Electronic Supplementary Information for

A Red-Emissive Aminobenzopyrano-xanthene Dye: Elucidation of the Fluorescence Emission Mechanism in Solution- and Aggregate-state

Shinichiro Kamino,*[a] Atsuya Muranaka,[bc] Miho Murakami,[d] Asana Tatsumi,[d] Noriyuki Nagaoka,[d] Yoshinao Shirasaki,[d] Keiko Watanabe,[a] Kengo Yoshida,[b] Jun Horigome,[e] Seiji Komeda,[f] Masanobu Uchiyama,[bg] and Shuichi Enomoto*[ad]

[a]Multiple Molecular Imaging Research Laboratory, RIKEN-CMIS, Kobe, Hyogo 650-0047, Japan. E-mail: skamino@riken.jp

[b]Advanced Elements Chemistry Research Team, RIKEN-ASI, Wako, Saitama 351-0198, Japan

[c]PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

[d]Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Okayama University, Okayama 700-8530, Japan. E-mail: senomoto@pharm.okayama-u.ac.jp

[e]Hitachi High-Technologies Co., Ltd., Hitachinaka, Ibaraki 312-8504, Japan

[f]Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science, Suzuka, Mie 513-8670, Japan

[g]Graduate School of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

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1. General Remarks

Materials. Reagents were purchased from Wako, Nacalai Tesque, TCI Japan or other commercial suppliers. All solvents were used without further purification. Experiments were conducted under an atmosphere of dry nitrogen or using a guard tube. All solvents were of spectral grade unless otherwise noted. Water for spectrophotometric measurements was obtained from a Millipore Milli-Q purification system. Liquid column chromatography was conducted over silica gel (Merck Silica Gel 60 mesh 70-230). Developed TLC plates were visualized under a short-wave UV lamp by staining with an I_2-SiO_2 mixture and by heating plates that were dipped in ammonium phosphomolybdate sulfate solution.

Instruments. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with an ECA600 spectrometer. The solvent used for NMR measurements was $CDCl_3$. Mass spectra were acquired using a JMX-700 (JEOL Co., Ltd.) MS instrument. Particle morphology was examined by scanning electron microscopy (SEM; DS-720, Topcon, Tokyo, Japan), and elemental analysis was accomplished by EDX equipment (EMAX-7000).

2. Figures and Tables

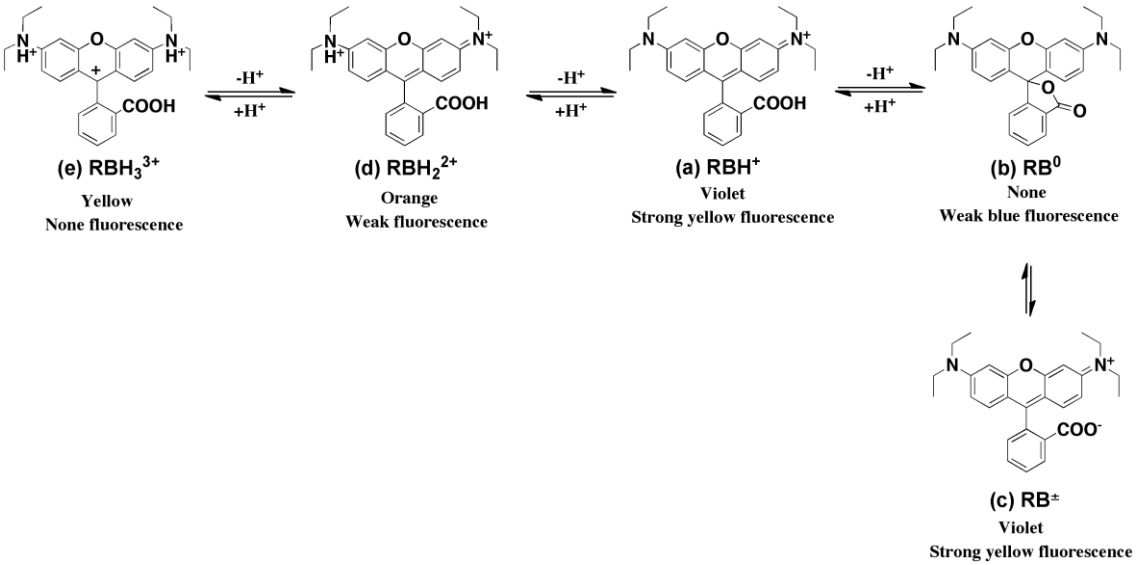


Fig. S1 Chemical equilibrium of rhodamine B (RB).[1] Respective chemical species and their color and fluorescence emission are described in below.

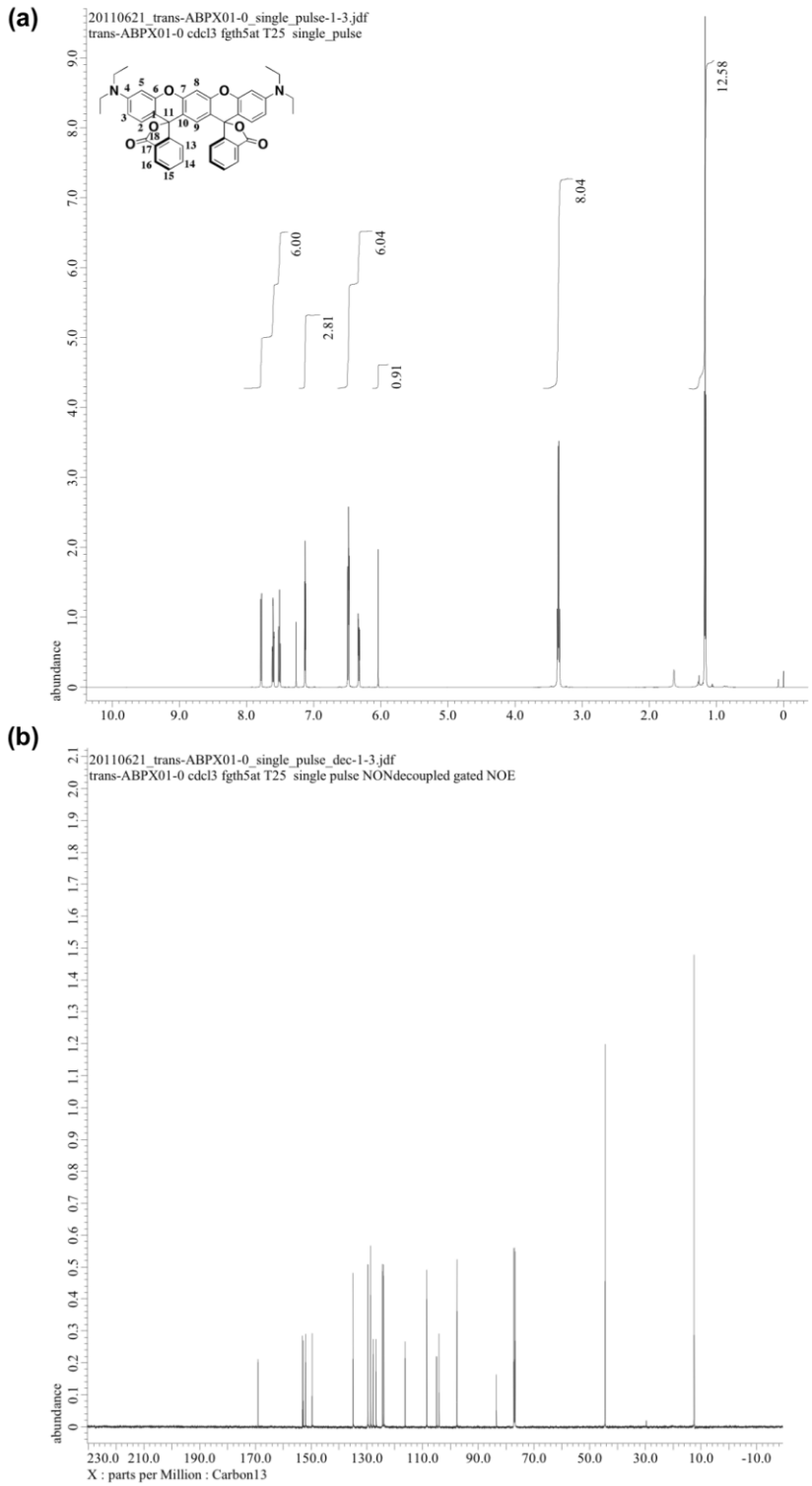


Fig. S2 (a)^{1}H- and (b) ^{13}C-NMR spectra of *trans*-ABPX01^{0} in $CDCl_3$. Inset: labeled atoms in the chemical structure of *trans*-ABPX01^{0}.

Table S1 NMR spectral data of *trans*-ABPX01^0 in $CDCl_3$.

Position	δ_H		*J* /Hz	^{1}H-^{1}H COSY	δ_C	HMBC (C)
1					152.83	
2	6.48	d	8.7	3	128.63	1,3,4,5,6,11
3	6.32	dd	8.9, 2.5	2,5	108.47	1,2,5,6,
4					149.67	
5	6.48	sd	2.3	3	97.65	1,3,4,6,11
6					104.95	
7					153.15	
8	7.12	s			104.10	7,10,11
9	6.04	s			127.69	7,8,10,11
10					116.27	
11					83.48	
12					151.98	
13	7.12	d	7.8	14,15	123.94	10,11,15,16,17
14	7.60	td	7.4, 0.93	13,15	134.97	11,12,13,15,16,17
15	7.51	td	7.5, 0.97	13,14,16	129.61	12,13,14,16,17,18
16	7.78	d	7.8	14,15	124.46	12,13,14,18
17					126.65	
18					169.12	
19	3.35	q	7.0	20	44.44	4,20
20	1.17	t	7.1	19	12.46	19

