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New asymmetric N-heterocyclic-bridged mixed-valent dinuclear complexes of rhenium and ruthenium

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Abstract

Two new mixed-metal mixed-valent complexes, of formulae: $[(CO)_3(bpy)Re^I(bpe)Ru^{III}(NH_3)_5]^{4+}$ and $[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+}$ (where bpy = 2,2′-bipyridine, bpe = *trans*-1,2-bis(4-pyridil)ethene, 4-CNpy = 4-cyanopyridine), were prepared and characterized as solids and in acetonitrile solutions. From their spectroscopic, electrochemical and photophysical properties, the values for the reorganization energies λ and electronic coupling elements H_{AB} for the metal-to-metal intramolecular electron transfers mediated by the N-heterocyclic bridges were calculated, using the Marcus–Hush formalism. For the 4-CNpy derivative, the reverse ruthenium-to-rhenium charge recombination—that should follow light excitation—is expected to be in the normal region, while for the bpe derivative this reaction is predicted to lie in the inverted region. The differences in redox potentials and in λ for both species account for these changes, which are relevant in the design of efficient photoconverters.

Keywords: Mixed-valence; Ruthenium complexes; Rhenium complexes; Intramolecular electron transfer; Energy conversion

1. Introduction

The control of the reorganization energies for intramolecular electron transfers in mixed-valent complexes is relevant to the design of efficient molecular photochemical devices that convert solar into chemical or electrical energy [1]. The possibility of rapid intramolecular electron transfer process in asymmetric dinuclear complexes has been discussed by Lin and Guarr [2]. Related to that study, we have demonstrated that increasing the redox asymmetry in simple dinuclear mixed-metal systems can eventually lead to intramolecular charge transfers in the inverted region [3]. We now discuss in this work how to induce these changes by choosing two metallic centers of very different redox potentials—such as rhenium and ruthenium—and N-heterocyclic ligands with suitable lengths in novel asymmetric mixed-valent dinuclear complexes.

2. Experimental

2.1. Materials and techniques

All chemicals used were p.a. MeCN was distilled over $KMnO_4$ and dried over molecular sieves. IR spectra were measured (as KBr pellets) by using a double-beam Perkin–Elmer 983G spectrophotometer or a Perkin–Elmer 1600 FT IR spectrophotometer. UV–Vis spectra were recorded on a Shimadzu UV-160A UV–Vis spectrophotometer, provided with 1-cm cells. Electrochemical data were carried out with a EQMAT-S1 cyclic voltammetry equipment. A standard three-electrode compartment cell was used with Ag/AgCl (3 M KCl) as a reference electrode and Pt as working and auxiliary electrodes. All values of redox potentials, $E_{1/2}$, were referred to Ag/AgCl. Emission studies were performed by using a spectrofluorometer Shimadzu RF-5301 PC, provided with 1-cm fluorescence cells. Ar was bubbled through the solutions prior to electrochemical and photophysical measurements. Chemical analyses were done at INQUIMAE, University of Buenos Aires, Argentina.

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2.2. Syntheses of complexes

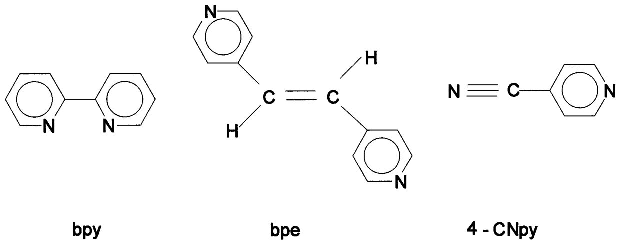
The PF_6^- salts of the ions $[Re(CO)_3(bpy)(bpe)]^+$ (**1**) and $[Re(CO)_3(bpy)(4\text{-}CNpy)]^+$ (**2**) (bpy = 2,2′-bipyridine, bpe = *trans*-1,2-bis(4-pyridil)ethene, 4-CNpy = 4-cyanopyridine), were prepared and purified using a similar method to that described for the 4,4′-bpy analogue [3]. For the complex (**1**)(PF_6), the yield obtained was 86% (*Anal.* Found: C, 38.2; H, 2.4; N, 7.7. Calc.: C, 38.4; H, 2.3; N, 7.2%). For the complex (**2**)(PF_6), the yield obtained was 78% (*Anal.* Found: C, 34.5; H, 2.6; N, 8.2. Calc.: C, 33.8; H, 1.8; N, 8.3%).

