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Synthesis of Fumed-Pr-Pi-TCT as a Fluorescent Chemosensor for the Detection of Cyanide Ions in Aqueous Media

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Abstract: In this research, fumed silica scaffolds modified via treatment with (3-chloropropyl)-triethoxysilane, piperazine, and trichlorotriazine groups were deployed for the specific detection of cyanide ions, thus paving the way for the detection of environmental hazards and pollutants with high specificity. Fumed-propyl -piperazine-trichlorotriazine (fumed-Pr-Pi-TCT) was synthesized in three steps starting from fume silica. It was functionalized subsequently using 3-(choloropropyl)-trimethoxysilane, piperazine, and trichlorotriazine, and then, the product was characterized through several methods including Fourier-transform infrared spectroscopy (FTIR) spectrum, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Fumed-Pr-Pi-TCT was exposed as a nanoparticle sensor to a range of different anions in aqueous media. This novel sensor could detect cyanide ions as a hazardous material, with the limit of detection being 0.82×10^{-4} M.

Keywords: Fumed-Pr-Pi-TCT; piperazine; trichlorotriazine; fluorescent spectroscopy; cyanide ions

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1. Introduction

Cyanide (CN^-) is a multifaceted toxin that can cause poisoning and death in humans [1,2] and is associated with many environmental hazards [2–4]. Despite its high toxicity, cyanide has been widely utilized on an industrial scale, which can lead to water pollution [5–7]. Recently, chemical sensors have received much attention due to their rapid response, simplicity, sensitivity, and low cost [8,9]. Chemical sensors that operate in conditions without a solvent or the use of an aqueous solvent have found a special place in analytical sensing or diagnostic methods as they follow the principles of green chemistry [10–13]. On the other hand, photochemistry is a branch of science that deals with the interaction between matter and light [14]. It can be employed in different areas, such as medicine, energy, and environmental sciences [15]. In this context, the construction of nanostructures with unique photochemical properties (light absorption/emission, energy, and electron transfer) via intermolecular interactions has been investigated by researchers [16–19].

Luminescence silica is broadly employed in many applications, from chemical sensing [20] to interfacial interactions, like immunoassays [21–23], bio-analysis [24], nucleic acid studies [25], and drug delivery [26–29]. These nanoparticles, with intrinsic properties, can be considered promising candidates for designing chemical fluorescence sensors; silica is a transparent material with visible light, which is not tangled in energy- and electron-transfer procedures alone [30]. All fluorescence properties of silica particles are due to the association between organic and inorganic groups on their surface [31,32]. Silica (nano)particles are not inherently toxic; thus, they are environmentally friendly and suitable for in vivo applications [33]. These materials have many active sites on their surface that can be used as scaffolds to react with a variety of organic and inorganic components. Silica scaffolds can protect the entry of foreign chemicals [34,35]. This allows the use of silica particles as chemosensors for the analysis of small dimensions, reducing the possibility of undesired photoreactions [36]. Chemical sensors made from silica (nano)particles have shown the advantages of cost-effectiveness, simplicity, requirement of mild conditions, and ease of separation [37]. Piperazine is a heterocycle with reactive nitrogen groups and was first introduced as an anthelmintic in 1953 [38]. Due to its high reactivity, this compound has been used in many chemical sensors in recent years, as the ensuing material can bind different anions via strong coordination [39,40]. The organic fluorophore moieties bound at the surface of the fumed silicas have become an important research area for selective adsorption and sensing applications [41]. Herein, fumed silica scaffolds, improved by (3-chloropropyl)-triethoxysilane, piperazine, and trichlorotriazine groups, were deployed for the specific detection of cyanide ions. Phenothiazines have notable sensitivity and selectivity for CN^- among other anions [42]. 5-(4-(Diphenylamine)phenyl) thiophen-2-formaldehyde was synthesized as a turn-on fluorescent reply to CN^-, which has the advantage of a lower detection limit [43]. In continuation of our previous research, the anion detection ability of the chemosensor among different anions was examined and characterized [18,44]. In this research, the fumed silica surface was modified through treatment with 3-(choloropropyl)-trimethoxysilane, piperazine, and trichlorotriazine, followed by the appropriate structural characterization of the synthesized material; the efficiency of this chemical sensor was demonstrated for the detection of cyanide ion from water.

