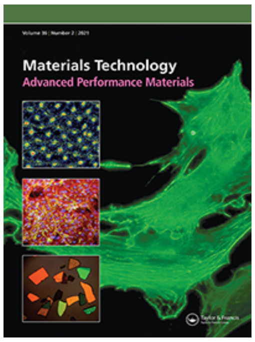

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A novel chitosan based fluorescence chemosensor for selective detection of Fe (III) ion in acetic aqueous medium

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ABSTRACT

Within this study, we have prepared 3-hydroxy-6H-benzo[c]chromen-6-one analogue grafted chitosan polymer. Mainly, 3-(3-chloropropoxy)-6H-benzo[c]chromen-6-one was synthesized from urolithin B and it was grafted on medium molecular weight chitosan (Uro-g-Ch). Employing our previous experience and observation on the characterisation of Urolithin B as a selective, fluorescent probe for sensing Iron (III), we have questioned its application in a polymer chain. Following that, we have conducted a serious of experiments to identify the fluorometric properties of the grafted polymer. Employing the λmax values detected for excitation and emission of fluorescent active-grafted polymer, the quenching effect of various metals on fluorescence was investigated based on grafted polymer–metal interactions. It was found that the grafted polymer displayed selective interaction with Iron (III) among the other metals tested (e.g. various +1, +2, +3 metals).

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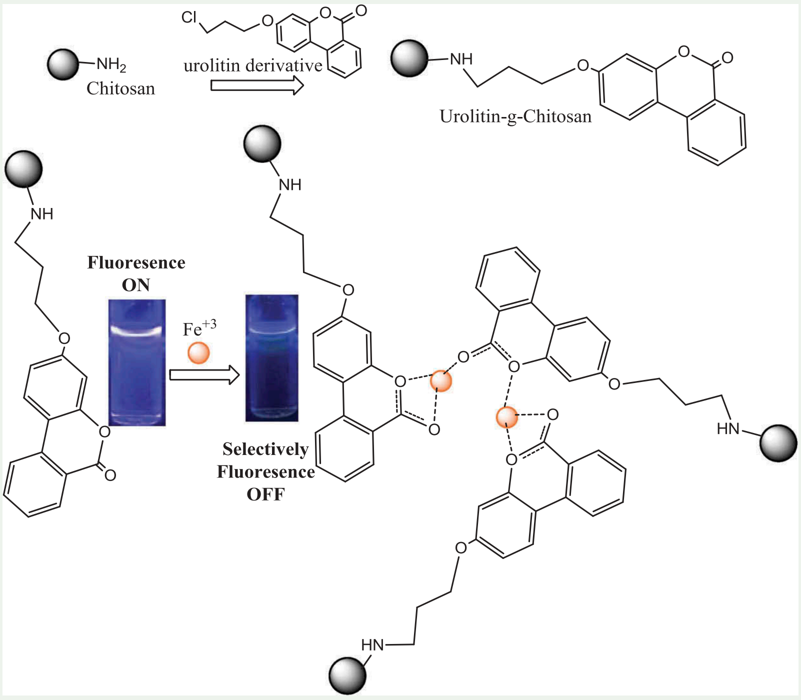
Chitosan; urolitin B; iron(III) ion; fluorescent; chemosensor; selective detection



Introduction

Regarding the technological development and related requirements, heavy metal use continuously rises up [1]. This results in the accumulation of heavy metals in the environment [2,3]. Indeed, heavy metals are now categorized as one of the important pollutants [4]. Toxicological studies indicate iron, nickel, cobalt, cupper, mercury, and lead heavy metals of particular concern [5,6]. From this point of view, the detection and treatment studies on heavy metals in various environmental sources are very significant to control their levels in order to prevent possible damages to living things [7,8]. Health associations point out the severe health problems such as cancer development and nervous system damages through exposure to heavy metals [4,5,9,10].

So far, numerous methods have been developed for the detection of heavy metals. Chemical reaction based, adsorption based [11,12], and biotechnological methods [13] are some of them. It is very important to

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develop novel methods that have properties such as cheaper, easy to access and applicable to various conditions.

