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Ester derivatives of hexahomotrioxacalix[3]naphthalenes: conformational and binding properties with alkali metal cations†

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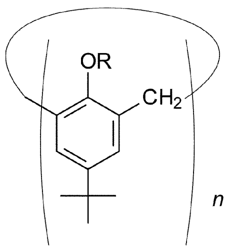
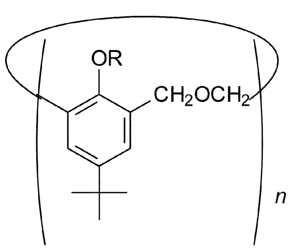
The syntheses of the triesters formed between ethyl bromoacetate and hexahomotrioxacalix[3]naphthalene **8**, and its *tert*-butyl analogue **11**, are described. Depending on the conditions employed, *cone* or *partial cone* conformers are produced. The conformations appear to have some influence on their complexation in neutral medium, with alkali metal cations. The X-ray structure of the *partial cone* triester **10** is presented.

Introduction

It is well-known that lower-rim unsubstituted calix[*n*]arenes such as **1** have the ability to accommodate various small neutral molecules within their cavities to form inclusion compounds.[1] On the other hand, these compounds show very little ionophoric preference for alkali metal cations, as determined for example, by their inability to transport such ions from neutral aqueous solutions across a chloroform membrane.[2] Ketone- and ester carbonyl group-bearing derivatives of calixarenes however, have been shown to selectively form complexes with alkali metal cations.[3–5] The tetrakis(ethoxycarbonylmethoxy) ester ("tetraester") of calix[4]arene, **2**, forms strong complexes with Na^+ and K^+, as does **3**, the tetrakis(*tert*-butoxycarbonylmethoxy) ester.[6] These tetraesters were shown to be in *cone* conformations. On the other hand, the centrosymmetric hexaester of calix[6]arene **4** forms strong complexes with Cs^+, Rb^+ and K^+, but relatively weak complexes with Na^+ ions.[7]

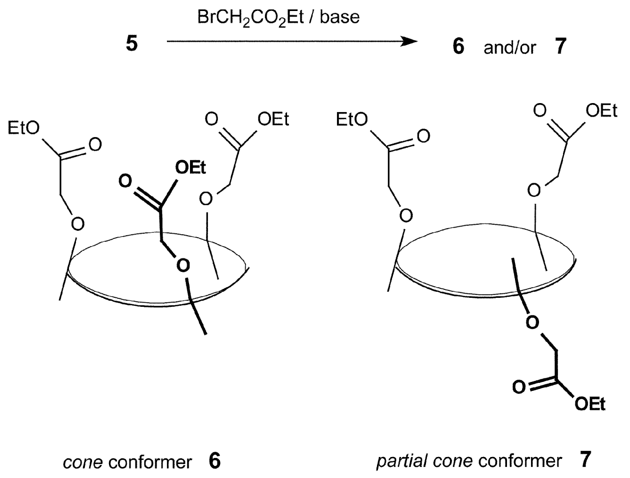


1 R = H ; *n* = 4
2 R = CH_2CO_2Et ; *n* = 4
3 R = $CH_2CO_2Bu^t$; *n* = 4
4 R = CH_2CO_2Et ; *n* = 6



5 R = H ; *n* = 3

In 1993 Shinkai *et al.* reported[8] that the related hexahomotrioxacalix[3]arene **5** forms analogous tris(ethoxycarbonylmethoxy) esters ("triesters") **6** and **7** which respectively are in *cone* and *partial cone* conformations, and also that they show ionophoric selectivities (Scheme 1). They reasoned that these compounds had several structural features including the presence of the ether oxygen atoms of the 18-membered intra-annular macrocycle which could act cooperatively with the phenolic oxygens upon the binding of metal ions. Slight selectivity for Na^+ over K^+ and Cs^+ was shown by **6**, but **7** showed selectivity towards K^+ and Cs^+ over Na^+. The observed selectivities roughly paralleled those shown by the corresponding tetraesters **2**.



cone conformer **6**

partial cone conformer **7**

Scheme 1

We report herein the synthesis of the ester derivatives of hexahomotrioxacalix[3]naphthalene, **8**,[9] namely, tris((ethoxycarbonyl)methoxy)hexahomotrioxacalix[3]naphthalenes **9** and **10**, which exist respectively in the *cone* and the *partial cone* conformations. Also reported are the esters of the corresponding *tert*-butyl derivative **11** of **8**, namely, **12** and **13**. Their abilities to form complexes with alkali metal cations and Ag^+ are discussed.

