Supporting Information

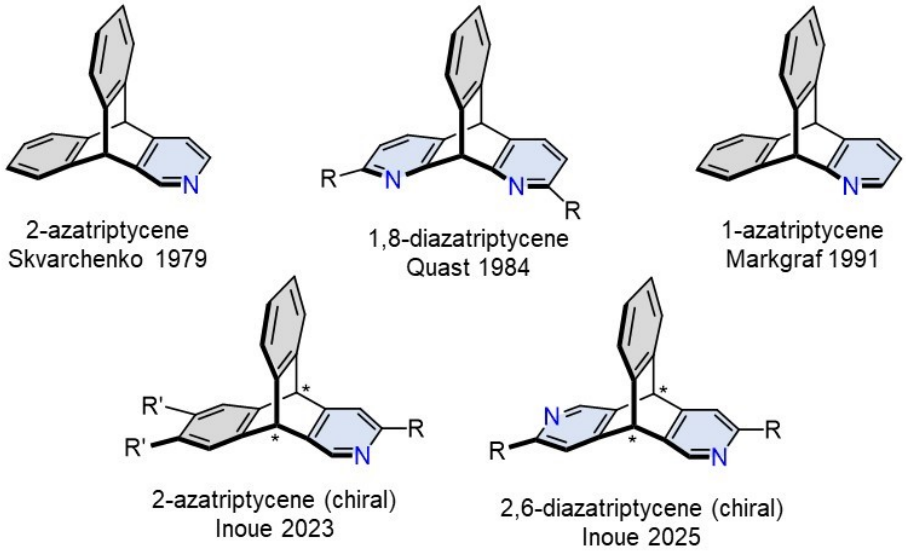


Figure S1. Chemical structures of azatriptycenes in the previous works.

General

^{1}H and ^{13}C spectra were recorded on a JNM-ECZ-600R instrument at 600 and 151 MHz, respectively. Samples were analyzed by $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Analytical thin layer chromatography (TLC) was performed with silica gel 60 F_{254} plates or silica gel 60 NH_2 F_{254S} plates. Column chromatography was performed with Silica gel 60N SiO_2 or CHROMATOREX NH-DM1020 NH-SiO_2. Preparative gel-permeation chromatography (GPC) was carried out by a JAI LC-9204 recycling preparative high-performance liquid chromatography (HPLC) equipped with a JAI JAIGEL-2HR Plus GPC column (solvent: CH_2Cl_2). HRMS data were obtained on a Thermo Fisher Scientific Orbitrap Eclipse Tribrid mass spectrometer (ESI). The PL lifetime measurement was performed on a Hamamatsu Photonics Quantaurus-Tau fluorescence lifetime spectrometer C16361-02 system. UV-vis spectra were recorded on a JASCO V-670 spectrometer. Absolute PL quantum efficiency was calculated on a JASCO FP-8500 with an ILF-835 integrating sphere.

Materials

Commercially available compounds:

1 M KO^{t}Bu tetrahydrofuran (THF) solution, BF_3OEt_2, 1 M KHMDS THF solution, TfOH, Tf_2NH, HBr solution, and Na_2SO_4

THF (dehydrated), toluene (dehydrated), $CHCl_3$, CH_2Cl_2, hexane, MeCN

Compounds prepared as described in the literature:

TCBO:

R. Inoue, K. Furumoto, T. Osada, Y. Morisaki, *Eur. J. Org.Chem*. **2022**, e202200041.

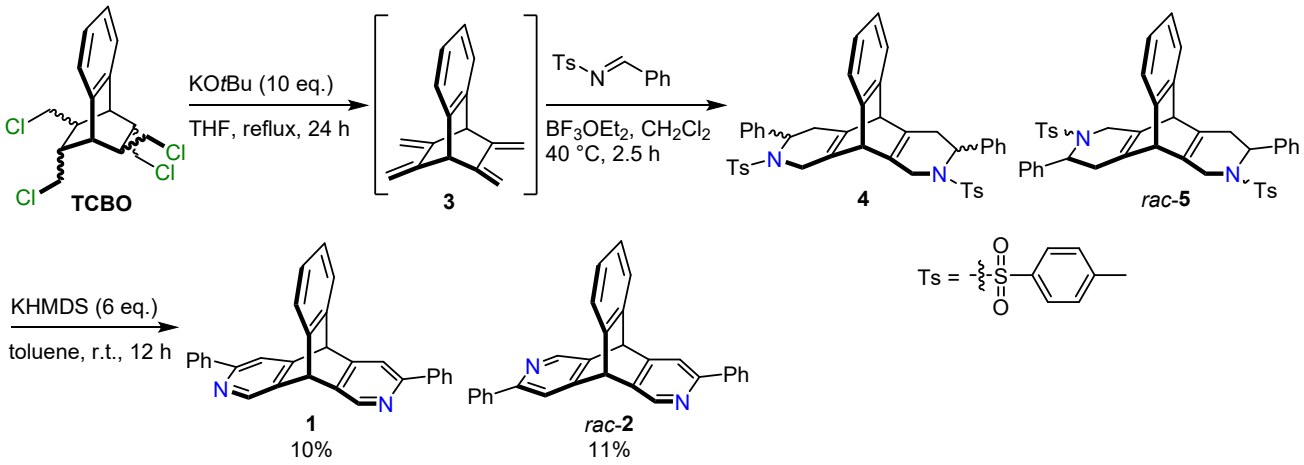
Tetrakis(methylene)-benzobicyclo[2.2.2]octane:

R. Inoue, S. Namba, Y. Morisaki, *Bull. Chem. Soc. Jpn.* **2023**, 96, 775–777.

X-ray structure determination

Crystals suitable for X-ray diffraction studies were analyzed using a Rigaku MicroMax-007HFM MoKa rotating anode generator equipped with VariMax optics, an AFC1 goniometer, and MERCURY CCD-2 detector. The reflection data were integrated, scaled and averaged using Rigaku CrysAlis^{PRO}. The structures were solved by a direct method (SHELXT) and refined using a full-matrix least-squares method on F2 for all reflections (SHELXL-2018/3). The calculations were performed on the Olex2 program package. Crystallographic data are given in Table S2. CCDC-2498092–2498098 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

Scheme S1. Synthesis of **1**.[a]



1 M KO^{t}Bu THF solution (5 mL, 5 mmol) was added to a solution of **TCBO** (176.10 mg, 0.50 mmol) in THF (12.5 mL) under Ar. After refluxing for 16 h, SiO_2 was added to the reaction mixture and dried under vacuum. The residue was purified by column chromatography on dried SiO_2 (CH_2Cl_2 as an eluent) to obtain a solution of **3** in CH_2Cl_2 (around 25 mL). The solution of **3** was added to a mixture of phenyl *N*-tosylimine (518.6 mg, 2.00 mmol), BF_3OEt_2 (0.19 mL, 1.50 mmol) in CH_2Cl_2 (5 mL) under Ar. After the mixture was heated at 40 ℃ for 2.5 h, the residue was purified by column chromatography on NH-SiO_2 (CH_2Cl_2/hexane = 1/1 as an eluent), affording **4** and *rac*-**5**. KHMDS, obtained by drying a 1 M KHMDS THF solution (3 mL, 3 mmol) under vacuum to remove the solvent, was dissolved in toluene (5 mL) under Ar. The solution was added to a solution of **4** and *rac*-**5** in toluene (15 mL) under Ar. After the mixture was stirred 16 h, water was added to the mixture. The organic layer was extracted with toluene three times. The combined organic layer was dried over Na_2SO_4. Na_2SO_4 was removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on NH-SiO_2 (hexane/CH_2Cl_2 = 4/1 to 1/3 as an eluent) and purified by GPC to obtain **1** (21.3 mg, 0.052 mmol, 10%) and *rac*-**2** (21.8 mg, 0.053 mmol, 11%) as a white solid.

[a] Under the same conditions as previously reported (toluene, 80 °C, 5 h), the isolated yield of **1** and *rac*-**2** was 6% and 7% in our hands.

1

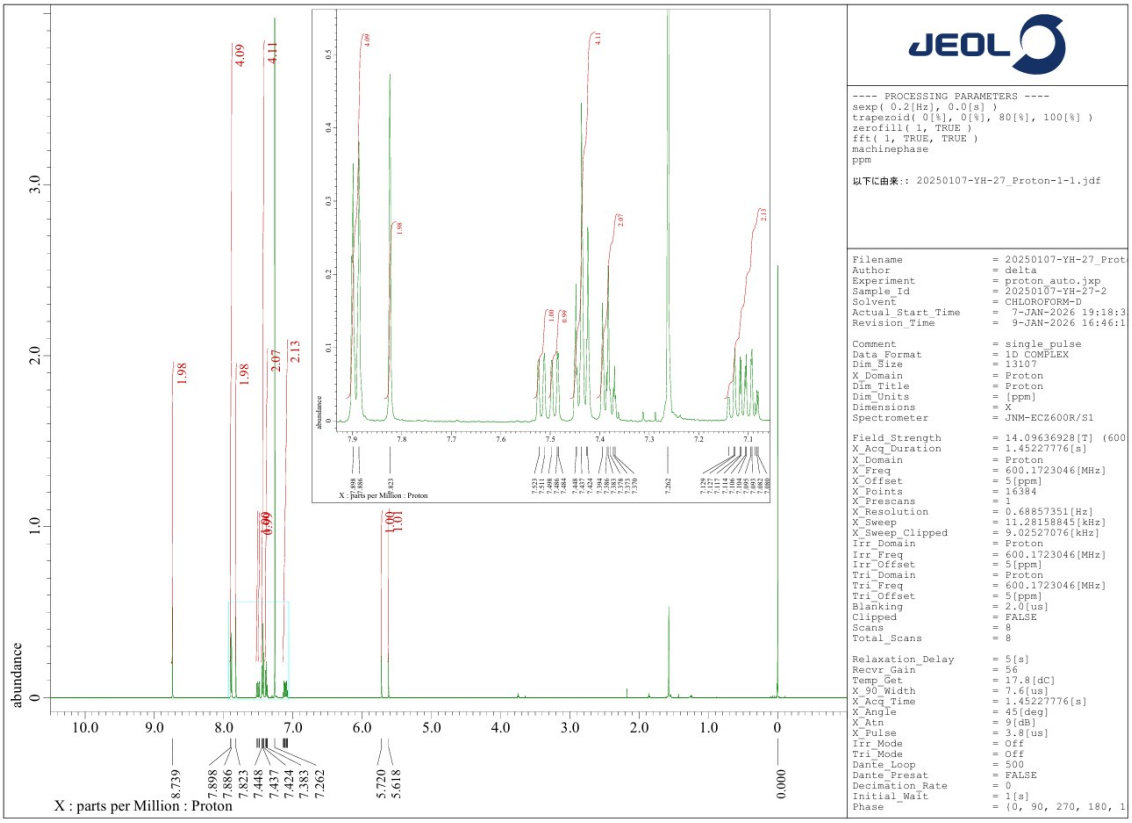
R_f = 0.28 (hexane/CH_2Cl_2 = 1:4 as an eluent, NH_2-SiO_2)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.62 (s, 1H), 5.72 (s, 1H), 7.07–7.15 (m, 2H), 7.43 (dd, J = 7.6 Hz, 2H), 7.43 (dd, J = 7.6 Hz, 4H), 7.49 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.82 (s, 2H), 7.89 (d, J = 6.9 Hz, 4H), 8.74 (s, 2H) ppm;

^{13}C NMR ($CDCl_3$, 151 MHz) δ 47.5, 53.5, 116.5, 124.4, 124.7, 126.0, 126.6, 127.1, 128.8, 129.0, 138.5, 139.4, 142.3, 143.6, 143.8, 153.6, 155.8 ppm.

HRMS (ESI+): *m/z* calcd for $C_{30}H_{21}N_2$ $[M+H^+]^+$: 409.16993; found: 409.17038.

