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Study of the correlations of the MLCT Vis absorption maxima of 4-pentacyanoferrate-4′-arylsubstituted bispyridinium complexes with the Hammett substituent parameters and the solvent polarity parameters E_T^N and AN

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In this work six new 4-aryl substituted bispyridinium salts have been synthesized using 2,4-dinitrophenyl-bispyridinium chloride as the starting material, which was arenamine exchanged via the Zincke reaction. These aromatic heterocyclic salts were used as ligands, acting as Lewis bases to form a series of 4-pentacyanoferrate-4′-aryl substituted bispyridinium complex salts in high yields. The complex salts were characterized using several spectroscopic techniques including ^{1}H as well as ^{13}C NMR spectroscopy, UV–Vis and FTIR spectrophotometry. These materials present a number of interesting electronic and optical properties. Herein we mainly focused on the electronic absorption of these materials. The visible metal-to-ligand-charge-transfer (MLCT) band of these materials assigned as dπ(Fe^{II}) → π^*(L) was proved to be affected by substituent changes (of the benzene ring of the complexes) but mainly by solvent polarity changes. Band shifts of even 4000 cm^{-1} were induced by small solvent polarity changes (e.g., water to methanol). The Vis absorption spectra were investigated in four protic solvents (water, 2,2,2-trifluoroethanol, ethylene glycol, and methanol). The substituent effects were then quantified using the Hammett equation which correlates the MLCT absorption wavenumbers with the Hammett constant (σ_x). Furthermore, two of the most successful solvent polarity parameters (the acceptor number AN and the normalized solvent polarity scale E_T^N) were used to quantify the solvent polarity effects on the MLCT absorption wavenumbers. The correlations obtained in all cases proved to be satisfactory. The dominant interaction responsible for the solvent polarity effects proved to be the hydrogen-bond formation between the cyano groups of the complex salts and the protic solvents.

Keywords: pentacyanoferrate complex salts; substituent effects; solvatochromism; Hammett equation; LFERs

INTRODUCTION

Complexes of several transition metals, such as ruthenium, osmium, and iron with aromatic heterocyclic ligands such as *N*-monosubstituted bispyridines are interesting materials which in recent years have been examined for their unique optical and electronic properties. Coe *et al.*[1] have reported the synthesis and Non-Linear-Optical properties (NLO) of such products, Toma and Takasugi[2] as well as Blandamer *et al.*[3] have reported that complexes like these are markedly solvatochromic, Pinheiro *et al.*[4] have also studied some ruthenium (II) complexes for use as highly sensitive sensors for water in aprotic solvents using simple UV–Vis spectrophotometry. Dyes with an analogous molecular structure have been also used as molecular switches,[5] as solvatochromic probes,[6] and in many other new technologies. In this work six new 4,4′-bispyridinium-1-aryl-1′-pentacyanoferrate (II) complex salts **4a-f** (Scheme 1) were synthesized, characterized, and their UV–Vis spectra were recorded in four protic solvents, [water, 2,2,2-trifluoroethanol (TFE), ethylene glycol (EG) and methanol], and the electron donor–acceptor effect of the aryl substituents as well as the influence of the solvent polarity on the Vis spectra were examined.

For substituent effects on the electronic absorption maxima, the simple type of the Hammett equation was used [Eqn (1)]. In this equation $\tilde{\nu}_x$ is the wavenumber of the absorption maximum of a compound with substituent X on its benzene ring, σ_x is the Hammett constant of the substituent X, $\tilde{\nu}_o$ is the absorption maximum wavenumber of the compound for X = H and $\Delta\tilde{\nu}$ is the difference between $\tilde{\nu}_x$ and $\tilde{\nu}_o$.[7,8]

$$\Delta\tilde{\nu} = \tilde{\nu}_x - \tilde{\nu}_o = \rho.\sigma_x \quad \text{or} \quad \tilde{\nu}_x = \tilde{\nu}_o + \rho.\sigma_x \qquad (1)$$

The solvatochromism of these products was also examined. For the solvent polarity effects on the electronic absorption maxima of these compounds we have examined the correlation of the absorption wavenumbers with the normalized Reichardt solvent polarity scale E_T^N[9] and Gutmann's acceptor number (AN),[10] two

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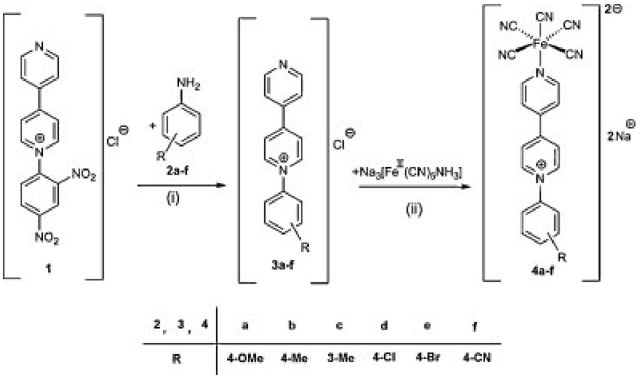


Scheme 1. Synthetic route for the preparation of complex salts **4a-f**. (i) EtOH, reflux, 4–48 h (ii) H_2O, r.t., Ar atmosphere, 6 h

of the most successful quantitative measures of solvent polarity. In both cases regression analysis resulted in six linear relations (one for each compound) which were of the type

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{Do}} + a_{\mathrm{D}} E_T^N \tag{2}$$

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{Go}} + a_{\mathrm{G}} \mathrm{AN} \tag{3}$$

In Eqns (2) and (3) α is the slope and $\tilde{\nu}_o$ is the intercept resulting from the analysis mentioned before (the subscript D corresponds to the correlation with the E_T^N solvent polarity scale and the subscript G to the correlation with the AN parameter). The intercept in both cases corresponds to the regression value of the absorption wavenumber of a certain compound in the solvent where the E_T^N scale [for Eqn (2)] or the AN parameter [for Eqn (3)] is zero. The slope α in both equations has a physical meaning by indicating the sensitivity of the absorption wavenumbers to the solvent polarity. Afterwards the experimental absorption wavenumbers were compared to those calculated from the above two equations.

