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Synthesis of a β-cyclodextrin derivate and its molecular recognition behavior on modified glassy carbon electrode by diazotization

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ABSTRACT

A novel β-cyclodextrin (β-CD) derivative containing mono-phenylamino (MPA-β-CD) was newly synthesized by classical Mitsunobu reaction in good yield, and its structure has been confirmed by ^{1}H NMR, ^{13}C NMR and electrospray ionization mass spectra. The compound MPA-β-CD was immobilized onto glassy carbon electrode (GCE) by diazotization, and with this modified electrode the binding behavior of MPA-β-CD for ferrocene (Fc) was investigated qualitatively, and the comparison of differential pulse voltammetry before and after immersion in ferrocene solution indicated that the MPA-β-CD immobilized GCE exhibited the molecular recognition behavior between β-CD and ferrocene.

1. Introduction

Cyclodextrin(CDs),[1]a class of cyclic oligosaccharides with 6–8 D-glucose units, gained prominence in recent years in diverse fields, such as molecular reactors,[2]drug delivery systems,[3]artificial enzymes,[4]catalysis,[5] molecular machines,[6]or supramolecular sensing.[7] Cyclodextrins, in their native state, are rigid molecules, and offer limited utility in terms of size, shape, and availability of chemically useful functional groups. Cyclodextrins have thus been called structural and functional straightjackets.[8] Consequently, in the past few decades a great deal of effort has been directed toward conversion of hydroxyl groups of cyclodextrins to other useful functional groups.[9–12]

The modification of cyclodextrins offers both enormous opportunities and challenges for chemists. Among all the possible types of modifications, Monomodifications of cyclodextrins to give selectively 2-, 3-, or 6-substituted product is a challenging task because of the number of hydroxyl groups that can potentially react with the incoming reagent.[13,14] Many researchers have been accustomed to prepare monosubstituted cyclodextrins derivatives by the tosylation of native cyclodextrins extensively,[10,15,16,17] However, by this method, the desired products are painstakingly separated out from other isomers and homologues by chromatographic methods and always in the poor yield. A way to overcome this problem is to protect the primary side of CDs by reversible silylation, because the protected compounds can be readily purified by flash chromatography. Consequently, here, we report a monosubstituted β-Cyclodextrin derivative with mono-phenylamino group by Mitsunobu reaction in good yield.

In the former work, the studies on the abilities of native or modified cyclodextrin were extensively carried out in some special kind of solutions by differential circular dichroism spectroscopy or spectrofluorometric titration in combination with computational methods.[15,18,19] Simultaneously, The functionalization of surfaces is of considerable interest in applications, such as sensors and biocompatible surfaces. Consequently, many researchers have successfully prepared a variety of mercaptocyclodextrin derivatives and studied the host-guest molecular recognition through their immobilization on gold surfaces, which was achieved by the oxidative adsorption of thiols covalent S–Au bond.[20–23]Recent reports showed that the electrochemical reduction of aryl diazonium salts is proven to be an excellent method to irreversibly attach molecules to some special conducting substrates.[24] Firstly, it avoids the use of oxidative conditions, which can lead to the detrimental oxidation of the carbon substrate, moreover because it allows the presence of selected functional groups on the aryl groups. Lastly, diazonium salts are easily and rapidly prepared in one step from a wide range of anilines and its reduction takes place within seconds to minutes. However, until now, there have not been literatures about the studies on the electrochemical immobilization of β-CD on electrode surface by diazotizatin.

In this work, we demonstrate for the first time the synthesis of a novel β-cyclodextrin derivative containing one phenylamino by

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Mitsunobu reaction, at the same time, we prepared a MPA-β-CD-modified electrode by the electrochemical reduction of aryl diazonium salts on glassy carbon electrode. Furthermore, with the modified electrode we investigated qualitatively the binding behavior of MPA-β-CD for ferrocene, which was detected by differential pulse voltammetry in Fc solution.