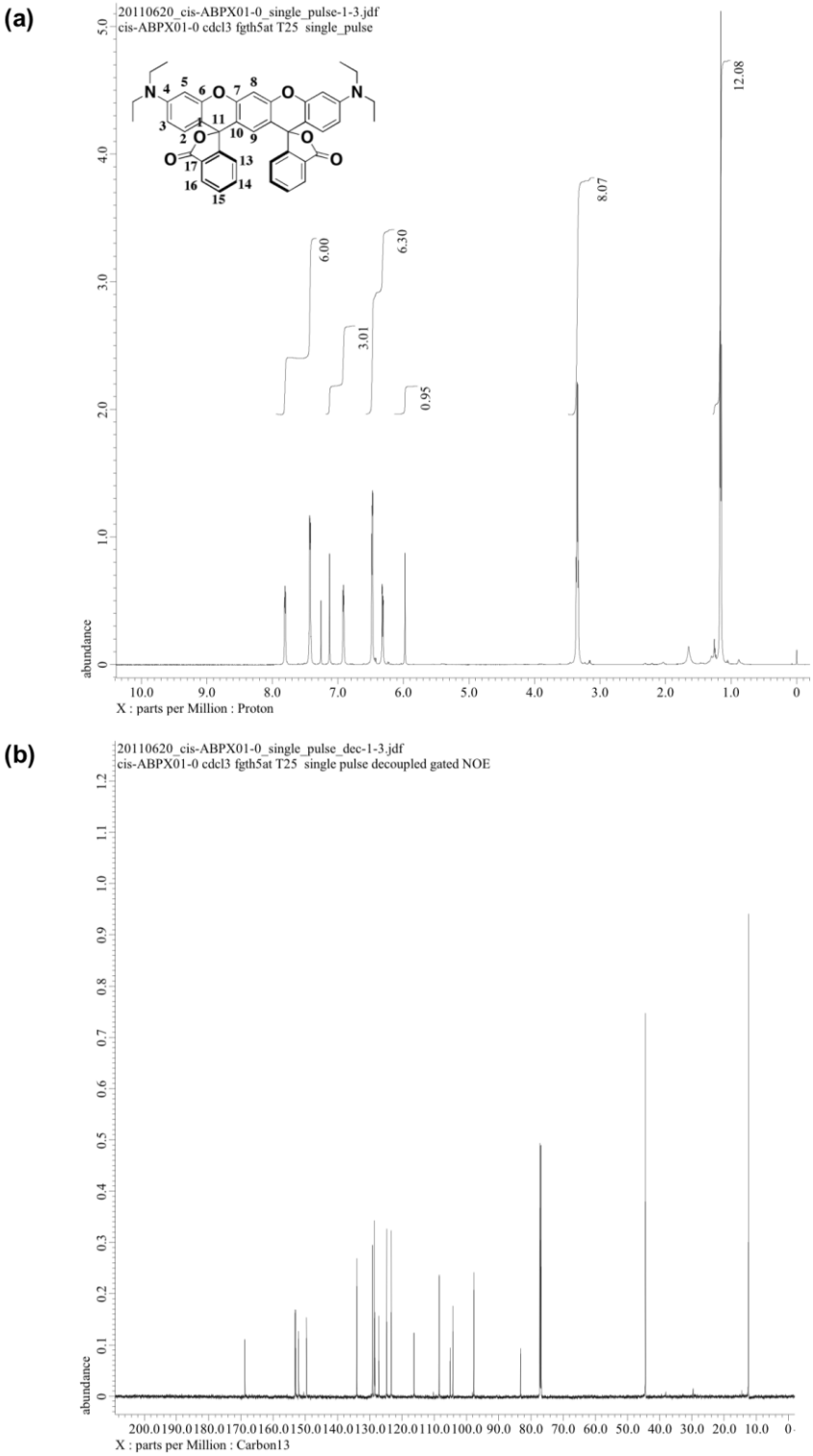


Fig. S3 (a) ^{1}H- and (b) ^{13}C-NMR spectra of *cis*-ABPX01^{0} in $CDCl_3$. Inset: labeled atoms in the chemical structure of *cis*-ABPX01^{0}.

Table S2 NMR spectral data of *cis*-ABPX01^{0} in $CDCl_3$.

Position	δ_H		*J* /Hz	^{1}H-^{1}H COSY	δ_C	HMBC (C)
1					153.06	
2	6.48	d	8.7	3	128.59	1,3,4,5,6,11
3	6.32	dd	9.2, 2.3	2, 5	108.44	5,6,
4					149.66	
5	6.48	sd	2.8	3	97.72	1,2,3,4,6,11
6					105.08	
7					153.20	
8	7.13	s			104.22	7,10,11
9	5.98	s			128.44	7,11
10					116.27	
11					83.19	
12					152.06	
13	6.92	dd	6.9, 1.3	14,15	123.37	11,12,15,17
14	7.43	t	6.9	13,15	134.04	12,13,15,16
15	7.43	t	6.7	13,14,16	129.19	12,13,14,16
16	7.81	dd	6.9, 1.3	14,15	124.79	12,14,17,18
17					127.21	
18					168.79	
19	3.35	q	6.9	20	44.45	4,20
20	1.16	t	6.9	19	12.54	19

Table S3 Crystal and experimental data for *trans*- and *cis*-ABPX01^0.

	trans-ABPX01^0	*cis*-ABPX01^0
Formula	$C_{42}H_{37}N_2O_6$	$C_{42}H_{37}N_2O_6$
Mw	665.76	665.76
Temperature (K)	293	93
Crystal system	orthorhombic	monoclinic
Space group	*Fdd2*	$P2_1/c$
a (Å)	17.5837(11)	10.8756(5)
b (Å)	23.2759(11)	16.1912(7)
c (Å)	18.2237(9)	20.1235(8)
α, β, γ (˚)	90	90, 94.485(7), 90
V (Å^3)	7458.5(7)	3532.7(3)
Z	8	4
D_{calc} (g/cm^3)	1.186	1.250
F(000)	2808	1404
μ (cm^{-1})	0.793 (Mo-Kα)	6.76 (Cu-Kα)
$2\theta_{max}$ (˚)	54.9	45.0
No. of unique reflections	4211	2,843
No. of reflections ($I > 2.00\sigma(I)$)	3761	1961
No. of parameters	252	460
R1 ($I > 2.00\sigma(I)$)	0.0705	0.0814
R (all reflections)	0.0772	0.1112
Goodness of fit	0.999	1.000
CCDC No	779022	894956

Table S4 Intramolecular bond lengths [Å] and angles [°] in the crystal structure of *trans*-ABPX01[0].

O(1)	-	C(6)	1.383(3)	O(1)	-	C(7)	1.373(3)
O(2)	-	C(11)	1.491(3)	O(2)	-	C(18)	1.363(4)
O(3)	-	C(18)	1.210(4)	N(1)	-	C(4)	1.371(4)
N(1)	-	C(19)	1.467(5)	N(1)	-	C(21)	1.469(5)
C(1)	-	C(2)	1.398(4)	C(1)	-	C(6)	1.382(3)
C(1)	-	C(11)	1.508(3)	C(2)	-	C(3)	1.370(4)
C(3)	-	C(4)	1.418(4)	C(4)	-	C(5)	1.404(4)
C(5)	-	C(6)	1.386(4)	C(7)	-	C(8)	1.382(3)
C(7)	-	C(10)	1.397(3)	C(9)	-	C(10)	1.393(3)
C(10)	-	C(11)	1.510(3)	C(11)	-	C(12)	1.500(3)
C(12)	-	C(13)	1.391(4)	C(12)	-	C(17)	1.377(4)
C(13)	-	C(14)	1.371(6)	C(14)	-	C(15)	1.371(7)
C(15)	-	C(16)	1.422(6)	C(16)	-	C(17)	1.376(5)
C(17)	-	C(18)	1.485(5)	C(19)	-	C(20)	1.575(7)
C(21)	-	C(22)	1.469(13)				

C(6)	-	O(1)	-	C(7)	118.38(17)	C(11)	-	O(2)	-	C(18)	111.04(19)
C(4)	-	N(1)	-	C(19)	120.3(3)	C(4)	-	N(1)	-	C(21)	120.0(4)
C(19)	-	N(1)	-	C(21)	116.5(4)	C(2)	-	C(1)	-	C(6)	116.22(19)
C(2)	-	C(1)	-	C(11)	121.56(19)	C(6)	-	C(1)	-	C(11)	122.21(18)
C(1)	-	C(2)	-	C(3)	122.4(3)	C(2)	-	C(3)	-	C(4)	121.0(3)
N(1)	-	C(4)	-	C(3)	121.5(3)	N(1)	-	C(4)	-	C(5)	121.6(3)
C(3)	-	C(4)	-	C(5)	116.9(3)	C(4)	-	C(5)	-	C(6)	120.2(3)
O(1)	-	C(6)	-	C(1)	123.13(19)	O(1)	-	C(6)	-	C(5)	113.7(2)
C(1)	-	C(6)	-	C(5)	123.2(2)	O(1)	-	C(7)	-	C(8)	115.19(19)
O(1)	-	C(7)	-	C(10)	123.49(17)	C(8)	-	C(7)	-	C(10)	121.31(18)
C(7)	-	C(8)	-	C(7)*	119.4(3)	C(10)	-	C(9)	-	C(10)*	122.2(3)
C(7)	-	C(10)	-	C(9)	117.82(18)	C(7)	-	C(10)	-	C(11)	121.36(16)
C(9)	-	C(10)	-	C(11)	120.82(19)	O(2)	-	C(11)	-	C(1)	108.00(15)
O(2)	-	C(11)	-	C(10)	108.79(15)	O(2)	-	C(11)	-	C(12)	102.64(16)

C(1)	-	C(11)	-	C(10)	111.22(17)	C(1)	-	C(11)	-	C(12)	111.87(17)
C(10)	-	C(11)	-	C(12)	113.79(16)	C(11)	-	C(12)	-	C(13)	129.1(3)
C(11)	-	C(12)	-	C(17)	110.0(2)	C(13)	-	C(12)	-	C(17)	120.9(3)
C(12)	-	C(13)	-	C(14)	117.7(3)	C(13)	-	C(14)	-	C(15)	122.0(4)
C(14)	-	C(15)	-	C(16)	120.8(4)	C(15)	-	C(16)	-	C(17)	116.4(4)
C(12)	-	C(17)	-	C(16)	122.3(3)	C(12)	-	C(17)	-	C(18)	108.1(3)
C(16)	-	C(17)	-	C(18)	129.6(3)	O(2)	-	C(18)	-	O(3)	121.4(3)
O(2)	-	C(18)	-	C(17)	108.0(3)	O(3)	-	C(18)	-	C(17)	130.6(3)

*Symmetry operators (-*x*+1/2, -*y*+1/2 ,*z*)

Table S5 Intramolecular bond lengths [Å] and angles [°] in the crystal structure of *cis*-ABPX01[0].

