

Thermal-responsive ground-state spin switching in novel butterfly-shaped overcrowded ethylene featuring a benzodithiophene core

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1. Experimental Section

Materials and General Methods: All reactions were carried out under nitrogen atmosphere in oven-dried glassware unless otherwise mentioned. All chemicals were purchased from Energy Chemical. Tetrahydrofuran, dichloromethane, petroleum ether, hexane, toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. 400 MHz ¹H, 101 MHz ¹³C spectra were recorded on a Bruker spectrometer. X-ray single crystals were obtained on a Bruker D8 X-ray single crystal Venture diffractometer using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). SAINT5.0 and SADABS programs are used for the reduction and absorption correction of crystal data. The resolution and refinement of the crystal structure are obtained on the SHELXTL-97 software. Using the direct or Patterson methods, all non-hydrogen source coordinates are obtained by using the differential Fourier method and the least square method. Then the geometric method and the difference value are used. The hydrogen atom coordinates were obtained by Fourier method, and the crystal structure was obtained. UV-visible absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer. The fluorescence data was measured on an Edinburgh Instruments FLS980 spectrophotometer. Fluorescent quantum efficiencies were determined using a Hamamatsu Quantaaurus-QY spectrometer (C11347-11). ESR was measured on Bruker A300-10/12.

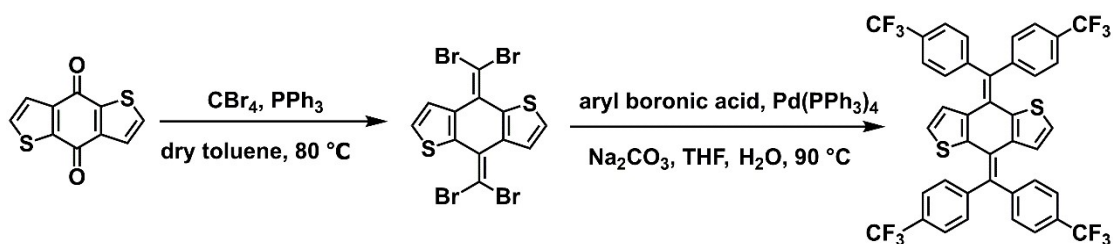
Computational Methods

Gaussian 16¹ package was used to perform the electronic structure theory calculations. The molecules were optimized using hybrid density functional, B3LYP, and 6-31G (d, p) basis set.^{2,3} BD molecule was optimized with all atoms relaxed. Constraint optimizations were carried on BD-42° and BD-87° molecules with dihedral fixed to 42° and 87°. The local minima of the optimized structures were verified with frequency calculations. The ground state of BD molecule is closed-shell singlet. The ground state of BD-42° and BD-87° molecules is triplet.

Table S1. Relative energy (kcal/mol) of singlet and triplet of the molecules with different dihedral at UB3LYP/6-31G(d,p) level of theory.

dihedral	BD	BD-42°	BD-87°
Singlet (open-shell) (Kcal/mol)	-	7.6	17.4
Singlet (closed-shell) (Kcal/mol)	0.0	8.5	36.1
Triplet (Kcal/mol)	4.7	5.5	17.1

2. Synthetic Procedures



4,8-bis(dibromomethylene)-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene (1)

A mixture of CBr_4 (6.63g, 20 mmol) and PPh_3 (10.48 g, 40 mmol) in 100 ml of dry toluene was stirred for 1 hour at room temperature before benzo [1,2-b:4,5-b'] dithiophene-4,8-dione (1.1 g, 5 mmol) was added in one portion and the solution was heated to 80 °C for 24 h. The reaction mixture was cooled to room temperature; the solid was removed by filtration and washed with toluene. The filtrates were rotavaped and the crude product obtained. The crude product was purified by flash chromatography on silica gel column using hexanes as eluent in 36% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) (ppm): 7.82 (d, 2H, $J = 4$ Hz), 7.30 (d, 2H, $J = 4$ Hz); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 138.3, 137.9, 132.4, 126.2, 124.4, 88.8. ESI-HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_5\text{Br}_4\text{S}_2$, 532.6526; found, 532.6520.

4,8-bis(bis(4-(trifluoromethyl)phenyl)methylene)-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene (BD) : 4,8-bis(dibromomethylene)-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene(213 mg, 0.4 mmol), (4-(trifluoromethyl)phenyl)boronic acid (380 mg, 2 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (120 mg, 0.1 mmol) were put into a 100 mL two-necked flask. A degassed THF (16 mL) was added under argon, the resulted solution was degassed by freeze-pump-thaw cycles. An aqueous solution (4 mL) of Na_2CO_3 (339 mg, 3.2 mmol) was added under argon. The mixture was further degassed by freeze-pump-thaw cycles and then stirred at 90°C overnight. The mixture was cooled to room temperature, THF was evaporated and the resulted residue was extracted with CH_2Cl_2 . The organic phase was washed with water and brine, dried with anhydrous Na_2SO_4 . Compound BD was isolated by column chromatography (Hexane/ $\text{CH}_2\text{Cl}_2 = 20:1$) as a yellow solid in 75% yield. $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2) (ppm): 7.63 (d, 4H, $J = 8$ Hz), 7.47 (t, 8H, $J = 8$ Hz), 7.30 (d, 4H, $J = 8$ Hz), 6.67 (d, 2H, $J = 8$ Hz), 6.20 (d, 2H, $J = 4$ Hz); ^{13}C NMR could not be obtained accurately due to the abundance is very low, $^{13}\text{C-NMR}$ (101 MHz, CD_2Cl_2) δ 147.3, 146.2, 140.2, 137.4, 135.2, 131.7, 131.0, 127.0, 126.1, 125.5, 124.8; ^{19}F NMR (400 MHz, CD_2Cl_2): -62.83 (d, 3F, $J = 24$ Hz); ESI-HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{40}\text{H}_{21}\text{F}_{12}\text{S}_2$ 793.0894; found, 793.0876.

