Electronic Supplementary Information

A Facile Synthesis of Molecularly Imprinted Polymer and its Properties as Electrochemical Sensor for Ethyl Carbamate Analysis

1. The FT-IR spectroscopy

The Fourier transform infrared spectroscopy (IR) was used to detect the structure of β-cyclodetrin (β-CD), β-cyclodetrin aldehyde (β-CDA) and molecularly imprinted polymer (MIP). The IR spectra recorded are shown in Fig. S1, and the spectral peaks are also listed in Table S1.
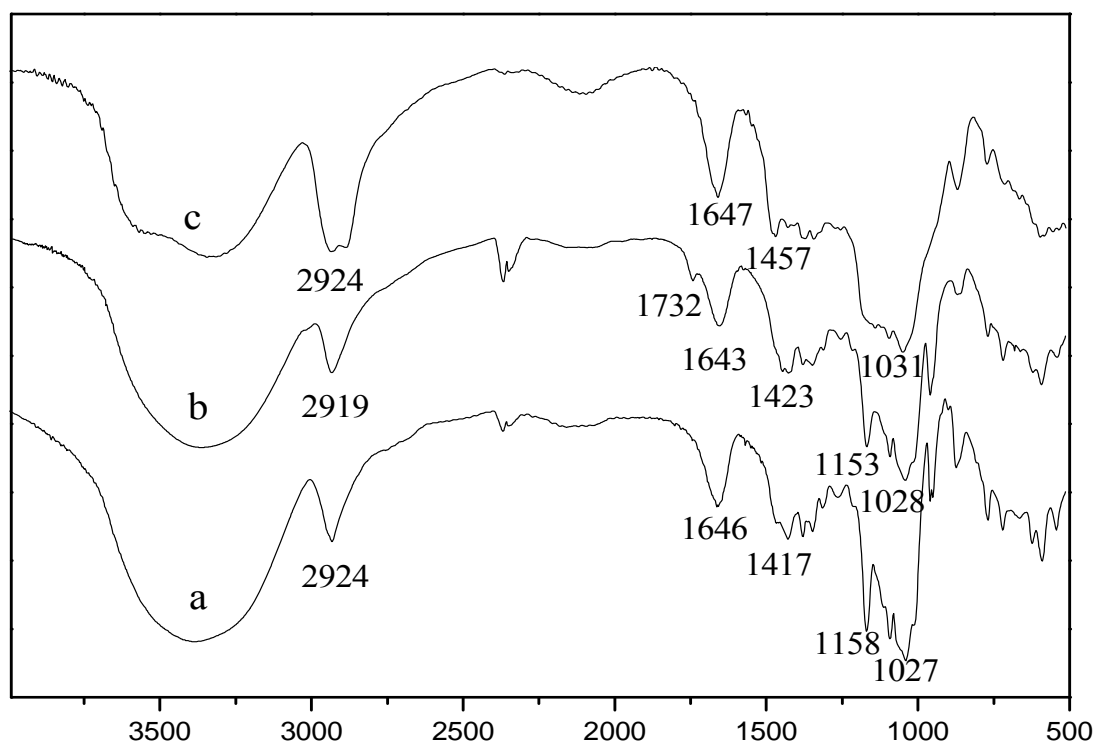

Fig. S1. FT-IR spectra of raw β-CD (a), β-CDA (b) and MIP(c)

Table S1. Infrared Absorption Characteristics of β-CD, β-CDA and MIP

Wave Number (cm^{-1})	Functional Group	Wave Number (cm^{-1})	Functional Group
3500-3200	β-CD -OH (s, ν)	1417	β-CD C-H (δ)
2924(2950-2850)	β-CD -CH$_2$, -CH (s, ν_{as}, ν_s)	1158, 1027	β-CD C-OH (s, δ)
1646	β-CD C=O (m, ν)	1153, 1028	β-CDA C-OH (s, δ)
3500-3200	β-CDA -OH (s, ν)	1643	β-CDA C=O (m, ν)
2919(2950-2850)	β-CDA -CH (s, ν_s)	1423	β-CDA C-H (δ)
1732	β-CDA -HC=O (s, ν)	1647	MIP C=O (m, ν)
3500-3200	MIP -OH (s, ν)	1457	MIP C-H (w, δ)
2924(2950-2850)	MIP -CH$_2$-, -CH$_3$, -CH (m, ν_{as}, ν_s)	1031	MIP C-OH(m, δ)

