†Electronic Supplementary Information

For

Development of a multi-responsive fluorescence switch system based on a pyrimidine functionalized tetrarylethylene compound

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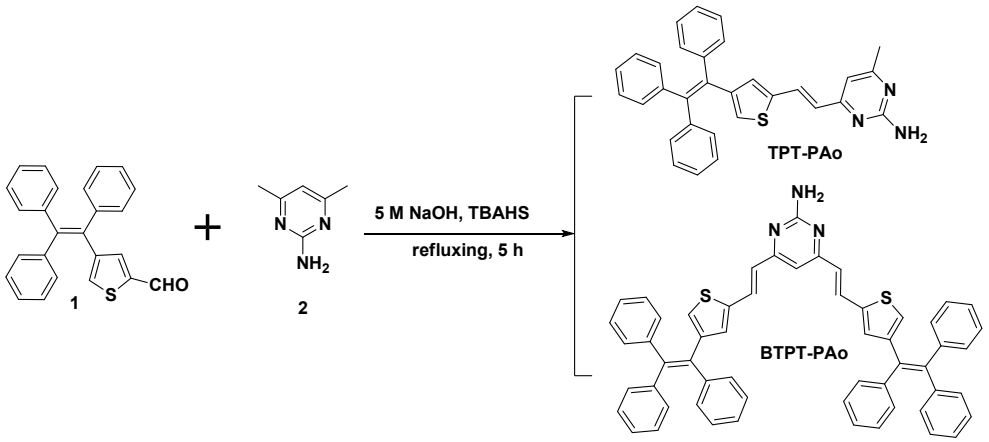
1. Experimental section

1.1 General methods

All the chemicals and reagents used for the synthesis of **1** and **2** were purchased from a variety of commercial sources without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker AV500 (500 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as the internal standard. Agilent 1100 ion trap MSD spectrometer was used for mass spectrometry. UV/Vis spectra were tested on Agilent 8454 spectrophotometer. Fluorescence spectra were captured by a Hitachi F−4600 spectrophotometer. Quantum yield was measured with Hamamatsu Absolute PL Quantum Yield Spectrometer C11347-11. WRS-1B melting point apparatus was used to gained the melting point. The UV and visual light sources were irradiated with MUA-165 and MVL-210, respectively. Luminescent decay experiments were determined by Edinburgh FLS 980 spectrophotometer.

1.2 Synthesis

The synthetic route of **TPT-2-PAo** and **BTPT-2-PAo** are shown in Scheme S1. First of all, compound **1** was synthesized by the method reported [1]. Then, the target molecules **TPT-2-PAo** and **BTPT-2-PAo** were synthesized by one-pot condensation reaction.



Scheme S1. The synthetic route of **TPT-2-PAo** and **BTPT-2-PAo**.

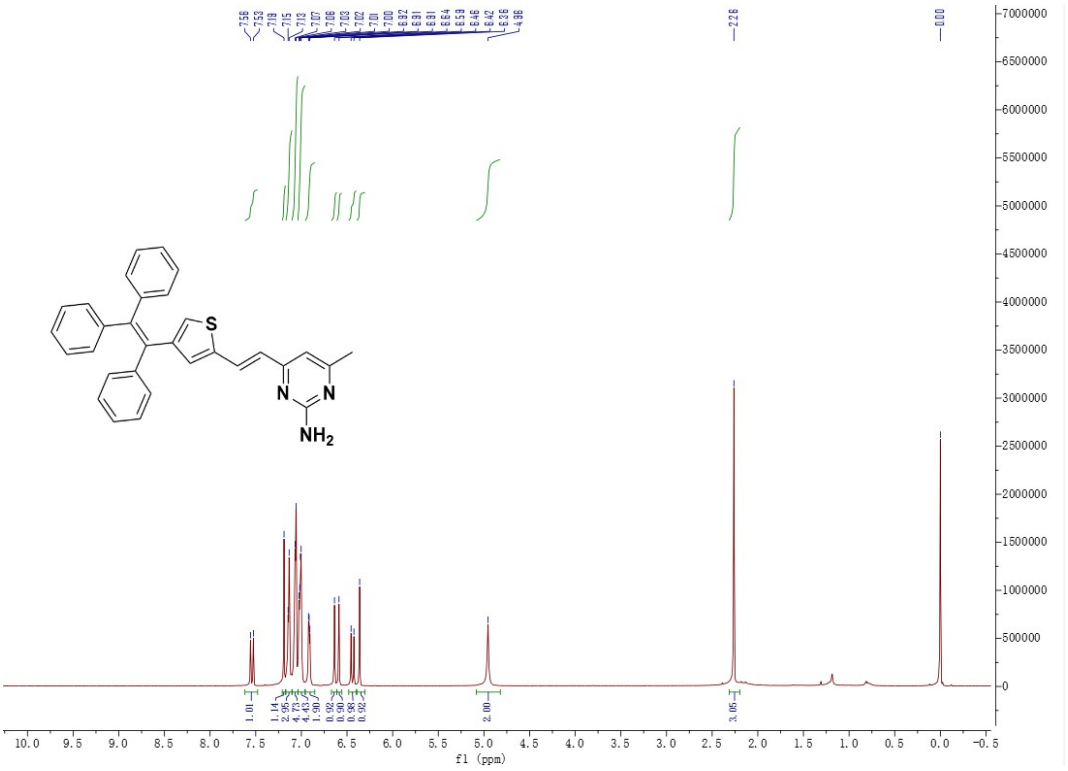
1.2.1 Synthesis of 4-methyl-6-(2-(4-(1,2,2-triphenylvinyl)thiophene-2-yl)vinyl)pyrimidine-2-amine (TPT-2-PAo)

4-(1, 2, 2-Triphenylvinyl)thiophene-2-carbaldehyde (**1,** 1.00 g, 2.70 mmol) and TBAHS (0.92 g, 2.70 mmol) were put into a 100 mL three-necked flask, with 80 mL 5M sodium hydroxide. Then, argon was fed into and stirred, 4,6-dimethylpyrimidin-2-amine (**2**, 0.67 g, 5.40 mmol) were added after 5 min. The reaction was heated reflux for 5 h at 120 °C. Subsequently, the crude products were dissolved in dichloromethane, and extracted. It was dried with anhydrous sodium sulfate and then purified by column chromatography. In the first place, petroleum ether and ethyl acetate (v:v = 5:1) was used as the eluate to obtained crude product **TPT-2-PAo**, then dichloromethane and ethyl acetate (*v:v* = 10:1) mixed solvent as the eluate continue to separated and obtained crude product **BTPT-2-PAo**. After that, two products were recrystallized with *n*-hexane and dried. The last, a light yellow solid is the target product **TPT-2-PAo** (0.40 g, 0.85 mmol) in 31% yield. M. p.: 196–197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (s, 3H), 4.98 (s, 2H), 6.36 (s, 1H), 6.44 (d, J = 20.0 Hz, 1H), 6.59 (s, 1H), 6.64 (s, 1H), 6.91 (t, J = 5.0 Hz, 2H), 7.00–7.03 (m, 4H), 7.06 (d, J = 5.0 Hz, 5H), 7.14 (d, J = 10.0 Hz, 3H), 7.19 (s, 1H), 7.54 (d, J = 15.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 22.76, 108.14, 123.72, 125.44, 125.71, 126.00, 126.58, 126.66, 126.74, 127.08, 128.30, 129.71,130.08, 130.13, 131.17, 133.80, 138.57, 140.15, 141.84, 142.12, 142.60, 143.85, 161.37, 161.92, 167.13 (Fig. S1). HRMS-ESI (*m/z*): $[M + H]^+$ Calcd. For ($C_{31}H_{25}N_3S^+$), 472.1769, found: 472.1828 (Fig. S2A).

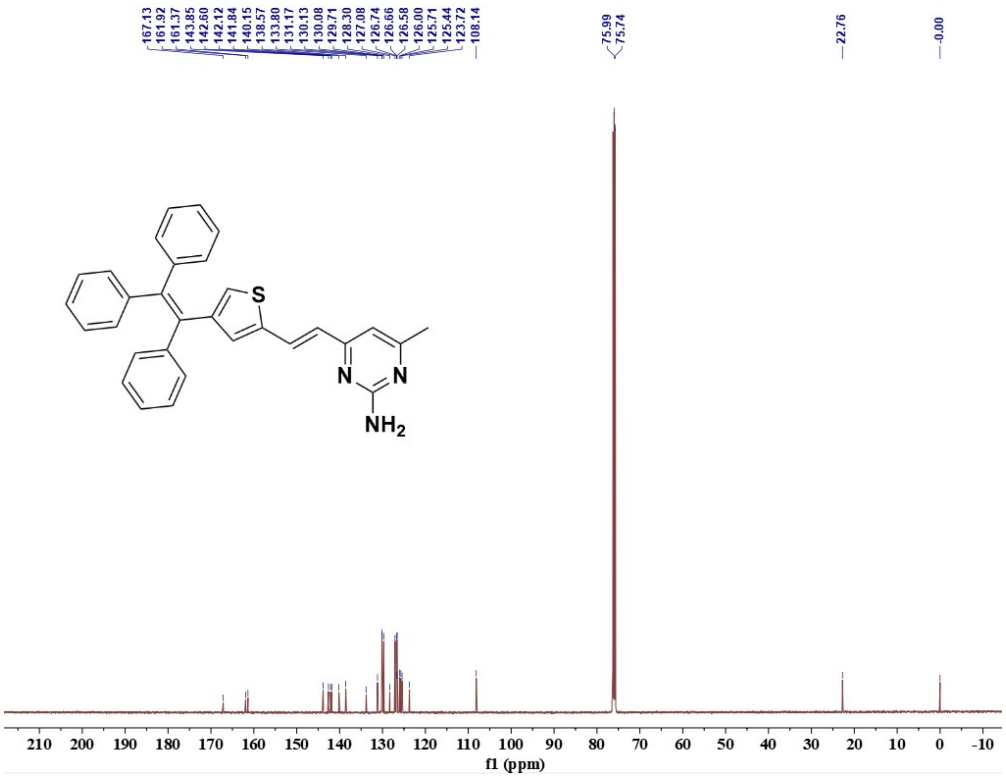
1.2.2 4,6-Bis-2-(4-(1,2,2-triphenylvinyl)thiophen-2-yl)vinyl)pyrimidine-2-amine (BTPT-2-PAo)

BTPT-2-PA (0.35 g, 0.43 mmol) was recrystallization from dichloromethane, yielding 16%. M.

p.:141–142℃ . ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.90 (s, 2H), 6.47 (s, 1H), 6.53 (d, J = 15.0 MHz, 2H), 6.65 (s, 2H), 6.71 (s, 2H), 6.99 (t, J = 5.0 MHz, 4H), 7.07–7.10 (m, 10H), 7.14 (d, J = 5.0 MHz, 10H), 7.22 (t, J = 5.0 MHz, 6H), 7.61 (d, J = 15.0 MHz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 107.01, 123.97, 125.43, 125.71, 126.01, 126.58, 126.74, 127.08, 128.00, 129.71, 130.09, 130.14, 131.12, 133.81, 138.64, 140.13, 141.85, 142.14, 142.60, 143.85 (Fig. S3). HRMS-ESI (*m/z*): $[M + H]^+$ Calcd. For ($C_{56}H_{42}N_3S_2^+$), 820.2820, found: 820.2695 (Fig. S2B).

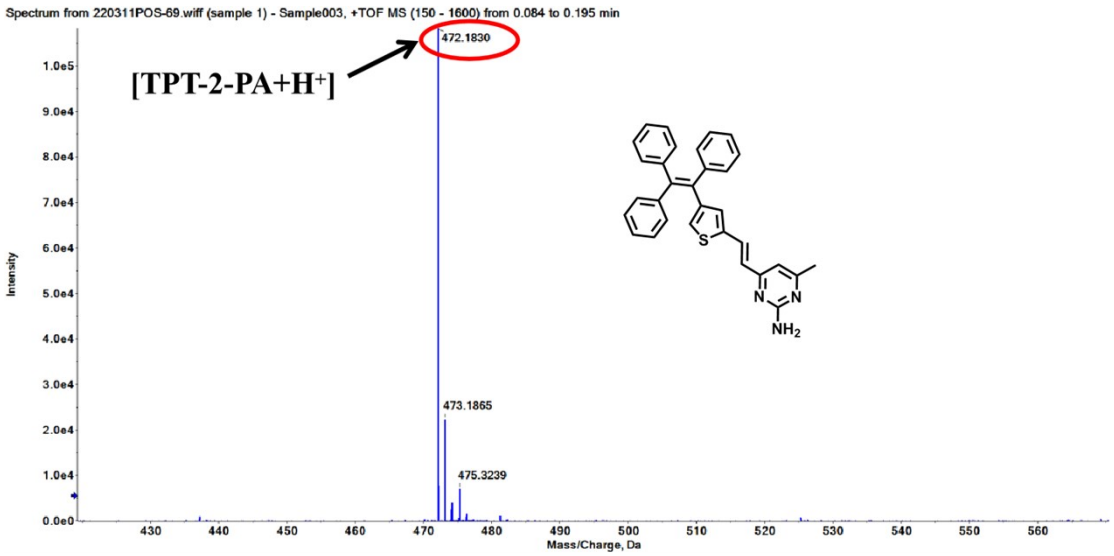


(A)

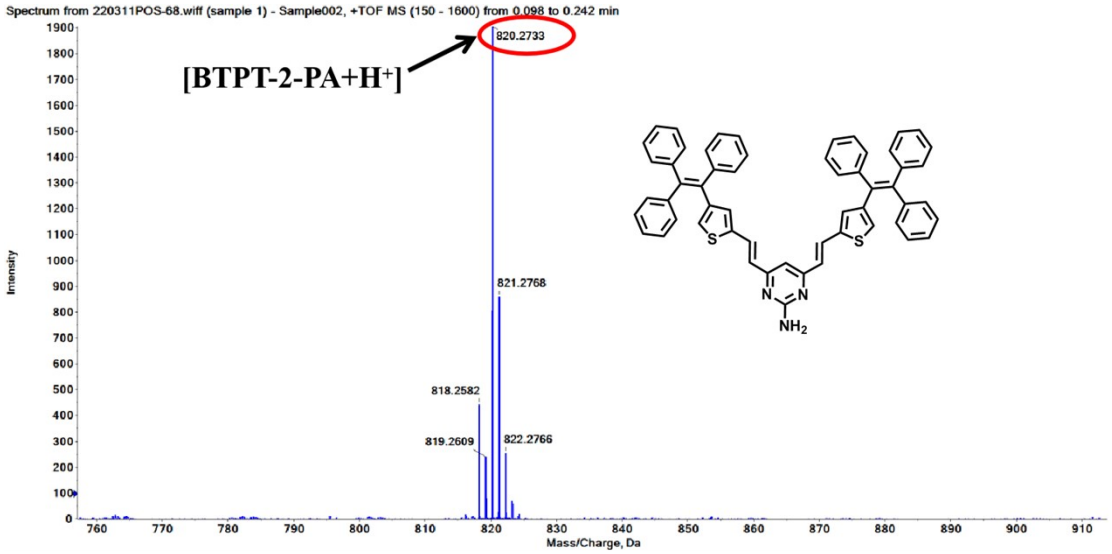


(B)

Figure S1. NMR spectra data for **TPT-2-PAo** in $CDCl_3$: (A) ^{1}H-NMR spectrum; (B) ^{13}C-NMR spectrum.

