Absorption and luminescence as a function of pH for carboxylic acid-functionalized Re(I) tricarbonyls

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Abstract

Six new ester- and carboxylic acid-derivatives of the fac-Re(I)(CO)$_3$(2,2′-bipyridine)Cl and [fac-Re(I)(CO)$_3$(2,2′-bipyridine)(pyridine)]CF$_3$SO$_3$ type have been prepared, in which the functions reside on the bipy or py fragments, in their 5- and 3-positions, respectively: the compounds are Re(I)(CO)$_3$(bipyCOOCH$_3$)Cl (**2**), Re(I)(CO)$_3$(bipyCOOH)Cl (**3**), [Re(I)(CO)$_3$-(bipyCOOH)(pyCOOCH$_3$)]CF$_3$SO$_3$ (**4**), [Re(I)(CO)$_3$(bipyCOOCH$_3$)(pyCOOH)]CF$_3$SO$_3$ (**5**), [Re(I)(CO)$_3$(bipyCOOCH$_3$)-(pyCOOCH$_3$)]CF$_3$SO$_3$ (**6**) and [Re(I)(CO)$_3$(bipyCOOH)(pyCOOH)]CF$_3$SO$_3$ (**7**). These Re(I) complexes are air- and moisture-stable, and it has been possible to study their properties in aqueous solution (water–dioxane 1:4), as a function of pH. The pK_as of the carboxylic acid(s)-containing species have been determined by means of potentiometric titration experiments and the absorbing and emitting properties of the six complexes related to the deprotonation processes. In particular, it has been possible to ascertain that the MLCT band of the rhenium chromophore is related, as expected, to an electron transfer process taking place always towards the bipy fragments, even in the py containing species **4**–**7**, independently on the substituent (ester, carboxylic acid or carboxilate) residing on it. Interestingly, the sharp and intense luminescence versus pH variation found for **3** makes it a suitable candidate for a luminescence-based pH sensor. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

The availability of Re(CO)$_5$Cl as a stable, straightforwardly functionalizable starting product [1] for Re(I) chemistry has led, especially during the last 10 years, to a noteworthy number of papers based on the [fac-Re(I)(CO)$_3$(L–L)L′]$^+$ core, for which an easy, well defined two step synthetic procedure has been established: the reaction of Re(CO)$_5$Cl with a variety of bidentate ligands (L–L), containing sp^2 nitrogen donors belonging to an extended π-system (e.g. L–L = bipyridine or phenantroline), leads to the fac-Re(I)(CO)$_3$(L–L)Cl species [2], which are air-stable, moisture-stable and kinetically inert, this latter feature
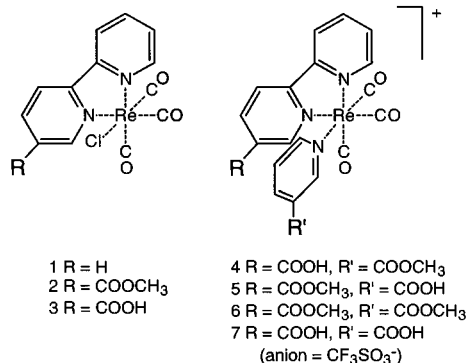
being typical of the low spin Re(I) d^6 cation; Cl$^-$ can then be removed in a second, separate step (reflux with Ag$^+$ salts) and substituted with L′, a monodentate ligand usually featuring an sp^2 nitrogen atom as donor, which belongs to a π-delocalized system (e.g. L′ = pyridine) [3]. What is obtained is [fac-Re(I)(CO)$_3$(L–L)L′]$^+$, which also is air- and moisture-stable and kinetically inert. It is of great interest, the fact that both the L–L and the L′ ligand can bear any desired substituent, this making [fac-Re(I)(CO)$_3$(L–L)L′]$^+$ available for more chemistry at its periphery. Moreover, both the fac-Re(I)(CO)$_3$(L–L)Cl and the [fac-Re(I)(CO)$_3$(L–L)L′]$^+$ species display respectively moderate and strong emitting properties [2–4], whose nature has been studied in detail during the last two decades. Due to the sum of these features, a variety of molecular or supramolecular systems was described, with particular emphasis on omo- and etero- bi- or polinuclear compounds, which have been employed, inter alia, in intramolecular elec-

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tron transfer studies [5], as sensors for metal cations [6], and in the photocatalytic reduction of CO_2 [7].