O(1)	-	C(6)	1.385(9)	O(1)	-	C(7)	1.373(10)
O(2)	-	C(11)	1.527(9)	O(2)	-	C(18)	1.340(13)
O(3)	-	C(18)	1.209(12)	O(11)	-	C(36)	1.403(10)
O(11)	-	C(37)	1.370(10)	O(12)	-	C(41)	1.521(9)
O(12)	-	C(48)	1.333(7)	O(13)	-	C(48)	1.206(7)
N(1)	-	C(4)	1.372(10)	N(1)	-	C(19)	1.455(9)
N(1)	-	C(21)	1.468(10)	N(11)	-	C(34)	1.361(12)
N(11)	-	C(49)	1.455(9)	N(11)	-	C(51a)*	1.527(19)
N(11)	-	C(51b)*	1.50(2)	C(1)	-	C(2)	1.386(11)
C(1)	-	C(6)	1.392(13)	C(1)	-	C(11)	1.508(11)
C(2)	-	C(3)	1.354(12)	C(3)	-	C(4)	1.434(13)
C(4)	-	C(5)	1.385(10)	C(5)	-	C(6)	1.359(11)
C(7)	-	C(8)	1.354(12)	C(7)	-	C(10)	1.417(13)
C(8)	-	C(37)	1.387(12)	C(9)	-	C(10)	1.387(11)
C(9)	-	C(40)	1.386(11)	C(10)	-	C(11)	1.494(11)
C(11)	-	C(12)	1.513(11)	C(12)	-	C(13)	1.389(10)
C(12)	-	C(17)	1.354(15)	C(13)	-	C(14)	1.390(13)
C(14)	-	C(15)	1.374(16)	C(15)	-	C(16)	1.366(13)
C(16)	-	C(17)	1.388(13)	C(17)	-	C(18)	1.476(11)
C(19)	-	C(20)	1.525(11)	C(21)	-	C(22)	1.514(11)
C(31)	-	C(32)	1.398(10)	C(31)	-	C(36)	1.388(12)
C(31)	-	C(41)	1.474(10)	C(32)	-	C(33)	1.364(12)
C(33)	-	C(34)	1.393(13)	C(34)	-	C(35)	1.406(11)
C(35)	-	C(36)	1.361(11)	C(37)	-	C(40)	1.409(13)
C(40)	-	C(41)	1.489(11)	C(41)	-	C(42)	1.519(10)
C(42)	-	C(43)	1.375(11)	C(42)	-	C(47)	1.379(9)
C(43)	-	C(44)	1.395(11)	C(44)	-	C(45)	1.391(15)
C(45)	-	C(46)	1.371(10)	C(46)	-	C(47)	1.382(6)
C(47)	-	C(48)	1.483(6)	C(49)	-	C(50)	1.485(10)
C(51A)*	-	C(52A)*	1.53(3)	C(51B)*	-	C(52B)*	1.52(3)

C(36)	-	O(11)	-	C(37)	118.3(6)	C(41)	-	O(12)	-	C(48)	111.8(4)
C(4)	-	N(1)	-	C(19)	122.3(7)	C(4)	-	N(1)	-	C(21)	121.4(6)
C(19)	-	N(1)	-	C(21)	116.0(6)	C(34)	-	N(11)	-	C(49)	121.4(8)
C(34)	-	N(11)	-	C(51a)*	117.6(10)	C(34)	-	N(11)	-	C(51b)*	118.4(10)
C(49)	-	N(11)	-	C(51a)*	114.5(10)	C(49)	-	N(11)	-	C(51b)*	114.9(9)
C(2)	-	C(1)	-	C(6)	114.9(7)	C(2)	-	C(1)	-	C(11)	122.6(8)
C(6)	-	C(1)	-	C(11)	122.4(7)	C(1)	-	C(2)	-	C(3)	123.6(8)
C(2)	-	C(3)	-	C(4)	119.9(7)	N(1)	-	C(4)	-	C(3)	120.9(7)
N(1)	-	C(4)	-	C(5)	121.8(8)	C(3)	-	C(4)	-	C(5)	117.3(7)
C(4)	-	C(5)	-	C(6)	119.9(8)	O(1)	-	C(6)	-	C(1)	120.8(7)
O(1)	-	C(6)	-	C(5)	114.8(8)	C(1)	-	C(6)	-	C(5)	124.4(7)
O(1)	-	C(7)	-	C(8)	118.4(8)	O(1)	-	C(7)	-	C(10)	121.8(7)
C(8)	-	C(7)	-	C(10)	119.8(8)	C(7)	-	C(8)	-	C(37)	121.9(8)
C(10)	-	C(9)	-	C(40)	123.3(8)	C(7)	-	C(10)	-	C(9)	117.8(7)
C(7)	-	C(10)	-	C(11)	121.1(7)	C(9)	-	C(10)	-	C(11)	121.0(8)
O(2)	-	C(11)	-	C(1)	107.1(6)	O(2)	-	C(11)	-	C(10)	107.2(5)
O(2)	-	C(11)	-	C(12)	100.3(6)	C(1)	-	C(11)	-	C(10)	112.2(7)
C(1)	-	C(11)	-	C(12)	114.2(6)	C(10)	-	C(11)	-	C(12)	114.6(6)
C(11)	-	C(12)	-	C(13)	128.0(8)	C(11)	-	C(12)	-	C(17)	111.3(6)
C(13)	-	C(12)	-	C(17)	120.7(7)	C(12)	-	C(13)	-	C(14)	117.3(8)
C(13)	-	C(14)	-	C(15)	121.8(8)	C(14)	-	C(15)	-	C(16)	120.0(9)
C(15)	-	C(16)	-	C(17)	118.7(8)	C(12)	-	C(17)	-	C(16)	121.5(7)
C(12)	-	C(17)	-	C(18)	108.4(8)	C(16)	-	C(17)	-	C(18)	130.1(10)
O(2)	-	C(18)	-	O(3)	121.9(8)	O(2)	-	C(18)	-	C(17)	108.6(8)
O(3)	-	C(18)	-	C(17)	129.4(10)	N(1)	-	C(19)	-	C(20)	112.6(5)
N(1)	-	C(21)	-	C(22)	114.8(6)	C(32)	-	C(31)	-	C(36)	113.6(7)
C(32)	-	C(31)	-	C(41)	123.2(7)	C(36)	-	C(31)	-	C(41)	123.1(7)
C(31)	-	C(32)	-	C(33)	123.1(8)	C(32)	-	C(33)	-	C(34)	122.3(8)
N(11)	-	C(34)	-	C(33)	123.5(8)	N(11)	-	C(34)	-	C(35)	121.1(8)
C(33)	-	C(34)	-	C(35)	115.4(7)	C(34)	-	C(35)	-	C(36)	120.9(7)
O(11)	-	C(36)	-	C(31)	121.0(7)	O(11)	-	C(36)	-	C(35)	114.4(7)
C(31)	-	C(36)	-	C(35)	124.6(7)	O(11)	-	C(37)	-	C(8)	116.5(8)
O(11)	-	C(37)	-	C(40)	123.4(7)	C(8)	-	C(37)	-	C(40)	120.1(8)

C(9)	-	C(40)	-	C(37)	117.1(7)	C(9)	-	C(40)	-	C(41)	122.7(8)
C(37)	-	C(40)	-	C(41)	120.2(7)	O(12)	-	C(41)	-	C(31)	107.0(5)
O(12)	-	C(41)	-	C(40)	106.2(6)	O(12)	-	C(41)	-	C(42)	100.7(6)
C(31)	-	C(41)	-	C(40)	112.6(7)	C(31)	-	C(41)	-	C(42)	114.2(6)
C(40)	-	C(41)	-	C(42)	114.7(5)	C(41)	-	C(42)	-	C(43)	128.9(7)
C(41)	-	C(42)	-	C(47)	110.5(6)	C(43)	-	C(42)	-	C(47)	120.6(7)
C(42)	-	C(43)	-	C(44)	117.4(8)	C(43)	-	C(44)	-	C(45)	121.0(8)
C(44)	-	C(45)	-	C(46)	121.5(8)	C(45)	-	C(46)	-	C(47)	116.8(6)
C(42)	-	C(47)	-	C(46)	122.7(5)	C(42)	-	C(47)	-	C(48)	107.8(5)
C(46)	-	C(47)	-	C(48)	129.5(4)	O(12)	-	C(48)	-	O(13)	122.4(5)
O(12)	-	C(48)	-	C(47)	109.1(4)	O(13)	-	C(48)	-	C(47)	128.4(5)
N(11)	-	C(49)	-	C(50)	112.3(5)	N(11)	-	C(51A)*	-	C(52a)*	108.0(16)
N(11)	-	C(51b)*	-	C(52b)	100.3(15)						

*Disordered atoms

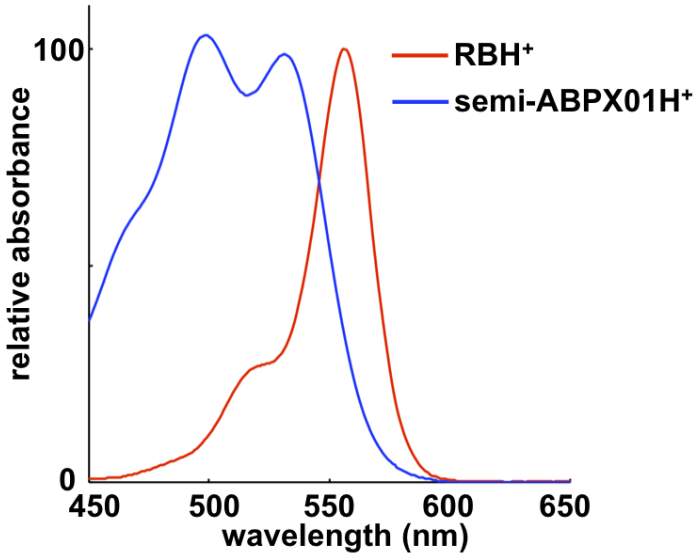


Fig. S4 Absorption spectra of RBH^+ in $CHCl_3$ solution containing 1% TFA and semi-$ABPX01H^+$ in THF solution containing 1% TFA.

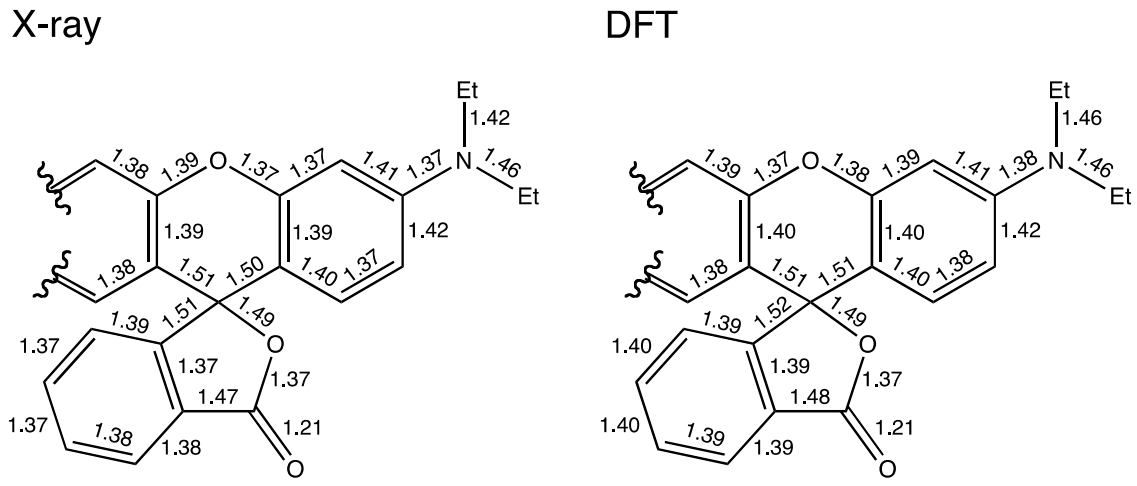


Fig. S5 Comparison of bond lengths (Å) in the crystal structure of *trans*-ABPX01^{0} with those in the optimized geometry.

