

Electronic Supplementary Information (ESI)

Asymmetric organic semiconductors for high performance single crystalline field-effect transistors with low activation energy

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Experimental Section

Modification of substrates

The heavily doped n-type Si wafers with a 300 nm thick SiO₂ layer were used as substrates of OFETs, which were cleaned with deionized water, piranha solution (70/30 vol./vol. H₂SO₄/H₂O₂), deionized water, isopropanol and blow-dried by N₂. Then, the substrates were treated with plasma for 5 min at 100 W and modification of octadecyltrichlorosilane (OTS).

Fabrication of thin film transistors

Bottom-gate top-contact thin film transistors were fabricated on OTS treated SiO₂/Si. 50nm thin films of three compounds were thermally deposited on the OTS treated SiO₂/Si. The deposition parameters of three thin films were kept the same (0.1 Å/s for the first 10nm, 0.2 Å/s for the 10-20nm and 0.3 Å/s for the 20-50nm). Then 50nm Au as drain and source electrodes was deposited on thin film under shadow mask with a defined channel length of 30 μm and a width of 215 μm. All the evaporations were conducted under a high vacuum level of 10⁻⁴ Pa. Thin film transistors were characterized by Agilent 1500A.

Fabrication of single crystals transistors

High quality single crystals were grown on OTS treated SiO₂/Si substrate by physical vapor transport (PVT) method in a horizontal tube furnace under argon atmosphere. In a tube furnace, 2-phA, 2-phvA and 2-pheA were placed in a quartz boat at the high temperature zone of 125 °C, 120 °C and 145 °C and kept at argon atmosphere at 1 atm, 20 pa and 1 atm, respectively. Single crystals could be obtained on substrate at the low temperature zone. The temperature of the tube furnace was gradually increased to target temperature, then maintained for 2 h. The thin Au electrodes (about 100 nm) were pasted onto the crystals to fabricate the bottom-gate top-contact devices with the help of the mechanical probes.¹ Devices were characterized by Agilent 1500A.

Material Synthesis

Synthesis of compound 2-phA

A mixture of compound 2-trifluoromethanesulfonate-anthracene (1 g, 3.07 mmol), (4-hexylphenyl) boronic acid (822 mg, 6.75 mmol) and Pd(PPh₃)₄ (177 mg, 0.15 mmol) was dissolved in 40 mL 1,4-dioxane under argon. Then 6 mL K₂CO₃ aqueous solution (2 M) has already bubbled with argon was added. The mixture was stirred for 12 h at 90 °C. The resulting precipitate was collected by filtration and was washed with triethylamine, dichloromethane, water and ethanol in turn. The product was further purified by vapor sublimation. Finally, 0.65 g pure product (2-phA) was obtained as a yellow solid in a yield of 84%. ¹H NMR (300 MHz, CDCl₃) δ 8.47 (2 H, d, *J* = 10.6), 8.21 (1 H, d, *J* = 0.7), 8.09 (1 H, d, *J* = 8.9), 8.02 (2 H, dd, *J* = 6.5, 3.2), 7.80 (1 H, d, *J* = 1.4), 7.77 (2 H, dd, *J* = 8.4, 2.0), 7.56 - 7.45 (4 H, m), 7.44 - 7.37 (1 H, m). ¹³C NMR (75 MHz, CDCl₃) δ 141.03 (s), 137.78 (s), 132.27 - 131.47 (m), 130.84 (s), 128.83 (d, *J* = 10.8), 128.18 (d, *J* = 5.6), 127.39 (d, *J* = 5.9), 126.56 (s), 126.01 (s), 125.51 (dd, *J* = 11.5, 9.1). MS (EI): *m/z* 254 (M⁺).

