

AIE-active Luminophore with tunable and remarkable fluorescence switching based on the piezo and protonation-deprotonation control†

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Experimental

Materials

1-Bromo-1,2,2-triphenylethene (P₃Br, compound **a**), 4-formylphenylboronic acid, tetrabutyl ammonium bromide (TBAB), tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄], potassium carbonate (K₂CO₃), 6-methoxybenzo[d]thiazol-2-amine (compound **c**), potassium hydroxide (KOH) and borontribromide (BBr₃) purchased from Alfa Aesar were used as received. The compounds **b**¹ and **d**² were prepared by the literature methods. Ultra-pure water (18 MΩ cm) was used in the experiments. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. The water/ethanol mixtures with different water fractions were prepared by slowly adding distilled water into the ethanol solution of samples under ultrasound at room temperature.

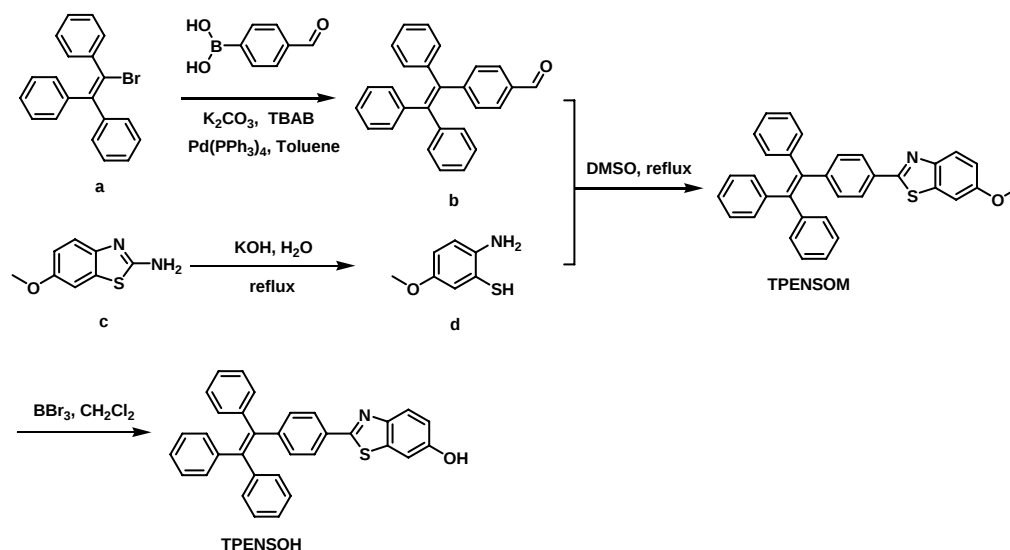
Characterization

Proton and carbon nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra were measured on a Mercury-Plus 300 spectrometer [CDCl₃, tetramethylsilane (TMS) as the internal standard]. Mass spectra were measured with Thermo spectrometers (DSQ). FT-IR spectra were obtained on a Nicolet NEXUS 670 spectrometer (KBr pellet). UV-visible absorption spectra (UV) were determined on a Hitachi U-3900 spectrophotometer. Fluorescence spectra (PL) were measured on a Shimadzu RF-5301PC spectrometer with a slit width of 1.5 nm for excitation and 3 nm for emission. Thermal behaviors were determined by differential scanning calorimetry (DSC) at heating and cooling rate of 10 °C/min under N₂ atmosphere using a NETZSCH thermal analyzer (DSC 204F1). Time-resolved emission decay behaviors were measured on an Edinburgh Instruments Ltd spectrometer (FLSP920). Wide-angle X-ray diffraction (WAXD) measurements were performed at 293 K by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with an X-ray source of Cu Kα (λ = 0.15406 nm) at 40 kV and 40 mA, at a scan rate of 6° (2θ) per min. Fluorescence quantum yields of solid powders and single crystals were measured on an integrating sphere (C-701, Labsphere Inc.), with a 405 nm Ocean Optics LLS-LED as the excitation source, and the light was introduced into the integrating sphere through optical fiber. The geometry optimization was carried out at the B3LYP/6-31G(d) level of the theory using TD-DFT method. The excited states were computed at the

B3LYP/6-31G+(d) level of the theory with TD-DFT method in the Gaussian 09 software.

Single crystals of TPENSOH (**T1**) were grown from dichloromethane (DCM) while the others of protonated TPENSOH (**T2** and **T3**) were obtained from ethanol and THF solutions under HCl vapors, respectively. For **T1** and **T2**, the single-crystal X-ray diffraction data was collected on a Rigaku R-Axis SPIDER IP diffractometer at 153(2) K using Mo-K α radiation ($\lambda=0.71073$ Å). For **T3**, the corresponding diffraction data was obtained from an Agilent Technologies Gemini A Ultra system with Cu-K α radiation ($\lambda=1.54178$ Å) at 150(2) K. All the three structures were solved by direct methods following difference Fourier syntheses, and all non-hydrogen atoms were refined anisotropically through least-squares on F^2 using the SHELXTL program suite.³ Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms attached to carbon were placed in idealized positions and refined using a riding model to the atom to which they were attached, and the hydrogen atoms attached to nitrogen and oxygen atoms were located in the difference Fourier map and refined isotropically. The pictures of the three structures were produced using Diamond 3.1.⁴ CCDC 981044, 981046 and 981049 contain the supplementary crystallographic data for this paper.

Synthesis



Scheme S1. Synthetic routes of the desired compound.

Synthesis of 6-methoxy-2-(4-(1,1,2-triphenylvinyl)phenyl)benzo[d]thiazole (TPENSOM) A mixture of 2-amino-5-methoxybenzenethiol (10.0 mmol, 1.55 g) and compound **b** (10.0 mmol, 3.60 g) in DMSO (10 mL) was heated at 170 °C for 12 h. After workup, the mixture was cooled to room temperature, poured into excess ice-cold water, and extracted with dichloromethane for three times. The dichloromethane solution was washed with water and dried over anhydrous Na_2SO_4 . Following filtration, the solvent was evaporated under vacuum. The resulting crude product was then chromatographed on a silica gel column with *n*-hexane/ CH_2Cl_2 (3:1, v/v) as eluent to afford a pale yellow powder (2.60 g, yield 52%). 1H NMR (300 MHz, $CDCl_3$) δ ppm: 3.89 (s, 3 H, $J=0.40$ Hz), 6.96–7.20 (m, 18 H), 7.32 (dd, 1 H, $J=0.40$ Hz, 2.47 Hz), 7.78 (dd, 2 H, $J=0.40$ Hz, 8.24 Hz), 7.91 (dd, 1 H, $J=0.40$ Hz, 8.92 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 165.54, 157.85, 148.75, 146.45, 143.41, 141.93, 139.97, 136.30, 132.13, 131.48, 127.99, 126.99, 126.80, 123.75, 115.81, 104.39, 56.12; FT-IR (KBr): 3023, 1602, 1465, 1272, 702; MS (EI), m/z : 495 (calcd. for $C_{34}H_{25}NOS$ 495); Anal. Calc. for $C_{34}H_{25}NOS$: C 82.39, H 5.08, N 2.83, O 3.23, S 6.47; Found: C 82.34, H 5.11, N 2.80, S 6.51.

