Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Non-conjugated fluorescent molecular cages of salicylaldehyde-based tri-Schiff bases: AIE, enantiomers, mechanochromism, anion hosts/probes, and cell imaging properties

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EXPERIMENTAL SECTION

Materials and Instrumentation. All reagents were purchased from commercial suppliers and used without further purification. All the Salen ligands were prepared according to previous reports.[14] ^{1}HNMR (400MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. UV/vis absorption spectra were recorded using a U5100 (Hitachi) spectrophotometer with quartz cuvettes of 1 cm pathlength. Fluorescence spectra were obtained using F-7000 Fluorescence spectrophotometer (Hitachi) at room temperature. The slit width was 2.5 nm for both excitation and emission. The photon multiplier voltage was 400 V. Samples in solution and powder were contained in 1 cm path length quartz cuvettes (3.5 mL volume) and quartz tube, respectively. The single-crystals of **TSB**, **3-F**, **3,5-Cl**, **3-OMe**, and **3-*t*-Bu**, were obtained by a slow diffusion/evaporation of CH_2Cl_2/hexane solution at room temperature during about two weeks.

Measurement of Fluorescence Quantum Yield (Φ). The quantum yield of a solution sample was measured by the optical dilute method of Demas and Crosby[18] with a standard of quinine sulfate (Φ_r = 0.55, quinine in 0.05 mol dm^{-3} sulfuric acid) calculated by: $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, where the subscripts s and r refer to the sample and reference standard solution respectively; *n* is the refractive index of the solvents; D is the integrated intensity. The excitation intensity *B* is calculated by: $B = 1 - 10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length (L = 1 cm in all cases). The refractive indices of the solvents at room temperature are taken from standard source. Errors for Φ values (± 10%) are estimated. The quantum yield of a solid sample was measured by an integrating sphere.

Computational Details. Calculations were carried out using the Gaussian 09 software package (B3LYP 6-31G(d,p)). The geometry optimization and absorption transition and spectrum were carried out by DFT and TD-DFT, respectively. The theoretical modelling was performed in the isolated molecule approximation ignoring the effect of the aggregation state or solvent. For the atoms of **TSB**, the standard split-valence basis sets B3LYP 6-31G(d,p) augmented with polarization d-functions for the non-hydrogen atoms and p-functions for the hydrogen atoms were used. Full geometry optimization corresponding to the minima on the potential energy surface (PES) was conducted until a gradient of 10^{-5} at.u. The spin multiplicities and charges of the **TSB** were set equal to 1 and 0, respectively. The spin

multiplicities and charges of the **TSB** (in form of O^-) were set equal to 1 and –3, respectively. The other parameters were set to default values.

Cell Culture Methods and Imaging. The imaging of HeLa cells was finished by Fluorescence Vertical Microscope LEICA DM2500. HeLa cells were cultured in dulbecco's modified eagle medium (DMEM) supplemented with 10 % fetal bovine serum, penicillin (100 units mL^{-1}), streptomycin (100 mg mL^{-1}) and 5 % CO_2 at 37 °C. After removing the incubating media and rinse with PBS for three times, the cells were incubated with the dye (1.0×10^{-5} mol dm^{-3}) in PBS for 2 h at room temperature. Then, the cells were washed three times with PBS and incubated with aqueous alkali for 20 min. At last, the cells were imaged with confocal microscope.

Measurement of Anion hosts/probes: Anion titration experiment was started with the dye (6 mL) of known concentration (1.0×10^{-5} mol dm^{-3} in MeCN or DMSO). For the titration, various sodium or potassium salts (1.0–0.10 mol dm^{-3} in water) were added by a microsyringe. All types of absorption and fluorescence measurement were monitored at about 1 hours after the addition of the anion to the dye solution at room temperature.

Synthesis of Organic Dyes: **TSBs** were prepared by a similar method according to previous reports.[14] The mixture of salicyaldehyde or salicylaldehyde derivatives (3.1 mmol) and the corresponding triamine (1.0 mmol) in 20 mL ethanol solution was refluxed at 78 °C for 5 h. After the reaction was complete, the mixture was cooled to 0 °C and then the product in crystal or powder was collected by filtration.

TSB (84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.78 (s, 3H), 7.81 (s, 3H), 7.24 – 7.28 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 3H), 6.93 (d, *J* = 8.2 Hz, 3H), 6.59 (td, *J* = 7.5, 1.1 Hz, 3H), 6.08 (dd, *J* = 7.7, 1.7 Hz, 3H), 3.57 – 3.49 (t, 6H), 2.86 – 2.79 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 161.13, 131.91, 131.79, 118.62, 118.55, 116.77, 58.01, 55.93. HRMS (ESI):Calculated for $C_{27}H_{30}N_4O_3$[[M+Na]$^+$] 481.2215, found 481.2187. Anal. Calcd. (Found): C, 70.72 (70.67); H, 6.59 (6.60); N, 12.22 (12.20).

3-F-TSB (80% yield): ^{1}H NMR (400 MHz, DMSO) δ 14.20 (s, 3H), 8.40 (s, 3H), 7.17 (ddd, *J* = 11.9, 7.9, 1.5 Hz, 3H), 6.88 (d, *J* = 7.8 Hz, 3H), 6.52 (td, *J* = 7.9, 4.5 Hz, 3H), 3.66 (t, *J* = 5.8 Hz, 6H), 2.88 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 166.66, 153.42, 151.00, 127.83, 119.42, 118.90, 115.60, 54.69, 54.44. HRMS (ESI): Calculated for $C_{27}H_{27}N_4O_3F_3$ [[M+Na]$^+$] 535.1932, found 535.1898. Anal. Calcd. (Found): C, 63.27 (63.21); H, 5.31 (5.29); N, 10.93 (10.96).

3-Cl-TSB (72% yield**):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.85 (s, 3H), 7.92 (s, 3H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 3H), 6.46 (t, *J* = 7.8 Hz, 3H), 6.31 (dd, *J* = 7.8, 1.6 Hz, 3H), 3.65 – 3.55 (t,

6H), 2.91 – 2.80 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97, 159.05, 132.57, 130.29, 121.89, 118.61, 117.82, 56.13, 55.34. HRMS (ESI): Calculated for $C_{27}H_{27}N_4O_3Cl_3$[[M+Na]$^+$] 583.1149, found 583.1134. Anal. Calcd. (Found): C, 57.71 (57.67); H, 4.84 (4.85); N, 9.97 (9.96).

3-Me-TSB (74% yield**):** ^{1}H NMR (400 MHz, DMSO) δ 13.89 (s, 3H), 8.25 (s, 3H), 7.18 (d, *J* = 7.2 Hz, 3H), 6.83 – 6.76 (m, 3H), 6.67 (t, *J* = 7.5 Hz, 3H), 3.61 (t, *J* = 5.8 Hz, 6H), 2.86 (t, *J* = 6.0 Hz, 6H), 2.14 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 166.89, 159.75, 133.36, 129.65, 125.36, 118.18, 118.06, 57.24, 55.40, 15.69. HRMS (ESI): Calculated for $C_{30}H_{36}N_4O_3$ [[M+Na]$^+$] 523.2684, found 523.2650. Anal. Calcd. (Found): C, 71.97 (71.99); H, 7.25 (7.24); N, 9.59 (9.57).

3-*t*-Bu-TSB (70% yield**):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.47 (s, 3H), 7.73 (s, 3H), 7.28 (dd, *J* = 7.8, 1.6 Hz, 3H), 6.53 (t, *J* = 7.7 Hz, 3H), 5.78 (dd, *J* = 7.6, 1.5 Hz, 3H), 3.57 – 3.46 (t, 6H), 2.90 – 2.81 (t, 6H), 1.41 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 160.40, 137.10, 130.21, 128.95, 118.56, 117.78, 58.10, 56.33, 34.79, 29.33. HRMS (ESI): Calculated for $C_{39}H_{54}N_4O_3$ [[M+Na]$^+$] 649.4196, found 649.4203. Anal. Calcd. (Found): C, 74.72 (74.77); H, 8.68 (8.66); N, 8.94 (8.92).

3-OMe-TSB (82% yield**):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.29 (s, 3H), 7.81 (s, 3H), 6.86 (dd, *J* = 8.0, 1.3 Hz, 3H), 6.52 (t, *J* = 7.9 Hz, 3H), 5.84 (dd, *J* = 7.9, 1.3 Hz, 3H), 3.89 (s, 9H), 3.57 – 3.51 (t, 6H), 2.88 – 2.80 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.30, 152.65, 148.47, 123.49, 118.17, 117.34, 113.63, 57.24, 56.08, 55.88. HRMS (ESI): Calculated for $C_{30}H_{36}N_4O_6$ [[M+Na]$^+$] 571.2532, found 571.2500. Anal. Calcd. (Found): C, 65.68 (65.64); H, 6.61 (6.62); N, 10.21 (10.23).

3-OH-TSB (79% yield): ^{1}H NMR (400 MHz, DMSO) δ 13.71 (s, 3H), 8.78 (s, 3H), 8.27 (s, *J* = 30.7 Hz, 3H), 6.84 – 6.73 (m, 3H), 6.60 – 6.40 (m, 6H), 3.61 (t, *J* = 5.7 Hz, 6H), 2.87 (t, *J* = 5.7 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 166.94, 153.62, 146.67, 122.36, 117.83, 117.55, 117.24, 55.81, 55.29. HRMS (ESI): Calculated for $C_{27}H_{30}N_4O_6$ [[M+Na]$^+$] 529.2156, found 529.2162. Anal. Calcd. (Found): C, 64.02 (64.07); H, 5.97 (5.98); N, 11.06 (11.04).

3-NO_2-TSB (82% yield): ^{1}H NMR (400 MHz, DMSO) δ 14.25 (s, 3H), 8.45 (s, 3H), 7.91 (dd, *J* = 7.9, 1.9 Hz, 3H), 7.31 (dd, *J* = 7.8, 1.9 Hz, 3H), 6.22 (t, *J* = 7.8 Hz, 3H), 3.75 (t, 6H), 2.93 (t, *J* = 5.5 Hz, 6H). HRMS (ESI): Calculated for $C_{27}H_{27}N_7O_9$ [[M+Na]$^+$] 616.1870, found 616.1881 Anal. Calcd. (Found): C, 54.64 (54.68); H, 4.59 (4.58); N, 16.52 (16.54).

