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Supplementary Information

New Charge Transfer-based High-Efficiency Organic Room Temperature Phosphorescent Trace Doping Systems

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Materials and Instruments

Unless otherwise noted, all reagents for chemical synthesis were obtained from commercial suppliers and were used without further purification. 2-amino-6-bromobenzothiazole (BT) was purchased as follows Adamas (Shanghai, China). BT has been purified by three rounds of column chromatography and recrystallization. All guest molecules have been purified by three rounds of column chromatography and recrystallization. Flash chromatography was carried out on silica gel (200-300 mesh). ^{1}H-NMR spectra were recorded using BRUKER DRX 400 or BRUKER DRX 500 spectrometer and ^{13}C-NMR was recorded using BRUKER DRX 400 or BRUKER DRX 500 spectrometer. Chemical shifts were expressed in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HR-MS) was recorded with Agilent-1100 HPLC/TOF mass spectrometer (Agilent Technologies, USA). The crystal diffraction data for complex were collected at 293 K using a Bruker ASX D8 VENTURE, and structures were solved by direct methods using the programme SHELXL2014. The thermal analyses were carried out on METTLER-TOLEDO TGA/DSC HT 1600 simultaneous thermal analyzer, under a nitrogen atmosphere, at heating rate of 10 °C min^{-1}. The UV-Vis absorption spectrum was collected from the UV-240IPC spectrophotometer by the dual light path method. The fluorescence spectrum of solution is obtained from a F97XP FL spectrophotometer with a 1 cm standard quartz cell. The excitation slits and emission slits are 5 nm and the voltage is 650 V during the test. The fluorescence spectrum of power is obtained from a F-380 spectrophotometer (GANGDONG SCI.&TECH.CO, LTD, Tianjin, China). The excitation slits and emission slits are 5 nm and the voltage is 450 V during the test. The phosphorescence spectrum of power is obtained from a F-380 spectrophotometer (GANGDONG SCI.&TECH.CO, LTD, Tianjin, China). The excitation slits and emission slits are 5 nm and the voltage is 450 V during the test. Phosphorescence emission lifetimes were performed on Horiba FL-3 and analyzed by the use of a program for exponential fits. Fluorescence quantum yields measurements of pure host and guests were performed on Edinburgh FLS1000 fluorescence spectrophotometer. Fluorescence quantum yields and phosphorescence quantum yields of doped system measurements were performed on Edinburg FLS1000.

Experimental Procedures

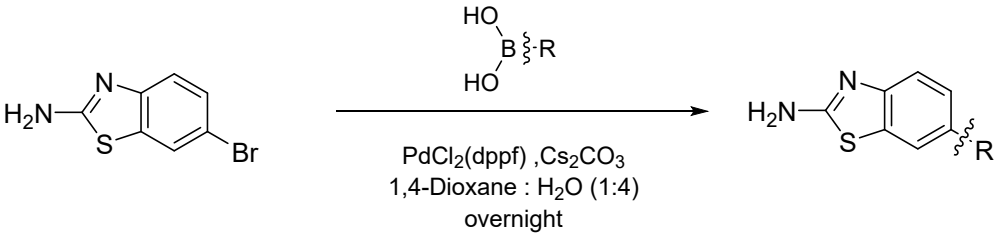
Computational Methods

DFT/TD-DFT calculations

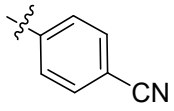
Molecular geometry optimization, vibration frequency analysis and single point energy were carried out within the density functional theory (DFT) framework using the Gaussian 09 software.[1] Since it is not necessary to use a large basis set for molecular structure optimization and vibration analysis, we use the B3LYP [2] functional with dispersion correction (D3), [3]which has the most robust performance in structural optimization, and a small basis set (6-31G*)[4] for molecular structure geometric optimization and vibration analysis. All the optimized molecular structures showed no imaginary vibrations in the frequency calculations. We employ time-dependent density functional theory (TD-DFT) for those at excited state calculation and optimization. In order to better reproduce the experimental results, PBE0[5] were chosen to perform tests shows the optimal performance (Fig. S3-S8). After comparing the calculation results and time consumption of different functional and basis set, PBE0 (D3) functional and

def2-TZVP [6] basis set are selected for excited state energy calculation of small molecule, and PBE0 (D3) functional and def2-SVP [6] are used for time-consuming molecular cluster excited state calculation. PBE0 functional combined with the linear re-sponse solvent formalism was used for describing S_1 potential energy in acetonitrile. In order to accurately describe the effects of solvents, all implicit solvent model uses an SMD (solvent model density) [7] model that considers both polar and non-polar components. The hole-charge analysis, molecular orbital and Independent Gradient Model (IGM) analysis were calculated using Multiwfn 3.8, [8] and the molecular visualization were performed using Visual Molecular Dynamics (VMD) package.[9]

Molecule synthesis

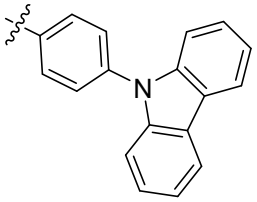


R =



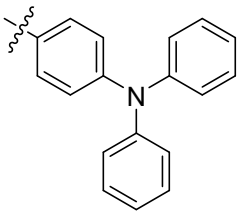
BCN

Yield = 26.5 %



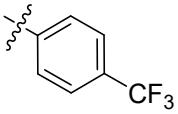
BCz

Yield = 11.2 %



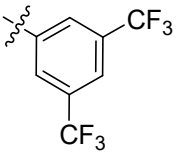
BTPA

Yield =21.4 %



BCF_3

Yield = 13.6 %

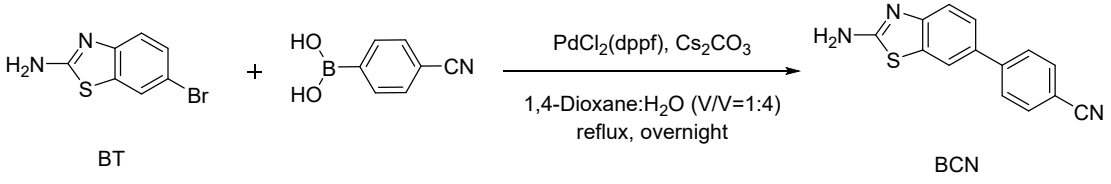


$B2CF_3$

Yield =30.6 %

Scheme S1 Guest molecular synthesis route and structure schematic

The synthesis of **BCN** compound



BT

BCN

Scheme S2 BCN synthesis route and structure schematic

The compound BT (753.15 mg, 3 mmol), 4-Cyanophenylboronic acid (481.8 mg, 3.3 mmol), catalyst $PdCl_2$(dppf) (90 mg, 0.13 mmol) and Cs_2CO_3 (1075.1 mg, 3.3 mmol) were added to a 50 mL single-necked flash, and followed by the addition of 12 mL 1,4-dioxane and 3 mL water. Under argon, the reaction mixture was stirred in an oil bath at 96 ℃ for overnight. After the reaction was completed, the mixture was concentrated under reduce pressure, and then extracted with dichloromethane for 3 times. To combine the extract, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified on silica column chromatography (PE: EA=5:1) to obtain pale brown solid **BCN** in 26.5% yield

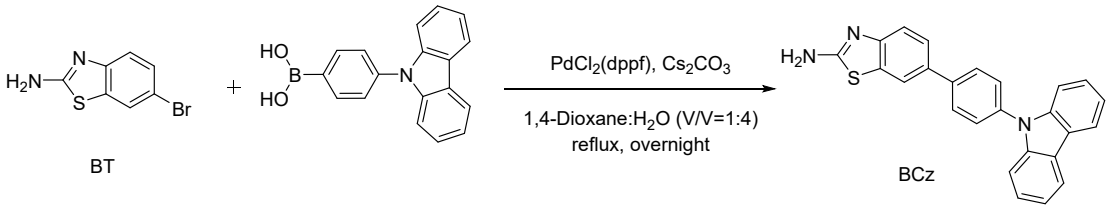
^{1}H NMR (500 MHz, DMSO-d6) δ 8.12 (d, J = 2.0 Hz, 1H), 7.88 (s, 4H), 7.66 (s, 2H), 7.62 (dd, J = 8.4, 2.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H).

^{13}C NMR (125 MHz, DMSO) δ 168.13, 153.98, 145.17, 133.25, 131.24, 127.46, 125.17, 120.03, 118.45, 109.50.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}N_3S$ 252.0595; Found 252.0592.

Melting point: 242.7 ℃

The synthesis of **BCz** compound



Scheme S3 BCz synthesis route and structure schematic

The synthesis method of **BCz** was similar to the **BCN**. White solid was obtained in 11.2 % yield.

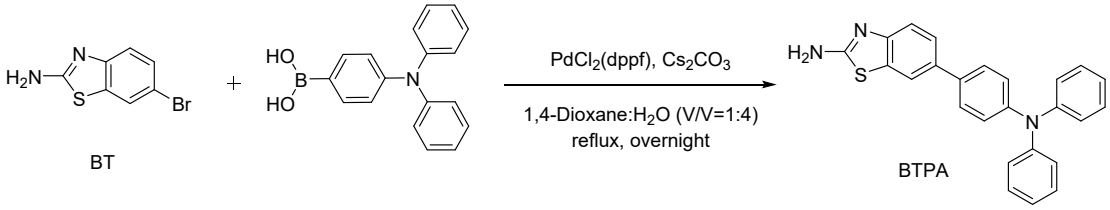
^{1}H NMR (400 MHz, DMSO-d6) δ 8.27 (d, J = 7.7 Hz, 2H), 8.13 (d, J = 1.9 Hz, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.73 – 7.59 (m, 5H), 7.51 – 7.41 (m, 5H), 7.31 (ddd, J = 8.0, 4.7, 3.4 Hz, 2H).

^{13}C NMR (100 MHz, DMSO) δ 167.61, 153.19, 140.61, 139.89, 135.92, 132.55, 128.39, 127.47, 126.73, 124.90, 123.24, 121.00, 120.54, 119.59, 118.49, 110.17.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{17}N_3NaS$ 414.1041; Found 414.1033.

Melting point: 302.2 ℃

The synthesis of **BTPA** compound



Scheme S4 BTPA synthesis route and structure schematic

The synthesis method of **BTPA** was similar to the **BCN**. White solid was obtained in 21.4 % yield.

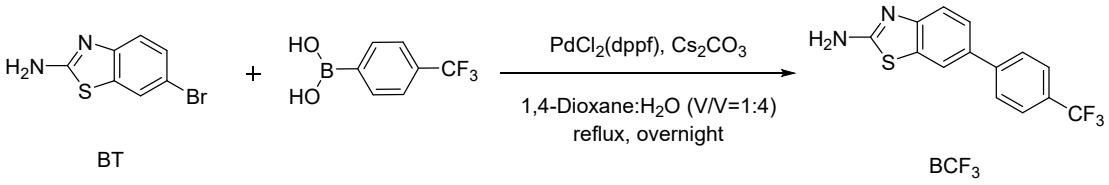
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.09 – 7.01 (m, 8H).

^{13}C NMR (125 MHz, DMSO) δ 167.17, 152.55, 147.62, 146.51, 134.98, 133.04, 132.41, 130.03, 127.79, 124.38, 124.19, 123.74, 123.540, 119.56, 118.92, 118.34.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3S$ 394.1378; Found 394.1373.

Melting point: 277.8 ℃

The synthesis of **BCF_3** compound



BT BCF_3

Scheme S5 BCF_3synthesis route and structure schematic

The synthesis method of **BCF_3** was similar to the BCN. White solid was obtained in 13.6 % yield.

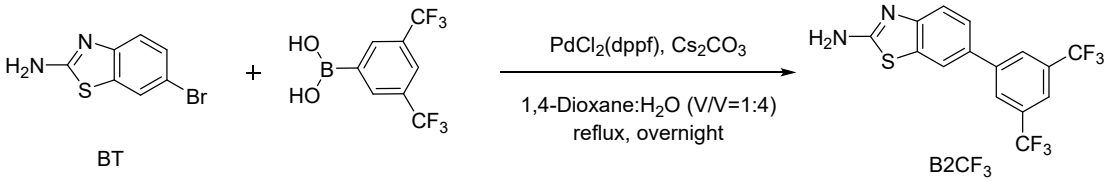
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.66 (s, 2H), 7.60 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H)。

^{13}C NMR (100 MHz, DMSO) δ 167.51, 153.40, 144.86, 134.63, 132.79, 132.69, 127.19, 125.67, 125.63, 124.90, 119.44, 118.71.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}F_3N_2S$ 295.0517; Found 295.0507.

Melting point: 236.9 ℃

The synthesis of **$B2CF_3$** compound



BT $B2CF_3$

Scheme S6 $B2CF_3$synthesis route and structure schematic

The synthesis method of **$B2CF_3$** was similar to the **BCN**. White solid was obtained in 30.6 % yield.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.33 (s, 2H), 8.26 (d, *J* = 2.0 Hz, 1H), 8.00 (s, 1H), 7.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (s, 2H), 7.44 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (125 MHz, DMSO) δ 167.84, 153.88, 143.54, 134.19, 132.96, 131.87, 131.54, 130.86, 126.98, 125.02, 119.80, 118.77.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_9F_6N_2S$ 363.0391; Found 363.0386.

Melting point: 209.0 ℃

Purity analysis of compounds performed by HPLC

HPLC analysis of host and guest was performed using the Reversedphase (RP)-HPLC (Agilent Technologies 1200 Series) following chromatographic conditions: Agilent Eclipse XDB C18 column (5 μm, 150 × 4.60 mm) eluted at 1 mL/min with a gradient of methanol (MeOH):H_2O, starting at 30% MeOH for 1 min, increased uniformly to 100% MeOH over 30 min and maintained at 100% MeOH for 5 min. This was uniformly reduced to 30% MeOH during the last 5 min. column temperature: 20°C, The samples were detected with the help of a UV detector at 254 nm.

Standard protocol for doping material

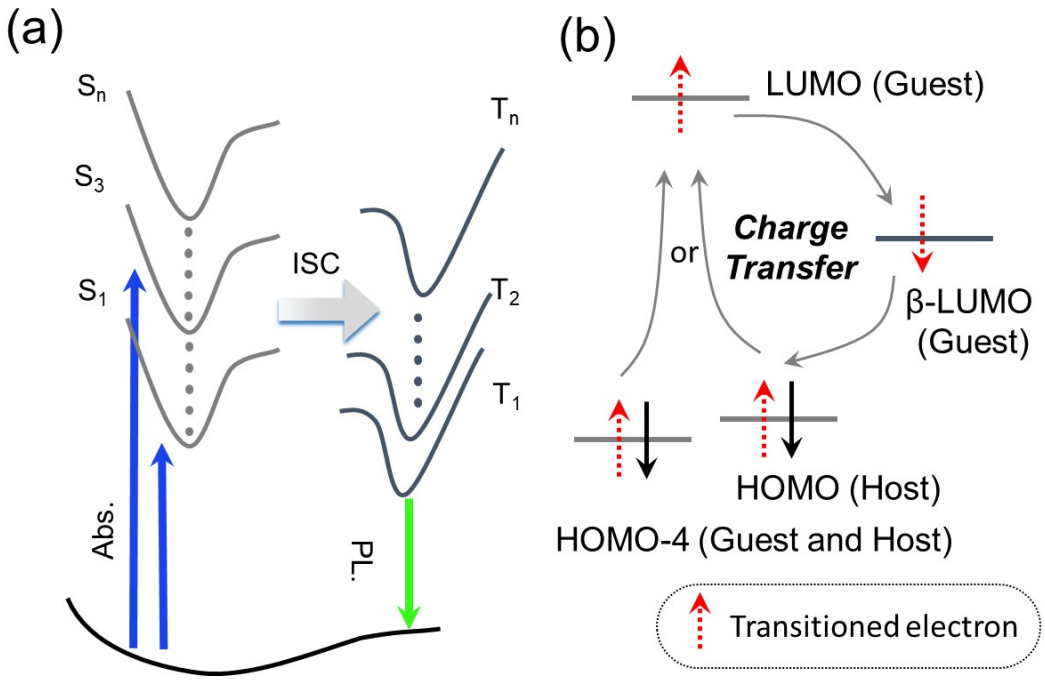
The doped materials were prepared using the solvent evaporation method. To begin, 10 mL of ethyl acetate was used to dissolve the appropriate amount of the guest material. The guest reserve that was produced has a concentration of 10 mM. Accurately weigh 100 mg **BT** and completely dissolve it in ethyl acetatel. The corresponding guest stock solution was added to the **BT** solution according to the molar ratio calculation. After mixing the two solutions, the solvent was distilled under reduced pressure with an oil pump to obtain the resulting mixture.

