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Building blocks for cyclotriveratrylene-based coordination networks

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The incorporation of three-fold symmetric organic host molecules into coordination polymers should allow for the construction of new and interesting network structures, capable of multiple inclusion behaviour. A range of new multi-dentate bridging ligands/molecular hosts have been prepared by appending nitrogen-containing heterocycles to either cyclotricatechylene, or cyclotriguaiacylene cores. These compounds were obtained in a single-step reaction from readily available precursors, with moderate to good yields, and characterised by a combination of NMR spectroscopy, mass spectrometry and elemental analysis. Two of the new compounds were characterised by X-ray crystallography, revealing different modes of self inclusion behaviour, which indicate the potential importance of π-donor stabilisation by CTV derivatives in host–guest chemistry.

Introduction

Host–guest or inclusion chemistry, where the two or more molecules form a non-covalently bound complex, has generated, and continues to receive, wide attention in the chemical sciences.[1] In this area, which provided much of the initial impetus in the development of supramolecular chemistry, some of the more successful hosts have been macrocycles such as the tubular cyclodextrins, or the bowl-shaped calixarenes.[1] Typically, successful host molecules completely encapsulate or shroud the guest within a molecular cavity, relying on weak supramolecular interactions to stabilise the non-covalent complex. These hosts have found application as receptors and sensors for biologically important guests, ions and small molecules, and in the field of separation science.[2] Other hosts include the cyclic trimer of veratrole, cyclotriveratrylene (CTV, **1**),[3–5] shown in Fig. 1, and macrocyclic crown ethers.[6]

Another area of supramolecular chemistry, which has seen a dramatic increase in study over the past decade, is the synthesis of coordination polymers or metal–organic frameworks.[7,8] Porous metal-containing compounds, constructed from transition metal ions and organic bridging ligands, have the potential to allow the formation of new and unusual structures. These materials can possess properties not available to purely organic or inorganic compounds, including new magnetic, electrochemical, optical and catalytic properties.[8] Such 3-D network structures can be constructed and tailored by judicious choice of the transition metal and/or organic bridging ligand.[8,9]

The unification of these two fields of supramolecular science by employing molecular hosts as building blocks for the construction of coordination polymers has been briefly studied.[10,11] The incorporation of molecular hosts also introduces the potential for a number of interesting properties not necessarily attainable with conventional ligands such as (i) multiple inclusion behaviours; (ii) unusual ligand topologies; (iii) employing host–guest interactions as supramolecular synthons. Some examples of this approach have been reported using sulfonated calixarenes,[11,12] for example a 2-D coordination polymer has been reported with sulfonatocalix[4]arene and scandium triflate.[11] Calixarenes substituted with nitrogen-containing heterocycles have been prepared,[13] but their use primarily directed toward improving the host–guest chemistry and complexation of alkali metals.[13] In contrast to the use of calixarene-based host molecules to build transition metal coordination polymers, CTV has not been extensively employed in such studies. Recently, we prepared the first example of a transition metal coordination polymer incorporating a CTV derivative.[14]

CTV is a rigid bowl-shaped molecule that, while being a poor host to small organic molecules, has been shown to bind large molecules such as *o*-carborane,[15] fullerenes,[16,17] and organometallic complexes[18] within its molecular cavity. With small molecules, CTV typically forms crystalline clathrate compounds whereby the guests are located in channels between pillars of stacked CTV molecules.[3] To enhance the properties of **1** as a host, CTV-based covalently-bonded cavitands, cryptophanes and extended arm derivatives have been prepared which more readily bind small guests.[5,19,20] For instance, a series of cyclotriveratrylene derivatives, with extended cavities possessing electron-withdrawing groups, were recently prepared by reaction of *p*-substituted fluorobenzene derivatives with cyclotriguaiacylene (CTG, **4**).[21] These extensions allow the

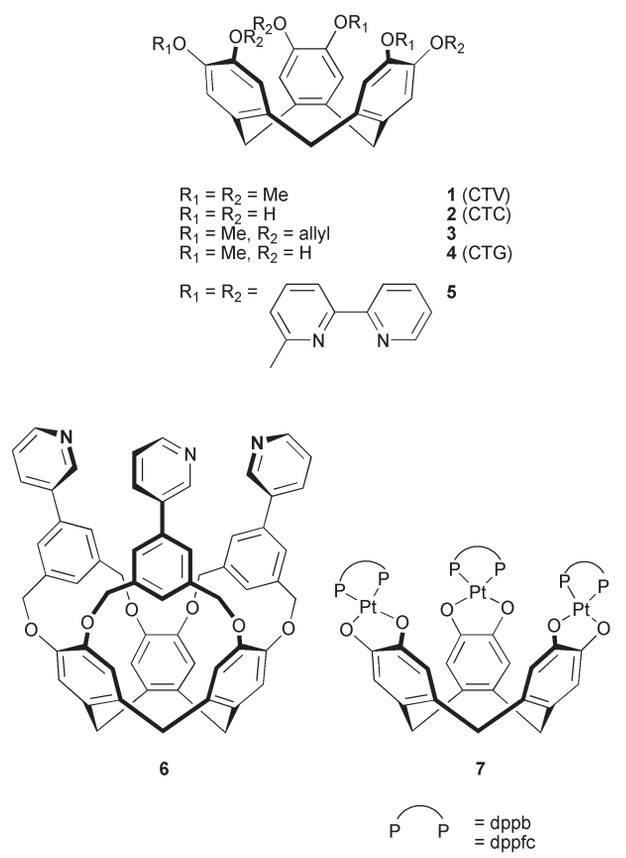

Fig. 1 Derivatives of cyclotriveratrylene (CTV, **1**), including examples with appended nitrogen-containing heterocyclic groups (**5** and **6**)[24,25] and the use of deprotonated cyclotricatechylene (CTC, **2**) as a ligand for platinum(II).[28] (dppb = diphenylphosphinobenzene, dppfc = diphenylphosphinoferrocene).

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CTV derivatives to completely encapsulate the guest within the molecular cavity.

