Synthesis and photophysical characterization of highly luminescent complexes of Ru(II) containing 4,4′-di-(*p*-carboxyphenyl)-2,2′-bipyridine

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Abstract

The synthesis and photophysical characterization of several complexes of Ru(II) containing 4,4′-di(carboxyphenyl)-2,2′-bipyridine (DCPB) and related bipyridine ligands are reported. In all complexes studied the lowest excited state is associated with Ru→DCPB charge transfer (CT) transition. The introduction of phenyl groups between the peripheral carboxyl group and the bipyridine framework caused a red-shifted, more intense absorption but the excited state properties (luminescence and transient absorption) remain nearly the same. The acid–base properties in the ground and excited state are different. With respect to 4,4′-carboxy-2,2′-bipyridine (dcbpy) derivative, the ground state pK_a of Ru(DCPB)$_3$ increases by about 2.5 pH units and a further extremely small increase in the pK_a is observed upon visible light excitation. The results suggest that the charge density is largely localized in the diimine unit and does not carry through the phenyl group. This could account for inefficient sensitization ($\leq 8\%$ monochromatic photon-to-current conversion efficiency) obtained on TiO$_2$ electrodes. Possible implication of the present results on the design of photosensitizers is also discussed.

Introduction

Due to their potential application as photosensitizers, polypyridyl complexes of Ru(II) have received extensive scrutiny in the last two decades [1–5]. An important goal of these studies has been the tuning of ground and excited state properties. Tuning of the energy of the CT state is achieved by changing the energy of the relevant molecular orbitals involved in the transition, viz, Ru^{II}(dπ) level or π^* level of the bipyridine ligand [6]. Key approaches involve usage of non-chromophoric ligands, peripheral substitution of the parent 2,2′-bpy with electron-donating or electron-withdrawing groups or polyimine ligands such as bipyrimidine, biquinoline etc. The lower lying π^* levels of these polyimine ligands cause a large decrease in the energy of the Ru→L CT transition. Unfortunately the red-shifted absorption and emission are often accompanied by very weak emission and short-lived excited states. The other extreme case of using electron-withdrawing non-chromophoric ligands to lower the Ru(t$_{2g}$) level (and hence increase the energy gap) can be found [6c] in [Ru(bpy)(CNMe)$_4$]$^{2-}$. This complex with the lowest energy CT absorption at 307 nm is emissive in aqueous solutions at room temperature (em. maximum at 476 nm) with excited state lifetime ≥ 8 μs. In an ideal photosensitizer, one would like to have the MLCT state energy as low as possible, yet the complex be highly emissive and long-lived in fluid solutions.

Amongst various substituted bpy/phen complexes, those involving dicarboxybipyridine (dcbpy)** are unique. They show interesting photophysical properties [7–12] and high efficiency as water-oxidation catalysts [13–17]. By controlling the extent of ionization of the peripheral carboxyl groups it is possible to have Ru complexes that are electrically neutral, anionic or cationic. Acid–base behaviour in the ground and excited state allow probing into the nature of the CT excited state [18–21]. Esterification of the carboxyl groups is known to produce complexes that are highly emissive and have a long lived excited state in fluid solutions ($\tau \geq 2$ μs) [7, 8, 10, 12]. Significant differences exist in

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**Ligand abbreviations used: 2,2′-bipyridine (bpy); 4,4′-dicarboxy-2,2′-bipyridine (dcbpy); 4,4′-dimethoxy-2,2′-bipyridine (DMB); 4,4′-dimethyl-2,2′-bipyridine (DMe$_2$B); 4,4′-diphenyl-2,2′-bipyridine (DPB) and 4,4′-di(p-carboxy-phenyl)-2,2′-bipyridine (DCPB); 4,4′-di(ethylcarboxy)-2,2′-bipyridine (DECB); 4,4′-di(*p*-(isopropyl)carboxyphenyl)-2,2′-bipyridine (DPCPB).

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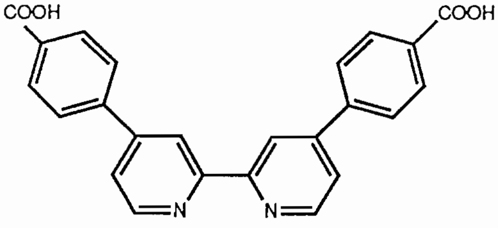
the spectral, redox and photophysical properties of 4,4′-disubstituted versus 5,5′-disubstituted complexes. In our studies on the visible light sensitization of polycrystalline TiO_2 electrodes [22–25], Ru(II)–polypyridine complexes carrying peripheral carboxyl substituents have been found to have efficient interaction with the TiO_2 surface. Possible application of carboxybipyridines in the sensitization of single-crystal semiconductor electrodes was examined earlier by Sutin, Goodenough, Memming and others [26–28].

It is also known that Ru(II) complexes having phenyl-substituted bpys have much stronger visible light absorption and longer lived excited states than the parent bpy complexes [29–32]. In an approach that combines these two key features, we sought to examine the properties and sensitizing role of complexes of Ru(II) composed of a ligand that contains these two key elements: 4,4′-di(*p*-carboxyphenyl)-2,2′-bpy (DCPB). We have managed to synthesize this key hitherto unknown ligand DCPB by an appropriate synthetic route and a number of Ru(II) complexes derived from it.



