

# Photoinduced charge separation in R–CO<sub>2</sub>–Re(CO)<sub>3</sub>(2,2'-bipyridine) complexes. Two emitting charge transfer excited states

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Excited state properties of the newly prepared complexes R–CO<sub>2</sub>–Re(CO)<sub>3</sub>(2,2'-bipy), where R–CO<sub>2</sub><sup>–</sup> = naphthalene-2-carboxylate, anthracene-9-carboxylate, pyrene-1-carboxylate and acetate, were investigated by steady state and time resolved spectroscopy. The X-ray structure revealed that the R containing ligand is coordinated through the carboxylate group to Re(I). Results showed that two emitting excited states play a major role in the photophysics of the complexes. The fast component of the complexes luminescence was associated with the charge transfer excited state, MLCT, Re-to-2,2'-bipyridine, while experimental evidence led to the long lived component being attributed to a ligand-to-ligand charge transfer excited state. This emissive LLCT excited state can also evolve to a photo-dissociative state which ultimately produces the complex decarboxylation. On the other hand, the carboxylate bridge was shown to be able to impede connection between R and the Re(CO)<sub>3</sub>(2,2'-bipy) chromophore.

## Introduction

Early studies on the photochemistry of XRe(CO)<sub>3</sub>L<sub>2</sub> compounds, where X = halide or mono-azine and L = mono-azine or di-azine, have shown that the photophysical and photochemical properties are largely associated with either or both MLCT<sub>L</sub> → Re and IL<sub>L</sub> excited states.<sup>1,2</sup> In these excited states the azine functions as an electron acceptor, *i.e.*, in a MLCT<sub>L</sub> → Re, or undergoes changes in its electronic configuration, *i.e.*, in a IL<sub>L</sub> state, similar to those undergone by a free ligand.<sup>1</sup> In some cases biradical intermediates were detected in irradiations that populated electronic states above the lowest MLCT<sub>L</sub> → Re.<sup>3,4</sup> In most of these Re compounds X functions as a “spectator ligand”.<sup>5</sup> Nevertheless, conversions between <sup>3</sup>MLCT and <sup>3</sup>LLCT excited states appear to control the rate of the luminescence in some Re compounds where X is a dimethylaniline derivative.<sup>5</sup> On the other hand, in (4-nitrobenzoate)Re(CO)<sub>3</sub>L<sup>6</sup> a charge transfer excited state, MLCT<sub>4-nitrobenzoate</sub> → Re is produced by a complex photochemical mechanism. Photogeneration of a Re to L ligand charge transfer excited state, MLCT<sub>L</sub> → Re, and its equilibration with a precursor, I, precedes the formation of the MLCT<sub>4-nitrobenzoate</sub> → Re. The photophysical and photochemical properties of (4-nitrobenzoate)Re(CO)<sub>3</sub>L,<sup>6</sup> (pyrazine-2-carboxylate)Re(CO)<sub>3</sub>(2,2'-bipy)<sup>7</sup> and (anthraquinone-2-carboxylate)Re(CO)<sub>3</sub>(2,2'-bipy)<sup>8</sup> have strongly suggested that the carboxylate electronically insulates the Re(I) chromophore from the pendant 4-nitrobenzyl, pyrazine and anthraquinone groups. In this work, we have studied the photophysics and photochemistry of a series of R–CO<sub>2</sub>–Re(CO)<sub>3</sub>(2,2'-bipy) compounds, to obtain more insight into the role of the carboxylate bridge on these properties.

## Experimental

### Materials

The Re(I) complexes, R–CO<sub>2</sub>–Re(CO)<sub>3</sub>(2,2'-bipy), where R–CO<sub>2</sub><sup>–</sup> = naphthalene-2-carboxylate, anthracene-9-carboxylate,

pyrene-1-carboxylate and CH<sub>3</sub>CO<sub>2</sub><sup>–</sup>, were prepared by modification of literature procedures.<sup>6–8</sup> The XRe(CO)<sub>3</sub>(2,2'-bipy) complexes, (X = Cl, Br), were reacted with Ag(RCO<sub>2</sub>), the silver salt of R-carboxylate. Small fractions of solid Ag(RCO<sub>2</sub>), in the form of a fine powder, were added to a warm solution of the Re(I) complex in CH<sub>2</sub>Cl<sub>2</sub> until the materials were in a 1 : 1 stoichiometry. This mixture was stirred and refluxed for 9 h under a N<sub>2</sub> atmosphere. The Re(I) complex in CH<sub>2</sub>Cl<sub>2</sub> solution was precipitated by adding n-pentane and was separated from the other product, solid AgX, on a Soxhlet extractor. The complex solution was rotoevaporated to dryness and recrystallized from a concentrated solution in dichloromethane by adding n-pentane. This recrystallization procedure was repeated until molar extinction coefficients, emission spectra and emission lifetimes remained constant.

Elemental analysis, X-ray diffraction and UV-visible spectra were used for the characterization of the materials and to ascertain their purity. (Found: C, 47.81; N, 4.80; H, 2.67; naphthalene-2-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy). Calc. C, 48.24; N, 4.69; H, 2.51%). (Found: C, 51.24; N, 4.13; H, 2.80; anthracene-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy). Calc. C, 51.93; N, 4.33; H, 2.63%). (Found: C, 53.54; N, 4.33; H, 2.65; pyrene-1-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy). Calc. C, 53.65; N, 4.17; H, 2.53%). (Found: C, 36.94; N, 5.71; H, 2.20; CH<sub>3</sub>CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy). Calc. C, 37.11; N, 5.77; H, 2.26%).

Double displacement reactions of Na(RCO<sub>2</sub>) with Ag(CF<sub>3</sub>SO<sub>3</sub>) or AgNO<sub>3</sub> were used for the preparation of Ag(RCO<sub>2</sub>). Complexes XRe(CO)<sub>3</sub>(2,2'-bipy) were available from previous work.<sup>7–9</sup> The sodium salt was prepared by titrations of RCO<sub>2</sub>H (Aldrich) with NaOH. Other materials were reagent grade and used without further purification.

### Determination of the crystal structure

Crystals of Re(CO)<sub>3</sub>(2,2'-bipy)O<sub>2</sub>C-9-anthracene were grown by slow evaporation of the solvent from a concentrated solution of the complex in CH<sub>3</sub>CN. The red prismatic crystal used for X-ray crystallography had the approximate dimensions of

**Table 1** Crystal data, structure solution methods and refinement results for anthracene-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy)

Empirical formula	C <sub>28</sub> H <sub>17</sub> N <sub>2</sub> O <sub>5</sub> Re
Formula weight	647.64
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	8.951(1) <sup>a</sup>
<i>b</i> /Å	15.089(2)
<i>c</i> /Å	18.253(3)
$\beta$ /°	97.53(1)
Volume/Å <sup>3</sup>	2443.9(6)
<i>Z</i>	4
Absorption coefficient/mm <sup>-1</sup>	5.013
Diffractometer/scan	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$
Radiation, graphite monochromator	Mo-K $\alpha$ , $\lambda$ = 0.71073 Å
Reflections collected	6054
Independent reflections	5876 [ <i>R</i> (int) = 0.035]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4158
Data reduction and correction <sup>b</sup>	XCAD-4 <sup>9</sup>
Structure solution <sup>c</sup> and	SHELXS-97 <sup>11</sup>
Refinement <sup>d</sup> programs	SHELXL-97 <sup>12</sup>
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	5876/0/326
Final <i>R</i> indices <sup>e</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0339, <i>wR</i> 2 = 0.0846
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0666, <i>wR</i> 2 = 0.0978

<sup>a</sup> Cell constants determined by least-squares refinement of  $[(\sin\theta)/\lambda]^2$  values for 24 reflections in the 23.28 < 2 $\theta$  < 40.84° range. <sup>b</sup> Corrections: Lorentz, polarization and absorption.<sup>10</sup> Maximum and minimum transmission factors of 0.348 and 0.203. <sup>c</sup> Neutral scattering factors and anomalous dispersion corrections. <sup>d</sup> Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms. <sup>e</sup> *R* indices defined as: *R*1 =  $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ ; *wR*2 =  $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ .

**Table 2** Bond distances (Å) and angles (°) around rhenium in anthracene-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy)

Re–C(3)	1.903(6)	Re–O(11)	2.127(3)
Re–C(2)	1.905(6)	Re–N(21)	2.168(4)
Re–C(1)	1.934(6)	Re–N(22)	2.177(4)
C(3)–Re–C(2)	88.7(32)	C(1)–Re–N(21)	172.4(2)
C(2)–Re–C(1)	88.6(3)	O(11)–Re–N(21)	76.7(2)
C(3)–Re–C(1)	88.9(2)	C(2)–Re–N(22)	170.6(2)
C(2)–Re–O(11)	93.5(2)	C(3)–Re–N(22)	97.1(2)
C(3)–Re–O(11)	173.0(2)	C(1)–Re–N(22)	98.9(2)
C(1)–Re–O(11)	97.8(2)	O(11)–Re–N(22)	79.8(2)
C(2)–Re–N(21)	96.9(2)	N(21)–Re–N(22)	75.1(2)
C(3)–Re–N(21)	96.5(2)		

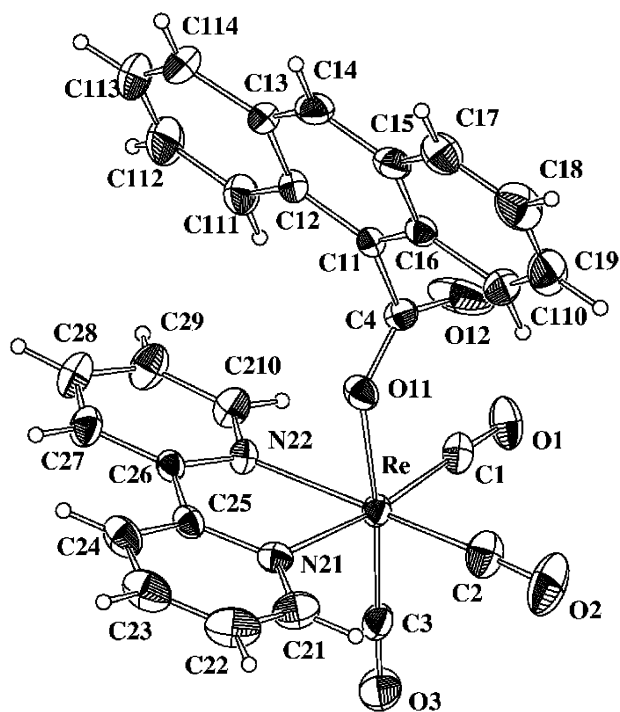
0.24 × 0.32 × 0.35 mm and was mounted on a glass fiber in a random orientation.

**Diffraction data, structure solution and refinement.** Crystal data, data collection procedures, structure determination methods and refinement results are summarized in Table 1.<sup>9–12</sup>

Most H-atoms were detected at approximate locations in a difference Fourier map. They, however, were positioned stereo-chemically and refined with the riding model employing a common isotropic displacement parameter which in the final run converged to *U* = 0.067(5) Å<sup>2</sup>.

Bond distances and angles around rhenium are reported in Table 2. Fig. 1 is an ORTEP<sup>13</sup> drawing of the complex where it can be seen that the anthracene-9-CO<sub>2</sub><sup>-</sup> is coordinated to Re by its carboxylate group.

The rhenium atom is in a distorted octahedral environment. It is coordinated by two carbonyl groups [Re–C distances of 1.905(6) and 1.934(6) Å] and a 2,2'-bipy molecule acting as a bidentate ligand [Re–N distances of 2.168(4) and 2.177(4) Å] which define an equatorial plane. These bond distances agree within experimental accuracy with the corresponding values found for the related pyrazine-2-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) complex.<sup>8</sup> The octahedral coordination is completed at the axial positions by another CO ligand [*d*(Re–C) = 1.903(6) Å] and a carboxylic oxygen of an anthracene-9-carboxylate [*d*(Re–O) = 2.132(3) Å]. This Re–O bond distance is 0.073(8) Å shorter than the corresponding value in the pyrazine complex.

**Fig. 1** Molecular plot of anthracene-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) showing the labeling of the non-H atoms and their vibrational ellipsoids at the 30% probability level.

As expected, the 2,2'-bipy rings and the anthracene and carboxylate C–CO<sub>2</sub> groups are planar to within experimental accuracy. The two 2,2'-bipy rings are slightly tilted (by 2°) from each other. The carboxylate plane is close to perpendicularity to both the anthracene group [dihedral angle of 85.7(2)°] and to the N<sub>2</sub>C<sub>2</sub> equatorial plane of ligands to rhenium [angle of 98.5(1)°]. The 2,2'-bipy plane is tilted by 12.1(2)° from this plane. The Re atom lies approximately on the intersection of the equatorial N<sub>2</sub>C<sub>2</sub> plane and the carboxylate plane.

CCDC reference number 171630.

See <http://www.rsc.org/suppdata/dt/b1/b108349j/> for crystallographic data in CIF or other electronic format.

## General methods

UV-vis spectra were recorded on a Cary 3 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 625 and NMR spectra on a Bruker AC 250. FTIR spectra were recorded on a Bruker IFS 113v.

## Electrochemistry

Tetra(1-butyl)ammonium hexafluorophosphate,  $[N(n-C_4H_9)_4](PF_6)$  (Fluka), was recrystallized from ethanol and vacuum dried. UV-grade  $CH_3CN$  (Merck, Uvasol), was dried over aluminium oxide 90 active basic (Merck) before electrochemical measurements. Cyclic voltammograms were obtained in 0.1 M  $[N(n-C_4H_9)_4](PF_6)/CH_3CN$  solutions, using a glassy carbon working electrode, with a LYP M2 potentiostat, a 3-module LYP sweep generator, and a Houston Omnigraphic 2000 pen recorder. Rhenium complex concentration was kept at  $1 \times 10^{-3}$  M and the ferrocene/ferrocenium couple was used as the internal standard. All half-wave potentials are reported vs. the SCE reference electrode.

