Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Dual Fluorescent Zwitterionic Organogel of a Quinoxalinone Derivative using Cation–Anion Detection Keys

Yuta Nakane, Takashi Takeda, Norihisa Hoshino, Ken-ichi Sakai, and Tomoyuki Akutagawa

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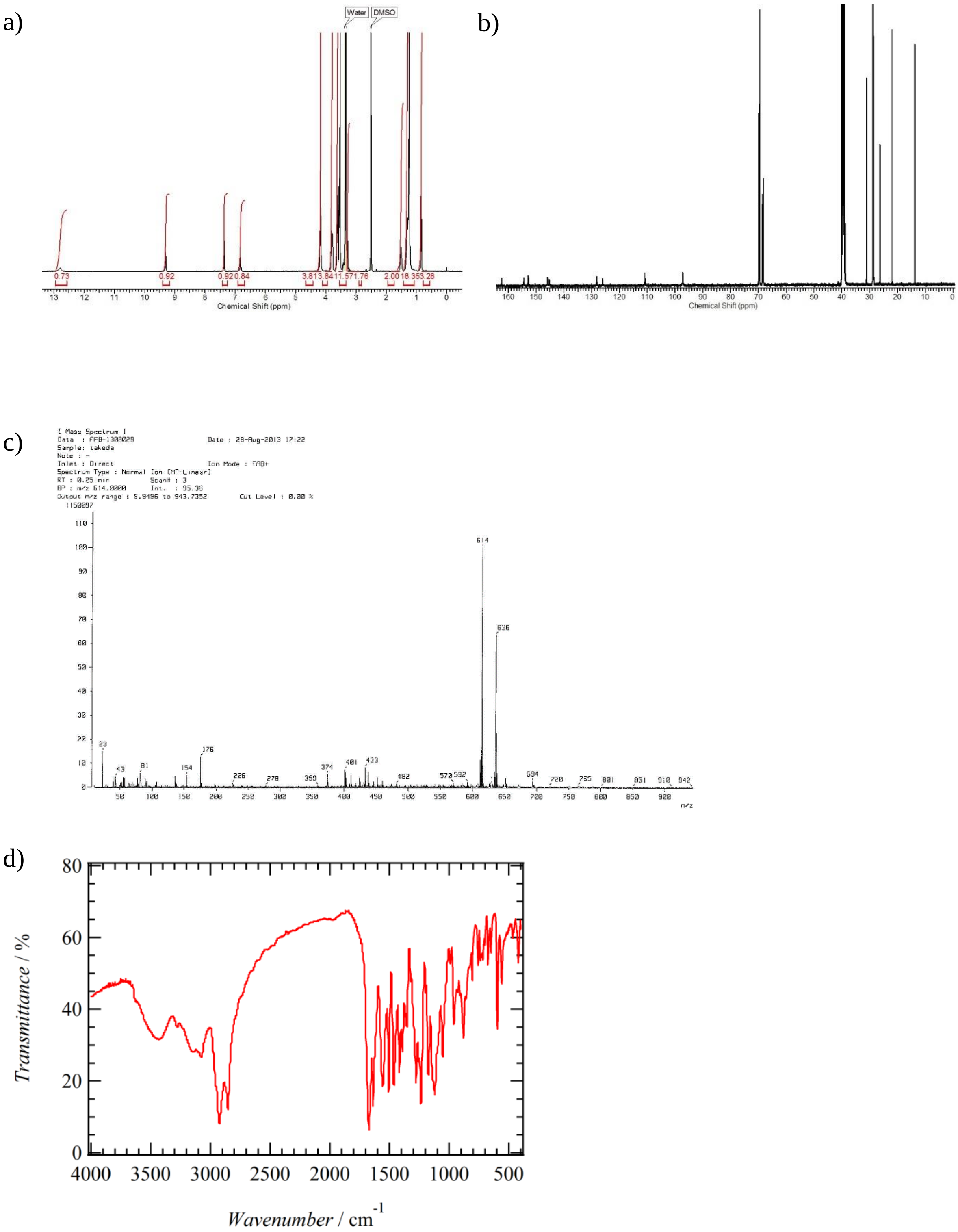

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Sample: takeda
Note : -
Inlet : Direct                        Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.25 min           Scan# : 3
BP : m/z 614.0000       Int.   : 95.36
Output m/z range : 5.9196 to 943.7352        Cut Level : 0.00 %
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Figure S1. Characterization of **1**. a) ^{1}H NMR, b) ^{13}C NMR, c) Mass, and d) IR spectra of **1**.

