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# Paper-Based Portable Sensor and Nanosensor For Sulfur Dioxide Detection

Thuy Le<sup>1</sup>, Samantha Macchi<sup>1</sup>, Amanda Jalihal<sup>1</sup>, Sylvia Szwedo<sup>1</sup>, and Noureen Siraj<sup>1\*</sup>

<sup>1</sup>Department 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](mailto:nxsiraj@ualr.edu)

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### Abstract

Sulfur dioxide ( $\text{SO}_2$ ) 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  $\text{SO}_2$  in the atmosphere. In order to design and generate an effective sensor that detects low levels of  $\text{SO}_2$ , 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  $\text{SO}_2$  gas. It has been shown that these dyes can provide an economic and efficient colorimetric detection of  $\text{SO}_2$ . In this work, (pR-HCl) is converted into an ionic material (IM) via a facile ion exchange reaction with bis (trifluoromethane) sulfonamide ( $\text{NTF}_2$ ) counterion. The new, hydrophobic derivative, pararosaniline bis (trifluoromethane) sulfonamide (pR- $\text{NTF}_2$ ) IM was converted into stable aqueous ionic nanomaterials (INMs) by a reprecipitation method. Examination of absorption spectra results revealed that pR- $\text{NTF}_2$  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  $\text{SO}_2$ . A paper based portable  $\text{SO}_2$  sensor was also developed and tested for its ability to colorimetric detection of  $\text{SO}_2$ . 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:**  $\text{SO}_2$  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 ( $\text{SO}_2$ ) is a very toxic gas that has a sharp odor.  $\text{SO}_2$  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].  $\text{SO}_2$  is emitted from natural processes such as volcanic eruptions, pollen grains [2] and natural decays [3]. The presence of  $\text{SO}_2$  gas in the atmosphere also cause acid rain when the rain water reacts with  $\text{SO}_2$  gas in air [4]. Since  $\text{SO}_2$  is highly soluble in water, it easily absorbs into respiratory tract and eyes of human where it is converted into sulfuric acid ( $\text{H}_2\text{SO}_4$ ). In addition, a short-term exposure to  $\text{SO}_2$  causes irritation in nose, throat, lungs and respiratory tract in human. The U.S. Environmental Protection

Agency (EPA) has listed  $\text{SO}_2$  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],  $\text{SO}_2$  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  $\text{SO}_2$  can cause many adverse health and environmental effects. For this reason, monitoring  $\text{SO}_2$  at low concentrations has gained attention to protect environment, living organisms as well as human health.

Various methods have been developed for monitoring  $\text{SO}_2$  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  $\text{SO}_2$ . However, these instruments are very expensive, and are difficult to use in the field to monitor  $\text{SO}_2$ . Developing an inexpensive portable sensor that is highly selective and sensitive (at ppm level) to  $\text{SO}_2$  is necessary for the prevention of the adverse effects of  $\text{SO}_2$  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  $\text{SO}_2$  gas pollution [7, 8]. These dyes play a significant role in the regulation of  $\text{SO}_2$  gas by providing an economical and relatively efficient colorimetric method for determining  $\text{SO}_2$ . However, further improvement in these dyes can enhance the sensitivity of fuchsine dyes towards  $\text{SO}_2$  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  $\pi$ -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 (NTF<sub>2</sub>) anion via ion exchange and applied as a stable nanosensor. The INMs were developed using pR-NTF<sub>2</sub> in water. The nanoparticle-based sensor for detection of SO<sub>2</sub> using fuchsin 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 fuchsin dye which can impact the sensitivity of the dyes towards SO<sub>2</sub>. Moreover, the potential application to use the hydrophobic dye to develop an inexpensive, stable and portable paper-based sensor for prompt detection of SO<sub>2</sub> 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 (NaNTF<sub>2</sub>) 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 (H<sub>2</sub>SO<sub>4</sub>), 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.