4-NEt_2-TSB(70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.08 (s, 3H), 7.51 (s, 3H), 6.18 – 5.81 (m, 9H), 3.43 (t, 6H), 3.36 (q, *J* = 6.9 Hz, 12H), 2.76 (t, *J* = 3.9 Hz, 6H), 1.20 (t, *J* = 7.0 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.92, 164.15, 151.88, 134.24, 108.32, 102.67, 98.65, 56.23, 54.57, 44.50, 12.87. HRMS (ESI): Calculated for $C_{39}H_{57}N_7O_3$ [[M+Na]$^+$]

694.4523, found 694.4518 Anal. Calcd. (Found): C, 69.71 (69.74); H, 8.55 (8.56); N, 14.59 (14.56).

4-OH-TSB (82% yield): ^{1}H NMR (400 MHz, DMSO) δ 13.86 (s, 3H), 9.91 (s, 3H), 8.05 (s, 3H), 6.76 (d, *J* = 8.3 Hz, 3H), 6.13 (dt, *J* = 3.5, 2.2 Hz, 6H), 3.48 (t, *J* = 5.8 Hz, 6H), 2.77 (t, *J* = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 166.38, 165.56, 162.43, 133.92, 111.48, 107.02, 103.22, 55.65, 55.56. HRMS (ESI): Calculated for $C_{27}H_{30}N_4O_6$ [[M+Na]$^+$] 529.2156, found 529.2159. Anal. Calcd. (Found): C, 64.02 (64.06); H, 5.97 (5.96); N, 11.06 (11.03).

5-OMe-TSB (75% yield**):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.35 (s, 3H), 7.90 (s, 3H), 6.86 (dd, *J* = 2.5, 1.6 Hz, 6H), 6.02 (d, *J* = 2.2 Hz, 3H), 3.62 (s, 9H), 3.58 – 3.51 (t, 6H), 2.91 – 2.83 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.77, 155.15, 151.87, 119.02, 118.38, 117.40, 114.86, 58.03, 56.26, 55.67. HRMS (ESI): Calculated for $C_{30}H_{36}N_4O_6$ [[M+Na]$^+$] 571.2532, found 571.2519. Anal. Calcd. (Found): C, 65.68 (65.65); H, 6.61 (6.59); N, 10.21 (10.22).

5-NO_2-TSB (87% yield**):** ^{1}H NMR (400 MHz, DMSO) δ 14.10 (s, 3H), 8.56 (s, 3H), 8.10 (d, *J* = 3.1 Hz, 3H), 7.84 (dd, *J* = 9.7, 3.1 Hz, 3H), 6.46 (d, *J* = 9.7 Hz, 3H), 3.73 (t, 6H), 2.92 (t, *J* = 5.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 177.96, 167.77, 134.08, 132.91, 129.28, 122.92, 113.71, 53.43, 50.58. HRMS (ESI): Calculated for $C_{27}H_{27}N_7O_9$ [[M+Na]$^+$] 616.1870, found 616.1877 Anal. Calcd. (Found): C, 54.64 (54.67); H, 4.59 (4.60); N, 16.52 (16.51).

3,5-Cl-TSB (90% yield**):** ^{1}H NMR (400 MHz, DMSO) δ 14.49 (s, 3H), 8.30 (s, 3H), 7.43 (d, *J* = 2.7 Hz, 3H), 6.98 (d, *J* = 2.7 Hz, 3H), 3.66 (t, *J* = 4.9 Hz, 6H), 2.92 – 2.84 (t, 6H). ^{13}C NMR (101 MHz, DMSO) δ 166.03, 164.34, 133.33, 130.48, 125.09, 117.12, 116.72, 54.14, 52.30. HRMS (ESI): Calculated for $C_{27}H_{24}N_4O_3Cl_6$ [[M+Na]$^+$] 684.9877, found 684.9886. Anal. Calcd. (Found): C, 48.75 (48.77); H, 3.64 (3.63); N, 8.42 (8.43).

3,5-NO_2-TSB (78% yield**):** ^{1}H NMR (400 MHz, DMSO) δ 13.29 (s, 3H), 8.78 (s, 3H), 8.54 (d, *J* = 3.1 Hz, 3H), 8.42 (d, *J* = 3.1 Hz, 3H), 3.85 (t, 6H), 3.03 (t, 6H). ^{13}C NMR (101 MHz, DMSO) δ 175.93, 170.02, 140.52, 130.04, 129.98, 127.38, 117.81, 55.40, 51.87. HRMS (ESI): Calculated for $C_{27}H_{24}N_{10}O_{15}$ [[M+Na]$^+$] 751.1423, found 751.1427. Anal. Calcd. (Found): C, 44.51 (44.54); H, 3.32 (3.31); N, 19.23 (19.27).

Naph-TSB (71% yield**):** ^{1}H NMR (400 MHz, DMSO) δ 13.96 (dd, *J* = 10.5, 5.2 Hz, 3H), 9.08 (d, *J* = 10.7 Hz, 3H), 8.02 (d, *J* = 8.3 Hz, 3H), 7.73 – 7.54 (m, 6H), 7.36 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 3H), 7.20 – 7.10 (m, 3H), 6.67 (d, *J* = 9.4 Hz, 3H), 3.75 (t, *J* = 11.8, 6.1 Hz, 6H), 2.97 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 178.25, 159.57, 137.53, 134.84, 129.27, 128.23, 126.21, 125.54, 122.47, 118.89, 106.15, 55.18, 49.89. HRMS (ESI): Calculated for $C_{39}H_{36}N_4O_3$ [[M+Na]$^+$] 631.2787 found 631.2781. Anal. Calcd. (Found): C, 76.95 (76.86); H, 5.96 (5.95); N, 9.20 (9.22).

Table. S1 Photophysical data of **TSBs**. Sample without emission data means that it is non-emissive. The amount of X^- is 100 equivalent to **TSBs**.

TSBs	medium	λ_{abs} /nm (ε/dm³ mol⁻¹cm⁻¹)	λ_{em} /nm	Stokes shift /nm	Φ	*f* /%
TSB	MeCN	253(4.85×10^4); 314(2.27×10^4)	426		0.0028	
	Water	328; 382	497	115	0.015	60
	Solid		497		0.018	
TSB+F^-	MeCN	314(4.83); 404(2.13×10^3)	418		0.0029	
	DMSO	316(1.73×10^4); 399(8.87×10^3)	464		0.023	
TSB+OH^-	MeCN	351(8.90×10^4)	432		0.036	
	DMSO	262(3.18×10^4); 370(2.83×10^4)	457		0.23	
TSB+HCO_3^-	MeCN	314(6.48×10^4); 404(4.47×10^3)	420		0.0081	
	DMSO	284(1.52×10^4); 411(3.10×10^3)	433		0.29	
3-F	MeCN	311(1.02×10^4); 409(4.77×10^3)	435		0.0037	
	Water	382	501	119	0.025	60
	Solid		512		0.13	
3-F+F^-	MeCN	312(9.70×10^4); 409(5.27×10^3)	482		0.021	
	DMSO	262(4.40×10^4); 390(3.25×10^3)	449		0.37	
3-F+OH^-	MeCN	345(2.70×10^4)	450		0.035	
	DMSO	260(3.97×10^4); 365(2.54×10^4)	450		0.42	
3-Cl	MeCN	319(5.41×10^3); 416(3.92×10^3)	432		0.0065	
	Water	392	505	113	0.025	60
	Solid		526		0.12	
3,5-Cl	MeCN	330(8.4×10^3); 428(1.16×10^4)	494		0.018	
	Water	403	510	107	0.048	60
	Solid		522		0.18	
3,5-Cl+F^-	MeCN	331(8.00×10^3); 426(1.33×10^4)	490		0.039	
	DMSO	263(4.53×10^4); 416(4.00×10^4)	462		0.41	
3,5-Cl+OH^-	MeCN	366(2.98×10^4)	444		0.040	
	DMSO	257(5.38×10^4); 409(3.54×10^4)	463		0.44	
3-CH_3	MeCN	254(3.55×10^4); 320(1.30×10^4)	406		0.0039	
	Water	335	502	167	0.0043	60
	Solid		514		0.022	
3-OMe	MeCN	328(8.43×10^3); 420(1.56×10^3)	453		0.0052	
	Water	393	492	99	0.0024	50
	Solid		537		0.010	
3-tBu	MeCN	256(3.57×10^4); 320(1.67×10^4)	406		0.0036	
	Solid		516		0.0058	
3-*t*-Bu+OH^-	MeCN	287(5.56×10^4); 377(4.73×10^3)	434		0.0096	
	DMSO	304(4.20×10^4)	468		0.47	
3-NO_2	MeCN	357(3.48×10^4); 409(3.63×10^4)	481		0.00088	
	Water	359 ; 392				
	Solid		556		0.0048	

3-OH	MeCN	295(1.34×10^4); 425(4.77×10^3)	460		0.0025	
	Water	286 ; 322	427	105	0.0028	60
	Solid		550		0.0067	
4-OH	MeCN	305(1.12×10^4); 380(5.37×10^3)	406		0.00076	
	Water	335	430	95	0.00081	60
	Solid		470		0.0051	
4-NEt_2	MeCN	329(7.05×10^4)	406		0.0062	
	Solid		487		0.011	
5-OMe	MeCN	343(1.71×10^4)	432		0.0068	
	Water	405	486	81	0.013	60
	Solid		532		0.028	
5-NO_2	MeCN	440(1.22×10^4)				
	Water	435				
	Solid		548		0.044	
3,5-NO_2	MeCN	381(2.67×10^4)				
	Water	370				
	Solid		558		0.0085	
Naph	MeCN	305(3.74×10^4); 401(3.03×10^4); 420(3.12×10^4)	450		0.00059	
	Water		454	43	0.0018	80
	Solid		488		0.011	

