Supporting Information for

A molecular design principle towards luminescent polymorphic organic heterostructured architectures

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Supplementary Methods

Polymorph-selective growth of γ-Co/β-DPA heterostructures using γ-Co ribbons as seeds through a stepwise crystallization route. Typically, the preparation procedure was performed by co-evaporation of one drop of the mixture solution of Co and DPA in DMF/THF (C_{Co} = 4 mM, C_{DPA} = 2 mM, v:v = 1:10) on a silicon or quartz substrate by a drop-casting method.
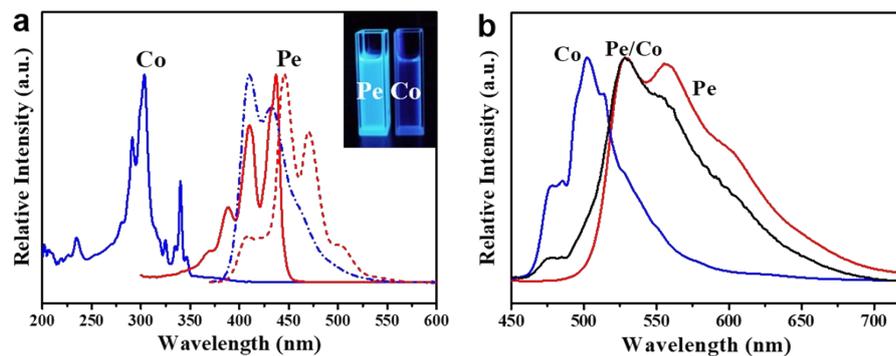
Supplementary Figures:

Fig. S1 (a) Absorption and PL spectra of the monomer solutions of Pe and Co in THF. Blue and red solid lines present the absorption spectra of Co and Pe, respectively. While blue and red dashed lines represent the PL spectra of Co and Pe, respectively. Inset shows the photographs of Pe and Co under a 365 nm UV lamp. (b) PL spectra of β-Pe plates, γ-Co, and Pe/Co heterostructures when excited by 420 nm light.

Table S1 Crystallographic parameters of different polymorphs of three organic crystals.

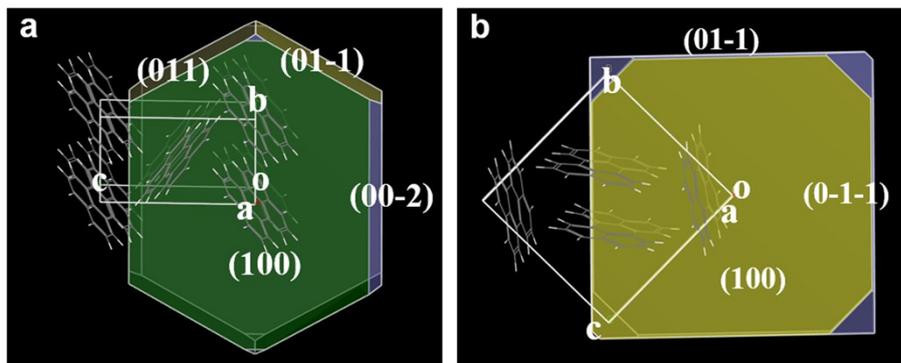| Polymorphs	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å³)
α-Pe	10.239	10.786	11.132	90	100.92	90	1207.13
β-Pe	9.7630	5.8430	10.608	90	96.770	90	600.916
β-Co	10.385	3.821	17.211	90	96.235	90	678.984
γ-Co	10.008	4.6651	15.5437	90	106.57	90	695.592
α-DPA	10.690	13.580	12.290	90	90.600	90	1784.04
β-DPA	9.497	20.413	10.084	90	112.307	90	1808.78
γ-DPA	9.216	21.111	10.041	90	111.404	90	1818.83

