



Paper-Based Portable Sensor and Nanosensor For Sulfur Dioxide Detection

Thuy Le¹, Samantha Macchi¹, Amanda Jaliha¹, Sylvia Szvedo¹, and Noureen Siraj^{1*}

¹Department of Chemistry, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock AR 72204, USA.

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*Corresponding Author: Noureen Siraj, Department of Chemistry, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock AR 72204, USA. E-mail: nxsiraj@ualr.edu

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Abstract

Sulfur dioxide (SO₂) pollution has become an increasing issue world-wide as it is produced both naturally and as industrial waste. Thus, it is critical to develop a sensor and detection methods to analyze SO₂ in the atmosphere. In order to design and generate an effective sensor that detects low levels of SO₂, fuchsine dyes have been used as a potential sensor material. New hydrophobic derivatives of Pararosaniline hydrochloride (pR-HCl) is developed to further improve the sensitivity of fuchsine dyes towards SO₂ gas. It has been shown that these dyes can provide an economic and efficient colorimetric detection of SO₂. In this work, (pR-HCl) is converted into an ionic material (IM) via a facile ion exchange reaction with bis (trifluoromethane) sulfonamide (NTF₂) counterion. The new, hydrophobic derivative, pararosaniline bis (trifluoromethane) sulfonamide (pR-NTF₂) IM was converted into stable aqueous ionic nanomaterials (INMs) by a reprecipitation method. Examination of absorption spectra results revealed that pR-NTF₂ IM exhibits enhanced molar absorptivity in comparison to the parent dye (pR-HCl). The improved photophysical properties allowed a framework for a highly sensitive nanosensor for detection of SO₂. A paper based portable SO₂ sensor was also developed and tested for its ability to colorimetric detection of SO₂. The cost effective and stable paper-based sensor exhibited the rapid response to decolorize the fuchsine dyes in few seconds as compared to their parent compound.

Keywords: SO₂ Detection, Portable and Low-cost Sensor, Nanosensor.

Introduction

Air pollution has contributed many issues to the global warming and human health. Among those air pollutants, sulfur dioxide (SO₂) is a very toxic gas that has a sharp odor. SO₂ is released in the process of generating electricity from sulfur-containing non-renewal energy sources (coal, oil, and gas), the fuel combustion in vehicles, and the extraction of metal ores [1]. SO₂ is emitted from natural processes such as volcanic eruptions, pollen grains [2] and natural decays [3]. The presence of SO₂ gas in the atmosphere also cause acid rain when the rain water reacts with SO₂ gas in air [4]. Since SO₂ is highly soluble in water, it easily absorbs into respiratory tract and eyes of human where it is converted into sulfurous acid (H₂SO₃). In addition, a short-term exposure to SO₂ causes irritation in nose, throat, lungs and respiratory tract in human. The U.S. Environmental Protection

Agency (EPA) has listed SO₂ as one of the six common air pollutants that needed to set National Ambient Air Quality Standards (NAAQS) to protect human health and environment [1]. According to U.S. Department of the Interior National Park Services [5], SO₂ becomes toxic to human health when its concentration exceeds from 5 parts per million (ppm) in the duration of 15 minutes [5]. It suggests that a very low concentration of SO₂ can cause many adverse health and environmental effects. For this reason, monitoring SO₂ at low concentrations has gained attention to protect environment, living organisms as well as human health.

Various methods have been developed for monitoring SO₂ such as acidimetry, conductimetry, colorimetry, flame photometry, potentiometry and coulometry [6]. The instruments such as gas chromatography, Fourier Transform Infrared (FTIR), Ozone Monitoring Instrument (OMI), etc. was also used to detect the presence of SO₂. However, these instruments are very expensive, and are difficult to use in the field to monitor SO₂. Developing an inexpensive portable sensor that is highly selective and sensitive (at ppm level) to SO₂ is necessary for the prevention of the adverse effects of SO₂ on human, environment, and other living organisms. Fuchsine dyes like pararosaniline hydrochloride (pR-HCl) and rosaniline hydrochloride (R-HCl) have been widely used as colorimetric sensor molecules for the detection of atmospheric SO₂ gas pollution [7, 8]. These dyes play a significant role in the regulation of SO₂ gas by providing an economical and relatively efficient colorimetric method for determining SO₂. However, further improvement in these dyes can enhance the sensitivity of fuchsine dyes towards SO₂ detection.

