

Chromogenic signaling of water traces by 1,8-naphthalohydrazone-anion complex in organic solvents



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ARTICLE INFO

Article history:

Received 20 July 2015

Received in revised form

25 February 2016

Accepted 1 March 2016

Available online 3 March 2016

Keywords:

Chromogenic signaling

Hydrazone receptors

Water detection

DFT

ABSTRACT

A naphthalo-1, 8-bis[(2,4-dinitrophenyl)hydrazone] sensor (**K**) was synthesized and characterized using UV–vis, ¹H NMR and fluorescence spectroscopy. The sensor showed strong colorimetric and spectral response upon the molar addition of acetate or fluoride ion (AcO[−] or F[−]) in acetonitrile. The complexed state (**KF** or **KAcO**) of the system showed significant reversibility properties, both in color and spectra, upon the addition of small traces of water. Subsequently, in addition to sensing of fluoride or acetate ions, the complexed **KF** or **KAcO** adducts can be used in colorimetric signaling of water traces in different organic mediums. In order to have more understanding of the interaction between **K** and the anions, the study was supplemented using density functional theory computations.

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1. Introduction

Molecular recognition has been the epic center of supramolecular chemistry in the past few decades. Anion recognition and sensing have received a fair share of attention. The study of anion sensing using colorimetric and fluorescent sensors has been actively explored. This is due to the fundamental roles anions play in biological, environmental and chemical processes [1–10]. As a result, the development of chromogenic and fluorogenic sensors through visual detection became more popular because it does not involve expensive equipment, as the color change is detected by naked eye [11–14]. The identity of a chromogenic/fluorogenic sensor is based on a specific overall design which consists of signaling units and binding sites that are covalently or non-covalently linked to the receptor moiety. Most of chromogenic and fluorogenic sensors in ureas [15–17], amides [18–20], pyrroles [19–23], thioureas [24–26] and hydrazine [27–29] are characterized by hydrogen bonding receptors as the binding sites. Hydrazone-based NH receptors are well-known for biologically

important acetate (AcO[−]) and fluoride (F[−]) sensors and they can be further polarized to increase the acidity through the insertion onto the molecular framework of electron withdrawing groups such as NO₂ [27–29]. However, extreme polarization leads to deprotonation upon the addition of a strong basic anion such as F[−]. Hydrazone based receptors display logic operation behaviors based on their reversible colorimetric activities [30–33]. Signaling units play a major role in transforming the events at the binding sites into useful information such as colorimetric or spectral activities, which can be quantified. There is variety of anion sensors bearing different signaling units, including anthracene [34], naphthalene [35], indole [36–38], BODIPY [30,39–41], ferrocene [42–45] and naphthalimides groups [46–48], which can be used in colorimetric only, or colorimetric and fluorescent. The signaling unit largely lies with the choice or preference of the designer.

Naphthalimide-based signal reporters have been utilized for this functionality, due to their favorable factors such as good thermal stability, strong fluorescence, large Stokes shift, high quantum yield and tunability for specific functions [49–54]. Consequently, their photophysical properties can be manipulated to suit specific functions through judicious structural modifications. Structural modification has seen naphthalimide-based moieties being applied as anion or cation sensors, while still performing the same signaling

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reporter function [48,49,51]. According to literature, the most substituted positions on the structure are the imide group and the C-4 position, which display a major influence on the sensor's sensitivity and selectivity. There is limited information in literature showing the modification of naphthalimide-based moieties through any other position than the imide or C-4 position [46–57]. Based on its general suitable properties in terms of its stability and strong responses, further explorations and manipulations remain a possibility.

On the other hand, hydrazone based sensors have proved to be selective only to acetate, fluoride and dihydrogen phosphate ions through hydrogen bonding. The association constant towards these anions favors the Y-shaped acetate over fluoride ions. The strong basicity of F^- results in the deprotonation of the sensor [30,58] when strong electron withdrawing groups (EWGs) such as NO_2 or CF_3 moiety are incorporated in the structure. Most of the activities observed in hydrazone based sensors in the presence of guest anion species such as color changes and spectral shifts are reversible upon the addition of different species like metal ions or other species. These lead to the exploration of logic operation functions in these sensors [59–62]. In addition to the anion sensing ability of hydrazone based receptors, their reversibility properties through the molar addition of several species (cations, anions, water) can be exploited further to a multi-purpose functioning system. Water is one of the species which can reverse colorimetric and structural activities in hydrazone-based sensors, ascribed to strong hydrogen bond formation [63]. Since the anion recognition in organic solvents is via hydrogen bonding interaction, the non-competitiveness of organic environments made the interaction possible. The presence of competitive species such as water results to the weakening and breaking of the anion-hydrogen bonding association. Therefore, hydrazone-based sensor-anion adducts can be used as a sensing tool for water in organic systems [27–33,58–65].

