Derivatives of Bis(2,2′-bipyridyl)dicyanoiron(II) with Long Alkyl Chains − Versatile Solvatochromic Probes that Form Metalloaggregates in Water-Rich Media

Paula Gameiro,*[a] Eulália Pereira,[a] Paula Garcia,[a] Sónia Breia,[a] John Burgess,[b] and Baltazar de Castro[a]

Keywords: Aggregation / Iron / Surfactants / Solvatochromism

We report on the preparation, characterisation, and solvatochromic behaviour of four new $[FeL_2(CN)_2]$ complexes, where L is the ligand 4,4′-diisobutyl-2,2′-bipyridine, 4,4′-di-*n*-pentyl-2,2′-bipyridine, 4,4′-di-*n*-heptyl-2,2′-bipyridíne, or 4-*n*-heptyl-4′-methyl-2,2′-bipyridine. The solvatochromic properties of these complexes show that the hydrophobicity imposed by the alkyl chains controls the response of the complexes towards the solvent, and that they are ideal to use as solvation probes in heterogeneous/organised media. An interesting result emerging from this work is the demonstration of the self-aggregating properties of the complexes *cis*-$[Fe(Pe_2bpy)_2(CN)_2]$, *cis*-$[Fe(He_2bpy)_2(CN)_2]$, and *cis*-$[Fe(Hebpy)_2(CN)_2]$ which are, without doubt, metallosurfactants.

Introduction

Iron(II) cyanide complexes such as *cis*-$[FeL_2(CN)_2]$, with L = 2,2′-bipyridyl, *o*-phenanthroline, or one of various Schiff base diimines, are strongly solvatochromic.[1−3] This property makes them suitable for the monitoring of their local solvation environment, not only in pure solvents, but also in binary media where they are used to assess preferential solvation and to study possible synergic solvation effects.[4,5] By varying the nature of the diimine, it is possible to control the hydrophilicity or lipophilicity of the complex. They have also been used to probe solvation in organised aqueous media, such as micelles and microemulsions.[6−9]

These inorganic complexes can complement E_T dyes, the most widely used organic solvatochromic polarity probes, since most of these dyes are not very soluble in water and are not ideal for investigating solvation in water-rich binary aqueous solvent mixtures.[10] Since systematic changes in the electrostatic/hydrophobic properties of the probes are necessary to investigate solvation in a wide range of solvents, metal complexes have proved to be particularly versatile. These metal complexes can be tuned by varying the inner coordination sphere of the metal centre while maintaining (or not) the overall charge of the probe molecule, or by appending aliphatic chains to the ligands and retaining the inner coordination sphere of the metal centre. As a result, the electrostatic or hydrophobic interactions of the complexes can be varied. This approach allows the construction of a set of solvation probes that may be used to analyse the relative importance of electrostatic/hydrophobic interactions in binary aqueous media, and also in organised media.

The most common inorganic solvatochromic probes, *cis*-$[FeL_2(CN)_2]$, with L = 2,2′-bipyridyl or 1,10-phenanthroline, are soluble in water and other protic solvents, but sparingly soluble or insoluble in nonpolar solvents. On the other hand, iron(II) complexes with lipophilic Schiff base diimines are soluble in some nonpolar solvents, and are much less sensitive to solvent polarity than those with 2,2′-bipyridyl and 1,10-phenanthroline.[3] The use of substituted 2,2′-bipyridyl ligands, containing one or two hydrophobic chains of varying length, seems a good route to isolate the changes in the inner coordination sphere of the metal centre from the changes in the hydrophobicity of the complexes. These compounds with substituted 2,2′-bipyridyl ligands combine the sensitivity of the bipyridyldicyanoiron(II) complex and the solubility of Schiff base diimines in nonpolar solvents.

In a recent paper we reported on the solvatochromic properties of the complex *cis*-$[Fe(PeMebpy)_2(CN)_2]$, where PeMebpy is bis(4-methyl-4′-*n*-pentyl-2,2′-bipyridyl).[12] This complex represents the first example of a solvatochromic compound which is soluble in water and in *n*-alkanes, and which is as sensitive to its solvent environment as the parent complex *cis*-$[Fe(bpy)_2(CN)_2]$. The solvatochromic behaviour of this complex has shown that attaching aliphatic chains to 2,2′-bipyridyl can lead to the development of versatile inorganic solvatochromic indicators for a wide range of solvent media.

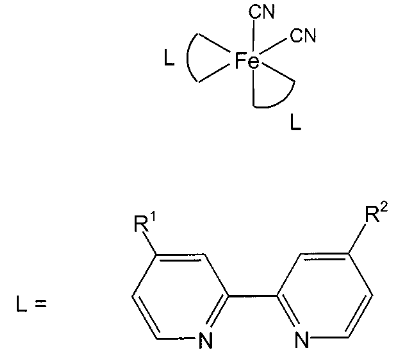
In this paper we report on the preparation, characterisation and solvatochromic behaviour of four new $[FeL_2(CN)_2]$ complexes, where L is the ligand Bu_2bpy, Pe_2bpy, Hp_2bpy, or HpMebpy (Scheme 1).

Their solvatochromism was studied in pure solvents and in mixed solvents (water/methanol, water/acetonitrile, and

---

[a] CEQUP/Departamento de Química, Faculdade de Ciências, Universidade do Porto,
4169-007 Porto, Portugal
E-mail: agsantos@fc.up.pt
[b] Department of Chemistry, University of Leicester,
Leicester LE1 7RH, UK

1434−1948/01/1111−2755 $ 17.50+.50/0



Compound		
1	$R^1 = R^2 = i\text{-}C_4H_9$:	Bu$_2$bpy
2	$R^1 = R^2 = n\text{-}C_5H_{11}$:	Pe$_2$bpy
3	$R^1 = R^2 = n\text{-}C_7H_{15}$:	Hp$_2$bpy
4	$R^1 = CH_3$, $R^2 = n\text{-}C_7H_{15}$:	HpMebpy
5	$R^1 = CH_3$, $R^2 = n\text{-}C_5H_{11}$:	PeMebpy

Scheme 1

water/acetone). Their solvatochromic characteristics are compared with those of the Reichardt dyes (E_T scale), as well as with those of *cis*-[Fe(bpy)$_2$(CN)$_2$], which is the most common solvatochromic inorganic probe, and of *cis*-[Fe(PeMebpy)$_2$(CN)$_2$], which is the first solvatochromic inorganic probe to be soluble in water and *n*-alkanes.

