

Naked Eye Colorimetric Fluoride Ion Sensors

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Supporting Information

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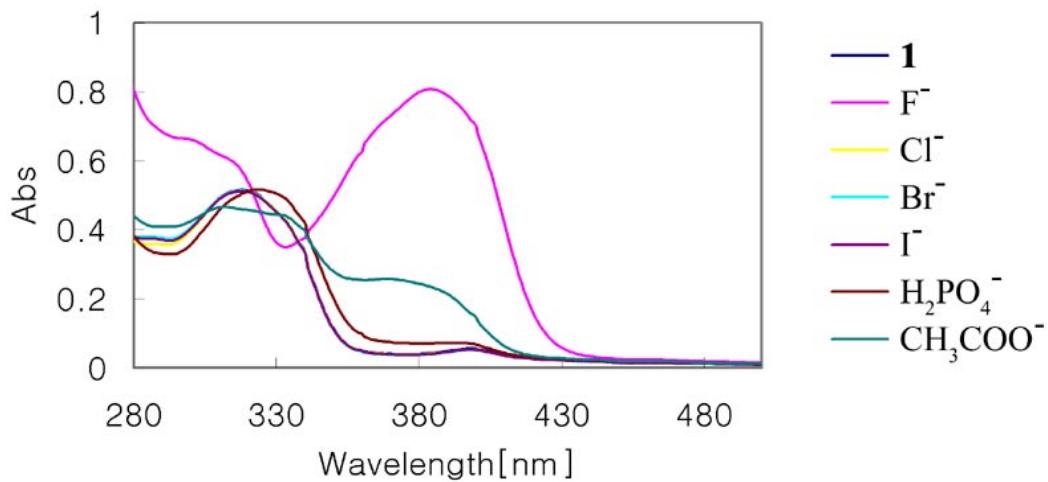


Figure S1. Absorption spectra of **1** (3 × 10⁻⁵ M) upon addition of tetrabutylammonium fluoride, chloride, bromide, iodide, dihydrogen phosphate and acetate (3 × 10⁻³ M) in DMSO.

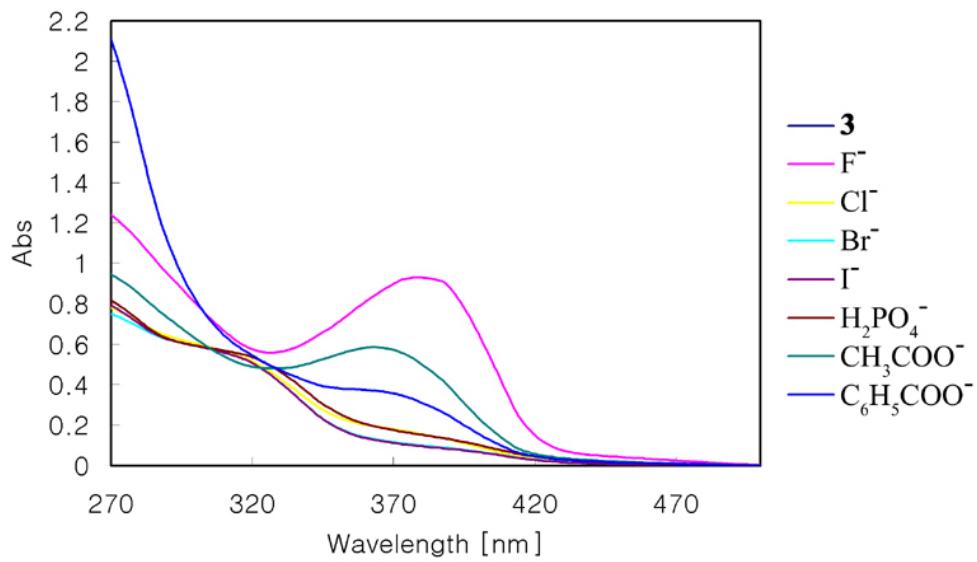


Figure S2. Absorption spectra of **3** (3 × 10⁻⁵ M) upon addition of tetrabutylammonium fluoride, chloride, bromide, iodide, dihydrogen phosphate, benzoate and acetate (3 × 10⁻³ M) in DMSO.

