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Pyridine-functionalised C_4 symmetric resorcinarenes

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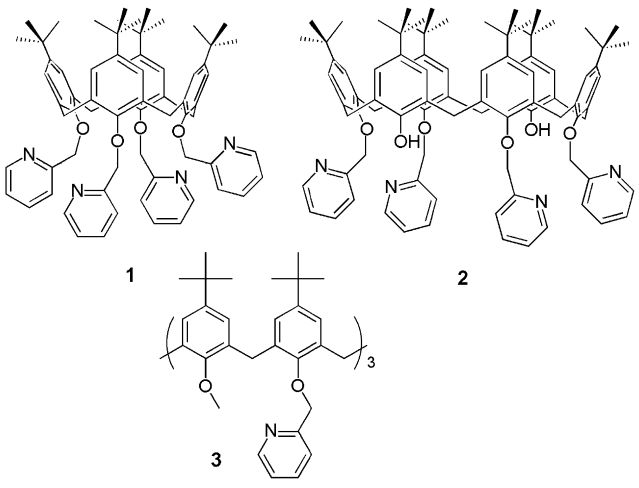
Abstract—Racemic mixtures of C_4 symmetric resorcinarenes have been functionalised by adding 2- and 3-picolyl ether functional groups. Three of the resulting macrocycles were structurally characterised. The aim of the work was to enable the resolution of the racemic mixture by forming salts with chiral acids. While the formation of diastereomers was demonstrated using NMR spectroscopy, isolation of the salts was not successful. Metal complexation was also investigated. The pyridine-functionalised ligands solubilise copper and nickel salts in dichloromethane, and form insoluble products with silver and palladium. A copper complex was structurally characterised, and shown to form a linear polymer containing two structurally distinct copper bridges.

1. Introduction

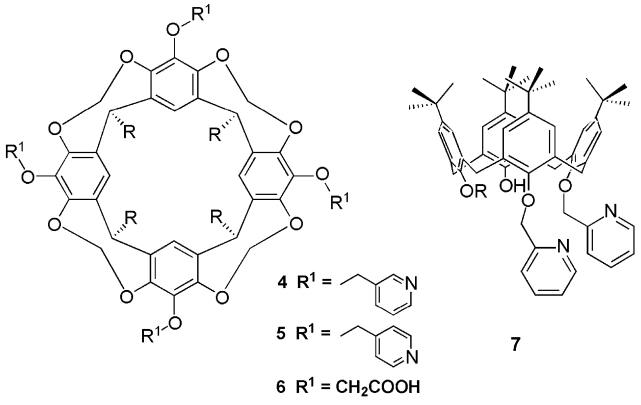
Since the publication of our initial paper describing the synthesis of racemic C_4 symmetric resorcinarenes[1] there has been a number of groups utilising this family of macrocycles.[2–5] We report here the functionalisation of C_4 symmetric resorcinarenes with picolyl ether moieties. One aim of the work was to determine if it is possible to resolve the resulting racemic mixtures by forming salts with chiral acids. Another aspect of interest was the potential to form metal complexes with the picolyl ether functionalised resorcinarenes.



The 2-picolyl ethers of calix[4]arenes and calix[6]arenes, such as **1** and **2**, were first reported by Pappalardo et al.[6–9] Their aim was to produce pre-organised ligands much like the calix[4]arene tetraester,[10] tetraketone[11] and tetraamides.[12] The hexamer **3** was found to bind copper(II)[13] but failed to form a zinc(II) complex.[14]

Shinkai et al. also produced several calixarene derivatives with pyridine attached at the upper rim[15–17] all of which were applied to palladium coordination. A number of lower rim picolyl ethers of a dihomooxacalixarene were described by Marcos et al.[18] The only resorcinarene analogues functionalised with picolyl moieties appears to have been the cavitands **4** and **5** prepared by Reinhoudt et al.[19] These compounds were mixed with the tetra-acid **6** to prepare capsular structures, however, no X-ray structural determination of the adducts was presented.

Of the chiral pyridine substituted derivatives, the most significant contribution appears to have been made by



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Pappalardo et al. with the picolyl substituted chiral calixarenes of the general structure **7** (where R≠H).[20–24]

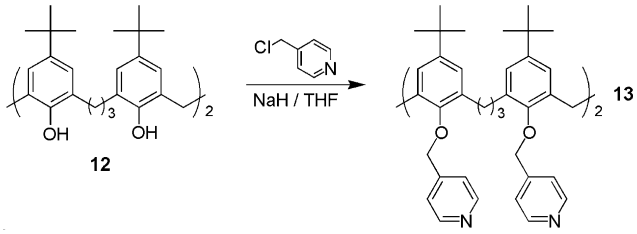
2. Results and discussion

2.1. Synthesis of the resorcinarenes

The alkylation of calixarene and resorcinarenes with the picolyl chlorides appears to have been investigated fairly thoroughly for the 2-picolyl ethers but significantly less for the 3- and 4-picolyl ethers. The derivatives were prepared by a standard Williamson ether synthesis involving a base, a solvent and the appropriate alkylating agent. The choice of base and solvent for the preparation of 2-picolyl ethers appears to be substrate dependant. Combinations such as sodium hydride,[6,8,9,18,22] caesium carbonate,[7] sodium carbonate[7] and potassium carbonate[7,18,21] in dimethylformamide and potassium carbonate in acetonitrile[9] have afforded good yields of alkylated products.

In our hands the alkylation of the racemic *C*-heptylresorcinarene **8**, and *C*-propylresorcinarene **9** with 2-picolyl chloride hydrochloride with potassium carbonate in acetonitrile at reflux afforded the tetra-picolyl ethers **10** and **11** in 84 and 80% yields, respectively (Scheme 1). The corresponding preparation of **10** using sodium hydride in dimethylformamide at room temperature yielded 81% of the desired product with identical physical and spectroscopic properties. Quite clearly the method of choice in this case is to use the more convenient and less hazardous base.

