

A Fluorescent Nanosensor Based on Magnetic Silica Nanoparticles as Illicit Drug Vapor Logic Gate

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ABSTRACT

Herein we report a fluorescent nanosensor based on magnetic silica nanoparticle as illicit drug logic gate. A novel naphthlimide derivative was synthesized (F), characterized and doped into the magnetic silica nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$). Its fluorescence intensity was markedly enhanced by adding of methamphetamine.

Keywords: naphthalimide, sensor, logic gate, emission, nano magnet, silica nanoparticle, Illicit Drug.

1 INTRODUCTION

Growing up abuse of amphetamine-type stimulants (ATS) over the 20 last years, particularly, involving amphetamines (amphetamine and methamphetamine) and substances of the “ecstasy”-group, among teen-agers has become a global problem. Methamphetamine “meth” can be found in the form of pills, capsules, powder or chunks, called crank, speed, crystal or ice. It can be smoked, snorted, injected or eaten. Meth is a powerful, highly toxic, addictive drug that is illegally “cooked” in household labs. Abuse of methamphetamine can result in a stimulant psychosis which may present with a variety of symptoms (e.g. paranoia, hallucinations, and delusions).

Different techniques for determination of methamphetamine and related compounds are used such as gas GC/MS, HPLC/MS, FTIR, voltammetry, capillary electrophoresis and Surface ionization [1-4]. These conventional methods, however, require large and expensive instruments, complicated experimental procedures. Thus, there is a need for development of a simple, rapid, and sensitive MA detection method. In recent years fluorescent sensing has been considerable attention for its high sensitivity, real time, online detection and easy operation. Our group has reported the design and synthesis of fluorescence dyes for sensor application [5-7].

In recent years nanoparticles have been of great interest because of their potential applications in cell targeting, drug delivery, bio separation, and magnetic resonance imaging.

Magnetic and fluorescent nanoparticles are of particular importance due to their broad range of potential applications [8]. It is expected that the combination of magnetic and fluorescent properties in one nanocomposite would enable the engineering of unique multifunctional nanoscale devices, which could be manipulated using external magnetic fields. In this way, there are only few reports about the fluorescence sensing of methamphetamine. Cheng and coworkers reported a highly fluorescent polyfluorene capable of producing high sensitivity for methamphetamine [9]. They also developed a fluorescent chemosensor for methamphetamine vapor sensing based on fluorene–thiophene-based thin-film [10]. Recently we reported the synthesis of a novel naphthalimide fluorescence derivative for selective recognition of methamphetamine [11].

Herein we report a fluorescent nano chemosensor based on magnetic silica nanoparticles as illicit drug logic gate based on naphthalimide derivative.

2 EXPERIMENTAL

2.1 Materials

Ferric chloride hexahydrate (FeCl_3), ferrous chloride tetrahydrate (FeCl_2), dichloromethane (DCM), ammonium hydroxide (28wt%), tetraethyl orthosilicate (TEOS), and potassium carbonate, Acenaphthene and 3-amino propyl triethoxysilane (APTES), were obtained from Merck. All used amines obtained from Merck Chemical Co. and used as received.

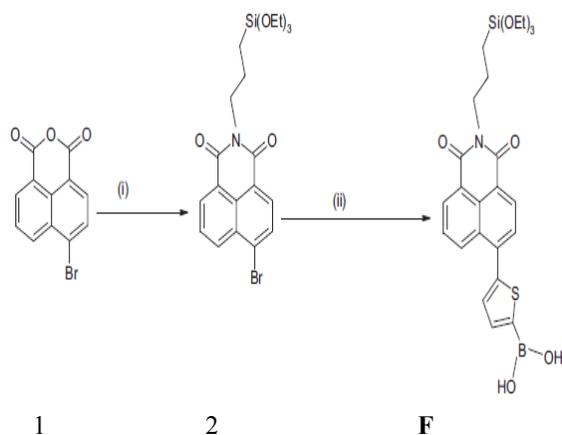
2.2 Synthesis

Fe_3O_4 NPs were prepared according to reported literature [12]. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2g, 0.01mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4 g, 0.02 mol) were dissolved in 120mL of deionized water. $\text{NH}_3 \cdot \text{H}_2\text{O}$ (60 mL, 28 wt%) was added under vigorous mechanical stirring. The color of the suspension turned black immediately. Afterward, the mixture was kept at 70°C for 30 min. The mechanical stirring and nitrogen

atmosphere were used. After cooling down, the precipitated powders were collected by magnetic separation and washed with deionized water. The core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs were synthesized by a sol-gel process through the hydrolysis and condensation of TEOS in ethanol and ammonia mixture. Briefly, 0.56 g citrate-functionalized Fe_3O_4 NPs and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (5.0 mL, 28 wt%) were stirred in a flask charged with 120 mL ethanol.