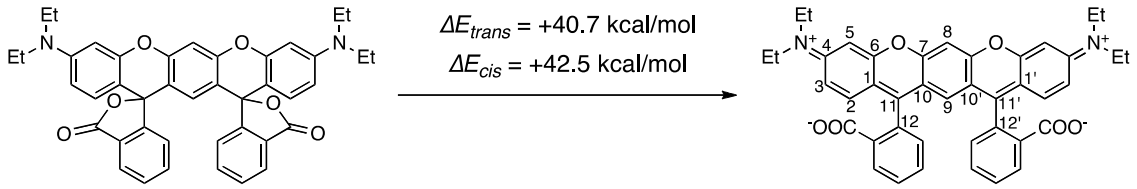


Fig. S6 Energy differences between ABPX01^{0} and ABPX01$^{2\pm}$.

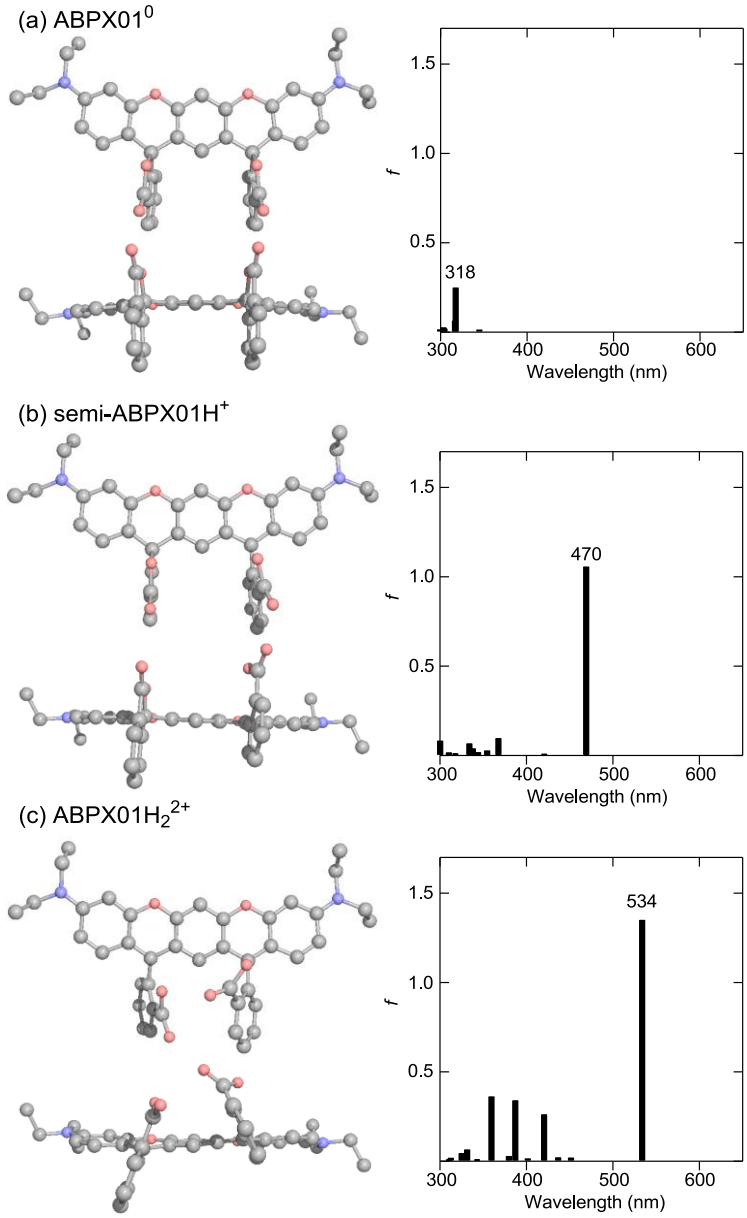


Fig. S7 Optimized geometries (left) and absorption spectra (right) of *cis*-ABPX01^0 (a), *cis*-semi-ABPX01H$^+$ (b), and *cis*-ABPX01H$_2^{2+}$ (c). Geometry optimizations were performed at B3LYP/6-31G(d,p) level. Hydrogen atoms were omitted for clarity. The absorption spectra in water were calculated at the same level using the self-consistent reaction field (SCRF) approach.

Table S6 Optical properties of *trans*-ABPX01 in various solvents.

Solvent	λ_{abs} [nm]	λ_{fl} [nm]	ε [$M^{-1}cm^{-1}$]	Φ_{fl} [*1]	Brightness $\varepsilon \times \phi_{fl}$
Chloroform	599	615	51045	0.069	3522
Methanol	593	618	74159	0.073	6378
Ethanol	594	618	5147	0.013	77
Acetone	594	618	64589	0.049	2067

[*1]Fluorescence quantum yields of ABPX01 were determined by using the reference standard dye RB (ϕ_{fl} = 0.73 in ethanol).

Table S7 Optical properties of *cis*-ABPX01 in various solvents.

Solvent	λ_{abs} [nm]	λ_{fl} [nm]	ε [$M^{-1}cm^{-1}$]	Φ_{fl} [*1]	Brightness $\varepsilon \times \phi_{fl}$
Chloroform	599	619	106090	0.209	22173
Methanol	592	618	66819	0.076	5947
Ethanol	593	618	3855	0.008	35
Acetone	593	619	56726	0.046	2950

[*1]Fluorescence quantum yields of ABPX01 were determined by using the reference standard dye RB (ϕ_{fl} = 0.73 in ethanol).

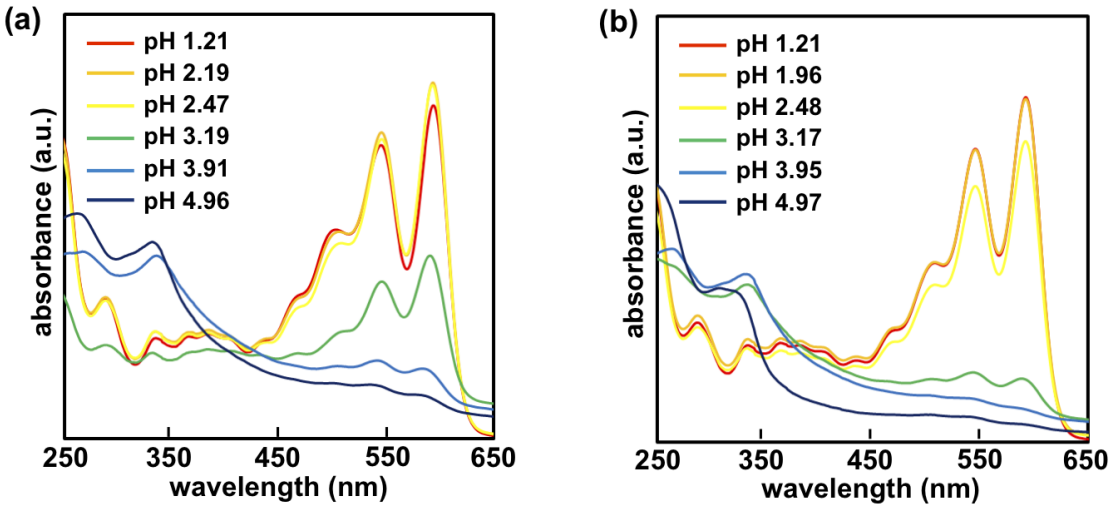


Fig. S8 Absorption spectra of (a) *trans*- and (b) *cis*-ABPX01 at various pH. The absorption spectra of 5 μM ABPX01 in 0.1 M acetate/HCl buffers of integral pH values ranging from 1 to 5 were measured.

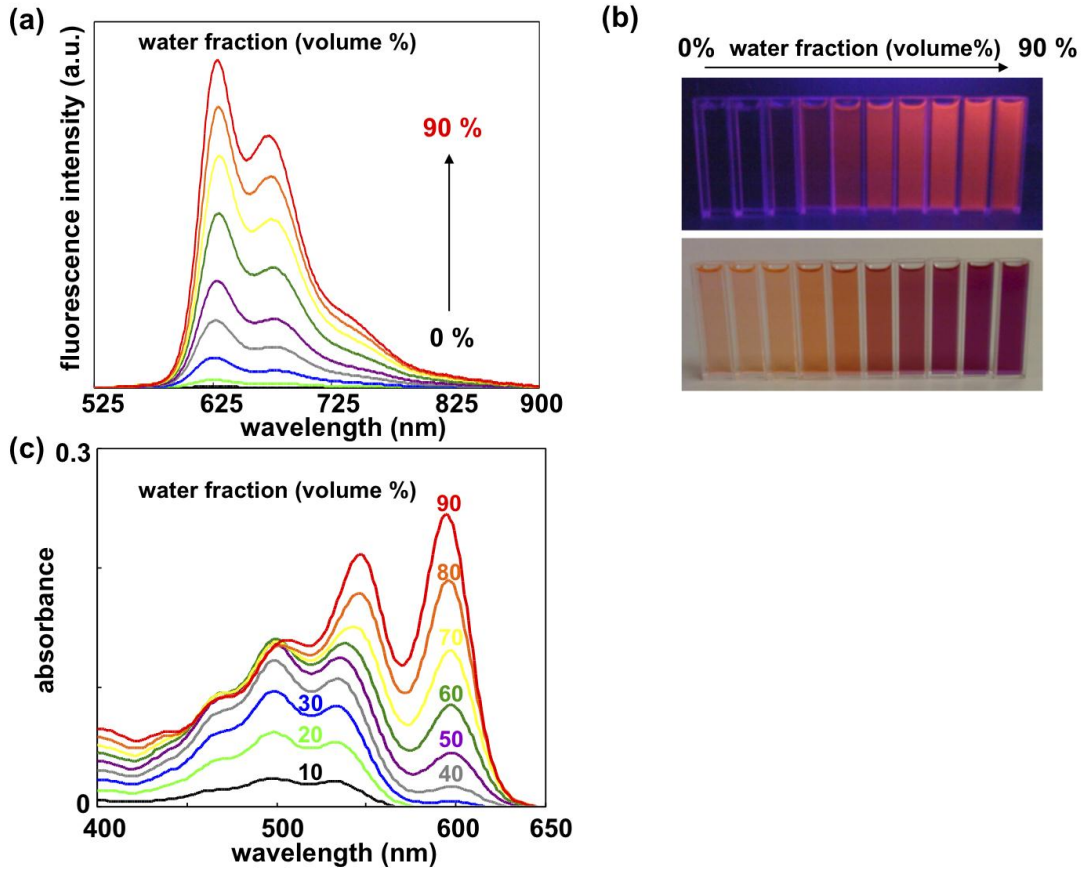


Fig. S9 (a) Fluorescence emission spectra of 500 μM ABPX01 in water/THF mixtures obtained by surface photometric method. λ_{ex} = 365 nm. (b) Photograph of the solutions, top: under 365 nm irradiation, bottom: under room light. (c) Absorption spectra of 5 μM ABPX01 in water/THF mixtures. Fluorescence emission and absorption spectra of ABPX01 were measured immediately after preparation, respectively.

