Supporting information

High Contrast Electroswitching of Emission and Coloration Based on Single-Molecular Fluoran Derivatives

Kenji Kanazawa, Kazuki Nakamura,* and Norihisa Kobayashi*

Department of Image and Materials, Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

**E-mail: Nakamura.Kazuki@faculty.chiba-u.jp; koban@faculty.chiba-u.jp; Fax: +81-43-290-3490; Tel: +81-43-290-3457*

Table of Contents

1. Absorption spectra of neutral and protonated fluoran molecule

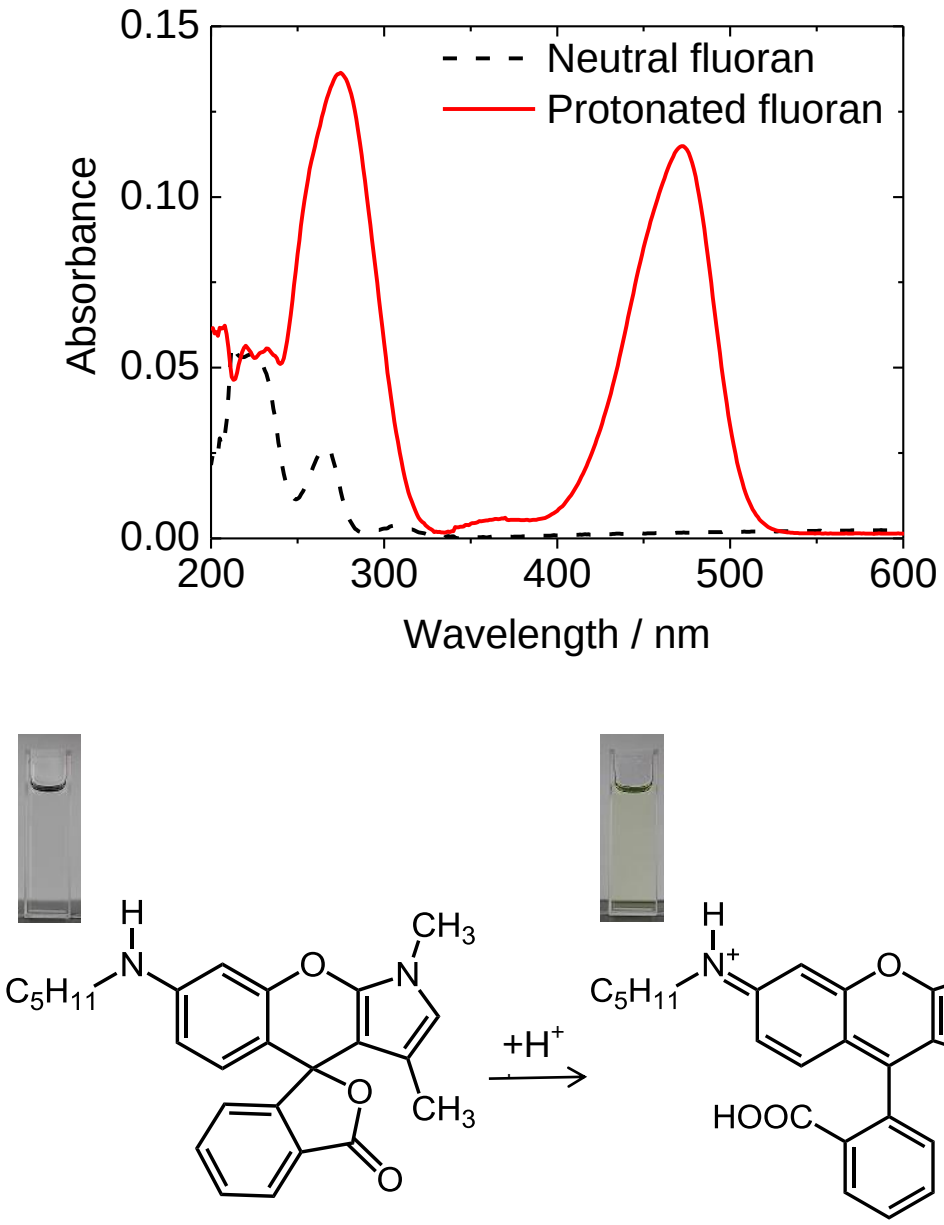

Figure S1. Absorption spectra measured for neutral fluoran molecule (1 μM) /PC solution (black line) and protonated fluoran molecule with H_2SO_4 (10 μM) (red line). Schemes indicate changes in coloration and molecular structures of fluoran molecule with protonation.