Synthesis of compound 2-phvA

A mixture of compound 2-bromoanthracene (1.0 g, 3.89 mmol), trans-beta-styrylboronic acid pinacol ester (1.16 g, 5.06 mmol) and Pd(PPh₃)₄ (219 mg, 0.19 mmol) was dissolved in 60 mL toluene under argon. Then 6 mL methanol and 8 mL K₂CO₃ aqueous solution (2M) has already bubbled with argon was added. The mixture was refluxed for 12 h at 110 °C. After that the mixture was allowed to cool to room temperature. The resulting precipitate was collected by filtration and was washed with dichloromethane, water and ethanol successively. The product was further purified by vapor sublimation. Finally, 0.87 g pure product (2-phvA) was obtained as a yellow solid in a yield of 80%. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (2 H, d, *J* = 6.3), 7.99 (4 H, d, *J* = 9.4), 7.80 - 7.75 (1 H, m), 7.59 (2 H, d, *J* = 7.5), 7.46 (2 H, dd, *J* = 5.3, 4.1), 7.39 (3 H, dd, *J* = 15.9, 8.0), 7.30 (2 H, d, *J* = 12.8). MS (EI): *m/z* 280 (M⁺). ¹³C NMR was not obtained because of 2-phvA was difficult to dissolve.

Synthesis of compound 2-pheA

A mixture of compound 2-bromoanthracene (1.0 g, 3.89 mmol), phenylacetylene (0.52 g, 5.06 mmol), Pd(PPh₃)₂Cl₂ (137 mg, 0.195 mmol) and CuI (74 mg, 0.389 mmol) was dissolved in 60 mL THF under argon. Then triethylamine (1.18g, 11.67 mmol) was added via syringe. The mixture was stirred for 48 h at 70 °C. After that the mixture was allowed to cool to room temperature, and then precipitated. The resulting precipitate was collected by filtration and was washed with dichloromethane, water and ethanol successively. The product was then further purified by vapor sublimation. Finally, 0.90 g pure product (2-pheA) was obtained as a yellow solid in yield of 83%. ¹H NMR (300 MHz, CDCl₃) 8.40 (2 H, s), 8.23 (1 H, s), 8.07 - 7.93 (3 H, m), 7.61 (2 H, dd, *J* = 7.2, 2.4), 7.54 (1 H, dd, *J* = 8.8, 1.4), 7.49 (2 H, dd, *J* = 6.6, 3.2), 7.43 - 7.34 (3 H, m). ¹³C NMR (75 MHz, CDCl₃) δ 133.87 (s), 134.97 - 130.93 (m), 130.67 (s), 129.21 - 127.27 (m), 127.27 - 127.08 (m), 126.34 (s), 126.28 - 124.60 (m), 123.29 (s), 119.98 (s). MS (EI): *m/z* 278 (M⁺).

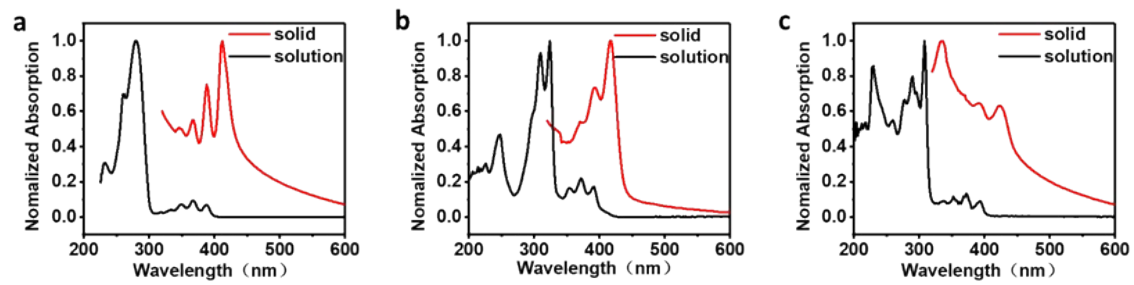


Fig. S1 Solution and solid absorption spectra of 2-phA, 2-phvA and 2-phEA.

