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Multi-functionality of cationic porphyrin-immobilized polymeric microspheres prepared by synchronously synthesizing and immobilizing pyridylporphyrin on surfaces of polymeric microspheres

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ABSTRACT

Pyridylporphyrin (PyP) was synchronously synthesized and immobilized on the surfaces of crosslinked polystyrene microspheres (CPS microspheres) via an Adler reaction between solid–liquid phases, resulting in PyP-immobilized microspheres, PyP-CPS microspheres. Then the cationic porphyrin-immobilized microspheres, MPyP-CPS microspheres ("M" represents methyl group that comes from iodomethane), was prepared via the quaternization reaction of PyP-CPS microspheres with iodomethane as reagent. In the current work, the efficiency of the above route to immobilize pyridylporphyrin PyP on CPS microspheres was first researched by a comparison method, and then the multi-functionality of the cationic porphyrin-immobilized microspheres MPyP-CPS were mainly tested and examined from many aspects. The investigation results show that: (1) the above route to immobilize pyridylporphyrin on the surfaces of CPS microspheres is highly efficient, and the immobilization amount of PyP on CPS microspheres can get up to about 0.2 mmol g^{-1}; (2) the cationic porphyrin-immobilized microspheres MPyP-CPS are a kind of multifunctional polymeric microspheres because of their special surface structure, and they can be used to construct different host-guest systems, resulting in many applications. MPyP-CPS microspheres can used as triphase-transfer catalysis in organic synthesis, can coordinate to transition metal ion to form immobilized metalloporphyrin catalysts to be used in the green catalytic oxidations, can be used as support of heteropoly acid to prepare heterogenous heteropoly acid catalyst, and MPyP-CPS microspheres also can used as solid adsorbent in the removal of toxic chromate ion from water medium. In a word, the polymeric microspheres supporting cationic porphyrin, MPyP-CPS microspheres, will have vast application prospect in various fields because they have special surface chemical structure.

1. Introduction

Porphyrins and metalloporphyrins are an important large class of macrocycle compounds, and exist extensively in nature and living bodies. The unique chemical structure of porphyrins with a big π-orbital on the carbon–nitrogen framework affords them unusual biological activity and physicochemical property. They can carry and transfer oxygen, transfer electron, catalyze chemical reactions, recognize molecules, have photosensitive activity [1–5], and so on. In present material science, to simulate the structure and function of natural porphyrins and to synthesize various porphyrins and metalloporphyrins with different structures and functions have become a very active study field. Among the great diversity of porphyrins with a specific pattern of substituents, pyridylporphyrins are a class of specific porphyrins in which the pyridine ring is directly attached to the porphyrin core. Pyridylporphyrins and their metal complexes have unique ability to form supramolecular assemblies [6–8]. Besides, the metal complexes of pyridylporphyrins have also special catalytic activity for hydrocarbon oxidation [9,10]. The cationic pyridylporphyrins coming from pyridylporphyrins are also a class of interesting substances. Their metal complexes also can be used as catalyst in hydrocarbon oxidations [11,12]. Besides, the cationic pyridylporphyrins coming from pyridylporphyrins also can form many host–guest systems because of their special structure in which more cations are contained, and these host–guest systems can be used in biology, medicine, molecular recognition and sensors [13–16]. The host–guest chemistry and applications of cationic pyridylporphyrins remain to be further developed.

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In recent years, porphyrin and metalloporphyrin unit-containing polymeric materials, linear-type or crosslinked polymer materials, are an important class of functional materials, they have attracted much attention and have been used in many field [17–19]. In particular, in catalytic organic synthesis, it is an attractive research area to immobilize porphyrin onto polymeric microspheres to prepare heterogeneous metalloporphyrin catalysts [20,21]. A great effort has been contributed to immobilizing various porphyrins and metalloporphyrins on polymeric microspheres or films [22–25]. There are basically two ways to immobilize porphyrins and metalloporphyrins on polymeric microspheres. One is the crosslinking copolymerization of the monomer containing porphyrin unit and other monomer, and the other one is bonding porphyrins onto the matrix microspheres. Because it is more difficult to synthesize porphyrin-containing monomers, usually the second route is widely used to realize the immobilization of porphyrins and metalloporphyrins on polymeric microspheres [24,26–28]. Even so, actually, the second route suffers some disadvantages from the complicated preparations of active porphyrins and polymer supports to create the connection between the support polymers and porphyrins as well as from the tedious preparation, separation and purification process of small-molecular porphyrins. By the way, among the various polymers that can be used for immobilizing porphyrins, crosslinked polystyrene (CPS) microspheres and its derivatives are often employed as solid matrixes, due to their cheapness, ready availability, mechanical robustness, chemical inertness and facile functionalization [29,30]. Taking the above disadvantages of the second route into consideration, it is important to adopt new strategies and design new routes to realize the immobilization of porphyrins and metalloporphyrins with CPS microspheres as matrix so that the porphyrin and metalloporphyrin-immobilized functional polymer microspheres are further developed to meet the needs of various science and technology fields.