2. Emission spectra of neutral and protonated fluoran molecule

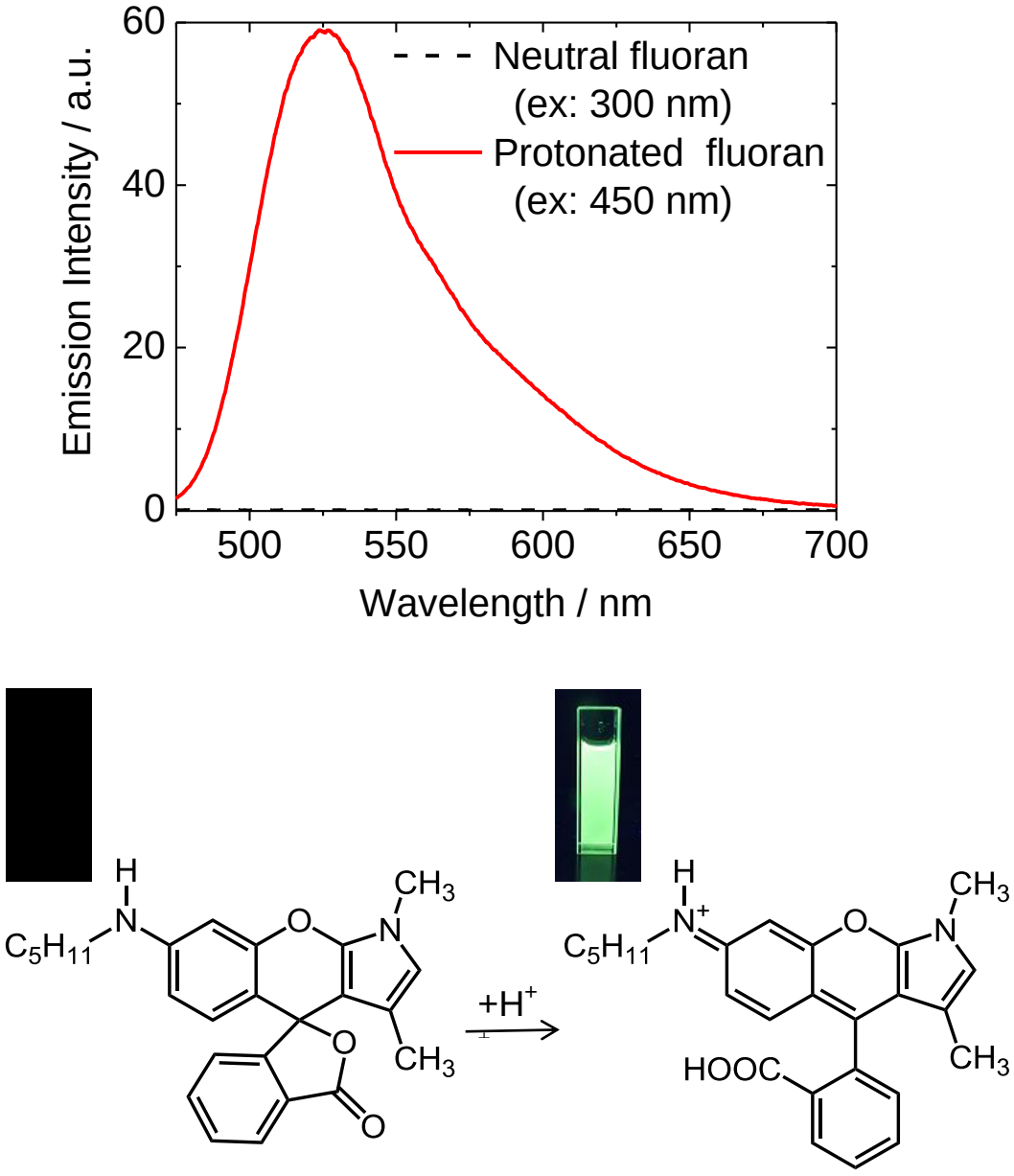

Figure S2. Emission spectra for measured fluoran molecule (1 μM) /PC solution (black line) and protonation with H_2SO_4 (10 μM) (red line) irradiated at 300 nm and 450 nm, respectively. Photographs of the neutral and protonated fluoran molecules-emission irradiated with UV light at 365 nm. Schemes indicate mechanism of fluoran molecule with protonation.

3. Emission decay profiles for protonated fluoran molecule

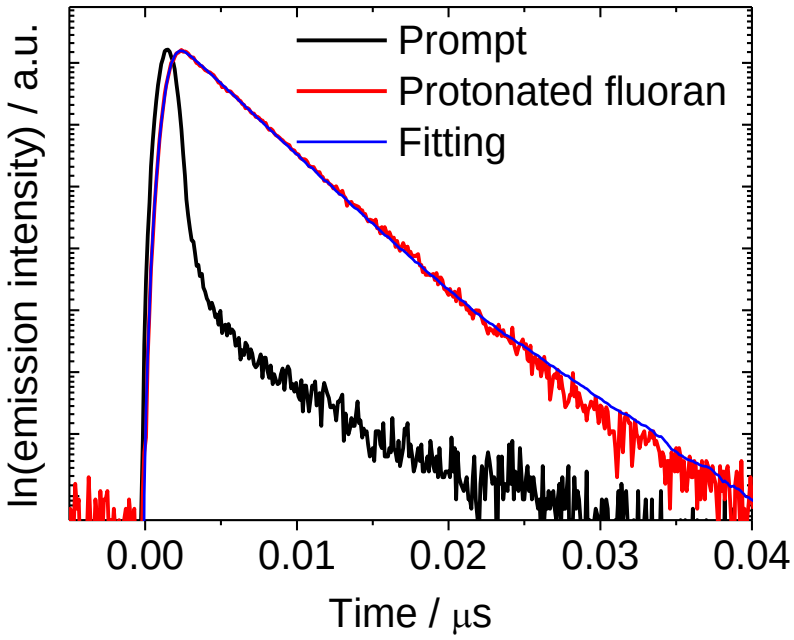

Figure S3. Emission decay plofiles obtained with the time-resolved fluorescence measurements of fluoran molecule (1 μM) /H_2SO_4 (10 μM)-PC solution. Blue line denotes fitting profiles based on the single exponential decay with time constants presented in Table S1.

Table S1. Emission quantum yields (ϕ), emission lifetime (τ), radiative rate constant (k_r), and non-radiative rate constant (k_{nr}) of the samples.

Compounds	ϕ [a]	τ [ns] [b]	k_r [$\times 10^8$ s^{-1}]	k_{nr} [$\times 10^7$ s^{-1}]
Neutral fluoran	—	—	—	—
Protonated fluoran	0.76	4.03	1.89	6.00

[a] The photophysical properties of the samples were measured in H_2SO_4 (10 μM)/PC solution. [b] Fluorescent quantum yields at room temperature; the sample concentration of 1 μM. [c] Fluorescence decay profiles are presented in **Figure S3**. The radiative (k_r) and non-radiative rate (k_{nr}) constants were calculated from the values of emission lifetime (τ) and quantum yields (ϕ).

