Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Multi-stimuli fluorescent responsive of a strongly emissive difluoroboron complex in both solution and solid states

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1 ^{1}H and ^{13}C NMR of target compound TC and its precursor

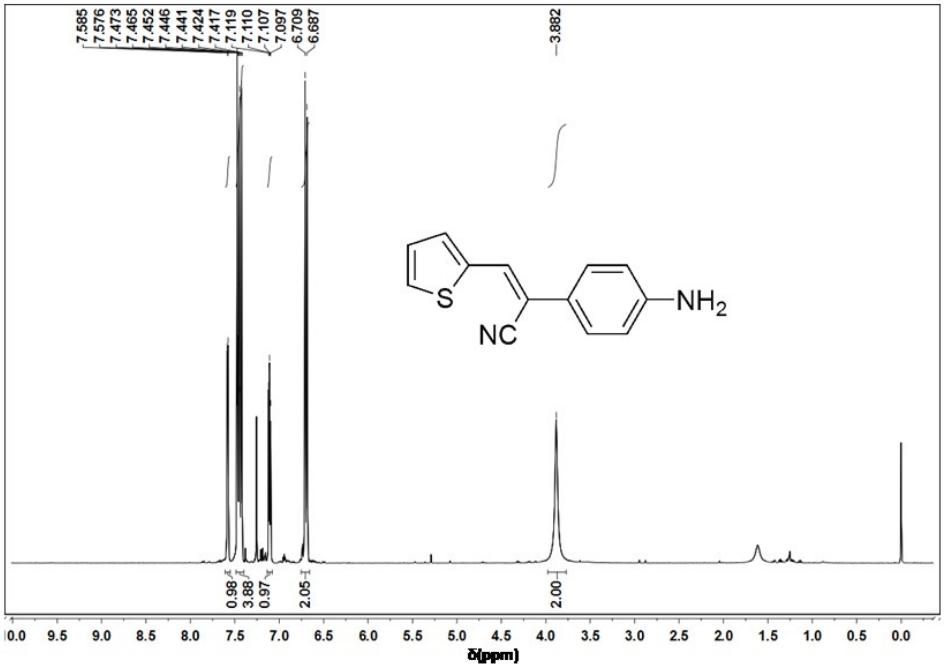

Fig. S1 ^{1}H NMR of **S2**

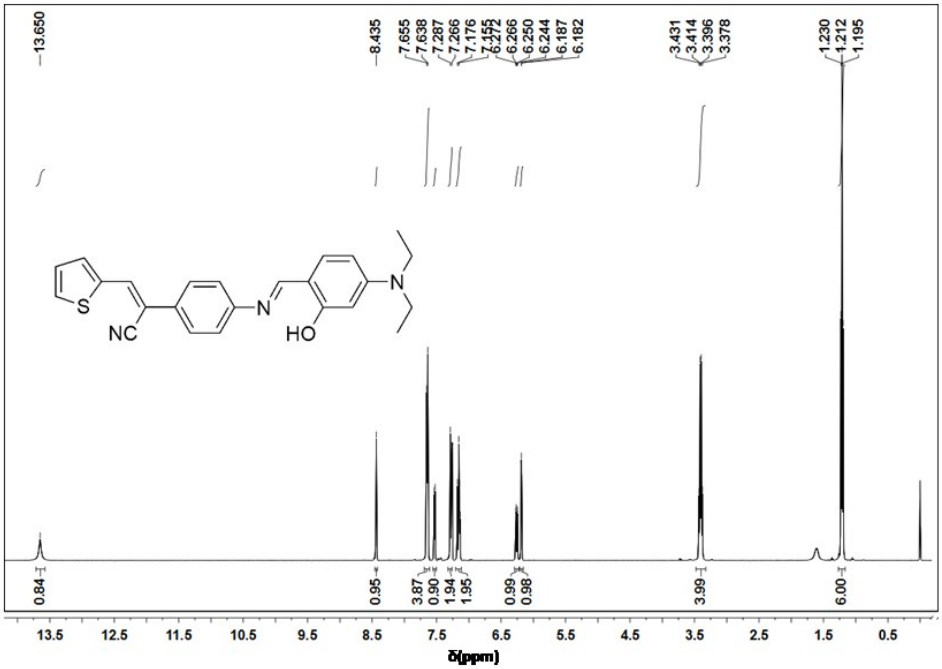

Fig. S2 ^{1}H NMR of **S3**

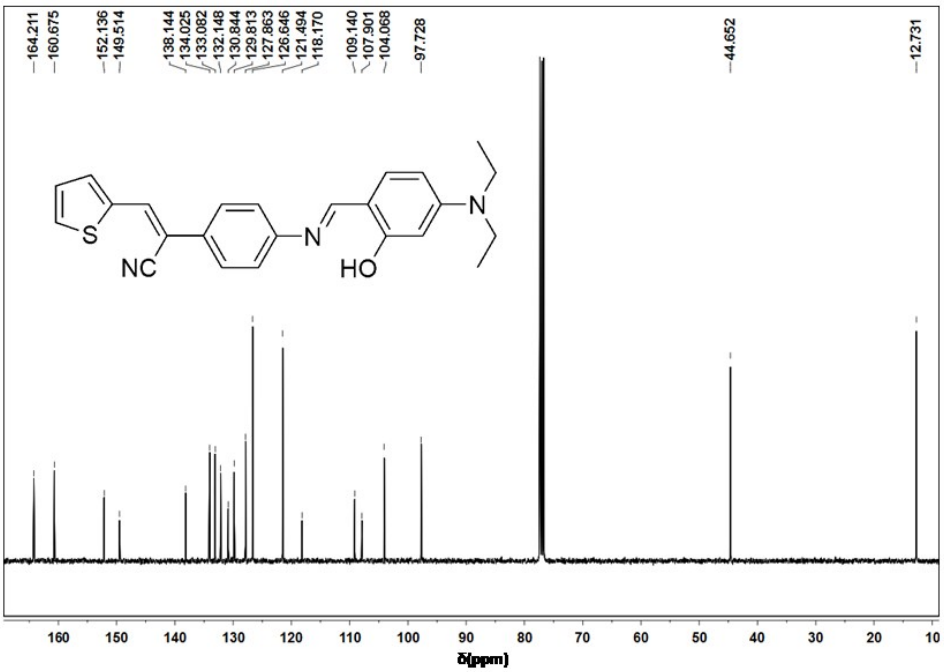

Fig. S3 ^{13}C NMR of **S3**

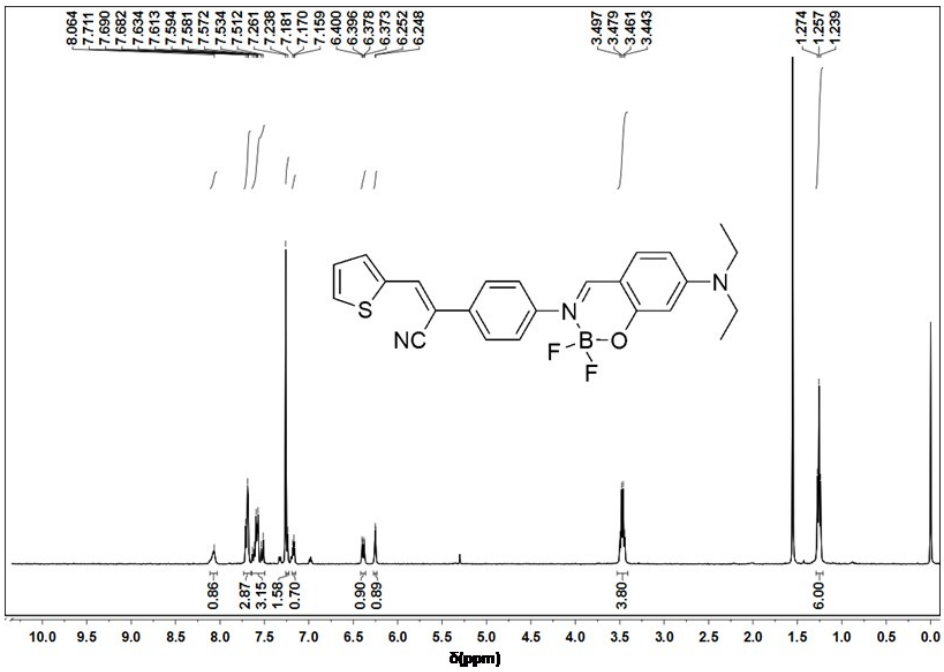

