Supporting information for

Enhanced Emission under Proton Stimuli Based on Phenanthroimidazole Derivative by Switching of Excited State type from CT to LE State

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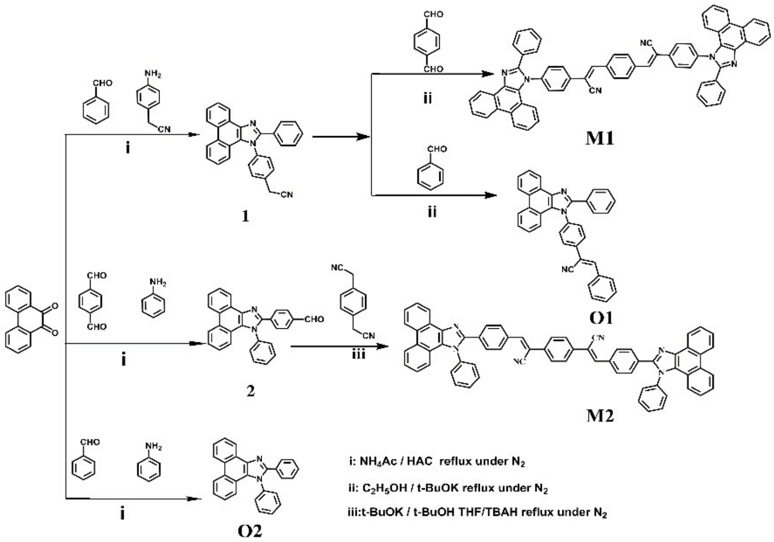
Materials and Instruments

All solvents and chemicals were purchased from Alfa Aesar or TCI and used without further purification. The reactions were performed under a dry nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-600 MHz spectrometer, using DMSO-d$_6$ as solvent and tetramethyl-silane (TMS) as internal standard. Absorption spectra were recorded using a Cary 50 Bio UV-visible spectrometer with samples in solution and a quartz cuvette (path length 1 cm). The steady state photoluminescence (PL) curves were measured with Edinburgh Instruments FLS980 and the time-resolved photoluminescence (TRPL) decay curves were measured under the excitation of a hydrogen flash lamp with the wavelength at 377 nm (nF 920, Edinburgh Instruments). Absolute fluorescence quantum yields in solid powder state ($\Phi_{F)}$ were determined using an integrating sphere on Edinburgh Instruments of FLS 980. The powder X-ray diffraction (PXRD) patterns were recorded on Rigaku Ultima IV with the 2θ range from 2° to 50°. The single crystal structure was measured on Bruker D8 Venture X-ray diffraction on a CCD detector using graphite-monochromated Mo K*a* radiation. Dynamic Light Scattering measurement were measured using Malvern Mastersizer. The electron spin resonance spectra were measured on electronic paramagnetic resonance spectrometer (EMXPLUS10/12, Bruker).

Theoretical calculation

The initial geometry of isolated M1 molecule was derived from the corresponding single-crystal structures. The ground state (S0) structures of both isolated and protonated molecules were optimized at the B3LYP/6-31g* level. The absorption spectra based on S0 state and the emission spectra based on optimized excited state were calculated at TD/B3LYP level. All calculations included density functional dispersion correction using BJ-damping (DFT-D3 (BJ)) and were performed using the Gaussian 16 program package.



Scheme S1 Synthetic routes and chemical structure of the target molecules (M1, M2, O1 and O2) in this paper.

Synthetic procedure

2-(4-(2-phenyl-1H-phenanthro[9,10-d]imidazol-1-yl)phenyl)acetonitrile (1)

The product was prepared by refluxing 9, 10-phenanthrenequinone (1.04 g, 5 mmol), benzaldehyde (1.14 g, 6 mmol), 2-(4-amino-phenyl) acetonitrile (0.793 g, 6 mmol) and ammonium acetate (4.9 g) in glacial acetic acid (60 mL) for 24 hours under an argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water, stirring for several minutes. The result mixture was filtered off, and the separated solid was washed with water and ethanol. The solid was purified by column chromatography (petroleum ether: CH_2Cl_2, 3:1) on silica gel, giving a pale milky solid finally. ^{1}HNMR (600 MHz, DMSO) δ 8.95 (d, J = 8.1 Hz, 1H), 8.89 (d, J = 8.2 Hz, 1H), 8.69 (d, J = 7.6 Hz, 1H), 7.77 (dd, J = 20.0, 7.8 Hz, 3H), 7.72 – 7.68 (m, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.2 Hz, 3H), 7.37 (dd, J = 14.9, 7.5 Hz, 4H), 7.10 (d, J = 8.3 Hz, 1H), 4.29 (s, 2H). ^{13}C NMR (151 MHz, DMSO) δ 151.27 (s), 137.97 (s), 136.98 (s), 133.89 (s), 130.68 (s), 130.38 (s), 130.21 (s), 129.72 (s), 129.56 (s), 128.98 (s), 128.73(s), 128.16 (d, J = 4.6 Hz), 127.99 (s), 127.17 (s), 126.28 (s), 125.75 (s),125.05 (s), 124.17 (s), 122.92 (s), 122.49(s), 120.58 (s), 119.50 (s), 22.77 (s). MS (ESI$^+$): m/z 410.1652 (MH$^+$), Calc. 409.1832.

4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)benzaldehyde (2)

The compound 2 was prepared with the similar procedure as that of the compound 1. ^{1}H NMR (600 MHz, DMSO) δ 10.00 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 8.90 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.83 – 7.67 (m, 9H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 193.10 (s), 149.67 (s), 138.38 (s), 137.23 (s), 136.24 (s), 136.02 (s), 130.98 (s), 130.02 (s), 129.70 (s), 129.57 (s), 129.26 (s), 128.75 (s), 128.29 (s), 128.09 (s), 127.23 (s), 127.06 (s), 126.50 (s), 126.07 (s), 125.06 (s), 124.22 (s), 122.84 (s), 122.52 (s), 120.83 (s).

（2Z,2'Z)-3,3'-(1,4-phenylene)bis(2-(4-(2-phenyl-1H-phenanthro[9,10-d]imidazol-1-yl)phenyl)acrylonitrile) (M1)

Compounds of 1 (0.205 g, 0.5 mmol) and terephthalaldehyde (0.034 g, 0.25 mmol) were dissolved in ethanol (20 mL) at 80 ℃, and the *t*-BuOK (0.11 g, 1.0 mmol) was added to the mixture solution subsequently. The reaction was monitored by TLC. After termination of reaction, the mixture was filtered and washed with ethanol. The obtained solid was purified by column chromatography (petroleum ether: CH_2Cl_2, 2:1) on silica gel, dried in vacuum and give a yellow solid.^{1}H NMR (600 MHz, DMSO) δ 8.97 (d, *J* = 7.6 Hz, 2H), 8.91 (d, *J* = 7.4 Hz, 2H), 8.71 (d, *J* = 7.4 Hz, 2H), 8.41 (s, 2H), 8.19 (s, 4H), 8.12 (d, *J* = 7.2 Hz, 4H), 7.92 (d, *J* = 7.3 Hz, 4H), 7.79 (d, *J* = 6.4 Hz, 2H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.61 (d, *J* = 15.8 Hz, 6H), 7.42 (s, 8H), 7.22 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 162.77 (s), 151.25 (s), 143.85 (s), 139.44 (s), 137.10 (s), 136.17 (s), 135.39 (s), 130.62 (s), 130.31 (s), 129.78 (s), 129.70 (d, *J* = 22.5 Hz), 129.02 (s), 128.80 (s), 128.30 – 127.80 (m), 127.35 (s), 127.14 (s), 126.32 (s), 125.81 (s), 125.06 (s), 124.17 (s), 122.88 (s), 122.53 (s), 120.73 (s), 118.02 (s), 111.09 (s). MS (ESI$^+$): m/z 917.3376 (MH$^+$), Calc.916.3314.

(Z)-3-phenyl-2-(4-(2-phenyl-1H-phenanthro[9,10-d]imidazol-1-yl)phenyl)acrylonitrile (O1)

O1 was prepared with the similar procedure as that of M1. ^{1}H NMR (600 MHz, DMSO) δ 8.96 (d, *J* = 7.9 Hz, 1H), 8.90 (d, *J* = 8.0 Hz, 1H), 8.70 (d, *J* = 7.4 Hz, 1H), 8.33 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 6.9 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.79 (t, *J* = 6.6 Hz, 1H), 7.71 (t, *J* = 6.9 Hz, 1H), 7.64 – 7.53 (m, 6H), 7.41 (d, *J* = 12.1 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR

(151 MHz, DMSO) δ 162.77 (s), 151.25 (s), 143.85 (s), 139.44 (s), 137.10 (s), 136.17 (s), 135.39 (s), 130.62 (s), 130.31 (s), 129.78 (s), 129.70 (d, J = 22.5 Hz), 129.02 (s), 128.80 (s), 128.30 – 127.80 (m), 127.35 (s), 127.14 (s), 126.32 (s), 125.81 (s), 125.06 (s), 124.17 (s), 122.88 (s), 122.53 (s), 120.73 (s), 118.02 (s), 111.09 (s).MS (ESI$^+$): m/z 498.1962 (MH$^+$), Calc. 497.1892.

