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# Reversible 2D Pseudopolyrotaxanes Based On Cyclodextrins and Cucurbit[6]uril

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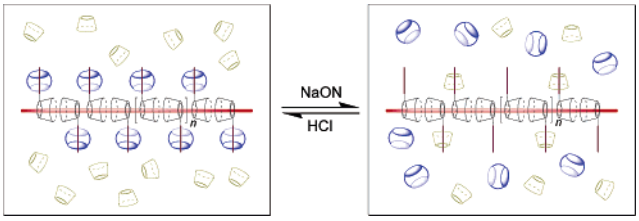


In this paper, a pseudorotaxane (**2**) was synthesized by reaction of cucurbit [6]uril with 6-[(6-aminohexyl)amino]-6-deoxy-$\beta$-cyclodextrin chloride. Subsequently, pseudorotaxanes **2** were further assembled to form a 2D pseudopolyrotaxane (**3**) through an $\alpha,\omega$-PPG2000 diamino polymer threading the cavities of cyclodextrins in **2**, and the resulting pseudopolyrotaxane was comprehensively characterized by FT-IR, NMR, TG-DTA, elemental analysis, and transmission electron microscopy. Significantly, the 2D pseudopolyrotaxane can turn into a main-chain pseudopolyrotaxane in the presence of base, and then the addition of $\alpha$-cyclodextrins may result in a reversible switch between two different 2D pseudopolyrotaxanes.

Pseudorotaxanes not only are the supramolecular precursors of rotaxanes and catenanes but also viewed as the most interesting prototypes for molecular machines because of their dethreading/rethreading motions,[1] so investigations on pseudorotaxanes have gained extensive attention in recent decades.[2] In this respect, pseudopolyrotaxanes, in which many cyclic molecules are threaded onto either a polymeric main chain (entitled "main chain pseudopolyrotaxanes") or the side chains of a polymer (entitled "side chain pseudopolyrotaxanes"),[3−5] are especially fascinating due to their unusual architectures and the different properties from conventional polymers. Therefore, designing and synthesizing pseudopolyrotaxanes with novel topologies is desirable for both polymer science and supramolecular chemistry. Recently, we successfully constructed not only a series of pseudopolyrotaxanes based on $\beta$-cyclodextrins ($\beta$-CDs)[6] and modified $\beta$-CDs,[7] but also bis(pseudopolyrotaxane)s based on bridged bis($\beta$-CD)s.[8] Here, we report a simple way to prepare 2D pseudopolyrotaxane **3** in which cyclic molecules are threaded onto both the polymeric main chain and its side chains (Scheme 1). Furthermore, the 2D pseudopolyrotaxane can turn into a main-chain pseudopolyrotaxane in the presence of base because of the cyclic cucurbit[6]uril (CB[6]) molecules dethreading from the side chain of **3**, and vice versa. Addition of $\alpha$-CDs may result in a reversible switch between two different 2D pseudopolyrotaxanes by acid−base control.

To obtain the 2D pseudopolyrotaxane **3**, pseudorotaxane **2** was first synthesized by reaction of CB[6] with 6-[(6-aminohexyl)amino]-6-deoxy-$\beta$-CD chloride (**1**) in 81% yield. The 1:1 **1**/CB[6] complexation in **2** was confirmed by the results of elemental analysis, MS, and $^1$H NMR spectroscopy. In the ESI-MS spectrum of pseudorotaxane **2**, a signal was observed at $m/z$ ($M^{2+}$) = 1115.8, indicating the formation of the pseudoro-