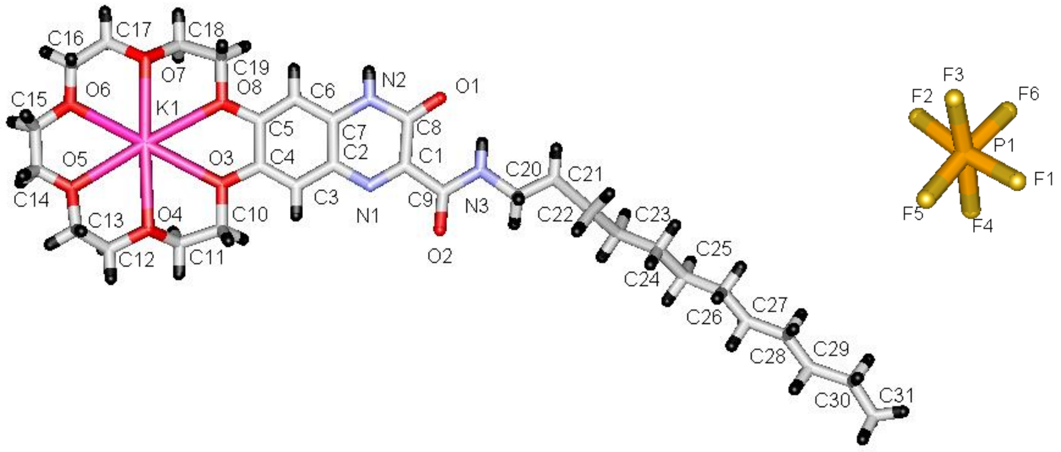

Figure S2. Atomic numbering scheme of single crystal K^+•**1**•PF_6^-.

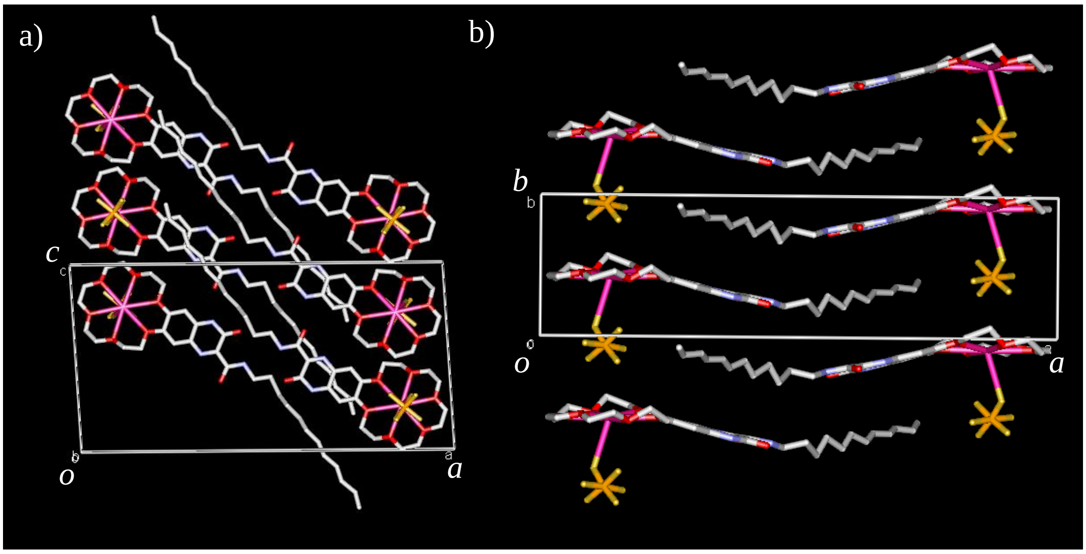

Figure S3. Unit cells of K^+•**1**•PF_6^- viewed a) along the *b* and b) along the *c* axis.

