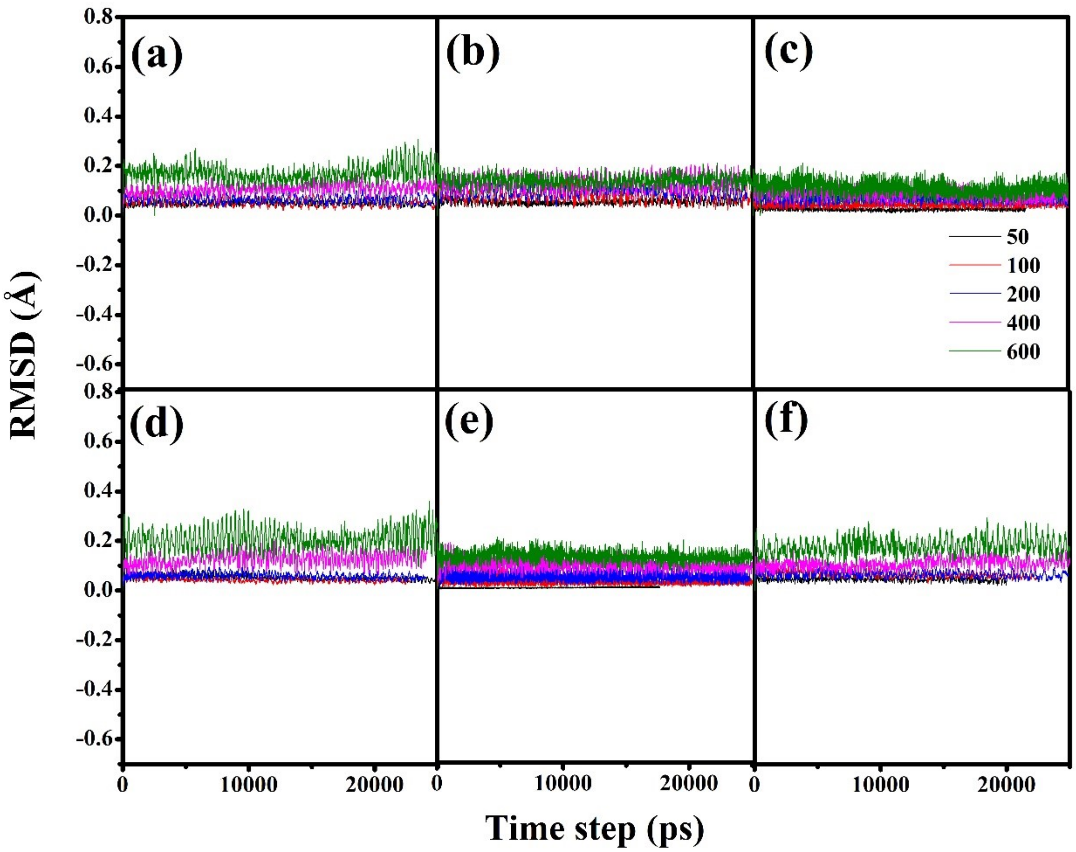


Figure S7. *RMSD vs MD time frame plots showing stability of the structure* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-).*

