

Iron(III) Selective Fluorescence Probe Based on Perylene Tetracarboxylic Diimide¹

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Abstract—Responses of organic fluorophore, perylenediimide derivative N,N'-di[3-[2-(3-thienyl)ethyl]phenyl]perylene-3,4,9,10-bis-(dicarboxyimide) (**PDII**) was investigated in polymer matrix of polyvinyl chloride (**PVC**) by emission spectrometry. Its response to Fe(III) ions was evaluated in terms of the effect of pH. The properties of time dependent response, reversibility, limit of detection, linear concentration range for the metal ion and repeatability characteristics of the sensing element also have been studied. The offered sensor exhibited remarkable fluorescence intensity quenching at pH 6.0 in the concentration range of 1×10^{-6} to 2.5×10^{-3} M Fe(III) ions. The reproducibility of the sensor membrane was investigated by alternately changing the solution between 1×10^{-4} M Fe(III) in Na_2HPO_4 (4×10^{-2} M) and NaH_2PO_4 buffer (2×10^{-3} M).

Keywords: organic fluorophore, Fe(III) sensor, perylenediimide, thiophene

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As an essential element for life, iron is one of the most important metals that plays an important role in numerous biological processes, typically in the storage and transport of oxygen to tissues. Many enzymatic reactions involving iron are related to redox reactions in numerous cellular functions such as the oxygen transport of hemoglobin and the electron transfer of heme-containing cytochromes [1–3]. If the iron concentration exceeds the normal level in the body, it can induce health problems such as liver and kidney damage; Alzheimer's and Parkinson's diseases are related to the iron accumulation in brain. On the other hand, iron deficiency leads to anemia [4]. Therefore, the development of analytical methods for the sensitive and selective determination of ionic iron, e.g. Fe(III), is highly desirable. Because of its operational simplicity, low cost, feasibility of real time monitoring and high selectivity, fluorescent detection has become a promising strategy used for Fe(III) detection [5]. Various analytical techniques were used for the detection of heavy metals including atomic absorption spectrometry, inductively coupled plasma emission spectrometry, and anodic stripping voltammetry. These methods can offer good detection limits and wide linear ranges, but they are expensive and do not easily apply themselves to miniaturization [6, 7]. Ion-selective sensors offer simple, rapid and reliable tool to

detect heavy metals. Plasticized PVC-membranes are believed to be useful for analytical applications because of their good mechanical properties, homogeneity, simplicity of preparation and optical transparency [8]. Oter et al. used benzofuran derivative *bis*-(7-methoxybenzofuran-2-yl)ketoxime for Fe(III) ions. They investigated fluoroionophores in different solvents and in polymer matrices of PVC and ethyl cellulose and tested corresponding absorption and emission spectrometry methods [9]. Ozturk et al. examined the photophysical and photochemical properties of azlactone derivative 4-(2-furylmethylene)-2-phenyl-5-oxazolone in different solvents and in solid matrix of PVC [10].

Fluorescent probes for sensing and monitoring chemical analytes are a topical and attractive field for chemical, biological and environmental science due to their high sensitivity and simplicity. To make a useful probe, a compound must contain a "receptor," which can selectively interact with the analytes, and a "signaling site," normally a strongly emitting fluorophore. A communication mechanism between the binding and signaling site must exist. Among the numerous mechanisms which induce signal changes upon the receipt ion of analytes, photoinduced receptor to fluorophore electron transfer has been widely used in the design of new sensors [11].

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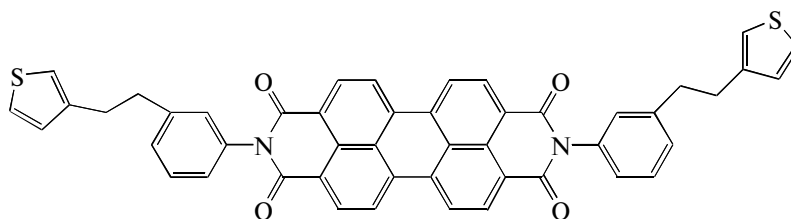
Perylenediimide (PDI) derivatives are highly versatile molecules, which attract a great interest owing to their applications such as organic solar cells, organic light emitting diodes, organic field effect transistors. PDIs are characterized by strong absorption in the visible region of spectrum and strong fluorescence. The fluorescence quantum yield is near 1. Also the PDI dyes have excellent photostability, thermal stability and chemical inertness [12–18]. Liwei et al reported a new PDI ligand functionalized with a dipicolylethylenediamine moiety which was synthesized and firstly used as a colorimetric and fluorometric dual-channel sensor to specifically detect Cu^{2+} over a wide range of other cations [19]. Also Zhao et al. reported PDI has excellent selectivity for Zn^{2+} ions. PDI is also used as metal ions receptor [20].

