SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES OF A SERIES OF SUBSTITUTED POLYPYRIDINE Co(II)/Co(III) COUPLES AND THEIR POTENTIALITY AS MEDIATORS FOR SOLAR CELLS.

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ABSTRACT

This paper reports the synthesis, characterization and spectroscopic and electrochemical study of a series of polypyridine Co(II) and Co(III) complexes. The effect on the redox potential of the presence of donor or acceptor substituents on the ligand, as well as the effect of an increased ligand aromaticity, was analyzed. Specifically, complexes of $[\text{Co}(\text{L-L})_3]^{n+}$ type were prepared, with $n = 2, 3$, and $\text{L-L} = 1,10$ -phenanthroline (phen), 5-amino-1,10'-phenanthroline (phen- NH_2), 3,4,7,8-tetramethyl phenanthroline (phen-4Me), pyrazino[2,3- f][1,10]phenanthroline (ppl), 2-methylpyrazino[2,3- f][1,10]phenanthroline (ppl-Me), dipyrro[3,2- a :2',3'- c]phenazine (dppz), 7-methyldipyrro[3,2- a :2',3'- c]phenazine (dppz-Me) and 7-aminodipyrro[3,2- a :2',3'- c]phenazine (dppz- NH_2). The results of this study open the possibility to have a battery of potential mediators for photoelectrochemical solar cells. Ultimately, the election of a determined couple as mediator will depend mainly on the electronic properties of the specific dye in a given cell.

Keywords: Cobalt polypyridine complexes, redox potential, substituent effect.

INTRODUCTION

Solar radiation is an inexhaustible energy source and probably one of the best candidates to be used in devices in order to cover the increasing world energy demands. While efficient solar energy conversion has been around for decades, the cost of electricity production from solar conversion is still higher than from conventional coal-based sources.¹ Photoelectrochemical cells based on dye sensitized semiconductor photoanodes have been mentioned for a long time in literature,² but it was only on 1991, after O'Regan and Graetzel's report of a photovoltaic device based on the sensitization of nanoparticulated TiO_2 electrodes,³ that this possibility came to be intensely considered as an alternative energy source. The functioning of the frequently called "Graetzel cells" basically consists of light absorption by a chromophore attached to the surface of a TiO_2 nanoparticulated photoanode, followed by the injection of an electron into the TiO_2 conduction band by the excited dye. This electron, which is the source of the photocurrent, is driven by an external circuit to the counter electrode. A redox shuttle in solution is employed to regenerate the dye. Diffusion of the oxidized form of the shuttle to the counter electrode completes the circuit.^{1, 2} Scheme 1 shows a description of this photoelectrochemical Grätzel type cell. Regarding the redox shuttle or mediator, a key aspect to be considered is its redox potential that should permit a thermodynamically favored reduction of the dye, but at the same time possess a sufficiently high ΔV value to permit the functioning of the cell. Ultimately, the optimum redox mediator for a given cell will depend on the nature and redox properties of the specific dye incorporated in it.

Scheme 1

Until now, the best efficiencies have been obtained with polypyridine Ru(II) dyes used in conjunction with I^-/I_3^- as mediator. As a mediator, I^-/I_3^- seems to have ideal kinetic properties;⁴ specifically, the regeneration of the dye by I^- is very fast, while the detrimental recombination of I_3^- with photoinjected electrons in the TiO_2 is a slow two electron transfer process.⁵ Nevertheless, regardless of these positive characteristics and its efficiency, alternatives to this shuttle should be considered, given first, its corrosive nature and volatility, that affects the durability of eventual commercial modules,⁶ and second, its absorption in the visible region, that competes with the absorption of the dye.

Alternative mediators, as one-electron outer sphere redox systems with rapid electron exchange kinetics such as ferrocene/ferricinium, give low photovoltages and low photocurrents as a consequence of rapid back reaction of photoinjected electrons with the oxidized redox component.^{5,8}

Other outer-sphere one electron mediators, as Cobalt polypyridyl couples, have also been considered as alternative shuttles,⁷ because they are expected to have the capacity to satisfy the main requirements these redox mediators should have, as efficient reduction of the dye with minimal overpotential, fast reduction at the cathode, slow interception of electrons contained in the photoanode, nonvolatility, and little light absorption in the spectral region where the dye absorbs, both in oxidized and reduced form.⁶ The slower rate of interaction with electrons in the photoanode for the Co polypyridyl couples when compared to the ferrocene/ferricinium couple arises mainly from the change in spin multiplicity involved in the former.⁴ On the other hand, when compared to the iodine couple, that possesses a sole redox potential, the possibility to tune the redox potential by changes in the ligand electronic properties appears as an additional advantage of Cobalt polypyridine type complexes.

