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SYNTHESIS OF IMIDAZOLIUM SALTS BEARING TWO CYCLODEXTRINS

Susumu Tsuda,[1]* Yohei Minami,[2] Ryoji Ueda,[2] Takanori Iwasaki,[2,3] Shin-ichi Fujiwara,[1] Hitoshi Kuniyasu,[2] and Nobuaki Kambe[2]*

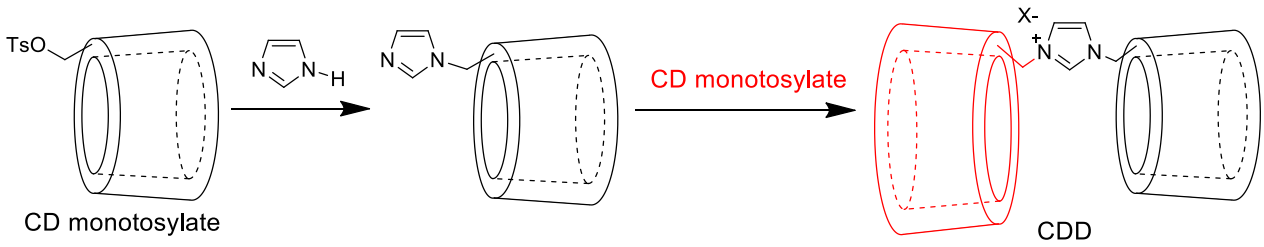
[1]Department of Chemistry, Osaka Dental University, 8-1 Kuzuhahanazono-cho, Hirakata, Osaka 573-1121, Japan. [2]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka, 565-0871, Japan. [3]Department of Chemistry and Biotechnology, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: tsuda-s@cc.osaka-dent.ac.jp

Abstract – Cyclodextrin (CD) homo and hetero dimers including an imidazolium salt were prepared from imidazolyl CDs and the corresponding CD monotosylates. The CD dimer imidazolium salts were characterized by MALDI-TOF mass and NMR spectroscopies.

Cyclodextrins (CDs) are cyclic oligosaccharides composed from six or more α-glucopyranoses. CDs are known as host molecules which can include various organic compounds into their cavities in aqueous media.[1] Therefore, a variety of modified CD derivatives have been designed as biomimetic functional molecules including artificial enzymes.[2-4] Host molecules bearing two CDs, called CD dimers, have two holding cavities closely located each other, and so tend to bind specific guest molecules more strongly compared with native CDs.[5] Although β-CD homo dimers have been synthesized and extensively studied, CD hetero dimers composed of two different cyclodextrins have been rarely reported.[6-10] Lincoln and coworkers found that an urea-linked CD hetero dimer recognizes more strongly Brilliant Yellow, a type of dyes, compared to native CDs and similar CD homo dimers,[8] demonstrating usefulness of CD hetero dimer. This mean that the CD hetero dimers provide a powerful tool for selective recognition of specific guest molecules, and will be employed as promising materials for development of supramolecular catalysts[11] and chemical sensors.[12] Aiming to lay the groundwork for development of these functional molecules, we herein investigated synthesis for homo and hetero CD dimers including an imidazolium salt which can be easily converted to a N-heterocyclic carbene (NHC)[11a,11c,13] which attracted much

attention in synthetic chemistry in recent years.

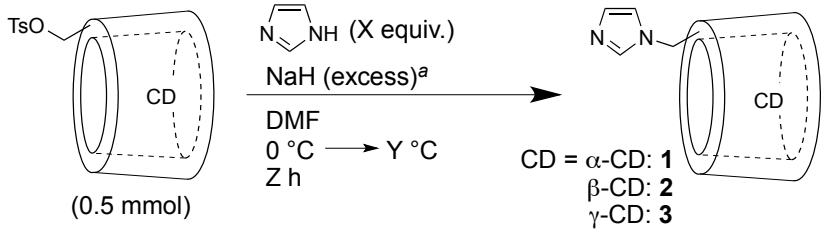
As shown in Scheme 1, we designed a route including two stepwise substitution reactions to prepare CD hetero dimers bearing an imidazolium salt. In first step, a CD monotosylate is converted to an imidazolyl CD with excess imidazole. Then the resulting CD-substituted imidazole is subjected to the second substitution with another CD monotosylate to give the desired CD dimers (abbreviated as CDD).