Synthesis of 6-hydroxy-2-(4-(1,1,2-triphenylvinyl)phenyl)benzo[d]thiazole (TPENSOH) To a stirring solution of

TPENSOM (2 mmol, 0.99 g) in CH₂Cl₂ (30 mL), BBr₃ (4 mmol, 1.00 g) in anhydrous CH₂Cl₂ (4 mL) was added slowly under argon atmosphere at -78 °C. Then, the mixture was gradually warmed to room temperature and stirred for an additional 20 h. After being neutralized with a saturated NaHCO₃ solution, the mixture was extracted with CH₂Cl₂ for three times. The resulting dichloromethane solution was washed with water and dried over anhydrous Na₂SO₄. Following filtration, the solvent was evaporated under vacuum. The crude product was chromatographed on a silica gel column with CH₂Cl₂ as eluent to afford a pale yellow powder (0.65 g, yield 92%). ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 6.96—7.08 (m, 7 H), 6.96—7.08 (m, 7 H), 7.41 (s, 1 H), 7.78 (d, 2 H, *J* = 0.40 Hz, 7.89 Hz), 7.82 (d, 1 H, *J* = 0.40 Hz, 8.81 Hz), 9.92 (s, 1 H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ ppm: 163.45, 156.26, 147.60, 146.16, 143.33, 142.03, 140.19, 136.38, 132.02, 131.64, 131.16, 128.46, 127.23, 126.67, 123.89, 116.62, 107.23; FT-IR (KBr): 3537, 2959, 1739, 1610, 1561, 1281, 815, 702 MS (EI), *m/z*: 481 (calcd. for C₃₃H₂₃NOS 481); Anal. Calc. for C₃₃H₂₃NOS: C 82.30, H 4.81, N 2.91, O 3.32, S 6.66; Found: C 82.28, H 4.79, N 2.93, S 6.62.

- 1 X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang, J. Xu, *Chem.-Asian J.* 2011, **6**, 808.
- 2 C. A. Mathis, Y. M. Wang, D. P. Holt, G. F. Huang, M. L. Debnath, W. E. Klunk, *J. Med. Chem.* 2003, **46**, 2740.
- 3 SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.
- 4 W. T. Pennington, *J. Appl. Crystallogr.* 1999, **32**, 1028.

Tables and Figures

Table S1. Solid-state fluorescence lifetime data of the samples in different conditions

	τ_1 (ns) ^a	A_1 ^b	τ_2 (ns) ^a	A_2 ^b	τ_3 (ns) ^a	A_3 ^b	$\langle\tau\rangle$ (ns) ^c
B ₁	0.90	0.98	1.71	0.02	—	—	0.92
G ₁	0.53	0.69	1.42	0.28	3.01	0.03	0.85
Y _{fa1}	0.96	0.29	2.28	0.57	3.95	0.14	2.13
O _{fa1}	0.87	0.52	2.19	0.44	8.07	0.04	1.74

^a Fluorescence lifetime, ^b fractional contribution, ^c weighted mean lifetime; (B₁) as-prepared sample; (G₁) ground sample; (Y_{fa1}) B₁ in the vapors of HCl for 10 min; (O_{fa1}) G₁ in the vapors of HCl for 10 min.

Table S2. Crystal data and structure refinement for the three single crystals

compound	T1	T2	T3
formula	C ₃₃ H ₂₃ NOS	C ₃₃ H ₂₄ NOSCl	C ₄₁ H ₄₀ NO ₃ SCl
fw	481.58	518.05	662.26
crystal system,	monoclinic	monoclinic	monoclinic
<i>T</i> (K)	153(2)	153(2)	150(2)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	23.642(3)	21.1014(11)	25.4332(6)
<i>b</i> /Å	5.7597(6)	9.2666(6)	13.2344(3)
<i>c</i> /Å	19.018(3)	13.5115(7)	10.6949(3)
α /°	90	90	90
β /°	105.496(3)	100.062(1)	96.568(2)
γ /°	90	90	90
<i>V</i> /Å ³ , <i>Z</i>	2495.6(5), 4	2601.4(3), 4	3576.2(2), 4
<i>F</i> (000)	1008	1080	1400
crystal size / mm ³	0.37×0.21×0.12	0.32×0.21×0.15	0.34×0.22×0.14
reflections collected / unique (<i>R</i> _{int})	14896/5666 (<i>R</i> _{int} = 0.0396)	16944/5839 (<i>R</i> _{int} = 0.0526)	12877/6204 (<i>R</i> _{int} = 0.0395)
obsd reflns [<i>I</i> ≥2σ(<i>I</i>)]	4052	4205	4787
data/restraints/parameter	5666/0/329	5839/0/338	6204/0/429
<i>D</i> _c / Mg·m ⁻³	1.282	1.323	1.230
μ / mm ⁻¹	0.157	0.255	1.790
goodness-of-fit on <i>F</i> ²	1.055	1.090	1.070
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> ≥2σ(<i>I</i>)]	0.0505, 0.1264	0.0598, 0.1448	0.0727, 0.1999
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0714, 0.1393	0.0838, 0.1597	0.0922, 0.2171

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}, \text{ where } w = 1/[^2(F_o)^2 + (aP)^2 + bP] \text{ and } P = (F_o^2 + 2F_c^2)/3.$$

Table S3. Summary of the supramolecular interactions in the three crystals

Single crystal	Orientation of interaction		d (Å) ^a	A (°) ^b
T1	I	BT ^c →BT	3.639(2)	--
	II	O-H→Ben ^d	2.606(3)	138(2)
	III	C-H···O	2.670(1)	136.6(1)
	IV	C-H→BT	2.953(1)	118.9(1)
	V	C-H→Ben	3.009(1)	159.1(1)
	VI	C-H→Ben	3.172(1)	149.9(1)
	VII	C-H···O	2.416(1)	133.5(1)
T2	I	BT→BT	3.771(1)	--
	II	O-H···Cl ⁻	2.034(3)	166(4)
	III	N-H···Cl ⁻	2.202(2)	145.7(3)
T3	I	N-H···Cl ⁻	2.13(5)	167(4)
	II	O-H···Cl ⁻	2.201(1)	170.6(2)
	III	C-H···Cl ⁻	2.929(1)	133.6(2)
	IV	C-H···O	2.487(6)	141.1(3)
	V	C-H···O	2.588(5)	146.0(3)
	VI	C-H···O	2.667(3)	165.3(4)

^a Distance of the ring→ring, H→ring, O···H or the Cl⁻···H interaction. ^b angle of the O-H→ring, C-H→ring, C-H···O, O-H···Cl⁻, N-H···Cl⁻ or the C-H···Cl⁻ interaction. ^c benzothiazole. ^d benzene ring.

