Electronic Supplementary Information (ESI)

Hydrostatic Pressure Effect on Charge Transport Properties of Phenacenes Organic Semiconductors.

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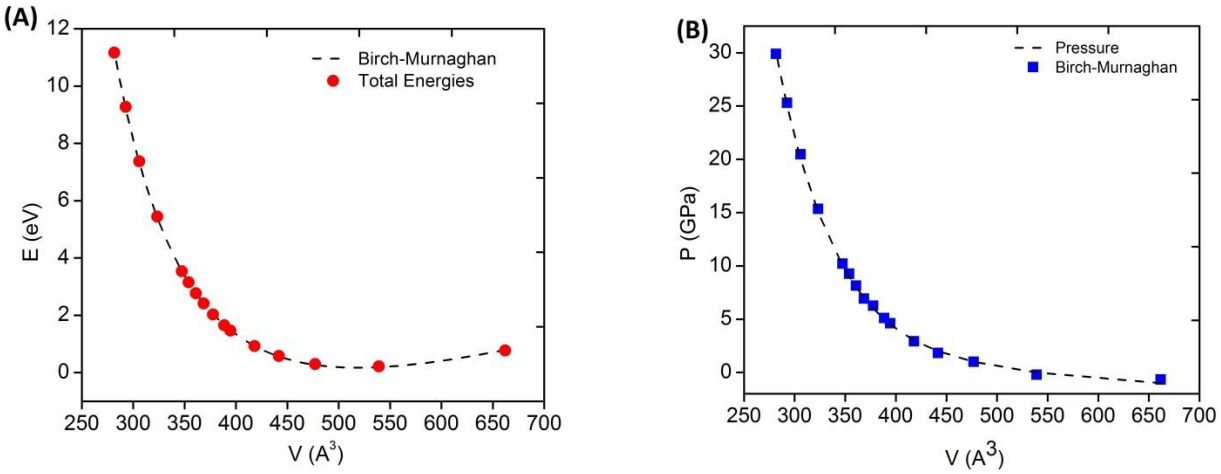

Figure S1. EOS of phenanthrene crystal from DFT calculations. (A) Energy vs volume relation where the total energies (red dot) is fitted with Birch-Murnaghan equation of state (dashed line). (B) Corresponding pressure (P) vs volume (V) relation.

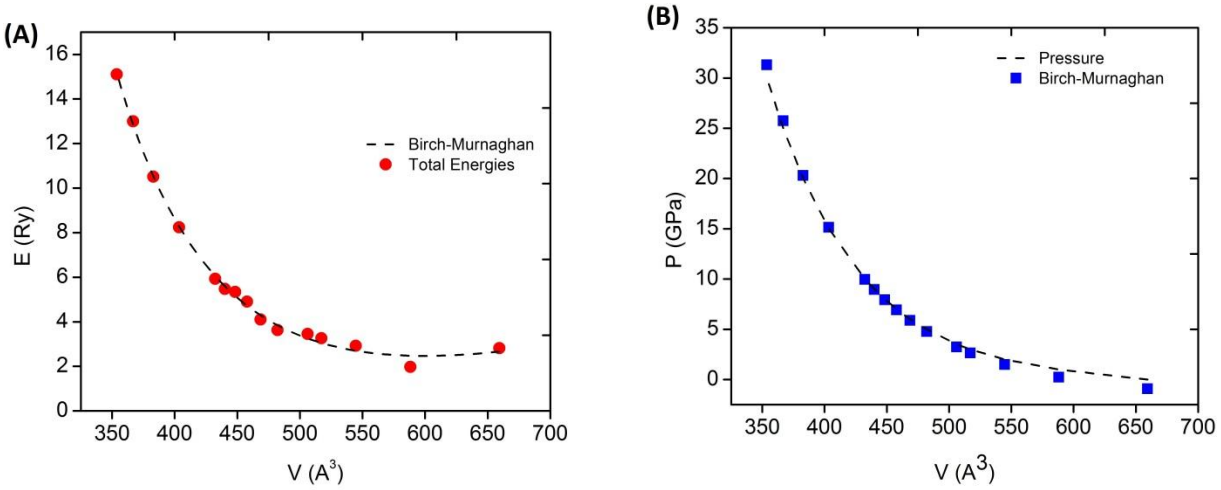

Figure S2. EOS of solid chrysene from the DFT calculations. (A) Energy vs volume (V) relation where the total energies (red dot) is fitted with Birch-Murnaghan equation of state (dashed line). (B) Pressure (P) vs volume (V) relation.

