

Supporting Information:

Selective Colorimetric Sensing of Anions in Aqueous Media through Reversible Covalent Bonding

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FIGURE S1. Color change of compound **2** (0.05 mM in CH₃CN) upon addition of anions (10 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).

FIGURE S2. Color change of compound **3** (0.05 mM) in MeOH–H₂O (10:1) upon addition of anions (250 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).

FIGURE S3. Color change of DNPA **1** (0.05 mM) MeOH–H₂O (10:1) upon addition of anions (50 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).

FIGURE S4. (a) UV-vis absorption change of DNPA **1** (2.0×10^{-5} M) in CH₃CN upon addition of 1.0 equiv of KOH. (b) UV-vis absorption change of DNPA **1** (5.0×10^{-5} M) upon addition of 2.0 equiv of KOH in MeOH–H₂O (10/1).

FIGURE S5. Color change of compound **3** (0.05 mM in CH₃CN) upon addition of

anions (10 equiv): no anion, CN^- , F^- , OAc^- , and H_2PO_4^- (from the left).

FIGURE S6. Color change of reference compound **2** (0.05 mM) in MeOH–H₂O (10:1) upon addition of anions (250 equiv): no anion, CN^- , F^- , OAc^- , and H_2PO_4^- (from the left).

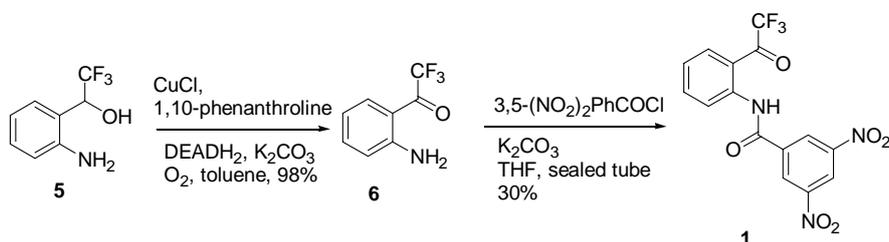
FIGURE S7. A plot of the absorbance normalized versus cyanide concentration (1.0 – 50 μM range). From this plot, an approximate detection limit for CN^- by DNPA **1** in MeOH–H₂O (10:1) is estimated to be $\sim 3 \mu\text{M}$.

FIGURE S8. Color change of DNPA **1** (0.1 mM) in MeOH–H₂O (10:1) upon addition of anions: no anion, an equimolar mixture of all the anions (F^- , OAc^- , H_2PO_4^- , HSO_4^- , SCN^- , Cl^- , and Br^-), and CN^- (from the left). All the anions used as their Bu_4N^+ -salts.

FIGURE S9. Color change of DNPA **1** (0.1 mM in CH_2Cl_2) upon addition of NaCN (1.0 mM in water). The left set: no NaCN but with distilled water; in the absence; and in the presence of a phase-transfer catalyst, $\text{Bu}_4\text{N}^+\text{Br}^-$ (from the left). The right set: the same combinations but with a higher concentration of DNPA **1** (1.0 mM).

(5) Copies of ^1H and ^{13}C NMR spectra of the compounds synthesized -----S14-S24

Synthesis of compounds 1 – 3:



(*o*-Trifluoroacetyl)aniline (6). A 25-mL two-necked flask fitted with a reflux condenser and an oxygen inlet were charged with toluene (10 mL), CuCl (9.9 mg, 0.1 mmol), and phenanthroline (18 mg, 0.1 mmol) sequentially, and the resulting black mixture was stirred at room temperature for 10 min. To the mixture was added diethylhydrazinodicarboxylate (DEADH₂, 88 mg, 0.5 mmol) followed by solid K₂CO₃ (552 mg; 4 mmol) and it was stirred for another 5 min. To this mixture was added the alcohol **5** (382 mg, 2 mmol)¹ as neat and the resulting solution was heated at 90 °C under a gentle stream of oxygen. After being stirred for 1 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celigel (50% silica gel mixed with 50% Celite), and concentrated in vacuo to afford the keto compound **6** as a brownish solid in 98% yield (370 mg): *R*_f = 0.48 (EtOAc/Hexane = 1/9); ¹H NMR (300 MHz, CDCl₃): δ 7.5 (dt, *J* = 6.6 and 1.8 Hz, 1H), 7.4 (dt, *J* = 7.8 and 1.8 Hz, 1H), 6.9 (dt, *J* = 7.8 and 0.9 Hz), 6.7 (d, *J* = 8.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 181.7, 181.2, 180.8, 180.3 [q, *J* = 33.2 Hz (coupled with F), -COCF₃], 153.4, 136.8, 131.62, 131.57, 131.51, 131.46 [q, *J* = 4.1 Hz (coupled with F), an aromatic carbon], 123.1, 119.2, 115.3, 111.5 [q, *J* = 292.5 Hz (coupled with F), -CF₃], 117.7, 116.6, 111.3; ¹⁹F (300 MHz, CDCl₃): δ 6.7; MS (EI) *m/z* for C₈H₆F₃NO (M⁺) calcd 189.04, found 189.09.