1,2-diphenyl-1H-phenanthro[9,10-d]imidazole (O2)

O_2 was synthesized with similar procedure as sample **1**. 1H NMR (600 MHz, DMSO) δ 8.94 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H), 8.69 (d, J = 7.9 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.70 (dd, J = 14.4, 6.4 Hz, 6H), 7.61 – 7.53 (m, 3H), 7.41 – 7.31 (m, 4H), 7.08 (d, J = 8.3 Hz, 1H).

(2Z,2’Z)-2,2'-(1,4-phenylene)bis(3-(4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)acrylonitrile) (M2)

Compounds of **2** (0.2 g, 0.5 mmol) and 2,2'-(1,4-phenylene) diacetonitrile (0.04 g, 0.25 mmol) were dissolved in mixture solution of tert-butanol (5 mL) and THF (5 mL). The mixture was heated to 46 ^{o}C and stirred for one hour. After then, mixture of potassium *tert*-butoxide (1 M solution in tetrahydrofuran, 0.25 mL) and tetrabutylammonium hydroxide (TBAH, 1 M solution in methanol, 0.25 mL) were added drop by drop, and the mixture was continuous stirred and monitored using the TLC plate to ensure the reaction completely. The orange resulting precipitate was collected by filtering and washing with methanol and then purified by column chromatography using dichloromethane as eluent to give an orange yellow powder (200 mg). ^{1}H NMR (600 MHz, DMSO) δ 8.92 (d, J = 8.5 Hz, 2H), 8.87 (d, J = 8.5 Hz, 2H), 8.70 (d, J = 7.9 Hz, 2H), 8.13 (s, 2H), 7.92 (d, J = 8.3 Hz, 4H), 7.89 (s, 2H), 7.80 – 7.66 (m, 20H), 7.56 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 167.47 (s), 149.99 (s), 138.47 (d, J = 14.2 Hz), 137.19 (s), 132.13 (d, J = 10.7 Hz), 131.02 (s), 129.89 (d, J = 37.9 Hz), 129.89 (d, J = 37.9 Hz), 129.63 (dd, J = 77.6, 55.5 Hz), 128.29 (s), 128.07 (s), 127.22 (s), 127.08 (s), 126.44 (s), 125.99 (s), 125.05 (s), 124.23 (s), 122.53 (s), 120.77 (s), 118.06 (s). MS (ESI$^+$): m/z 917.3389 (MH$^+$), Calc.916.3314.

Table S1 Summarized data of photo-physical properties for M1, M2, O1 and O2 at original state, TFA fumed state and recovery state.

Samples	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	τ_1Rel.%	τ_2Rel.%	τ_3Rel.%	χ^2	τ(ns)	Φ_F(%)	Kr (s^{-1})	Knr (s^{-1})
M1 (Original)	583	4.54	22.91	74.55	10.87	38.31	50.82	1.205	47.16	2.05	4.35×10^{5}	2.08×10^{7}
M1 (TFA fumed)	503	0.92	5.39		91.4	8.6		0.662	1.30	7.53	5.02×10^{7}	7.11×10^{8}
M1 (NH_3 recovery)	582	1.22	15.08	51.99	8.98	32.64	58.37	1.092	35.38	2.64	7.46×10^{5}	2.75×10^{7}
M2 (Original)	605	2.32	11.04		70.02	29.98		1.128	4.93	12.13	2.46×10^{7}	1.78×10^{8}
M2 (TFA fumed)	547	0.96	3.11		85.85	14.15		0.861	1.26	15.84	1.26×10^{8}	6.68×10^{8}
M2(NH_3 recovery)	600	1.70	8.39		69.0	31.0		1.198	3.77	7.56	2.00×10^{7}	2.45×10^{8}
O1 (Original)	482	3.83	21.98		56.24	43.76		1.146	11.77	3.33	2.83×10^{6}	8.21×10^{7}
O1 (TFA fumed)	438	0.56	4.33		89.51	10.49		1.213	0.96	8.53	8.89×10^{7}	9.53×10^{8}
O2 (Original)	395	1.07	7.27		2.22	97.78		0.886	7.13	76.55	1.08×10^{6}	3.29×10^{7}
O2 (TFA fumed)	413	2.09	9.87		77.76	22.24		1.091	3.82	46.52	1.22×10^{8}	1.4×10^{8}

Φ_F = fluorescence quantum yield determined using a calibrated integrating sphere,

τ = lifetime,

K_r = radiative transition rate constant ($K_r=\Phi_F/\tau$),

K_{nr} = nonradiative transition rate constant ($K_{nr}=(1-\Phi_F)/\tau$).

Table S2 Summarized data of AIE properties for M1, M2, O1, O2.

Sample	^{a}Abs$_{max}$ (nm)		^{b} Em$_{max}$ (nm)		$^{c}\Phi_{F(AIE)}$	
	0%	100%	0%	100%	0%	100%
M1	361,384	364,392	439	568	ND	5.81
M2	410	421	561	571	26.25	10.51
O1	316/360	320/365	386/620	493	ND	4.7
O2	312/360	318/370	372/387	374/392	52.92	47.33

[a] Maximum wavelength of absorption spectra in DMF/H_2O mixture with different water content;

[b] Maximum wavelength of emission spectra in DMF/H_2O mixture with different water content;

[d] fluorescent quantum yield in DMF/H_2O mixture with different water content;

Table S3 Summarized data of lifetime for the compounds in DMF/H_2O mixture with different water content of 0 % and 100 %.

Samples	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	τ_1Rel.%	τ_2Rel.%	τ_3Re%	χ2	τ(ns)
M1(0%)	439	0.50	6.49		62.31	37.69		0.596	2.76
M1(100%)	568	3.29	22.45	61.69	5.51	39.53	54.96	0.982	42.96
M2 (0%)	561	1.60	5.39		97.14	2.86		0.541	1.71
M2 (100%)	571	1.68	8.08		56.41	43.59		0.731	4.47
O1 (100%)	493	12.51	52.45		46.84	53.16		1.011	33.74
O2 (100%)	392	1.83	6.38		51.4	48.6		0.871	4.04

Table S4 Summarized data of lifetime for M1 at longer wavelength (L W) and short wavelength (S W) emission in THF solvent.

Samples	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	τ_1Rel.%	τ_2Rel.%	τ_3Rel.%	χ^2	τ(ns)
M1((L W)	612	1.43	5.30		0.88	0.12		0.88	1.89
M1(S W)	427	0.27	2.06		0.73	0.27		0.84	0.77
O1 (L W)	566	0.29	3.16		0.85	0.15		0.91	0.73
O1(S W)	404	1.39	4.87	9.86	0.19	0.37	0.44	1.14	0.38