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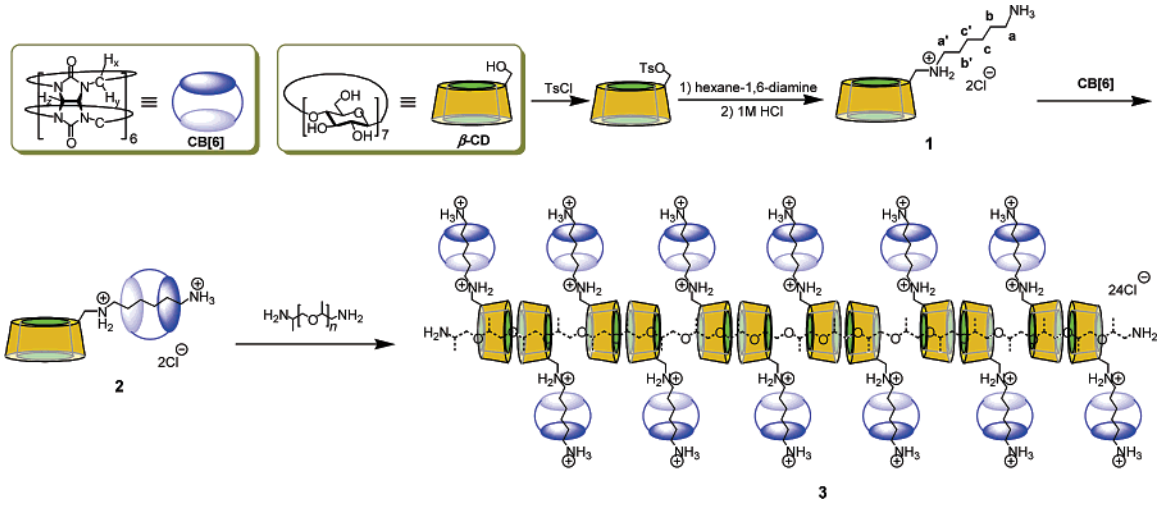
**SCHEME 1. Preparation Processes of 2D Polypseudorotaxane 3**




taxane **2**. In the $^1$H NMR experiments, the resonance signals of $H_{a/a'}$, $H_{b/b'}$, and $H_{c/c'}$ of CD in **2** shift upfield ca. 0.04, 1.02, and 0.91 ppm, respectively, relative to the free **1**, as shown in Figure 1. On the other hand, the chemical shift of $H_x$ protons of the CB[6] molecule in **2** shifts downfield accompanying its signal to split to quadruple peaks from its original double peaks, which should be attributed to the asymmetry guest penetrating into the cavity of CB[6].[9] All of these observations suggest that the methylene groups of CD moiety must be included to the cavity of CB[6].

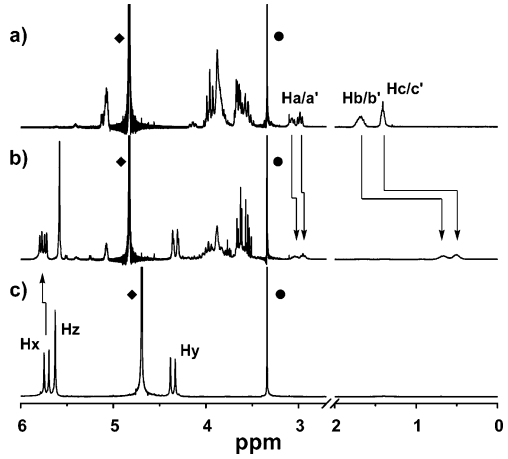



**FIGURE 1.** $^1$H NMR spectra of (a) **1**, (b) **2**, and (c) CB[6] in $D_2O$ containing 0.2M $Na_2SO_4$. Symbols ◆ and ● indicate the solvent and MeOH resonances, respectively.

Pseudopolyrotaxane **3** was prepared by adding amino-terminated PPG2000 to a saturated aqueous solution of **2** in 21% yield. From $^1$H NMR data of **3** in $D_2O$ (Figure 4a), we could calculate the number of $\beta$-CD units by comparing the integral of signals at 0.51 ppm ($H_{c/c'}$ of $\beta$-CD) or 4.34 ppm ($H_y$ of CB[6]) with those at 1.15 ppm ($CH_3$ of PPG). The obtained values were $11.8 \pm 0.7$, which means that PPG2000 could thread about 12 pseudorotaxanes **2** to form pseudopolyrotaxane **3**. The consistency between both values calculated form $H_{c/c'}$ and $H_y$ indicates that no CB[6]s dethread off during this procedure, which is attributed to the strong binding ability between hexane-1,6-diamine and CB[6] ($K = 4.49 \times 10^8$ $M^{-1}$) in aqueous solution.[10] Cross-peaks of protons of $CH_3$ of PPG and H-3/H-5 of CD in 2D ROESY spectrum of **3** also reveals that PPG thread into the CDs cavities.

