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A novel sensing membrane for the determination of ferric ion in aqueous solutions

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Abstract

A new fluorescent sensing membrane in which naphthalimide derivative containing two long hydrophobic hydrocarbon chains, amphiphilic molecule castor oil polyoxyethylene ether and PVC were respectively used as fluorescence indicator, plasticizer and matrix for specific recognition of Fe$^{3+}$ was prepared based on physical entrapment method. The results show the fluorescence of the sensing membrane is selectively quenched by the Fe$^{3+}$ ions over other common metal ions in aqueous solutions. A good linear response range of the sensing membrane is from $5.0 \times 10^{-5}$ to $1.5 \times 10^{-3}$ M ($R^2 = 0.9906$), with a detection limit of $4.0 \times 10^{-7}$ M. The sensing membrane shows a good reversibility, fast response of less than 20 s and satisfactory stability with a relative standard deviation of $\pm 1.5\%$. Moreover, it was successfully applied in the detection of Fe$^{3+}$ in tap water with recoveries of 97.6 - 101.2%.

Key words: Sensing membrane, Naphthalimide derivative, Castor oil polyoxyethylene ether, Fluorescence, Fe$^{3+}$

Introduction

As one of the most abundant transition metal, iron is widely distributed in the nature.$^{1,2}$ And it plays an essential role in many physiological processes such as oxygen transport,$^3$ electron transfer,$^4$ enzymatic catalysis$^5$ and DNA synthesis.$^6$ Iron deficiency or overloading
can cause a variety of diseases like anemia, liver damages and heart disease.\textsuperscript{7-9} Thus it is of great importance for the environment and human health to develop a simple, reliable and selective detection method for Fe\textsuperscript{3+}. There are some successful analysis methods for the detection of Fe\textsuperscript{3+} including atomic absorption spectrometry,\textsuperscript{10,11} inductively coupled plasma mass spectrometry,\textsuperscript{12} electrochemical methods,\textsuperscript{13} colorimetry\textsuperscript{14} and chromatographic analysis\textsuperscript{15} and so on. However, to some extent, these methods are relative to the expensive instrumentation, sophisticated pretreatment procedures, and they are inappropriate for on-line monitoring.\textsuperscript{16,17}

Owing to the advantages of low cost, easy operation and real-time monitoring, fluorescent optical sensors was developed as a tool for the determination of Fe\textsuperscript{3+},\textsuperscript{18} in which sensing membranes plays a decisive role for its detection performance. Polyvinyl chloride (PVC) is the most widely used polymer matrix in preparing fluorescent sensing membrane for its low cost, good mechanical performance and easy plasticizing.\textsuperscript{19,20} Plasticizer such as phthalate is usually added into PVC matrix in order to improve the flexibility of the sensing membrane. However, the conduction of the strong polar hydrophilic substance for this kind of sensing membrane is unfavorable for both PVC and phthalate are hydrophobic substance.\textsuperscript{21} In addition, the immobilization of the fluorescent indicator is a crucial step, which vastly affects the performance of the sensing membrane with respect to stability, response time, and sensitivity.\textsuperscript{22,23} Covalent immobilization of the fluorescent indicator could inhibit the indicator leaching and then prolong the lifetime. However, the preparation process is relative sophisticated.\textsuperscript{24} Physical entrapment is a simple operation and low cost method, but the leaking of indicator from the sensing membrane is still a problem for the losses of indicator
results in the shortage of the using life of the membrane. Developing a fluorescence sensing membrane with good stability, fast response and satisfactory reversibility by physical entrapment is still a challenge.

