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[Raffaello Papadakis](#)\*

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Article

# Chromotropism of Iron(II) Complexes with Non-Symmetric Heterocyclic Ligands: Polarity Sensing in Aqueous Urea Solutions

Raffaello Papadakis

Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences, 756 51 Uppsala, Sweden; rafail.papadakis@slu.se

**Abstract:** In this work, two pentacyanoferrate(II) complexes are synthesized and characterized, and their intense solvatochromic properties are examined in various solvents and solvent mixtures. These complexes feature ligands with flexible xylylene bridges and distinct heterocycles: one combining 4-dimethylaminopyridine (DMAP) with 4,4'-bipyridine, and the other isoquinoline with 4,4'-bipyridine. This structural diversity leads to intriguing solvatochromic behavior, enabling various intermolecular interactions and motifs in solution among the solvents and the complexes acting as solutes. The determined dipole moment changes between ground and excited states of both compounds highlight their sensitivity to small changes in dipolarity within polar media, such as water and polar organic solvents and mixtures thereof. Linear solvation energy relationships are employed to investigate their dependencies on solvent polarity and their responsiveness to different media. Additionally, the solvatochromic aptitude of the molecules examined is utilized to determine the polarity properties of aqueous solutions containing the bio-based molecule urea, a major player in bio-based resins and adhesives and other imminent applications.

**Keywords:** Chromotropism; 4,4'-bipyridine; iron(II) complexes; solvatochromism; urea sensing; specific solvent-solute interactions

## Introduction

Cyanoferrate(II) complexes have gained significant attention in recent years due to their versatile applications in various fields, including catalysis,<sup>i,ii,iii</sup> materials science,<sup>iv,v,vi</sup> and medicinal chemistry.<sup>vii</sup> These complexes are particularly noted for their unique electronic properties and their ability to form stable complexes with a variety of ligands.<sup>viii,ix,x</sup> Recent trends in the study of cyanoferrate(II) complexes have focused on enhancing their functional properties through innovative ligand design and exploring their potential in new applications.<sup>xi</sup> One of the key features in developing these complexes is the incorporation of 4,4'-bipyridine as a ligand.<sup>xii</sup> 4,4'-Bipyridine is a bidentate ligand that can coordinate with metal centers to form robust, versatile structures. Its ability to undergo redox reactions and its electrochromic properties make it an attractive component in the design of multifunctional materials.<sup>xiii</sup> The use of 4,4'-bipyridine in cyanoferrate(II) complexes has led to the development of compounds with enhanced stability, improved electronic properties, and increased responsiveness to environmental changes.<sup>xiii,xiv,xv,xvi,xvii,xviii,xix,xx</sup>

Medium-responsive materials, which change their properties in response to external stimuli such as temperature, pH, or solvent polarity, constitute an exciting area of research of high scientific and technological relevance.<sup>xxi,xxii,xxiii</sup> Pentacyanoferrate(II) complexes with 4,4'-bipyridine ligands have shown promising results as medium-responsive materials.<sup>xii</sup> These materials can exhibit significant changes in their optical and electronic properties when exposed to different solvents or solvent mixtures. This solvatochromic behavior is beneficial for sensing applications, where the material's response to environmental changes can be used to detect and measure various parameters/properties of the environment. The combination of cyanometallate complexes with 4,4'-

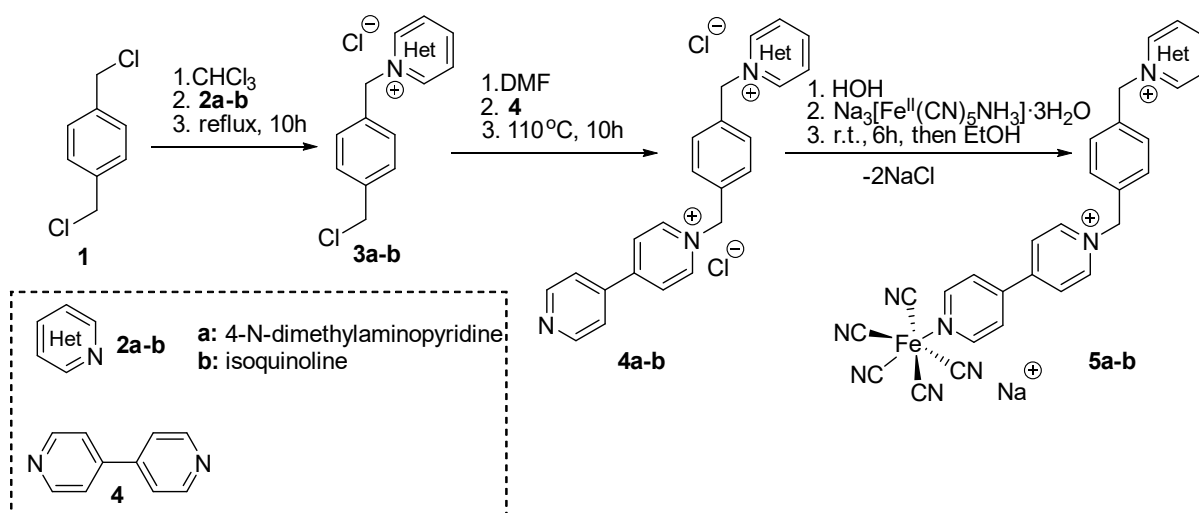
bipyridine and related ligands and their medium-responsive properties opens up new possibilities for the design of advanced materials.<sup>xii,xxiv,xxv</sup> These materials can be tailored for specific applications, such as sensors<sup>xxvi</sup> and smart coatings,<sup>xxvii</sup> where their ability to respond to environmental changes can be harnessed for practical use. The ongoing research in this field aims to further understand the mechanisms behind these responses and to develop new materials with enhanced performance and broader applicability. For these reasons, various attempts have been made to investigate solvation effects in diverse media, with a special interest in solutions (aqueous or not) of molecules acting as modifiers.<sup>xxviii,xxix,xxviii</sup> However, studies on the alteration of the ionicity of solute indicators due to the dielectric effects of the medium remain scarce. Embracing these facts, this work features two pentacyanoferrate(II) complexes that are synthesized and fully characterized, exhibiting intense solvatochromic properties. Their solvatochromism is examined in various solvents and solvent mixtures. These complexes feature ligands with flexible xylylene bridges and distinct heterocycles: one bearing DMAP and 4,4'-bipyridine, and the other isoquinoline and 4,4'-bipyridine. This structural diversity leads to an interesting solvatochromic behavior, enabling various intermolecular interactions between solvents and these complexes as solutes. Linear solvation energy relationships are employed to investigate their dependencies on solvent polarity and their responsiveness to different media. A further goal of this work is to explore polarity sensing and solvation effects in aqueous urea. There are several reasons why urea has been chosen as a key polarity modifier in water. Firstly, urea is widely used in numerous processes and materials of industrial importance, most prominently in urea-formaldehyde<sup>xxx,xxxi</sup> and urea-phenol-formaldehyde resins,<sup>xxxii</sup> which have immense applications in adhesives,<sup>xxxiii, xxxiv, xxxv</sup> and coatings of global technological significance.<sup>xxxvi,xxxvii</sup> Additionally, urea is considered a bio-based compound, and its use in new "green" adhesive formulations and polymers is currently being highly promoted.<sup>xxxviii</sup> To facilitate its use in novel applications, its properties as a solute require more investigation. Furthermore, the study of aqueous urea solutions is crucial for understanding their dielectric properties and the specific effects of H-bonding solute-solvent interactions. This study attempts to investigate the solvent-solute interactions in the presence of urea in water solutions of the title solvatochromic probes. FTIR and UV-Vis spectrophotometric experimental results and different mathematical models are employed to rationalize the complex solvation effects in aqueous urea solutions.

## Results and Discussion

### *Synthesis and Characterization*

The solvatochromic pentacyanoferrate(II) complex **5a** has been synthesized and characterized before.<sup>xviii</sup> An analog of **5a** lacking the polar dimethylamino functional group and further benzanullated (complex **5b** involves an isoquinoline-bearing ligand, see Scheme 1) was synthesized for the first time.

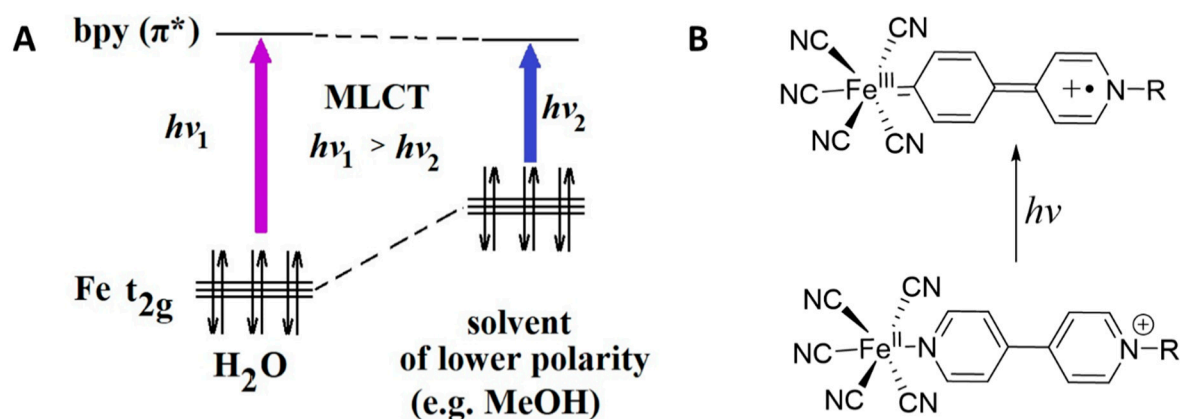
Two different heterocyclic compounds were used for the synthesis of the ligands (**4a-b**). The 4-dimethylaminopyridine (**2a**) and isoquinoline (**2b**) reacted in a 1:2 ratio with  $\alpha,\alpha'$ -dichloro-*p*-xylene (**1**), while 4,4'-dipyridine (**4**) reacted in a 2:1 ratio to yield the respective products (**4a-b**). Through the reaction of products **3a** and **3b** with 4,4'-dipyridine, products **4a-b**, which were subsequently used as "ligands," were produced. The general synthesis method of the heterocyclic products **4a-b**, as well as their structural evaluation, is described in the Materials and Methods section. Note: An excess of the electrophile was used to avoid di-substitution, as the introduction of the first heterocyclic group activates the other electrophilic carbon (of the chlorine).



