Electronic supplementary information (ESI)

Expression of Anti-Kasha's emission from amino benzothiadiazole and

its utilizations for fluorescent chemosensors and organic light emitting

materials

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Experimental Section

Material and Instruments

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. For the purpose of the measurement of photophysical properties, toluene was distilled from sodium, while acetonitrile was distilled from CaH2. Melting points were measured with a micro melting point apparatus. Infrared spectra were obtained with an FTIR spectrometer. NMR spectra were operated at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR. All the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet. Coupling constants J were reported in hertz. Highresolution mass spectra (HRMS) data were obtained with an electron ionization time-of-flight (EI-TOF) mass spectrometer. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254. The absorption spectra were measured using UV-vis spectrometer. FL spectra were recorded on a fluorospectro photometer with a xenon lamp excitation source. PL decay dynamics were measured on a timecorrelated single-photon counting (TCSPC) spectrofluorometer at room temperature, and the compounds were excited by a 405 nm picosecond laser diode. Cyclic voltammetry measurements were performed on an electrochemical analyzer in acetonitrile at room temperature. Thermogravimetric Analysis (TGA) was obtained with a thermal analyzer at heating and cooling rates of 10 K/min under an N₂ atmosphere.

PMMA Fabrication: a certain amount of fluorophore was added into a certain volume of 10% PMMA in chlorobenzene. The resulting mixture was pasted on the glass slide under 2500r/min to produce a wet film. The wet film was dried under 90 °C for 1h.

Device Fabrication: Before device fabrication, the ITO glass substrates were pre-cleaned carefully. Then hole transporting material PEDOT:PSS was made with 4000 r/s for 45 s and annealing 25 min at 150 °C. Emission Layer was prepared in chlorobenzene with 30 mg/mL. Then it was made with 2000 r/s for 45 s and annealing 25 min at 50 °C. After the organic film deposition, 40 nm of TPBi, 1.5 nm of LiF and 50 nm of aluminum were thermally evaporated onto the organic surface. Preparation of compounds 1-7



To a 100 mL round bottom flask with magnetic stir bar was added 4,7dibromobenzo[c][1,2,5]thiadiazole (735 mg, 2.5 mmol), (4-methoxyphenyl)boronic acid (456 mg, 3.0 mmol), Pd(PPh₃)₄ (145mg, 0.125 mmol), K₂CO₃ (690mg, 5mmol), and was suspended in a mixture of Toluene and water (35ml) and stirred at reflux under N₂ for 12h. After cooling to room tempeteture, the solvent was removed via vacuum. Purification of the residue by flash chromatography on silica gel using DCM/HEX (1:4) as eluent afforded the desired product as a green solid. The yield is 51%.



To a 25 mL shrek tube with magnetic stir bar was added 4-bromo-7-(4methoxyphenyl)benzo[c][1,2,5]thiadiazole (64mg, 0.2 mmol), amino (0.25 mmol), $Pd_2(dba)_3$ (18.3mg, 0.02 mmol), (t-Bu)₃HP⁺BF₄⁻ (17.5mg, 0.06 mmol), t-BuNa (38.5mg, 0.4 mmol) and was suspended in Toluene (4ml) and stirred at reflux under N₂ for 12h. After cooling to room tempeteture, the solvent was removed via vacuum. Purification of the residue by flash chromatography on silica gel using DCM/HEX as eluent afforded the desired product.



Compound **1**: Red solid, yield 71.6%, mp 87-88°C. ¹H NMR (400 MHz, DMSO): δ 7.85 (d, *J* = 8.8Hz, 2H), 7.65 (d, *J* = 8.0Hz, 1H), 7.03 (d, *J* = 8.8Hz, 2H), 6.67 (t, *J* = 5.6Hz, 1H), 6.49 (d, *J* = 8.0Hz, 1H), 3.81 (s, 3H), 3.33-3.28 (m, 2H), 1.70-1.63 (m, 2H), 1.46-1.37 (m, 2H), 0.94 (t, *J* = 7.2Hz, 3H).

¹³C NMR (100MHz, DMSO): δ 158.5, 154.1, 148.2, 140.1, 130.8, 130.6, 129.5, 118.9, 114.3, 101.8, 55.6, 42.7, 30.7, 20.3, 14.3. HRMS (EI-TOF): cacld. for C₁₇H₁₉N₃OS [M⁺], 313.1249; found: 313.1254. IR: 2959, 2933, 1568, 1504, 1371, 1309, 1274, 1244, 1175, 1141, 1036.



