RESEARCH PAPER

Graphene Oxide-terpyridine Conjugate: A Highly Selective Colorimetric and Sensitive Fluorescence Nano-chemosensor for Fe^{2+} in Aqueous Media

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ABSTRACT

A graphene oxide-terpyridine conjugate (GOTC) based colorimetric and fluorescent nano-chemosensor was synthesized. It showed high selectivity and sensitivity for Fe^{2+} and Fe^{3+} ions in neutral aqueous solution over other metal ions such as Li^{+}, Na^{+}, Ba^{2+}, Ca^{2+}, Al^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Ag^{+}. In absorption spectra, upon addition of Fe^{2+} or Fe^{3+}, the sensor displayed a peak at 568 nm, by changing the color of the solution from light pink for GOTC to light magenta and deep magenta for Fe^{3+} and Fe^{2+}, respectively. Also, the fluorescence studies revealed that, Fe^{2+}, Fe^{3+} and Co^{2+} quench the emission of GOTC at 473 nm, while other metal ions do not quench the fluorescence of GOTC in solution. Colorimetric and fluorescence techniques could be used for detection of Fe^{2+} ion concentration at least about 6-10 µM in water solution. The sensing on test paper was also investigated for the naked-eye detection of Fe^{2+}.

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INTRODUCTION

The design and development of new materials for the recognition and sensing of transition-metal ions in aqueous solution have received great attention in environmental chemistry and biology [1-4]. In particular, colorimetric methods are of interest because they allow naked-eye detection of color change without any use of a complicated analytical instrument [5-9]. Also, due to their convenient use, high sensitivity, and real-time detection, a tremendous attention has been paid to the development of fluorescent chemo sensors for metal ions [10-15].

Iron is the most abundant intracellular metal ion and one of the most essential trace elements in biological systems. It is an essential element for the formation of hemoglobin and various enzymes in the human body [16] and plays crucial role in many biological processes [17-19], and deficiencies or excesses of iron ions cause a variety of diseases [20]. Therefore, the development of sensitive and selective sensors for iron ions is of considerable interest. Although, examples of colorimetric and fluorescent chemical sensors for Fe^{3+} were reported [21-26], which most of them rely on small organic molecules with low solubility in water having no application for iron ion detection in biological environments, there are only a few fluorescent sensors reported for Fe^{2+} until now [27,28].

Terpyridine ligands have not been generally used for sensors, due to possessing an excellent ability to coordinate with a large variety of transition metal ions with high binding constants. However, there are some limited reports on the sensing of iron metal ions by terpyridine containing sensors. In this context, Liang *et al.* reported a colorimetric

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chemosensor containing terpyridine moiety for Fe^{2+} and Fe^{3+} ions in aqueous solution [29]. Also, a europium-based metal-organic framework (Eu-MOF), EuL_3 (L = 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine), was reported as a luminescence sensor for Fe^{3+} ions [30].

Graphene oxide (GO), a highly dispersed derivative of graphene in water, has found important applications, especially in sensors for detecting DNA [31-34], small molecules [35,36], proteins [37], and cells [38], because of its distinguished electronic properties [39,40]. In continuing our research on the sensors [41], herein we wish to report a new graphene oxide-terpyridine conjugate for the selective and sensitive recognition of Fe^{2+} ion in aqueous solution.

EXPERIMENTAL

Materials and Apparatus

All chemicals were purchased from Merck and Sigma-Aldrich and used without any further purification. Solvents were used as received from commercial suppliers. FT-IR spectra were obtained using a Perkin Elmer 781 spectrometer. UV-Vis spectra were recorded using Shimadzu UV-1800 spectrophotometer and fluorescence spectra were measured using JASCO-FP-750, Rev. 1.00 fluorometer. TEM images were recorded using a Philips CM120 microscope. SEM images were recorded using a MIRA3 TESCAN microscope.