Ionic materials (IMs) have been attracted great attention due to their unique tunable photophysical property, high thermal stability, environmentally friendly nature and economic synthesis approach [9]. Therefore, many fluorescent [10], magnetic [11], colorimetric [12], hydrophobic [13]. IMs have been developed for variety of applications such as sensor [12], solar cells [14], organic light emitting diodes (OLEDs) [15], cancer therapy [16]. IMs with extended π -conjugated system can shift the absorption or emission wavelength maxima of the molecule [17]. Simply by changing the counterion of the IMs, improved photophysical and electronic property can be attained [18, 19]. Moreover, hydrophobic characteristics can be introduced to molecules which aids to develop stable nanostructures termed ionic nanomaterials (INMs) via simple methodology such as reprecipitation [20-23].

In the recent year, nanoparticles are getting tremendous interest of many researchers due to its amazing characteristics such as optical, electrical, and magnetic property [24, 25]. Several methods have been explored to design the nanomaterials [22, 26]. The size, shape, and surface charge of nanoparticles play an important role in many different applications such as biomedical, industrial, pharmaceutical, environment, electronics, textiles, energy, and sensing use [10, 23, 27]. It has been shown that nanoparticle-based sensors have several advantages over others such as greater sensitivity and faster response time [28]. However, the typical nanostructures used are metal based (gold, silver, etc.) which are expensive and not environmentally friendly [29]. Thus, implementing nanostructures based on organic molecules could prove to be an economic way to introduce effective sensors of pollutants.

In this project, a new hydrophobic derivative of pR-HCl is synthesized by combining pR cation with bis (trifluoromethane) sulfonamide (NTF₂) anion via ion exchange and applied as a stable nanosensor. The INMs were developed using pR-NTF₂ in water. The nanoparticle-based sensor for detection of SO₂ using fuchsine dyes is sought out for the first time. Photophysical characterization of parent compound, IMs and INMs are studied in detail to investigate the

colorimetric sensor performance of pR based IMs and INMs. Herein, a new, simple, and inexpensive approach is introduced to tune the hydrophobicity and photophysical properties of fuchsine dye which can impact the sensitivity of the dyes towards SO₂. Moreover, the potential application to use the hydrophobic dye to develop an inexpensive, stable and portable paper-based sensor for prompt detection of SO₂ is presented. This study can be used to developed highly efficient nanoparticles or hydrophobic potable, stable sensor. Quantitative analysis will be performed in future.

Materials and methods

Materials

pR-HCl, R-HCl and sodium bis (trifluoromethanesulfonyl) imide (NaNTF₂) were purchased from Sigma-Aldrich and their chemical structures are presented in Figure 1. The 18 MΩ-cm triple deionized ultrapure distilled (DI) water was used. Sulfuric acid (H₂SO₄), ethanol (EtOH), dichloromethane (DCM) and copper (Cu) were purchased from VWR. Plastic cuvet was used for Dynamic Light Scattering (DLS). 150 mesh copper grids with a formvar/carbon coating (EMS cat# FCF150-Cu) were used for transmission electron microscopy (TEM) imaging.