2. Materials and Methods

2.1. Instruments and Materials

IR spectra were prepared using the FT-IR device TENSOR 27 from the Brooker Company. For thermal gravimetric analysis of the samples, the TGA model Q600, made in America, was used. To acquire scanning electron microscope (SEM) images, a MIRA III FESEM machine made in the Czech Republic was used. PL Spectroscopy model G9800A, from Agilent Company, was used for the investigation and study of the fluorescence spectroscopy of the ensuing material. The chemicals used in this research were purchased from Merck. The raw materials and solvents used in this section include the following: fumed silica, (3-chloropropyl)trimethoxysilane (CPTMS), piperazine, trichlorotriazine (TCT), toluene and methanol as solvents, and metal ions of different anions of Br^-, NO_3^-, HSO_3^-, SO_4^{2-}, OH^-, Cl^-, I^-, F^-, CH_3COO^-, $H_2PO_4^-$, CO_3^{2-}, NO_2^-, SCN^-, and CN^- with a concentration of 0.01 M in distilled water.

2.2. Methods

2.2.1. General Synthesis of Fumed-Pr–Pi-TCT

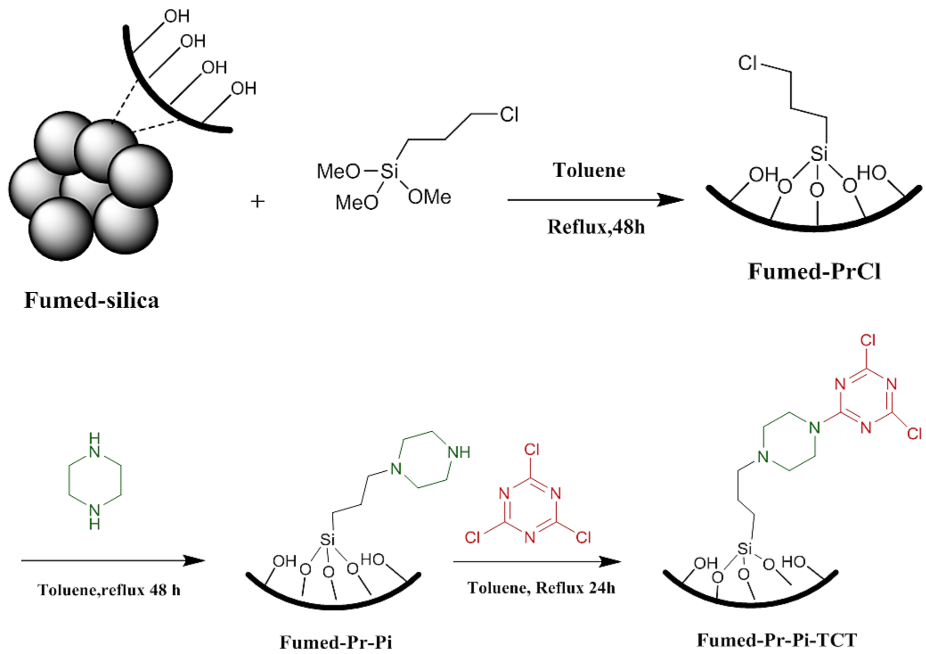
At first, fumed-Pr–Cl and fumed-Pr–Pi were synthesized as in our reported procedure [45], and then, after activating fumed-Pr–Pi (1 g) at 100 °C, it was refluxed with trichlorotriazine (1 mmol) and dry toluene solvent for 12 h. To obtain the final product (fumed-Pr–Pi-TCT), the resulting precipitate was subjected to a Soxhlet apparatus using methanol as a solvent for 24 h.

2.2.2. Preparation of 10^{-3} M Aqueous Solution of Fumed-Pr-Pi-TCT in H_2O

In volumetric flasks, the aqueous solution of fumed-Pr-Pi-TCT (0.02 g L^{-1}) was prepared in H_2O. The aqueous solution of fumed-Pr-Pi-TCT (3 mL) was placed into the sample tubes, and then, an aqueous solution of various anions (200 µL, 10^{-2} M) was added.

2.2.3. Synthesis of Fumed-Pr-Pi-TCT

In the first step, the surface of fumed silica particles was improved using (3-chloropropyl)-triethoxysilane (ClPTES). In the next steps, it was functionalized with piperazine and trichlorotriazine (TCT), respectively (Scheme 1).



Scheme 1. Preparative process for fumed-Pr-Pi-TCT chemosensor.

