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The synthesis of calix[4]crown based dendrimer

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Abstract—A second generation of dendrimer with calixcrown as repeat unit was first synthesized. Its structure and conformation was determined by ^{1}H NMR and MALDI-TOF mass spectra.

1. Introduction

Dendrimers are macromolecules that radiate out from a central core and have at least one branch at each repeat unit. A typical of dendrimer contains three different regions: core, branches, and periphery, and all of them can be modified to exhibit certain function. Due to their unique physical property and structure, such as, highly branched structure, monodispersed molecular weight, globular and symmetrical conformation, and high density of peripheral functionalities, the researches based on them has expanded exponentially in recent years.[1]

There are two basic approaches for the stepwise synthesis of dendrimers: The divergent approach[2] and convergent approach.[3] In the divergent approach, the synthetic sequence is from the core to periphery; while the convergent approach is from the periphery to core.

Calixarene are well-defined macrocyclic molecules, which are readily available in large quantities and easily modified by chemical reaction to bind various kinds of anions, cations, and neutral molecules.[4] It is an original idea to integrate calixarenes and dendrimers as well as their unique properties to form new structural host, and there have several examples about dendrimers with calixarene as core.[5] However, it may be due to the serious steric problem caused by the large sized calixarenes, there are only a few examples on dendrimers with calixarenes as branched units reported,[6] and in most of these works, only the first-generation dendrimers was obtained, except one example of second-generation dendrimer with seven calixarene moieties.[6e] Therefore, the research on this field is still largely unexplored.

If the 1,3-calix[4]crown, an excellent ionphore could be introduced to the dendrimers as repeat unit, a 'multi-metal recognition central' dendrimer will be obtained. It may be helpful to mimic the ion channel, a very important biological structure. Here, we report the synthesis and conformation of a second generation of dendrimer with 1,3-calix-[4]-benzocrown-6 as repeat unit.

2. Results and discussion

2.1. Synthesis of monomer

In order to obtain a dendrimer with calixcrown as repeat unit, we needed to synthesize a calixcrown monomer with three functional groups in two different types. For a 1,3-calix[4]crown, the positions where functional group could be introduced included the four upper rim carbon atoms and two low rim oxygen atoms. If the monomer was a calixazacrown or calixbenzocrown, the nitrogen atom or the phenyl unit could be another position. However, the upper rim was not a good choice for introducing functional groups, because of much harsh synthetic conditions and low yield. At the same time, a rather large group at the upper rim facing the ether crown ring would hinder the ether crown to recognize the guest.[7] Therefore, a calixbenzocrown **4** (Scheme 1), which had two ester groups at lower rim and one aldehyde group at the phenyl unit, was chosen as the monomer.

There were several advantages for choosing **4** as the monomer: (1) it was easy to synthesize; (2) the ester groups and aldehyde group located at each end of the molecule, which could reduce the steric repulsion to a very low

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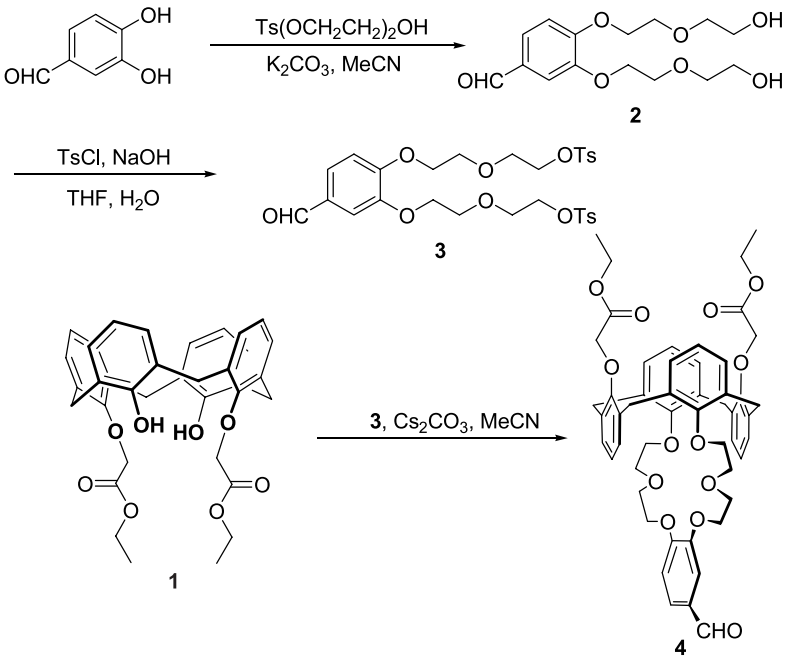


Scheme 1.

degree; (3) because the ester group and aldehyde group did not react each other under common conditions, we did not need to use protection and deprotection strategy during the synthesis of dendrimer. On the other hand, they were easy to be converted to carboxyl group and benzyl alcohol group, and then linked together under mild condition with high yield; (4) the three functional groups had little effect on the recognition ability of the ether crown ring.