2. Results and discussion

2.1. Synthesis

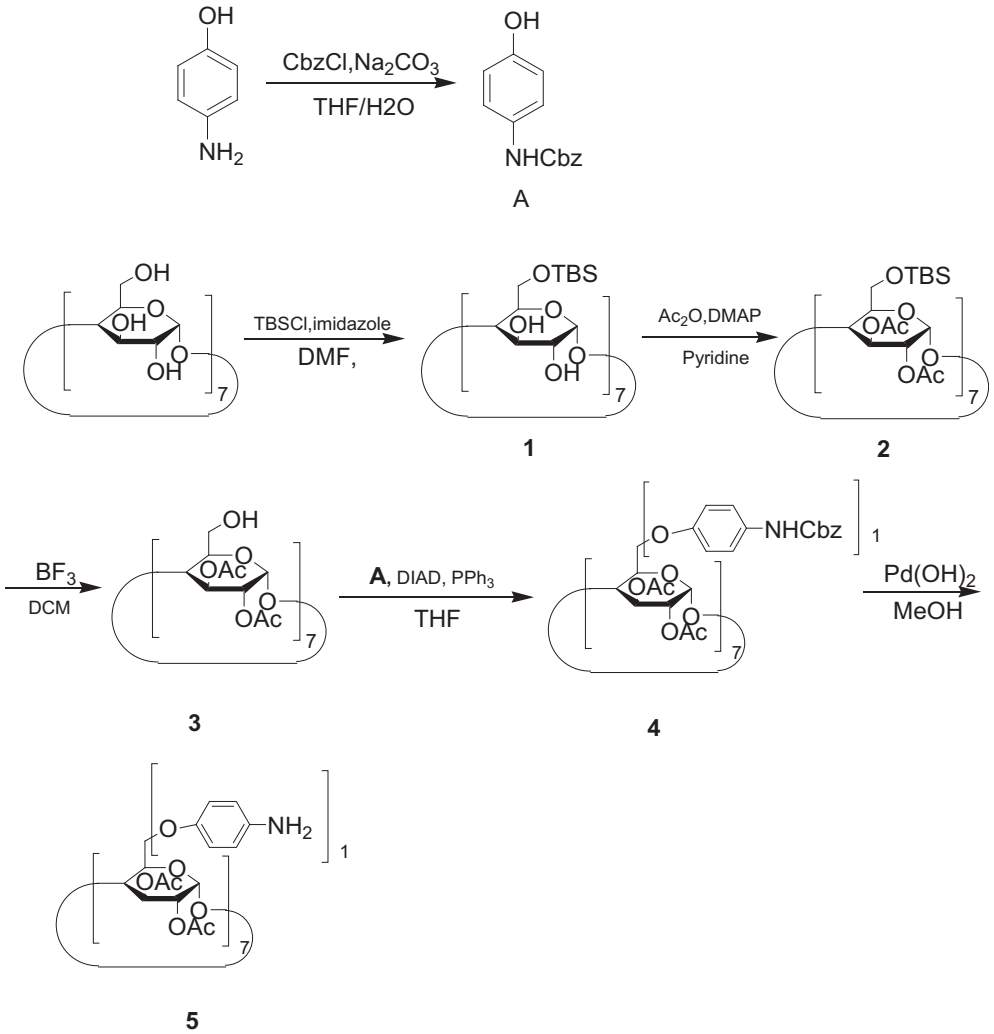
The synthesis of MPA-β-CD was shown schematically in Scheme 1. Hydroxyl groups present at the 2-, 3-, and 6-positions compete for the reagent and make selective modification extremely difficult, and thereby, the synthesis of monofunctionalization of native cyclodextrin involves in sequence (1) protection of the primary side with silyl groups, (2) protection of the secondary side with acetyl groups, (3) desilylation of the primary side, (4) Mitsunobu reaction, monosubstitution of the primary hydroxyl group of β-cyclodextrin was achieved. Although the process was slightly long, the purification of every step reaction was easily achieved by flash chromatography. In this strategy, each reaction is carefully chosen to give a high yield and the products were easily separable and purifiable by flash column chromatography.

During the course of the preparation of the target compound **5**. The Mitsunobu reaction is a key step. In recent years, the scope of the Mitsunobu reaction in natural products synthesis has been extensively discussed and reviewed.[25]The application of this classical reaction is the synthesis of some types of ethers.[26]In this nucleophilic substitution reaction, we tried a variety of reaction conditions, such as ratio of the reactants, reaction time, the adding sequence, and finally we got the optimal condition as described in the Experiment section. The Monosubstitution was in good yield under the optimal condition. More importantly the selectivity of this reaction was well controlled according to the final product.

