

Supporting Information

Cocrystal Engineering of Molecular Rearrangement: A “Turn-On” Approach for High-Performance N-type Organic Semiconductor

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Experimental Procedures

Materials: Perylene were purchased from Luminescence Technology Corp. TCAF was synthesized as follows: first, di-cyanodiazafuorene (DCAF) was synthesized from the cyclo-condensation between 1Hindene-1,2,3-trione and 2,3-diaminomaleonitrile (DAMN) with a high yield of 85.0%; then TCAF was obtained from the atom-economical Knoevenagel condensation between DCAF and malononitrile with an excellent 91.5% yield.¹ Chlorobenzene (C₆H₅Cl, HPLC) were purchased from Sigma-Aldrich, and used directly as received without further purification.

Cocrystal Growth and Structural Analysis: For the growth of α - and β -phase single crystal, equimolar amounts of TCAF (0.5 mg) and perylene (0.5 mg) were dissolved in chlorobenzene (2 mL) for the growth of α - and β -phase single crystal. In order to ensure that the solution was completely dissolved, put the solution into sample heater with setting temperature 120 °C for 4 hours. The black crystals (α -cocrystal) were obtained by room-temperature solution cooling for 12 hours and without any vibrations. While for the growth of β -cocrystal, as dark needle-like complexes, the dissolved solution was shaken vigorously and then placed on a flat workbench. The crystals were then found on the bottom of the bottle in 5-7 min. The Bruker Smart-1000-CCD diffractometer using graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) measured the crystal structures of α - and β -cocrystals. The data were collected at room temperature and the structure was resolved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 program,² and analyzed using Mercury and Diamond. CCDC number: 2047151 (α -cocrystal), 2047153 (β -cocrystal). These crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Growth of the Micro/nanocrystals and Device Fabrication: Organic field-effect transistors (OFETs) with a top-contact/bottom-gate configuration were constructed to investigate the electric properties. Here, highly n-doped Si wafers were employed as the gate electrode, with 500 nm thermally oxidized SiO₂ as the gate dielectric (the capacitance is 7.5 nF·cm⁻²). The substrates used in the present study were successively cleaned with deionized water, hot acid/hydrogen peroxide solution (H₂SO₄:H₂O₂ 2:1), and isopropyl alcohol, then blow dried by a N₂ gun. Si/SiO₂ wafers are treated with OTS by vapor deposition method to obtain a hydrophobic surface. For eliminating the effect of moisture, dry the silicon wafer under vacuum environment with setting temperature 90 °C for 75 min after cleaning. Until the silicon wafer was cooled to room temperature, took one drop of OTS on a glass dish and heat it to 120 °C for 135 minutes under vacuum environment. After natural cooling, the OTS modified wafers were washed with n-hexane, chloroform and isopropyl alcohol, dried under ambient N₂ before use. Afterwards 80 μ L chlorobenzene solution of perylene/TCAF mixture (0.5 mg/mL, molar ratio 1:1) were drop-cast onto 1 \times 1 cm² substrates in a nitrogen-filled glove box at room temperature; after the solvent evaporation, α -phase cocrystals were obtained on the substrates. For phase change, we tried to drop hot chlorobenzene solvent onto the substrate containing α -phase crystals for dissolution and regrowth. The β -cocrystals were obtained through several times of such re-drop-casting process. Drain and source electrodes (50 nm) were deposited on the single crystal by thermal evaporation with copper grid as a mask. Finally, the copper grid was removed to obtain a gap between the source and drain electrodes.

Measurements: The UV-vis-NIR absorption spectra were recorded by a LAMBDA 35 spectrometer. FT-IR spectra were recorded on a PE-Spectrum Two spectrometer with KBr slice under ambient atmosphere. X-ray diffraction (XRD) was carried out on a D/max2500 with a Cu K α source ($\lambda = 1.541 \text{ \AA}$), the data were collected in the 2θ range of 3-30° at room temperature. The current-voltage (I - V) characteristics of the OFETs were recorded using a Keithley 4200 SCS and a Micromanipulator probe station with a high-resolution microscope in the ambient

condition. The charge carrier motilities were extracted from the saturated regime according to the following equation (1):

$$I_D = \frac{W}{2L} C_i \mu (V_{GS} - V_T)^2 \quad (1)$$

where I_D is the drain current, W and L are the channel width and length, respectively, C_i is the dielectric capacitance per unit area, μ is the field-effect charge carrier mobility, V_{GS} and V_T is the gate-source voltage and threshold voltage.

