ChemPubSoc Europe

DOI: 10.1002/chem.201500333

CHEMISTRY
A European Journal
Full Paper

Host–Guest Systems

Highly Efficient Chirality Transfer from Diamines Encapsulated within a Self-Assembled Calixarene–Salen Host

Luis Martínez-Rodríguez,[a] Nuno A. G. Bandeira,[a] Carles Bo,[a, b] and Arjan W. Kleij*[a, c]

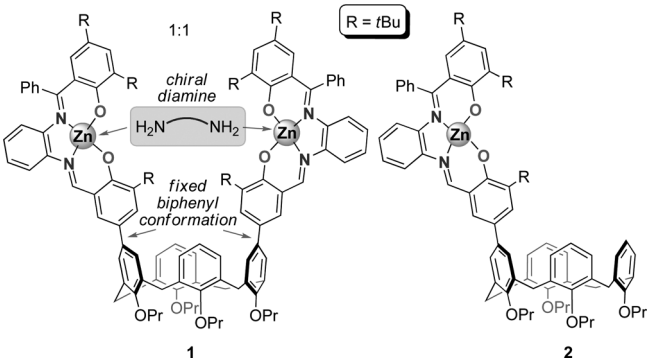
Abstract: A calix[4]arene host equipped with two bis-[Zn(salphen)] complexes self-assembles into a capsular complex in the presence of a chiral diamine guest with an unexpected 2:1 ratio between the host and the guest. Effective chirality transfer from the diamine to the calix–salen hybrid host is observed by circular dichroism (CD) spectroscopy, and a high stability constant $K_{2,1}$ of 1.59×10^{11} M^{-2} for the assembled host–guest ensemble has been determined with a substantial cooperativity factor α of 6.4. Density functional calculations are used to investigate the origin of the stability of the host–guest system and the experimental CD spectrum compared with those calculated for both possible diastereoisomers showing that the *M*,*M* isomer is the one that is preferentially formed. The current system holds promise for the chirality determination of diamines, as evidenced by the investigated substrate scope and the linear relationship between the *ee* of the diamine and the amplitude of the observed Cotton effects.

Introduction

The creation and transfer of chirality, sometimes referred to as chirogenesis, plays a key role in biological processes that involve proteins and other natural systems such as DNA.[1] Chiral transmission has also been shown to be crucial in the catalytic asymmetric synthesis of various organic compounds, in which a metal or organic catalyst favors the formation of one preferred chiral product in the enantiocontrolling step.[2] Furthermore, to date highly efficient methodologies have been designed to create materials with reversible and responsive features, and smart materials have also been developed with predesigned sensing purposes.[3] The field of chirality sensing has rapidly advanced over the last five years with a strong focus on newly designed systems that may facilitate fast and efficient determination of the concentration, absolute configuration, enantiomeric excess, and/or molecular identity of a chiral analyte.[4] Whereas bis-porphyrins have been and still continue to be popular hosts in chirality transfer processes,[4e, 5] we have recently started to use modular and easy to assemble dinuclear and trinuclear [Zn(salen)]-based hosts that show (strong) chirogenesis effects in the presence of chiral carboxylic acids,[4d] diamines, amino alcohols, and diols[6] induced by 1:1 complex formation between the host and the guest.

With most reported supramolecular host systems, the transfer of chiral information by interaction with chiral diamines is hampered by the requirement of a pretreatment of the analyte with additives, the use of a (large) excess of diamine, the requirement of air-sensitive reagents, and/or a relatively low binding constants between the host and guest partners; owing to such challenges, the quest for an efficient host system remains an important undertaking.

Herein, we present a new type of supramolecular host for chiral diamine guests that is based on a calix[4]arene–salen hybrid structure. Each calixarene unit is functionalized by two distal [Zn(salphen)] complexes connected to the upper rim of the calixarene incorporating two prochiral biphenyl units (Scheme 1; host **1**). These [Zn(salphen)] complexes are known to form stable complexes with amine donors[7] and, as such, we anticipated the easy formation of 1:1 complexes with chiral



Scheme 1. Structures of calix–[Zn(salphen)] hosts **1** and **2** and the expected coordination stoichiometry (1:1) and induction of chirality in host **1** by binding to one molecule of a ditopic chiral diamine.

[a] *L. Martínez-Rodríguez, Dr. N. A. G. Bandeira, Prof. Dr. C. Bo, Prof. Dr. A. W. Kleij*
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
E-mail: akleij@iciq.es

[b] *Prof. Dr. C. Bo*
Departament de Química Física i Inorgànica, Universitat Rovira i Virgili
Marcel·lí Domingo s/n, 43007 Tarragona (Spain)

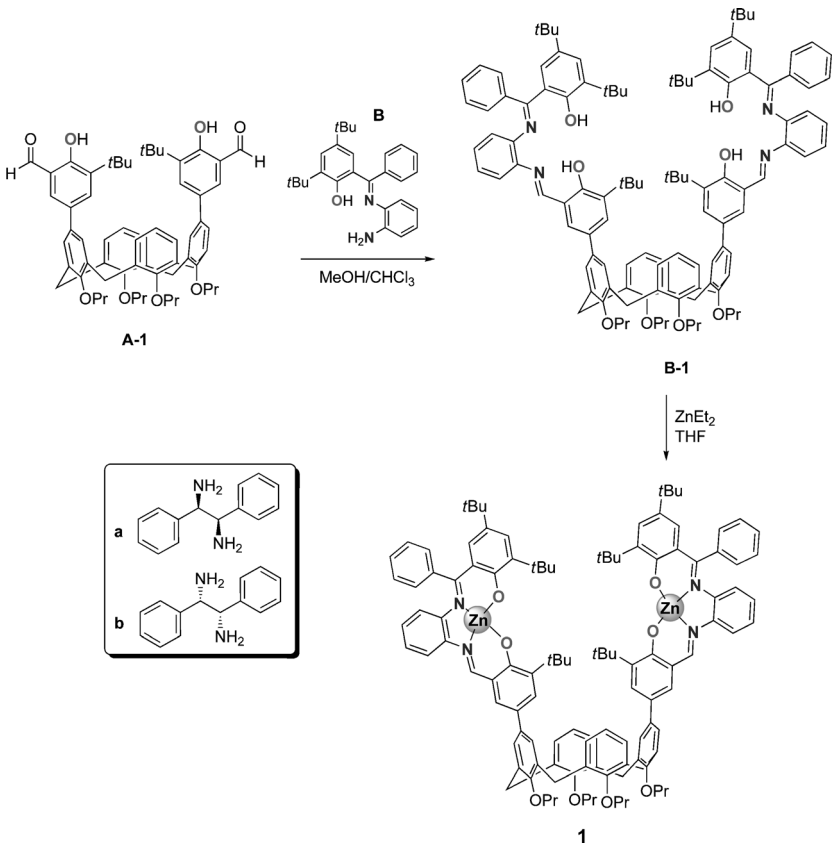
[c] *Prof. Dr. A. W. Kleij*
Catalan Institute of Research and Advanced Studies (ICREA)
Pg. Lluís Companys 23, 08010 Barcelona (Spain)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201500333.

diamines; each molecule of complex **1** would thus bind one molecule of diamine. However, the unusual formation of 2:1 host–guest assemblies, in which two molecules of calixarene–bis-[Zn(salphen)] interact with only one diamine molecule, was noted with concomitant, cooperative and diastereo-selective encapsulation of the chiral diamine guest. The underlying reasons for this unusual observation have been investigated in detail by using various experimental and computational methods, and the use of these types of calix–salen host systems in the determination of the absolute configuration and *ee* of the diamine is also detailed.

