

# Three-phase transport studies of benzimidazole ligands bearing hydrophobic N-alkyl substituents: transport of metal(II) ions (Ni, Cu, Zn, Cd) in single- and multiple-ion experiments †

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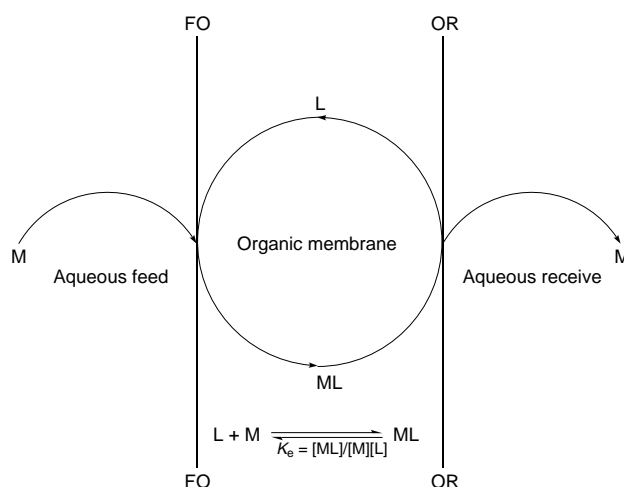
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New ligands having two benzimidazole units, or one benzimidazole and one carboxylic acid unit, the two functions linked by a chain, and bearing hydrophobic N-alkyl substituents have been tested as transfer agents for metal(II) ions (Ni, Cu, Zn, Cd) using three-phase transport techniques. The transport was pH-dependent, so all comparisons were made with buffered feed and receiving phases at fixed pH. Variations in the nature and number [single and double N-alkyl-substituted bis(benzimidazole) ligands] of N-alkyl substituents, linker chain and its donor atoms were explored and resultant transport trends are discussed. While single-ion transport results were ambivalent (singly alkylated 2-oxapropane derivatives being the best extractants for copper, and the analogous 2-thiapropane ligands for zinc), in multiple-ion experiments copper was always transported in preference to zinc. Even for ligands with a longer linking chain (based on 2,5-dioxaoctane) the order for extraction of metal(II) ions was always Cu > Zn > Cd and the transport of Ni was negligible. From the benzimidazole ligands screened, those having a carboxylic acid moiety reveal the highest metal-ion selectivity.

The measurement of transport rates through bulk liquid membranes<sup>1</sup> is a well established technique and has been used extensively over the last twenty years to screen new and novel carriers (transfer agents) with respect to selectivity. The transport of substrates through membranes has received much attention because of the potential applications of the technique.<sup>2–6</sup> It has been used to model biological membrane-transport systems, to develop ion-selective electrodes, to separate metal ions and to treat wastewater flows. The transport of a single substrate species through a bulk liquid membrane by a suitable carrier (L) is depicted in Scheme 1. The substrate (M) is initially located in the aqueous feed in the carrier (L) in the organic membrane with no substrate residing in the receiving phase. The rate at which the substrate is transported through the bulk liquid membrane is expressed as  $J_m$ , the number of moles of substrate transported per  $24 \text{ h} \times 10^7$ . The factors that influence the transport rate  $J_m$  and which have been altered during this study are the carrier and metal ion.

In this work a range of new bis(benzimidazole) (**3f**, **3h–10f**, **10h**, Table 1, Scheme 2) and benzimidazole carboxylic acid (**11–15**, Table 1, Scheme 3) ligands bearing hydrophobic N-alkyl substituents have been screened for potential metal-ion selectivity, complementing earlier work<sup>7</sup> on *N*-octadecylbenzimidazoles **1** and **2**. Rushton and co-workers<sup>7</sup> assumed that passive transport applied for fully alkylated bis(benzimidazole) carriers. However, our preliminary results indicated an effect of pH on transport of metal(II) ions. Thus the comparisons are all made at fixed pH although benzimidazoles of different p*K* are involved. To obviate the problems of comparison between different ligands the pH (receiving and feed phases) was buffered using a sodium acetate buffer.<sup>8,9</sup> Lindoy and co-workers<sup>10</sup> have adopted this approach when screening Schiff-base-derived macrocycles for metal-ion selectivity. Sodium cations and acetate anions present in the receive and source (feed) phases are believed to have little or no effect on the transport rates or the



**Scheme 1** Representation of carrier-facilitated diffusion of a single substrate across an organic membrane. Aqueous ‘feed’ and aqueous ‘receive’ refer to the adopted industrial nomenclature for in and out phases respectively; FO and OR represent the interfacial areas between the aqueous feed–organic membrane and organic membrane–aqueous receive phases respectively

metal-ion selectivity. Benzimidazole ligands show no affinity for sodium cations, especially in the presence of transition-metal ions, and acetate is known to be a poorer co-transported anion than fluoride.<sup>11</sup> The only transport considered, therefore, is between the benzimidazole ligand and the metal nitrate salt introduced into the feed solution. In the impending Discussion section direct comparisons are made only between the benzimidazole ligands developed in this study.

## Experimental

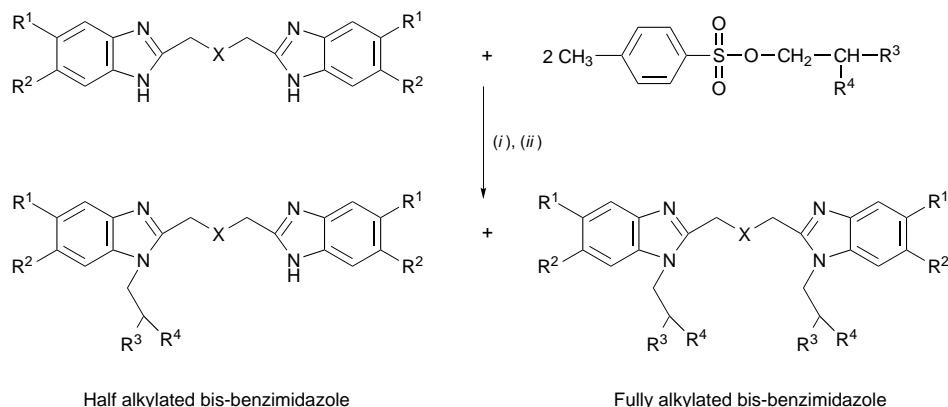
Reagents and solvents used were of commercially available reagent grade quality. The alcohols 2-hexyldecanol, 2-octyl-dodecanol and isooctadecanol were received from Zeneca Specialties and were of industrial grade quality. 3,6,9-Trioxaundecanedioic acid was supplied by Hoescht chemical company. Dimethylformamide (dmf) was distilled over calcium

† Supplementary data available: relative differences in transport rates. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/79/>, otherwise available from BLDSC (No. SUP 57310, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

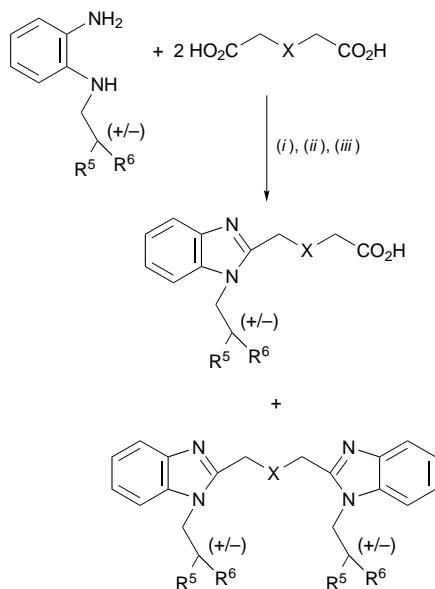
**Table 1** N-Alkylated hydrophobic bis(benzimidazole) and benzimidazolecarboxylic acid ligands **3f**, **3h**–**10f**, **10h**, **11**–**15**

N,N'-dialkyl	N-Alkyl	Carboxylic acid <sup>a</sup>	X	R <sup>3 a,b</sup>	R <sup>4 a,b</sup>
<b>3f</b>	<b>3h</b>	<b>11</b>	S	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
<b>4f</b>	<b>4h</b>	—	S	(CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
<b>5f</b>	<b>5h</b>	—	O	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
<b>6f</b>	<b>6h</b>	—	O	(CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
<b>7f</b>	<b>7h</b>	<b>12</b>	O	(CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	CH(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>
<b>8f<sup>b</sup></b>	<b>8h<sup>b</sup></b>	<b>13</b>	OCH <sub>2</sub> CH <sub>2</sub> O	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
<b>9f</b>	<b>9h</b>	<b>14</b>	OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> O	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
<b>10f</b>	<b>10h</b>	<b>15</b>	OC <sub>6</sub> H <sub>4</sub> O- <i>o</i>	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>

<sup>a</sup> For N-alkylated hydrophobic benzimidazolecarboxylic acid ligands (**11**–**15**): R<sup>5</sup> = CH<sub>2</sub>CH<sub>3</sub>, R<sup>6</sup> = (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> (Scheme 3). <sup>b</sup> R<sup>1</sup> = R<sup>2</sup> = H, except for compounds **8f** and **8h** for which R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub> (Scheme 2).



**Scheme 2** Synthesis of N-alkylated hydrophobic bis(benzimidazole) ligands. (i) Dry dimethylformamide, dry powdered K<sub>2</sub>CO<sub>3</sub>, 80 °C, 72 h; (ii) flash chromatography



**Scheme 3** Synthesis of N-branched alkylbenzimidazolecarboxylic acids. (i) Finely ground reagents; (ii) molten mass heated for 2 h with efficient stirring; (iii) flash chromatography [35–70 μm silica, eluent CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (10:1)]

hydride and used immediately. Melting points were determined with a Gallenkamp apparatus and are uncorrected. Proton and <sup>13</sup>C NMR spectra were run on Bruker WP200, WB300 and AMX500 spectrometers; chemical shifts (δ) are reported in parts per million (ppm) relative to deuteriated solvents as internal standards. Merck silica gel 60F<sub>254</sub> plates for thin-layer chromatography were developed in the solvent systems stated. Elemental analysis was performed on a Carlo Erba 1106 Elemental Analyser; fast atom bombardment (FAB) and electron impact (EI) mass spectra were obtained on a Kratos MS80 RF instrument. Inductively coupled plasma (ICP) analysis was

performed on a UNICAM 701 optical emission spectrophotometer or at Zeneca Specialties. All three-phase transport experiments were performed in triplicate in an apparatus similar to that described previously;<sup>7</sup> the reproducibilities for three-phase metal-ion transport are estimated as ±15% respectively. In comparisons of *J<sub>m</sub>*, values that lie within the boundaries of error are represented as approximately equivalent by the sign (≈). Blank experiments (no carrier present in the organic membrane) were performed to determine membrane leakage; in each case the amount of leakage was regarded as negligible (*M<sup>n+</sup>* ca. <0.05 ppm). Metal-ion concentrations in aqueous solutions were determined using ICP techniques. 1,3-Bis(benzimidazol-2-yl)-2-thiopropane,<sup>12a</sup> 1,3-bis(benzimidazol-2-yl)-2-oxapropane,<sup>12a</sup> 1,6-bis(5,6-dimethylbenzimidazol-2-yl)-2,5-dioxahexane<sup>12b</sup> and 1,2-bis(benzimidazol-2-yl)methoxybenzene<sup>12c</sup> were prepared *via* the Phillips<sup>12d</sup> condensation reaction. 1,3-Bis(*N*-stearylbenzimidazol-2-yl)-2-oxapropane **1** and 1,3-bis(5,6-dimethyl-*N*-stearylbenzimidazol-2-yl)-2-oxapropane **2** have been reported elsewhere<sup>7</sup> and *N*-2-(±)-ethylhexylamino-*o*-phenylenediamine was prepared according to a method described by Zeneca Specialties.