Synthesis of 4'-[4-(hydroxyethoxy)phenyl]-2,2':6',2"-terpyridine 3. A mixture of chloroethanol (41 mmol, 3.3 g), 4-hydroxybenzaldehyde 1 (41 mmol, 5.0 g) and Na_2CO_3 (56 mmol, 5.9 g) in 15 ml DMF was heated under reflux conditions for 24 h. Then, water was added and extracted by EtOAc three times. The combined organics were dried over anhydrous $MgSO_4$ and evaporated to give 4-(2-hydroxy-ethoxy)benzaldehyde 2 as a yellow viscose oil [42], which was used in next step without further purification. Obtained 2 and 2-acetylpyridine (105 mmol, 12.7 g) were dissolved in 600 ml MeOH/dioxane (1/1; v/v) mixture, and stirred at 50 °C for 5 min. Then, 40 ml $NH_3{\cdot}H_2O$ and 240 ml NaOH (15% water solution) were added to obtained solution and heated at 70 °C for 12 h. Then, the mixture was cooled to room temperature, and obtained white solid was filtered and washed with MeOH/water (1/1, v/v), and then dried at room temperature for 2 days (3: m.p.: 200 °C) [43].

Synthesis of 2-{4-[(2,2':6',2"-terpyridin)-4'-yl] phenoxy}ethyl acrylate 4. Acryloyl chloride (5.5 mmol, 0.5 g) was added drop wise to a cold solution of 3 (1.35 mmol, 0.5 g) and Et_3N (0.5 g) in 20 ml $CHCl_3$ in an ice bath, and stirred at the same temperature for 5 h. After completion of the reaction, the mixture was diluted with CH_2Cl_2 and washed with brine. Then, the organic was dried using anhydrous $MgSO_4$, and evaporated to give 4 as a light brown solid. M.p.: 132-134 ºC; FT-IR (KBr) υ = 3051 (CH_{Ar}), 2928 ($CH_{aliphatic}$), 1727 (C=O), 1605, 1582, 1514 (C=C), 1399 ($CH_{2\text{-bending}}$), 1253, 1184 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 4.32 (t, *J* = 4.8 Hz, 2H, CH_2), 4.59 (t, *J* = 4.8 Hz, 2H, CH_2), 5.89-5.92 (dd, *J* = 1.2, 10.4 Hz, CH_{vinyl}), 6.18-6.25 (dd, *J* = 10.4, 17.6 Hz, CH_{vinyl}), 6.48-6.52 (dd, *J* = 1.2, 17.6 Hz, CH_{vinyl}), 7.06-7.09 (m, 2H, CH_{Ar}), 7.37-7.40 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 2H, CH_{Ar}), 7.89-7.93 (m, 4H, CH_{Ar}), 8.69 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 8.73 (S, 2H, CH_{Ar}), 8.75-8.77 (m, 2H, CH_{Ar}) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 62.9, 66.0, 114, 118.2, 121.4, 123.8, 128.0, 128.6, 131.5, 136.9, 149.1, 149.6, 155.8, 156.3, 159.4, 166.1 (CO_{ester}) ppm.

Synthesis of 2-{4-[(2,2':6',2"-terpyridin)-4'-yl] phenoxy} ethyl-3-[(2-hydroxyethyl)amino]propanoate 5. $MnCl_2{\cdot}4H_2O$ was added to a solution of ethanol amine (1.11 mmol, 0.066 g) and 4 (1.11 mmol, 0.47 g) in 15 ml MeOH, and stirred at room temperature for 3 h. Then, the solvent was evaporated under reduced pressure, and obtained solid was washed with water. The yellow solid with m.p.: 140-143 °C was obtained [44].

Synthesis of graphene oxide. 400 ml solution of H_2SO_4/HNO_3 (9/1 v/v) was added to a mixture of graphite flakes (3.0 g) and $KMnO_4$ (18.0 g), and stirred at 50 °C for 12 h. After cooling to room temperature, 400 ml ice and 3 ml H_2O_2 (30%) was added to mixture, and the obtained solid was isolated by centrifuge at 4000 rpm, washed twice with DI water, three times with HCl 35%, and twice with EtOH. GO solution in water was obtained by ultrasonic irradiation for 20 min, followed by centrifuge at 5000 rpm for 10 min. The supernatant containing GO was isolated and stored at 4 °C for further uses [45].

