FULL PAPER

Dalton
www.rsc.org/dalton

Dinuclear zinc(II) dithiocarbamate macrocycles: ditopic receptors for a variety of guest molecules

Wallace W. H. Wong, David Curiel, Andrew R. Cowley and Paul D. Beer*

Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: paul.beer@chem.ox.ac.uk

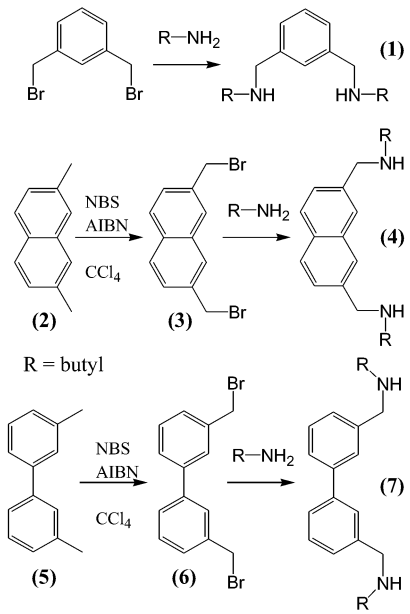
Received 14th October 2004, Accepted 12th November 2004
First published as an Advance Article on the web 8th December 2004

The synthesis of a series of dinuclear zinc(II) dithiocarbamate (dtc) macrocyclic receptors containing aryl spacer groups of different sizes is reported. As evidenced from ^{1}H NMR titration investigations, these receptors have the ability to bind various neutral and anionic bidentate guests species, including 1,4-diazabicyclo[2.2.2]octane (DABCO), isonicotinate and terephthalate in a cooperative 1 : 1 intramolecular inclusion complex. Stability constant determinations reveal a correlation between the strength of complexation and complementary receptor cavity : guest molecule size. In particular, the X-ray structure of a 1 : 1 host–guest complex between a dinuclear zinc(II) dtc receptor and DABCO illustrates the cooperative nature in which the dinuclear receptor associates with the bidentate guest.

1 Introduction

The method of metal-directed self-assembly has lead to the synthesis of numerous two- and three-dimensional macrocyclic and cage-like systems for host–guest complexation.[1] By choosing appropriate polydentate ligands and metal centers, complicated and unusual molecular architectures, such as helical structures, tubes, ladders and grids, are attainable.[1] In particular, some of these examples highlight the extensive uses of polydentate pyridyl and oligocatecholate ligands with a variety of metals.[2]

We have been exploiting the application of dithiocarbamate based ligands in the metal directed self-assembly of a large variety of supramolecular architectures such as calixarene[3] and resorcarene[4] based assemblies, catenanes[5], assorted macrocycles[6], trinuclear cages[7] and cryptands.[8] In this paper we present a new series of dinuclear zinc(II) dtc receptors covering a range of sizes to enable the study of host : guest size correspondence. The affinity of these receptors to bind a series of neutral and anionic bidentate guests with varying functionalities and sizes was investigated by ^{1}H NMR titration experiments. In addition, a single crystal structure determination of a 1 : 1 dinuclear zinc(II) dtc receptor: 1,4-diazabicyclo[2.2.2]octane (DABCO) complex highlights the importance of cooperativity in the binding of bidentate guests by these ditopic receptors.



Scheme 1

2 Results and discussion

2.1 Syntheses

The general strategy used for the synthesis of the dinuclear zinc(II) dtc macrocyclic compounds involved the metal-directed assembly of the appropriate dtc ligand with zinc(II) acetate. The dtc ligands were generated *in situ* from the appropriate secondary amines, carbon disulfide and base. The secondary amine precursors were prepared by simple alkylation reactions of the appropriate dichloro, dibromo or ditosyl spacer compound and primary amine.

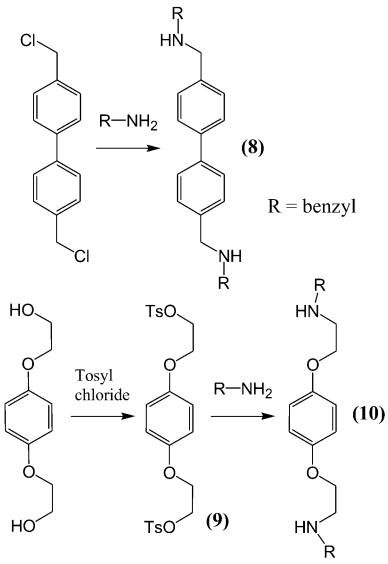
Diamine (**1**) was obtained by treating α,α′-dibromo-*m*-xylene with excess of butylamine (Scheme 1). Compounds (**4**) and (**7**) were similarly synthesised with excess butylamine and 2,7-bis(bromomethyl)naphthalene[9] (**3**) and 3,3′-bis(bromomethyl)-1,1′-biphenyl[10] (**6**), respectively (Scheme 1). The reaction between benzylamine and 4,4′-bis(chloromethyl)-1,1′-biphenyl gave compound (**8**) while tosylation of hydroquinone 2,2′-bis(hydroxyethyl) ether followed by displacement of the tosyl groups with excess benzylamine gave compound (**10**) (Scheme 2).