In view of the above, we hereby report on the design of a 1,8-naphthalo-dinitrophenylhydrazone (**K**), a chromogenic and fluorogenic sensing system to discriminate AcO^- and F^- in acetonitrile. When little amount of water was added, reversible responses, impeded colorimetric or spectral changes were observed. The two dinitrophenylhydrazone groups are linked to the 1, 8-naphthalic anhydride via the two carbonyl groups at position C1 and C3 (Scheme 1). The 1,8-naphthalic anhydride forms a signaling subunit while the 1,4-dinitrophenylhydrazone serves as a binding unit. These two are excellent functional units which together displayed exceptional good sensing properties toward acetate and fluoride ions, as well as the detection ability of water contents in organic systems.

2. Experimental section

2.1. Reagents and physical measurements

All chemicals and reagents used were of reagent grade and were used as received from the commercial source. UV–Vis spectra were obtained on a Tu-1901 UV–vis spectrophotometer (1 cm quartz cell), 1H NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer, steady state excitation and emission spectra were obtained on a RF-5301 PC Shimadzu spectrophotometer. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240C analytical instrument. All the measurements were carried out at room temperature (25 °C).

2.2. Synthesis of **K**

A solution of 2,4-dinitrophenylhydrazine (0.1 g, 0.45 mmol) in 20 ml of ethanol was mixed with the ethanolic solution (15 ml) of 1,8-naphthalic anhydride (0.041 g, 0.2 mmol) at room temperature and the mixture was magnetically stirred. H_3PO_4 (5 ml) was then added as a catalyst and the mixture was refluxed with vigorous stirring overnight (18 h). The light yellow precipitate was filtered off and washed several times with hot ethanol, removing all of the unreacted hydrazine. The light-yellow powder was dried in vacuum at room temperature and recrystallized from acetonitrile. Yield 80%. 1H NMR (300 MHz, $DMSO-d_6$): δ : 10.59 (2H, NH), δ : 8.95 (2H, ArH_{NO_2}), 8.60 (2H, ArH_{NO_2}), 8.19 (2H, Ar), 7.98 (2H, Ar), 7.95 (2H, ArH_{NO_2}), 7.51 (2H, Ar); Elemental Analysis calcd (%) for $C_{24}H_{14}N_8O_9$: C 51.62, H 2.53, N 20.07, O 25.79, Found: C 51.54, H 2.73, N 19.58, O 24.92. The UV–Vis spectrum of **K** exhibits a band at 336 nm ($\epsilon = 44\,000\,dm^3\,mol^{-1}\,cm^{-1}$) due to $\pi-\pi^*$ transition.

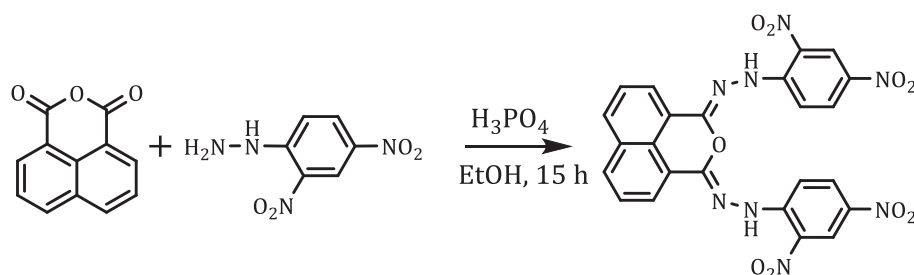
3. Results and discussions

3.1. UV–vis absorption studies

The photophysical properties of **K**, in acetonitrile, were defined by two prominent absorption bands at 230 nm and 336 nm, attributed to internal-charge transfer (ICT) of the nitrophenyl moiety and naphthyl moiety respectively. **K** displayed a weak fluorescent emission in the UV region characterized by two vibronic transitions at 360 nm and 376 nm and the weakened emission is presumably attributed to the presence of EWG NO_2 groups.

3.2. Influence of anions on the photophysical properties of **K**

In order to understand the selectivity and sensitivity behaviors of **K** towards anions, the examination of receptor's interaction with anions was carried out using both UV–vis and fluorescent spectroscopy. Upon gradual addition of 5 equiv. of TBA^+



Scheme 1. Synthetic route of **K**.

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