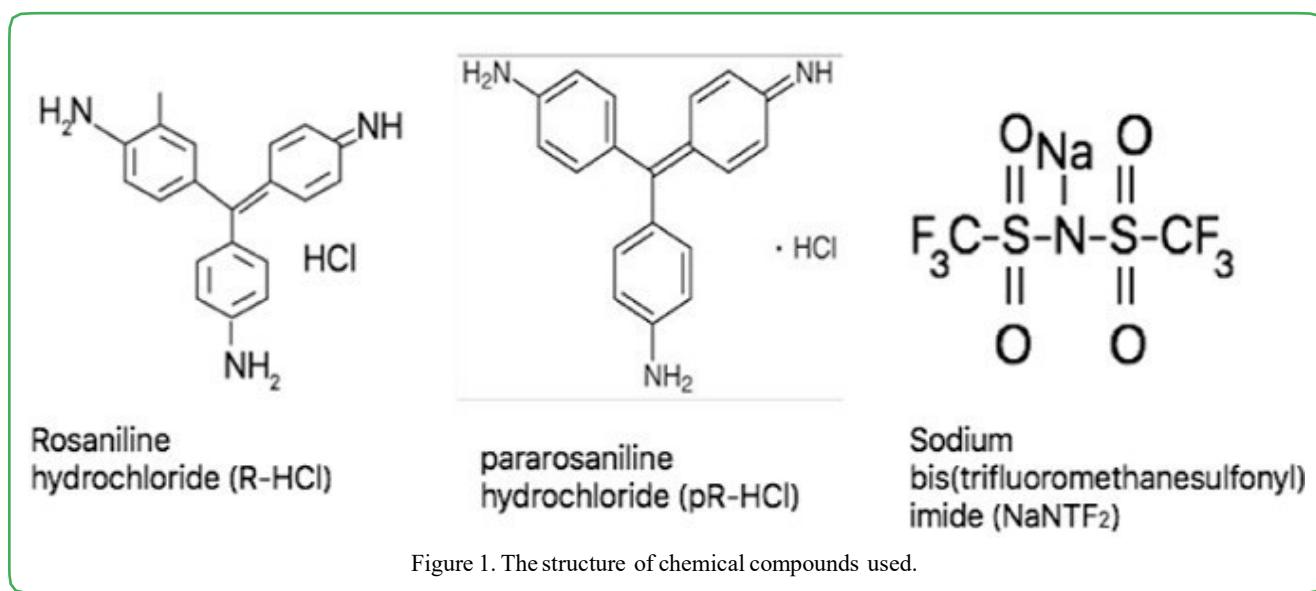


Figure 1. The structure of chemical compounds used.

### 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 NaNTF<sub>2</sub> were dissolved in water, stirred for 24 hours (Figure 2). After 24 hours, hydrophobic compound (pR-NTF<sub>2</sub>) 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 pararosaniline bis (trifluoromethanesulfonyl) imide (pR-NTF<sub>2</sub>) were obtained as depicted in Figure 2.

