Electronic Supplementary Information:
Iron(III)-selective materials based on catechol-bearing amide for optical sensing

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Synthesis of amide ***L***

Compound 1: a mixture of 3,4-dihydroxybenzoic acid (5.6 g, 36.5 mmol), acetic anhydride (14 mL, 148 mmol), and a drop of conc. sulfuric acid was magnetically stirred for 15 minutes at 55 °C. Subsequently, it was poured to cold, distilled water (75 mL). The resulting precipitate was filtered off and crystalized from an aqueous ethanol solution (c= 15%). Yield: 66%; $R_f = 0.09$ ($CHCl_3$: acetone, 10:1, v/v); ^1H NMR (200 MHz, d_6-DMSO, δ [ppm]): 2.28 (3H, s), 2.29 (3H, s), 7.40 (1H, d, *J*= 8.8 Hz), 7.79 (1H, s), 7.87 (1H, d, *J*= 8.8 Hz), 13.3 (1H, s).

Compound 2: to the round-bottom two-neck flask, containing compound **1** (1.6 g, 7 mmol) and DMF (0.2 mL), thionyl chloride (0.6 mL, 8.2 mmol) was added stepwise within 15 minutes. Reaction mixture was magnetically stirred for 40 minutes at 50°C. Subsequently, the excess of thionyl chloride was evaporated under reduced pressure. The obtained acid chloride was used without purification in the next step.

Compound 3: to the solution of *p*-nitroaniline (1.4 g, 10 mmol) in dry pyridine (10 mL) the solution of the acid chloride from previous step (compound 2) in dry acetone (25 mL) was added within 30 minutes. The reaction mixture was magnetically stirred at room temperature for 1 hour and next, it was poured to cold, distilled water (50 mL). The organic products were extracted with dichloromethane (5×10 mL). The organic extracts were combined, washed with 1 M HCl (5×10 mL), with saturated $NaHCO_3$ (10 mL) and subsequently dried with anhydrous $MgSO_4$. The resulting solution was concentrated under reduced pressure. The pure product **3** was obtained after crystallization from an aqueous solution of ethanol (c= 75%). Yield: 58%; R_f= 0.69 ($CHCl_3$: acetone, 10:1, v/v); ^1H NMR (500 MHz, d_6-DMSO, δ [ppm]): 2.33 (3H, s), 2.34 (3H, s); 7.48 (1H, d; *J*= 8.6 Hz); 7.89-7.97 (3H, m); 8.04 (2H, d, *J*= 9.3 Hz); 8.28 (2H, d, *J*= 9.3 Hz); 10.86 (1H, s, NH).

Compound L: compound **3** (1.4 g, 5 mmol) was added to 10 mL of 1 M KOH. The reaction mixture was magnetically stirred at 50°C until the compound was completely dissolved. Then the reagents were cooled to room temperature and neutralized with 1 M HCl. The obtained precipitate was filtered off and crystalized from the aqueous ethanol solution (75 %). Yield: 41%; mp = 271°C; R_f= 0.47 (CH_2Cl_2:MeOH, 10:1, v/v); FTIR (KBr pellet) cm^{-1}: 3523, 3382, 3181, 1648, 1611, 1592, 1511, 1486, 829, 748; ^1H NMR (500 MHz, d_6-DMSO, δ [ppm]): 6.85 (1H, d, *J*=9.3 Hz); 7.38-7.43 (2H, m); 8.04 (2H, d, *J*= 9.4 Hz); 8.24 (2H, d, *J*=9.4 Hz); 9.50 (2H, s, OH); 10.51 (1H, s, NH); ^{13}C NMR (125 MHz, d_6-DMSO, δ [ppm]): 115.7; 116.3; 120.2; 120.9; 125.5; 125.7; 142.7; 145.8; 146.7; 150.3; 166.6; HRMS(EI) m/z: [M$^+$]: 273.0505 for compound $C_{13}H_9N_2O_5$, calculated: 273.0511; UV-Vis (DMSO): λ(ε)= 345 nm (1.9×10^4).

