Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementry Information(ESI)

Tunable RGB luminescence of single molecule with high quantum yields through a rational design

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Contents

1.Experimental Section

1.1 Materials

4-aminosalicylic acid (99%), 2-aminothiophenol (98%), tetrabutylammonium fluoride trihydrate (98%), tert-butyldimethylsilyl chloride (98%), trifluoroacetic acid (99%), tert-Butyldimethylsilyl chloride(99%) were purchased from Energy Chemical .4-dimethylaminopyridine (99%), Rhodamine B (95%) were perchased from Aladdin, polyphosphoric acid (AR), benzoyl chloride (AR) were purchased from Sinopharm Chemical Reagent. All the reagents were used directly without further purification.

1.2 Instrument Characterization

^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker AVANCEIII 500M NMR spectrometer. LC-HRMS spectral data were recorded on a Bruker Agilent1290-micrOTOF Q II spectrometer. UV-VIS absorption spectra were measured on SHIMADZU UV-2550 UV-VIS spectrophotometer. Fluorescence emission spectra were obtained using SHIMADZU RF-5301pc spectrofluorophotometer at 298 K. Absolute quantum yields were measured on a FLS920 steady state and transient state fluorescence spectrometer from Edinburgh Instrument. Refractive index was measured on ATAGO NAR-3T abbe refractometer.

1.3 Parameters of the single crystal of RHBT-G

Table S1. Summary of crystal data and intensity collection parameters for **RHBT-G**

Compound	**RHBT-G**
Formula	C41H38N4O3S
Formula mass	666.81
Space group	P2(1)/c
a/Å	18.9533(12)
b/Å	9.1195(6)
c/Å	21.5823(13)
α/°	90
β/°	113.281
γ/°	90
V/ $Å^3$	3426.6(4)
Z/mg.m^{-3}	4 4
F_{000}	1408.0
Theta max/°	25.230
R(reflections)	0.0584(3391)
wR2(reflections)	0.1604(6158)
CCDC No.	**1416546**

1.4 PL spectra of RHBT-G demonsrating AIEE property

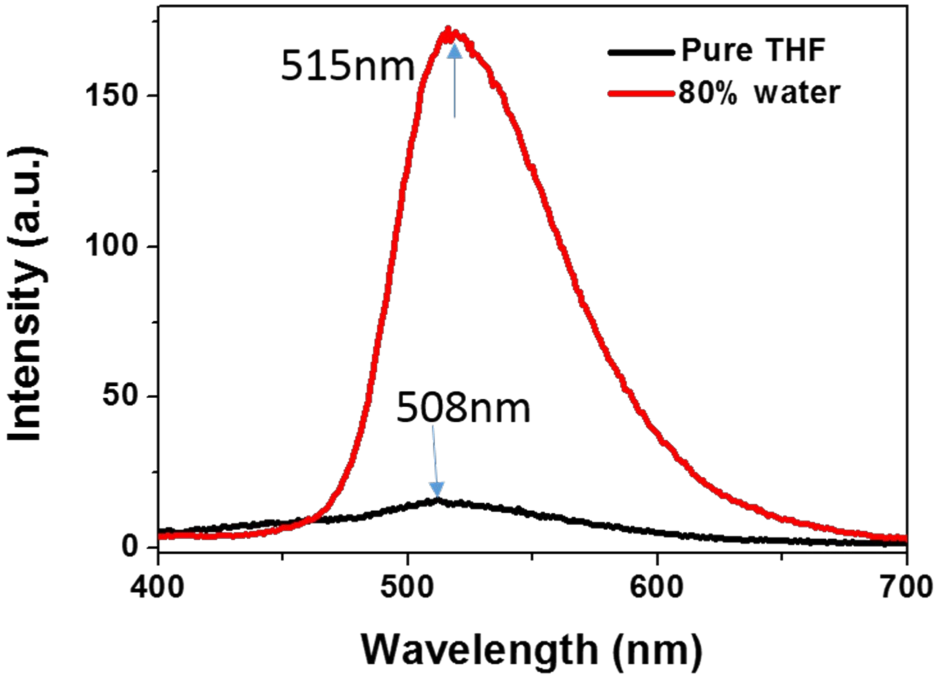


Fig. S1: PL spectra of 1.0×10^{-5} M **RHBT-G** in THF and a mixed solvent with water fraction of 80%.

1.5 TD-DFT calculation of the J-aggregation

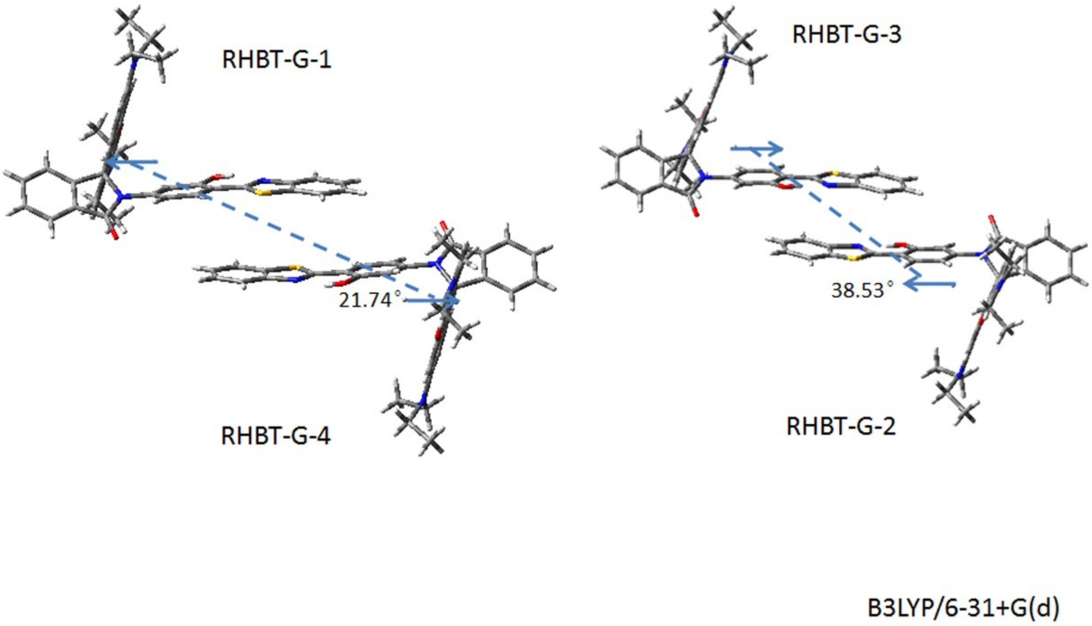


Fig.S2: The angle between the transition dipole and interconnected axis calculated based on the two disordered crystal structure. (All the transition dipole were drew using the dipole moment with the largest f value.)

Ground to excited state transition electric dipole moments (Au):

RHBT-G-1

state	X	Y	Z	Dip. S.	Osc.
1	0.2589	-0.2089	-0.0101	0.1108	0.0085
2	0.1026	0.0123	0.0817	0.0174	0.0014
3	-0.1749	-0.1299	-0.1656	0.0749	0.0066
4	0.3101	0.0933	0.0639	0.1089	0.0098
5	**-2.3377**	**0.442**	**0.2995**	**5.7498**	**0.5284**
6	1.0559	-0.2612	-0.2412	1.2413	0.1168
7	0.6119	0.9362	-0.2034	1.2922	0.1302
8	0.1905	-0.1084	-0.3177	0.149	0.015
9	0.9536	-0.4254	-0.3307	1.1997	0.1227
10	0.304	0.4005	-0.1636	0.2796	0.0288

RHBT-G-2

state	X	Y	Z	Dip. S.	Osc.
1	0.2573	-0.0839	0.0199	0.0736	0.0057
2	-0.1984	0.0946	-0.0761	0.0541	0.0043
3	-0.5727	0.2506	0.0245	0.3914	0.0349
4	**2.1129**	**-0.8171**	**0.6916**	**5.6103**	**0.5061**
5	0.0361	0.121	-0.0808	0.0225	0.0021
6	-0.5081	0.0976	-0.108	0.2794	0.0264
7	0.5832	-0.173	0.0705	0.3751	0.037
8	0.2104	0.8872	0.0266	0.8321	0.0836
9	0.4919	0.5156	0.4352	0.6972	0.0707
10	-0.1405	-0.176	0.038	0.0521	0.0054

RHBT-G-3

state	X	Y	Z	Dip. S.	Osc.
1	-0.2574	-0.084	0.0199	0.0737	0.0057
2	0.1985	0.0946	-0.0762	0.0542	0.0043
3	0.5713	0.25	0.0247	0.3895	0.0347
4	**-2.1133**	**-0.8173**	**0.6915**	**5.6122**	**0.5063**
5	-0.0362	0.1209	-0.0808	0.0225	0.0021
6	0.5081	0.0976	-0.108	0.2794	0.0264
7	-0.5832	-0.1728	0.0705	0.3749	0.0369
8	-0.2085	0.8854	0.0249	0.8279	0.0831
9	-0.4922	0.5179	0.4361	0.7006	0.0711
10	0.1406	-0.1755	0.0372	0.0519	0.0054

RHBT-G-4

state	X	Y	Z	Dip. S.	Osc.
1	-0.2587	-0.2088	-0.0101	0.1106	0.0084
2	-0.1027	0.0123	0.0817	0.0174	0.0014
3	0.1751	-0.1299	-0.1658	0.075	0.0066
4	-0.3098	0.0934	0.0639	0.1088	0.0098
5	**2.3369**	**0.4418**	**0.2992**	**5.7459**	**0.528**
6	-1.0568	-0.2614	-0.2412	1.2433	0.117
7	-0.6258	0.9245	-0.2289	1.2988	0.1309
8	-0.1389	-0.1862	-0.299	0.1434	0.0145
9	-0.9535	-0.4253	-0.3299	1.1989	0.1226
10	-0.3046	0.3993	-0.1646	0.2793	0.0287

Fig.S3: The dipole moment of each structure calculated using B3LYP/6-31+G(d). Bold contents: dipole moment with the largest f value.

Excited State	Involved orbitals	Energy(eV)	Oscillator strength
1	HOMO—LUMO (0.69614)	3.1159	0.0085
2	HOMO-1—LUMO (0.69017) HOMO-1—LUMO+1 (-0.10553)	3.2166	0.0014
3	HOMO—LUMO+1 (0.69174)	3.5928	0.0066
4	HOMO-1—LUMO (0.11172) HOMO-1—LUMO+1 (0.68014)	3.6737	0.0098
5	HOMO-2—LUMO (0.69056)	3.7508	0.5284

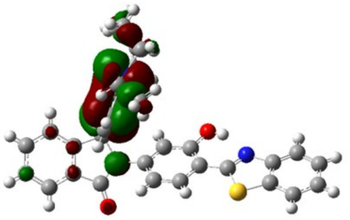
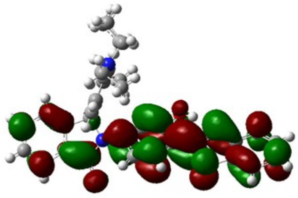
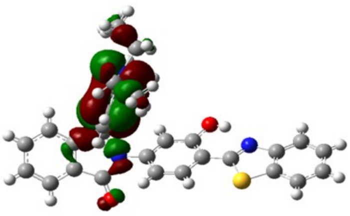
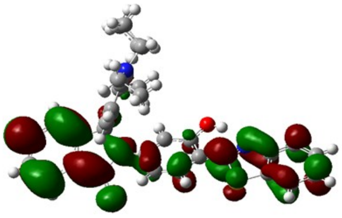
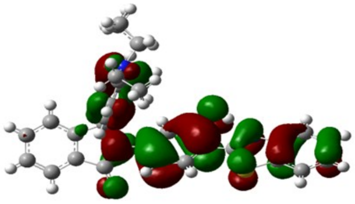
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2			

Fig.S4: Molecular orbitals of RHBT-G-1

Excited State	Involved orbitals	Energy(eV)	Oscillator strength
1	HOMO—LUMO (0.69771)	3.1378	0.0057
2	HOMO-1—LUMO (0.69116) HOMO-1—LUMO+1 (-0.10403)	3.2670	0.0043
3	HOMO-2—LUMO (-0.19137) HOMO—LUMO+1 (0.66536)	3.6386	0.0349
4	HOMO-2—LUMO (0.66499) HOMO—LUMO+1 (0.19608)	3.6823	0.5061

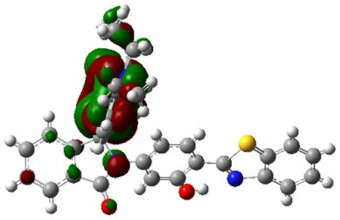
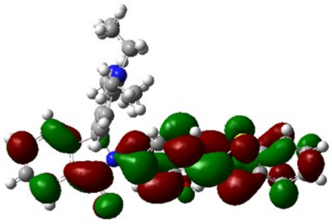
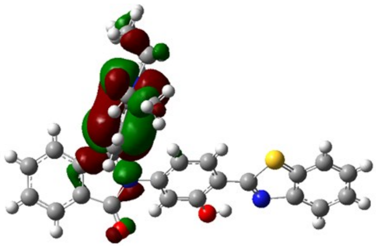
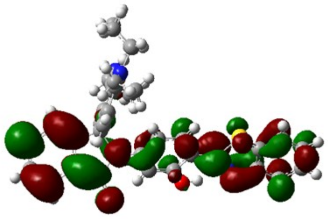
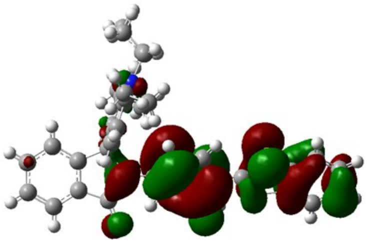
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2			

Fig.S5: Molecular orbitals of RHBT-G-2

Excited State	Involved orbitals	Energy(eV)	Oscillator strength
1	HOMO—LUMO (0.69773)	3.1377	0.0057
2	HOMO-1—LUMO (0.69117) HOMO-1—LUMO+1 (-0.10404)	3.2669	0.0043
3	HOMO-2—LUMO (-0.19097) HOMO—LUMO+1 (0.66549)	3.6385	0.0347
4	HOMO-2—LUMO (0.66511) HOMO—LUMO+1 (0.19569)	3.6822	0.5063

