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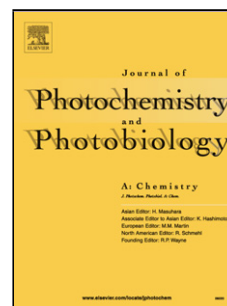
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Salicylaldimine-based receptor as a material for iron(III) selective optical sensing

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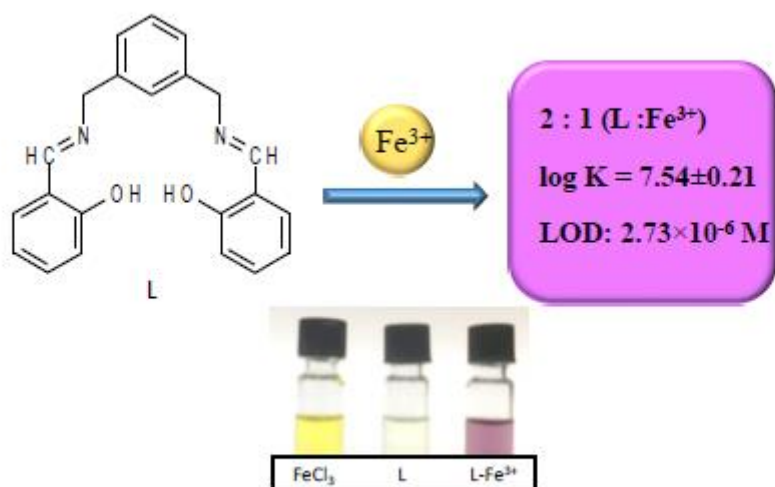
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## Graphical abstract

**Highlights**

- Application of microwave irradiation ensures  $\alpha,\alpha$ -bis(salicylimino)-*m*-xylene synthesis in easy, fast, and efficient way.
- The reported compounds shows ability to colorimetric iron(III) recognition in aqueous solutions, what is shown by color change from yellow to purple.
- Incorporation of the ligand into polymeric matrix enables to iron(III) detection at pH 2.9 in aqueous solution with detection limit  $2.73 \times 10^{-6} \text{ M}$ .
- Mechanism of ligand – iron(III) interactions on the basis of spectroscopic methods is proposed.

Abstract:

$\alpha,\alpha$ -Bis(salicylimino)-*m*-xylene (**L**) was prepared using both conventional and microwave-assisted procedure. The compound exhibits ability to colorimetric recognition of iron(III) ions in aqueous environment, what is manifested by significant color change from yellow to purple. In DMSO : water (9:1 v/v) solvent system, receptor creates with iron(III) cations complexes of 2:1 stoichiometry (L:Fe<sup>3+</sup>) with stability constant (log K) 7.54±0.21. Incorporation of ligand into polymeric matrix (cellulose triacetate) enables iron(III) detection in 100% aqueous solution at pH 2.9 with detection limit 2.73×10<sup>-6</sup> M.

Keywords: Schiff base, tautomerism, iron(III) receptor, optical sensor, UV-Vis spectrophotometry

## 1. Introduction

Iron, one of the most essential trace element, plays a significant role in many biochemical cellular processes. It is involved in oxygen transport and storage in diverse metalloenzymes [1]. Iron is also crucial in cellular metabolism and enzymatic reactions. Its deficiency is the most common cause of anemia, low blood pressure, and hyp immunity [2]. On the other hand, high level of iron within an organism is associated with an increased risk of cancer and dysfunction of several organs like heart or liver [3]. Therefore, reliable, sensitive and selective methods for qualitative and quantitative iron(III) detection are needed in the field of clinical, environmental, and industrial analysis.

In aqueous solutions iron(III) exists in several forms depending on pH i.e. at low pH [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ions are predominant, but above pH ~ 3 hydroxo species [Fe(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup>, [Fe(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub>]<sup>+</sup>, or [Fe(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>4</sub>]<sup>-</sup> appear [4]. For this reason, a form of iron ions existing in solution must be taken into account for an appropriate method development.

Due to fast and easy detection, relatively low costs, and high sensitivity optical chemosensors gained vast popularity [5-7]. Color change occurring during recognition process between receptor and complementary ion provides easy to measure analytical signal and even “naked-eye” detection without a need of use of the expensive equipment. Among metal cation receptors Schiff bases derived from salicylaldehyde are an important group of compounds. Due to the presence of chromogenic azomethine moiety and hydroxyl group being additional binding site they are often applied for spectrophotometric ion recognition and sensing. Velmathi *et al.* [8] used salophene (*N,N'*-bis(salicylidine)-*o*-phenylenediamine) as colorimetric and fluorescent reagent for transition metal cation detection in acetonitrile and its mixtures with water. Spectrofluorimetric response of salophene towards copper(II) cation in aqueous solution at pH



8.2 was also reported [9]. Amani *et al.* [10] described recognition ability of imines derived from salicylaldehyde towards fluoride anions in acetonitrile-DMSO mixtures.

Among reported iron(III)-selective chemosensors majority of them cannot operate in fully aqueous solutions due to their low binding affinity or hydrophobicity [11-15]. The necessity of addition of organic solvent may limit potential applications of described probes. What is more, from practical point of view operation with ligand solution is less convenient than with a ligand incorporated into membrane (optode) that may ensure on-line monitoring [16-17].

Taking all above into consideration, we present here the synthesis and ion-binding ability of  $\alpha,\alpha$ -bis(salicylimino)-*m*-xylene (**L**) (Scheme 1) towards metal cations and anions in aqueous environment. This compound was previously reported by Maverick *et al.* [18]. Its complexes with copper(II) and palladium(II) were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR as well as by X-Ray analysis. To the best of our knowledge (according to Chemical Abstracts), interactions of ligand **L** with ions in aqueous solution have not been studied so far. Besides studies in solution (DMSO : water mixture) compound **L** was also incorporated into polymeric matrix and adsorbed on the test strips for easy, “naked-eye” detection of the analyte in 100% aqueous solutions.