(a)



(b)

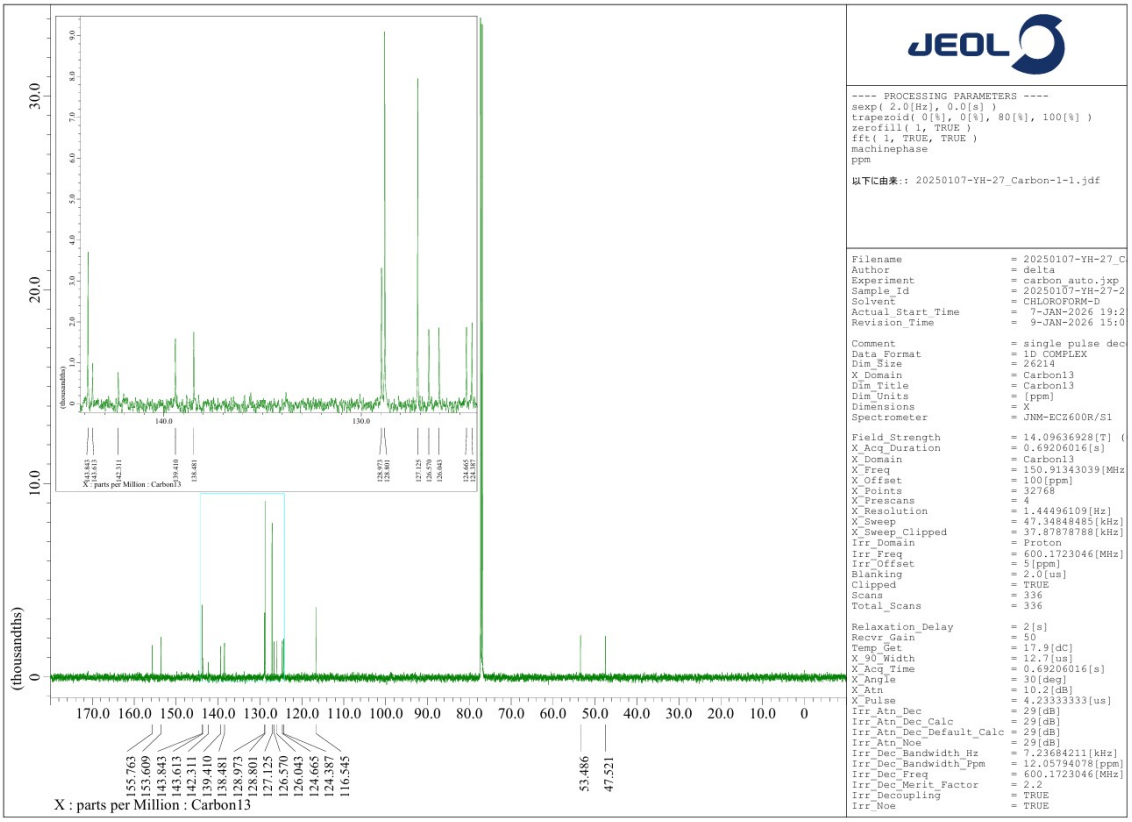


Figure S2. (a) ^{1}H NMR spectra ($CDCl_3$, 600 MHz) of **1**. (b) $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of **1**.

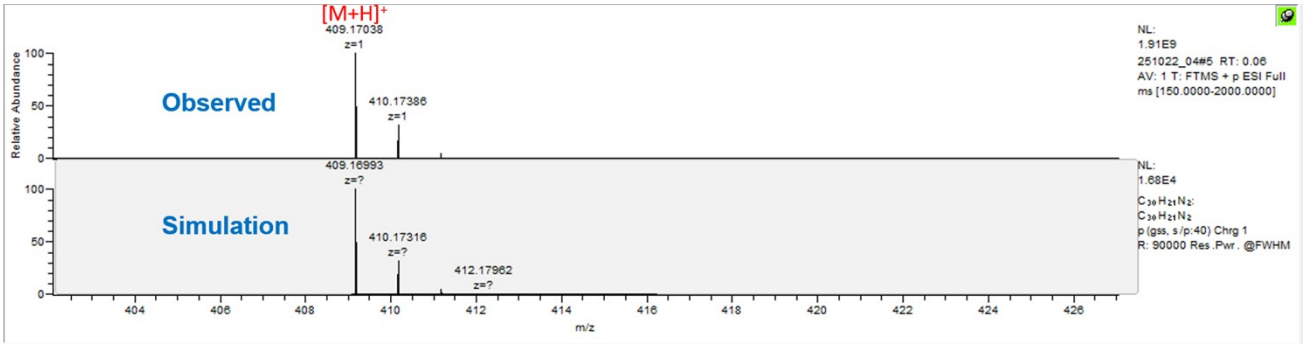


Figure S3. Mass spectra (ESI) and data of **1**. Top: experimental spectrum and bottom: theoretical spectrum.

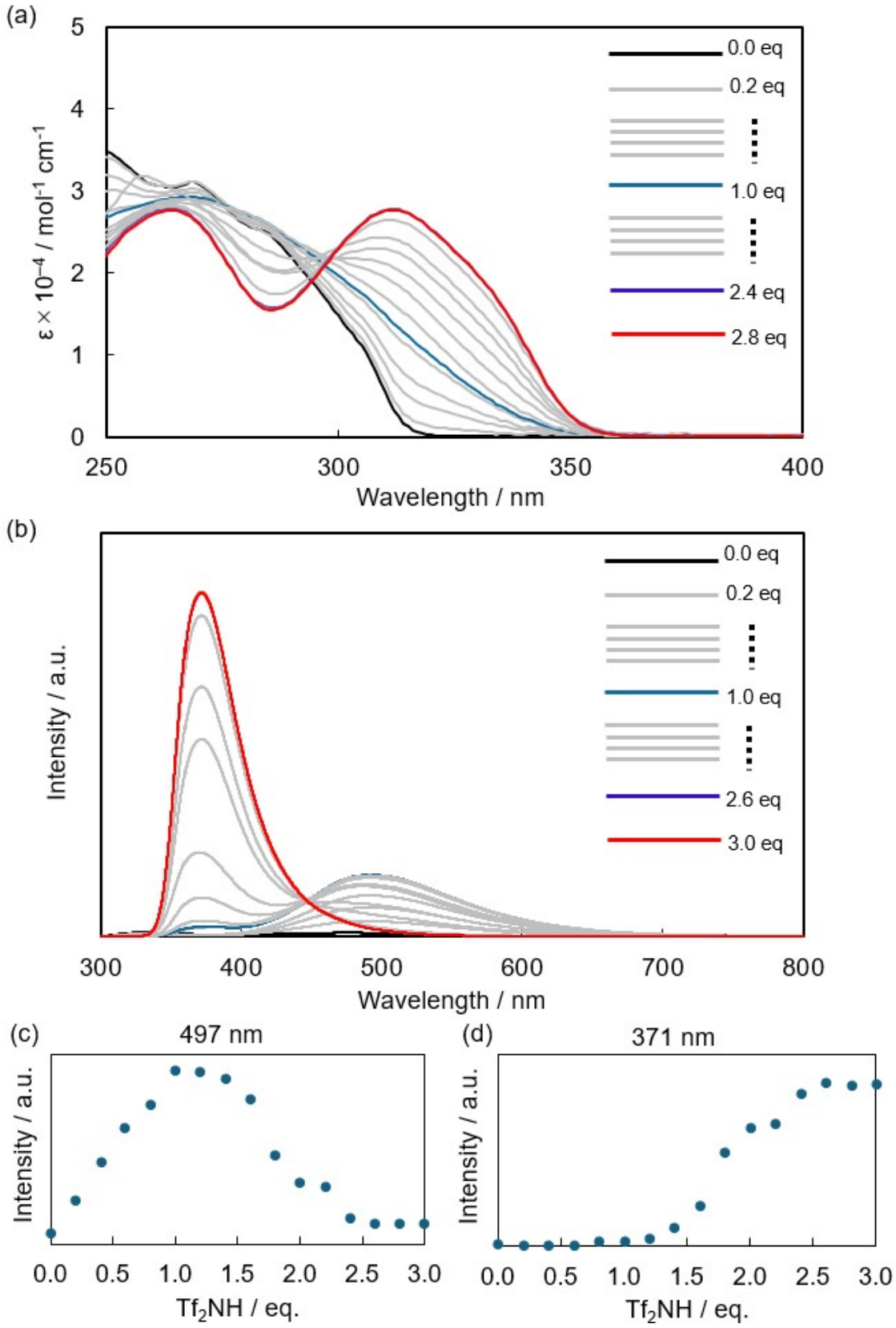


Figure S4. Spectral changes of (a) UV/vis absorption, (b) fluorescence spectra of **1** on the addition of Tf_2NH (5.0×10^{-6} M, CH_2Cl_2). (c,d) Fluorescence intensity plots for the acid titration at (c) 497 nm and (d) 371 nm.

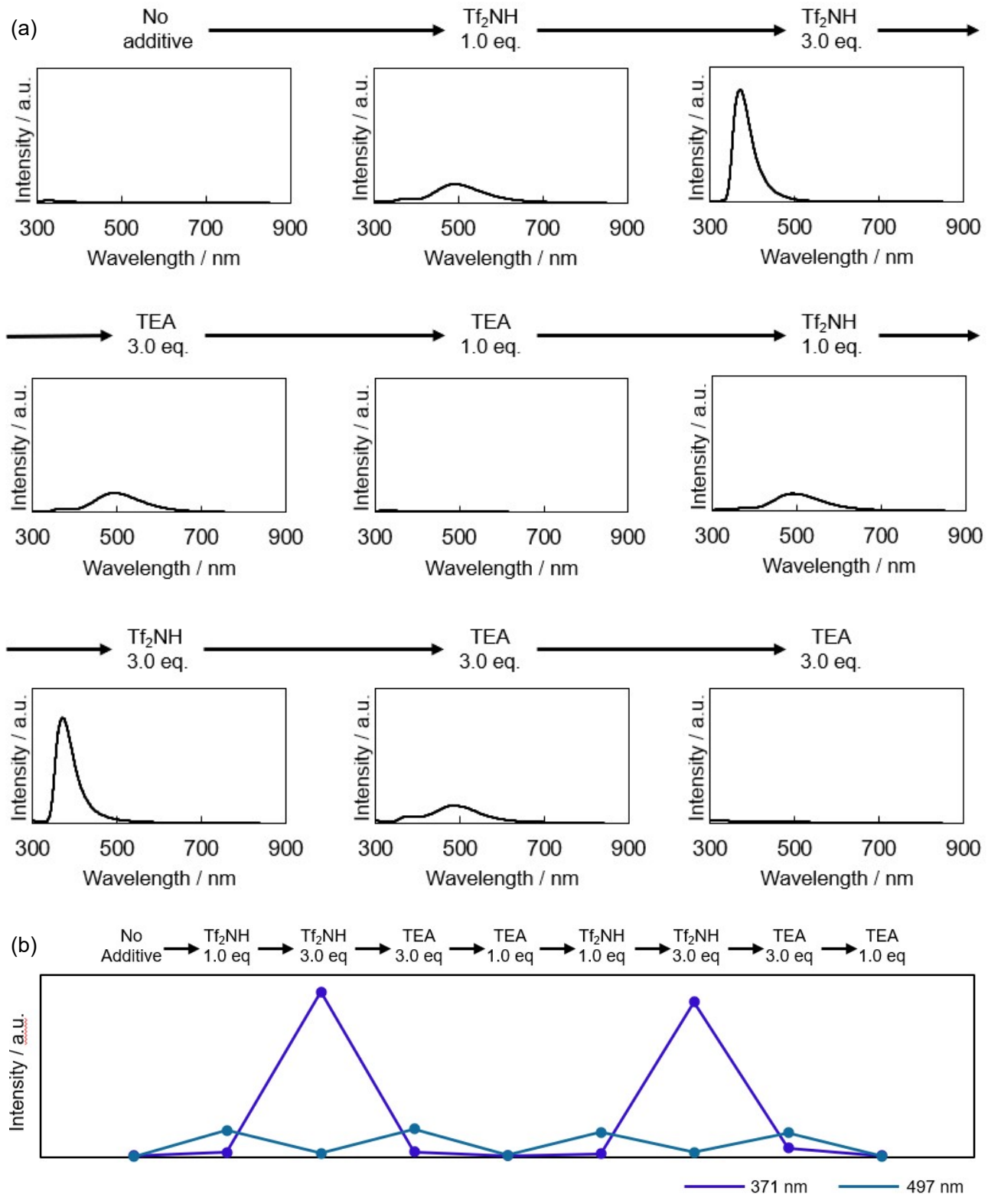


Figure S5. (a) PL spectral changes of **1** upon the addition of Tf_2NH and TEA. To a solution of **1** in CH_2Cl_2 (5.0×10^{-6} M, 3.0 mL) was added a CH_2Cl_2 solution of Tf_2NH (5.0×10^{-4} M) and a CH_2Cl_2 solution of TEA (3.8×10^{-4} M). (b) Switching of the emission intensity of **1** upon addition of Tf_2NH and TEA at 371 nm and 497 nm.

