Photophysical properties of -Re(I)(CO)₃(phen) pendants grafted to a poly-4-vinylpyridine backbone. A correlation between photophysical properties and morphological changes of the backbone

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Key words: photophysics; poly(4-vinylpyridine); -Re(CO)₃(phen) pendants

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Abstract

Photochemical and photophysical properties of a polymer, Re-P4VP, consisting of - Re(I)(CO)₃(phen) pendants grafted to a poly-4-vinylpyridine backbone, P4VP, were interpreted on the bases of morphological transformations. These transformations are responsible of a significant increase of the MLCT_{Re(I) → phen} excited state luminescence lifetime when the polymer concentration is increased. Also a nearly 8-fold increase in the luminescence quantum yield resulted from the protonation of Re-P4VP with consequent changes of the excited state decay kinetics. Results of TEM and AFM morphological studies on P4VP and Re-P4VP in the presence of HClO₄ acid, i.e., to form Re-P4VPH_nⁿ⁺, revealed that they have concentration dependent morphologies. From low to large concentrations of the Re-P4VP polymer, the morphology of Re-P4VP varies from a nonhomogeneous distribution of spherical nanoaggregates coexisting with micrometer size fibers to an homogeneous distribution of spherical nanoaggregates with diameters around 25 nm. The Re-P4VP morphology is also altered when the polymer pyridines are protonated. Protonation of diluted solutions of Re-P4VP polymers decrease the sizes of the nanoaggregates and small objects with diameters smaller than 10 nm appear.

Introduction

Among the third row of transition metal compounds, Re(I) tricarbonyl complexes coordinated to mono or bidentate azines of the type fac-XRe(CO)₃L (where X= halide and/or substituted azine and L= α -diimine) show exceptionally rich excited-state behavior and redox chemistry as well as thermal and photochemical stability [1]. Broad structural variations of the L ligand allowed to utilize them in electron transfer studies [2], solar energy conversion [3-5], catalysis [6], as luminescent sensors [7-9], molecular materials for non-linear optics [10-11] and optical switching [12]. Besides, variation of the X/L ligands allows to incorporate these chromophores into several media, such as proteins [13-15], polymers [16-26], intercalate them to DNA [27-28] or make them part of supramolecular structures [29].

The polymers used here and in previous works have an average of ~200 – [Re(CO)₃L]⁺ pendants grafted on a poly-4-vinylpyridine, P4VP, backbone, Scheme I [16-23, 26, 30]. These Re(I) polymers, which are polyelectrolytes, exhibit interesting properties from a photochemical and nanoscience stand points. The pendants show marked differences in their photophysical properties when compared to single [Re(CO)₃L]⁺ molecules in diluted solutions. For example, Re $\rightarrow$ L charge transfer excited states (MLCT) in the Re(I) polymers undergo a

Scheme I: Structural formulae of Re-P4VP polymer

more efficient annihilation and/or secondary photolysis than in $-\text{[Re(CO)}_3\text{L]}^+$ complexes, eq.1-2, where $[\text{Re(CO)}_3\text{L}]^{+*}$ denotes an excited state higher in energy than the MLCT [26].

The $-\text{[Re(CO)}_3\text{L]}^{+*}$ is an intra-ligand, IL, excited state which is formed in eq. 2 by the annihilation of two ${}^3\text{MLCT}$ excited states. In contrast to the ${}^3\text{MLCT}$, the ${}^3\text{IL}$ excited states can oxidize solvents like CH_3OH . When the Re-free pyridines of the Re(I) polymers were peralkylated, the 350 nm irradiation of the Re(I) chromophores induced charge transfer processes between the chromophores [30]. The latter charge transfer process stands in contrast with the intrastrand energy transfers that occur during the irradiation of a P4VP polymer containing pendent $-\text{[Re(CO)}_3(\text{phen})]^+$ chromophores [26].

From the nanoscience viewpoint, AFM and TEM observations have revealed that Re(I) polymers form nanometer scale structures where several hundreds of polymer strands are associated in nearly spherical aggregates [18, 20, 22]. Multiple morphologies of those polymers aggregates were obtained by using different solvents [18]. Moreover, in a common realm of photochemistry and nanoscience, significant mechanistic differences are observed when the respective luminescence of $[\text{Re(CO)}_3\text{L}]^+$ molecules and polymers containing pendent Re(I) chromophores are compared. In both materials the luminescence, originated in the ${}^3\text{MLCT}$ excited state, is quenched by amines. For instance, the observed rate constants for the quenching of the ${}^3\text{MLCT}$ luminescence of a P4VP polymer containing pendants $-\text{Re(CO)}_3(\text{bpy})^+$ chromophores by amines shows “vestiges” of the inverted effect predicted by Marcus. In contrast with the latter mechanism, the quenching of $[\text{pyRe(CO)}_3(\text{bpy})]^+$ luminescence follows a Rehm-Weller type of mechanism [17]. The lower value obtained for the total reorganization energy of the Re(I) polymer than that for $[\text{pyRe(CO)}_3(\text{bpy})]^+$ was due to the retarded solvent motions inside the nanoaggregates formed by the Re(I) polymer in acetonitrile solutions [17].

In this paper we have used steady state and time resolved techniques to study the effect of nanoaggregation on the photophysical properties of a polymer, Re-P4VP, containing $-\text{[Re(CO)}_3(\text{phen})]^+$ pendants grafted to P4VP. It was found that the Re-P4VP luminescence

lifetime increases with increasing polymer concentration. In addition, the protonation of the Re-free pyridines of Re-P4VP by HClO_4 acid in CH_3CN changes the aggregation pattern of the Re-P4VP aggregates as established using Atomic Force Microscopy and TEM methods. Protonation of the pyridines induce morphological changes which affect, in turn, the photophysical properties of the Re(I) polymer.

Experimental Section

Photophysical Measurements. UV-vis spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Emission spectra were obtained with a computer-interfaced Near-IR Fluorolog-3 Research Spectrofluorometer, and were corrected for differences in spectral response and light scattering. Solutions were deaerated with O_2 -free nitrogen in a gas-tight apparatus before recording the spectra. Lifetime measurements were performed using the Time-correlated Single-Photon Counting (TCSPC) unit of the Fluorolog-3 with a 341 nm NanoLED excitation source.