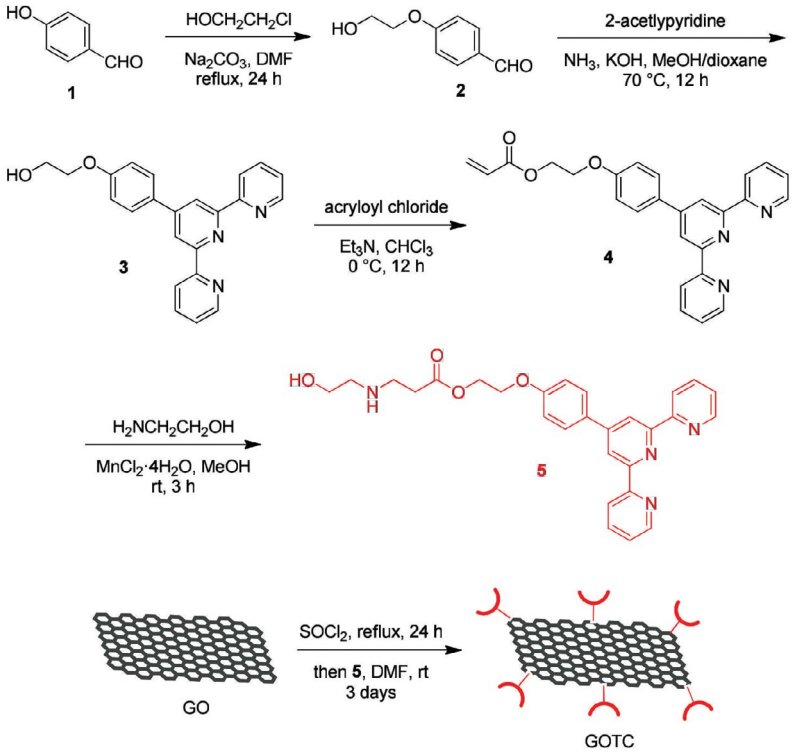
Synthesis of GO-terpyridine conjugate (GOTC). 0.005 g GO was mixed with 10 ml $SOCl_2$ and heated under reflux at 70 °C for 24 h, and then the mixture was dried using rotary evaporator. The obtained solid was mixed with 5 (0.07 g) in 10 ml

dry DMF and heated at 120 °C for 3 days. The solid was isolated by centrifuging at 4000 rpm for 10 min and washed with MeOH.

RESULTS AND DISCUSSION

Synthesis and Characterization of GOTC

The schematic representation of the synthesis of compound 5 and GOTC is shown in Scheme 1. The FT-IR of GO and GOTC is shown in Fig. 1, in which the O-H stretching vibration of GO was appeared as a broad signal at 3415 cm^{-1}, and C=O of carboxylic acid groups was appeared at 1720 cm^{-1}. Peaks at 1621 and 1219 cm^{-1} are related to the C=C and C-O stretching vibrations, respectively. In the FT-IR spectra of GOTC, O-H is appeared at 3415 cm^{-1} as a broad peak, and the C-H stretching vibration of aromatic rings of 5 is appeared at 3062 cm^{-1}, and distinguished bands corresponding to the asymmetric and symmetric stretching modes of CH_2 groups of 5, are appeared at 2924 and 2853 cm^{-1}, respectively. Peak at 1726 cm^{-1} is attributed to the stretching vibration of C=O of ester. Also, in