Two- and three-dimensional crystal-engineered materials have been prepared using the dimethoxy functionality of CTV as either a hydrogen bond donor[22] or as a ligand for alkali metals.[23] Incorporation of CTV into coordination networks has been shown to enhance the properties of CTV as a molecular host. However, despite being able to construct 2-D and 3-D networks from CTV incorporating specific host–guest interactions, the resulting materials are not of a sufficiently predictable nor robust nature to be suitable for the aforementioned applications of coordination networks.[8] Thus, herein we describe a series of tri- and hexa-substituted CTV derivatives where, by incorporating nitrogen-containing heterocyclic donor groups, we have both extended the molecular cavity and improved the metal binding properties of the parent compound.

There have been a limited number of reported extended arm derivatives of CTV incorporating metal binding domains. These include a copper complex of the 2,2-bipyridyl compound (**5**), which has been investigated as a redox-induced conformational switch.[24] Cram *et al.* reported the synthesis of extended cavitand derivatives,[20] while the tripod (**6**) was prepared by Wytko and Weiss.[25] Nickel complexes have been described with an extended salicylaldiminato derivative of CTV.[26] CTV can also be improved as a ligand by demethylation with boron tribromide to give the hexahydroxy compound, cyclotricatechylene (CTC, **2**).[27] Deprotonated CTC has been shown to form discrete trinuclear complexes with platinum(II) (**7**).[28] Indicative of the recent interest in metal–organic analogues of organic macrocycles, a metal–organic mimic of CTV has also been described.[29]

Results and discussion

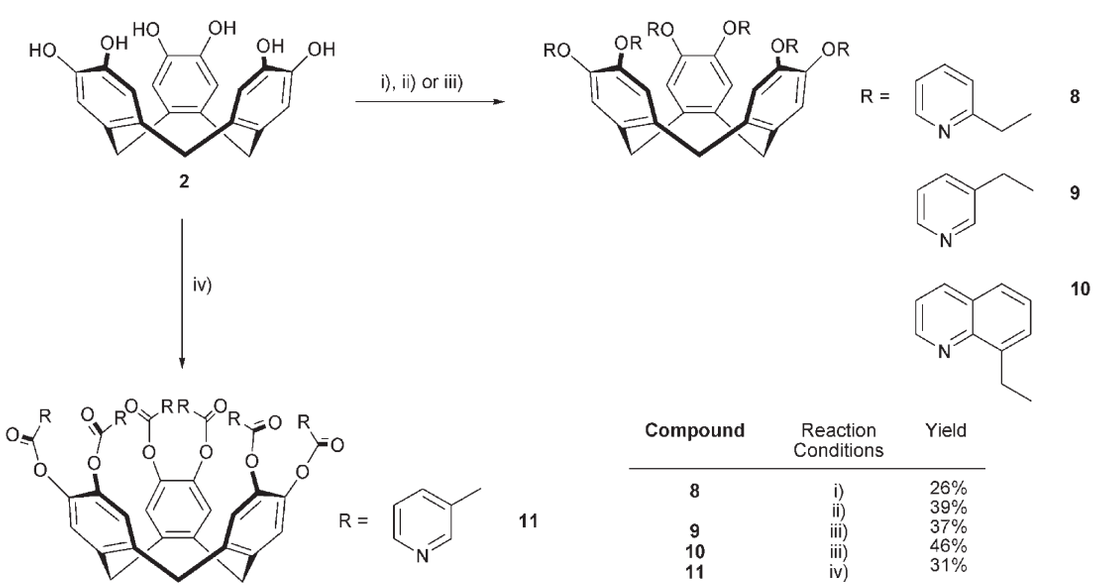
Synthesis

The heterocycle functionalised CTV compounds were all prepared by reaction of the appropriately demethylated derivative, cyclotricatechylene or cyclotriguaiacylene, with the desired electrophile in the presence of a suitable base. As noted above, CTC is easily prepared, on a multi-gram scale, by demethylation of CTV,[27,30] while the trihydroxy derivative, CTG, can be readily prepared from the trisallyl-protected compound (**3**)[31,32] as described by Brotin and co-workers.[33] It is worth noting here that the individual tri-substituted CTV compounds (*i.e.* **4**) are chiral but the bulk material is prepared as a racemic mixture. In this work the enantiomers were not separated, but the possibility exists for doing so in the future.

The hexa-substituted derivatives were prepared by reacting six equivalents of an electrophile with **2** to give a series of new ligands in yields ranging from 26% to 46%. Specifically, reaction of **2** with 2-bromomethylpyridine hydrobromide or 3-chloromethylpyridine hydrochloride, in the presence of potassium carbonate, gave the new ligands **8** and **9**, in moderate yields of 26% and 37%, respectively (Scheme 1). The sterically hindered quinoline derivative **10** was isolated in 46% yield following extended heating in DMF using cesium carbonate as a base. Shorter reaction times gave an inseparable mixture of incompletely reacted derivatives, which could be converted to the final product (**10**) by addition of further equivalents of 8-bromomethylquinoline. The ester (**11**) was prepared by stirring **2** and nicotinoyl chloride hydrochloride at room temperature in THF. This compound was isolated in 31% yield as a white solid by trituration with ethanol.