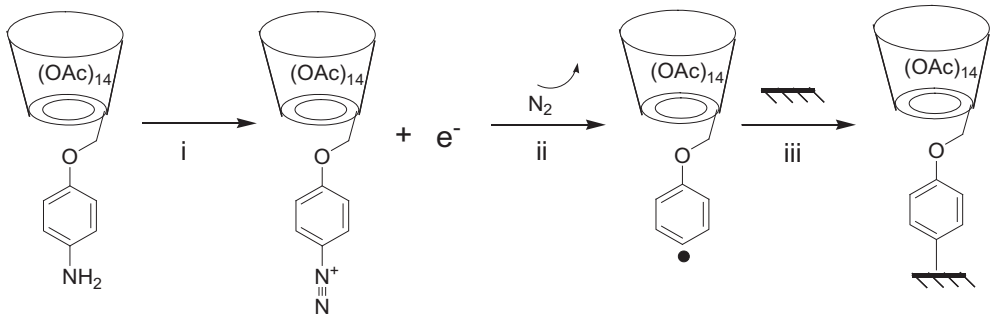
The special structure of the target compound MPA-β-CD was confirmed by ^{1}H NMR, ^{13}C NMR, and ESI-Mass. Judging by the ration of the aromatic protons in the aminophenoxy group at 7.14–7.40 and the proton of β-cyclodextrin at the C-5, only one hydroxyl group of β-cyclodextrin at the 6-position was substituted by aminophenoxy group. In addition, ESI-Mass spectra also showed the presence of monosubstitution.

2.2. Immobilization of MPA-β-CD on GCE

The formation of MPA-β-CD diazonium was shown in Scheme 2, which occurred via diazotization of MPA-β-CD to form the aryl diazonium in aqueous acidic medium. The diazonium cations generated in situ from MPA-β-CD was investigated by cyclic



Scheme 1. Schematic representation of MPA-β-CD.



Scheme 2. Schematic illustration of MPA-β-CD-modified GCE via diazotization.

voltammetry. The whole procedure involved: (i) the diazotation of the compound MPA-β-CD, (ii) the electroreduction of diazonium cation, and (iii) the covalent linkage to the GCE surface.

As shown in Figure 1, the first cycle exhibited a well-defined, reproducible, and irreversible reduction peak at −700 mV, corresponding to the reduction of the aryl diazonium salt, generating the radical. During the second and subsequent cycles, the redox peak disappears and the cyclic voltammogram exhibits only a small reduction current. This feature gave an evidence of electrode surface saturation, simultaneously showed that a monolayer of fixed molecules was achieved.

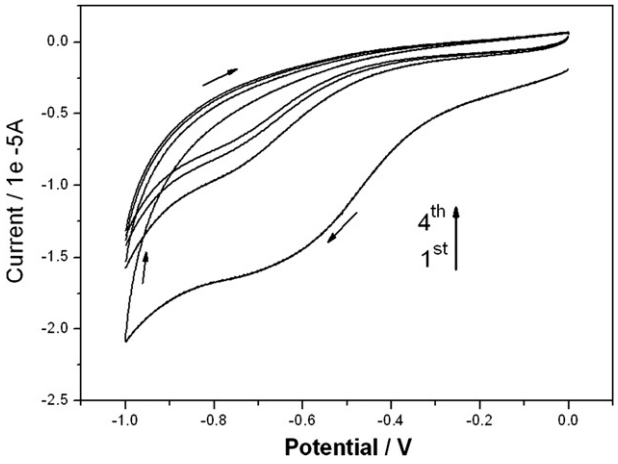


Figure 1. Cyclic voltammogram of MPA-β-CD diazonium in 1.0 M HCl. Potential scanned from 0 to −1 V versus GCE. Four cycles were performed at a scan rate of 100 mV/s.