11. Fig. S8. Standard deviation for the normalized area.

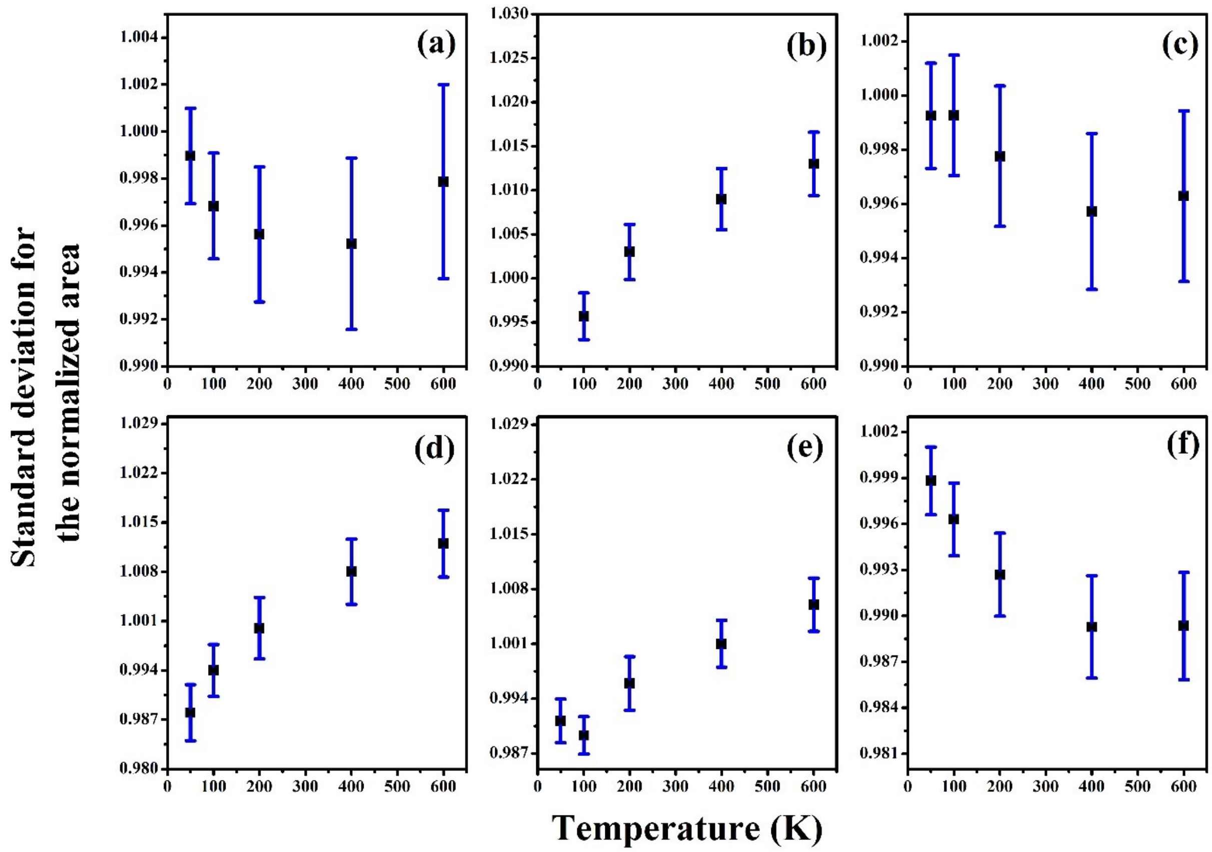


Figure S8. *The standard deviation plots for Normalized area vs Temperature for* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-).*

12. Table ST3. The standard deviation values at different temperatures.

Temperature	**50K**	**100K**	**200K**	**400K**	**600K**
6,6,12-	0.00203	0.00225	0.00287	0.00365	0.00413
14,14,14-	0.00275	0.00266	0.00314	0.00347	0.00360
α (18,18,18-)	0.00194	0.00222	0.00259	0.00288	0.00315
β (12,12,12-)	0.00398	0.00368	0.00436	0.00462	0.00476
γ (6,6,6-)	0.00279	0.00239	0.00342	0.003	0.00339
δ (6,6,14-)	0.00221	0.00237	0.00271	0.00335	0.00350

13. Table ST4. Biaxial Negative thermal expansion of different Graphyne materials.

1. 6,6,12- Gy

Temperature (K)	x (Å)	y (Å)
0	35.2404	24.7312
50	35.2398	24.7309
100	35.2401	24.7301
200	35.2386	24.7295
400	35.1868	24.7303
600	35.1788	24.7264

2. 14,14,14- Gy

Temperature (K)	x (Å)	y (Å)
0	30.7207	33.5166
50	30.7186	33.5155
100	30.72	33.5166
200	30.7251	33.5182
400	30.7212	33.5191
600	30.7245	33.5193

3. α (18,18,18-) Gy

Temperature (K)	x (Å)	y (Å)
0	34.808	34.818
50	34.815	34.8076
100	34.8103	34.8056
200	34.8114	34.8099
400	34.8125	34.8112
600	34.8178	34.8112

4. β (12,12,12-) Gy

Temperature (K)	x (Å)	y (Å)
0	28.4162	28.4162
50	28.4108	28.416
100	28.415	28.4105
200	28.4162	28.4158
400	28.4178	28.4162
600	28.418	28.4171

