

**Three-dimensional supramolecular network structure
cooperative hydrogen bond and π - π interaction:
synthesis, structure, and the fluorescence detection of
balsalazide disodium**

Chen Wang^a, Zi Xin You^a, Yong-Heng Xing^{a*}, Feng-Ying Bai^a, Zhan Shi^b

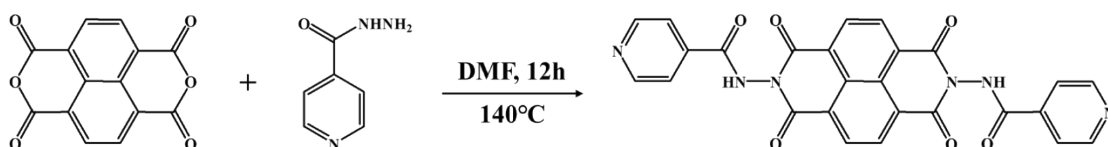
^a *College of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, P. R. China*

^b *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China*

E-mail: xingyongheng2000@163.com (Yong-Heng Xing);

Materials and methods: The elemental analyses were carried out on a Perkin-Elmer 240C automatic analyzer. Infrared spectra were measured on a Bruker AXSTENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 400-4000 cm^{-1} at room temperature. UV-vis spectra were recorded on JASCOV-570 spectrometer (200-2500 nm, in form of solid sample) and Lambda 35 UV/VIS Spectrometer (200-800 nm, in form of liquid sample). X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu $K\alpha$ radiation, in the range $5^\circ <2\theta < 50^\circ$, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step. Thermogravimetric analysis (TG) was performed on a Perkin Elmer Diamond TG/DTA under the conditions of the N_2 atmosphere in the temperature range from 30 to 800 $^\circ\text{C}$. The photoluminescent spectra of the coordination polymers were measured on a HORIBA Fluoromax-4-TCSPC spectrofluorometer equipped with Spectra LED Pulsed LED sources at room temperature (200-1000 nm). The ^1H -NMR spectra were measured on Nuclear Magnetic Resonance Spectrometer (Bruker Avance II 400).

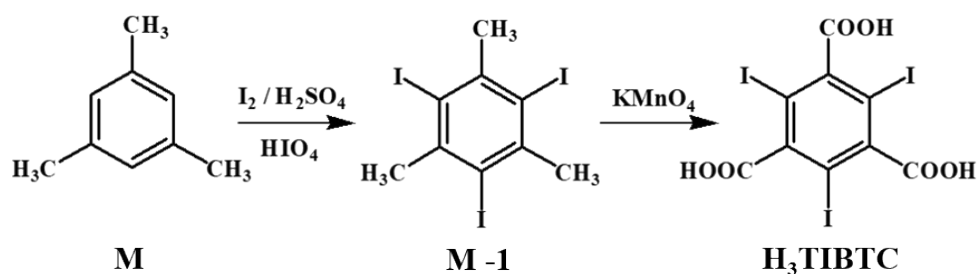
Synthesis of NDI-A: The NDI-A was successfully composed according to the previous literature^[1]. IR (KBr, cm^{-1}): 3492, 3159, 1693, 1595, 1409, 1306, 1244, 1198, 919, 846, 751. ^1H NMR (400 MHz, DMSO- d_6) δ 11.93 (d, $J = 15.9$ Hz, 2H), 8.89 (dt, $J = 4.5$ Hz, 4H), 8.86 (d, $J = 1.7$ Hz, 4H), 7.95 (m, 4H).



Scheme S1: Synthesis of ligand NDI-A

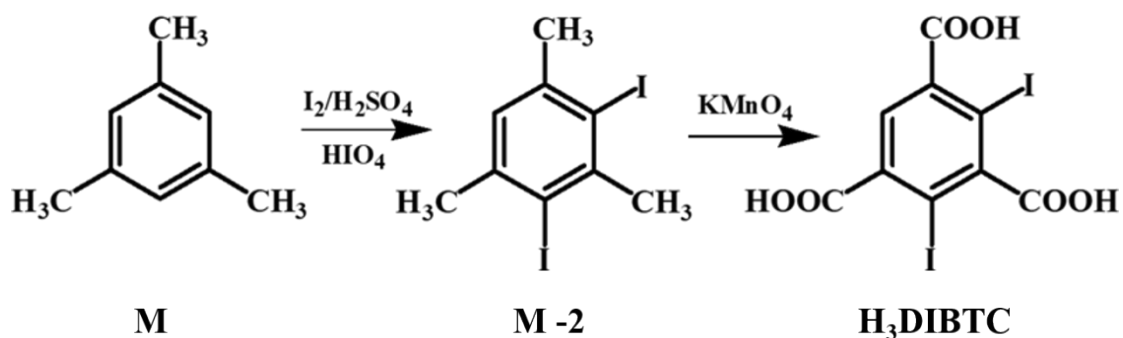
Synthesis of H_3TIBTC : Based on the reported literature^[2], we have improved the synthesis of H_3TIBTC . **2,4,6-triiodo-1,3,5-trimethylbenzene (M -1):** Combine 1,3,5-trimethylbenzene (M) (12.0 g), iodine (38.8 g), $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ (14.0 g), CH_3COOH (100 mL) and deionized water (20 mL) were added to the three-necked flask. After stirring for a while, 3 mL of concentrated H_2SO_4 was added dropwise. The mixture was heated to reflux at 90 °C for 10 hours, then filtered with suction and repeatedly washed with deionized water, and finally purified with acetone to obtain 2,4,6-triiodo-1,3,5-trimethylbenzene (M-1). **H_3TIBTC :** Add 5.0 g of 2,4,6-triiodo-1,3,5-trimethylbenzene, 70 mL of pyridine and 25 mL of deionized water to a three-necked flask, and stir until the solid is completely dissolved to obtain milky white liquid. The temperature was then raised to 90 °C and solid KMnO_4 (10.0 g) was added every 1 hour for a total of 6 times. The mixture was heated to reflux for 10-12 hours. After the reaction was completed, it was filtered while hot, the solid in the solution was washed with 35 mL of 5% KOH solution, and then the pyridine was removed by