***N*-(2-(2,2,2-Trifluoroacetyl)phenyl)-3,5-dinitrobenzamide (DNPA 1).** To a mixture of aniline **6** (100 mg, 0.52 mmol) and K₂CO₃ (85 mg, 0.63 mmol) in dry THF

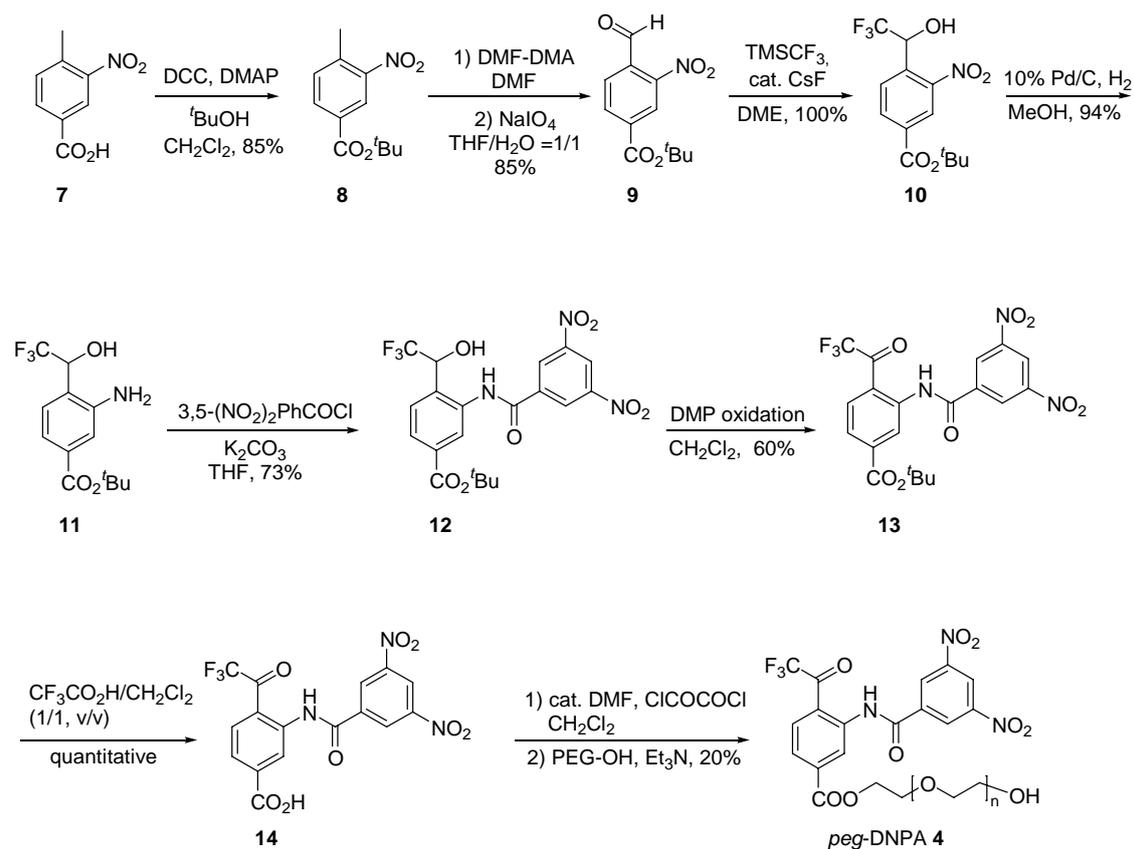
(6 mL) in a sealed tube was added slowly a solution of 3,5-dinitrobenzoyl chloride (146 mg, 0.63 mmol) in THF (1 mL). The resulting mixture was stirred at room temperature for 4 h and concentrated under reduced pressure. The residue was partitioned between EtOAc (10 mL) and water (10 mL), and the organic layer was separated, washed with water (2 × 10 mL) successively, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography (EtOAc/Hexane = 1/20) to afford DNPA **1** as a white solid in 30% yield (60 mg): *R*_f = 0.23 (EtOAc/Hexane = 1/4); mp 153.2 °C; ¹H NMR (300 MHz, CDCl₃): δ 12.2 (s, 1H), 9.25 (t, *J* = 3 Hz, 1H), 9.2 (d, *J* = 2 Hz, 2H), 9.0 (d, *J* = 8.5 Hz, 1H), 8.2–8.1 (m, 1H), 7.9 (dt, *J* = 7.9 and 1.3 Hz, 1H), 7.4 (dt, *J* = 7.9 and 0.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 185.48, 185.00, 184.55, 184.07 (q, *J* = 34.7 Hz, –COCF₃), 162.0, 149.7, 143.2, 139.0, 138.5, 133.25, 133.20, 133.14, 133.07 [q, *J* = 4.8 Hz (coupled with F), an aromatic carbon], 133.1, 128.1, 125.0, 122.5, 122.2, 116.6, 122.5, 119.0, 115.2, 111.3 [q, *J* = 292.0 Hz (coupled with F), –CF₃]; ¹⁹F NMR (300 MHz, CDCl₃): δ 7.24; HRMS (FAB) *m/z* for C₁₅H₉F₃N₃O₆ (M + H⁺) calcd 384.0443, found 384.0443.

