Tailoring mixed-valence Co^{III}/Fe^{II} complexes for their potential use as sensitizers in dye sensitized solar cells†

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Dinuclear class II Co^{III}/Fe^{II} mixed-valence complexes of type $[L_nCo^{III}(\mu\text{-NC})Fe^{II}(CN)_3L_2]^{m-}$ (where L_n represents a pentadentate macrocycle and L_2 a bpy ligand or two cyanides) have electronic properties that make them possible sensitizers in DSSC (dye sensitized solar cells). For this purpose the new complex $Na_2[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]$ has been prepared and characterized by the usual methods and its sensitizer properties compared with those of the already known $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_3(bipy)_{eq,ax}](ClO_4)$. The complex $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^{2-}$ has been designed for the actuation of an electron injection from the cobalt centre on MMCT, while the $[\{trans\text{-}L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_3(bipy)]^+$ structure can produce a tuned injection from the iron centre *via* an MLCT electronic state, as described for similar systems. The characterization on solid oxide semiconductor supports has been carried out for these two complexes and the results have been compared with the behaviour observed in aqueous solution and in solvents of varying polarities. Their use in DSSC has been checked and, while a sensitizer response is observed for $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^{2-}$, complex $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_3(bipy)_{eq,ax}]^+$ does not produce any electrical current on illumination. The low efficiency of the built DSSC can be easily related both with the very low value of the extinction coefficient of the MMCT band responsible for the electron injection, and with the small driving force for the reduction of the complex with the standard I_2/I_3^- system used after electron injection.

Introduction

The use of dye sensitized solar cells (DSSC) as an alternative approach to the "classical" photovoltaic silicon panels for the production of electrical power is not new and the subject has been the centre of important efforts and advances in recent years, both basically and industrially.[1] The importance of the field from a sustainable point of view is immense and the need of a fast response in the field is generally accepted.[2] The basic principles of the actuation of these cells are already well understood, the role of the sensitizers fully established, and a great amount of literature exists in this respect.[3] The fact that the cells have to work at relatively high temperatures creates one of the most serious deterrents for the implementation of such cells, as constructed nowadays.[4] The use of volatile solvents for the redox mediator of the systems is not ideal, consequently there is a need for new sensitizers and redox mediator electrolytes that can be contained in cells with more innocent, resistant and ecological solvents.[5]

We have been involved in recent years both in the improvement of the characteristics of such devices[6,7] and in the development of synthetic strategies allowing the formation of molecular, very robust and simple weakly-coupled (they belong to the class II Robin and Day classification)[8] mixed-valence complexes.[9–11] The Co^{III}/Fe^{II} cyanide-bridged complexes prepared (Chart 1) show an interesting MMCT (metal-to-metal charge-transfer) band generally centred in the 550 nm area. This fact makes them suitable for their use in devices containing systems requiring visible light for their electron transfer processes.[12] In fact, some developments on this area with implications on smart windows have already been published.[13]

In this paper we present the intended use of two new tailor-made dinuclear Co^{III}/Fe^{II} mixed valence complexes (Scheme 1) designed to ensure the possibility of two different electron injection pathways from the molecule to the mesoporous oxide semiconducting electrode of an DSSC.[14,15] The relative orientation of these metal dyads, as a key point for the electron injection, has also been looked into.[16,17]

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† Electronic supplementary information (ESI) available: Fig. S1: UV-Vis spectral changes on addition of solid $Na_2S_2O_8$ to $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^{2-}$ in water. Fig. S2: IR spectra of $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^{2-}$ dispersed in KBr and anchored of mesoporous TiO_2. Fig. S3: Comparison of the IPCE curve of a complete solar cell built on mesoporous TiO_2 electrodes using $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^{2-}$ as sensitizer and the visible spectrum of the sensitizer on the same surface. See DOI: 10.1039/b716855a