Spectral characterization of amide ***L***

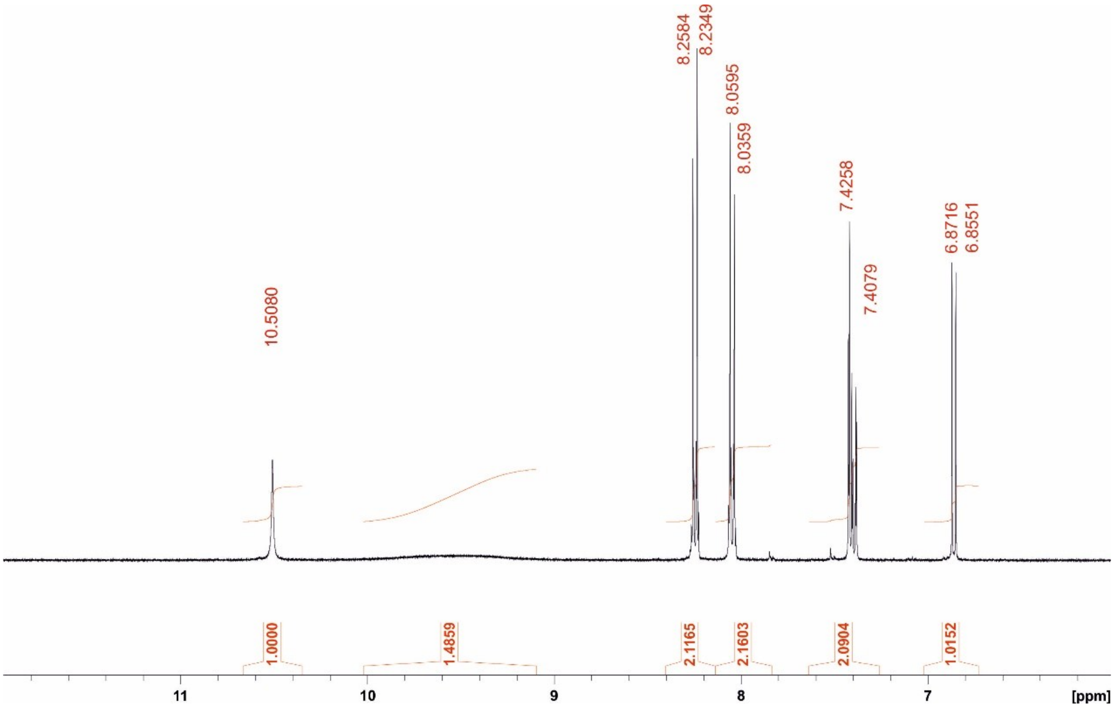
