Inorganic Chemistry Communications 70 (2016) 22–26

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

A novel artificial metallocyclodextrins polymer: Synthesis and photoactive properties in imprinting of molecular recognition

Yantao Qi [a], Jie Tang [a], Pingang He [b], Fan Yang [a,*]

[a] Shanghai Engineering Research Center of Molecular Theraputics and New Drug Development, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, SCME, East China Normal University, Shanghai 200062, China
[b] Department of Chemistry, SCME, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 6 March 2016
Received in revised form 13 May 2016
Accepted 15 May 2016
Available online 19 May 2016

Keywords:
Cyclodextrins
Metallocyclodextrin
Host-guest recognition
Molecular imprinting
Electrochemiluminescence

ABSTRACT

A novel metallocyclodextrins polymer was synthesized as artificial polymeric receptor. The polymer showed excellent adsorption stability on the surface of glassy carbon electrode. More interestingly, the receptor could be prepared by using molecular imprinting technique conveniently and the resulting polymer template exhibited excellent selectivity. These attractive characteristics will be significant for constructing ultrasensitive ECL sensors.

A novel metallocyclodextrins polymer was successfully developed and it exhibited excellent sensitivity and selectivity in the imprinting of molecular recognition for drug molecules based on electrochemiluminescence (ECL) analysis.

Over the years cyclodextrins (CDs) have been proven to be very efficient host molecules for binding of a large number of organic guest molecules in aqueous solution [1]. However, monomeric cyclodextrin hosts are usually not selective in their choices of guest molecules [2]. Nevertheless, incorporation of supramolecular moieties into a polymer could enhance the selectivity, especially when combined with molecular imprinting method [3]. In addition, the incorporated polymers would be endowed with improved physicochemical properties such as stronger rigidity and lower solubility [4], and photoactive properties such as fluorescence and electrochemiluminescence. Electrochemiluminescence (ECL) is a type of luminescence that arises from the high-energy electron-transfer reaction between electro-generated species at electrode surface. As a versatile detection method, ECL has been receiving increasing attention in analytical chemistry due to its unique advantages such as rapidity, low cost, simplified optical set-up, low background signal, and high sensitivity [5]. ECL has also been combined with molecular imprinting technique, which not only improved the selectivity of ECL analysis, but also effectively enhanced the detection sensitivity of the host–guest recognition [6].

Recently, we have reported a supramolecular metallocyclodextrin constructed from an inclusion complex of β-cyclodextrin and bipyridines by coordination with ruthenium (III) ion. The supramolecular metallocyclodextrin exhibited strong fluorescence and electrochemiluminescence as well as excellent quenching efficiency because of their good performance in host–guest recognition [7].

Herein, we report a novel artificial metallocyclodextrins polymeric receptor for a variety of large guest molecules. Preliminary investigation of its fluorescence and ECL characteristics was carried out. Furthermore, molecular imprinting polymer (MIP) based on the compound was constructed by using the molecular imprinting technique and its selectivity to the guests based on host–guest recognition was studied. The polymer was prepared as depicted in Scheme 1.

Complex I was synthesized by Mitsunobu reaction and isolated in 30% yield [8]. Afterwards, compound II was obtained through the coupling of the cyclodextrin derivative with 4′-((benzyloxy)carbonyl)-[2,2′-bipyridine]-4-carboxylic acid by the HATU and DIPEA promoted acid-amine condensation in DMF. Subsequently(yield 73%), mixing compound II with a slight excess of complex *cis*-Ru(bpy)$_2$Cl$_2$ in ethanol/water under refluxing, followed by deprotecting the amino and carboxyl groups respectively, furnished the crude compound III that was purified through a C-18 reversed-phase column(yield 39% in three steps). Its structure was confirmed by 1H NMR and MALDI-TOF MS analysis. Last, the self-condensation of compound III afforded the polymer IV. However, prolonged reaction time was needed due to the steric hindrance of the bulky groups. Actually, the self-condensation reaction completed after being stirred for five days, and an orange precipitate

* Corresponding author.
E-mail addresses: pghe@chem.ecnu.edu.cn (P. He), fyang@chem.ecnu.edu.cn (F. Yang).

http://dx.doi.org/10.1016/j.inoche.2016.05.006
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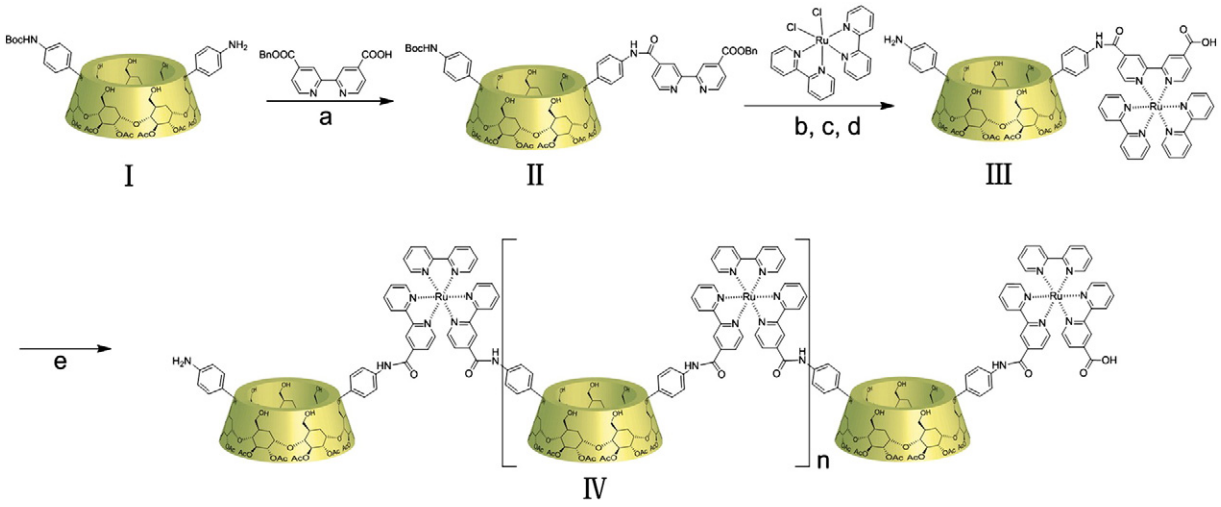