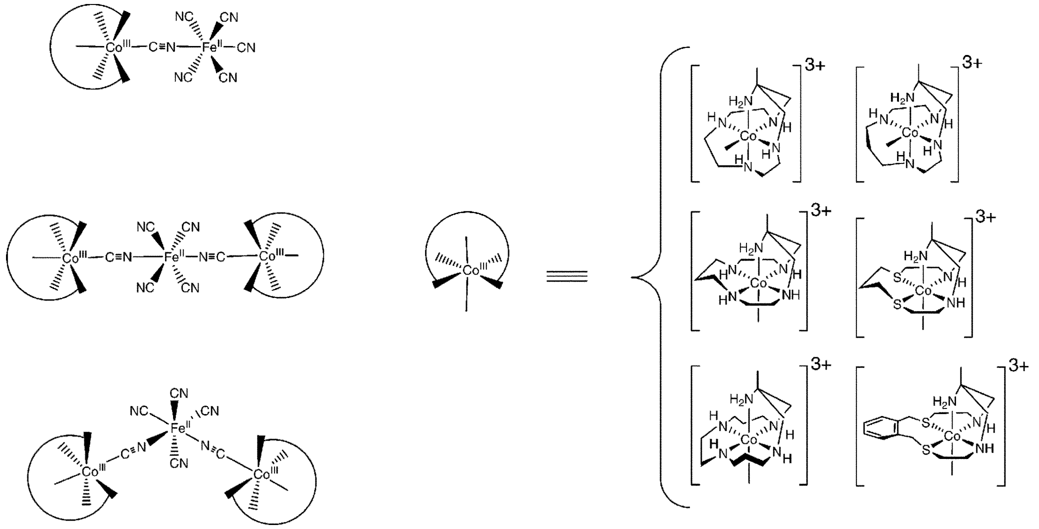
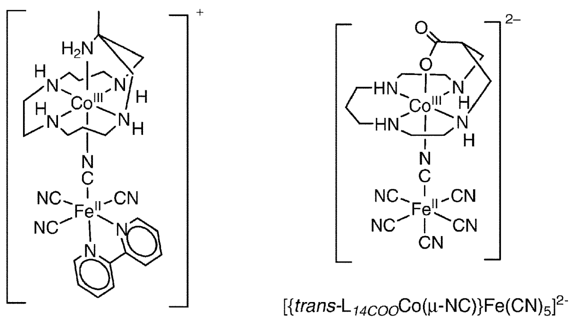


Chart 1



[{*trans*-L_{15}Co(μ-NC)}Fe$(CN)_3$$(bipy)_{eq,ax}$]$^+$

[{*trans*-L_{14COO}Co(μ-NC)}Fe$(CN)_5$]$^{2-}$

Scheme 1

The results obtained indicate that although for the [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}$(CN)_3$$(bpy)_{eq,ax}$]$^+$ complex no sensitization response is observed, for the carboxylato [{*trans*-L_{14COO}Co^{III}(μ-NC)}Fe^{II}$(CN)_5$]$^{2-}$ complex a typical sensitizer response is obtained. The results are interpreted in view of a dominant MMCT process that acts disfavouring the electron injection (direct or MLCT-assisted) from the iron centre and enables the electron transfer from the Co^{II} centre generated on illumination. The values obtained for efficiency of the DSSC are poor, the reason probably being the relatively low extinction coefficient of the complex compared with those for accepted well behaved sensitizers. Nevertheless, the real possibility of increasing the nuclearity and extinction coefficient of these mixed-valence species makes the results obtained very promising for future work.

Experimental

Synthesis

***trans*-[CoClL_{14COO}](ClO_4).** The precursor mononuclear cobalt complex for the preparation of Na_2[{*trans*-L_{14COO}Co^{III}-(μ-NC)}Fe^{II}$(CN)_5$] was obtained from the reaction of the new ligand L_{14COO}[18] with Co^{II}, following the same standard preparative procedure described for this family of complexes.[9,19–22] Ligand L_{14COO} was obtained as described for the analogous L_{15COO} but using the 2,3,2-tet linear amine instead of 3,2,3-tet used in the literature.[23] To a solution of 4 g of HL_{14COO}·4HCl in 50 cm^3 of water 2.6 g of $CoCl_2$·$6H_2O$ dissolved in 50 cm^3 of water were added and the pH set to 9 with 1 M NaOH solution. After bubbling air for 2 h, 1.5 g of activated charcoal and 15 cm^3 of concentrated HCl were added and the solution stirred for *ca.* 12 h to destroy any peroxo-complexes formed. The final solution was filtered and diluted to 1 dm^3 before loading it into a 20 × 2 cm column of Dowex 50 W × 2 resin in H$^+$ form. Washing with 0.2 M HCl eliminated any unreacted Co^{2+} and elution with 1–2 M HCl produced a first green band that was discarded while a second red one was collected and concentrated at reduced pressure and 40 °C to *ca.* 15 cm^3. A few drops of concentrated $HClO_4$ were added and the product was left to crystallize by slow evaporation in a 18% yield. ^{13}C NMR (100 MHz, D_2O, 298 K), δ/ppm: 30.0, 50.8, 53.8, 55.6, 57.4, 61.4, 183.8. UV-Vis, λ_{max}/nm: 376, 536; $\varepsilon_{376}/\varepsilon_{536}$ = 1.54. No further characterization of this complex was carried out given its intermediate nature for the new mixed-valence compound indicated below.