Reinhoudt has appended both 3- and 4-picolyl groups to cavitands **4** and **5** derived from pyrogallol using a caesium carbonate in acetonitrile protocol.[19] This method, however, produced the per-ethers in only 37 and 25% yields, respectively. Reinhoudt indicated that the low yields could be attributed to competing alkylation of the pyridine ring either in the picolyl chlorides or the alkylated resorcinarene products. Yamato et al. obtained a significantly a higher yield with his tetrahydroxy[3.1.3.1]metacyclophane (**12**) using sodium hydride and 4-picolyl chloride hydrochloride in THF, recovering 80% of the peralkylated material **13** (Scheme 2).[25] Using caesium carbonate as the base he obtained a 65% recovery and with potassium carbonate an intractable mixture.



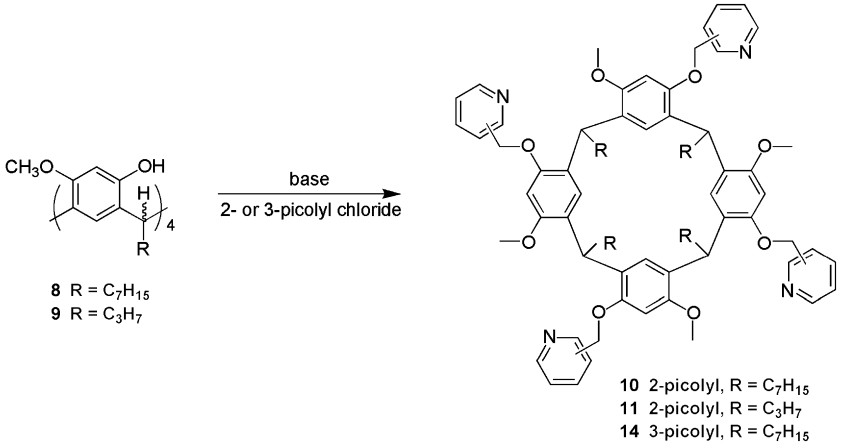
Scheme 2. Synthesis of pyridine-functionalised cyclophanes.

The increased yields obtained utilising sodium hydride as the base are presumably due to more effective deprotonation of the macrocyclic components. With these results in mind we applied the sodium hydride/dimethylformamide system to alkylate **8** with 3-picolyl chloride obtaining 72% yield of **14**. A reduction in the yield of **10** when **8** was alkylated with 2-picolyl chloride and potassium carbonate (rather than NaH) was not observed. The alkylation of **8** with 3-picolyl chloride using potassium carbonate gave a lower yield (15%), in accordance with the previous findings.

2.2. Interaction of the resorcinarenes with chiral acids

One aim of this work was to exploit the basic pyridine moiety to form a diastereomeric salt as a rational scheme for the separation of the chiral species. If this could be achieved, then the picolyl ether group can also potentially be removed from substrates that are not degraded under hydrogenation conditions.[26]

Interaction of **10** with chiral acids was demonstrated initially with ^{1}H and ^{13}C NMR experiments. On addition of one mole equivalent of (+)-10-camphorsulfonic acid (CSA) to a sample of **10** in deuterated chloroform, a significant downfield shift (and broadening) of the pyridine proton signals was observed. In addition, the methylene protons of the picolyl ether, which appear as an AB quartet were split into two AB signals of equal intensity (Fig. 1). The splitting of the AB signal in such a manner is indicative of formation of diastereomeric species. However, the mechanism by which



Scheme 1. Synthesis of the pyridine-functionalised resorcinarenes.

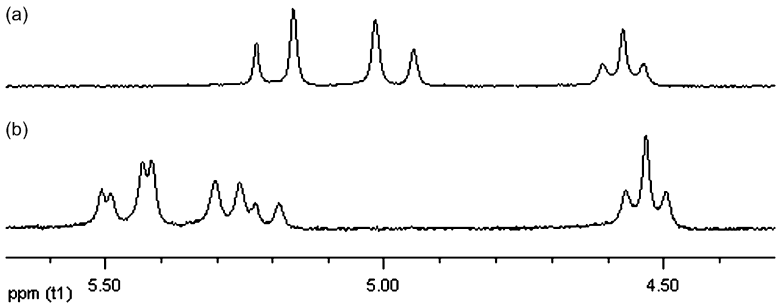


Figure 1. Proton NMR spectrum of (a) **10**, and (b) **10** with 1 equiv of (+)-10-camphorsulfonic acid.

the diastereomeric species are generated is not obvious. The splitting effect in the proton NMR may be a result of inclusion of the CSA within the cavity of the resorcinarene rather than an acid–base interaction.

The ^{13}C NMR spectrum of **10** on addition of the CSA clearly shows significant shifting of the 2, 4 and 6 carbons of the pyridine ring (Fig. 2). The upfield shift of the 2 and 6 carbon signals and the downfield shift of the 4 carbon are typical of protonation at the pyridine nitrogen.

Based on these observations, attempts were made to resolve the racemic products by addition of chiral acids including (+)-10-camphorsulfonic acid, (+)-tartaric acid, (+)-camphoric acid, and (*S*)-(+)-2-(6-methoxy-2-naphthyl)propionic acid. After fractional crystallisation only neutral racemic starting material was isolated in all cases.

2.3. Structures of the pyridine-functionalised resorcinarenes

Resorcinarenes **10**, **11** and **14** crystallised from dichloromethane/methanol solutions. Single crystal X-ray analysis provided confirmation of the proposed structures. Solvent was found in **10** and **14**, and was modelled as a methanol, and methanol and water molecule, respectively.