Results and discussion

Synthesis

We previously described the syntheses of **8** and **11**.[9] Picrate extraction studies with these compounds **8** and **11** showed that they only weakly bind alkali metal cations and Ag^+.[9] It was anticipated however, that by analogy with calixarenes and the hexahomotrioxacalix[3]arenes, that the (ethoxycarbonyl)methoxy derivatives of **8** and/or **11** could result in molecules having a high degree of phase-transfer affinity for alkali metal cations.

Shinkai *et al.* found that a metal ion-template effect (see below) was clearly evident for the selective syntheses of the conformational isomers **6** and **7**.[8] They found that the *partial cone* conformer **7** is formed exclusively from **5** with ethyl

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† Electronic supplementary information (ESI) available: ^1H NMR spectra for the triesters **9** and **10**. The crystallographic files in .cif or other electronic format for the structure of **10**; CCDC reference number 194366. See http://www.rsc.org/suppdata/ob/b2/b209046p/

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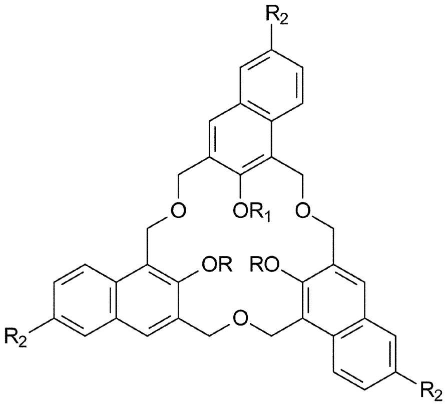
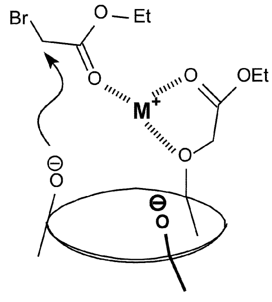
Table 1 Distribution of alkylation products from reaction of **8** or **11** with ethyl bromoacetate under different basic conditions

Substrate	Base	Solvent	Product	Yield (%)
8	K_2CO_3	Acetone	**10** (*partial cone*)	47
8	NaH	THF	**9** (*cone*)	25
			10 (*partial cone*)	10
11	K_2CO_3	Acetone	**13** (*partial cone*)	24
			Diester **14** (*cone*)	26
11	NaH	THF	**12** (*cone*)	25
			13 (*partial cone*)	17



8 $R = R_1 = R_2 = H$
9 $R = R_1 = CH_2CO_2Et$; $R_2 = H$ *cone* conformer
10 $R = R_1 = CH_2CO_2Et$; $R_2 = H$ *partial cone* conformer
11 $R = R_1 = H$; $R_2 =$ *t*-Bu
12 $R = R_1 = CH_2CO_2Et$; $R_2 =$ *t*-Bu *cone* conformer
13 $R = R_1 = CH_2CO_2Et$; $R_2 =$ *t*-Bu *partial cone* conforme
14 $R = CH_2CO_2Et$; $R_1 = H$; $R_2 =$ *t*-Bu *cone* conformer

bromoacetate, when K_2CO_3 or Cs_2CO_3 is used as the base with acetone as the solvent. They also reported that some of the *cone* conformer **6** can be obtained (20–22%) when NaH or *t*-BuOK is used as the base with THF as solvent. To account for the formation of the *cone* products in the latter cases, Shinkai *et al* proposed a metal-ion coordinated/templated intermediate which is formed when a strong base containing Na^+ (or K^+ in *t*-BuOK) is used (Scheme 2). Such an intermediate could overcome the steric hindrance which would tend to favour the formation of the corresponding *partial cone* conformers.