Scheme 1. Synthesis of GOTC

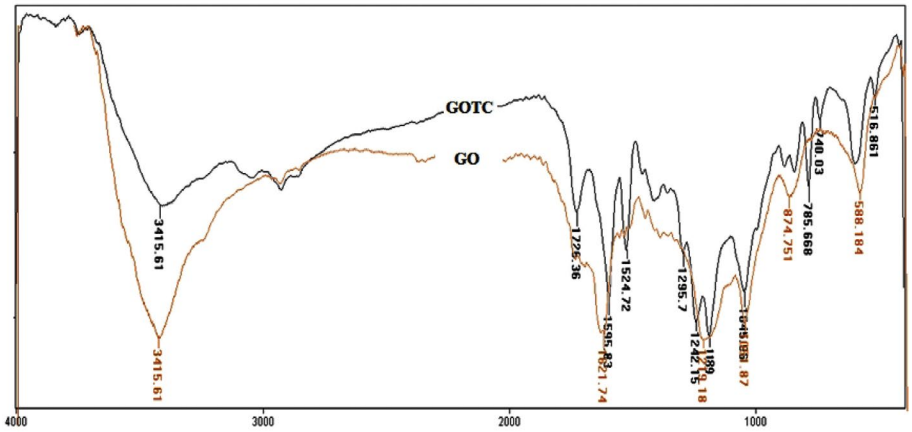


Fig. 1. FT-IR spectra of GO and GOTC.

the C=C bond region, in addition to C=C double bonds of GO at 1595 cm^{-1}, peaks at 1468 and 1525 cm^{-1} are attributed to the aromatic rings of phenyl and terpyridine moieties. Peak at 1413 cm^{-1} is related to the CH_2 bending vibration, and peaks at 1189, 1242 and 1296 cm^{-1} are attributed to C-O and C-N bond stretching vibrations, indicating the covalently linkage of 5 onto GO.

TEM image of an aqueous dispersion of GOTC (Fig. 2a) supported the existence of sheet like material, and revealed that the GOTC nanosheets are highly dispersed in water. Also, SEM image of GO shows single flakes of GO (Fig. 2b), which was shown as randomly aggregated crumpled sheets in the case of GOTC, indicating the modification on the surface of GO (Fig. 2c).

Colorimetric Fe^{2+} Sensing

Free GOTC (0.2 mg ml^{-1}) in water shows a weak absorption band centered at 568 nm. Upon addition of Fe^{2+} to GOTC solution (the final concentration of GOTC and Fe^{2+} are 0.2 mg ml^{-1} and 0.33 μM, respectively), band at 568 nm increased, whereas addition of Fe^{3+} caused lower increase than Fe^{2+} at the band. Addition of Co^{2+} resulted in a week absorption band centered at 516 nm, and in the case of other relevant metal ions, such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Ag^+, Cu^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+} and Cr^{3+} there are no any changes in the absorption spectra (Fig. 3). GOTC showed color changes from plum to dark magenta in the presence of Fe^{2+} and from plum to violet-red and yellow in the presence of Fe^{3+} and Co^{2+}, respectively,

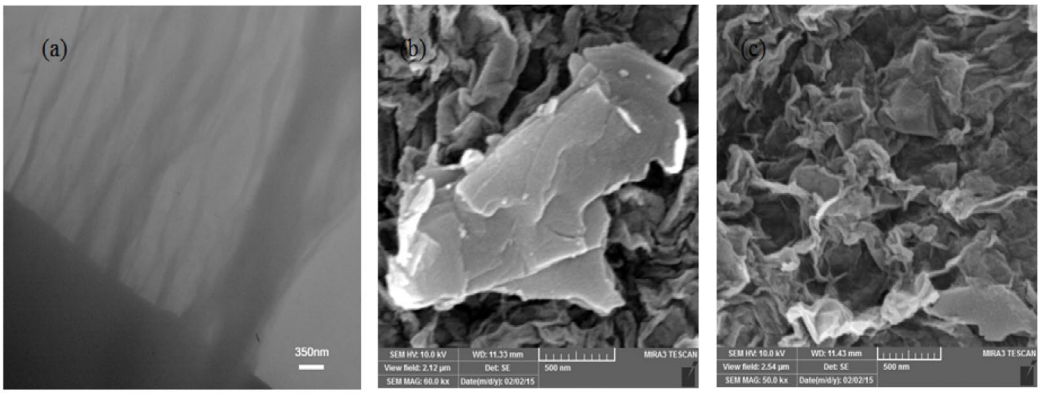


Fig. 2. TEM image of GOTC (a), and SEM images of GO (b) and GOTC (c).