Hence, we designed a novel fluorescence sensing membrane (SM) in which PVC, naphthalimide derivative containing long hydrocarbon chains (D6) and castor oil polyoxyethylene ether (EL-60) were used as matrix, fluorescence indicator and plasticizer, respectively. For D6 with two long hydrophobic hydrocarbon chains and relatively big molecular weight, in some extent its properties are compatible with PVC, and then it could result in the migrations of D6 from SM to the aqueous solution slow down, so the leaking of D6 may be effectively restrained. EL-60 as an amphiphilic molecule could improve the hydrophility as well as the flexibility of SM, thus Fe$^{3+}$ could fast penetrate into SM and shorten the response time. The results show that SM can recognize Fe$^{3+}$ in aqueous solutions based on the fluorescence quenching, and it exhibits a high selectivity for Fe$^{3+}$ over a series of common metal ions. Meanwhile, the recognition to Fe$^{3+}$ is barely influenced by other coexisting metal ions. Further, SM shows a good reversibility, fast response of less than 20 s, satisfactory stability with a relative standard deviation (RSD) of ± 1.5% and a low detection limit of 4.0 × 10^{-7} M. Moreover, it is successfully used for the determination of Fe$^{3+}$ in tap water solution.

**Experimental**

**Materials**

Polyvinyl chloride (PVC) was purchased from Mudanjiang HuaQing Corp, China. Castor oil polyoxyethylene ether (EL-60) was obtained from Zhejiang Real Madrid Corp,
China. 4-bromine-1,8-naphthalene anhydride was purchased from Anshan Huifeng Chemical Co., Ltd, China. Dibutyl phthalate (DBP), other synthetic raw materials and solvents are commercially available chemicals. The stock solutions (0.050 M) of Na$^+$, K$^+$, Al$^{3+}$, Cu$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Ca$^{2+}$, Cr$^{3+}$, Mg$^{2+}$, Fe$^{3+}$ and Ag$^+$ were prepared by nitrate compounds. A stock solution of 0.10 M HAc-NaAc buffer solution was used. The pH value was adjusted by HCl or NaOH solutions.

**Apparatus**

Mass spectra were recorded on a HP 1100 API-ES LC/MS mass spectrometer (HP Co., USA). IR spectra were conducted on an Avtar-370 fourier transform infrared spectrometer (USA Nicolet Co., KBr pellets). NMR was performed on a Varian INOVA 400 (400 MHz) nuclear magnetic resonance instrument (USA Varian Co., TMS as an internal standard). Elemental analysis was examined by Elementar Vario EL III elemental analyzer (Germany). Melting point was conducted using X-6 microscopic melting point apparatus (Teck instrument Co., Ltd, Beijing). BS-210s one over ten thousand electronic balance (Sartorius, Germany) was used. All pH measurements were made by a PB-20 standard pH meter (Sartorius, Germany). The thickness of the membrane was measured by the Elcometer 456 Coating Thickness Gauge (Shanghai, China). Ultra pure water through all experiments was made by Milli-Q (Billerica, MA, USA) purification system. A set of assembly fluorescence detection device was fabricated using WGD-3 grating spectrometer (Tianjin port east technology development co., Ltd., China) connected with Silica fiber ($\Phi$ 35 $\times$ 1000 mm, Beijing glass institute, China), an 8 W light source at 365 nm (WFH-204B ultraviolet lamp, Shanghai Jingke industrial Co., Ltd, China) and computer as shown in Figure S1(see ESI†). The
fluorescence spectra of the membrane were obtained by above fluorescence detection device and the emission wavelength was 490 nm.

**Synthesis of fluorescent indicator**

**Scheme 1**

Reference to the literature,\textsuperscript{26} fluorescent indicator (D6) was synthesized as shown in Scheme 1. 4-bromine-1,8-naphthalene anhydride (16.6 g, 60 mmol) and lauryl amine (11.1 g, 60 mmol) in 200 mL of methylbenzene were stirred and refluxed for 16 h. After removing the solvent by reduced pressure evaporation, the black solid was obtained. The solid was purified by silica gel column chromatography separation with dichloromethane as the eluent to afford light tawny powder. The power was recrystallized with alcohol to afford white crystal. Yield: 21.5 g (81%), mp: 75.8-76.2 °C.

