Lithium calix[4]arenes: structural studies and use in the ring opening polymerization of cyclic esters†

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We have structurally characterized a number of lithiated calix[4]arenes, where the bridge in the calix[4]arene is thia (−S−, L5H4), sulfynil (−SO−, L5SOH4), sulfonyl (−SO2−, L5SO2H4), dimethylenedioxy (−CH2OCH2−, L5OCC4H4) or metylene (−CH2−, LH4). In the case of LH4, interaction with LiOtBu led to the isolation of the complex [Li6(LH2)2(THF)4]−·5THF (1·5THF), whilst similar interaction of L5SOH4 led to the isolation of [Li4(L5SOH2)2(THF)2]−·5THF (2·5THF). Interestingly, the mixed sulfynil/sulfonyl complexes [Li6(calix[4]arene(SO)(SO2)(SO1.68)2)2(THF)6]−·5THF (3·5THF) and [Li6(calix[4]arene(SO)(SO2)(SO1.68)2)2(THF)6]−·7.5THF (4·7.5THF) have also been characterized. Interaction of LiOtBu with L5SOH4 and L5OCC4H4 afforded [Li6(L5SO(OH)2)2(THF)4]−·2THF (5·2THF) and [Li6(L5OCC4H2)2(OH2)2]−·0.78THF·1.22hexane (6·0.78THF·1.22hexane), respectively. In the case of LH4, reaction with LiOtBu in THF afforded a monoclinic polymorph [Li8Li2(thf)(OH)2]3·3THF (7·3THF) of a known triclinic form of the complex, whilst reaction of the de-butylated analogue of LH4, namely de-BuLH4, afforded a polymeric chain structure {[Li3(de-BuL)(OH)(NCMe)3]·2MeCN}n (8·2MeCN). For comparative catalytic studies, the complex [Li8(LH2)2(THF)4]−·hexane (9·hexane), where L5SOH4 = 1,3,5-tri-n-propylxycalix[4]arene+H2, was also prepared. The molecular crystal structures of 1−9 are reported, and their ability to act as catalysts for the ring opening (co-)polymerization (ROP) of the cyclic esters ε-caprolactone, δ-valerolactone, and rac-lactide has been investigated. In most of the cases, complex 6 outperformed the other systems, allowing for higher conversions and/or greater polymer Mn.

Introduction

The search for alternative plastics to petroleum-based products continues at a pace. One avenue of exploration is to develop new, greener biodegradable polymers, but which retain the desirable features of traditional plastics.1 With this in mind, one promising route is to exploit the ring opening polymerization (ROP) of cyclic esters, a process which can be controlled by a metal-based catalyst. For the catalyst, it is important that the ancillary ligands present can be easily adjusted in terms of their steric and electronic properties. There has been considerable interest in the use of the phenolic macrocycles called calixarenes in a broad range of catalysis.2 Indeed, we have been interested in employing such species in the ROP of cyclic esters to afford biodegradable polymers.3 Both the upper- and lower-rim of a calixarene can readily be modified, and for the latter the introduction of ether groups allows the charge to be altered.4 Moreover, different bridging groups can be used to link the phenols, and the range of conformations available to calixarenes allows for further structural flexibility.5 In terms of the metal employed, it is important it is relatively cheap and non-toxic. Lithium is the 25th most abundant element, and lithium systems have shown promise as ROP catalysts.6 Over the last decade or so, a number of routes to lithiated calix[4]arenes and their thia-bridged analogues have been developed. The early work on calix[n]arenes involved the use of 7Li NMR spectroscopy,7 whilst for p-tert-butylcalix[4]arene (L1H4), early structural work involved the use of lithium amide,8 whilst Davidson et al. employed nBuLi in the presence of either wet or dried hexamethylphosphoramide (hmpa) and isolated L4 LiOH·4hmpa or [Li4Li4·2hmpa], respectively.9 Floriani et al. also employed nBuLi in the presence of naphthalene to prepare lithiated calix[4]arenes.10 Fromm et al. structurally characterized the complex [Li6(LH2)2(THF)4]−·3THF, possessing a core containing two face-shared Li2O cubes from the reaction of L1H4 and LiOtBu; the partial hydrolysis product [Li6(LH2)2(H2O)(μ3-H2O)(THF)]·3THF was also characterized.11 Hanna et al. also studied reactions of calix[4 and 8]arene as well as p-tert-

† Electronic supplementary information (ESI) available: Alternative views of 1, 2, 3 and 6; polymer 1H and 2D-resolved NMR spectra, MALDI-TOF spectra. CCDC 2038615–2038623. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra00175b

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butylcalix[4 and 8]arene with LiOtBu or LiOSiMe₃ respectively, and isolated monoanions. In later studies, Hanna et al. extended their studies to the reaction of p-tert-butylcalix[5]arene with a number of lithiated reagents, namely LiOH, nBuLi and LiH. Moreover, a number of molybdocalix[4]arenes incorporating lithium, primarily as part of a bridging ligand have also been reported, as have mixed lithium–strontium complexes. We have previously structurally characterized the two complexes \([L_4H_2(OMe)(OLi)]_2 \cdot 4MeCN\) and \([L_4H_2(OLi)[OLi(NCMe)_2]]_2 \cdot 8MeCN\) resulting from the use of nBuLi.

For p-tert-butyltetra(thi)calix[4]arene \([L_{54}H_4]_x\), Zeller and Radius employed nBuLi to access \(L_{54}Li_4\), which proved problematic to crystallize and only the decomposition product \([L_{54}Li_5(OH)(THF)]_4\) was structurally characterized; the complex could be isolated directly using LiOH·H₂O/\(L_{54}H_4\). We have reacted a lower rim 1,3-diacid calix[4]arene with either Li₂CO₃ or tBuLi and isolated helical nanotubes or infinite chains, respectively. The structure of a supramolecular lithium calix[4] arene complex has also been reported.

Despite this synthetic activity, applications of such lithiated calixarene species have not been forthcoming. With this in

Chart 1 Lithium-calixarene complexes 1–9 prepared herein.
mind, we have embarked upon a programme to screen the potential for lithiated calixarenes for the ring opening polymerization (ROP) of cyclic esters. Herein, we present our findings on calix[4]arene systems for which the calixarene bridge has been varied, viz –S–(L4SH4), –SO–(L4SOH4), –SO2–(L4SO2H4), –CH2OCH2–(L4COCH4), –CH2–(L4H4), and in the case of the latter 1,3-propoxide groups have also been introduced at the lower-rim. Structural studies and the ROP of the cyclic esters 3-caprolactone, d-valerolactone and rac-lactide are reported. The nine lithium-calixarenes prepared herein are shown in Chart 1. We note that a number of lithium-containing cages, rings, and ladders, supported primarily by phenolate-type ligation, have previously been employed for the ROP of cyclic esters.\textsuperscript{21} The use of calixarenes though, is somewhat limited.\textsuperscript{4,22}