Table S4. Theoretical calculated frontier orbitals contribution in the three crystals

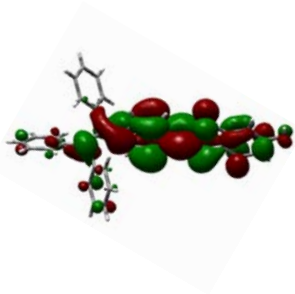
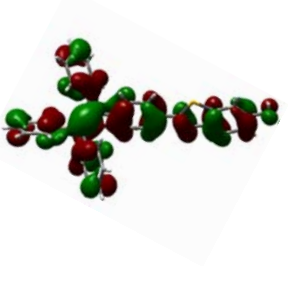
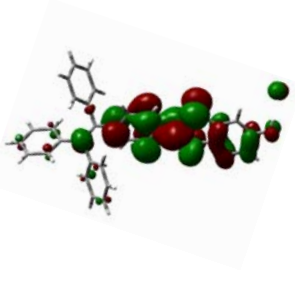
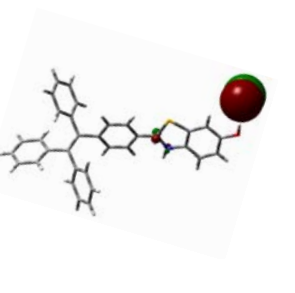
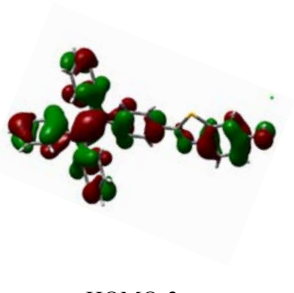
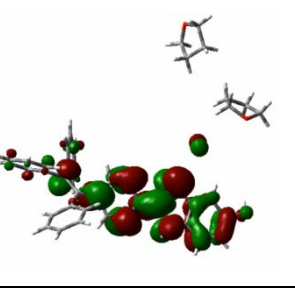
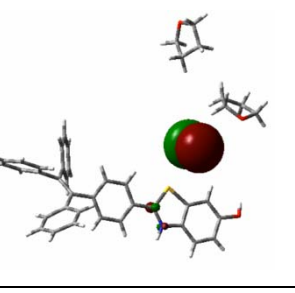
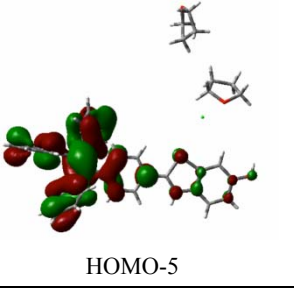
Single crystal	LUMO	HOMO	HOMO-n
T1			—
T2			
T3			

Table S5. Dihedral angles of the selected planes of the molecules in single crystals and free molecule

Plane	A ^a -B ^a	A-D ^a	C ^a -D	D-E ^a
Free molecule ^b	76.2	58.7	75.3	0.7
Molecule in T1	82.2	67.5	80.3	3.6
Molecule in T2	68.5	60.6	78.5	14.6
Molecule in T3	77.2	58.9	71.7	4.7

^a Planes of A, B, C, D, and E were shown in Fig. S6; ^b Geometry from calculation using Gaussian 03

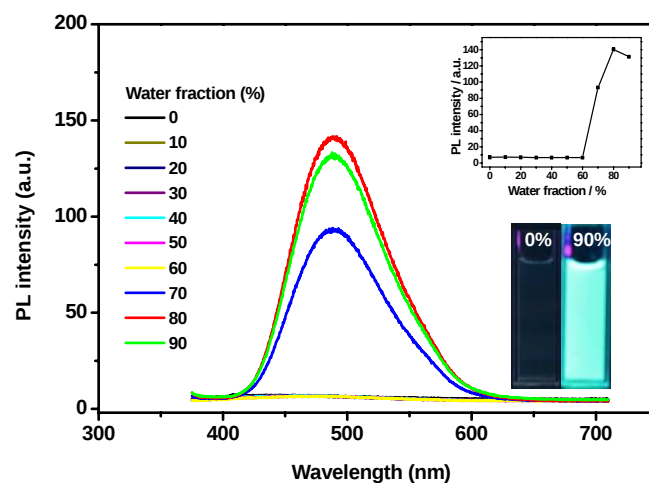


Fig. S1 PL spectra of the dilute solutions of TPENSOH in water/ethanol mixtures with different water fractions (concentration: 10 μ M; excitation wavelength: 365 nm). The insets depict the changes in PL peak intensity (up) and emission images of TPENSOH in pure ethanol and water/ethanol (9:1, v/v) under 365 nm UV illumination (down).

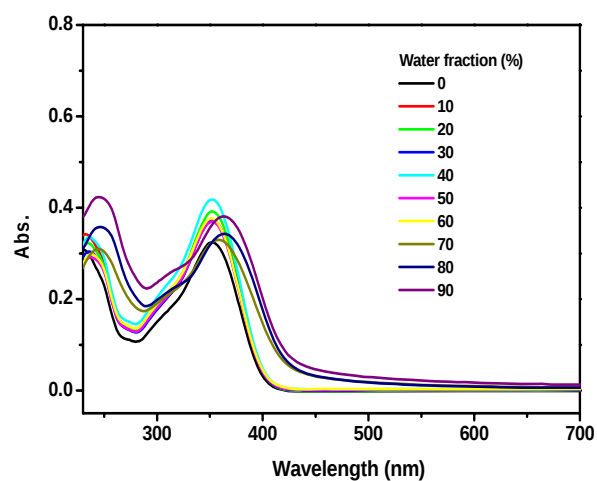


Fig. S2 UV-visible spectra of the dilute solutions of TPENSOH in water/ethanol mixtures with different water fractions (concentration: 10 μ M).

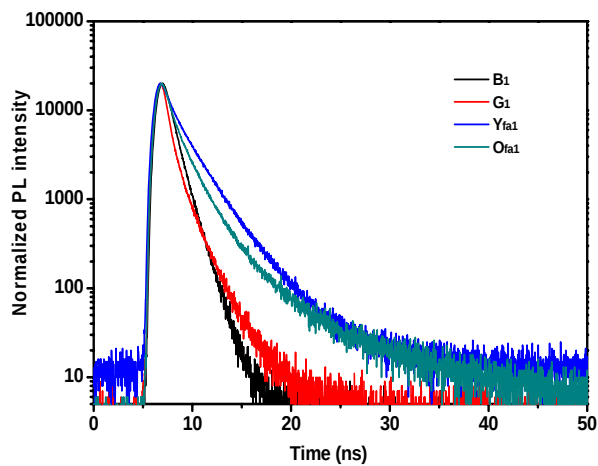


Fig. S3 Time-resolved emission decay curves of the samples: (B_1) as-prepared sample; (G_1) ground sample; (Y_{fa1}) B_1 in the vapors of HCl for 10 min; (O_{fa1}) G_1 in the vapors of HCl for 10 min.

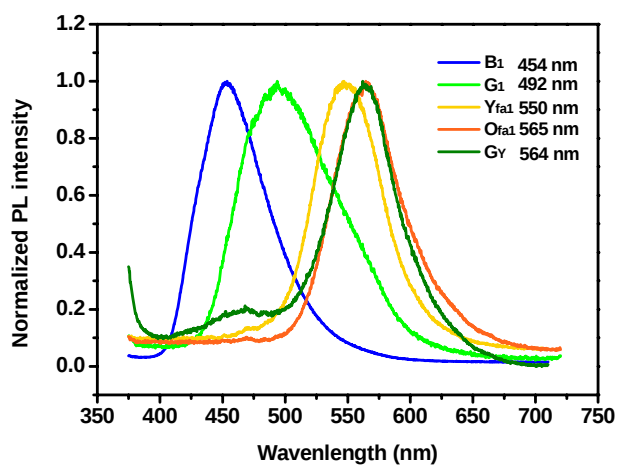


Fig. S4 PL spectra of the powders treated by different stimuli: (B_1) as-prepared TPENSOH; (G_1) ground sample from B_1 ; (Y_{fa1}) B_1 in the vapor of HCl for 10 min; (O_{fa1}) G_1 in the vapor of HCl for 10 min; (G_Y) ground sample from Y_{fa1} .