### Synthesis

**1,9-Bis(benzimidazol-2-yl)-2,5,8-trioxanonane.** To 3,6,9-trioxaundecanedioic acid (11.56 g, 0.05 mol) was added *o*-phenylenediamine (11.26 g, 0.10 mol); the two reagents were finely ground and intimately mixed. The mixture was stirred and heated to 140–160 °C in a molten fluid state for 4 h and cooled to room temperature to produce a brown glass-like solid which was extracted with portions of hot ethanol (5 × 50 cm<sup>3</sup>). The ethanolic solution was refluxed with decolourising charcoal for 1 h, filtered whilst hot and reduced *in vacuo* to yield a pale yellow oil. The oil was dissolved in dichloromethane (3 × 200 cm<sup>3</sup>) and washed with water (5 × 150 cm<sup>3</sup>) until the orange colouration was no longer evident in the aqueous washings. The organic extracts were dried over anhydrous magnesium sulfate,

filtered and slowly reduced in volume *in vacuo* until the first signs of precipitation. The resultant solution was kept at  $-20^{\circ}\text{C}$  overnight which resulted in a white precipitate forming. Yield 6.12 g (36%), m.p.  $141^{\circ}\text{C}$  (Found: C, 65.5; H, 5.7; N, 14.9.  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_3$  requires C, 65.6; H, 6.05; N, 15.3%).  $^1\text{H}$  NMR [200 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  3.71–3.83 (m, 8 H,  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ ), 4.81–4.84 (s, 4 H,  $\text{C}_7\text{H}_5\text{N}_2\text{CH}_2\text{O}$ ), 7.25–7.27 (m, 2 H,  $\text{H}^{5,6}$  of aryl, AA'BB', in slow exchange), 7.57–7.61 (m, 4 H,  $\text{H}^{4,7}$  of aryl, AA'BB' in slow exchange) and 12.6 (br s, 2 H, NH). (FAB) mass spectrum;  $m/z$  (assignment, relative intensity) 367 ( $M + \text{H}^+$ , 40%). EI mass spectrum:  $m/z$  (assignment, relative intensity) 366.1686 ( $M^+$ , 95%);  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_3$  requires 366.1692.

The hydrophobic alkyl tosylates (toluene-*p*-sulfonates) were prepared<sup>13</sup> according to the general procedure outlined below.

**2-Hexyldecyl tosylate.** To a stirred solution of 2-hexyldecanol (196.2 g, 0.81 mol) in cold dry pyridine (previously dried over molecular sieves) was added a slight excess of toluene-*p*-sulfonyl chloride (158.2 g, 0.83 mol) in small portions ensuring the temperature did not exceed  $-5^{\circ}\text{C}$ . The solution was then allowed to stir for 6 h at  $-10^{\circ}\text{C}$  in an ice-salt bath and then overnight in a cold room. The reaction mixture was poured over an ice (3 l) and concentrated HCl (700  $\text{cm}^3$ ) mixture ensuring the pH  $\approx$  1 with Congo Red indicator paper, at a temperature  $<10^{\circ}\text{C}$ . The mixture was then stirred for 1 h and allowed to settle, upon which the tosylated alcohol separated to the top of the aqueous layer to yield a pale yellow oil. The aqueous waste was removed and the oil extracted into dichloromethane (450  $\text{cm}^3$ ). The organic extracts were washed with 0.1 M HCl (3  $\times$  200  $\text{cm}^3$ ), saturated brine (3  $\times$  200  $\text{cm}^3$ ) and finally distilled water (3  $\times$  200  $\text{cm}^3$ ). The organic extracts were dried with magnesium sulfate, filtered and reduced in volume *in vacuo* to yield a viscous pale yellow oil. Yield 272.5 g, 85% (Found: C, 69.7; H, 10.6; S, 8.1. Calc. for  $\text{C}_{23}\text{H}_{40}\text{O}_3\text{S}$ : C, 69.7; H, 10.2; S, 8.1%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.66–0.71 [m, 6 H,  $2 \times \text{CH}_3$  (R)], 1.01–1.05 [m, 24 H, alkyl (R)], 1.35–1.42 [m, 1 H, CH (R)], 2.27 (s, 3 H, aryl- $\text{CH}_3$ ), 3.71–3.74 [d, 2 H,  $\text{OCH}_2$  (R)], 7.12–7.18 (d, 2 H, aryl) and 7.59–7.63 (d, 2 H, aryl). EI mass spectrum:  $m/z$  241.2522 ( $M^+ - \text{C}_7\text{H}_7\text{O}_2\text{S}$ , 30%);  $\text{C}_{16}\text{H}_{33}\text{O}$  requires 241.2531.

**2-Octyldodecyl tosylate.** From 2-octyldodecanol (241.8 g, 0.81 mol) and toluene-*p*-sulfonyl chloride (158.2 g, 0.83 mol) in the same manner as described above a viscous golden oil was obtained. Yield 273.0 g, 74% (Found: C, 72.3; H, 9.5; S, 6.1. Calc. for  $\text{C}_{27}\text{H}_{48}\text{O}_3\text{S}$ : C, 71.6; H, 10.7; S, 7.1%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.52–0.64 [m, 6 H,  $2 \times \text{CH}_3$  (R)], 0.91–0.99 [m, 32 H, alkyl (R)], 1.28–1.42 [m, 1 H, CH, (R)], 2.17 (s, 3 H, aryl- $\text{CH}_3$ ), 3.62–3.65 [d, 2 H,  $\text{OCH}_2$  (R)], 7.05–7.09 (d, 2 H, aryl), and 7.49–7.57 (d, 2 H, aryl). EI mass spectrum:  $m/z$  297.3152 ( $M^+ - \text{C}_7\text{H}_7\text{O}_2\text{S}$ , 30%);  $\text{C}_{20}\text{H}_{41}\text{O}$  requires 297.3157.

**Isooctadecyl tosylate.** From isooctadecanol (179.1 g, 0.81 mol) and toluene-*p*-sulfonyl chloride (158.2 g, 0.83 mol) in the same manner as described above was obtained a viscous golden oil. Yield 212.0 g, 62% (Found: C, 70.5; H, 9.1; S, 7.4. Calc. for  $\text{C}_{25}\text{H}_{44}\text{O}_3\text{S}$ : C, 70.7; H, 10.4; S, 7.6%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.58–1.36 [m, 35 H, alkyl (R)], 2.13 (s, 3 H, aryl- $\text{CH}_3$ ), 3.55–3.72 [m, 2 H,  $\text{OCH}_2$  (R)], 7.02–7.06 (d, 2 H, aryl) and 7.47–7.51 (d, 2 H, aryl). EI mass spectrum:  $m/z$  269.2832 ( $M^+ - \text{C}_7\text{H}_7\text{O}_2\text{S}$ , 30%);  $\text{C}_{18}\text{H}_{37}\text{O}$  requires 269.2844.

N-Alkylation of the bis-benzimidazoles to yield the half and fully alkylated hydrophobic bis-benzimidazoles (**3f**, **3h**–**10f**, **10h**) was carried out according to the general procedure outlined below. The singly and the doubly N-alkylated products were separated from a one-pot reaction mix using flash chromatography (35–70  $\mu\text{m}$  silica; fully alkylated ligands  $R_f \approx 0.85$  and half-alkylated ligands  $R_f \approx 0.35$ ) with the relevant eluent.

**1,3-Bis(N-2-hexyldecylbenzimidazol-2-yl)-2-thiapropane 3f.** To 1,3-bis(benzimidazol-2-yl)-2-thiapropane (20.1 g, 0.07 mol)

previously dried under vacuum at  $60^{\circ}\text{C}$  was added finely ground dry potassium carbonate (21.2 g, 0.15 mol) under a nitrogen atmosphere in freshly distilled dry dimethylformamide (500  $\text{cm}^3$ ). The suspension was gently warmed to  $80^{\circ}\text{C}$  for 4 h and 2-hexyldecyl tosylate (62.7 g, 0.16 mol) was added slowly over 2 h. The suspension was stirred for 72 h at  $80^{\circ}\text{C}$  under a nitrogen atmosphere then cooled to room temperature and filtered through Celite to yield an orange solution which was concentrated *in vacuo* to yield a golden oil. The oil was diluted with water (500  $\text{cm}^3$ ), extracted into dichloromethane ( $5 \times 500 \text{ cm}^3$ ) and washed with water ( $5 \times 300 \text{ cm}^3$ ). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and reduced in volume *in vacuo* to yield a golden oil. Thin-layer chromatography of the crude oil indicated the presence of two major alkylated products. The oil was purified *via* flash chromatography [35–70  $\mu\text{m}$  silica; eluent ethyl acetate–light petroleum (b.p.  $60$ – $80^{\circ}\text{C}$ ) (40:60)] to yield the fully alkylated product as a pale yellow oil. Yield (8.54 g, 16%) (Found: C, 77.9; H, 10.6; N, 7.2; S, 4.1.  $\text{C}_{48}\text{H}_{78}\text{N}_4\text{S}$  requires C, 77.6; H, 10.6; N, 7.5; S, 4.3%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.76–0.87 [m, 12 H,  $4 \times \text{CH}_3$  (R)], 1.15–1.23 [m, 48 H, alkyl (R)], 1.84–1.98 [br m, 2 H, CH, (R)], 3.91–3.94 [d, 4 H,  $\text{NCH}_2$  (R)], 4.05 (s, 4 H,  $\text{CH}_2\text{S}$ ), 7.15–7.37 (m, 6 H,  $\text{H}^{4,6}$  of aryl) and 7.58–7.67 (m, 2 H,  $\text{H}^7$  of aryl).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.8 ( $\text{C}^2$ ), 142.6 ( $\text{C}^9$ ), 135.9 ( $\text{C}^8$ ), 122.7 ( $\text{C}^5$ ), 122.2 ( $\text{C}^6$ ), 119.8 ( $\text{C}^4$ ), 110.1 ( $\text{C}^7$ ), 48.6 ( $\text{CH}_2\text{S}$ ), 38.6 ( $\text{NCH}_2$ ), 35.6–14.0 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  742.5980 ( $M^+$ , 30%);  $\text{C}_{48}\text{H}_{78}\text{N}_4\text{S}$  requires 742.5947.

**1-Benzimidazolyl-3-(N-2-hexyldecyl)benzimidazolyl-2-thiapropane 3h.** The half-alkylated bis-benzimidazole product was isolated from the column as a pale yellow oil. Yield 14.54 g, 40%. (Found: C, 73.8; H, 8.5; N, 10.4; S, 5.9.  $\text{C}_{32}\text{H}_{46}\text{N}_4\text{S}$  requires C, 74.1; H, 8.9; N, 10.8; S, 6.2%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.60–0.72 [m, 6 H,  $2 \times \text{CH}_3$  (R)], 1.04–1.11 [m, 24 H, alkyl (R)], 1.79–1.82 [m, 1 H, CH (R)], 3.60 (s, 2 H,  $\text{CH}_2\text{S}$ ), 3.77 (s, 2 H,  $\text{CH}_2\text{S}$ ), 3.88–3.96 [m, 2 H,  $\text{NCH}_2$  (R)], 7.04–7.21 (m, 5 H,  $\text{H}^{4,5,5',6,6'}$  of aryl), 7.46–7.49 (m, 2 H,  $\text{H}^{4,7}$  of aryl), 7.51–7.70 (m, 1 H,  $\text{H}^7$  of aryl) and 12.98 (br s, 1 H, NH).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.6 ( $\text{C}^2$ ), 150.6 ( $\text{C}^2$ ), 141.5 ( $\text{C}^9$ ),  $\ddagger$ ( $\text{C}^9$ ),  $\ddagger$ ( $\text{C}^8$ ), 135.8 ( $\text{C}^8$ ), 123.5 ( $\text{C}^{5,6}$ ), 122.9 ( $\text{C}^5$ ), 122.5 ( $\text{C}^6$ ), 119.5 ( $\text{C}^4$ ),  $\ddagger$ ( $\text{C}^4$ ),  $\ddagger$ ( $\text{C}^7$ ), 110.6 ( $\text{C}^7$ ), 48.9 ( $\text{CH}_2\text{S}$ ), 38.7 ( $\text{NCH}_2$ ) and 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). FAB mass spectrum:  $m/z$  519 ( $M + \text{H}^+$ , 100%). EI mass spectrum:  $m/z$  518.3424 ( $M^+$ , 30%);  $\text{C}_{32}\text{H}_{46}\text{N}_4\text{S}$  requires 518.3443.

