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Anthracene-based fluorescence turn-on chemodosimeter for the recognition of persulfate anion

Pooja S. Badekar and Anupa A. Kumbhar*

The anthracenethiosemicarbazone (ATSC) fluorescent 'turn- on' chemodosimeter, for detection of the persulfate anion $(S_2O_8^{-2})$ in 90% DMSO has been developed. ATSC is simple and exhibits high selectivity toward $S_2O_8^{-2}$ anion in the presence of large interferences from other anions or cations. A fluorescence change from blue to green visualized under the UV light makes it possible to detect the persulfate anion with naked-eye. A mechanism underlying the molecular recognition has been explained from the ¹H-NMR and single crystal X-ray structure experiments.

Introduction

Development of selective and sensitive methods for detection and monitoring of anions are in great demand as anions are ubiquitous in nature and are crucial for a variety of biological and chemical phenomena, health, environment, as components of fertilizer and food industries.¹ Fluorescence signalling has been preferred over other detection methods owing to its selectivity and high sensitivity. A recognition unit attached to fluorophore is known to be responsible for selective and efficient binding of analytes for sensing of the molecule. The diffused nature and wide variation in structure of anions pose a great challenge in the designing of sensors for the detection of a specific anion. Anion receptors reveal different binding or sensing mechanisms consequent to analyte binding² or hydrogen bonding interactions³ which results in the perturbation of π -conjugation. The chemical reaction between analyte and the sensing molecule, accompanied by spectral changes, have been reported in the literature. The synthetically challenging scaffolds like peptides⁴, cholic acids,⁵ protonated quinoxaline,⁶ metal-based Lewis acid centers,⁷ thiouronium,⁸ thiocalix[4]arenes,⁹ amine or polyamine functionalities¹⁰ have been utilized for sensing of the ions.

It has been realized that polarized HN groups present in the recognition unit are H-bond donor toward anions and find applications as receptors for the recognition and sensing.

Molecules containing chromophores covalently linked to guanidium,¹¹ pyrrole,¹² phenol,¹³ amide,¹⁴ indolocarbazoles¹⁵

and urea/thiourea¹⁶ bind effectively to anions through directional H-bonding interactions. The receptors containing thiourea (which is stronger acid than urea, pKa values being 21.1 and 26.9 respectively) bring stronger H-bond interactions conducing stable anion complexes.^{9a} Further the ease of synthesis, high yields and highly specific responses at low detection limits makes them fascinating. The urea/thiourea derivatives have successfully been incorporated as neutral ionophores in ion selective electrodes (ISEs) to quantify chloride,¹⁷ sulphide¹⁸ and acetate anions¹⁹ or in optical anion sensing.²⁰

Chemodosimeters are a class of sensing system based on an irreversible chemical reaction between the analyte and the dosimeter molecule leading to a change in the fluorescence or colour of the receptor.²¹ Usually, the response of the dosimeter is cumulative and thus can be related to the concentration of the analyte. Fluorescent dosimeters have been known for the detection of formaldehyde,^{22a} hypochlorous^{22b} and hypobromous acids,^{22c} reactive oxygen species (.OH),^{22d} and metal ions such as Cu(II),²³ Hg(II),²⁴ Al(III),²⁵ Fe(III),²⁶ etc. However, to the best of our knowledge, a chemodosimeter for the detection of anions has not been reported so far.

Persulfate (or peroxydisulfate) being a strong oxidizing agent, serves as an initiator for olefin polymerization, microetchant in printed circuit boards,²⁷ for bleaching of textiles, cosmetics²⁸ and as polymerization activator²⁹ in industries. It has further been used as an efficient decolorizing agent in azo dyes³⁰ and photochemical oxidant for decomposition of environmentally persistent perfluorocarboxylic acid in water.³¹ Being highly reactive, contact with persulfate may lead to skin diseases³² and occupational asthama.³³ The detection and quantitation of persulfate has thus become imperative in industrial environments to ensure the safety of the personal.