Molecular dynamics

All molecular dynamics (MD) simulations were performed using the GROMACS 2019.6 suite of programs.[10] The force field parameters of **BT** and **BCN** were built from the general amber force field (GAFF). [11] The restrained electrostatic potential (RESP) of **BT** and **BCN** was calculated by Multiwfn 3.8 [8] based on the optimized geometry at B3LYP/6-31+G* level. The top file of small molecule is generated by Sobtop software. [12] All simulations are performed under periodic boundary conditions. First, we perform an energy minimum on the system until the maximum force < 100.0 kJ/mol/nm. Then 100 ps NVT simulation was performed under conditions that constraint small molecules (harmonic restraint of 1,000.0 kJ/mol/nm). An annealing simulation (298-373-298 K / 0 ns-2.5 ns-5 ns) was run all 100 ns followed under the NPT ensemble. Finally, we performed 1000 ns MD simulation under NPT ensemble removing constraints. The temperature is coupled by a Velocity rescaling (V-rescale) thermostat.[13] The pressure in the pre-equilibrium and annealing simulation stages is coupled by a Berendsen barostat.[14] The pressure in the formal simulation is coupled by a more accurate Parrinello-Rahman barostat. [15] The coupling times of temperature and pressure were 0.1 ps and 1.0 ps, respectively. The fast smooth particle-mesh ewald (SPME) electrostatics is used to calculate the long-distance electrostatic interactions. The short-range neighborlist cutoff and electrostatic cutoff value is 1.4 nm. The short-range van der Waals interaction is calculated at 1.4 nm. Bond parameters are holonomic constrained by LINCS constraint-algorithm, and the time step of integration is 2 fs.

Spectroscopic Methods

Accurately weigh a certain amount of **BT**, **BCN**, **BCz**, **BTPA**, **BCF_3**, and **$B2CF_3$** then dissolved in a certain volume of ethyl acetate to prepare a probe stock solution with a concentration of 10.0 mM to prepare for the subsequent experiments. When preparing for the test, take 3.0 μL of the stock solution and dilute it into the 3.0 mL acetonitrile to prepare a final concentration of 10.0 μM test solution. Then, an appropriate amounts of test solution was transfered to a standard quartz cuvette of 1.0 cm × 1.0 cm to collect UV-visible absorption and fluorescence emission spectra. In addition, the absorption and emission spectra in Fig. S28 were normalized. The solid state emission tests were performed by uniformly distributing the compound powder between two circular quartz plates (ϕ=2 cm) and then fixing them on the spectrometer test clips.



Scheme S7 (a) The Jablonski Diagram of **BCN/BT** molecular cluster absorbance (Abs.) and phosphorescence (PL.). (b) Probable paths of charge transfer between host and guest in **BCN/BT** molecular cluster.

TD-DFT Calculation For pure host or guests

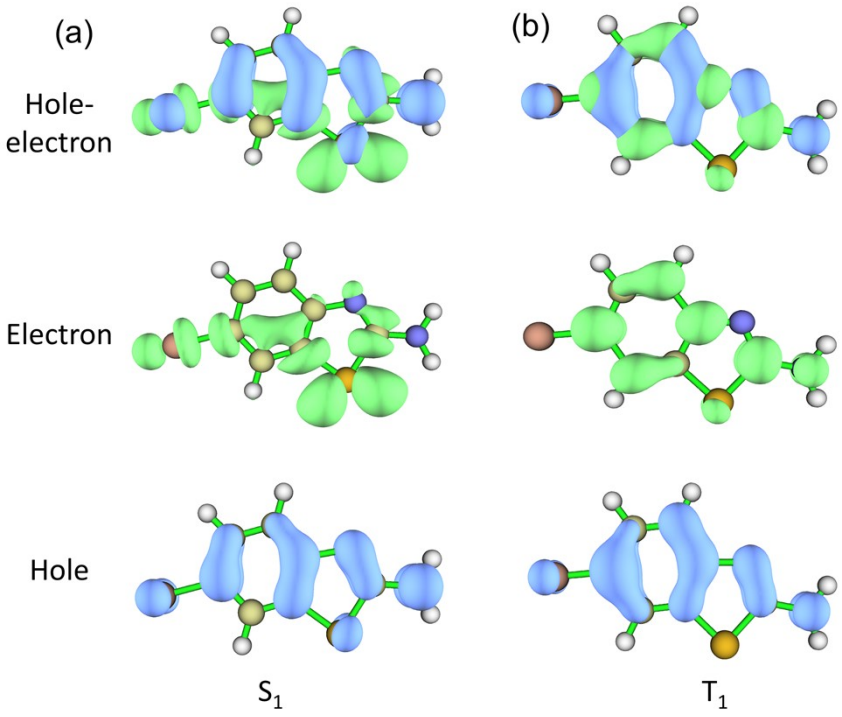


Fig. S1 Schematic diagram of the hole charge distribution in the principal least-excited singlet (S_1) and triplet states (T_1).

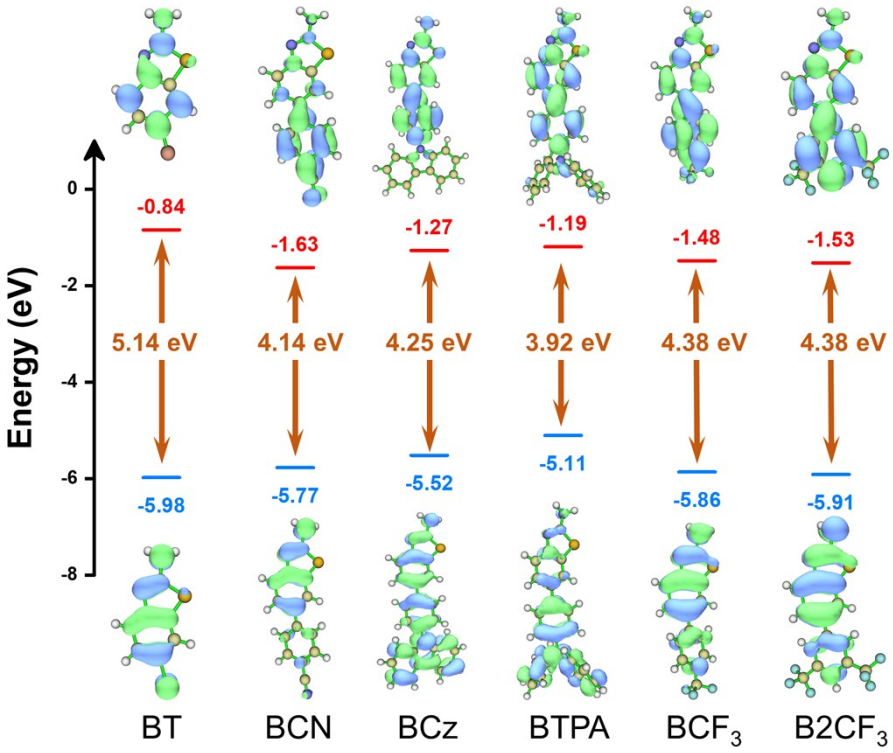


Fig. S2 Schematic diagram of frontier molecular orbital energy and electron density distribution of host and guests.

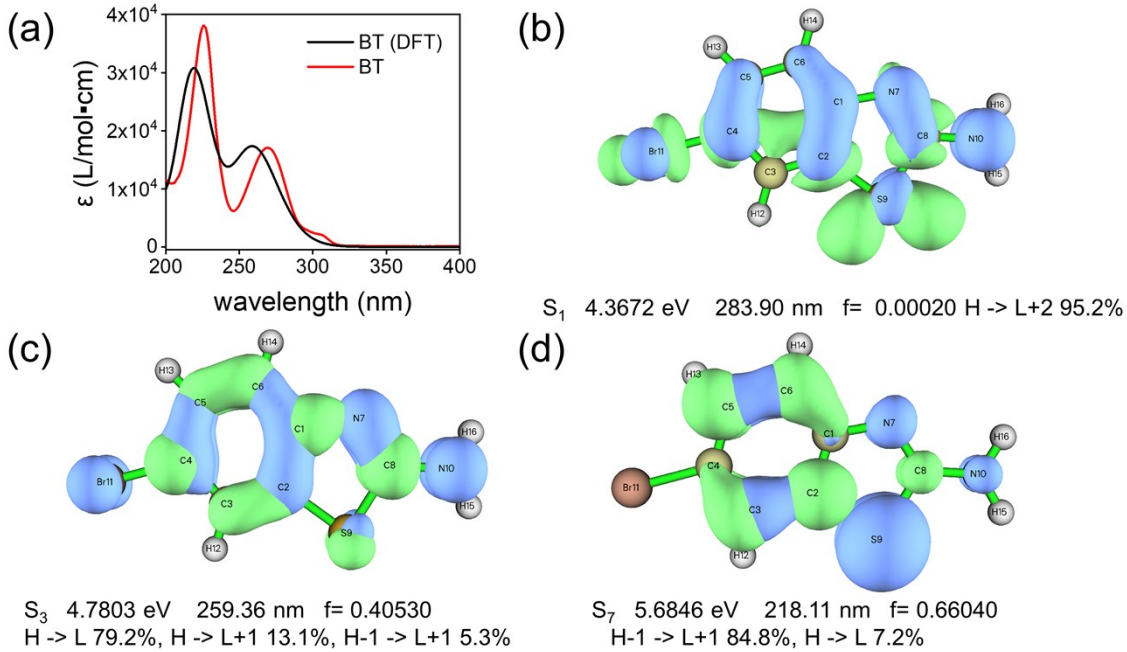


Fig. S3 Uv-vis spectra of **BT**, red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **BT**. (c) Visualize the hole electron distribution of S_3 for **BT**. (d) Visualize the hole electron distribution of S_7 for **BT**. Bule and green isosurfaces represent hole and electron distributions, respectively.

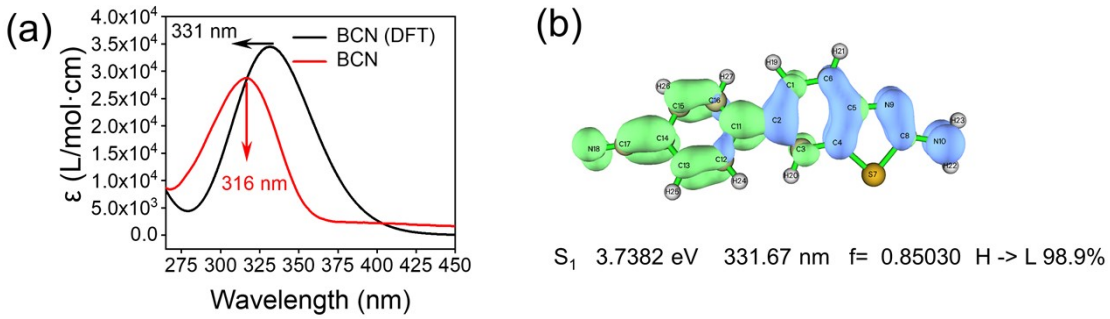


Fig. S4 (a) Uv-vis spectra of **BCN**, red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **BCN**. Bule and green isosurfaces represent hole and electron distributions, respectively.

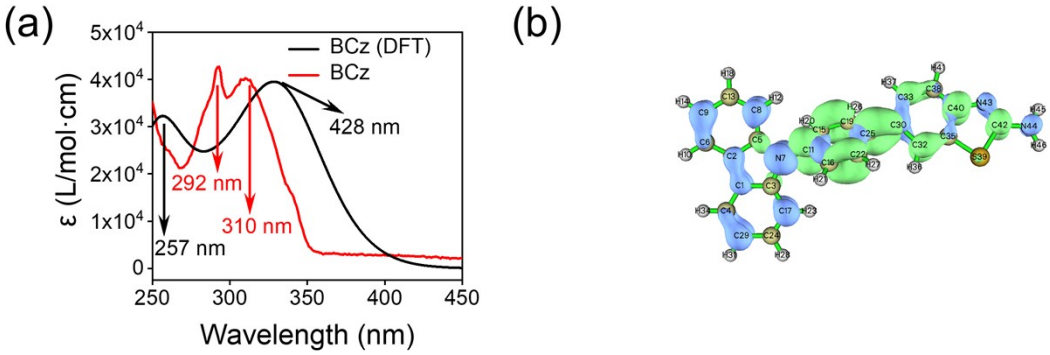


Fig. S5 (a) Uv-vis spectra of **BCz**, red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **BCz**. Bule and green isosurfaces represent hole and electron distributions, respectively.

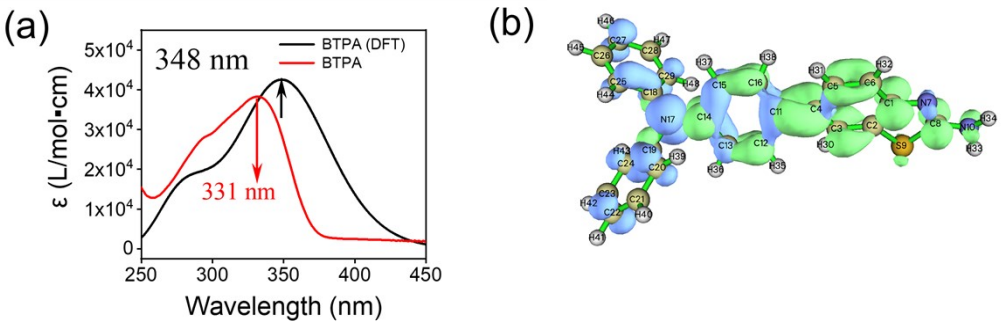


Fig. S6 (a) Uv-vis spectra of **BTPA**, red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **BTPA**. Bule and green isosurfaces represent hole and electron distributions, respectively.

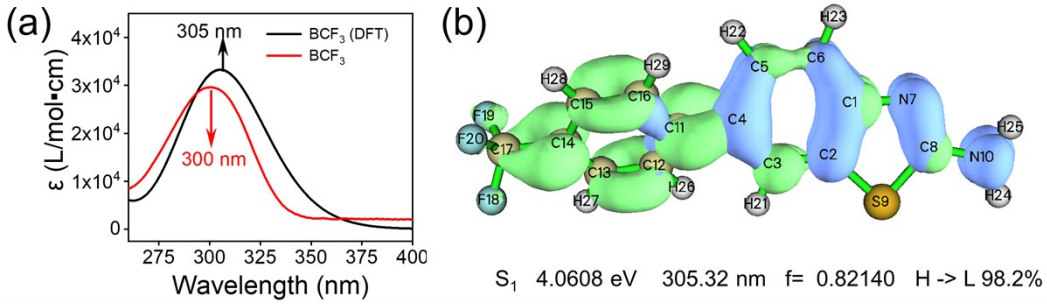


Fig. S7 (a) Uv-vis spectra of **BCF_3,** red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **BCF_3**. Bule and green isosurfaces represent hole and electron distributions, respectively.

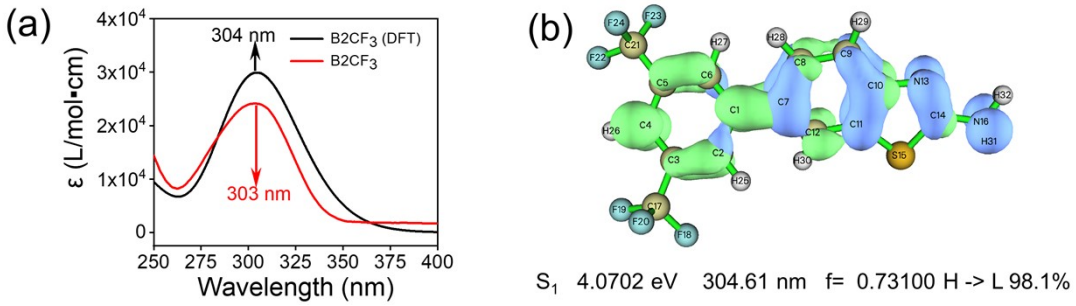


Fig. S8 (a) Uv-vis spectra of **$B2CF_3$**, red solid line represents measured (10 μM) in acetonitrile, blank solid line represents obtained with DFT calculation use PBE0/def2-TZVP with acetonitrile (SMD). (b) Visualize the hole electron distribution of S_1 for **$B2CF_3$**. Bule and green isosurfaces represent hole and electron distributions, respectively.