rotary evaporation. Then, 75 mL of distilled water was added to remove insoluble materials, and the filtrate was adjusted to pH = 1 with concentrated HCl. Finally, it was extracted with 125 mL of ethyl acetate, washed with 20 mL of water, and then rotary evaporation to give 2,4,6-triiodo-1,3,5-trimellitric acid (H_3TIBTC) as a solid. Yield: 86%, m.p. > 280 °C. IR (KBr, cm^{-1}): 3444, 1616, 1501, 1373, 1308, 1160. 1H NMR (M -1) (400 MHz, $CDCl_3$) δ 3.00 (d, $J = 0.9$ Hz, 1H).



Scheme S2: Synthesis of ligand H_3TIBTC

Synthesis of H_3DIBTC : The synthesis route of the H_3DIBTC was similarly to the H_3TIBTC ^[3]. The only difference is that the molar ratio of 1,3,5-trimethylbenzene to iodine is changed from 1:3 to 1:2.5. IR (KBr, cm^{-1}): 3466, 1627, 1518, 1408, 1247, 1153. 1H NMR (Compound M-2) (400 MHz, $CDCl_3$), δ 2.44 (s, 6H), δ 2.94 (s, 3H), δ 7.01 (s, 1H).



Scheme S3: Synthesis of ligand H_3DIBTC

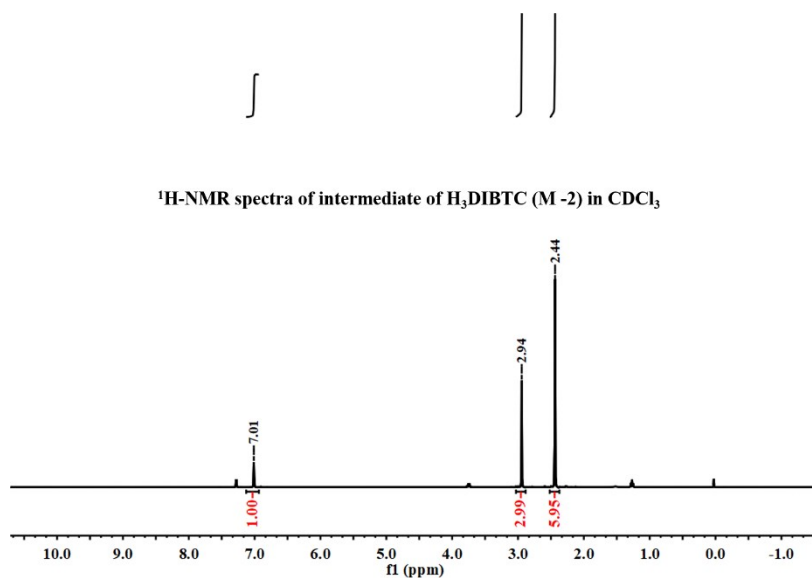
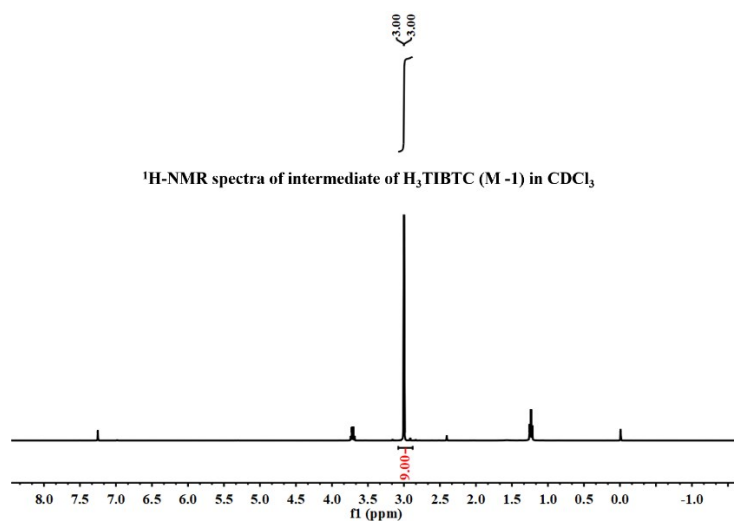
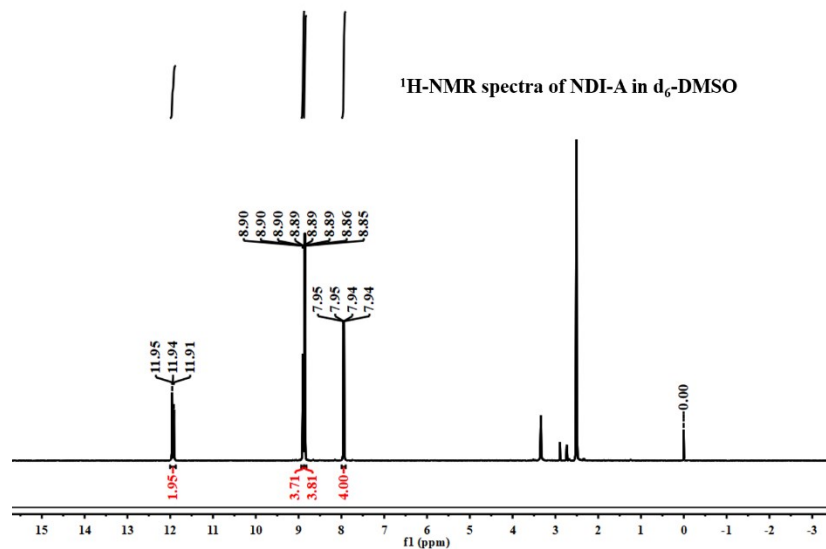


