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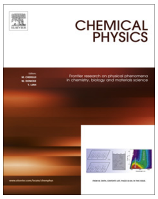

The solvatochromic behavior and degree of ionicity of a synthesized pentacyano (N-substituted-4,4′-bipyridinium) ferrate(II) complex in different media. Tuning the solvatochromic intensity in aqueous glucose solutions

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ABSTRACT

A new solvatochromic pentacyanoferrate(II) complex with a 4,4′-bipyridine based dicationic ligand was synthesized and characterized. Its chromotropic behavior markedly affected by solvent polarity was examined in different media *i.e.* neat solvents, binary solvent mixtures, and aqueous glucose solutions, and quantified using suitable solvent polarity parameters. The metal to ligand charge transfer (MLCT) energy shows a linear correlation with the Reichardt solvent polarity parameter as well as the Kirkwood dipolarity function and suitable functions expressing polarizability. Using suitable Linear Solvation Energy Relationships (LSERs) it was concluded that mainly specific solute–solvent interactions contribute to the solvatochromic phenomenon. The investigation of the solvatochromic behavior of the title compound in aqueous glucose solutions revealed a different response to medium polarity. Tuning of the solvatochromic intensity of the title compound by changing the type of medium was further studied focusing on aqueous glucose solutions.

1. Introduction

Pentacyanoferrate(II) complexes with suitable electron accepting ligands, are a widely known class of solvatochromic coordination compounds [1–5]. Their intense solvatochromism resulting from the solvent polarity dependent metal-to-ligand-charge-transfer (MLCT) is pronounced in systems possessing the electron-donating Fe^{II} center coordinated to an electron-deficient ligand, such as aryl-substituted 4,4′-bipyridines [6], 4-aryl or 4-heteroaryl-substituted 4′-vinylpyridines [7], or N-methyl-pyrazine [8]. Their medium responsive character has been shown to be affected by Lewis acidity [6] and hydrogen-bond-donor (HBD) acidity [7], as well as the dipolarity and polarizability of solvents [6,7,9]. They present negative solvatochromism attributed to the lowering of the dipole moment in their excited states with respect to their ground states [10]. The latter effect results in bathochromic shifts of the visible MLCT bands in their electronic absorption spectra, by decreasing solvent polarity. The changes in most of the cases are obvious by naked-eye [1]. Their intense responses to small solvent polarity changes (*e.g.* between water and methanol) have been also reported [6–8]. The aforementioned marked medium responsive character reinforced their use as sensors of special modifiers in mutual aqueous solutions. Pinheiro et al. used a tetracyano Ru^{II} solvatochromic complex as a sensor of traces of water in aprotic organic solvents [11]. In this work the solvatochromic behavior of a new synthesized and fully-characterized pentacyanoiron(II) complex in different media, including aqueous glucose solutions, neat solvents and binary solvent mixtures is examined, taking into account both specific and non-specific solute–solvent interactions. To the best of the author's knowledge, just a few works related to the use of medium responsive probes in glucose solutions have been published so far. The work of Spange et al. for the determination of the values of E_T^N (normalized Reichardt polarity scale [10]) of aqueous and DMSO sugar solutions, and the solvatochromic parameters α and π^* (HBD acidity and dipolarity/polarizability parameters respectively of the Kamlet, Abboud and Taft equation [12]) of sugar DMSO solutions, being the most significant [13]. Nevertheless the use of pentacyanoiron(II) complexes for such a purpose has never been reported, albeit the use of the latter complexes can give valuable informations for Lewis and HBD-acidity as well as dipolarity and polarizability of aqueous glucose solutions. Besides, using different probes leads to a better understanding of the solvating ability, dielectric effects as well as specific solute–solvent effects in glucose solutions. The

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rationalization of the aforementioned effects are of high interest mainly because of the biological importance of glucose. For that purpose suitable solvatochromic probes such as the title complex can be used. Since glucose modifies significantly both dipolarity [14,15] and polarizability [16] as well as Lewis acidity of water [13], a pentacyanoferrate(II) complex could serve as suitable solvatochromic probe. In this work the degree of ionicity of the title compound which is a measure of solvatochromic intensity (degree of charge transfer) in all types of media examined, was determined and its relation with the medium responsive character of the title compound is discussed. Rationalizing the different responses of the MLCT energy of the title compound, strongly dependent on the type of medium, leads to the ability of controlling solvatochromic intensity.

2. Experimental part

2.1. Materials and methods

All products were purchased from ACROS Organics. The solvents were HPLC-grade and they were purified prior to use, according to literature [17]. Water was purified with a Barnstead EASY pure RF compact ultrapure water system and then distilled twice. Experimental details regarding the synthesis of compounds **1**–**4**, in Supporting Information: Paragraphs 1.1–1.3.

2.2. Physical measurements

NMR spectra were obtained using a Varian Gemini 300 spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C). ^{1}H spectra were recorded in D_2O at 25 ± 1 °C. The ^{13}C NMR spectra were recorded in D_2O containing drops of DMSO-d_6. ^{1}H NMR spectra were calibrated by using residual undeuterated solvent peak. UV–Vis spectra were recorded using a Varian CARY 1E UV–Vis spectrophotometer. Regarding the solvatochromism of compound **4**, typically solutions with a concentration of 750 ppm (approx. 1 mM) were prepared right before any measurement, and measured at 25 ± 1 °C. Each measurement was repeated three times; therefore, each of the values of MLCT energies listed in Tables 1 and 2 correspond to the average of three measurements (standard deviation 0.5 nm). IR spectra were recorded on a Perkin–Elmer Spectrum 1 FTIR spectrophotometer in the solid state (without any preparation of the samples) using the attenuated total reflectance technique (ATR) in the region 600–4000 cm^{-1}. Elemental analyses were performed on a Perkin–Elmer Elemental Analyzer 2400 CHN. Thermogravimetric analyses (TGA) were performed under N_2 on a Mettler Toledo TGA/SDTA 851. Finally cyclic voltammetry measurements were performed in aqueous NaCl solutions 1 M, using a glassy carbon working electrode at scan rates varying between 10 and 500 mV/s. The reference electrode was Ag/AgCl and the counter electrode was Pt. All measurements were performed at 25 °C.

3. Calculations

All correlations were performed using the program *QtiPlot*. Structures of different conformers of **4** were generated with Molecular Mechanics conformational searching using *Avogadro 1.0.0*. The structure was first drawn in *Chemtool* and then optimized using UFF force field. The resulted configuration was further used as input for conformational searching. The donor–acceptor distance needed for calculation of ground and MLCT-excited state dipole moments difference, through the methodology of Saito, was calculated based on the as optimized structure. Van der Waals radius of compound **4**, was calculated using 3 V: Voss volume voxalator, available on-line. The latter was directly used as the cavity term in Suppan–Tsiamis equation.

4. Results and discussion

4.1. Synthesis and characterization of the solvatochromic Fe^{II} complex

The pentacyanoferrate complex (compound **4**) used in this work possesses a dicationic 4,4′-bipyridine based ligand as shown in Scheme 1. As depicted in Scheme 1 4,4′-bipyridine reacts with the precursor **2** (a 1:1 product of 4-dimethylamino-pyridine: 4-DMAP and *a*,*a*′-dichloro-*p*-xylene) to give in high yield the desired ligand (compound **3**). After subsequent reaction of the latter with $Na_3[Fe^{II}(CN)_5NH_3]$ in water, solvatochromic compound **4**, was produced as a deep blue solid. Product **4**, was isolated as a monosodium salt, very soluble in water and polar organic solvents. All products were analyzed by means of several spectroscopic techniques (such as FTIR, ^{1}H and ^{13}C NMR, and UV–Vis spectroscopy as well as elemental analysis, see paragraphs 1.1–1.4, Supporting Information).

Solvatochromic product **4**, is isolated as a hydrated salt, containing 9 water molecules per molecule as confirmed by thermogravimetric and elemental analyses (**4**.9H_2O). The structure of **4**, corresponds to the type of bolaform electrolytes. These kind of small bolaform amphiphiles containing *p*-xylene as the hydrophobic flexible spacer, have been synthesized in the past for uses in

Table 1
MLCT energies of **4** in ten solvents and binary solvent mixtures and corresponding solvent polarity parameters.