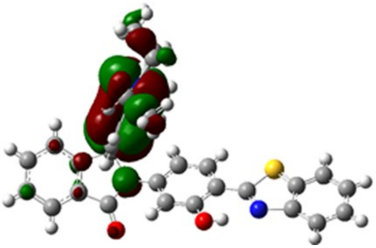
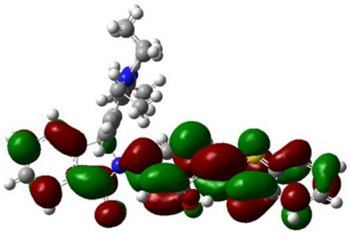
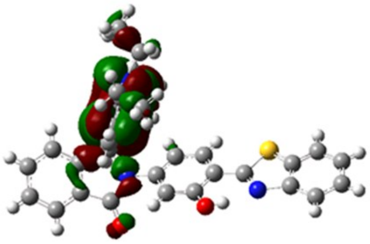
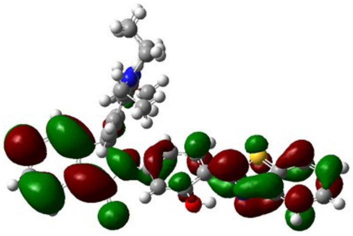
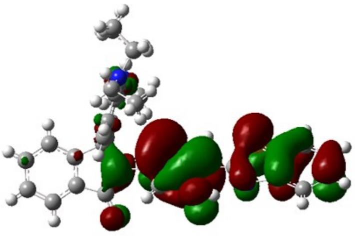
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2			

Fig.S6: Molecular orbitals of RHBT-G-3

Excited State	Involved orbitals	Energy(eV)	Oscillator strength
1	HOMO—LUMO (0.69612)	3.1162	0.0084
2	HOMO-1—LUMO (0.69015) HOMO-1—LUMO+1 (-0.10553)	3.2167	0.0014
3	HOMO—LUMO+1 (0.69172)	3.5930	0.0066
4	HOMO-1—LUMO (0.11172) HOMO-1—LUMO+1 (0.68012)	3.6738	0.0098
5	HOMO-2—LUMO (0.69054)	3.7509	0.5280

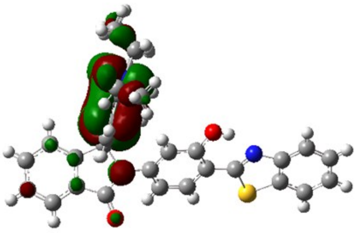
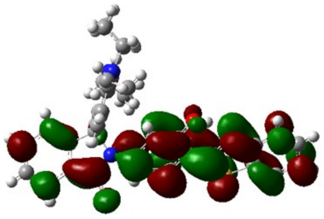
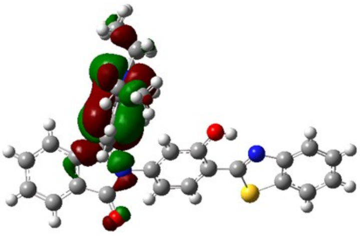
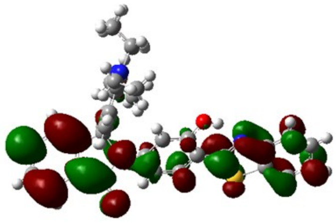
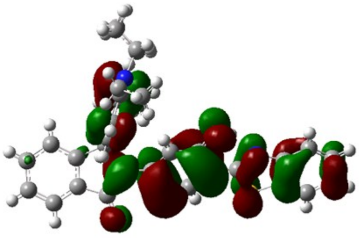
HOMO		LUMO	
HOMO-1		LUMO+1	
HOMO-2			

Fig.S7: Molecular orbitals of RHBT-G-4

1.6 Optical properties in response to acid of RHBT-G

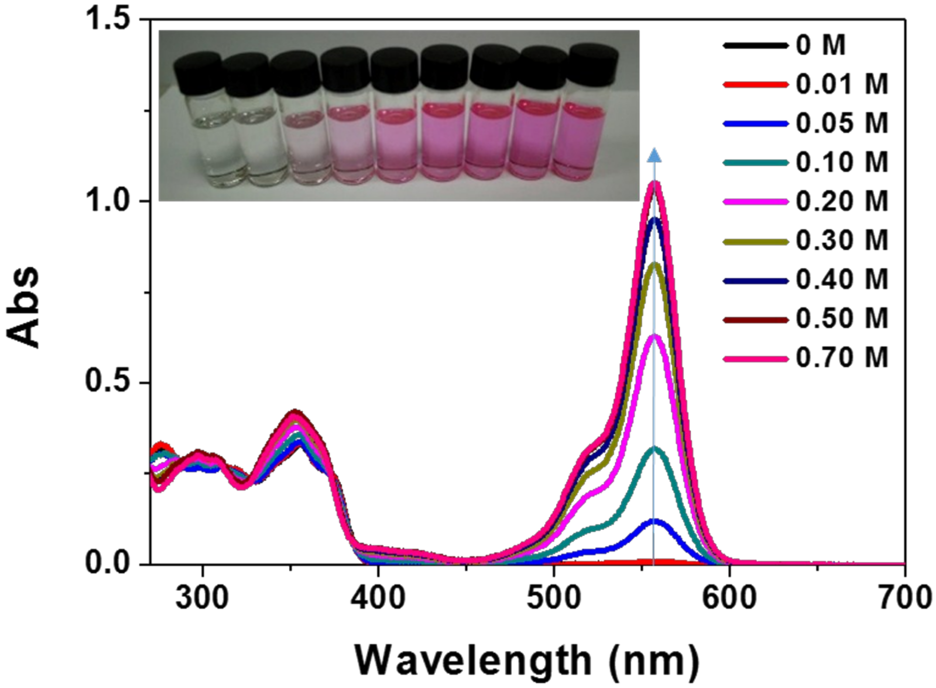


Fig.S8: Absorption of 1.0×10^{-5} M **RHBT-G** in THF with different concentration of TFA. Inset: photograph of the solutions under visible light.

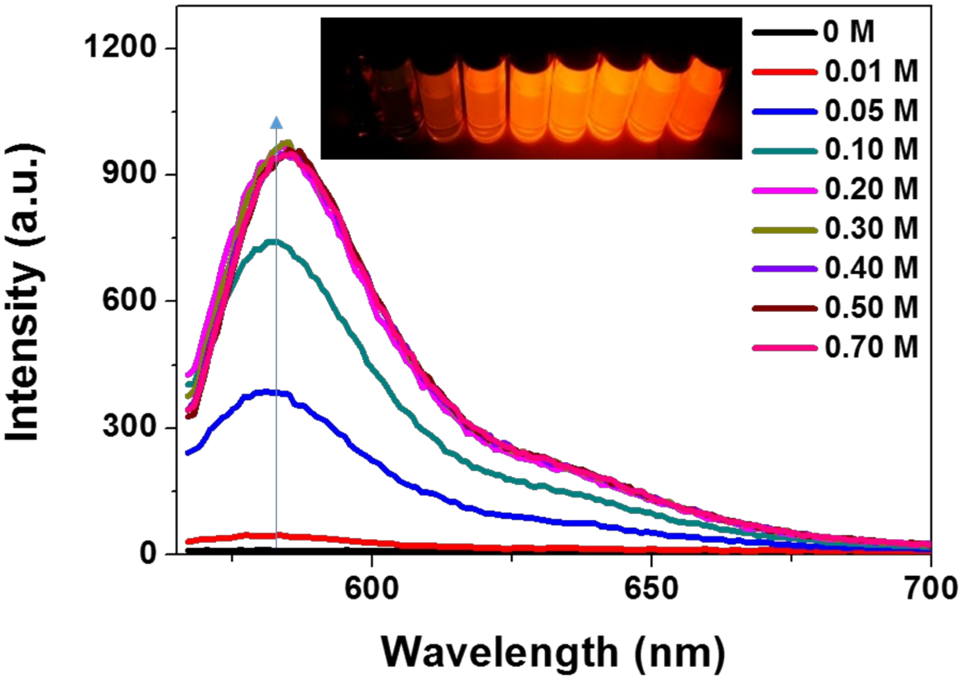


Fig.S9: PL spectra of 1.0×10^{-5}M **RHBT-G** in THF with different concentration of TFA. Inset: photograph of the solutions under 365 nm.

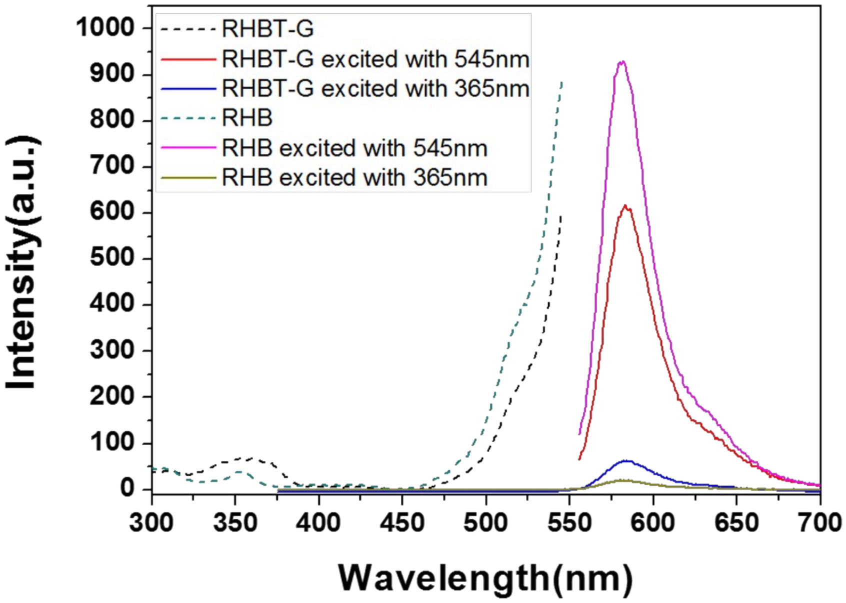


Fig.S10: Excitation (dash) and emission (solid) spectra of 1.0×10^{-5} M RHBT-G and Rhodamine B THF solutions with 0.2M TFA.

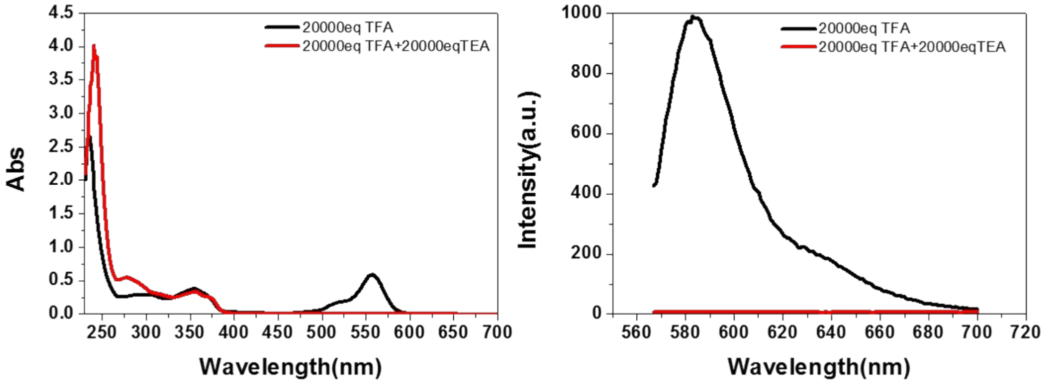


Fig.S11: UV-Vis and PL spectra of 1.0×10^{-5} M RHBT-G THF solution with 20000eq. TFA and then 20000eq.TEA was added to neutralize the acid.

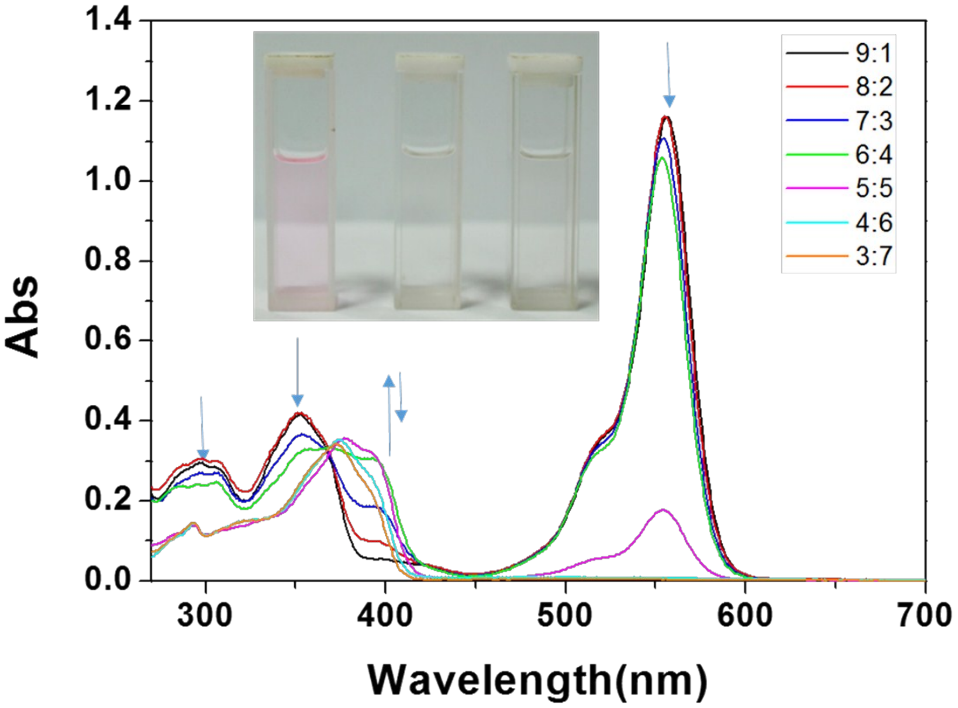


Fig.S12: UV-Vis spectra of 1.0×10^{-5} M RHBT-G solution with different volume ratio of THF/TFA. Inset:photograph of the solutions at the ratio of 5:5, 4:6 and 3:7.