## 2. Experimental

### 2.1 General

All chemicals of the highest available purity were purchased from commercial sources and used without further purification. The reaction progress was monitored by TLC using aluminium sheets covered with silica gel 60F<sub>254</sub> (Merck). Microwave-assisted synthesis was carried out in Plazmatronika RM 800 microwave reactor (power 300 W).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian INOVA-550 apparatus at 500 MHz and 125 MHz respectively. Chemical shifts are reported as  $\delta$  [ppm] values in relation to TMS. ATR FTIR spectra were taken on a Nicolet iS10 apparatus. Mass spectra were recorded on a SYNAPT G2-S HDMS (Waters) (ESI) spectrometer. Molar conductivities of the ligand and its complex with iron(III) ions were measured in DMF ( $\sim 10^{-3}$  M) at room temperature using Philips PW 9527 conductivity meter. UV-Vis titrations in DMSO (Sigma-Aldrich) and its mixtures with water were carried out using an UNICAM UV 300 spectrophotometer. For spectrophotometric measurements 1 cm quartz cuvettes were used. In measurements carried out in aqueous solution deionized water (conductivity  $< 1 \mu\text{S}\cdot\text{cm}^{-1}$ , Hydrolab, POLAND) was used.

### 2.2 Synthesis



Schiff base (**L**) –  $\alpha,\alpha$ -bis(salicylimino)-*m*-xylene – was obtained using both conventional heating (oil bath) and microwave-assisted synthetic procedures.

#### *Conventional synthesis*

To the solution of 1,3-xylylenediamine (0.75 mmol, 0.1 mL) in absolute ethanol (5 mL) salicylaldehyde (1.50 mmol, 0.156 mL) was added stepwise. The reaction mixture was magnetically stirred at reflux for 5 h. The resulting precipitate was filtrated off and the pure product was obtained after crystallization from ethanol. Yield: 67% (0.171 g).

#### *Microwave-assisted synthesis*

A mixture of 1,3-xylylenediamine (0.75 mmol, 0.1 mL), salicylaldehyde (1.50 mmol, 0.156 mL), and absolute ethanol (5 mL) was exposed to microwave irradiation for 10 minutes at room temperature (300 W). Purification process was similar as describe above for conventional route of synthesis. Yield: 97 %.

$\alpha,\alpha$ -Bis(salicylimino)-*m*-xylene: yellow crystals,  $R_f = 0.93$  ( $\text{CHCl}_3$ :acetone, 10:1, v/v),  $R_f = 0.16$  (chloroform), mp. 56-57°C,  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  [ppm]): 4.81 (4H, s); 6.86 (2H, d,  $J=7.9$  Hz); 6.90 (2H, td,  $J=7.6$  Hz); 7.26 (2H, d,  $J=7.7$  Hz); 7.35-7.31 (3H, m); 7.38 (1H, t,  $J=7.6$  Hz); 7.47 (2H, dd,  $J_1=7.6$  Hz,  $J_2=1.5$  Hz); 8.72 (2H, s); 13.41 (2H, s); FTIR (ATR) 3051; 3009; 2897; 2845; 2516; 1621; 1614; 1577; 1496; 1458; 1440; 1422; 1374; 1338; 1284; 1212; 1150; 1114; 1047; 1027; 895; 880; 796; 796; 767; 749; 703; 647  $\text{cm}^{-1}$ . UV-Vis (DMSO):  $\lambda(\epsilon) = 317$  nm ( $8.3 \times 10^3$ ), 405 nm ( $2.4 \times 10^2$ ).

### 2.3 Ligand-ion interaction studies

Ligand-ion interactions both in solution and after immobilization of ligand into organic matrix were investigated. Binding properties of obtained Schiff base were tested using UV-Vis spectrophotometry, FTIR and  $^1\text{H NMR}$  spectroscopy. Spectrophotometric response of ligand towards many metal cations (alkali, alkaline earth, heavy, and transition metal cations) in the form of perchlorate salts as well as anions of different size and shape (as tetra-*n*-butylammonium salts, TBA) was studied. Iron(II) was used as  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  and iron(III) as anhydrous chloride  $\text{FeCl}_3$ . All spectrophotometric titrations were carried out in the DMSO : water (9:1 v/v) solvent mixture. On the basis of experimental data stability constant values and stoichiometry of formed species were determined using OPIUM program [19]. In competition studies the absorbance of ligand solution ( $\lambda = 550$  nm) in the presence of iron(III) chloride at fixed concentration (1 equivalent) was recorded before ( $A_0$ ) and after ( $A$ ) addition of interfering



metal cations (as perchlorate salts) at the concentration 10 times higher than the analyte. The influence of tested interfering ions on spectrophotometric response towards iron(III) cations is presented as the relative response. The value of the relative response was determined as % RR =  $[(A-A_0)/A_0] \times 100\%$ .

#### *Complex preparation and characterization*

Iron(III) complex was prepared by dissolving of ligand and FeCl<sub>3</sub> (molar ratio L : FeCl<sub>3</sub> = 2:1) in methanol. The respective mixture was refluxed till homogenous solution was obtained. Sample was analyzed, after solvent evaporation under reduced pressure and crystallization from water.

FTIR (ATR): 3377; 3050; 3021; 2899; 2844; 1611; 1541; 1469; 1445; 1398; 1316; 1201; 1150; 1148; 1124; 1046; 1027; 901; 752; 702; 598 cm<sup>-1</sup>.

UV-Vis:  $\lambda$  ( $\epsilon$ ) = 320 nm ( $1.2 \times 10^4$ ), 524 nm ( $2.2 \times 10^3$ ).

#### *Ligand immobilization into organic matrix*

Schiff base was incorporated into polymeric matrix based on cellulose triacetate. For membrane preparation the respective quantities of ligand (0.01 g, 1.7% w/w), cellulose triacetate (0.25 g, 41.9% w/w), and triethylene glycol (0.3 mL, 56.4% w/w) in chloroform (6 mL) were dissolved. The mixture was magnetically stirred for several hours till homogenous solution was obtained and then poured onto a clean and dry Petri dish for solvent evaporation.

#### *Test strips preparation*

Test strips were prepared by absorption of ligand directly on a glass microfibre filter (Whatman GF/C). Ligand solution (concentration 2, 4 or 6 mM) in methanol was poured into a chromatographic chamber and then a strip of glass filter was placed in it, similarly as a TLC plate. When ligand solution covered the whole the strip, it was taken out of the chamber and left for solvent evaporation.