The structure of the ligands is shown in Scheme 1.

The new dinuclear PF_6^- salts of the complexes $[(CO)_3(bpy)Re(bpe)Ru(NH_3)_5]^{3+}$ (**3**) and $[(CO)_3(bpy)Re(4\text{-}CNpy)Ru(NH_3)_5]^{3+}$ (**4**) were synthesized as described for the 4,4′-bpy analogue [3]. Thus, 0.1 mmol of $[Re(CO)_3(bpy)(L)](PF_6)$ (with L = bpe, 4-CNpy) were stirred in Me_2CO (10 ml) under Ar for 1 h, and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (54 mg, 0.1 mmol; prepared as in [4]) was added, followed by continuous stirring under Ar for 2 h in the dark. One hundred ml of ether were added to precipitate the complex, which was dissolved in MeOH and purified by chromatography on Sephadex LH-20, using MeOH as the eluting solvent. The second fraction was collected, roto-evaporated to 5 ml, cooled and precipitated with ether (100 ml). The solids were filtered, washed with ether and dried in vacuo under P_4O_{10}. For complex (**3**)$(PF_6)_3$, the yield obtained was 32% (*Anal.* Found: C, 24.5; H, 2.8; N, 9.8. Calc.: C, 24.4; H, 2.7; N, 10.3%). For complex (**4**)$(PF_6)_3$, the yield obtained was 42% (*Anal.* Found: C, 19.7; H, 2.7; N, 9.7. Calc.: C, 19.8; H, 2.4; N, 10.9%).

The mixed-valent ion $[(CO)_3(bpy)Re(bpe)Ru(NH_3)_5]^{4+}$ (**5**) was generated in situ by adding Br_2 vapor to an MeCN solution of **3**. $[(CO)_3(bpy)Re(bpe)Ru(NH_3)_5](PF_6)_4 \cdot 2MeCN$ was generated by adding excess of Br_2 (0.7 ml) to an acetonitrile solution (7 ml) of **3** (13 mg) after adding stoichiometric amounts of $Bu_4{}^nNPF_6$ (4 mg). After 30 min of reaction, 100 ml of ether was added to precipitate the complex. The solid was filtered, washed with ether and dried under vacuo over P_4O_{10}. Yield: 7 mg (48%) (*Anal.* Found: C, 24.7; H, 3.2; N, 10.8. Calc.: C, 24.2; H, 2.7; N, 10.7%).

The mixed-valent ion $[(CO)_3(bpy)Re(4\text{-}CNpy)Ru(NH_3)_5]^{4+}$ (**6**) was generated in situ by adding stoichiometric amounts of *p*-fluorobenzene-diazonium hexafluorophosphate in MeCN (prepared as in [5]) or generated spectroelectrochemically, by using the same voltammetry equipment described above and a spectroeletrochemical cell designed ad hoc, provided with a Pt grid as a working electrode, and Au and Ag wires as auxiliary and reference electrodes, respectively.



Scheme 1.

3. Results and discussion

3.1. IR spectra

PF_6^- salts of complexes **3** and **4** present similar spectra. Three intense carbonyl stretching frequencies $\nu(CO)$, characteristic of C_s symmetry [6], appear at 2032, 1927 and 1913 cm^{-1} for complex (**3**)$(PF_6^-)_3$ and at 2032, 1933 and 1915 cm^{-1} for complex (**4**)$(PF_6^-)_3$. The slightly higher values of $\nu(CO)$ for the 4-CNpy derivative point to a higher π-acceptor ability of 4-CNpy when compared with bpe [6]. Besides, the typical ammonia deformation frequencies δ_{sym} (NH_3), that appear at 1282 cm^{-1} for complex (**3**)$(PF_6^-)_3$ and at 1281 cm^{-1} for complex (**4**)$(PF_6^-)_3$, indicate localized oxidation state (II) for the Ru center in both complexes [7]. The nitrile streching frequency, $\nu(C{\equiv}N)$, appears at 2177 cm^{-1} in complex (**4**)$(PF_6^-)_3$, which is a clear indication of nitrile N coordination to the $Ru^{II}(NH_3)_5$ moiety, since free 4-CNpy has the same band at 2241 cm^{-1} [8].