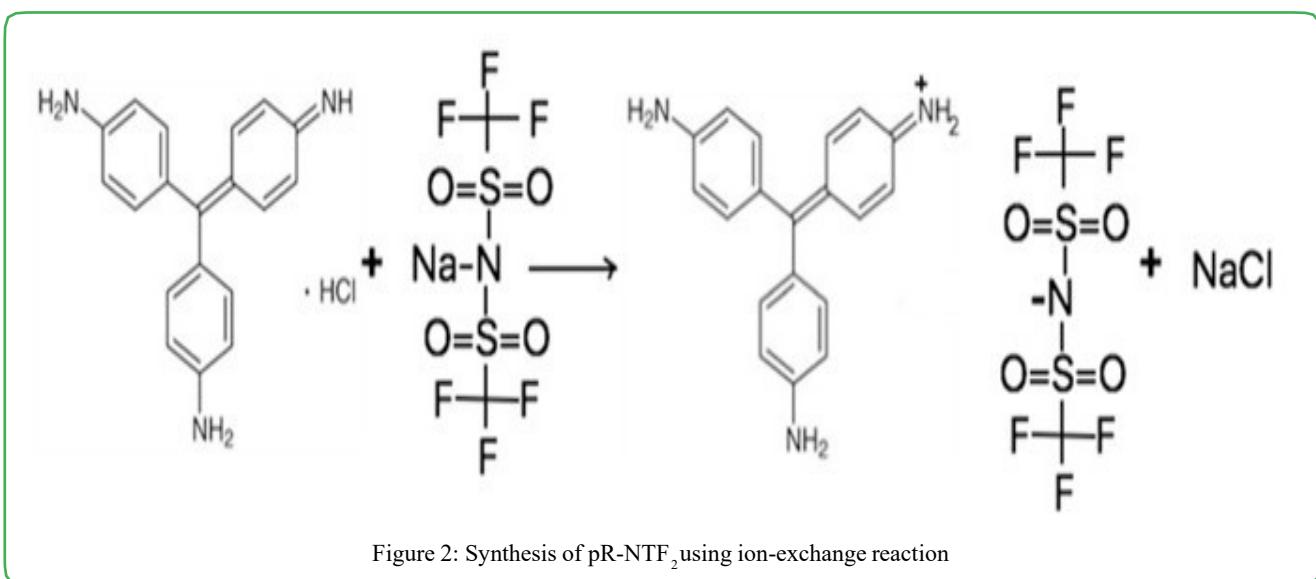


Figure 2: Synthesis of pR-NTF<sub>2</sub> using ion-exchange reaction

## Synthesis of nanoparticles

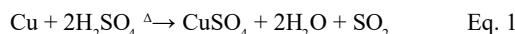
Reprecipitation method was used to prepare INMs of pR-NTF<sub>2</sub> as described earlier [20, 30]. Briefly, a concentrated solution was prepared in ethanol and dropwise added to vials containing DI water while under sonication waves for 5 minutes. The INMs were allowed a 20 minutes rest time and characterized using TEM and DLS. INMs' photophysical characteristics were studied in detail to investigate their sensitivity towards detection of SO<sub>2</sub>.

## 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 pRNTF<sub>2</sub> 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 SO<sub>2</sub> are recorded to investigate the most sensitive sensor for prompt detection of SO<sub>2</sub>.

## Synthesis of SO<sub>2</sub> 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 SO<sub>2</sub> gas from the chemical reaction presented in **Eq. 1**. Cu trimmings and H<sub>2</sub>SO<sub>4</sub> were placed in the middle test tube chamber where it generates copper sulfate (CuSO<sub>4</sub>), water and SO<sub>2</sub> 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 SO<sub>2</sub> gas from the test tube into the vial containing fuchsine 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-NTF<sub>2</sub> 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-NTF<sub>2</sub> 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 SO<sub>2</sub>.

## Results and discussions

### IMs and INMs Characterizations

#### MS

Newly synthesized pR-NTF<sub>2</sub> 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-NTF<sub>2</sub> 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 NTF<sub>2</sub> anion (280.15 g/mol) indicating the pR-NTF<sub>2</sub> 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-NTF<sub>2</sub> was generated by heating under continuous air flow from 25-800 °C (**Figure S3**). pR-NTF<sub>2</sub> possesses one major degradation occurring at 495 °C. This indicates that upon conversion from chloride salt to NTF<sub>2</sub> 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-NTF<sub>2</sub> 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-NTF<sub>2</sub> 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  $215.12 \pm 3.95$  nm with a polydispersity index of  $0.178 \pm 0.020$ . Such a low polydispersity index indicates that the nanoparticles are uniform in size. The zeta potential value was found to be  $-28.46 \pm 3.48$  mV indicating that the INMs are colloidally stable and possess a negative surface charge. This negative charge indicates the presence of NTF<sub>2</sub> 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 SO<sub>2</sub> gas by fuchsine 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 SO<sub>2</sub>. Two solvents, water and EtOH were used. The dye absorption wave length maxima of R-HCl, pR-HCl, and pR-NTF<sub>2</sub> 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 (x104) L mol <sup>-1</sup> cm <sup>-1</sup>	
Compounds	545 nm
R-HCl in water	4.58
pR-HCl in water	4.68
pR-HCl in EtOH	0.830
pR-NTF <sub>2</sub> Nanoparticle in water	4.06
pR-NTF <sub>2</sub> in EtOH	12.7

Table 1: Molar Extinction Coefficient for the Dyes

Detailed examination of results revealed that pR-NTF<sub>2</sub> 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 NTF<sub>2</sub> 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 SO<sub>2</sub>.

