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Synthesis and Characterization of New bis-Symmetrical Adipoyl, Terepthaloyl, Chiral Diimido-di-L-alanine Diesters and Chiral Phthaloyl-L-alanine Ester of Tripropoxy *p-tert*-Butyl Calix[4]arene and Study of Their Hosting Ability for Alanine and Na^+

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ABSTRACT

Bis-symmetrical tripropoxy *p-tert*-butyl calix[4]arene esters were prepared from the reaction of tripropoxy calix[4]arene ($1HPr_3$) with di-acyl chlorides as bridges in the presence of sodium hydride. The esters, which were synthesized from L-alanine acyl chloride derivatives, are optically active. In all of these esters, calix[4]arene cavities have a pinched cone conformation. The structures of these esters were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, elemental analysis and ion positive FAB mass spectrometry.

KEYWORDS

Synthesis, tripropoxy calix[4]arene, acyl chloride, double calix[4]arenes, L-alanine.

1. Introduction

Calixarenes, which are phenol-formaldehyde cyclic oligomers, are receiving increasing attention in the field of supramolecular chemistry. Calix[4]arenes can be selectively functionalized easily, both at the phenolic OH groups (lower rim)[1] and at the *para* positions of the phenol rings (upper rim). Consequently they are useful building blocks for host molecules with different properties.[2,3] It was recognized by Cornforth[4] that a calix[4]arene can exist in four main conformations. The first bis-calix[4]arenes connected *via* a single bridge between the narrow rims were prepared by reacting the triester monoacid chloride with 1,2-diaminoethane or ethylene glycol in benzene. X-ray structural studies showed the usual pinched cone conformation of the two calix[4]arene units.[5]

In this study, we report the synthesis of new calix[4]arene esters by the reaction of tripropoxy calix[4]arene ($1HPr_3$) with acyl chloride bridges (Table 1) in the presence of NaH as base (Scheme 1). One of them is a type of mono-optically active ester (phthaloyl-L-alanine ester of $1HPr_3$) and it adopts a pinched cone conformation. The others are double calix[4]arenes with symmetrical structures and cone conformations (Table 2). Many calixarene derivatives have been incorporated as neutral ionophores into ion-selective electrodes for alkali metal ions.[6,7] This property was used successfully for the analysis of Na^+ in blood using both steady-state and flow-injection analysis (FIA) techniques[8–10] and plays a critical role in maintaining homeostasis in metabolism.[11]

To date, various calixarenes that possess ester,[12] amide[13] or other functional groups have been synthesized for separation,[14] recognition,[15] discrimination[16] and catalysis.[17] Among them, chiral recognition[18] is one of the more essential reaction processes occurring in living systems. Among the most popular chiral building blocks used, amino acids[19] offer a wide range of possibilities for providing calix[4]arenes with asymmetric features. Many of the chiral calix[4]arene derivatives have shown remarkable recognition properties toward achiral cations and anions;[20] however, more interestingly, some of them have exhibited significant chiral discrimination abilities for chiral guests such as amino acids.[21]

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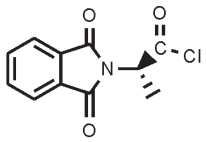
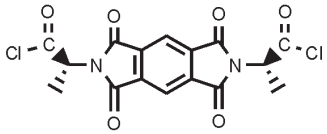
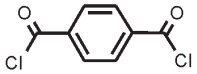
2. Results and Discussion