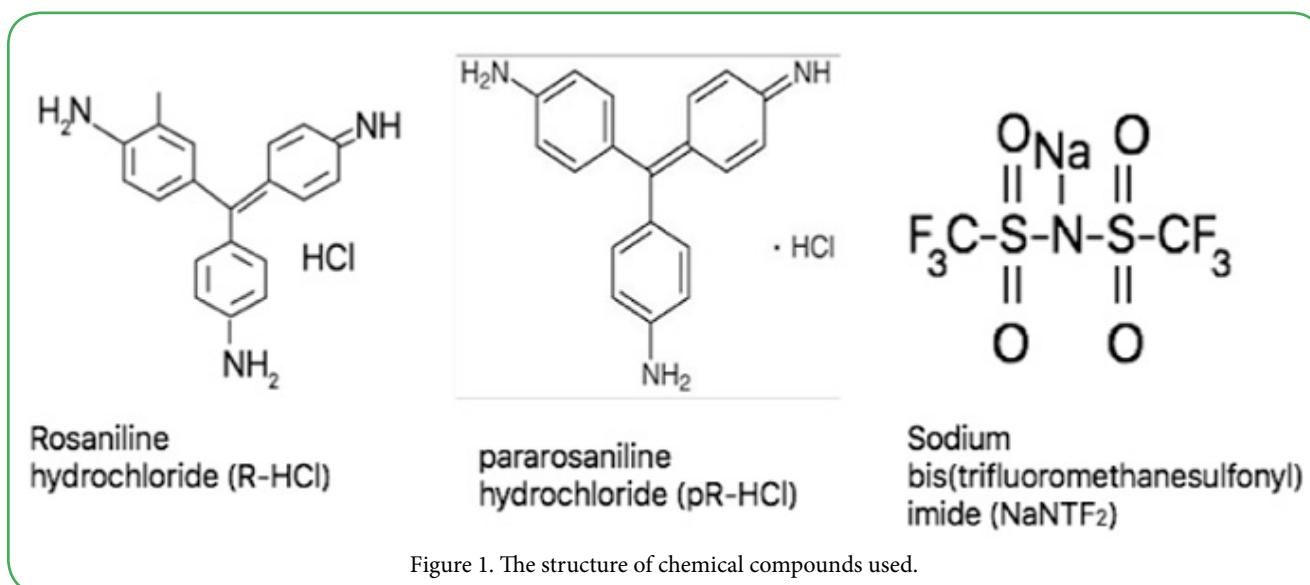


Figure 1. The structure of chemical compounds used.

Synthesis of new hydrophobic derivatives of fuchsine dyes

Hydrophobic compound was synthesized using a simple and single step ion-exchange method. A 1:1 ratio of parent dyes (pR-HCl) to NaNTF₂ were dissolved in water, stirred for 24 hours (Figure 2). After 24 hours, hydrophobic compound (pR-NTF₂) was extracted

with DCM, then DCM was evaporated via Rotary Evaporator (Rotavap) and the final product was freeze dried in the lyophilizer for 24 hours to remove any excessive moisture. In result, the hydrophobic compounds of pararosanine bis (trifluoromethanesulfonyl) imide (pR-NTF₂) were obtained as depicted in Figure 2.