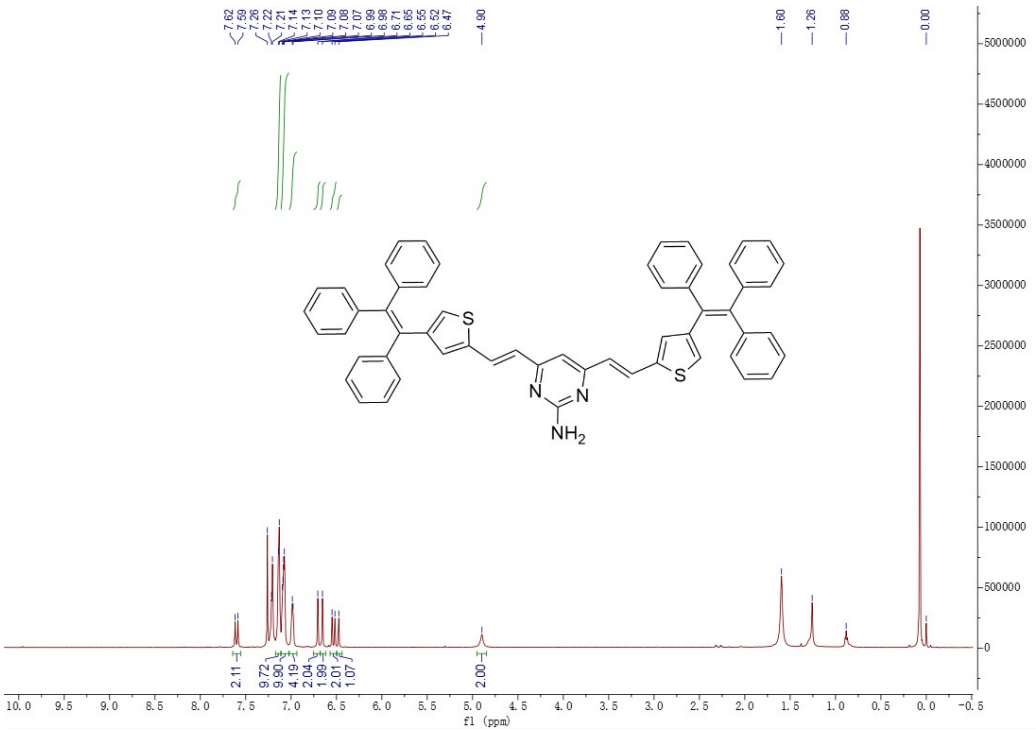


(A)

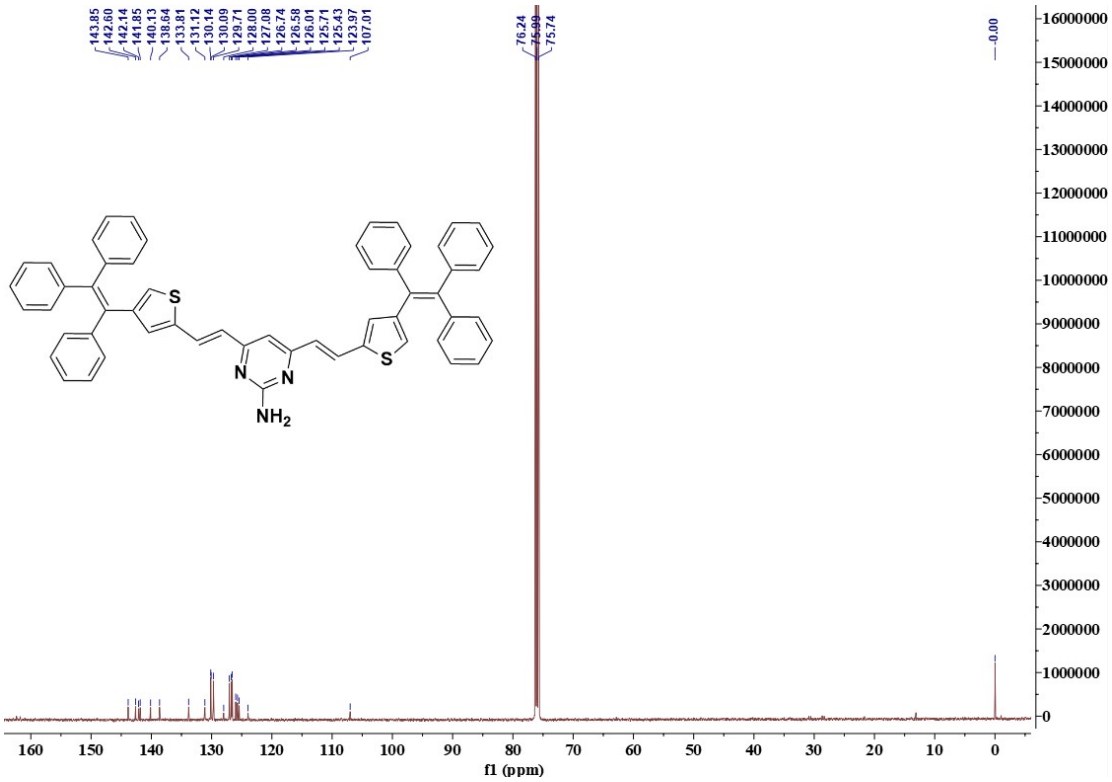


(B)

Figure S2. (A) HRMS-ESI spectra of **TPT-2-PAo** in methanol and (B) **BTPT-2-PAo** in acetonitrile.

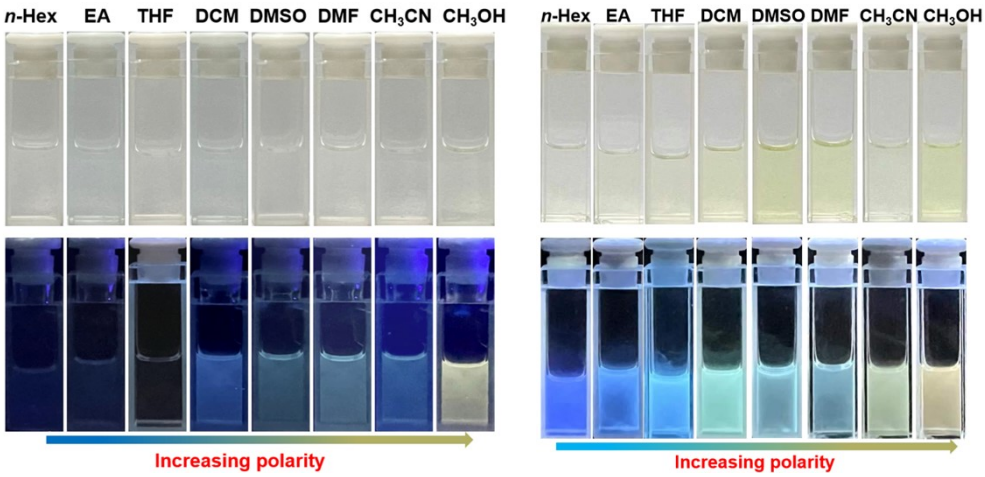


(A)



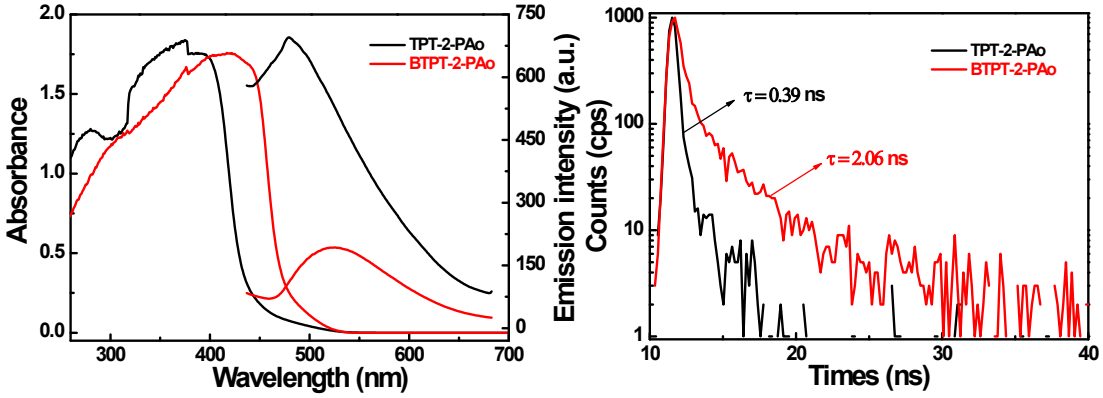
(B)

Figure S3. NMR spectra data for **BTPT-2-PAo** in $CDCl_3$: (A) ^{1}H-NMR spectrum; (B) ^{13}C-NMR spectrum.



(A) (B)

Figure S4. (A) Photograph showing the color changes of **TPT-2-PAo**, and (B) **BTPT-2-PAo** in different solvents ((λ_{ex} = 365 nm).



(A) (B)

Figure S5. (A) The absorption and PL spectra of **TPT-2-PAo** and **BTPT-2-PAo** in solid states, and (B) fluorescence decay cures of them in solid states.

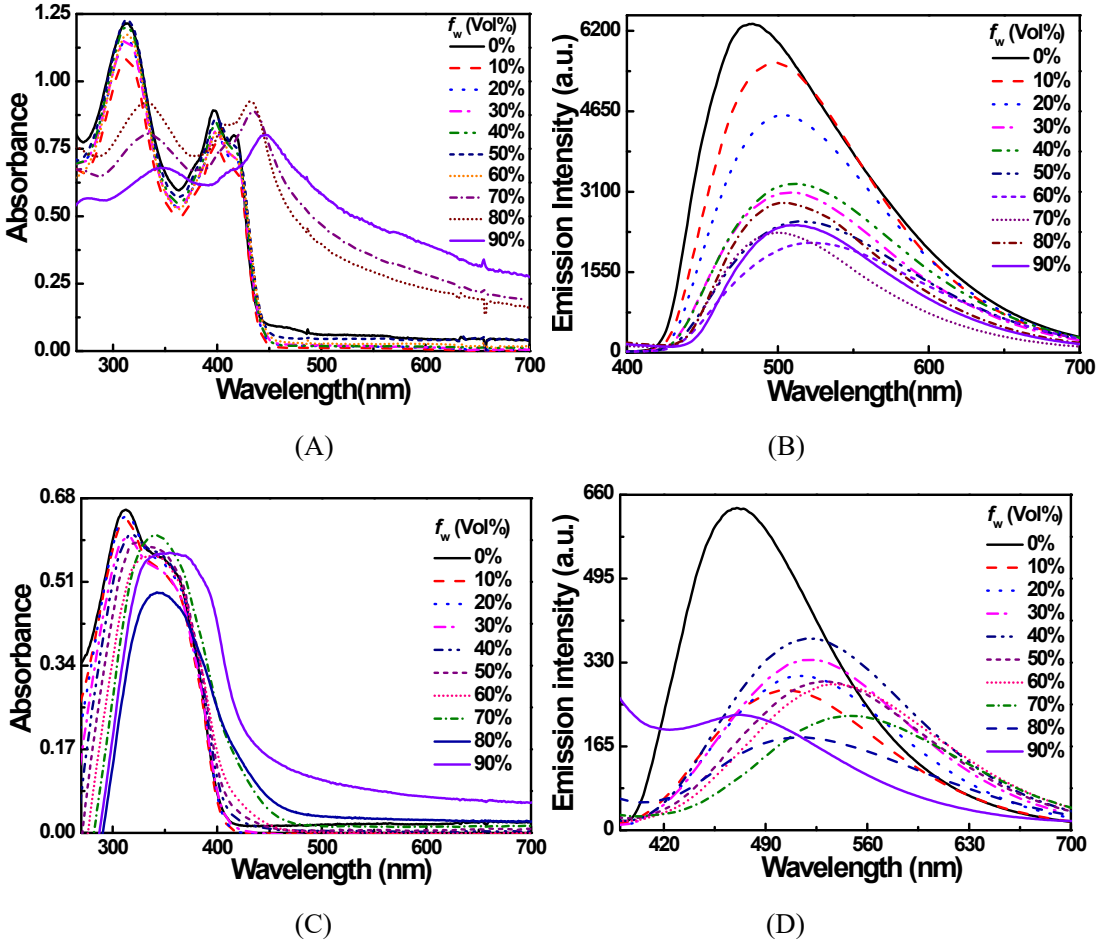
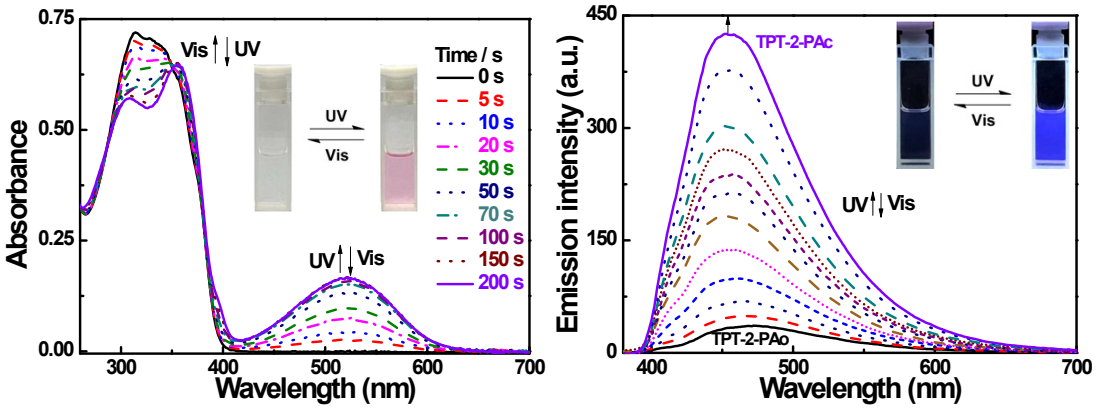
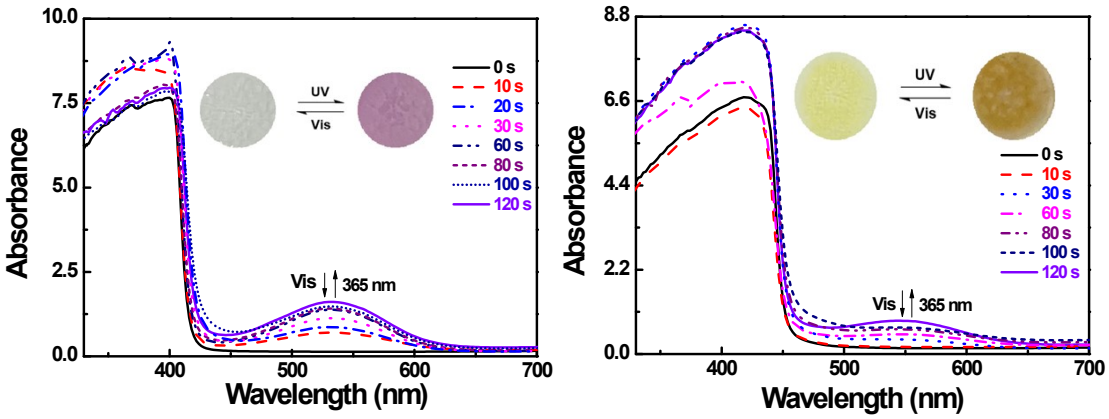


Figure S6. Changes of absorption and PL spectra for **TPT-2-PAo** and **BTPT-2-PAo** in THF/H_2O ($C = 2.0 \times 10^{-5}$ mol L^{-1}) mixtures with different fractions: (A) absorption spectra for **BTPT-2-PAo**, (B) PL intensity for **BTPT-2-PAo**, (C) absorption spectra for **TPT-2-PAo**, and (D) PL intensity for **TPT-2-PAo**.