Theoretical calculation: The calculations of the molecular energy levels were calculated by DFT at the B3LYP/6-31G level. The calculation of DCT was performed with the Mulliken population analysis. The crystal structures of the two perylene-TCAF complexes were optimized by using VASP 5.4 (Vienna Ab initio Simulation Package) program within the Perdew-Burke-Ernzerhof (PBE) functional³⁻⁵. The reciprocal space was covered by a Γ -centered Monkhorst-Pack lattice of $3 \times 3 \times 3$ K -points. The convergence criteria of the total energy and ionic force were set as 10^{-5} eV and $0.001 \text{ eV \AA}^{-1}$ for the geometry optimization, respectively. The effective transfer integral of the two cocrystals was calculated using the molecular-fragment orbit approach in combined with the basis set orthogonalization method. The super-exchange coupling along the donor-accept stacking direction, t^{eff} are estimated with the energy-splitting method by performed with Gaussian 09 at level of B3LYP/6-31G.

$$t^{\text{eff}} = (E_{L+1} - E_L)/2$$

Where E_L and E_{L+1} refer to the LUMO+1 and LUMO of the neutral state of the A-D-A triad.

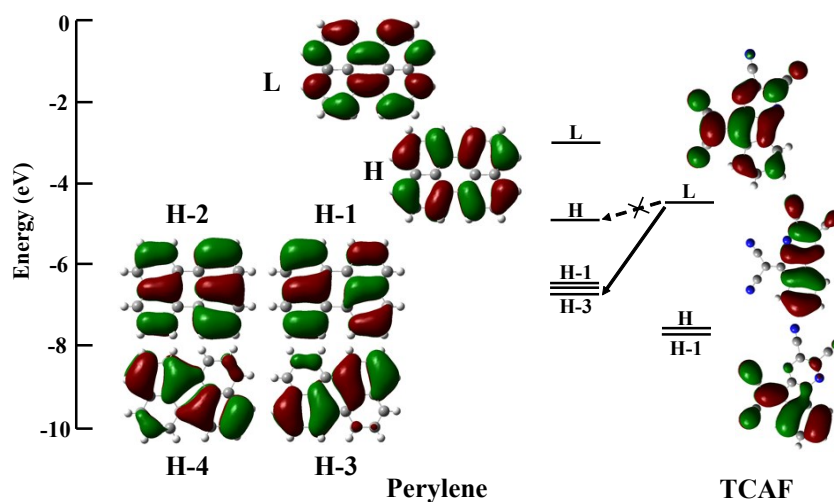


Fig. S1. Molecular orbitals of perylene and TCAF. The TCAF LUMO has a stripe symmetry, but the perylene HOMO has a horizontal node, so the charge carrier integrals calculated are opposite to cancel out hole transport. By contrast, the D HOMO-3 has a similar stripe symmetry, which causes the efficient electron transport.

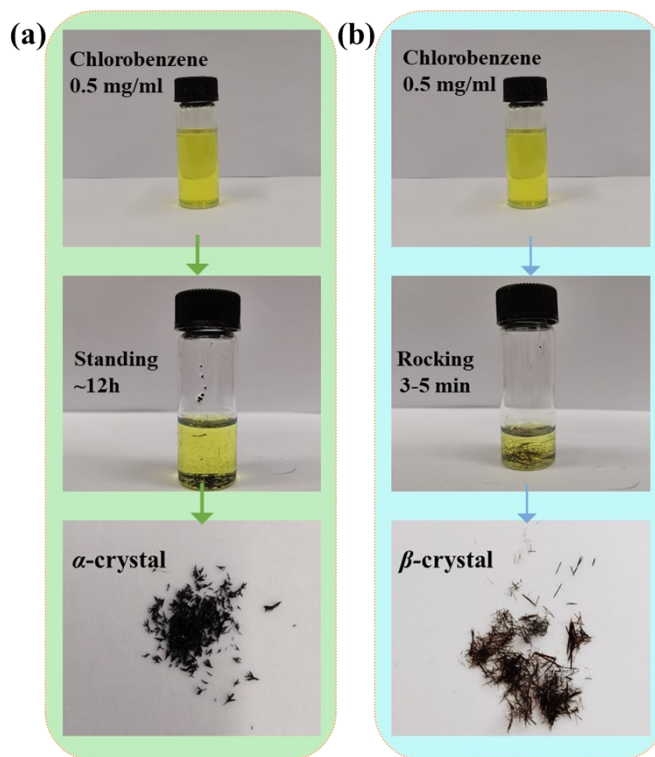


Fig. S2. Selective growth of (a) α - and (b) β -phase complexes.