3. Results and Discussion

3.1. Characterization Data

3.1.1. FT-IR Studies

The FT-IR spectra of fumed-Pr-Cl, fumed-Pr-Pi, and fumed-Pr-Pi-TCT are shown in Figure 1. According to the FT-IR spectrum, the organic moieties bonded on the silica fume were proven. The two peaks at 1100 and 800 cm^{-1} depend on the asymmetric stretching vibrations of Si-O-Si groups. The band was about 3420 cm^{-1} and can also be considered to be related to the stretching O-H of Si-OH functional groups on the surface. The absorbance bands at 3431 and 1101 cm^{-1} fit the stretching and bending of N-H in fumed-Pr-Pi, respectively [45]. Finally, the peak at 1700 cm^{-1} is related to the C=N groups, and the peaks at 1560 to 1400 cm^{-1} are also related to the aromatic groups in the TCT.

3.1.2. Thermogravimetric Analysis (TGA) Studies

Thermogravimetric analysis (TGA) established the loading of organic compounds on the fumed silica (Figure 2). In the TGA diagram, two weight-loss steps were observed. The first weight loss, which occurred up to 200 °C, is related to the loss of H_2O in the fumed silica cavities. Weight loss in the range 200–800 °C is related to the decomposition of existing organic components on the fumed silica. TGA curves indicated, respectively, the weight losses of organic compounds for 8% (fumed-PrCl), 17% (fumed-Pr-Pi), and 45% (Fumed-Pr-Pi-TCT), as predicated for materials with increasing loadings of organic content.

3.1.3. SEM Studies

Fumed silica and Fumed-Pr-Pi-TCT SEM images are shown in Figure 3, which could be used to determine morphology. The image shows that the spherical particle scale of the silica fume had not changed much after functionalization.

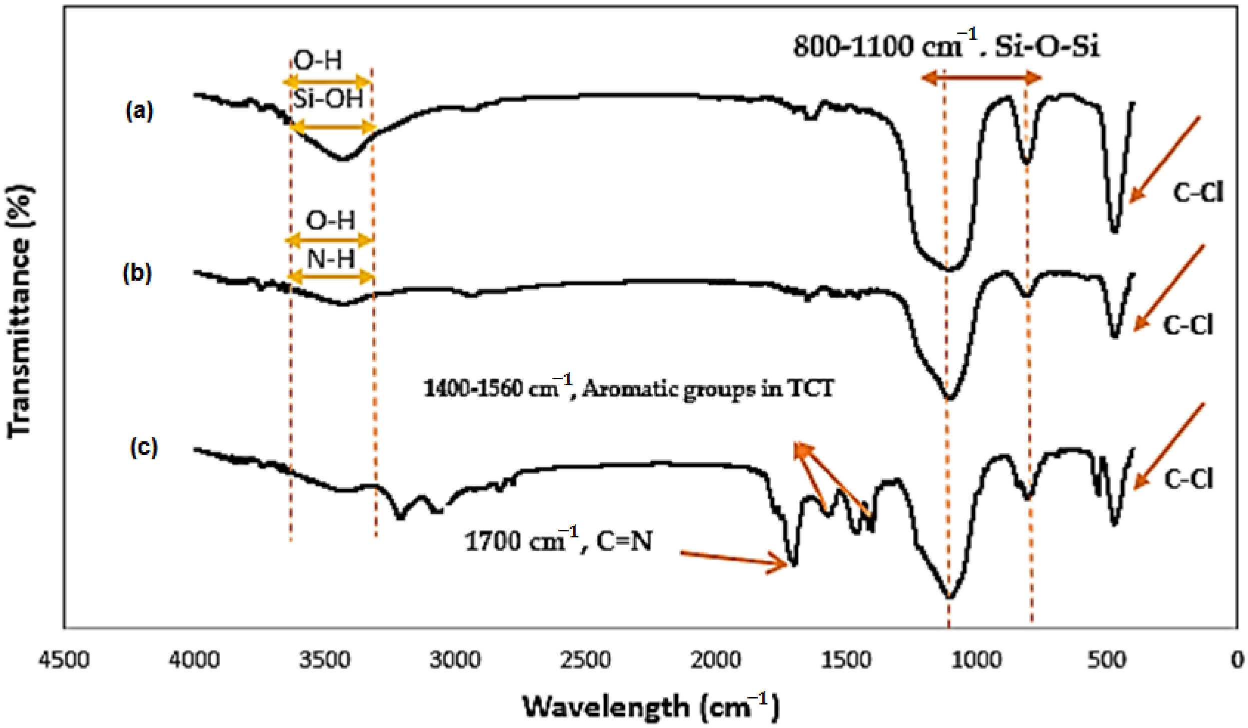


Figure 1. FT-IR analysis of (**a**) fumed-Pr-Cl, (**b**) fumed-Pr-Pi, and (**c**) fumed-Pr-Pi-TCT.