Fluorescent measurements are very important techniques with respect to their high sensitivity and low amount of quantification and application properties [14,15]. In our previous works [16,17], we had discovered a natural coumarin compound, 3-hydroxybenzo[c] chromen-6-one, also referred to as urolithin B, as a potent, selective fluorescent probe for the selective detection of Iron (III) among other metals. Employing this feature, within this study, we have prepared a spacer linked Uro-g-Ch polymer. Following the synthesis and structure identification studies, the polymer prepared was investigated in terms of interaction with heavy metals. Particularly considering the fact that the urolithin B itself acts as a selective probe for Iron (III) determination, we have questioned both the metal interaction potential of the polymer probe prepared and its property to act as an on-off fluorescent probe for selective Iron (III) binder in acetic acid aqueous solution.

Experimental

Materials

Medium molecular weight chitosan, sodium chloride, silver nitrate, potassium chloride, cobalt(II) nitrate hexahydrate, iron (III) nitrate nonahydrate, nickel(II) nitrate hexahydrate, barium sulphate, zinc sulphate heptahydrate, mercury(II) chloride, aluminium sulphate, boric acid, sodium hydride, 1-bromo-3-chloroprpane, sodium hydroxide and 2-iodobenzoic acid were purchased from Sigma-Aldrich Co. Resorcinol, acetone, 1-4dioxan and acetic acid were obtained from Merck Co. Unless otherwise stated, the reagent and the solvent were used without further purification.

Synthesis of 3-hydroxy-6H-benzo[c]chromen-6-one (UroB)

UroB was synthesized according to a previous procedure [17,18]. Briefly, 10 g resorcinol was dissolved in 4.4 g NaOH containing 60 ml distilled water. Then, 7.5 g 2-iodobenzoic acid was added to the reaction flask. The mixture was refluxed for 1 h. Following the time, 10 ml of 25% cupper sulphate solution was added drop wise. The product precipitated was filtered and washed with ice-cold water. Yield 90%.

Synthesis of 3-(3-chloropropoxy)-6H-benzo[c] chromen-6-one (Uro-Cl)

To the solution of 3 g Uro B in 40 ml DMF was added 1.5-g sodium hydride. After stirring for 5 min at RT, 10 g 1-bromo-3-chloropropane was added to the reaction mixture. Reaction was stirred for 1 h at rt. Then, the reaction mixture was poured into 50 ml 0.1 N aqueous NaOH solution and the product precipitated was filtered off and washed with n-hexane. Yield 85%.

Preparation of urolithin grafted chitosan (Uro-g-Ch)

0.2 g low molecular weight chitosan was dissolved in 30 ml 2% aqueous acetic acid solution. 50 mg of 3-(3-chloropropoxy)-6H-benzo[c]chromen-6-one in 20 ml 1,4-dioxane was added to the chitosan solution. The mixture was heated under reflux for 12 h. Following the time, a mixture of 200 mL 1,4-dioxane and acetone solution (3:4) was added. The precipitate formed was filtered off and washed with acetone [19].

Result and discussion

Synthesis and characterization

The synthetic scheme followed for the preparation of the propylene linked urolithin and chitosan probe is shown in Figure 1.

FTIR spectra of the chitosan, Uro-Cl and Uro-g-Ch

FTIR spectrum was utiliszd to prove the grafted of the urolithin derivative on chitosan with a spacer. As seen in Figure 2, the IR spectrums of chitosan, Uro-Cl and Uro-g-Ch are shown. Accordingly, chitosan displays vibrations: above 3000 cm^{-1} with respect to the hydroxyl groups. On the other hand, Uro-Cl has no vibration above 3000 cm^{-1} through the lackey of hydroxyl group; however, the lactone carbonyl stretching has been shown to appear of 1727 cm^{-1}. The grafted polymer prepared has shown to have both of these features. It is important to state that there has been observed as shift in the carbonyl stretching (i.e. 1656 cm^{-1}) of the grafted chitosan. This has been attributed to the presence of hydrogen bonding, possible between the carbonyl oxygen of urolithin and the available hydroxyl and unreacted amine groups of chitosan.