Scheme 1. A synthetic route of CDDs including an imidazolium salt

We optimized reaction conditions, such as the equivalents of imidazole and sodium hydride (NaH), temperature and reaction times, and the results are shown in Table 1. Firstly, α-CD monotosylate was reacted with 90 equivalents of imidazole activated with excess NaH at 60 °C for 3 days (entry 1, Table 1). Although the desired imidazolyl α-CD **1** was obtained, multi-imidazolylated CDs were also formed and the desired compound **1** could be isolated in pure form only in 39% yield by a reversed-phase (C18) silica gel column chromatography due to the insufficient separation. The formation of the multi-imidazolylates

Table 1. Preparation of imidazolyl CDs **1**-**3**



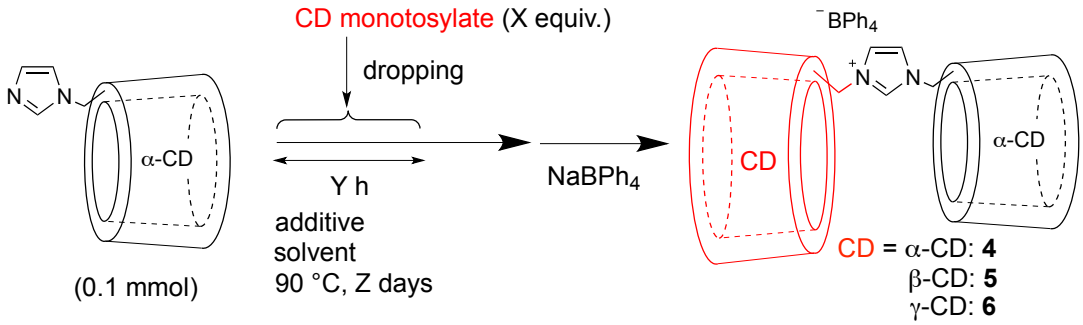
Entry	imidazole X (equiv.)	temperature Y (°C)	reaction time Z (h)	yield (%)[b]
1	90	60	72	39
2	90	rt	20	40
3	90	rt	3	31
4	30	rt	3	43
5	15	rt	3	20
6	30	40	4	57
7	30	40	4	54 [c]
8	30	40	4	55 [d]

[a]1.2 equiv. based on imidazole. [b]Isolated yield. [c]6-Imidazolyl-β-CD. [d]6-Imidazolyl-γ-CD.

could not be also suppressed by conducting the reaction at room temperature or for a short time (entries 2-3, Table 1). Since the reaction was almost completed in a relatively shorter time (entry 3, Table 1), we optimized the reaction conditions employing less amounts of imidazole for 3 or 4 h (entries 4-6, Table 1) and found that pure α-CD **1** was obtained in 57% yield using 30 equivalents of imidazole under the conditions of entry 6. In addition, imidazolyl β-CD **2** and imidazolyl γ-CD **3** were also obtained from the corresponding CD monotosylates under identical conditions (entries 7-8, Table 1). These imidazolyl CDs were characterized by mass spectroscopy (MALDI-TOF) and NMR spectroscopies.

Then, thus obtained imidazolyl α-CD **1** was allowed to react with another CD monotosylate to give targeted CDDs as shown in Table 2. Although imidazolyl α-CD **1** was reacted with an equivalent of α-CD monotosylate at 90 °C for 2 days in dimethyl sulfoxide (DMSO) under our previous reported procedure[14] (entry 1, Table 2), the imidazolyl CD **1** reacted only very lowly (conversion: 6%). Breslow and a coworker synthesized a homo CDD including an imidazolium salt by the reaction of imidazolyl β-CD with β-CD monoiodide.[15] We repeated the reaction of entry 1 in the presence of one equivalent of sodium iodide (NaI) and the conversion of **1** was increased to 18% (entry 2, Table 2). We assumed that low reactivity of imidazolyl α-CD **1** might arise from the facile self-inclusion phenomenon[16] of **1**, due to