Figure S4 ¹³C NMR of compound 2 in CDCl₃.

Compound **2**: Red solid, yield 62.6%, mp 188-189°C. ¹H NMR (400 MHz, DMSO): δ 7.839 (d, *J* = 8.8Hz, 2H), 7.59 (d, *J* = 8.0Hz, 1H), 7.04 (d, *J* = 8.8Hz, 2H), 6.87 (d, *J* = 7.6Hz, 1H), 5.53 (s, 1H), 3.81 (s, 3H), 2.15-2.09 (m, 9H), 1.77-1.69 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 158.6, 154.1, 149.3, 137.0, 130.9, 130.4, 129.5, 129.4, 114.0, 105.0, 55.4, 52.2, 42.2, 36.5, 29.6. HRMS (EI-TOF): cacld. for C₂₃H₂₅N₃OS [M⁺], 391.1718; found: 391.1715. IR: 2917, 2854, 1557, 1501, 1375, 1358, 1307, 1244, 1188, 1140, 1036.



Figure S5 ¹H NMR of compound 3 in DMSO- d_6 .



Compound **3**: Orange solid, yield 55.5%, mp 136-137°C. ¹H NMR (400 MHz, DMSO): δ 8.89 (s, 1H), 7.90 (d, J = 8.8Hz, 2H), 7.68 (d, J = 8.0Hz, 1H), 7.44-7.34 (m, 4H), 7.27 (d, J = 8.0Hz, 1H), 7.08-7.01 (m, 3H), 3.82 (s, 3H). ¹³C NMR (100 MHz, DMSO): δ 159.0, 154.2, 149.2, 141.9, 135.6, 130.3, 129.9, 129.7, 129.6, 122.8, 122.5, 120.5, 114.4, 107.1, 55.7. HRMS (EI-TOF): cacld. for C₁₉H₁₅N₃OS [M⁺], 333.0936; found: 333.0937. IR: 2834, 1605, 1591, 1557, 1505, 1477, 1414, 1309,

1278, 1247, 1179, 1034.







Figure S8 ¹³C NMR of compound **4** in DMSO- d_6 .

Compound **4**: Red solid, yield 70.5%, mp 152-153°C. ¹H NMR (400 MHz, DMSO): δ 8.68 (s, 1H), 7.88 (d, *J* = 8.8Hz, 2H), 7.62 (d, *J* = 8.0Hz, 1H), 7.35 (d, *J* = 9.2Hz, 2H), 7.05 (d, *J* = 8.8Hz, 2H), 7.00-6.96 (m, 3H), 3.81 (s, 3H), 3.77 (s, 3H). ¹³C NMR (100 MHz, DMSO): δ 158.8, 155.8, 154.2, 148.7, 137.2, 134.4, 130.5, 129.9, 129.7, 123.9, 121.4, 115.0, 114.3, 104.8, 55.8, 55.6.. HRMS (EI-TOF): cacld. for C₂₀H₁₇N₃O₂S [M⁺], 363.1041; found: 363.1046. IR: 2929, 1607, 1590, 1560, 1511, 1461, 1369, 1276, 1245, 1173.



Figure S10 ¹³C NMR of compound 5 in DMSO- d_6 .

Compound **5**: Yellow solid, yield 86.0%, mp 234-235°C. ¹H NMR (400 MHz, DMSO): δ 9.52 (s, 1H), 7.93 (d, *J* = 8.8Hz, 2H), 7.76 (d, *J* = 7.6Hz, 1H), 7.70 (d, *J* = 8.8Hz, 2H), 7.55(d, *J* = 7.6Hz, 1H), 7.41 (d, *J* = 8.4Hz, 2H), 7.09 (d, *J* = 9.2Hz, 2H), 3.83 (s, 3H). ¹³C NMR (100 MHz, DMSO): 158.9, 153.7, 149.5, 147.0, 133.6, 132.0, 129.8, 129.4, 128.3, 125.9, 119.7, 117.0, 114.0, 113.5, 101.1, 55.2. HRMS (EI-TOF): cacld. for C₂₀H₁₄N₄OS [M⁺], 358.0888; found: 358.0887. IR: 2915, 2217, 1607, 1584, 1551, 1531, 1375, 1328, 1247, 1179.