**1,3-Bis(N-2-octyldodecylbenzimidazol-2-yl)-2-thiapropane 4f.** From the preparation using 1,3-bis(benzimidazol-2-yl)-2-thiapropane (20.5 g, 0.07 mol) and 2-octyldodecyl tosylate (72.9 g, 0.16 mol) the crude oil was purified *via* flash chromatography [35–70  $\mu\text{m}$  silica; eluent ethyl acetate–light petroleum (b.p.  $60$ – $80^{\circ}\text{C}$ )] to give a viscous golden oil. Yield 6.54 g, 11% (Found: C, 78.4; H, 10.5; N, 7.0; S, 3.9.  $\text{C}_{56}\text{H}_{94}\text{N}_4\text{S}$  requires C, 78.6; H, 11.1; N, 6.6; S, 3.8%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.70–0.88 [m, 12 H,  $4 \times \text{CH}_3$  (R)], 1.19–1.27 [m, 64 H, alkyl (R)], 1.85–1.97 [br, m, 2 H, CH (R)], 3.92–3.96 [d, 4 H,  $\text{NCH}_2$  (R)], 4.06 (s, 4 H,  $\text{CH}_2\text{S}$ ), 7.16–7.34 (m, 6 H,  $\text{H}^{4,6}$  of aryl) and 7.64–7.72 (m, 2 H,  $\text{H}^7$  of aryl).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.8 ( $\text{C}^2$ ), 142.6 ( $\text{C}^9$ ), 135.9 ( $\text{C}^8$ ), 122.8 ( $\text{C}^5$ ), 122.1 ( $\text{C}^6$ ), 119.8 ( $\text{C}^4$ ), 110.1 ( $\text{C}^7$ ), 48.6 ( $\text{CH}_2\text{S}$ ), 38.6 ( $\text{NCH}_2$ ) and 32.4–14.3 (remaining C atoms of hydrophobic alkyl chains). (FAB) mass spectrum;  $m/z$  855 ( $M + \text{H}^+$ , 25%). (EI) mass spectrum:  $m/z$  854 ( $M^+$ , (5%);  $\text{C}_{56}\text{H}_{94}\text{N}_4\text{S}$ ) requires 854.7199.

$\ddagger$  Owing to the prototropy of the unalkylated benzimidazole unit these carbons are in a state of fast exchange and their signals are not observed at room temperature on this NMR time-scale.

$\S$  Fast atom bombardment and EI mass spectrometry were obtained on a Kratos MS80 RF instrument. Owing to the high molecular mass of the fully alkylated ligands **4f** and **6f**–**10f** an accurate mass to four decimal places was unobtainable.

**1-Benzimidazolyl-3-(N-2-octyldodecyl)benzimidazolyl-2-thiopropane 4h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 17.0 g, 42% (Found: C, 76.1; H, 10.1; N, 9.4; S, 5.6.  $C_{36}H_{54}N_4S$  requires C, 75.2; H, 9.5; N, 9.8; S, 5.6%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.77–0.83 [m, 6 H,  $2 \times CH_3$  (R)], 1.14–1.22 [m, 32 H, alkyl (R)], 1.79–1.84 [m, 1 H, CH (R)], 3.71 (s, 2 H,  $CH_2S$ ), 3.88 (s, 2 H,  $CH_2S$ ), 3.99–4.07 [m, 2 H,  $NCH_2$  (R)], 7.15–7.35 (m, 5 H,  $H^{4,5,5',6,6'}$  of aryl), 7.40–7.62 (m, 2 H,  $H^{4,7}$  of aryl), 7.63–7.78 (m, 1 H,  $H^7$  of aryl) and 12.96 (br s, 1 H, NH).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  151.6 ( $C^2$ ), 150.6 ( $C^2$ ), 141.5 ( $C^9$ ),  $\ddagger(C^9)$ , 135.8 ( $C^8$ ), 123.5 ( $C^{5,6}$ ), 122.9 ( $C^5$ ), 122.5 ( $C^6$ ), 119.5 ( $C^4$ ),  $\ddagger(C^4)$ ,  $\ddagger(C^7)$ , 110.6 ( $C^7$ ), 48.9 ( $CH_2S$ ), 38.7 ( $NCH_2$ ) and 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  574.4062 ( $M^+$ , 30%);  $C_{36}H_{54}N_4S$  requires 574.4069.

**1,3-Bis(N-2-hexyldecylbenzimidazol-2-yl)-2-oxapropane 5f.** From the preparation using 1,3-bis(benzimidazol-2-yl)-2-oxapropane (16.4 g, 0.06 mol) and 2-hexyldecyl tosylate (53.5 g, 0.13 mol), the crude oil was purified *via* flash chromatography [35–70  $\mu m$  silica; eluent ethyl acetate–light petroleum (b.p. 60–80 °C)] to give a viscous golden *oil* 5f. Yield 9.38 g, 22% (Found: C, 78.9; H, 9.0; N, 7.2.  $C_{48}H_{78}N_4O$  requires C, 79.3; H, 10.8; N, 7.7%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.75–0.85 [m, 12 H,  $4 \times CH_3$  (R)], 1.14–1.22 [m, 48 H, alkyl (R)], 1.89–1.97 [br m, 2 H, CH (R)], 3.93–3.97 [d, 4 H,  $NCH_2$  (R)], 4.84 (s, 4 H,  $CH_2O$ ), 7.14–7.29 (m, 6 H,  $H^{4,6}$  of aryl) and 7.67–7.73 (m, 2 H,  $H^7$  of aryl).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  150.1 ( $C^2$ ), 142.6 ( $C^9$ ), 135.9 ( $C^8$ ), 123.2 ( $C^5$ ), 122.3 ( $C^6$ ), 120.3 ( $C^4$ ), 110.3 ( $C^7$ ), 65.1 ( $CH_2O$ ), 48.7 ( $NCH_2$ ) and 35.6–14.0 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  726.6230 ( $M^+$ , 10%);  $C_{48}H_{78}N_4O$  requires 726.6176.

**1-Benzimidazolyl-3-(N-2-hexyldecyl)benzimidazolyl-2-oxapropane 5h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 14.0 g, 46% (Found: C, 76.8; H, 9.5; N, 11.4.  $C_{32}H_{46}N_4O$  requires C, 76.5; H, 9.2; N, 11.1%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.77–0.87 [m, 6 H,  $2 \times CH_3$  (R)], 1.13–1.24 [m, 24 H, alkyl (R)], 1.80–1.99 [m, 1 H, CH (R)], 3.70–3.74 [d, 2 H,  $NCH_2$  (R)], 4.77 (s, 2 H,  $CH_2O$ ), 4.82 (s, 2 H,  $CH_2O$ ), 7.14–7.27 (m, 5 H,  $H^{4,5,5',6,6'}$  of aryl), 7.58–7.66 (m, 2 H,  $H^{4,7}$  of aryl), 7.67–7.71 (m, 1 H,  $H^7$  of aryl) and 13.08 (br s, 1 H, NH).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  151.1 ( $C^2$ ), 150.4 ( $C^2$ ), 141.8 ( $C^9$ ),  $\ddagger(C^9)$ ,  $\ddagger(C^8)$ , 135.5 ( $C^8$ ), 123.3 ( $C^{5,6}$ ), 123.3 ( $C^5$ ), 122.6 ( $C^6$ ), 119.6 ( $C^4$ ),  $\ddagger(C^4)$ ,  $\ddagger(C^7)$ , 110.6 ( $C^7$ ), 66.9 ( $CH_2O$ ), 65.2 ( $CH_2O$ ), 48.5 ( $NCH_2$ ) and 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). (FAB) mass spectrum:  $m/z$  519 ( $M + H^+$ , 100%). EI mass spectrum:  $m/z$  502.3688 ( $M^+$ , 30%);  $C_{32}H_{46}N_4O$  requires 502.3672.

**1,3-Bis(N-2-octyldodecylbenzimidazol-2-yl)-2-oxapropane 6f.** From the preparation using 1,3-bis(benzimidazol-2-yl)-2-oxapropane (16.7 g, 0.06 mol) and added 2-octyldodecyl tosylate (64.0 g, 0.14 mol), the crude oil was purified *via* flash chromatography [35–70  $\mu m$  silica; eluent ethyl acetate–light petroleum (b.p. 60–80 °C)] to give a viscous golden *oil* 6f. Yield 10.2 g, 20% (Found: C, 79.7; H, 11.5; N, 7.0.  $C_{56}H_{94}N_4O$  requires C, 80.1; H, 11.3; N, 6.7%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.76–0.81 [m, 12 H,  $4 \times CH_3$  (R)], 1.09–1.17 [m, 64 H, alkyl (R)], 1.87–1.98 [br m, 2 H, CH (R)], 3.93–3.97 [d, 4 H,  $NCH_2$  (R)], 4.81 (s, 4 H,  $CH_2O$ ), 7.11–7.25 (m, 6 H,  $H^{4,6}$  of aryl) and 7.63–7.70 (m, 2 H,  $H^7$  of aryl).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  150.2 ( $C^2$ ), 142.5 ( $C^9$ ), 135.9 ( $C^8$ ), 123.2 ( $C^5$ ), 122.3 ( $C^6$ ), 119.9 ( $C^4$ ), 110.3 ( $C^7$ ), 65.1 ( $CH_2O$ ), 48.7 ( $NCH_2$ ) and 35.6–14.0 (remaining C atoms of hydrophobic alkyl chains). FAB mass spectrum:  $m/z$  839 ( $M + H^+$ , 5%). EI mass spectrum:  $m/z$  838 ( $M^+$ , 5%);  $C_{56}H_{94}N_4O$  requires 838.7428.

**1-Benzimidazolyl-3-(N-2-octyldodecyl)benzimidazolyl-2-oxapropane 6h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 15.3 g, 46% (Found: C, 76.4; H, 10.4; N, 9.5.  $C_{36}H_{54}N_4O$  requires C, 77.4; H, 9.8; N, 10.0%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.59–0.69 [m, 6 H,  $2 \times CH_3$  (R)], 0.83–1.07 [m, 32 H, aryl (R)], 1.50–1.60 [m, 1 H, CH (R)], 3.93–3.97 [m, 2 H,  $NCH_2$  (R)], 4.64 (s, 2 H,  $CH_2O$ ), 4.68 (s, 2 H,  $CH_2O$ ), 6.97–7.11 (m, 5 H,  $H^{4,5,5',6,6'}$  of aryl), 7.14–7.41 (m, 2 H,  $H^{4,7}$  of aryl), 7.51–7.64 (m, 1 H,  $H^7$  of aryl), 13.03 (br s, 1 H, NH);  $^{13}C$  NMR (50 MHz,  $CDCl_3$ )  $\delta$  151.1 ( $C^2$ ), 150.4 ( $C^2$ ), 141.8 ( $C^9$ ),  $\ddagger(C^8)$ ,  $\ddagger(C^9)$ , 135.5 ( $C^8$ ), 123.4 ( $C^{5,6}$ ), 123.3 ( $C^5$ ), 122.6 ( $C^6$ ), 119.6 ( $C^4$ ), 110.6 ( $C^7$ ),  $\ddagger(C^4)$ ,  $\ddagger(C^7)$ , 66.9 ( $CH_2O$ ), 65.2 ( $CH_2O$ ), 48.5 ( $NCH_2$ ), 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  558.4252 ( $M^+$ , 30%);  $C_{36}H_{54}N_4O$  requires 558.4298.