Table 2. Preparation of homo and hetero CDDs bearing an imidazolium salt



Entry	solvent	additive	monotosylate (X equiv.)	drop time Y (h)	reaction time Z (d)	conv. (%) of imidazolyl CD[a]	yield (%) of CDD[b]
1	DMSO	none	1	0	2	6	---
2	DMSO	NaI (1 eq.)	1	0	2	18	---
3	DMSO/toluene (4/1)	NaI (1 eq.)	1	0	2	29	---
4	DMSO/toluene (4/1)	none	1	0	2	16	---
5	DMF/toluene (4/1)	NaI (1 eq.)	2	24	2	40	---
6	DMF/toluene (4/1)	NaI (1 eq.)	2	40	2	63	---
7	DMF/toluene (4/1)	NaI (1 eq.)	2	90	4	85	26[c]
8	DMF/toluene (4/1)	NaI (1 eq.)	2	90	7	90	43
9	DMF/toluene (4/1)	NaI (1 eq.)	2[d]	90	7	88	39
10	DMF/toluene (4/1)	NaI (1 eq.)	2[e]	90	7	75	53

[a]Determined by ^{1}H NMR spectroscopy. [b]Isolated yield. [c]without $NaBPh_4$. [d]β-CD monotosylate. [e]γ-CD monotosylate.

the good fitting of the imidazole group in the α-CD cavity of **1**, which can obstruct the reaction of **1** with the tosylate. Therefore, we used toluene as a co-solvent and the conversion of **1** was improved to 29% (entry 3, Table 2). This result indicated that sterically protected imidazole part of the self-inclusion complex was forced out from the α-CD cavity by a toluene molecule, and thus the imidazole moiety reacted easier with the tosylate. In addition, this effect was also observed in the case without NaI when compared between entry 1 and 4. We finally found that conversion of imidazolyl α-CD **1** was drastically improved by slow addition of the monotosylate (entries 5-8, Table 2). When α-CD monotosylate was added over 90 h by using a micro syringe pump device, 85% of imidazolyl α-CD reacted in 4 days. However, α-CD homo dimer (αα-CDD) imidazolium tosylate salt was isolated in only 26% yield by a reversed-phase column chromatography (entry 7, Table 2) due to the tailing of the imidazolium tosylate salt in the chromatography. After an anion exchange of the αα-CDD tosylate salt to the corresponding tetraphenylborate salt by the treatment with sodium tetraphenylborate ($NaBPh_4$), the tailing was efficiently improved leading to the successful isolation of the desired dimer **4** in 43% yield (entry 8, Table 2). By a similar operation, CD hetero dimers **5** and **6** (αβ-CDD and αγ-CDD) were also obtained in moderate yields by using corresponding β- and γ-CD monotosylates, as shown in entries 9 and 10 of Table 2. These CDDs were characterized by mass spectroscopy (MALDI-TOF) and NMR spectroscopies. The ^{1}H NMR spectra of CDDs **4**-**6** including an imidazolium salt were shown in Figure 1. In general, the secondary hydroxyl groups (-O^{2}H and -O^{3}H) on the wider rim of the CD skeleton form hydrogen bonding network.[17] Therefore, protons of CD's secondary OH groups are much more deshielded than those of normal secondary OH groups and their proton signals shift downfield to appear between 5 and 6 ppm in DMSO-d_6. In addition, the secondary OH signals of α-CD are more shielded than those of β- and γ-CD. As shown in Figure 1, secondary OH signals of α-CD included in hetero CDDs (**5** and **6**) were separately observed from those of β- and γ-CD at 5.3 ~ 5.8 ppm. This observation, together with the results from the mass spectroscopy and the column chromatography, strongly supported that hetero CDDs are