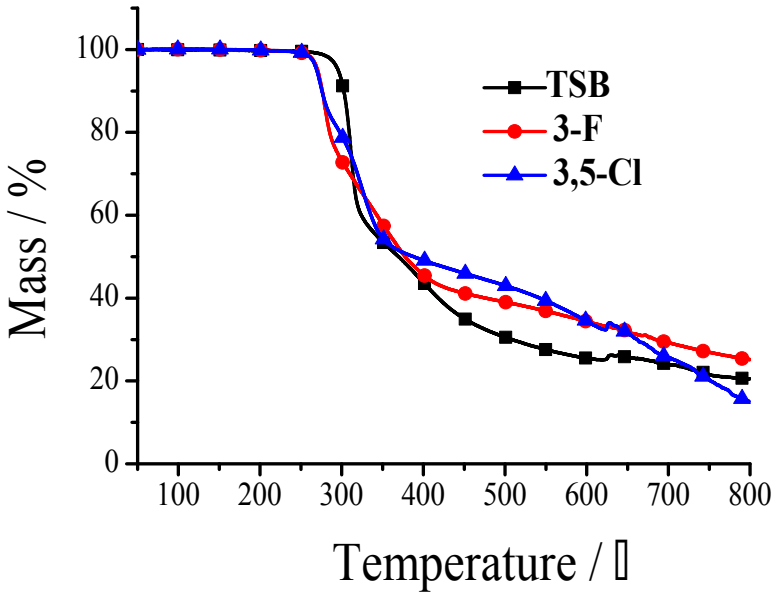

Fig. S1 Thermogravimetric Analysis (TGA) experiments of **TSB**, **3-F**, and **3,5-Cl** (25℃–800℃, 10℃/min).

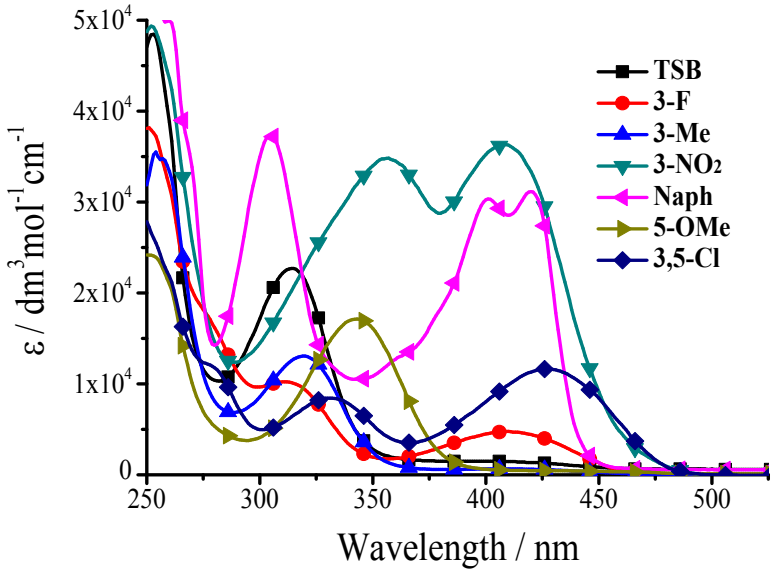

Fig. S2 Absorption spectra of some selected **TSBs** in MeCN.

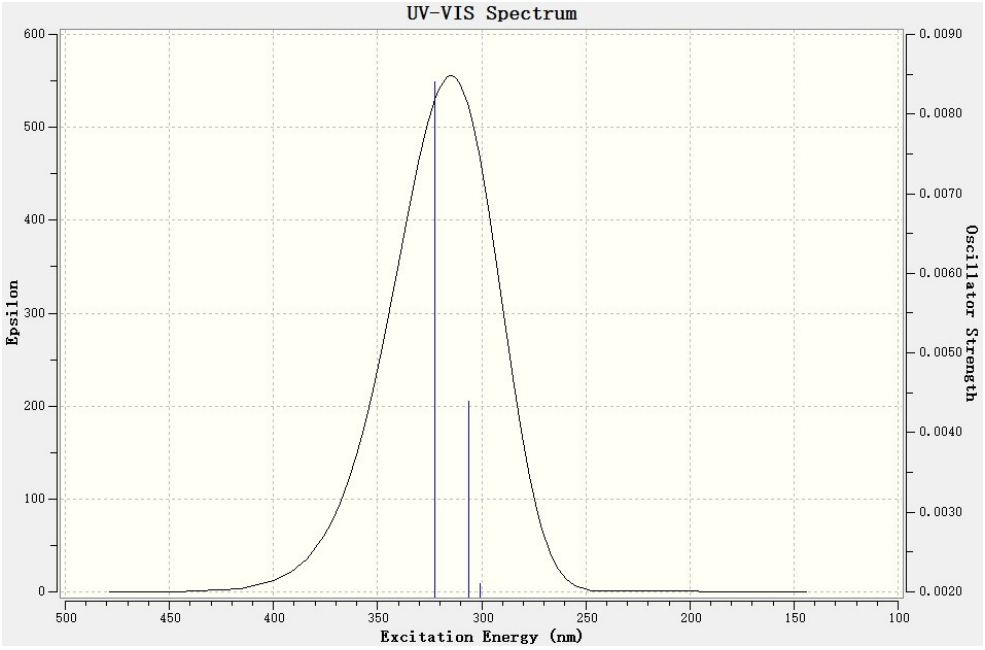

Fig. S3 computational (gas-phase) absorption spectra of **TSB**.

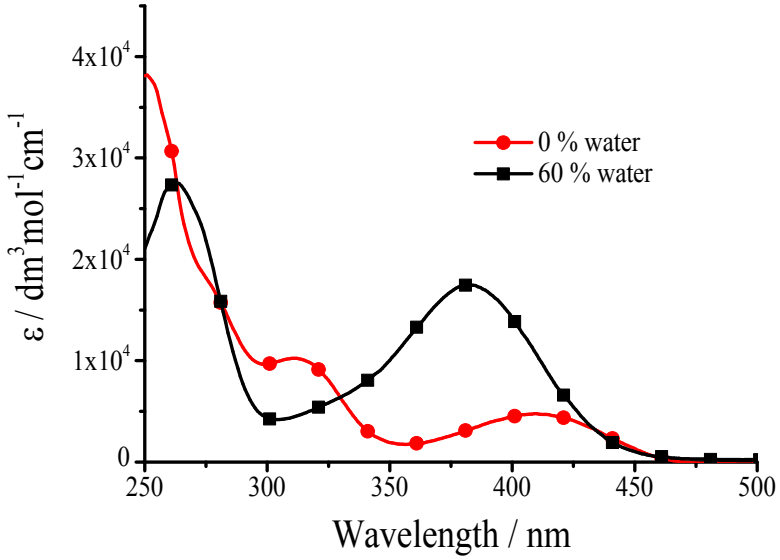

Fig. S4 Absorption spectra of **3-F** in MeCN-H_2O with different *f* values (3.0×10^{-5} mol dm^{-3}).

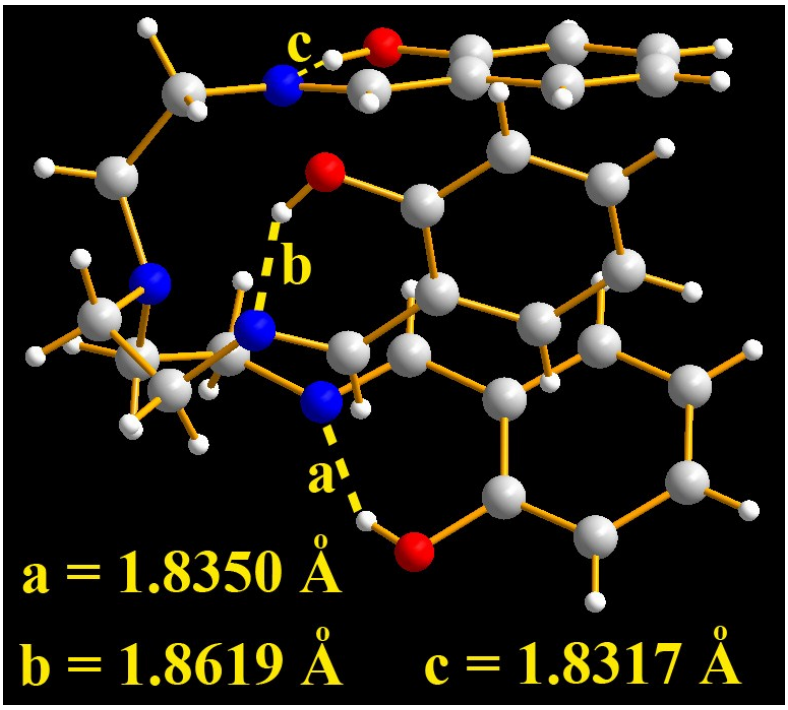

Fig. S5 Intramolecular N···H hydrogen bonds in the X-ray single crystal structure of **TSB** molecule.