In this paper, we report a PDI derivative based probe which acts as an Fe(III) selective fluorescent sensor. In this probe, PDI unit is connected to

thiophene group. Also we investigated spectral characteristics.

EXPERIMENTAL

Reagents and apparatus. The polymer membrane components, PVC of high molecular weight and the plasticizer, *bis*-(2-ethylhexyl)phthalate, were obtained from Fluka. Absolute ethanol, tetrahydrofuran (THF), dichloromethane (DCM), hydrochloric acid and chloroform were of analytical grade. Solvents for the spectroscopic studies were used without further purification. However, buffer components and metal salts were of spectrophotometric grade and used as received from Merck and Fluka. All solutions were prepared with glass-distilled water. We investigated sensor properties of perylenediimide derivative based on thiophene (PDI1) synthesized earlier [21]:



Molecular structure of PDI1

N,N'-Di-[3-[2-(3-thienyl)ethyl]phenyl]perylene-3,4,9,10-bis(dicarboximide)

Absorption spectra were recorded using a Perkin-Elmer UV-1601 UV-Vis spectrophotometer. Fluorescence emission and excitation spectra were measured using Perkin Elmer spectrourometer.

Polymer film preparation. The optode membranes were prepared to contain 120 mg of PVC, 240 mg of plasticizer, 7.2 mg of PDI dye (2 mmol/kg polymer), equivalent amount (1 : 2) of potassium *tetrakis*-(4-chlorophenyl)borate and 1.5 mL of THF. The prepared cocktails contained 33% PVC and 66% plasticizer by weight which is quite common [22, 23]. The resulting cocktails were spread onto a polyester support (Mylar TM type) located in a THF-saturated desiccator. Absorption and fluorescence emission spectra of PVC-membranes were recorded in quartz cells filled with Fe(III) solution. The polymer films were placed in diagonal position in the quartz cell. The advantage of this kind of placement was to improve the reproducibility of measurements.

Synthesis of PDI1. Triphenylphosphine dibromide (20.05 g, 48.6 mmol) was added to solution of 2-(3-thienyl)ethanol (4.60 g, 35.9 mmol) in dry acetonitrile (75 mL), with the temperature being kept below 8°C. After stirring at room temperature for 20 h, the reaction mixture was filtered and concentrated. The resi-

due was purified by column chromatography (silica gel, *n*-hexane) yielding a colorless oil (4.64 g, 68%). $^1\text{H NMR}$ (CDCl_3): ($\text{C}_6\text{H}_7\text{SBr}$) δ 7.27 (m, 1H, Th-H), 7.01 (m, 2H, Th-H), 3.55 (t, 2H, $-\text{CH}_2$), 3.18 (t, 2H, $-\text{CH}_2$) ppm. A similar synthetic procedure given in the literature was followed for the synthesis of 3-(2-bromoethyl)thiophene [10]. A 100 mL three-necked round-bottom flask equipped with a nitrogen inlet–outlet was charged with 1 M Na_2CO_3 (10 mL) and THF (15 mL). The mixture of the solvents had previously been bubbled with nitrogen over a period of 1 h and refluxed under nitrogen for 4 h. A 20 mL three-necked round-bottom flask was charged under an inert atmosphere with 0.62 mmol of 3-(2-bromoethyl)thiophene (0.1191 g), 3 mmol (0.579 g) of 3-aminophenylboronic acid hemisulfate, and 0.02 mmol (0.0276 g) of $\text{Pd}(\text{PPh}_3)_4$. The solvent mixture (12 mL) was introduced. The mixture was refluxed under nitrogen for 5 days. The mixture was cooled till room temperature and then extracted with chloroform. The organic phase was dried over MgSO_4 and filtered followed by evaporating the solvent. Purification was performed by passing the product through a silica gel column using chloroform as eluent (0.127 g, 23%). $^1\text{H NMR}$ (CDCl_3 ; δ , ppm): 7.60–6.95 (m, 4H,

