Electronic Supplementary Information

For

Fluorescence modulation in anion sensing by introducing intramolecular H-bonding interactions in host-guest adducts

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Fig. S6 Plausible intermediates in the host-guest interactions in the cases of reference compounds *para*-TFADA (**2**) and *N*-Ph-DA (**3**).

Fig. S1 UV absorption spectrum of *ortho*-TFADA (**1**) in CH_3CN.

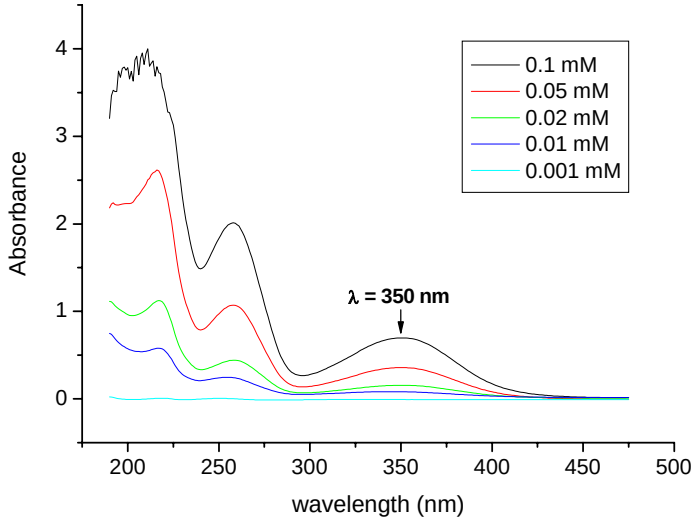
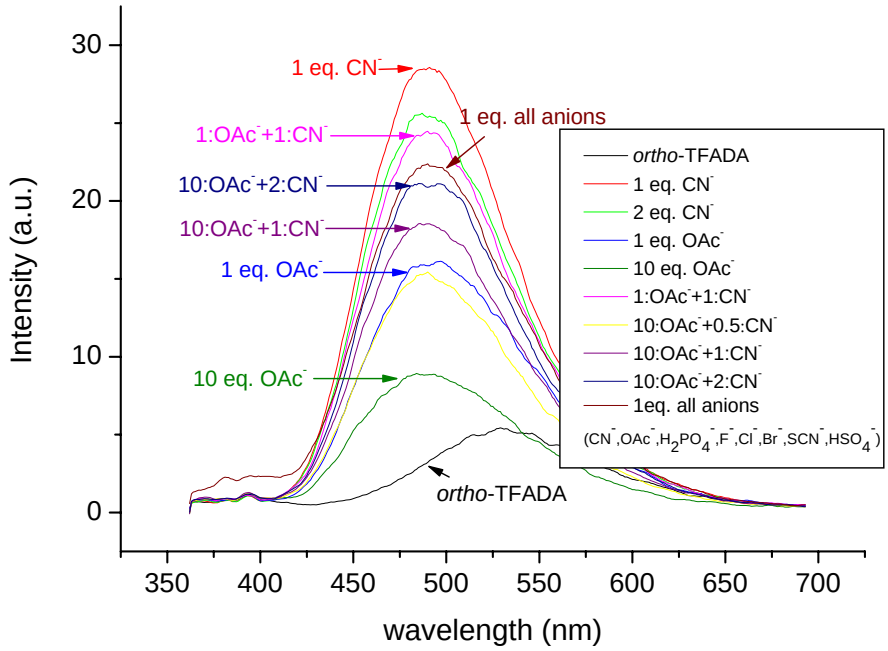


Fig. S2 Fluorescence emission changes of *ortho*-TFADA (**1**) (20 μM) in the presence of various competing anions, as indicated.



Fluorescence intensity enhanced as followed: 1.0 equiv. CN^- > (1 equiv. ^-OAc + 1.0 equiv. ^-CN) > all anions (each 1.0 equiv.) > (10 equiv. ^-OAc + 2.0 equiv. ^-CN) > (10 equiv. ^-OAc + 1.0 equiv. ^-CN) > 1.0 equiv. ^-OAc > 10 equiv. ^-OAc > *ortho*-TFADA, where all anions are ^-CN, ^-OAc, $H_2PO_4^-$, F^-, Cl^-, Br^-, ^-SCN, HSO_4^-.