Absorption spectra of R-HCl, pR-HCl, pR-NTF<sub>2</sub> and INMs were recorded when exposed to SO<sub>2</sub> gas to determine the sensitivity of compounds towards SO<sub>2</sub> detection in solution. The changes in photophysical properties of the compounds upon exposure of SO<sub>2</sub> 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 SO<sub>2</sub> gas. The dye is still very colorful which shows the R-HCl limit to sense

SO<sub>2</sub>. For pR-HCl (Figure 5d), the absorption of pR-HCl was slightly decreased after 30 seconds exposure to SO<sub>2</sub> 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 SO<sub>2</sub> detection in ethanolic solution.

In aqueous solution, the absorption of R-HCl (Figure 5c) was dramatically decreased as the exposure time of SO<sub>2</sub> increased and the peak maxima was red-shifted. After 60 seconds, the absorbance was quenched completely. The longer the exposure of SO<sub>2</sub> 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 SO<sub>2</sub> at different time interval. A significant decreased in intensity is observed after 45 seconds exposure to SO<sub>2</sub>. This appeared to be more time sensitive than R-HCl in water. Then at 80 seconds the strong magenta color disappeared suggesting that SO<sub>2</sub> completely decolorize the dye.

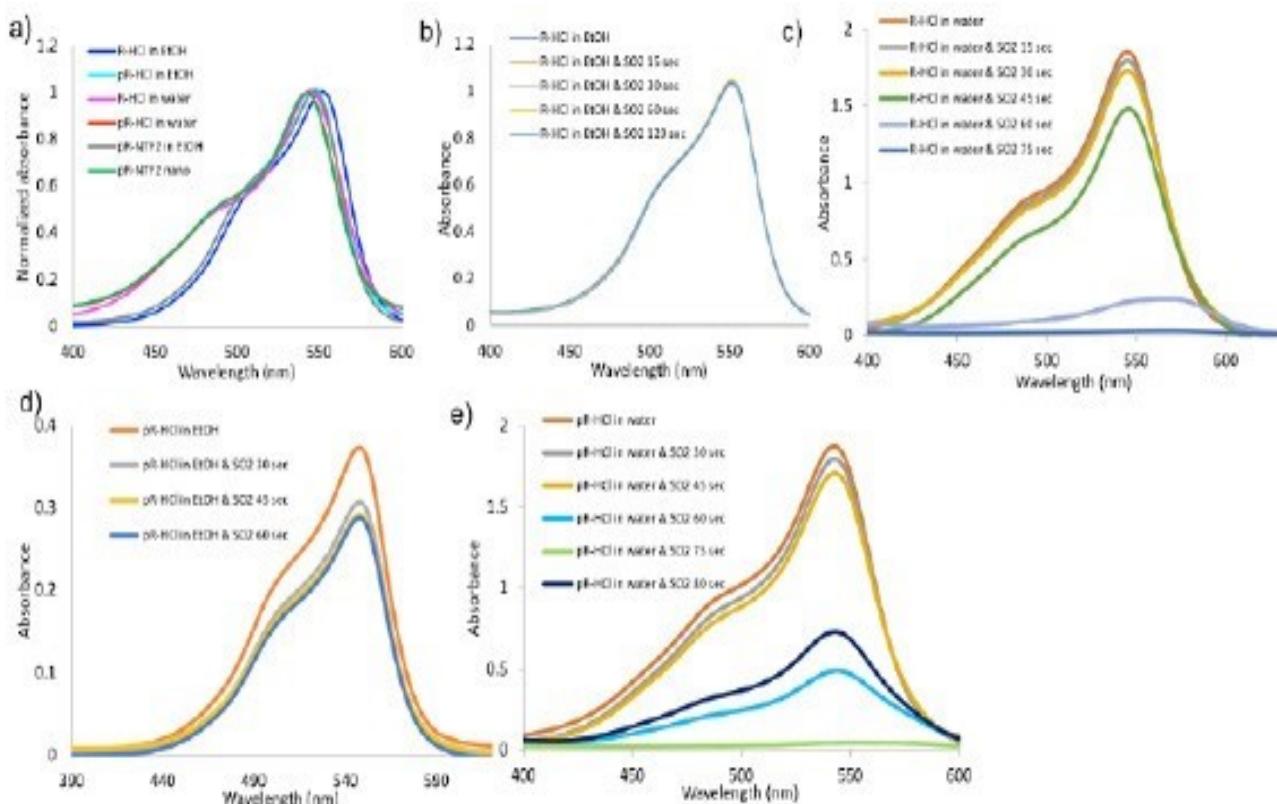


Figure 5. (a) The normalized absorption spectra of parent compounds, IMs and its INMs in different solvents. The absorption spectra of R-HCl in (b) EtOH and (c) water. The absorption spectra of pR-HCl in (c) EtOH and (d) water

