Supporting Information

Electronic Bandgap Engineering of Pyrene-Modified α-Graphyne through Chemical Functionalization and Mechanical Strain

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Figure S1: The polar plots on the radial representation of elastic moduli, Young's modulus, Shear modulus and Poisson's ratio.

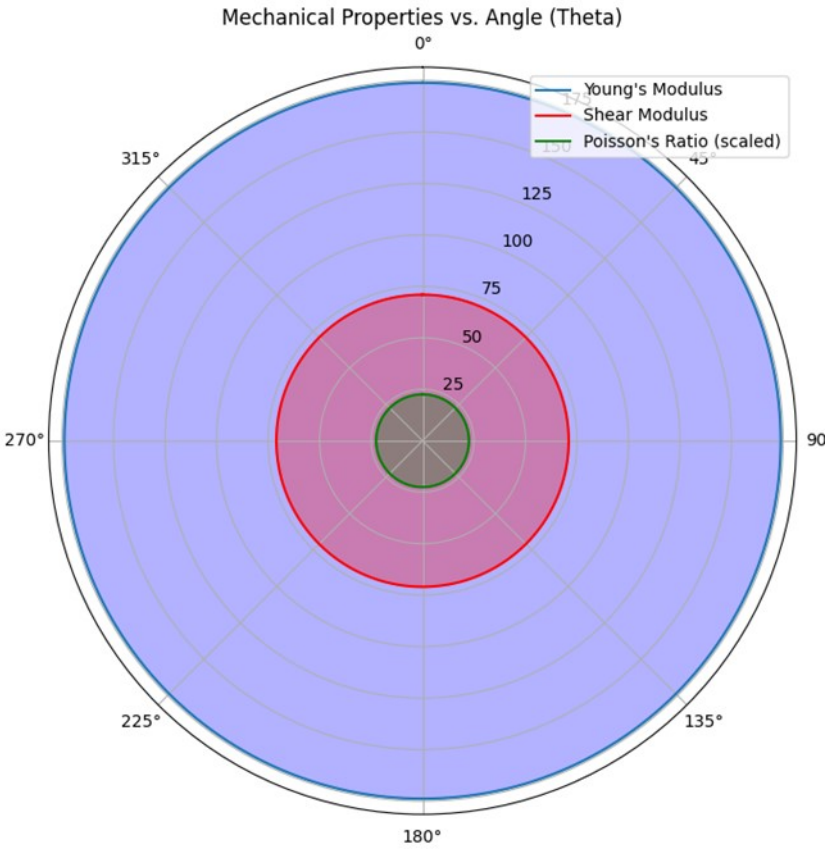

Table S1: Strain-induced bandgap along x and y axis

strain	along x (zig-zag)	along y (armchair)
-0.030	0.0186	0.02000
-0.025	0.0095	0.01290
-0.020	0.0043	0.00910
-0.015	0.0026	0.00470
-0.010	0.0017	0.00250
-0.005	0.0006	0.00060
0.000	0.0000	0.00000
0.005	0.0006	0.00100
0.010	0.0015	0.00230
0.015	0.0026	0.00380
0.020	0.0041	0.00670
0.025	0.0076	0.01030
0.030	0.0112	0.01430

Geometrical Parameter	Pyrene-modified α-graphyne	H-all sites	H-non acetylenic	F-all sites	F-non-acetylenic	Cl-all sites	Cl-non-acetylenic
a(Å)	14.41	14.48	14.41	14.53	14.41	14.53	14.41
b(Å)	14.41	14.48	14.41	14.53	14.41	14.53	14.41
c(Å)	14.57	9.96	14.57	15.85	14.57	15.85	14.57
α	90°	90°	90°	91.11°	90°	91.11°	90°
β	90°	90°	90°	89.50°	90°	89.50°	90°
Γ	120°	120°	120°	120.06°	120°	120.05°	120°
Cell volume	2619	1808	2619	2896	2620	2896	2619
C-C	1.40	1.56	1.55	1.54	1.55	1.54	1.40
C≡C	1.22	1.21	1.21	1.34	1.21	1.34	1.22
C-X or -H		1.11	1.51	1.39	1.40	1.49	1.75

Table S2: The geometrical parameters of the optimized unit cell of pyrene modified α-graphyne and the functionalized structures

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Figure S2: The phonon band structure of full Hydrogenation.