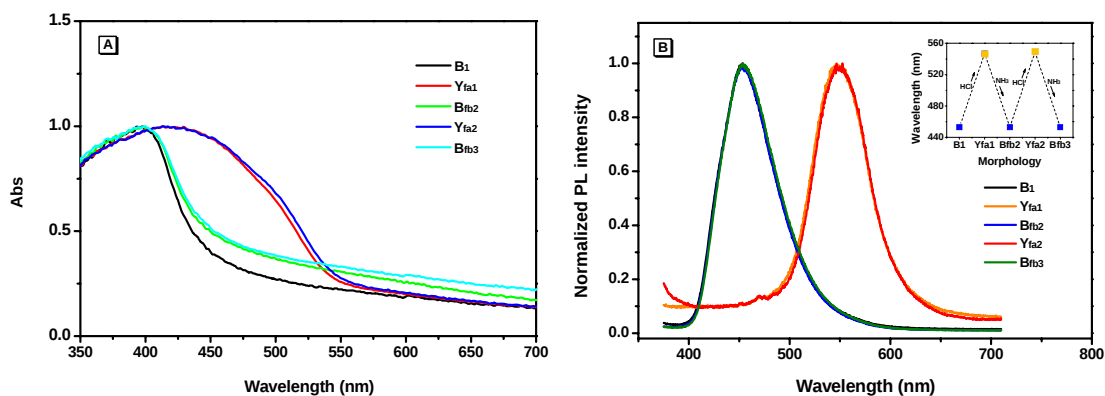


Fig. S5 UV-visible curves (A) and normalized PL spectra (B) of pristine TPENSOH: (B_1) as-prepared sample; (Y_{fa1}) acid fumed sample (B_1 in the vapors of HCl for 10 min); (B_{fb2}) base fumed sample (Y_{fa1} in the vapors of NH_3 for 10 min.); (Y_{fa2}) acid re-fumed sample; (B_{fb3}) base re-fumed sample. The inset depicts the reversibility of the PL wavelengths of pristine TPENSOH by the treatment of fuming in the vapors of HCl or NH_3 .

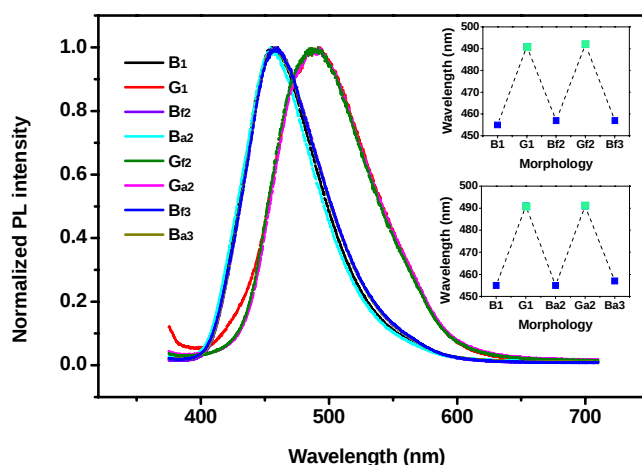


Fig. S6 Normalized PL curves of TPENSOH powders: (B_1) as-prepared sample; (G_1) ground sample; (B_{f2}) fumed sample (ground sample in dichloromethane vapors for 10 min.); (B_{a2}) annealed sample (ground sample in homoiothermal at 200 °C for 10 min, and then, cooled down to room temperature.); (G_{f2}) re-ground sample from B_{f2} ; (G_{a2}) re-ground sample from B_{a2} ; (B_{f3}) re-fumed sample from G_{f2} ; (B_{a3}) re-annealed sample from G_{a2} . The insets depict the reversibility of the PL wavelengths of TPENSOH powders: by grinding and fuming treatments (up); and by grinding and annealing treatments (down).

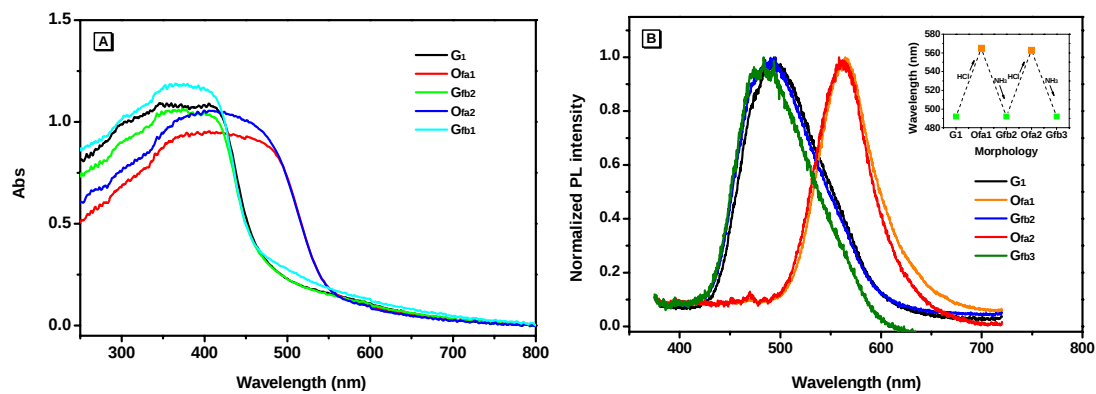


Fig. S7 UV-visible curves (A) and normalized PL spectra (B) of ground TPENSOH: (G_1) ground sample; (O_{fa1}) acid fumed sample (G_1 in the vapors of HCl for 10 min); (G_{fb2}) base fumed sample (O_{fa1} in the vapors of NH₃ for 10 min.); (O_{fa2}) acid re-fumed sample from G_{fb2} ; (G_{fb3}) base re-fumed sample from O_{fa2} . The inset depicts the reversibility of the PL wavelengths of ground TPENSOH by the treatment of fuming in the vapors of HCl or NH₃.