### **3. Results and discussion**

#### *3.1 Synthesis*

Schiff base **L** was obtained as shown in Scheme 1 using salicylaldehyde and 1,3-xylylenediamine as substrates. The resulting imine is already known in literature. Its synthetic procedure described by Maverick *et al.* [18] provides desired product obtainment with good yield i.e. 90%, however carcinogenic benzene was there applied as a solvent. Proposed by us

conventional method employs a safer solvent i.e. ethanol and allows preparation of **L** without the use of catalysts with moderate yield. Application of microwave irradiation - green chemistry approach - enables shorter reaction time (10 minutes instead of 5 hours in the conventional procedure) and higher yield of desired product, i.e. 97 %. Shorter reaction times and higher yields are often reported for MW assisted protocols [20], however the mechanism of reaction acceleration and yield improvement are not always clear. One of the reason which is considered in literature and supported by many experiments (cf. amide synthesis [21]) is the more effectual heating of polar species under microwave irradiation. In Schiff bases' synthesis from an aldehyde and a primary amine as substrates, the rate determining step is dehydration of hemiacetal, preceded by the formation of charged intermediate (see Fig. SD1, Supplementary Data). On the other hand, the reverse reaction i.e. the hydrolysis of imine is a process which must be taken into account, when water is not removed from reaction environment. This can lower the final yield of Schiff base, especially when reaction is carried out for a long time. Microwave supported preparation of **L** occurs in a short time, thus the probable hydrolysis of the product can be limited. This can be an additional explanation of the more effective MW assisted synthesis of **L** comparing to conventional heated reaction.

### 3.2 Tautomeric equilibrium

Tautomeric equilibrium can be affected by many factors, among the others by the nature of the solvent [22]. Possible tautomers: enol ( $L_E$ ) and keto ( $L_K$ ) form and zwitterionic form ( $L_Z$ ) which can be considered for **L** are shown in Fig. 1a. To study of keto-enol tautomerism of **L** solvents of different properties and polarities were used in spectroscopic measurements: UV-Vis,  $^1H$  and  $^{13}C$  NMR. The comparison of the absorption UV-Vis spectra of **L** registered in benzene, hexane, methanol, DMSO and the mixture DMSO:water (9:1) is shown in Fig. 1b. In nonpolar hexane three bands at 217, 257 and 322 nm are observed. The band at 322 nm is also observable in nonpolar benzene (bands at shorter wavelengths are overlapped by solvent). This spectral pattern is characteristic for the enol tautomer [23], whereas the existence of the keto tautomer in UV-Vis spectra is manifested by the presence of band over 400 nm. This band ~ 400 nm and yellow color of solution (Fig. SD2, Supplementary data), can suggest the change of tautomeric equilibrium towards keto form in methanol, DMSO, and mixture of DMSO with water (Fig. 1b). The intensity of this band depends on polarity of the solvent system (comparing normalized  $E_T(30)$  solvent polarity parameter [22a]):  $DMSO < Methanol < DMSO:water$ .

We compared  $^1H$  and  $^{13}C$  NMR spectra of **L** registered in solvents of different polarity (for details see Supplementary Data).  $^1H$  NMR spectra (Fig. 1d) in all cases show signal distribution



characteristic for aromatic protons (region 6.50-7.40 ppm). The presence of the pure keto form (**L<sub>K</sub>**) should change this spectral pattern due to the partial loss of the aromaticity of the system or additional signals should be present in the case of co-existence of two tautomeric forms in solution. In <sup>13</sup>C NMR spectra (Fig. SD3a-c) signal characteristic for ketone carbon atom C=O, typically seen above 180 ppm [24] here is not observed. These results prompt us to conclude that in polar solvents the zwitterionic keto form (**L<sub>Z</sub>**) is present. Moreover, it is well seen from Fig. 1c that increasing water content shifts the enol-keto tautomeric equilibrium of **L** towards zwitterionic form **L<sub>Z</sub>**.

### 3.3 Ligand- ion interactions studies

#### *Ion complexation in solution – UV-Vis spectroscopy*

Alkali, alkaline earth and heavy metal cations complexation studies were preliminary performed in DMSO. Spectral changes were observed in the presence of copper(II), lead(II), zinc(II), iron(III) and iron(II) salts. The use of only organic solvent limits application of investigated ligand as possible ion sensor thus further studies were carried out in water containing solvent mixture. In DMSO : H<sub>2</sub>O (9:1, v/v) the most significant changes in UV-Vis spectrum of ligand **L** solution were observed in the presence of iron(III) salt. Upon titration with iron(III) chloride a new band appears at ~530 nm where absorption of ligand is not observed. This change in UV-Vis spectrum, which can be assigned to a phenolate-iron(III) charge transfer band [25], is connected with well observable color change from yellow to purple. Changes in absorption spectrum of **L** upon titration with iron(III) chloride are shown in Fig. 2a. In Fig. 2 also color change of ligand solution in the presence of equimolar amount of iron(III) salt in DMSO : water (9:1 v/v) solvent system can be seen.

Molar ratio and Job plots obtained from titration experiments in DMSO-water mixture point out that under titration conditions one metal ion can participate in complex formation with two ligand molecules (Fig. SD4). Thus we assumed that in a mixed solvent system, 2:1 (**L**:Fe) complex is formed. The stability constant value was calculated with OPIUM software [19] as (log K) 7.54±0.21.

Iron(II) also causes changes in absorption spectra of **L** with color change from yellow to reddish ( $\lambda = 510$  nm) (Fig. SD5). Absorption band of the **L**-Fe<sup>2+</sup> complex is partially overlapped by the absorption band of the used salt - iron(II) sulfate. Estimated binding constant value (log K) for **L**: Fe(II) (2:1) complex is about 7 (in experiment FeSO<sub>4</sub>·xH<sub>2</sub>O was used, thus stability constant

should be taken as approximate value) and it is comparable with stability constant value for iron(III) complex.