Na_2[{*trans*-L_{14COO}Co^{III}(μ-NC)}Fe^{II}$(CN)_5$]. The mixed-valence dinuclear complex was obtained from the redox/substitution sequence established for the preparation of this family of complexes.[10,11,24,25] 0.6 g of the mononuclear cobalt complex indicated above were dissolved in 100 cm^3 of water, the pH was set to 8–9 with 1 M NaOH and stirring was maintained for *ca.* 10 min. 0.5 g of Na_4[Fe$(CN)_6$] dissolved in 50 cm^3 of water were added, the pH value was reset at 9, and the solution was left stirring at 60 °C overnight. The final dark solution was diluted to 2 dm^3 and loaded into a 20 × 2 cm column with Sephadex DEAE-25 resin in ClO_4^- form; after washing with water the product was eluted with 0.1 M $NaClO_4$ as a red band. The solution was diluted 10-fold, the chromatography procedure repeated with 0.05 M $NaClO_4$, and the central portion of the diffuse red brown band was collected and concentrated at reduced pressure and 45 °C to 15 cm^3. 150 cm^3 of cold EtOH was added and the precipitate in a 11%

yield was dried in air. ^{13}C NMR (100 MHz, D_2O, 298 K), δ/ppm: 30.0, 50.8, 53.8, 55.6, 57.4, 61.4, 177.0, 178.0 (×4), 184.1, 197.0. IR, ν_{CN}/cm^{-1}: 2054, 2090, 2130. MS (ES$^+$), *m/z* 267.0; $\{[\{L_{14COO}Co(\mu\text{-}NC)\}Fe(CN)_5] + 4H^+\}^{2+}$. UV-Vis, λ_{max}/nm (ε/M^{-1} cm^{-1}): 324 (400), 442 (450), 502 (370). Voltammetry, $E_{\frac{1}{2}}$/mV: −330, 610. Elemental analysis indicated a C : N ratio of 1.67 in good agreement with the presence of six cyanide ligands and the L_{14COO} macrocyclic ligand in the complex (C : N = 1.64). As indicated in the Compounds/Results and discussion section, the lability of the coordinated carboxylate arm of the macrocycle during the chromatography separation procedures does not allow for a sensible CHN elemental analysis to be carried out.

[{*trans*-$L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}](ClO_4)$. The *trans*-$[CoClL_{15}](ClO_4)_2$ and $K_2[Fe(CN)_4(bpy)]$ precursor complexes were prepared according to published procedures.[19,21,25,26] The procedure for the preparation of the dinuclear complex has been recently reported as occurring *via* a base-assisted substitution process.[27] Characterization was carried out accordingly.

Physical methods

NMR spectra were recorded on a Varian Mercury-400 (^{1}H, 400 MHz or ^{13}C 100.6 MHz) instrument in D_2O and using NaTSP as external standard at the Serveis Científico-Tècnics of the Universitat de Barcelona. Elemental analyses were carried out also by the Serveis Científico-Tècnics of the Universitat de Barcelona. Electrospray mass spectrometry was carried out in a VG Quatro Instrument from Fisons at the Servei d'Espectrometría de Masses of the Universitat de Barcelona. UV-Vis spectra were recorded on a Cary5 or J&M TIDAS instruments depending on the circumstances. IR spectra were carried out in an FT-IR Impact 400 NICOLET instrument on KBr disk or on an FT-IR 200 NICOLET instrument using a ATR accessory for the oxide-supported samples. Electrochemistry in solution was carried out on a 263A instrument of EG&G using a glassy carbon working electrode, a Ag/AgCl (3 M KCl) reference electrode and platinum wire secondary electrode on 1×10^{-3} M solutions of the sample and using 0.1 M $NaClO_4$ as supporting electrolyte. For the electrochemical experiments carried out on mesoporous oxide films the working electrode consisted of a conducting glass with mesoporous Sb-doped SnO_2 deposited, to which the relevant complex had been chemisorbed, and soaked in a acetonitrile solution of the relevant electrolyte.

