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Designing and fabricating of single and double alkyl-chain indazole derivatives self-assembled monolayer for corrosion inhibition of copper

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ABSTRACT

Two novel long alkyl-chain indazole derivatives namely, 1-dodecyl-1H-indazole (DI), N,1-didodecyl-1H-indazol-5-amine (DDIA), were synthesized and fabricated on copper surface. Comprehensive characterizations were used to evaluate the appearance and structural properties of studied SAMs, implying a more stable and hydrophobic film of DDIA than IA. The anticorrosion ability of the SAMs was investigated by electrochemical methods allied to an immersion test, which suggest that DDIA-SAMs harbor more superior inhibition performance than IA ones. Besides, Fukui functions indicates that N2 and N10 in DDIA molecule are likely to form coordinate bonds with Cu atoms, whereas N2 in DI is the active site during absorption process.

1. Introduction

Self-assemble monolayers (SAMs) preventing corrosion are important for metallic materials in many industries ranging from electronic and engineering to medical fields owing to its fast film-forming, high coverage, few defects, favorable efficiency, and low cost [1–5]. SAMs are compact and highly ordered molecular layers formed by the spontaneous adsorption process of organic molecules on the substrate via covalent bonds [6,7]. Numerous organic compounds such as thiol [8], dithiol [9], fatty acid [10–12], and some other heterocyclic compounds containing N [13,14], S [15], atoms have been employed as adsorptive inhibitors for metal corrosion. Among these compounds, the organics containing a head group of N-heterocyclic and a long-chain tail have attracted significant attention due to their excellent performance and environment friendly in recent years [16,17]. However, despite obtaining some achievement of the N-heterocyclic SAMs for metal corrosion, the investigations normally involve in the influence of only chain length and head group on inhibition effect [18–20]. To the best of our knowledge, the role of single and double alkyl-chain tails on inhibition behavior has been barely reported.

As known that copper can be corroded severely in an ocean environment owing to the presence of abundant chloride ions, which will deteriorate its appearance and performance simultaneously [21]. Thus, it is of great significance to explore available methods to harness copper corrosion. Our previous research firstly indicates that 1H-indazole (IA) and 5-amino-1-H-indazole (5-AIA) can adsorb on copper surface to suppress the corrosion of copper effectively [22]. It is well known that the compounds containing long alkyl chain are beneficial to generate SAMs with a superior inhibition ability. Therefore, in this work, single and double long-chain indazole derivatives based on IA and 5-AIA were synthesized and then fabricated on copper surface, respectively. Field emission scanning electron microscope (FE-SEM), atomic force microscope (AFM), optical microscope (OM), Energy-dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and contact angle (CA) meter were employed to evaluate the appearance and structural properties of these SAMs. After that, the corresponding inhibition capacities of studied SAMs were captured by using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization measurement as well as an immersion test. Finally, the relevant inhibition mechanism was elucidated by quantum chemical calculation at the atomic level. The understanding of the correlation between the corrosion resistance capacity and inhibitor structure may have important implications in design and preparation of outstanding SAMs.

2. Experimental section

2.1. Materials

Testing specimens were cut from a pure copper sheet (99.99 wt%, Aldrich Corporation). The copper specimens were sealed in epoxy, leaving a 1 cm^2 area exposed to the aggressive solution for electrochemical tests. Sodium chloride (NaCl, 99.5 wt%, Chongqing Chuandong Chemical Ltd), absolute ethanol (C_2H_5OH, 99.7%, Chongqing Chuandong Chemical Ltd), potassium 2-methylpropan-2-