4. HOMO-LUMO gap of oxidized fluoran molecule

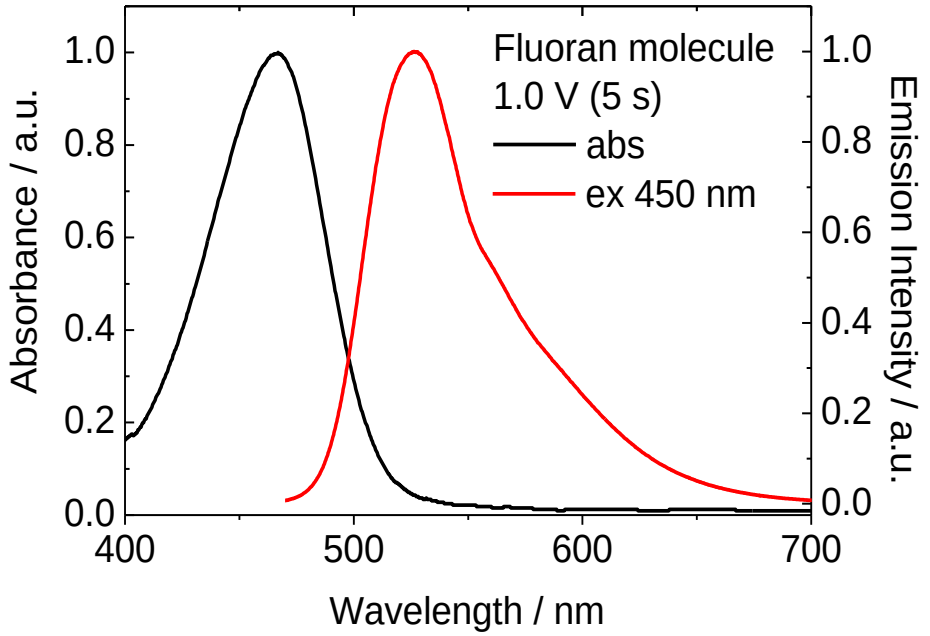

Figure S4. Absorption (black line) and emission spectra (red line) of oxidized fluoran molecule / PC solution when potential was applied at 1.0 V (vs. Ag/Ag^{+}) for 5 s.

5. Quantum chemical calculations for neutral fluoran molecule by Gaussian 09

Table S2. Electronic excitation energies [eV], corresponding oscillator strengths (*f*), and main configurations, and CI coefficients of the low-lying electronically excited states of neutral fluoran molecule [a]

	TDDFT//RB3LYP/6-31G(d)			
Electronic transition	Energy [eV] [b]	*f* [c]	Composition [d]	CI
$S_0 \rightarrow S_1$	3.44 (360.05 nm)	0.0013	H-1 → L	0.1661
			H → L	0.6848
$S_0 \rightarrow S_2$	3.64 (340.96 nm)	0.0030	H-1 → L	0.6846
			H → L	0.1672
$S_0 \rightarrow S_3$	4.24 (292.35 nm)	0.0087	H-1 → L+1	0.1409
			H → L+1	0.6879
$S_0 \rightarrow S_4$	4.35 (284.95 nm)	0.0019	H-2 → L	0.6946
$S_0 \rightarrow S_5$	4.43 (279.72 nm)	0.0153	H-1 → L+1	0.6554
			H-1 → L+2	0.1492
			H → L+1	0.1238
			H → L+2	0.1450
$S_0 \rightarrow S_6$	4.55 (272.50 nm)	0.0318	H-1 → L+1	0.2079
			H-1 → L+2	0.3144
			H-1 → L+3	0.1905
			H → L+2	0.5449
			H → L+3	0.1078
$S_0 \rightarrow S_7$	4.64 (267.12 nm)	0.0101	H-3 → L+3	0.1037
			H-1 → L+2	0.4318
			H → L+2	0.3925
			H → L+3	0.3513
$S_0 \rightarrow S_8$	4.88 (254.17 nm)	0.0300	H-6 → L	0.5215
			H-4 → L	0.2075
			H-3 → L	0.3446
			H → L+3	0.1347
$S_0 \rightarrow S_9$	4.90 (252.95 nm)	0.3533	H-3 → L	0.2718
			H-1 → L+2	0.2694
			H-1 → L+3	0.1545