3,5-Dinitro-*N*-phenylbenzamide (2).² A sealed-tube amide formation similarly as described above afforded the reference compound **2** as a solid in 36 % yield; mp 235.8 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.2 (t, *J* = 1.8 Hz, 1H), 9.1 (d, *J* = 2.1 Hz, 2H), 7.65 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.5 (t, *J* = 7.5 Hz, 2H), 7.3 (s, 1H); ¹⁹F NMR (300 MHz, CDCl₃): δ 4.6; HRMS (FAB) *m/z* for C₁₃H₁₀N₃O₅ (M + H⁺) calcd 288.0620, found 288.0623.

***N*-(4-(2,2,2-Trifluoroacetyl)phenyl)-3,5-dinitrobenzamide (3).** A sealed tube amide coupling reaction similarly as described above gave the *para*-analogue of **1** as a yellowish solid in 56% yield: *R*_f = 0.5 (Hexane/EtOAc = 7/3); mp 168.6 °C; ¹H NMR

(300 MHz, CDCl₃): δ 9.3 (t, $J = 2.0$ Hz, 1H), 9.1 (d, $J = 2.0$ Hz, 2H), 8.6 (s, 1H), 8.2 (d, $J = 8.2$ Hz, 2H), 8.0 – 7.9 (m, 2H); ¹⁹F NMR (300 MHz, CDCl₃): δ 4.55; HRMS (FAB) m/z for C₁₅H₉F₃N₃O₆ (M + H⁺) calcd 384.0443, found 384.0443.

Synthesis of *peg*-DNPA 4:



***tert*-Butyl 4-methyl-3-nitrobenzoate (8).**³ A stirred solution of commercially available 4-methyl-3-nitrobenzoic acid (**7**) (5.0 g, 27.6 mmol), DMAP (337 mg, 2.76 mmol), and *t*-BuOH (3.1 mL, 33 mmol) in dry CH₂Cl₂ was treated with DCC (6.83 g, 33 mmol) at 0 °C. After being stirred for 5 min, the cooling bath was removed and the mixture was further stirred for 5 h at room temperature. The precipitate was suction-filtered, washed with CH₂Cl₂, and the filtered solution was concentrated under reduced pressure. Purification of the residue by column chromatography (EtOAc/Hexane = 1/9)

afforded ester **8** as a white solid (5.58 g, 85 %): $R_f = 0.45$ (EtOAc/Hexane = 1/4); mp 69.9 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.5 (d, $J = 2.1\text{ Hz}$, 1H), 8.1 (dd, $J = 8.0$ and 1.8 Hz, 1H), 7.4 (d, $J = 7.8\text{ Hz}$, 1H), 2.7 (s, 3H), 1.6 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 164.2, 149.7, 138.3, 133.9, 133.4, 131.9, 126.1, 82.8, 28.7, 21.1; HRMS (FAB) m/z for $\text{C}_{12}\text{H}_{16}\text{NO}_4$ ($\text{M} + \text{H}^+$): calcd 238.1079, found 238.1081.

