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Cocrystal Engineering for Constructing Two-photon Absorption Materials by Controllable Intermolecular Interactions

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1. Experimental

1.1. Chemicals and reagents

Benzo[b]naphtho[1,2-d]thiophene (BDBT, CAS:205-43-6, 98 %+) was purchased from TCI Co., 1,2,4,5-tetracyanobenzene (TCNB, CAS:712-74-3, 97 %) was purchased from Aldrich Co., and octafiuoronaphthaene (OFN, CAS:313-72-4, 96 %) was purchased from Aldrich Co.; Acetonitrile (CH_3CN, HPLC) was purchased from Beijing Chemical Co. China; Dichloromethane ($CHCl_3$, GR) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd., China. All of them were directly used without further purification. Deionized water (18.2 MΩ·cm^{-1}) was made by a Mill-Q water purification machine.

1.2. Cocrystal characterization

Single crystal structure of BDBT-OFN cocrystals were obtained on a Rigaku mm007 X-ray diffractometer (Rigaku, Japan), under a Mo target (50 kV, 16 mA). Single crystal structure of BDBT-TCNB cocrystals were conducted on an X-ray diffractometer (XtaLAB FRX) with Cu Kα radiation (40 kV, 30 mA). The powder X-ray diffraction pattern was obtained on a Rigaku SmartLab 9 kW instrument under 45 kV, 200 mA, Cu Kα radiation (λ = 1.542 Å). Ultraviolet–visible absorption (UV) spectra were obtained by the UV-3600 Plus UV-Vis-NIR spectrophotometer (SHZMADZU, Japan) combined with the diffuse reflection mode of the integrating sphere. Fourier transform infrared (FTIR) spectra were measured on the Bruker Vertex 70 FTIR spectrometer, which was made in Germany. Differential scanning calorimetry (DSC) diagram was obtained on a DSC 214 polyma (Germany) with a heating rate of 10 °C·min^{-1}. Thermogravimetric analysis (TGA) curve was measured on a Mettler Toledo TGA (Switzerland) instrument under a nitrogen atmosphere, and the heating rate was 10 °C·min^{-1}. Photoluminescence (PL) spectroscopy was acquired using Edinburgh Instruments (FLS1000). The absolute photoluminescence quantum yield (Φ_f, PLQY) was measured on the FLS1000 spectrometer in Edinburgh with an integrating sphere. The PL lifetime was measured with 3B laser product (EPL-375) and nF920 nanosecond lamp controller as the excitation source. The excited Raman spectrum was measured on a RENISHAW laser Raman spectrometer (UK) under a 785 nm laser. The two-photon correlation detection was acquired under a Nikon AIR-MP+ multiphoton microscope. The intermolecular potentials were calculated using UNI force field by Mercury software (copyright CCDC). And the calculated Bravais Friedel donnay Harker (BFDH) morphology was shown by Mercury software according to the crystal structure. Moreover, the energy levels were obtained at the B3lyp/6-31G(d) level of theory by Gaussian 09 package. The molecular orbital surfaces were visualized with GaussianView. The calculation of ESP map adopts MOPAC in Mercury software. MOPAC (Molecular Orbital PACkage) is a semiempirical quantum chemistry program based on Dewar and Thiel's NDDO approximation.

2. Supplemental Figures

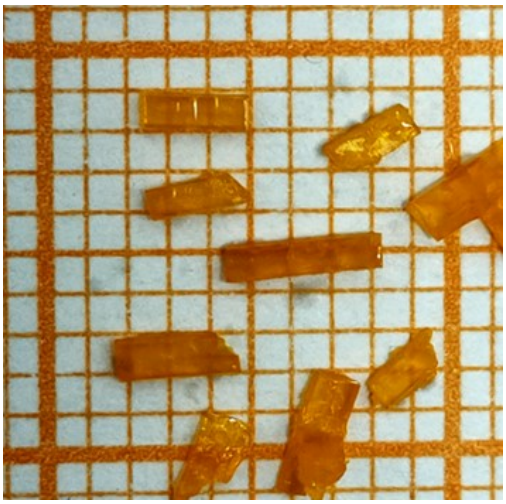

Fig. S1 Large crystal photo of BDBT-TCNB cocrystal.