The resorcinarene molecules **10**, **11**, and **14** are shown in Figures 3–5. In all cases, the macrocycles possess pseudo-2 symmetry rather than possible four-fold symmetry resulting from opposite Ar rings being either approximately coplanar (i.e., 'horizontal') to or perpendicular ('vertical') to the C_4 'plane' of the four methylene groups. The dihedral angles between the planes of the 'vertical' rings and the C_4 plane are 109.28(7), 83.56(7)° (**10**), 75.4(2), 101.5(2)° (**14**), and 96.82(7), 87.36(8)° (**11**). Those between the 'horizontal' rings and the C_4 plane are 14.49(7), 3.02(7)° (**10**), 19.1(2), 13.2(2)° (**14**), and 4.24(8), 7.24(8)° (**11**).

In **14**, the macrocycle forms a centrosymmetric hydrogen-bonded cluster through a Py nitrogen atom, N2, with the solvent water and methanol molecules as seen in Figure 4(b). Relevant contact distances and angles are: N2···H9B 1.96(8) Å, N2···H9B–O9 177(6)°; O9···H10 1.886(6) Å, O9···H10–O10 177.5(4)°; H9A···O10(1−x,−y,−z) 1.97(5) Å, O9–H9A···O10(1−x,−y,−z) 170(7)°.

2.4. Complexation with transition metal cations

The picolyl functionalised resorcinarene may also serve as a multidentate ligand for the coordination of some transition metals such as palladium, zinc, nickel and copper. The use of calixarenes as ligands for transition metals is of significant interest and has been reviewed.[27] The catalytic application of transition metals and their complexes is also well known.[28]

Preliminary ^{1}H NMR experiments clearly showed that on addition of 1 equiv of $Zn(ClO_4)_2\cdot 6H_2O$ to a solution of **10** in d_6-acetone significant signal shifts and broadening occurred (Fig. 6). The addition of excess $Zn(ClO_4)_2\cdot 6H_2O$ did not appear to cause any significant change from that already induced by the addition of 1 equiv, although the determination of the stoichiometry is not conclusive. These signal changes are very similar to the NMR data obtained by

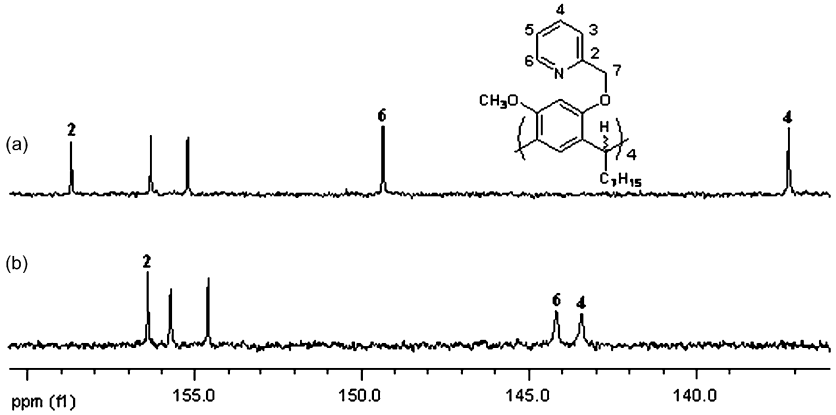


Figure 2. ^{13}C NMR spectra (136.0–165 ppm) of (a) **10**, (b) **10** with 1 equiv of (+)-10-camphorsulfonic acid.

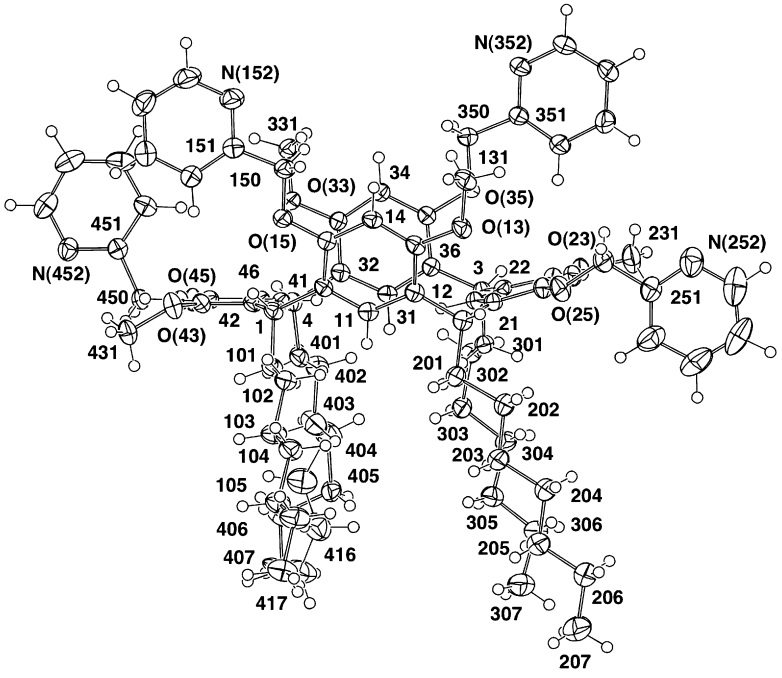


Figure 3. A molecule of **10** showing the numbering scheme. Non-hydrogen atoms ellipsoids are shown at the 50% probability level.

Pappalardo and Parisi[24] on addition of $Zn(CF_3SO_3)_2$ to a $CDCl_3$ solution of picolyl functionalised calix[4]crowns.