3. Characterization of BD

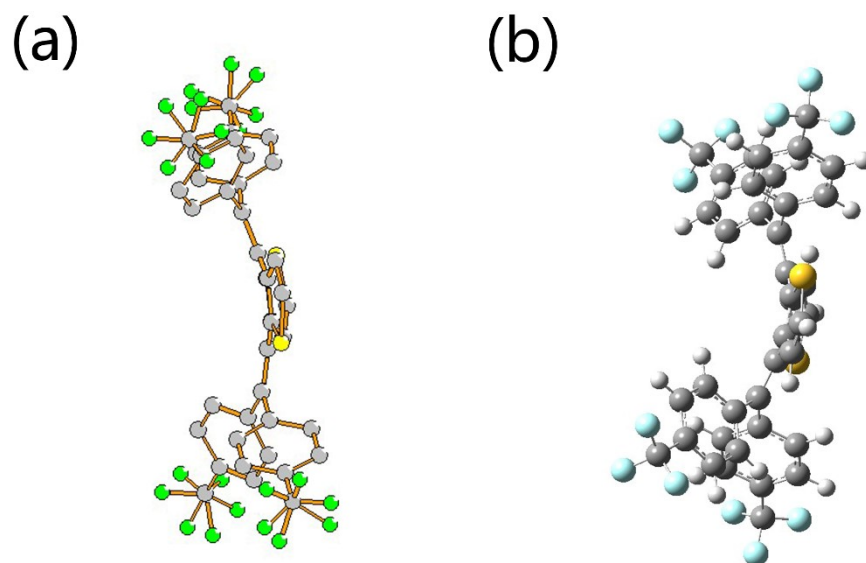
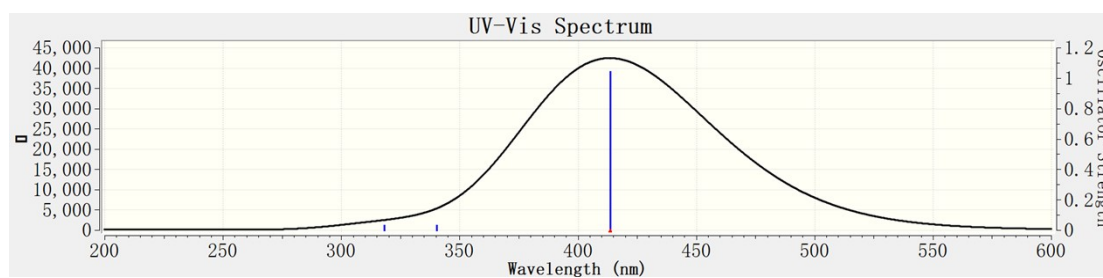
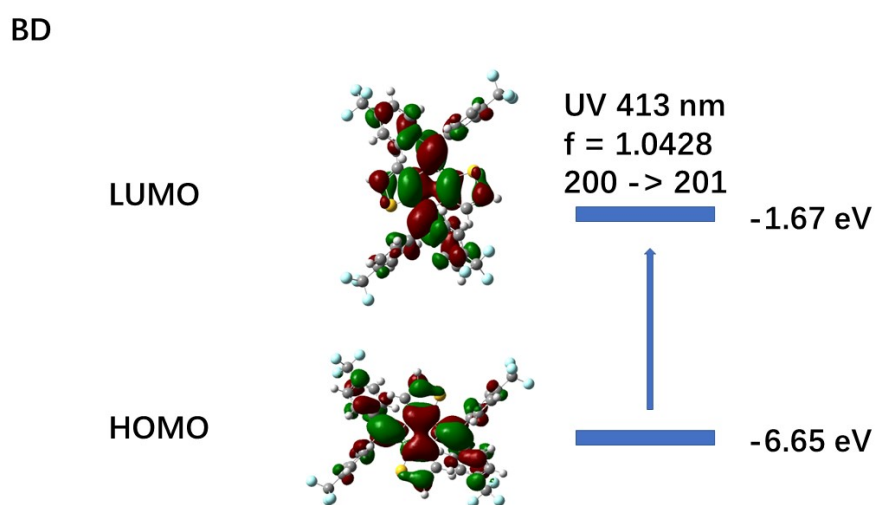
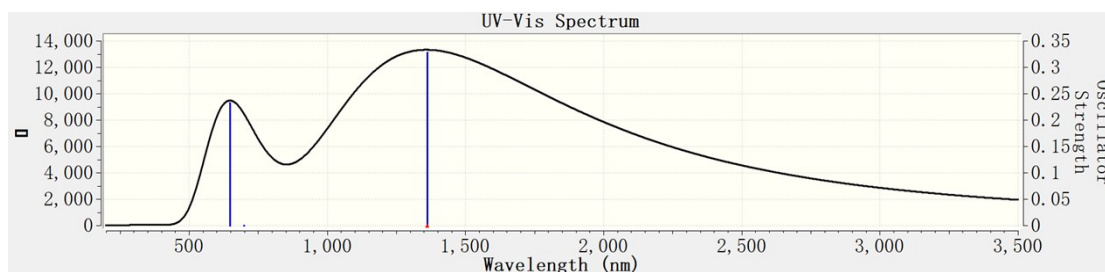
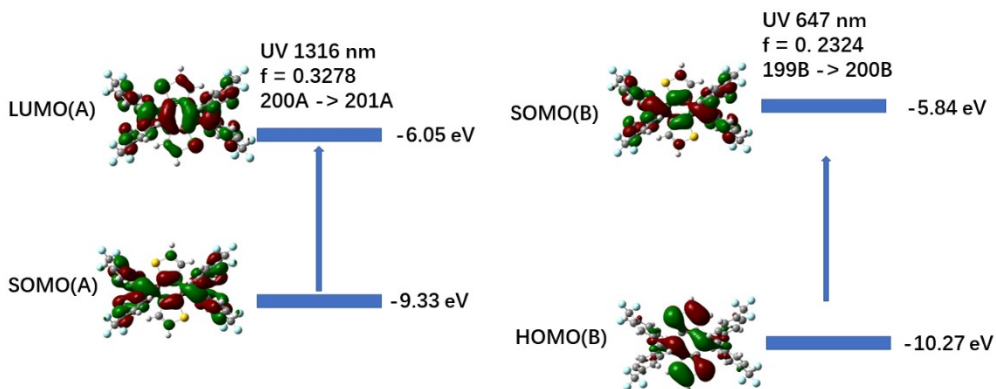


Figure S1. (a). X-ray structures of BD (b). Optimized structural by DFT calculations at the B3LYP- 6-31G (d, p) level of theory.



BD⁺



BD²⁺

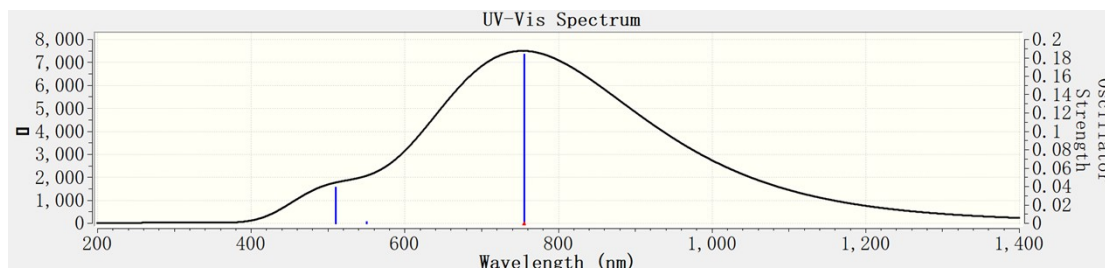
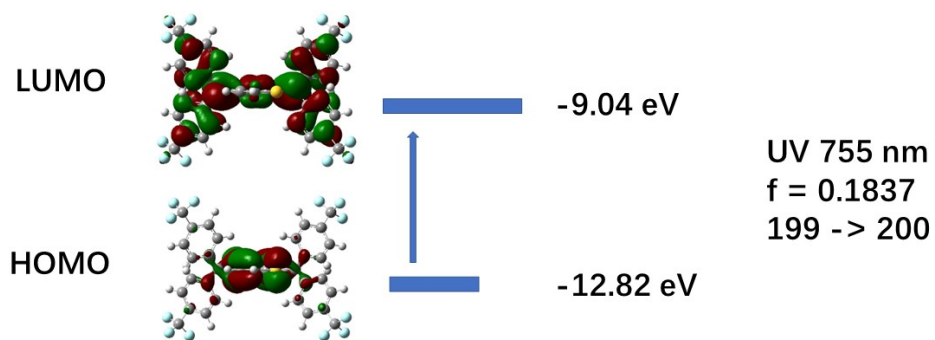


Figure S2. TD-DFT calculated results. (B3LYP/6-31G (d, p)).

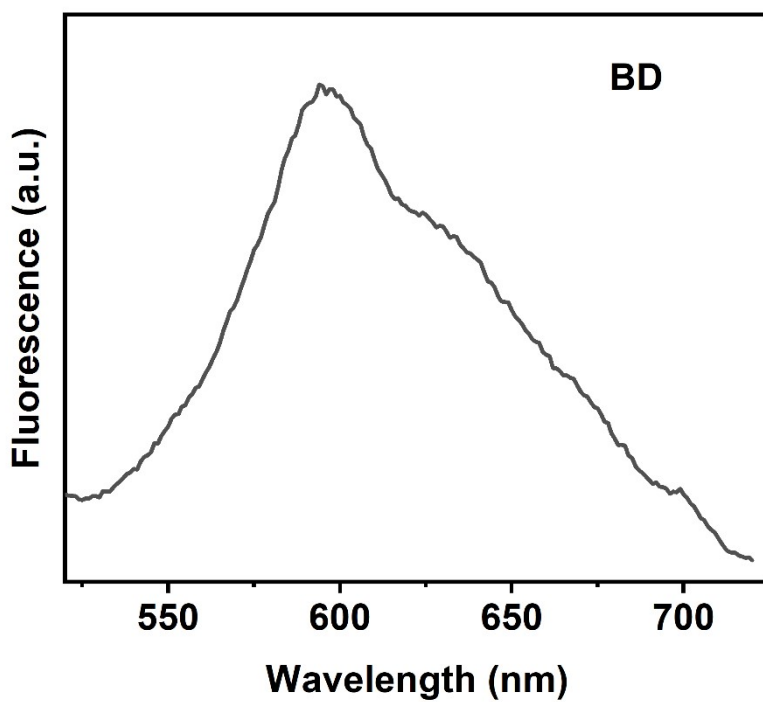


Figure S3. Solid fluorescence spectra of BD.