2. The CP/MAS ^{13}C-NMR

^{13}C-NMR spectra of β-CD, β-CDA and MIP were recorded by Avance II /400M Hz nuclear magnetic resonance spectrometer, and the ^{13}C-NMR spectra are shown in Fig. S2 and S3. The chemical shifts are summarized in Table S2.
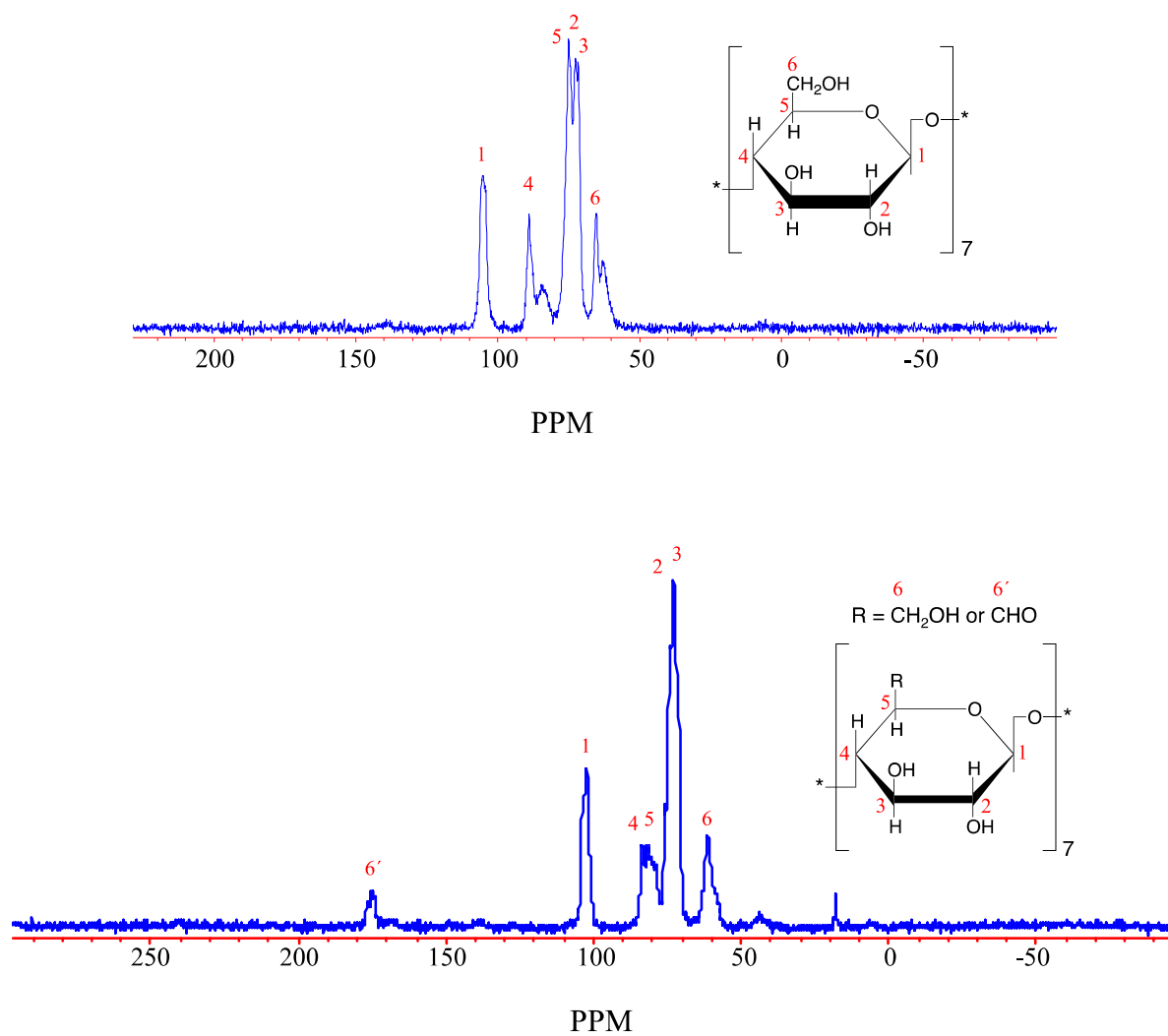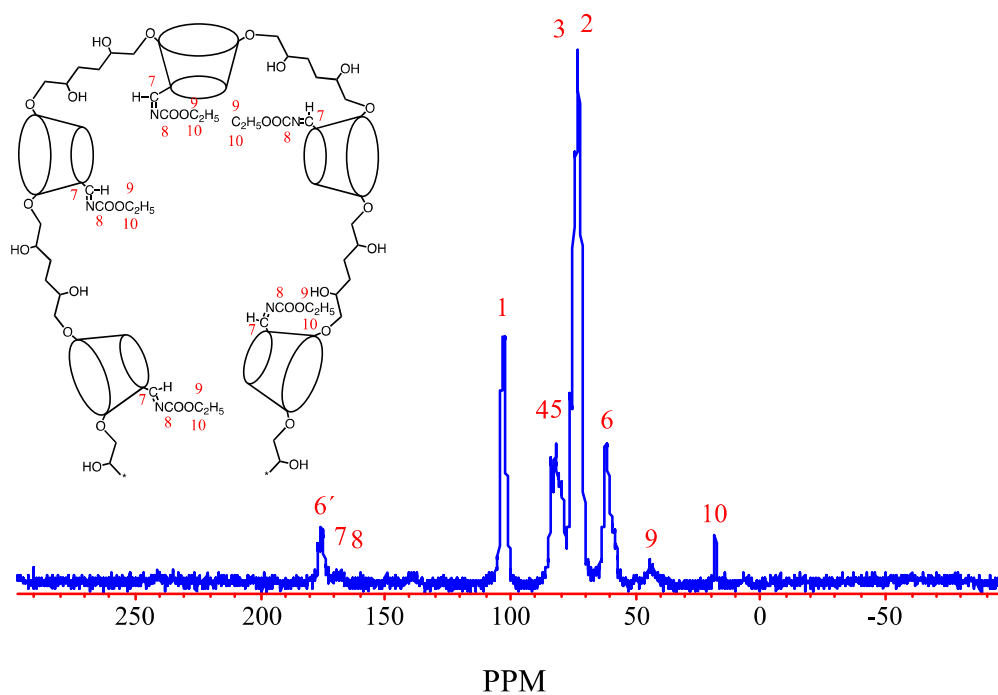