The cyclic voltammogram of soluble electroactive species provides a convenient tool to study the presence of grafted films and their blocking properties. The influence of the glassy carbon electrode modification conditions on the cyclic voltammetric response of $Fe(CN)_6^{3-/4-}$ oxido-reduction was investigated for different layers grafted by electrochemical reduction of the in situ generated diazonium cations. Figure 2 shows the cyclic voltammogram recorded at bare glassy carbon electrode and MPA-β-CD-modified electrodes. The voltammogram of the $Fe(CN)_6^{3-/4-}$ redox system presents a quasireversible behavior at the bare electrode with an apparent redox potential of 0.23 V. However, the MPA-β-CD-modified electrodes exhibit a significant blocking behavior for the oxidation and reduction reactions of the $Fe(CN)_6^{3-/4-}$ redox system. Therefore, in this case, this feature can be explained that MPA-β-CD-modified electrodes have been successfully prepared.

FT-IR spectra were used to confirm surface attachment to electrodes, as shown in the spectra of MPA-β-CD (Fig. 3). Compared with the FT-IR spectrum of pristine GCE (Fig. 3a), the spectrum of

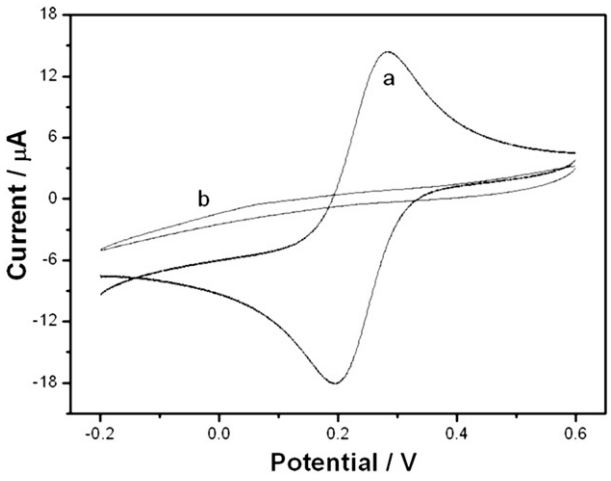


Figure 2. Cyclic voltammogram at a scan rate of 100 mV/s for a 1 mM $K_3Fe(CN)_6$ solution before (a) and after grafting of the MPA-β-CD diazonium (b).

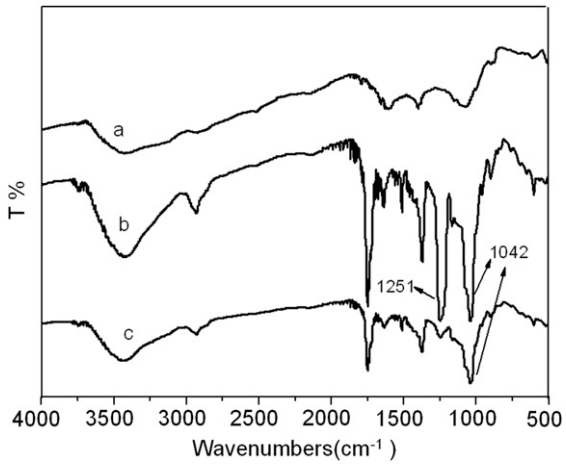


Figure 3. FT-IR spectra of GCE (a), MPA-β-CD (b), GCE modified by grafting aryl diazonium salt of MPA-β-CD film (c).

both MPA-β-CD and the diazonium/CNTs share two intense band at about between 1155 and 1042 cm^{-1} correspond to the antisymmetric glycosidic νa(C—O—C) vibrations, and the coupled ν(C—C/C—O) stretch vibration. On the other hand, the peak seen at 2928 and 2931 cm^{-1} for them, which is attributed to the asymmetric methylene stretches. The O—H vibrational band at about 3435 cm^{-1} is broadened in figure b and c spectra, presumably due to inter- and intramolecular hydrogen bonding. The deformation vibrations δ

(C–H) and δ(O–H) of the CH_2 and OH groups between 1460 and 1299 cm^{-1} and the characteristic ring vibrations at 945 and 705 cm^{-1} are seen in figure b and c spectra. Furthermore, of note is the sharp peak at 1754 cm^{-1} common to both MPA-β-CD and its GCE/diazonium film spectrum. This absorption stretch is characteristic of 14 carbonyl groups at the 2- and 3-position of MPA-β-CD. The peak assignments for the various C–H, C–O, and C–C vibrations could not be determined, owing in part to the difficulty in determining the dipole moment of the cyclodextrin ring, and in part to the added complication of the spacer units in the derivatized cyclodextrin. Nevertheless, all the above information of the spectrum to some extent provided strong evidence for the presence of MPA-β-CD at GCE. The peak at 1251 cm^{-1} attributed to the aryl C–N stretch vibration in MPA-β-CD, while in the diazonium/GCE this peak disappeared, which is indicative of surface attachment by reduction of the aryl diazonium cation.

