Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 151 (2015) 655–661

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Novel azo dye-based color chemosensors for fluoride ions

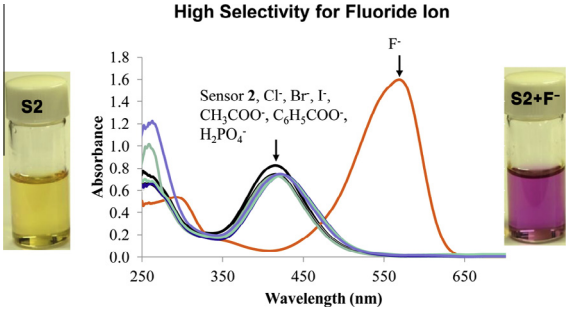
Eun Jin Cho [a,*], Yongjun Lee [b], Hyeun-Jong Bae [a,c], Young Ju Lee [b,*]

[a] Bio-energy Research Institute, Chonnam National University, Gwangju 500-757, Republic of Korea
[b] Gwangju Center, Korea Basic Science Institute, Gwangju 500-757, Republic of Korea
[c] Department of Bioenergy Science and Technology, Chonnam National University, Gwangju 500-757, Republic of Korea

HIGHLIGHTS

- Simple and easy-to-make colorimetric sensors were synthesized.
- These chemosensors exhibited high selectivity towards fluoride.
- These chemosensors showed a large red shift (154 nm) in absorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2015
Received in revised form 27 May 2015
Accepted 7 July 2015
Available online 8 July 2015

Keywords:
Fluoride sensor
Color change
Azo dye
Chemosensor
Naked eye

ABSTRACT

Two novel fluoride (F^-) sensors based on an azo dye (solvent yellow 4) were designed and synthesized. The chemosensors exhibited selectivity and high sensitivity towards F^- over other anions such as Cl^-, Br^-, I^-, CH_3COO^-, $C_6H_5COO^-$, and $H_2PO_4^-$, as noted by the naked eye and UV–vis spectral changes in DMSO/CH_3CN (1:9, v/v). An obvious change in the color of the sensor solution from pale yellow to pink occurred after the addition of F^-, while the addition of other anions did not cause any change in color. These results imply that the two sensors are viable, portable chemosensors for the detection of F^- ions in various biological and environmental fields.

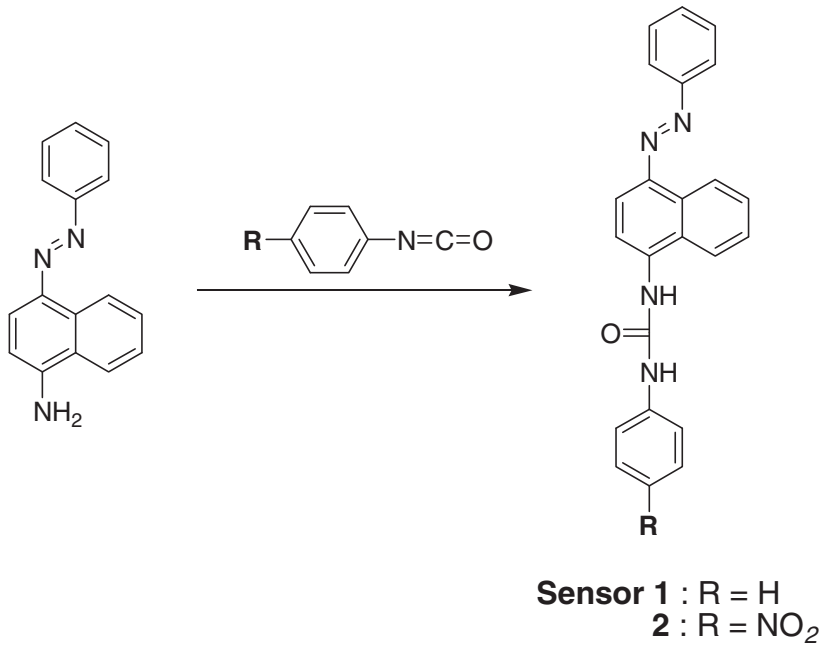
1. Introduction

Anions play a significant role in a wide range of biological, environmental, medical, and chemical processes. In addition, they exhibit large variations in size, shape, and charge distribution, along with strong solvation in polar and/or H-bond donor solvents. Therefore, the design and development of synthetic receptors and sensors for the detection of anions have attracted considerable attention in recent years [1–6]. In particular, fluoride (F^-) sensing has garnered increasing interest in the molecular recognition community because of its pivotal importance in biological and chemical sciences [7–12]. F^- is a useful additive that may benefit human health, in that it prevents and cures dental conditions and osteoporosis. However, a substantive intake of F^- can cause environmental pollution, and excessive ingestion can disrupt the immune system, and can cause kidney damage and cancer [13,14]. Thus, the development of reliable sensors for F^- ions is crucial.