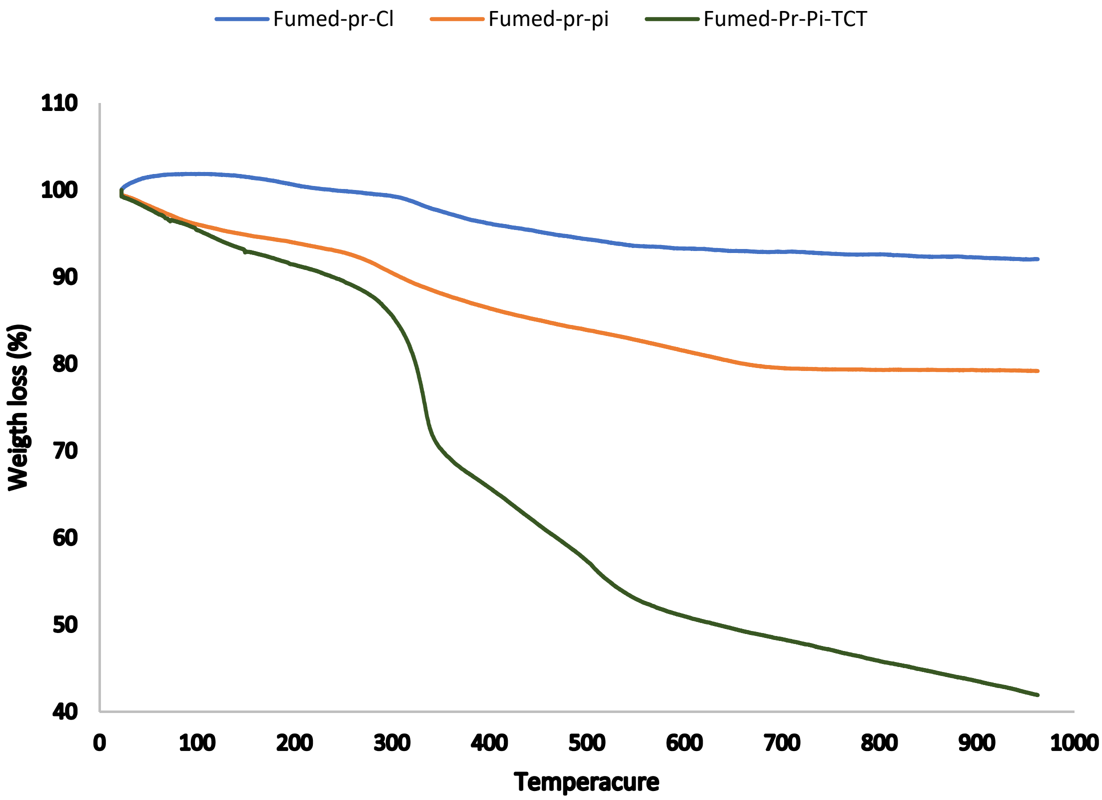


Figure 2. TGA curves of fumed-Pr-Cl, fumed-Pr-Pi, and fumed-Pr-Pi-TCT.

