Reversible mechanochromism in dipyridylamine-substituted unsymmetrical benzothiadiazoles

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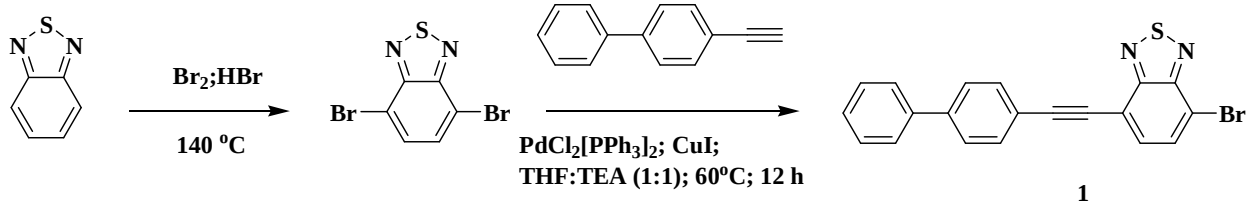
I. Experimental Section: Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on on the Bruker Avance (III) 400 MHz instrument by using $CDCl_3$. Chemical shifts for ^{1}H NMR spectra are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard {$CDCl_3$, 7.26 ppm}. Chemical shifts for ^{13}C NMR spectra are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as internal standard {$CDCl_3$, 77.0 ppm}. The ^{1}H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". Thermogravimetric analyses were performed on the Metler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The excitation and emission slits were 2/2 nm for the emission measurements. All of the measurements were done at 25°C. The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G** level for C, N, S, H in the Gaussian 09 program. HRMS was recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer. The XRD measurements were performed using Rigaku SmartLab, Automated Multipurpose Xray diffractometer. The X-rays were produced using a sealed tube and the wavelength of the X-ray was 0.154 nm (Cu K-alpha).

Reaction Scheme



1

Preparation of benzothiazole 1.

To a stirred solution of the 4-ethynylbiphenyl (1 mmol), and dibromo-BTD **1** (1 mmol) in THF, and TEA (1:1, v/v) were added [$PdCl_2(PPh_3)_2$] (10 mg, 0.014 mmol) and CuI (2 mg, 0.01 mmol) under an argon flow at room temperature. The reaction mixture was stirred for 12 h at 60 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure, and the mixture was purified by SiO_2 chromatography with DCM/hexane (1:3, v/v), followed by recrystallization in DCM:hexane (1:3) to obtain **1**. Pale yellowish solid (203 mg, Yield: 52 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.85 (d, 1H, J = 7.5 Hz), 7.75–7.72 (m, 2H), 7.68 (d, 1H, 7.5 Hz), 7.65–7.62 (m, 4H), 7.49–7.44 (m, 2H), 7.40–7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 154.1, 153.1, 141.8, 140.1, 132.7, 132.4, 132.0, 128.9, 127.8, 127.1, 127.0, 121.2, 116.7, 114.6, 96.8, 85.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{11}BrN_2S$ + Na: 412.9719 [M + Na]$^+$, found 412.9683 [M+ Na]$^+$.

Preparation of benzothiadiazole 2.

To a stirred solution of the 3-ethynylpyridine (1 mmol), **1** (1 mmol) in THF, and TEA (1:1, v/v) were added [$PdCl_2(PPh_3)_2$] (10 mg, 0.014 mmol) and CuI (2 mg, 0.01 mmol) under an argon flow at room temperature. The reaction mixture was stirred for 24 h at 60 °C, and then cooled to room temperature. The solvent was then evaporated under reduced pressure, and the mixture was purified by SiO_2 chromatography with DCM/hexane (2:2, v/v), to obtain **2.** Yellowish green solid (322 mg, Yield: 78 %); ^{1}H NMR (400 MHz, ($CDCl_3$, δ in ppm): 8.91 (s, 1H), 8.63 (m, 1H), 7.98–7.95 (m, 1H), 7.86–7.82 (m, 2H), 7.77–7.74 (m, 2H), 7.67–7.63 (m, 4H), 7.49–7.45 (m, 2H), 7.41–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 154.3, 154.2, 152..5, 149.2, 141.9, 140.1, 138.7, 132.8, 132.4, 132.2, 128.9, 127.8, 127.1, 127.0, 123.1, 121.2, 119.8, 117.9,

116.2, 97.9, 93.6, 88.4, 85.9, HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{15}N_3S$ + H: 414.1059 $[M + H]^+$, found 414.1058 $[M + H]^+$.

Preparation of benzothiadiazole 3.

2,2'-Dipyridylamine (4.0 mmol), **1** (3.0 mmol), anhydrous potassium carbonate (12.0 mmol), cupric sulfate (0.63 mmol), and 1,2-dichlorobenzene (10 mL) were added to a round bottom flask, degassed, and flushed with N_2. The reaction mixture was heated at 180 °C for 48 h, and then cooled to room temperature. Dichloromethane and water were added. The organic phase was washed with water and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by SiO_2 column chromatography, using DCM: Ethylacetate (9 : 1) mixture as eluent to afford **3**. Yellow solid (313 mg, Yield: 65 %); ^{1}H NMR (400 MHz, ($CDCl_3$, δ in ppm): 8.30-8.28 (m, 2H), 7.81 (d, 1H, J = 7.8 Hz), 7.75-7.72 (m, 2H), 7.66-7.61 (m, 6H), 7.49-7.45 (m, 2H), 7.41-7.35 (m, 2H), 7.14-7.12 (m, 2H), 7.03-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 157.5, 156.1, 151.5, 148.6, 141.4, 140.3, 137.8, 137.6, 133.3, 132.3, 128.9, 127.7, 127.04, 127.0, 125.6, 121.7, 119.1, 117.2, 114.2, 95.5, 86.1; HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{19}N_5S$ + H: 482.143 $[M + H]^+$, found 482.143 $[M + H]^+$.