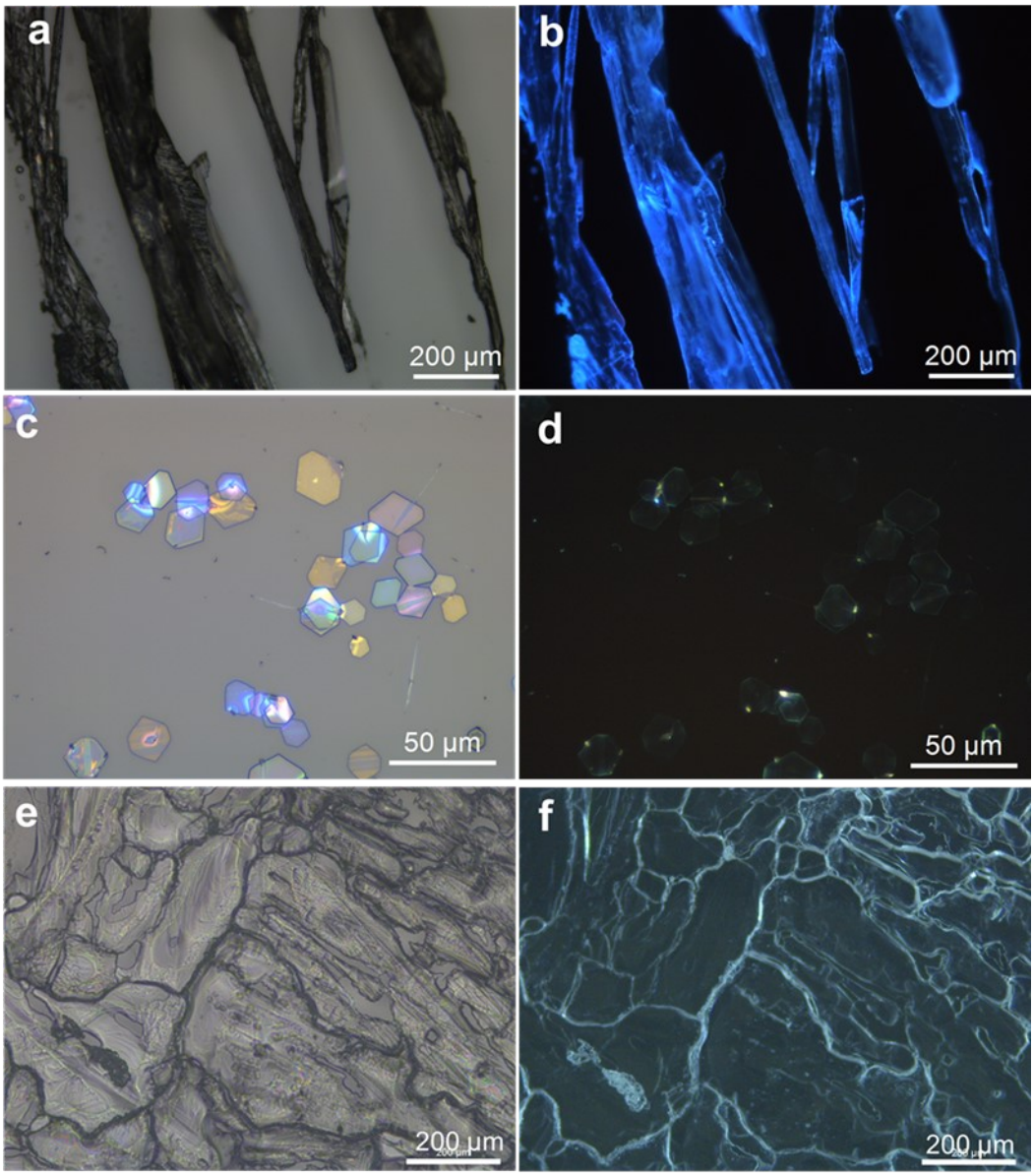

Fig. S2 Optical images of (a) BDBT, (c) TCNB and (e) OFN crystals obtained from acetonitrile solution drop casting on the glass substrate. Corresponding confocal laser scanning microscope (CLSM) images of (b) BDBT, (d) TCNB and (f) OFN crystals under the excitation of an unfocused UV light (330-380 nm).

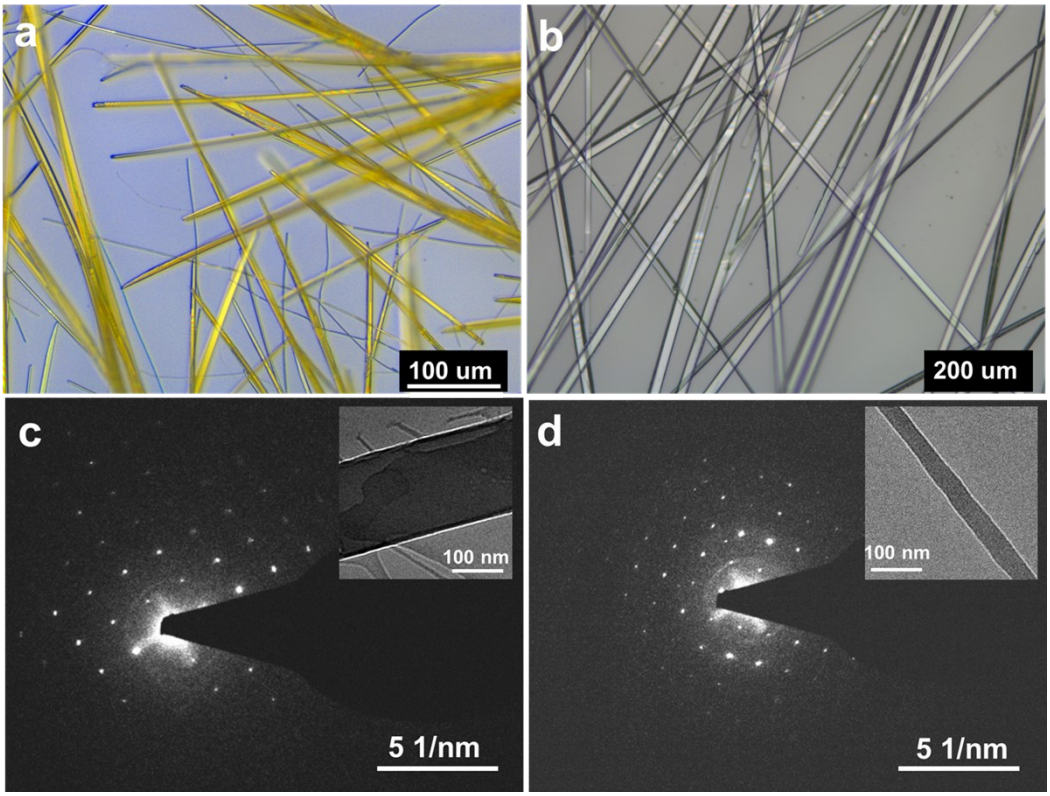

Fig. S3 Optical images of (a) BDBT-TCNB and (b) BDBT-OFN crystals obtained from acetonitrile solution drop casting on the glass substrate. Typical TEM and SAED images of (c) BDTC-TCNB cocrystals and (d) BDBD-OFN cocrystals.