1 R = H
2 R = COOCH$_3$
3 R = COOH

4 R = COOH, R' = COOCH$_3$
5 R = COOCH$_3$, R' = COOH
6 R = COOCH$_3$, R' = COOCH$_3$
7 R = COOH, R' = COOH
(anion = CF$_3$SO$_3^-$)

Interestingly, most of the reported works on *fac*-Re^I(CO)$_3$(L–L)Cl and the [*fac*-Re^I(CO)$_3$(L–L)L']$^+$ species deal with solution chemistry which excludes water as solvent, thus preventing the possibility of studying the properties of the systems as a function of pH, a fundamental and easy tunable parameter. In this work, we present a series of new compounds of the [*fac*-Re^I(CO)$_3$(L–L)L']$^+$ type, in which L–L is a 2,2'-bipyridine and L' a pyridine (or the starting Cl$^-$ anion), which bear substituents of the –COOH or –COOCH$_3$ type (compounds 2–7). These rhenium(I) complexes are soluble and stable in aqueous solution and this allowed us to study their properties as a function of pH. In particular, the pK_a values of the carboxylic acid-functionalized derivatives were determined by means of potentiometric titrations. The luminescence of systems 3, 4, 5, 7 was examined as a function of pH, both in the absence and in the presence of metal cations, and compared with that of the pertinent, pH-independent species 1, 2, 6, and the observed variations were put in relation with the disclosed equilibria.

2. Experimental

2.1. Syntheses

2,2'-Bipyridine-5-carboxylic acid [8], 2,2'-bipyridine-5-carboxylic acid methyl ester [9] and compound 1 [4d] were prepared according to literature methods. All the other reagents were purchased from Aldrich and used without further purification.

[Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid methyl ester)Cl] (2). Re(CO)$_5$Cl (0.1 g, 0.28 mmol) was dissolved in 30 cm^3 methanol, under a nitrogen atmosphere. 2,2'-bipyridine-carboxylic acid methyl ester (0.060 g, 0.28 mmol) was then added as a solid, and the obtained colorless solution heated at reflux for 2 h, under a nitrogen atmosphere, after which time the solution became deep yellow. The volume of the solution was reduced to 15 cm^3 on a rotary evaporator and,

after cooling at room temperature, 2 precipitated as a pure, yellow solid. Yield: 82% Anal. Found: C, 34.69; H, 1.90; N, 5.37%. Anal. Calc. for C$_{15}$H$_{10}$ClN$_2$O$_5$Re, C, 34.66; H, 1.92; N, 5.39%. NMR (CD$_3$CN): δ 9.10 (s, 1H), 8.93 (d, 1 H), 8.55 (d, 1H), 8.4 (m, 2H), 8.10 (t, 1H), 7.58 (t, 1H): hydrogens of the bipy ring; δ 3.97 (s, 3H, COOCH_3).

[Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid)Cl] (3), was prepared according to an analogous procedure. Yield 90%. Anal. Found: C, 33.20; H, 1.60; N, 5.51%. Anal. Calc. for C$_{14}$H$_8$ClN$_2$O$_5$Re, C, 33.24; H, 1.58; 5.53%. NMR (CD$_3$CN): δ 9.52 (s, 1H), 9.12 (d, 1H), 8.7 (m, 3H), 8.32 (t, 1H), 7.79 (t, 1H), hydrogens of the bipy ring.

[Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid) (pyridine-3-carboxylic acid methyl ester)]CF$_3$SO$_3$ (4) was prepared by dissolving compound 3 (0.122 g, 0.24 mmol) in 40 cm^3 methanol and treated with 0.067 g (0.26 mmol) AgCF$_3$SO$_3$. The solution was kept at reflux temperature for 24 h, under a nitrogen atmosphere and in the dark, then filtered over a bed of dry celite, under a nitrogen flux. The obtained clear solution was then treated with 0.26 g (1.89 mmol) of pyridine-3-carboxylic acid methyl ester and heated at the reflux temperature for further 24 h. The solvent was then removed on a rotary evaporator and the obtained semisolid thoroughly washed with diethyl ether (5 × 10 cm^3), in order to remove the excess of pyridine ester. A bright yellow powder was obtained as the final product, which was pure according to elemental analysis, mass and NMR spectroscopy. Yield 45%. Anal. Found: C, 34.96; H, 1.99; N 5.58%. Anal. Calc. for C$_{22}$H$_{15}$F$_3$N$_3$O$_{10}$SRe, C, 34.93; H, 1.98; N, 5.55%. NMR (CD$_3$OD): δ 9.78 (s, 1H), 9.41 (d, 1H), 9.11 (s, 1H), 8.8–8.3 (m, 5H), 7.98 (t, 1H), 7.75 (t, 1H), 7.54 (t, 1H), hydrogens of the bipy and py rings; 4.02 (s, 3H, COOCH_3). Mass (ESI): 608 ([Re(CO)$_3$(bipyCOOH)(pyCOOCH$_3$)]$^+$).

[Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid methyl ester)(pyridine-3-carboxylic acid)]CF$_3$SO$_3$ (5), [Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid methyl ester)(pyridine-3-carboxylic acid methyl ester)]CF$_3$SO$_3$ (6) and [Re^I(CO)$_3$(2,2'-bipyridine-5-carboxylic acid)(pyridine-3-carboxylic acid)]CF$_3$SO$_3$ (7) were prepared with similar procedures starting from the appropriate parent compound (2 or 3).

5: yield 34%, Anal. Found: C, 34.90; H, 1.97; N, 5.57%. Anal. Calc. for C$_{22}$H$_{15}$F$_3$N$_3$O$_{10}$SRe, C, 34.93; H, 1.98; N, 5.55%. NMR (CD$_3$OD): δ 9.57 (s, 1H), 9.28 (d, 1H), 9.12 (s, 1H), 8.7 (d, 1H) 8.5 (m, 4H), 8.24 (t, 1H), 7.65 (t, 1H), 7.4 (t, 1H), hydrogens of the bipy and py rings; 4.02 (s, 3H, COOCH_3). Mass (ESI): 608 ([Re(CO)$_3$(bipyCOOCH$_3$)(pyCOOH)]$^+$).

6: yield 47%. Anal. Found: C, 35.88; H, 2.22; N, 5.43%. Anal. Calc. for C$_{23}$H$_{17}$F$_3$N$_3$O$_{10}$SRe, C, 35.85; H, 2.21; N, 5.45%. NMR (CD$_3$OD) δ 9.60 (s, 1H), 9.2 (m, 2H), 8.81 (d, 1H) 8.3–8.5 (m, 5H), 7.71 (t, 1H), 7.3 (t,

1H) hydrogens of the bipy and py rings; 4.06 + 3.95 (s + s, 3H + 3H, COOCH_3 on the bipy and py rings). Mass (ESI): 622 ([Re(CO)$_3$(bipyCOOCH$_3$)(pyCOO-CH$_3$]$^+$).

7: yield 39%. Anal. Found: C, 34.01; H, 1.76; N, 5.64%. Anal. Calc. for $C_{21}H_{13}F_3N_3O_{10}SRe$, C, 33.97; H, 1.75; N, 5.66%. NMR (CD$_3$OD): δ 9.52 (s, 1H), 9.31 (d, 1H), 9.04 (s, 1H), 8.81 (d, 1H) 8.6–8.2 (m, 5H), 7.65 (t, 1H), 7.23 (t, 1H) hydrogens of the bipy and py rings. Mass (ESI): 594 ([Re(CO)$_3$(bipyCOOH)(pyCOOH)]$^+$).