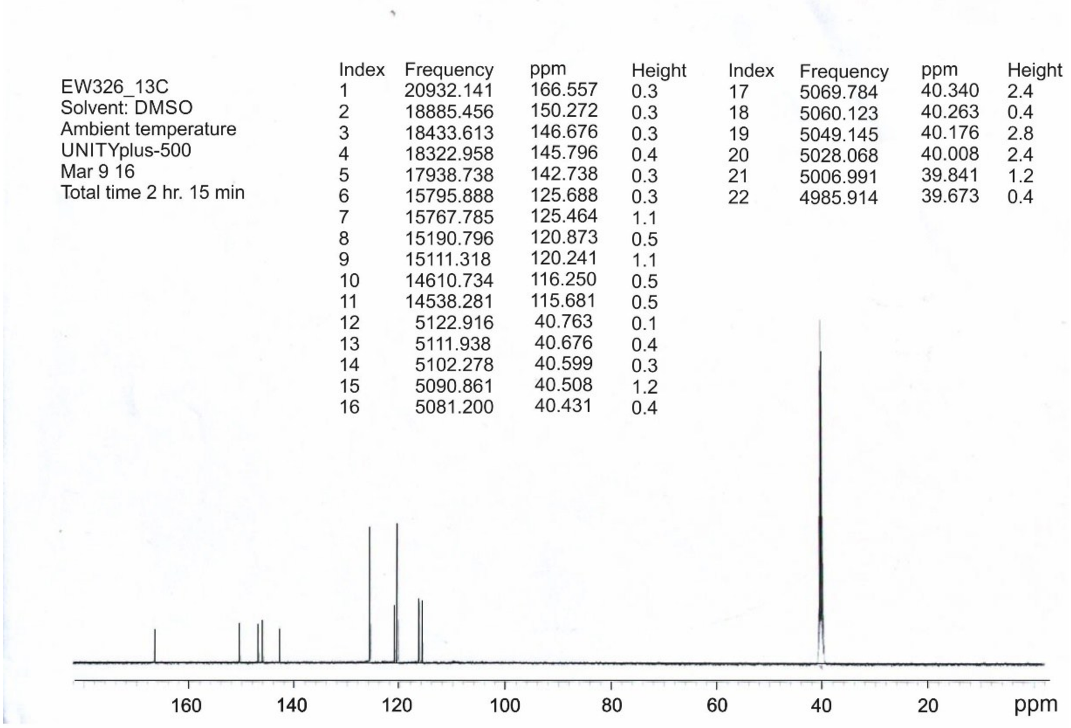
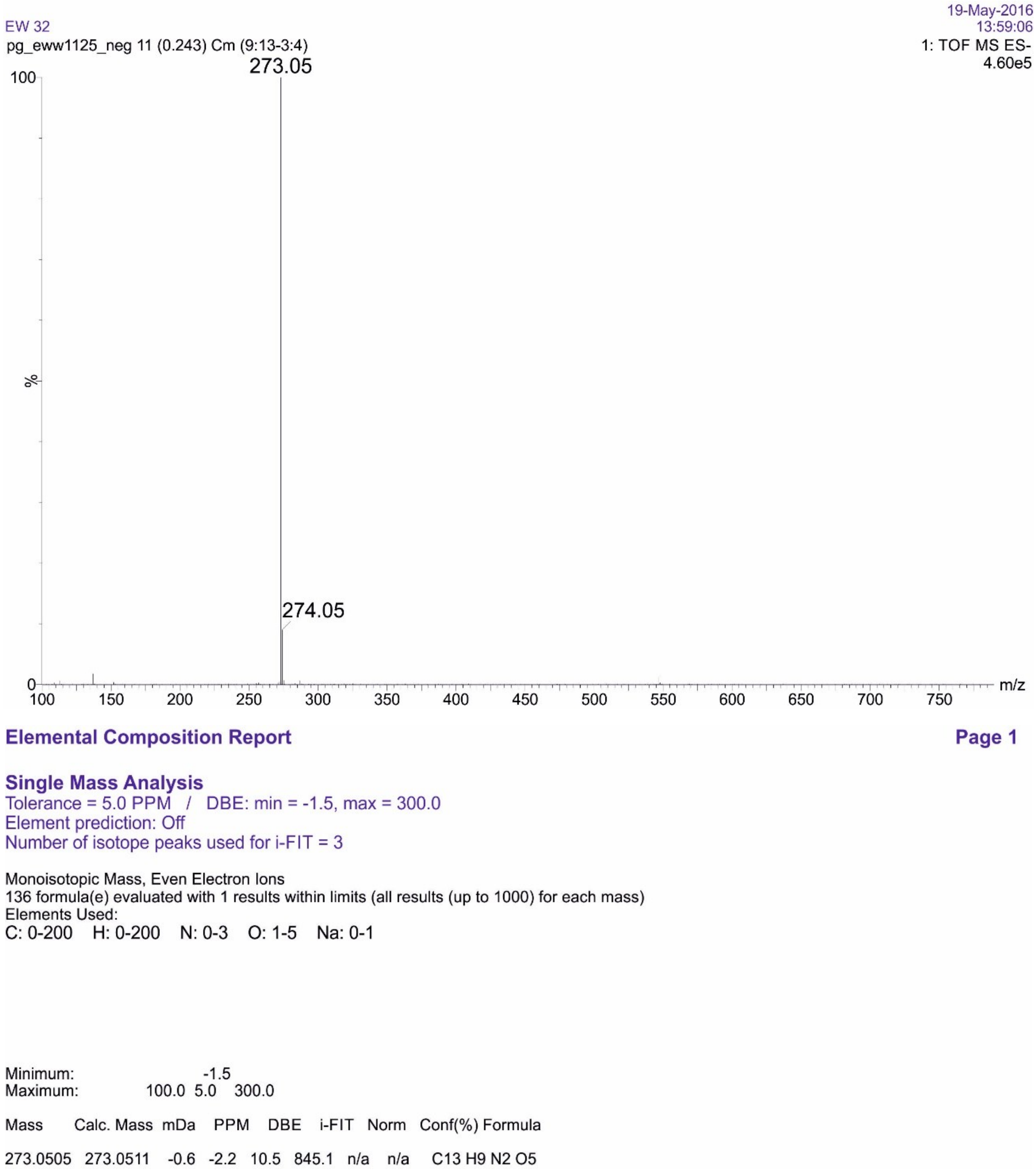