RESULTS AND DISCUSSION

The 4,4′-bispyridinium-1-aryl-1′-pentacyanoferrate (II) complex salts **4a-f** were prepared in two steps. 2,4-dinitrophenyl-4,4′-bispyridinium chloride **1** was used as starting material for the synthesis of the *N*-aryl substituted 4,4′-bispyridinium chloride salts **3a-f** (Scheme 1). **1** was arenamine-exchanged via the Zincke reaction[11] giving products **3a-f** in high yields. Then these products were reacted with **$Na_3[Fe^{II}(CN)_5NH_3]$** to afford the complex salts **4a-f**.[12]

These new compounds have interesting optical and electronic properties. In this work we are interested in the UV–Vis spectra of these materials.

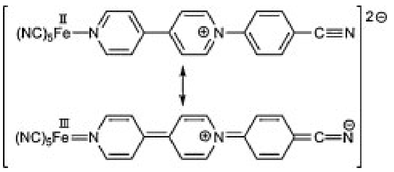
The 4,4′-bispyridinium-1-aryl-1′-pentacyanoferrate(II) complex salts exhibit two absorption bands in their UV–Vis spectra. The first one lies in the region of $\lambda_{max} = 310$–330 nm and presents molecular extinction coefficients (ε_{max}) which vary from 5.10^3 to 6.10^3 ($M^{-1}\,cm^{-1}$) corresponding to π-π^* intraligand excitations. In all cases these UV bands are sharp and generally their position in the UV–Vis spectrum does not seem to be considerably affected neither by substituent changes (of their benzene ring) nor by solvent polarity changes. The second Vis absorption band is an intense broad metal-to-ligand-charge-transfer (MLCT) band assigned as $d\pi(Fe^{II}) \rightarrow \pi^*(L)$, the energy of which depends on the electron-donor ability of the Fe^{II} center and the electron-acceptor ability of the ligand (L).[1] These bands are affected mainly by solvent polarity changes, but also by substituent changes as shown in Table 1. Their position in the UV–Vis spectrum lies in the region of $\lambda_{max} = 550$–750 nm and their molecular extinction coefficients (of the maximum absorptions) vary from 3.10^3 to 4.10^3 ($M^{-1}\,cm^{-1}$). In this work we focus on the substituent and solvent polarity effects on the MLCT bands of these complex salts.

Table 1. Wavenumbers of the MLCT Vis absorption maxima of **4a-f**, measured in four solvents of different polarity

$\tilde{\nu}_{MLCT}$ /($10^3\,cm^{-1}$)	H_2O	TFE	EG	MeOH
4a (*p*-OMe)	17.699	17.482	14.970	13.755
4b (*p*-Me)	17.668	17.483	14.970	13.699
4c (*m*-Me)	17.759	17.094	14.981	13.680
4d (*p*-Cl)	17.483	17.007	14.641	13.500
4e (*p*-Br)	17.452	16.920	14.620	13.495
4f (*p*-CN)	17.065	16.447	14.205	13.245

Bathochromic band shifts of the MLCT bands are induced when electron-withdrawing substituents are introduced in the benzene ring. These bathochromic band shifts are probably associated with the stabilization of the excited state by delocalization of the charge transferred from the metal to the aromatic system of the ligand taking place during the excitation of molecules (Scheme 2). Electron-withdrawing substituents stabilize more the MLCT excited state than electron-donating substituents, by attracting effectively the charge transferred from the metal to the ligand, so the MLCT bands are shifted to longer wavelengths (bathochromism) in the case of electron-withdrawing substituents. The steady red shift of the MLCT bands is in agreement with the increasing acceptor strength order *p*-OMe < *p*-Me < *m*-Me < *p*-Cl < *p*-Br < *p*-CN of substituents on the benzene ring of the examined compounds.

The Hammett equation is satisfactory even in its simplest type in quantifying substituent effects in spectral data (obtained from UV–Vis, NMR, or IR spectroscopy) and that is why it has been widely used in the past for this purpose for many cases in organic[7,13–16] and coordination chemistry.[17] For the use of this equation we consider that the benzene ring which is attached to the 4,4′-bispyridine moiety, plays little role in the electronic MLCT excitation process or in other words the electron density changes in the benzene ring are minimal. Under this condition the substituents attached to the ring may influence the position of the MLCT band indirectly by their electron-donating or withdrawing effect and thus the transition energy of the MLCT band will be in proportion to the Hammett substituent constant σ_x.[7]



Scheme 2. Limiting resonance structures of the complex anion **4f**

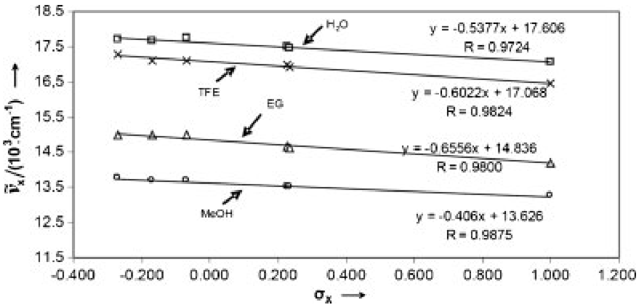


Figure 1. Correlation between Hammett's substituent constants, σ_x, and the wavenumbers of **4a-f**, $\tilde{\nu}_x$, measured in four protic solvents at room temperature