2.2. Physical and spectroscopic measurements

NMR spectra were recorded on a Bruker AMX 400 instrument. Mass spectra (ESI) were obtained on a Finnigan TSQ 700 instrument. UV-vis absorption spectra were taken with a Hewlett-Packard HP8453 diode array spectrophotometer or with a Perkin Elmer λ 16 spectrophotometer. IR spectra were recorded (NaCl cells, Nujol mull) with a Mattson 5000 FT-IR instrument. Uncorrected emission and corrected excitation spectra were obtained with a Perkin Elmer LS 50 spectrofluorimeter.

The excited state lifetimes (uncertainty $\pm$ 5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D$_2$. Luminescence quantum yields (uncertainty $\pm$ 15%) were determined using [Ru(bpy)$_3$]$^{2+}$ in aqueous solution ($\Phi = 0.028$ [10]) as a reference. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects, and phototube sensitivity were performed [11]. Emission spectra at 77 K were obtained using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen.

2.3. Potentiometric titrations

Potentiometric titrations (pK_a determination) were performed in water–dioxane (1:4 v/v) solutions (50 ml, made 0.1 M in sodium perchlorate) containing ligand (10^{-3} to 5×10^{-4} M) and excess standard perchloric acid, by addition of standard aqueous NaOH, under a nitrogen atmosphere, in a cell thermostatted at 25°C. In each titration 60–70 points were recorded. The pH scale was calibrated prior to each experiment by the Gran method [12]. Refinement of the potentiometric data was made using the Hyperquad package [13], which minimizes a least squares function. Fit between calculated and experimental emf data was evaluated through the σ and χ^2 parameters [14], whose values, in each treatment, were found to be 1($\pm$0.3) and < 10%, respectively. The calculated pK_a values, which are reported in the text, bear an uncertainty lower than $\pm$0.03.

2.4. Spectrophotometric titrations

Spectrophotometric titrations (coupled with pH-metric titrations) were performed in water–dioxane solutions, 1:4 v/v, made 0.1 M in sodium perchlorate. 30–50 cm^3 volumes were employed, with samples in the 2.5×10^{-4} to 5×10^{-4} M concentration range. Solutions (in which the pH-reading electrode was immersed; the pH scale was calibrated prior to each experiment by the Gran method [12]) were kept under a nitrogen atmosphere and thermostated at 25°C. After each base addition, 2.5–3.0 cm^3 solution samples were quickly transferred to a quartz cuvette which, after measuring spectrum, were transferred back to the bulk solution. One minute of time was allowed for the bulk solution to re-equilibrate before a further base addition.

2.5. Fluorimetric titrations

Spectrofluorimetric titrations coupled with pH-metric titrations were performed in water–dioxane solutions, 1:4 v/v; 20 cm^3 of 2.0×10^{-4} M solution were freshly prepared each time. After each base addition, 2.5–3.0 cm^3 solution samples were quickly transferred to a quartz cuvette which, after measuring spectrum, were transferred back to the bulk solution, in which the pH-reading electrode was immersed. The pH scale was calibrated prior to each experiment by the Gran method [12].

2.6. Electrochemistry

Electrochemical experiments (DPV, Differential Pulse Voltammetry) were carried out with a P.A.R. 273 potentiostat/galvanostat, under the control of a PC with dedicated software, on 5–10 cm^3 solutions of the examined compound (concentration: $1-2 \times 10^{-3}$ mol l^{-1}) in a 4:1 dioxane–water mixture, made 0.1 mol l^{-1} in [(n-but)$_4$N]ClO$_4$. A platinum microsphere electrode was used as the working electrode, a SSCE as the reference (connected to the electrochemical solution through a jacket filled with 0.1 mol l^{-1} aqueous NaClO$_4$) and a platinum foil as the counter electrode.

