



Layer-by-layer assembly of anionic-/cationic-pillar[5]arenes multilayer films as chiral interface for electrochemical recognition of tryptophan isomers

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ARTICLE INFO

Article history:

Received 25 January 2018

Received in revised form

10 April 2018

Accepted 26 April 2018

Available online 28 April 2018

Keywords:

Layer-by-layer assembly

pillar[5]arene

Molecular recognition

Chiral interface

Tryptophan isomers

ABSTRACT

The rational design of electrochemical methods for chiral recognition is a focus of research in the detection fields of biomolecules and pharmaceuticals. In this work, a novel, rapid, and convenient electrochemical approach for recognition of tryptophan isomers (L-/D-Trp) was constructed based on the alternating layer-by-layer assembly of water-soluble cationic and anionic pillar[5]arene on a carboxylic graphene (C-Gra) modified glass carbon electrode. Differential pulse voltammetry (DPV) was employed to study the electrochemical recognition of tryptophan isomers. The results reveal that both the peak currents of L-Trp and D-Trp decreased with the increasing of the layer number of the assembled pillar[5]arene, whereas the peak current value's difference between the L-Trp and D-Trp increased with the increased layers, which demonstrated an efficient route for discriminating the L-Trp and D-Trp. The recognition mechanism was studied by ¹H NMR spectra and molecular docking. The host–guest interaction is different for D- and L-Trp due to the opposite steric configurations of the Trp isomers, resulting in significantly discernible electrochemical differences in both peak currents and consequently effective chiral recognition of Trp isomers. This study is the first example that shows the construction of electrochemical chiral separation platform based on pillar[5]arene. This method shows potential applications in many fields, including separation, purification, storage of chiral molecule, drug detection and analysis.

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1. Introduction

The separation of chiral amino acids is especially important in the biochemistry, pharmaceuticals, and medical science [1]. The design and development of convenient methods for differentiating chiral amino acids have been long-term challenges for chemists. Although there are many methods for discrimination of these chiral

amino acids isomers [2,3], such as high-performance liquid chromatography [4], gas chromatography [5], and fluorescence spectroscopy [6], the electrochemical method is an alternative and promising approach for recognition chiral isomers. Because it has enormous merits which overcome the shortcomings of high cost, time-consuming process, and complicated pretreatment. Therefore, searching a nanocomposite or macrocyclic host compound as modifying the electrode materials for recognition and separation the chiral amino acids such as tryptophan isomers is highly important.

The advancement of artificial receptors, especially macrocyclic hosts, has pointed a new avenue out for recognition of chiral compounds. Recently, electrochemical recognition of Trp isomers has been demonstrated in Kong's group by using β -cyclodextrin (β -CD) as a chiral receptor [7–9]. Pillar[n]arenes are new macrocyclic

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hosts, mainly including pillar[5]arene and pillar [6]arene, first reported by Ogoshi and co-workers [10,11]. Compared with other macrocycles such as crown ethers [12,13], cyclodextrins [14–17], calixarenes [18–22], and cucurbiturils [23–26], the pillararenes have much more outstanding advantages, such as easier synthesis, functionalization, and excellent properties of host-guest recognition. The applications of pillararenes such as self-assembly [27–29], supramolecular polymers [30–32], and materials [33–39], have been reported in recent years. However, its application in the recognition of chiral isomers has not been explored. According to the property of cavity size and charge of the pillar[5]arenes from the previous papers [40,41], the different charged pillar[5]arene assembled films may have special interaction to the chiral tryptophan isomers. Therefore, it is necessary and worth to investigate the function of pillar[5]arene in chiral isomers separation.

Herein, we reported a novel electrochemical strategy for discrimination of chiral tryptophan (D-Trp and L-Trp) based on the alternating layer-by-layer (LbL) assembly of multilayer films of water-soluble anionic pillar[5]arene (WP5) and cationic pillar[5]arene (CP5) on a carboxylic graphene (C-Gra) modified glass carbon electrode (GCE) [42,43]. The multilayer films can be obtained by LbL assembly due to the distinct pillar-shaped architecture and alternating charges at two rims of different pillar[5]arenes.

Multilayer films based on the pillar[5]arene can show excellent molecular recognition capability towards guest molecules owing to the intrinsic pores from the pillar[5]arene cavities. As shown in Fig. 1, pillar[5]arene multilayers were constructed by the alternating LbL assembly of cationic (P+) and anionic (P-) pillar[5]arenes on the negatively charged C-Gra modified-GCE. Firstly, the C-Gra modified-GCE was immersed in an aqueous solution of P+ for 1.0 h to introduce P+ molecules onto the anionic surface, washed with a large amount of water to remove excessive unmodified P+ molecules, and dried for 1.0 h at room temperature to obtain the cationic monolayer (1L). Secondly, 1L was immersed in an aqueous solution of P- for 1.0 h to introduce P- molecules onto 1L, washed with a large amount of water, and dried at room temperature to give the bilayer with an anionic surface (2L). Multilayer films (nL, n is the number of deposited layers) were obtained by repeating the alternating assembly steps in P+ and P- solutions. Differential pulse voltammetry (DPV) was employed to study the

electrochemical recognition of tryptophan isomers. The results implied that both the peak currents of L-Trp and D-Trp decreased with the increasing of the layer number of the assembled pillar[5]arene, whereas the peak current value's difference between the L-Trp and D-Trp increased with the increased layers. These results provided an efficient route for discriminating the L-Trp and D-Trp.