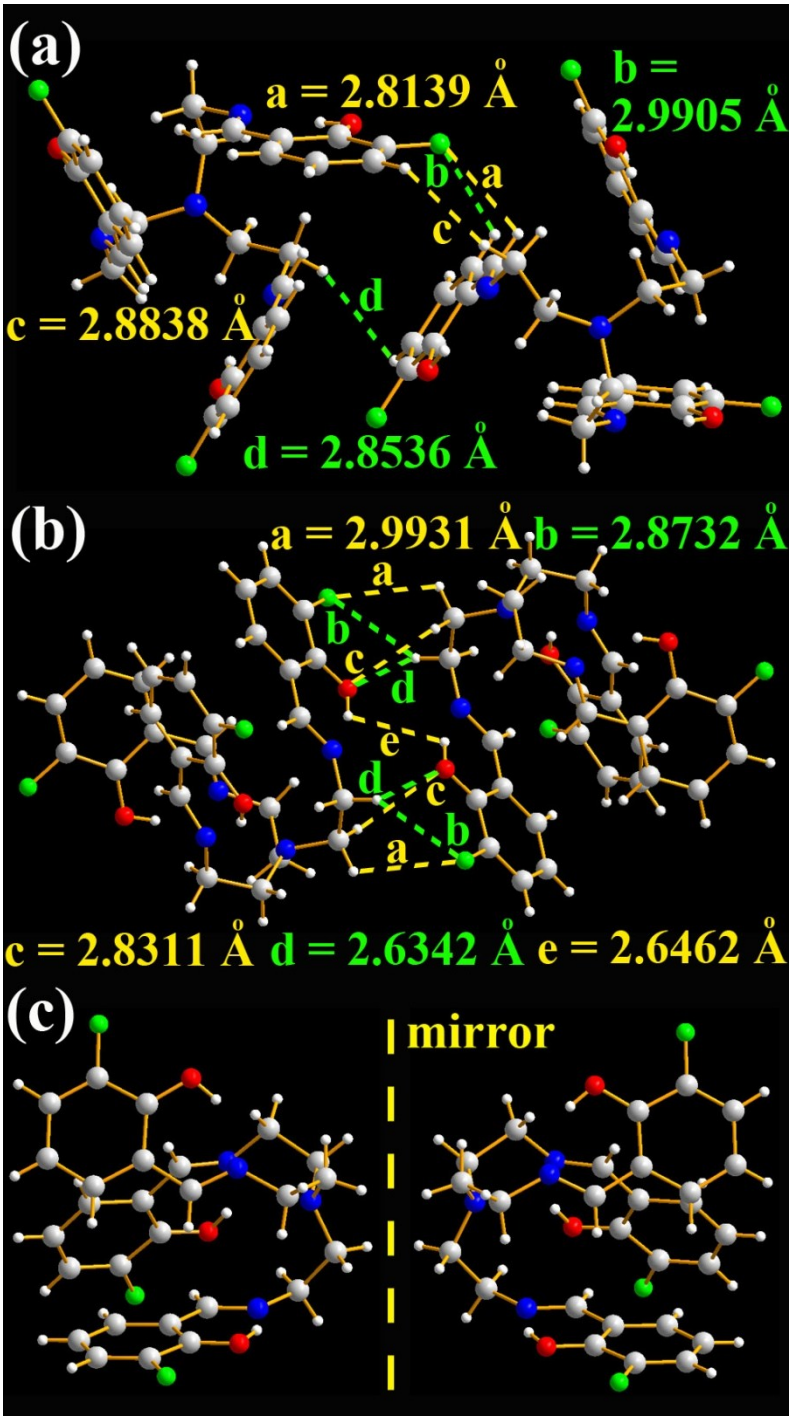

Fig. S6 X-ray single crystal structures and packing of **3-F** molecules: (a) and (b), intermolecular interactions of the two closest molecules; (c) enantiomers.

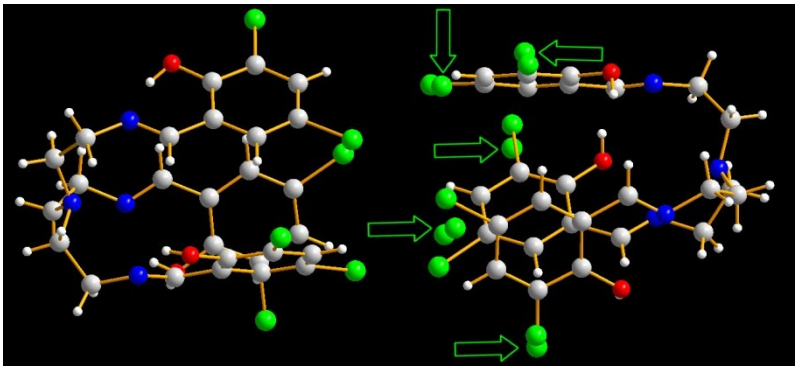

Fig. S7 X-ray single crystal structure of two close **3,5-Cl** molecules. In one **3,5-Cl** molecule, the positions of Cl atoms are not fixed, due to the disorders of Cl atoms.

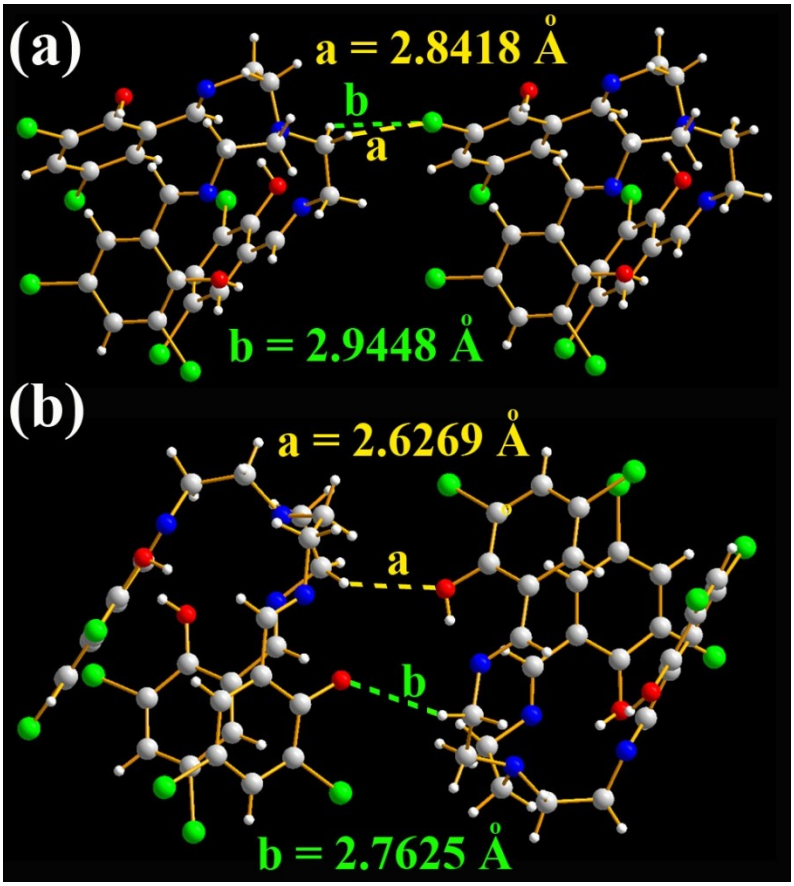

Fig. S8 X-ray single crystal structures and packing of **3,5-Cl** molecules: (a) and (b), intermolecular interactions of the two closest molecules.

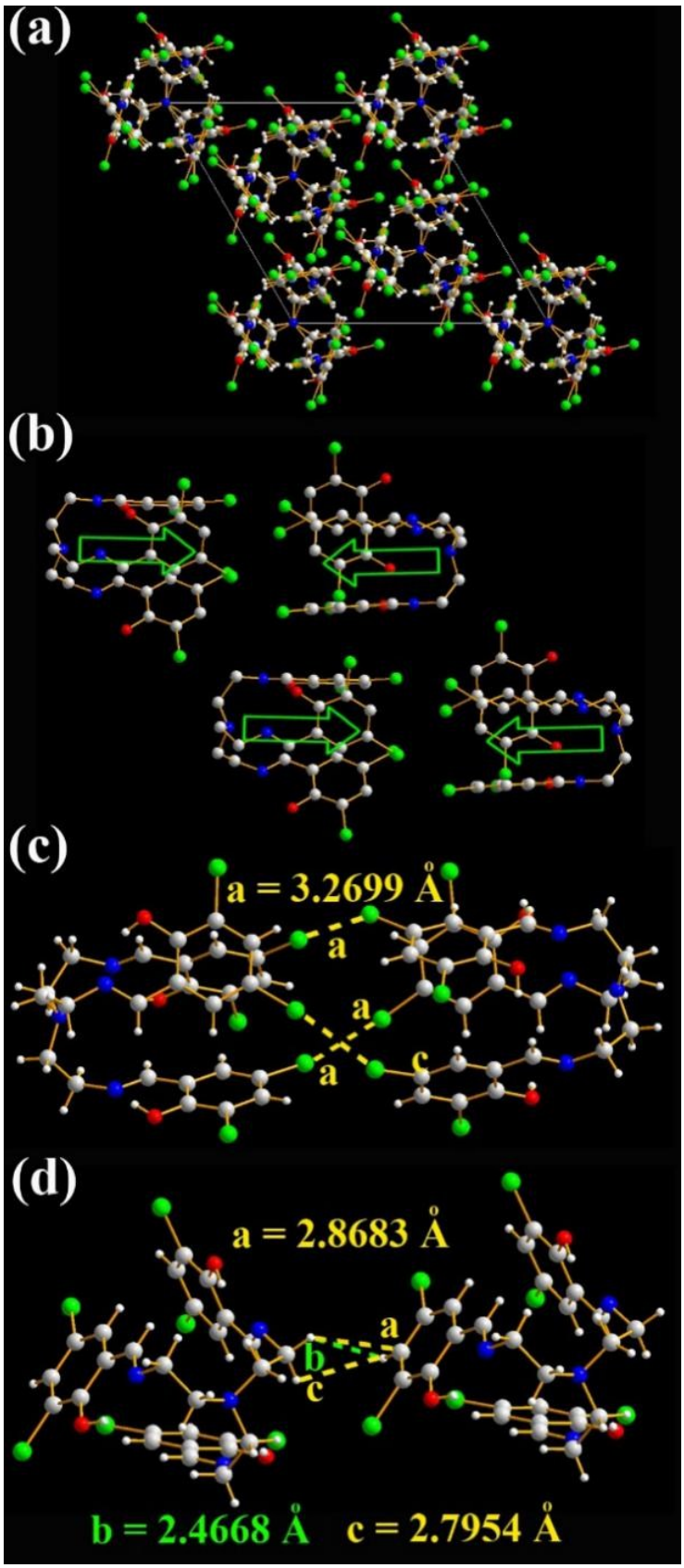

Fig. S9 X-ray single crystal structures and packing of **3,5-Cl** molecules: (a) packing in a unit cell (H atoms are omitted); (b) packing of some selected molecules (blue arrows indicate the opening direction of molecular cages); (c) and (d) intermolecular interactions of the two closest molecules.