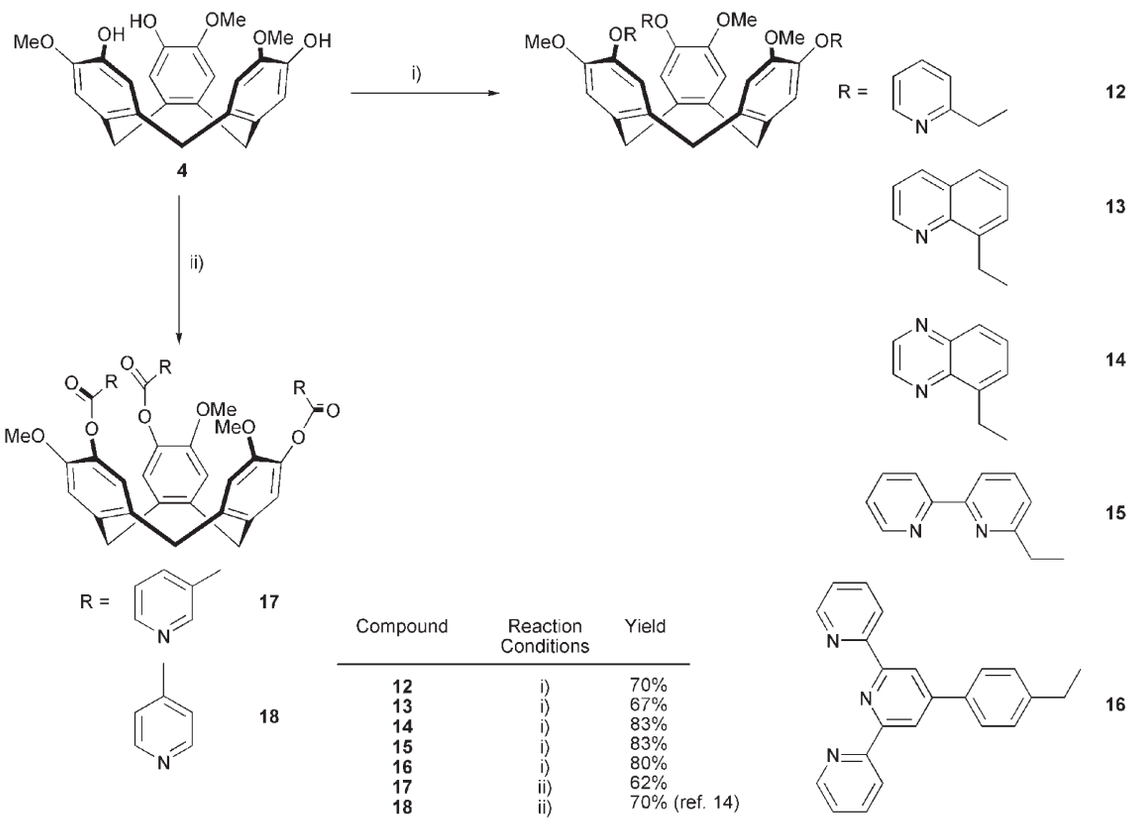
All the new hexa-substituted compounds were characterised by a combination of ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and CHN analysis. Compounds **8**–**11** all provided NMR spectra commensurate with a symmetrical CTV core; *i.e.* a pair of doublets in the range 3.4–5.0 ppm, corresponding to the methylene protons of the cyclononene core, and a signal at *ca.* 5–6 ppm for the protons of the benzene ring. The functionalised arms of compounds **8** and **9** appear to be freely rotating in solution as evidenced by the singlets observed for the methylene protons in the ^{1}H NMR spectra, while the corresponding protons of the more sterically hindered derivative, **10**, appeared as a broadened quartet. This indicated the considerable steric bulk of the hexa-substituted compounds and prompted us to investigate related ligands constructed around a cyclotriguaiacylene core.

In contrast to the syntheses of **8**–**11**, which proceeded in low to moderate yields, the syntheses of the tri-substituted derivatives were considerably more facile (Scheme 2). Typically under less aggressive conditions than previously used, the tri-substituted compounds **12**–**17** were obtained in yields ranging from 62–83%. Thus, reaction of cyclotriguaiacylene with 2-bromomethylpyridine hydrobromide gave **12** in 70% yield, whereas reaction with CTC gave only a 26% yield of **8** under identical conditions. Similarly, reaction of **4** with 8-bromomethylquinoline or 5-bromomethylquinoxaline gave the new derivatised cyclotriveratrylenes (**13** and **14**) in good yields of 67% and 83%, respectively. The new tris-bidentate compound, **15**, was prepared in 83% yield, while the corresponding terpyridine derivative (**16**) was obtained in 80% yield after only 48 hours reflux. Compound **17** was prepared by reacting CTG with nicotinoyl chloride hydrochloride using the method employed for compound **11**. An isomer of **17**, tris(isonicotinoyl)cyclotriguaiacylene (**18**), has been recently reported by us.[14]



Compound	Reaction Conditions	Yield
8	i)	26%
	ii)	39%
9	iii)	37%
10	iii)	46%
11	iv)	31%

Scheme 1 *Reagents and conditions*: i) RBr, K_2CO_3, acetone; ii) RBr, KOH, DMSO; iii) RX (X = Cl, Br), K_2CO_3 or Cs_2CO_3, DMF; iv) RCOCl, Et_3N, THF.



Compound	Reaction Conditions	Yield
12	i)	70%
13	i)	67%
14	i)	83%
15	i)	83%
16	i)	80%
17	ii)	62%
18	ii)	70% (ref. 14)

Scheme 2 *Reagents and conditions*: i) RBr, K_2CO_3, acetone; ii) RCOCl, Et_3N, THF.

Like the hexa-substituted compounds, all the new cyclotriguaiacylene derivatives were characterised by a combination of ^1H and ^{13}C NMR spectroscopy, mass spectrometry and CHN analysis. The symmetry of the CTV core is absent in these compounds and the benzene protons appeared as two singlets in the ^1H NMR spectra. Other features are commensurate with a central cyclononene core.

Structural studies

There has been limited structural characterisation of CTV derivatives with extended and functionalised cavities.[20,34] Many of the proposed uses of such compounds involve taking advantage of the host–guest chemistry of these derivatives, but limited information is available about the conformations such derivatives adopt in either the solid-state, or in solution.

Crystals of the hexa-substituted derivative, **8**, were obtained by slow cooling and evaporation of a dilute methanol solution. Compound **8** crystallises in the hexagonal space group *R*3*m*, with three molecules of **8** in the unit cell and solvate water filling the voids between the molecules of **8**. The oxygen atoms of the water molecules are modelled isotropically and the hydrogen atoms on these oxygen atoms were not located in the difference map. The crystal structure confirms that the precursor, CTC, has indeed yielded to six-fold substitution and, as shown in Fig. 2, the pyridine rings of **8** further extend the bowl-shaped cavity of the parent compound. The torsion angles reveal that, in the solid-state structure, each face of the extended CTV bowl is almost planar forming the three sides of a trigonal pyramid. The bond distances and angles of the core of the molecule are unremarkable and typical of other structurally characterised CTV derivatives.