3. Results and discussion

3.1. Synthesis

The kinetically inert nature of the Re^I center allows to follow a useful two step synthesis, in which a first generation of compounds is obtained by substitution of two CO ligands with a functionalized bipyridine, and a second generation of compounds becomes available by taking the Cl$^-$ off the Re center and replacing it with a functionalized pyridine. For both the first and the

Table 1
IR data (C–O stretching frequencies) for compounds **1–7**

Compound	IR bands, wavenumber (cm^{-1})			
1	2022	1895	1880	
2	2029	1902, br		1727 [a]
3	2023	1915	1900	1730 [a]
4	2034	1920	1907	1734 [a], 1702 [a]
5	2035	1910, br		1727 [a], 1712 [a]
6	2031	1936, br		1737 [a], 1728 [a]
7	2024	1909	1887	1720 [a], 1704 [a]

[a] Relative to C=O stretching frequencies of –COOH and –COOCH$_3$ groups; br, broad peak; IR spectra, Nujol mull with NaCl cells.

second step, the chosen functions were –COOH and –COOCH$_3$. This led to a group of 2 and 4 new compounds in which the species containing only the ester group were prepared for comparative purposes, the ester function being supposed to display similar effects on the bipy or py fragments than the carboxylic acid group but also to display no sensitivity towards pH.

The choice of the position on which 2,2′-bipyridine and pyridine bear their substituents (5- and 3-, respectively) comes from a series of considerations: positions 6- and 3- for 2,2′-bipyridine were not taken into consideration due to steric hindrance problems, in the light of further, external coordination of the –COO$^-$ group [15]. The 5-position has been preferred to 4- thanks to the easier synthetic availability of the ester and carboxylic acid derivatives. As regards the pyridine ligand, position 2- has been not taken into consideration again for steric hindrance problems. Pyridines substituted in position 4- were not employed (even if commercially available) due to separation problems in the synthetic procedure, connected with the use of an excess of the pyridine acid or ester and to the different solubility

properties between 3- and 4- derivatives (see Section 2.1).

3.2. Spectroscopic properties

IR stretching frequencies for C≡O and C=O groups are reported in Table 1. All the spectra are well settled in what literature reports for fac-Re^I(CO)$_3$(L–L)Cl and [fac-Re^I(CO)$_3$(L–L)L′]$^+$ compounds [16]: a sharp band is always observed between 2022 and 2035 cm^{-1} (ν_{sym}(CO)) while the two expected remaining bands between 1880 and 1936 cm^{-1} overlap in almost all cases (except **1** and **3**) to give a single, broad band, in which sometimes the two components are sufficiently separated to observe a shoulder.

On passing from Cl$^-$- to py-substituted species, an increment of the stretching frequencies is observed, which gives account of a decrease of π-back donation towards the carbonyl ligands, due to the increased positive charge density on the Re$^+$ cation.

Uv-vis spectra (Table 2) display the characteristic [4e–h] MLCT band of fac-[Re^I(CO)$_3$(L–L)Cl] and [fac-Re^I(CO)$_3$(L–L)L′]$^+$ compounds. In the Cl-substituted series when a carbonyl function is appended to the bipy ligand the position of the absorption maximum shifts at longer wavelengths. This is due to the electron withdrawing effect played by –COOH or –COOCH$_3$, which decreases significantly the energy of the π* acceptor orbitals while it plays only a moderate effect on the electron density at the rhenium center, as shown also by the very small shift towards higher energies of the CO stretching bands in the IR spectrum on passing from **1** to **2** and **3**. When py-substituted compounds **4–7** are taken into consideration, λ_{max} values are observed not far from that of compound **1**: stabilization of the ligands π* orbitals is in this case compensated by a significant increase in the positive

Table 2
UV–vis and luminescence data [a]

Complex	Absorption		Luminescence (298 K)			Luminescence (77 K)	
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	Φ	τ (ns)	λ_{max} (nm)	τ (μs)
1	368	3690	605	4×10^{-3}	29	536	2.9
2	394	3070	678	1×10^{-4}	1.5	580	0.7
3	390	3150	648	2×10^{-4}	0.5	541	0.9
3 (pH 8)[b]	375	3600	625	2×10^{-3}	7		
4	366 (sh)	2970	592	1.5×10^{-2}	77	523	3.1
4 (pH 8)[b]	350 (sh)	3450	583	4.5×10^{-2}	75		
5	370	4390	612	4×10^{-3}	12	533	1.5
5 (pH 8)[b]	370	4390	610	5×10^{-3}	10		
6	360	3440	614	5×10^{-3}	48	521	2.8
7	370 (sh)	2450	605	5×10^{-3}	12	528	1.5
7 (pH 8)[c]	355 (sh)	2900	587	4×10^{-2}	50		