In order to prove that decolorization for R-HCl and pR-HCl is caused by SO<sub>2</sub> 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-NTF<sub>2</sub>, has demonstrated a higher molar extinction coefficient (Table 1) which could be used as a highly sensitive colorimetric sensor for SO<sub>2</sub>. After full characterization and performing the sensor response of parent fuchsine dyes, IMs are tested as a sensor for SO<sub>2</sub> detection (Figure 6). The absorption intensity of pR-NTF<sub>2</sub> in EtOH solution slowly decreases after prolonged exposure to SO<sub>2</sub> (Figure 6a). However, when pR-NTF<sub>2</sub>

inanoparticle in water (Figure 6b) was exposed to SO<sub>2</sub> a significant decrease in the absorbance intensity was observed within 15 seconds time lapse. pR-NTF<sub>2</sub> nanoparticles exhibited a tremendous decreased in absorbance intensity after 45 seconds when exposed to SO<sub>2</sub> gas. At 60 seconds, the magenta color was completely colorless. It indicates the sensitive performance of nanoparticles towards SO<sub>2</sub> sensing. The stability of the pR-NTF<sub>2</sub> 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-NTF<sub>2</sub> nanoparticles are stable.

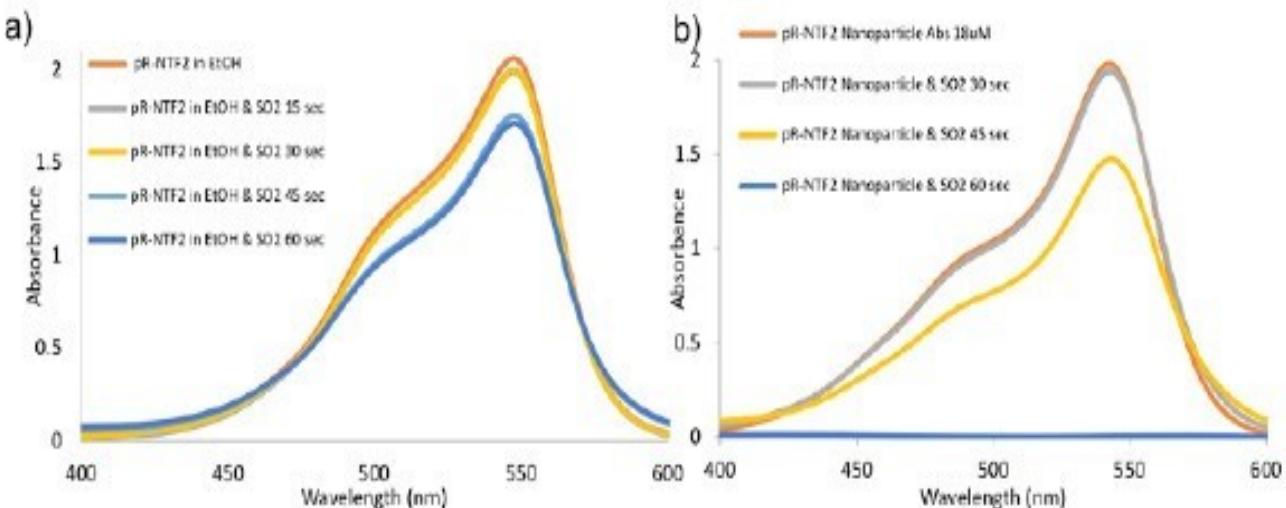


Figure 6. Spectra of pR-NTF<sub>2</sub> (a) in EtOH and (b) its nanoparticle in water when exposed to SO<sub>2</sub>

### Sensing results using portable filter paper sensor

The ultimate goal of the study was to develop a low-cost portable sensor to detect SO<sub>2</sub>. 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 SO<sub>2</sub> 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 SO<sub>2</sub>. In comparison to parent dyes' sensor, pR-NTF<sub>2</sub> IMs paper-based sensor showed a very rapid response and decolorize the dyes in less than 10 seconds when exposed with SO<sub>2</sub> (Figure 7a). This proves that the paper-based sensor from the newly

synthesized compound, pR-NTF<sub>2</sub>, was successfully enhanced the sensitivity of colorimetric sensor for SO<sub>2</sub> detection due to improved photophysical properties. When the nanosensor of pR-NTF<sub>2</sub> were exposed to SO<sub>2</sub>, an even shorter amount of time was required to detect the SO<sub>2</sub> 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 fuchsine dyes towards SO<sub>2</sub> 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 SO<sub>2</sub>.