Solubilisation experiments with copper(II) salts also demonstrated the significant ligating ability of **10** and **14**. When solid copper acetate hydrate was added to a dichloromethane solution of **10**, two mole equivalents of the salt (per mole of calix ligand) were taken into solution. The stoichiometry of the **14** complexes could not be determined in this manner due to partial insolubility of the complexes.

Addition of soft metal cations such as silver(I) and palladium(II) to solutions of **10**, **11** and **14** resulted in the rapid formation of insoluble precipitates that could not be readily characterised. Despite efforts to obtain crystalline metal complexes for a range of metal:ligand combinations, microcrystalline products were produced in almost all cases. A single crystal of sufficient quality for X-ray structural studies was eventually obtained for a copper complex of **11** by slow evaporation of solvent from a methanol/dichloromethane solution.

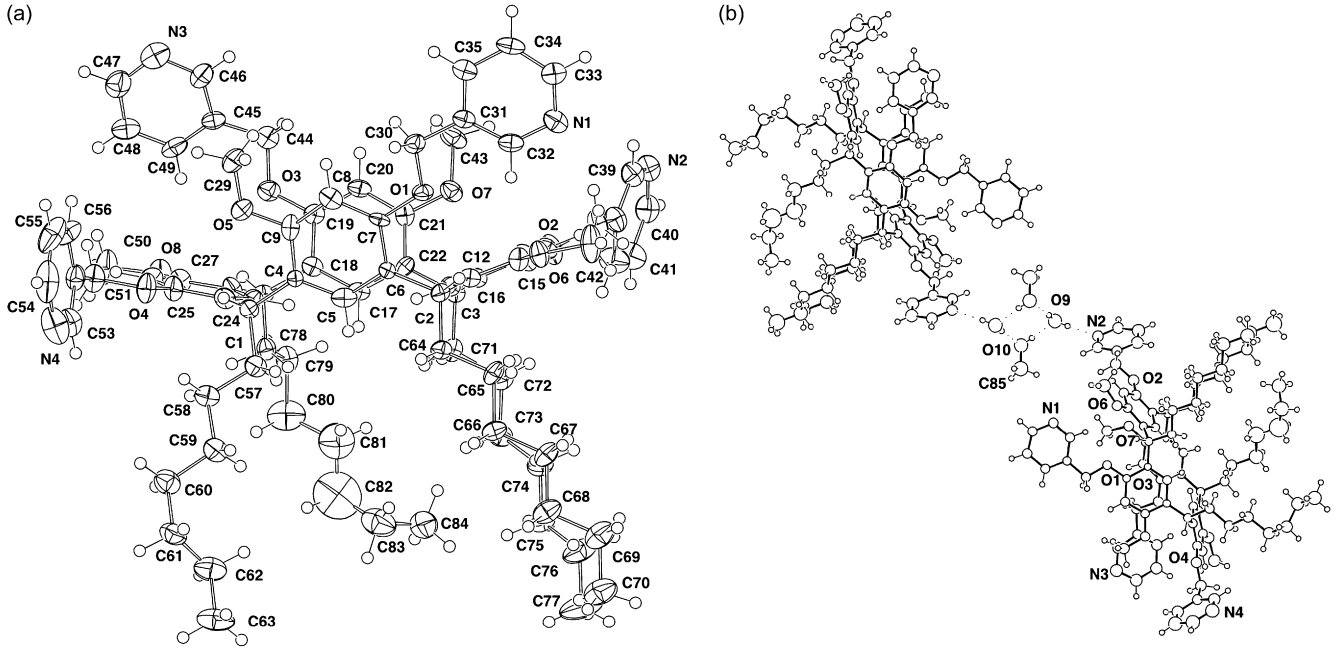


Figure 4. (a) A molecule of **14** showing the numbering scheme. Non-hydrogen atoms ellipsoids are shown at the 50% probability level. (b) The centrosymmetric H-bonded cluster. The atoms have been drawn with arbitrary radii for clarity.

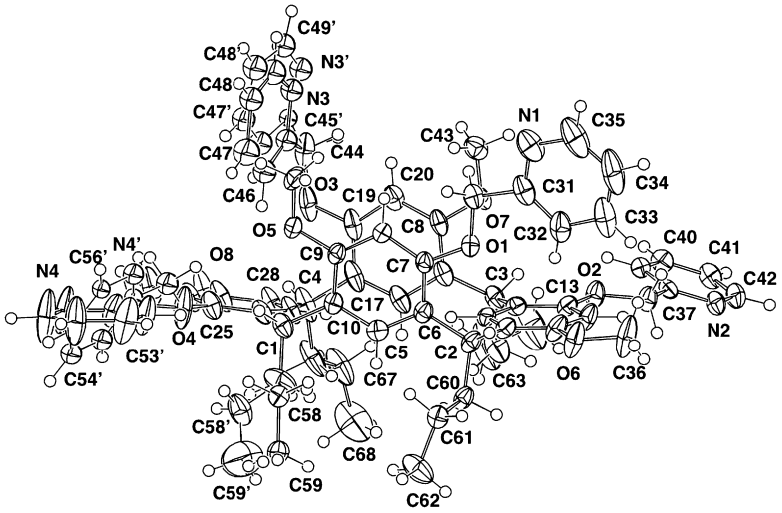


Figure 5. A molecule of **11** showing the numbering scheme. Non-hydrogen atoms ellipsoids are shown at the 50% probability level.

The structure is a linear polymer of resorcinarene/copper acetate, remarkable for the fact that the resorcinarene molecules are bridged by two different copper acetate moieties, one the well known $Cu_2(O_2CCH_3)_4$ 'paddlewheel' structure, and the other a mononuclear $Cu(O_2CCH_3)_2$ unit.