The packing diagram in Fig. 3 illustrates that this trigonal pyramidal extended-cavity provides a natural host for another molecule of **8**, resulting in infinite stacks of the ligand with the solvated water molecules filling the voids between those stacks. The stacks are stabilised by off-set face-to-face π–π stacking interactions between the CTV cores of the adjacent molecules of **8**. The shortest carbon–carbon distance, between carbon

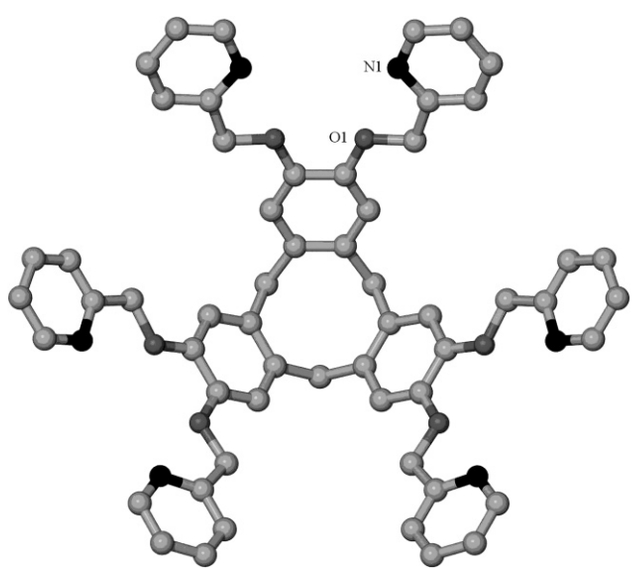


Fig. 2 A perspective view of the bowl-shaped CTV derivative **8**, from the X-ray crystal structure of **8**·4½H_2O. Hydrogen atoms and solvated water molecules are omitted from the diagram for clarity.

atoms in the CTV core, is 3.58(1) Å. No solvent host–guest inclusion behaviour is observed in the solid state for **8**. This packing is similar to the α-phase observed for CTV, whereby solvate molecules fill the voids surrounding pillars formed from stacks of CTV.[3]

The tri-substituted compound, **13**, was also characterised by X-ray crystallography. The crystals of **13**·2CH_3CN were obtained by vapour diffusion of ether into an acetonitrile solution of **13**. Compound **13** crystallises in the triclinic space group, *P*-1, with a centre of inversion relating two molecules of **13**, which form a self-complementary host–guest association. Two lattice included acetonitrile solvate molecules also occupy the asymmetric unit. A perspective view of **13** is shown in Fig. 4, revealing that the more bulky quinoline substituents twist out of the plane of the benzene core to which they are appended. This is in

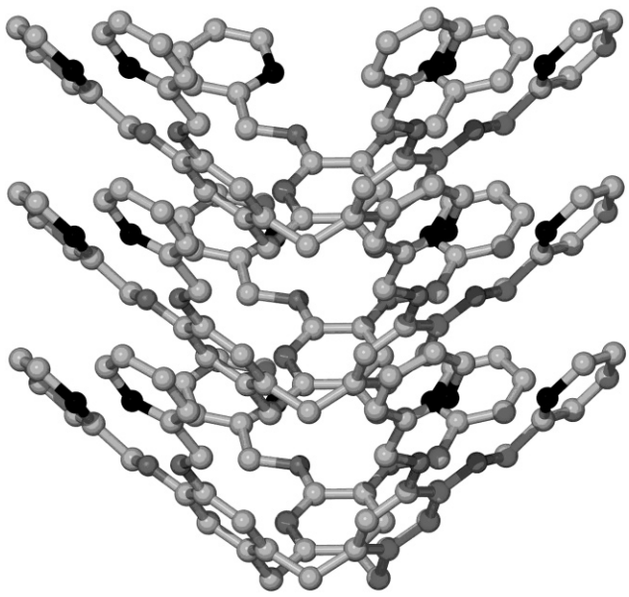


Fig. 3 A perspective view of a pillar (viewed perpendicular to the *c*-axis) formed by host–guest associations between adjacent molecules of **8**.

contrast to the trigonal pyramidal conformation of **8**. The torsion angles for the O–CH_2–C_{quin}–C_{quin} bonds are between 79.2(3) and 171.2(4)°. In this structure, one of the carbon atoms of a methoxy group (C43) on the cyclotriguaiacylene core is heavily disordered and this atom modelled over the two positions. Such disorder of the methoxy groups of CTV derivatives is, in our experience, relatively uncommon because mesomeric effects stabilise the in-plane conformation of the methoxy groups.

The packing diagram in Fig. 5 shows the self-complementary host–guest association between two molecules of **13**. The quinoline ring from one molecule lies directly over the 9-membered ring of the CTV core of the second molecule of **13**. An edge-to-face C–H···π interaction between the quinoline ring of one molecule and the phenyl ring of the CTV core stabilises the dimer (C39–benzene centroid distance of 3.46(1) Å). The dimer is skewed to accommodate this interaction and the CTG cores of the two molecules are not located directly opposite each other. No evidence of dimerisation of this compound is observed in solution however.

Interestingly, the edge-to-face C–H···π interaction observed for compound **13** is consistent with π-donation by the CTV core being an important factor in the stabilisation of host–guest complexes of CTV derivatives with π-deficient guests.[16,23,35] Additionally, this interaction between the π-deficient quinoline ring and the CTV core appears to be favoured over inclusion of solvent in the molecular cavity of **13**. The mode of self-inclusion observed here is entirely different to that usually encountered in CTV chemistry, where typically the molecules stack in the mode observed for compound **8**.

Notably, the previously described ester compound (**18**) also packs as a face-to-face dimer in the solid state.[14] The orientation of the carbonyl groups and the pyridine rings in that compound appear to prevent it from packing in the manner described above for compound **8**.

Conclusions

In summary, a series of new multi-dentate nitrogen-containing bridging ligands/molecular hosts have been prepared, in moderate to good yields, by appending nitrogen-containing heterocycles to either cyclotricatechylene or cyclotriguaiacylene precursors. Two of these compounds were characterised by X-ray crystallography revealing different forms of host–guest behaviour in the solid state. Transition metal complexes and potential coordination polymers of the new nitrogen-donor ligands described in this paper are currently under investigation.