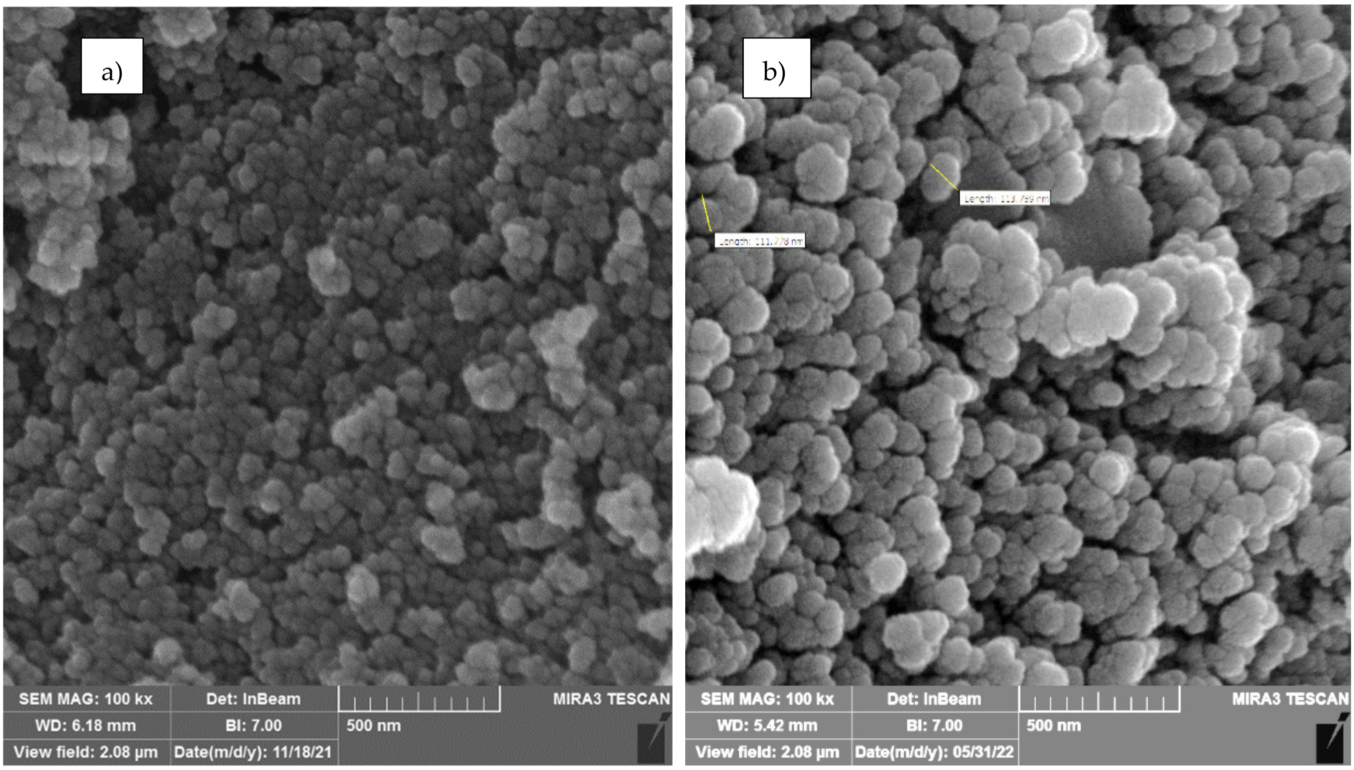


Figure 3. SEM images of (**a**) fumed silica and (**b**) fumed-Pr-Pi-TCT.

3.2. Fluorescence Response of Fumed-Pr–Pi-TCT for CN^-

To investigate the fluorescence properties of fumed-Pr-Pi-TCT, its solution (0.02 g L^{-1}) was made in an aqueous solvent. Then, its fluorescence response was studied using different anions, such as Br^-, NO_3^-, HSO_3^-, SO_4^{2-}, OH^-, Cl^-, I^-, F^-, CH_3COO^-, $H_2PO_4^-$, CO_3^{2-}, NO_2^-, SCN^-, and CN^-. By adding a 10^{-2} M concentration of different anions to 3 mL of fumed solution(0.2 g L^{-1}), the spectra were recorded after 30 s. The fluorescence intensity of fumed-Pr–Pi-TCT decreased significantly after the addition of CN^- but did not change significantly compared to that with other anions, which affirmed that this ligand could be applicable to detect CN^- among other anions (Figure 4).

3.2.1. Selectivity Studies

To evaluate the selectivity, a CN^- competition test was performed against other anions. For this purpose, the spectra were recorded by adding anions (100 μL × 10^{-2} M) to the mixture of fumed-Pr-Pi-TCT (3 mL H_2O suspension, 0.2 g L^{-1}) and CN^- (100 μL × 10^{-2} M). The results presented in Figure 5 demonstrate that the CN^- anion has high selectivity against other anions according to the fluorescence intensity.

3.2.2. Titration Studies

To evaluate the detection potential of this chemical sensor, a titration test was performed. For this purpose, diverse concentrations of CN^- (1×10^{-4} M to 100×10^{-4} M) were added to fumed-Pr-Pi-TCT. After each addition, the fluorescence spectrum was recorded. It gradually decreased after adding different amounts of anion (Figure 6).