[a] UV–vis and luminescence data have been obtained in 1:4 (v/v) water–dioxane mixtures, pH 2.5, unless otherwise stated. sh, shoulder.
[b] Carboxylate form.
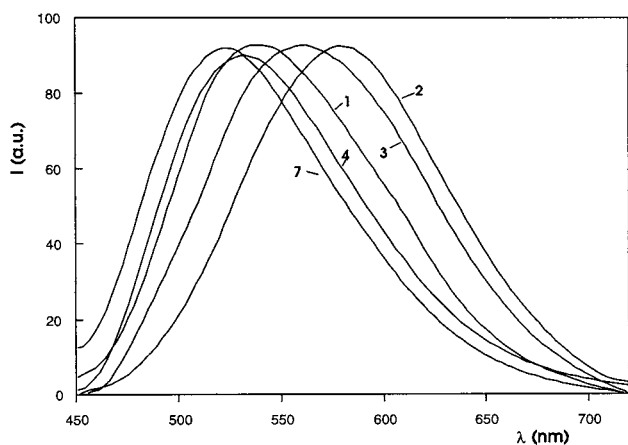[c] Bis-carboxylate form.

Fig. 1. (Normalized) luminescence spectra of selected complexes in rigid matrix at 77 K. Spectra of **5** (very similar to that of **4**) and of **6** (very similar to that of **7**) have been omitted for sake of clarity.

charge density on the Re^+ cation, which is reflected in the already mentioned decrease of back donation towards CO ligands observed in the IR spectra.

The luminescence spectra of complexes of the type of *fac*-$Re^I(CO)_3$(L–L)X are also usually dominated by MLCT transitions, except for few examples [4e, 16, 17], in which a ligand centered (LC) excited state lies close, or even below, in energy to the MLCT one. The assignment to a LC emission can usually be done on the basis of a relatively long lifetime at 77 K, and of the similarity with the phosphorescence band of the free ligand present in the complex. A MLCT transition is instead structureless, solvent dependent, and also much more sensitive on the rigidity of the medium (the so called rigidochromism), so that substantial spectral shift can be observed on passing from fluid solution to a frozen matrix [4f, 17].

As can be seen from Table 2 and Fig. 1, the luminescence of complexes **2**–**7** can be attributed, as already done for **1** [4f] and according to the properties described above, to a MLCT transition. In agreement to this attribution, as described for the MLCT absorption band, the maximum of the luminescence band, both at room temperature and at 77 K in the Cl-substituted series is found at longer wavelengths when a carbonyl function is appended to the bipy ligand. At room temperature, a decrease of the quantum yield was also observed. This was an expected results, since usually in the Re complexes the non radiative rate constant increases (and the quantum yield decreases) as the energy of the MLCT state decreases, in agreement with the so-called energy gap law.

As observed for the absorption MLCT band, when py-substituted compounds **5**–**7** are taken into consideration, λ_{max} values are observed not far from that of compound **1**. For compound **4**, in which the acid function is on the bpy ligand, the luminescence maxi-

mum is instead observed at shorter wavelengths, in line with the trend observed in the Cl-substituted series. According to the energy gap law, this complex possesses the highest luminescence quantum yield among the complexes reported here.