Flash Photochemical Procedures. Transient absorption spectra were performed by excitation with a Lambda Physik SLL-200 excimer laser (25 ns FWHM and 20-30 mJ/pulse at 351 nm), For transient absorption studies, the excitation beam was at a right angle with the white-light monitoring beam provided by a 1000-W Xe arc lamp probe source. The light was passed through a monochromator (PTI-1695) and detected by a HamamatsuR758 photomultiplier. Decays typically represented the average of 10 to 30 pulses and were collected on a HP-54600B digital oscilloscope interfaced with a PC computer. Solutions for the photochemical work were deoxygenated with streams of ultrahigh-purity N_2 before and during the irradiations. A flow system ensured that the fresh solution was brought to the reaction cell in experiments where the decomposition of the Re(I) complexes and/or formation of products interfered with the optical measurements. The concentration of the complexes were adjusted to provide homogeneous concentrations of the photogenerated intermediates within the volume of the irradiated solution, *i.e.*, optical densities equal to or less than 0.1 (optical length = 1 cm) at 355 nm. In all the flash photolysis experiments, the concentration of the polymer was adjusted, in chromophore units, to $[\text{Re chromophore}] = 1.8 \times 10^{-4} \text{ M}$.

Protonation studies and spectroscopic analysis. Spectrophotometric titrations were performed by following changes in the UV-vis spectrum after the addition of different volumes of HClO_4 acid to the Re(I) polymer solution in CH_3CN . In each experiment, to a volume of 2 ml of a

CH₃CN solution containing the Re(I) polymer ([Re chromophore] = 6x10⁻⁵M in Re(I) pendants and a concentration of uncomplexed pyridines in Re-P4VP, [py] = 1.2x10⁻⁴M), 50 or 100 µl aliquots of HClO₄ (3x10⁻⁴M in CH₃CN) were successively added and the absorption spectrum of the resulting solution was recorded. When it was necessary, the absorbances were corrected by the appropriate dilution factors. By this way, spectral changes following the mixing of the Re(I) polymer and HClO₄ solutions were recorded for [HClO₄]/[P4VP] initial ratios between 0 and 1.5. We used chemometric-techniques in order to retrieve, from the absorbance matrix, the concentration profiles and the spectra of each contributing factor [31-32]. A bilinear regression analysis [33] was applied to the experimental absorption matrix in order to obtain information on the spectra of the absorbing species. These methods can be applied to bilinear spectroscopic data from a chemical reaction to provide information about composition changes in the presence of multiple species. In the present work we used the alternating least-squares (ALS) algorithm to simultaneously estimate concentration and spectral profiles [34]. ALS extracts useful information from the experimental data matrix $\mathbf{A}(i \times j)$ by the iterative application of the following matrix product: $\mathbf{A} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$ where $\mathbf{C}(i \times n)$ is the matrix of the concentrations profiles; $\mathbf{S}^T(n \times j)$ is that containing the spectral profiles, and $\mathbf{E}(i \times j)$ represents the error matrix. The indexes i , n and j denote the samples, contributing factors and recorded wavelengths, respectively. Resolving matrix $\mathbf{A}$ may be a rather difficult task [35] since on the one hand, n is usually unknown [36] and on the other hand, curve resolution methods cannot deliver a single solution because of rotational and scale ambiguities [37]. We applied Singular Value Decomposition to the experimental matrix for the estimation of n . In order to reduce rotational ambiguities we used some chemically relevant constraints [38] such as non-negativity, closure and unimodality.

AFM. Formation of the Re(I) polymer aggregates from neat CH₃CN or HClO₄/CH₃CN solutions was monitored by Atomic Force Microscopy (AFM). In all the experiments, the concentration of the polymer was adjusted, in chromophore units, to [Re chromophore] = 2 x 10⁻⁷ M, and a 10 µl aliquot was spotted stepwise on freshly cleaved muscovite mica. After, the sample was dried under N₂. All images were obtained in ambient conditions using MultiMode Scanning Probe Microscope (Veeco, Santa Barbara, CA. USA) equipped with a Nanoscope V controller (Veeco, Santa Barbara, CA). All the measurements were obtained with tapping mode, using probes doped with silicon nitride (RTESP, Veeco with tip radius of 8-12 nm, 271-311 kHz, force constant 20-80 N/m). Typical scan rates were 1 Hz-1.5 Hz.

TEM. Transmission electron micrographs were recorded on a JEOL JEM 1200 EX II electron microscope using a carbon-coated 300-mesh copper grid. The polymer films were obtained by room temperature solvent evaporation of acetonitrile solutions of the Re-P4VP and Re-P4VPH_nⁿ⁺, respectively. When taking photos, the polymer films were not stained with any chemicals, and the contrast of the image in the TEM photos can only originate from the rhenium complexes incorporated to the polymers. The Re(I) complexes in the polymer Re-P4VP aggregate and form isolated nanodomains that are dispersed in the polymer matrix film.

Materials. The polymer Re-P4VP and poly(4-vinylpyridine), P4VP, were available from a previous work [26]. The reproduction of photochemical and structural data literature was used to assess the materials purity. Other materials were reagent grade and used as received.

Results

As shown in previous communications, the interpretation of the photophysical and photochemical properties of photoactive coordination complexes grafted into a polymer must be based on the understanding of the morphological conditions of the polymeric medium. Therefore the analysis of the species distribution and the morphological studies are presented in sections 1, and 2, ahead of the sections dealing with pendent $[\text{Re}(\text{CO})_3(\text{phen})]^+$ photophysical properties.