**1,3-Bis(N-2-isooctyldecylbenzimidazol-2-yl)-2-oxapropane 7f.** From the preparation using 1,3-bis(benzimidazol-2-yl)-2-oxapropane (15.2 g, 0.055 mol) and added 2-isooctyldecyl tosylate (52.6 g, 0.12 mol), a crude oily product was purified *via* flash chromatography [35–70  $\mu m$  silica; eluent ethyl acetate–light petroleum (b.p. 60–80 °C)] to give a viscous golden *oil* 7f. Yield 1.8 g, 4% (Found: C, 78.7; H, 11.5; N, 7.3.  $C_{52}H_{86}N_4O$  requires C, 79.7; H, 11.1; N, 7.2%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.62–1.43 [m, 68 H, alkyl (R)], 1.66–1.79 [br m, 2 H, CH (R)], 3.75–4.09 [br m, 4 H,  $NCH_2$  (R)] 4.91 (s, 4 H,  $CH_2O$ ), 7.19–7.30 (m, 6 H,  $H^{4,6}$  of aryl) and 7.62–7.77 (m, 2 H,  $H^7$  of aryl).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  150.2 ( $C^2$ ), 142.5 ( $C^9$ ), 135.9 ( $C^8$ ), 123.2 ( $C^5$ ), 122.3 ( $C^6$ ), 119.9 ( $C^4$ ), 110.3 ( $C^7$ ), 65.1 ( $CH_2O$ ), 47.6 ( $NCH_2$ ) and 35.6–14.0 (remaining C atoms of hydrophobic alkyl chains). FAB mass spectrum:  $m/z$  784 ( $M + H^+$ , 25%). EI mass spectrum:  $m/z$  783 ( $M^+$ , 5%);  $C_{52}H_{86}N_4O$  requires 782.6801.

**1-Benzimidazolyl-3-(N-2-isooctyldecyl)benzimidazolyl-2-oxapropane 7h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 15.3 g, 52% (Found: C, 76.3; H, 10.1; N, 9.8.  $C_{34}H_{50}N_4O$  requires C, 76.9; H, 9.5; N, 10.6%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.47–1.18 [m, 34 H, alkyl (R)], 1.75–1.86 [m, 1 H, CH (R)], 3.54–3.86 [br m, 2 H,  $NCH_2$  (R)], 4.72 (s, 2 H,  $CH_2O$ ), 4.74 (s, 2 H,  $CH_2O$ ), 7.03–7.13 (m, 5 H,  $H^{4,5,5',6,6'}$  of aryl), 7.28–7.51 [br m, 2 H,  $H^{4,7}$  of aryl], 7.60–7.63 (m, 1 H,  $H^7$  of aryl) and 13.10 (br s, 1 H, NH).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  151.3 ( $C^2$ ), 150.6 ( $C^2$ ), 141.9 ( $C^9$ ),  $\ddagger(C^9)$ ,  $\ddagger(C^8)$ , 135.7 ( $C^8$ ), 123.3 ( $C^{5,6}$ ), 123.3 ( $C^5$ ), 122.7 ( $C^6$ ), 119.6 ( $C^4$ ),  $\ddagger(C^4)$ ,  $\ddagger(C^7)$ , 110.6 ( $C^7$ ), 65.9 ( $CH_2O$ ), 65.6 ( $CH_2O$ ), 47.7 ( $NCH_2$ ) and 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  530.3917 ( $M^+$ , 5%);  $C_{34}H_{50}N_4O$  requires 530.3985.

**1,6-Bis(N-2-hexyldecyl-5',6-dimethylbenzimidazol-2-yl)-2,5-dioxahexane 8f.** From the preparation using 1,6-bis(5,6-dimethylbenzimidazol-2-yl)-2,5-dioxahexane (3.34 g, 8.84 mmol) and added 2-hexyldecyl tosylate (7.96 g, 20.08 mmol), the crude oil was purified *via* flash chromatography (35–70  $\mu m$  silica; eluent methanol–dichloromethane) to give a viscous golden *oil* 8f. Yield 1.32 g, 18% (Found: C, 78.7; H, 11.3; N, 6.8.  $C_{54}H_{90}N_4O_2$  requires C, 78.4; H, 11.0; N, 6.8%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.80–0.89 [m, 12 H,  $4 \times CH_3$  (R)], 1.15–1.24 [m, 48 H, alkyl (R)], 1.96–2.07 [br m, 2 H, CH (R)], 2.34–2.36 (d, 12 H, aryl- $CH_3$ ), 3.57 (s, 4 H,  $OCH_2$ ), 3.98–4.02 [d, 4 H,  $NCH_2$  (R)], 4.78 (s, 4 H,  $C_7H_2N_2CH_2O$ ), 7.02 (s, 2 H,  $H^7$  of aryl) and 7.46 (s, 2 H,  $H^4$  of aryl).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  149.7 ( $C^2$ ), 140.9 ( $C^9$ ), 134.5 ( $C^8$ ), 132.0 ( $C^5$ ), 130.8 ( $C^6$ ), 120.0 ( $C^4$ ), 110.4 ( $C^7$ ), 69.2 ( $C_7H_2N_2CH_2O$ ), 66.1 ( $CH_2O$ ), 48.3 ( $NCH_2$ ) and 35.6–14.0 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum:  $m/z$  826 ( $M^+$ , 60%);  $C_{54}H_{90}N_4O_2$  requires 826.7064.

**1-(*N*-2-Hexyldecyl)-5,6-dimethylbenzimidazolyl)-6-(5,6-dimethylbenzimidazolyl)-2,5-dioxahexane 8h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 1.82 g, 34% (Found: C, 75.2; H, 9.6; N, 9.2. C<sub>38</sub>H<sub>58</sub>N<sub>4</sub>O<sub>2</sub> requires C, 75.7; H, 9.7; N, 9.3%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.85–0.91 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.24 [br s, 24 H, alkyl (R)], 1.78–2.05 [br m, 1 H, CH (R)], 2.34 (s, 6 H, un-*N*-alkylated aryl CH<sub>3</sub>), 2.40–2.44 (d, 6 H, *N*-alkylated aryl CH<sub>3</sub>), 3.75–3.89 (m, 4 H, CH<sub>2</sub>O), 4.07–4.11 [d, 2 H, NCH<sub>2</sub> (R)], 4.85 (s, 2 H, CH<sub>2</sub>O), 4.99 (s, 2 H, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 7.02 (s, 1 H, H<sup>7</sup> of aryl), 7.25 (br s, 2 H, H<sup>4,7</sup> of aryl), 7.46 (s, 1 H, H<sup>4</sup> of aryl) and 13.03 (br s, 1 H, NH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 151.3 (C<sup>2</sup>), 149.9 (C<sup>2</sup>), 140.8 (C<sup>9</sup>), ‡(C<sup>9</sup>), ‡(C<sup>8</sup>), 134.3 (C<sup>8</sup>), 132.5 (C<sup>5,6</sup>), 131.4 (C<sup>5</sup>), 130.7 (C<sup>6</sup>), 119.7 (C<sup>4</sup>), ‡(C<sup>4</sup>), ‡(C<sup>7</sup>), 110.6 (C<sup>7</sup>), 71.5 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 69.0 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 67.5 (CH<sub>2</sub>O), 65.3 (CH<sub>2</sub>O), 65.2 (CH<sub>2</sub>O), 48.5 (NCH<sub>2</sub>) and 32.0–14.3 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum: *m/z* 602.4630 (*M*<sup>+</sup>, 20%); C<sub>38</sub>H<sub>58</sub>N<sub>4</sub>O<sub>2</sub> requires 602.4560.

**1,9-Bis(*N*-2-hexyldecylbenzimidazol-2-yl)-2,5,8-trioxanonane 9f.** From the preparation using 1,9-bis(benzimidazol-2-yl)-2,5,8-trioxanonane (3.17 g, 8.66 mmol) and added 2-hexyldecyl tosylate (7.54 g, 19.01 mmol), the crude oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane; 1 : 10); to give a viscous golden oil **9f**. Yield 0.64 g, 8% (Found: C, 77.1; H, 10.8; N, 6.4. C<sub>52</sub>H<sub>86</sub>N<sub>4</sub>O<sub>3</sub> requires C, 76.6; H, 10.6; N, 6.9%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.82–0.85 [m, 12 H, 4 × CH<sub>3</sub> (R)], 1.17–1.24 [m, 48 H, alkyl (R)], 1.98–2.07 [br m, 2 H, CH (R)], 3.50–3.60 (m, 8 H, OCH<sub>2</sub>), 4.0–4.11 [d, 4 H, NCH<sub>2</sub> (R)], 4.79 (s, 4 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>O), 7.17–7.29 (m, 6 H, H<sup>4–6</sup> of aryl) and 7.67–7.72 (m, 2 H, H<sup>7</sup> of aryl). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 150.6 (C<sup>2</sup>), 142.3 (C<sup>9</sup>), 135.9 (C<sup>8</sup>), 122.9 (C<sup>5</sup>), 122.1 (C<sup>6</sup>), 120.1 (C<sup>4</sup>), 110.2 (C<sup>7</sup>), 70.3 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>O), 69.6 (CH<sub>2</sub>O), 66.1 (CH<sub>2</sub>O), 48.5 (NCH<sub>2</sub>) and 38.2–14.1 (remaining C atoms of hydrophobic alkyl chains). FAB mass spectrum: *m/z* 816 (*M* + H<sup>+</sup>, 100%). EI mass spectrum: *m/z* 814 (*M*<sup>+</sup>, 10%); C<sub>52</sub>H<sub>86</sub>N<sub>4</sub>O<sub>3</sub> requires 814.6700.

**1-Benzimidazolyl-9-(*N*-2-hexadecylbenzimidazolyl)-2,5,8-trioxanonane 9h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 0.62 g, 12% (Found: C, 73.2; H, 9.2; N, 9.6. C<sub>36</sub>H<sub>54</sub>N<sub>4</sub>O<sub>3</sub> requires C, 73.2; H, 9.2; N, 9.5%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.74–0.82 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.13–1.28 [br m, 24 H alkyl (R)], 1.93–2.05 [br m, 1 H, CH (R)], 3.60–3.72 (m, 8 H, CH<sub>2</sub>O), 4.01–4.05 [d, 2 H, NCH<sub>2</sub> (R)], 4.83 (s, 2 H, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 4.91 (s, 2 H, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 7.04–7.29 (m, 5 H, H<sup>4,5,5,6,6</sup> of aryl), 7.31–7.43 [br m, 2 H, H<sup>4,7</sup> of aryl], 7.64–7.70 (m, 1 H, H<sup>7</sup> of aryl) and 12.80 (br s, 1 H, NH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 152.1 (C<sup>2</sup>), 150.7 (C<sup>2</sup>), 141.9 (C<sup>9</sup>), ‡(C<sup>9</sup>), ‡(C<sup>8</sup>), 135.8 (C<sup>8</sup>), 123.2 (C<sup>5,6</sup>), 122.4 (C<sup>5</sup>), 122.1 (C<sup>6</sup>), 119.9 (C<sup>4</sup>), ‡(C<sup>4</sup>), ‡(C<sup>7</sup>), 110.4 (C<sup>7</sup>), 70.7 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 70.5 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 69.3 (CH<sub>2</sub>O), 67.4 (CH<sub>2</sub>O), 65.7 (CH<sub>2</sub>O), 48.6 (NCH<sub>2</sub>) and 31.9–14.1 (remaining C atoms of hydrophobic alkyl chains). FAB mass spectrum: *m/z* 591 (*M* + H<sup>+</sup>, 70%). EI mass spectrum: *m/z* 590.4190 (*M*<sup>+</sup>, 100%); C<sub>36</sub>H<sub>54</sub>N<sub>4</sub>O<sub>3</sub> requires 590.4196.