II. Copies of ^{1}H NMR, ^{13}C NMR spectra and HRMS of the New Compounds

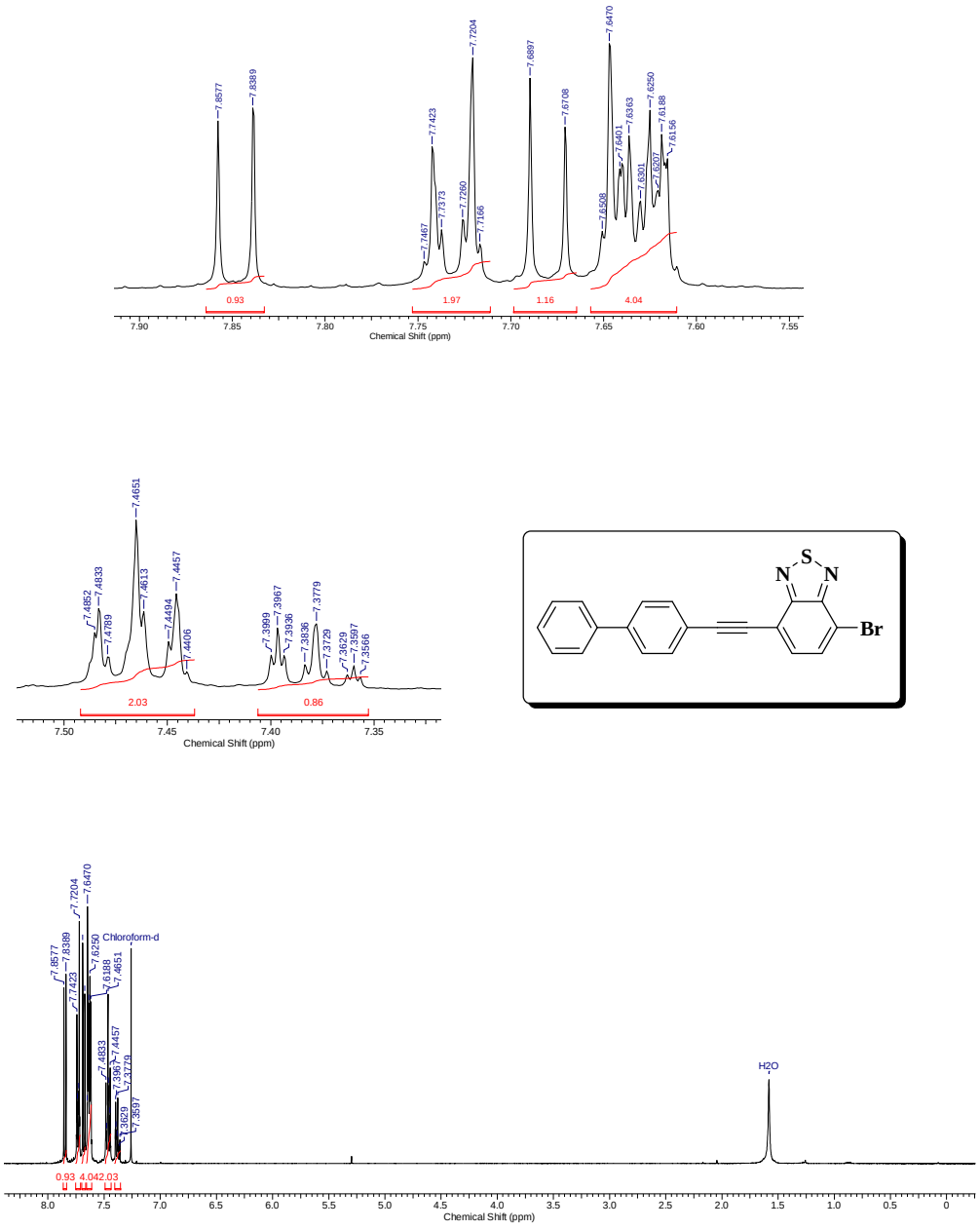


Fig. S1 ^{1}H NMR Spectra of **1**.

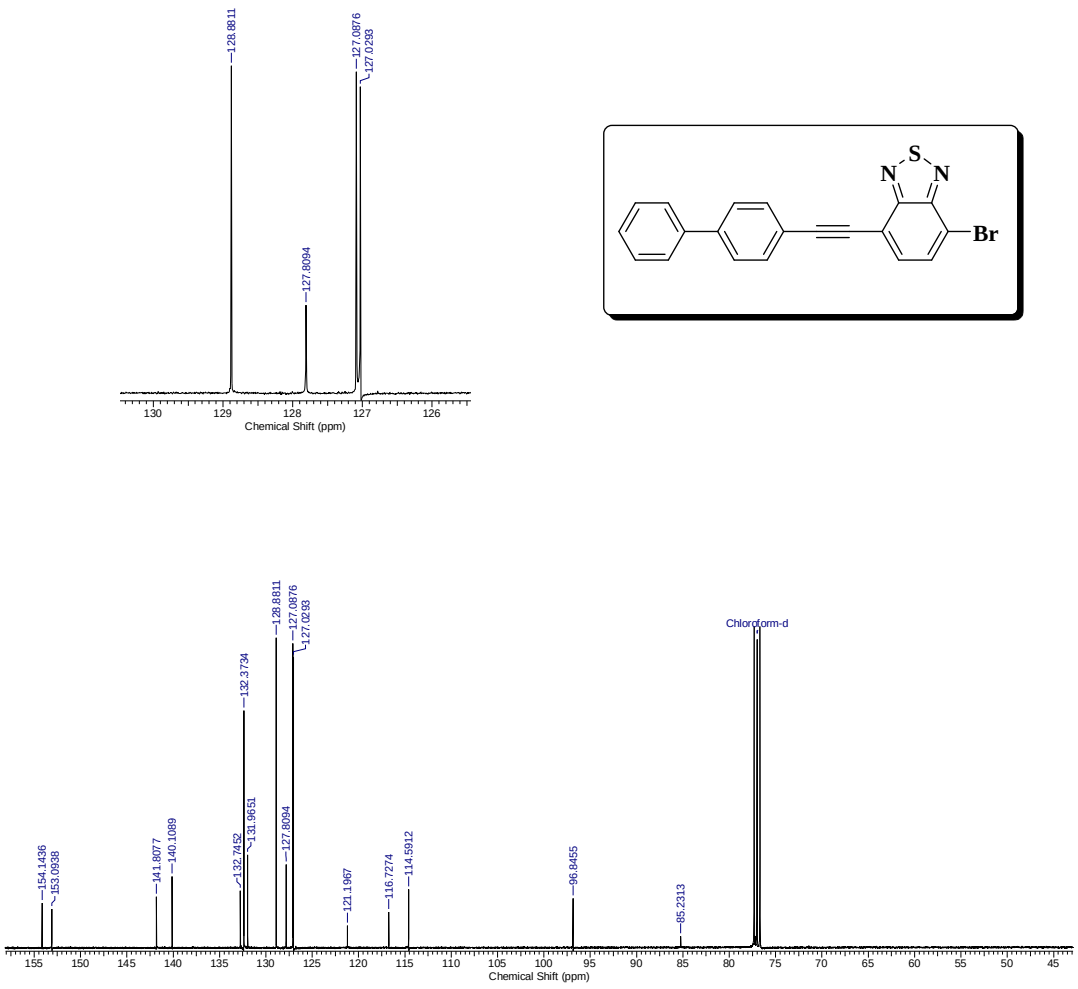


Fig. S2 ^{13}C NMR Spectra of **1**.

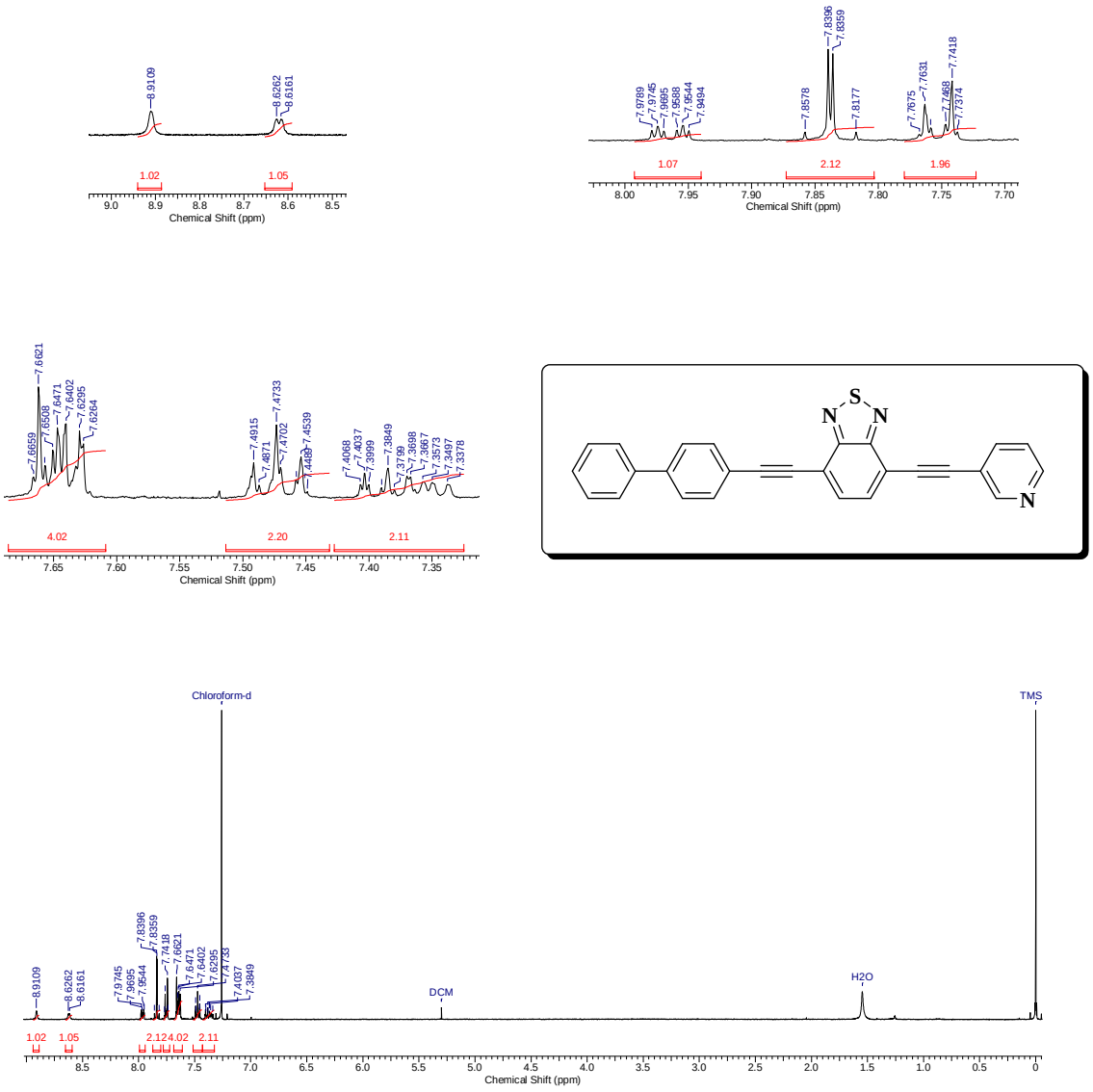


Fig. S3 ^{1}H NMR Spectra of **2**.