According to the titration diagram, the fluorescence intensity was reduced by adding CN^-. By plotting the ratio of fluorescence intensity to different CN^- concentrations (Figure 7), a linear relationship could be established between them that followed the equation $y = -0.0069x + 0.8262$, with a regression coefficient of $R^2 = 0.9541$. The $DL = 3\,S_d/m$ equation was used to calculate the detection limit (DL is the detection limit, Sd is the standard derivation of the blank, and m is the slope of fluorescence intensity) [46]. According to the above equation, the detection limit was obtained 0.82×10^{-4} M.

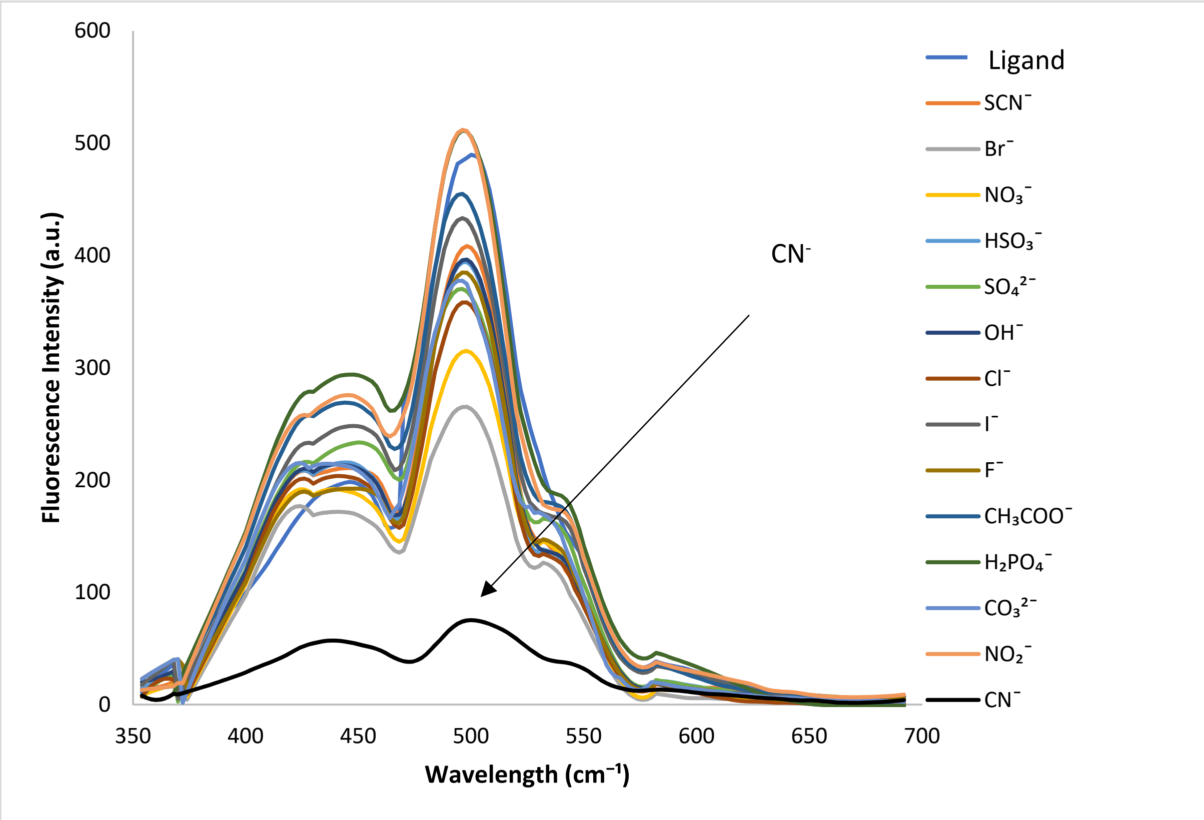


Figure 4. Fluorescence spectra of the aqueous suspended fumed-Pr–Pi-TCT (3 mL H_2O suspension, 0.2 g L^{-1}) using different anions.