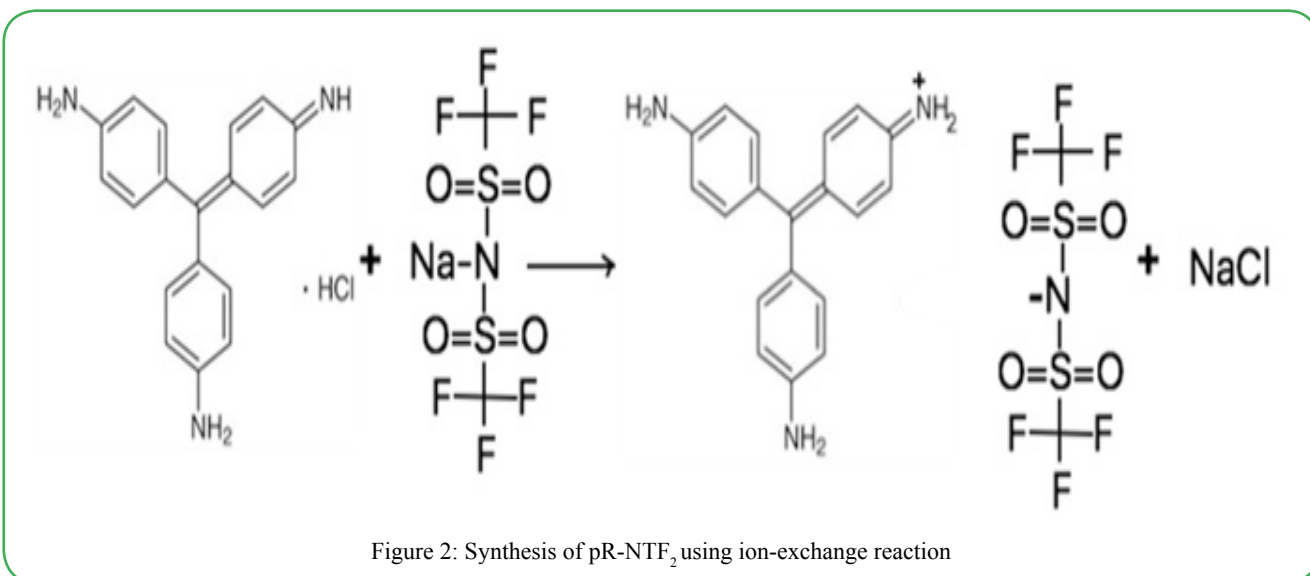


Figure 2: Synthesis of pR-NTF₂ using ion-exchange reaction

Synthesis of nanoparticles

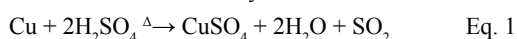
Reprecipitation method was used to prepare INMs of pR-NTF₂ as described earlier [20, 30]. Briefly, a concentrated solution was prepared in ethanol and dropwise added to vials containing DI water while under sonication waves for 5 minutes. The INMs were allowed a 20 minutes rest time and characterized using TEM and DLS. INMs' photophysical characteristics were studied in detail to investigate their sensitivity towards detection of SO₂.

Instrumentation

The Rotavapor Buchi RE 111 was used to evaporate the solvent after the synthesis of the IMs. The newly synthesized hydrophobic derivative is characterized using ESI high-resolution mass spectrometry (Shimadzu IT-TOF) or MS. Nanoparticles are prepared using reprecipitation methods via Fisher Scientific FS20H ultrasonicator. The morphology of nanoparticles are characterized using a FEI Tecnai F20 80kV TEM and a Broo khaven NanoBrook 90plus Zeta for DLS [7]. INMs of pRNTF₂ were prepared in water to investigate the hydrodynamic diameter and dry diameter by using DLS and TEM respectively. Thermogravimetric analysis (Mettler Toledo) or TGA was performed to analyze the thermal stability of synthesized material. Samples were heated in air at a rate of 10 °C/min over a range of 25-800 °C and were plotted as a function of mass lost. A plot of the 1st derivative of mass lost is used to determine the onset degradation temperature, Tonset. The single beam Varian Cary 60 UV-Vis-NIR absorption spectrophotometer was utilized for photophysical characterization. A 2-sided quartz cuvette was used for absorption experiment. The changes in the absorption spectra of newly developed IMs and INMs are recorded and compared with parent compounds. All parent samples, IMs and INMs absorption spectra upon exposure with SO₂ are recorded to investigate the most sensitive sensor for prompt detection of SO₂.

Synthesis of SO₂ gas