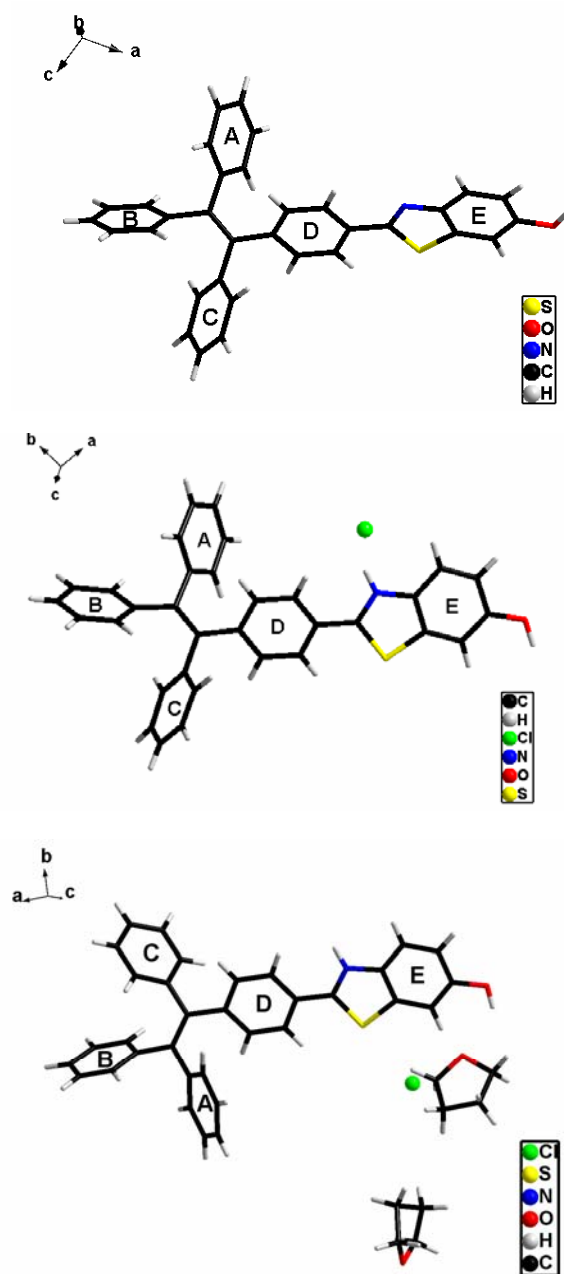


Fig. S8 Chemical structures of the three crystals of **T1** (upper), **T2** (middle) and **T3** (bottom).

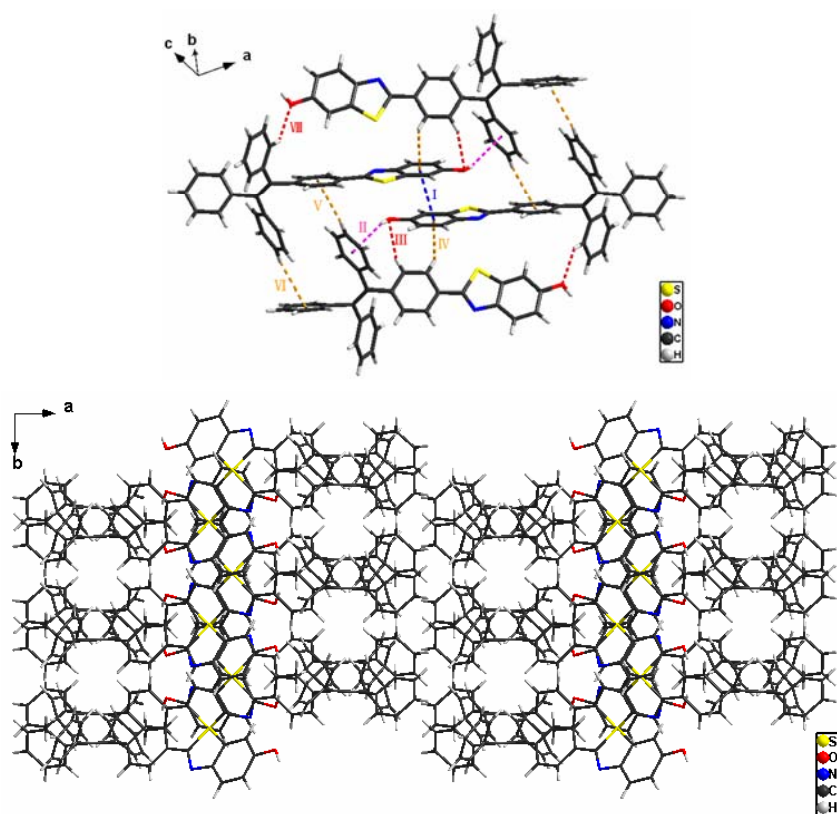


Fig. S9 Aggregating state of molecules in **T1**.

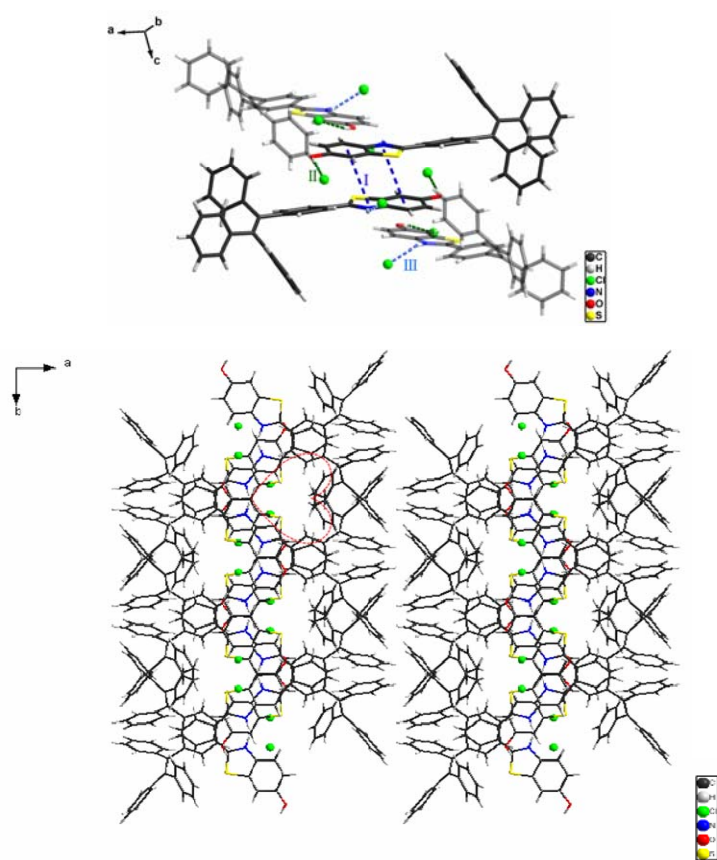


Fig. S10 Aggregating state of molecules in **T2**.

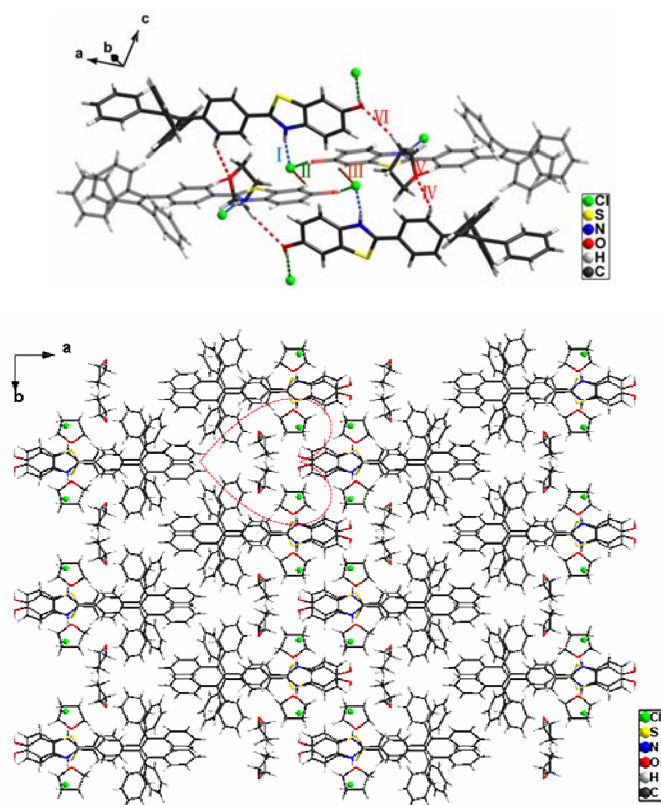


Fig. S11 Aggregating state of molecules in T3.