Preparation of TiO_2 and Sb-doped SnO_2 films and chemisorption of the complexes

Mesoporous TiO_2 electrodes were prepared on conducting glass substrates (TEC 8, Pilkington). TiO_2 powder (Degussa P25) was added to ethanol to a concentration of 20 wt%, followed by stirring. The resulting suspension was applied onto a substrate by doctor blading using scotch tape as frame and spacer. After evaporation of the ethanol, the substrate with the attached powder film was put between two planar steel press plates and 1360 kg cm^{-2} pressure was applied by using a hydraulic press followed by heating to 450 °C for 30 min. Sb-doped SnO_2 oxide surface electrodes, having a much lower conduction band, were used to verify the feasibility of the electron injection processes in DSSC cells, as well as the electrochemical experiments needing high conductivity supports.[28] The preparation procedure started with 10 g of a water colloidal dispersion of Sb-doped SnO_2 (15%, Alfa) that was added to 0.75 g of M_w = 2000 poly(ethylene glycol) and stirred for 1 h. Addition of 2 cm^3 of ethanol started gelification, the mixture was stirred for further 15 min and then left overnight. The final gel was stirred for 15 min and diluted with H_2O–EtOH to the desired viscosity suitable for "doctor blading". The films obtained in this way were also sintered at 450 °C for 30 min.

Once any of the two types of electrodes reached 80 °C, on cooling, they were soaked overnight in a (4–8) × 10^{-3} M solution of the mixed-valence complexes studied, either in acetonitrile for $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$, or in water at pH = 2 ($HClO_4$) for $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$. The electrodes were subsequently washed with ethanol and air dried.

For their use in DSSC the electrodes were assembled with a TEC8 counter-electrode thermally platinised and using a thermoplastic (Surlyn) frame separator. The electrolyte used for the experiments was I_2–LiI (0.05 : 0.5 M) for $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ or I_2–$(NBu_4)I$ (0.05 : 0.5 M) for $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ in acetonitrile.[29]

Results and discussion

Compounds

$[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bipy)_{eq,ax}]^+$. This already known complex has recently been reported and is prepared *via* a direct substitution process of the hydroxo ligand in *trans*-$[Co^{III}(OH)L_{15}]^{2+}$ by $[Fe^{II}(CN)_4(bipy)]^{2-}$.[20,27,30,31] As reported, the potential of the $[Fe^{III}(CN)_4(bipy)]^-$/$[Fe^{II}(CN)_4(bipy)]^{2-}$ couple does not allow for the sequence of reactions operating for the preparation of other mixed-valence dinuclear Co^{III}/Fe^{II} of this type (see below).

$[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$. The preparation of this species has been achieved by the, now well established,[9] outer-sphere oxidation/substitution/inner-sphere oxidation sequence between *trans*-$[Co^{III}L_{14COO}(H_2O)]^{2+}$ and $[Fe^{II}(CN)_6]^{4-}$. This general process has been proved to be a keystone for the preparation of discrete di- and trinuclear mixed-valence complexes of this family.[9,10,32] The complex has been characterized by its UV-Vis, IR and NMR spectra, as well as mass spectrometry and show the expected Fe^{II}-to-Co^{III} MMCT band in the 450–550 nm zone that bleaches on addition of $S_2O_8^{2-}$ as expected.[33] The preparation of the initial parent cobalt mononuclear complex from the new L_{14COO} ligand has been achieved in the same manner as that established for the equivalent ligand with a 15-membered macrocycle.[23] The chromatography procedures, nevertheless, proved to be a bit more delicate due to the facile protonation reactivity of the dangling carboxylate arm of the L_{14COO} ligand that introduces a quasi-variable charge character to the complex. As a result, the complex collected is a mixture of dangling arm on and off, thus making meaningless any elemental analysis data collected.

The nature of the isomerism of the macrocycle around the cobalt centre is established by the number of signals in the ^{13}C NMR spectrum. These indicate that the structure is fully symmetric with only six types of non-carboxylic carbons, which corresponds to a *trans*-I or *trans*-III macrocycle isomeric form,[19] as defined for cyclam complexes.[34] Interestingly the same form of the $\{CoL_{14COO}\}^{2+}$ unit is obtained both for the mononuclear and the dinuclear complex as in the L_{14} equivalents, despite the much more complicated behaviour observed for the L_{15} and L_{14S} systems.[11,19,21,35] The coordinating nature of the carboxylato arm is fully established by the vibrational spectrum in the COO bond stretching zone.[36] Two signals at 1630 (ν_{asym}) and 1400 (ν_{sym}) cm^{-1} are observed the separation of which (230 cm^{-1}) clearly indicates a monodentate coordination mode of the $-COO^-$ group.[37]