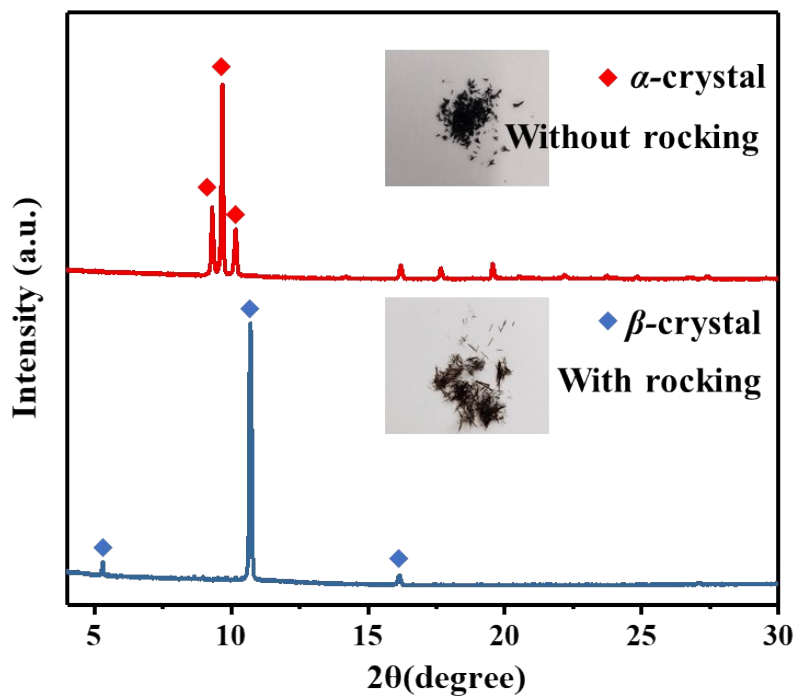


Fig. S3. The XRD peaks of (a) α -phase and (b) β -phase complexes. Inserts are α - and β -phase cocrystals.

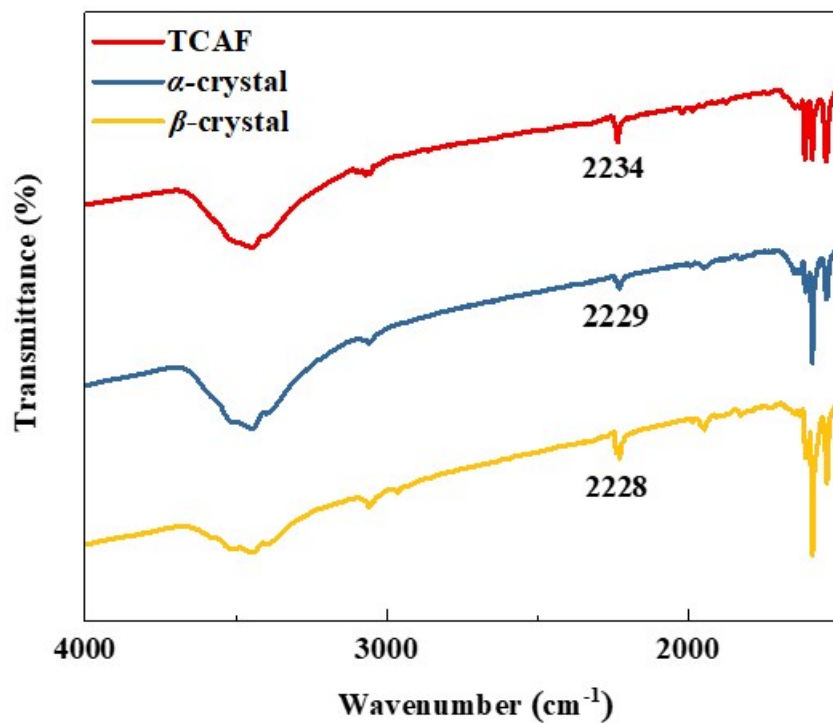


Fig. S4. FT-IR spectra of α -, β -phase cocrystal and TCAF compound powders.

