Supplementary Information

Selective electrochemical sensing of acidic organic molecules via a novel guest-to-host proton transfer reaction

H. Miyaji, G. Gasser, S. J. Green, Y. Molard, S. M. Strawbridge, J. H. R. Tucker

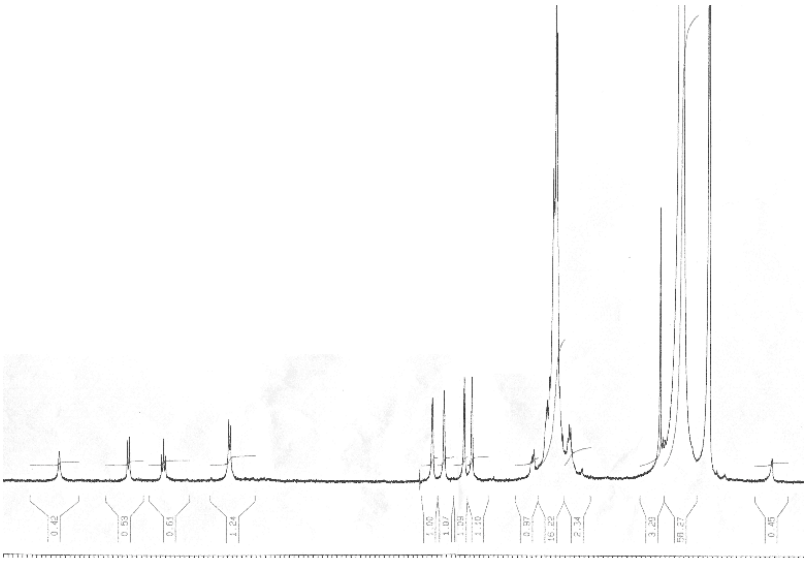
Synthesis of the perchlorate salt of L-Phe:
L-Phe (Aldrich, 500 mg, 3 mmol) was suspended in MeOH (10 mL). Perchloric acid solution (68%, 448 mg, 3 mmol) was then added dropwise to the stirred suspension, causing the amino acid to dissolve. The solvent was removed and benzene (30 mL) added which in turn was removed to give the product as a white solid in quantitative yield. The salt was recrystallised from $CH_3CN/CHCl_3$ and dried *in-vacuo*.

^{1}H NMR (CD_3CN, 300 MHz): δ 7.39 (m, Ar-H, 5H), 7.06 (s, NH_3, 3H), 4.28 (m, CH, 1H), 3.34 (dd, HCH, 1H), 3.17 (dd, HCH, 1H).

Synthesis of receptor 2:
1-chlorocarbonyl-1'-[{(6-methyl-2-pyridyl)amino}carbonyl]ferrocene[6] (50 mg, 0.13 mmol) and 2-(aminomethyl)-18-crown-6 (Aldrich, 38 mg, 0.13 mmol) were mixed together in dry THF (10 mL) containing triethylamine (13 mg, 0.13 mmol) and DMAP (1 mg). The solution was stirred under N_2 for 2 hours, after which time the solvent was removed and the resulting mixture subjected to column chromatography on silica (eluent: $CHCl_3/MeOH/NH_3(aq)$ = 88/10/2). The largest fraction was collected and purified further by column chromatography on neutral alumina. The pure product **2** (16 mg, 19 % yield) was isolated as an orange viscous oil using the eluent mixture $CH_3CN/CHCl_3/MeOH$ = 4/1/0.5.

^{1}H NMR (CD_3CN, 400 MHz): δ 8.76 (s, NH, 1H), 8.04 (d, py-H, 1H), 7.67 (tr, py-H, 1H), 6.98 (m, py-H and NH, 2H), 4.85 (s, Cp-H, 2H), 4.72 (s, Cp-H, 2H), 4.51 (s, Cp-H, 2H), 4.43 (s, Cp-H, 2H), 3,78 (m, OCH, 1H), 3.45-3.75 (m, OCH_2, 22H), 3.41 (m, NCH_2, 2H), 2.46 (s, CH_3, 3H); ^{13}C-{^{1}H} NMR (CD_3CN, 100 MHz): δ 170.00 (C=O), 169.25 (C=O), 157.84 (py-C), 152.20 (py-C), 139.31 (py-CH), 119.62 (py-CH), 111.80 (py-CH), 79.27, 78.45, 78.22, 73.18, 72.52, 72.43, 71.5-70.5 (11 carbon signals), 69.20, 39.92 (NCH_2), 24.20 (CH_3); HRMS (ES+): calc. for $C_{31}H_{42}N_3O_8Fe$ m/z 640.2321; found 640.2321.