Table S1 Lowest singly excited state (S_1) properties of compounds

Compound	Energy (eV)	D_{ict} (Å)	Strength oscillator (*f*)	Contribution
BT	4.367	1.273	0.0002	H -> L+2 95.2%
BCN	3.215	4.224	0.0395	H -> L 98.9%
BCz	3.717	2.880	0.8551	H -> L 96.9%
BTPA	3.505	3.371	0.9356	H -> L 96.3%
BCF_3	4.061	2.816	0.8214	H -> L 98.2%
$B2CF_3$	4.070	2.938	0.7310	H -> L 98.1%

H: HOMO, highest occupied molecular orbital; L: LUMO, lowest unoccupied molecular orbital

NMR and HR-MS spectra

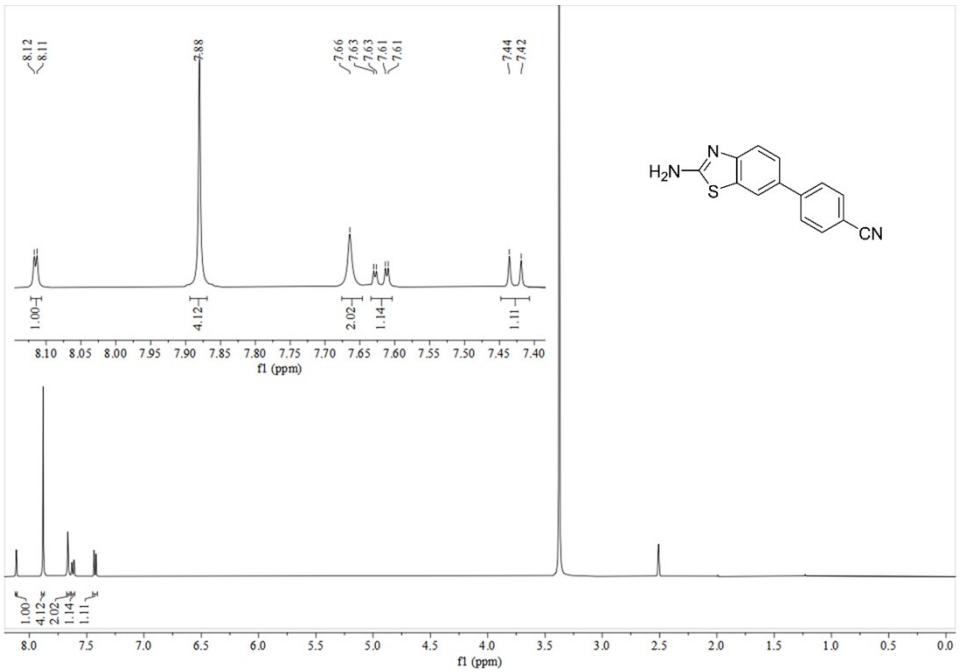


Fig. S9 ^{1}H-NMR of **BCN** (400 Hz, DMSO-d_6)

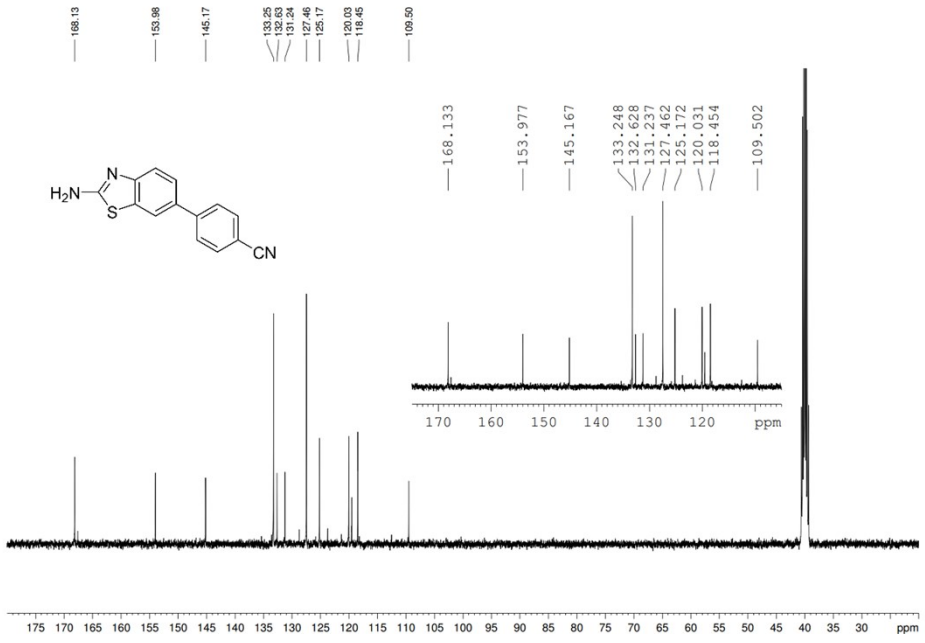


Fig. S10 ^{13}C-NMR of **BCN** (100 Hz, DMSO-d_6)

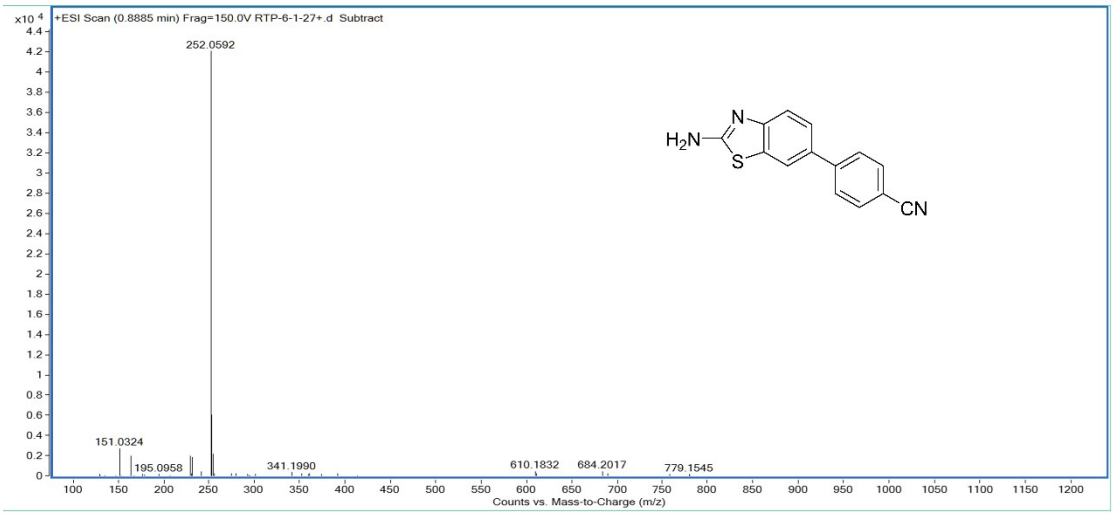


Fig. S11 HR-MS (ESI) of **BCN**

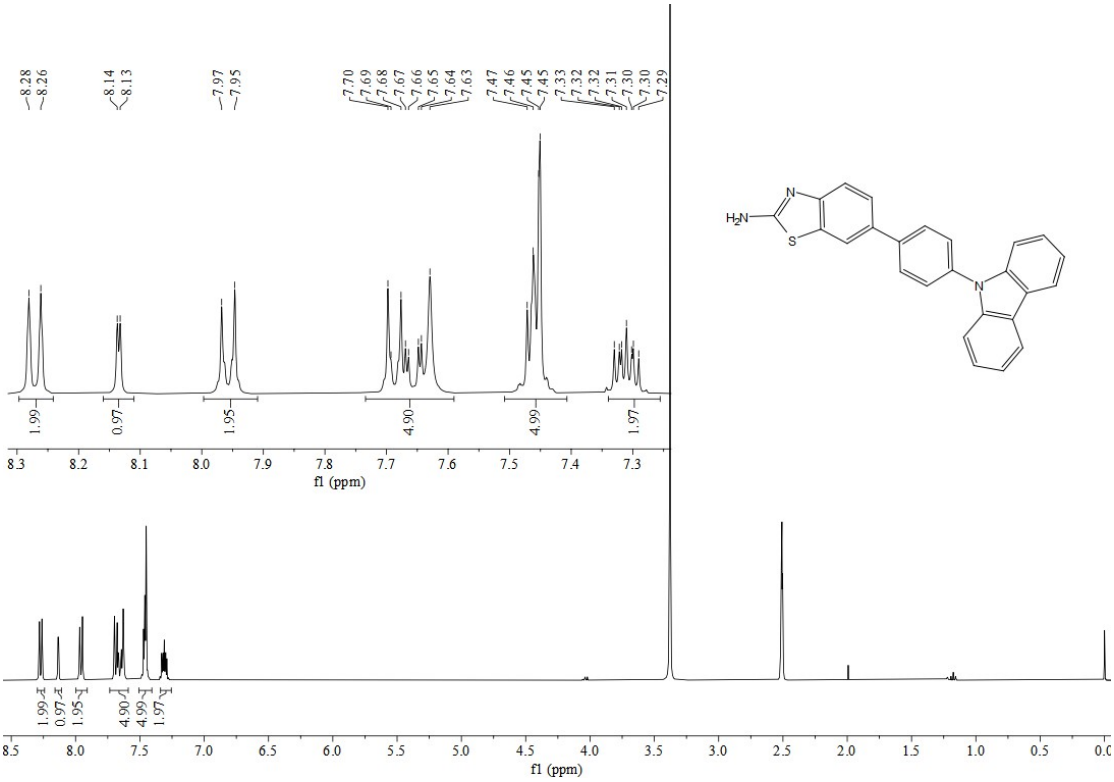


Fig. S12 ^{1}H-NMR of **BCz** (400 Hz, DMSO-d_6)

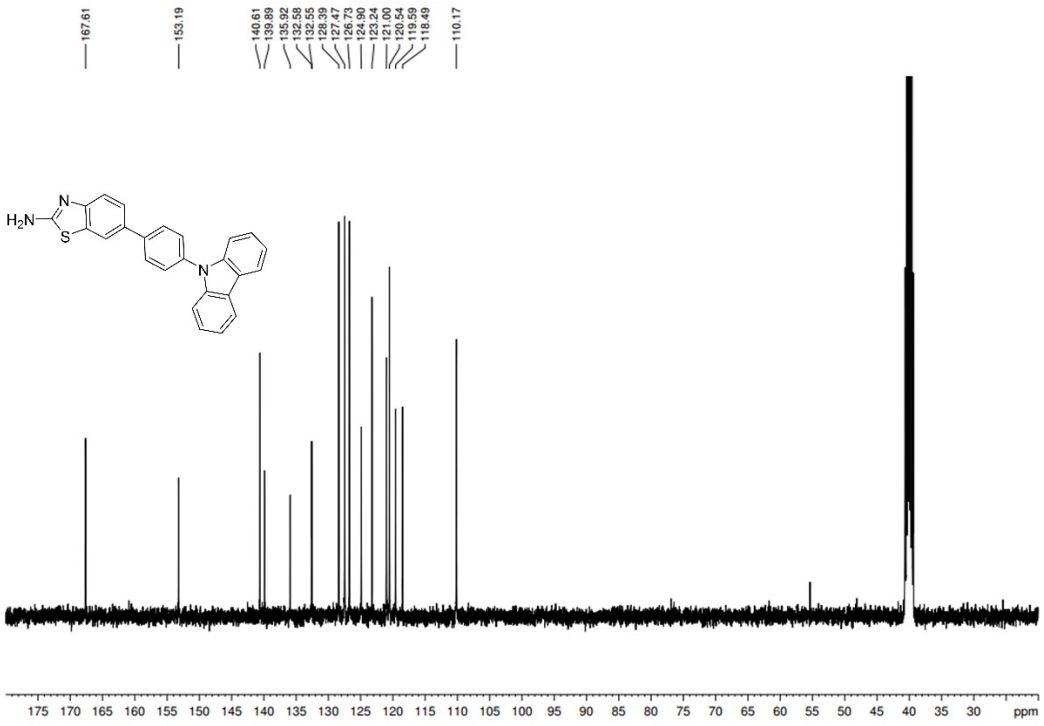


Fig. S13 ^{13}C-NMR of **BCz** (100 Hz, DMSO-d_6)

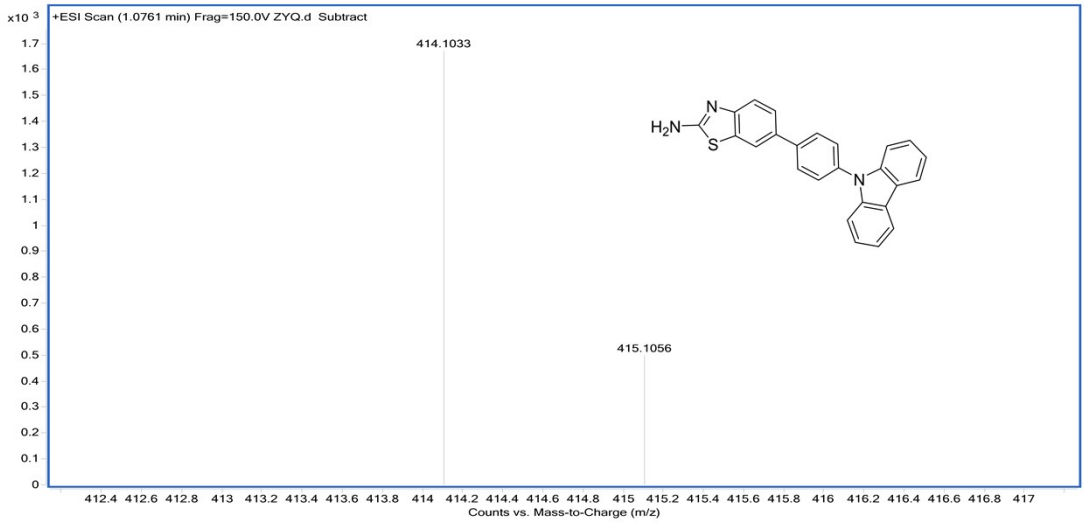


Fig. S14 HR-MS (ESI) of **BCz**

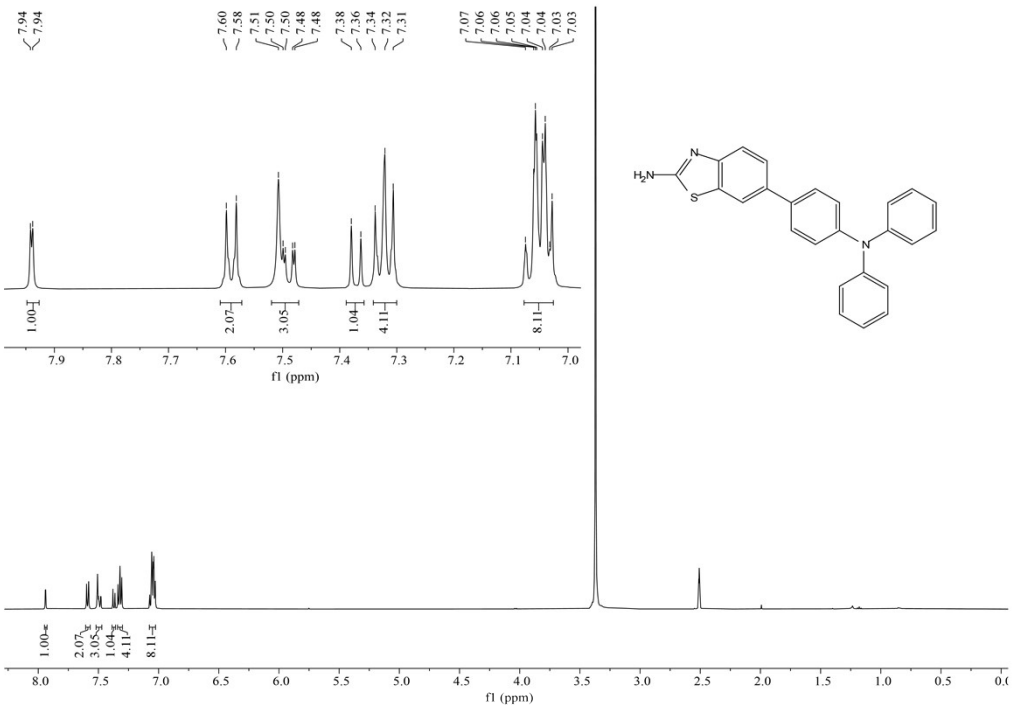


Fig. S15 ^{1}H-NMR of **BTPA** (400 Hz, DMSO-d_6)