Different procedures for the estimation of persulfate³⁴ ion based on sulphate detection encompassing iodimetric,³⁵ reductometric,³⁶ polarographic,³⁷ electrochemical³⁸ and

Department of Chemistry,

Savitribai Phule Pune University, Ganeshkhind Road, Pune 411007, India.

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spectrophotometric³⁹ methods have been developed. The indirect methods used for the detection of persulfates are time consuming, complex in operation and not suitable for routine analysis⁴⁰ and therefore a simple, rapid and sensitive analysis method for its determination is necessary.⁴¹ The instability of persulfate in aqueous medium with respect to its decomposition into sulphate (SO_4^{2-}) , hydrogen sulphate (HSO_4^{2-})) or sulphite (SO_3^{2}) anions pose a great challenge in this regard. Detailed investigations on the kinetics and mechanism of thermal decomposition of persulphate ion in aqueous alkaline, neutral or dilute acid medium showed that rate of decomposition of persulfate in aqueous alkaline and neutral media at the ambient temperature /pressure conditions was hours in the absence of any catalyst.⁴² On the other hand $S_2O_8^{2-}$ in DMSO solutions is stable and does not undergo any further decomposition⁴³ which can be utilized as an effective medium for frontal polymerization of different monomers. The present endeavour demonstrates the detection of persulfate anion in 90% DMSO solution using the anthracenethiosemicarbazone. 1, as the fluorescent chemodosimeter.

Experimental Section

Materials and methods

All the starting materials were obtained from commercial suppliers and used as received. The potassium salts in the present study were AR grade, obtained from SRL or S.D. Fine Chemicals Limited (India). Dry DMSO (HPLC grade,) was procured from Aldrich Chemicals. All samples were prepared at room temperature, in dry DMSO and de-ionized water and equilibrated for 110 min before recording the emission spectra. Aqueous solution (300μ L) of anions and cations used to prepare samples has no effect on the emission intensity of **1**. UV-VIS spectra were recorded on the Shimadzu UV-1601 spectrophotometer. Fluorescence spectra were measured with Jasco FP-8300 Spectrofluorometer. Both excitation and emission slit widths were set at 2.5 nm. Samples were exited at 392 nm. Infrared spectra of solid samples were recorded on BRUKER platinum ATR Tensor-37.

Synthesis and characterization of anthracenethiosemicarbazone (ATSC, 1)

1 was synthesized according to the previously reported procedure,⁴⁴ by reacting 9-anthracene carboxaldehyde and thiosemicarbazide in 1:1.2 ratio in ethanol (20 mL) taken in a round bottom flask equipped with a stir bar. Two to three drops of glacial acetic acid was added to reaction mixture and was refluxed for 3 h. Yellow color product was collected by filtration, washed several times with diethyl ether and dried in vacuum (yield = 63%). ¹H NMR (DMSO-d⁶) - 11.8 (s, 1H), 9.4 (s, 1H), 8.6 (s, 1H), 8.7 (doublet 2H), 8.2 (t, 8H), 8.4 (broad 1H), 7.6 (m); ESI-MS, m/z =280 [M + H]⁺ (Fig. S1 and Fig. S2 for ¹H NMR and ESI-MS respectively).

1 (10 mg, 0.036 mmol) was reacted with (2.9 g, 10.72 mmol) of potassium persulphate in ethanol. The yellow

solution obtained on stirring the reaction mixture at 37°C for 24 h was concentrated on rotary evaporator and loaded on silica gel column. Progress of the reaction was monitored by TLC. After 24 h, TLC showed a spot at solvent front and another spot at the point of application which did not move through the column. The product was separated using ethyl acetate : hexane (50/50 v/v) solvent system. Slow evaporation of this solution gave yellow needles of the isolated oxidation product **2** suitable for single crystal X-ray diffraction. Yield (~15%); ¹H NMR (DMSO-d⁶) – 7.94 (m, 4H), 8.23 (m, 4H); ESI-MS, m/z =274.27 [M + 2 MeOH + H]⁺ (Fig. S5 and Fig. S6 for ¹H NMR and ESI-MS respectively).

