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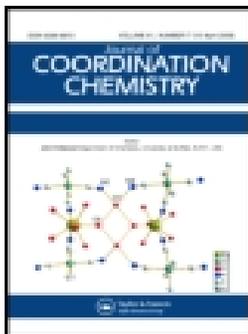
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Probe **1**, which contains an anilinopyridine chromophore and an aza-oxa macrocyclic subunit, presented an absorption band centered at 340 nm in acetonitrile. Addition of Fe(III), Cr(III) and Hg(II) induced growth of a new absorption band centered at *ca.* 430 nm (with a concomitant color change from colorless to yellow), whereas in the presence of Cu(II), Zn(II) and Pb(II) less marked changes were observed. The prominent color changes observed upon addition of Fe(III), Cr(III) and Hg(II) were ascribed to the formation of 1:1 stoichiometry complexes with probe **1**. Coordination of Fe(III), Cr(III) and Hg(II) with the pyridine fragment of **1** induced an enhancement of the charge transfer character accompanied with a marked bathochromic shift that was reflected in a color change from colorless to yellow. The strength of the interaction between probe **1** and Fe(III) cation was modulated upon interaction with selected anions. Moreover, of all the anions tested, only cyanide was able to induce the bleaching of the yellow **1**·Fe(III) complex solution. This bleaching was ascribed to the formation of **1**·Fe(III)-CN complex that restored, to some extent, the optical features of the free probe allowing the chromogenic sensing of cyanide; **1**·Fe(III) complex was used to detect cyanide in acetonitrile-water 90:10 v/v mixtures with good recoveries (in the 73-90% range).

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Anions play vital roles in biological systems but abnormal concentrations can cause several diseases [1]. Inside the vast realm of anions, cyanide is one of the most toxic and dangerous for the environment [2]. Concentrations of this anion in the 0.5–3.5 mg/kg body weight interval are lethal to humans. At these concentrations, cyanide strongly binds to the cytochrome c active sites resulting in inhibition of oxygen transport and cellular respiration with subsequent central nervous system damage [3]. However, despite its toxicity, cyanide is extensively used in the chemical industry. For instance, cyanide derivatives are used in metal mining processes (isolation of gold and silver from its ores), organic chemical industries (fabrication of nylon and other synthetic fibers and resins), wastewater treatment facilities and iron and steel plants. All these industries can potentially be sources of water contamination with cyanide. The World Health Organization (WHO) established a permissive concentration of cyanide in drinking water of 1.9 μM while in industrial effluents this level is fixed below 1 μM [4].

Taking into account the above mentioned facts, easy and affordable detection methods for cyanide are of interest. Currently, cyanide detection is achieved using colorimetric, titrimetic and electrochemical methods [5]. Among them, chromo-fluorogenic protocols for the detection of cyanide has attracted attention due to the high degree of selectivity usually achieved and the use of common and simple instrumentation or the visual detection to the naked eye [6]. In fact chromo-fluorogenic protocols are not time consuming and do not require trained personnel. Traditionally, chromo-fluorogenic sensors for anions have been developed using the "binding site-signaling unit" paradigm. In this approach a binding site, designed by taking into account the chemical features of the guest in order to achieve a high complementarity degree, is covalently linked with a signaling unit that is expected to transform the coordination event into an easily measurable optical macroscopic signal [7]. Another approach, developed by Anslyn and co-workers, is the use of a competition assay between a chromophore bounded to a receptor and a certain anion [8]. In a first step a sensing ensemble between a synthetic receptor and a dye/fluorophore was formed. In the presence of a target anion its coordination with the synthetic receptor displaced the dye/fluorophore to the solution. If the optical properties of the dye/fluorophore alone are different to that presented in the sensing ensemble an output signal is

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observed. Finally, the use of anion-induced chemical reactions coupled with color and/or emission changes have been extensively explored (chemodosimeter approach) [9].