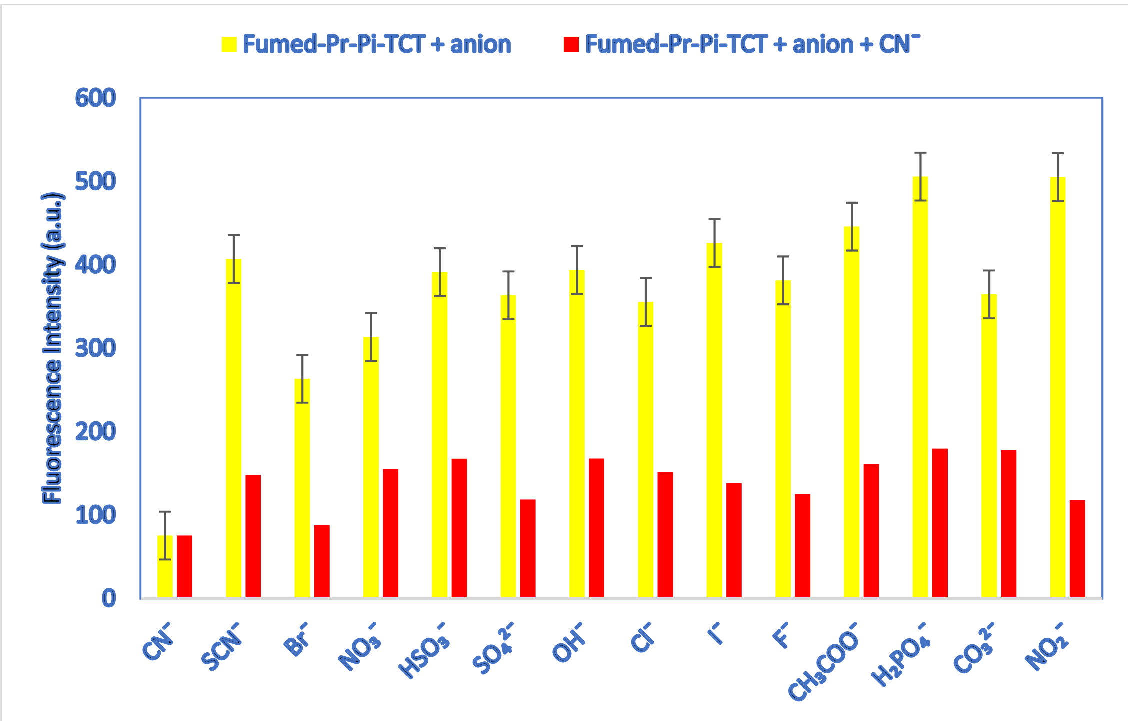


Figure 5. Selectivity of fumed-Pr–Pi-TCT (3 mL H_2O suspension, 0.2 g L^{-1}) for CN^- (100 µL, 1×10^{-2} M) with equal amounts of interfering anions (λem = 500 nm, λex = 350 nm).

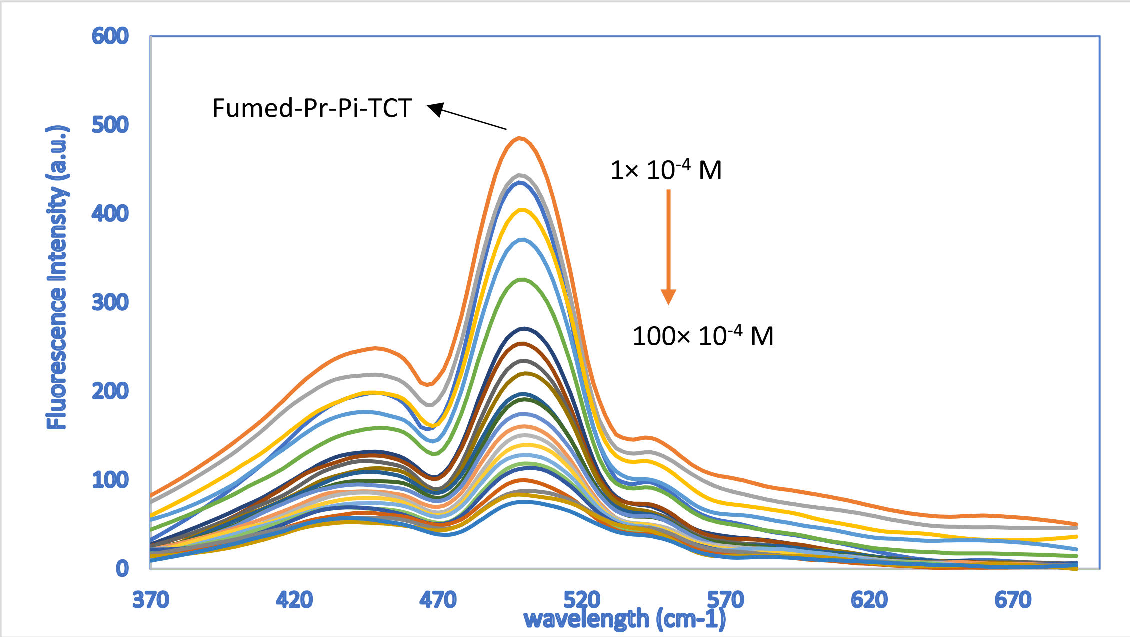


Figure 6. Fluorescence response of fumed-Pr-Pi-TCT (3 mL H_2O suspension, 0.2 g L^{-1}) after adding different concentrations of CN^-.