The results obtained demonstrated that complexes **1**−**4** combine the sensitivity of the bipyridyldicyanoiron(II) complexes with the solubility of the analogous, but less sensitive, complexes of Schiff base diimines in nonpolar solvents. On the other hand, the response of complexes **2**−**4** to solvent polarity in nonpolar solvents was found to be completely different from that observed for the Reichardt dyes. Finally, in water-rich media, it must be stressed that the hydrophobicity imposed by the alkyl tails clearly controls the response of the complexes to solvent polarity, and thus gives access to the synthesis of complexes for probing solvation in heterogeneous/organised solvent media.

An interesting result of complexes **2**−**4** is that they form metalloaggregates in the water-rich region of the mixed solvents used. The water content at which aggregation starts is dependent on the length and number of the alkyl chains.

Results and Discussion

Solutions of complexes **1**−**4** are violet in polar solvents, but blue in nonpolar solvents. The solvatochromic properties of these complexes were studied by visible spectrophotometry in several pure solvents, ranging from water to paraffins, and in the following mixed solvents: water/methanol, water/acetonitrile and water/acetone. The electronic absorption spectra of all complexes are identical to that reported for *cis*-[Fe(bpy)$_2$(CN)$_2$],[13] and the solvatochromic behaviour presented in this work is based on the wavenumber of the maximum absorption of the lowest-energy metal-to-ligand charge-transfer band, $\tilde{\nu}_{max}$(MLCT).

Solvatochromic Behaviour in Water and in Non-Aqueous Solvents

Table 1 includes the values of $\tilde{\nu}_{max}$(MLCT), in water and in a wide range of non-aqueous solvents, for each complex, and the values of the Reichardt parameter E_T,[14,15] and of Gutmann's acceptor number (*AN*),[16] for the solvents used. Solvatochromic data in water are restricted to *cis*-[Fe(*i*Bu$_2$-bpy)$_2$(CN)$_2$], the only complex that is water-soluble.

Comparison of solvent sensitivity of the *cis*-[FeL$_2$(CN)$_2$] complexes prepared in this work (**1**−**4**) with that of *cis*-[Fe(bpy)$_2$(CN)$_2$], the inorganic species whose solvatochromic behaviour has been most extensively studied, can be made by plotting their $\tilde{\nu}_{max}$(MLCT) values against those of *cis*-[Fe(bpy)$_2$(CN)$_2$], for solvents in which they are soluble. These plots gave straight lines, with correlation coefficients higher than 0.99±0.02, and with slopes close to unity (the average for complexes **1**−**4** is 1.05±0.05). Thus, it is possible to conclude that these complexes are as sensitive as *cis*-[Fe(bpy)$_2$(CN)$_2$] to the solvent environment, and that they also extend the range of solvents in which they can be used as probes. However, since *cis*-[Fe(bpy)$_2$(CN)$_2$] is not soluble in nonpolar solvents, it is of interest to note that a comparison of plots of $\tilde{\nu}_{max}$(MLCT) values for complexes **1**−**4** against those of the similar complex *cis*-[Fe(MePebpy)$_2$(CN)$_2$], which is soluble in solvents ranging from water to paraffins,[12] reveals that they have the same sensitivity, within experimental error (average slope: 1.00±0.02). All these results indicate that alkyl chains appended to 2,2′-bipyridine allow for a fine tuning of complex solubility, without changing the solvatochromic sensitivity of the "*cis*-[Fe(bpy)$_2$(CN)$_2$]" moiety.

It is also important to assess the solvatochromic response of complexes **1**−**4** against the E_T scale, the most widely used for empirical measurements of solvent polarity. The plots of $\tilde{\nu}_{max}$(MLCT) for similar inorganic complexes versus the solvent E_T values found in the literature typically exhibit two correlation lines, which correspond to hydroxylic and non-hydroxylic solvents.[1,17,18] Such plots for complexes **1**−**4** exhibit roughly the same behaviour, but with a novel feature: a third correlation line is observed for nonpolar solvents. This feature is absent from the plots reported in the literature, since the complexes were not soluble in nonpolar solvents. This effect is observed more clearly for the more hydrophobic complexes **3** and **4**. Figure 1 shows such a plot for *cis*-[Fe(Hp$_2$bpy)$_2$(CN)$_2$].

A comparison with Gutmann's acceptor number *AN*[16,19] (another empirical solvent polarity scale) was also carried out. For complexes **1**−**4**, plots of $\tilde{\nu}_{max}$(MLCT) against *AN* values, for all polar solvents for which this value is available, show one reasonable correlation line (average correlation coefficient: 0.90±0.05). However, as with the comparison of $\tilde{\nu}_{max}$(MLCT) with E_T data, a different line is also obtained for nonpolar solvents.

Before suggesting a possible explanation for the difference in behaviour of complexes **1**−**4** with that of the Reichardt dyes, it is important to recall that Reichardt defines solvent polarity as "the overall solvation capability of sol-

Table 1. Wavenumber of the maximum absorption ($\tilde{\nu}_{max}$/cm^{-1}) for the lowest-energy MLCT band for complexes **1−4**