The new dinuclear zinc(II) dithiocarbamate macrocycles were prepared in one-pot syntheses from the appropriate diamine, triethylamine, carbon disulfide and zinc acetate hydrate to give white solids in yields ranging from 70–85% (Scheme 3 and 4). Mononuclear zinc(II) bis-diethyldithiocarbamate (**16**) was prepared following a literature procedure.[11] All products were characterised by ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis.

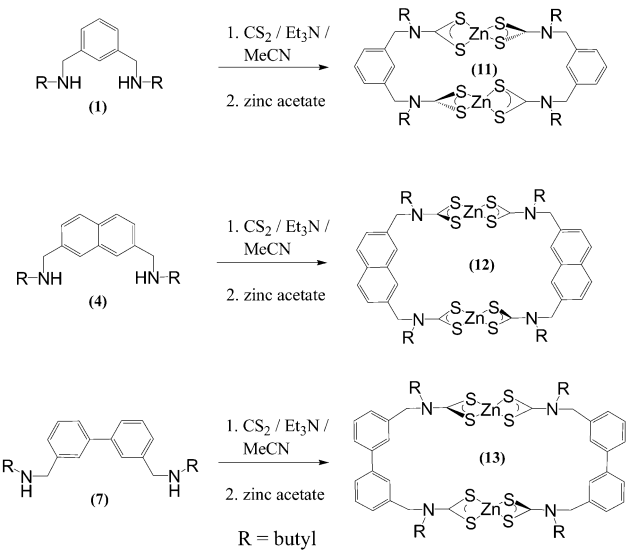
2.2 X-Ray crystal structures

Crystals of 1,4-diazabicyclo[2.2.2]octane (DABCO) bound five-coordinate zinc(II) dtc complexes suitable for single crystal X-ray structure determination were grown by the slow diffusion of diethyl ether into dichloromethane solutions of receptor–guest mixtures. The structure of the 2 : 1 complex of zinc(II) bis-diethyldithiocarbamate (**16**) and DABCO is shown in Fig. 1. The bridging DABCO ligand is disordered over two positions which are approximately related by a non-crystallographic centre of inversion, as are the two $Zn(S_2CNEt_2)_2$ groups. The large and highly-anisotropic thermal parameters of the disordered C atoms suggest that there is very little hindrance to rotation

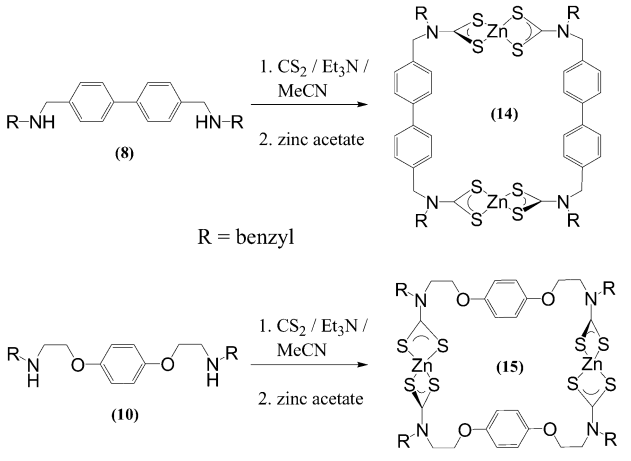
DOI: 10.1039/b415935g



Scheme 2



Scheme 3



Scheme 4

of the bridge about the N···N axis. Each zinc atom is five coordinate, being bonded to two dithiocarbamate ligands with Zn–S distances 2.357(1)–2.560(1) Å and to a DABCO nitrogen with a Zn–N distance of 2.123(3) Å. The coordination geometry about each of the Zn(1) and Zn(2) atoms can be considered as square pyramidal with the nitrogen atom occupying the axial position. Similar structures have been reported by Lai and

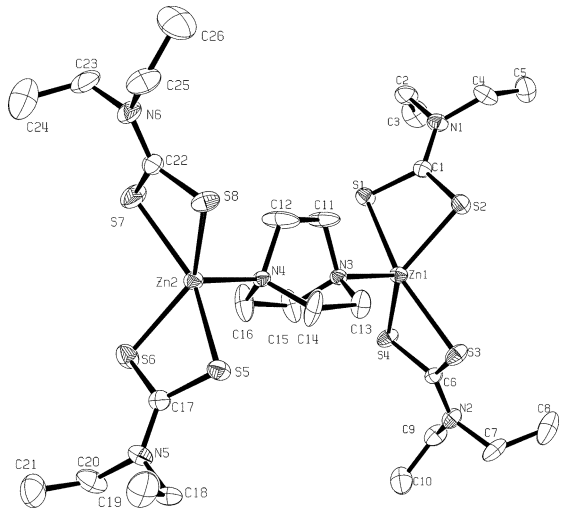


Fig. 1 Thermal ellipsoid plot at 40% probability of two $Zn(S_2CNEt_2)_2$ groups with a bridging DABCO. This view shows one orientation of the disordered DABCO bridge and hydrogen atoms have been omitted.