The $E_{\frac{1}{2}}$ values for the cobalt and iron centres (Table 1) show shifts of 270 and −20 mV, respectively, from the $[\{trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ parent compound. In all cases the peak-to-peak difference for the iron redox moiety is in good agreement with the reversibility observed (60–67 mV), while for the Co^{III}/Co^{II} moiety the cyclic voltammetry evidences the already reported irreversible behaviour under these conditions.[9] The very small difference for the iron centre agrees, again, with the class II nature of the mixed-valence complex prepared[8] and a small inductive influence of the anionic dangling arm on the cobalt moiety. On the other hand the large difference found for the cobalt centre is in line with, as seen for other compounds of this family,[25] an N_5O environment of the cobalt centre that stabilizes the Co^{II} oxidation state[38] despite the presence of a negative donor carboxylate group. The UV-Vis spectra shows the typical MMCT band at 542 nm (Table 1) that bleaches on addition of $Na_2S_2O_8$ due to the iron centre oxidation (Fig. S1, ESI†);[33] the band is shifted to lower energies with respect to the $[\{trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ equivalent. The decreased difference between the reduction potentials produces a lower ΔG° value that translates to the charge transfer energy. However, a similar ΔG° difference had already been observed between $[\{trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ and $[\{trans\text{-}L_{14S}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ complexes, where two amines have been changed to thioether groups, leading to a MMCT band at 566 nm, much lower in energy. The fact seems to indicate that the reorganization energy of the $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ system must play a role in the energy of the optical charge transfer, increasing it in a measurable way.[32,39,40] In fact some differences in the reorganization energy have already been found between *cis* and *trans* complexes of the L_{14} ligand. It was concluded that the more flexible the conformation of the ligand the larger the reorganization energy needed.[40] In our case the dangling arm is, *de facto*, longer and possibly the decrease in the ΔG° is partially compensated by and increase in the value of the reorganization energy.

Attachment to mesoporous oxide surfaces

The anchorage of the two tailor-made mixed-valence complexes on mesoporous TiO_2 or SnO_2 oxide films deposited on conducting oxide slides has been achieved and characterization of the resulting transparent electrodes carried out by UV-Vis, IR and electrochemistry.

$[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$. The nature of the linkage to the oxide surface of this species is clearly shown by the IR spectrum of the electrodes prepared. While the KBr dispersed complex showed a $\nu COO_{asym-sym}$ separation corresponding to monodentate coordination, the samples attached to the oxides (Fig. S2, ESI†) have a much smaller separation, indicative of a unsymmetrical bridging of the $-COO^-$ group.[36,37] That is, the nature of the dinuclear mixed-valence anchorage to the oxide surface corresponds to a strong ester linkage,[41] as indicated in Fig. 1(a). Even the presence of small cation electrolyte solutions does not affect the linkage, unlike for systems with a weaker attachment (see below). The results of UV-Vis spectroscopy and electrochemistry on the iron centre for these surfaces are also collected in Table 1. The shift of the MMCT band maximum to higher energies on oxide surface attachment is parallel to that observed on protonation in solution, indicating that the linkage to the oxide surface has a similar effect on the band. This attachment effect is related with the strong attachment to the cobalt moiety of the mixed-valence complex to M^{IV}

Table 1 Characterization data for the species $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$, $[\{trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ and $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ prepared

	$E_{\frac{1}{2}}$ /mV			
Species	$Fe^{III/II}$	$Co^{III/II}$	λ_{MMCT}/nm	Solvent or support
$[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$	610	−330	542	H_2O
	890[a]	—[b]	446	SnO_2
	—[b]	—[b]	444	TiO_2
$[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$	775	−530	470[c]	H_2O
	550	−740	540	CH_3CN
	930[a]	—[b]	515	SnO_2
	—[b]	—[b]	500	TiO_2
$[\{trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ [d]	630	−600	513	H_2O
$[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ [d]	600	−580	530	H_2O

[a] With CH_3CN electrolyte solution. [b] Not measured. [c] From ref. 27. [d] From ref. 9.

