Organic Nanoparticles as Sensor for toxic metals in Aqueous Medium Based On Fluorescent quenching

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Abstract:

Molecule N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle (DPCNPs) was synthesized for detect cadmium metal in Aqueous Medium Based on Fluorescent quenching. Cd^{+2} particularly is emitted into the environment via fertilizers of abundant phosphate, and prolonged Cd^{+2} contact can cause bone weakening and damage to the internal organs. Its characteristics and fluorescence behavior were studied. Dynamic light scattering (DLS) was utilized to test the prepared NDPCNPs which reveal a narrower distribution of the sizes of the particles of 60 nm which is the average particles size. The scanning electron microphotograph (SEM) shows distinctive nano-particles of morphology in a spherical shape. The (DPCNPs) aqueous suspension fluorescence spectra and UV-absorption are blue shifted from the congruous of N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide solution spectra in acetonitrile. Such shifted blue color indicates the Aggregation Induced Enhanced Emission (AIEE) and H-aggregates from nano-particles. The (DPCNPs) nano-particles are of stability being high with surfactant of Tween80. Therefore, the effects of few metal cations on the fluorescent (DPCNPs) intensity were investigated. It was detected that fluorescence modified (DPCNPs) intensity was quenched selectively through Cd (II) ion addition compared to with other tested cations. The (DPCNPs) can be utilized as chemosensor being fluorescent bulk for Cd (II) ions detection. The quenching of fluorescent is linear at 25 to 225 µM range of ions of Cd (II). The detection limit was 1.47µM. The nanosensor displays a great selectivity versus ions of Cd (II) compared to communal metal ions. The suggested method applicability for detecting Cd+ metal in water samples collected from the Al Habbaniya Lake (Iraq) were calculated.

Keywords: N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide, Nano-particles, Sensor, Fluorescent quenching.

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Introduction

Soil and Water contamination through ions as heavy metals is a severe issue globally for the reason that their persistence biology and toxicity [1]. Monitoring the contaminant presence in H_2O is of general attention for ensuring the surface quality, ground, and drinking H_2O. Ions as heavy metal among several H_2O pollutants, such as waste or plastic, pesticides or chemical fertilizers, and pathogens, are recognized for their great toxicity. Although few of them are nutrients being essential (for example, Fe, Zn, or Co), at greater concentrations, they are toxic. At trace levels, Cd, Pb, and Hg are extremely poisonous even, presenting a nearby relationship to neuro-degenerative or cancer diseases [2-4]. Moreover, ions as heavy metals are substances being non-biodegradable and of accumulative influence in human the body once they enter, normally, by beverages, air, and the food chain, where H2O has a key function. Thus, metal ions can be detected owing to batteries, vehicle emissions, or activities of industries. Therefore, at small concentrations, their detection is a primacy matter for the conservation of environment and prevention of viruses [5-7]. Cd exists in rocks of phosphate and the utilization of fertilizers of phosphate presents Cd to sources of food and into the environment. Furthermore, emissions of anthropogenic Cd are quickly growing from combustion of fossil fuel, Zn smelting, Pb, and Cu ores, pigment manufacture, and from sewage sludge and municipal incinerators [8-10]. The main exposure routes to Cd are through contaminated food ingestion or H_2O and cigarettes smoking [8-11]. Chronic exposure of Cd cause numerous negative health effects on kidneys, lungs and liver damage [12]. Also, Cd interferes with bone structure and mineralization, causing osteomalacia, osteoporosis, and Itai- Itai disease, as well severe spine and joint pain [13]. WHO Cd guidelines for drinking H2O are 3 ug/L (3 ppb). Guidelines of Environmental Protection Agency (EPA) in the USA reports that the maximum level of contaminant for Cd in drinking H2O is 5 ppb [14]. For Cd contamination detecting in H_2O sources is pivotal to minimize human intake and prevent negative health influences. Numerous techniques were stated for Cd detection such as AAS, fluorescence spectroscopy (FS), calorimetry, plasma-mass inductively coupled spectrometry, and electrochemical voltammetry [15]. Fluorescence spectroscopy, compares favorably to other techniques in terms of selectivity, sensitivity, affordability, simplicity, and extremely low detection limits, for instance. Fluorescent organic nano-particles (FONs) are of high consideration because of its character as selective binding with molecules of analysis. FONs have encouraged rising research efforts because of their high organic molecules diversity being available including the material synthesis flexibility, good H2O solubility and being optical. The characteristics of fluorescence and absorption spectral properties are distinct because of charge transfer exciton evolution effect with enlarged ratio of surface to volume, enhanced and various emissions [16-18]. In this paper, N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle (DPCNPs) was synthesized in suspension as aqueous done through a reprecipitation technique to the sensitive and selective Cd^{+} according to quenching of fluorescence.

