Supporting Information

Full-Colour Solvatochromic Fluorescence Emitted from A Semi-aromatic Imide Compound Based on ESIPT and Anion Formation

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1. Experimental Section

Synthesis of 3-acetylamino-N-cyclohexylphthalimide. 3-aminophthalic acid (0.50 g, 2.8 mmol) was dissolved in acetic anhydride (10 mL) and the solution was stirred at 80 °C under a nitrogen atmosphere for 4 h. After cooled to 20 °C, the mixture was kept in refrigerator overnight. Then white precipitate of 3-acetylamino-phthalic anhydride was filtered and dried under vacuum. To the solution of the precipitate (0.35 g, 2.1 mmol) in mixed solvent of anhydrous DMAc (4 ml) and o-xylene (6 mlL), cyclohexylamine (0.22 g, 2.2 mmol) was added dropwise with cooling and stirring. Then the solution was refluxed using a Dean-stark apparatus at 140 °C for 5 h. After cooling to 20 °C, the solution was added to excess water, and the precipitate was filtered and dried under vacuum. The crude product was purified by recrystallization from ethyl acetate / hexane to give white solid (0.30 g, 38%). For ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.18-1.45 (3H, br *m*, CH_2), 1.68-2.07 (5H, br *m*, CH_2), 2.11-2.23 (2H, br *m*, CH_2), 2.25 (3H, *s*, CH_3), 4.03 (1H, *m*, N-CH), 7.45(1H, *d*, aryl), 7.73 (1H, *t* aryl), 8.70 (1H, *d*, aryl), 9.58 (1H, br *s*, NH) (**Figure S4**).

HRMS (FAB) m/z $[M + H]^+$ calcd for $C_{16}H_{18}N_2O_3$ 287.1396; found 287.1390.

Anal. Calced for $C_{16}H_{18}N_2O_3$: C, 67.12; H, 6.34; N, 9.78; O, 16.76. Found: C, 67.11; H, 6.26; N, 9.81; O, 16.72.

Synthesis of 3-Trifluoroacetylamino-N-cyclohexylphthalimide. Compound 3 (0.50 g, 2.0 mmol) and sodium hydrogen carbonate (0.17g, 2.0 mmol) were added to 1,4-dioxane (4 mL), trifluoroacetic anhydride (0.35 mL, 2.5 mmol) was added dropwise with stirring, and the mixture was stirred for 30 min. The reaction solution with excess water was filtered and dried. White needle-like crystals were obtained by recrystallisation from hexane (yield, 65%). For ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] 1.25–1.42 (3H, br *m*, CH_2), 1.55–1.90 (5H, br *m*, CH_2), 2.09–2.22 (2H, br *m*, CH_2), 4.09 (1H, *m*, N-CH), 7.63 (1H, *d*, aryl), 7.75 (1H, *t* aryl), 8.68 (1H, *d*, aryl), 10.55 (1H, br *s*, NH) (**Figure S5**).
HRMS (FAB) m/z $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_3F_3$ 341.1113; found 341.1119.
Anal. Calced for $C_{16}H_{15}N_2O_3F_3$: C, 56.47; H, 4.44; N, 8.23; O, 14.10; F, 16.75. Found: C, 56.85; H, 4.19; N, 8.23; O+F, 30.73.

Synthesis of 3-Methansulfonylamino-N-cyclohexylphthalimide. Compound 3 (0.68 g, 2.8 mmol) and methansulfonyl chloride (0.38 g, 3.3 mmol) were dissolved in pyridine (0.7 mL) and stirred for 12 h. The white solid reprecipitated with water was filtered. The solid obtained was stirred with sodium hydroxide (0.1 g) in methanol (5 mL). When all the solids were dissolved, the solution was stirred dropwise into 1 N HCl aq (30 mL) and the precipitate was filtrated. White needle-like crystals were obtained by recrystallisation from ethanol (yield, 26%). For ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] 1.21–1.43 (3H, br *m*, CH_2), 1.62–1.91 (5H, br *m*, CH_2), 2.11–2.21 (2H, br *m*, CH_2), 3.15 (3H, *s*, S- CH_3), 4.07 (1H, *m*, N-CH), 7.51 (1H, *d*, aryl), 7.67 (1H, *t* aryl), 7.86 (1H, *d*, aryl), 8.89 (1H, br *s*, NH) (**Figure S6**).
HRMS (FAB) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_2O_4S$ 323.1066; found 323.1064.

2. Figures and Tables.

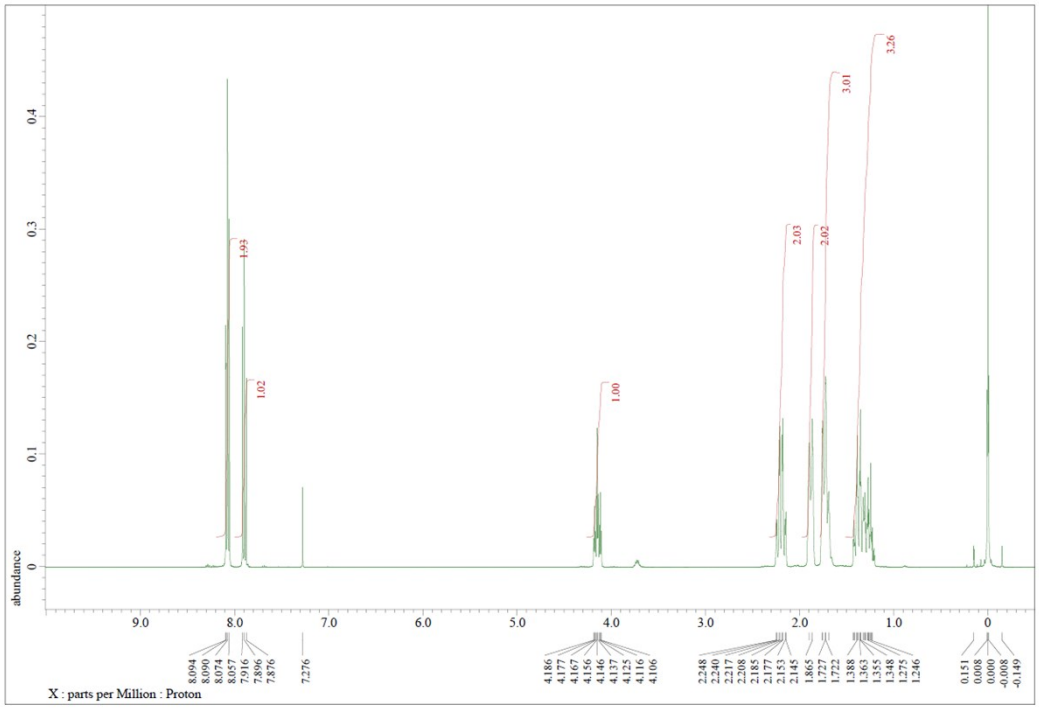


Figure S1. ^{1}H NMR spectrum of 3-Nitro-*N*-cyclohexylphthalimide (**2**).