4,4'-di(p-carboxyphenyl)-2,2'-bipyridine
(DCPB)

In this work, after a brief description of the syntheses, we describe the electronic absorption and luminescence properties (including acid–base behaviour in the ground and excited state) of the homo tris- and mixed ligand complexes of Ru(II): $[Ru(DCPB)_3]^{2+}$, $[Ru(DCPB)_2(DMB)]^{2+}$ and $Ru(DCPB)(DMB)_2]^{2+}$. A comparison is made between the dcbpy and DCPB complexes and their implications in the design of efficient photosensitizers for sensitization processes is indicated.

Experimental

Materials

Synthesis of the ligand 4,4′-di(p-carboxyphenyl)-2,2′-bipyridine (DCPB)

The 4,4′-di(p-carboxyphenyl)-2,2′-bipyridine (DCPB) ligand was synthesized from pyridine, following the reaction pathway shown in Scheme 1. Compounds **1**, **2**, **3** and **4** were synthesized as described in the literature [33]. The melting point data are in good agreement with the reported values.

Compound **5** was prepared by mixing compound **4** (5.9 mmol, 2 g), *N*-bromosuccinimide (35.6 mmol, 6.34 g) and benzoyl peroxide (0.59 mmol, 0.14 g) in CCl_4 (100 ml) and refluxing with stirring. After 10 h additional amounts of *N*-bromosuccinimide (16.0 mmol, 3 g) and benzoyl peroxide (0.20 mmol, 0.05 g) were added. The mixture was then refluxed for 24 h. The hot reaction mixture was filtered and the tarry residue was washed with hot CCl_4. The combined liquors were washed with 4% aq. sodium hydroxide, then with water, then dried over anhydrous sodium sulfate and concentrated *in vacuo*. The solid residue was crystallized from ethanol. Yield 70%. m.p. 126–128 °C. Proton NMR chemical shifts for compounds **4**, **5** and **6** are listed in Table 1.

Compound **6** was prepared by treating compound **5** (1.9 mmol, 1 g) with 30% aq. sulfuric acid (200 ml) and refluxing the mixture for 8 h. The pH of the sulfuric acid solution was adjusted to 3 with gaseous ammonia. The precipitate was collected and crystallized from ethanol. Yield 60%. m.p. > 335 °C. IR bands of the carboxyl at 3500–2500 (broad), 1705 strong and 1260 (strong) cm^{-1}. NMR (DMSO-d_6): 6H [8.86, d, *J*(6,5) 18 Hz]; 3H[8.79, d, *J*(3,5) 7 Hz]; 8H [8.14, d, *J*(8,9) 27 Hz]; 9H [7.99, d, *J*(9,8) 27 H7]; 5H [7.87, dd, *J*(5,6,3) 0.1, 6Hz].

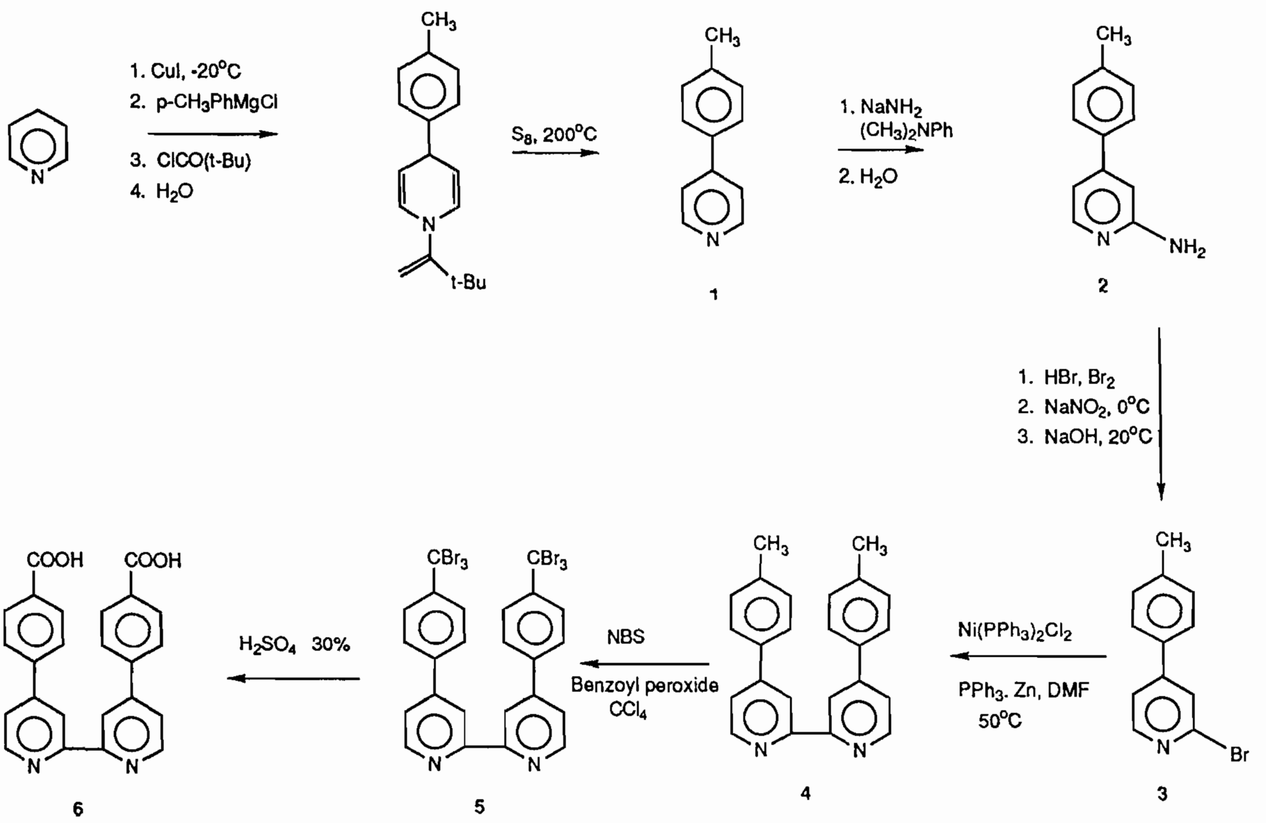
2.2′-bpy (Fluka) and 4,4′-dcbpy (Alfa Inorganics) ligands are commercial samples and were used as received. 4,4-DMB was prepared using the procedure described by Maerker and Case [34].

