Electronic Supplementary Information

For

Selective recognition and electrochemical sensing of dicarboxylates with a ferrocene-based bis(*o*-trifluoroacetylcarboxanilide) receptor

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Synthesis of ditopic receptor 1: To a solution of *o*-trifluoroacethylaniline (98 mg, 0.52 mmol) and triethylamine (0.3 mL) in anhydrous THF (3 mL) was added 1,1'-dichlorocarbonylferrocene (80 mg, 0.26 mmol) dissolved in anhydrous THF (3 mL). The reaction mixture was stirred overnight at room temperature. THF was removed on a rotary evaporator and the residue was dissolved in chloroform and then washed with water. The aqueous layer was extracted with chloroform, and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The ditopic receptor **1** was isolated as a reddish brown solid (110 mg, 30%) by column chromatography on silica gel ($CHCl_3$: EtOAc = 10 : 1; R_f = 0.5). ^{1}H NMR (300 MHz, CD_3CN): δ 11.03 (s, NH, 2H), 8.36 (d, J =8.6 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.7 Hz, 2H), 5.06 (t, J = 1.9 Hz, Cp-H, 4H), 4.64 (t, J = 1.9 Hz, Cp-H, 4H); ^{19}F NMR (282 MHz, CD_3CN) δ 5.52; Mass (MALDI) calc. for $C_{28}H_{18}F_6FeN_2O_4$ 616.0520, found (*m/z*) 616.0565.

Synthesis of receptor 2: To solution of ferrocenecarboxylic acid (500 mg, 2.17 mmol) dissolved in anhydrous dichloromethane (30 mL) at room temperature was added oxalyl chloride (1.5 mL) dropwise, and the resulting mixture was stirred overnight at room temperature, and then it was refluxed for 2 h. The solvent was evaporated and the residue was dried in vacuum to give a crude chlorocarbonylferrocene, which was dissolved in anhydrous THF (10 mL) transferred to a solution of *o*-trifluoroacethylaniline (400 mg, 2.12 mmol) and triethylamine (1.3 mL) dissolved in anhydrous THF (10 mL). The reaction mixture was stirred at room temperature overnight. THF was evaporated and the residue was dissolved in chloroform and washed with water. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo.* The product **2** was isolated as an orange solid (387 mg, 52%) by column chromatography on silica gel ($CHCl_3$:EtOAc=20:1; R_f = 0.5). ^{1}H NMR (300 MHz, CD_3CN): δ 10.95 (s, NH, 1H), 8.69 (d, J =8.1 Hz, 1H), 7.99 (d, J = 6.1 Hz, 1H), 7.77 (t, J = 8.5 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 4.87 (t, J = 1.9 Hz, Cp-H, 2H), 4.54 (t, J = 1.9

Hz, Cp-H, 2H), 4.28 (s, Cp-H, 5H); ^{19}F NMR (282 MHz, $CDCl_3$) δ 5.33; Mass (MALDI) calc. for $C_{19}H_{14}F_3FeNO_2$ 401.0326, found (*m/z*) 400.0042 (M-1).

^{1}H NMR studies:

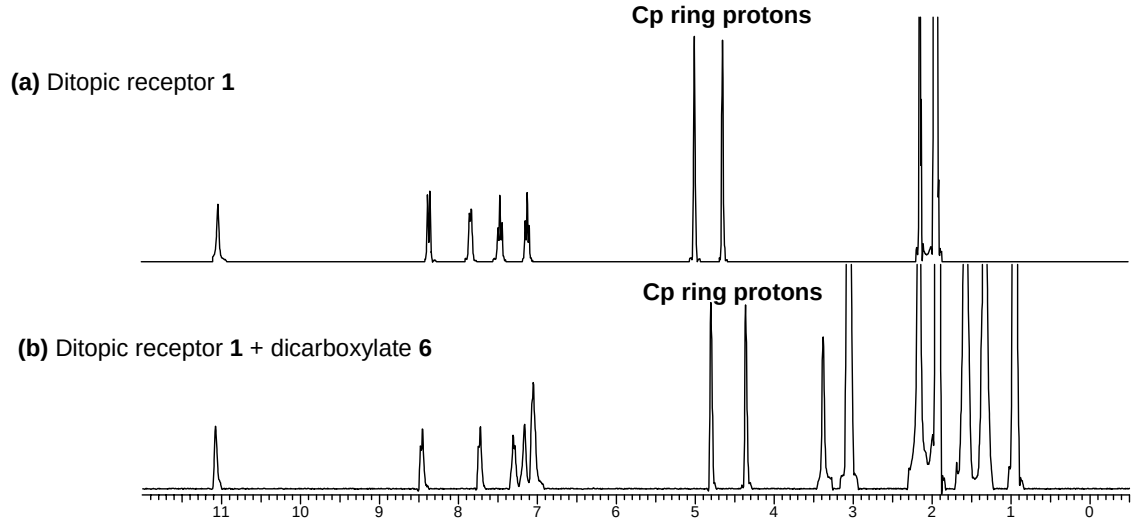


Fig. S1 ^{1}H NMR spectra of (a) the ditopic receptor **1** and (b) the ditopic receptor **1** plus one equivalent of the dicarboxylate **6,** in CD_3CN.