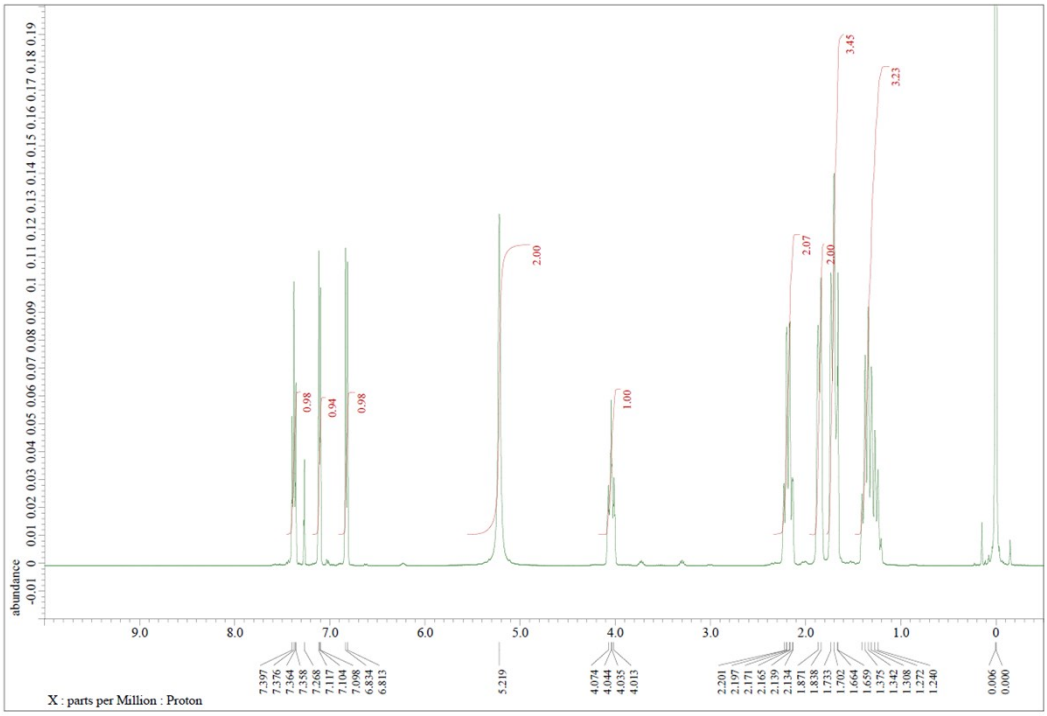


Figure S2. ^{1}H NMR spectrum of 3-Amino-*N*-cyclohexylphthalimide (**3**).

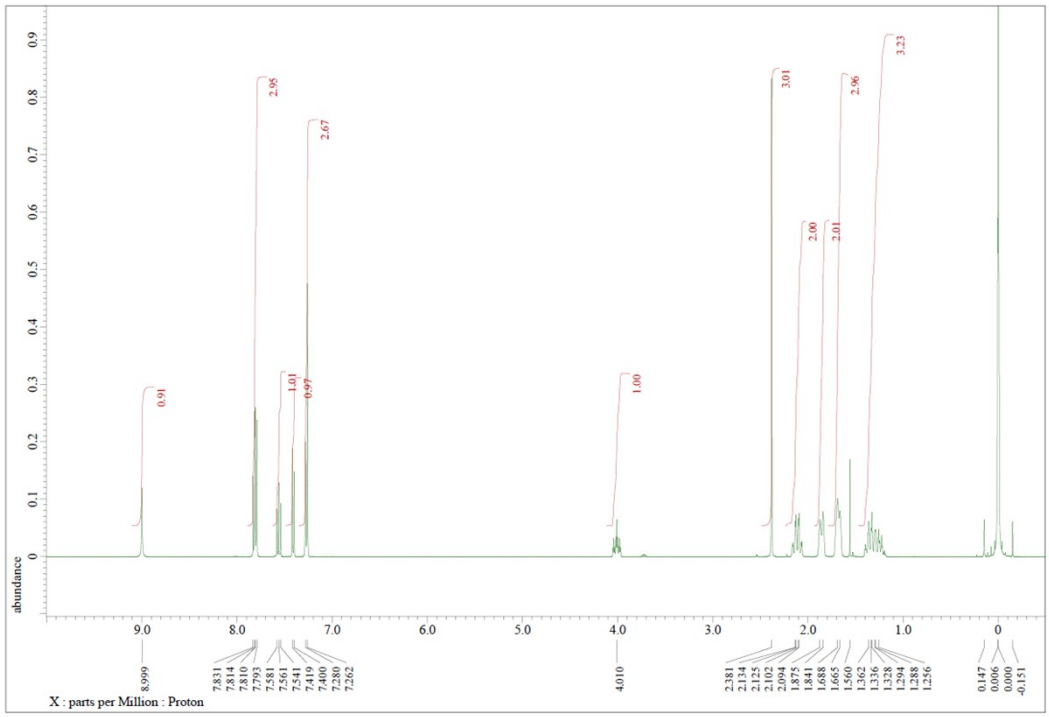


Figure S3. [1]H NMR spectrum of 3-Tosylamino-*N*-cyclohexylphthalimide (**3TsAPI**).

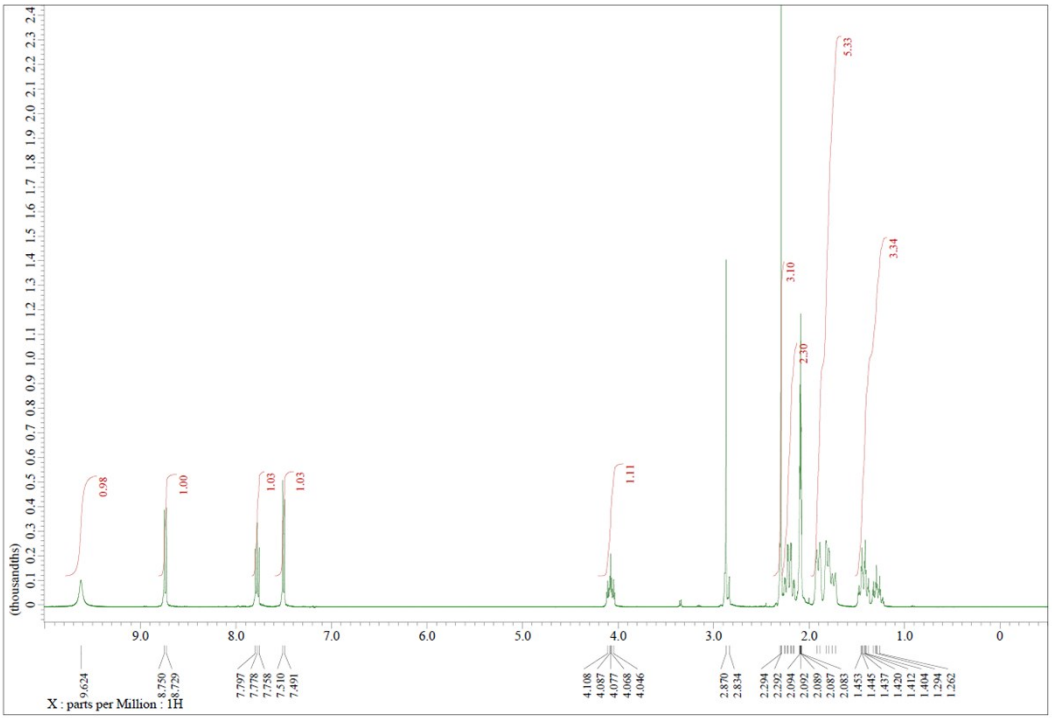


Figure S4. [1]H NMR spectrum of 3-acetylamino-*N*-cyclohexylphthalimide.

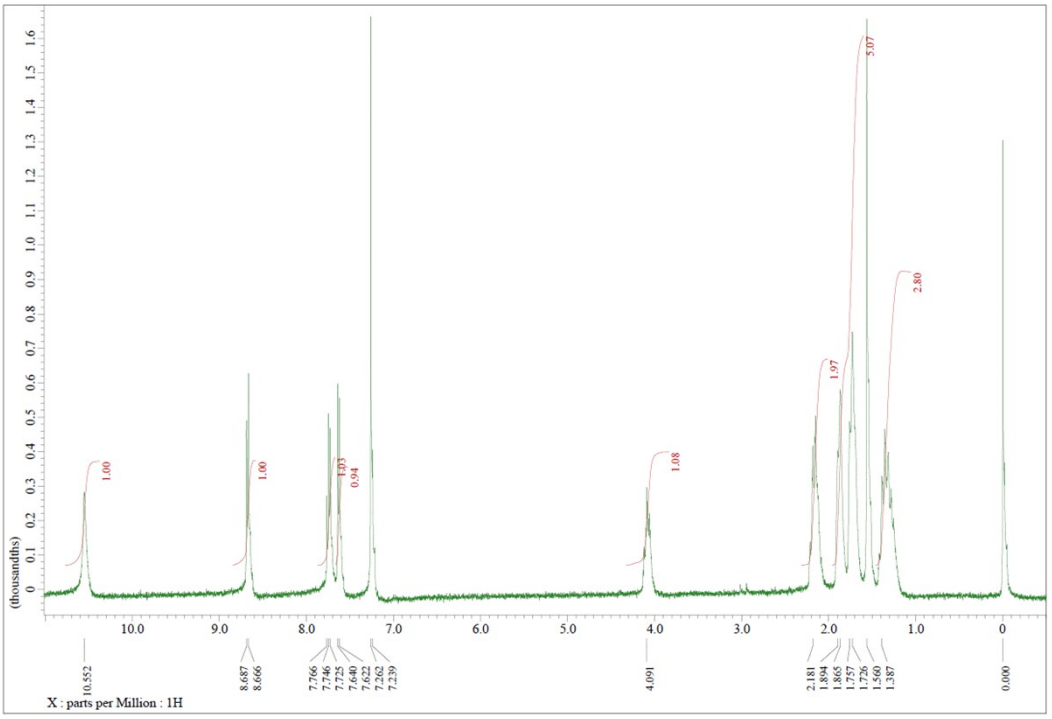


Figure S5. ^{1}H NMR spectrum of 3-Trifluoroacetylamino-*N*-cyclohexylphthalimide.