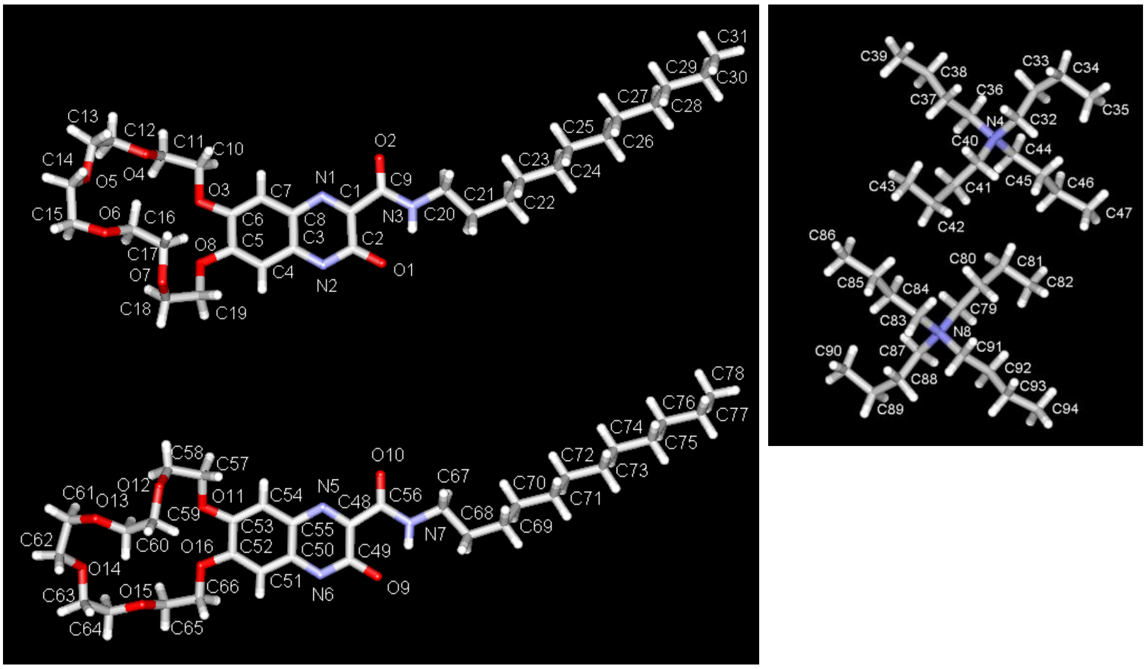

Figure S4. Atomic numbering scheme of single crystal TBA$^+$•**1**$^-$•$(H_2O)_2$.

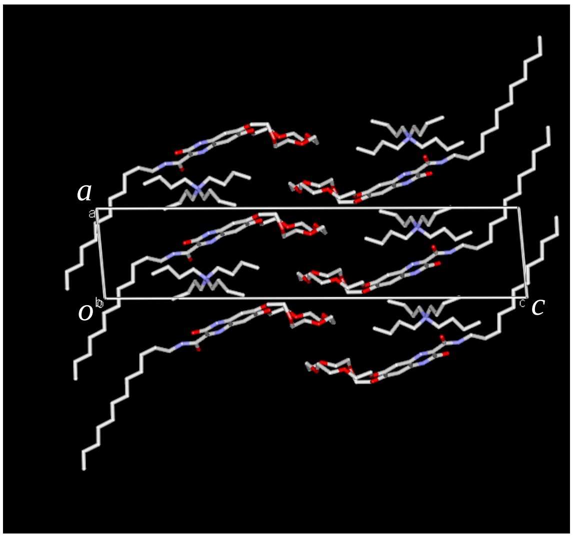

Figure S5. Packing structure of TBA$^+$•**1**$^-$•$(H_2O)_2$ viewed along the *b* axis.