Results and Discussion

We first designed host **1** (Scheme 2; see the Supporting Information, Schemes S1 and S2 and Figures S1–S16, for more details) incorporating two co-facially orientated [Zn(salphen)] units that should accommodate the binding of suitable chiral diamine guests and block C_{aryl}–C_{aryl} rotation of the biphenyl units leading to chirality transfer effects.



Scheme 2. Synthesis of bis-[Zn(salphen)] host **1** and structures of chiral diamines **a** and **b**.

The synthesis of host **1** started off by using known calixarene–disalicylaldehyde **A-1** and treatment with the ketamine reagent **B** (see the Supporting Information, Scheme S1) furnishing the calixarene–bis-salphen ligand **B-1** in 70% yield. The Zn-based host **1** was then prepared from **B-1** by reaction with a stoichiometric amount of $ZnEt_2$ in THF to give the desired calixarene–bis-[Zn(salphen)] complex in 83% yield. Likewise, the mono-Zn host **2** (see the Supporting Information, Scheme S2) was prepared in a similar way in 99% yield from its calixarene—salphen precursors. Complex **2** represents a control compound in the chirality transfer experiments, as will be discussed below.

The potential induction of chirality by chiral diamines and thus a conformational control within host structure **1** was first probed in the presence of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine **a** (Scheme 2) and the UV/Vis and circular dichroism (CD) features of **1** in the presence of this chiral diamine were studied. Titration of a solution of **1** (CH_2Cl_2; 6×10^{-5} M) with a solution of the diamine **a** (CH_2Cl_2; 6×10^{-4} M) showed typical UV/Vis changes of a [Zn(salphen)]-derived complex (Figure 1a). A small but detectable bathochromic shift ($\Delta\lambda = 6$ nm) was noted together with a significant decrease of the absorption upon addition of higher amounts of diamine **a**. Similar bathochromic shifts of [Zn(salphen)] species were detected in the presence of pyridine donors.[8] However, in these cases an increasing absorption was detected at higher concentrations of analyte due to aggregate-to-monomer transitions of these materials. Thus, in the present case it seems that host molecule **1** does not seem to be in an aggregated state, rendering it useful for interaction with suitable ditopic substrates such as diamine **a**. The CD spectra of **1** (Figure 1b and 1d) showed typical Cotton effects at $\lambda = 416$ and 476 nm, with an unexpected saturation point after the addition of 0.5 equivalents of diamine **a**, that is, at a 2:1 host–guest ratio (Figure 1c).[9] The species formed at this ratio proved to be rather stable as a large excess of 40 equivalents of the diamine guest were required to fully disrupt the 2:1 assembly (see the Supporting Information, Figure S28).

The binding constant $K_{2,1}$ represents the binding of each diamine with two equivalents of calixarene host **1**; if this binding process is cooperative (i.e., $K_{1,1} < K_{1,1\rightarrow2,1}$) then $K_{2,1} = \alpha K_M^2$ where α is the cooperativity factor and K_M represents the microscopic binding constant. The K_M value can be derived from the equation $K_{1,1} = 2\,K_M$ with two possible and identical binding sites for the amine. To evaluate possible cooperative effects in the formation of $(\mathbf{1})_2$·**a**, we first determined $K_{1,1}$ by titration of model complex **2** (Scheme 1) with benzylamine, giving a value of $3.14\times10^5\ M^{-1}$. The binding constant $K_{2,1}$ was hereafter deter-

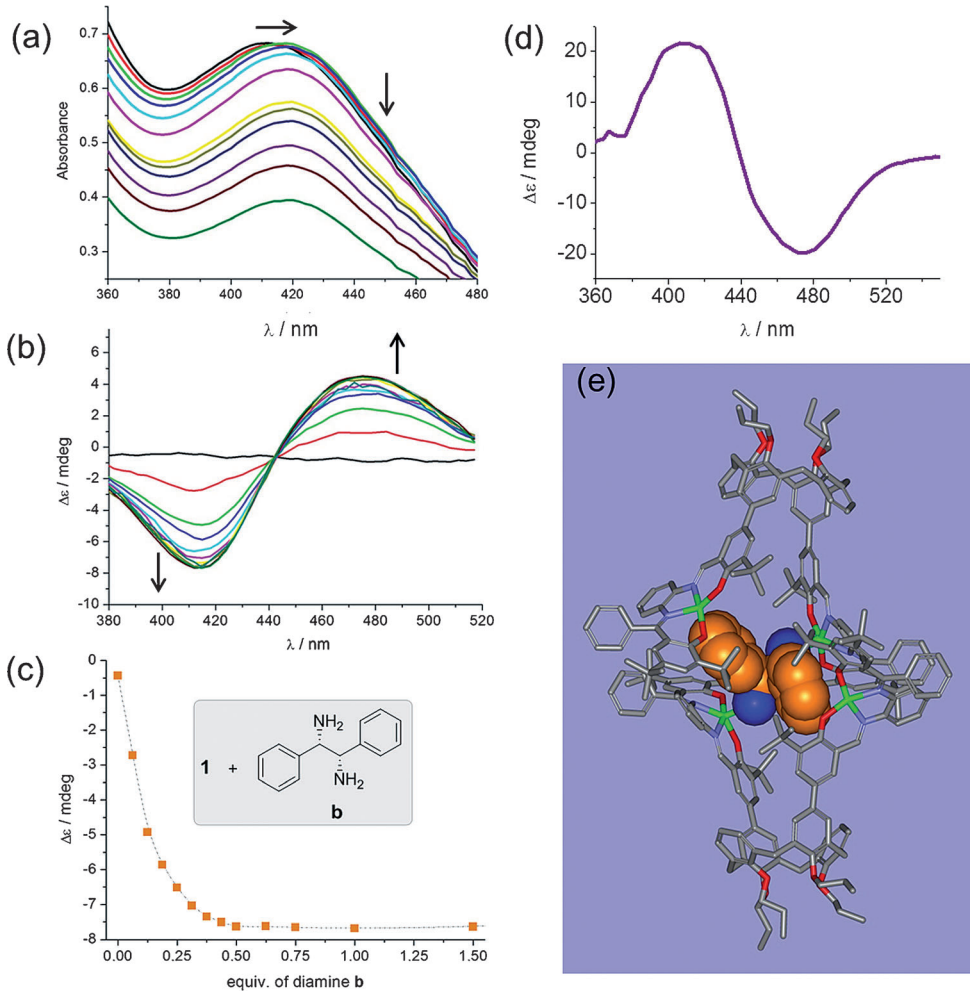


Figure 1. a) Detail of the UV/Vis spectrum for **1** (6×10^{-5} M; CH_2Cl_2) in the presence of increasing amounts of diamine **a** (0–100 equiv); b) CD spectroscopic changes for host **1** (6×10^{-5} M; CH_2Cl_2) in the presence of 0.06–1.50 equivalents of diamine **b**; c) titration curve for **1** using the CD data at $\lambda = 416$ nm; d) CD response for **1** in the presence of 0.5 equivalents of diamine **a** at [**1**] $= 2\times10^{-4}$ M (CH_2Cl_2); e) computed structure of assembly (**1**)$_2$·**b**.

