Electronic Supplementary Material (ESI) for CrystEngComm
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Halogen bond cocrystal polymorphs of the 1,4–di(4'–pyridyl)–1,3–diacetylene

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Electronic Supporting Information (ESI†)

Ⅰ Synthesis of 1,4-di(4'-pyridyl)-1,3-diacetylene (DPDA) donor.

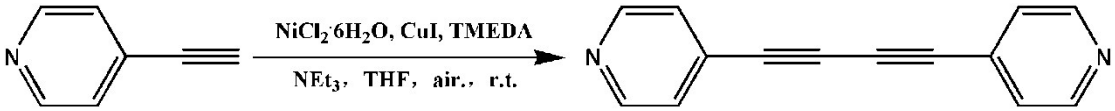
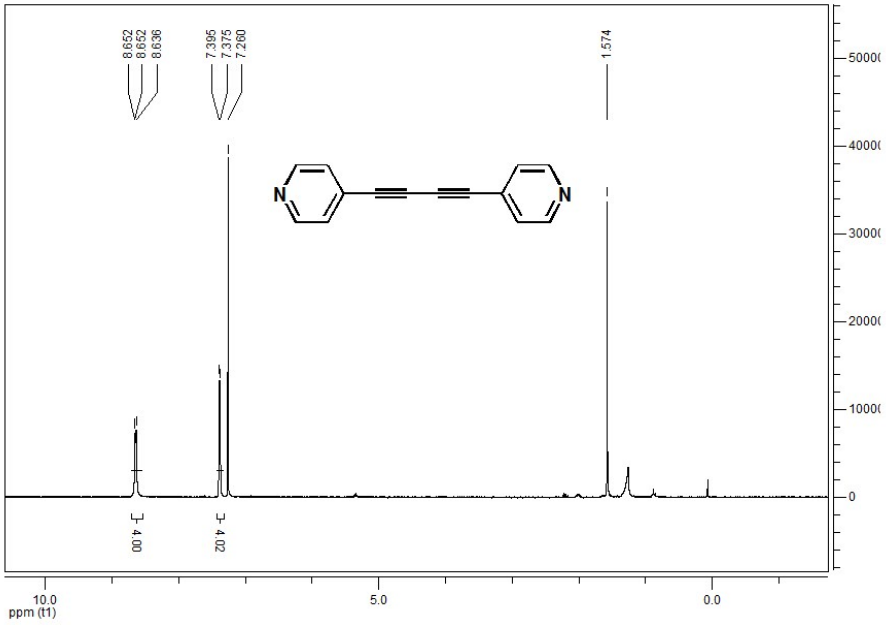


Figure S1. Synthesis of 1,4-di(4'-pyridyl)-1,3-diacetylene (DPDA) donor.

A solution of 4-Ethynylpyridine (CAS registry no. 2510-22-7, 97+%) (206.2426 mg, 2.0 mmol), which was purchased from Ark Pharm Co., $NiCl_2 \cdot 6H_2O$ (23.769mg, 0.05mmol), CuI (19.045mg, 0.05mmol) and TMEDA (0.06 mL,0.2mmol), NEt_3(0.835mL,3mmol) in 7.5 mL of THF was stirred rapidly. After 12 h, the solvent was removed and the solid was extracted with methylene chloride, Then methylene chloride was removed. The product was then recrystallized from ethanol/water to give a yellow solid (80%). It has been verified by ^1H NMR of DPDA is shown below:



Ⅱ Thermodynamic nature of stable DPDA crystal and DPDA–IFB cocrystals.