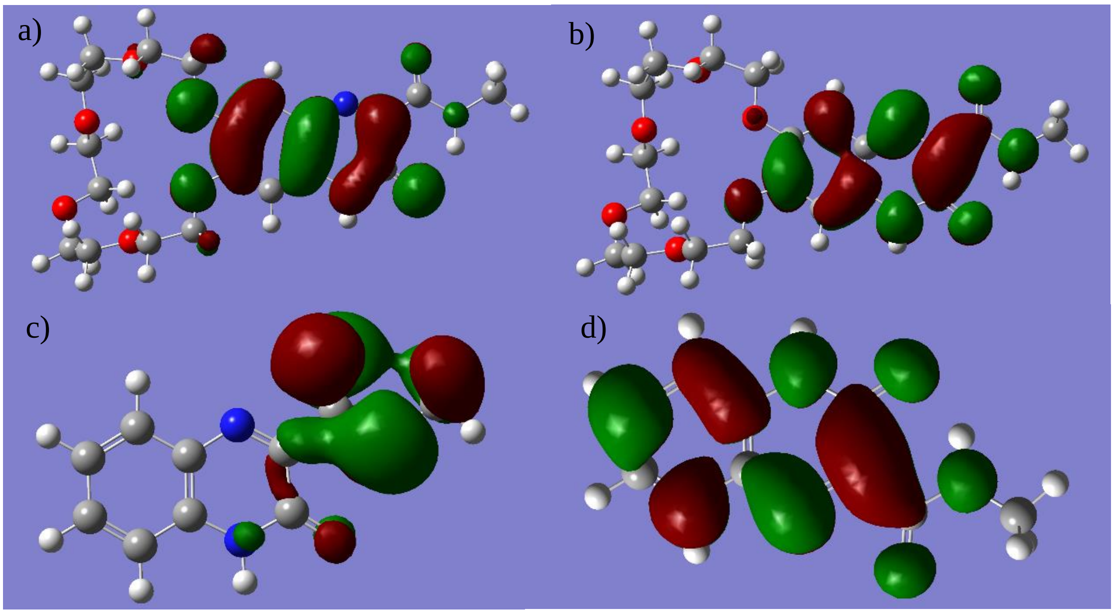

Figure S6. Frontier orbitals of **1** a) for HOMO, b) for LUMO and of **C1QXa** c) for HOMO, d) for LUMO based density functional theory (DFT) calculations using the B3LYP-6-31G (*d*, *p*) basis set in Gaussian 09W.

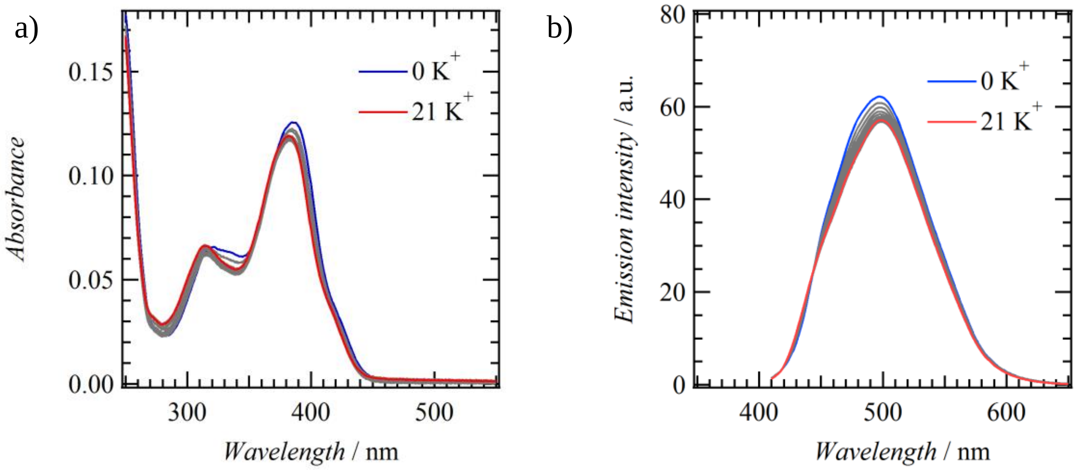

Figure S7. K^+ titration spectra of **1** in CH_3CN. a) Absorption and b) fluorescence spectra by the addition of 21 equivalents of K^+ in CH_3CN.

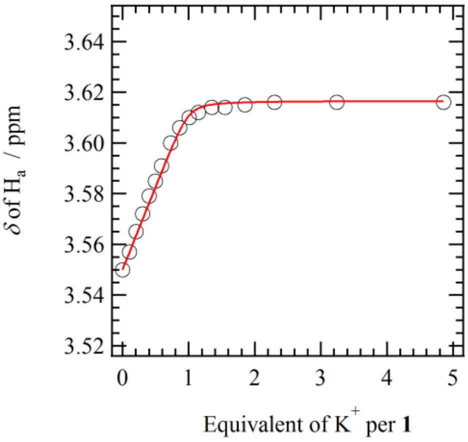

Figure S8. ^{1}H NMR titration spectra of **1** (2.0 mM) in CD_3CN using $K^+ \bullet PF_6^-$. Plots of chemical shift of H_a and titration amount of K^+ ion per **1**. Red line was a fitting curve of 1:1 complex formation between **1** and K^+ ion.