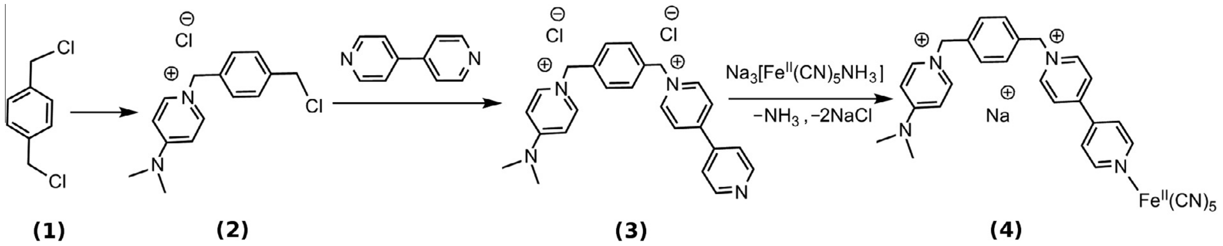
Solvent	E_{MLCT}[a] (kcal/mol)	ε[b]	n[c]	$E_T(30)$[d] (kcal/mol)	E_T^N[e]	E[f] (kcal/mol)
H_2O	53.592	78.5	1.3325	63.1	1.000	21.736
EG	47.652	41.4	1.4318	56.3	0.790	14.895
Gly	47.258	42.5	1.4746	57.0	0.812	15.371
FA	45.527	109.5	1.4475	55.8	0.775	13.704
MeOH	42.610	33.8	1.3264	55.4	0.762	14.756
NMF	45.684	182.4	1.4319	54.1	0.722	11.907
EtOH–H_2O, 50% (v/v)[g]	48.874	38.1	1.3617	56.5	0.797	15.562
AcMe–H_2O, 50% (v/v)[g]	47.731	30.0	1.3583	54.9	0.747	14.256
EG–H_2O, 50% (v/v)[g]	49.810	44.7	1.4051	59.7	0.895	18.355
MeOH–H_2O, 50% (v/v)[g]	48.459	51.9	1.3363	58.4	0.856	17.332

[a] MLCT energy.
[b] Static dielectric constants of the solvents used, measured at 25 °C [26].
[c] Refractive indices of the solvents used (25 °C) [27].
[d] Reichardt's solvent polarity scale [23].
[e] Reichardt's normalized polarity scale [23].
[f] Solvent Lewis acidity parameter of Koppel–Palm equation [23].
[g] Values ε [28], n [29], $E_T(30)$ [30], and E for these solvent mixtures are determined according to Supporting Information, Paragraphs 2 and 3.

Table 2
MLCT energies of **4** in aqueous glucose solutions at eight different concentrations of glucose and corresponding solvent polarity parameters.

Glucose concentration (g/L)	E_{MLCT}[a] (kcal/mol)	ε[b]	n[c]	$E_T(30)$[d] (kcal/mol)	E_T^N[e]	E[f] (kcal/mol)
0	53.592	78.54	1.3325	63.10	1.000	21.736
40	53.492	77.61	1.3386	62.21	0.973	20.830
80	53.492	76.64	1.3446	61.57	0.953	20.170
120	53.442	75.62	1.3507	61.12	0.939	19.689
160	53.243	74.55	1.3567	60.79	0.929	19.336
200	53.144	73.44	1.3628	60.55	0.921	19.071
240	53.144	72.28	1.3689	60.37	0.916	18.862
280	53.045	71.06	1.3749	60.21	0.911	18.688
320	52.947	69.80	1.3810	60.08	0.907	18.533

[a] MLCT energy.
[b] Static dielectric constants of the solutions used, measured at 25 °C [14]. (See also: Supporting Information, paragraph 4).
[c] Refractive indices of the solutions used at 25 °C (Supporting Information, paragraph 4).
[d] Reichardt's solvent polarity scale [13]. Also: Supporting Information, paragraph 5.
[e] Reichardt's normalized polarity scale [13].
[f] Solvent Lewis acidity parameter of Koppel–Palm equation.



Scheme 1. Synthetic route followed for the preparation of solvatochromic compound **4**.

coloration technologies [18], rotaxanes and pseudorotaxanes synthesis [19,20] as well as conformational probes of hydrophobic, π-stacking interactions in water solutions [21], or even for the adsorption of anionic molecules on monolayers for the constructions of multilayers [22]. In case of compound **4**, the incorporation of a pentacyanoferrate(II) group on the bolaform backbone of **3**, renders the title compound capable of developing, in solution, hydrogen bonds (HBD-solvents with cyano groups of $[Fe^{II}(CN)_5]^{-3}$) as well as dipole–dipole interactions. The aforementioned interactions are of great interest for the study of solvatochromism of compound **4** [23]. In Fig. 1, different conformers of the title bolaform pentacyanoferrate complex are depicted. Both conformers correspond to geometrically optimized structures. In both cases (a) and (b) 4,4′-bipyridine and DMAP branches lie on different sites of the plane of the xylene bridge, resulting in *quasi* helical conformations.

Cyclic voltammetry measurements revealed a reversible Fe^{II}/Fe^{III} oxidation as shown in Supporting Information, Figs. S1 and S2. $E_{1/2}$ for Fe^{II}/Fe^{III} was determined to be 0.56 V *vs* Normal Hydrogen Electrode (NHE). This value is very close to the $E_{1/2}$ values of published pentacyanoferrate(II) with N-substituted-4,4′-bipyridinium ligands in water [24] (according to Coe et al. solvent effects become very important for pentacyanoferrate complexes with N-substituted-4,4′-bipyridines [7]). Nevertheless the value reported herein is slightly lower than the values reported by Coe et al. for N-methyl- and N-phenyl-bipyridinium corresponding pentacyanoferrate(II) complexes [7]. This is attributed to the much different N-substituent of 4,4′-bipyridine of compound **4**. It is though closer to the $E_{1/2}$ for Fe^{II}/Fe^{III} reported by Almaraz et al. for $[4\text{-CN-}py\text{-}Fe^{II}(CN)_5]^{3-}$ were *py* symbolizes pyridine [24]. The latter observation is an indication that the monocationic substituent $[a,a'\text{-DMAP-xylene}]^{1+}$ behaves as anticipated as a worse electron accepting substituent than aryls do. This is consistent with the results of UV–Vis experiments as will be analyzed. The complexation of the dicationic ligand **3** with pentacyanoiron(II) induced important shifts in the proton NMR spectra, especially to protons of 4,4′-bipyridyl (Supporting Information, Fig. S3). All signals became broader after complexation and the expected splitting patterns were not observed. This has been reported for other pentacyanoferrate(II) complexes [25].

*4.2. UV–Vis spectra and solvatochromism of compound **4***

Complex **4**, as mentioned, is an intensely solvatochromic compound. Its electronic absorption spectra include two important features in the wavelength range 200–900 nm. The lower energy band

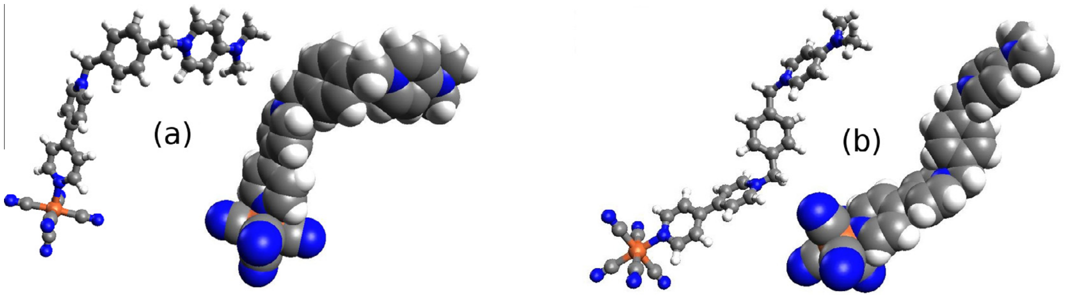


Fig. 1. Two different conformers of the anion $(\mathbf{4})^{1-}$.

appears at about 270 nm, it is sharp and is attributed to the intraligand (aromatic) π–π^* excitation [6,7]. This band is not significantly altered in terms of shape, absorbance or position, when compound **4** is dissolved in solvents of different polarity [6]. The second band is a significantly broader band of lower absorbance as compared to the π–π^* band and appears in the visible region (533 to even 750 nm) strongly depending on solvent polarity [6,7,9]. The latter band is attributed to a MLCT band assigned as $d\pi(\text{Fe}^{\text{II}}) \rightarrow \pi^*(\text{L})$. The value 533 nm (position of MLCT absorption maximum in water) is very close to the one reported by Coe et al. for pentacyano (N-methyl-4,4′-bipyridinium) ferrate (II) (534 nm) [7], but shifted hypsocromically as compared to (N-aryl substituted 4,4′-bipyridinium)ferrates (II) [*e.g.* for pentacyano (N-*p*-tolyl-4,4′-bipyridinium) ferrate (II), $\lambda_{\text{MLCT(max)}} = 566$ nm, as reported earlier by the author et al. [6]]. The latter observation reflects the decrease of the MLCT energy when the nitrogen substituent of the ligand is in conjugation with the aromatic 4,4′-bipyridinium spacer. As shown in Fig. 2, red-shifts as high as *approx.* 140 nm (3,840 cm^{-1}) were observed when going from water to MeOH, which corresponds to a relatively small change in solvent polarity (*i.e.* $\Delta\lambda = 137.5$ nm for $\Delta E_T^N = 0.238$, where E_T^N is Reichardt's normalized polarity scale). The vis MLCT band of **4** in different solvents and solvent mixtures, is shown in Fig. 2. The results are listed in Table 1 along with corresponding solvent polarity parameters.

