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Steroidal 1,2,3-triazole-based sensors for Hg^{2+} ion and their logic gate behaviour

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ABSTRACT

1,2,3-Triazole-based sensors for Hg^{2+} ion have been developed which exhibit NOR and OR logic gate behaviour on using Hg^{2+} and H^+ as inputs.

The environmental pollution due to mercury has always been a matter of concern as mercury is highly toxic and is continuously released in the environment through several natural and industrial processes such as oceanic and volcanic emissions, coal-burning and gold-mining.[1] The elementary mercury is oxidized to Hg^{2+} which is accumulated in plants, soil and water. Mercury is also converted into methylmercury, a highly potent neurotoxin, by microorganisms.[2] The exposure to mercury even at low concentration leads to various health problems, especially neurological disorders. Hence, there has been considerable interest in the development of chemosensors that can show high selectivity and sensitivity for Hg^{2+} ion.[3]

Recently, click reactions[4] involving Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between an azide and a terminal alkyne to yield 1,4-disubstituted 1,2,3-triazoles have attracted much attention in synthetic organic chemistry, polymer science, materials science, bio- and peptide chemistry.[5] More recently, the importance of the role of 1,2,3-triazole as a potential ligand for the binding of metal ions has also been realized.[6]

Herein, we report bile acid-based receptors containing 1,2,3-triazole moieties which show high selectivity and sensitivity for Hg^{2+} ion and display some interesting logic gate properties.

The steroidal 1,2,3-triazole-based receptors **4** and **5** were synthesized by the coupling of the diazido derivative[7] of deoxycholic acid **1** with salicylaldehyde and 2-hydroxy-1-naphthaldehyde-based terminal alkynes **2** and **3**, respectively, using click chemistry (Scheme 1). The alkynes **2** and **3** were synthesized by the reactions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively, with propargyl bromide in alkaline medium.[8]

First, we investigated the affinity of compound **4** towards Hg^{2+} ion by monitoring the absorbance changes on addition of $Hg(ClO_4)_2$ to the solution of compound **4** (4×10^{-5} M) in $CHCl_3$/MeOH (7:3, v/v). As shown in Figure 1, the absorbance bands at 254 and 317 nm decreased and a new band around 279 nm developed with two sharp isosbestic points at 271 and 284 nm, by incremental addition of Hg^{2+} ion (0–1.3 equiv). Compound **5** (2.5×10^{-5} M) also showed similar type of behaviour with Hg^{2+} ion (Fig. 2). Job's plots indicated the 1:1 complex formation in both cases. Their binding constants were calculated using Hildebrand–Benesi equation (see the Supplementary data). The binding constants for receptors **4** and **5** were found to be 3.7×10^4 and 1.2×10^4 M^{-1}, respectively.

We also examined the binding behaviour of **4** and **5** with other metal ions such as Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Mg^{2+}. In all cases, their perchlorate salts were used for the UV–vis titration. We have also found that these receptors show very weak binding with anions. Among the above mentioned metal ions, only Cu^{2+} and Pb^{2+} showed appreciable binding towards these receptors. The binding constants for receptor **4** with Cu^{2+} and Pb^{2+} were 1.4×10^3 and 1.0×10^3 M^{-1}, respectively. In the case of receptor **5**, these values were found to be 2.2×10^3 and 1.3×10^3 M^{-1}, respectively. The remaining metal ions did not show any binding affinity for these receptors. These results clearly indicate that receptors **4** and **5** are selective for Hg^{2+} ion.

The mode of binding of Hg^{2+} ion with compounds **4** and **5** was ascertained by ^1H NMR spectroscopy. After addition of Hg^{2+} ion to the solution of compound **4** (10 mM) in $CHCl_3$/MeOH (7:3, v/v), C–H protons of 1,2,3-triazole rings shifted downfield by δ 0.6 ppm and –CHO protons attached to phenyl rings shifted upfield by δ 0.28 ppm (Fig. 3). Similar shifts of triazole-protons and aldehydic protons were also observed in the case of compound **5**. This indicates the involvement of both 1,2,3-triazole rings and –CHO groups during the binding of compounds **4** and **5** with Hg^{2+} ion.

We also studied the UV–vis absorbance behaviour of receptors **4** and **5** towards TFA. Addition of TFA (0–20 equiv) to the solution of compound **4** (4×10^{-5} M) in $CHCl_3$/MeOH (7:3, v/v) also results in the decrease of absorbance bands at 254 and 317 nm and appearance of a new band around 279 nm with two sharp isosbestic points at 271 and 284 nm (Fig. 4). Compound **5** (2.5×10^{-5} M) also showed similar type of behaviour for TFA under these conditions giving isosbestic points at 270 and 296 nm.

The ^1H NMR study with addition of TFA gave similar results as described above in the case of their interactions with Hg^{2+} ion.