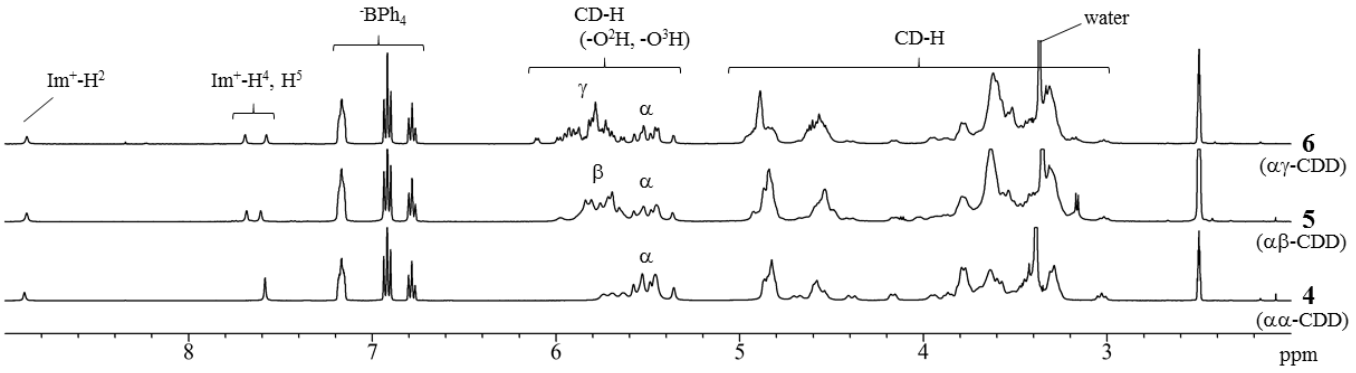


Figure 1. ^{1}H NMR spectra (400 MHz) of CDDs **4**-**6** including an imidazolium salt in DMSO-d_6

successfully synthesized and isolated. Unlike hetero CDDs, the protons (H^4 and H^5) of the imidazolium salt unit included in homo CDD **4** were equivalent giving a single peak, which indicated that the homo CDD **4** has C_2 symmetry in the DMSO solution.

In conclusion, we have prepared a new homo and hetero CDDs **4**-**6** including an imidazolium salt moiety as the tether unit. Use of NaI as an additive and toluene as the co-solvent and slow addition of the CD monotosylates is the key to this success. These CD derivatives were characterized by mass spectroscopy (MALDI-TOF) and NMR spectroscopies. Further studies aiming at developing functional molecules incorporating homo and hetero CDD units possessing two molecule recognition sites are underway.

EXPERIMENTAL

Melting points were measured with a Stanford Research Systems MPA100 apparatus. Optical rotations were recorded by a Jasco P-2200 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded by a JEOL JNM-Alice 400 (for 400 MHz and 100 MHz, respectively) spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with 2,5-dihydroxy benzoic acid as a matrix on a BRUKER autoflex III. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

Materials. All reagents were purchased from commercial sources and used without further purification.

Typical procedure for the preparation of imidazolyl CD.

Under nitrogen, NaH (18 mmol) was suspended in DMF (5.0 mL) at 0 °C. To the suspension, 3.0 mol/L imidazole DMF solution (5.0 mL) was slowly added at 0 °C, the resulting reaction mixture was stirred at 0 °C for 10 min. Next, α-CD monotosylate (0.5 mmol) was added at once to the reaction mixture, and then the mixture was stirred at 40 °C. After 4 h, the reaction mixture was neutralized with 1 M HClaq, and solvents were removed in vacuo. To the residue, EtOAc was added, and then the mixture was vigorously stirred. After standing, the top clear layer was removed. The precipitate was washed another two times with EtOAc by the same decantation process. The residue was dried in vacuo to give a white solid. The crude was purified with column chromatography (ODS; KP-C18-HS 60 g (Biotage), water/MeOH = 100/0 → 0/100) to obtain the desired imidazolyl α-CD **1** (57%) as a white solid.