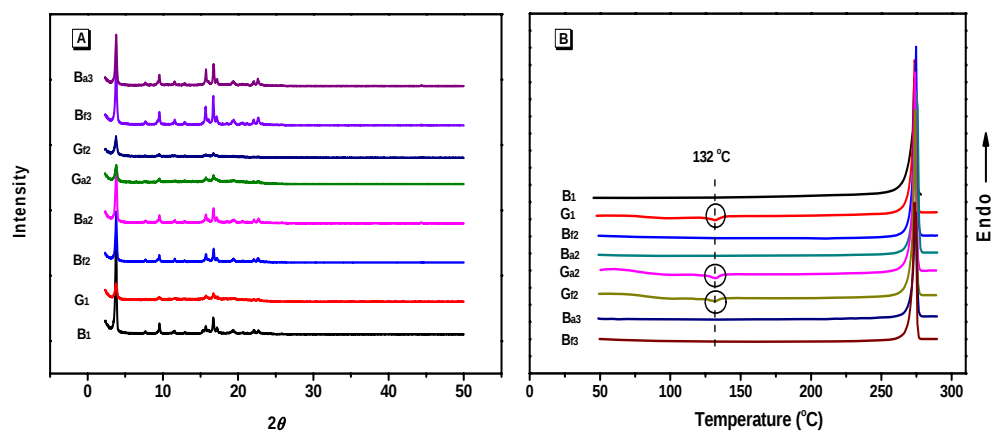


Fig. S12 A) Powder WXR D patterns and B) DSC curves of TPENSOH in different morphologies: (B₁) as-prepared sample; (G₁) ground sample; (B_{f2}) fumed sample (ground sample in dichloromethane vapors for 10 min.); (B_{a2}) annealed sample (ground sample in homoiothermal at 200 °C for 10 min, and then, cooled down to room temperature.); (G_{f2}) re-ground sample from B_{f2}; (G_{a2}) re-ground sample from B_{a2}; (B_{f3}) re-fumed sample from G_{f2}; (B_{a3}) re-annealed sample from G_{a2}.

Structure Information

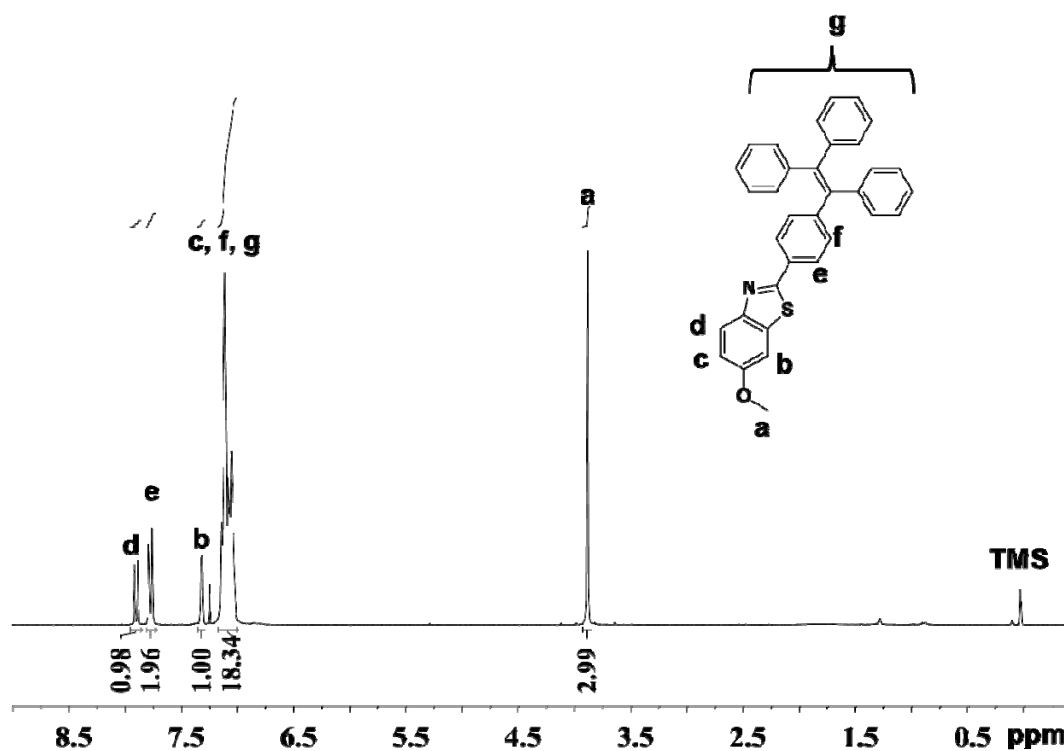


Fig. S13 ¹H NMR spectrum of TPENSOH.

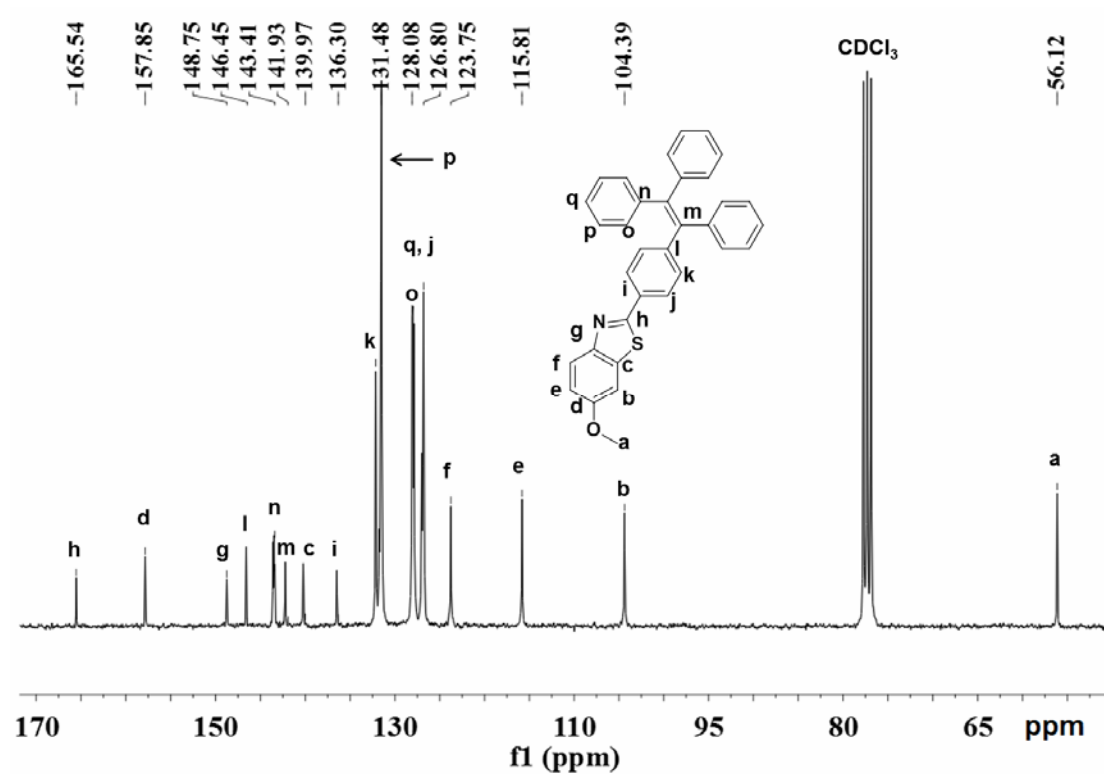


Fig. S14 ^{13}C NMR spectrum of TPENSOM.