Characterization of the Uro-g-Ch employing fluorometric measurement

Previously we have shown that urolithin B itself displays fluorometric characteristics. As know, chitosan has no fluorescence feature. From this point of view, we have questioned whether the novel Uro-g-Ch polymer, possesses fluorometric capacity. Regarding this, 1% acetic acid-water solution of the novel polymer was prepared and its excitation spectrum is obtained (Figure 3). As seen λ_{max} was obtained within the 290–350 nm range. In order to obtain emission spectrum, a λ_{max} emission was obtained at

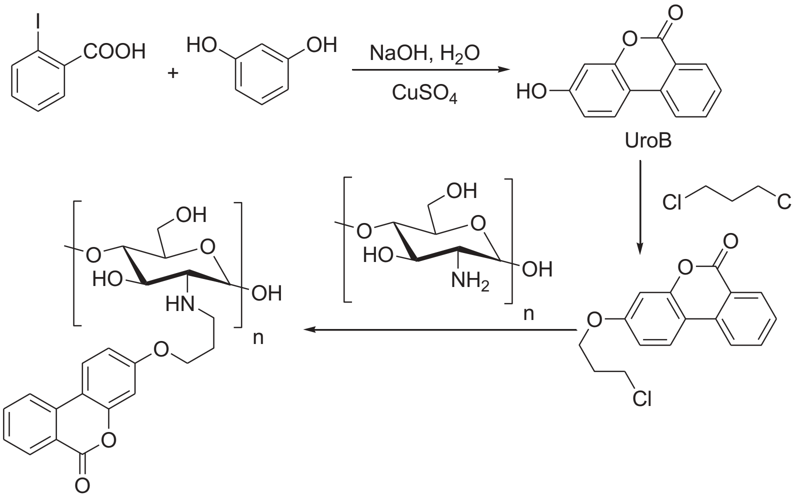

Figure 1. Synthetic scheme for the preparation of the Uro-g-Ch.

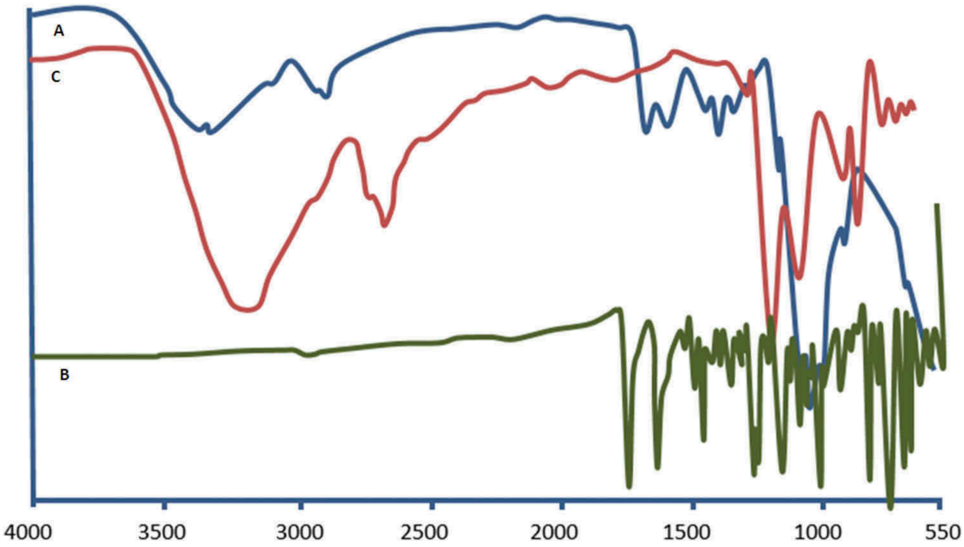

Figure 2. The FTIR pattern of (a) Uro-g-Ch, (b) chitosan and (c) URO-Cl.

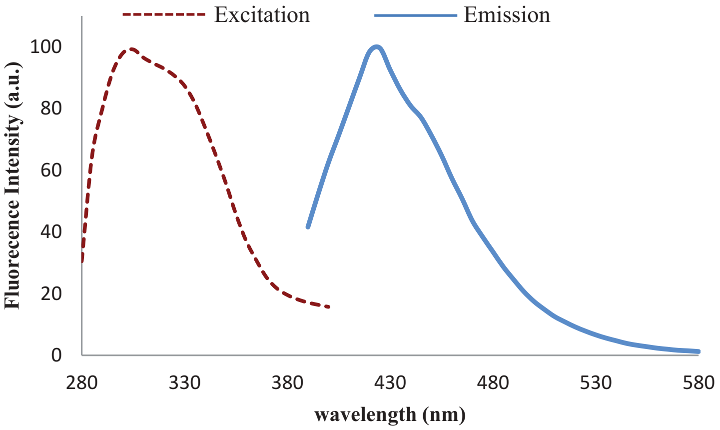

Figure 3. Excitation and emission spectra of Uro-g-Ch.