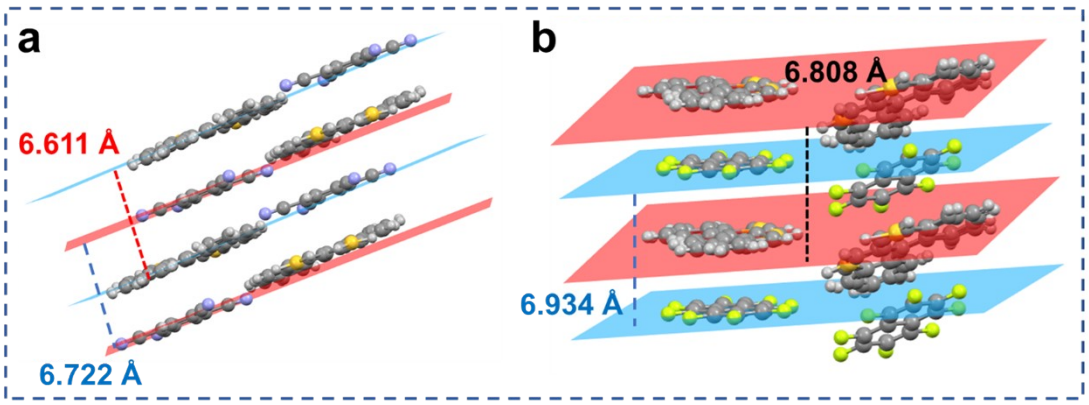

Fig. S4 The following formula is used to calculate the distance between receptor molecules: $$l = \frac{\mathbf{L}_{\mathbf{donor}} + \mathbf{L}_{\mathbf{acceptor}}}{4}$$ (L_{donor}: The distance between the two donors in the cocrystal molecule; $L_{acceptor}$: The distance between the two acceptors in the cocrystal molecule.).

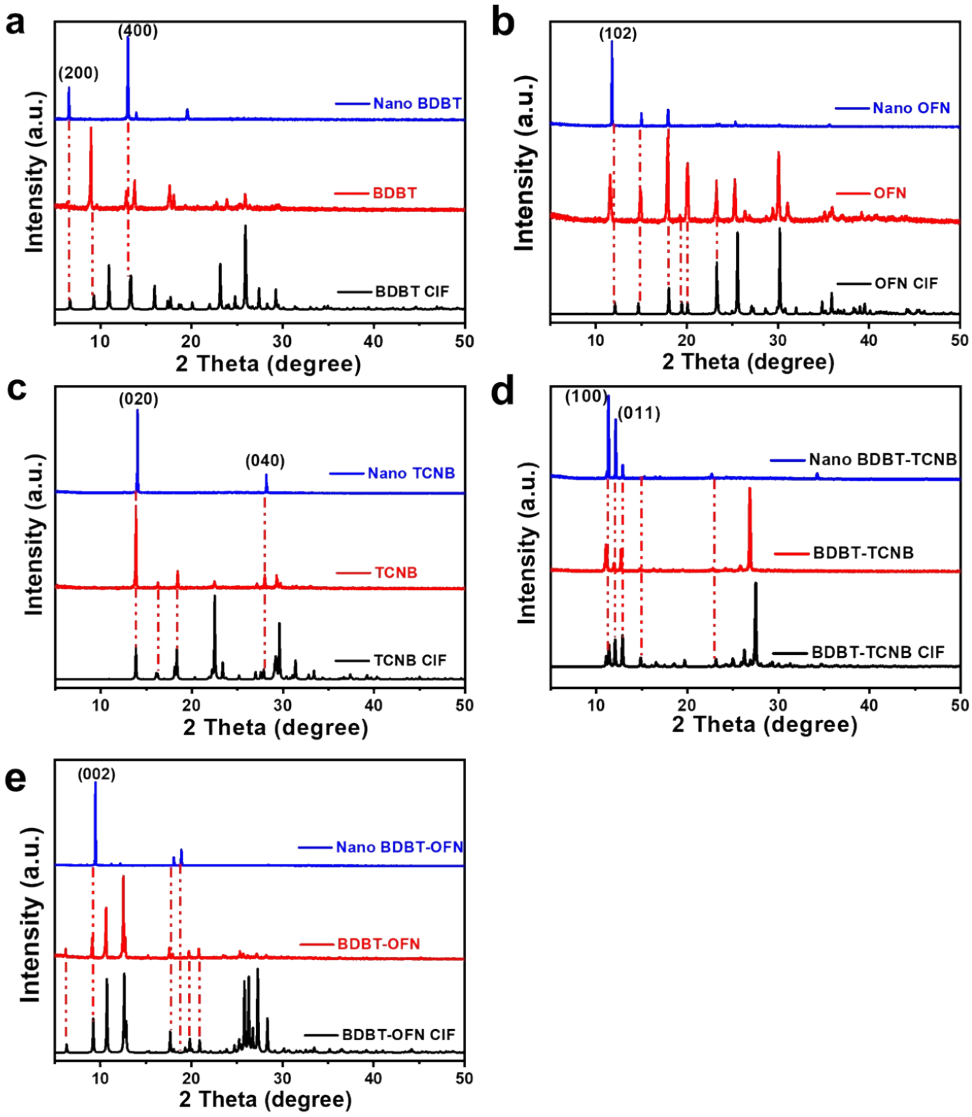

Fig. S5 XRD result of (a) BDBT, (b) OFN, (c) TCNB, (d) BDBT-TCNB and (e) BDBT-OFN on a glass substrate (blue curve), powder (red curve) and the calculated XRD from cif file (black curve).

