Chemical Physics Letters 696 (2018) 106–111

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Instilling exploitable INHIBIT logic gate response for F^-/H^+ in 'end-off' anthracene-diamine hybrid by simple functional group manipulation: Experimental study aided by DFT calculations

Arghyadeep Bhattacharyya, Subhash Chandra Makhal, Aniruddha Ganguly, Nikhil Guchhait *

Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

ARTICLE INFO

Article history:
Received 16 October 2017
In final form 14 February 2018
Available online 15 February 2018

Keywords:
Chromogenic
Fluoride sensor
Naked eye
INHIBIT logic gate
DFT
Paper strip

ABSTRACT

Two anthracene based receptors **ADAMN** and **ANOPD** were synthesized and characterized. The response of both towards F^- ion has been monitored by UV–Vis and ^1H NMR spectroscopy as well as naked eye color change. Interestingly, change in acceptor unit endows **ADAMN** to behave as a **INHIBIT** logic gate with F^- and H^+ as inputs whereas **ANOPD** remains totally silent towards F^-. The reason for this differential behavior has been explored by DFT calculations. The practical utility of the logic gate response of **ADAMN** was explored by successful paper strip experiment.

1. Introduction

The design and synthesis of fluoride specific receptors have been gaining impetus over the last few decades principally due to the Janus faced effect F^- causes on human physiology. Within permissible limits, F^- in indispensable in preventing dental caries, treatment of osteoporosis [1,2] as well as its industrial utility as a component of cockroach poisons, anesthetic drugs [3–5] cannot be ignored. When taken in excess, the dreaded disease Fluorosis accompanied with thyroid activity depression and bone disorders are a few of the pathological conditions [6–8] that is brought about by F^-. China, Africa as well as the Indian subcontinent are affected by fluoride pollution, which is a matter of serious concern [9]. Reports claim that approximately 40 blocks of 7 districts in West Bengal are endemic to Fluorosis [10]. Thus, it is of utmost importance to design new, cheap and sensitive sensors for fluoride ion. The colorimetric sensors are user friendly and can detect analyte(s) without any sort of instrumental assistance. Of late, several colorimetric sensors capable of detecting F^- have been reported. However, the main drawback of some of these sensors is their inability to distinguish fluoride from acetate due to their comparable basicity as also poor detection limit restricts the practical utility of such sensors when trace amount of Fluoride is to be detected [11,12]. Hence, the necessity of selective and sensitive chromogenic F^- sensors can be envisaged. At this juncture, we report a comparative study involving chromogenic response of two anthracene based probes 2-((anthracen-10-yl)methyleneamino)-3-aminomaleonitrile **(ADAMN)** (obtained by the condensation between anthracene aldehyde and diaminomaleonitrile) and (*E*)-N^1-((anthracen-10-yl)methylene)-5-nitrobenzene-1,2-diamine **(ANOPD)** (obtained by the condensation between anthracene aldehyde and 4-nitro *ortho*-phenylenediamine) towards F^-. **ADAMN** undergoes a sharp change in color from yellow to pink associated with considerable spectral modification of the same in presence of Fluoride. The detection limit of **ADAMN** towards Fluoride was found out to be 5.0×10^{-6} (M) which is comparable to the same obtained from more sensitive method in the form of fluorescence [13,14]. In addition, **ADAMN** shows excellent recyclability of its optical response towards F^- with respect to protic acid, thereby exhibiting a 'write-read-erase' type of logic function, the associated logic gate known as 'INHIBIT' logic gate. Surprisingly, **ANOPD** neither shows any sort of naked eye color change/spectroscopic modification in presence of F^- or any other anionic radicals; nor does it show any sort of logic gate response. We conducted Density Function Theory (**DFT**) based calculations to reveal the differential behavior of two similar probes as far as anion recognition/logic gate response is concerned and concluded that structural linearity was the determining factor. Thus, a successful chromogenic reusable F^- sensor was constructed by simple modification of functional groups.

---

* Corresponding author.
E-mail address: nguchhait@yahoo.com (N. Guchhait).