Figure S1 The ¹H-NMR spectra of the ligand NDI-A, intermediate of H₃TIBTC (M -1),
intermediate of H₃DIBTC (M-2)

X-ray crystallographic determination

Suitable single crystals of three co-crystals (**1-3**) were mounted on glass fibers for X-ray structure determination. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All absorption corrections were performed using the SADABS program^[4]. All calculations were performed using the SHELX-97 program^[5, 6] and OLEX-2 program^[7]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropic-ally. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. Structures were checked for additional symmetry using PLATON^[8].

Table S1. Crystallographic data for the co-crystals **1-3***

co-crystals	1	2	3
Formula	C ₃₃ H ₁₉ N ₆ O ₆	C ₁₄ H ₇ I ₃ NO ₆	C ₁₄ H ₈ I ₂ NO ₆
Molecular weight	595.54	665.91	540.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> /Å	10.7535(7)	8.9598(5)	14.811(6)
<i>b</i> /Å	8.9587(6)	21.9155(11)	9.023(4)
<i>c</i> /Å	27.8995(19)	9.5862(5)	24.110(10)
α (°)	90	90	90
β (°)	96.3210(10)	116.7110(10)	106.673(7)
γ (°)	90	90	90
<i>V</i> (nm ³)	2671.4(3)	1681.46(15)	3086(2)
<i>Z</i>	4	4	8
D _{calc} /(g·cm ⁻³)	1.481	2.630	2.324
F(000)	1228	1220	2024
μ (Mo K α)/nm	0.105	5.607	4.106
θ range/(°)	1.469-28.292	1.858-31.113	2.675-28.609

Reflections collected	16538	11463	9783
Independent reflections [$I > 2\sigma(I)$]	6468	4822	3827
Parameters	406	218	209
Goodness of fit	0.995	1.076	1.030
R ^a (R ^b)	0.0578 (0.1367) ^b	0.0341(0.0390) ^b	0.0375(0.0637) ^b
wR ₂ ^a (R ₂ ^b)	0.1396 (0.1774) ^b	0.0843 (0.0866) ^b	0.0800(0.0892) ^b
$\Delta(\rho)$ (e Å ⁻³)	0.31 and -0.52	1.15 and -2.00	1.27 and -0.90

* a. $R = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$; b. $[F_o > 4\sigma(F_o)]$; b. based on all data.

Table S2. Selected bond lengths (Å) and angles (°) for the co-crystals **1-3***

co-crystal 1			
C1-C2	1.419(3)	C12-O3	1.212(3)
C1-C3	1.409(3)	C18-N1	1.324(3)
C5-N3	1.408(3)	N2-N3	1.393(3)
C10-O4	1.397(3)	C16-O6	1.217(3)
C3-C1-C2	119.0(2)	O1-C13-C17	122.3(2)
O6-C16-N5	122.5(2)	O5-C8-N4	119.8(2)
N4-C8-C4	116.0(2)	C32-C27-C28	125.6(13)
N2-N3-C12	116.48(19)	N1-C18-C20	124.0(3)
co-crystal 2			
I3-C5	2.105(4)	O3-C9	1.281(5)
I1-C1	2.103(4)	O2-C8	1.310(5)
I2-C3	2.094(4)	C12-C12 ^{#1}	1.497(8)
C11-C10	1.388(8)	C13-C14	1.378(8)
C4-C5-I3	118.5(3)	C13-C12-C12 ^{#1}	120.9(6)
C2-C1-I1	118.9(3)	C4-C3-I2	119.4
O6-C7-O5	125.4(4)	C14-N1-C10	121.7(5)
co-crystal 3			
I1-C4	2.091(4)	I2-C6	2.081(4)
O3-C9	1.240(6)	O4-C9	1.241(5)