Solvent	No.	E_T[a]	AN[b]	$\tilde{\nu}_{max}$ bpy[c]	$\tilde{\nu}_{max}$ **1**	$\tilde{\nu}_{max}$ **2**	$\tilde{\nu}_{max}$ **3**	$\tilde{\nu}_{max}$ **4**
Water	1	63.1	54.8	19194	19342	[d]	[d]	[d]
2,2,2-Trifluoroethanol	2	59.8	[e]	18975	19084	19084	19048	19120
Methanol	3	55.4	41.5	18018	17986	18083	18149	18051
Diethylene glycol	4	53.8	[e]	17668	17762	17668	17575	17730
Ethanol	5	51.9	37.1	17606	17606	17637	17637	17857
1-Propanol	6	50.7	33.7	17483	17483	17483	17544	17483
1-Butanol	7	49.7	32.2	17422	17483	17331	17301	17391
Acetylacetone	8	49.2	[e]	16367	16529	16447	16447	16502
1-Hexanol	9	48.8	[e]	17212	17271	17301	17271	17331
2-Propanol	10	48.4	33.5	17301	17271	17271	17212	17271
1-Octanol	11	48.1	30.4	17241	17271	17422	17422	17361
Nitromethane	12	46.3	20.5	16892	17094	17065	17065	17065
Acetonitrile	13	45.6	18.9	16611	16474	16474	16420	16502
Dimethyl sulfoxide	14	45.1	19.3	16207	16207	16234	16234	16234
tert-Butyl alcohol	15	43.3	27.1	16807	16779	16667	16694	16722
Dimethylformamide	16	43.2	16	16181	15949	16000	15974	15974
Acetone	17	42.2	12.5	15974	16000	15873	15773	15848
Nitrobenzene	18	41.2	14.8	16051	16129	16077	16129	16129
2-Pentanone	19	41.1	63.3	16420	16447	16420	16393	16340
Dichloromethane	20	40.7	20.4	16287	16340	16340	16340	16420
Acetophenone	21	40.6	15	16000	16051	16077	16129	16051
Pyridine	22	40.5	14.2	15898	15823	15848	15848	15848
Cyclohexanone	23	39.8	18	16077	15625	15798	15773	15699
Isobutylmethylacetone	24	39.4	[e]	16026	16026	16129	16077	15949
Chloroform	25	39.1	23.1	16474	16474	16502	16502	16502
Ethylacetate	26	38.1	9.3	[d]	15723	15773	15723	15723
Tetrahydrofuran	27	37.4	8	[d]	15129	15060	15083	15152
Chlorobenzene	28	36.8	11.9	15974	15848	15748	15898	15798
Diethyl ether	29	34.5	3.9	[d]	[d]	15337	15291	[d]
Toluene	30	33.9	6.8	[d]	15385	15456	15408	15432
Tetrachloromethane	31	32.4	8.6	[d]	[d]	15848	15723	15674
n-Pentane	32	31.1	[e]	[d]	[d]	15848	15924	[d]
n-Heptane	33	31	[e]	[d]	[d]	[d]	16077	15848
n-Hexane	34	30.8	0	[d]	[d]	[d]	15873	15748

[a] E_T values are in kcal mol^{-1}. − [b] AN = acceptor number. − [c] $\tilde{\nu}_{max}$ for the lowest energy MLCT band for $[Fe(CN)_2(bpy)_2]$ cm^{-1}. − [d] Not soluble. − [e] Not determined.

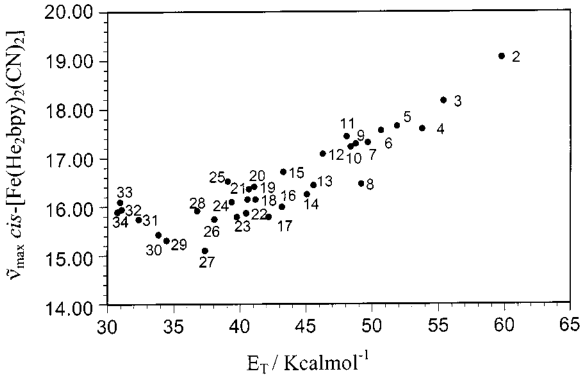


Figure 1. Wavenumber of the maximum absorption ($\tilde{\nu}_{max}$/10^3 cm^{-1}) for the lowest-energy MLCT band of *cis*-$[Fe(Hp_2bpy)_2(CN)_2]$, plotted versus Reichardt E_T values; the numbering of the points corresponds to the numbering of solvents in Table 1

vents, which in turn depends on the action of all possible, non-specific and specific intermolecular interactions between solute ions or molecules and solvent molecules".[15,20] From this definition it is clear that the solvatochromic band of the Reichardt dyes (the lowest-energy charge-transfer absorption band) is not related to properties of the solvent considered as a non-structured continuum.

As the response of complexes **2−4**, and **5** correlates in a different manner with the E_T values, they must be responding to a different solvent property, probably to a physical property of the solvent considered as non-structured continuum. In fact a reasonable correlation is obtained when $\tilde{\nu}_{max}$(MLCT) is plotted against the dipole moment of the nonpolar solvents (correlation coefficient = 0.92).

Solvatochromic Behaviour in Binary Aqueous Solvent Mixtures

The solvatochromic behaviour of complexes **1−4** was also studied in three binary solvents; water/methanol, water/acetone, and water/acetonitrile. The first co-solvent is protic, and although the other two are non-protic, acetonitrile is also known as a protogenic solvent since a strongly basic solute induces the formation of hydrogen bonds with the hydrogen atoms from the methyl group adjacent to the CN group.[19]

For complexes **1−4** in the three binary aqueous mixtures, $\tilde{\nu}_{max}$(MLCT) data can be divided into two sets. The behaviour of the complex *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$] (**1**) is practically identical to that of *cis*-[Fe(PeMebpy)$_2$(CN)$_2$], and is similar to that observed for other inorganic iron(II) diimine cyanide complexes.[4,12,21] However, for complexes **2−4**, which have longer alkyl chains attached to the 2,2′-bipyridine moiety, the $\tilde{\nu}_{max}$(MLCT) dependence on solvent composition for regions of high water content is completely different. The $\tilde{\nu}_{max}$(MLCT) values become independent of solvent composition. This unexpected result is, to the best of our knowledge, unparalleled in the literature for diimine-iron(II) cyanide complexes.

cis-[Fe(iBu$_2$bpy)$_2$(CN)$_2$] (1)

In water/methanol, plots of $\tilde{\nu}_{max}$(MLCT) against volume content (v/v) of methanol are linear, which indicates similar solvation by water and methanol in the full composition range. Analogous plots for acetone and acetonitrile as the co-solvents indicate strong preferential hydration in acetonitrile or acetone-rich media, but similar solvation by water and co-solvent in water-rich media (Figure 2). A comparable behaviour is observed for *cis*-[Fe(bpy)$_2$(CN)$_2$] in the first two solvent mixtures, but in water/acetone preferential solvation by water occurs over the full composition range, as has been reported in the literature.[4]