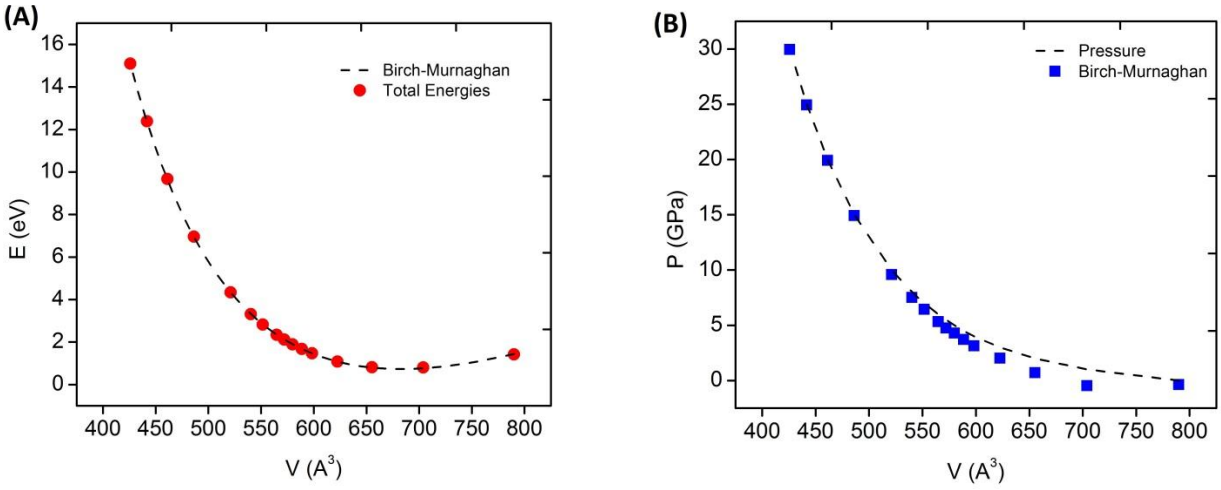

Figure S3. Equation of state of solid picene, from DFT calculations. (A) Energy vs volume (V) relation where the total energies (red dot) is fitted with Birch-Murnaghan equation of state (dashed line). (B) Pressure (P) vs volume (V) relation.

Fig. S1, S2 and S3(A) depicts the EOS based on the calculated volume and energy for phenanthrene, chrysene and picene along with a fit to the Birch-Murnaghan relation. From the EOS, we take the first derivative and obtain the pressure along the volume compression as shown in Fig. S1, S2 and S3(B).

Table S1. The bulk modulus of phenacenes and isomeric acenes as well as the equilibrium volume V_0 under the effect of compression

Formula		B_0	V_0^{theo}	V_0^{exp}
$C_{14}H_{10}$	Phenanthrene	7.92	518.6	484.4[b]
	Anthracene	8.40[a]	-------	-------
$C_{18}H_{12}$	Chrysene	12.24	599.1	587.5[c]
	Tetracene	9.00[a]	-------	-------
$C_{22}H_{14}$	Picene	17.56	682.5	708.0[d]
	Pentacene	9.60[a]	-------	-------

a) Ref. 1 b) Ref. 2 c) Ref. 3 d) Ref. 4

In Table. S1, the calculated equilibrium volume of phenanthrene is V_0^{exp} = 518.6 Å^3, 7% different from the experimental volume of 484.4 Å^3. We estimate the bulk modulus as B_0 = 7.92 GPa. The calculated modulus B_0 is in range of agreement with the reported bulk modulus for its isomeric form anthracene of 8.4 GPa.

The bulk modulus obtained in chrysene is 12.24 GPa exhibits a resistance under compression by an amount of applied pressure better than phenanthrene. Compared to tetracene with bulk modulus of 9.0 GPa, phenacene-type molecules has better stability under pressure than acene-type molecules. The equilibrium volume of chrysene obtained is 599.1 Å^3, 2% higher than the experimental structure of 587.5 Å^3.

In picene, we obtain the equilibrium volume of 682.5 Å^3, which is closer to the experimental value of 708 Å^3 with the bulk modulus is 17.56 GPa, much higher than the reported bulk modulus of pentacene of 9.6 GPa. We notice that our results are in agreement with the previous report of equilibrium V_0 = 613 Å^3 and the bulk modulus B_0 = 18.5 GPa in the same system using (Local-density approximation) LDA functional [5].