**1,2-Bis(*N*-2-hexyldecylbenzimidazol-2-ylmethoxy)benzene 10f.** From the preparation using 1,2-bis(benzimidazol-2-ylmethoxy)benzene (3.72 g, 10.02 mmol) and added 2-hexyldecyl tosylate (8.15 g, 20.56 mmol), a crude oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane; 1 : 10) to give a viscous golden oil **10f**. Yield 2.2 g, 27% (Found: C, 79.8; H, 10.2; N, 6.8. C<sub>54</sub>H<sub>82</sub>N<sub>4</sub>O<sub>2</sub> requires C, 79.2; H, 10.1; N, 6.8%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.71–0.82 [m, 12 H, 4 × CH<sub>3</sub> (R)], 1.01–1.24 [br s, 48 H, aryl (R)], 1.87–2.02 [br m, 2 H, CH (R)], 3.99–4.03 [d, 4 H, NCH<sub>2</sub> (R)], 5.28 (s, 4 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>O), 6.79–6.97 (m, 2 H, aryl), 7.04–7.13 (m, 2 H, aryl) and 7.15–7.21 (m, 6 H, aryl). <sup>13</sup>C

NMR (50 MHz, CDCl<sub>3</sub>): δ 149.5 (C<sup>2</sup>), 148.3 (aryl), 142.3 (C<sup>9</sup>), 136.0 (C<sup>8</sup>), 123.1 (C<sup>5</sup>), 122.6 (aryl), 122.2 (C<sup>6</sup>), 120.2 (C<sup>4</sup>), 115.2 (aryl), 110.3 (C<sup>7</sup>), 65.02 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>O), 48.4 (NCH<sub>2</sub>) and 38.3–14.1 (remaining C atoms of hydrophobic alkyl chains). EI mass spectrum: *m/z* 819, (*M*<sup>+</sup>, 100%); C<sub>54</sub>H<sub>82</sub>N<sub>4</sub>O<sub>2</sub> requires 818.6438.

**1-(Benzimidazol-2-ylmethoxy)-2-(*N*-2-hexyldecyl)benzimidazolylmethoxybenzene 10h.** The half-alkylated bis(benzimidazole) *product* was isolated from the column as a pale yellow oil. Yield 1.86 g, 31% (Found: C, 77.5; H, 8.5; N, 9.4. C<sub>38</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub> requires C, 76.7; H, 8.5; N, 9.4%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.64–0.72 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.05–1.15 [br m, 24 H, alkyl (R)], 1.87–2.06 [br m, 1 H, CH (R)], 3.93–3.96 [d, 2 H, NCH<sub>2</sub> (R)], 5.30 (s, 2 H, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 5.32 (s, 2 H, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 6.70–6.86 (m, 1 H, aryl), 6.87–6.99 (m, 2 H, aryl), 7.03–7.27 (m, 6 H, aryl), 7.41–7.58 (br m, 1 H, aryl), 7.60–7.66 (br m, 1 H, aryl), 7.68–7.72 (m, 1 H, aryl) and 13.38 (br s, 1 H, NH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 150.7 (C<sup>2</sup>), 150.2 (C<sup>2</sup>), 149.6 (aryl), 147.5 (aryl), 142.9 (C<sup>9</sup>), ‡(C<sup>9</sup>), ‡(C<sup>8</sup>), 135.5 (C<sup>8</sup>), 124.6 (C<sup>5,6</sup>), 124.6 (C<sup>5</sup>), 123.5 (C<sup>6</sup>), 122.8 (aryl), 122.7 (aryl), 119.9 (C<sup>4</sup>), ‡(C<sup>4</sup>), ‡(C<sup>7</sup>), 115.6 (aryl), 110.6 (C<sup>7</sup>), 65.9 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 65.3 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>CH<sub>2</sub>O), 69.3 (CH<sub>2</sub>O), 48.7 (NCH<sub>2</sub>) and 31.9–14.1 (remaining C atoms of hydrophobic alkyl chains) EI mass spectrum: *m/z* 594.3910 (*M*<sup>+</sup>, 5%); C<sub>38</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub> requires 594.3934.

**4-[*N*(±)-2-Ethylhexylbenzimidazolyl]-3-thiobutanoic acid 11.** To thiadiglycolic acid [2'-thiobis(acetic acid)] (5.12 g, 34.09 mmol) was added *N*(±)-2-ethylhexylamino-*o*-phenylenediamine (3.75 g, 17.03 mmol). The mixture was finely ground and stirred with heating to 140–160 °C in a molten fluid state for 4 h, then cooled to room temperature to produce a brown glassy solid which was extracted with portions of hot ethanol (5 × 50 cm<sup>3</sup>). The ethanolic solution was refluxed with decolourising charcoal for 1 h, filtered whilst hot and reduced in volume *in vacuo* to yield a pale brown oil. The oil was dissolved in dichloromethane (3 × 200 cm<sup>3</sup>), washed with water (5 × 150 cm<sup>3</sup>) and dried over anhydrous magnesium sulfate. The organic extracts were filtered and reduced *in vacuo* to yield a brown oil. Thin-layer chromatography of the crude oil indicated the presence of two major products [the desired *N*-alkylated benzimidazole acid *R*<sub>f</sub> ≈ 0.3 and the unwanted fully condensed *N*-alkylated bis(benzimidazole) *R*<sub>f</sub> ≈ 0.9]. The oil was purified *via* flash chromatography (35–70 μm silica; eluent CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>2</sub>OH, 10 : 1) to yield the *N*-alkylated benzimidazole acid as a colourless oil. The oil was triturated with diethyl ether to yield a pure white solid **11**. Yield 1.08 g, 19%; m.p. 108 °C (Found: C, 64.6; H, 7.6; N, 8.5. C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 64.6; H, 7.8; N, 8.4%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.90–0.98 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.19–1.79 [m, 8 H, alkyl (R)], 1.97–2.17 [br m, 1 H, CH (R)], 3.30 (s, 2 H, CH<sub>2</sub>CO<sub>2</sub>), 4.12–4.16 (d, 2 H, NCH<sub>2</sub>), 4.30 (s, 2 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 7.28–7.42 (m, 3 H, H<sup>4–6</sup> of aryl), 7.81–7.89 (m, 1 H, H<sup>7</sup> of aryl) and 11.33 (br s, OH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 172.1 (C=O), 150.6 (C<sup>2</sup>), 139.4 (C<sup>9</sup>), 135.1 (C<sup>8</sup>), 123.6 (C<sup>5</sup>), 123.1 (C<sup>6</sup>), 118.9 (C<sup>4</sup>), 110.3 (C<sup>7</sup>), 48.3 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 40.0 (NCH<sub>2</sub>), 36.4 (CH<sub>2</sub>CO<sub>2</sub>) and 30.9–10.9 (remaining C atoms of alkyl chains). FAB mass spectrum: *m/z* 335 (*M* + H<sup>+</sup>, 100%).

The benzimidazole carboxylic acid ligands **12–15** were prepared according to the general procedure outlined above.

**4-[*N*(±)-2-Ethylhexylbenzimidazolyl]-3-oxabutanoic acid 12.** To diglycolic acid [2-oxybis(acetic acid)] (4.43 g, 33.04 mmol) was added *N*(±)-2-ethylhexylamino-*o*-phenylenediamine (3.64 g, 16.53 mmol). The oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane; 1 : 10) to give a viscous colourless oil which was triturated with diethyl

¶ No attempt has been made to separate the (+) and (–) isomers.

ether to yield a pure white *solid*. Yield 1.98 g, 38%; m.p. 105 °C (Found: C, 68.3; H, 8.5; N, 8.8. C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub> requires C, 67.9; H, 8.2; N, 8.8%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.86–0.94 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.16–1.42 [m, 8 H, alkyl (R)], 1.96–2.02 [br m, 1 H, CH (R)], 4.13 (s, 2 H, CH<sub>2</sub>CO<sub>2</sub>), 4.13–4.17 (d, 2 H, NCH<sub>2</sub>), 5.13 (s, 2 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 7.26–7.41 (m, 3 H, H<sup>4+6</sup> of aryl), 7.77–7.83 (m, 1 H, H<sup>7</sup> of aryl) and 12.05 (br s, OH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 172.0 (C=O), 149.1 (C<sup>2</sup>), 138.5 (C<sup>9</sup>), 134.2 (C<sup>8</sup>), 123.1 (C<sup>5</sup>), 122.4 (C<sup>6</sup>), 118.3 (C<sup>4</sup>), 109.8 (C<sup>7</sup>), 66.0 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 62.4 (CH<sub>2</sub>CO<sub>2</sub>), 47.6 (NCH<sub>2</sub>) and 38.9–10.0 (remaining C atoms of alkyl chains). FAB mass spectrum: *m/z* 319 (M + H<sup>+</sup>, 60%). EI mass spectrum: *m/z* 318.1958 (M<sup>+</sup>, 15%); C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub> requires 318.1943.

**7-[N-(±)-2-Ethylhexylbenzimidazolyl]-3,6-dioxahexanoic acid 13.** To 3,6-dioxaoctanedioic acid (4.85 g, 27.23 mmol) was added *N*-(±)-2-ethylhexylamino-*o*-phenylenediamine (3.00 g, 13.36 mmol). The oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane, 1:10) to give a viscous colourless *oil*. Yield 1.65 g, 34% (Found: C, 66.6; H, 8.2; N, 7.5. C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> requires C, 66.3; H, 8.3; N, 7.7%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.84–0.92 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.15–1.40 [m, 8 H, alkyl (R)], 1.94–2.01 [br m, 1 H, CH (R)], 3.74 (s, 4 H, OCH<sub>2</sub>), 4.14 (s, 2 H, CH<sub>2</sub>CO<sub>2</sub>), 4.14–4.17 (d, 2 H, NCH<sub>2</sub>), 4.97 (s, 2 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 7.24–7.39 (m, 3 H, H<sup>4+6</sup> of aryl), 7.77–7.83 (m, 1 H, H<sup>7</sup> of aryl) and 10.05 (br s, OH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 173.0 (C=O), 150.2 (C<sup>2</sup>), 140.0 (C<sup>9</sup>), 135.0 (C<sup>8</sup>), 123.7 (C<sup>5</sup>), 123.0 (C<sup>6</sup>), 119.3 (C<sup>4</sup>), 110.5 (C<sup>7</sup>), 70.7 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 69.3 (OCH<sub>2</sub>), 69.2 (OCH<sub>2</sub>), 64.2 (CH<sub>2</sub>CO<sub>2</sub>), 48.4 (NCH<sub>2</sub>) and 39.7–10.8 (remaining C atoms of alkyl chains). FAB mass spectrum: *m/z* 363 (M + H<sup>+</sup>, 85%). EI mass spectrum: *m/z* 362.2217 (M<sup>+</sup>, 90%); C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> requires 362.2206.