**Scheme 1.** Synthetic route to solvatochromic products **5a-b**.

### Solvatochromism

Compounds **5a** and **5b** exhibit marked solvatochromism, similar to other ferrocyanide(II) complexes encompassing 4,4'-dipyridine-based ligands (see recent works by Papadakis and coworkers<sup>xiii,xv,xvii,xviii,xx</sup>). What is noteworthy with compounds **5a** and **5b** is their ligands' flexible backbone, which can potentially diversify solvent-solute interactions and give rise to unique solvation phenomena. Recently, the unique structural properties of **5a** have been tested in the context of glucose sensing.<sup>xviii</sup> In a study by the author, it was shown that there is a bimodal chromotropic behavior: with one mode encountered in molecular solvents and their mixtures, and another mode in glucose solution associated with the attenuation of ionicity of **5a** in aqueous glucose.<sup>xviii</sup> The solvatochromism of ferrocyanide(II) complexes encompassing 4,4'-dipyridine-based ligands is associated with the medium-influenced character of the  $\text{Fe}^{\text{II}}(dp) \rightarrow \pi^*(bpy)$  transition (see Scheme 2a). As shown in Scheme 2a, the energy gap between the ground and MLCT excited state of **5ab** is larger in highly polar solvents such as water than in less polar solvents e.g. MeOH. This effect drastically influences the visible spectra of these compounds by inducing sizable bathochromic shifts in the vis spectra upon decreasing solvent polarity. The "solvatochromic backbone" experiencing this effect involves the 4,4'-bipyridinium part of the molecule and the pentacyanoiron(II) part of the complex (see Scheme 2b)



**Scheme 2.** A) Illustration of the  $Fe^{II}(dp) \rightarrow \pi^*(bpy)$  transition observed in complexes like **5a-b** and comparison of the energy gaps in two solvents of different polarity. B) Scheme depicting the “solvatochromic backbone” of compounds **5ab** and the photoinduced MLCT transition and how the structure is influenced.

Here, the author attempts to go a step further and investigate the properties of a relative compound to **5a**, which differs only in the use of an N-heterocycle opposite to 4,4'-dipyridine, specifically isoquinoline instead of DMAP (the latter appearing in the structure of **5a**). Due to the lower dipolarity of isoquinoline compared to DMAP and the lack of hydrogen bonding possibilities, the chromotropic behaviour of **5b** is anticipated to be influenced mostly by the dipolarity and likely by the polarizability of the medium. This can lead to a polarity indicator that encompasses only one hydrogen-bond sensing side, that of the  $-Fe^{II}(CN)_5$  moiety which plays a dominant role in the observed solvatochromism, and thus, this structural feature could attenuate the role of other sites of the molecule which give rise to solute-solvent interactions of lower importance for the core transition [e.g. the H-bonding of the type Sol-H $\cdots$ NMe<sub>2</sub>py (where Sol: a solvent with H-Bond donating aptitude and NMe<sub>2</sub>py being DMAP)]. To have a meaningful comparison of the two complexes the same molecular media used for **5a** previously were also used for **5b**. More details about the used solvents and solvent mixtures are found in Table 1.

**Table 1.** Solvents and solvent mixtures used for the study of solvatochromism of **5a** and **5b** and corresponding solvent polarity parameters and functions.\*

Solvent	$\alpha^{[xxxix]}$	$\beta^{[xxxix]}$	$\pi^{*[xxxix]}$	$E_T30^{[xxxix]}$ (kcal/mol)	$E_T^N$ ■	$\epsilon^{[xl]}$	$n^{[xlii]}$	$\varphi(\epsilon)^{\dagger}$	$\varphi(n^2)^{\dagger}$
HOH	1.17	0.47	1.09	63.1	1.000	78.5	1.3325	0.9810	0.3408
TFE	1.51	0.00	0.73	59.8	0.898	26.7	1.2907	0.9449	0.3074
Glycerol	1.14	0.87	0.92	57.0	0.812	42.5	1.4746	0.9651	0.4391
‡EtOH50%	1.10	0.54	0.96	56.5	0.796	38.1	1.3617	0.9611	0.3628
EG	0.90	0.52	0.92	56.3	0.790	41.4	1.4318	0.9642	0.4118
FA	0.71	0.48	0.97	55.8	0.775	109.5	1.4475	0.9864	0.4220
MeOH	0.98	0.66	0.60	55.4	0.762	33.8	1.3264	0.9563	0.3361
‡AcMe50%	0.96	0.47	1.00	54.9	0.747	30.0	1.3583	0.9508	0.3603
NMF	0.62	0.80	0.90	54.1	0.722	182.4	1.4319	0.9918	0.4118

\* Solvents are displayed in decreasing  $E_T(30)$  mode (top to bottom). † Calculated through equation 6 with  $x=\epsilon$  for  $\varphi(\epsilon)$  and  $x=n^2$  for  $\varphi(n^2)$ . ‡ Determined through the interpolation method described in [xxiv]. ■ Normalized Reichardt's solvent polarity scale<sup>xxxix</sup>.

Through the spectrophotometric study of compounds **5a** and **5b** in various solvents and solvent mixtures, intriguing effects were observed. Qualitatively, the most noticeable observation is the negative solvatochromism of both compounds, corresponding to a bathochromic shift in the MCLT band as the solvent polarity decreases. Quantitatively, compound **5a** exhibited a maximal bathochromic shift of  $\Delta_{HOH}^{NMF} \lambda_{CT} = 92 \text{ nm}$  (or  $\Delta_{HOH}^{NMF} \tilde{\nu}_{CT} = -2766 \text{ cm}^{-1}$ ) between water (the solvent with the highest  $E_T(30)$  value in this study) and NMF (the solvent with the lowest  $E_T(30)$  value). For compound **5b**, the corresponding shift was 88 nm (or  $-2606 \text{ cm}^{-1}$ ). Interestingly, while NMF has the lowest  $E_T(30)$  value in this study, it was not the solvent in which the highest solvatochromic shift was observed. Instead, MeOH exhibited the most significant shift, with  $\Delta_{HOH}^{MeOH} \lambda_{CT} = 137 \text{ nm}$  (or  $\Delta_{HOH}^{MeOH} \tilde{\nu}_{CT} = -3841 \text{ cm}^{-1}$ ) for **5a** and 153 nm ( $-4118 \text{ cm}^{-1}$ ) respectively for **5b**. This is not surprising, as NMF, despite its low  $E_T(30)$  value due to its low Lewis acidity (significantly lower than MeOH), also has one of the highest dielectric constants ( $\epsilon = 182.4$ ), indicating stronger dipolarity among molecular solvents (including water). Indeed the author has recently reported on an observation of the high-polarity-driven behaviour of NMF in binary solvent mixtures.<sup>xiii</sup> This finding suggests that both compounds are more influenced by dielectric effects than by the Lewis acidity of the medium. It furthermore underscores the importance of interpreting solvatochromic shifts using

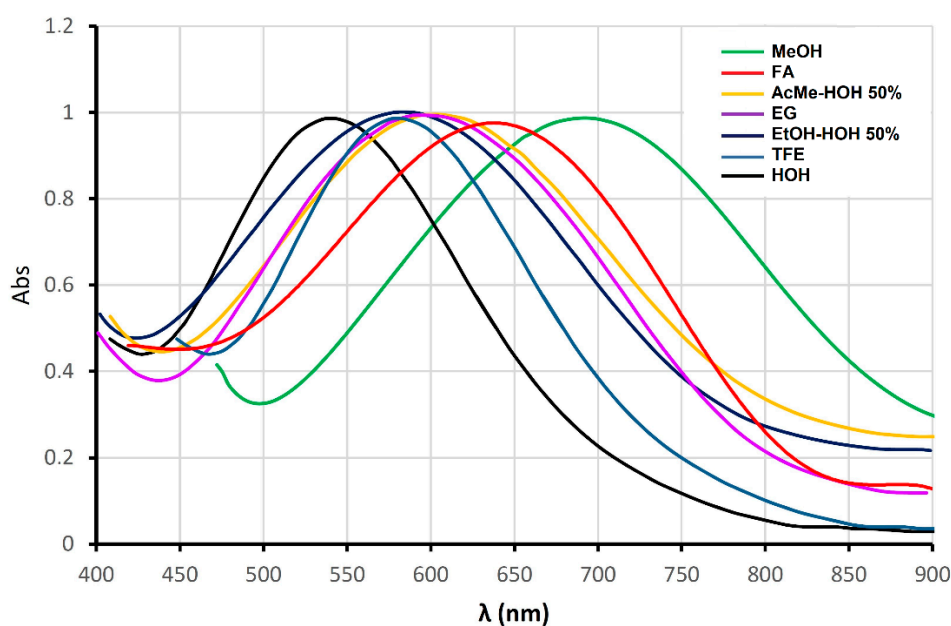
various scales and parameters (empirical or otherwise) to gain a better understanding of the dominant solute-solvent interactions.

Moreover, small but noticeable differences in the measured MLCT maxima wavelengths were observed when comparing **5a** to **5b** in different solvents. The most prominent differences are a 19 nm shift observed in neat MeOH and a 10 nm shift in FA, with the band of **5b** being more redshifted than **5a** in both cases. Additionally, the general observation in most solvents/mixtures examined, excluding NMF and EG, is that the visible MLCT band of **5b** is either centered at an identical wavelength or redshifted compared to **5a**. Although it is difficult to draw definitive conclusions from these observations, the DMAP group is likely capable of pushing electron density into the “solvatochromic backbone” of the molecule (i.e., 4,4'-bipyridine-Fe<sup>II</sup>(CN)<sub>5</sub>) more effectively than isoquinoline. It has been shown earlier by Papadakis and Tsolomitis<sup>xx</sup> that electron-withdrawing substituents bound to the N-end of the 4,4'-bipyridine-Fe<sup>II</sup>(CN)<sub>5</sub> backbone result in redshifts in the visible spectra of compounds relative to **5a** and **5b**. For a thorough study focusing on these effects, please refer to the relevant literature. [xx]).

**Table 2.** Measured MLCT wavelength maxima of **5a** and **5b** in different solvents and corresponding MLCT wavenumbers.

Solvent	$\lambda_{CT}^{5a}$ (nm)*	$\lambda_{CT}^{5b}$ (nm)†	$\tilde{\nu}_{CT}^{5a}$ (10 <sup>3</sup> cm <sup>-1</sup> )	$\tilde{\nu}_{CT}^{5b}$ (10 <sup>3</sup> cm <sup>-1</sup> )
HOH	534	537	18.744	18.622
TFE	572 <sup>†</sup>	577	17.470	17.341
Glycerol	605	610	16.529	16.389
EtOH50%	585	585	17.094	17.094
EG	600	599	16.667	16.705
FA	628	638	15.923	15.664
MeOH	671	690	14.903	14.497
AcMe50%	599	604	16.694	16.564
NMF	626	625	15.978	16.009

\* Data reported previously by the author<sup>xviii</sup>. † Measurements in TFE have not been previously reported for **5a**. ‡ Results reported in this study.



**Figure 1.** Normalized vis absorption spectra of compound **5b** (MLCT band) in different solvents.

### Types of Solute-Solvent Interactions

Compounds **5a** and **5b** can interact with solvent molecules in various ways due to the diversity of their functional groups. Understanding these interactions is crucial for rationalizing solvation phenomena. This study identifies the following main types of solute-solvent interactions.