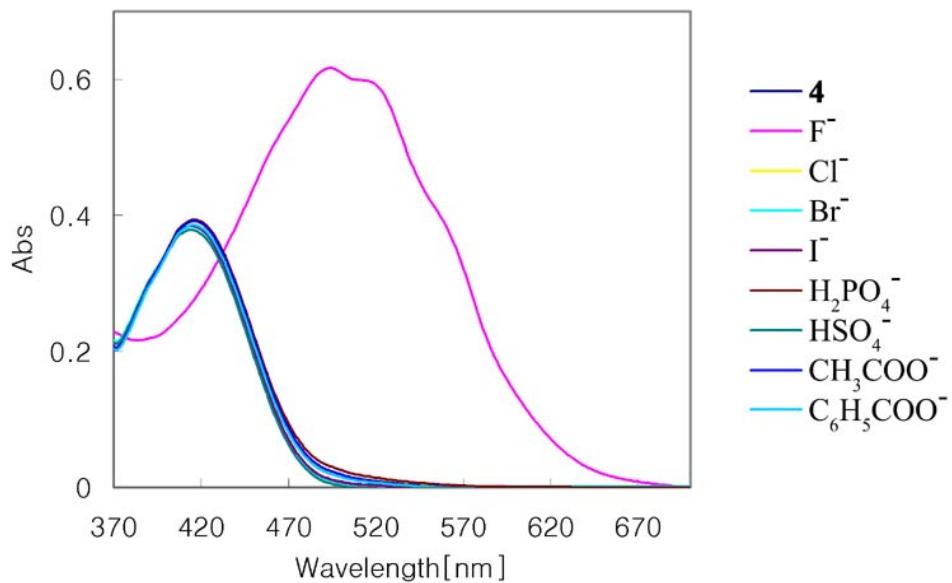


Figure S3. Absorption spectra of **4** (3 × 10⁻⁵ M) upon addition of tetrabutylammonium fluoride, chloride, bromide, iodide, dihydrogen phosphate, hydrogen sulfate, benzoate and acetate (3 × 10⁻³ M) in DMSO.

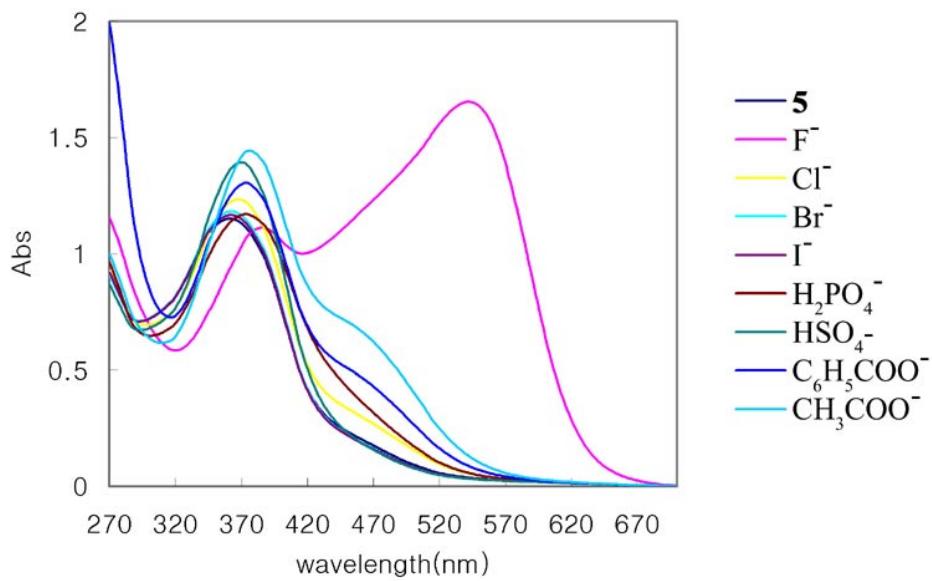


Figure S4. Absorption spectra of **5** (3 × 10⁻⁵ M) upon addition of tetrabutylammonium fluoride, chloride, bromide, iodide, dihydrogen phosphate, hydrogen sulfate, benzoate and acetate (3 × 10⁻³ M) in DMSO.

