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Probing the presence of hydrophobic sites in anionic polyelectrolytes with tris(polypyridine)chromium(III) complexes

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Abstract

The emission properties of tris(polypyridine)chromium(III) complexes, $[Cr(LL)_3]^{3+}$ (LL = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,7-dimethylphenanthroline (dim), and 4,7-diphenylphenanthroline (dip)), in air-saturated aqueous solutions, are dramatically modified in the presence of anionic polyelectrolytes. Investigated polyions included poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), and sodium poly(styrenesulfonate) (PSS). All four chromium complexes displayed tunable emission properties in the polyelectrolyte microenvironment, in a degree that depended on the hydrophobic character of both the macromolecule and the polyamine. The largest effect was observed for 2.5×10^{-5} M aqueous solutions of $[Cr(dip)_3]^{3+}$ in 4×10^{-3} M PMA at approximately pH 5 and $t = 15^{\circ}$ C, where $I_{PMA}/I_w = 25.66$ ($I_{PMA} =$ emission intensity in aqueous solutions containing PMA; $I_w =$ emission intensity in water). Decay lifetimes revealed that $[Cr(dip)_3]^{3+}$ units are distributed in hydrophobic and hydrophilic sites of the PMA, giving rise to short and long-lived intermediates. Distribution of $[Cr(dip)_3]^{3+}$ units in PAA and PSS is homogeneous throughout the polyelectrolyte, and the excited-state intermediates decay following a first order exponential rate law. All other investigated chromium polypyridines showed a homogeneous distribution in solutions containing PMA, PAA or PSS. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The photophysical and photochemical properties of chromium(III) polypyridyl complexes have been the subject of extensive investigation [1]. Luminescence from the lowest-energy excited states consists of two bands from the thermally equilibrated states ${}^{2}E/{}^{2}T_{1}$, and has been identified as of metal-centered ligand-field character, d-d or LF [2,3]. Values for decay lifetimes (τ) for $({}^{2}E/{}^{2}T_{1})[Cr(LL)_{3}]^{3+}$ result from contribution of different modes of decay, $1/\tau = k_{rad} + k_{nr} + k_{rx} + k_{g}[{}^{4}A_{2}] + k_{q}[Q] (k_{rad}$, rate constant for luminescence decay; k_{nr} , rate constant for non-radiative decay; k_{q} , rate constant for reactive decay, such as photoaquation; k_{g} , rate constant for other quenching modes) [3]. Infinite diluted solutions in the absence of quenchers display an intrin-

sic lifetime of ${}^{2}T_{1}/{}^{2}E$, τ_{o} , given by $1/({}^{2}k_{nr} + {}^{2}k_{rx})$ [3]. Lifetime measurements and absorption decays showed that the excited-state lifetimes have a strong dependence on the nature of the ligands, the pH of the solution, and the presence of added salts [4]. Chromium(III) polypyridines are good target compounds for solar energy conversion for their long lifetimes and strong oxidizing properties ($*E^{\circ} = 1.2 - 1.5$ V) [1]. A recent report described the ability of $[Cr(LL)_{3}]^{3+}$ to interact with DNA and the potential use of chromium(III) polyamines to serve as probes of DNA binding [5].

Polypyridyl complexes of Cr(III) display low activity toward photoaquation upon excitation with light $(\lambda_{exc} = 313-464 \text{ nm}) [1b,3]$, being $[Cr(bpy)_3]^{3+}$ the most reactive species with a quantum yield, $\Phi = 0.11$ (pH 9.6, in air-saturated, 1 M NaCl at 11°C) [4b]. The low photochemical reactivity of these complexes is explained via deactivation mechanisms that involve competing reactive, radiative and non-radiative modes. The

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proposed seven-coordinate intermediate, $[Cr(bpy)_3-(H_2O)]^{3+}$, is believed to undergo deprotonation followed by loss of bpy, to yield the final product, $[Cr(bpy)_2(OH)_2]^+$ [6]. Biphotonic studies proved that visible excitation of the long-lived doublet states of $[Cr(phen)_3]^{3+}$ promotes overall ligand labilization [7]. These photochemical processes depend strongly on the pH, ionic strength and temperature of the reaction medium. Quantum yields for photoaquation decrease at lower temperature and increasing ionic strength.

Polyelectrolyte microenvironments have been reported to modify different steps associated with photoinduced processes, such as: (i) rates of forward and back reactions; (ii) luminescence quantum yields; and (iii) decay lifetimes [8]. Electrostatic interactions between positively charged transition metal complexes and anionic polyelectrolytes have been used to enhance the rate of photoinduced electron transfer processes, and retard recombination reactions [8]. Binding affinities for chromium(III) complexes with the polyelectrolytes depend on a series of experimental parameters, in which the hydrophobic character of both the ligand and the macromolecule plays a major role [9]. In this context, we investigated binding properties between guest and host molecules and compared them with emission intensities and decay lifetimes of a series of $[Cr(LL)_3]^{3+}$ containing ligands with a varying degree of hydrophobicity. Lifetime and intensity measurements were conducted as a function of the concentration of chromium units and polyelectrolytes, ionic strength, pH and temperature.