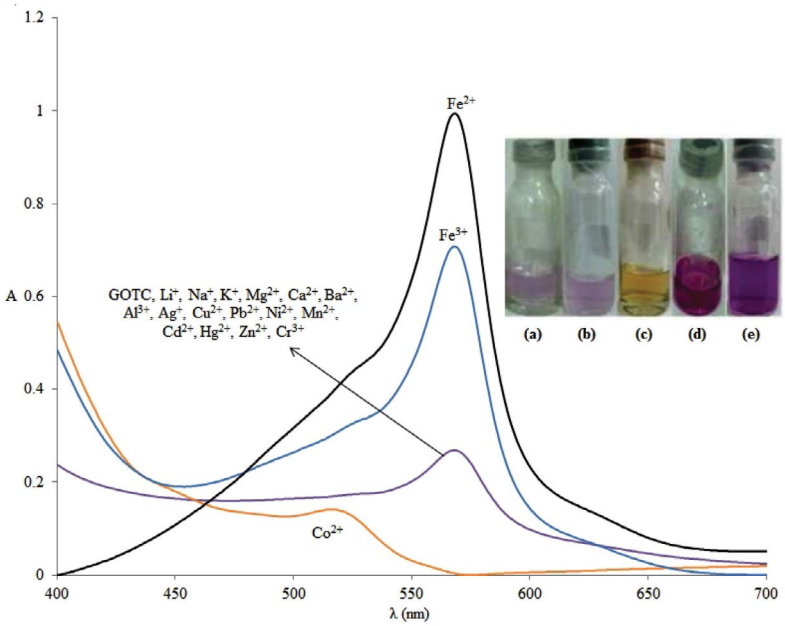


Fig. 3. The color changes of GOTC upon addition of various metal ions: (a) free GOTC (0.2 mg ml^{-1}), (b) after addition of relevant metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Ag^+, Cu^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+} and Cr^{3+}), (c) Co2+, (d) Fe^{3+} and (e) Fe^{2+}.

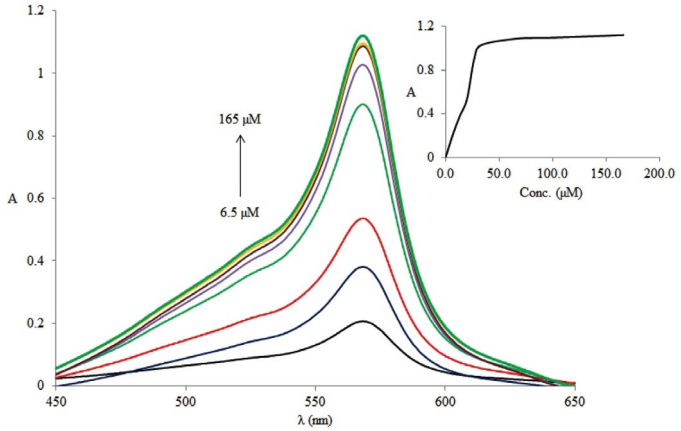


Fig. 4. Titration of GOTC with Fe^{2+}.

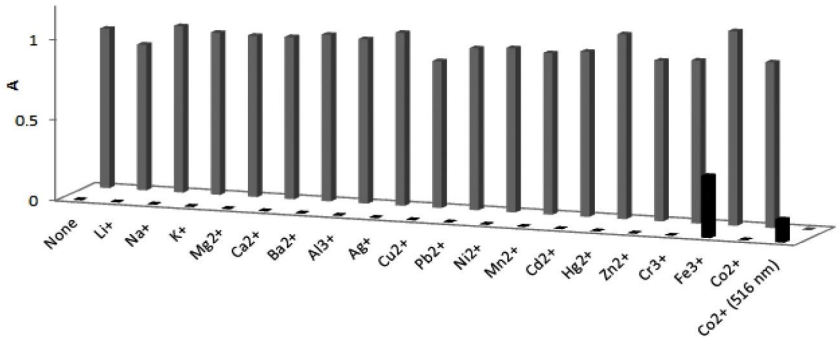


Fig. 5. Competitive metal ion titrations with Fe^{2+}, absorbance is at 568 nm, unless that is mentioned, black bars: absorbance of a solution of GOTC (0.2 mg ml^{-1}) + metal ions (0.33 µM), gray bars: absorbance of a solution of GOTC (0.2 mg ml^{-1}) + metal ions (0.33 µM) + Fe^{2+} (0.33 µM); data in parenthesis are the final concentration in 3 ml solution).