mined using fluorescence titration data of **1** in the presence of diamine **a** and was found to be very high ($1.59\pm0.14\times10^{11}$ M^{-2}) with an α value of 6.4, in line with a strong, cooperative binding of **a** (for full details, see the Supporting Information). Interestingly, a similar preferred 2:1 stoichiometry between host **1** and diamines **b** and **d** (Figures S29–S32) was found as evidenced by their titration data, thus pointing to more general and similar chirality transfer behavior for **1** in the presence of chiral diamines.

To understand in more detail the binding mode in (**1**)$_2$·**b**, a number of additional experiments were conducted. Structures for both the 1:1 and the 2:1 assemblies based on **1** and diamine **b** were generated and fully optimized using a ONIOM QM/QM strategy (see also Supporting Information for details and Figure 1e). Interestingly, the 1:1 host–guest complex shows a higher degree of distortion within each [Zn(salphen)] unit as a consequence of the ditopic binding of diamine **b**. In the 2:1 model, this effect is less pronounced, showing this system to be of significantly lower energy (−36.3 versus −27.4 kcal mol^{-1}; see the Supporting Information, Figures S38 and S39). Furthermore, in the 2:1 system (see Figure 1e) two key features were observed. The first is the presence of multiple π–π stacking interactions (virtually absent in the 1:1 complex; see the Supporting Information, Figure S40) between the phenyl groups of the guest and the phenyl groups of the coordinated [Zn(salphen)] units of two calix[4]arene–bis-[Zn(salphen)] hosts, which helps to stabilize the assembled 2:1 complex. In line with this observation is the significant ^{1}H NMR upfield shift detected for the imine H of host **1** in the presence of diamine guest **a** ([D$_6$]acetone).[10] As for the free host **1**, this resonance is located at $\delta = 9.09$ ppm. In the presence of **a** it is shifted to 8.64 ppm ($\Delta\delta = -0.45$ ppm; for completeness, calixarene–bis-salphen **B-1** gives rise to a resonance at $\delta = 8.80$ ppm). Such an upfield shift is much larger than has been previously reported for pyridine coordination to [Zn(salphen)], which typically results in very small shifts for the imine H.[8b] Therefore, it seems reasonable to suggest that the imine protons in **1** are affected by the encapsulation process and are located near to the π surface of the diamine guest **a** (see the Supporting Information, Figures S40 and S42).

The second remarkable feature is the conformation of the two non-coordinated [Zn(salphen)] units (one present in each calix[4]arene–bis-[Zn(salphen)] host), which shows some degree of distortion of the N_2O_2 tetradentate coordination plane of the salphen ligand with the Zn ion pushed "inwards" (see the Supporting Information, Figure S41). As a result, these non-coordinated [Zn(salphen)] units are sterically congested and not easily approached by incoming ligands (cf., diamines such as **b**). Both features (Figures S40 and S41) support the high stability found for the 2:1 assembly, and the coordination of the diamine **b** to two molecules of **1** results in the cooperative and full encapsulation of the diamine guest.

^{1}H DOSY NMR spectroscopy (CD_2Cl_2; see the Supporting Information, Figure S43) was also carried out, suggesting a molecular radius of 11.0 Å that is close to the estimation derived from the computed structure for assembly (**1**)$_2$·**b** by DFT (11.4 Å; see the Supporting Information, Figure S39). Since the CD results for (**1**)$_2$·**b** point to a clear transfer of chirality from the diamine to the host, the CD traces of both possible (*M*,*M*)

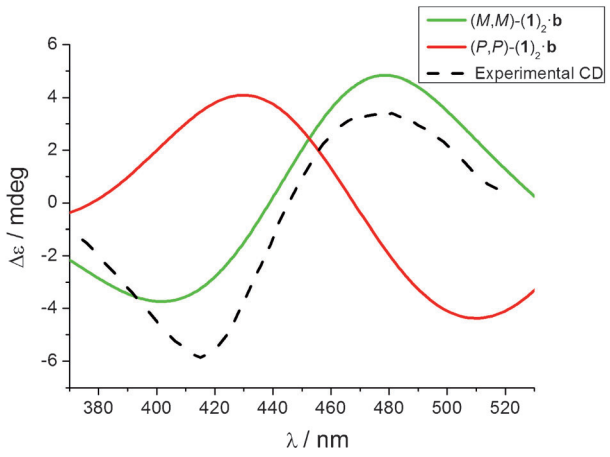
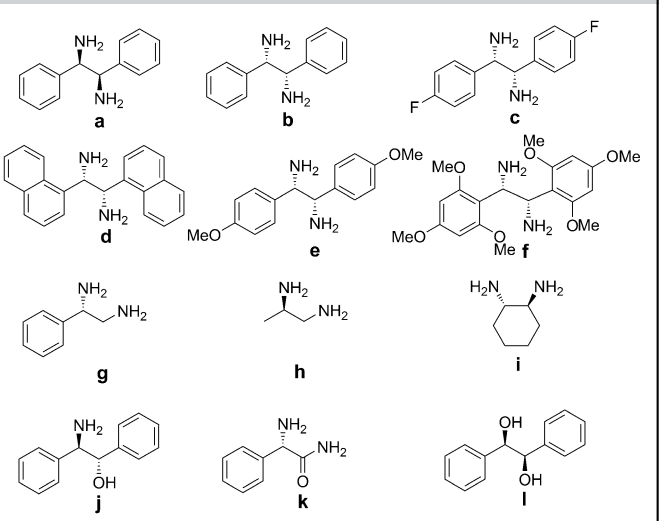


Figure 2. Comparison between the computed CD spectra for diastereoisomeric assemblies (*P,P*)-(**1**)$_2$·**b** (red) and (*M,M*)-(**1**)$_2$·**b** (green) and the experimental observed one (dashed).

and (*P,P*) configured diastereoisomers were calculated by DFT methods.[11] The calculated CD spectrum for (*M,M*)-(**1**)$_2$·**b** showed a remarkable resemblance to the experimental one, suggesting that this diastereoisomer should be the predominant species in solution (Figure 2). The large resemblance of the experimental and calculated CD traces for the 2:1 assembly (**1**)$_2$·**a** is further support for a selective encapsulation process.