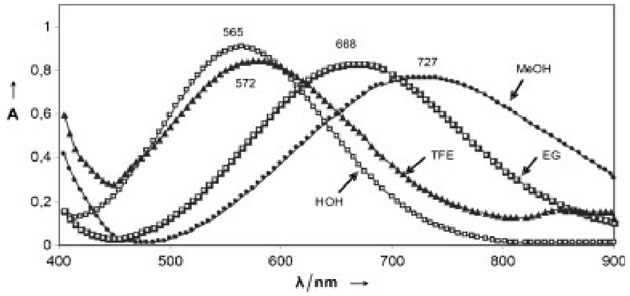


Figure 2. Vis absorption spectra of **4a**, measured in H_2O, TFE, EG, and MeOH at room temperature

For the quantitative assessment of the substituent effects on the MLCT band absorption wavenumbers of our products we have used the simple type of the Hammett equation [Eqn (1)] using the σ_p substituent constants for the *para* substituents (*p*-OMe, −0.268; *p*-Me, −0.170; *p*-Cl, +0.227; *p*-Br, +0.232),[18] the σ_m substituent constant for *m*-Me (−0.069)[18] and finally the σ_α^- constant for *p*-CN (+1.00).[18,19] The σ_α^- value for *p*-CN (+1.00) was derived by Zollinger, Wittwer,[19] concerning the acidity constants of substituted anilinium ions. Four linear relationships were gained from the Hammett correlation, one for each solvent. These correlations are shown in Fig. 1. The same slopes were obtained for both donors (*p*-OMe, *p*-Me, *m*-Me) and acceptors (*p*-Cl, *p*-Br, *p*-CN). In all four solvents used, the correlation between the measured wavenumbers of the MLCT bands and the Hammett substituent constant σ, was quite good (in all cases $R > 0.970$). There was no reason in using a more sophisticated type of the Hammett equation.

In all cases the slope ρ of the correlation equations was negative which means that an increase in the acceptor strength of a substituent of a compound induces a decrease of the MLCT maximum absorption wavenumber of the UV–Vis spectrum of this compound. The sensitivity of the MLCT absorption wavenumbers to the substituent changes, proved to be greater in the case of ethylene glycol as solvent (in that case ρ had the highest absolute value).

The influence of the solvent polarity on the absorption spectra of **4a-f** was also investigated. As it is shown in Fig. 2 when the solvent polarity is reduced (going from water to methanol) a bathochromic band shift is induced (negative solvatochromism).[9] The complexes of the transition metals (such as Fe, Ru, Os, etc.) with heterocyclic ligands are known as solvatochromic and have been examined intensively in the past.[2,3,20] **4a-f** present a very intense solvatochromism. For example, a relatively small change in the solvent polarity, e.g., from water (with $\boldsymbol{E_T}\mathbf{(30)} = 63.1\,\text{kcal mol}^{-1}$) to methanol (with $\boldsymbol{E_T}\mathbf{(30)} = 55.4\,\text{kcal mol}^{-1}$), induces a bathochromic band shift of $\Delta\lambda \cong 200\,\text{nm}$ ($\Delta\tilde{\nu} = -3944\,\text{cm}^{-1}$) as shown in Fig. 2.

This was observed also for some similar complexes of ruthenium by Curtis *et al.*[20] In general, it is known that substances the dipole moment (μ) of which decreases upon excitation in solution show negative solvatochromism ($\mu_g > \mu_e$, where the subscript g corresponds to the ground state and the subscript e to the excited state). Generally, such substances usually present intramolecular charge-transfer bands as it happens in the case of the substances studied here.[9]

The lack of theoretical expressions for calculating solvent effects has driven to attempts to introduce empirical solvent polarity scales.[21] These empirical scales can be used to quantify solvent effects on the UV–Vis–NIR spectra.[9] In the past years several successful attempts for the correlation of the MLCT bands of complexes of several transition metals such as Fe, Ru, W, etc. which contain organic ligands such as 2,2′-bispyridine or *N*-alkyl substituted 4,4′-bispyridines, with the Dimroth–Reichardt $\boldsymbol{E_T}\mathbf{(30)}$ polarity scale and the Kosower's ***Z*** scale[22,23] have been made as well as with Gutmann's acceptor and donor number.[2,20]

In order to quantify the impact of the solvent polarity on the MLCT absorption maxima wavenumbers, we have chosen to use the normalized, dimensionless E_T^N solvent polarity scale and Gutmann's acceptor number, AN, two of the most satisfactory solvent polarity scales. The polarity information for the solvents used in this work is listed in Table 2.