**10-[N-(±)-2-Ethylhexylbenzimidazolyl]-3,6,9-trioxadecanoic acid 14.** To 3,6,9-trioxadecanedioic acid (7.52 g, 33.86 mmol) was added *N*-(±)-2-ethylhexylamino-*o*-phenylenediamine (3.61 g, 16.37 mmol). The oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane, 1:10) to give a viscous colourless *oil*. Yield 2.46 g, 37% (Found: C, 66.1; H, 8.6; N, 7.0. C<sub>22</sub>H<sub>34</sub>N<sub>2</sub>O<sub>5</sub> requires C, 65.0; H, 8.4; N, 6.9%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.79–0.87 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.18–1.34 [m, 8 H, alkyl (R)], 1.88–2.10 [br m, 1 H, CH (R)], 3.55–3.72 (m, 8 H, OCH<sub>2</sub>), 4.06–4.09 (d, 2 H, NCH<sub>2</sub>), 4.13 (s, 2 H, CH<sub>2</sub>CO<sub>2</sub>), 4.85 (s, 2 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 7.20–7.32 (m, 3 H, H<sup>4+6</sup> aryl), 7.70–7.77 (m, 1 H, H<sup>7</sup> of aryl) and 10.05 (br s, OH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 173.1 (C=O), 150.5 (C<sup>2</sup>), 140.4 (C<sup>9</sup>), 135.1 (C<sup>8</sup>), 123.5 (C<sup>5</sup>), 122.8 (C<sup>6</sup>), 119.4 (C<sup>4</sup>), 110.4 (C<sup>7</sup>), 71.0 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 70.6 (OCH<sub>2</sub>), 70.4 (OCH<sub>2</sub>), 69.6 (OCH<sub>2</sub>), 69.4 (OCH<sub>2</sub>), 69.0 (OCH<sub>2</sub>), 64.7 (CH<sub>2</sub>CO<sub>2</sub>), 48.3 (NCH<sub>2</sub>) and 39.7–10.8 (remaining C atoms of alkyl chains). FAB mass spectrum: *m/z* 407 (M + H<sup>+</sup>, 40%). EI mass spectrum: *m/z* 406.2458 (M<sup>+</sup>, 40%). C<sub>22</sub>H<sub>34</sub>N<sub>2</sub>O<sub>5</sub> requires 406.2468.

**7-[2-N-(±)-2-Ethylhexylbenzimidazolyl]-catechol-*o,o*-acetic acid 15.** To catechol-*o,o*-diacetic acid (5.35 g, 23.65 mmol) was added *N*-(±)-2-ethylhexylamino-*o*-phenylenediamine (2.60 g, 11.83 mmol). The oil was purified *via* flash chromatography (35–70 μm silica; eluent methanol–dichloromethane, 1:10) to give a viscous colourless oil which was triturated with diethyl ether to yield a pure white *solid*. Yield 1.31 g, 27%; m.p. 138 °C (Found: C, 70.2; H, 7.4; N, 6.8. C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> requires C, 70.2; H, 7.4; N, 6.8%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.82–0.91 [m, 6 H, 2 × CH<sub>3</sub> (R)], 1.23–1.52 [m, 8 H, alkyl (R)], 1.98–2.12 [br m, 1 H, CH (R)], 4.21–4.25 (d, 2 H, NCH<sub>2</sub>), 4.65 (s, 2 H, CH<sub>2</sub>CO<sub>2</sub>), 5.46 (s, 2 H, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 6.68–7.03 (m, 4 H, aryl), 7.22–7.37 (m, 3 H, aryl), 7.76–7.81 (m, 1 H, aryl) and 12.05 (br s, OH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 171.6 (C=O), 149.1 (C<sup>2</sup>), 149.0 (aryl), 146.7 (aryl), 139.3 (C<sup>9</sup>), 134.7 (C<sup>8</sup>), 124.1 (aryl), 123.5 (C<sup>5</sup>), 121.9 (C<sup>6</sup>), 119.1 (C<sup>4</sup>), 113.8 (aryl), 110.7 (C<sup>7</sup>), 66.4

**Table 2** Transport from single and binary mixtures of metal(II) ions

Ligand	Cu	Zn	Cd	Cu	Zn
<b>1</b>	144.6	209.7	27.5	171	68.7
<b>3f</b>	165.2	125.8	65.3	168.1	23.8
<b>4f</b>	143.5	127.9	58.6	137	25.2
<b>5f</b>	92.8	131.1	23.8	99.8	27.8
<b>6f</b>	88.6	188.8	18.9	104.1	10
<b>3h</b>	231.1	233.8	10.4	294	11
<b>4h</b>	226.6	275.8	10.4	303.2	13.6
<b>5h</b>	302.2	81.8	19.5	422.4	3.7
<b>6h</b>	247.1	66.1	16.5	355	4.7
<b>7h</b>	327	76.6	21.4	431.6	4.7

pH 5.05, NaO<sub>2</sub>CMe buffer. Columns 2–4; single-ion transport, feed solution, [M<sup>II</sup>] = 0.1 mol dm<sup>-3</sup>. Columns 5 and 6; transport from binary mixtures, feed solution, [M<sup>II</sup>] = 0.2 mol dm<sup>-3</sup>. pH receive 3.42.

(C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>2</sub>), 64.2 (CH<sub>2</sub>CO<sub>2</sub>), 48.6 (NCH<sub>2</sub>) and 39.9–10.8 (remaining C atoms of alkyl chains). FAB mass spectrum: *m/z* 411 (M + H<sup>+</sup>, 35%). EI mass spectrum: *m/z* 410.2186 (M<sup>+</sup>, 20%); C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> requires 410.2206.

## Results

The hydrophobic benzimidazoles transported Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> at transport rates [or flux (*J<sub>m</sub>*)] shown in Tables 2–7. The transport rates and potential metal-ion selectivity of the hydrophobic benzimidazole ligands are considered in terms of hydrophobicity and branching, N-alkyl substitution and the nature (by systematic alteration of the bridge length using additional ether donor atoms and methylene spacer groups) of the linking bridge under conditions of multiple-ion transport (*i.e.* more than one metal present).

### Three-phase single-ion transport

The ligands **1**, **3f**, **3h–6f**, **6h** and **7h** were found to transport Cu<sup>2+</sup> (*J<sub>m</sub>*, 88.5–327.0) and Zn<sup>2+</sup> (*J<sub>m</sub>*, 66.1–275.8) effectively (Table 2, columns 2–4) under the conditions of single-ion transport (feed phase; [M<sup>2+</sup>]<sub>total</sub> = 0.1 mol dm<sup>-3</sup>, pH = 5.05 with NaO<sub>2</sub>CMe buffer). Significant transport of Cd<sup>2+</sup> is only effected by the fully alkylated thioether bridged ligands **3f** (*J<sub>m</sub>*, 65.3) and **4f** (*J<sub>m</sub>*, 58.6). Transport of Ni<sup>2+</sup> by the series of ligands **1**, **3f**, **3h–6f**, **6h** and **7h** was found to be negligible which is probably kinetic in origin due to the slow substitution of [Ni<sup>2+</sup>](aq).

**Hydrophobicity.** In considering the effect of increasing hydrophobicity, ligands **1**, **3f**, **3h–6f**, **6h** and **7h** were examined under single-ion transport conditions (Table 2, columns 2–4). These ligands contain comparable ether and thioether linking bridges but possess alkyl chains of differing hydrophobicity. Increasing the degree of hydrophobicity (stearyl < hexadecyl < octadecyl < iso-octadecyl) has little or no effect on metal-ion selectivity as expected. The hydrophobic alkyl chains, lacking potential co-ordinating sites, are believed to anchor the ligand to the organic membrane and are remote from the ligand's co-ordinating environment. It is apparent that there is no clear trend linking an increase in ligand hydrophobicity to an increase in the transport rate under the conditions of single-ion transport and using chloroform as the organic membrane.

**Nature of alkyl substitution (single or double N-alkylation).** The number of alkyl groups on the bis(benzimidazole) ligands (**3f**, **3h–6f**, **6h**) has a considerable impact on metal-ion selectivity and the transport rate of flux (*J<sub>m</sub>*) of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> in single-ion transport experiments (Table 2, columns 2–4). A trend for the metal-ion transport rates (*J<sub>m</sub>*) for these ligands is identified in Table 3. The half (singly) alkylated ligands have Cu<sup>2+</sup> fluxes (*J<sub>Cu<sup>2+</sup></sub>*) 2–3 times higher than their fully (doubly) alkylated analogues. This phenomenon is also observed for the transport of Zn<sup>2+</sup> by the half-alkylated thioether-bridged lig-

**Table 3** Trend observed in metal-ion selectivity and transport rate ( $J_m$ ) from single-ion transport experiments due to the influence of alkyl substitution

Metal ion	Hydrophobic bis(benzimidazole) ligands	
	Thioether bridged	Ether bridged
Cu <sup>2+</sup>	h > f	h > f
Zn <sup>2+</sup>	h > f	f > h
Cd <sup>2+</sup>	f > h	f > h

h = Half-alkylated, f = fully alkylated.

**Table 4** Trend observed in metal-ion selectivity from single-ion transport experiments due to the influence of the linking bridge

N-Alkylation	Hydrophobic bis-benzimidazoles	
	Ether bridged	Thioether bridged
N-Alkyl	Cu <sup>2+</sup> > Zn <sup>2+</sup> ≧ Cd <sup>2+</sup>	Zn <sup>2+</sup> > (≈) Cu <sup>2+</sup> ≧ Cd <sup>2+</sup>
N,N'-Dialkyl	Zn <sup>2+</sup> > Cu <sup>2+</sup> ≧ Cd <sup>2+</sup>	Cu <sup>2+</sup> > (≈) Zn <sup>2+</sup> ≧ Cd <sup>2+</sup>

ands **3h** and **4h**. These ligands promote Zn<sup>2+</sup> fluxes ( $J_{Zn^{2+}}$ ) twice those of their fully alkylated analogues **3f** and **4f** but the reverse situation arises for the ether-bridged ligands; ( $J_{Zn^{2+}}$ ) **5f**, **6f** > **5h**, **6h**. Although the transport of Cd<sup>2+</sup> by the hydrophobic bis(benzimidazole) ligands is relatively low, the trend cannot be ignored. The fully alkylated ligands promote a higher Cd<sup>2+</sup> flux ( $J_{Cd^{2+}}$ ) than do their half-alkylated analogues under the conditions of single-ion transport.

**Nature of linking bridge.** The effect of alkyl substitution on metal-ion selectivity is also associated with the nature of the linking bridge. The half-alkylated ligands containing an ether bridge (**5h–7h**) have a higher Cu<sup>2+</sup> flux ( $J_{Cu^{2+}}$ ) in comparison to the Zn<sup>2+</sup> fluxes ( $J_{Zn^{2+}}$ ), *i.e.*  $J_{Cu^{2+}} > J_{Zn^{2+}}$  (Table 2). This phenomenon is reversed for the fully alkylated analogues (**1**, **5f** and **6f**), *i.e.*  $J_{Zn^{2+}} > J_{Cu^{2+}}$ . Concerning the thioether-bridged ligands a complete reversal in trend arises; half-alkylated ligands **3h** and **4h** have higher Zn<sup>2+</sup> fluxes  $J_{Zn^{2+}} > J_{Cu^{2+}}$  whereas the fully alkylated ligands **3f** and **4f** have higher Cu<sup>2+</sup> fluxes  $J_{Cu^{2+}} > J_{Zn^{2+}}$ . The fully alkylated thioether-bridged ligands **3f** and **4f** display a marginal affinity for transporting Cd<sup>2+</sup>  $J_{Cd^{2+}} = 65.3$  and  $J_{58.6}$  respectively. The remaining ligands of the series showed little propensity to transport Cd<sup>2+</sup>;  $J_{Cd^{2+}} = 10.4–27.5$ . The trend is identified in Table 4. Overall, the single-ion transport results suggested copper and zinc selectivity might be established with the half-alkylated ether-bridged (**5h–7h**) and fully alkylated bridged (**1**, **5f**, **6f**) ligands respectively, irrespective of the degree of hydrophobicity.