Monomer **4** could be obtained using the method developed by Reinhoudt et al.,[8] so we needed to synthesize the corresponding diethylene glycol ditosylate **3**, first. This compound could be prepared from 3,4-dihydroxybenzaldehyde through two steps in a fairly good yield (Scheme 1). In the presence of Cs_2CO_3, **3** reacted with 25,27-diethoxycarbonylmethoxycalix[4]arene (**1**) in MeCN under argon affording the monomer **4** in 55% yield. The signal at 37.6 ppm in its ^{13}C NMR spectrum indicated it fixed in 1,3-alternative conformation (Schemes 2–4).[9]

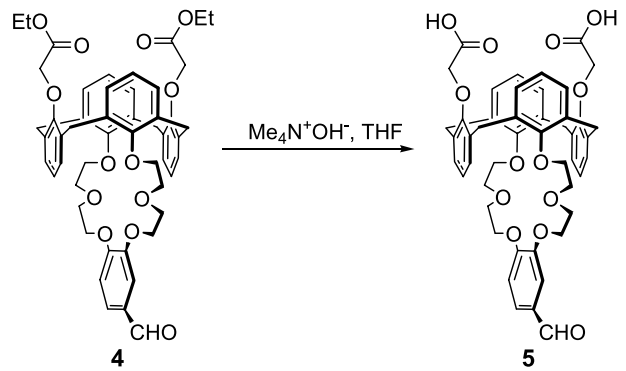
2.2. The 1st generation of dendrimer

Because the ester and aldehyde groups could not react each other, we needed to activate them respectively before preparing 1st generation of dendrimer.

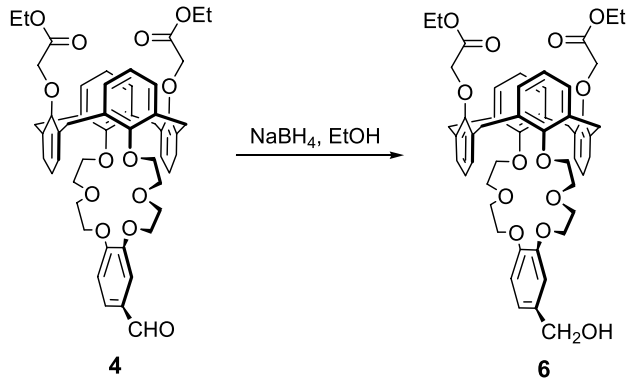
Hydrolysis of **4** using 10% tetramethylammonium hydroxide aqueous solution under room temperature afforded the diacid **5**, in nearly quantitative yield.

Reduction of **4** with $NaBH_4$ under ice bath, the aldehyde group could be converted to benzyl alcohol group in 60% yield. The relatively low yield was contributed to that the ester group at the low rim could be reduced to ethylene glycol under similar condition. To prevent this side reaction, the quantity of $NaBH_4$ was not allowed to exceed 2 equiv of the compound **4**, the reaction temperature must be low, and reaction time must be short. However, under this condition, the reaction could not acquire completion. The exceeding reactant could be retrieved by chromatography.