while other metal ions caused no change in color (Fig. 3, inset). Upon titration of GOTC with Fe^{2+}, the absorbance at 568 nm increased sharply (Fig. 4), which may be attributed to the interaction of Fe^{2+} ions with the terpyridyl moiety leading to the metal-to-terpyridine-charge-transfer. Whereas, the increasing of Fe^{3+} and Co^{2+} concentration caused little increase at the corresponding bands at 586 nm and 516 nm, respectively.

In order to investigate the practical utility of GOTC to detect Fe^{2+} ions selectively in the presence of other metal ions, competitive metal ion titrations were carried out by titration of a solution of GOTC and different metal ions with Fe^{2+}. In the case of Co^{2+}, the absorption band at 516 nm disappeared, while absorbance at 568 nm increased as a function of the addition of Fe^{2+}. By addition of Fe^{2+} to a solution of Fe^{3+} and GOTC, a little change was observed at 568 nm at low concentrations of Fe^{2+}, but increased when the concentration of Fe^{2+} reached to the Fe^{3+} ones. In all other cases absorbance at 568 nm increased as a function of the addition of Fe^{2+} (Fig. 5).

Due to the distinct color change of GOTC upon addition of Fe^{2+} solution, and to obtain a naked-eye detection method, the sensing on the test paper was also investigated by immersing a piece of filter paper into a sensor solution, followed by drying under vacuum at 50 °C. By immersing the obtained test paper into the solution of various metals ions, no color changes were observed, except for Fe^{2+} solution, which led to the color change from light pink to magenta. However, in the case of Fe^{3+} solution, the slightly yellowish color was observed (Fig. 6).

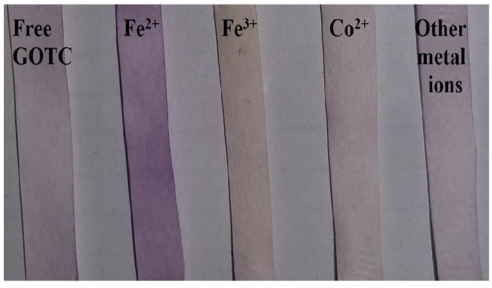


Fig. 6. Paper sensing of Fe^{2+} ions.