Fig. S4 ^{1}H NMR of **TC**

2 TGA and DTG curve of TC

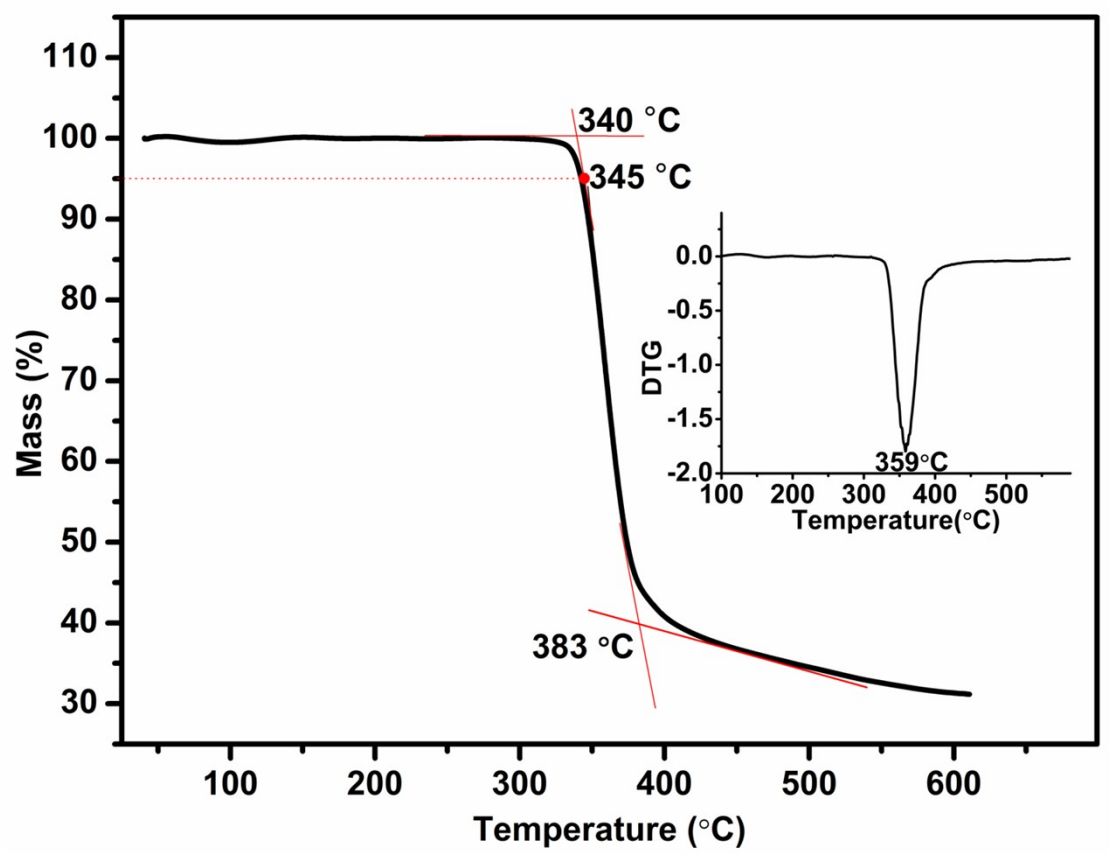

Fig. S5 The TGA curve of **TC** recorded under nitrogen at a heating rate of 10 °C/min. The inserts is DTG curves.

3 The time-dependent DFT (TD-DFT) calculations

Table S1 The wavelength of absorption maximum, oscillator strength and major contributions for the **TC** and **S3**

Compound	Experimental λ (nm)	Theoretical λ (nm)	Osc. strength	Major contributions (% coefficients)
TC	420	423	1.3757	H→L (64%)
S3	415	412	0.1064	H-3→L (43%) H→L + 1 (43%)

4 Single crystal parameter

Table S2 The data of single crystal **S3**

empirical formula	$C_{24}H_{23}N_3OS$	Z	8
formula weight	401.52	T (K)	296(2) K
crystal system	Monoclinic	Dcalcd (g cm^{-3})	1.282
space group	C2/c	μ (mm^{-1})	0.176
a (Å)	26.886(3)	θ range (deg)	1.74 to 24.99
b (Å)	10.6027(18)	total no. of reflns	14422
c (Å)	16.7359(18)	no. of unique reflns	3657
α (deg)	90	no. of params refined	265
β (deg)	119.293(2)	R1	0.0396
γ (deg)	90	wR2	0.1184
V (Å^3)	4160.8(10)	GOF	1.074
CCDC number	96763		