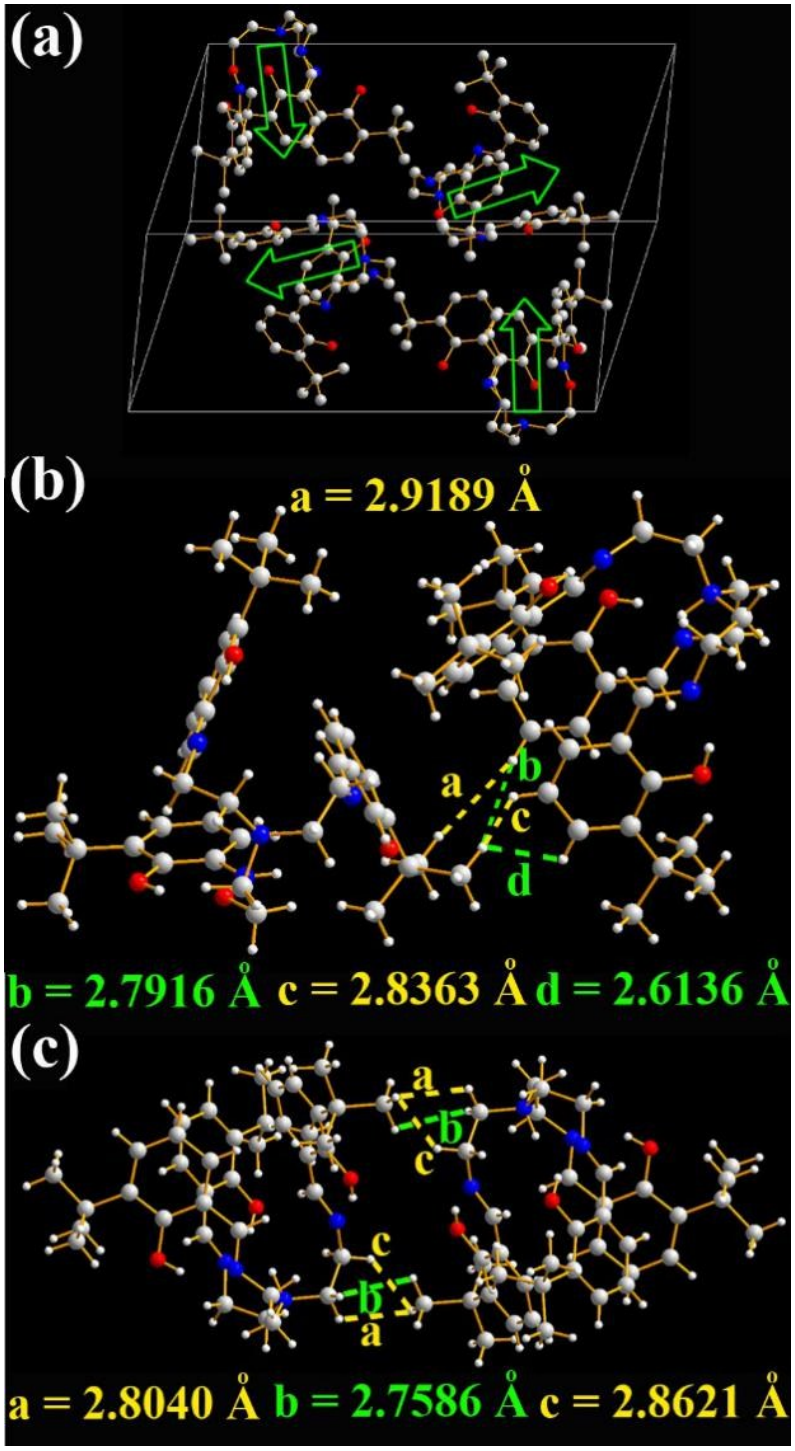

Fig. S10 X-ray single crystal structures and packing of **3-*t*-Bu** molecules: (a) packing in a unit cell (H atoms are omitted and blue arrows indicate the opening direction of molecular cages); (b) and (c) intermolecular interactions of the two closest molecules.

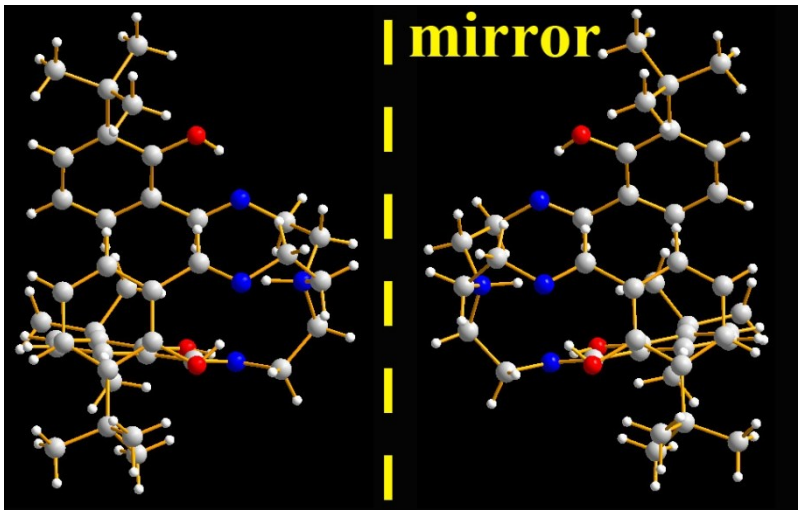

Fig. S11 X-ray single crystal structures and packing of **3-*t*-Bu** enantiomers.

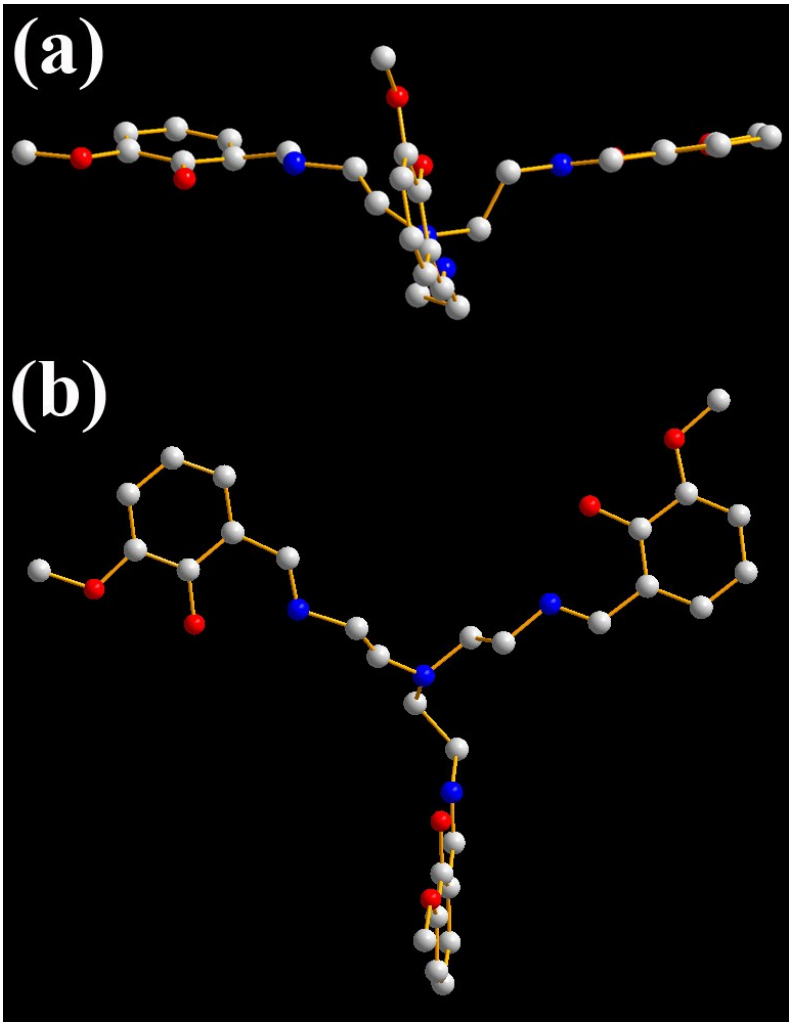

Fig. S12 X-ray single crystal structure of **3-OMe** molecule: (a) side view; (b) top view.

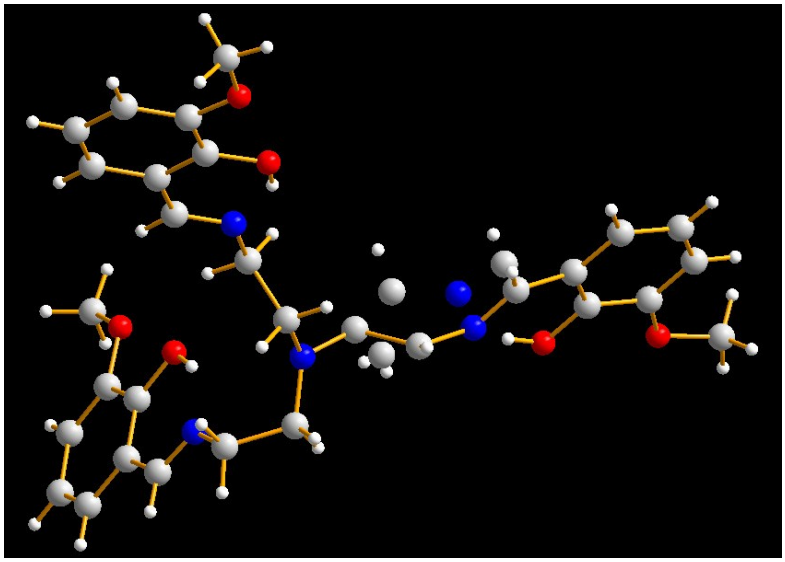

Fig. S13 Dissoder of X-ray single crystal structure of **3-OMe** molecule.