Here we report the synthesis and chromogenic behavior of probe **1** that contains an aza-oxa macrocycle embedded in an anilinopyridine conjugated chromophore [10]. This chemosensor forms colored complexes with several metal cations that were characterized by the presence of a charge transfer band in the visible zone. Moreover, the **1**·Fe(III) complex is able to detect CN⁻; only the presence of cyanide induced a clear color change from yellow to colorless allowing the "naked eye" detection of this dangerous anion.
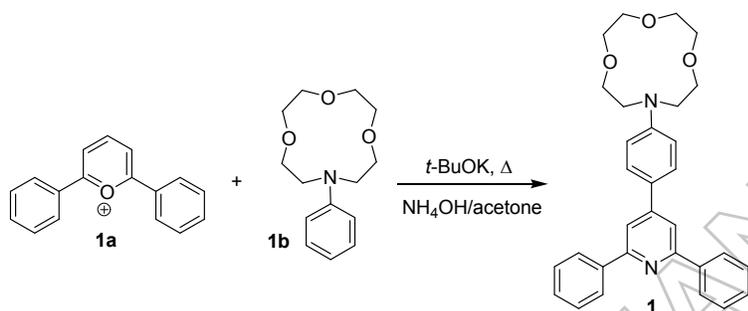
Scheme 1. Synthesis and structure of chemosensor **1**.

The synthesis of probe **1** was previously published [11]. However we used here a slightly modified procedure in order to enhance the yields for the preparation of **1b** and **1**. Briefly, an electrophilic aromatic substitution of 2,6-diphenylpyrylium perchlorate (**1a**) with 10-phenyl-10-aza-1,4,7-trioxacyclododecane (**1b**) in DMF at 150 °C was used to obtain **1**. Subsequent treatment with ammonium hydroxide and column chromatography with aluminum oxide afforded the desired receptor in 70% yield as a pallid yellow solid (see scheme 1). ¹H and ¹³C NMR, mass spectra and elemental analyses were in accord with the proposed formulation.

The chemical structure of **1** consists of a chromophore composed of an aniline donor unit (D) and a pyridine acceptor moiety (A) endowing charge transfer character to the probe [12]. Moreover, **1** contains two nitrogens with potential metal cation coordination ability. One nitrogen is located in the 2,6-diphenylpyridine subunit and the other in the aniline group. In spite of the fact that simple aniline derivatives weakly coordinate certain transition metal cations, the donor site of probe **1** was additionally functionalized with a small aza trioxa macrocycle as

"shielding group" [10]. This modification inhibits interaction with the aniline donor group and led to preferential coordination of metal cations with the pyridine unit (*vide infra*).

Acetonitrile solutions of probe **1** (9.0×10^{-5} M) show an absorption band centered at 343 nm with charge transfer features (see figure 1a). In fact, certain solvatochromism was observed for the probe. The absorption band of **1** was found at 333, 337 and 343 nm in hexane, diethyl ether and acetonitrile, respectively [11]. Figure 1b shows the color changes observed upon addition of one eq. of selected metal cations (Fe(III), Cr(III), Ni(II), Zn(II), Cu(II), Cd(II), Hg(II) and Pb(II)) to acetonitrile solutions of probe **1**. As could be seen, addition of Fe(III), Cr(III) and Hg(II) induced a bright yellow color due to the growth of a new absorption band centered at *ca.* 440 nm with molar absorptivities of 22450, 22110 and 21440 M^{-1} cm^{-1} for Fe(III), Cr(III) and Hg(II), respectively (see figure 1a). Other metal cations such as Cu(II), Zn(II) and Pb(II) changed the color of the solution to pale yellow, whereas Ni(II) and Cd(II) did not induce any noticeable color change (see also figure 1b). The color changes observed and the remarkable bathochromic shift of the absorption band, upon addition of Fe(III), Cr(III) and Hg(II), were ascribed to a preferential coordination of these metal cations with the 2,6-diphenylpyridine acceptor subunit of probe **1**. This coordination induced an increase in the charge transfer character of the band due to the higher electron deficiency of the pyridine acceptor subunit in the formed complexes. The pale yellow color observed in the presence of Cu(II), Zn(II) and Pb(II) indicated less affinity of these cations to probe **1**. Titration experiments of **1** with Fe(III), Hg(II), Cu(II), Zn(II) and Pb(II) clearly indicated the formation of 1:1 probe-metal stoichiometry complexes. From the titration data the log K values for the complex formation of probe **1** with the corresponding cations were calculated and are shown in table 1. The obtained log K values are similar to that found in the literature for other pyridine derivatives with transition metal cations [13].