Solvatochromism was also investigated in aqueous glucose solutions of different glucose concentrations. The results are listed in Table 2 and the MLCT band shifting depending on glucose concentration is depicted in Fig. 3. Increasing dipolarity and/or HBD-acidity of the medium, induces hypsochromic shifts of the MLCT vis bands of **4**. This behavior corresponds to negative solvatochromism since the ground state is more polar than the excited MLCT state [6–10]. The effect of glucose concentration on the solvatochromic behavior of pentacyanoferrate(II) complexes has never been reported before. Qualitatively the solvatochromic effect remains the same in case of different media like pure solvents, binary solvent mixtures and aqueous sugar solutions. Increasing medium Lewis acidity and HBD-acidity, results in an increased tendency of development of hydrogen bonds between hydrogen atoms of the solvent molecules and the cyano groups of compound **4**. Thus electron density is removed from the CN ligands and the π-back-bonding with the metal is increased. The latter increase leads to a higher separation of the metal π and ligand π^* orbitals, therefore the MLCT energy is higher. That is also observed when solvent dipolarity increases. Since the ground state is more polar than the MLCT excited state, dipolar solvents tend to stabilize more the ground state increasing the MLCT energy. In both cases (*i.e.* when either acidity or dipolarity increases) hypsochromic shifts of the vis MLCT band are observed. Since increasing glucose content in aqueous solutions results in lower dipolarity and Lewis acidity of the medium, bathochromism is observed in the vis spectrum of **4**, as shown in Fig. 3. The MLCT energy of **4** in a 320 g/L glucose solution is lower by roughly 0.645 kcal mol^{-1} (226 cm^{-1}) than in water. As will be analyzed, this small change reflects the significantly lower sensitivity on overall solvent polarity, as compared to that observed in the group of solvents and binary solvent mixtures examined.

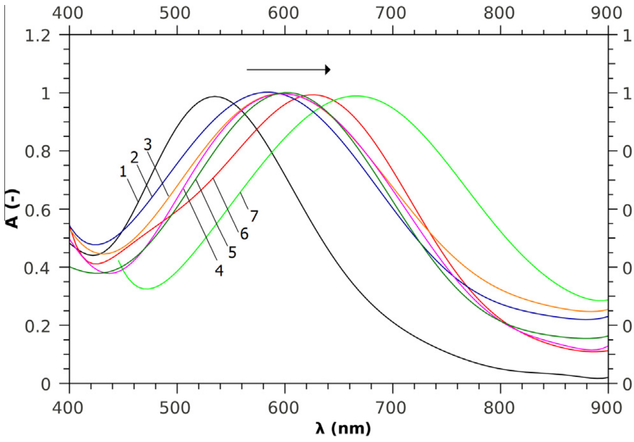


Fig. 2. Normalized vis absorption spectra of **4** (MLCT band) in different solvents: H_2O:black (1); EtOH-H_2O, 50% (v/v): blue (2); acetone–H_2O, 50% (v/v): orange (3); EG (ethylene glycol): magenta (4); glycerol (Gly): olive (5); FA (Formamide): red (6); MeOH: green (7). Arrow indicates redshift of MLCT band when decreasing solvent polarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

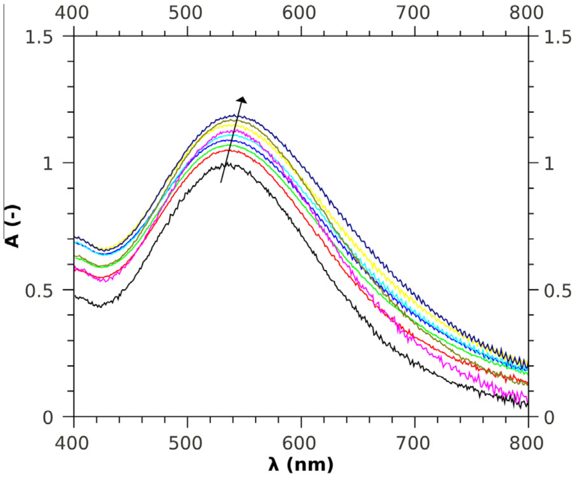


Fig. 3. Vis MLCT band of **4** in glucose aqueous solutions varying glucose concentration between 0 and 320 g/L. The bands absorbances are set in increasing mode with increasing glucose concentration to better visualize the solvatochromic effect.

Another very interesting feature of the solvatochromic effect of **4** in different media, is the increasing tendency of the bandwidth at half-height of the MLCT band, which keeps up with the bathochromic effect induced by lowering solvent dipolarity and Lewis acidity. The bandwidths seem to be proportional to the square root of the MLCT absorption maxima wavenumbers as shown in Supporting Information, Fig. S6. The impact of glucose concentration on the MLCT bandwidth is depicted in Fig. 4 (MLCT bandwidths were determined according to Supporting Information, paragraph 6). A steady linear increase of the MLCT bandwidth is observed up to 120 g/L. After this concentration the bandwidths increasing tendency becomes smaller until 320 g/L (which was the highest glucose concentration examined). These broadening of the MLCT band upon increasing glucose content (lowering polarity of the medium) may be associated with the alteration of solvent (water) relaxation time, an effect which can be related to water-glucose hydrogen bonding, which gets more intense when glucose content increases. Interestingly a linear dependence of the MLCT bandwidths on Reichardt's solvent polarity scale $E_T(30)$ was observed (Supporting Information, Fig. S7b). Increased MLCT bandwidths are also observed as going from polar solvents to less polar ones. This is obvious for instance between water and MeOH in Fig. 2.

4.3. Quantifying solvent effects

As mentioned compound **4**, exhibits negative solvatochromism in neat solvents, binary solvent mixtures as well as in aqueous glucose solutions. In order to quantify solvent polarity effects of **4**, arising from the interactions of its molecules with molecules of

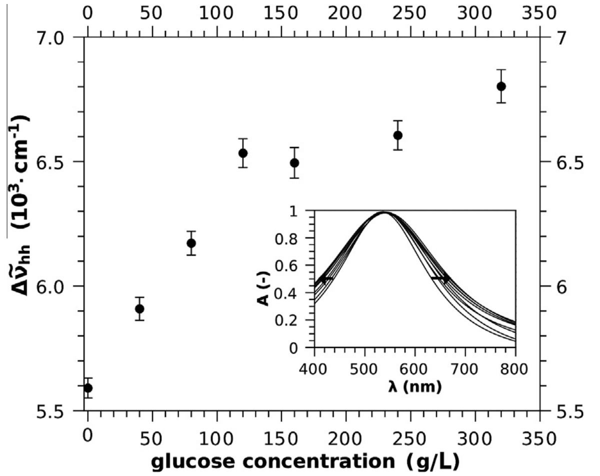


Fig. 4. Dependence of MLCT bandwidths of **4** (determined at half band height) on glucose concentration. Error bars correspond to the regression errors (Supporting Information: paragraph 6). Inset: broadening of vis MLCT band of compound **4** in aqueous glucose solutions.