tert-Butyl 4-formyl-3-nitrobenzoate (9).⁴ A solution of the toluene derivative **8** (5.58 g, 23.5 mmol) and *N,N*-dimethylformamide dimethylacetal (DMA, 4.0 mL, 30 mmol) in DMF (47 mL) was stirred under nitrogen at 140 °C for 7 h. Concentration of the reaction mixture *in vacuo* provided the corresponding enamine intermediate as a dark purple oil: $R_f = 0.32$ (EtOAc/hexane = 3/7], which was dissolved in 50% aqueous THF (100 mL) and treated with NaIO_4 (14.8 g, 70 mmol), and the resulting mixture was stirred at room temperature for 1 h (The reaction was monitored by TLC). Insoluble materials were removed by filtration using CH_2Cl_2 , and the filtered solution was washed with brine (50 mL, two times). The organic layer was dried over Na_2SO_4 , concentrated *in vacuo*, and purified by column chromatography (EtOAc/Hexane = 1/9) to afford the aldehyde **9** as a white solid (4.0 mg, 67%): $R_f = 0.23$ (EtOAc/Hexane = 1/9); mp 110.3 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.4 (s, 1H), 8.7 (s, 1H), 8.4 (d, $J = 8.58\text{ Hz}$, 1H), 8.0 (d, $J = 9.0\text{ Hz}$, 1H), 1.7 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 188.3, 163.1, 149.9, 137.7, 135.1, 134.4, 130.4, 126.0, 84.1, 28.6; HRMS (FAB) m/z for $\text{C}_{12}\text{H}_{14}\text{NO}_5$ ($\text{M} + \text{H}^+$) calcd 252.0872, found 252.0873.

tert-Butyl 3-amino-4-(2,2,2-trifluoro-1-hydroxyethyl)benzoate (10). To a stirred solution of the aldehyde **9** (4.0 g, 15.9 mmol) containing a catalytic amount of dry CsF (~10 mg) in DME (53 mL) at 0 °C was added a solution of TMSCF_3 (8.0 mL, 2 M in THF, 15.9 mmol) under an argon atmosphere. After being stirred for 5 h at room

temperature, the reaction mixture was treated with 10% HCl (30 mL) and diluted with EtOAc (30 mL). Extractive workup and purification by column chromatography (EtOAc/Hexane = 1/9) afforded the corresponding alcohol **10** as a yellowish solid (5.1 g, 100%): $R_f = 0.50$ (EtOAc/Hexane = 1/4); mp 101.3 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.5 (d, $J = 1.5$ Hz, 1H), 8.2 (dd, $J = 8.2$ and 1.5 Hz, 1H), 8.1 (d, $J = 8.2$ Hz, 1H), 6.3 – 6.2 (m, 1H), 4.5 (d, $J = 4.6$ Hz, 1H), 1.6 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 164.4, 148.9, 134.5, 134.4, 133.7, 130.5, 126.3, 129.9, 126.1, 122.4, 118.7 [q, $J = 277.5$ Hz (coupled with F), $-\text{CF}_3$], 84.3, 67.8, 67.4, 67.0, 66.5 [q, $J = 30.0$ Hz (coupled with F), $-\text{C}(\text{OH})\text{CF}_3$] 28.6; $^{19}\text{F NMR}$ (300 MHz, CDCl_3): δ -1.60, -1.62 (The $-\text{CF}_3$ group can have pseudo-equatorial and -axial position owing to intramolecular H-bonding); HRMS (FAB) m/z for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}_5$ ($\text{M} + \text{H}^+$) calcd 322.0902, found 322.0905.