An apparatus was constructed using a triconnected test tubes hooked on a ring stand as depicted in **Figure S1** in the supporting information to effectively generate SO₂ gas from the chemical reaction presented in **Eq. 1**. Cu trimmings and H₂SO₄ were placed in the middle test tube chamber where it generates copper sulfate (CuSO₄), water and SO₂ gas as a result of chemical reaction in the presence of heat. A plastic tube is used to connect the test tube with a vial to transfer SO₂ gas from the test tube into the vial containing fuchsin parent dyes solution, IM solution, INM dispersion and filter paper coated with these sensor dyes.



Preparation of portable paper-based sensor and nanosensor

A solution of R-HCl, pR-HCl were prepared in EtOH and water separately and used to develop filter paper-based sensor. pR-NTF₂ was prepared in EtOH and water separately to develop paper-based sensor and nanosensor coated filter paper respectively. Strips of filter paper (ashy) were soaked into the dye solution and nanoparticles of pR-NTF₂ for one hour to allow adequate absorption onto the paper. The paper is then removed from the solution, dried and placed into the vial connected to the apparatus generating SO₂.

Results and discussions

IMs and INMs Characterizations

MS

Newly synthesized pR-NTF₂ IMs was confirmed via high-resolution MS. Based on the mass to charge (M/Z) ratio of fragment ions in positive and negative ion mode, the mass of pR-NTF₂ can be evaluated. The observed peaks (**Figure S2**) from positive ion mode and negative ion mode were 288.15 and 279.92, respectively. These values matched with theoretical molecular weight of pR cation (288.37 g/mol) and NTF₂ anion (280.15 g/mol) indicating the pR-NTF₂ was successfully synthesized via ionexchange method. Thermal stability of IMs was also investigated and presented it in SI.

TGA

The newly synthesized compound is investigated for its thermal stability using TGA. Thermal stability curve of pR-NTF₂ was generated by heating under continuous air flow from 25-800 °C (**Figure S3**). pR-NTF₂ possesses one major degradation occurring at 495 °C. This indicates that upon conversion from chloride salt to NTF₂ IM, there is not a significant loss in thermal stability.