Afterward, 4.0 mL TEOS was added drop wise. The mixture was kept at room temperature for 8 h under N_2 with violent mechanical stirring. The products were collected with a magnet and washed with ethanol and toluene.

The intermediate, compound 1, was synthesized from acenaphthene, according to the reported method in literature [13]. The intermediate compound 2 was prepared at 76% yield by the reaction of 0.52 mmol of compound 1 with 2.88 mmol of 3-aminopropyl-triethoxysilane, in ethanol. The solvent evaporated by rotary evaporation, and the crude product recrystallized with ethanol to give compound 2 (Scheme 1)



Scheme 1. Synthesis route for fluorescence sensor

Compound **F** was synthesized through the palladium-catalyzed Suzuki reaction [14]. The intermediate (0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.011 mmol), K_3PO_4 (0.78 mmol) and 2,5-thiophenediyl-bisboronic acid (0.8 mmol) in toluene were mixed, stirred and reflux for 24 h. The crude products were concentrated under vacuum, and purified by chromatography. Synthesis compounds were characterized by $^1\text{H NMR}$, $^{13}\text{C NMR}$, FTIR and elemental analysis.

3 RESULTS AND DISCUSSION

The TEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ NPs were obtained. The average diameter of magnetic silica NPs was about 28 nm. The $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ NPs have uniform spherical morphology.

The variation of functional groups on $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ NPs was characterized by FT-IR (Figure 1). Fig. 1, shows new bands refer to bonding of compound **F** on the silica surfacfter and before bonding on nanoparticles. The peak at 1661 corresponds to C=O stretching. The band at 1544 cm^{-1} is due to the C=C stretching, which comes from the aromatic ring. The band at 1343 cm^{-1} is C-N stretching which is corresponded to naphthalimide ring. As expected, strong Si-O-Si stretching band in 1115 cm^{-1} and Si-OH stretching band in 810 cm^{-1} are observed in $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$.

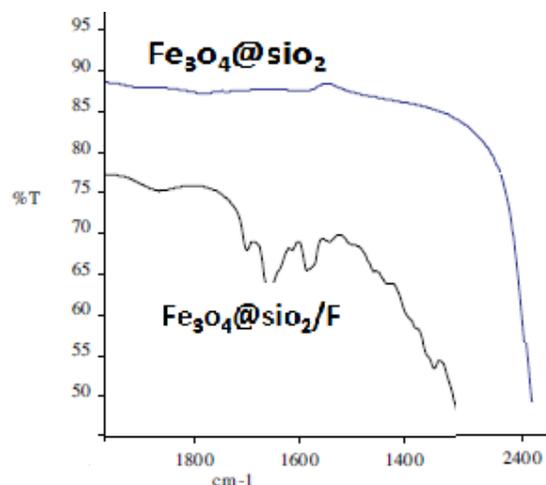


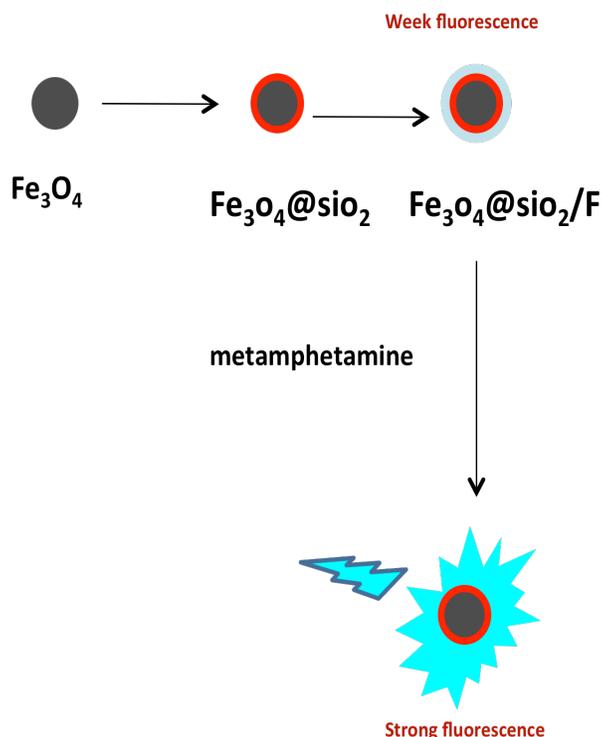
Fig 1. FTIR spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2$

The UV-Vis and fluorescence property of synthesized compound in chloroform and solid state were investigated. The synthesized nano hybrid can emit blue emission against metaamphetamine vapor (Scheme 2).

It exhibited selective recognition towards metaamphetamine among different amines. Its fluorescence emission changes by the inputs of metaamphetamine can be viewed as a logic gate at the nanoscale level. Fluorescence intensity markedly changed as 190% by adding of metaamphetamine, the detection limits for metaamphetamine vapor were estimated to be 16 ppm.