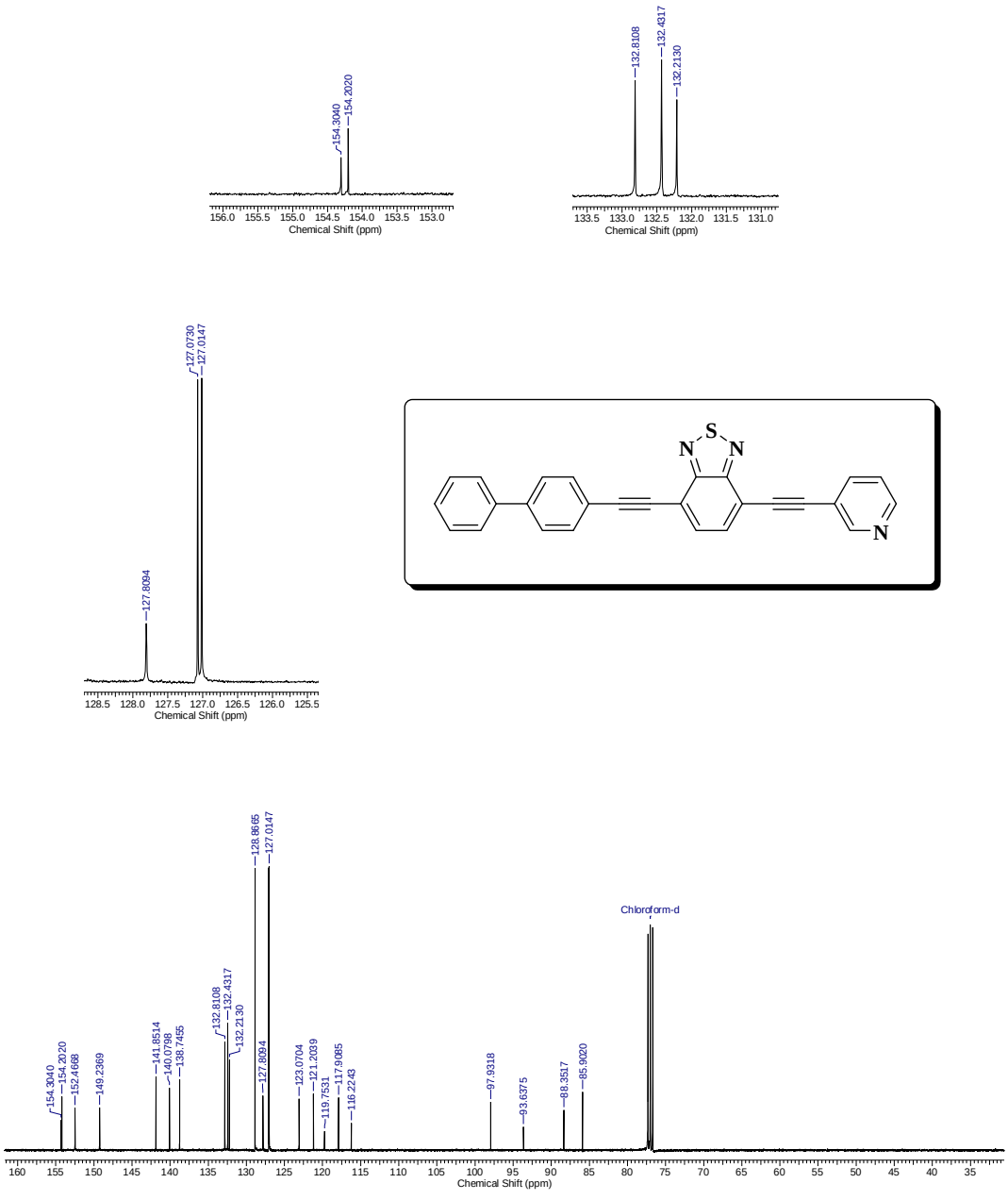


Fig. S4 ^{13}C NMR Spectra of **2**.

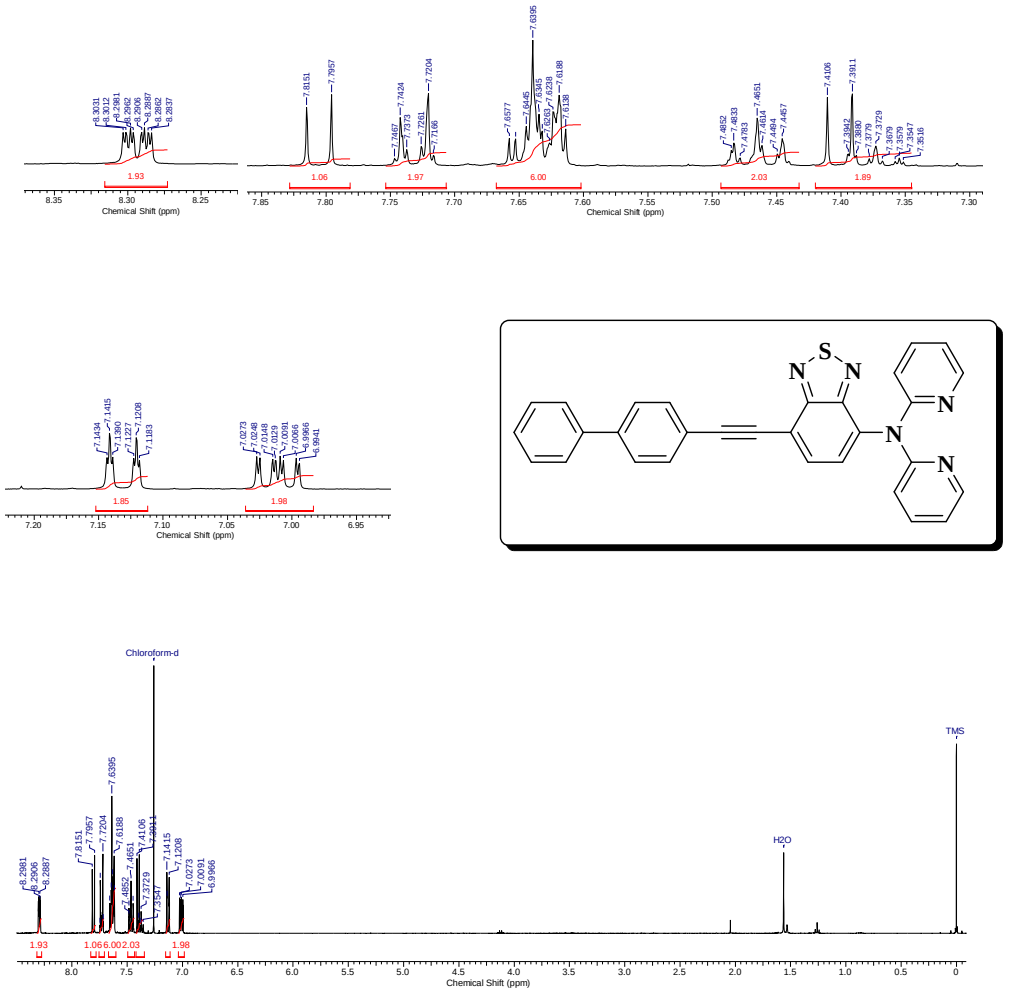


Fig. S5 ^{1}H NMR Spectra of **3**.