Scheme 2

Alkylation of **8** and **11** with ethyl bromoacetate was carried out using NaH/THF or K_2CO_3/acetone conditions. The products from these reactions which were isolated by preparative TLC, are summarized below, and in Table 1. Alkylation of **8** with ethyl bromoacetate using NaH in THF produces both *cone* **9** and *partial cone* **10** products; alkylation of **11** under similar conditions, also produces both *cone* **12** and *partial cone* **13** products, with a preference in both cases, however, for the *cone* conformers. Using K_2CO_3 in acetone instead, alkylation of **8** afforded the *partial cone* product **10** exclusively. With **11**, under similar conditions using K_2CO_3 in acetone, the *partial cone* product **13** and the *diester*, **14**, were produced in roughly equal amounts. NOED experiments failed to establish unequivocally the conformation of **14**, however, molecular modeling calculations[10] suggest that the most likely conformer is the *cone* form. Longer reaction times failed to result in the complete conversion of **14** to **13**. In their work, Shinkai *et al* did not report isolating the corresponding diester of **5** but inferred its intermediacy in the formation of both *cone* and *partial cone* products **6** and **7**.[8]

In summary, therefore, both **8** and **11** formed *partial cone* triesters as the predominant conformers when the weaker base (K_2CO_3/acetone) conditions were employed, whereas with NaH/THF, both **8** and **11** formed the *cone* triesters as the major conformers. This latter observation contrasts with Shinkai's findings that under similar NaH/THF conditions, the hexahomotrioxacalix[3]arene **5** formed the *partial cone* triester as the major conformer with the corresponding *cone* conformer being formed as the minor product. In our case, therefore it would appear that the Na^+ ion template effect is more pronounced in holding the carboxylate group(s) on the same side of the hexahomotrioxacalix[3]naphthalene molecule, thus leading to the *cone* conformer. With the weaker base, the undissociated hydroxy group forms intramolecular hydrogen bonds with the dissociated hydroxy group(s), thus inhibiting any metal template effect arising from the $M^+ \cdots O^-$ interactions, leading to the predominance of the *partial cone* conformer which is also favoured sterically.

The ^1H NMR spectrum of **9**[11] shows one triplet centered at δ 1.38 ppm (J = 6.9 Hz), coupled to the quartet centered at δ 4.34 ppm (J = 6.9 Hz) and is therefore consistent with a *cone* conformation. The spectrum also reveals three AB systems; one centered at δ 4.47 ppm (J = 15.3 Hz), the other at δ 4.86 ppm (J = 16.5 Hz) and the third at δ 5.22 ppm (J = 12.6 Hz). The first two AB systems are due to the two sets of the macrocyclic ring-bridging methylene protons and the one which is centered at δ 5.22 ppm is due to the diastereotopic O–$\mathbf{CH_2}$–CO methylene protons. Similar splitting patterns are also observed for **12**, in addition to the singlet at δ 1.26 ppm corresponding to the *tert*-butyl methyl protons.

In the ^1H NMR spectrum ($CDCl_3$) of the *partial cone* triester **10** the methyl groups of the ethyl esters appear as three distinct sets of triplets in a 1:1:1 ratio. The shielding effect of the two distal naphthalene rings on one of the methyl groups is clearly shown by the high-field (δ 0.40 ppm) location of one of these methyl triplets. This spectrum also reveals very complex splitting patterns in the aromatic regions and in the methylene regions due to diastereotopic effects. Similar splitting patterns were observed for the *partial cone* triester of **13** which contains additionally, three singlets at δ 1.33 ppm, 1.37 ppm, and 1.42 ppm due to each of the *tert*-butyl groups.

The X-ray structure of **10** shows that the compound also adopts a *partial cone* conformation in the solid state (Fig. 1). The structure clearly shows the positioning of one of the ethoxy groups as being sandwiched between the two naphthalene rings.

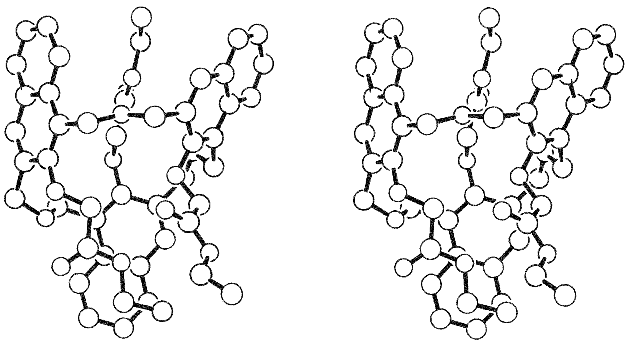


Fig. 1 PLUTO stereoview of *partial cone* conformer **10**.