Interference studies of the response of probe **1** toward Fe(III), Hg(II) and Cr(III) in the presence of the other selected cations was tested. The obtained results in the presence of one eq. of Ni(II) and Cd(II) are shown in figure 2. As could be seen, Ni(II) and Cd(II) were unable to modify the chromogenic response of probe **1** in the presence of Fe(III), Hg(II) and Cr(III) cations.

In a second step, the ability to chromogenically detect anions using the $\mathbf{1} \cdot M^{+n}$ complexes as probes was tested. For this purpose, potential color changes of acetonitrile solutions of $\mathbf{1} \cdot M^{+n}$

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complexes (9.0×10^{-5} M) were studied in the presence of selected anions (*i.e.* fluoride, chloride, bromide, iodide, acetate, benzoate, cyanide, nitrate, dihydrogenphosphate and hydrogensulfate). Complexes **1**·Cu(II), **1**·Pb(II) and **1**·Zn(II) presented low levels of selectivity (data not shown). For instance yellow solutions of **1**·Cu(II) turned colorless in the presence of fluoride, acetate, cyanide and dihydrogenphosphate. Moreover, yellow acetonitrile solutions of **1**·Pb(II) and **1**·Zn(II) became colorless with fluoride, chloride, acetate, benzoate, cyanide, dihydrogenphosphate and hydrogensulfate. In contrast, a more selective response was obtained with **1**·Hg(II) and **1**·Fe(III) complexes. Figure 3 shows the UV-vis spectra and the color changes observed upon addition of selected anions to acetonitrile solutions of **1**·Fe(III) (9.0×10^{-5} M). Of all the anions tested, only cyanide was able to induce a nearly complete disappearance of the charge-transfer band of the **1**·Fe(III) complex (figure 3a). This fact was reflected in a complete bleaching of the yellow **1**·Fe(III) complex solution (figure 3b). A similar behavior, in terms of UV-visible and color changes, was observed for the **1**·Hg(II) complex in the presence of selected anions. Titration experiments of acetonitrile solutions of **1**·Fe(III) with cyanide showed the formation of 1:1 stoichiometry adducts. Log K value for the **1**·Fe(III)·CN$^-$ adduct formation, calculated through nonlinear least-squares treatment of the titration profile, was 6.6 ± 0.2.

In order to understand the chromogenic behavior observed in the presence of cyanide with **1**·Hg(II) and **1**·Fe(III) complexes, ^{1}H NMR studies were performed. ^{1}H NMR in the presence of Fe(III) cannot be carried out due to the paramagnetic character of the iron cation, but a similar coordination behavior with cyanide to that shown by Hg(II) complex was expected to occur. ^{1}H NMR studies on the **1**·Hg(II) system clearly showed that metal cation coordinated with the 2,6-diphenylpyridine acceptor moiety. At this respect, the singlet of the pyridine protons centered at 7.72 ppm was shifted downfield to 7.85 ppm whereas the *ortho* protons of the monosubstituted benzene rings were shifted upfield from 8.16 to 7.90 ppm. Besides the other protons of the monosubstituted benzene were shifted by +0.10 ppm. The observed changes together with the fact that macrocycle protons suffers negligible shifts (between 0.01 and 0.03 ppm) pointed to a preferential coordination of Hg(II) cation with the pyridine ring. Upon addition of cyanide, the ^{1}H NMR of **1** is not completely retrieved, suggesting that cyanide coordinates with the cation, forming a ternary molecular adduct, without completely removing Hg(II) from the pyridine heterocycle [11]. Coordination of cyanide with the metal bounded with probe **1** diminished the strength of the cation-pyridine interaction with subsequent reduction of