An effective chemosensor must convert the anion recognition event by the ionophore into an easily monitored and highly sensitive signal by the chromophore. Currently, the development of colorimetric anion sensors is particularly challenging because

* Corresponding authors at: 300 Yongbong-dong, Chonnam National University, Republic of Korea.
E-mail addresses: choej47@gmail.com (E.J. Cho), yjlee@kbsi.re.kr (Y.J. Lee).

http://dx.doi.org/10.1016/j.saa.2015.07.042
1386-1425/



Scheme 1. Synthesis of sensors **1** and **2**.

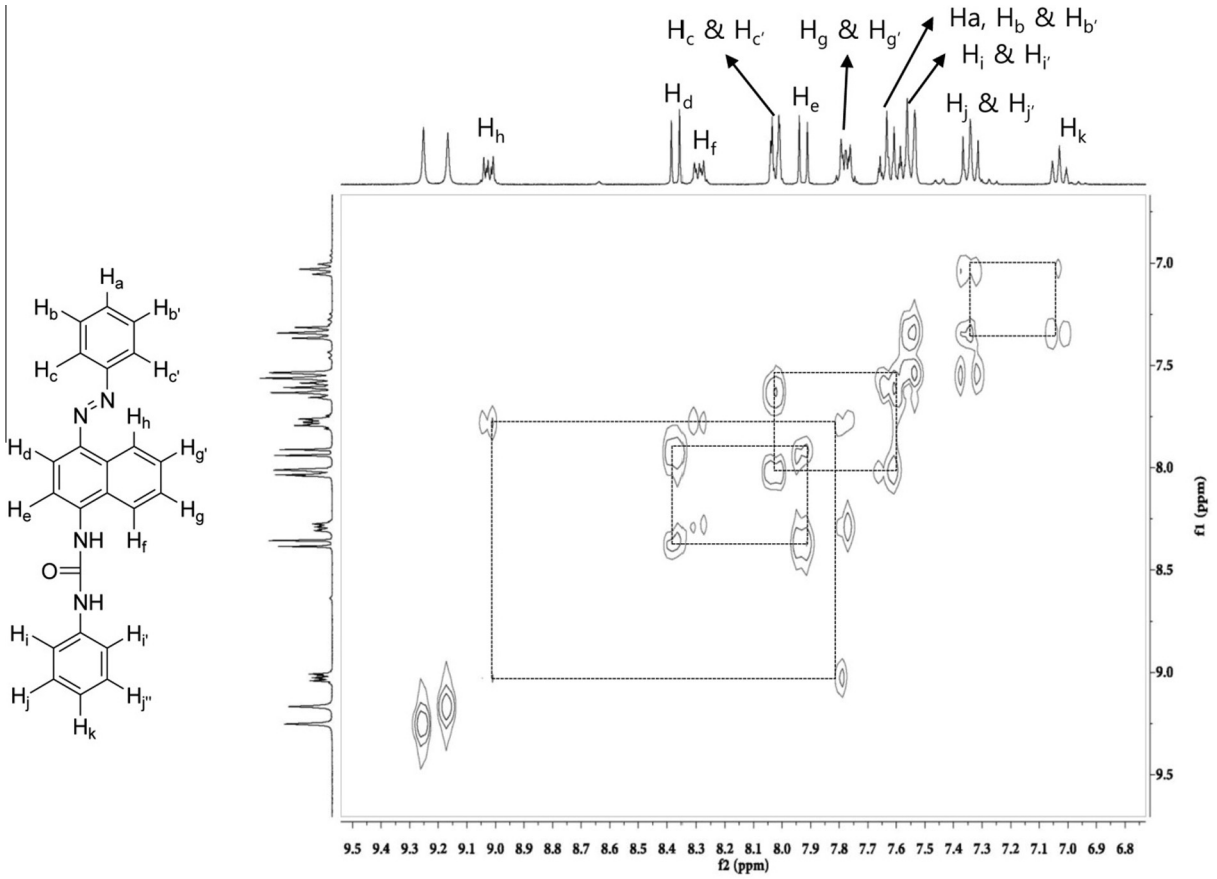


Fig. 1. Partial ^{1}H–^{1}H COSY NMR spectrum of sensor **1** recorded in DMSO-d_6.

signaling events, such as color changes, that can be detected by the naked eye are widely used owing to the low cost and minimal equipment requirement. In general, such chemosensors are constructed according to the receptor-chromophore binomial, which involves the binding of a specific anion substrate to receptor sites and a chromophore, which is responsible for translating the receptor–anion association into an optical signal. Color changes occur when a charge-transfer complex is formed [15–25].