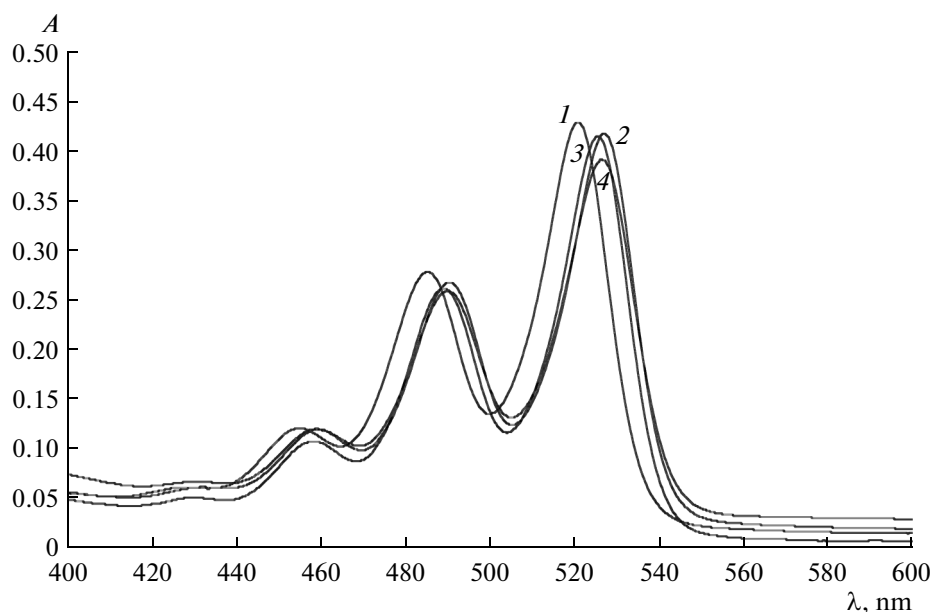


Fig. 1. Absorption spectra of the 1×10^{-6} M PDI1 dye in: (1) THF, (2) toluen, (3) DCM, (4) chloroform.

Ar-H), 6.7 (m, 3H, Th-H), 3.5 (t, 2H, $-\text{CH}_2$), 2.9 (t, 2H, $-\text{CH}_2$), 2.8 (s, 2H, $-\text{NH}_2$), $\text{C}_{12}\text{H}_{13}\text{NS}$.

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (0.49 mmol, 192 mg) 3-[2-(3-thienyl)ethyl]aniline (0.98 mmol, 200 mg) and imidazole (3.5 g) were heat-

ed at 140°C for 4.5 h under Ar atmosphere. Then 2 M HCl (200 mL) was added to the reaction solution and the resulting mixture was stirred for 1 h at room temperature, then extracted with chloroform (600 mL). The organic phase was evaporated under vacuum and the crude product was purified by column chromatography (silica gel; CH_2Cl_2 - CH_3OH , 12 : 1). Yield: 60%, FT-IR (KBr cm^{-1}): 2928, 2841, 1702 and 1649 (imide group), 1587 (aromatic C=C), 1404, 1346 (C-N), 1250, 1173. ^1H NMR (CDCl_3 ; δ , ppm): 8.65 (dd, 8H, perylene-H), 7.8-7.42 (m, 8H, Ar-H), 7.3 (m, 6H, Th-H), 1.6 (t, 4H, $-\text{CH}_2$), 1.3 (t, 4H, $-\text{CH}_2$). $\text{C}_{48}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_2$.