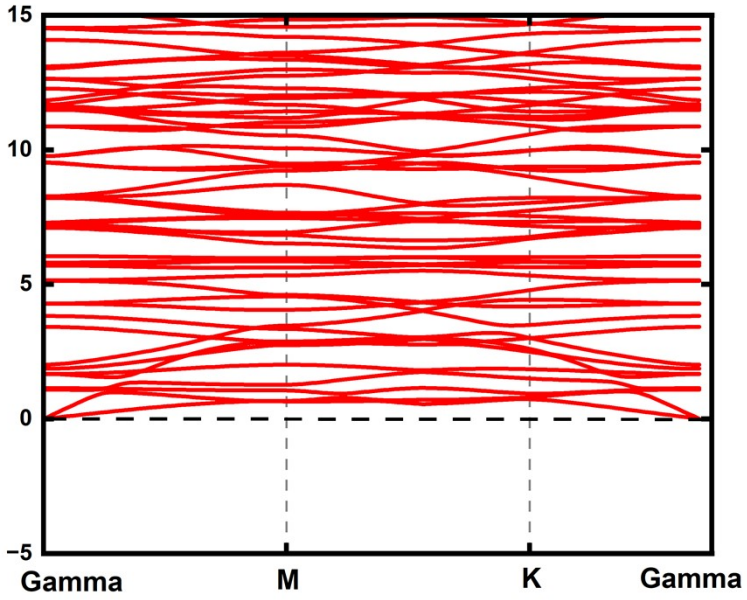


Figure S3: The phonon band structure of partial Hydrogenation.

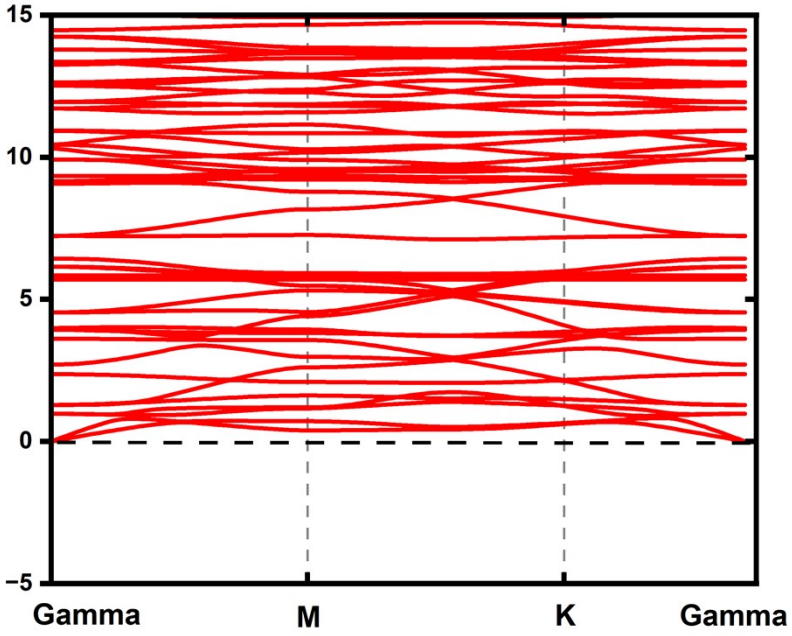


Figure S4: The phonon band structure of full Fluorination.