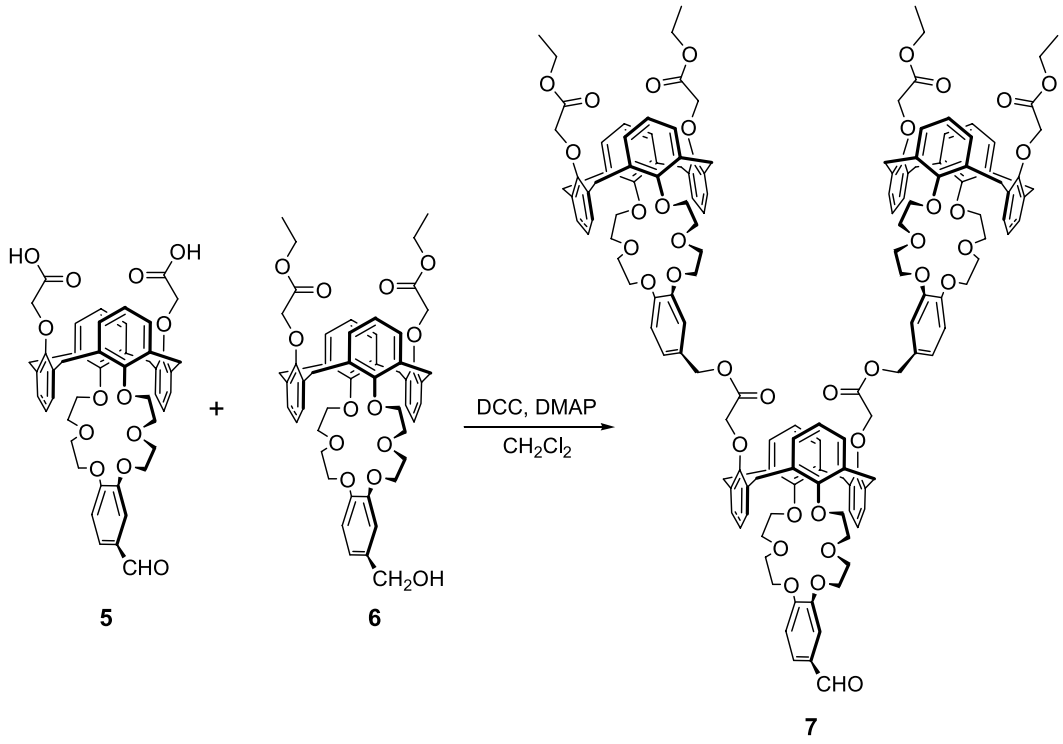
With the two blocks in hand, the 1st generation of dendrimer could be obtained by the condensation of 1 equiv of **5** and 2 equiv of **6** under the treatment of DCC/DMAP in high yields (91%).



Scheme 2.



Scheme 3.



Scheme 4.

The two carbon signals at 37.7 and 37.5 in its ^{13}C NMR spectra indicated that all of the calix[4]crown were fixed in 1,3-alteralternative conformation.[9]

2.3. The 2nd generation of dendrimer

There are two ways to prepare the 2nd generation of dendrimer: the divergent approach and the convergent approach.

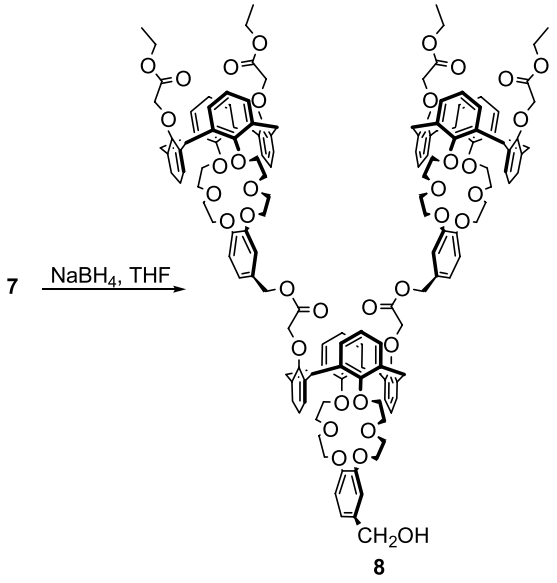
If the convergent approach were chosen, we would face the same problem of over reduction we had encountered in the synthesis of **6**, and the much larger 1st generation dendrimer would cause more serious steric problem during the synthesis of 2nd generation of dendrimer. But if the divergent way were chosen, we would face much more difficult problems: (1) because there were six ester groups, it would be very difficult to selectively saponify the four peripheric ones; (2) even the saponification could acquire success, the total yield would be low since the next condensation step needed the relative low-yield compound **6** as reactant; (3) the divergent way required four reaction positions during the process of the condensation, but the convergent way only need two.

Due to the inherent shortcomings of the divergent way, we chose convergent way for the preparation of the 2nd generation of dendrimer.