Fig. S3 (a) Fluorescence emission changes of *para*-TFADA (**2**) (0.1 mM) upon addition of $^{-}$OAc (as Bu_4N^+ salt) in CH_3CN following 376 nm excitation (at which the maximum absorption was observed). (b) Fluorescence emission changes of *para*-TFADA (**2**) (0.1 mM) with increasing concentration of $^{-}$CN in CH_3CN following 376 nm excitation.

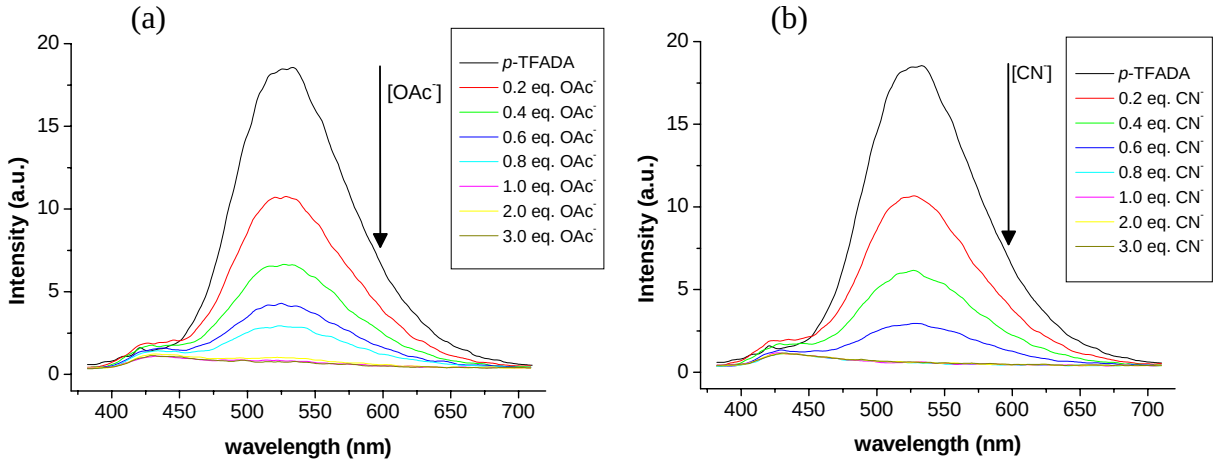
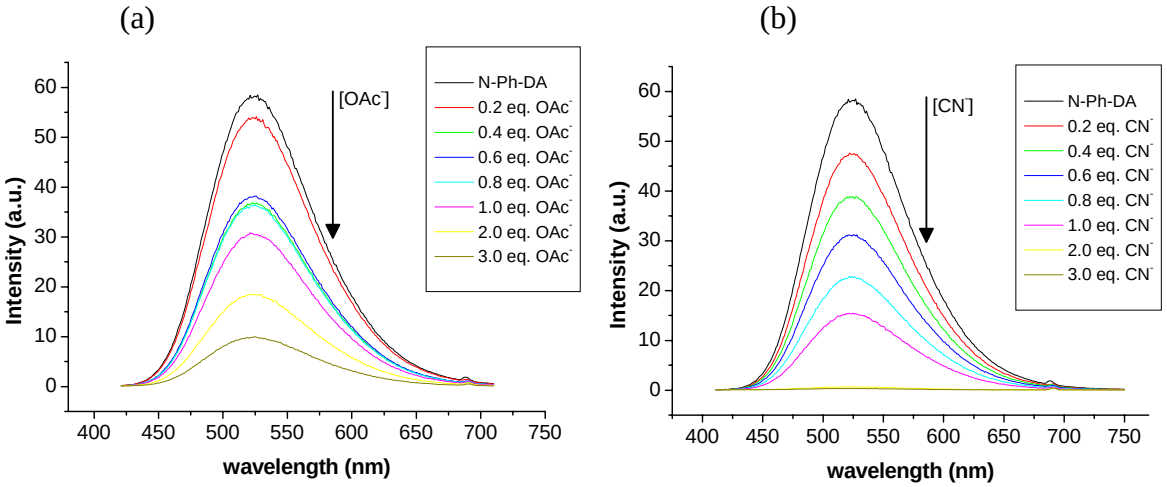