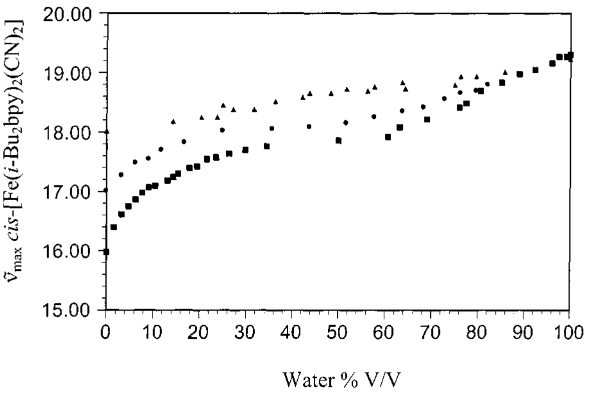


Figure 2. Wavenumber of the maximum absorption ($\tilde{\nu}_{max}/10^3$ cm^{-1}) for the lowest-energy MLCT band of *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$] in methanol (▲), acetonitrile (●) and acetone (■) solvent mixtures

It is also of interest to compare the results for complex **1** and *cis*-[Fe(bpy)$_2$(CN)$_2$] with those for *cis*-[Fe(PeMebpy)$_2$(CN)$_2$].[12] In water/methanol and water/acetonitrile mixtures all these complexes exhibit the behaviour described above for **1**: (a) similar solvation by water and methanol in the full composition range; (b) preferential solvation by water in acetonitrile-rich media and similar solvation by water and acetonitrile in water-rich media. However, in the acetone-rich region of the water/acetone media all complexes exhibit preferential solvation by water, but for regions of high water content they exhibit different solvatochromic properties; *cis*-[Fe(bpy)$_2$(CN)$_2$] is preferentially solvated by water, *cis*-[Fe(PeMebpy)$_2$(CN)$_2$] by acetone and *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$] is similarly solvated by water and acetone (Figure 3). These different solvatochromic characteristics must be related not only to solvent polarity, but also to differences between the hydrophobicity of the complexes (see below).

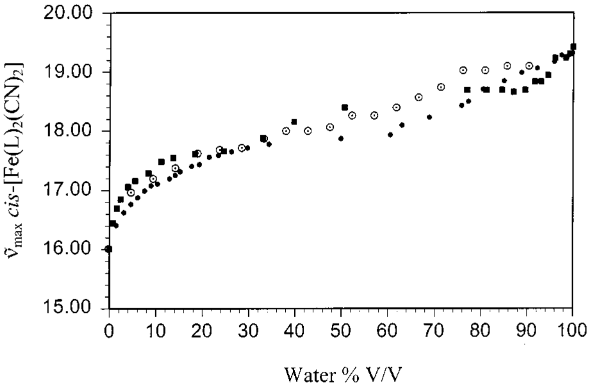


Figure 3. Wavenumber of the maximum absorption ($\tilde{\nu}_{max}/10^3$ cm^{-1}) for the lowest-energy MLCT band of *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$] (●), *cis*-[Fe(PeMebpy)$_2$(CN)$_2$] (■) and *cis*-[Fe(bpy)$_2$(CN)$_2$] (⊙) in water/acetone mixtures; composition 0−100% H_2O, by volume before mixing, at 298 K

A plot of $\tilde{\nu}_{max}$(MLCT) of complex **1** against $\tilde{\nu}_{max}$(MLCT) of *cis*-[Fe(bpy)$_2$(CN)$_2$] in water/acetone and water/acetonitrile mixtures is linear with a slope of 0.93±0.05. This indicates that both complexes have comparable sensitivities for these mixtures. In contrast, the slope in water/methanol is 0.78±0.05, an indication that complex **1** is less sensitive in methanol/water than *cis*-[Fe(bpy)$_2$(CN)$_2$]. This behaviour, which has already been found for *cis*-[Fe(PeMebpy)$_2$(CN)$_2$], indicates that the hydrophobicity, imparted by the presence of the aliphatic chains, renders the complexes less sensitive to small changes in the composition of a mixture of two very polar solvents.

Finally, a comparison with the Reichardt E_T scale can be made, as the E_T values are known for mixtures of water with methanol, acetone, or acetonitrile as the co-solvent.[21−23] When values of $\tilde{\nu}_{max}$(MLCT) were plotted against E_T, for all mixed solvents, linear correlations were obtained (average correlation coefficient: 0.98). This trend suggests that complex **1** is similarly affected by the mixed solvent components as is the organic betaine, upon whose spectra the E_T scale is based.

Complexes with Longer Alkyl Chains − *cis*-[Fe(Pe$_2$bpy)$_2$(CN)$_2$] (2), *cis*-[Fe(Hp$_2$bpy)$_2$(CN)$_2$] (3), and *cis*-[Fe(HeMebpy)$_2$(CN)$_2$] (4)

Plots of $\tilde{\nu}_{max}$(MLCT) against water content for complexes **2−4** can be divided into two regions, co-solvent-rich and water-rich media (Figure 4).

In the co-solvent-rich region, all complexes exhibit a behaviour analogous to that of *cis*-[Fe(PeMebpy)$_2$(CN)$_2$], *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$], and *cis*-[Fe(bpy)$_2$(CN)$_2$]: similar solvation by water and methanol in water/methanol, and preferential solvation by water in water/acetone and water/acetonitrile. Plots of $\tilde{\nu}_{max}$(MLCT) for complexes **2−4** versus $\tilde{\nu}_{max}$(MLCT) of *cis*-[Fe(bpy)$_2$(CN)$_2$] are linear, with an average slope of 1.02±0.05 in water/acetone and water/acetonitrile, but with a slope of 0.78±0.05 in water/methanol.

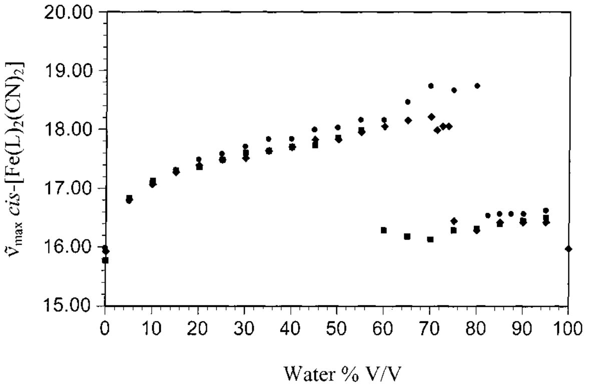


Figure 4. Wavenumber of the maximum absorption ($\tilde{\nu}_{max}/10^3$ cm^{-1}) for the lowest-energy MLCT band of *cis*-[Fe(Pe$_2$bpy)$_2$(CN)$_2$] (◆), *cis*-[Fe(Hp$_2$bpy)$_2$(CN)$_2$] (■), and *cis*-[Fe(HpMebpy)$_2$(CN)$_2$] (●) in water/acetone mixtures; composition 0−100% H_2O, by volume before mixing, at 298 K

This indicates less sensitivity to solvent polarity in this latter mixture. This situation is identical to that found for *cis*-[Fe(PeMebpy)$_2$(CN)$_2$] and *cis*-[Fe(*i*Bu$_2$bpy)$_2$(CN)$_2$] in water/methanol, and must reflect the reduced ability of hydrophobic complexes to discriminate between very polar complexes.