The E_T^N solvent polarity scale is the normalized Reichardt solvent polarity scale which associates with the Dimroth–Reichardt solvent polarity parameter [$\boldsymbol{E_T}\mathbf{(30)}$] as shown in Eqn (4).[9]

$$E_T^N = \frac{E_T(30)_{(solvent)} - E_T(30)_{(SiMe_4)}}{E_T(30)_{(H_2O)} - E_T(30)_{(SiMe_4)}} = \frac{E_T(30)_{(solvent)} - 30.7}{32.4} \tag{4}$$

The regression analysis resulted in six linear relations of the type

$$\tilde{\nu} = \tilde{\nu}_{Do} + a_D E_T^N \tag{2}$$

In this equation [Eqn (2)] $\tilde{\nu}$ is the wavenumber of a MLCT band (absorption maximum) of a compound in a certain solvent, α_D and $\tilde{\nu}_{Do}$ are the slope and the intercept respectively (obtained from the regression analysis) and E_T^N is the value of the normalized Reichardt polarity scale of the solvent. The regression value $\tilde{\nu}_{Do}$ corresponds to the wavenumber of the MLCT absorption maximum of a substance when the E_T^Nscale is set to zero [i.e., for tetramethylsilane ($SiMe_4$) as shown in Eqn (4)]. The regression values of α_D and $\tilde{\nu}_{Do}$ as well as the correlation coefficients for each case are shown in Table 3. The correlation of

Table 2. Polarity parameters of the four solvents used

Solvents	μ (D)[24]	E_T (30)[9] (kcal mol^{-1})	E_T^N[9]	AN
H_2O	1.85	63.1	1.000	54.8[4]
TFE	2.46	59.8	0.898	53.3[25]
EG	2.28	56.3	0.790	43.5[26]
MeOH	1.70	55.4	0.762	41.3[4]

Table 3. Results of the regression analysis for the linear correlation between the wavenumbers of the MLCT absorption maxima of **4a-f** and the E_T^N solvent polarity scale

Compound	$\tilde{\nu}_{Do}$[a]	α_D	R[b]
4a	1.865	16.300	0.9445
4b	1.918	16.162	0.9513
4c	1.609	16.544	0.9554
4d	1.336	16.604	0.9496
4e	1.440	16.443	0.9536
4f	1.417	16.027	0.9630

[a] $\tilde{\nu}/(10^3\,\mathrm{cm}^{-1})$.

[b] Correlation coefficient.

Table 4. Results of the regression analysis for the linear correlation between the wavenumbers of the MLCT absorption maxima of **4a-f** and the AN solvent polarity parameter

Compound	$\tilde{\nu}_{Go}$[a]	α_G	R[b]
4a	2.753	0.273	0.9909
4b	2.934	0.268	0.9876
4c	2.721	0.273	0.9910
4d	2.283	0.277	0.9931
4e	2.434	0.274	0.9930
4f	2.486	0.265	0.9950

[a] $\tilde{\nu}/(10^3\,\mathrm{cm}^{-1})$.

[b] Correlation coefficient.

the wavenumbers of the MLCT bands with the E_T^N solvent polarity scale is successful. In all cases of the six products in all four solvents used, the correlation coefficient was greater than 0.900 as shown in Table 3. It should be mentioned that α_D has a physical meaning. The slope (α_D) indicates the sensitivity of the MLCT absorption maximum of a product to the polarity of the solvent in which it is dissolved. Increased values of α_D correspond to a more intense solvatochromism or in other words when α_D increases, the MLCT band wavenumbers become more sensitive to the changes of solvent polarity.

The positive sign of α_D corresponds to the bathochromism ($\tilde{\nu}_{MLCT}$ reduction) induced when E_T^N is being reduced, so the sign (negative or positive) of the α_D parameter reflects the type of solvatochromism. The positive sign of the slop in all cases studied here is in agreement with the observed negative solvatochromism. In order to check the success of the correlation, we compared the experimentally obtained MLCT maxima absorption wavenumbers to the calculated ones from the Eqn (2) for all six products in different solvents. The results are shown in the plot of Fig. 3.

In addition to the previously described correlation, we attempted to investigate the correlation of the experimentally obtained MLCT absorption maxima wavenumbers, with Gutmann's acceptor number (AN) which is another quantitative empirical parameter of solvent polarity. This solvent polarity parameter introduced by Gutmann *et al.* quantifies the ability of a solvent to act as a Lewis acid by accepting electron pairs and thus quantifies the electrophilic properties of a solvent. That is why it can be used in deciding which would be the most appropriate solvent for a given reaction taking into account the electrophilic properties of solvents.[10] In this work, we are interested in the impact of the electrophilic properties of the solvents used in our experiments, on the MLCT absorption maxima wavenumbers of the compounds studied. The regression analysis between $\tilde{\nu}_{MLCT(max)}$ and the AN parameter resulted in six linear relationships (one for each product) of the type

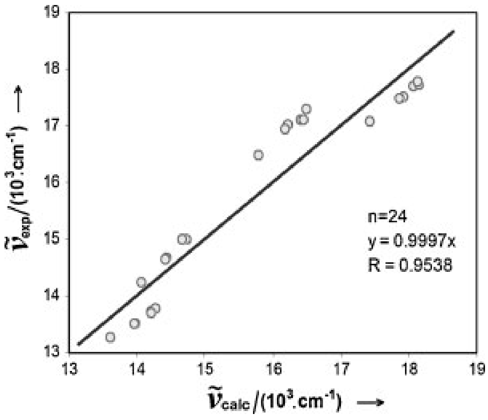


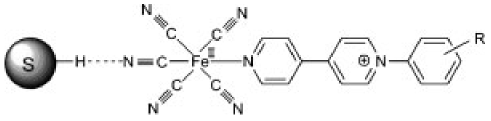
Figure 3. Correlation of the experimentally obtained wavenumbers of the MLCT absorption maxima *versus* the calculated ones (from Eqn (2)) for **4a-f** in the four solvents used

$$\tilde{\nu}=\tilde{\nu}_{Go}+a_G\mathrm{AN} \qquad (3)$$

where $\tilde{\nu}$ is the wavenumber of a MLCT band (absorption maximum) of a product in a certain solvent, α_G and $\tilde{\nu}_{Go}$ are the slope and the intercept, respectively, and AN is the acceptor number of the solvent. The results of the regression analysis are shown in Table 4.