To further investigate the scope, a series of other (potentially) ditopic substrates (Table 1; **b**–**l**) were then combined with host **1** and their CD spectra recorded.[12] As expected, (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine **b** showed opposite Cotton effects to those of diamine **a**. Other diamine substrates having a (1*S*,2*S*) configuration (**c**–**f**) showed similar Cotton effects to **b**, suggesting that host **1** could be useful to determine the absolute configurations of chiral diamines. Interestingly, when chiral diamines **g** and **h** (incorporating only one chiral center) were used, similar CD behavior was noted to that for **b**–**f**, and therefore the presence of only one chiral center in the diamine substrate seems to be required for effective chirality transmission. A more rigid diamine such as **i** did not lead to any observable chirality transfer; apparently, the rigidity of this diamine does not allow for productive diamine complexation as noted for **a**–**h**. The absence of any CD signals in the presence of ditopic systems **j**–**k** (at [**1**] = 6×10^{-5} M) emphasizes the requirement for the presence of two (electron-rich) N-donor atoms in the guest structure. The fact that O-donor-based amino alcohol **j**, amide-based **k**, and diol **l** did not produce any useful CD output is in line with previous work on the coordination behavior of [Zn(salphen)] species that (strongly) prefer N-donor over alcohol ligands.[13] Finally, various ratios of **a** and **b** in the presence of host **1** were then analyzed by CD spectroscopy and the amplitude of the Cotton effects compared with the actual *ee* values of the diamine samples (see the Supporting Information). A linear dependence was found and the calibration showed low absolute errors in the *ee* determinations (around 1%), a feature potentially useful for practical applications, as detection by CD/fluorescence spectroscopy allows for very low concentrations (10^{-5}–10^{-6} M) of diamine to be determined.

Table 1. Collected CD data for host **1** in the presence of chiral ditopic ligands **a**–**l**.[a]



Diamine guest	λ [nm]	Δε [M^{-1}cm^{-1}][b,c]	Δε [M^{-1}cm^{-1}][b,c]
a	416	5.6	21
	476	−6.4	−20
b	416	−5.4	−23
	476	6.6	20
c	420	−3.2	−6.6
	484	1.2	1.8
d	426	−4.0	−15
	475	0.3	4.7
e	413	−9.5	−13
	476	6.3	14
f	424	−6.4	26
	481	3.0	24
g	424	−1.8	−6.1
	480	0	2.0
h	420	−2.3	−3.6
	480	0	0.7
i–l	–	0	0

[a] Measured in CH_2Cl_2 at [**1**] = 6×10^{-5} M. [b] ΔA values are $\Delta\varepsilon/32982$. [c] Data refer to the CD output at [**1**] = 2×10^{-4} M. Note that for potentially ditopic substrates **i**–**l**, no output was observed at either concentration of **1** except for **j** ($\Delta\varepsilon = 13.0$ M^{-1}cm^{-1} at $\lambda = 464$ nm). For representative CD spectra, see Figures 1d and 2; see also the Supporting Information.

Conclusion

In summary, we have presented a unique self-assembled host–guest system with an unexpected binding motif between the host and the guest. Two molecules of host **1** bind one diamine guest molecule to form an encapsulated system with effective chirality transfer from the guest to the host, as indicated by CD spectroscopy. The high stability of this new host–guest system prospectively allows for the determination of low concentrations of chiral diamines, their absolute configuration, and their enantiomeric excess.

Experimental Section

General methods and materials: Compound **A-1**,[14] mono-5-bromotetrapropoxycalix[4]arene,[15] 3-(*tert*-butyl)-2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde,[16] (*S*)-1-phenyl-

ethane-1,2-diamine,[17] and (*S*)-2-amino-2-phenylacetamide[18] were prepared as reported previously. All others chemicals are commercially available from Aldrich and were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 500 NMR spectrometers at 297 K. Chemical shifts are reported in ppm relative to the residual solvent peaks in $CDCl_3$ ($\delta = 7.26$ ppm) and [D_6]DMSO ($\delta = 2.50$ ppm). Mass analyses were carried out by the High Resolution Mass Spectrometry Unit at the ICIQ in Tarragona, Spain. UV/Vis and CD spectra were recorded on an Applied Photophysics Circular Dichroism Chirascan Spectrophotometer using host **1** at 6×10^{-5} M in DCM, using the following parameters: step-size 2 nm, time-per-point 0.5 s, 3 repeats per sample, $T = 24\,^{\circ}$C. Further details are mentioned in each respective section provided below.

Syntheses

Precursor (3,5-di-*tert*-butyl-2-hydroxyphenyl)(phenyl)methanone (A): Under an argon atmosphere, 3,5-di-*tert*-butylsalicylic acid (1.0 g, 4 mmol) was dissolved in dry THF (30 mL). A phenyllithium solution (1.8 M in dibutyl ether, 13 mL, 25 mmol) was added dropwise at 0 °C. The solution was then stirred at 10 °C for 18 h. Then, freshly distilled Me_3SiCl (7 mL, 56 mmol) was added, and the reaction mixture was stirred for 1 h. Dilute aqueous HCl (3 M, 30 mL) was then added, and the organic phase was extracted with diethyl ether (3×30 mL) and the combined extracts were dried over Na_2SO_4. The product was purified by column chromatography (5:95 up to 10:90 v/v ethyl acetate/hexane) to give **A** as a yellow solid (yield: 92%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (s, 9H), 1.49 (s, 9H), 7.44 (d, $J = 2.4$ Hz, 2H), 7.71–7.48 (m, 5H), 12.71 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.6$, 31.4, 34.4, 35.4, 118.2, 128.0, 128.3, 129.4, 131.4, 131.7, 138.0, 138.9, 140.0, 160.1, 202.7 ppm; HRMS (ESI+, MeOH): *m/z* calcd for $C_{21}H_{26}O_2Na$: 333.1825; found: 333.1828.

Precursor (*E*)-2-{[(2-aminophenyl)imino]-(phenyl)methyl}-4,6-di-*tert*-butylphenol (B): Compound **A** (300 mg, 0.88 mmol) was dissolved in toluene (20 mL) and *o*-phenylenediamine (191 mg, 1.76 mmol) and *p*-toluenesulfonic acid (8 mg, 0.09 mmol) were added to the mixture. The reaction was performed using a Dean–Stark apparatus (120–130 °C) for 30 h. The reaction mixture was allowed to cool and the resultant precipitate was filtered off and washed with MeOH (3×10 mL) to give **B** as a yellow solid (yield: 74%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.15$ (s, 9H), 1.51 (s, 9H), 3.84 (s, 2H), 6.27 (dd, $J = 1.5$ Hz; 8.0 Hz, 1H), 6.40 (td, $J = 1.4$ Hz; 7.6 Hz, 1H), 6.67 (dd, $J = 1.4$ Hz; 8.0 Hz, 1H), 6.81 (td, $J = 1.5$ Hz; 7.6 Hz, 1H), 6.96 (d, $J = 2.5$ Hz, 1H), 7.17–7.23 (m, 2H), 7.30–7.34 (m, 3H), 7.46 (d, $J = 2.5$ Hz, 1H), 14.90 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.7$, 31.4, 34.3, 35.4, 115.2, 118.1, 119.0, 122.2, 125.6, 127.0, 128.1, 128.3, 128.5, 129.1, 134.2, 135.1, 136.7, 137.4, 139.1, 139.4, 159.9, 176.2 ppm; HRMS (ESI+, MeOH): *m/z* calcd for $C_{27}H_{33}ON_2$: 401.2587; found: 401.2584.