Four different conformers for calix[4]arenes exist. These conformations are driven by substitution of the four bulky substituents at the phenolic oxygen atoms and the conformations are named cone, partial cone, 1,2-alternate and 1,3-alternate. The structures of these conformers can be easily distinguished by their characteristic ^{1}H NMR patterns arising from the $ArCH_2Ar$ methylene protons. The splitting patterns for $ArCH_2Ar$ protons of these four conformers are: a pair of doublets for cone, two pairs of doublets for partial cone, one singlet and a pair of doublets for 1,2-alternate and one singlet for 1,3-alternate.[22–24] The conformations of calix[4]arenes can be deduced from the ^{13}C NMR chemical shifts of the methylene groups connecting each pair of aromatic rings.[25] When the phenol rings adjacent to each methylene are in a *syn* orientation (in cone conformations), the methylene signals appear around δ 31 ppm, whereas they appear around δ 37 ppm when both phenol rings are *anti* oriented (in 1,3-alternate conformations). However, an inspection of the proton-decoupled ^{13}C NMR spectra of all the series revealed that the methylene carbon chemical shift always ranged around two values: δ 31 and 37 ppm. In cone conformations, adjacent phenol rings are in a *syn* orientation only (δ 31 ppm); while in the other conformations, adjacent phenol rings are in both *syn* and *anti* orientations.

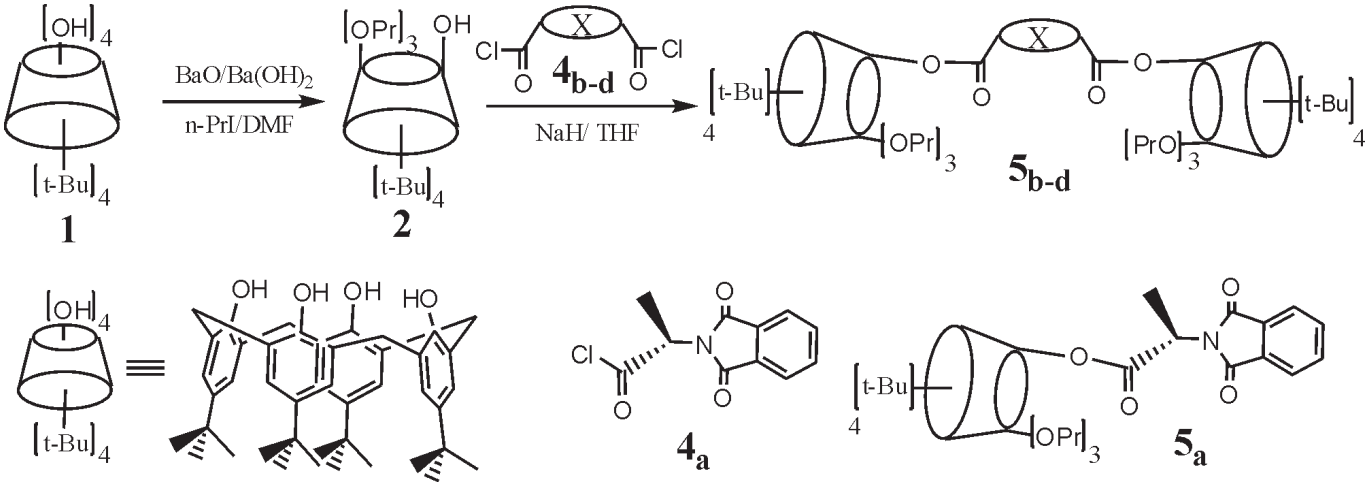
Compound **2** ($1HPr_3$) has only one hydroxyl group in the lower rim, therefore its reactions with acyl halides are more selective and do not produce any other by-products. Because of the lower

Table 1 Esterification conditions and yields.

Compound no.	Structure of bridging sample	Molar ratio of NaH to **4a–d**	Reaction time/h	Product name	Yield/%
4a		2	5	**5a**	28
4b		7.5	5	**5b**	23
4c		7.5	4	**5c**	53
4d		6	4	**5d**	56

acidity of the proton of the OH group in compound **2**, it was activated by using NaH as a strong base; also the small size of NaH is very useful for this type of reaction. All of the esters are soluble in low polarity solvents such as CH_2Cl_2 and $CHCl_3$, but they are insoluble in polar solvents such as DMSO, DMF, MeOH and H_2O. This phenomenon is attributed to the existence of the bulky non-polar moiety in their structures, so they are categorized as non-polar molecules.