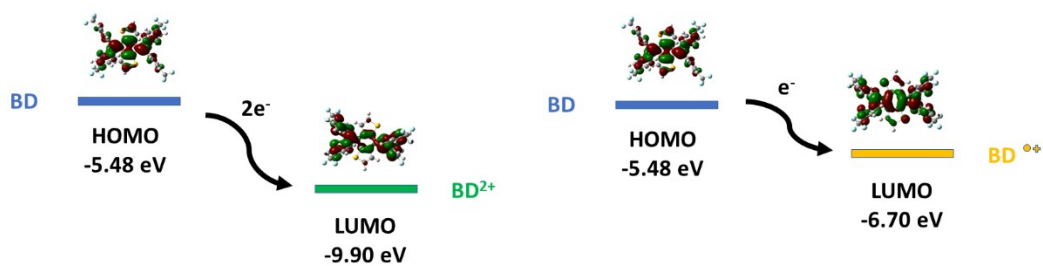


Figure S4. Energy diagram and frontier orbitals from the DFT calculation at the B3LYP/6-31G (d, p).

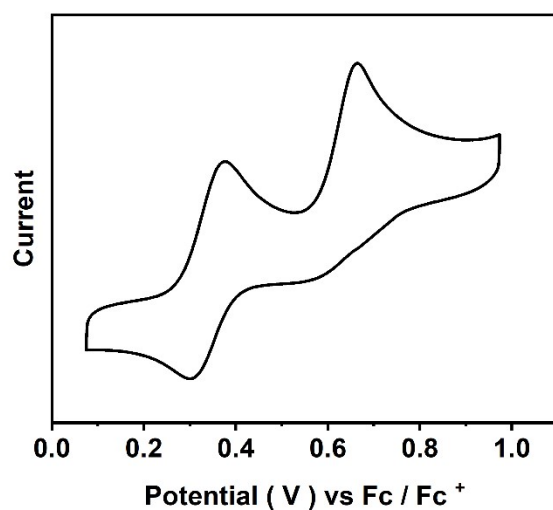


Figure S5. Cyclic voltammogram (CV) diagrams of BD showing the oxidation waves (recorded in CH_2Cl_2) vs Fc/Fc^+ , using $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) as the electrolyte, $v = 100$ mV/s.

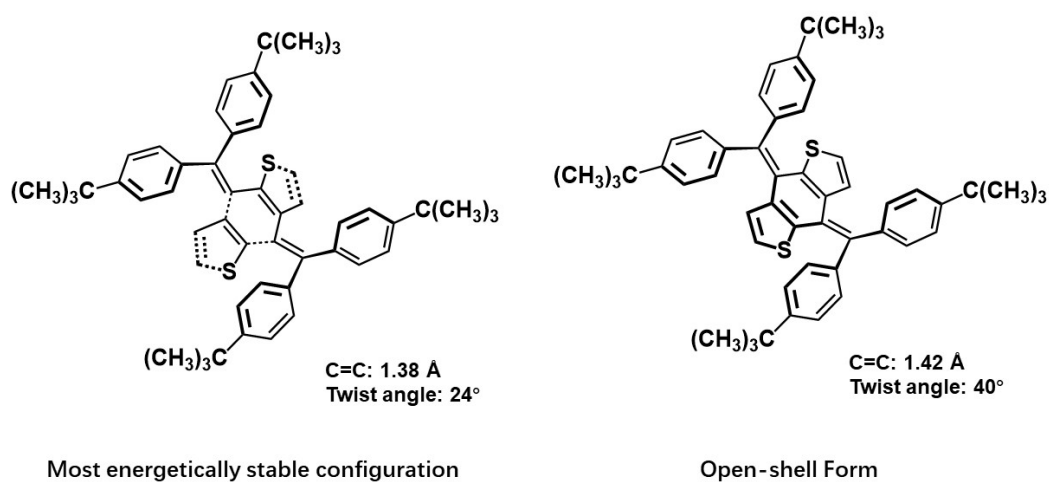


Figure S6. Various twisted geometries of BD- *t*Bu based on DFT calculations at the UB3LYP/6-31G (d, p) level of theory.

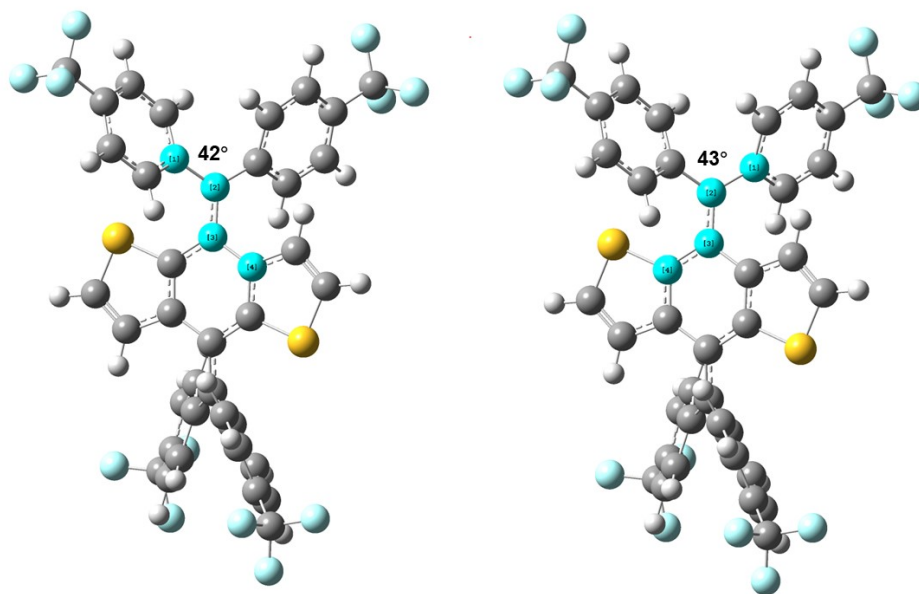


Figure S7. The definition of dihedral angles.

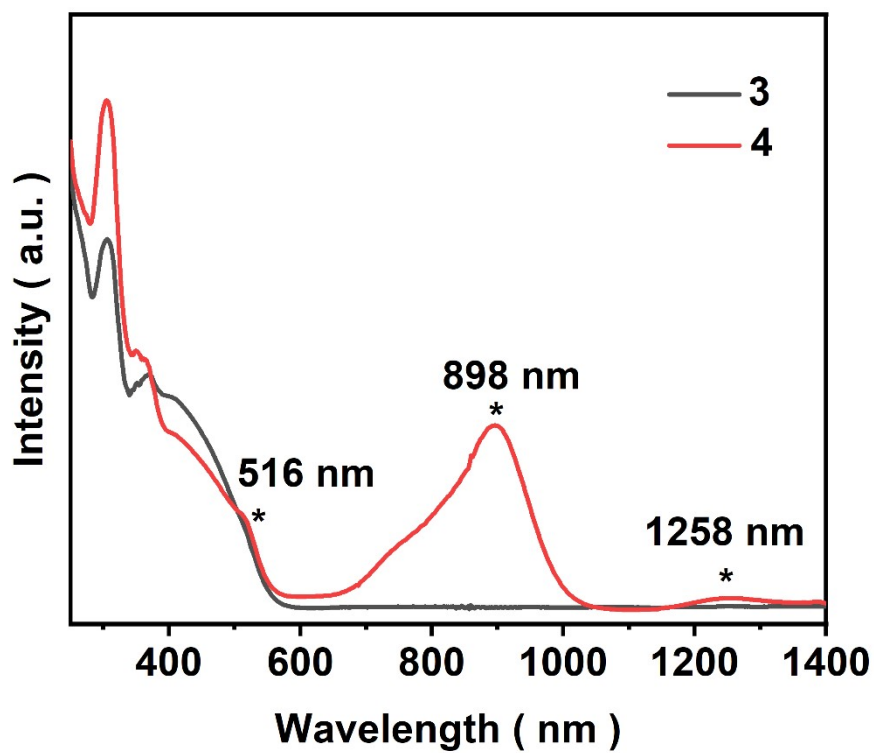


Figure S8. Absorption spectral of 1eq MB to 1eq BD (3); Absorption spectral of 1 eq BD to 1eq MB (4). The tests are carried out under nitrogen and anhydrous conditions.