(A) (B)

Figure S7. Changes in absorption (A) and fluorescence (B) spectra for **TPT-2-PAo** by photoirradiation with UV and visible in hexane ($C = 2.0 \times 10^{-5}$ mol L^{-1}) at room temperature (inset: color changes by photoirradiation).



(A) (B)

Figure S8. Changes in absorption spectral for **TPT-2-PAo** (A) and **BTPT-2-PAo** (B) by photoirradiation with UV and visible light at room temperature in PMMA films (inset: color changes by photoirradiation).

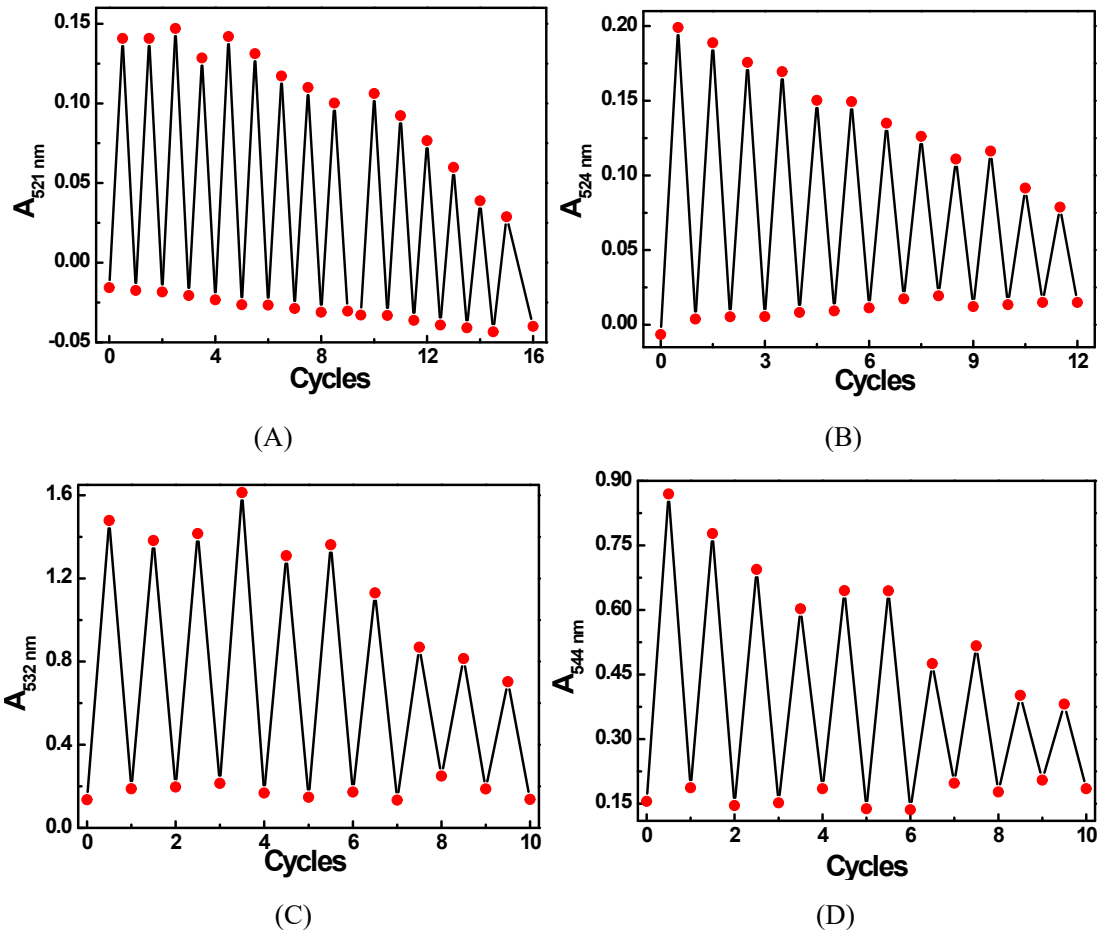
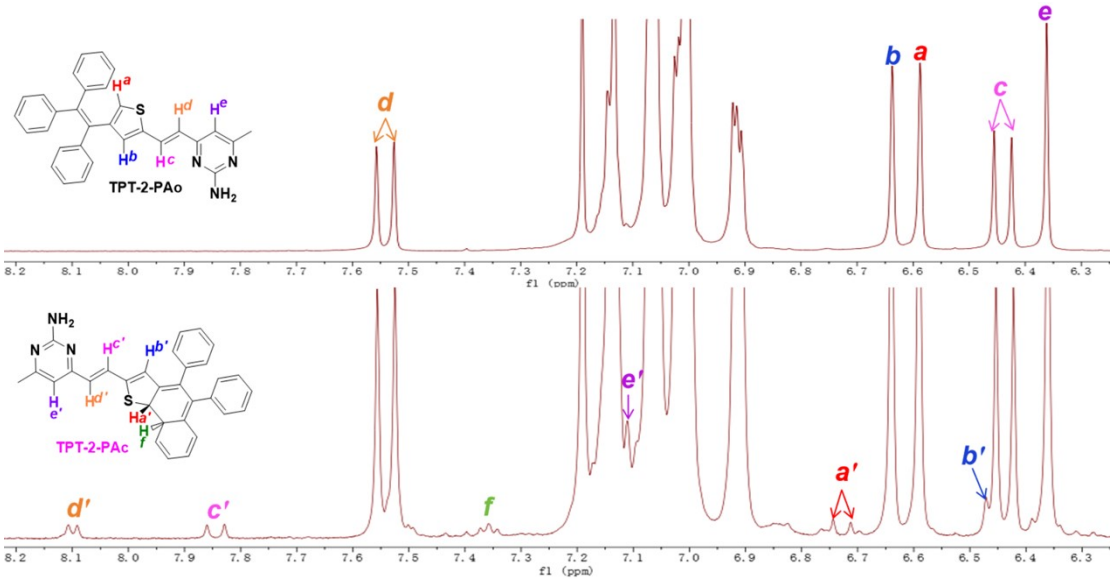
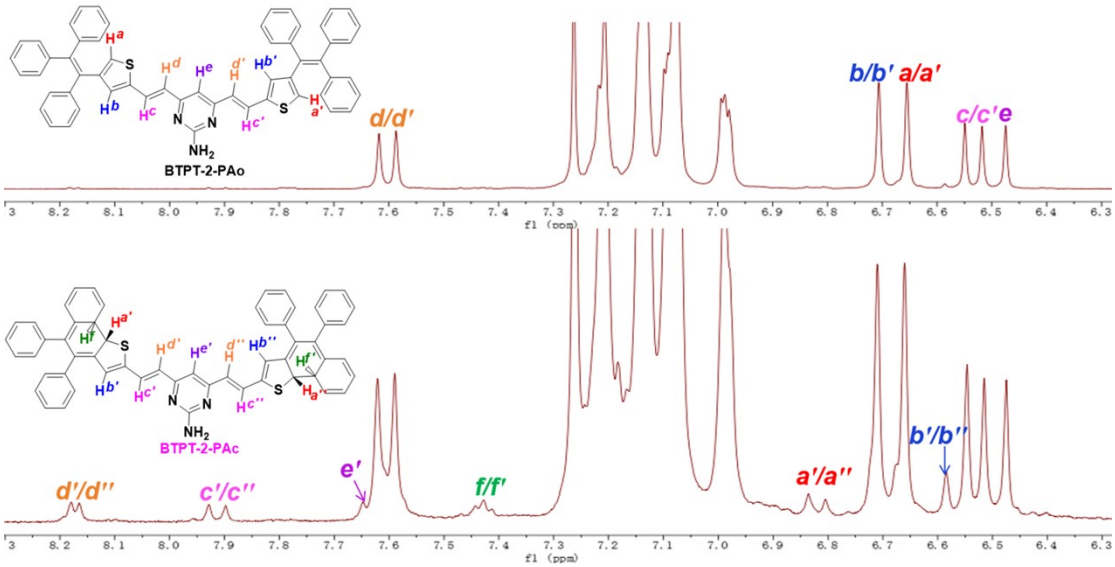


Figure S9. Fatigue resistance of **TPT-2-PAo** and **BTPT-2-PAo** upon alternating irradiation with UV and visible light: (A) and (B) in THF, (C) and (D) in PMMA film.



(A)



(B)

Figure S10. Comparison of ^{1}H NMR spectra of **TPT-2-PAo** (A) and **BTPT-2-PAo** (B) in $CDCl_3$ before and after UV irradiation (insets: corresponding structures).

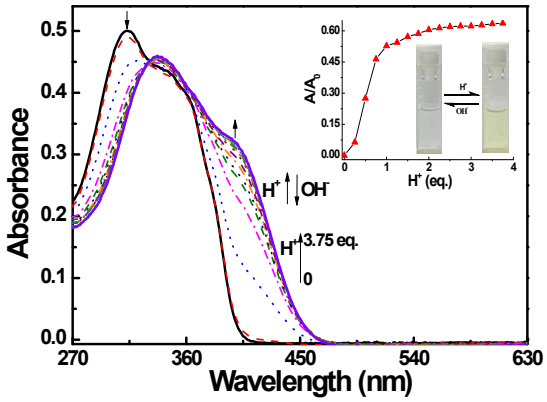


Figure S11. Absorption spectral and color changes of **TPT-2-PAo** by HCl/NaOH stimuli in THF ($C = 2.0 \times 10^{-5}$ mol L^{-1}).

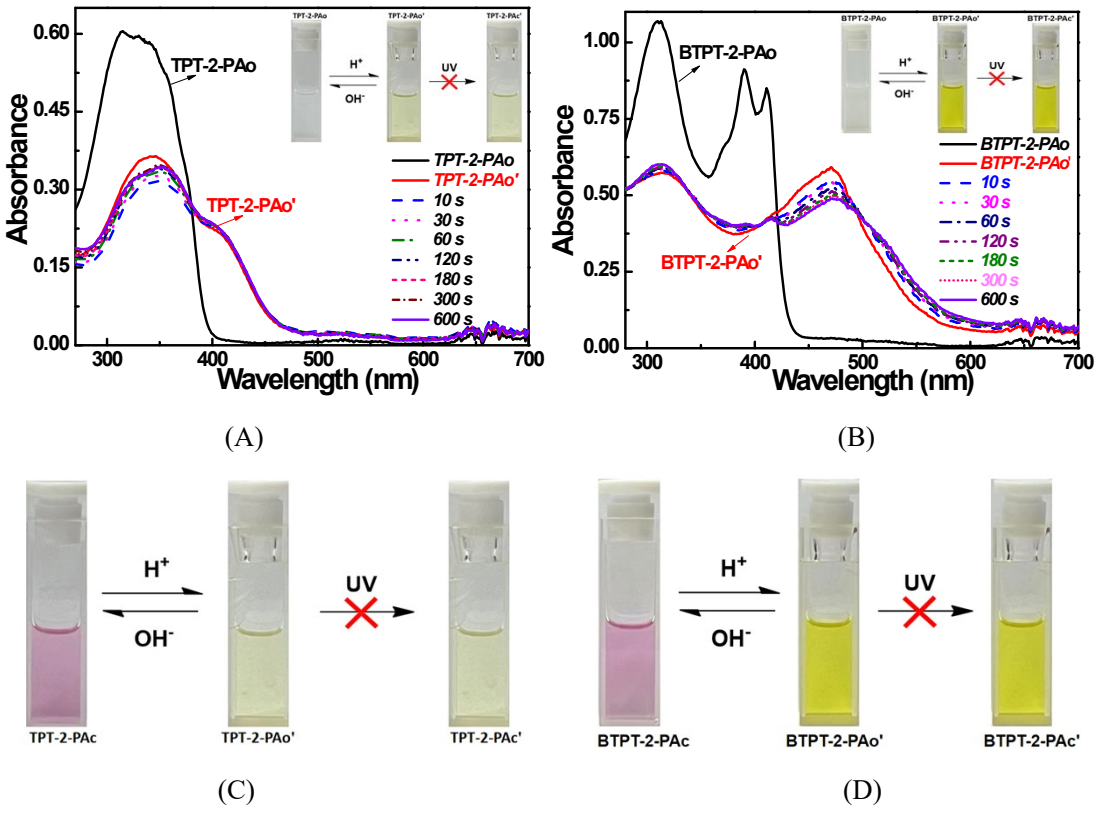


Figure S12. (A) Changes in absorption spectral of **TPT-2-PAo′**, and (B) **BTPT-2-PAo′** by photoirradiation with UV and visible light in *n*-hexane ($C = 2.0 \times 10^{-5}$ mol L^{-1}) at room temperature (inset: color changes by photoirradiation), (C) and (D) color changes for their closed-ring isomers by stimuli with acid/base and UV light.

