Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Vapor-Phase π-π Molecular Recognition: A Fast and Solvent-free Strategy to the Formation of Co-crystalline Hollow Microtube with 1D Optical Waveguide and Up-conversion Emission

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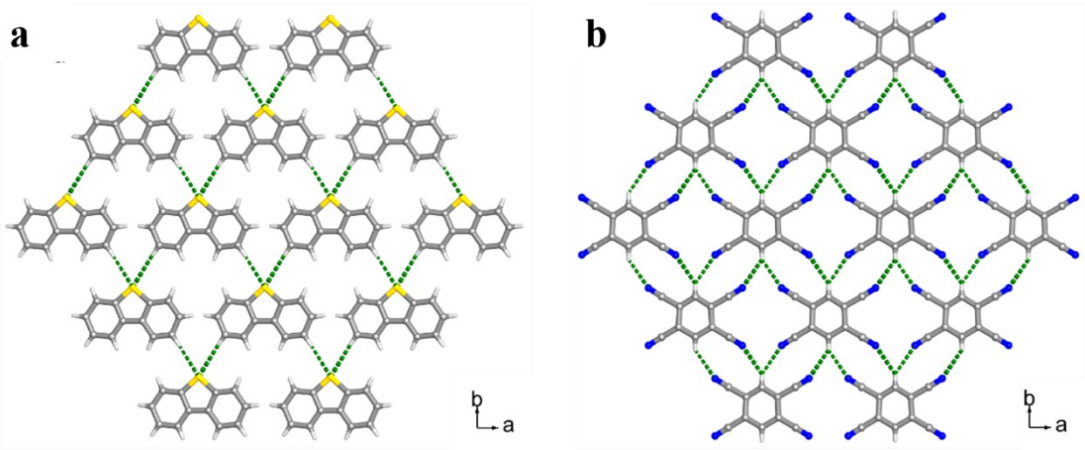

Figure S1. The layers of DBT (a) and TCNB (b) in the co-crystal. The green dash represents the hydrogen bond interactions.

Table S1. Single crystal structure data for DBT@TCNB.

Crystal	**DBT@TCNB**
Empirical formula	$C_{22}H_{10}N_4S$
Formula weight	296(2)
Temperature / K	102.2
Crystal system	monoclinic
Space group	*C*2/*m*
***a* / Å, *b* / Å, *c* / Å**	9.435(6), 12.771(8), 7.237(5)
***α*/°, *β*/°, *γ*/°**	90, 93.021(9), 90
Volume / Å^3	870.8(10)
Z	2
ρ_{calc} / mg mm^{-3}	1.382
***μ* / mm^{-1}**	0.200
***F*(000)**	372.0

Crystal size / mm^3	0.290 ×0.270 ×0.250
2θ range for data collection	5.374° to 50.998°
Index ranges	$-8 \le h \le 11$, $-15 \le k \le 14$, $-8 \le l \le 8$
Reflections collected	2152
Independent reflections	842[R(int) = 0.0334]
Data/restraints/parameters	842 / 6 / 71
Goodness-of-fit on F^2	1.019
Final R indexes [I>2σ (I) i.e. F$_o$>4σ (F$_o$)]	$R_1 = 0.0596$, $wR_2 = 0.1679$
Final R indexes [all data]	$R_1 = 0.0659$, $wR_2 = 0.1756$
Largest diff. peak/hole / e Å^{-3}	0.27/-0.40