The splitting pattern for $ArCH_2Ar$ protons (a pair of doublets with a typical AX pattern) shows that the compounds **5c** (terephthaloyl diester of $1HPr_3$) and **5d** (adipoyl diester of $1HPr_3$) adopt a cone conformation. We used the DEPT-135 technique to distinguish signals relevant to methylene carbons in the products. The compound **5c** DEPT-135 spectrum has two signals relevant to the methylene carbons that are contracted together at δ 30.96 ppm. This confirms that **5c** adopts a cone conformation. The compound **5d** DEPT-135 spectrum has one signal relevant to the methylene carbons at δ 30.71 ppm. This confirms that **5d** adopts a cone conformation. There is a signal at δ 33.63 ppm in the DEPT-135 spectrum of compound **5d** which is relevant to the compound **4d** (adipoyl chloride) methylene carbons. The conformation recognition of **5a** (phthaloyl-L-alanine ester of $1HPr_3$) *via* the ^{1}H NMR spectrum is difficult; but the DEPT-135 spectrum does not show a signal at δ 37 ppm; it has three signals in the range δ 30.8, 31.2 and 31.36 ppm. These results show that the compound adopts a pinched cone conformation and the symmetry in this molecule is low. There is a signal at δ 30.28 ppm in this spectrum which is relevant to CH_2*-CH_3 carbon(s) in propyl group(s). Similar to compound **5a**, the characterization of **5b** (diimido-di-L-alanine diester of $1HPr_3$) *via* the ^{1}H NMR



Scheme 1
General synthetic pathway for synthesis of double calix[4]arenes.

Table 2 Properties of final products.

Compound no.	M.p./°C	Conformation	Product type	$[\alpha]_D^{20}$/deg cm^2 g^{-1}	Optical activity	Ex % of Na^+Pic^-	Ex % of alanine
5a	239–40	pinched cone	mono	–17.3	active	24.2	19.2
5b	>311	pinched cone	bis	–19.2	active	43.1	33.4
5c	>309	cone	bis	0	inactive	31.5	39.5
5d	>314	cone	bis	0	inactive	32.4	42.1

spectrum is also difficult, but in its DEPT-135 spectrum, there is no signal in the region δ 37 ppm, but it has three signals at δ 30.72, 31.2 and 31.31 ppm. These results show that it adopts a pinched cone conformation. There is a signal at δ 30.54 ppm in this spectrum which is relevant to CH_2*-CH_3 carbon(s) in the propyl group(s). With comparison of the ^{1}H NMR and ^{13}C NMR spectra for compounds **5a** and **5b** in the aliphatic and aromatic regions, we realized that the symmetry in **5b** is decreased toward **5a** and maximum similarity of these compounds is related to the splitting pattern for $ArCH_2Ar$ protons (Table 3). In the synthesis of **5a** and **5b**, we used L-alanine; therefore, both products are optically active and can potentially exhibit importance in pharmaceutical applications.[26] When acyl chlorides were used in the synthesis of more bulky **5a** and **5b** compounds, the yields of these products were low. General results are summarized in Table 1.

The extraction ability of a calixarene for neutral guests depends on the size of the calixarene cavity and its conformation. A fixed cone conformer is more effective for extraction of neutral guests in solution. All of our novel products are fixed in the cone conformation; therefore they should be suitable for extraction of α-amino acids (e.g. alanine) from aqueous solution to the organic phase. We performed the extraction of neutral guest experiments only for D,L-alanine following Pedersen's procedure.[27] The results of these experiments are summarized in Table 2. The enantioselective recognition ability of the receptors was studied by UV/visible absorption spectroscopy. All receptors efficiently extracted D,L-alanine; however, whether chiral or achiral, they did not show any enantioselectivity towards either alanine enantiomer. The percentage extraction value (Ex %) for **5d** is higher than for the other compounds. This is attributed to the size-fitting of **5d** and alanine.