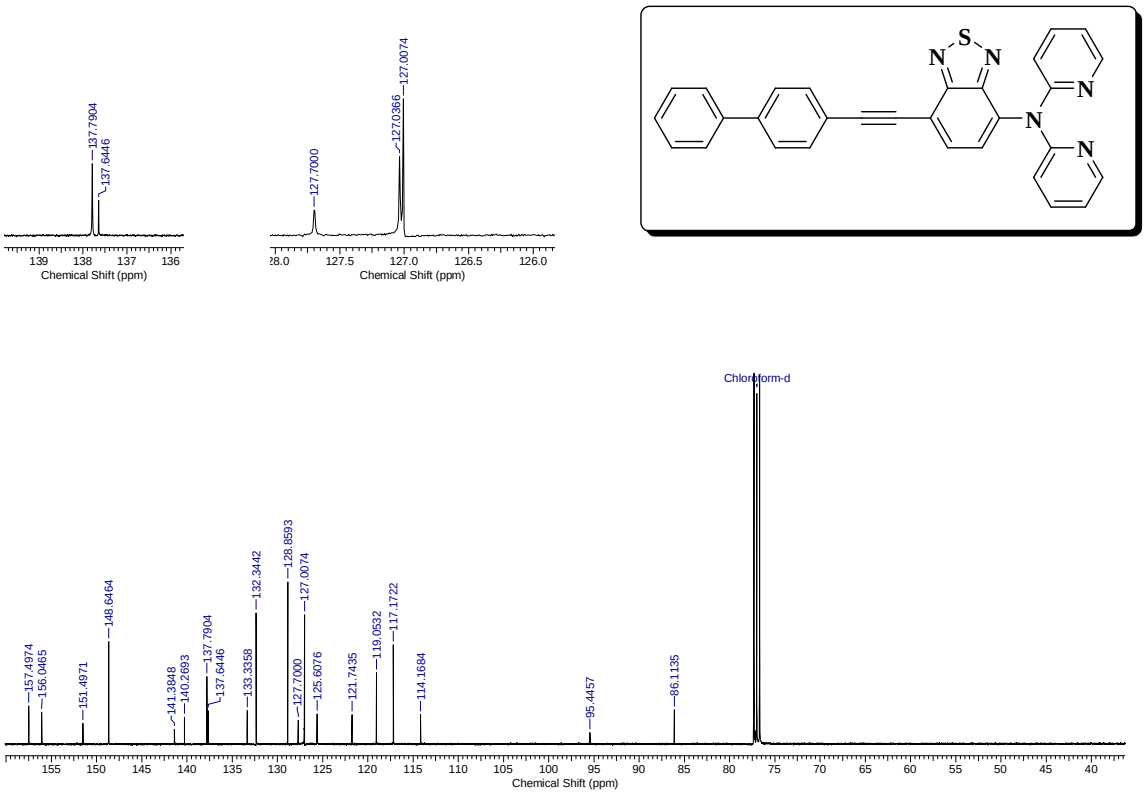


Fig. S6 ^{13}C NMR Spectra of **3**.

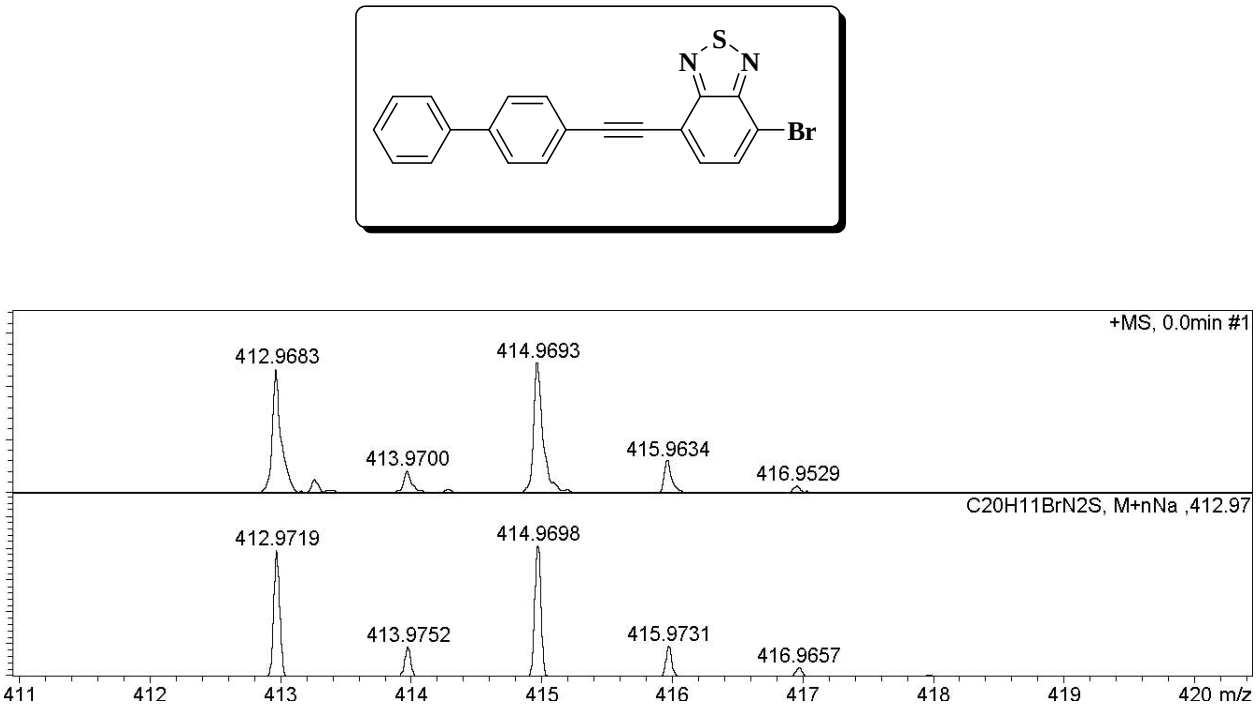
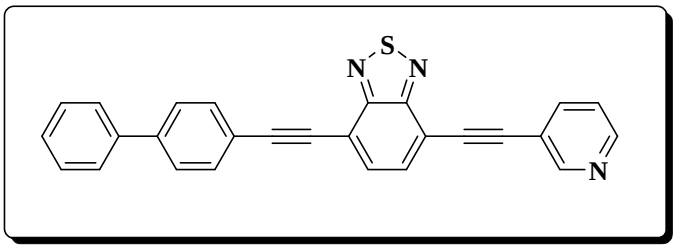


Fig. S7 HRMS of **1**.



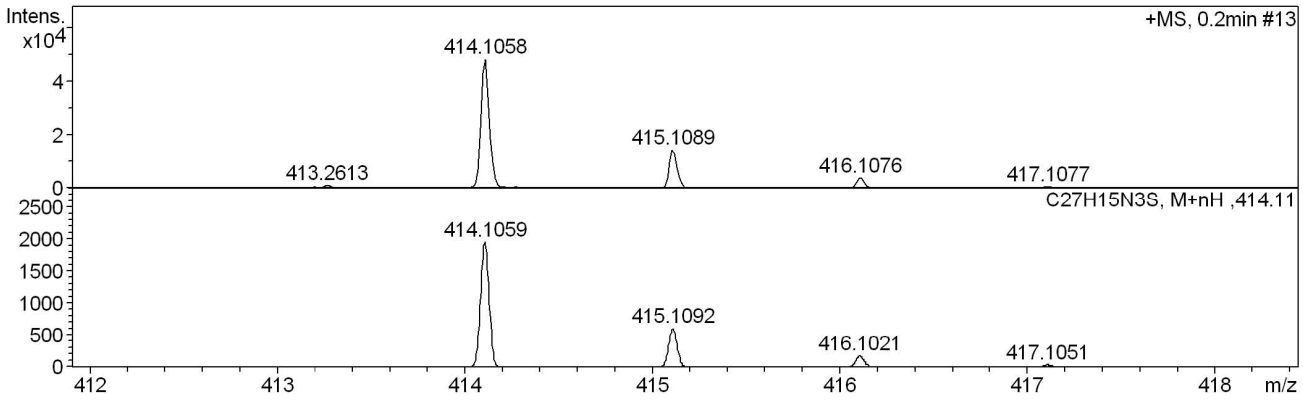
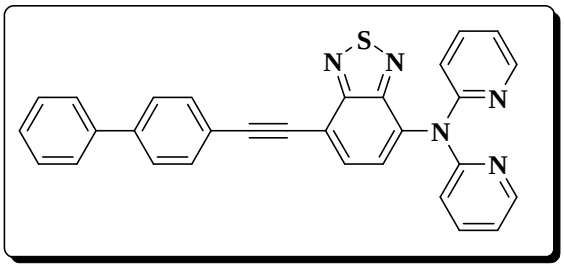


Fig. S8 HRMS of **2**.