1. Absorption spectroscopy and species distribution

Fig. 1 shows the spectral changes in the UV-vis spectrum of the Re(I) polymer after the acidification with HClO₄ acid and the spectral changes recorded for the protonation of P4VP in CH₃CN. Fig. 1a shows that the absorbance of the Re(I) polymer grows at 221, 254 and 263 nm. In Fig. 1b it is observed that the initial spectrum of P4VP changes abruptly when [HClO₄]/[py] varies between 0.01 and 0.1. In the wavelength range between 200 and 240 nm, a new sharp band appears centered at $\lambda_{\text{max}} = 223$ nm and the former band centered at $\lambda_{\text{max}} = 257$ nm shifts to $\lambda_{\text{max}} = 255$ nm. In addition, a shoulder centered at $\lambda_{\text{max}} \approx 275$ nm is developed. The broad band centered at $\lambda_{\text{max}} \approx 360$ nm experiences only small changes after protonation. After that, when the

Fig. 1: (a) Spectrophotometric titrations performed by following the absorbance changes in the UV-vis spectrum after the addition of different volumes of HClO_4 acid to the Re(I) polymer ($[\text{Re chromophore}] = 6 \times 10^{-5} \text{ M}$.) solution in CH_3CN . (b) Spectrophotometric titrations performed by following the absorbance changes in the UV-vis spectrum after the addition of different volumes of HClO_4 acid to P4VP ($[\text{P4VP}] = 4 \times 10^{-4} \text{ M}$). The arrows show the progress of the change at different $[\text{HClO}_4]/[\text{P4VP}]$ ratios. In (a) is $[\text{HClO}_4]/[\text{P4VP}] = 0; 0.125; 0.1875; 0.25; 0.3125; 0.375; 0.4375; 0.5; .5625; 0.625; 0.75; 0.875; 1.0; 1.125; 1.25; 1.375; 1.5$. In (b) is $[\text{HClO}_4]/[\text{P4VP}] = 0; 0.01; 0.02; 0.03; 0.04; 0.05; 0.06; 0.07; 0.08; 0.09; 0.1; 0.15; 0.2; 0.25; 0.3; 0.35; 0.4; 0.45; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 1.5$.

$[\text{HClO}_4]/[\text{P4VP}]$ ratio is increased between 0.1 and 1.5 the spectrum increases in intensity smoothly. The analysis of both matrices of UV-vis spectra shown in Fig. 1 was performed using

Fig. 2: Spectral shapes and relative concentration profiles obtained from chemometric analysis of UV-vis spectral changes of Fig. 1. (a) Re-P4VPH_n^{nt+}: C1 = contribution of the deprotonated polymer; C2 = contribution of protonated pyridines; C3 and C4 = contributions of conformational changes induced by protonation. (b) P4VP/HClO₄: C1 = contribution of the deprotonated polymer; C2 = contribution of protonated pyridines; C3 = contribution of conformational changes induced by protonation.

chemometric techniques including Singular Value Decomposition, Evolving Factor Analysis and ALS algorithm. Spectral changes recorded for the solutions of Re(I) polymer were properly modeled by considering 4 contributing factors. On the other hand, for the set of UV-vis spectra obtained for P4VP solutions only 3 contributions were necessary. Fig. 2 shows the spectra obtained by ALS algorithm for each composition whereas insets to Fig. 2 show the corresponding concentration profiles. The comparison of the concentration and the spectral

profiles shows a common feature in both polymeric systems, i.e. at low $[\text{HClO}_4]/[\text{py}]$ ratios (below 0.15) relatively sharp spectral changes occur in the wavelength range 240-265 nm as the $[\text{HClO}_4]/[\text{py}]$ ratio is increased. Afterwards, the dependencies of the spectral changes with the $[\text{HClO}_4]/[\text{py}]$ ratio are smoother in both cases. It is worth to mention that the spectral changes observed for low $[\text{HClO}_4]/[\text{py}]$ ratios in the 240-265 nm wavelength range are very similar to those recorded for the protonation of single pyridines in CH_3CN solutions [39]. Moreover, similar absorbance changes to those of Fig. 1 were observed after protonation of P4VP by trifluoroacetic acid in 1,2-dichloroethane [40]. Therefore, the absorption behavior observed for both polymers at $[\text{HClO}_4]/[\text{py}]$ ratios below 0.15 can be mainly ascribed to the protonation of the pyridine moieties.

It should be noted that the molar extinction coefficient of P4VP is at least one order of magnitude smaller than that of Re-P4VP in the 230-300 nm range. Therefore, the spectral changes of P4VP for $[\text{HClO}_4]/[\text{py}]$ ratios equal to or smaller than 0.15 can be almost completely ascribed to the protonation of the pyridines in the polymer while lesser changes are caused by the pyridine protonation on the overall spectral shapes of Re-P4VP. This is evident from the concentration profile associated to the second contribution in Fig. 2a, which is less than 20%. This is indicative, see below, that the Re-P4VP protonation should be occurring simultaneously with a change in the aggregation of polymer strands.

2. Morphology of Re-P4VP and Re-P4VPH_n^{n+} aggregates

The understanding of the Re-P4VP photophysical and photochemical properties requires a knowledge of the polymer's morphology. To ascertain the various morphologies of the polymers Re-P4VP and Re-P4VPH_n^{n+} under different conditions, samples of the polymers were studied using both transmission electron microscopy (TEM) and AFM techniques.

TEM observations. The films used in TEM experiments were prepared using two different concentrations of Re-P4VP, i.e. $[\text{Re chromophore}] = 2 \times 10^{-5} \text{ M}$ and $2 \times 10^{-4} \text{ M}$ in chromophore units. In addition, Re-P4VPH_n^{n+} polymer films were prepared in the presence of HClO_4 acid concentrations so that $[\text{HClO}_4]/[\text{py}] = 1.5$ at both Re-P4VP concentrations. In all TEM images, a polymer matrix film is observed, which is always at the rear, consisting of a disordered perforated bilayer [41] encompassing the pores of the supporting grid. Fig. 3 shows TEM images of Re-P4VP polymer films prepared with $[\text{Re chromophore}] = 2 \times 10^{-5} \text{ M}$. Isolated and scattered

nanodomains of shapes that, in conjunction with AFM observations, must have near spherical symmetry. Shapes with about 200 nm diameters were observed dispersed in the polymer matrix film. In addition, nanodomains consisting of fibers at a micrometer scale were observed. Fig. 4 shows TEM images for Re-P4VPH_nⁿ⁺ polymer films ([HClO₄]/[py] = 1.5) prepared with [Re

Fig. 3: TEM images of Re-P4VP polymer films prepared with $\text{Re(I)} = 2 \times 10^{-5} \text{ M}$. Top left panel shows the TEM image of the bare carbon-coated 300-mesh copper grid without Re-P4VP polymer film.