In the dinuclear PF_6^- salt of complex **5**, the carbonyl frequencies are hardly changed when compared with the mononuclear parent complex, evidencing a slight inter-

Table 1
Electronic spectral data in MeCN

Complex	λ_{max} (nm) (10^{-3} ε_{max}, M^{-1} cm^{-1}) [a]
$[Re(CO)_3(bpy)(bpe)]^+$ (**1**)	331(8.3), 319(12.2), 306(12.3), 283(sh), 246(6.6)
$[Re(CO)_3(bpy)(4\text{-}CNpy)]^+$ (**2**)	344(5.4), 318(12.0), 306(13.1), 268(13.9), 244(16.8), 207(23.6)
$[(CO)_3(bpy)Re^I(bpe)Ru^{II}(NH_3)_5]^{3+}$ (**3**)	543(6.8), 334(12.3), 316(18.2), 305(18.4), 290(17.2), 243(13.0), 206(22.8)
$[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{II}(NH_3)_5]^{3+}$ (**4**)	486(5.9), 346(4.9), 319(10.6), 306(10.3), 246(15.3), 205(20.0)
$[(CO)_3(bpy)Re^I(bpe)Ru^{II}(NH_3)_5]^{4+}$ (**5**) [b]	477(0.6), 345(12.8), 319(19.2), 310(17.6), 283(sh), 241(11.2)
$[(CO)_3(bpy)Re^I(4\text{-}CNpy)Ru^{III}(NH_3)_5]^{4+}$ (**6**) [c]	454(1.2), 346(4.5), 318(8.1), 305(7.8)

[a] At 22 °C error: ±2 nm in λ_{max}, ±5% in ε_{max}.
[b] In MeCN 0.1 M CF_3COOH.
[c] By spectroelectrochemical titration of **4**.

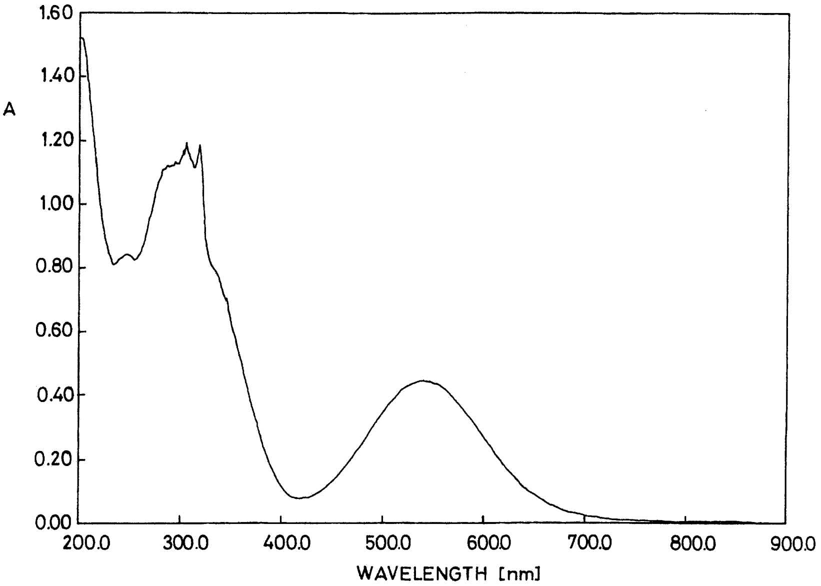


Fig. 1. UV–Vis spectrum of $[(CO)_3(bpy)Re(bpe)Ru(NH_3)_5]^{3+}$, in MeCN ($C = 6.5 \times 10^{-5}$ M).

action between both metallic centers [6]. On the other hand, δ_{sym} (NH_3) appears at 1330 cm^{-1}, with indicates localized oxidation state (III) for the Ru center [7].

3.2. UV–Vis spectra

Table 1 shows the UV–Vis absorptions of all complexes at 22 °C in MeCN. Figs. 1 and 2 show the complete UV–Vis spectrum of complexes **3** and **4**, respectively. The UV absorptions between 200 and 300 nm in all species can be assigned to characteristic intraligand $\pi \rightarrow \pi^*$ transitions of the pyridinic ligands [9].The absorptions at $\lambda_{max} = 334$ and 346 nm in **3** and **4**, respectively, correspond to those at 331 and 344 nm in the mononuclear parent complexes **1** and **2**, and thus can be assigned to metal-to-ligand charge transfer (MLCT) transitions $d_\pi(Re) \rightarrow \pi^*(bpy)$. The absorptions at $\lambda_{max} = 543$ and 486 nm in **3** and **4** are absent in **1** and **2** and so can be assigned to MLCT transitions $d_\pi(Ru) \rightarrow \pi^*(L)$, with L = bpe and 4-Cnpy, respectively. These bands are shifted to lower energies than those of the corresponding bands in $[Ru(NH_3)_5(bpe)]^{2+}$ ($\lambda_{max} = 500$ nm in MeCN, [10]) and $[Ru(NH_3)_5(4\text{-}CNpy)]^{2+}$) (nitrile-bonded, ($\lambda_{max} = 425$ nm in H_2O, [8]), indicating some degree of electronic communication between both metallic centers in **3** and **4**.