## Conductivity measurements

Conductivity measurements were performed using a CONSORT C835 multichannel analyser. A solution of KCl = 0.01 M was used for calibration ( $1413 \mu S cm^{-1}$ ). Complex concentrations were kept at  $2 \times 10^{-4}$  M in  $CH_3CN$ .

## Photophysical measurements

Emission spectra were obtained with a computer-interfaced SLM-Aminco 4800 or a Perkin-Elmer LS 50B spectrofluorimeter. Spectra 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. Spectra at 77 K in MeOH/EtOH (1 : 4) glasses were recorded by placing photolytes in cells with cylindrical geometries. The cells were located in a low temperature accessory of the LS50B spectrofluorimeter. Emission quantum yields were measured relative to Rhodamine B in ethanol. Quantum yields were calculated according to the equation:

$$\phi_{em} = (A_{standard}/A_{sample})(I_{sample}/I_{standard})\phi_{em,standard}(n_{sample}/n_{standard})^2$$

where  $I$  is the integral of the emission spectrum and  $A$  is the absorbance of the sample or standard at the excitation wavelength and  $n$  is the solvent refraction index.

Emission lifetimes, nanosecond transient absorption spectra and kinetics were mostly measured with a nitrogen laser set-up. In these experiments, 10 ns flashes of monochromatic (337 nm) light were generated with a nitrogen laser as described elsewhere.<sup>14</sup> For transient absorption studies, the excitation beam was at a right angle with the white-light monitoring beam provided by a 100 W Xe arc lamp probe source. The light was passed through a monochromator (PTI-1695) and detected by a modified 1P28 PTM photomultiplier. Decays typically represented the average of 20–100 pulses and were collected on a HP-54600B digital oscilloscope interfaced with a PC. Some experiments were carried out on a Eximer (351 nm) and Nd-Yag (354 nm) laser set-up described elsewhere.<sup>8,15</sup>

## Steady state photolysis

Steady state photolysis experiments (350, 300 and 254 nm) were carried out in an irradiator with appropriate Rayonet lamps. A  $Co(NH_3)_5Br^{2+}$  actinometer was used for the measurements of the light intensities ( $I_0 \approx 4 \times 10^{-4}$  Einstein  $l^{-1} min^{-1}$ ). The concentration of the photolyte was adjusted for absorbing more than 99.99% of the incident light and magnetic bars were used for stirring the solutions while they were irradiated.

In a large scale photolysis experiment,  $CO_2$  formation was detected by IR analysis of the gases above the photolyzed

solution after 12 h of 300 nm photolysis of 45 mg of  $CH_3CO_2Re(CO)_3(2,2'-bipy)$  dissolved in 50 ml of  $CH_3CN$ . To take the IR spectrum the volatile gases, at 195 K, contained in the photolysis cell were condensed at 77 K in the IR cell using a sealed system and then allowed to evaporate at room temperature. The nature of the products other than  $CO_2$  formed after 14 h of 254 or 300 nm photolysis of 15 mg of  $CH_3CO_2Re(CO)_3(2,2'-bipy)$  dissolved in 10 ml of  $CH_3CN$  were investigated by following their FTIR spectra in the liquid phase. Attempts at isolation of these products and further purification by chromatographic techniques failed due to their decomposition while passing through the column.

## Results

### (a) Absorption and emission spectra

The UV-visible spectra of Nap-2- $CO_2Re^I(CO)_3(2,2'-bipy)$  (Nap: Naphthalene), An-9- $CO_2Re^I(CO)_3(2,2'-bipy)$  (An: anthracene), Pyr-1- $CO_2Re^I(CO)_3(2,2'-bipy)$  (Pyr: pyrene),  $CH_3CO_2Re(CO)_3(2,2'-bipy)$  and  $BrRe^I(CO)_3(2,2'-bipy)$  in  $CH_3CN$  are shown in Fig. 2. A  $d\pi(Re) \rightarrow \pi^*(2,2'-bipy)$  metal-

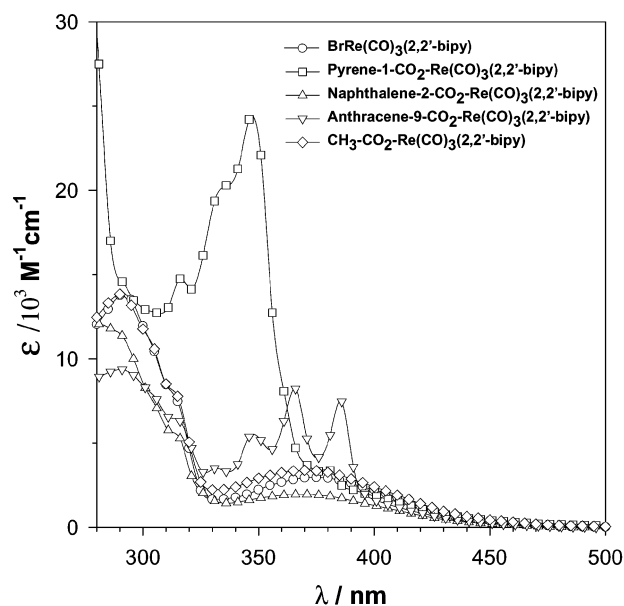
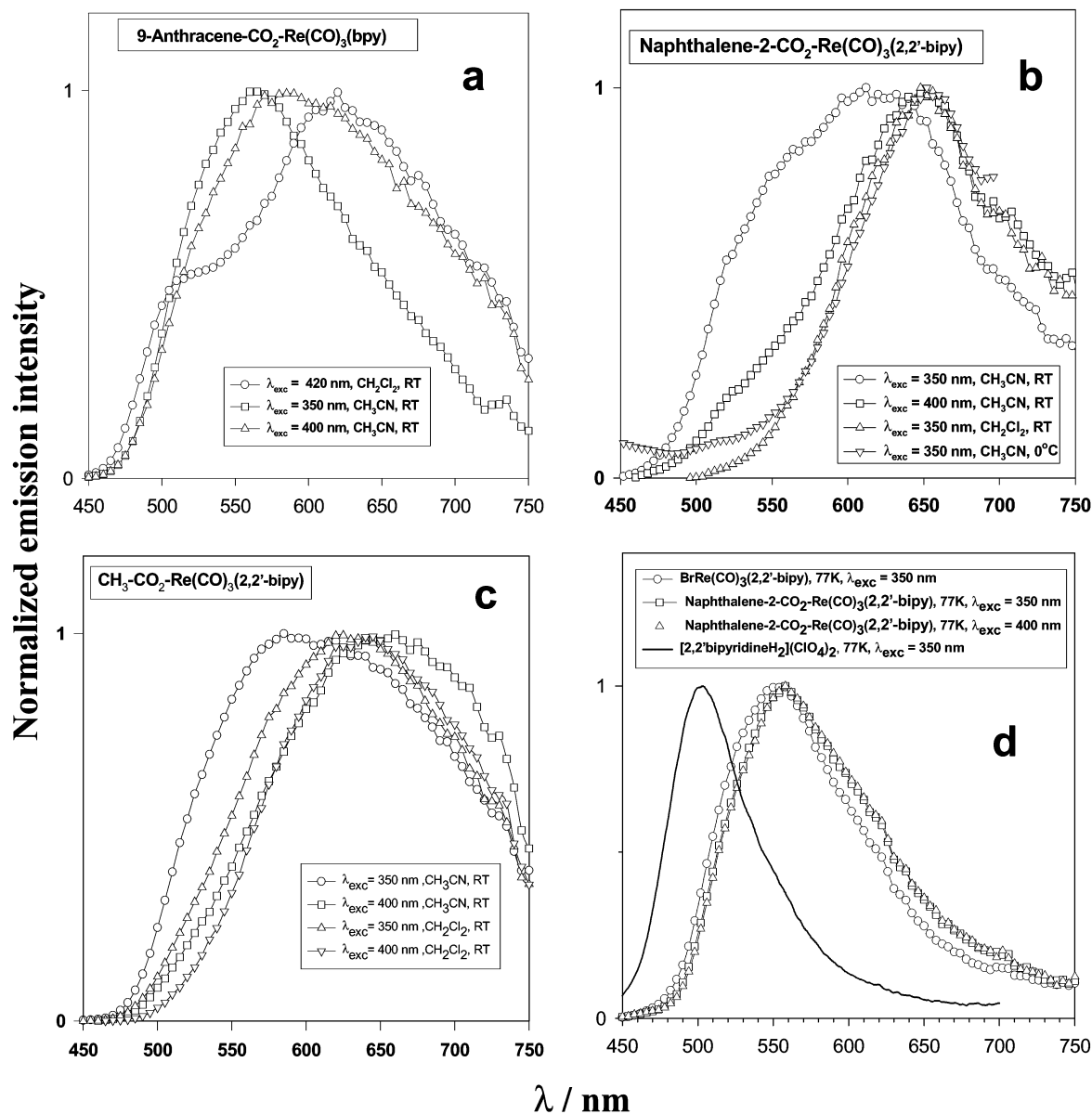


