



# First phenalenone based receptor for selective iodide ion sensing



Amrita Mitra<sup>a,1</sup>, Anand Pariyar<sup>b,2</sup>, Suranjana Bose<sup>a</sup>, Pinaki Bandyopadhyay<sup>a</sup>,  
Arindam Sarkar<sup>c,\*</sup>

<sup>a</sup> Department of Chemistry, University of North Bengal, Raja Rammohunpur, Siliguri 734013, India

<sup>b</sup> Indian Institute of Science Education and Research Kolkata (IISER Kolkata), Kolkata 700064, India

<sup>c</sup> India Innovation Research Centre, 465 Patparganj Industrial Area, Delhi 110092, India

## ARTICLE INFO

### Article history:

Received 23 September 2014

Received in revised form 8 January 2015

Accepted 9 January 2015

Available online 17 January 2015

### Keywords:

Chemosensor

Fluorescence

Iodide

Job's plot

Phenalenone

Stern–Volmer plot

## ABSTRACT

A novel phenalenone based molecular receptor, 1,1,1-tris(1-oxophenalenyl-9-N-ethyl)amine (**3**) bearing PLY moiety as the fluorophore has been synthesized and characterized. A thorough study on the binding behaviour of the compound with I<sup>-</sup> and other biologically relevant anions (viz. F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, N<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) in solution was performed by quantitative UV–vis and fluorescence spectroscopy. The novel compound evolved as a highly selective sensor for I<sup>-</sup> ion, discriminating all other biologically important anions in solution.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Phenalenone based compounds have left their mark as novel materials due to their unique molecular properties. Most of the novel phenalenone molecules are either in the form of radical, salt or in complexed form with elements such as Zn, B or Si [1–4]. Chemosensors are capable of interacting with ions in solution and signal their presence by changing optical properties (absorption or emission) [5]. Phenalenone based compounds are rarely reported as a fluorescent material in non radical or non complexed form [6]. Particularly, the application of phenalenone based molecules as chemosensor is not known. Phenalenone is a natural product which can be found in the plant extracts [7]. Designing a fluorescent chemosensor by simple modification of the original phenalenone framework would be biocompatible and can be utilized as biomarker in future. Phenalenones or 9-hydroxy phenalenones have never been attractive fluorescent materials due to their weak fluorescent property. This is due to the presence of non bonding electrons in the oxygen atoms which do

not contribute to the conjugation, but deactivate fluorescence by inter-combinational conversions [8]. Introduction of –NHR moiety in conjugated  $\pi$  systems has been effective to enhance the fluorescence signals [9]; due to the participation of nitrogen lone pair electrons to the conjugation. Introduction of –NR<sub>2</sub> to the 9 position of phenalenone has been shown to enhance fluorescence signals more than alkoxy substitutions [8] because participation of nitrogen lone pair to the  $\pi$  conjugation lower the  $\pi$ – $\pi^*$  excitation below that of  $n$ – $\pi^*$  excitation to have minimum possibility of inter-combinational conversion. On the other hand, tripodal amine based receptors have been widely used as chemosensors [10] and remain as an attractive backbone for anion and cation sensing molecules. A simple tripodal amine substitution to the 9-position of the phenalenone is expected to enhance the fluorescence as well as could lead to selective ion/molecule sensing. Scheme 1 shows the importance of the design of tris-amino-phenalenone molecule (**3**).