Fig. 4: TEM images for Re-P4VPH_nⁿ⁺ polymer films ([HClO₄]/[P4VP] = 1.5) prepared with [Re chromophore] = $2 \times 10^{-5} \text{ M}$.

chromophore] = 2×10^{-5} M. The top panel shows small nearly spherical objects, whose dimensions are below 10 nm in diameter, representing objects at polymer scales [20]. The middle panel shows large compound vesicles. Besides, at a micrometer scale, the fiber-type aggregation

Fig. 5: TEM images for Re-P4VP polymer films prepared with {Re chromophore] = 2×10^{-4} M.

is clearly observed (bottom panel). Fig. 5 shows TEM images for Re-P4VP polymer films prepared with $\text{Re(I)} = 2 \times 10^{-4}$ M. The Re-P4VP polymer aggregate in nearly spherical nanodomains with mainly 25 nm in diameters. Some scattered bigger structures appear, however, with diameters between 50 and 75 nm as well as some large compound nanodomains at the micrometer scales. Fig.6 shows a TEM image for Re-P4VPH_n^{n+} polymer films ($[\text{HClO}_4]/[\text{P4VP}] = 1.5$) where a bicontinuous bilayer [41] is observed. In addition, objects that are nearly spherical with diameters smaller than 10 nm were observed. They appear attached to the bicontinuous bilayer structure.

Fig. 6: TEM image for Re-P4VPH_nⁿ⁺ polymer films ($[\text{HClO}_4]/[\text{py}] = 1.5$) with $[\text{Re chromophore}] = 2 \times 10^{-4} \text{ M}$.

AFM observations. Samples were loaded onto a mica surface and observed under AFM to characterize the morphologies of the aggregates formed by Re-P4VP under different experimental conditions. The dimensions of the oligomers were estimated by measuring their heights with the use of the Nanoscope 7.30 software. Fig. 7 and 8 show AFM images of Re-P4VP and Re-P4VPH_nⁿ⁺. Re-P4VP was characterized by a non-homogeneous distribution of oligomers, Fig. 7. Most of them showed distorted spherical islands with diameters ranging from 100 to 200 nm and 5 nm in height, though some objects with diameters between 300 and 400 nm can be identified in that Fig. 7. In addition, fibers of 10 nm in width, 5 nm in height and lengths between 600 and 1000 nm can be observed. Fig. 8 shows that the Re-P4VPH_nⁿ⁺ polymer is characterized by a different and somewhat more homogeneous distribution of oligomers than ReP4VP. Oligomers in Fig. 8 are mainly spherical in shape. A minor proportion of them have heights around 10 nm, the majority of them showing heights between 30 and 60 nm. Also, some 150 nm height clusters were detected. Also in Fig. 8, pearl necklaces [41] show the connection between the oligomers but neither fibers nor islands are evident in the preparation.

Fig. 8: AFM images for Re-P4VPH_n⁺ polymer films ([HClO₄]/[P4VP] = 1.5) prepared with [Re chromophore] = 2 × 10⁻⁷ M.

Fig. 7: AFM images for Re-P4VP polymer films prepared with [Re chromophore] = 2 × 10⁻⁷ M.

The diverse morphologies of ReP4VP and Re-P4VPH_n⁺ evidenced in these studies have a direct influence over the polymers photophysical properties. They appear as the dependences in acid and polymer concentrations communicated in the following sections.

3. Dependence of the luminescence lifetime on Re-P4VP concentration. A broad unstructured band centered at ~550 nm is observed in the emission spectrum of Re-P4VP when a deaerated solution of the polymer in CH₃CN is irradiated at 350 nm. Luminescence lifetimes determined under various experimental conditions are summarized in Table I, In this work, a complementary study to one in the literature [26], it has been established that the luminescence lifetime is dependent on the polymer concentration. Luminescence lifetimes were calculated from traces

Table I. Lifetimes from time-resolved luminescence and flash photochemical experiments.

[Re-P4VP], M	[HClO ₄]/[P4VP]	τ , ns	Other Conditions
2×10^{-5} to 1×10^{-4} ^a	0	$\tau_{EM,1} = 55.9 \pm 1$ $\tau_{EM,2} = \text{varies from}$ 240 ± 25 to 491 ± 9	EM, ^b $\lambda_{exc} = 350$ nm $\lambda_{ob} = 550$ nm
$> 2 \times 10^{-4}$	0	$\tau_{EM} = 581 \pm 10$	EM, ^b $\lambda_{exc} = 350$ nm $\lambda_{ob} = 550$ nm
4×10^{-5}	0.1 to 1.5	$\tau_{EM} = 450 \pm 10$	EM, ^b $\lambda_{exc} = 350$ nm $\lambda_{ob} = 550$ nm
1.6×10^{-4}	0.1 to 1.5	$\tau_{EM} = 560 \pm 10$	EM, ^b $\lambda_{exc} = 350$ nm $\lambda_{ob} = 550$ nm
1.8×10^{-4} M ^a	0	$\tau_{FP,1} = 104 \pm 25$; $\tau_{FP,2} = 628 \pm 22$	LP, ^b $\lambda_{exc} = 351$ nm, $n_{hv} = 5 \times 10^{-5}$ Einstein L ⁻¹ sec ⁻¹
1.8×10^{-4} M ^a	140	$\tau_{FP,1} = 147 \pm 14$; $\tau_{FP,2} = 819 \pm 62$	LP, $\lambda_{exc} = 351$ nm, $n_{hv} = 5 \times 10^{-5}$ Einstein L ⁻¹ sec ⁻¹
1.8×10^{-4} M ^a	0	$\tau_{FP,1} = 147 \pm 14$; $\tau_{FP,2} = 1340 \pm 230$	LP, $\lambda_{exc} = 351$ nm, $n_{hv} = 1.5 \times 10^{-4}$ Einstein L ⁻¹ sec ⁻¹
1.8×10^{-4} M ^a	140	$\tau_{FP,1} = 169 \pm 8$; $\tau_{FP,2} = 1180 \pm 70$	LP, $\lambda_{exc} = 351$ nm, $n_{hv} = 1.5 \times 10^{-4}$ Einstein L ⁻¹ sec ⁻¹

^abiexponential decay, ^b EM = single photon counting measurements; LP = laser flash photochemical measurements.

obtained with polymer concentrations corresponding to a total chromophore concentration varying from [Re chromophore] = 2×10^{-5} M to 4×10^{-4} M. In the range of [Re chromophore] = 2×10^{-5} M to 1×10^{-4} M, the luminescence traces could only be fitted by a sum of two exponentials.