In all cases the correlation coefficient (R) was close to 0.9900 or more. In all cases we obtained positive slopes (α_G) which means that an increase of the acceptor number induces an increase of the MLCT absorption maximum wavenumber of a product. It means that solvents which do not behave as good Lewis acids by acting as worse electron-pair acceptors stabilize more the MLCT excited state of the products causing a bathochromic shift of the MLCT band. On the other hand, solvents which act as better Lewis acids (such as water) can donate more easily their proton in order to form a hydrogen bond with the nitrogen atom of a cyano group bound to the iron (II) atom of a complex molecule (Scheme 3) and destabilize strongly the MLCT excited state.

It is known that in the presence of strong Lewis acids the nitrogen atom of a cyano group of complexes of the general type $\mathrm{LFe^{II}(CN)_5}$ where L is a heterocyclic ligand, can be even protonated causing then the destabilization of the MLCT excited state since the electron transfer in that case becomes more difficult.[27] The slope here (α_G) reflects the impact of the Lewis acidity of protic solvents on the MLCT bands energies or, in other words, the sensitivity of the MLCT absorption maxima wavenumbers of the substances to the Lewis acidity. The successful correlation for all six cases of products indicate that probably the dominating interaction, responsible for the negative solvatochromism of all the products, is the H-bond donating ability of



Scheme 3. Hydrogen bond between the hydrogen atom of a solvent (S stands for Solvent) and a nitrogen atom of a cyano group of **4a-f**

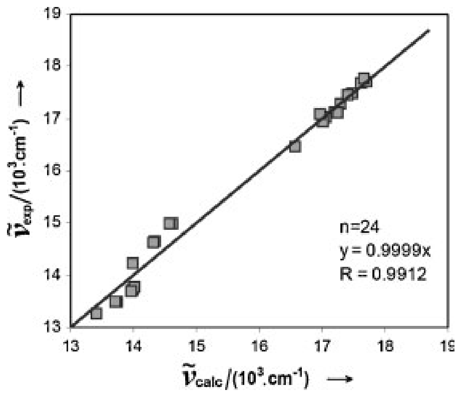


Figure 4. Plot of the experimentally obtained wavenumbers of the MLCT absorption maxima *versus* the calculated ones (from Eqn (3)) for **4a-f** in all four solvents used

the solvents used, with the cyano groups of the products, since Gutmann's acceptor number indicates the ability of solvents to act as Lewis acids either by giving a proton in order to protonate a group or by forming hydrogen bonds by proton donation to an electronegative atom such as nitrogen.

Finally, the experimentally observed values of the wavenumbers of the MLCT absorption maxima of all products in all four solvents were compared to the theoretical ones calculated from the family of Eqns (3), and the plot of Fig. 4 was obtained.

CONCLUSION

The impact of the solvent polarity on the position of the MLCT absorption maxima in the visible region, of **4a-f**, proved to be higher than the impact of the substituent in the benzene ring of these compounds. Solvent polarity changes induced band shifts of even $\Delta\tilde{\nu} \approx 4000\,cm^{-1}$, however substituent changes induced shifts up to $\Delta\tilde{\nu} \approx 1000\,cm^{-1}$. The successful Hammett correlation of the UV–Vis MLCT band maxima wavenumbers in all solvents indicates that the Hammett equation is also applicable in the case of the organometallics studied in this work and capable to quantify substituent effects on UV–Vis spectra of such compounds. The satisfactory results even when the simplest type of the Hammett equation is used confirm the high applicability of this linear-free-energy relationship (LFER). Concerning the solvent polarity effects on the UV–Vis spectra of **4a-f**, it was shown that the MLCT bands are very sensitive in solvent polarity changes even if that changes are small. The correlation with the acceptor number (AN) was more successful ($R = 0.9912$) than that attempted one with the E_T^N solvent polarity scale, which was also satisfactory ($R = 0.9538$). This shows that probably the dominating interaction between the solvent molecules and the dye molecules is in all cases the H-bond formation. The acceptor number proved to be a perfect solvent polarity parameter at least in the case of the protic solvents used in this work.

EXPERIMENTAL SECTION

Materials and procedures

Sodium nitroprusside $Na_3[Fe^{II}(CN)_5NO]$ and chloro-2,4-dinitrobenzene were purchased from ACROS Organics, 4,4′-bispyridine was obtained from Fluka as well as the substituted anilines (*p*-methoxy, *p*- and *m*-methyl, *p*-chloro, *p*-bromo, *p*-cyano). The solvents used were degassed for several minutes with argon before use. Water was purified with a Barnstead EASYpure RF compact ultrapure water system and then distilled. In all cases of complex formation reactions, the reaction mixture was kept under argon atmosphere in the dark. The final products were dried under vacuum over anhydrous $CaCl_2$ for several days until they were brought to constant weight.

Physical measurements

NMR spectra were obtained using a Varian Gemini 300 spectrometer (300 MHz ^1H, 75 MHz ^{13}C). Both ^1H and ^{13}C NMR spectra were recorded in deuterium oxide (D_2O) at 25 °C. In the case of ^{13}C NMR measurements, $[D_6]DMSO$ was used as an internal reference (39.39 ppm)[28]. The ^1H NMR spectra were calibrated by using residual undeuterated solvent (H_2O) as an internal reference (4.79 ppm)[28]. 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}. UV–Visible spectra were recorded using a Varian CARY 1E UV–Visible spectrophotometer at 25 °C. Melting points were determined in open capillary tubes using a Gallenkamp HFB-595 melting point apparatus and are uncorrected. Elemental and thermogravimetric analyses (TGA) were performed by the microanalytical laboratory of CNRS (France).