In the work described herein, we report the ability of $[Cr(dip)_3]^{3+}$ (dip = 4,7-diphenylphenanthroline) to



probe the presence of hydrophobic sites in aqueous solutions containing polyelectrolyte microenvironments. In order to gain a better understanding on hydrophobic and hydrophilic interactions between guest and host molecules, we compared the emission changes observed in $[Cr(dip)_3]^{3+}$ with luminescence changes in solutions containing chromium(III) complexes with less hydrophobic ligands, such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 4,7-dimethylphenanthroline (dim) (see Scheme 1)¹.

2. Experimental

2.1. Materials

All materials were reagent grade and used without further purification. $[Cr(LL)_3](ClO_4)_3$ complexes were prepared by literature procedures. $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ were prepared by reducing $CrCl_3$ with Zn/Hg in acidic aqueous solution under an Ar atmosphere [10]. A flurry containing the ligand in deaerated ethanol was added to the Cr(II) solution, and allowed to react for ten minutes. Solution handling was conducted with Hamilton air-tight syringes. Oxidation of $[Cr(LL)_3]^{2+}$ was achieved by bubbling chlorine or oxygen. $[Cr(dim)_3]^{3+}$ and $[Cr(dip)_3]^{3+}$ were prepared by dissolving anhydrous CrCl₂ in deoxygenated methanol [11]. A flurry containing the ligand in air-free methanol was added to this solution, and was allowed to react for ten minutes. Oxidation of the Cr(II) complex was achieved by gently bubbling oxygen. The complexes were precipitated as the perchlorate salts by dissolving them in the minimum amount of methanol followed by a dropwise addition of HClO₄. Purity of the chromium complexes was verified by their UV-Vis spectra [12]. **Caution:** perchlorate salts of transition metal complexes are potentially explosive and should be handled with extreme care!

Poly(sodium 4-styrenesulfonate) ($M_r = 70\ 000$) and poly(acrylic acid) ($M_r = 250\ 000$) were purchased from Aldrich and used without further purification. Poly(methacrylic acid) sodium salt (25% aqueous solution; $M_r = 15\ 000$) was purchased from Polysciences. Polyelectrolyte concentrations were calculated on the basis of the monomeric unit formula weight. Solutions of $[Cr(LL)_3]^{3+}$ -polyelectrolyte were prepared by adding appropriate amounts of chromium complex to aqueous solutions containing a known concentration of

¹ Abbreviations used in this paper: bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; dim = 4,7-dimethylphenanthroline; dip = 4,7-diphenylphenanthroline; PAA = poly(acrylic acid); PMA = poly(meth-acrylic acid); PSS = poly(sodium 4-styrenesulfonate).

polyelectrolyte. A known amount of acid or base, determined from a titration curve of the corresponding $[Cr(LL)_3]^{3+}$ -polyelectrolyte system, was added to the solution to adjust the pH. For O₂ quenching experiments the solutions were air-saturated and concentrations were calculated using Ostwald solubility coefficients [13]. Bimolecular rate constants for quenching with O_2 were calculated by measuring emission lifetimes and intensities in the presence and absence of dissolved O₂, and assuming an oxygen concentration of 2.5×10^{-4} M at 25°C in solutions of ionic strength, I = 0.01 M (KH₂PO₄). Unless otherwise noted, experiments were carried out at 25°C. Steady temperatures were maintained with a circulating bath and measured inside the cuvettes with a high precision digital thermometer (Fischer Scientific) ($t \pm 0.01^{\circ}$ C) prior to intensity and lifetime measurements.

2.2. Photophysical measurements

UV-Vis spectra were obtained on a Hewlett-Packard 8452 A diode array spectrophotometer. Luminescence spectra were measured with a Spex Fluoromax spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. Emission lifetimes were measured with a laser flash photolysis instrument that uses a Surelite II Nd/YAG laser (10 Hz) as the excitation source ($\lambda_{exc} = 355$ nm). Emission was monitored at 90° to the excitation beam with a Bausch & Lomb monochromator and a Hamamatsu R928 photomultiplier tube powered by a Betran high voltage power supply. The output of the detector was digitized with a 400 MHz Hewlett-Packard 54504A digital scope (200 M samples s^{-1}) and sent to a PC through an IEEE card where it was analyzed. Each decay trace represents the average of 64 experiments.