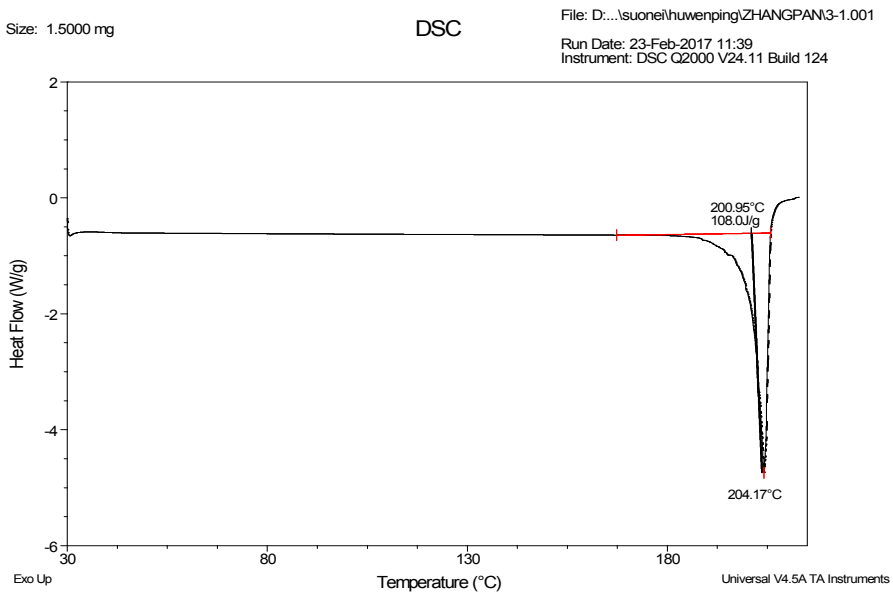


Figure S2. Monotropy of DPDA in DSC recorded at 5 ℃ heating rate.

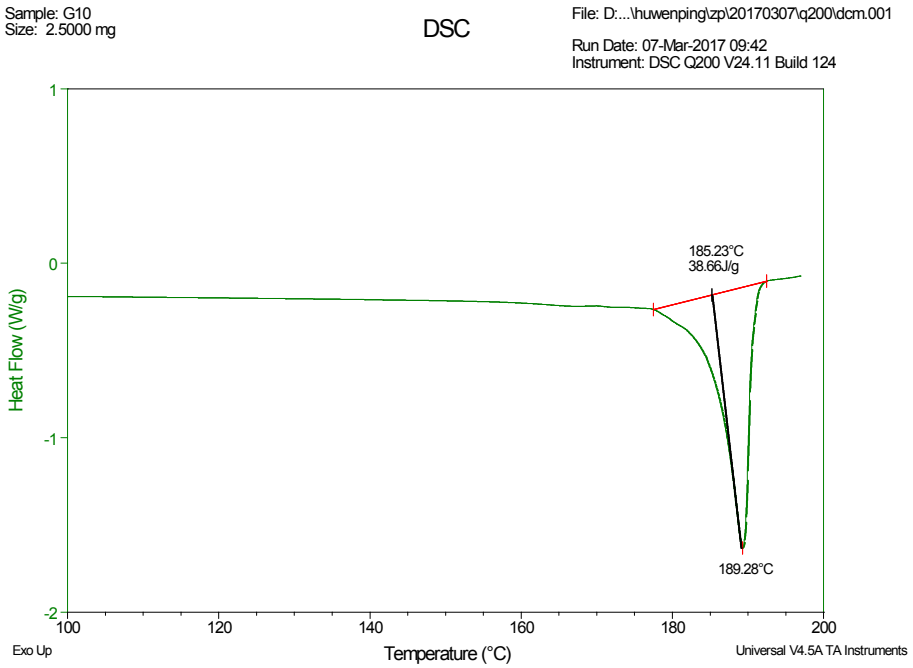


Figure S3. Monotropy of DPDA–IFB–I in DSC recorded at 5 ℃ heating rate.

