

## The phosphorescent cocrystals of 1,4-diiodotetrafluorobenzene and bent 3-ring-N-heterocyclic hydrocarbons by C-I $\cdots$ N and C-I $\cdots$ $\pi$ halogen bonds

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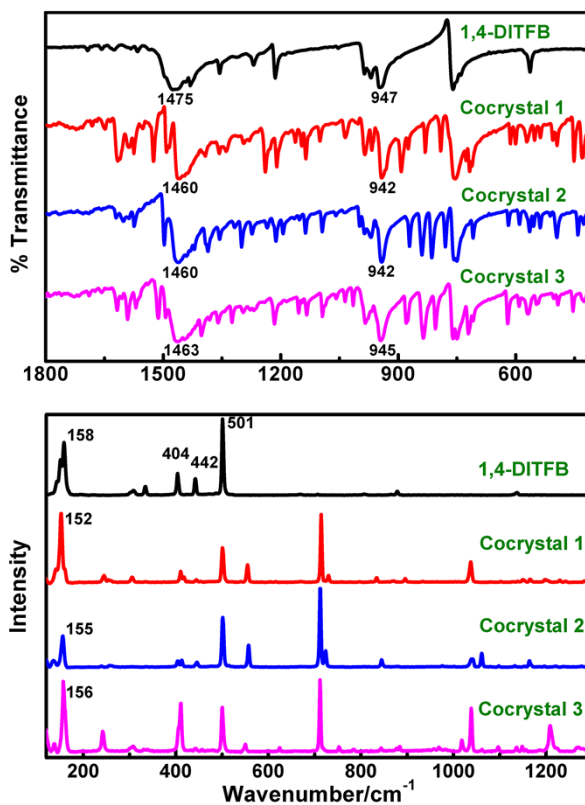
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**Table S1.** The main bonding properties and geometrical parameters of cocrystals.

Cocrystals	Interactions	$d/(\text{\AA})$		$\theta/^\circ$
<b>1</b>	C1-I1 $\cdots$ N1	2.858(3)	-19.0%	169.68(11)
<b>2</b>	C1-I1 $\cdots$ N2	2.975(8)	-15.7%	171.6(3)
	C10-I4 $\cdots$ N1	2.971(8)	-15.8%	171.7(3)
	C4-I2 $\cdots$ I3	3.7858(9)	-4.4%	166.3(2)
	C7-I3 $\cdots$ $\pi$ (C31)	3.628(11)	-5.3%	171.4(4)
	C1-C37	3.500(13)	-5.4%	4.1 $^\phi$
	C2-C38	3.579(14)	-3.3%	
	C3-C35	3.559(12)	-3.8%	
	C12-C22	3.524(11)	-4.8%	6.2 $^\phi$
	C10-C24	3.504(12)	-5.3%	
<b>3</b>	C7-I3 $\cdots$ N1	3.003(1)	-14.9%	177.52(17)
	C1-I1 $\cdots$ $\pi$ (C14)	3.564(6)	-6.9%	162.62(18)
	C1-I1 $\cdots$ $\pi$ (C15)	3.492(6)	-8.8%	174.50(19)
	C4-I2 $\cdots$ $\pi$ (C19)	3.536(6)	-7.6%	167.37(19)
	C4-I2 $\cdots$ $\pi$ (C20)	3.651(6)	-4.7%	168.94(19)

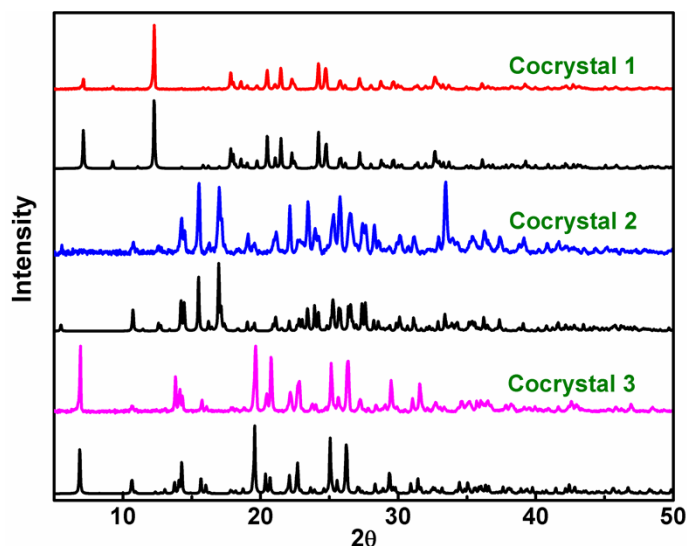
$^\phi$  means the dihedral angle of  $\pi_n$ - $\pi$  or  $\pi$ - $\pi$  interaction.