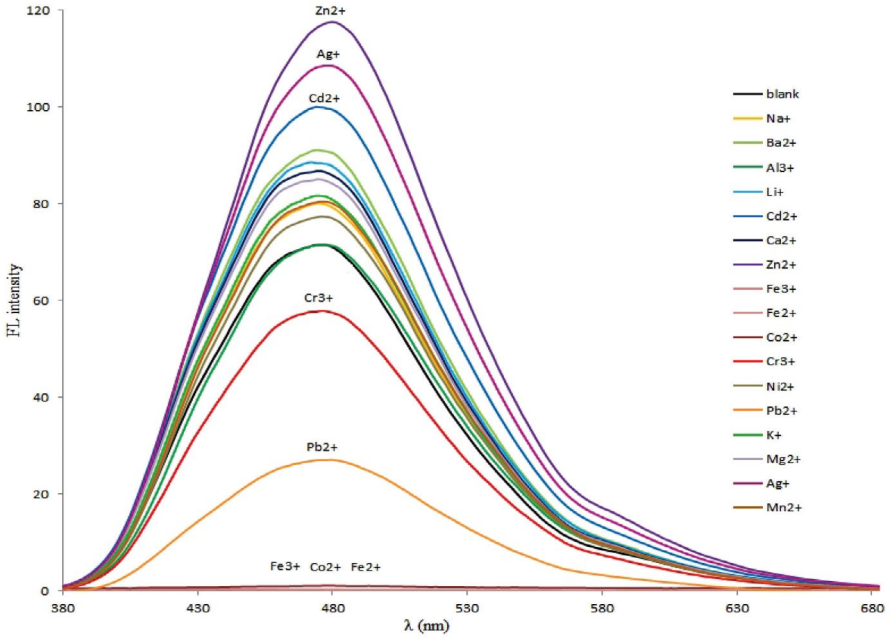


Fig. 7. Fluorescence of GOTC (0.2 mg ml^{-1}) upon addition of various metal ions (0.33 μM).

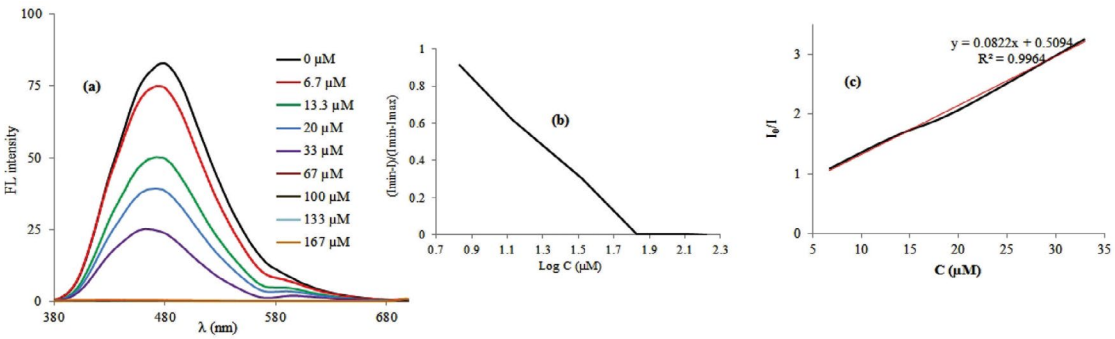


Fig. 8. Fluorescence intensity of GOTC upon titration with Fe^{2+} (a), the normalized intensity $[(I_{min} - I)/(I_{min} - I_{max})]$ plot against logC (μM) of Fe^{2+} (b), and Stern-Volmer plot for GOTC in the presence of Fe^{2+} (c).

Fluorescence Fe^{2+} Sensing

The fluorescence response behavior of GOTC was examined upon treatment with various metal ions in water. Fig. 7 shows that the addition of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Ni^{2+}, Mn^{2+} causes a little fluorescence increase, and the addition of Cd^{2+}, Ag^+ and Zn^{2+} results in a pronounced fluorescence enhancement, whereas addition of Cr^{3+} and Pb^{2+} leads to a decrease in fluorescence of GOTC, and the addition of Fe^{2+}, Fe^{3+} and Co^{2+} causes full quenching of the fluorescence of GOTC. To determine the sensitivity range of GOTC toward Fe^{2+}, the fluorescence properties of GOTC were investigated upon addition of different amounts of Fe^{2+} (Fig. 8a). The normalized intensity $[(I_{min} - I)/(I_{min} - I_{max})]$ was plotted against logC (μM) of Fe^{2+}, which exhibited good linearity in the range of 6.5 × 10^{-6} M-67 × 10^{-6} M (Fig. 8b). The most abundant complex formed within the range of 6.5-33 μM of Fe^{2+}, showed a 1:1 (host/guest) stoichiometry, using the Stern-Volmer plot, as shown in Fig. 8c.

CONCLUSIONS

In summary, a nano-chemical sensor for Fe^{2+} ions was developed based on terpyridine conjugated on GO. Both colorimetric and fluorescence method were investigated, in which the sensor exhibited good linearity in the range of 6.5 × 10^{-6}-33 × 10^{-6} M and 6.5 × 10^{-6} M-67 × 10^{-6} M, respectively. Also, competitive metal ion titrations

were carried out, that exhibited best selectivity for Fe^{2+} ions. The solubility of designed sensor in water is an important advantage, leading to detection of Fe^{2+} ions in aqueous solution.

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