Table 2 %E values for two-phase solvent extraction of alkali metal and silver picrates with triesters **9**–**13** in $CHCl_3$

		Metal picrate					
Triester	Run	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
9	1	5.0	4.5	5.0	4.8	3.2	4.2
	2	4.2	6.0	7.0	5.4	3.7	5.4
Mean values		4.6 ± 0.4	5.3 ± 0.7	6.0 ± 1.0	5.2 ± 0.4	3.5 ± 0.2	4.8 ± 0.4
10	1	1.6	1.1	1.9	4.1	0.7	0.1
	2	2.8	1.9	1.3	4.5	1.1	0.3
Mean values		2.2 ± 0.6	1.5 ± 0.4	1.6 ± 0.3	4.3 ± 0.2	0.9 ± 0.2	0.2 ± 0.1
12	1	6.0	4.7	9.7	4.4	5.2	2.0
	2	5.3	5.6	9.6	5.0	5.1	3.2
Mean values		5.6 ± 0.3	5.2 ± 0.4	9.7 ± 0.1	4.7 ± 0.3	5.2 ± 0.1	2.6 ± 2.6
13	1	5.1	3.9	3.8	5.9	3.6	1.6
	2	5.1	4.0	3.9	5.8	3.8	2.1
Mean values		5.1 ± 0.1	4.0 ± 0.1	3.9 ± 0.1	5.9 ± 0.1	3.7 ± 0.1	1.8 ± 0.3

Complexation of triesters with metal ions. Two-phase solvent extraction experiments with alkali metal cations and silver ions with each of the triesters **9**–**13**, in $CHCl_3$ were conducted at 25 °C (Table 2). Overall, the percent extraction (%E) values are small, but a trend can be discerned that suggest that they are affected by the conformation of the receptor. The *cone* conformers in general, have higher %E values, albeit that they are overall still relatively low, than the *partial cone* conformers, implying that the lower-rim ionophoric region formed by the three alkoxyester groups in the *cone* conformer may be more efficient for metal binding. Furthermore, the *cone* conformers in both **9** and **12** show some selectivity toward K^+ over the other alkali metal cations, with **12** showing the greater selectivity (Fig. 2).

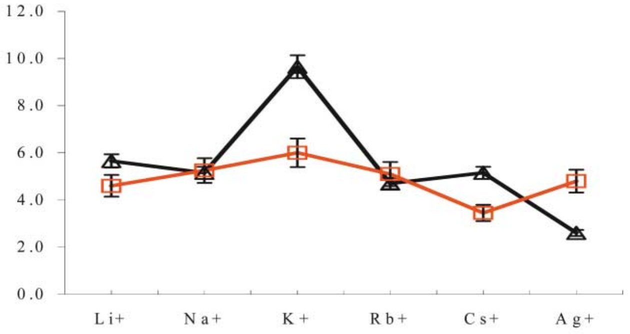


Fig. 2 %E values for *cone* triesters **12** (higher) and **9** (lower values).

The *partial cone* conformers **10** and **13**, show some selectivity towards Rb^+ (Fig. 3). Whether or not there is additional (optimal) interaction between the Rb^+ ion and the π orbitals of the naphthalene ring and the two alkoxyester groups which are all *syn* to each other in the *partial cone* conformers is open to conjecture at this stage.

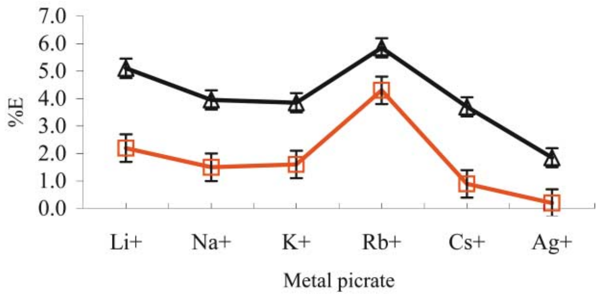


Fig. 3 %E values for *partial cone* triesters **13** (higher) and **10** (lower values).

The %E values obtained with Ag^+ in all but with **9** are the lowest with no clear trend apparent. Finally, it should be noted that the two-phase solvent extraction of alkali metal cations with the triesters **6** and **7** which was reported by Shinkai *et al.*,[8] employed metal picrates in a basic medium. It is therefore not appropriate to compare our results directly with those of Shinkai's group. Nevertheless, data presented herein suggest that the esters obtained with hexahomotrioxacalix[3]naphthalene **8** or **9** may show greater relative selectivities for extracting alkali metal cations from neutral solutions.

Experimental

For general experimental conditions see ref. 9.