2. Materials and methods

The experimental procedures are provided in Supporting Information.

3. Results and discussion

3.1. Characterizations of the CP5@C-Gra material

The structural feature of C-Gra and CP5@C-Gra were characterized via SEM as shown in Figs. S5A and B. The result indicates that the C-Gra consist of randomly aggregated thin and wrinkled sheets, and the morphology of CP5@C-Gra is similar to that of C-Gra. However, it is difficult to discriminate the CP5 molecules on the SEM, thus we used the FTIR and TGA to further characterize the complex of CP5@C-Gra. The FTIR spectra of C-Gra, CP5 and CP5@C-Gra were shown in Fig. S5C. The FTIR spectrum of C-Gra displays the stretching vibrations of —OH (3440 cm^{-1}), $\text{C}\equiv\text{C}$ (1630 cm^{-1}) conjugation, and O—H bending vibrations (1405 cm^{-1}) [44]. As for CP5@C-Gra, the FTIR spectrum exhibit the typical CP5 absorption features at 1500 cm^{-1} of the phenyl plane bending vibrations, which indicates that CP5 molecules have been introduced to the C-Gra. As shown in Fig. S5D, from the TGA results, we found that the pyrolysis of the remaining oxygen-containing functional groups in C-Gra resulted in approximately 42 wt% loss in mass at a temperature of approximately 450°C . The mass loss of the CP5@C-Gra reached about 68 wt% when the temperature was 450°C . The mass loss caused by the decomposition of CP5 was calculated to be 26 wt% by deducting the mass loss of the C-Gra, revealing that 26 wt% CP5 was loaded on the C-Gra. XPS analysis was used to characterize the composite CP5@C-Gra. As shown in Fig. S6, the significant N 1s peak is observed for the resultant CP5@C-Gra, which comes from the —NH_3^+ of CP5, further indicating the

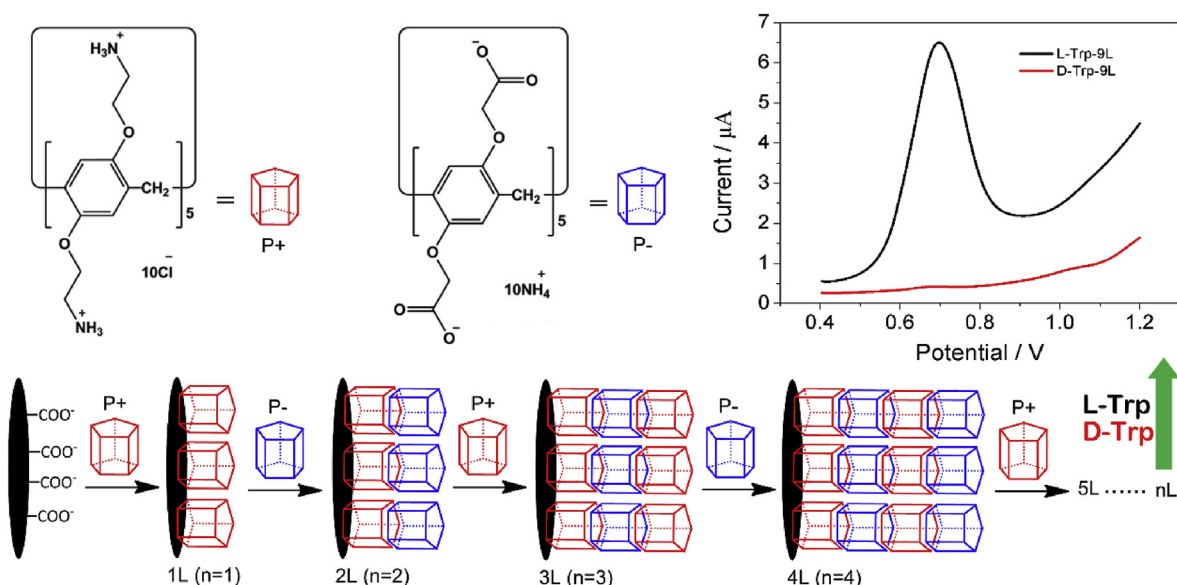


Fig. 1. Schematic illustrating the LbL assembly of anionic/cationic-pillar[5]arenes multilayer films and the recognition of Trp isomers.

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