X-ray crystal structure refinement

Data of compound **2** (Fig. S7) was collected on a Bruker D8 venture PHOTON 100 CMOS diffractometer using graphite monochromatized Cu-K α radiation ($\lambda = 1.54178$ Å) at 100 K. Data integration was carried out by Bruker SAINT program and Empirical absorption corrections were applied using the SADABS program. The programs are integrated in APEX III package. The structure of the ligand was solved on Olex2⁴⁵ using SHELXT program and refined (full matrix least-squares refinement on F²) using SHELXL program.^{46,47} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Determination of quantum yield

The effect of addition of increasing equivalents of persulfate on the quantum yield of **1** was determined in 90% DMSO solvent. The refractive index (RI) for 90% DMSO was calculated using the equation(1):

$$\label{eq:n} \begin{split} n &= [\% \ H_2 O / 100 \ x \ RI_{H2O} + \% \ DMSO / 100 \ x \ RI_{DMSO}] \end{split} \tag{1} \\ & \text{where, } n \ \text{is the } RI \ \text{of } 90\% \ DMSO \ \text{which turned out to be} \\ 1.46467, \text{ and used further for determination of quantum yields} \\ & \text{using:} \end{split}$$

$$\Phi_{\rm S} = \Phi_{\rm R} \left(I_{\rm S}/I_{\rm R} \right) (A_{\rm R}/A_{\rm S}) (nS_2/nR_2) \tag{2}$$

In the above equation, S and R indicate the sample and reference standard solution respectively, Φ being the quantum yield and I the area under the emission curve, A represents absorbance at the excitation wavelength and n is the refractive index of solvent. Anthracene in chloroform was used as standard (Φ_{CHCI3} = 0.11).⁴⁸ All the solutions used in determination of quantum yields were aerated.

Results and Discussion



Scheme 1 Synthesis of 1

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Fig. 2 Emission intensity of **1** (10 μ M) with (A) different anions such as HSO₄⁻, SO₄²⁻, SO₃²⁻, H₂PO₄²⁻, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CO₃²⁻, ClO₄⁻, and CH₃COO⁻ (4.6 mM) and (B) cations such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Hg²⁺, Cd²⁺, and Pb²⁺ (4.6 mM). All spectra are acquired in 90% DMSO solution at 37 $^{\circ}$ C.

1 was prepared in one step reaction in reasonably high yield (Scheme 1), giving orange crystalline compound exhibiting weak blue fluorescence (90% DMSO, 10μ M, pH 7.2).

Selectivity for persulfate anion by fluorescence spectroscopic method

The absorption spectra of **1** recorded in dry DMSO shows absorption band at 247 nm which can be attributed to π - π * transitions whereas the peak centered at 392 nm is assigned to n- π * transitions. On excitation at 392 nm, the emission spectra emerge with a peak centered at 474 nm as displayed in Fig. 1.



Fig. 1 Absorption and emission spectra of 1 (10 $\mu M)$ in dry DMSO ($\lambda_{ex}{=}392$ nm).

To evaluate the selectivity of 1, changes in the fluorescence properties caused by addition of potassium salts of HSO₄, SO_4^{2-} , SO_3^{2-} , $H_2PO_4^{-}$, F⁻, Cl⁻, Br⁻, l⁻, NO_3^{-} , CO_3^{2-} , ClO_4^{-} , and CH_3COO^{-} was monitored at the 474 nm ($\lambda_{ex}\text{=}$ 392 nm). As evidenced from Fig. 2A, only the persulfate anion reveal around 20-fold increase in the emission intensity with 11 nm shift in the emission band at 485 nm. 1 demonstrated remarkable selectivity toward the persulfate anion over others. The persulfate solution (100 mM) was prepared freshly in de-ionized water, and added immediately to solution of 1 in dry DMSO in such a way that total volume of water in the mixture does not exceed 300 µL. The solution (90% DMSO) was then equilibrated for 110 min before measuring the response. Same procedure was followed for other anions including the persulphate decomposition products HSO_4 , SO_4^2 , and SO_3^{2-} anions which do not reveal any noticeable change for their fluorescence intensity. Based on the conditions used in the present study, it may thus be inferred that the fluorescence response obtained can either be attributed to hydrogen bonding interactions between intact persulfate anion and 1 or formation of new oxidation products via the processes involving the cleavage of thiosemicarbazone molecule from 1.