Figure S11 ¹H NMR of compound **6** in DMSO- d_6 .



Compound **6**: Orange-red solid, yield 80%, mp 136-137°C. ¹H NMR (400 MHz, DMSO): δ 7.94 (d, J = 8.8Hz, 2H), 7.76 (d, J = 8Hz, 1H), 7.30-7.26 (m, 5H), 7.11-7.00 (m, 5H), 3.84 (s, 3H). ¹³C NMR (100 MHz, DMSO): δ 159.6, 154.8, 151.8, 147.7, 138.2, 130.6, 129.9, 129.7, 129.2, 128.4, 125.3, 123.9, 123.6, 114.5, 55.7. HRMS (EI-TOF): cacld. for C₂₅H₁₉N₃OS [M⁺], 409.1249; found: 409.1254. IR: 2899, 1607, 1590, 1548, 1486, 1350, 1276, 1249, 1178, 1034.





Compound **7**: Red solid, yield 85%, mp 136-137°C. ¹H NMR (400 MHz, DMSO): δ 7.89 (d, *J* = 8.8Hz, 2H), 7.67 (d, *J* = 7.6Hz, 1H), 7.07 (d, *J* = 8.8Hz, 2H), 6.99 (d, *J* = 8.0Hz, 1H), 6.95-6.92 (m, 4H), 6.89-6.86 (m, 4H), 3.82 (s, 3H), 3.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 155.8,

155.0, 150.9, 141.4, 139.5, 130.2, 130.0, 127.9, 127.6, 125.7, 121.0, 114.5, 114.0, 55.44, 55.36. HRMS (EI-TOF): cacld. for $C_{27}H_{23}N_3O_3S$ [M⁺], 469.1460; found: 469.1458. IR: 2839, 1607, 1543, 1505, 1480, 1351, 1241, 1179, 1102, 1070, 1034.



Figures S15. Thermogravimetric analysis curves of compounds1-7.

Compounds	1	2	3	4	5	6	7
Formula	$C_{17}H_{19}N_30S$	C ₂₃ H ₂₅ N ₃ 0S	$C_{19}H_{15}N_{3}OS$	$C_{20}H_{17}N_3O_2S$	C ₂₀ H ₁₄ N ₄ OS	$C_{25}H_{19}N_30S$	$C_{27}H_{23}N_3O_3S$
CCDC	1813982	1813986	1813987	1813988	1813989	1813990	1813991
a [Å]	8.4386	18.4571	14.3135	15.0345	9.1703	10.2716	13.9070
b [Å]	9.4891	16.2012	14.6015	7.1821	19.850	10.9546	5.0220
c [Å]	11.2415	6.5052	15.5923	31.643	18.7033	11.2649	33.693
α[°]	106.972	90	90	90	90	99.583	90
β[°]	102.465	90	101.462	93.706	102.929	111.659	93.091
γ[°]	107.518	90	90	90	90	113.273	90
Z	2	4	8	8	8	2	4
V [ų]	774.17	1945.23	3193.8	3409.6	3318.2	1007.19	1349.8
D [g cm ⁻³]	1.334	1.337	1.387	1.416	1.435	1.350	1.327
Space group	P -1	P n a 21	P 21	P 21 / c	P 21 / c	P -1	P 21 / n
Hall group	-P 1	P 2c -2n	P 2yb	-P 2ybc	-P 2ybc	-P 1	-P 2yn
Mu [mm ⁻¹]	0.215	0.186	0.213	0.210	0.213	0.183	0.172
R (reflections)	0.0499	0.0444	0.0549	0.1028	0.0490	0.0452	0.0595
wR2 (reflections)	0.1282	0.1107	0.1347	0.3098	0.1339	0.1211	0.1571

 Table S1. Single crystal analysis.



Figure S16. Absorption and emission spectra of compounds**1-7** in toluene (a-c) and in CH₃CN (d-f), excited at the maximum absorption wavelength.



Figure S17. Excitation dependant emissions of compounds **2-7** in toluene (a-f) and in acetonitrile (A-E).

	Compound 1	Compound 2	Compound 7	
380 nm	9.0%	7.3%	5.0%	
400 nm	2.5%	2.6%	4.1%	
420 nm	1.2%	1.3%	1.2%	
440 nm	0.6%	0.9%	0.6%	

 Table S2 Relationship of QY and excited wavelength for compound 1, 2, 7 in toluene.