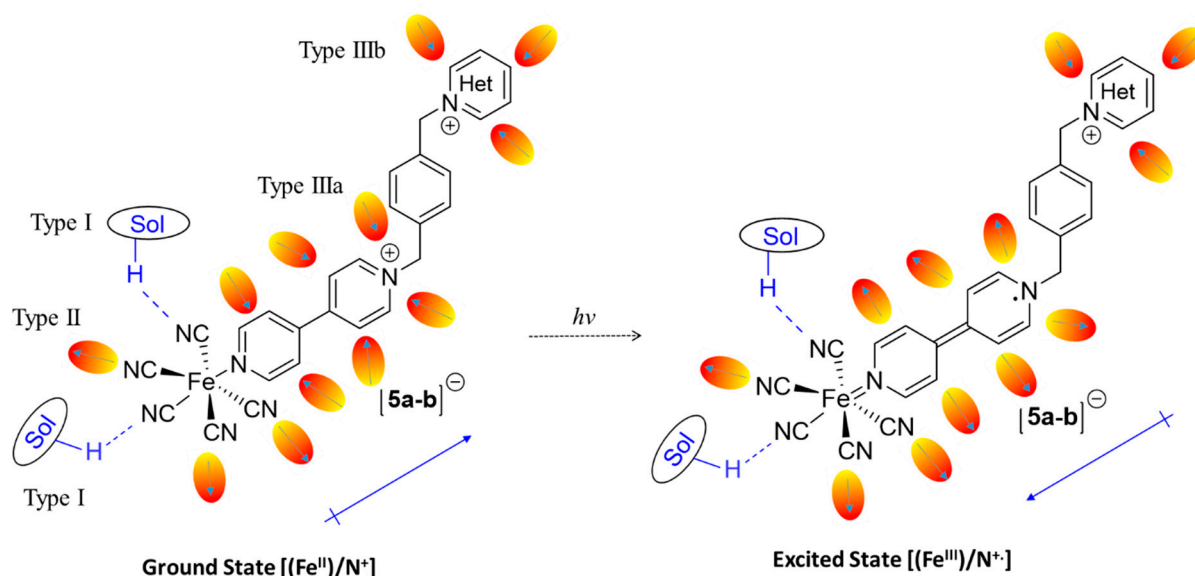
The  $(C\equiv N)^-$  groups of the pentacyanoferrate(II) "head" of the molecules can effectively hydrogen bond to a variety of hydrogen bond donor (HBD) molecules, such as hydroxylated solvents (e.g., water, alcohols) and amides (e.g., FA and NMF).<sup>xiii,xx</sup> This type of interactions is identified here as **Type I**; see Scheme 3. These interactions are highly relevant to the chromic behavior of pentacyanoferrates(II) since H-bonding attenuates the  $Fe^{II}-CN$  bond strength. Hence, MLCT becomes less efficient, and its energy increases. This has a direct impact on solvatochromism. Indeed Brønsted acids capable of protonating the CN groups while kept bound on the Fe(II) center, have been found to drastically change the chromic and non-linear-optical (NLO) properties of pentacyanoferrate(II) complexes.<sup>xlii</sup>

Moreover, the  $(C\equiv N)^-$  groups can also interact specifically with solvent dipoles (anion-dipole interactions; **Type II** interactions; Scheme 3). Such interactions clearly influence the MLCT energy and therefore the solvatochromism of **5a** and **5b** in a similar fashion as in **Type I** interactions i.e. by energetically disfavoring the MLCT.<sup>xx</sup>

The charged backbone of the ligand, i.e. the bipyridinium part adjacent to the pentacyanoferrate(II), also exhibits an aptitude to interact with the dipoles of solvent molecules through cation-dipole interactions (see Scheme 3). Support for this type of interactions has been provided through <sup>1</sup>H-NMR studies on pyridinium salts.<sup>xliii</sup> These interactions (here called **Type IIIa**) can influence the solvatochromism of **5a** and **5b** by attenuating the electron-withdrawing aptitude of the bipyridinium positively charged core. Such interactions will obviously hamper the transfer of charge from iron(II) to the heterocycle (note: the MLCT transition is the  $Fe^{II}(dp) \rightarrow \pi^*(bpy)$  transition; *vide supra*).

On the other hand, not only bipyridinium but also the quaternized N-heterocycle (DMAPyridinium for **5a** and quinolinium for **5b**) is also capable of developing interactions cation-dipole interactions with dipoles of polar solvents. (**Type IIIb** interactions). In contrast to quinoline, DMAP can also develop hydrogen bonding with HBD-solvents such as water, formamide, and methanol (MeOH) as a result of the mild HBA-capacity of the dimethylamino group of DMAP (**Type IV**).

The latter two types (**Type IIIb** and **IV**) of interactions do not directly affect the core of the molecule and hence their contribution to the solvatochromic is rather minor. Nonetheless, as described above, small shifts in the visible spectra of **5a** and **5b** can be attributed to the heterocyclic substituent and could be explained based on **Type IIIb** and **IV** interactions, which are dependent on the nature of the side-heterocycle.



**Scheme 3.** Illustrations representing the interactions of compounds **5a** and **5b** with solvent molecules (dipoles) in ground and excited state after reorientation (Sol: corresponds to solvent).

#### Using LSERs to Rationalize the Solvatochromic Effects

To elucidate the solute-solvent interactions that influence the solvatochromism of **5a** and **5b**, selected LSERs were employed (see Methods section). The choice of LSERs was based on a series of previous studies on pentacyanoferrate(II) complexes with variously substituted 4,4'-bipyridines as ligands.<sup>xiii,xiv,xvii,xviii,xix,xx</sup>

Correlations between measured  $\tilde{\nu}_{CT}$  values for **5a** and **5b** using the LSER models (Eq. 1-4) help in understanding the solvent polarity parameters that influence the observed solvatochromism of both compounds. The correlation between  $\tilde{\nu}_{CT}$  and  $E_T^N$  resulted in a good fit ( $r^2=0.712$  for **5a** and  $r^2=0.617$  for **5b**; see Table 3 for more details) with a positive slope of  $10.54 \times 10^3 \text{ cm}^{-1}$  for **5a** and  $10.39 \times 10^3 \text{ cm}^{-1}$  for **5b** (see Table 3).  $E_T^N$  is a polarity scale encompassing Lewis acidity and dipolarity/polarizability character<sup>xxxix</sup> and these correlations are in line with the specific role of Lewis acidity of solvents in **Type I** interactions as well as with the role of dipolarity on **Type II** and **Type III** interactions and their overall influence on solvatochromism. Similar results have been shown by the author in a range of recent studies and are characteristic of ferrocyanides.<sup>xiv,xviii-xx</sup> The positive slopes in both cases indicate a negative solvatochromic effect, corresponding to bathochromism (lowering of  $\tilde{\nu}_{CT}$ ) when solvent polarity increases.

**Table 3.** Results of application of LSERs 1-4 to the spectrally determined MLCT energies  $E_{CT}$  of **5a** and **5b**.

Compound/ Equation #	Solvent Parameter/Correlation coefficient					$r^2$	rse
	$\tilde{\nu}_o(10^3 \cdot \text{cm}^{-1})$	$E_T^N(10^3 \cdot \text{cm}^{-1})$	$\pi^*(10^3 \cdot \text{cm}^{-1})$	$A(10^3 \cdot \text{cm}^{-1})$	$\beta(10^3 \cdot \text{cm}^{-1})$		
<b>5a/1</b>	$8.119 \pm 2.0$ 64	$10.54 \pm 2.5$ 31	-	-	-	0.71 2	0.6 18
<b>5a/2</b>	$9.547 \pm 1.6$ 36	-	$5.486 \pm 1.1$ 51	$9.547 \pm 1.6$ 36	$0.730 \pm 0.83$ 9	0.88 1	0.4 70
<b>5a/3</b>	$8.733 \pm 1.3$ 14	-	$5.487 \pm 1.1$ 27	$2.972 \pm 0.6$ 30	-	0.86 4	0.4 60
<b>5a/4</b>	$8.594 \pm 2.8$ 33	$10.14 \pm 3.0$ 90	-	-	$0.288 \pm 1.07$ 2	0.71 6	0.6 64

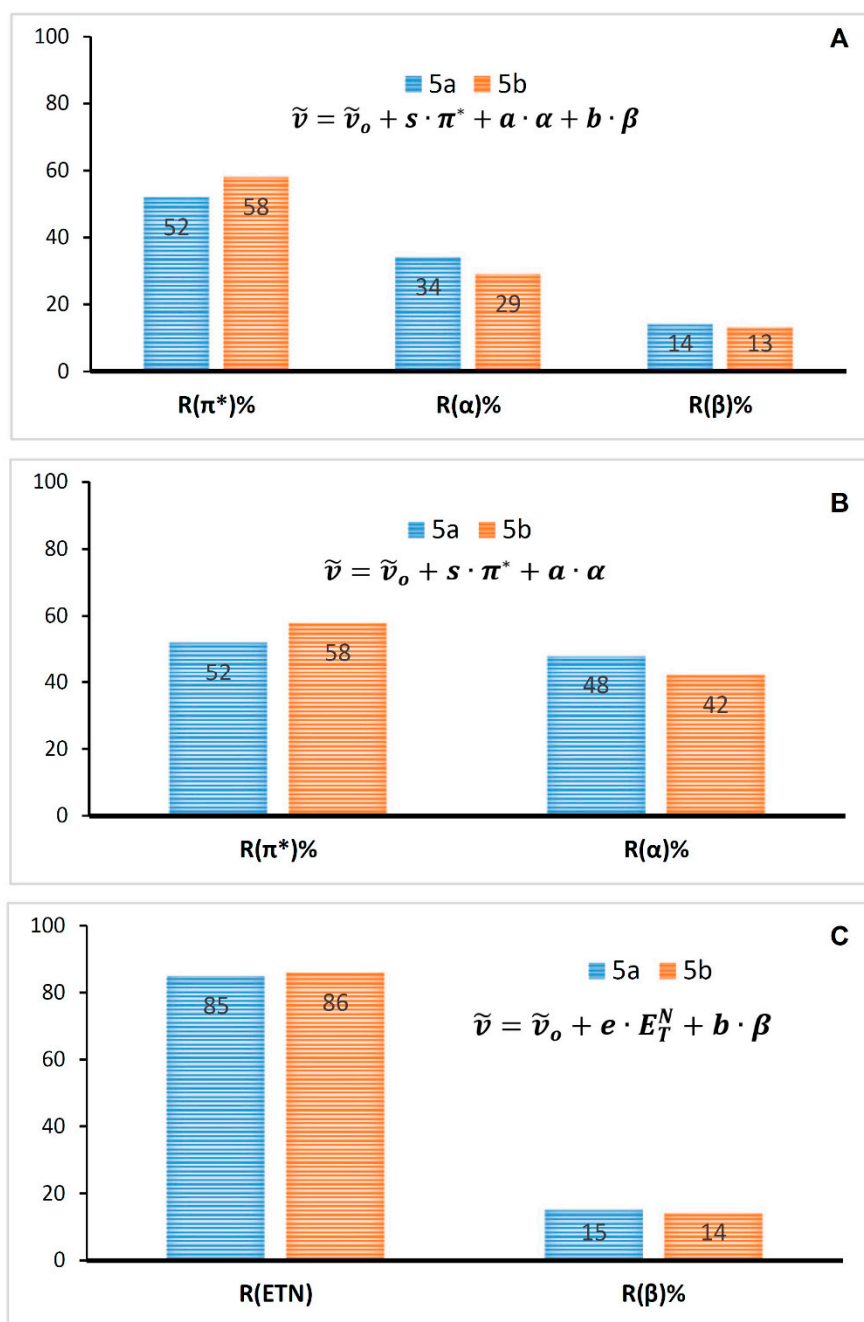
<b>5b/1</b>	8.121±2.5 25	10.39±3.0 96	-	-	-	0.61 7	0.7 56
<b>5b/2</b>	9.052±1.9 71	-	5.958±1.3 87	2.509±0.9 68	- 0.731±1.01 2	0.84 7	0.5 66
<b>5b/3</b>	8.238±1.5 51	-	5.959±1.3 30	2.928±0.7 43	-	0.83 1	0.5 43
<b>5b/4</b>	8.513±3.4 77	10.06±3.7 92	-	-	- 0.238±1.31 5	0.61 9	0.8 15