A solution of the alcohol **10** (1.7 g, 6.2 mmol) was dissolved in methanol (20 mL) and was subjected to hydrogenolysis in the presence of Pd/C (200 mg, 10 wt%) under hydrogen atmosphere (1 atm) at room temperature for 5 h. The reaction mixture was filtered through Celite and the filtrate was concentrated to give the aniline **11** as a solid (1.7 g, 94%): $R_f = 0.35$ (EtOAc/Hexane = 1/4); mp 130.2 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.33 (d, $J = 8.0$ Hz, 1H), 7.28 (s, 1H), 7.2 (d, $J = 8.0$ Hz, 1H), 5.1 (q, $J = 7.3$ Hz, 1H), 4.3 (s, 3H), 1.6 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 164.8, 144.3, 133.2, 130.0, 126.2, 122.5, 118.7 (q, $J = 300.0$ Hz), 122.5, 129.1, 119.8, 119.1, 80.9, 72.4, 72.0, 71.5, 71.1 [q, $J = 277.5$ Hz (coupled with F), $-\text{CF}_3$], 27.7; $^{19}\text{F NMR}$ (300 MHz, CDCl_3): δ -1.14, -1.16 (The $-\text{CF}_3$ group can have pseudo-equatorial and -axial position owing to intramolecular H-bonding); HRMS (FAB) m/z for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{NO}_3$ ($\text{M} + \text{H}^+$) calcd 292.1161, found 292.1164.

***tert*-Butyl-3-(3,5-dinitrobenzamido)-4-(2,2,2-trifluoro-1-hydroxyethyl)benzoate**

(12). To a mixture of the aniline **11** (200 mg, 0.68 mmol) and K_2CO_3 (187 mg, 1.36 mmol) in dry THF (2.3 mL) was added slowly a solution of 3,5-dinitrobenzoyl chloride (189 mg, 0.82 mmol). The resulting mixture was stirred at ambient temperature for 6 h and concentrated under reduced pressure. The residue was partitioned between EtOAc (10 mL) and water (10 mL). The organic layer was separated, washed with water (2×10 mL) successively, dried over Na_2SO_4 , and concentrated under reduced pressure to give a crude product. Purification by column chromatography (EtOAc/Hexane = 3/7) afforded the amide **12**, which was recrystallized from Et_2O /Hexane as a pure white solid (240 mg, 73%). $R_f = 0.38$ (EtOAc/Hexane = 3/7); mp 186.5 °C; 1H NMR (300 MHz, $CDCl_3$): δ 10.2 (s, 1H), 9.2 (t, $J = 1.9$ Hz, 1H), 9.1 (d, $J = 2.0$ Hz, 2H), 9.0 (d, $J = 1.3$ Hz, 1H), 7.8 (dd, $J = 8.0$ and 1.5 Hz, 1H), 7.3 (d, $J = 8.0$ Hz, 1H); 5.4 – 5.3 (m, 1H), 4.6 (d, $J = 4.8$ Hz, 1H), 1.6 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ + four drops of $DMSO-d_6$): δ 165.0, 160.8, 149.1, 138.5, 137.7, 134.0, 130.4, 130.56, 126.2, 123.1, 119.4 (q, $J = 232.5$ Hz, $-CF_3$), 128.8, 127.9, 126.9, 124.4, 121.6, 82.0, 73.7, 73.3, 72.8, 72.4 (q, $J = 37.5$ Hz, $-C(OH)CF_3$), 28.5; ^{19}F NMR (300 MHz, $CDCl_3$): δ -1.46, -1.48 (The $-CF_3$ group can have pseudo-equatorial and -axial position owing to intramolecular H-bonding); HRMS (FAB) m/z for $C_{20}H_{18}F_3N_3O_8$ (M^+) calcd 485.1046, found 485.1041.

***tert*-Butyl 3-(3,5-dinitrobenzamido)-4-(2,2,2-trifluoroacetyl)benzoate (13).** To a stirred solution of the Dess-Martin periodinane (DMP, 20 g, 47.5 mmol) in dry CH_2Cl_2 (20 mL) was added the alcohol **12** (5.8 g, 11.9 mmol) dissolved in CH_2Cl_2 (20 mL), and the resulting solution was stirred at room temperature for 48 h. The reaction mixture was diluted with CH_2Cl_2 (40 mL) and poured into a 40 mL of 0.26 M solution of sodium thiosulfate in saturated aqueous sodium bicarbonate. Extractive workup with CH_2Cl_2 and purification by column chromatography (EtOAc/Hexane = 3/7) afforded the