Job plots:

^{1}H NMR Job plots in CD_3CN, determined by integrating the ratio of the Cp ring protons of the receptor: [complex] = [host] x (integration ratio of complex) / (integration ratio of host + integration ratio of complex).

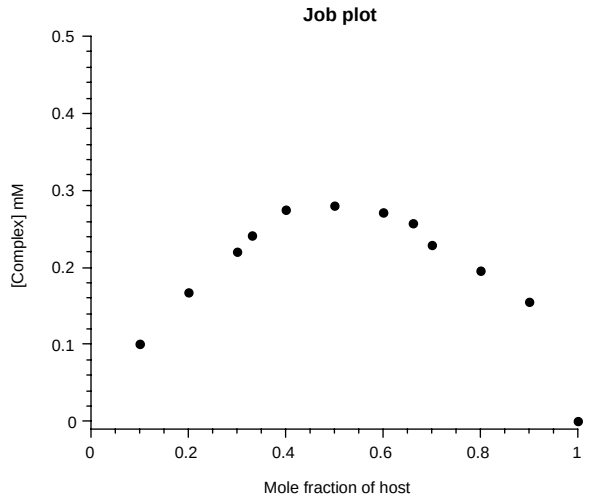


Fig. S2 Job plot of the receptor **2** with the acetate **3** in CD_3CN at 298 K.

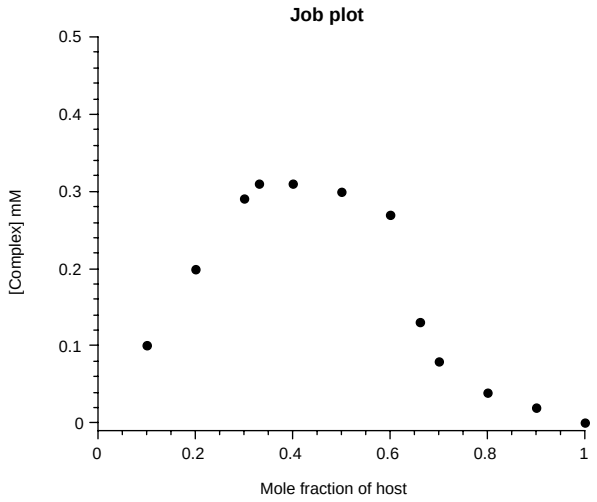


Fig. S3 Job plot of the ditopic receptor **1** with the acetate **3** in CD_3CN at 298 K.

The isothermal titration calorimetry (ITC) analysis:

The binding affinity and thermodynamic data were determined by ITC, using an isothermal titration calorimeter (MicroCal, Inc.).

A typical procedure:

To a solution of host in the calorimetry cell, 5 μL of guest solution was injected 40 times at 303 K. In all titrations, dilution effects were corrected, which were done by carrying out a separate titration experiment. Thus, the titration result obtained by adding the same guest solution into pure CH_3CN at 303 K was subtracted from the raw titration data to produce the final binding curve. The titration data was analyzed by a curve-fitting software implemented, which gave a number of sites, apparent binding affinity K, and the standard enthalpy change ΔH^o.