Synthesis of Ru(II) complexes

Mononuclear bis and tris-chelated complexes of DCPB, RuL_2Cl_2 and RuL_3 (L = DCPB, DMB) were prepared by reacting $RuCl_3$ with two- or three-fold excess of the ligand L under reflux in DMF for a period of 4–6 h. After removal of the solvent under rotavap, the complex was thoroughly washed with ether and dissolved in alkaline water (pH ≈ 10). The complex was isolated as the neutral salt from the aqueous solution upon lowering of the pH to ≈ 3.5. The isopropyl ester of the $Ru(DCPB)_3$ complex was prepared by refluxing the complex in acidified isopropanol and subsequent removal of the solvent on a rotavap. Bis(hydroxy/aquo) complexes RuL_2X_2 were prepared from RuL_2Cl_2 by digesting the complex in dilute NaOH for a couple of hours and precipitation of the required complex upon acidification. Mixed ligand complex RuL_2L' (L' = DMB or DCPB) was subsequently prepared by replacement of aquo ligands by L′ in DMF.

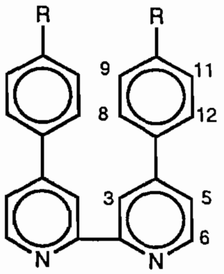
Methods

UV–Vis absorption spectra were recorded on a HP 8450A diode array spectrophotometer. Emission spectra were recorded with a Spex Fluorolog spectrofluorimeter equipped with a R9628 Hamamatsu photomultiplier tube. All the emission spectral data reported have been corrected for variations in the instrumental and photo-



Scheme 1. Reaction scheme for the synthesis of 4,4′-(*p*-dicarboxyphenyl)-2,2′-bipyridine (DCPB).

TABLE 1. Proton chemical shifts for various 4,4′-(di(substituted phenyl)-2,2′-bipyridines



Compound (R)	Solvent	3	5	6	8	9	11	12	CH_3
4 (CH_3)	$CDCl_3$	8.74	7.56	8.74	7.71	7.29	7.29	7.71	2.44
5 (CBr_3)	$CDCl_3$	8.80	7.59	8.80	8.17	7.83	7.83	8.17	
6 (COOH)	DMSO-d_6	8.79	7.87	8.86	8.14	7.99	7.99	8.14	

multiplier response using a NBS standard quartz tungsten–halogen lamp. Emission lifetimes were measured using a J&K system 2000 laser flash photolysis system (frequency doubled Nd laser, 530 nm, pulse width of 15 ns) in a single shot mode. The detection unit consists of a Hamamatsu R928 PM interfaced to a Tetronix 7612 transient digitizer and HP 300 series computer. The solutions were deoxygenated by bubbling Ar for at least 15 min prior to emission lifetime measurements. Estimated error in various reported values are as follows: absorption and emission maxima ± 3 nm; emission lifetimes ± 10% and quantum yields ± 25%.

Results and discussion

Peripheral substitution of 2,2′-bipyridine or 1,10-phenanthroline with electron-donating or -withdrawing ligands constitute a simple, yet powerful way of tuning the redox and photophysical properties of resulting polypyridine complexes of Ru(II). As elaborated in the introductory paragraphs, the goal of the present investigation was to explore the possibility of having both phenyl and carboxyl groups at the same 4,4′-positions of the 2,2′-bpy framework. The required ligand DCPB and a number of Ru(II) complexes were prepared as described in 'Experimental'. In our experience, the best way of purifying carboxybipyridine complexes is via repeated reprecipitation from aqueous solutions (dissolution in alkaline solutions (pH$\geqslant$10) and subsequent lowering of pH). The complexes are isolated as internally charge compensated electrically neutral salts. The isopropyl ester is fairly soluble in acetonitrile and ethanol.

As isolated, the solubility of the DCPB complexes in aqueous or organic solvents (polar and non-polar) is extremely limited. The peripheral carboxyl groups can be readily deprotonated at pH$\geqslant$7 as discussed above. In the deprotonated form, the complexes however are fairly soluble in aqueous alkaline solutions (pH$\geqslant$8, concentrations $\geqslant$0.1 mM) and in alkaline ethanol–water mixtures (1:1 vol./vol.). For this reason, studies reported herein are restricted to these two solvent systems. In addition to homo/tris chelates, mixed ligand complexes containing DCPB and 4,4′-dimethoxy-2,2′-bipyridine, $[\mathrm{Ru(DCPB)}_n(\mathrm{DMB})_{3-n}]$ were examined. It is known that in mixed ligand complexes of this type carrying electron-donating and electron-withdrawing bpy units, the lowest energy CT excited state is associated with that of the electron-withdrawing bpy. Thus in all of the DCPB complexes examined herein the lowest excited state is Ru→DCPB CT.