2.3. Quantum yield measurements

A medium-pressure Hg spectral lamp was used, in conjunction with fused silica optics, for continuous photolysis of [Cr(LL)₃]³⁺ at 313 nm. Photoaquation quantum yields, $\Phi_{\rm aq}$, were calculated by following absorbance changes in the UV-Vis spectra as a function of irradiation time. The absorption spectrum of the photolyte was recorded after each irradiation up to $\sim 10\%$ change in absorbance at the monitoring wavelength ($\lambda_{mon} = 344$ nm). A sample of non-irradiated solution was kept as a blank and analyzed in the same way. Light intensity ($\sim 1 \times 10^{-6}$ einstein dm⁻³ s⁻¹) was determined by ferrioxalate actinometry [14]. Photolyte concentrations were adjusted to absorb 99.99% or more of the incident light at the excitation wavelength. Quantum yields $\Phi_{\rm rx}$ were determined from extrapolation of the linear portions of plots of $\phi_{rx}(t)$ versus time. Each quantum yield value represents the average of five experiments.

2.4. Binding constant measurements

Binding constants, K (M⁻¹), for chromium polypyridines bound to polyelectrolyte were measured by following emission changes with increasing polyelectrolyte concentration, and calculated from log { $f_b/(1 - f_b)$ } = log K + n log ([polyelectrolyte]/3), where f_b is the fraction of complex bound to the polyelectrolyte [15]. As a control method, some binding constants were also measured by a reported method using dialysis membranes [9].

3. Results and discussion

3.1. Binding and emission properties in the polyelectrolyte architecture

The binding affinities of a series of chromium(III) polypyridines with polyelectrolytes were investigated in aqueous solutions by following emission intensities at increasing polyelectrolyte concentrations. The polyelectrolyte architecture modifies the photophysical properties of these complexes due to a strong association between guest and host units, and to an increase in the medium viscosity. All investigated solutions displayed 'tunable' luminescence properties that varied as a result of the association with the macromolecules, and leveled off at large polyelectrolyte concentrations. All four studied Cr(III) polypyridines showed emission changes upon addition of polyelectrolytes, indicative of good binding affinity between guest and host components. Chromium polyamines interact electrostatically with carboxylate and sulfonate groups from the polyions. No changes in the UV-Vis spectra of the chromium complexes proved no complexation with the polyelectrolytes. Binding constants follow the order bpy < phen < dip < dim. Emission changes are also reflected in the decay lifetimes, which follow a similar trend than emission intensities. Fig. 1 and Table 1 exemplify the effect of PMA in all four complexes. These changes depend on experimental conditions, such as pH of the solution, ionic strength, and nature of the polyelectrolyte, ligands and added salts. Chromium polypyridines containing ligands with significant hydrophobic character, such as dim and dip, displayed large changes in the emission properties when bound to PMA, PSS or PAA. The largest effect observed was for 2.5×10^{-5} M aqueous solutions of $[Cr(dip)_3]^{3+}$ in 4×10^{-3} M PMA (pH 5.0) with maximum emission intensities, $I_{\rm PMA}/I_{\rm w} =$ 25.66 at $t = 15^{\circ}$ C (I_{PMA} = emission intensity in PMA; $I_{\rm w}$ = emission intensity in pure water; $\tau_{\rm PMA}$ = decay lifetime in PMA; τ_w = decay lifetime in water). The effect of the PMA architecture on the photophysics of transition metal complexes has been previously explained using a micelle-like model. In PMA aqueous solutions,



Fig. 1. (a) pH-dependence of the emission intensity of 2.5×10^{-5} M [Cr(LL)₃]³⁺ in 1.25×10^{-3} M PMA: (i) [Cr(dip)₃]³⁺; (ii) [Cr(dim)₃]³⁺; (iii) [Cr(phen)₃]³⁺; (iv) [Cr(bpy)₃]³⁺. (b) Changes in the relative emission intensity of 2.5×10^{-5} M [Cr(dip)₃]³⁺ by the addition of PMA (pH 4.5).

the methyl groups are located inside of the polymer coil and the -COO- and -COOH functional groups are oriented towards the water interface [16]. Binding has been explained as electrostatic in nature, where the molecules are severely restricted in a hydrophobic environment. PMA undergoes conformational changes from a tight coil at approximately pH 2.0 to an extended chain at approximately pH 7.0. At pH 4-5 the polymer ionizes and swells, allowing some water molecules to penetrate into PMA. At pH 5.0 a significant fraction of the carboxylate functional groups is deprotonated (\sim 24%). At pH > 9, the degree of ionization is > 97% and the polymer exists as uncoiled species with a strong negative charge [16]. PMA shows much sharper transitions with pH than PAA. These transitions are associated with a stronger hydrophobic character leading to large emission changes in the species attached to it. It has been reported that hydrophobic Ru(II) complexes have appreciable affinity to PAA at low pH and induce conformational changes of the polymer upon binding [9]. Our experimental observations showed that Cr(III) complexes containing hydrophobic ligands, dim and dip, in PAA display increased luminescence properties that are a function of pH with maximum intensities at pH 5.5 and 6.00, respectively. Similar experiments with $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ failed to show this pH effect. These observations support the view that PAA might be in a compact conformation when is attached to dip or dim complexes.