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the charge transfer character in the final adduct (see scheme 2). This reduction in the charge transfer character was the responsibility of the hypsochromic shift observed upon cyanide addition to solutions of **1**·Hg(II) and **1**·Fe(III) complexes.
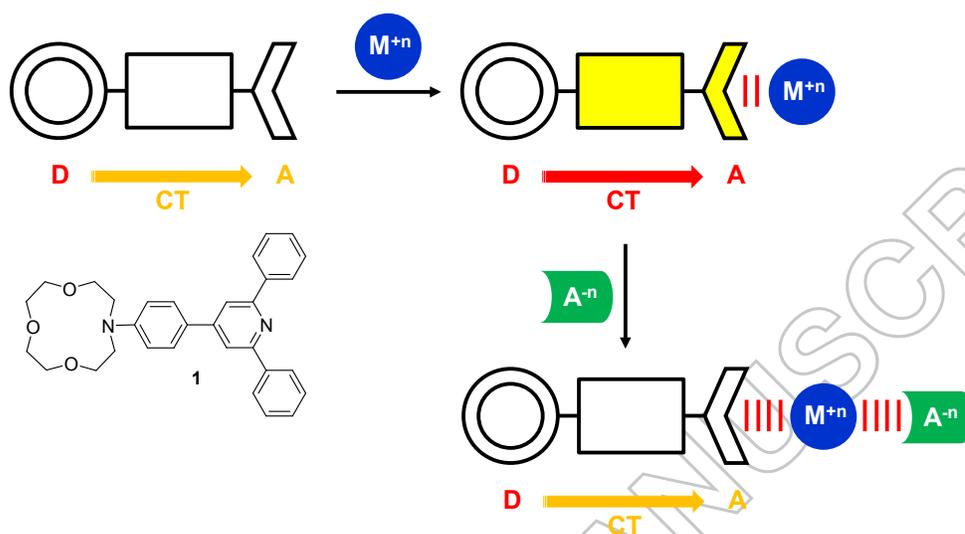
Scheme 2. Signaling protocol for chromogenic cyanide recognition using coordinative complexes of probe **1** with metal cations. D is the donor part of the probe (aniline) whereas A designed the acceptor region (pyridine). CT indicated the charge transfer nature of the electronic transition in the free probe and in the complexes. The strength of the CT is indicated by a colored arrow (orange for a weak CT and red for a stronger CT).

Finally, in order to test the potential utility of **1**·Fe(III) complex for the selective detection of cyanide in water further experiments were carried out [14]. Although the above described selective chromogenic behavior was not perceived in pure water it was still observed in acetonitrile-water 90:10 v/v mixtures. Therefore we used calibration curves for cyanide in acetonitrile-water 90:10 v/v solutions (see figure 4) for cyanide determination in water. From figure 4 a limit of detection for cyanide in acetonitrile-water 90:10 v/v solutions was calculated to be 3.16×10^{-5} M. The limit of detection concurs with the inflection point of the two slopes observed for the concentration range studied. In a typical experiment for the detection of cyanide, 0.5 mL of water containing a certain amount of cyanide was mixed with 4.5 mL of an acetonitrile solution containing the **1**·Fe(III) complex. Cyanide solution in water also contained other typically water-present anions (chloride, nitrate, sulfate, sodium and potassium in

concentration ranges $1.0 \times 10^{-4} - 8.0 \times 10^{-4}$ M). Using the calibration curve shown in figure 4 the concentration of cyanide was determined quite accurately in different water samples (see table 2) with recoveries in the 73-90% range.

In summary, we have shown herein the synthesis and characterization of new chromogenic cyanide sensors based on Fe(III) and Hg(II) complexes of an anilinopyridine-containing derivative (**1**). The method uses a colorless probe that is switched ON (yellow color) in the presence of certain metal cations. This produces the colored **1**·Fe(III) and **1**·Hg(II) complexes that are selectively bleached (switched OFF) by the cyanide anion. Further studies will be carried out to determine the applicability of this simple method for the determination of cyanide in a large range of locations.

Experimental

Materials and methods

Commercially available reagents were used without purification. Air/water-sensitive reactions were performed in flame-dried glassware under argon. Acetonitrile was dried with CaH_2 and distilled prior to use. Perchlorate salts of Cr(III), Pb(II), Fe(III), Ni(II), and Cd(II) and triflate salts of Hg(II) and Zn(II) were purchased from Aldrich, whereas the triflate salt of Cu(II) was purchased from Acros. The selected anions (fluoride, chloride, bromide, iodide, acetate, benzoate, cyanide, nitrate, dihydrogenphosphate and hydrogensulfate) were used as tetrabutylammonium salts and were purchased from Aldrich. UV-visible spectra were recorded with a JASCO V-650 spectrophotometer. ^{1}H and ^{13}C-NMR spectra were acquired in a BRUKER AVANCE III (400 MHZ), where mass spectra were carried out in a TRIPLETOF T5600 (ABSciex, USA) spectrometer.