Fig. S2. ^{13}C-NMR spectra of β-CD and β-CDA

Fig. S3. ^{13}C-NMR spectra of MIP

Table S2 ^{13}C-NMR spectral peaks ascription of β-CD, β-CDA and MIP

Carbon	β-CD (ppm)	β-CDA (ppm)	MIP (ppm)
C_1	105.11 (s)	102.61 (s)	105.8 (C_1, d)
C_2	75.01 (s)	76.81 (s)	75.01 (C_2, s)
C_3	72.46 (s)	72.87 (s)	71.25(C_3, s)
C_4	88.86 (s)	83.67 (s)	88.91(C_4, s)
C_5	81.53 (s)	81.93 (s)	82.56(C_5, s)
C_6-CHOH	65.23 (s)	65.05 (s)	65.05 (s)
$C_{6'}$-CHO		174.93 (d)	174.93 (d)
C_7			168.54 (s)
C_8			161.01 (s)
C_9			45.83 (d)
C_{10}			18.46 (d)

3. The SEM

Fig. S4 shows the morphology of β-CD, β-CDA and MIP by using the scanning electron microscope (SEM, δ is the unit of scale, and × is the magnification).

SEM of β-CD ×1000 δ=10.0 μm   SEM of β-CDA ×1000 δ=10.0 μm   SEM of MIP×1000 δ=10.0 μm
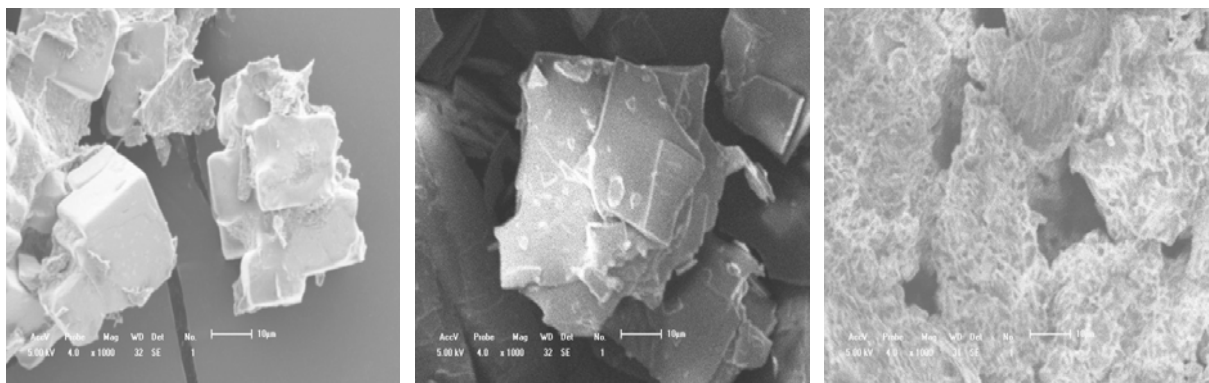
Fig. S4. SEM of β-CD, β-CD A and MIP (×1000)

As shown in the SEM photos, the surface topography of β-CD is very smooth and glossy. However, after selective oxidation of β-CD, although the β-CDA retains the basic morphologic structure of β-CD, some corrugations and cracks appear on the main structure. The structure of MIP appears porous with a number of distributed cavities, which will be involved in EC adsorption and separation.
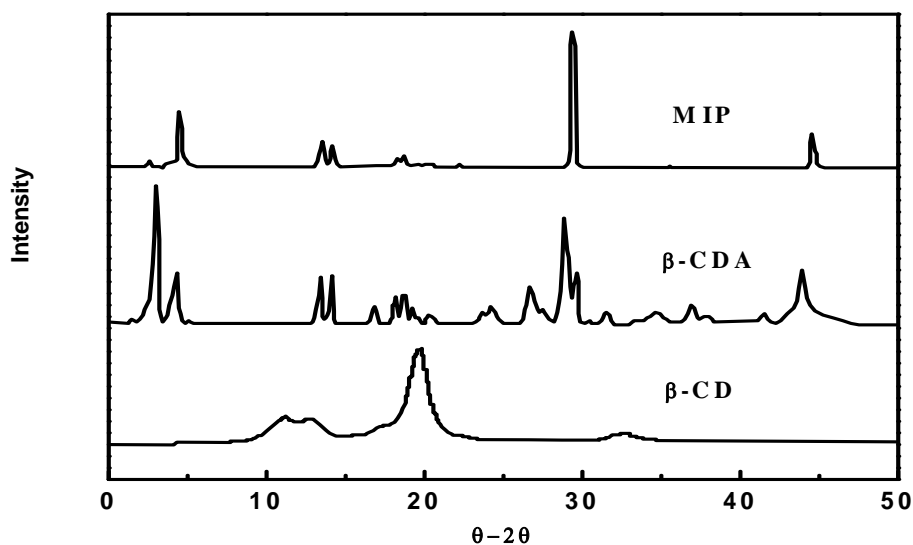
4. The XRD

Fig. S5. X-ray diffraction spectra of β-CD, β-CDA and MIP

Table S3 The crystallinity of β-CD, β-CDA and MIP

Sample	*K* value	Scanning range	Crystallinity
β-CD	0.10	0°- 60°	56.5
β-cyclodextrin aldehyde	0.10	0°- 60°	75.9
MIP	0.10	0°- 60°	38.1

From Fig. S5 and Table S3, it is evident that the structure of β-CD consists of crystalline as well as amorphous regions. The crystallinity of β-CD is 56.5%. The diffraction peaks at 2θ=12.2° and 2θ=13.3° exhibit amorphous characteristics while the diffraction peak at 2θ=19.6° exhibit crystal characteristics. After selective oxidation of β-CD, the intensity of the crystal diffraction peaks are significantly decreased. Around 2θ=18.0° there is a group of narrow crystal diffraction peaks. At 2θ=3.6°, 2θ=14.5°, 2θ=26.8°, 2θ=29.5° and 2θ=44.4°, high strength crystal diffraction

peaks appear. The crystallinity of β-CDA is 75.9 %. After the cross-linking polymerization, the crystallinity decreases and is 38.1 %. For the MIP. At 2θ=4.4°, 2θ=31.1° and 2θ=44.9°, crystal diffraction peaks appear, which means that new forces were built during the process of association and polymerization.