2.Experimental

2.1 Materials

The chemicals used in this study were obtained from commercial centers of materials. N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide purchased from Merck Co. (Germany). All metal salts were from sigma Aldrich. The solvents from Alfa Aaser. Throughout the investigation period, distilled water was used in all work steps.

2.2Apparatus

N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide spectrum was determined from the absorbance spectrum at standard incidence above the range (200 –800) nm by utilizing UV-VIS spectrophotometer type (SHIMADZU) (UV-1600). Fluorescent spectra were measured in the Molecular Spectroscopy Laboratory in the Physics Department of the college of Science using a Shimadzu RF-5301PC spectrofluorophotometeras. The acidity of the resulting solution was measured in the department of chemistry using a digital pH meter, model ph7110 (in lab, India), with a collective glass electrode. The nano-particle zeta and size potential were examined and measured in Iran utilizing a Malvern Zetasizer (nano ZS-90) device. The BDNPs morphology was measured through (SEM), activated at 20 kV as voltage of accelerating.

2.3. Preparation of (DPCNPs)

DPCNPs were done through method of reprecipitation utilizing template of tween-80. To prepare this nanopartical, a certain amount of N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide is measured and dissolved in the acetonitrile solvent to obtain solution at a concentration of 1×10^{-4} molar. The solution is placed on the stirrer for 15-20 minutes. A quantity of tween-80 in 100 ml of H2O with concentration 3×10^{-3} molar was dissolved and then put on the stirrer for 20 minutes. 5 ml of N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide solution were added and injected directly into tween-80 solution with stirrer retention. The mixture was stirred for half an hour. Then the mixture is placed in an ultrasonic device for 15 minutes. Finally, the suspended solution remained constant or standing for half an hour. Transparent nano-particle suspension as yellow colored was undertaken extra for distribution of particles size and morphology of surface studies. The nano-particles suspension was prepared through a sample and surfactant solution changing concentration. In the DLS histogram, the suspension displayed a narrow particle size distribution, which was defined as monodispersity for fluorescence and photophysical quenching studies.

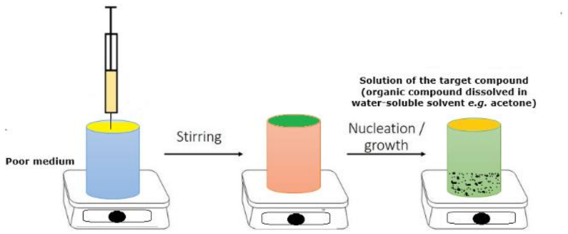

Fig.1 Reprecipitation Method

3.Results and Discussion

3.1. (DPCNPs) Morphology and Particles Size

The possible interaction between nano-particles determines the possibility of forming nano-particles. The process of formation and stability of nano-particles is influenced by a series of important parameters, including the size of the massive and ionic additives, the flow conditions, the nature of the charge and the low molecular weight molecules. All these factors determine the stability of nano-particles DPCNPs [19,20].