Figures S18. Purity analysis by HPLC



Figure S19. Excitation spectra of compounds **2-7**, monitored at one or two emissive bands (as indicated in parenthesis) in toluene (a-f and in acetonitrile (A-E).



Figure S20. Fluorescence decay traces of compounds **1**-**7** in toluene or acetonitrile monitored at specified emission wavelengths, excited at 404 nm.

Compound		Toluene		MeCN			
Compound	λ	Life Time	χ ²	λ	Life time	χ ²	
1	483	τ ₁ =1.32(66.32%)	0.005				
		τ ₂ =10.96(33.68%)					
	505	τ ₁ =1.65(90.83%)	1 2 4 1				
	595	τ ₂ =4.85(9.17%)	1.241				
2	502	τ=10.56(100%)	1.273				
	599	τ ₁ =1.90(93.32%)	1 210				
		τ ₂ =12.24(6.68%)	1.319				
3	582	τ=4.01(100%)	0.887	545	τ_1 =1.11(14.81%)	1.103	
					τ ₂ =12.67(85.19%)		
				611	τ ₁ =0.94(93.11%)	1.403	
					τ ₂ =5.50(6.89%)		
4	600	τ=3.46(100%)	1.313				
5	569	T=6 84(100%)	1 150	560	τ ₁ =2.11(52.98%)	- 1.103	
		(-0.84(100%)	1.150	509	τ ₂ =12.38(47.02%)		
6	575	τ=15.26(100%)	1.117	611	τ=6.80(100%)	0.970	
7	481	τ ₁ =2.91(92.31%)	1 200				
		τ ₂ =13.60(7.69%)	1.209				
	630	τ ₁ =2.69(83.66%)	1 002				
		τ ₂ =7.22(16.34%)					

Table S3 Fluorescent lifetimes of compounds 1-7 in toluene and in acetonitrile



Figure S21. Emission spectra of compounds **1-7** in powders (a) and crystals (b), excitation wavelength is maximum absorption wavelength in toluene.



Figure S22. (a) Absorption spectra of compounds 2-7 in films; (b) Emission spectra of compounds 1, 5, 6 in films.



Figure S23 Absorption (a) and emission (b) spectra of compounds **1-7** in PMMA film doping with compounds **1-7** (9×10^{-5} mol / 1 g PMMA).



Figures S24 Emission of compounds **1-7** in powders as excitation wavelength changes from 360 nm to 420nm.



Figure S25 Emission spectra of compounds 1-7 in toluene under 77K as excitation wavelength changes from 360 nm to 420nm.



Figure S26. UV-vis absorption and FL of compounds 1-6 (5 x 10^{-5} M) before (up) and after (down) in the presence of HCl (0.1M) in MeCN.



Figure S27. Reversible color change of silica plate (doping with compound **2**) as a function of HCl and NH₃.



Figure S28. The frontier orbital plots of the HOMO and LUMO of compounds 1-7.



Figure S29. Cyclic voltammograms of compound1-7.



Figure S30. Energy gaps (HOMO/LUMO) from CV (a); from theoretical calculation (b); and from UV observation (c) *versus* compounds **1-7**.

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	номо		LUMO		Eg		
compound	CVa	Calcd ^b	CVc	Calcd	CV	Calcd	UV ^d
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
1	-5.288	-5.387	-2.850	-2.669	2.438	2.718	2.311
2	-5.241	-5.114	-2.724	-2.649	2.517	2.466	2.285
3	-5.314	-5.316	-2.829	-2.883	2.485	2.433	2.320
4	-5.036	-5.173	-2.810	-2.809	2.226	2.363	2.267
5	-5.449	-5.677	-2.910	-3.216	2.539	2.461	2.393
6	-5.320	-5.271	-2.869	-2.876	2.451	2.395	2.311
7	-5.103	-5.018	-2.834	-2.767	2.269	2.251	2.179

Table S4. The value of HOMO, LUMO, and energy gap of compounds 1-7.

^a Potentials vs reference electrode SCE, working electrode glassy carbon, auxiliary electrode Pt, 0.1 M Bu₄N⁺PF₆⁻-MeCN, scan rate 100 mV/s, HOMO = E_{ref} - E_{ox} . ^b Obtained from DFT using the B₃LYP functional and the 6-31G* basis set. ^c LUMO= E_{ref} - E_{red} . ^d E_g = 1241 / $\lambda_{(UV onset in toluene)}$.