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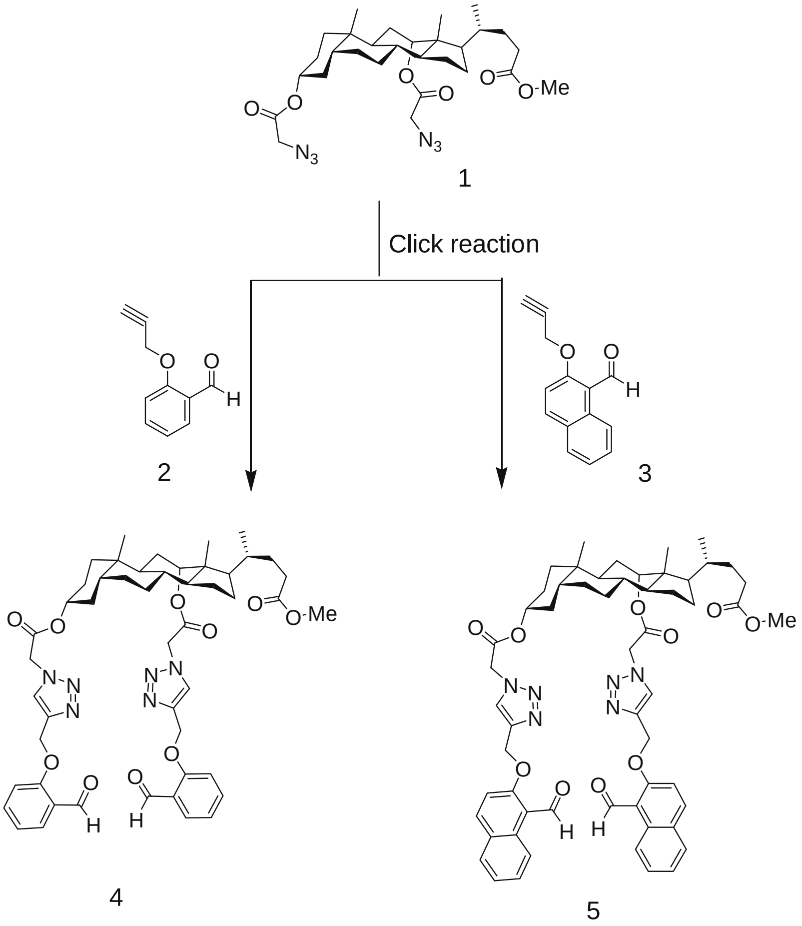

Scheme 1. Synthesis of compounds **4** and **5**.

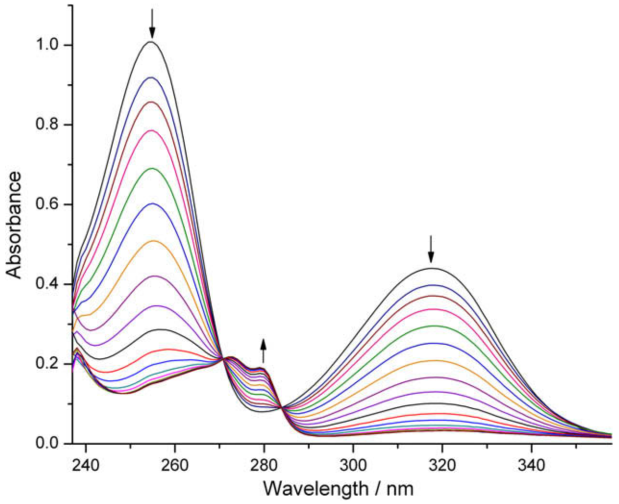

Figure 1. Absorbance spectra of compound **4** (4×10^{-5} M) in $CHCl_3$/MeOH (7:3, v/v) in the presence of Hg^{2+} (0–1.3 equiv).

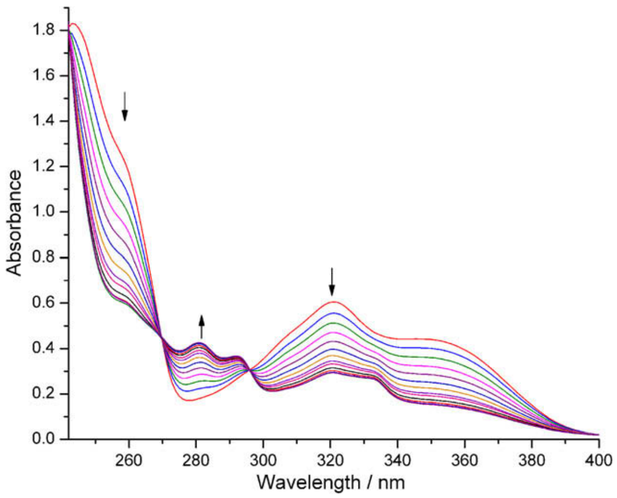

Figure 2. Absorbance spectra of compound **5** (2.5×10^{-5} M) in $CHCl_3$/MeOH (7:3, v/v) in the presence of Hg^{2+} (0–4 equiv).