References

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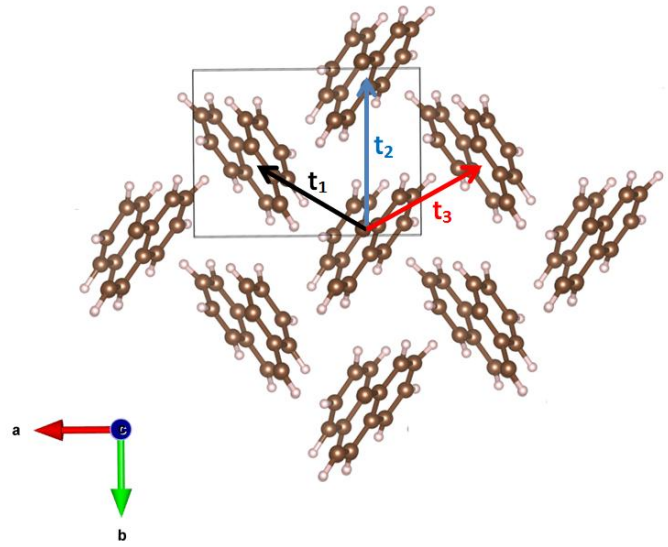

Figure S4. Directions of hopping pathways for phenanthrene crystal throughout the compression study.

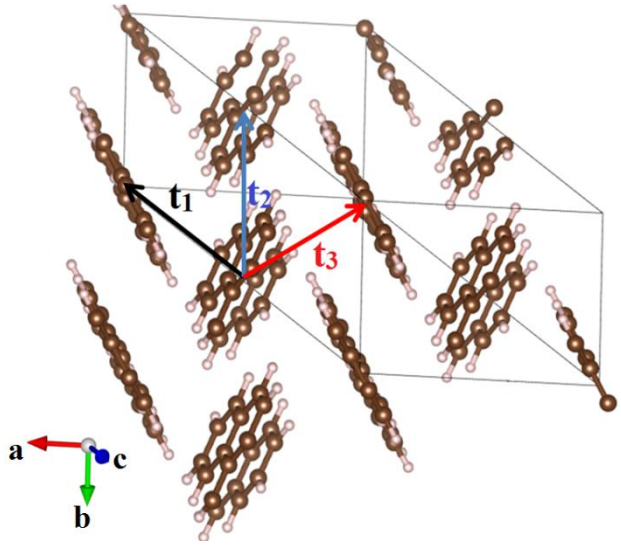

Figure S5. Directions of hopping pathways for chrysene crystal throughout the compression study.

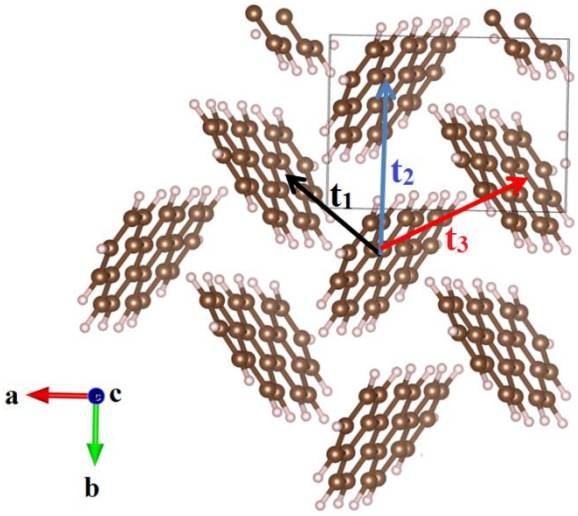

Figure S6. Directions of hopping pathways for picene crystal throughout the compression study.

Table S2. Applied Pressure (P), Corresponding Volume (V), Energy Gap (E_g), Intermolecular Distance (D), Hole Transfer Integral (t_{hole}) for channel 1 (t_1), channel 2 (t_2), channel 3 (t_3), and the Hole Mobility (μ_{hole}) of phenanthrene.