3.3. Protonation equilibria [2]

Potentiometric titration experiments were carried out in water–dioxane mixtures (1:4 v/v) on each of the –COOH functionalized derivatives, by addition of standard base on solutions containing the chosen compound plus excess acid. A pK_a value of 5.39 (± 0.01) was obtained for compound **3** (equilibrium: $[Re^I(CO)_3(bipyCOOH)Cl] \rightleftharpoons [Re^I(CO)_3(bipyCOO)Cl]^- + H^+$). Unfortunately, no literature data are available [18] for protonation equilibria of 2,2′-bipyridine-5-carboxylic acid, so the effect of the complexation of the bipy nitrogens to the rhenium center can not be evaluated directly. Literature reports protonation constants for the somewhat comparable bis-carboxylic acids $[Ru(2,2′\text{-bipyridine})_2(3,3′\text{-dicarboxy-2,2′-bipyridine})]^{2+}$ and $[Ru(2,2′\text{-bipyridine})_2(4,4′\text{-dicarboxy-2,2′-bipyridine})]^{2+}$, for both of which a decrease of $1-2$ log units was found in the pK_{a1} and pK_{a2} values on passing from the free to the complexed bipyridine-bis-carboxylic acid molecule [19]. This increase in acidity upon coordination was attributed to the electrostatic (electron withdrawing) effect upon coordination overbalancing metal to ligand π back-donation [19b]. With our compound, we can try to compare the obtained value at least with those reported for uncoordinated pyridine-3-carboxylic acid and pyridine-2-carboxylic acid. The pK_as (4.83 and 5.47, respectively, in water [20]) are similar to what found for **3** and this indicates that the possible favorable effect on the –COOH acidity played by nitrogen complexation to the positively charged Re^I center is compensated by back donation to the bipy rings or, more likely, by the presence in the Re coordination sphere of the negatively charged chloride ion. It has also to be noted that, due to solubility problems in water, all the experiments with our compounds were carried out in water–dioxane mixtures. Changing the nature of the solvent could certainly modify the measured pK_as, but the effect of adding a less polar solvent to water seems to be not dramatic and, in any case, it cannot be predicted if it would rise or lower the acidity of the –COOH group [21]. The deprotonation equilibrium for compound **3** can be followed also by means of coupled pH-metric and UV-vis and fluorimetric titrations. What is observed is a shift of the absorption MLCT band from 390 to 375 nm (with a slight increment in intensity: ε changes from 3150 to 3600 mol^{-1} l

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[2] In the remaining part of the discussion, the *fac*- prefix is omitted for sake of graphical simplicity.

cm^{-1}) and of the MLCT luminescence band from 648 to 625 nm, accompanied, in this case, by a ten-fold intensity increase, this latter feature being of particular interest, as it makes feasible the use of complex **3** as a luminescence-based pH-sensor [6a].

The ascending A_{375} versus pH and I_{625} versus pH profiles superimpose well to the percent of $[Re^I(CO)_3(bipyCOO)Cl]^-$ species versus pH profile which can be drawn from the calculated pK_a value, and the blue shift of the absorption and luminescence maxima is connected with the metal-to-ligand nature of the transition associated with the considered band, as the energy necessary to transfer an electron from the Re^I center to the bipy ligand increases when a negative charge is set up on the latter fragment. As expected, in the same experiment carried out on the ester-functionalized compound **2**, no variations (absorbance or luminescence) were observed in the 2–12 pH range, indicating also that no significant hydrolytic processes take place at the ester function, at least along the time required for a spectrophotometric or fluorimetric titration (30 min).

With the second generation series of compounds, in which the Cl^- anion has been substituted with a functionalized pyridine, higher pK_a values then in **3** were measured for **4** ($pK_a = 5.6$) and **5** ($pK_a = 6.02$), while for the bis-acid **7**, the first pK_a ($pK_{a1} = 5.07$) is only 0.3 log units lower than for **3**. However, an increased acidity for the –COOH groups (and *distinctly lower* pK_as) should be expected on the basis of (i) the increase of the charge density on the Re^+ cation; (ii) the decrease of π-back donation on the py or bipy groups, connected to the latter point. The observed opposite trend should then be explained with a different effect: in particular, it could be hypothesized that intramolecular –OH···O=C hydrogen bond between carboxylic acid–ester or carboxylic acid–carboxylic acid groups can be effective in stabilizing the protonated form of the studied acids, as indicated also by molecular modeling calculation (Hyperchem 3.0 package) and as it has been already found in the literature for the comparable bis-carboxylic acid $[Ru^{II}(2,2'\text{-bipyridine})_2(3,3'\text{-dicarboxy-}2,2'\text{-bipyridine})]$ [2, 19a]. Finally, a $pK_{a2} = 6.48$ has been calculated for the bis-acid **7**: in this case, the further decrease of acidity can be obviously accounted for with the overall charge decrease which sets on the molecule after the first deprotonation, or even with the more favorable –OH···O=C hydrogen bond which could hold between the undissociated and dissociated carboxylic groups.