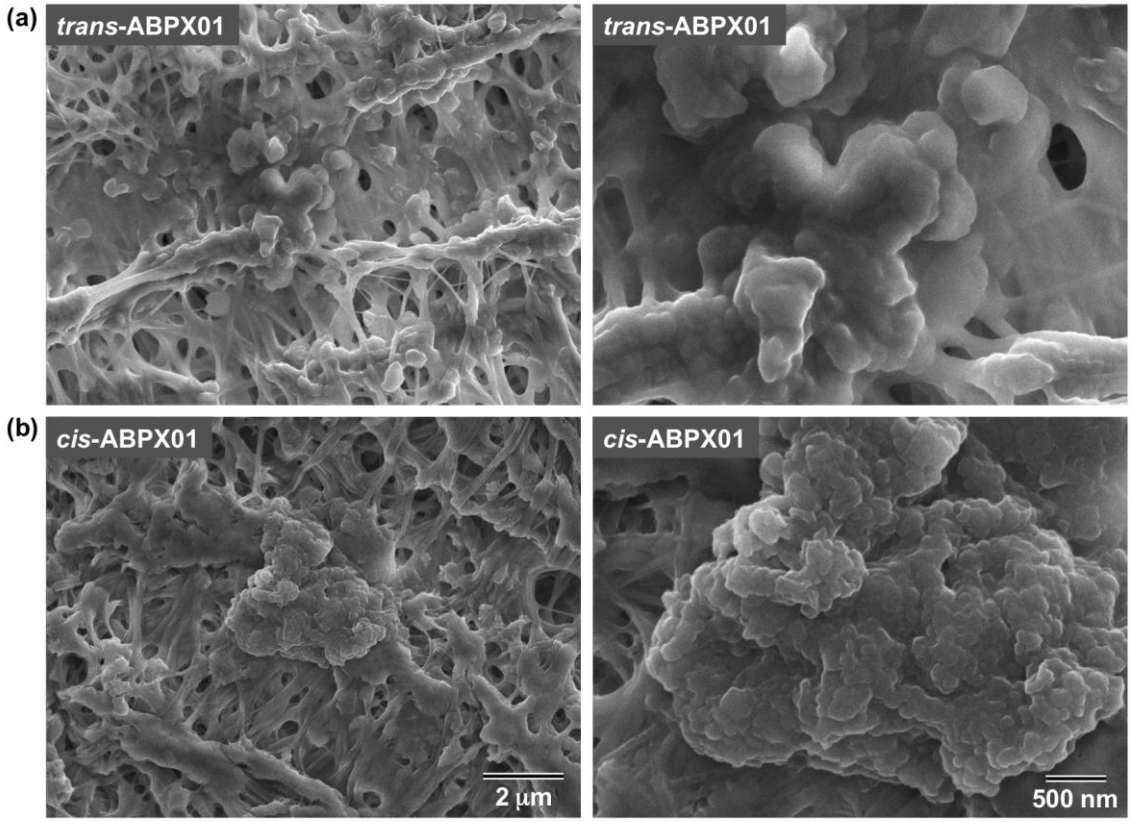


Fig. S10 SEM images of ABPX01-chloride ion pairs on PTFE membrane filter. The aggregates were obtained from 1 M HCl aqueous solution. (a) *Trans*-ABPX01 and (b) *cis*-ABPX01.

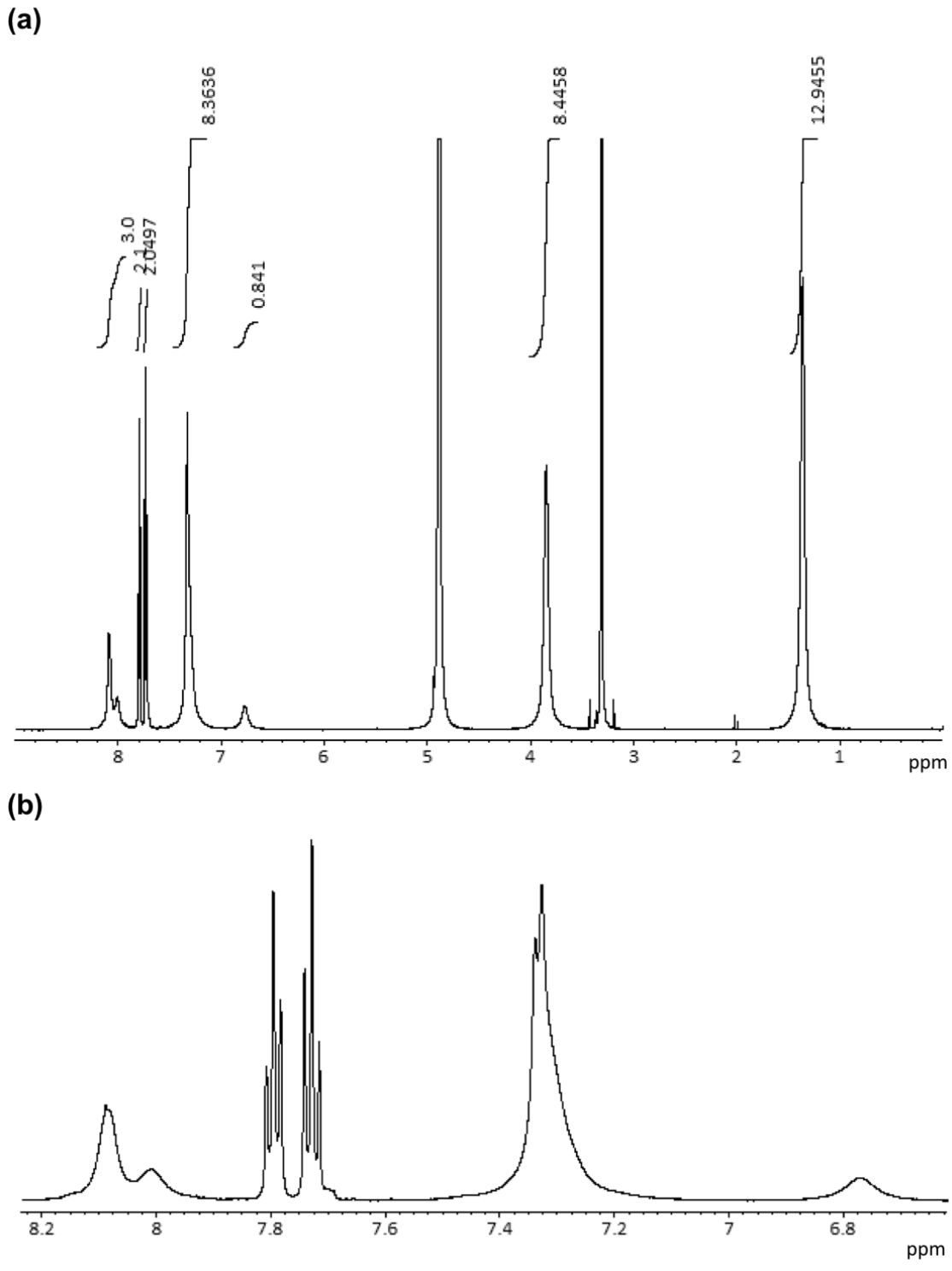


Fig. S11 (a) ^{1}H-NMR spectra of *trans*-ABPX01 hydrochloride in CD_3OD. (b) Expanded aromatic proton region (δ = 8.2-6.7 ppm) of xanthene and carboxylic benzene moieties of *trans*-ABPX01 hydrochloride.

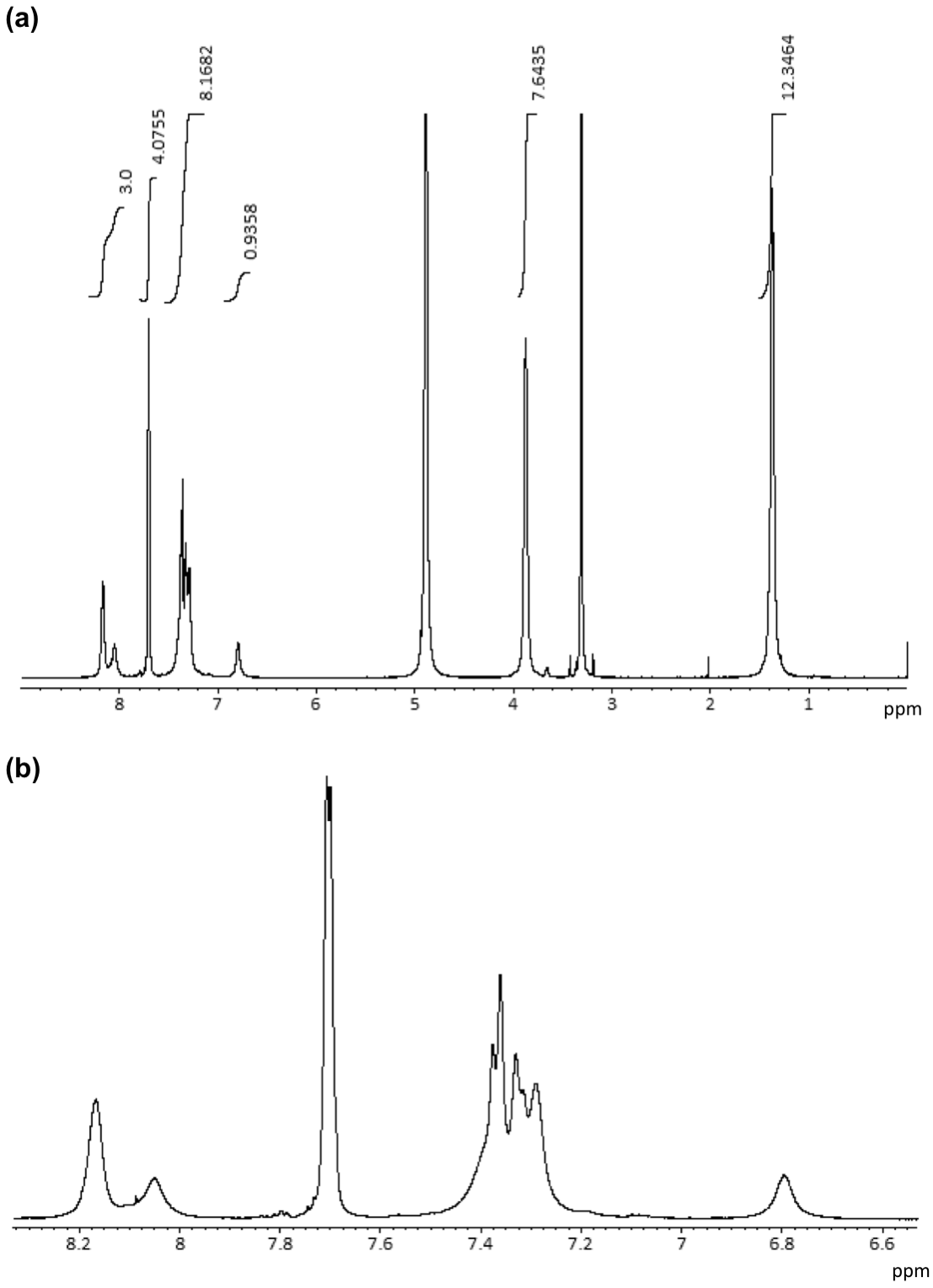


Fig. S12 (a) ^{1}H-NMR spectra of *cis*-ABPX01 hydrochloride in CD_3OD. (b) Expanded aromatic proton region (δ = 8.3-6.6 ppm) of xanthene and carboxylic benzene moieties of *cis*-ABPX01 hydrochloride.