trifluoroacetyl compound **13**, which was recrystallized from Et₂O/EtOAc to give a pure white solid (3.5 g, 60%): $R_f = 0.38$ (EtOAc/Hexane = 3/7; mp 168.1 °C; ¹H NMR (300 MHz, CDCl₃): δ 12.1 (s, 1H), 9.47 (d, $J = 1.5$ Hz, 1H), 9.3 (t, $J = 2.0$ Hz, 1H), 9.2 (d, $J = 2.0$ Hz, 2H), 8.2-8.1 (m, 1H), 7.9 (dd, $J = 8.5$ and 1.6 Hz, 1H), 1.6 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 185.4, 184.9, 184.4, 184.0 (q, $J = 37.5$ Hz, -COCF₃), 164.1, 161.9, 149.7, 143.0, 140.9, 138.2, 132.99, 132.93, 132.88, 132.82 (q, $J = 3.75$ Hz, an aromatic carbon coupled with the F), 128.1, 126.3, 124.1, 122.0, 122.8, 119.6, 115.7, 111.9 (q, $J = 292.5$ Hz, -CF₃), 118.8, 83.8, 28.7; ¹⁹F NMR (300 MHz, CDCl₃): δ 6.47; HRMS (FAB) m/z for C₂₀H₁₇F₃N₃O₈ (M + H⁺) calcd 484.0968, found 484.0969.

3-(3,5-Dinitrobenzamido)-4-(2,2,2-trifluoroacetyl)benzoic acid (14). To a solution of the *tert*-butyl ester **13** (100 mg, 0.27 mmol) in dichloromethane (1.5 mL) was added trifluoroacetic acid (1.5 mL), and the resulting solution was stirred for 3 h at room temperature. The solvent was then removed under reduced pressure, and the residue was azeotropically dried by using toluene (2 × 3 mL) to give the acid **14** as a yellowish solid (82.3 mg, 100%): $R_f = 0.11$ (EtOAc/Hexane = 3/7); mp 216.9 °C; ¹H NMR (300 MHz, CDCl₃): δ 12.1 (s, 1H), 9.66 (s, 1H), 9.3 (s, 1H), 9.2 (d, $J = 1.8$ Hz, 2H), 8.3 – 8.2 (m, 1H), 8.06 – 8.04 (m, 1H), 1.63 (s, 9H); ¹⁹F NMR (300 MHz, CDCl₃): δ 6.49; HRMS (FAB) m/z for C₁₆H₉F₃N₃O₈ (M + H⁺) calcd 428.0342, found 428.0337.

peg-DNPA 4. To a solution of the acid **14** (300 mg, 0.7 mmol) and a few drops of DMF in dichloromethane (2 mL) was added oxalyl chloride (122 μL, 2.0 equiv) dropwise at 0 °C, and the resulting solution was stirred for 9 h at room temperature. The reaction mixture was concentrated under reduced pressure to give the corresponding acid chloride. To this acid chloride dissolved in dichloromethane (4 mL) at room temperature was added a mixture of poly(ethyleneglycol) (PEG-OH, MW 1100, 616 mg,

0.56 mmol) and triethylamine (195 μ L, 1.4 mmol) in dichloromethane (10 mL) through a cannula. The resulting mixture was stirred at room temperature for 7 h. Then, Et₂O was added to the reaction mixture, the solid obtained was removed by filtration, and the filtered solution was evaporated under reduced pressure to give a crude product. Purification by flash chromatography (DMF/EtOAc = 6 mL/100 mL) afforded the desired product as a brownish solid (211 mg, 20% yield). ¹H NMR (300 MHz, CDCl₃): δ 9.30 (d, J = 2.0 Hz, 2H), 9.24 (t, J = 2.0 Hz, 1H), 8.26 (d, J = 1.4 Hz, 1H), 8.20 (dd, J = 8.3, 1.6 Hz, 1H), 87.78 (d, J = 8.0 Hz, 1H), 4.6 (t, J = 4.8 Hz, 2H), 3.88 (t, J = 5.4 Hz, 9H), 3.65 (br s, ~120H).