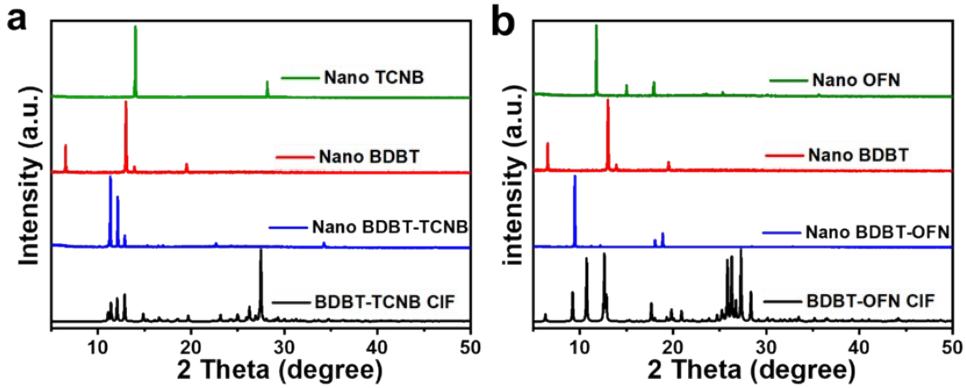

Fig. S6 (a) Comparison of XRD results of BDBT, TCNB and BDBT-TCNB on glass substrates. (b) Comparison of XRD results of BDBT, OFN and BDBT-OFN on glass substrates.

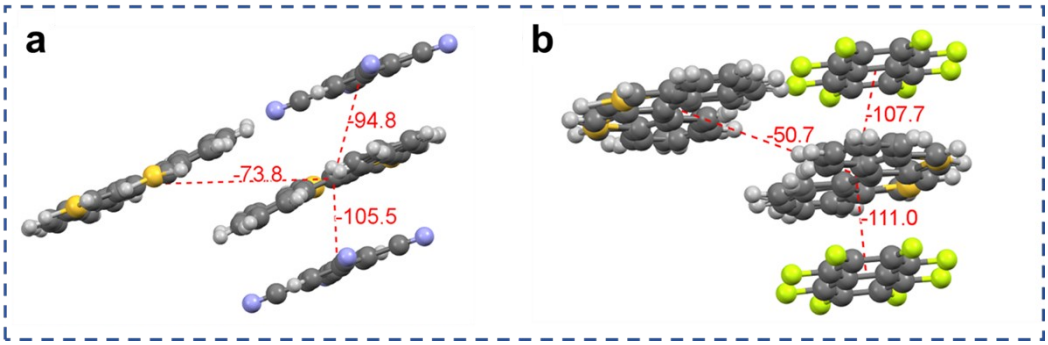

Fig. S7 The intermolecular potential energy of (a) BDBT-TCNB and (b) BDBT-OFN cocrystal.

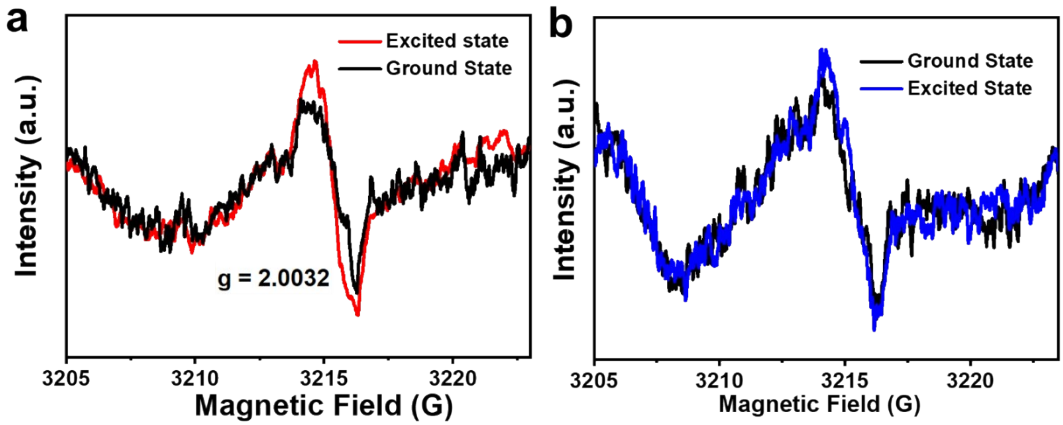

Fig. S8 ESR spectrum of (a) BDBT-TCNB cocrystal and (b) BDBT-OFN cocrystal.

