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A steroid–coumarin conjugate for cascade recognition of copper ion and dihydrogen phosphate: Microstructural features and IMPLICATION logic gate properties

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ABSTRACT

A fluorescent probe 1 based on deoxycholic acid-coumarin was synthesized, and its cascade recognition for Cu^{2+} ion, $H_2PO_4^-$ ion, and amino acids were investigated by spectroscopic techniques and microstructural features, respectively. It exhibits the high selectivity toward Cu^{2+} ion by forming a 1:2 complex with 1,2,3-triazole motif as the binding sites, and the resulting [$1{\cdot}Cu^{2+}$] complex shows the turn-on recognition ability in fluorescence for $H_2PO_4^-$ ion and amino acids. Consequently, an IMPLICATION (IMP) logic gate has been generated by using Cu^{2+} ion and $H_2PO_4^-$ ion as inputs and the emission of 1 as the output signal, respectively. This research may enrich the field of multi-functional chemosensors in natural products.

1. Introduction

Molecular and ionic recognition has drawn great attentions in the past decades due to its crucial role in biological, medical, environmental, and chemical fields [1]. Although it is not difficult to obtain the single selective chemosensors, the reports on multi-functional ones which allow the differential response to multiple analytes, such as dual-responsive receptors [2], ion-pair sensors [3], and relay recognition systems [4], are still rare. Inspired by the requirement of developing multi-functional chemosensors, a novel concept named as 'cascade recognition' has emerged recently, in which the second analyte is detected by the coordinative complex of the host molecule and the first analyte [5]. Obviously, such chemosensors in cascade recognition are recyclable, cost effective, and would be highly desirable from the viewpoint of practical applications [5h]. For example, Rao and co-workers reported a calix [4] arene-based sensor for cascade recognition of Ag^+ ion and cysteine ratiometrically [5c]. Li and co-workers developed a nanochannel for cascade recognition, which can selectively chelate Zn^{2+} ion first, and then be used as a sensing device for phosphate anions [5g].

As two essential components in biological processes, Cu^{2+} ion and $H_2PO_4^-$ ion are involved in many life functions, such as enzymes and proteins expression [6], energy transduction [7], genetic information storage [8], and membrane transport [9]. Therefore, the detection and discrimination of these ions remains the focus in ionic recognition. Though several works about the recognition of Cu^{2+} ion [10] and $H_2PO_4^-$ ion [11] have been reported individually, there is no report of a cascade recognition system that can detect Cu^{2+} ion first followed by $H_2PO_4^-$ ion yet.

Herein, we exploited a novel fluorescent tweezer molecule **1** as shown in Fig. 1, in which deoxycholic acid, coumarin, and 1,2,3-triazole motif were used as molecular scaffold, fluorophore, and linker, respectively. As a member of the steroids family, deoxycholic acid is an ideal scaffold for receptors [12], due not only to its low toxicity and biocompatibility [13], but also its unique microstructural features in assembly [14], which could be used to reflect the recognition processes. Meanwhile, as a class of naturally occurring fluorophores with high quantum yield and high photostability [15], coumarins have been widely used in fluorescent probes [16]. In addition, the 1,2,3-triazole motif was introduced as the linker by 'CuAAC click chemistry' [17] for its potential binding ability to transition metal ions [18]. Apparently, it is a typical naturally florescent probe, and its ability in fabricating the cascade recognition system was evaluated by recognizing the different ions and amino