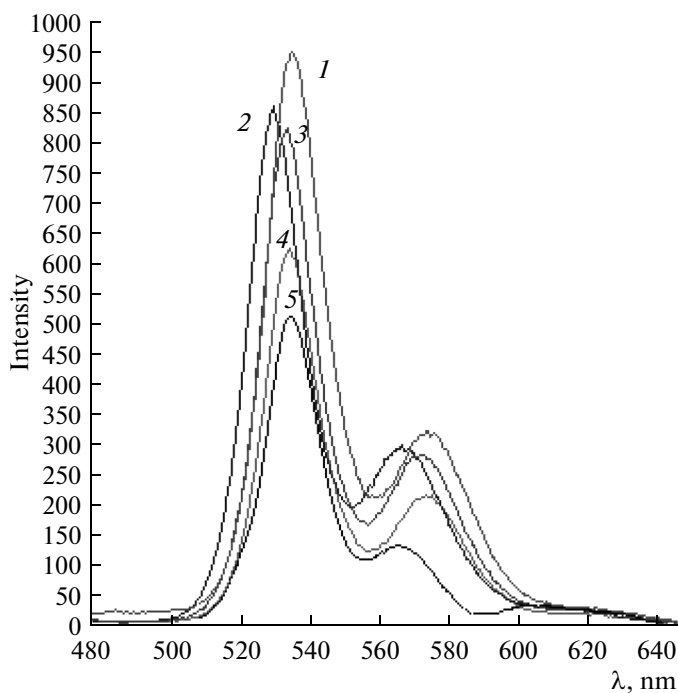


Fig. 2. Emission spectra of the 1×10^{-6} M PDI1 dye in: (1) (480, 526 nm), (2) toluen (490, 536 nm), (3) DCM (488, 531 nm), (4) chloroform (485, 531 nm), (5) PVC (488, 531 nm).

RESULTS AND DISCUSSION

UV-visible absorption and fluorescence emission spectroscopy studies. In order to perform the spectral characterization of the PDI1 dye, the absorption, excitation and emission spectra were recorded in THF, chloroform, DCM and toluene. PDI1 was excited at 480, 485, 488 and 490 nm, respectively, and the emission spectra were recorded. In order to obtain the excitation spectra, PDI1 was excited at 526, 531 and 536 nm, respectively. The UV-visible absorption of PDI1 (1×10^{-5} M) is shown Fig. 1; it has three absorption bands in the UV-visible region, which result from π - π^* -transition. Emission spectra of the dye in the solvents that have different polarity such as toluene (polarity index: 2.4), dichloromethane (polarity index: 3.1), chloroform (polarity index: 4.1), tetrahydrofuran (polarity index: 4.0) are shown in Fig. 2. It is understood that the higher the polarity of the solvents, the shorter the wavelengths of the emission maxima of

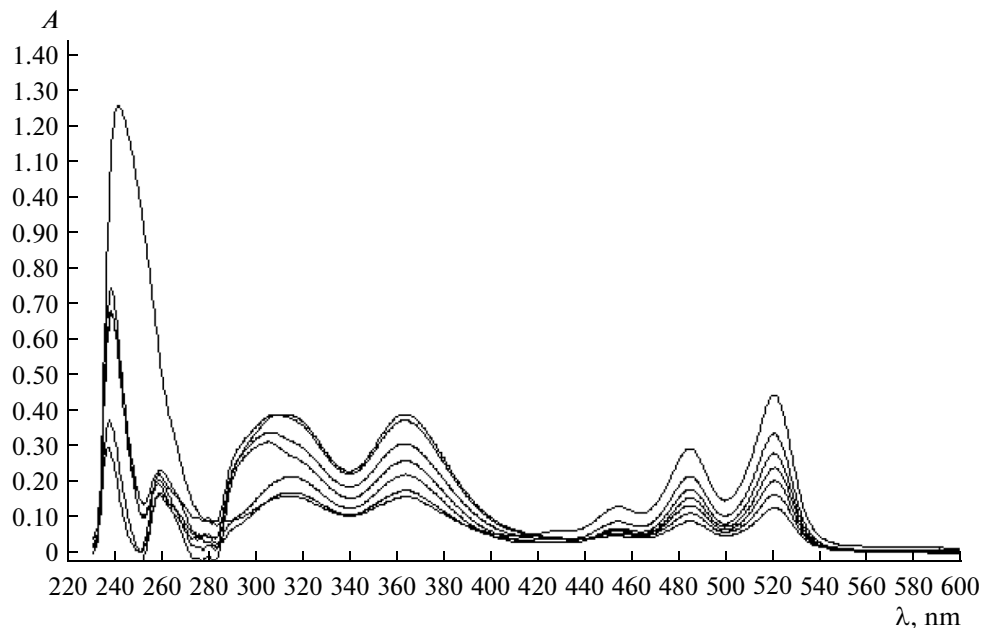


Fig. 3. Absorption spectra using Job method of PDI1 and Fe(III) between 280–340 nm.

the dye. It is seen that solute molecules have an excited state less polar than the ground state. Increasing solvent polarity will stabilize the excited state less than the ground state [21]. Therefore, a blue shift is observed for the dye molecules in toluene medium.