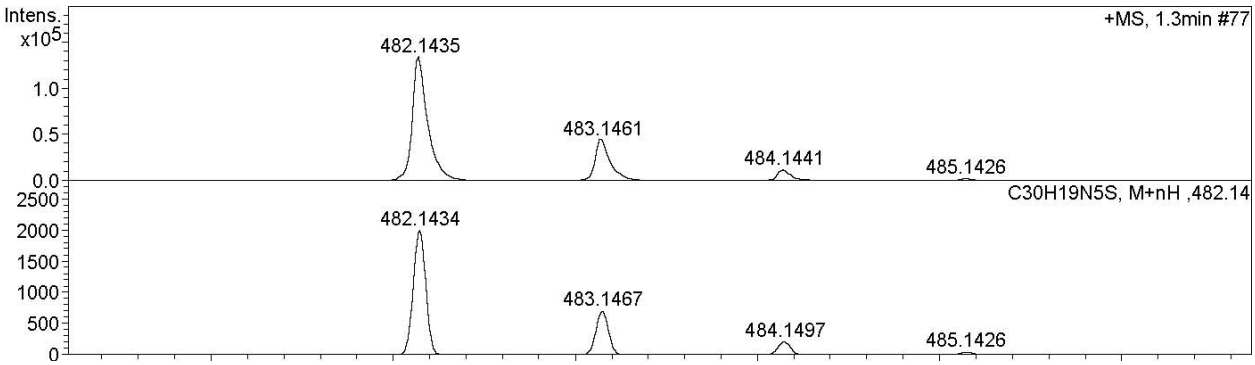


Fig. S9 HRMS of **3**

III. TGA of BTD 2 and 3

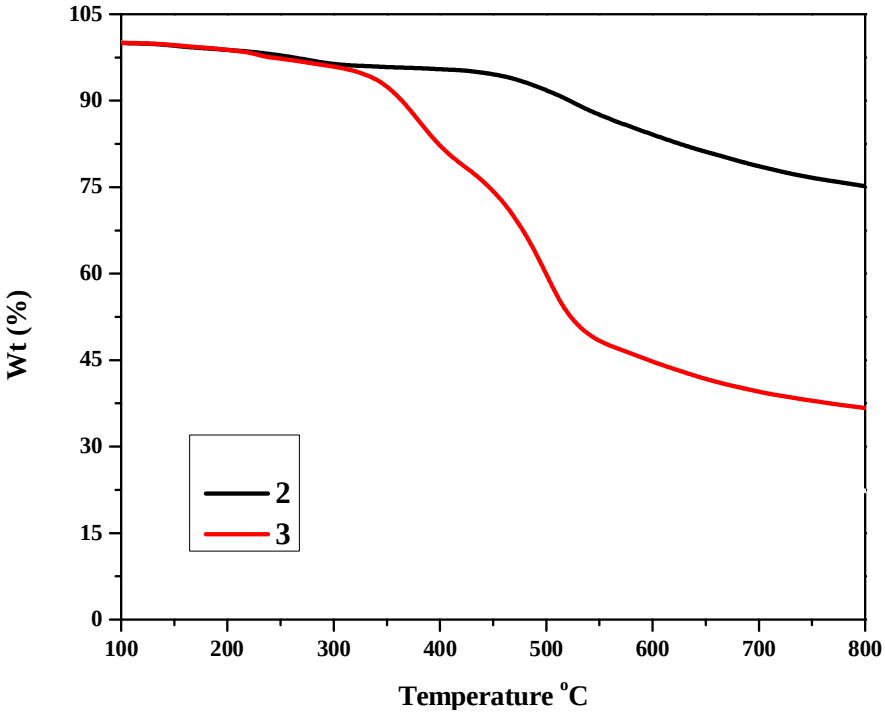


Fig. S10 TGA plots of **2** and **3** at a heating rate of 10 °C min^{-1}, under nitrogen atmosphere.

IV. UV/vis and Emission Data of BTD 2 and 3

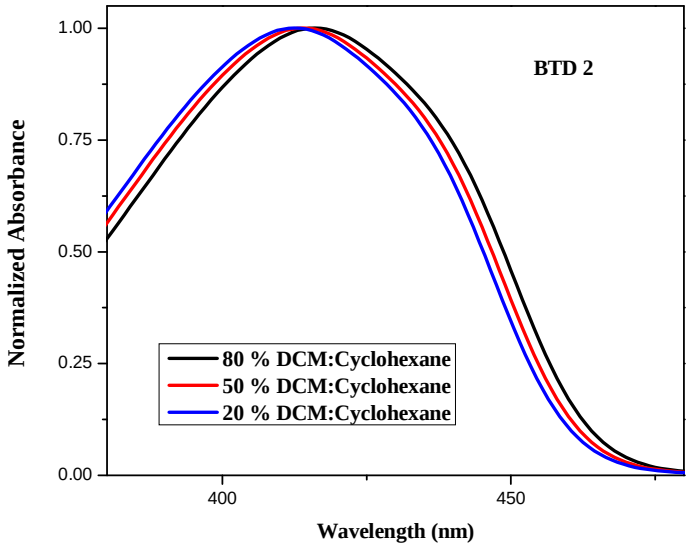


Fig. S11 UV/vis absorption spectra of **2.**

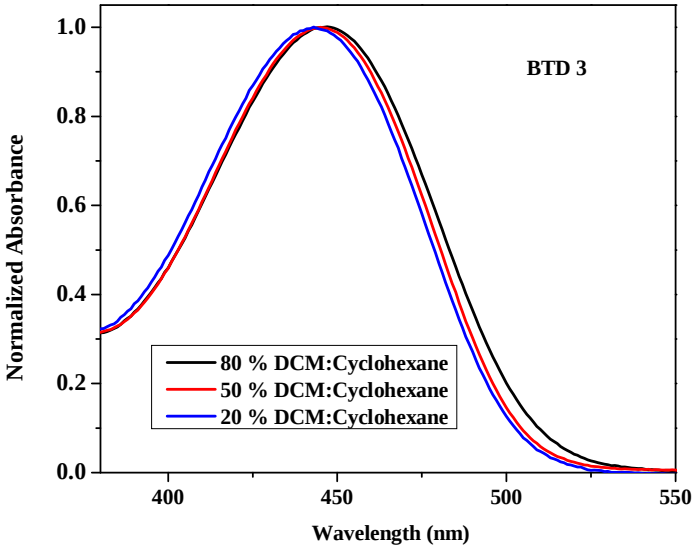


Fig. S12 UV/vis absorption spectra **3**.