In order to investigate the fluorescence sensing of synthesized fluorophore (**F**) against metaamphetamine, titration of **F** (1×10^{-8} mol) was performed in acetonitrile solution with 1×10^{-1} mol of metaamphetamine. As can be seen in Fig. 2 a) and b) fluorescence emission of nanosensor displayed enhancements upon the addition of 0–100 equivalent of metaamphetamine. Fluorescence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ upon addition of metaamphetamine under 360 nm excited UV lamp gradually increases with 190% enhancement at emission maximum wavelength. We suggest that the fluorescence “turn-on” sensing mechanism

could be due to the binding induced weakening of internal heavy-atom effect as previously reported by Cheng . Sulfur, as a heavy atom, may strengthens the spin-orbit coupling and increases the intersystem crossing transitions from S1 → T1, so leading to decrease the fluorescence quantum yield of the molecules. Thus, **F** emits weak fluorescence because of thiophene units. However, when amines such as metaamphetamine bind to thiophene unit, their interaction weakens the internal heavy atom effect and lead to fluorescence enhancement



Scheme 2. Schematic response of nanosensor

To evaluate the selectivity of the nanosensor, fluorescence emission changes were obtained in the presence of different amines. The fluorescence intensity shows a little change against several different amines. But fluorescence intensity considerably increased just against metaamphetamine. In order to study the interfering effects, the intensity changes of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ upon addition of different amines in the presence of metaamphetamine (MA:amine, 1:10) were investigated. As can be seen in fig. 2 the excellent selectivity of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ for metaamphetamine against different amines obtained. Therefore, it seems these amines do not interfere with the determination of metaamphetamine. Consequently, it is concluded that the new nanohybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$ can be used as a chemosensor for the detection of different concentrations of metaamphetamine with high selectivity.

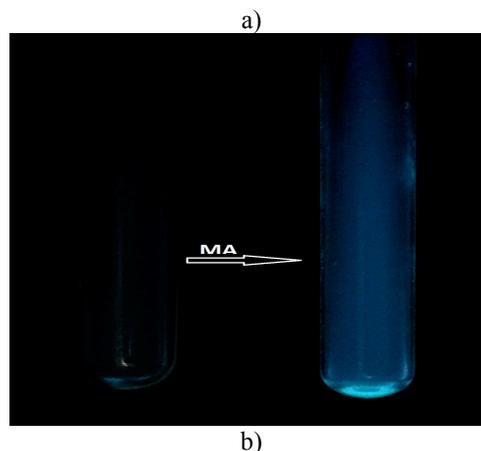
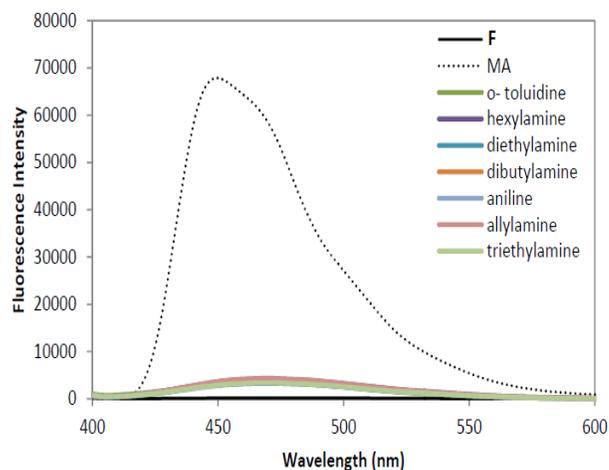


Fig. 2. $\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{F}$ in the absence and presence of metaamphetamine. a) emission spectra in the presence of various amine, b) visual change under uv irradiation.

In order to evaluate the applicability of the proposed nanosensor, metaamphetamine was determined in laboratory prepared samples containing different amounts of interfering amines by two methods of HPLC and proposed nanosensor. Recovery of two techniques illustrated in Table 1. As can be seen there is a satisfactory agreement between results of the presented method and those obtained by (HPLC). The results given in Table 1 show that the recovery of MA from samples are good (relative standard deviation (RSD) less than 4.16% (n = 6)).

Sample	Known amount	Found amount	RSD%
1	12	13±0.5	2.74
2	60	59±0.4	3.1

Table 1. Real sample analysis of metaamphetamine ($\mu\text{mol L}^{-1}$).

4 CONCLUSION

A fluorescence “turn-on” molecular logic gate system ($\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{F}$) was developed based on a functionalized naphthalimide dye derivative linked to the magnetic silica nanoparticles surface. Reusable logic gate nanosensor shows high selectivity toward metaamphetamine vapor in ultra trace level.

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