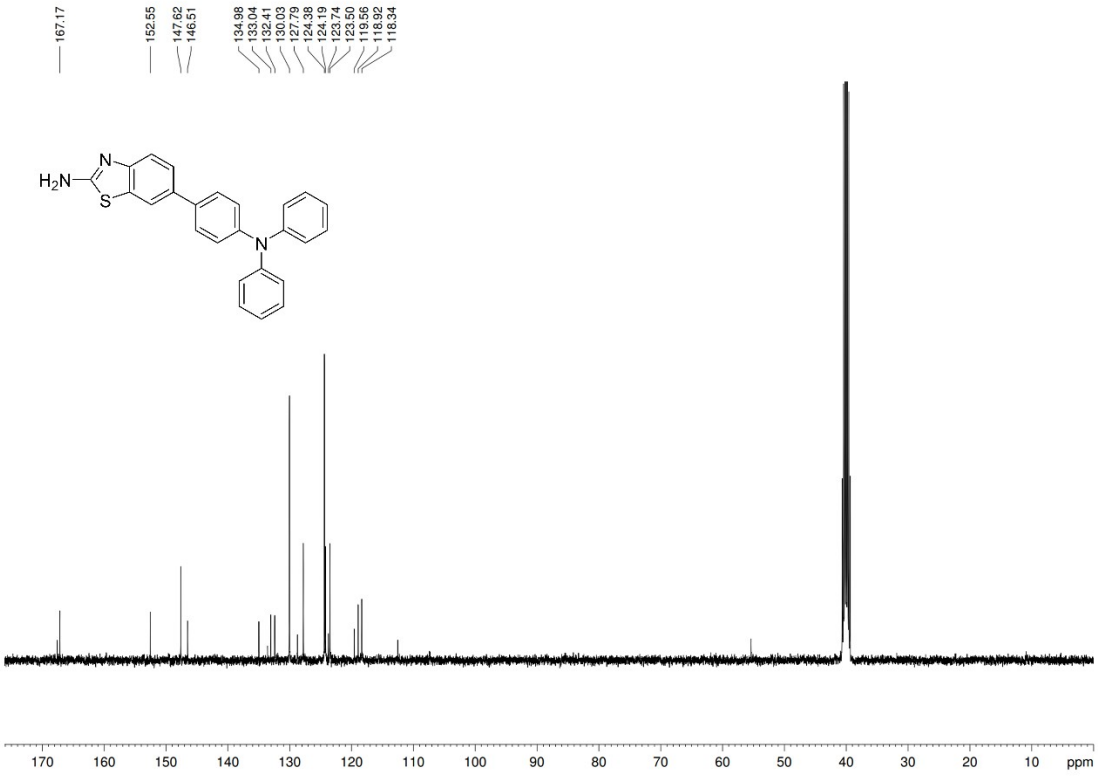


Fig. S16 ^{13}C-NMR of **BTPA** (100 Hz, DMSO-d_6)

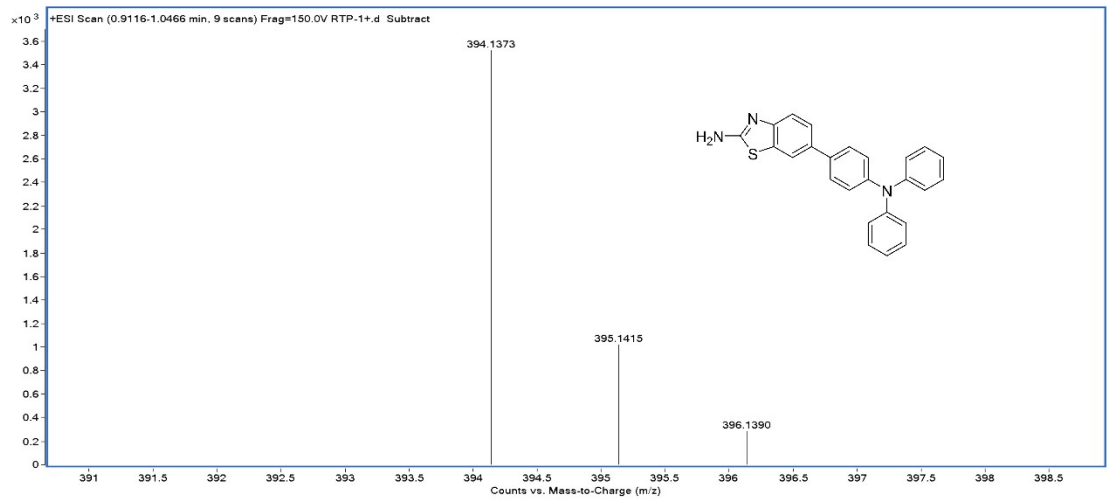


Fig. S17 HR-MS **(ESI)** of **BTPA**

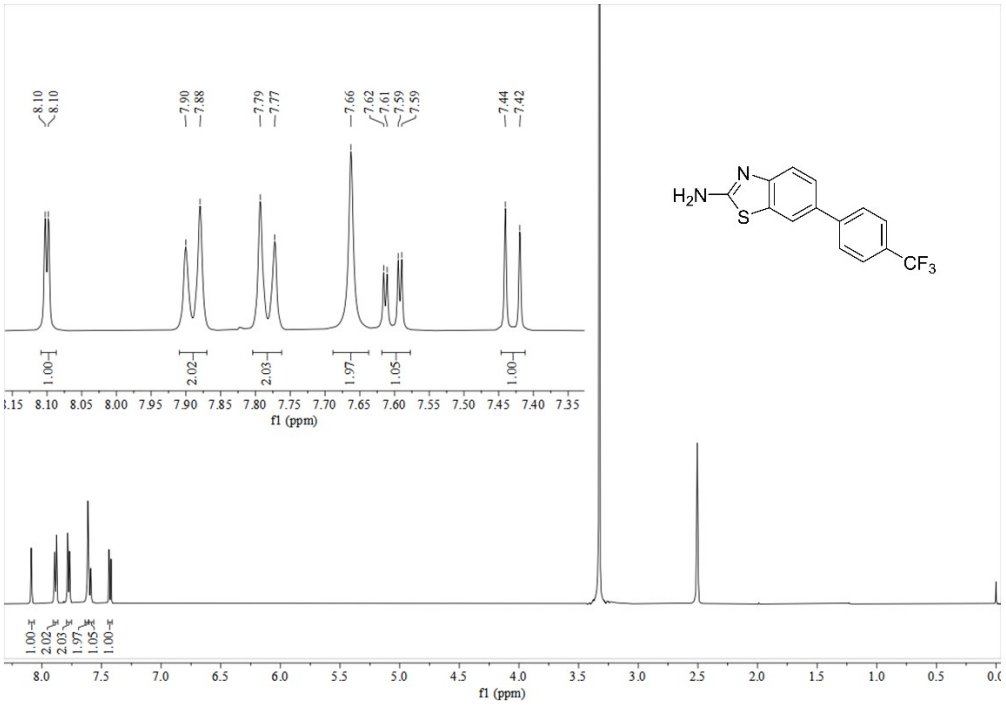


Fig. S18 ^{1}H-NMR of **BCF_3** (400 Hz, DMSO-d_6)

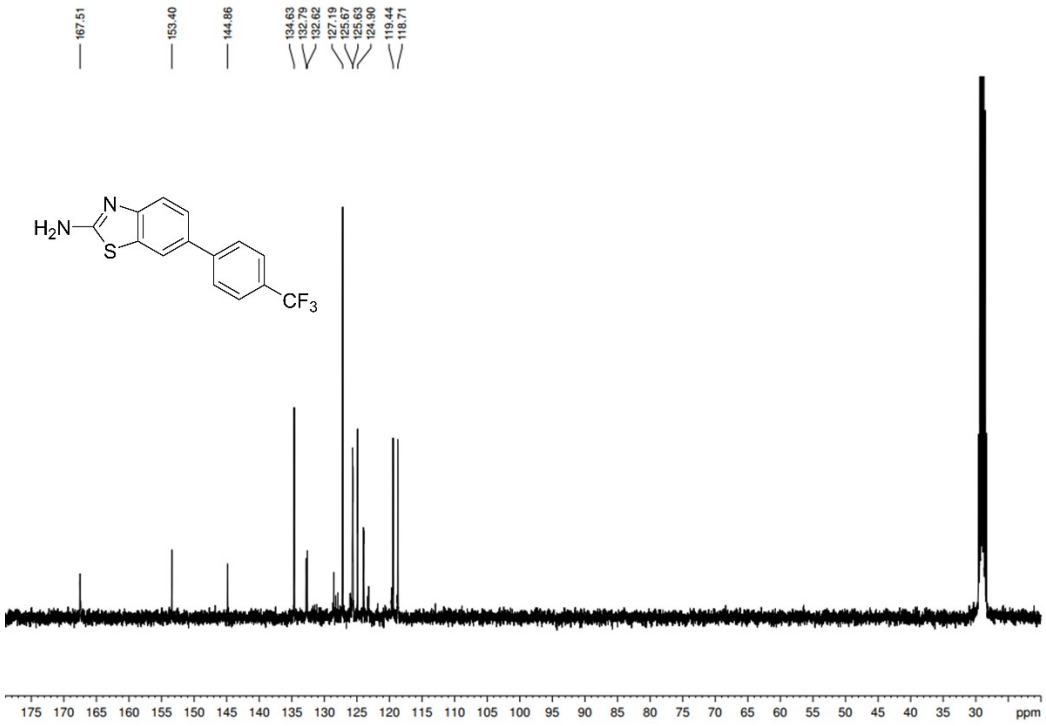


Fig. S19 ^{13}C-NMR of **BCF$_3$** (100 Hz, DMSO-d_6)

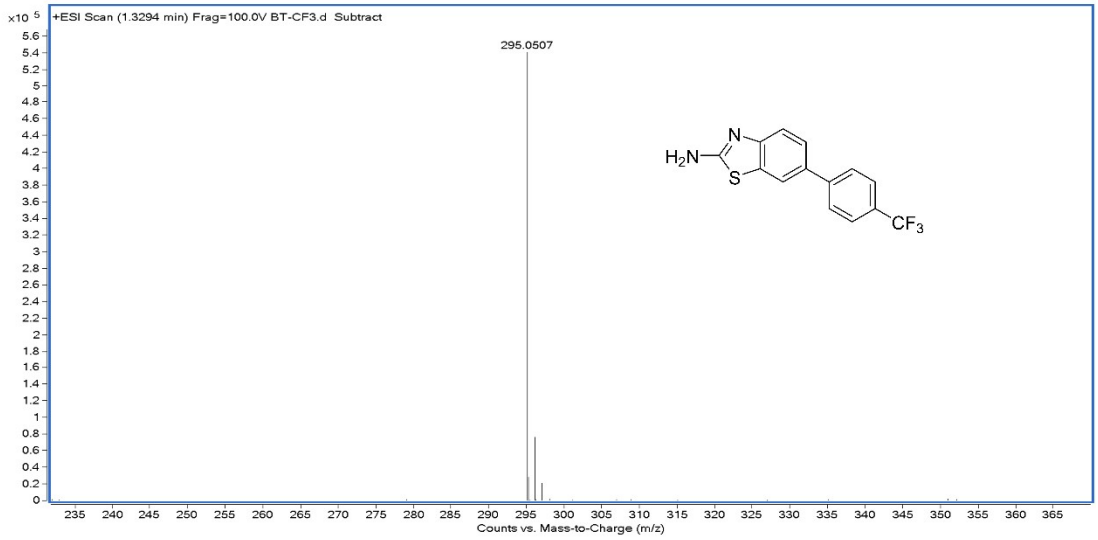


Fig. S20 HR-MS (ESI) of **BCF$_3$**

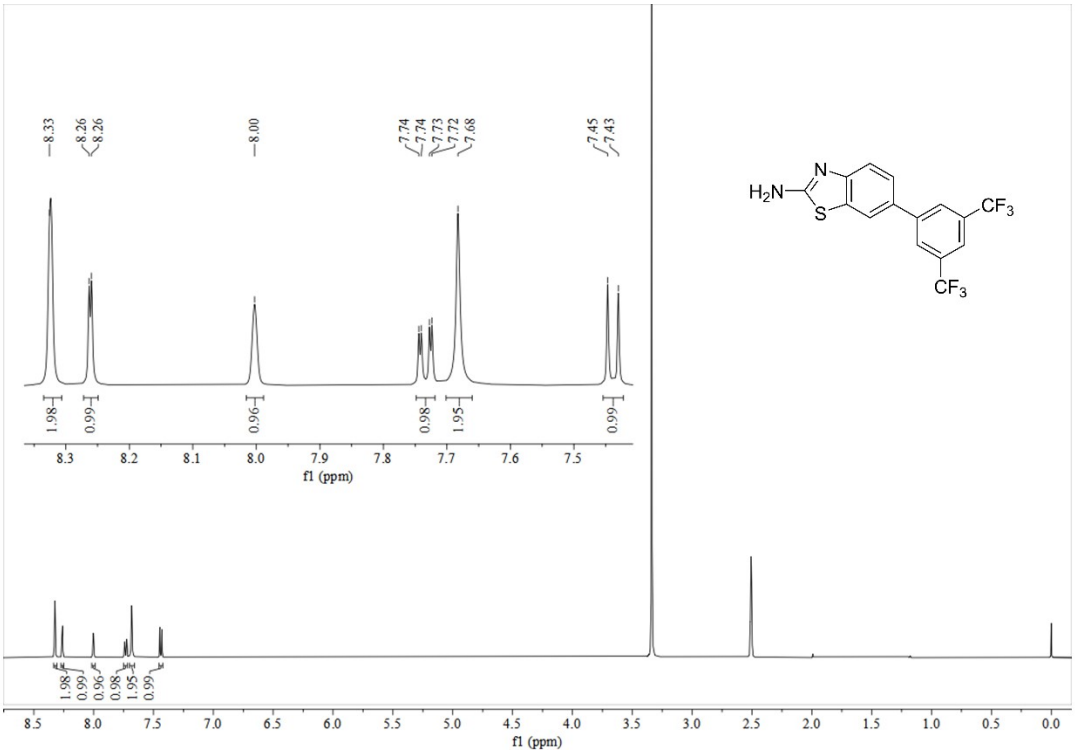


Fig. S21 ^{1}H-NMR of **B2CF$_3$** (400 Hz, DMSO-d_6)

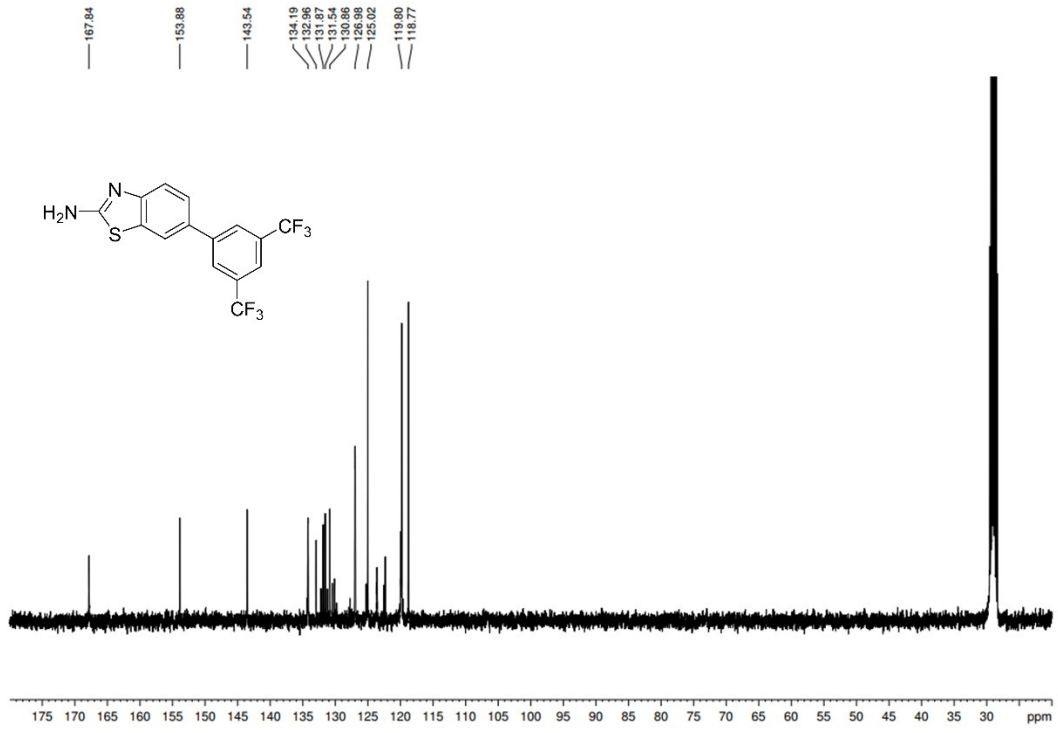


Fig. S22 ^{13}C-NMR of **B2CF$_3$** (100 Hz, DMSO-d_6)