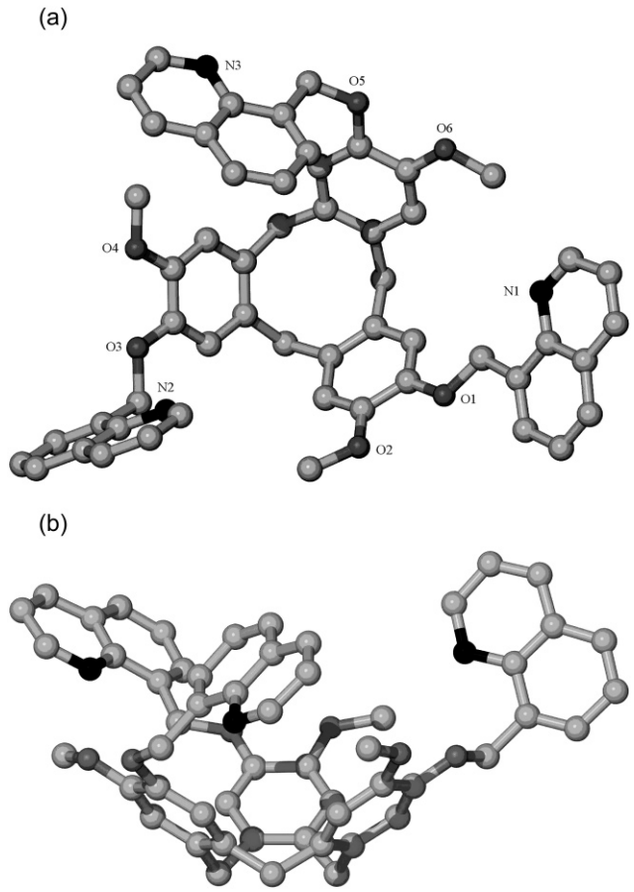


Fig. 4 Two views of the cyclotriguaiacylene derivative **13** from the crystal structure of **13**·$2CH_3CN$, showing (a) the twisting of the three quinoline arms looking into the cavity and (b) a side view. Solvate molecules, along with the hydrogen atoms and the disorder of the methoxy group, are not shown in the diagram.

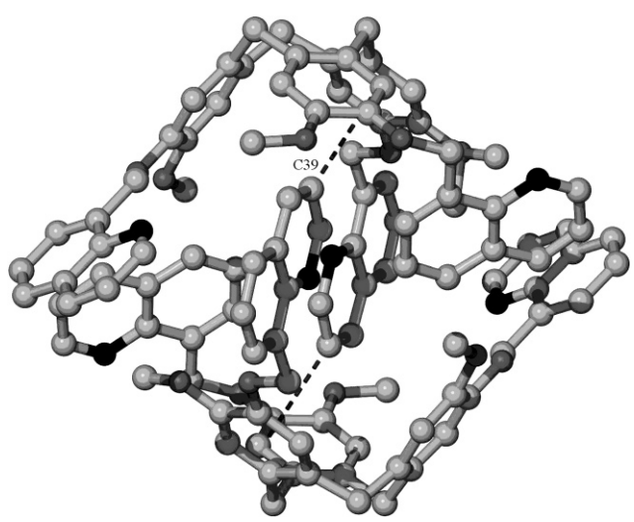


Fig. 5 A perspective view of the self-complementary host–guest association between two molecules of **13**, with the stabilising edge-to-face C–H···π interactions indicated (dashed bonds).

Acknowledgements

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Experimental

General experimental

Melting points were recorded on a Bibby melting point apparatus and are uncorrected. The University of Leeds microanalytical

laboratory performed elemental analyses. Electrospray (ES) mass spectra were recorded using a Micromass LCT mass spectrometer. NMR spectra were recorded on a Bruker 250 MHz spectrometer at 23 °C, using a 5 mm probe. Unless otherwise stated reagents were obtained from commercial sources and used as received. Solvents were dried using standard procedures. The following compounds were prepared by literature procedures: cyclotriveratrylene (**1**),[32] cyclotricatechylene (**2**),[27] tris(allyl)-trimethoxycyclononene (**3**),[31,32] cyclotriguaiacylene (**4**)[33] and 8-bromomethylquinoline.[36]

Syntheses

Hexakis(2-pyridylmethyl)cyclotriveratrylene (8). ***Method A***. Under nitrogen, cyclotricatechylene (250 mg, 0.682 mmol) and potassium carbonate (3.93 g, 28.4 mmol) were refluxed in acetone (40 mL) for 30 minutes before 2-bromopyridine hydrobromide (1.16 g, 4.59 mmol) was added. The resulting solution was refluxed for 50 hours, the solid removed by filtration and the filtrate evaporated to dryness. The residue was taken up in dichloromethane (50 mL), washed with two portions of water (50 mL) and dried over sodium sulfate. The filtrate was evaporated to dryness and the residue triturated with methanol to give a cream precipitate that was filtered and dried. Yield 160 mg (26%).

*Method B***.** Cyclotricatechylene (249 mg, 0.680 mmol) and potassium hydroxide (1.05 g, 28.4 mmol) were stirred for 30 minutes in DMSO (40 mL), under nitrogen. 2-Bromopyridine hydrobromide (1.15 g, 4.55 mmol) was added to the deep blue solution. The reaction mixture was stirred at room temperature for three days, then poured into water (50 mL) and extracted with dichloromethane (4 × 50 mL). The chlorinated extracts were dried over sodium sulfate and the solvent removed *in vacuo.* The residue was triturated with methanol to give a cream precipitate that was filtered and dried. Yield 241 mg (39%). Crystals were obtained by slow cooling and evaporation of a dilute methanol solution.

Mp 186–187 °C. *m/z* (ES) 913.3680 (56%, MH^+, $C_{57}H_{49}N_6O_6^+$ requires 913.3714). Analysis: calc. for $C_{57}H_{48}N_6O_6{\cdot}H_2O$ C 73.5, H 5.4, N 9.0; found C 73.7, H 5.1, N 8.6%. ^{1}H NMR ($CDCl_3$) δ 3.42 (d, 3H, CH_2), 4.63 (d, 3H, CH_2), 5.26 (s, 12H, CH_2–O), 6.82 (s, 6H, arom. CH), 7.14 (dd, 6H, pyH5), 7.55 (d, 6H, pyH3), 7.66 (t, 6H, pyH4), 8.57 (d, 6H, pyH6). ^{13}C NMR ($CDCl_3$) δ 35.42, 71.09, 115.51, 120.29, 121.56, 131.76, 135.80, 146.28, 148.07, 156.64.