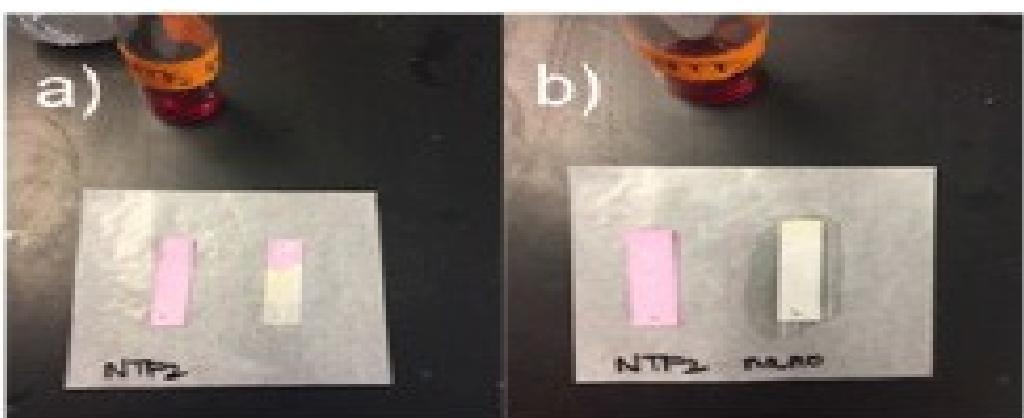


Figure 7. Exposure of SO<sub>2</sub> for 10 seconds (a) pR-NTF<sub>2</sub> (prepared in EtOH) and (b) pR-NTF<sub>2</sub> nanoparticle (prepared in water)

### Conclusion

The hydrophobic derivative pR-HCl, was successfully synthesized via ion-exchange reaction. Absorption characteristics significantly improved by changing the counterion from chloride to NTF<sub>2</sub><sup>-</sup>. The molar extinction coefficient of pR-NTF<sub>2</sub> was dramatically enhanced indicating the potential to develop a highly sensitive colorimetric method for SO<sub>2</sub> detection. In the study, the hydrophobic derivative, pR-NTF<sub>2</sub>, was used to develop nanoparticle-based sensor using fuchsine dye for SO<sub>2</sub> detection for the first time. INMs of pR-NTF<sub>2</sub> has demonstrated the quick response and rapid decolorization of fuchsine dyes when exposed to SO<sub>2</sub> gas. The hydrophobic

derivative of fuchsine dye, pR-NTF<sub>2</sub> 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 SO<sub>2</sub> 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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## References

