Supporting Information

Polymorphism-Based Luminescence and Morphology-Dependent Optical Waveguide Property in the 1:1 Charge Transfer Cocrystals

Jing Wang,[a,b] Shuping Xu,[c] Aisen Li,[c] Lei Chen,[a,b] Weiqing Xu*[c] and Hongyu Zhang[c]*

Table S1 The Crystallographic data of form α and form β cocystals derived from single-crystal X-ray diffraction measurements.

Crystal	**form *α***
Formula	$C_{26}H_{14}N_4O$
Formula weight(g/mol)	398.41
Crystal system	monoclinic
Space-group	P 21/c
Lattice parameter a (Å)	7.4866(4)
Lattice parameter b (Å)	28.6968(18)
Lattice parameter c (Å)	9.5251(6)
cell parameter α(°)	90
Lattice parameter β(°)	92.720(3)
Lattice parameter γ(°)	90
Cell volume (Å^3)	2044.1(2)
Formula units per cell Z	4
Calculated density (g•cm^{-3})	1.295
Mu(mm^{-1})	0.082
F(000)	824.0
F(000)'	824.31
h,k,l,(max)	9, 35, 11
Nref	4172
R reflections	0.0481(2653)
wR2	0.1196
CSD	NAFJIR

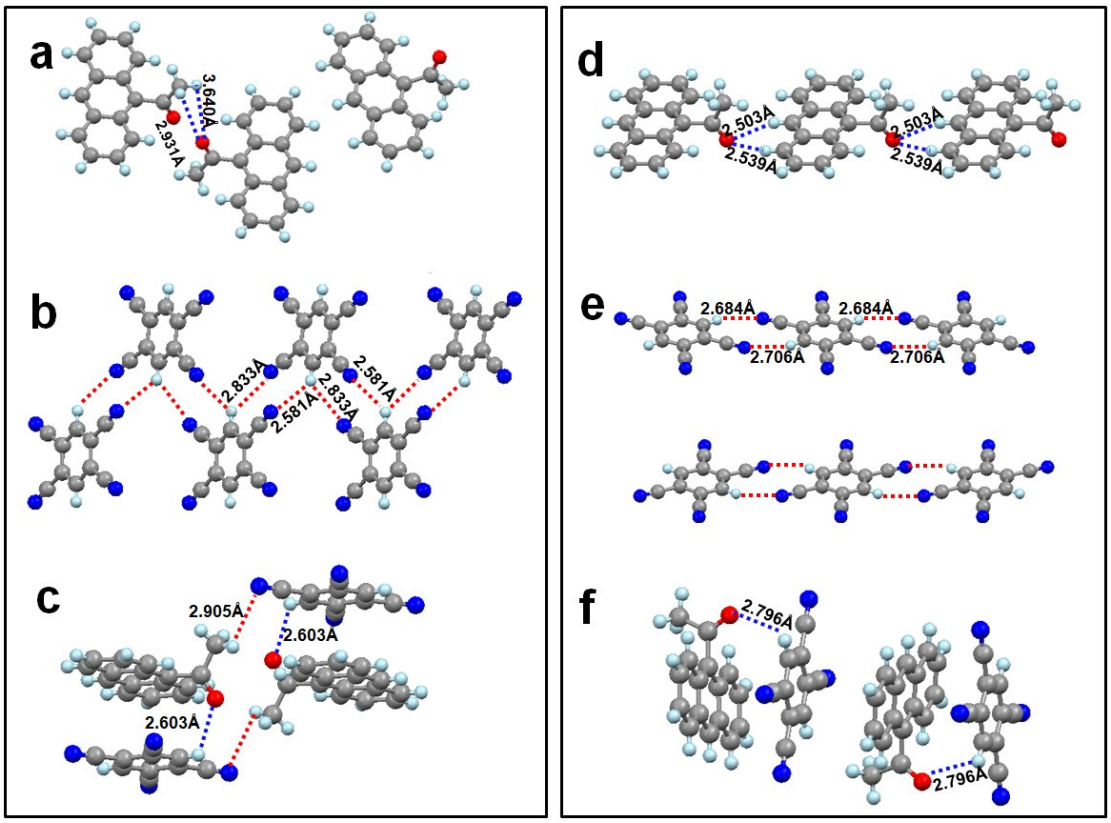

Fig. S1 The intermolecular interactions of (a-c) form *α* and (d-f) form *β* cocrystals.