\textit{N}-dodecyl-4-bromine-1,8-naphthalimide (4.44 g, 10 mmol) and piperazine (2.15 g, 25 mmol) in 50 mL of glycol monomethyl ether were refluxed under nitrogen atmosphere for 10 h. After removing the solvent, the mixture was dissolved using CH$_3$OH/CHCl$_3$ (1:5, v/v) and purified by silica gel column chromatography separation to afford yellow solid (M3).

**M3:** Yield: 3.16 g (70%), mp: 79.9-80.3 °C. $^1$H-NMR (CDCl$_3$) $\delta$ (*10$^{-6}$): 8.57 (d, $J = 7.8$ Hz, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.40 (d, $J = 8.4$ Hz, 1H), 7.68 (t, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 4.16 (t, $J = 7.4$ Hz, 2H), 3.27 (s, 4H), 3.25 (s, 4H), 2.7 (br, 1H), 1.72 (br, 2H), 1.27-1.43 (m, 18H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$) $\delta$ (*10$^{-6}$): 164.46, 163.99, 156.23, 132.53, 131.08, 120.17, 130.03, 126.39, 125.72, 123.56, 117.13, 115.12, 54.51, 46.41,
40.58, 32.14, 29.84, 29.64, 29.55, 28.45, 27.43, 22.90, 14.31. HRMS Calcd for C_{28}H_{40}N_{3}O_{2} ([M+H]^+) 450.3115, Found 450.3129. IR (cm\(^{-1}\)): 3131.99, 2917.14, 2847.67, 1688.47, 1649.43, 1587.60, 1386.91, 1349.49, 1234.92, 1071.42, 780.03, 758.11, 720.90, 669.11.

M3 (225 mg, 0.50 mmol), N,N-dichloroacetyl-o-phenylenediamine (52 mg, 0.20 mmol) and 0.50 mL DIEA in 25 mL of acetonitrile were refluxed under nitrogen atmosphere for 10 h. After removing the solvent, the mixture was dissolved using CH\(_3\)OH/CHCl\(_3\) and purified by silica gel column chromatography separation to afford yellow solid (D6). The structure of D6 was characterized by \(^1\)H-NMR and \(^{13}\)C-NMR in Figure S2 and Figure S3 (see ESI†).

D6: Yield: 170 mg (78%), mp: 146.5-147.8 °C. \(^1\)H NMR (CDCl\(_3\), 400 M, 60 °C), \(\delta (\times10^{-6})\): 0.87 (t, 6H, \(J = 6.8 \) Hz), 1.24-1.42 (br, 36H), 1.72 (m, 4H, \(J = 7.2 \) Hz), 2.99 (br, 8H), 3.36 (br, 4H), 3.39 (s, 8H), 4.16 (t, 4H, \(J = 6.6 \) Hz), 7.25-7.27 (m, 4H), 7.56 (dd, \(J = 4.0 \) Hz, \(J = 1.2 \) Hz, 2H), 7.70 (dd, \(J = 7.6 \) Hz, \(J = 8.4 \) Hz, 2H), 8.39 (d, \(J = 8.0 \) Hz, 2H), 8.53 (d, \(J = 8.0 \) Hz, 2H), 8.59 (d, \(J = 8.0 \) Hz, 2H), 9.40 (br, 2H, -CONHar). \(^{13}\)C-NMR \(\delta (\times10^{-6})\): 14.41, 22.94, 27.42, 28.43, 29.59, 29.65, 29.87, 32.16, 40.63, 53.17, 54.00, 62.17, 115.25, 117.49, 123.52, 125.22, 126.03, 126.28, 126.63, 129.95, 130.09, 130.16, 131.26, 132.44, 155.34, 163.97, 164.37, 168.88. API-ES-MS (positive) \(m/z\): 1039.6 ([M+H]\(^+\)), 1061.6 ([M+Na]\(^+\)). IR (cm\(^{-1}\)): 3432.7, 2923.6, 2852.2, 1697.0, 1654.6, 1591.0, 1390.4, 1359.6, 1236.2, 783.0, 759.8. C\(_{66}\)H\(_{86}\)N\(_8\)O\(_6\): Calcd. C 72.90, H 7.97, N 10.30; Found. C 72.66, H 8.13, N 10.09.