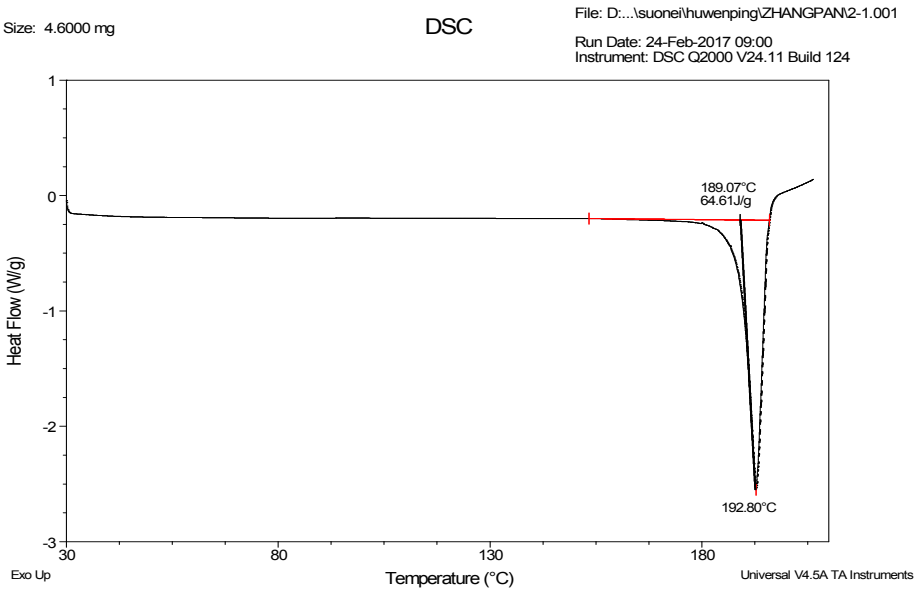


Figure S4. Monotropy of DPDA–IFB–II in DSC recorded at 5 ℃ heating rate.

Ⅲ Co-crystals structure characterization.

Table S1. Crystalgraphic parameters of DPDA–IFB polymorphs.

Identification code	DPDA–IFB–I	DPDA–IFB–II
Empirical Formular	C_{20} H_8 F_3 I_3 N_2	C_{20} H_8 F_3 I_3 N_2

Formula weight	713.98	713.98
Temperature	173.1500 K	173.1500 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 1 21/c 1	P 1 21/n 1
Unit cell dimensions	a = 6.6699(5) Å α= 90°. b = 34.308(3) Å β= 102.639(5)°. c = 9.1378(10) Åγ = 90°.	a = 10.309(2) Å α= 90°. b = 8.9709(18) Å β= 97.88(3)°. c = 22.251(5) Å γ = 90°
Volume	2040.3(3) $Å^3$	2038.4(7) $Å^3$
Z	**4**	**4**
Density (calculated)	2.324 Mg/m^3	2.327 Mg/m^3
Absorption coefficient	4.630 mm^{-1}	4.635 mm^{-1}
F(000)	1312	1312
Crystal size	0.285 x 0.121 x 0.103 mm^3	0.248 x 0.121 x 0.071 mm^3
Theta range for data collection	2.574 to 27.501°.	2.080 to 27.486°.
Index ranges	-8<=h<=8, -44<=k<=44, -11<=l<=10	-13<=h<=13, -11<=k<=11, -28<=l<=28
Reflections collected	14316	14221
Independent reflections	4623 [R(int) = 0.0325]	4621 [R(int) = 0.0379]
Completeness to theta = 26.000°	99.3 %	99.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.68536	1.00000 and 0.40112
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4623 / 0 / 253	4621 / 0 / 253
Goodness-of-fit on F^2	1.201	1.260
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0614	R1 = 0.0413, wR2 = 0.0641
R indices (all data)	R1 = 0.0351, wR2 =	R1 = 0.0462, wR2 =

	0.0630	0.0657
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.625 and -1.006 e.Å^{-3}	0.561 and -0.544 e.Å^{-3}