the solvent, either specific or not, different solvent polarity parameters can be used. It has been pointed out in earlier publications that the position of MLCT bands of pentacyanoferrate(II) complexes with 4,4′-bipyridine based ligands, mainly depends on Lewis acidity and dipolarity/polarizability of solvents [1,6,9]. Linear correlations of the MLCT energies measured in different solvents with Reichardt's solvent polarity parameter $E_T(30)$ [6,31] as well as parameters describing solvent Lewis acidity *e.g.* Gutmann's acceptor number (AN) [6,31–33] and hydrogen-bond-donor (HBD) acidity parameter $a_{(KAT)}$ of the Kamlet–Abboud–Taft (KAT) equation [9] have been reported. The group of neat solvents/solvent mixtures used herein is well chosen including both protic and non-protic solvents, spanning a polarity range, as described by $E_T(30)$ polarity scale of Reichardt, of nearly 9 kcal mol^{-1}. MLCT energies of compound **4** correlate well to Reichardt's solvent polarity scale, as shown in Fig. 5a. As parameter $E_T(30)$ increases, the MLCT energy increases linearly. The MLCT energies in binary solvent mixtures do not deviate from this linear behavior. The slope of the obtained line is in the order of magnitude of already described pentacyanoferrate(II) complexes, thus exhibiting a typical sensitivity to solvent dipolarity/polarizability and Lewis acidity. Additionally, MLCT energies of compound **4** measured in different solvents and solvent mixtures are correlated slightly better with the empirical parameter *E* of Koppel–Palm equation describing Lewis acidity (Fig. 5b). For a given solvent this parameter is derived from Reichardt's parameter $E_T(30)$ by excluding the influence of non-specific effects [23]. The meaning of the latter two correlations is that solvent Lewis acidity is very important for the observed solvatochromic effect, thus specific solute–solvent effects seem to have a significant contribution.

On the other hand MLCT energies show poorer correlations with parameters expressing dipolarity and polarizability of solvents. Kirkwood polarity function $f(\varepsilon)$ (Eq. (1)) and function $f(n^2)$ (Eq. (2)) were used herein as measures of dipolarity and polarizability, respectively. Kirkwood function has been widely used in the past in order to quantify solvent effects on the spectra of solvatochromic compounds [23,34] as well as solvent effects on chemical reactions [35]. MLCT energies of **4**, tend to increase as Kirkwood function $f(\varepsilon)$ increases (Fig. 6a; ε is the static dielectric constant of the solvent). This is consistent with the positive slope of the line shown in Fig. 5a ($E_{MLCT} \propto E_T(30)$), since $E_T(30)$ is also a measure of dipolarity of solvents. Some deviations from linearity were observed for solvents FA and NMF. These solvents present very

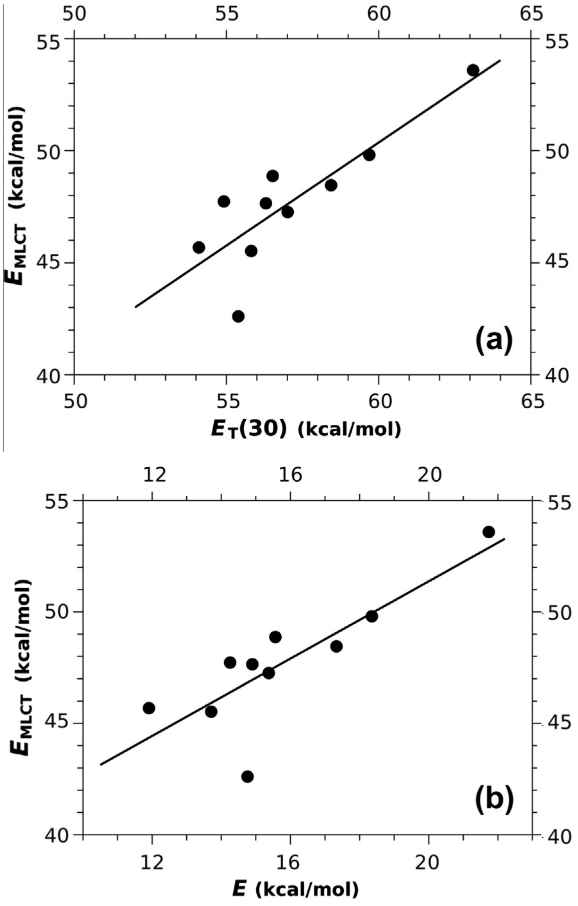


Fig. 5. Dependence of MLCT absorption maxima energies of **4** in neat solvents and binary solvent mixtures (listed in Table 1) on the solvent polarity parameters $E_T(30)$ (a) and *E* (b).

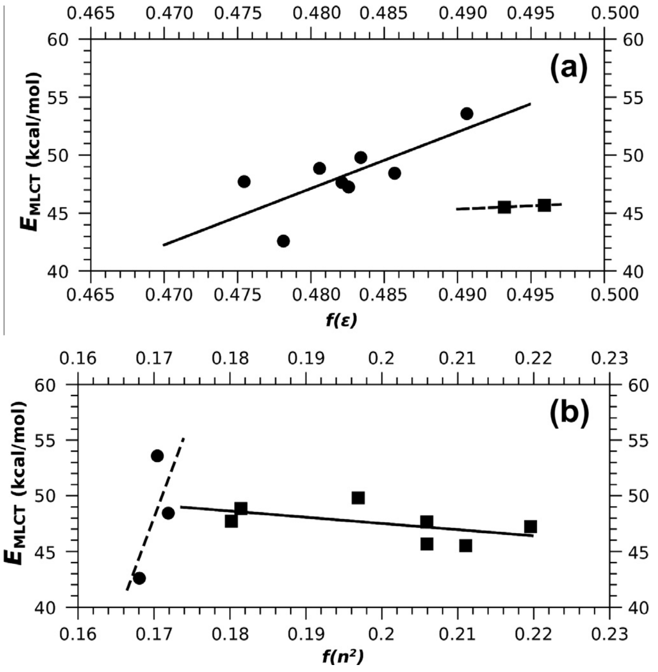


Fig. 6. Dependence of MLCT absorption maxima energies of **4** in neat solvents and binary solvent mixtures (listed in Table 1) on the functions $f(\varepsilon)$ (a) and $f(n^2)$ (b).

high static dielectric constants than all the other solvents used (even water) nevertheless, they are characterized by $E_T(30)$ values lower than water. This is an indication that specific solute–solvent interactions play here a more important role than specific ones. Furthermore a linear dependence of E_{MLCT} on function: $f(n^2)$ expressing polarizability was observed. The latter function expresses solvent polarizability (n is the refractive index of the solvent). Interestingly some hydroxylic solvents/solvent mixtures tend to deviate as shown in Fig. 6b. For most of the selected group of solvents and solvent mixtures though, the general observation is that increasing polarizability (as expressed by function $f(n^2)$) results in decreasing the MLCT energy of **4**. The results of all linear correlations of MLCT energies of **4** in different solvents with different solvent polarity parameters are listed in Table S1 of Supporting Information.

$$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1} \tag{1}$$

$$f(n^2) = \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

Correlations of MLCT energies of **4** in glucose aqueous solutions with the solvent polarity parameters $E_T(30)$, E, and functions $f(\varepsilon)$ and $f(n^2)$ revealed a different sensitivity to solvent polarity (see Table S1 of Supporting Information). Concerning polarity parameters describing non-specific solute–solvent interactions, the results obtained were comparable to those in case of neat solvents and solvent mixtures. First of all regarding the dependence of the MLCT energies on dipolarity as expressed by Kirkwood's function $f(\varepsilon)$ in glucose aqueous solutions, a linear correlation was observed. The slope in this case was positive meaning that as glucose content of a glucose aqueous solution increases causing a drop of the permittivity of the medium, the MLCT energy of **4**, decreases linearly. This is consistent with the results in case of the group of solvents and solvent mixtures. Nevertheless, a smaller slope in case of glucose solutions was observed, as shown in Fig. 7b (see also Supporting Information Table S1). Such a linear correlation is anticipated since the permittivity of a glucose aqueous solution is decreasing linearly with increasing glucose concentration (Supporting Information, Fig. S4), whereas the MLCT energy tends to decrease linearly as glucose concentration increases (Fig. 7a). Small discrepancies of the sensitivities (slopes) of MLCT energies on parameter $f(\varepsilon)$ were observed within glucose concentration range 0–320 g/L (values listed in Table S1 of Supporting Information). On the other hand a decreasing tendency of E_{MLCT} of **4** is observed when the function $f(n^2)$ increases (Fig. 7c). This is also consistent with the behavior observed in most of the solvents (shown in Fig. 6b). The slope in that case was slightly smaller than in case of solvents (excluding MeOH and MeOH/H_2O 50%). Some small but notable discrepancies of the sensitivities (slopes) of MLCT energies on parameter $f(n^2)$ were also observed within glucose concentration range 0–320 g/L (values listed in Table S1 of Supporting Information).