**Preparation of SM**

SM was prepared according to the following procedure. 32 mg of PVC, appropriate amounts of plasticizers (EL-60 and DBP), additive sodium tetraphenylborate (NaTPB), and a certain amounts of D6 were dissolved in 2.0 mL of cyclohexanone solution by heating in
water bath. Then cooling down to room temperature, 1.0 mL of the solutions was casting to the clean glass slide. Thereafter, the glass slide was kept horizontally till the cyclohexanone evaporated completely. At last, SM was leaved on the surface of the glass slide. The thickness of SM was about 8 µm. A series of SMs with different components, such as plasticizers, NaTPB and D6 were listed in Table 1.

Table 1

Fluorescence measurements

A piece of SM was cut and mounted on the top of the optical fiber then it was immersed into water in the cuvette. The fluorescence intensity was measured with the excitation wavelength of 365 nm UV light source. After the fluorescence intensity of SM remained stability, the fluorescence emission spectrum was obtained by above detection device.

Results and discussion

The effect of the composition on the response of SM

It is well known that the membrane composition mainly influences the response characteristics and working concentration ranges.\textsuperscript{27,28} Refer to the literature,\textsuperscript{29} the best ratio of the plasticizer/PVC is 1.6-2.2. So, the ratio of plasticizer/PVC of SM was chosen in the range of 2.0 to 2.1. The effect of the plasticizers DBP and EL-60 on the response of SM to Fe\textsuperscript{3+} were examined, respectively. Through the quantitative detection of Fe\textsuperscript{3+} by SM (see ESI†), the linear range and detection limit is obtained and listed in the Table 2. As shown in Table 2, the linear range and detection limit of SM for EL-60 as plasticizer are similar with that of
Fig. 1

As shown in Fig. 1, the response time of SM-1 is less than 25 s, and SM-2 to Fe$^{3+}$ is more than 40 s. It indicates that EL-60 as plasticizers not only enhanced the flexibility, as an amphiphilic molecule but also improved the hydrophility of SM-2, and then promoted Fe$^{3+}$ fast penetrating into SM-2 and shorten the response time.

As it is documented in the literature, the presence of lipophilic anionic additive NaTPB can accelerate ion exchange equilibrium. It can be seen from Table 2, adding 1.0 mg of NaTPB to SM-3, the response characteristic of wider linear range and lower detection limit is obtained. Increasing the amount of NaTPB up to 2.0 mg, the detection limit of SM-4 is higher than SM-3. In addition, SM-5 with higher concentration of D6 provides a narrow linear range. Thus, SM with PVC: EL-60: NaTPB: D6 wt% ratio 32 : 66 : 1 : 1 was used for the further studies.

Table 2

Effect of pH

For the protonation or deprotonation of fluorescent indicators containing amino could affect the properties of the sensing membranes, and the varied pH of solution could affect the status of Fe$^{3+}$, so the effect of pH on the fluorescence and the recognition properties of
SM were studied. As shown in Fig. 2, the fluorescence intensity of SM in solution is gradually reduced with increasing of pH from 2.0 to 7.0. It might be due to the protonation or deprotonation of N atom in piperazine of D6. In acidic condition, an eyeable enhancement of the fluorescence intensity of SM is attributed to the protonation of N atom in piperazine of D6 for the photo-induced electron transfer (PET) progress is blocked. When continue to increase pH of the aqueous solution, an observable decrease of the fluorescence intensity of SM is due to the deprotonation of N atom in piperazine of D6 for the PET is proceed.31