Table S3 The data of single **TC**

empirical formula	$C_{24}H_{22}BF_2N_3OS$	Z	4
formula weight	449.32	T (K)	296(2)
crystal system	Monoclinic	Dcalcd (g cm^{-3})	1.395
space group	P2(1)/c	μ (mm^{-1})	0.074
a (Å)	6.500(7)	θ range (deg)	1.54 to 25.00
b (Å)	26.53(3)	total no. of reflns	13926
c (Å)	12.800(13)	no. of unique reflns	6885
α (deg)	90	no. of params refined	542
β (deg)	beta = 104.287(14)	R1	0.0766
γ (deg)	90	wR2	0.2566
V (Å3)	2139(4)	GOF	0.977
CCDC number	96829		

Table S4 Selected Dihedral Angles and Interaction Patterns in the Crystals of **S3** and **TC**

		Dihedral Angle (°)	interaction	d (Å)	interaction	d (Å)
S3	P_A-P_B	40.127	O_1-H_1…N_2	1.892	C_{13}-H_{13}…π	3.250
	P_B-P_C	25.272	O_2-H $_2$…N_5	1.882	C_{30}-H_{30}…π	2.984
	$P_{A'}$-$P_{B'}$	40.539	C_{28}-H_{28A}…N_3	2.700	C_{31}-H_{31}…π	2.958
	$P_{B'}$-$P_{C'}$	25.611	C_8-H_8…π	2.995	C_{46}-H_{46}…π	3.351
TC	P_A-P_B	28.982	C_3-H_3…O_1	2.576	C_{24}-H_{24B}…F_2	2.521
	P_B-P_C	37.156	C_7-H_7…F_1	2.611	C_{16}-H_{16}…N_3	2.415
	P_A-P_D	1.024	C_9-H_9…F_2	2.630	C_7-H_7…π	3.449
			C_{21}-H_{21A}…F_2	2.636		

5 Parameter of solvents

Table S5 The value of the refractive index (n), relative permittivity (ε) and orientation polarizability (Δf)

Solution	ε	n	Δf
Benzene	2.28	1.5011	0.0026
DCM	9.10	1.4244	0.2185
THF	7.58	1.407	0.2097
EA	6.02	1.3724	0.1997
EtOH	25.70	1.3614	0.2903
AN	37.50	1.3441	0.3055
DMF	36.71	1.4282	0.2751
DMSO	47.2	1.4795	0.2632