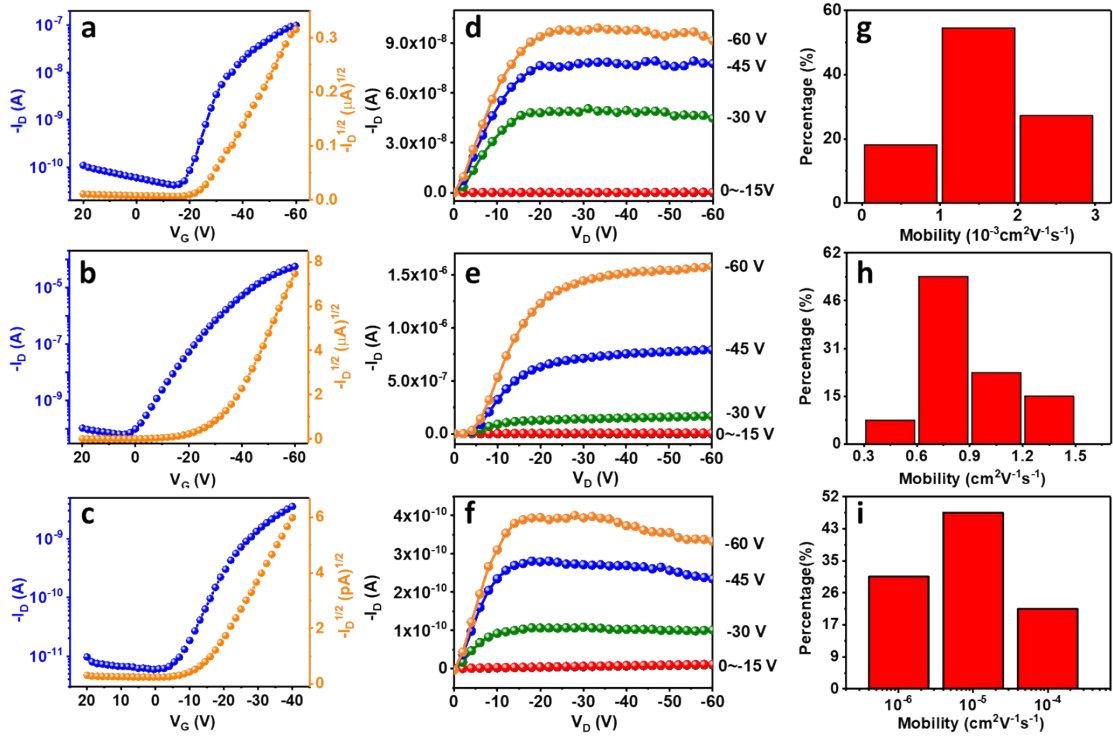


Fig. S2 Typical transfer (a, b and c), output (d, e and f) curves and mobility distribution (g, h and i) of thin film transistors of 2-phA, 2-phvA and 2-pheA.

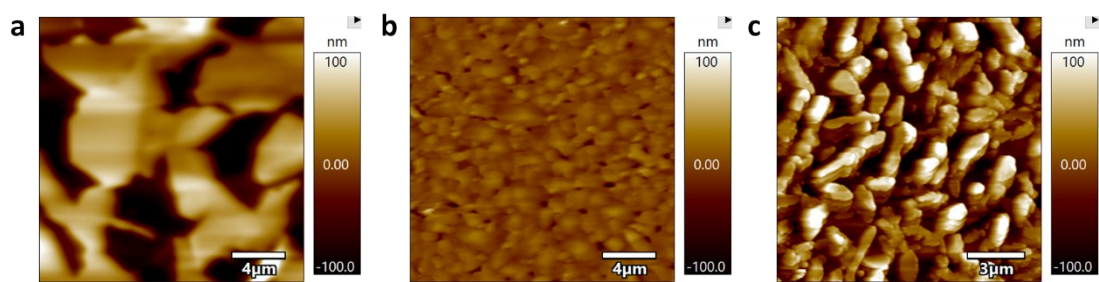


Fig. S3 AFM of thin film of (a) **2-phA**, (b) **2-phvA** and (c) **2-pheA** with roughness (R_q) of 43.1 nm, 10.6 nm and 49.8 nm, respectively.