Solvent extraction of metal salts, mostly picrates, from water into an organic solvent, usually CH_2Cl_2 or $CHCl_3$ was performed at 25 °C. The esters are suitable for encapsulating guest cations, and excellent selectivity in favour of Na^+ was obtained. The results of the extraction ability of **5a–d** for Na^+ are summarized in Table 2. Although the Na^+ selectivity of ionophoric calix[4]arenes can be changed by conformation, the Na^+ affinity observed for cone conformers is always the highest amongst all four possible conformers.[30] Amide and ester groups in calix[4]arenes possess a high affinity for Na^+, also double calix[4]arenes have two metal complexing sites. The induced 3D cavity (size-fitting) of the parent calixarene platform and the attached side arms upon complexation play an important role in cation binding ability and selectivity. The percentage extraction value for **5b** is higher than for the other compounds; this is attributed to the existence of more donor carbonyl groups in **5b** than in the others.

3. Experimental

3.1. General Procedure

Melting points of all compounds were recorded on Philip Harris C4954718 apparatus (Birmingham, UK) without calibration.

Table 3 Characteristic spectral data of final products.

Sample no.	^{1}H NMR ArH $CDCl_3$ δ/ppm	Splitting pattern of ArH protons	^{1}H NMR $ArCH_2Ar$ $CDCl_3$ δ/ppm	Splitting pattern of $ArCH_2Ar$ protons	J/Hz	^{13}C NMR C=O $CDCl_3$ δ/ppm	^{13}C NMR $ArCH_2Ar$ δ/ppm	FABMS [a] data/m e^{-1}
5a	6.78–88	multiplet	3.15–3.19	doublet	12.6	167.81	30.80	976
	7.73–75	multiplet	3.25–3.29	doublet	12.9	170.19	31.20	
	7.88–91	multiplet	3.96–4.01	doublet	12.9		31.36	
			4.27–4.31	doublet	12.9			
			4.46–4.50	doublet	12.3			
			4.49–4.53	doublet	12.3			
5b	6.74	singlet	3.16–3.20	doublet	12.3	169.95	30.72	1875
	6.96	singlet	3.27–3.32	doublet	12.9	170.00	31.20	
	8.36	singlet	3.96–4.00	doublet	12.9		31.31	
			4.30–4.34	doublet	12.9			
			4.47–4.51	doublet	12.3			
			4.51–4.55	doublet	12.3			
5c	6.86	singlet	3.16–3.21	doublet	12.6	166.38	30.96	1681
	6.94	singlet	3.27–3.31	doublet	12.9		31.01	
	7.04	singlet	4.22–4.26	doublet	12.6			
	8.93	singlet	4.51–4.55	doublet	12.3			
5d	6.49–50	doublet	3.17–3.21	doublet	12.3	174.48	30.71	1661
	6.59–60	doublet	3.18–3.23	doublet	13.2			
	7.16–18	doublet	4.07–4.11	doublet	12.9			
			4.53–4.57	doublet	12.3			

[a] 976 = $(M+1)^+$; rest of numbers are equal to $(M+2)^+$.

Optically active samples were analyzed by EHARTNACK apparatus (Paris, France) at 20 °C with dichloromethane solvent. IR spectra were determined on a Thermo Nicolet 610 Nexus FT-IR spectrometer (Waltham, MA, USA) in KBr disks. Ultraviolet spectra were recorded on a Shimadzu UV-2401/PC spectrometer (Columbia, MD, USA). ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR measurements were recorded on a Bruker AVANCE 300 spectrometer (Ettlingen, Germany) in $CDCl_3$ or CD_3OD using TMS as the internal reference. Elemental analyses were performed using a Heraeus CHN-O-Rapido analyzer (Austin, TX, USA). Positive ion FAB mass spectra were recorded using a JEOL AX505HA spectrometer (Tokyo, Japan) and *m*-nitro benzyl alcohol as matrix. Thin layer chromatography (TLC) analyses were carried out on silica gel plates. All chemicals were purchased from Merck (Tehran, Iran) and used as received by standard procedures, such as difunctional reagent **4c** (terephthaloyl chloride) and **4d** (adipoyl chloride). All reactions were carried out under a nitrogen or argon atmosphere. All of the instruments, chemicals and solvents for esterification were dried according to standard methods. Freshly distilled solvents were used throughout, and anhydrous solvents were dried according to Perrin and Armarego.[28] THF was freshly distilled over sodium/benzophenone ketyl.