Tiekink for coordination complexes with the same mononuclear zinc(II) dtc compound and *trans*-1,2-bis(4-pyridyl)ethylene[12] and with 4,4′-bipyridine.[13]

A 1 : 1 receptor–guest mixture was used to obtain crystals of the inclusion complex of dinuclear zinc(II) dtc macrocycle (**12**) and DABCO. The structure of the complex is located on a crystallographic centre of inversion, which results in disorder of the DABCO bridge over two positions (Fig. 2). Each zinc atom is five coordinate, being bonded to two dithiocarbamate ligands with Zn–S distances 2.408(1)–2.495(1) Å and to a DABCO nitrogen with a Zn–N distance of 2.157(2) Å. Allowing for distortions caused by the chelating four-membered ring of the zinc dithiocarbamate, the metal environment can be considered as square pyramidal with the nitrogen atom occupying the axial position.

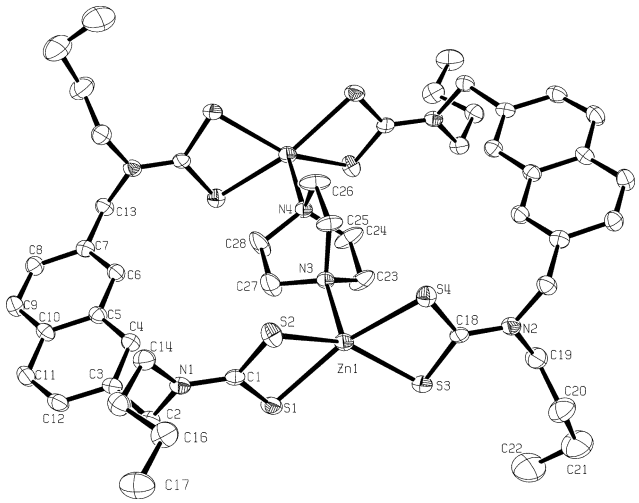


Fig. 2 Thermal ellipsoid plot of the structure of receptor (**12**) and DABCO showing only one orientation of the DABCO bridge with thermal ellipsoids at 40% probability. Hydrogen atoms have been omitted.

By comparing the crystal structure of receptor (**12**) and DABCO to that of the mononuclear zinc(II) dtc compound (**16**) and DABCO, it is apparent that the naphthyl spacer group provides an ideal distance for the coordination of DABCO between the two zinc centres in the dinuclear macrocycle. The Zn(1)–Zn(2) distance in the structure of (**16**) and DABCO is 6.83 Å and can be interpreted as the thermodynamically favoured distance in a DABCO-bridged structure as there are no steric constraints (Fig. 1). In the crystal structure of receptor (**12**) and DABCO, the Zn(1)–Zn(2) distance is 6.92 Å. This small difference in the Zn(1)–Zn(2) distance between the two

structures is attributed to the rigid naphthyl spacer groups that hold the zinc(II) dtc centres apart.

2.3 Host–guest binding properties

The incorporation of the zinc(II) dithiocarbamate Lewis acid centre into a cyclic framework structure allows the potential coordination of axial ligands converting the tetrahedral $Zn(dtc)_2$ moiety into a five-coordinate square pyramidal $Zn(dtc)_2L$ complex. [12–14] The new series of ditopic dinuclear zinc(II) dtc macrocyclic receptors are designed to cooperatively bind appropriate bidentate guest species. The mononuclear zinc(II) bis-diethyldithiocarbamate compound (**16**) was used for comparison in the binding studies. Moreover, with the aim of studying the effect of size complementarity on the magnitude of receptor-guest binding, the interaction between the dinuclear zinc(II) dtc macrocycles and a range of bidentate guests 4,4′-bipyridine, DABCO, pyrazine and tetrabutylammonium (TBA) salts of terephthalate and isonicotinate, were investigated.

The binding of the guests of different sizes by dinuclear zinc(II) dtc macrocycles was examined by ^{1}H NMR titration studies. Preliminary titration experiments were performed by titrating the potential coordinating guests into solutions of receptors in 9 : 1 mixtures of $CDCl_3$: DMSO-d_6. No significant change in the proton chemical shift values of the receptors was observed, however, substantial perturbations in the proton chemical shifts of the guest species were apparent.

In order to determine stability constant values, further titration experiments were carried out by adding small aliquots of the receptor dissolved in a 9 : 1 or 3 : 1 mixture of $CDCl_3$: DMSO-d_6, depending on solubility requirements, to a solution of the coordinating guest in the same mixture of solvents and the change in chemical shift of the guest molecule protons was monitored. Typically, significant downfield shifts were detected in the proton resonances of the bidentate guests as a result of the deshielding effect caused by the interaction with the zinc centres (Fig. 3).

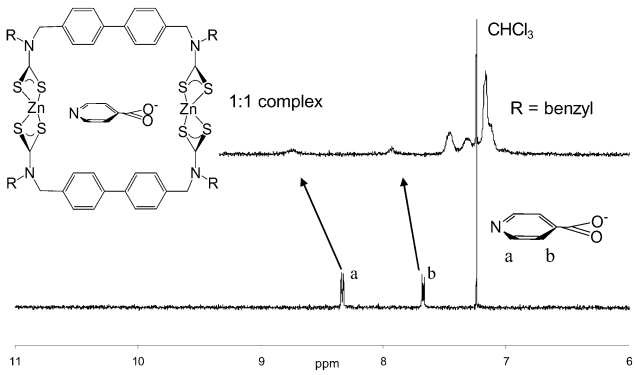


Fig. 3 ^{1}H NMR spectra of isonicotinate and after the addition of one equivalent of receptor (**14**) in $CDCl_3/d_6$-DMSO.

