

Supporting information:

The phenomena of polymorphs widely exist in crystals.¹ Siegrist et al found that pentacene single crystals from PVT had tighter molecular stacking than those from solution, and this tight molecular stacking structure effectively improved the physical performance such as the effect-field mobility could be up to 3 cm²/Vs at room temperature.² The crystals obtained by PVT method should be a kind of thermodynamically stable form. The reason may be the molecules in vapor have more flexible than that in solution because of the influence of high-temperature growth conditions and carrier gas molecules. Taken *trans*-DPDSB molecule for example, the crystal from vapor is strip shape with molecules staggered parallel stacking and that from solution is needle shape with molecules crossed stacking.^{3,4} On the basis of different molecular stacking modes, we performed B3LYP/6-311+G(2d, p) and MP2/6-31G(d, p) calculation method on dimer molecules respectively and the obtained results are similar which had been shown in Table 3. The values of potential energy of staggered parallel stacking in crystal are 1276.31 KJ/mol (B3LYP/6-311+G(2d, p)) and 1316.74 KJ/mol (MP2/6-31G(d, p)) lower than that of crossed stacking mode, respectively, through different calculation method. We could conclude that the crystals grown from PVT are apt to form a stable conformation.

Table S1. The potential energy of dimer molecules based on different stacking modes by B3LYP/6-311+G(2d, p) and MP2/6-31G(d, p) calculation

Calculation method	Potential energy of cross stacking (KJ/mol)	Potential energy of staggered parallel stacking (KJ/mol)	ΔE (KJ/mol)
B3LYP/6-311+G(2d, p)	-6884666.01	-6885942.32	1276.31
MP2/6-31G(d, p)	-6861266.52	-6862583.26	1316.74

References:

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