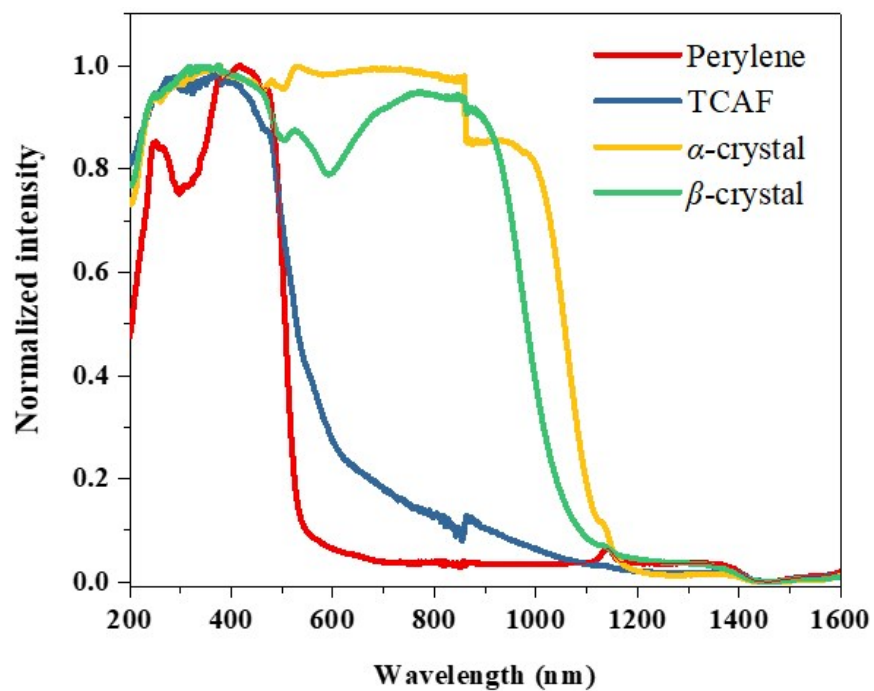


Fig. S5. Solid-state UV-vis absorption spectra of pristine perylene, TCAF and two phase complexes.

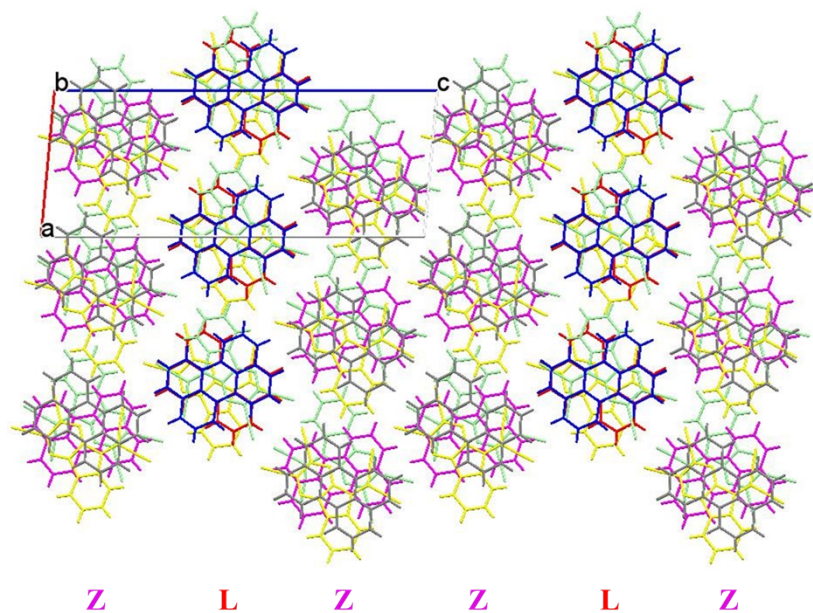


Fig. S6. Two alignment columns at a molar ratio of 2:1. Z represents Zig-zag mixed stacking, L represents typical mixed alignments.