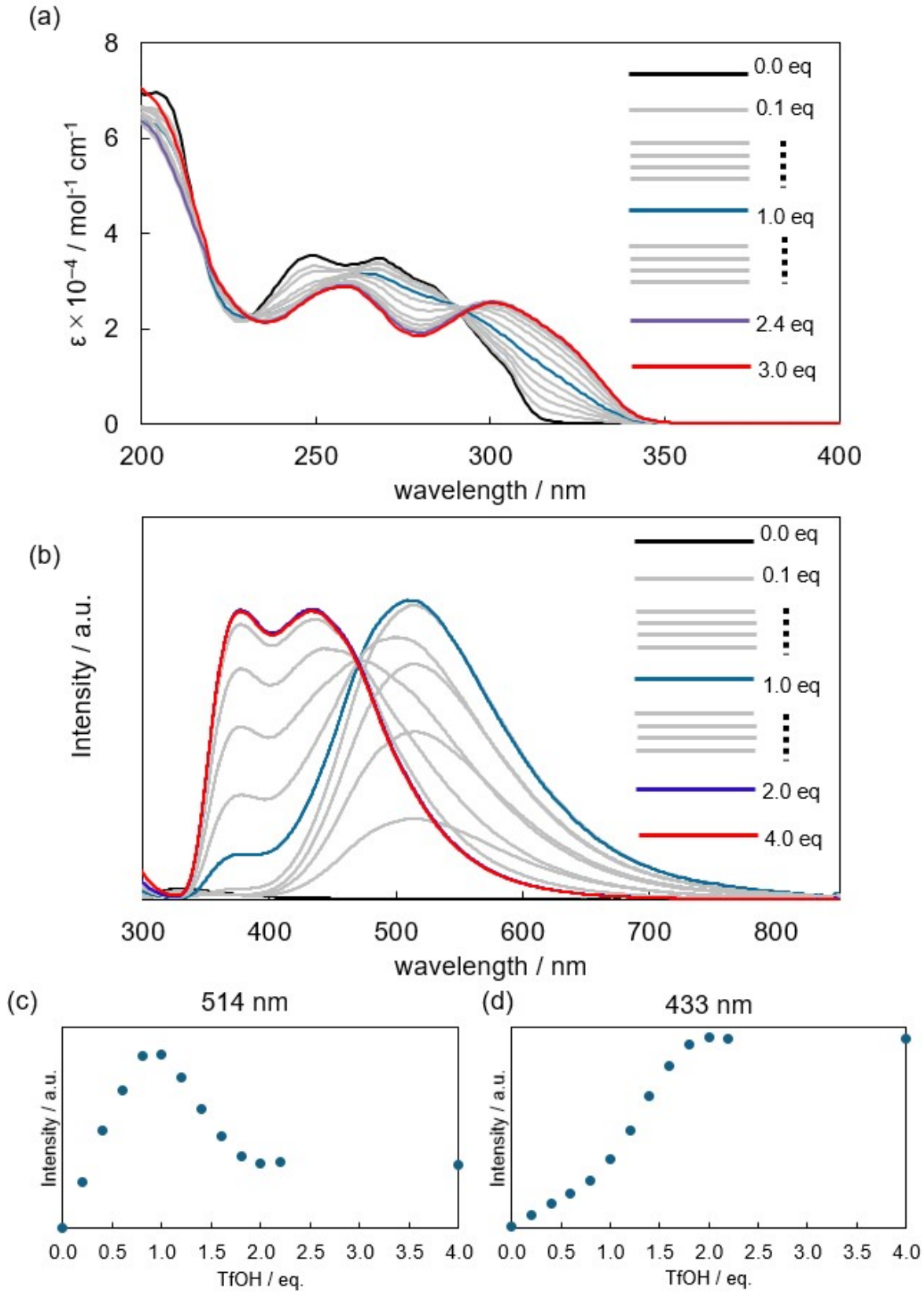


Figure S6. Spectral changes of (a) UV/vis absorption, (b) fluorescence spectra of **1** on the addition of TfOH (2.0×10^{-5} M, MeCN). (c,d) Fluorescence intensity plots for the acid titration at (c) 514 nm and (d) 433 nm.

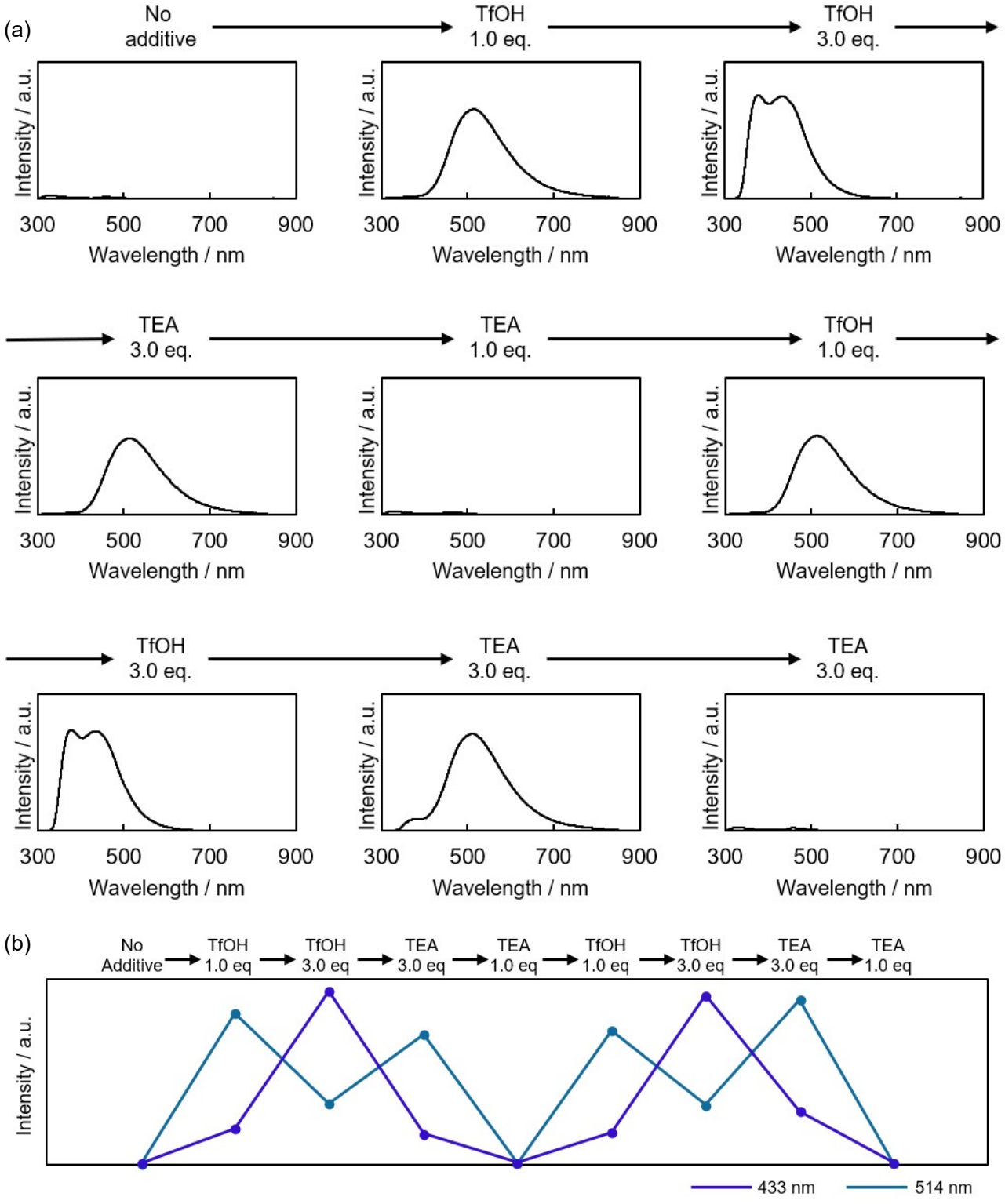


Figure S7. (a) PL spectral changes of **1** upon the addition of TfOH and TEA. To a solution of **1** in MeCN (2.0×10^{-5} M, 3.0 mL) was added a CH_3CN solution of TfOH (2.3×10^{-3} M) and a CH_3CN solution of TEA (1.6×10^{-3} M). (b) Switching of the emission intensity of **1** upon addition of TfOH and TEA at 371 nm and 497 nm.

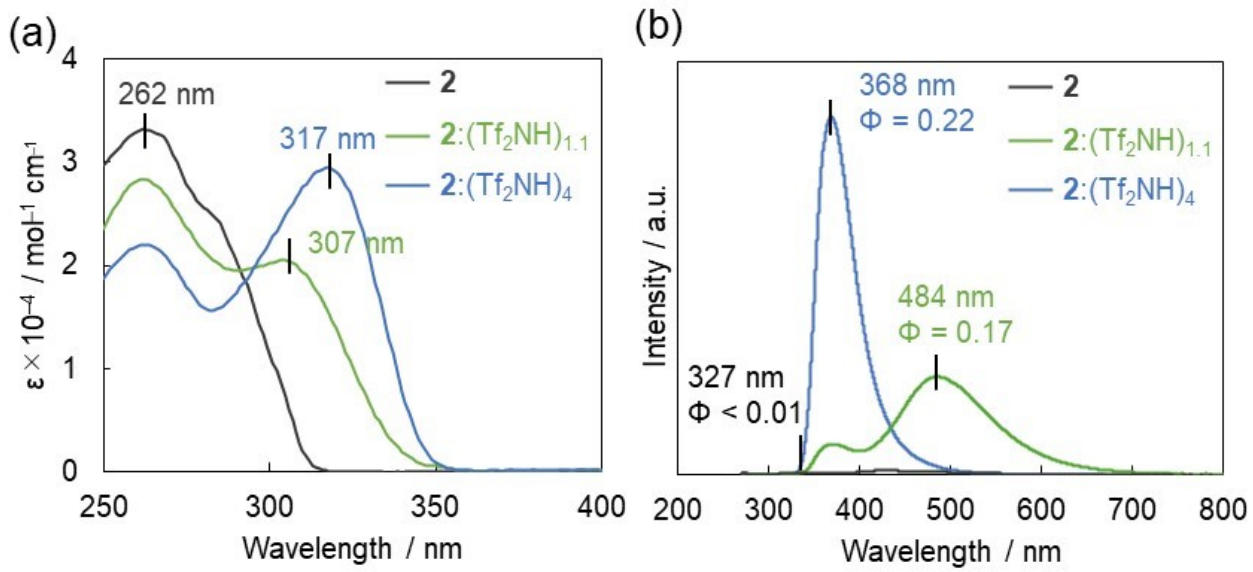


Figure S8. Spectral changes in (a) UV/vis absorption, (b) fluorescence spectra of **2** on the addition of Tf_2NH (5.0×10^{-6} M, CH_2Cl_2).

