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Self-assembly of new dendrimers basing on strong π-π intermolecular interaction for application to protect copper

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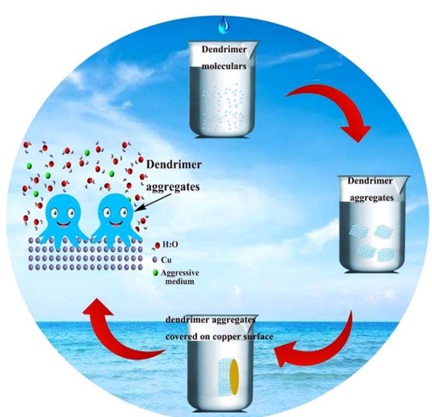
HIGHLIGHTS

- Novel target amphiphilic dendimer including triple triazols was synthesized.
- Self-assembly dendrimer aggregates were obtained basing on π-π interactions.
- Chemical adsorption of the dendrimer aggregates on copper was demonstrated.
- Corrosion inhibition of the dendrimer aggregates for copper were determined.

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents a novel amphiphilic target dendrimer including triple triazol segments and a linear molecule containing single triazol part. Self-assembly dendric molecular aggregates are produced basing on strong π-π interactions for protecting copper in 3 wt% NaCl solution. In contrast, the prepared linear molecule cannot form molecular aggregates. Scanning electron microscopy, transmission electron microscopy and dynamic light scattering are employed to characterize the morphologies and sizes of the yielded dendrimer aggregates. Chemical adsorption evidences of the dendrimer aggregates on the studied copper specimens are acquired by Fourier transform infrared spectroscopy, Raman spectroscopy as well as X-ray photoelectron spectroscopy. Corrosion inhibition efficiencies of the dendrimer aggregates for the surveyed copper specimens in NaCl solution are determined by electrochemical methods and weight loss experiments. The results suggest that the dendrimer aggregates could adsorb on the investigated copper specimen surfaces efficiently to achieve anticorrosion effects in 3 wt% NaCl solution.

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1. Introduction

Suppression of metal corrosion in an aggressive environment is one of the significantly important tasks in the chemical engineering field [1,2]. For instance, copper has been used extensively for industrial applications owing to its electrical and thermal conductivities, mechanical workability and resistance to atmospheric and chemical agents. However, copper is susceptible to corrosion in sea water, which is applied in industrial manufacturing instead of clean water. In aqueous chloride environment, copper corrosion products have been identified as a few main species: Cu_2O, CuCl, $CuCl_2^-$ [3,4]. As long as copper corrosion occurs in aggressive aqueous chloride solution, it is easy to form a clathrate Cu(I)-organic inhibitor film due to the chelation interaction between the organic inhibitor molecules containing heteroatoms (such as O, N, S and P) and d orbitals of copper atoms, which is considered as an efficient approach to alleviate metal corrosion [5,6].

Hence, chemical coordination between organic inhibitor molecules and copper ions could determine protection film qualities as well as corrosion inhibition properties for a corroded metal. It is known that copper ions present metal organic complexes with polydentate ligands [7]. As a consequence, more heterocyclic parts in an organic inhibitor molecular skeleton could yield stronger chelation with copper ions, and thus a tougher adsorption film on copper surface could be produced.

A number of studies have documented applications of N-heterocyclic molecules including benzotriazole [8], azoles [9], pyridine derivatives [10], pyrazole derivatives [11] and benzimidazole derivatives [12] as organic corrosion inhibitors for copper in NaCl solution. The results suggest that it could be not easy for single N-heterocyclic organic inhibitors to produce strong chemical interaction on copper surface for forming neat compact adsorption protection films.

Some organic surfactants, such as alkyl dimethylisopropylammonium hydroxide cationic surfactants that yielded self-assembly molecular aggregates to adsorb on metal surface through physical adsorption, were employed as the corrosion inhibitors [13]. On the other hand, it could be more possible to yield better organic inhibitors adsorbed film on copper surface by chemical adsorption as compared with physical adsorption.

In this study, we propose to use organic molecular self-assembly aggregates to strengthen chemical coordination interaction with copper ions. In other words, such “super molecules” could carry a large number of chelation centers such as N-heterocycles. So, more robust adsorbed films could be formed by chemical adsorption. However, it is a challenge to form molecular aggregates of small organic inhibitors via self-assembly due to the lack of strong π-π interaction as well as hydrogen bonding.