Pseudopolyrotaxane **3** is more thermally stable than both pseudorotaxane **2** and its precursor **1**. The TGA analysis (Figure 2) shows that **1**−**3** exhibit small initial weight loss corresponding to hydration before 230 °C. And then, **1** loses 94.0% of its original weight at 507 °C, corresponding to the loss of CDs backbone. Remarkably, **2** and **3** exhibit a similar change profile after 298 °C, but the decomposition temperatures of **3** in every step are ca. 60 °C higher than those of **2**, suggesting that the threading of PPG increases the stability of **3**. Similar increases in thermal stability were also observed in main-chain[3c] and side-chain[3d] pseudopolyrotaxanes incorporating CB[6].

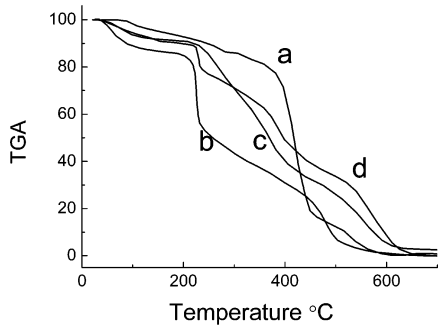



**FIGURE 2.** TGA curves of (a) CB[6], (b) **1**, (c) **2**, and (d) **3**.

TEM was performed to provide further insight into the size and shape of pseudopolyrotaxane **3**. From Figure 3a, we may note that there exist some sticklike nanowires on the substrate. The lengths of these nanowires are in the range of 14−25 nm, which is consistent with those of PPG2000. To obtain their width data, we also tried to further magnify the samples to obtain higher resolution TEM images, but unfortunately, these samples melt. Hence, their widths are just roughly estimated from Figure 3a. They are about 3 nm. As is well-known, the diameter of the $\beta$-CD's periphery is about 1.5 nm, and the height of CB[6]

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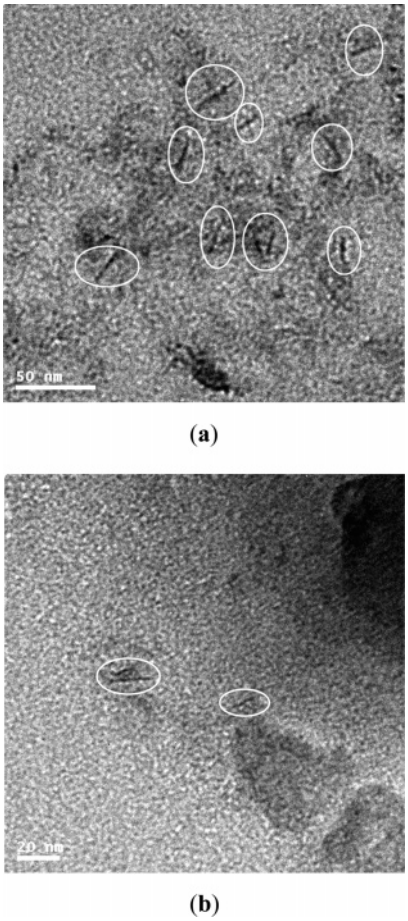


**FIGURE 3.** TEM images of (a) free **3** and (b) **3** in the presence of NaOH. Nanowires were highlighted by the white ellipses.

is 0.9 nm, so the extra width of the nanowires in excess of 1.5 nm should be attributed to the CB[6] molecules threading the side chain of CDs. That is, these nanowires in the TEM image belong on pseudopolyrotaxane **3**.

Interestingly, while the sample of **3** for TEM experiments was prepared in the presence of NaOH, the width of nanowires became thinner, as shown in Figure 3b. The observation should be attributed to CB[6]s dethreading off the side chain of pseudopolyrotaxane **3**.[3d] $^1$H NMR spectra of **3**-$D_2O$ solutions in the presence and absence of NaOD also confirm unambiguously this process.