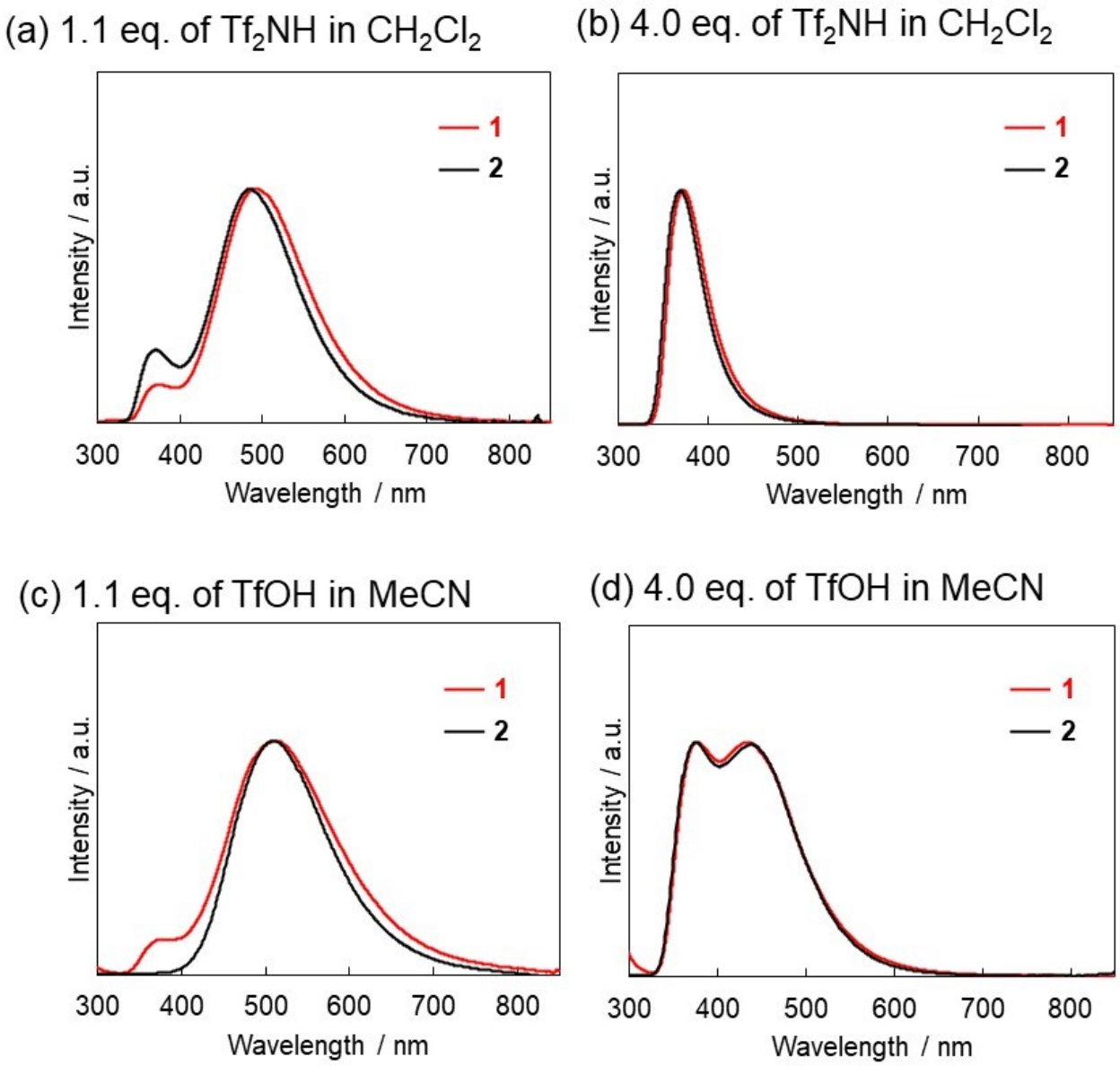
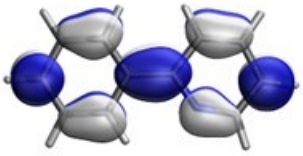


Figure S9. PL spectra of **1** and **2** under protonated conditions: (a) in the presence of 1.1 eq. of Tf_2NH in CH_2Cl_2, (b) in the presence of 4.0 eq. of Tf_2NH in CH_2Cl_2, (c) in the presence of 1.1 equiv. of TfOH in MeCN, and (d) in the presence of 4.0 eq. of TfOH in MeCN.

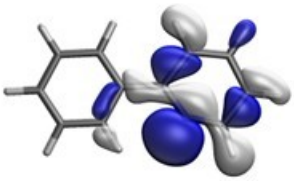
Table S1. Photophysical data for **1** and **2**. [a,c]

Compound	Solution	$\lambda_{abs,max}$ [nm] ($\varepsilon \times 10^4$ / $M^{-1}cm^{-1}$)	$\lambda_{lum,max}$ [nm]	Φ[c]	τ [ns] (χ^2)	k_r [10^7 s^{-1}]	k_{nr} [10^7 s^{-1}]
1	CH_2Cl_2	269 (3.06)	330	<0.01	-	-	-
1:$(Tf_2NH)_{1.1}$	CH_2Cl_2	269 (2.93)	497	0.03	12.4 (1.0)	0.24	7.8
1:$(Tf_2NH)_{4.0}$	CH_2Cl_2	310 (2.79)	371	0.07	1.67 (1.0)	4.2	55.7
1	MeCN	268 (3.48)	329	<0.01	-	-	-
1:$(TfOH)_{1.1}$	MeCN	264 (3.16)	514	0.03	-	-	-
1:$(TfOH)_{4.0}$	MeCN	310 (2.31)	433	0.03	-	-	-
(9*S*,10*S*)-**2**	CH_2Cl_2	262 (3.32)	327	<0.01	-	-	-
(9*S*,10*S*)-**2**:$(TfOH)_{1.1}$	CH_2Cl_2	307 (2.05)	484	0.17	10.7 (1.0)	1.6	7.8
(9*S*,10*S*)-**2**:$(TfOH)_{4.0}$	CH_2Cl_2	317 (2.94)	368	0.22	2.23 (1.0)	9.9	35.0
(9*S*,10*S*)-**2**	MeCN	203 (8.60)	416	< 0.01	-	-	-
(9*S*,10*S*)-**2**:$(TfOH)_{1.1}$	MeCN	204 (7.57)	510	0.12	11.9 (1.0)	1.0	7.4
(9*S*,10*S*)-**2**:$(TfOH)_{4.0}$	MeCN	201 (6.59)	438	0.17	6.1 (1.0)	2.8	13.5

[a] Emission spectra, quantum efficiencies, and emission decays were measured in CH_2Cl_2 solution (5.0×10^{-6} M) or MeCN solution (2.0×10^{-5} M) at room temperature. [b] Determined by the absolute method using an integrating sphere. [c] Data of **2** in MeCN obtained from ref 12.



LUMO



HOMO–1

λ = 330 nm, f = 0.0006

n-π* transition

Figure S10. Selected molecular orbitals in the S_1 states, λ, and oscillator strength f of ppy (TDA-TD-LC-wHPBE, 6–31g(d)).

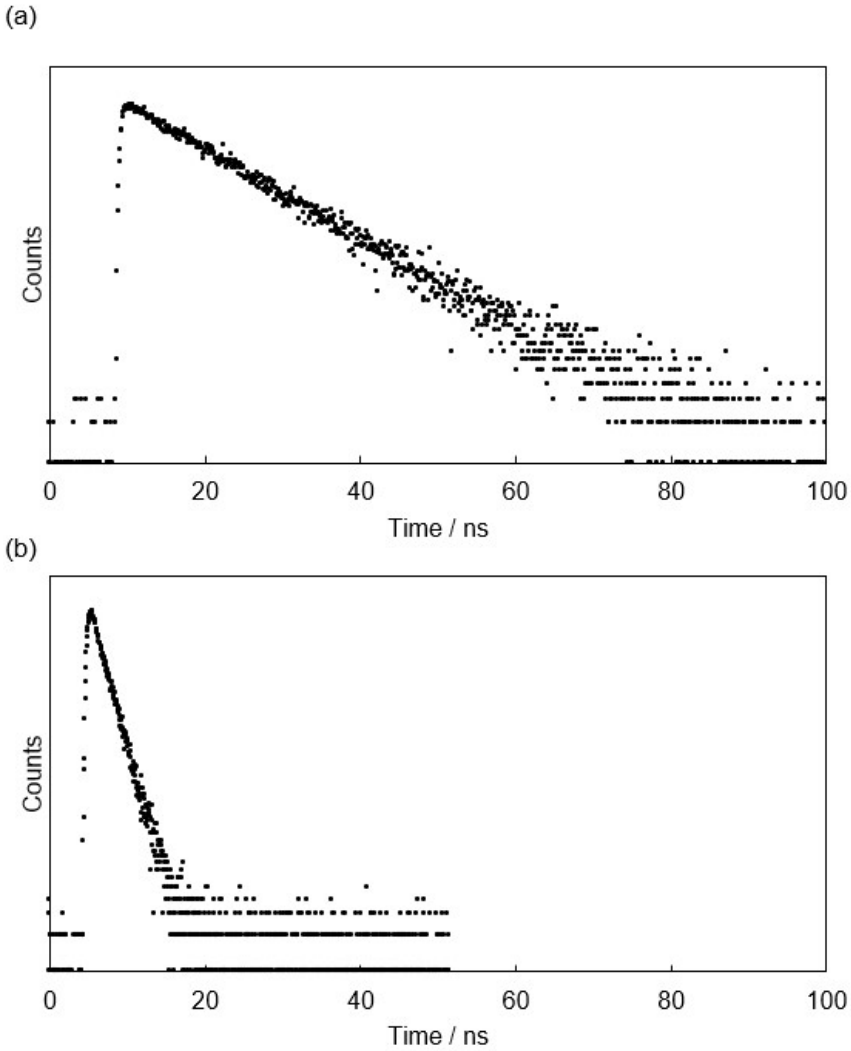


Figure S11. Emission decay curves for (a) **1**:$(Tf_2NH)_{1.1}$ and (b) **1**:$(Tf_2NH)_4$ in CH_2Cl_2 (5.0×10^{-6} M) monitored at (a) 497 nm (b) 410 nm (λ_{ex} = 280 nm).