Due to the fact that Lewis acidity and dipolarity/polarizability are entangled in the empirical scale of Reichardt,  $E_T^N$ , Kamlet-Taft-Abboud (KAT) equation in its triparametric form (see Methods section; equation 2) can help to separate acidity (specifically HBD-acidity), basicity (HBA-basicity) and dipolarity/polarizability of solvents.<sup>xliv</sup> The triparametric linear fits of the spectrally obtained  $\tilde{\nu}_{CT}$  values to the three parameters  $\pi^*$ ,  $\alpha$ , and  $\beta$  for **5a** and **5b** were satisfactory ( $r^2=0.881$  for **5a** and  $0.847$  for **5b**; see Table 3 for more details). A general observation for both **5a** and **5b** is that positive coefficients (also known as sensitivities) were obtained for  $\pi^*$  and  $\alpha$ , whereas negative ones were obtained for  $\beta$  (See Table 3). The positive coefficients  $s$  (corresponding to  $\pi^*$ ) are in line with the assumption of negative solvatochromism since the increase of dipolarity/polarizability triggers a hypsochromic effect in the vis-spectra of **5a** and **5b** (characteristic of most bipyridine-bearing pentacyanoferrate(II) complexes).<sup>xx</sup> The positive coefficient of  $\alpha$  parameter ( $a$ ) is also in line with the expected effect of HBD-acidity on **5a** and **5b** (see **Type I** interactions above). On the other hand, the negative response to changes in parameter  $\beta$  (reflected in the negative  $b$  values for both compounds; see Table 3) is potentially associated with the channelling of electron density towards the core of the complex induced by the interactions with solvent molecules acting as HBA/Lewis bases. Such an effect is expected to have an opposite impact compared to acidity or dipolarity, as it can enhance the electron-pushing towards the electron-deficient parts of compounds **5a** and **5b**. Additionally, solvents interacting with the pyridinium entities of **5a** and **5b** in a **Type IIIa** fashion (*vide supra*), for example, by interacting with the *ortho*-hydrogen atoms of the bipyridinium, could lead to further polarization, resulting in a more energetically favoured MLCT when basicity increases, inducing bathochromism while solvent-basicity increases. Such phenomena have not been extensively studied, yet there are indications of the effects of HBA- and Lewis-basicity on the solvatochromism of pentacyanoferrate(II) complexes.<sup>xix</sup> Nonetheless, the overall role of basicity on the studied solvatochromic effects was found to be statistically much less important than the role of dipolarity/polarizability and HBD-/Lewis acidity ( $R_\beta$  was determined to be 14% for **5a** and 13% for **5b**; see Table 4 and Fig 2A). For that reason, the author has recently attempted to employ a reduced form of the KAT equation having two parameters instead of three.<sup>xix</sup> This approach is attempted in this study too. Specifically, parameter  $\beta$  is neglected in the analysis of solvatochromism of **5a** and **5b**. In this study use of Equation 3 (involving merely  $\pi^*$ ,  $\alpha$ ; see methods section for details) resulted in very good fitting, being comparable to the triparametric KAT equation. Through the statistical analysis, it was found that parameter  $\pi^*$  exhibits higher importance than parameter  $\alpha$  and this effect is slightly more pronounced in compound **5b** than **5a** (see Table 4 and Figure 2B). This finding is in line with the structural diversity of **5a** and **5b** and specifically the difference in side-pyridinium substituents; DMAP for **5a** and quinolinium for **5b**. Because isoquinoline compared to DMAP lacks hydrogen bonding capacity, the chromotropic behavior of **5b** is more significantly affected by the dipolarity and polarizability of the medium. Interestingly, the application of Equation 3 can be viewed as a disentanglement of Equation 1. While the latter (Eq. 1) fits the spectrally obtained  $\tilde{\nu}_{CT}$  to  $E_T^N$ , Equation 3 breaks down the fitting into the two components of  $E_T^N$ , namely Lewis acidity and dipolarity/polarizability, which are described in Eq. 3 through the linear combination of  $\pi^*$  and  $\alpha$ . Indeed, the connection of  $E_T(30)$  to parameters  $\pi^*$  and  $\alpha$  has been reported in past (e.g.:  $E_T(30) = 31.2 + 15.2 \cdot \alpha + 11.5 \cdot \pi^*$ ,  $r^2 = 0.9585$ )<sup>xlv</sup>.

Finally, an LSER complementary to KAT-equation is further used (see Eq. 4). The latter involves  $E_T^N$  expressing a combination of dipolarity/polarizability and Lewis acidity with parameter  $\beta$  expressing HBA-basicity. This LSER can be regarded as analogous to the Krygowski-Fawcett equation.<sup>xlvi</sup> In this form, Equation 4, provides the benefit of using KAT-parameter  $\beta$  which allows to draw a complementary conclusion to that of the KAT equation (Eq. 2). Interestingly, Equation 4, provides qualitatively the same results as KAT-equation. While positive sensitivities to  $E_T^N$  ( $10.14 \times 10^3 \text{ cm}^{-1}$  for **5a** and  $10.06 \times 10^3 \text{ cm}^{-1}$  for **5b**) were obtained, negative sensitivities to KAT-parameter  $\beta$  were observed ( $-0.288 \times 10^3 \text{ cm}^{-1}$  for **5a** and  $-0.238$  for **5b**). The interpretation of this finding is the same as in KAT-equation (*vide supra*). Additionally, the sensitivities to  $E_T^N$  were very close to those obtained through Equation 1 (involving solely Reichardt's polarity scale; see Table 3 for details). This underlines the minimal role of parameter  $\beta$  which is moreover manifested through the very low relative importance of this parameter (15% and 14% respectively for **5a** and **5b**; see Table 4 and Fig.2c). The complementarity of Equations 2 and 4 is also manifested through the very close relative importance of parameters  $E_T^N$  and  $\pi^*$  and  $\alpha$  the latter two combined i.e.  $\%R_{E_T^N} = 85\% \cong (\%R_{\pi^*} + \%R_{\alpha}) = (52\% + 34\%) = 86\%$  for **5a** and  $\%R_{E_T^N} = 86\% \cong (\%R_{\pi^*} + \%R_{\alpha}) = (58\% + 29\%) = 87\%$  for **5b**. The overall interpretation of the qualitative and quantitative results obtained through Equations 1-4 indicates that the dipolarity/polarizability of the medium, along with HBD- and/or Lewis- acidity, are the most important solvent polarity features for the observed solvatochromic effects, in both compounds examined. The results clearly indicate a negative solvatochromic effect, and the impact of HBA-basicity is found to be of minor importance, given the set of solvent/solvent mixtures examined, which, interestingly, involves solvents of relatively high basicity.(e.g. NMF with  $\beta=0.80$ , glycerol with  $\beta=0.87$ , and MeOH with  $\beta=0.66$ ).

**Table 4.** Relative Importance of parameters  $E_T^N$ ,  $\pi^*$ ,  $\alpha$ , and  $\beta$  in LSERs 2,3, and 4 for compounds **5a** and **5b**.

Compound/Equatio n #	$R_{E_T^N}$	$R_{\pi^*}$	$R_{\alpha}$	$R_{\beta}$
<b>5a/2</b>	-	0.52	0.34	0.14
<b>5a/3</b>	-	0.52	0.48	-
<b>5a/4</b>	0.85	-	-	0.15
<b>5b/2</b>	-	0.58	0.29	0.13
<b>5b/3</b>	-	0.58	0.42	-
<b>5b/4</b>	0.86	-	-	0.14



**Figure 2.** Bar graphs depicting the relative importance of the polarity parameters involved in Equations 2 (A), 3 (B) and 4 (C).

#### *Determination of Electronic Ground and Excited State Dipole Moments*

Determining the dipole moments of solvatochromic dyes is essential for understanding their molecular polarity and optimizing their electronic properties. Knowledge of dipole moments in the ground and excited states can assist in enhancing the performance of these dyes in applications like sensors<sup>xviii,xlvii</sup> and molecular electronics,<sup>xlviii</sup> where the precise tuning of electronic properties is crucial.<sup>xlix</sup> Additionally, it helps predict spectroscopic behavior, providing valuable insights into the electronic structure and bonding patterns of these dyes. Taking these facts into account, ground and excited state dipole moments of **5a** and **5b** were determined. The dipole moments were determined by employing a model introduced by Suppan and Tsiamis<sup>1</sup> (see Methods section; Equations 5-6) which allows the determination of ground and excited dipole moments of non-emissive

solvatochromic compounds.<sup>ii</sup> The author recently determined the dipole moment difference between the ground and MLCT-excited state of **5a**, nonetheless,<sup>18</sup> the current study included an additional molecular solvent (TFE) which was now also taken into account and for a complete comparison with the results obtained for **5b** (also including TFE). The complete results of the application of the model for **5a** and **5b** are presented in Table 5. The obtained values for **5a** were very close to the reported ones in a recent publication by the authors. Small differences in dipole moments between **5a** and **5b** were observed and **5b** was found to exhibit a slightly more polar excited state than **5a** as well as a larger difference  $\vec{\mu}_e - \vec{\mu}_g$  which is in line with the overall more dipolar nature of **5b** compared to **5a** (see discussion above) with  $\vec{\mu}_e = -1.423\vec{\mu}_g$  for **5a** and  $\vec{\mu}_e = -1.479\vec{\mu}_g$  for **5b**. Qualitatively, the model predicts a higher dipolar moment for the MLCT excited state compared to the ground state in both cases of compounds which is in line with the hypothesis of negative-solvatochromism. Practically, an increase of “pure” dipolarity expressed by an increase of the function:  $g(\epsilon, n^2) = \varphi(\epsilon) - \varphi(n^2)$  which excludes polarizability ( $\varphi(n^2)$ ) of the medium results in an increase of  $E_{CT}$  i.e. it induces hypsochromism.