Synthesis of 10-phenyl-10-aza-1,4,7-trioxacyclododecane (1b)

In a typical procedure *N,N*-phenyldiethanolamine (1 g, 5.5 mmol) was dissolved in anhydrous acetonitrile (100 mL) in an inert atmosphere (Ar). Then, potassium *tert*-butoxide (1.54 g, 13.7 mmol) was added at room temperature in small portions during 180 min. Afterward the crude solution was heated to reflux and 3-oxapentane-1,5-dimethanesulfonate (1.44 g, 5.5 mmol) was slowly added during 10 h. The reaction was refluxed overnight. The crude was filtered off and concentrated in a rotary evaporator to give an orange oil. This oil was then purified through

column chromatography using aluminium oxide and dichloromethane as eluent to give 10-phenyl-10-aza-1,4,7-trioxacyclododecane (**1b**) as a pale yellow oil (0.83 g, 3.3 mmol, 60% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.55 (t, 4H), 3.64 (m, 8H), 3.83 (t, 4H), 6.68 (t, 2H), 6.70 (d, 1H), 7.18 (t, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 52.4, 69.6, 69.8, 71.5, 112.2, 116.0, 129.0, 148.4. HRMS-EI m/z: calcd for C$_{14}$H$_{21}$NO$_5$ 251.1521; found: 252.1603 (M+H$^+$).

Synthesis of probe 1

10-Phenyl-10-aza-1,4,7-trioxacyclododecane (**1b**, 350 mg, 1.39 mmols) and 2,6-diphenylpyrylium perchlorate (**1a**, 925 mg, 2.78 mmols) were dissolved in anhydrous dimethylformamide (15 mL) and heated at 150 °C for six hours. Then, and at room temperature, diethyl ether (60 mL) was added and the crude reaction was stirred overnight. A magenta oil precipitate was separated by decantation. This magenta oil was dissolved in dry acetone and excess of ammonium hydroxide were added. The crude was concentrated in a rotary evaporator and then purified through column chromatography using dichloromethane-hexane 1:1 v/v as eluent. Probe **1** was obtained as pale yellow solid (468 mg, 0.97 mmol, 70% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.62 (m, 12H), 3.90 (t, 4H), 6.84 (d, 2H), 7.41 (t, 3H), 7.47 (t, 3H), 7.63 (d, 2H), 7.72 (s, 2H), 8.16 (d, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 53.1, 70.1, 70.5, 72.1, 113.2, 116.5, 127.7, 128.4, 129.2, 129.4, 140.6, 150.0, 150.4, 157.9. HRMS-EI m/z: calcd for C$_{31}$H$_{32}$N$_2$O$_3$ 480.2413; found: 481.2489 (M+H$^+$).

Stability constants of selected metal ion complexes of 1

The intensity of the 440 nm band of 9.0×10^{-5} M solutions of **1** in acetonitrile was monitored during a titration with increasing amounts of the metal ions Fe(III), Hg(II), Cu(II), Zn(II) and Pb(II), which allowed us to determine the complex stability constants. In these three cases, the formation of 1:1 ligand-to-metal complexes was found and the calculated log*K* values, through nonlinear least-squares fitting of the titration profiles, are provided in table 1.

Interaction of 1 with metal cations

The interaction of **1** with certain cations was studied by UV-Vis spectrophotometry. Receptor **1** consists of an anilino-type donor moiety attached through a single bond to a 2,6-diphenylpyridine acceptor group, exhibiting π electron delocalization over the entire

chomogenic system. As a consequence, **1** shows an intramolecular charge transfer band, typical for such donor-acceptor-substituted dyes, centered at 340 nm in acetonitrile. Upon addition of different metal cations to **1** in acetonitrile, three different behaviors were observed.

- The addition of the metal cations Fe(III), Cr(III) and Hg(II) induced the development of a new band at *ca.* 430 nm with the corresponding change of the solution from colorless to yellow. This bathochromic shift of the charge transfer band is consistent with a coordination-induced increase in the acceptor strength of the pyridine unit and thus attributed to coordination of the metal ions to the pyridine group. Less marked color changes were observed upon addition of Cu(II), Zn(II) and Pb(II), indicating a weaker affinity of these cations for probe **1**.

- Several other first row transition metal cations, such as Ni(II) and Cd(II), are unable to change the UV-Vis spectral profile of receptor **1** distinctly at micromolar concentrations, suggesting that no coordination takes place.