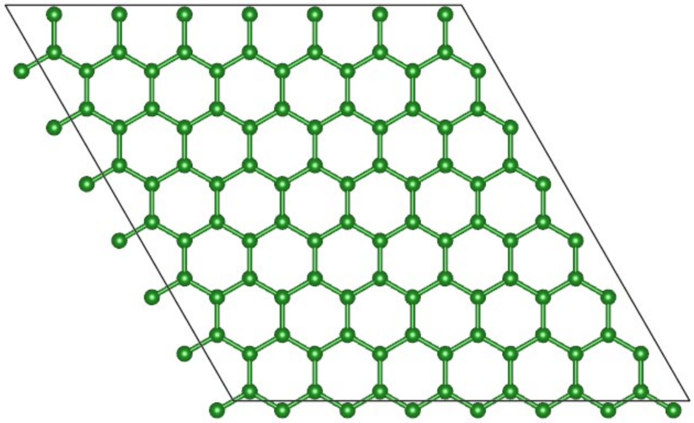
5. γ (6,6,6-) Gy

Temperature (K)	x (Å)	y (Å)
0	33.0415	31.6168
50	33.0418	31.6127
100	33.0416	31.6157
200	33.0416	31.6172
400	33.0411	31.6127
600	33.0401	31.7916

6. δ (6,6,14-) Gy

Temperature (K)	x (Å)	y (Å)
0	28.3416	28.283
50	28.3113	28.3112
100	28.3111	28.31
200	28.309	28.304
400	28.316	28.301
600	28.3083	31.319

14. Figure S9. Visualization of graphene.



15. Figure S10. Relative magnitudes for the thermal expansion coefficient of graphene with the graphyne systems.

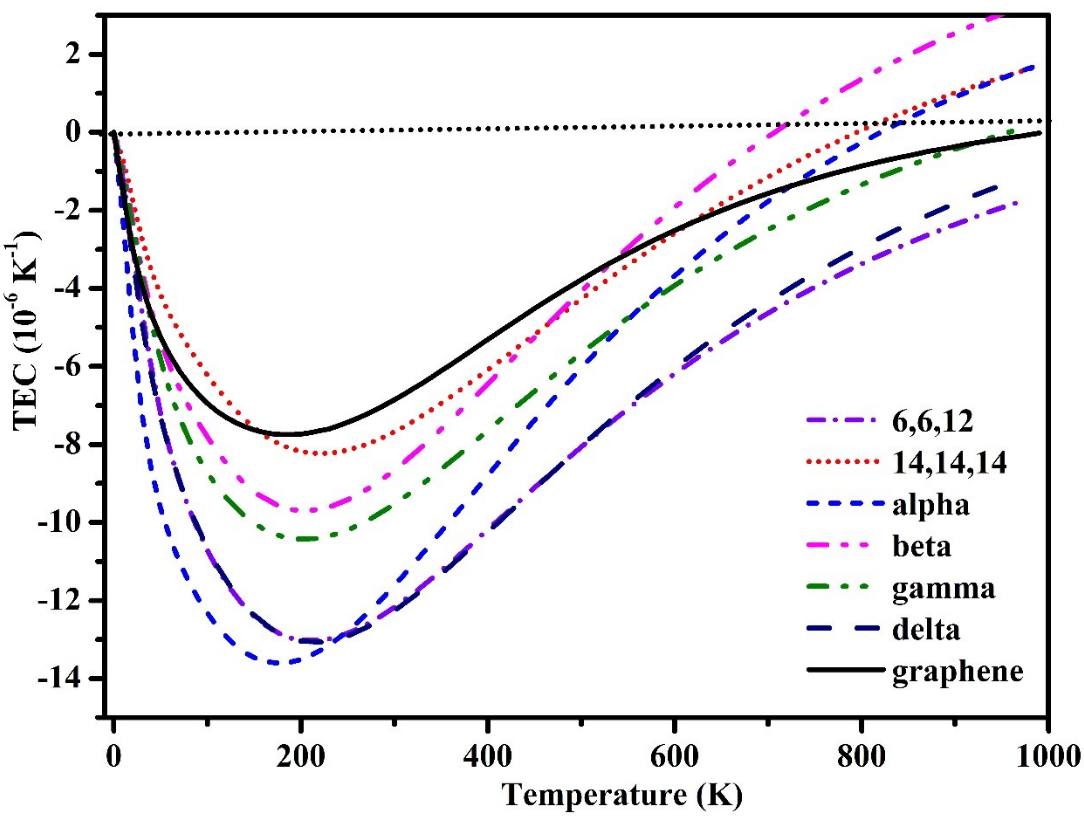


Figure S10. *Thermal expansion coefficient of* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-)* ***(g)*** *graphene.*

Graphene the two-dimensional Carbon allotrope, is one of the first two-dimensional sheet that showed the Negative thermal expansion, is evident in innumerable research articles. The negative thermal expansion of graphene arises from the rigid unit modes. The thermal expansion coefficient for the lowest acoustic mode in graphene exhibits negative values at low temperatures, indicating an unusual behavior. This phenomenon arises because, at lower temperatures, only the lower acoustic modes are thermally excited. Consequently, the unique characteristics of these modes contribute to the observed negative thermal expansion coefficient in graphene. The temperature variation of the Grüneisen parameter which is mainly responsible for the negative values of the TECs are negative for acoustic modes (ZA, TA, LA) till 20 THz (See supporting information file **Figure S11**).