Nevertheless MLCT of **4**, responds in a much different way to changes of Lewis acidity in glucose-aqueous solutions, than does in neat solvents and solvent mixtures. As shown in Fig. 8a, starting form neat water and up to roughly 120 g/L the MLCT energies seem to be practically insensitive to the changes of $E_T(30)$ (slope: 0.070, Table S1, Supporting Information). In glucose concentration range $120 \leqslant C_{glu} \leqslant 320$ g/L, the sensitivity of MLCT energies of **4** on $E_T(30)$ becomes higher (slope: 0.380, that is approx. 5.5 times greater than observed for range $0 < C_{glu} \leqslant 120$ g/L). This is also obvious in Fig. 8a. This bigger slope is still significantly lower than the slope (sensitivity) obtained for the examined group of solvents and binary solvent mixtures (Supporting Information: Table S1 and Fig. S11a). Correlations of the MLCT energies of **4** with the Lewis acidity of solvents parameter E (Fig. 8b), result in the same pattern as in case of $E_{MLCT} \propto E_T(30)$ correlations.

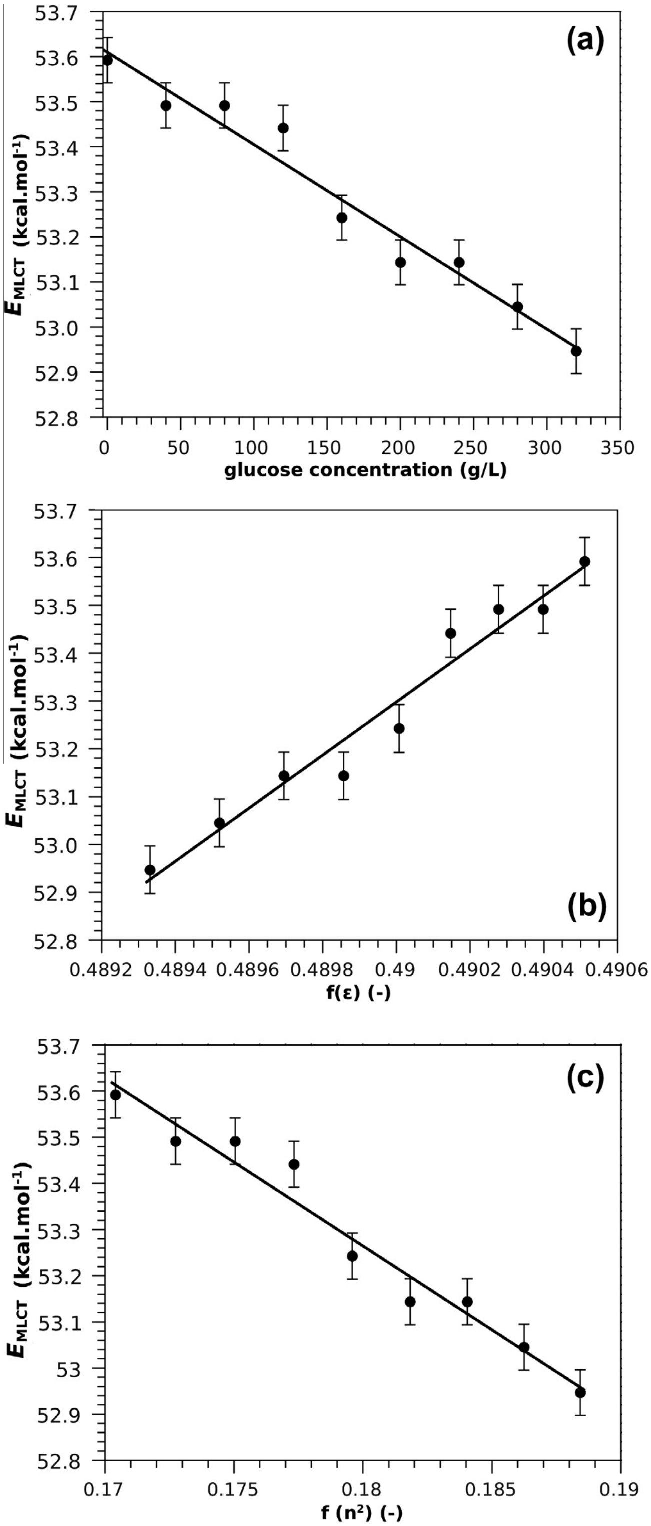


Fig. 7. Dependence of MLCT absorption maxima energies of **4** in glucose aqueous solutions, on glucose concentration (a), and polarity functions $f(\varepsilon)$ (b) and $f(n^2)$ (c). Error bars in plots are based on the resolution uncertainty, which corresponds to an uncertainty of ±0.05 kcal/mol.

The latter effect has been reported before in case of solvatochromic organic betaines exhibiting intramolecular charge transfer [36,37]. In those cases different sensitivity on $E_T(30)$ was also

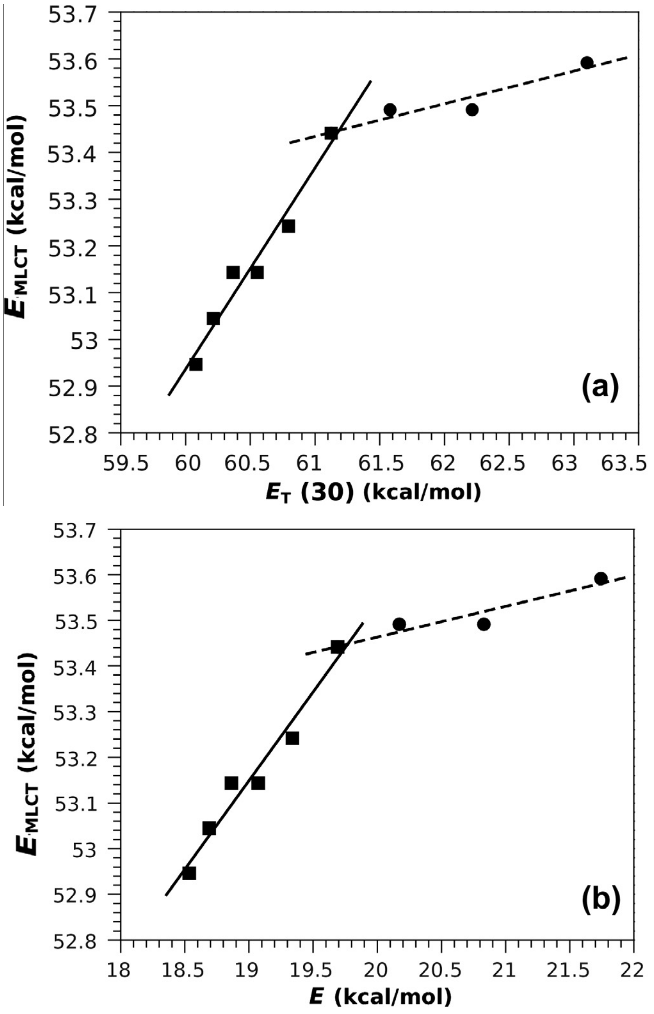


Fig. 8. Dependence of MLCT absorption maxima energies of **4** in glucose aqueous solutions, on solvent polarity parameters $E_T(30)$ (a) and E (b).

observed depending on the type of solvents. These differentiations within a given range of solvent polarity are connected to the dipole moment differences between the ground and excited state of solvatochromic molecules [36–38]. Analyzing the different polarity in ground and excited states can provide insights of the nature of solvatochromism and rationalize those different behaviors depending on the nature of the medium.