The dependences of $\tau_{EM,1}$ and $\tau_{EM,2}$ on the Re chromophore concentration between 2×10^{-5} M and 4×10^{-4} M is shown in Fig. 9. The shorter lifetime, $\tau_{EM,1} = 55 \pm 7$ ns, remains essentially constant between 2×10^{-5} M and 1×10^{-4} M while the longer lifetime, $\tau_{EM,2}$, increased monotonically from

240 to 490 ns. When $[\text{Re chromophore}] > 1 \times 10^{-4} \text{ M}$, the luminescence decay was fitted without deviation to a single exponential with a lifetime, $\tau_{\text{EM}} = 581 \pm 10 \text{ ns}$ which is independent of polymer concentration in the concentration range $1 \times 10^{-4} \text{ M} < [\text{Re chromophore}] < 8 \times 10^{-4} \text{ M}$.

4. Effect of the pyridine pendants protonation on the Re-P4VP luminescence

The degree of polymer protonation at different $[\text{HClO}_4]/[\text{P4VP}]$ ratios was followed also by spectrofluorometric techniques. In the steady-state experiments, the total chromophore concentration, $[\text{Re chromophore}] = 2 \times 10^{-5} \text{ M}$, was kept constant and the deaerated solutions were irradiated at 350 nm. A large increase in the luminescence of Re-P4VP was observed when Re-free pyridines in Re-P4VP were protonated with HClO_4 , Fig. 10. The inset to Fig.10 shows that the protonation of the Re-free pyridines in Re-P4VP causes more than an 8-fold increase in the total luminescence. Neither changes on the band shape nor a band shift accompanied the increase in the luminescence quantum yield.

Fig.9: Dependence of the luminescence lifetimes, $\tau_{\text{EM},1}$ and $\tau_{\text{EM},2}$ on the concentration of Re-P4VP.

Fig.10: Luminescence spectra of the Re-P4VP at different $[\text{HClO}_4]/[\text{P4VP}]$ ratio. Inset shows the relative increase in the luminescence quantum yield as a function of $[\text{HClO}_4]/[\text{P4VP}]$ ratio. $[\text{HClO}_4]/[\text{P4VP}] = 0; 0.01; 0.02; 0.03; 0.04; 0.05; 0.075; 0.10; 0.125; 0.15; 0.20; 0.25; 0.50; 0.75; 1.00$.

The effect of pyridine protonation on the Re-P4VP luminescence lifetime was studied at two Re-P4VP concentrations, i.e. [Re chromophore] = 4.0×10^{-5} and 1.6×10^{-4} M, with [HClO₄]/[py] ratios varying from 0.1 to 1.5. It has been shown in the morphological observations that these Re-P4VP concentrations are those where the decay of the luminescence respectively exhibits biexponential and monoexponential kinetics. In solutions where [Re-P4VP] = 4×10^{-5} M, the kinetics of the luminescence decay changes from a biexponential regime (when no acid is present) to a monoexponential law over the whole [HClO₄]/[P4VP] range. A lifetime, $\tau_{EM} = 450 \pm 10$ ns, was calculated for the monoexponential decay of the luminescence. When the total concentration of pendants is 1.6×10^{-4} M, a longer lifetime, $\tau_{EM} = 560 \pm 10$ ns, was obtained for the monoexponential decay of the luminescence over the whole range of [HClO₄]/[P4VP] values. The time-resolved absorption spectroscopy technique was used for the elucidation of other photophysical effects caused by the Re-P4VP concentration and protonation of the ground and excited states.

5. Change of the ³MLCT excited state properties by the protonation of Re-P4VP.

Solutions of Re-P4VP in deaerated CH₃CN were flash irradiated at 351 nm. The transient absorption spectrum, recorded ~20 ns after the irradiation, has spectral features attributed to the ³MLCT excited state of the pendent $[\text{Re}(\text{CO})_3(\text{phen})]^+$. Oscillographic traces were recorded at a given wavelength λ_{ob} , within a 300 -700 nm wavelength span. They were fitted to a biexponential function, $A_1 \exp(-t/\tau_{FP,1}) + A_2 \exp(-t/\tau_{FP,2})$, with $\tau_{FP,1}$ and $\tau_{FP,2}$ being about 10^{-7} and 10^{-6} s, respectively. Lifetimes calculated for the absorbance decay are summarized in Table 1. Moreover 351 nm laser flash irradiations of Re-P4VP and Re-P4VPH_nⁿ⁺ were carried out using two different laser powers. Both laser powers produced nearly identical transient absorption spectra respectively assigned to the ³MLCT excited states of Re-P4VP and Re-P4VPH_nⁿ⁺. No significant differences were observed between the excited state spectra, $\lambda_{max} \approx 460$ nm and $\lambda_{max} \approx 700$ -750 nm, generated when different number of photons, i.e. laser powers $n_{hv} = 5 \times 10^{-5}$ Einstein L⁻¹ flash⁻¹ and $n_{hv} = 1.5 \times 10^{-4}$ Einstein L⁻¹ flash⁻¹, were absorbed by Re-P4VP or Re-P4VPH_nⁿ⁺ Fig.11a, 12a, and a chromophore concentration [Re chromophore] = 1.8×10^{-4} M. In these experimental conditions the ratio between the number of incident photons to the number of Re(I) chromophores is $n_{hv}/[\text{Re chromophore}] = 0.083$ and 0.83. The maximum absorbance change, ΔA_{max} , was about 10% smaller in the photolysis of Re-P4VPH_nⁿ⁺ than in the Re-P4VP

experiments when irradiated with a laser power $n_{\text{hv}} = 1.5 \times 10^{-4}$ Einstein $\text{L}^{-1} \text{flash}^{-1}$. This disparity on ΔA_{max} was not observed however when Re-P4VP and Re-P4VPH_nⁿ⁺ were irradiated with the lower laser power $n_{\text{hv}} = 5 \times 10^{-5}$ Einstein $\text{L}^{-1} \text{flash}^{-1}$. Oscillographic traces showing the decay of the transient absorbance, ΔA , were collected at different wavelengths between 750 and 350 nm. Transient decay lifetimes, $\tau_{\text{FP}, 1}$ and $\tau_{\text{FP}, 2}$, were calculated for Re-P4VP and Re-P4VPH_nⁿ⁺