Lifetime and intensity measurements in PSS do not show a strong pH-dependence, as expected by the na-

Table 1 Emission lifetimes ^a and binding constants ^b of [Cr(LL)₃] ³⁺ in PMA

Ligand	τ (us)	$\tau_{\rm o}$ (us)	$\tau/\tau_{}$	$K (M^{-1})$
	- (Fre)	-0 (P)	• / • W	()
bpy	30	43	0.69	212
phen	118	233	2.01	1.18×10^{3}
dim ^c	158	570	3.95	2.21×10^{5}
dip °	140, 510	1010	9.33, 34	1.00×10^4

^a [Cr(III)] = 2.5×10^{-5} M, [PMA] = 4×10^{-3} M, non-controlled ionic strength, pH 4.5; τ , decay lifetimes of air-saturated PMA solutions; τ_0 , decay lifetimes of Ar-saturated PMA solutions; τ_w , decay lifetimes of air-saturated solutions in pure water.

^b K, binding constants for $[Cr(LL)_3]^{3+}$ with PMA.

^c Sequential first-order decays (see text).

ture of the functional group. Association of PSS with metal complexes has been described as a combination of electrostatic and π -electron overlap interactions in a microdomain, in which the number of monomer units does not depend on the concentration of the polymer or the ionic strength [17].

In contrast with complexes containing hydrophobic ligands, bpy and phen complexes showed smaller effects for all three polyelectrolytes under our experimental conditions, see Table 1 and Fig. 1. These observations suggest that the most predominant interactions between these chromium units and carboxylate or sulfate groups are electrostatic. A systematic study conducted with 2.5×10^{-5} M solutions of $[Cr(LL)_3]^{3+}$ in 4×10^{-3} M polyelectrolyte revealed that bpy complexes display smaller emission intensities and shorter decay lifetimes in PMA ($I_{PMA}/I_w = 0.69$, $\tau_{PMA}/\tau_w = 0.81$, pH 4.5), PSS $(I_{\rm PSS}/I_{\rm w}=0.66,\ \tau_{\rm PSS}/\tau_{\rm w}=0.82,\ {\rm pH}\ 6.00)$ and in PAA $(I_{\rm PAA}/I_{\rm w} = 0.63, \ \tau_{\rm PAA}/\tau_{\rm w} = 1.03, \ {\rm pH} \ 6.00)$ than in water. Phen complexes show a similar trend than for the two substituted phenanthrolines, in which the emission properties are enhanced upon addition of polyelectrolytes $(I_{PAA}/I_w = 2.5, \tau_{PAA}/\tau_w = 1.93, I_{PMA}/I_w = 3.06,$ $\tau_{\rm PMA}/\tau_{\omega} = 3.55$, and $I_{\rm PSS}/I_{\rm w} = 1.29$, $\tau_{\rm PSS}/\tau_{\rm w} = 1.44$).

Decay lifetimes were measured under different experimental conditions (see Tables 1 and 2). Air-saturated aqueous solutions, 2.5×10^{-5} M in Cr(III) and $4 \times$ 10⁻³ M in PMA, PSS or PAA, exhibit emission lifetimes that are significantly longer than those measured in pure water except for bpy. Once again, a larger effect was observed for complexes containing the more hydrophobic ligands, such as dip and dim. Emission lifetimes for bpy, phen and dim complexes in all three polyelectrolytes followed a first-order rate law, suggesting a uniform chromium distribution throughout the macromolecule. $[Cr(dip)_3]^{3+}$ showed decay lifetimes that fit an exponential first-order rate law in PAA and PSS. The emission lifetimes of $[Cr(dip)_3]^{3+}$ upon binding to PMA followed a double-exponential behavior that can be fit to a decay with two clear first-order components, $I_{t} = I_{0}[\alpha \exp((-k_{1}t) + (1-\alpha) \exp((-k_{2}t))] (\alpha \text{ is the frac-}$

Table 2 Effect of the polyelectrolytes on the luminescence properties of $[Cr(dip)_3]^{3+}$ in aqueous solutions ^a

Medium	τ_0 (µs)	τ (μs)	$ au/ au_{0}$	I/I_0	$K (\mathrm{M}^{-1})$
Water, pH 4.91	345	15	0.04	0.10	
PAA, pH 6.26	145	36	0.25	0.21	5.45×10^{6}
PMA ^b , pH 4.91	1 010	140 (τ_1) , 510 (τ_2)	0.14, 0.51	0.48	1.00×10^4
PSS, pH 5.00	240	43	0.18	0.21	2.94×10^{6}

^a [Cr(dip)₃³⁺] = 2.5×10^{-5} M; [polyelectrolyte] = 4×10^{-3} M, non-controlled ionic strength; 25°C; τ_0 = decay lifetime in air-free solutions;

 $\tau =$ decay lifetime in air-saturated solutions; I and $I_0 =$ emission intensities in air-saturated and air-free solutions, respectively.