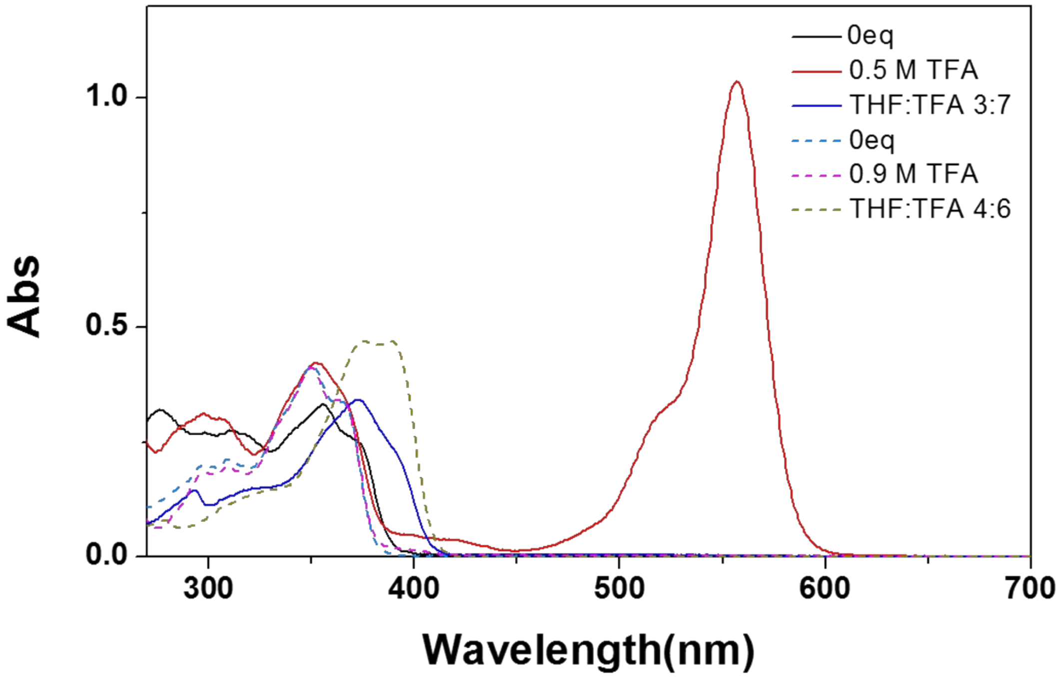


Fig.S13: UV-Vis spectra of 1.0×10^{-5} M RHBT-G (solid),PHBT-G (dash) THF solution with different amounts of TFA.

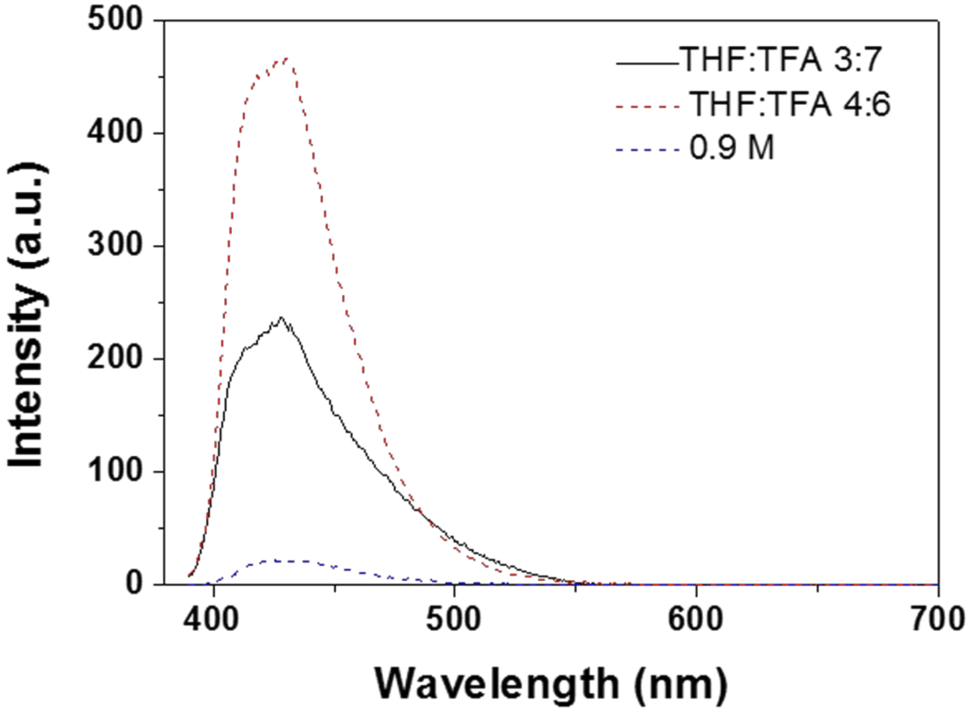
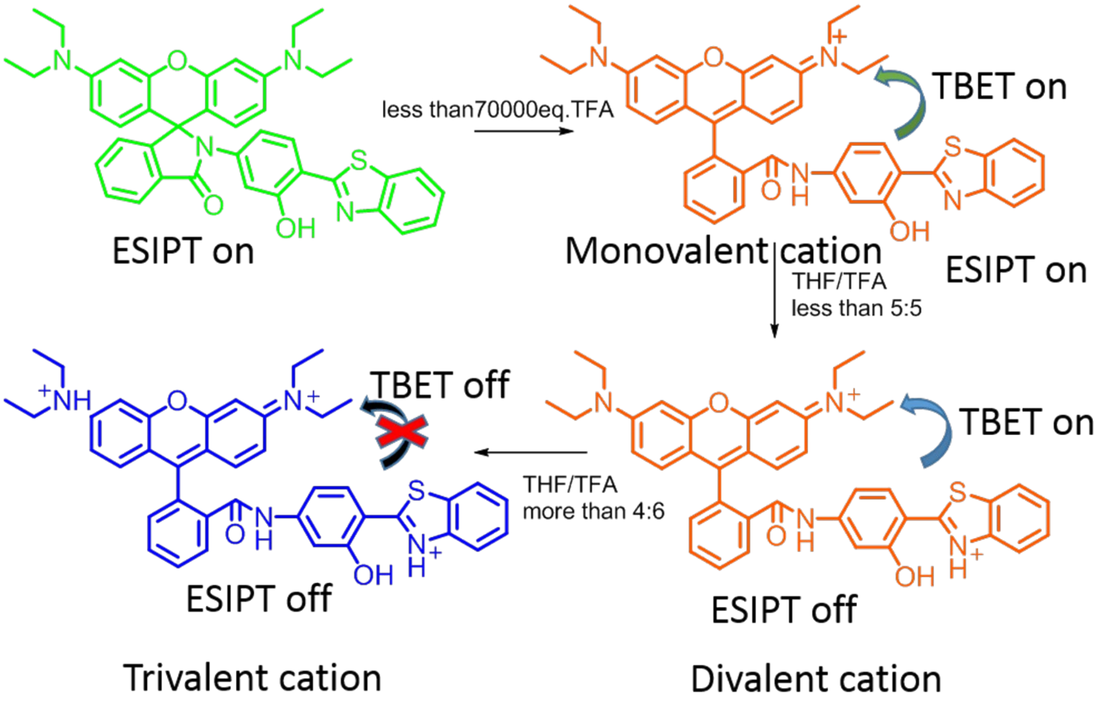


Fig.S14: PL spectra of 1.0×10^{-5} M RHBT-G (solid), PHBT-G (dash) THF solution with different amounts of TFA.



Scheme S1: Different forms of RHBT-G with different amounts of TFA.