5. The Biodegradation test

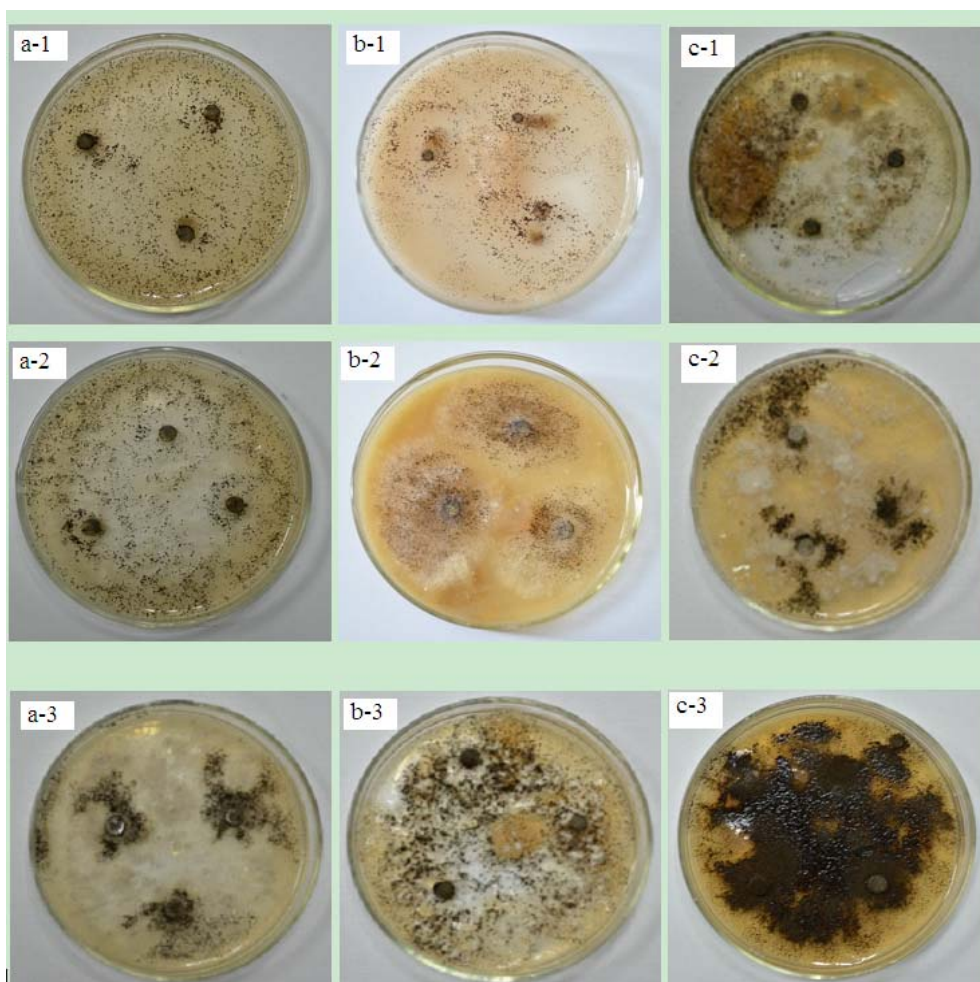Fig. S6 shows the growth of *Aspergillus niger* colonies after incubation for 7, 14 and 21 days, respectively.

Fig. S6. Growth of *Aspergillus niger* on agar media containing β-CD (a), β-CDA (b) and MIP (c) as only carbon source.

From Fig. S6, it is obvious that the colony of bacteria is widely distributed on the medium containing MIP, which means that the MIP has a better biodegradability than β-CD or β-CDA.