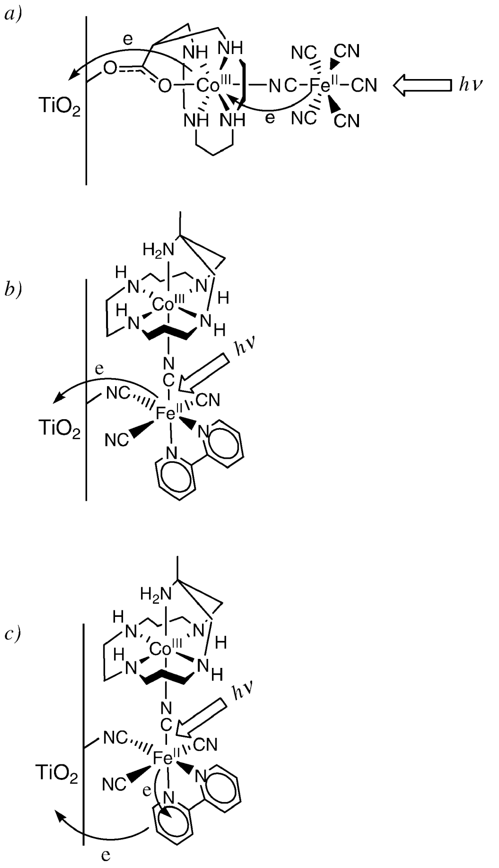


Fig. 1 Expected electron flow upon irradiation of: (a) [{*trans*-L_{14COO}Co^{III}(μ-NC)}Fe^{II}(CN)$_5$]$^{2-}$ (from a MMCT excited state), (b) [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ (direct), and (c) [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ (from a MLCT excited state) when attached to TiO$_2$ surfaces.

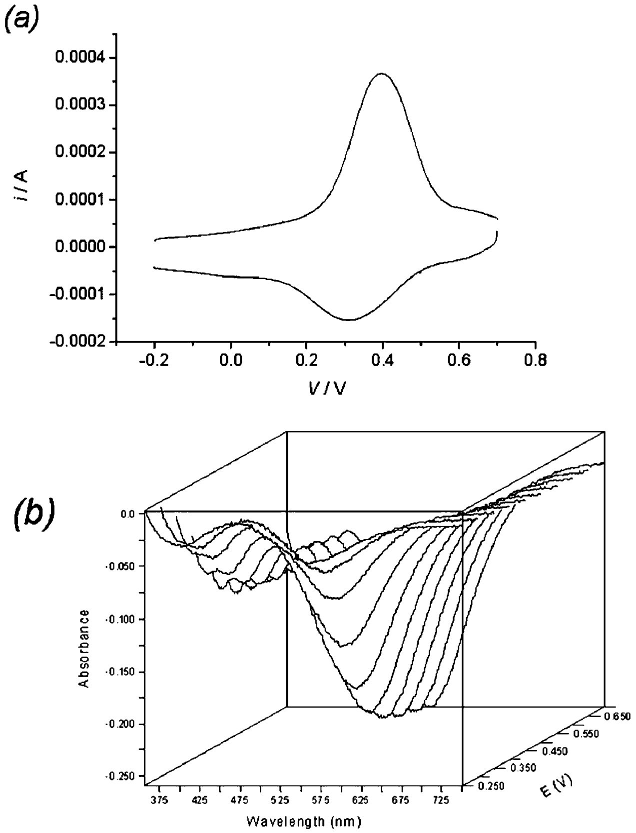


Fig. 2 Cyclic voltammetry, (a), and spectro-electrochemical experiment, (b), of the [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ species attached to a Sb-doped SnO$_2$ surface. Electrolyte solvent MeCN, I = 0.1 M (NBu$_4$)PF$_6$, Ag/AgCl reference, 5 mV s^{-1}.

centres of the oxide surface, producing important inductive effects on the iron centre[9,33] and increasing its measured $E_{\frac{1}{2}}$ value, as seen in Table 1. As a result the difference between the reduction potential of the two metal centres will increase and produce more energetic demands for the MMCT band.