Hexakis(3-pyridylmethyl)cyclotriveratrylene (9). Cyclotricatechylene (251 mg, 0.685 mmol) and potassium carbonate (2.50 g, 18.1 mmol) were stirred in DMF (10 mL), under nitrogen. This suspension was heated at 90 °C for 30 minutes before 3-chloropyridine hydrochloride (738 mg, 4.50 mmol) was added. The resulting suspension was heated for 96 hours, poured into water (100 mL) and extracted with dichloromethane (3 × 75 mL). The extracts were dried over magnesium sulfate, evaporated to dryness and the residue triturated with methanol to give a cream precipitate that was filtered and dried. Yield 230 mg (37%).

Mp 191–193 °C. *m/z* (ES) 913.3707 (55%, MH^+, $C_{57}H_{49}N_6O_6^+$ requires 913.3714), 822.3 (11%), 729.3 (40%), 638.2 (37%) 545.2 (37%). Analysis: calc. for $C_{57}H_{48}N_6O_6{\cdot}2H_2O$ C 72.1, H 5.5, N 8.9; found C 71.9, H 5.5, N 8.6%. ^{1}H NMR ($CDCl_3$) δ 3.41 (d, 3H, CH_2), 4.62 (d, 3H, CH_2), 4.97 (s, 12H, CH_2–O), 6.76 (s, 6H, arom. CH), 7.19 (t, 6H, pyH5), 7.65 (d, 6H, pyH4), 8.45 (d, 6H, pyH6), 8.59 (d, 6H, pyH2). ^{13}C NMR ($CDCl_3$) δ 35.49, 68.63, 116.56, 122.51, 131.71, 132.30, 134.26, 146.70, 147.84, 148.45.

Hexakis(8-quinolinylmethyl)cyclotriveratrylene (10). Cyclotricatechylene (252 mg, 0.688 mmol) and cesium carbonate (2.68 g, 8.23 mmol) were mixed in DMF (40 mL), under nitrogen. This suspension was refluxed for 30 minutes before 8-bromomethylquinoline (1004 mg, 4.52 mmol) was added. The resulting solution was refluxed for 48 hours, two further equivalents of 8-bromomethylquinoline (1004 mg, 4.52 mmol) added and the reaction refluxed for a further 120 hours. Water (50 mL) was added and the reaction extracted with dichloromethane (2 × 75 mL), dried over sodium sulfate and evaporated to dryness *in vacuo.* The residue was triturated with methanol to give a pale brown precipitate, which was filtered and dried *in vacuo.* Yield 383 mg (46%).

Mp 216–219 °C (dec.). *m/z* (ES) 1213.5 (MH^+). Analysis: calc. for $C_{81}H_{60}N_6O_6{\cdot}3H_2O$ C 76.8, H 5.3, N 6.6; found C 76.7, H 5.7, N 5.9%. ^{1}H NMR ($CDCl_3$) δ 3.47 (d, 3H, CH_2), 4.68 (d, 3H, CH_2), 5.64–5.91 (dd, 12H, CH_2–O), 7.03 (s, 6H, arom. CH), 7.24 (dd, 6H, quinH), 7.50 (t, 6H, quinH), 7.60 (d, 6H, quinH), 7.92 (dd, 6H, quinH), 8.02 (dd, 6H, quinH), 8.75 (dd, 6H, quinH). ^{13}C NMR ($CDCl_3$) δ 35.24, 66.40, 119.75, 125.43, 125.83, 126.38, 126.71, 131.35, 134.75, 134.94, 144.44, 146.50, 148.17, 148.33.

Hexakis(nicotinoyl)cyclotriveratrylene (11). Under an argon atmosphere, cyclotricatechylene (253 mg, 0.691 mmol) was dissolved in dry THF (30 mL) and cooled to 0 °C in an ice bath. Triethylamine (2.3 mL, 16.5 mmol) was added to the reaction mixture, which was then stirred for 5 minutes. Nicotinoyl chloride hydrochloride (740 mg, 4.16 mmol) was added in portions to this solution, the solution stirred at 0 °C for one hour and then at room temperature for 4 days. The solution was taken to dryness *in vacuo* and the residue triturated with ethanol to give a white solid. Yield 213 mg (31%).

Mp 265–267 °C (dec.). *m/z* (ES) 997.2475 (100%, MH^+, $C_{57}H_{37}N_6O_{12}^+$ requires 997.2469). ^{1}H NMR ($CDCl_3$) δ 3.91 (d, 3H, CH_2), 4.98 (d, 3H, CH_2), 7.33 (dd, 6H, pyH5), 7.45 (s, 6H, arom. CH), 8.28 (d, 6H, pyH4), 8.75 (d, 6H, pyH6), 9.22 (s, 6H, pyH2). ^{13}C NMR ($CDCl_3$) δ 35.43, 122.48, 123.64, 123.88, 136.51, 136.71, 139.71, 150.21, 153.22, 161.67.

Tris(2-pyridylmethyl)cyclotriguaiacylene (12). Under nitrogen, a suspension of cyclotriguaiacylene (205 mg, 0.501 mmol) and potassium carbonate (695 mg, 5.03 mmol) were stirred at reflux in acetone (30 mL) for 30 minutes. 2-Bromomethylpyridine hydrobromide (420 mg, 1.66 mmol) was added and the reaction refluxed for 96 hours. After cooling the acetone was removed *in vacuo*, water (50 mL) added and the suspension extracted with dichloromethane (3 × 50 mL). The combined extracts were dried over sodium sulfate and taken to dryness to give a brown oil that solidified on standing. A white solid was obtained by triturating the oily solid in methanol. This was collected by filtration and dried. Yield 240 mg (70%).