In this work, it is necessary to point out the importance of the use of surfecant particles that surround nano-particles and thus inhibit aggregation of nano-particles forming larger volumes outside of nanoscale measurements. It is known that the composition of nano-particles is formed in different sizes, but the higher-velocity is the dominant size. The distribution of DPCNPs particles size histogram of aqueous suspension, detected through (DLS) technique, is illustrated in Figure 2 in which the size particles distribution observed is narrow remarkably, with 65 nm diameter as average particle. The zeta (ξ) potential value measured on size as zeta is −14.8 mV which confers a great nano-particles level stability. SEM illustrated in Figure (3) exposes that the DPCNPs are of spheres being distinct and monodispersity. The average particle size calculated is 50 nm, which is similar to the DLS histogram estimate.

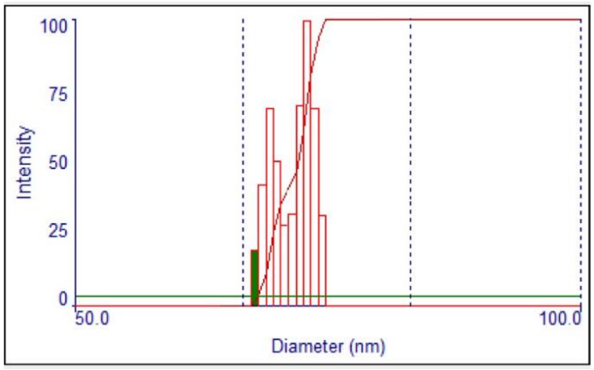

Fig.2 The particle size distribution histogram of DPCNPs

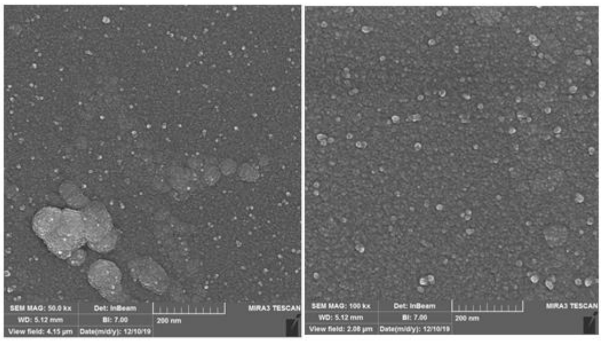

Fig. 3 Scanning electron microphotograph of DPCNPs

3.2. (DPCNPs) Photophysical Properties

Nano-particles formation in suspension as aqueous is extra verified through fluorescence and absorption spectroscopy. Figure 4 displays the absorption of the dilute solution spectra of DPC in acetone (A) and aqueous DPCNPs (B) suspension. The absorption spectra of dilute DPC sample solution has a broad band peaking at 285 nm, whereas DPCNPs have blue shifted structured sharp bands at (235,250) nm, which because to the $\pi^* \longrightarrow \pi$ transition. The observed structured absorption spectrum and blue shift show that the molecule of DPC aggregates in cluster as planar. The spectrum structured with a band of absorption at 235 nm and 250 nm make us consider the individual molecules contribution. The big blue shift in the spectrum of absorption additionally reveals that the aggregates of H-type are fashioned because of strong interaction of lateral π-stacking [21]. Figure (5) shows that the fluorescence DPCNPs spectrum of aqueous suspension broad band of emission enhanced at 530 nm. Because of the face-face π stacking influence in nano-aggregates, the enhanced strong spectrum at 537 nm is given to the best likely π*⟶π evolution. Because the electronic dipoles of every monomer transition paralleled to one another according to a regular rise in the excitonic coupling influence where the exciton relaxes to a lower lying excited state energetically, the interaction of dipoledipole between closely neighboring molecules stacked in H- aggregates. The emission is assumed to be caused by a lower nano-aggregate lying excited state than the excited solitary DPCNPs molecule in suspension, and hence the nano-emission is bathochromically changed. The bar diagram explaining the influence of pH on fluorescence intensity is illustrated in Figure 6. The highest fluorescence intensity was reported at pH=6, indicating high power colloidal stability at that pH. The colloidal stability altered by the tween-80 disruption cage at high and low pH decreased fluorescence intensity due to nanoparticle disaggregation.