1. EPA. (2019). Sulfur Dioxide (SO<sub>2</sub>) Pollution. Retrieved from United States Environmental Protection Agency website: <https://www.epa.gov/so2-pollution/sulfur-dioxide-basics#what is so2>.
2. Kumar Jha, D., Sabesan, M., Das, A., Vinithkumar, N. V., & Kirubagaran, R. (2011). Evaluation of Interpolation Technique for Air Quality Parameters in Port Blair, India. *Universal Journal of Environmental Research and Technology*, 1(3), 301–310. Retrieved from <http://www.environmentaljournal.org/1-3/ujeft-1-3-10.pdf>
3. Thurston, G. D. (2017). Outdoor Air Pollution: Sources, Atmospheric Transport, and Human Health Effects. In *International Encyclopedia of Public Health (Second Edition)* (Second Edi, Vol. 5).<https://doi.org/10.1016/B978-0-12-803678-5.003209>
4. Pohl, H., Liccione, J., & Iannucci, A. (2002). Toxicological Profile for Sulfur Dioxide. In *Agency for Toxic Substances and Disease Registry's Toxicological Profiles*.[https://doi.org/10.1201/9781420061888\\_ch144](https://doi.org/10.1201/9781420061888_ch144)
5. DINPS. (2018). Sulfur Dioxide Effects on Health. Retrieved from U.S. Department of the Interior National Park Service website: <https://www.nps.gov/subjects/air/humanhealth-sulfur.htm>
6. Spetz, A. L. (2014). SiC-FET based SO<sub>2</sub> sensor for power plant emission applications. *Sensors and Actuators, B: Chemical*, 194(194), 511–520. <https://doi.org/10.1016/j.snb.2013.11.089>
7. Goyal, S. K. (2001). Use of rosaniline hydrochloride dye for atmospheric SO<sub>2</sub> determination and method sensitivity analysis. *Journal of Environmental Monitoring*, 3(6), 666–670. <https://doi.org/10.1039/b106209n>
8. Pate, J. B., Lodge, J. P., & Wartburg, A. F. (1962). Effect of Pararosaniline in the Trace Determination of Sulfur Dioxide. *Scientific Communications*, 34(12), 1660–1662.
9. Warner, I. M., El-Zahab, B., & Siraj, N. (2014). Perspectives on moving ionic liquid chemistry into the solid phase. *Analytical Chemistry*, 86(15), 7184–7191. <https://doi.org/10.1021/ac501529m>
10. McNeel, K. E., Siraj, N., Bhattarai, N., & Warner, I. M. (2019). Fluorescence-Based Ratiometric Nanosensor for Selective Imaging of Cancer Cells. *ACS Omega*, 4(1), 1592–1600. <https://doi.org/10.1021/acsomega.8b02765>
11. Berton, P., Siraj, N., Das, S., de Rooy, S., Wuilloud, R. G., & Warner, I. M. (2020). Efficient Low-Cost Procedure for Microextraction of Estrogen from Environmental Water Using Magnetic Ionic Liquids. *Molecules (Basel, Switzerland)*, 26(1), 1–12. <https://doi.org/10.3390/molecules26010032>
12. Galpothdeniya, W. I. S., Regmi, B. P., McCarter, K. S., De Rooy, S. L., Siraj, N., & Warner, I. M. (2015). Virtual colorimetric sensor array: Single ionic liquid for solvent discrimination. *Analytical Chemistry*, 87(8), 4464–4471. <https://doi.org/10.1021/acs.analchem.5b00714>
13. Al Ghafly, H., Siraj, N., Das, S., Regmi, B. P., Magut, P. K. S., Galpothdeniya, W. I. S., ... Warner, I. M. (2014). GUMBOS matrices of variable hydrophobicity for matrix-assisted laser desorption/ionization mass spectrometry. *Rapid Communications in Mass Spectrometry*, 28(21), 2307–2314. <https://doi.org/10.1002/rcm.7027>
14. Kolic, P. E., Siraj, N., Cong, M., Regmi, B. P., Luan, X., Wang, Y., & Warner, I. M. (2016). Improving energy relay dyes for dye-sensitized solar cells by use of a group of uniform materials based on organic salts (GUMBOS). *RSC Advances*, 6(97), 95273–95282. <https://doi.org/10.1039/c6ra21980b>
15. Siraj, N., Hasan, F., Das, S., Kiruri, L. W., Steege Gall, K. E., Baker, G. A., & Warner, I. M. (2014). Carbazole-derived group of uniform materials based on organic salts: Solid state fluorescent analogues of ionic liquids for potential applications in organic-based blue light-emitting diodes. *Journal of Physical Chemistry C*, 118(5), 2312–2320. <https://doi.org/10.1021/jp410784v>
