



Anion response of dimeric hydrazide derivatives: Dependence on the nature of terminal substituents



Zhenhua Wei^{a,b}, Jue Wei^a, Binglian Bai^{a,*}, Haitao Wang^b, Min Li^{b,*}

^a College of Physics, Jilin University, Changchun 130012, PR China

^b Key Laboratory for Automobile Materials (JLU), Ministry of Education, College of Materials Science and Engineering, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form 23 January 2015

Accepted 28 January 2015

Available online 2 February 2015

Keywords:

Anion sensing

Hydrazide derivatives

Highly selective detection

Terminal substituent

ABSTRACT

Three dimeric hydrazide derivatives with nitro, phenyl, and methyl terminal substituents were synthesized and their anion responsive behaviors were studied. The UV–vis spectra showed that the compounds with methyl groups and phenyl groups can allow highly selective fluoride detection, whereas the compound with terminal nitro substituent can respond to F^- , AcO^- and $H_2PO_4^-$, due to the distinction on acidity of compounds which is caused by electronic effect and field effect of terminal substituents. The 1H NMR spectra revealed that the anion responsive mechanism for F^- , AcO^- and $H_2PO_4^-$ was different due to the much lower basicity of AcO^- and $H_2PO_4^-$ compared to F^- . Whereas the number of hydrazide groups and the nature of the terminal substitute do not affect the fluoride anion responsive mechanism. It demonstrates that, by altering terminal substituent groups, the anionic recognition ability of compounds could be adjusted and controlled.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The research for the recognition and sensing of biologically important ions has emerged as a research field which has considerable attention [1–4]. The majority of these synthetic chemosensors generally contains an optical-signaling chromophoric fragment linking to a neutral anion receptor with urea [1,5–7], thiourea [6,8], calix [4]pyrrole [9], indole [10] and amide [11] subunits which can provide one or more hydrogen bond (H-bond) donor sites for selective binding and recognizing of special anions. Among numerous anions, the fluoride anion is significantly important for health and environmental issues. For example, fluoride can be applied on dental care and treatment of osteoporosis, whereas superfluous intake of F^- would cause fluorosis [12]. So the recognizing and sensing of F^- have received considerable attention.

The selectivity mainly relate to the structure of the synthetic chemosensors and the basicity of the anions [13,14]. As the most electronegative atom, F^- usually forms strong H-bond interaction with –NH or –OH fragment [12] of the receptor, and then the processes of charge displacement and deprotonation take place [13,15,16], which mainly depend on the inherent acidity of the H-bond donor fragment of the artificial chemosensors.

Recently, we reported the anion responsive behavior of the 4-nitrobenzohydrazide derivative C8 (Scheme 1) (containing one hydrazide per molecule) and proposed the possible mechanism for the F^- responsive process [17]. In order to study the influence of the number of

hydrazide groups, we synthesized the dimeric 4-nitrobenzohydrazide derivative (containing two hydrazide groups per molecule) with more target sites for forming H-bond with anions, namely, 1,6-Bis[N-(4-nitrobenzoyl)-N'-(benzoyl-4'-oxy)hydrazine]hexane (N6). In addition, in order to study the properties of the terminal substituent groups in the anion responsive process, the dimeric hydrazide derivatives with methyl groups and phenyl groups, namely, 1,6-bis[N-(4-nitrobenzoyl)-N'-(benzoyl-4'-oxy)hydrazine]hexane (N6), 1,6-bis[N-(4-biphenylcarbonyl)-N'-(benzoyl-4'-oxy)hydrazine]hexane (B6) and 1,6-bis[N-(4-methylbenzoyl)-N'-(benzoyl-4'-oxy)hydrazine]hexane (M6) (as shown in Scheme 1) were also synthesized. Compound N6 with terminal nitro substituents can respond to F^- , AcO^- and $H_2PO_4^-$, which is similar to that of the reported hydrazide derivatives C8, whereas M6 with methyl groups and B6 with benzene groups can allow highly selective fluoride detection.

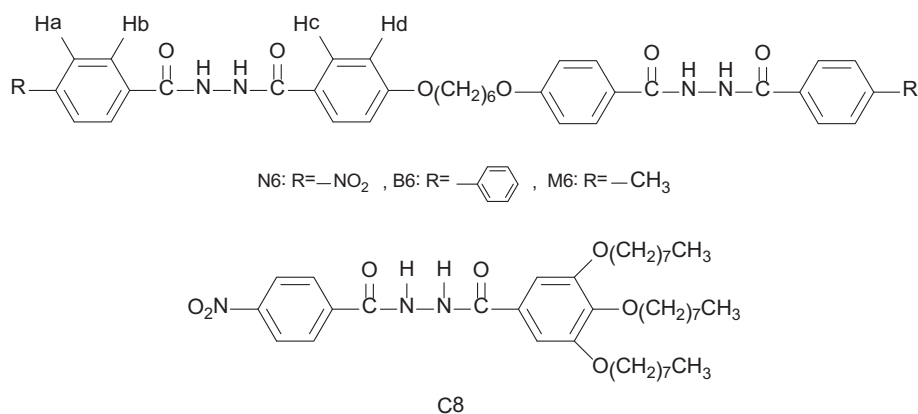
2. Experimental and characterization

The compounds N6, B6 and M6 were synthesized in our laboratory, and their structures confirmed by FTIR, 1H NMR spectra and elemental analysis. The synthetic details were reported elsewhere [18]. Spectrophotometric titrations were performed on solutions of receptors in DMSO at room temperature. Anions (F^- , Cl^- , Br^- , I^- , AcO^- and $H_2PO_4^-$) were used in solution by adding relative alkylammonium salts [16,19].