Several research articles have already proven the high ductility and NTE of graphene till 1000K. But, 14,14,14, alpha and beta Gys start showing postitive thermal expansion much before 1000K.

16. Figure S11 Grüneisen parameter vs frequency plot for graphene.

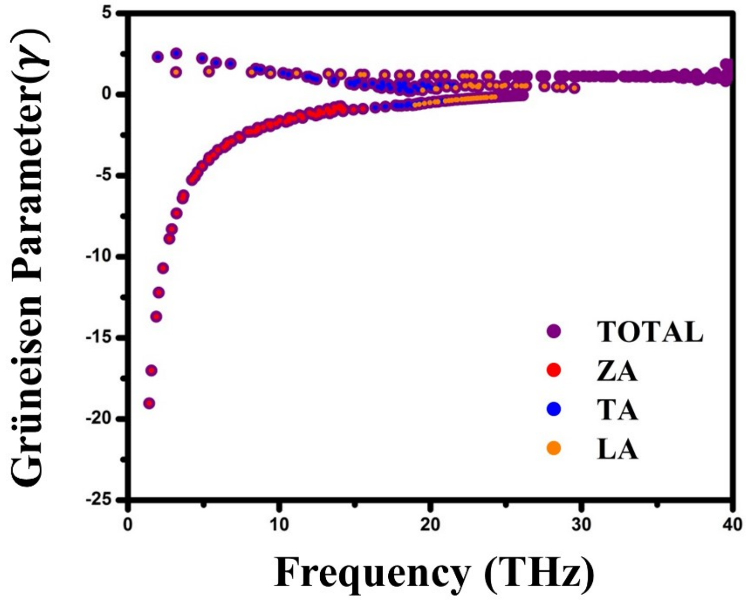
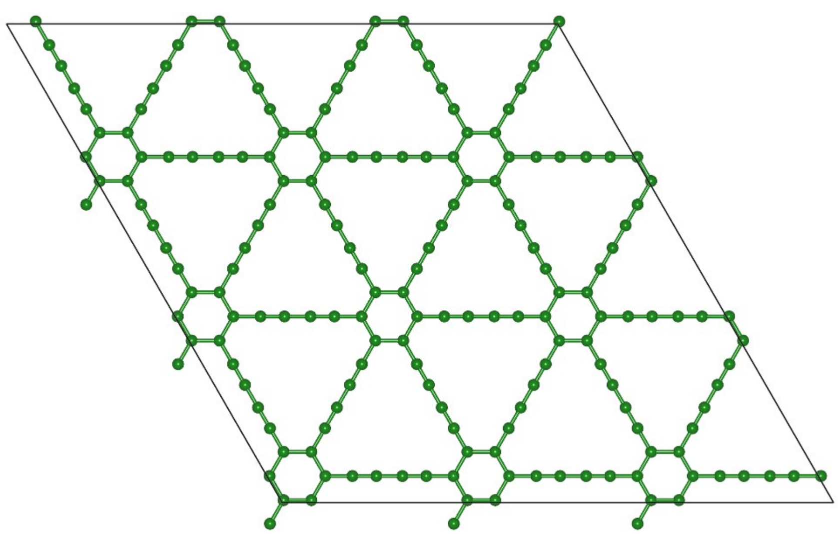


Figure S11 *Grüneisen parameter vs frequency plot for graphene.*

17. Figure S12. Visualization of graphdiyne.



18. Figure S13. Relative magnitudes for the thermal expansion coefficients in graphdiyne (GDy) with the graphyne systems and other carbon allotropes at room temperature.