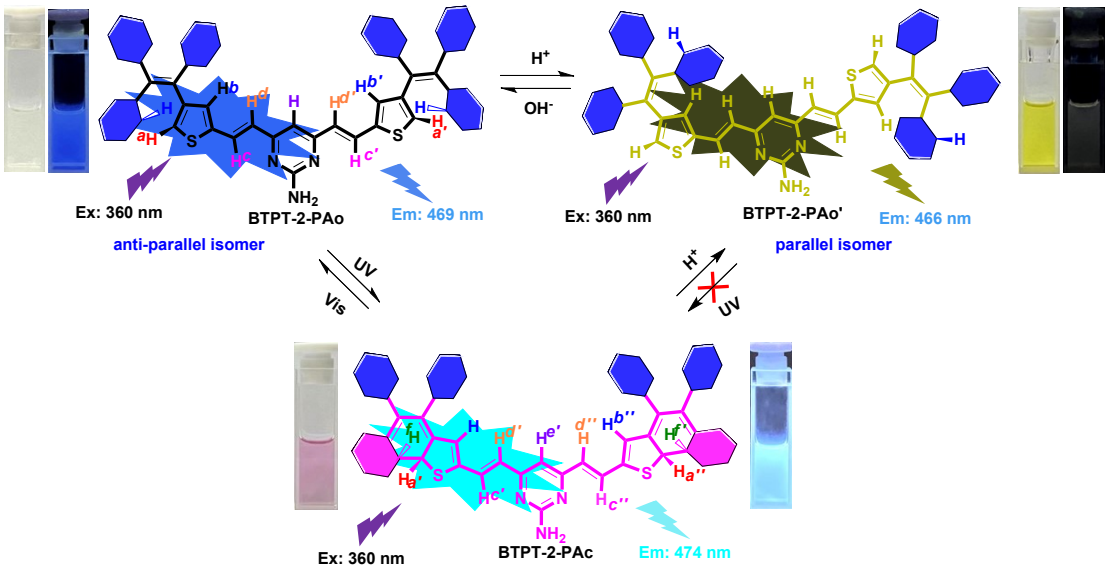
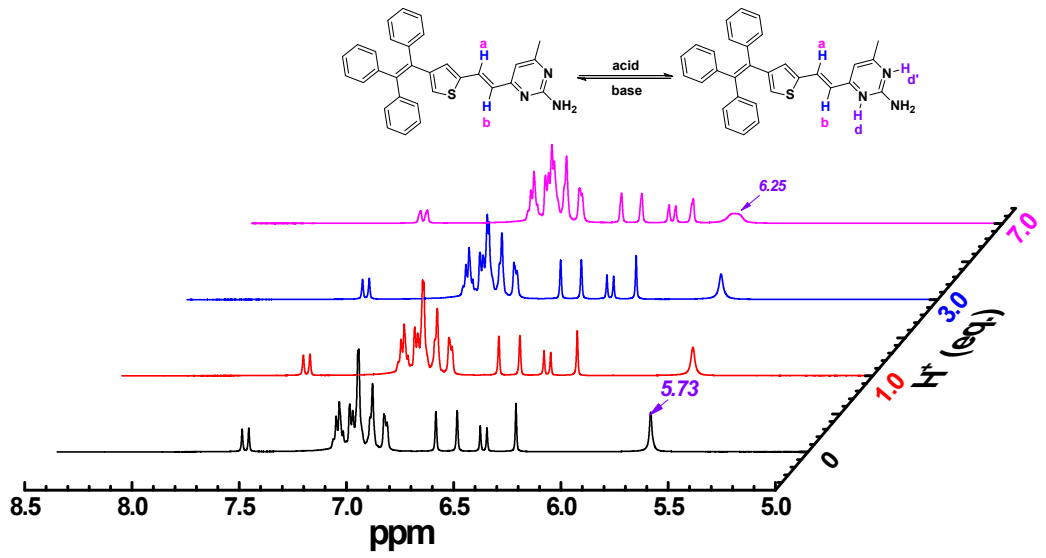
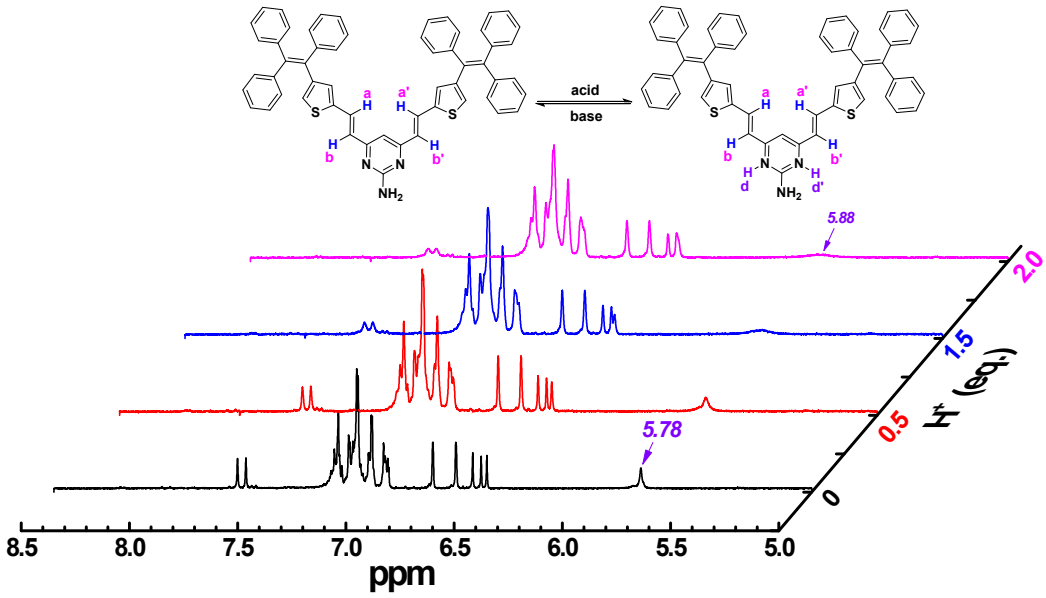


Figure S13. Structural, fluorescence and color changes between **BTPT-2-PAo**, and **BTPT-2-PAo′** induced by base and light.



(A)



(B)

Figure S14. Changes in ^{1}H NMR spectra of **TPT-2-PAo** (A) and **BTPT-2-PAo** (B) stimuli by different H^{+} concentration in THF-d_8.

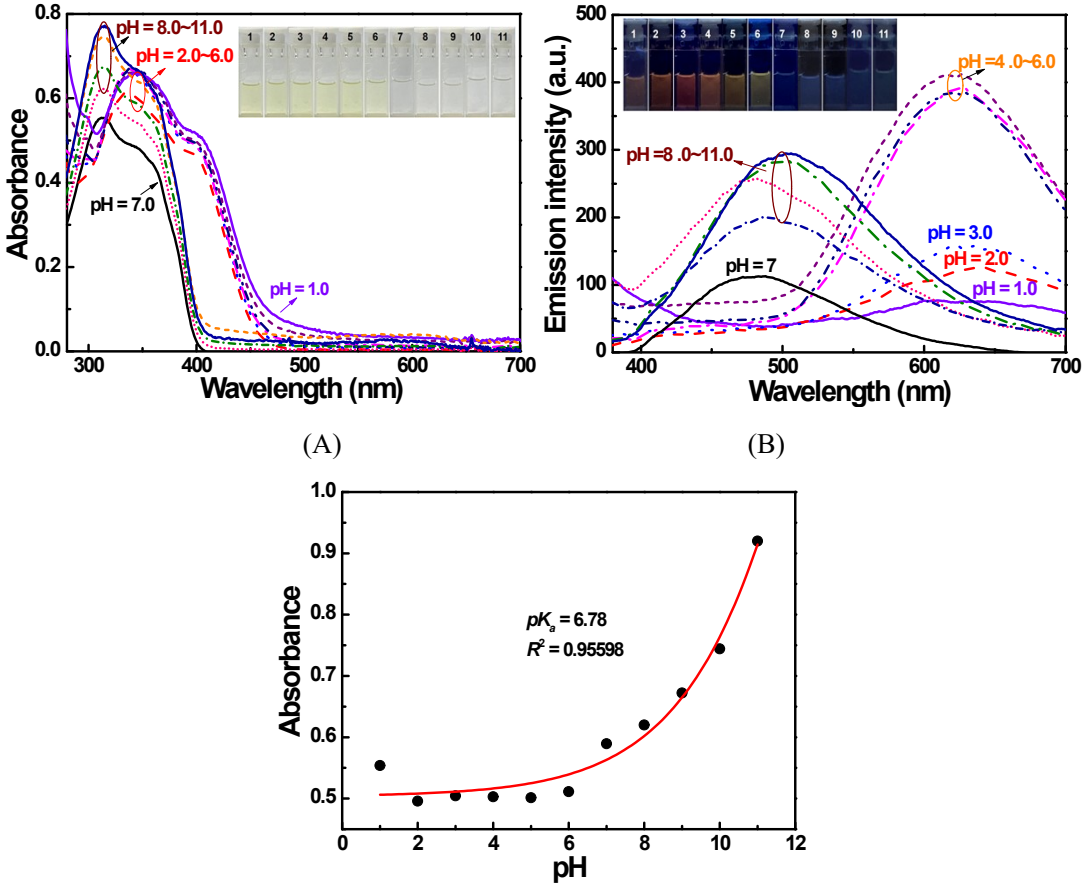
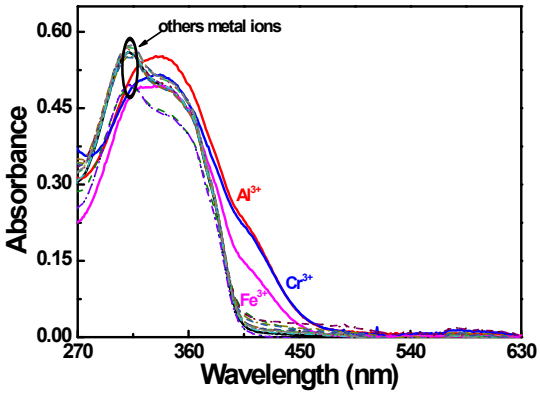
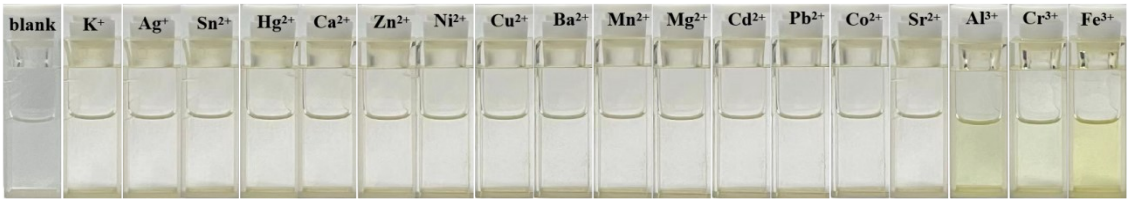


Figure S15. Absorption / PL spectra and color changes of **TPT-2-PAo** in various pH values solutions: (A) absorption spectra, (B) PL spectra (λ_{ex} = 360 nm), and (C) changes of the absorbance spectra of **TPT-2-PAo** with increasing pH from 1.0 to 11.0: sigmoidal fitting of the pH-dependent absorbance intensity at 400 nm.

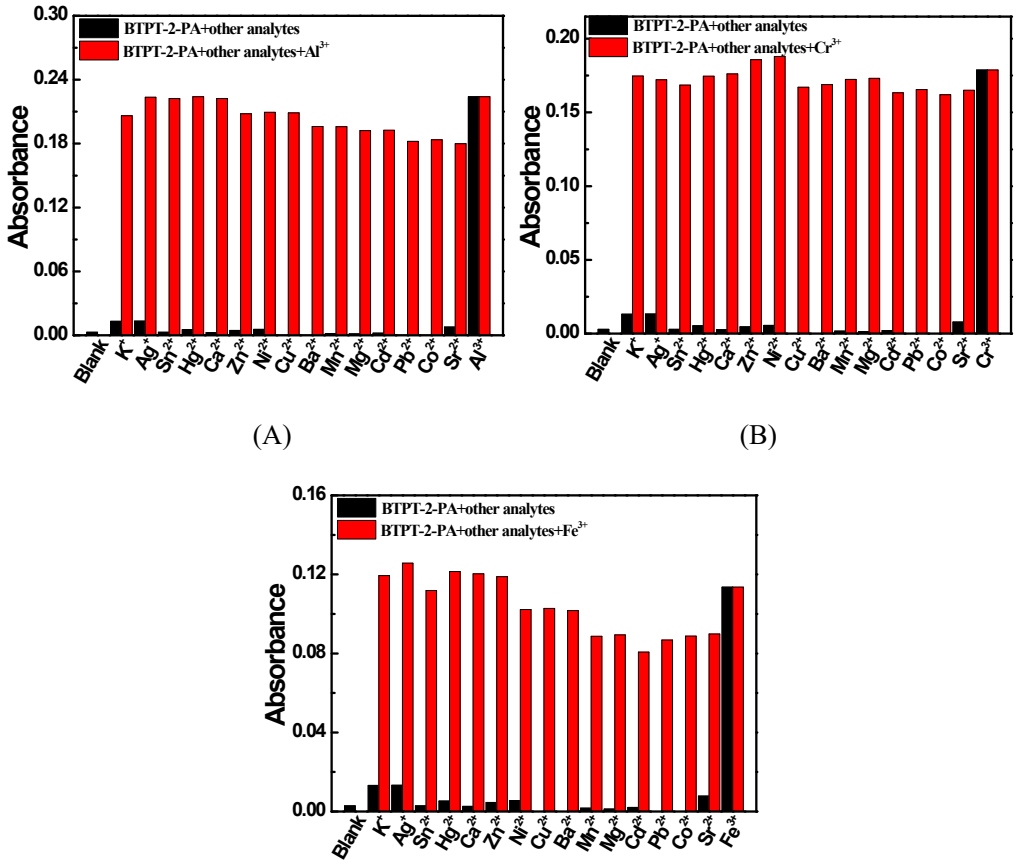


(A)



(B)

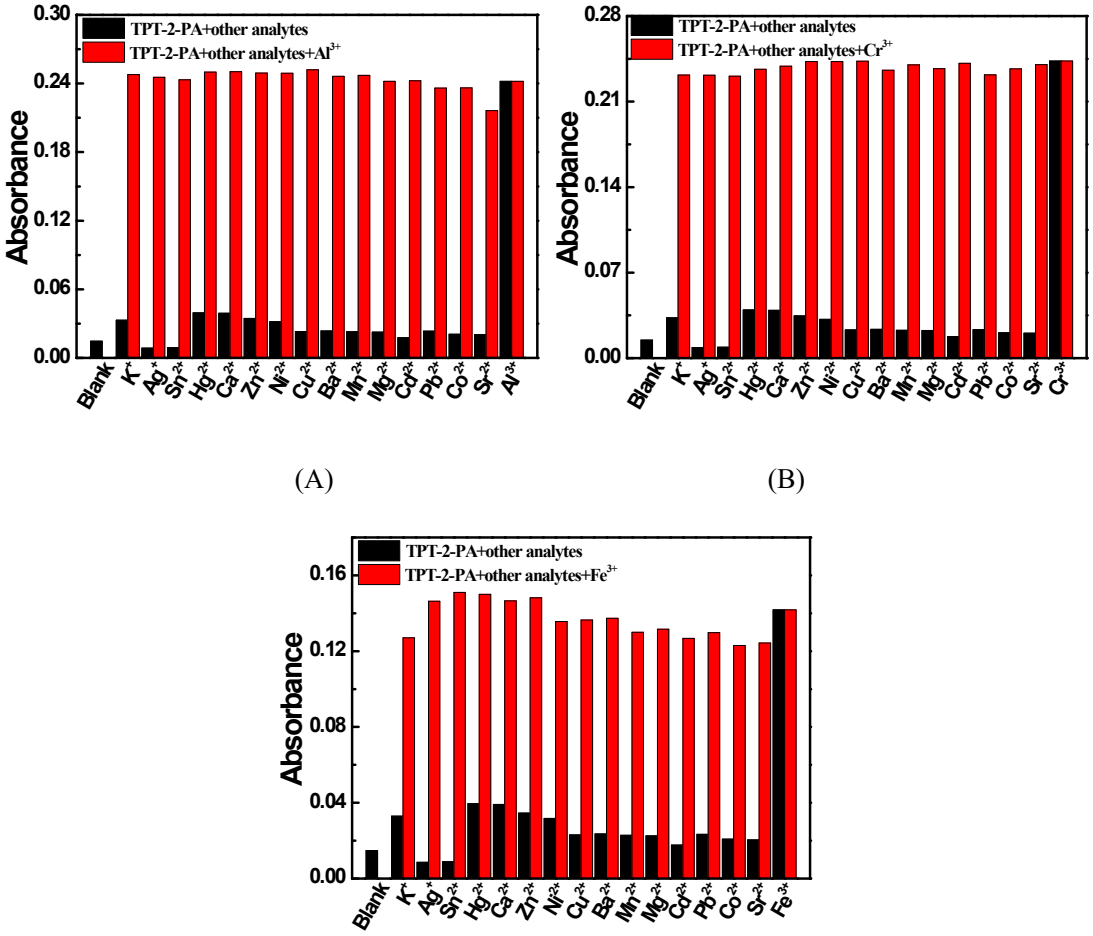
Figure S16. Changes in the absorption of **TPT-2-PAo** induced by various metal ions (5.0 equiv) in THF ($C = 2.0 \times 10^{-5}$ mol L^{-1}): (A) absorption spectra, (B) photos of color changes.