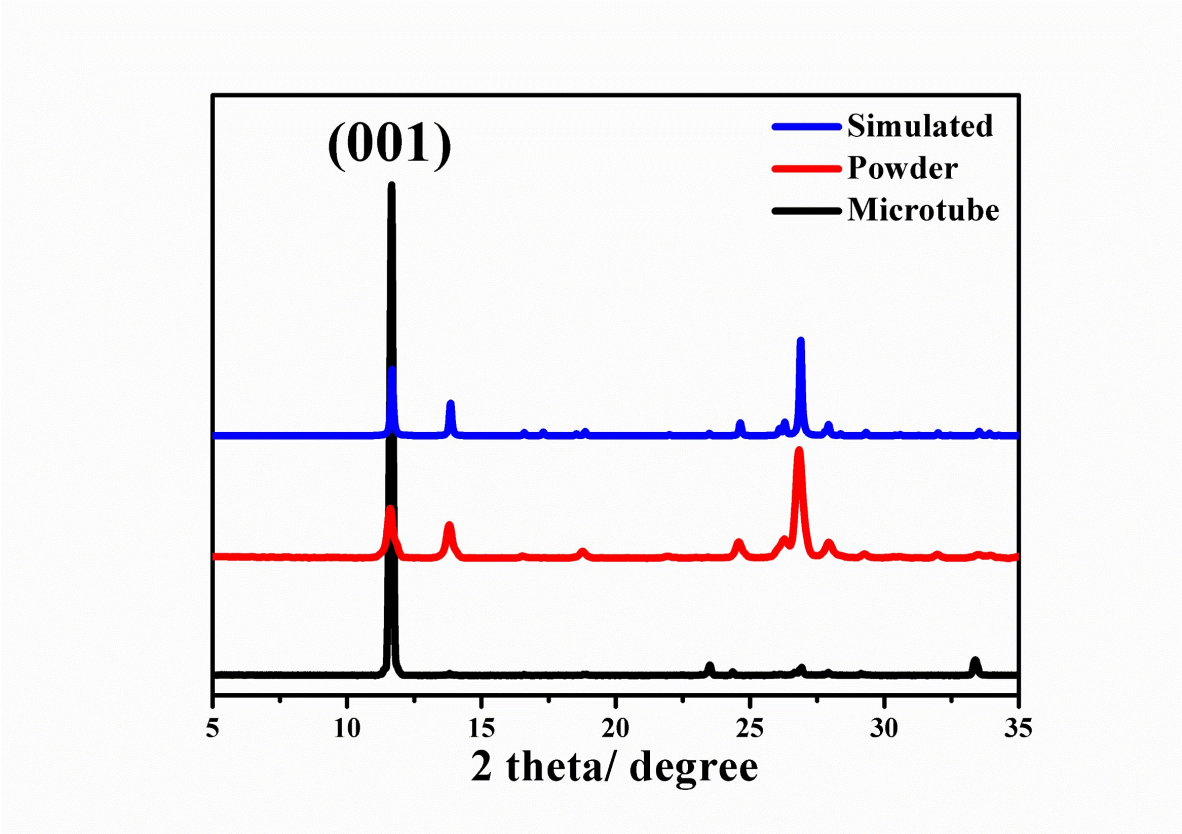

Figure S2. The X-ray diffraction (XRD) pattern simulated from the single crystal structure data (top), the XRD pattern of the DBT@TCNB co-crystal powder (middle) and microtube (down).

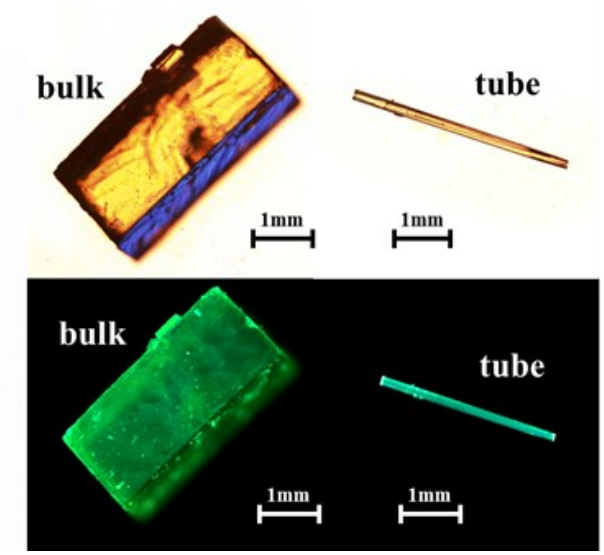

Figure S3. Fluorescence microscopy images of co-crystal in bulk (left) and microtube (right) forms under daylight (top) and UV light (down).