As can been seen from Figure 4a,b, upon the addition of NaOD, the resonance signals of $H_{b/b'}$ and $H_{c/c'}$ of CD in **3** shift downfield (ca 0.8 ppm) and those of $H_{a/a'}$ shift upfield (ca. 0.3−0.4 ppm). Meanwhile, the signal of $H_x$ in CB[6] turned to double peaks from the original quadruple peaks. These phenomena completely contrast with those of CB[6] threading the cavity of CD in **1**, indicating that the dethreading process of CB[6]s from their axle is due to the deprotonation of 1,6-hexane diamino units. From the $^1$H NMR spectrum of **3** in the presence of NaOD, 100% CB[6] molecules dethread, while CDs were still threaded on PPG2000. That is, the 2D pseudopolyrotaxane **3** decomposed to a "main-chain pseudopolyrtoaxane", as illustrated in Figure 5a,b. Furthermore, when the solution pD value was adjusted to acidity by adding DCl, all CB[6]s rethreaded on the side chain of **1** to re-form the 2D pseudopolyrotaxane (Figure 4c). This process may be repeated at least four times upon addition of base or acid.

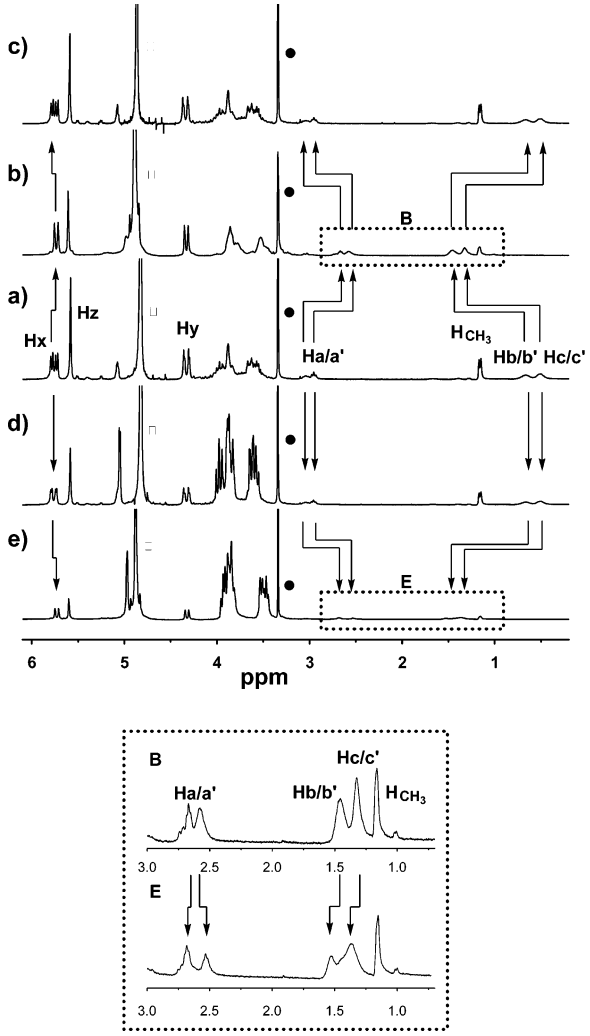


**FIGURE 4.** $^1$H NMR spectra of (a) **3** (0.33 mM); (b) **3** (0.33 mM) + NaOD (39.6 mM); (c) **3** (0.32 mM) + NaOD (39.1 mM) + excess DCl; (d) **3** (0.33 mM) + α-CD (22.6 mM); (e) **3** (0.32 mM) + α-CD (22.6 mM) + NaOD (39.4 mM). Symbols ◆ and ● indicate the solvent and MeOH resonances, respectively.

When α-CDs exist in the above systems, two interconvertible 2D pseudopolyrotaxanes could be obtained by acid−base control. In the case of acidity, α-CDs do not interact with the protonated 1,6-hexanediamino residue of CD (Figure 4d), so the structure of 2D pseudopolyrotaxane **3** is stable. Upon the addition of NaOD, the original protonated 1,6-hexanediamino residues first become neutral side chains resulting in CB[6]s dethreading, and then α-CDs thread on the bare side axle to form a new 2D pseudopolyrotaxane, as shown in Figure 5d. This process was recorded by $^1$H NMR spectroscopy. As can been seen from Figure 4e, upon addition of base, the resonance signals of $H_{a/a'}$ in **3** shift upfield, and those of $H_{b/b'}$ and $H_{c/c'}$ shift downfield, suggesting that CB[6]s dethread from the side chains of *β*-CDs. It is noted that these resonance signals corresponding to the side chains of *β*-CDs are different from those in the absence of α-CDs (B and E in Figure 4), which might be attributed to the inclusion of 1,6-hexanediamino residues into the cavities of α-CD molecules. In all NMR spectra, the chemical shift of the methyl protons in PPG is invariable, indicating that the structure of the main chain pseudopolyrtoaxane is stable.