Synthesis of $Na_3[Fe^{II}(CN)_5NH_3].3H_2O$

This compound was prepared according to the Kenney, Flynn and Gallini method.[29] Sodium nitroprusside (15.00 g, 0.0526 mol) was finely powdered and then added to concentrated NH_4OH (60 ml) containing anhydrous sodium acetate (5.00 g). The reaction mixture was kept at 4 °C in the refrigerator overnight, and the formed bright yellow solid was filtered off by suction. The solid product was reprecipitated twice from an aqueous solution by adding cold ethanol. Finally, the product was dried under vacuum over anhydrous $CaCl_2$ for about a week until its weight was stabilized. The yield of the reaction was about 50% (8.60 g, 0.0263 mol).

Synthesis of 2,4-dinitrophenyl-4,4′-bispyridinium chloride [2,4-DNPhQ$^+$]Cl

According to Coe *et al.*[12] to a solution of chloro-2,4-dinitrobenzene (4.30 g, 21 mmol in 35 ml EtOH) 4,4′-bispyridine was added (3.35 g, 21 mmol) and the solution was refluxed for 24 h. The dark brown solution after cooling at room temperature was added to diethyl ether (350 ml), with stirring. A golden-brown precipitate was obtained which was filtered by suction and washed several times with diethyl ether. The solid was stored under vacuum over anhydrous $CaCl_2$ (higly hygroscopic solid which turns to a sticky brown solid when exposed to air) to give 6.25 g (17.42 mmol) 82%: mp 158–159 °C.

General procedure for the synthesis of *N*-substituted 4,4′-bispyridinium chloride (3a-f)

To a solution of **$[2,4\text{-DNPhQ}^+]$Cl (1)** (538 mg, 1.5 mmol in 8 ml EtOH) an excess of the substituted aniline (**2a-f**) was added (6.0 mmol). The solution turned immediately to deep red–violet and it was refluxed under an argon atmosphere for a period varying between 4 and 48 h depending on the substituent of compounds **2a-f**. After cooling the dark solution, water was added (20 ml) and a yellow precipitate (2,4-dinitroaniline) was formed immediately. The mixture was filtered and the filtrate was concentrated to dryness. The solid was dissolved in EtOH and reprecipitated by adding diethyl ether. Finally, the solid was filtered off by suction, washed with ethyl acetate and diethyl ether, and dried under vacuum for several hours. The products were recrystalized from EtOH or EtOH/ ^{i}PrOH. Compounds **3a**, **3d**, and **3e** are known[30] as well as compound **3f**[31] but their melting points are not mentioned.

N-(4-methoxyphenyl)-4,4′-bispyridinium chloride, [*p*-MeOPhQ$^+$]Cl (3a)

4 h reflux. Pale yellow powder 380 mg, 85%, mp: 192–194 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.18$ (d, $J = 6.9$ Hz, 2 H; C_5H_4N), 8.81 (d, $J = 5.6$ Hz, 2 H; C_5H_4N), 8.56 (d, $J = 6.9$ Hz, 2 H; C_5H_4N), 8.00 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 7.60 (d, $J = 9.0$ Hz, 2 H; Ph), 7.29 (d, $J = 6.9$ Hz, 2 H; Ph), 3.94 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 162.81$, 155.29, 151.59, 145.93, 143.70, 136.95, 127.34,126.86, 124.00, 117.14, 57.38 (Me); elemental analysis calcd (%) for $C_{17}H_{15}N_2ClO$: C 68.34, H 5.03, N 9.92, found: C 68.52, H 4.80, N 9.73.

N-(4-methylphenyl)-4,4′-bispyridinium chloride, [*p*-MePhQ$^+$]Cl (3b)

4 h reflux. Pale yellow powder 372 mg, 88%, mp: 164–166 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.24$ (d, $J = 6.0$ Hz, 2 H; C_5H_4N), 8,83 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 8.61 (d, $J = 6.3$ Hz, 2 H; C_5H_4N), 8.04 (d, $J = 5.1$ Hz, 2 H; C_5H_4N), 7.72 (d, $J = 8.1$ Hz, 2 H; Ph), 7.60 (d, $J = 8.1$ Hz, 2 H; Ph), 2.50 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 155.62$, 151.58, 146.02, 144.31, 143.67, 141.35,132.54, 127.38, 125.04, 124.02, 21.77 (Me); elemental analysis calcd (%) for $C_{17}H_{15}N_2Cl$: C 72.21, H 5.31, N 9.92, found: C 72.48, H 5.02, N 10.10.

N-(3-methylphenyl)-4,4′-bispyridinium chloride, [*m*-MePhQ$^+$]Cl (3c)

4 h reflux. Pale yellow powder 380 mg, 90%, mp: 246–247 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.18$ (d, $J = 6.3$ Hz, 2 H; C_5H_4N), 8.74 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 8.55 (d, $J = 6.0$ Hz, 2 H; C_5H_4N), 7.95 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 7.58 (m, 4 H; Ph), 2.47 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 155.36$, 151.54, 145.88, 143.48, 143.32, 142.85, 133.78, 131.81, 127.21, 125.61, 123.92, 122.24, 21.91 (Me); elemental analysis calcd (%) for $C_{17}H_{15}N_2Cl$: C 72.21, H 5.31, N 9.92, found: C 72.47, H 5.14, N 10.11.