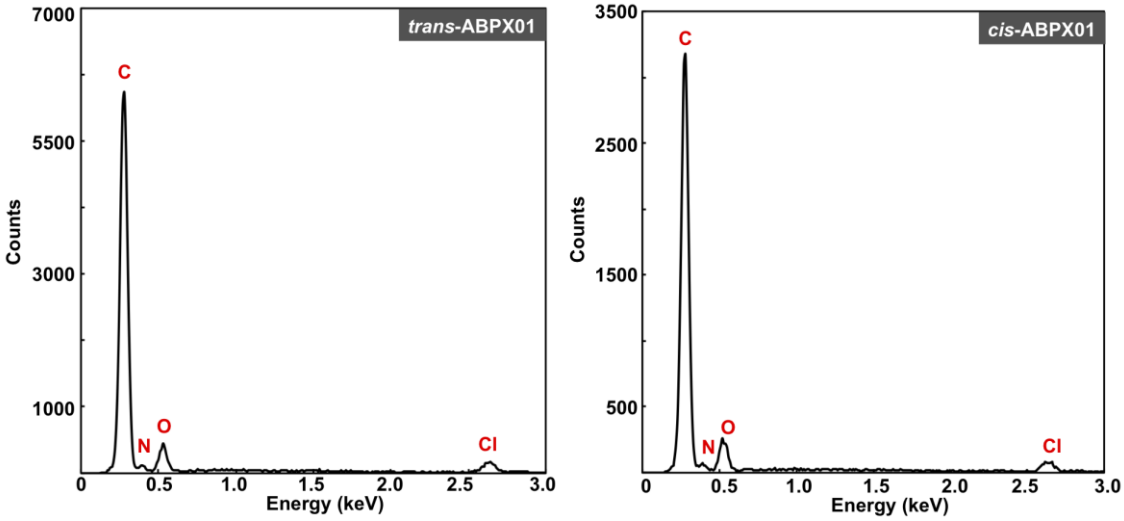


Fig. S13 Spot EDX analysis spectra of ABPX01 hydrochloride. The aggregates were obtained from 1 M HCl in diethyl ether/CH_2Cl_2 solution. (a) *Trans*-ABPX01 and (b) *cis*-ABPX01.

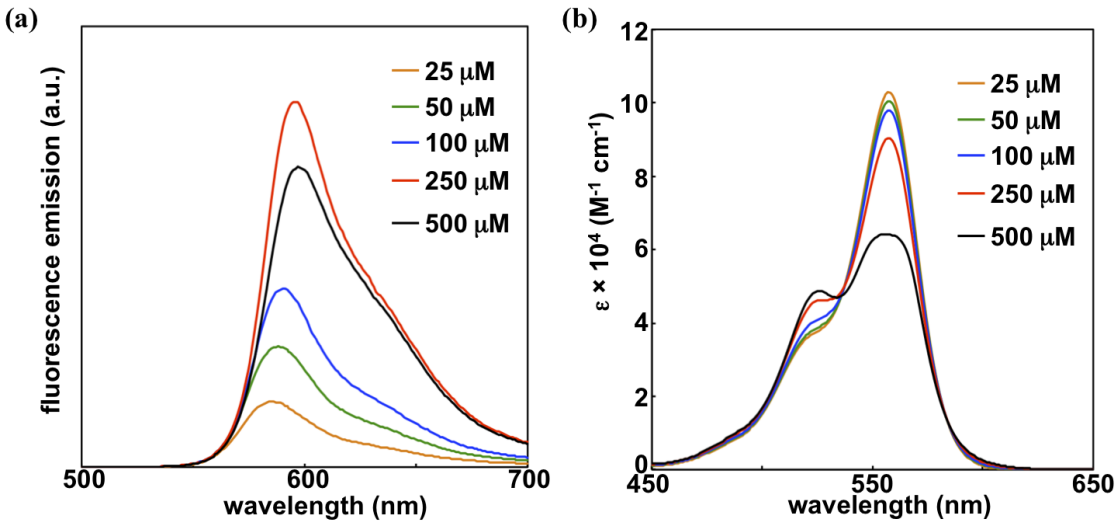
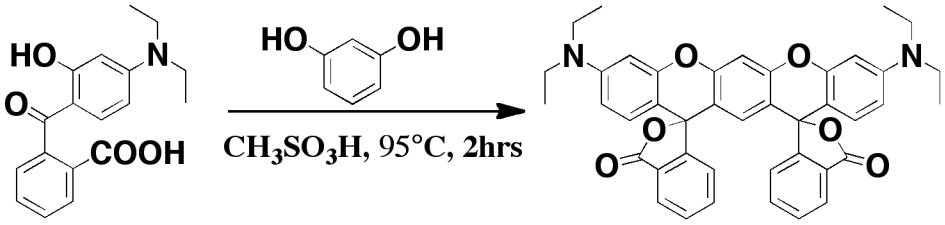


Fig. S14 Concentration-dependent (a) fluorescence emission and (b) absorption spectra of RBH in 0.05 M HCl aqueous solution.

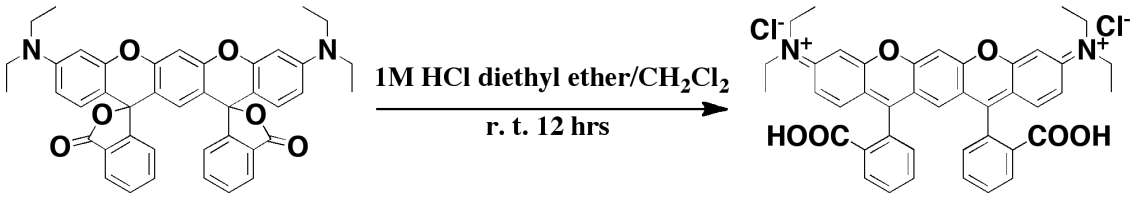
3. Syntheses

3-1. Syntheses of *trans*- and *cis*-ABPX01 **(Scheme S1)**.



2-[4-(Diethylamino)-2-hydroxybenzoyl]benzoic acid (2.0 equiv) and resorcinol (1.0 equiv) were combined in methanesulfuric acid (2.0 mL) in a sealed tube and heated at 95 ℃ for 2 hrs. The reaction was poured into stirred ice water, its pH was adjusted to 11-12 with 1.0 M sodium hydroxide aqueous solution, and the mixture was stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 three times. The organic layers were dried over $MgSO_4$ and evaporated to give a crude product that was subsequently purified by silica gel column chromatography. *Trans*-ABPX01^0 (eluent: CH_2Cl_2 : MeOH = 10 : 1, Rf = 0.80) was firstly eluted, followed by *cis*-ABPX01^0 (eluent: CH_2Cl_2 : MeOH = 10 : 1, Rf = 0.65). ***Trans*-ABPX01^0:** HRMS (ESI) calcd for $C_{42}H_{37}N_2O_6$ (M+H): 665.2651, Found: 665.2657. ***Cis*-ABPX01^0:** HRMS (ESI) calcd for $C_{42}H_{37}N_2O_6$ (M+H): 665.2651, Found: 665.2648.

3-2. Syntheses of ABPX01 hydrochloride **(Scheme S2)**.



ABPX01^0 (50 mg, 75 μmol) dissolved in 2 mL of CH_2Cl_2 was rapidly added to 10 mL of 1 M HCl in diethyl ether solution. The mixture was stirred under nitrogen at r.t. for 12 hrs to induce the formation of precipitates. The precipitates were then filtered on PTFE membrane filter of 500 nm pore size, extensively rinsed with diethyl ether, and then dried under vacuum at r.t. The obtained products were pulverized in agate mortar before analysis. Samples for SEM, EDX, and XRD measurements were prepared as follows: the sample was dropped onto a carbon tape (for SEM and EDX) or a glass

substrate (for XRD). ***Trans*-ABPX01 hydrochloride:** HRMS (ESI) calcd for $C_{42}H_{37}N_2O_6$ $(M+H)^+$: 665.2653, Found: 665.2652. ***Cis*-ABPX01 hydrochloride:** HRMS (ESI) calcd for $C_{42}H_{37}N_2O_6$ $(M+H)^+$: 665.2651, Found: 665.2648.

4. Single Crystal X-ray Structure Analysis

Crystallographic Data Collection and Structure Refinement. Data collections and structure refinements for *trans*-ABPX01^0 and *cis*-ABPX01^0 are described below. Further details of the crystal structure determination of *trans*-ABPX01^0 and *cis*-ABPX01^0 are given in Table S1 and Table S2, respectively. Their intramolecular bond lengths and angles are listed in Tables S3-S5. Structural drawings and geometrical calculations were performed with ORTEP[2] and PLATON,[3] respectively. Crystallographic data (excluding structure factors) for the two stereoisomers reported in this paper are deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 779022 (*trans*-ABPX01^0) and 894956 (*cis*-ABPX01^0). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Trans-ABPX01^0. Single crystals of *trans*-ABPX01^0 were obtained by slow evaporation of its saturated acetonitrile solution. X-ray diffraction data were collected on a Rigaku RAXIS-RAPID II imaging plate area detector using graphite-monochromated Mo-Kα radiation (λ = 0.710690 Å) at 293 K. Frame data were integrated and the data set was corrected for absorption using a Rigaku/MSC CrystalClear program package. All calculations were performed with a Rigaku/MSC CrystalStructure program package and structures were solved by Direct Methods (SIR97)[4] and refined by full-matrix least squares techniques against F^2. Anisotropic refinement was applied to all non-hydrogen atoms and all hydrogen atoms were put at the calculated positions.