2.3. Host-guest including behavior for Fc on the MPA-β-CD-modified electrode

The formation of inclusion complexes between β-cyclodextrin and Fc has been widely reported, and the structural nature of such complexes has been successfully used to the study of the modified electrode with cyclodextrins and their derivative.[27]Therefore, in order to further investigate the characteristic of molecular recognition on the MPA-β-CD-modified electrode, we carried out the research of binding interactions between ferrocene and MPA-β-CD-modified GCE. MPA-β-CD-modified GCE was immersed in a solution of 1 mM ferrocene (Fc) in ethanol for 30 min. After a washing procedure, differential pulse voltammetry was performed from −0.2 to 0.6 V at a scan rate of 100 mV/s in PBS buffer. The result was shown in Figure 4. By contrast with the bare electrode, an obvious peak current was obtained, and the potential response was recorded at 0.27 V, which falls within the typical redox potential range of Fc. Furthermore, a slight current wave was observed in the Figure 4a, which was explained that a small quantity of adsorption occurred between Fc and the bare electrode after immersion in the Fc solution. This adsorption was reported in the previous research.[28]Therefore, in this case, during the course of the inclusion of MPA-β-CD for Fc, the electrochemical response becomes the sum of contributions both from the Fc in solution and Fc included in MPA-β-CD cavity, as shown in the Scheme 3. For all this, compared to the bare electrode, just by the distinct increase of the peak current, we could draw a qualitative conclusion that large numbers of Fc were included in the β-CD cavity except a small adsorption.

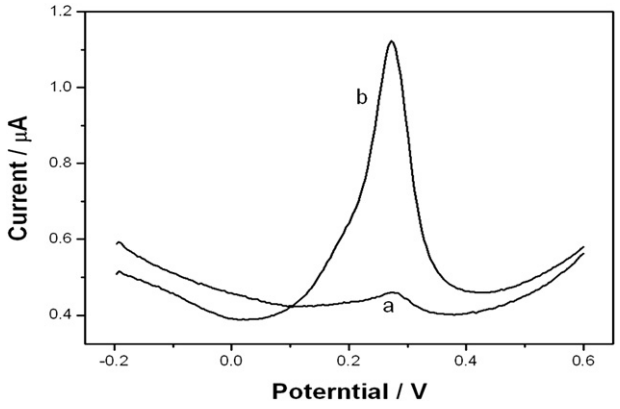
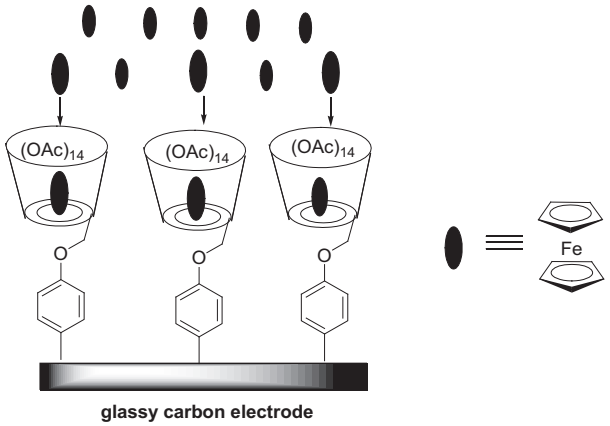


Figure 4. Comparison of differential pulse voltammetry curves for 1 mM Fc in Ethanol, recorded using a bare GCE (a) and MPA-β-CD-modified electrode (b) after immersion in 1 mM Fc for 30 min, respectively. Scan rate 100 v/s.



Scheme 3. Schematic illustration of inclusion of MPA-β-CD for Fc in 1 mM Fc solution onto the GCE.