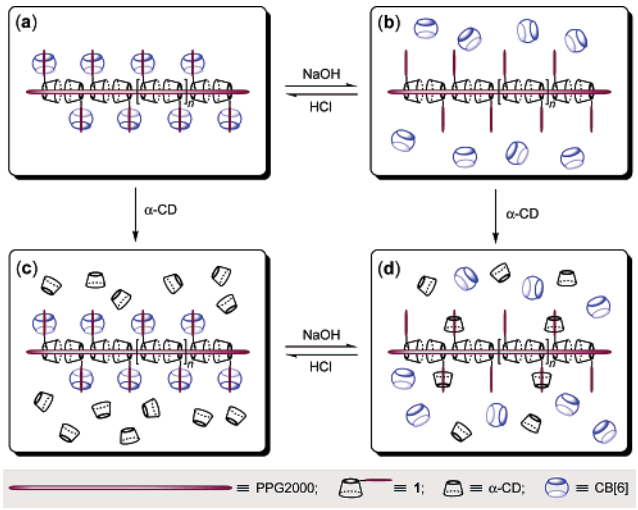


**FIGURE 5.** Schematic interconvertible processes between 2D pseudopolyrotaxane **3** and the main chain pseudopolyrtoaxane (a and b) and two 2D pseudopolyrotaxanes (c and d).

The experiments of microcalorimetric titrations further confirmed the inclusion of hexanediamine side chain in α-CD. We measured the binding constant of α-CD with 6-[(6-aminohexyl)-amino]-6-deoxy-$\beta$-CD by microcalorimetric titrations under the basic conditions at 298 K. The value of the binding constant obtained is 46 $M^{-1}$. Considering each 2D pseudopolyrotaxane bearing 12 hexanediamino residue units, therefore, the concentration of 6-[(6-aminohexyl)amino]-6-deoxy-$\beta$-cyclodextrin should be about 3.84 mM, and the concentration of α-CD is 22.6 mM. As a result, we can calculate the ratio of the inclusion of hexanediamine side chain in α-CD. It is about 49%. That is to say, almost half of α-CDs are threaded on pseudopolyrotaxane.

We have synthesized a 2D pseudopolyrotaxane **3** through α,$\omega$-PPG2000 diamino polymer threading the cavities of CDs in pseudorotaxane **2**. This novel 2D pseudopolyrotaxane can change to a familiar main-chain pseudopolyrotaxane in the presence of base. Furthermore, α-CDs can be threaded onto the side chains of the main-chain pseudopolyrotaxane, forming another 2D pseudopolyrotaxane. The two 2D pseudopolyrotaxanes can interconvert by acid−base stimuli. The topological structures of the pseudopolyrotaxanes and their reversible behavior would not only be useful for designing novel supramolecular polyrotaxanes and multicatenanes but also afford the opportunity to design and develop molecular switches and machines based on the pseudopolyrotaxane structure as scaffolds.

## Experimental Section

**General Methods.** α,$\omega$-Diaminopolypropylene glycols (PPG, average molecular weight of 2000) and $\beta$-cyclodextrin (CD) were purchased from commercial suppliers. Cucurbit[6]uril (CB[6]) was prepared according to previous reports.[11] FT-IR spectra were recorded on a Shimadzu Bio-Rad FTS 135 instrument. Thermogravimetric (TG) and differential thermal analyses (DTA) were obtained by using a RIGAKU standard-type spectrometer. The samples were put into platinum pans, which were hung in the heating furnace. The weight percentage of material remaining in the pan was recorded, while the temperature was increased from room temperature to 700 °C at a heating rate of 10 °C/min.

NMR spectra were recorded in $D_2O$. All chemical shifts were referenced to the internal 0.05 M MeOH signal at 3.341 ppm, which had been determined using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the standard.[12]

**Transmission Electron Microscopic (TEM) Measurements.** A drop of sample solution was dropped on a carbon-coated copper grid. The grid was then air-dried. The samples were examined by a high-resolution transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV.