However, in regions of high water content and for all co-solvents, the solvatochromic behaviour of complexes **2**−**4** is completely different. An unexpected and abrupt bathochromic shift in $\tilde{\nu}_{max}$(MLCT) to the same final value of $\tilde{\nu}_{max}$(MLCT) for each complex is observed at a specific co-solvent volume content. This shift implies that nonpolar molecules must surround the complexes, since the final value of $\tilde{\nu}_{max}$(MLCT) is very similar to that observed in pure non-protic solvents. This is a very strange occurrence since the complexes are in water-rich media. This abrupt change in $\tilde{\nu}_{max}$(MLCT) is not only dependent on the complex, but also on the co-solvent (Table 2). The volume fraction of water at which the abrupt change occurs is: (a) for each complex roughly the same for acetonitrile and acetone as the co-solvents, and lower for methanol, and (b) increases in the order *cis*-[Fe(HpMebpy)$_2$(CN)$_2$] > *cis*-[Fe(Pe$_2$bpy)$_2$(CN)$_2$] > *cis*-[Fe(Hp$_2$bpy)$_2$(CN)$_2$]. For water contents above this critical value, the resulting solutions are blue and show a slight turbidity; however, the scattering does not prevent the observation of the lowest-energy MLCT band. Obviously, complexes **2**−**4** can only be used as probes for water concentrations smaller than that at which the abrupt change in $\tilde{\nu}_{max}$(MLCT) occurs, and in this region their sensitivity is similar to that of other bipyridyldicyanoiron(II) complexes.

Metalloaggregate Formation

A possible explanation for the anomalous solvatochromic behaviour of complexes **2**−**4** can be given by the formation of aggregates. These complexes have hydrophobic tails that not only have a reasonably strong affinity for themselves, but are also segregated from the polar liquid, largely due to the hydrogen bonding between the polar molecules. These factors lead to an exclusion of water molecules from the immediate environment of the complexes which sense a non-protic environment.

Solutions of complexes **2**−**4** (concentration ca. $1.5 \cdot 10^{-5}$ M) have been prepared in water/co-solvent mixtures with a water mol fraction higher than that at which the abrupt change in $\tilde{\nu}_{max}$(MLCT) occurs. Light-scattering analysis of these mixtures showed the existence of aggregates with a mean diameter of 1000±250 nm, and with very large polydispersion (1.00).

This observation supports the assumption that the abrupt change in $\tilde{\nu}_{max}$(MLCT) may be ascribed to the formation of metalloaggregates in regions of high water content. Formation is clearly solvent-dependent, and in the more polar water/methanol mixtures it occurs at a lower water content than in the less polar mixtures with acetone or acetonitrile (Figure 4). This is an expected result since the tails of the complexes render the monomers less soluble in the more polar mixtures. Obviously, the alkyl chains markedly control complex hydrophobicity, and the ease of formation of metalloaggregates is related to the size and number of the aliphatic chains. For complex **4**, which has four chains with seven carbon atoms, aggregation starts at a smaller water content than that for complex **2**, which has four alkyl chains with five carbon atoms each. Finally, the monomers of complex **3**, which have only two alkyl chains with seven carbon atoms each, are more soluble in water-rich media than either complex **2** or **4**.

Concluding Remarks

The complexes prepared in this work have been shown to be solvatochromic probes as sensitive to solvent polarity as [Fe(bpy)$_2$(CN)$_2$], the most studied inorganic probe, but with the added advantage of being soluble in a wider range of solvents. The hydrophilic-lipophilic balance, which in turn depends on the length of the alkyl chain, controls their solvation behaviour; short chains make the complexes insoluble in nonpolar solvents, whereas long chains render them insoluble in water. The complex [Fe(PeMebpy)$_2$(CN)$_2$], already reported in the literature, is still the only complex of this type with a hydrophilic-lipophilic balance that makes it soluble in both water and in *n*-alkanes.[12] The use of

Table 2. Water molar percent at which there is an abrupt change in the wavenumber of the maximum absorption

Solvent	[Fe(Pe$_2$bpy)$_2$(CN)$_2$]	[Fe(He$_2$bpy)$_2$(CN)$_2$]	[Fe(Hebpy)$_2$(CN)$_2$]
Acetone	92%	85%	95%
Acetonitrile	89%	84%	95%
Methanol	77%	70%	90%

iron(II) complexes with substituted 2,2′-bipyridyl ligands, which contain one or two hydrophobic chains of varying length, as solvatochromic probes combines the sensitivity of the bipyridyldicyanoiron(II) complexes with the solubility of the analogous, but less sensitive, complexes of Schiff base diimines in nonpolar solvents.

In binary mixtures the results obtained show that in cosolvent rich media, all new complexes exhibit similar behaviour: in acetone and acetonitrile, they are as sensitive as $[Fe(bpy)_2(CN)_2]$ to hydration, but less sensitive in methanol to changes in solvent polarity. In water-rich media, the hydrophobicity imposed by the alkyl tails clearly controls the behaviour of the complexes. With these new complexes we have begun the construction of a good basic set of solvation probes that seem to be ideal for the analysis of the relative importance of electrostatic/hydrophobic interactions in binary aqueous media. These complexes are very versatile solvation probes and may well prove to be valuable in assessing solvent polarity in a variety of novel heterogeneous/organised solvent media.