The copper complex (**Cu–11**) consists of a linear polymer of copper(II) acetate with the ligand in the Cu/OAc/**11** ratio of 1.5:3:1 (Fig. 7). The Py groups on opposite sites of the ligand containing the 'horizontal' phenyl rings bind to two Cu atoms. Py ring N2 is coordinated to a Cu1 of a $Cu(OAc)_2$ group situated on a crystallographic inversion centre. The N atom on the opposite Py group N4 is bound to a Cu2 of a $Cu_2(OAc)_4$ 'paddlewheel' group, which is also situated on a crystallographic inversion centre thus forming the polymeric chain, which is parallel to the $1\bar{1}1$ direction. The coordination around Cu1 is therefore square planar, Cu1–N2, OAc 2.003(3), 1.971(3) Å, O101–Cu1–N2 89.6(1)° (the acetate anion is considered to be unidentate, the other Cu···O distance being 2.611(3) Å). The coordination around Cu2 is a slightly distorted octahedral arrangement with the Cu2–OAc bonds being 1.967(3), 1.969(3), 1.980(3) Å and the Cu2–N4 2.200(3) Å. The angles around the Cu2 atom range from 92.0(1)–95.8(1)° with the Cu2···Cu2 distance in the $Cu_2(OAc)_4$ group being 2.643(1) Å. Table 1 shows geometries around the Cu atoms.

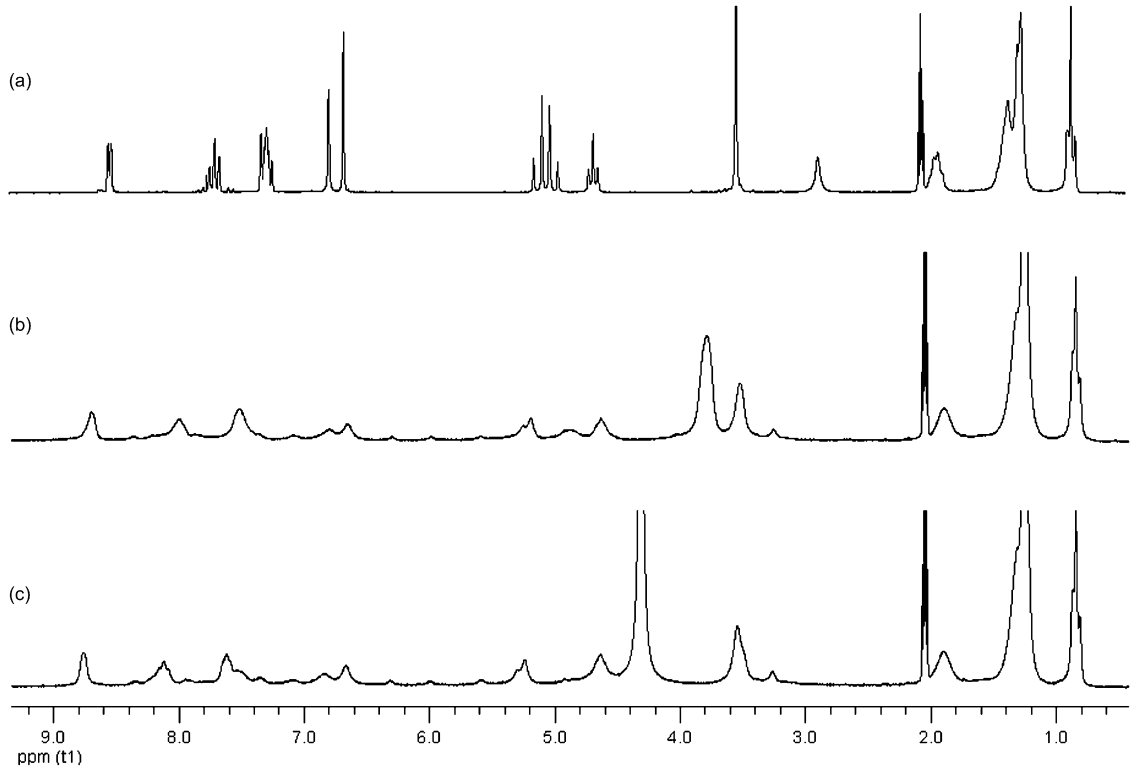


Figure 6. ^1H NMR spectra of (a) **10**, (b) **10** with 1 equiv of $Zn(ClO_4)_2 \cdot 6H_2O$, (c) **10** with excess of $Zn(ClO_4)_2 \cdot 6H_2O$.