Cis-ABPX01^0. *Cis*-ABPX01^0 was saturated in a solution of dimethylsulfoxide and 2-methyl-2,4-pentanediol (1 : 1 (v : v)). The solution was then slowly evaporated to give single crystals. X-ray diffraction data were collected using a Rigaku VARIMAX with a RAPID system (Cu-Kα radiation, λ = 1.54187 Å) at 93 K. Frame data were integrated and the data set was corrected for absorption using a Rigaku/MSC CrystalClear program package. Structures were solved by Direct Methods (SIR97) and refined on F^2 by full-matrix least squares techniques (SHELXL 97).[5] Anisotropic refinement was applied to all non-hydrogen atoms other than the disordered atoms (C20a, C21a, C20b, and C21b). All hydrogen atoms were put at the calculated positions.

5. Computational Details

Calculations were performed with the Gaussian09 program package.[6] Geometry optimizations in the gas phase were performed at the B3LYP density functional[7] and the 6-31G(d,p) basis set. TD-DFT calculations in aqueous solution were carried out with the same level. The solvent effect was taken into account using the self-consistent reaction field (SCRF) method.

Constrained geometry optimizations of *trans*- and *cis*-ABPX01$^{2\pm}$ were performed with dihedral angles of C(12)-C(10)-C(11)-C(1) and C(12')-C(10')-C(11')-C(1') fixed at 175.8°, as shown in Fig. S6. Both structures had two imaginary frequencies and the total electron energies were approximately 40 kcal/mol higher than the energies of *trans*- and *cis*-ABPX01^{0}. The results suggested that the zwitterionic structures were unstable and hardly existed.

Cartesian Coordinates (*trans*-ABPX01) and Total Electron Energies

***trans*-ABPX01^{0}**

E(RB3LYP) = -2183.05760646

O	2.32864600	-2.08869100	-0.14785300
O	2.65015500	3.52508600	-2.50810300
N	7.05388600	-2.71235000	-0.08884700
C	0.00005700	-2.02546600	-0.00009400
C	0.00002800	0.74642000	-0.00000300
C	1.19995700	-1.32345200	-0.07909700
C	2.62087200	2.05790100	0.67968500
C	3.70956300	-0.08662500	-0.12715400
C	1.22385700	0.08011400	-0.07932000
C	3.55982200	-1.47509800	-0.13231500
C	2.52487000	0.84152400	-0.23036400
C	5.96475000	-1.85925500	-0.09864500
C	2.67991500	3.20920500	-0.09488800
C	2.65107000	2.13599200	2.06968200
C	2.62429800	2.82375200	-1.52481600
C	6.12702000	-0.44709100	-0.08070000
C	5.02816400	0.39334100	-0.10040700
C	4.64442700	-2.34996400	-0.11774500
C	8.42084600	-2.21498100	-0.22399300
C	2.80011200	4.56503900	1.86413200
C	2.73966300	3.40358000	2.65111800
C	2.77114300	4.47951400	0.47302600
C	9.08874100	-1.85894500	1.11053300
C	6.89020000	-4.16136900	-0.01270900
C	6.67486200	-4.83682900	-1.37379000
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H	5.19355500	1.46662200	-0.09129400
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H	2.75812700	3.49331600	3.73338200
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H	0.00006800	-3.10877300	-0.00012700
H	0.00001700	1.83164100	0.00003300
O	-2.32853000	-2.08874900	0.14766800
O	-2.65014000	3.52500900	2.50810400
N	-7.05388900	-2.71232800	0.08888500
C	-1.19985800	-1.32348200	0.07895500
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C	-1.22378800	0.08008300	0.07927100
C	-3.55972000	-1.47518000	0.13222800
C	-2.52481500	0.84146300	0.23035300
C	-5.96464800	-1.85937300	0.09862700
C	-2.67989500	3.20914400	0.09488700
C	-2.65113800	2.13593300	-2.06968700
C	-2.62416400	2.82369100	1.52480900
C	-6.12694600	-0.44722300	0.08084900
C	-5.02810600	0.39323000	0.10055200
C	-4.64430800	-2.35006800	0.11765400
C	-8.42070600	-2.21461200	0.22411600
C	-2.80023600	4.56497600	-1.86412700
C	-2.73979300	3.40352000	-2.65111700
C	-2.77119600	4.47945000	-0.47302100
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H	-7.78958600	-4.56936600	-0.46257000
H	-9.00553400	-2.99077100	0.73043300
H	-8.42900400	-1.35206700	0.89806900
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H	-8.53676600	-1.07110200	-1.63146600
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H	-5.77514100	-4.45740100	1.86499800
H	-6.57104500	-5.92072800	1.25333000
H	-7.52378200	-4.65046000	2.04014800
O	2.53198700	1.46001600	-1.58513400
O	-2.53191300	1.45994900	1.58512100

trans-ABPX01H$^+$

E(RB3LYP) = -2183.47425074

O	2.39460400	-2.07617800	0.06675400
O	2.47904800	3.49890200	-2.64248600
N	7.13006500	-2.63141200	-0.00474000
C	0.07659700	-2.09720200	0.08020700
C	0.02862100	0.68025900	-0.28608500
C	1.26423200	-1.36217800	-0.02104200
C	2.62090200	2.05159600	0.55019900
C	3.74683100	-0.07320500	-0.25357900
C	1.25228600	0.04611300	-0.19860700
C	3.63113500	-1.44752700	-0.05752800
C	2.54678000	0.83226000	-0.36298000
C	6.03447100	-1.80634900	-0.08916000
C	2.61643300	3.20233100	-0.22832300
C	2.70169900	2.13174900	1.93768300
C	2.53161200	2.81277800	-1.65397400
C	6.16680800	-0.40381800	-0.29768500
C	5.05758300	0.41707600	-0.37438800
C	4.71807100	-2.30744800	0.03020000
C	8.48891500	-2.14041500	-0.24980300
C	2.76715200	4.56469900	1.72376700
C	2.77297500	3.40356100	2.51366500
C	2.68916900	4.47650700	0.33448200
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H	9.07208000	-2.98160000	-0.63836300
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H	6.20444900	-4.17459600	1.07191900
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H	9.24543100	-2.32152600	1.78619100
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C	-3.62072100	-0.20346500	-0.24158000
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C	-2.39749400	2.46338700	-1.92489200
C	-3.03965500	2.78170000	1.84522400
C	-6.04085300	-0.53814800	-0.26779200
C	-4.95822000	0.28766900	-0.35485800
C	-4.56898700	-2.46552800	0.04829700
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C	-8.93671200	-2.11793600	-1.40581000
C	-6.84001400	-4.23433100	0.11656500
C	-6.70878900	-4.73668400	1.55788900
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H	-5.10773700	1.34788000	-0.52437300
H	-2.17004700	1.71547900	-2.67831200
H	-2.36332600	4.08776700	-3.33130600
H	-2.90596400	5.81257500	-1.61392100
H	-3.21720800	5.11628000	0.76195200
H	-7.02773000	-0.11150500	-0.38157700
H	-7.73065500	-4.66374700	-0.35042500
H	-8.95291600	-2.95985600	0.58978100
H	-8.39205100	-1.30899300	0.54377400
H	-5.99330800	-4.55903400	-0.49350200
H	-8.37361100	-1.39653000	-2.00478600
H	-9.97470100	-1.77754300	-1.34658600
H	-8.92604900	-3.07589500	-1.93400500
H	-5.81504500	-4.33593000	2.04417500
H	-6.64224900	-5.82861700	1.56553000
H	-7.57755400	-4.44841600	2.15711400
O	2.50558100	1.43527200	-1.70659500
O	-2.71053100	1.52107200	2.21968300
H	-2.84936200	1.48462900	3.18166500

trans-ABPX01H$_2^{2+}$

E(RB3LYP) = -2183.81005663

O	2.33154700	-2.18852000	0.03825100
O	1.52633100	3.21229200	-3.28081400
N	7.05132600	-2.66071700	0.12486200
C	0.00008500	-2.17241600	-0.00002300
C	0.00003500	0.64384200	0.00004600
C	1.19237300	-1.45873000	0.01276400
C	2.57721200	2.11709600	0.06850000
C	3.65634300	-0.15191100	0.04972600
C	1.22568300	-0.03639400	0.00287300
C	3.55559700	-1.58705200	0.06238000
C	2.50809200	0.62829700	0.00964800
C	5.96476900	-1.87430300	0.09457000
C	2.29206600	2.96644700	-1.02687300
C	2.89239900	2.69110600	1.31016900
C	1.98577700	2.50175400	-2.41504700
C	6.08735100	-0.43015000	0.06515200
C	4.99329800	0.37661900	0.04357900
C	4.64363800	-2.41962800	0.08744400
C	8.43050000	-2.12759700	0.03903500
C	2.63181000	4.91204300	0.39469800
C	2.92021200	4.07690700	1.47386900
C	2.32032400	4.35591600	-0.84342200
C	9.02179600	-1.77085700	1.40518200
C	6.95893800	-4.13203800	0.24291800
C	6.85076000	-4.83599900	-1.11280600
H	4.46548600	-3.48543100	0.07401800
H	5.12116100	1.45239100	0.02292900
H	3.10043200	2.04539000	2.15795400
H	3.16420800	4.49710700	2.44436400
H	2.65509300	5.99019800	0.51457500
H	2.10304700	4.98409100	-1.70038900
H	7.06768000	0.02539700	0.07469700
H	7.86059100	-4.45738500	0.76782400
H	9.02968500	-2.90473500	-0.44184400
H	8.44400100	-1.27307300	-0.63993000
H	6.11967200	-4.38482000	0.89432500
H	8.45299900	-0.97655600	1.89689100
H	10.05151700	-1.42562800	1.27775500
H	9.03929500	-2.63853200	2.07086200
H	5.94418000	-4.54274300	-1.64970600
H	6.82470600	-5.91860900	-0.96101600
H	7.71072700	-4.60729900	-1.74846300
H	0.00010000	-3.25563800	-0.00003900
H	0.00001000	1.72659300	0.00009700
O	-2.33137800	-2.18859500	-0.03826800
O	-1.52806900	3.21285600	3.28123700
N	-7.05114800	-2.66092700	-0.12481400
C	-1.19222700	-1.45876600	-0.01278000
C	-2.57720900	2.11701900	-0.06850000