It can be seen from Fig. 2, the fluorescence intensity of SM in 1.0 mM Fe$^{3+}$ aqueous solutions is quenched obviously, and the effect of varied pH on the fluorescence intensity of SM in Fe$^{3+}$ solutions is notably. The fluorescence of SM is constant and remained at a lower intensity when pH was lower than 5.1. As pH is in the range of 5.1 to 6.5, an slightly fluorescence enhancement of SM is obtained, it may be corresponding to the generation of Fe(OH)$_3$ precipitation which causes the reduction of the concentration of free Fe$^{3+}$. As pH value is higher than 6.5, the fluorescence intensity of SM obviously changed for more precipitation of Fe$^{3+}$ forming in the solution. The fluorescence quenching mechanism of SM by Fe$^{3+}$ in solution may result from that Fe$^{3+}$ combined with the carbonyl of naphthalimide which leaded to the electron transfer or electronic energy transfer (see ESI† Figure S4).22 Therefore, the following determination was carried out at pH = 5.0.

![Fig. 2](image-url)

**Selectivity and interference**
The fluorescence response of SM to various metal ions was investigated. As shown in Fig. 3A (Black bars), the fluorescence intensity of SM decreases obviously upon the addition of Fe$^{3+}$ at the pH = 5.0, while the fluorescence intensity of SM in the presence of other metal ions does not show a significant decrease relative to Fe$^{3+}$. The results indicate that SM had a good selectivity towards Fe$^{3+}$ based on the fluorescence quenching. Interference from other coexisting metal ions to the recognition of Fe$^{3+}$ was further studied. As seen from Fig. 3A (Red bars), upon the addition of other metal ions to Fe$^{3+}$, the fluorescence intensity of SM is changed unobviously. It can be seen from Fig. 3B, the relative error (RE) of the fluorescence intensity is less than ± 5%. It implies the tolerance of SM to interference ions is acceptable. And RE is defined as $\text{RE (\%) = } \left[ \frac{(F - F_0)}{F_0} \right] \times 100$ ($F_0$ is the fluorescence intensity of SM in Fe$^{3+}$ solution, $F$ is the fluorescence intensity of SM in Fe$^{3+}$ solution which added other metal ions).$^{32,33}$

Fig. 3

Quantitative detection

In order to evaluate the sensitivity of SM, the effect of Fe$^{3+}$ concentrations on the fluorescence response was studied. We recorded the fluorescence intensity of SM by immersing it into the increasing concentrations of Fe$^{3+}$ buffer solution in the cuvette. The effect of the concentration of Fe$^{3+}$ to the fluorescence spectrum of SM is as shown in Fig. 4A. The maximum emission wavelength of SM is 490 nm. With increasing the concentration of Fe$^{3+}$, the maximum emission wavelength of SM basically remains steady while the intensity is
decreased. The fluorescence intensity of SM presents a linear decreased relation to the increasing concentration of Fe\(^{3+}\) (Fig. 4B), which indicates that SM could be potentially used for the quantification of Fe\(^{3+}\). A linear regression equation of \(y = -61.61x + 161.34\) (\(R^2 = 0.9906\)) is obtained in which \(y\) and \(x\) respectively stand for the fluorescence intensity of SM and the concentration of Fe\(^{3+}\). By calculating the detection limit is \(4.0 \times 10^{-7} \text{ M} (3\sigma / \text{slope})\). The changes upon the addition of Fe\(^{3+}\) and the low detection limit indicate that SM can be used for the detection of Fe\(^{3+}\) with high sensitivity.

**Fig. 4**

**Reversibility and reproducibility**

The fluorescence intensity of SM was studied by alternately switching the solution in the cuvette by the buffer solution and Fe\(^{3+}\) buffer solution. It reveals that the fluorescence intensity of SM presents a cyclical reversible changes between HAc-NaAc buffer solution and Fe\(^{3+}\) solution added alternately (Fig. 5). Relative to buffer solution, the fluorescence intensity of SM in Fe\(^{3+}\) solution decreases and its response time is less than 20 s before reaching a steady-state fluorescence signal. The results disclose that SM has a satisfactory reversibility and reproducibility for Fe\(^{3+}\) sensing.