			H → L+2	0.1200
			H → L+3	0.5475
$S_0 \rightarrow S_{10}$	4.96 (249.76 nm)	0.0660	H-6 → L	0.3954
			H-3 → L	0.5299
			H → L+3	0.1718
$S_0 \rightarrow S_{11}$	5.05 (245.39 nm)	0.1201	H-6 → L	0.1412
			H-5 → L	0.1657
			H-5 → L+1	0.2666
			H-4 → L	0.5339
			H-3 → L	0.1407
			H-2 → L+1	0.1464
			H-1 → L+3	0.2029
$S_0 \rightarrow S_{12}$	5.15 (240.58 nm)	0.5063	H-4 → L	0.1543
			H-3 → L+2	0.1231
			H-2 → L+1	0.1105
			H-1 → L+2	0.2601
			H-1 → L+3	0.5801
$S_0 \rightarrow S_{13}$	5.19 (238.89 nm)	0.0220	H-4 → L	0.1604
			H-2 → L+1	0.6727
$S_0 \rightarrow S_{14}$	5.53 (224.21 nm)	0.1569	H-5 → L	0.5099
			H-4 → L	0.1383
			H-4 → L+1	0.1583
			H-2 → L+2	0.4135
$S_0 \rightarrow S_{15}$	5.58 (222.12 nm)	0.0611	H-5 → L	0.3599
			H-4 → L	0.1033
			H-4 → L+1	0.1607
			H-2 → L+2	0.5610
$S_0 \rightarrow S_{16}$	5.74 (215.96 nm)	0.0401	H-3 → L+1	0.6867
$S_0 \rightarrow S_{17}$	5.79 (214.31 nm)	0.0022	H-2 → L+3	0.6817
			H → L+5	0.1108
$S_0 \rightarrow S_{18}$	5.98 (207.41 nm)	0.0250	H-7 → L	0.6490
			H-6 → L	0.1116
			H → L+4	0.1381
$S_0 \rightarrow S_{19}$	6.02 (205.99 nm)	0.0963	H-7 → L	0.1555
			H-3 → L+2	0.1607
			H-3 → L+3	0.2768

			H-1 → L+4	0.3688
			H → L+4	0.4039
			H → L+5	0.1661
$S_0 \rightarrow S_{20}$	6.09 (203.63 nm)	0.0327	H-3 → L+2	0.1394
			H-1 → L+4	0.4825
			H → L+4	0.4508
$S_0 \rightarrow S_{21}$	6.14 (201.81 nm)	0.0074	H-6 → L+1	0.6818
			H-4 → L+1	0.1272
$S_0 \rightarrow S_{22}$	6.19 (200.38 nm)	0.2278	H-7 → L+2	0.1306
			H-7 → L+3	0.1149
			H-3 → L+2	0.5125
			H-3 → L+3	0.2069
			H-1 → L+3	0.1049
			H-1 → L+4	0.2441
			H → L+5	0.2041
$S_0 \rightarrow S_{23}$	6.29 (197.06 nm)	0.1613	H-8 → L	0.1504
			H-5 → L+1	0.2453
			H-4 → L	0.1248
			H-4 → L+1	0.1652
			H-4 → L+2	0.5331
			H → L+6	0.1633
$S_0 \rightarrow S_{24}$	6.30 (196.78 nm)	0.1590	H-5 → L+1	0.1016
			H-3 → L+2	0.1849
			H-3 → L+3	0.1169
			H-2 → L+4	0.2674
			H-1 → L+4	0.1201
			H → L+4	0.1694
			H → L+5	0.5183
			H → L+6	0.1089

[a] Calculated by TDDFT//RB3LYP/6-31G(d), based on the DFT//RB3LYP/6-31G(d) optimized ground state geometries. [b] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [c] Oscillator strength. [d] H stands for HOMO, and L stands for LUMO. [e] CI coefficients are in absolute values.

6. Quantum chemical calculations for protonated fluoran molecule by Gaussian 09

Table S3. Electronic excitation energies [eV], corresponding oscillator strengths (*f*), and main configurations, and CI coefficients of the low-lying electronically excited states of protonated fluoran molecule [a]