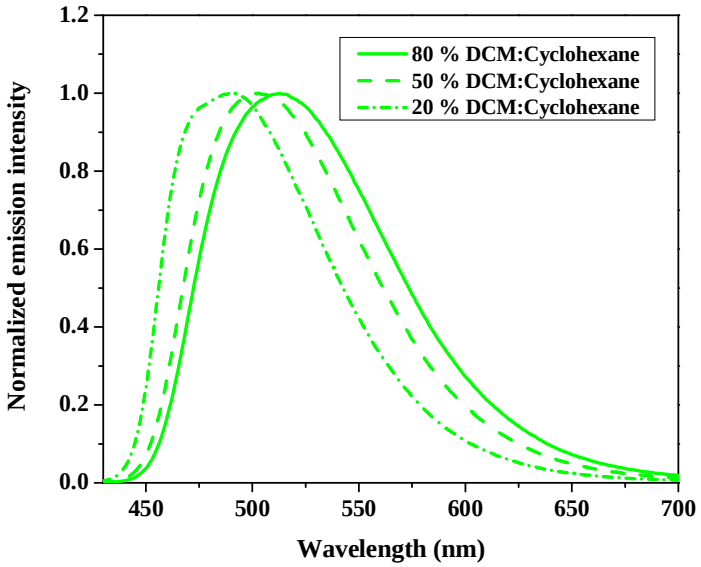


Fig. S13 Emission spectra of **2.**

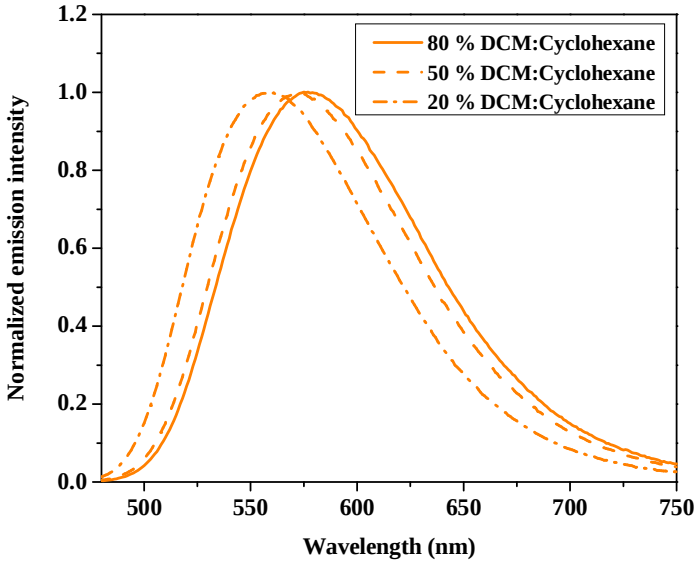


Fig. S14 Emission spectra of **3.**

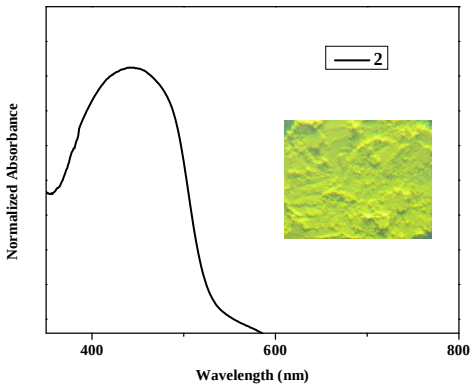


Fig. S15 Normalized absorbance and photograph of the solid sample of BTD **2** as prepared.

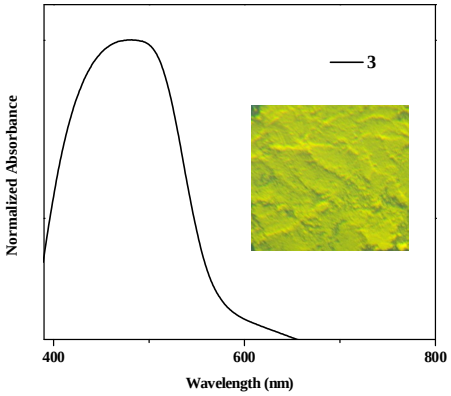


Fig. S16 Normalized absorbance and photograph of the sample of BTD **3** as prepared.

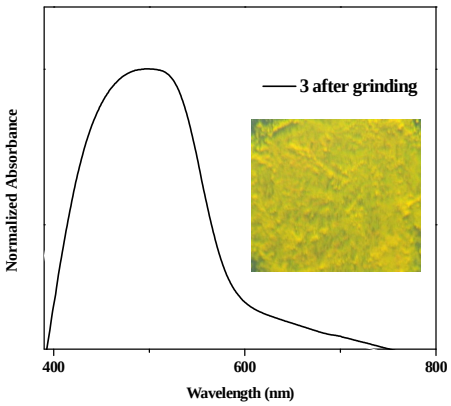


Fig. S17 Normalized absorbance and photograph of the sample of BTD **3** after grinding.

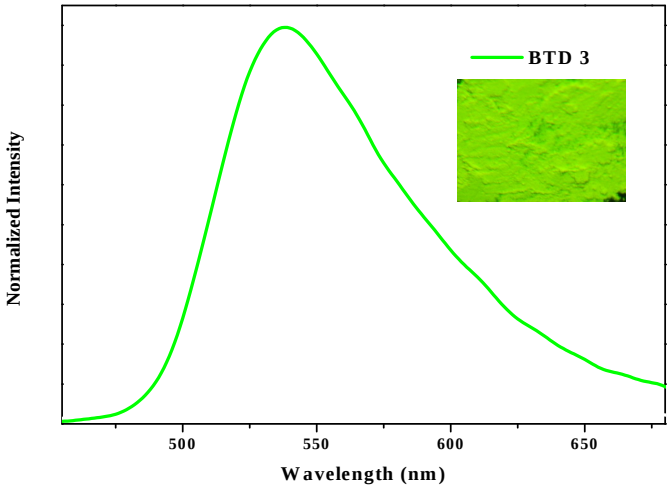


Fig. S18 Normalized emission and photograph of the solid sample of BTD **2** as prepared.

Table S1. Photophysical data of BTD **2** and **3**

BTD	Photophysical data[a]										
	In dichloromethane solution[a]					In solid state				Optical Gap (eV)[b]	HOMO-LUMO Gap (eV)[c]
	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Stoke's shift (nm)	Φ_F	λ_{abs} (nm) as prepared	λ_{abs} (nm) after grinding	λ_{em} (nm) as prepared	λ_{em} (nm) after grinding		
2	312	50437	513	96	0.47	443	–	538	538	2.68	2.79
	417	40382									
3	319	90273	578	130	0.14	481	498	556	582	2.47	2.69
	448	52841									

[a] measured in DCM; Stoke's shift calculated from the difference of λ_{max}abs and λ_{max}em. Φ_F calculated with Quinine sulfate (Φ = 0.55) in 0.1M H_2SO_4 as standard;
[b]Optical gap determined from λ_{onset}; [c] HOMO–LUMO gap: calculations performed at the B3LYP/6-31G** level.

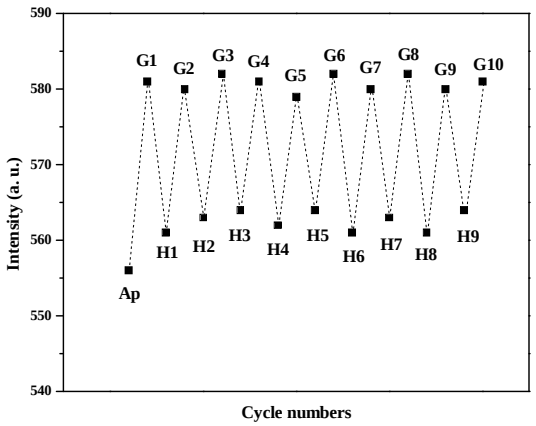


Fig. S19 BTD **3** as prepared (**Ap**) and repeated switching of the solid-state fluorescence by repeated grinding (**G**) and heating (**H**) cycles.

