Supplementary Material for Chemical Society Reviews

Supporting Information

MS: "An enantioselective imprinted receptor for…." by Manesiotis et al.

Experimental Section

^{1}H NMR titrations and estimation of association constant for (1) and TBABz

All ^{1}H NMR titrations were performed in DMSO-d_6. Association constants (K_{SL}) for the interactions between hosts and guests were determined by titrating an increasing amount of guest (tetrabutylammonium benzoate, TBABz) into a constant amount of functional monomer (1). The concentration of functional monomer was 1mM and the amounts of added guest were 0, 0.5, 1, 2, 3, 4, 5, 7.5 and 10 equivalents, respectively. The complexation induced shifts (Δ□) of the host urea protons were followed and titration curves were then constructed of Δ□ versus guest concentration. The raw titration data were fitted to a 1:1 binding isotherm by nonlinear regression using Microcal^{TM} Origin 5.0 from which the association constants could be calculated.

Polymer preparation

An imprinted polymer using monomer (1) (P1) was prepared in the following manner. The template molecule, *Z*-D-Glu-OH (1mmol), if not otherwise stated, functional monomer (1) (2mmol) and EDMA (20mmol) were dissolved in DMF (5.6mL). To the solution were added TEA (2mmol) and the initiator ABDV (1%w/w of total monomers). The solution was transferred to a glass ampoule, cooled to 0^{o}C and purged with a flow of dry nitrogen for 10 minutes. The tubes were then flame-sealed while still under cooling and the polymerization initiated by placing the tubes in a thermostatted water bath pre-set at 40^{o}C. After 24h the tubes were broken and the polymers lightly crushed. Removal of the template molecule from the polymers was achieved by extraction with methanol in a Soxhlet apparatus for 24 hours. Thereafter, the polymers were crushed and sieved to obtain particles in the size range 25-50□m. A non-imprinted polymer (P_N1) was prepared in the same way as described above, but with the omission of the template molecule and TEA from the pre-polymerisation solution.

Elemental analyses of extracted polymers: P1/P_N1: Calculated: C 60.97; H 6.81; N 1.86. Found: P1: C 60.0; H 7.0; N 1.7. P_N1: C 59.9; H 7.1; N 1.6

HPLC Evaluation

The 25-50μm particle size fraction was repeatedly sedimented (80/20: methanol /water) to remove fine particles and then slurry-packed into HPLC columns (125mm x 5mm, i.d.) using the same solvent mixture as pushing solvent. Subsequent analyses of the polymers were performed using an Agilent HP1050 system equipped with a diode array-UV detector and a workstation. Analyte detection was performed at 260nm.

Binding isotherms

Imprinted or non-imprinted polymer (10mg of 25-50μm particles) were weighed into 2mL HPLC vials. Solutions (1mL) of Z-D-Glu-OH and Z-L-Glu-OH in a mixture of acetonitrile (92%) – water (7%) – TEA (1%) made up to the following concentrations: 0, 0.1, 0.2, 0.5, 0.75, 1, 2, 5, 10mM, were then added. After 24h incubation, the concentration of the non-bound analyte in each vial was quantified by HPLC, using a C-18 reversed phase column (Phenomenex Luna (5μm), 150mm x 4.6mm) and calibration using the method of external standards. The mobile phase consisted of methanol (40%) – H_2O (59.4%) – Trifluoroacetic acid (0.6%). Each experiment was performed in duplicate.

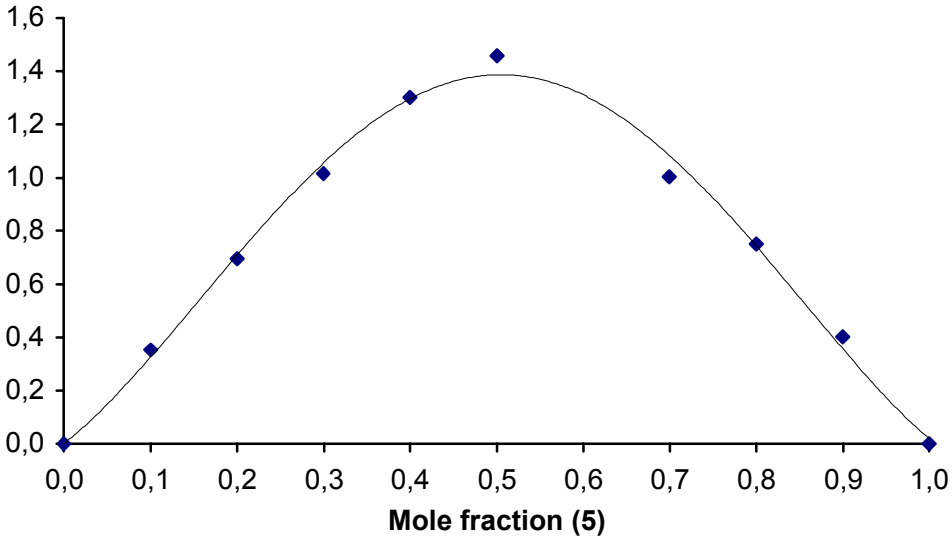

Figure 1. Job Plot for the 1,3-diarylsubstituted urea monomer (1) with TBA benzoate in DMSO-d_6. Mother solution concentrations of both host and guest were 2mM.

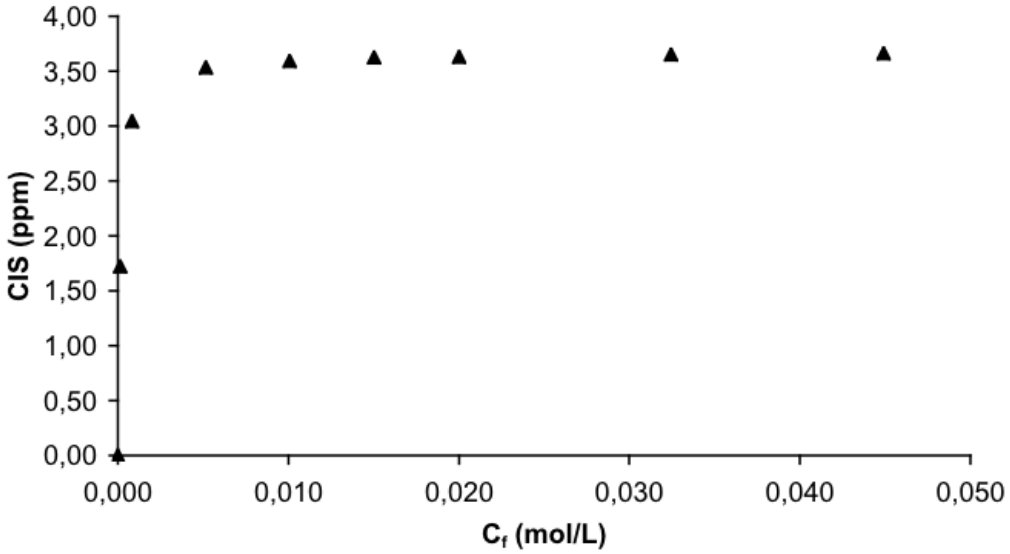

Figure 2. ^{1}H NMR titration curves reflecting the complexation of TBA benzoate by urea monomer (1) in DMSO-d_6 ([1] = 5mM, [TBA benzoate] = 0 - 50mM). C_f=concentration of free guest. CIS= complexation induced shift of one of the urea protons.