Coupled pH-metric, spectrophotometric and spectrofluorimetric titrations gave some more information on the deprotonation processes along the **4**–**7** series. In particular, for compound **4**, which bears a –COOH group on the 2,2'-bipyridine ligand, a shift of the MLCT absorption (shoulder, from 366 to 350 nm) and

luminescence (from 592 to 583 nm, accompanied by a three-fold increase of the luminescence intensity) bands to shorter wavelengths was observed on going from pH 4.5 to 6.5, i.e. on deprotonation of the –COOH group. The observed blue shift gives account of the more energy demanding CT transition from the metal center to the bipyCOO$^-$ fragment. On the other hand, for compound **5**, which bears a –COOH group on the pyridine ligand, no change in the MLCT band position was observed over the 2–10 pH range, while a very small shift (from 612 to 610 nm) was observed in the luminescence spectrum (accompanied by a 0.3-fold increase in intensity), on going from acidic (pH < 5) to basic (pH > 7) solutions. These findings indicate that, as it could be expected, the ester-substituted bipyridine ligand is the preferred fragment for electron transfer, independently from the presence of a carboxylic acid or a carboxylate group on the pyridine ligand. Finally, with compound **7** a blue shift (from 370 nm, shoulder, to 355 nm, shoulder) was observed on the addition of the first equivalent of OH$^-$, i.e. on deprotonation of the first –COOH group, while no further variations were observed on addition of the second equivalent of OH$^-$ (i.e. on deprotonation of the second –COOH group). Similarly, a eight-fold increase of the luminescence intensity was observed after the first deprotonation process, while negligible changes were observed thereafter. Comparison of these results with what found for compounds **4** and **5** suggests that the first deprotonation, in complex **7**, takes place on the –COOH appended to the 2,2'-bipyridine ligand [22].

3.4. Electrochemistry

Coupled pH-metric and electrochemical titration experiments were carried out on compounds **2**–**7**, in the 2–12 pH range, by adding microquantities of standard base to solutions containing the chosen compound plus excess acid. It has to be noted that the employed experimental conditions (1:4 water–dioxane mixture as solvent, made 0.1 mol l^{-1} in $[(n\text{-but})_4N]ClO_4$) made the potential window quite narrow, due to the presence of huge quantities of water. Moreover, a cathodic shift of the solvent anodic discharge was obviously observed as standard base was added to the electrochemical solution. According to this, it was possible to observe a quasi-reversible oxidation wave (Re^{II}/Re^I couple) only for compounds **2** and **3**. In particular, the oxidation wave for compound **2** displayed an $E_{1/2}$ value of 1.39 V versus SCE in the 2–12 pH range, while the oxidation wave for compound **3** shifted from $E_{1/2} = 1.36$ V versus SCE (pH < 4.5) to 1.14 V versus SCE (pH > 6.1), in correspondence to the deprotonation of the carboxylic group. These values are well set in what reported in the literature [6b, 15] for comparable compounds and are also in accord with what was measured under our

experimental conditions for compound **1** (1.33 V versus SCE). In particular, the slight increase of the oxidation potential for **3** and **2** with respect to **1** (60 and 30 mV, respectively) gives also in this case account of the electron withdrawing effect played by carboxylic acid and ester group on the metal center, through the bipy ligand. When the second generation series of compounds (**4**–**7**) was taken into consideration, no oxidation wave was observed, in the 2–12 pH range, in the allowed potential window. Substitution of a Cl^- anion with a pyridine ligand increases the positive charge on the Re^I center, making its oxidation more difficult, so that it would take place at a potential higher than that of the solvent oxidation.

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[22] Confirming what is observed for compound **2**, further addition of base for compounds **4** and **5** did not affect the spectra recorded for the –COO^- species, indicating that the ester function is not hydrolized along the time required for the experiment (20–30 min). In accord with these observations, the spectrum of the bis-ester compound **6** did not vary in the 2–12 pH range.