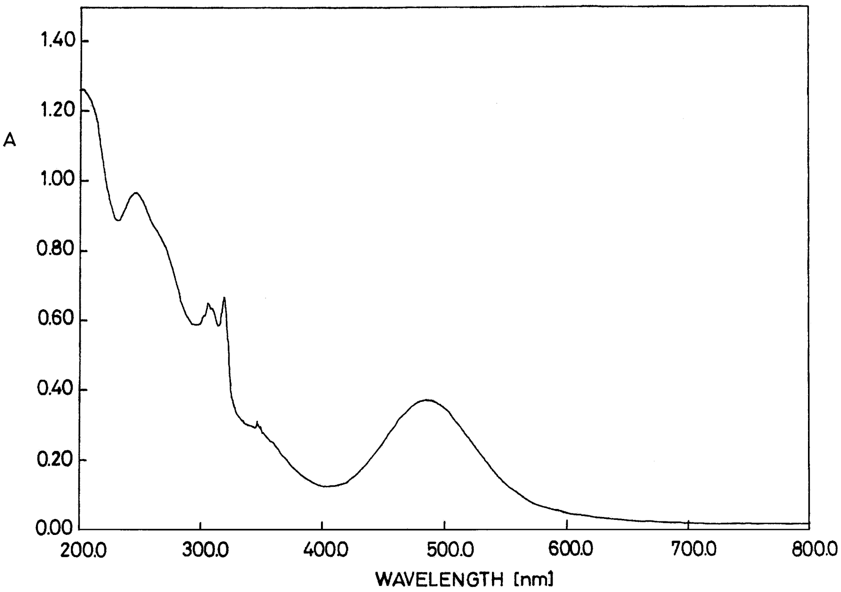


Fig. 2. UV–Vis spectrum of $[(CO)_3(bpy)Re(4\text{-}CNpy)Ru(NH_3)_5]^{3+}$, in MeCN ($C = 6.3 \times 10^{-5}$ M).

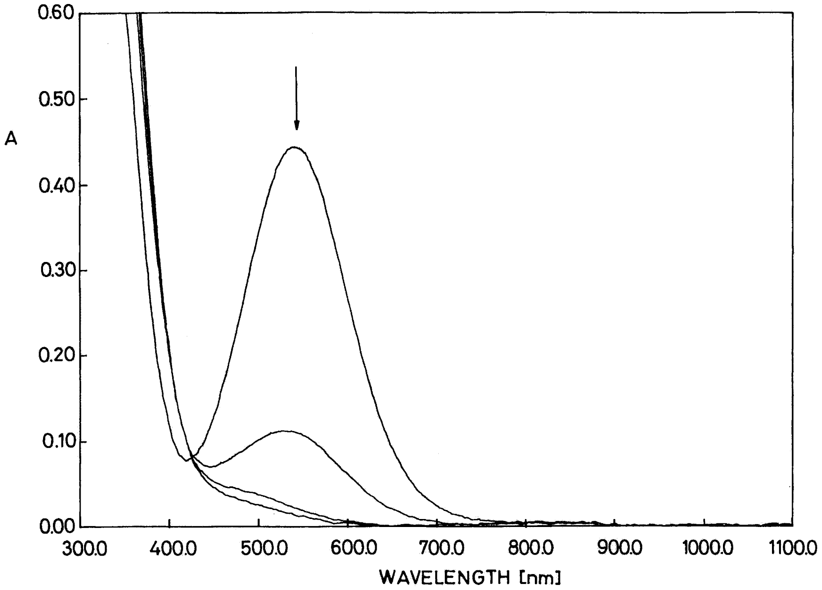


Fig. 3. Spectrophotometric titration of $[(CO)_3(bpy)Re(bpe)Ru(NH_3)_5]^{3+}$ by Br_2, in MeCN ($C = 6.0 \times 10^{-5}$ M). The arrow indicates increasing amounts of oxidant from a mole relation $[Br_2]/[Ru] = 0–1.25$.

