

Electronic Supplementary Information for

Synthesis and photophysical properties of charge transfer cocrystals based on TCNB and fluorene and its derivatives

Wenxiu Yao,^a Pengfei Wu,^a Yidan Xie,^a Xinyu Shen,^a Shuwei Xia^{*a} and Liangmin Yu^{*a}

^a Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

* Corresponding author

E-mail: shuweixia@ouc.edu.cn; yuyan@ouc.edu.cn

Table S1. Bond length in TCNB, TCNB anion and cocrystals. (a, b, c, d, and e represent the corresponding bond length shown in the right figure.)

	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)
TCNB	1.4009	1.3924	1.0214	1.4432	1.1382
TCNB anion	1.4356	1.3872	0.9152	1.4310	1.1521
TCNB-FR	1.4114	1.3880	0.9501	1.4392	1.1455
TCNB-2-BrFR	1.3885	1.3967	0.9497	1.4429	1.1495
TCNB-CZ	1.4035	1.3892	0.9500	1.4418	1.1461
TCNB-2-BrCZ	1.4024	1.3883	0.9502	1.4388	1.1436

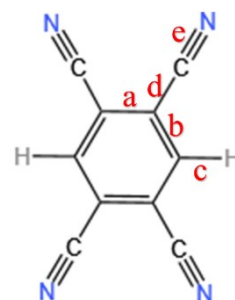


Table S2. Binding energy of cocrystals.

	TCNB-FR	TCNB-2-BrFR	TCNB-CZ	TCNB-2-BrCZ
E_D (eV)	-2174.990	-2524.327	-2275.140	-2624.474
E_A (eV)	-2660.325	-2660.327	-2660.325	-2660.325
E_{DA} (eV)	-4835.444	-5184.749	-4935.615	-5284.916
ΔE (kJ/mol)	-12.414	-9.152	-14.440	-11.249
E (kJ/mol)	12.414	9.152	14.440	11.249

Table S3. ADCH charge difference of TCNB-FR, TCNB-2-BrFR.

TCNB-FR				TCNB-2-BrFR			
TCNB		FR		TCNB		2-BrFR	
N1	-0.0909	C9	0.0579	N24	-0.2064	Br1	-0.0598
N2	-0.0236	H10	-0.6606	N25	-0.0486	C2	-0.0849
C3	-0.1410	C11	1.5985	C26	0.1477	H3	-0.1327
C4	-0.0536	H12	-0.5394	C27	-0.0832	C4	0.0286
C5	0.0572	C13	-0.2094	C28	-0.0208	H5	0.0346
C6	0.0914	H14	0.2498	C29	0.4324	H6	-0.0377
C7	-0.0273	C15	-0.5394	H30	-0.2474	C7	1.2732
H8	-0.0098	C16	-0.1711	C31	0.1796	H8	-0.5855
N32	-0.0262	C17	0.4764	N32	0.3888	C9	-0.1715
N33	-0.0848	H18	-0.2759	N33	-0.0987	C10	-0.3491
C34	-0.0815	C19	0.0873	C34	0.3083	C11	0.3117
C35	0.2352	H20	-0.0375	C35	-0.1400	H12	-0.1361
C36	-0.0331	H21	0.0347	C36	0.0909	C13	-0.0984
C37	-0.0374	C22	0.1299	C37	-0.0340	C14	-0.1121
C38	0.4211	C23	0.5159	H38	-0.0139	H15	0.1842
H39	-0.2417	H24	-0.4264	C39	-0.6901	C16	0.3569

		C25	-0.1603			H17	-0.2721
		H26	0.0076			C18	-0.1086
		C27	-0.2438			C19	-0.4807
		C28	0.2664			C20	1.4980
		H29	-0.2468			H21	-0.5286
		C30	0.4354			C22	0.1860
		H31	-0.3033			H23	-0.6799
Total	-0.0459	Total	+0.0459	Total	-0.0354	Total	+0.0354

Table S4. ADCH charge difference of TCNB-CZ, TCNB-2-BrCZ.

TCNB-CZ				TCNB-2-BrCZ			
TCNB		CZ		TCNB		2-BrCZ	
N1	0.2411	C9	0.4408	N2	0.3590	Br1	-0.0509
N2	-0.0557	H10	-0.2855	N5	-0.1755	N3	-0.4586
C3	-0.0989	C11	0.3323	N6	0.2897	H4	0.1187
C4	0.2086	H12	-0.2413	C7	0.1880	C18	0.0096
C5	0.3701	C13	0.2324	C8	0.2282	C19	-0.1062
H6	-0.1818	H14	-0.3933	C9	-0.6591	C20	0.0934
C7	-0.5071	C15	0.3645	N10	-0.0726	C21	0.1504
C8	0.0146	C16	0.0822	C11	-0.1078	H22	-0.1173
N31	-0.0070	C17	-0.2985	C12	0.3803	C24	0.0969
N32	-0.1592	H18	0.0064	H13	-0.1843	C26	0.3419
C33	-0.1558	C19	0.0793	C14	0.4704	H27	-0.2706
C34	-0.1599	C20	-0.0500	H15	-0.2184	C28	-1.8419
C35	0.4507	N21	-0.6227	C16	0.1568	H29	0.4531
H36	-0.2019	H22	0.1422	C17	-0.1580	C30	0.2016
C37	0.0135	C23	1.0218	C23	-0.5845	H31	-0.1483
C38	0.1480	H24	-0.4930	C25	0.0212	C32	-0.0426
		C25	-0.8235			C33	0.9620
		H26	0.0339			H34	-0.2415
		C27	0.7755			C35	1.2203
		H28	-0.4546			H36	-0.5328
		C29	0.5730			C37	0.5691
		H30	-0.3413			H38	-0.3396
Total	-0.0807	Total	+0.0807	Total	-0.0667	Total	+0.0667

Table S5. Topological parameters of the cocrystals.