Fig. 11: (a) Spectral changes in the 351 nm laser flash irradiations ($n_{\text{hv}} = 5 \times 10^{-5}$ Einstein $\text{L}^{-1} \text{flash}^{-1}$, [Re chromophore] = 1.8×10^{-4} M) of Re-P4VP and Re-P4VPH_nⁿ⁺ ([HClO₄] = 0.05 M) in CH₃CN. The spectrum of the MLCT excited state was recorded at the time corresponding to the maximum absorbance change from the laser trigger. (b) Oscillographic traces recorded at $\lambda_{\text{ob}} = 465$ nm showing the decay of MLCT excited states of Re-P4VP and Re-P4VPH_nⁿ⁺ polymers.

Fig.12: (a) Spectral changes in the 351 nm laser flash irradiations ($n_{\text{hv}} = 1.5 \times 10^{-4}$ Einstein $\text{L}^{-1} \text{flash}^{-1}$, [Re chromophore] = 1.8×10^{-4} M) of Re-P4VP and Re-P4VPH_nⁿ⁺ ([HClO₄] = 0.05 M) in CH₃CN. The spectrum of the MLCT excited state was recorded at the time corresponding to the maximum absorbance change from the laser trigger. (b) Oscillographic traces recorded at $\lambda_{\text{ob}} = 465$ nm showing the decay of MLCT excited states of Re-P4VP and Re-P4VPH_nⁿ⁺ polymers.

polymers, Table 1. The lifetimes calculated from the traces obtained with a laser power $n_{\text{hv}} = 5 \times 10^{-5}$ Einstein $\text{L}^{-1} \text{ flash}^{-1}$ were $\tau_{\text{FP}, 1} = 104 \pm 23$ ns and $\tau_{\text{FP}, 2} = 628 \pm 22$ ns for Re-P4VP and $\tau_{\text{FP}, 1} = 147 \pm 35$ ns and $\tau_{\text{FP}, 2} = 819 \pm 61$ ns for Re-P4VPH_nⁿ⁺. The decay lifetimes, $\tau_{\text{FP}, 1} = 147 \pm 14$ ns and $\tau_{\text{FP}, 2} = 1340 \pm 230$ ns for Re-P4VP and $\tau_{\text{FP}, 1} = 169 \pm 8$ ns and $\tau_{\text{FP}, 2} = 1180 \pm 70$ ns for Re-P4VPH_nⁿ⁺, were calculated for the irradiations made with the laser power, $n_{\text{hv}} = 1.5 \times 10^{-4}$ Einstein $\text{L}^{-1} \text{ flash}^{-1}$. It can be seen that significantly longer decay lifetimes are obtained for the photolysis with the laser power, $n_{\text{hv}} = 1.5 \times 10^{-4}$ Einstein $\text{L}^{-1} \text{ flash}^{-1}$, than with the laser power $n_{\text{hv}} = 5 \times 10^{-5}$ Einstein $\text{L}^{-1} \text{ flash}^{-1}$. Protonation of Re-P4VP also lengthened the lifetimes of the absorbance decay as seen for the luminescence lifetimes, Table 1. Furthermore, the transient spectra generated when Re-P4VP or Re-P4VPH_nⁿ⁺ were flash irradiated under the experimental conditions indicated above decayed leaving no evidence of any product formation.

Discussion

The results have shown that the photophysical and photochemical properties of the Re-P4VP are intrinsically associated with the medium-imposed polymer's morphologies. To understand the complexities of the medium-imposed polymer's morphologies, it is useful to compare the morphology of Re-P4VP with that of closely related Re- containing polystyrene-block-poly(acrylic acid) (PS-b-PAA).

6. Comparison of the morphologies of Re-containing polymers. The self-assembly of amphiphilic block copolymers in selective solvents usually tend to form spherical aggregates that consist of a core and a corona shell. The insoluble blocks constitute the core while the corona contains the soluble blocks swollen by the solvent. In highly asymmetric polystyrene-block-poly(acrylic acid) (PS-b-PAA), the addition of electrolytes like CaCl_2 , NaCl or HCl changed the morphologies of those spherical aggregates to rod like, univesicular or lamellar aggregates and sometimes to large compound vesicles [42]. It was suggested that those morphological changes are probably induced by a decrease in the steric and electrostatic repulsion among the hydrophilic segments due to the protonation or ion binding to PAA, or bridging [42]. In polymers consisting of polystyrene-block-poly-(4-vinylpyridine) (PS-b-P4VP) functionalized with pendants $-\text{Re}(\text{CO})_3(\text{bpy})^+$ groups, the Re(I) complexes could induce the self-assembly of the copolymers into nanometer size aggregates with different shapes and dimensions. Those polymer aggregates were prepared by using a common good solvent for both blocks to dissolve

the copolymer. Then a poor solvent for one of the blocks was added. The shapes of the aggregates depended on the chemical nature of the copolymers and the solvent used. In the copolymers, one of the blocks expands while the other condenses due to their difference in solubility in the common solvent. The aggregation driving force being related to the repulsive interactions between one of the blocks and the solvent. Spherical, disk-like and rod-like structures were observed, where the P4VP block constituted the outer shell of the particles [24]. It is noteworthy that the dimensions of these nano sized aggregates are much larger than the full stretch length of the polymers. Therefore, those aggregates are likely to contain more than one layer of polymers. Those PS-b-P4VP-Re(CO)₃(bpy)⁺ polymers, are not pure diblock copolymers due to the fact that Re(I) complexes are distributed randomly within the P4VP block [24]. The morphological properties of several inorganic polymers containing around 200 pendant – [Re(CO)₃L]⁺ chromophores (L= 1,10 phenanthroline, 2,2' bipyridine, 3,4,7,8-tetramethyl-1,10 phenanthroline and 5-nitro-1,10 phenanthroline) attached to the P4VP backbone have been previously studied by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) techniques [18, 20, 22]. Those studies revealed in all cases that at the polymer concentration used, i.e. [Re chromophore] ~ 2x10⁻⁴ M, the Re(I) polymers are aggregated in CH₃CN solutions forming nearly spherical clusters whose dimensions vary from 100 to 400 nm in diameter. Coordination of Cu(II) species to the Re (I) polymers causes a decrease in the aggregates radii and a distortion from the spherical shape [20]. In fact, polymers derived from P4VP functionalized with –[Re(CO)₃L]⁺ pendants behave morphologically in a similar way to amphiphilic block copolymers. For instance, in acetonitrile solutions, P4VP grafted with [Re(CO)₃L]⁺, where L= 3,4,7,8-tetramethyl-1,10 phenanthroline and/or 5-nitro-1,10 phenanthroline, aggregate to form spherical nanodomains whose dimensions are between 80 and 160 nm. However, these same polymers form non homogeneous large compound vesicles in dichloromethane [18].