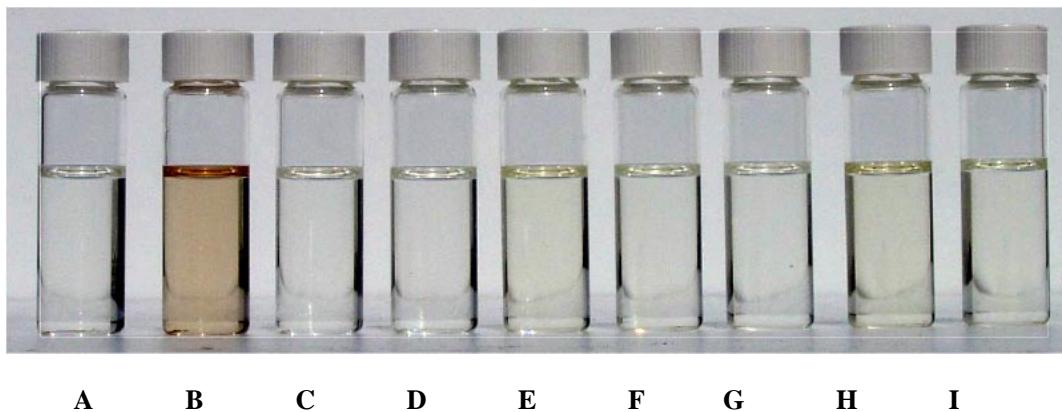


Figure S5. Color changes of ligand **3** (2×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (2×10^{-3} M). A= Free receptor, B= Fluoride, C=Chloride, D=Bromide, E=Iodide, F=Dihydrogen phosphate, G= Hydrogen sulfate, H=Acetate, I=Benzoate.

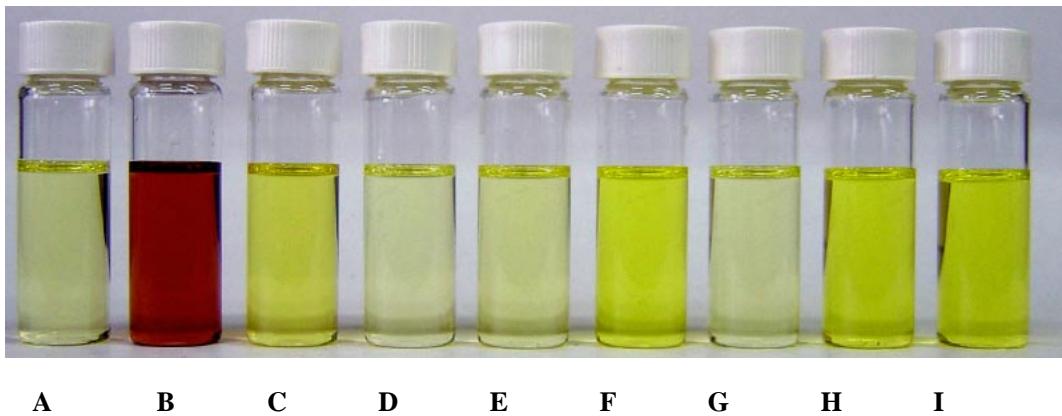
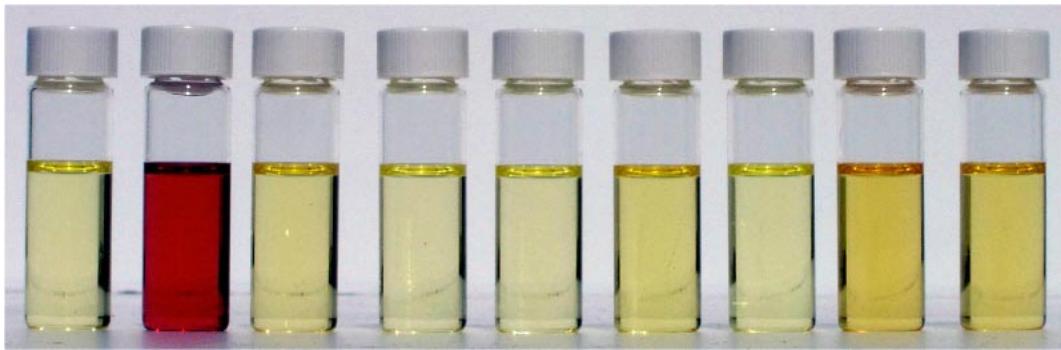