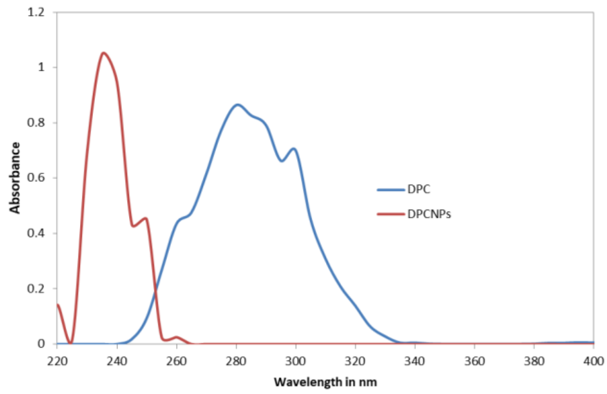

Fig.4 Absorption spectrum of DPCNPs

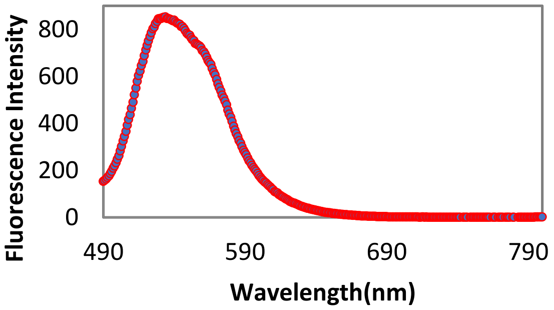

Fig.5. fluorescence spectrum of DPCNPs

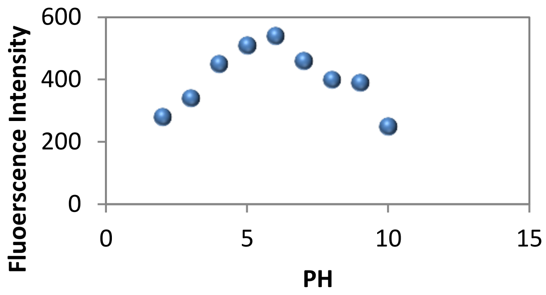

Fig. 6. Effect of pH on the fluorescence spectrum of DPCNPs

3.3. Selective DPCNPs Fluorescence 'Turn-Off' through Ions of Cd^{2+}

The negative DPCNPs zeta potential −14.8 mV in suspension as aqueous showsits capability for binding cations. The capability of binding was test via changes measuring results in the DPCNP molecule spectra following the addition of metal salt suspensions aqueous. Figure 7. Illustrates the fluorescence aqueous DPCNPs suspension spectra recorded in the metal ions presence. It is noticed that Cd^{2+} presence reveals quenching fluorescence whereas other cations are enhancement fluorescence responding oppositely. The fluorescence change intensity ΔF/F is depicted in Figure 8 as a bar diagram with F = F -F^0. In the presence and absence of interfering cations, F^0 and F are the fluorescence and nan-oparticle intensities, respectively. The spectrum intensity decrease is only observed for cadmium cation. The DPCNP coordination with Cd2+ upsurges the molecular aggregation rigidity through limiting the free carbonyl carbon rotations with regard to the ring of indole leading to a noteworthy reduce of the intensity of fluorescence that is recognized as chelation-quenched fluorescence (CHQF). Other metals are not showing interference in $Cd2^{+}$ distinguishing in liquid as aqueous. The fluorescence aqueous DPCNPs suspension spectral changes after and before Cd2+ addition are illustrated in Figure 9. Fluorescence aqueous DPCNP suspension solution spectra in Cd2+ presence from 25 to 225 μM concentration range detected at room temperature. The fluorescence nano-particles intensity is regularly declining with no spectral shifts. The data of quenching was analyzed through utilizing conventional Stern-Volmer relation. Figure 10 shows the Fluorescence spectra of DPCNPs for many days. The transform in the spectrum intensity in the metal concentration (Cd) is shown in Figure 11. The obtained Practical results in Cd^{2+} fitted favorably to the following experimental equation: Y = 0.001733x +0.984