(A) (B)

(C)

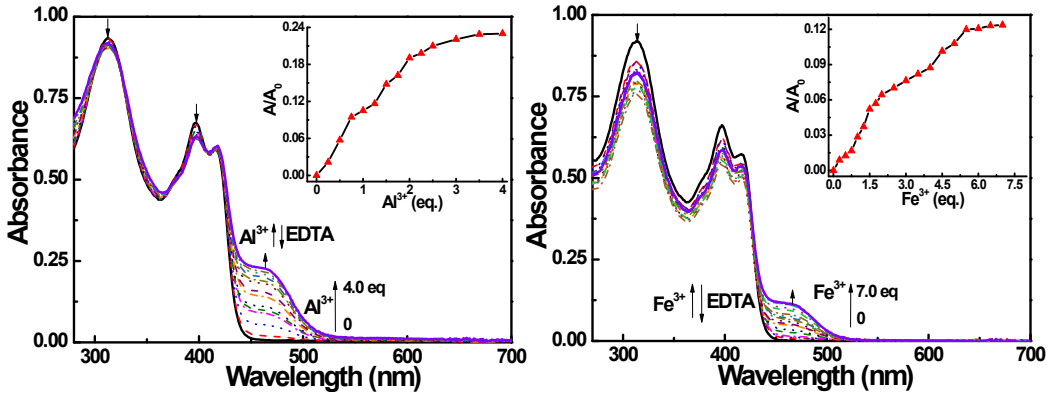
Figure S17. Competitive test showing the absorbance response of **BTPT-2-PAo** to different metal ions (20.0 equiv.) in THF ($C = 2.0 \times 10^{-5}$ mol L^{-1}). Black bars: **BTPT-2-PAo** with various metal ions; red bars: **BTPT-2-PAo** with different competing metal ions and Al^{3+} (A), Cr^{3+} (B), and Fe^{3+} (C).



(A) (B)

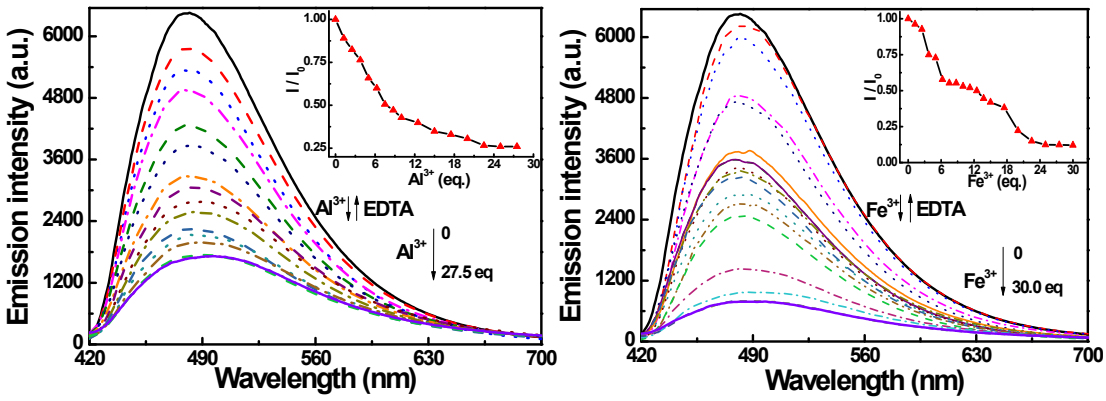
(C)

Figure S18. Competitive test showing the absorbance response of **TPT-2-PAo** to different metal ions (5.0 equiv.) in THF ($C = 2.0 \times 10^{-5}$ mol L^{-1}). Black bars: **TPT-2-PAo** with various metal ions; red bars: **TPT-2-PAo** with different competing metal ions and Al^{3+}(A), Cr^{3+} (B), and Fe^{3+} (C).



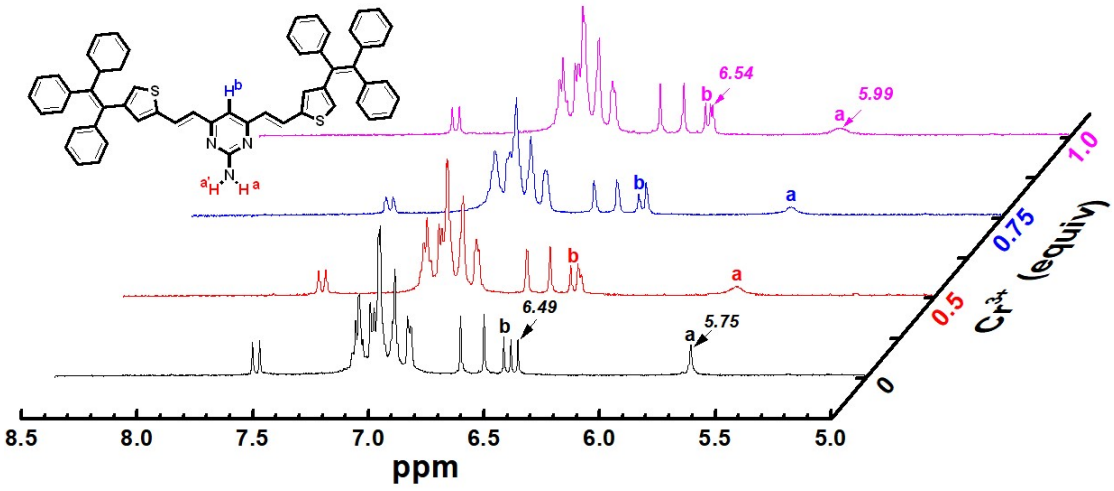
(A) (B)

Figure S19. Absorption spectral changes of **BTPT-2-PAo** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) by stimulation with metal ions: (A) Al^{3+} (inset: the effect of Al^{3+} concentration on absorption intensity at 467 nm), and (B) Fe^{3+} (inset: the effect of Fe^{3+} concentration on absorption intensity at 465 nm).

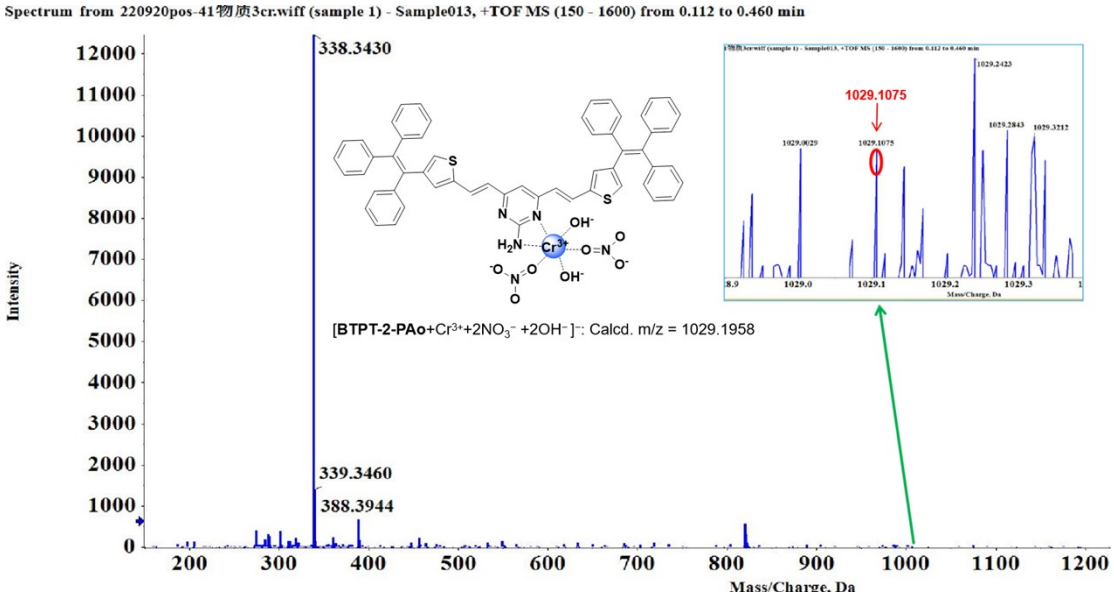


(A) (B)

Figure S20. PL intensity changes of **BTPT-2-PAo** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) by stimulation with metal ions: (A) Al^{3+}, and (B) Fe^{3+} (inset: the effect of Cr^{3+} concentration on emission intensities of **BTPT-2-PAo** at 482 nm. I_0: initial emission intensity of **BTPT-2-PAo**, I: emission intensity of **BTPT-2-PAo** in the presence of Al^{3+} and Fe^{3+}).

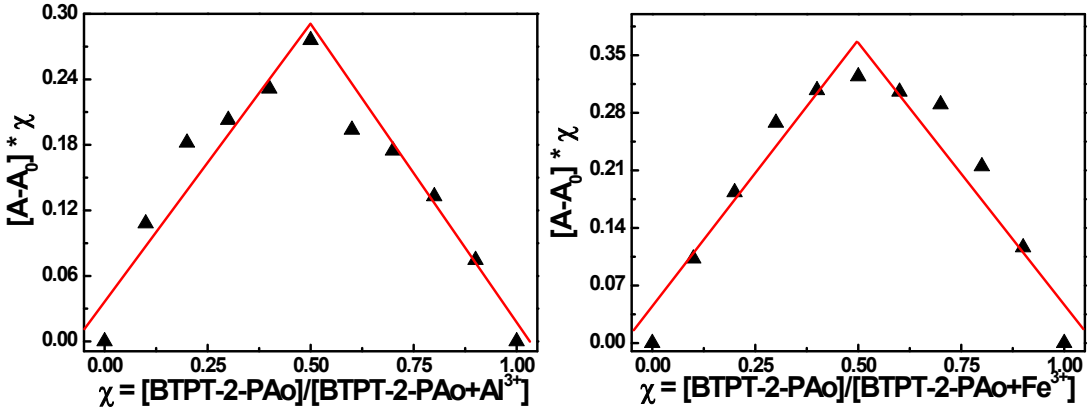


（A）



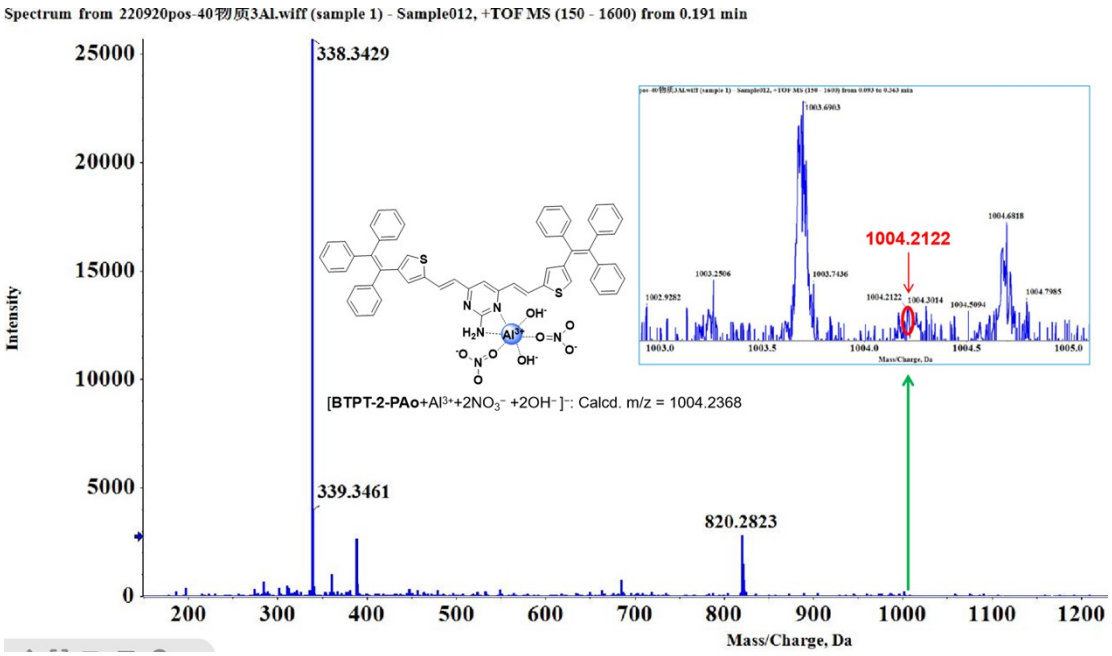
(B)

Figure S21. Changes in ^{1}H NMR spectra of **BTPT-2-PAo** stimuli by different Cr^{3+} concentration in THF-d_8 (A), and HRMS-ESI spectra of [**BTPT-2-PAo**+Cr^{3+}] in acetonitrile (B).

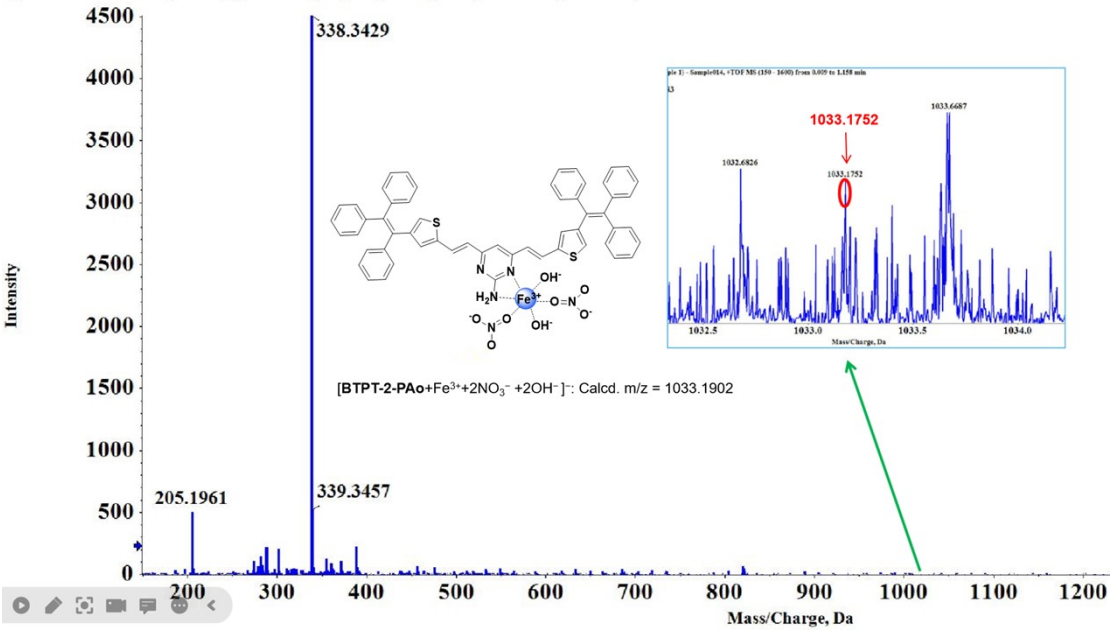


(A) (B)

Figure S22. Job's plot for **BTPT-2-PAo** with Al^{3+} (A), and Fe^{3+} (B).