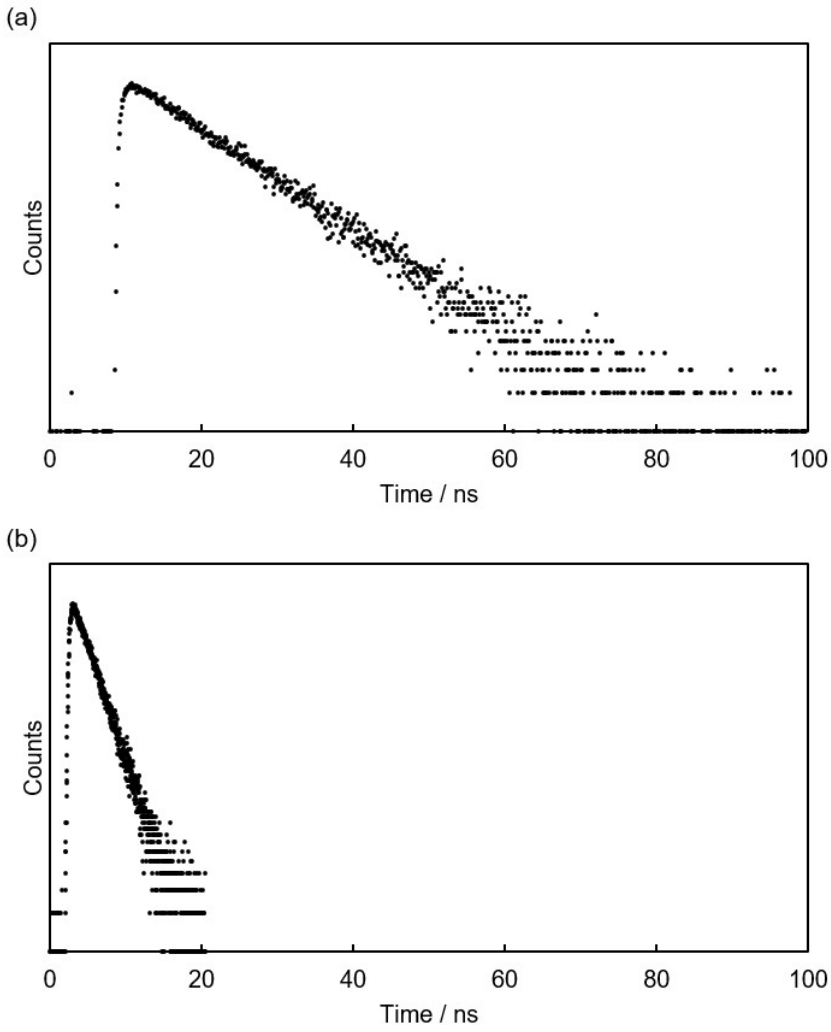


Figure S12. Emission decay curves for (a) **2**:$(Tf_2NH)_{1.1}$ and (b) **2**:$(Tf_2NH)_4$ in CH_2Cl_2 (5.0×10^{-6} M) monitored at (a) 490 nm (b) 400 nm (λ_{ex} = 280 nm).

Computational methods

TD-DFT calculations were carried out by using the Gaussian 16 program package, with the 6–31G(d) basis set for C, H, and N atoms. Optimized geometries, as well as molecular orbitals in the S_1 states were determined by TD-DFT calculations with the LC-wHPBE functional with Tamm-Dancoff Approximation. Analysis of the molecular orbital pair contributions to the transition dipole moment was performed using Multiwfn.[30] Selected excited-state data together with Cartesian coordinates are provided in Table S8–S14.

1 (HOMO: 107, LUMO: 108)

Excited State 1: Singlet-A 3.8686 eV 320.49 nm f=0.0028 <S**2>=0.000

105 ->108 0.56529

105 ->117 -0.12999

106 ->108 0.29279

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1263.66256885

1H^{+} (HOMO: 107, LUMO:108)

Excited State 1: Singlet-A 3.8044 eV 325.89 nm f=0.0115 <S**2>=0.000

101 ->108 0.13026

102 ->108 0.14586

105 ->108 -0.15160

107 ->108 0.62792

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1264.06893961

1H$_2$ $^{2+}$ (HOMO: 107, LUMO:108)

Excited State 1: Singlet-A" 4.2179 eV 293.95 nm f=0.9336 <S**2>=0.000

100 ->108 -0.10273

105 ->108 0.19494

106 ->109 -0.41647

107 ->108 0.47385

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1264.36977788

ppy (HOMO: 41, LUMO: 42)

Excited State 1: Singlet-A 3.7569 eV 330.02 nm f=0.0006 <S**2>=0.000

40 -> 42 0.66958

40 -> 45 -0.19579

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -478.816413830

2 (HOMO: 107, LUMO: 108)

Excited State 1: Singlet-A 3.8606 eV 321.15 nm f=0.0026 <S**2>=0.000

105 ->108 0.63162

105 ->117 -0.14205

106 ->108 -0.11889

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1263.66269747

2H^{+} (HOMO: 107, LUMO:108)

Excited State 1: Singlet-A 3.7542 eV 330.26 nm f=0.3561 <S**2>=0.000

101 ->108 0.19483

105 ->108 0.12305

107 ->108 0.62124

107 ->110 0.16091

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1264.09310126

2H$_2$ $^{2+}$ (HOMO: 107, LUMO:108)

Excited State 1: Singlet-A 4.2525 eV 291.56 nm f=1.2480 <S**2>=0.000

105 ->109 0.20208

106 ->108 0.50042

107 ->109 -0.37364

This state for optimization and/or second-order correction.

Total Energy, E(CIS/TDA) = -1264.36936913

Table S2. Molecular orbital pair contributions to transition dipole moment of monocation **1H**$^{+}$.

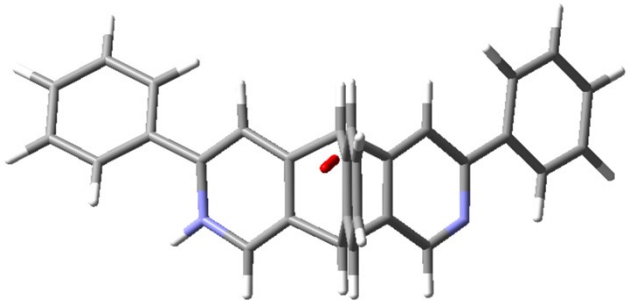
#Pair	Orbital trans.	Coefficient	Transition dipole X/Y/Z			Norm (a.u.)
1	101 -> 108	0.130570	0.119000	0.152870	0.077456	0.208637
2	102 -> 108	0.145320	-0.250011	-0.265772	-0.161117	0.398871
3	105 -> 108	-0.151570	0.065220	0.041781	-0.052725	0.093697
4 (main transition)	107 -> 108	0.627950	-0.070100	0.146996	-0.004665	0.162922
TDM of main transition (Pair 4) 						

Table S3. Molecular orbital pair contributions to transition dipole moment of monocation **2H**$^{+}$.

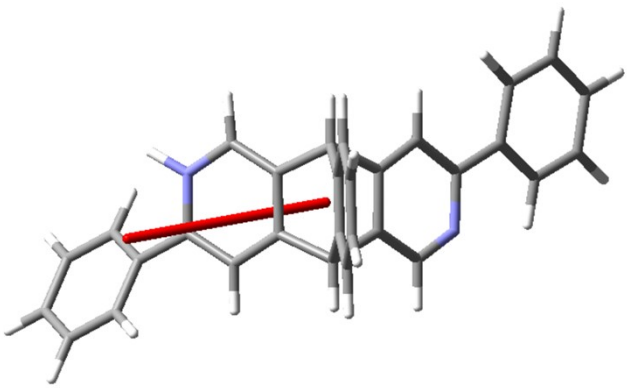
#Pair	Orbital trans.	Coefficient	Transition dipole X/Y/Z			Norm (a.u.)
1	101 -> 108	0.194830	0.050109	0.064888	0.161371	0.181003
2	105 -> 108	0.123050	-0.042064	-0.046469	0.045675	0.077556
3 (main transition)	107 -> 108	0.621240	1.175564	0.332206	0.193506	1.236834
4	107 -> 110	0.160910	0.560828	0.380724	-0.134281	0.691021
TDM of main transition (Pair 3) 						

Table S4. Molecular orbital pair contributions to transition dipole moment of monocation **1H$_2$**$^{2+}$.

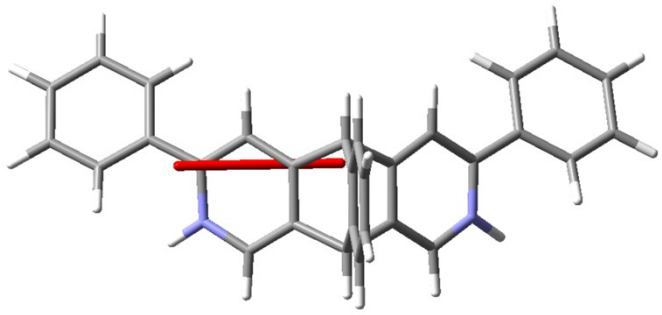
#Pair	Orbital trans.	Coefficient	Transition dipole X/Y/Z			Norm (a.u.)
1	100 -> 108	-0.103070	0.000000	0.000000	0.004339	0.004339
2	105 -> 108	0.194990	0.000000	0.000000	0.378516	0.378516
3	106 -> 109	0.416310	0.000000	0.000000	1.345696	1.345696
4 (main transition)	107 -> 108	0.473880	0.000000	0.000000	0.991690	0.991690
TDM of main transition (Pair 4) 						

Table S5. Molecular orbital pair contributions to transition dipole moment of monocation **2H$_2$**$^{2+}$.

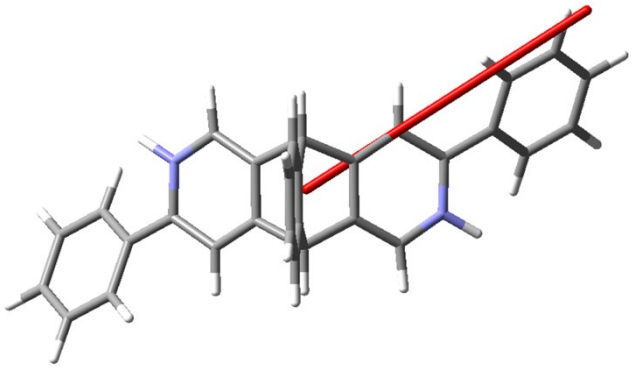
#Pair	Orbital trans.	Coefficient	Transition dipole X/Y/Z			Norm (a.u.)
1	105 -> 109	0.202080	0.460487	0.000000	-0.143208	0.482241
2 (main transition)	106 -> 108	0.500420	1.979468	0.000004	-0.501775	2.042075
3	107 -> 109	-0.373640	0.676063	-0.000005	-0.452843	0.813712
TDM of main transition (Pair 2) 						

Table S6. Crystallographic data and structure refinements.

Molecule	**1**	**1**•TfOH•EtOH•H_2O	**1**•$(TfOH)_2$•$(H_2O)_{2.5}$
Formula	$C_{30}H_{20}N_2$	$C_{33}H_{29}F_3N_2O_5S$	$C_{37}H_{28}F_{12}N_4O_9S_4$
Formula weight	408.48	622.64	1028.87
Temperature (K)	150	150	150
Crystal color, habit	colorless, plate	yellow, plate	colorless, plate
Crystal size, mm	0.1× 0.1 × 0.03	0.5× 0.3 × 0.02	0.2× 0.2 × 0.05
Crystal system	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$ (#2)	*P*bca (#61)	$P\bar{1}$ (#2)
a, Å	11.5316(3)	13.7158(4)	11.6575(3)
b, Å	12.1045(4)	19.9625(6)	13.2664(4)
c, Å	15.9135(5)	21.2858(7)	14.5139(5)
α, deg	97.883(3)	90	86.097(2)
β, deg	105.717(3)	90	81.085(2)
γ, deg	104.068(3)	90	74.851(2)
V, Å^3	2024.48(11)	5828.1(3)	2139.55(11)
Z value	4	8	2
D_{calcd}, g cm^{-3}	1.340	1.419	1.597
μ (MoKα), cm^{-1}	0.78	1.76	3.33
F(000)	856.0	2592.0	1044.0
$2\theta_{max}$, deg	56.406	56.670	56.314
No. of reflections measured	18321	29903	17967
No. of observed reflections	7992	6341	8339
No. of variables	6633	5311	7468
R_1 (I > 2σ(I))[a]	0.0397	0.0403	0.0841
wR_2 (all reflns)[b]	0.1028	0.1030	0.2472
Goodness of fit	1.013	1.067	1.021
Radiation_type	MoKα	MoKα	MoKα
Recrystallization solvent	CH_2Cl_2, MeOH	EtOH, $CHCl_3$	Acetone, CH_2Cl_2
CCDC-number	2498092	2498093	2498094

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table S6. Continued.