Figure S6. Color changes of ligand **4** (2×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (2×10^{-3} M). A= Free receptor, B= Fluoride, C=Chloride, D=Bromide, E=Iodide, F=Dihydrogen phosphate, G= Hydrogen sulfate, H=Acetate, I=Benzoate.



A B C D E F G H I

Figure S7. Color changes of ligand **5** (2×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (2×10^{-3} M). A= Free receptor, B= Fluoride, C=Chloride, D=Bromide, E=Iodide, F=Dihydrogen phosphate, G= Hydrogen sulfate, H=Acetate, I=Benzoate.

S8. Spectroscopic data for **2**; ^1H NMR (DMSO-d₆) δ 9.58 (s, 2H, NH), δ 8.79 (s, 2H, NH), δ 7.99 (d, 4H, ArH, J = 9.8 Hz), δ 7.83 (d, 2H, ArH, J = 7.9 Hz), δ 7.58 (d, 2H, ArH, J = 7.3 Hz), δ 7.51 (t, 2H, ArH, J = 7.7 Hz), δ 7.51 (d, 4H, ArH, J = 12.0 Hz); ^{13}C NMR δ 153.2 (-CO), 146.9, 140.9, 135.9, 133.0, 126.6, 125.8, 125.1, 124.7, 124.1, 117.4, 112.7 (Ar). FAB MS m/z 486 (M+1, Calcd 487). Anal. Calcd for C₂₄H₁₈N₆O₆: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.19; H, 3.78; N, 17.10. **3**; ^1H NMR (DMSO-d₆) δ 9.36 (s, 2H, NH), δ 8.74 (s, 2H, NH), δ 8.31 (s, 2H, ArH), δ 7.82 (d, 2H, ArH, J = 7.8 Hz), δ 7.58 (m, 8H, ArH), δ 7.36(t, 2H, ArH, J = 7.8 Hz); ^{13}C NMR δ 114.3 (-CO), 108.8, 102.3, 96.7, 94.1, 90.7, 87.2, 86.5, 85.3, 84.8, 84.7, 76.7, 72.9 (Ar). FAB MS m/z 486 (M+1, Calcd 487). Anal. Calcd for C₂₄H₁₈N₆: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.17; H, 3.80; N, 17.14. **4**; ^1H NMR (DMSO-d₆) δ 10.05 (s, 2H, NH), δ 7.95 (d, 2H, ArH, J = 8.7 Hz), δ 7.39 (t, 4H, ArH and NH, J = 7.0 Hz), δ 7.20 (t, 2H, ArH, J = 8.4 Hz), δ 7.10 (d, 2H, ArH, J = 7.8 Hz), δ 7.0 (d, 2H, ArH, J = 8.4 Hz), δ 6.61 (t, 2H, ArH, J = 6.6 Hz).