Mp 162–164 °C. *m/z* (ES) 682.2943 (100%, MH^+, $C_{42}H_{40}N_3O_6^+$ requires 682.2917), 497.7 (8%), 405.8 (7%). Analysis: calc. for $C_{42}H_{39}N_3O_6{\cdot}H_2O$ C 72.1, H 5.9, N 6.0; found C 72.3, H 6.0, N 5.8%. ^{1}H NMR ($CDCl_3$) δ 3.39 (d, 3H, CH_2), 3.69 (s, 9H, O–CH_3), 4.63 (d, 3H, CH_2), 5.20 (s, 6H, CH_2–O), 6.62 (s, 3H, arom. CH), 6.77 (s, 3H, arom. CH), 7.17 (dd, 3H, pyH5), 7.46 (d, 3H, pyH3), 7.61 (t, 3H, H4), 8.54 (d, 3H, H6). ^{13}C NMR ($CDCl_3$) δ 36.45, 56.27, 71.69, 113.69, 115.28, 121.28, 122.60, 131.66, 132.56, 137.03, 146.57, 148.14, 148.89, 157.67.

Tris(8-quinolinylmethyl)cyclotriguaiacylene (13). The procedure for the synthesis of **12** was followed but using 8-bromomethylquinoline (370 mg, 1.67 mmol) in place of 2-bromomethylpyridine hydrobromide. Thus, reaction of cyclotriguaiacylene (204 mg, 0.500 mmol) gave **13** as a cream solid. Yield 280 mg (67%). Crystals were obtained by vapour diffusion of ether into an acetonitrile solution of **13**.

Mp 124–126 °C (dec.). *m/z* (ES) 832.3384 (100%, MH^+, $C_{54}H_{46}N_3O_6^+$ requires 832.3387). Analysis: calc. for $C_{54}H_{45}N_3O_6{\cdot}4\frac{1}{2}H_2O$ C 71.0, H 6.0, N 4.6; found C 70.9, H 5.8, N 4.1%. ^{1}H NMR ($CDCl_3$) δ 3.31 (d, 3H, CH_2), 3.52 (s, 9H, O–CH_3), 4.57 (d, 3H, CH_2), 5.88 (s, 6H, CH_2–O), 6.54 (s, 3H, arom. CH), 6.87 (s, 3H, arom. CH), 7.42 (dd, 3H, quinH), 7.50

(d, 3H, quinH), 7.72 (d, 3H, quinH), 7.83 (d, 3H, quinH), 8.16 (d, 3H, quinH), 8.89 (d, 3H, quinH). ^{13}C NMR ($CDCl_3$) δ 36.29, 55.99, 67.15, 113.32, 114.79, 121.13, 126.79, 127.01, 127.31, 128.02, 131.64, 131.97, 135.32, 136.56, 145.80, 146.81, 147.91, 149.21.

Tris(5-quinoxalinylmethyl)cyclotriguaiacylene (14). ***Step 1.*** A catalytic amount of benzoyl peroxide was added to a solution of 5-methylquinoxaline (2.02 g, 14.0 mmol) and *N*-bromosuccinimide (2.49 g, 14.0 mmol) in carbon tetrachloride (20 mL). The solution was refluxed for 4 hours, cooled and then filtered to remove the precipitated succinimide. The filtrate was washed with dilute sodium hydroxide solution (50 mL), then water (50 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* to give an orange–brown solid that was purified by chromatography on silica, eluting with 4 : 1 ethyl acetate–hexane. This gave a yellow coloured oil of 5-bromomethylquinoxaline which was used without further purification. Yield 2.59 g (83%).

m/*z* (ES) 222.9868 (44%, MH^+, $C_9H_8N_2Br^+$, requires 222.9871). ^{1}H NMR ($CDCl_3$) δ 5.09 (s, 2H, CH_2), 7.53 (t, 1H, H7), 7.62 (d, 1H, H6), 7.99 (d, 1H, H8), 8.77 (m, 2H, H1/H2). ^{13}C NMR ($CDCl_3$) δ 28.24, 130.27, 130.71, 131.38, 137.09, 141.21, 143.50, 144.91, 145.69.

Step 2. The procedure for the synthesis of **12** was followed but using 5-bromomethylquinoxaline (282 mg, 1.26 mmol) in place of 2-bromomethylpyridine hydrobromide. Thus, reaction of cyclotriguaiacylene (154 mg, 0.377 mmol) gave **14** as a pale brown solid. Yield 260 mg (83%).

Mp 120–123 °C (dec.). *m*/*z* (ES) 835.3208 (100%, MH^+, $C_{51}H_{43}N_6O_6^+$ requires 835.3244), 693.3 (26%), 550.2 (9%). Analysis: calc. for $C_{51}H_{42}N_6O_6{\cdot}H_2O$ C 71.8, H 5.2, N 9.9; found C 71.8, H 5.5, N 9.2%. ^{1}H NMR ($CDCl_3$) δ 3.33 (d, 3H, CH_2), 3.58 (s, 9H, O–CH_3), 4.59 (d, 3H, CH_2), 5.78 (dd, 6H, CH_2–O), 6.54 (s, 3H, arom. CH), 6.85 (s, 3H, arom. CH), 7.70 (t, 3H, quinH7), 7.90 (d, 3H, quinH6), 7.99 (d, 3H, quinH8), 8.76 (d, 3H, quinH1 or quinH2), 8.82 (d, 3H, quinH1 or quinH2). ^{13}C NMR ($CDCl_3$) δ 36.75, 56.46, 67.10, 113.99, 115.68, 128.55, 129.10, 130.65, 132.14, 132.78, 136.46, 140.90, 143.12, 144.20, 145.24, 148.58.

Tris(2,2′-bipyridyl-6′-methyl)cyclotriguaiacylene (15). The procedure for the synthesis of **12** was followed but using 6-bromomethyl-2,2′-bipyridine (461 mg, 1.85 mmol) in place of 2-bromomethylpyridine hydrobromide. Thus, reaction of cyclotriguaiacylene (220 mg, 0.539 mmol) gave a brown oil that was triturated with ethanol to give **15** as a cream solid. Yield 380 mg (83%).