Hydrogen bonding	r (Å)	ρ (a.u.)	$\nabla^2\rho$ (a.u.)	G (a.u.)	V (a.u.)	H (a.u.)	E_{HB} (kcal/mol)	-G/V
TCNB-FR								
C21-H22...N63	2.8255	0.0051	0.0174	0.0035	-0.0027	0.0008	-0.3912	1.3039

N63...H16-C15	2.4658	0.0097	0.0318	0.0069	-0.0059	0.0010	-1.4208	1.1729
C87-H88...N72	2.6916	0.0065	0.0219	0.0045	-0.0035	0.0010	-0.6975	1.2774
N72...H18-C17	2.6096	0.0074	0.0239	0.0050	-0.0041	0.0009	-0.8974	1.2297
C102-H103...N64	2.6109	0.0073	0.0239	0.0050	-0.0041	0.0009	-0.8936	1.2301
N64...H49-C48	2.6924	0.0064	0.0219	0.0045	-0.0035	0.0010	-0.6955	1.2777
C131-H132...N71	2.4648	0.0097	0.0318	0.0069	-0.0059	0.0010	-1.4252	1.1725
N71...H107-C106	2.8248	0.0051	0.0174	0.0035	-0.0027	0.0008	-0.3927	1.3037
C69-H70...N9	2.4660	0.0097	0.0318	0.0069	-0.0059	0.0010	-1.4224	1.1715
N125...H78-C77	2.4653	0.0097	0.0318	0.0069	-0.0059	0.0010	-1.4255	1.1713

TCNB-2-BrFR

C84-H85...N87	2.6798	0.0066	0.0217	0.0045	-0.0036	0.0009	-0.7310	1.2601
N87...H17-C16	2.5438	0.0088	0.0303	0.0064	-0.0052	0.0012	-1.2307	1.2346
N87...H15-C14	2.9179	0.0049	0.0162	0.0033	-0.0025	0.0008	-0.3477	1.3266
C130-H131...N118	2.3454	0.0122	0.0393	0.0089	-0.0079	0.0010	-1.9903	1.1224
C76-H77...N118	2.9096	0.0046	0.0164	0.0033	-0.0024	0.0008	-0.2846	1.3386
N118...H85-C84	2.6462	0.0072	0.0239	0.0050	-0.0040	0.0010	-0.8603	1.2527
C53-H54...N88	2.6469	0.0072	0.0238	0.0050	-0.0040	0.0010	-0.8580	1.2528
N88...H46-C45	2.9088	0.0046	0.0164	0.0033	-0.0024	0.0008	-0.2861	1.3384
N88...H61-C60	2.3450	0.0123	0.0393	0.0089	-0.0079	0.0010	-1.9917	1.1223
C107-H108...N117	2.9178	0.0049	0.0163	0.0033	-0.0025	0.0008	-0.3484	1.3265
C109-H110...N117	2.5429	0.0089	0.0303	0.0064	-0.0052	0.0012	-1.2344	1.2343
N117...H54-C53	2.6796	0.0066	0.0217	0.0045	-0.0036	0.0009	-0.7318	1.2599
C92-H93...N56	2.3451	0.0123	0.0392	0.0089	-0.0079	0.0010	-1.9960	1.1201
N126...H123-C122	2.3450	0.0123	0.0392	0.0089	-0.0079	0.0010	-1.9960	1.1201

TCNB-CZ

C41-H42...N62	2.9816	0.0038	0.0131	0.0026	-0.0019	0.0007	-0.1081	0.0072
N62...H40-C39	2.7211	0.0063	0.0212	0.0044	-0.0035	0.0009	-0.6678	0.0118
N62...H90-C89	2.5034	0.0090	0.0304	0.0065	-0.0054	0.0011	-1.2726	0.0169
C15-H16...N69	2.6530	0.0070	0.0241	0.0050	-0.0039	0.0011	-0.8201	0.0136
N69...H42-C41	2.5097	0.0090	0.0293	0.0063	-0.0052	0.0011	-1.2556	0.0182
C111-H112...N61	2.5096	0.0090	0.0294	0.0063	-0.0052	0.0011	-1.2558	0.0182
N61...H130-C129	2.6522	0.0070	0.0242	0.0050	-0.0039	0.0011	-0.8228	0.0136
C49-H50...N70	2.5035	0.0090	0.0304	0.0065	-0.0054	0.0011	-1.2723	0.0169
C109-H110...N70	2.7200	0.0063	0.0213	0.0044	-0.0035	0.0009	-0.6711	0.0118
N70...H112-C111	2.9807	0.0038	0.0131	0.0026	-0.0019	0.0007	-0.1092	0.0072
C65-H66...N86	2.5028	0.0091	0.0304	0.0065	-0.0054	0.0011	-1.2782	0.0169
N46...H74-C73	2.5035	0.0090	0.0304	0.0065	-0.0054	0.0011	-1.2756	0.0169

TCNB-2-BrCZ

N101...H34-C33	2.5288	0.0089	0.0302	0.0064	-0.0052	0.0012	-1.2425	0.0175
N101...H29-C28	3.0296	0.0041	0.0135	0.0027	-0.0020	0.0007	-0.1675	0.0078

C97-H98...N100	2.9424	0.0042	0.0139	0.0028	-0.0021	0.0007	-0.1987	0.0081
N78-H79...N100	2.0820	0.0195	0.0639	0.0151	-0.0142	0.0009	-3.5969	0.0357
C73-H74...N105	2.6295	0.0074	0.0245	0.0051	-0.0041	0.0010	-0.9082	0.0149
N105...H67-C66	2.9160	0.0046	0.0162	0.0032	-0.0024	0.0008	-0.2779	0.0083
N105...H10-C9	2.4422	0.0101	0.0326	0.0072	-0.0063	0.0010	-1.5161	0.0186
C49-H50...N99	2.4236	0.0104	0.0330	0.0074	-0.0065	0.0009	-1.5756	0.0191
N99...H74-C73	2.7612	0.0057	0.0187	0.0039	-0.0030	0.0008	-0.5386	0.0113
C107-H108...N7	2.4410	0.0102	0.0326	0.0072	-0.0063	0.0009	-1.5269	0.0186
N39...H110-C109	2.4243	0.0104	0.0329	0.0073	-0.0065	0.0009	-1.5729	0.0191