Hz), δ 6.51 (d, 2H, ArH, J = 7.2 Hz). FAB MS m/z 486 (M+1, Calcd 487). Anal. Calcd for C₂₄H₁₈N₆O₆: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.20; H, 3.80; N, 17.13. **5**; ¹H NMR (DMSO-d₆) δ 9.38 (s, 2H, NH), 8.84 (s, 2H, NH), 7.77 (m, 10H, ArH), 7.67 (d, 2H, ArH, J = 7.2 Hz), 7.59 (d, 4H, ArH, J = 5.6 Hz), 7.49 (m, 8H, ArH); ¹³C NMR (DMSO-d₆) δ 153.1 (-CO), 152.1, 146.5, 1493.4, 135.7, 133.3, 130.6, 129.3, 125.7, 125.5, 123.7, 123.4, 122.2, 118.0 (ArH). FAB MS m/z 604 (M+1, Calcd 605). Anal. Calcd for C₃₆H₂₈N₈O₂: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.46; H, 4.72; N, 18.60. **6**; ¹H NMR (DMSO-d₆) δ 9.33 (s, 2H, NH), 8.83 (s, 2H, NH), 8.19 (d, 4H, ArH, J = 8.7 Hz), 7.79 (t, 8H, ArH, J = 9.0 Hz) 7.66 (d, 4H, ArH, J = 8.7 Hz), 7.59 (d, 2H, ArH, J = 7.5 Hz), 7.50 (m, 8H, ArH). FAB MS m/z 694 (M+1, Calcd 695). Anal. Calcd for C₃₆H₂₆N₁₀O₆: C, 62.24; H, 3.77; N, 20.16. Found: C, 62.16; H, 3.75; N, 10.98.