Fig. S4 (a) Fluorescence emission changes of *N*-Ph-DA (**3**) (0.1 mM) upon addition of $^{-}$OAc (as Bu_4N^+ salt) in CH_3CN following 344 nm excitation (at which the maximum absorption was observed). (b) Fluorescence emission changes of *N*-Ph-DA (**3**) (0.1 mM) upon addition of $^{-}$CN (as Bu_4N^+ salt) in CH_3CN following 344 nm excitation.



Fluorescence Titration Experiments

Fluorescence spectra were recorded on a Photon Technical International Fluorescence system. Fluorescence experiments were carried out in 10 mm quartz cuvette at 25 ºC. Stock solutions of hosts and guests were prepared in acetonitrile. Test solutions were obtained by adding an appropriate aliquot of the stock solutions and diluting to 2 mL in the cuvette. Both excitation and emission slit widths were of 2 nm.

Fig. S5 (a) ^{1}H NMR spectra of *ortho*-TFADA (**1**) in $CDCl_3$; (b) **1** + 1.0 equiv. of $^{-}$CN (as Bu_4N^+ salt); at 25 °C (only NH and aromatic protons are shown).

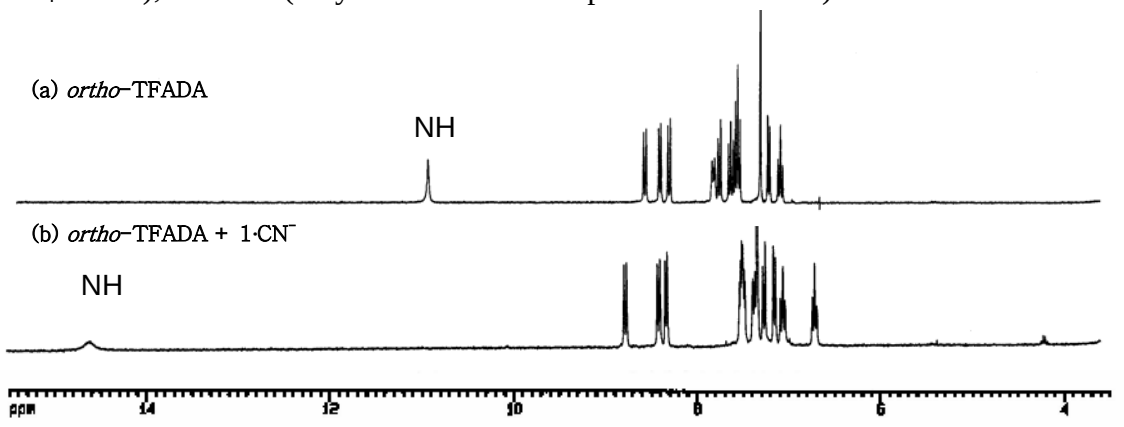
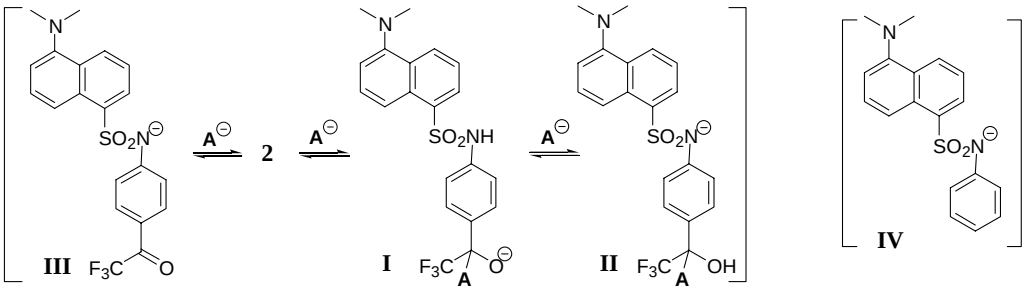
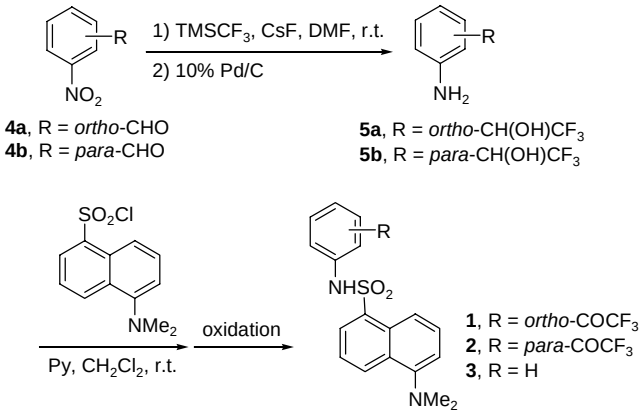