The effect of other heavy metal cations: copper(II), zinc(II), and lead(II) on iron(III) binding by investigated Schiff base **L** was also studied. From spectra registered during spectrophotometric titrations of ligand solution in DMSO : water solvent system (9:1 v/v) with copper(II), zinc(II) or lead(II) perchlorate solutions (Fig. 3a-c) it can be seen that absorption bands of formed complexes of ligand **L** with tested metal cations are not in the same region as band of **L-Fe<sup>3+</sup>**. Analysis of spectrophotometric data revealed that under measurement conditions 2:1 (L:M) complexes are formed with stability constant values (log K)  $9.16 \pm 0.03$  and  $6.96 \pm 0.08$  for **L-Cu<sup>2+</sup>** and **L-Zn<sup>2+</sup>** respectively. Evaluation of reliable value of binding constant for **L-Pb<sup>2+</sup>** was not possible due to relatively small changes in absorption spectra. Application of tested metal cations salts in concentration 10-fold higher than iron(III) salt revealed that the most significant effect on spectrophotometric response of ligand **L** towards iron(III) have copper(II) cations. The influence of interfering ions on iron(III) determination expressed as %RR is shown in Fig. 3d (see also Fig. SD6).

Schiff base **L** due to the presence of O-H and azomethine C-H groups in the structure can be a potential anion receptor. Ability of ligand to anions of different size and shape complexation was tested in DMSO and DMSO : water (9:1 v/v) solvent system. Among studied ions changes in UV-Vis spectrum of ligand solution only in the presence of fluoride and hydroxide (tested as tetra-*n*-butylammonium salts) were noticed. Large bathochromic shift and similarities in changes caused by those strongly basic anions suggest that under measurement conditions the ligand deprotonation is a dominant process (Fig. SD7).

#### *Iron(III)-L complex characterization*

The nature of iron(III) binding by tested here ligand was analyzed using spectroscopic methods. Comparison of FTIR (ATR) spectra of Schiff base **L** and its iron(III) complex is shown in Fig. 4. In free imine spectrum a broad band c.a.  $2560 \text{ cm}^{-1}$ , which can be assigned to O-H...N intramolecular hydrogen bond, is observed [26-27]. This and the presence of strong bands at  $1621$  and  $1284 \text{ cm}^{-1}$  indicate that in a solid state ligand **L** exists in a phenol-imine tautomeric form. The most significant differences between **L** and iron(III) complex are observed in absorption region of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{C})_{\text{ar}}$  bands, which in free ligand are present as a purely resolved doublet at  $1621$  and  $1614 \text{ cm}^{-1}$ . In the complex those bands, seen as a singlet, are shifted



towards lower frequencies ( $1611\text{ cm}^{-1}$ ), what may indicate that metal ion is coordinated through the nitrogen atom of azometine group. In N, O donor Schiff bases metal cation is usually coordinated also by oxygen atom of deprotonated OH group in *ortho* position to azometine residue [28-29]. In IR spectra of the reported here free ligand **L** the well observable  $\nu(\text{OH})$  broad band signal  $\sim 2600\text{ cm}^{-1}$  is absent in the spectrum of complex. Concurrently, the  $\nu(\text{C-O})$  band seen in the imine spectrum at  $1284\text{ cm}^{-1}$  in the complex spectrum is broaden and less intense (however, its position is nearly the same). Changes of intensity and position of  $\nu(\text{C-C})_{\text{ar}}$  and  $\delta(\text{C}_{\text{ar}}\text{-H})$  bands are also observed. It may suggest that in metal coordination phenolic group is involved.

In the mass spectrum of the obtained complex a base peak at  $m/z = 813.14$  is observed. Peaks at  $m/z$ : 345.16 and 398.07 of intensity of 26% and 32% respectively are also seen, which correspond to ligand ion  $[\text{M} + \text{H}]^+$  and an adduct of the deprotonated ligand and iron(III) ion (Fig. SD8). Molar conductivities of **L-Fe**<sup>3+</sup> complex and free **L** in DMF are  $37.7$  and  $1.7\text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  respectively, what indicates their nonelectrolyte properties. This means that in solution complex exists mostly in neutral form and there are no anions in the coordination sphere [30-32]. Additionally, test for chloride ions with the use of silver nitrate excluded its participation in the complex formation.

Taking into account all the obtained results it may be concluded that one iron(III) ion is coordinated by 2 molecules of ligand through two nitrogen atoms and two oxygen atoms from each molecule of the compound. It is possible that complex is stabilized by 4 molecules of water interacting with azomethine CH protons of the ligand molecules *via* hydrogen bonds. The base peak observed in the mass spectrum at  $m/z = 813.14$  may thus correspond to  $[\text{M} + \text{H}]^+$  ion.

The reversibility of complexation process is an important feature in regard to usage of the ligand as an analytical reagent. Performed studies reveal that anionic species have an impact on stability of **L-Fe**<sup>3+</sup> complex. Strongly basic anions namely: fluoride, hydroxide, acetate, benzoate, and dihydrophosphate ions (in the form of tetra-*n*-butylammonium salts) cause the reversibility of complexation process in **L-Fe**<sup>3+</sup> system. During spectrophotometric titration of **L-Fe**<sup>3+</sup> solution in DMSO : water (9:1 v/v) with one of the mentioned above salt the band  $\sim 550\text{ nm}$ , characteristic for complex of the Schiff base with iron(III), disappears. Addition of other tested anions: chlorides, bromides, iodides, nitrates(V), monohydrogen sulfates, thiocyanates, *p*-toluenesulfonates, and perchlorates does not influence on the complex stability.

*Metal cation recognition by ligand incorporated into organic matrix*

A remarkable color change of ligand **L** solution upon iron(III) coordination from yellow to purple makes the proposed here imine an interesting candidate for an optical sensor (optode). This is why Schiff base **L** was incorporated into polymeric matrix i.e. cellulose triacetate and its ability to iron(III) recognition in fully aqueous solution was examined. The use of triacetate cellulose material based on natural polymer - instead of popular PCV matrix is the advantage of our system as such materials seem nowadays to be biodegradable [33]. Similarly to UV-Vis spectrum of ligand solution in DMSO : water solvent system, in the optode spectrum a new band at ~ 530 nm upon iron(III) chloride addition was observed, what was accompanied by optode color change (Fig. 5).

Iron(III) due to its small size and relatively high charge reveals strong tendency to hydrolyze in aqueous solution [4]. This is why, iron(III) determination needs to be carried out at fixed and low value of pH. The influence of pH value on absorbance of the optode doped with ligand **L** was tested (Fig. 6a). At low pH ~ 2 complete decrease of membrane absorbance at the analytical wavelength is observed. In such conditions hydrolysis of imine may take place and the prepared optode cannot operate. Keeping constant pH value at around 3 during all measurements is preferable from stability of both the optode, and iron ions point of view.