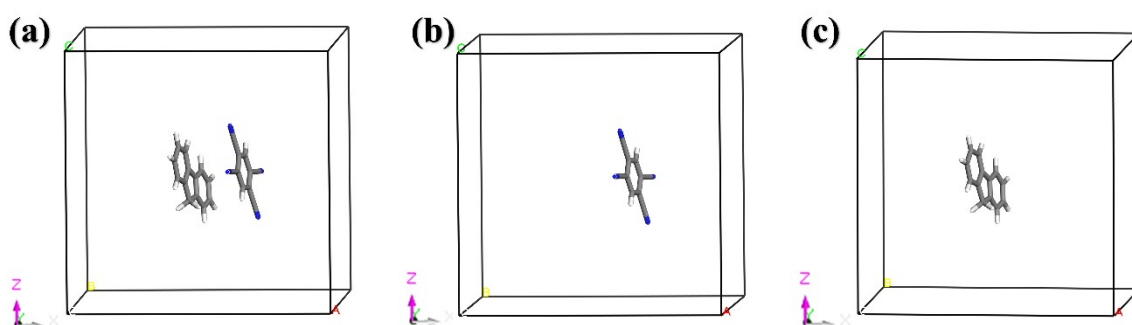


Figure S1. Binding energy calculation model of (a) TCNB-FR, (b) TCNB, (c) FR.

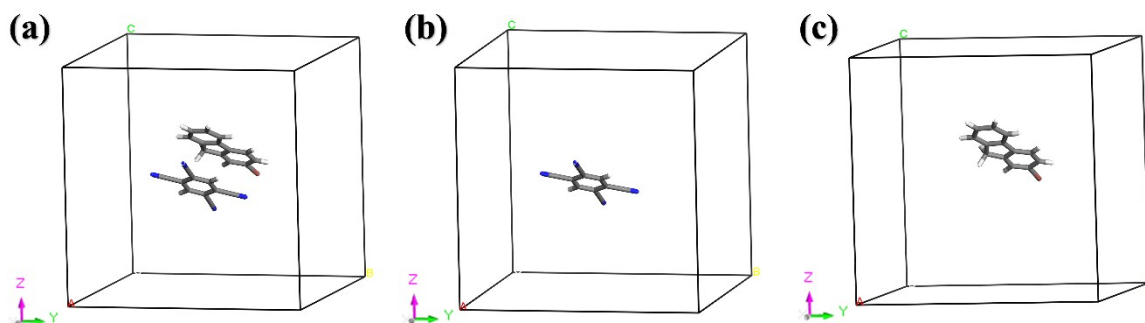


Figure S2. Binding energy calculation model of (a) TCNB-2-BrFR, (b) TCNB, (c) 2-BrFR.

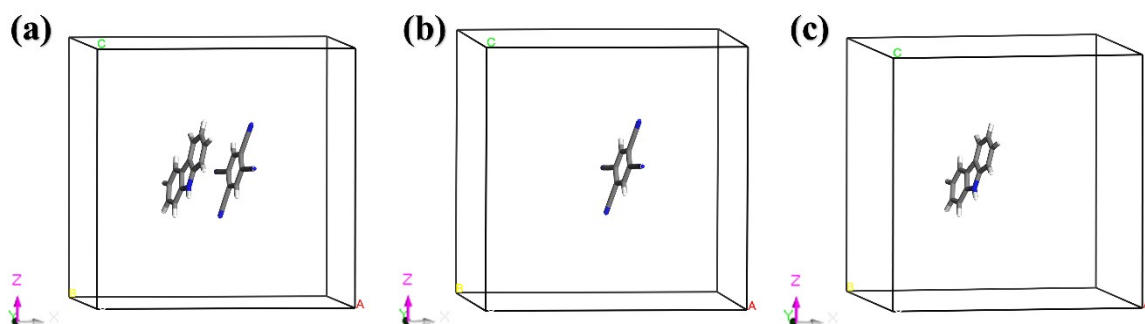


Figure S3. Binding energy calculation model of (a) TCNB-CZ, (b) TCNB, (c) CZ.

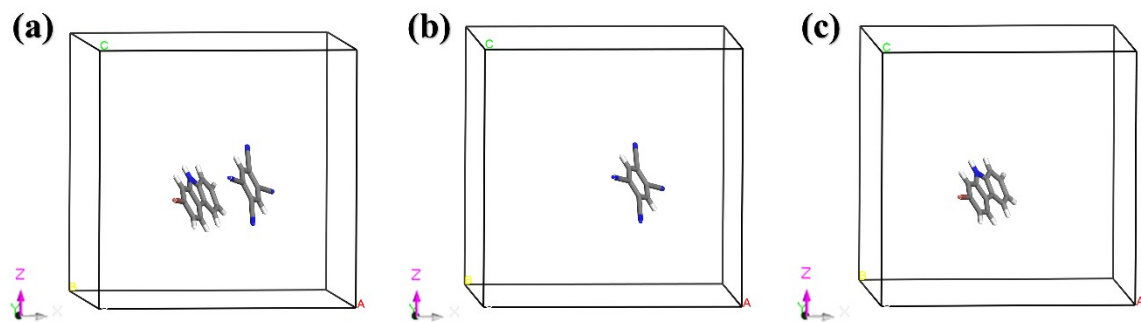


Figure S4. Binding energy calculation model of (a) TCNB-2-BrCZ, (b) TCNB, (c) 2-BrCZ.