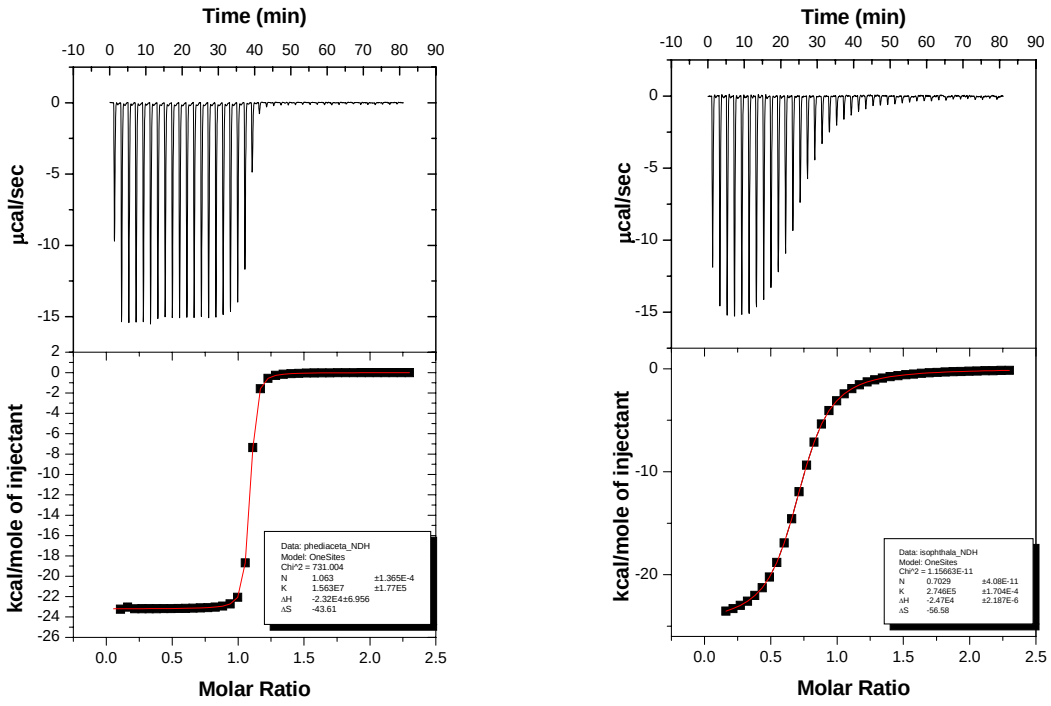


Fig. S4 ITC data of the ditopic receptor **1** (0.16 mM) with the dicarboxylate **6** (2.4 mM) (left side), with the dicarboxylate **5** (2.4 mM) (right side) in CH_3CN at 303 K.

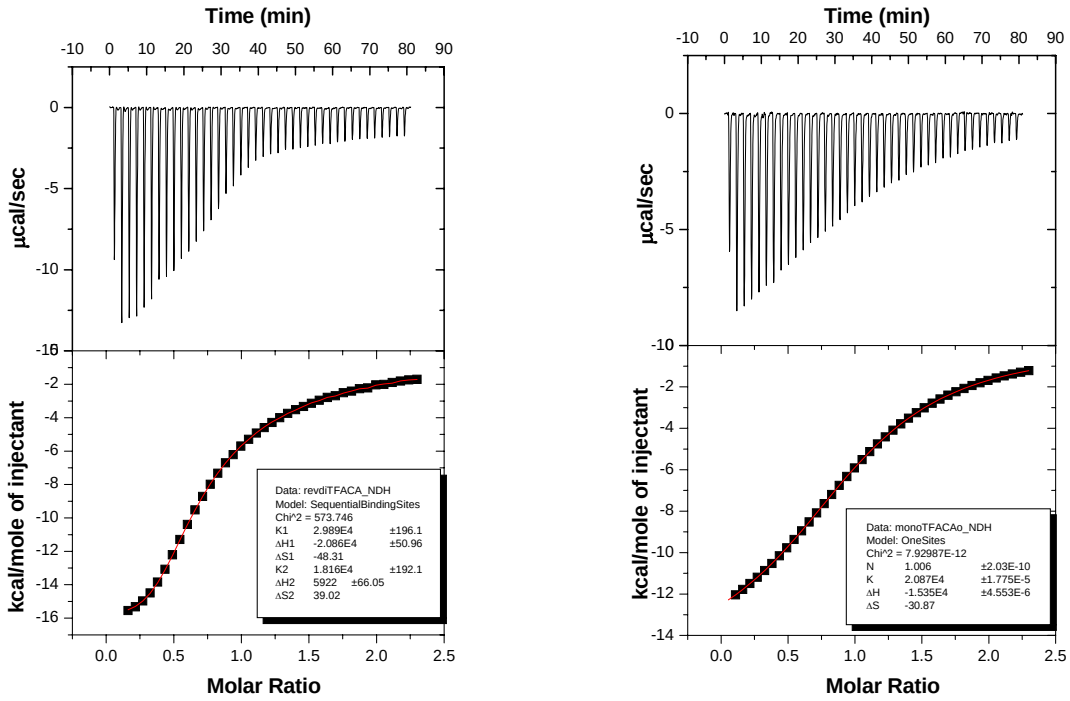
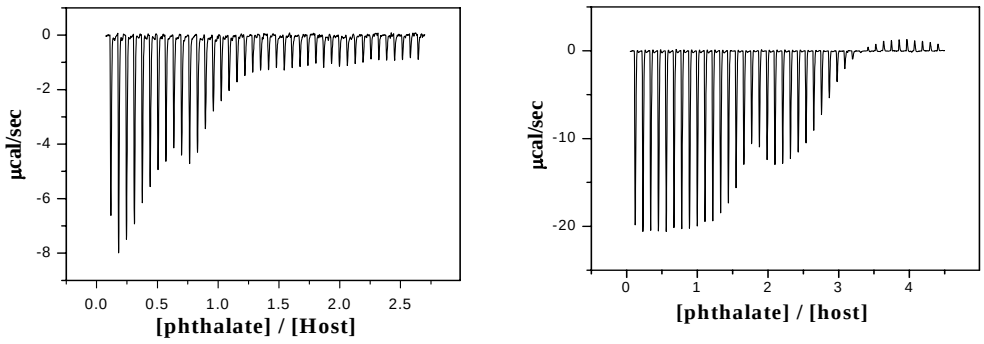