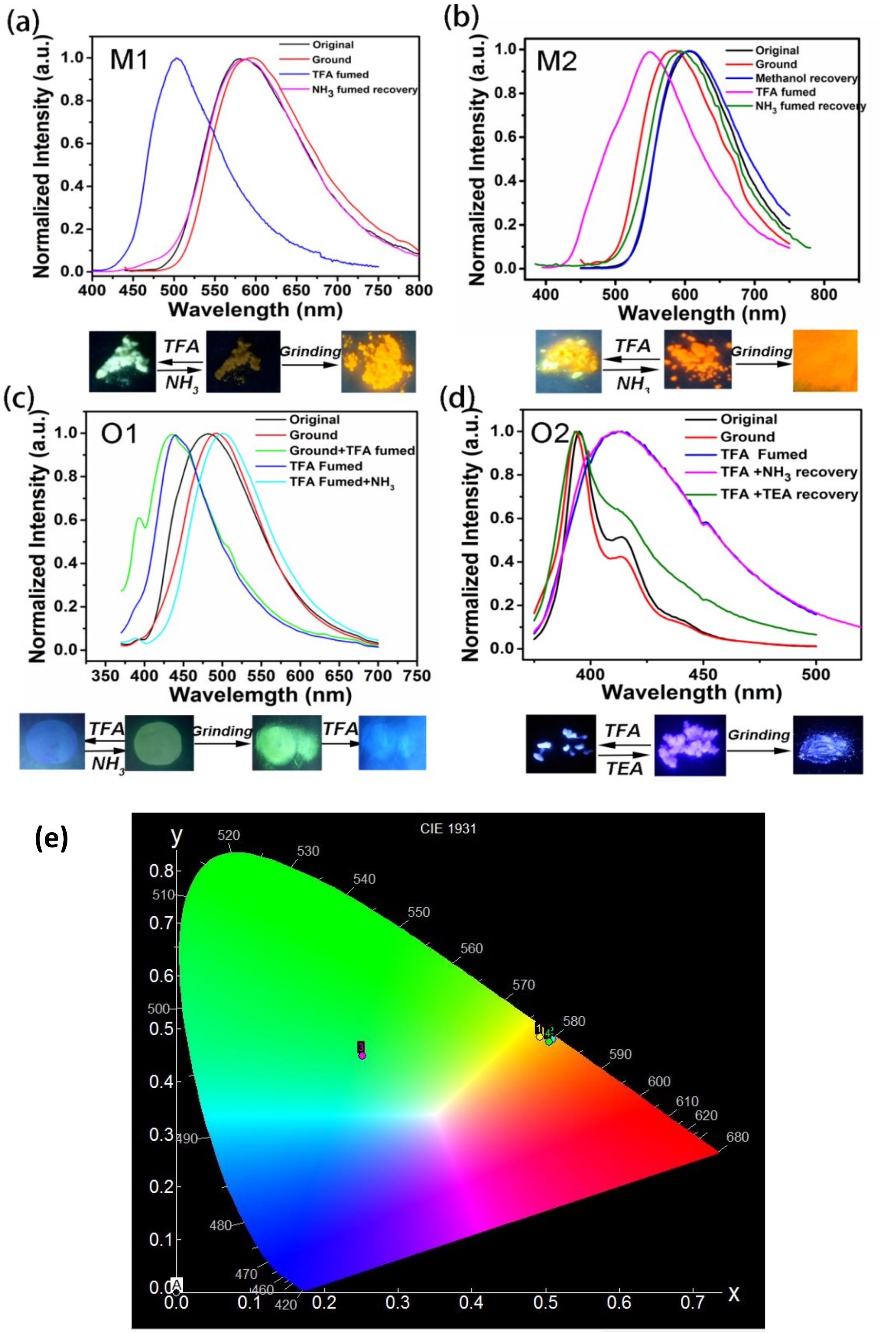


Fig.S1 (a-d) Solid state fluorescent spectra of **M1**, **M2**, **O1 and O2** in the original state, TFA fumed and ground state, respectively. The photographs are taken under 365 nm lamp excitation. (e) The CIE coordinates of M1 under different states corresponding for emission spectra in (a).

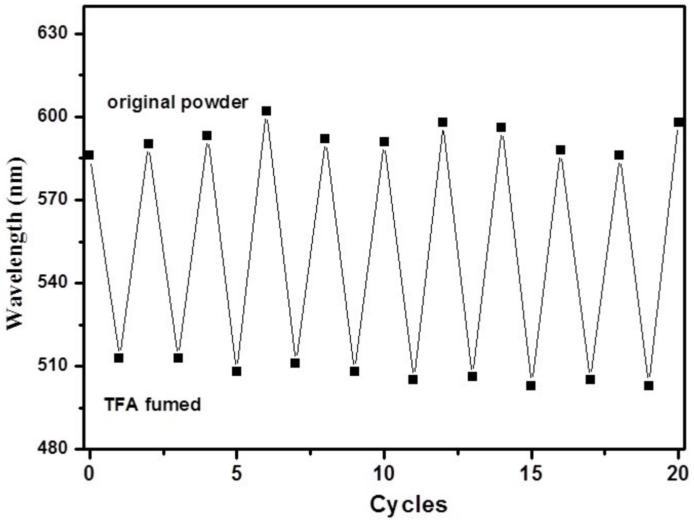


Fig.S2 Cycle experiments of solid powder state of M1 with TFA fumed and restoring.

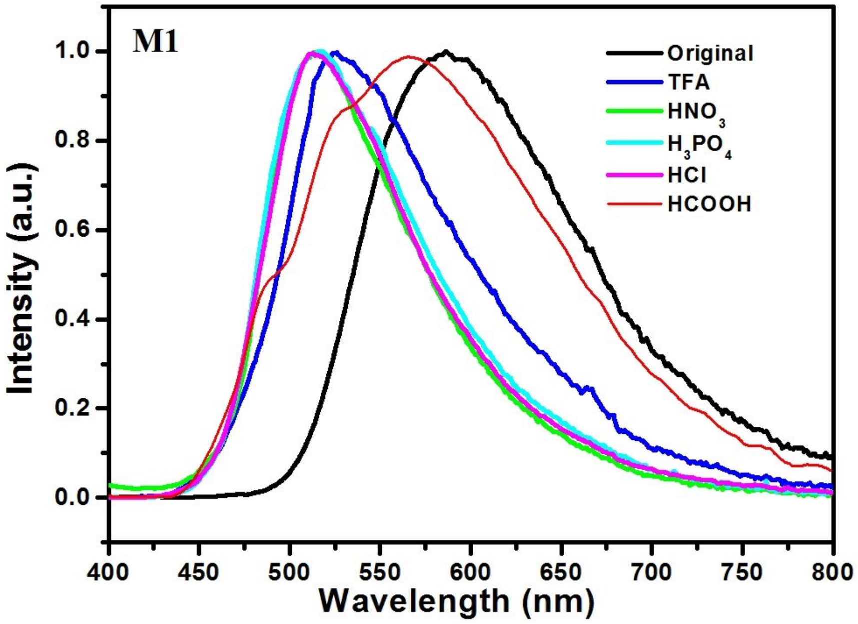


Fig.S3 Fluorescent spectra of solid state of M1 under different acid stimuli.

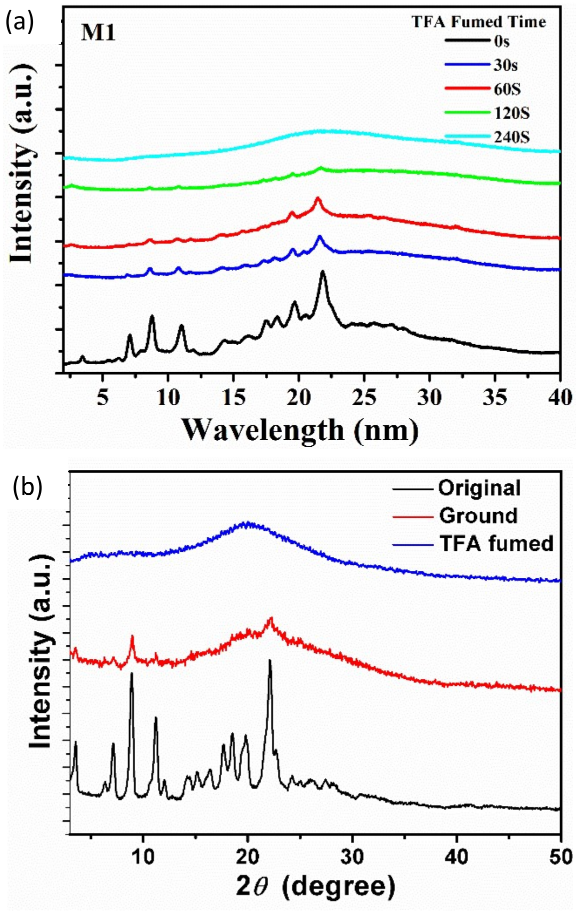


Fig.S4 PXRD of M1 (a) at original state, ground sample and TFA fumed sample; (b) with TFA fumed for increasing time.

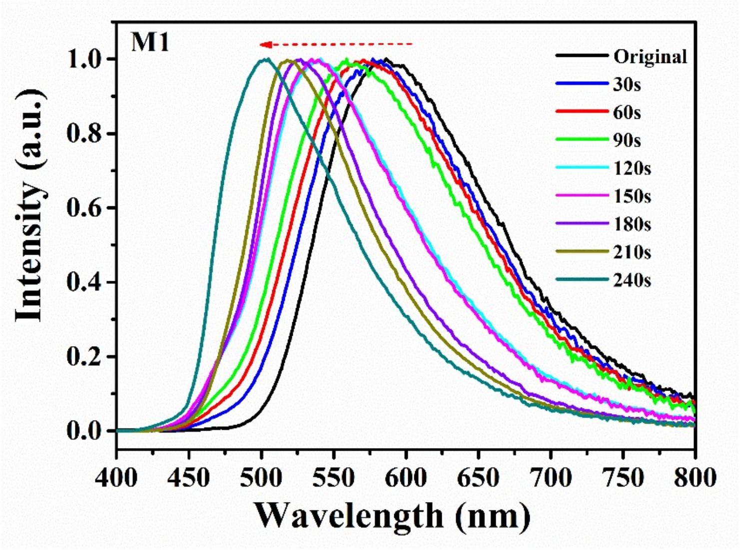


Fig.S5 Fluorescent spectrum of solid state M1 under TFA fuming with increasing time.