One of the important features of chemical sensor is its response time. Figure 6b shows the time-dependent response characteristics of reported here optode immersed in solution containing 1.6 mM of FeCl<sub>3</sub>. The optical membrane gives stable response after short time i.e. 50 seconds. This response is proportional to iron(III) concentration in whole tested concentration range: from  $8.1 \times 10^{-4}$  M to  $1.5 \times 10^{-2}$  M with correlation factor  $R^2=0.998$ . The detection limit, estimated as a concentration of analyte generating a signal equal to three times of standard deviation of blank membrane [34], is  $2.73 \times 10^{-6}$  M. In order to determine the sensor selectivity the influence of several metal cations on the membrane absorbance was tested. In competition studies the absorbance of optode in the presence of iron(III) chloride in hydrochloric acid solution ( $10^{-3}$  M) at fixed concentration ( $c_{\text{salt}} = 1.60 \times 10^{-3}$  M) was recorded before ( $A_0$ ) and after ( $A$ ) addition of interfering metal cations at the concentration 10 times higher than the analyte ( $\lambda=550$  nm). The influence of tested interfering ions on spectrophotometric determination of iron(III) cations is presented as the relative response (Fig. 7a). The most significant influence on the optode response towards iron(III) chloride have calcium and copper(II) ions. Sodium, potassium, magnesium, and lead(II) cations cause negligible effect on absorbance changes.

Regeneration of bulk optode by the use of EDTA solution (0.1 M) was provided. After 2 minutes of immersion of membrane in EDTA solution iron(III) ions were efficiently removed and the membrane absorbance returned to its initial value. Before next iron(III) determination the optode was kept for 1 minutes in water. The same membrane can be used 2 times without significant loss of effectiveness. In the third cycle the response decreases to 50% (Fig. 7b).

For comparative purpose linear range, detection limit and working media of the presented here sensor and several other colorimetric reagents for iron(III) recognition are summarized in Table 1. Most of iron(III)-selective sensors reported in [5-7, 11] work in solutions containing organic solvents whereas the proposed optode operates in 100% aqueous environments. Other important feature of the proposed sensor is that the ligand can be obtained in fast way with very high yield from commercially available, inexpensive reagents, what makes it a cheap and effective tool for iron(III) recognition.

#### *Metal cation recognition by ligand adsorbed on test strips*

For fast, qualitative experiments the test strips are a convenient tool. In presented here studies, the effect of ligand concentration ( $c_L$ :  $2.20 \times 10^{-3}$ ,  $4.10 \times 10^{-3}$ , and  $6.00 \times 10^{-3}$  M) on iron(III) “naked-eye” detection in aqueous solution was examined. As described above, the strongest influence on iron(III) recognition by optode with ligand **L** has copper(II) ion (Fig. 7a). For this reason response of the test strip towards iron(III) in the presence of copper(II) ions (10-fold molar excess to iron(III) concentration) was tested. As an optimum ligand concentration  $4.10 \times 10^{-3}$  M was chosen (because of color change) (Fig. 8). A characteristic, for iron(III) recognition, change of color of the test strip even in the presence of interfering ion was observed. The limit for “naked-eye” detection for test strips is on the level of  $10^{-3}$  M  $\text{FeCl}_3$ .

## **4. Conclusions**

Ligand **L** -  $\alpha,\alpha$ -bis(salicylimino)-*m*-xylene is obtained in eco-friendly synthetic route (etanol, microwave heating) with a high yield (97%) from simple, commercially available substrates. **L** exhibits ability to iron(III) recognition in water containing systems. In DMSO : water solvent mixture (9:1 v/v) the imine interacts with iron(III) creating  $\text{ML}_2$  complexes with stability constant ( $\log K$ )  $7.54 \pm 0.21$  (it can act as a chromogenic reagent for metal ion detection and determination). The presence of iron(III) chloride causes the appearance of a new band at around 530 nm in UV-Vis spectrum of ligand solution, what is accompanied by remarkable



color change from yellow to purple. Incorporation of ligand into polymeric matrix based on cellulose triacetate, considered as a biodegradable material, provides iron(III) detection in 100% aqueous solution at pH 2.9 in concentration range from  $8.1 \times 10^{-4}$  M to  $1.5 \times 10^{-2}$  M with detection limit  $2.73 \times 10^{-6}$  M. It is worth to point out, that the determined detection limit is lower than the one recommended by World Health Organization in drinking water ( $5.36 \times 10^{-6}$  M) [35].

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found , in the online version, at