**Fig. 5**

**Stability**
The stability of SM was tested by exposing SM to the HAc-NaAc buffer solution in the absent or present of 1.0 mM Fe$^{3+}$ for 5 h. The fluorescence intensity of SM was recorded at an interval of 15 min as shown in Fig. 6. The fluorescence intensity of SM basically remains stable. By calculating the relative standard deviation (RSD) are 1.1% and 1.5%, respectively.

In conclusion, the stability of SM in HAc-NaAc buffer of aqueous solution is ideal. The strong hydrophobic property and relative large molecular weight of D6 results in the improvement of the consistency of PVC with D6 embedded in SM as well as the reduction of the migration of D6 from SM to the aqueous solution, so the leakage of D6 is effectively restrained, finally improves the stability of SM.

Fig. 6

Practical application

SM was applied to determine Fe$^{3+}$ in tap water solutions in order to verify the application of SM. A standard addition method was prepared according to the literature.\textsuperscript{35} The results show that the fluorescence intensity of SM changed with the increase of the concentration of Fe$^{3+}$ (Fig. 7). In combination with the standard equations in Fig. 4B, recovery rate was calculated. According to the dates (Table 3), the recovery rate is between 97.6% and 101.2% which means that the determination of Fe$^{3+}$ in the tap water solutions by SM is accurate relatively, so SM has practical applications.

Fig. 7
Conclusion

In this article, a novel fluorescence sensing membrane was reported by the physical entrapment method for selectively recognition of Fe$^{3+}$ in the aqueous solution based on the fluorescence quenching. The fluorescence sensing membrane shows a good reversibility, fast response of less than 20 s and satisfactory stability with a relative standard deviation (RSD) of ± 1.5% and is successfully applied to detect the content of Fe$^{3+}$ in the tap water solution. It is an extensive potential application value and the preparation method of the sensing membrane can be used as a reference in the similar research.

Acknowledgements

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Reference


4631-4634.


10022-10028.


List of Figures and Tables

Scheme 1 Synthesis of the fluorescence probe (D6).

Fig. 1 Response time of SM-1 and SM-2 to Fe$^{3+}$ (1.0 mM) in HAc-NaAc (10 mM) aqueous solutions at pH = 5.0. $\lambda_{ex}$ = 365 nm.

Fig. 2 Effect of pH on the fluorescence intensity of SM at 490 nm in the absent or present of Fe$^{3+}$ (1.0 mM). $\lambda_{ex}$ = 365 nm.

Fig. 3 Selectivity and interference of SM to Fe$^{3+}$ (1.0 mM) from common metal ions (1.0 mM) in HAc-NaAc (10 mM) aqueous solutions at pH = 5.0. $\lambda_{ex}$ = 365 nm. (A) Black bars and Red bars are in the absent or present of Fe$^{3+}$. (B) Relative error of SM exposing other metal ions in the present of Fe$^{3+}$.

Fig. 4 Fluorescence spectra (A) and fluorescence intensity (B) of SM versus different concentrations of Fe$^{3+}$ in HAc-NaAc (10 mM) aqueous solutions at pH 5.0. $\lambda_{ex}$ = 365 nm.

Fig. 5 Reversibility of SM exposed to Fe$^{3+}$ (1.0 mM) and HAc-NaAc (10 mM) aqueous solutions at pH 5.0. $\lambda_{ex}$ = 365 nm.

Fig. 6 Effect of time on the fluorescence intensity of SM in HAc-NaAc (10 mM) aqueous solutions with or without Fe$^{3+}$ (1.0 mM) at pH 5.0. $\lambda_{ex}$ =365 nm.

Fig. 7 Fluorescence intensity of SM in tap water solutions of HAc-NaAc (10 mM) with increasing concentrations of Fe$^{3+}$ at pH 5.0. $\lambda_{ex}$ = 365 nm.

Table 1 Preparation of SM with different components.

Table 2 Effect of the membrane composition on the linear range and limit detection.