Fig. S2 (a, b) BFDH simulation results of (a) β- and (b) α-Pe crystals along [100] direction using Material Studio software.
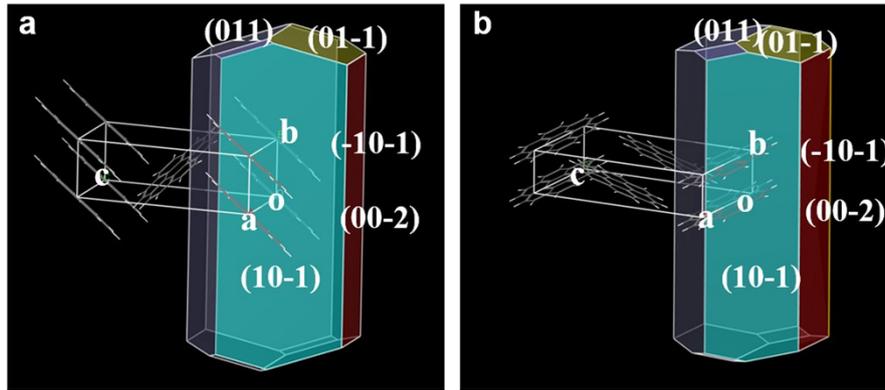
Fig. S3 (a, b) BFDH simulation results of (a) γ- and (b) β-Co crystals along [10-1] direction using Material Studio software.
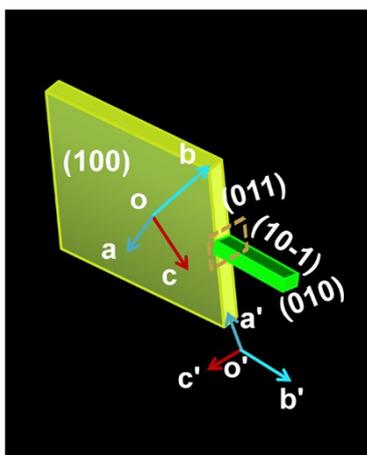
Fig. S4 Schematic showing β-Pe/β-DPA heterogeneous configuration at the junction interface.
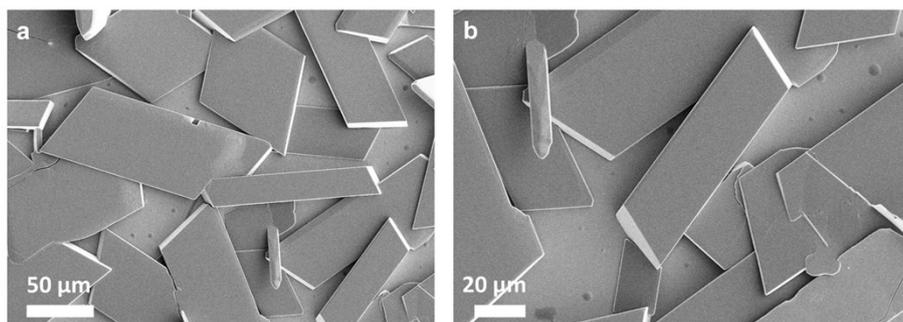
Fig. S5 (a, b) SEM images of β-DPA microplates at (a) low and (b) high-magnification formed by sublimation of DPA powder at 230 ℃ at ambient pressure.
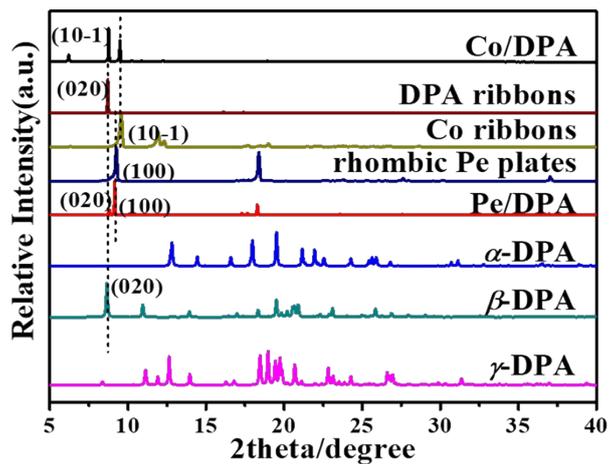
Fig. S6 PXRD patterns of two types of heterostructures including Pe/DPA and Co/DPA and three organic assemblies including Pe plates, Co ribbons, and DPA ribbons. Single-crystal XRD patterns of α-DPA, β-DPA, and γ-DPA were also simulated based on their respective crystallographic data.
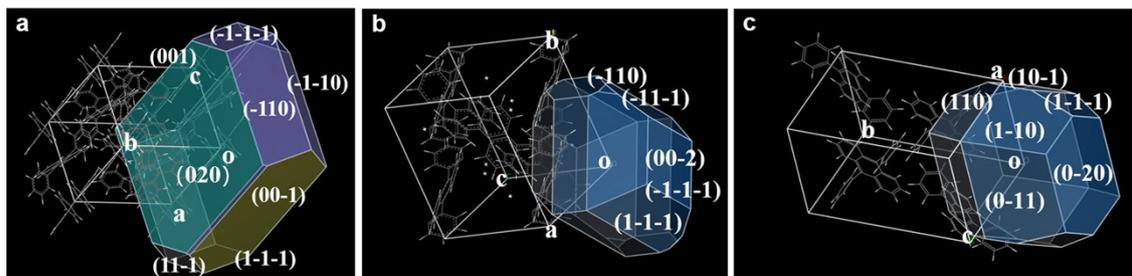
Fig. S7 (a-c) BFDH simulation results of β-DPA, α-DPA, and γ-DPA using Material Studio software.