^b Sequential first-order decays.

tion of chromium units that decays with rate constant k_1 , and k_2 are exponential decays of excited chromium species, and I_0 and I_t are emission intensities at time 0 and t, respectively). α values were calculated from the double exponential equation as described by Thomas et al.[16]. The short-lived component, $\tau_1 \sim 140 \ \mu s$ and $\alpha = 0.46$, may be assigned to chromium units located in the polyelectrolyte-water interface that are attracted to carboxylate groups by electrostatic interactions, and to free forms. The long-lived component, $\tau_2 \sim 510 \ \mu s$, may be assigned to chromium bound to PMA sites by hydrophobic interactions, see Table 2. In the absence of O₂, exponential decays for PMA solutions follow a first-order rate law with lifetimes, $\tau_0 = 1.01$ ms $(1/\tau_0 =$ $k_{\rm nr} + k_{\rm r})^2$. This observation suggests that hydrophobic interactions between metal complex and polyelectrolyte lead to a significant shielding from oxygen quenching. Also, the fact that the emission intensities and decay lifetimes are enhanced in the presence of PMA for both aerated and deaerated solutions suggests that the rate of nonradiative decay is decreased in the polyelectrolyte microenvironment [9]. This can be interpreted in terms of a more rigid environment created by the polyelectrolyte that restricts the vibrational freedom of the ligands around the metal center, and that replaces some of the water molecules in the solvation sphere [3]. The slight decrease in the emission properties of $[Cr(bpy)_3]^{3+}$ in the polyelectrolyte was investigated by evaluating $k_{\rm nr}$ and $k_{\rm rx}$ values at 25°C. This decrease, observed in emission intensities and lifetimes, approaches a limiting value at higher polyelectrolyte concentrations. It has been reported that $[Cr(bpy)_3]^{3+}$ is photochemically active with photoaquation quantum yields (Φ_{aq}) defined as $\Phi_{aq} = k_{rx} \tau_{air}^{-1}$, and that $\tau_0^{-1} =$ $k_{\rm nr} + k_{\rm rx}^3$. All other chromium(III) polypyridines showed non-significant photochemical reactivity in

PMA ($\Phi_{aq} < 0.013$). Photoaquation quantum yields in PMA, reach a lower limit at acidic pHs while show an upper limit plateau in alkaline solutions $(\Phi_{aq}(H_2O)/$ $\Phi_{aq}(PMA) = 1.00 \text{ (pH 4.5); } \Phi_{aq}(H_2O)/\Phi_{aq}(PMA) = 1.31$ (pH 9)) describing a 'titration curve', as previously observed for aqueous solutions [3]. Both rate constants, $(k_{\rm nr} = 1.44 \times 10^4; k_{\rm rx} = 9.43 \times 10^3 \text{ s}^{-1})$, are slightly higher for $[Cr(bpy)_3]^{3+}$ in PMA (pH 4.5, $t = 25^{\circ}C$) than in pure water $(k_{\rm nr} = 1.29 \times 10^4; k_{\rm rx} = 7.05 \times 10^3$ s⁻¹). These observations seem to suggest that both non-radiative and reactive pathways contribute to decreased emission lifetimes and intensities under our experimental conditions⁴. Photoaquation quantum yields of $[Cr(bpy)_3]^{3+}$ in PAA and PSS, 0.0155 and 0.0107, lead to non-significant contributions of the reactive pathway in the overall decay scheme with rate constants $k_{\rm rx} = 449$ and 328 s⁻¹, respectively, and leave $k_{\rm nr}$ as the major contribution to the intrinsic decay of the excited state. The assumption that k_{nr} is increased in the polyelectrolyte microenvironment agrees well with luminescence lifetimes for $[Cr(dip)_3]^{3+}$ in PAA or PSS in the absence of O_2 (see Table 2). Only hydrophobic complexes, [Cr(dip)₃]³⁺ and [Cr(dim)₃]³⁺, bound to PMA showed a decrease in k_{nr} values, probably due to strong binding of Cr(III) to sterically restricted hydrophobic sites inside the polymer coil.

The temperature dependence of the emission properties of $[Cr(dip)_3]^{3+}$ in the polyions was investigated in a temperature range between 280 and 310 K, see Fig. 2. Static and dynamic measurements in PSS and PAA show the same trend for emission intensity and decay lifetime changes in the temperature range under investigation. For PMA solutions the temperature dependence reflects the chromium distribution throughout the polyion and was found that $I/I_w = (\alpha \tau_1 + (1 - \alpha)\tau_2)/\tau_w$.