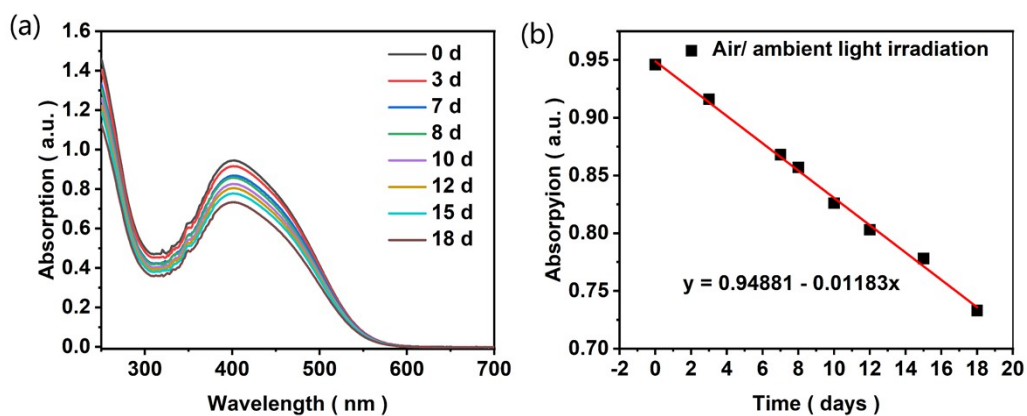


Figure S9. (a). Changes of the absorption spectra of BD with irradiation time under ambient light irradiation and exposure to ambient air (measured in dichloromethane). (b). Change of the optical density at the absorption maxima of BD as a function of irradiation time under ambient light irradiation and exposure to ambient air conditions.

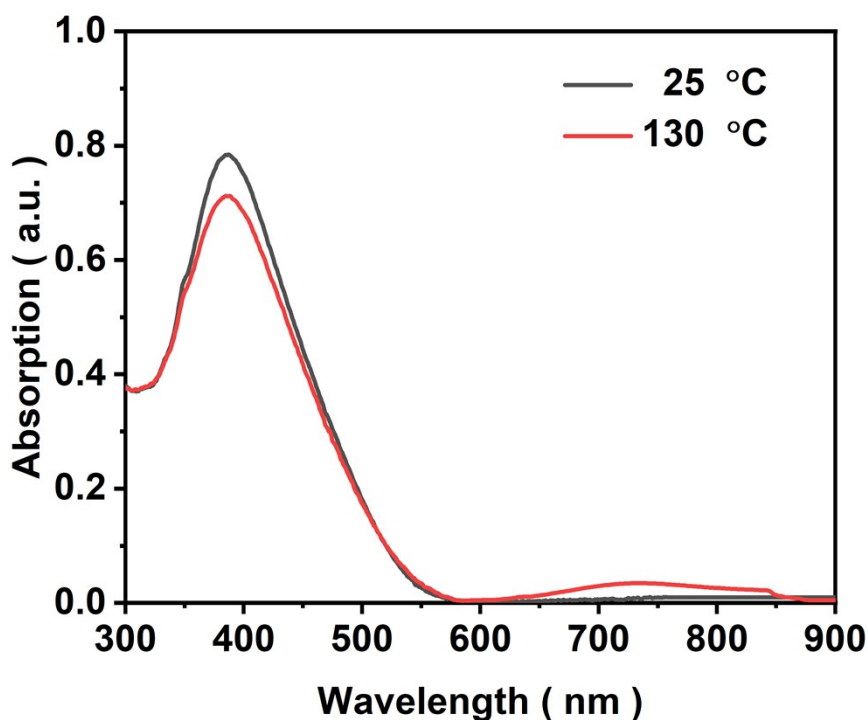


Figure S10. UV-Vis-NIR absorption spectrum of BD in DMF recorded at different temperatures. The tests are carried out under nitrogen and anhydrous conditions.

Table S2.X-ray crystallographic data for BD
CCDC: 2239887

Compound	Date
Empirical formula	C ₄₆ H ₃₄ F ₁₂ S ₂
<i>M_r</i> (g mol ⁻¹)	878.85
Temperature/K	298
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.6287(8)
<i>b</i> (Å)	13.8939(8)
<i>c</i> (Å)	16.745(3)
α (°)	87.821(12)
β (°)	76.267(15)
γ (°)	80.835(6)
<i>V</i> /Å ³	2148.3(5)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.225
μ mm ⁻¹	0.201
<i>F</i> (000)	800
Crystal size/mm ³	0.2 × 0.15 × 0.2
limiting indices	-12 ≤ <i>h</i> ≤ 12 -17 ≤ <i>k</i> ≤ 17 -21 ≤ <i>l</i> ≤ 21
no. of reflections collected	26361
no. of independent reflections	9286
data/restrains/parameters	9286/0/593
largest difference peak and hole (e Å ⁻³)	0.196, -0.242
Theta range/°	2.460 to 26.999
<i>R</i> _{int}	0.0332
GooF 或 GoF	1.057
<i>R</i> [<i>I</i> > 2σ]	<i>R</i> ₁ = 0.0483 <i>wR</i> ₂ = 0.1222
<i>R</i> (all data)	<i>R</i> ₁ = 0.0758 <i>wR</i> ₂ = 0.1322
$R_1 = \sum(F_o - F_c)/\sum F_o $, $wR_2 = \{\sum[w(F_o - F_c)^2]/\sum[w(F_o)^2]\}^{1/2}$.	

Table S3. DFT Computational Methods and Cartesian Coordinates Density functional theory (DFT) calculations of various possible geometries at the B3LYP/6-31 (d, p) level of theory.

BD-singlet

C	0.51945900	1.30454700	-1.11233200
C	-0.86097400	1.10665400	-1.14533000
C	-1.47039500	-0.19827800	-0.88433000
C	-0.51938800	-1.30458800	-1.11256500
C	0.86104800	-1.10668800	-1.14549200
C	1.47046000	0.19820500	-0.88428400
C	0.88368600	2.66236200	-1.40482600
C	-0.18950100	3.47059700	-1.61170400
S	-1.69113400	2.61754100	-1.46587800
C	-0.88359600	-2.66232900	-1.40544700
C	0.18960200	-3.47051200	-1.61247200
S	1.69122800	-2.61750400	-1.46631300
C	2.76254700	0.40095900	-0.44516400
C	-2.76249500	-0.40105600	-0.44523400
C	3.83870100	-0.62512800	-0.58024500
C	3.20526300	1.63377200	0.25941300
C	-3.20524100	-1.63383500	0.25939300
C	-3.83863800	0.62504500	-0.58030600
C	4.44188900	-1.19855100	0.55248400
C	5.48606400	-2.10735800	0.42109600
C	5.96456400	-2.44135400	-0.84993900
C	5.39251000	-1.86488300	-1.98490900
C	4.33601100	-0.96651300	-1.84900200
C	4.45871600	2.21322300	-0.01403700
C	4.90028800	3.33378400	0.68262800
C	4.10542600	3.88933900	1.68817900
C	2.86767800	3.31448100	1.99141100
C	2.42536600	2.20170000	1.28580600
C	-4.44175900	1.19852600	0.55243100
C	-5.48593100	2.10733900	0.42105900
C	-5.96449700	2.44128300	-0.84996400
C	-5.39251500	1.86475300	-1.98494100
C	-4.33601800	0.96637700	-1.84905200
C	-4.45862200	-2.21337900	-0.01419700
C	-4.90025400	-3.33388400	0.68252100
C	-4.10554100	-3.88927800	1.68827800
C	-2.86788300	-3.31430800	1.99166900
C	-2.42550600	-2.20158800	1.28601000
C	7.14034500	-3.37071400	-0.98704400