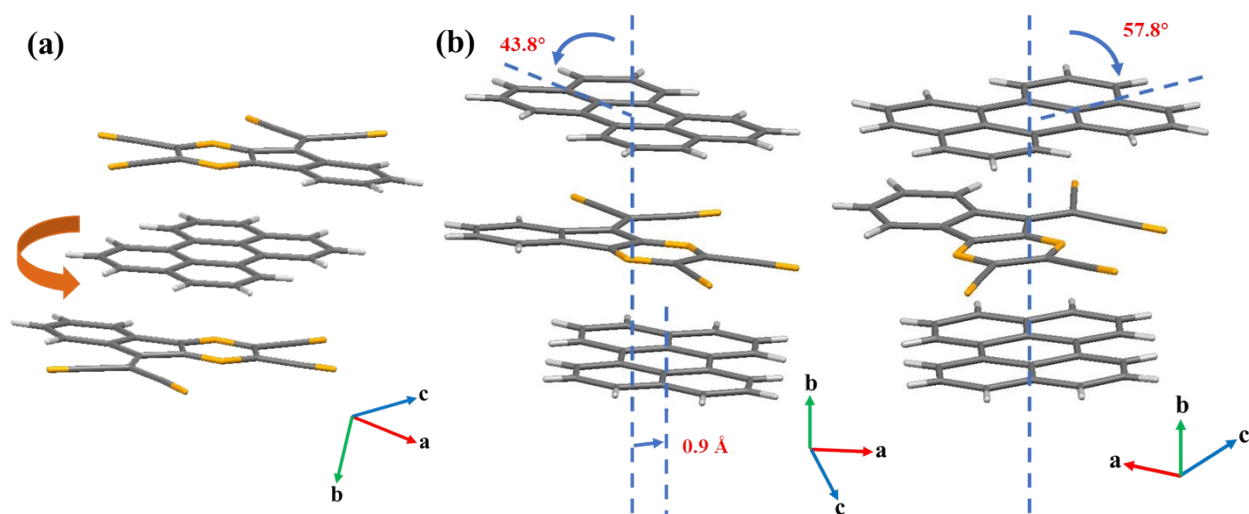


Fig. S7. Crystal stacking pattern of α -phase cocrystal: (a) A-D-A and (b) D-A-D.

