Highly pure pentacene crystals grown by physical vapor transport: the critical role of the carrier gas

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Fig. S1. Molecular structures of (a) pentacene, (b) pentacenyl radical (6PR\(^\cdot\)), and (c) dihydropentacene (DHP).
Fig. S2. Mass spectrum of commercial pentacene powder ( Sigma-Aldrich). It is expressed as a relative intensity in % between \( m/z = 270 \) and 285, based on pentacene at \( m/z = 278 \). A relatively large amount of \( m/z \) at 279 and 280 indicates the presence of impurities with similar molecular weights of pentacene, such as 6PR and DHP.
**Fig. S3.** Mass spectrum of pentacene powder after annealed at 503 K for 60 minutes in an inert environment. Upon heating, it shows an increase of the impurities, compared to 298 K (without further treatment).
Fig. S4. Calculated mass spectrum of isotopic pentacene (C$_{22}$H$_{14}$).
Fig. S5. Kinetic parameters of various carrier gases at 625 K. (a) Equation of root mean square velocity defined by the molecular weight of gas and temperature. (b) Comparison of the molecular weight and the average velocity of gases. The velocity of $H_2$ is 4.5 times faster than that of Ar as molecular weight is inversely proportional to the velocity of each gas molecule. In accordance with similar molecular weight, Ar-N$_2$ and H$_2$-He have a similar trend in the velocity.

(a) $v_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}}$

- $v_{\text{r.m.s.}}$ = Root mean square velocity of the gas
- $R$ = Gas constant
- $T$ = Absolute temperature
- $M$ = Molecular weight of the gas

(b) | Molecular weight (g mol$^{-1}$) | $v_{\text{r.m.s.}}$ (m s$^{-1}$) |
<table>
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<tbody>
<tr>
<td>Ar</td>
<td>39.94</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2.016</td>
</tr>
<tr>
<td>$N_2$</td>
<td>28.01</td>
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<tr>
<td>He</td>
<td>4.003</td>
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Fig. S6. Equation and parameters for Rayleigh number (Ra). (a) Equation of dimensionless Rayleigh number defined by thermofluid parameters, such as viscosity and thermal diffusivity. (b) Comparison of Rayleigh numbers of carrier gases, which determine the flow type in a quartz tube. As the convective flow becomes dominant for larger Rayleigh number than 1,296 (critical Rayleigh number). Ar-N₂ and H₂-He show similar trends of convective flow and laminar flow, respectively.
**Fig. S7.** The differences of remaining materials and products grown in Ar and H$_2$ environments. (a, b) Summary of PVT reactions from starting materials to residue in the crucible in (a) Ar and (b) H$_2$ environment. (c) The composition and percentage ratio of remaining impurities after crystal growth.

In the Ar environment, the impurities increased by about 3.7 mg compared to before the reaction, whereas in the H$_2$ environment, only 0.08 mg increased. These results clearly show that the formation of impurities is well suppressed under the H$_2$ environment.
Fig. S8. Mass spectra of the residue in (a) Ar and (b) H$_2$ which consists of the distribution of m/z peaks occurring in the hydrogenation from bipentacene to fully fused PP. The intensity ratio of PP to pentacene in Ar environment remains much larger than in H$_2$ environment. Hence, the disproportionation reaction rarely occurs in H$_2$ environment, while it occurs actively in Ar environment.
The PXRD pattern is almost identical to that of pentacene (magenta), which indicates the formation of DHP-pentacene cocrystal. It should be noted that the peaks with two theta values of ~6°, 12°, 18°, and 24° (grey with dashed line) come from plate-shaped pentacene crystals.

Fig. S9. (a) SEM image and (b) PXRD pattern (purple) of resulting crystals grown in N\textsubscript{2} environment.
Fig. S10. (a) SEM image and (b) PXRD pattern (sky-blue) of the resulting crystals grown in He environment. The diffraction pattern of pentacene$^{\text{H}_2}$ (blue) is identical to that of pentacene$^{\text{H}_2}$ having two theta values of $\sim 6^\circ$, $12^\circ$, $18^\circ$, and $24^\circ$ (grey with dashed line).
Fig. S11. PL properties of pentacene$^{Ar}$ and pentacene$^{H2}$ in the aggregate and solution states measured at 298 K; while pentacene$^{Ar}$ is still highly emissive in solution state, pentacene$^{H2}$ is non-emissive.
**Fig. S12.** PL spectra of pentacene$^{12}$ measured at 298 K (grey) and 194 K (blue).
Fig. S13. Schematic of the field-effect transistor (FET) device.
Fig. S14. Pentacene\textsuperscript{H2} with controlled thicknesses for fabricating OFET devices. (a, b) SEM images of pentacene\textsuperscript{H2} obtained from; (a) original condition and (b) modified condition of PVT.
Fig. S15. Mass spectra of commercially available pentacene powder (TCI (Japan)) with (a) no further treatment and (b) thermal annealing at 503 K for 60 min under Ar flow. Like as pentacene powder purchased from Sigma-Aldrich, a drastic increase in peak intensities of the impurities (6PR and DHP) is shown by heat.
Fig. S16. SEM images and mass spectrum of (a, b) pentacene$^+$ and (c, d) pentacene$^{12}$ grown using pentacene powder purchased from TCI (Japan). The scale bar in the inset image is 10 µm.
Fig. S17. PL and electrical properties of pentacene$^{Ar}$ and pentacene$^{H2}$. (a) PL spectra of pentacene$^{Ar}$ (magenta) and pentacene$^{H2}$ (blue). (b) $I-V$ characteristics of insulating pentacene$^{Ar}$. (c, d) Transfer and output curves of pentacene$^{H2}$ indicating $p$-type semiconducting behavior.
**Fig. S18.** PXRD patterns of resulting crystals grown in (a) Ar and (b) H$_2$ environments at low pressure. The PXRD result of (a) pentacene$^{Ar}$ and (b) pentacene$^{H_2}$ grown at low pressure is almost identical to that of pentacene$^{Ar}$ and pentacene$^{H_2}$ grown at atmospheric pressure (dots), respectively.