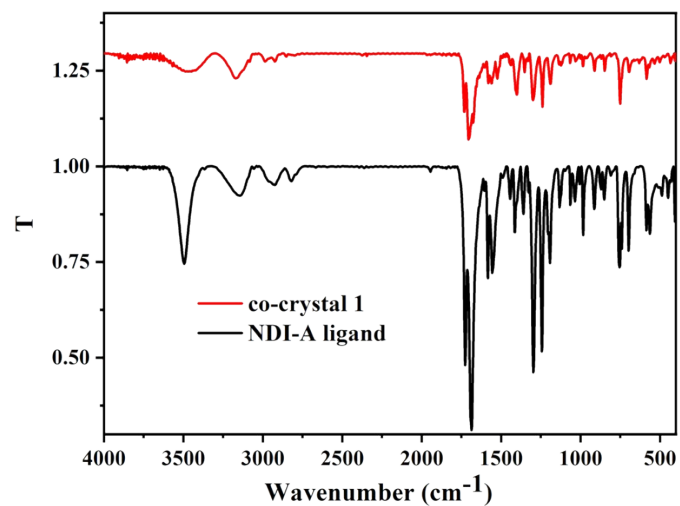
N1-C10	1.313(8)	N1-C14	1.321(8)
C12-C12#1	1.475(9)	C11-C10	1.379(8)
C5-C6-I2	119.7(13)	C1-C6-I2	118.8(3)
C10-N1-C14	120.4(5)	C13-C12-C12#1	122.2(5)
C11-C12-C12#1	120.3(6)	N1-C10-C11	121.1(6)
C3-C4-I1	119.7(3)	O1-C7-C1	114.1(4)

*co-crystal **2**: #1: $x+1/2, -y+3/2, z+1/2$. co-crystal **3**: #1: $x+1/2, y-1/2, z$.

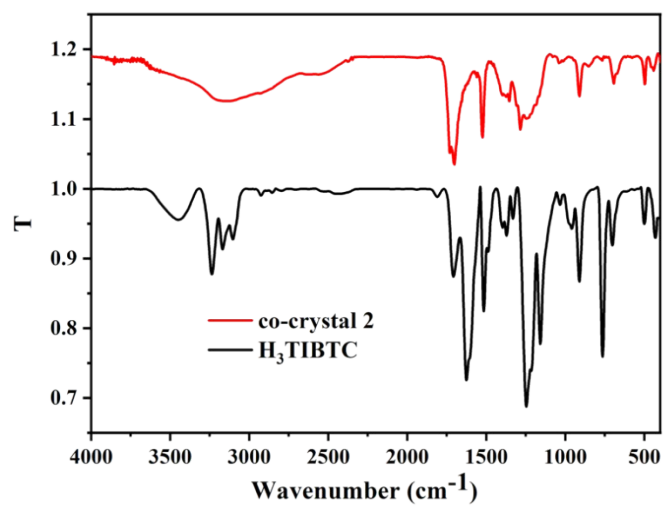
Table S3. Hydrogen bond lengths (Å) and angles (°) for the co-crystals **1-3***

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
co-crystal 1				
N5-H5...O1#1	0.86	2.08	2.836(3)	146.8
N2-H2...N1#2	0.86	2.10	2.941(3)	164.8
C21-H21...N6#3	0.93	2.50	3.399(4)	162.1
C33-H33B...O2#4	0.97	2.49	3.427(6)	163.4
C7-H7...O5#5	0.93	2.57	3.199(3)	125.3
co-crystal 2				
O2-H2...O3#1	0.82	1.75	2.524(4)	156.4
co-crystal 3				
O5-H5...O4#1	0.82	1.70	2.514(5)	175.2
C14-H14...O6#2	0.93	2.36	3.288(7)	174.6

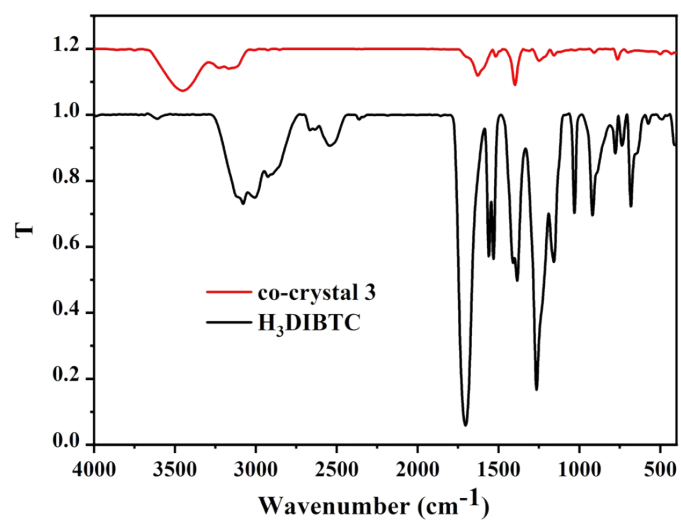
*co-crystal **1**: #1: $-x+1, -y+2, -z$; #2: $-x+2, y-1/2, -z+1/2$; #3: $-x+1, y+1/2, -z-1/2$; #4: $-x+2, -y+2, -z$; #5: $x, y+1, z$. co-crystal **2**: #1: $x+1/2, -y+3/2, z+1/2$. co-crystal **3**: #1: $x+1/2, y-1/2, z$; #2: $-x+2, y, -z+1/2$.