Results and discussion

Syntheses and solid-state structures

–Thia–. Of the number of synthetic routes to lithiated calixarenes outlined above,\textsuperscript{9–14} we chose as our entry point the use of LiO\textsubscript{t}Bu. Reaction of LiO\textsubscript{t}Bu (5 equiv.) with L4SH4 led to the isolation of the complex [Li\textsubscript{8}(L\textsuperscript{45}SH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{4}]·5THF (1·5THF). Single crystals were grown, in ca. 65% isolated yield, from a saturated THF solution at ambient temperature and an X-ray structure determination revealed the structure shown in Fig. 1; for an alternative view of the core see Fig. S1, ESI.\textsuperscript{†} Table 6 presents the crystal data for this and the other crystal structures reported herein. A closely related structural motif has been reported previously for [Li\textsubscript{4}L\textsuperscript{4}·2hmpa]\textsubscript{2} (Chart 2), whilst related sodium and potassium-containing motifs have also been reported.\textsuperscript{6,12,13} The molecule lies on a 2-fold axis which passes through Li(3)···Li(4). Thus, half of the molecule is unique as are $\eta_2$ THF
molecules of crystallization. The $\frac{1}{2}$ THF was modelled using Platon Squeeze. All four S atoms make contacts with one or more lithium centres, namely Li(1)···S(4) = 2.720(15), Li(2)···S(1) = 2.610(17), Li(2)···S(2A) = 2.644(15), Li(4)···S(3) = 2.734(10), Li(4)···S(3A) = 2.734(10) Å. Furthermore, Li(5) is involved in C(π) contacts, viz Li(5)···C(1) = 2.74(2) and Li(5)···C(31) = 2.670(18) Å. In the packing of 1, the calixarene complexes are well separated with THFs in the voids. The compound is not so soluble in toluene, which is problematic for the ROP studies vide infra.

**Sulfinyl.** Interaction of LiOTBu with L$_4$SO$_4$H$_4$ afforded small prisms of [Li$_6$(L$_4$SOH)$_2$(THF)$_2$]$\cdot$8(THF) in ca. 30% yield on standing (2 days) at ambient temperature. The molecular structure was determined using synchrotron radiation, and is shown in Fig. 2; the core is shown in Fig. S2, ESI.† Whilst the data was weak, the connectivity was clearly established. The molecule lies on a centre of symmetry, and so half is unique. Given there are six lithium ions present, and analysis of the bond lengths and relative positions of the phenolate oxygens, we conclude that O(3) is protonated; the position of O(2) also suggests it forms an H-bond with O(3). Two of the SO oxygens bind to lithium centres, namely Li(1) and Li(3), whilst Li(2) remains 4-coordinate. The phenolate oxygens O(2) and O(3) bridge three lithium centres, whilst O(1) and O(4) bridge only two Li centres. The SO groups have the O partially disordered at the alternative tetrahedral site on the S with minor component occupancies between ca. 0.1 and 0.2.

On one occasion, reaction of L$_4$SO$_4$H$_4$ with LiOTBu led to the isolation of a mixed sulfinyl/sulfonyl complex, namely [Li$_8$(calix[4]arene(SO)(SO$_2$)(SO$_{1.68}$)$_2$)$_2$(THF)$_6$]$\cdot$8(THF) ($\cdot$8THF). The

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**Fig. 3** Molecular structure (left) and core (right) of [Li$_6$(L$_4$SOH)$_2$(THF)$_2$]$\cdot$8(THF) $\cdot$8(THF). H atoms, and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)···O(1) 1.957(5), Li(1)···O(2) 1.954(5), Li(1)···O(2A) 2.247(6), Li(1)···O(5) 2.145(6), Li(2)···O(1) 1.870(6), Li(2)···O(2A) 1.931(6), Li(2)···O(4) 1.852(6), Li(2)···O(10) 2.041(6); Li(1)···O(1)···Li(2) 89.4(2), Li(1)···O(2)···Li(2A) 110.7(2), Li(2)···O(10)···Li(4) 121.8(2).

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**Fig. 4** Repeating unit (left) and 1D zigzag polymer chains (right) in the structure of [Li$_6$Na(L$_4$SOH)$_2$(THF)$_2$]$\cdot$7.5(THF) $\cdot$4.75THF. H atoms not involved in H-bonding, minor disorder components and non-coordinated THFs omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)···O(1) 1.876(8), Li(1)···O(4) 1.970(8), Li(1)···O(10) 1.988(8), Li(1)···O(12) 1.969(8), Li(1)···O(16) 2.352(8), Li(1)···S(4) 2.932(7), Li(1)···O(16) 1.974(8), Li(2)···O(2) 2.081(8), Li(2)···O(5) 2.135(9), Li(2)···O(12) 2.259(8), Li(2)···O(16) 2.147(8), Li(3)···O(2) 1.945(8), Li(3)···O(3) 1.996(7), Li(3)···O(12) 1.926(7), Li(3)···O(15) 2.016(7), Li(3)···S(2) 2.837(7), Li(3)···S(6) 2.968(7); Li(1)···O(1)···Li(2) 83.5(3), Li(1)···O(12)···Li(2) 74.3(3), Li(1)···O(12)···Li(3) 116.8(3), Li(2)···O(2)···Li(3) 87.2(3), Li(2)···O(12)···Li(3) 82.8(3).
molecular structure is shown in Fig. 3 (for an alternative view, see Fig. S3, ESI†), with selected bond lengths and angles given in the caption. The molecule lies on a centre of symmetry, and so half of this formula is unique. Interestingly, only one of the bridging S centers on each calix {S(2)} has just one O group bound (i.e. a sulfonyl), whilst the other three have two oxygens (i.e. sulfonyls), though it should be noted two of these actually have ca. 1.68 oxygens rather than 2, indicating some slight variability in the degree of oxidation at sulfur in these calixar- enes. There are weak Li(1)--S(2') and Li(2)--S(2') interactions of 2.929(5) and 3.099(5) Å, respectively, which are both longer than seen in 1-5THF. Each calixarene possesses a cone conformation. The molecules pack forming layers in the b/c plane (see Fig. S4, ESI†). The presence of the sulfonyl [-SO2–] bridges was thought to arise from adventitious oxidation during the reaction; mass spectra of the parent L4SOH4 did not exhibit higher peaks associated with the presence of -SO2– bridges.

We also isolated a Na-bridged polymer [Li$_3$Na(L$^{SO/3SO_{2}}$H)$_2$ (THF)$_7$]·7.5(THF) (4·7.5(THF)) from the reaction of $L^{SOCH_4}$ with LiOH. The molecular structure is shown in Fig. 4, with selected bond lengths and angles given in the caption. Both Li(1) and Li(4) are distorted squared-based pyramidal, whilst Li(2) is distorted octahedral and Li(5) distorted tetrahedral. Li(3), whilst forming 4 bonds to neighbouring oxygens, also forms two weaker interactions to S(2) and S(6). For all but one of the SO$_2$ groups present, one of the oxygen atoms binds to Li or Na, whilst for S(5) one O bridges Li(1) and Li(2) and the other bonds to Na(1). In the case of the SO groups, the S binds weakly to Li(3) and the O binds to either Li(5) or Na(1). The slight variability in oxidation at S is manifested here with O(20) being 78.0(18)% occupied.

Complex 4 forms 1D chains linked via octahedral Na$^+$ ions (Fig. 4, right). We have previously noted the incorporation of Na from drying agents in metallocalixarene chemistry. In 4, to balance the overall charge, two phenols remain protonated, one on each calix[4]arene.