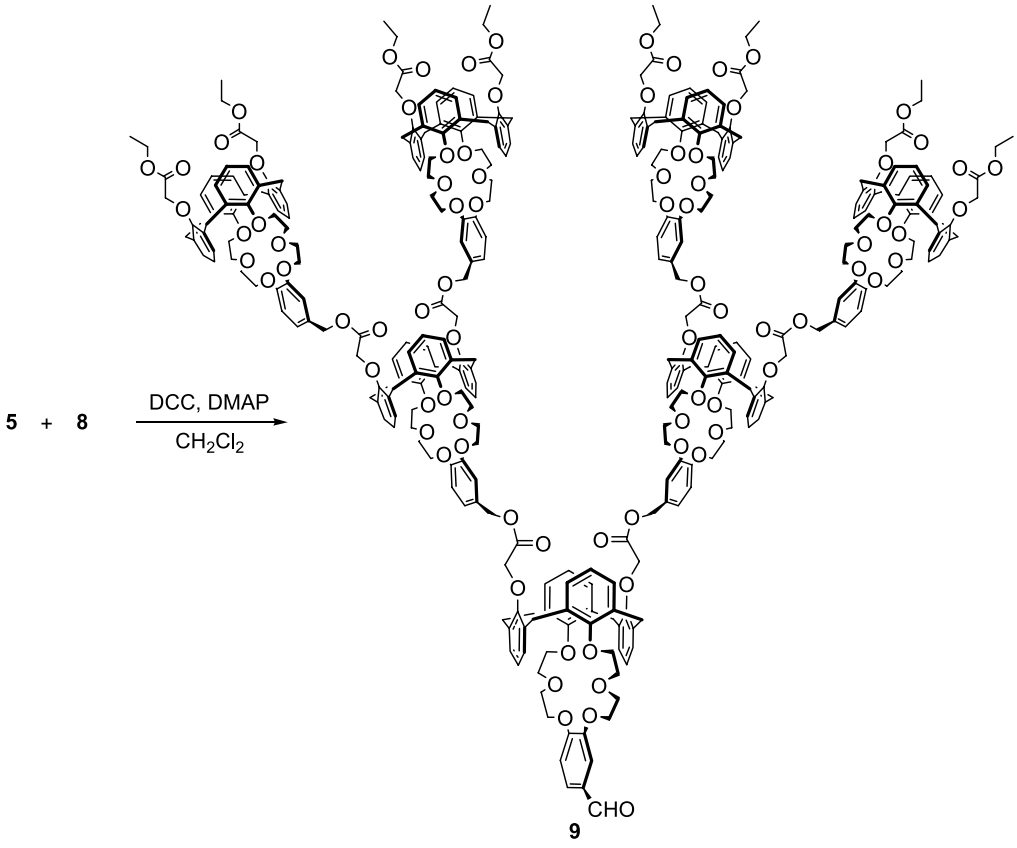
First, we intended to obtain the corresponding benzyl alcohol compound **8** from **7** by the same method in the synthesis of compound **6**, but failed. The reason may be that both **7** and **8** were hardly dissolved in EtOH. So we used THF instead of EtOH as solvent, and the **8** was obtained in a fairly good yield (Scheme 5).

The 2nd generation of dendrimer **9** can be obtained by the condensation of 2 equiv of **8** and 1 equiv of **5** in high yields using the same method for the preparation of 1st generation dendrimer (Scheme 6).

In conclusion, we have synthesized the first 2nd generation of dendrimer based on calixcrown. Its structure and conformation were confirmed by ^{1}H NMR and MALDI-TOF mass spectra. The recognition properties of the dendrimers are under investigation.



Scheme 5.



Scheme 6.

3. Experimental

3.1. General

Melting points were determined on an electrothermal melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were obtained at 300 and 75 MHz ($CDCl_3$, TMS as internal standard) respectively on a Bruker DMX300 NMR. MALDI-TOF MS was recorded on a Bruker BIFLEXIII mass spectrometer with CCA (2-cyano-4′-hydroxycinnamic acid) as the matrix. Elemental analyses were performed by the Analytical Laboratory of the Institute. IR Spectra were recorded on a JASCO 480 spectrometer. Preparative column chromatography was performed with silica gel (200–300 mesh). Petroleum ether for column chromatography refers to that of 60–90 °C boiling range. MeCN was dried over 4 Å molecular sieve. THF was freshly distilled over Na before used. All other chemicals were reagent grade and were used without further purification. Compound **1** was prepared according to literature procedures.[10]