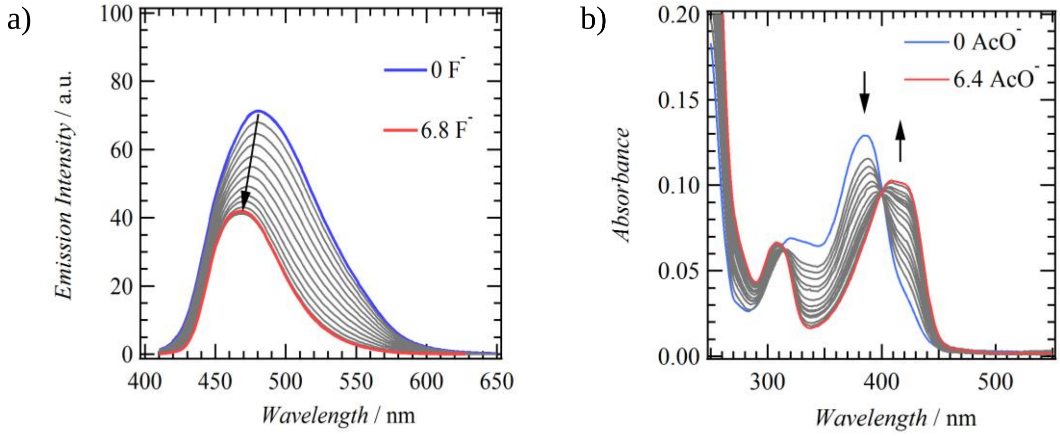

Figure S9. Titration spectra of **1** using a) 6.8 equivalent of F^- at fluorescence spectra and b) 6.4 equivalent of AcO^- anions at UV-vis spectra in CH_3CN. The excitation wavelength was fixed at 399 nm.

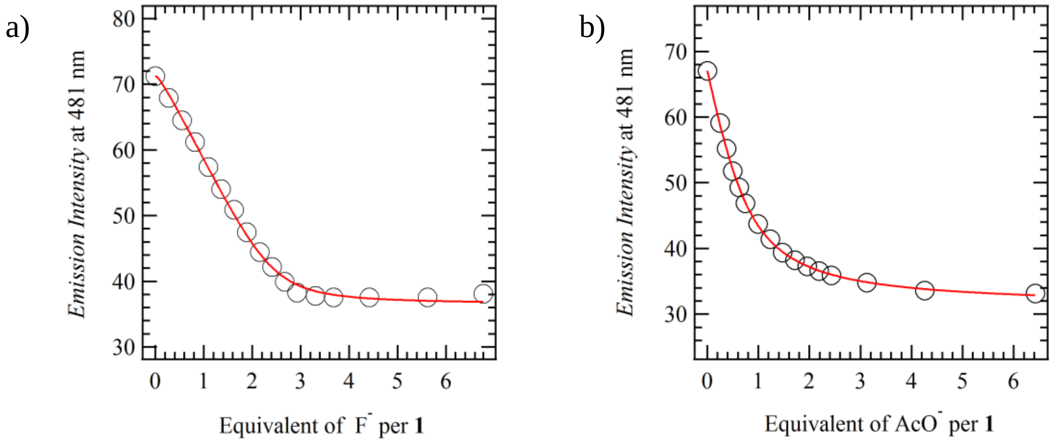

Figure S10. Fitting curves of two steps a) F^- and b) AcO^- recognitions processes using the fluorescence titration spectra of **1**.