Fig. 2 Absorption spectra of  $LRe(CO)_3(2,2'-bipy)$  complexes in  $CH_3CN$ .

to-ligand charge transfer (MLCT) band is observed in the 370 nm region, while the near UV is dominated by ligand-based  $\pi \rightarrow \pi^*$  bands. Compounds containing the anthracene and pyrene moieties, show the characteristic vibronic progression for the  $S_0 \rightarrow S_1$  of the ligands superimposed on the MLCT band. The basic inference from these spectra is that the ground-state spectrum for each of these complexes is an additive composite of  $Re(CO)_3(2,2'-bipy)$  and R chromophores without any significant interaction between them.

In Figs. 3a–c show emission spectra taken at room temperature. When the spectra were taken in dichloromethane, emission occurred peaking at 640 nm like that observed in the parent complex,  $BrRe(CO)_3(2,2'-bipy)$ . That emission spectrum has been attributed to the  ${}^3MLCT_{2,2'-bipy} \rightarrow Re$  excited state.<sup>16,17</sup> In this solvent, as the excitation wavelength goes from 350 to 400 nm, the emission intensity decreases though no spectrum shape changes are observed. However, when the solvent was acetonitrile a strong wavelength effect could be seen and by irradiating at the shorter wavelength the emission spectrum was blue shifted. When the emission spectrum in acetonitrile was taken at 0 °C (Fig. 3b),  $\lambda_{exc} = 350$  nm, some features present at room temperature almost disappeared and the emission



**Fig. 3** Emission spectra of  $\text{LRe}(\text{CO})_3(2,2'\text{-bipy})$  complexes recorded by the respective irradiations at 350, 400 or 420 nm of its deaerated solutions in  $\text{CH}_2\text{Cl}_2$  (RT),  $\text{CH}_3\text{CN}$  (RT or 0 °C) and  $\text{EtOH}/\text{MeOH}$  4 : 1 v/v (77 K). See key to the spectra in the figure.

peaking at 640 nm dominated the emission spectrum. Excitation spectra taken in acetonitrile solutions of Nap-2- $\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$  (Fig. 4) confirm the presence of two excited states preferentially populated at different wavelengths. It is worthy of note that for complexes like  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$  and  $[(\text{CH}_3\text{CN})\text{Re}(\text{CO})_3(2,2'\text{-bipy})]^+$  no such solvent and wavelength effect was observed.

Emission quantum yields irradiating at 350 nm, in acetonitrile, were  $7.8 \times 10^{-3}$  for  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$  and  $1.3 \times 10^{-3}$  and  $1.1 \times 10^{-3}$  for Nap-2- $\text{Re}(\text{CO})_3(2,2'\text{-bipy})$  and  $\text{CH}_3\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$ , respectively. Emission quantum yields measured in similar conditions in dichloromethane were  $1.6 \times 10^{-2}$  for  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$ , and  $2.4 \times 10^{-3}$  and  $4.0 \times 10^{-3}$  for Nap-2- $\text{Re}(\text{CO})_3(2,2'\text{-bipy})$  and  $\text{CH}_3\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$ , respectively. These results showed that in both solvents the emission quantum yield is, for the carboxylate containing compounds, several times lower than for  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$ .

In Fig. 3d emission spectra at 77 K of Nap-2- $\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$ ,  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$  and  $[\text{2,2'-bipyridineH}_2](\text{ClO}_4)_2$  are shown. No significant differences can be observed between both complexes. A featureless emission, blue shifted about 100 nm from that observed in dichloromethane at RT, was present. This emission can be attributed to the  ${}^3\text{MLCT}_{2,2'\text{-bipy}} - \text{Re}$

because the emission maximum shown by the protonated 2,2'-bipy at 77 K is still located 60 nm towards higher energy (see Fig. 3d).

### (b) Electrochemical measurements

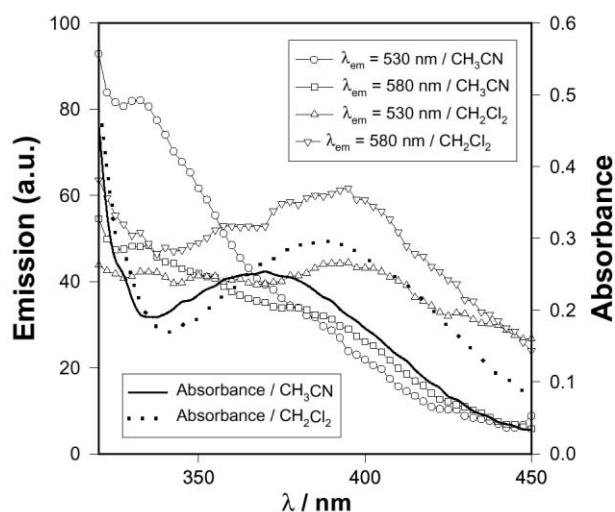
Some relevant electrochemical data acquired in  $\text{CH}_3\text{CN}$  are compiled in Table 3. All the complexes displayed a characteristic, reversible cathodic wave at  $E_{1/2}$  values ranging from 1.30 to 1.34 V which is due to reduction of the coordinated 2,2'-bipy ligand.<sup>16</sup> The irreversible cathodic wave, at  $E_{\text{peak}} = 1.88$ , 1.86 and 1.79 V for Nap-2- $\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$ , An-9- $\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$  and Pyr-1- $\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$ , respectively, should be attributed to the  $\text{R}^{0/-1}$  couple. In addition, the complexes displayed an irreversible anodic wave at  $E_{\text{peak}} = 1.34$  V, which was observed in the parent complex  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$  as well, corresponding to the couple  $\text{Re}^{+1/+2}$ .<sup>8</sup> All the compounds showed another irreversible wave at more positive potentials attributable to the R moiety and/or to the carboxylate group.