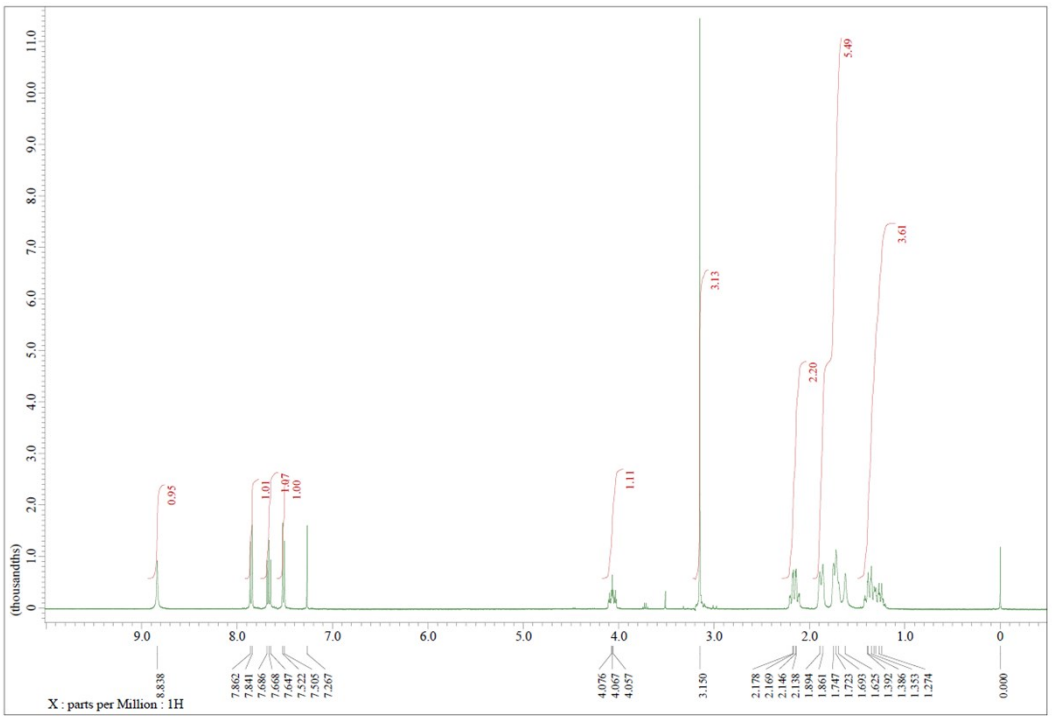


Figure S6. ^{1}H NMR spectrum of 3-Methansulfonylamino-*N*-cyclohexylphthalimide.

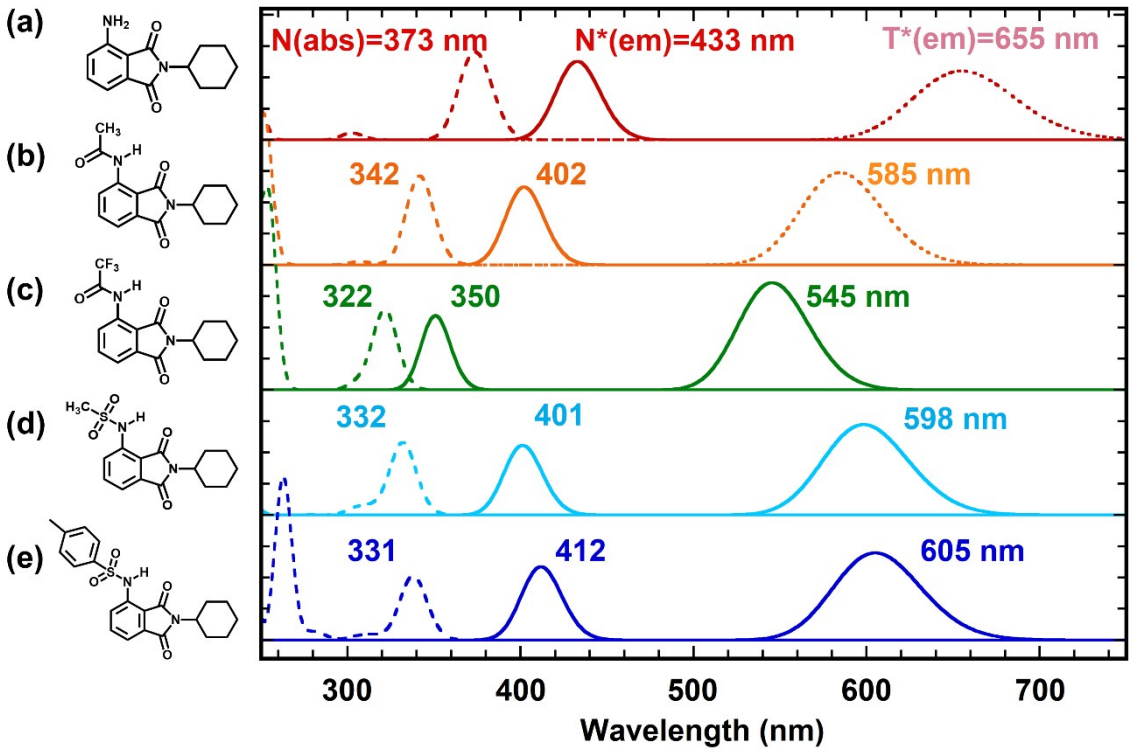


Figure S7. Chemical structures and calculated UV-vis absorption (331−373 nm) and emission (350−655 nm) spectra of *N*-cyclohexylphthalimides substituted with (a) amino (-NH_2), (b) acetyl (-$NHCOCH_3$), (c) trifluoroacetyl (-$NHCOCF_3$), or (d) methansulfonylamino (-$NHSO_2CH_3$) group and (e) tosylamino (−$NHSO_2C_6H_4$-CH_3, **3TsAPI**) in normal (N*) and tautomer form (T*) in toluene. The emission spectra of the T* state in (a) and (b) are drawn as dotted lines because they are energetically very unstable compared with the N* state.