(a)



(b)

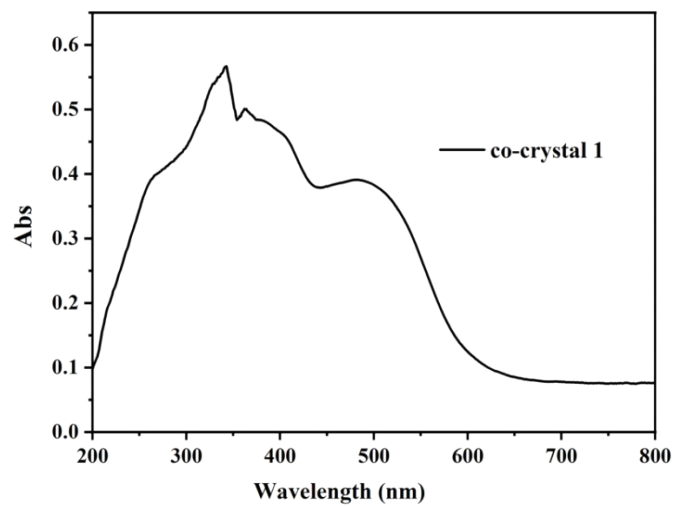


(c)

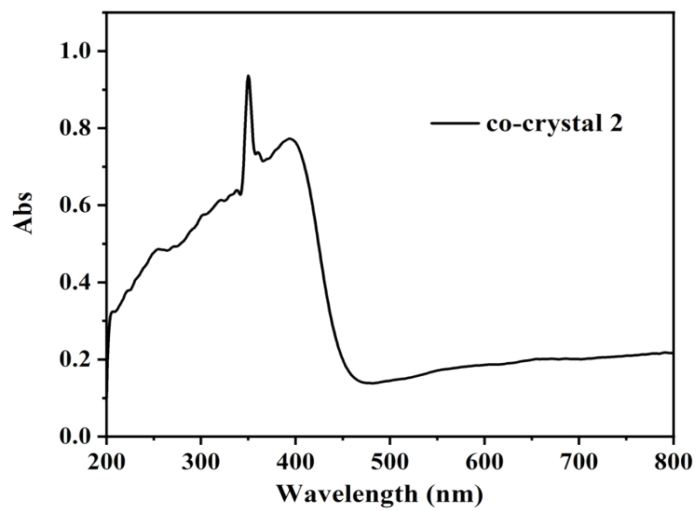
Figure S2 The FT-IR spectra of the moieties and the co-crystal 1-3

Table S4. Detailed attribution of IR data of the starting compounds and co-crystal **1-3** (cm⁻¹)

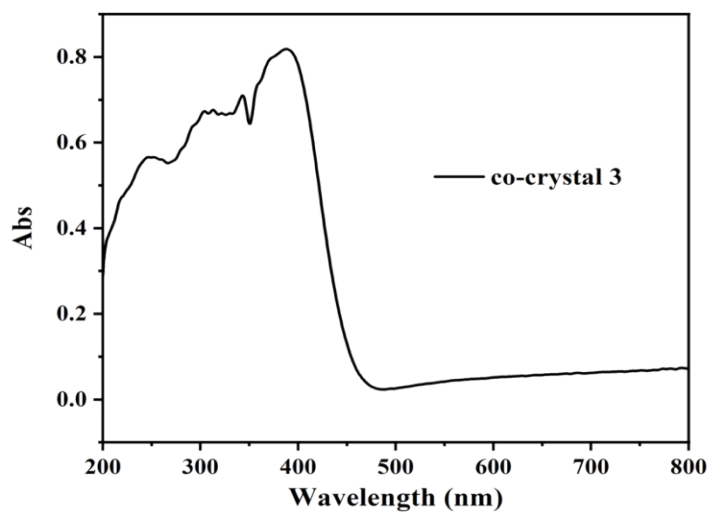
	NDI-A	H ₃ TIBTC	H ₃ DIBTC	co-crystal 1	co-crystal 2	co-crystal 3
$\nu_{\text{N-H}}$	3496	-	-	3473	-	-
$\nu_{\text{Ar-H}}$	3144	-	3126	3170	3168	3104
$\nu_{\text{C=O}}$	1687, 1413	1692, 1405	1683, 1403	1703, 1400	1616, 1385	1627, 1408
$\nu_{\text{C=N}}$	1580	-	-	1576	1520	1521
$\nu_{\text{C=C}}$	1306	1307	1244	1302	1288	1247
$\nu_{\text{C-C}}$	1237	1201	1137	1243	1136	1153
$\nu_{\text{C-N}}$	1189	-	-	1195	-	-
$\delta_{\text{Ar-H}}$	915, 846, 758	-	-	921, 852, 755	960, 910, 766	905, 858, 763



(a)



(b)