(A)



(B)

Figure S23. HRMS-ESI spectra of [**BTPT-2-PAo** + Al^{3+}] (A) and [**BTPT-2-PAo** + Fe^{3+}] (B) in acetonitrile.

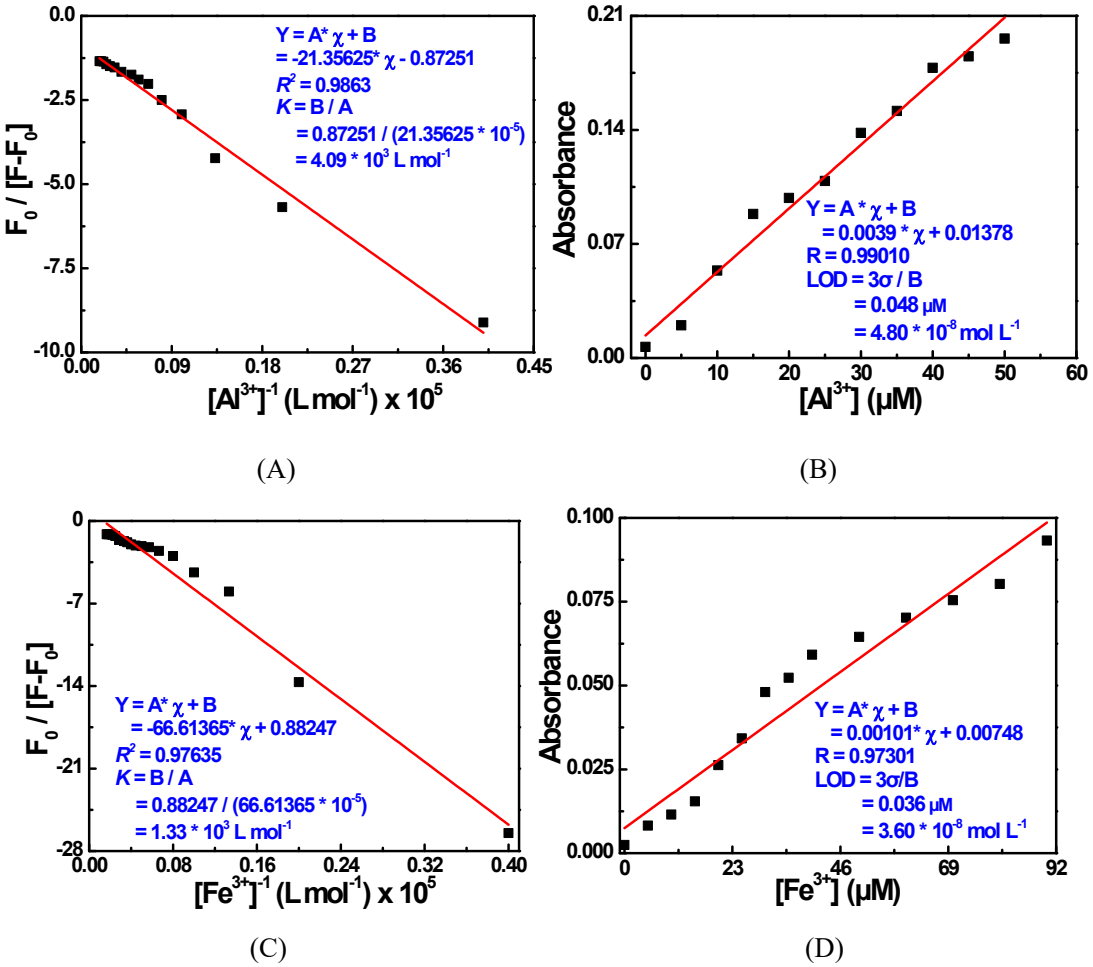
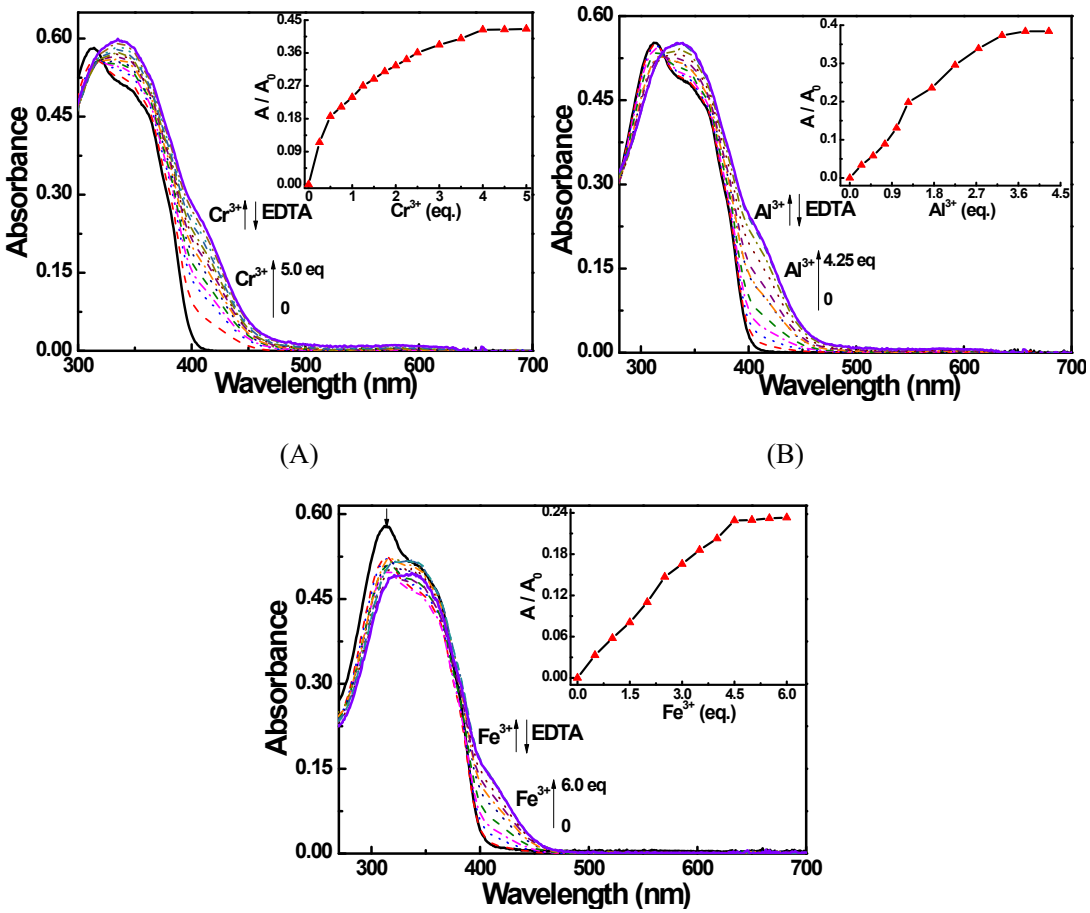


Figure S24. (A) The binding constant for **BTPT-2-PAo** with Al^{3+} was calculated to be 4.09×10^3 L mol^{-1}, (B) the limit of detection (LOD), LOD is 4.80×10^{-8} mol L^{-1}, (C) The binding constant for **BTPT-2-PAo** with Fe^{3+} was calculated to be 1.33×10^3 L mol^{-1}, and (D) the limit of detection (LOD), LOD is 3.60×10^{-8} mol L^{-1}.



(A) (B)

(C)

Figure S25. Absorption spectral changes of **TPT-2-PAo** by stimulation with metal ions in THF (C = 2.0 × 10^{-5} mol L^{-1}): (A) Cr^{3+}, (B) Al^{3+}, and (C) Fe^{3+}((inset: the effect of Cr^{3+} concentration on absorption intensity of **TPT-2-PAo** at 410 nm, A_0: initial absorption intensity of **TPT-2-PAo**, A: absorption intensity of **BTPT-2-PAo** in the presence of M^{3+}).

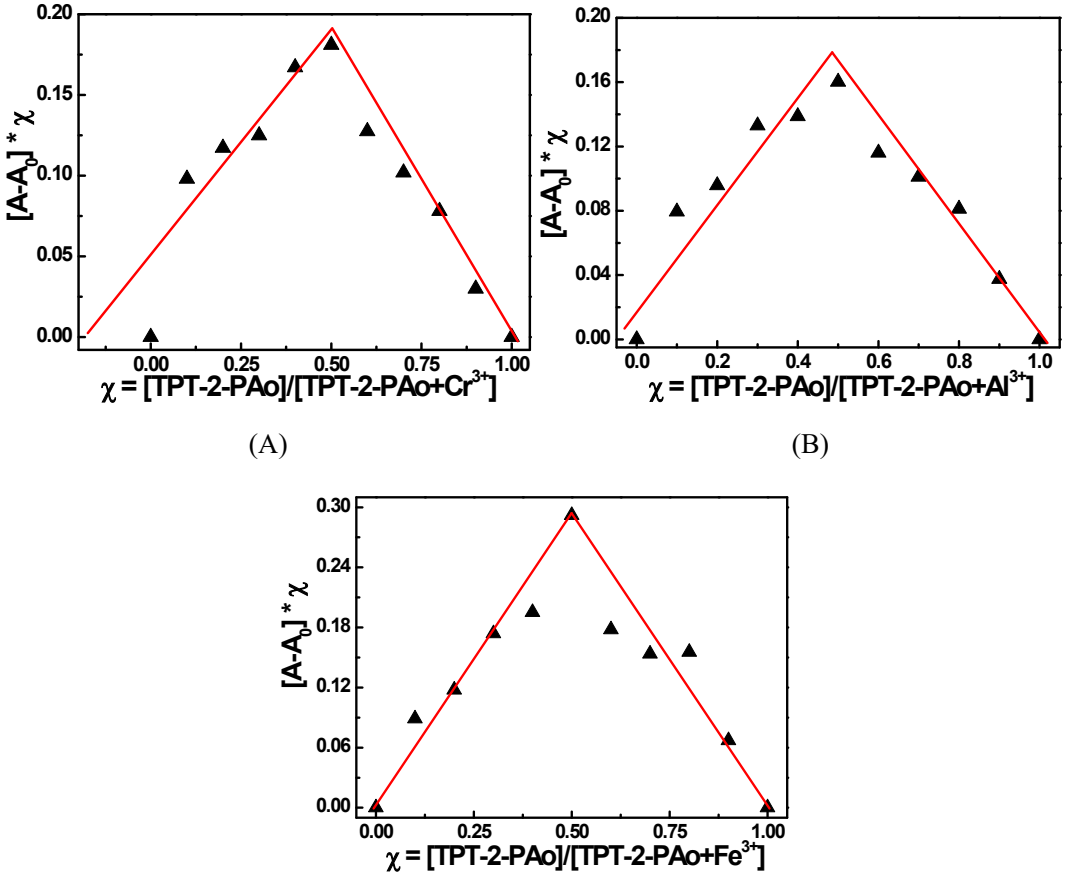
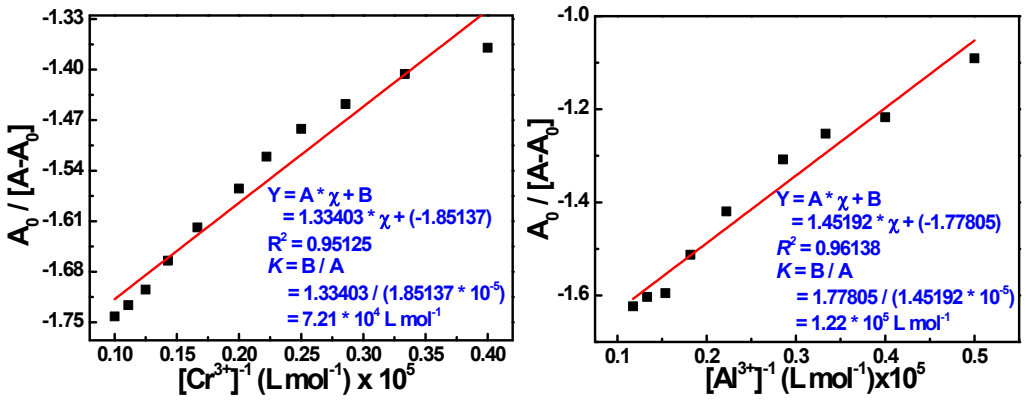
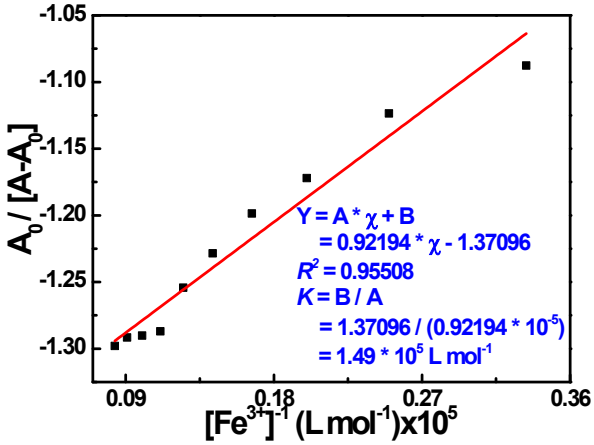


Figure S26. Job's plot for **TPT-2-PAo** with Al^{3+} (A), Cr^{3+} (B), and Fe^{3+} (C).



(A) (B)



(C)

Figure S27. Hildebrand-Benesi plot based on the 1:1 ratio between **TPT-2-PAo** and M^{3+} (M = Al, Cr, Fe): (A) the binding constant for **TPT-2-PAo** with Cr^{3+} was calculated to be 7.21×10^4 L mol^{-1}; (B) the binding constant for **TPT-2-PAo** with Al^{3+} was calculated to be 1.22×10^5 L mol^{-1}; (C) the binding constant for **TPT-2-PAo** with Fe^{3+} was calculated to be 1.49×10^5 L mol^{-1}.