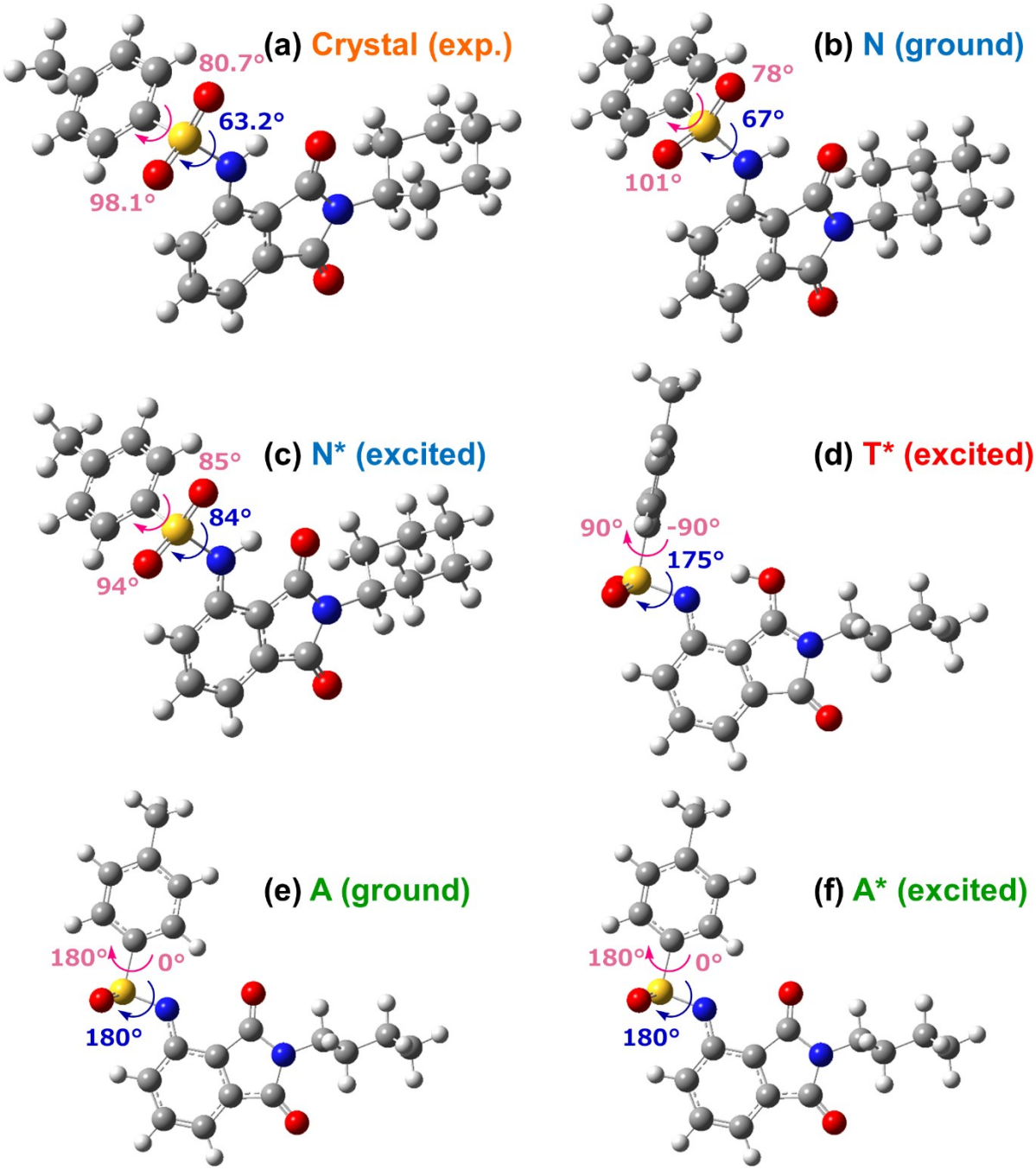


Figure S8. (a) Crystal structure (experimental) and the calculated optimized structures of **3TsAPI** in the (b) ground states (N), (c) one-electron excited state (N*), (d) proton transferred excited state (T*), (e) anion form in the ground state (A) and (f) that in the excited state (A*).

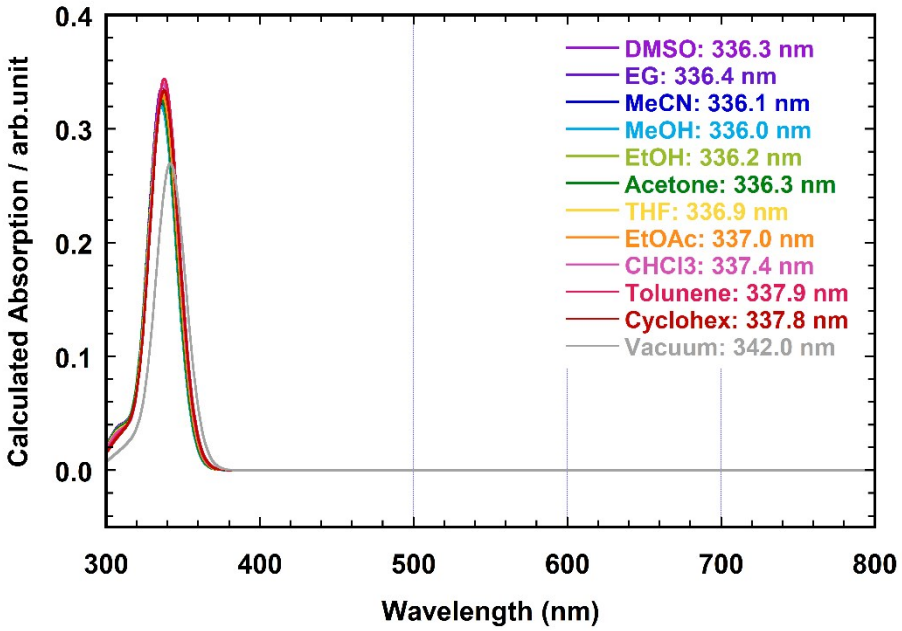


Figure S9. Calculated absorption spectra of **3TsAPI** in the ground states in various solutions and under vacuum condition.

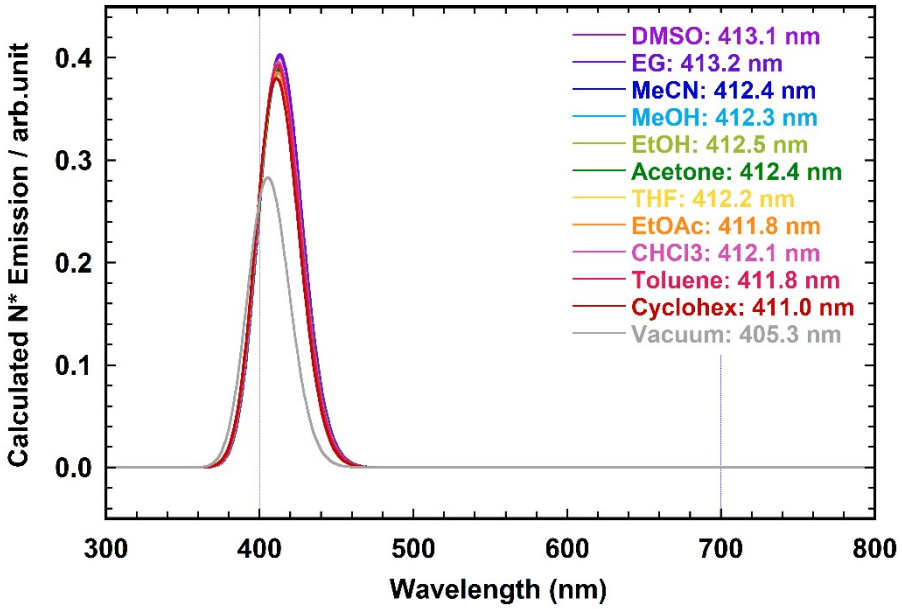
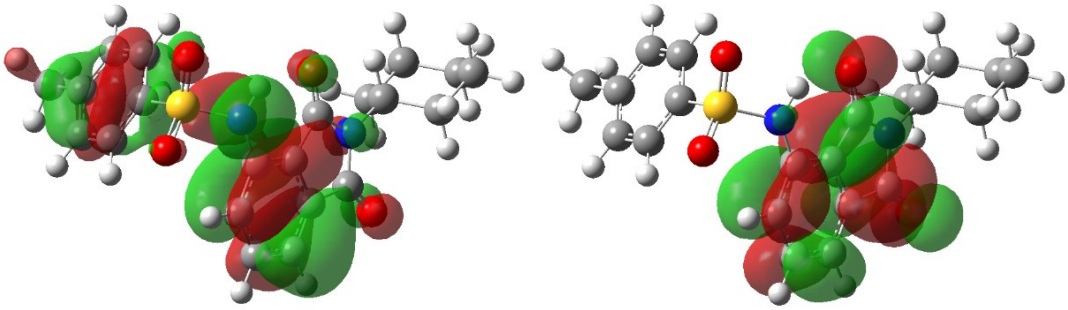
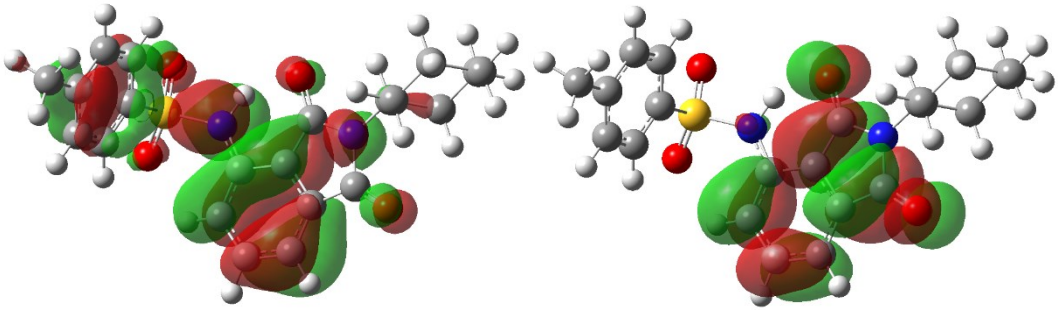


Figure S10. Calculated emission spectra of the N* form of **3TsAPI** in various solutions and under vacuum condition.