Furthermore, in order to further investigate the ability of binding of the MPA-β-CD for Fc, based on the above comparison experiment, we conducted a series of experiments with the MPA-β-CD-modified GCE by varying the immersion time in the same concentration of Fc solution. One is differential pulse voltammetry, and the other is the peak current dependence of immersion time in Fc solution. The results were shown in Figure 4 and 5. As can be seen from the Figure 4, compared to the bare electrode, after immersion in the Fc solution, a distinct current increased was found. In addition, as seen from the Figure 5, the response of the peak current was enhanced gradually with time increased from 5 to 70 min until the equilibrium was obtained, which indicated that surface binding of Fc by the MPA-β-CD monolayer reached the equilibrium at the same concentration of Fc solution. Similarly under the same condition the insert of peak current dependence of immersion time showed that the peak current was linear versus immersion time. Still the eventual equilibrium was observed. Herein, we could draw a conclusion that a large amount of Fc was included in the MPA-β-CD cavity by host-guest molecular recognition, simultaneously, this kind of binding of host-guest would reach the equilibrium at the definite condition, the explanation about, which was reported in the previous literature.[29]

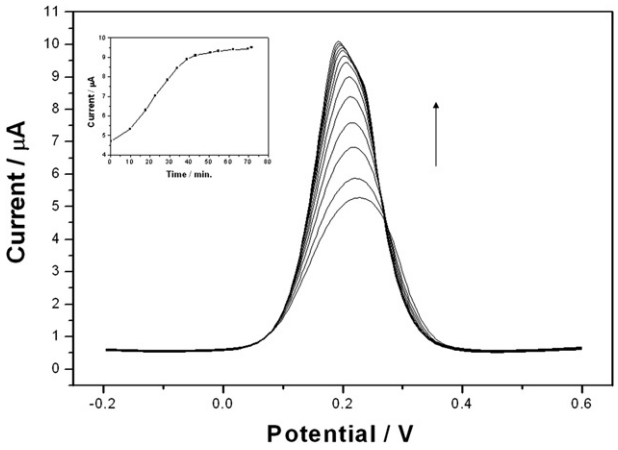


Figure 5. Differential pulse voltammetry curves for the MPA-β-CD-modified glassy carbon electrode with varying immersion time (5–70 min) in 1 mM Fc. Insert is response cure of peak current with the immerse time in 1 mM Fc solution. Potential recorded from −0.2 to 0.6 V. Scan rate 100 v/s.

3. Conclusions

MPA-β-CD has been successfully synthesized via Mitsunobu reaction in good yield and its structure has been confirmed by ^1H

NMR, ^{13}C NMR, and ESI-MS. Specially, for the studied object MPA-β-CD, we achieved in both facilitating our synthetic work and enhancing the solubility of the derivative in common organic solvents, especially for the molecular recognition process, good solubility of host molecular to some extent promotes the forming of the inclusion.

In the study for application of this derivative in electrochemistry, here, we achieved in immobilizing MPA-β-CD on the GCE via diazotization. Finally using the MPA-β-CD-modified electrode we investigated the binding ability for Fc by host-guest molecular recognition. The results showed that we have obtained a practical analyte-responsive modified electrode, furthermore, the application of this MPA-β-CD-modified electrode has been in progress in our group.

4. Experimental section

4.1. Materials

Reagent grade β-cyclodextrin was recrystallized twice from water and dried in vacuo at 100 °C for 24 h prior to use. *N*,*N*-dimethylformamide, dichloromethane, tetrahydrofuran, pyridine, acetic anhydride, diisopropyl azodicarboxylate, triphenylphosphine, 4-Aminophenol, benzyl carbonochloridate, imidazole, potassium ferricyanide, hydrochloric acid, ferrocene, potassium chloride, were commercially available and used without further purification.

4.2. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker 500 MHz spectrometer. ESI-Mass spectrometry experiments were performed with Bruker microTOfII. Electrochemical experiments were carried out using a CHI 660A electrochemical workstation (Chen Hua instruments Co., Shanghai, China). A three-electrode single-compartment cell was used for cyclic voltammetry. A 4 mm diameter glassy carbon electrode (GCE) disk was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode (in saturated KCl aqueous solution) as the reference electrode. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet Nexus 670 FT-IR spectrophotometer (ThermoNicolet, USA).