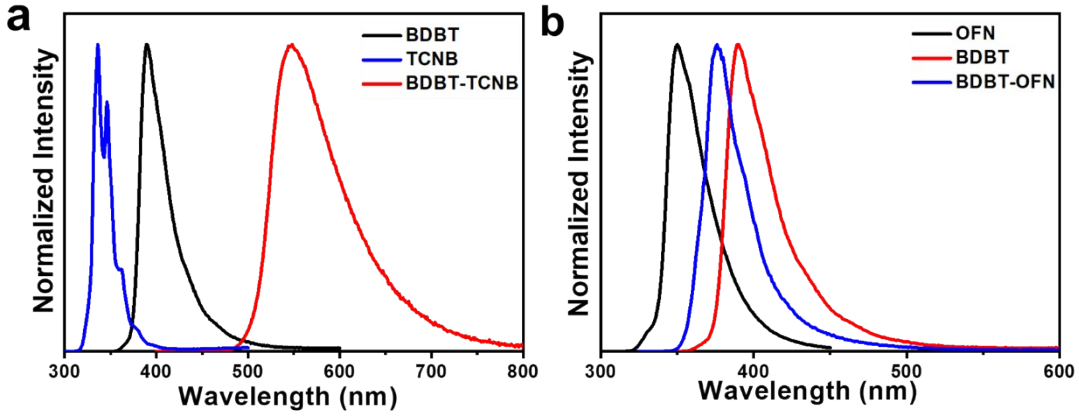

Fig. S9 (a) Fluorescence spectra of BDBT, TCNB and BDBT-TCNB; (b) Fluorescence spectra of BDBT, OFN and BDBT-OFN.

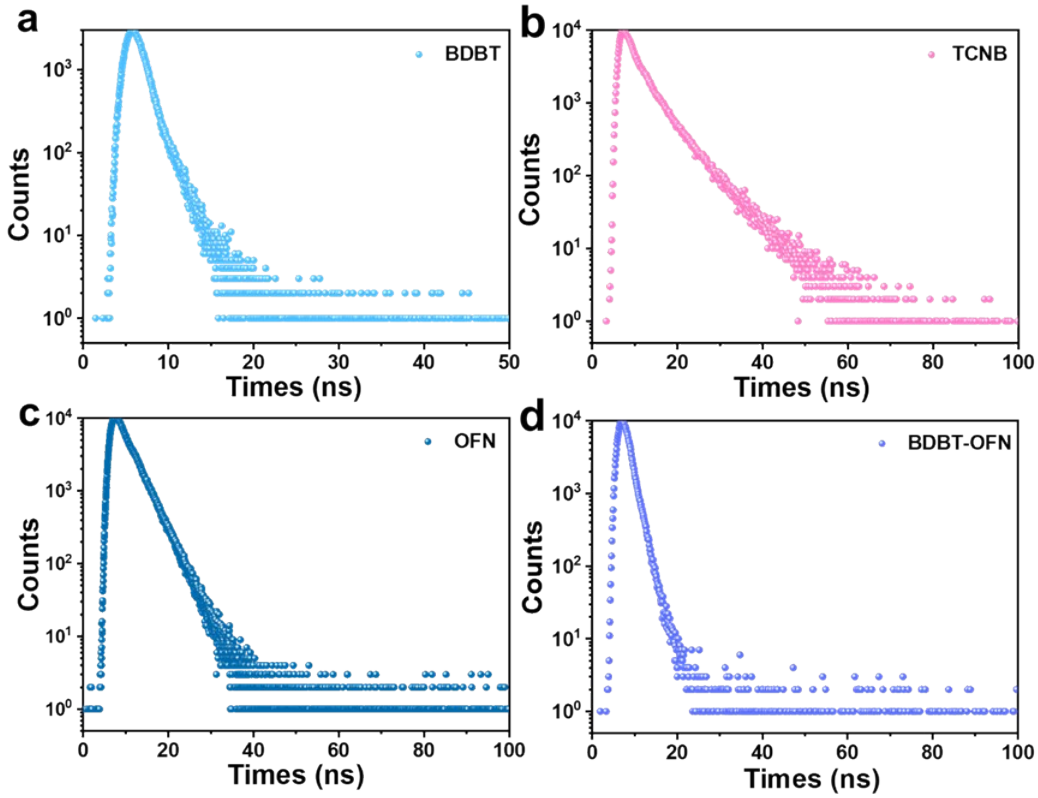

Fig. S10 Fluorescence decay curve of (a) BDBT donor, (b) TCNB acceptor, (c) OFN acceptor and BDBT-OFN cocrystal.

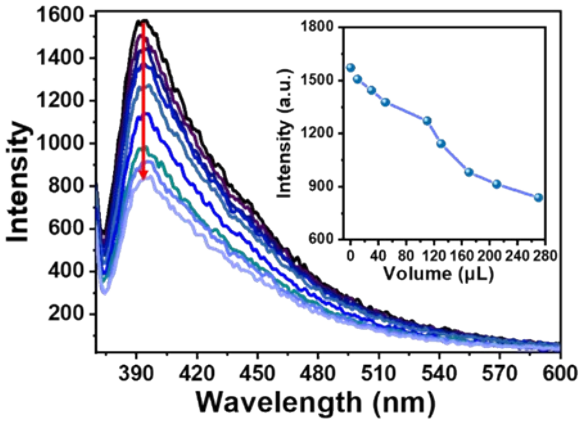

Fig. S11 Fluorescence spectra of BDBT (C = 1 × 10^{-5} M, 10 mL) with increasing volume of OFN in dichloromethane (C = 2 × 10^{-3} M, 0–270 μL).