**Table 5.** Results of application of Suppan-Tsiamis model in **5a** and **5b**.

	$a_r(\text{\AA})$	$k_c^* \left[ \frac{\vec{\mu}_g \cdot (\vec{\mu}_g - \vec{\mu}_e)}{a_r^3} \right]$	$k_c \left[ \frac{(\mu_e^2 - \mu_g^2)}{a_r^3} \right]$	$\left( \frac{\ \vec{\mu}_g\ }{(D)} \right)$	$\ \vec{\mu}_e\  (D)$	$r^2$	$rse^{\blacksquare}$
<b>5a</b>	5.01	$4.408 \cdot 10^{-19} \pm 7.106 \cdot 10^{-20}$	$1.869 \cdot 10^{-19} \pm 1.107 \cdot 10^{-19}$	15.1	21.5	0.997	$2.168 \cdot 10^{-20}$
<b>5b</b>	5.03	$4.263 \cdot 10^{-19} \pm 7.538 \cdot 10^{-20}$	$2.044 \cdot 10^{-19} \pm 1.174 \cdot 10^{-19}$	14.8	21.9	0.996	$2.299 \cdot 10^{-20}$

\* $k_c$ : Coulomb's constant;  $k_c = \frac{1}{4\pi\epsilon_0} \cong 8.988 \cdot 10^9 \text{ Nm}^2\text{C}^{-2}$ .  $\blacksquare$ rse: residual standard error (see details in materials and methods section).

### Polarity Sensing in Aqueous Urea

The intense solvatochromic behavior of compounds **5a** and **5b** can be conveniently used to quantify solvent polarity in aqueous solutions of polarity modifiers. The author has previously reported the sensing aptitude of compound **5a** in aqueous glucose solutions.<sup>xviii</sup> In the current study, the author attempts to quantify and rationalize the behavior of the polarity sensors **5a** and **5b** in aqueous urea solutions. To the best of the author's knowledge, studies on solvation effects in aqueous urea solutions are scarce and mainly focus on their dielectric properties.<sup>lii</sup> Nonetheless, there are only a few studies pertaining to the use of solvent polarity indicators that could probe specific effects such as H-bonding solute-solvent interactions.<sup>xxix</sup> To shed more light on this, the influence of urea concentration on polarity in water-based solutions is investigated using compounds **5a** and **5b**.

**Background studies:** In the study of urea-water solutions, it has been observed that dimers of urea form up to a concentration of 2M, while above this concentration, urea aggregates into chain-like structures.<sup>liii</sup> Rezus and Bakker, using polarization-resolved mid-infrared pump-probe spectroscopy, measured the orientational dynamics of water molecules and examined the rigidity of hydrogen bonds in urea-water mixtures. They found that water-structured networks are retained in the mixture, and urea interacts with only a few water molecules, leading to the formation of specific urea-water molecular arrangements<sup>liv</sup>. Moreover, Soper, Castner, and Luzar reported that urea can form hydrogen bonds with either water or urea molecules without significant preference.<sup>lv</sup> Additionally, quantitative analysis of spectra by Hayashi, et al. showed that the number of hydration water molecules is approximately two per urea molecule for concentrations below 5.0 M, while previous molecular dynamics studies predicted approximately six water molecules.<sup>lii</sup> Different authors have shown that there is a nearly linear increase of static permittivity with increasing urea content (see Table 6 and the ESI). Interestingly, moving from neat water to urea concentration of 9 M

the static permittivity of aqueous urea solutions increases from 78.4 to nearly 102 at 25 °C, i.e. a static permittivity nearly as high as that of formamide.<sup>lii</sup> This marked dielectric properties alteration is presumably associated with the formation of H-bonded clusters of urea and unbound water molecules resulting in highly dipolar species contributing to a high static permittivity. Different researchers have concluded via theoretical and experimental observations that urea hardly breaks the structure of water and this holds true both in low concentration urea solutions as well as high.

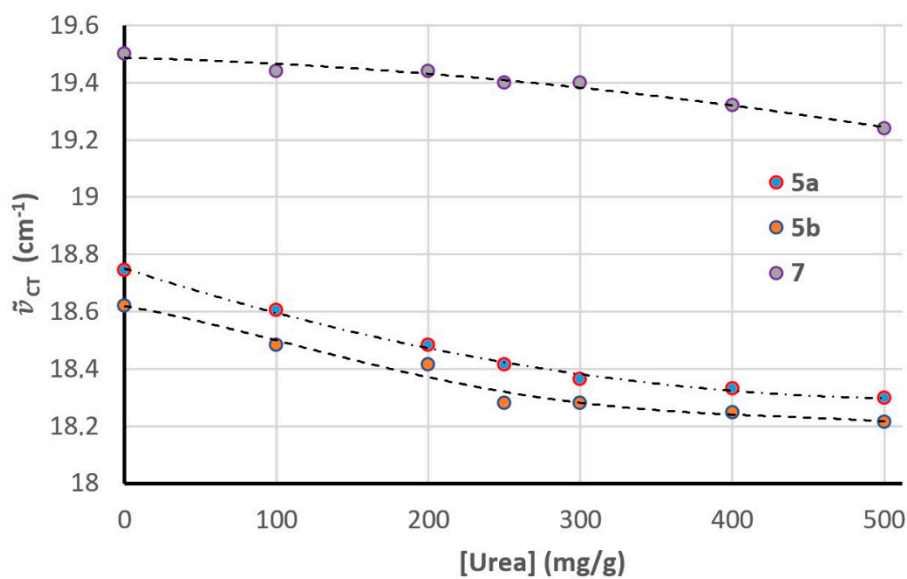
In terms of the polarity characteristics of aqueous urea solutions, apart from the aforementioned drastic increase of permittivity observed when increasing urea concentration, a milder yet sizable increase in the refractive index is also observed (see Table 6). However, using polarity parameter  $f(x)$  (see Methods section for details) the increase in dipolarity of aqueous urea as urea's concentration increases (expressed through function  $f(\epsilon)$ ) is more subtle compared to the observed increase in polarizability expressed through  $f(n^2)$ ; see the ESI for details). In turn, Dimroth-Reichardt's polarity scale decreases upon the increase of urea's concentration from 63.1 kcal/mol for neat water to 61.2 kcal/mol at a urea concentration of 500 mg/g (approx 9.5 M; see Table 6 for more data and the ESI for corresponding plots). The fact that  $E_T(30)$  is a measure of Lewis acidity and dipolarity/polarizability of the medium the above-described observations on  $f(\epsilon)$ ,  $f(n^2)$ , and  $E_T(30)$  indicate a significant decrease of Lewis acidity with the increase in urea concentration. Additionally, another solvatochromic compound namely Dicyanobis(1,10-phenanthroline)iron(II) (**7**) has been shown to be responsive to urea in a concentration-dependent fashion<sup>xxix</sup> however of low sensitivity (*vide infra*). The observed response of **7** was recorded as a hypsochromic effect in its vis-spectra (specifically the MLCT band) upon increasing urea concentration.<sup>xxix</sup>

Taking into account these findings on aqueous urea, the present study focuses both on dilute solutions lower than 2M as well as solutions with urea concentration up to approx. 9.5 M. Notably, both compounds exhibited a mild response to polarity changes induced when increasing urea's concentration (average 47.5 cm<sup>-1</sup>/M for **5a** and 35.9 cm<sup>-1</sup>/M for **5b**; see Table 7 and Figure 3 and 4B). Taking into account the positive solvatochromic response of **5a** and **5b** to the increase of  $f(\epsilon)$  or  $f(n^2)$  i.e. bathochromism upon the increase of dipolarity/polarizability the question that arises is "Is there an inversion of solvatochromism when moving from molecular solvents to aqueous urea?".

**Table 6.** Physicochemical and polarity properties of the studied aqueous urea solutions.

Urea Conc. (mg/g)	$\rho$ (g/L) <sup>lii</sup>	[Urea] (mol/L)	$E_T(30)$ <sup>xxix</sup> (kcal/mol)	$\tilde{\nu}_{CT}^7$ <sup>xxix</sup> (10 <sup>3</sup> cm <sup>-1</sup> )	$\epsilon$ <sup>lii</sup>	$n$ <sup>lvi</sup>	$f(\epsilon)$ <sup>▲</sup>	$f(n^2)$ <sup>▲</sup>
0	998.68	0.00	63.1	19.50	78.48	1.33100	0.4905	0.1706
100	1023.4	1.70	62.5	19.44	83.74	1.34720	0.4911	0.1760
200	1049.7	3.50	62.1	19.44	87.76	1.36210	0.4915	0.1816
250	1063.5	4.43	61.8	19.40	90.10	1.36980	0.4917	0.1844
300	1077.7	5.38	61.6	19.40	92.48	1.37780	0.4919	0.1873
400	1107.2	7.37	61.4	19.32	96.45	1.39430	0.4923	0.1931
500	1138.3	9.48	61.2	19.24	102.1	1.41180	0.4927	0.1992

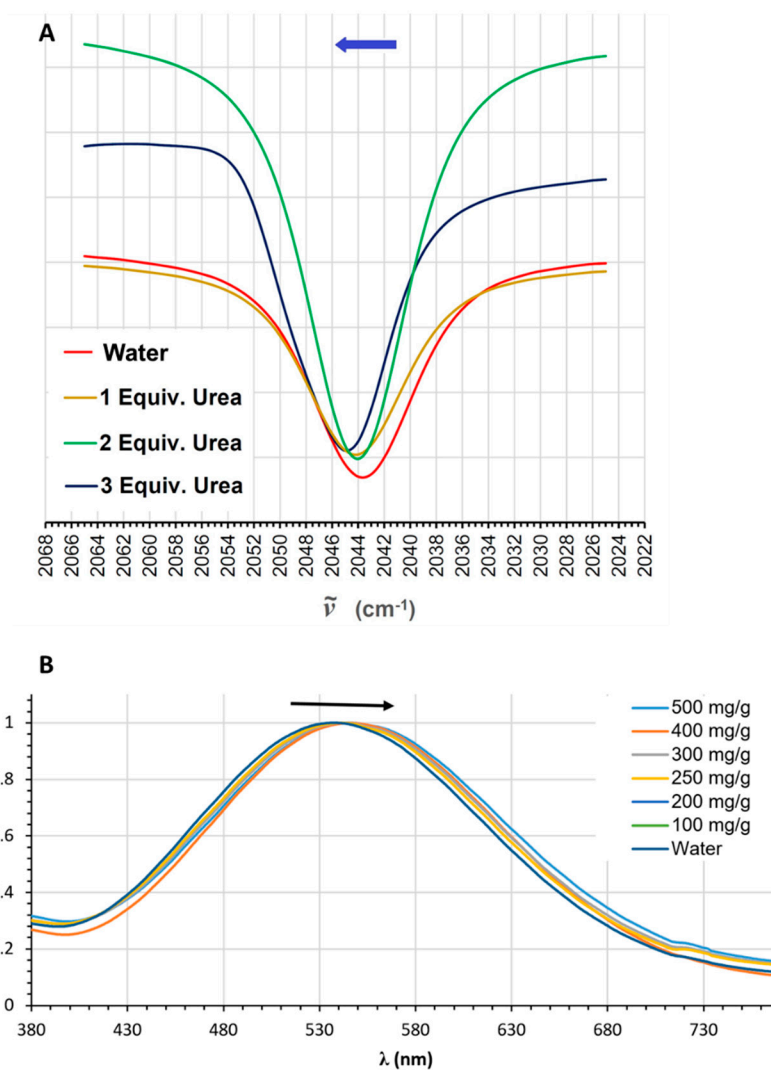
▲General Polarity function:  $f(x) = \frac{x-1}{2x+1}$ .