The linear relationship between the increased concentration 25 – 225 µM of the metal and the fluorescent intensity was demonstrated to have a correlation coefficient R = 0.9915. The detection limit was computed through the equation.

$$LOD=3.3\sigma/K$$

Here, σ is the standard reversion lines deviation and k is the correction chart slope. In the experimental equation above, the detection limit for iron metal was calculated as a value of LOD was 0.47 µM. This finding indicates the ability of DPCNP nano-particles to sensitize and select Cd by effective fluorescent suppression.

Table (1) compares this technique with other several reported techniques for the sensing of Cd^{2+}.

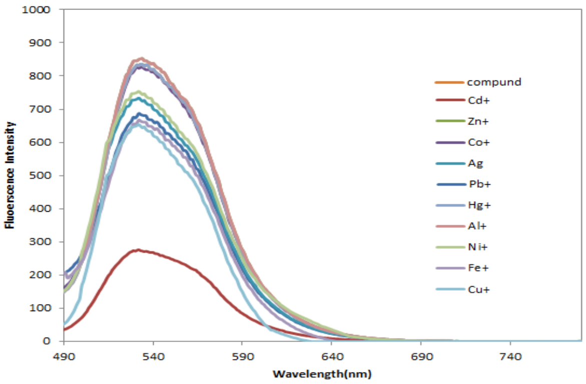

Fig. 7 fluorescence spectrum of DPCNPs with metals

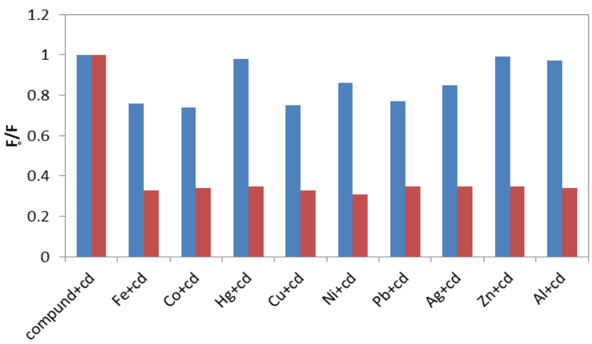

Fig. 8. scheme exhibiting fluorescence spectrum response [(ΔF)/F] of DPCNPs

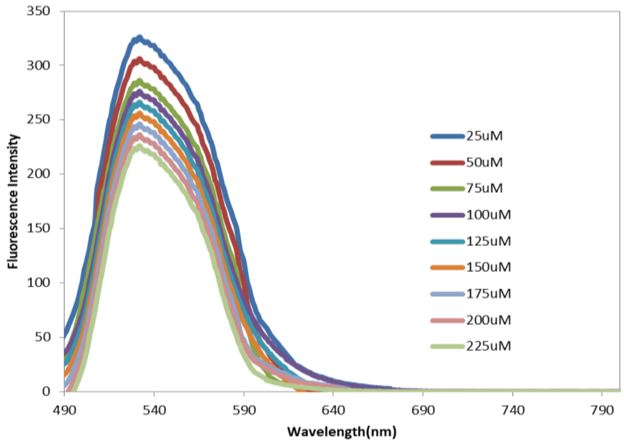

Fig. 9. Spectrum intensity of DPCNPs after add of different concentrations of Cd2+ ions