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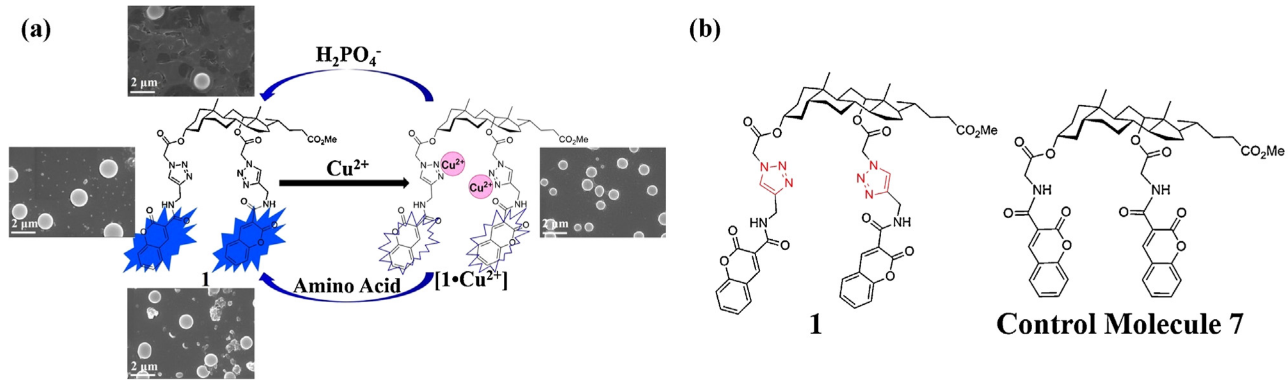
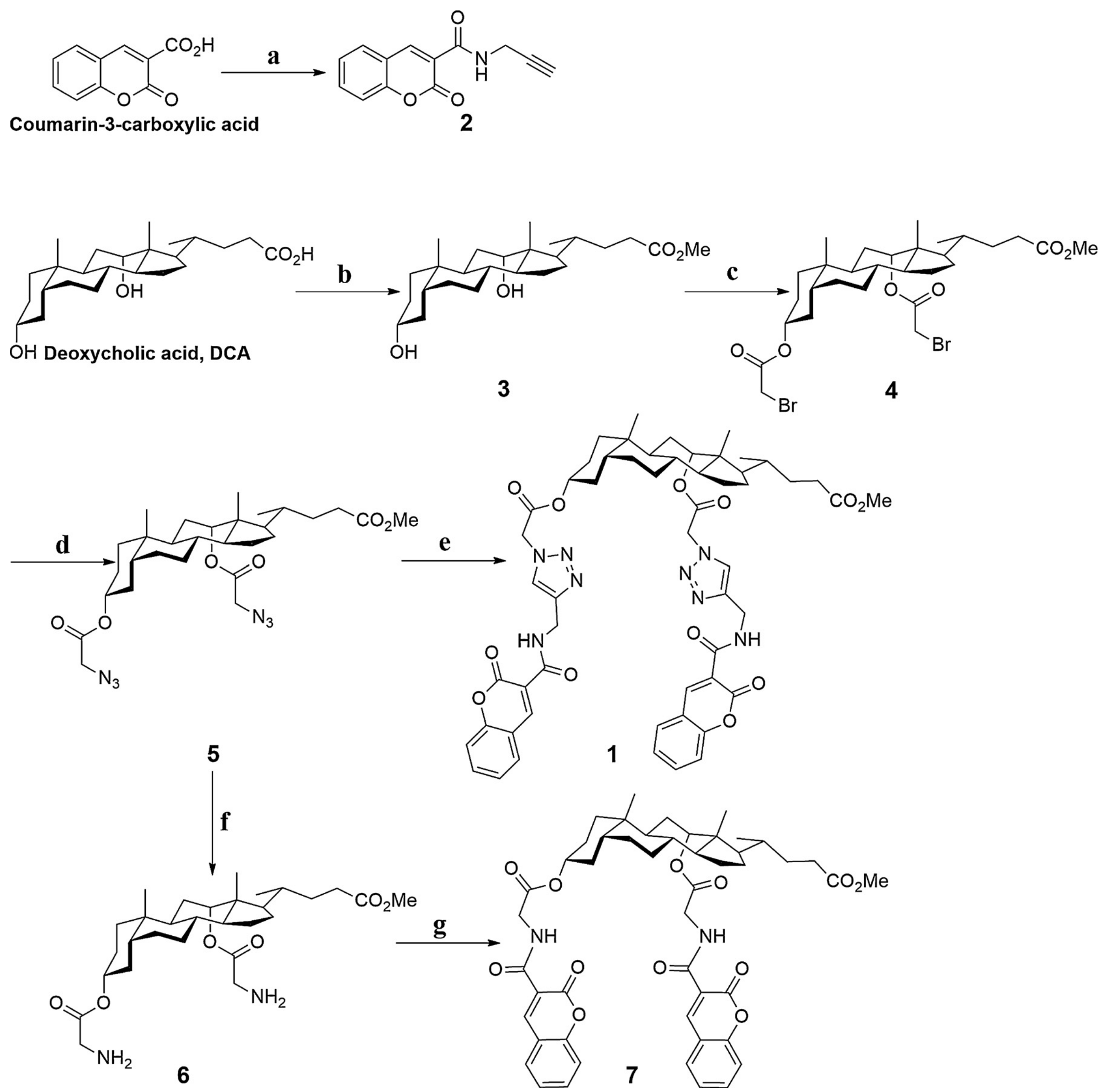


Fig. 1. (a) The schematic representation of the cascade recognition of **1**, and the morphology changes of the aggregates assembled from **1** during the recognition processes; (b) molecular structures of **1** and control molecule **7**.



Scheme 1. The synthetic route of **1** and **7**: (a) i. $SOCl_2$, DCM, reflux, 6 h; ii. 2-propynylamine, DCM, Et_3N, 0 °C to rt, 8 h, 80%; (b) MeOH, HCl (conc.), rt, 10 h, 90%; (c) bromoacetyl bromide, K_2CO_3, 0 °C to rt, 8 h, 76%; (d) NaN_3, DMF, 50 °C, 10 h, 92%; (e) **2**, $CuSO_4{\cdot}5H_2O$, sodium L-ascorbate, *t*-BuOH:THF:H_2O = 5:1:1 (volume ratio), 65 °C, 8 h, 53%; (f) PPh_3, THF, H_2O, 45 °C, 8 h, 86%; (g) coumarin-3-carboxylic acid chloride, DCM, Et_3N, 0 °C to rt, 8 h, 81%.