Finally, an interesting result emerging from this work is the demonstration of the self-aggregating properties of the complexes *cis*-$[Fe(Pe_2bpy)_2(CN)_2]$, *cis*-$[Fe(He_2bpy)_2(CN)_2]$, and *cis*-$[Fe(Hebpy)_2(CN)_2]$ which are, without doubt, metallosurfactants. Surfactants containing transition metal ions have only recently begun to be investigated. The use of a transition metal ion in the head-group permits the incorporation of useful properties such as colour, paramagnetism, variable charge, and pH sensitivity. Moreover, as transition metal complexes possess a wide range of reactivity, such as redox behaviour and catalytic activity, they can provide a good method of localising this kind of activity at interfaces.

Experimental Section

Instrumentation: Elemental analyses (C, H N) were performed by the Micro Analytical Laboratory, Department of Chemistry, University of Manchester (UK). No elemental analyses were performed for the complexes since compounds with cyanides always give unreliable results. − IE and FAB mass spectra at "Unidade de Espectrometria de Masas, Facultad de Química, Universidade de Santiago de Compostela" (Spain), using 3-nitrobenzyl alcohol (NBA) as the matrix. − ^1H NMR spectra were recorded with a Bruker AC 200 at 200 MHz (298 K). Chemical shifts are reported in ppm referred to TMS, used as an internal standard. − UV/Vis spectra were recorded in the 800−200 nm range with a Unicam UV-2, at room temperature, using quartz cells with 1 cm optical path. Light-scattering measurements were performed with a Malvern Instruments ZetaSizer 5000, using the 633-nm line of a He-Ne 5-mW laser.

Solvents and Reagents: All solvents were from Merck and all chemicals from Aldrich, except for 4,4′-dimethyl-2,2′-bipyridyl and the *n*-bromoalkanes which were from Fluka; all were used as received.

Ligand Synthesis

4,4′-Diisobutyl-2,2′-bipyridine (*i*Bu₂bpy): The ligand was prepared according to a published procedure[24] with 4,4′-dimethylbipyridine (Me_2bpy; 5.0 g; 27 mmol) and 2-bromopropane (7.7 ml; 82 mmol). All other reagents and solvents were used in the amounts described for the synthesis of the symmetric bipyridine derivatives.[24] Purification by chromatography on silica gel 60 (70−230 mesh ASTM) using 1,4-dioxane as the eluent afforded a pale yellow oil (yield: 58%, 4.20 g). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 3 H), 1.36 (m, 2 H), 1.70 (m, 4 H), 2.44 (s, 3 H), 2.69 (t, 2 H), 7.13 (m, 2 H), 8.22 (s, 2 H), 8.54 (m, 2 H). − $C_{18}H_{24}N_2$ (268.4): C 80.55, H 9.01, N 10.44; found C 80.55, H 9.01, N 10.38.

4,4′-Di-*n*-pentyl-2,2′-bipyridine (Pe_2bpy): A procedure similar to that described above was applied using 1-bromobutane (8.8 ml; 82 mmol). Purification by basic alumina column chromatography (3 × 20 cm, activity grade 1) using dichloromethane as the eluent, followed by chromatography of the appropriate fraction on silica gel (3 × 20 cm, 230−400 mesh) with a gradient starting with 10% up to 40% diethyl ether in petroleum ether, afforded the pure compound as a pale yellow oil (yield: 60.0%, 4.80 g). − ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.78−0.88 (m, 6 H, 2 × $-CH_3$), 1.25−1.34 [m, 8 H, 2 × $-(CH_2)_2-CH_3$], 1.60−1.67 (m, 4 H, 2 × $Ar-CH_2-CH_2$), 2.63 (t, $J_{H,H}$ = 7.79 Hz, 4 H, 2 × $Ar-CH_2-$), 7.06 (dd, $J_{H,H}$ = 4.99, 1.28 Hz, 2 H, 2 × Ar-5-H), 8.30 (s, 2 H, 2 × Ar-3-H), 8.55 (d, $J_{H,H}$ = 5.02 Hz, 2 H, 2 × Ar-6-H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 13.5 (2 × $-CH_3$), 34.9 (2 × $Ar-CH_2$), 120.7, 123.3 (Ar-C3, Ar-C5), 148.4 (Ar-C4), 152.1 (Ar-C6), 155.6 (Ar-C2). − MS (70 eV, EI): *m*/*z* (%) = 296 (9) [$M^{+\cdot}$]. − $C_{20}H_{28}N_2$ (296.5): C 81.03, H 9.52, N 9.45; found C 80.92, H 9.81, N 9.58.

4,4′-Di-*n*-heptyl-2,2′-bipyridíne (Hp_2bpy): A similar procedure was applied using 1-bromohexane (11.5 ml; 81.9 mmol). Purification by column chromatography (3 × 35 cm) with dichloromethane as the eluent afforded a white powder that was further purified by recrystallisation from ethanol (yield: 66.1%, 6.28 g), m.p. = 32−34 °C. − ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, *J* = 6.81 Hz, 6 H, 2 × $-CH_3$), 1.24−1.37 [m, 16 H, 2 × $-(CH_2)_4-CH_3$], 1.66−1.72 (m, 4 H, 2 × $ArCH_2-CH_2$), 2.69 (t, $J_{H,H}$ = 7.80 Hz, 4 H, 2 × $Ar-CH_2$), 7.13 (dd, $J_{H,H'}$ = 5.0, 1.64 Hz, 2 H, 2 × Ar-5-H), 8.22, 8.23 (s, 2 H, 2 × Ar-3-H), 8.56 (d, $J_{H,H}$ = 5.13 Hz, 2 H, 2 × Ar-6-H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.1 (2 × $-CH_3$), 35.5 (2 × $Ar-CH_2$), 121.3, 123.9 (2 × Ar-C3, 2 × Ar-C5), 148.9 (Ar-C4), 152.9 (Ar-C6), 156.1 (Ar-C2). − MS (70 eV, EI): *m*/*z* (%) = 352 (14) [$M^{+\cdot}$]. − $C_{24}H_{36}N_2$ (352): C 81.76, H 10.29, N 7.94; found C 81.66, H 10.39, N 8.26.