The absorption and fluorescence spectra of PDI1 show consistent mirror-image behavior. Generally perylene dyes display an intense absorption band in the visible spectrum located between 400–600 nm corresponding to a $\pi-\pi^*$ singlet transition. PDI1 dye shows characteristic absorption peaks for the perylenediimide at 458, 490, and a greater shoulder peak at 526 nm, which are denoted to their (0, 2), (0, 1), and (0, 0) transitions, respectively. Also, the emission spectra of the PDI dyes resemble each other. Fe(III) ions have absorption at 240–400 nm, which do not interfere with the investigation of PDI1. A gradual decrease in the absorption of PDI1 is obtained with the addition of Fe(III) ion at 490 and 520 nm. Blue-shift was observed from 316 to 308 nm (Fig. 3).

Coordination compound between Fe(III) ion and PDI1 is formed with the electronic pair transit from the oxygen and nitrogen atoms to the 3d orbital of Fe(III) ion. The stoichiometry of the complex formed by PDI1 and Fe(III) was calculated by Job method. A Job plot and fluorescence experiments were performed at room temperature. The stoichiometry of the complex is 1 : 2. In fluorescence studies, it is important to understand what kind of interaction is taking place between PDI1 and the Fe(III) ion. Excitation and emission spectra of the films were recorded for spectral characterization of the PVC doped PDI1. PDI1 was

excited at 488 nm and its emission spectrum was observed at 531 nm in PVC, as shown in Fig. 4. A gradual decrease in the intensity of PDI1 is obtained with the addition of Fe(III) ion.

Photostability test results. The short-term photostability test of PDI1 dye in CHCl_3 , THF, DCM and PVC was carried out in the mode of “time based measurements.” The PDI1 dye was excited at 480 nm in THF, at 490 nm in toluene, at 488 nm in DCM, at 485 nm in chloroform, at 488 nm in PVC, and the data were acquired at maximum emission wavelength of 526 nm in THF, 536 nm in toluene, 531 nm in DCM, 531 nm in chloroform, 531 nm in PVC during 1 h of monitoring. The acquired data of PDI1 is shown in Fig. 5 which reveals the excellent short time photostability in all of the employed solvents and PVC-matrix.

Effect of pH on sensor response. In order to determine the useful pH range over which the dye doped membrane can be used without any pH interference, the potential of the dye doped membrane was determined over a pH range of 4–10; pH was adjusted by dropwise addition of 0.1 M $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}^-$ (pH 4–6), 0.1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ (pH 7–8) and 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_3$ (pH 9–10). The intensity of the dye doped membrane was measured at each pH value. Optimum pH values were investigated at 1×10^{-3} M Fe(III) ions. It is clear from Fig. 6 that the intensity had the maximum value at pH 6 which can be taken as the pH optimum of the proposed sensor. At lower pH values the fluorescence intensity decreased, which was attributed to the proton binding by amide nitrogen. At

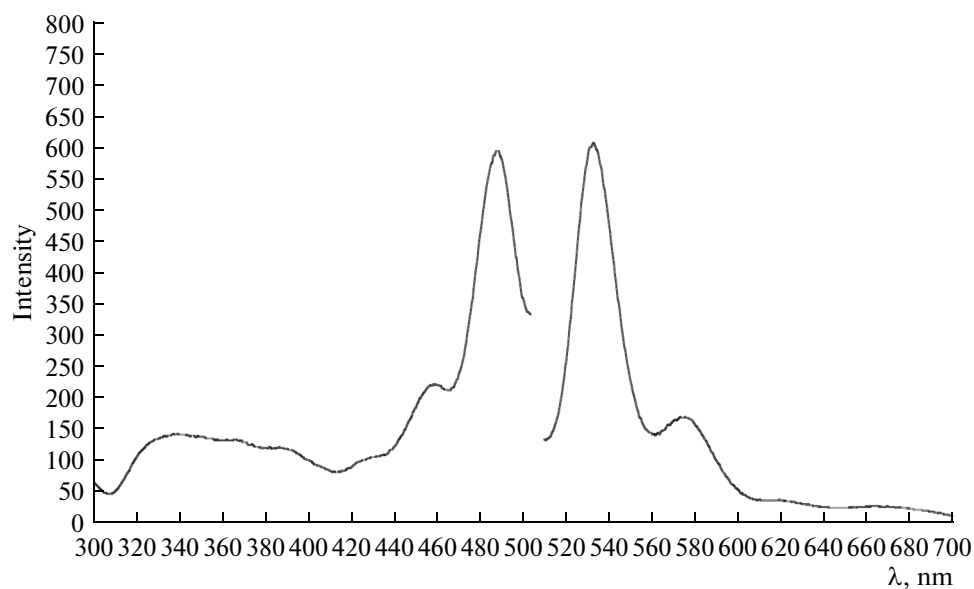


Fig. 4. Emission and excitation spectra of the PDI1 dye in PVC (488, 531 nm).

