Tetrahedron Letters 50 (2009) 2782–2786

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

ICT-based Cu(II)-sensing 9,10-anthraquinonecalix[4]crown

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ARTICLE INFO

Article history:
Received 14 February 2009
Revised 20 March 2009
Accepted 23 March 2009
Available online 26 March 2009

Keywords:
ICT
Chromogenic
Anthraquinone
Calixarenes
Copper ion

ABSTRACT

A series of calix[4]arene-based chromogenic sensors bearing the 9,10-anthraquinone moiety have been synthesized and examined for their abilities to recognize various cations such as Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} by UV–vis spectroscopy. In acetonitrile, the presence of Cu^{2+} induces the formation of the 1:1 ligand/metal complex, which exhibits a new absorption band centered at 450 nm, and leads to an obvious color change from yellow to red.

The development of specific chemosensors for the efficient detection of metal ion analytes is one of the most important areas in organic and supramolecular chemistry due to their pivotal role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals.[1,2]

Over the last few decades, chemosensors for the detection and measurement of Cu^{2+} ions have been actively investigated as this metal ion is a significant environmental pollutant and an essential trace element in the human body. Copper(II) also plays an important role in various biological processes. However, it is toxic at higher concentrations and, for example, the accumulation of Cu^{2+} in the liver and kidney may cause gastrointestinal problems, Wilson disease, hypoglycemia, dyslexia, and infant liver damage.[3,4]

Calixarenes have been found to be outstanding platforms for creating attractive host molecules. Modifications of calixarenes give rise to a great variety of derivatives with tunable binding properties. For instance, calix[4]arene derivatives such as esters, amides, crown ethers, azacrown ethers, and carboxylic acids have been shown to extract and form complexes with metal ions, also displaying interesting selectivity.[5,6] As one of the calixarene derivatives, calixcrown compounds in which one crown ether unit or two crown ether units are incorporated into the lower rim of a calix[4]arene skeleton are also well described because of their high selectivity toward metal ions.[7,8]

An anthraquinone chromophoric system may be important as a chemosensor because its optical properties can be significantly perturbed by chemical stimuli. It is also important to note that the carbonyl group of 9,10-anthraquinone ligands is known to interact with various metal ions to cause a pronounced color change.[9,10]

Even though the 9,10-anthraquinone moiety has been recently utilized as a chemosensor for metal ions and anions,[9,10] there have been only a few examples with *p-tert*-butylcalix[4]arene bearing the 9,10-anthraquinone sensing moiety.[11] This report describes the synthesis and binding properties of a series of 9,10-anthraquinone pendant calix[4]crowns amongst which compound **1** displays a highly selective color change for Cu^{2+}.

Our synthesis began with the preparation of the 9,10-anthraquinone derivative **4**. Under a N_2 atmosphere, the treatment of 1,8-dihydroxy-9,10-anthraquinone with 2-(2-chloroethoxy)ethyl 4-methylbenzenesulfonate and Cs_2CO_3 in CH_3CN led to **4**. Subsequently, **1–3** were synthesized using the reaction of **4** with **6–8** in the presence of Cs_2CO_3 in CH_3CN/DMF (1:1 v/v) with a catalytic amount of NaI. As a reference compound, **5** was also obtained by the reaction of 1,8-dihydroxy-9,10-anthraquinone with 2-(2-hydroxyethoxy)ethyl 4-methylbenzenesulfonate and K_2CO_3 in CH_3CN (Scheme 1). Their molecular structures were fully characterized by ^1H NMR, ^{13}C NMR, MS, and X-ray analysis (see Supplementary data). Synthetic details are described in Ref.15.

The UV–vis spectra of the 9,10-anthraquinone-appended calix[4]arenes **1–3** showed a new absorption band at 380 nm in CH_3CN. Excess perchlorate salts (50 equiv) of Li^+, Na^+, K^+, Rb^+, Cs^+,

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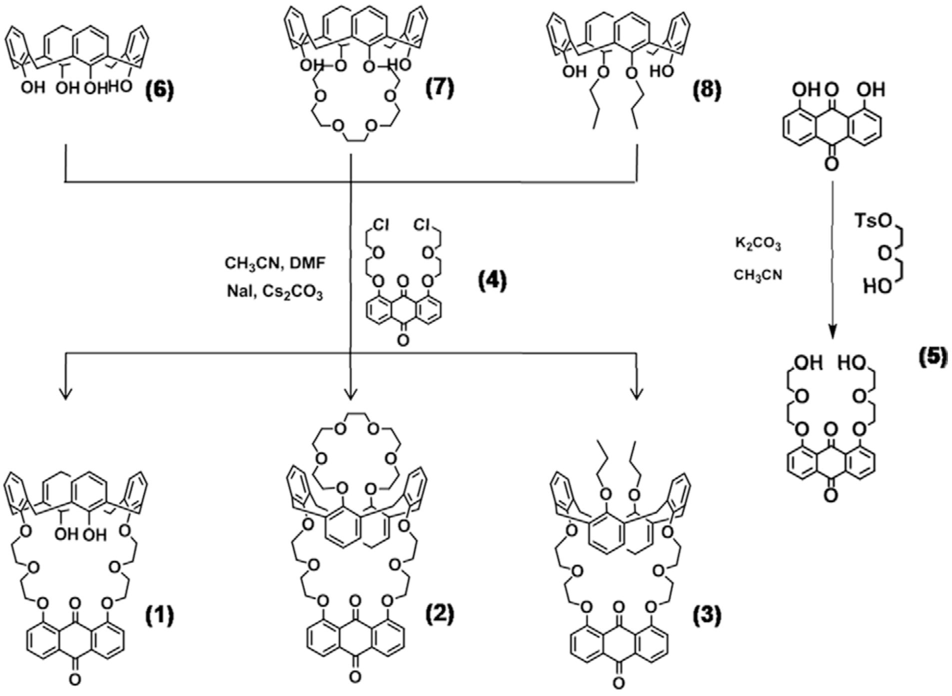
doi:10.1016/j.tetlet.2009.03.149