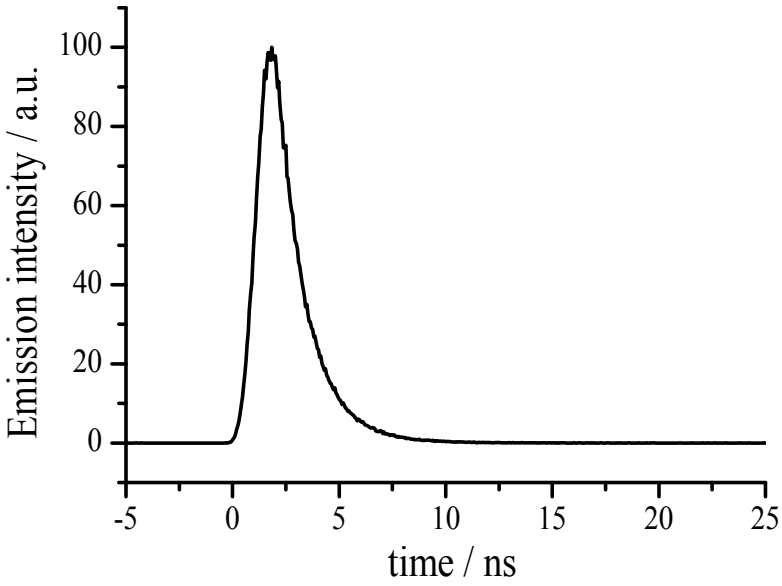

Fig. S14 Time-resolved emission decay spectra (excited at 370 nm) of **3,5-Cl** powder samples.

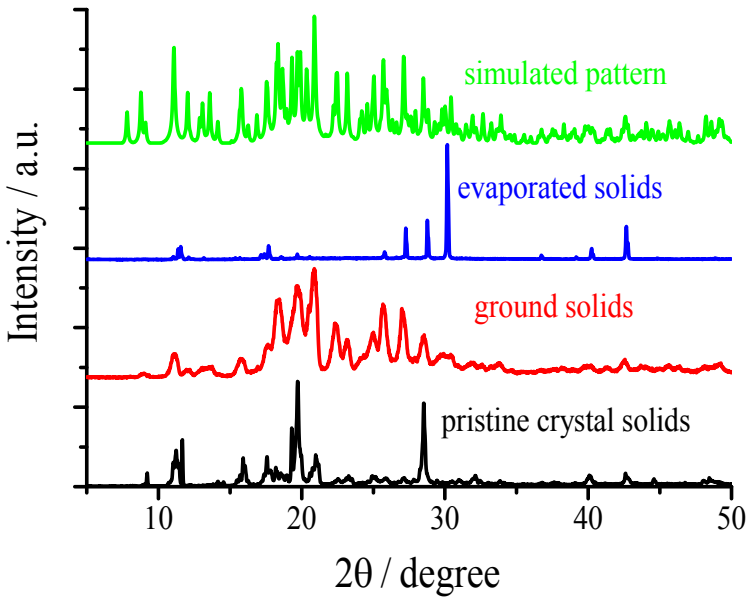

Fig. S15 X-ray powder diffraction of **TSB** solids.

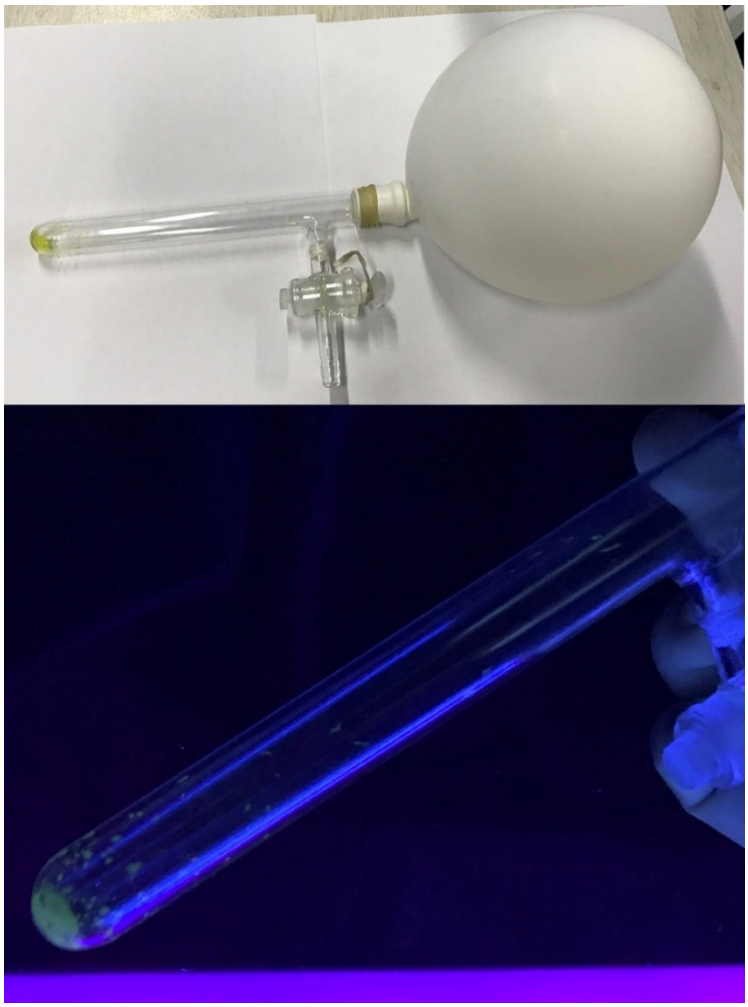

Fig. S16 Amorphous samples of **TSB** prepared via the rapid cooling (ice-water bath) from the melted state (~120 ^{o}C in N_2) under room light (top) and UV light (bottom).

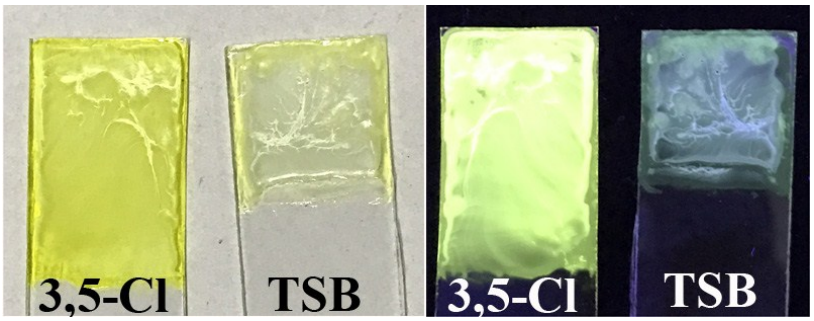

Fig. S17 Casting films of **TSB** and **3,5-Cl** in PMMA (5.0 wt%) under room light (left) and UV light (right).

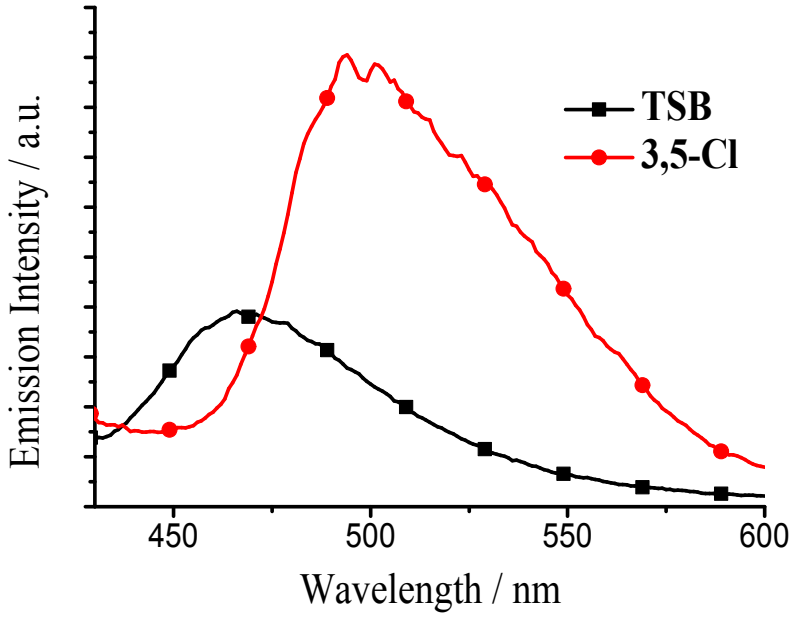

Fig. S18 Emission spectra (excited at 370 nm) of **TSB** and **3,5-Cl** in THF at 77 K (3.0×10^{-5} mol dm^{-3}).

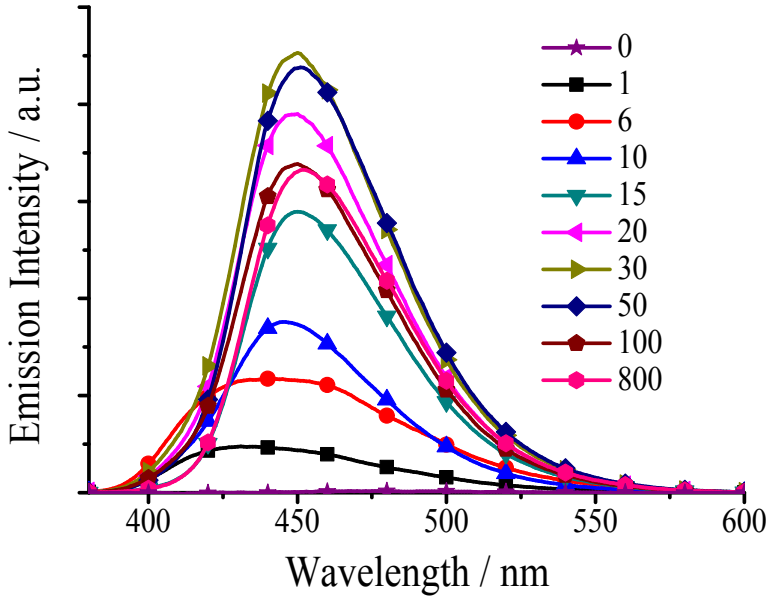

Fig. S19 Emission spectra of **3-F** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 365 nm) upon the addition of different equivalents of OH^-.