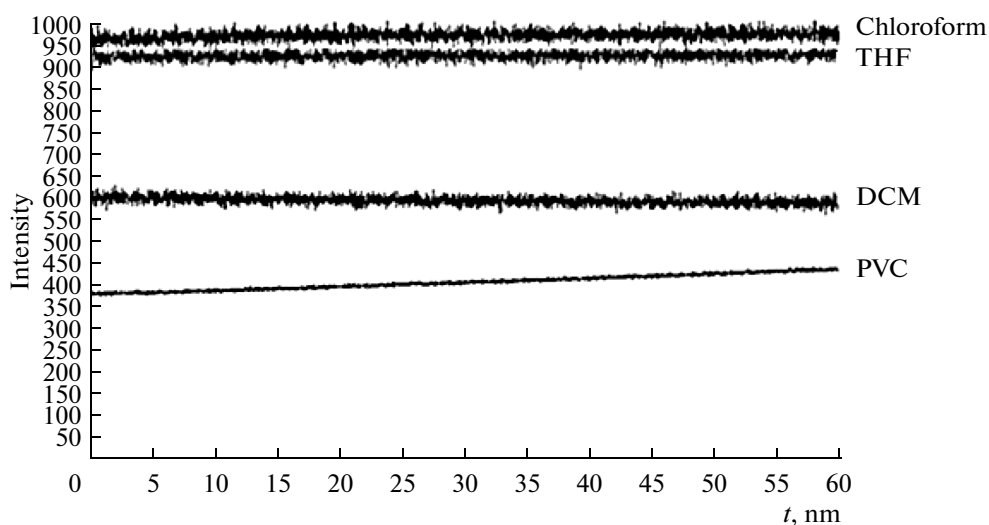


Fig. 5. Short-time photostability test result of 1×10^{-6} M PDI1 in all studied solvents (CHCl_3 , THF, DCM) and PVC after exposure to xenon arc lamp for 1 h of monitoring.

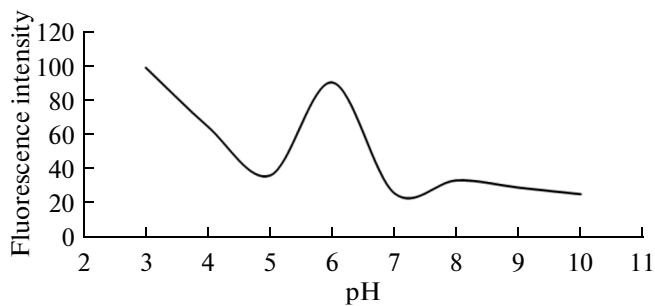


Fig. 6. Effect of pH on the response of the Fe(III) sensor at 1×10^{-3} M Fe(III).

higher pH values ($\text{pH} > 6$), the polymeric film could slightly swelling; therefore, the fluorescence intensity decreased.

Sensor response to Fe(III). The selectivity behavior is one of the most important characteristics of ion-selective sensors, determining whether a reliable measurement in the target sample is possible. To investigate the selectivity of the sensor to iron, its potential response was assessed in the presence of some cations and anions. The sensor was highly selective for iron compared with many cations such as Li^+ , Cu^{2+} , Hg^{2+} , Ca^{2+} , K^+ , Pb^{2+} , As^{3+} , Cr^{3+} , Mn^{2+} , Bi^{3+} , Ba^{2+} , Sn^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Ag^+ , Ni^{2+} , Na^+ as given Fig. 7a.