Fig. ESI 1 ^{1}H NMR spectrum (500 MHz) of ligand **L** in *d$_6$*-DMSO.


EW326_13C
Solvent: DMSO
Ambient temperature
UNITYplus-500
Mar 9 16
Total time 2 hr. 15 min

Index	Frequency	ppm	Height
1	20932.141	166.557	0.3
2	18885.456	150.272	0.3
3	18433.613	146.676	0.3
4	18322.958	145.796	0.4
5	17938.738	142.738	0.3
6	15795.888	125.688	0.3
7	15767.785	125.464	1.1
8	15190.796	120.873	0.5
9	15111.318	120.241	1.1
10	14610.734	116.250	0.5
11	14538.281	115.681	0.5
12	5122.916	40.763	0.1
13	5111.938	40.676	0.4
14	5102.278	40.599	0.3
15	5090.861	40.508	1.2
16	5081.200	40.431	0.4
17	5069.784	40.340	2.4
18	5060.123	40.263	0.4
19	5049.145	40.176	2.8
20	5028.068	40.008	2.4
21	5006.991	39.841	1.2
22	4985.914	39.673	0.4

Fig. ESI 2 ^{13}C NMR spectrum (125 MHz) of ligand **L** in *d$_6$*-DMSO.



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Elemental Composition Report                                          Page 1

Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 300.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
136 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-200    H: 0-200    N: 0-3    O: 1-5    Na: 0-1


Minimum:                     -1.5
Maximum:           100.0  5.0    300.0

Mass      Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%) Formula

273.0505   273.0511   -0.6   -2.2   10.5   845.1   n/a    n/a     C13 H9 N2 O5
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Fig. ESI3 Mass spectrum (TOF MS ES-) of ligand **L**.

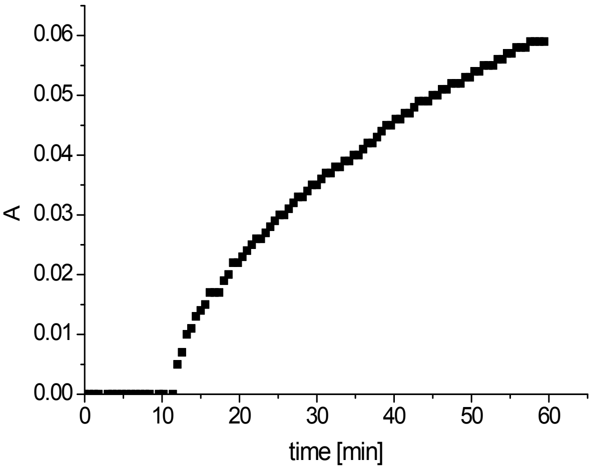


Fig. ESI4 Changes of absorbance of amide **L** solution (c = 5.08×10^{-5} M, λ = 700 nm) in DMSO in the presence of equimolar amount of iron(III) nitrate *vs.* time.