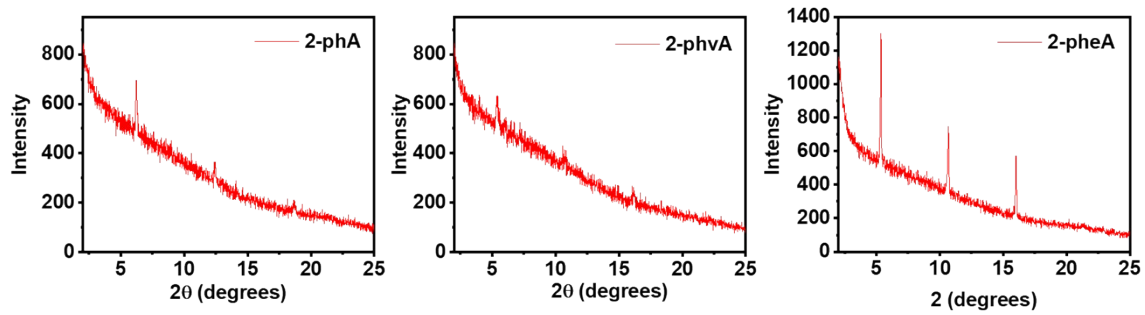


Fig. S4 XRD of film of 2-phA, 2-phvA and 2-pheA.

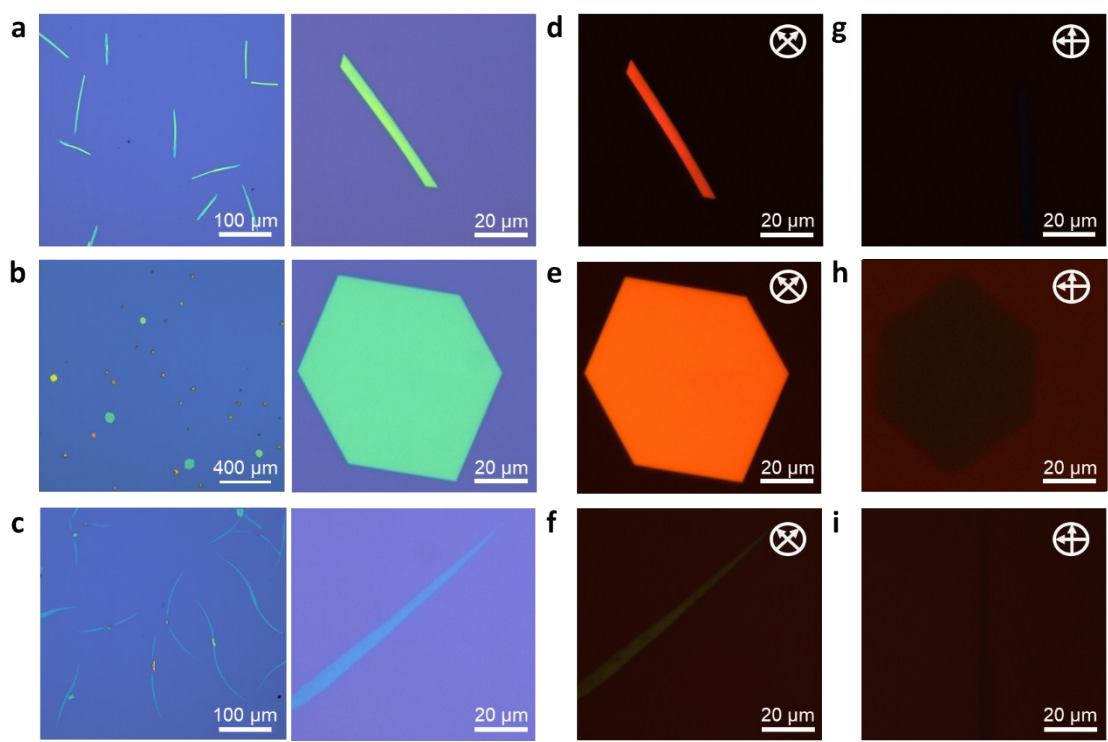


Fig. S5 (a, b and c) optical microscope and (d-i) orthogonal polarizing microscope (OPM) picture of **2-phA**, **2-phvA** and **2-pheA**.