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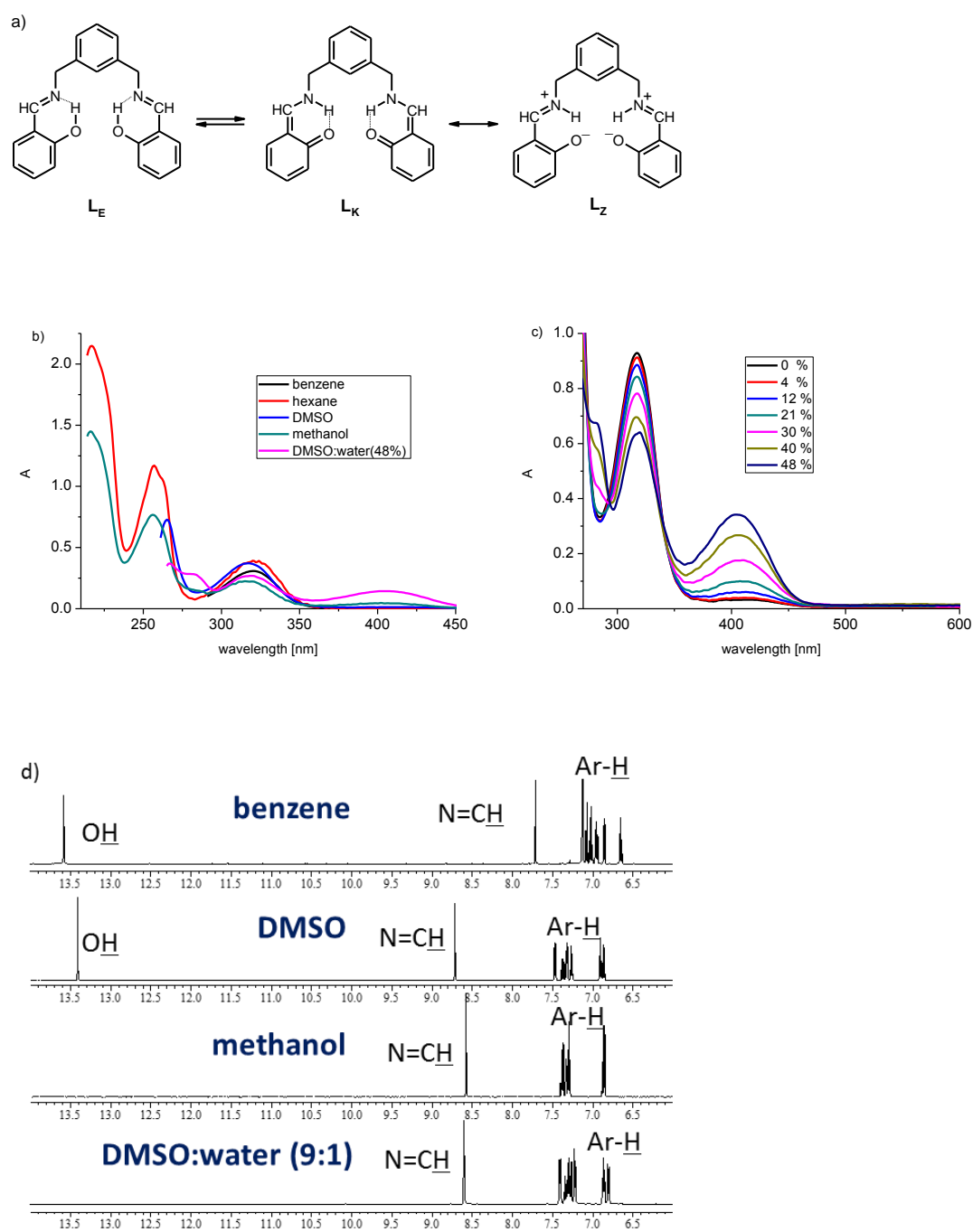
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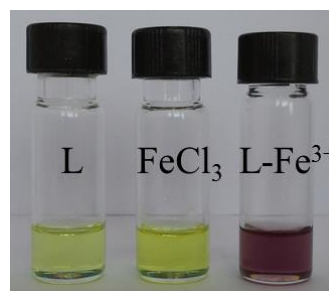
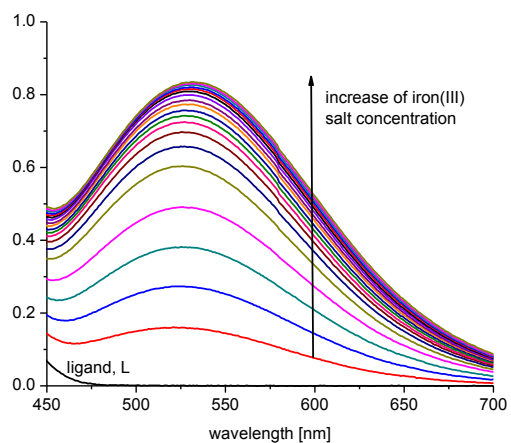
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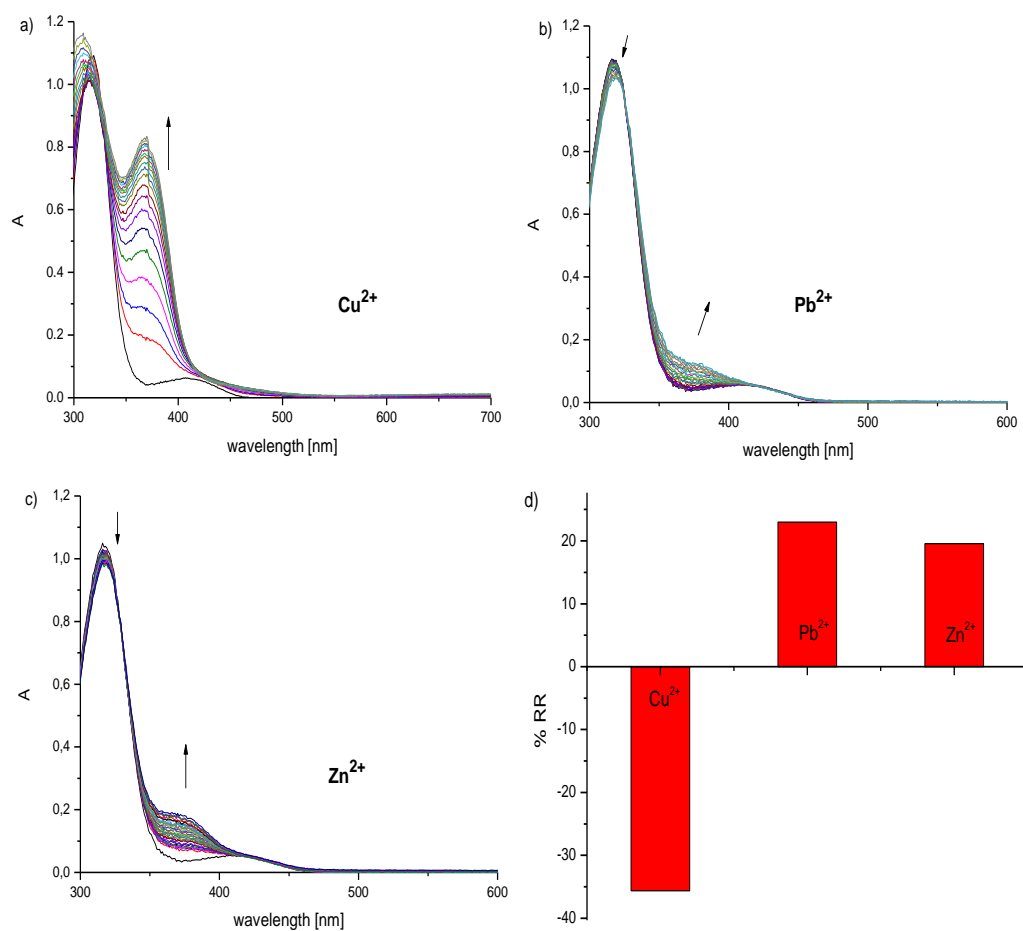