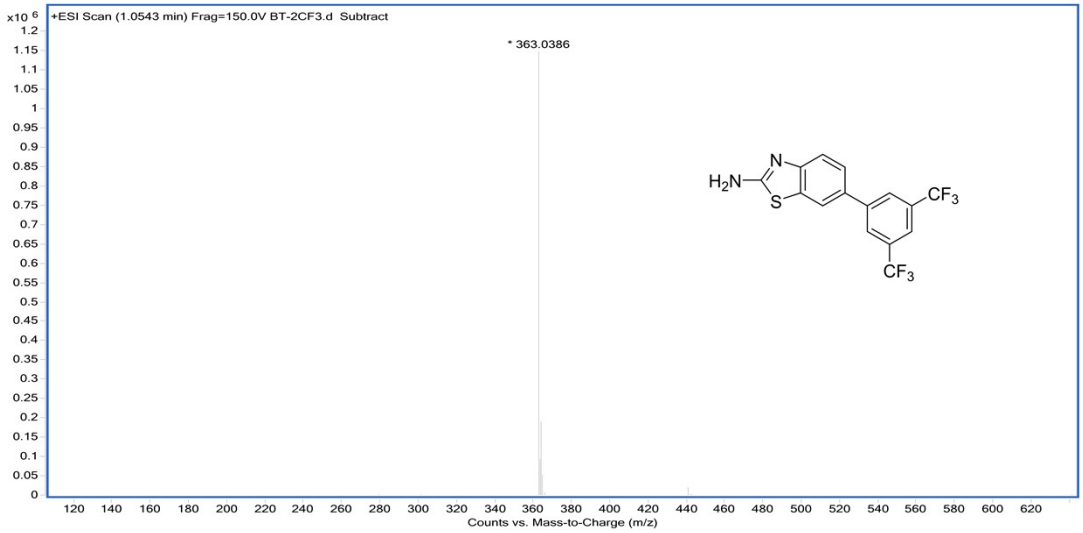


Fig. S23 HR-MS (ESI) of **B2CF$_3$**

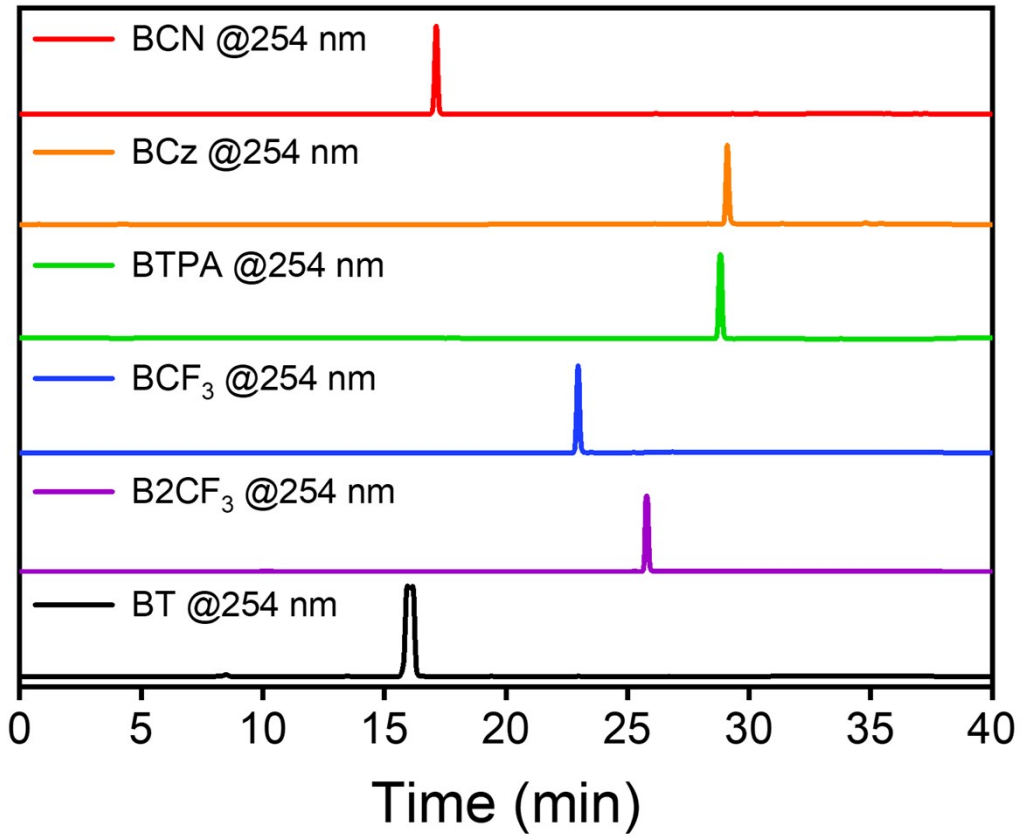


Fig. S24 HPLC purity assessment of the host and synthesized guests.

Photophysical Property

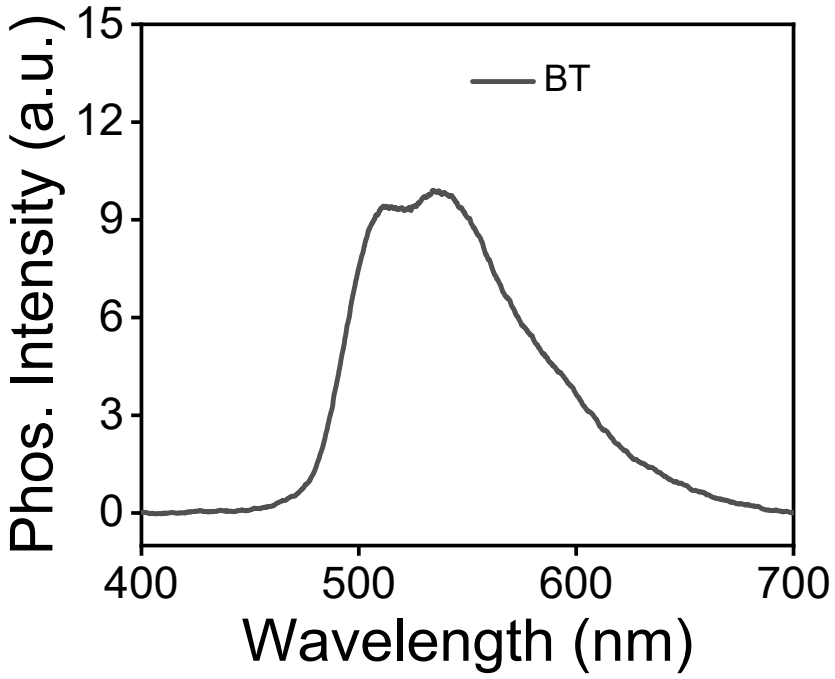


Fig.S25 Delayed emission spectra of the host (**BT**)

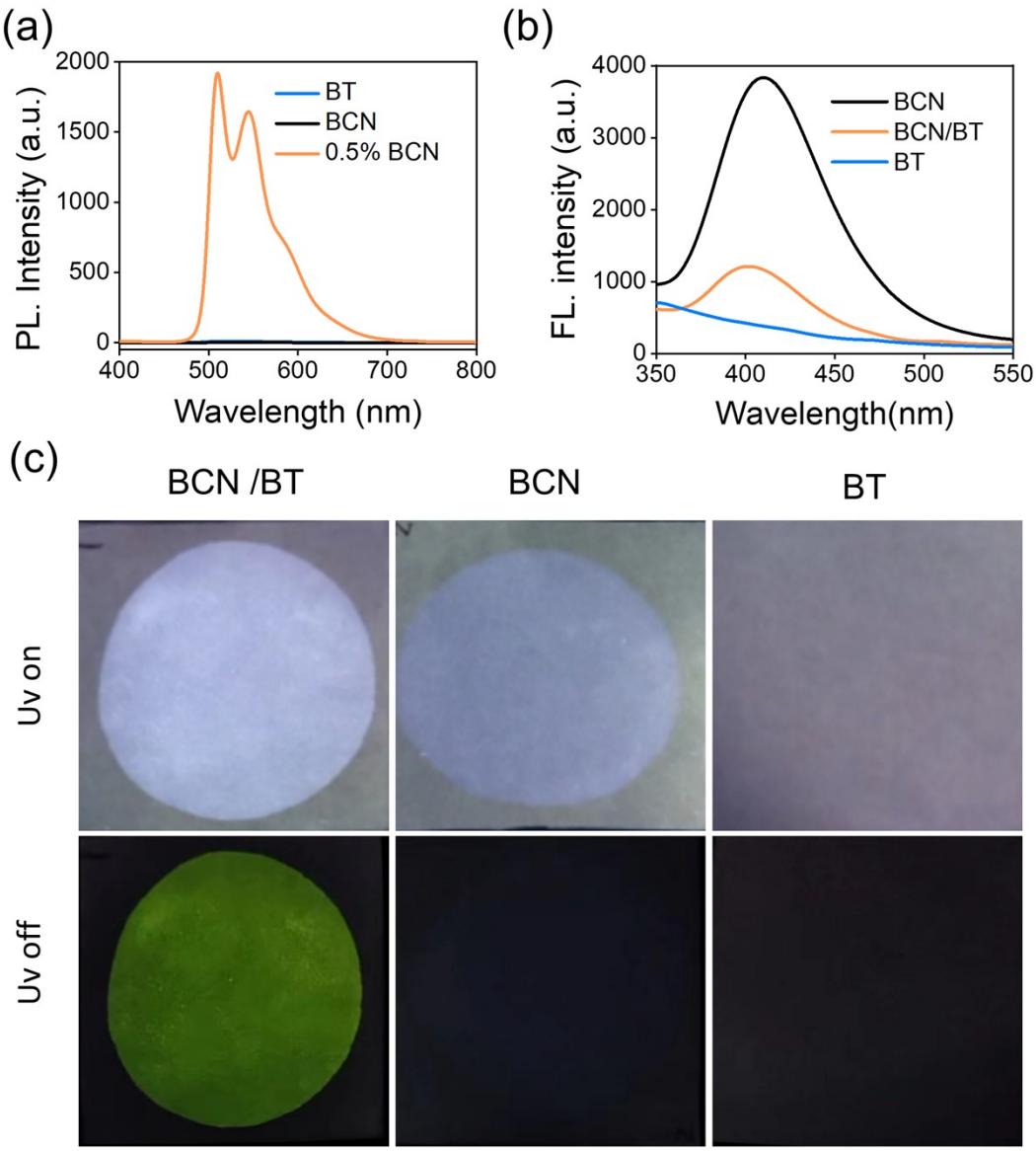


Fig.S26 (a) Delayed emission spectra of the host (BT), guest (BCN), and Host-Guest doped materials (0.5% BCN in BT). (b) Steady state fluorescence spectral of the host (2 mM BT in filter paper), guest (0.01 mM **BCN** in filter paper), and Host-Guest doped materials (0.01 mM **BCN** and 2 mM BT in filter paper). (Delayed emission spectra: Ex. = 365 nm, Delayed time: 25 ms) (c) Luminescence photos of the Host-Guest doped materials in filter paper.

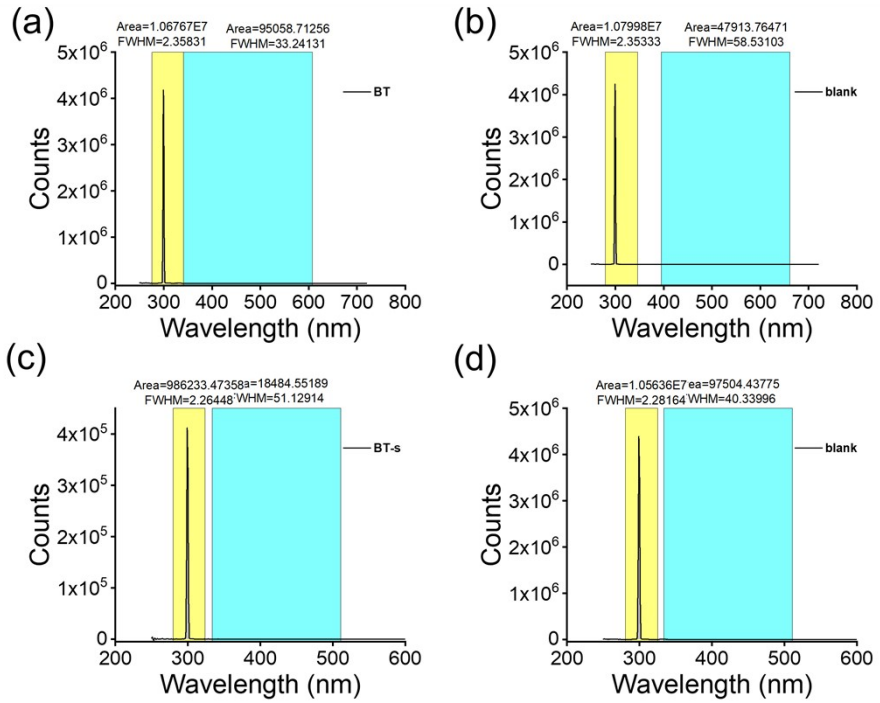


Fig.S27 (a) Fluorescence spectra obtained using an integrating sphere of the **BT** in acetonitrile (10 μM). (b) Fluorescence spectra obtained using an integrating sphere of the acetonitrile. (c) Fluorescence spectra obtained using an integrating sphere of the **BT** (powder). (d) Fluorescence spectra obtained using an integrating sphere of the blank.

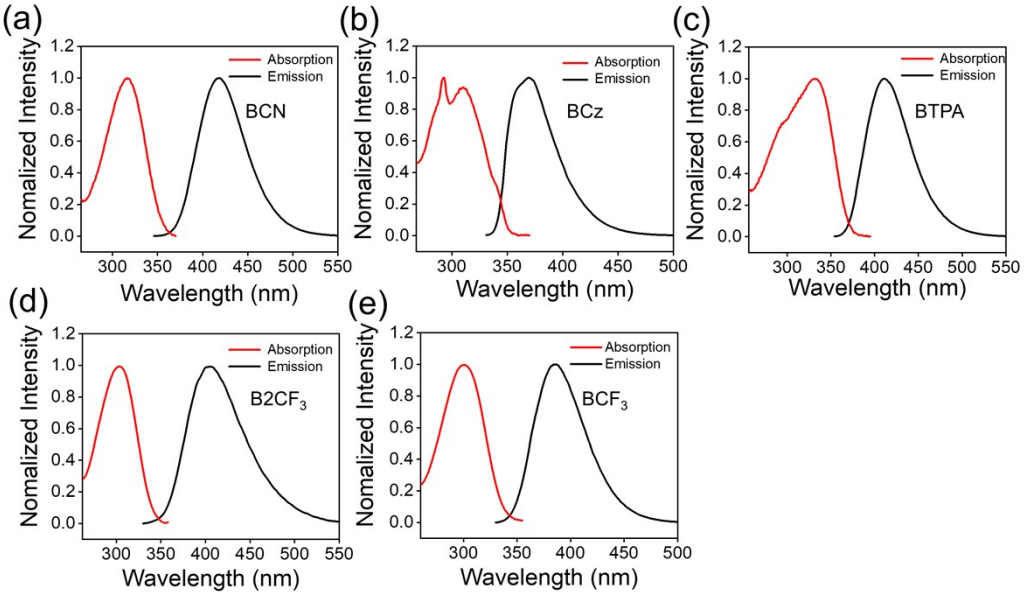


Fig. S28 Normalized Uv-visible absorption and fluorescence spectra of guest molecules (10 μM) in acetonitrile.

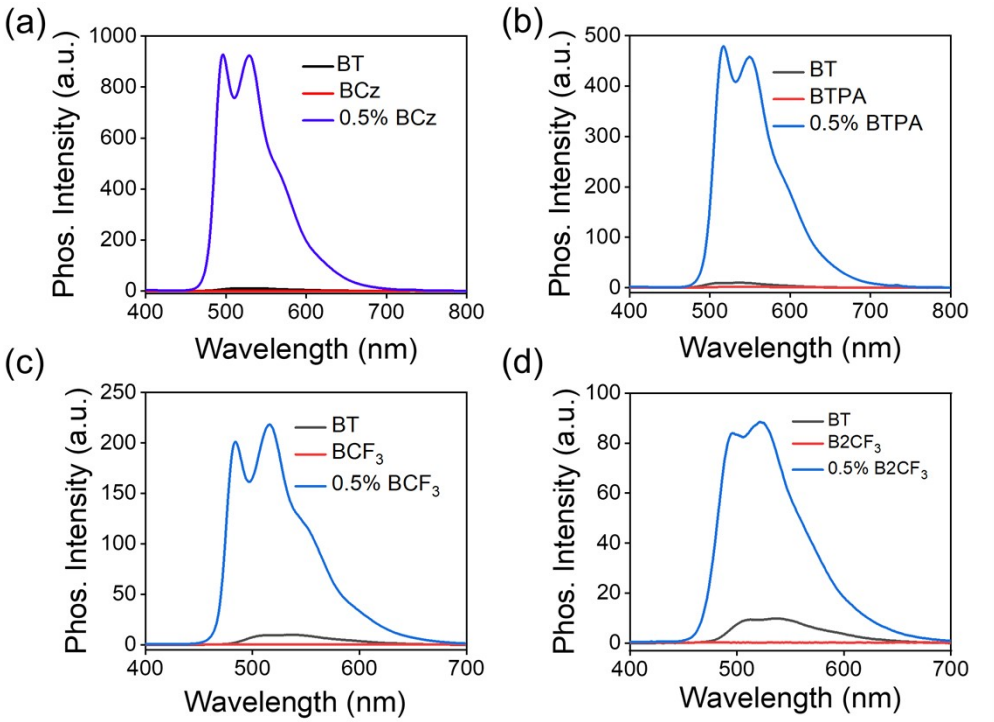


Fig.S29 (a)Delayed emission spectra of the host (BT), guest (BCz), and Host-Guest doped materials (0.5% BCz in BT). (b)Delayed emission spectra of the host (BT), guest (BTPA), and Host-Guest doped materials (0.5% BTPA in BT). (c)Delayed emission spectra of the host (BT), guest (BCF3), and Host-Guest doped materials (0.5% BCF3 in BT). (d)Delayed emission spectra of the host (BT), guest (B2CF3), and Host-Guest doped materials (0.5% B2CF3 in BT).