**Sulfonyl.** Extension of the LiOttBu methodology to the sulfonyl-[–SO$_2$–] bridged calix[4]arene system, afforded single crystals suitable for X-ray diffraction from a saturated tetrahydrofuran solution at 0°C in ca. 60% isolated yield. The molecular structure of [Li$_3$L$^{SO2}$–OH–(THF)$_4$]·2THF (5·2THF) is shown in Fig. 5, with selected bond lengths and angles given in the caption. The complex contains the Li$_2$OH motif noted by Davidson et al., and Zeller and Radius, and, like the latter, lies on a 4-fold axis and possesses four lithium-bound THF ligands. The difference in S is that an oxygen of each of the bridging sulfonyl groups is bound to each of the ‘outer’ lithium centres. The lithium atom Li(2) is 0.580 Å above the plane formed by the phenolate oxygens, whilst the Li(2)–O(5) bond length is 1.958(13) Å cf. 2.055(10) Å for the Zeller and Radius structure.\(^{18}\) Each of the lithium centres is 5-coordinate with the other four adopting what can best be described as trigonal bipyramidal geometries, whilst the inner lithium centre Li(2)
adopts a square pyramidal geometry. Both the THFs of crystallization are substantially disordered on the 4-fold axis and were modelled as diffuse regions of electron density by using Platon Squeeze. One THF resides in the calixarene cavity, the other lies above the OH beyond the four coordinated THF molecules.

**Dimethyleneoxa.** Reaction of L COCH₄ with LiO tBu led, following work-up, to the complex [Li₆(LCOCH₄)₂(HO tBu)₂] $·0.78$THF $·1.22$hexane (6 $·0.78$THF $·1.22$hexane) in ca. 45% isolated yield. Two views of the molecular structure are shown in Fig. 6, with selected bond lengths and angles given in the caption. The core of the complex comprises a pseudo-cubane Li₆O₆ unit, which contains four, boat-shaped, six-membered faces of two Li₃O₃ units. A tBuOH molecule is bound to Li(2) and resides within the calixarene cavity and, being disordered, H-bonds to either O(2) (for the major component) or O(6) (minor). Pairs of molecules sit in a slipped face-to-face or cavity-to-cavity motif with tBuOH molecules pointing approximately towards each other.

**Methylene.** In the case of LH₄, reaction with LiO tBu (2.2 equiv.) in THF afforded [LH₄Li₃(THF)(OH)₂] $·3$THF $·7·3$THF, which is a monoclinic polymorph of a known, triclinic, structure reported by Fromm et al. The crystals were very small and very weakly diffracting, even at the synchrotron, which resulted in the poor $R$ factor. The absolute structure could not be determined due to the combination of radiation wavelength and lack of an anomalous scatterer. The H atoms on the terminal water molecule could not be located in difference maps, but the proximity of this water molecule and two H-bond acceptors is perfectly logical. The H atoms on the bridging waters were placed geometrically, while those between calixarene oxygens are heavily restrained. In reality they are probably

Fig. 7 Molecular structure of the H-bonded dimer of [LH₂Li₂(THF)(OH)₂] $·3$THF (7 $·3$THF). H atoms not involved in H-bonding and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)–O(1) 1.86(3), Li(1)–O(2) 1.99(3), Li(1)–O(5) 1.97(3), Li(1)–O(6) 1.94(3), Li(1)–Li(2) 3.06(4), Li(2)–O(3) 1.95(3), Li(2)–O(4) 1.89(3), Li(2)–O(5) 2.00(3), Li(2)–O(7) 1.92(3), Li(3)–Li(4) 3.10(4), Li(1)–O(5)–Li(2) 100.7(12), O(1)–Li(1)–O(2) 104.2(14), O(3)–Li(2)–O(4) 105.3(14).

Fig. 8 (Left) Molecular structure of the repeating unit in the polymeric structure [Li₆(LtBuL)(OH)(NCMe)₃]$·2$MeCN, (8 $·2$MeCN); (right) 1D zig-zag chain polymer propagating in the b direction. Most H atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)–O(2B) 1.999(15), Li(1)–O(3) 1.910(16), Li(1)–O(4) 1.988(14), Li(1)–N(1) 2.071(16), Li(2)–O(1) 1.961(14), Li(2)–O(2) 1.963(3), Li(3)–O(3A) 1.948(3), Li(2)–O(4) 1.973(3), Li(1)–O(2B)–Li(2) 78.64(13), Li(1)–O(4)–Li(3A) 102.41(13), O(2)–Li(3)–O(4A) 166.43(16).

Fig. 9 Molecular structure of [Li₆(LtBuL)(H₂O)₂]·hexane (9 hexane). Most H atoms and hexane of crystallization omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)–O(2) 1.913(3), Li(1)–O(4) 1.935(3), Li(1)–O(5) 1.885(3), Li(2)–O(1) 1.883(3), Li(2)–O(2) 1.963(3), Li(3)–O(3A) 1.948(3), Li(2)–O(4) 1.973(3), Li(1)–O(2B)–Li(2) 138.7(7), Li(1B)–O(4)–Li(2) 130.3(6).
more asymmetric. Their presence is required for charge balance and supported by the better, known structure. There are two molecules of the Li2 complex and six THFs of crystallisation in the asymmetric unit. They form a H-bonded cluster involving both complexes and four THFs (see Fig. 7; a view of a single complex), with an additional THF in each calixarene cavity. The same motif is seen in the asymmetric unit. They form an H-bonded cluster involving two THFs H-bonded to two ipso carbons and, as a result, a pinched-cone conformation for the calixarene is observed. The calixarenes are linked via centrosymmetric Li2O2 diamonds involving Li(2) and O(2). The Li(3)⋯C(6) distance is 2.734(6) Å. Li(1), which is not involved in the chain propagation, bears an NCMe ligand, as does Li(3) in the cavity. The complex packs with the 1D zig–zag chain polymer propagating in the b direction (Fig. 6, right).

For our catalytic studies, we were also interested in evaluating the effect of the presence of alkyl chains at the lower rim. With this in mind, 1,3-di-n-propyloxycalix[4]arene, 1,3-L(OH)2(nPrO)2, which we abbreviate as LPr2H2, was treated with nBuLi in hexane. Following work-up, small crystals suitable for X-ray diffraction using synchrotron radiation were obtained. The molecular structure (Fig. 9) revealed the complex to be [Li40(LPr)2(H2O)2]hexane (9 hexane). Half of the complex and half a solvent molecule are unique, both on i. The core comprises two face-sharing distorted cubes. The distortion arises because Li(1) and O(3) are not directly bound, and instead Li(1) makes a π-interaction with C(23), bound to phenolate oxygen O(3). Additionally, Li(3) binds to the water molecule which resides in the calixarene cavity. Each calixarene adopts a pinched conformation with rings attached to O(2) and O(4) splayed out, whilst those at O(1) and O(4) are pinched together.

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Table 1 ROP of ε-CL catalysed by the Li complexes

| Run | Catalyst | ε-CL : Li | T (°C) | Time (h) | Conversion (%) |
|-----|----------|-----------|-------|---------|----------------|
| 1   | 1        | 100 : 1 : 1| 130   | 24      | 16             |
| 2   | 2        | 100 : 1 : 1|       | 0       |                |
| 3   | 4        | 100 : 1 : 1|       | 0       |                |
| 4   | 5        | 100 : 1 : 1|       | 18      |                |
| 5   | 6        | 100 : 1 : 1|       | 10      |                |
| 6   | 7        | 100 : 1 : 1|       | 20      |                |
| 7   | 8        | 100 : 1 : 1|       | 11      |                |
| 8   | 9        | 100 : 1 : 1|       | 7       |                |

* Determined by 1H NMR spectroscopy on crude reaction mixture.