Conductivity measurements have been made to ensure that the carboxylate complexes were not dissociated in solution. Results (Table 4) showed that dissociation was negligible.

**Table 3** Electrochemical data (in CH<sub>3</sub>CN) and lifetimes observed in flash photolysis and flash fluorescence in deaerated solutions of arene-CO<sub>2</sub>-Re(CO)<sub>3</sub>(2,2'-bipy) and related compounds

Compound	$E_{1/2}/V$ (bipy 0/-I)	$E_{peak}/V$ (R-CO <sub>2</sub> - 0/-I)	$E_{peak}/V$ (Re I/II)	$E_{peak}/V$ (R-CO <sub>2</sub> - oxidation)	Lifetimes of OD changes/ns	Luminescence lifetimes/ns
Naphthalene-2-CO <sub>2</sub> Re(CO) <sub>3</sub> (2,2'-bipy)	-1.34	-1.88 irr	1.35	1.85	CH <sub>3</sub> CN 20 CH <sub>2</sub> Cl <sub>2</sub> 15, 80	CH <sub>3</sub> CN 370, 50 CH <sub>2</sub> Cl <sub>2</sub> 110
Anthracene-9-CO <sub>2</sub> Re(CO) <sub>3</sub> (2,2'-bipy)	-1.31	-1.86 irr	1.38	1.21; 1.43	CH <sub>3</sub> CN 6900 CH <sub>2</sub> Cl <sub>2</sub> 5500	CH <sub>3</sub> CN 389, 20 CH <sub>2</sub> Cl <sub>2</sub> 53
Pyrene-1-CO <sub>2</sub> Re(CO) <sub>3</sub> (2,2'-bipy)	-1.30	-1.79 irr	1.37	1.43; 1.59	CH <sub>3</sub> CN 7400 CH <sub>2</sub> Cl <sub>2</sub> 6800	CH <sub>3</sub> CN 428 CH <sub>2</sub> Cl <sub>2</sub> 61
CH <sub>3</sub> CO <sub>2</sub> Re(CO) <sub>3</sub> (2,2'-bipy)	-1.25 irr -1.47	-1.72 rev	1.33			CH <sub>3</sub> CN 474 CH <sub>2</sub> Cl <sub>2</sub> 244, 31
BrRe(CO) <sub>3</sub> (2,2'-bipy)	-1.32		1.34			CH <sub>3</sub> CN 60 CH <sub>2</sub> Cl <sub>2</sub> 100
Anthracene-9-CO <sub>2</sub> H				1.50	CH <sub>3</sub> CN 2500	
Naphthalene-2-CO <sub>2</sub> H				1.89		
Pyrene-1-CO <sub>2</sub> H				1.37; 1.58		
CH <sub>3</sub> CO <sub>2</sub> H		-2.0 <sup>a</sup>		1.58 <sup>a</sup>		

<sup>a</sup> Taken from ref. 24.



**Fig. 4** Excitation spectra for naphthalene-2-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>. Left axis shows the emission intensity monitored at 530 and 580 nm in both solvents when varying the excitation wavelength while the right axis shows the absorbance of the solutions used in those experiments for comparison.

### (c) Emission lifetimes

The luminescence kinetics of the Re(I) complexes investigated, at room temperature, by 351 and/or 337 nm flash photolysis of their acetonitrile deaerated solutions, revealed dual emissions that were differentiated by means of their absorption spectra and/or corresponding emission lifetimes. However, in dichloromethane solutions a short lived monoexponential emission was mostly observed. Emission lifetimes are listed in Table 3. On the other hand, no significant temperature dependence was observed between 273 and 313 K for both lifetimes,  $\tau_1$  and  $\tau_2$ , after 337 nm excitation of acetonitrile solutions of R-CO<sub>2</sub>-Re(CO)<sub>3</sub>(2,2'-bipy) complexes.

### (d) Absorption transients

For the An-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) and Pyr-1-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) compounds the absorption transient spectra were dominated by the triplet excited states<sup>18,19</sup> of the corresponding arene (Fig. 5a). The triplet was probably formed because, at the irradiation wavelength (337 nm), the arene moiety absorptions were significant. However, for the Nap-2-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) complex, where the naphthalene group does not absorb at the irradiating wavelength, only a transient decaying with the same lifetime as the short-lived emission (Fig. 5b) could be observed. This transient could be identified<sup>20</sup>

**Table 4** Conductivity measurements of  $2 \times 10^{-4}$  M solutions of XRe(CO)<sub>3</sub>(2,2'-bipy) in CH<sub>3</sub>CN

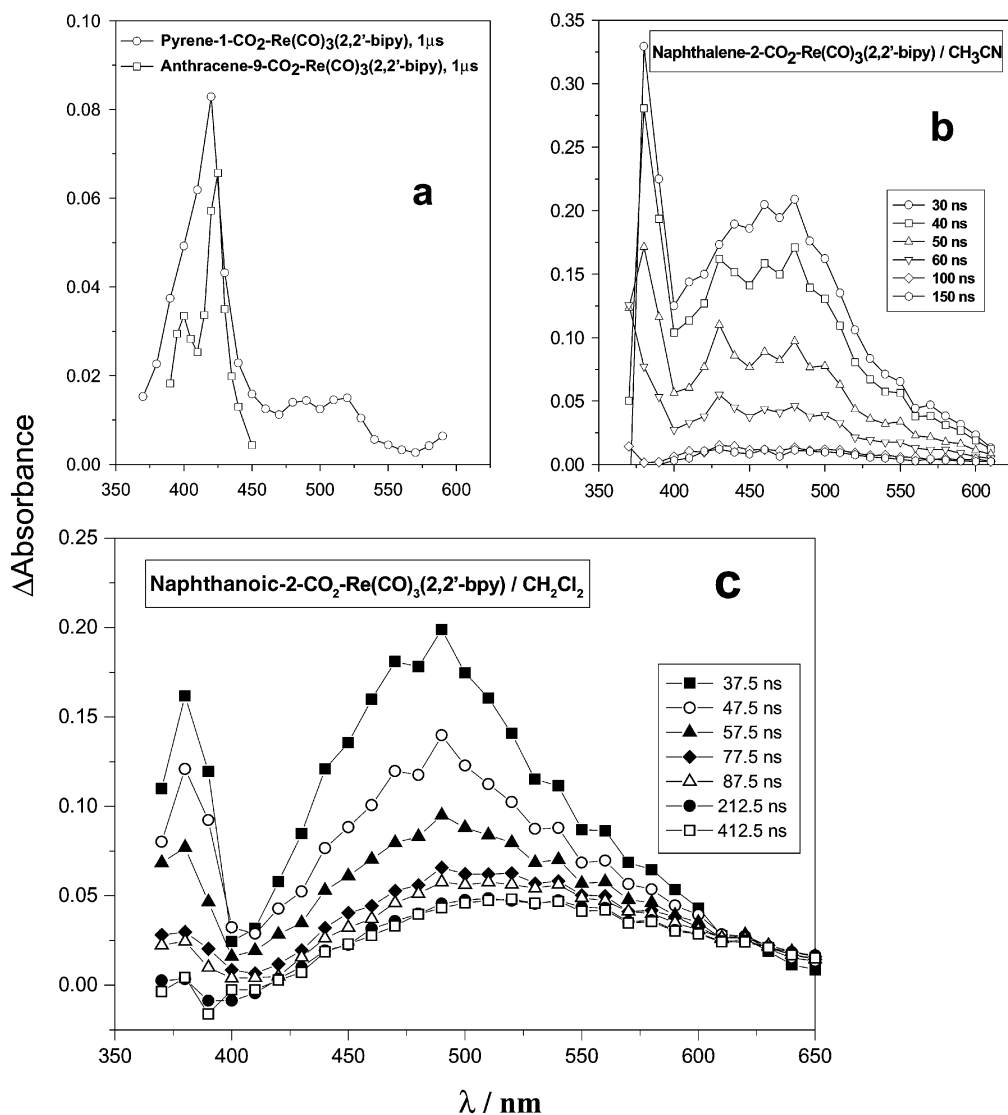
Compounds	Specific conductivity/ $\mu\text{S cm}^{-1}$
CH <sub>3</sub> CN	0.16
CH <sub>2</sub> -CO <sub>2</sub> -Re(CO) <sub>3</sub> (2,2'-bipy)	0.30
Br-Re(CO) <sub>3</sub> (2,2'-bipy)	0.31
CF <sub>3</sub> -SO <sub>3</sub> -Re(CO) <sub>3</sub> (2,2'-bipy)	34.10