TEM

TEM is used to visualize the shape and dimension of nanoparticles in the absence of any media. To prepare the TEM grid, a small aliquot of pR-NTF₂ INMs was drop casted onto a hydrophobic copper grid. After drying, the grids are analyzed to determine particle size and morphology using TEM instrument. As shown in **Figure S4**, the pR-NTF₂ INMs are spherical in shape and have an approximate diameter in the range of 180-200 nm.

DLS

DLS is used to determine the size distribution of solvated nanoparticles. Average hydrodynamic diameter was found to be 215.12 ± 3.95 nm with a polydispersity index of 0.178 ± 0.020. Such a low polydispersity index indicates that the nanoparticles are uniform in size. The zeta potential value was found to be -28.46 ± 3.48 mV indicating that the INMs are colloidal stable and possess a negative surface charge. This negative charge indicates the presence of NTF₂ anion on the surface of nanoparticles while the pR cation dye is mostly present at the core of the nanoparticles.

Photophysical characterization and sensing of SO₂ gas by fuchsin dyes and hydrophobic derivative

The detailed photophysical properties of all parent dyes and synthesized IM and their nanoparticles are recorded with and without exposure to SO₂. Two solvents, water and EtOH were used. The dye absorption wave length maxima of R-HCl, pR-HCl, and pR-NTF₂ have been observed primarily at 545 nm wavelengths while a shoulder is observed at 504 nm. The normalized absorption spectra of all compounds are shown in **Figure 5a**. A slight shift in absorption wavelength maxima is observed from 550 nm to 545 nm upon changing the solvent from EtOH to water. In addition, the changes in molar absorptivity is also recorded. The molar extinction coefficient has been calculated at wavelengths maxima. The results for molar extinction coefficients for all dyes in different solvents are as tabulated in **Table 1**.

Molar Extinction Coefficient (x10 ⁴) L mol ⁻¹ cm ⁻¹	
Compounds	545 nm
R-HCl in water	4.58
pR-HCl in water	4.68
pR-HCl in EtOH	0.830
pR-NTF ₂ Nanoparticle in water	4.06
pR-NTF ₂ in EtOH	12.7

Table 1: Molar Extinction Coefficient for the Dyes

Detailed examination of results revealed that pR-NTF₂ exhibited the highest value of molar absorptivity as compared to its parent compound. Thus, it proved that replacement of small chloride ion with a bulky NTF₂ ion significantly improved the absorption characteristics of fuchsine dyes. Therefore, it is expected that a highly sensitive sensor can be developed using IMs and INMs which also permit to develop a portable paper-based sensor for the toxic SO₂.

Absorption spectra of R-HCl, pR-HCl, pR-NTF₂ and INMs were recorded when exposed to SO₂ gas to determine the sensitivity of compounds towards SO₂ detection in solution. The changes in photophysical properties of the compounds upon exposure of SO₂ at different time intervals were recorded.

In EtOH solution, the absorption intensity of R-HCl (**Figure 5b**) was not changed after increasing the exposure time with SO₂ gas. The dye is still very colorful which shows the R-HCl limit to sense

SO₂. For pR-HCl (**Figure 5d**), the absorption of pR-HCl was slightly decreased after 30 seconds exposure to SO₂ while after exposure of 45 seconds no further decrease in absorbance intensity is observed. This result shows the limitation of pR-HCl for used as a sensor for SO₂ detection in ethanolic solution.

In aqueous solution, the absorption of R-HCl (**Figure 5c**) was dramatically decreased as the exposure time of SO₂ increased and the peak maxima was red-shifted. After 60 seconds, the absorbance was quenched completely. The longer the exposure of SO₂ to the strong magenta color of R-HCl, the more colorless it becomes. The absorption of pR-HCl (**Figure 5e**) in water is recorded upon exposure to SO₂ at different time interval. A significant decreased in intensity is observed after 45 seconds exposure to SO₂. This appeared to be more time sensitive than R-HCl in water. Then at 80 seconds the strong magenta color disappeared suggesting that SO₂ completely decolorize the dye.