[{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$. Again the nature of the linkage of the dinuclear complex on the oxide surface has been studied by IR spectroscopy. The electrodes containing the [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ species showed $\nu_{(CN)}$ stretching signals in exactly the same position than those observed for the complex dispersed in KBr, which indicates that the cyanide linkage to the mesoporous surface (Fig. 1(b) and (c)) is not strong enough to change the CN bond strength.[38,42] In this respect, the fact that small cation (Na$^+$ or Li$^+$) electrolyte solutions produced immediate desorption of the complex from the electrodes when soaked, agree with this fact; (NBu)$_4$PF$_6$ had to be used as electrolyte for the experiments with electrodes containing this complex. The results of UV-Vis spectroscopy and electrochemistry on the iron centre for these electrodes are collected in Table 1. The shifts of the MLCT/MMCT band maximum to lower energies compared to the values in water solution agrees fairly well with the weak nature of the interaction of the complex with the oxide surface (acting as a solvent).[10,43] In fact the value obtained for the spectrum in MeCN solution is indicative of the shift expected for a practically non-interacting solvent.[44] As for the reduction potential of the iron centre in the attached samples Fig. 2 shows, as an example, the cyclic voltammetry obtained, as well as the associated spectro-electrochemical experiment. The results are comparable with those observed for the complex mentioned in the previous paragraph, [{*trans*-L_{14COO}Co^{III}(μ-NC)}Fe^{II}(CN)$_5$]$^{2-}$. The voltammogram is clearly reversible, despite the implicit slow interfacial electron transfer and uncompensated resistance phenomena,[28] with a $E_{\frac{1}{2}}$ value much higher than that observed for the unattached species (Table 1). The cyanide nitrogen linkage to the oxide surface can easily account for the difference, attachment of a Sn^{IV} unit to the cyanide nitrogen produces important positive shifts on the reduction potential of the iron moiety, as observed for the [Fe(CN)$_4$(bpy)]$^{2-}$ → [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ (see above) or [Fe(CN)$_6$]$^{4-}$ → [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_5$]$^-$ → [{*trans*-L_{15}Co^{III}(μ-NC)}$_2$Fe^{II}(CN)$_4$]$^{2+}$ → [{*trans*-L_{15}Co^{III}(μ-NC)}Fe^{II}(CN)$_3$(CNH)$_2$]$^+$ sequences.[9,10,27,33,39] The spectro-electrochemical experiment shown also clearly indicates that the application of the oxidation potential measured to the sample results in a bleaching of the MMCT/MLCT bands in the visible spectrum as already described chemically.[27]

Dye-sensitized solar cells

Solar cells constructed as indicated in the experimental section where prepared with both $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ and $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ complexes.[45] As indicated in Fig. 1 complex $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ is a perfect candidate for electron injection from the cobalt centre through the light generated by the MMCT excited state, while the cyanide bound complex, $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bipy)_{eq,ax}]^+$ is a good candidate for electron transfer into the semiconductor *via* direct iron injection or through a MLCT state centred on the bpy ligand, tuned by the presence of the $\{CoL_n\}^{3+}$ moiety attached.

The cells with $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ anchored on mesoporous TiO_2 electrodes did not produce any current on illumination. They were prepared again with Sb-doped SnO_2, despite its worse characteristics, in order to ascertain that the possible non-matching energy levels between the semiconductor and the sensitizer were not responsible for this lack of response observed.[46] No photocurrent was obtained either with this low energy conduction band semiconductor, indicating that the relative energy levels of the semiconductor and sensitizers are not responsible for this fact.

The cells built on mesoporous TiO_2 electrodes with chemisorbed $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ showed a much more promising response, as seen in Fig. 3, even in the absence of any of the standard additives used to improve efficiency.[47] The intensity–voltage curves at different illumination power in Fig. 3(a) show that, although the V_{OC} and photocurrent values (0.42 V and 0.031 mA cm^{-2} at 1000 W m^{-2}) are low compared to other sensitizers in the literature,[2] this complex shows a good behaviour as sensitizer. In the incident to photon current efficiency curve (IPCE) of Fig. 3(b), the highest value obtained was 4% at 440 nm, which corresponds to the position of the MMCT band of the sensitizer attached to TiO_2 (Table 1, Fig. S3, ESI†). This is an indicative that the optical Co^{III}/Fe^{II}-to-Co^{II}/Fe^{III} charge transfer is responsible for the electron injection, as schematized in Fig. 1. One of the possible reasons for the poor efficiency (0.1%) of the system could be the low absorption coefficient of the sample (*ca.* 500 M^{-1} cm^{-1} in water), when compared with the best behaved sensitizers (10 000–100 000 M^{-1} cm^{-1}).[14,48]