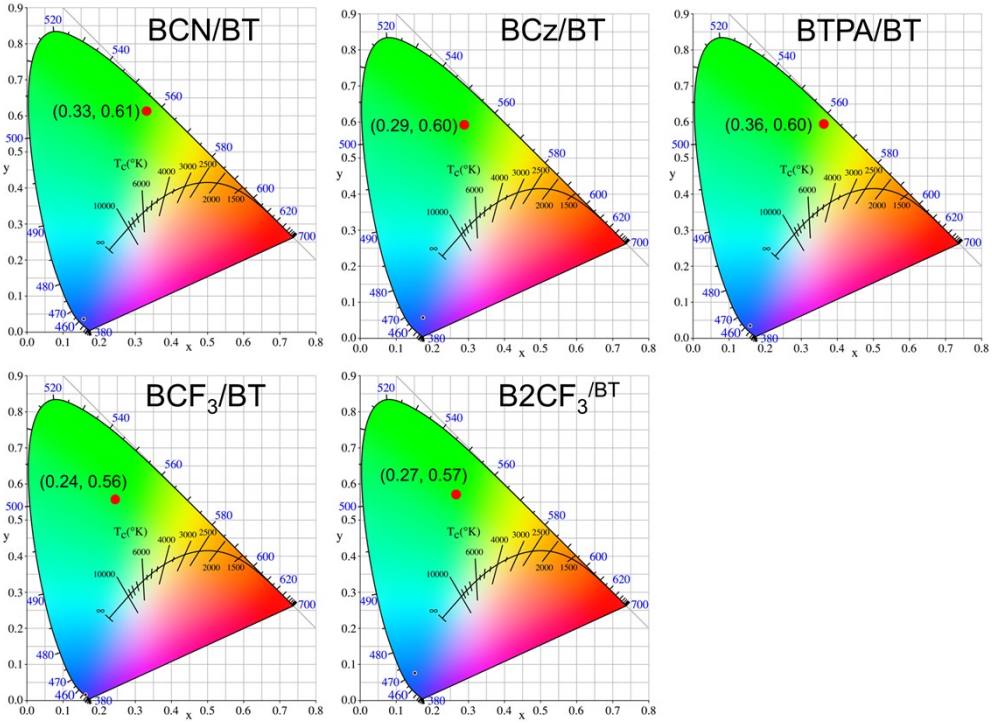


Fig.S30 Commission Internationale de l'Eclairage (CIE) coordinates of the doping system

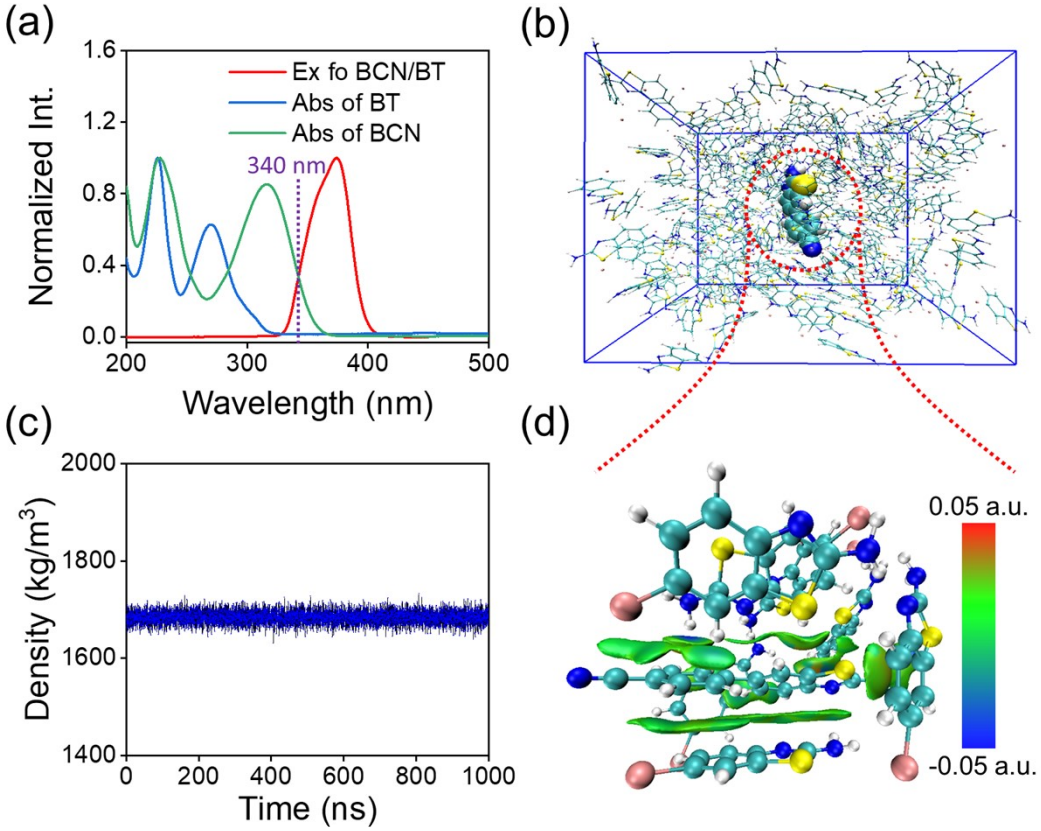


Fig. S31. (a) The Uv-visible absorption spectra of **BCN** and **BT**, and the excitation spectra of the **BCN/BT** doped system. (b) Schematic representation of the molecular dynamics simulation of the **BCN/BT** system. (c) Density curves during the MD simulation. (d) The intermolecular interaction was visualized by IGM.

Table S2 photophysical property parameters of pure host and guests

	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	Φ_{FL} (%)	$\Phi_{FL\text{-}S}$ (%)
BCN	315	416	101	≈100	3.87
BCz	310	369	59	60.96	1.36
BTPA	331	411	80	75.79	14.61
BCF_3	302	405	103	81.07	13.75
$B2CF_3$	301	386	85	14.66	NS
BT	271	NS	NS	NS	NS

Φ_{FL}: The absolute fluorescence quantum yield of the dilute solution in acetonitrile (10 μM) was determined using an integrating sphere; $\Phi_{FL\text{-}S}$: The absolute fluorescence quantum yield of the powder was determined using an integrating sphere. NS: no signal, indicates that no signal is detected.

Table S3 photophysical property parameters of doped materials

	λ_{FL} (nm)	λ_{PL} (nm)	τ_{PL} (ms)	Φ_{FL} (%)	Φ_{PL} (%)
BCN/BT	415	511	88.68	18.23	8.34
BCz/BT	375	497	28.36	8.17	4.02
BTPA/BT	402	517	53.69	5.48	0.91
BCF_3/BT	380	516	10.03	2.90	0.66

B2CF$_3$/BT	372	522	7.99	3.23	0.58
BT(Host)		534	4.35	2.34	0.20

λ_{FL}: Maximum fluorescence emission wavelength; λ_{PL}: Maximum phosphorescence emission wavelength; Φ_{FL}: The absolute fluorescence quantum yield of the doped system were determined using an integrating sphere; Φ_{PL}: The absolute phosphorescence quantum yield of the doped system were determined using an integrating sphere. T_{PL}: Phosphorescence emission lifetimes of the doped system.

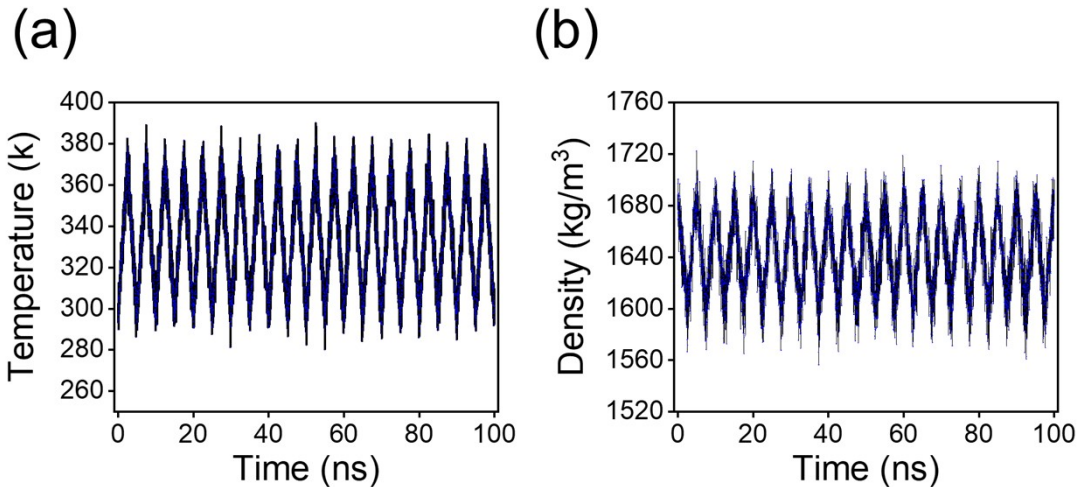


Fig.S32 Temperature and density variation during periodic annealing simulation

Table S4 Singlet excited state parameters and orbital contributions of **BCN/BT** molecular clusters

Excited state	Energy (eV)	Strength oscillator (*f*)	Contribution
S_1	3.215	0.0395	H -> L 98.9%
S_2	3.523	0.0011	H-1 -> L 94.0%
S_3	3.675	0.0007	H-2 -> L 96.7%
S_4	3.8518	0.2185	H-4 -> L 90.1%
S_5	3.8846	0.0012	H-3 -> L 92.0%
S_6	3.9109	0.0097	H-1 -> L+1 61.4%; H-1 -> L+2 21.3%; H-2 -> L+1 6.7%
S_7	3.9441	0.0033	H -> L+1 27.6%; H -> L+4 21.5%; H -> L+3 14.9%; H -> L+10 6.2%; H -> L+5 5.8%; H -> L+2 5.6%
S_8	3.9777	0.0002	H -> L+1 44.0%; H -> L+2 20.3%; H -> L+4 13.6%; H -> L+3 6.3%

S_9	4.0384	0.0073	H-5 -> L 45.2%; H -> L+3 22.4%; H-6 -> L 10.7%; H -> L+2 8.0%
S_{10}	4.0479	0.0031	H -> L+2 43.8%; H-5 -> L 19.4%; H -> L+1 13.7%; H -> L+3 7.9%; H -> L+4 7.4%

H: HOMO, highest occupied molecular orbital; L: LUMO, lowest unoccupied molecular orbital

Crystallography

Table S6 Crystallographic parameters of **BT**, **BCN** and **BCz**

	BT	**BCN**	**BCz**
CCDC	2259073	2092483	2108890
Empirical formula	$C_{14}H_{10}Br_2N_4S_2$	$C_{14}H_9N_3S$	$C_{25}H_{17}N_3S$
Formula weight	458.2	251.3	391.47
Temperature (K)	301(2)	302(2)	301(2)
Wavelength (Å)	0.71073	1.54178	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	Pna21	$P2_1/n$	$P2_1/c$
a (Å)	17.2218(7)	7.51440(10)	10.7111(3)
b (Å)	4.0384(2)	8.8611(2)	8.8354(3)
c (Å)	22.4366(10)	17.9123(3)	21.0030(7)
α (°)	90	90	90
β (°)	90	101.2480(10)	101.7500(10)
γ (°)	90	90	90
V(Å^3)	1560.43(12)	1169.80(4)	1946.01(11)
Z_{value}	4	4	4
ρ(g·cm^{-3})	*1.95*	1.427	1.336
μ (mm^{-1})	*5.462*	2.309	0.183
F(000)	896	520	816
Crystal size (mm)	0.250 x 0.220 x 0.200	0.240 x 0.210 x 0.170	0.240 x 0.200 x 0.160
Limiting indices	-22<=h<=22, -5<=k<=5, -29<=l<=29	-9<=h<=9, -10<=k<=10, -21<=l<=21	-12<=h<=12, -10<=k<=10, -25<=l<=25
Completeness to theta = 67.679	99.70%	99.10%	99.60%
Goodness-of-fit on F^2	1.133	1.029	1.035
R1,wR2 [I>2σ(I)]	0.0548, 0.1542	0.0405, 0.1078	0.0465, 0.1147
R indices (all data)	0.0661, 0.1608	0.0486, 0.1186	0.0686, 0.1320

Table S7 Crystallographic parameters of **BTPA**, **BCF_3** and **$B2CF_3$**

	BTPA	**BCF_3**	**$B2CF_3$**
CCDC	2098590	2098589	2092484
Empirical formula	$C_{25}H_{19}N_3S$	$C_{14}H_9N_2F_3S$	$C_{15}H_8F_6N_2S$
Formula weight	393.49	294.29	362.29
Temperature (K)	298(2)	298(2)	302(2)
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	P-1
a (Å)	17.3606(13)	12.0962(12)	8.5804(3)
b (Å)	10.3859(7)	9.1516(9)	9.4893(4)
c (Å)	11.4467(7)	11.7094(10)	10.4129(4)
α (°)	90	90	102.4300(10)
β (°)	97.743(3)	97.352(5)	109.290(2)
γ (°)	90	90	107.080(2)
V(Å^3)	2045.1(2)	1285.6(2))	717.67(5)
Z_{value}	4	4	2
ρ(g·cm^{-3})	1.278	1.521	1.677
μ (mm^{-1})	0.174	0.278	2.691
F(000)	824	600	364
Crystal size (mm)	0.300 x 0.200 x 0.100	0.240 x 0.140 x 0.120	0.320 x 0.200 x 0.160
Limiting indices	-20<=h<=20, -12<=k<=12, -13<=l<=13	-14<=h<=14, -10<=k<=10, -14<=l<=13	-10<=h<=10, -11<=k<=11, -12<=l<=12
Completeness to theta = 67.679	99.90%	96.6%	99.10%
Goodness-of-fit on F^2	1.178	1.194	1.095
R1,wR2 [I>2σ(I)]	0.1001, 0.1225	0.0825, 0.1523	0.0806, 0.2296
R indices (all data)	0.1601, 0.1824	0.1973, 0.2110	0.0882, 0.2403