Bis-(4,6-di-*tert*-butylphenol-salphen)calix[4]arene ligand (B-1): Compounds **A-1** (150 mg, 0.16 mmol) and **B** (134 mg, 0.33 mmol) were dissolved in a 50:50 v/v MeOH/$CHCl_3$ solvent mixture (10 mL). The reaction mixture was heated at reflux for 48 h (until all aldehyde had been consumed, as monitored by TLC). The solvent was then removed by evaporation to afford a yellow solid, which was washed and triturated with MeOH to give **B-1** (yield: 70%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$–1.00 (m, 12H), 1.11 (s, 18H), 1.36 (s, 18H), 1.53 (s, 18H), 1.84–2.03 (m, 8H), 3.23 (d, $J = 13.5$ Hz, 4H), 3.66–3.80 (m, 4H), 3.99–4.12 (m, 4H), 4.52 (d, $J = 13.0$ Hz, 4H), 6.16–6.35 (m, 8H), 6.86–6.92 (m, 2H), 7.03–7.33 (m, 18H), 7.46 (d, $J = 9.5$ Hz, 4H), 7.63 (s, 2H), 8.53 (s, 2H), 13.88 (s, 2H), 14.70 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 10.0$, 11.0, 23.2, 23.7, 29.4, 29.8, 31.1, 31.4, 34.2, 35.2, 35.4, 76.6, 77.4, 118.4, 118.5, 119.3, 122.3, 123.6, 125.3, 126.8, 127.0, 127.7, 128.3, 128.4, 128.8, 129.3, 131.2, 133.2, 134.4, 135.6, 137.4, 138.2, 138.7, 139.5, 142.1, 155.4, 157.4, 160.0, 160.3, 162.8, 176.0 ppm; HRMS (ESI+, MeOH): *m/z* calcd for $C_{116}H_{133}O_8N_4$: 1710.0118; found: 1710.0064.

Bis-(4,6-di-*tert*-butylphenol-salphen)calix[4]arene zinc complex (1): Under an argon atmosphere, compound **B-1** (100 mg, 0.059 mmol) was dissolved in dry THF (10 mL), and then a solution of $ZnEt_2$ (1 M, 0.12 mL, 0.118 mmol) was added dropwise and the reaction mixture was stirred for 4 h. The solvent was then removed by evaporation to afford **1** as a bright orange solid (yield: 83%). ^{1}H NMR (500 MHz, DMSO): $\delta = 0.91$ (t, $J = 7.5$ Hz, 6H), 1.02 (s, 18H), 1.09–1.15 (m, 24H), 1.45 (s, 18H), 1.83–1.90 (m, 4H), 1.95–2.03 (m, 4H), 3.22–3.26 (m, 4H), 3.62–3.68 (m, 4H), 4.01–4.07 (m, 4H), 4.38–4.45 (m, 4H), 4.94 (s, 4H), 6.21–6.28 (m, 8H), 6.33 (d, $J = 6.7$ Hz, 2H), 6.48 (d, $J = 7.9$ Hz, 2H), 6.57–6.81 (m, 4H), 7.07 (t, $J = 8.0$ Hz, 2H), 7.23–7.28 (m, 4H), 7.37–7.45 (m, 10H), 7.56–7.69 (m, 4H), 9.04 ppm (s, 2H); ^{13}C NMR (125 MHz, DMSO): $\delta = 10.0$, 11.0, 22.8, 23.3, 29.6, 29.8, 30.3, 31.3, 33.6, 35.0, 35.3, 35.6, 76.1, 77.0, 114.7, 115.9, 119.1, 119.7, 121.9, 125.5, 126.0, 126.4, 127.3, 127.6, 128.0, 128.2, 128.5, 129.0, 132.0, 132.9, 134.9, 136.5, 136.8, 140.2, 140.3, 140.7, 141.2, 141.7, 155.0, 156.0, 159.6, 162.9, 170.1, 171.4, 174.2, 175.8 ppm; HRMS (MALDI+, dctb): *m/z* calcd for $C_{116}H_{130}O_8N_4Zn_2$ $(M+2H)^+$: 1836.8628; found: 1836.8772.

5-Mono-[1-(3-*tert*-butyl-2-hydroxy-1-formylphenyl)]-25,26,27,26-tetra-propoxy-calix[4]arene (B-2): Under an argon atmosphere, $Pd(OAc)_2$ (10 mg, 0.045 mmol) and P(*o*-tol)$_3$ (27 mg, 0.089 mmol) were dissolved in previously deoxygenated toluene (25 mL). After stirring the mixture for 30 min, mono-5-bromotetrapropoxycalix[4]-arene (500 mg, 0.74 mmol)[15] and 3-(*tert*-butyl)-2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (268 mg, 0.89 mmol)[16] were dissolved in deoxygenated MeOH (5 mL) and added to the mixture with an aqueous solution of K_2CO_3 (2 M, 5 mL). After 40 h stirring at 65 °C, the reaction mixture was allowed to cool and water (10 mL) and aqueous HCl (1 M, 5 mL) were added. The crude product was filtered through Celite and extracted with ethyl acetate (3×30 mL). The organic phases were combined and dried over Na_2SO_4. The solvent was removed by evaporation and the white solid obtained was further triturated with MeOH to give **B-2** (yield: 71%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.4$ Hz, 6H), 1.04 (t, $J = 7.4$ Hz, 3H), 1.07 (t, $J = 7.4$ Hz, 3H), 1.40 (s, 9H), 1.86–2.01 (m, 8H), 3.15 (d, $J = 13.4$ Hz, 2H), 3.20 (d, $J = 13.4$ Hz, 2H), 3.76 (t, $J = 7.1$ Hz, 2H), 3.81 (t, $J = 7.1$ Hz, 2H), 3.91–3.98 (m, 4H), 4.46 (d, $J = 13.4$ Hz, 2H), 4.50 (d, $J = 13.4$ Hz, 2H), 6.06 (t, $J = 7.5$ Hz, 1H), 6.31 (d, $J = 7.5$ Hz, 2H), 6.51 (s, 2H), 6.74 (t, $J = 7.5$ Hz, 2H), 6.85 (d, $J = 7.5$ Hz, 2H), 6.89 (d, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 7.5$ Hz, 2H), 9.86 (s, 1H), 11.65 ppm (s. 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 10.3$, 10.7, 23.3, 23.5, 23.6, 29.4, 29.8, 31.1, 31.3, 35.0, 77.0, 77.1, 77.4, 120.6, 121.8, 122.0, 126.2, 127.7, 128.7, 128.8, 129.7, 132.9, 133.4, 133.7, 134.4, 134.9, 136.0, 136.3, 138.0, 155.8, 156.1, 157.4, 160.0, 197.5 ppm; HRMS (ESI+, MeOH): *m/z* calcd for $C_{51}H_{60}O_6Na$: 791.4282; found: 791.4281.