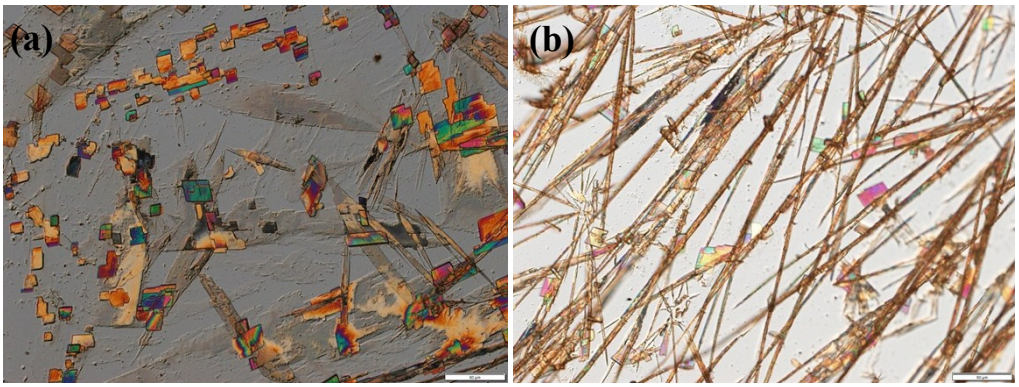
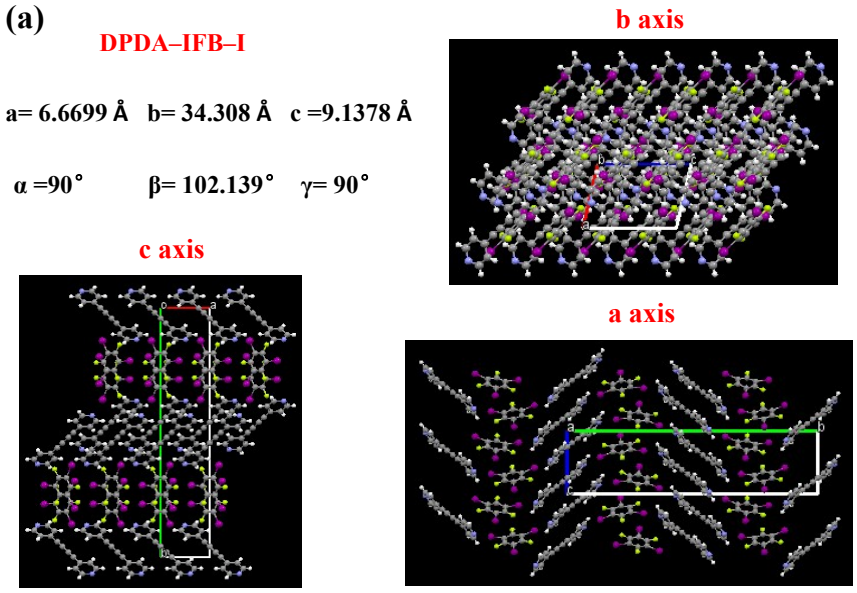


Figure S5. Optical images of (a) DPDA–IFB–I and (b) DPDA–IFB–II obtained by solution drop–casting.



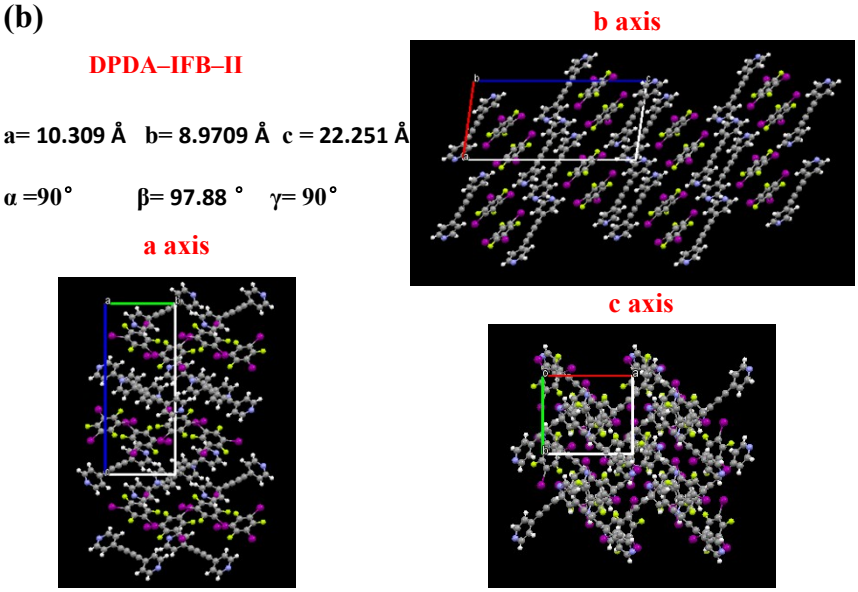


Figure S6. Co-crystals structure of (a) DPDA–IFB–I and (b) DPDA–IFB–II.

References

1 J. G. Rodríguez, C. D. Oliva, *Tetrahedron,* 2009, **65**, 2512-2517.

2 P. M. García, M. Gulcur, D. Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang, A. S. Batsanow, M. R. Bryce, C. Lambert and T. Wandlowski, *J. Am. Chem. Soc*. 2013, **135**, 12228−12240.