**Figure 3.** Plots of measured  $\tilde{\nu}_{CT}$  of solvatochromic compounds **5a**, **5b** and **7** against urea concentration. Lines in all cases are polynomial fits added for visualization purposes.

**Table 7.** Solvatochromic shifts observed in aqueous urea of compounds **5a** and **5b**.

Urea Concentration (mg/g)	$\lambda_{CT}^{5a}$ (nm)	$\tilde{\nu}_{CT}^{5a}$ ( $10^3 \text{cm}^{-1}$ )	$\lambda_{CT}^{5b}$ (nm)	$\tilde{\nu}_{CT}^{5b}$ ( $10^3 \text{cm}^{-1}$ )
0	533.5	18.744	537.0	18.622
100	537.5	18.605	541.0	18.484
200	541.0	18.484	543.0	18.416
250	543.0	18.416	547.0	18.282
300	544.5	18.365	547.0	18.282
400	545.5	18.332	548.0	18.248
500	546.5	18.298	549.0	18.215

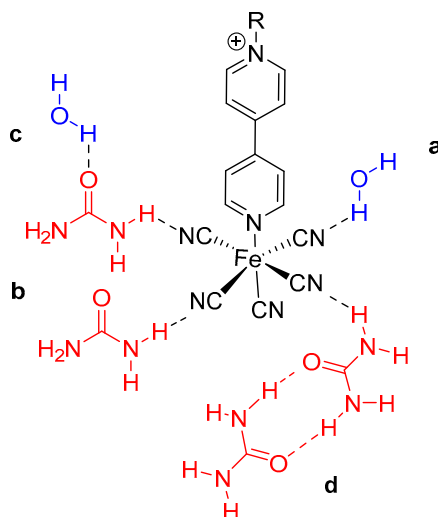


**Figure 4.** (A) Partial FTIR spectra of **5a** ( $C\equiv N$  stretching band) in water and in the presence of 1 (0.5 M), 2 (1 M), and 3 (1.5 M) equivalents of urea (at a constant **5a** concentration of 0.5 M). The arrow indicates the slight blue shift of the band with increasing urea equivalents. (B) Partial normalized UV-Vis spectra of **5a** in water at varying urea concentrations (0 to 9.48 M).

#### *An Inverted Solvatochromic Effect or a Pronounced Specific Effect?*

Answering this question is not trivial since it is not clear which type of interactions dominate at different urea concentrations. The author herein attempts an FTIR study (see experimental details) to complement this analysis. Through this study, small shifts and slight broadening of the  $C\equiv N$  stretching bands of **5ab** were observed when varying urea concentration from 0 to 9.48 M. The shift in reference to water solution was as anticipated more obvious yet a clear shift was observed while increasing the concentration of urea in the aqueous phase (see Fig. 4A). The results for both **5a** and **5b** were very similar. Small but noticeable shifts in the  $C\equiv N$  stretching band of both compounds were observed while increasing the concentration of urea solutions. This effect is associated with the development of hydrogen bond interactions between an HBD molecule and the CN groups of a cyanoferrate. The aforementioned H-bonding interaction can cause a shift in the vibrational frequency of the CN stretching mode. This shift can be observed as a blue shift in the infrared or Raman spectra and as anticipated, the extent of this shift depends on the strength of the hydrogen bond and the nature of the hydrogen bond donor and acceptor.<sup>lviii</sup> In the case of **5ab**, it was observed that, regardless of the concentration increase, no further shift of the  $C\equiv N$  stretching bands was

detected when there was an excess of urea. Once complete hydrogen bonding between the CN-groups of **5ab** and urea is achieved, any further changes in the dielectric properties of the solution have no significant effect on the C≡N stretching bands of the pentacyanoferrates. However, understanding how urea, water, and their complexes can hydrogen bond to pentacyanoferrates is not straightforward and is beyond the scope of this study. Potential H-bonding motifs are proposed in Figure 5 based on the background analysis (*vide supra*).



**Figure 5.** Plausible H-bonding motifs encountered in aqueous urea solutions of to **5a** and **5b** with low to intermediate urea concentration (< 5 M) (a: water molecule; b: urea molecule; c: a water-urea dimer; d: a urea dimer) R: substituent representing the remaining, non-displayed part of **5a/5b**.

#### Setting a Suitable Equation Describing Aqueous Urea Polarity Sensing

A good way to represent the observed aqueous urea polarity sensing mathematically is through an equation involving parameters expressing key medium polarity properties. Unfortunately, there are no theoretical properties describing the acidity of such solutions, in contrast to dipolarity and polarizability.<sup>lviii</sup> In light of this, a hybrid equation involving the empirical  $E_T(30)$  parameter by Reichardt and the functions  $f(\epsilon)$  and  $f(n^2)$  is employed (see Equation 10). Equation 10 attempts to represent the MLCT maxima wavenumbers  $\tilde{\nu}_{CT}$  in a very specific manner. It does so by subtracting dipolarity and polarizability from the empirical parameter  $E_T(30)$  through the functions  $f(\epsilon)$  and  $f(n^2)$ , thus removing their proportional contribution for the given medium (aqueous urea). The sensitivities  $m_2$  and  $m_3$  and the intercept  $m_1$  are determined through regression using the experimental  $\tilde{\nu}_{CT}$  data (Table 7) and the corresponding values of  $E_T(30)$ ,  $f(\epsilon)$ , and  $f(n^2)$ , at different urea concentrations (see Table 6; also for more details on the methodology see Materials and Methods Section).

Practically, Eq.10 provides  $\tilde{\nu}_{CT}$  as a function of Lewis acidity since the proportion of dipolarity that  $E_T(30)$  imparts is removed by subtracting the function  $f(\epsilon) - f(n^2)$  expressing dipolarity of the medium.

The results of Eq. 10 for **5a** and **5b** are included in Table 8.

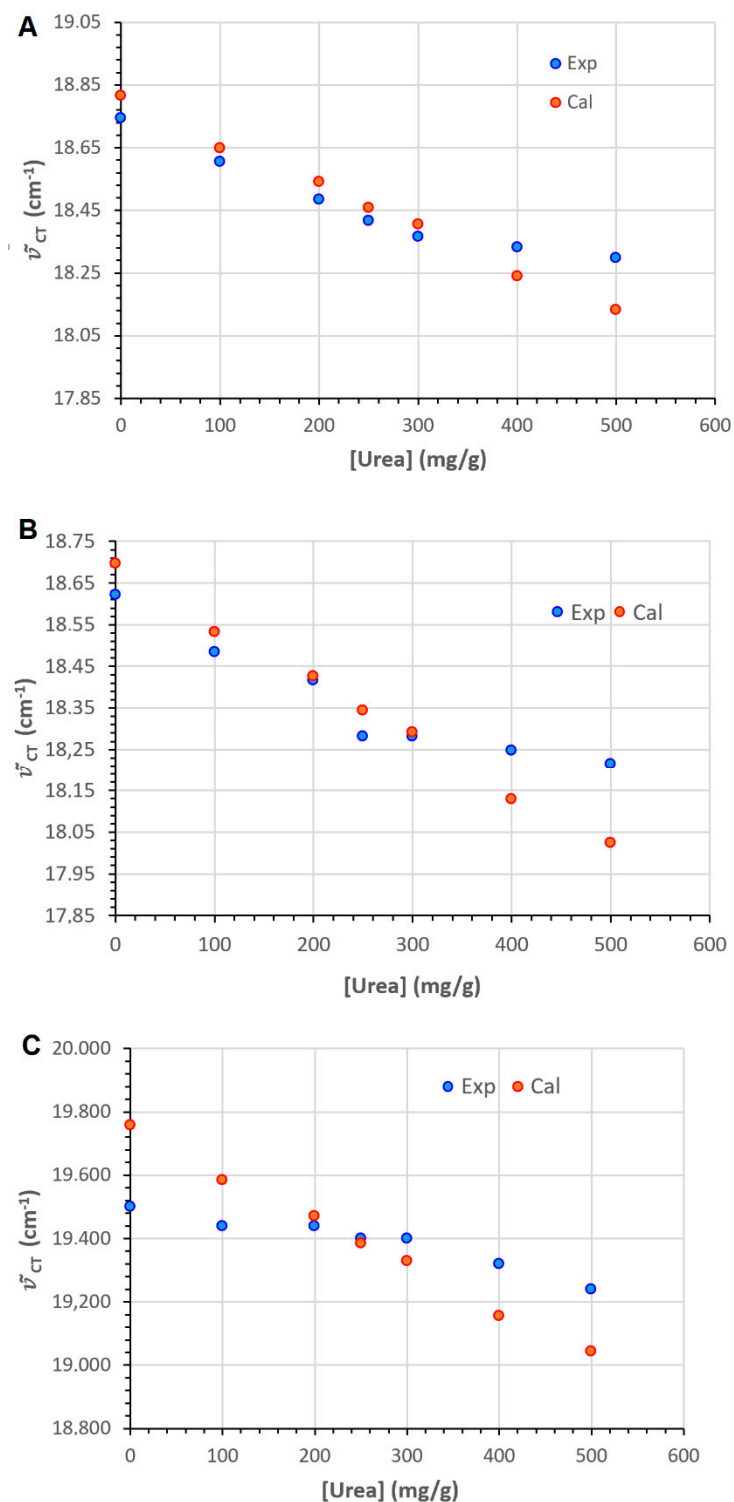
**Table 8.** Results of application of the model Equation 10 in **5a** and **5b**.