6 The molecular structure, dihedral angle and the distances of TC molecular interplanar.

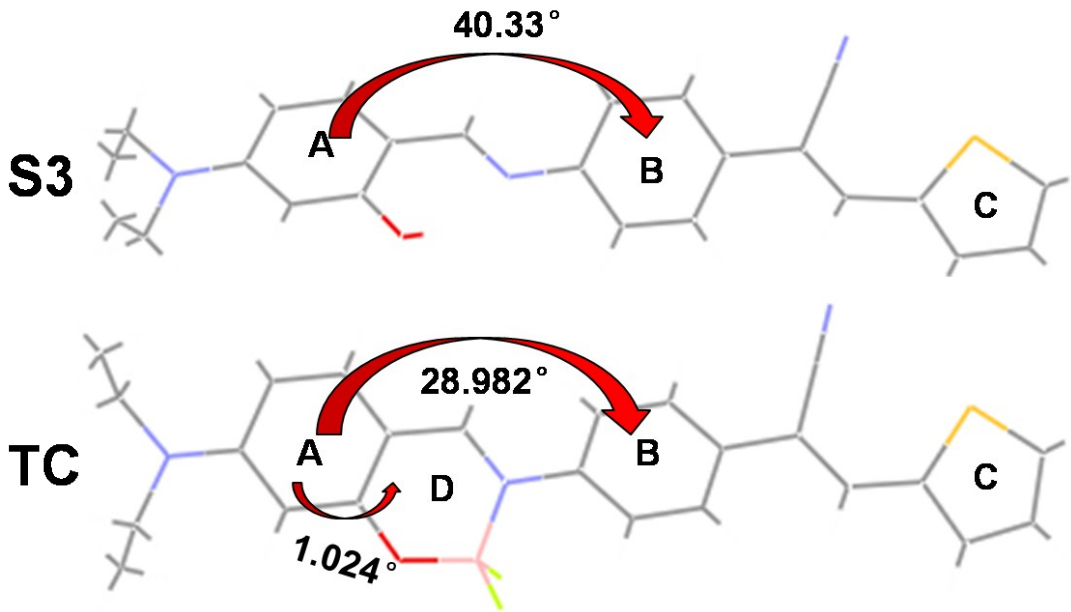

Fig. S6 The dihedral angle between aromatic ring A and B in molecular structure of **S3** and **TC**.

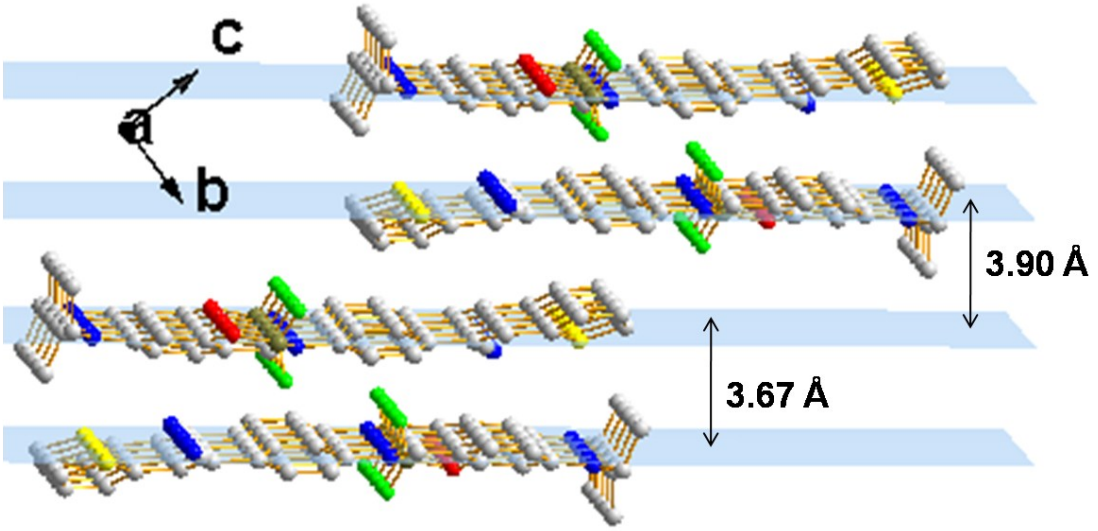

Fig. S7 . The interplanar distances of **TC**.

7 Electron density distributions of the frontier molecular orbitals

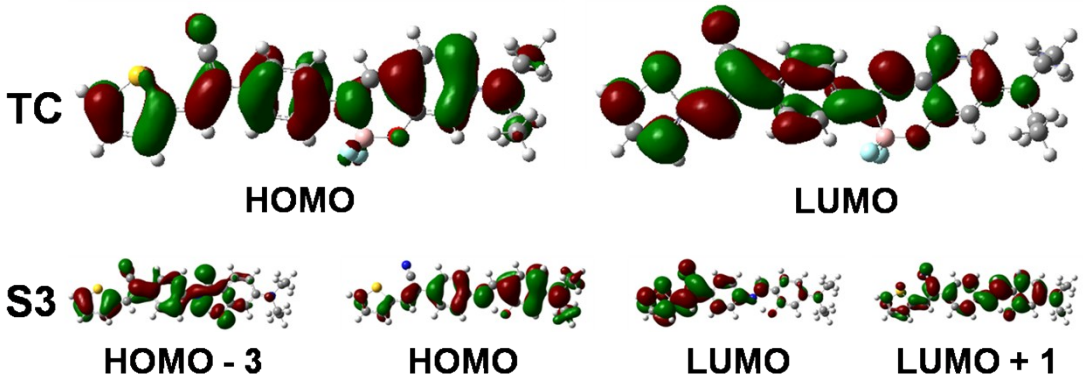

Fig. S8 Electron density distributions of the frontier molecular orbitals of compounds **TC** and **S3** calculated at the B3LYP/6-31+G(d) level..