430 nm once the polymer was exited at 330 nm. It was also shown that the polymer prepared has a large stock shift of 100nm. Therefore, it has been indicated that the grafted chitosan prepared has a fluorescence feature.

The fluorescence response of the polymer in the presence of metals

The solutions of various +1t to +3 charge metals have been prepared and they were used to investigate the possible interaction of the new polymer prepared with these metals employing fluorometric measurement. Accordingly, 165 µL of solution of 0.15% each metal ions in 1% acetic acid solution (i.e. Na^+, Ag^+, K^+, Co^+, Ni^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+}, B^{3+}) were added into the 165 µL of 0.15% grafted chitosan solution. The results are shown in Figure 4. It was observed that only Iron (III) has quenching effect among other metals tested. This indicated selectivity of the chitosan polymer probe to Iron (III) under the experimental condition polymers. Furthermore, anti-interference study was employed to investigate the effect of other metals on selective interaction of the fluorescent polymer probe with iron(III). Accordingly, it was observed that the presence of other metals has no interference on the interaction of probe and iron(III) (Figure 5).

The selective response of the Uro-g-Ch to iron (III)

Under the same experimental conditions explained for the interaction of metals and the polymer various Iron (III) concentration (0.10–0.080 mM) were employed

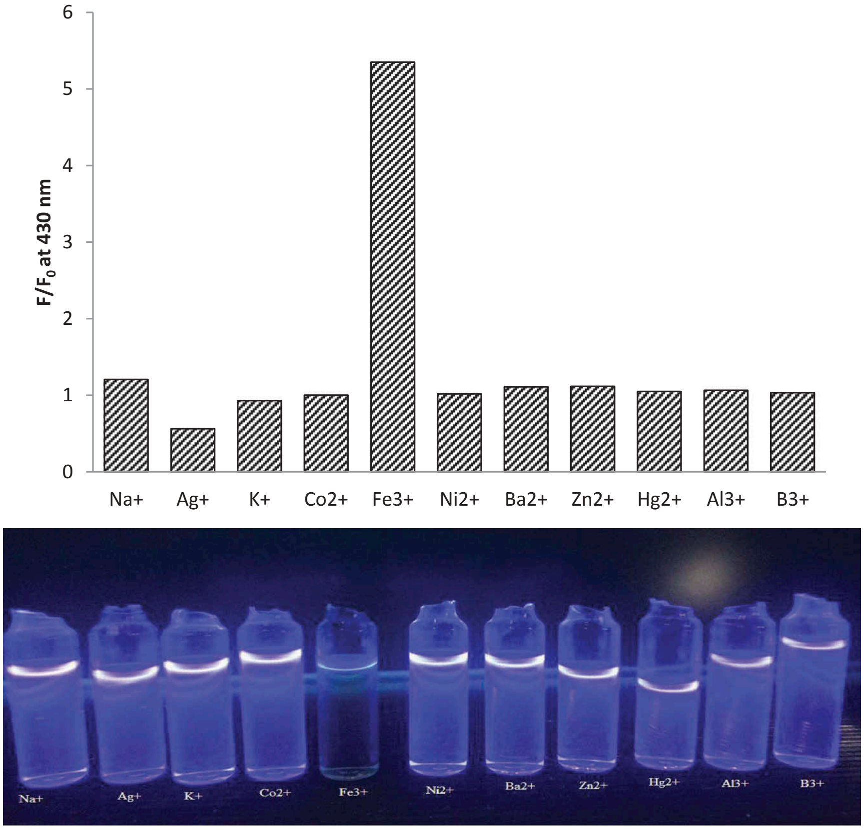

Figure 4. Selectivity of Uro-g-Ch probe (0.15%) in the presence of Na^+, Ag^+, K^+, Co^+, Ni^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+}, B^{3+} solutions in CH_3COOH/H_2O 1% (v/v).