$\tilde{\nu}_{CT} = m_1 + m_2 E_T(30) - m_3 (f(\epsilon) - f(n^2))$						
	$m_1$ (cm <sup>-1</sup> )	$m_2$ (cm <sup>-1</sup> mol.kcal <sup>-1</sup> )	$m_3$ (cm <sup>-1</sup> )	$*r^2$	%RET(30)	%R <sub>f(ε)-f(n<sup>2</sup>)</sub>
<b>5a</b>	0.988	0.291	1.750	0.849	63	37
<b>5b</b>	1.168	0.286	1.621	0.898	59	41
<b>7</b>	1.182	0.302	1.580	0.556	11	88

\* $r^2$  corresponds to the regression coefficient of the linear fit:  $\tilde{\nu}_{CT}(exp)$  vs  $\tilde{\nu}_{CT}(cal)$  where *cal* values correspond to calculated values obtained through Eq. 10 whereas *exp* values correspond to the experimentally obtained values.

The obtained  $m_1, m_2$ , and  $m_3$  values provide accurate predictions of the  $\tilde{\nu}_{CT}$  for both compounds as implied by the high regression coefficients of the linear fitting of experimental and calculated  $\tilde{\nu}_{CT}$  values (see Figure 6). The model's prediction of a positive dependency of the  $\tilde{\nu}_{CT}$  on  $E_T(30)$  aligns with the assumption of a more stabilizing environment for the MLCT excited state of the compounds in aqueous urea when increasing urea concentration. This increase is associated with a decrease in Lewis acidity, as expressed by the  $E_T(30)$  parameter. Additionally, the relative importance of  $E_T(30)$  in the observed solvatochromism of both compounds was found to be the highest, around 60% in both cases (see Table 8) being slightly lower in the case of compound **5b**. The negative sensitivity of  $\tilde{\nu}_{CT}$  to  $f(\epsilon) - f(n^2)$  observed in both cases (since  $m_3$  was positive in both cases; Table 8 and Eq. 10), along with the very low contribution of dipolarity (expressed via  $f(\epsilon) - f(n^2)$ ), suggests that the phenomenon should not be attributed to an inverted solvatochromism. Instead, it potentially indicates the dominance of specific interactions, particularly hydrogen bonding, in the cybotactic region involving compounds **5a** and **5b** as solutes.

Compound **7** (a dicyanoferrate(II) solvatochromic complex) on the other hand exhibited qualitatively the same behaviour as probes **5a** and **5b** i.e. a decrease of  $\tilde{\nu}_{CT}$  (hypsochromism) upon increasing urea concentration. Nonetheless, the sensitivity of **7** to the solvent polarity changes that the increase of urea concentration imparts to the medium, was lower than any of the compounds **5a** or **5b** (6 nm for **7**, 13 nm, and 12 nm respectively for **5a** and **5b** within the range of urea concentration 0 and 9.48 M respectively). This finding underlies their superiority over this renowned solvatochromic compound. Model Eq. 10 was not as successful in describing the solvatochromic effect for **7** as compared to **5a** and **5b** (see Table 8 and Figure 6 for details).



**Figure 6.** Experimental and calculated through Eq. 10  $\tilde{\nu}_{CT}$  values for solvatochromic compounds A) 5a, B) 5b and C) 7.

## Conclusions:

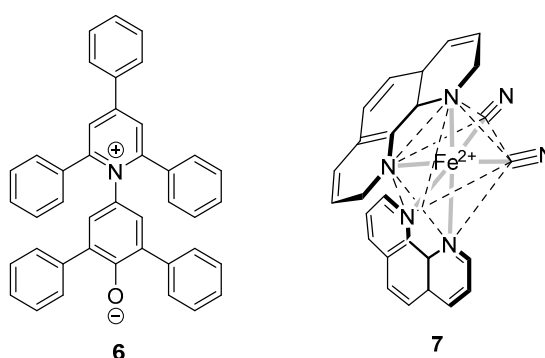
Two intensely solvatochromic pentacyanoferrate(II) complexes were synthesized and characterized. Their solvatochromism was examined in a set of solvents, including both protic and non-protic solvents, and binary mixtures of molecular solvents. A strong negative solvatochromic effect was observed. Small differences between the two examined compounds were attributed to the structural diversity of the ligands.

Rationalization of the solvatochromic shifts in terms of solute-solvent interactions revealed a strong dependency on Lewis acidity as well as on the dipolarity/polarizability of the medium. This analysis was based on a well-defined set of LSERs, offering complementary information on specific and non-specific solute-solvent effects. Moreover, the dipole moments in the excited and ground states of both compounds were determined using the Suppan-Tsiamis method based on spectral data. It was found that compound **5b** exhibits a more polar excited state as well as a larger difference between the excited and ground states than compound **5a**. This effect was attributed to the different side-heterocycles, the only differing structural feature between the two compounds.

Additionally, the evaluation of the urea-sensing aptitude in aqueous solutions indicated that both compounds are prone to probe a significant difference in Lewis acidity upon an increase in urea concentration. However, the dipolarity of the medium exhibited a relatively lesser impact on the solvatochromic sensitivity of both compounds. Compared to compound **7**, a known solvatochromic probe, compounds **5a** and **5b** were proved to be more sensitive to changes in urea concentration. The behavior of the two compounds is quantitatively comparable to Reichardt's solvatochromic betaine **5**.

## Materials and Methods

### Materials:



**Figure 7.** Reference solvatochromic compounds.

### Computations

#### Linear Solvation Energy Relationships (LSERs)

In the context of the study of correlations of  $\tilde{\nu}_{CT}$  with different solvent polarity parameters the following mono- and multi-parametric LSERs were employed:

$$\tilde{\nu}_{CT} = \tilde{\nu}_o + e \cdot E_T^N \quad (1)$$

$$\tilde{\nu}_{CT} = \tilde{\nu}_o + s \cdot \pi^* + a \cdot \alpha + b \cdot \beta \quad (2)$$

$$\tilde{\nu}_{CT} = \tilde{\nu}_o + s \cdot \pi^* + a \cdot \alpha \quad (3)$$

$$\tilde{\nu}_{CT} = \tilde{\nu}_o + e \cdot E_T^N + b \cdot \beta \quad (4)$$

Eq. 1 correlates  $\tilde{\nu}_{CT}$  with the normalized polarity scale by Reichardt<sup>xxxix</sup>, Eq. 2 is the so-called Kamlet, Taft and Abboud (KAT) equation<sup>xliv</sup> and Eq. 3 its reduced form excluding parameter  $\beta$ .<sup>xix</sup>

Equation 4 is analogous to Krygowski-Fawcett equation which is often used to quantify and rationalize the effects of solvent polarity on a variety of physicochemical properties and spectroscopic data.<sup>xlvi</sup> In its original form the model employs Dimroth-Reichardt  $E_T(30)$  parameter and the Gutmann's donor numbers DN. In fact, the author has used in the past this equation encompassing normalized parameters (i.e. normalized Reichardt solvent polarity scale and  $DN^N$  (normalized donor number) yet, here it is employed with parameter  $\beta$  instead of  $DN^N$ .<sup>lix</sup> One of the benefits of using the normalized versions is that both parameters involved are dimensionless and very within the same

range i.e. 0 to 1. More details can be found in a recent publication where Equation 4 was utilized to rationalize solvatochromic data in binary solvent mixtures.<sup>xiv</sup>

All linear correlations (both mono- and multi-parametric) were performed using *RStudio* (ver: 2024.09.1+394). The calculations included the determination of standard errors for the parameters, as well as the calculation of the residual sum of squares (*rss*) and the coefficient of determination ( $r^2$ ). The *RStudio* environment provided the necessary tools and packages to accurately perform these statistical analyses.

### Dipole Moment Calculations

For the determination of dipole moments in ground and MLCT excited states of compounds **5a** and **5b** the model by Suppan and Tsiamis<sup>1</sup> (Eq. 5) was used. The model is ideal for dyes that are not emissive.

$$E_{CT} = \frac{1}{4\pi\epsilon_0} \left[ \frac{\mu_g \cdot (\mu_g - \mu_e)}{a^3} (\varphi(\epsilon) - \varphi(n^2)) + \frac{(\mu_e^2 - \mu_g^2)}{a^3} \varphi(n^2) \right] \quad (5)$$

$$\varphi(x) = \frac{2(x-1)}{2x+1} \quad (6)$$

The cavity terms (Van der Waals radii) of both compounds ( $a$  (Å)) were determined using the following procedure: First, the structures were drawn in *Chemtool* 1.6.15 and then optimized using Molecular Mechanics on *Avogadro* 1.2.0. The UFF force field was used in both cases. The resulting configurations were further used as input for the determination of the Van der Waals radii using 3V:VossVolume Voxalator, available online. The latter was directly used as the cavity term.

### Determination of Relative Importance (Contribution) of Each of the Parameters Involved in the LSERS

For the calculation of the relative importance (contribution) of each of the parameters involved in the LSERS and other equations (Eq. 1-4 and 10), the following methodology was employed. A general multiparametric LSER model can be assigned as in the general Equation the quantity  $Q$  with the parameters  $X_1, \dots, X_i, \dots, X_n$ , according to Eq. 3 is assumed<sup>lix</sup>:

$$Q = Q_0 + \sum_{i=1}^n (x_i X_i) \quad (7)$$

$$P(X_i) = \frac{100x'_i}{\sum_{i=1}^n x'_i} \quad (8) \text{ where } x'_i = |x_i| \sqrt{\frac{\sum_{j=1}^m (X_{ij} - \bar{X}_i)}{\sum_{j=1}^m (Q_j - \bar{Q})}} \quad (9)$$

In this equation,  $Q_0$  is the regression value of the intercept of this linear model, and  $x_1, \dots, x_i, \dots, x_n$  are the coefficients of the parameters  $X_1, \dots, X_i, \dots, X_n$ , respectively. These coefficients reflect the sensitivity of the quantity  $Q$  to the parameters  $X_1, \dots, X_i, \dots, X_n$ . The coefficients  $x_1, \dots, x_i, \dots, x_n$  are obtained through linear multiparametric regression analysis. (In this work,  $n=3$  for Eq. 2;  $n=2$  for Eqs: 3-4). Furthermore, assuming that we have  $m$  series of data, e.g.  $m$  different cases of solvents (in the case of this work  $m=9$  solvents), the relative contribution of each one of the parameters  $X_i$  [symbolized as  $P(X_i)$ ] to the quantity  $Q$ , can be calculated through Eq. 8. In Eq. 8,  $(x_i)'$  is calculated through Eq. 9, where  $\bar{X}_i$  and  $\bar{Q}$  are the mean values of the parameter  $X_i$  and of the quantity  $Q$ , respectively, and finally  $|x_i|$  is the absolute regression value of  $x_i$  obtained from the regression analysis.