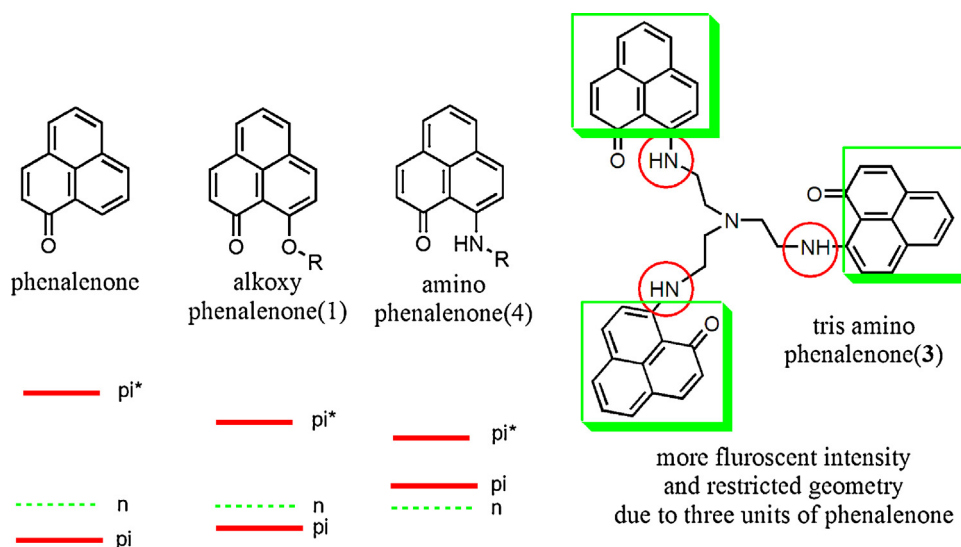
With the above underlying objective, we report, the synthesis and characterization of a highly fluorescent novel phenalenone based receptor 1,1,1-tris (1-oxophenalenyl-9-N-ethyl) amine (**3**) which bears PLY moiety as the fluorophore. The receptor was tested for anion sensing because it has two probable anion interaction sites such as –NH– (–N–H – anion hydrogen bond interaction; marked as red circle) and phenalenone (C–H – anion hydrogen bond interaction or anion –  $\pi$  charge transfer interaction; marked as green square in Scheme 1). These interactions are observed

\* Corresponding author. Tel.: +91 1140532692; fax: +91 1140532692.

E-mail address: [sararindam@gmail.com](mailto:sararindam@gmail.com) (A. Sarkar).

<sup>1</sup> Tel.: +91 353 2776381; fax: +91 353 2699001.

<sup>2</sup> Tel.: +91 336 4510539.



**Scheme 1.** A qualitative and schematic representation of electronic states of phenalenone and its derivatives towards chemosensor design. (a) Electronic states in phenalenone, alkoxyphenalenone and aminophenalenone. (b) Tris-amino phenalenone (**3**) studied in the present work.

in many published chemosensors including few pyrrole based molecules [11,12].

The inorganic anions, such as halide ions, nitrate, nitrite, phosphate, sulphate, sulphide, cyanide, acetate, carbonate, etc. play vital role in biological systems, industrial fields, biomedical stream and medical sciences. Their presence in accurate proportion is very important for the maintenance of lethal limit [13,14]. With this background their selective detection and quantification is very important in various fields of experimental science. Iodide ion is one of the most biologically essential anion since it has pronounced utility in sustaining neurological activity and thyroid gland function [15]. In recent years a number of selective fluorescent sensors have been developed for the detection of iodide ion by the change in photophysical or colorimetric properties of the receptor without substantial interferences from other anions [16–18]. In this context, the work by Chen et al. requires special mention where the change in the optical properties of gold nano particles was utilized to sense iodide ions [19]. Thus development of a biocompatible chemosensor for iodide ion in presence of other biologically relevant anions is important. The encapsulation of iodide ion or other anion is mainly dependent on the basicity of anions; however the compatible size of the host and guest molecules is also very important.

In our present study, the receptor (**3**) has shown selective and efficient binding of iodide ion in solution which is facilitated by the compatible size of pseudocavity furnished by the newly synthesized compound.