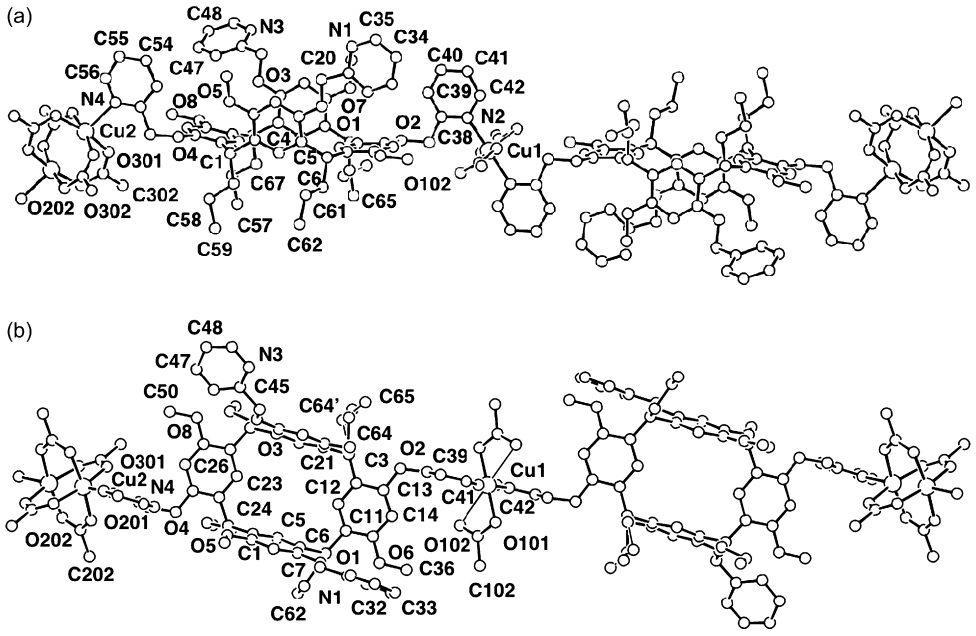


Figure 7. Showing two views of (**Cu–11**) oblique to (a) and perpendicular to (b) the plane of the methylene groups showing the numbering scheme and its polymeric nature. Non-hydrogen atoms are shown as circles of arbitrary radii. Hydrogen atoms have been omitted for clarity.

Table 1. Coordination geometries for compound **Cu–11** in Å and °

Cu1–O101	1.971(3)
Cu1–N2	2.003(3)
Cu2–O301	1.967(3)
Cu2–O201	1.969(3)
Cu2–O302′	1.980(3)
Cu2–O202′	1.967(3)
Cu2–N4	2.200(3)
Cu2···Cu2′	2.643(1)
O301–Cu2–O202′	87.8(1)
O301–Cu2–O201	92.0(1)
O202′–Cu2–O201	168.8(1)
O301–Cu2–O302′	167.7(1)
O202′–Cu2–O302′	87.7(1)
O201–Cu2–O302′	90.1(1)
O301–Cu2–N4	95.9(1)
O202′–Cu2–N4	98.16(1)
O201–Cu2–N4	93.00(1)
O302′–Cu2–N4	96.13(1)

Primed atoms are at −x,2−y,−z.

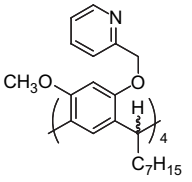
The ligand also shows the pseudo-2 symmetry, similar to that observed in the structures of the resorcinarenes **10**, **11**, and **14** above. The dihedral angles between the pairs of opposite Ph rings and the plane through the four methylene groups are 77.4(1), 98.9(1)° and 3.2(1), 12.8(1)°.

3. Experimental

3.1. General

Nuclear magnetic resonance spectra were acquired using Varian Gemini 200 (^{1}H NMR at 200 MHz and ^{13}C NMR at 50.3 MHz) or Bruker ARX 500 (^{1}H NMR at 500.13 MHz and ^{13}C NMR at 125.8 MHz) spectrometers. Chemical shifts are expressed in parts per million relative to an internal standard of chloroform, taken as being 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C spectra (relative to TMS). Melting points were recorded using an Electrothermal-IA 9100 melting point instrument. Elemental microanalyses were carried out by the Central Science Laboratory, University of Tasmania, Australia. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium-backed plates coated with Merck Kieselgel 60 F_{254} silica gel. TLC plates were visualised by UV radiation at a wavelength of 254 nm. All solvents were purified by distillation and were dried according to standard methods.

3.2. Synthesis of 2,8,14,20-tetraheptyl-4,10,16,22-tetra-(2-picolyloxy)-6,12,18,24-tetramethoxy calix[4]arene (10)

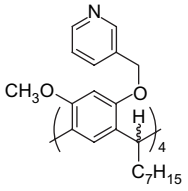


(a) A mixture of resorcinarene **8** (0.5 g, 0.53 mmol), potassium carbonate (1.47 g, 10.6 mmol) and 2-picolyl chloride hydrochloride (1.05 g, 6.40 mmol) in acetonitrile (20 mL) was heated at reflux overnight. The reaction mixture was then cooled and the solvent was removed at reduced pressure. To the residue was added sodium hydroxide solution (3 M, 50 mL) and the mixture was stirred for 30 min. The mixture was extracted with dichloromethane (3×30 mL) and the combined organic layers were washed with water (2×30 mL) and then dried (Na_2SO_4). The solvent was removed at reduced pressure and the residual solid recrystallised from methanol to give **10** as off-white needles (0.58 g, 84%) mp 99.5–100.0 °C. ^{1}H NMR ($CDCl_3$) δ 0.84 (br t, 12H, CH_2CH_3), 1.13–1.48 (m, 40H, CH_2), 1.83–1.99 (m, 8H,

CH_2CH), 3.42 (s, 12H, OCH_3), 4.59 (t, 4H, J=7.4 Hz, $CHCH_2$), 4.90, 5.09 (AB quartet, J=13.5 Hz, 8H, CH_2O), 6.42, 6.71 (s, 2×4H, ArH), 7.27–7.39 (m, 8H, pyr), 7.69 (apparent d of t, 4H, pyr), 8.56 (br d, 4H, J=4.8 Hz, pyr). ^{13}C NMR ($CDCl_3$) δ 14.8 (CH_3), 23.4, 29.1, 30.1, 30.7, 32.7, 35.2, 36.6 (CH and CH_2), 56.4 (OCH_3), 70.1 (OCH_2), 97.9, 123.3, 124.0, 126.5, 127.11, 127.18, 140.2, 146.6, 154.9, 156.4 and 157.2 (Ar). Found: C, 77.5; H, 8.4; N, 4.2%. $C_{84}H_{108}N_4O_8$ requires C, 77.5; H, 8.4; N, 4.3%.