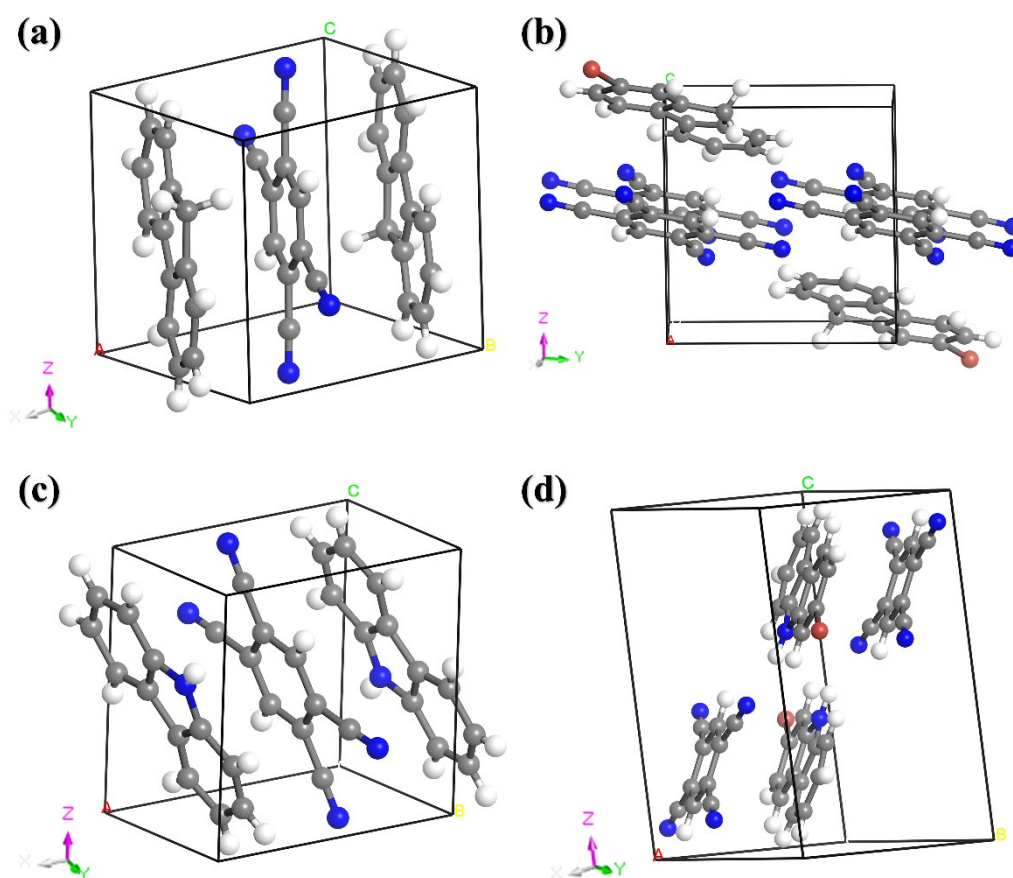


Figure S5. Unit cell of cocrystals (a) TCNB-FR, (b) TCNB-2-BrFR, (c) TCNB-CZ, (d) TCNB-2-BrCZ.

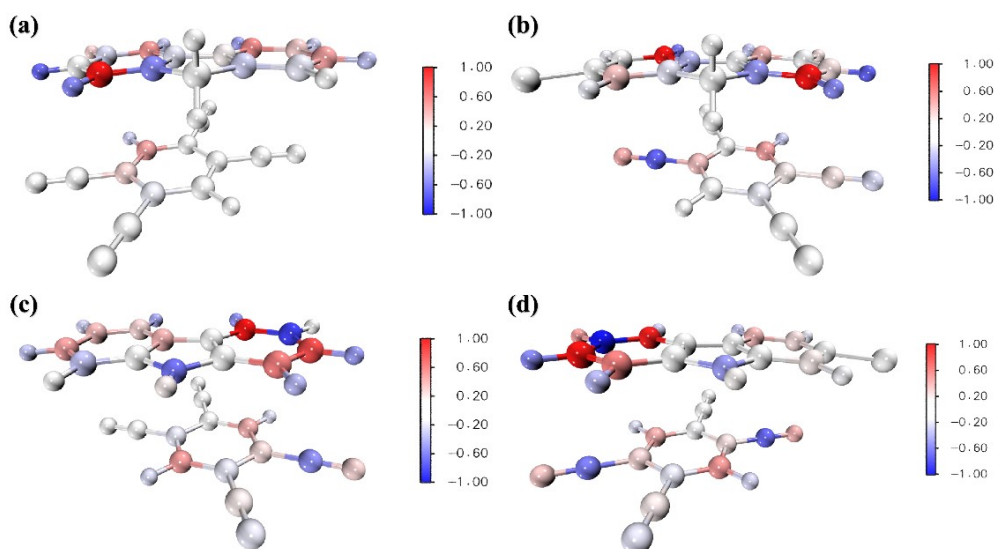


Figure S6. Dimer charge difference distribution of the cocrystals.