N-(4-chlorophenyl)-4,4′-bispyridinium chloride, [*p*-ClPhQ$^+$]Cl (3d)

24 h reflux. Yellow powder 355 mg, 78%, mp: 293–294 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.24$ (d, $J = 5.7$ Hz, 2 H; C_5H_4N), 8.79 (d, $J = 4.5$ Hz, 2 H; C_5H_4N), 8.61 (d, $J = 5.7$ Hz, 2 H; C_5H_4N), 8.00 (d, $J = 4.5$ Hz, 2 H; C_5H_4N), 7.82 (m, 4 H; Ph); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 156.03$, 151.59, 146.10, 143.47, 142.13, 138.86, 132.10, 127.45, 127.02, 124.03; elemental analysis calcd (%) for $C_{16}H_{12}N_2Cl_2$: C 63.37, H 3.96, N 9.24, found: C 63.63, H 3.79, N 9.43.

N-(4-bromophenyl)-4,4′-bispyridinium chloride [*p*-BrPhQ$^+$]Cl (3e)

24 h reflux. Yellow powder 415 mg, 80%, mp: 284–286 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.39$ (d, $J = 6.3$ Hz, 2 H; C_5H_4N), 9.00 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 8.77 (d, $J = 5.4$ Hz, 2 H; C_5H_4N), 8.20 (d, $J = 5.1$ Hz, 2 H; C_5H_4N), 8.13 (d, $J = 8.1$ Hz, 2 H; Ph), 7.94 (d, $J = 8.7$ Hz, 2 H; Ph); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 155.61$, 151.55, 145.90, 143.20, 142.51, 138.86, 134.92, 127.21, 126.84, 123.90; elemental analysis calcd (%) for $C_{16}H_{12}N_2BrCl$: C 55.25, H 3.45, N 8.06, found: C 55.02, H 3.21, N 7.89.

N-(4-cyanophenyl)-4,4′-bispyridinium chloride [*p*-CNPhQ$^+$]Cl (3f)

48 h reflux. Pale yellow powder 330 mg, 75%, mp: 185–186 °C; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.34$ (d, $J = 6.3$ Hz, 2 H; C_5H_4N), 8.84 (d, $J = 4.8$ Hz, 2 H; C_5H_4N), 8.68 (d, $J = 5.7$ Hz, 2 H; C_5H_4N), 8.21 (d, $J = 8.1$ Hz, 2 H; Ph), 8.07 (m, 4 H; arom); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 156.76$, 151.61, 146.54, 146.16, 143.43, 136.25, 127.55, 126.74, 124.09, 119.24, 116.17; elemental analysis calcd (%) for $C_{17}H_{12}N_3Cl$: C 69.51, H 4.09, N 14.31, found: C 69.66, H 3.94, N 14.51.

General Procedure for the synthesis of compounds 4a-f: $Na_2[Fe^{II}(CN)_5(R\text{-}PhQ^+)]$

To an aqueous solution of the *N*-substituted-4,4′-bispyridinium chloride **3a-f** (0.900 mmol in 10 ml of water), 1.000 mmol (325 mg) of $Na_3[Fe^{II}(CN)_5NH_3].3H_2O$ was added. The color of the solution directly turned to deep purple–blue. The solution was stirred in the dark under an argon atmosphere at room temperature for 6 h. A sixfold volume of ethanol was then added and the reaction mixture was kept at 4 °C overnight. The precipitate was filtered off by suction, washed with ethanol, and then dried for several hours *in vacuo* before storage. The yield in all cases was above 60%. All products have melting points above 300 °C.

$Na_2[Fe^{II}(CN)_5(p\text{-MeOPhQ}^+)]$ (4a)

Deep blue solid, 352 mg (0.567 mmol) 63%; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.21$ (m, 4 H; C_5H_4N), 8.53 (d, $J = 4.5$ Hz, 2 H; C_5H_4N), 7.73 (m, 4 H; Ph), 7.30 (d, $J = 6$ Hz, 2 H;) 3.96 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/$[D_6]$DMSO): $\delta = 170.71$ (CN), 162.52, 154.66, 151.47, 146.27, 143.34, 136.67, 127.56, 126.90, 124.03, 117.02, 57.31 (Me); IR: $\tilde{\nu}(C{\equiv}N) = 2045\ cm^{-1}$; UV–Vis ($H_2O$, λ_{nm} ($\log\varepsilon$)): 332 (3,70) (π-π^*), 565 (3,45) (d-π^*); elemental analysis calcd (%) for $C_{22}H_{15}N_7FeNa_2O$. $7H_2O$: C 42.53, H 4.70, N 15.78, found: C 42.34, H 4.49, N 16.02; TGA: loss of *ca*. 6.5 molecules of H_2O upon heating.

$Na_2[Fe^{II}(CN)_5(p\text{-MePhQ}^+)]$ (4b)

Blue solid, 355 mg (0.586 mmol) 65%; ^{1}H NMR (300 MHz, D_2O): $\delta = 9.18$ (d, $J = 6$ Hz, 2 H; C_5H_4N), 8.57 (d, $J = 6$ Hz, 2 H; C_5H_4N), 8.50 (d, $J = 4.5$ Hz, 2 H; C_5H_4N), 7.89 (d, $J =$ Hz, 2 H; C_5H_4N), 7.70 (d, *J* = 9 Hz, 2 H; Ph), 7.60 (d, *J* = 6.6 Hz, 2 H; Ph), 2.76 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/[D_6]DMSO): δ = 170.14 (CN), 154.97, 151.51, 146.96, 143.83, 143.39, 141.19, 132.43, 127.30, 125.06, 123.99, 21.82 (Me). IR $\tilde{\nu}$(C≡N): 2043 cm^{-1}; UV–Vis (H_2O, λ_{nm} (logε)): 327 (3,90) (π-π^*), 566 (3,77) (d-π^*); elemental analysis calcd (%) for $C_{22}H_{15}N_7FeNa_2.7H_2O$: C 43.65, H 4.83, N 16.20, found: C 43.46, H 5.05, N 15.84; TGA: loss of *ca*. 6.8 molecules of H_2O upon heating.