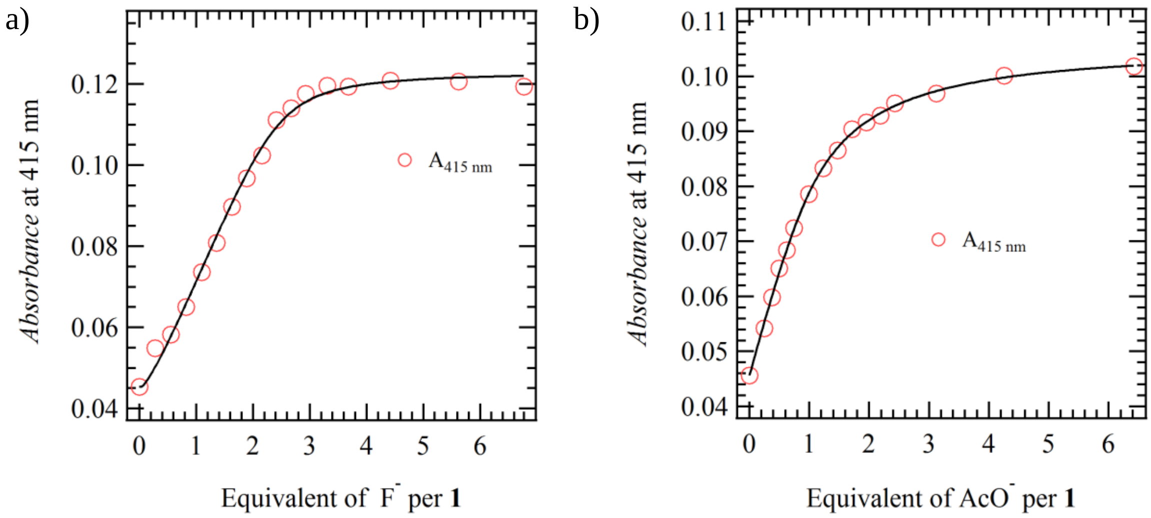

Figure S11. Fitting curves of two steps a) F^- and b) AcO^- recognitions processes using the UV-vis titration spectra at 415 nm of **1**.

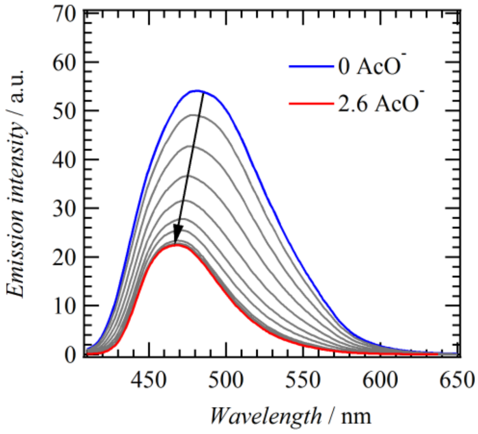

Figure S12. Fluorescence titration spectra of K^+•**1** by the addition of 2.6 equivalent of AcO^- anion.

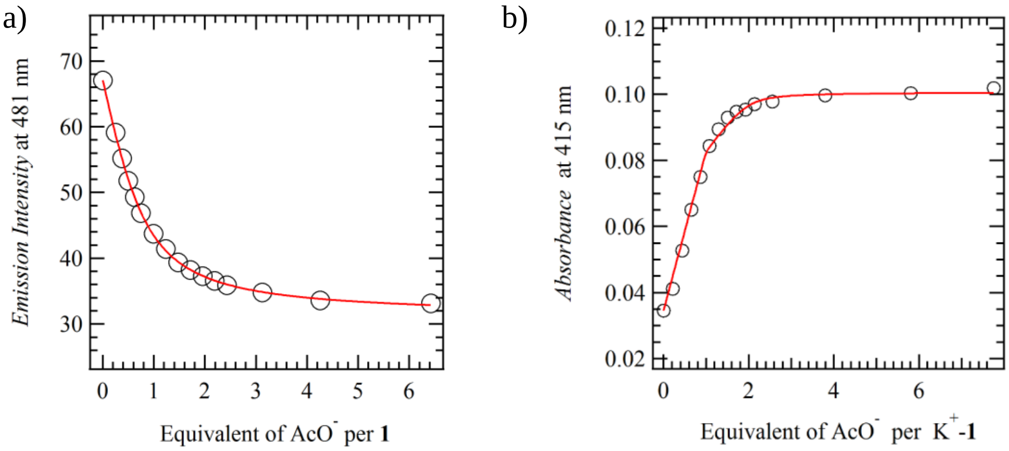

Figure S13. Fitting curve of the two-step AcO^- anion recognition processes of K^+•**1** in CH_3CN. Titration data of a) fluorescence band at 481 nm and b) UV-vis band at 415 nm.