Alkylation of 8 with ethyl bromoacetate

(a) K_2CO_3/acetone conditions

Ethyl bromoacetate (0.03 mL, 0.27 mmol) was added to a mixture of **8** (19 mg, 0.034 mmol) and K_2CO_3 (28 mg, 0.20 mmol) in anhydrous acetone (10 mL) at rt. The mixture was refluxed for 48 h, and worked up by first evaporating the solvent, then dissolving the crude product in $CHCl_3$ (20 mL) and then washing with aqueous 1% HCl. The organic layer was separated and washed with H_2O (10 mL). Drying over $MgSO_4$, filtered and evaporating the solvent afforded a residue, from which excess ethyl bromoacetate was evaporated under high vacuum. The crude product was purified by PLC using ethyl acetate:hexane (3:7) to afford **10** (13 mg, 47%), mp 113–115 °C, ^1H NMR ($CDCl_3$): δ 0.40 (t, J = 7.2, 3H), 0.86 (t, J = 7.2, 3H), 1.10 (t, J = 7.2, 3H), 2.26 (d, J = 15.9, 1H), 2.65–2.75 (m, 1H), 2.85–3.00 (m, 1H), 3.15 (d, J = 15.3, 1H), 3.28–3.40 (m, 1H), 3.80–3.90 (m, 1H), 3.92–4.02 (dt, J = 9.5, 3.0, 2H), 4.30 (s, 1H), 4.17–4.42 (m, 4H), 4.59 (d, J = 9.3, 1H), 4.71(d, J = 12.9, 1H), 4.84 (d, J = 5.1, 1H), 4.90 (d, J = 10.5, 1H), 4.98 (d, J = 2.7, 1H), 5.01 (s, 2H), 5.22 (d, J = 9.6, 2H), 5.25 (d, J = 9.6, 2H), 5.41 (t, J = 12, 2H), 7.37 (t, J = 7.8, 2H), 7.46 (t, J = 8.1, 3H), 7.56 (t, J = 5.4, 1H), 7.71 (m, 3H), 7.83 (m, 3H), 8.09 (d, J = 8.1, 1H), 8.12 (d, J = 7.8, 1H), 8.33 (d, J = 8.4, 1H); ^{13}C NMR ($CDCl_3$): δ 13.2, 13.7, 14.0, 59.4, 60.3, 60.4, 60.8, 63.3, 67.3, 69.3, 69.9, 70.3, 72.4, 72.7, 123.3, 124.4, 125.0, 125.1, 125.7, 126.2, 126.4, 127.6, 127.9, 128.2, 130.2, 130.3, 130.4, 130.6, 130.7, 130.9, 131.6, 131.7, 133.5, 133.9, 153.3, 154.6, 155.9, 168.5, 169.5, 169.6; $ES^+(+NH_3)$ calcd for $C_{48}H_{48}O_{12}$ NH_4^+ 834.35, found 834.2.

(b) NaH/THF conditions. To a solution of **8** (50 mg, 0.09 mmol) in anhydrous THF (20 mL) at rt was added NaH (15 mg, 0.62 mmol). The mixture was stirred for 5 min at rt and then ethyl bromoacetate (0.08mL, 0.7 mmol) was added. The reaction mixture was refluxed for 8 h, cooled to rt and then the solvent was evaporated on a rotary evaporator. The crude product was dissolved in $CHCl_3$ (20 mL) and the mixture was washed carefully with aqueous 5% HCl. The organic layer was separated and washed with H_2O (10 mL). Drying over $MgSO_4$, filtration and evaporation of the solvent afforded a residue from which excess ethyl bromoacetate was evaporated under high vacuum. The crude product was then purified by tlc using ethylacetate:pet.ether (3:7) to give: (*i*) 7 mg (10%) of **10** and (*ii*) 18 mg (25%) of **9**: mp 60–62 °C; ^1H NMR ($CDCl_3$): δ 1.38 (t, J = 6.9 Hz, 9H), 4.34 (q, J = 6.9 Hz, 6H), 4.47 (q, J = 15.3 Hz, 6H), 4.86 (q, J = 16.5 Hz, 6H), 5.22 (q, J = 12.6, 3H), 6.76 (d, J = 8.1 Hz, 3H), 7.00 (s, 3H), 7.16 (ddd, J = 7.6, 7.2, 1.0 Hz, 3H), 7.46 (ddd, 7.6, 6.9, 1.0 Hz, 3H), 8.20 (d, J = 8.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): 14.2, 61.2, 64.9, 68.3, 71.5, 123.5, 124.4, 124.5, 125.5, 127.4, 127.9, 130.5, 130.9, 132.2, 151.9, 168.7; ESI$^+$-(+NH_3) calcd for $C_{48}H_{48}O_{12}$ NH_4^+ 834.35, found 834.2.