C	4.60982100	5.05785300	2.48934000
F	7.16445300	-4.29759500	-0.00393800
F	7.12799400	-4.02811700	-2.16749600
F	8.31506600	-2.70039000	-0.92273800
F	5.43637400	5.84490100	1.76507700
F	3.59800400	5.83375400	2.93833600
F	5.30676300	4.65483800	3.57826700
C	-7.14027600	3.37065000	-0.98704600
F	-7.16432100	4.29757400	-0.00398000
F	-7.12798200	4.02800200	-2.16752800
F	-8.31500100	2.70034200	-0.92264800
C	-4.61001500	-5.05772300	2.48948800
F	-5.43639400	-5.84490500	1.76517200
F	-3.59823600	-5.83351500	2.93876000
F	-5.30717500	-4.65461700	3.57824200
H	1.90509900	3.00814300	-1.47523900
H	-0.19277200	4.52191500	-1.86457700
H	-1.90500300	-3.00809000	-1.47604000
H	0.19288500	-4.52176100	-1.86563300
H	4.07894100	-0.93326700	1.54039400
H	5.92971500	-2.56130800	1.30052300
H	5.76691800	-2.12281100	-2.96944200
H	3.88902600	-0.52080900	-2.73204100
H	5.08642900	1.78540700	-0.78878400
H	5.85934700	3.78063900	0.44427300
H	2.25398600	3.73931600	2.77834000
H	1.46735700	1.75677100	1.53108500
H	-4.07876000	0.93328100	1.54033400
H	-5.92952800	2.56133400	1.30049000
H	-5.76697700	2.12263800	-2.96946500
H	-3.88909300	0.52062100	-2.73209600
H	-5.08622400	-1.78568500	-0.78910200
H	-5.85924800	-3.78081800	0.44405000
H	-2.25431300	-3.73900700	2.77876600
H	-1.46757500	-1.75656500	1.53142500

BD-T42-singlet

C	0.64502700	0.26133900	1.25763200
C	-0.75724200	0.33136900	1.17136700
C	-1.48782100	0.23979000	-0.06887900
C	-0.64599700	0.26930800	-1.25475100
C	0.75626600	0.33783800	-1.16805600
C	1.48679200	0.23769800	0.07155200

C	-1.10478800	0.32240400	-2.61940400
C	-0.09295100	0.35525000	-3.52227500
S	1.47482800	0.36155500	-2.77398400
C	1.10387700	0.30647900	2.62257400
C	0.09211000	0.33406000	3.52567500
S	-1.47570800	0.34503400	2.77750000
C	2.89689800	0.10770600	0.14102700
C	-2.89807100	0.11159800	-0.14044400
C	3.76772300	0.91153400	-0.73995300
C	3.52680300	-0.83762000	1.08009600
C	-3.52558800	-0.83117700	-1.08430100
C	-3.77040000	0.90937600	0.74379100
C	2.84204800	-2.01250000	1.47368600
C	3.45051000	-2.98104500	2.25795300
C	4.80078500	-2.85945500	2.60259200
C	5.48761700	-1.68862900	2.27042700
C	4.85428100	-0.68651200	1.54337800
C	3.39835500	2.23961400	-1.05254800
C	4.24060700	3.07779100	-1.76785700
C	5.52275000	2.64855900	-2.12380500
C	5.89483800	1.32456200	-1.87089800
C	5.02345400	0.46559500	-1.20906500
C	-2.84019200	-2.00696500	-1.47274200
C	-3.44525600	-2.97517000	-2.25960600
C	-4.79255300	-2.85337500	-2.61523600
C	-5.47950200	-1.68080000	-2.28812800
C	-4.84982800	-0.67909000	-1.55672000
C	-3.39893000	2.23261800	1.07551000
C	-4.24332100	3.06486300	1.79569700
C	-5.53010200	2.63456600	2.13343700
C	-5.90474900	1.31518400	1.86251500
C	-5.03056900	0.46122600	1.19858200
C	5.46903700	-3.92114200	3.43018500
C	6.44571000	3.56403500	-2.87852200
C	-5.45615000	-3.91469600	-3.44675600
C	-6.45696100	3.54394100	2.89102000
F	4.97232900	-5.15000400	3.16562100
F	6.80199300	-3.96269600	3.21136000
F	5.29550100	-3.70664500	4.75654200
F	6.26236600	4.85753100	-2.53172600
F	7.74395200	3.26119300	-2.65610700
F	6.24738000	3.48532700	-4.21570200
F	-6.26717600	4.84088100	2.56080900
F	-7.75416200	3.24749000	2.65430100

F	-6.27010400	3.44931400	4.22885400
F	-4.96136200	-5.14368000	-3.17938600
F	-6.79036100	-3.95572300	-3.23561800
F	-5.27490000	-3.70004400	-4.77202500
H	-2.14681600	0.34104900	-2.90346100
H	-0.16891800	0.40867800	-4.59977100
H	2.14591200	0.32339200	2.90667300
H	0.16812700	0.38101100	4.60346900
H	1.82675400	-2.17287300	1.13100100
H	2.90446200	-3.87798500	2.53003700
H	6.52008100	-1.56322800	2.57844700
H	5.40135200	0.22074900	1.31664300
H	2.44546600	2.61850200	-0.70025600
H	3.93740100	4.09777700	-1.97858400
H	6.86916400	0.96848700	-2.18778800
H	5.32486500	-0.56138200	-1.03806500
H	-1.82739100	-2.16885900	-1.12346400
H	-2.89812200	-3.87298900	-2.52683000
H	-6.50961600	-1.55349800	-2.60325300
H	-5.39763300	0.22876600	-1.33384600
H	-2.44236300	2.61255700	0.73452400
H	-3.93886100	4.08108600	2.02188700
H	-6.88290200	0.95912400	2.16733000
H	-5.33311000	-0.56302100	1.01422700

BD-T42-triplet

C	0.70644100	-0.01085600	-1.21647600
C	-0.71921600	-0.02326400	-1.17485300
C	-1.45650800	-0.01556700	0.01804900
C	-0.70669600	-0.01323500	1.21865900
C	0.71894900	-0.02452900	1.17704000
C	1.45626900	-0.01435600	-0.01584500
C	-1.20081100	-0.01263000	2.57334000
C	-0.21027800	-0.00506100	3.49930100
S	1.39442100	-0.00902300	2.80422700
C	1.20050100	-0.00803300	-2.57118400
C	0.20993700	0.00019800	-3.49710800
S	-1.39474400	-0.00582400	-2.80201700
C	2.94453100	-0.00220600	-0.02310600
C	-2.94483400	-0.00427200	0.02567700
C	3.64341300	-1.15919100	0.51665100
C	3.62027500	1.15935900	-0.57809200
C	-3.62046900	1.15762100	0.58072400
C	-3.64349800	-1.16055800	-0.51513500

C	2.94861900	2.40778500	-0.65097900
C	3.57162600	3.53847500	-1.15592500
C	4.89847900	3.47508200	-1.59662000
C	5.57176000	2.24879900	-1.57743500
C	4.94450900	1.11206000	-1.08757000
C	3.00259900	-2.42452800	0.55011500
C	3.64947900	-3.55201400	1.03147600
C	4.96965500	-3.46696400	1.48754300
C	5.61116700	-2.22371100	1.50856800
C	4.95972500	-1.09070300	1.04189900
C	-2.94926500	2.40634100	0.64961800
C	-3.57188900	3.53783600	1.15301400
C	-4.89773500	3.47562900	1.59670900
C	-5.57028200	2.24879100	1.58192700
C	-4.94353100	1.11108700	1.09329400
C	-3.00095700	-2.42503500	-0.55550100
C	-3.64783000	-3.55177900	-1.03879300
C	-4.97013600	-3.46643400	-1.48876400
C	-5.61350300	-2.22413500	-1.50324500
C	-4.96176900	-1.09188400	-1.03553900
C	5.56144600	4.69220300	-2.17774300
C	5.65841600	-4.68245400	2.04158400
C	-5.55988100	4.69395700	2.17611100
C	-5.65961400	-4.68089500	-2.04428000
F	5.10240400	5.83144800	-1.61389100
F	6.90198300	4.66282400	-2.00764500
F	5.33774100	4.79697000	-3.50976300
F	5.23337500	-5.81698200	1.44205200
F	6.99922300	-4.61465000	1.88389300
F	5.42668300	-4.82997800	3.36770400
F	-5.23089900	-5.81695700	-1.45027200
F	-6.99988800	-4.61528400	-1.88117800
F	-5.43284300	-4.82365900	-3.37179000
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F	-6.90075400	4.66361000	2.00890600
F	-5.33340100	4.80221100	3.50737100
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H	-0.31608700	-0.00270700	4.57579400
H	2.25319100	-0.00817300	-2.82265300
H	0.31572700	0.00415200	-4.57359800
H	1.93286000	2.48253200	-0.28046000
H	3.04205600	4.48475100	-1.17882200
H	6.58777400	2.18697000	-1.95219100
H	5.47233100	0.16679600	-1.12132900