 $^{^2}$ In these assumptions we are not considering a non-radiative photoaquation pathway. Previous reports in aqueous solutions indicated that photoaquation quantum yields for phen, dim, and dip complexes are non-significant and $k_{\rm rx}$ negligible in the overall decay scheme.

³ No ground-state quenching was observed for our experimental conditions. See Ref. [1a].

⁴ A full investigation of the effect of the electrostatic interactions in the emission properties of $[Cr(byy)_3]^{3+}$ attached to anionic polyelectrolytes is currently under investigation. $\Phi_{aq}(H_2O) = 0.31$; $\Phi_{aq}(PMA) = 0.33$; $\tau_{air}(H_2O) = 44$ µs; $\tau_{air}(PMA) = 35$ µs; τ_0 (H₂O) = 50 µs; $\tau_0(PMA) = 42$ µs.

3.2. Excited-state quenching

Bimolecular rate constants for the quenching of the excited-states of all four complexes with I^- , O_2 , and Fe^{2+} ions were measured in pure water (pH 4.5 and 6), PMA (pH 4.5), PAA (pH 6.0), and PSS (pH 6.0) (see



Fig. 2. Temperature-dependence of emission properties of 2.5×10^{-5} M [Cr(dip)₃]³⁺ in 4×10^{-3} M polyelectrolyte; (a) PMA; (b)(i) PSS; (ii) PAA. Solid and open circles are emission intensity and decay lifetime measurements, respectively.

Table 3 Quenching of $[Cr(LL)_3]^{3+}$ in polyelectrolyte solutions at 25°C ^a

Medium	k (polyelectrolyte)/k (water	r)

	Вру	phen	dim	dip				
(i)I ⁻								
PAA	0.874	0.359	0.00957	0.0165				
PSS	0.202	0.0147	0.00425	0.00105				
PMA ^b	0.930	0.773	0.0765	0.0197,				
				0.00460				
(ii)Fe ²⁺								
PAA	1.64	2.87	3.40×10^2	97.2				
PSS	4.42×10^{3}	2.52×10^3	1.42×10^{3}	1.82×10^{2}				
PMA ^b	1.36	1.13	1.64×10^2	3.20×10^2 , 37.5				
(iii)O ₂								
PAA	0.967	0.324	0.449	0.970 (0.327)				
PSS	1.03	0.280	0.453	0.176 (0.299)				
PMA ^b	1.00	1.00	0.744	0.463, 0.0611				
				(0.152, 0.0152)				

^a [Cr(III)] = 1×10^{-5} M; [polyelectrolyte] = 1×10^{-4} M; [KH₂PO₄] = 0.01 M unless stated. Results in parentheses correspond to [Cr(III) = 2.5×10^{-5} M; [polyelectrolyte] = 4×10^{-3} M with no added salt.



Fig. 3. Stern–Volmer plots for the bimolecular reaction between $[Cr(LL)_3]^{3+}$ and I⁻ in the presence of PMA: (i) phen; (ii) bpy; (iii) dim; (iv) dip. $[Cr(LL)_3^{3+}] = 1 \times 10^{-5}$ M; $[PMA] = 1 \times 10^{-4}$ M; $[KH_2PO_4] = 0.01$ M.

Table 3). All quenching reactions were measured in air-saturated solutions at the pH of the most pronounced emission change. Static quenching was evaluated by following emission intensity changes at the wavelength of maximum intensity in the emission spectra. Stern-Volmer plots showed a perfectly linear behavior in the concentration range under study for all four complexes with PSS, PMA and PAA⁵ [18]. Fig. 3 exemplifies the behavior of all four chromium polypyridines with I⁻ in the presence of PMA. The hydrophobic nature of both ligand and macromolecule played a major role in the quenching reactions for all tested solutions, despite of the charge of the quencher. The more hydrophobic ligand, dip, has the largest affinity for the hydrophobic pockets of PSS and PMA, and hence feels the steric shielding effect of the polyelectrolyte backbone in a larger extent. On the other hand, smaller effects observed for bpy complexes indicate smaller binding affinities with the polyelectrolyte and coulombic interactions between chromium and polyelectrolyte. The data collected with PMA and

^b Results indicate both short and long-lived intermediates with $\alpha = 0.79$ for these experimental conditions.

⁵ Stern–Volmer parameters were determined by plotting: $I_0/I = 1 + K_{\rm SV}[Q]$. I_0/I , ratio of the emission intensity in the absence of quencher to that in the presence of quencher; $K_{\rm SV}$, Stern–Volmer coefficient. Bimolecular rate constants for the quenching reactions, $k_{\rm q}$, were calculated as: $1/\tau = k_{\rm obsd} = k_0 + k_{\rm q}[Q]$ where $\tau_{\rm o} = 1/k_0$ is the decay time without the quencher, and [Q] is the quencher concentration [8a].