The response measured in the presence of metal ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Hg²⁺, Cd²⁺, and Pb²⁺ has been described in Fig. 2B. As may be observed, even with the large excess of metal ions, a significant response was obtained only for the persulfate anion. The high selectivity of **1** toward S₂O₈²⁻ anion thus is transparent. Since maximum 300 μ L of the aqueous solutions of anions and cations were added to **1** during measurements

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further experiments to understand the effect of water on emission intensity of **1**, as depicted in Fig. S3 revealed that water do not promote any changes in fluorescence intensity under the identical experimental conditions.

It can be noted that nearly non-fluorescent **1** generated strongly fluorescent green species which emits at around 485 nm with persulfate anion ($S_2O_8^{2^-}$, λ_{ex} = 370 nm). A dramatic fluorescence off-on behaviour of **1** in response to $S_2O_8^{2^-}$ (Φ_f , 0.007 \rightarrow 0.1012) necessitated further investigations of the detection of persulfate anion.



Fig. 3 Change in emission intensity of 1 as a function of increasing concentrations of persulfate anion. Inset: Emission intensity at 485 nm.

Therefore, fluorescence performance of ${\bf 1}$ for detection of $S_2O_8^{\ 2^-}$ in DMSO/water 90:10 (v/v) solution was studied. Fig. 3 shows an increase in the fluorescence intensity with respect to



Fig. 4 Selectivity of 1 (10 μ M) toward anions and cations in 90% DMSO solution. The red bars represent the fluorescence emission of 1 (10 μ M) with anions and cations (4.6 mM). The black bars represent the fluorescence changes that occur upon addition of competing ions (4.6 mM) to the solution containing 1 (10 μ M) and S₂O₈²⁻ (4.6 mM). 1: 1; 2: S₂O₈²⁻; 3:F⁻; 4:Cl; 5: HSO₄⁻; 6: H₂PO₄⁻; 7: CH₃COO⁺;



Fig. 5 Photograph of **1** with different anions under UV-light in UV-chamber. Note the color change and intensified emission of **1** on addition of persulfate anion (4.6 mM) after 110 min incubation at 37°C.

the added amounts of $S_2O_8^{2-}$ ion reaching saturation at 460 equivalents. Further, the emission intensity was found to increase with time giving stable response after 110 min (Fig. S4). Therefore, the interaction of **1** with other interfering anions and cations was studied at 4.6 mM concentrations individually as well as in presence of persulphate anion after 110 min incubation of reaction mixtures at 37 °C.

As may readily be noticed from Fig. 4, presence of large amounts (4.6 mM) of other anions and cations did not affect the intensity of persulfate anion significantly. This makes **1** a very selective and sensitive probe for detection of persulfate anion in presence of large interferences allowing easy and rapid detection. In addition, we have also verified the response of **1** with other oxidants like hydrogen peroxide and tert-butyl peroxide in absence and presence of persulphate anion (Fig.4, bars 20 and 21 respectively). The simultaneous presence of peroxides and persulphate has reduced the response drastically, may be due to radical-radical annihilation thereby inhibiting the oxidation of **1**. In addition, the color change could be observed visually under UV light as shown in Fig. 5.