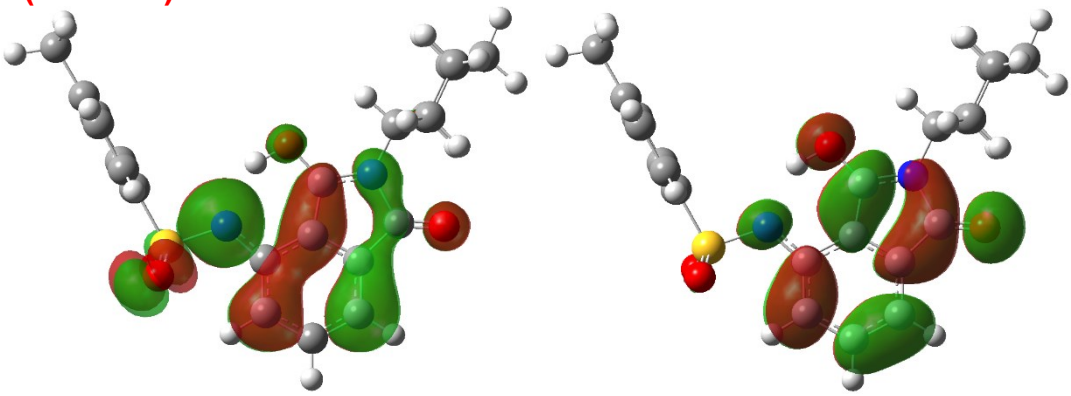
a) N (ground)



b) N* (excited)



c) T* (excited)



d) A* (excited)

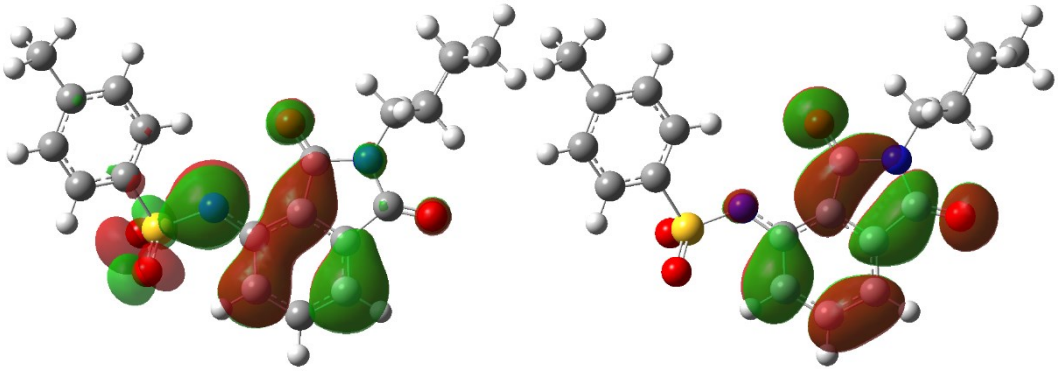


Figure S11. The calculated spatial distribution of the HOMOs (left) and LUMOs (right) of **3TsAPI** in the optimized geometries under vacuum for a) the ground state (N), (b) the excited state (N*), (c) the excited proton transferred state (T*), and (d) the excited anionic state (A*).

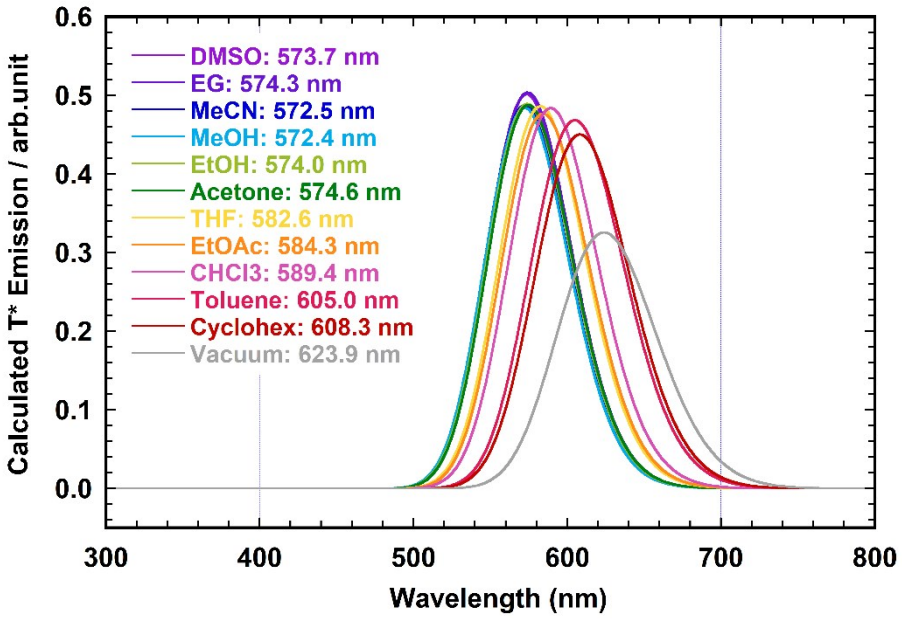


Figure S12. Calculated emission spectra of the T* form of **3TsAPI** in various solutions and under vacuum condition.

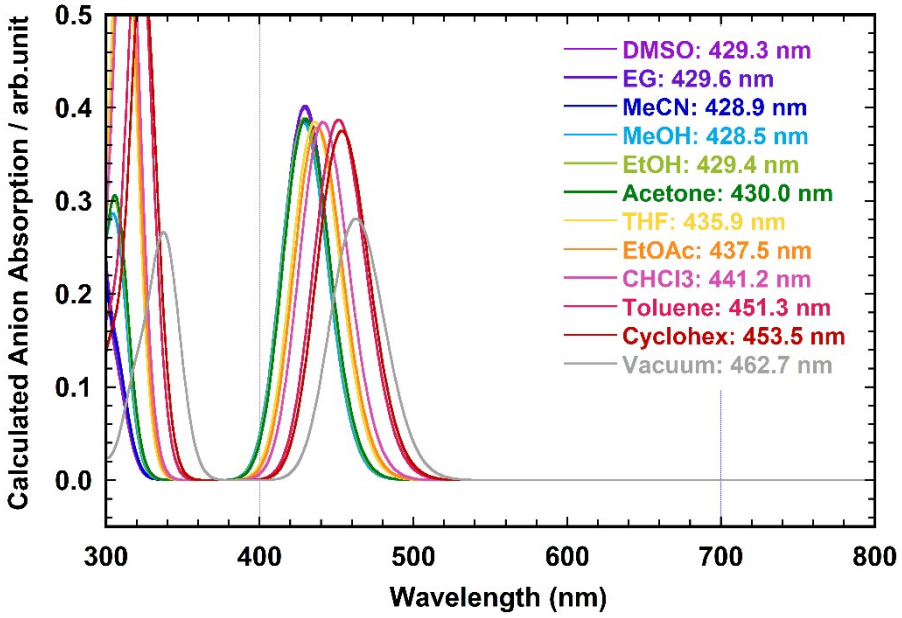


Figure S13. Calculated absorption spectra of the anion form of **3TsAPI** in various solutions and under vacuum condition.