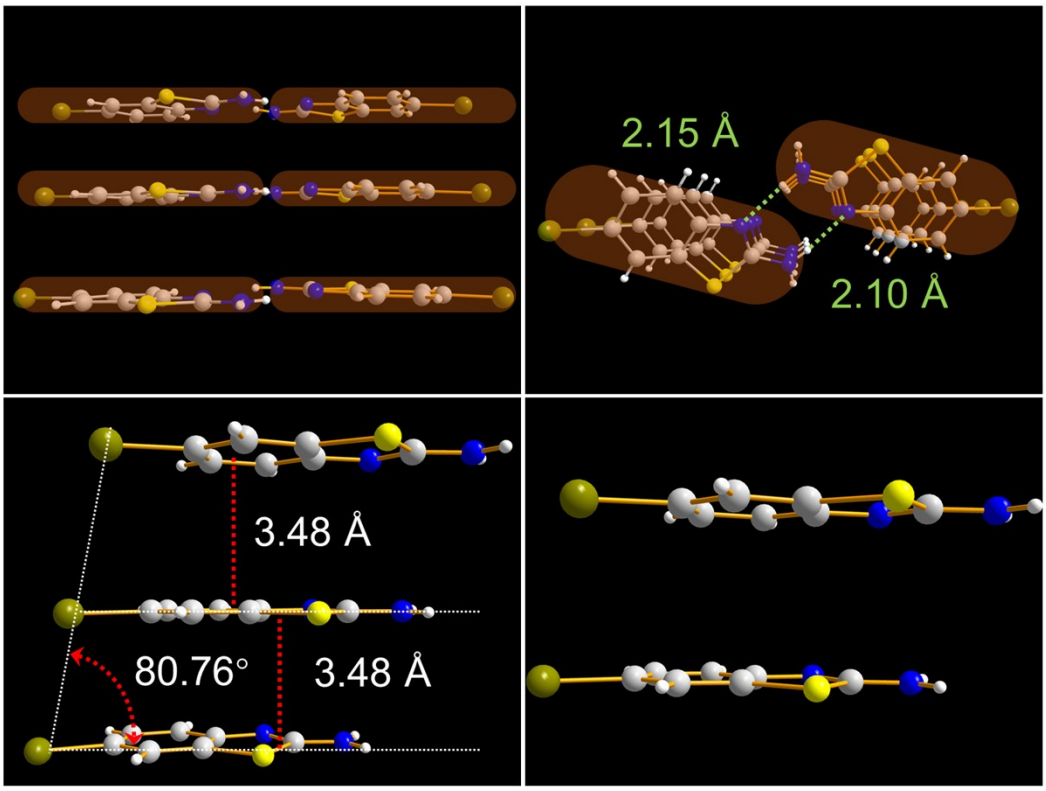


Fig. S33 The bulk form of the host (**BT**) molecule

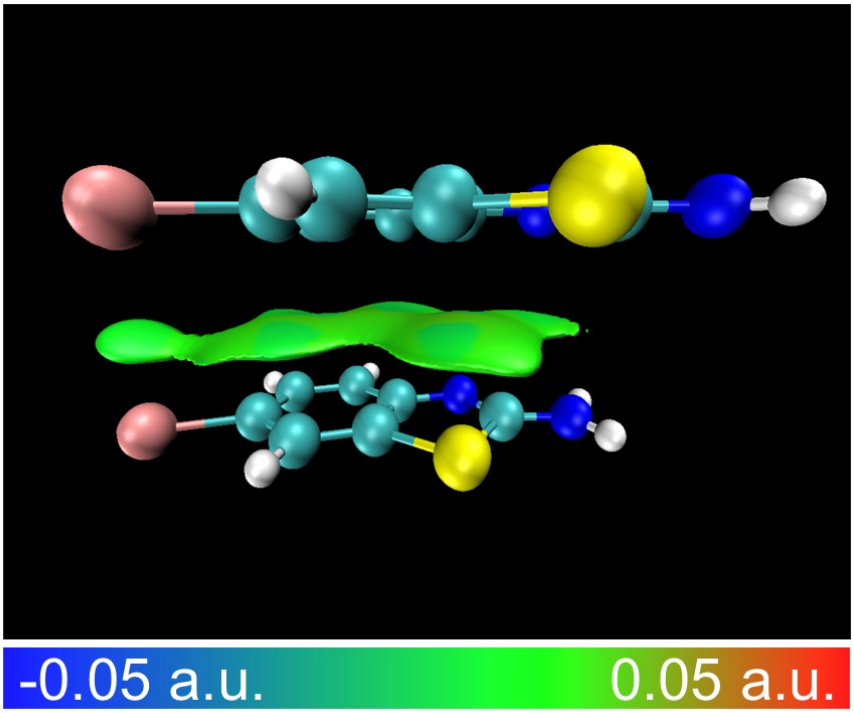


Fig. S34 The intermolecular interaction of **BT** was visualized by IGM.

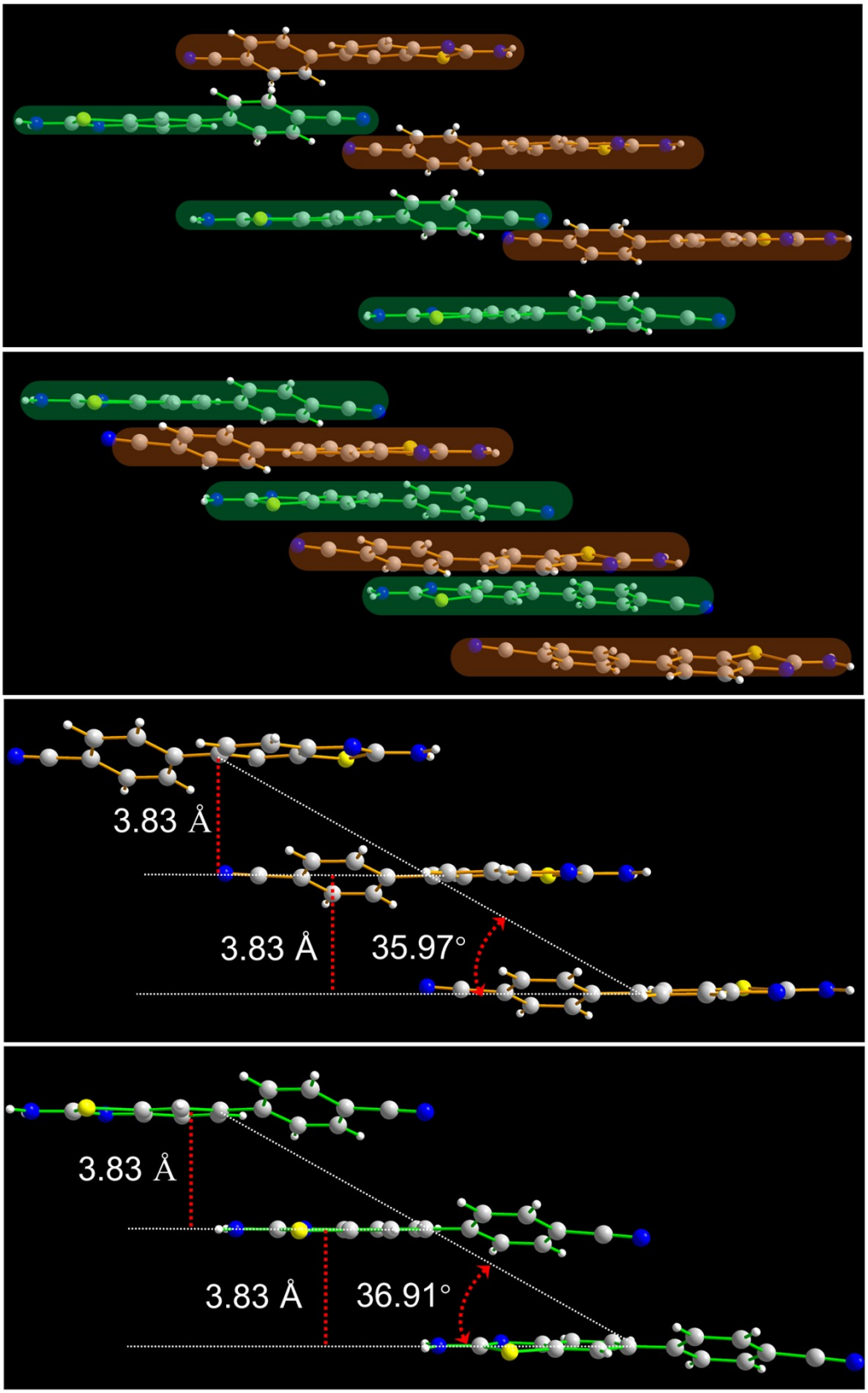


Fig. S35 The bulk form of the **BCN**

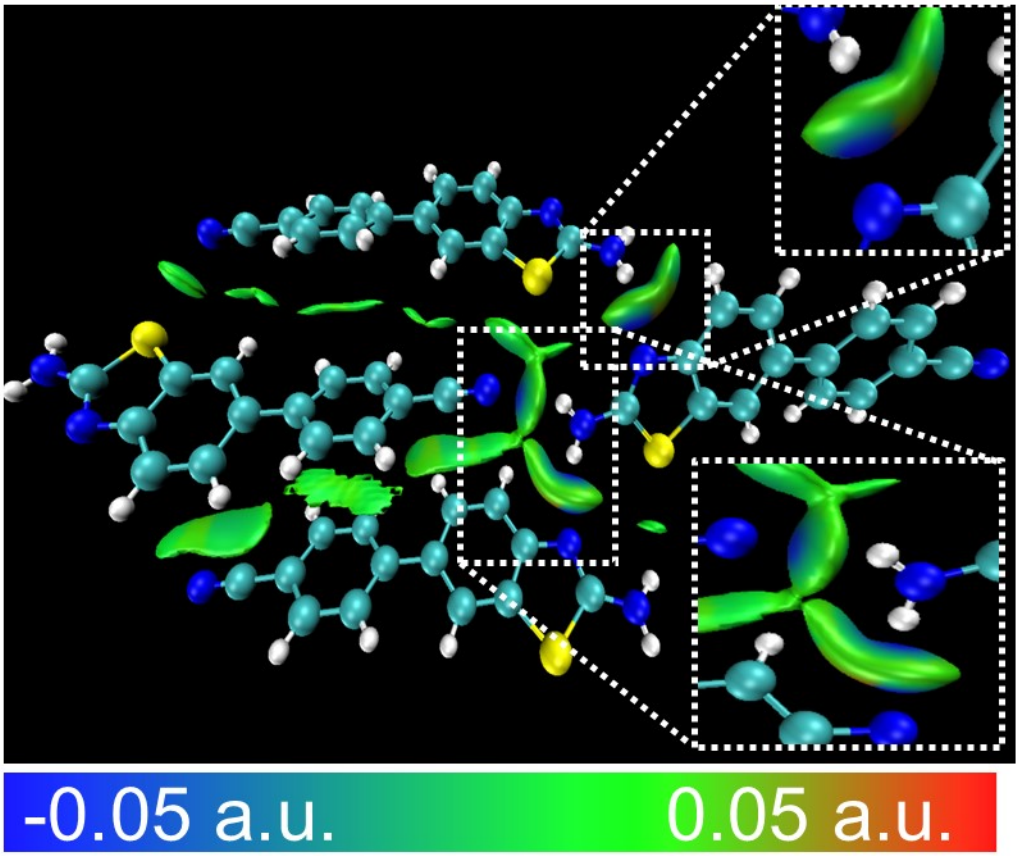


Fig. S36 The intermolecular interaction of **BCN** was visualized by IGM.

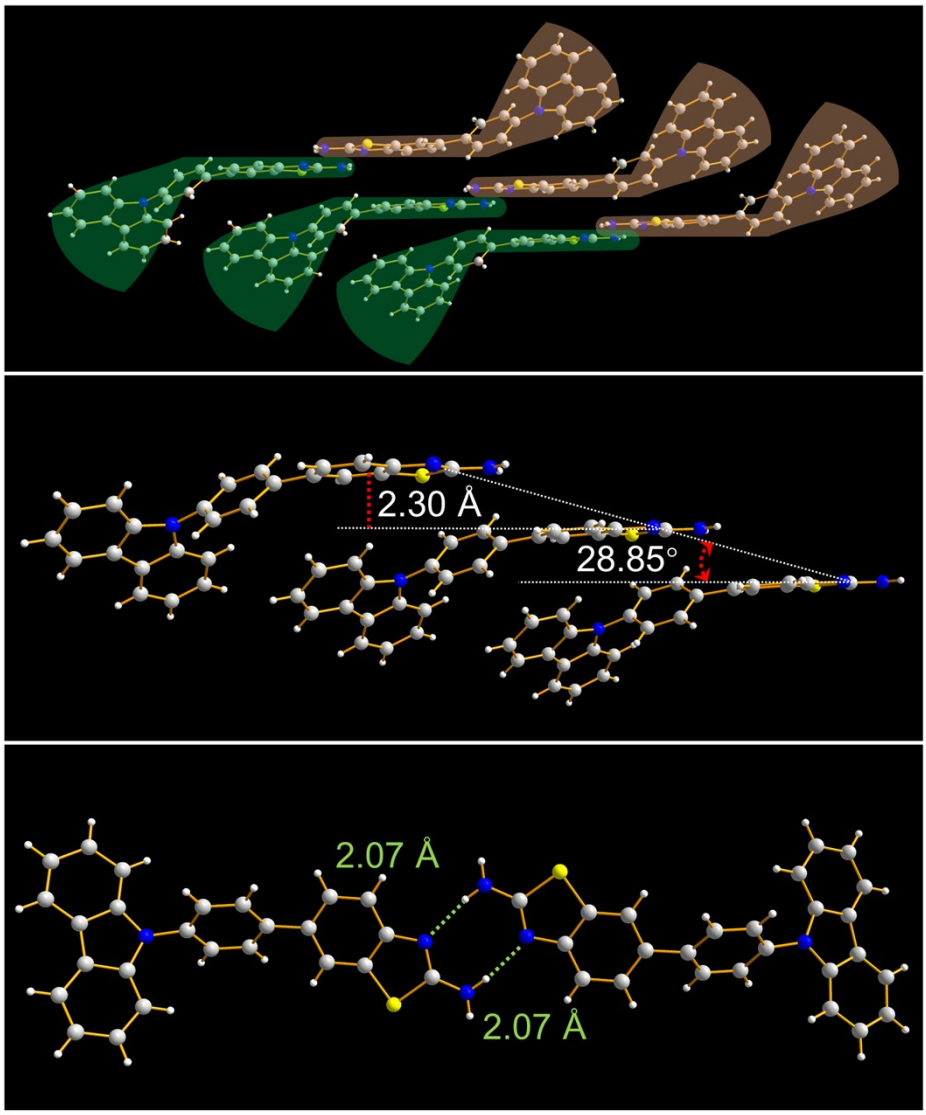


Fig. S37 The bulk form of the **BCz**

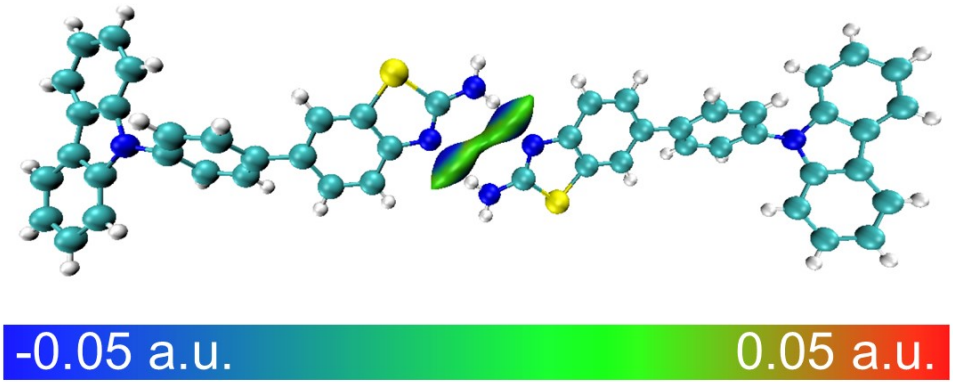


Fig. S38 The intermolecular interaction of **BCz** was visualized by IGM.