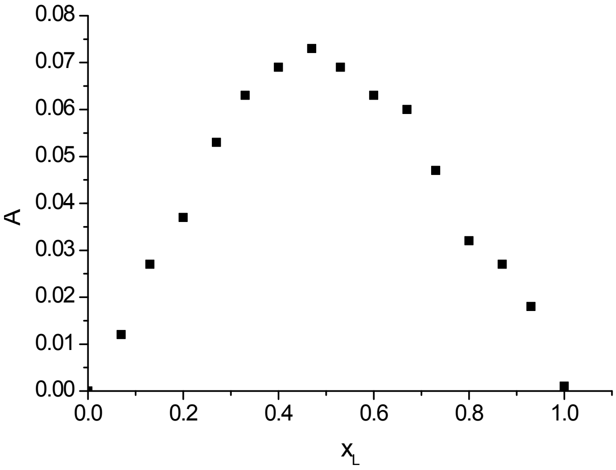


Fig. ESI5 Job plot for **L**-iron(III) system in DMSO (c_L = 10^{-4} M, c_s = 10^{-4} M, λ = 700 nm).

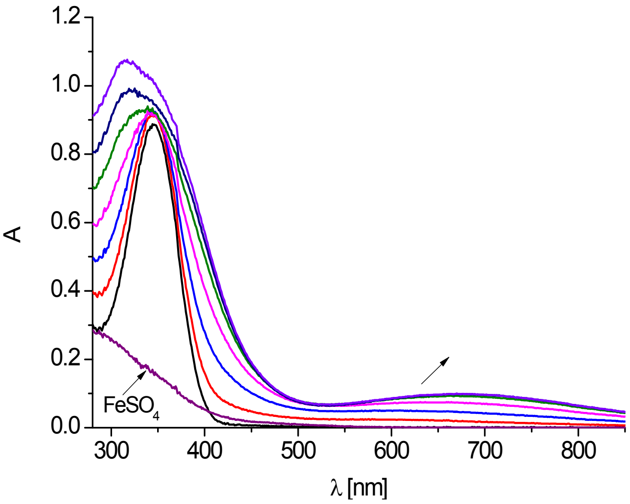


Fig. ESI6 Spectral changes in ligand **L** solution (c = 4.28×10^{-5} M) in the presence of iron(II) sulfate(VI) (0-2.57×10^{-4} M) in DMSO. Spectrum of “free” salt (purple line) is also added.

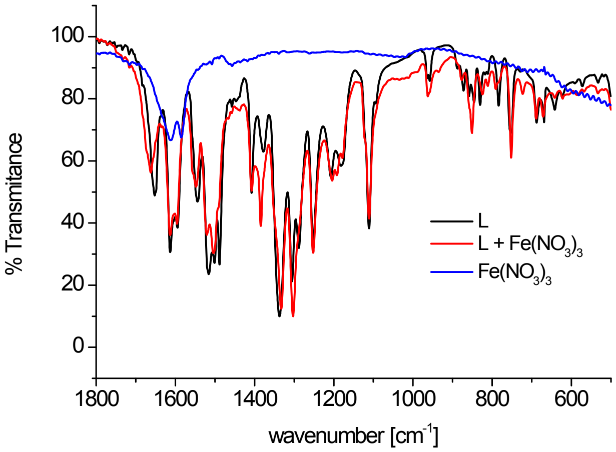


Fig. ESI7 Comparison of partial (1800-500cm^{-1}) FTIR (KBr pallets) spectra of “free” amide **L**, **L**-Fe^{3+} complex (L:Fe^{3+} molar ratio 1:1), and iron(III) nitrate.