Table 2 ROP of ε-CL catalysed by the Li complexes under solvent-free conditions

| Run | Catalyst | ε-CL : Li | T (°C) | Time (h) | Conversion (%) | Mw,b | Mnc,b | PDI,b |
|-----|----------|-----------|-------|---------|----------------|------|-------|-------|
| 1   | 1        | 100 : 1 | 130   | 24      | None           | —    | —     | —     |
| 2   | 2        | 100 : 1 | 24    | 24      | None           | —    | —     | —     |
| 3   | 4        | 100 : 1 | 45    | 24      | 1800           | 5130 | 1.25  |       |
| 4   | 5        | 100 : 1 | 40    | 24      | None           | —    | —     | —     |
| 5   | 6        | 100 : 1 | 17%   | 24      | 14 640         | 4560 | 2.01  |       |
| 6   | 7        | 100 : 1 | 99    | 24      | 27 000         | 11 290 | 1.67  |       |
| 7   | 8        | 100 : 1 | 80    | 24      | 16 130         | 9130 | 1.78  |       |
| 10  | 9        | 100 : 1 | 14    | 15 min  | 72             | 8210 | 1.76  |       |
| 12  | 10       | 100 : 1 | 77    | 24      | None           | —    | —     | —     |
| 13  | 11       | 100 : 1 | 77    | 6       | 17 040         | 8780 | 2.05  |       |
| 14  | 12       | 100 : 1 | 7    | 24      | None           | —    | —     | —     |

* Determined by 1H NMR spectroscopy on crude reaction mixture.

ε-caprolactone (ε-CL). We have examined the ability of the complexes prepared herein (not 3) to act as catalysts for the ROP of ε-CL (Table 1). When conducting the reaction in toluene at 130 °C, poor activity was observed upon using a monomer to catalyst ratio of 100 : 1 and in the presence of one equiv./Li of BnOH as co-activator. In fact, the conversions observed were in the range of 10–20%. The reaction was then repeated under solvent-free conditions in the absence of a co-activator (Table 2). While no reactivity was obtained after 24 h for compound 1 and...
in the presence of the Na-containing species 4 (runs 1 and 4), complete monomer conversion was achieved within 10 minutes in the presence of the dimethyleneoxa-derivative 6 (run 7). Moreover, interesting reactivity was exhibited by the SO₂₆₆·bridged congener 5 and the methylene-bridged compound 7. Indeed, the formation of polymer blocking the stirring of the mixture took place within 1 h, affording 40 and 80% conversion for 5 and 7, respectively. Good activity was also shown by 2 and 9 (45 and 77% conversion, respectively), albeit requiring longer reaction times. The activity trend (6 > 7 > 8 > 5 > 9 > 2) indicated a positive effect of the dimethyleneoxa bridge systems, compared with its CH₂CH₂ and S-containing congener. Interestingly, similar behaviour has been previously observed for ethylene polymerization promoted by V-based catalysts. Such higher activity could be attributed to the greater flexibility of the dimethyleneoxa bridge (over CH₂CH₂ and S-) allowing the monomer better access to active centres and/or to the presence of oxygen atoms which help stabilize the active species. With respect to the CH₂₂₂-bridged complexes, the higher activity of complex 7 over its de-butylated analogue 8 could be attributed to its higher solubility in the reaction medium. Finally, the lower activity of 9 could be due to the steric encumbrance of its propoxy groups. In all cases, $M_n$ higher than the calculated values were observed, suggesting a concentration of the active species lower than expected. Moreover, the rather broad $M_w/M_n$ values indicated poor control over the polymerization, possibly due to the forcing reaction conditions as well as to the heterogeneous nature of the reaction medium. These factors impeded the rigorous study of the kinetics aspects of the reaction. The ¹H NMR spectrum of the PCL synthesized with 6 showed the presence of a triplet at δ 3.6 ppm, compatible with linear –CH₂OR (R = H or tBu) terminated polymers (Fig. S6, ESI†). This was confirmed by mass spectrometry. In fact, the MALDI-ToF spectrum of the sample (Fig. S7†) displayed one population of peaks (separated by 114 m/z units) compatible with an α-tBuO-ω-OH terminated linear PCL. This suggested that the tert-butoxy group of 6 serves as initiating group of the ROP process. Upon performing the reaction in air, low conversion (14–17%) was

| Table 3 | ROP of δ-VL catalysed by the Li complexes under solvent-free conditions |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Run     | Catalyst       | δ-VL : Li       | $T$ (°C)        | Time (h)        | Conversiona (%) | $M_n$bc          | $M_{calc}$d      | PDIb            |
|---------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|
| 1       | 1              | 100 : 1        | 130            | 24             | 18             | nd              | 1800            | nd              |
| 2       | 2              | 24             | 10             | 1320           | 1000           | 1.29            |
| 3       | 5              | 10 minf        | 58             | 30 100         | 5800           | 2.12            |
| 4       | 6              | 12             | >99            | 2990           | 9900           | 1.57            |
| 5       | 7              | 1t            | 46             | 16 360         | 4600           | 1.29            |
| 6       | 8              | 30 minf        | 60             | 21 680         | 6000           | 1.52            |
| 7       | 9              | 12f            | 64             | 31 650         | 6400           | 2.08            |

a Determined by ¹H NMR spectroscopy on crude reaction mixture. b From GPC. c Values corrected considering Mark–Houwink factor (0.56) from polystyrene standards in THF. d Calculated from $\left[\text{[Monomer]}_0/\text{[Cat.]}_0\right] \times \text{conv.} \times \text{monomer molecular weight.}$ e Stirring stopped due to the polymer formation.

| Table 4 | ROP of r-LA catalysed by the Li complexes |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Run     | Catalyst       | r-LA : Li       | $T$ (°C)        | Time (h)        | Conversiona (%) | $M_n$bc          | $M_{calc}$d      | PDIb            |
|---------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|
| 1       | 1              | 100 : 1        | 150            | 24             | 57             | 17 340          | 8210            | 1.73            |
| 2       | 2              | 100 : 1        | 18             | nd             | 3600           | nd              | nd              |
| 3       | 3              | 100 : 1        | 25             | nd             | 1150           | nd              | nd              |
| 4       | 5              | 100 : 1        | 69             | 12 530         | 1.72           | 0.90            |
| 5       | 6              | 100 : 1        | 87             | 18 470         | 1.72           | 0.90            |
| 6       | 7              | 100 : 1        | 18             | nd             | 1150           | nd              | nd              |
| 7       | 8              | 100 : 1        | 57             | 22 650         | 1.71           | 0.88            |
| 8       | 9              | 100 : 1        | 66             | Liquid oligomers |

a Determined by ¹H NMR spectroscopy on crude reaction mixture. b From GPC. c Values corrected considering Mark–Houwink factor (0.56) from polystyrene standards in THF. d Calculated from $\left[\text{[Monomer]}_0/\text{[Cat.]}_0\right] \times \text{conv.} \times \text{monomer molecular weight.}$ e Determined 2D $J$-resolved ¹H NMR spectroscopy.