Fig. 3 shows a spectrophotometric redox titration of complex **3** with Br_2 in MeCN, and Fig. 4 shows a spectroelectrochemical oxidation of **4**. In the mixed-valent species **5** and **6**, the intense bands at 543 and 486 nm disappear completely and new bands appear at $\lambda_{max} \approx 477$ nm ($\varepsilon_{max} \approx 600$ M^{-1} cm^{-1}) and at $\lambda_{max} \approx 454$ nm ($\varepsilon_{max} \approx 1200$ M^{-1} cm^{-1}), respectively; they can be assigned to metal-to-metal charge transfer (MMCT) transitions $Re^{I} \rightarrow Ru^{III}$. In complex **4**, a chemical oxidation with the p-fluorobenzene-diazonium cation gives the same final spectrum as that of Fig. 4. Moreover, in the analogous species bridged by 4,4′-bipyridine (4,4′-bpy), $[(CO)_3(bpy)Re(4,4'\text{-bpy})Ru(NH_3)_5]^{4+}$, the same band is observed at $\lambda_{max} \approx 480$ nm ($\varepsilon_{max} \approx 980$ M^{-1} cm^{-1}) [3]. The appearance of MMCT bands in the visible region can be accounted for by the high redox asymmetry in these mixed-valent species, as discussed below.

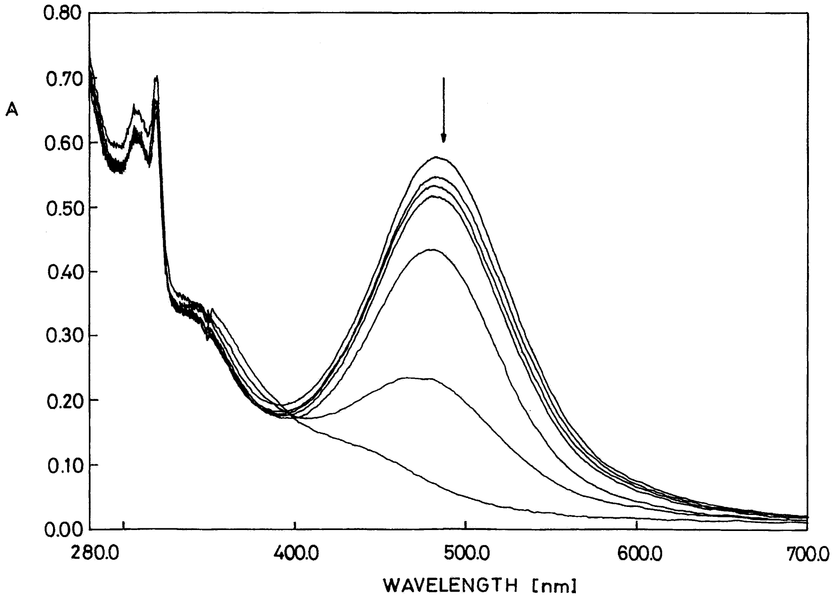


Fig. 4. Spectroelectrochemical titration of $[(CO)_3(bpy)Re(4\text{-}CNpy)Ru(NH_3)_5]^{3+}$ in MeCN ($C = 8.0 \times 10^{-5}$ M). The arrow indicates increasing applied potential from 0.5 up to 1 V.