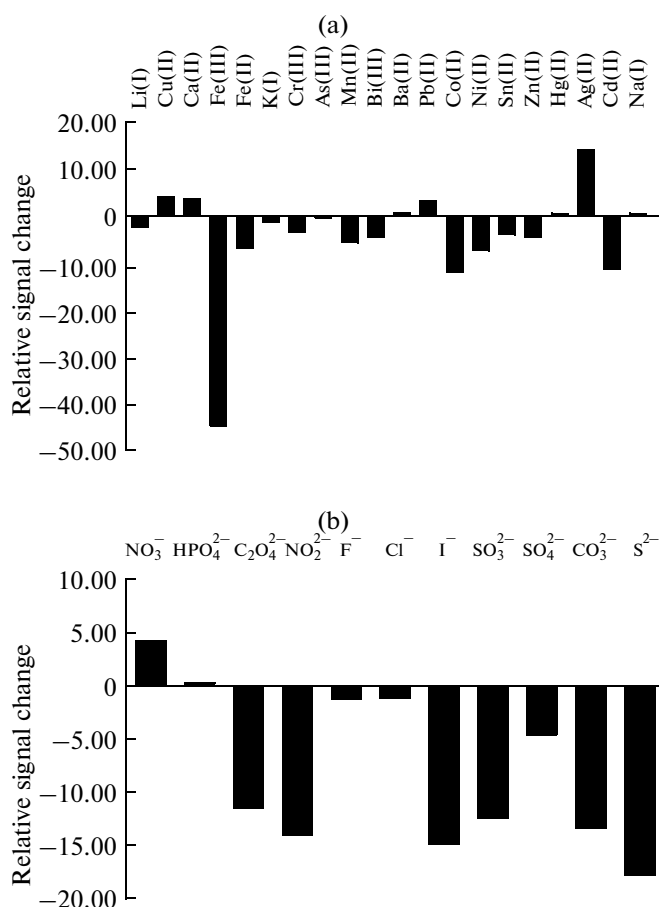


Fig. 7. Response of cations (a) and anions (b), relative signal change $-(I - I_0/I_0) \times 100$.

The effects of some anions such as NO₃⁻, HPO₄²⁻, C₂O₄²⁻, NO₂⁻, F⁻, Cl⁻, I⁻, SO₃²⁻, SO₄²⁻, CO₃²⁻, S²⁻ were also examined (Fig. 7b). Maximum relative signal change was observed with Fe(III). The other cations and anions do not interact with the dye. The selective and strong response of PDI1 dye to Fe(III) can also be attributed to the strong quencher characteristic of Fe(III). The fluorescence was quenched to a greater extent by Fe(III) than by Fe(II) and other possible interferent cations.

The dye-doped PVC membrane exhibited remarkable fluorescence intensity quenching upon exposure to Fe(III) ions at pH 6.0. Figure 8 shows the fluorescence spectra of the PDI1 membrane exposed to a solution containing different concentrations of Fe(III), which are recorded at 488 nm. The fluorescence intensities of the sensor membrane decrease with increasing concentration of Fe(III), which constitutes the basis for the determination of Fe(III) with the fluorescent sensor proposed in this paper. Figure 8 shows the absorption spectral changes of PDI1 upon addition of different amounts of Fe(III) at room temperature. Upon exposure to Fe(III) concentrations from 1.0×10^{-6} to 2.5×10^{-3} M, the membrane exhibits a 45% relative decrease in fluorescence intensity. The PDI1 dye is supposed to form a complex with Fe(III) and statically quench in ground state.

The data on Fig. 9 presented are mean of five measurements all with different fresh fiber tips. In the concentration range from 1×10^{-6} to 2.5×10^{-3} M a good linear correlation was obtained with R^2 value of 0.97 for Fe(III). The limit of detection for Fe(III) was defined as the concentration at which the signal is equal to the blank