| Table 5 | ε-CL/r-LA copolymerization catalysed by the Li complexes under solvent-free conditions |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Run     | Catalyst       | CL : LA : Li    | $T$ (°C)        | Time (h)        | Conversion CL/LAa (%) |
|---------|----------------|----------------|----------------|----------------|-----------------|----------------|----------------|
| 1       | 1              | 100 : 100 : 1   | 130            | 24             | 0/66            |
| 2       | 2              |                | 0/80            |
| 3       | 5              |                | 0/79            |
| 4       | 6              |                | 0/99            |
| 5       | 7              |                | 0/70            |
| 6       | 8              |                | 0/83            |
| 7       | 9              |                | 0/71            |

a Determined by ¹H NMR spectroscopy on crude reaction mixture.
obtained in the presence of 5, 6, and 7 (runs 5, 7, and 9) while no reaction was observed for 1, 8 and 9 (runs 2, 11, and 13). This significant drop of activity was attributed to the hydrolysis of the complexes affording catalytically inactive parental calixarenes; separate runs using the parent calixarenes failed to produce any PCL.

δ-valerolactone (δ-VL). The ROP of δ-valerolactone (δ-VL) was also investigated. By performing the reaction in toluene and in the presence of BnOH as co-activator, none of the catalysts proved active, affording either nil or trace polymer after 24 h at 130 °C. Furthermore, the tests were repeated under solvent-free conditions (Table 3). Due to the disappointing results achieved in the CL case, the Na-containing species 4 was not further tested. Poor activity was exhibited by complexes 1 and 2, allowing for 18 and 10% conversion, respectively, after 24 h (runs 1 and 2). Good conversion (58%) was obtained in the presence of the SO2-bridged derivative 5 after 10 minutes (run 3); however, further reaction was impeded by the formation of a highly viscous mixture. A similar outcome was observed in the presence of complexes 7–9, albeit with longer reaction times (30 min to 12 h, runs 4–6). Finally, complete conversion was attained after 12 h with the dimethyleneoxa-derivative 6, affording a PVL with $M_n$ lower than the expected values and rather broad polydispersity (1.57, run 4). This indicated the occurrence of extensive transesterification. Noteworthy, the $M_n/M_w$ values observed for the PCLs and PVLs do not present significant differences (with respect to the uncertainty of the GPC measurements). Thus, the same extent of transesterification can be assumed for both monomers. This was primarily attributed to the lack of homogeneity of the reaction medium, as the formation of polymer often impeded efficient stirring of the mixture. On the other hand, $M_n$ higher than the expected values were obtained in the presence of complexes 5 and 7–9, indicating partial catalyst activation. Similar to the CL case, the $^1H$ NMR spectrum of the PVL synthesized with 6 suggested the formation of linear $\sim$CH2OH capped polymer chains (Fig. S8†). The MALDI-ToF spectrum of the sample highlighted the presence of a main set of peaks (Fig. S9†) compatible with an $α$-hydroxyl-$ω$-[carboxylic acid]-terminated PVL, suggesting that, unlike the PCL case, the polymerization was initiated by adventitious water. Two minor distributions accountable to cyclic species and Na-doped linear adducts were also observed (Fig. S10 and S11, † respectively).

rac-Lactide (r-LA). The complexes were then employed as catalysts in the ROP of r-LA under solvent-free conditions at 150 °C (Table 4). While low molecular weight oligomers were obtained with 2, 4, 5, 7, and 9, wax-like materials were isolated in the presence of 1, 6, and 8. $M_n$ higher than the calculated values and polydispersities of ca. 1.7 suggested partial catalyst activation as well as the occurrence of transesterification. Again, here the dimethyleneoxa-bridged complex 6 performed best. The samples showed high heterotactic enrichment ($P_r$ 0.88–0.91), as observed by 2D $J$-resolved $^1H$ NMR spectroscopy (Fig. S12–S14†). However, due to the poor activity of the catalysts in solution, it has not been possible to perform mechanistic investigations by NMR spectroscopy in order to assess the type of stereocontrol involved. The MALDI-ToF spectrum of the PLA prepared in the presence of 6 (Fig. S15†) highlighted the presence of only one population accountable to cyclic species. In addition, the fact that the peaks are separate by 72 $m/z$ units (mono-lactyl group) suggested the occurrence of transesterification.

ω-pentadecalactone (ω-PDL). All complexes were found to be inactive in the ROP of the more challenging 15-membered ring monomer ω-pentadecalactone, both in solution and under solvent-free conditions.

ε-CL/r-LA co-polymerization. Lastly, the co-polymerization of ε-CL and r-LA was investigated in bulk at 130 °C (Table 5). While ε-CL was completely unreacted, the conversion of r-LA was observed, as highlighted by $^1H$ NMR spectroscopy on the crude reaction mixtures (see for example Fig. S16†). Liquid PLA oligomers, whose separation from the residual monomers proved problematic, were obtained in all cases.

**Conclusions**

In conclusion, the use of LiOBU (or LiOH or nBuLi in the case of 4 and 7) on interaction with a series of calixarenes containing a range of bridging groups, namely $\sim$CH2$\sim$, $\sim$S$\sim$, $\sim$SO$\sim$, $\sim$SO2$\sim$ or $\sim$CH2OCH$\sim$ allowed access to a number of lithiated calix[3 and 4] arenes (see Chart 1). In the case of the $\sim$SO2$\sim$, adventitious oxidation can result in the formation of mixed $\sim$SO/$\sim$SO2 bridging.

All complexes (except 1 and 4) proved active in the ROP of ε-CL, δ-VL and r-LA under solvent-free conditions and in the case of ε-CL, the activity trend was found to be 6 > 7 > 8 > 5 > 9. Similar results were also observed in the case of the other monomers, with the dimethyleneoxa-bridged derivative outperforming the other systems. The higher activity of 6 was thought to be due to the higher flexibility of the $\sim$CH2OCH$\sim$ bridge allowing better access to the active centre(s) and/or to the stabilization of the active species by the oxygen atoms of said bridge. In most of the cases, incomplete catalyst activation and lack of control were observed. The NMR spectroscopy characterization of selected samples suggested the formation of linear $\sim$CH2OH capped PCLs and PVLs and highly heterotactic PLAs. None of the catalysts proved active in the ROP of the larger monomer ω-pentadecalactone, while the conversion of only r-LA was observed during ε-CL/r-LA co-polymerization.