as <sup>3</sup>MLCT<sub>2,2'-bipy</sub> → Re. After this excited state was depleted a residual absorption peaking around 500 nm remained. This behavior is similar in both solvents though in CH<sub>2</sub>Cl<sub>2</sub> the amount of the product absorbing at 500 nm is notably higher.

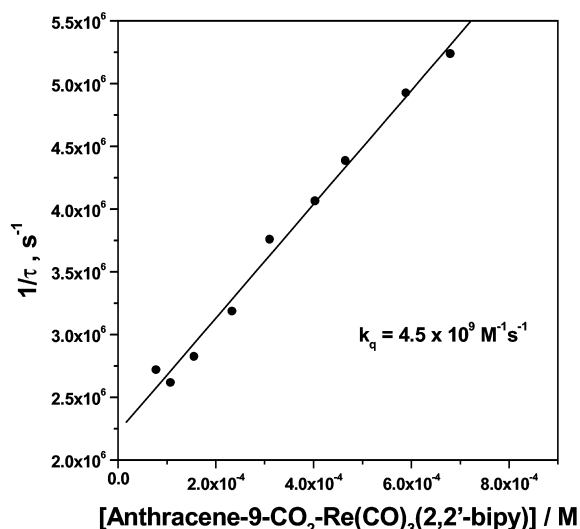
It has been observed that for An-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) and Pyr-1-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) complexes the emission lifetime depends on the concentration of the complex (Fig. 6). To avoid this bimolecular quenching all the studies have been performed at the lowest concentration where the emission could be measured.

### (e) Steady state photolysis results

Steady state photolysis experiments, performed on acetonitrile solutions of CH<sub>3</sub>CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy), Nap-2-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) and An-9-CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy), irradiating with light of 350 nm wavelength did not reveal any change in the UV-visible spectrum. However, when the irradiation wavelength was 300 nm, photochemistry was evident. A product showing new absorption features with a maximum at 500 nm was formed, see Figs. 7a and b. Photolysis in CH<sub>2</sub>Cl<sub>2</sub> produced different spectral changes suggesting that the solvent was intervening in the reaction. On the other hand, photolysis at 300 nm produced carbon dioxide which was detected by its IR spectrum (see Fig. 7c). 254 and 300 nm photolysis of CH<sub>3</sub>CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) in acetonitrile were followed by FTIR spectroscopy in the region of CO stretching vibrations. As can be seen in Fig. 8, the CO frequencies at 2019, 1913 and 1892 cm<sup>-1</sup>, belonging to the parent complex, decrease and the formation of a new species is evidenced by the new CO-stretching vibrations at 1934, 1902, 1860 and 1823 cm<sup>-1</sup>. FTIR spectra recorded after 14 h of irradiation at 254 nm show that about 93% of the parent complex underwent photolysis. This can be inferred from the decrease of the 2019 cm<sup>-1</sup> peak, where no new absorptions can interfere. Nevertheless, when photolysis is carried out at 300 nm under identical photochemical conditions only 50% of the CH<sub>3</sub>CO<sub>2</sub>Re(CO)<sub>3</sub>(2,2'-bipy) was photolyzed. For the new CO-stretching vibrations, the absorbance ratio  $A_v(\lambda_{\text{phot}} = 254 \text{ nm}) / A_v(\lambda_{\text{phot}} = 300 \text{ nm})$  was 1.67, 1.33 and 1.22 at  $\nu = 1823, 1860$  and  $1934 \text{ cm}^{-1}$ , respectively. This absorbance ratio dependence on



**Fig. 5** Transient spectra of species generated after the 337 (Fig. 5a, in  $\text{CH}_3\text{CN}$ ) and 351 nm (Figs. 5b and c) irradiations of deaerated  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  solutions of  $\text{LRe}(\text{CO})_3(2,2'\text{-bipy})$  complexes. See key to the spectra in the figure.



**Fig. 6** Concentration dependence of the luminescence lifetime of anthracene-9- $\text{CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  in  $\text{CH}_3\text{CN}$ .

the wavelength suggests that more than one product is formed with their relative amounts depending on the irradiation wavelength.