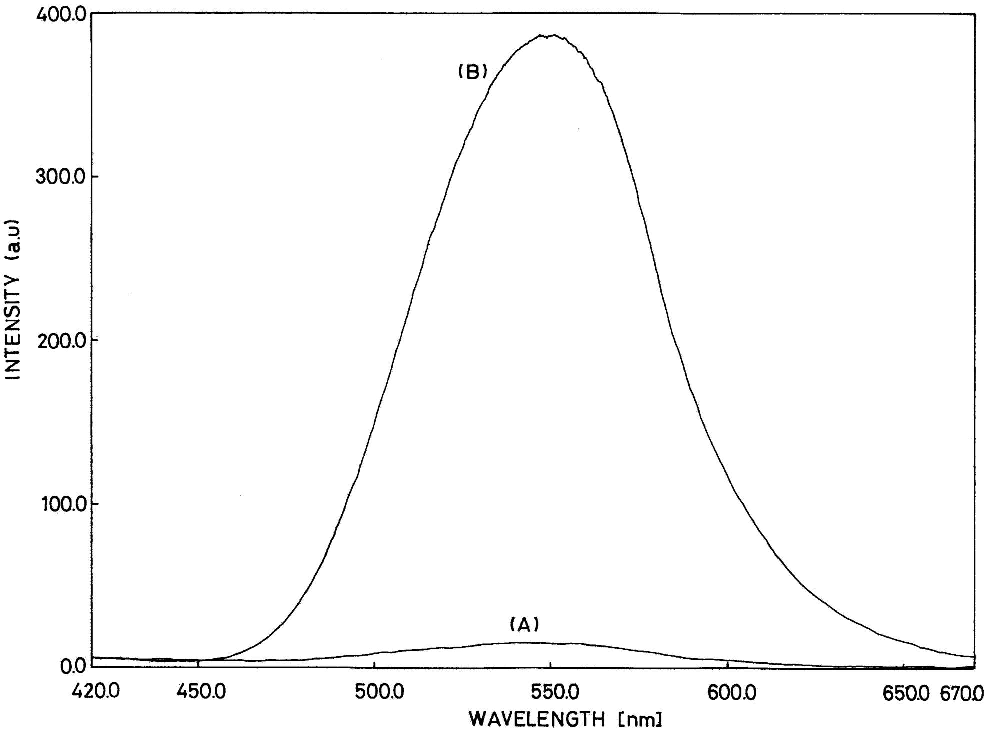


Fig. 5. (A) Emission spectrum of complex **6**, $[(CO)_3(bpy)Re(4\text{-}CNpy)Ru(NH_3)_5]^{4+}$. (B) Emission spectrum of complex **2**, $[Re(CO)_3(bpy)(4\text{-}CNpy)]^+$ (isoabsorbative solutions in MeCN, $\lambda_{ex} = 340$ nm, $t = 22$ °C).

3.3. Electrochemistry

The voltammperometric studies of the dinuclear complexes **3** and **4** in MeCN, 0.1 M TBAH, and scan rate $v = 200$ mV s^{-1}, in the oxidative range shows two waves that can be assigned to the couples Re^{II}/Re^{I} ($E_{1/2} = 1.76$ and 1.89 V for the complexes bridged by bpe and 4-CNpy, respectively) and Ru^{III}/Ru^{II} ($E_{1/2} = 0.42$ and 0.73 V for the same species, respectively). In the series $[(CO)_3(bpy)Re(L)Ru(NH_3)_5]^{3+}$, the values obtained for $\Delta E_{1/2} = E_{1/2}(Re^{II}/Re^{I}) - E_{1/2}(Ru^{III}/Ru^{II})$ are: $\Delta E_{1/2} = 1.34$ eV for L = bpe, and $E_{1/2} = 1.16$ V for L = 4-CNpy. Previously, we had measured the corresponding value of $\Delta E_{1/2} = 1.40$ eV for L = 4,4′-bpy [3].

3.4. Luminiscence

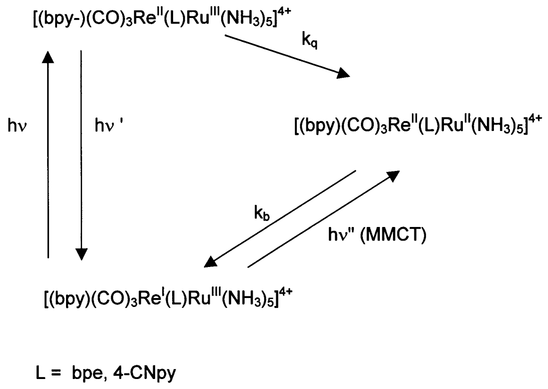
Fig. 5 shows the emission spectra at 22 °C ($\lambda_{ex} = 340$ nm) of the mixed-valent species **6**, as compared with the mononuclear parent complex **2**. The results are similar when comparing the mixed-valent species **5** with its parent complex **1**. In both cases, as in the previous study with the 4,4′-bpy derivative [3], the emission of the rhenium chromophore ($\lambda_{em} = 540$ nm for **1** and $\lambda_{em} = 546$ nm for **2**) in the mononuclear complexes is quenched, although not completely, in both dinuclear species, evidencing the possibility of electron transfer in the excited state, as discussed before [2,3], and shown in Scheme 2.