(b) A mixture of resorcinarene **8** (0.52 g, 0.55 mmol), sodium hydride (1.12 g, 60% in oil, 28.0 mmol) and imidazole (1 crystal) in dry dimethylformamide (20 mL) was stirred at room temperature for 30 min. 2-Picolyl chloride hydrochloride (0.459 g, 2.80 mmol) was then added in portions and the mixture was stirred at room temperature overnight. The majority of the solvent was then removed at reduced pressure and the resulting residue was dissolved in dichloromethane (50 mL). The solution was washed with water (5×50 mL) and dried (Na_2SO_4). The solution was concentrated at reduced pressure and the residue crystallised from methanol to afford colourless needles (0.58 g, 81%). The NMR and physical data were identical to that given above.

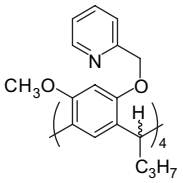
3.3. Synthesis of 2,8,14,20-tetraheptyl-4,10,16,22-tetra-(3-picolyloxy)-6,12,18,24-tetramethoxy calix[4]arene (14)



(a) A mixture of resorcinarene **8** (0.50 g, 0.53 mmol), sodium hydride (1.07 g, 60% in oil, 26.7 mmol) and imidazole (1 crystal) in dry dimethylformamide (20 mL) was stirred at room temperature for 30 min. 3-Picolyl chloride hydrochloride (0.70 g, 4.24 mmol) was then added in portions and the mixture was stirred at room temperature overnight. The majority of the solvent was then removed at reduced pressure and the resulting residue was dissolved in dichloromethane (50 mL). The solution was washed with water (5×50 mL) and dried (Na_2SO_4). The solvent was removed at reduced pressure and the residue crystallised from dichloromethane/methanol to afford **14** as off-white needles (0.50 g, 72%) mp 133–134 °C. ^1H NMR (d_6-acetone) δ 0.85 (br t, 12H, CH_2CH_3), 1.14–1.46 (m, 40H, CH_2), 1.80–1.97 (m, 8H, CH_2CH), 3.51 (s, 12H, OCH_3), 4.60 (t, 4H, J=7.4 Hz, $CHCH_2$), 4.89, 5.15 (AB quartet, J=11.6 Hz, 8H, CH_2O), 6.68, 6.76 (s, 2×4H, ArH), 7.31 (dd, 4H, J=4.8 Hz, J=7.8 Hz, pyr), 7.56–7.66 (m, 4H, pyr), 8.48–8.61 (m, 8H, pyr). ^{13}C NMR (d_6-acetone) δ 14.8 (CH_3), 23.7, 29.6, 30.6, 31.0, 33.1, 35.6 (CH_2), 37.0 (CH), 56.2 (OCH_3), 69.7 (OCH_2), 99.2, 124.4, 126.8, 127.1, 134.7, 136.4, 150.2, 150.3, 156.5 and 157.1 (Ar); note—one coincident Ar signal. Found: C, 74.9; H, 8.3; N, 4.0%. $C_{84}H_{108}N_4O_8$. ½CH_3OH.½CH_2Cl_2 requires C, 75.0; H, 8.2; N, 4.1%.

(b) A mixture of resorcinarene **8** (0.25 g, 0.27 mmol), potassium carbonate (0.74 g, 5.3 mmol) and 3-picolyl chloride hydrochloride (0.52 g, 3.20 mmol) in acetonitrile (10 mL) was heated at reflux overnight. The reaction mixture was then cooled and the solvent was removed at reduced pressure. To the residue was added sodium hydroxide solution (3 M, 20 mL) and the mixture stirred for 30 min. The mixture was extracted with dichloromethane (3×20 mL) and the combined organic layers were washed with water (2×30 mL) and then dried (Na_2SO_4). The solvent was removed at reduced pressure and the residual solid recrystallised from dichloromethane–methanol to give **14** as off-white needles (0.05 g, 15%). The NMR and physical data were identical to that given above.

3.4. Synthesis of 2,8,14,20-tetrapropyl-4,10,16,22-tetra-(2-picolyloxy)-6,12,18,24-tetramethoxy calix[4]arene (11)



A mixture of resorcinarene **9** (0.5 g, 0.70 mmol), potassium carbonate (1.94 g, 14.0 mmol) and 2-picolyl chloride hydrochloride (1.38 g, 8.40 mmol) in acetonitrile (20 mL) was heated at reflux overnight. The reaction mixture was then cooled and the solvent was removed at reduced pressure. To the residue was added sodium hydroxide solution (3 M, 50 mL) and the mixture was stirred for 30 min. The mixture was extracted with dichloromethane (3×30 mL) and the combined organic layers were washed with water (2×30 mL) and then dried (K_2CO_3). The solvent was removed at reduced pressure and the residue passed through a silica plug (dichloromethane/ethyl acetate 4:1 followed by dichloromethane/ethyl acetate 4:1 with 5% triethylamine). The crude solid was recrystallised from methanol to give **11** as colourless plates (0.60 g, 80%) mp 184–185 °C. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.94 (t, 12H, J=7.4 Hz, CH_2CH_3), 1.41 (apparent sextet, 8H, CH_2CH_3), 1.85–1.96 (m, 8H, CH_2CH), 3.43 (s, 12H, OCH_3), 4.61 (t, 4H, J=7.5 Hz, $CHCH_2$), 4.90, 5.08 (AB quartet, J=13.2 Hz, 8H, CH_2O), 6.40, 6.71 (s, 2×4H, ArH), 7.15–7.19 (m, 4H, pyr), 7.27 (br d, 4H, pyr), 7.53 (apparent d of t, 4H, pyr), 8.53–8.55 (m, 4H, pyr ArH). ^{13}C NMR ($CDCl_3$) δ 15.0 (CH_3), 22.2 (CH_2CH_3), 36.5 (CH), 37.4 ($CHCH_2$), 56.1 (OCH_3), 71.8 (OCH_2), 97.6, 121.8, 123.0, 126.4, 126.8, 127.0, 137.3, 149.4, 155.2, 156.3 and 158.7 (Ar).