We also investigated the logic gate behaviour of these systems. There has been considerable interest in recent years in the development of supramolecular systems behaving as molecular logic gates. Since the pioneering work of de Silva et al., a large number of molecular systems showing AND, NAND, OR, NOR, INHIBIT, XOR, YES, NOT and XNOR logic gates have been reported.[9,10] They change their properties such as absorbance, fluorescence, and redox potential in a specific fashion in response to a particular input. These systems can be used as molecular switches which can have potential applications in the design and development of molecular electronic devices for information, processing, sensing and computation.

These bile acid-based 1,2,3-triazole-containing systems show **NOR** and **OR** type logic gates by using different combinations of

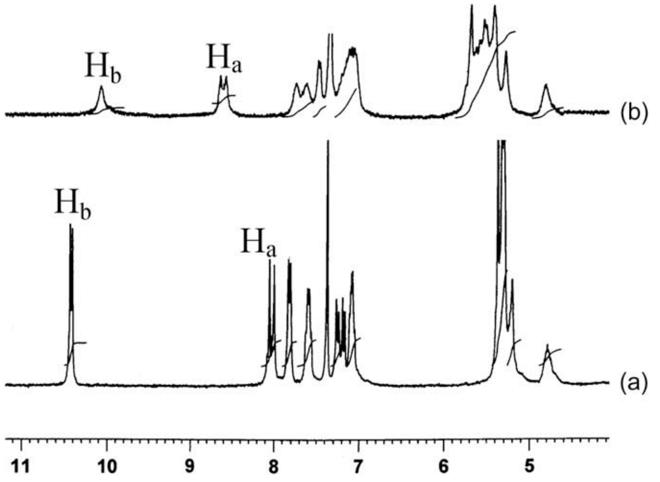

Figure 3. Partial ^{1}H NMR spectra of (a) compound **4** and (b) compound **4** + 2 equiv of $Hg(ClO_4)_2$. H_a = CH–triazole; H_b = –CHO.

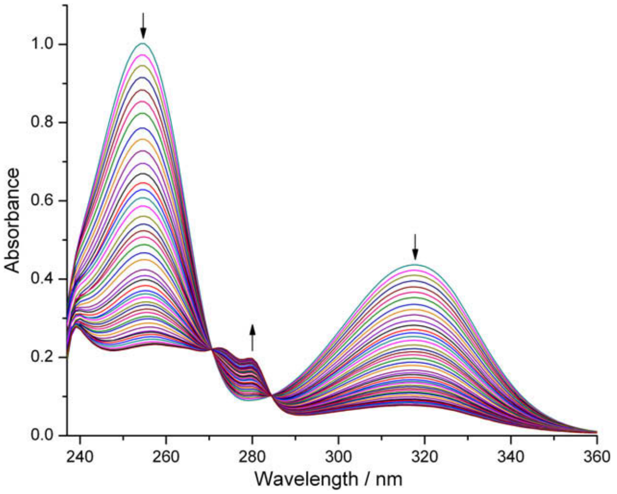

Figure 4. Absorbance spectra of compound **4** (4×10^{-5} M) in $CHCl_3$:MeOH (7:3, v/v) with TFA (0–20 equiv).

Hg^{2+} and H^+ as inputs and monitoring absorbance changes as output signals. To our knowledge, this is the first report on the 1,2,3-triazole-based molecular logic gate as absorbance sensor for Hg^{2+} and H^+ ions.

Thus, Boolean functions can be achieved by considering compound **4** as a logic gate using Hg^{2+} and H^+ as inputs and the resulting absorbance changes as outputs. When the inputs, Hg^{2+} and H^+, are 0, 0; three outputs at 254, 279 and 317 nm are 1, 0 and 1, respectively. On the other hand, the 1, 0; 0, 1 and 1, 1 input combinations give 0, 1 and 0 outputs, respectively (Table 1). Thus, the system behaves as **NOR** type logic gate at 254 nm and 317 nm, and **OR** type logic gate at 279 nm for the same input.

Table 1
Truth table for logic functions of compounds **4** and **5** operating with two inputs Hg^{2+} and H^+.

Input		Output		
Hg^{2+}	H^+	*a*	*b*	*c*
0	0	1	0	1
1	0	0	1	0
0	1	0	1	0
1	1	0	1	0

Compound **5** also displayed the same kind of **NOR** and **OR** logic functions for Hg^{2+} and H^+ considering the absorption changes at 257, 280 and 320 nm.

In summary, we have developed a new type of chemosensors based on 1,2,3-triazole system which show high selectivity and affinity for Hg^{2+} ion. In addition, these systems also exhibit logic gate properties showing **NOR** and **OR** type logic gates on using Hg^{2+} and H^+ as inputs.

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Supplementary data

Supplementary data (experimental details, characterization data for compounds and UV–vis titration curves) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.007.

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