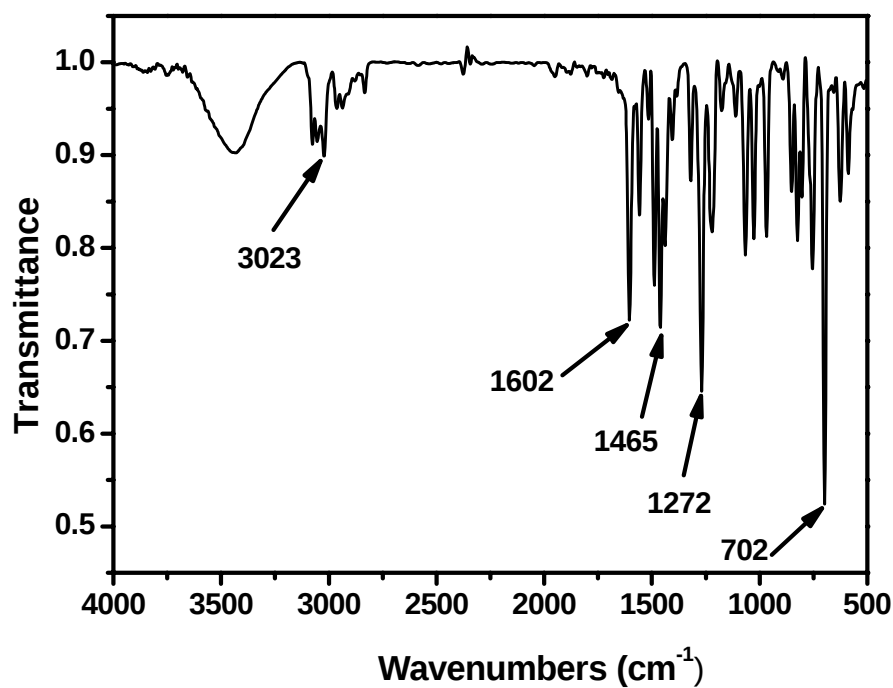


Fig. S15 FT-IR spectrum of TPENSOM.

052305 #65 RT: 1.68 AV: 1 NL: 5.45E4
 T: + c Full ms [45.00-800.00]

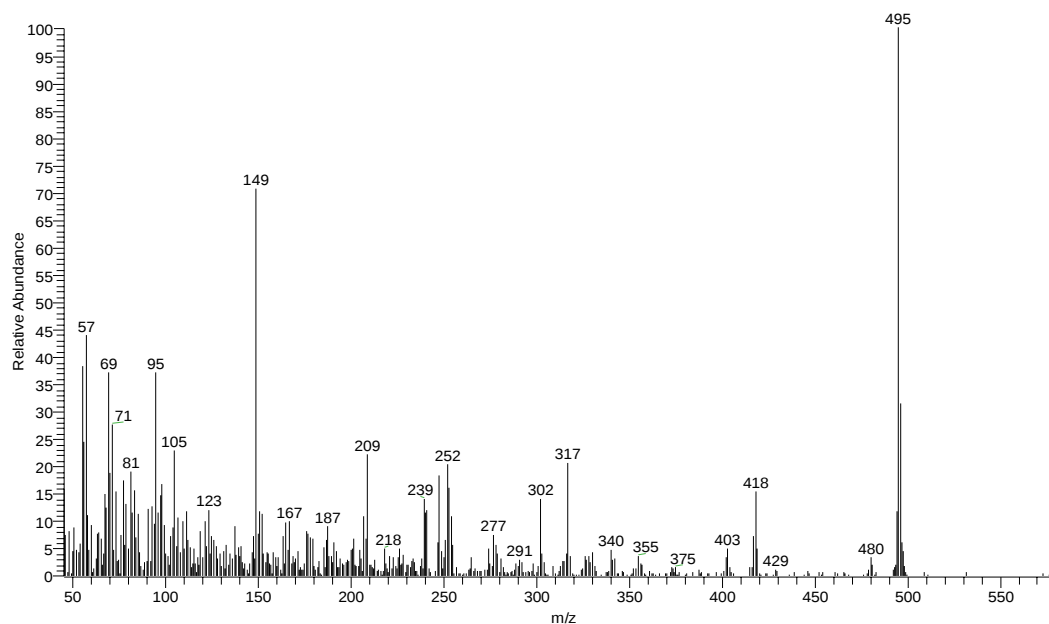


Fig. S16 EI-MS spectrum of TPENSOM.

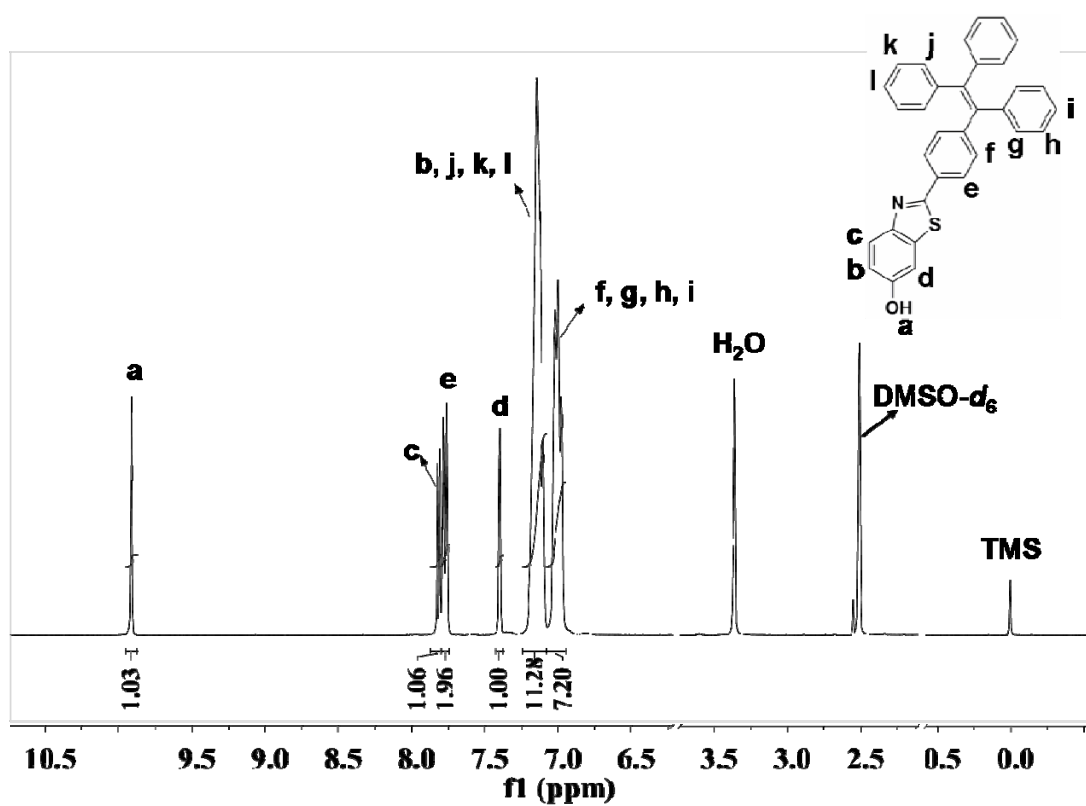


Fig. S17 ¹H NMR spectrum of TPENSOH.