4.3. Synthesis

4.3.1. Benzyl 4-hydroxyphenylcarbamate(A). To a cold solution of *p*-aminophenol (5.0 g, 45.82 mmol) and Na_2CO_3 (7.7, 3.31 mmol) in a mixed solution (THF/H_2O, 50 mL/50 mL) was added dropwise a solution of benzyl carbonochloridate in THF at ice-bath. After addition, the reaction mixture was slowly warmed to room temperature. The mixture was extracted with ethyl acetate (100 mL×3), the combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography to afford the desired product as white solid (10 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 9.43 (s, 1H), 9.11(s, 1H), 7.49–7.35 (m, 5H), 7.22 (d, 2H), 6.66–6.68 (d, 2H), 5.11 (s, 2H).[30]

*4.3.2. Heptakis(6-O-tert-butyldimethylsi-lyl)-β-CD (**1**).* β-cyclodextrin (4 g, 3.52 mmol, dried at 100 °C in vacuum) was dissolved in 60 mL anhydrous DMF, imidazole (3.35 g, 49.28 mmol) was added. At 0–5 °C, *tert*-butyldimethylsilyl chloride (7.43 g, 49.28 mmol) in dry DMF was added in 20 min. The mixture was stirred overnight, then was poured into ice/water (150 mL) and followed by stirring for 30 min. The white precipitate was filtered and dissolved in ethyl acetate (100 mL), washed with aqueous HCl (50 mL×2), then washed with brine (50 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo yielding 8 g crude product. The crude product was purified by silica gel column chromatography (eluted by dichloromethane and methanol 10/1,v/v) to give a pure product (5.6 g, 82.4%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.73(s, 7H), 5.27(s, 7H), 4.89(d, *J*=5.00 Hz, 7H), 4.00(t, *J*=15 Hz, 7H), 3.90(d, *J*=10 Hz, 7H), 3.72–3.58(m, 28H), 0.87(s, 63H), 0.03(d, *J*=20 Hz, 42H). Mp 299–302 °C (dec)[31]

*4.3.3. Acetylated heptakis(6-O-tert-butyldimethylsilyl)-β-CD (**2**).* Heptakis (6-*O*-*tert*-butyldimethylsilyl)-β-CD(5 g, 2.58 mmol) was dissolved in 20 mL of dry pyridine. Acetic anhydride (12 mL) and 94 mg of 4-dimethylamino pyridine were added, and then the mixture was stirred at room temperature overnight. The solvent was distilled off in vacuo to give a slurry. The residue was dissolved in ethyl acetate (50 mL), washed with aqueous HCl (0.2 M, 50 mL×3), then washed with saturated $NaHCO_3$ solution (50 mL×3), finally with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude as a white solid. The crude was purified by silica gel column chromatography (eluted by dichloromethane and methanol) to yield the desired product (5.8 g, 89%). It is unnecessary for the purification of this step. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.37–5.31 (m, 7H), 5.15 (d, *J*=3.5 Hz, 7H), 4.70 (dd, *J*=3.5 and 3.5 Hz, 7H), 4.05–3.70(m, 21H), 2.09–2.04(m, 49H), 0.88(s, 63H), 0.04(d, *J*=8.5 Hz, 42H).[31]

*4.3.4. Heptakis(2,3-O-diacetyl)-β-CD (**3**).* To a solution of compound **2** (2 g, 0.79 mmol) in 20 mL of dry dichloromethane was added dropwise boron trifluoride etherate in ether (48%, 2.9 mL, 33 mmol) at room temperature. The mixture was stirred for about 6 h. The reaction mixture was poured into ice water. The organic layer was separated and washed with saturated $NaHCO_3$ solution (20 mL×3) and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a crude product. The crude product was purified by silica gel column chromatography to afford 1.2 g of desired product (88%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 5.25(t, 7H), 5.09 (d, *J*=3.4 Hz, 7H), 4.80–4.78 (m, 7H), 4.59 (dd, *J*=3.45 and 3.45 Hz, 7H), 3.86–3.80 (m, 21H), 3.62(d, *J*=7.15 Hz, 7H). Mp 184–188 °C (dec).[31]