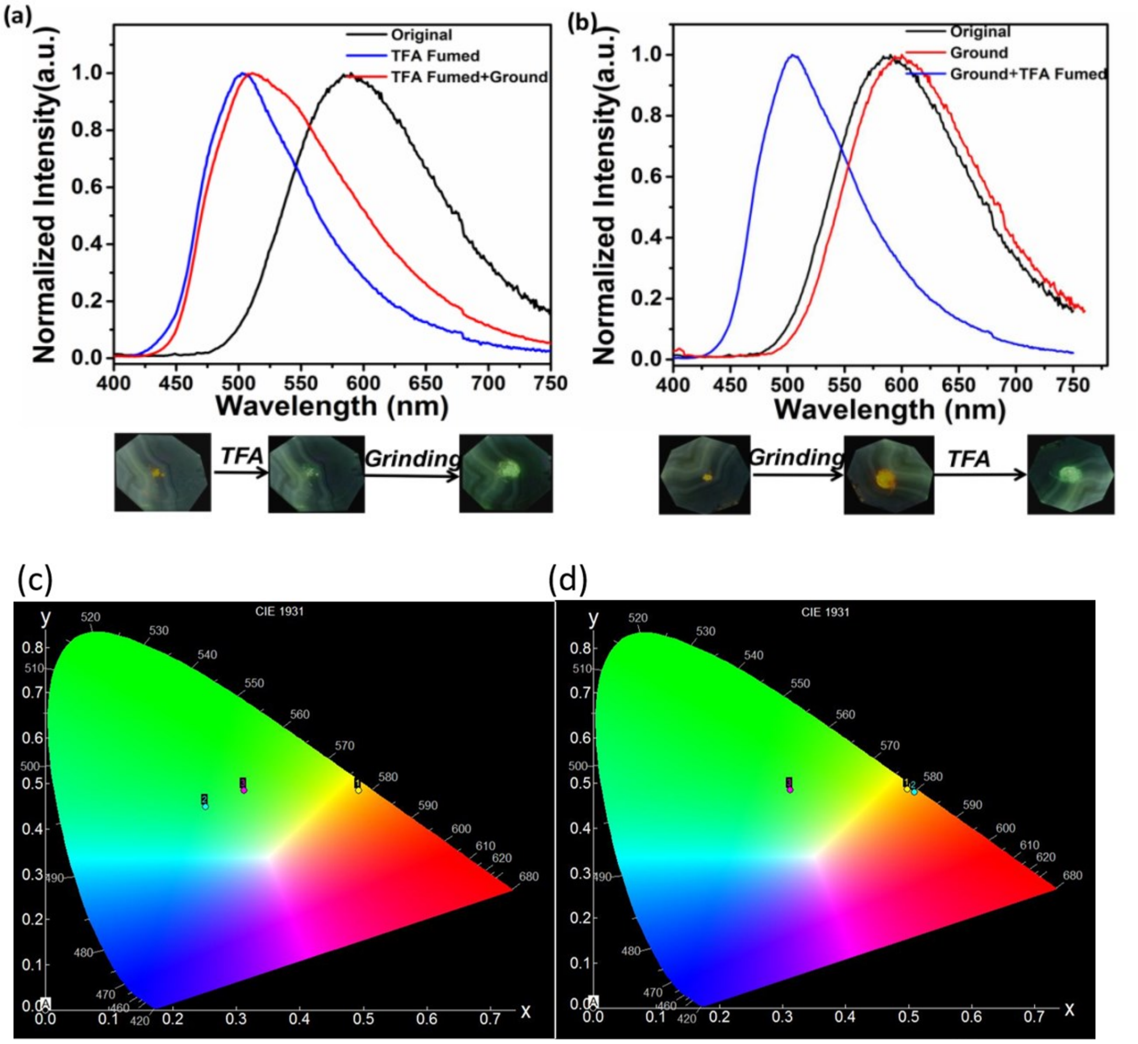
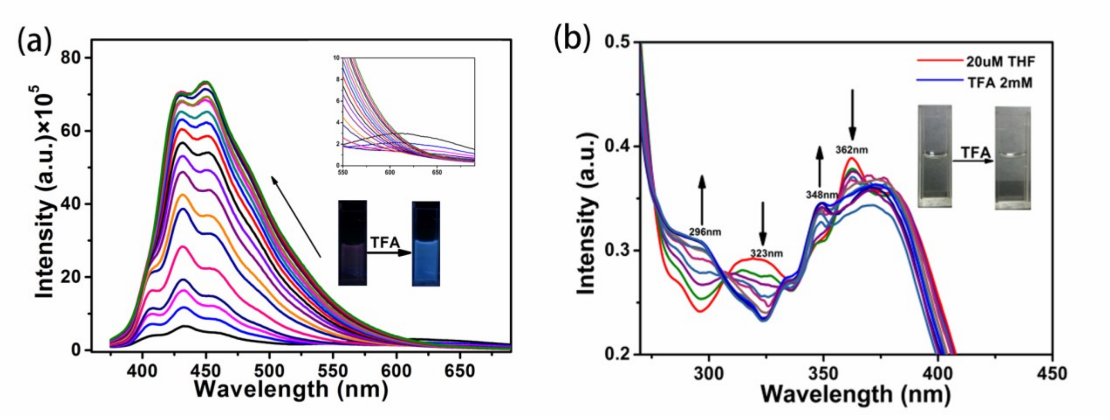


Fig.S6 Solid state emission spectra of M1 for: (a) original state and then TFA fumed and subsequently ground; (b) original state and then ground and subsequently TFA fumed. Inset photos are taken under 365 nm UV lamp excitation. (c) and (d) are CIE coordinates of corresponding emission spectra of M1 for (a) and (b), respectively.



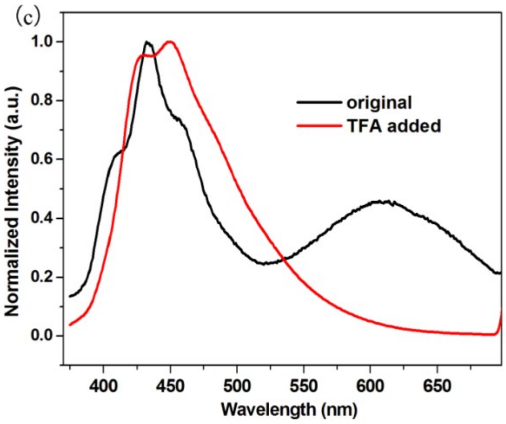


Fig.S7 (a) Fluorescence emission spectra and (b) UV–Vis absorption spectra of M1 in THF (1.0×10^{-5} M) upon different amounts of TFA (0–200 equiv) added; (c) Normalized emission spectra of M1 in original state and after protonation in THF solution. Inset: Photos of M1 in THF before and after addition of TFA under UV light and daylight, respectively.

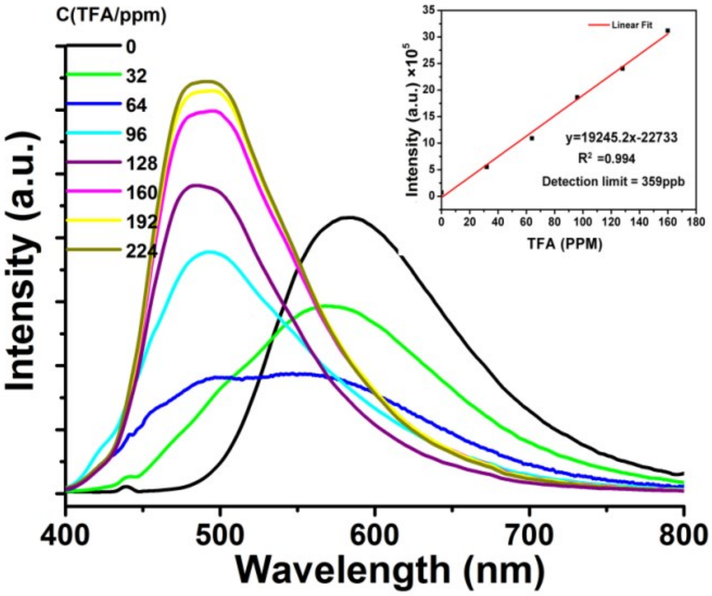


Fig.S8 Fluorescence emission spectra of the film of **M1** upon exposure to different amounts of TFA vapor (0–224 ppm) (λ_{ex}=360 nm).

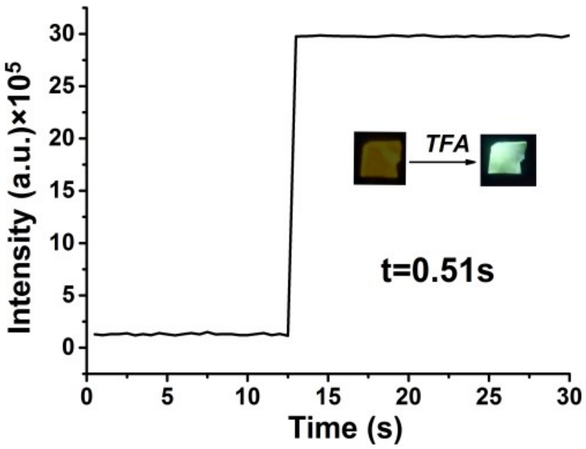


Fig.S9 Time course of fluorescence increasing of **M1** in the film (filter paper) upon exposure to TFA vapor at 224 ppm,and the intensity was monitored at 495 nm (λ_{ex}=360 nm). Inset: Photos of the film before and after exposed to the TFA vapor under UV light.