**Experimental**

**General**

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and Cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. THF-$d_8$ was stirred over CaH2 for 48 h, vacuum transferred and then stored over 3A molecular sieves. Elemental analyses were performed by the microanalytical services at the London Metropolitan University or the Chemistry Department at the University of Hull. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 MHz; chemical shifts are referenced to the residual proton impurity of the deuterated solvent. IR spectra (nujol mulls, KBr windows) were recorded on
### Table 6  Crystallographic data for complexes 1–9

| Compound | 1·5THF | 2·5THF | 3·8THF | 4·7.5THF | 5·2THF |
|----------|--------|--------|--------|----------|--------|
| Formula  | C₁₂H₁₆₀S₆Li₆O₁₈ | C₁₆₈H₂₄₆Li₆O₃₂S₆ | C₃₀₆H₅₀₀Li₆O₈₄S₆ | C₆₀H₅₈S₄Li₆O₁₈ | C₆₀H₅₈S₄Li₆O₁₈ |
| Formula weight | 2138.43 | 2110.36 | 2702.48 | 2687.55 | 1257.21 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic | Tetragonal |
| Space group | P2/a | P1 | P2₁/c | C2 | P4/n |
| Unit cell dimensions | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) |
| Crystal size (mm³) | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 | 0.28 | 0.34 | 0.34 |
| Transmission factors (min./max.) | 0.980 and 0.993 | 0.984 and 0.998 | 0.965 and 0.982 | 0.965 and 0.982 | 0.974 and 0.997 | 0.974 and 0.997 | 0.990 and 0.993 | 0.990 and 0.993 | 0.990 and 0.993 | 0.990 and 0.993 | 0.990 and 0.993 | 0.990 and 0.993 |
| GOOF, S | 0.93 | 0.93 | 0.88 | 0.88 | 1.10 | 1.07 | 1.05 | 1.05 | 1.05 | 1.05 | 1.05 | 1.05 |
| Largest difference peak and hole (e Å⁻³) | 0.41 and −0.32 | 0.53 and −0.31 | 1.08 and −0.88 | 1.17 and −0.40 | 0.67 and −0.43 |

| Compound | 6·0.78THF | 1.22hexane | 7·3THF | 8·2MeCN | 9·hexane |
|----------|-----------|----------|--------|---------|--------|
| Formula  | C₉₀H₁₄₃Li₆O₁₄.₇₇ | C₆₀H₆₀Li₂O₁₀ | C₅₈H₃₈Li₅N₅O₅ | C₁₀₀H₁₃₆Li₆O₁₀ |
| Formula weight | 1498.68 | 985.19 | 677.42 | 1539.72 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | P1 | P2₁ | P2₁/m | P1 |
| Unit cell dimensions | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) | a (Å) | b (Å) | c (Å) |
| Crystal size (mm³) | 0.24 | 0.11 | 0.09 | 0.31 | 0.18 | 0.25 | 0.32 | 0.20 | 0.12 | 0.30 | 0.02 | 0.08 |
| Number of reflections | 748 | 707 | 965 | 1657 | 191 |
| Number of parameters | 493 | 1333 | 298 | 561 |
| GOOF, S | 0.93 | 0.93 | 0.88 | 0.88 | 1.10 | 1.07 | 1.05 | 1.05 |
| Largest difference peak and hole (e Å⁻³) | 0.44 and −0.36 | 0.56 and −0.49 | 0.40 and −0.52 | 0.66 and −0.36 |

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PerkinElmer 577 and 457 grating spectrophotometers. The compounds 1,3-di-n-propyloxycalix[4]arene and tert-butyldihexahomotrioxacalix[3]arene were prepared from using the literature methods. The compound tert-butyldihexacalix[4]arene was purchased from TCI UK, whilst the ligands tert-butyldihexalix[4]arene and p-tert-butyldihexalix[4]arene were gifts from Dr Hitoshi Kumagaya of the Cosmo oil company. The complex [L₄Li₆(OH)(THF)]₅ was prepared by the method of Zeller and Radius. All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of [Li₆(L⁵⁰)₃(THF)]₅THF (1·5THF)

A solution of lithium tert-butoxide (7.21 ml, 1 M in THF, 7.21 mmol) was added to Li₄H₄ (1.00 g, 1.39 mmol) in THF (30 ml) at ambient temperature. After stirring for 1 h, the orange solution was concentrated to about 20 ml, and was left to stand for 48 h at room temperature to afford colourless crystals of 1·5THF suitable for X-ray diffraction analysis in 65% yield (0.90 mmol, 1.90 g). Anal. cald. for C₆₀H₈₅S₄Li₅O₁₈: C, 57.32; H, 6.82%; found C, 57.21; H, 6.85%. IR: 3182 bw, 1609 m, 1514 m, 1396 bw, 1316 m, 1292 m, 1261 s, 1214 m, 1197 m, 1155 m, 1127 s, 1080 bs, 1019 bs, 962 m, 902 w, 866 w, 796 s, 735 w, 722 w, 685 w, 660 w, 631 m, 562 m, 523 w, 495 w, 478 w. ¹H NMR (THF-δ, 194.3 MHz, 298 K) δ: 7.61 (s, 16H, ArH), 1.31 (s, 72H, (CH₃)₃C). ³Li NMR (THF-δ, 194.3 MHz, 298 K) δ: 1.50 (s).

Preparation of [Li₆(L⁵⁰)₃(THF)]₅THF (2·5THF)

A solution of lithium tert-butoxide (2.01 ml, 1 M in THF, 2.01 mmol) was added to Li₆H₄ (0.51 g, 0.65 mmol) in THF (10 ml) at ambient temperature. After stirring for 1 h, the solution was concentrated to about 10 ml, and was left to stand for 48 h at room temperature, to afford colourless crystals of 2·5THF suitable for X-ray diffraction analysis in 31% yield (0.20 mmol, 0.22 g). Anal. cald. for C₆₈H₁₀₂Li₁₈O₁₈S₆ (sample dried in vacuo for 12 h, −5THF) requires C 60.40, H 6.11% Found C 59.87, H 6.09%. IR: 3182 bw, 1609 m, 1514 m, 1396 m, 1316 m, 1292 m, 1261 s, 1214 m, 1197 m, 1155 m, 1127 s, 1080 bs, 1019 bs, 962 m, 902 w, 866 w, 796 s, 735 w, 722 w, 685 w, 660 w, 631 m, 562 m, 523 w, 495 w, 478 w. ¹H NMR (THF-δ, 194.3 MHz, 298 K) δ: 7.99 (s, 8H, ArH), 1.34 (s, 36H, (CH₃)₃C). O₃H signal not detected. ³Li NMR (THF-δ, 194.3 MHz, 298 K) δ: 1.12 (s).

Preparation of [Li₆(L⁵⁰)(HO(Bu)]₅THF (6·0.78THF·1.22hexane)

A solution of lithium tert-butoxide (9.02 ml, 1 M in THF, 9.02 mmol) was added to Li₂S₄H₄ (1.00 g, 1.73 mmol) in THF (30 ml) at ambient temperature. After stirring for 1 h, the volatiles were removed in vacuo, and the residue was taken up in hexane (30 ml). Filtration of the solution under nitrogen atmosphere on a POR4 frit and cooling at 0 °C afforded colourless crystals of 6·0.78THF·1.22hexane suitable for X-ray diffraction analysis in 11% yield (0.19 mmol, 0.25 g). Further crops of crystals can be obtained by concentration of the mother liquor to 10 ml and standing at −40 °C for 10 days (total isolated yield 45%, 0.78 mmol, 1.02 g). Cₙ₀H₄₃Li₃₃S₄O₇ requires C 72.48, H 8.97%. Found C, 71.96; H, 8.49%. IR: 3662 bs, 2727 w, 1636 m, 1304 w, 1260 w, 1260 w, 1211 m, 1094 m, 1018 m, 975 w, 875 w, 802 m, 722 m, 530w. ¹H NMR (THF-δ, 400 MHz, 298 K) δ: 7.14 (s, 16H, ArH), 0.61 (m, 72H, (CH₃)₃C). ³Li NMR (THF-δ, 194.3 MHz, 298 K) δ: 0.14 (bs), 0.13 (s).