Molecule	**1**•$(Tf_2NH)_2$•Acetone	**1**•$(Tf_2NH)_2$•EtOH	**1**•$(HBr)_2$•$(H_2O)_2$
Formula	$C_{37}H_{28}F_{12}N_4O_9S_4$	$C_{36}H_{26}F_{12}N_4O_9S_4$	$C_{30}H_{24}Br_2N_2O_2$
Formula weight	1028.87	1014.85	604.33
Temperature (K)	150	150	150
Crystal color, habit	colorless, plate	colorless, block	colorless, block
Crystal size, mm	0.2× 0.2 × 0.05	0.1× 0.1 × 0.08	0.4× 0.2 × 0.2
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1$ (#4)	P 2_1/c (#14)
a, Å	11.6575(3)	13.2970(4)	8.1489(3)
b, Å	13.2664(4)	21.4099(7)	18.9495(7)
c, Å	14.5139(5)	14.5936(4)	17.1033(6)
α, deg	86.097(2)	90	90
β, deg	81.085(2)	92.730(3)	90.103(3)
γ, deg	74.851(2)	90	90
V, Å^3	2139.55(11)	4149.9(2)	2641.05(17)
Z value	2	2	4
D_{calcd}, g cm^{-3}	1.597	1.624	1.520
μ (MoKα), cm^{-1}	3.33	3.42	31.0
F(000)	1044.0	2056.0	1216.0
$2\theta_{max}$, deg	56.314	56.532	56.614
No. of reflections measured	17967	37484	11870
No. of observed reflections	8339	15952	5266
No. of variables	7468	13424	4431
R_1 (I > 2σ(I))[a]	0.0841	0.0537	0.0380
wR_2 (all reflns)[b]	0.2472	0.1364	0.1152
Goodness of fit	1.021	1.045	1.047
Radiation_type	MoKα	MoKα	MoKα
Recrystallization solvent	Acetone, CH_2Cl_2	EtOH	MeOH, THF, H_2O, HBr
CCDC-number	2498095	2498096	2498097

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

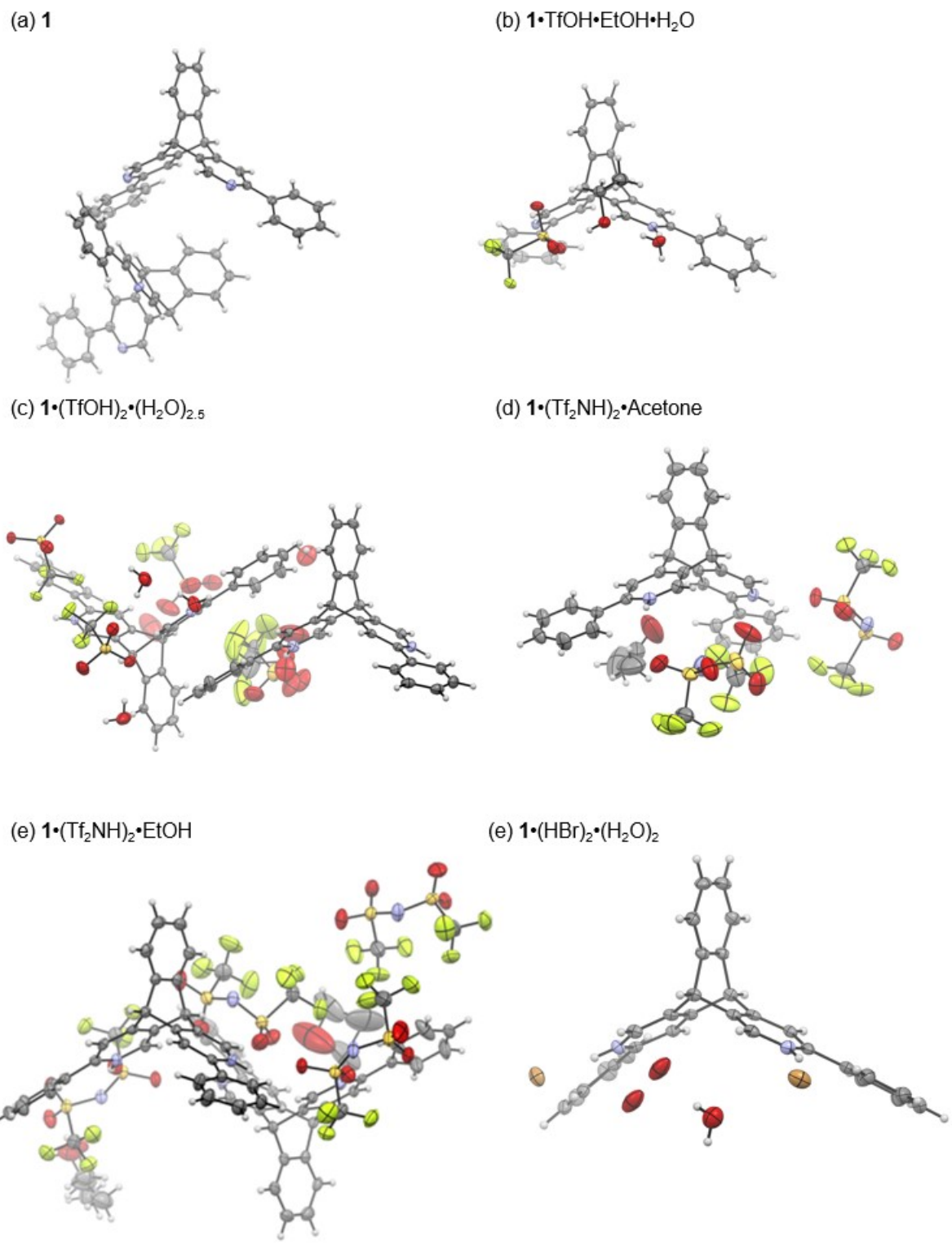


Figure S13. ORTEP drawing of (a) **1**, (b) **1**•TfOH•EtOH•H_2O, (c) **1**•$(TfOH)_2$•$(H_2O)_{2.5}$, (d) **1**•$(Tf_2NH)_2$•Acetone, (e) **1**•$(Tf_2NH)_2$•EtOH, and (f) **1**•$(HBr)_2$•$(H_2O)_2$. Thermal ellipsoids are drawn at the 50% probability level. C: gray, H: off-white, N: blue, O: red, F: yellow-green, and S: yellow.

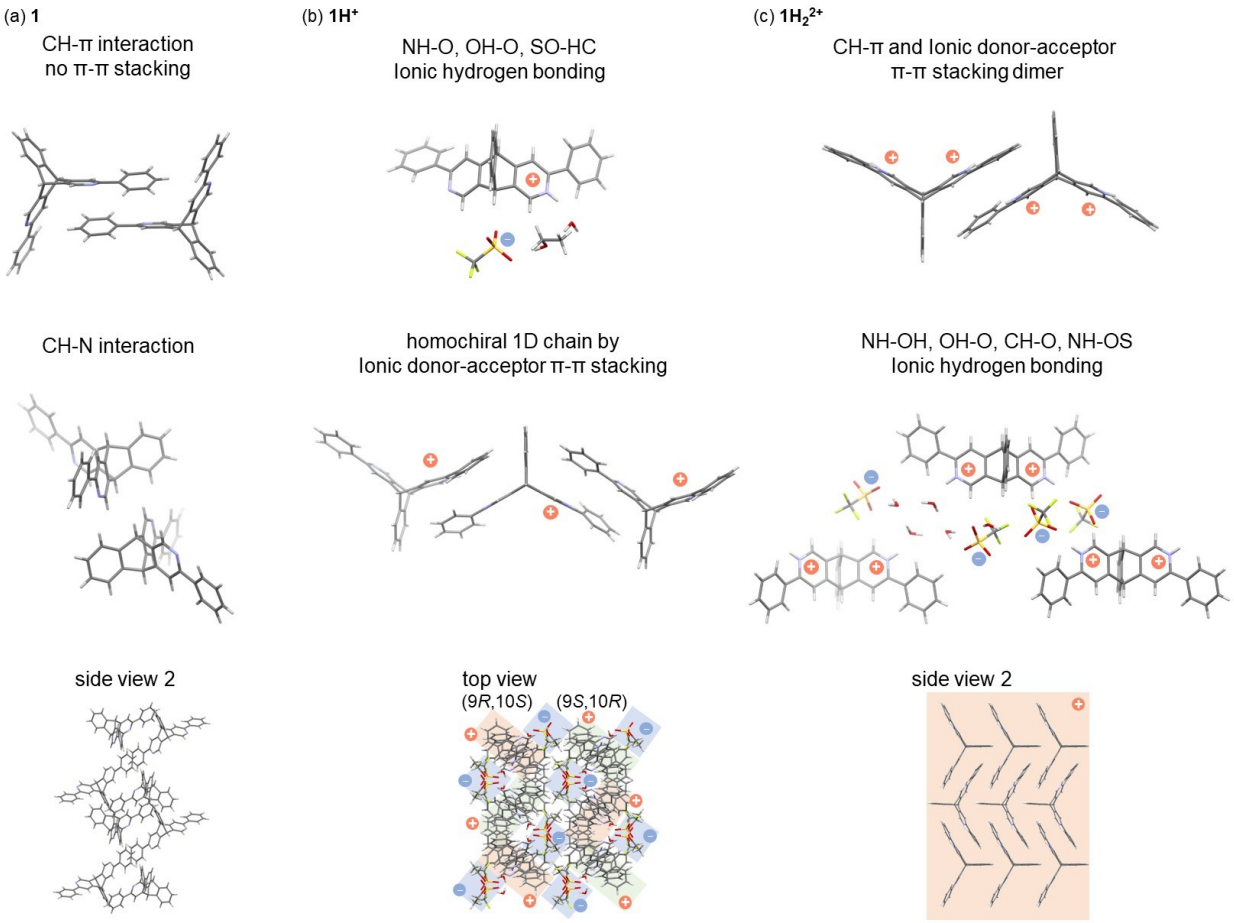


Figure S14. Selected intermolecular interactions and packing structures for (a) **1**, (b) **1**•TfOH•EtOH•H_2O, and (c) **1**•$(TfOH)_2$•$(H_2O)_{2.5}$ in crystalline state.

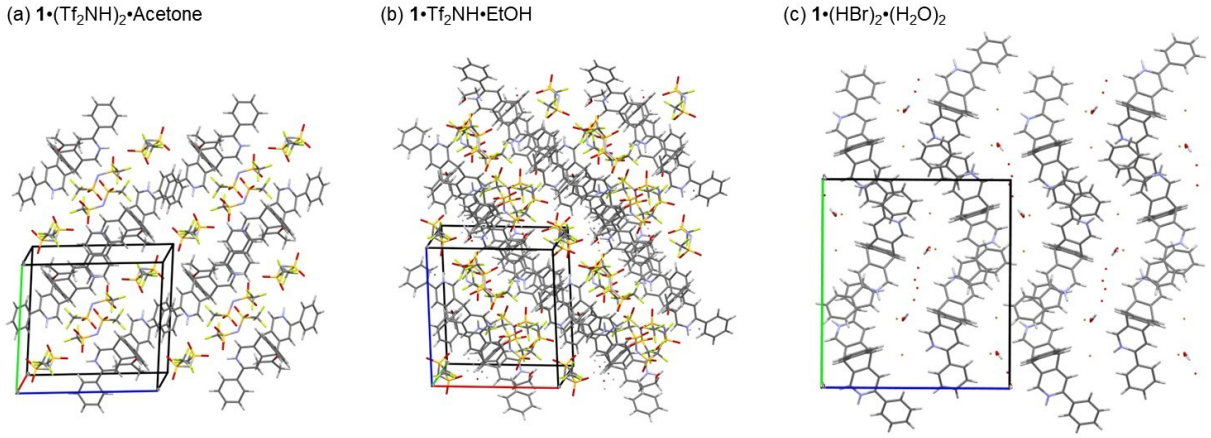


Figure S15. Crystal packing structures for (a) **1**•$(Tf_2NH)_2$•Acetone, (b) **1**•$(Tf_2NH)_2$•EtOH, and (c) **1**•$(HBr)_2$•$(H_2O)_2$.