Cyanide detection using 1·Fe(III) complex

In a typical experiment 0.5 mL of water containing cyanide (0.80, 2.35 and 3.54 ppm) was mixed with 4.5 mL of an acetonitrile solution containing the **1**·Fe(III) complex. Cyanide solution in water also contained other typically water-present anions (chloride, nitrate, sulfate, sodium and potassium in concentration ranges $1.0 \times 10^{-4} – 8.0 \times 10^{-4}$ M). Then, the absorbance of the resulting mixture was measured and the concentration of cyanide measured using the calibration curve shown in figure 3. Cyanide was determined quite accurately in the different water samples with recoveries in the 73-90% range.

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Table 1. Values of the logarithm of the stability constant for formation of metal complexes with probe **1**. Values in parentheses are standard deviation of the last digit.

Fe(III)	Hg(II)	Cu(II)	Zn(II)	Pb(II)
6.90(2)	5.11(1)	6.40(2)	4.30(1)	3.81(1)

Table 2. Concentration of cyanide (in ppm) in different samples of water.
Concentration of cyanide was determined using the calibration curve in figure 3.

| Real concentration (ppm)	Determined using **1**·Fe(III) (ppm)	Recovery (%)
0.80	0.72	90
2.35	1.72	73
3.54	2.83	80
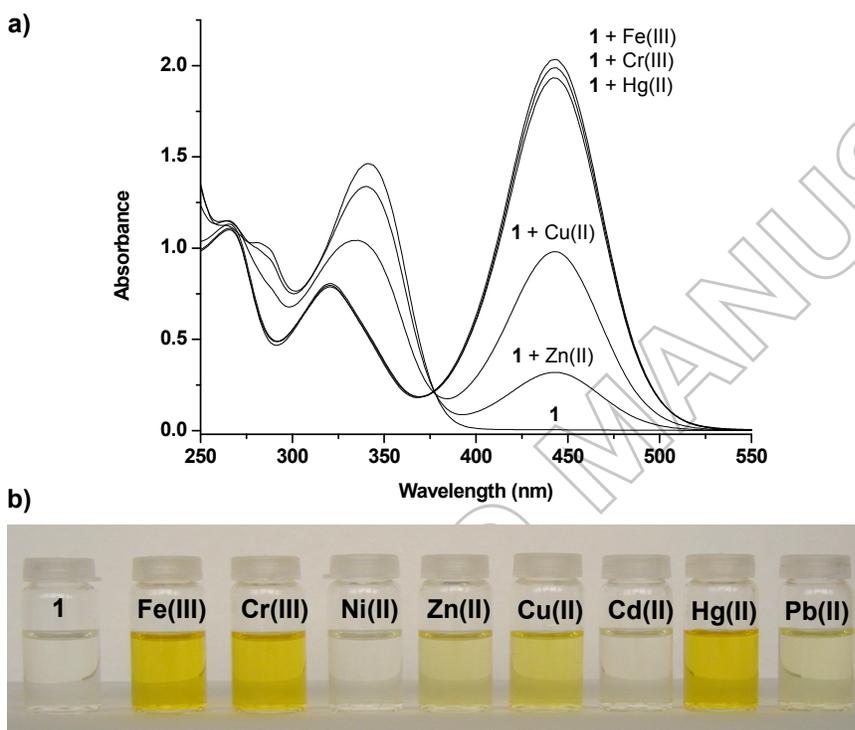
Figure 1. a) UV-visible spectra of probe **1** (9.0×10^{-5} M in acetonitrile) alone and in the presence of one eq. of selected metal cations. b) Color changes observed upon addition of one eq. of selected metal cations to acetonitrile solutions of probe **1** (9.0×10^{-5} M).
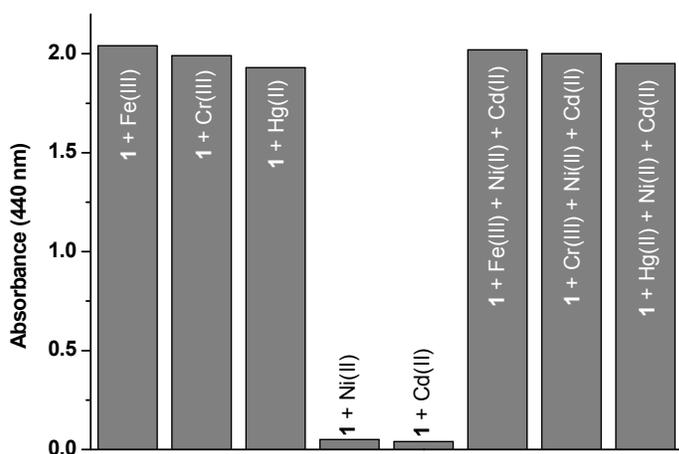
Figure 2. Absorbance at 440 nm of acetonitrile solutions of probe **1** (9.0×10^{-5} M) in the presence of one eq. of selected metal cations.
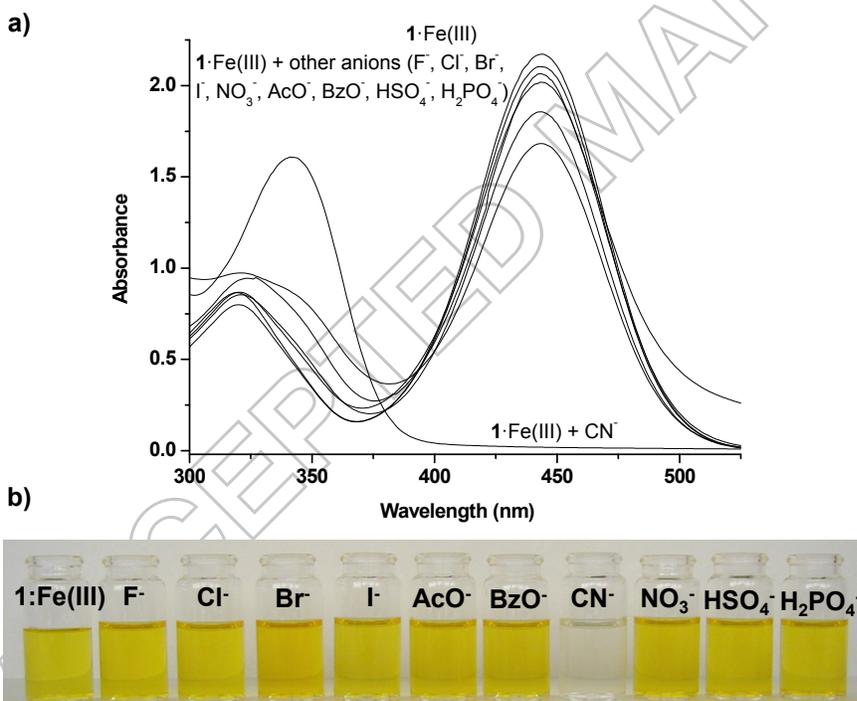