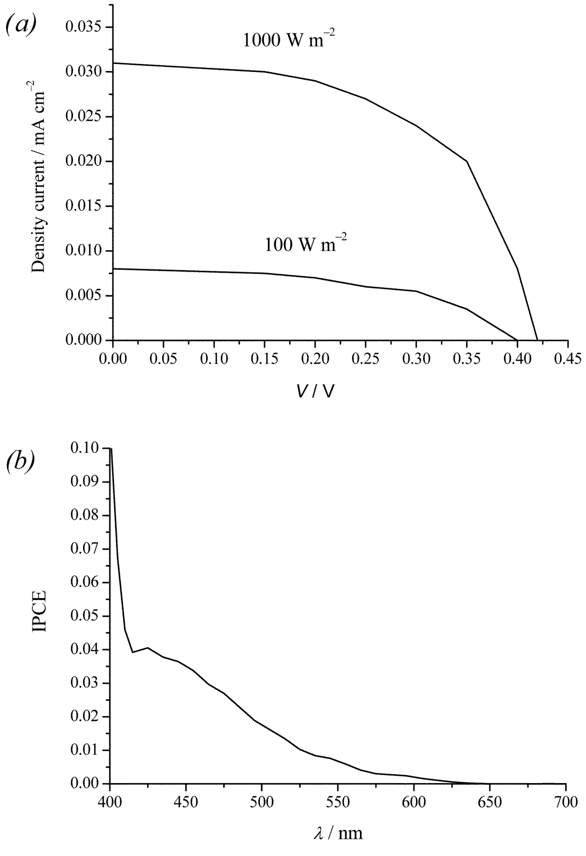


Fig. 3 Measurements carried out on a complete solar cell using $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ as sensitizer and using I_2–LiI (0.05 : 0.5 M) as electrolyte in acetonitrile. (a), *i–V* curves at different light intensities; (b), IPCE curve.

Another feasible explanation of the low efficiency observed is the fact that the $E_{\frac{1}{2}}$ for the $Fe^{III/II}$ couple in our complex is only 0.61 V, very close to the value of the redox mediator ($E^\circ(I_2/I_3^-) = 0.54$ V in water)[49] compared with that of the best behaved N719 dye ($E^\circ(Ru^{III/II}) = 0.79$ V).[50] The combination of the low absorptivity and the possible slow regeneration of the dye due to the small difference in redox potential can be held responsible for the low efficiency obtained.

As a whole the results indicate that the MMCT is dominant in the features of these mixed-valence complexes as sensitizers in solar cells. For the $[\{trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ complex the Fe^{II}-to-Co^{III} charge transfer, occurring on illumination, disfavours the observed direct and indirect electron transfer paths from $[Fe^{II}(CN)_4(bpy)]^{2-}$ (Fig. 1(b) and (c)), and no electrical response is obtained. For the carboxylato attached complex, $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$, the optical electron transfer to the cobalt from the iron centre, at 440 nm, favours a direct electron injection to the semiconductor from the strongly anchored Co^{III} unit (Fig. 1(a)). Presumably the absence of low-lying MLCT states for the $\{Co^{II}L_{14COO}\}$ unit prevents the occurrence of any indirect injection path.

Conclusions

Tailoring of discrete mixed-valence cyanide-bridged Co^{III}/Fe^{II} complexes in order to obtain characteristics of electron injection processes dominated by the MMCT band has been proved to be possible. The Fe^{II}-to-Co^{III} charge transfer band has been proved important both to disrupt processes based on injection from the iron centre and to promote new electron transfer processes from the cobalt unit of the dinuclear complex. The efficiencies of the prepared DSSC are poor, although the behaviour of the active complexes as sensitizers is remarkable taking into account the value of the extinction coefficient for the MMCT band (*ca.* 500 M^{-1} cm^{-1}), two orders of magnitude lower that the best well behaved dyes. The possibility of increasing the nuclearity of these complexes *via* a mechanistic-based preparative procedure, with the consequent increase in the extinction coefficient of the MMCT band, remains an extremely interesting field that could be explored for these purposes.

The data obtained indicate that $[\{trans\text{-}L_{15}Co^{III}\text{-}(\mu\text{-}NC)\}Fe^{II}(CN)_3(bipy)_{eq(ax)}]^+$ is attached to the surface *via* the terminal cyanide ligands while complex $[\{trans\text{-}L_{14COO}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^{2-}$ attains the interaction *via* a carboxyester direct linkage. The latter complex seems to be involved in an electron injection from the cobalt centre through the MMCT excited state (Co^{II}/Fe^{III}), while the former does not produce any electron injection either from the MLCT exited state (Co^{III}/Fe^{III}bipy$^-$)or directly from the Fe^{II} centre.

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