Alkylation of 11 with ethyl bromoacetate

(a) K_2CO_3/acetone conditions. Ethyl bromoacetate (0.03 mL, 0.3 mmol) was added to a mixture of **11** (25 mg, 0.034 mmol) and K_2CO_3 (29 mg, 0.21 mmol) in 10 mL anhydrous acetone at rt. The mixture was refluxed for 48 h, and worked up by first evaporating the solvent, and then dissolving the crude product in $CHCl_3$ (20 mL) and washed carefully with aqueous 1% HCl. The organic layer was separated and washed with H_2O (10 mL). Drying over $MgSO_4$, filtration and evaporation of the solvent afforded a residue from which excess ethyl bromoacetate was evaporated under high vacuum. The crude product was purified by tlc using ethyl acetate:hexane (3:7) to afford: *diester* **14**, as a colorless solid (8 mg, 26%), mp 120–122 °C; ^1H NMR ($CDCl_3$): δ 0.62 (t, J = 6.9 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H),1.38 (s, 9H), 1.42 (s, 9H), 1.44 (s, 9H), 3.12–3.42 (m, 1H), 3.40–3.62 (m, 4H), 3.91 (d, J = 16.2 Hz, 1H), 4.21 (t, J = 15.9 Hz, 2H), 4.45 (d, J = 11.7 Hz, 1H), 4.55 (d, J = 13.8 Hz, 1H) 4.77 (d, J = 4.8 Hz, 1H), 4.84 (d, J = 4.8 Hz, 1H), 4.90 (t, J = 12.3 Hz, 2H), 5.00–5.13 (m, 4H), 5.31 (t, J = 11.7 Hz, 1H) 7.54–7.98 (m, 10H), 8.17 (d, J = 9.0 Hz, 1H), 8.34 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.5, 13.7, 14.1, 29.7, 34.7, 59.9, 60.1, 61.2, 62.0, 63.1, 66.2, 68.6, 70.0, 71.2, 115.4, 120.2, 122.0, 123.3, 123.4, 123.5, 124.4, 124.7, 125.5, 125.6, 126.1, 128.0, 129.3, 130.2, 130.3, 130.5, 130.6, 130.7, 131.2, 131.4, 131.7, 145.5, 147.1, 147.8, 153.1, 154.5, 168.9, 169.2; ES$^+$ calcd for $C_{60}H_{72}O_{12}$ 985.2, found 985.3; and *triester* **13**, as a colorless solid (8 mg, 24%), mp 114–116 °C; ^1H NMR ($CDCl_3$): δ 0.36 (t, J = 7.2 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H), 1.37 (s, 9H), 1.42 (s, 9H), 2.12 (d, J = 15.6 Hz, 1H), 2.56 (m, 1H), 2.86 (m, 1H), 3.05 (m, 1H), 3.22 (d, J = 15.6 Hz, 1H), 3.97 (m, 2H), 3.95 (m, 2H), 4.13–4.40(m, 4H), 4.53 (d, J = 8.4 Hz, 1H), 4.72 (m, 2H), 4.89–5.11 (m, 8H), 5.45 (m, 2H), 7.49 (d, J = 4 Hz, 1H), 7.54 (m, 2H), 7.57 (d, 1H), 7.65 (m, 3H), 7.70 (s, 1H), 7.75 (d, J = 4 Hz, 2H), 7.76 (s, 1H), 7.82 (s, 1H), 7.96 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 9.0 Hz, 1H), 8.29 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.2, 13.8, 14.0, 31.1, 31.2, 34.6, 34.7, 59.2, 59.9, 60.2, 60.4, 60.8, 63.2, 67.5, 69.6, 69.8, 70.7, 72.5, 73.1, 122.9, 123.1, 124.1, 124.3, 125.3, 125.4, 125.7, 126.1, 127.5, 130.1, 130.3, 130.6, 130.7, 130.8, 131.6, 131.7, 132.0, 148.2, 148.3, 152.2, 152.7, 153.3, 154.2, 155.7, 168.7, 169.3, 169.8, 171.2; ES$^+$ calcd for $C_{60}H_{72}O_{12}$ 985.2, found 985.3.