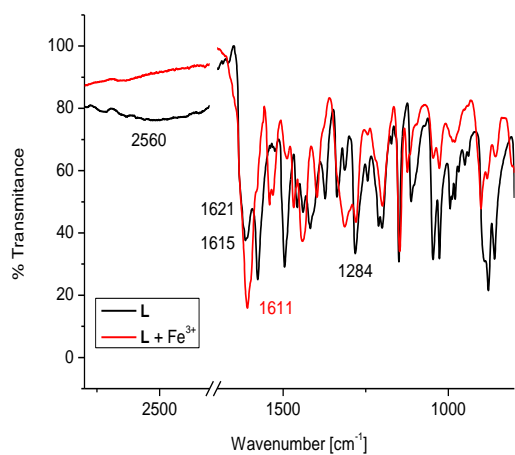
**Fig. 1.** (a) Possible: enol ( $L_E$ ) and keto ( $L_K$ ) tautomers and zwitterionic ( $L_Z$ ) form of **L**; (b) the comparison of UV-Vis spectra of **L** ( $\sim 4 \times 10^{-5}$  M) in different solvents; (c) changes in UV-Vis spectrum of ligand **L** ( $9.90 \times 10^{-5}$  M) in the presence of different amounts of water; (d) partial  $^1\text{H}$  NMR spectra of **L** registered in solvents of different polarity.



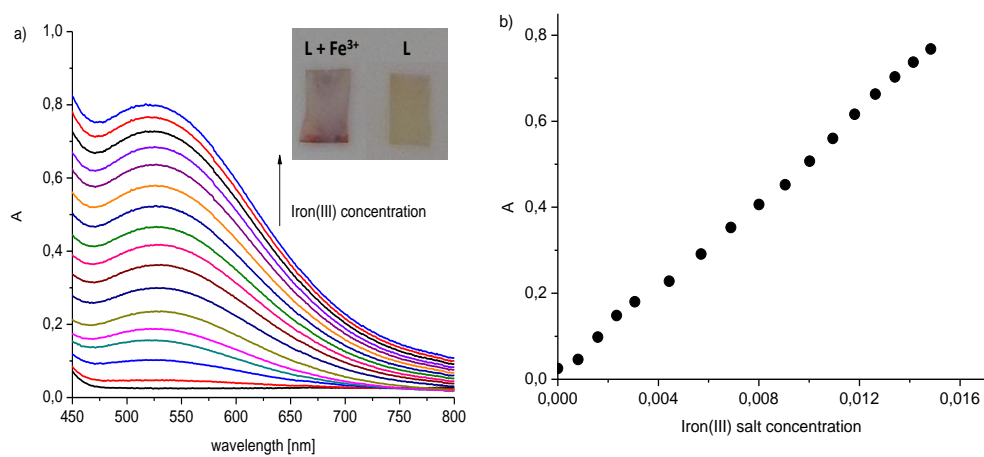
**Fig. 2.** Photo: color change of ligand solution in the presence of equimolar amount of iron(III) chloride in mixed DMSO : water (9:1, v/v) solvent system. Spectrophotometric titration (spectral range 450-700 nm) of ligand solution ( $6.69 \times 10^{-4}$  M) with iron(III) chloride ( $0-8.0 \times 10^{-4}$  M) in mixed DMSO : water (9:1, v/v) solvent system.



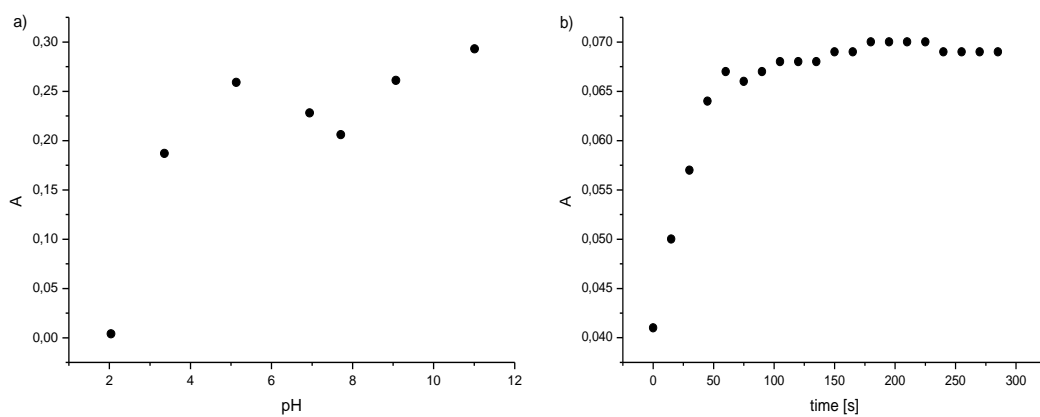
**Fig. 3.** Changes in UV-Vis spectra of ligand solution ( $c_L = 1.40 \times 10^{-4}$  M) upon addition of (a) copper(II) perchlorate ( $c_{\text{Cu}} = 0-2.16 \times 10^{-4}$  M); (b) lead(II) perchlorate ( $c_{\text{Pb}} = 0-3.38 \times 10^{-3}$  M); (c) zinc(II) perchlorate ( $c_{\text{Zn}} = 0-6.85 \times 10^{-4}$  M); (d) the influence of metal cation (10-fold molar excess) on spectrophotometric response of ligand solution ( $c_L = 2.10 \times 10^{-4}$  M) towards iron(III) chloride ( $c_{\text{Fe}} = 5.17 \times 10^{-5}$  M) in DMSO : water (9:1) solvent system ( $\lambda = 550$  nm).



**Fig. 4.** Comparison of FTIR (ATR) spectra of Schiff base **L** and its iron(III) complex (**L** : Fe<sup>3+</sup> = 2:1, w/w).