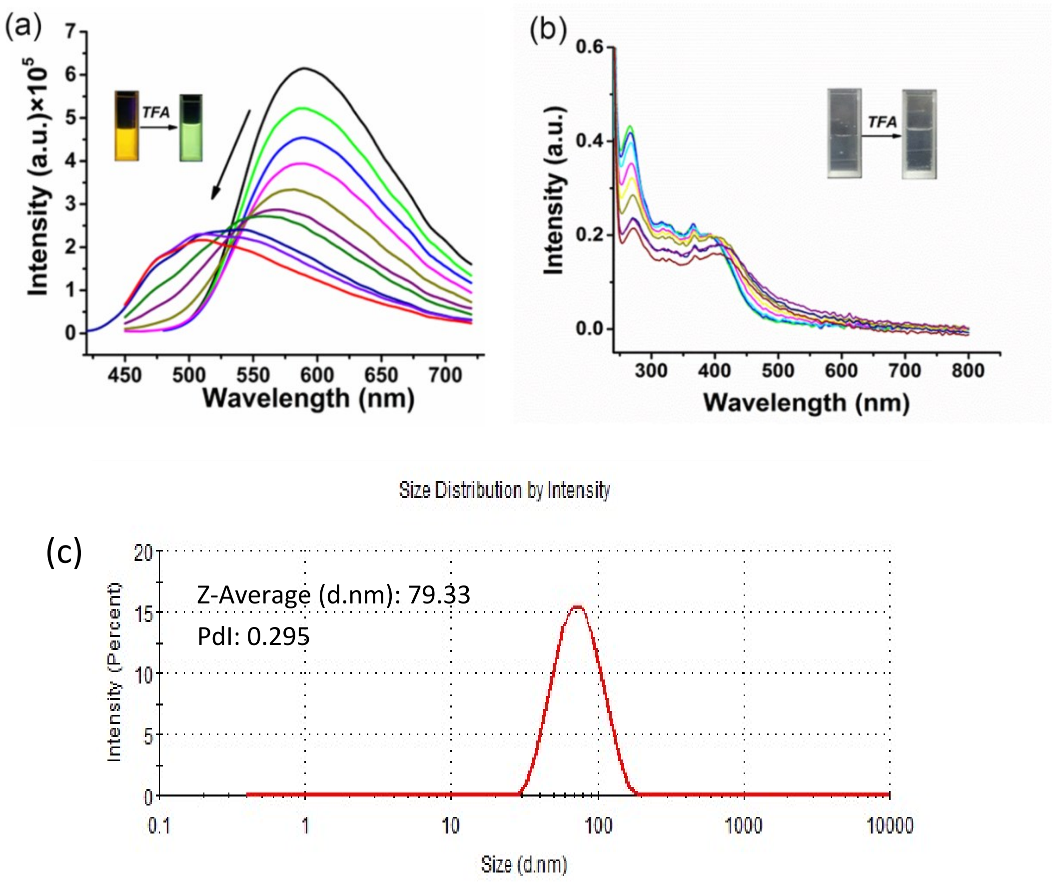


Fig.S10 (a) The fluorescence emission and (b) UV-vis absorption spectra of **M1** in H_2O (10 μM) with additional TFA from 0~ 90 equiv. Insert: Photographs of **M1** in H_2O before and after adding TFA under 365 nm UV lamp excitation. (c) The dynamic light scattering (DLS) of M1 in in H_2O (10 μM).

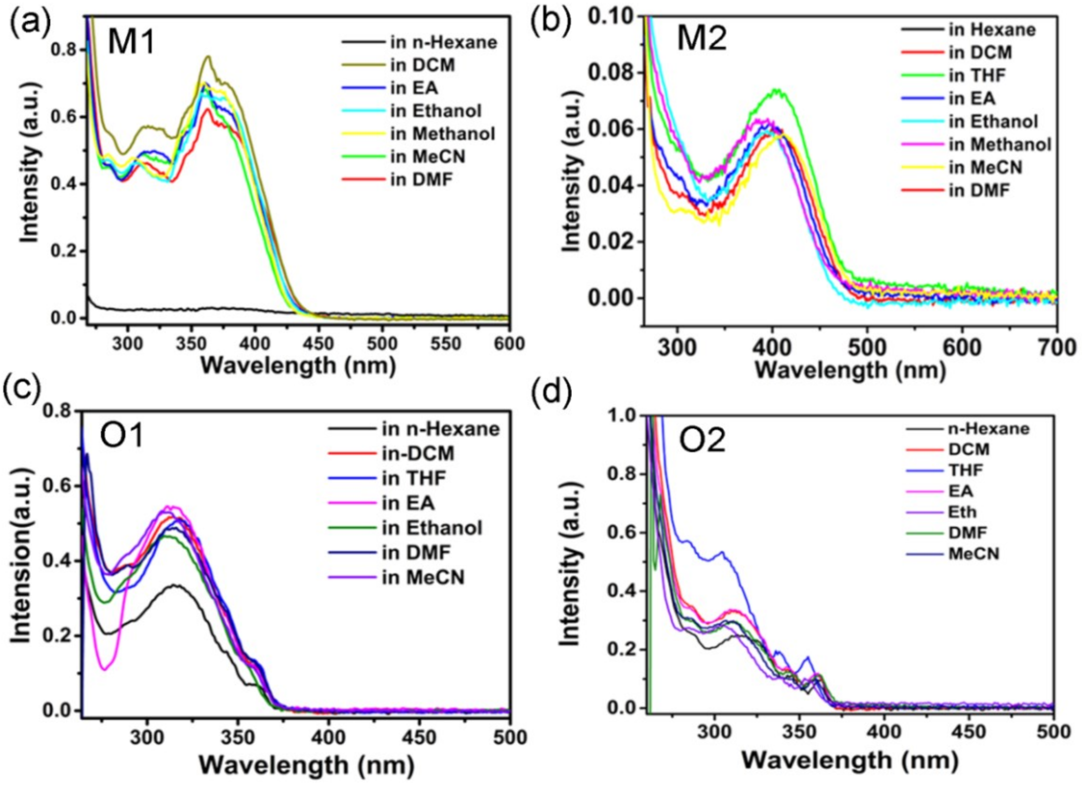


Fig.S11 UV-Vis absorption spectra of **M1**, **M2**, **O1**, **O2** in solvents of different polarity (10 μM).

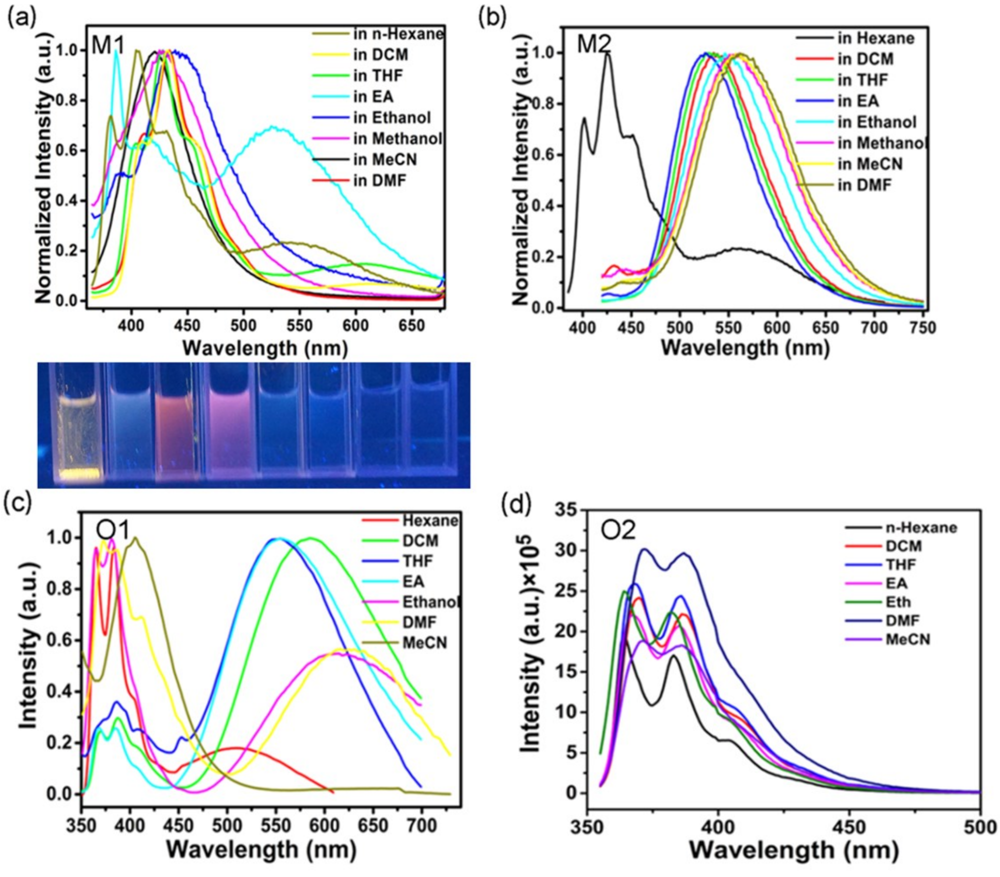


Fig.S12 Fluorescent spectra of **M1**, **M2**, **O1, O2** in solvents of different polarity (10 μM).