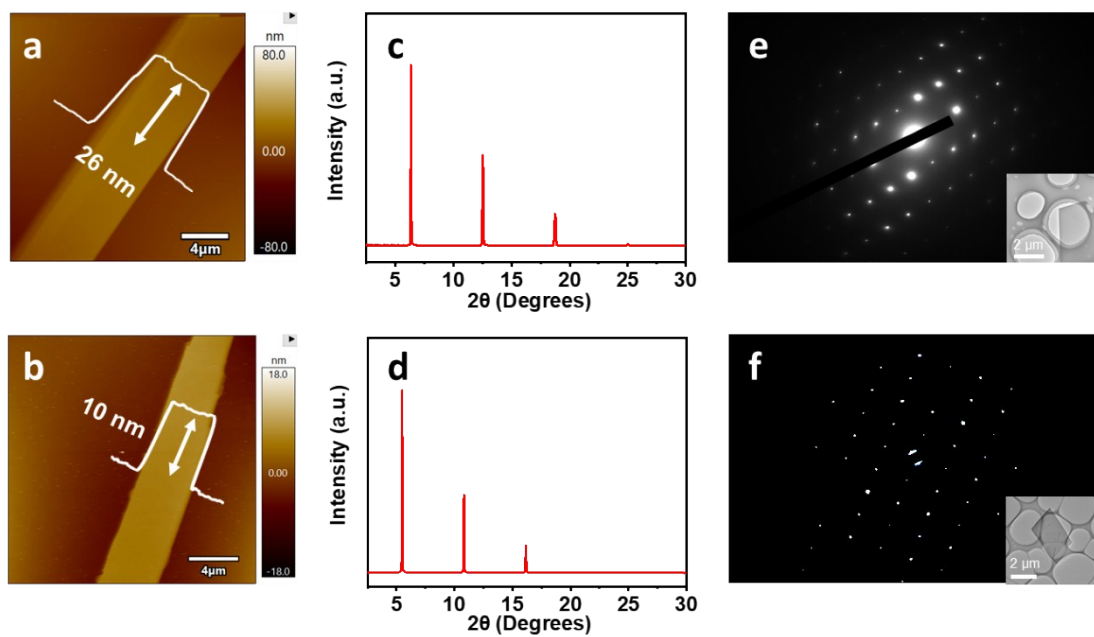


Fig. S6 AFM (a, b), XRD (c, d) and TEM (e, f) for 2-phA and 2-pheA.

Table S1. Crystal data and structure refinement for 2-phvA

Empirical formula	C ₄₄ H ₃₂
Formula weight	560.69
Temperature/K	169.99(12)
Crystal system	monoclinic
Space group	Pc
a/Å	5.90880(10)
b/Å	7.4390(2)
c/Å	33.1005(8)
α/°	90
β/°	90.919(2)
γ/°	90
Volume/Å ³	1454.76(6)
Z	2
ρ _{calc} /cm ³	1.28
μ/mm ⁻¹	0.547
F(000)	592
Crystal size/mm ³	0.21 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.34 to 151.14
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -41 ≤ l ≤ 41
Reflections collected	25929
Independent reflections	5488 [R _{int} = 0.0484, R _{sigma} = 0.0379]
Data/restraints/parameters	5488/2/397
Goodness-of-fit on F ²	1.086
Final R indexes [I > 2σ (I)]	R ₁ = 0.0649, wR ₂ = 0.1723
Final R indexes [all data]	R ₁ = 0.0766, wR ₂ = 0.1800
Largest diff. peak/hole / e Å ⁻³	0.36/-0.27
Flack parameter	-1.2(10)