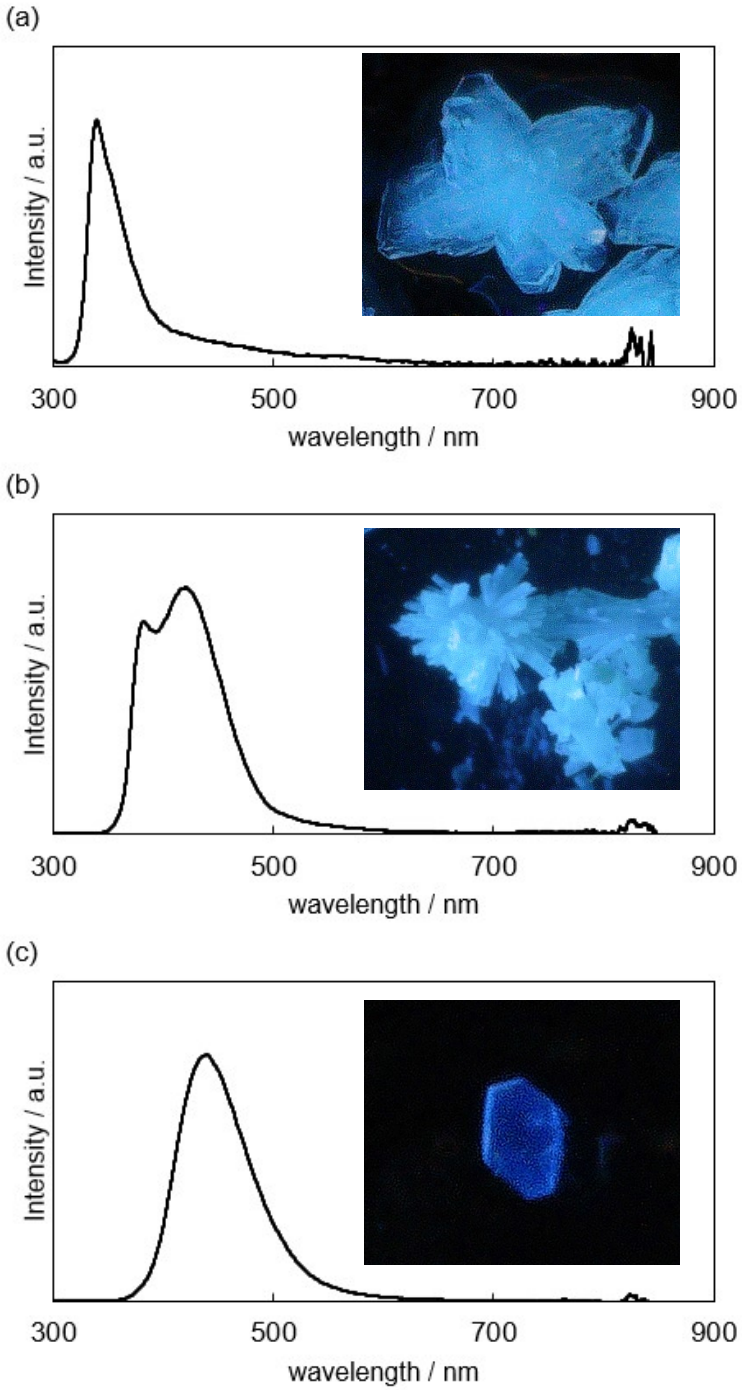


Figure S16. PL spectra charts of (a) **1**, (b) **1**•TfOH•EtOH•H_2O and (c) **1**•$(TfOH)_2$•$(H_2O)_{2.5}$ in crystalline state. The inset photograph shows fluorescence from crystals under UV light.

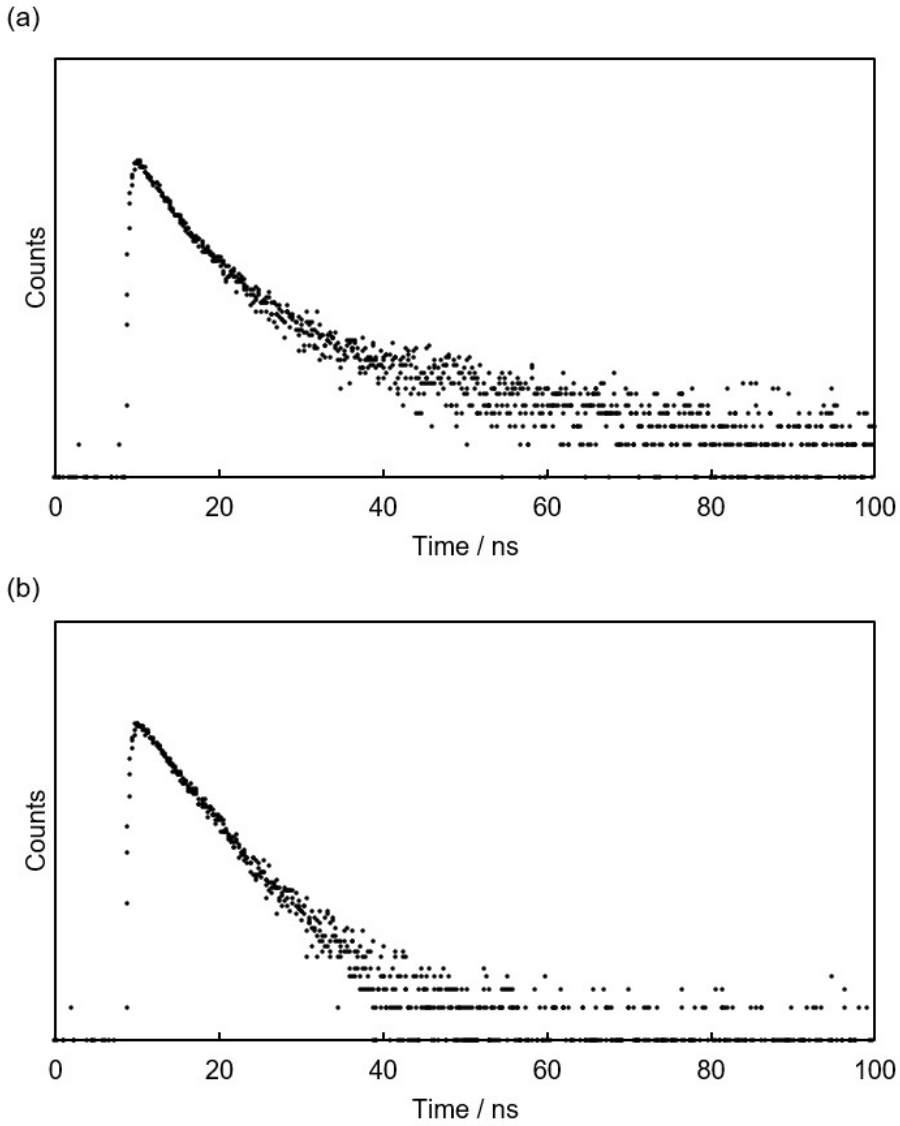


Figure S17. Emission decay curves for (a) **1**•TfOH•EtOH•H_2O and (b) **1**•$(TfOH)_2$•$(H_2O)_{2.5}$ in crystalline state monitored at (a) 455 nm and (b) 500 nm (λ_{ex} = 280 nm).

Table S7. Photophysical data for **1** in crystalline state. [a]

Compound	$\lambda_{lum,max}$ [nm]	Φ[b]	τ [ns] (χ^2)
1	339	0.08	-
1•TfOH•EtOH•H_2O	420	0.37	3.9, 15.2 (1.0)
1•$(TfOH)_2$•$(H_2O)_{2.5}$	439	0.25	4.4 (1.0)

[a] Emission spectra, quantum efficiencies, and emission decays were measured at room temperature.
[b] Determined by the absolute method using an integrating sphere.

Table S8. Cartesian coordinates of **1** in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	-0.050765	2.996312	-0.248730
C	-0.029586	2.425047	1.026931
C	-0.003192	3.228067	2.150722
C	-0.002164	4.612915	2.001861
C	-0.024329	5.179623	0.737349
C	-0.047642	4.370171	-0.395838
H	0.015190	2.783230	3.142263
H	0.015316	5.249436	2.881544
H	-0.024251	6.260113	0.627591
H	-0.064669	4.815390	-1.387297
C	2.193443	-0.303511	0.601603
C	1.186483	0.499081	0.200171
C	1.153464	1.095751	-1.115900
C	2.208805	0.804446	-1.941180
H	2.206522	-0.747099	1.592569
H	2.331166	1.177069	-2.954836
C	-3.268338	-0.623076	-0.366664
C	-2.244663	-0.364043	0.553435
C	-1.227463	0.486763	0.182711
C	-1.248735	1.062968	-1.087856
C	-2.306367	0.762705	-1.920377
H	-2.266031	-0.803595	1.545344
H	-2.372580	1.197358	-2.917176
C	-0.061558	1.963620	-1.363910
H	-0.084068	2.410118	-2.360443
C	-0.029494	0.904377	1.015199
H	-0.034264	0.470932	2.017315
N	-3.294844	-0.058653	-1.572083
C	-4.398175	-1.532559	-0.033156
C	-4.268413	-2.546716	0.913268
C	-6.689337	-2.204259	-0.388057
C	-5.338624	-3.377891	1.210424
H	-3.315900	-2.711945	1.408495
C	-6.554143	-3.206145	0.564284
H	-7.636419	-2.066192	-0.901819
H	-5.218256	-4.168755	1.945189

H	-7.392855	-3.855747	0.797529
N	3.131371	0.018386	-1.450103
C	3.314189	-0.616006	-0.279151
C	-5.618930	-1.377476	-0.687387
H	-5.708633	-0.598131	-1.436747
C	4.450511	-1.452255	-0.017526
C	5.432329	-1.634429	-1.007507
C	4.630079	-2.111709	1.211422
C	6.535967	-2.436745	-0.775990
H	5.319054	-1.136274	-1.966450
C	5.736182	-2.909392	1.429789
H	3.897300	-1.999890	2.004383
C	6.701033	-3.081989	0.441493
H	7.277749	-2.558349	-1.560736
H	5.849068	-3.406999	2.389155
H	7.567473	-3.710663	0.620825

Table S9. Cartesian coordinates of **1H**$^+$ in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	0.034055	3.119923	0.266351
C	0.014869	2.619830	-1.038241
C	-0.000613	3.487944	-2.116257
C	0.004014	4.857907	-1.883280
C	0.031302	5.352962	-0.584945
C	0.052148	4.483940	0.499209
H	-0.019097	3.103803	-3.132306
H	-0.011801	5.546525	-2.722250
H	0.034394	6.425070	-0.415540
H	0.071341	4.871696	1.513929
C	-2.155306	-0.301537	-0.620712
C	-1.140413	0.601678	-0.267348
C	-1.123641	1.107327	1.069677
C	-2.036570	0.693644	1.975505
H	-2.235728	-0.675221	-1.635825
H	-2.056339	1.017038	3.009601
C	3.166859	-0.602872	0.291369
C	2.188173	-0.232117	-0.663147
C	1.198235	0.641017	-0.302239
C	1.193898	1.149390	1.019011
C	2.213363	0.724448	1.908882
H	2.208462	-0.640806	-1.665407
H	2.235290	1.102457	2.929378
C	0.041694	2.041934	1.335984
H	0.065445	2.437304	2.352923
C	0.004375	1.104536	-1.104953
H	0.002392	0.718672	-2.125567
N	3.156692	-0.104862	1.563791
C	4.232333	-1.530872	-0.003592
C	4.391634	-2.120154	-1.277668
C	6.178286	-2.749360	0.771764
C	5.420580	-3.000896	-1.514570
H	3.711075	-1.886278	-2.087166
C	6.316032	-3.319179	-0.491054
H	6.878743	-2.999761	1.561082
H	5.537938	-3.447903	-2.495724