16. Bhattarai, N., Mathis, J. M., Chen, M., Perez, R. L., Siraj, N., Magut, P. K. S., ... Warner, I. M. (2018). Endocytic Selective Toxicity of Rhodamine 6G nanoGUMBOS in Breast Cancer Cells. *Molecular Pharmaceutics*, 15(9), 3837–3845. <https://doi.org/10.1021/acs.molpharmaceut.8b00339>
17. Hanson, K., Roskop, L., Djurovich, P. I., Zahariev, F., Gordon, M. S., & Thompson, M. E. (2010). A paradigm for blue- or red-shifted absorption of small molecules depending on the site of  $\pi$ -extension. *Journal of the American Chemical Society*, 132(45), 16247–16255. <https://doi.org/10.1021/ja1075162>
18. Gayton, J. N., Autry, S., Fortenberry, R. C., Hammer, N. I., & Delcamp, J. H. (2018). Counter Anion Effect on the Photophysical Properties of Emissive Indolizine-Cyanine Dyes in Solution and Solid State. *Molecules*, 23(12). <https://doi.org/10.3390/molecules23123051>
19. Jordan, A. N., Das, S., Siraj, N., De Rooy, S. L., Li, M., El-Zahab, B., ... Warner, I. M. (2012). Anioncontrolled morphologies and spectral features of cyanine-based nanoGUMBOS - An improved photosensitizer. *Nanoscale*, 4(16), 5031–5038. <https://doi.org/10.1039/c2nr30432e>
20. Haber, L. H., Karam, T. E., Siraj, N., Ranasinghe, J. C., Kolic, P. E., Regmi, B. P., & Warner, I. M. (2020). Efficient photoinduced energy transfer in porphyrin-based nanomaterials. *Journal of Physical Chemistry C*, 124(44), 24533–24541. <https://doi.org/10.1021/acs.jpcc.0c08985>
21. Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A., & Danquah, M. K. (2018). Review on nanoparticles and nanostructured materials: History, sources, toxicity and regulations. *Beilstein Journal of Nanotechnology*, 9(1), 1050–1074. <https://doi.org/10.3762/bjnano.9.98>
22. Jordan, A. N., Siraj, N., Das, S., & Warner, I. M. (2014). Tunable near-infrared emission of binary nanoand mesoscale GUMBOS. *RSC Advances*, 4(54), 28471–28480. <https://doi.org/10.1039/c4ra03256j>
23. Karam, T. E., Siraj, N., Warner, I. M., & Haber, L. H. (2015). Anomalous Size-Dependent Excited-State Relaxation Dynamics of NanoGUMBOS. *Journal of Physical Chemistry C*, 119(50), 28206–28213. <https://doi.org/10.1021/acs.jpcc.5b09729>
24. Hung, T.-F., & Liu, R.-S. (2012). Chapter 1: An Introduction of Controlled Sizes and Shapes of Nanostructured Materials and Their Applications. In R.-S. Liu (Ed.), *Controlled Nanofabrication: Advances and Applications*. <https://doi.org/10.4032/9789814364515>
25. Kumar, G., Sharma, and M. K. (2013). Effect of size and shape on the vibrational and thermodynamic properties of nanomaterials. *Journal of Thermodynamics*, 1(1), 1–5. <https://doi.org/10.1155/2013/328051>
26. Zamiri, R., Zakaria, A., Ahangar, H. A., Darroudi, M., Zak, A. K., & Drummen, G. P. C. (2012). Aqueous starch as a stabilizer in zinc oxide nanoparticle synthesis via laser ablation. *Journal of Alloys and Compounds*, 516, 41–48. <https://doi.org/10.1016/j.jallcom.2011.11.118>

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27. Simon-Deckers, A., Loo, S., Mayne-L'Hermite, M., Herlin-Boime, N., Menguy, N., Reynaud, C., ... Carriere, M. (2009). Size-, composition- and shape-dependent toxicological impact of metal oxide nanoparticles and carbon nanotubes toward bacteria. *Environmental Science and Technology*, 43(21), 8423–8429. <https://doi.org/10.1021/es9016975>
28. Yuan, Z., Li, R., Meng, F., Zhang, J., Zuo, K., & Han, E. (2019). Approaches to enhancing gas sensing properties: A review. *Sensors (Switzerland)*, 19(7). <https://doi.org/10.3390/s19071495>
29. Charitidis, C. A., Georgiou, P., Koklioti, M. A., Trompeta, A. F., & Markakis, V. (2014). Manufacturing nanomaterials: From research to industry. *Manufacturing Review*, 1(11), 19.
30. Kolic, P. E., Siraj, N., Hamdan, S., Regmi, B. P., & Warner, I. M. (2016). Synthesis and Characterization of Porphyrin-Based GUMBOS and NanoGUMBOS as Improved Photosensitizers. *Journal of Physical Chemistry C*, 120(9), 5155–5163. <https://doi.org/10.1021/acs.jpcc.5b12013>