Job plot experiments revealed 1 : 1 and 2 : 1 host–guest binding stoichiometries depending on the relative sizes of the hosts and guests (Fig. 4). Due to the small macrocyclic cavity size, receptor (**11**) with the *m*-xylyl spacer group only forms 2 : 1 host–guest complexes. On the other hand, 4,4′-bipyridine is too large for any of the macrocycles in this study and the binding stoichiometry for receptors (**12**)–(**15**) with 4,4′-bipyridine was also found to be 2 : 1 host–guest in Job plot experiments (Fig. 4b).[14] The host–guest binding stoichiometry for receptors (**12**)–(**15**) with bidentate guests DABCO, isonicotinate and terephthalate was found to be 1 : 1 indicating the formation of intramolecular inclusion complexes (Fig. 4a).

EQNMR[15] analysis of the resulting titration curves gave stability constant values shown in Table 1. Interestingly, all stability constant values obtained by applying 2 : 1 host–guest binding stoichiometry are similar in magnitude (Table 1). The binding of bidentate guest species outside the receptor cavity is expected to be unaffected by receptor macrocyclic ring size.

In general for the 1 : 1 complexes, Table 1 reveals a correlation between host–guest size complementarity and the magnitude of stability constant values. All the receptors (**12**)–(**15**) bind strongly the bidentate anionic guest, terephthalate (Table 1). Simple molecular models[16] reveal the terephthalate guest (~7.2 Å in length) fits best between the two zinc(II) dtc centers of receptors (**12**) and (**13**), which have Zn–Zn distances of 8.1 and 8.7 Å, respectively. It is difficult to rationalise why receptors (**14**) and (**15**) form such strong complexes as the Zn–Zn distances in these hosts are much larger *ca.* 12 Å. The flexible ethylene linkers to the hydroquinone spacer groups of receptor (**15**) may allow for variation in the intramolecular Zn–Zn distance of the receptor.

The strongest host–guest complex for isonicotinate was obtained with receptor (**14**) bearing a *p*-biphenyl spacer (Table 1). Related to the recognition of terephthalate and isonicotinate it is worth mentioning that none of the zinc(II) dtc receptor systems interacted with benzoate in control experiments carried out during this study. This again highlights the importance of the cooperativity between the two Lewis acidic zinc(II) dtc centers in the dinuclear systems for the binding of bidentate guests. Additional evidence for the formation of 1 : 1 inclusion complexes was observed using electrospray mass spectrometry (ESMS). The molecular ion for the host–guest complex of isonicotinate and receptor (**15**) were observed in the negative ion mode of ESMS (Fig. 5).

In the binding studies of DABCO, a large stability constant value (6000 M^{-1}) was obtained for zinc(II) dtc receptor (**12**). Evidence for the formation of an inclusion complex of receptor (**12**) and DABCO in solution was observed by NOE experiments. An *intermolecular* NOE signal was detected between the DABCO protons and the receptor naphthalene protons at the 1-position. The crystal structure of receptor (**12**) and DABCO highlights the host–guest complementarity of the complex in the solid state (Fig. 2).

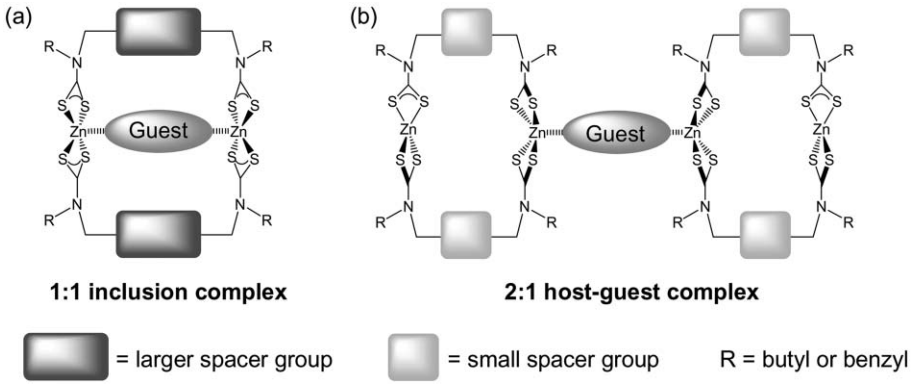


Fig. 4 Illustrations of the two binding modes observed in ^{1}H NMR titration experiments.

Table 1 Stability constant values (M^{-1}) for zinc(II) dtc receptors and a variety of guests[a]

		Increasing size of macrocyclic cavity →				
		(**11**)	(**12**)	(**13**)	(**14**)	(**15**)
Larger guest ↑	4,4′-Bipyridine	[b]	5400/250	5500/250	5200/300	4000/300
	Terephthalate[c]	5000/200	5000	>10000	8000	>10000
	Isonicotinate	[b]	700	3500	6500	2000
	DABCO	3000/300	6000	3800	1500	>10000
	Pyrazine	[b]	400	[b]	[b]	[b]

[a] Titrations were performed at 295 K in $CDCl_3/d_6$-DMSO 9 : 1 unless stated otherwise. Stability constant values (error = ±10%) were calculated from 1 : 1 (K) and 2 : 1 (K_1/K_2) host–guest stoichiometric models. [b] Negligible change in the chemical shifts of the guest protons was observed. [c] Titration experiments with terephthalate were performed in $CDCl_3/d_6$-DMSO 3 : 1.