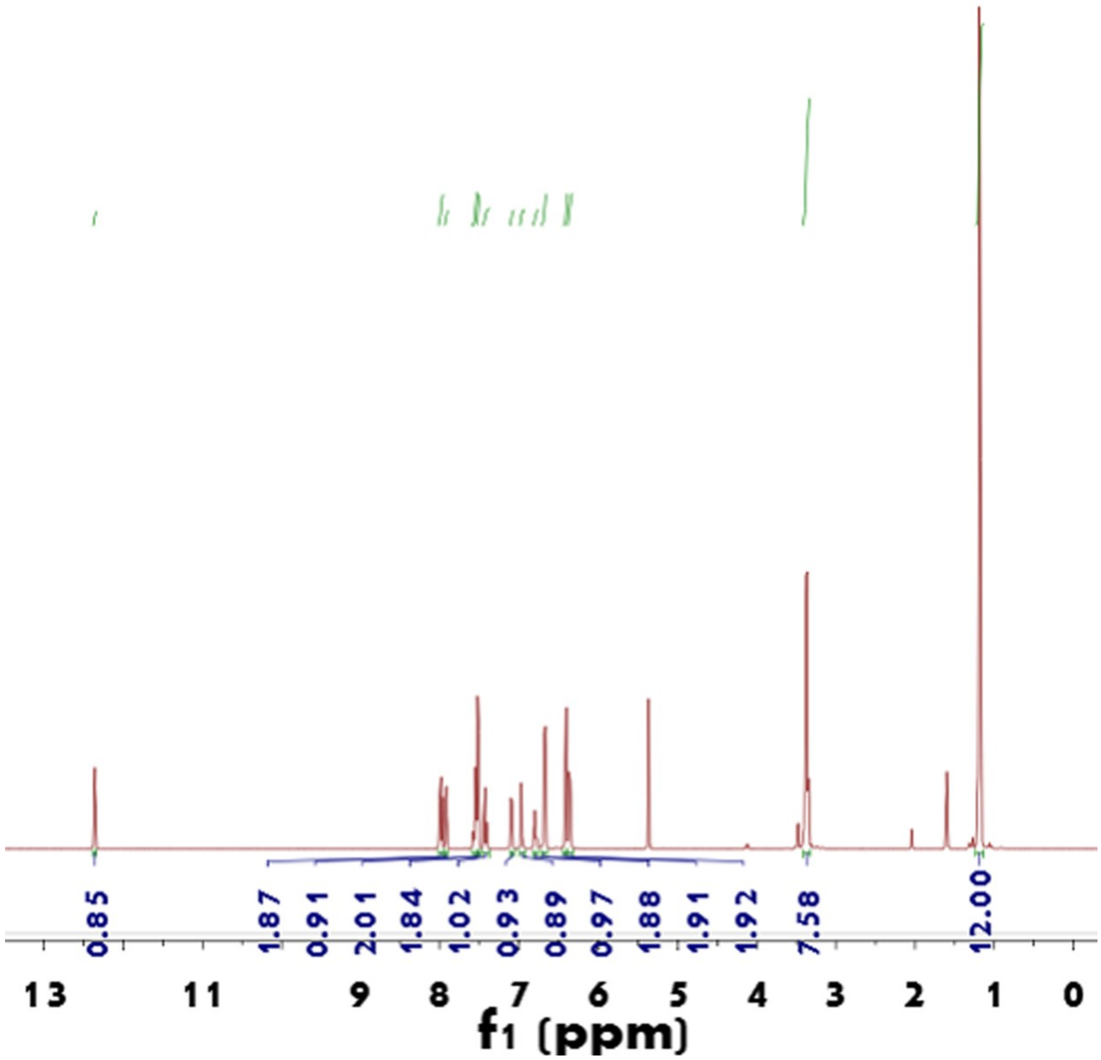


Fig. S15: ^{1}H NMR of RHBT-G in CD_2Cl_2

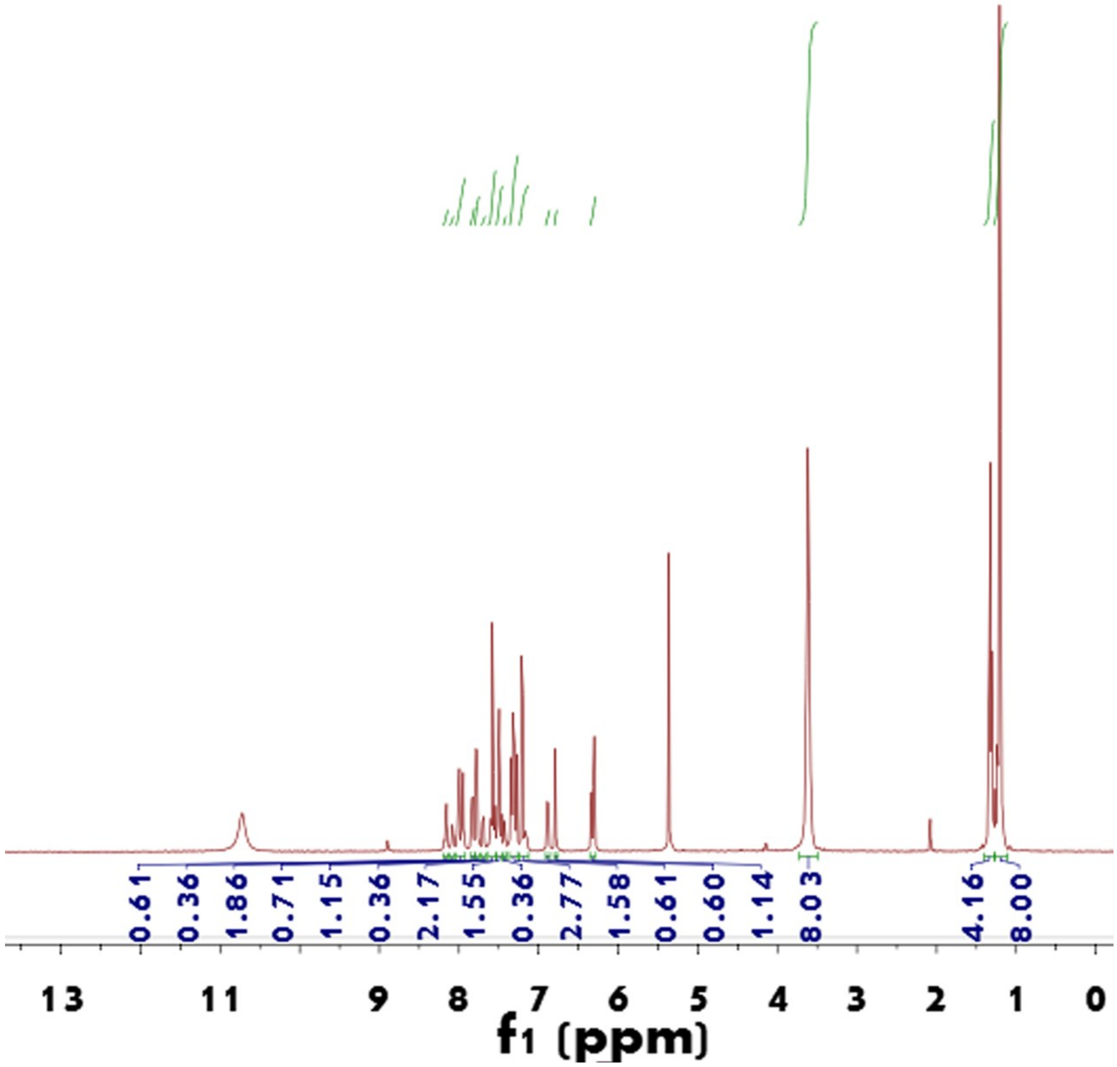


Fig. S16: ^{1}H NMR of RHBT-G in 0.5 ml CD_2Cl_2 with 0.05 ml CF_3COOD

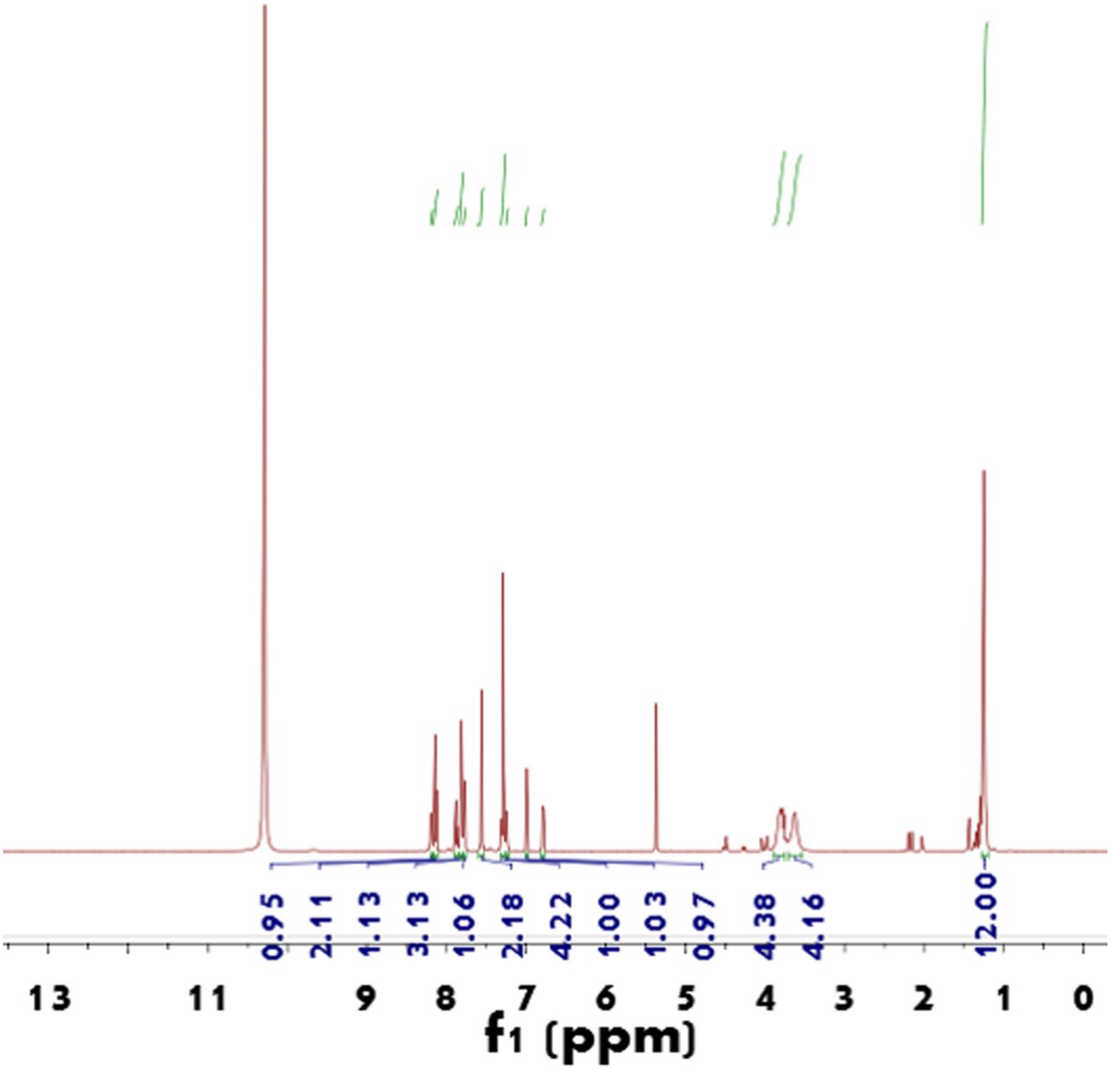


Fig. S17: ^{1}H NMR of RHBT-G in 0.5 ml CD_2Cl_2 with 0.1 ml CF_3COOD

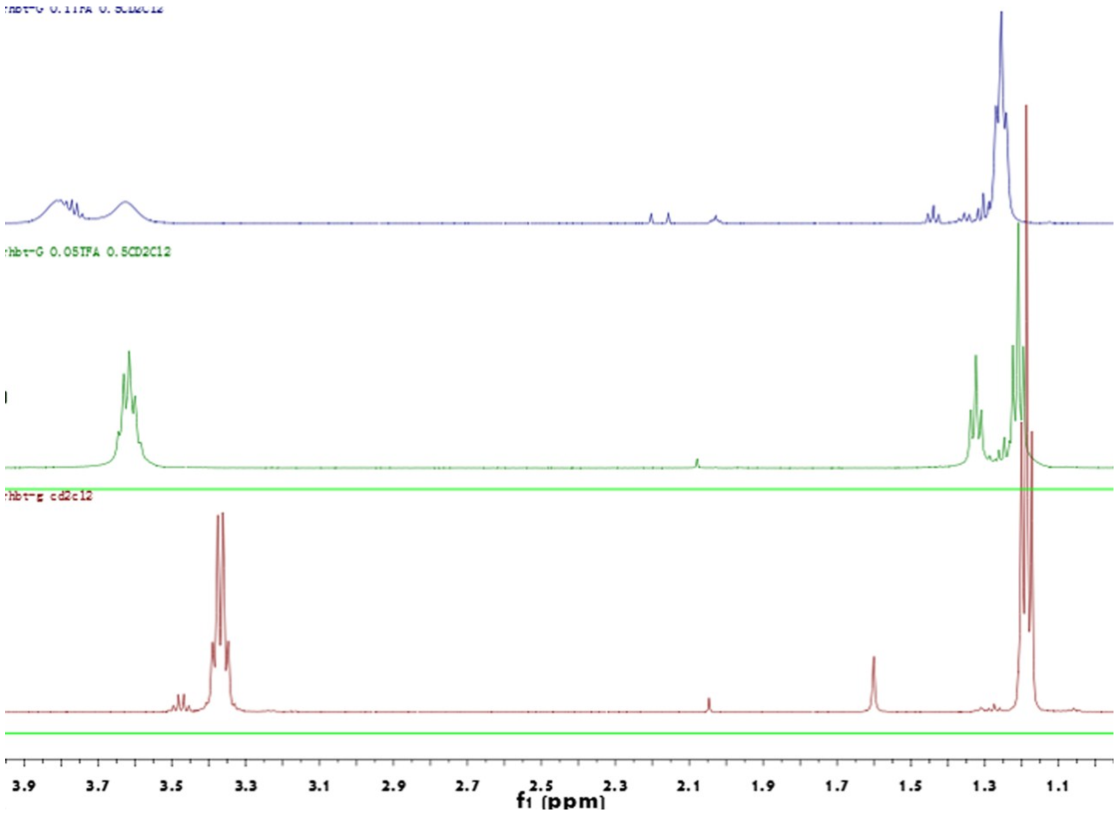


Fig.S18: Amplified ^{1}H NMR of diethylamino group of RHBT-G in 0.5ml CD_2Cl_2 (bottom), 0.5 ml CD_2Cl_2 with 0.05 ml CF_3COOD (middle), 0.5 ml CD_2Cl_2 with 0.1 ml CF_3COOD (up).

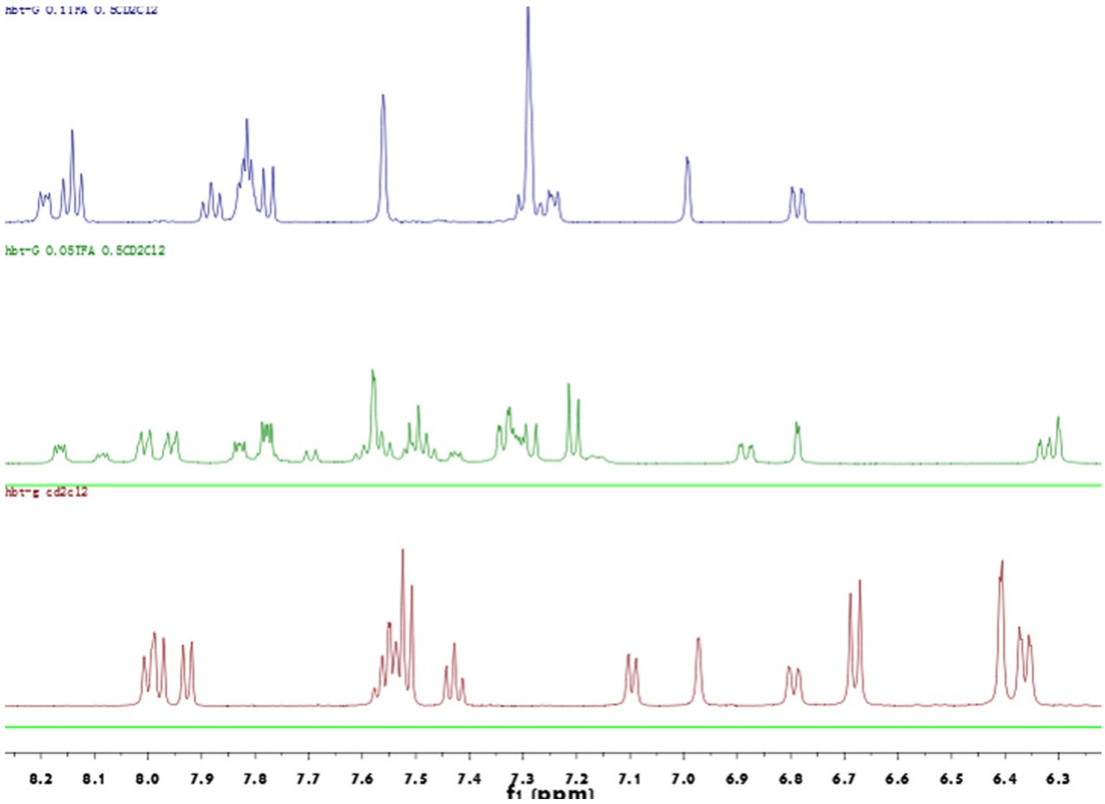


Fig.S19: Amplified ^{1}H NMR of aromatic hydrogens of RHBT-G in 0.5ml CD_2Cl_2 (bottom), 0.5 ml CD_2Cl_2 with 0.05 ml CF_3COOD (middle), 0.5 ml CD_2Cl_2 with 0.1 ml CF_3COOD (up).

1.6 Optical properties in response to base of RHBT-G

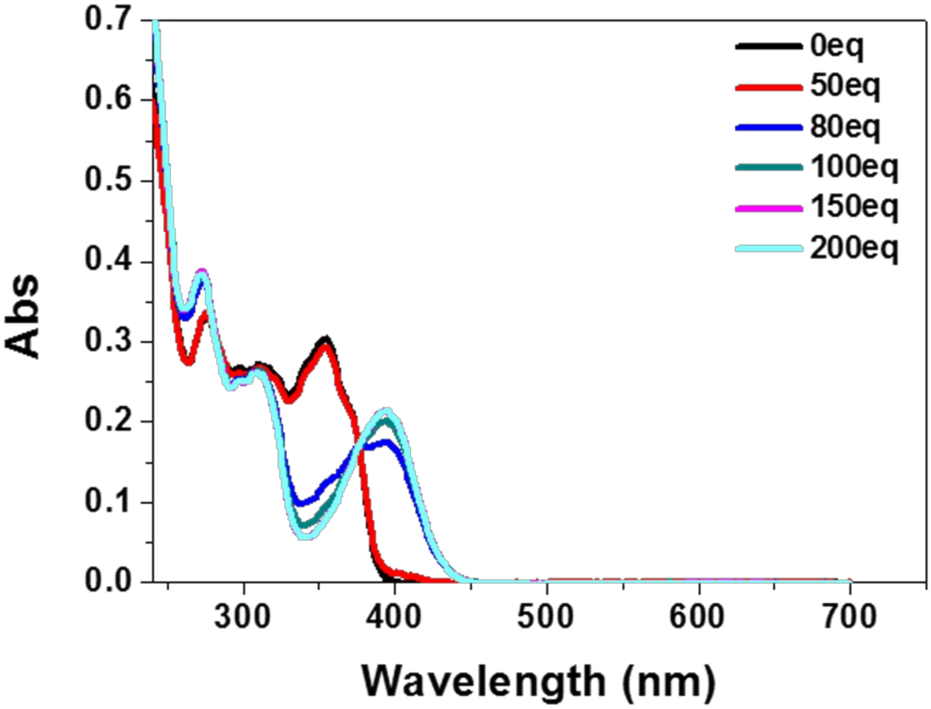


Fig.S20: UV-Vis spectra of 1.0×10^{-5} M RHBT-G in the THF/Methanol (volume ratio:80/20) mixture with different amounts of sodium methoxide.

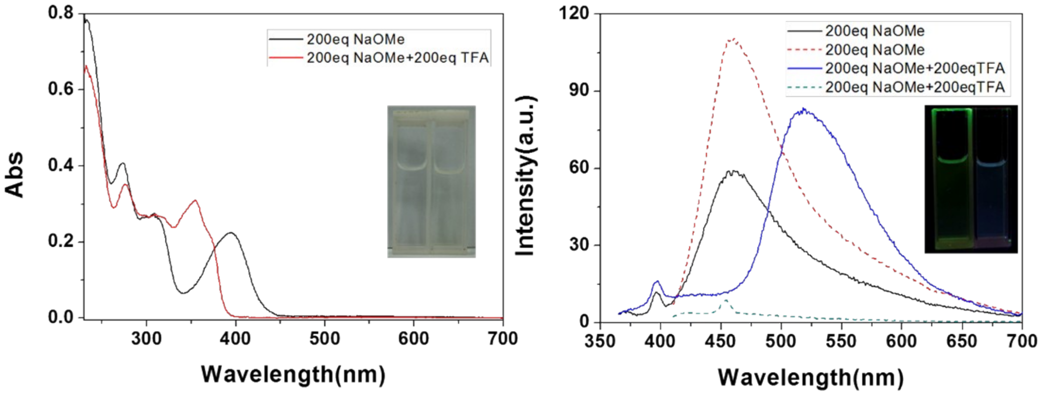
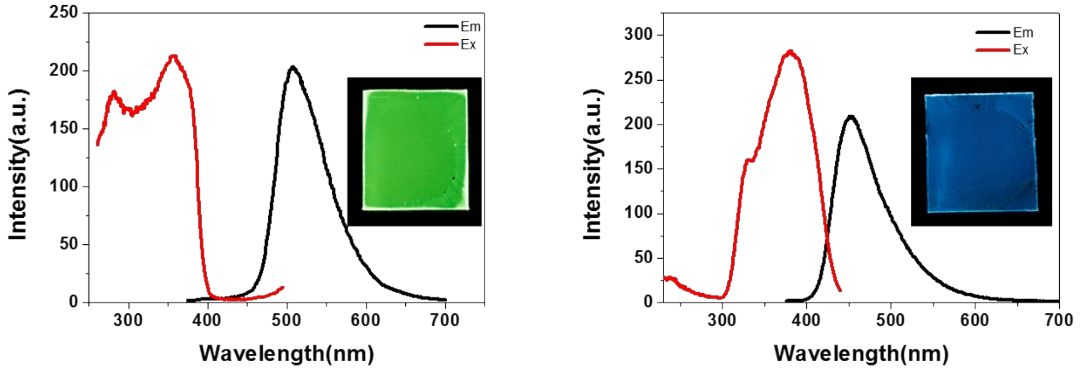


Fig.S21: UV-Vis and PL spectra of 1.0×10^{-5} M RHBT-G in the THF/Methanol (volume ratio: 80/20) mixture with 200eq. sodium methoxide and then 200 eq. TFA was added to neutralize the base. (Solid: excited with 355nm, Dash: excited with 400nm).