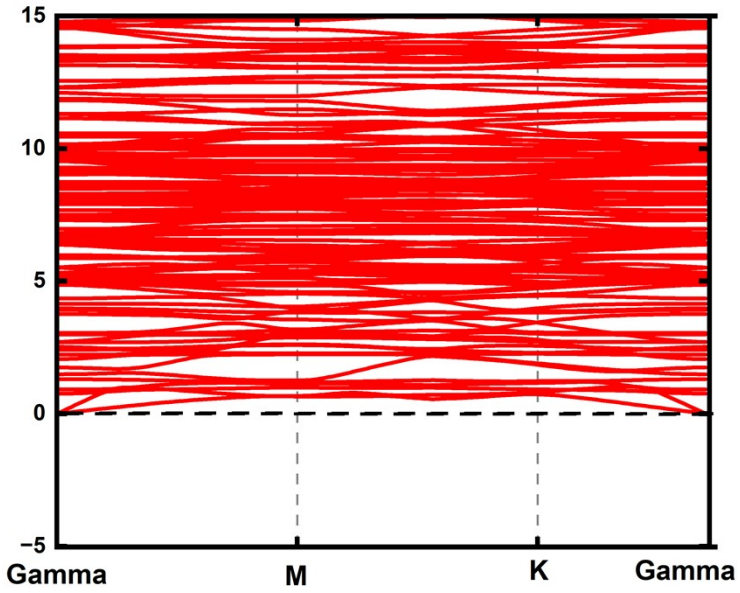


Figure S5: The phonon band structure of partial Fluorination.

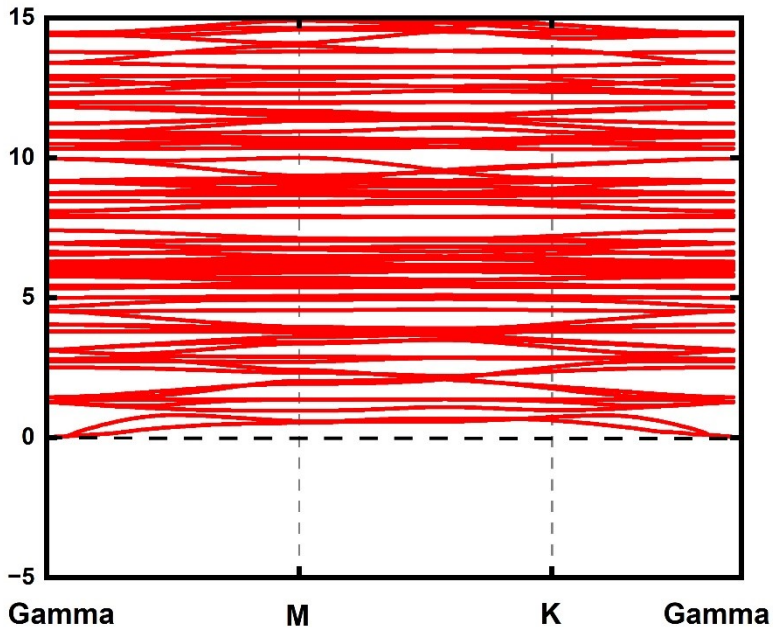
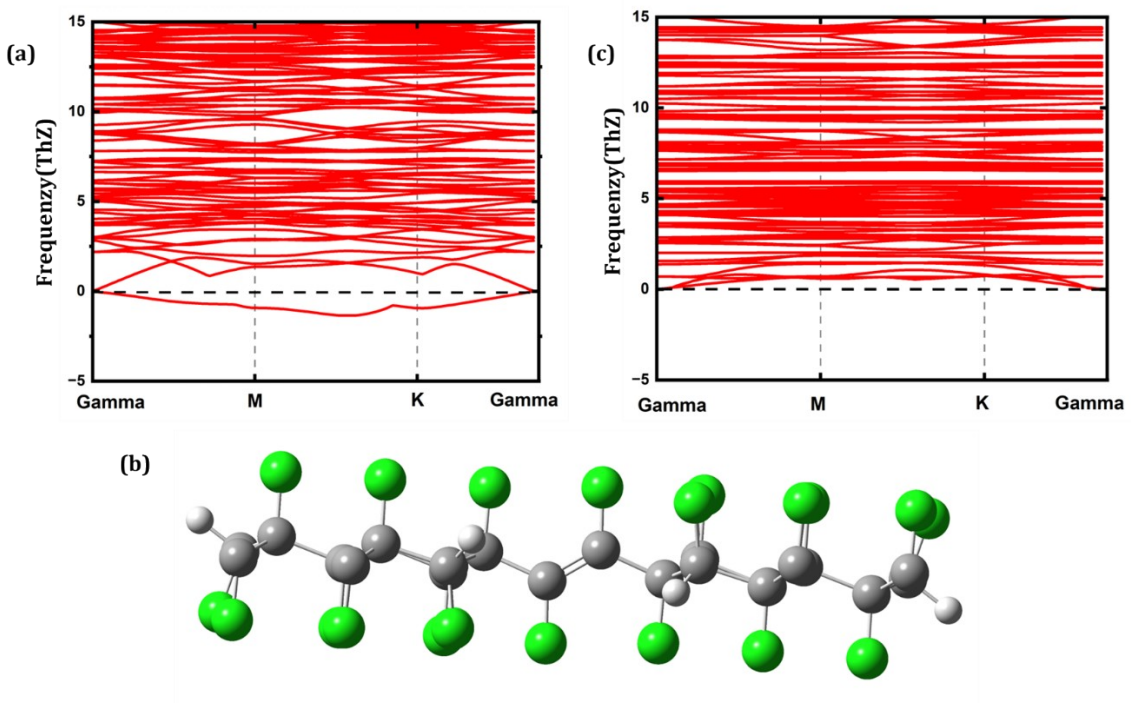