**Fig. S1** FT-IR (top) and Raman (bottom) spectra of the cocrystals **1-3** and the corresponding 1,4-DITFB.

## PXRD

For confirming the phase purity and homogeneity of the cocrystals, powder X-ray diffraction (PXRD) patterns were obtained at room temperature. As shown in **Fig. S2**, the peak positions of the simulated spectra (black curves) by single crystal structure data are in agreement with the experimental PXRD patterns (color curves), indicating a good phase purity of the bulk crystal products. The few discrepancies in intensity between simulated and experimental values may be the consequence of preferred orientations of the crystal powder samples.



**Fig. S2.** Powder X-ray diffraction patterns of the cocrystals. Experimental patterns (colorful curve) and simulated patterns from single crystal XRD data (black curve).

#### **Differential scanning calorimetry thermogram and thermogravimetric analysis.**

In order to better understand the thermal properties of cocrystals **1-3** as phosphorescent materials, the TGA and DSC analysis were also investigated. As shown in **Fig. S3**, a sharp increase can be observed in the enthalpy relaxation as the cocrystals are heated to a temperature above the glass transition temperature. The areas of the endothermic peaks indicating melting points at  $T_p$  of 149.4 °C (cocrystal **1**), 117.5 °C (cocrystal **2**) and 64.7 °C (cocrystal **3**) in the DSC scans give comparable enthalpies ( $\Delta H$ ) as -102.7, -67.9 and -42.2 J·g<sup>-1</sup>, respectively. The starting decomposed temperature as well as the rate of thermal decomposition of the cocrystals **1-3** can be obtained by TGA curves, they are 148.0 °C/99.4%, 141.0 °C/99.4% and 80.3 °C/99.7%, respectively. And from the TGA curves, it can be noticed that the region is considered as the main decomposition step for these samples. Other relevant data of the cocrystals and raw materials are listed in **Table S2**.

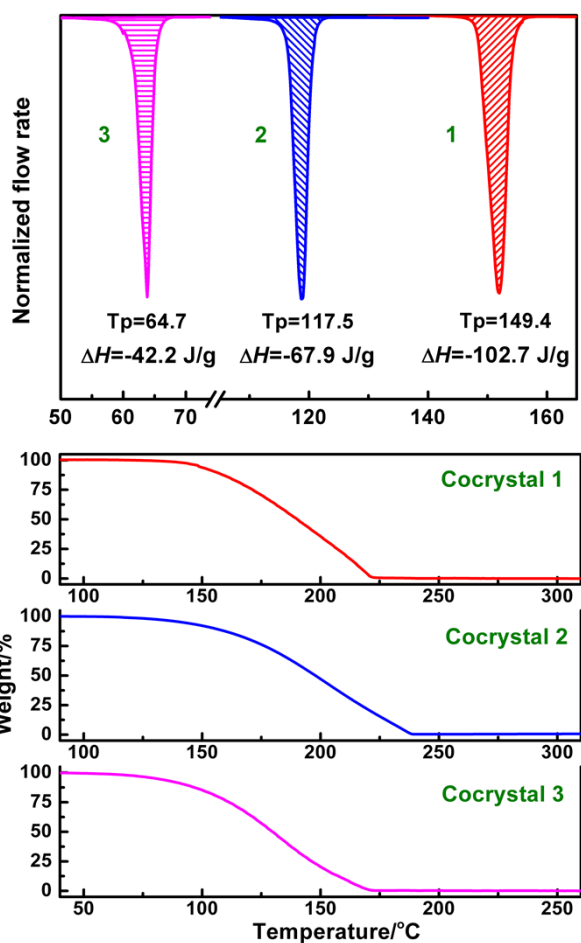


Fig. S3 The DSC (top) and TGA (bottom) curves of the cocrystals 1-3.

Table S2. DSC and TGA results of the cocrystals and their raw materials

	Differential scanning calorimetry (DSC)			Thermogravimetric analysis (TGA)	
	Initial melting temperature ( $T_{onset}$ ) °C	Endothermic peak ( $T_p$ ) °C	Enthalpy ( $\Delta H$ ) J·g <sup>-1</sup>	Initial decomposition temperature ( $T_{in}$ ) °C	Weight loss rate (Wt.) %
1,4-DITFB	106.2	107.3	-45.3	/	/
PHN	107.4	108.3	-125.4	/	/
BfQ	90.7	92.3	-82.4	/	/
BhQ	51.2	52.7	-70.3	/	/
<b>1</b>	147.9	149.4	-102.7	148.0	99.4
<b>2</b>	116.1	117.5	-67.9	141.0	99.4
<b>3</b>	63.2	64.7	-42.2	80.3	99.7