### Three-phase multiple-ion transport in binary mixtures

Pairwise comparisons of transport rate were made for the series of ligands with a buffered feed solution equimolar in both Cu<sup>2+</sup> and Zn<sup>2+</sup> ( $[M^{2+}]_{total} = 0.1 + 0.1 = 0.2 \text{ mol dm}^{-3}$ ), shown in Table 2, last two columns.

**Hydrophobicity.** As in the single-ion experiments no definitive relationship between hydrophobicity and transport rate was observed. However, results for the binary mixtures (Table 2, last two columns) suggested a slight trend, although not apparent in every case, of a decrease in transport rate by fully alkylated bis(benzimidazole) ligands for Cu<sup>2+</sup> and Zn<sup>2+</sup>, while the trend is reversed for the half-alkylated ligands.

**Nature of alkyl substitution (single or double N-alkylation).** No reversal in metal-ion selectivity between half (h) and full (f) alkyl substitution was found, contrary to the finding with single-ion transport experiments; thus for L<sup>f</sup> and L<sup>h</sup>, Cu<sup>2+</sup> > Zn<sup>2+</sup>, where L = bis(benzimidazole) ligand. Frequently, com-

**Table 5** Trend observed in metal-ion selectivity and transport rate ( $J_m$ ) from multiple-ion transport experiments due to the influence of alkyl substitution

Metal ion	Hydrophobic bis(benzimidazole) ligands	
	Thioether bridged	Ether bridged
Cu <sup>2+</sup>	h > f <sup>a</sup>	h > f <sup>a</sup>
Zn <sup>2+</sup>	f > h <sup>b</sup>	f > h <sup>a</sup>

<sup>a</sup> This trend is also observed in single-ion transport experiments. <sup>b</sup> Reverse of trend observed in single-ion transport experiments.

petitive experiments between pairs of cations have shown suppression of transport of one metal ion relative to its single-ion rate.<sup>7,14</sup> In the competition experiments described here the transport rate of Cu<sup>2+</sup> by the fully alkylated ligands remained approximately the same as in single-ion experiments but the Zn<sup>2+</sup> transport rate was dramatically suppressed. However, the half-alkylated ligands displayed an increase in the transport of Cu<sup>2+</sup> and a suppression of the Zn<sup>2+</sup> transport rate to an almost negligible level. The increase in  $J_{Cu^{2+}}$  probably reflects the use of a more concentrated binary feed solution *i.e.* an increase in total  $[M^{2+}]$  and  $[NO_3^-]$ . The relative differences in Cu<sup>2+</sup> and Zn<sup>2+</sup> transport rates arising from experiments conducted in isolation and competition are shown in SUP 57310. The half-alkylated ligands exhibited a superior discriminatory behaviour for the transport of Cu<sup>2+</sup> and Zn<sup>2+</sup> compared to their fully alkylated analogues which can be clearly seen in Table 2. The trend observed in single-ion transport was slightly altered under conditions of competition (Table 5), the half-alkylated ether and thioether ligands having a higher Cu<sup>2+</sup> flux ( $J_{Cu^{2+}}$ ) than the analogous fully alkylated ligands whereas the Zn<sup>2+</sup> flux ( $J_{Zn^{2+}}$ ) was higher for the fully alkylated ligands.

**Nature of linking bridge.** The fully alkylated ether- and thioether-bridged bis(benzimidazole) ligands displayed comparable metal-ion selectivity for Cu<sup>2+</sup> over Zn<sup>2+</sup> in binary mixtures. For the half-alkylated ligands a higher selectivity for Cu<sup>2+</sup> over Zn<sup>2+</sup> was displayed, and the oxygen-bridged ligands **5h**, **6h** and **7h** were best (Table 2, last two columns).

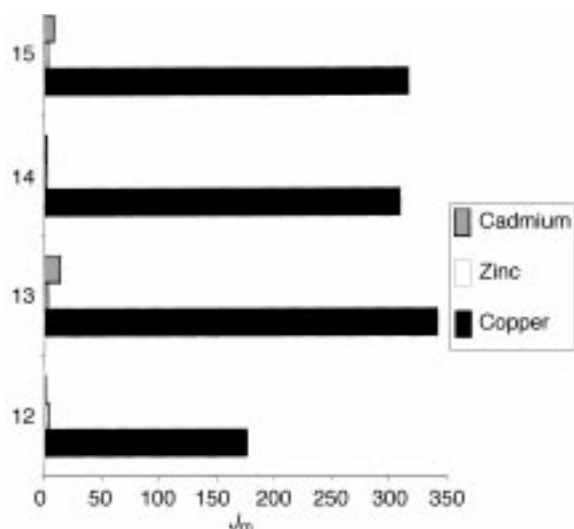
### Multiple-ion transport: tertiary mixtures

Since a direct comparison of transport rates under conditions of competition is the one of consequence in any future application, tertiary mixtures containing an aqueous buffered equimolar solution of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> were also examined as a feed solution (source phase;  $[M^{2+}]_{total} = 0.1 + 0.1 + 0.1 = 0.3 \text{ mol dm}^{-3}$ ) to determine the ultimate selectivity of the half, fully alkylated ligands (**1**, **2**, **5f**, **5h**, **8f**, **h–10f,h**) and the N-alkylated benzimidazolecarboxylic acids **12–15**. The linking bridges of these ligands were systematically altered using additional ether donor atoms and methylene spacer groups to effect a possible increase in the Zn<sup>2+</sup>, Cd<sup>2+</sup> transport rates and selectivities, thus omitting ligands **3f**, **3h**, **4f**, **4h**, **6f**, **6h** and **7h** from this study. Only one type of branched alkyl chain was used to supply hydrophobicity (hexadecyl). The effort in synthesizing ligands with a range of hydrophobic chains seemed futile following discoveries that the variation of hydrophobicity had no effect on metal-ion selectivity or flux in a chloroform organic membrane. To ensure this observation still holds using a tertiary feed of equimolar metal ions, the fully alkylated straight-chain ligands **1** and **2** were screened as a control. Variation in aromatic substitution was also considered for ligands **2** and **8**. The following results are described in terms of the nature of the linking bridge and (N- and aromatic) alkyl substitution.

**Nature of alkyl substitution (single and double N-alkylation).** As is clear from Table 6, the trend in metal-ion selectivity in tertiary mixtures for ligands **8f**, **8h–10f**, **10h** was unaffected

**Table 6** Influence of alkyl substitution on the trend in metal-ion selectivity for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in tertiary mixtures of metal(II) ions

Ether-bridged bis-benzimidazole	$J_{\text{Cu}^{2+}}$	$J_{\text{Zn}^{2+}}$	$J_{\text{Cd}^{2+}}$	Selectivity trend
<b>5h</b>	271.2	3.5	1.3	$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$
<b>5f</b>	190.4	12.4	8.3	$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$
<b>8h</b>	163.4	9.0	15.0	$\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$
<b>8f</b>	164.5	5.5	31.5	$\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$
<b>10h</b>	72.4	8.8	32.4	$\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$
<b>10f</b>	124.4	35.8	46.1	$\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$
<b>9h</b>	79.8	17.5	10.1	$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$
<b>9f</b>	86.7	23.4	17.0	$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$



**Fig. 1** Transport profile of alkylated benzimidazolecarboxylic acid ligands **12–15** for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  from multiple-ion transport experiments. Feed phase;  $[\text{M}^{2+}]_{\text{total}} = 0.3 \text{ mol dm}^{-3}$ , pH 5.05,  $\text{NaO}_2\text{CMe}$  buffer. Bars represent  $J_m$  (moles transported 24 h)  $\times 10^7$

by the single *vs.* double N-alkylation. The enhancement in  $\text{Cu}^{2+}$  transport rate ( $J_{\text{Cu}^{2+}}$ ) previously observed for the singly alkylated ligands **3h–7h** (Table 2) was not apparent for the ligands **8f**, **8h–10f**, **10h** (Table 6) when the bridge length was increased. Indeed, the fully alkylated ligands **8f–10f** were found to exhibit higher metal-ion fluxes compared to their half-alkylated analogues **8h–10h**; the exception is **5f** which has a lower copper flux ( $J_{\text{Cu}^{2+}}$ ;  $190.4 < 271.2$ ) than that of ligand **5h**. This phenomenon was previously observed with binary equimolar mixtures of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  (Table 2). Aromatic substitution with methyl groups also enhanced the transport rate and metal-ion selectivity, *cf.* ligand **2** [ $J_{\text{Cu}^{2+}}$ , 236.7;  $J_{\text{Zn}^{2+}}$ , 2.2;  $J_{\text{Cd}^{2+}}$ , 0.9] > ligand **1** [ $J_{\text{Cu}^{2+}}$ , 146.3;  $J_{\text{Zn}^{2+}}$ , 20.0;  $J_{\text{Cd}^{2+}}$ , 9.9]. As outlined earlier, the use of straight alkyl chains (ligands **1** and **2**) as opposed to branched alkyl chains does not alter the metal-ion selectivity.

**Nature of the linking bridge.** The selectivity of  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$  for the series of ligands held as the bridge length was increased through the addition of methylene spacer groups and ether donor atoms (Table 6). However, the overall selectivity for copper decreased. In general, the flux of  $\text{Cu}^{2+}$  ( $J_{\text{Cu}^{2+}}$ ) was suppressed as the bridge length was increased whereas the flux of  $\text{Zn}^{2+}$  ( $J_{\text{Zn}^{2+}}$ ) and  $\text{Cd}^{2+}$  ( $J_{\text{Cd}^{2+}}$ ) was slightly raised. The sequence of metal-ion selectivity displayed by the series of ligands is represented in Table 7.

**N-Alkylated benzimidazolecarboxylic acids.** It is evident that the benzimidazolecarboxylic acids (for which a transport profile is shown in bar graph form in Fig. 1) are extremely selective for  $\text{Cu}^{2+}$  over  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The transport rate and metal-ion

selectivity for copper were dramatically increased in comparison to those for the half (**8h–10h**) and fully alkylated (**1**, **2**, **8f–10f**) ligands. The increase in  $\text{Cu}^{2+}$  ( $J_{\text{Cu}^{2+}}$ ) flux from 176.7 for ligand **12** reached a plateau with increasing bridge length, at a  $J_m$  value of 310–340 for **13–15**; this coincided with a suppression of the  $\text{Zn}^{2+}$  ( $J_{\text{Zn}^{2+}}$ ) and  $\text{Cd}^{2+}$  ( $J_{\text{Cd}^{2+}}$ ) fluxes, 2.4–3.8 and 0.84–13.7 respectively.

## Discussion

The present study has revealed that variation in the hydrophobicity of the N-alkyl substituent of a benzimidazole had little or no effect on the metal-ion selectivity of the benzimidazole in chloroform three-phase transport. However, the choice of alkyl substituent has important implications in the hydrometallurgical industry, where the degree of hydrophobicity often governs the choice and amount of modifier that is added with the ligand to the extracting medium (to obviate surface effects and prevent leaching of the extracting medium). It had been hoped that the addition of an alkyl chain to the secondary nitrogen of a benzimidazole might also provide a more rigid ligand backbone which could enhance metal-ion selectivity because a more exact fit of the metal cation with the ligand would then be required. Previously, alkyl chains with amide and carbonyl functional groups have been used to provide benzimidazoles with hydrophobicity and extra co-ordinating sites in an attempt to improve metal-ion selectivity.<sup>7b</sup> The amide carbonyl groups supplied were found to be non-co-ordinating and these substituted alkyl chains less effective than unsubstituted alkyl chains for metal-ion transport.<sup>7c</sup>

Single-ion transport measurements permitted (Table 2) comparison of structural features of the bis-benzimidazoles with their efficacy in metal-ion transport. A subtle alteration in the number and type of donor atoms in the bridge, number of methylene spacer groups in the bridge, optimum alkyl chain length and the effect of aromatic ring substitution could increase or decrease the rate at which the ligand transported a particular metal ion. Once the optimum structural features have been established for a ligand which successfully transports the metal ion of interest, the ability to transport the metal ion in competition with other metal ions must be tested in order to ascertain if any genuine selectivity has been engineered. It seemed, following establishment of single-ion transport results, that the optimum structural features to remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  selectively from a mixture of metal ions (multiple ion) were displayed by the half (**5h–7h**) and the fully alkylated (**1**, **5f**, **6f**) ether-bridged ligands respectively; the thioether-bridged ligands (**3f**, **3h**, **4f**, **4h**) displayed comparable  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  transport rates and offered no real discrimination between the two metal ions (Table 2). The transport of  $\text{Cd}^{2+}$  by the series of ligands **1**, **3f**, **3h–6f**, **6h** and **7h** was negligible: transport was only effected by the fully alkylated thioether-bridged ligands **3f** and **4f**.