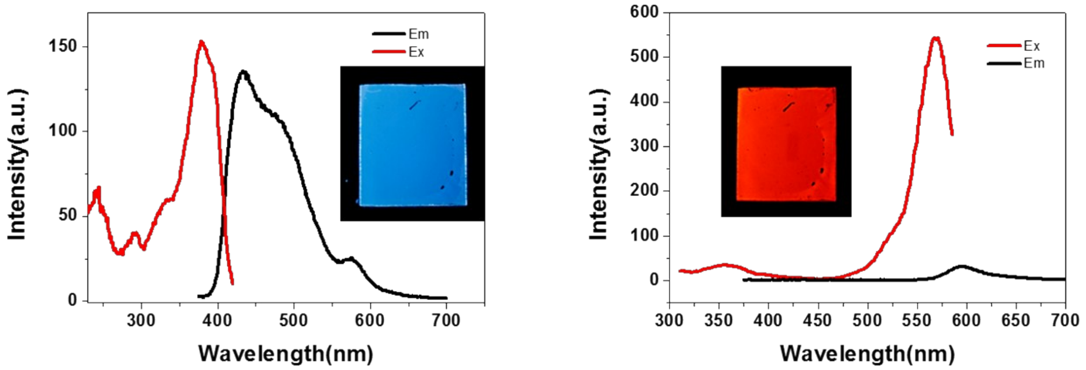
1.7 Optical properties of the PMMA film of RHBT-G in response to acid and

base.



(a):As-prepared film

(b):Fumed with diethylamine



(c):Fumed with TFA

(d):Fumed with TFA and heated under70°C

Fig.S22: Excitation and emission (excited with 365 nm) spectra of 1% RHBT-G PMMA film under different conditions.

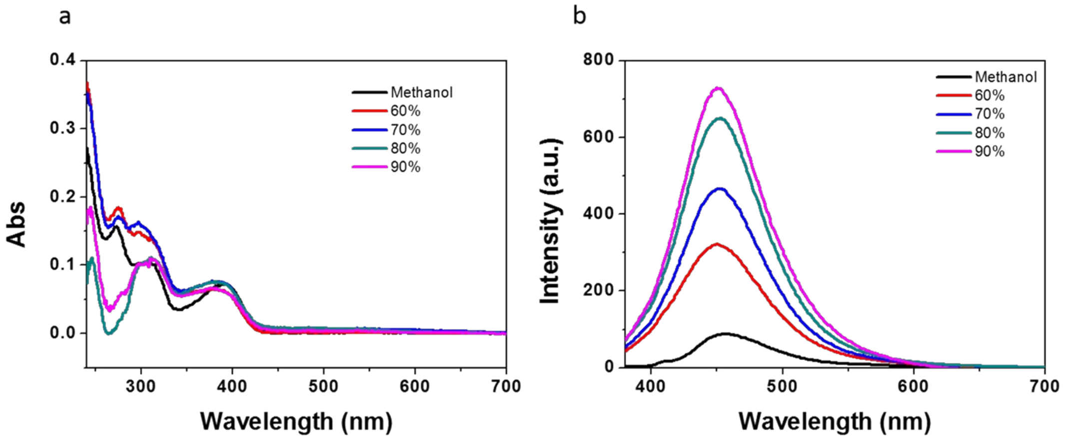


Fig.S23: UV-Vis and PL spectra of 1.0×10^{-5}M RHBT-G-ONa with 5.4 mg sodium methoxide in methanol with different volume ratio of glycerol.

RHBT-G-ONa was prepared through washing RHBT-G in DCM with 1M sodium hydroxide aqueous solution and extract from the mixed solution using DCM. The DCM was evaporated and the final product was dried as yellow solids.

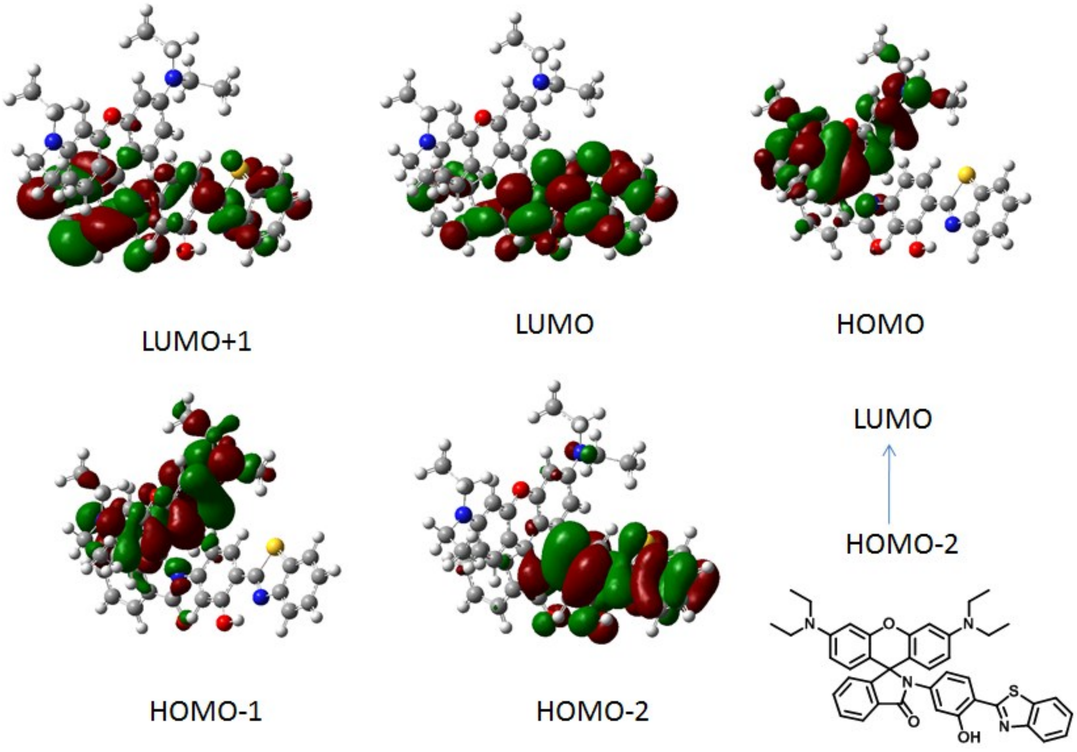


Fig.S24: Optimized molecular orbitals of the neutral form at the ground state.

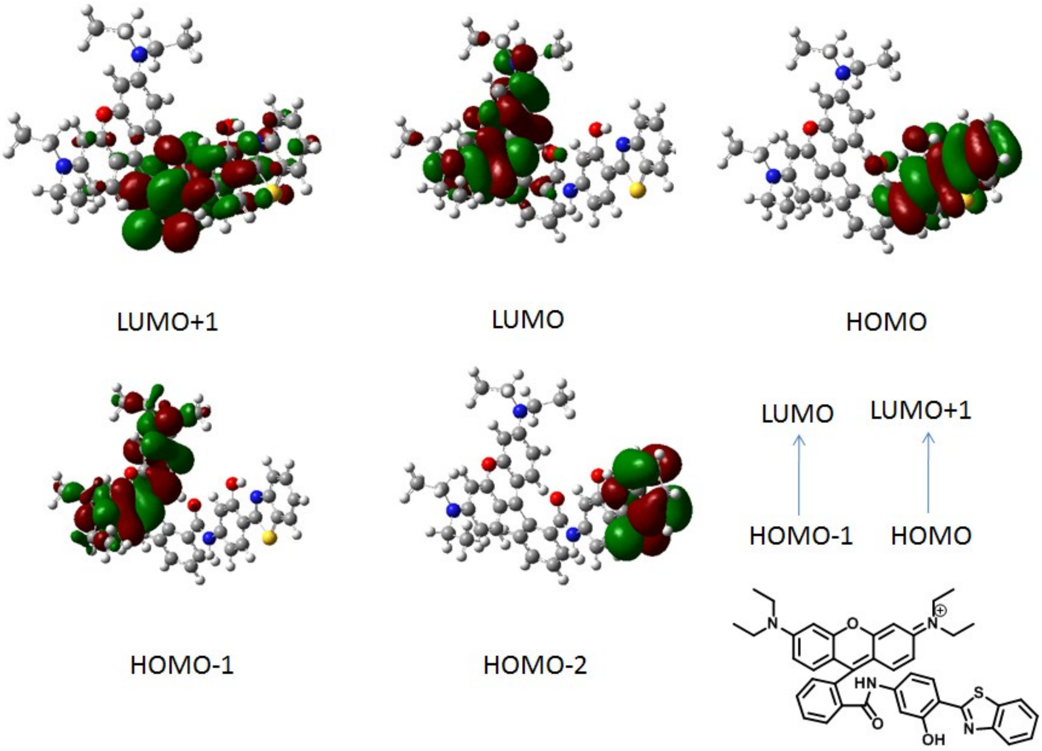
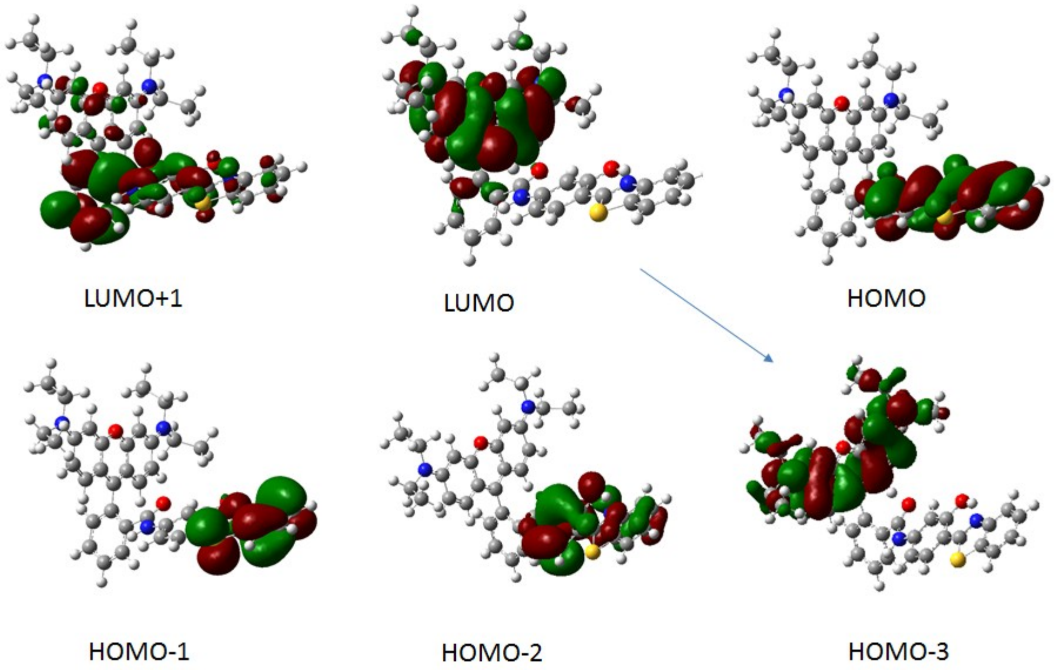


Fig.S25: Optimized molecular orbitals of the monovalent cation form at the ground state.



LUMO+1

LUMO

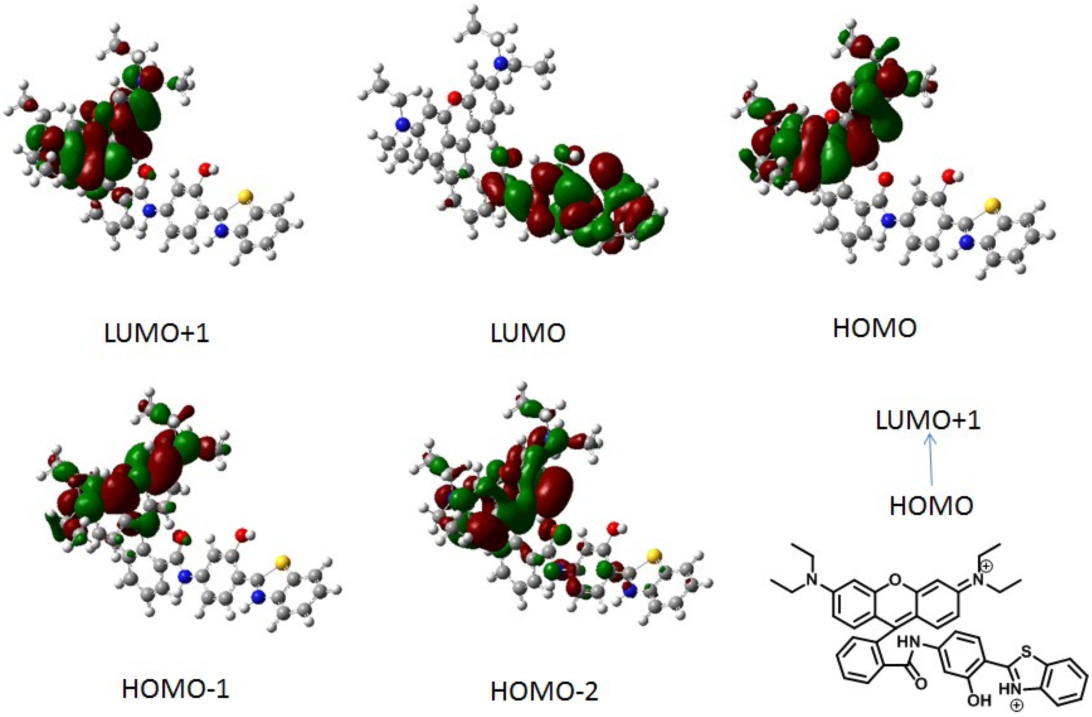
HOMO

HOMO-1

HOMO-2

HOMO-3

Fig.S26: Optimized molecular orbitals of the monovalent cation form at the excited state.