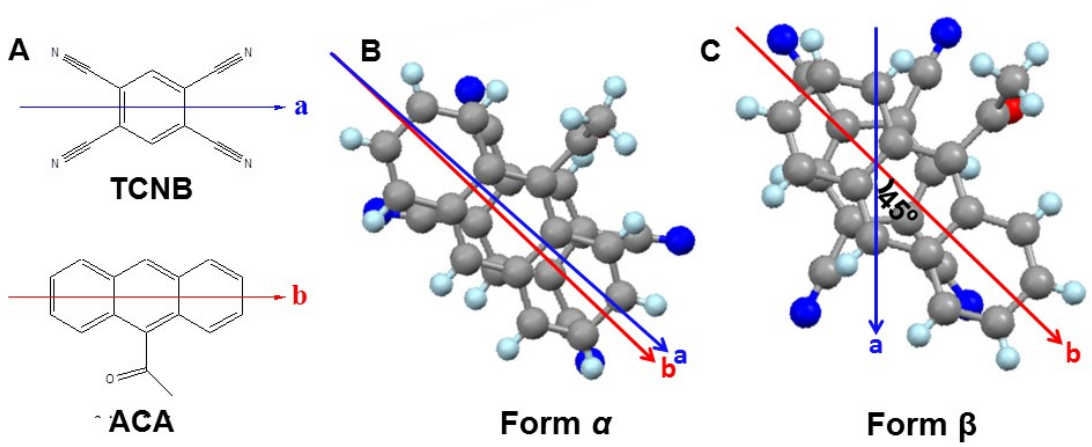

Fig. S2 (A) Directions of ACA (marked as a) and TCNB (marked as b) are marked by arrowhead with different color. The Intermolecular π-π interaction of ACA and TCNB with different rotation angles in (B) form *α* and (C) form *β* cocrystals.

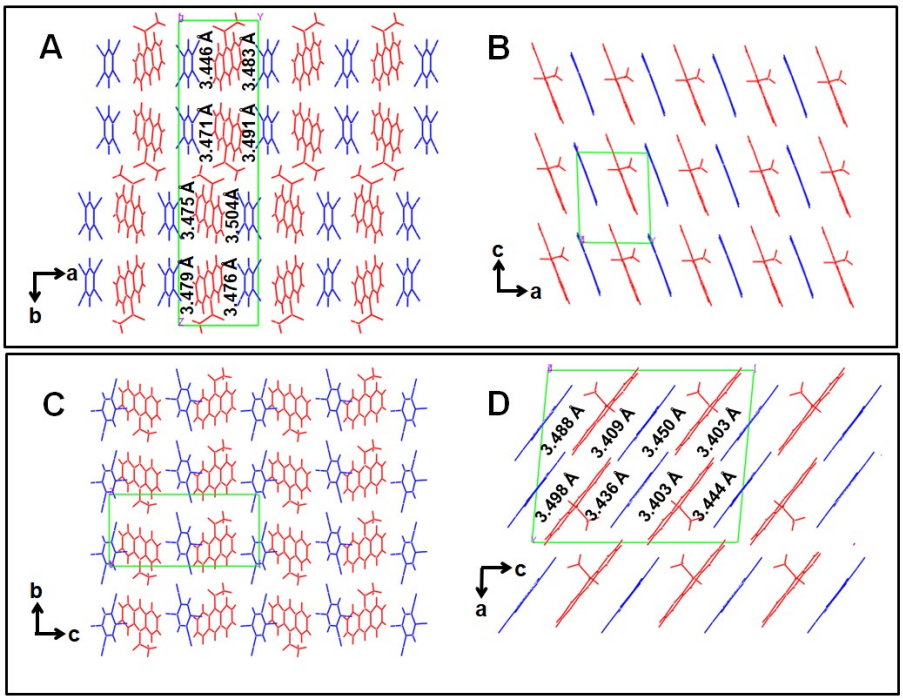

Fig. S3 The interplanar distances between ACA and TCNB in the (A and B) form *α* and (C and D) form *β* cocrystals.

Table S2 The interplanar distances between ACA and TCNB in the form *α* and form *β* from Fig. S3

Crystal	$d_{D\text{-}A}$ (Å)	*mean distance* (Å)
form *α*	3.504, 3.491, 3.483, 3.479 3.476, 3.475, 3.471, 3.446	3.478
form *β*	3.498, 3.488, 3.450, 3.444 3.436,3.409, 3.403, 3.403	3.441

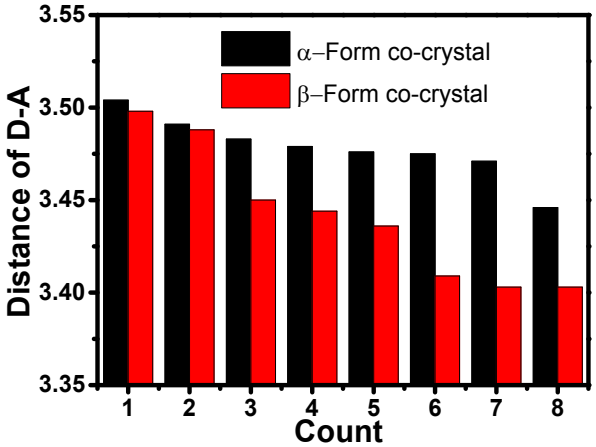

Fig. S4 The Histogram of interplanar distances between ACA and TCNB in form *α* (Black) and form *β* (Red) cocrystals from Table S2.