			D (Å)			$\lvert t_{hole} \rvert$ (eV)			μ_{hole} ($cm^2\ V^{-1}\ s^{-1}$)		
P (GPa)	V (Å^3)	E_g (eV)	t_1	t_2	t_3	t_1	t_2	t_3	t_1	t_2	t_3
-0.22	539.13	2.994	5.333	6.371	5.591	0.045	0.028	0.034	0.521	0.284	0.327
1.00	476.98	2.857	5.101	6.116	5.326	0.064	0.036	0.051	0.964	0.438	0.667
1.82	441.80	2.769	4.976	5.893	5.119	0.076	0.040	0.060	1.293	0.497	0.880
2.93	418.20	2.675	4.864	5.723	5.085	0.089	0.042	0.070	1.694	0.522	1.146
4.60	394.65	2.556	4.765	5.575	4.969	0.102	0.045	0.082	2.136	0.569	1.501
5.10	388.63	2.522	4.734	5.555	4.930	0.107	0.046	0.086	2.320	0.590	1.625
6.25	377.76	2.454	4.675	5.500	4.874	0.116	0.048	0.093	2.659	0.630	1.858
6.92	368.59	2.398	4.628	5.474	4.808	0.124	0.052	0.103	2.978	0.733	2.218
8.13	360.93	2.341	4.584	5.423	4.775	0.132	0.052	0.107	3.311	0.719	2.360
9.26	353.93	2.289	4.548	5.396	4.729	0.140	0.055	0.115	3.665	0.796	2.674
10.20	347.49	2.241	4.516	5.363	4.687	0.145	0.056	0.123	3.877	0.816	3.005
15.34	323.40	2.030	4.383	5.246	4.540	0.176	0.061	0.153	5.381	0.926	4.363
20.47	305.99	1.850	4.285	5.158	4.430	0.201	0.066	0.180	6.708	1.048	5.750
25.29	292.69	1.698	4.210	5.090	4.340	0.223	0.070	0.206	7.969	1.148	7.227
29.89	281.66	1.557	4.146	5.024	4.268	0.242	0.073	0.230	9.102	1.216	8.713

Table S3. Applied Pressure (P), and Electron Mobility ($\mu_{electron}$) of phenanthrene for channel 1 (t_1), channel 2 (t_2) and channel 3 (t_3).

	$\mu_{electron}$ (cm^2 V^{-1} s^{-1})		
P (GPa)	t_1	t_2	t_3
-0.22	0.016	0.117	0.044
1.00	0.033	0.277	0.075
1.82	0.022	0.541	0.072
2.93	0.024	0.814	0.11
4.60	0.024	1.208	0.123
5.10	0.028	1.288	0.133
6.25	0.033	1.542	0.149
6.92	0.042	1.677	0.172
8.13	0.042	1.958	0.182
9.26	0.048	2.135	0.194
10.20	0.055	2.335	0.205
15.34	0.081	3.395	0.261
20.47	0.106	4.442	0.306
25.29	0.134	5.495	0.337
29.89	0.393	6.63	0.144

Table S4. Applied Pressure (P), Corresponding Volume (V), Energy Gap (E_g), Intermolecular Distance (D), Electron Transfer Integral ($t_{electron}$) for channel 1 (t_1), channel 2 (t_2), channel 3 (t_3), and the Hole Mobility ($\mu_{electron}$) of chrysene. Blue mark shows the pressure in which the ambipolar characteristic was observed and red mark shows the pressure in which the n-type characteristic happened.

			D (Å)			$\lvert t_{electron} \rvert$ (eV)			$\mu_{electron}$ (cm^2 V^{-1} s^{-1})		
P (GPa)	V (Å^3)	E_g (eV)	t_1	t_2	t_3	t_1	t_2	t_3	t_1	t_2	t_3
-0.93	659.39	2.598	5.462	6.486	5.462	0.008	0.034	0.008	0.017	0.445	0.017
0.23	588.22	2.459	5.217	6.215	5.217	0.012	0.050	0.012	0.035	0.884	0.034
1.49	544.63	2.351	5.070	6.059	5.070	0.013	0.065	0.013	0.037	1.419	0.037
2.64	517.13	2.268	4.960	5.956	4.960	0.013	0.077	0.013	0.040	1.910	0.040
3.24	506.07	2.198	4.936	5.814	4.936	0.016	0.092	0.016	0.056	2.618	0.056
4.78	482.19	2.141	4.815	5.830	4.815	0.016	0.094	0.016	0.054	2.748	0.054
5.87	468.62	2.019	4.789	5.616	4.789	0.020	0.122	0.020	0.084	4.317	0.084
6.93	457.89	1.975	4.736	5.595	4.735	0.020	0.128	0.020	0.084	4.690	0.082
7.93	448.39	1.911	4.700	5.527	4.700	0.022	0.140	0.021	0.098	5.479	0.089
8.95	440.07	1.867	4.662	5.498	4.662	0.022	0.147	0.022	0.096	5.978	0.096
9.95	432.46	1.817	4.523	5.46	4.63	0.024	0.156	0.023	0.108	6.639	0.104
15.14	403.48	1.631	4.495	5.332	4.495	0.026	0.189	0.024	0.125	9.294	0.107
20.30	382.87	1.459	4.400	5.245	4.400	0.028	0.216	0.027	0.139	11.75	0.129
25.74	366.84	1.312	4.322	5.176	4.323	0.027	0.241	0.028	0.120	14.24	0.134
31.31	353.67	1.186	4.258	5.121	4.258	0.026	0.261	0.028	0.112	16.35	0.130