Preparation of [Li₆Li₆(THF)]₅THF (7·3THF)

A solution of lithium tert-butoxide (4.33 ml, 1 M in THF, 4.33 mmol) was added to Li₄ (1.00 g, 1.73 mmol) in THF (30 ml) at ambient temperature. After stirring for 1 h, the system was filtered, concentrated to about 20 ml, and was left to stand for 48 h at room temperature affording colourless prisms of 7·3THF suitable for X-ray diffraction analysis in 31% yield (0.19 mmol, 0.25 g). Anal. cald. for C₈₀H₉₇Li₅S₃O₂₅ requires C 59.87, H 6.09%. IR: 3182 bw, 1610 m, 1509 m, 1396 w, 1365 m, 1328 w, 1292 m, 1261 s, 1214 m, 1197 m, 1155 m, 1127 s, 1080 bs, 1019 bs, 962 m, 902 w, 866 w, 796 s, 735 w, 722 w, 685 w, 660 w, 631 m, 562 m, 523 w, 495 w, 478 w. ¹H NMR (THF-δ, 400 MHz, 298 K) δ: 7.99 (s, 8H, ArH), 1.74 (s, 36H, (CH₃)₃C). O₃H signal not detected. ³Li NMR (THF-δ, 194.3 MHz, 298 K) δ: 1.23 (s).

Preparation of [Li₆(S₄O₂)(OH)(THF)]₅THF (7·5THF)

To Li₂S₄H₄ (1.00 g, 1.27 mmol) and LiOH (0.16 g, 6.68 mmol) in THF (30 ml) at ambient temperature. After stirring for 12 h, the system was filtered, concentrated to about 20 ml, and was left to stand for 48 h at room temperature affording colourless prisms of 7·5THF suitable for X-ray diffraction analysis in 31% yield (0.19 mmol, 0.25 g). Anal. cald. for C₈₀H₉₇Li₅S₄O₂₅ requires C 59.87, H 6.09%. IR: 3530 bs, 2826 w, 2360 m, 2341 w, 1604 m, 1261 s, 1220 w, 1092 s, 1020 s, 866 w, 799 s, 723 m, 678 w, 634 w, 563 w. ¹H NMR (THF-δ, 400 MHz, 298 K) δ: 8.82 (bs, 2H, −OH), 7.97–7.27 (m, 16H, ArH), 1.25–1.03 (m, 72H, (CH₃)₃C). ³Li NMR (THF-δ, 194.3 MHz, 298 K) δ: 0.14 (bs).
ambient temperature. After stirring for 4 h, the solution was concentrated to about 20 ml, and was left to stand for 48 h at room temperature to afford colourless crystals of 7 suitable for X-ray diffraction analysis in 45% yield (0.59 g, 0.78 mmol). 

Preparation of \( \text{[Li}_6\text{(LPr)}_2\text{(H}_2\text{O})_2\text{]} \) (m, 8H, Ar \(_\text{endo}\))

1H NMR (THF-\(_d_8\), 400 MHz, 298 K) \( \delta \): 7.13–7.67 (m, 16H, Ar\( \text{H}, \text{ArH} \)), 5.08 (d, 2H, \( J = 12 \text{ Hz}, \text{endo-CH}_2 \)), 4.66 (d, 2H, \( J = 12 \text{ Hz}, \text{endo-CH}_2 \)), 4.57 (d, 2H, \( J = 12 \text{ Hz}, \text{endo-CH}_2 \)), 4.14 (d, 2H, \( J = 12 \text{ Hz}, \text{endo-CH}_2 \)), 3.40–3.02 (m, 8H, \( \text{exo-CH}_2 \)), 1.43–1.11 (m, 72H, \( \text{CH}_3\text{)}_2\text{C} \)) \( \text{OH} \) signal not detected. \(^7\) Li NMR (THF-\(_d_8\), 194.3 MHz, 298 K) \( \delta \): 2.44 (bs), 1.77 (bs).

Preparation of \([\text{Li}_4\text{(de-Bu)}_4\text{(OH)}\text{(NCMe)}_4\text{]}_2\text{MeCN})_n\) (8·2MeCN)

A solution of lithium tert-butoxide (12.25 ml, 1 M in THF, 12.25 mmol) was added to de-BuLH\(_4\) (1.00 g, 2.36 mmol) in THF (30 ml) at ambient temperature. After stirring for 4 h the volatiles were removed in vacuo, and the residue was taken up in MeCN (30 ml). Filtration under nitrogen atmosphere on a POR4 frit and cooling to 0 °C led to a fraction of the polymer, which was dried in air at room temperature. The monomer (9.0 mmol) was then added and the reaction was stirred at 130 °C for 12–24 h, or until a mass of polymer blocking the stirrer formed. The mixture was then taken up in CH\(_2\text{Cl}_2\) and quenched with acidified methanol (200 ml). The resultant polymer was then collected on filter paper and dried in air at room temperature.

Ring open polymerization (ROP) procedures

Reaction in toluene. Under inert atmosphere, a THF solution of the complex (1 mM) was added into a Schlenk tube and the solvent was removed under reduced pressure at room temperature. Toluene (2 ml) was added along with the monomer (4.5 mmol) and the required amount of BnOH (as a toluene solution). The reaction mixture was then placed into an oil bath preheated to the required temperature, and the solution was stirred for the prescribed time. The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 ml) into the solution, and the resultant solution was then poured into methanol (200 ml). The resultant polymer was then collected on filter paper and dried in air at room temperature.

Solvent-free conditions. Under an inert atmosphere, a THF solution of the complex (1 mM) was added into a Schlenk tube and the solvent was removed under reduced pressure at room temperature. The monomer (9.0 mmol) was then added and the reaction was stirred at 130 °C for 12–24 h, or until a mass of polymer blocking the stirrer formed. The mixture was then taken up in CH\(_2\text{Cl}_2\) and quenched with acidified methanol (200 ml). The resultant polymer was then collected on filter paper and dried in air at room temperature.