3.1.1. Compound 2. 3,4-Dihydroxy-benzaldehyde (690 mg, 5 mmol) was dissolved in MeCN (50 mL), then diethylene glycol mono-tosylate (2.6 g, 10 mmol) and potassium carbonate (1.38 g, 10 mmol) were added. The mixture was refluxed under argon for 36 h. After cooling to room temperature, the mixture was filtered, and the solvent was removed under reduced pressure. The crude product was purified on a silica column using petroleum ether/acetone = 2/1. The product was obtained as colorless oil: yield 86%; IR (KBr): 3378, 2755, 1682, 1586 cm^{-1}; ^{1}H NMR: δ 9.84 (s, 1H, ArC*H*O), 7.47–7.41 (m, 2H, Ar*H*), 6.98 (d, 1H, J = 8.1 Hz, Ar*H*), 4.26–4.21 (m, 4H, Ar–OCH_2CH_2O–), 3.97–3.92 (m, 4H, Ar–OCH_2CH_2O–), 3.77–3.75 (m, 4H, –OCH_2CH_2OH), 3.70–3.68 (m, 4H, –OCH_2CH_2OH), 3.52 (s, 2H, CH_2O*H*); ^{13}C NMR: δ 190.8 (Ar*C*HO), 153.8, 148.8, 130.2, 126.9, 111.7, 110.6 (Ar*C*), 72.8, 72.7, 69.0, 68.8, 68.5, 68.4, 61.6 (–O*C*H_2*C*H_2O–); MS (EI): 314 (27), 164 (32), 89 (23), 45 (100). Anal. Calcd for $C_{15}H_{22}O_7 \cdot 0.25H_2O$ C, 56.51; H, 7.11. Found, C, 56.66; H, 7.06.

3.1.2. Compound 3. Compound **2** (950 mg, 3 mmol) was dissolved in THF (15 mL), and a solution of NaOH (360 mg, 9 mmol) in H_2O (10 mL) was added. The mixture was cooled to 0 °C, then a solution of *p*-toluenesulfonyl chloride (1.2 g, 6.3 mmol) in THF (15 mL) was added dropwise during a period of 2 h. The mixture was stirred under ice bath for another 2 h, and then 1 mol L^{-1} of HCl was added until the pH value of the solution reach to 3. THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (30 mL × 2). The combined organic phase was dried with Na_2SO_4. Then purified on silica column, using ether/acetone = 3/1 as eluant to afford a colorless oil: yield 75%; IR (KBr): 3559, 1686, 1593, 1509, 1437, 1354, 1270 cm^{-1}; ^{1}H NMR: δ 9.84 (s, 1H, ArC*H*O), 7.78 (d, 4H, J = 8.1 Hz, Ar*H*), 7.46 (d, 1H, J = 8.2 Hz, Ar*H*), 7.38 (s, 1H, Ar*H*), 7.30 (d, 4H, J = 8.1 Hz, Ar*H*), 6.97 (d, 1H, J = 8.2 Hz, Ar*H*), 4.19–4.10 (m, 8H, Ar–OCH_2CH_2O–), 3.86–3.75 (m, 8H, –OCH_2CH_2O–), 2.41 (s, 6H, ArCH_3); ^{13}C NMR: δ 190.8 (Ar*C*HO), 154.1, 149.0, 144.8, 132.9, 130.3, 129.8, 127.9, 126.8, 112.4, 111.5 (Ar*C*), 69.6, 69.5,

69.3, 69.0, 68.9, 68.6 (–O*C*H$_2$*C*H$_2$O–), 21.6 (Ar*C*H$_3$); MS (MALDI-TOF): 622.9 (M+H$^+$), 644.9 (M+Na$^+$), 660.8 (M+K$^+$). Anal. Calcd for: $C_{29}H_{34}O_{11}S_2$ C, 55.94; H, 5.50. Found, C, 55.83; H 5.72.

3.1.3. Compound 4. 25,27-Diethoxycarbonylmethoxycalix[4]arene (**1**) (596 mg, 1 mmol) was dissolved in MeCN (250 mL), and **3** (653 mg, 1.05 mmol), cesium carbonate (652 mg, 2 mmol) was added under argon. The mixture was refluxed for 30 h, and then cooled to room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 (30 mL) and 1 mol L^{-1} HCl (30 mL). The organic layer was separated, and washed with water (30 mL×2), dried with Na_2SO_4. Then the crude product was purified on silica column, using ether/acetone=5/1 as eluant to afford a white solid: yield 55%; mp 65–67 °C; IR (KBr): 2730, 1752 cm^{-1}; ^{1}H NMR: δ 9.88 (s, 1H, ArC*H*O), 7.53–7.51 (m, 2H, Ar*H*), 7.15–7.09 (m, 9H, Ar*H*), 6.80 (t, 2H, J=7.5 Hz, Ar*H*), 6.68 (t, 2H, J=7.5 Hz, Ar*H*), 4.26–4.21 (m, 4H, Ar–O–C*H*$_2$CH$_2$–), 4.09 (q, 4H, J=7.2 Hz, CH$_3$C*H*$_2$O–), 4.05 (d, 4H, J=14.1 Hz, ArC*H*$_2$Ar), 3.87–3.80 (m, 6H, Ar–OCH$_2$-C*H*$_2$O–, ArC*H*$_2$Ar), 3.74–3.67 (m, 6H, –OCH$_2$C*H*$_2$O–), 3.60–3.45 (m, 4H, –OCH$_2$C*H*$_2$O–), 3.40 (s, 4H, –OC*H*$_2$–CO–), 1.22 (t, 6H, J=7.2 Hz, C*H*$_3$CH$_2$–); ^{13}C NMR: δ 190.8 (Ar*C*HO), 170.0 (–O*C*O–), 156.8, 155.3, 154.4, 149.2, 134.5, 133.9, 133.8, 130.6, 130.5, 130.4, 127.0, 123.1, 122.5, 112.9, 112.4 (Ar*C*), 70.4, 70.3, 70.2, 70.0, 69.9, 69.4, 69.3, 68.4, 60.3 (–O*C*H$_2$*C*H$_2$O–, –O*C*H$_2$CO–, –*C*H$_2$CH$_3$), 37.6 (Ar*C*H$_2$Ar), 14.1 (–CH$_2$*C*H$_3$); MS (MALDI-TOF): 897.5 (M+Na$^+$), 913.5 (M+K$^+$). Anal. Calcd for: $C_{51}H_{54}O_{13}$ C, 70.01; H, 6.22. Found, C, 69.61; H, 6.19.