LUMO+1

LUMO

HOMO

HOMO-1

HOMO-2

Fig.S27: Optimized molecular orbitals of the divalent cation form at the ground state.

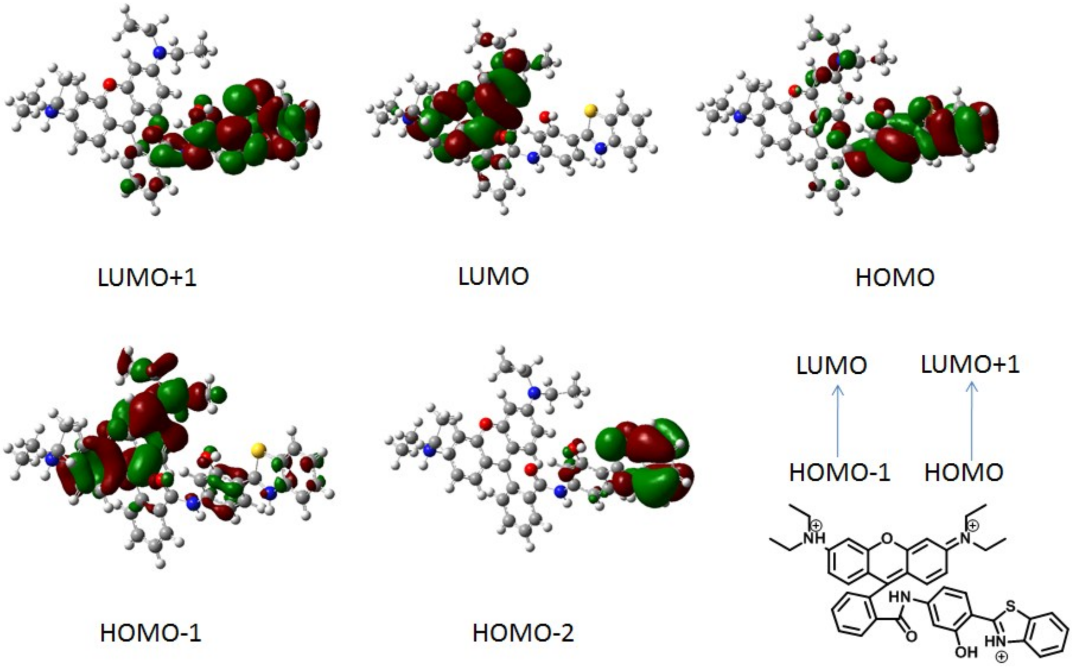


Fig.S28: Optimized molecular orbitals of the trivalent cation form at the ground state.

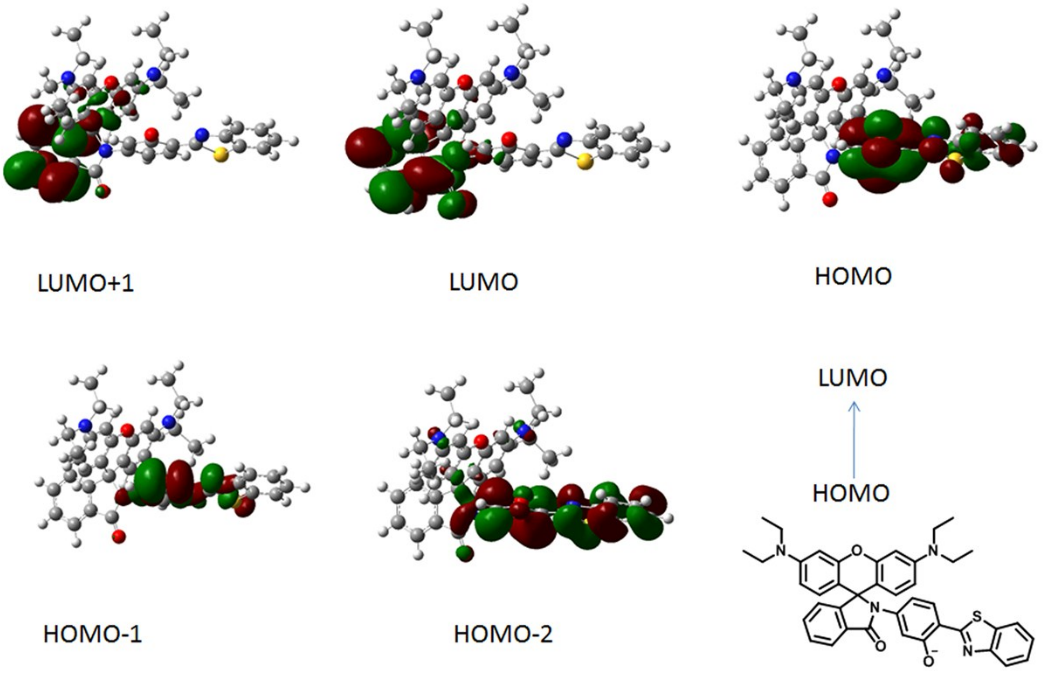


Fig.S29: Optimized molecular orbitals of the trivalent phenoxide anion form at the ground state.

1.8 Measurement of the relative quantum yields

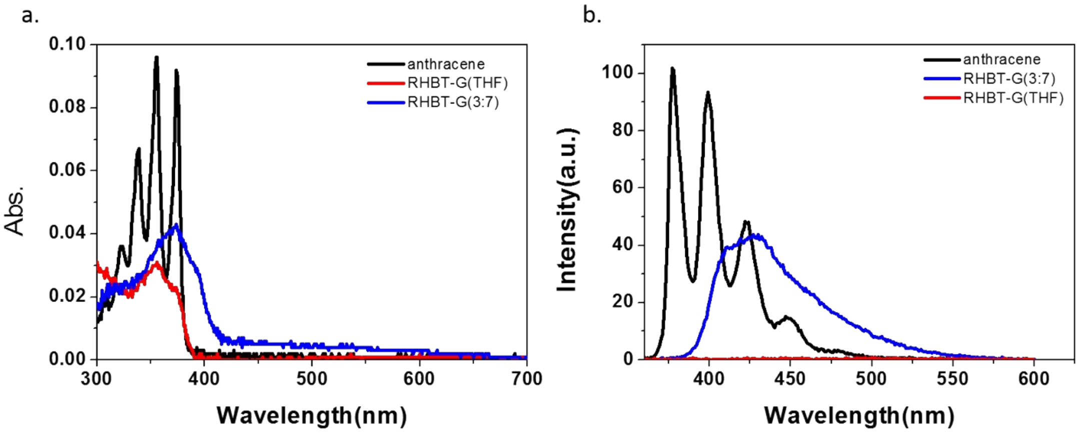


Fig.S30: Abs and PL spectra of dilute anthracene in EtOH and **RHBT-G** in THF or in the mixture of THF/TFA 3:7.

Anthracene in ethanol was reported to be 0.27.[1]

Peak area of the anthracene, free **RHBT-G** in THF, **RHBT-G** in THF/TFA 3:7 were calculated to be 3477, 62, 3155.

The absorption at 350nm were 0.063, 0.029, and 0.033 independently.

The refractive index of THF, EtOH, and THF/TFA 3:7 were 1.407, 1.361, and 1.323.

The relative quantum yield (ϕ_{ref}) of the emission of free RHBT-G in THF and the mixture were calculated to be 1% and 44% according to the formula $\phi = Ys \cdot Fu/Fs \cdot As/Au \cdot (Ru/Rs)^2$

Ys refers to the quantum yield of the reference.

Fs refers to the peak area of the reference and As refers to the absorption of the reference.

Fu refers to the peak area of the unknown compound and Au refers to the absorption of the unknown compound.

R refers to the refractive index of the solvent.

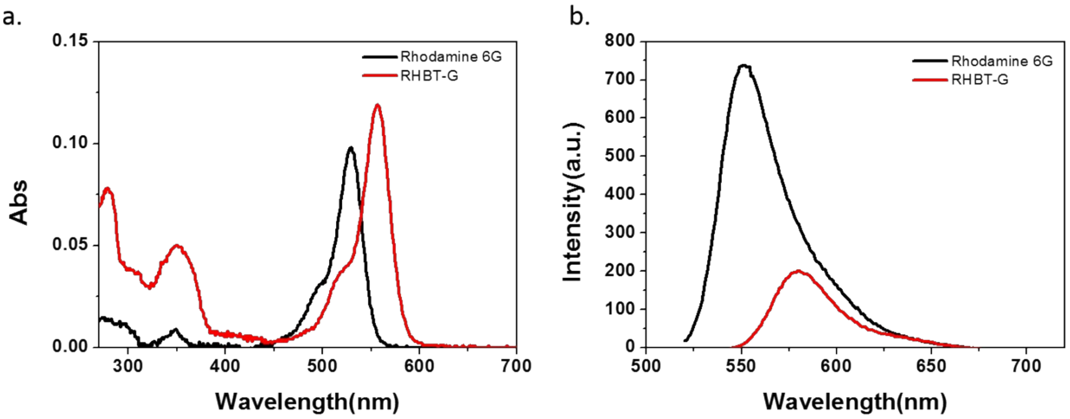


Fig.S31: Abs and PL spectra of dilute Rhodamine 6G in EtOH and **RHBT-G** in THF with 20000eq. of TFA.

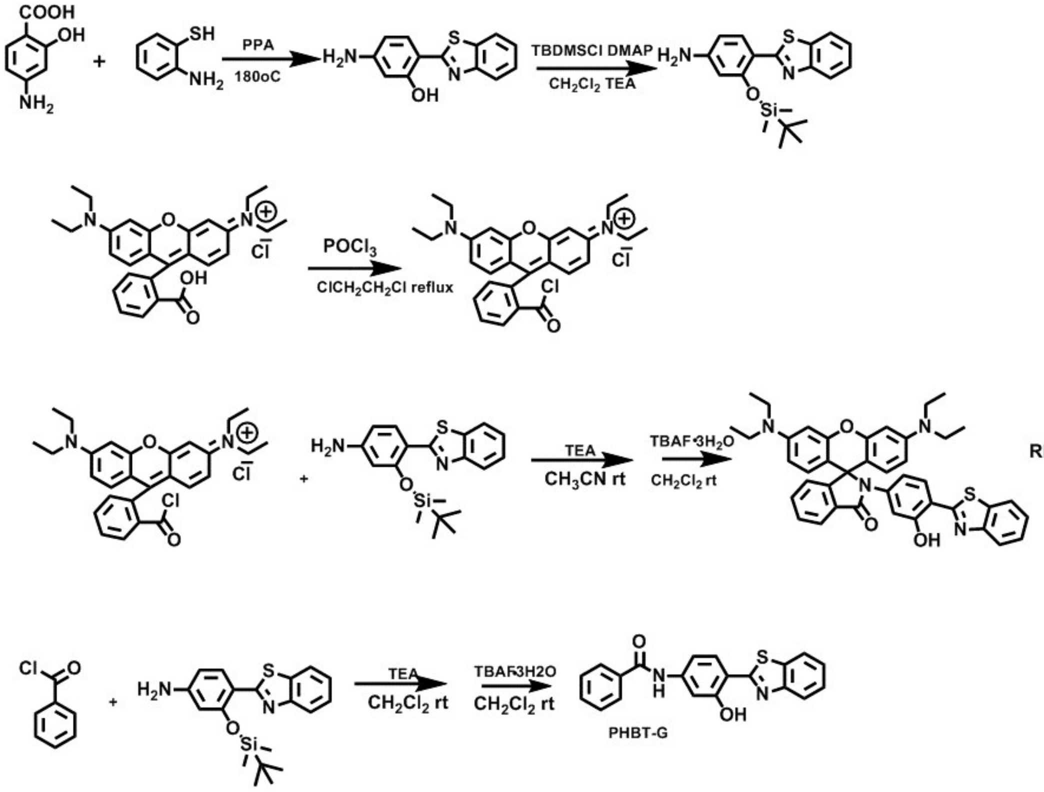
Rhodamine 6G in ethanol was reported to be 1.[2]

Peak area of Rhodamine 6G and **RHBT-G** in THF with 20000eq. of TFA were calculated to be 32673, 9290.

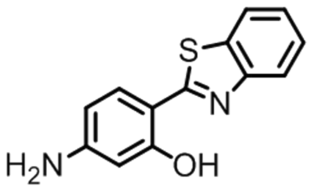
The absorption at 510nm were 0.043, 0.03.

The quantum yield of the red emission in THF was calculated to be 44%, which is lower than the Rhodamine B in EtOH reported to be 65%[2] suggesting the ring-opening form of RHBT-G still suffered from the rotation and vibration.

1.9 Synthesis of RHBT-G and PHBT-G



Synthesis of 5-amino-2-(benzo[d]thiazol-2-yl)phenol

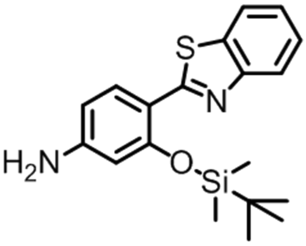


4-aminosalicylic acid (3 g, 20 mmol) and 2-aminothiophenol (2.5 g, 20 mmol) and 30 ml polyphosphoric acid were mixed into a round-bottom flask with a magneton stirring vigorously and heated under 180 ^{o}C for 3 hours. The mixture were poured into cold water and adjust the pH of the mixture to 7-8. The crude solid product were filtered and recrystalized with dioxane/water to get pure yellow needle shaped product. (1.8 g ,35 %) HRMS (ESI) m/z calcd $[M+H]^+$ for $C_{13}H_{11}N_2OS$ 243.0592, found 243.0592. Melting point: 216.8-217.3 ^{o}C.

^{1}H NMR (500 MHz, DMSO) δ 11.75 (s, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.51 – 7.42 (t, 1H), 7.38 – 7.30 (t, 1H), 6.26 (dd, J = 8.6, 2.0 Hz, 1H), 6.18 (d, J = 2.0 Hz, 1H), 5.95 (s, 2H).

^{13}C NMR (126 MHz, DMSO) δ 168.25, 159.07, 154.05, 152.11, 132.73, 130.33, 126.76, 124.55, 122.17, 121.18, 107.56, 106.63, 99.76.