	TDDFT//RB3LYP/6-31G+(d)			
Electronic transition	Energy [eV] [b]	*f* [c]	Composition [d]	CI
$S_0 \rightarrow S_1$	3.03 (409.52 nm)	0.2660	H-1 → L	0.2664
			H → L	0.6486
$S_0 \rightarrow S_2$	3.30 (375.88 nm)	0.2547	H-1 → L	0.6427
			H → L	0.2561
$S_0 \rightarrow S_3$	3.66 (338.98 nm)	0.0076	H-3 → L	0.3123
			H-2 → L	0.6298
$S_0 \rightarrow S_4$	3.78 (327.71 nm)	0.0024	H-3 → L	0.6323
			H-2 → L	0.3134
$S_0 \rightarrow S_5$	3.98 (311.86 nm)	0.0077	H → L+1	0.7020
$S_0 \rightarrow S_6$	4.16 (298.20 nm)	0.0031	H-5 → L	0.6701
			H → L+2	0.1816
$S_0 \rightarrow S_7$	4.18 (296.31 nm)	0.0003	H-4 → L	0.7045
$S_0 \rightarrow S_8$	4.52 (274.40 nm)	0.0026	H-1 → L+1	0.6868
			H → L+2	0.1423
$S_0 \rightarrow S_9$	4.57 (271.26 nm)	0.1421	H-5 → L	0.1782
			H-1 → L+1	0.1510
			H → L+2	0.6388
$S_0 \rightarrow S_{10}$	4.67 (265.75 nm)	0.0015	H-4 → L+1	0.6739
			H-2 → L+1	0.1106
$S_0 \rightarrow S_{11}$	4.80 (258.19 nm)	0.1309	H-7 → L	0.1504
			H-6 → L	0.5836
			H-2 → L+1	0.2067
			H-1 → L+2	0.1588
			H-1 → L+4	0.1091
			H → L+4	0.1268
$S_0 \rightarrow S_{12}$	4.87 (254.82 nm)	0.0118	H-6 → L	0.2069
			H-3 → L+1	0.1800

			H-3 → L+2	0.1189
			H-3 → L+3	0.2388
			H-2 → L+1	0.5478
			H-1 → L+2	0.1028
$S_0 \rightarrow S_{13}$	4.95 (250.66 nm)	0.0078	H-2 → L+1	0.1081
			H → L+3	0.6856
$S_0 \rightarrow S_{14}$	5.03 (246.38 nm)	0.0013	H-7 → L	0.6762
			H-6 → L	0.1940
$S_0 \rightarrow S_{15}$	5.07 (244.67 nm)	0.0000	H-8 → L	0.7032
$S_0 \rightarrow S_{16}$	5.20 (238.36 nm)	0.3907	H-1 → L+2	0.1424
			H → L+4	0.6534
$S_0 \rightarrow S_{17}$	5.23 (236.93 nm)	0.1179	H-10 → L	0.2471
			H-6 → L	0.1548
			H-1 → L+2	0.6043
			H-1 → L+4	0.1044
			H → L+4	0.1147
$S_0 \rightarrow S_{18}$	5.28 (234.85 nm)	0.0348	H-10 → L	0.6594
			H-1 → L+2	0.2221
$S_0 \rightarrow S_{19}$	5.29 (234.20 nm)	0.0000	H-9 → L	0.7031
$S_0 \rightarrow S_{20}$	5.36 (231.18 nm)	0.1421	H-4 → L+1	0.1066
			H-3 → L+1	0.5844
			H-2 → L+1	0.1962
			H-2 → L+2	0.1351
			H-2 → L+3	0.1620
			H → L+5	0.2021
$S_0 \rightarrow S_{21}$	5.37 (230.73 nm)	0.0248	H-3 → L+1	0.1748
			H → L+5	0.6631
$S_0 \rightarrow S_{22}$	5.50 (225.29 nm)	0.0299	H-5 → L+1	0.1162
			H-1 → L+3	0.6878
$S_0 \rightarrow S_{23}$	5.56 (222.90 nm)	0.0249	H-5 → L+1	0.6870
			H-1 → L+3	0.1070
$S_0 \rightarrow S_{24}$	5.68 (218.37 nm)	0.0670	H-1 → L+4	0.5733
			H → L+6	0.3740

[a] Calculated by TDDFT//RB3LYP/6-31G+(d), based on the DFT//RB3LYP/6-31G+(d) optimized ground state geometries. [b] Only selected excited states were considered. The

numbers in parentheses are the excitation energy in wavelength. [c] Oscillator strength. [d] H stands for HOMO, and L stands for LUMO. [e] CI coefficients are in absolute values.