Supplementary Material (ESI) for Chemical Communications

Double Loading of $ZnCl_2$ by Polytopic Ligands which Co-extract Zn^{2+} and Tetrachloridozincate

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Supplementary Information

All reagents were used as received, unless otherwise specified.

Synthetic details for L^1-L^3

4,4'-Di-*tert*-butyl-6,6'-bis(dihexylaminomethyl)-2,2'-(ethylenedinitrilodimethylidyne)diphenol (L^1) To a stirred solution of 5-*tert*-Butyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde[1] (6.44 g, 17 mmol) in ethanol (50 ml) was added a solution of ethylenediamine (0.54 g, 8.9 mmol) in acetonitrile (25 ml). The mixture was stirred overnight and the solvents were removed *in vacuo*. The product was dissolved in dichloromethane (50 ml) and extracted with water (3 × 25 ml). The organic fraction was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a viscous yellow oil (6.54 g, 99%). (Found: C, 77.25; H, 11.5; N, 7.4. Calc. for $C_{50}H_{86}N_4O_2$: C, 77.5; H, 11.2; N, 7.2%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 0.87 (12H, t, $N(CH_2)_5CH_3$), 1.27 (24H, m, $NCH_2CH_2(CH_2)_3CH_3$), 1.30 (18H, s, $C(CH_3)_3$), 1.50 (8H, m, $NCH_2CH_2(CH_2)_3CH_3$), 2.46 (8H, t, $NCH_2(CH_2)_4CH_3$), 3.65 (4H, s, $ArCH_2N$), 3.92 (4H, s, $N(CH_2)_2N$), 7.19 (2H, d, Ar-*H*), 7.51 (2H, d, Ar-*H*), 8.43 (2H, s, N=C*H*); ESIMS *m/z* 776 (MH^+).

4,4'-Di-*tert*-butyl-2,2'-(ethylenedinitrilodimethylidyne)diphenol (L^2) A solution of ethylenediamine (0.54 g, 8.9 mmol) in acetonitrile (25 ml) was added to a stirred solution of 5-*tert*-butyl-2-hydroxybenzaldehyde[2] (3.09 g, 17 mmol) in ethanol (50 ml). The mixture was stirred overnight and the solvents were removed *in vacuo*. The product was dissolved in dichloromethane (50 ml) and extracted with water (3 × 25 ml). The organic fraction was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a viscous yellow solid which was recrystallized from ethanol to afford the product as a light yellow solid (3.12 g, 96%). (Found: C, 75.9; H, 8.45; N, 7.35. Calc. for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.5; N, 7.4%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.29 (18H, s, $C(CH_3)_3$), 3.94 (4H, s, $N(CH_2)_2N$), 6.90 (2H, d, Ar-*H*), 7.21 (2H, d, Ar-*H*), 7.35 (2H, dd, Ar-*H*), 8.37 (2H, s, N=C*H*); ESIMS *m/z* 381 (MH^+); mp 161-162 °C.

1-*tert*-Butyl-4-(dihexylamino)methylbenzene (L^3) An excess of dihexylamine (30.0 g, 162 mmol) was added to a solution of 4-*tert*-butylbenzylbromide (11.9 g, 52.5 mmol) in dichloromethane (150 ml) at 0 °C. The mixture was stirred overnight at room temperature and the solvents then removed *in vacuo*. The product was washed with 4 M NaOH aqueous solution (150 ml), extracted with diethyl ether (2 × 50 ml), dried over $MgSO_4$, concentrated *in vacuo* and purified by silica-60 wet flash column chromatography (eluting with 10% methanol in dichloromethane) to afford a brown oil (10.8 g, 62%). (Found: C, 83.2; H, 12.2; N, 4.5. Calc. for $C_{23}H_{41}N$: C, 83.3; H, 12.3; N, 4.2%);δ_H (250 MHz; $CDCl_3$; Me_4Si) 0.89 (6H, t, $N(CH_2)_5CH_3$), 1.28 (12H, m, $NCH_2CH_2(CH_2)_3CH_3$), 1.33 (9H, s, $C(CH_3)_3$), 1.52 (4H, m, $NCH_2CH_2(CH_2)_3CH_3$), 2.48 (4H, t, $NCH_2(CH_2)_4CH_3$), 3.62 (2H, s, $ArCH_2N$), 7.29 (2H, d, Ar-*H*), 7.35 (2H, d, Ar-*H*); ESIMS *m/z* 332 (MH^+).

Loading/stripping data of L^1

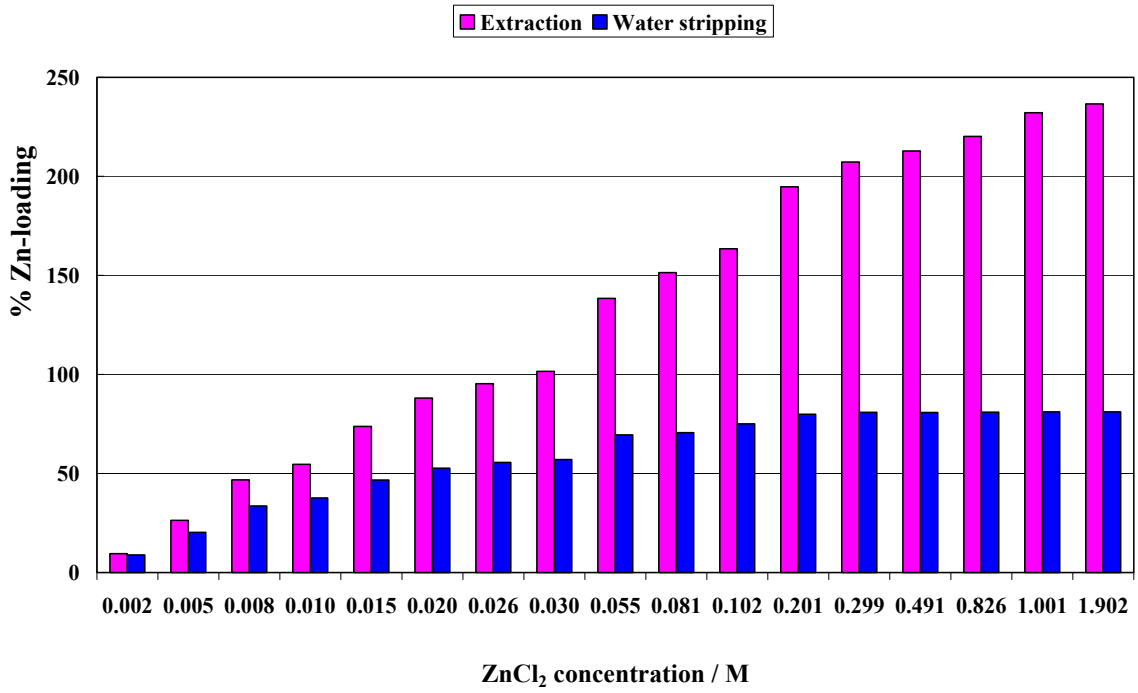

Fig. S1 Extraction and water stripping by L^1 (0.01 M) from $ZnCl_2$ solutions of varied concentrations. The 100% Zn loading is based on 0.01 M zinc content in the organic phase.

Reference

1 H. Adams, N. A. Bailey, D. E. Fenton and G. Papageorgiou, *Dalton Trans.*, 1995, 1883-1886.

2 R. Aldred, R. Johnston, D. Levin and J. Neilan, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1823-1831.