3.5. Crystallography

Colourless prisms of **10**, **11** and **14** suitable for single crystal X-ray analysis were obtained by slow evaporation of solvent from a filtered solution of the appropriate resorcinarene (20–40 mg) in methanol (~5 mL) and dichloromethane (~5 mL). Blue prisms of the copper complex of **Cu–11** suitable for single crystal X-ray analysis were obtained by slow evaporation of solvent from a filtered solution of **11** (~20 mg) and excess copper(II) acetate in methanol (~5 mL) and dichloromethane (~5 mL).

The data for **10** were collected on a Bruker SMART diffractometer, ω scans, Mo Kα radiation, λ=0.71073 Å. Those for **11**, **14** and **Cu–11** were collected on an Oxford Diffraction Xcalibur-S diffractometer using φ and ω scans, T=100 K. Following multiscan absorption corrections, the structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX97.[29] Residuals $R1$ are quoted for 'observed' reflections ($I>2\sigma(I)$), and $wR2$ for all data. Except where stated, all non-hydrogen atoms were refined with anisotropic displacement parameters.

Compound **10**·CH_3OH: $C_{84}H_{108}N_4O_8\cdot CH_3OH$, M=1333.79. Triclinic, space group $P\bar{1}$, a=14.962(2), b=14.972(2), c=17.762(2) Å, α=105.740(2), β=94.113(2), γ=92.176(2)°, V=3813.0(8) Å^3. D_{calc} (Z=2)=1.162 g cm^{-3}. μ (Mo Kα)=0.074 mm^{-1}; specimen: 0.40×0.32×0.19 mm; $T_{min/max}$=0.91. $2\theta_{max}$=58°; T=170 K. N_{total}=34,868; N_{unique}=18,118 (R_{int}=0.044), $N(I>2\sigma(I))$=12,321; $R1$, $wR2$=0.077, 0.247.

The solvent was modelled as a molecule of methanol, disordered over two sites each with site occupancies set at 0.5 after trial refinement. Three atoms, C404–C407, of one chain were found to be disordered over two sites and assigned occupancy factors of 0.5 after initial trial refinement. The atoms of the solvent and the disordered atoms were refined with isotropic displacement parameters.

Compound **14**·$CH_3OH\cdot H_2O$: $C_{84}H_{108}N_4O_8\cdot CH_3OH\cdot H_2O$, M=1351.80. Triclinic, space group $P\bar{1}$, a=10.004(3), b=18.280(6), c=22.807(8) Å, α=68.33(3), β=78.73(3), γ=82.08(3)°, V=3791(2) Å^3. D_{calc} (Z=2)=1.184 g cm^{-3}. μ (Mo Kα)=0.077 mm^{-1}; specimen: 0.35×0.26×0.15 mm; $T_{min/max}$=0.98. $2\theta_{max}$=50°; T=100 K. N_{total}=32,659; N_{unique}=13,225 (R_{int}=0.089), $N(I>2\sigma(I))$=4819; $R1$, $wR2$=0.101, 0.283 (all data).

Water molecule hydrogen atoms were refined with geometries restrained to ideal values.

Compound **11**: $C_{68}H_{76}N_4O_8$, M=1351.80. Triclinic, space group $P\bar{1}$, a=12.929(3), b=15.093(5), c=16.100(2) Å, α=85.49(1), β=67.98(1), γ=77.55(2)°, V=2844(1) Å^3. D_{calc} (Z=2)=1.258 g cm^{-3}. μ (Mo Kα)=0.082 mm^{-1}; specimen: 0.64×0.47×0.08 mm; $T_{min/max}$=0.98. $2\theta_{max}$=50°; T=100 K. N_{total}=51,364; N_{unique}=10,000, (R_{int}=0.032), $N(I>2\sigma(I))$=5480; $R1$, $wR2$=0.068, 0.218.

Two CH_2py groups (C44–N3 and C51–N4) and one ^{n}Pr group (C57–C59) were modelled as being disordered, each over 2 sites with site occupancy factors set at 0.5 for C44–N3 and C57–C59 after trial refinement, and 0.750(4) and 1–0.750(4) for the C51–N4 ring.

Disordered atoms were refined with isotropic displacement parameters.

Compound **Cu–11**: $C_{148}H_{170}Cu_3N_8O_{28}\cdot 2(CH_2Cl_2)\cdot 0.538(CH_3OH)$, M=2886.63. Triclinic, space group $P\bar{1}$, a=12.933(2), b=15.996(6), c=18.917(3) Å, α=92.56(2), β=94.96(1), γ=108.09(2)°, V=3695(2) Å^3. D_{calc} (Z=1)=1.297 g cm^{-3}. μ (Mo Kα)=0.573 mm^{-1}; specimen: 0.18×0.10×0.04 mm; $T_{min/max}$=0.94. $2\theta_{max}$=50°; N_{total} 31,297; T=100 K. N_{unique}=12,896, (R_{int}=0.087), $N(I>2\sigma(I))$=6250; $R1$=0.071, $wR2$=0.146.

One solvent was identified clearly as a CH_2Cl_2. The second was modelled as CH_2Cl_2 refined with site occupancy factor complementary of the first. Remaining peaks near the second CH_2Cl_2 site were modelled as a solvent CH_3OH with site occupancy refined to 0.269(4), methyl and hydroxyl H atoms not being included. One propyl group (C63–C65) was found to be disordered over 2 sites with site occupancy of the major component found to be similar to those of CH_2Cl_2 (**1**) and thus these were restrained to be the identical.

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