## 2. Experimental

### 2.1.1. General

All reagents were procured from Aldrich, SD Fine Chemicals and/or Fluka and were used without further purification unless otherwise stated. All the reactions were done with dried and freshly distilled solvents under anhydrous atmosphere. Compound 9-ethoxy-1-oxophenalene (**1**) was prepared according to reported procedure [20,21]. The  $^1\text{H}$  NMR data were collected from JEOL ECS 400 spectrometer with  $\text{CDCl}_3/\text{THF-d}_8$  solvent and tetramethylsilane (TMS) as internal standard. UV–vis spectra were recorded on Agilent 8543 spectrometer. Fluorescence experiment was carried out with PTI spectrofluorometer using Felix-Gx software. The slit widths were fixed at 1 mm for the entrance slit, 1 mm for the

intermediate and 1 mm for the exit slit and Xenon lamp was used as the source of radiation for steady state fluorescence experiments. For anion binding studies tetrabutyl ammonium salts of halide ions and sodium salts of other anions were used. Synapt G2 HDMS instrument was used to record HRMS and Leucine enkephalin used for lock mass.

### 2.1.2. Synthesis of 1,1,1-tris (1-oxophenaleny-9-N-ethyl)amine (**3**)

A solution of 1,1,1-tris (aminoethyl) amine (**2**) (0.42 mg, 2.9 mmol) in 1,2-dichloro ethane (5 mL) was added to a solution of 9-ethoxy-1-oxophenalene (**1**) (2 g, 8.9 mmol) in the same solvent (30 mL). The mixture was refluxed for 24 h. The progress of reaction was observed by comparative TLC analysis with 1:2 hexane–chloroform mixtures as an eluent. After completion of the reaction the solvent was removed under reduced pressure. The dark yellow crude oily product was purified by column chromatography on active neutral  $\text{Al}_2\text{O}_3$  (for column chromatography) with chloroform. Yield of the crude product: 1.5 g (25%). M.P. 87 °C.

UV/vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  [nm]( $\epsilon$  in  $\text{M}^{-1} \text{cm}^{-1}$ ): 255 ( $1.2 \times 10^5$ ), 279 ( $5 \times 10^4$  sh), 341 ( $3 \times 10^4$  sh), 357 ( $5.1 \times 10^4$ ), 422 ( $1.7 \times 10^4$  sh), 449 ( $3.4 \times 10^4$ ), 477 ( $4.9 \times 10^4$ ); FT-IR (KBr,  $\nu \text{ cm}^{-1}$ ): 3384 (w, br), 3029 (w), 2950 (ms), 2359 (ms), 1634 (s), 1572 (s); Anal. Calcd. for  $\text{C}_{45}\text{H}_{36}\text{N}_4\text{O}_3$ : C, 79.4; H, 5.33; N, 8.23. Found: C, 78.8; H, 5.128; N, 8.13; ESI MS:  $m/z$  703.3 ( $\text{M}+\text{Na}^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) in ppm:  $\delta$  12.25(s, 3H); 7.135 (d, 3H); 7.26 (t, 3H); 7.58 (d, 3H); 7.73 (d, 3H); 7.66(m, 6H); 6.78(d, 3H); 3.15 (t, 6H); 3.74 (t, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) in ppm: 42.9, 54.9, 108.0, 114.5, 121.6, 124.3, 124.9, 128.0, 129.6, 131.2, 131.5, 137.9, 138.4, 156.1, 183.9.

### 2.1.3. Synthesis of 9-(propylamino)-1-phenalenone (**4**)

Compound **4** was synthesized by minor modification of reported procedure [21,22]. 30 mL of n-propyl amine was added to a solution of 9-ethoxy phenalenone (500 mg, 2.23 mmol) in 10 mL 1,2-dichloroethane. The resulting mixture was refluxed at 90 °C for 12 h. The progress of the reaction was monitored by TLC analysis (1:1 n-hexane– $\text{CHCl}_3$ ). After refluxing the solvent was removed under reduced pressure and the crude product was purified by column chromatography on alumina using  $\text{CHCl}_3$  as eluent.

Download English Version:

<https://daneshyari.com/en/article/741931>

Download Persian Version:

<https://daneshyari.com/article/741931>

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