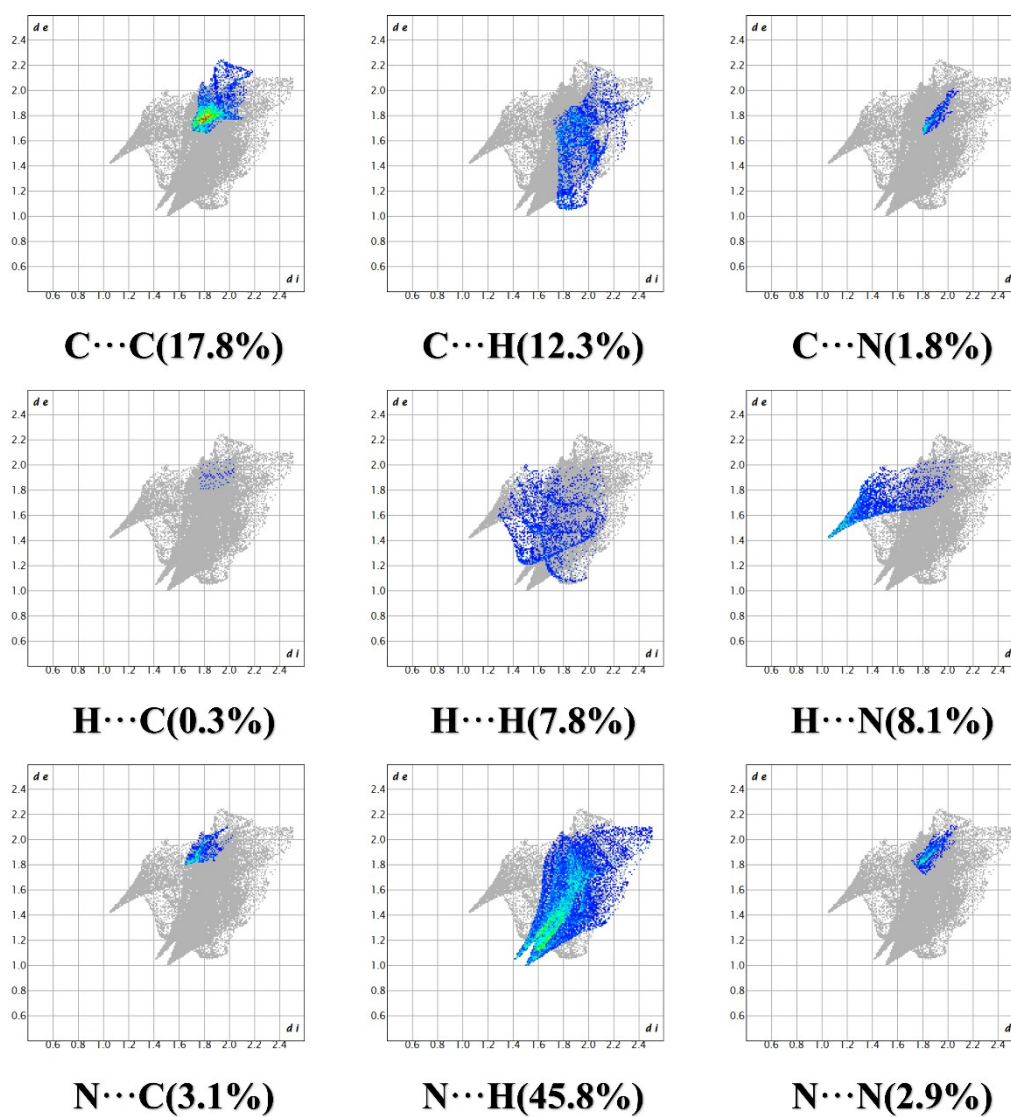


Figure S7. 2D fingerprint distribution and interaction proportion of TCNB-FR.

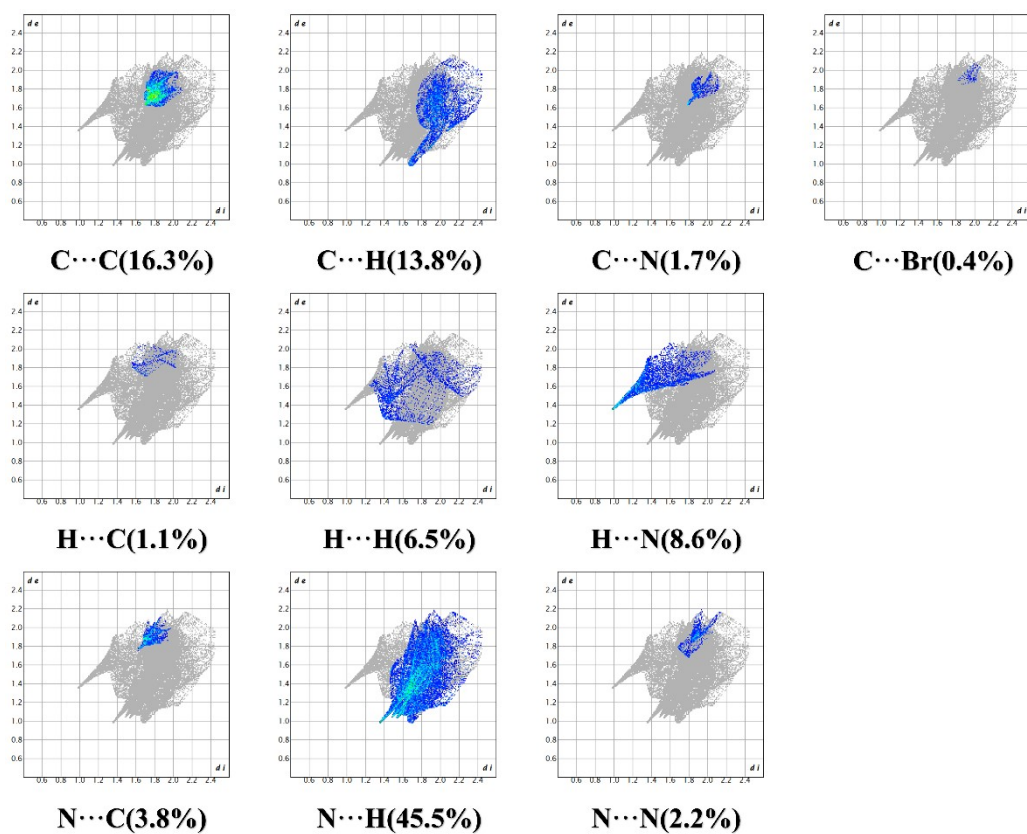


Figure S8. 2D fingerprint distribution and interaction proportion of TCNB-2-BrFR.