UV–Vis absorption and luminescence properties of the tris chelate Ru(DCPB)$_3$

Figure 1 presents the absorption and emission spectra of the homo tris-chelate $[\mathrm{Ru(DCPB)_3}]^{4-}$ in aqueous alkaline solution (pH 10.5) at room temperature. At this pH, the carboxyl groups are fully deprotonated and the complex is tetraanionic. Data on the absorption and emission for the homoleptic and mixed ligand complexes are listed in Table 2. For comparison the Table also includes relevant data on the parent bpy and dcbpy complexes. The spectra of the phenyl-substituted carboxybipyridine complexes are typical of polypyridine complexes of Ru(II). The absorption spectra consist of three MLCT bands in the near UV–Vis region. In the UV, the ligand π–π^* transitions appear as two bands with maximum at 298 and 264 nm, respectively.

In the RuL$_3$ complexes with L = bpy, dcbpy and DCPB, there is a gradual red-shift of the lowest energy CT band along the series, consistent with the increased electron-withdrawing nature of the ligand L. Also along this series there is an increase in the observed emission lifetimes and quantum yields. A priori this observation of longer lifetimes for a red-shifted CT emission may appear unusual. Energy gap law considerations predict the emission quantum yields and lifetimes to decrease with decreasing energy of the CT excited state. The observed increase can be traced to the increased absorption intensity of the CT transition. Both phenyl and carboxyl substituents on the bpy ligand are known to have pronounced increase on the molar absorbance of the Ru→bpy CT transitions. For example, the molar absorbances of $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Ru(dcbpy)_3}]^{4-}$, $[\mathrm{Ru((COOEt)_2\text{-}bpy)_3}]^{2+}$ and $[\mathrm{Ru}(\phi_2\text{-bpy})_3]^{2+}$ have been reported to be 14 500, 18 000, 25 000 and 28 000 M^{-1} cm^{-1}, respectively.

In spite of the red-shifted nature of the absorption and emission maxima, the excited state lifetimes of $[\mathrm{Ru(DCPB)_3}]^{4-}$ and $\mathrm{Ru(dcbpy)_3}]^{4-}$ complexes (in a given solvent) are strikingly similar. Unfortunately, dcbpy and DCPB complexes are not soluble in many organic solvents. Limited studies in various solvent mixtures do indicate high solvent sensitivity of the emission. For all of the DCPB complexes and $\mathrm{Ru(dcbpy)_3}]^{4-}$ a two-fold increase in excited state lifetime (and quantum yield) is obtained in 1:1 ethanol–water mixtures. The high quantum yield of emission and the associated long lifetime for the CT excited state in fluid solutions are partly due to increased radiative rate. Amongst various Ru(II) complexes known to date, the dcbpy and DCPB complexes are the most highly emissive and have potential applications as probes.

Protonation of the peripheral carboxyl groups in bipyridine complexes causes considerable decrease in the emission quantum yields and lifetimes (cf. discussions on this later). This type of proton-induced quenching has been studied in detail earlier. Esterification of the carboxyl group can reduce significantly this quenching pathway. Indeed esters of 4,4′-carboxybipyridine complexes have been reported to have very high emission quantum yield and long lifetimes. The ethyl ester of [Ru(4,4′-dcbpy)$_3$] has been reported to have $\tau \approx 2.3$ μs and $\phi = 0.30$. We have reconfirmed these earlier reports. Data obtained on these are also included in Table 3.

For the present DCPB case it is interesting to ask if these two effects, viz. introduction of the phenyl group and esterification of the carboxyl group, are additive in the DCPB complexes. Emission quantum yield of 0.30 in fluid solutions at ambient temperature is already substantial but any further increase would indicate any limitations imposed by concurrent non-radiative pathways inherent in these bipyridine-framework-based Ru(II) complexes. Table 3 presents data obtained on the isopropyl ester of the tris-DCPB complex (labelled as $[\mathrm{Ru(DPCPB)_3}]^{2+}$) and related complexes in fluid solutions at room temperature. In neat ethanol and acetonitrile, the emission quantum yield