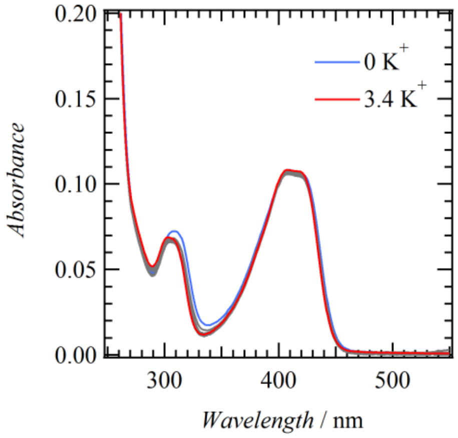

Figure S14. UV-vis spectra of **1**$^-$ anion by the addition of 3.4 equivalent of K$^+$.

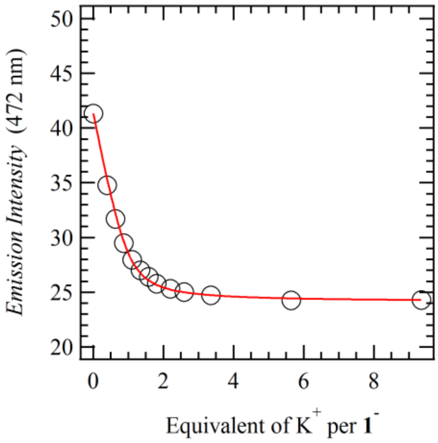

Figure S15. Fitting curve of K$^+$ recognition process of anionic **1**$^-$ at the fluorescence spectra using the 1:1 complex formation model.

Determination of complex formation constants.

Titration data were fitted by non-linear regression analyses using the global fitting program of Igor Pro 5.03J. The two steps complex formation model in the equations (1), (2), and (3) is applied to determine the K_1 and K_2 values form the optical titration data.

$$\mathbf{1} + X^- \overset{K_1}{\rightleftharpoons} \mathbf{1{\cdot}X^-} + X^- \overset{K_2}{\rightleftharpoons} \mathbf{1^-} + \mathbf{HX_2^-} \quad (1)$$

$(X^- = F^-$ or $AcO^-)$

$$K_1 = \frac{[1{\cdot}X^-]}{[1][X^-]} \quad (2)$$

$$K_2 = \frac{[1^-][H^+X^-]}{[1{\cdot}X^-]} \quad (3)$$

Absorbance (A) and Fluorescence intensity (F) are represented by equations(4) and (5), respectively.

$$\mathbf{A} = \frac{\varepsilon_{\mathrm{LH}} + \varepsilon_{\mathrm{LH\cdot X}}\,\mathrm{K_1}\,[\mathrm{X}] + \varepsilon_{\mathrm{L}}\mathrm{K_1}\,\mathrm{K_2}[\mathrm{X}]}{1+\mathrm{K_1}\,[\mathrm{X}]+\mathrm{K_1K_2}[\mathrm{X}]^2} \quad (4)$$

$$\mathbf{F} = \frac{k_{\mathrm{LH}} + k_{\mathrm{LH\cdot X}}\,\mathrm{K_1}\,[\mathrm{X}] + k_{\mathrm{L}}\mathrm{K_1}\,\mathrm{K_2}[\mathrm{X}]}{1+\mathrm{K_1}[\mathrm{X}]+\mathrm{K_1K_2}[\mathrm{X}]^2} \quad (5),$$

where the constant k is corresponding to a proportionality factor $F = k\,[c]$ in fluorescence spectra.

The [X] is a solution of three order equation (6),

$$\mathrm{A[X]^3 + B[X]^2 + C[X] + D = 0} \quad (6),$$

$$\mathrm{A = K_1K_2,\ \ B = K_1 + 2K_1K_2[LH]_t - K_1K_2[X]_t}$$

$$\mathrm{C} = 1 + \mathrm{K}_1[H]_t - K_1[X]_t \ , \ \ \mathrm{D} = -[\mathrm{X}]_\mathrm{t}$$

The binding constants of K_1 and K_2 were obtained by the fitting procedure of equations (4) and (5), where the unknown parameters of $\varepsilon_{\mathrm{LH\bullet X}}$, ε_{L}, $k_{\mathrm{LH\bullet X}}$, and k_{L} are also determined by the regression analysis. Newton method is used in the regression program of equation (6).