Reference

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- (2) Cline, G. W.; Hanna, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 3087.
- (3) Rawson, D. J.; Dack, K. N.; Dickinson, R. P.; James, K. Indole derivatives useful as endothelin receptor antagonist. PCT Patent WO 97/43260, November 20, 1997.
- (4) Zask, A.; Diane, B.; Kees, K. L.; Coghlan, R. D.; Yardley, J. Preparation of bicyclic antagonists selective for the α v β 3 integrin. PCT Patent WO 01/07036, February 1, 2001.

ITC experiments

The ITC experiments were carried out by using a MicroCal calorimeter. A typical procedure is as follows: To a solution of DNPA **1** (0.2 mM, 1.5 mL) in CH₃CN taken in the calorimetry cell, each 5 μL of the guest solution (3.0 mM in CH₃CN, except for Bu₄N⁺H₂PO₄⁻ in which case 10 mM solution was used) was injected in total 40 times at 303 K (The reference power value of the calorimeter was set between 15 and 28, depending on the anion guests). In all titrations dilution effect was corrected, which was done by carrying out separate titration experiment: Thus, the titration result obtained by adding the same guest solution into the cell in the absence of the sensor was subtracted from the raw titration data to get the final binding curve. The titration data was analyzed by a curve-fitting software implemented, which gave thermodynamic values such as the apparent binding affinity K , and the standard enthalpy change ΔH° as well as the binding stoichiometry n .

Titration Experiments



FIGURE S1. Color change of compound **2** (0.05 mM in CH₃CN) upon addition of anions (10 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).



FIGURE S2. Color change of compound **3** (0.05 mM) in MeOH–H₂O (10:1) upon addition of anions (250 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).



FIGURE S3. Color change of DNPA **1** (0.05 mM) MeOH–H₂O (10:1) upon addition of anions (50 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).

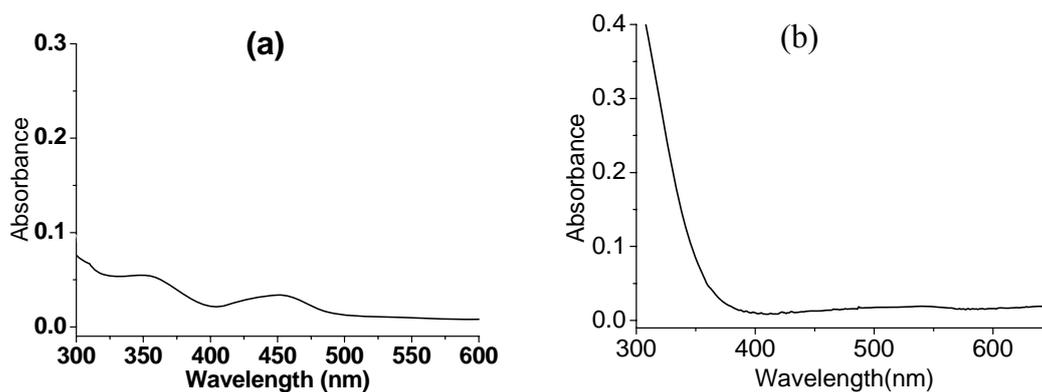


FIGURE S4. (a) UV-vis absorption change of DNPA **1** (2.0×10^{-5} M) in CH₃CN upon addition of 1.0 equiv of KOH. (b) UV-vis absorption change of DNPA **1** (5.0×10^{-5} M) upon addition of 2.0 equiv of KOH in MeOH–H₂O (10/1).



FIGURE S5. Color change of compound **3** (0.05 mM in CH₃CN) upon addition of anions (10 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).



FIGURE S6. Color change of reference compound **2** (0.05 mM) in MeOH–H₂O (10:1) upon addition of anions (250 equiv): no anion, CN⁻, F⁻, OAc⁻, and H₂PO₄⁻ (from the left).