### Model Describing Aqueous Urea Solvatochromic Sensing

$$\tilde{\nu}_{CT} = m_1 + m_2 E_T(30) - m_3 (f(\epsilon) - f(n^2)) \quad (10)$$

$$\text{with } m_1, m_2, m_3 > 0 \text{ and } f(x) = \frac{x-1}{2x+1} \quad (11)$$

from **Kirkwood-Bauer-Mataga (KBM)** equation.<sup>xxxix</sup>

Description on method: The R package *nloptr* (Version 2.1.1) was used to perform the optimization (see Eq. 10). An objective function was constructed to minimize the sum of squared residuals between the observed and predicted values. The function was defined to include the

parameters of interest, and initial values for these parameters were set to  $c(1,1,1)$ . The lower and upper bounds for the parameters were defined as  $c(0,0,0)$  and  $c(\infty,\infty,\infty)$ , respectively in order to ensure that  $m_1, m_2, m_3 > 0$ . The optimization was performed using the *NLOPT\_LN\_COBYLA* algorithm with a relative tolerance of  $1 \times 10^{-6}$ . The optimized parameters *aa*, *bb*, and *cc* were extracted from the result object obtained after the optimization process (are listed in Table 8).

### Spectroscopic and Analytical Methods

NMR spectra were obtained using a Varian Gemini 300 spectrometer (300 MHz  $^1\text{H}$ , 75 MHz  $^{13}\text{C}$ ). Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO-*d*<sub>6</sub> at  $25 \pm 1$  °C. The  $^1\text{H}$  NMR spectra were calibrated by using residual undeuterated solvent as an internal reference (4.79 ppm) and  $^{13}\text{C}$  NMR spectra were calibrated using the DMSO-*d*<sub>6</sub> signal at 39.52 ppm.<sup>lx</sup> Abbreviations used for multiplicity in the text: s = single; d = doublet; m = multiplet; arom = aromatic; Ph = phenyl.

Elemental Analyses were performed on a Perkin-Elmer Elemental Analyzer 2400 CHN.

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  $25 \pm 1$  °C. Each measurement was repeated three times; therefore, each of the values of CT energies listed in Tables 2 and 7 correspond to the average of three measurements (standard deviation 0.5 nm).

Fourier-transform infrared spectroscopy: Infrared spectrum were recorded using a Fourier-transform infrared spectrophotometer (Spectrum Two, Perkin-Elmer, Llantrisant, UK) equipped with a Universal Attenuated Total Reflectance diamond. All FTIR spectra were collected at a spectrum resolution of  $4 \text{ cm}^{-1}$ , with 32 scans from  $4000$  to  $500 \text{ cm}^{-1}$ .

Thermogravimetric analysis: Thermograms were made with a Mettler-Toledo TGA2 (Mettler Toledo, Greifensee, Switzerland), under nitrogen with a flow rate of  $40 \text{ mL min}^{-1}$ , using alumina pans. 5 to 10mg of each sample were put in a standard TGA alumina crucible pan at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### Syntheses

#### General Method for the Synthesis of Products (**3a-b**)

In a solution of  $\alpha,\alpha'$ -dichloro-*p*-xylene (**1**) (171 mg, 1 mmol in 5 mL  $\text{CHCl}_3$ ), half the stoichiometric amount (0.5 mmol) of the heterocyclic compound (**2a-b**) is added. The solution is then left to boil under stirring for 10 hours, during which a white precipitate forms. This precipitate is filtered under vacuum and washed with  $\text{CHCl}_3$  and then with diethyl ether. The solids are dried under vacuum for several hours and stored in a vacuum desiccator in the presence of  $\text{P}_2\text{O}_5$ .

#### 2-(4-(. chloromethyl)benzyl)isoquinolin-2-ium (**3b**)

White hygroscopic solid, 118 mg, 78%, mp  $> 250$  °C.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 9.81$  (s, 2H: isoq.), 8.56 (d,  $J = 6.3 \text{ Hz}$ , 2H: isoq.), 8.39 (m, 3H, arom.), 8.17 (m, 3H, arom.), 7.98 (t,  $J = 5.7 \text{ Hz}$ , 1H: isoq.), 7.65 (s, 2H: (- $\text{CH}_2$ )-isoq.), 6.00 (s, 2H: (- $\text{CH}_2$ )-Cl).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}/[\text{D}_6]\text{DMSO}$ ): 150.95, 139.25, 139.02, 136.38, 135.56, 133.13, 131.81, 131.56, 129.31, 128.82, 128.35, 65.35 (-( $\text{CH}_2$ )-py), 40.09 (-( $\text{CH}_2$ )-Cl).

#### Preparation of Products (**4a-b**)

Dissolve product **3a-b** (0.427 mmol) in 5 mL of DMF. Addition of 4,4'-Dipyridine: An excess of 4,4'-dipyridine (135 mg, approximately 0.855 mmol, which is 2 times the amount of **3a-b**) was added to the solution. The solution was placed in an oil bath at a temperature of  $100$ - $110$  °C for 10 hours. 20 mL of anhydrous acetone was added to the solution, and immediately a white precipitate of product (**4a-b**) was formed. The solid was filtered with suction and washed several times with ethanol (to

remove DMF) and diethyl ether. Finally, the product was dried under vacuum for several hours. Both products (**4a-b**) are highly hygroscopic and should be stored in a vacuum desiccator with P<sub>2</sub>O<sub>5</sub>.

#### 2.-(4-([4,4'-bipyridin]-1-ium-1-ylmethyl)benzyl)isoquinolin-2-ium: Ligand: Ligand **4b**

Off-white hygroscopic powder, 140 mg, 72%, mp>250 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ =9.44 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.36 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.84 (d, J = 6.6 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.75 (d, J = 7.2 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.63 (d, J = 6.9 Hz, 1H: C<sub>5</sub>H<sub>4</sub>N), 8.55 (d, J = 6.9 Hz, 1H: isoq.), 8.42 (d, J = 6.3 Hz, 1H: isoq.), 8.10 (d, J = 6.3 Hz, 2H: isoq.), 7.99 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 7.11 (d, J = 7.2 Hz, 4H: Ph), 5.93 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O/[D<sub>6</sub>]DMSO): 152.32, 149.85, 146.18, 144.89, 144.32, 142.77, 140.17, 131.42, 130.56, 128.92, 128.00, 127.36, 127.21, 126.23, 124.67, 121.39, 62.4 (CH<sub>2</sub>), 61.9 (CH<sub>2</sub>).

#### General Method for the Synthesis of Solvatochromic Products (**5a-b**)

In an aqueous solution of the heterocyclic ligand (**5a-b**) (0.450 mmol in 5 mL H<sub>2</sub>O), add 0.500 mmol (163 mg) of freshly prepared Na<sub>3</sub>[Fe<sup>II</sup>(CN)<sub>5</sub>NH<sub>3</sub>]<sub>3</sub>H<sub>2</sub>O salt. The solution immediately takes on a characteristic violet color (due to complex formation). The solution was stirred in the dark under an inert atmosphere (Ar) at room temperature for 6 hours. Then, add ethanol (EtOH) in a volume six times that of the solution (30 mL) and leave the mixture in the dark at 4°C for 12 hours, during which a colored precipitate forms in all cases. Collect the precipitate by vacuum filtration, and wash it sequentially with cold EtOH and diethyl ether (Et<sub>2</sub>O) several times. Finally, dry the product under vacuum at a temperature above 40°C.

#### Solvatochromic Complex **5b**

Deep blue solid, 237 mg (0.305 mmol) 68% mp> 300 °C (dec.). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):9.52 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 9.42 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.90 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.83 (d, J = 6.9 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 8.69 (d, J = 7.2 Hz, 1H: C<sub>5</sub>H<sub>4</sub>N), 8.59 (m, 2H: isoq.), 8.16 (d, J = 6.9 Hz, 2H: isoq.), 8.07 (d, J = 7.2 Hz, 2H: C<sub>5</sub>H<sub>4</sub>N), 7.21 (d, J = 9.2 Hz, 4H: Ph), 5.99 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O/[D<sub>6</sub>]DMSO): 172.34 (CN), 152.96, 150.15, 146.83, 144.99, 144.82, 143.17, 140.53, 132.02, 130.86, 129.12, 128.66, 127.82, 127.91, 126.79, 124.78, 121.94, 62.69 (CH<sub>2</sub>), 62.81 (CH<sub>2</sub>). TGA: loss of approx. 6 molecules of H<sub>2</sub>O.

## Nomenclature

$\alpha_r$	Van der Waals cavity parameter of a solvatochromic compound
$a$	HBD-acidity parameter (involved in KAT equation)
$a$	Coefficient of parameter $a$
$\beta$	HBA-basicity parameter (involved in KAT equation)
$b$	Coefficient of parameter $\beta$
bpy	4,4'-bipyridine
$\delta$	Chemical shift (NMR)
$e$	Coefficient of parameter $E_T^N$ in Eq.: 1 and 4
EG	Ethylene glycol
$E_T^N$	Normalized Reichardt's polarity scale
$E_T(30)$	Dimroth-Reichardt's polarity scale
$\epsilon$	Permittivity of the medium
$\epsilon_0$	Vacuum permittivity
$f(\epsilon)$	Dipolarity function
$f(n^2)$	Polarizability function
FA	Formamide
$\varphi(\epsilon)$	Dipolarity function in Suppan-Tsiamis equation
$\varphi(n^2)$	Polarizability function in Suppan-Tsiamis equation
$g(\epsilon, n^2)$	"Pure dipolarity" function: $g(\epsilon, n^2) = \varphi(\epsilon) - \varphi(n^2)$
HBD	Hydrogen Bond Donor
HBA	Hydrogen Bond Acceptor
$J$	Coupling constant in <sup>1</sup> H-NMR
KAT	Kamlet Taft Abboud (Equation)
$k_C$	Coulomb's constant; $k_C = \frac{1}{4\pi\epsilon_0} \cong 8.988 \cdot 10^9 \text{ Nm}^2\text{C}^{-2}$

LSER	Linear solvation energy relationship
$\lambda_{CT}^{5a}, \lambda_{CT}^{5b}, \lambda_{CT}^7$	MLCT maximum wavelength of compound <b>5a</b> , <b>5b</b> and <b>7</b> respectively
$m_1, m_2, m_3$	Intercept and two coefficients involved in Eq.10
$\overrightarrow{\mu}_g$	Ground state dipole moment
$\overrightarrow{\mu}_e$	Excited state dipole moment
$\tilde{\nu}_{CT}^{5a}, \tilde{\nu}_{CT}^{5b}, \tilde{\nu}_{CT}^7$	MLCT maximum wavenumber of compound <b>5a</b> , <b>5b</b> and <b>7</b> respectively
$\tilde{\nu}_o$	Intercept MLCT wavenumber involved in LSERs:1-4
$n^2$	Polarizability of the medium
$n$	Refractive index of the medium
NMF	N-methyl formamide
$\pi^*$	Dipolarity/polarizability parameter involved in KAT equation
$Q$	Physicochemical parameter involved in the generic LSER equation:
$Q_o$	Intercept involved in the generic LSER equation:
$P$	Density of an aqueous urea solution
$s$	Coefficient of parameter $\pi^*$ (KAT equation)
TFE	2,2,2-trifluoroethanol
$x_i$	Coefficient of parameter $X_i$
$X_i$	Parameter involved in the generic LSER model

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