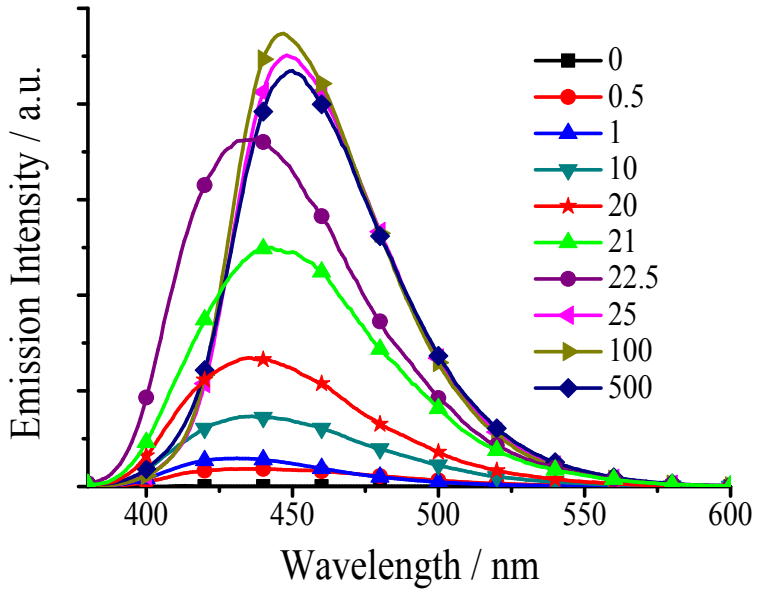

Fig. S20 Emission spectra of **3-F** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 365 nm) upon the addition of different equivalents of F^-.

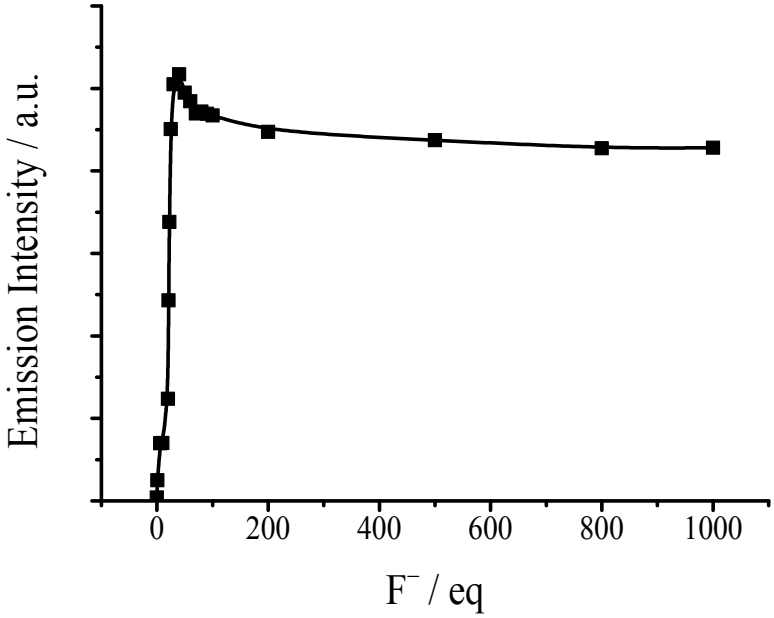

Fig. S21 Plot of emission intensity of **3-F** (1.0×10^{-5} mol dm^{-3} in DMSO) at 450 nm (excited at 365 nm) as a function of F^- concentration.

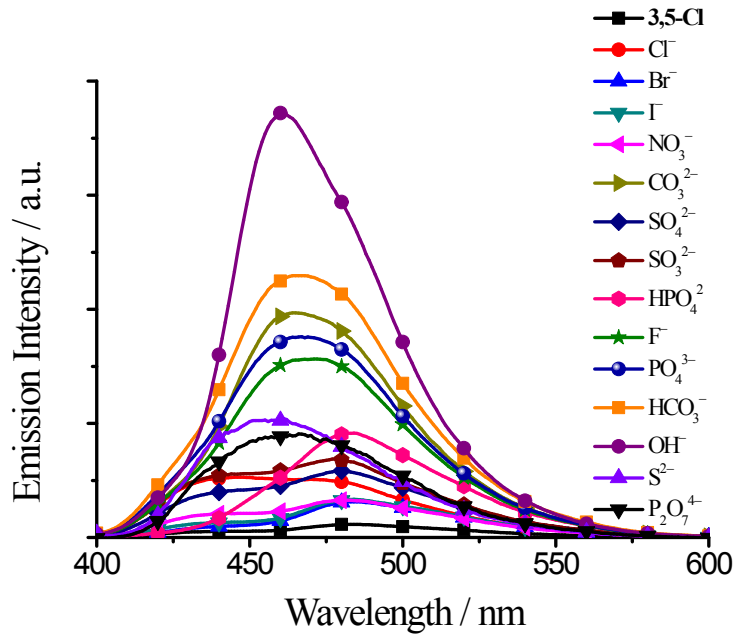

Fig. S22 Emission spectra of **3,5-Cl** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 365 nm) upon the addition of 100 equivalent of different anions.

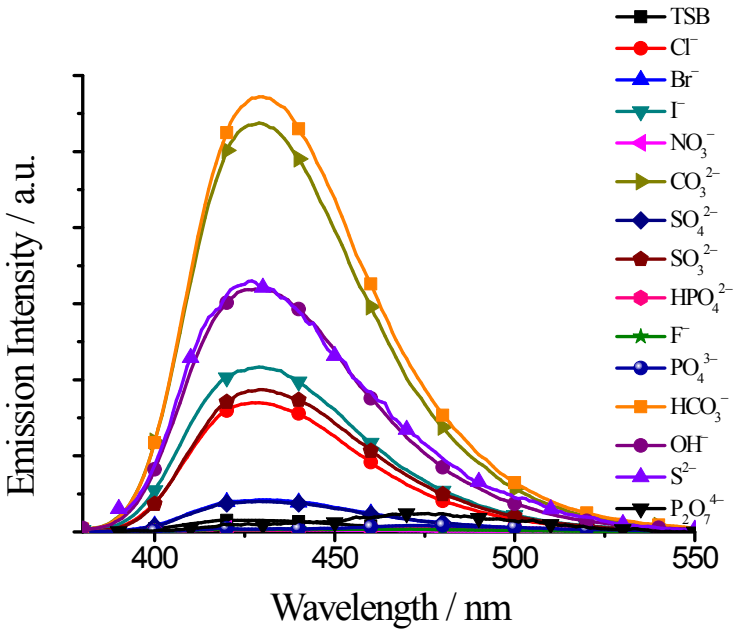

Fig. S23 Emission spectra of **TSB** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 370 nm) upon the addition of 100 equivalent of different anions.

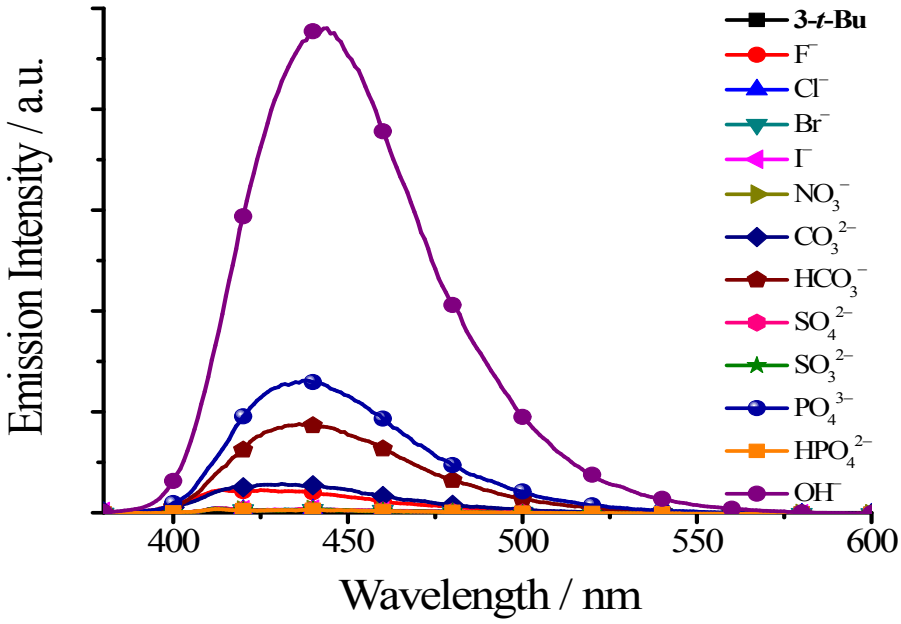

Fig. S24 Emission spectra of **3-*t*-Bu** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 370 nm) upon the addition of 100 equivalent of different anions.

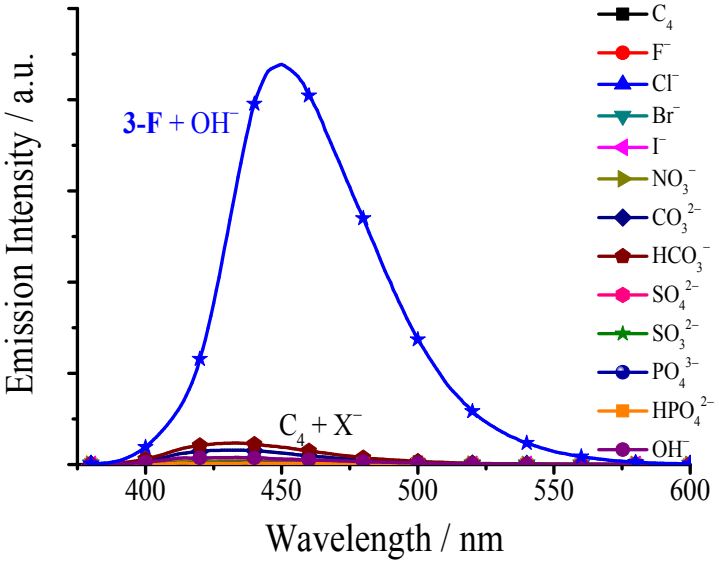

Fig. S25 Emission spectra of C_4 (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 365 nm) upon the addition of 100 equivalent of different anions and emission spectrum of **3-F** (1.0×10^{-5} mol dm^{-3} in DMSO, excited at 365 nm) upon the addition of 100 equivalent of OH^-.