Scheme 1. Synthesis of compound IV. Reagents and conditions: (a) HATU and DIPEA in anhydrous DMF under N_2, 12 h at rt; (b) $Pd(OH)_2$ in MeOH, under H_2, 2 h at rt.; (c)EtOH/H_2O, reflux overnight under N_2; (d) TFA in DCM, 12 h at 5 °C; (e) HATU and DIPEA in anhydrous DMF under N_2, 5d at rt.

was isolated in 90% yield by solidifying in ether. The polymer is characterized by 1H NMR and MALDI-TOF MS. As shown in Fig. 1a, molecular weight of the β-CD polymer increases in multiples, and the aberration values of the adjacent peaks are related to the molecular weight of the monomer, indicating at least six molecules of the monomer were polymerized in the polymer IV.

Further characterization was performed by scanning atomic force microscopy (AFM) at concentration of 1.0×10^{-5} M, which gave an insight about the size and shape of the polymer constructed from bipyridine ruthenium and β-cyclodextrin. The image (Fig. 1b) presents a phenomenon of polymer cluster and the resulting network structure at high concentration, verifying the structural characteristic of polymer IV.

To investigate the photoactive properties of the β-CD polymers, its fluorescence (Fig. 2a) upon excitation in their metal–ligand charge transfer (MLCT) band was monitored and compared with that of the monomer III. Complex III and IV exhibited an MLCT absorption at 470 nm and an emission with the maximum at 655 nm and 661 nm, respectively. This red shift phenomenon may come from the electron-withdrawing effect of the amide group that forms a bridge to link each monomer [9]. Furthermore, compared with compound III, the reduce in the fluorescence intensity of IV was attributed to the greater steric hindrance of cyclodextrins after forming one huge rigid structure.

In contrast to fluorescence, ECL detection method has higher sensitivity and thus allows lower sample concentration [10]. We investigated the luminescence behavior of III and IV by ECL and the result is shown in Fig. 2b. The ECL intensity of the two compounds showed the same trend as their fluorescence characteristic. This trend may still result from the steric hindrance of cyclodextrin that decreases the electron-transfer rate of the luminescent center on the surface of the electrode [11].

Based on the above ECL property of these compounds, we further studied their luminescence behavior by host-guest recognition. As shown in Fig. 3a and b, before and after the addition of the guest, significant difference of the absolute (415.3 for III, 7219.2 for IV) and relative (18.8% for III, 26.8% for IV) ECL intensity of the two compounds was observed, suggesting that there was a distinct ECL quenching effect for both products. The highly efficient quenching effect of ECL may be not only from electron transfer but also from the strong binding between β-CD and the guest. In the polymer, cyclodextrins were connected via a spacer, and thus cooperative interactions between the neighboring cavities would occur, leading to significantly stronger binding activity than that from the monomeric species. These characteristics of the multiruthenium metallocyclodextrins enable it to be suitable for constructing ultrasensitive ECL sensors.

In addition to their luminescent characteristics, we also investigated the adsorption stability of β-CD polymers on the glassy carbon electrode

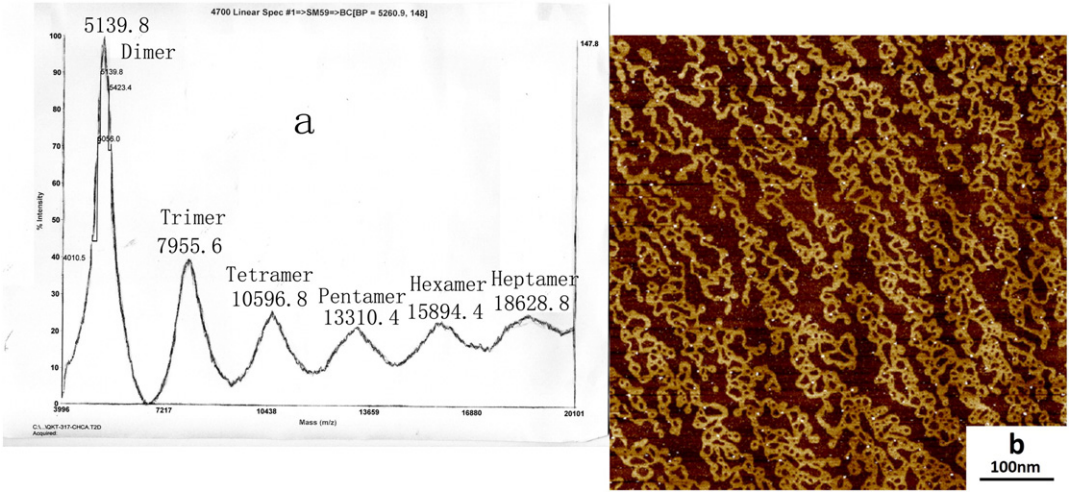

Fig. 1. (a) MALDI-TOF MS spectra of polymer IV. (b) AFM images of compound IV.