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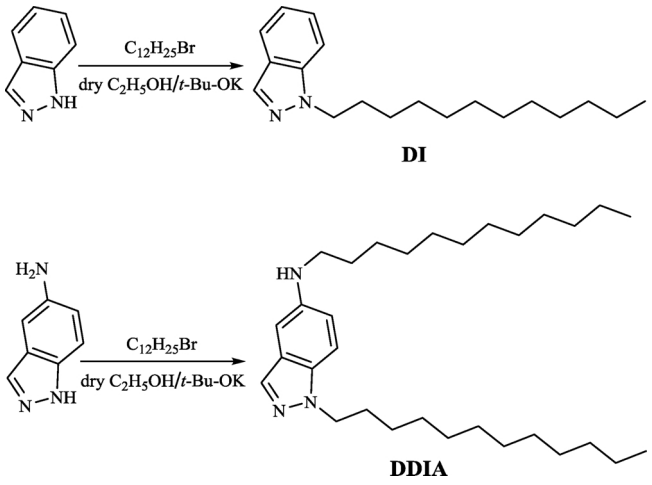

Fig. 1. The synthetic routes of the target inhibitors.

olate (t-Bu-OK, 98.0 wt%, Tansoole Corporation), 1-Bromododecane ($C_{12}H_{25}Br$, 98.0 wt%, Tansoole Corporation), 1H-Indazole (99.0 wt%, Aladdin Corporation), and 5-amino-1H-indazole (98.0 wt%, Aladdin Corporation) were used as received.

2.2. Synthesis of DI and DDIA

1-dodecyl-1H-indazole (DI) and N,1-didodecyl-1H-indazol-5-amine (DDIA) were synthesized in our laboratory through some simple synthetic routes as shown in Fig. 1. 1H-Indazole, 1-Bromododecane and potassium 2-methylpropan-2-olate were added into dry ethanol with a mole ratio of 1:1.2:1. The mixture was heated at 80 °C with stirring for 12 h. After the solvent was removed in vacuum, the crude product was purified by silica gel column chromatography with ethanol/cyclohexane (1/5, V/V) as the eluent to obtain the pure products with yields 89–93%. Similarly, 5-amino-1H-indazole, 1-Bromododecane and potassium 2-methylpropan-2-olate were added into dry ethanol with a mole ratio of 1:2.2:1. The mixture was heated at 80 °C with stirring for 12 h. After the solvent was removed in vacuum, the crude product was purified by silica gel column chromatography with ethanol/cyclohexane (1/5, V/V) as the eluent to obtain the pure products with yields 67–72%.

Fig. 2 gives the typical 1H NMR spectra of synthesized compounds. **DI**, 1-dodecyl-1H-indazole, oil product (yield 96%). ^{1}H-NMR (D^6-DMSO, 600 MHz) δ (ppm): 8.007 (s, 1H, Ar−H), 7.722-7.708 (d, J = 8.4 Hz, 1H, Ar−H), 7.557-7.543 (d, J = 8.4 Hz, 1H, Ar−H), 7.189-7.164 (t, J = 7.5 Hz, 1H, Ar−H), 6.994-6.970 (t, J = 7.2 Hz, 1H, =CH), 4.377-4.354 (t, J = 6.9 Hz, 2H, N−CH_2), 1.788-1.764 (m, 2H, −CH_2−), 1.241-1.183 (m, 18H, −CH_2−), 0.837-0.806 (m, 3H, −CH_3). **DDIA**, N,1-didodecyl-1H-indazol-5-amine, (yield 75%). ^{1}H-NMR (D^6-DMSO, 600 MHz) δ (ppm): 7.704 (s, 1H, Ar−H), 7.230-7.215 (d, J = 9 Hz, 1H, Ar−H), 6.794-6.779 (d, J = 9 Hz, 1H, Ar−H), 6.569 (s, 1H, Ar−H), 4.547-4.523 (t, J = 7.2 Hz, 2H, N−CH_2), 4.044 (s, 1H, −NH), 2.947-2.923 (t, J = 7.2 Hz, 2H, N−CH_2), 1.561-1.512 (m, 2H, −CH_2−), 1.354-1.209 (m, 38H, −CH_2−), 0.830-0.807 (m, 6H, −CH_3).