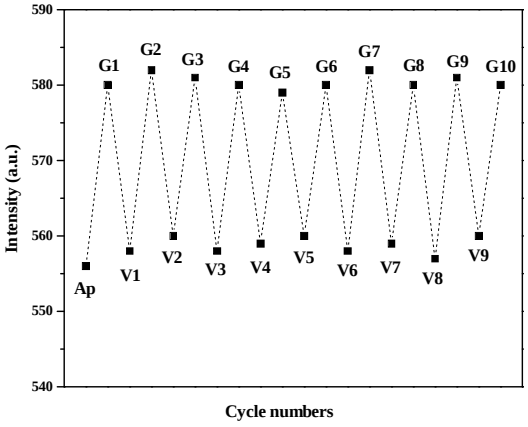


Fig. S20 BTD **3** as prepared (**Ap**) and repeated switching of the solid-state fluorescence by repeated grinding (**G**) and fuming (**V**) cycles

I. Crystallographic Data

Single crystal X-ray structural studies of benzothiadiazole **3** was collected at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. The crystal, and refinement data are summarized in Table 1. The CCDC number **1020099** contains the supplementary crystallographic data for BTD **3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S2. Crystal data and structure refinement for BTD 3.

BTD	3
Identification code	rm108
Empirical formula	$C_{30}\,H_{19}\,N_5\,S$
Formula weight	481.56
Temperature	273(2) K
Wavelength(A)	1.5418 A
Crystal system, space group	Monoclinic, P 21/c
***a*/ (Å)**	20.8735(5)
***b*/ (Å)**	11.8292(3)
***c*/ (Å)**	9.8383(3)
α /(°)	90
β/ (°)	101.978(3)
γ/ (°)	90

Volume	2376.35(11) $Å^3$
Z, Calculated density (mg m^{-3})	4, 1.346
Absorption coefficient /(mm^{-1})	1.438
F(000)	1000
Crystal size	0.22 x 0.18 x 0.14 mm
θ range for data collection/(°)	4.32 to 71.98
Limiting indices	-25<=h<=24, -14<=k<=10, -12<=l<=11
Reflections collected / unique	15657 / 4584 [R(int) = 0.0256]
Completeness to theta	θ = 25.00; 99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8240 and 0.7426
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4584 / 0 / 400
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1274
R indices (all data)	R1 = 0.0529, wR2 = 0.1393
Largest diff. peak and hole ($eÅ^{-3}$)	0.312 and -0.397

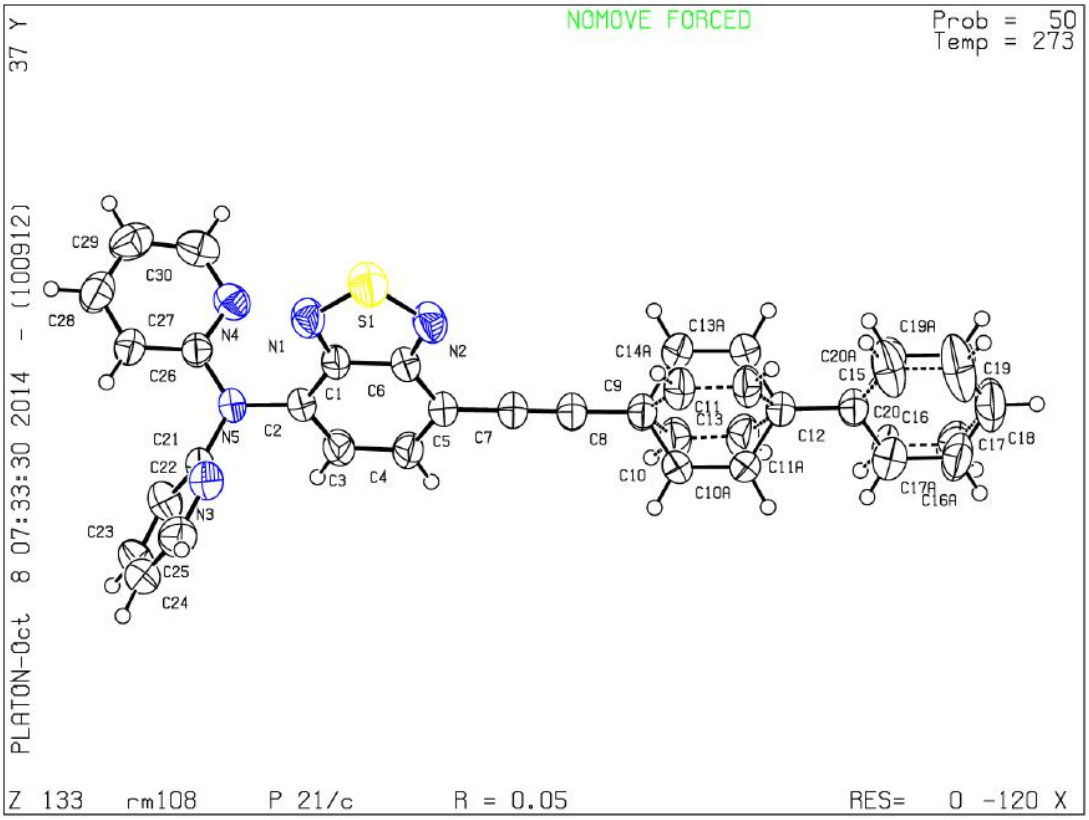


Fig. 21 ORTEP view of **3** and the atom-labelling scheme. Thermal ellipsoids are plotted at the 50 % level.

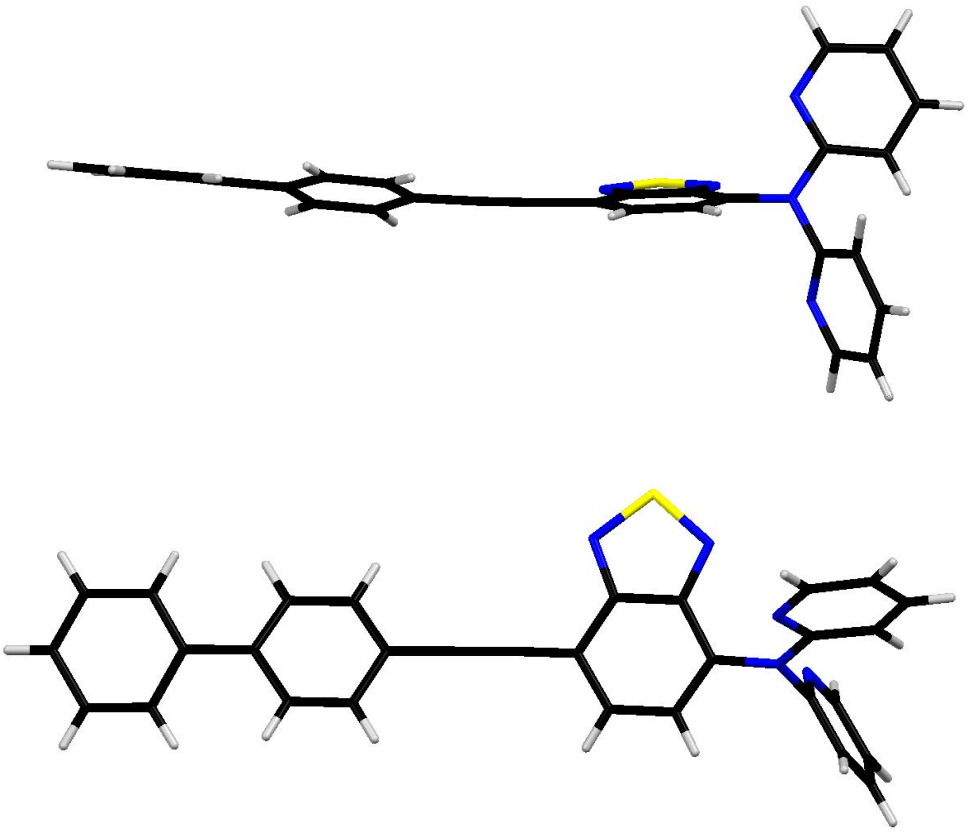


Fig. S22 Crystal structure of **3** side view (above) and top view (below)**.**

Table S3. Selected bond length and bond angle of BTD **3**

Bond lengths [Å]		Bond angles [°]	
For 3			
S(1)-N(2)	1.6035(18)	**N(2)-S(1)-N(1)**	101.64(8)
S(1)-N(1)	1.6086(17)	**C(1)-N(1)-S(1)**	105.76(12)
N(1)-C(1)	1.341(2)	**C(6)-N(2)-S(1)**	106.07(12)
N(2)-C(6)	1.339(2)	**N(1)-C(1)-C(2)**	126.49(15)
C(2)-N(5)	1.416(2)	**N(1)-C(1)-C(6)**	113.32(15)
C(21)-N(5)	1.429(2)	**C(3)-C(2)-N(5)**	121.05(16)
C(21)-N(3)	1.320(2)	**N(5)-C(2)-C(1)**	121.69(15)
C(25)-N(3)	1.347(3)	**N(2)-C(6)-C(5)**	125.63(15)
C(26)-N(4)	1.336(2)	**N(2)-C(6)-C(1)**	113.21(15)
C(26)-N(5)	1.394(2)	**N(3)-C(21)-C(22)**	123.75(17)
N(4)-C(30)	1.350(3)	**N(3)-C(21)-N(5)**	115.47(15)
		C(22)-C(21)-N(5)	120.77(17)
		N(3)-C(25)-C(24)	123.5(2)
		N(3)-C(25)-H(25)	118.3
		N(4)-C(26)-C(27)	123.23(16)