Mp 179–181 °C. *m*/*z* (ES) 913.3688 (100%, MH^+, $C_{57}H_{49}N_6O_6^+$ requires 913.3714), 745.3 (33%), 575.2 (58%). Analysis: calc. for $C_{57}H_{48}N_6O_6{\cdot}H_2O$ C 73.5, H 5.4, N 9.0; found C 73.4, H 5.9, N 8.6%. ^{1}H NMR ($CDCl_3$) δ 3.35 (d, 3H, CH_2), 3.56 (s, 9H, O–CH_3), 4.59 (d, 3H, CH_2), 5.25 (s, 6H, CH_2–O), 6.58 (s, 3H, arom. CH), 6.74 (s, 3H, arom. CH), 7.24 (dd, 3H, bpyH5), 7.44 (d, 3H, bpyH4′), 7.71 (m, 6H, bpyH4/H6′), 8.23 (d, 3H, bpyH3), 8.23 (d, 3H, bpyH3′), 8.62 (d, 3H, bpyH6). ^{13}C NMR ($CDCl_3$) δ 36.86, 56.56, 72.52, 114.00, 115.77, 120.35, 121.50, 124.17, 132.05, 132.91, 137.30, 138.20, 147.12, 148.54, 149.54, 149.64, 155.84, 156.37, 157.70.

Tris(4-[2,2′,6′,2″-terpyridyl]benzyl)cyclotriguaiacylene (16). The procedure for the synthesis of **12** was followed but using 4′-(*p*-bromomethyl)-2,2′,6′,2″-terpyridine (332 mg, 0.852 mmol) in place of 2-bromomethylpyridine hydrobromide and a reaction time of 48 hours. Thus, reaction of cyclotriguaiacylene (103 mg, 0.252 mmol) gave **16** as a cream solid. Yield 277 mg (80%).

Mp >240 °C (dec.). *m*/*z* (ES) 1372.2 (MH^+). Analysis: calc. for $C_{90}H_{69}N_9O_6{\cdot}3½H_2O$ C 75.3, H 5.4, N 8.8; found C 75.3, H 5.4, N 8.2%. ^{1}H NMR ($CDCl_3$) δ 3.41 (d, 3H, CH_2), 3.66 (s, 9H, O–CH_3), 4.64 (d, 3H, CH_2), 5.09 (s, 6H, CH_2–O), 6.46 (s, 3H, arom. CH), 6.63 (s, 3H, arom. CH), 7.28 (dd, 6H), 7.47 (d, 6H), 7.77 (m, 12H), 8.60 (d, 6H), 8.66 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 35.53, 55.19, 70.45, 112.91, 115.56, 117.75, 120.38, 122.83, 126.49, 126.49, 130.75, 131.89, 135.88, 136.87, 137.65, 146.06, 147.61, 148.11, 148.77, 154.98, 155.20.

Tris(nicotinoyl)cyclotriguaiacylene (17). Under an argon atmosphere, cyclotriguaiacylene (204 mg, 0.500 mmol) was dissolved in dry THF (20 mL) and cooled to 0 °C in an ice bath. Triethylamine (0.84 mL, 6.02 mmol) was added to the reaction, which was stirred for 5 minutes. Nicotinoyl chloride hydrochloride (293 mg, 1.65 mmol) was added in portions to this solution, the solution stirred at 0 °C for one hour and then at room temperature for 4 days. The solution was taken to dryness *in vacuo* and the residue washed with triturated ethanol to give a white solid. Yield 257 mg (62%).

Mp 254–256 °C. *m*/*z* (ES) 724.2308 (100%, MH^+, $C_{42}H_{34}N_3O_9^+$ requires 724.2295), 619.2 (22%). Analysis: calc. for $C_{42}H_{33}N_3O_9{\cdot}2H_2O$ C 66.4, H 4.9, N 5.5; found C 66.9, H 4.7, N 5.6%. ^{1}H NMR ($CDCl_3$) δ 3.63 (d, 3H, CH_2), 3.73 (s, 9H. CH_3), 4.78 (d, 3H, CH_2), 6.89 (s, 3H, arom. CH), 7.12 (s, 3H, arom. CH), 7.39 (dd, 3H, pyH5), 8.38 (d, 3H, pyH4), 8.77 (d, 3H, pyH6), 9.31 (s, 3H, pyH2). ^{13}C NMR ($CDCl_3$) δ 36.92, 56.65, 114.62, 123.89, 124.34, 126.05, 131.86, 138.36, 138.66, 148.09, 150.24, 151.67, 153.95, 163.69.

Crystallography

The crystal data, data collection and refinement parameters are given below. Measurements were made with a Nonius Kappa CCD diffractometer using graphite monochromatised Mo Kα (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS-97,[37] and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL-97.[38] Hydrogen atoms were included at calculated positions with isotopic displacement parameters 1.2 times the isotropic equivalent of their carrier carbon atoms. Additional refinement details for each structure are given below.

Crystal data for 8. $C_{57}H_{51}N_6O_{10.5}$, *FW* 988.04, trigonal, *R*3*m*, *a* 31.0859(7), *c* 4.6544(1) Å, *V* 3895.12(15) Å^3, *Z* 3, ρ 1.264 g cm^{-3}, μ 0.088 mm^{-1}, *F*(000) 1557, colourless needle 0.31 × 0.07 × 0.05 mm, $2\theta_{max}$ 49.98°, *T* 150 K, 9404 reflections, 1618 unique, R_{int} 0.0849, 115 parameters, GOF 1.125, *wR*2 0.2296 for all data, R_1 0.0831 for 1493 data with $I > 2\sigma(I)$. The oxygen atoms of the solvate water molecules in compound **8** are modelled isotropically and refined without hydrogen atoms.

Crystal data for 13. $C_{58}H_{51}N_5O_6$, *FW* 914.04, triclinic, *P*-1, *a* 12.036(2), *b* 12.090(2), *c* 18.469(2) Å, α 104.18(3), β 98.27(3), γ 109.89(3)°, *V* 2372.9(8) Å^3, *Z* 2, ρ 1.279 g cm^{-3}, μ 0.084 mm^{-1}, *F*(000) 964, colourless block 0.49 × 0.43 × 0.30 mm, $2\theta_{max}$ 50°, *T* 150 K, 38302 reflections, 8349 unique, R_{int} 0.1536, 633 parameters, GOF 1.056, *wR*2 0.1780 for all data, R_1 0.0627 for 6554 data with $I > 2\sigma(I)$. In the crystal structure of **13** one of the carbon atoms of the methoxy groups (C43) on the cyclotriguaiacylene core is heavily disordered. The carbon atom modelled over the two positions with the carbon atom in part 2 modelled isotropically.

CCDC reference numbers 238548 and 238549. See http://www.rsc.org/suppdata/ob/b4/b407165d for crystallographic data in .cif or other electronic format.

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