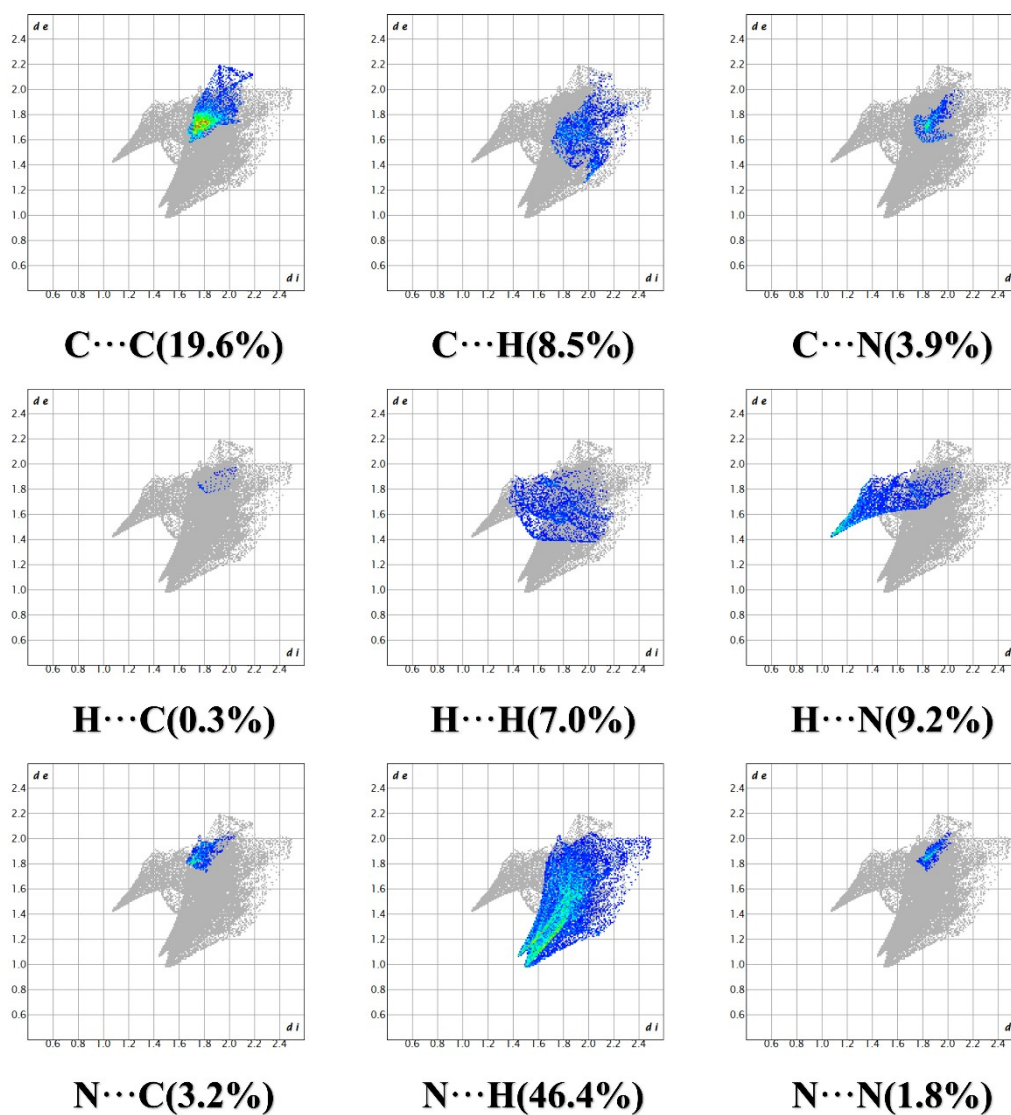


Figure S9. 2D fingerprint distribution and interaction proportion of TCNB-CZ.

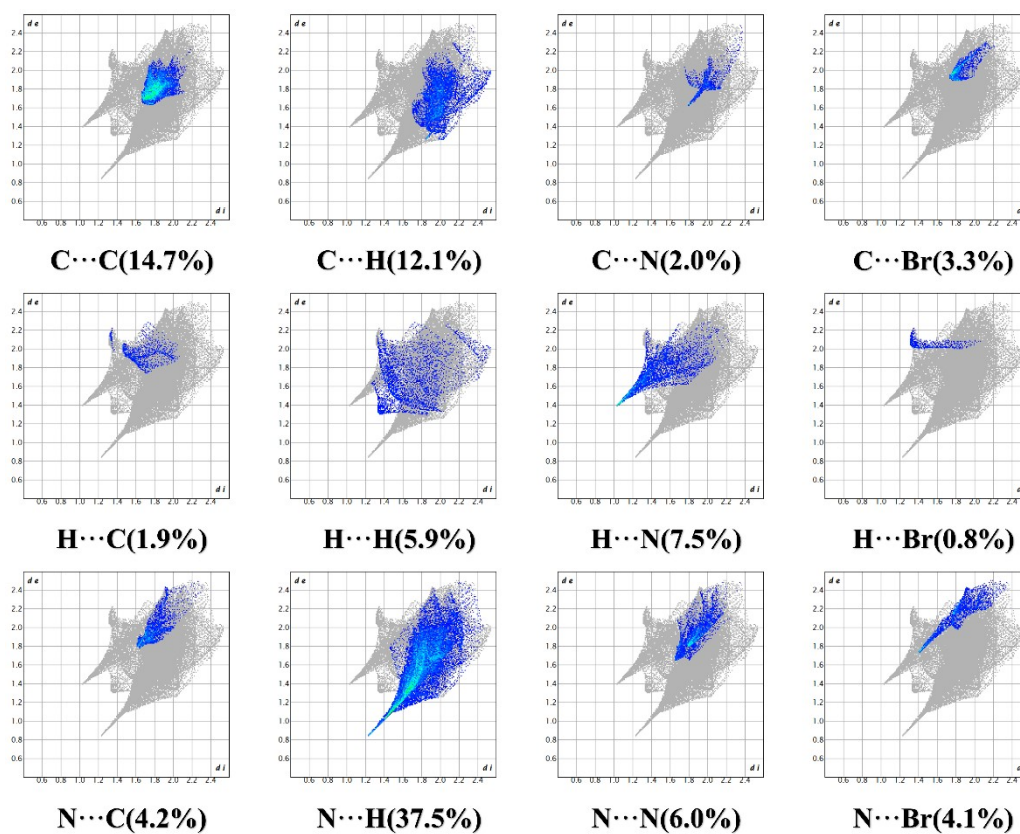


Figure S10. 2D fingerprint distribution and interaction proportion of TCNB-2-BrCZ.