https://doi.org/10.1016/j.cplett.2018.02.046

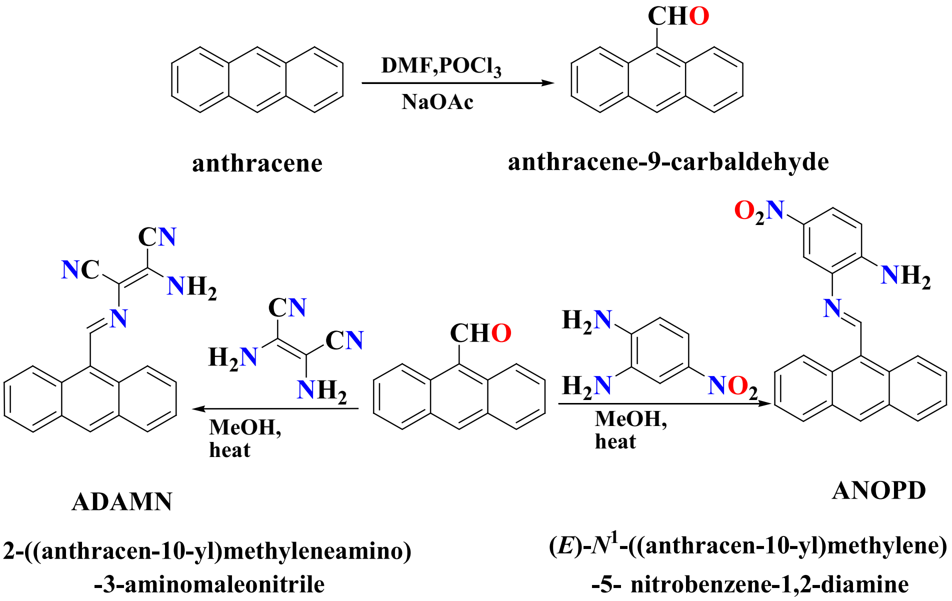
2. Experimental

Anthracene-9-aldehyde was synthesized using Vilsmeir-Haack formylation of anthracene nucleus (Scheme 1) [15]. Diaminomaleonitrile, 4-nitroprthophenylene diamine, Tetrabutylammonium salts of anions and perchlorate salts of metals were purchased from Merck and used as received. Trifluoroacetic acid (TFA) was purchased from SRL. Acetonitrile used for naked eye color change experiments and UV–Vis spectroscopic experiments was of spectroscopic grade and obtained from Spectrochem, India. ^{1}H NMR and ^{13}C NMR were recorded on Bruker Advanced Supercon 300 MHz and chemical shifts are expressed in ppm using TMS as internal standard. IR spectrum was recorded on Perkin Elmer spectrum-100 and UV–Vis titrations and related experiments were conducted in Hitachi U-3501 Spectrophotometer. Mass spectrum was recorded on Waters Xevo G2-S Q TOF mass spectrometer. Theoretical calculations were carried out using Gaussian 09 W software at DFT level with 6-31G** basis set and B3LYP functional [16]. For optimizing the fluoride complexes of the receptors, tetramethylammonium unit was chosen as counter cation for the sake of simplicity.

3. Results and discussion

Receptors **ADAMN** and **ANOPD** were synthesized by simple condensation reaction of 9-anthracene aldehyde with their respective amines and have been characterized by NMR, IR and ESIMS (ESI, Figs. S1–S9). To a 50 μM acetonitrile solution of **ADAMN** anions (5 equivalents) were added individually. Addition of fluoride resulted in an instantaneous change in color from yellow to pink whereas addition of other anions produced too little a change to be taken into consideration (Fig. 1). On the other hand, addition of anions (5 equivalents) to a 50 μM acetonitrile solution of **ANOPD** did not result in any sharp color change (ESI, Fig. S10). Since many metal sensors are reported where diaminomaleonitrile is a constituent, the naked eye response of metal ions (5 equivalents each) was checked only to find no observable naked eye change in color. Moreover, **ADAMN** could successfully recognize fluoride even in a mixture of metals (ESI, Fig. S11).

The UV–Visible responses of both receptors towards cations/anions were checked in acetonitrile solvent keeping concentrations of both at 10 μM. **ADAMN** shows structured absorption band feature with peaks at ~452 nm, ~350 nm and ~267 nm (ESI, Fig. S12). These absorption bands are red-shifted with respect to the bare anthracene due to the presence of substitution having the possibility of extensive delocalization. These bands are nothing but the π-π* type transitions to different electronic states of the aromatic unit. The molecule **ANOPD** shows similar bands with most red-shifted peak at ~415 nm due to less delocalization possibility due to the presence of bulky substituted phenyl unit. Addition of fluoride resulted in bathochromic shift of the most red-shifted band by ~79 nm whereas other bands remained almost



Scheme 1. Synthetic outline of title compound **ADAMN** and control compound **ANOPD**.

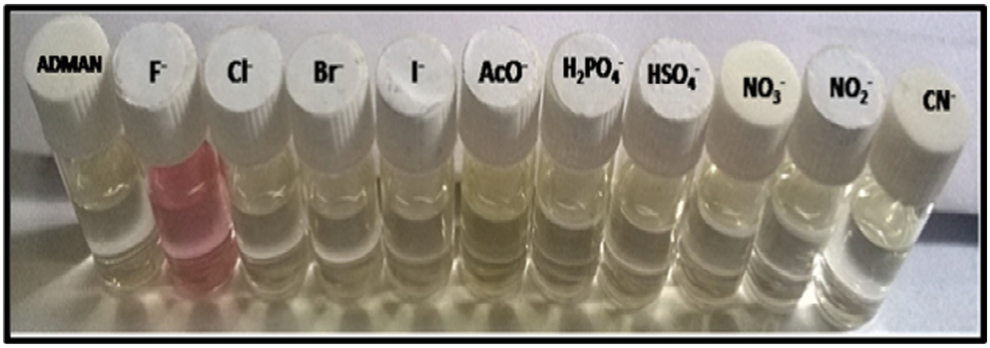


Fig. 1. Change in color of **ADAMN** (50 μM) upon addition of 5 equivalents of F$^-$.