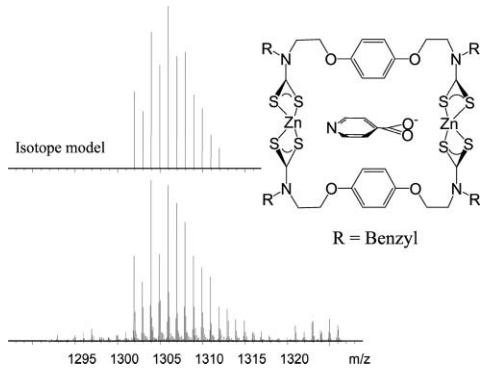


Fig. 5 Negative ion ESMS spectrum of the inclusion complex of receptor (**15**) and isonicotinate.

It is noteworthy that the magnitude of DABCO stability constant values decreases in the order (**12**) > (**13**) > (**14**) as the macrocycle cavity size increases. Interestingly, although of similar size to (**14**), receptor (**15**) forms a very stable 1 : 1 complex with DABCO which, as observed with the terephthalate guest, may reflect this macrocycle's ability to alter its cavity size.

Despite the similarity in size between pyrazine and DABCO, pyrazine does not interact significantly with any of the zinc(II) dtc receptors except for receptor (**12**) (Table 1). A stability constant value of 6000 M^{-1} was found for DABCO with receptor (**12**) compared to 400 M^{-1} for pyrazine. This difference between the stability of the complexes is probably due to the different electron density distributions of DABCO and pyrazine whereby DABCO is a better σ donor than pyrazine. This is in agreement with earlier work reported by Maverick *et al.*[17] They found DABCO and their dinuclear copper(II) acetoacetonate-type (acac) macrocycle with naphthyl spacer groups formed a relatively strong 1 : 1 inclusion complex ($K = 220$ M^{-1} in $CDCl_3$) but the binding of pyrazine ($K = 5$ M^{-1} in $CDCl_3$) by their receptor was significantly weaker.

The mononuclear zinc(II) bis-diethyldithiocarbamate receptor (**16**) was titrated with the whole series of bidentate guests. In general, binding was found to be extremely weak. Only small changes in the chemical shifts of the guest species were observed and the stoichiometry of binding did not fit well with either 1 : 1 or 1 : 2 guest–host models. As a consequence, reliable stability constant values could not be determined.

Conclusion

A series of new dinuclear zinc(II) dithiocarbamate macrocyclic receptors containing various aryl spacer groups of different sizes have been prepared. ^{1}H NMR titration studies revealed these ditopic receptor systems form strong 1 : 1 inclusion complexes with a variety of bidentate guests such as terephthalate, isonicotinate and DABCO where the guest is bound in a cooperative intramolecular manner between the receptors' two Lewis acidic zinc(II) dtc centers. A correlation between the strength of complexation and complementary receptor cavity : guest molecule size was observed generally. For example, the biphenyl spaced receptor (**14**) preferably binds terephthalate over DABCO whereas with the smaller rigid naphthalene spaced receptor (**12**), the reverse trend is observed. This highlights the importance of cooperative binding of bidentate guests of complementary size between the respective receptor's zinc(II) dtc centers.

3 Experimental

3.1 General details

NMR spectra were recorded on a Varian 300 MHz and 500 MHz spectrometers. Mass spectrometry was carried out on a Micromass LCT electrospray mass spectrometer (ESMS, cone voltage = 20–50 V, desolvation temperature = 80 °C, source temperature = 60 °C). Elemental analysis was performed at the Inorganic Chemistry Laboratory, Oxford.

3.2 Syntheses

Mononuclear zinc(II) bis-diethyldithiocarbamate[11] (**16**) was prepared by following procedures in the literature as were 2,7-bis(bromomethyl)naphthalene[9] (**3**) and 3,3′-bis(bromomethyl)-1,1′-biphenyl[10] (**6**). Tetrabutylammonium terephthalate and isonicotinate were prepared from their respective acids by reacting with tetrabutylammonium hydroxide (40% wt/v *aq.*). All other reagents were obtained from commercial sources and used without further purification.

Hydroquinone 2,2′-bis(tosylethyl) (9). An aqueous sodium hydroxide solution (14 g in 20 ml) was added to a solution of hydroquinone bis(hydroxyethyl) ether (11.5 g) in THF (100 ml) and the mixture was cooled to 0 °C with stirring. Tosyl chloride (25 g) in THF (50 ml) was added dropwise and the mixture was stirred for 2 h at 0 °C. The reaction mixture was poured into ice water (100 ml) and the product was extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous $MgSO_4$. A white powder (30 g, 82% yield) was collected on solvent removal.