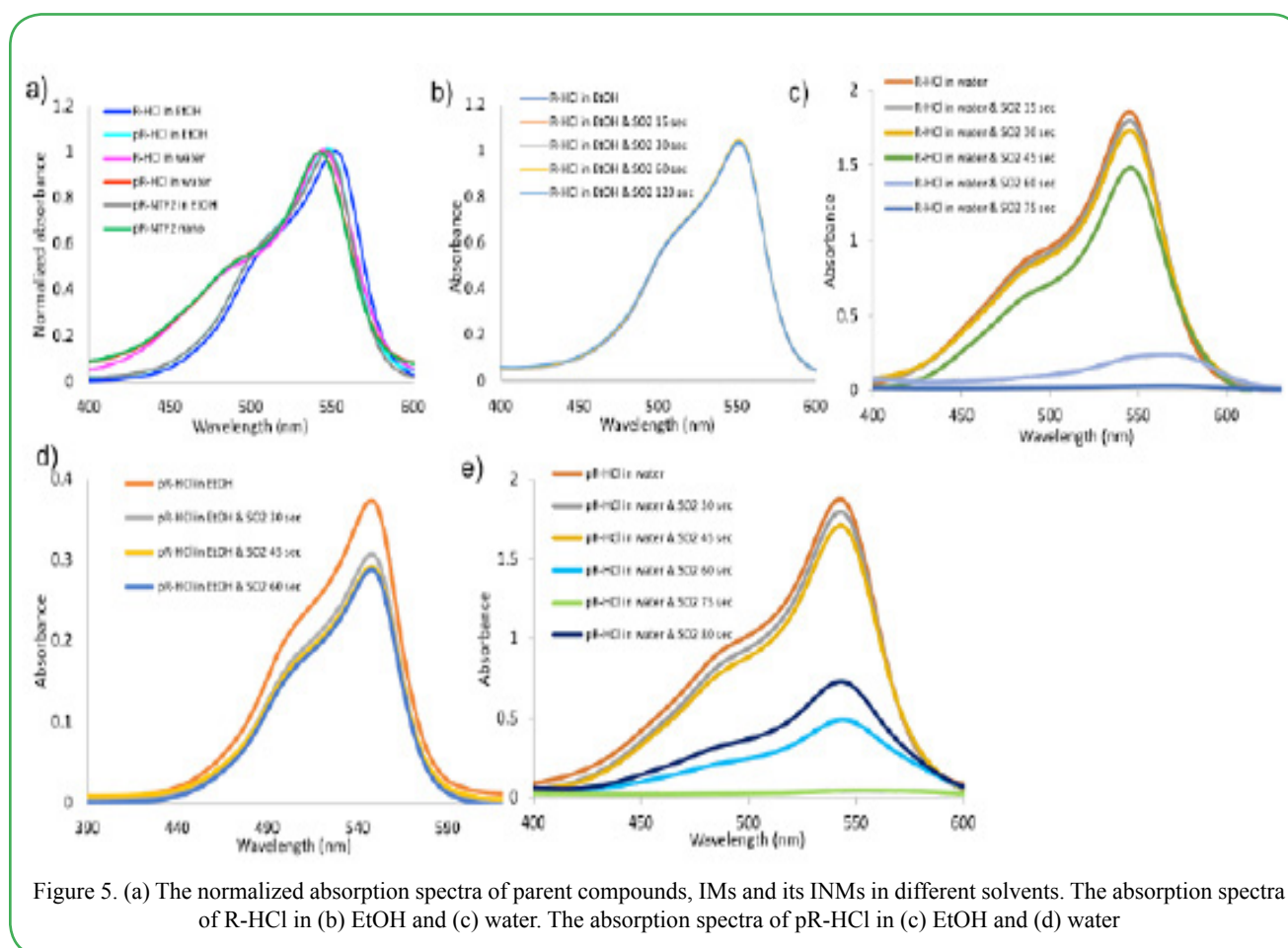
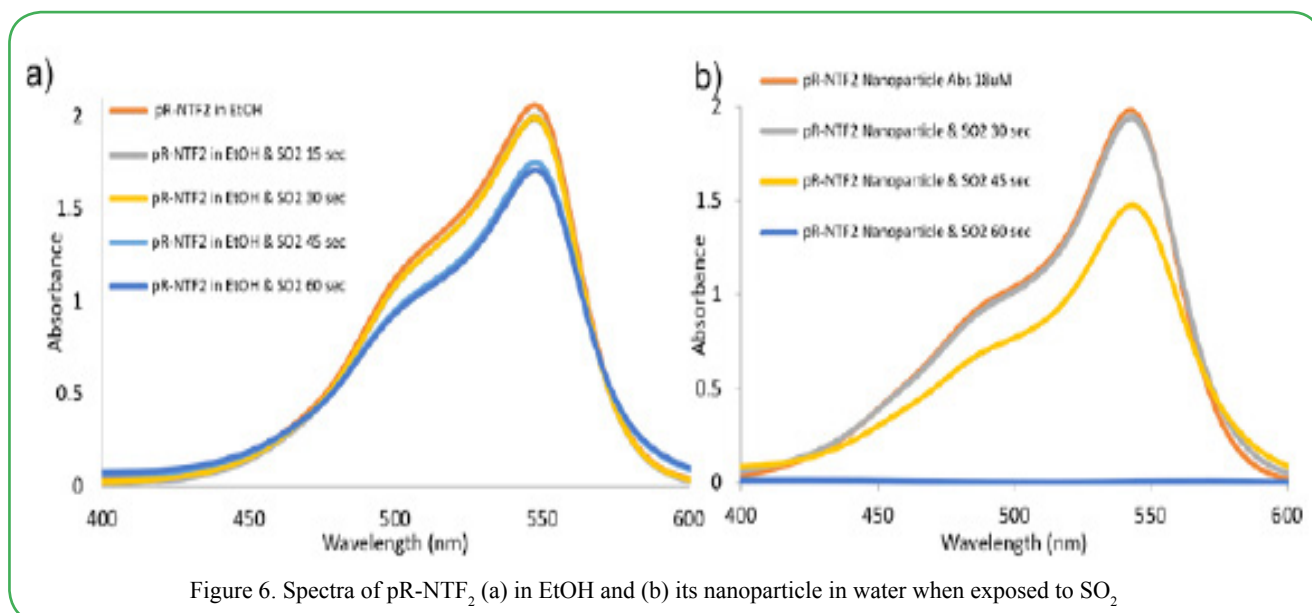