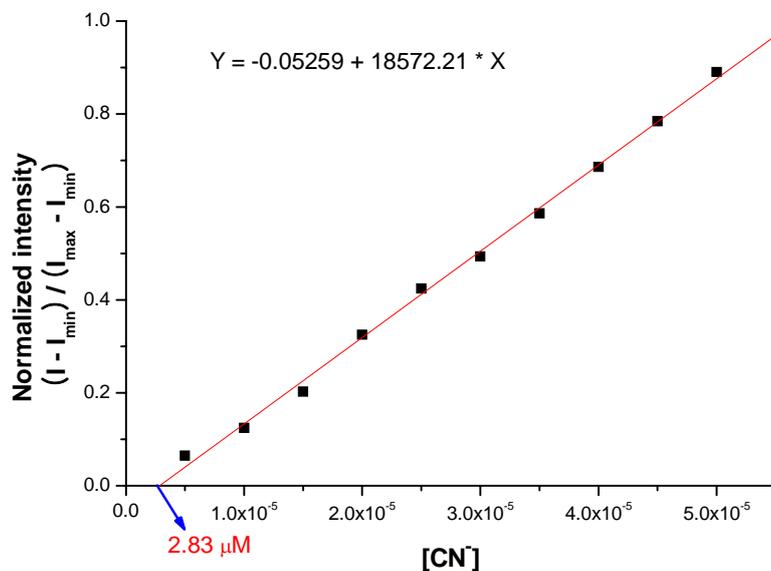


FIGURE S7. A plot of the absorbance normalized versus cyanide concentration (1.0 – 50 μM range). From this plot, an approximate detection limit for CN^- by DNPA **1** in MeOH–H₂O (10:1) is estimated to be $\sim 3 \mu\text{M}$.

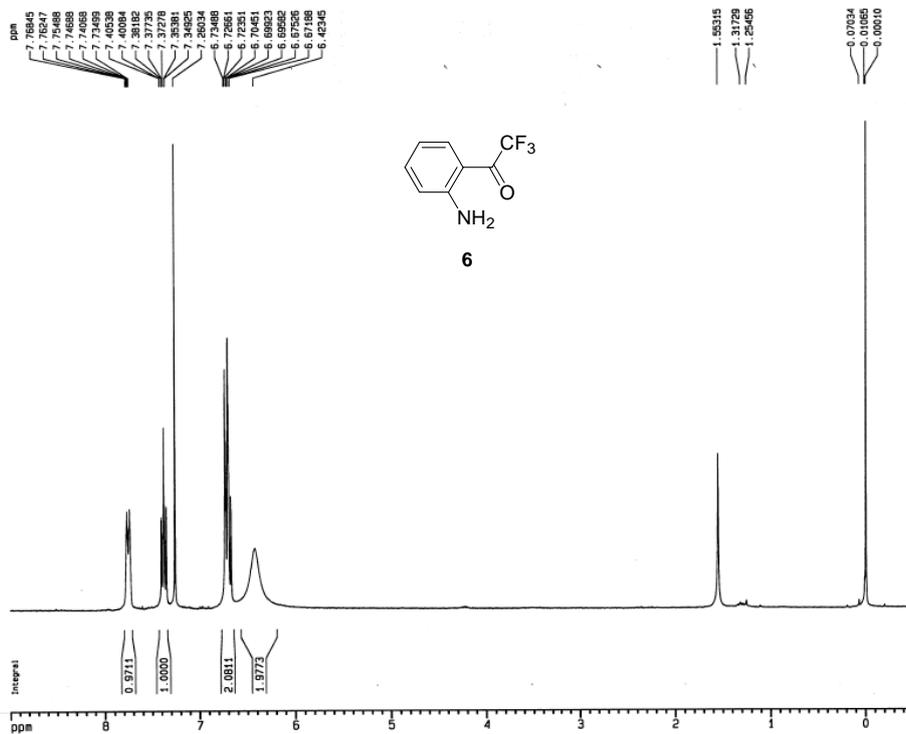


FIGURE S8. Color change of DNPA **1** (0.1 mM) in MeOH–H₂O (10:1) upon addition of anions: no anion, an equimolar mixture of F^- , OAc^- , H_2PO_4^- , HSO_4^- , SCN^- , Cl^- , and Br^- , and an equimolar mixture of F^- , OAc^- , H_2PO_4^- , HSO_4^- , SCN^- , Cl^- , Br^- , and CN^- (from the left). All the anions used as their Bu_4N^+ -salts.



FIGURE S9. Color change of DNPA **1** (0.1 mM in CH_2Cl_2) upon addition of NaCN (1.0 mM in water). The left set: no NaCN, in the absence a phase-transfer catalyst, $\text{Bu}_4\text{N}^+\text{Br}^-$, and in the presence of the phase-transfer catalyst (from the left). The right set: in the same order but with a higher concentration of DNPA **1** (1.0 mM).

TFAAniline



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