^{1}H NMR (300 MHz, $CDCl_3$, 288 K) $\delta = 7.80$ (d, 6.3 Hz, 2H, tosyl), 7.33 (d, 6.3 Hz, 2H, tosyl), 6.66 (s, 4H, hydroquinone), 4.30 (t, 6.6 Hz, 4H, -CH_2-), 4.06 (t, 6.6 Hz, 4H, -CH_2-), and 2.42 (s, 6H, CH_3). MS (ESI positive ion, MeOH/CH_2Cl_2): m/z 507 [M + H$^+$].

Secondary diamine compounds (1), (4), (7), (8) and (10). Ditosyl, bis(chloromethyl) and bis(bromomethyl) compounds were treated with excess amine (butylamine or benzylamine). The reaction mixtures were stirred overnight and the excess amine was removed under vacuum. The residue was redissolved in CH_2Cl_2 (50 ml) and washed with water (3 × 50 ml). The

organic layer was collected and dried over anhydrous $MgSO_4$. Oily solids were obtained on solvent removal.

(**1**): A pale yellow oil was collected after drying *in vacuo* (0.5 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.2–7.3 (m, 4H, ArH), 3.81 (s, 4H, $ArCH_2$-), 2.67 (t, J = 7.2 Hz, 4H, N–CH_2-), 1.54 (m, 4H, -CH_2-), 1.36 (m, 4H, -CH_2-), 0.94 (t, J = 7.2 Hz, 6H, CH_3). MS (ESI positive ion, MeOH/CH_2Cl_2) m/z: 249 [M + H]$^+$.

(**4**): A yellow oil was collected after drying *in vacuo*. (0.45 g, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76 (d, J = 8.4 Hz, 2H, $ArH^{4/5}$), 7.70 (s, 2H, $ArH^{1/8}$), 7.41 (d, J = 8.7 Hz, 2H, $ArH^{3/6}$), 3.94 (s, 4H, $ArCH_2$), 2.66 (t, J = 7.2 Hz, 4H, NHC$H_2$$CH_2$), 1.53 (m, 4H, $NHCH_2CH_2$), 1.36 (m, 4H, C$H_2$$CH_3$), 0.91 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ = 137.75, 133.29, 131.68, 128.37, 127.04, 125.61 (ArC), 54.10, 49.11, 32.20, 20.57 (CH_2), 14.11 (CH_3). MS (ESI positive ion, MeOH/CH_2Cl_2) m/z: 298.6 [M]$^+$, 227.2 [M − NHBu]$^+$

(**7**): A yellow oil was collected after drying *in vacuo* (0.89 g, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55 (t, J = 1.5 Hz, 2H, $ArH^{2/2'}$), 7.46 (dt, J = 7.5 Hz, J' = 1.5 Hz, 2H, $ArH^{6/6'}$), 7.37 (t, J = 7.5 Hz, 2H, $ArH^{5/5'}$), 7.29 (dt, J = 7.8 Hz, J' = 1.5 Hz, 2H, $ArH^{4/4'}$), 3.88 (s, 4H, $ArCH_2$), 2.66 (t, J = 7.2 Hz, 4H, NHC$H_2$$CH_2$), 1.52 (m, 4H, $NHCH_2CH_2$), 1.36 (m, 4H, C$H_2$$CH_3$), 0.92 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ = 141.08, 140.59, 128.63, 126.98, 126.88, 125.66 (ArC), 54.08, 49.02, 32.17, 20.56 (CH_2), 14.11 (CH_3). MS (ESI positive ion, MeOH/CH_2Cl_2) m/z: 325.3 [M + H]$^+$, 252.2 [M − NHBu]$^+$

(**8**): A yellow oil was collected after drying *in vacuo* (1.0 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.57 (d, J = 8.1 Hz, 4H, ArH), 7.41 (d, J = 8.1 Hz, 4H, ArH), 7.31 (s, 10H, benzyl), 3.84 (s, 4H, $ArCH_2$-). MS (ESI positive ion, MeOH/CH_2Cl_2) m/z: 393 [M + H]$^+$.

(**10**): A yellow oil was collected after drying *in vacuo* (0.9 g, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 288 K) δ = ^{1}H NMR (300 MHz, $CDCl_3$, 288 K) δ = 7.31 (m, 10H, benzyl), 6.80 (s, 4H, hydroquinone), 4.02 (t, J = 5.1 Hz, 4H, -$NHCH_2CH_2$O-), 3.85 (s, 4H, Ar–CH_2-), 2.98 (t, J = 5.1 Hz, 4H, -NH$CH_2$$CH_2$O-). MS (EI$^+$): m/z 377 (MH$^+$).

Dinuclear zinc(II) dithiocarbamate receptors. Diamine compound (**1**), (**4**), (**7**), (**8**) or (**10**) was dissolved in THF/MeCN and two equivalents of Et_3N and CS_2 were added. The mixture was stirred at room temperature for 2 h and an equivalent of zinc acetate hydrate was added. The mixture was stirred overnight and solvent removed. The remaining solid was extracted with CH_2Cl_2 (100 ml) and the organic solution was washed with water (50 ml) followed by brine (50 ml). The organic layer was dried over anhydrous $MgSO_4$ and then filtered. The filtrate was concentrated *in vacuo* to leave a solid residue as the product. The zinc(II) dtc macrocycles were further purified by recrystallisation from CH_2Cl_2/MeOH.