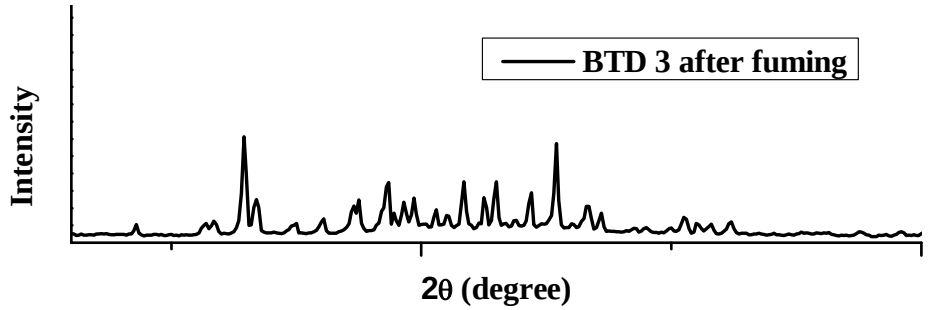


Fig. S23 Powder-XRD patterns of BTD 3 after fuming with DCM vapor.

DFT Calculations for 2 and 3. [1]

BTD 2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.186558	3.018415	-0.198171
2	7	0	0.906723	1.989942	-0.136800
3	7	0	3.426868	1.942778	-0.128510
4	6	0	1.418570	0.758746	-0.059130
5	6	0	2.868360	0.731796	-0.054262
6	6	0	3.579870	-0.518633	0.025101
7	6	0	2.804238	-1.670056	0.094133
8	1	0	3.306442	-2.629892	0.154940
9	6	0	1.390007	-1.644076	0.089265
10	1	0	0.851816	-2.584296	0.146512
11	6	0	0.658325	-0.464011	0.015181
12	6	0	-0.754436	-0.444004	0.012766
13	6	0	-1.972005	-0.423371	0.011959
14	6	0	-3.391561	-0.375649	0.011462
15	6	0	-4.066580	0.860778	-0.058713
16	6	0	-4.159169	-1.556195	0.082093
17	6	0	-5.454303	0.907395	-0.057184
18	1	0	-3.486390	1.775444	-0.123716
19	6	0	-5.546623	-1.497354	0.083790
20	1	0	-3.653251	-2.514191	0.146347
21	6	0	-6.226201	-0.267129	0.014722
22	1	0	-5.952489	1.868516	-0.139390
23	1	0	-6.116502	-2.417668	0.167514
24	6	0	-7.708329	-0.209768	0.019353
25	6	0	-8.388358	0.824073	0.686938
26	6	0	-8.472080	-1.187192	-0.642431
27	6	0	-9.781119	0.878340	0.692556
28	1	0	-7.820103	1.574510	1.228429
29	6	0	-9.864900	-1.132855	-0.636623
30	1	0	-7.968561	-1.979226	-1.188727
31	6	0	-10.525938	-0.099903	0.030930
32	1	0	-10.285508	1.681508	1.222327
33	1	0	-10.434632	-1.893942	-1.162275
34	1	0	-11.611181	-0.057583	0.035305
35	6	0	4.993580	-0.553764	0.031770
36	6	0	6.210318	-0.583682	0.038124
37	6	0	7.630094	-0.587743	0.043909
38	6	0	8.351629	0.624794	-0.030181
39	6	0	8.374133	-1.779848	0.122682
40	7	0	9.681920	0.698329	-0.029427
41	1	0	7.806346	1.564063	-0.092189
42	6	0	9.762192	-1.706447	0.123626
43	1	0	7.860517	-2.734174	0.181459
44	6	0	10.368375	-0.450646	0.046334

45	1	0	10.368373	-2.604888	0.183224
46	1	0	11.453081	-0.361763	0.045148

Total Energy (HF) = -1600.2309089 Hartree

BTD 3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.743098	-2.197647	2.184761
2	7	0	-0.461369	-1.485540	1.443324
3	7	0	-2.981151	-1.449663	1.408020
4	6	0	-0.970461	-0.627776	0.555183
5	6	0	-2.422219	-0.607967	0.533900
6	6	0	-3.120828	0.266205	-0.363311
7	6	0	-2.357249	1.072450	-1.178333
8	1	0	-2.863029	1.748969	-1.859705
9	6	0	-0.938337	1.064813	-1.152129
10	1	0	-0.401861	1.728977	-1.821418
11	6	0	-0.208750	0.235068	-0.312741
12	6	0	1.206123	0.225377	-0.293309
13	6	0	2.423193	0.217360	-0.276809
14	6	0	3.843732	0.195303	-0.241910
15	6	0	4.526693	-0.656245	0.650841
16	6	0	4.604629	1.021052	-1.094401
17	6	0	5.914912	-0.676161	0.684736
18	1	0	3.952369	-1.303461	1.305646
19	6	0	5.992599	0.992984	-1.051859
20	1	0	4.093111	1.689157	-1.779880
21	6	0	6.679789	0.145890	-0.163337
22	1	0	6.418704	-1.359372	1.361787
23	1	0	6.556745	1.657748	-1.698962
24	6	0	8.162335	0.120122	-0.121837
25	6	0	8.848204	-0.038165	1.095232
26	6	0	8.920956	0.253171	-1.298047
27	6	0	10.241326	-0.062650	1.134524
28	1	0	8.283888	-0.115251	2.019860
29	6	0	10.314108	0.228823	-1.258692
30	1	0	8.412698	0.348833	-2.253000
31	6	0	10.980950	0.070786	-0.042201
32	1	0	10.750064	-0.177368	2.087545
33	1	0	10.879563	0.324537	-2.181374
34	1	0	12.066448	0.051739	-0.011495
35	7	0	-4.542659	0.313511	-0.384666
36	6	0	-5.169916	1.513628	0.045117
37	6	0	-6.430309	1.907856	-0.439069
38	6	0	-6.950606	3.116986	0.001727

39	1	0	-6.979634	1.280238	-1.126850
40	6	0	-4.969310	3.429570	1.292475
41	6	0	-6.213408	3.905512	0.890004
42	1	0	-7.922167	3.446969	-0.355162
43	1	0	-4.350625	4.005752	1.978539
44	1	0	-6.588796	4.856102	1.253827
45	6	0	-5.260349	-0.863682	-0.688515
46	6	0	-4.675282	-1.853067	-1.503465
47	6	0	-7.181113	-2.097159	-0.463281
48	6	0	-5.399858	-3.008305	-1.761137
49	1	0	-3.686817	-1.708362	-1.922993
50	6	0	-6.685089	-3.147931	-1.230202
51	1	0	-8.181944	-2.148963	-0.037434
52	1	0	-4.969521	-3.788138	-2.383064
53	1	0	-7.283705	-4.034097	-1.411308
54	7	0	-6.493535	-0.983581	-0.187489
55	7	0	-4.454816	2.261739	0.890005

Total Energy (HF) = -1826.5141315 Hartree

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1 (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, 1988, **37**, 785− 789. (c) Becke, A. D. *J. Chem. Phys.*, 1993, **98**, 1372−1377.