Synthesis of 4-(benzo[d]thiazol-2-yl)-3-((tert-butyldimethylsilyl)oxy)aniline

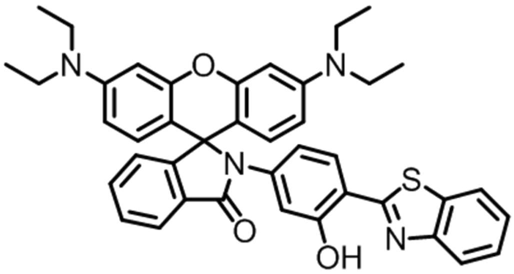


5-amino-2-(benzo[d]thiazol-2-yl)phenol (0.96 g, 4 mmol), tert-Butyldimethylsilyl chloride (TBDMSCl) (0.9 g, 6 mmol) and 4-dimethylaminopyridine (0.85 g, 7 mmol) were mixted into 30 ml dry CH_2Cl_2 with 1 ml dry triethylamine added. The mixture was stirred under room temperature for 5 hours with the solution becoming transparent. Then the mixture was mixed with silica gel and the product was purified by column chromatography using CH_2Cl_2: EtOAc 20:1 as the eluent. The eluent was evaporated and the solid product was further recrystallized with EtOAc and hexane to get the pure product of the needle shaped crystal with light yellow color. (1.2 g, 84 %). HRMS (ESI) m/z calcd $[M+H]^+$ for $C_{19}H_{25}N_2OSSi$ 357.1457, found 357.1457. Melting point: 157.9-158.3 ^oC.

^1H (500 MHz, DMSO) 8.02 (2 H, dd, J 15.0, 8.1), 7.88 (1 H, d, J 8.1), 7.44 (1 H, t, J 7.4), 7.31 (1 H, t, J 7.4), 6.38 – 6.29 (2 H, m), 5.88 (2 H, s), 1.00 (9 H, s), 0.43 (6 H, s).

^{13}C (126 MHz, DMSO) 164.05, 155.69, 153.33, 152.41, 134.94, 130.79, 126.27, 124.11, 121.84, 121.77, 111.69, 108.52, 103.29, 26.70, 19.21, -2.73.

Synthesis of RHBT-G



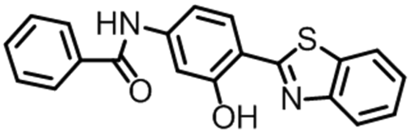
1 g Rhodamine B (2 mmol) and 1.8 g $POCl_3$ (12 mmom) were dissolved with dichloroethane and reflux for 4 hours. Dichloroethane was evaporated and the solid residue was dissolved with acetonitrile. 0.365 g 4-(benzo[d]thiazol-2-yl)-3-((tert-butyldimethylsilyl)oxy)aniline (1 mmol) was dissolved in acetonitrile with 1 ml triethylamine added. The acetonitrile solution of acyl chloride of Rhodamine B was dropped into the above mentioned mixture with vigorously stirring and stirred under room temperature for 12 hours. Then acetonitrile was evaporated and the residue was dissolved with CH_2Cl_2 and washed with saturated $NaHCO_3$ aqueous solution for three times. The organic phase was dried with anhydrous sodium sulfate and was filtered. 0.315g TBAF·$3H_2O$ (1 mmol) was added to the solution with stir for 10 minutes. The final product was purified by column chromatography (silic gel) using CH_2Cl_2: EtOAc 25:1 as the eluent. White powder was gained as the pure product. (0.1 g, 15%) HRMS (ESI) m/z calcd [M+H]+ for $C_{41}H_{39}N_4O_3S$ 667.2743, found 667.2782.

Melting point: 302.3-302.8 ^oC.

^1H (500 MHz, $CDCl_3$) 12.36 (1 H, s), 8.04 (1 H, d, J 8.0), 7.90 (1 H, d, J 8.1), 7.85 (1 H, d, J 7.9), 7.48 (4 H, ddd, J 24.8, 14.9, 7.9), 7.37 (1 H, t, J 7.5), 7.14 (1 H, d, J 7.9), 6.96 (1 H, s), 6.71 (1 H, d, J 8.5),

6.67 (2 H, d, J 8.8), 6.38 (2 H, d, J 2.3), 6.32 (2 H, d, J 8.9), 3.41 – 3.27 (8 H,q), 1.18 (12 H, t, J 7.0).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.03, 168.12, 158.02, 153.96, 152.79, 151.79, 148.86, 141.47, 133.23, 132.46, 129.76, 128.48, 128.38, 128.11, 126.57, 125.29, 123.83, 123.46, 121.95, 121.43, 116.64, 114.51, 114.41, 108.26, 106.36, 97.93, 67.42, 44.31, 12.63.

Synthesis of PHBT-G



0.5 g 4-(benzo[d]thiazol-2-yl)-3-((tert-butyldimethylsilyl)oxy)aniline (1.4mmol) was dissolved in CH_2Cl_2 with 1ml triethylamine added, and then 0.2 ml benzoyl chloride (1.7 mmol) was dropped into the solution with vigorously stir. The solution was stirred under room temperature for 3 hours and then washed with saturated $NaHCO_3$ aqueous solution for three times. The organic phase was dried with and filtered. 0.6 g TBAF·$3H_2O$ (2 mmol) was added to the solution with stir for 10 minutes. CH_2Cl_2 was evaporated and the solid residue was recrystallized with EtOAc to gain the white powder. (0.05 g, 10%) HRMS(ESI) m/z calcd [M+H]+ for $C_{20}H_{15}N_2O_2S$ 347.0854, found 347.0830. Melting point: 275.8-276.2 ^oC.
^1H (500 MHz, DMSO) 11.68 (1 H, s), 10.48 (1 H, s), 8.19 – 8.10 (2 H, m), 8.03 (1 H, d, J 8.1), 7.98 (2 H, d, J 7.4), 7.81 (1 H, s), 7.63 (1 H, t, J 7.3), 7.59 – 7.50 (3 H, m), 7.48 – 7.38 (2 H, m).
^{13}C (126 MHz, DMSO) 166.42, 157.29, 152.05, 143.47, 135.28, 134.38, 132.18, 129.40, 128.90, 128.19, 126.79, 125.30, 122.38, 122.25, 114.43, 112.34, 107.78.

2. ^{1}H NMR and ^{13}C NMR of the compounds

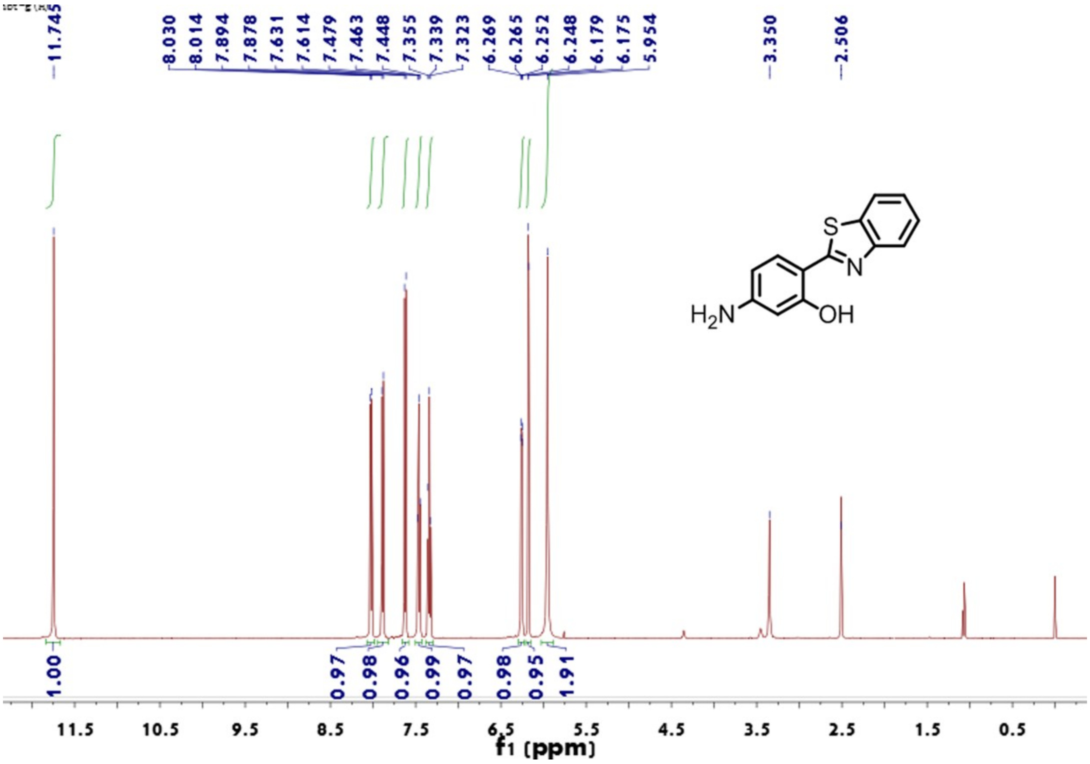


Fig.S32 ^{1}H NMR spectra of 5-amino-2-(benzo[d]thiazol-2-yl)phenol in DMSO.

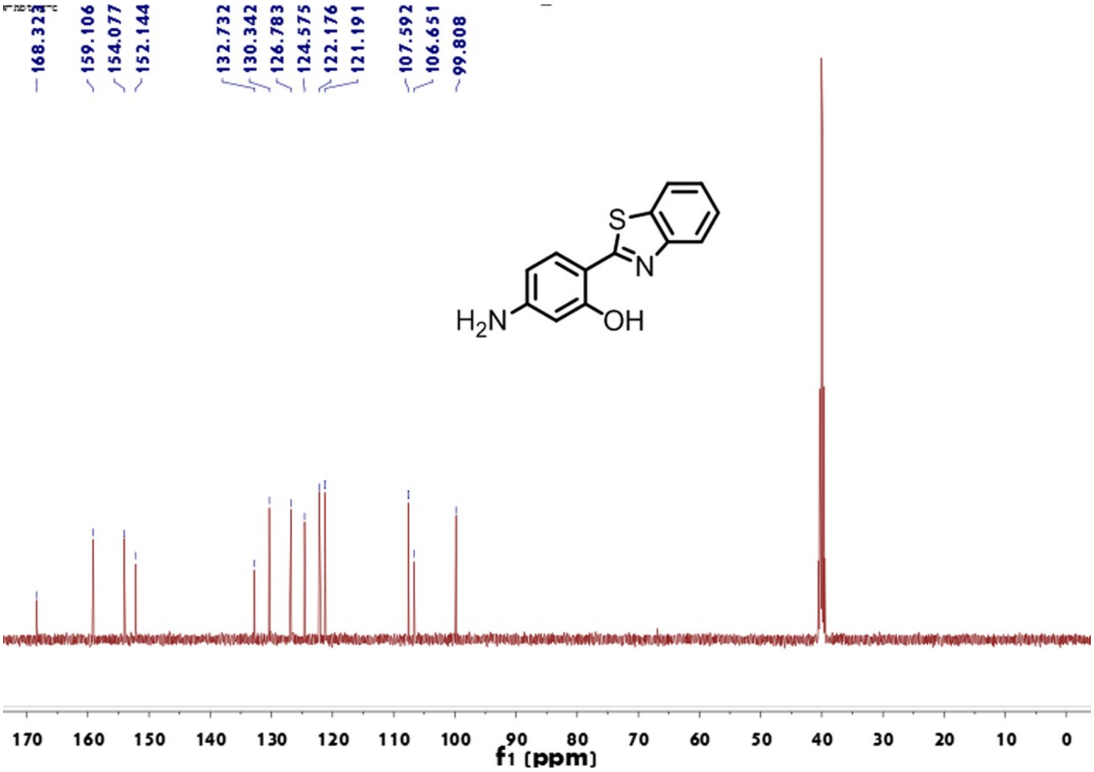


Fig.S33 ^{13}C NMR spectra of 5-amino-2-(benzo[d]thiazol-2-yl)phenol in DMSO.

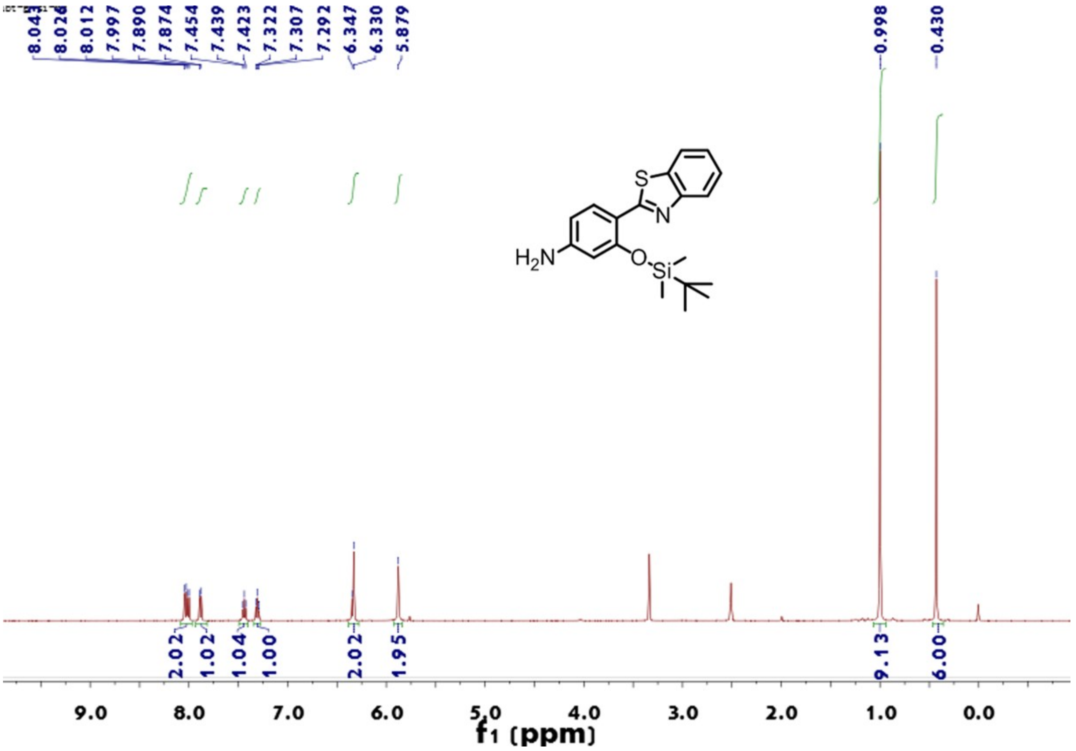


Fig.S34 ^{1}H NMR spectra of 4-(benzo[d]thiazol-2-yl)-3-((tert-butyldimethylsilyl)oxy)aniline in DMSO.