*4.3.5. Mono(6-O-benzyl-4-hydroxyphe-nylcarbamate) heptakis(2,3-O-diacetyl)-β-CD (**4**).* The compound **4** was synthesized according to modified literature methods.[32] A solution of compound **3** (500 mg, 0.29 mmol), benzyl 4-hydroxyphenylcarbamate (423 mg, 1.74 mmol), and PPh_3 (684 mg, 2.61 mmol) was stirred in dry THF (20 mL) at 0 °C at a nitrogen atmosphere. To this mixture was added dropwise a solution of diisopropyl azodicarboxylate(5.1 mL, 2.61 mmol) in THF (5 mL) over a period of 30 min, and the reaction was monitored by TLC. The starting material wasn't consumed completely. The reaction mixture was poured into ice water, extracted with ethyl acetate (30 mL×3), the organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to give a crude oil. The crude was purified by flash column chromatography (dichloromethane/methanol) to give 260 mg of the desired product (45.8%). The by-product was a mixture of bi-and tri-substituted at the 6-position of β-CD. ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 9.59 (s, 1H), 7.34–7.43 (m, 7), 6.85–6.87 (d, 2H), 5.24–5.29 (m, 7H), 5.05–5.13 (m, 9H), 4.55–4.78 (m, 13H), 4.35 (d, *J*=0.3 Hz, 1H), 4.22 (d, *J*=0.3 Hz, 1H), 4.08 (m, 2H), 3.76–3.83 (m, 16H), 3.63–3.65 (m, 5H), 3.58(m, 2H), 3.29 (d, *J*=0.3 Hz, 1H), 2.00–2.04 (m, 42H). ^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 170.75, 170.63, 169.34, 162.67, 154.21, 131.55, 128.50, 128.10, 114.73, 96.69, 96.26, 69.82–72.77, 66.77, 60.26–61.25, 53.37, 29.35, 20.63–20.90. MS (ESI) *m*/*z* 1970.5893 $[M+Na]^+$.

*4.3.6. Mono(6-O-4-aminophenoxy)heptakis(2,3-O-diacetyl)-β-CD (**5**).* The compound **4** (200 mg, 0.103 mmol) was dissolved in 10 mL of methanol, palladium hydroxide (20 mg, 10%m/m) under

hydrogen was added to the solution. The mixture was stirred at room temperature for about 1 h. The reaction mixture was filtered over Celite, the filtrate was concentrated in vacuo to give the desired product (180 mg, 96.2%) without purification. ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 6.64–6.66 (d, 2H), 6.51–6.53 (d, 2H), 5.25–5.28 (m, 7H), 5.07–5.11 (m, 7H), 4.52–4.68 (m, 15H), 4.27 (d, J=0.3 Hz, 1H), 4.13 (d, J=0.3 Hz, 1H), 3.93–4.06 (m, 2H), 3.78–3.84 (m, 16H), 3.60–3.67 (m, 7H), 3.36 (d, J=0.3 Hz, 1H), 1.99–2.02 (m, 42H). ^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 170.58, 169.50, 117.61, 115.39, 96.55, 67.64–72.08, 60.58–60.97, 53.37, 20.66–21.91. MS (ESI) m/z 1814.5690 $[M+H]^+$, 1836.5469 $[M+Na]^+$.

4.4. Electrochemistry

4.4.1. Preparation of MPA-β-CD diazonium. The compound MPA-β-CD (42 mg) was dissolved in 1 mL of aqueous solution containing 1.0 M HCl, the solution was treated by deaerating and cooled to 0 °C, then a solution of 1.4 mg $NaNO_2$ in cold water was added dropwise to the mixture. The mixture was stirred under argon at this temperature for about 10 min. The diazonium solution formed was then immediately used to perform electro-addressing.

4.4.2. Electrodeposition of Diazonium of MPA-β-CD on GCE. The diazonium of MPA-β-CD formed in the above step was used to modify the prepared GCE by electrodeposition. The surface derivatization was carried out by electrochemical reduction, in the diazonium cation-generating solution by scanning from 0 V to −1.0 V versus Ag/AgCl at 0.1 V/s for four cycles. After deposition, the carbon electrodes were fully rinsed with distilled water and also sonicated to wash out all unbound molecules.

Acknowledgements

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Supplementary data

^{1}H NMR of the compound **A**, **1**, **2**, and **3**, ^{13}C NMR of compound **4** and compound **5**, ^{1}H NMR and ESI-MS of the compound **4** and **5**. Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.07.052.

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