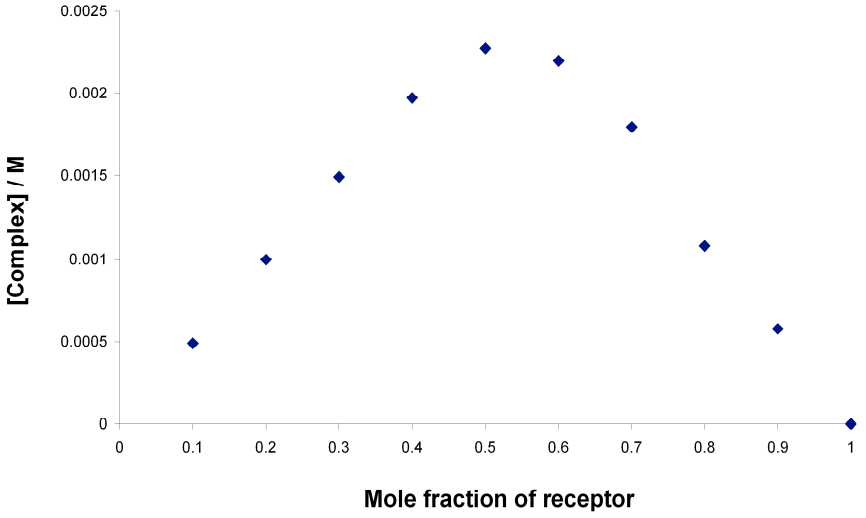
^{1}H NMR spectrum of **2** in CD_3CN:



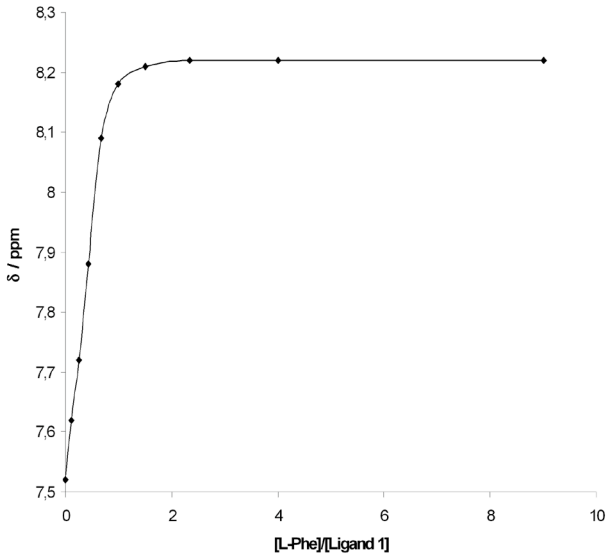
Electrochemistry: Cyclic voltammograms were obtained at 293 K using a three-electrode cell connected to a BAS workstation. The cell contained a nitrogen-purged acetonitrile solution of receptor (0.5 mM) and $[NBu_4][ClO_4]$ as supporting electrolyte (0.1 M). Ag/AgCl (3M NaCl) was used as the reference electrode, with Pt wire as both counter and working electrodes. The scan rate was 250 mVs^{-1}.

Binding studies:

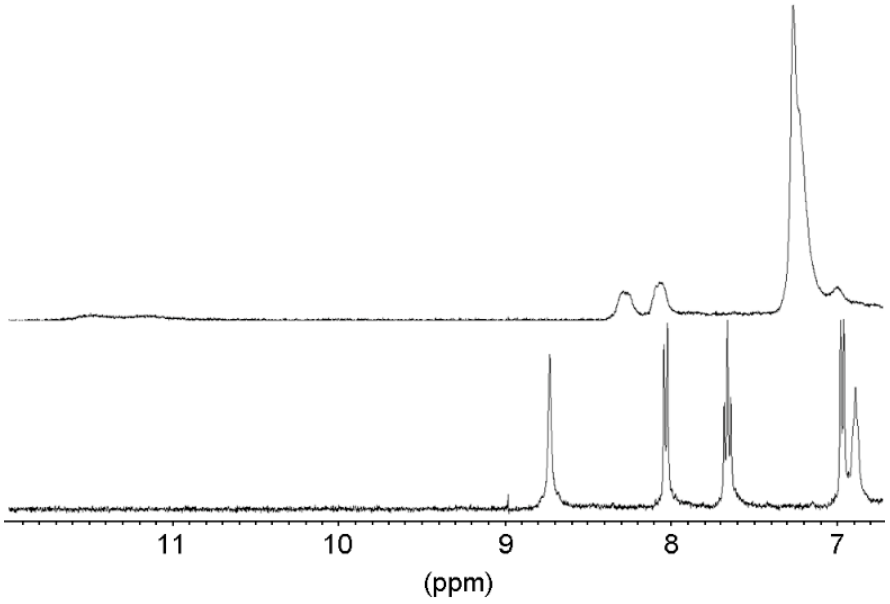
^{1}H NMR Job plot of complex concentration (taken from the δ value of the amide proton of receptor **1** in CD_3CN) against mole fraction of receptor (guest: perchlorate salt of **L-Phe**). The maximum at 0.5 indicates a complex stoichiometry of 1/1:



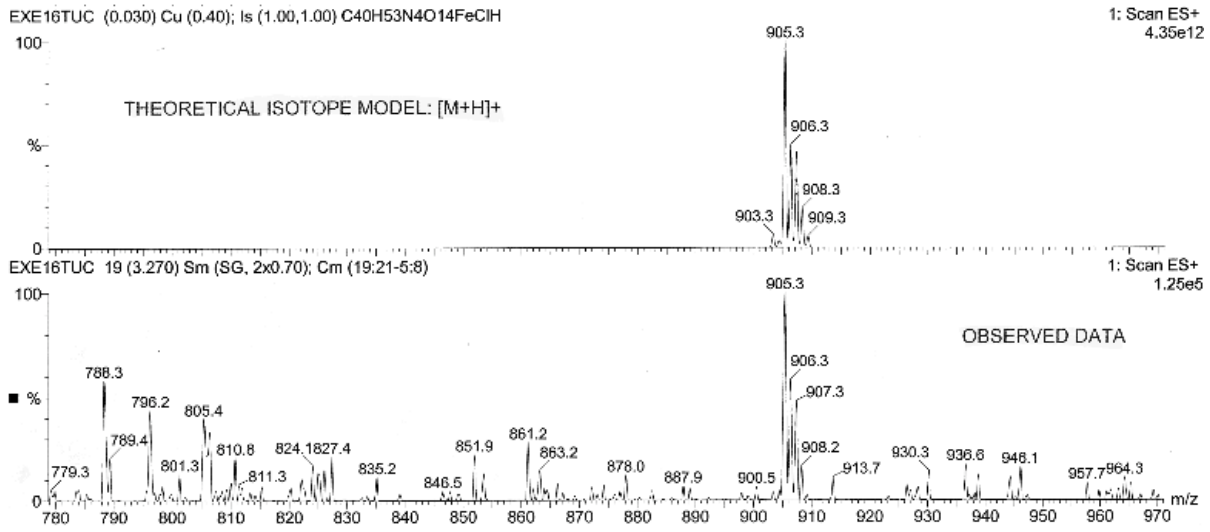
^{1}H NMR titration of the downfield shift of the signal for the H_b proton of receptor **1** *vs*. molar equivalents of **L-Phe** salt:



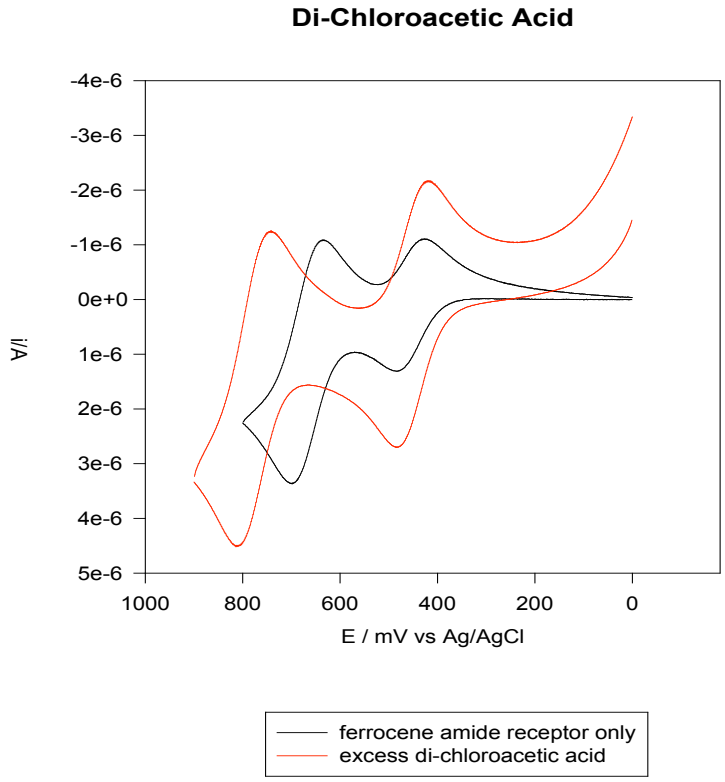
NMR spectra (aromatic and amide NH region) of receptor **2** in CD_3CN (10 mM) in the absence (bottom) and presence (top) of one molar equivalent of the perchlorate salt of **L-Phe**:



ES+ mass spectrum of the complex $[M+H]^+$, where M = **2**:**L-Phe**.ClO_4:



Cyclic voltammograms of ferrocene receptor **1** in the absence and in the presence of an excess amount (*ca*. 5 equivalents) of dichloroacetic acid (ferrocene used as internal reference):



NMR spectra in CD_3CN of (a) ferrocene receptor **1**, (b) **1** plus one molar equivalent of chloroacetic acid, (c) **1** plus one molar equivalent of dichloroacetic acid.