Crystal structure determinations

Diffraction data for 1·5THF, 5·2THF, and 8·2MeCN were collected on a Bruker Apex 2 CCD diffractometer using a sealed tube source; for 2·5THF & 7·3THF at the Diamond Light Source synchrotron, station I19, equipped with Rigaku Saturn724+ CCD or Crystallographic diffractometers; for 3·8THF, 4·7.5THF, and 6·0.78THF·1.22hexane, on Rigaku Saturn 724+ CCD diffractometers equipped with sealed tube (3·8THF and 4·7.5THF) or rotating anode (6·0.78THF·1.22hexane) sources; and for 9·hexane at the Advanced Light Source synchrotron, Station 11.3.1, equipped with a Bruker Apex 2 CCD diffractometer. Further details are given in Table 6 and in the deposited cif files. All crystal structures were collected at low temperature. Data were corrected for absorption and Lp effects. The structures were solved using direct methods \(^{39}\) or a dual-space, charge-flipping algorithm and refined on \( F^2,30,31\) This set of lithium-containing calixarene structures were challenging due to often weak diffracting power caused by their light-atom make-up, and the often-encountered \( \text{Bu} \) group and solvent of crystallization disorder. Some \( \text{Bu} \) groups needed to be modelled with the methyl groups or the whole moiety split over two sets of positions. Solvent molecules of crystallization were often disordered and needed to be modelled with split positions, or as diffuse electron density via the Platon Squeeze procedure (for 1·5THF, 2·5THF, 4·7.5THF, 5·2THF and 6·0.78THF·1.22hexane). \(^{32}\) The ‘squeezed’ solvent contribution is included in the chemical formula in each case. The number of solvent molecules of crystallization should only be taken as approximate. Where disorder has been modelled, restraints were applied to anisotropic displacement parameters and the geometry of the affected and immediately adjacent atoms. For 2·5THF there was some evidence of partial disorder in the O atom on each –SO– bridging group, with the O sometimes...
positioned in the tetrahedral site on the S; this was modelled and the major components at O(5), O(6), O(7), and O(8) were 88.4(8), 91.4(7), 81.6(8), and 81.9(9)% respectively. For 3·8THF the occupancies of O(6) and O(11) were refined as 68.1(10) and 68.0(10)%, respectively. For 4·7.5THF O(20) was only 78.0(18)% occupied. For 5·2THF both THFs are disordered along the 4-fold axis and both were modelled with ‘Squeeze’. One resides in the calixarene cavity, the other above the coordinates were re

except for those on hetero atoms in structures with good data, atoms were placed in geometrically determined positions, occupancy 85.2(4)%. The di

were also modelled as two-fold disordered with major site occupancy 54.9(12)% while atoms O(6)/C(36) and the associated hydrogens only 78.0(18)% occupied. For

O(8) were 88.4(8), 91.4(7), 81.6(8), and 81.9(9)%, respectively. For

Notes and references

1 (a) R. E. Drumright, P. R. Gruber and D. E. Henton, Adv. Mater., 2000, 12, 1841–1846; (b) C. K. Williams and M. A. Hillmyer, Polym. Rev., 2008, 48, 1–10; (c) M. A. Woodruff and D. W. Hutmacher, Prog. Polym. Sci., 2010, 35, 1217–1256; [d] A. L. Sisson, D. Ekinci and A. Lendlein, Polymer, 2013, 54, 4333–4350.

2 (a) Arbaoui and C. Redshaw, Polym. Chem., 2010, 1, 801–826; (b) I. Nifant’ev and P. Ichenko, Molecules, 2019, 24, 4117; (c) O. Santoro, X. Zhang and C. Redshaw, Catalysts, 2020, 10, 800.

3 D. Homden and C. Redshaw, Chem. Rev., 2008, 108, 5086–5130.

4 O. Santoro and C. Redshaw, Catalysts, 2020, 10, 210.

5 C. Floriani and R. Floriani-Moro, Adv. Organomet. Chem., 2001, 47, 167–233.

6 See for example (a) B. Maschi, in Calixarenes 2001, ed. Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens, Kluwer Academic Publishers, 2001, ch. 12; (b) N. Morohashi, F. Narumi, N. Iki, T. Hattori and S. Miyano, Chem. Rev., 2006, 106, 5291–5316; (c) K. Cottet, P. M. Marcos and P. J. Cragg, Beilstein J. Org. Chem., 2012, 8, 201–226.

7 (a) A. K. Sutar, T. Maharana, S. Dutta, C.-T. Chen and C. Lin, Chem. Soc. Rev., 2010, 39, 1724–1746; (b) J. Gao, D. Zhu, W. Zhang, G. A. Solan, Y. Ma and W.-H. Sun, Inorg. Chem. Front., 2019, 6, 2619–2652.

8 (a) C. D. Gutsche, M. Iqbal, K. S. Nam, K. See and I. Alam, Pure Appl. Chem., 1988, 60, 483–488; (b) R. Abidi, M. V. Baker, J. M. Harrowfield, D. S.-C. Ho, W. R. Richmond, B. W. Skelton, A. H. White, A. Varnek and G. Wipff, Inorg. Chim. Acta, 1996, 246, 275–286; (c) K. C. Nam, D. S. Kim and J. M. Kim, Bull. Korean Chem. Soc., 1997, 18, 636–640; (d) For FTIR studies see B. Brzezinski, F. Bartl and G. Zundel, J. Phys. Chem. B, 1997, 101, 5611–5653.

9 H. Bock, A. John, C. Nather and Z. Havlas, J. Am. Chem. Soc., 1995, 117, 9367–9368.

10 M. G. Davidson, J. A. K. Howard, S. Lamb and C. W. Lehmann, Chem. Commun., 1997, 1607–1608.

11 G. Guillemot, E. Solari, C. Rizzoli and C. Floriani, Chem.–Eur. J., 2002, 8, 2072–2080.

12 E. D. Gueneau, K. M. Fromm and H. Goesmann, Chem.–Eur. J., 2003, 9, 509–514.

13 T. A. Hanna, L. Liu, A. M. Angeles-Boza, X. Kou, C. D. Gutsche, K. Ejsmont, W. H. Watson, L. N. Zakharov, C. D. Incarvito and A. L. Rheingold, J. Am. Chem. Soc., 2003, 125, 6228–6238.

14 D. Mendoza-Espinosa, B. A. Martinez-Ortega, M. Quiroz-Guzman, J. A. Golen, A. L. Rheingold and T. A. Hanna, J. Organomet. Chem., 2009, 694, 1509–1523.

15 L. Liu, L. N. Zakharov, J. A. Golen, A. L. Rheingold, W. H. Watson and T. A. Hanna, Inorg. Chem., 2006, 45, 4247–4260.

16 N. P. Clague, J. D. Crane, D. J. Moreton, E. Sinn, S. J. Teat and N. A. Young, J. Chem. Soc., Dalton Trans., 1999, 3535–3536.

17 D. S. Lee, M. R. J. Elsegood, C. Redshaw and S. Zhan, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2009, 65, m291–m295.

18 J. Zeller and U. Radius, Inorg. Chem., 2006, 45, 9487–9492.

19 C. Redshaw, O. Rowe, D. L. Hughes, A. M. Fuller, I. Alvarado Ibarra and S. M. Humphrey, Dalton Trans., 2013, 42, 1983–1986.

20 M. Yamada, M. R. Gandhi and F. Hamada, Acta Crystallogr., Sect. E: Crystallogr. Commun., 2018, 74, 575–579.

21 (a) B.-T. Ko and C.-C. Lin, J. Am. Chem. Soc., 2001, 123, 7973–7977; (b) M. H. Chisholm, C.-C. Lin, J. C. Galluccio and B.-T. Ko, Dalton Trans., 2003, 406–412; (c) C.-A. Huang and C.-T. Chen, Dalton Trans., 2007, 5561–5566; (d) W. Clegg, M. G. Davidson, D. V. Graham, G. Griffen, M. D. Jones, A. R. Kennedy, C. T. O’Hara, L. Russo and C. M. Thomson, Dalton Trans., 2008, 1295–1301; (e) Y. Huang, Y.-H. Tsai, W.-C. Hung, C.-S. Lin, W. Wang, J.-H. Huang, S. Dutta and C.-C. Lin, Inorg. Chem., 2010, 49, 9416–9435; (f) W.-Y. Lu, M.-W. Hsiao, S. C. N. Hsu, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, Y.-C. Lai, Y. Chen and H.-Y. Chen,