The TEM studies on Re-P4VP were carried out using films prepared from CH₃CN solutions of [Re chromophore] = 2 x 10⁻⁵ M and 2 x 10⁻⁴ M, which for the sake of simplicity will be named hereafter as TEM-1 and TEM-2 studies, respectively. The effect on polymer concentration on the morphological properties of the polymer was evidenced by those experiments: while at dilute polymer concentrations TEM-1 experiments show mainly the formation of a disordered perforated bilayer with some scattered spherical nanodomains of about 200 nm in diameter as

well as fiber structures, TEM-2 experiments showed clearly that Re-P4VP polymer aggregate in a huge collection of nearly spherical nanodomains whose dimensions are mainly 25 nm in diameter. Besides, the protonation of Re-P4VP polymers altered profoundly their aggregation pattern. From an even distribution of spherical objects mainly of 25 nm in diameter for the bare Re-P4VP polymers the morphology shifts to a bicontinuous bilayer with attached objects at polymer scales after protonation of Re-P4VP.

Due to an experimental requirement of the technique, the concentration of the polymer used for AFM studies was [Re chromophore] $\sim 2 \times 10^{-7}$ M. Therefore, AFM studies reflect the morphology of polymer aggregates in a much more diluted (1000-fold) regime than TEM and DLS studies. The morphological patterns of AFM studies are similar to those of TEM-1 studies and differ substantially from those of TEM-2 ones. In AFM studies, in addition to the 100-400 nm clusters, also long (~ 600 -1000 nm) and thin (10 nm width) fibers are observed. AFM images from Re-P4VPH_nⁿ⁺ show that: (i) the shapes of the distorted spherical aggregates is smaller than in the Re-P4VP, (ii) no fibers are observed and (iii) almost pearl necklaces appear instead of the isles observed in the Re-P4VP. Moreover, as noted before, absorption changes in Fig. 1 at [HClO₄]/[P4VP] ratios higher than 0.15 reflect nano-aggregation changes induced by polymer protonation as well as absorbance changes due to the protonation of the Re-free pyridines of Re-P4VP. In this regard, absorption changes in Fig. 1 as well as the differences encountered in the morphological properties of Re-P4VP and Re-P4VPH_nⁿ⁺ may be reflecting inter or intra-molecular interactions that may occur such as cross-linking via H-bonded interactions, i.e. py-H-py, thus linking different pyridines of the same polymer and/or crosslinking different polymers. Therefore, from TEM and AFM studies it can be concluded that the morphology of the Re-P4VP polymer at low concentrations ([Re chromophore] between 2×10^{-7} and 2×10^{-5} M) can be described by the coexistence of small objects at polymer scales (diameters below 10 nm) with larger nano aggregates (diameters between 200 and 1000 nm) as well as long fibers at the micrometer scales in a not homogeneous distribution of aggregates sizes. When the concentration of the polymer is higher ([Re chromophore] = 2×10^{-4} M) TEM experiments show that the morphology of the Re-P4VP polymer is characterized by nearly spherical nanodomains exhibiting a homogeneous distribution centered at about 25 nm in diameter. After protonation of the Re-P4VP polymers, their morphology is strongly affected: at low concentration of the Re-P4VP polymers, small objects at polymer scales are clearly observed and the fiber-structure is

more evident than in TEM-1 experiments. At higher concentration of the Re-P4VP polymers, the morphology of the polymers shifts after protonation from a homogeneous distribution of spherical nanodomains (TEM-2 experiments) to a bicontinuous bilayer with attached small objects at polymer scales sizes.

7. Morphological effects on the Re-P4VP luminescence. The dependence of $\tau_{EM, 2}$ on polymer concentration, Fig. 9, is another manifestation of the different environments where the luminescent $^3\text{MLCT}$ excited state is formed. Accordingly the luminescence decay of Re-P4VP is bi-exponential at $[\text{Re chromophore}] < 1 \times 10^{-4} \text{M}$ but becomes mono-exponential when $[\text{Re chromophore}] > 1 \times 10^{-4} \text{M}$. Observations made via TEM and AFM show that these environments are the result of a concentration dependent morphology. The photophysical observations are interpreted therefore in terms of medium-destabilized charge-transfer excited states, labeled $^3\text{MLCT}_{\text{md}}$, present in some chromophores within a strand of polymer. $^3\text{MLCT}_{\text{md}}$ excited states may decay to the ground state or they can transfer their excess electronic energy to other chromophores producing medium-stabilized charge-transfer excited states, $^3\text{MLCT}_{\text{ms}}$. The multiple types of aggregates seen by TEM and AFM in diluted solutions of Re-P4VP are consistent with the coexistence of $^3\text{MLCT}_{\text{md}}$ and $^3\text{MLCT}_{\text{ms}}$ excited states. By contrast, at higher polymer concentrations, e.g. $[\text{Re chromophore}] = 2 \times 10^{-4} \text{M}$, inspection of the samples using TEM reveals the presence of nearly spherical aggregates with $\sim 25 \text{ nm}$ diameters. Therefore, some critical mass of polymer between $[\text{Re chromophore}] < 1 \times 10^{-4} \text{M}$ and $[\text{Re chromophore}] = 2 \times 10^{-4} \text{M}$ must provide enough material to form the spherical aggregates. Based on the change in the mechanism of the luminescence decay accompanying the formation of spherical aggregates, it can be concluded that the distribution of oligomers when $[\text{Re chromophore}] = 2 \times 10^{-4} \text{M}$ is more homogeneous than when $[\text{Re chromophore}] = 2 \times 10^{-5} \text{M}$. Accordingly, the regime change from a bi-exponential decay to a mono-exponential decay of the luminescence is tuned by the concentration-dependent morphology of the Re-P4VP.