3.1.1. *p-tert*-butyl calix[4]arene (**1**) was prepared according to Gutsche's method[29] as white crystals.

3.1.2. The cone conformer of 25,26,27-tripropoxy-28-hydroxy-*p-tert*-butyl calix[4]arene (**2**) was prepared by the previously reported method[30,31] as white crystals.

3.1.3. 2-(1,3-dioxoisoindolin-2-yl) propanoic acid (**3a)** was prepared by the previously reported method[32] as a white solid.

3.1.4. 2-(1,3-dioxoisoindolin-2-yl) propanoyl chloride (phthaloyl-L-alanine chloride) (**4a**)

Compound **3a** (1 g) was refluxed in $SOCl_2$ (20 mL) for 12 h. The solvent was evaporated. Then 2 drops of formic acid were added to the residue and this was recrystallized from CH_2Cl_2/n-hexane to give colourless crystals. This compound is very sensitive to moisture; therefore, the melting point is not reported.

3.1.5. 2,2′-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl) dipropanoic acid (N,N′-pyromelliticdiimido-di-L-alanine chloride) (**3b**)

1,2,4,5-benzene-tetra carboxylic-1,2:4,5-dianhydride (2.18 g, 10 mmol) and L-alanine (1.78 g, 20 mmol) were refluxed in acetic acid (50 mL) for 24 h. The solvent was evaporated. The residue was recrystallized from H_2O/MeOH to give a white solid.

3.1.6. 2,2′-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl) dipropanoyl chloride (**4b**)

Compound **3b** (1 g) was refluxed in a mixture of $SOCl_2$ (15 mL) and ethyl acetate (5 mL) for 12 h. The solvent was evaporated. Then 2 drops of formic acid were added to the residue and this was recrystallized from CH_2Cl_2/n-hexane to give colourless crystals. This compound is very reactive and sensitive to moisture; therefore, the melting point is not reported.

3.1.7. 25-[2-(1,3-dioxoisoindolin-2-yl)propanoate]-5,11,17,23-tetra-*tert*-butyl-26,27,28-tripropoxy calix[4]arene (**5a**)

To a solution of 775 mg (1 mmol) of compound **2** and 18 mg (3 mmol) NaH (60 % dispersion in oil) in THF (20 mL), 355 mg (1.5 mmol) of compound **4a** in THF (5 mL) was added at once while stirring on an ice bath. The reaction mixture was stirred for 5 h at room temperature and the solvent was evaporated. The residue was triturated with MeOH and recrystallized from CH_2Cl_2/MeOH to give colourless crystals.

3.1.8. Bis-[25-(5,11,17,23-tetra-*tert*-butyl-26,27,28-tripropoxy calix[4]arene)]-2,2′-(1, 3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6(1H,3H,5H,7H)-diyl) dipropanoate (**5b**)

To a solution of 1.55 g (2 mmol) of compound **2** and 35 mg (6 mmol) NaH (60 % dispersion in oil) in THF (20 mL), 395 mg (1 mmol) of compound **4b** in THF (5 mL) was added at once while stirring on an ice bath. The reaction mixture was stirred for 5 h at room temperature and the solvent was evaporated. The residue was triturated with MeOH and recrystallized from CH_2Cl_2/MeOH to give a white powder.