Table 3 Analytical application of SM for the determination of Fe$^{3+}$ in tap water solution (n=3)
Scheme 1

\[ \text{C}_{12}H_{25}\text{NH}_2 \rightarrow \text{C}_{12}H_{25}\text{N} \rightarrow \text{C}_{12}H_{25}\text{N} \rightarrow \text{M3} \]

\[ \text{C}_{12}H_{25}\text{N} + \text{Cl} \rightarrow \text{DIEA} \rightarrow \text{CH}_3\text{CN Reflux} \rightarrow \text{D6} \]
Fig. 1

Fluorescence Intensity (a.u.)

Time (s)

SM-1
SM-2

buffer solution

Fe$^{3+}$ solution
Fig. 2

Fluorescence Intensity (a.u.)

2 3 4 5 6 7

100 120 140 160 180

pH

- the membrane + Fe^{3+}
- the membrane
Fig. 3

A

Fluorescence Intensity (a.u.)

Species

Absent

B

Relative Error (%)

Metal ions

Ca^{2+}

Al^{3+}  Pb^{2+}  Hg^{2+}  Ni^{2+}  Cu^{2+}  Zn^{2+}  Cr^{3+}  Mg^{2+}  Na^{+}  Ag^{+}
Fig. 4

A

[B] = 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6

Fluorescence Intensity (a.u.)

Wavelength (nm)

B

y = -61.61x + 161.34

R^2 = 0.9906

Fluorescence Intensity (a.u.)

[Fe^{3+}] (mM)
Fig. 5

Fluorescence Intensity (a.u.)

Time (s)

buffer solution

Fe$^{3+}$
Fig. 6

Fluorescence Intensity (a.u.)

[Graph showing fluorescence intensity over time for SM + Fe³⁺ and SM]
Fig. 7

Fluorescence Intensity (a.u.)

$y = -64.82 \times + 161.78$

$R^2 = 0.9843$
<table>
<thead>
<tr>
<th>Membrane number</th>
<th>EL-60 (mg)</th>
<th>DBP (mg)</th>
<th>D6 (mg)</th>
<th>NaTPB (mg)</th>
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<tbody>
<tr>
<td>SM-1</td>
<td>-</td>
<td>67</td>
<td>1.0</td>
<td>-</td>
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<tr>
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<td>-</td>
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* PVC: 32 mg; cyclohexanone: 2.0 mL.
<table>
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<tr>
<th>Membrane number</th>
<th>Linear range (M)</th>
<th>R²</th>
<th>Limit detection (M)</th>
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<tr>
<td>SM-1</td>
<td>$5.0 \times 10^{-5}$ - $3.5 \times 10^{-4}$</td>
<td>0.9983</td>
<td>$3.2 \times 10^{-7}$</td>
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<td>SM-2</td>
<td>$2.5 \times 10^{-5}$ - $2.2 \times 10^{-4}$</td>
<td>0.9936</td>
<td>$3.9 \times 10^{-7}$</td>
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<tr>
<td>SM-3</td>
<td>$5.0 \times 10^{-5}$ - $1.5 \times 10^{-3}$</td>
<td>0.9906</td>
<td>$4.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>SM-4</td>
<td>$5.0 \times 10^{-5}$ - $2.7 \times 10^{-3}$</td>
<td>0.9901</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>SM-5</td>
<td>$5.0 \times 10^{-5}$ - $6.4 \times 10^{-4}$</td>
<td>0.9903</td>
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Table 3

<table>
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<th>Added (mM)</th>
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<th>0.370</th>
<th>0.540</th>
<th>0.740</th>
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<tr>
<td>Found (mM)$^a$</td>
<td>0.101±0.01</td>
<td>0.218±0.01</td>
<td>0.361±0.01</td>
<td>0.541±0.01</td>
<td>0.730±0.02</td>
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<tr>
<td>Recovery (%)</td>
<td>101.2</td>
<td>99.2</td>
<td>97.6</td>
<td>100.1</td>
<td>98.6</td>
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$^a$ Average value of three determinations.