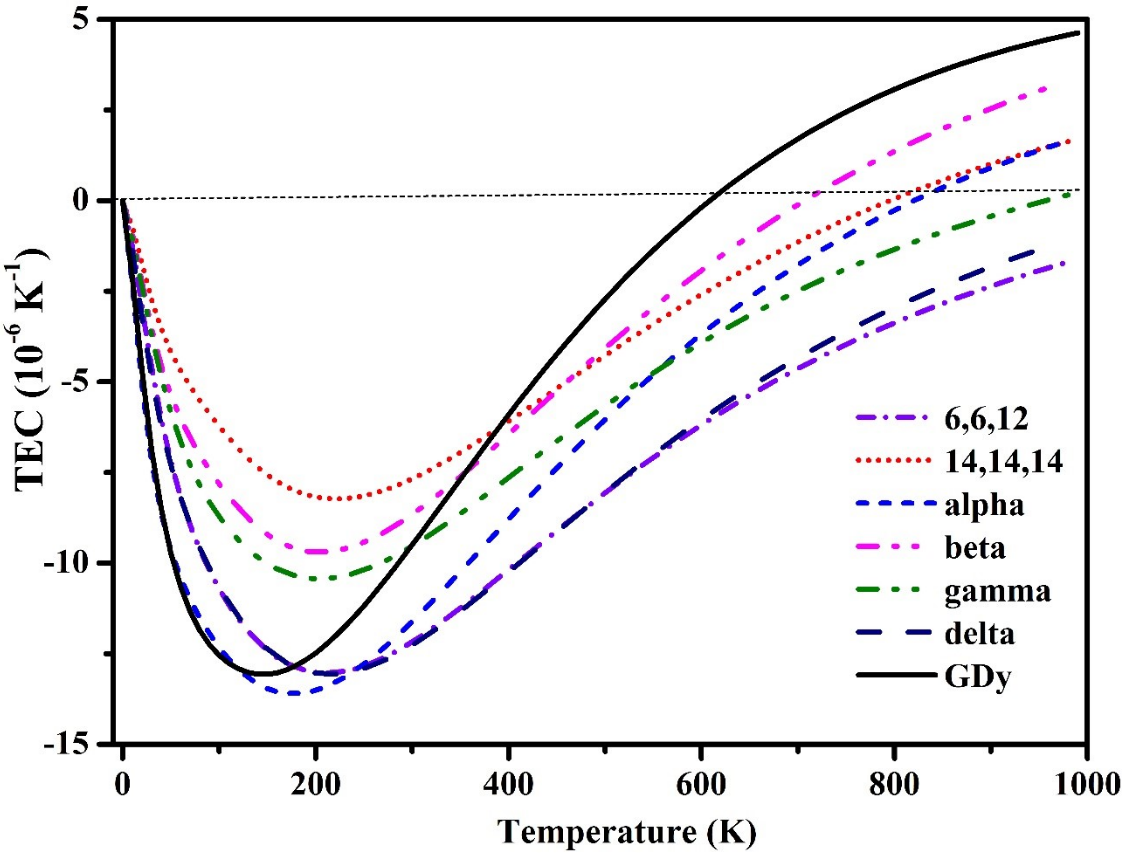


Figure S13. *Thermal expansion coefficient of* ***(a)*** *(6,6,12-),* ***(b)*** *(14,14,14-),* ***(c)*** *α (18,18,18-),* ***(d)*** *β (12,12,12-),* ***(e)*** *γ (6,6,6-) and* ***(f)*** *δ (6,6,14-)* ***(g)*** *GDy (Graphdiyne).*

The mechanical property of graphdiyne is similar to graphyne[3-5], i.e. it is brittle in nature, which makes it attain PTE at lower temperature. GDy has 5 different types of bond connectivities (sp-sp-sp-sp, sp^2-sp^2-sp^2-sp^2, sp^2-sp^2-sp-sp, sp-sp^2-sp^2-sp, and sp^2-sp^2-sp^2-sp) which is highest among Gy family making it most anharmonic and shoots up the NTE value.

19. Table ST5. Thermal expansion coefficient (TEC) values of **(a)** (6,6,12-), **(b)** (14,14,14-), **(c)** α (18,18,18-), **(d)** β (12,12,12-), **(e)** γ (6,6,6-) **(f)** δ (6,6,14-), **(g)** **(h)** GDy (graphdiyne) at room temperature (r.t).

2D Carbon allotropes	TEC values at r.t (10^{-6} K^{-1})
(6,6,12-)	-4.59013
(14,14,14-)	-2.71835
α (18,18,18-)	-7.19711
β (12,12,12-)	-3.52966
γ (6,6,6-)	-3.68903
δ (6,6,14-)	-4.87272
graphene	-3.93952
GDy (graphdiyne)	-6.86171

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