In order to yield molecular aggregates of organic inhibitors via self-assembly, this work proposes to use dendric molecules to increase the intermolecular interactions. However, owing to steric hindrance of large dendrimers, it is hard for dendric molecules to undergo molecular aggregation. In this work, planar amphiphilic dendrimers carrying multiple π bonds are employed to form molecular aggregates that include a large amount of N-heterocyclic centers (Scheme 1). In this manner, organic aggregates-based metal complexes adsorbed onto a copper surface through chemical chelation could yield good protective films.

Therefore, one of main concerns of this article is to utilize strong π-π interaction to yield self-assembled dendrimer aggregates carrying thousands of N-heterocyclic rings. The yielded aggregates could coordinate with copper ions effectively to form stiff adsorption films on copper surface in NaCl solution. To the best of our knowledge, there are few studies on protective films yielded by organic aggregates that could react with the copper surface through chemical interactions.

In order to further understand dendrimer aggregates as corrosion inhibitors, this study also prepares the corresponding linear molecule containing single N-heterocyclic ring, which is also used as a corrosion inhibitor (Scheme 1). It is further shown that this inhibitor molecule could not yield organic aggregates because of weak π-π interaction.

The prepared dendrimer aggregates are characterized by scanning electron microscopy, transmission electron microscopy as well as dynamic light scattering. Chemical adsorption of the studied dendrimer aggregates on the studied copper specimen surface is further demonstrated by Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy as well as X-ray photoelectron spectroscopy (XPS).

This work further investigates the corrosion inhibition properties of the studied dendrimer aggregates as well as the corresponding linear inhibitor for copper in 3 wt% NaCl solution by a variety of means including polarization curves, electrochemical impendence spectroscopy (EIS) and weight loss analyses. The adsorption mechanism of the studied aggregates on the surveyed copper surface is further analyzed by Langmuir isotherm plot.

2. Experimental procedures

2.1. Materials and characterizations

The new studied target molecules of 4,4′,4″-((2*E*,2′*E*,2″*E*)-3,3′,3″-(benzene-1,3,5-triyl)-tris-(acryloyl))-tris-(2-(2*H*-benzo[*d*][1,2,3]-triazol-2-yl)-phenyolate)-potassium (**TTP**) and potassium 2-(2*H*-benzo[*d*][1,2,3]-triazol-2-yl)-4-cinnamoylphenolate (**PTC**) were prepared through multi-step synthetic routes in our laboratory (Scheme 1), which used the starting materials provided by Sigma-Aldrich Chemical Corporation. All organic solvents reagents were of analytical grade (99.5%) supplied by Acros Chemical Corporation.

Bruker nuclear magnetic resonance (NMR) apparatus (600 MHz) was used to determine ^{1}H and ^{13}C NMR spectra of the intermediates and targets (Scheme 1) in standard NMR tubes at 303 K, which employed tetramethylsilane (TMS) as an internal reference zero point of chemical shift of NMR peak. Fourier transform infrared (FT-IR) spectroscopy of the samples was measured by Fourier transform infrared apparatus of Nicolet iS50 of Thermo Scientific. High-resolved mass spectra of the samples were conducted by Acquity SQD from WATERS using the electro spray ionization (ESI) technique. Elemental analysis of the samples was performed by a CE440 elemental analysis meter from Exeter Analytical Inc. The melting points of the samples were carried out by a Beijing Fukai melting point apparatus.

The working electrodes were cut from a sheet copper (10 cm × 10 cm × 1 cm, 99.99% copper content). Besides, the copper specimens for weight loss measurements were processed into the metal samples with 3.0 cm × 1.5 cm × 1.5 cm dimensions mechanically. The emery papers (400, 800, 1600, 2000, 3000 grits) were employed to grind the studied copper specimens surfaces.

2.2. Synthesis of the target molecules

The detail description of synthetic routes as well as chemical structural characterizations of the target molecules including ^{1}H and ^{13}C NMR spectra, high resolution mass spectra, FT-IR spectra and elemental analysis are shown in Supplementary materials.

2.3. Formation of molecular aggregates of dendric inhibitors and preparation of the studied copper electrodes with protection films

Fig. 1 shows the diagrammatic drawing of the entire experimental process of this section. A stock solution of **TTP** in organic solvents such as THF (1×10^{-3} mol/L) was titrated promptly by using a micro-syringe into a THF/NaCl solution mixture (THF volume fraction was varied from 20% to 80%) with vigorous stirring at 303 K. Sharp variations of the solvent polarities could lead to the formation of **TTP** molecular aggregates. It is generally thought that organic molecular aggregation in mixed organic solvents/water solution arises from two primary factors, (a) the sharp variations of the solvent polarities could provide a certain amount of tension for molecular aggregation; and (b) dissolving