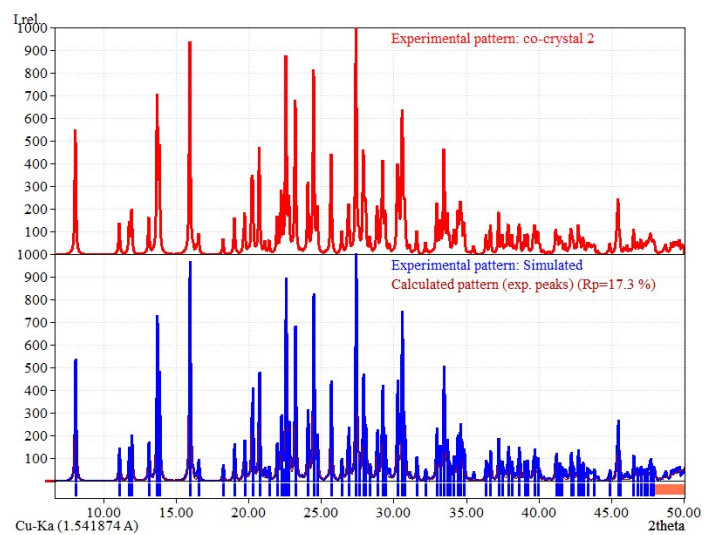
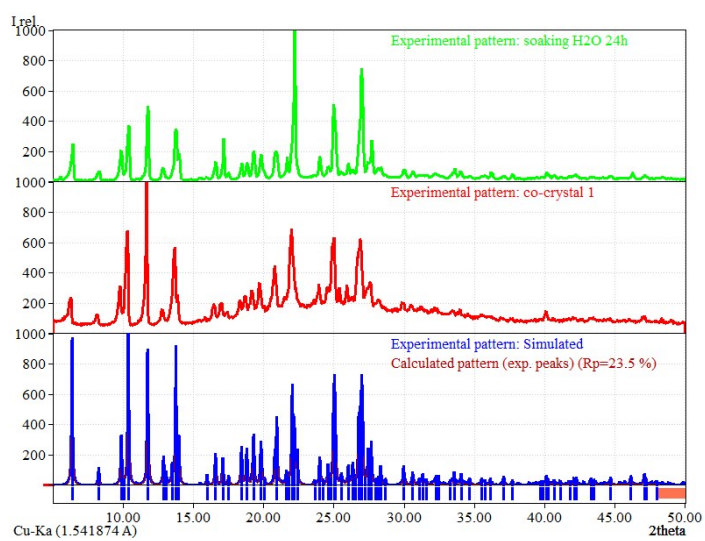


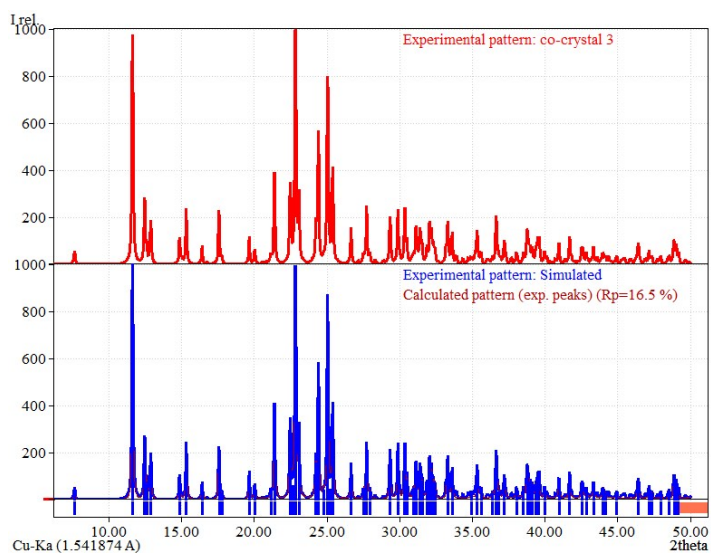
(c)

Figure S3 The solid UV-Vis spectra of the co-crystal 1-3

Table S5 UV-vis spectra identifications of co-crystal compounds **1-3**

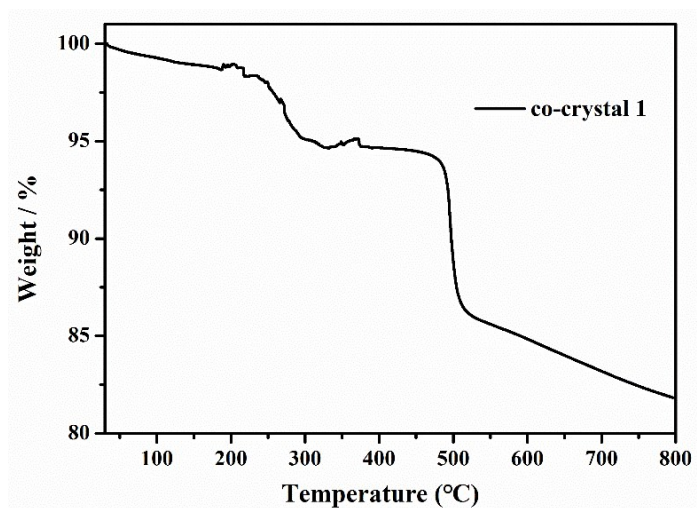
co-crystal	LLCT		Intramolecular charge transfer
	π - π^*	n- π^*	
1	342	362	486
2	256	315	395
3	248	307	395