3.1.4. Compound 5. Compound **4** (175 mg, 0.2 mmol) was dissolved in THF (5 mL), and then 1 mL of 10% tetramethylammonium hydroxide was added. The mixture was stirred under argon for 4 h, then acidified with 1 mol L^{-1} HCl until white precipitation was occurred, filtered to afford white solid, yield 95%; mp 211–213 °C; IR (KBr): 3420, 1778, 1758, 1732 cm^{-1}; ^{1}H NMR: δ 9.89 (s, 1H, ArC*H*O), 7.56–7.50 (m, 2H, Ar*H*), 7.13–7.04 (m, 9H, Ar*H*), 6.90 (t, 2H, J=7.5 Hz, Ar*H*), 6.80 (t, 2H, J=7.5 Hz, Ar*H*), 4.18 (t, 2H, J=4.8 Hz, Ar–O–C*H*$_2$CH$_2$–), 4.14 (t, 2H, J=4.8 Hz, Ar–O–C*H*$_2$CH$_2$–), 4.11 (s, 4H, –OC*H*$_2$–CO–), 3.94 and 3.80 (AB, 8H, J=16.2 Hz, ArC*H*$_2$Ar), 3.70 (t, 2H, J=4.8 Hz, Ar–O–C*H*$_2$CH$_2$–), 3.65–3.57 (m, 6H, Ar–O–CH$_2$C*H*$_2$–), 3.48 (t, 4H, J=5.7 Hz, Ar–O–CH$_2$C*H*$_2$–); ^{13}C NMR: δ 190.9 (Ar*C*HO), 168.4 (–O*C*O–), 156.1, 154.5, 153.4, 149.3, 133.7, 133.6, 130.7, 130.2, 130.1, 129.6, 127.1, 124.4, 113.2, 112.8 (Ar*C*), 70.4, 70.2, 70.1, 70.0, 69.9, 69.8, 67.1 (–O*C*H$_2$*C*H$_2$O–, –O*C*H$_2$CO–), 37.5 (Ar*C*H$_2$Ar); MS (MALDI-TOF): 840.8 (M+Na$^+$), 856.7 (M+K$^+$). Anal. Calcd for: $C_{47}H_{46}O_{13}\cdot H_2O$ C, 67.45; H, 5.78. Found, C, 67.61; H, 5.56.