Fig. S6. Plausible intermediates in host-guest interactions in the cases of reference compounds *para*-TFADA (**2**) and *N*-Ph-DA (**3**).



All intermediates **I**-**IV** are possible fluorescence quenching species.

Synthesis and Characterization of Compounds 1–3



1-(2-Aminophenyl)-2,2,2-trifluoroethanol (5a)

To a stirred solution of the aldehyde **4a** (151 mg, 1.0 mmol) and carefully dried cesium fluoride (*cat*.) in DME (5 mL) was added $TMSCF_3$ (2.0 M in THF, 0.06 mL, 1.2 mmol) at 0 ℃ under an argon atmosphere. After being stirred for 5 h at room temperature, the reaction mixture was treated with 10% aq. HCl (1 mL) and diluted with EtOAc (10 mL). An extractive workup with EtOAc and purification by column chromatography (Hexane/EtOAc, 4:1) afforded 2,2,2-trifluoro-1-(2-nitrophenyl)ethanol as a yellowish solid (210 mg, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (t, J = 7.8 Hz, 2H), 7.71 (t, J = 7.8 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 6.20 (q, J = 6.3 Hz, 1H) and 4.13 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 134.5, 130.9, 130.0, 129.6, 126.4, 130.1, 126.4, 122.6, 118.9 (q, J = 280.8 Hz), 67.95, 67.52, 67.08 and 66.66 (q, J = 32.6 Hz). HRMS (EI): calc. for $C_8H_6F_3NO_3$ (M^+) 221.0300, found (*m*/*z*) 221.0296. A solution of this nitro compound (221 mg, 1.0 mmol) in methanol (5 mL) was subjected to hydrogenolysis in the presence of 10 wt % Pd/C (25 mg) under hydrogen atmosphere (about 1 atm) at room temperature for 5 h. The reaction mixture was filtered through Celite and the filtrate was concentrated to give **5a** as a solid (181 mg, 95%): ^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD) δ 7.23 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 5.06 (q, J = 7.5 Hz, 1H) and 3.66 (br, 2H); HRMS (EI^+): calc. for $C_8H_8F_3NO$ (M^+) 191.0558, found (*m*/*z*) 191.0550.

5-(Dimethylamino)naphthalene-1-sulfonic acid [2-(2,2,2-trifluoroacetyl)phenyl]-amide (*ortho*-TFADA, 1)

To a solution of aniline **5a** (191 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added pyridine (87 mg, 1.1 mmol), followed by dansyl chloride (297 mg, 1.1 mmol) under an argon atmosphere, and the resulting mixture was stirred further for 6 h. The reaction