Table S3 Intermolecular hydrogen bond interactions in form α and form β.

Crystal Intermolecular interactions	form α C–H···X (X = O, N)	Length of C–H···X	form β C–H···X (X = O, N)	Length of C–H···X
Interactions of ACA and adjacent ACA	C_{26}-H_{26A}···O_1	3.640 Å	C_{17}-H_{17}···$O_{1;}$	2.503 Å
	C_{26}-H_{26B}···O_1	2.931 Å	C_{19}-H_{19}···O_1	2.539 Å
Interactions of TCNB and adjacent TCNB	C_3-H_3···N_4	2.581 Å	C_3-H_3…N_3	2.684 Å
	C_3-H_3···N_2	2.833 Å	C_6-H_6…N_2	2.706 Å
Interactions of TCNB with stacking ACA	C_6-H_6···O_1	2.603 Å	C_6-H_6···O_1	2.794 Å
	C_{26}-H_{26A}··· O_1	2.905 Å		

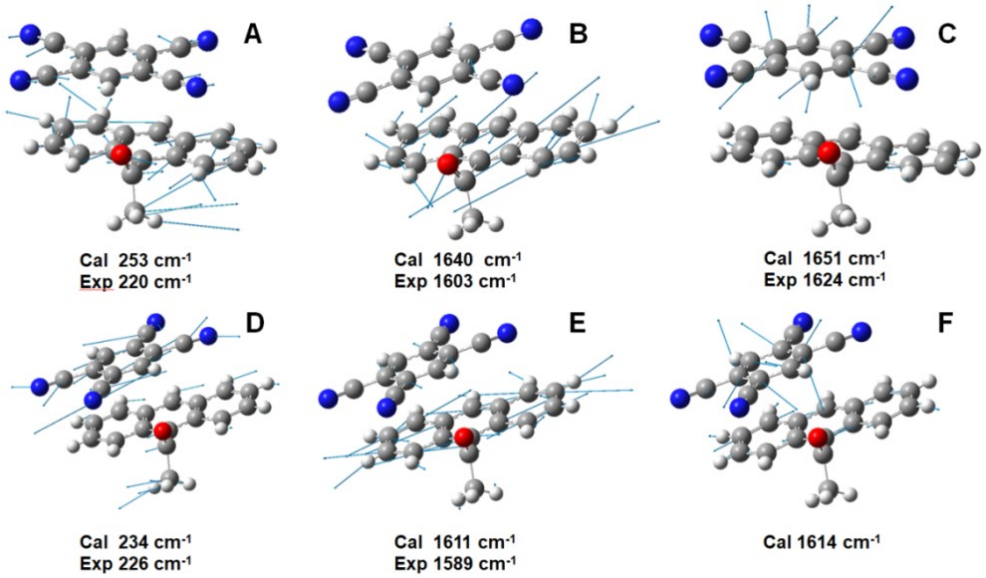

Fig. S5 In-plane π-π vibration between ACA and TCNB in the (A-C) form α and (D-F) form β.

Table S4. The fluorescent lifetime of the form α at 570, 580 and 590 nm, respectevily.

570nm		580 nm		590 nm	
Value(ns)	Rel %	Value(ns)	Rel %	Value(ns)	Rel %
6.73	9.88	7.37	9.66	9.16	15.23
18.72	90.12	18.75	90.04	19.25	84.77

Table S5 The fluorescent lifetime of the form β at 590, 610 and 630 nm, respectevily.