C	-3.65623400	-0.15202300	-0.04976200
C	-1.22558600	-0.03643700	-0.00283600
C	-3.55544400	-1.58716200	-0.06238500
C	-2.50801600	0.62821800	-0.00959300
C	-5.96461100	-1.87448400	-0.09458800
C	-2.29236700	2.96648600	1.02685900
C	-2.89228600	2.69090600	-1.31025900
C	-1.98627200	2.50194500	2.41512000
C	-6.08723500	-0.43033200	-0.06526900
C	-4.99320500	0.37646800	-0.04370500
C	-4.64346300	-2.41976900	-0.08743600
C	-8.43033200	-2.12783900	-0.03896600
C	-2.63217700	4.91194200	-0.39489200
C	-2.92025600	4.07668700	-1.47406100
C	-2.32084500	4.35594300	0.84331900
C	-9.02171800	-1.77126500	-1.40511500
C	-6.95873000	-4.13225500	-0.24277000
C	-6.85046500	-4.83611500	1.11299100
H	-4.46527900	-3.48556700	-0.07398500
H	-5.12109700	1.45223900	-0.02314200
H	-3.10012600	2.04510400	-2.15802600
H	-3.16414200	4.49678800	-2.44462700
H	-2.65560500	5.99008500	-0.51484800
H	-2.10385800	4.98419000	1.70030600
H	-7.06757600	0.02518700	-0.07489000
H	-7.86040200	-4.45765900	-0.76760800
H	-9.02946600	-2.90493800	0.44204100
H	-8.44381500	-1.27323600	0.63990000
H	-6.11949300	-4.38506200	-0.89420600
H	-8.45297700	-0.97699600	-1.89694100
H	-10.05144300	-1.42605700	-1.27766600
H	-9.03922800	-2.63901000	-2.07070500
H	-5.94390200	-4.54274200	1.64985600
H	-6.82431800	-5.91873300	0.96127200
H	-7.71044100	-4.60745400	1.74865000
O	2.29091000	1.19736300	-2.63301900
H	2.08276500	1.02572600	-3.56814000
O	-2.29003000	1.19717200	2.63274200
H	-2.08222200	1.02565900	3.56796000

trans-ABPX01$^{2\pm}$

E(RB3LYP) = -2182.99271539

*Number of Imaginary Freq = 2

O	2.33479300	-2.06371300	0.04962800
O	2.67812500	2.24885300	-3.68380100
N	7.05627300	-2.61162300	0.34572300
C	0.00000000	-2.02723100	0.00001800
C	-0.00000100	0.77175200	0.00000500
C	1.19584400	-1.31907700	0.01907500
C	2.59929100	2.26896600	-0.09988700
C	3.68638600	-0.04984100	0.10397900
C	1.22147100	0.09362100	-0.00427400
C	3.55780700	-1.45264000	0.12398400
C	2.51264000	0.77298400	-0.03148400
C	5.95949200	-1.78560200	0.27373900
C	2.66454100	2.86055000	-1.36301400
C	2.61974600	3.07418600	1.04679800
C	2.62805300	1.88895300	-2.51024800
C	6.09942700	-0.36472600	0.28098100
C	4.99928800	0.45929900	0.19688600
C	4.64844300	-2.30593200	0.19796200
C	8.42351700	-2.09022400	0.29545700
C	2.77486300	5.04685800	-0.35901700
C	2.70696000	4.46208900	0.91019900
C	2.75306100	4.24367100	-1.49917500
C	8.99083000	-1.71184800	1.66896600
C	6.92002200	-4.06609600	0.43355000
C	6.80503200	-4.75892600	-0.93008200
H	4.44951600	-3.36826400	0.17041800
H	5.13843400	1.53500000	0.20203300
H	2.56328200	2.62711900	2.03543100
H	2.71870600	5.08764400	1.79795100
H	2.84219300	6.12702700	-0.45319500
H	2.80221800	4.65643800	-2.50231400
H	7.07841200	0.08746500	0.36629300
H	7.79806400	-4.44382100	0.96820900
H	9.04979200	-2.86345300	-0.16193700
H	8.46193700	-1.23625900	-0.38708400
H	6.05996800	-4.31001700	1.06454600
H	8.39400800	-0.92684300	2.14192400
H	10.01948800	-1.34929400	1.57041000
H	8.99956500	-2.57619400	2.34073000
H	5.92783900	-4.40818400	-1.48062200
H	6.72050000	-5.84313700	-0.80137400
H	7.68804600	-4.55893300	-1.54525700
H	0.00000000	-3.11018000	0.00002100
H	-0.00000200	1.85517400	-0.00000100
O	-2.33479400	-2.06371400	-0.04959500
O	-2.67812700	2.24892300	3.68380800
N	-7.05627100	-2.61163300	-0.34572900
C	-1.19584500	-1.31907700	-0.01904600
C	-2.59929400	2.26896800	0.09988600
C	-3.68638900	-0.04984300	-0.10397500
C	-1.22147200	0.09362100	0.00429100
C	-3.55780700	-1.45264300	-0.12396700
C	-2.51264300	0.77298400	0.03149400
C	-5.95949200	-1.78561000	-0.27374100
C	-2.66454300	2.86057200	1.36300600
C	-2.61975000	3.07417300	-1.04681000
C	-2.62805200	1.88899900	2.51026300
C	-6.09942800	-0.36473300	-0.28099600
C	-4.99929000	0.45929300	-0.19689800
C	-4.64844200	-2.30593600	-0.19794800
C	-8.42351600	-2.09023500	-0.29548200
C	-2.77487000	5.04686400	0.35897600
C	-2.70696700	4.46207700	-0.91023100
C	-2.75306500	4.24369500	1.49914400
C	-8.99081400	-1.71186600	-1.66899900
C	-6.92001700	-4.06610700	-0.43354500
C	-6.80503700	-4.75892600	0.93009300
H	-4.44951500	-3.36826800	-0.17039300
H	-5.13843700	1.53499400	-0.20205600
H	-2.56328700	2.62709200	-2.03543700
H	-2.71871500	5.08761900	-1.79799300
H	-2.84220000	6.12703500	0.45313600
H	-2.80222200	4.65647600	2.50227700
H	-7.07841200	0.08745600	-0.36632100
H	-7.79805400	-4.44383700	-0.96820800
H	-9.04979600	-2.86346300	0.16190800
H	-8.46194600	-1.23626700	0.38705500
H	-6.05995800	-4.31003100	-1.06453200
H	-8.39398700	-0.92686200	-2.14195300
H	-10.01947300	-1.34931300	-1.57045800
H	-8.99953900	-2.57621500	-2.34076000
H	-5.92785000	-4.40817700	1.48063800
H	-6.72050200	-5.84313800	0.80139400
H	-7.68805700	-4.55893100	1.54526000
O	2.53719400	0.66999600	-2.06444200
O	-2.53718300	0.67003000	2.06449100

cis-ABPX01^{0}

E(RB3LYP) = -2183.05517127

cis-ABPX01H^{+}

E(RB3LYP) = -2183.47334157

cis-ABPX01H$_2^{2+}$

E(RB3LYP) = -2183.81224142

***cis*-ABPX01$^{2\pm}$**

E(RB3LYP) = -2182.98742068

*Number of Imaginary Freq = 2

6. Surface photometric method

A number of experimental difficulties have hindered the quantitative fluorophotometric analysis of fluorescent compounds in concentrated solution. One difficulty was that the recorded fluorescence emission intensity was not proportional to the concentration of the fluorophore owing to the inner-filter effect. This was due to the absorption of incident light before it reached the point in the sample at which fluorescence emission was observed in the cuvette, and the re-absorption of some of the emitted light before it left the cuvette. Because of the inner-filter effect, the observed fluorescence emission intensity would not be dependent on the optical density of the sample at both excitation and emission wavelengths, and would not be a linear function of the fluorophore concentration. Then, the fluorescence spectra of $ABPX01H_2^{2+}$ were measured at various concentrations in chloroform containing 1% TFA by the conventional photometric method. A random shift of the maximum wavelength was observed and the linearity of the fluorescence emission intensity at 616 nm plotted against concentration was good in the concentration range of 1 μM to 10 μM, as shown in Fig. S15 (a). The problem of the inner-filter effect was solved by using the surface photometric method that detected fluorescence emission on the cuvette surface. The sample holder in the surface photometric method was set at an angle of 30° with respect to the excitation light to prevent the propagation of incident light to the detector. Shown in Fig. S15 are the respective equipment configurations. By using the surface photometric method, the fluorescence emission intensity at 616 nm was linearly increased as the concentration was increased from 1 μM to 100 μM, as shown in Fig. S15 (b).

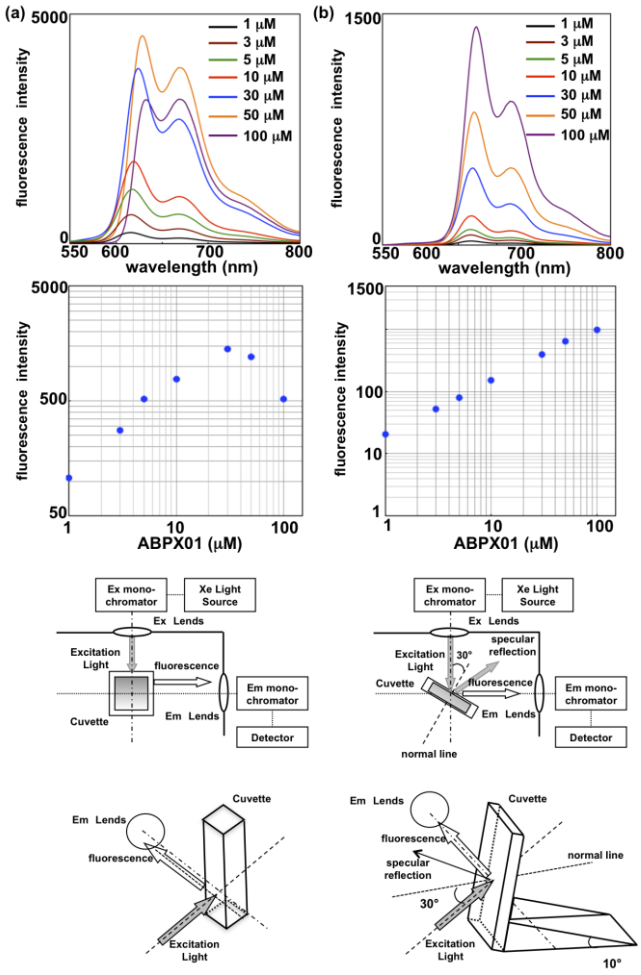

Fig. S15 Photometric system for $ABPX01H_2^{2+}$ in chloroform containing 1% TFA in (a) conventional photometric method and (b) surface photometric method. First panel fluorescence emission spectra at various concentrations of $ABPX01H_2^{2+}$. Second panel: linearity of fluorescence intensity at 616 nm against concentration. Third drawer: top-down view of equipment configuration. Last panel: side view of equipment configuration.

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