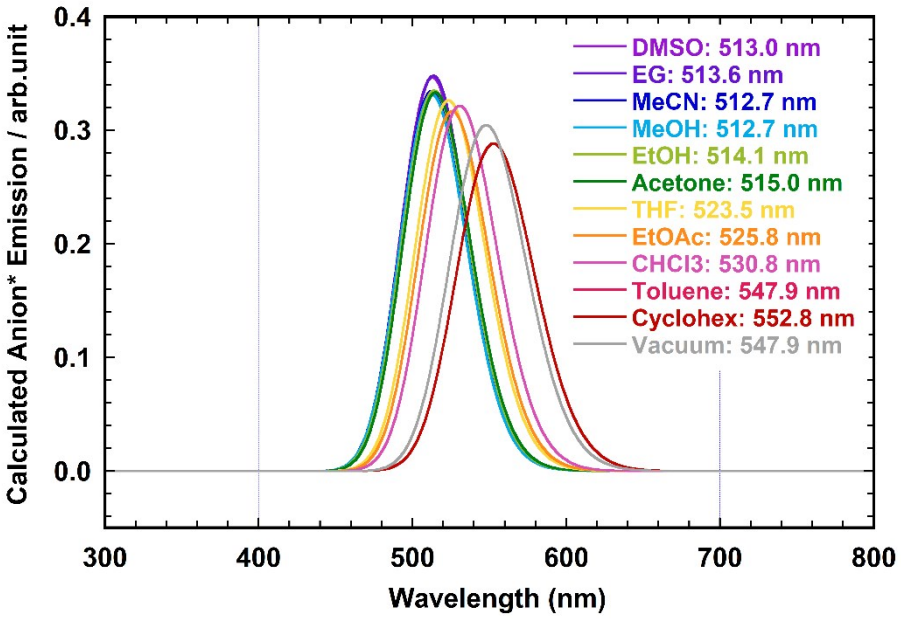


Figure S14. Calculated emission spectra of the anion form of **3TsAPI** in various solutions and under vacuum condition.

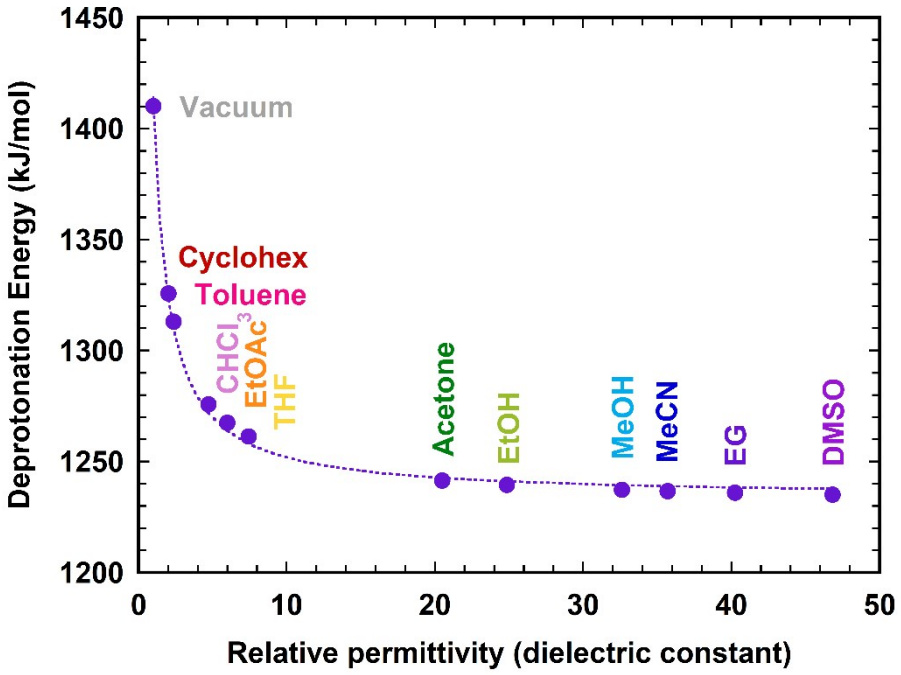


Figure S15. Relationship between the relative permittivity (dielectric constants) and the calculated deprotonation energy of **3TsAPI** in various solvents and under vacuum condition.

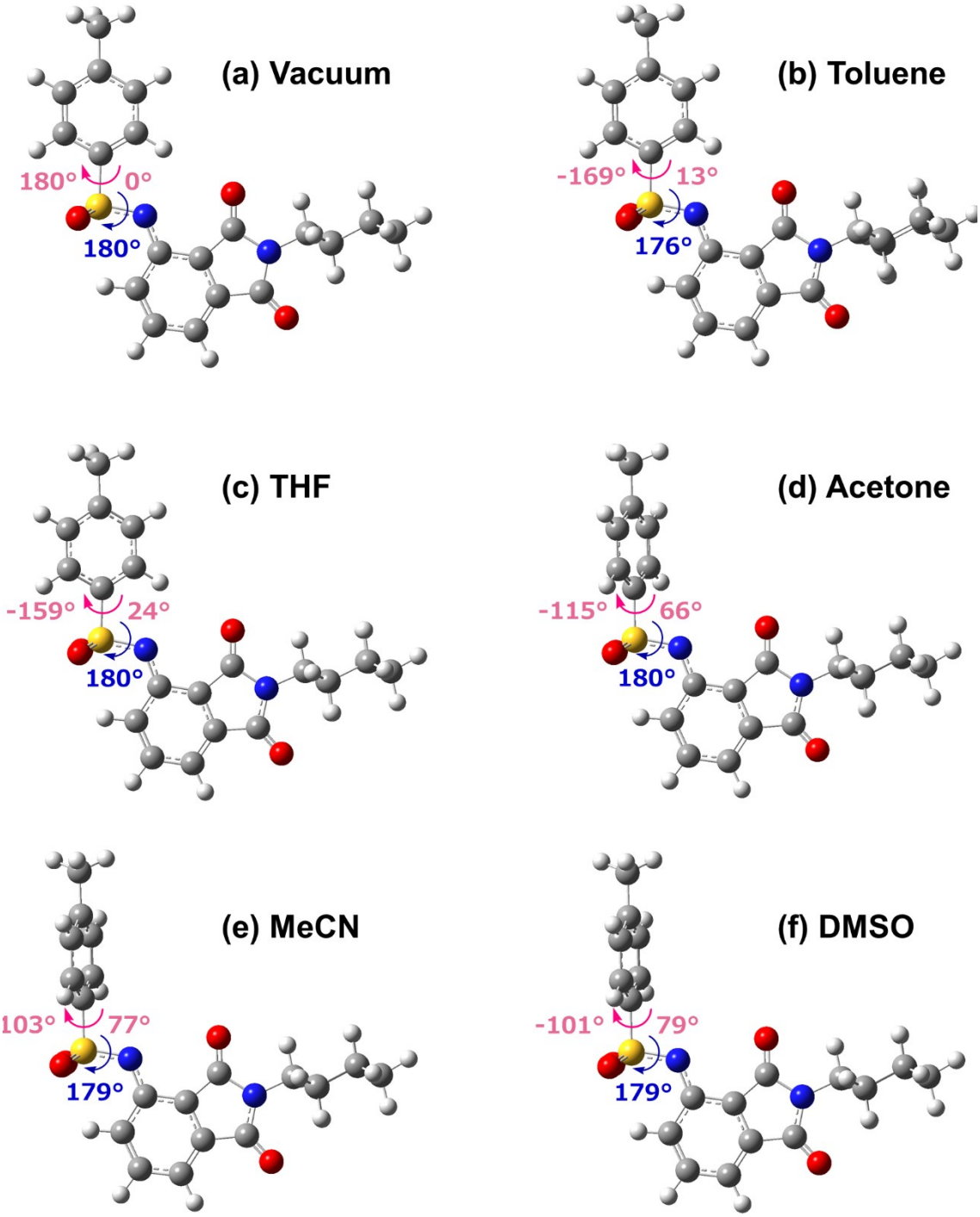


Figure S16. Optimized structures of the anion forms of **3TsAPI** in the ground state (a) under vacuum, (b) in toluene, (c) THF, (d) in acetone, (e) in MeCN, and (f) in DMSO.

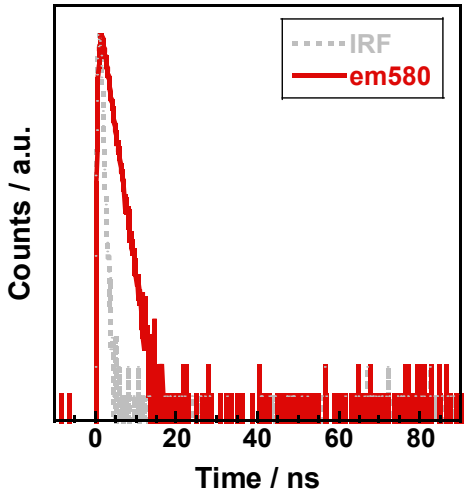


Figure S17. Fluorescence decay curve of **3TsAPI** in the crystalline state. The decay time was estimated as 1.1 ns. IRF is the instrument response function.