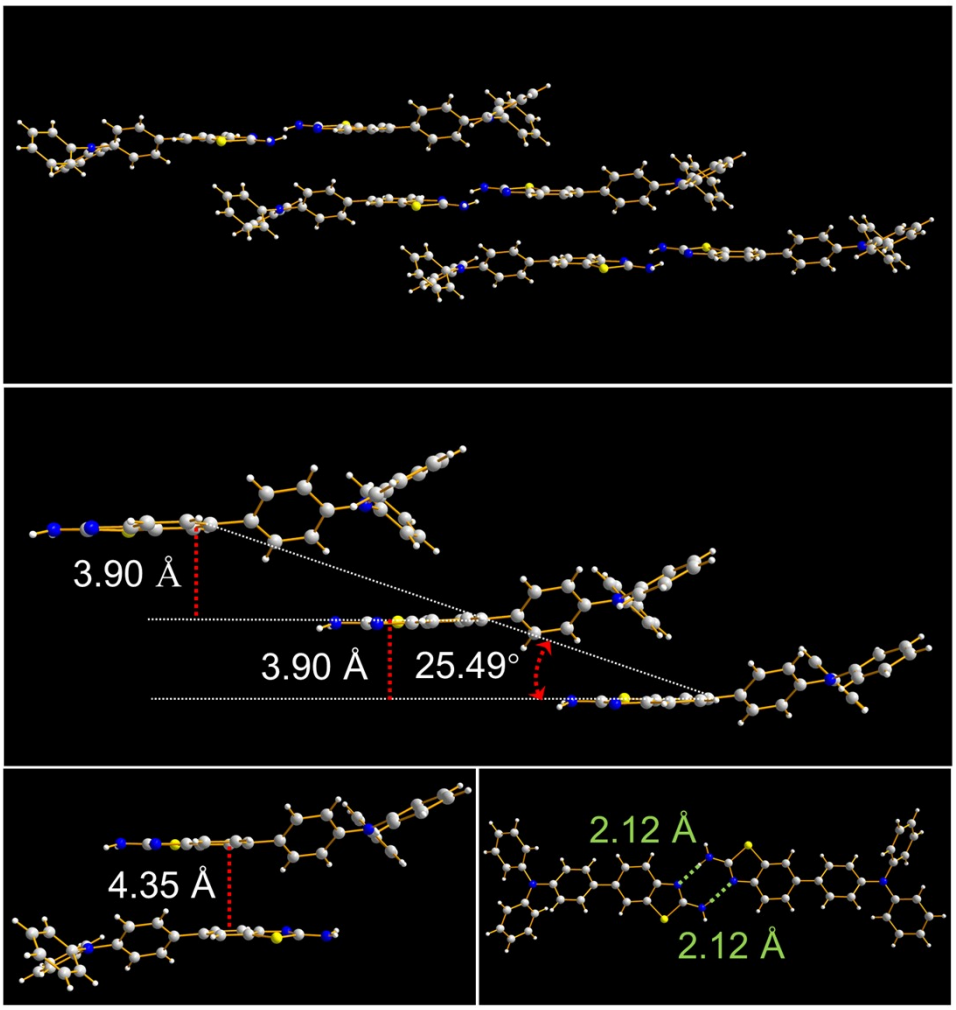


Fig. S39 The bulk form of the **BTPA**

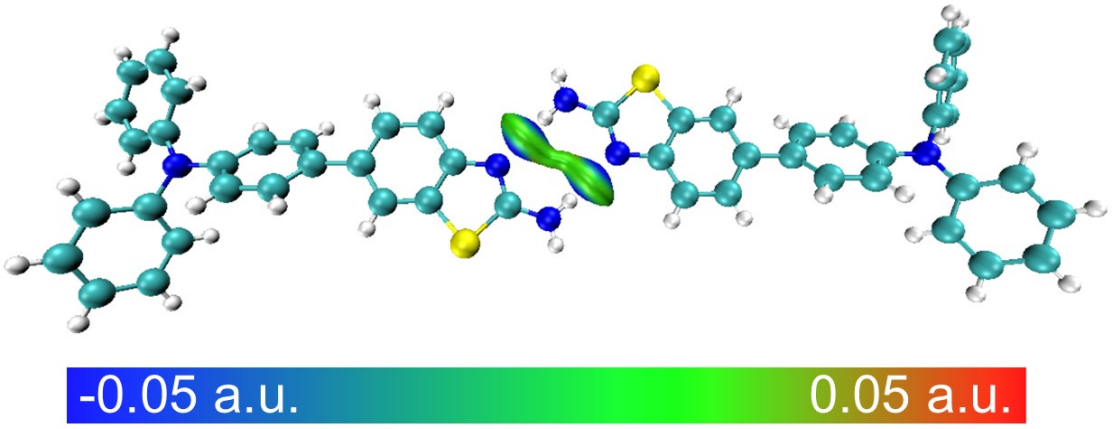


Fig. S40 The intermolecular interaction of **BTPA** was visualized by IGM.

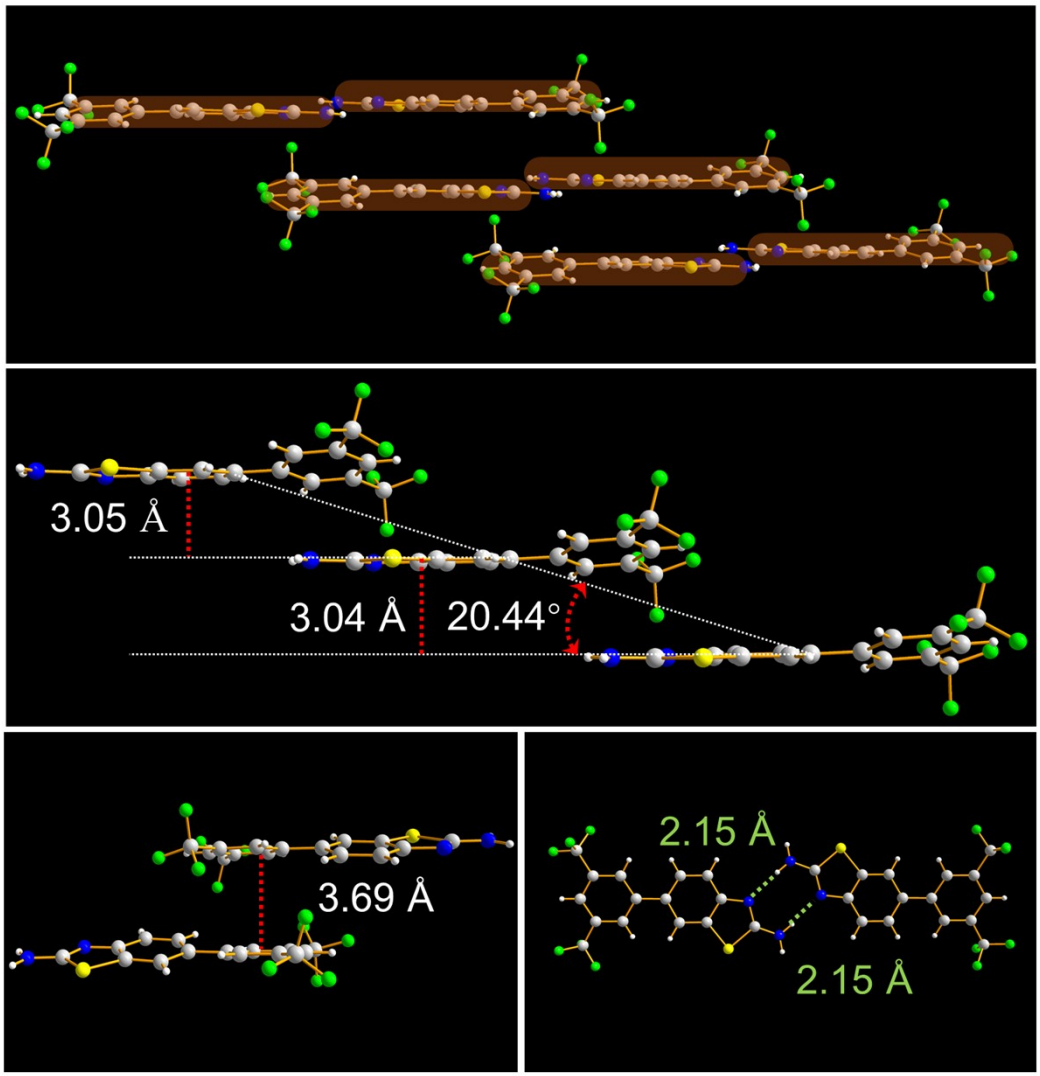


Fig. S41 The bulk form of the **B2CF$_3$**

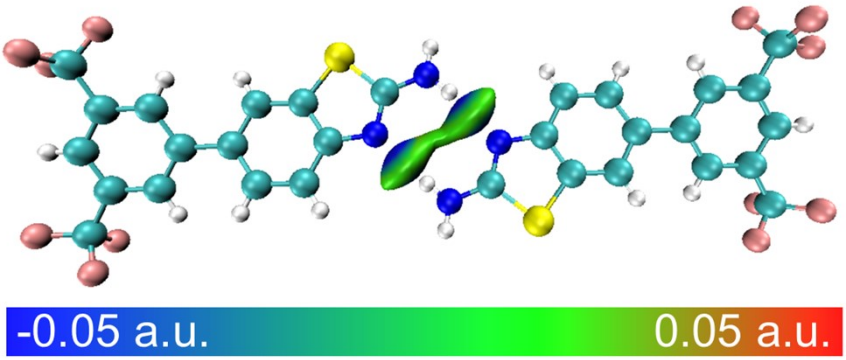


Fig. S42 The intermolecular interaction of **B2CF$_3$** was visualized by IGM.

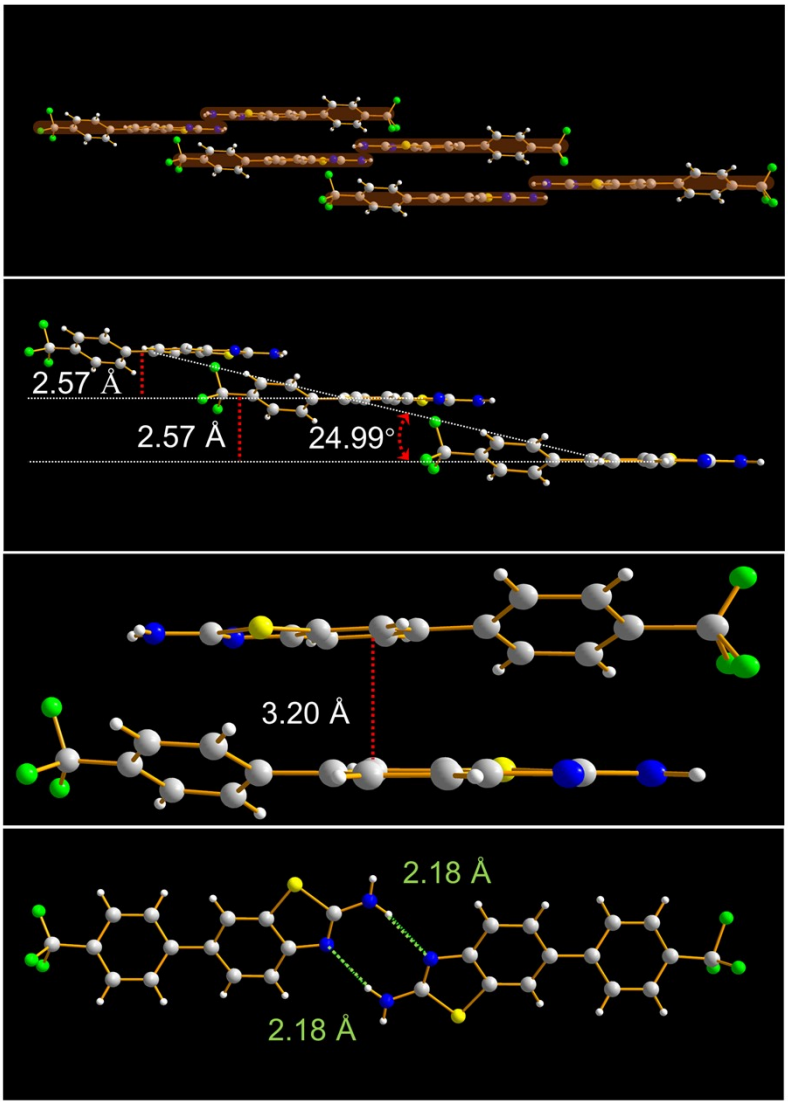


Fig. S43 The bulk form of the **BCF_3**

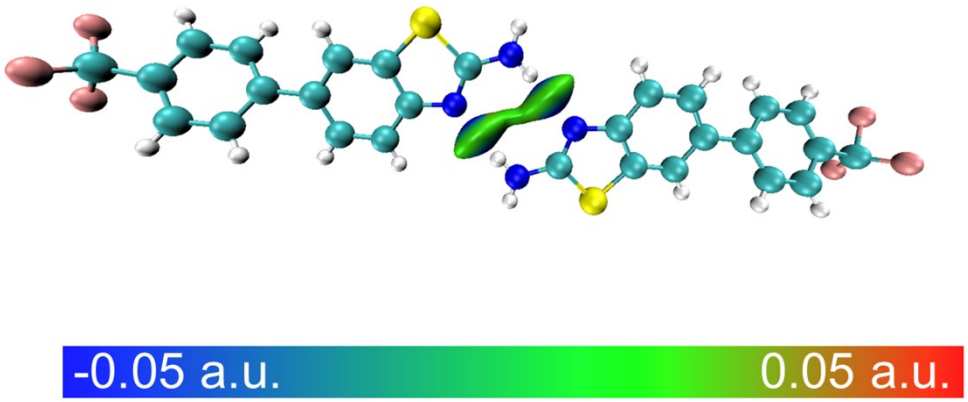


Fig. S44 The intermolecular interaction of **BCF_3** was visualized by IGM.

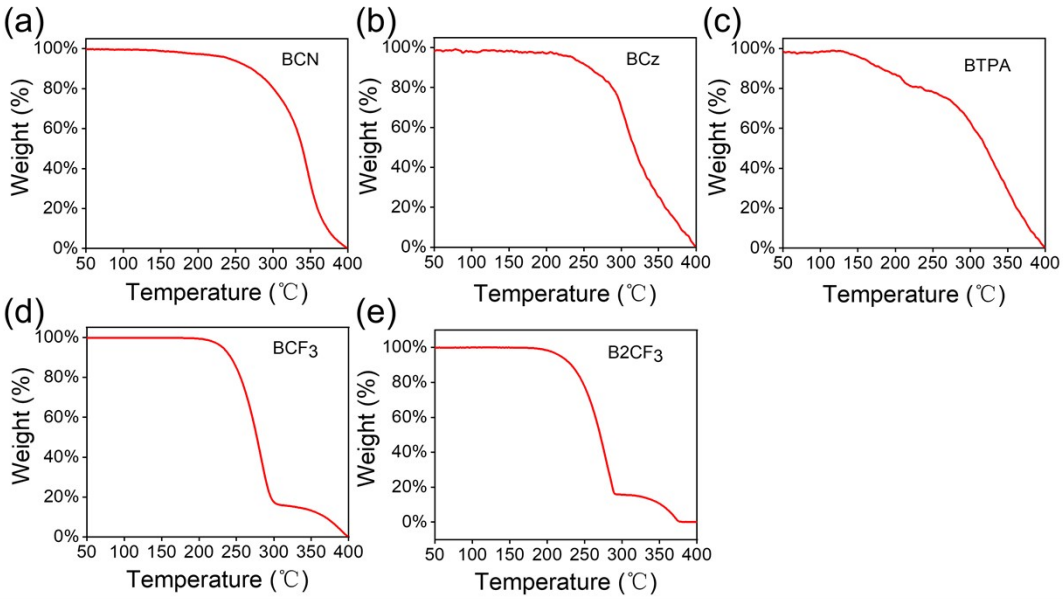


Fig.S45 TG curves of guest molecules.

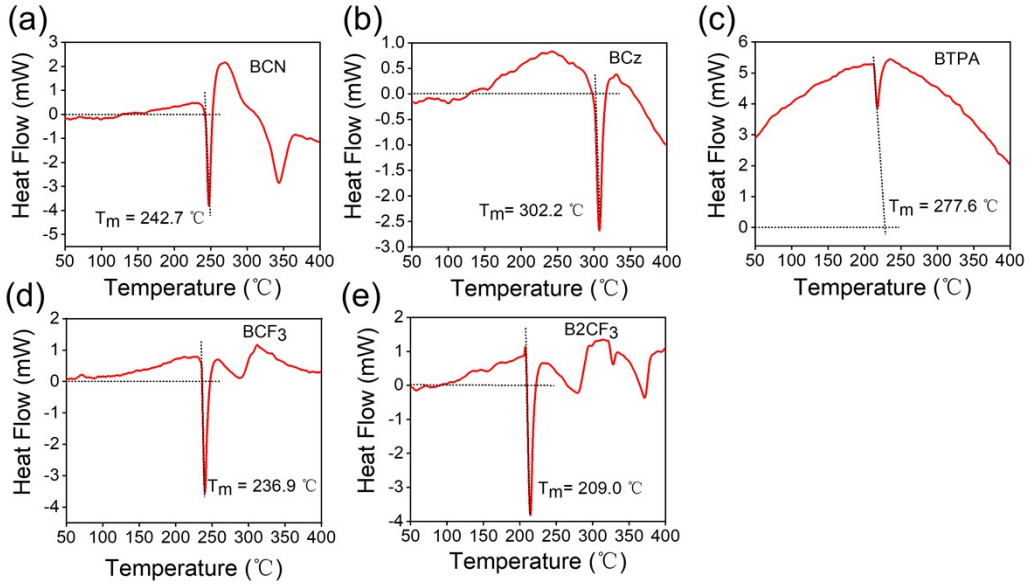


Fig.S46 DGS curves of guest molecules.

Cartesian coordinate

BT

C	-1.27526157	0.95510561	0.00000232
C	-0.88623503	-0.40876425	-0.00000274
C	0.44757554	-0.80033826	-0.00000939
C	1.40322455	0.21565923	-0.00000405
C	1.06397772	1.57042783	0.00000145
C	-0.28246163	1.94383196	0.00000155
N	-2.65198981	1.20181283	0.00000106

C	-3.36430743	0.10562525	-0.00000093
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Br	5.99433636	4.79216362	-1.70791480

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