H	7.126298	-4.015353	-0.684202
C	-3.100490	-0.685102	0.290471
C	5.151308	-1.864742	1.016466
H	5.027817	-1.407510	1.990363
C	-4.229149	-1.578217	-0.001834
C	-5.472408	-1.381792	0.605187
C	-4.078740	-2.643350	-0.892983
C	-6.535557	-2.225655	0.324497
H	-5.628975	-0.535174	1.269222
C	-5.144130	-3.480739	-1.175564
H	-3.110164	-2.831226	-1.346814
C	-6.375738	-3.277491	-0.565944
H	-7.497922	-2.052290	0.795951
H	-5.009653	-4.307077	-1.866629
H	-7.208450	-3.938266	-0.784786
H	-3.655172	-0.543338	2.279429
N	-3.029308	-0.166108	1.584793

Table S10. Cartesian coordinates of $\mathbf{1H_2^{2+}}$ in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	2.885757	-0.156930	0.000000
C	2.263836	1.092035	0.000000
C	3.015497	2.252283	0.000000
C	4.403562	2.152692	0.000000
C	5.022374	0.910232	0.000000
C	4.265162	-0.256819	0.000000
H	2.535773	3.226898	0.000000
H	5.006056	3.055335	0.000000
H	6.105760	0.847024	0.000000
H	4.753572	-1.227203	0.000000
C	-0.446296	0.524137	2.250592
C	0.373048	0.172602	1.201479
C	1.010413	-1.096588	1.198711
C	0.794861	-1.949487	2.240418
H	-0.911716	1.502827	2.285739
H	1.230145	-2.940621	2.309855
C	-0.635706	-0.351518	-3.329104
C	-0.446296	0.524137	-2.250592
C	0.373048	0.172602	-1.201479
C	1.010413	-1.096588	-1.198711
C	0.794861	-1.949487	-2.240418
H	-0.911716	1.502827	-2.285739
H	1.230145	-2.940621	-2.309855
C	1.904610	-1.322107	0.000000
H	2.392241	-2.298427	0.000000
C	0.740954	1.016042	0.000000
H	0.260234	1.995375	0.000000
C	-1.416544	-0.044418	-4.507918
C	-2.498083	0.865596	-4.432720
C	-1.870849	-0.348821	-6.868904
C	-3.244997	1.152642	-5.550836
H	-2.766829	1.312092	-3.480843
C	-2.937638	0.546452	-6.772042
H	-1.627200	-0.800636	-7.824690
H	-4.080410	1.841538	-5.483908
H	-3.530679	0.775548	-7.652328

C	-0.635706	-0.351518	3.329104
C	-1.117450	-0.644049	-5.754996
H	-0.254121	-1.295252	-5.864576
C	-1.416544	-0.044418	4.507918
C	-1.117450	-0.644049	5.754996
C	-2.498083	0.865596	4.432720
C	-1.870849	-0.348821	6.868904
H	-0.254121	-1.295252	5.864576
C	-3.244997	1.152642	5.550836
H	-2.766829	1.312092	3.480843
C	-2.937638	0.546452	6.772042
H	-1.627200	-0.800636	7.824690
H	-4.080410	1.841538	5.483908
H	-3.530679	0.775548	7.652328
H	-0.191651	-2.243107	4.002636
N	0.005119	-1.567637	3.273804
H	-0.191651	-2.243107	-4.002636
N	0.005119	-1.567637	-3.273804

Table S11. Cartesian coordinates of **ppy** in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	-1.573841	1.244183	-0.001467
C	-2.719885	-1.253926	0.000929
H	-1.098955	2.219979	-0.002704
H	-3.052745	-2.288740	0.001758
N	-1.445635	-1.019415	-0.001331
C	-0.682831	0.083706	-0.001183
C	0.750747	0.047233	-0.000503
C	1.426099	-1.186543	-0.000671
C	1.528517	1.218766	0.000313
C	2.808754	-1.240631	-0.000016
H	0.850572	-2.108064	-0.001406
C	2.908114	1.150528	0.000922
H	1.049352	2.192677	0.000611
C	3.564701	-0.076547	0.000776
H	3.301869	-2.209013	-0.000166
H	3.483598	2.072265	0.001572
H	4.649166	-0.121696	0.001265
C	-2.920159	1.116467	0.000072
H	-3.528897	2.016189	0.000140
C	-3.571928	-0.160271	0.001705
H	-4.644242	-0.295479	0.002983

Table S12. Cartesian coordinates of **2** in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	0.233736	2.642708	-0.62949
C	-0.19999	2.611992	0.699108
C	-0.4437	3.789474	1.379366
C	-0.24949	5.006952	0.731397
C	0.181394	5.037269	-0.58551
C	0.424361	3.850643	-1.27285
H	-0.7822	3.765812	2.411905
H	-0.43639	5.935676	1.262322
H	0.33136	5.989831	-1.0851
H	0.76144	3.874614	-2.30598
C	-2.50373	-0.08566	0.689454
C	-1.34809	0.510581	0.332704
C	-0.89073	0.548348	-1.03741
C	-1.69033	-0.07493	-1.96204
H	-2.8372	-0.10921	1.722394
H	-1.47686	-0.14847	-3.02525
C	1.743924	-0.15642	1.945095
C	0.96415	0.505977	1.020882
C	1.399101	0.540282	-0.30447
C	2.588288	-0.06928	-0.63798
H	1.437144	-0.22299	2.988263
H	2.935105	-0.0836	-1.66619
C	0.43189	1.25902	-1.22657
H	0.768969	1.285692	-2.26499
C	-0.36038	1.205623	1.253713
H	-0.67215	1.193119	2.300153
N	-2.78259	-0.62882	-1.50646
C	-3.36761	-0.72403	-0.30129
C	-4.63992	-1.35669	-0.10173
C	-5.32078	-1.92694	-1.192
C	-5.24922	-1.43372	1.163207
C	-6.5487	-2.54186	-1.02127
H	-4.87162	-1.88406	-2.18042
C	-6.47457	-2.05133	1.320194
H	-4.7612	-1.00426	2.032417

C	-7.13866	-2.61177	0.232934
H	-7.05052	-2.97372	-1.88298
H	-6.92201	-2.09616	2.309385
H	-8.10144	-3.09531	0.364637
C	3.32558	-0.69528	0.374666
N	2.89917	-0.7419	1.635055
C	4.623881	-1.36368	0.087058
C	5.065079	-2.39132	0.918689
C	5.420725	-0.98428	-0.99096
C	6.26466	-3.03657	0.666385
H	4.449503	-2.6699	1.767446
C	6.624258	-1.62705	-1.24172
H	5.116731	-0.16044	-1.63027
C	7.047746	-2.65875	-0.41669
H	6.591434	-3.84034	1.319938
H	7.237293	-1.31368	-2.08186
H	7.9893	-3.16341	-0.6132

Table S13. Cartesian coordinates of **2H**$^+$ in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	-0.28534	2.832064	0.660794
C	0.130685	2.826456	-0.67278
C	0.293571	4.014688	-1.36462
C	0.055217	5.21715	-0.70691
C	-0.35184	5.22449	0.622036
C	-0.52614	4.029522	1.312741
H	0.613982	4.010948	-2.40324
H	0.190094	6.155859	-1.23587
H	-0.5372	6.169001	1.124685
H	-0.84759	4.038242	2.351126
C	2.462758	-0.02941	-0.639
C	1.30109	0.690679	-0.30307
C	0.886336	0.729905	1.065008
C	1.614633	0.097453	2.011028
H	2.784579	-0.12133	-1.67124
H	1.356463	0.078039	3.063925
C	-1.60357	-0.12434	-1.94247
C	-0.88608	0.661438	-0.99611
C	-1.35469	0.679847	0.344053
C	-2.47232	-0.03195	0.664849
H	-1.25614	-0.18514	-2.97238
H	-2.8326	-0.04467	1.686402
C	-0.43277	1.447436	1.261679
H	-0.77346	1.460457	2.298533
C	0.369577	1.431964	-1.22957
H	0.693464	1.428681	-2.27177
C	3.195965	-0.64973	0.335076
C	4.419386	-1.42938	0.086086
C	4.67485	-2.60232	0.801364
C	5.346987	-1.00431	-0.86749
C	5.829451	-3.33388	0.564353
H	3.948813	-2.97322	1.521481
C	6.497015	-1.7405	-1.10562
H	5.179978	-0.07518	-1.40542
C	6.743248	-2.90582	-0.38959

H	6.010477	-4.24902	1.12032
H	7.213345	-1.39448	-1.84486
H	7.647358	-3.47817	-0.57384
C	-3.14863	-0.75768	-0.35376
N	-2.67072	-0.79977	-1.63589
C	-4.36595	-1.48767	-0.114
C	-4.93069	-2.25431	-1.1624
C	-5.02867	-1.46429	1.136981
C	-6.09429	-2.96449	-0.96362
H	-4.42334	-2.27337	-2.11951
C	-6.19151	-2.17455	1.324983
H	-4.63926	-0.87702	1.960289
C	-6.72776	-2.92871	0.277323
H	-6.51598	-3.55211	-1.7726
H	-6.69513	-2.14716	2.2858
H	-7.64514	-3.48886	0.432898
H	3.378023	-0.90711	2.374402
N	2.760162	-0.56779	1.651151

Table S14. Cartesian coordinates of $\mathbf{2H_2^{2+}}$ in the S_1 state (TDA-TD-LC-wHPBE, 6-31g(d)).

Atom	X	Y	Z
C	0.211687	2.551599	-0.66483
C	-0.21169	2.551599	0.664832
C	-0.4239	3.741841	1.335899
C	-0.20999	4.939831	0.661539
C	0.20997	4.939831	-0.66155
C	0.423889	3.741841	-1.3359
H	-0.75269	3.746659	2.371282
H	-0.37374	5.881526	1.175486
H	0.373716	5.881526	-1.17549
H	0.752676	3.746659	-2.37129
C	-2.57972	-0.10545	0.647018
C	-1.36763	0.457077	0.317401
C	-0.93129	0.455987	-1.03358
C	-1.72833	-0.10308	-1.98605
H	-2.91793	-0.13197	1.676909
H	-1.48569	-0.12025	-3.04304
C	1.728333	-0.10307	1.986049
C	0.931292	0.455994	1.033581
C	1.367637	0.457084	-0.3174
C	2.579729	-0.10544	-0.64702
H	1.4857	-0.12024	3.043039
H	2.917941	-0.13196	-1.67691
C	0.395825	1.153642	-1.24428
H	0.722237	1.156966	-2.28542
C	-0.39583	1.153642	1.244277
H	-0.72224	1.156966	2.285424
C	-3.38951	-0.67959	-0.3451
C	-4.66592	-1.31328	-0.09486
C	-5.14213	-2.34883	-0.93533
C	-5.46957	-0.89485	0.993225
C	-6.36889	-2.92754	-0.70052
H	-4.52328	-2.7365	-1.7405
C	-6.69308	-1.47989	1.218907
H	-5.14111	-0.07862	1.62858
C	-7.14975	-2.49521	0.373542

H	-6.72443	-3.72715	-1.34183
H	-7.31126	-1.1445	2.044945
H	-8.11805	-2.95231	0.554155
C	3.389516	-0.67957	0.345097
C	4.665921	-1.31327	0.094863
C	5.142131	-2.34882	0.935327
C	5.469581	-0.89485	-0.99322
C	6.368886	-2.92754	0.700515
H	4.523273	-2.73649	1.740497
C	6.693081	-1.47989	-1.21891
H	5.141122	-0.07861	-1.62858
C	7.149751	-2.49522	-0.37355
H	6.724422	-3.72716	1.341826
H	7.311268	-1.14451	-2.04494
H	8.118042	-2.95232	-0.55416
H	-3.53136	-0.97818	-2.37286
N	-2.91406	-0.66136	-1.63454
H	3.531365	-0.97816	2.372858
N	2.914062	-0.66135	1.634541