3.1.9. Bis-[25-(5,11,17,23-tetra-*tert*-butyl-26,27,28-tripropoxy calix[4]arene)] terephthalate (**5c**)

To a solution of 1.55 g (2 mmol) of compound **2** and 35 mg (6 mmol) NaH (60 % dispersion in oil) in THF (20 mL), 162 mg (0.8 mmol) of compound **4c** in THF (5 mL) was added at once while stirring on an ice bath. The reaction mixture was stirred for 4 h at room temperature and the solvent was evaporated. The residue was triturated with MeOH and recrystallized from CH_2Cl_2/MeOH to give a white powder.

3.1.10. Bis-[25-(5,11,17,23-tetra-*tert*-butyl-26,27,28-tripropoxy calix[4]arene)] adipoyl dioate (**5d**)

To a solution of 1.55 g (2 mmol) of compound **2** and 35 mg (6 mmol) NaH (60 % dispersion in oil) in THF (25 mL), 157 mg (0.8 mmol) of compound **4d** (liquid) was added at once while stirring on an ice bath. The reaction mixture was stirred for 4 h at room temperature and the solvent was evaporated. The residue was triturated with MeOH and recrystallized from CH_2Cl_2/MeOH to give a white powder.

3.2. Analytical Procedure (D,L-alanine Extraction)

To prepare the ammonium picrates, an aqueous solution of alanine hydrochloride salt was treated with a saturated Na_2CO_3 solution and extracted three times with CH_2Cl_2. The organic phase was then dried over $MgSO_4$. The solvent was evaporated to dryness to give the pure alanine. Then alanine and picric acid in the molar ratio of 1:1 were dissolved in deionized water. The stock solution was diluted to 2.0×10^{-5} mol L^{-1} and then used in liquid–liquid extraction experiments. Picrate extraction experiments were performed following Pedersen's procedure:[27] 10 mL of 2.0×10^{-5} mol L^{-1} aqueous picrate and 10 mL of 1.0×10^{-3} mol L^{-1} solution of **5a–d** in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 25 °C for 1 h, and finally left to stand for an additional 30 min. Then the concentration of picrate ion remaining in the aqueous phase was determined spectrophotometrically at 357 nm. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

3.3. Analytical Procedure (Na^+ Extraction)

The organic phase (5 mL of CH_2Cl_2) containing **5a–d** (2.50 mmol L^{-1}) and aqueous phase (5 mL) containing Na^+Pic^- (0.25 mmol L^{-1}), NaOH (0.10 mol L^{-1}) and NaCl (0.50 mol L^{-1}) were mixed and the mixture was shaken for 12 h at 25 °C. Extraction percentage values were determined spectrophotometrically at 357 nm. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

3.4. Spectral Data

3.4.1. (**4a**)

Yield: 61 % (0.66 g). ^{1}H NMR ($CDCl_3$): δ 1.79–1.81 (d, 3H, J = 7.5 Hz, Me), 5.14–5.22 (q, 1H, J = 7.5 Hz), 7.79–7.82 (m, 2H, ArH) and 7.92–7.95 ppm (m, 2H, ArH).

3.4.2. (**3b**)

Yield: 86 % (3.1 g). M.p. 280–282 °C. IR (KBr): ν = 3097, 3035, 1781, 1716, 1465, 1382 and 1258 cm^{-1}. ^{1}H NMR (CD_3OD): δ 1.70–1.73 (d, 6H, J = 7.5 Hz, Me), 5.01–5.08 (q, 2H, J = 7.5 Hz) and 8.31 ppm (s, 2H, ArH). ^{13}C NMR (CD_3OD): δ 13.84, 22.83, 117.64, 137.19, 165.61 and 171.29 ppm.

3.4.3. (**4b**)

Yield: 92 % (1 g). ^{1}H NMR ($CDCl_3$): δ 1.85–1.88 (d, 6H, J = 7.5 Hz, Me), 5.21–5.28 (q, 2H, J = 7.5 Hz) and 8.43 ppm (d, 2H, ArH).