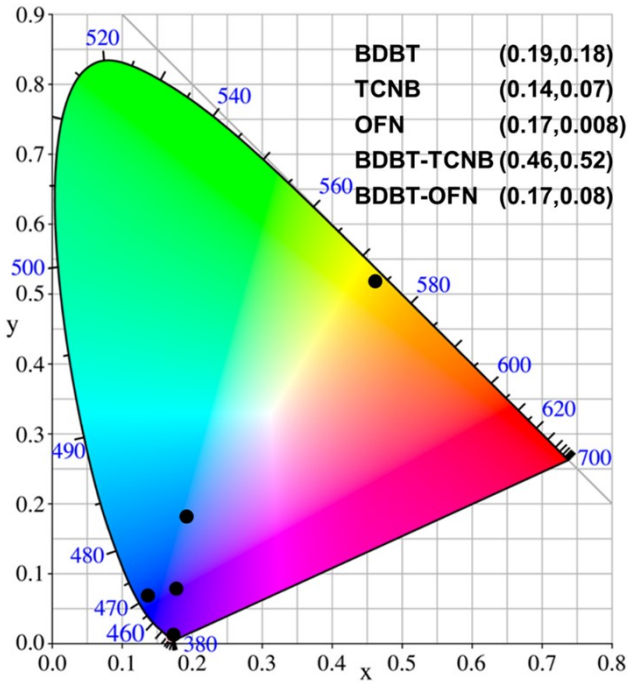

Fig. S12 CIE chromaticity diagram of BDBT, TCNB, OFN, BDBT-TCNB and BDBT-OFN.

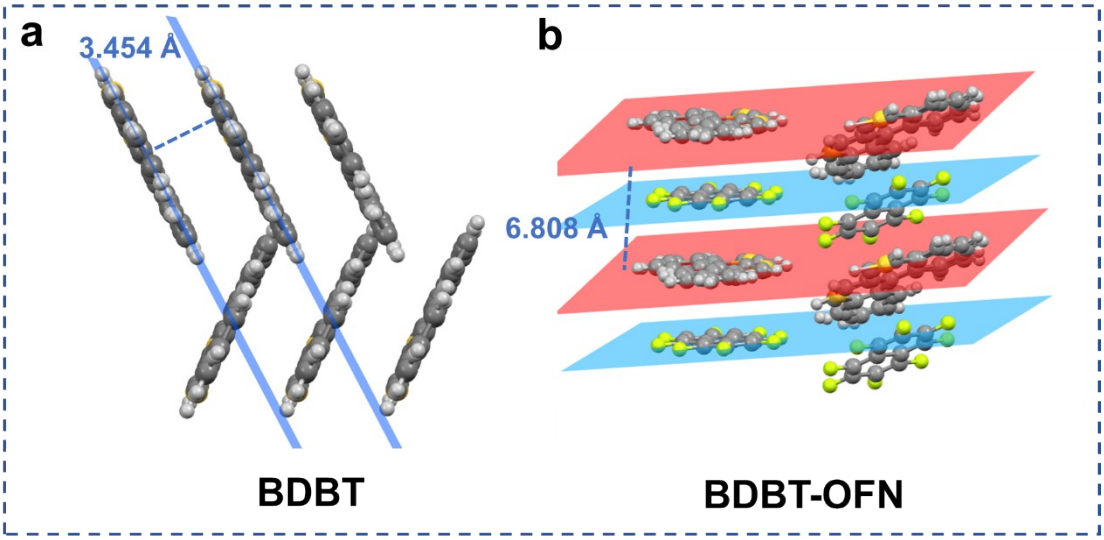

Fig. S13 The distance between BDBT molecules in BDBT single crystal and BDBT-OFN cocrystal.

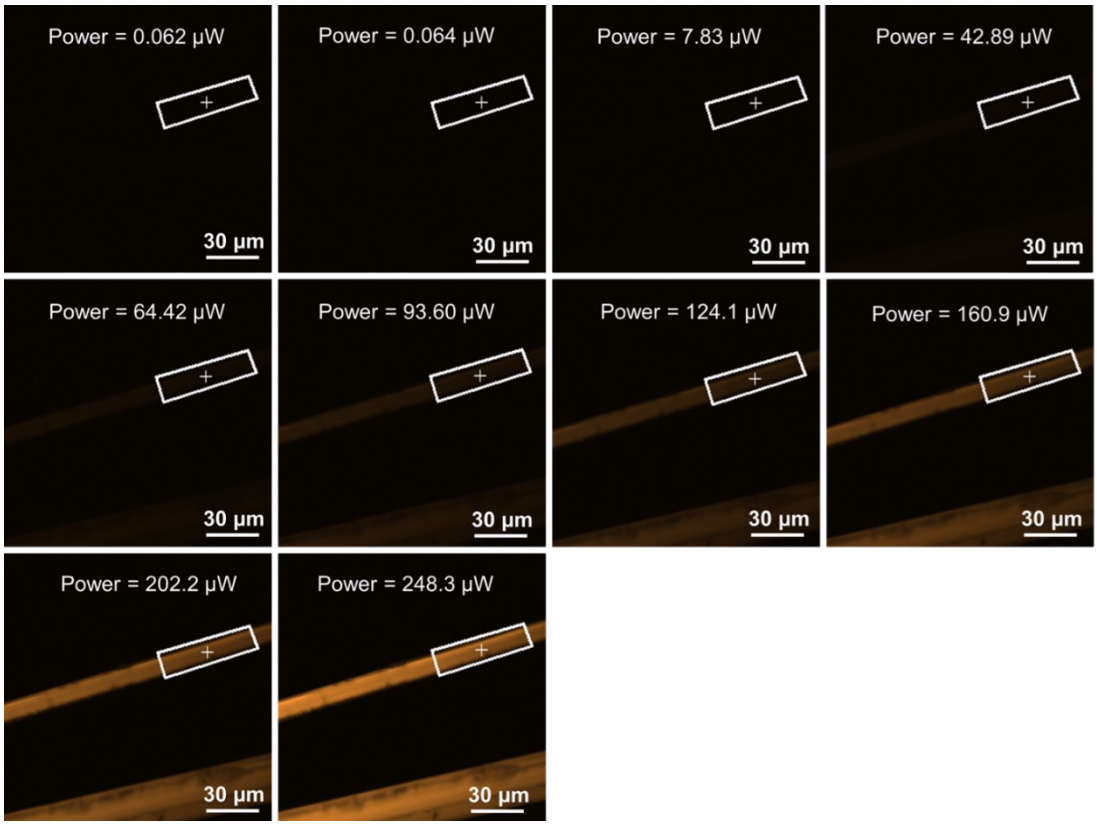

Fig. S14 The two-photon microscopy images of BDBT-TCNB excited at 800 nm with tunable powers.