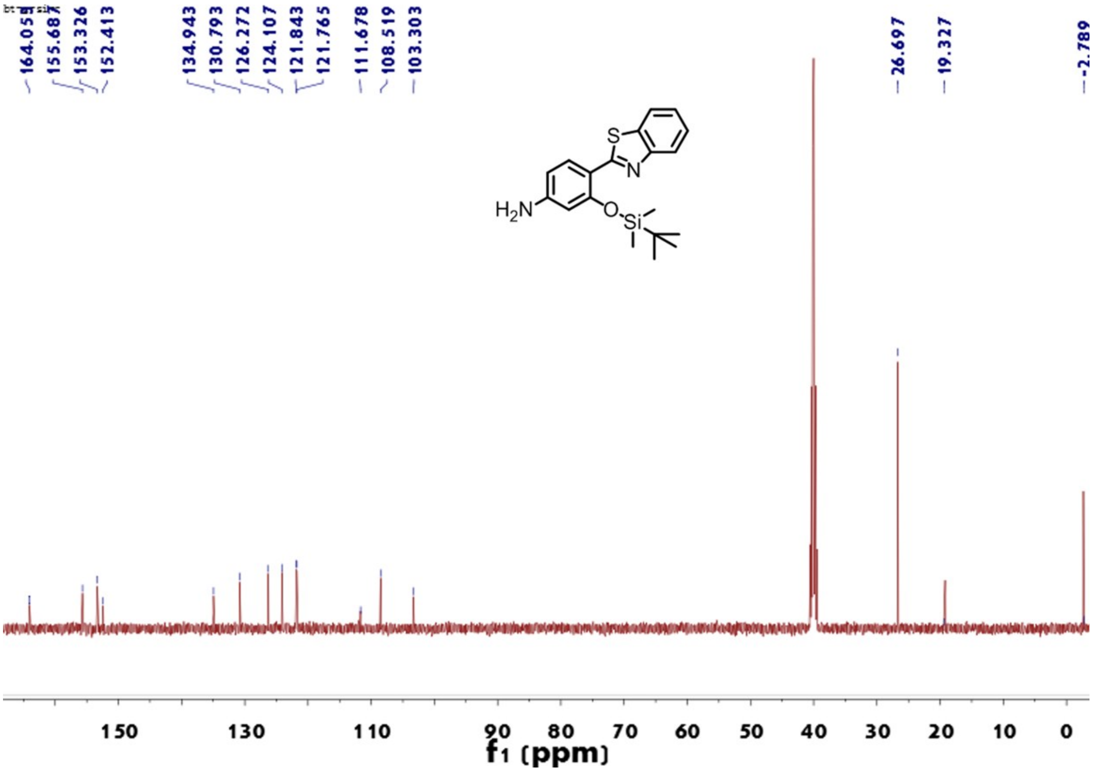


Fig.S35 ^{13}C NMR spectra of 4-(benzo[d]thiazol-2-yl)-3-((tert-butyldimethylsilyl)oxy)aniline in DMSO.

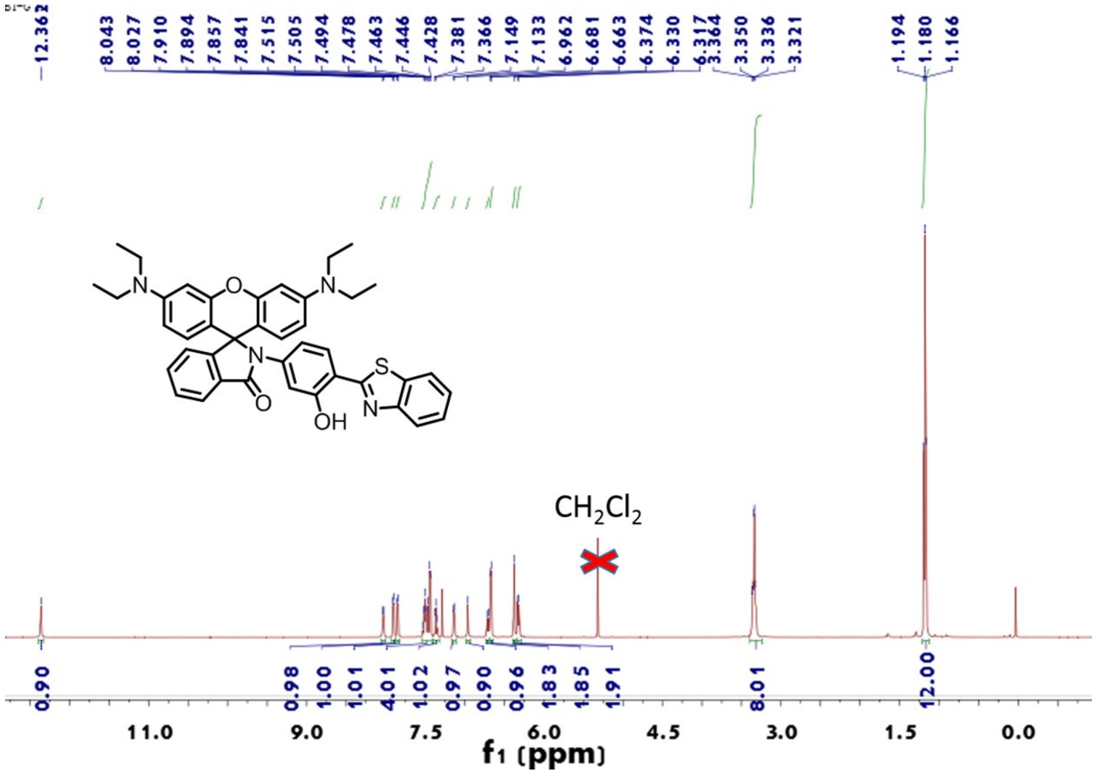


Fig.S36 ^{1}H NMR spectra of RHBT-G in CDCl$_3$.

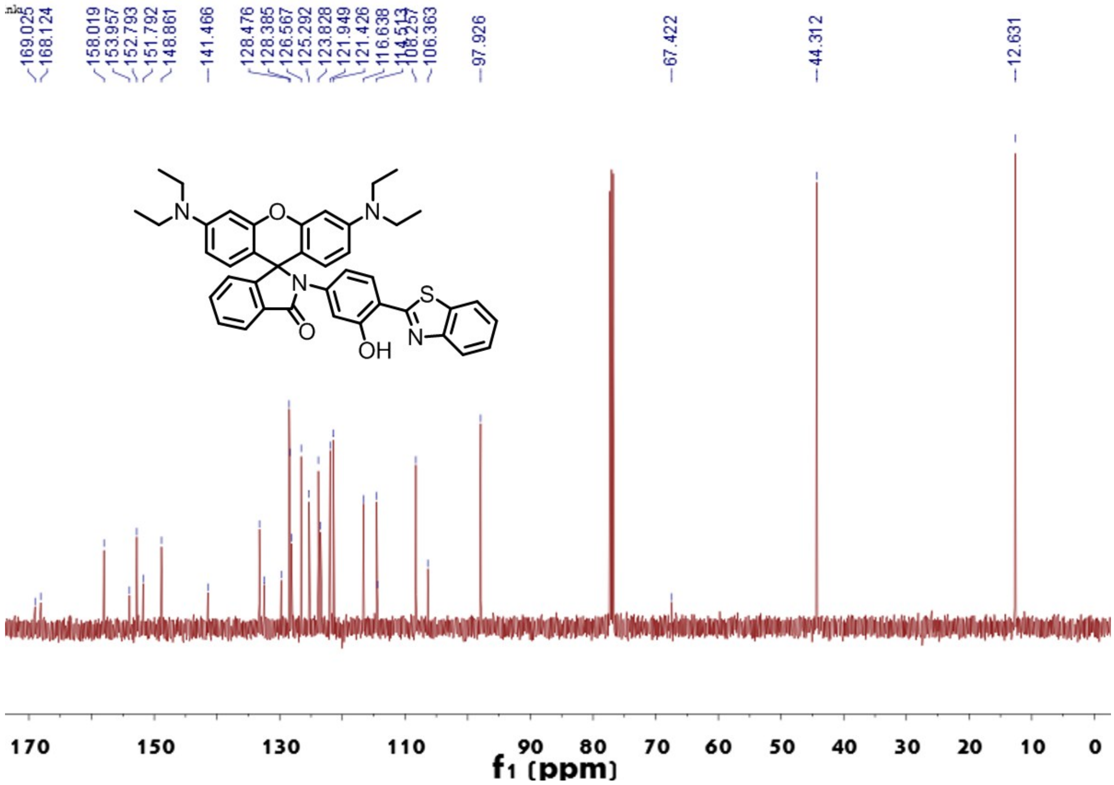


Fig.S37 ^{13}C NMR spectra of RHBT-G in CDCl$_3$.

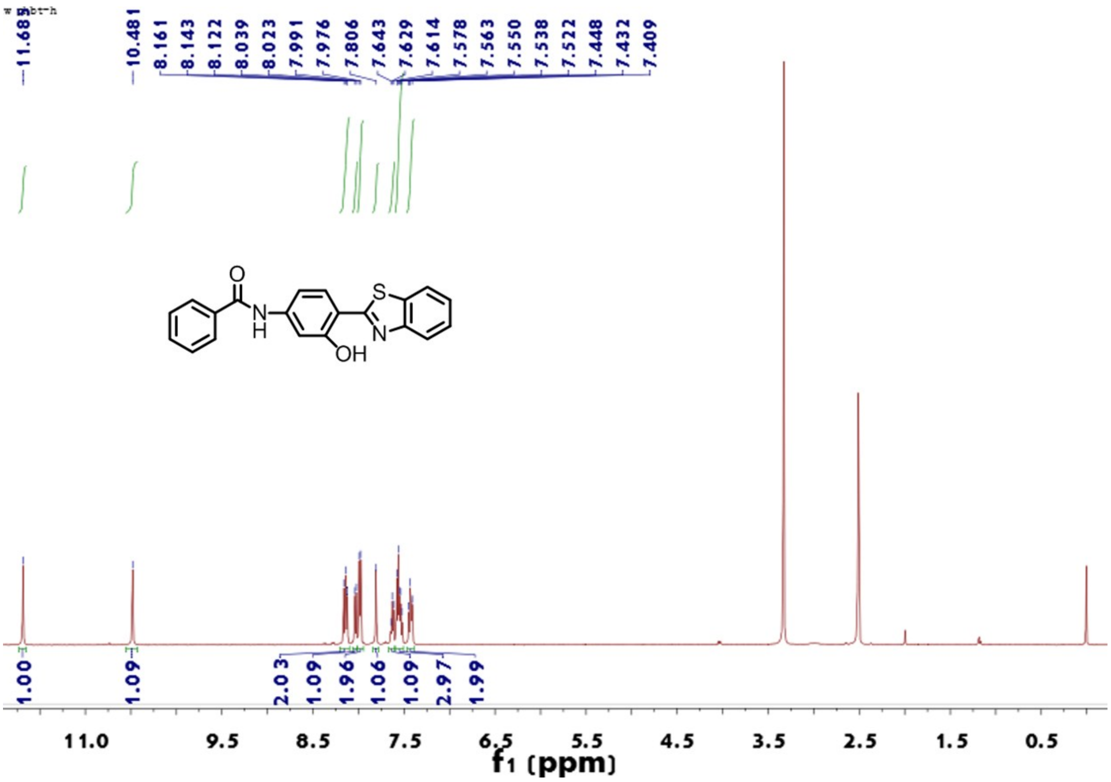


Fig.S38 ^{1}H NMR spectra of PHBT-G in DMSO.

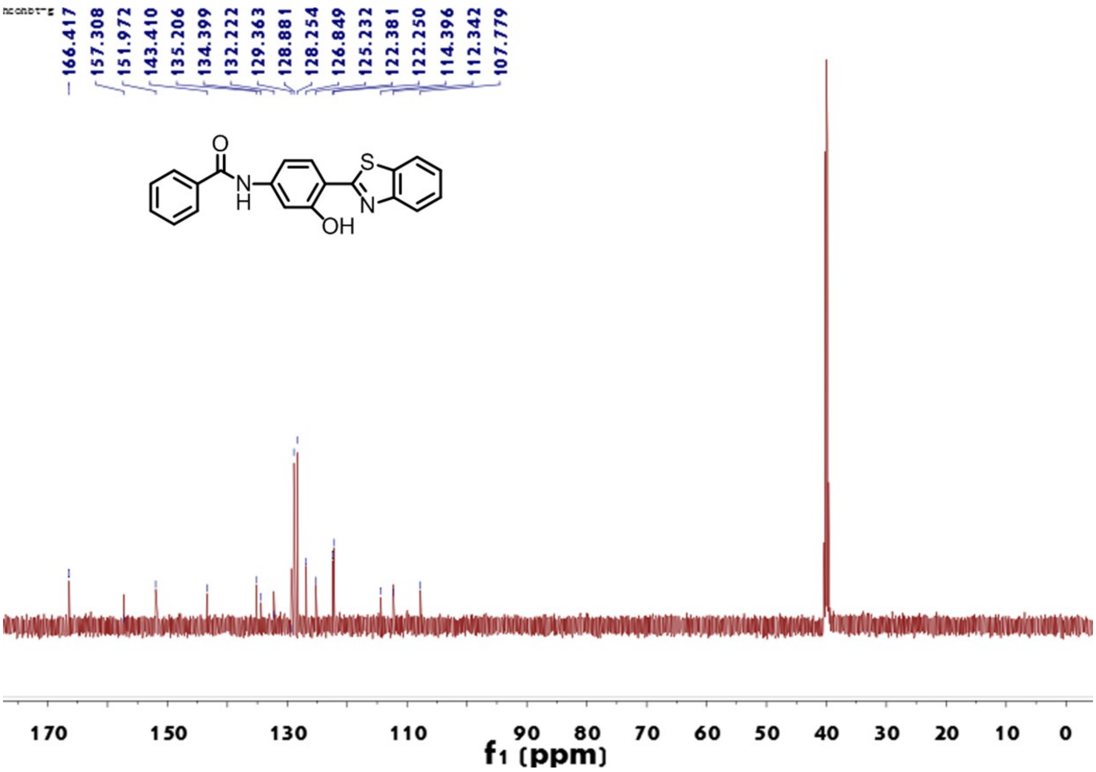


Fig.S39 ^{13}C NMR spectra of PHBT-G in DMSO.

Reference

1. W. H. Melhuish, *J. Phys. Chem.*, **64**, 762 (1960).

2. Trombay, Mumbai, *Appl. Phys. B,* **75**, 85–90 (2002).