About the immobilization of pyridylporphyrins on polymer materials including the immobilization of metallo-pyridylporphyrins and cationic pyridylporphyrins, in general, the second route described above is adopted, namely, pyridylporphyrin species are first synthesized, separated and purified, and then are supported on the resin matrixes by right of the quaternization reaction between the pyridyl group and the alkyl halide group of the resin matrixes [31,32]. It is obvious that in this process, the synthesis, separation and purification of small-molecular pyridylporphyrins are all involved, and the process to immobilize pyridylporphyrins on polymer materials is very backward.

In our previous study, a new and simple route to immobilize *meso*-tetra-4-pyridylporphyrin (shorted as pyridylporphyrin, PyP) on CPS microspheres was designed [33], and it was to synchronously synthesize and immobilize pyridylporphyrin on CPS microspheres, obtaining the functionalized polymeric microspheres PyP-CPS as well as cationic pyridylporphyrin-immobilized microspheres, MPyP-CPS microspheres (“M” came from the cationic reagent iodomethane). In this designed reaction process, 4-pyridylaldehyde (PyAL) was first bound onto the surfaces of chloromethylated crosslinked polystyrene microspheres (CMCPS microspheres) via the quaternization reaction, forming the modified microspheres PyAL-CPS, and then synchronously synthesizing and immobilizing pyridylporphyrin (PyP) on CPS microspheres were carried out via an Adler reaction between solid–liquid phases, in which, PyAL-CPS microspheres, pyrrole and 4-pyridylaldehyde in a solution were used as co-reactants, resulting in PyP-immobilized microspheres, PyP-CPS microspheres. In this method, the tedious synthesis, separation and purification process of small-molecular pyridylporphyrin species were completely avoid, and at the same time, the immobilization process of small-molecular pyridylporphyrin species was also omitted. By adopting the new route, the total immobilization process of PyP was simplified greatly.

In this paper, we report the new research results. In the further investigation, we found the following facts: (1) the immobilization amount of pyridylporphyrin on the porphyrin-supporting microspheres is much higher than that of phenyl porphyrins (PP) on the porphyrin-supporting microspheres, which was also prepared by using the same way, namely synchronously synthesizing and immobilizing phenyl porphyrin on CPS microspheres, but then one of the reactants in the solution was not 4-pyridinealdehyde, but was benzaldehyde. This fact indicates the high efficiency of the above route to immobilize pyridylporphyrin, PyP, on CPS microspheres, and this character is largely determined by the nature of the former reaction system. (2) The prepared cationic pyridylporphyrin-immobilized microspheres, MPyP-CPS microspheres, are multi-functional owing to their special surface structure, and they can be used to construct different host-guest systems, leading to many applications. In this paper, the high-efficiency character of this new route is first discussed through a comparison way, and then the multi-functionality of MPyP-CPS microspheres is mainly investigated. This highly efficient route to synthesize and immobilized pyridylporphyrins and cationic pyridylporphyrins on polymeric microspheres is quite valuable and significant in many science and technology fields, and the multi-functional microspheres MPyP-CPS will have the extensive application prospect.

2. Experimental

2.1. Materials and instruments

Crosslinked polystyrene microspheres (CPS, Changzhou Tenlong Chemical Ltd., Province Jiangsu, China) were received, and they were about 0.32–0.45 mm in diameter and had a crosslinking degree of 4%; chloromethylated crosslinked polystyrene microspheres (CMCPS microspheres) were self-synthesized via chloromethylation reaction of CPS microspheres with 1,4-bis (chloromethoxy) butane (BCMB) without carcinogenic toxicity as chloromethylation reagent [34], and the used CMCPS microspheres in this work had a chlorine content of 14 wt%, i.e. 0.349 mol/100 g; 4-pyridinealdehyde (PyAL, Jinan Dexin Biotechnology Co., Ltd., Jinan City, China) was of analytical grade; Pyrrole (Fenke Chemical Reagent Company, Shanghai, China) was of analytical grade; propionic acid (Tientsin Bodi Chemical Co., Ltd., Tientsin City, China); dimethyl sulfoxide (DMSO, Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade; benzaldehyde (Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade; Other chemicals were all commercial reagents with analytical pure and were purchased from Chinese companies.

The instruments used in this study were as follows: a Perkin–Elmer 1700 infrared spectrometer (FTIR, Perkin–Elmer Company, USA) was used for FTIR analyses, a Unic UV/Vis-2602 spectrophotometer (Unic Company, USA) was used for determining the electronic absorption spectrum of the product microspheres, and a calorimetric meter of oxygen-bomb type made in China was used for analysis of chlorine element content of the intermediate microspheres with Volhard method.

2.2. Preparation of functional microspheres PyP-CPS and MPyP-CPS

By referring to Ref. [33], the synchronic synthesis and immobilization of pyridylporphyrin on CPS microspheres was performed