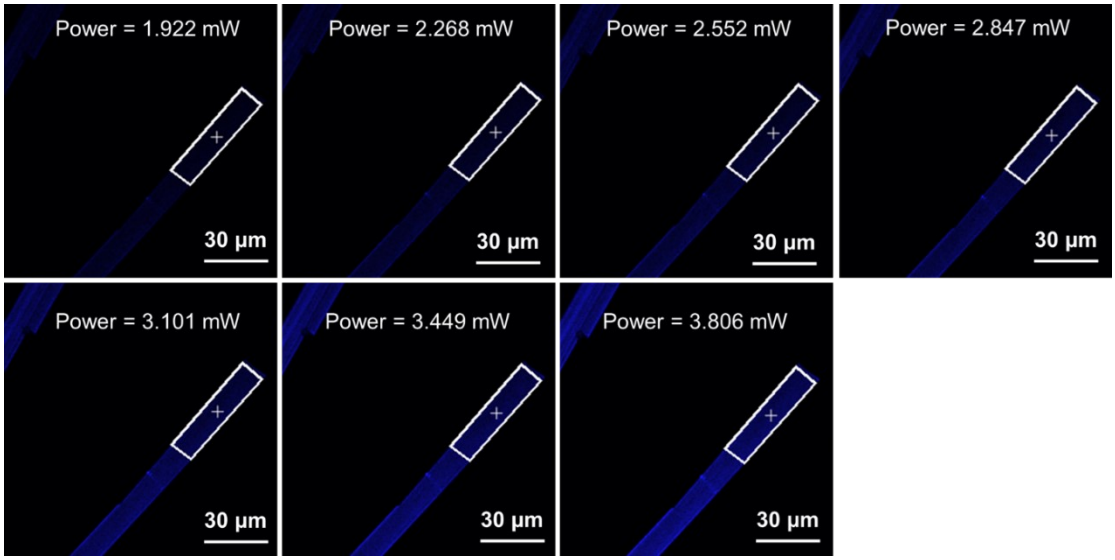

Fig. S15 The two-photon microscopy images of BDBT excited at 700 nm with tunable powers.

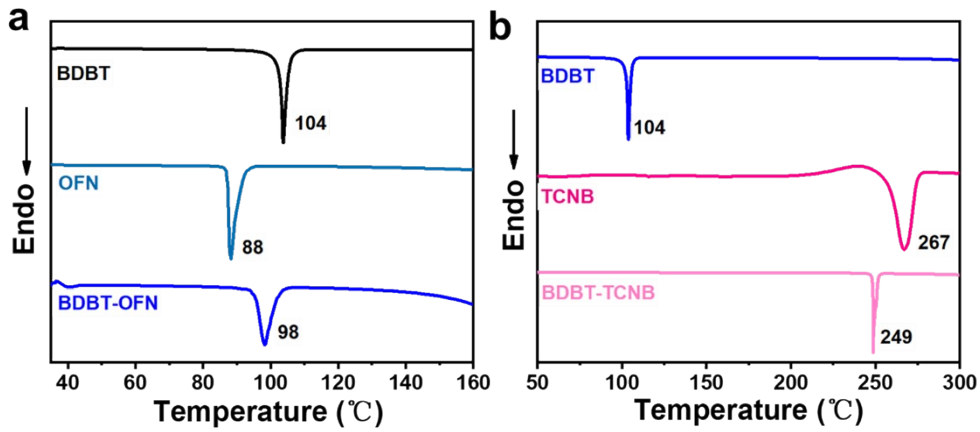

Fig. S16 (a) DSC spectra of TCNB, BDBT and BDBT-TCNB; (b) DSC spectra of OFN, BDBT and BDBT-OFN.

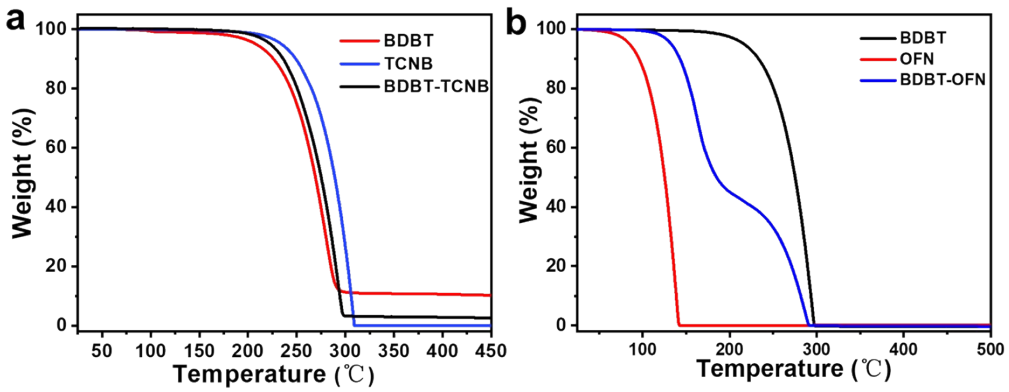

Fig. S17 (a) TGA spectra of TCNB, BDBT and BDBT-TCNB; (b) TGA spectra of OFN, BDBT and BDBT-OFN.