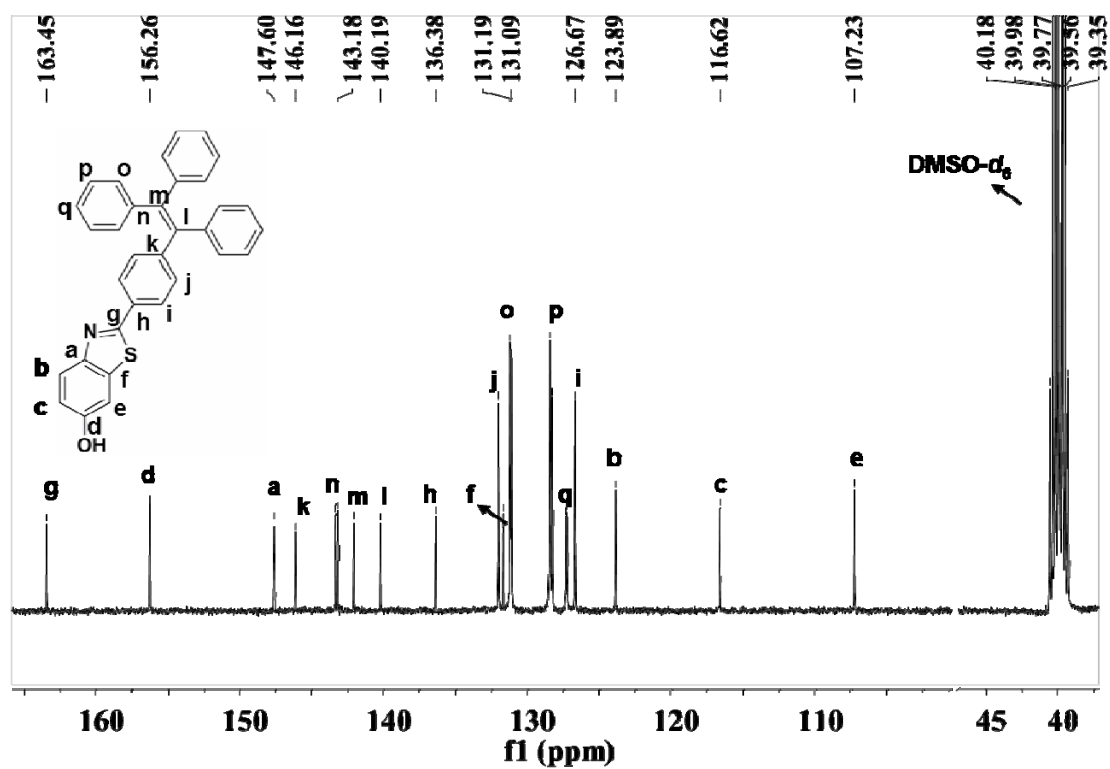


Fig. S18 ^{13}C NMR spectrum of **TPENSOH**.

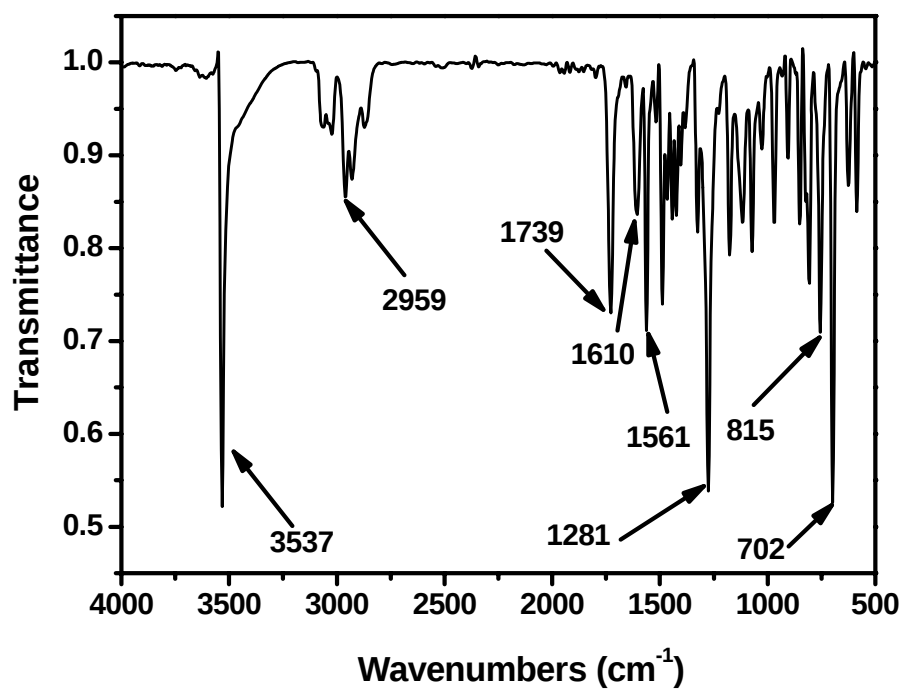


Fig. S19 FT-IR spectrum of **TPENSOH**.

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T: + c Full ms [45.00-800.00]

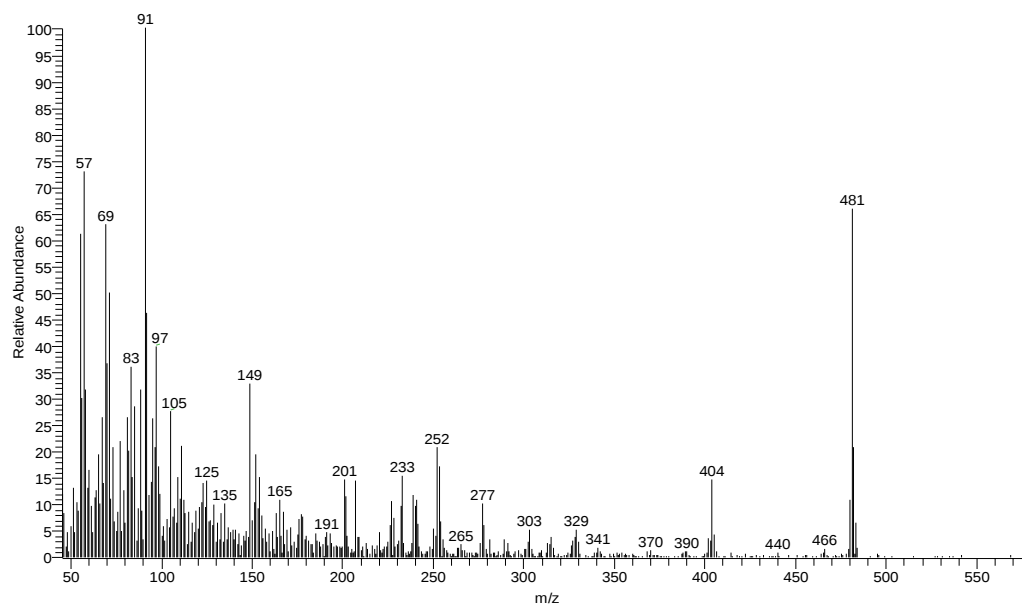


Fig. S20 EI-MS spectrum of **TPENSOH**.