3.1.5. Compound 6. Compound **4** (175 mg, 0.2 mmol) was suspended in EtOH (5 mL) under ice bath, and then $NaBH_4$ (17 mg, 0.45 mmol) was added. After stirred for 10 min, 5 mL of water was added. The solution was extracted with CH_2Cl_2 (10 mL×2), and the combined organic layer was washed successively with 1 mol L^{-1} HCl (10 mL×2), and water (10 mL×2), dried with Na_2SO_4. The pure product was obtained as white solid by chromatography (silica column, petroleum ether/acetone=5/1): yield: 63%; mp 57–59 °C; IR (KBr): 3441, 1753 cm^{-1}; ^{1}H NMR: δ 7.13 (d, 4H, J=7.5 Hz, Ar*H*), 7.09 (d, 4H, J=7.5 Hz, Ar*H*), 7.04 (s, 1H, Ar*H*), 6.97 (s, 2H, Ar*H*), 6.79 (t, 2H, J=7.5 Hz, Ar*H*), 6.70 (t, 2H, J=7.5 Hz, Ar*H*), 4.65 (s, 2H, ArC*H*$_2$OH), 4.17–4.12 (m, 4H, Ar–O–C*H*$_2$CH$_2$–), 4.08 (q, 4H, J=7.2 Hz, CH$_3$C*H*$_2$–), 4.04 (d, 4H, J=15.9 Hz, ArC*H*$_2$Ar), 3.80–3.74 (m, 8H, ArC*H*$_2$Ar, Ar–O–C*H*$_2$CH$_2$–), 3.70 (t, 4H, J=6.0 Hz, Ar–O–CH$_2$C*H*$_2$–), 3.50 (t, 4H, J=6.0 Hz, Ar–O–CH$_2$C*H*$_2$–), 3.35 (s, 4H, –OC*H*$_2$–CO–), 1.21 (t, 3H, J=7.2 Hz, C*H*$_3$CH$_2$–); ^{13}C NMR: δ 170.1 (–O*C*O–), 157.0, 155.3, 149.4, 148.6, 134.9, 134.7, 133.8, 130.6, 130.5, 123.1, 122.7, 120.5, 115.6, 114.3 (Ar*C*), 70.6, 70.5, 70.3, 69.9, 69.7, 68.4, 65.2 (–O*C*H$_2$*C*H$_2$O–, –O*C*H$_2$CO–, Ar*C*H$_2$-OH), 60.3 (–O*C*H$_2$CH$_3$), 37.7 (Ar*C*H$_2$Ar), 14.1 (–OCH$_2$*C*H$_3$); MS (MALDI-TOF): 899.4 (M+Na$^+$), 915.4 (M+K$^+$). Anal. Calcd for: $C_{51}H_{56}O_{13}$ C, 69.85; H, 6.44. Found, C, 69.59; H, 6.50.

3.1.6. Compound 7. Compound **5** (82 mg, 0.1 mmol) and **6** (175 mg, 0.2 mmol) was dissolved in 3 mL of dried CH_2Cl_2, then DCC (42 mg, 0.2 mmol) and DMAP (5 mg, 0.04 mmol) was added under argon. After the mixture was stirred for 12 h, DCU was filtered. The organic layer was washed successively with 1 mol L^{-1} HCl (5 mL×2) and water (10 mL×2), dried with Na_2SO_4. The crude product was purified on a silica column, using petroleum ether/acetone=3/1 as eluant to afford white solid: yield 91%; mp 102–104 °C; IR (KBr): 1755, 1734, 1687 cm^{-1}; ^{1}H NMR: δ 9.88 (s, 1H, ArC*H*O), 7.51 (s, 2H, Ar*H*), 7.12 (d, 8H, J=7.5 Hz, Ar*H*), 7.08–7.06 (m, 17H, Ar*H*), 6.99 (s, 2H, Ar*H*), 6.96 (s, 4H, Ar*H*), 6.79 (t, 4H, J=7.5 Hz, Ar*H*), 6.71–6.61 (m, 8H, Ar*H*), 5.02 (s, 4H, ArC*H*$_2$–O–CO–), 4.23–4.03 (m, 24H, Ar–O–C*H*$_2$CH$_2$–, ArC*H*$_2$Ar, CH$_3$C*H*$_2$–), 3.97 (AB, J=16.6 Hz, 12H, ArC*H*$_2$Ar) 3.84–3.61 (m, 32H, Ar–O–C*H*$_2$CH$_2$–, Ar–O–CH$_2$C*H*$_2$–), 3.59–3.47 (m, 12H, Ar–O–CH$_2$C*H*$_2$–), 3.40 (s, 4H, Ar–O–C*H*$_2$CO–), 3.35 (s, 8H, Ar–O–C*H*$_2$CO–), 1.21 (t, 12H, J=7.2 Hz, C*H*$_3$CH$_2$–); ^{13}C NMR: δ 190.8 (Ar*C*HO), 170.0, 169.8 (–O*C*O–), 156.9, 155.3, 154.4, 149.4, 149.3, 149.1, 134.6, 134.5, 133.8, 130.7, 130.5, 130.4, 129.3, 123.1, 122.6, 122.5, 116.2, 115.2, 112.9, 112.4 (Ar*C*), 70.5, 70.2, 70.1, 69.9, 69.8, 69.7, 69.4, 69.3, 68.5, 68.3 (–O*C*H$_2$*C*H$_2$O–, –O*C*H$_2$CO–), 60.3 (–O*C*H$_2$CH$_3$), 37.7, 37.5 (Ar*C*H$_2$Ar), 14.1 (–OCH$_2$*C*H$_3$); MS: (MALDI-TOF): 2557.1 (M+Na$^+$). Anal. Calcd for: $C_{149}H_{154}O_{37}$ C, 70.55; H, 6.12. Found, C, 70.67; H, 6.64.