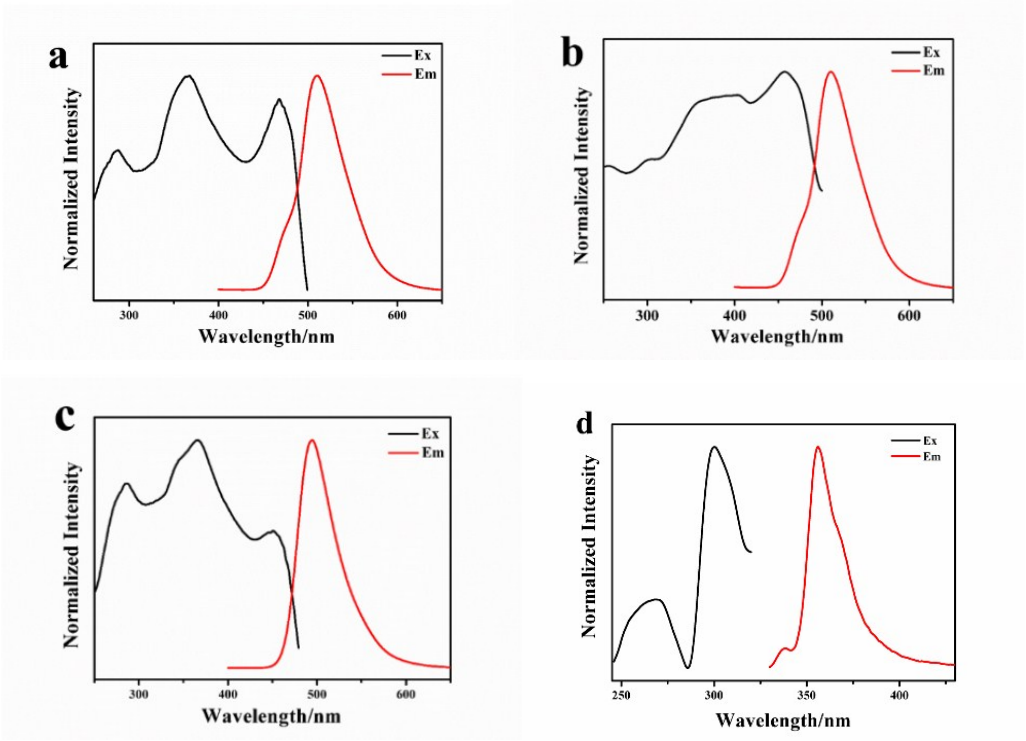

Figure S4. Fluorescence (FL) spectra of DBT@TCNB at different states (excitation wavelength: 360 nm) and DBT at room temperature (excitation wavelength: 300 nm). The black line represents the excitation spectra, and the red line represents the emission spectra: (a) in the state of bulk; (b) in the state of microtube; (c) in the state of powder, as obtained by grinding the microtube. (d) FL spectra of DBT.

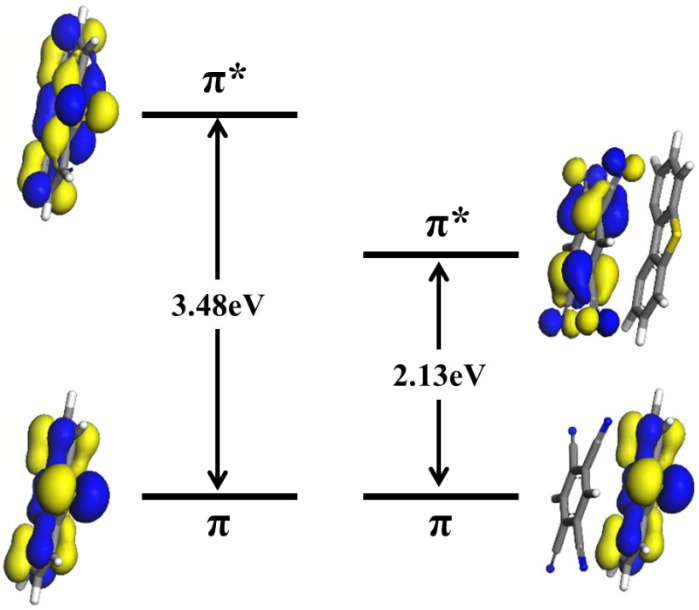

Figure S5. Calculated molecular orbital diagrams for the pristine DBT (left) and DBT@TCNB co-crystal (right).