Table S5. Applied Pressure (P), Corresponding Volume (V), Energy Gap (E_g), Intermolecular Distance (D), Hole Transfer Integral (t_{hole}) (for channel 1 (t_1), channel 2 (t_2), channel 3 (t_3)) and the Hole Mobility (μ_{hole}) of picene. Red mark shows the pressure in which the isotropic characteristic happens.

			D (Å)			$\lvert t_{hole} \rvert$ (eV)			μ_{hole} ($cm^2\ V^{-1}\ s^{-1}$)		
P (GPa)	V ($Å^3$)	E_g (eV)	t_1	t_2	t_3	t_1	t_2	t_3	t_1	t_2	t_3
-0.470	703.97	2.37	5.193	6.133	5.338	0.065	0.068	0.064	1.520	2.330	1.560
0.690	655.23	2.239	5.035	6.000	5.165	0.082	0.082	0.080	2.279	3.236	2.282
2.020	622.54	2.134	4.959	5.763	5.116	0.095	0.087	0.092	2.967	3.361	2.962
3.120	598.32	2.031	4.883	5.647	5.083	0.106	0.093	0.104	3.581	3.687	3.680
3.710	588.64	1.992	4.842	5.634	4.994	0.112	0.098	0.110	3.932	4.075	4.034
4.280	579.9	1.938	4.817	5.580	4.973	0.117	0.100	0.114	4.246	4.162	4.297
4.750	572.03	1.900	4.788	5.552	4.943	0.122	0.102	0.119	4.561	4.287	4.625
5.310	567.78	1.865	4.763	5.572	4.914	0.126	0.105	0.123	4.815	4.502	4.884
6.430	551.68	1.797	4.715	5.481	4.862	0.135	0.109	0.132	5.416	4.771	5.506
7.510	540.27	1.735	4.673	5.442	4.816	0.144	0.113	0.140	6.053	5.060	6.077
9.570	521.17	1.624	4.600	5.381	4.736	0.159	0.121	0.156	7.151	5.667	7.297
14.91	486.24	1.395	4.469	5.258	4.590	0.191	0.137	0.190	9.740	6.937	10.167
19.90	461.23	1.210	4.372	5.17	4.481	0.219	0.150	0.218	12.255	8.040	12.757
24.93	441.81	1.047	4.296	5.098	4.395	0.243	0.162	0.244	14.569	9.118	15.374
29.96	425.87	0.891	4.233	5.037	4.323	0.265	0.174	0.268	16.822	10.269	17.944

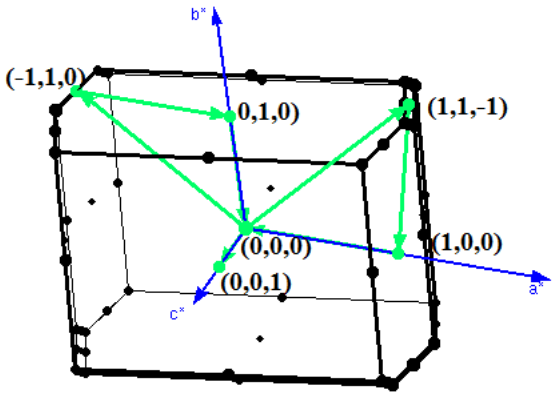

Figure S7. Brillouin zone of chrysene crystal. The path for the calculation of band structure is indicated by a green line.