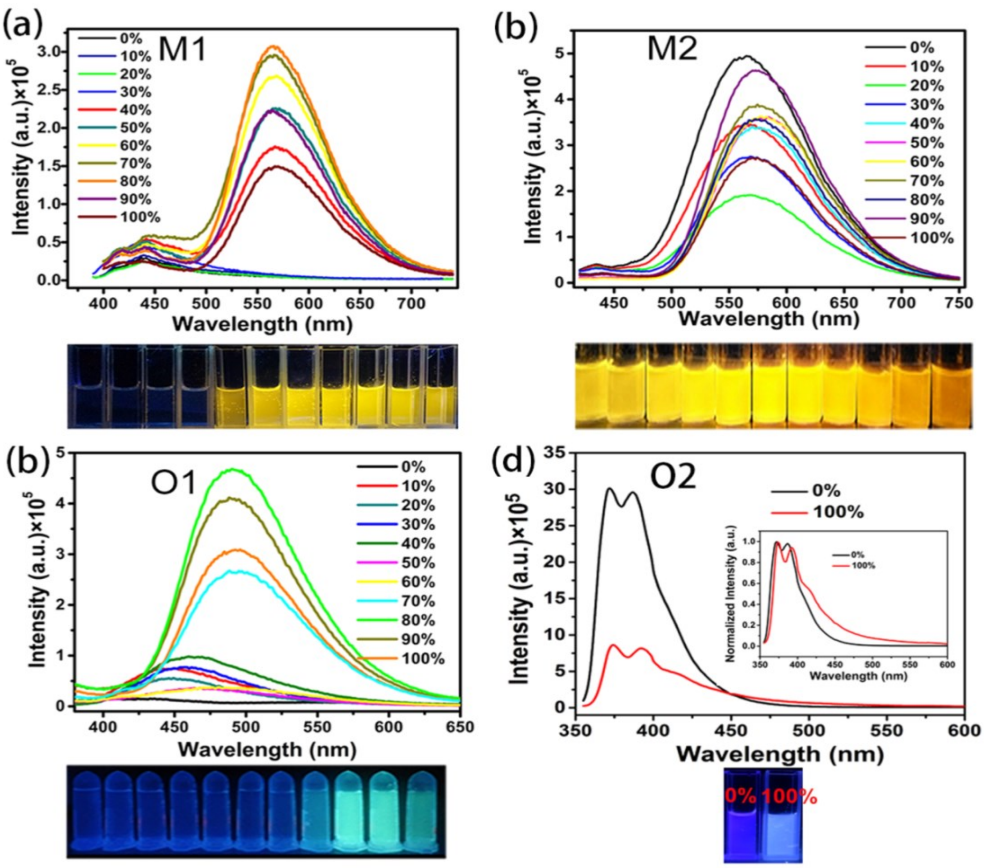


Fig.S13 Emission spectra of **M1**, **M2**, **O1**, **O2** in a mixture of DMF and water with different water content from 0 to 100% (10 μM).

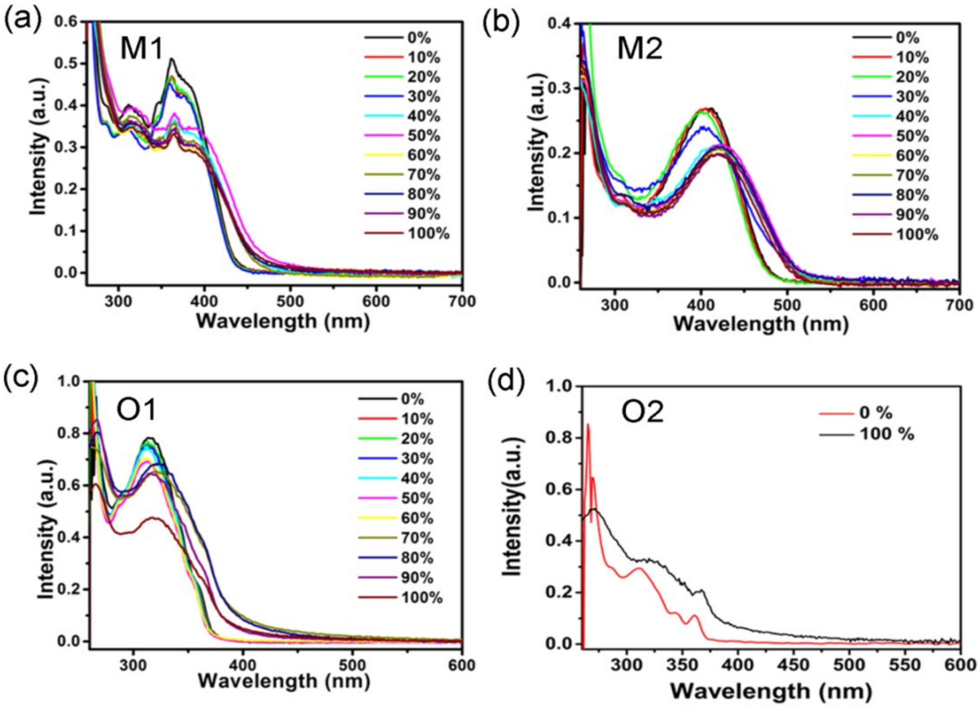


Fig.S14 UV-Vis absorption spectra of **M1**, **M2**, **O1**, **O2** in a mixture of DMF and water with different water content from 0 to 100% (10 μM).

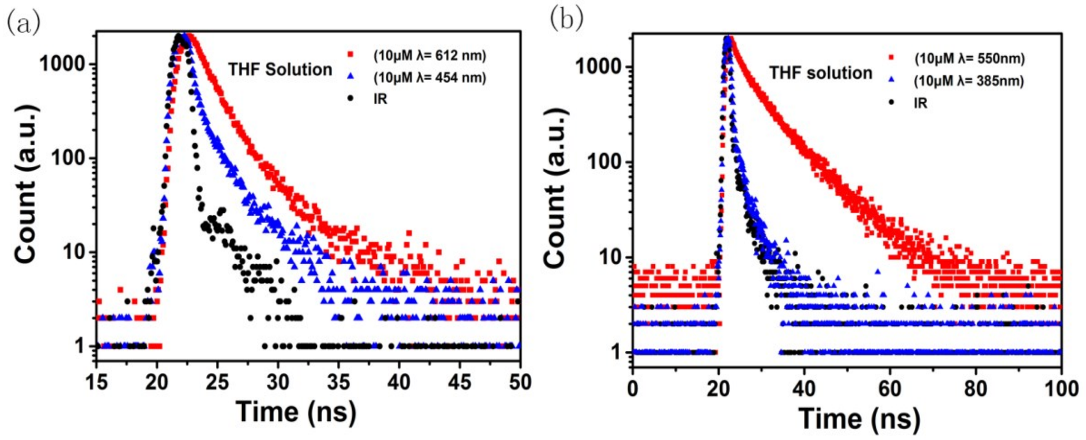


Fig.S15 Emission life-time of M1and O1 at longer wavelength and short wavelength emission in THF solvent.

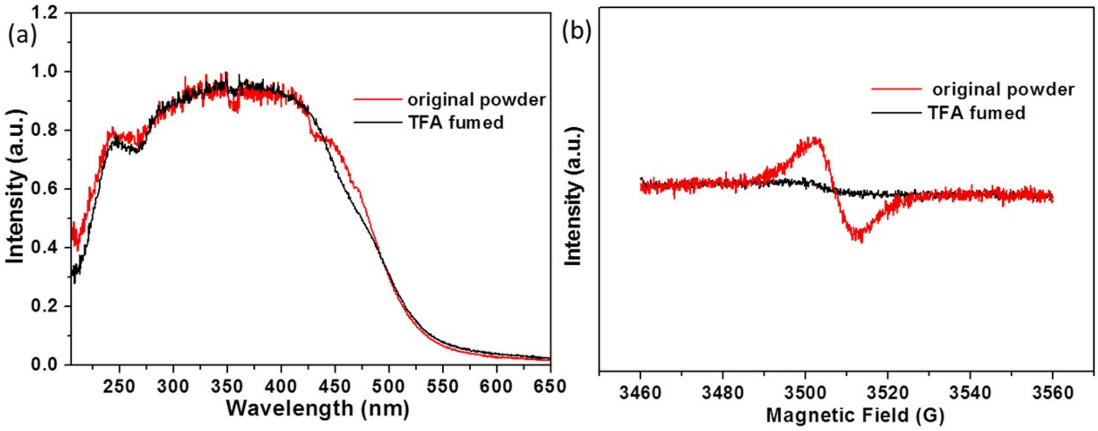


Fig.S16 Solid state of UV-Vis absorption and electron spin resonance spectrum (ESR) before and after TFA stimuli.