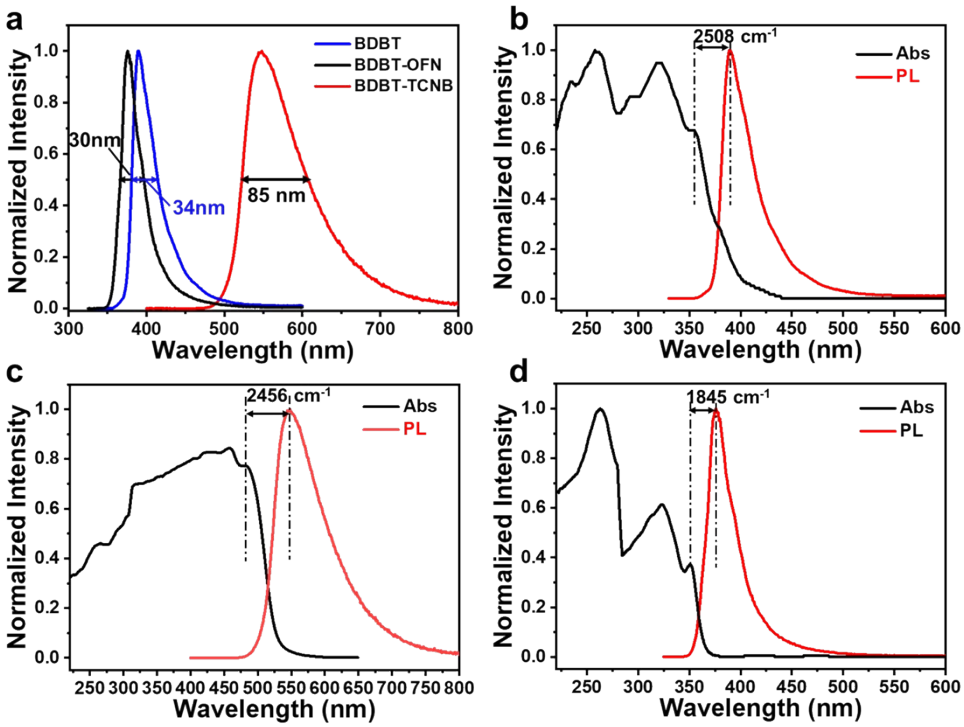

Fig. S18 (a)The full width at half maximum (FWHM) of BDBT, BDBT-OFN and BDBT-TCNB. Absorption and PL spectra of (b) BDBT, (c) BDBT-TCNB cocrystal and (d) BDBT-OFN cocrystal.

Table S1 Single crystal structure of BDBT-TCNB cocrystal and BDBT-OFN cocrystal.

Crystal	BDBT-TCNB	BDBT-OFN
Empirical formula	$C_{26}H_{12}N_4S$	$C_{26}H_{10}F_8S$
Formula weight	412.46	294.15
Temperature/K	113.15	113.15
Crystal system	Triclinic	Monoclinic
Space group	P1 (2)	P21 /n
a /Å	7.2920 (3)	7.2054 (2)
b/Å	8.0111 (4)	10.1966 (3)
c/Å	15.7519 (9)	28.0448 (7)
α/°	93.915 (4)	90
β/°	98.871 (4)	92.672 (4)
γ/°	93.579 (4)	90
Volume/Å^3	966.59 (8)	2058.23 (10)
Z	2	2
ρcalcg/cm^3	1.417	1.634
F (000)	424.0	1016.0
Crystal size/mm^3	0.18 × 0.16 × 0.14	0.20 × 0.18 × 0.16
Reflections collected	10224	11862
Independent reflections	3948 [Rint = 0.0266, Rsigma = 0.0292]	4038 [Rint = 0.0276, Rsigma = 0.0221]
Goodness-of-fit on F^2	1.106	1.137

Table S2 Fluorescence decay of the cocrystals and single component crystals.

	m	τi (ns)	Ai	<τ>(ns)	χ2
OFN	1	3.4459	11008.5215	3.4459	1.06
BDBT	2	1.1875	3209.0073	1.3224	1.10
		3.0479	97.7358		
TCNB	2	2.4187	4517.2461	4.8346	1.09
		6.3855	2665.2747		
BDBT-TCNB	3	16.5315	12123.3408	122.4279	1.22
		61.3301	483.6035		
		860.4195	36.2775		
BDBT-OFN	3	0.4718	13567.0039	1.17	1.28
		2.9103	241.2669		
		8.4700	53.4047		

m represents the mono-, double- or triple exponential fitting of the fluorescence decay curve; τ_i is the fluorescence lifetime; A_i stands for the fractional weights. The fitting goodness is indicated by the value of χ^2. In the mono-exponential case, lifetime is τ1; In the double-exponential case, $<\tau> = (\tau2\ 1\cdot A_1 + \tau2\ 2\cdot A_2)/(\tau_1\cdot A_1 + \tau_2\cdot A_2)$; In the triple exponential case, $<\tau> = (\tau3\ 1\cdot A_1 + \tau3\ 2\cdot A_2 + \tau3\ 3\cdot A_3)/(\tau_1\cdot A_1 + \tau_2\cdot A_2 + \tau_3\cdot A_3)$.