$Na_2[Fe^{II}(CN)_5$(*m*-MePhQ$^+$)] (4c)

Blue solid, 405 mg (0.651 mmol) 72%; ^{1}H NMR (300 MHz, D_2O): δ = 9.27 (d, *J* = 6.3 Hz, 2 H; C_5H_4N), 9.16 (d, *J* = 6.9 Hz, 2 H; C_5H_4N), 8.56 (d, *J* = 6.6 Hz, 2 H; C_5H_4N), 7.71 (d, *J* = 6.6 Hz, 2 H; C_5H_4N), 7.63 (m, 4 H; Ph), 2.51 (s, 3 H; Me); ^{13}C NMR (75 MHz, D_2O/[D_6]DMSO): δ = 171.34 (CN), 167.93, 155.71, 151.54, 146.32, 143.74, 142.90, 133.70, 131.77, 127.62, 125.90, 124.13, 122.43, 21.913 (Me); IR $\tilde{\nu}$(C≡N): 2035 cm^{-1}; UV–Vis (H_2O, λ_{nm} (logε)): 315 (3,70) (π-π^*), 563 (3,60) (d-π^*); elemental analysis calcd (%) for $C_{22}H_{15}N_7FeNa_2.8H_2O$: C 42.46, H 5.02, N 15.75, found: C 42.27, H 4.81, N 15.66; TGA: loss of *ca*. 7.8 molecules of H_2O upon heating.

$Na_2[Fe^{II}(CN)_5$(*p*-ClPhQ$^+$)] (4d)

Blue powder, 365 mg (0.552 mmol) 61%; ^{1}H NMR (300 MHz, D_2O): δ = 9.23 (m, 4 H; C_5H_4N), 8.55 (d, *J* = 4.2 Hz, 2 H; C_5H_4N), 7.62 (m, 4 H; arom.), 7.64 (d, *J* = 4.5 Hz, 2 H; arom.); ^{13}C NMR (75 MHz, D_2O/[D_6]DMSO): δ = 171.17 (CN), 167.69, 151.50, 146.51, 143.46, 138.67, 132.03, 127.76, 127.62, 127.15, 124,12; IR $\tilde{\nu}$(C≡N): 2038 cm^{-1}; UV–Vis (H_2O, λ_{nm} (logε)): 321 (3,74) (π-π^*), 572 (3,65) (d-π^*); elemental analysis calcd (%) for $C_{21}H_{12}N_7FeNa_2Cl^{\cdot}.9H_2O$: C 38.11, H 4.57, N 14.82, found: C 38.38, H 4.37, N 14.59; TGA: loss of *ca*. 8.2 molecules of H_2O upon heating.

$Na_2[Fe^{II}(CN)_5$(*p*-BrPhQ$^+$)] (4e)

Blue powder, 425 mg (0.617 mmol) 68.5%; ^{1}H NMR (300 MHz, D_2O): δ = 9.14 (m, 4 H; C_5H_4N), 8.31 (s, 2 H; C_5H_4N), 7.62 (s, 2 H; C_5H_4N), 7.55 (m, 4 H; Ph); ^{13}C NMR (75 MHz, D_2O/[D_6]DMSO): δ = 170.90 (CN), 167.21, 151.50, 146.38, 143.39, 142.53, 135.04, 127.71, 127.32, 126.88, 124.12; IR $\tilde{\nu}$(C≡N): 2040 cm^{-1}; UV–Vis (H_2O, λ_{nm} (logε)): 321 (3,76) (π-π^*), 573 (3,67) (d-π^*); elemental analysis calcd (%) for $C_{21}H_{12}N_7FeNa_2Br.8H_2O$: C 36.65, H 4.10, N 14.25, found: C 36.90, H 3.87, N 14.44; TGA: loss of *ca*. 7.4 molecules of H_2O upon heating.

$Na_2[Fe^{II}(CN)_5$(*p*-CNPhQ$^+$)] (4f)

Deep blue powder, 350 mg (0.537 mmol) 60%; ^{1}H NMR (300 MHz, D_2O): δ = 9.30 (d, *J* = 6.9 Hz, 2 H; C_5H_4N), 9.18 (d, *J* = 5.1 Hz, 2 H; C_5H_4N), 8.55 (s, 2 H; C_5H_4N), 8.16 (d, *J* = 8.1 Hz, 2 H; Ph), 8.01 (d, *J* = 8.7 Hz, 2 H; arom), 7.70 (2H, *J* = 6.3 Hz 2 H; arom); ^{13}C NMR (75 MHz, D_2O/[D_6]DMSO): δ = 171.27 (CN-Fe^{II}), 167.94, 151.46, 150.94, 146.74, 146.10, 136.24, 127.97, 126.99, 124.12, 119.276, 115.86; IR $\tilde{\nu}$(C≡N): 2043 cm^{-1}; UV–Vis (H_2O) λ_{nm} (logε)): 323 (3,83) (π-π^*), 586 (3,63) (d-π^*); elemental analysis calcd (%) for $C_{22}H_{12}N_8FeNa_2.9H_2O$: C 40.51, H 4.64, N 17.18, found: C 40.33, H 4.84, N 17.01; TGA: loss of *ca*. 8.4 molecules of H_2O upon heating.

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