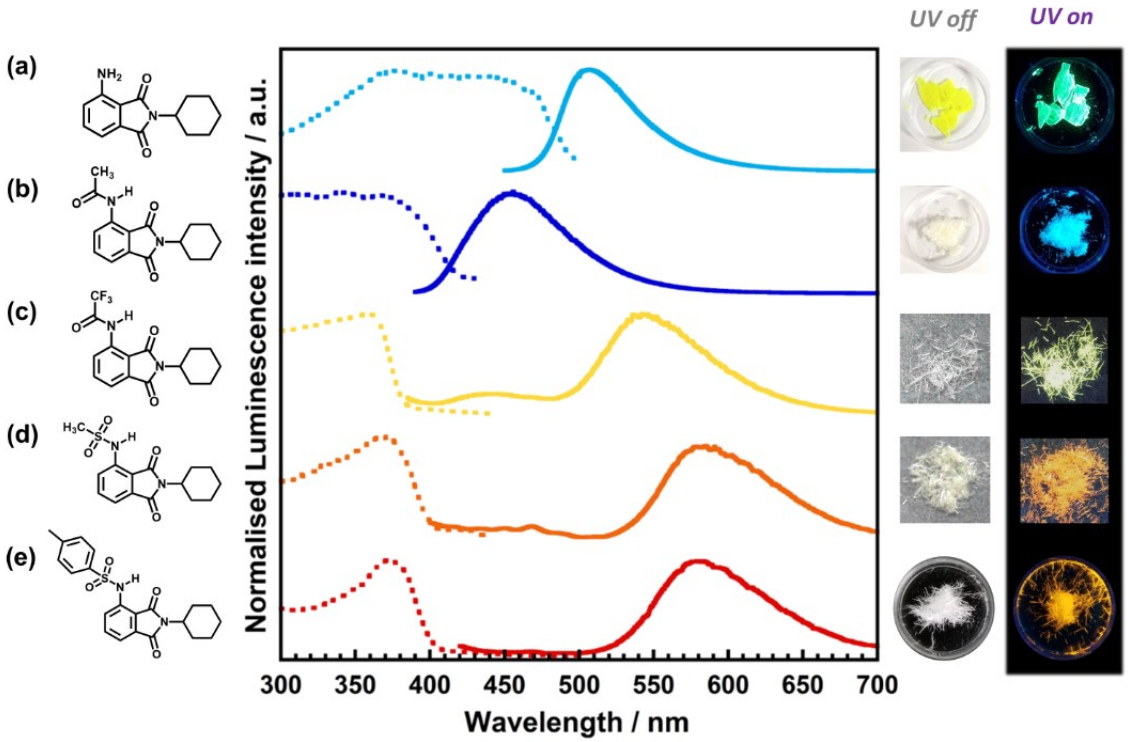
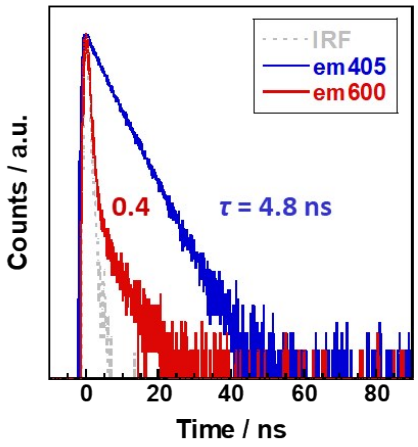


Figure S18. Chemical structures and excitation (dotted line)/emission (solid line) spectra of *N*-cyclohexylphthalimides substituted with (a) amino (-NH_2), (b) acetyl (-$NHCOCH_3$), (c) trifluoroacetyl (-$NHCOCF_3$), or (d) methansulfonylamino (-$NHSO_2CH_3$) group and (e) tosylamino (−$NHSO_2C_6H_4$- CH_3, **3TsAPI**) in the crystalline state, and their photographs under white light (UV off) and UV light (λ = 365 nm) irradiation (UV on).

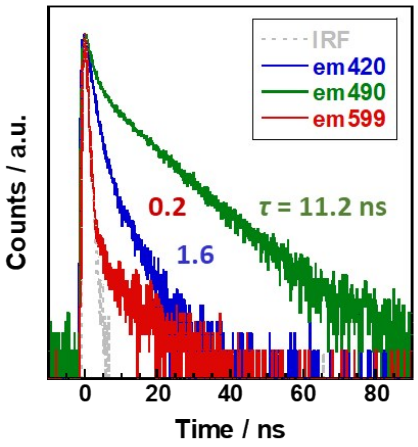
Table S1. Excitation and emission wavelengths (λ_{ex}, λ_{em}), and quantum yields (Φ) of *N*-cyclohexylphthalimides substituted with amino (−NH_2), acetyl (−$NHCOCH_3$), trifluoroacetyl (−$NHCOCF_3$), or methansulfonylamino (−$NHSO_2CH_3$) group and tosylamino (−$NHSO_2C_6H_4$- CH_3, 3TsAPI) at the 3-position in the crystalline state.

Substituents	λ_{ex} /nm	λ_{em} /nm	Φ
-NH_2	375	503	0.76
-$NHCOCH_3$	370	456	0.07
-$NHCOCF_3$	365	542	0.34
-$NHSO_2CH_3$	365	585	0.08
−$NHSO_2C_6H_4CH_3$	370	580	0.22

