Electronic supplementary information

Cooperative intramolecular interaction of diazacrown ether bearing β-diketone fragments on an ionic liquid extraction system

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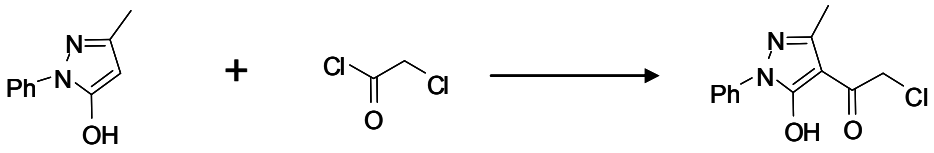
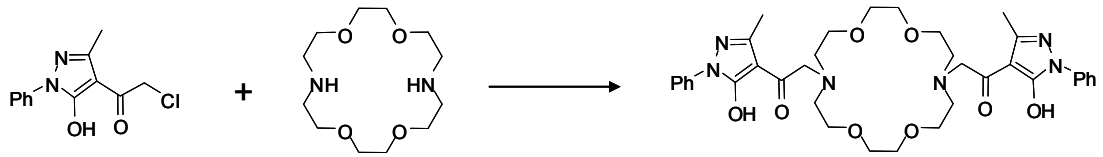
Synthesis of H2βDA18C6



1-phenyl-3-methyl- 5-pyrazolone chloroacetyl chloride 1

Under a nitrogen atmosphere, 1-phenyl-3-methyl-5-pyrazolone (8.71 g, 0.05 mol) was added to a three-neck flask and was dissolved in 1,4-dioxane (80 mL) by heating to 70 °C. $Ca(OH)_2$ (7.72 g, 0.1 mol) was added to the solution and subsequently chloroacetyl chloride (11.65 g, 0.1 mol) was delivered by the slow addition of drops of this reagent to the solution. The mixture was heated to reflux at 110 °C for 1 h. After cooling, the resulting brown solution was poured into 2 mol/L HCl (100 mL). The organic materials were extracted with dichloromethane and were washed three-times with fresh 2 mol/L HCl. After the organic layer was dried with anhydrous sodium sulfate, the solvent was removed in vacuo. The crude residue was recrystallized from methanol to obtain chloride **1**.



1 diazacrown H2βDA18C6

Under a nitrogen atmosphere, a solution of diazacrown (0.52 g, 1.98 mmol), chloride **1** (1.5 g, 5.98 mmol) and triethylamine (0.81g, 8 mmol) in ethanol (10 mL) was refluxed at 92 °C for 1 day. After cooling, the resulting red-wine colored solution was poured into distilled water (50 mL) and extracted with chloroform. The organic layer was washed three-times with distilled water and dried with anhydrous sodium sulfate.

After evaporation of the solvent in vacuo, the crude residue was recrystallized from acetone and methanol to obtain H2βDA18C6; white powder 1.0 g (73.1 %); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ 2.44 (s, 6H, Py-C*H*$_3$), 3.29 (br m, 8H, N-C*H*$_2$-CH$_2$-O), 3.57 (s, 8H, O-C*H*$_2$-C*H*$_2$-O), 3.72 (br m, 8H, N-CH$_2$-C*H*$_2$-O), 4.22 (s, 4H, N-C*H*$_2$-C=O), 7.10 (t, 2H, *p-H* of Ph), 7.38 (t, 4H, *m-H* of Ph) and 7.87 ppm (d, 4H, *o-H* of Ph); MS, *m/e* (% relative intensity) 691.6 (MH^+, 100). Anal. Calc. for $C_{36}H_{46}O_8N_6$: C, 62.59; H, 6.71; N, 12.17. Found: C, 62.52; H, 6.72; N, 12.24.

Slope analysis

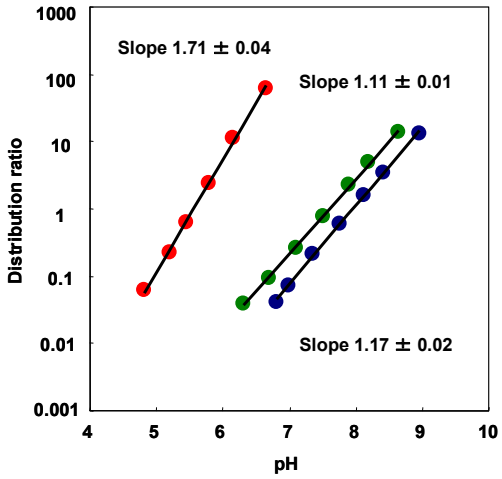


Fig. S1 Slope analysis of Sr^{2+} extraction as a function of the aqueous phase pH in the [C_2mim][Tf_2N] system. Aqueous phase: [Sr^{2+}] = 0.01 mM. Extracting phase: [HPMBP] = 2 mM, [DBzDA18C6] = 1 mM and [H2βDA18C6] = 1 mM. The DBzDA18C6 system (blue symbols), the HPMBP + DBzDA18C6 system (green symbols) and the H2βDA18C6 system (red symbols).