H	1.99230500	-2.51419200	0.16755700
H	3.14398400	-4.51161900	1.02443000
H	6.62087300	-2.14572400	1.89704400
H	5.46036900	-0.13244000	1.10885000
H	-1.93429200	2.48085700	0.27691400
H	-3.04248200	4.48431000	1.17244900
H	-6.58545100	2.18717400	1.95902400
H	-5.47097500	0.16571900	1.13042900
H	-1.98911800	-2.51450200	-0.17701700
H	-3.14107500	-4.51071700	-1.03737900
H	-6.62479900	-2.14639200	-1.88759200
H	-5.46372700	-0.13403700	-1.09784600

BD-T87-singlet

C	0.70954200	-0.08151200	1.28799700
C	-0.71980800	-0.09011400	1.24579700
C	-1.45298000	-0.09731000	0.05700600
C	-0.71338500	-0.09612000	-1.14484700
C	0.71623600	-0.09488800	-1.10270300
C	1.44937800	-0.09708900	0.08671100
C	-1.20548200	-0.08281500	-2.50049500
C	-0.21183200	-0.08638900	-3.42407800
S	1.39393700	-0.09357500	-2.72946800
C	1.20126200	-0.03343600	2.64315000
C	0.20746000	-0.02985200	3.56665000
S	-1.39827500	-0.06724700	2.87238700
C	2.94755300	-0.03391600	0.08444200
C	-2.95136000	-0.03971400	0.05811900
C	3.51831100	1.29562200	-0.01953000
C	3.62667800	-1.31333400	0.13438800
C	-3.62371300	-1.31922800	-0.05981200
C	-3.52703800	1.29112300	0.09080600
C	5.03773400	-1.51604500	0.19354500
C	5.60346700	-2.77992100	0.15519600
C	4.80159500	-3.92157100	0.05665400
C	3.41157000	-3.76944400	0.02229200
C	2.84427600	-2.50785100	0.05882300
C	4.89932200	1.60803300	-0.19399400
C	5.36770100	2.91179800	-0.19199300
C	4.49261000	3.98743100	-0.01148700
C	3.12702500	3.72739300	0.14239300
C	2.65701700	2.42579200	0.14000200
C	-5.03014400	-1.52926900	-0.17760500
C	-5.58766400	-2.79726400	-0.19945400

C	-4.78286000	-3.93670900	-0.10109200
C	-3.39693100	-3.77717000	-0.00072800
C	-2.83806800	-2.51158100	0.02266800
C	-4.91580100	1.60169800	0.19000600
C	-5.38844100	2.90231300	0.12532000
C	-4.50897800	3.97654400	-0.04183400
C	-3.13621700	3.71910900	-0.11532300
C	-2.66205200	2.42055700	-0.05092600
C	5.42471000	-5.28338900	-0.05436100
C	5.01622000	5.39291500	0.06214800
C	-5.40037100	-5.30482700	-0.05614000
C	-5.03312600	5.37654400	-0.18377300
F	6.60922900	-5.34807900	0.59421500
F	4.62491100	-6.24492100	0.45774700
F	5.66604500	-5.61973600	-1.34407400
F	6.13485400	5.55213200	-0.67986000
F	4.10538400	6.29176500	-0.37216800
F	5.33606500	5.74132500	1.33182800
F	-6.18849800	5.55197100	0.49573600
F	-4.14872400	6.29253400	0.26901200
F	-5.28962800	5.68562900	-1.47777200
F	-6.55668400	-5.35713500	-0.75476900
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F	-5.69213200	-5.68091500	1.21201200
H	-2.25763200	-0.07832900	-2.75504000
H	-0.31670200	-0.08008400	-4.50070500
H	2.25334900	-0.01327100	2.89744200
H	0.31215600	-0.00224400	4.64296900
H	5.70556700	-0.68727700	0.36005800
H	6.68090000	-2.88483700	0.22257600
H	2.77425000	-4.64502800	-0.03556600
H	1.76655100	-2.42867300	0.01196700
H	5.61129900	0.83454700	-0.42979100
H	6.42373800	3.09967900	-0.35281300
H	2.43195200	4.55046200	0.26770900
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H	-1.76431200	-2.42788000	0.12225800
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H	-2.43839800	4.54193400	-0.22602900
H	-1.59582300	2.26087200	-0.13323600

BD-T87-triplet

C	0.70690300	-0.04228600	1.25181100
C	-0.72004000	-0.05273300	1.21164800
C	-1.45460000	-0.05067700	0.02310400
C	-0.71098200	-0.04994000	-1.17580100
C	0.71599900	-0.05359400	-1.13565100
C	1.45062300	-0.05303800	0.05329800
C	-1.20684200	-0.04099900	-2.52968400
C	-0.21673400	-0.04333400	-3.45647300
S	1.39060000	-0.05177200	-2.76267200
C	1.20241000	-0.00530700	2.60541300
C	0.21225300	-0.00296100	3.53215800
S	-1.39505200	-0.03582700	2.83856400
C	2.95356600	-0.01888600	0.05562600
C	-2.95765800	-0.02056700	0.02113500
C	3.55264200	1.31032000	-0.00061800
C	3.61193700	-1.31916800	0.08690400
C	-3.61202300	-1.32228500	-0.04635500
C	-3.55890600	1.30850100	0.03746700
C	5.01537100	-1.54508400	0.15380300
C	5.56043500	-2.81983600	0.10711400
C	4.73931600	-3.94401700	-0.01215000
C	3.35338600	-3.76649500	-0.05830700
C	2.80877400	-2.49382400	-0.00899700
C	4.93735100	1.59986100	-0.15352700
C	5.42947900	2.89635800	-0.11584500
C	4.57103800	3.98067900	0.08168000
C	3.20024400	3.74106400	0.21405500
C	2.70839800	2.44663100	0.17238400
C	-5.01285500	-1.55528200	-0.14022300
C	-5.55131500	-2.83365500	-0.12522200
C	-4.72653100	-3.95542300	-0.01003200
C	-3.34293700	-3.77100100	0.06696900
C	-2.80503600	-2.49470400	0.04924000
C	-4.94818300	1.59572600	0.14642500
C	-5.44257100	2.88991100	0.07513800
C	-4.58131600	3.97399800	-0.11152300
C	-3.20641000	3.73696400	-0.19757400
C	-2.71241100	2.44478700	-0.12283500
C	5.33823400	-5.31680100	-0.13187300
C	5.11698300	5.37601200	0.19343900
C	-5.31972800	-5.33326700	0.07490500
C	-5.12751000	5.36584800	-0.25970200
F	6.51876900	-5.40845600	0.52042700