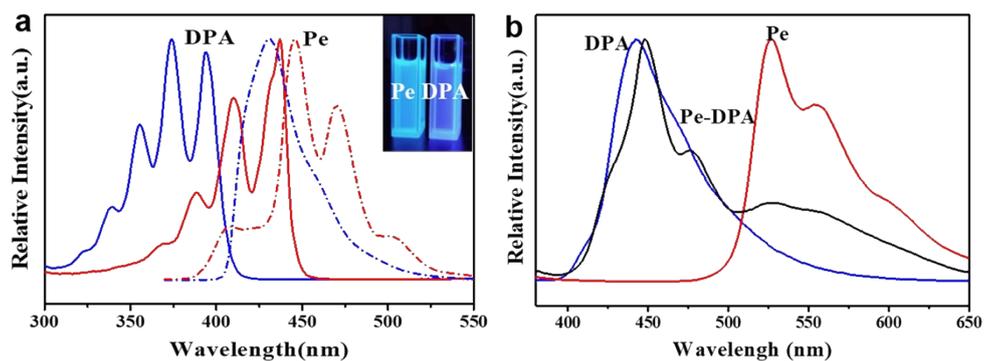
Fig. S8 (a) Absorption and PL spectra of the monomer solutions of DPA and Pe in THF. Blue and red solid lines present the absorption spectra of DPA and Pe, respectively. While blue and red dashed lines represent the PL spectra of DPA and Pe, respectively. Inset shows the photographs of Pe and DPA under a 365 nm UV lamp. (b) Steady-state PL spectra of β-DPA ribbons (blue line), β-Pe plates (black line), and Pe/DPA heterostructures (red line) when excited by 380 nm light.
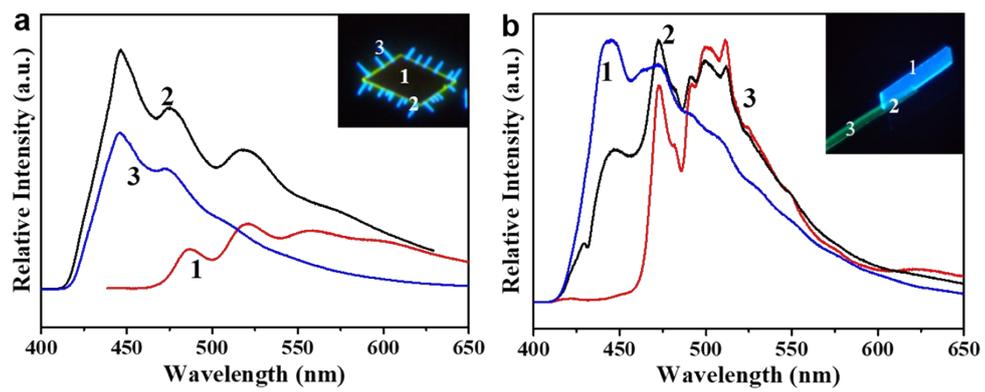
Fig. S9 (a, b) Micro-area PL spectra of each domain of (a) Pe/DPA and (b) Co-DPA heterostructures. Insets show the corresponding single typical heterojunction.
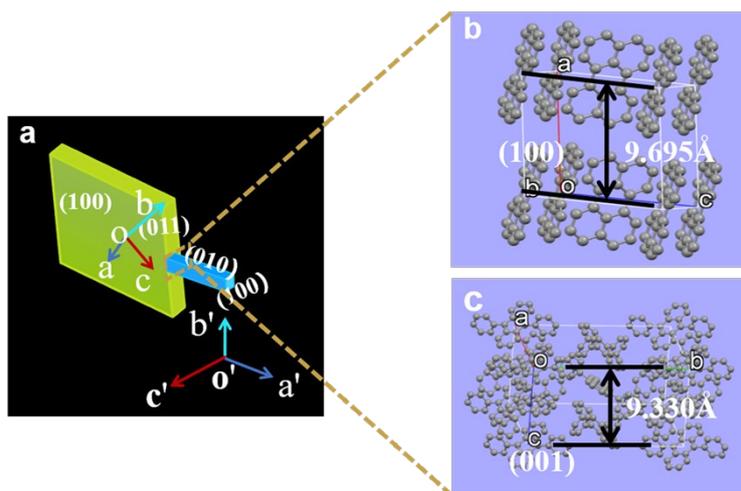
Fig. S10 (a) Schematic showing β-Pe/β-DPA heterogeneous configuration at the junction region. (b, c) Molecular packing motifs and lattice distances of (b) β-Pe along [100] direction and (c) β-DPA along [001] direction, respectively.