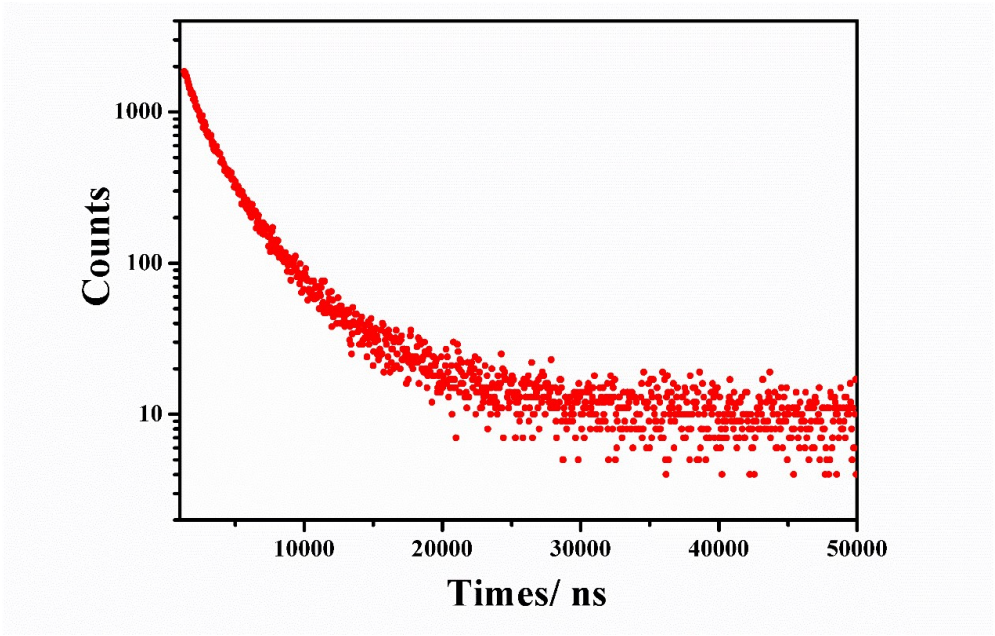

Figure S6. Fluorescence decay curve of the co-crystal microtube.

Table S2. Fluorescence decay of the co-crystal microtube

m	τ_i (ns)	A_i	<τ>(ns)	χ^2
1	2118.3	3177.44698	2118.3	1.35
2	3471.3	1193.02266	2328.0	1.09
	1082.3	3511.82215		

m stands for the mono- or double-exponential fitting of the fluorescence decay curve; τ_i is the fluorescence lifetime, for m = 1, lifetime is τ_1, and for m = 2, two lifetimes are τ_1 and τ_2; A_i stands for the fractional weights. The fitting goodness is indicated by the value of χ^2. In the double-exponential case, $<\tau>=(\tau 2\ 1\cdot A_1 + \tau 2\ 2\cdot A_2)/(\tau_1\cdot A_1 + \tau_2\cdot A_2)$.

Table S3. Surface area percentage of important facets of co-crystal by BFDH method

hkl	Multiplicity	d_{hkl}	Distance	Total facet area%
{ 1 1 0}	4	7.57	13.21	52.13
{ 0 0 1}	2	7.22	13.85	31.32
{ 0 2 0}	2	6.39	15.66	13.51
{ 1 1 -1}	4	5.34	18.74	3.04

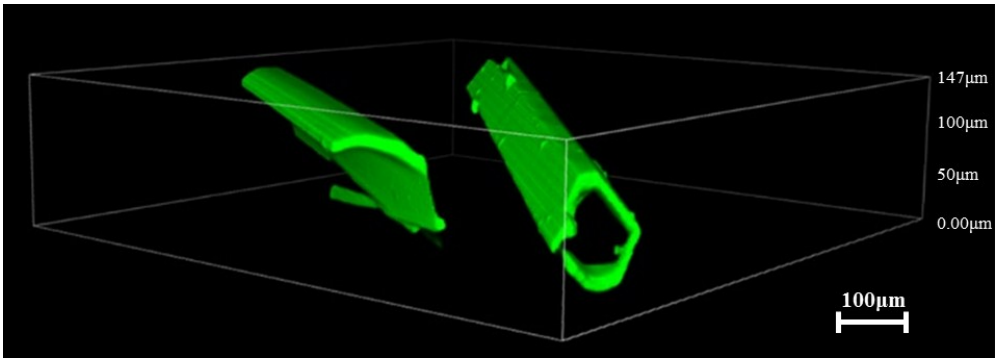

Figure S7. Image of the reconstructed 3D structures of unclosed co-crystalline microtube based on the fluorescence signal using a laser confocal microscope.