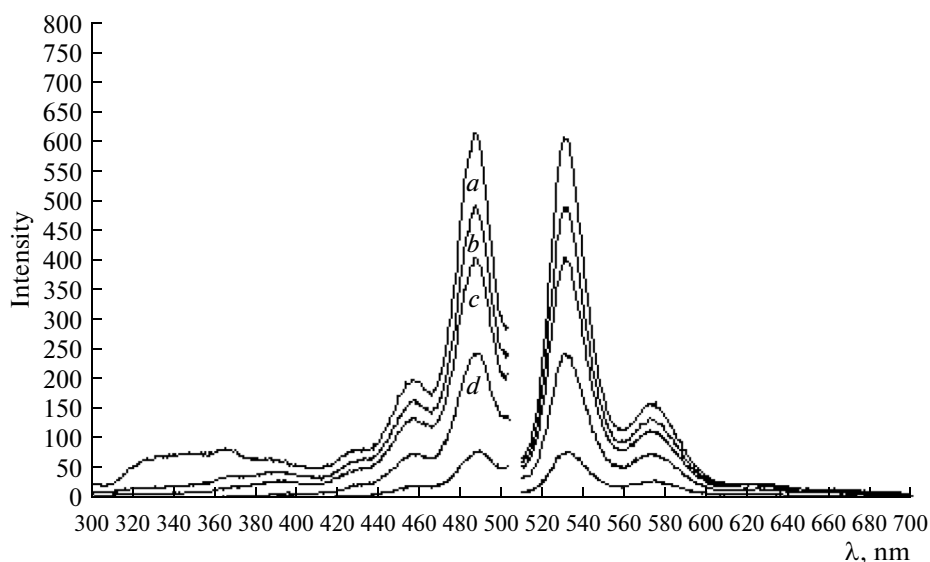


Fig. 8. Emission and excitation spectra based response of the sensor membrane after exposure to certain concentrations of Fe(III), M: (a) 1×10^{-6} , (b) 5×10^{-4} , (c) 1×10^{-3} , (d) 2.5×10^{-3} .

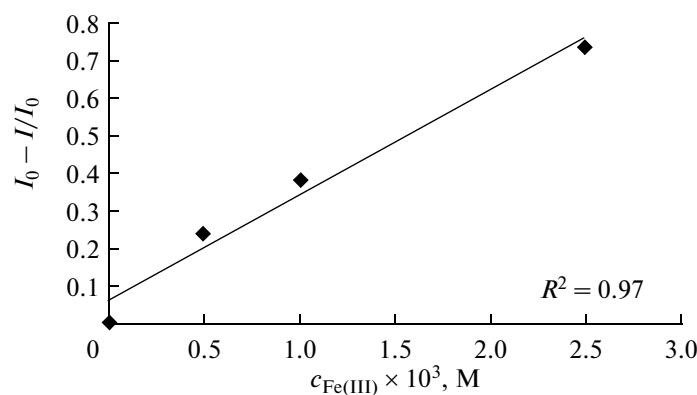


Fig. 9. Calibration plot of Fe(III)-selective sensor in the concentration range of 1.0×10^{-6} to 2.5×10^{-3} M in acetic acid/acetate buffer solution at pH 6.0.

signal plus 3σ and found to be 5.0×10^{-7} M. At constant pH (6.0) the response is reproducible.

Reproducibility studies. The sensor was fully reversible and can be regenerated with $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ solution with 100% efficiency as shown in Fig. 10. The membrane should be washed first with 0.01 M HCl solution and then with blank buffer solution ($\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$) after each measurement. The membrane can be easily regenerated by washing once with 0.01 M HCl solution followed by blank buffer solution at the concentration level 6.0×10^{-6} to 6.0×10^{-4} M Fe. Between the first and third cycles, the reproducibility of the upper signal level was quite good. One sensor film could be used for about 30 repetitive cycles and then kept in a THF-saturated desiccator in the dark. The sensor film was found to be stable for 4 months.

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We successfully investigated the effect of ferric ions on the emission intensity of the fluorophore PDII. We

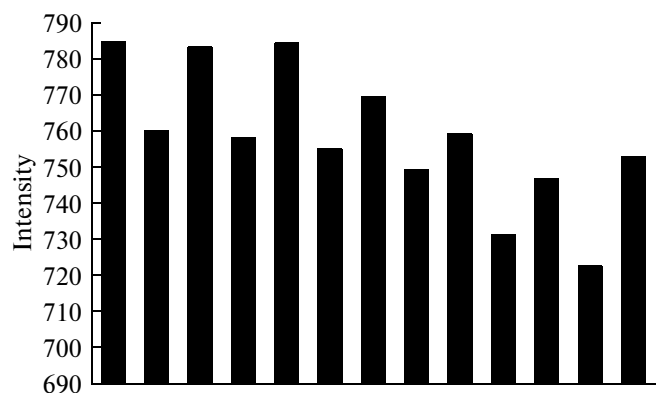


Fig. 10. Successive responses of the PDII membrane to 1.0×10^{-4} M Fe(III) and buffer $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ at pH 6.0.

demonstrated that fluorescent perylenediimide derivative (PDII) containing a thiophene group can be used for reversible Fe(III) sensing in plasticized PVC-matrix. The sensor exhibited a decrease in emission intensity and absorbance in the presence of Fe(III) by the quenching effect. The dynamic working range was 1×10^{-6} to 2.5×10^{-3} M Fe(III). The sensor had a reproducible response and provided an inexpensive and quick method for the detection of Fe(III).

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