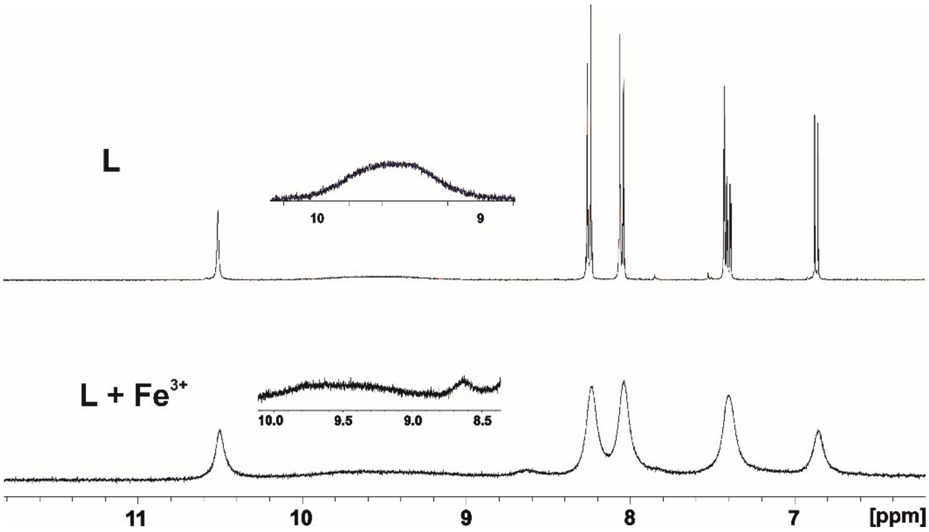


Fig. ESI8 Comaprison of ^{1}H NMR spectra of the ligand **L** solution (c = 13.6 mM) (top) and its complex with iron(III) nitrate (L : Fe^{3+} = 1:1, w/w) (bottom) in DMSO-*d*$_6$.

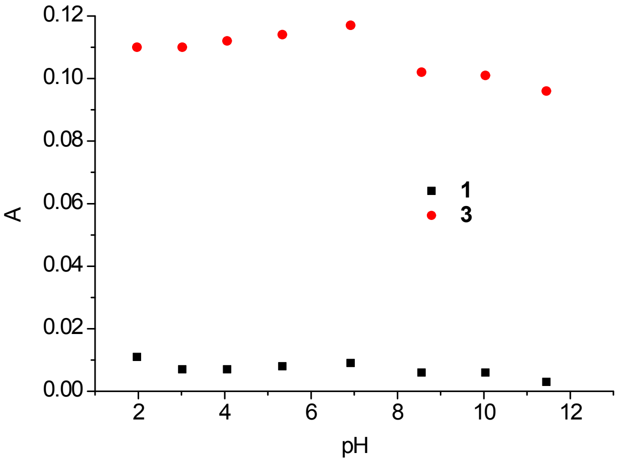


Fig. ESI9 Measurement of the absorbance of amide **L** incorporated into polymeric matrix (**1**- cellulose triacetate, **3**- PVC) as a function of pH (λ = 700 nm).