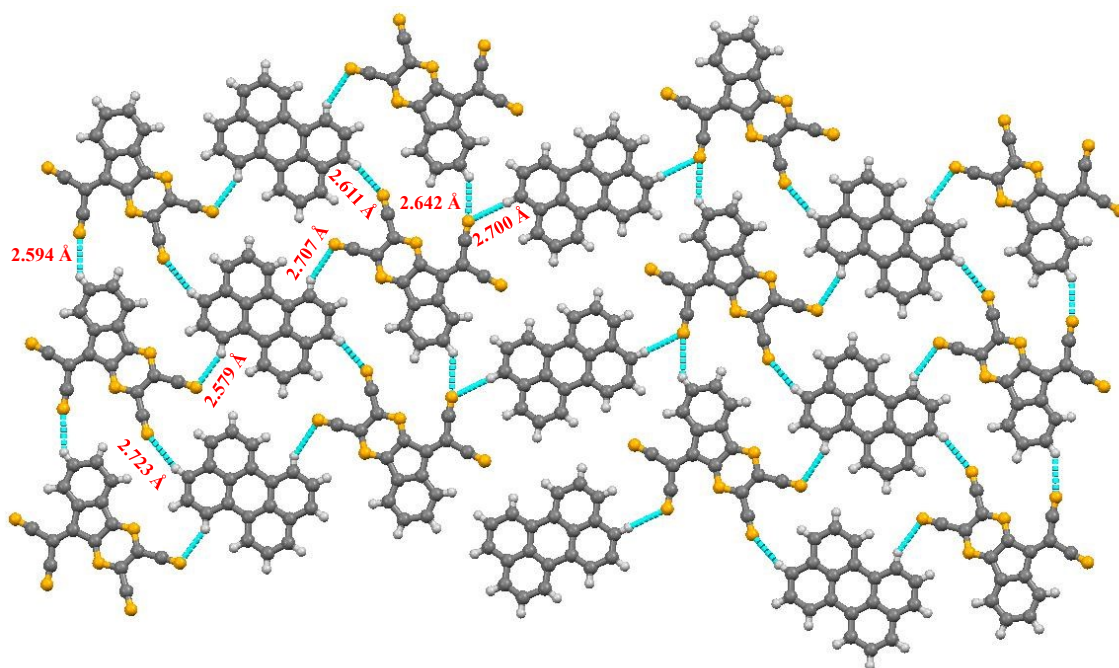


Fig. S8. The hydrogen bonding interactions in α -phase cocrystal. Each TCAF molecule is surrounded by three perylene molecules and two TCAF molecules in ac plane. The extended π -conjugated system of TCAF led to C-H \cdots N contacts (2.594 and 2.642 Å) between adjacent acceptor molecules, short C-H \cdots N distances (2.579-2.723 Å) were observed between TCAF and perylene molecules from neighboring columns.

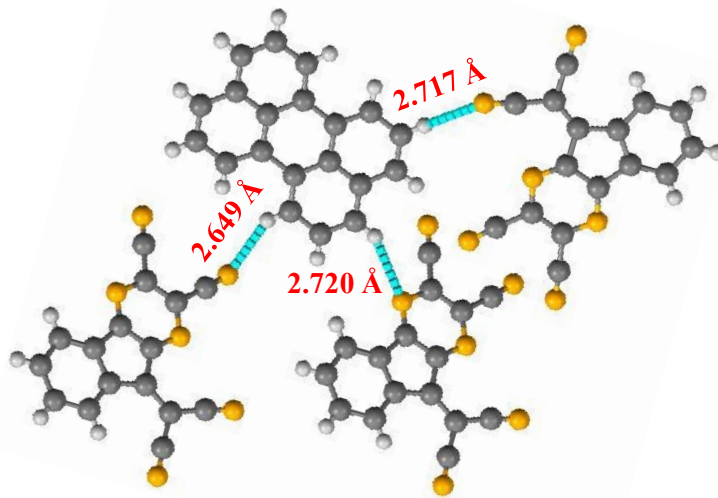


Fig. S9. The hydrogen bonds in the β -phase cocrystal. Each perylene molecule is surrounded by three TCAF molecules in ac plane. Perylene and TCAF in the neighboring columns were observed from the short C-H \cdots N distance (2.649-2.720 Å).

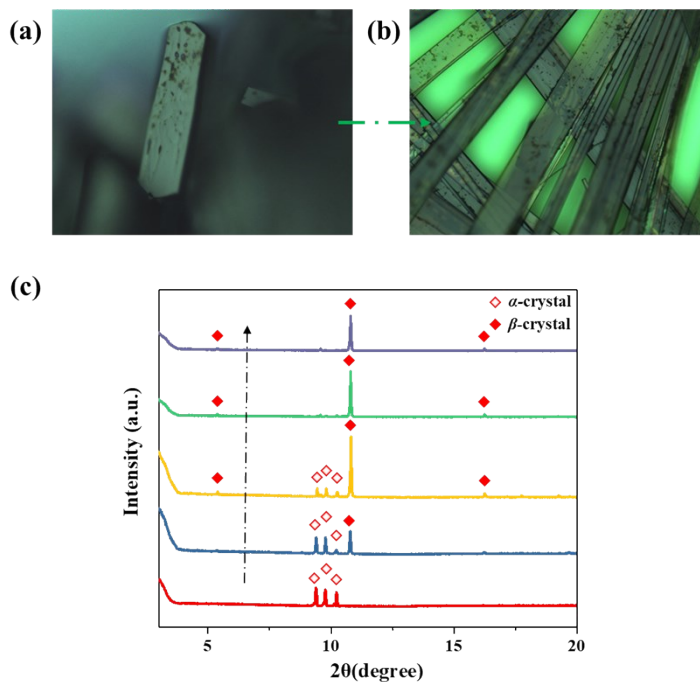


Fig. S10. Optical micrographs of (a) α -phase microcrystals obtained via a solution drop-casting method and (b) β -phase microcrystals obtained through multi re-drop-casting processes. (c) Diffraction pattern changes of cocrystal transition from α -phase to β -phase complex via gradual toluene dip-casting.