3.4.4. (**5a**)

Yield: 28% (0.27 g). M.p. 239–240 °C. IR (KBr): ν = 2962, 2874, 1756, 1720, 1480, 1388 and 1196 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.92–1.01 (m, 9H, CH_2-CH_3*), 1.05–1.07(d, 18H, J = 5.7 Hz, *t*-Bu), 1.1–1.15 (d, 18H, J = 14.4 Hz, *t*-Bu), 1.89–2.03 (m, 6H, CH_2*-CH_3), 2.31–2.33 (d, 3H, J = 7.5 Hz, CH-CH_3*), 3.15–3.19 (d, 3H, Ar-CH_2-Ar), 3.25–3.29 (d, 1H, Ar-CH_2-Ar), 3.80–3.95 (m, 6H, OCH_2), 3.96–4.01 (d, 1H, Ar-CH_2-Ar), 4.27–4.31 (d, 1H, Ar-CH_2-Ar), 4.46–4.53 (dd, 2H, Ar-CH_2-Ar), 5.59–5.67 (q, 1H, J = 7.5 Hz, CH*-CH_3), 6.78–6.88 (m, 8H, ArH), 7.73–7.75 (m, 2H, ArH) and 7.88–7.91 ppm (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 10.03, 10.15, 10.21, 15.82, 23.09, 23.12, 30.28, 30.8, 31.2, 31.36, 31.39, 31.42, 31.51, 31.63, 33.84, 33.98, 49.22, 77.1, 77.27, 123.36, 124.78, 124.91, 125.03, 125.06, 125.2, 125.35, 125.42, 132.16, 132.97, 133.03, 133.25 133.55, 133.7, 133.8, 133.91, 134, 143.67, 144.37, 144.49, 144.54, 147.13, 152.82, 152.87, 153.77, 167.81 and 170.19 ppm. $C_{64}H_{81}NO_7$ (975.60): calcd. C 78.73, H 8.36, N 1.43 %; found C 78.81, H 8.29, N 1.44 %.

3.4.5. (**5b**)

Yield: 23% (0.43 g). Compound **5b** decomposes above 311 °C thus the melting point was not determined. IR (KBr): ν = 2962, 2875, 1759, 1719, 1481, 1386 and 1197 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.90–0.98 (m, 18H, CH_2-CH_3*), 1.00–1.03 (d, 36H, J = 8.1 Hz, *t*-Bu), 1.18–1.22 (d, 36H, J = 12 Hz, *t*-Bu), 1.85–2.02 (m, 12H, CH_2*-CH_3), 2.43–2.45 (d, 6H, J = 7.8 Hz, CH-CH_3*), 3.16–3.2 (d, 6H, Ar-CH_2-Ar), 3.27–3.32 (d, 2H, Ar-CH_2-Ar), 3.72–3.95 (m, 12H, OCH_2), 3.96–4.0 (d, 2H, Ar-CH_2-Ar), 4.30–4.34 (d, 2H, Ar-CH_2-Ar), 4.47–4.55 (dd, 4H, Ar-CH_2-Ar), 5.7–5.8 (q, 2H, J = 7.8 Hz, CH*-CH_3), 6.74 (s, 8H, ArH), 6.96 (s, 8H, ArH) and 8.36 ppm (s, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 10.06, 10.12, 10.24, 15.71, 23, 23.09, 23.12, 30.54, 30.72, 31.2, 31.31, 31.35, 31.42, 31.6, 33.8, 33.93, 34.08, 50.06, 77.21, 77.54, 118.46, 124.89, 125.06, 125.18, 125.32, 125.43, 132.4, 132.7, 133.39, 133.5, 134.04, 134.1, 134.51, 137.26, 143.73, 144.48, 144.52, 144.57, 147.53, 152.46, 155.76, 169.95 and 170 ppm. $C_{122}H_{156}N_2O_{14}$ (1873.16): calcd. C 78.17, H 8.39, N 1.49 %; found C 78.47, H 8.44, N 1.47 %.