The protonation of the Re(I) polymer induces an 8-fold increase in the luminescence quantum yield and a significant increase in $\tau_{EM, 2}$ from 300 ns to 450 ns for $[\text{Re chromophore}] = 4 \times 10^{-5} \text{M}$. Moreover, nearly identical luminescence lifetimes were obtained for the mostly protonated Re(I) polymer and the Re-P4VP in the absence of HClO_4 acid with solutions having in both cases $[\text{Re chromophore}] = 1.6 \times 10^{-4} \text{M}$. These facts suggest that the increase in the luminescence quantum yield and the lengthening are the result of morphological changes caused

Scheme II

by the Re-P4VP protonation in diluted solutions. To some extent the morphologies of Re-P4VP in concentrated solutions and in diluted acid solutions must be alike or that although being different they exert similar perturbations on the photophysics of the chromophores. More information on the photophysical and photochemical processes of Re-P4VP were assessed using the flash photolysis technique.

8. Polymer effect on the ³MLCT decay regime. The main difference between the photophysical properties of single molecules like fac-XRe(CO)₃L and those of the Re(I) pendants in scheme 1 is that ³MLCT-³MLCT annihilation reactions, eq. 1-2, are bimolecular diffusion controlled reactions for fac-XRe(CO)₃L complexes while inside a polymer strand they occur between close neighbor chromophores as represented in scheme II.

The main cause of these differences is the photogeneration of MLCT excited states in close proximity when $-\text{[Re(CO)}_3\text{L)]}^+$ chromophores are bound to P4VP. Thus, using high power lasers

(20-30 mJ/pulse) as excitation sources usually favor the annihilation and/or the photolysis of MLCT excited states in close proximity [21, 26]. A manifestation of this is that the luminescence decays are bi-exponential in this regime. Reducing the laser power to lower levels (~ 5 mJ/pulse), thus generating much lower amounts of MLCT excited states in close vicinity, restores the luminescence decays to a mono-exponential function [21]. Also, the shift from a mono-exponential to a bi-exponential regime has been tuned by varying solvent polarity and temperature, inducing by that way conformational changes which ultimately affected the photophysical properties [21]. Ground state depletion is also important in flash photolysis experiments with laser powers of $n_{\text{hv}} = 1.5 \times 10^{-4}$ Einstein L⁻¹ flash⁻¹. In each case, however, the transient decay could only be fitted with a sum of two exponential functions. This experimental observation implies the coexistence of $^3\text{MLCT}_{\text{md}}$ and $^3\text{MLCT}_{\text{ms}}$ excited states, where $^3\text{MLCT}_{\text{md}}$ could stand, for instance, for several $^3\text{MLCT}$ in close vicinity to participate in annihilation reactions of eq. 1-2 inside a polymer strand, scheme 2. Since aggregation of polymer strands also contributes to crowd excited chromophores in reduced spaces, it is a phenomenon which affects the overall photophysical properties of the polymers. The augment of the decay lifetimes after polymer protonation is a manifestation of the tuning of the photophysical properties by the variations in the state of the polymer strands nano-aggregation.

Striking differences can be seen between the luminescence and absorbance decay kinetics. While the luminescence decay exhibits mono and biexponential kinetics depending on the Re-P4VP and acid concentrations, the regime of the transient spectrum decay is always biexponential, Table I. Moreover, the longest lifetime of the absorbance decay, $\tau_{\text{FP}, 2}$, is much longer than the longest lifetime of the luminescence decay, $\tau_{\text{EM}, 1}$ or $\tau_{\text{EM}, 2}$. Therefore the second component of the transient spectrum decay with a lifetime $\tau_{\text{FP}, 2}$ cannot be attributed to the decay of a luminescent excited state. Possible processes associated with the slow spectral change, i.e., with $\tau_{\text{FP}, 2}$, are reorganizations of the $-\text{[Re(CO)}_3\text{(phen)]}^+$ pendants' environment after the relaxation of the $^3\text{MLCT}$ excited state. Recovery of the pendants' original environment will return the spectra of the Re-P4VP and Re-P4VPH_n^{n+} to the condition they had before the flash irradiation.

Conclusions

TEM and AFM studies on Re-P4VP and Re-P4VPH_n^{n+} polymers have shown that (i) the morphology of Re-P4VP polymers is concentration dependent and (ii) protonation of Re-P4VP

polymers alters strongly their morphology. At low concentration of the Re-P4VP polymers their morphology is characterized by a not homogeneous distribution of spherical nano aggregates in coexistence with fibers at micrometer size scales. At high concentration of the Re-P4VP polymers, their morphology is characterized by a homogeneous distribution of spherical nanoaggregates with diameters around 25 nm. Protonation of diluted solutions of Re-P4VP polymers decrease the sizes of the nano aggregates and small objects at polymer size scales are clearly observed in TEM images. However, protonation of concentrated solutions of Re-P4VP polymers shifted their morphology to a bicontinuous bilayer. Those morphological changes, have direct impact on the photophysical properties of the Re-P4VP polymers and are responsible of (i) the enhancement of the luminescence lifetime upon increasing polymer concentration and (ii) the nearly 8-fold increase of the luminescence quantum yield after protonation of the Re(I) polymer.

Acknowledgments

This work was supported in part by ANPCyT (PICT 1435), CONICET (PIP 0389), and Universidad Nacional de La Plata (UNLP X533 and X611) of Argentina. A.S.M thanks CONICET for a research scholarship. G.T.R. F.G.E and E.W. are Research Members of CONICET (Argentina). Part of this work was also carried out in the Notre Dame Radiation Laboratory (NDRL). The NDRL is supported by the Division of Chemical Sciences, Geosciences and Biosciences, Basic Energy Sciences, Office of Science, United States Department of Energy through grant number DE-FC02-04ER15533. This is contribution number NDRL 5084.

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