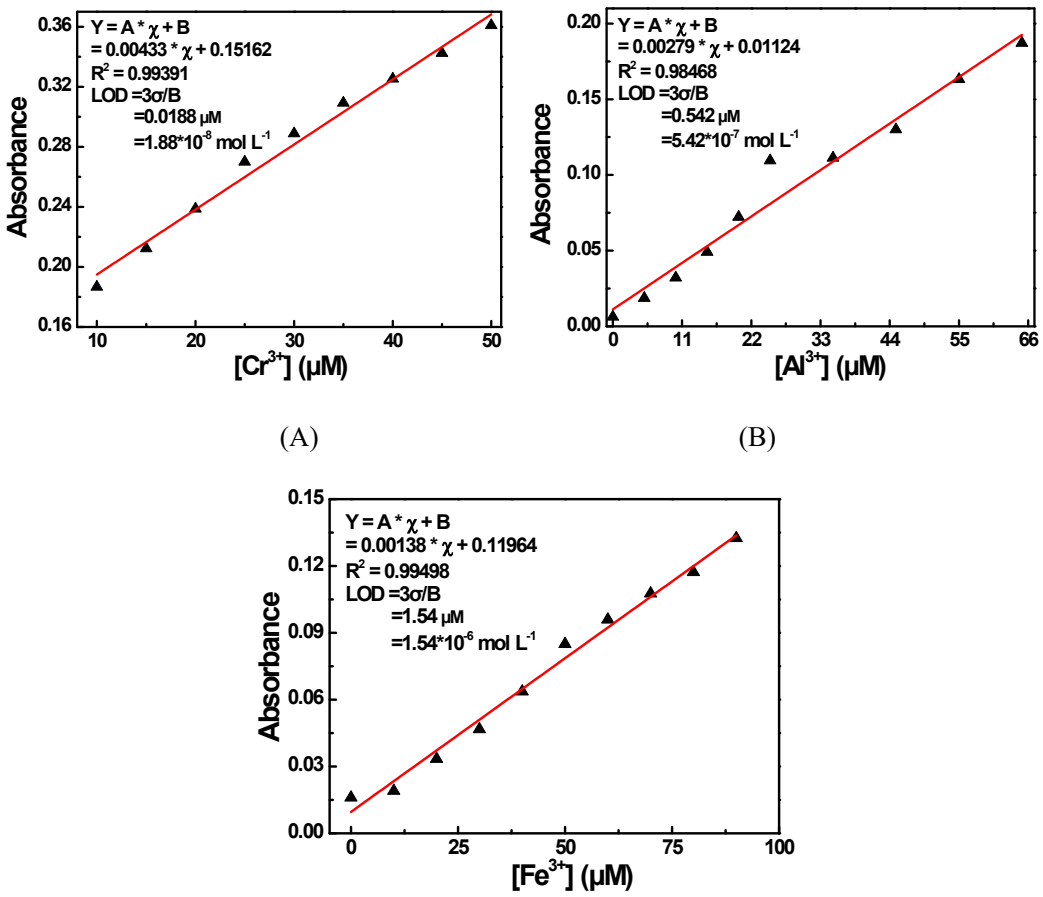
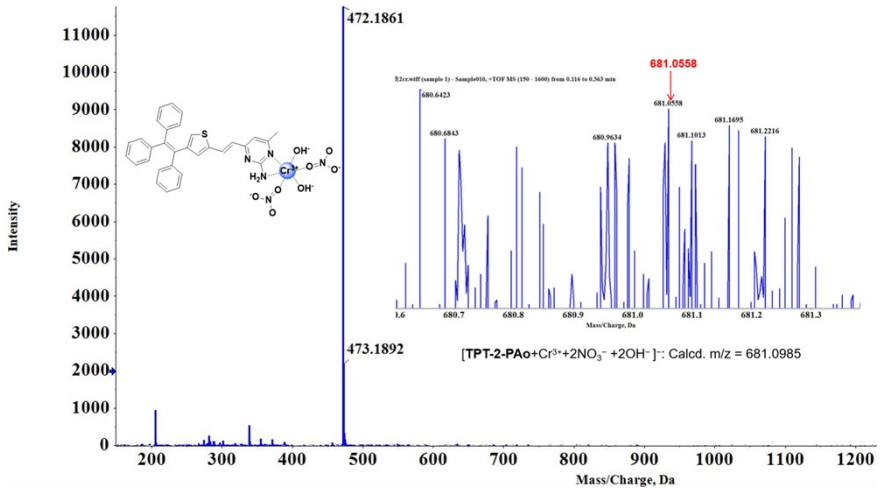
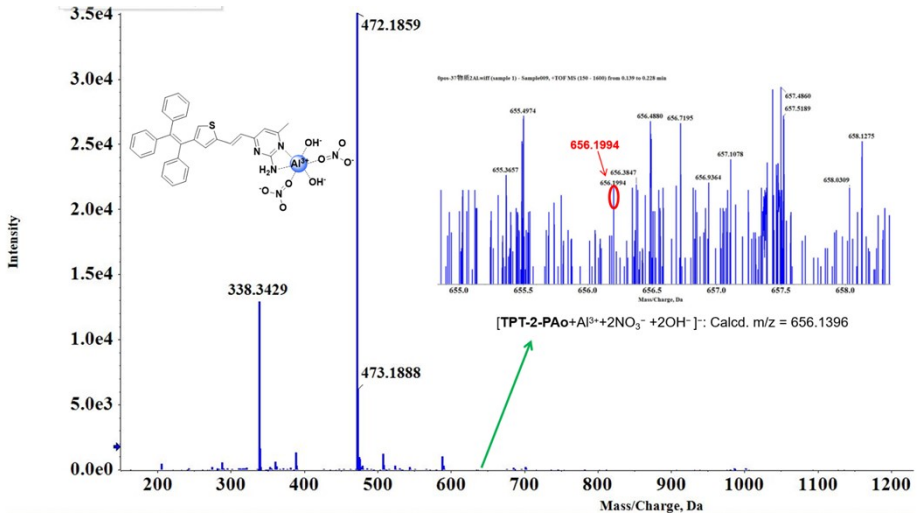


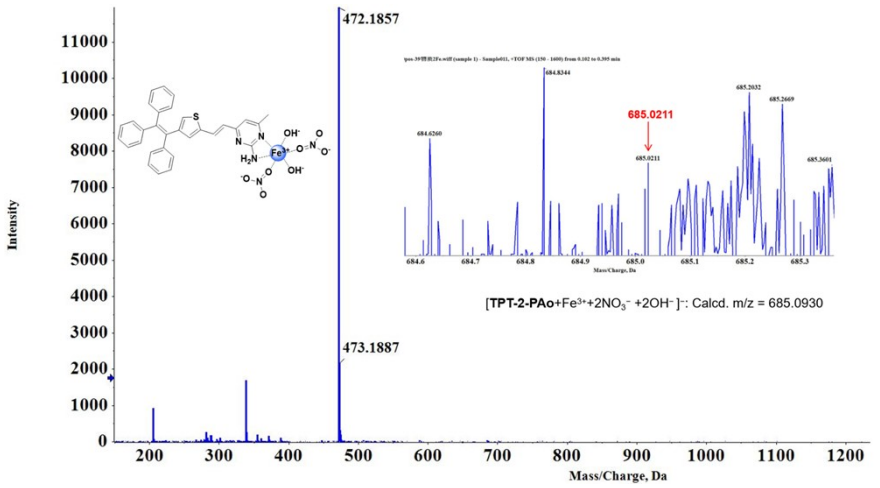
Figure S28. (A) The limit of detection (LOD) of **TPT-2-PAo** with Cr^{3+}, LOD is 1.88×10^{-8} mol L^{-1}; (B) the limit of detection (LOD) of **TPT-2-PAo** with Al^{3+}, LOD is 5.42×10^{-7} mol L^{-1}; (C) the limit of detection (LOD) of **TPT-2-PAo** with Fe^{3+}, LOD is 1.54×10^{-6} mol L^{-1}.



(A)



(B)



(C)

Figure S29. HRMS-ESI spectra of [**TPT-2-PAo**+M^{3+}] in acetonitrile: (A) [**TPT-2-PAo**+Cr^{3+}], (B) [**TPT-2-PAo**+Al^{3+}], and (C) [**TPT-2-PAo**+Fe^{3+}].

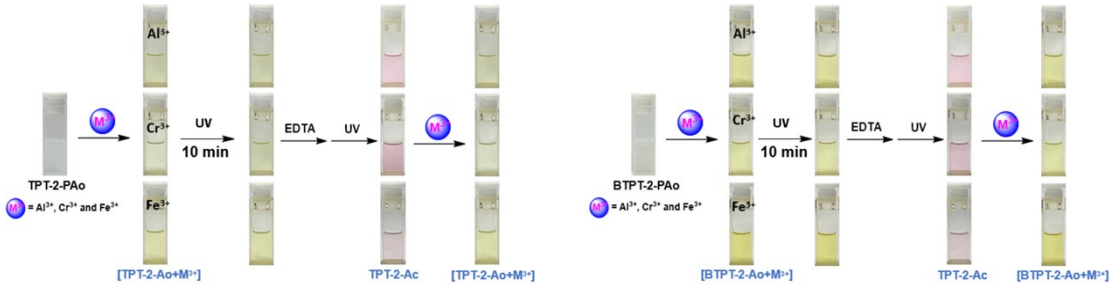


Figure S30. The color changes of **TPT-2-PAo** and **BTPT-2-PAo** under various stimuli including UV, EDTA and metal ions.

Table S1. The characteristics of **TPT-2-PAo** in different solvents.

TPT-2-PAo	*n*-hex	EA	THF	DCM	DMSO	DMF	MeCN	MeOH
Δf^a	0.001	0.201	0.21	0.218	0.263	0.274	0.307	0.309
λ_{abs} (nm)^b	315	311	320	316	314	311	310	314
λ_{em} (nm)^c	480	484	470	523	505	487	532	563
Stokes (nm)^d	165	173	150	207	191	176	222	249
Φ^e	0.034	0.014	0.009	0.006	0.014	0.01	0.003	0.015
ε (mol^{-1} L cm^{-1})^f	3.3× 10^4	3.2×10^4	2.7×10^4	3.0×10^4	3.1×10^4	3.1×10^4	2.9×10^4	3.1×10^4

[a] Directed polarizability (Δf); [b] maximum absorption wavelength; [c] maximum emission wavelength; [d] Stokes displacement (nm); [e] fluorescence quantum yield; [f] molar extinction coefficient.

Table S2. The characteristics of **BTPT-2-PAo** in different solvents.

BTPT-2-PAo	*n*-hex	EA	THF	DCM	DMSO	DMF	MeCN	MeOH
Δf^a	0.001	0.201	0.21	0.218	0.263	0.274	0.307	0.309
λ_{abs}(nm)^b	309	312	314	311	315	312	314	313
λ_{em}(nm)^c	469	479	482	518	500	499	531	544
Stokes(nm)^d	160	167	168	207	185	187	217	231
Φ^e	0.043	0.065	0.077	0.053	0.055	0.034	0.038	0.017
ε (mol^{-1} L cm^{-1})^f	5.5×10^4	5.8×10^4	5.9×10^4	5.7×10^4	5.6×10^4	5.3×10^4	5.2×10^4	5.6×10^4

[a] Directed polarizability (Δf); [b] maximum absorption wavelength; [c] maximum emission wavelength; [d] Stokes displacement (nm); [e] fluorescence quantum yield; [f] molar extinction coefficient.

Table S3. Photophysical properties of **TPT-2-PAo** aggregates at different pH.

pH	1	2	3	4	5	6	7	8	9	10	11
λ_{abs} (nm)[a]	348	344	344	337	337	337	313	313	314	313	312
λ_{em} (nm)[b]	645	639	637	627	628	626	470	481	485	504	506
Stokes (nm)[c]	297	295	293	290	291	289	157	168	171	191	194
Φ[d]	0.001	0.007	0.01	0.043	0.041	0.048	0.009	0.024	0.021	0.028	0.034
ε (mol^{-1} L cm^{-1})[e]	3.6×10^4	3.3×10^4	3.4×10^4	3.4×10^4	3.3×10^4	3.1×10^4	2.8×10^4	3.1×10^4	3.4×10^4	3.7×10^4	4.6×10^4

[a] Maximum absorption wavelength; [b] maximum emission wavelength; [c] Stokes displacement (nm); [d] fluorescence quantum yield; [e] molar extinction coefficient.

Table S4. Photophysical properties of **BTPT-2-PAo** aggregates at different pH.

pH	1	2	3	4	5	6	7	8	9	10	11
λ_{abs} (nm)[a]	465	465	465	465	463	465	313	313	313	313	313
λ_{em} (nm)[b]	606	607	630	630	620	621	482	485	489	493	493
Stokes (nm)[c]	141	142	165	165	157	156	169	172	176	180	180
Φ[d]	0.003	0.009	0.005	0.008	0.012	0.011	0.077	0.069	0.064	0.061	0.075
ε (mol^{-1} L cm^{-1})[e]	4.6 × 10^4	4.7 × 10^4	4.5 × 10^4	4.6 × 10^4	4.5 × 10^4	4.5 × 10^4	5.3 × 10^4	5.4 × 10^4	5.6 × 10^4	5.9 × 10^4	6.6 × 10^4

[a] Maximum absorption wavelength; [b] maximum emission wavelength; [c] Stokes displacement (nm); [d] fluorescence quantum yield; [e] molar extinction coefficient.

Table S5. Symbolic Z-Matrix of **TPT-2-PAo**.

C	-7.41174	0.11846	-0.66001
C	-7.13019	-1.18151	-0.23571
C	-5.81689	-1.64744	-0.2311
C	-4.75699	-0.81675	-0.63003
C	-5.05601	0.48352	-1.06823
C	-6.36913	0.94652	-1.08212
C	-3.3615	-1.33065	-0.62751
C	-3.18736	-2.69742	-1.18708
C	-2.31031	-0.60248	-0.14826
C	-2.50613	0.63672	0.65453
C	-0.9022	-0.99395	-0.37676
C	-1.78337	1.804	0.36052
C	-1.9662	2.96372	1.11141
C	-2.86082	2.9715	2.18348
C	-3.56915	1.8101	2.4991
C	-3.39288	0.65438	1.74209
C	-2.45203	-3.67382	-0.49623
C	-2.28698	-4.95047	-1.02832
C	-2.85629	-5.27603	-2.26126
C	-3.60505	-4.31931	-2.95033
C	-3.77839	-3.04542	-2.41242
C	-0.53306	-2.13702	-1.05317
S	1.18213	-2.34309	-1.15044
C	1.44991	-0.86346	-0.23488
C	0.24857	-0.28061	0.09452
C	2.76071	-0.36772	0.1053
C	3.94052	-0.94456	-0.20562
C	5.26421	-0.43071	0.13895
N	6.29465	-1.19964	-0.25773
C	7.52646	-0.75446	0.04838
N	7.83737	0.36795	0.72058
C	6.80036	1.12778	1.10788
C	5.48253	0.77091	0.83421

C	7.14045	2.38801	1.85661
N	8.57658	-1.51072	-0.40202
H	-8.43573	0.48101	-0.66929
H	-7.93461	-1.83533	0.08976
H	-5.60159	-2.66177	0.09113
H	-4.24907	1.13008	-1.39607
H	-6.57957	1.9549	-1.42746
H	-1.08214	1.79858	-0.46845
H	-1.40835	3.86154	0.86008
H	-2.99991	3.87361	2.77248
H	-4.25814	1.80298	3.33905
H	-3.94694	-0.24606	1.98589
H	-2.00611	-3.4201	0.45998
H	-1.71475	-5.69269	-0.47898
H	-2.72456	-6.27049	-2.67804
H	-4.05722	-4.56651	-3.90683
H	-4.36724	-2.30451	-2.94485
H	-1.19016	-2.86727	-1.50424
H	0.18839	0.6384	0.664
H	2.74514	0.56618	0.66378
H	3.96453	-1.87941	-0.76107
H	4.66353	1.40162	1.15712
H	6.24301	2.93636	2.15535
H	7.72463	2.14859	2.75192
H	7.76223	3.04029	1.23329
H	9.46774	-1.34407	0.04284
H	8.36269	-2.46503	-0.6537

Table S6. Total energies of **TPT-2-PAo**.