3.4.6. (**5c**)

Yield: 53% (0.89 g). Compound **5c** decomposes above 309 °C so the melting point was not recorded. IR (KBr): ν = 2961, 2875, 1728, 1480, 1259 and 1198 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.74–0.79 (t, 12H, J_1 = 7.5 Hz, J_2 = 7.2 Hz, CH_2-CH_3*), 1.0–1.03 (m, 6H, CH_2-CH_3*), 1.06 (s, 36H, *t*-Bu), 1.19–1.2 (d, 36H, J = 3.3 Hz, *t*-Bu), 1.6–1.72 (m, 8H, CH_2*-CH_3), 1.97–2.05 (m, 4H, CH_2*-CH_3), 3.16–3.21 (d, 4H, Ar-CH_2-Ar), 3.27–3.31 (d, 4H, Ar-CH_2-Ar), 3.70–3.85 (m, 8H, OCH_2), 3.96–4.04 (m, 4H, OCH_2), 4.22–4.26 (d, 4H, Ar-CH_2-Ar), 4.51–4.55 (d, 4H, Ar-CH_2-Ar), 6.86 (s, 8H, ArH), 6.94 (s, 4H, ArH), 7.04 (s, 4H, ArH) and 8.93 ppm (s, 4H, compound **4c**). ^{13}C NMR ($CDCl_3$): δ 10.15, 22.95, 23.06, 30.97, 31.01, 31.37, 31.47, 31.57, 33.85, 33.92, 34.1, 77.15, 77.27, 124.96, 125.07, 125.52, 131, 133.16, 133.86, 134.18, 134.25, 143.79, 144.53, 144.61, 147.26, 152.44, 153.63 and 166.38 ppm. $C_{114}H_{150}O_{10}$ (1679.12): calcd. C 81.48, H 9.00 %; found C 81.59, H 8.93 %.

3.4.7. (**5d**)

Yield: 56% (0.93 g). Compound **5d** decomposes above 314 °C so the melting point was not recorded. IR (KBr): ν = 2962, 2874, 1751, 1481, 1198 and 1129 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.85 (s, 36H, *t*-Bu), 0.95-1 (t, 6H, J = 7.2 Hz, CH_2-CH_3*), 1.05–1.1 (t, 12H, J = 7.5 Hz, CH_2-CH_3*), 1.35–1.37 (d, 36H, J = 6.3 Hz, *t*-Bu), 1.88–2.06 (m, 16H, CH_2*-CH_3 and compound **4d**), 3.17–3.23 (dd, 8H, Ar-CH_2-Ar), 3.6–3.7 (m, 8H, OCH_2), 3.73–3.78 (m, 4H, OCH_2), 4.07–4.11 (d, 4H, Ar-CH_2-Ar), 4.13–4.16 (m, 4H, CH_2-C=O), 4.53–4.57 (d, 4H, Ar-CH_2-Ar), 6.49–6.50 (d, 4H, ArH), 6.59–6.60 (d, 4H, ArH) and 7.16–7.18 ppm (d, 8H, ArH). ^{13}C NMR ($CDCl_3$): δ 9.8, 10.77, 22.96, 23.58, 24.56, 25.35, 30.72, 30.95, 31.12, 31.15, 31.63, 31.78, 33.63, 34.06, 34.23, 50.89, 77.25, 77.84, 124.78, 124.82, 125.08, 125.43, 131.48, 132.24, 135, 135.43, 144.36, 144.68, 147.38, 151.95, 154.62 and 174.48 ppm. $C_{112}H_{154}O_{10}$ (1659.15): calcd. C 81.02, H 9.35 %; found C 80.93, H 9.24 %.

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