590nm		610 nm		630 nm	
Value(ns)	Rel %	Value(ns)	Rel %	Value(ns)	Rel %
14.04	5.56	11.07	4.43	9.16	5.24

56.06	94.44	55.48	95.57	56.01	94.76

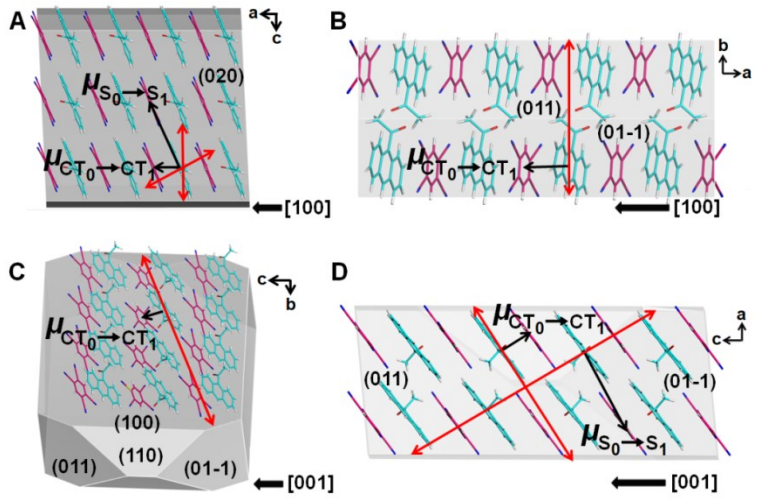

Fig. S6 Transition dipole moments vector of CT_0 to CT_1 and S_0 to S_1 in the form α viewed along the (A) [010], (B) [001] directions, and that in form β viewed along the (C) [100], (D) [010] directions, The vector μ are marked as black single-headed arrows. The directions of the light propagation in the crystal are marked as red double-headed arrows. (A-D) Growth morphologies of the two forms are simulated using materials studio software.

The growth morphologies of the form α and the form β polymorphic cocrystals were simulated via materials studio software. The ACA and TCNB molecules appear mixed stacking ···D–A–D–A··· along the direction of [100] in the form α (Fig. S6A and S6B) and along the direction of [001] in the form β (Fig. S6C and S6D). Therefore, the form α and the form β polymorphic cocrystals grow along the [100] and [001] directions, respectively.

The emitting light can travel around in the same plane which perpendicular to transition dipole moment (μ). Therefore, light propagation in the crystal were predicted by the vectors of μ which from donor to acceptor. In the form α, the composition vectors of μ contain a CT_0 to CT_1 transition with parallel direction of the [100] and a S_0 to S_1 transition with an angle of ≈ 60° along the [100] direction (Black unfilled arrows represented the direction of μ in the Fig. S6A and S6B), which lead to the optical wave can be transmitted along two directions of [001] and [100] with an angle of ≈ 30°. The directions of the light-wave propagation in form β are plotted in the Fig. S6C and S6D, the emitting light produced by CT_0 to CT_1 and S_0 to S_1

transitions can be travel in the crystal along the direction of [001] with an angle of ≈ 60° and 30°, respectively (Fig. S6C).

Table S6 The distances of light propagation $D_{b\text{-}t}$ and spatially resolved PL intensity from Fig. 4C.

No	$D_{b\text{-}t}$ (mm)	Fluorescent Intensity (I_{body} or I_{tip})
1	0	21926
2	0.15	8601
3	0.25	5248
4	0.4	1757
5	0.42	978
6	0.5	726
7	0.625	612
8	0.77	535
9	0.92	577
10	1.1	615
11	1.2	477

Table S7 The distances of light propagation $D_{b\text{-}t}$ and spatially resolved PL intensity from Fig. 4E.

No	$D_{b\text{-}t}$ (mm)	Fluorescent Intensity (I_{body} or I_{tip})
1	0	37246
2	0.15	21291
3	0.2	7119
4	0.25	2134
5	0.35	1890
6	0.5	1158