4.4. Ionicity of 4 in different media

As mentioned the overall solvatochromic sensitivity in glucose solutions on solvent polarity changes as described by Reichardt's polarity scale, is significantly lower than in neat solvents. According to Saito et al. it is possible to determine the ionicity of a molecule of the type $D^{\delta+}$-π-$A^{\delta-}$ [38], where D represents the electron donating group and A the electron accepting group of a solvatochromic compound. π represents the π-linkage of A and D [38]. Finally δ is the ionicity of the compound in its ground state [38]. In case of compound **4**, the Fe(II) center plays the role of the electron donor, being able to donate one electron (by being thus oxidized to Fe(III)) to the quaternary nitrogen of the neighboring pyridinium ring of the ligand. The latter acts as the electron withdrawing group, and charge transfer occurs through the aromatic backbone of 4,4′-bipyridyl, as depicted in Supporting Information, Scheme S1. The molecule $D^{\delta+}$-π-$A^{\delta-}$, in the ground state, is thus transformed to $D^{(1-\delta)+}$-π-$A^{(1-\delta)-}$ in the excited state (MLCT excited state for **4**). For **4**, this transition can be written as: Fe^{II}-π-N^{+} → Fe^{III}-π-$N^{+\cdot}$. When δ is very close to the value 0.5, it is obvious that the ionicity between the ground and excited state is roughly the same, thus the difference between ground and excited dipole moments approaches zero. Taking into account that the driving force of solvatochromism is the aforementioned difference, no solvatochromism is expected when $\delta \approx 0.5$, whereas maximization of the intensity of solvatochromism is anticipated when $\delta = 1$. Saito points out that the difference $(\mu_g - \mu_e)$ decreases and approaches zero when $\delta \approx 0.5$, as implied by Eq. (3).

$$(\mu_e - \mu_g) = (1 - 2\delta) \cdot er \tag{3}$$

In this equation μ_g is the ground state dipole moment, μ_e is the excited state dipole moment, e is the electron charge, and r is the distance between $D^{\delta+}$ and $A^{\delta-}$. In order to estimate δ, Saito et al. introduced a method which takes into account that Reichardt's solvatochromic zwitterionic dye depicted in Supporting Information, Scheme S2, when $\delta = 1$. It is then concluded that ionicity of a compound of the type $D^{\delta+}$-π-$A^{\delta-}$ can easily be determined by Eq. (4):

$$\frac{a}{a_1} = (2\delta - 1) \tag{4}$$

where a_1 and a are the slopes of the lines determined by Eq. (5) (a_1 for Reichardt's dye, a for the solvatochromic dye of interest).

$$E_{CT} = aE_T(30) + b \tag{5}$$

In Eq. (5), E_{CT} is the charge transfer energy for a given solvatochromic dye of the type $D^{\delta+}$-π-$A^{\delta-}$, $E_T(30)$ is the Reichardt's solvent polarity scale and b is the intercept of this linear equation corresponding to the charge transfer energy when $E_T(30)$ is minimized to zero (the case of TMS: tetramethylsilane or gas phase [23]). a_1 is the slope for Reichardt's zwitterionic dye and a the slope determined for a solvatochromic dye of the type: $D^{\delta+}$-π-$A^{\delta-}$. It is obvious that for Reichardt's dye it is: $a_1 = 1$, because $\delta = 1$. Assuming now that for the solvatochromic dye: $D^{\delta+}$-π-$A^{\delta-}$ it is $\alpha = 1$ when ionicity is equal to 1 ($\delta = 1$), the ionicity $D^{\delta+}$-π-$A^{\delta-}$ can easily be determined through Eq. (4). As mentioned before for a given solvatochromic compound, it is possible to observe different sensitivity on solvent polarity (as expressed by parameter $E_T(30)$) within a given range of solvent polarity. In those cases this effect can be attributed in terms of the theory analyzed above, to the alteration of the ionicity of the solvatochromic compound within this range of solvent polarity. According to those regression values and Eq. (4) three different cases are recognized within solvent polarity range: $54.1 \leqslant E_T(30) \leqslant 63.1$ kcal mol^{-1}, including all types of media examined herein. The corresponding three ionicity values of **4**, regarding these three cases, are mentioned in Fig. 9.

The difference between the the excited MLCT state dipole moment and the ground state dipole moment, calculated through Eq. (3), considering a distance between Fe(II) and N^{+} (para quaternized nitrogen) of approx. 9 Å (Supporting Information, Fig. S8) is equal to $(\mu_e - \mu_g)_a = -32$D, for case (a) of Fig. 9. The negative sign is consistent with the negative character of observed solvatochromism (the ground state more polar than the MLCT excited state). The same equation gave a significantly lower dipole moment difference in case (b) of Fig. 9, regarding the case of glucose aqueous solutions with concentrations within the range $120 \leqslant C_{\mathrm{glu}} \leqslant 320$ g/L *i.e.* $(\mu_e - \mu_g)_b = -16.4$ D. As anticipated Eq. (3) results in a lower $(\mu_e - \mu_g)_b$ difference since the slope of Eq. (5) in that case is lower (roughly half as compared to the slope in case of solvents). Finally concerning the concentration range $0 < C_{\mathrm{glu}} \leqslant 120$ g/L (Fig. 9(c)) Eq. (3) gave $(\mu_e - \mu_g)_c = -3$D. The as mentioned results are of course consistent with the theory developed by Saito et al. Lower sensitivity of the experimental charge transfer energies to parameter $E_T(30)$ reflects a lower dipole moment difference between the

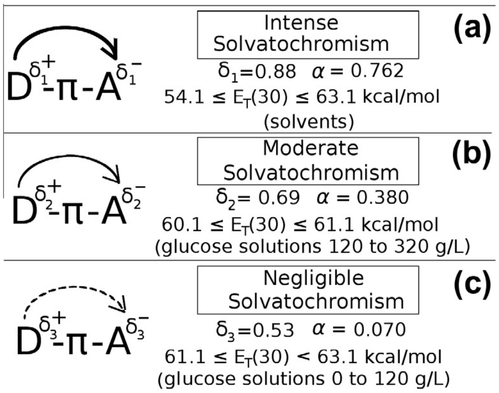


Fig. 9. MLCT of **4** in different media, with respect to ionicity of **4**. Calculated differences between MLCT excited and ground state dipole moments through Eq. (3): (a) $(\mu_e - \mu_g)_a = -32$D, (b) $(\mu_e - \mu_g)_b = -16.4$D, and (c) $(\mu_e - \mu_g)_c = -3$D.

MLCT excited state and the ground state. Interestingly the values obtained for **4** by means of the described methodology, in case of the glucose solutions, are close to the ones obtained through another method, the method of Suppan and Tsiamis [39]. This theory allows the determination of ground and excited dipole moments of solvatochromic compounds by using only absorption spectral data [39,40]. That is very important for non-emitting compounds (for instance compound **4**). Eq. (6) is an extension of earlier Suppan's equation [41] containing only the first term which is the permanent dipole interaction term. The second term represents the stabilization difference of the ground state and excited state dipoles ($\boldsymbol{\mu_g}$ and $\boldsymbol{\mu_e}$ respectively) [39]. Since the MLCT energy of **4** in glucose solutions correlated very well with both polarity functions $\varphi(\varepsilon)$ and $\varphi(n^2)$, Eq. (6) can give accurate results (Supporting Information, Figs. S9 and S10). Ground and excited state dipoles are considered as collinear in case of **4**. For the determination of both terms of the biparametric linear equation (6), the value 5.01 Å was used for the cavity radius (α). The latter is the Van der Waals radius of **4**, determined as described in calculations part. This approach has been applied in the past for the determination of ground and excited state dipole moments when no other data concerning the cavity term are available [42–43] (*e.g.* the density of the solute [44]). Finally the scaling factor $(4\pi\varepsilon_o)^{-1}$ where ε_o is vacuum permittivity, was used for SI units [41].