## Discussion

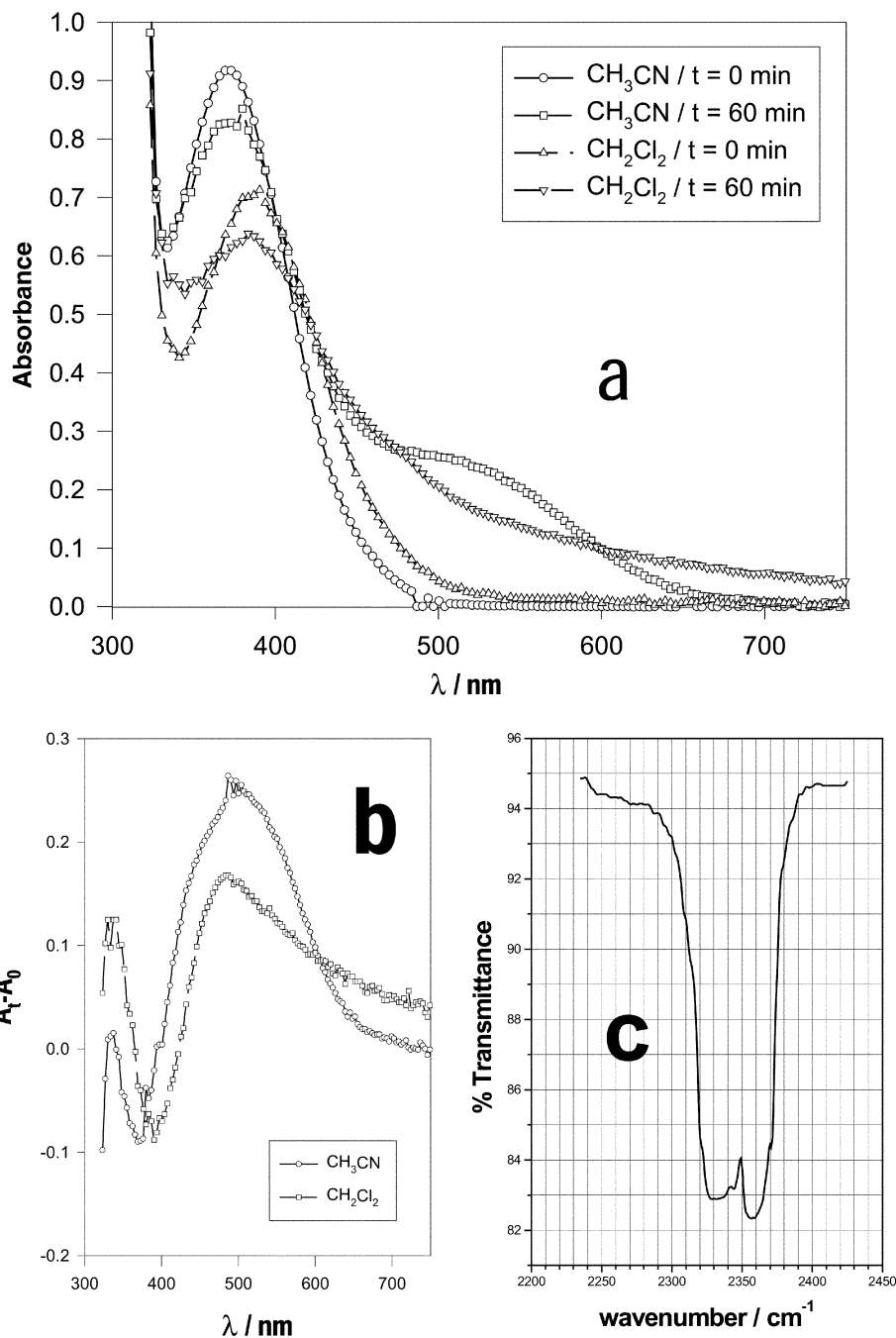
A common feature in the photophysics of all the  $\text{R-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  complexes studied here was that two emissive excited states resulted from irradiation at wavelengths higher than 300 nm. The short-lived excited state could be easily identified with the  ${}^3\text{MLCT}_{2,2'\text{-bipy} \rightarrow \text{Re}}$ , however, the nature of the long-lived excited state is not straightforwardly inferred.

In the first place, NMR results showed (see Table 5), in accordance with the Rx, no evidence for the existence of more than one species in the ground state in solution or the solid phase. On the other hand, conductivity measurements lead

**Table 5**  ${}^1\text{H}$  NMR resonances in  $\text{CH}_3\text{-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})^{a,b}$

Solvent	Aromatic protons			Aliphatic protons	
$\text{CDCl}_3$	$\delta_{\text{H}_{6,6'}}$	$\delta_{\text{H}_{5,5'}}$	$\delta_{\text{H}_{4,4'}}$	$\delta_{\text{H}_{3,3'}}$	$\delta_{\text{Methyl}}$
	9.21sd	7.54st	8.08st	8.17d	1.60s
$\text{CD}_3\text{CN}$	$\delta_{\text{H}_{6,6'}}$	$\delta_{\text{H}_{5,5'}}$	$\delta_{\text{H}_{4,4'}}$	$\delta_{\text{H}_{3,3'}}$	$\delta_{\text{Methyl}}$
	9.06d	7.62st	8.20st	8.40d	1.43s

<sup>a</sup> Aromatic protons named as  $\text{H}_{i,i'}$  correspond to the H atoms bonded to the  $\text{C}_{i,i'}$  in the 2,2'-bipyridine molecule. Shifts are in ppm from  $\text{SiMe}_4$ . Instrument frequency: 300 MHz. <sup>b</sup> s = Singlet, d = Doublet, sd = Pseudodoublet and st = Pseudotriplet.

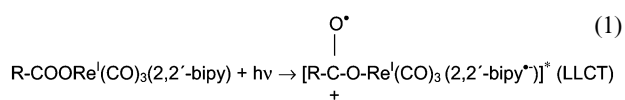


**Fig. 7** Steady state photolysis of  $\text{CH}_3\text{-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$ . (a) Spectral changes upon 300 nm irradiation of  $\text{N}_2$ -deaerated solutions in  $\text{CH}_3\text{CN}$  ( $2.6 \times 10^{-4}$  M, optical path = 1 cm) and  $\text{CH}_2\text{Cl}_2$  ( $2.3 \times 10^{-4}$  M, optical path = 1 cm). (b) Differential spectra obtained after subtracting the initial spectrum from that recorded after 60 min of photolysis. (c) IR spectrum of  $\text{CO}_2$  formed after 12 h of 300 nm photolysis of a  $\text{N}_2$ -deaerated  $1.9 \times 10^{-3}$  M solution in  $\text{CH}_3\text{CN}$ . See text for details.

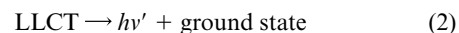
us to discard the possible presence of dissociated species in solution. These results indicated that the double emission did not originate from two different species in the ground state.

Secondly, previous studies on  $\text{XRe}(\text{CO})_3(2,2'\text{-bipy})$  complexes (where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CH}_3\text{CN}$  or mono-azine) showed only a single emission attributed to the  $^3\text{MLCT}_{2,2'\text{-bipy} \rightarrow \text{Re}^{17,20}}$ . Moreover, emission lifetimes and emission spectra led us to discount the view that the long-lived emitting excited state was a 2,2'-bipy intraligand excited state decaying to the ground state.

In addition, emission spectra and emission lifetimes were very similar, being independent of the nature of the R moiety. This fact would mean that the bridging carboxylate group might be playing a major role in the nature of the long-lived emission excited state. For instance,



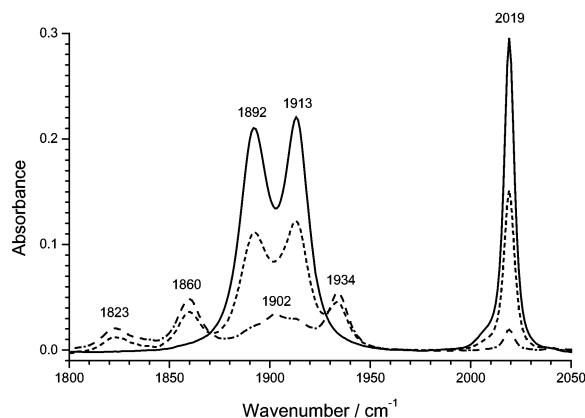
Such an excited state could return to the ground state,



or decompose by decarboxylation.