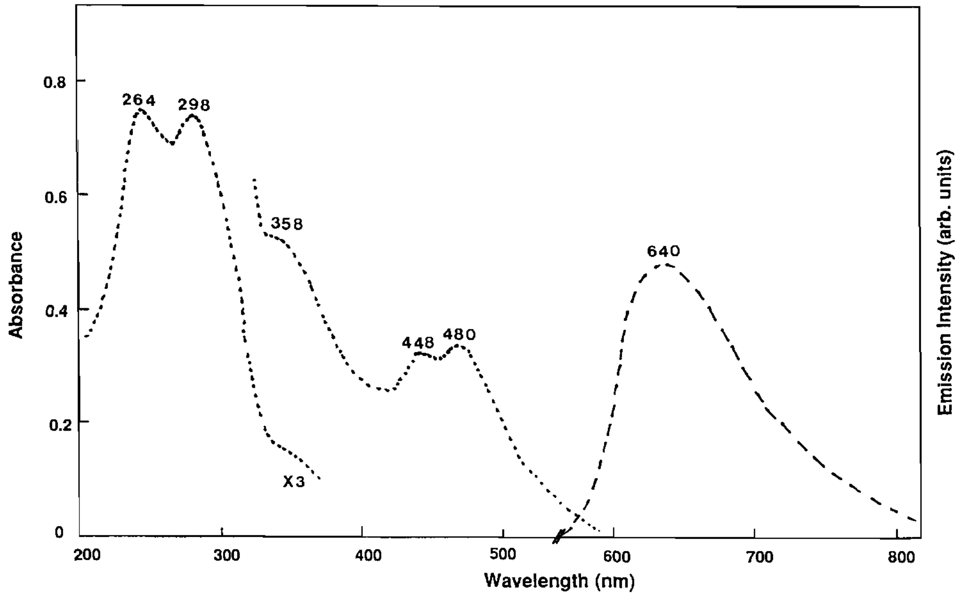


Fig. 1. Absorption and emission spectra of $Ru(DCPB)_3^{4-}$ in aqueous alkaline solutions (pH 10.5).

TABLE 2. Absorption and luminescence properties of di(phenyl-substituted)bipyridine complexes of Ru(II) in fluid solutions (alkaline, pH ≈10) at ambient temperature (293 K)

Complex[a]	Solvent	CT absorption			CT emission			Reference
		max. (nm)			max (nm)	τ (μs)	ϕ[b]	
		I	II	III				
$Ru(DCPB)_3]^{4-}$	H_2O	480	448	358	640	0.80	0.058	this work
	$EtOH–H_2O$	478	452	370sh	634	1.62	0.0996	this work
$[Ru(DCPB)_2(DMB)]^{2-}$	H_2O	492	454	372	666	0.40	0.0269	this work
	$EtOH–H_2O$	488	452	368	657	1.09	0.0286	this work
$[Ru(DCPB)(DMB)_2]$	H_2O	512	454sh	367sh	700	0.35	0.0063	this work
$[Ru(bpy)_3]^{2+}$	H_2O	450	428	360	621	0.62	0.042	29
$[Ru(dcbpy)_3]^{4-}$	H_2O	464	436	350	635	0.80	0.05	this work
$[Ru(DECB)_3]^{2+}$	CH_2Cl_2	467			629	2.23	0.30	10
$[Ru(DECB)_2(DMe_2B)]^{2+}$	CH_2Cl_2	483			658	1.42	0.10	10
$[Ru(DECB)(DMe_2B)_2]^{2+}$	CH_2Cl_2	493			694	0.85	0.07	10
$[Ru(DPB)_3]^{2+}$ [b]	EtOH	473			637	1.95	0.31	

[a] For ligand abbreviations used see footnote on p. 831. [b] Quantum yield values were measured relative to $[Ru(bpy)_3]^{2+}$ in water for which the yield is taken as 0.042 (cf. ref. 29).

and lifetime of the isopropyl ester of DCPB complex show only a marginal increase. This is a rather disappointing result. The results can be taken either to confirm above cited anxieties that in carboxy–bipyridine esters one has already reached the possible limits or failure of the additivity hypothesis.

Even within the same bipyridine framework, the nature of the peripheral substitution (type of the substituents and their position of linkage) is known to affect the absorption and photophysical properties of the resulting Ru(II) complexes. For example, the 5,5′-dicarboxy-2,2′-bipyridine complexes behave quite differently from the 4,4′-dicarboxy-2,2′-bipyridine derivatives. The lowest energy CT absorption in the former complexes are red-shifted and the complexes are very weak emitters. As shown by the data presented in Table 3, even esterification does not improve the situation. We have reconfirmed the earlier observations of Cook *et al.* [8] that the emission lifetime of the ethyl ester of $[Ru(5,5'\text{-dcbpy})_3]$ is only 210 ns, an order of magnitude less than that of the 4,4′-derivative. The emission quantum yields are also correspondingly low. Theoretical calculations on the charge densities and nodal planes on these and related complexes would help in understanding the subtle factors that control the formation and decay of charge transfer excited state.

TABLE 3. Absorption and luminescence properties of ester derivatives of carboxybipyridine and related complexes of Ru(II) in fluid solutions at ambient temperature (293 K)

Complex[a]	Solvent	CT absorption			Emission			Reference
		max. (nm)			max (nm)	τ (μs)	ϕ^{b}	
		I	II	III				
Ru(4,4'-DPCPB)$_3$]$^{2+}$	EtOH	476	450	360	636	1.85	0.19	this work
	CH_3CN	480	452	360	643	1.98	0.14	this work
Ru(4,4'-DECB)$_3$]$^{2+}$	EtOH	464	438	356	638	2.00	0.113	this work
	EtOH	464			655	1.65	0.20	10
	CH_3CN	466	436	356	638	1.52	0.10	this work
	CH_2Cl_2	466	436	353	629	2.55	0.26	this work
	CH_2Cl_2	467			629	2.23	0.30	8
[Ru(4,4'-DPB)$_3$]$^{2+\,b}$	EtOH	473			637	1.95	0.30	29
Ru(5,5'-DECB)$_3$]$^{2+}$	EtOH	495	464	360	720	0.23	0.004	8
	CH_2Cl_2	500	464	360	674	0.21	0.012	this work
[Ru(4,4'-dcbpy)$_3$]$^{4-}$	H_2O	464	436	350	635	0.80	0.05	this work
	CH_3CN-H_2O	464	434	343	632	1.20	0.074	this work
	EtOH-H_2O	464	434	342	632	1.68	0.097	this work

[a] For ligand abbreviations used see footnote on p. 831. [b] quantum yield values were measured relative to [Ru(bpy)$_3$]$^{2+}$ in water for which the yield is taken as 0.042 (cf. ref. 29).