$$E_{CT} = \frac{1}{4\pi\varepsilon_o}\left[\frac{\vec{\mu}_g\cdot(\vec{\mu}_g-\vec{\mu}_e)}{\alpha^3}(\varphi(\varepsilon)-\varphi(n^2)) + \frac{(\mu_e^2-\mu_g^2)}{\alpha^3}\varphi(n^2)\right] + const. \qquad (6)$$

where

$$\varphi(x) = \frac{2(x-1)}{2x+1} \qquad (7)$$

The dipole moment difference $(\mu_e - \mu_g)$ of **4** in glucose solutions obtained through Eq. (6) regarding the concentration range $0 < C_{glu} \leqslant 320$ g/L was $(\mu_e - \mu_g)_s = -11.8$ D (the index *s* denotes the value obtained through Eq. (6)). It is obvious that $(\mu_g - \mu_e)_c = 3\text{D} < (\mu_g - \mu_e)_s = 11.8\text{D} < (\mu_g - \mu_e)_b = 16.4\text{D}$. As mentioned MLCT energies of **4** measured in glucose solutions correlate linearly to polarity functions $\varphi(\varepsilon) - \varphi(n^2)$ and $\varphi(n^2)$ in the whole concentration range $0 < C_{glu} \leqslant 320$ g/L. Thus it is not possible to obtain more than one different values $(\mu_e - \mu_g)$ in the aforementioned concentration range. Nevertheless the value 11.8D is very well balanced between the values obtained through application of Saito's theory. Since $(\mu_e - \mu_g)_c = -3$D is valid in the range $0 < C_{glu} \leqslant 120$ g/L and $(\mu_e - \mu_g)_b = -16.4$D in the range $120 \leqslant C_{glu} \leqslant 320$ g/L, the balanced value of the dipole moment difference will be $(\mu_e - \mu_g)_w = -11.4\text{D} \approx (\mu_e - \mu_g)_s = -11.8$D (where the index *w* denotes the balanced value). This is very important since two different methods for determining differences between excited and ground state dipole moment result in very close results. Furthermore taking into account a general linear correlation in the whole glucose concentration range ($0 < C_{glu} \leqslant 120$ g/L) as shown in Fig. S11b gives according to Eq. (3): $(\mu_e - \mu_g)_{glu} = -11.5$D. This value is very close to the balanced dipole moment difference $(\mu_e - \mu_g)_w = -11.4$D. The as mentioned results prove that the use of the Van der Waals radius of **4**, (5.01 Å) as the cavity radius (α) in Eq. (6) is not mistaken. This observation is supported by the fact that even small errors of the cavity radius introduce higher errors to the determined dipole moments through the term α^3. Unfortunately equation (6), probably because of poor correlation of the MLCT energies of **4**, measured in solvents of Table 1, resulted in a value of $(\mu_e - \mu_g)_a \approx -22$D. This value is smaller from the calculated dipole moment difference through Eq. (3) (−32D), though still higher as compared to the one determined in glucose solutions. (Values −22D and −32D were determined using Suppan's and Saito's method respectively; see Supporting Information: Tables S1 and S2 and Figs. S9–S11a). This discrepancy is anticipated since correlation coefficients (R) for correlations E_{MLCT} *vs* $[\varphi(\varepsilon) - \varphi(n^2)]$ and E_{MLCT} *vs* $\varphi(n^2)$, regarding E_{MLCT} measured in solvents, were rather low, whereas as mentioned E_{MLCT} correlate excellently with $E_T(30)$, rendering Saito's method much more reliable in that case. The as determined values of $(\mu_e - \mu_g)$ for **4**, by means of different methods are listed in Table S2 of Supporting Information.

*4.5. Solvatochromic sensitivity of **4***

The fact that the ionicity of **4** differs depending on the medium, can explain the observed alteration of the medium responsive character of **4**, as depicted in Fig. 9. In order to answer why such alteration of the ionicity occurs, the analysis of contribution of different solvent polarity parameters on solvatochromism in neat solvents, binary solvent mixtures, as well as in glucose solutions, is needed. For that matter Linear Solvation Energy Relationships (LSER's) can be employed. [9,23,45–48] Herein the multiparametric equation of Koppel and Palm was used for different reasons. First of all, in order to include the solvatochromic shifts measured in glucose solutions in an LSER, one is obliged to know or to determine the values of the corresponding LSER parameters for each of the examined glucose solutions. Unfortunately as also mentioned in introduction, apart from Reichardt's polarity scale of aqueous glucose solutions (determined by Spange et al. [13]) refractive indices and static dielectric constants, no other solvent polarity parameters have been determined up to now. This decreases the number of applicable LSER's. Koppel–Palm equation in its extended form, correlates a physicochemical quantity X with four parameters [23,49] (see Eq. (8)). Two parameters describing non-specific solute–solvent interactions, (one expressing polarization: $Y(\varepsilon)$ where ε is the static dielectric constant of a solvent, the other expressing polarizability: $P(n^2)$ where n is the refractive index of a solvent) then two more describing specific solute–solvent effects. The latter two include both solvent Lewis acidity, expressed by parameter E (values of E listed in Tables 1 and 2) and Lewis basicity expressed by parameter B (to the best of the author's knowledge no data for this parameter are available for glucose solutions). Coefficients a_1 to a_4 represent the susceptibilities of physicochemical quantity X to the four parameters of equation 8 and are determined through linear regression. The most important solvent parameters to describe solvatochromism of pentacyanoferrate(II) complexes which do not bear substituents giving rise to significant overall Lewis acidity, are parameters describing dipolarity/polarizability of solvents as well as solvents' Lewis acidity. The latter is a general observation which has been made by different authors in the past [1,6,9,31–33]. According to Koppel and Palm, parameter E for a given solvent can be derived through Eq. (11) [23] (E, $E_T(30)$ as well as coefficients of $Y(\varepsilon)$ and $P(n^2)$ in kcal mol^{-1}). Thus knowing $E_T(30)$, ε, and n of glucose solutions, E can be determined (listed values in Table 2).

$$X(\varepsilon, n^2, E, B) = X_o + a_1 Y(\varepsilon) + a_2 P(n^2) + a_3 E + a_4 B \tag{8}$$

where:

$$Y(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2} \tag{9}$$

and

$$P(n^2) = \frac{n^2 - 1}{n^2 + 2} \tag{10}$$

$$E = E_T(30) - 25.10 - 14.84 \cdot Y(\varepsilon) - 9.59 \cdot P(n^2) \tag{11}$$

A second reason which excuses the choice of using Koppel–Palm equation is that it gives the possibility of separately determining the contribution of dipolarity and polarizability, by means of functions Y and P. Nevertheless, Koppel–Palm will be used herein in its reduced form containing three parameters for reasons analyzed above: Y, P, and E [50]. Correlation of MLCT energies of **4**, in all group of solvents, solvent mixtures and glucose solutions with the aforementioned parameters, resulted in linear equation (12) [51].

$$E_{MLCT}(\text{kcal mol}^{-1}) = 2.74 + 25.24 \cdot Y(\varepsilon) + 16.89 \cdot P(n^2) + 1.12 \cdot E(\text{kcal mol}^{-1}) \tag{12}$$

The success of Eq. (12) in describing solvatochromism of **4**, is proved by the high correlation coefficient ($R = 0.92$) of the experimental values of E_{MLCT} *vs* calculated ones, as shown in Fig. 10.