(a) NaH/THF conditions. To a solution of **11** (27 mg, 0.037 mmol) in anhydrous THF (20 mL) at rt was added NaH (15 mg, 0.62 mmol). The mixture was stirred for 5 min at rt and then ethyl bromoacetate (0.03 mL, 0.3 mmol) was added. The reaction mixture was refluxed for 8 h, cooled to rt and then the solvent was evaporated using a rotary evaporator. The crude product was dissolved in $CHCl_3$ (20 mL) and the mixture was washed with aqueous 5% HCl. The organic layer was separated and washed with H_2O (10 mL). Drying over $MgSO_4$, filtration and evaporation of the solvent afforded a residue from which excess ethyl bromoacetate was evaporated under high vacuum. The crude product was then purified by tlc using ethylacetate:-pet.ether (3:7) to afford **13** as a colorless solid (6 mg) whose spectral properties were identical to that of the product obtained from K_2CO_3/acetone conditions; and **12** as a colorless solid (9 mg, 25%) in the *cone* conformation, mp 75–77 °C; ^1H NMR ($CDCl_3$): δ 1.26 (s, 27H),1.36 (t, J = 6.9 Hz, 9H), 4.28 (d, J = 7.2 Hz, 4H), 4.33 (d, J = 6.9 Hz, 4H), 4.50 (d, J = 16.2 Hz, 4H), 4.74 (d, J = 14.1 Hz, 4H), 4.85 (d, J = 15.9 Hz, 4H), 5.01 (d, J = 12.3 Hz, 4H), 5.17 (d, J = 12.3 Hz, 4H), 7.08 (d, J = 2.1 Hz, 3H), 7.10 (s, 3H), 7.20 (dd, J = 1.8 Hz, 7.5, 3H), 7.76 (d, J = 9.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 14.1, 31.1, 34.4, 60.9, 64.2, 69.8, 71.6, 122.8, 123.4, 124.3, 124.6, 128.6, 130.4, 131.1, 146.8, 153.4, 169.6; ES$^+$ calcd for $C_{60}H_{72}O_{12}$ 985.2, found 985.3.

Metal picrate binding studies

Extractions of metal picrates from deionized water into chloroform (spectrograde) were performed according to the following typical[5] procedure: 5 ml of an aqueous 1.7×10^{-4} M solution of the metal picrate and 5 ml of a chloroform 1.7×10^{-4} M solution of triester **9** (or **10**), or triester **12** (or **13**) in $CHCl_3$ were mechanically shaken in a Teflon^R-lined stoppered glass tube for 24 h. The mixture was then equilibrated in a thermostated water bath at 25.0 ± 0.1 °C for 2 h in order to achieve a good phase separation. The absorbance of the metal picrate remaining in the aqueous phase was then determined spectrophotometrically at 358 nm on a HP 8452A diode array uv-vis spectrophotometer. The percentage extraction (%E) for each solution was calculated from the expression $\%E = 100(A_o - A)/A_o$. Where A_o is the absorbance of the aqueous solution of the metal picrate without the triesters. The results are summarized in Table 1.

X-Ray crystal data for 10.[12] (Ethyl acetate:hexane) $C_{48}H_{48}O_{12}$; orthorhombic, space group *Pbca* (#61), Z value = 8, a = 17.092(2) Å, b = 30.493(3) Å, c = 16.382(2) Å, V = 8538(2) Å^3, D_{calc} = 1.271 g cm^{-3}, F_{000} = 3456.00, μ(Cu-Kα) = 0.75 cm^{-1}, crystal dimension = 0.35 × 0.20 × 0.40 mm. Intensity data were measured at 299 ± 1 K on a Rigaku AFC6S diffractometer with graphite monochromated Cu-Kα (λ = 1.54178 Å) radiation to $2\theta_{max}$ (degree) = 120.1°; 7028 reflections were collected, of which 3274 were unique (R_{int} = 0.044) with $I > 1.00\sigma(I)$; Final R and R_w values were 0.087 and 0.080, respectively, gof = 2.01.

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12 The crystallographic files in .cif or other electronic format for the structure of **10** reported in this paper are available as ESI. † CCDC reference number 194366.