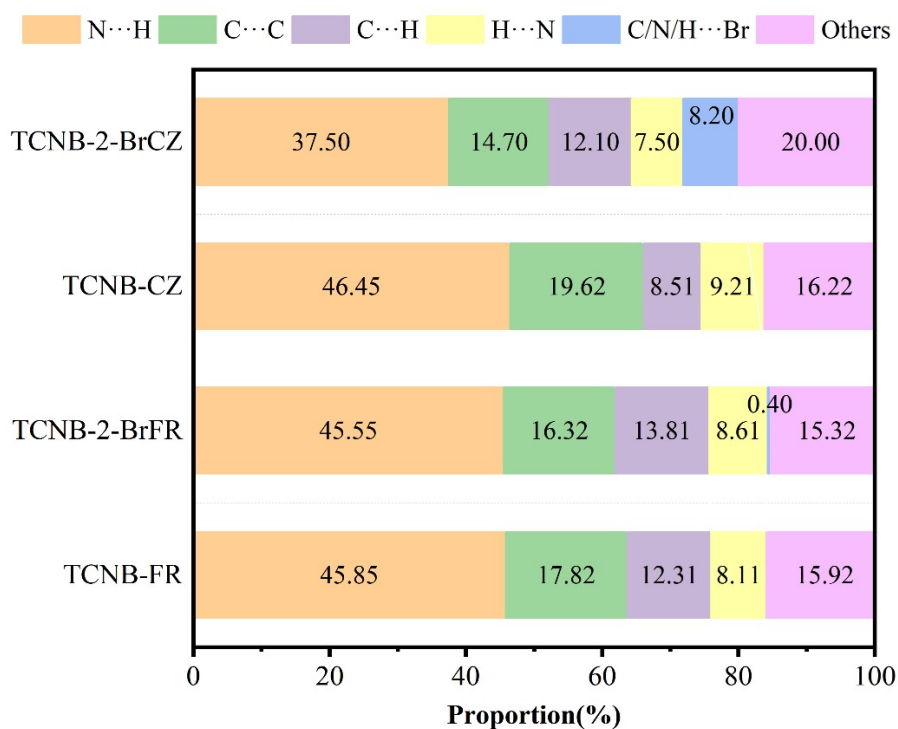


Figure S11. Contributions of various intermolecular contacts in the cocrystals to the Hirshfeld surface.

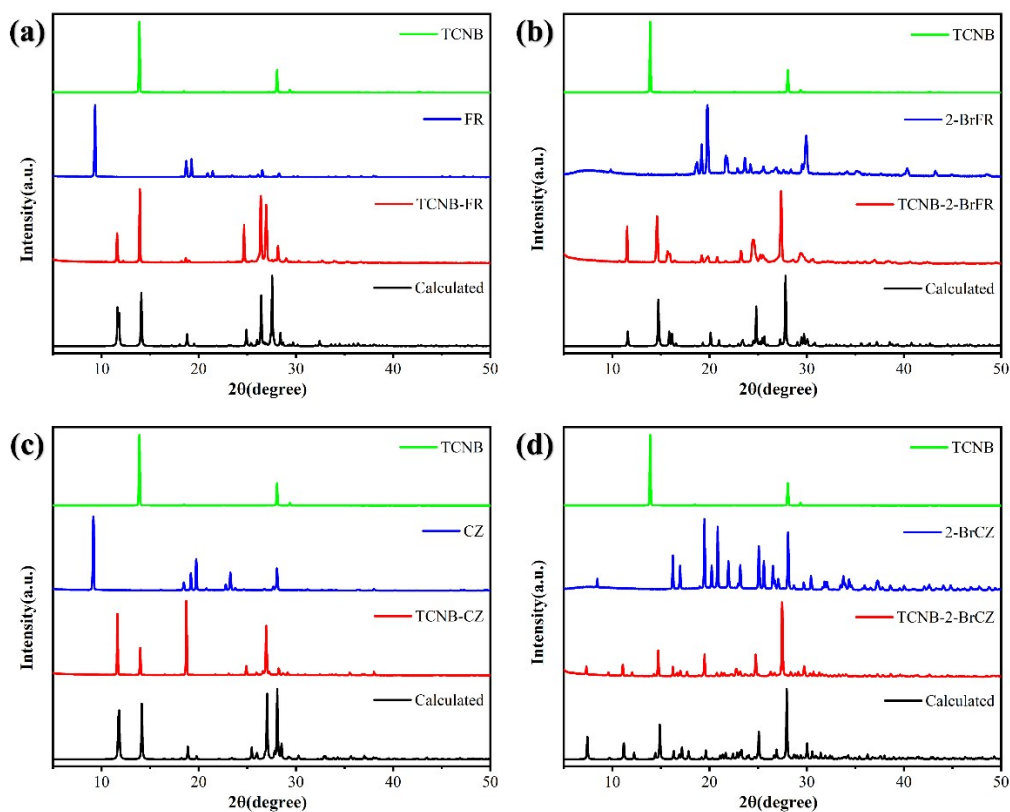


Figure S12. PXRD images of (a) TCNB, FR, TCNB-FR, calculated, (b) TCNB, 2-BrFR, TCNB-2-BrFR, calculated, (c) TCNB, CZ, TCNB-CZ, calculated, (d) TCNB, 2-BrCZ, TCNB-2-BrCZ, calculated.