3.5. Calculations of intramolecular electron transfer parameters

Using the Marcus–Hush formalism and the experimental spectral data of MMCT transitions in the mixed-valent complexes, the reorganization energy λ for the intramolecular electron transfers through the N-heterocyclic bridges can be calculated as:

$$\lambda = E_{op} - \Delta G^\circ - \Delta E_{ex} \quad (1)$$

where E_{op} is the energy of the absorption maximum (in eV), ΔG° is the free energy difference between both redox sites (obtained approximately as the difference in the redox potentials $\Delta E_{1/2}$, defined earlier) and ΔE_{ex} is an excited-state energy difference, estimated as 0.25 eV



Scheme 2.

Table 2
Intramolecular electron transfer parameters in the series of mixed-valent mixed-metal complexes of the type $[(CO)_3(bpy)Re^I(L)Ru^{III}(NH_3)_5]^{4+}$

L	r (Å)	E_{op} (eV)	ΔG° (eV)	λ (eV)	H_{AB} (cm^{-1})
4-CNpy	9.3	2.73	1.16	1.32	805
4,4′-bpy	11.3	2.58	1.40	0.93	749
bpe	13.8	2.60	1.34	1.01	467

for various ruthenium complexes [11]. We can also determine the electronic coupling elements H_{AB} through the well-known Hush formula [12]:

$$H_{AB} = \frac{2.06 \times 10^{-2}}{r}(\varepsilon_{max} \cdot \Delta\tilde{\nu}_{1/2} \cdot \tilde{\nu}_{max})^{1/2} \quad (2)$$

where H_{AB} is the donor–acceptor coupling element (in cm^{-1}), r is the metal-to-metal distance (in Å) and ε_{max}, $\Delta\tilde{\nu}_{1/2}$ and $\tilde{\nu}_{max}$ are the molar absorptivity (in M^{-1} cm^{-1}), bandwidth at half-height (in cm^{-1}) and energy maximum of the MMCT band (in cm^{-1}), respectively. Table 2 shows the obtained values for these parameters in the series of mixed-metal mixed-valent complexes $[(CO)_3(bpy)Re(L)Ru(NH_3)_5]^{4+}$, (with L = 4-CNpy, 4,4′-bpy and bpe).

For all mixed-valent species of Table 2, the values of $H_{AB} \ll \lambda$; therefore, these complexes can be classified as Class (II) (slightly delocalized) of Robin and Day nomenclature [12]. The electronic coupling H_{AB} decreases with increasing metal-to-metal distance, as expected [7]. However, the value of λ for the 4-CNpy complex **6** is much higher than expected, when considering the distance dependence of the reorganization energy [7], but this 'anomaly' can be accounted for if we consider that the metal-to-ligand distances in nitrile-bonded complexes are much shorter than those of pyridinic N-bonded species; for example, in $[Ru(NH_3)_5L]^{3+}$ complexes, Ru^{III}–N(L) bond length is 2.077 Å for L = pyridine, and 2.025 Å for L = benzonitrile [13]. Current theories predict that λ increases with decreasing metal-to-ligand distance [14]. The consequence of the higher value of λ and lower value of ΔG° in the 4-CNpy-bridged complex—as compared with the other two—is that the reverse intramolecular electron transfer $Ru^{II} \rightarrow Re^{II}$ (that may follow after light excitation) falls in the normal region [λ (= 1.32 eV) > $-\Delta G^\circ$ (= 1.16 eV)], while for the bpe-bridged species (as disclosed before for the 4,4′-bpy one [3]) the analogous charge recombination $Ru^{II} \rightarrow Re^{II}$ is predicted to be in the Marcus inverted region [14] [λ (= 1.01 eV) < $-\Delta G^\circ$ (= 1.34 eV)]. This tuning of the reorganization energies and the driving forces by the bridging ligands, as well as the tuning introduced by 'innocent' co-ligands described in a previous work [15], are important factors for enhancing the efficiency of molecular photoconverters.

4. Conclusions

We conclude that the reorganization parameters and driving forces for intramolecular electron transfers in the new mixed-valent asymmetric complexes of rhenium and ruthenium prepared and characterized in this work can be altered when changing the bridging N-heterocyclic ligands. Thus, we predict that the charge recombination that follows light excitation in **6** falls in the normal region, while the same reaction in the related complex **5** lies in the Marcus inverted region.

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