(**11**): A white solid (0.5 g, 81% yield) was collected. ^{1}H NMR (300 MHz, $CDCl_3$, 288 K) δ = 7.29 (m, 2H, ArH), 7.11 (m, 6H, ArH), 5.20 (br, 8H, $ArCH_2$), 3.80 (br, 8H, NC$H_2$$CH_2$), 1.68 (m, 8H, NCH_2CH_2), 1.28 (m, 8H, C$H_2$$CH_3$), 0.88 (m, 12H, CH_3). ^{13}C NMR (75.43 MHz, $CDCl_3$) δ = 205.6 (CS_2), 135.7, 128.6, 127.0 (ArC), 57.4, 54.3, 29.0, 20.0, (CH_2) 13.7 (CH_3). MS (ESI positive ion, MeCN): m/z 928 [M]$^+$. Anal. Calcd. for $C_{36}H_{52}N_4S_8Zn_2$: C, 46.59; H, 5.65; N, 6.04. Found: C, 46.45; H, 5.62; N, 6.06.

(**12**): A white solid (0.5 g, 80% yield) was collected. ^{1}H NMR (300 MHz, DMSO) δ = 7.92 (d, J = 8.4, 4H, ArH), 7.76 (4H, s, ArH), 7.51 (d, J = 8.4, 4H, ArH), 5.29 (s, 8H, $ArCH_2$), 3.76 (br, 8H, NC$H_2$$CH_2$), 1.65 (br, 8H, NCH_2CH_2), 1.20 (br m, 8H, C$H_2$$CH_3$), 0.83 (br, 12H, CH_3). ^{13}C NMR (75.43 MHz, DMSO) δ = 205.4 (CS_2), 134.4, 132.8, 131.8, 128.2, 125.7 (ArC), 57.1, 53.8, 28.3, 19.5 (CH_2), 13.7 (CH_3). MS (ESI positive ion, MeCN): m/z 1028 [M]$^+$. Anal. Calcd. for $C_{44}H_{56}N_4S_8Zn_2$: C, 51.40; H, 5.49; N, 5.45. Found: C, 52.11; H, 6.07; N, 5.96.

(**13**): A white solid (0.5 g, 77% yield) was collected. ^{1}H NMR (300 MHz, $CDCl_3$, 288 K) δ = 7.97 (s, 4H, ArH), 7.30 (d, J = 8.1 Hz, 4H, ArH), 7.41 (t, J = 7.5 Hz, 4H, ArH), 7.21 (d, J = 7.2 Hz, 4H, ArH), 5.21 (s, 8H, $ArCH_2$), 3.79 (br, 8H, NC$H_2$$CH_2$), 1.70 (m, 8H, NCH_2CH_2), 1.26 (m, 8H, C$H_2$$CH_3$), 0.88 (m, 12H, CH_3). ^{13}C NMR (75.43 MHz, $CDCl_3$) δ = 205.1 (CS_2), 141.0, 135.7, 129.1, 126.9, 126.2 (ArC), 57.4, 54.0, 28.8, 20.0, (CH_2) 13.7 (CH_3). MS (ESI positive ion, MeCN): m/z 1080 [M]$^+$. Anal. Calcd. for $C_{48}H_{60}N_4S_8Zn_2$: C, 53.36; H, 5.60; N, 5.19. Found: C, 50.21; H, 5.65; N, 5.06.

(**14**): A white solid (2 g, 70% yield) was collected. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61 (d, J = 7.2 Hz, 8H, $ArH^{2/6}$), 7.44 (d, J = 7.2 Hz, 8H, $ArH^{3/5}$), 7.37 (m, 20H, benzyl), 5.09 (s, 16H, $ArCH_2$). ^{13}C NMR (75.43 MHz, $CDCl_3$) δ = 206.1 (CS_2), 140.4, 134.4, 133.7, 128.9, 128.5, 128.3, 128.0, 127.6 (ArC), 52.9, 55.4 (CH_2). MS (ESI positive ion, CH_2Cl_2/MeOH): m/z 1214 [M]$^+$. Anal. Calcd. for $C_{60}H_{52}N_4S_8Zn_2$: C, 59.24; H, 4.31; N, 4.61. Found: C, 58.46; H, 4.49; N, 4.81.

(**15**): A white solid (5 g, 85% yield) was collected. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37 (m, 20H, benzyl) 6.82 (s, 8H, hydroquinone), 5.30 (s, 8H, -O$CH$$CH_2$N-), 4.29 (t, J = 5.4 Hz, 8H, -$OCH_2$$CH_2$N-), 4.11 (t, J = 5.4 Hz, 8H, NC$H_{22}$$CH_2$). ^{13}C NMR (75.43 MHz, $CDCl_3$) δ = 205.7, 152.6, 134.9, 134.7, 128.9, 128.0, 65.6, 59.7 and 52.3 ppm. MS (ESI positive ion, CH_2Cl_2/MeOH): m/z 1205 [M]$^+$. Anal. Calcd. for $C_{52}H_{52}N_4O_4S_8Zn_2$: C, 52.74; H, 4.43; N, 4.73. Found: C, 52.02; H, 4.56; N, 5.02.

