Supporting Information

Chemical Communications

A Sodium-Enabled 'Pourbaix Sensor': A Three-Input AND Logic Gate as a 'Lab-on-a-Molecule' for Na^+, pH and pE

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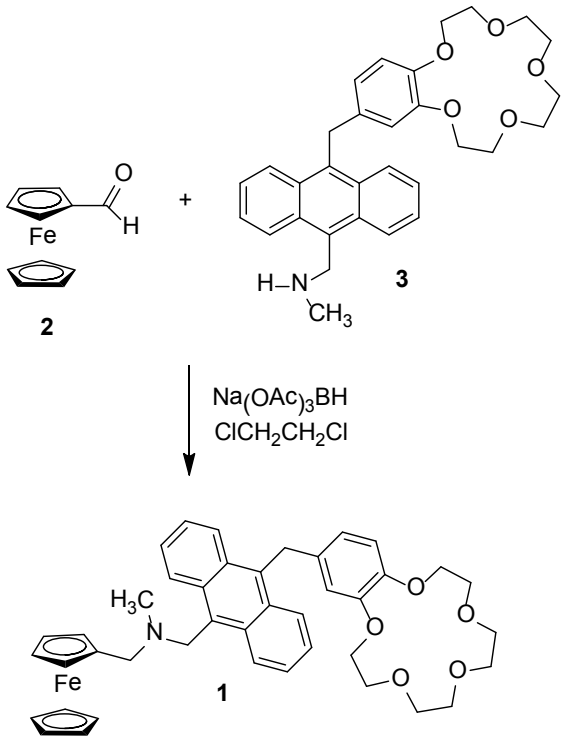
Experimental

Instrumentation

Melting points were recorded on a Stuart Griffin melting point with a Fisherbrand UK thermometer apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Bruker AM 250 NMR spectrometer equipped with a $^{1}H/^{13}C$ dual probe at room temperature. ^{1}H NMR spectra were recorded in $CDCl_3$ at 250.1 MHz. Chemical shifts are reported in ppm versus tetramethylsilane at $\delta = 0.00$ ppm. Infra-red spectra were recorded on a Shimadzu IR-affinity 1 FT-IR spectrometer calibrated against polystyrene at 1602 cm^{-1} as a thin film between NaCl plates prepared from $CHCl_3$. UV-visible absorption spectra were recorded on a Jasco V-650 spectrophotometer interfaced to a desktop computer using a medium response with a bandwidth of 2 nm and a scan speed of 200 nm min^{-1}. All spectra were corrected for the solvent by scanning the solvent blank prior to the experiments. Fluorimetric studies were performed on a Jasco FP-8300 spectrophotometer in emission mode with a bandwidth of 2.5 nm for both slits and a scan speed of 200 nm min^{-1}. Electrospray time-of-flight (ES-TOF) spectra were performed on a Waters LC Premier instrument.

Synthesis of compound 1: 220 mg (1.0 mmol) of ferrocenecarboxaldehyde **2** was reacted with 350 mg (0.70 mmol) of 4-(10-aminomethylanthracen-9-ylmethyl)benzo-15-crown-5-ether **3** by reduction amination.[S1] The reagents **2** and **3** were dissolved in 25 mL of 1,2-dichloroethane and to the solution was added 610 mg (2.9 mmol) of sodium triacetoxyborohydride and 3 drops of glacial acetic acid. The solution was stirred in the dark at room temperature for 72 hours. The product was recovered by solvent extraction with three portions of 10 mL of dichloromethane, washed twice with 15 mL of saturated $NaHCO_3$, dried over anhydrous magnesium sulfate, filtered and evaporated to yield an orange gum. The crude product was purified by column chromatography on silica gel using a gradient mixture of 98:2 CH_2Cl_2/MeOH to yield an orange crystalline solid in 24% yield.

Compound **1**: m.p. 172-175 ºC; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.17 (s, 3H, -NCH_3), 3.61 (s, 2H, CH_2 spacer$_1$), 3.45-3.95 (m, 16H, crown ether), 4.11 (s, 5H, C_5H_5), 4.03-4.29 (m, 4H, C_5H_4), 4.61 (s, 2H, CH_2 spacer$_2$), 4.94 (s, 2H, CH_2 spacer$_3$), 6.50-6.70 (m, 3H, phenyl crown), 7.37-7.47 (m, 2H, anthracene), 8.15-8.29 (m, 2H, anthracene), 8.37-8.40 anthracene); IR(NaCl/cm^{-1}): 3086, 3007, 2928, 2872, 1660, 1605, 1589, 1514, 1454, 1425, 1358, 1250, 1136, 1105, 1057, 1001, 937, 820, 754, 602; UV-vis (methanol) λ_{max}/nm (ε/cm^{-1} mol L^{-1}): 397 (9700), 376 (9700), 357 (6000); MS (ES-TOF) m/z (%): 723 (M+H+Na, 21), 722 (M+Na, 33), 701 (M+H, 38), 700 (M+, 100), 639 (15), 540 (14), 525 (15), 524 (48), 471 (21), 427 (12), 369 (13), 313 (21), 261 (32); HRMS Calcd. $C_{42}H_{46}N_1O_5{}^{56}Fe$ (M^+) 700.2725, found 700.2747.



Scheme S1: The synthesis of molecule **1** by reductive animation.

Synthesis of 3: 600 mg (1.1 mmol) of 4-(10-bromomethylanthracen-9-ylmethyl)benzo-15-crown-5-ether[S2] was dissolved in 15 mL of THF and 100 mL of toluene. The solution was added dropwise over 2 hours to a stirring solution of 15 mL of a 2.0 M methylamine solution in THF. The reaction mixture was left to stir for 5 hours at 40 ºC and monitored

by TLC in methanol. The solution was evaporated to yield a yellow-brown solid, which was used for synthesis without further purification.

Compound **3**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38, (s, 1H, -NH) 2.48 (s, 3H, -NCH_3), 3.53-4.10 (m, 16H, benzocrown), 4.83 (s, 2H, CH_2 spacer amine-anthracene), 5.15 (s, 2H CH_2 spacer anthracene-benzocrown), 6.47-6.55 (m, 1H, phenyl), 6.59-6.69 (m, 2H, phenyl), 7.42-7.53 (m, 2H, anthracene), 7.57-7.68 (m, 2H, anthracene), 8.21 (d, 2H, J = 8.7 Hz, anthracene); 8.39 (d, 2H, J = 8.7 Hz, anthracene); IR(NaCl/cm^{-1}): 3475 (br), 3054, 2921, 2866, 1669, 1588, 1511, 1447, 1425, 1353, 1251, 1138, 1057, 980, 602; MS (ESI) m/z (%): 525 (M+H+Na, 29), 502 (M+H, 100), 472 (12), 263 (28), 247 (100).

References

(S1) Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem*. **1996**, *61*, 3849-3862.

(S2) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *J. Am. Chem. Soc.* **1997**, *119,* 7891-7892.