Figure 3. a) UV-visible spectra of complex **1**·Fe(III) (9.0×10^{-5} M in acetonitrile) alone and in the presence of one eq. of selected anions. b) Color changes observed upon addition of one eq. of selected anions to acetonitrile solutions of complex **1**·Fe(III) (9.0×10^{-5} M).
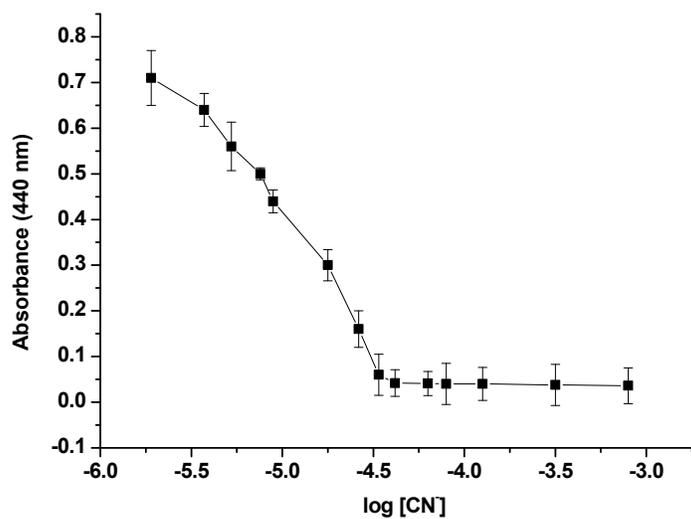
Figure 4. Absorbance at 440 nm for **1**·Fe(III) complex (1.0×10^{-4} M) in acetonitrile-water 90:10 v/v mixture upon addition of increasing quantities of cyanide.

Graphical abstract