F	4.51911200	-6.26734600	0.37002100
F	5.57740500	-5.64662800	-1.42321400
F	6.24965100	5.53201100	-0.52741900
F	4.22827800	6.29887400	-0.23617300
F	5.42147400	5.69137100	1.47499600
F	-6.28115300	5.52875700	0.42552900
F	-4.25426900	6.29770800	0.18198800
F	-5.39544900	5.66141600	-1.55405300
F	-6.48813800	-5.41961900	-0.59953500
F	-4.48654800	-6.27030500	-0.42924700
F	-5.57945600	-5.68726600	1.35582700
H	-2.26106100	-0.03646800	-2.77776700
H	-0.32287300	-0.03897200	-4.53291000
H	2.25662200	0.01151500	2.85324200
H	0.31824900	0.01762100	4.60842500
H	5.69743800	-0.72989800	0.32858400
H	6.63530100	-2.94417100	0.18132800
H	2.70050000	-4.62941900	-0.13093400
H	1.73267500	-2.39500700	-0.05581200
H	5.63963500	0.81937200	-0.39500000
H	6.49047000	3.06912900	-0.25977900
H	2.51712700	4.57264000	0.34852900
H	1.64346900	2.30048000	0.29094200
H	-5.69801100	-0.74172800	-0.30930100
H	-6.62406100	-2.96209400	-0.22020700
H	-2.68646200	-4.63124800	0.13915200
H	-1.73076600	-2.39142700	0.12060600
H	-5.65520900	0.81681200	0.37849800
H	-6.50790300	3.06148000	0.18425800
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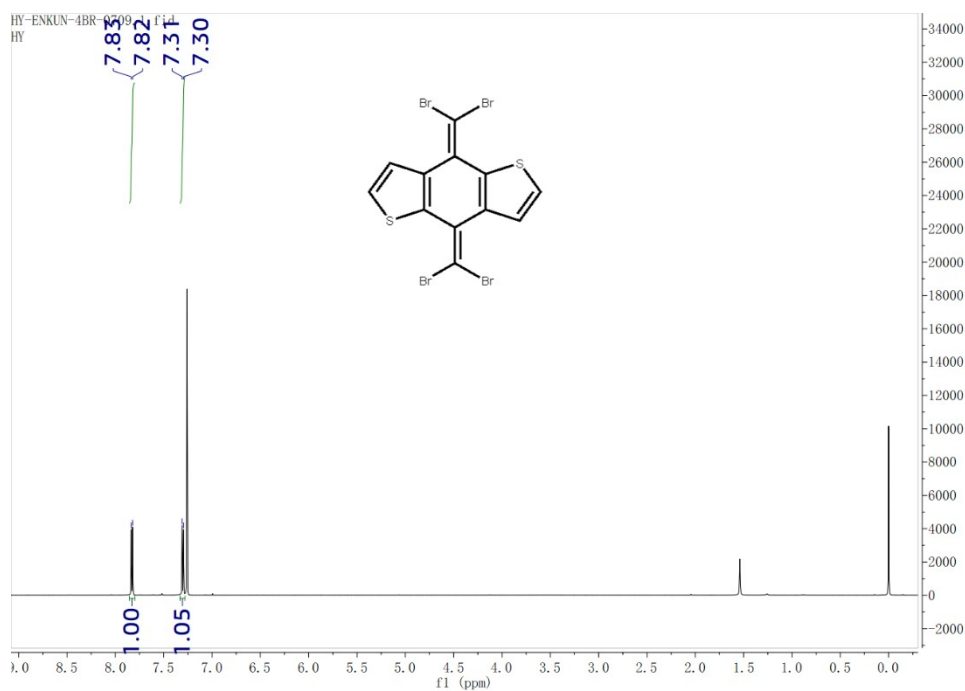
BD2+

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C	-1.44796800	0.07055600	-0.04024200
C	-0.68654000	0.05698100	-1.24542500
C	0.74133500	0.10826700	-1.18191700
C	1.44796700	0.07060700	0.04042300
C	1.15766100	0.06025000	2.60343900
C	0.14881200	0.06907400	3.51248400
S	-1.43607400	0.09326000	2.79417900
C	-1.15767100	0.06041400	-2.60325300
C	-0.14882400	0.06936800	-3.51229800

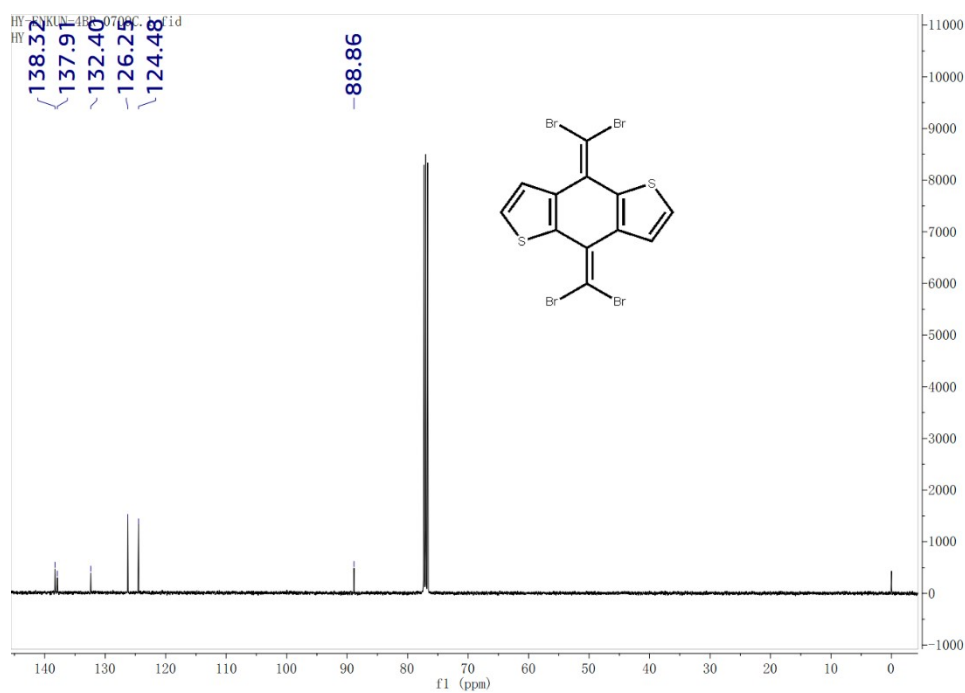
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C	-2.92257900	0.03365400	-0.07107300
C	3.66838000	1.04883500	-0.62843300
C	3.58989900	-1.02172400	0.78966600
C	-3.58980900	-1.02186000	-0.78960200
C	-3.66847100	1.04865300	0.62855100
C	4.94537500	0.77314100	-1.19478500
C	5.65243500	1.76592200	-1.85409700
C	5.11844200	3.05710800	-1.94380600
C	3.86028000	3.35373300	-1.39593300
C	3.13445700	2.36144300	-0.76467500
C	4.87741100	-0.82616000	1.36589700
C	5.51220700	-1.85716400	2.04010400
C	4.89271200	-3.10915500	2.13858800
C	3.62146300	-3.32580600	1.58465600
C	2.96916800	-2.29407400	0.93527200
C	-4.94548200	0.77289300	1.19484000
C	-5.65263300	1.76564000	1.85410400
C	-5.11872200	3.05685900	1.94382100
C	-3.86055300	3.35355500	1.39600300
C	-3.13464100	2.36130200	0.76478900
C	-4.87734700	-0.82636500	-1.36580300
C	-5.51204600	-1.85736300	-2.04010700
C	-4.89242700	-3.10928200	-2.13872400
C	-3.62115000	-3.32586300	-1.58483000
C	-2.96894800	-2.29413200	-0.93535000
C	5.92248800	4.16518200	-2.60467300
C	5.61738200	-4.26092500	2.81637700
F	6.77005100	3.66722000	-3.51650100
F	5.10870800	5.04637500	-3.20852800
F	6.63526200	4.81923200	-1.67251400
F	6.47751300	-3.81008400	3.74109900
F	4.74221300	-5.08916000	3.40945900
F	6.30563000	-4.96041500	1.89926300
C	-5.92286900	4.16489500	2.60463200
F	-6.77044800	3.66689400	3.51642400
F	-5.10917200	5.04614500	3.20851500
F	-6.63563400	4.81888700	1.67242600
C	-5.61699000	-4.26105600	-2.81662100
F	-6.47718300	-3.81020800	-3.74128200
F	-4.74174500	-5.08913900	-3.40980300
F	-6.30515000	-4.96071200	-1.89956700
H	2.20054000	0.05929800	2.88867400