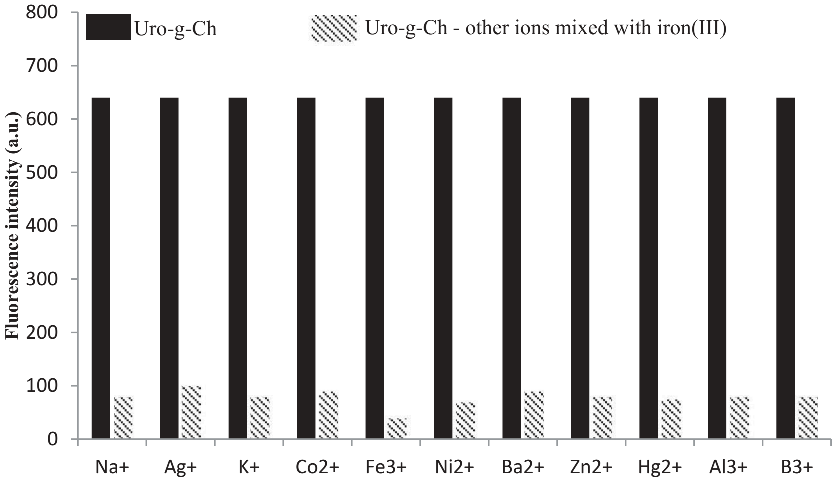

Figure 5. Fluorescence response of Uro-g-Ch probe 0.15% to Fe(III) (0.1 mM) in the presence of other metal ions in CH_3COOH/H_2O 1% (v/v).

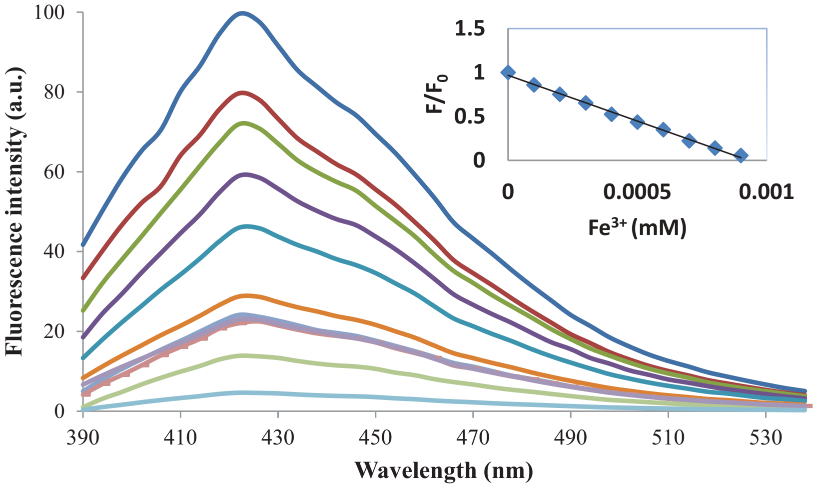

Figure 6. Fluorescence spectra (λex, 330) of 0.15% of Uro-g-Ch in presence of Fe^{3+} ion in CH_3COOH/H_2O 1% (v/v).

to test the effect on the quenching of the fluorescence of the novel polymer prepared. As shown in Figure 6, the gradual increase of iron(III) concentration has resulted in a linear decrease in fluorescence intensity reaching to an almost non-fluorescence point. Moreover, the emission intensity and the iron(III) concentration were found linear, that was statistically significant.

Conclusion

In summary, we have successfully synthesized an Uro-g-Ch fluorescence chemosensor which is capable selective detection of Fe^{3+} ion in the presence of variety of other metal ions in acetic aqueous medium without the involvement of any organic solvent. The result of fluorescence emission showed that the chitosan-based biopolymer has high selectivity and sensitivity for Fe^{3+} ion among all the metal ions investigated, such as sodium, potassium, cobalt, nickel, barium, zinc, mercury, aluminium, and boron ions. The fluorescence intensity quenching has linear relationship with ferric ion concentration indicates that Uro-g-Ch would be a highly efficient fluorescence chemosensor for ferric ion. This chitosan-based urolithin grafted chemosensor can also be used for the removal of Fe^{3+} ions from drinking water.

Disclosure statement

No potential conflict of interest was reported by the authors.

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