**6-[(6-Aminohexyl)amino]-6-deoxy-$\beta$-CD Chloride (1).** 6-[(6-Aminohexyl)amino]-6- deoxy-$\beta$-CD[13] (500 mg) was dissolved in water (8 mL) at room temperature, and then 1 mL of HCl (aq, 2 M) was added in under stirring. After 30 min, an additional 40 mL of acetone was added to form a white precipitate. Stirring was continued for another 30 min, and the precipitate was collected by filtration with 20 mL of acetone washing and dried under vacuum to obtain **1** with a yield of 99%. $^1$H NMR (300 MHz, $D_2O$, ppm): $\delta$ 4.97 (d, 7H), 3.83−3.64 (m, 42H), 2.71(q, 4H), 1.58 (m, 4H), 1.31 (s, 4H). FTIR (KBr): $\nu$ 3342, 2923, 1699, 1655, 1559, 1456, 1332, 1154, 1079, 1034, 943, 849, 756, 706, 608, 581, 533 $cm^{-1}$.

**Pseudorotaxane 2.** Compound **1** (500 mg) was dissolved in 20 mL of water with stirring at room temperature; after that, CB[6] (650 mg) was added in portions. Unsolved CB[6] was removed by centrifugation after 12 h, and the solution was dried under reduced pressure. Product was collected with a yield of 81%. $^1$H NMR (300 MHz, $D_2O$, ppm): $\delta$ 5.58 (tert, 12H), 5.40 (s, 12H), 4.17 (d, 12H), 3.81−3.18(m, 42H), 2.76 (d, 4H), 0.59 (s, 4H), 0.31 (s, 4H). ESI-MS: *m*/*z* 1115.87, ($M^{2+}$). FTIR (KBr): $\nu$ 3344, 2925, 1736, 1474, 1420, 1374, 1324, 1294, 1235, 1190, 1147, 1028, 964, 919, 816, 800, 758, 673, 629, 495, 445 $cm^{-1}$. Anal. Calcd for $(C_{84}H_{122}Cl_2N_{26}O_{46})(H_2O)_{14}$: C, 39.49; H, 5.92; N, 14.25. Found: C, 39.45; H, 6.07; N, 14.21.

**Pseudopolyrotaxane 3.** In a solution of **2** (800 mg in 5 mL of water), PPG 2000 was added at room temperature. The mixture was put in a supersonic bath for 2 h and then stirred for another 24 h. Then, the resulting solution was washed with ethyl acetate (10 mL × 3) to remove the unreacted PPG2000 and dried under reduce pressure. Crude product was purified with Sephadex G-25 to afford a white solid in 21% yield. $^1$H NMR (300 MHz, $D_2O$, ppm): 5.68 (tert, 11 × 12H of CB[6]), 5.50 (s, 11 × 12H of **1**), 4.27 (d, 11 × 12H of **1**), 3.86−3.31 (m, 11 × 42H of **1**, 34 × 3H of $-CH_2-CHO-$ of PPG), 2.85 (s, 11 × 4H of **1**), 1.07 (d, 34 × 3H of $-CH_3$ of PPG), 0.61 (s, 11 × 4H of **1**), 0.39 (s, 11 × 4H of **1**). FTIR (KBr): $\nu$ = 3342, 2929, 1735, 1558, 1474, 1420, 1374, 1324, 1294, 1236, 1190, 1147, 1029, 964, 923, 816, 800, 758, 673, 630, 445 $cm^{-1}$. Anal. Calcd for $(C_{84}H_{122}Cl_2N_{26}O_{46})_{12}(C_{102}H_{204}O_{34}N_2H_4)(H_2O)_{180}$: C, 40.61; H, 6.22; N, 13.36. Found: C, 40.31; H, 6.41; N, 13.37.

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(13) $^1$H NMR (300 MHz, $D_2O$, ppm): $\delta$ 4.96 (d, 7H), 3.79−3.62 (m, 42H), 2.66 (m, 4H), 1.44−1.33 (m, 4H), 1.19 (t, 4H). ESI-MS: *m*/*z* 1233.60 ($M + H^+$). Yang, X.-L.; Wang, Q.; Xu, H.-B. *Carbohydr. Res.* **2002**, *337*, 1309−1312.