3.3 X-Ray crystallography

Sinlge crystals of the zinc(II) bis-diethyldithiocarbamate and DABCO complex were grown by slow diffusion of methanol into a dichloromethane solution of a 1 : 1 mixture of zinc(II) bis-diethyldithiocarbamate (**16**) and DABCO while crystals of the complex of receptor (**12**) and DABCO were grown by slow diffusion of methanol into a dichloromethane solution of a 1 : 1 mixture of receptor (**12**) and DABCO. Crystals were mounted on a glass fibre and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit. Intensity data were processed using the DENZO-SMN package.[18] Structures were solved by direct methods using the SIR92 program.[19] Full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[20] Hydrogen atoms were positioned geometrically after each cycle of refinement. A Chebychev polynomial weighting scheme was applied.

Crystal data for zinc(II) bis-diethyldithiocarbamate (**16**) and DABCO, $C_{26}H_{52}N_6S_8Zn_2$, M = 836.03, Orthorhombic, a = 21.7324 (3), b = 7.2463 (2), c = 24.1595 (4) Å, α = β = γ = 90°, U = 3804.63 (13) Å^3, T = 150 K, space group Pca 2$_1$, Z = 4, μ = 1.727 mm^{-1}, 27083 reflections measured, 8373 unique (R_{int} = 0.041). The final $wR(F^2)$ was 0.0365 (all data).

Crystal data for receptor (**12**) and DABCO, $C_{50}H_{86}N_6S_8Zn_2$, M = 1140.42, Triclinic, a = 11.6711 (4), b = 11.9393 (4), c = 12.4675 (4) Å, α = 110.2029° (15), β = 100.1626° (15), γ = 115.6632° (17), U = 1360.59 (9) Å^3, T = 150 K, space group $P\bar{1}$, Z = 1, μ = 1.228 mm^{-1}, 16123 reflections measured, 6073 unique (R_{int} = 0.043). The final $wR(F^2)$ was 0.0509 (all data).

CCDC reference numbers 252800–252801.

See http://www.rsc.org/suppdata/dt/b4/b415935g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge the Marie Curie Fellowship of the European Union for a postdoctoral fellowship (DC) and the EPSRC for a studentship (WWHW).

References

1 (*a*) S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972. 1; (*b*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*c*) R. W. Saalfrank and I. Bernt, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 407; (*d*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*e*) C. J.

Jones, *Chem. Soc. Rev.*, 1998, **27**, 289; (*f*) S. J. Loeb and C. R. Bondy, *Coord. Chem. Rev.*, 2003, **240**, 77.
2 (*a*) M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249; (*b*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (*c*) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. VanDorsselaer, B. Kneisel and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10956; (*d*) C. O. Dietrich-Buchecker, J. F. Nierengerten, J. P. Sauvage, N. Armaroli, V. Balzani and L. Decola, *J. Am. Chem. Soc.*, 1993, **115**, 11237; (*e*) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 3644; (*f*) D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; (*g*) C. A. Schalley, A. Lützen and M. Albrecht, *Chem. Eur. J.*, 2004, **10**, 1072.
3 P. R. A. Webber, M. G. B. Drew, R. Hibbert and P. D. Beer, *Dalton Trans.*, 2004, **8**, 1127.
4 O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 136.
5 M. E. Padilla-Tosta, O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 4235.
6 (*a*) P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, **2001**, 199; (*b*) N. G. Berry, M. D. Pratt, O. D. Fox and P. D. Beer, *Supramol. Chem.*, 2001, **13**, 677.
7 P. D. Beer, A. G. Cheetham, M. G. B. Drew, O. D. Fox, E. J. Hayes and T. D. Rolls, *Dalton Trans.*, 2003, **4**, 603.
8 P. D. Beer, N. G. Berry, A. R. Cowley, E. J. Hayes, E. C. Oates and W. W. H. Wong, *Chem. Commun.*, **2003**, 2408.
9 P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, **2001**, 199.
10 N. G. Berry, M. D. Pratt, O. D. Fox and P. D. Beer, *Supramol. Chem.*, 2001, **13**, 677.
11 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.
12 C. S. Lai and R. T. Tiekink, *Appl. Organomet. Chem.*, 2003, **17**, 251.
13 C. S. Lai and R. T. Tiekink, *Appl. Organomet. Chem.*, 2003, **17**, 253.
14 In a previous study, 4,4′-bipyridine was found to form a 1 : 1 stoichiometric complex inside the large cavity of a dinuclear zinc(II) dtc macrocycle with terphenyl spacer groups.L. H. Uppadine, J. M. Weeks and P. D. Beer, *J. Chem. Soc., Dalton Trans.*, 2001, **22**, 3367.
15 M. J. Hynes, *J. Chem. Soc., Dalton. Trans.*, 1993, 311–312.
16 *Molecular modeling program used: Quantum Cache Version 3.2*, Oxford Molecular Ltd., 1999.
17 (*a*) A. W. Maverick, S. C. Buckingham, Q. Yao, J. R. Bradbury and G. G. Stanley, *J. Am. Chem. Soc.*, 1986, **108**, 7430; (*b*) A. W. Maverick, M. L. Ivie, J. H. Waggenspack and F. R. Fronczek, *Inorg. Chem.*, 1990, **29**, 2403.
18 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods Enzymol.*1997, vol. 276, ed. C. W. Carter and R. M. Sweet, Academic Press.
19 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Ploidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
20 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.