H	0.23421900	0.07424600	4.59136400
H	-2.20055200	0.05942200	-2.88848100
H	-0.23423100	0.07461900	-4.59117800
H	5.33750200	-0.23685700	-1.17108600
H	6.60761100	1.54469500	-2.31635200
H	3.46410100	4.35961600	-1.47599800
H	2.17122000	2.59401400	-0.32510200
H	5.33772500	0.15444700	1.33445000
H	6.47708800	-1.69534900	2.50693200
H	3.15782100	-4.30177200	1.67223600
H	1.99715400	-2.46814800	0.48870800
H	-5.33754700	-0.23712900	1.17113700
H	-6.60781800	1.54436100	2.31631500
H	-3.46444000	4.35946400	1.47607100
H	-2.17140300	2.59392900	0.32525000
H	-5.33775700	0.15419400	-1.33424900
H	-6.47694900	-1.69559700	-2.50690800
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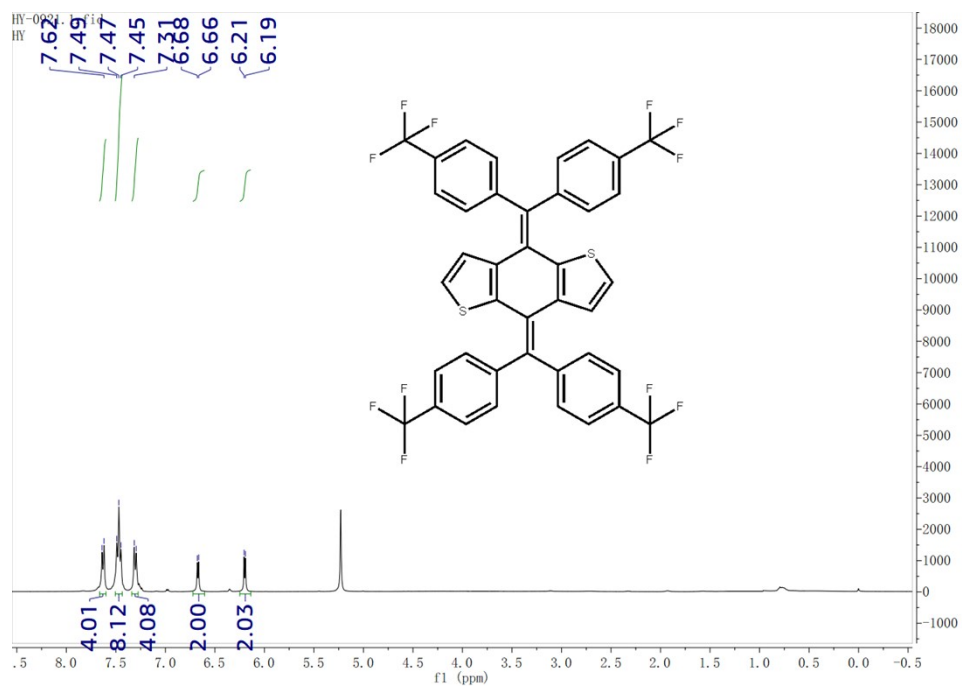
Characterization by NMR



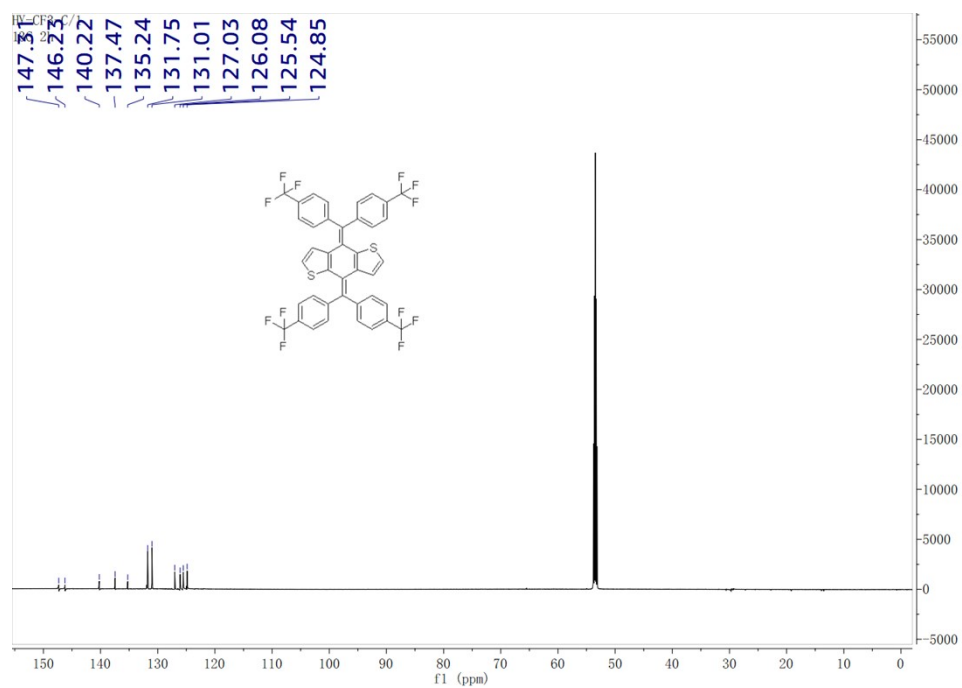
¹H NMR (400 MHz, CDCl₃) spectrum of 1



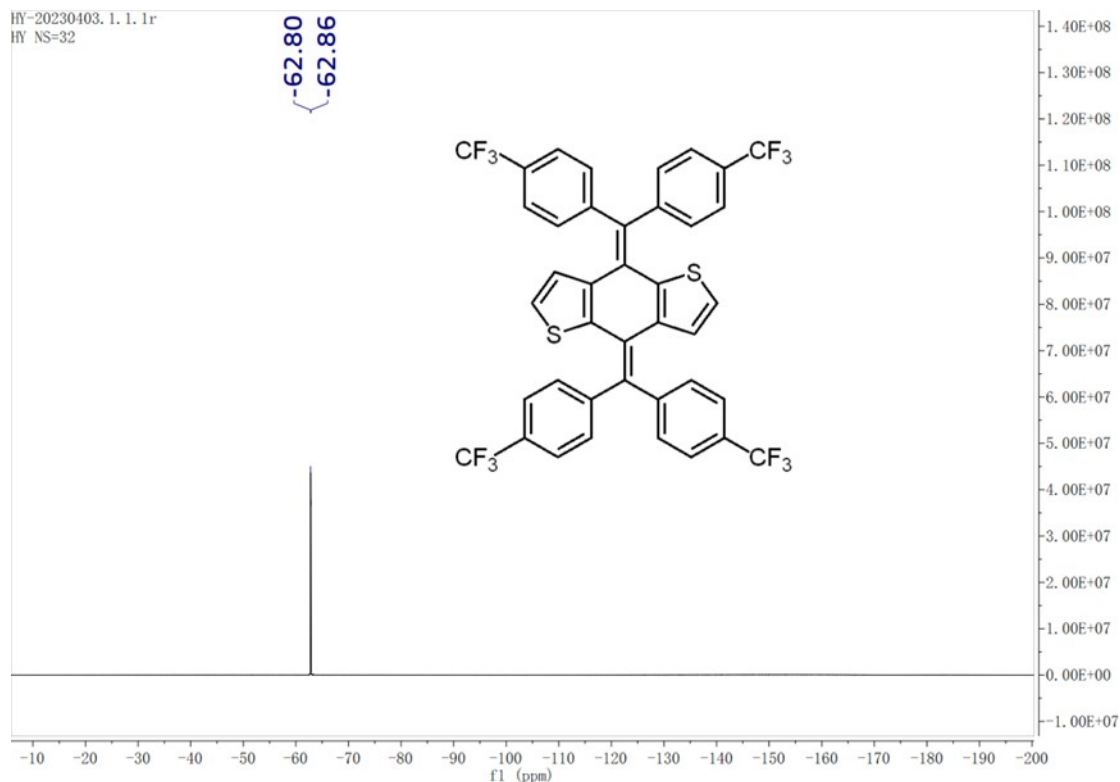
¹³C NMR (101 MHz, CDCl₃) spectrum of 1



¹H NMR (400 MHz, CD₂Cl₂) spectrum of BD



¹³C NMR (101 MHz, CD₂Cl₂) spectrum of BD



^{19}F NMR (400 MHz, CD_2Cl_2) spectrum of BD

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