Zero-point correction	0.479514 (Hartree/Particle)
Thermal correction to Energy	0.509779
Thermal correction to Enthalpy	0.510724
Thermal correction to Gibbs Free Energy	0.413522
Sum of electronic and zero-point Energies	-1758.475125
Sum of electronic and thermal Energies	-1758.444860
Sum of electronic and thermal Enthalpies=	-1758.443916
Sum of electronic and thermal Free Energies=	-1758.541117

Table S7. Symbolic Z-Matrix of **TPT-2-PAc**.

C	1.85442	1.83709	0
C	2.78108	2.51303	0.68862
C	3.53975	1.88071	1.59842
C	3.39922	0.57476	1.92624
C	2.51981	-0.08151	1.13192
C	1.74647	0.52073	0.21447
C	4.18359	-0.05026	2.85243
C	4.08165	-1.3901	3.05633
C	5.03357	0.57104	3.71945
C	4.82466	1.82484	4.19317
C	5.9857	-0.16911	4.33487
C	5.85691	2.64033	4.5002
C	5.66412	3.88101	4.97486
C	4.42055	4.34558	5.16331
C	3.38032	3.55471	4.86773
C	3.58243	2.3164	4.39056
C	2.89071	-1.96033	3.33126
C	2.75336	-3.2353	3.7312
C	3.79649	-4.05044	3.94735
C	5.04651	-3.61842	3.74246
C	5.31705	-2.2505	3.18802
C	6.48086	-1.45854	3.75869
S	7.36765	-2.08067	5.18415
C	7.25066	-0.93361	6.10307
C	6.49184	0.04212	5.56699
C	7.79598	-0.95857	7.33557
C	8.57796	-1.93814	7.83205
C	9.15696	-1.94514	9.05005
N	9.85196	-2.92614	9.45305
C	10.38496	-2.92914	10.60505
N	10.26196	-1.96214	11.41805
C	9.58696	-0.94714	11.08605
C	9.00096	-0.89814	9.88105

C	9.48296	0.15586	12.10905
N	11.06396	-3.94014	10.95805
H	1.23545	2.3399	-0.76133
H	2.93533	3.58571	0.48196
H	4.32104	2.51899	2.035
H	2.38574	-1.17288	1.16651
H	1.03273	-0.06829	-0.38695
H	6.90137	2.32861	4.32417
H	6.52973	4.52725	5.20065
H	4.25815	5.36256	5.55769
H	2.35318	3.92036	5.0324
H	2.68851	1.69719	4.20215
H	1.96398	-1.36021	3.32687
H	1.74237	-3.61735	3.9588
H	3.62563	-5.07562	4.31509
H	5.89551	-4.3032	3.90733
H	7.23322	-1.21322	2.96897
H	6.217	0.92373	6.16129
H	7.59393	-0.09887	8.00085
H	8.77668	-2.81859	7.19942
H	8.41096	-0.01214	9.60205
H	8.69496	0.89586	11.84405
H	9.22796	-0.24914	13.11505
H	10.44996	0.70286	12.18605
H	11.51496	-3.96914	11.90505
H	11.17896	-4.75614	10.30705
H	5.07295	-2.11736	4.22126

Table S8. Total energies of **TPT-2-PAc**.

Zero-point correction	0.480458 (Hartree/Particle)
Thermal correction to Energy	0.509974
Thermal correction to Enthalpy	0.510918
Thermal correction to Gibbs Free Energy	0.416849
Sum of electronic and zero-point Energies	-1758.445479
Sum of electronic and thermal Energies	-1758.415963
Sum of electronic and thermal Enthalpies=	-1758.415019
Sum of electronic and thermal Free Energies=	-1758.509088

Table S9. Symbolic Z-Matrix of **BTPT-2-PAo**.

C	-2.81395	-0.67442	0
C	-3.83061	-0.66347	-0.87299
C	-3.97323	0.36226	-1.72705
C	-3.12397	1.41325	-1.7495
C	-2.10596	1.36696	-0.8612
C	-1.95065	0.34999	0.00124
C	-3.25573	2.44593	-2.62726
C	-4.47232	2.79475	-3.12585
C	-2.14227	3.13334	-3.0093
C	-0.99323	2.44753	-3.25193
C	-2.20439	4.48034	-3.15034
C	0.23535	2.97894	-3.08141
C	1.36076	2.28664	-3.32564
C	1.2933	1.01936	-3.7515
C	0.0892	0.45519	-3.91672
C	-1.0248	1.16132	-3.66843
C	-4.59717	3.38681	-4.33284
C	-5.78341	3.76512	-4.83376
C	-6.9064	3.56407	-4.13313
C	-6.81592	2.98674	-2.92769
C	-5.62306	2.61016	-2.44171
C	-3.24467	5.29683	-2.90228
S	-2.98652	6.7177	-3.13492
C	-1.57075	6.59457	-3.50061
C	-1.20694	5.30234	-3.51674
C	-0.72157	7.60628	-3.76429
C	-1.01276	8.92211	-3.78242
C	-0.11276	9.91311	-3.95842
N	-0.47676	11.08311	-4.27642
C	0.37524	11.99911	-4.49042
N	1.62324	11.80111	-4.39642
C	2.08224	10.66811	-4.05842
C	1.20424	9.67611	-3.82342

C	3.40924	10.45211	-3.94942
N	-0.03476	13.15611	-4.81542
C	3.97485	9.28143	-3.5969
C	5.29195	9.01943	-3.50425
S	6.39194	9.95809	-3.75814
C	7.49044	9.03402	-3.47134
C	7.11586	7.79532	-3.11029
C	5.77367	7.8171	-3.14334
C	7.93328	6.76655	-2.77459
C	9.28405	6.95393	-2.80598
C	7.43609	5.55995	-2.39441
C	10.0791	5.94577	-3.25615
C	9.8095	8.13446	-2.38301
C	8.11749	4.76453	-1.54121
C	7.65673	3.56782	-1.14497
C	6.48091	3.11619	-1.60163
C	5.78623	3.87365	-2.46063
C	6.26209	5.06899	-2.84485
C	11.3503	5.7765	-2.83147
C	12.12698	4.76944	-3.26004
C	11.65288	3.88031	-4.14261
C	10.39407	4.01617	-4.57976
C	9.62906	5.02656	-4.13941
C	10.96515	8.6327	-2.87278
C	11.47636	9.80689	-2.4671
C	10.83319	10.53146	-1.54282
C	9.68143	10.06883	-1.03814
C	9.18287	8.89486	-1.45802
H	-2.68923	-1.51451	0.70272
H	-4.54093	-1.50805	-0.89713
H	-4.79822	0.27099	-2.45217
H	-1.37359	2.18833	-0.7801
H	-1.11344	0.35681	0.72049
H	0.37279	3.99176	-2.67061
H	2.34574	2.7531	-3.15738

H	2.21169	0.44524	-3.95513
H	0.01626	-0.58722	-4.26993
H	-1.9766	0.64176	-3.86931
H	-3.72348	3.56495	-4.98137
H	-5.83818	4.24721	-5.82513
H	-7.88283	3.88313	-4.53225
H	-7.72836	2.84739	-2.32452
H	-5.62659	2.20209	-1.41658
H	-4.20869	4.99453	-2.4706
H	-0.1928	4.97531	-3.78966
H	0.32243	7.30932	-3.9676
H	-2.06199	9.22562	-3.61797
H	1.56524	8.67411	-3.53942
H	4.07422	11.30917	-4.15264
H	0.65324	13.92811	-4.99842
H	-1.06176	13.35211	-4.90242
H	3.30168	8.44448	-3.33963
H	8.52754	9.37046	-3.60407
H	5.11827	6.9823	-2.86091
H	9.0722	5.08772	-1.09125
H	8.23755	2.95785	-0.43317
H	6.0974	2.13309	-1.28196
H	4.83101	3.50009	-2.8666
H	5.66723	5.60225	-3.60452
H	11.79344	6.43095	-2.06163
H	13.15541	4.65936	-2.87419
H	12.2849	3.0498	-4.49693
H	9.9918	3.29404	-5.31118
H	8.61653	5.08894	-4.57279
H	11.51587	8.12142	-3.67973
H	12.41486	10.18637	-2.90844
H	11.24256	11.49757	-1.20654
H	9.14711	10.65422	-0.26903
H	8.24815	8.56129	-0.97666

Table S10. Total energies of **BTPT-2-PAo**.

Zero-point correction	0.809478 (Hartree/Particle)
Thermal correction to Energy	0.861108
Thermal correction to Enthalpy	0.862052
Thermal correction to Gibbs Free Energy	0.711823
Sum of electronic and zero-point Energies	-3118.728500
Sum of electronic and thermal Energies	-3118.676870
Sum of electronic and thermal Enthalpies=	-3118.675926
Sum of electronic and thermal Free Energies=	-3118.826155

Table S11. Symbolic Z-Matrix of **BTBT-2-PAc**.

C	1.0775	1.94707	0
C	0.0495	1.18807	-0.412
C	-1.2025	1.67807	-0.528
N	-1.3645	2.98507	-0.227
C	-0.3475	3.75507	0.189
N	0.8825	3.23707	0.308
C	-2.2665	0.94807	-0.949
C	-3.0685	1.47807	-1.923
C	-2.4885	-0.30193	-0.458
N	-2.7085	2.54807	-2.681
C	-4.1835	0.81607	-2.306
C	-3.7785	-1.03893	-0.74
C	-3.5455	-2.49093	-1.007
C	-2.6135	-3.08493	-0.246
C	-1.8015	-2.33393	0.52
C	-1.7075	-0.99393	0.402
C	-3.6325	3.45407	-3.072
C	-3.3175	4.53107	-3.807
C	-2.0485	4.74007	-4.184
C	-1.1095	3.85907	-3.816
C	-1.4405	2.78707	-3.078
C	-4.7985	0.86007	-3.506
C	-5.7875	-0.02893	-3.733
C	-5.9755	-0.93793	-2.589
C	-4.8315	-0.19893	-1.428
C	-6.4755	-0.07393	-4.89
C	-7.4815	-0.91593	-5.204
C	-8.1615	-0.91293	-6.37
C	-9.1775	-1.77293	-6.577
C	-9.8535	-1.73493	-7.74
C	-9.4855	-0.88093	-8.603
C	-8.5215	-0.08793	-8.383
C	-7.8735	-0.09693	-7.294

S	-10.9035	-2.51993	-8.066
C	-17.69416	-9.78328	-9.97713
C	-16.72858	-8.89486	-10.26391
C	-16.23382	-8.00847	-9.3676
C	-16.90571	-7.99838	-8.1935
C	-17.87349	-8.87418	-7.87816
C	-18.26318	-9.79653	-8.76597
C	-15.2695	-7.09503	-9.68205
C	-14.70497	-6.20995	-8.8098
C	-14.69367	-7.0808	-10.91136
C	-14.52207	-6.50726	-7.49854
C	-14.11872	-5.09891	-9.31347
C	-14.44228	-5.78601	-11.64843
C	-13.34466	-5.88339	-12.66725
C	-12.87692	-7.07615	-13.05633
C	-13.28885	-8.20092	-12.45431
C	-14.12412	-8.2004	-11.40154
C	-14.54679	-5.56002	-6.53671
C	-14.36027	-5.85578	-5.24037
C	-14.13752	-7.12172	-4.86388
C	-14.10564	-8.08269	-5.79677
C	-14.2967	-7.77418	-7.0894
C	-13.12495	-4.36141	-8.77692
C	-12.60571	-3.37317	-9.53315
C	-13.26551	-3.30318	-10.84923
S	-14.4759	-4.61112	-10.68448
C	-11.58465	-2.54628	-9.22804
C	-8.1965	0.74707	-9.282
H	-12.6965	-4.5984	-7.79485
H	-11.27459	-1.82871	-10.00704
H	-11.2199	-3.22505	-7.27853
H	-9.4425	-2.48493	-5.782
H	-4.4865	1.53407	-4.318
H	-6.1855	0.67507	-5.648
H	-7.7895	-1.66093	-4.451

H	-15.49184	-4.1528	-10.62115
H	-5.4335	0.39207	-0.691
H	2.0925	1.51907	0.06
H	0.2915	0.15907	-0.726
H	-2.3605	3.46007	-0.277
H	-0.5215	4.81507	0.439
H	1.7245	3.86607	0.641
H	-4.2395	-3.07893	-1.625
H	-2.5125	-4.18293	-0.255
H	-1.0645	-2.85793	1.155
H	-0.8595	-0.54493	0.937
H	-4.6865	3.36507	-2.753
H	-4.0985	5.25707	-4.091
H	-1.7825	5.62307	-4.789
H	-0.0645	4.01007	-4.134
H	-0.6265	2.07807	-2.858
H	-18.047	-10.48951	-10.74768
H	-16.39039	-8.93219	-11.30985
H	-16.73095	-7.23536	-7.41934
H	-18.37784	-8.81861	-6.89842
H	-19.06927	-10.50861	-8.52663
H	-13.00382	-4.97119	-13.18245
H	-12.12338	-7.12948	-13.86066
H	-12.8352	-9.15684	-12.7731
H	-14.22447	-9.16679	-10.87663
H	-14.77507	-4.50801	-6.77874
H	-14.40492	-5.05834	-4.47969
H	-13.98349	-7.37069	-3.8006
H	-13.91201	-9.12768	-5.50062
H	-14.22104	-8.60469	-7.81334
H	-7.4025	1.41407	-9.123
H	-8.7185	0.77507	-10.192
H	-4.21111	-1.09698	0.23692
H	-15.31898	-5.65027	-12.24667

Table S12. Total energies of **BTPT-2-PAc**.

Zero-point correction	0.811868 (Hartree/Particle)
Thermal correction to Energy	0.861819
Thermal correction to Enthalpy	0.862763
Thermal correction to Gibbs Free Energy	0.719522
Sum of electronic and zero-point Energies	-3118.633682
Sum of electronic and thermal Energies	-3118.583731
Sum of electronic and thermal Enthalpies=	-3118.582787
Sum of electronic and thermal Free Energies=	-3118.726028