4-*n*-Heptyl-4′-methyl-2,2′-bipyridine (HpMebpy): 4,4′-Dimethylbipyridine (5.0 g; 27 mmol) and 1-bromohexane (11.5 ml; 81.9 mmol) were used. All other reagents and solvents were used in the amounts described for the synthesis of the asymmetric bipyridine derivatives.[24] Purification of the cream solid obtained was performed by recrystallisation from ethanol (yield: 32.0%, 2.32 g), m.p. 36−38 °C. − ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84−0.91 (m, 6 H, 2 × $-CH_3$), 1.27−1.33 [m, 8 H, 2 × $-(CH_2)_4-CH_3$], 1.65−1.79 (m, 2 H, 2 × $ArCH_2-CH_2$), 2.44 (s, 3 H, $Ar-CH_3$), 2.69 (t, $J_{H,H}$ = 8.0 Hz, 2 H, $Ar-CH_2$), 7.13 (d, $J_{H,H}$ = 5.0 Hz, 2 H, 2 × Ar-5-H), 8.22 (s, 2 H, 2 × Ar-3-H), 8.54 (d, $J_{H,H}$ = 4.8, 2 H, 2 × Ar-6-H). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.0 ($-CH_3$), 31.7 ($Ar-CH_3$), 35.51 ($Ar-CH_2$), 121.3, 122.0, 123.9, 124.6(2 × Ar-C5, 2 × Ar-5), 148.0, 148.9 (2 × Ar-C4), 152.9 (Ar-C6), 156.1 (Ar-C2). − MS (70 eV, EI): *m*/*z* (%) = 268 (10) [$M^{+\cdot}$]. − $C_{18}H_{24}N_2$ (268.4): C 80.55, H 9.01, N 10.44; found C 79.95, H 9.04, N 10.99.

Synthesis of Iron(II) Complexes

***cis*-Dicyanobis(4,4′-diisobutyl-2,2′-bipyridine)iron(II) [Fe(*i*Bu₂bpy)₂(CN)₂]:** The complex was prepared by Schilt's method,[13] with minor modifications. A stoichiometric amount of $(NH_4)_2FeSO_4\cdot 6H_2O$ in water (5 mL) was added to a solution of *i*Bu_2bpy (0.371 g; 1.38 mmol) in refluxing methanol (25 mL). After full development of the characteristic red colour, a stoichiometric amount of KCN was added. On standing at room temperature, a blue solid formed which was washed with petroleum ether (10 × 20 mL) and recrystallised from a mixture of 1:5 v/v dichloromethane/petroleum ether (yield: 74.7%, 0.22 g), m.p. > 300 °C. − ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS). δ = 0.85−0.97 (m, 6 H, 2 × $-CH_3$), 1.27−1.43 [m, 8 H, 2 × $-(CH_2)_2-CH_3$], 1.57−1.76 (m, 4 H, 2 × Ar-CH_2-CH_2-), 2.61, 2.77 (t, $J_{H,H}$ = 7.79, $J_{H,H}$ = 7.76 Hz, 4 H, 2 × Ar-CH_2-), 6.86, 7.20 (dd, $J_{H,H}$ = 5.71, 1.28 Hz, $J_{H,H}$ = 5.76, 1.27 Hz, 2 H, 2 × Ar-5-H), 7.12, 9.81 (d, $J_{H,H}$ = 5.75 Hz, $J_{H,H}$ = 5.80 Hz, 2 H, 2 × Ar-6-H), 7.82 (s, 2 H, 2 × Ar-3-H). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.0 (2 × $-CH_3$), 35.28 (2 × Ar-CH_2), 121.1, 125.0 (Ar-C5, Ar-C3), 150.1, 158.3 (2 × Ar-C6), 151.2, 151.4 (2 × Ar-C4), 157.7, 161.6 (2 × Ar-C2). − MS (10 keV, FAB+): *m/z* (%) = 700 (5) $[M^{+\cdot}]$, 674 (44) $[M^+ - CN]$, 648 (29) $[M^+ - (CN)_2]$.

***cis*-Dicyanobis(4,4′-di-*n*-pentyl-2,2′-bipyridine)iron(II) $[Fe(Pe_2bpy)_2(CN)_2]$:** A similar procedure was followed using Pe_2bpy (1.35 g; 4.57 mmol). The blue solid formed was washed with petroleum ether (10 × 20 cm^3) and recrystallised from a mixture of 2:10 v/v dichloromethane/petroleum ether (yield: 74.7%, 0.80 g), m.p. > 300 °C. − ^{1}HNMR (300 MHz, $CDCl_3$, 25 °C, TMS). δ = 0.85−0.97 (m, 6 H, 2 × $-CH_3$), 1.27−1.43 [m, 8 H, 2 × $-(CH_2)_2-CH_3$], 1.57−1.76 (m, 4 H, 2 × Ar-CH_2-CH_2-), 2.61, 2.77 (t, $J_{H,H}$ = 7.79, $J_{H,H}$ = 7.76 Hz, 4 H, 2 × Ar-CH_2-), 6.86, 7.20 (dd, $J_{H,H}$ = 5.71, 1.28 Hz, $J_{H,H}$ = 5.76, 1.27 Hz, 2 H, 2 × Ar-5-H), 7.12, 9.81 (d, $J_{H,H}$ = 5.75 Hz, $J_{H,H}$ = 5.80 Hz, 2 H, 2 × Ar-6-H), 7.82 (s, 2 H, 2 × Ar-3-H). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.0 (2 × $-CH_3$), 35.28 (2 × Ar-CH_2), 121.1, 125 (Ar-C5, Ar-C3), 150.1, 158.3 (2 × Ar-C6), 151.2, 151.4 (2 × Ar-C4), 157.7, 161.6 (2 × Ar-C2). − MS (10 keV, FAB+): *m/z* (%) = 700 (5) $[M^{+\cdot}]$, 674 (44) $[M^+ - CN]$, 648 (29) $[M^+ - (CN)_2]$.