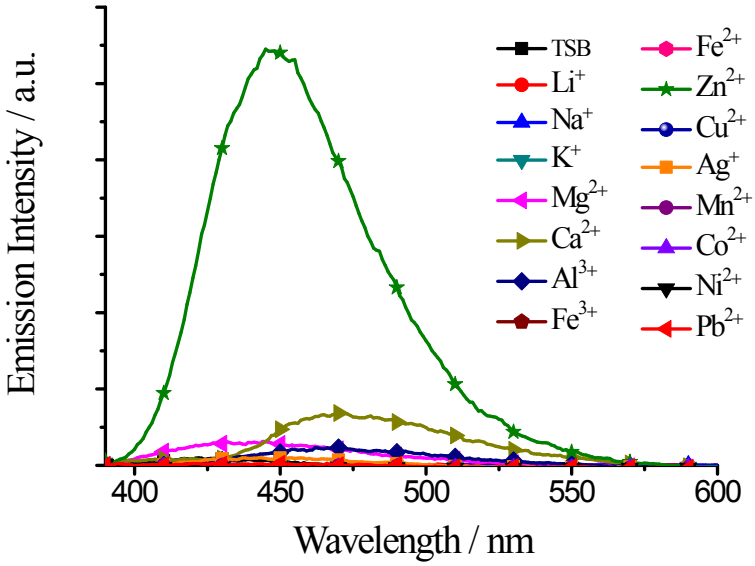

Fig. S26 Emission spectra of **TSB** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 370 nm) upon the addition of 5 equivalent of different metal ions.

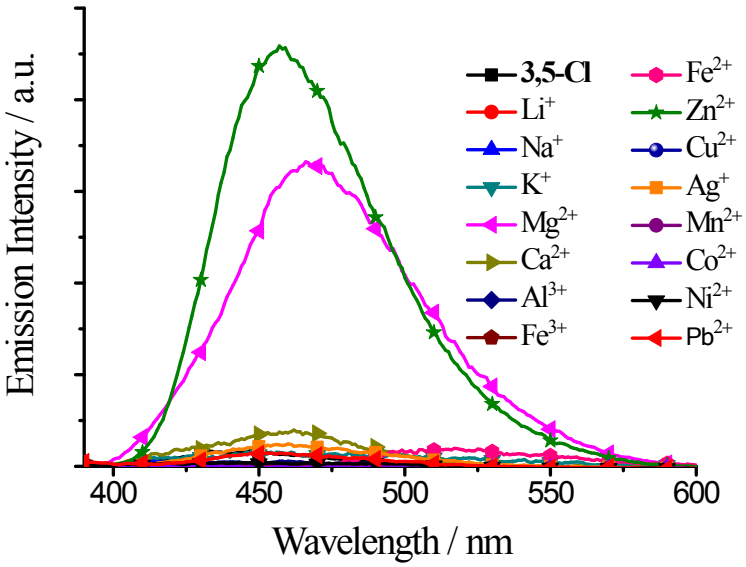

Fig. S27 Emission spectra of **3,5-Cl** (1.0×10^{-5} mol dm^{-3} in MeCN, excited at 370 nm) upon the addition of 5 equivalent of different metal ions.

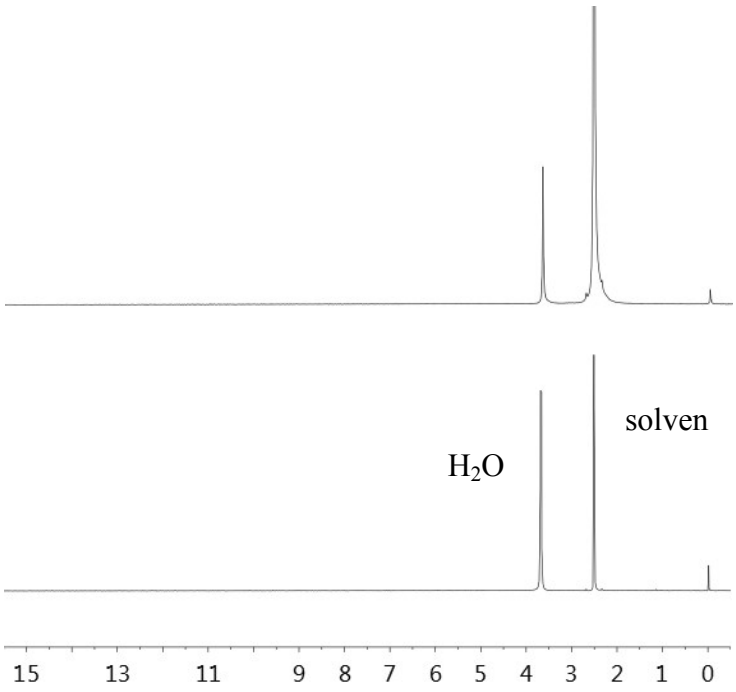

Fig. S28 ^{1}H NMR spectra of OH^- (top) and F^- (bottom) in DMSO-d_6.

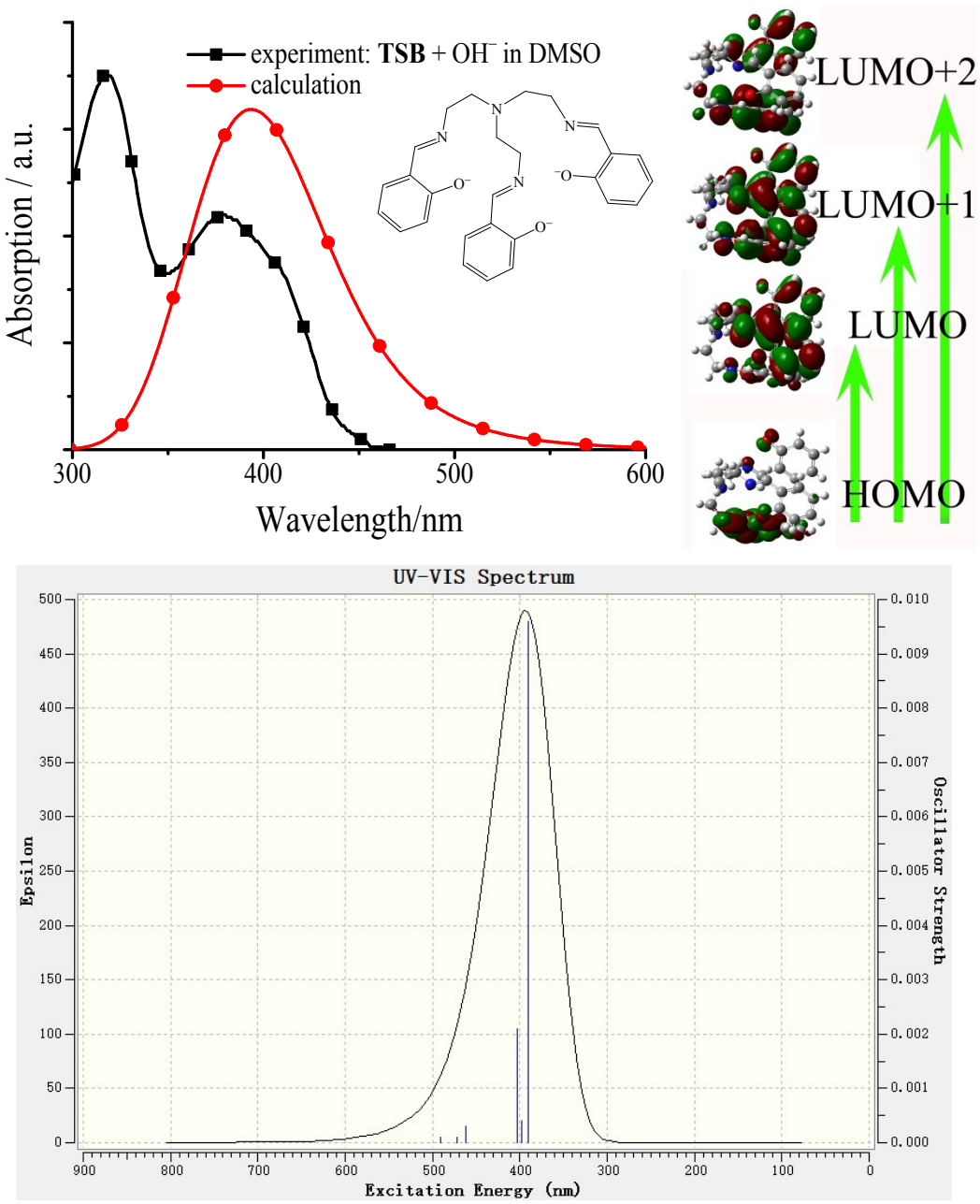

Fig. S29 Top: computational (gas-phase) and experimental (in DMSO + 100 equivalent of OH^-) absorption spectra, energy level diagram, and frontier molecular orbitals of **TSB** (in form of O^-). Botoom: computational (gas-phase) absorption spectra of **TSB** (in form of O^-).

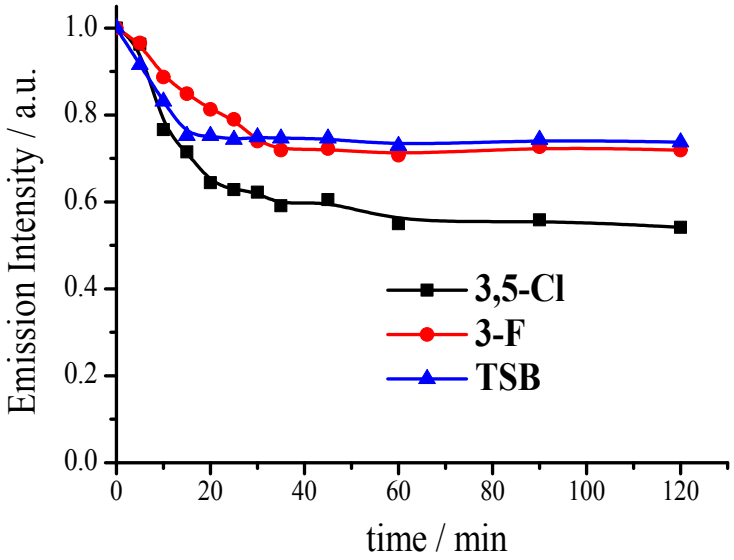

Fig. S30 Fluorescence (excited at 380 nm) intensity decay curve of several **TSBs** solids under 360 nm UV light (30 W) irradiation.