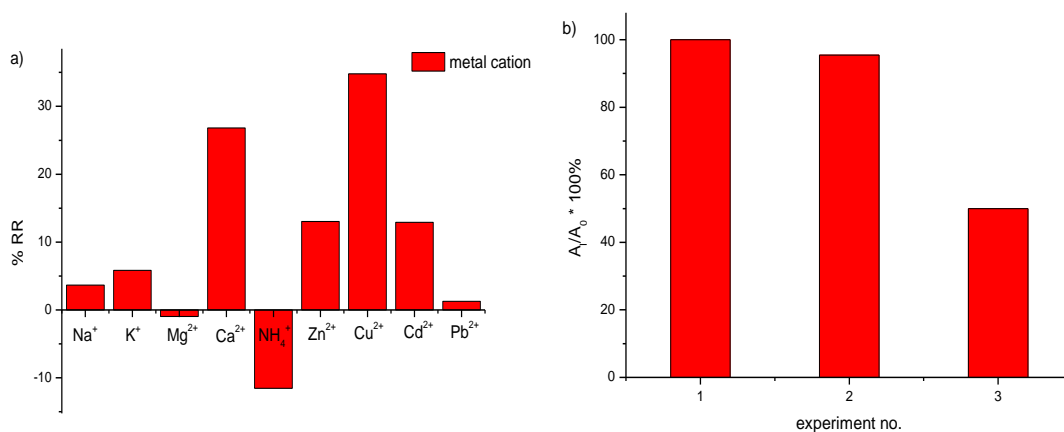


**Fig. 5.** a) Changes in UV-Visible spectrum of optode with ligand **L** in the presence of FeCl<sub>3</sub> ( $c = 0 - 1.48 \times 10^{-2}$  M) in HCl ( $10^{-3}$  M) at pH = 2.9; b) Absorbance of optode with ligand **L** vs. iron(III) chloride concentration ( $\lambda = 550$  nm).

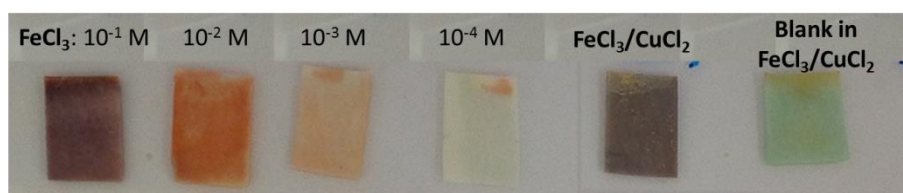


**Fig. 6.** (a) pH Effect on optode absorbance ( $\lambda=400$  nm); (b) Changes in absorbance of optode in the presence of  $\text{FeCl}_3$  ( $c = 1.60 \times 10^{-3}$  M) vs. time at pH= 2.9 ( $\lambda= 550$  nm).

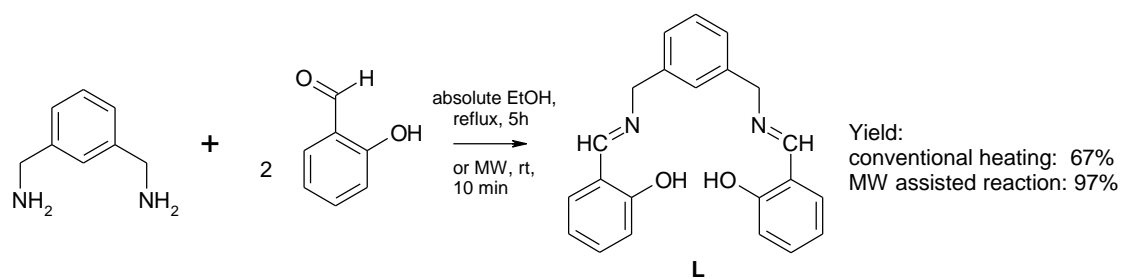




**Fig. 7.** (a) Interferences from several metal cations (10-fold molar excess) to the spectrophotometric response of optode with ligand **L** ( $\lambda = 550$  nm) towards FeCl<sub>3</sub> ( $c_{\text{salt}} = 1.60 \times 10^{-3}$  M) in HCl solution (pH=2.9); (b) Changes in optode response towards iron(III) before ( $A_0$ ) and after ( $A_1$ ) regeneration in 0.01 M EDTA solution and water ( $\lambda = 550$  nm).



**Fig. 8.** Changes of color of ligand ( $c_L = 4.10 \times 10^{-3} \text{ M}$ ) adsorbed on the test strip in the presence of different concentration of  $\text{FeCl}_3$  (from left) and mixture of  $\text{FeCl}_3/\text{CuCl}_2$  ( $c_{\text{Fe}} = 0.1 \text{ M}$ ,  $c_{\text{Cu}} = 1 \text{ M}$ ) in aqueous solution ( $\text{pH} = 2.9$ ). From right: color of test strip without ligand in the presence of  $\text{FeCl}_3/\text{CuCl}_2$  solution.



**Scheme 1.** Conventional or microwave-assisted (MW) synthesis of ligand **L**. Yield was added in scheme.

**Tab. 1** The comparison of the proposed sensor with some iron(III)-selective colorimetric reagents found in the literature

Colorimetric sensor	Linear range [M]	Detection limit [M]	Working media
Ref. [5]	n.d.	$1.7 \times 10^{-6}$	EtOH : Tris-HCl (1:1, v/v); pH 7
Ref. [6]	n.d.	$5.03 \times 10^{-8}$	CH <sub>3</sub> CN : H <sub>2</sub> O
Ref. [7]	$1 \times 10^{-6} - 1 \times 10^{-5}$	$1.9 \times 10^{-7}$	aqueous solution containing DMSO; pH 7
Ref. [11]	n.d.	$5.6 \times 10^{-7}$	EtOH : THF (99:1, v/v)
Ref. [12]	$1 \times 10^{-5} - 4 \times 10^{-4}$	$6.8 \times 10^{-6}$	DMF
Ref. [13]	n.d.	$1.18 \times 10^{-6}$	aqueous solution containing DMF; pH 7
Ref. [14]	n.d.	$9.5 \times 10^{-7}$	DMSO
Ref. [15]	$1 \times 10^{-9} - 1 \times 10^{-3}$	$6.2 \times 10^{-10}$	aqueous solution; pH 4.7
The proposed sensor	$8.1 \times 10^{-4} - 1.5 \times 10^{-2}$	$2.73 \times 10^{-6}$	aqueous solution; pH 2.9

n.d. not discussed