Figure S6: (a) Phonon structure of fully chlorinated pyrene-based α-graphyne, **(b)** The side view of the fully Chlorinated pyrene-based α-graphyne; **(c)** Phonon structure of partially Chlorinated pyrene-based α-graphyne.



Fully hydrogenated and fully fluorinated structures exhibit no imaginary phonon modes across the entire Brillouin zone (**Figures S4 and S5**), confirming robust harmonic stability arising from complete passivation of sp and sp^2 carbon sites. In contrast, selectively hydrogenated and fluorinated configurations remain dynamically viable but display low-frequency soft acoustic modes near the Γ point (**Figures S6 and S7**), indicative of enhanced lattice flexibility associated with unpassivated acetylenic linkers.

Complete chlorination introduces pronounced imaginary phonon modes along the M–K and K–Γ directions (**Figure S8a**), signaling dynamic instability. Structural inspection reveals significant out-of-plane distortions driven by steric repulsion between adjacent chlorine atoms (**Figure S8b**). When chlorination is restricted to non-acetylenic sites, the phonon spectrum becomes entirely positive (**Figure S8c**), restoring harmonic stability while retaining mild low-frequency softening. These trends are consistent with prior reports on chlorinated graphene, where excessive halogen coverage leads to phonon softening and buckling instabilities.[1]

(1) Şahin, H.; Ciraci, S. Chlorine Adsorption on Graphene: Chlorographene. *J. Phys. Chem. C* **2012**, *116* (45), 24075–24083. https://doi.org/10.1021/jp307006c.

Figure S7: The band structure of functionalization of modified α-4 graphyne with;(a) Hydrogen,(c) Fluorine, (e) Chlorine. The density of state plots of functionalization of modified α-4 graphyne with;(b) Hydrogen,(d) Fluorine, (f) Chlorine.