3.1.7. Compound 8. Compound **7** (126 mg, 0.05 mmol) was suspended in 5 mL of THF under ice bath, and then $NaBH_4$ (4 mg, 0.10 mmol) was added. After stirred for 10 min, 5 mL of water was added. The solution was extracted with CH_2Cl_2 (10 mL×2), and the combined organic layer was washed successively with 1 mol L^{-1} HCl (10 mL×2), then water (10 mL×2), dried with Na_2SO_4. The pure product was obtained as white solid by chromatography (silica column, petroleum ether/acetone=5/1): yield: 60%; mp 105–107 °C; IR (KBr): 3441, 1753, 1734 cm^{-1}; ^{1}H NMR: δ 7.12 (d, 8H, J=7.5 Hz, Ar*H*), 7.07 (d, 16H, J=7.5 Hz, Ar*H*), 7.04–6.92 (m, 9H, Ar*H*) 6.79 (t, 4H, J=7.5 Hz, Ar*H*), 6.69 (t, 6H, J=7.5 Hz, Ar*H*), 6.30 (t, 2H, J=7.5 Hz, Ar*H*), 5.01 (s, 4H, Ar–O–C*H*$_2$CO–), 4.65 (s, 2H Ar–O–C*H*$_2$CO–), 4.20–4.12 (m, 12H, Ar–C*H*$_2$–Ar, Ar–O–C*H*$_2$–), 4.08 (q, 8H,

$J=7.2$ Hz, CH_3CH_2–), 4.09–4.05 (m, 4H, Ar–CH_2–Ar), 3.98 (d, 8H, $J=15.2$ Hz, Ar–CH_2–Ar), 3.84–3.61 (m, 36H, Ar–CH_2–Ar, Ar–O–CH_2CH_2–, Ar–O–CH_2CH_2–), 3.59–3.43 (m, 12H, Ar–O–CH_2CH_2–), 3.35 (s, 8H, Ar–OCH_2CO–), 3.33 (s, 4H, Ar–OCH_2CO–), 1.21 (t, 12H, $J=7.2$ Hz, CH_3CH_2–); ^{13}C NMR: δ 170.1, 170.0 (–O*C*O–), 157.0, 155.3, 155.2, 149.4, 149.2, 148.6, 134.7, 134.6, 133.9, 133.8, 130.7, 130.6, 130.5, 129.4, 129.3, 123.2, 122.7, 116.2, 115.5, 115.3 (Ar*C*), 70.5, 70.3, 70.0, 69.9, 68.4, 66.0, 65.2 (–O*C*H_2*C*H_2O–, –O*C*H_2CO–, Ar*C*H_2OH), 60.3 (–O*C*H_2*C*H_3), 37.7 (Ar*C*H_2Ar), 14.1 (–OCH$_2$*C*H_3); MS (MALDI-TOF): 2560.1 ($M+Na^+$), 2576.1 ($M+K^+$). Anal. Calcd for: $C_{149}H_{156}O_{37}$ C, 70.49; H, 6.19. Found, C, 70.69; H, 6.56.

3.1.8. Compound 9. Compound **5** (8 mg, 0.01 mmol) and **8** (51 mg, 0.02 mmol) was treated in the same way as described in the synthesis of **7**: yield: 88%; mp 115–117 °C; IR (KBr): 1755, 1734 cm^{-1}; ^{1}H NMR: δ 9.88 (s, 1H, ArC*H*O), 7.52–7.50 (m, 2H, Ar*H*), 7.13–7.06 (m, 56H, ArH), 6.99–6.96 (m, 19H, ArH), 6.78 (t, $J=7.4$ Hz, 10H, ArH), 6.69–6.58 (m, 18H, ArH), 5.00 (s, 12H, Ar–CH_2–O–), 4.30–3.69 (m, 152H, Ar–CH_2–Ar, Ar–O–CH_2–CH_2–), 3.59–3.42 (m, 32H, 3.35 (s, 28H, ArO–CH_2–CO–), 1.21 (t, $J=7.2$ Hz, 24H, CH_3CH_2–); MS: (MALDI-TOF): 5879.1 ($M+Na^+$). Anal. Calcd for: $C_{345}H_{354}O_{85}$ C, 70.71; H, 6.09. Found, C, 70.41; H, 6.51.

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