Acid–base properties in the ground and excited states and sensitization of TiO_2 electrodes

The introduction of electron-rich phenyl groups as spacers between the bipyridine and carboxyl units can cause an increase in the local charge density. This can be probed using the acid–base properties of the complex. As expected, the absorption and emission spectra of [Ru(DCPB)$_3$]$^{4-}$ are strongly pH dependent. Figure 2 presents a comparison of the absorption and emission spectra at pH 10 and 4.0. In alkaline solutions (pH$\geqslant$8) the carboxyl groups are deprotonated and the complex is tetraanionic. Lowering of the pH leads to a gradual red-shift of the absorption spectrum. At pH 3.55 for example, the lowest energy CT band has moved by $\approx$10 nm (from 476 to 486 nm). Over the same pH range, the emission spectrum also shows distinct spectral and intensity changes. At pH 4.0 for example, the emission spectrum changes in shape and intensity decreased to less than 2.0% of the initial value. As shown in Fig. 2 (top panel), the change in the spectral shape becomes clear upon normalisation of the emission intensity at $\approx$644 nm of the spectra observed in neutral and mildly acidic solutions. The difference spectrum (corresponding to weak emission of the protonated form) has a maximum at 760 nm.

The red-shift in the absorption spectrum upon protonation and the decrease in emission intensity can be quantitatively examined to derive protonation constants in the ground and excited states. Figure 3 (top) presents the titration curve for the ground state absorption changes observed in the visible region. From this curve, the ground state pK_a has been estimated to be 5.20$\pm$0.10. Figure 3 (bottom) shows a similar titration curve for the emission intensity monitored at 642 nm. Quantitative analysis of the emission intensity changes indicate an apparent excited state pK_a (pK_a*) of 5.40$\pm$0.1. Over the pH range 1.0–4.0, the solubility of the partially protonated forms is very limited. Alkaline solutions acidified to the above pH appear to be metastable in that the solutions remain clear for several minutes. Upon standing on the bench top for several hours, the complex comes out of solution. For this reason, the absorption and emission spectral changes have not been studied in detail. There appears to be no hysteresis in the titration curves shown in Fig. 3, in that the absorption, emission intensities are readily reproduced in both directions.

The acid–base behaviour in the ground and excited states of [Ru(bpy)$_n$(dcbpy)$_{3-n}$]$^{m+}$ and related complexes has been investigated earlier [18–20]. The pK_a for protonation of the first dcbpy ligand in the ground state has been determined to be in the range of 2.2–2.8. The value depends on the ratio of bpy versus dcbpy ligands in the complex. Introduction of the phenyl group as a spacer between the carboxyl and bipyridine ring has caused two significant changes in the acid–base behaviour of the complex. The ground state pK_a has been raised by $\approx$2.5 pH units, in good agreement with expected increased charge density. There is a transfer of electron from the Ru(II) to the DCPB ligand upon formation of the CT excited state. In complexes with polyimine ligands, this is indicated by a pronounced increase in the basicity of the complex in the excited state (Δp$K\geqslant$5.5 pH units). For dcbpy complexes the effect is much less pronounced (the excited state pK_a values (pK_a*) are in the range of 4.20–4.60). For the

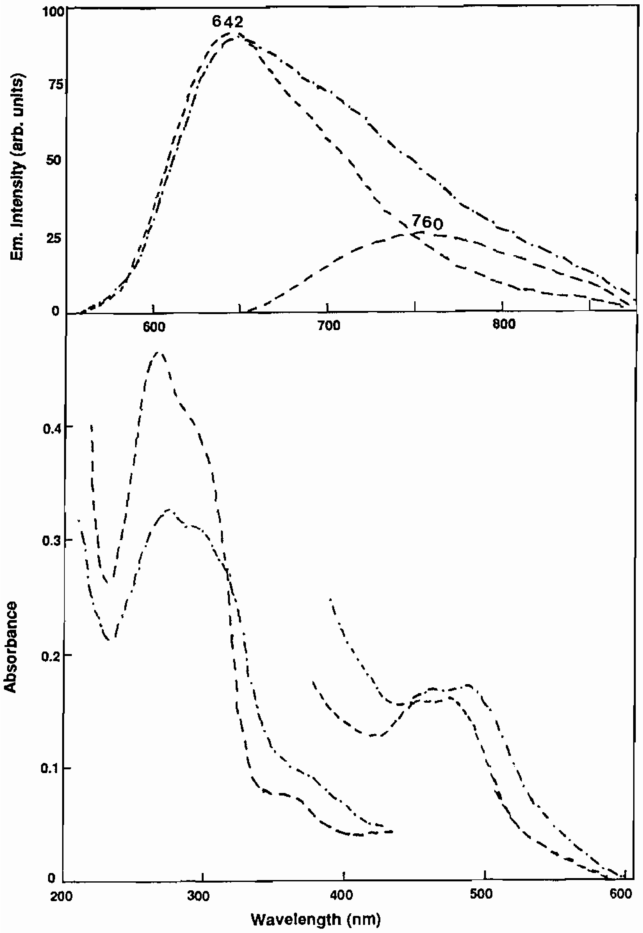


Fig. 2. Comparison of the absorption (lower panel) and emission (upper panel) spectra of freshly prepared solutions of Ru(DCPB)$_3^{4-}$ in water at two different pH values: 7.50 (– – –) and 3.55 (–·–·–). Shown also in the upper panel the difference emission spectrum (·····).