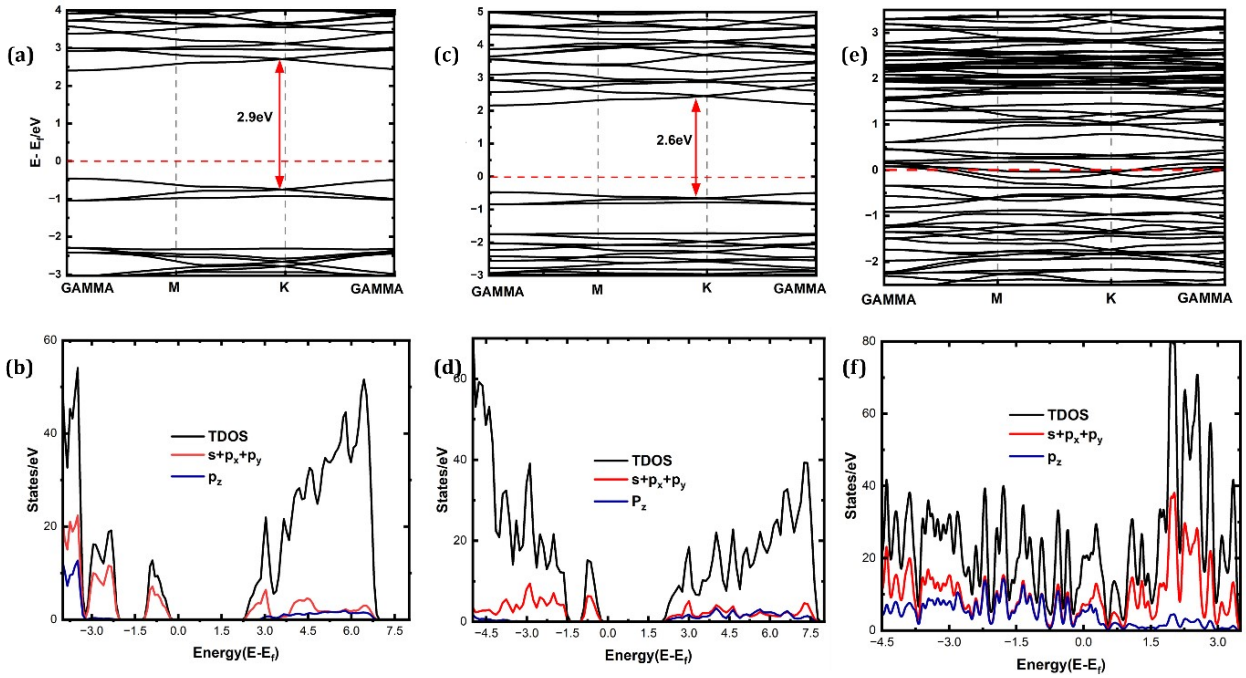
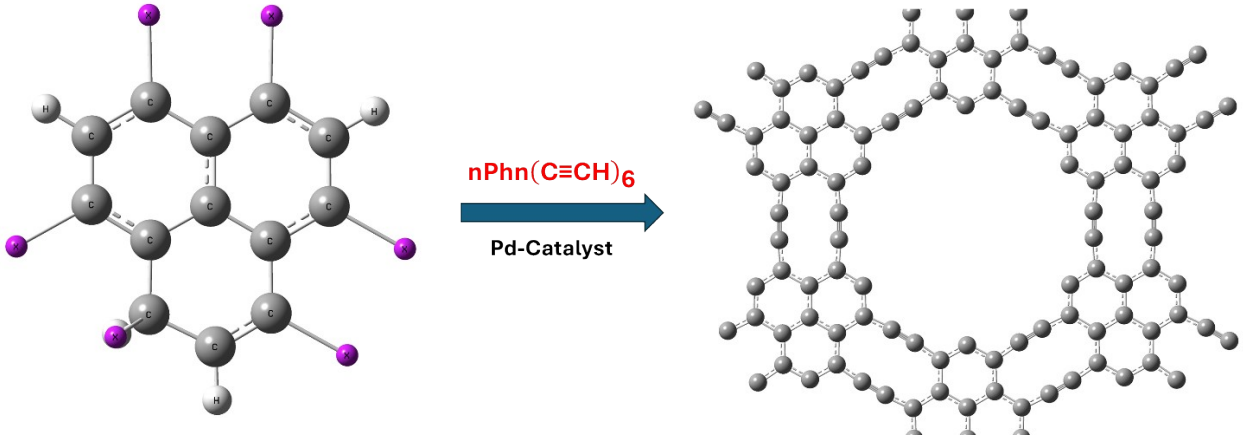


Table S3: The adsorption energies of gases(**eV**) Cl_2, F_2, NO, O_2, and CO_2 at sites S1 and S2.

S1		**S2**	
Gas Type	**E_{ad}**	**Gas Type**	**E_{ad}**
Cl2	-1.94	**Cl2**	-2.24
F2	-4.54	**F2**	-4.11
NO	-2.59	**NO**	-4.17
O2	-2.71	**O2**	-3.77
CO2	-3.68	**CO2**	-4.21

Scheme 1: Proposed Synthetic route for pyrene modified α-graphyne



A conceptual synthetic pathway for constructing a phenalene-linked sp/sp^2 carbon network via Pd/Cu-catalyzed Sonogashira coupling. In the first step, phenalene is regioselectively functionalized at edge positions (e.g., 4, 6, 8, 9, 10, 11) via iterative halogenation, yielding a multi-halogenated phenalene precursor ($PhnX_6$, X = Br or I).

Subsequently, the halogenated phenalene nodes undergo Pd/Cu-catalyzed Sonogashira cross-coupling with terminal or protected ethynyl groups to generate ethynyl-functionalized phenalene building blocks. Repetition of this coupling step under surface-confined or interfacial conditions enables the formation of extended –Phn–C≡C–Phn– linkages, giving rise to a two-dimensional sp/sp^2 carbon network.