Fig. S5 ITC data of the ditopic receptor **1** (3.0 mM) with the acetate **3** (0.2 mM)-inverse titration (left side), and ITC data of the ditopic receptor **2** (0.2 mM) with the acetate **3** (3.0mM) (right side) in CH_3CN at 303 K.



Inverse titration Normal titration

Fig. S6 ITC data of the ditopic receptor **1** (3.0 mM) with the dicarboxylate **4** (0.2 mM) (left side), and the ditopic receptor **1** (0.16 mM) with the dicarboxylate **4** (4.8 mM) (right side) in CH_3CN at 303 K.

Electrochemistry:

Cyclic voltammograms were obtained at 298K using a three-electrode cell connected to a potentiostat. The cell contained a nitrogen-purged acetonitrile solution of receptor (1.0 mM) and $[NBu_4][ClO_4]$ as supporting electrolyte (0.1 M). Ag/AgCl (3M NaCl) was used as the reference electrode, with glassy carbon as the working electrode, and Pt as the counter electrode. The scan rate was 250 mVs^{-1}. Ferrocene (*ca.* 1 mM) was added as an internal reference in each case (Fc^+/Fc: $E^{0'}$ = 0.51 V *vs* Ag/AgCl).

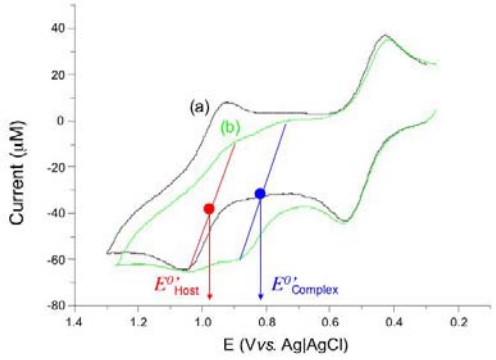


Fig. S7 Cyclic voltammograms of the ditopic receptor **1** (1.0 mM in CH_3CN): (a) in the absence of the dicarboxylate **6** and (b) in the presence of 0.7 equivalents of the dicarboxylate **6**. $E^{0'}_{Host}$ = 984 mV, $E^{0'}_{Complex}$ = 831 mV, $\Delta E^{0'} = E^{0'}_{Complex} - E^{0'}_{Host}$ = -153 mV.

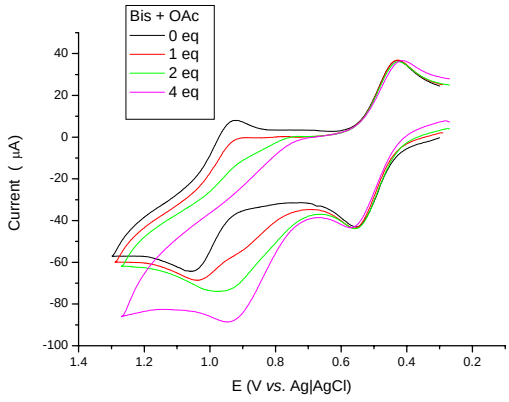


Fig. S8 Cyclic voltammograms of the ditopic receptor **1** (1.0 mM in CH_3CN) with the acetate **3**.

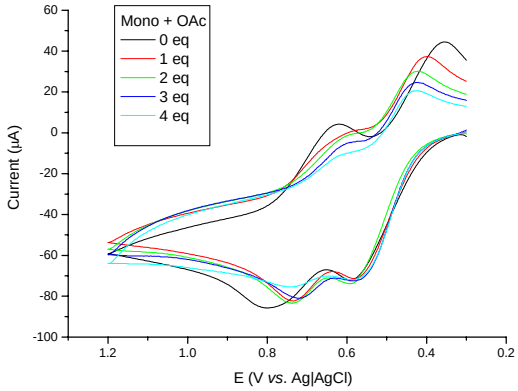


Fig. S9 Cyclic voltammograms of the receptor **2** (1.0 mM in CH_3CN) with the acetate **3**.