5-Mono-(4,6-di-*tert*-butylphenol-salphen)calix[4]arene ligand (C-2): Compounds **B-2** (100 mg, 0.13 mmol) and **B** (78 mg, 0.20 mmol) were dissolved in a 1:1 v/v MeOH/$CHCl_3$ solvent mixture (5 mL). The reaction mixture was stirred and heated at reflux for 30 h, after which TLC showed full consumption of the aldehyde reagent. The solvent was then removed by evaporation to afford a yellow solid, which was triturated with MeOH to give **C-2** (yield: 62%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.4$ Hz, 6H), 1.01–1.06 (m, 6H), 1.09 (s, 9H), 1.27 (s, 9H), 1.51 (s, 9H), 1.86–1.98 (m, 8H), 3.17 (dd, $J = 6.7$ Hz; 13.5 Hz, 4H), 3.78 (t, $J = 7.3$ Hz, 2H), 3.83 (t, $J = 7.3$ Hz,

2H), 3.92 (t, $J=7.5$ Hz, 4H), 4.47 (t, $J=13.5$ Hz, 4H), 6.15 (t, $J=7.5$ Hz, 1H), 6.38 (d, $J=7.5$ Hz, 2H), 6.58 (s, 2H), 6.69 (t, $J=7.5$ Hz, 2H), 6.76–6.91 (m, 6H), 7.00–7.13 (m, 8H), 7.20 (t, $J=7.3$ Hz, 2H), 7.42 (d, $J=2.3$ Hz, 1H), 8.31 (s, 1H), 13.72 (s, 1H), 16.64 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=10.3$, 10.6, 10.7, 23.3, 23.5, 23.6, 29.3, 29.8, 31.1, 31.3, 31.4, 34.1, 35.0, 35.4, 118.2, 118.5, 119.1, 122.0, 123.6, 125.2, 126.3, 126.7, 127.6, 128.8, 128.2, 128.6, 128.7, 128.8, 128.9, 129.6, 131.5, 134.5, 134.6, 134.9, 135.6, 135.8, 136.0, 137.4, 137.6, 138.7, 139.6, 142.1, 155.6, 156.2, 157.3, 159.7, 160.2, 162.8, 175.9 ppm; HRMS (ESI+, MeOH): *m/z* calcd for $C_{78}H_{91}N_2O_6$: 1151.6872; found: 1151.6850.

5-Mono-(4,6-di-*tert*-butylphenolsalphen)calix[4]arene zinc complex (2): Under an argon atmosphere, precursor compound **C-2** (100 mg, 0.086 mmol) was dissolved in dry THF (10 mL). A solution of $ZnEt_2$ (1 M, 0.09 mL, 0.09 mmol) was then added dropwise and the mixture was further stirred for 4 h. The solvent was removed by evaporation to afford **2** as a bright orange solid (yield: 99%). ^{1}H NMR (500 MHz, DMSO): $\delta=0.96$ (t, $J=7.5$ Hz, 6H), 0.99–1.05 (m, 15H), 1.39 (s, 9H), 1.52 (s, 9H), 1.87 (dt, $J=7.3$ Hz; 14.3 Hz, 8H), 3.14–3.24 (m, 4H), 3.70–3.88 (m, 4H), 4.30–4.42 (m, 4H), 6.04 (t, $J=7.7$ Hz, 1H), 6.33 (d, $J=7.5$ Hz, 2H), 6.57 (s, 2H), 6.68 (t, $J=7.3$ Hz, 2H), 6.76–6.88 (m, 6H), 6.96 (s, 1H), 7.03–7.42 (m, 14H), 8.88 ppm (s, 1H); ^{13}C NMR (125 MHz, DMSO): $\delta=10.2$, 10.4, 10.5, 22.8, 22.9, 23.0, 29.4, 29.5, 29.7, 30.2, 30.4, 30.7, 31.0, 31.1, 33.5, 34.6, 34.9, 35.0, 35.4, 76.3, 116.4, 118.9, 119.1, 121.5, 121.6, 121.8, 124.6, 124.7, 125.2, 125.3, 125.7, 126.5, 127.5, 128.0, 128.2, 128.3, 128.9, 129.7, 131.3, 131.8, 134.2, 134.4, 134.6, 135.1, 136.2, 137.8, 139.9, 140.0, 141.0, 154.3, 155.8, 155.9, 156.3, 156.6, 162.6, 170.9, 171.0, 174.0 ppm; HRMS (MALDI+, dctb): *m/z* calcd for $C_{78}H_{88}N_2O_6Zn$: 1212.5934; found: 1212.5929.

Titration studies: To determinate K_m, a UV/Vis spectroscopy was carried out on mono-[Zn(salphen)]–calix[4]arene complex **2** (Scheme 1) as a reference and benzylamine as the titrant (see the Supporting Information for more details). The titration data was imported to SPECFIT/32[19] and the association constant K_m was thus determined. Fluorescence spectra were also recorded (to determine $K_{2,1}$) by using a Fluorolog Horiba Jobin Yvon Spectrophotometer. To record the fluorescence spectra of compound **1**, an excitation wavelength of $\lambda=416$ nm was used. This titration data was imported to SPECFIT/32 and the constant $K_{2,1}$, using the previously determined K_m, was calculated. The constant $K_{2,1}$ was determined at 1.585×10^{11} M^{-2}.