In our cases, for 2-phA and 2-phvA, the mobility increases with the increase of crystal thickness in the range of 10-30 nm and reach its maximum in the range of 20-30 nm. Then it goes down when the crystal thickness is more than 20-30 nm (Fig. S7a-h, ESI⁺). For 2-pheA, only crystals with a thickness less than 10 nm can be obtained (it easily grows into twin crystals if the thickness is more than 10 nm), and an increase of the mobility is observed as increase of the thickness of the crystals (Fig. S7i-l, ESI⁺). Therefore, to ensure the best device performances, crystals with the thickness of 20-30 nm (2-phA and 2-phvA) and 10 nm (2-pheA) were selected to fabricate the single crystal OFETs.

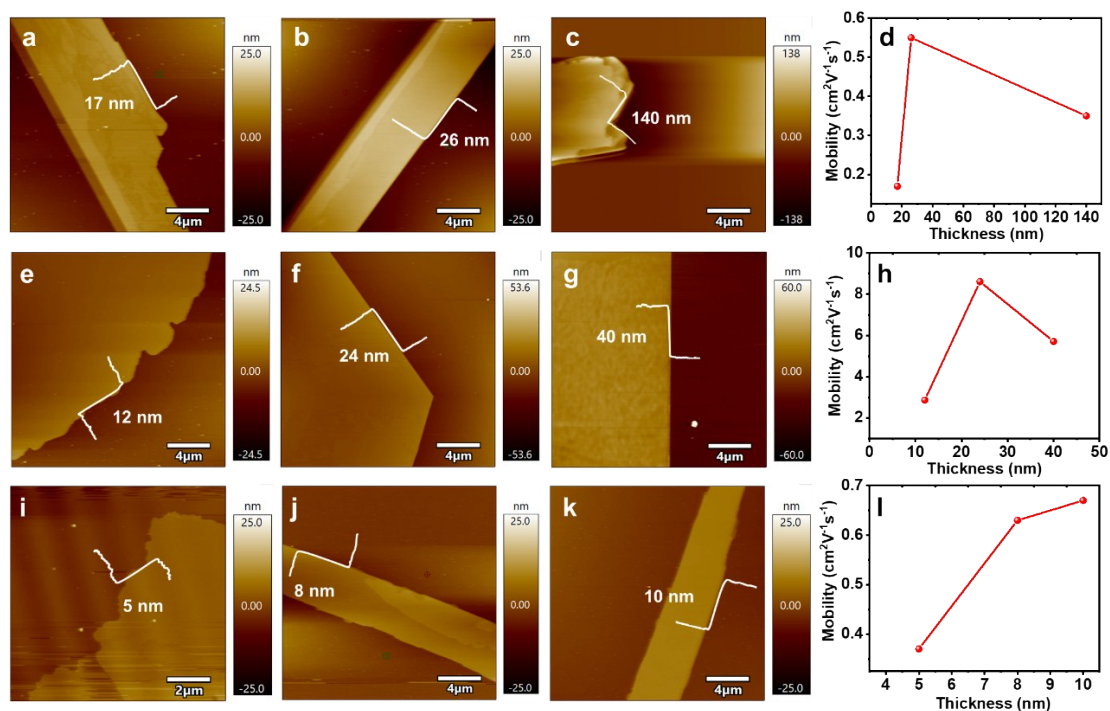


Fig. S7 AFM of different thickness single crystals and thickness dependence of mobility for (a-d) **2-phA**, (e-h) **2-phvA** and (i-l) **2-pheA**.