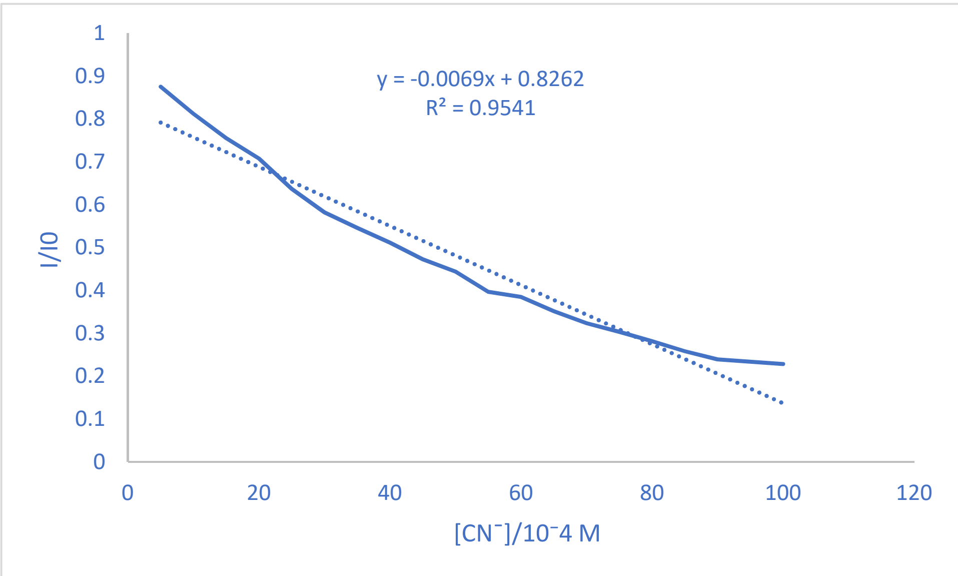


Figure 7. Stern–Volmer plot for the titration of fumed-Pr-Pi-TCT with different concentrations of CN^-.

3.2.3. Competition Studies

To compare our work with other previous research documented in the literature, in terms of the limit of detection (LOD), media with different structures are shown in Table 1. In recent years, the use of fumed silica as a scaffold for the production of organic–inorganic hybrids has garnered special attention due to its simple reactions, non-toxicity, and inexpensive nature, and hence, fumed silica was used in this research.

Table 1. Comparison between various sensors.

Sensors	Solvent System	Sensing Ions	LOD	Reference
SSA[1]	H_2O	CN^-	2×10^{-4} M	[46]
SBA-II	H_2O	CN^-	3.9×10^{-4} M	[47]
Fumed-Pr-Pi-TCT	H_2O	CN^-	0.82×10^{-4}	Present work

[1] SBA-15, (3-aminopropyl)triethoxysilane, salicylaldehyde; [2] SBA15, NaN_3, 1, 2, 3-triazole linked 8-hydroxyquinoline

4. Conclusions

Fumed-Pr-Pi-TCT was prepared successfully via functionalization with piperazine, and the trichlorotriazine and the ensued chemical sensor could selectively and successfully detect CN^-. The fluorescence intensity was significantly reduced after adding CN^- in the presence of different anions. In the field of environmental hazards and pollutants, cyanide is one of the most important pollutants in water, soil, and air, which has detrimental ecological impacts on the ecosystem and the environment; thus, its removal from the environment is vital. Fumed-Pr-Pi-TCT can be modified with different nucleophilic groups to yield other newer optical sensors, which could serve as scavengers of metal ions and assorted anions. Therefore, these types of compounds could be used for detecting pollutants successfully.

Author Contributions: S.S.A.: Writing-Original Draft, performing experimental works; G.M.Z., Supervision, Project administration, Editing; F.M., Validation-Supporting, editing Data Analysis, Graphical Abstract Design; A.B., Data Analysis, Editing of the article; S.I., Writing, Review & Editing; R.S.V., Review & Editing. All authors have read and agreed to the published version of the manuscript.

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