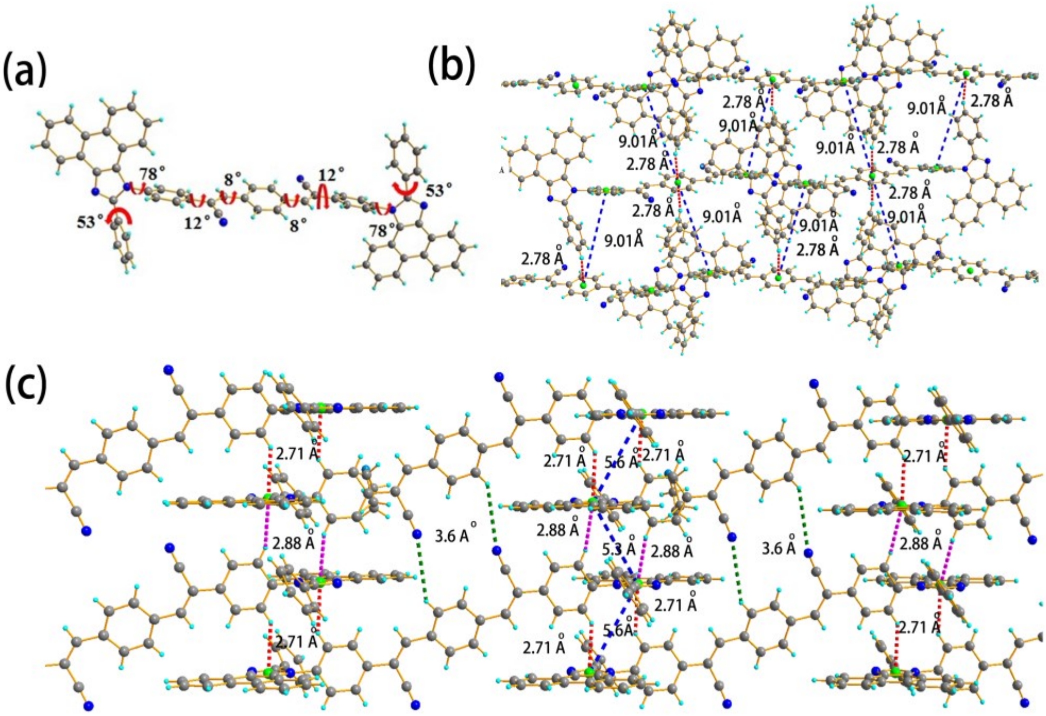


Fig.S17 Single crystal XRD analysis of M1: single molecule structure (a) and weak interactions in the packing pattern (b-c).

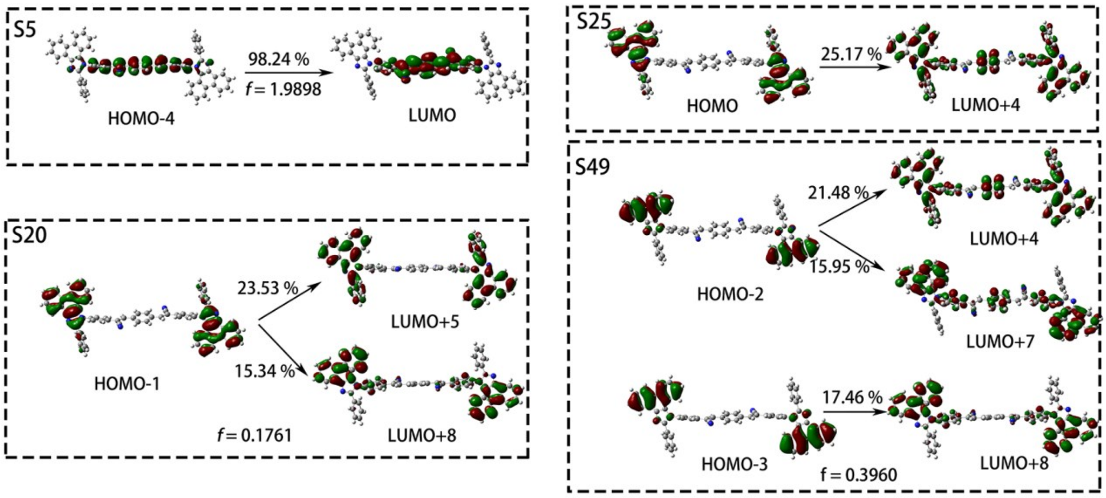


Fig.S18 Energy transitions of neutral M1 estimated by TD-DFT calculations at the B3LYP/6-31g* level.

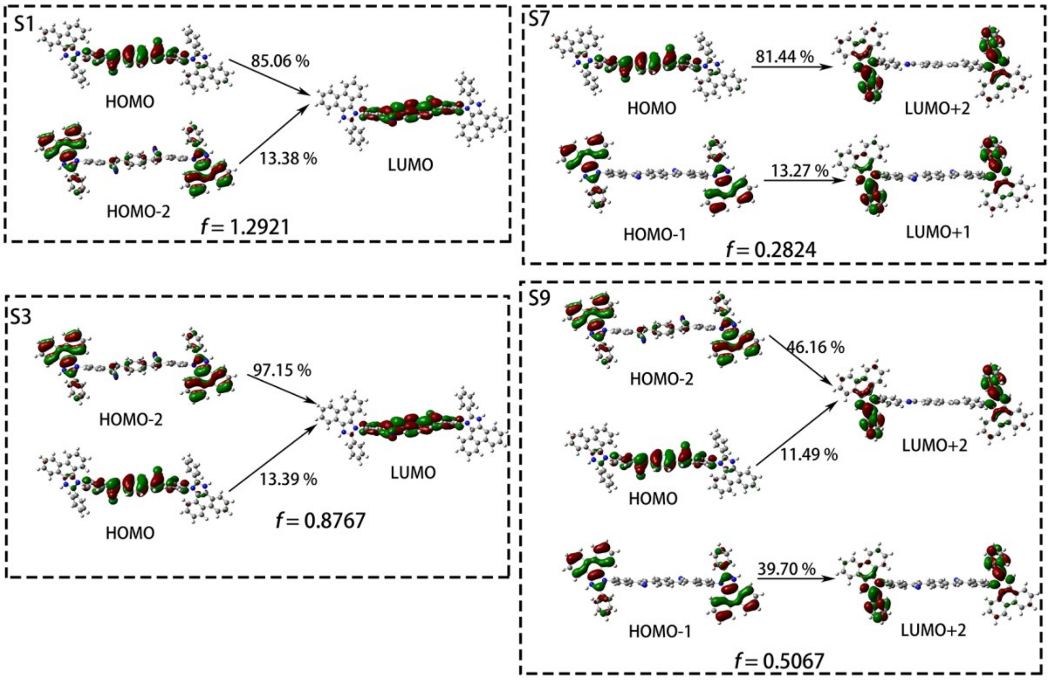


Fig.S19 Energy transitions of protonation M1 estimated by TD-DFT calculations at the B3LYP/6-31g* level.

H^1 NMR and C^{13} NMR spectra of all compounds in this paper.

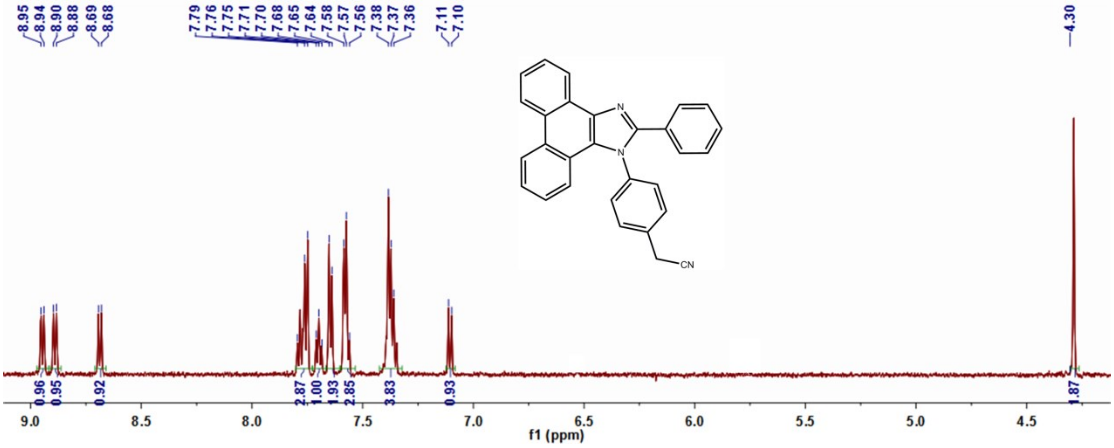


Fig.S20 ^{1}H NMR(600 MHz) spectrum of compound **1** in DMSO-*d6* .