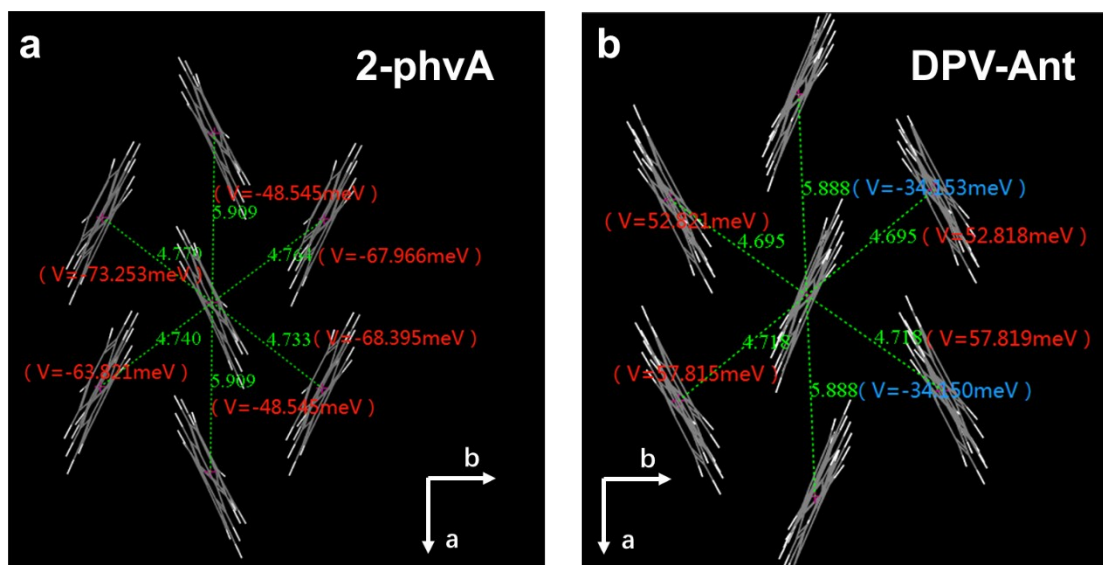


Fig. S8 The charge hopping pathways from center molecule to its neighbors for (a) **2-phvA** and (b) **DPV-Ant**.

Table S2 Data of theoretical calculation

	DPV-Ant	2-phvA
Recombination energy (meV)	160.47	156.49
Transfer integral (meV)	57.82	73.25
Mobility of single crystals ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	1.75 (Calculated data)	24.07 (Calculated data)

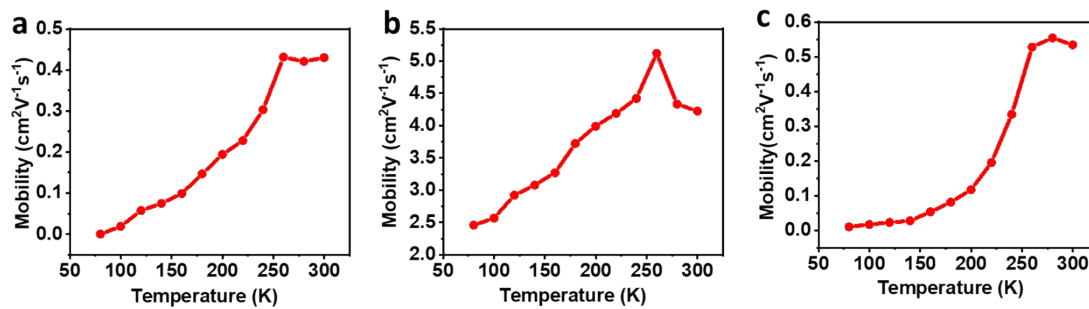


Fig. S9 Temperature dependences of charge-carrier mobility (a, b and c) for **2-phA**, **2-phvA** and **2-phA**.

Reference

1. L. Jiang, J. Liu, Y. Shi, D. Zhu, H. Zhang, Y. Hu, J. Yu, W. Hu and L. Jiang, *J. Mater. Chem. C*, 2019, 7, 3436-3442.