***cis*-Dicyanobis(4,4′-diheptyl-2,2′-bipyridine)iron(II) $[Fe(Hp_2bpy)_2(CN)_2]$:** A similar procedure was applied using Hp_2bpy (1.00 g; 2.84 mmol). Recrystallisation of the product from a mixture of 1:50 v/v dichloromethane/petroleum ether, afforded a dark blue solid (yield: 63.3%, 0.49 g), m.p. > 300 °C. − ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84−0.94 (m, 6 H, 2 × $-CH_3$), 1.19−1.40 [m, 16 H, 2 × $-(CH_2)_4-CH_3$], 1.59−1.75 (m, 4 H, 2 × ArCH_2-CH_2), 2.61, 2.77 (t, $J_{H,H}$ = 7.77, $J_{H,H}$ = 7.77 Hz, 4 H, 2 × ArCH_2), 6.86, 7.21 (d, $J_{H,H}$ = 5.19, $J_{H,H}$ = 4.89 Hz, 2 H, 2 × Ar-5-H), 7.12, 9.81 (d, $J_{H,H'}$ = 5.76 Hz, $J_{H,H}$ = 5.8 Hz, 2 H, 2 × Ar-6-H), 7.80, 7.81 (s, 2 H, 2 × Ar-3-H). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.10 (2 × CH_3), 35.32 (2 × ArCH_2), 121.2, 125.2 (Ar-C3, Ar-C5), 150.1, 158.4 (2 × Ar-C6), 151.2, 151.4 (2 × Ar-C4), 157.8, 161.6 (2 × Ar-C2). − MS (10 keV, FAB$^+$): *m/z* (%) = 812 (6) $[M^{+\cdot}]$, 786 (50) $[M^+ - CN]$, 760 (30) $[M^+ - (CN)_2]$.

***cis*-Dicyanobis(4-*n*-heptyl-4′-methyl-2,2′-bipyridine)iron(II) $[Fe(HpMebpy)_2(CN)_2]$:** A similar procedure was applied using HpMebpy (0.912 g; 3.40 mmol). The dark blue solid was purified twice by column chromatography (3 × 20 cm, silica gel 230−400 mesh) using a gradient of acetone/methanol as the eluent. The complex was further purified by recrystallisation from acetone/ethanol (yield 24.7%, 0.18 g), m.p. > 300 °C. − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.83−0.91 (m, 3 H, $-CH_3$), 1.20−1.36 [m, 8 H, $-(CH_2)_4-CH_3$], 1.52−1.61 (m, 2 H, ArCH_2-CH_2), 2.35−2.37 (m. 2 H, Ar-CH_2), 2.53 (s, 3 H, ArCH_3), 6.84, 7.19 (d, $J_{H,H}$ = 6.0 Hz, $J_{H,H}$ = 5.6 Hz, 2 H, 2 × Ar-5-H), 7.10, 9.77 (t, $J_{H,H}$ = 6.6 Hz, $J_{H,H}$ = 5.8 Hz, 2 H, 2 × Ar-6-H), 7.83, 7.88 (s, 2 H, 2 × Ar-3-H). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.0 ($-CH_3$), 31.6 (Ar-CH_3), 35.23 (Ar-CH_2), 121.3, 122.15, 125.28, 126.31(2 × Ar-C5, 2 × Ar-C3), 146.0, 151.6(2 × Ar-C4), 150.0, 158.3 (2 × Ar-C6), 157.6, 162.0 (2 × Ar-C2). − MS (10 keV, FAB$^+$): *m/z* (%) = 644 (3) $[M^{+\cdot}]$, 618(32) $[M^+ - CN]$, 592(24) $[M^+ - (CN)_2]$.

Acknowledgments

Partial financial support for this work was provided by "Fundação para a Ciência e Tecnologia" (FCT, Lisboa). P. G. thanks FCT for a fellowship.

[1] J. Burguess, *Spectrochim. Acta* **1970**, *26A*, 1369; J. Burguess, *Spectrochim. Acta* **1970**, *26A*, 1957−1962.

[2] H. Kobayashi, B. V. Agarwala, Y. Kaizu, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 465−468.

[3] M. Kotowski, R. Van Eldik, R. B. Ali, J. Burgess, S. Radulovic, *Inorg. Chim. Acta* **1987**, *131*, 225−228.

[4] J. Burgess, S. F. N. Morton, *J. Chem. Soc., Dalton Trans.* **1972**, 1712−1714.

[5] J. Burgess, M. V. Twigg, *J. Chem. Soc., Dalton Trans.* **1974**, 2032−2036.

[6] H. Elias, H. T. Macholdt, K. J. Wannowius, M. J. Blandamer, J. Burgess, B. C. Clark, *Inorg. Chem.* **1986**, *25*, 3048−3053.

[7] M. J. Blandamer, J. Burgess, B. Shraydeh, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 531−533.

[8] J. Burgess, R. C. Lane, K. Singh, B. Castro, P. Gameiro, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3071−3075.

[9] S. Ahmed, J. Burgess, G. Capper, N. C. Fellowes, M. S. Patel, *Polyhedron* **1993**, *12*, 1145−1148.

[10] C. Laurence, P. Nicolet, C. Reichardt, *Bull. Soc. Chim. Fr.* **1987**, 125−130.

[11] A. Al-Alousy, J. Burgess, *Inorg. Chim. Acta* **1990**, *169*, 167−170.

[12] P. Gameiro, A. Maia, E. Pereira, B. Castro, J. Burgess, *Trans. Met. Chem.* **2000**, *25*, 283−286.

[13] A. A. Schilt, *J. Am. Chem. Soc.* **1960**, *82*, 3000−3005.

[14] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, *Justus Liebigs Ann. Chem.* **1963**, *661*, 1- 37

[15] C. Reichardt, *Chem. Rev.* **1994**, 2319−2358.

[16] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, **1978**, pp. 29−33.

[17] J. Burgess, J. G. Chambers, R. I. Haines, *Trans. Met. Chem.* **1981**, *6*, 145−151.

[18] E. E. A. Abu-Gharib, J. Burgess, *Trans. Met. Chem.* **1983**, *18*, 625−628.

[19] Y. Marcus, *The Properties of Solvents*, John Wiley & Sons, Chichester, **1998**, pp. 140−155.

[20] J. L. M. Abboud, R. Notario, *Pure Appl. Chem.* **1999**, *71*, 645−718.

[21] H. E. Toma, M. S. Takasugi, *J. Sol. Chem.* **1983**, *12*, 547−561.

[22] J. G. Dawber, J. Ward, R. A. Williams, *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 713−727.

[23] R. D. Skwierczynski, K. A. Connors, *J. Chem. Soc., Perkin Trans. 2* **1994**, 467−472.

[24] C. G. Griggs, D. J. H. Smith, *J. Chem. Soc., Perkin Trans. 1* **1982**, 3041−3043.

Received May 30, 2001
[I01198]