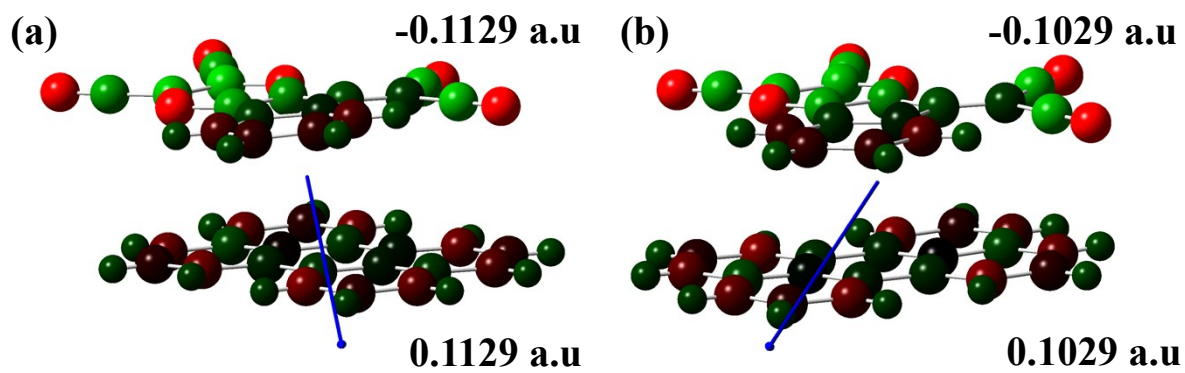


Fig. S11. The calculated mulliken charge distribution of (a) α -crystal and (b) β -crystal at the DFT level with B3LYP/6-31G*.

Table S1. Crystal data and structure refinement for α -phase and β -phase cocrystals.

	α -crystal	β -crystal
Empirical formula	C ₃₆ H ₁₆ N ₆	C ₃₆ H ₁₆ N ₆
Formula weight	532.55	532.55
Temperature (K)	296(2)	297(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	10.372(2)	10.665(4)
<i>b</i> (Å)	13.686(3)	7.297(3)
<i>c</i> (Å)	27.253(5)	32.830(14)
α (°)	96.390(5)	90
β (°)	94.921(4)	94.180(12)
γ (°)	92.968(5)	90
Volume (Å ³)	3823.0(13)	2548.1(18)
<i>Z</i>	6	4
Absorption coefficient (mm ⁻¹)	0.085	0.085
Calculated density (g/cm ³)	1.388	1.388
<i>F</i> (000)	1644	1096
Crystal size (mm)	0.180 × 0.150 × 0.130	0.220 × 0.210 × 0.200
ϑ range (°)	2.249 to 24.964	2.206 to 24.999
Limiting indices	-12 ≤ <i>h</i> ≤ 10 -16 ≤ <i>k</i> ≤ 16 -32 ≤ <i>l</i> ≤ 32	-12 ≤ <i>h</i> ≤ 9 -8 ≤ <i>k</i> ≤ 8 -38 ≤ <i>l</i> ≤ 39
Reflections collected	23270	14870
<i>R</i> (int)	0.0633	0.1178
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	12945/0/1136	4469/0/379
Goodness-of-fit on <i>F</i> ²	1.033	1.007
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0896 <i>wR</i> ₂ = 0.2195	<i>R</i> ₁ = 0.0886 <i>wR</i> ₂ = 0.1854
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1895 <i>wR</i> ₂ = 0.2508	<i>R</i> ₁ = 0.1951 <i>wR</i> ₂ = 0.2166

Table S2. The relative energy of the two perylene-TCAF complexes.

	Energy (meV)	atoms	Energy (eV/atom)	Relative energy (meV/atom)
α -phase	-2575.2677	348	-7.40	0.00
β -phase	-1714.6337	232	-7.39	9.53

References

- 1 B. Yang, J. Zhao, Z. Wang, Z. Yang, Z. Lin, Y. Zhang, J. Li, L. Xie, Z. An, H. Zhang, J. Weng and W. Huang, *Chinese Chemical Letters*, 2019, **30**, 1969-1973.
- 2 G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- 3 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
- 4 G. Kresse, J. Hafner and *J. Phys.: Condens. Matter*, 1994, **6**, 8245–8257.
- 5 P. E. Blöchl, *Phys. Rev. B: Condens. Matter. Mater. Phys.*, 1994, **50**, 17953-17979.