The trend in selectivity under the conditions of single-ion transport may be viewed in terms of the bridge length, donating atom (hard or soft) and the geometrical constraints provided by the ligands **1**, **3f**, **3h–6f**, **6h** and **7h**. In terms of size, the ionic radii are in the sequence<sup>15</sup>  $\text{Cd}^{2+}$  (0.97),  $\text{Zn}^{2+}$  (0.74) and  $\text{Cu}^{2+}$  (0.70 Å) while  $\text{Cd}^{2+}$  is soft and  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are borderline. The size of the metal ion may partly explain the lack of  $\text{Cd}^{2+}$  transport by the series of ligands which have a  $\text{CH}_2\text{XCH}_2$  ( $\text{X} = \text{S}$  or  $\text{O}$ ) linking bridge. The bridge length is apparently too small for effective transport of a relatively large  $\text{Cd}^{2+}$  ion in comparison to the smaller metal ions  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  which have comparable ionic radii. In general the softer  $\text{Cd}^{2+}$  prefers soft thioether donating atoms whereas  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are borderline and usually prefer ether and nitrogen donating atoms (hard-soft acid-base theory).<sup>16</sup> The presence of a soft thioether donor atom from the linking bridge may be responsible for the slight transport of  $\text{Cd}^{2+}$  by ligands **3f** and **4f**. The high transport rate



**Table 7** Sequence of metal-ion selectivity displayed by ligands **1**, **2**, **5f**, **5h**, **8f**, **8h–10f**, **10h**

	<b>5h</b>	>(≈) <b>2</b>	>	<b>5f</b>	>(≈) <b>8f</b>	>(≈) <b>8h</b>	>(≈) <b>1</b>	>	<b>10f</b>	>	<b>9f</b>	>(≈) <b>9h</b>	>(≈) <b>10h</b>			
$J_{\text{Cu}^{2+}}$	271.2	>(≈) 236.7	>	190.4	>(≈) 164.5	>(≈) 163.4	>(≈) 146.3	>	124.4	>	86.7	>(≈) 79.8	>(≈) 72.4			
	<b>10f</b>	>	<b>9f</b>	>(≈) <b>1</b>	>(≈) <b>9h</b>	>	<b>5f</b>	>	<b>8h</b>	>(≈) <b>10h</b>	>	<b>8f</b>	>	<b>5h</b>	>	<b>2</b>
$J_{\text{Zn}^{2+}}$	35.8	>	23.4	>(≈) 20.0	>(≈) 17.5	>	12.4	>	9.0	>(≈) 8.8	>	5.5	>	3.5	>	2.2
	<b>10f</b>	>	<b>10h</b>	>(≈) <b>8f</b>	>	<b>9f</b>	>(≈) <b>8h</b>	>	<b>9h</b>	>(≈) <b>1</b>	>	<b>5f</b>	>	<b>5h</b>	>	<b>2</b>
$J_{\text{Ca}^{2+}}$	46.1	>	32.4	>(≈) 31.5	>	17.0	>(≈) 15.0	>	10.1	>(≈) 9.9	>	8.3	>	1.3	>	0.9

(≈) Within the boundaries of experimental error  $\pm 15\%$ .

of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  is effected by the presence of an ether donating atom in the linking bridge of **1**, **5f**, **5h–6f**, **6h** and **7h**, and is more pronounced for  $\text{Cu}^{2+}$  with the combination of a secondary arylamine functionality (half-alkylated ligands **5h–7h**).

Behr *et al.*<sup>17</sup> have described how the selectivity of a system between two cations needs to be measured in competition and not isolation. The present study reinforces this analysis, since the potential  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  selectivity predicted from the single-ion transport rates alone is not found for the mixtures (comparisons in Table 2). The order of selectivity,  $\text{Cu}^{2+} > \text{Zn}^{2+}$ , is maintained throughout the series of ligands **1**, **3f**, **3h–6f**, **3h** and **7h** irrespective of the nature of alkyl substitution and the linking bridge (S or O donor), but the observed selectivity in competitive experiments was accompanied by a fluctuation of the transport rates for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  relative to their single-ion transport rates. The transport of  $\text{Zn}^{2+}$  by the series of ligands was dramatically suppressed. The transport of  $\text{Cu}^{2+}$  was maintained for the fully alkylated ligands (**1**, **3f–6f**) and increased for the half-alkylated ligands (**3h–7h**). The increased anion concentration in the mixed-ion solution is probably relevant. The changes in transport rate induced a superior selectivity for  $\text{Cu}^{2+}$  over  $\text{Zn}^{2+}$ ; those ligands containing ether donating atoms (**5h–7h**) were best.

Undoubtedly, the unalkylated secondary nitrogen of the bis(benzimidazole) ligands (**5h–7h**) is the rationale for the striking difference in  $\text{Cu}^{2+}$  transport rates in mixtures for these ligands compared to the f analogues. This phenomenon may be related to other features of the ligand co-ordination, namely hydrogen bonding, relative dissociation rates for the metal chelates, and orientation of the ligand (and/or complex) at the interface in transport cells. The 'free' NH might enhance the rate of transport by hydrogen bonding to the counter anion ( $\text{NO}_3^-$ ) in the fashion which is displayed in the solid state in various crystal structures,<sup>12,18</sup> which would be unavailable to the fully alkylated ligands, devoid of free NH. Further, the hydrophilic nature of the unalkylated half of the bis-benzimidazole could facilitate its orientation towards the metal ion at the organic–aqueous interface, while leakage of ligand to the aqueous medium is prevented by the anchoring of the molecule to the organic phase *via* the highly hydrophobic alkyl chain connected to the opposite half of the ligand.

In considering the effect of the hydrophobic chains allusion can be made to some biological situations. With carrier molecules like valinomycin a hydrophobic 'coat' of methyl groups from *e.g.* Val, Ala, Ile and Leu apparently enables the molecule to transport enclosed potassium ions through membranes. In lipids a much longer linear alkyl chain acts as an interface but is not itself mobile. The branched alkyl chains chosen here lack the ability of the lipid chain to stack and are likely to be more disordered. Since no attempt was made to separate the optical and other isomers (possibly also congeners) of the alkyl groups used here, the compounds are unlikely to be homogeneous, but they do have a strategic 'coat' of methyl groups to assist transport.

The co-ordinating environments provided by the ligands with a  $\text{CH}_2\text{XCH}_2$  (X = S or O) linking bridge have previously been examined crystallographically.<sup>18,19</sup> In the solid state, ether-bridged ligands provided the expected  $\text{N}_2\text{O}$  donor set from the tertiary nitrogen atoms of the benzimidazole heterocycle and

the ether donating atom from the linking bridge to both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The copper and zinc were five-co-ordinate in a pseudo-trigonal-bipyramidal geometry with halide anions completing the remaining co-ordination sites. The thioether-bridged ligands displayed a strikingly different co-ordination mode to  $\text{Zn}^{2+}$  since the  $\text{Zn}^{2+}$  was found to be in its 'preferred' four-co-ordinate tetrahedral environment. The benzimidazole ligand provided an  $\text{N}_2$  donor set only; the thioether donating atom of the linking bridge did not participate in the co-ordination of the central zinc atom, and the remaining co-ordination sites were filled by halide anions. If such a rigid tetrahedral co-ordinating environment were to be maintained in solution this could aid selectivity. Ligands which impose a defined geometric array of donor atoms may induce the selective binding of a particular metal ion. Nickel(II), copper(II) and iron(III) prefer octahedral/square planar, square planar and octahedral geometrical environments respectively whilst zinc(II) has a complete  $d^{10}$  electronic configuration and is not subject to any crystal field stabilisation energy effects or preferred co-ordinating environments. Therefore, a rigid tetrahedral donor environment<sup>20</sup> could co-ordinate  $\text{Zn}^{2+}$  in preference to other transition metals. The solid-state structural comparison of the thioether- and ether-bridged ligands may suggest stronger bonding to  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with ligands possessing ether donating atoms in the linking bridge rather than thioether donating atoms. It is probable that the smaller ether donating atom of the linking bridge can co-ordinate more readily to  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  in comparison to the larger thioether donating atom which is apparently sterically hindered and is unable to provide a co-ordination site for the central zinc atom when constrained.

The enhancement in  $\text{Cu}^{2+}$  transport rates occurring for the half-alkylated ligands possessing a  $\text{CH}_2\text{XCH}_2$  (X = S or O) bridge is diminished as the bridge length is increased for the series of ligands **1**, **2**, **5h**, **5f**, **8f**, **8h–10f**, **10h** (Table 6). The suppression of this effect (nature of alkyl substitution) with increasing bridge length demonstrates that the geometrical, structural, and donor atom properties of the linking bridge are the most important facets of a bis(benzimidazole) ligand when considering metal-ion selectivity. While the overall selectivity of  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$  for the series of ligands holds as the bridge length increases, nevertheless as the bridge length increases the selectivity for larger metal ions such as  $\text{Cd}^{2+}$  increases whereas the selectivity for smaller metal ions decreases.

The results of metal-ion selectivity for the entire series of ligands can be summarised for three-phase transport. In general  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ ; metal-ion selectivity diminishes as bridge length increases but the trend in selectivity holds.

The transport of a metal ion through a bulk liquid membrane is believed to be dominated by three major rate processes:<sup>12b,c,21</sup> the net rate at which the metal ion [and its anion(s)] crosses the feed phase and associates with the ligand, the rate at which the ligand–metal complex crosses the organic membrane and the rate at which the cation can dissociate itself from the ligand into the receive phase. Therefore at one, a combination, or all of these stages the  $\text{Cu}^{2+}$  is 'winning' against  $\text{Zn}^{2+}$ . The ligands **1**, **2**, **3f**, **3h–6f**, **6h** and **7h** which possess a short bridge length have discriminated against  $\text{Cd}^{2+}$ . Although as the bridge length increases for the series of ligands **1**, **2**, **5h**, **5f**, **8f**, **8h–10f**, **10h** the discrimination changes in favour of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  remains

the 'winning' metal ion. This phenomenon may be attributed to the kinetic lability (and thermodynamic stability)<sup>22</sup> of Cu<sup>2+</sup> in comparison to those of Zn<sup>2+</sup> and Cd<sup>2+</sup>.

The N-alkylated benzimidazolecarboxylic acids (12–15) proved to be the most selective ligands for the extraction of Cu<sup>2+</sup> in three-phase transport (Fig. 1). Introduction of a longer bridge reduced the overall Cu<sup>2+</sup> selectivity and could be viewed in the terms described above, but in general there remains a high selectivity for Cu<sup>2+</sup> throughout the series. It is probable that the benzimidazolecarboxylic acids do not behave as neutral carriers and may participate in counter-current transport: metal ions transported in one direction and protons in the opposite direction.<sup>23</sup> The transport process for carriers bearing carboxylate functionalities is known to be extremely pH dependent; a change in pH of the buffered regime may cause dramatic changes in transport rates and even alter metal-ion selectivities.<sup>24</sup>

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