Figure 5. (a) The normalized absorption spectra of parent compounds, IMs and its INMs in different solvents. The absorption spectra of R-HCl in (b) EtOH and (c) water. The absorption spectra of pR-HCl in (c) EtOH and (d) water

In order to prove that decolorization for R-HCl and pR-HCl is caused by SO₂ and not because of instability dye in water, photostability test of R-HCl and pR-HCl is also performed in water to prove the stability of the solution over the time span of 60 minutes (**Figure S5a, S5b**). Minimal to no differences in the absorption spectra are observed which proves R-HCl and pR-HCl dye are stable in water.

Hydrophobic IMs, pR-NTF₂, has demonstrated a higher molar extinction coefficient (Table 1) which could be used as a highly sensitive colorimetric sensor for SO₂. After full characterization and performing the sensor response of parent fuchsine dyes, IMs are tested as a sensor for SO₂ detection (**Figure 6**). The absorption intensity of pR-NTF₂ in EtOH solution slowly decreases after prolonged exposure to SO₂ (**Figure 6a**). However, when pR-NTF₂

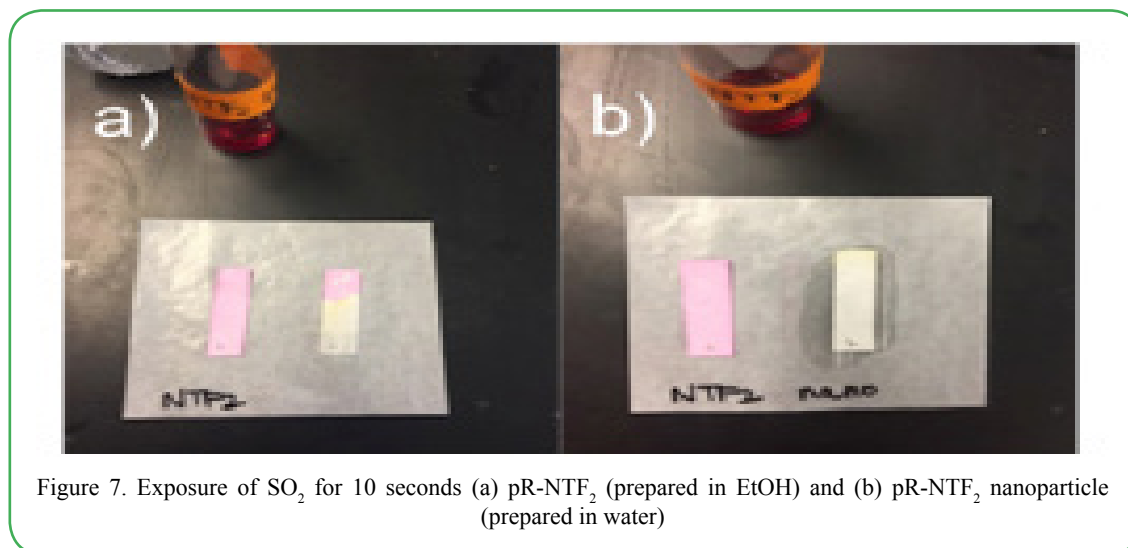
nanoparticle in water (**Figure 6b**) was exposed to SO₂, a significant decrease in the absorbance intensity was observed within 15 seconds time lapse. pR-NTF₂ nanoparticles exhibited a tremendous decreased in absorbance intensity after 45 seconds when exposed to SO₂ gas. At 60 seconds, the magenta color was completely colorless. It indicates the sensitive performance of nanoparticles towards SO₂ sensing. The stability of the pR-NTF₂ nanoparticle was also performed and demonstrated in **Figure S5c**. Absorbance spectra is recorded after every 20 minutes and minimal differences in the absorption spectra has been observed, indicating that the pR-NTF₂ nanoparticles are stable.



Sensing results using portable filter paper sensor

The ultimate goal of the study was to develop a low-cost portable sensor to detect SO₂. Examination of results obtained using paper-based sensor with parent dyes (prepared in EtOH) (**Figure S6**) indicated that both R-HCl and pR-HCl took approximately 20 seconds to start reacting with SO₂ and became colorless after 30 seconds. However, results of pR-HCl and R-HCl paper-based sensor (prepared in water) (**Figure S7**) became colorless after 20 seconds when exposed to SO₂. In comparison to parent dyes' sensor, pR-NTF₂ IMs paper-based sensor showed a very rapid response and decolorize the dyes in less than 10 seconds when exposed with SO₂ (**Figure 7a**). This proves that the paper-based sensor from the newly

synthesized compound, pR-NTF₂, was successfully enhanced the sensitivity of colorimetric sensor for SO₂ detection due to improved photophysical properties. When the nanosensor of pR-NTF₂ were exposed to SO₂, an even shorter amount of time was required to detect the SO₂ gas as shown in **Figure 7b**. Furthermore, filter paper-based sensor developed using hydrophobic INMs are more stable towards moisture and can be stored for a long time as compared to their hydrophilic parent compound. Thus, IM approach to develop a hydrophobic compound does not only improve the photophysical properties which enhanced the sensitivity of fuchsin dyes towards SO₂ but it also permits to develop a stable, economical, and portable paper-based sensor which can easily be used in the field for rapid detection of SO₂.



Conclusion

The hydrophobic derivative pR-HCl, was successfully synthesized via ion-exchange reaction. Absorption characteristics significantly improved by changing the counterion from chloride to NTF₂⁻. The molar extinction coefficient of pR-NTF₂ was dramatically enhanced indicating the potential to develop a highly sensitive colorimetric method for SO₂ detection. In the study, the hydrophobic derivative, pR-NTF₂ was used to develop nanoparticle-based sensor using fuchsin dye for SO₂ detection for the first time. INMs of pR-NTF₂ has demonstrated the quick response and rapid decolorization of fuchsin dyes when exposed to SO₂ gas. The hydrophobic

derivative of fuchsin dye, pR-NTF₂ permits the synthesis of stable paper-based sensor. A portable sensor was developed using inexpensive filter paper which can be used as an economical and stable sensor for SO₂ sensing. In future, many different anions can be combined with R-HCl and pR-HCl using IM approach to alter the hydrophobicity and photophysical characteristics of the synthesized product which can further tune the sensitivity of the sensor. The portable based sensor approach using the hydrophobic nanoparticles is thus successfully demonstrated.

Competing Interests: There is no conflict of interest.

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