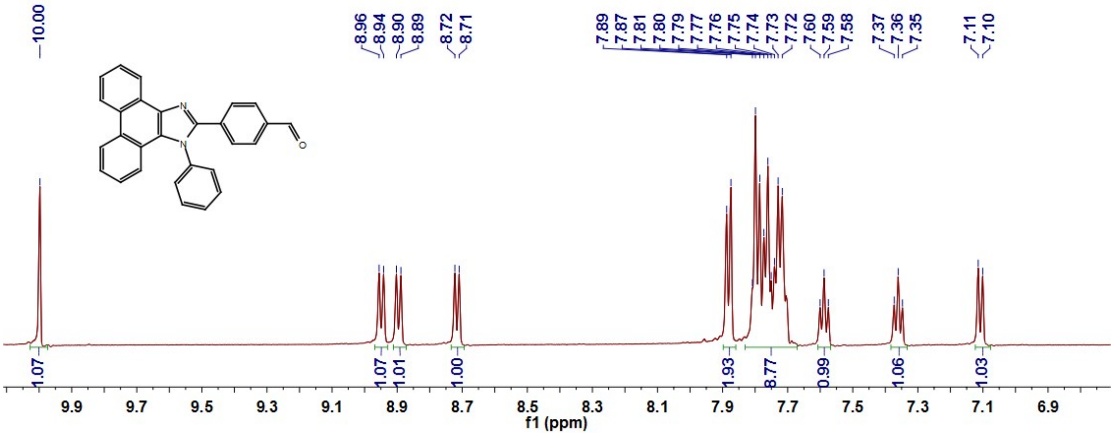


Fig.S21 ^{1}H NMR(600 MHz) spectrum of compound **2** in DMSO-*d6*.

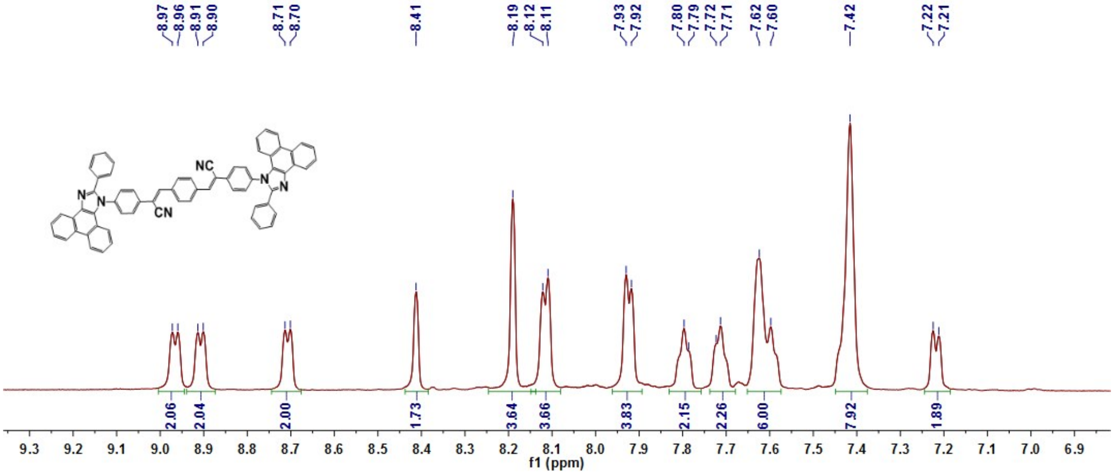


Fig.S18 ^{1}H NMR(600 MHz) spectrum of compound **M1** in DMSO-*d6*.

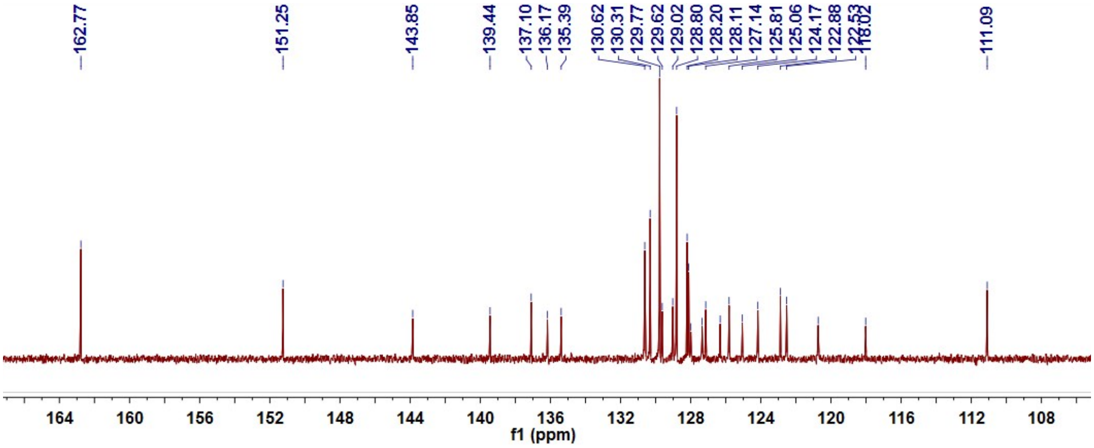


Fig.S22 ^{13}C NMR (151 MHz) spectrum of compound **M1** in DMSO-*d6*.

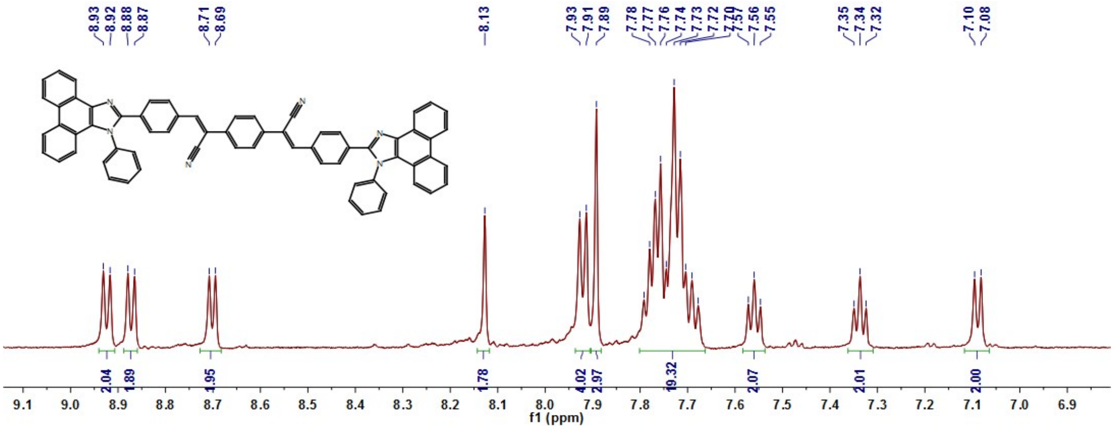


Fig.S23 ^{1}H NMR (600 MHz) spectrum of compound **M2** in DMSO-*d6*.

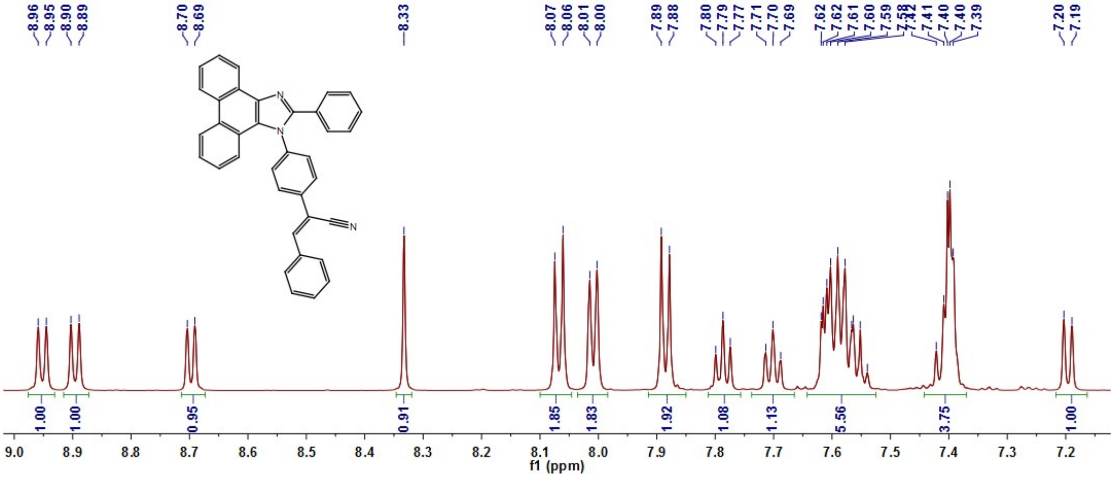


Fig.S24 ^{1}H NMR (600 MHz) spectrum of compound **O1** in DMSO-*d6*.