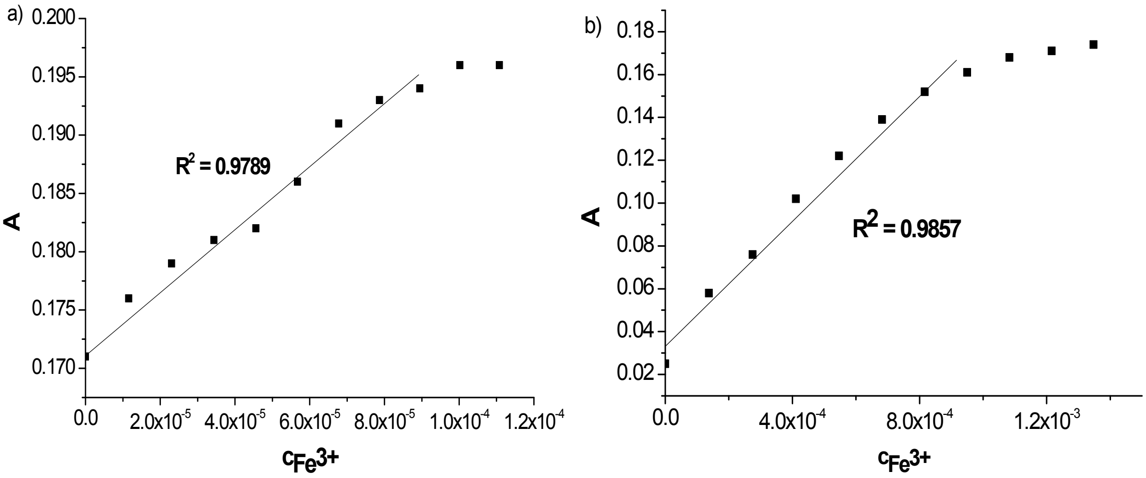
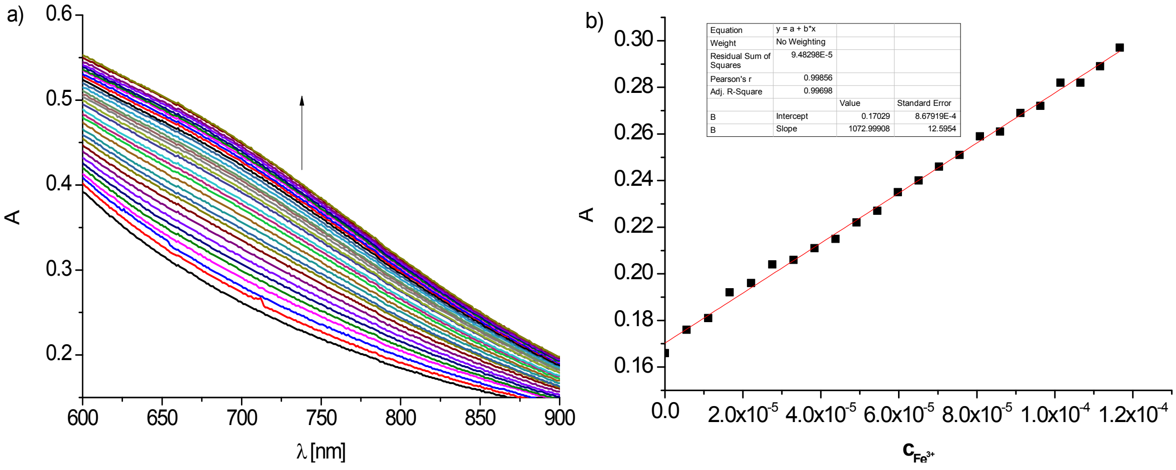


Fig. ESI10 Absorbance of optode a) **1**; b) **3** with compound **L** *vs.* concentration of iron(III) nitrate(V) (λ = 700 nm) at pH 2.9.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	9.48298E-5		
Pearson's r	0.99856		
Adj. R-Square	0.99698		
		Value	Standard Error
B	Intercept	0.17029	8.67919E-4
B	Slope	1072.99908	12.5954

Fig. ESI111 a) Changes in UV-Vis spectrum of amide **L** encapsulated into nanospheres **4** with NPOE in the presence of iron(III) nitrate (c = 0 – 1.27×10^{-4} M); b) Absorbance of **L** in nanospheres **4** *vs*. concentration of iron(III) nitrate (λ = 700 nm) in nitric(V) acid solution (pH 2.9).

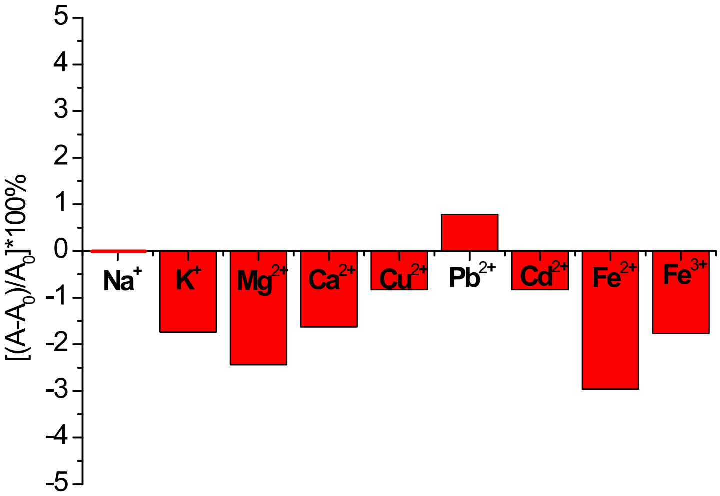


Fig. ESI12 Absorbance changes (λ = 700 nm) of “blank” micelles (without ionophore) in the presence of metal cations (c~ 5×10^{-4} M) registered in nitric acid solution (pH 2.9).