mixture was treated with 10% aq. HCl (1 mL) and diluted with CH_2Cl_2 (20 mL). An extractive workup with CH_2Cl_2 and purification by column chromatography (Hexane/EtOAc, 4:1) afforded 5-(dimethylamino)naphthalene-1-sulfonic acid [2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl]amide (399 mg, 94.3 %) as a yellowish solid: mp 167.1-167.4 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.59 (t, J = 8.1 Hz, 1H), 7.46-7.41 (m, 2H), 7.40-7.31 (br s, 1H), 7.31–7.06 (m, 3H), 6.75 (d, J = 7.8 Hz, 1H), 5.36 (q, J = 6.9 Hz, 1H), 3.21-3.12 (br, 1H) and 2.89 (s, 6H);^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 135.3, 134.1, 131.3, 130.2, 130.1, 130.0, 129.8, 129.3, 129.0, 126.9, 126.4, 125.2, 123.4, 122.6, 118.6, 115.6, 70.0 (q, J = 32.3 Hz) and 45.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -0.44; HRMS (E^+) calc. for $C_{20}H_{19}F_3N_2O_3S$ (M^+) 424.1068, found (*m*/*z*) 424.1062. To a stirred solution of Dess-Martin periodinane (1.272 g, 3 mmol) in dry toluene (10 mL) was added the obtained trifluoromethyl alcohol (424 mg, 1.0 mmol) in toluene (3 mL), and the resulting mixture was stirred at room temperature for 24 h and then at 40-45 ℃ for 24 h. The reaction mixture was diluted with EtOAc (20 mL) and poured into a solution of sodium thiosulfate (10 mL, 0.26 M) in a saturated aqueous sodium bicarbonate solution. An extractive workup with EtOAc and purification by column chromatography (Hexane:EtOAc, 4:1) afforded *ortho*-TFADA (**1**) as a solid (242 mg, 57%).

5-(Dimethylamino)naphthalene-1-sulfonic acid [4-(2,2,2-trifluoroacetyl)phenyl]-amide (*para*-TFADA, 2)

Prepared similarly as above starting from 5-(dimethylamino)naphthalene-1-sulfonic acid [4-(2,2,2-trifluoro-1-hydroxyethyl)phenyl]amide after purification by column chromatography (Hexane:EtOAc, 4:1) in 40% yield (170 mg). 5-(Dimethylamino)naphthalene-1-sulfonic acid [4-(2,2,2-trifluoro-1-hydroxyethyl)-phenyl]amide was in turn prepared similarly as above from 1-(4-aminophenyl)-2,2,2-trifluoroethanol in 95% yield as a pale green solid: ^1H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.53 (t, J = 8.4 Hz, 1H), 7.42 (t, J = 8.1 Hz, 1H), 7.19-7.14 (m, 3H), 6.95 (d, J = 8.4 Hz, 2H), 4.82 (q, J = 6.6 Hz, 1H) and 2.85 (s, 6H);^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 137.9, 134.3, 131.3, 130.7, 130.5, 130.0, 129.9, 129.7, 128.9, 128.6, 126.2, 126.1, 123.3, 122.4, 120.7, 118.6, 115.5, 72.3 (q, J = 31.8 Hz) and 45.6; ^{19} F NMR (282 MHz, $CDCl_3$) δ -2.08; HRMS (E^+) calc. for $C_{20}H_{19}F_3N_2O_3S$ (M^+) 424.1068, found (*m*/*z*) 424.1070.

5-(Dimethylamino)naphthalene-1-sulfonic acid phenylamide (*N*-Ph-DA, 3)

To a stirred solution of aniline (93 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added

pyridine (87 mg, 1.1 mmol) and followed by dansyl chloride (297 mg, 1.1 mmol) under an argon atmosphere, and the resulting mixture was stirred at room temperature for 6 h. The reaction mixture was treated with 10% aq. HCl (1 mL) and diluted with CH_2Cl_2 (20 mL). An extractive workup with CH_2Cl_2 and purification by column chromatography (Hexane:EtOAc, 4:1) afforded **3** as pale green solid (271 mg, 83 %): mp 141.6-141.8 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.7 Hz, 1H), 8.16 (dd, J = 7.5 and 1.2 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 6.90-7.13 (m, 6H), 6.75 (br s, 1H) and 2.87 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 136.7, 134.4, 131.1, 130.6, 130.1, 129.9, 129.4, 128.9, 125.6, 123.4, 121.9, 118.7 and 115.5; HRMS (E^+) calc. for $C_{18}H_{18}N_2O_2S$ (M^+) 326.1089, found (m/z) 326.1082.