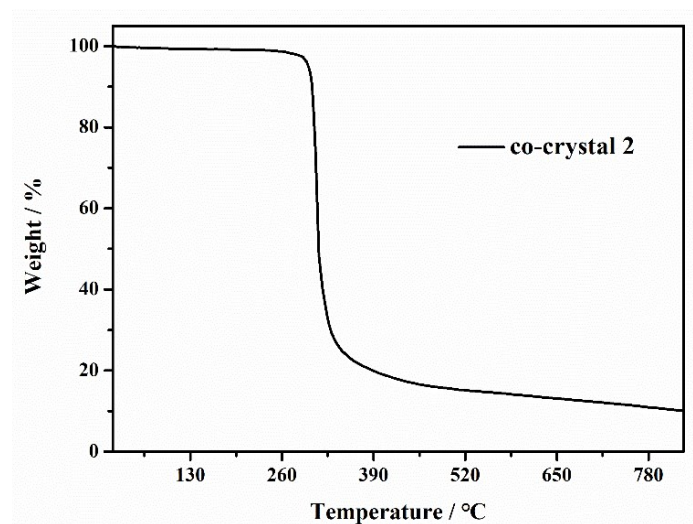


(c)

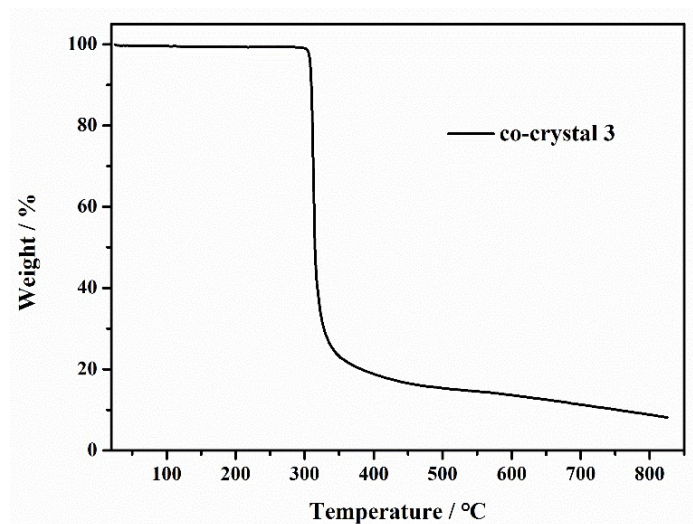
Figure S4 The PXR D patterns of the co-crystal 1-3



(a)



(b)



(c)

Figure S5 The TG curves of the co-crystal 1-3

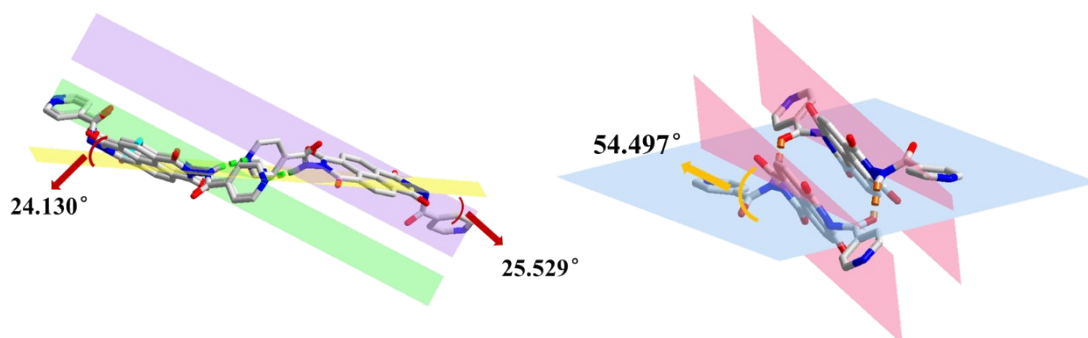


Figure S6 The angles of the planes of the NDI-A moieties in co-crystal **1** (yellow, blue: the plane constructed by hydrogen bond ring; green, purple, pink: the plane constructed by NDI-A moieties)