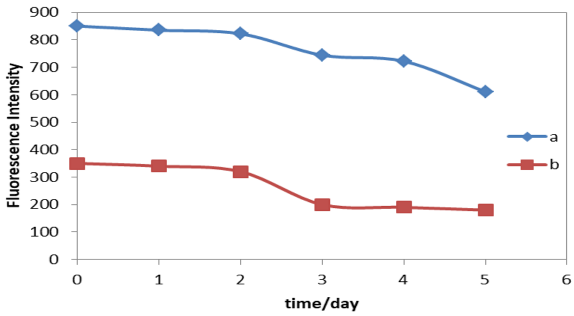

Fig. 10. Fluorescence spectra of DPCNPs for many days

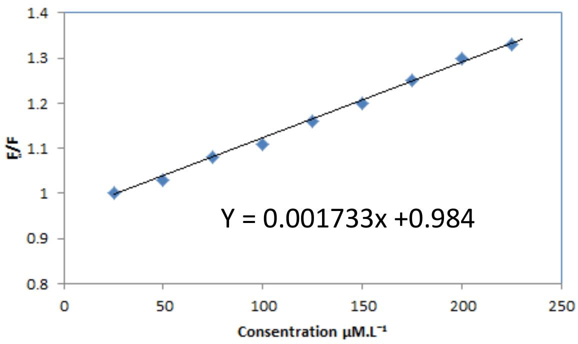

Fig. 11. Stern- volmer plot of fluorescence quenching data

Table 1 Comparison of this method with other several reported methods for the sensing of Cd^{2+}.

S.no.	Method used	Limit of detection (LOD)	Ref.
1	A quinoline based Schiff base	0.495 µM	[22]
2	N,N-dimethyl-4-(((2-(phenylamino)phenyl)imino)methyl)aniline (DMBA)	0.438 µM	[23]
3	Di-2-Picolylamine-Substituted Quinoline-Based Tolans	0.158 µM	[24]
4	N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle (DPCNPs)	0.47 µM	This method

3.4Application of DPCNPs for the selective of metal amounts in water samples

The ability to use N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle molecule with a fluorescence quenching method to detect metal within real models in the medium of a solution is the most significant goal. N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle was used in a practical application to detect metals in tap water samples using the fluorescence technique. The suggested method applicability for detecting Cd+ metal in water samples collected from the Al Habbaniya Lake (Iraq) was calculated. To remove contaminants, the specimens were first filtered by filter sheet. Tables 2 details the findings. Several facts are revealed as a result of these findings.

Cd^{+} values in the Al Habbaniya Lake ranged from 0.006 to0.00 8 miligrams per liliter in all samples. The experimental concentrations are similar to those seen in natural water. As a result of these findings, the chemosensor N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide nanoparticle can be utilized to measure Cd2+ in the real samples. Concentrations exceeding the EPA limit can induce gastrointestinal problems in the short term and long term.

Table .2- DPCNPs for the detection of metal amounts in water samples

Water samples	The amount of standard Cd^{2}+ added µM	Total Cd^{2+} Found µM	The amount of cd^{+2} discovery µM	Relative Error (%)
sampel 1	100	101.39	20.39	0.176
sampel 2	120	131.63	21.63	0.186
sampel 3	140	190	23.2	0.143
sampel 4	160	196	23.76	0.189
sampel 5	180	196	22.65	0.184
sampel 6	200	198.8	23.98	0.178

Conclusion

This work concludes that it is possible to prepare nanoparticles of N-[3-(Dimethylamino) phenyl] thiophene-2-carboxamide Molecule according to the conditions adopted by the method of reprecipitation, which was an easy, simple and cheap method. Also, there is no significant difference in thin films of nanoparticles which prepared in different ways. The ionic surface is very important in maintaining the nanoparticle structure of DPCNPs nanoparticles. The DPCNP nanoparticles have high spectral properties and distinct synthetic features that make them useful in many applications. Other conclusions are that the solution of the nanoparticles of DPCNPs is more effective and more stable at medium pH. One of the most important conclusion is the high sensitivity of nanoparticles to minerals, especially Cd^{+} metal in aqueous solutions. Another conclusion is the success of the method of fluorescent quenching in metal detection using DPCNPs.

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