Imidazolyl α-CD (1): a white solid; mp 240-244 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +115.7 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (s, 1H), 7.14 (s, 1H), 6.87 (s, 1H), 5.79-5.21 (m, 12H), 4.93-4.66 (m, 7H), 4.62-4.44 (m, 3H), 4.35-4.19 (m, 2H), 4.12 (m, 1H), 3.97 (m, 1H), 3.84-3.57 (m, 18H), 3.50-3.15 (m, overlapped with HOD), 2.85 (t, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.2, 127.9, 120.7, 102.0-101.9 (overlapped),101.5, 83.1, 82.8, 82.3, 82.1, 81.9, 81.8, 73.4-73.3 (overlapped), 73.1, 73.0, 72.5, 72.2-72.0 (overlapped), 71.8, 71.7, 70.1, 60.7-60.8 (overlapped), 60.0-59.8 (overlapped), 46.9; HR-MS (MALDI-TOF): (*m*/*z*) 1045.384 ([M+Na]$^+$, $C_{39}H_{62}N_2NaO_{29}^+$, calcd. 1045.333); Anal. Calcd

for $C_{39}H_{62}N_2O_{29}\cdot(H_2O)_6$: C, 41.42; H, 6.59; N, 2.48. Found: C, 41.82; H, 6.22; N, 2.23.

Imidazolyl β-CD (2): a white solid; mp 266-269 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +128.6 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (s, 1H), 7.16 (s, 1H), 6.85 (s, 1H), 5.94-5.47 (m, 14H), 4.86-4.78 (m, 8H), 4.65 (t, *J* = 5.3 Hz, 1H), 4.56-4.41 (m, 4H), 4.32 (t, *J* = 5.6 Hz, 1H), 4.09 (m, 1H), 3.89 (m, 1H), 3.79-3.50 (m, 24H), 3.43-3.03 (m, overlapped with HOD); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.1, 127.9, 120.6, 102.4-102.3 (overlapped), 102.1-101.9 (overlapped), 101.1, 83.8, 82.6, 81.9, 81.6-81.4 (overlapped), 80.7, 73.4-73.1 (overlapped), 72.7-72.1 (overlapped), 70.5, 60.7, 60.1-59.8 (overlapped), 59.1, 47.1; HR-MS (MALDI-TOF): (*m/z*) 1207.432 ($[M+Na]^+$, $C_{45}H_{72}N_2NaO_{34}^+$, calcd. 1207.386).

Imidazolyl γ-CD (3): a white solid; mp 244-248 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +153.6 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (s, 1H), 7.17 (s, 1H), 6.85 (s, 1H), 6.05-5.62 (m, 16H), 4.93-4.84 (m, 8H), 4.77-4.37 (m, 9H), 4.153 (m, 1H), 3.79-3.54 (m, 30H), 3.42-3.19 (m, overlapped with HOD), 3.06 (t, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.3, 127.9, 120.7, 102.4, 102.2, 101.9-101.5 (overlapped), 101.0, 83.6, 82.0, 81.3, 81.1, 81.0, 80.7-80.6 (overlapped), 80.2, 73.2-72.2 (overlapped), 70.5, 60.8, 60.2-59.8 (overlapped), 59.4, 46.9; HR-MS (MALDI-TOF): (*m/z*) 1369.496 ($[M+Na]^+$, $C_{51}H_{82}N_2NaO_{39}^+$, calcd. 1369.439.

Typical procedure for preparation of CD dimer (CCD) imidazolium salt.

Under nitrogen, dried imidazolyl α-CD **1** (0.2 mmol), NaI (0.2 mmol) was suspended in DMF (1.0 mL) and toluene (0.4 mL). The reaction mixture was stirred at 90 °C while extremely slowly adding (0.016 mL/h) 0.3 mol/L α-CD monotosylate DMF solution (1.4 mL) to the mixture with a micro syringe pump device. After 7 days, the mixture was poured in acetone, and then the resulting white precipitate was filtrated. The filtered residue was dissolved with a small amount of water, and $NaBPh_4$ (0.24 mmol) was added to the solusion. The crude was purified two times by column chromatography (ODS; KP-C18-HS 60 g (Biotage), water/ MeOH = 100/0 → 0/100) to obtain the desired αα-CDD imidazolium salt **4** (43%) as a white solid.