2.3. Preparation of SAMs on copper surface

The copper samples were ground with various grades of emery paper up to 3000 grit, then further sonicated continuously with alcohol and ultrapure water for 20 min to remove all contaminants, and finally dried with the flow of nitrogen gas. The test samples prepared as above were dipped in a 5 mM DI or DDIA ethanol solution for various self-assembly time (0.5 h–2 h) at 298 K, taken out and rinsed with ethanol followed by ultrapure water to remove physisorbed molecules. Besides, copper samples also treated by different concentrations (1, 2, 5 mM) of DI or DDIA ethanol solution at a same self-assembly time of 2 h.

2.4. Surface characterization

The morphology of copper samples modified with 5 mM DI and DDIA for 2 h at 298 K were observed by field emission scanning electron microscope (FE-SEM, JEOL-JSM-7800 F, JEOL Ltd., Japan) at high vacuum, atomic force microscope (AFM, MFP-3D-BIO, Asylum Research, America) using tapping mode, and optical microscope (OM, Axio Scope A1, ZEISS, Germany). Energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were used to investigate the composition and structure of the SAMs. XPS analysis was conducted on an PHI 5700 spectrometer with an Al Kα anode (1486.6 eV). The surface wettability was evaluated by a contact angle meter (Data-physics OCA20, Germany) under static condition.

2.5. Electrochemical determination

The electrochemical measurements were performed with CHI 760E electrochemical station. A three-electrode system was used, with a bare copper specimen, DI-modified or DDIA-modified copper specimen as the working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode (RE), and a 2 cm × 2 cm platinum plate as the counter electrode (CE). All of the reported potentials in this study were measured in regard to the SCE. At first, the WE was dipped in the test media for 1 h at the open circuit potential (E_{OCP}) to gain a stationary

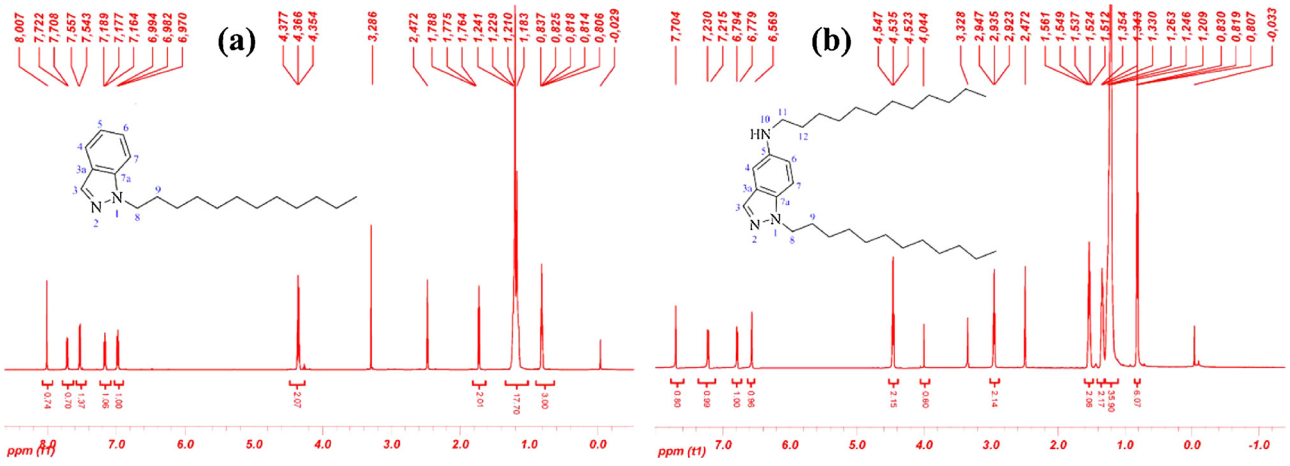

Fig. 2. The representative 1H NMR spectra of (a) DI and (b) DDIA.