PSS solutions indicates that the overall polyelectrolyte effect follows a trend that is in agreement with the hydrophobic character of the polyamines, bpy < phen < dim < dip.

Anionic polyelectrolytes are expected to decrease the interaction between cationic species, the Cr(III) complex, and a negatively charged quencher, I⁻, due to coulombic repulsions. Hydrophobic polyelectrolytes make this effect even more pronounced by isolating the chromium units from the water interface. PSS solutions show the largest effect among all the polyelectrolytes for all tested compounds with rate constant values between 4.74 (bpy) and 950 (dip) times smaller than in pure water. PMA solutions revealed strong hydrophobic interactions between the polyelectrolyte and chromium units, k_q (water)/ k_q (PMA) = 217 (dip) (k_q = bimolecular quenching rate constant, M⁻¹ s⁻¹).

A similar trend on both the polyelectrolyte and the nature of the coordinating ligand is observed in quenching experiments conducted with a positively charged quencher, Fe²⁺. In this case, the presence of the anionic polyelectrolyte increases the rate constant values, by bringing the reactants together due to a strong electrostatic interaction [8,15]. This effect was proved to be mainly a volume effect in which the reactants are condensed in the negative potential field of the microenvironment [8]. PSS solutions display a substantial increase in the bimolecular rate constants for all four complexes $(k_{a}(\text{PSS})/k_{a}(\text{water}) = 4.42 \times 10^{3}$ (bpy), 2.52×10^3 (phen), 1.42×10^3 (dim) and 1.82×10^3 10^2 (dip)). This trend shows a decreased rate constant for dip due to a strong shielding association with the polyelectrolyte and absorption of the cationic quencher



Fig. 4. Effect of added salts on the relative emission intensity of 1×10^{-5} M $[Cr(dip)_3]^{3+}$ in 1×10^{-4} M PMA at various pHs, [I] = 0.01 M: (i) \bigcirc NaClO₄, \blacksquare LiCF₃SO₃; (ii) KH₂PO₄.

in the polyelectrolyte chains. The same general trend was observed for PAA and PMA solutions. While bpy and phen complexes do not show much of an effect in the presence of either polycarboxylate, the differences between dip and dim complexes can be interpreted in terms of an unequal distribution of Cr(III) and Fe²⁺ ions throughout the macromolecule with a stronger shielding effect for dip. Fe²⁺ ions are known to form complexes with carboxylate and sulfonate groups [19] and expected to be located near the water interface. Complexation makes Fe^{2+} less accessible to the Cr(III) units. Preliminary results showed that bimolecular rate constants measured with $[Ru(bpy)_3]^{2+}$ as an electron transfer quencher follow the same trend, in which for dip the small value observed for PMA can be explained in terms of location of chromium and ruthenium units in different sites within the polyelectrolyte $(k_o(PMA)/$ k_{a} (water) = 0.24). One site is restricted and removed away from the water interface and the other is in close proximity to the water.

Bimolecular rate constants for the quenching reaction of the excited states of Cr(III) with dissolved O_2 were evaluated by assuming relationships such as $\tau^{-1} = k_{rad} + k_{nr} + k_q [O_2]$. The inhibition of O_2 quenching is greater for $[Cr(dip)_3]^{3+}$ in the presence of PMA at a pH of a compact conformation (pH 4.5). At this pH the macromolecules offer a rigid microenvironment in which the metal complexes are protected against quenching by oxygen and other nonradiative decay modes of the excited state [8].

3.3. Effect of added salts

As mentioned above, the photophysical properties of chromium(III) polyamines in polyelectrolytes are closely related to experimental parameters that influence binding affinities between guest and host components. Addition of salts modifies coulombic interactions with the macromolecules due to extensive ion-pairing between chromium units and added anions⁶ [20,21]. Ion-pairing decreases the overall charge of the chromium species bound to macromolecules, and therefore it modifies the electrostatic interactions between guest and host components. Additional positively charged ions 'screen' the interactions between these chromium species and host molecules [22]. Cr(III) units hydrophobically bound inside the polymer coils are expected to be sterically shielded and hence, to feel the ionic strength effect in a lesser extent. Fig. 4 and Table 4 exemplify the effect of added salts on the emission

⁶ The ion-pairing constant (K_{ip}) can be calculated as a function of the ionic strength by using the Fuoss equation. For {[Cr(bpy)₃]³⁺, ClO₄⁻} the ion-pairing equilibrium constant is expected to be larger than 5.73.