Based on the regression values of Eq. (12), and according to the treatment described in Supporting Information, Paragraph 10) the relative contributions of the parameters of Koppel–Palm relationship Y, P, and E (respectively $\%\text{P}_Y$, $\%\text{P}_P$, $\%\text{P}_E$) follow the decreasing sequence: $\%\text{P}_E = 78\% > \%\text{P}_Y = 12.5\% > \%\text{P}_P = 9.5\%$. The meaning of this sequence is that for the given data set (containing neat solvents, binary solvent mixtures as well as glucose solutions), Lewis acidity as expressed by polarity parameter E, contributes the most to the observed solvatochromism of **4**. The contribution of dipolarity and polarizability of the medium is minor as compared to the contribution of medium Lewis acidity. However the contribution of polarizability is lower than that of dipolarity. Obviously specific solute–solvent interactions play a very important role. Hydrogen-bonding between solvent molecules acting as Lewis acids, and cyano groups of solute molecules, is the expected dominating specific interaction. A good way to rationalize the different chromotropic behavior of **4** depending on the medium is to combine the information derived by applying Koppel–Palm equation, with the change in sensitivity of the MLCT energies of **4**, on each of the three parameters of Koppel–Palm equation ($Y(\varepsilon)$, $P(n^2)$, and E). The slopes of the corresponding correlations are considered as measures of sensitivities. In the histograms of Fig. 11, the sensitivities of MLCT energies of **4** (in kcal/mol) on the aforementioned three parameters, in all different types of media are depicted (herein classified in three categories according to the medium type: solvents and binary solvent mixtures, aqueous glucose solutions with concentration varying within $0 < C_{\text{glu}} \leqslant 120$ g/L, and finally aqueous glucose solutions with concentration varying within $120 \leqslant C_{\text{glu}} \leqslant 320$ g/L). As shown, there is a gradual decreasing of all sensitivities of **4** on $Y(\varepsilon)$, $P(n^2)$, and E ($\text{S}_{Y(\varepsilon)}$, $\text{S}_{P(n)}$, S_E respectively) when going from the set of solvents and solvent mixtures (of Table 1) to glucose aqueous solutions. This decrease becomes very intense in case of parameter E, practically leading to insensitivity of MLCT energy to Lewis acidity of the medium in case of glucose-aqueous solutions with concentration varying within $0 < C_{\text{glu}} \leqslant 120$ g/L. This is also observed in case of $\text{S}_{Y(\varepsilon)}$, $\text{S}_{P(n)}$, but in case of sensitivity on dipolarity $\text{S}_{Y(\varepsilon)}$ is far less intense than in case of S_E and slightly less than $\text{S}_{P(n)}$. Taking into account the results obtained through Koppel–Palm equation ($\%\text{P}_E > \%\text{P}_Y > \%\text{P}_P$), it is possible to deduce that in case of glucose solutions (especially at low concentrations of glucose) the solvatochromic dye seems to practically respond only in changes of dipolarity and slightly in changes of polarizability of the medium. On the other hand in case of solvents and solvent mixtures, compound **4** mainly responds to Lewis acidity changes (and rather less to dipolarity and polarizability), and it seems that this is the main tendency which shapes the overall contribution pattern. The answer why such an alteration of the solvatochromic behavior of **4** is observed in different media, has thus to be linked with glucose-water specific interactions which are very intense, as observed in the past [52,53]. Polyhydroxy compounds including sugars have a structure-breaking effect in water, because of the strong hydrogen bonding between glucose and water molecules [52]. Glucose can thus affect the hydration of the solute molecules (*e.g.* molecules of the solvatochromic dye **4**). As observed in the past, partial dehydration of hydrophilic molecules such as N,N-dimethylformamide (DMF) [52] or inorganic salts (such as NaCl, KCl *etc.*) [53] becomes energetically harder when increasing glucose content. The solvatochromic complex salt (**4**) which possesses five cyano groups coordinated to iron(II) per molecule, as well as other ionic parts along the molecule (*i.e.* two quaternized nitrogen atoms) is highly hydrophilic. Consequently increasing glucose content stabilizes the hydration shell of solvatochromic dye molecules. Since this effect is observed even at very low glucose concentrations, hydrogen-bond formation between solute (**4**) and water molecules which (according to the analysis based on Koppel–Palm equation) is the most dominant solute–solvent interaction, the gradual decrease of Lewis acidity as glucose content increases, does not affect intensely the cyano-water hydrogen bonding. Consequently it results in moderate solvatochromic shifts and thus to moderate sensitivity S_E. In comparison with glucose solutions (with concentrations between 0 and 320 g/L) neat solvents lead to much higher sensitivities to Lewis acidity, since comparing the solvating abilities of water and polar organic solvents used herein, water presents by far the highest Lewis acidity and Hydrogen-Bond-Donor ability. Thus the effect of different solvent leads to a much more significant

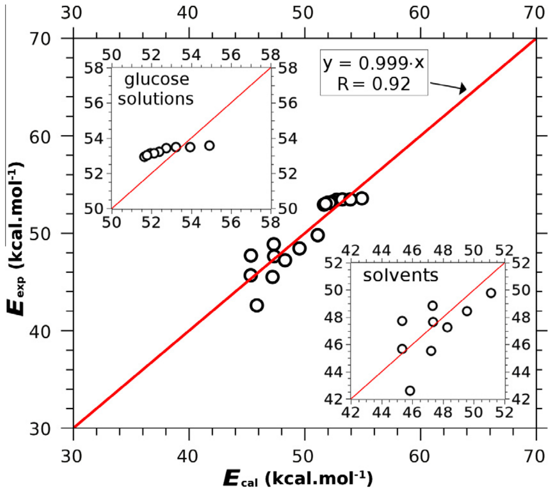


Fig. 10. Experimentally obtained E_{MLCT} values *vs* calculated E_{MLCT} values through Eq. (12).

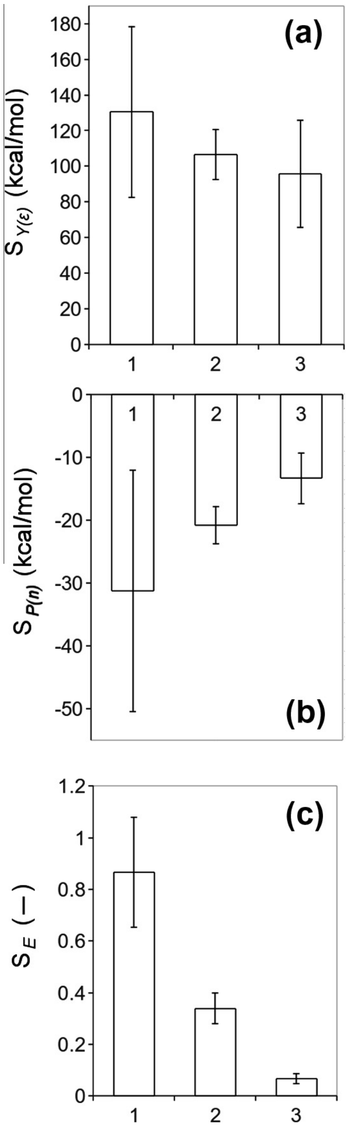


Fig. 11. Histograms showing the sensitivities of measured MLCT energies of **4**, to (a) dipolarity expressed by function $Y(\varepsilon)$, (b) polarizability expressed by function $P(n^2)$, and (c) Lewis acidity of the medium expressed by parameter E of Koppel and Palm. Values obtained through linear regression analyses between MLCT energies of **4** and corresponding solvent polarity parameters. (1) solvent set of Table 1, (2) glucose solutions $120 \leqslant C_{\text{glu}} \leqslant 320$ g/L, and (3) glucose solutions $0 < C_{\text{glu}} \leqslant 120$ g/L. Error bars in all cases are based on the regression errors of the slops of the corresponding lines obtained through linear regression.

sensitivity S_E. This is why Suppan–Tsiamis method used for the determination of dipole moments of **4**, gave much better results in case of aqueous glucose solutions (results consistent with Saito's method) but failed in case of the set of solvent/binary solvent mixtures, where sensitivity to Lewis acidity is much higher (since Suppan–Tsiamis method does not consider any specific solute–solvent effects).

Furthermore by comparing the ratios $[\Delta E/\Delta Y(\varepsilon)]_{\text{sol}} = 131.6$ kcal mol^{-1} [54] (regarding the set of solvents) and $[\Delta E/\Delta Y(\varepsilon)]_{\text{glu}} = 707.7$ kcal mol^{-1} [54] (regarding glucose solutions: the whole concentration range examined) it is apparent that the increase of glucose in solution, brings a smaller decrease of dipolarity than Lewis acidity. This is also in agreement with the results of the correlations between E_{MLCT} and $f(\varepsilon)$ and E concerning the set of solvents (of Table 1) and glucose solutions. Although for neat solvents and binary solvent mixtures E_{MLCT} shows an excellent linear correlation with E, the correlation with $f(\varepsilon)$ is much poorer. Things are inversed in glucose solutions where E_{MLCT} shows an excellent linear correlation with $f(\varepsilon)$, reflecting the fact that dipolarity becomes more important in glucose solutions. The same thing, in a different extent is observed for polarizability as expressed by parameter $P(n^2)$.

5. Conclusion

A new pentacyanoferrate solvatochromic complex was synthesized and fully characterized. Its solvatochromic behavior was very intense as examined in different media (pure solvents, binary solvent mixtures and glucose aqueous solutions). The general conclusion based on suitable Linear Solvation Energy Relationship was that the medium responsive behavior of the complex, is mainly affected by solute–solvent specific interactions. Hydrogen bond formation mainly affects the chromotropic phenomenon observed, with the solvent molecules acting as HBD-acids, readily interacting with cyano groups of the complex. Nevertheless it was observed that, quantitatively, the solvatochromic behavior of the pentacyanoferrate complex differed strongly depending on the type of medium. The solvatochromism was more intense in the examined group of pure solvents and binary solvent mixtures (including both HBD and HBA solvents) than was in aqueous glucose solutions. The "driving force" of solvatochromism which is the difference between ground and MLCT-excited state dipole moments, was much smaller in case of glucose solutions, reflecting the moderate or almost negligible (at lower glucose concentrations) solvatochromism. This discrepancy was attributed to the different environment, the molecules of the complex "feel" and the intense and steadily high hydrogen bond donor acidity of glucose solutions in water. These results reveal an interesting phenomenon narrowly connected to water–glucose interactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2013.12.008.

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[51] Number of points: 18; residual sum of squares: $rss = 36.276$. Intercept and coefficients of $Y(\varepsilon)$ and $P(n^2)$ in kcal mol^{-1}, coefficient of parameter E: dimensionless.
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