Scheme 1. Synthetic route to chromogenic ligands **1**–**3**.

Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (a total 16 metal ions) were tested to evaluate the metal ion-binding properties of **1–3**. Interestingly, we found unusual UV–vis changes in **1**; the addition of Cu^{2+} produced a new absorbance band at 450 nm in a solution of CH_3CN, as shown in Figure 1a. Based on the UV band and color changes, we noticed that compound **1** shows a pronounced selectivity for Cu^{2+} over other metal cations, whereas **2** and **3** do not show any UV and color changes (Fig. 1b).

In a function of Cu^{2+} concentration, the intensity of the new red-shifted absorption band centered at 450 nm increased. This band at 450 nm is attributable to an Internal Charge Transfer (ICT)[12] transition made possible by coordination of Cu^{2+} to **1**. When the Cu^{2+} ion interacts strongly with the lone pair electrons of the carbonyl oxygen atoms ($Cu^{2+}\cdots O{=}C$) with the aid of the two proximal OHs of the calix[4]arene platform, then the charge transfer from the 1,8 oxygen atoms to the electron-deficient carbonyl group becomes stronger (Fig. 3).

To elucidate how the two proximal OHs in **1** act to promote selective Cu^{2+} ion binding, **a** calixcrown having a dipropyl unit (**3**) was also prepared. However, we observed no absorbance changes of **3** toward any metal ions, including Cu^{2+} (Fig. 1b). In addition, **5** was synthesized to investigate the role of the calix[4]-

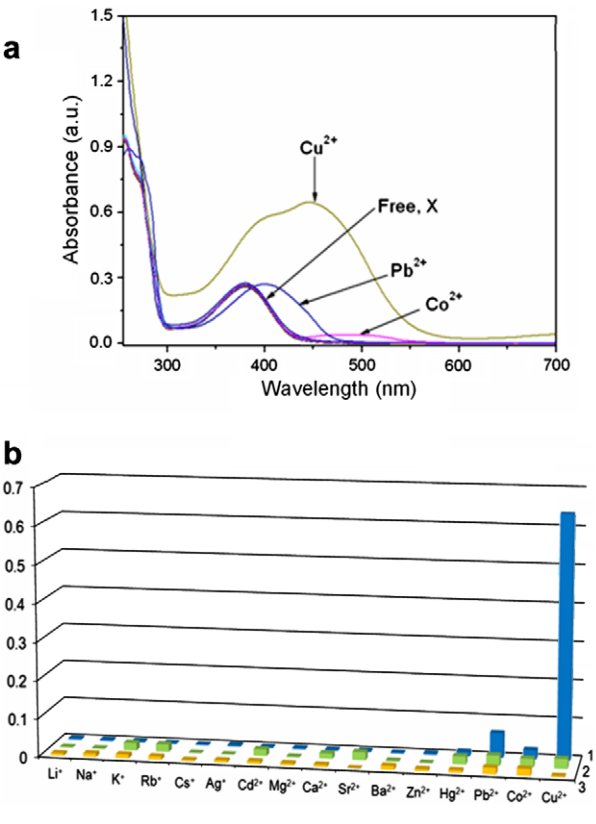


Figure 1. Absorption spectra of **1** (50.0 μM) (a) and relative responses at 450 nm of **1**–**3** (50.0 μM), (b) with the addition of ClO_4^- salts of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (50 equiv, respectively) in CH_3CN.

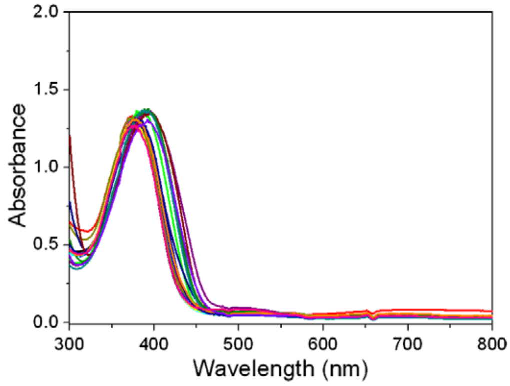


Figure 2. Absorption spectra of **5** (50.0 μM) with addition of ClO_4^- salts of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (50 equiv, respectively) in CH_3CN.