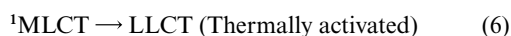
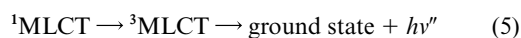
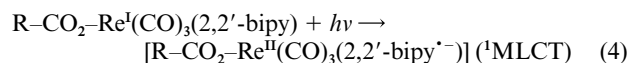
It can be seen in Fig. 8 that upon 254 and 300 nm photolysis of  $\text{CH}_3\text{CO}_2\text{Re}(\text{CO})_3(2,2'\text{-bipy})$  new IR bands appear at 1860 and  $1934 \text{ cm}^{-1}$  attributed to dimer formation by recombination of the  $\text{Re}(\text{CO})_3(2,2'\text{-bipy}')$ .<sup>21</sup> However, another band at 1823



**Fig. 8** FTIR spectral changes upon 254 and 300 nm steady state photolysis of a  $\text{N}_2$ -deaerated  $3 \times 10^{-3}$  M solution of  $\text{CH}_3\text{-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  in acetonitrile. (—)  $t = 0$ ; (---)  $t = 14$  h,  $\lambda_{\text{phot}} = 300$  nm; (- · -)  $t = 14$  h,  $\lambda_{\text{phot}} = 254$  nm. See text for details.

$\text{cm}^{-1}$ , characteristic of the bridging CO, shows up. It has been reported<sup>2</sup> that when photolyzing acetonitrile solutions of  $\text{ClRe}(\text{CO})_3(4\text{-phenylpyridine})_2$  CO bridged dimers are formed after losing the other carbon monoxide molecules. In Fig. 8 the characteristic bands belonging to the parent complex disappear during the photolysis indicating that CO coordinated to the Re is released, like in the photolysis of  $\text{ClRe}(\text{CO})_3(4\text{-phenylpyridine})_2$ .

Considering that when the temperature is reduced to 273 K the emission spectrum showed only the features corresponding to the  $^3\text{MLCT}$  luminescence though emission lifetimes were temperature independent between 273 and 313 K, and taking into account the lower emission quantum yield observed in these complexes compared with  $\text{BrRe}(\text{CO})_3(2,2'\text{-bipy})$ , it is possible to infer that actually:

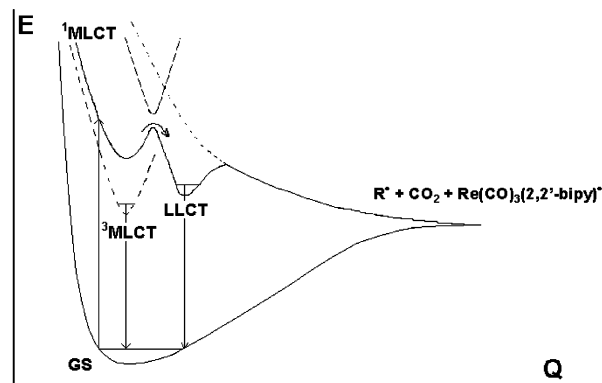


The fact that the long-lived emission is not observed in  $\text{CH}_2\text{Cl}_2$  could be attributed to the higher reactivity of the halocarbon solvents which introduces an additional pathway for the LLCT depletion.

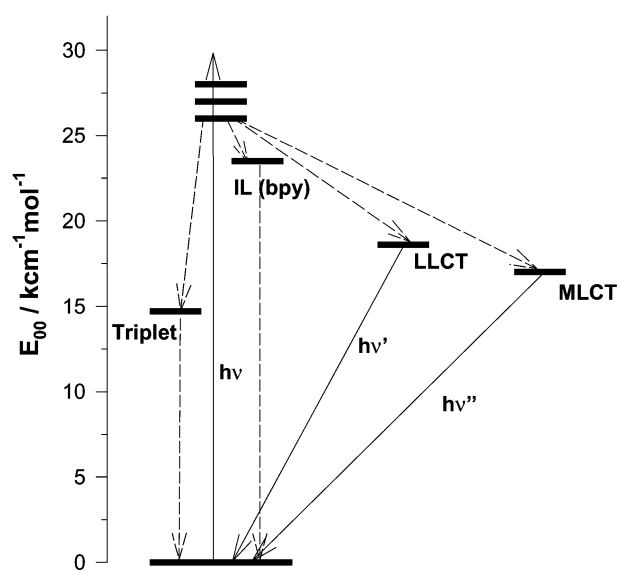
## Concluding remarks

The photophysical and photochemical properties of  $\text{R-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  complexes can now be related to the actual excited state properties. A schematic representation of the potential energy curves (Fig. 9) shows the relative positions of the excited states involved in the photophysics and photochemistry of  $\text{R-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  complexes when excited with photonic energies  $E_{h\nu} < 33.3 \text{ kJ mol}^{-1}$ . Redox potentials of the  $\text{Re}^{\text{II}}/\text{Re}^{\text{I}}$ ,  $2,2'\text{-bipy}/2,2'\text{-bipy}^{\cdot-}$  and  $\text{RCO}_2/\text{RCO}_2^-$  couples in Table 3 were used for the calculation of the 0–0 point energies,  $E_{00}$ , of  $^1\text{MLCT}$ ,  $^3\text{MLCT}$  and LLCT. A value of the 0–0 point energy,  $E_{00} \approx 23.5 \text{ kJ mol}^{-1}$ , was assigned to the IL based on the luminescence of the protonated  $2,2'\text{-bipy}$ .

When R is naphthalene, anthracene or pyrene we must take into account the arene triplet excited state. The values,  $E_{00} = 21.2 \text{ kJ mol}^{-1}$ ,  $E_{00} \approx 14.7 \text{ kJ mol}^{-1}$  and  $E_{00} \approx 16.8 \text{ kJ mol}^{-1}$ , for naphthalene, anthracene and pyrene triplets respectively, have been reported.<sup>22</sup> We can include all the relevant excited states in a Jablonski diagram (Fig. 10).



**Fig. 9** Schematic representation of the potential energy curves of the ground state,  $^1\text{MLCT}$ ,  $^3\text{MLCT}$ , LLCT and the dissociative state of  $\text{R-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  complexes. Excitation into the  $^1\text{MLCT}$  state may decay by two different ways: to the nonreactive  $^3\text{MLCT}$  and from there to the ground state by radiative and non-radiative processes or by crossing the barrier to the emissive LLCT state which eventually reaches the dissociative state.



**Fig. 10** Jablonski diagram showing  $E_{00}$  energies of  $^1\text{MLCT}$ ,  $^3\text{MLCT}$ , LLCT, Triplet (R = Anthracene) and IL ( $2,2'\text{-bipy}$ ) states of  $\text{R-CO}_2\text{-Re}(\text{CO})_3(2,2'\text{-bipy})$  complexes. See text for details.

A final comment is required concerning the absence of intramolecular quenching of the emitting excited states by the triplet of anthracene or pyrene, as usually observed.<sup>23</sup> This lack of intramolecular quenching should be attributed to the carboxylate-induced decoupling of donor and acceptor wavefunctions. This carboxylate-induced insulation has already been observed in several recently studied cases.<sup>6–8</sup>

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