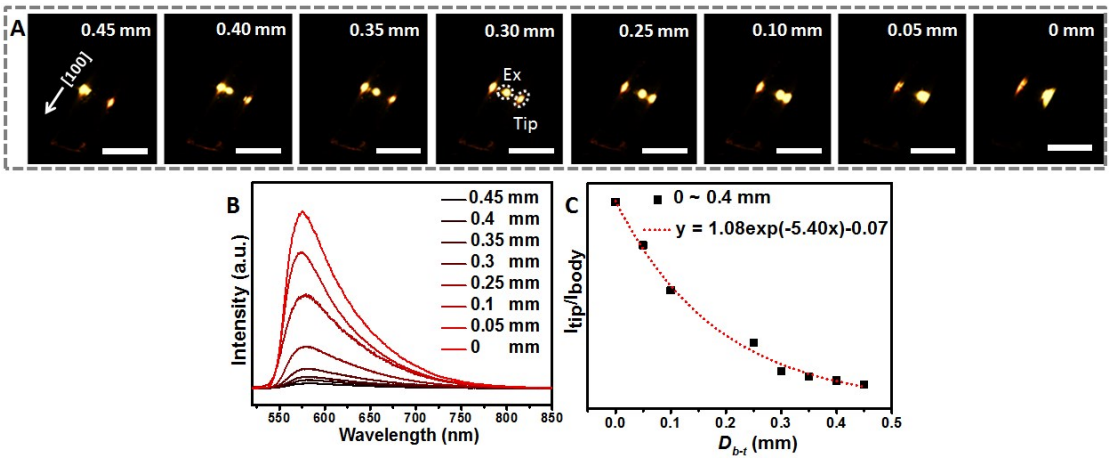

Fig. S7 (A) PL micro-imagings of optical propagation in the form α, the excitation spot moved perpendicular to the [100] axis (marked as 0.45 to 0 mm), white scale bars are 0.5 mm; (B) Spatially resolved PL spectra of out coupled lights at the location of "Tip" in form α from Fig. 7SA; (C) The fitting curves of I_{tip}/I_{body} with $D_{b\text{-}t}$ from Fig. 7SB.

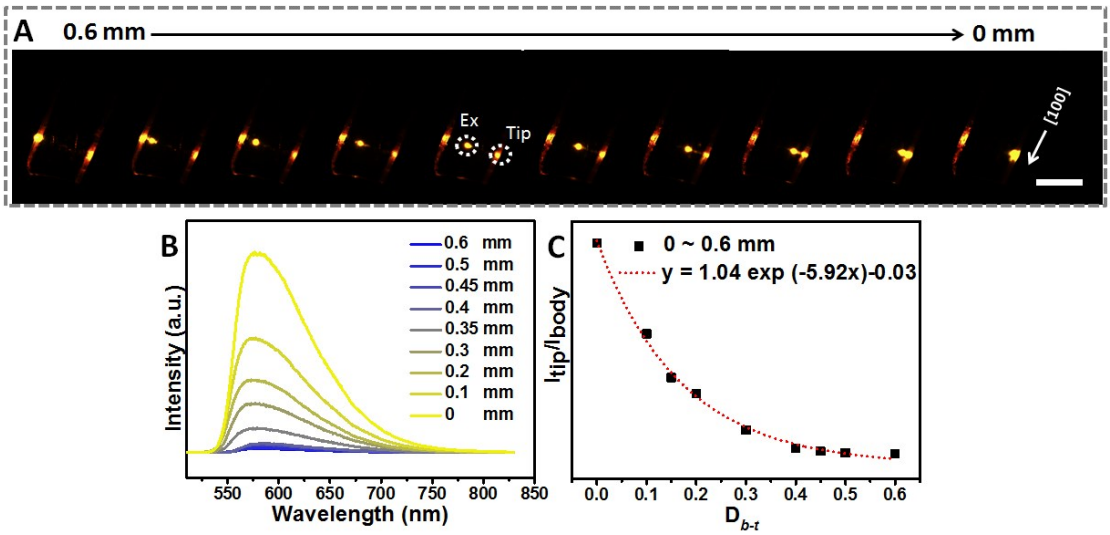

Fig. S8 (A) PL micro-imagings of optical propagation in the form *α*, the excitation spot moved perpendicular to the [100] axis (marked as 0.6 to 0 mm), white scale bar is 0.5 mm; (B) Spatially resolved PL spectra of out coupled lights at the location of "Tip" in form *α* from Fig. 8SA; (C) The fitting curves of I_{tip}/I_{body} with $D_{b\text{-}t}$ from Fig. 8SB.

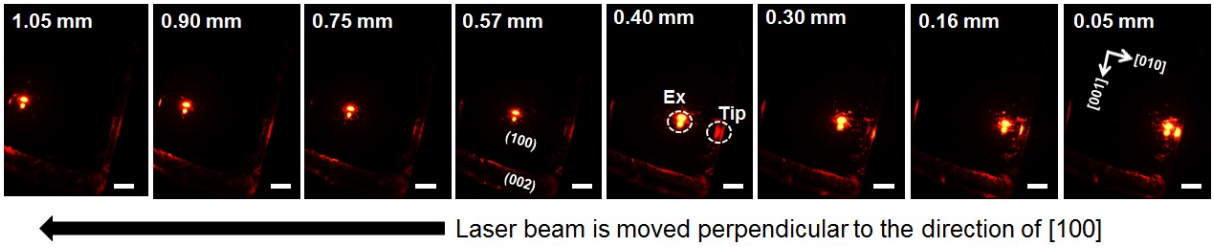

Fig. S9 PL micro-imagings of form *β*, the incident laser beam from crystal tip to crystal body perpendicular the [001] axis with different distance $D_{b\text{-}t.}$ The white scale bar is 0.25 mm.