DFT calculations

The Gaussian 09 software package[20] was used in a two tier (ONIOM2) approach.[21] The high layer was constituted of the simpler [Zn(salphen)] moiety and the bridging diamine whereas the remainder of the organic framework was modelled as the low layer (Figure S42). The high layer was described with the density functional approach, namely the B3LYP gradient-corrected hybrid three parameter functional[22,23] built upon the Slater local exchange,[24] and the Vosko, Wilk and Nusair's local[25] correlation (VWN formula 3) functionals. The basis set was of the Pople,type contracted 6–31G(d,p) split-valence basis set for all elements. The low layer was described through the semi-empirical parametric model 6 (PM6) of Stewart[26] employing valence-only Slater-type orbitals approximated by a primitive set of six Gaussian functions (STO-6G) on all the atoms. The layer interface was composed of hydrogen link atoms. The total energy of the system can thus be computed[21] as: $E(\text{ONIOM2})=E_{\text{high layer}}$ (subsystem) $+E_{\text{low layer}}$ (full system) $-E_{\text{low layer}}$ (subsystem)- The geometries were optimized without any constraints until the default convergence criteria were met. The electronic circular dichroism (ECD) rotatory strength values of the dinuclear complexes were computed with time dependent density functional theory (TDDFT)[27,28] as implemented in Gaussian 09 selecting thirty singlet to singlet transitions in an all electron single point calculation. The computed intensities were broadened by a Gaussian function to be comparable to the experimentally determined spectrum. For the tetranuclear complexes, the calculation of ECD spectra in Gaussian 09 was exceedingly demanding, as it involves a very large number of excitations, so it was opted to compute these ECD transitions with the ADF[29] program, in which a single-point calculation was performed on the previously optimized ONIOM geometry. A double-zeta basis set was employed on all the light atoms while employing a triple-zeta basis set on zinc. One advantage in favor of expediting this demanding calculation was the inclusion of [He] and [Ne] frozen cores on the light elements (apart from hydrogen) and zinc, respectively. The basis sets were further augmented with one polarization d function for C, N, and O and a p function for Zn. A total of three hundred singlet-to-singlet excitations were calculated to reproduce the excitation spectra of the tetranuclear zinc complexes. The GGA class BLYP functional was employed rather than the aforementioned B3LYP used in Gaussian to eschew the computation of exact exchange integrals.

Acknowledgements

We thank ICIQ, ICREA, and the Spanish Ministerio de Economía y Competitividad (MINECO) through projects CTQ-2014–60419-R and CTQ2014–52824-R, and the Severo Ochoa Excellence Accreditation 2014–2018 through project SEV-2013–0319. We also thank AGAUR for support through 2014-SGR-409. Dr. Noemí Cabello, Sofía Arnal, and Vanessa Martínez are acknowledged for the mass analyses, and Dr. Gemma Aragay for help with the binding studies and data interpretation. N.A.G.B. gratefully acknowledges the COFUND grant 291787-ICIQ-IPMP for financial support.

Keywords: calixarenes · chirality transfer · encapsulation · host–guest systems · salens

[1] a) G. A. Hembury, V. V. Borovkov, Y. Inoue, *Chem. Rev.* **2008**, *108*, 1–73; b) *Supramolecular Chemistry*, 1st ed. (Eds.: J. W. Steed, J. L. Atwood), John Wiley & Sons, Chichester, **2000**; c) *Biochemistry*, 2nd ed. (Eds.: D. Voet, J. G. Voet), John Wiley & Sons, New York, **1995**; d) M. V. Escárcega-Bobadilla, A. W. Kleij, *Chem. Sci.* **2012**, *3*, 2421–2428; e) M. R. Ringenberg, T. R. Ward, *Chem. Commun.* **2011**, *47*, 8470–8476.

[2] For some examples: a) P. Dydio, C. Rubay, T. Gadzikwa, M. Lutz, J. N. H. Reek, *J. Am. Chem. Soc.* **2011**, *133*, 17176–17179; b) A. J. Boersma, J. E. Klijn, B. L. Feringa, G. Roelfes, *J. Am. Chem. Soc.* **2008**, *130*, 11783–11790; c) C. J. Brown, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2009**, *131*, 17530–17531.

[3] a) H. Qiu, Y. Inoue, S. Che, *Angew. Chem. Int. Ed.* **2009**, *48*, 3069–3072; *Angew. Chem.* **2009**, *121*, 3115–3118; b) J. Wang, B. L. Feringa, *Science* **2011**, *331*, 1429–1432; c) N. Liu, G. R. Darling, R. Raval, *Chem. Commun.* **2011**, *47*, 11324–11326; d) G. Haberhauer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9286–9289; *Angew. Chem.* **2010**, *122*, 9474–9477; e) P. K. Hashim, N. Tamaoki, *Angew. Chem. Int. Ed.* **2011**, *50*, 11729–11730; *Angew. Chem.* **2011**, *123*, 11933–11934; f) K. Rijeesh, P. K. Hashim, S.-I. Noro, N. Tamaoki, *Chem. Sci.* **2015**, *6*, 973–980; g) H. Hayasaka, T. Miyashita, M. Nakayama, K. Kuwada, K. Akagi, *J. Am. Chem. Soc.* **2012**, *134*, 3758–3765.

[4] For a selection of recent examples: a) K. W. Bentley, Y. G. Nam, J. M. Murphy, C. Wolf, *J. Am. Chem. Soc.* **2013**, *135*, 18052–18055; b) L. A. Joyce, M. S. Maynor, J. M. Dragna, G. M. da Cruz, V. M. Lynch, J. W.

Canary, E. V. Anslyn, *J. Am. Chem. Soc.* **2011**, *133*, 13746 – 13752; c) L. You, G. Pescitelli, E. V. Anslyn, L. Di Bari, *J. Am. Chem. Soc.* **2012**, *134*, 7117 – 7125; d) S. J. Wezenberg, G. Salassa, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Angew. Chem. Int. Ed.* **2011**, *50*, 713 – 716; *Angew. Chem.* **2011**, *123*, 739 – 742; e) X. Li, M. Tanasova, C. Vasileiou, B. Borhan, *J. Am. Chem. Soc.* **2008**, *130*, 1885 – 1893; f) S. Nieto, V. M. Lynch, E. V. Anslyn, H. Kim, J. Chin, *J. Am. Chem. Soc.* **2008**, *130*, 9232 – 9233; g) M. Yamamura, T. Saito, T. Nabeshima, *J. Am. Chem. Soc.* **2014**, *136*, 14299 – 14306; h) M. Anyika, H. Gholami, K. D. Ashtekar, R. Acho, B. Borhan, *J. Am. Chem. Soc.* **2014**, *136*, 550 – 553; i) M. Balaz, A. E. Holmes, M. Benedetti, P. C. Rodriguez, N. Berova, K. Nakanishi, G. Proni, *J. Am. Chem. Soc.* **2005**, *127*, 4172 – 4173.

[5] a) V. V. Borovkov, G. A. Hembury, Y. Inoue, *Acc. Chem. Res.* **2004**, *37*, 449 – 459; b) J. Etxebarria, A. Vidal-Ferran, P. Ballester, *Chem. Commun.* **2008**, 5939 – 5941; c) V. V. Borovkov, I. Fujii, A. Muranaka, G. A. Hembury, T. Tanaka, A. Ceulemans, N. Kobayashi, Y. Inoue, *Angew. Chem. Int. Ed.* **2004**, *43*, 5481 – 5485; *Angew. Chem.* **2004**, *116*, 5597 – 5601; d) V. V. Borovkov, G. A. Hembury, Y. Inoue, *Angew. Chem. Int. Ed.* **2003**, *42*, 5310 – 5314; *Angew. Chem.* **2003**, *115*, 5468 – 5472; e) M. Siczek, P. J. Chmielewski, *Angew. Chem. Int. Ed.* **2007**, *46*, 7432 – 7436; *Angew. Chem.* **2007**, *119*, 7576 – 7580; f) I. C. Pintre, S. Pierrefixe, A. Hamilton, V. Valderrey, C. Bo, P. Ballester, *Inorg. Chem.* **2012**, *51*, 4620 – 4635; g) X. Huang, N. Fujioka, G. Pescitelli, F. E. Koehn, R. T. Williamson, K. Nakanishi, N. Berova, *J. Am. Chem. Soc.* **2002**, *124*, 10320 – 10335.