1H NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer, using dimethyl sulfoxide-d as solvent and tetramethylsilane (TMS) as an internal standard ($\delta = 0.00$). UV–vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer.

* Corresponding authors.

E-mail addresses: baibinglian@jlu.edu.cn (B. Bai), minli@mail.jlu.edu.cn (M. Li).



Scheme 1. Molecular structures of compounds N6, B6, M6, and C8 [17].

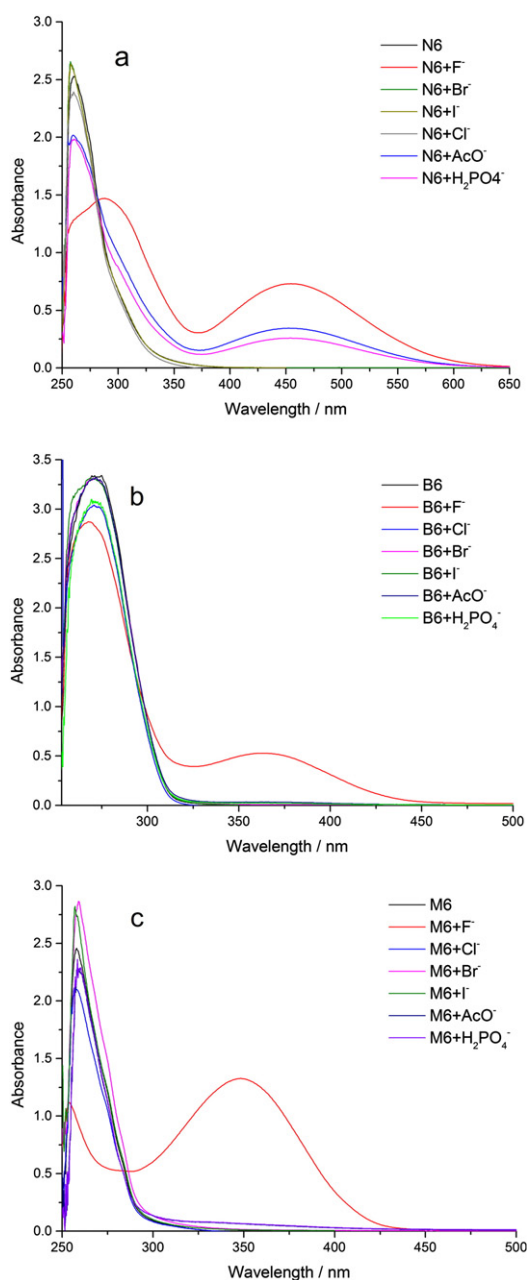


Fig. 1. UV-vis absorption spectra of a) N6, b) B6 and c) M6 in the presence of various anions (16 equiv.) in DMSO (5×10^{-5} mol/L).

3. Results and discussion

3.1. Anion-binding studies and color change

The interactions of receptors (N6, B6 and M6) with multiple anions (F^- , Cl^- , Br^- , I^- , AcO^- and H_2PO_4^-) were investigated in DMSO solutions through UV-vis spectra experiments. The anions were added as the state of TBA salts, stepwise into the solution of receptor at room temperature.

As shown in Fig. 1a, N6 exhibited various responses for anions. In addition of 16 equiv. F^- , the intrinsic maximum absorption of N6 at 257 nm, had an evident decrease and a bathochromic shift to 290 nm, and a new absorption band appeared at 456 nm. In contrast, in the presence of 16 equiv. AcO^- and H_2PO_4^- , the absorption band at 257 nm decreased with no red shift, and a new absorbance appear at 456 nm which is the same with the situation when F^- added, but the absorbance strength

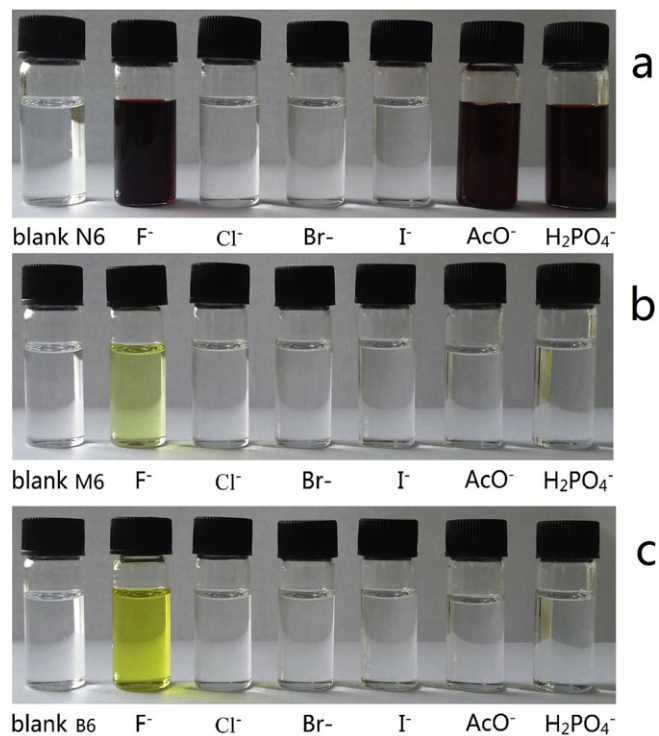


Fig. 2. The corresponding color changes of three dimeric hydrazide derivatives (1×10^{-2} mol/L) upon addition of 10 equiv. various anions in DMSO.

Download English Version:

<https://daneshyari.com/en/article/5411173>

Download Persian Version:

<https://daneshyari.com/article/5411173>

[Daneshyari.com](https://daneshyari.com)