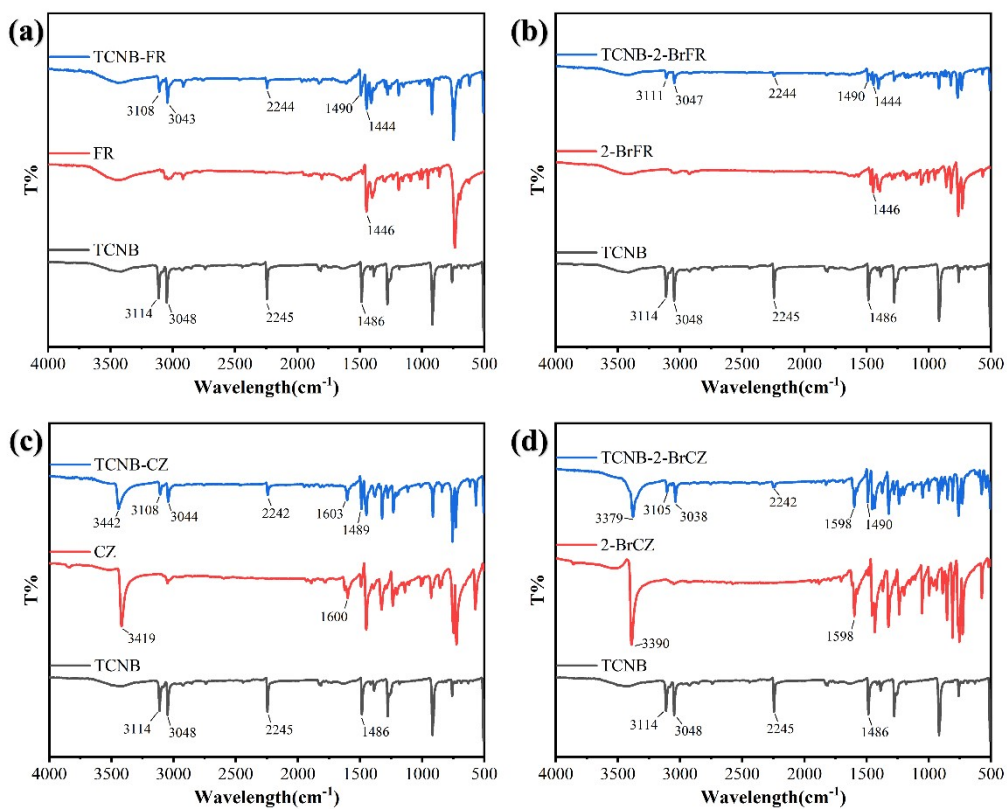


Figure S13. IR spectra of (a) TCNB, FR, TCNB-FR, (b) TCNB, 2-BrFR, TCNB-2-BrFR, (c) TCNB, CZ, TCNB-CZ, (d) TCNB, 2-BrCZ, TCNB-2-BrCZ.

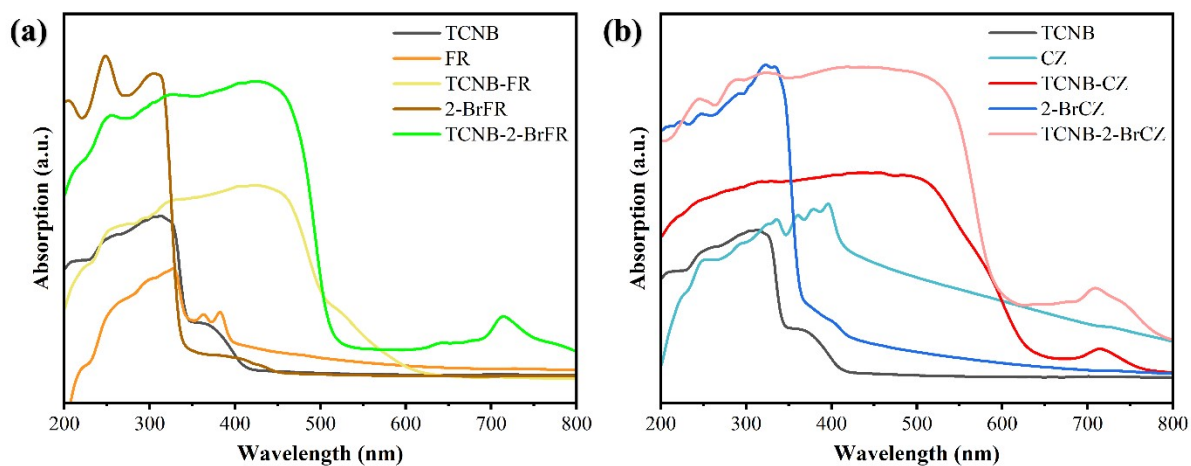


Figure S14. Solid-state absorption spectra of (a) TCNB, FR, TCNB-FR, 2-BrFR, TCNB-2-BrFR, (b) TCNB, CZ, TCNB-CZ, 2-BrCZ, TCNB-2-BrCZ.

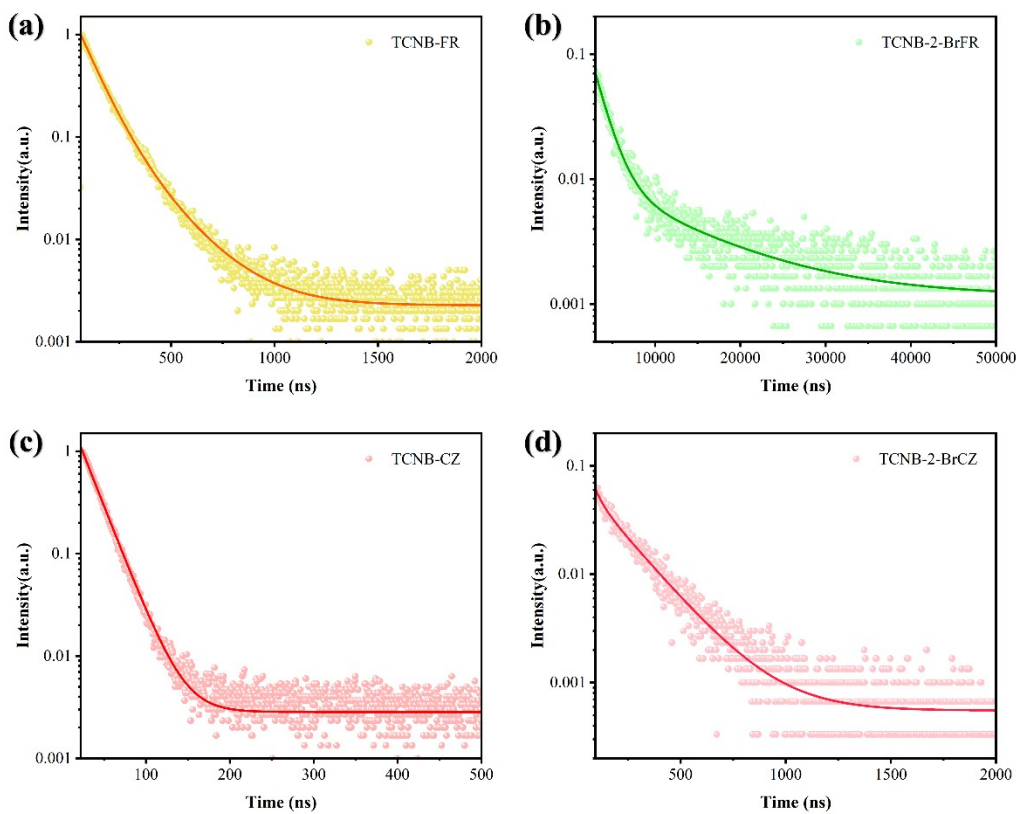


Figure S15. Fluorescence decay curves of cocystals (a) TCNB-FR, (b) TCNB-2-BrFR, (c) TCNB-CZ, (d) TCNB-2-BrCZ.