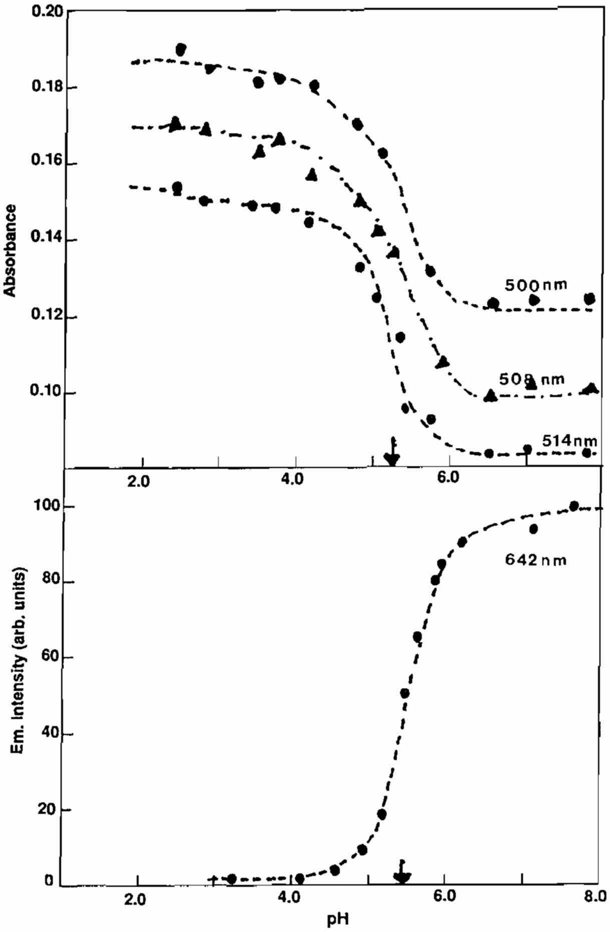


Fig. 3. pH dependence of absorbance (top) and emission intensity (bottom) of Ru(DCPB)$_3^{4-}$ at different wavelengths in aqueous solutions.

DCPB complex, ΔpK of $\leqslant 0.2$ pH units suggest an extremely small increase in the basicity. The results suggest that in the excited state the promoted electron resides primarily in the diimine framework.

In recent years a number of polypyridine complexes of Ru(II) have been found to be efficient sensitizers for charge injection using visible light on polycrystalline TiO_2 electrodes [22–25]. All these complexes contained at least one carboxybipyridine as a key anchoring ligand. When we examined the analogous DCPB complexes (including the cyano-bridged trinuclear complex, $[(CN)(bpy)_2Ru{-}CN{-}Ru(DCPB)_2{-}NC{-}Ru(bpy)_2(CN)])$ in similar sensitization experiments, the performance of DCPB-based ones was extremely low. The monochromatic photon-to-current conversion efficiency in the cyano-trimer, for example, was only 8% while $\geqslant 80\%$ efficiency has been obtained in the parent dcbpy derivative. One of the aims of the present photophysical study indeed was to understand this disappointing result. Clearly the charge injection efficiencies are related to the nature of charge density distribution in the ground and excited states of these complexes. If the promoted electron in the excited state does not find its way to the anchoring carboxyl group but is instead localized on the diimine framework, then this could result in inefficient sensitization. If this interpretation is correct, then the CT excited state of the DCPB complexes should not be heavily quenched on TiO_2 surfaces. We are currently examining this question by measuring the excited state decay both of dye-coated TiO_2 surfaces and dye-colloidal TiO_2 mixtures.

Photophysical properties of mixed ligand complexes $[Ru(DCPB)_n(DMB)_{3-n}]$

The series of complexes $[Ru(DCPB)_n(DMB)_{3-n}]$ ($n = 1$–3) illustrate another type of tuning of the energy of the CT excited state. In these mixed ligand complexes the lowest excited state is always associated with Ru→DCPB charge transfer transition. Successive replacement of the DCPB ligand by a ligand that is a more electron-donating ligand LL (such as 4,4′-$(MeO)_2$-2,2′-bpy) leads to a gradual red-shift of the longest wavelength CT band (and the emission). The lowering of the energy of the CT transition is caused by an upward shifting of the dπ orbital of Ru(t_{2g}) without affecting the nature of the lowest ligand π^* orbital (LUMO). This is shown schematically in Fig. 4. With $[Ru(DCPB)(DMB)_2]$, absorption/emission data indicate a lowering of the lowest energy CT transition by ≈ 0.17 V. The first oxidation of this complex occurs more readily (shift by 200 mV with respect to $Ru(DCPB)_3$), in consistency with the above lines of interpretation.

Table 2 also includes absorption and emission spectral data for the analogous series of complexes $[Ru(DECB)_n(DMe_2B)_{3-n}]$ ($n = 1$–3) of Wacholtz *et al.* [10]. Replacement of 4,4′-di(ethylcarboxy)-2,2′-bpy (DECB) by 4,4′-dimethyl-2,2′-bpy (DMe_2B) causes a similar raising of Ru(t_{2g}) level and a gradual red-shift of the absorption and emission takes place. It may be pointed out that, during the raising of the Ru(t_{2g}) level, all the shift in the metal complex oxidation potential does not appear in the energy of the CT transition. Nearly a quarter of the shift in the oxidation potential (increased charge density) is transferred to the bipyridine ligand involved in the CT transition via mixing of the Ru(dπ) and ligand π^* orbitals [6].