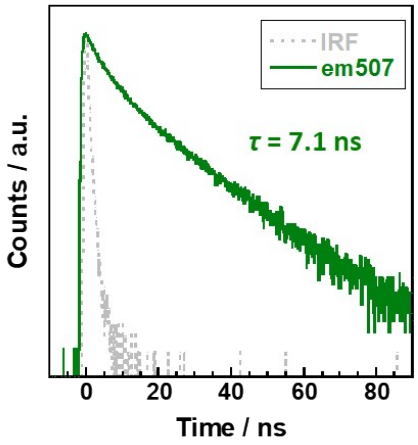
(a) Toluene



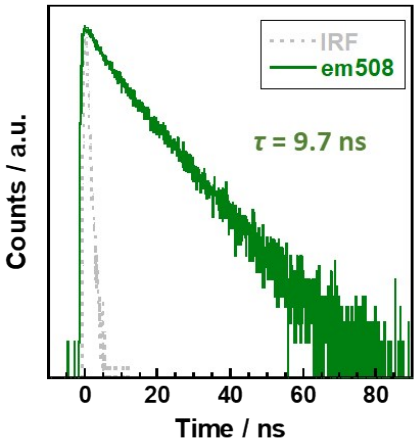
(b) Acetone



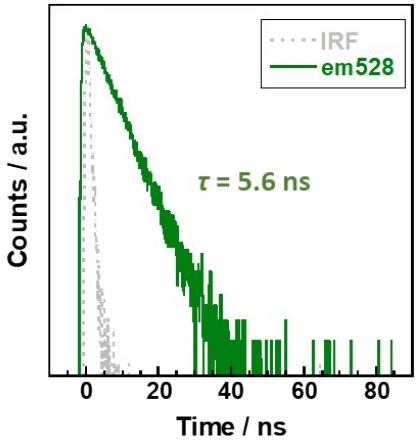
(c) EtOH



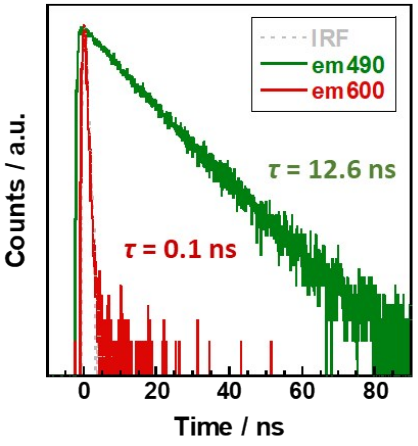
(d) MeOH



(e) DMSO



(f) EtOAc



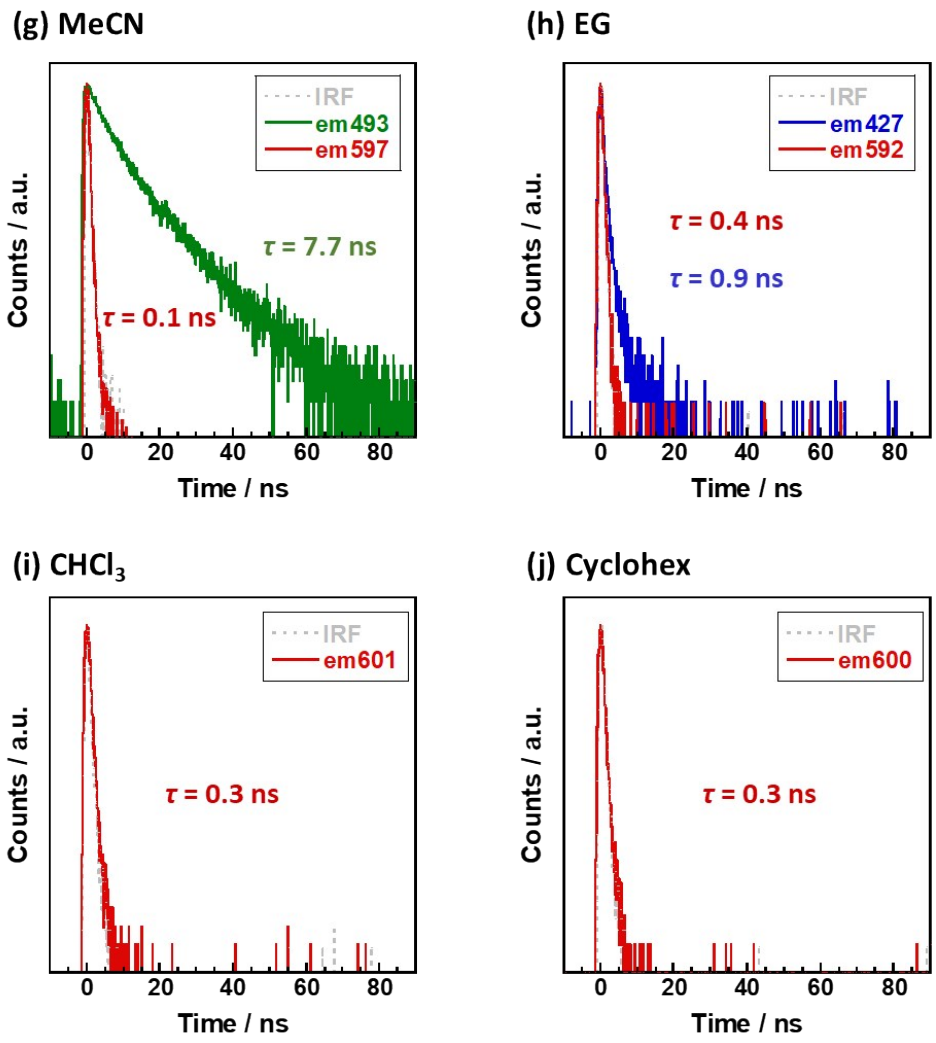


Figure S19. Fluorescence decay curves for **3TsAPI** dissolved in (a) Toluene, (b) Acetone, (c) Ethanol (EtOH), (d) Methanol (MeOH), (e) Dimethyl sulfoxide (DMSO), (f) Ethyl acetate (EtOAc), (g) Acetonitrile (MeCN), (h) Ethylene glycol (EG), (i) Chloroform (CHCl3), and (j) Cyclohexane (Cyclohex) solutions.

Table S2. Absorption wavelength (λ_{abs}), excitation and emission wavelengths (λ_{ex}, λ_{em}), Stokes shifts (ν), fluorescence lifetimes (τ), and quantum yields (Φ) of 3TsAPI in Acetone/TFA and EtOH/TFA mixed solutions.

Solvent	λ_{abs} /nm	λ_{ex} /nm	λ_{em} /nm	ν /cm^{-1}	τ /ns	Φ
Acetone/TFA	338	351	605	11972	0.1	0.02
		351	414	4312	1.7	
EtOH/TFA	339	350	605	11972	0.1	0.02
		350	400	3571	0.4	

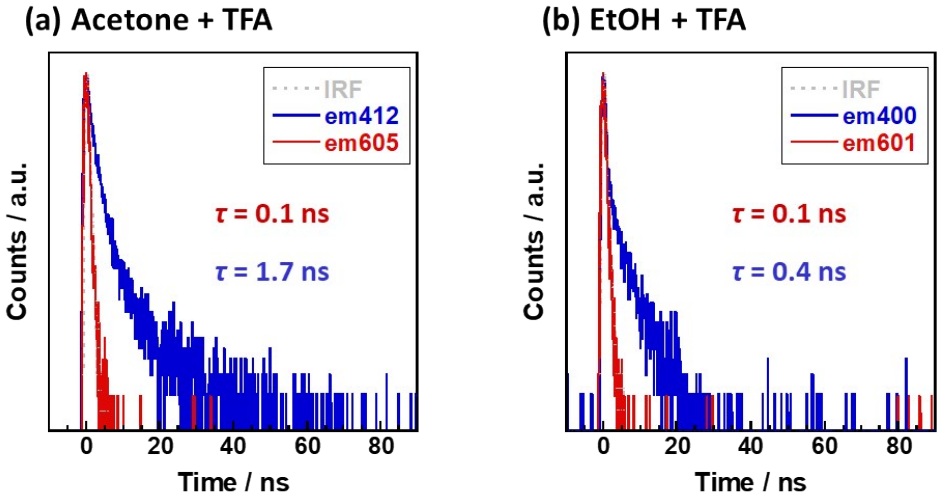


Figure S20. Fluorescence decay curves for **3TsAPI** dissolved in mixed solvent of (a) Acetone/TFA, (b) EtOH/TFA.

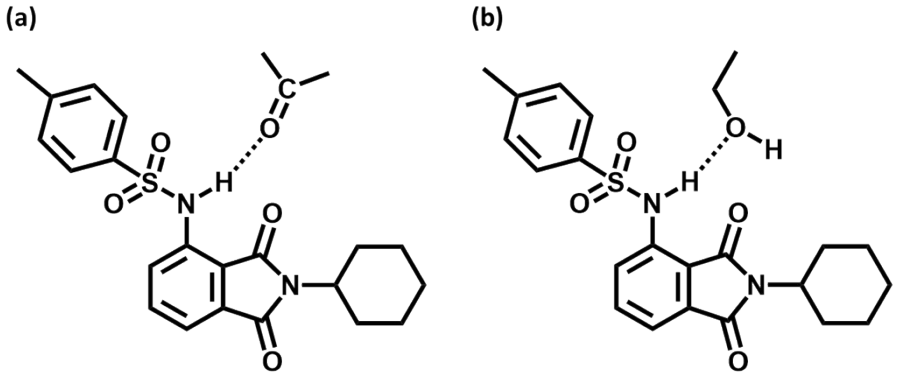


Figure S21. Schematic hydrogen bond formation between 3TsAPI in (a) acetone and (b) EtOH.

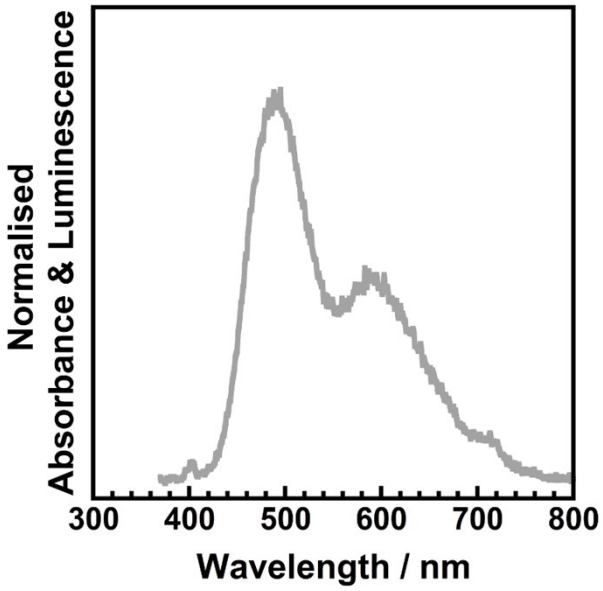


Figure S22. Emission spectrum of **3TsAPI** in ethyl acetate (EtOAc) excited at 360 nm.