αα-CDD imidazolium salt (4): a white solid; mp 220-224 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +79.7 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 7.58 (s, 2H), 7.17 (m, 8H), 6.92 (t, *J* = 7.3 Hz, 8H), 6.77 (t, *J* = 7.3 Hz, 4H), 5.74-5.36 (m, 24H), 4.87-4.82 (m, 16H), 4.70-4.53 (m, 12H), 4.38 (d, *J* = 13.4 Hz, 2H), 4.16 (d, *J* = 9.0 Hz 2H), 3.95-3.28 (m, overlapped with HOD), 3.03 (t, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.2, 163.7, 163.2, 162.7, 138.3, 135.7-135.6 (overlapped), 125.4-125.3 (overlapped), 123.4, 121.6, 102.2-101.6 (overlapped), 83.0, 82.3-82.1 (overlapped), 73.3-73.2 (overlapped), 73.0, 72.5, 72.2-72.0 (overlapped), 71.6, 61.1, 60.2-59.8 (overlapped), 49.7-49.6 (overlapped); HR-MS (MALDI-TOF): (*m/z*) 1977.699 ($[M-Ph_4B^-]^+$, $C_{75}H_{121}N_2O_{58}^+$, calcd. 1977.658;

Anal. Calcd for $C_{99}H_{141}BN_2O_{58}\cdot(H_2O)_9$: C, 48.33; H, 6.51; N, 1.14. Found: C, 48.66; H, 6.97; N, 1.14.

αβ-CDD imidazolium salt (5): a white solid; mp 218-223 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +91.3 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.88 (s, 1H), 7.68 (s, 1H), 7.61 (s, 1H), 7.17 (m, 8H), 6.92 (t, *J* = 7.3 Hz, 8H), 6.78 (t, *J* = 7.3 Hz, 4H), 5.84-5.37 (m, 26H), 4.91-4.83 (m, 16H), 4.66-4.35 (m, 14H), 4.13-3.16 (m, overlapped with HOD), 3.02 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 164.1, 163.6, 163.2, 162.7, 138.2, 135.6-135.5 (overlapped), 125.4-125.3 (overlapped), 123.4, 123.1, 121.6, 102.3, 102.0-101.6 (overlapped), 83.1, 82.7, 82.6, 82.3-81.1 (overlapped), 73.3-72.9 (overlapped), 72.5-71.9 (overlapped), 61.1, 60.8, 60.2-59.9 (overlapped), 59.7, 49.5; HR-MS (MALDI-TOF): (*m/z*) 2139.770 ($[M\text{-}Ph_4B^-]^+$, $C_{81}H_{131}N_2O_{63}^+$, calcd. 2139.710; Anal. Calcd for $C_{105}H_{151}BN_2O_{63}\cdot(H_2O)_9$: C, 48.09; H, 6.50; N, 1.07. Found: C, 48.24; H, 6.93; N, 0.99.

αγ-CDD imidazolium salt (6): a white solid; mp 220-223 °C, accompanied by decomposition; $[\alpha]_D^{20}$ +124.8 (c 1.0, H_2O); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.88 (s, 1H), 7.69 (s, 1H), 7.58 (s, 1H), 7.17 (m, 8H), 6.92 (t, *J* = 7.3 Hz, 8H), 6.77 (t, *J* = 7.3 Hz, 4H), 6.11-5.36 (m, 28H), 4.92-4.81 (m, 20H), 4.65-4.45 (m, 18H), 4.40 (m, 2H), 4.16 (m, 2H), 3.93-3.17 (m, overlapped with HOD), 3.02 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 164.2, 163.7, 163.2, 162.7, 138.3, 135.6-135.5 (overlapped), 125.5-125.4 (overlapped), 123.5, 123.2, 121.6, 102.3-101.3 (overlapped), 83.1, 82.5, 82.3-82.0 (overlapped), 81.5, 81.2-81.0 (overlapped), 80.9, 80.5, 80.1, 73.3-72.5 (overlapped), 72.2-72.0 (overlapped), 60.3-59.7 (overlapped), 49.6; HR-MS (MALDI-TOF): (*m/z*) 2301.821 ($[M\text{-}Ph_4B^-]^+$, $C_{87}H_{141}N_2O_{68}^+$, calcd. 2301.763; Anal. Calcd for $C_{111}H_{161}BN_2O_{68}\cdot(H_2O)_{15}$: C, 46.09; H, 6.66; N, 0.97. Found: C, 46.54; H, 6.76; N, 0.71.

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