Transient absorption spectra of the CT excited state

In view of the differences in the acid–base properties of the DCPB and dcbpy complexes in the excited state, the absorption spectra corresponding to the CT excited state of the DCPB complexes have been examined. Figure 5 presents the transient difference absorption spectra for $Ru(DCPB)_3{}^{4-}$ (top) and $[Ru(DCPB)_2(DMB)]^{2-}$ (bottom) measured at 50 ns following optical excitation using 530 nm Nd-laser pulses on a laser flash photolysis system. The assignment of the spectra to the corresponding CT excited states is based on matching decay of the transient absorption at several wavelengths with emission decay measured under similar conditions and sensitivity to dissolved oxygen. With respect to the transient spectrum of analogous $Ru(dcbpy)_3{}^{4-}$ complexes, all the absorption maxima are red-shifted by nearly 20 nm. This is consistent with similar red-shifts observed in the ground state absorption spectra of these complexes. As with the other bipyridine complexes of Ru(II), the 385 nm absorption maximum is assigned to the absorption of the reduced DCPB ligand ($DCPB^-\cdot$) formed in the CT excited state:

$$Ru(DCPB)_3{}^{4-} \xrightarrow{h\nu} [Ru(DCPB)_2(DCPB^-\cdot)]^{4-*} \qquad (1)$$

The observed absorption maximum at 385 nm for both the tris and mixed ligand complex is consistent with the model indicated earlier, viz the lowest energy CT excited state in all cases involve Ru → DCPB transition.

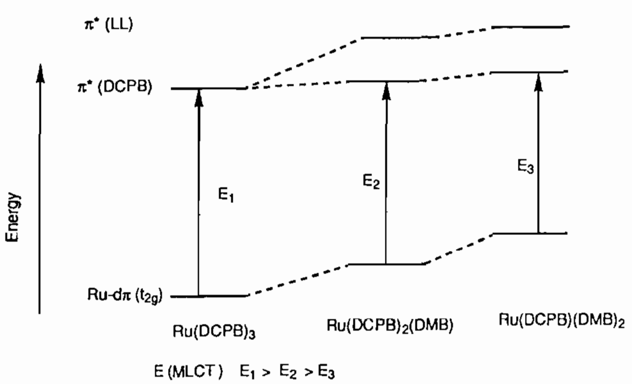


Fig. 4. A schematic representation of the shifting of the energies of the molecular orbitals that are predominantly localized on the Ru(t_{2g}) and ligand π^* orbitals in the series of mixed ligand complexes $[Ru(DCPB)_n(DMB)_{3-n}]$.

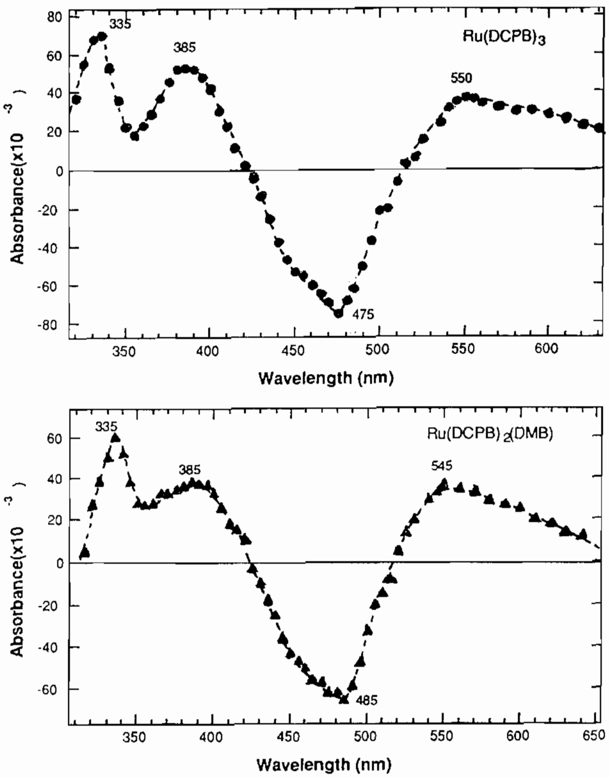


Fig. 5. Transient difference absorption spectrum corresponding to the formation of the charge transfer excited state, recorded at 50 ns following 530-nm laser pulse excitation of $Ru(DCPB)_3{}^{4-}$ (top) and $[Ru(DCPB)_2(DMB)]^{2-}$ in water (pH 10.5).

Conclusions

A study of the Ru(II) complexes containing DCPB ligands showed several features that allow better understanding of the tuning of the CT excited state via peripheral substitution of the bipyridine framework. But for the marked differences in the acid–base properties in the ground and excited states with respect to the parent dcbpy complexes, photophysical properties of DCPB and dcbpy complexes are strikingly similar. The present results indicate that in the excited state, the transferred charges remain largely localized on the diimine framework and do not extend through the phenyl spacers to the carboxyl unit. This may well account for the inefficient sensitization of the TiO_2 electrodes by the DCPB complexes.

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