[6] M. V. Escárcega-Bobadilla, G. Salassa, M. Martínez Belmonte, E. C. Escudero-Adán, A. W. Kleij, *Chem. Eur. J.* **2012**, *18*, 6805 – 6810.

[7] See: a) C. J. Whiteoak, G. Salassa, A. W. Kleij, *Chem. Soc. Rev.* **2012**, *41*, 622 – 631; b) A. W. Kleij, *Dalton Trans.* **2009**, 4635 – 4639; c) S. J. Wezenberg, A. W. Kleij, *Angew. Chem. Int. Ed.* **2008**, *47*, 2354 – 2364; *Angew. Chem.* **2008**, *120*, 2388 – 2399.

[8] For reports on N-donors coordinating to aggregated [Zn(salphen)]-type complexes and their UV/Vis behavior: a) G. Salassa, M. J. J. Coenen, S. J. Wezenberg, B. L. M. Hendriksen, S. Speller, J. A. A. W. Elemans, A. W. Kleij, *J. Am. Chem. Soc.* **2012**, *134*, 7186 – 7192; b) M. Martínez Belmonte, S. J. Wezenberg, R. M. Haak, D. Anselmo, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans.* **2010**, *39*, 4541 – 4550; c) J. A. A. W. Elemans, S. J. Wezenberg, M. J. J. Coenen, E. C. Escudero-Adán, J. Benet-Buchholz, D. den Boer, S. Speller, A. W. Kleij, S. De Feyter, *Chem. Commun.* **2010**, *46*, 2548 – 2550.

[9] To assess the generality of this saturation effect, similar titrations were conducted with diamines **b** and **d**, which also showed saturation points in the CD spectra at the addition of 0.5 equivalents of the diamine guest.

[10] [Zn(salphen)] species underwent some decomposition over time in non-coordinating solvents in the absence of a stabilizing donor ligand. Therefore ^{1}H NMR studies were conducted in [D_6]acetone, despite the limited solubility of **1** in this solvent. See also: S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2008**, *10*, 3311 – 3314.

[11] The (*M*,*M*) and (*P*,*P*) designations stand for the chiral conformations of both biphenyl units in **1** upon binding to chiral diamine **a**. Both (*M*,*P*) and (*P*,*M*) isomers of **1** are *meso* and should not give any signal in the CD experiments.

[12] The fact that no Cotton effects were observed for any of the substrates **a**–**l** in the presence of mononuclear complex **2** suggests that ditopic binding/coordination of the diamine substrate is requisite for efficient chirality transfer.

[13] a) A. W. Kleij, D. M. Tooke, M. Kuil, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743 – 4750; b) S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 2925 – 2927; c) E. Martin, M. Martínez Belmonte, E. C. Escudero-Adán, A. W. Kleij, *Eur. J. Inorg. Chem.* **2014**, 4632 – 4641.

[14] S. J. Wezenberg, A. W. Kleij, *Adv. Synth. Catal.* **2010**, *352*, 85 – 91.

[15] M. Cavazzini, A. Manfredi, F. Montanari, S. Quici, G. Pozzi, *Eur. J. Org. Chem.* **2001**, 4639 – 4649.

[16] J. Y. Jang, D. G. Nocera, *J. Am. Chem. Soc.* **2007**, *129*, 8192 – 8198.

[17] The synthesis is based on the reduction of amineamide (*S*)-2-amino-2-phenylacetamine **k** using $LiAlH_4$. See also: Y. Hsiao, L. S. Hegedus, *J. Org. Chem.* **1997**, *62*, 3586 – 3591.

[18] K. Lin, Z. Cai, W. Zhou, *Zhongguo Yiyao Gongye Zazhi* **2009**, *40*, 334 – 336. The synthesis of this aminoamide is based on the preparation of L-phenylglycine methyl ester from the amino acid precursor followed by amidation in ammonia, with an overall yield of about 65%.

[19] SPECFIT32: Specfit/32, version 3.0; Spectra Software Associates: Bradford-on-Avon, U. K., 2005. Specfit/32 is a multivariate data analysis program for modeling and fitting multi-wavelength titration datasets giving more reliable parameters than single-wavelength fits. For software details and the related nonlinear algorithms see: H. Gampp, M. Maeder, C. J. Meyer, D. A. Zuberbühler, *Talanta* **1985**, *32*, 95 – 101; H. Gampp, M. Maeder, C. J. Meyer, D. A. Zuberbühler, *Talanta* **1986**, *33*, 943 – 951.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, **2009**.

[21] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, K. Morokuma, *J. Phys. Chem.* **1996**, *100*, 19357 – 19363.

[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.

[23] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[24] J. C. Slater, *Phys. Rev.* **1951**, *81*, 385 – 390.

[25] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200 – 1211.

[26] J. Stewart, *J. Mol. Model.* **2007**, *13*, 1173 – 1213.

[27] C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* **2013**, *42*, 845 – 856.

[28] A. Rosa, G. Ricciardi, O. V. Gritsenko, E. J. Baerends, *Struct. Bonding (Berlin)* **2004**, *112*, 49 – 116.

[29] E. J. Baerends, J. Autschbach, A. Bérces, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. F. Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. v. d. Hoek, H. Jacobsen, L. Jensen, G. van Kessel, F. Kootstra, E. van Lenthe, D. A. McCormack, A. Michalak, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, F. Wang, E. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev, T. Ziegler, *ADF*, revision ADF-2013.01, http://www.scm.com, Scientific Computing and Modelling NV: Amsterdam, the Netherlands, **2013**.

Received: January 26, 2015
Published online on ■■ ■■, 0000

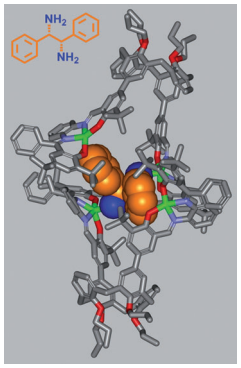
FULL PAPER

Host–Guest Systems

*L. Martínez-Rodríguez, N. A. G. Bandeira, C. Bo, A. W. Kleij**

■■ – ■■

Highly Efficient Chirality Transfer from Diamines Encapsulated within a Self-Assembled Calixarene–Salen Host



The host with the most: A calix[4]arene functionalized with two [Zn(salphen)] complexes shows highly effective chirality transfer effects in the presence of chiral diamines. The operating modus of the system involves a unique encapsulation of the diamine guest. This calixarene–salphen hybrid host holds promise for the determination of the absolute configuration and *ee* of diamines.