Table	4									
Effect	of add	ed salt	s on	the	emission	lifetimes	of $[Cr(dip)_3]^{3+}$	attached	to	PMA ^a

Salt	α	τ(μs) ^b	$ au/ au_{\mathbf{w}}$	$\tau_0^{\ c}$	$ au/ au_0$
NaClO ₄	0.46	$110(\tau_1), 410(\tau_2)$	11, 41	1160	0.10, 0.35
LiCF ₃ SO ₃	0.53	$135(\tau_1), 490(\tau_2)$	12.2, 44.5	1130	0.12, 0.43
KH ₂ PO ₄	0.77	$25(\tau_1), 103(\tau_2)$	2.4, 9.8	289	0.09, 0.36

^a $[Cr(dip)_{3}^{3+}] = 2.5 \times 10^{-5} \text{ M}; [PMA] = 4 \times 10^{-3} \text{ M}; I = 0.1 \text{ M}.$

^b Sequential first-order decays. α is the fraction of chromium units that decays with lifetime τ_1 .

^c First-order decays.

intensities and decay lifetimes of $[Cr(dip)_3]^{3+}$ in PMA. While the addition of 0.01 M perchlorate or triflate salts does not change emission patterns substantially, KH₂PO₄ favors an overall decrease in luminescence suggesting dominant coulombic interactions rather than hydrophobic⁷. This sharp decrease in emission intensity, together with shorter decay lifetimes in the presence of phosphate, indicates ion-pair formation and displacement of chromium units from inside the hydrophobic polymer coils. Perchlorate and triflate solutions display α values and τ/τ_{0} ratios comparable to those measured in the absence of added salts. Inspection of emission data in PMA solutions with KH₂PO₄ suggests that the chromium units are pushed out of the hydrophobic sites and placed near the water interface, where they are more exposed to O₂ quenching. Time-resolved experiments showed short-lived ($\tau_1 = 25 \ \mu s$) and long-lived $(\tau_2 = 103 \text{ } \mu\text{s})$ transients with decay lifetimes in the neighborhood of those measured for pure water ($\tau = 15$ us) and for electrostatically bound phenanthroline complexes ($\tau \sim 118 \ \mu s$), respectively.

The ionic strength effect on the emission decays was investigated by adding increasing amounts of NaClO₄ to PMA solutions of bpy and dip complexes, see Fig. 5. Both complexes showed opposite effects that reflect the different nature of the chromium/polyelectrolyte interaction. Addition of salt to $[Cr(dip)_3]^{3+}$ shortens emission lifetimes of both short-lived (τ_1) and long-lived (τ_2) components of the emission ($\tau_1 = 119 \ \mu s$ and 69 μs for $[NaClO_4] = 0$ and 0.6 M respectively; $\tau_2 = 510 \ \mu s$ and 395 µs for $[NaClO_4] = 0$ and 0.6 M respectively) as expected for a screened interaction between guest and host molecules. Decays for $[Cr(bpy)_3]^{3+}$ units in PMA become longer at increasing concentrations of the salt, and level off at $[NaClO_4] \sim 0.4$ M with $\tau = 67$ µs. This result matches decay lifetimes measured in aqueous solutions with no polyelectrolyte (I = 0.4 M). Thus, $[Cr(bpy)_3]^{3+}$ ions are surrounded by perchlorate anions that occupy interligand pockets and provide additional rigidity to the metal surrounding making emission lifetimes longer than those observed with no added salts. Longer lifetimes in a highly ionic medium have been explained by invoking ionic interferences of the ligand vibrations that promote non-radiative processes, and a change in the microstructure of the medium surrounding the metal complex [3].

4. Conclusions

The experimental data described above show that chromium(III) polypyridines can be used as sensitive probes for hydrophilic and hydrophobic sites in polyelectrolyte microenvironments. While the emission properties of $[Cr(dip)_3]^{3+}$ show the effect of a combination of hydrophobic and electrostatic interactions, $[Cr(bpy)_3]^{3+}$ solutions display the effect of only coulombic interactions with the polyelectrolyte backbone. From here we can conclude that electrostatic interactions between Cr(III) and anionic polyelectrolytes contribute to reduced emission properties, apparently due to an increase in k_{nr} . On the other hand, strong hydrophobic interactions place chromium units in restricted microenvironments, in which the excited state proper-



Fig. 5. Ionic strength effect on the decay lifetimes of 2.5×10^{-5} M [Cr(LL)₃]³⁺ in 4×10^{-3} M PMA. (a) bpy; (b) dip; (i) no NaClO₄; (ii) [NaClO₄] = 0.6 M.

⁷ The anion effect has been reported to result from a combination of phenomena such as ion-pairing, molecular events in interligand pockets, vibrational freedom of the ligands and the structure of the solvent [11].

ties are greatly enhanced. These emission properties may be finely tuned by controlling experimental parameters, such as ionic strength, nature of added salts and temperature.

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