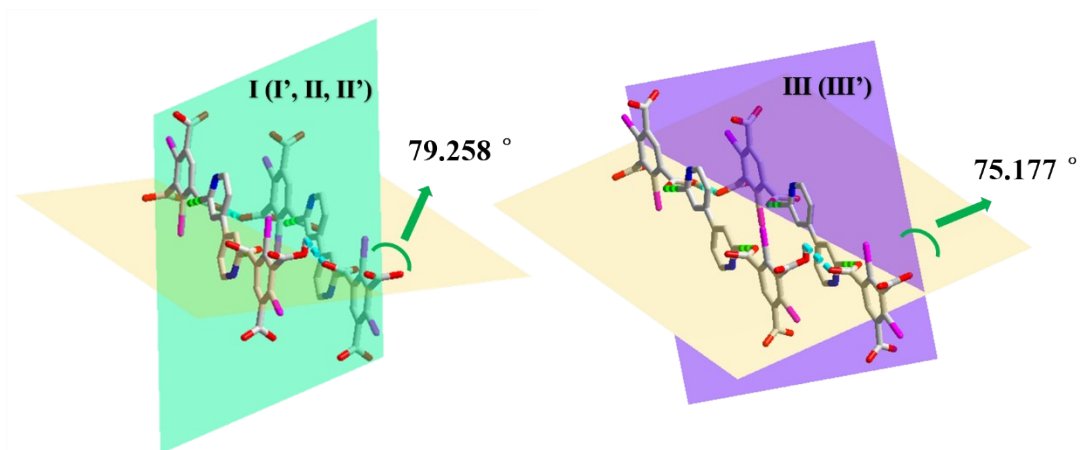


Figure S7 The angles of the planes of the H₃DIBTC and 4,4-bipy moieties in co-crystal **3** (yellow: the plane constructed by hydrogen bond ring; green: the I , I ' , II , II ' plane; purple: the III , III ' plane)

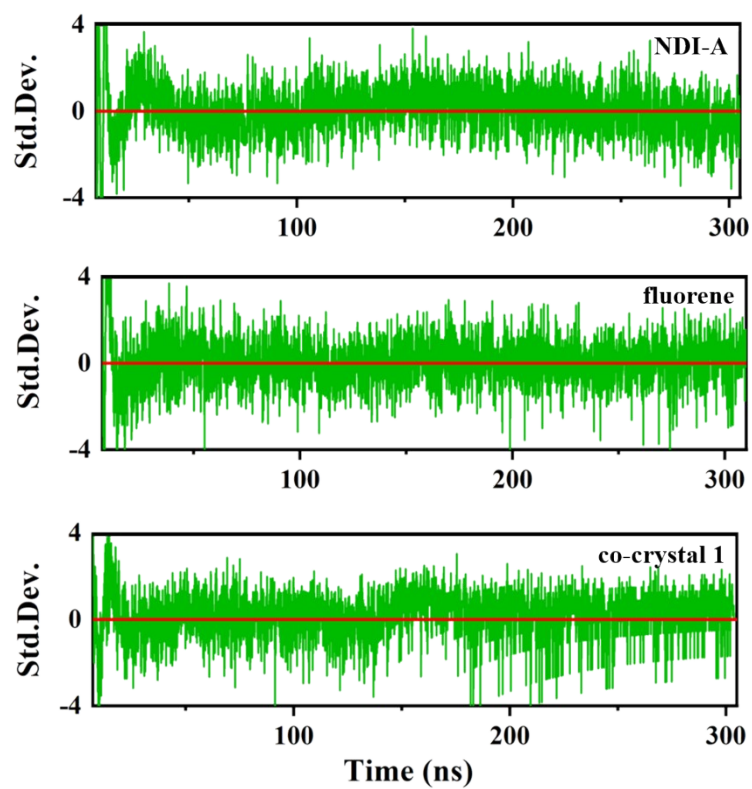


Figure S8 The residuals of the fits of the luminescence decay traces of NDI-A, fluorene, and co-crystal **1**

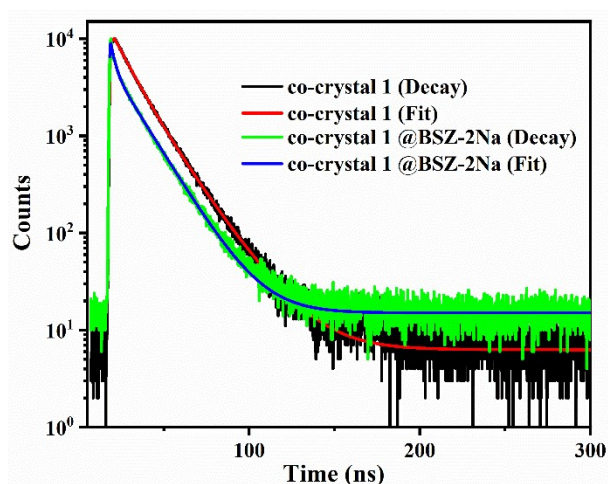


Figure S9 Comparison of the liquid fluorescence lifetime of co-crystal **1** before and after adding balsalazide disodium

References

- [1] S. Bhattacharjee, B. Maitia and S. Bhattacharya, *Nanoscale*, 2016, **8**, 11224-11233.
- [2] B. Wang, X. L. Lv, D. W. Feng, L. H. Xie, J. Zhang, M. Li, Y. B. Xie, J. R. Li and H. C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204–6216.
- [3] C. H. Liu, Q. L. Guan, X. D. Yang, F. Y. Bai, L. X. Sun and Y. H. Xing, *Inorg. Chem.*, 2020, **59**, 8081–8098.
- [4] G. M. Sheldrick, *Acta Crystallogr A.*, 2008, **64**, 112–122.
- [5] G. M. Sheldrick, *University of Göttingen, Göttingen*, 1996.
- [6] G. M. Sheldrick, *University of Göttingen, Göttingen*, 1997.
- [7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr.*, 2009, **42**, 339-341.
- [8] A.L. Spek, *J Appl Crystallogr.*, 2003, **36**, 7–13.