Fig.6 Changes in the absorption spectrum of 1 with increasing additions of persulphate anion till saturation (4.6 mM)

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Fig. 7. ¹H-NMR titration of **1** (10 μ M, in 90% DMSO-d₆ – 10 % D₂O) in (A) absence and presence of (B) 2, (C) 5 and (D) 50 equivalents of persulfate respectively. (E) shows the ¹H-NMR spectrum of the crude reaction product precipitated after addition of 460 equivalents of persulphate to the solution of **1** in DMSO-d₆.

Changes in the absorbance were also monitored with incremental additions of persulphate anions to **1**. It can be seen from Fig. 6, that at the end of the titration, complete change in the absorption spectrum of the **1** occurs indicative of *in situ* generation of new species during the titration thus ruling out the possibility of persulphate recognition via hydrogen bonding mechanism.

Since potassium persulfate is insoluble in neat DMSO-d₆, we monitored the interaction of persulfate anion with **1** (10 μ M) by ¹H-NMR titration in 90% DMSO-d₆-10% D₂O solution (Fig. 7). With increase in the amount of persulphate anion in the NMR tube (upto 50 equivalent), the peaks corresponding to **1** gradually disappeared and three singlets were observed which can be attributed to a transitory intermediate formed *in situ* during titration which could not be identified. Further increase in persulphate concentration resulted in precipitation of a yellow compound. This was filtered, washed and redissolved in DMSO-d6 and its ¹H-NMR spectrum was recorded (Fig 7 E). Interestingly, the ¹H-NMR of crude product matches with that of anthraquinone. This suggests that **1** detects persulphate indirectly by getting oxidized.

To confirm this, we carried out a reaction between **1** and 300 equivalents of potassium persulphate at 37 °C, and separated the product through column chromatography (silica gel, ethyl acetate:hexane (50/50, v/v). The single crystals obtained by slow evaporation of the eluted product gave yellow needles suitable for single-crystal X-ray diffraction. The identity of the product was thus confirmed to be anthraquinone (Fig. S7). The suggested mechanism of the reaction is given in Scheme 2. Under the experimental conditions used, potassium persulphate dissociates in water to give persulphate anion ($S_2O_8^{2-}$), which despite having a strong



Scheme 2 Plausible mechanism for oxidation of the probe 1 by persulphate anion.

oxidation potential reacts sluggishly.^{49,50} However, presence of 10% water gives OH- ion, which accept electrons from persulphate anion to form sulphate anion radical (SO4 •-); but the reaction rate is low. Therefore, maximum response was achieved after 110 min in 90% DMSO solution of 1. Production of sulphate anion radical is self-sustaining in neutral medium (OH- ion then reacts with SO4 - to produce OH which again reacts with $S_2O_8^{2-}$ to produce SO_4^{--}) Reaction is initiated by hydrogen abstraction by $OH^{-}/S_{2}O_{8}^{2-}$ at C-9 position of **1** (1) to form an anion (2). This anion attacks on persulfate to form (3) with removal of HSO_4 . In presence of water, imine bond in (5) gets cleaved and formation of anthraldehyde (6) takes place. This anthraldehyde gets protonated (6) with removal of formic acid and generates an anionic aromatic species (7). This anion again reacts with persulfate to form aromatic disulfate species (8) which in turn gets protonated by water (9) and formation of quinone takes place with removal of HSO₄. Though, we have isolated anthraquinone as the oxidation product, presence of other species contributing to fluorescence in solution cannot be excluded.⁵¹

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Conclusions

In summary, the fluorescence turn-on chemodosimeter that selectively recognizes the persulfate anion in presence of other competitive anions and cations under the UV-visible region has been developed.

Conflicts of interest

There are no conflicts of interest to declare.

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Anthracene-based fluorescence turn-on chemodosimeter for the recognition

of persulfate anion

Pooja S. Badekar and Anupa A. Kumbhar*

Department of chemistry, Savitribai Phule Pune University, Pune 411007, India.

Email: aak@chem.unipune.ac.in

A fluorescence turn-on chemodosimeter that recognizes the persulfate anion in presence of other competitive anions or cations under the UV-visible region has been developed.