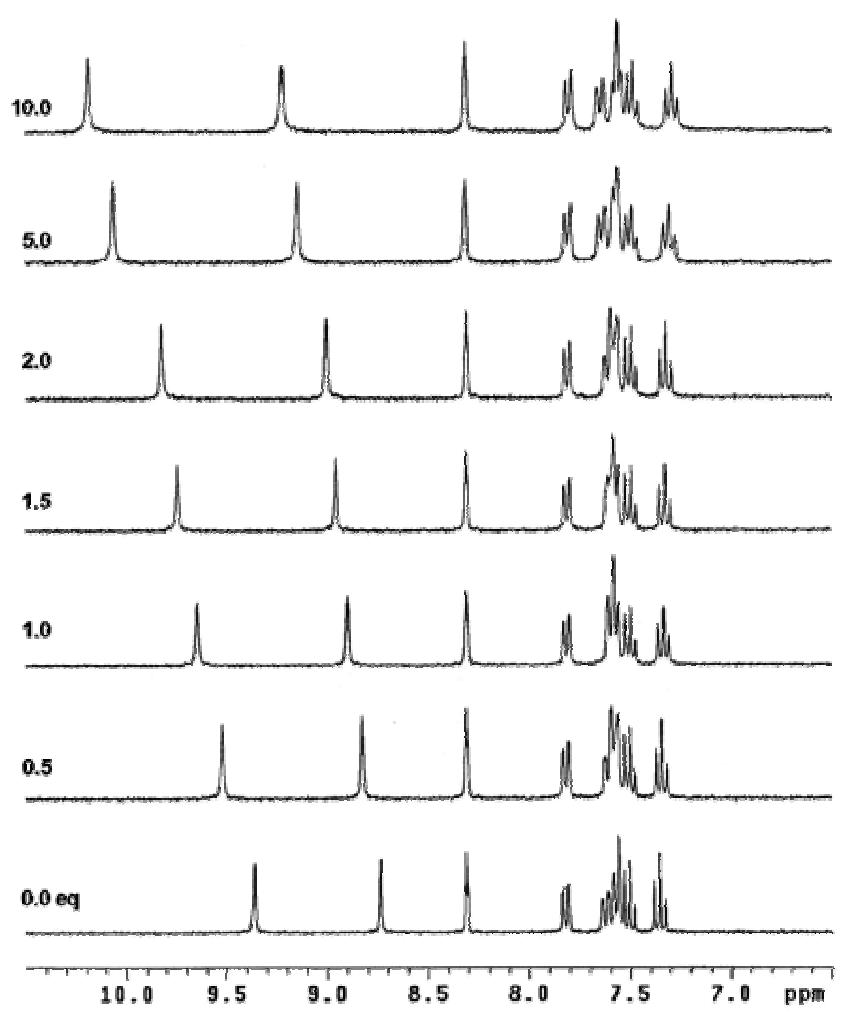


Figure S9. The partial ¹H NMR spectra of compound 3 in the presence of tetrabutylammonium chloride in DMSO-d₆. Numbers at the left side indicate the equivalent amounts of chloride added.

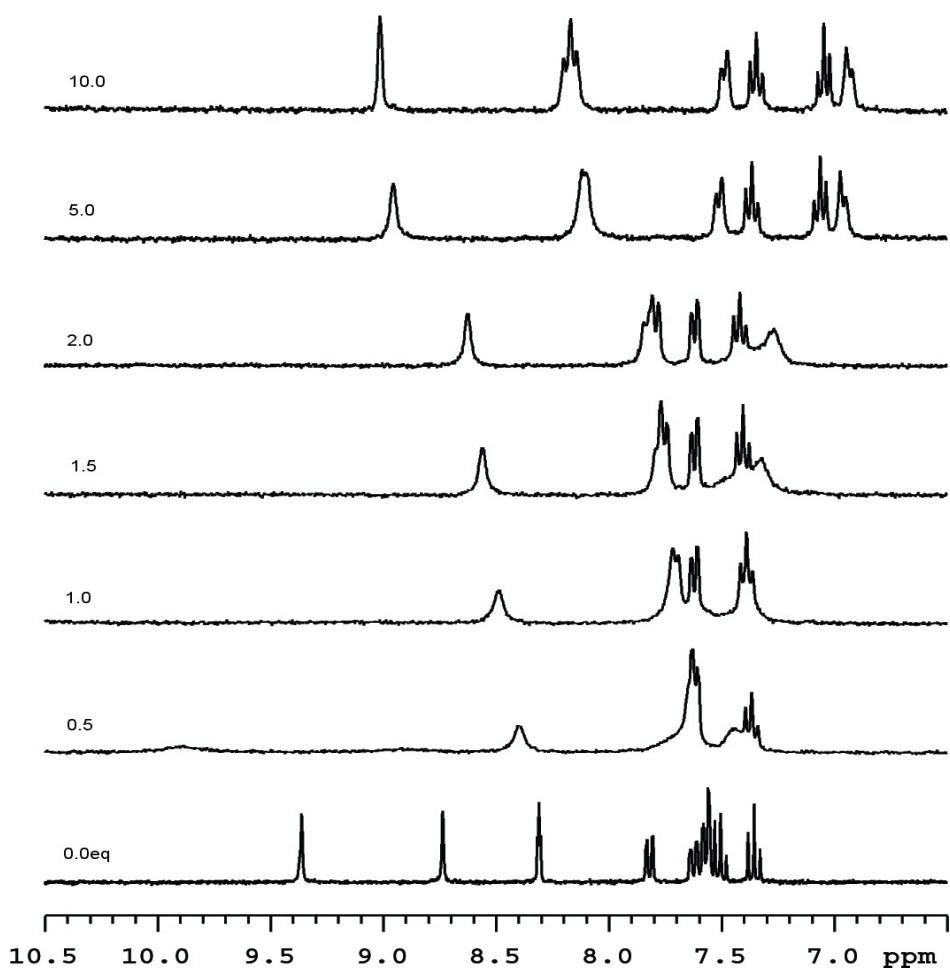


Figure S10. The partial ¹H NMR spectra of compound 3 in the presence of tetrabutylammonium fluoride in DMSO-d₆. Numbers at the left side indicate the equivalent amounts of fluoride added.