Although very promising results were reported for the cobalt based redox mediator $\text{Co(II)}(\text{dbbip})_2(\text{ClO}_4)_2$, with $\text{dbbip} = 2,6$ -bis(1'-butylbenzimidazol-2'-yl)pyridine,^{7d,e} other parent systems of the type $\text{Co(II)}(\text{LL})_3^{2+/3+}$, with $\text{LL} = \text{bpy}$, phen and substituted derivatives, have shown very low efficiency. Factors as slow diffusion and reduction of the Co(III) form of the mediator at the photoanode, have been discussed, among other variables, as the possible reasons for this rather low response. Ultrathin coating of the nanoparticulated TiO_2 with alumina has been tested as a protection to prevent the deactivation of the photogenerated electrons by the oxidized form of the redox mediator.^{7a}

In this work a series of polypyridine Cobalt(II) and Cobalt(III) complexes of the type $[\text{Co}(\text{L-L})_3]^{n+}$ with $\text{L-L} = 1,10$ -phenanthroline (phen), 5-amino-1,10'-phenanthroline (phen- NH_2), 3,4,7,8-tetramethyl phenanthroline (phen-4Me), pyrazino[2,3- f][1,10]phenanthroline (ppl), 2-methylpyrazino[2,3- f][1,10]phenanthroline (ppl-Me), dipyrro[3,2- a :2',3'- c]phenazine (dppz), 7-methyldipyrro[3,2- a :2',3'- c]phenazine (dppz-Me) and

7-aminodipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz-NH₂), were synthesized and systematically studied, mainly from a spectroscopic and electrochemical point of view. Differentiating from previous literature reports in this area, where the Co(III) species are generated *in situ*, in this work the Co(III) species were isolated as a solid, to permit its characterization, and a better control of the Co(II)/Co(III) concentration relation. The effect on the redox potential of the Co(II)/Co(III) couple of the presence of donor or acceptor substituents on the ligand, as well as the effect of an increased ligand aromaticity, was analyzed. The results of this study open the possibility to choose as alternative redox mediator - for a specific cell and according to the dye properties - some of the Co(II)/Co(III) couples here reported, especially in cases where the regeneration of the dye by the traditionally used iodine based mediator, is thermodynamically unattainable.

Experimental Section

Materials. Solvents were of ACS grade. All reagents and solvents were used as received. 1,10-phenanthroline (phen) and 3,4,7,8-tetramethylphenanthroline (phen-4Me) were obtained from Aldrich.

Analytical methods

UV-Vis and Emission Spectroscopy. UV-Vis absorbance measurements were made on a Shimadzu UV 3101PC spectrophotometer.

Infrared Spectra. Infrared (IR) spectra for the desired compounds and reactants were recorded as KBr mulls in a Bruker Vector 22 FTIR spectrometer.

Analytical Data: Elemental Analysis was performed on a Fisons Instrument Analyzer, model EA1108/CHN-S with PC NCR system 3225, while Mass Spectra were recorded with an LCQ Duo Ion Trap Mass Spectrometer (Thermo Finnigan, USA).

NMR. ¹H-NMR spectra were recorded on a Bruker ACL 200 200MHz spectrometer with TMS as reference or on a Bruker AVANCE 400 FT-NMR spectrometer.

Electrochemistry. Cyclic Voltammograms were taken in dry CH₃CN nitrogen saturated 1x10⁻³ M solutions of the corresponding complex, at 100 mV/s sweep rate, with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. A BAS model CV50w potentiostat was used in a standard three-electrode arrangement with a Pt or glassy platinum working electrode, a Pt gauze counter electrode, and a Ag/Ag⁺ AgNO₃ 0.01M reference electrode. The measured E_{1/2} values were adjusted to be referred v/s NHE.

Synthesis

Co(II) complexes:

All the Co(II) complexes were synthesized in a similar way as described by Shawn A. Sapp.^{7b} A solution of three equivalents of the corresponding ligand was dissolved in methanol with magnetic stirring, and the solution taken to reflux temperature until ligand dissolution. One equivalent of CoCl₂·5xH₂O in methanol was then added. The mixture was refluxed for 2 hours and then cooled to room temperature. The total volume was reduced to ca 70% with the use of rotary evaporation. Addition of NH₄PF₆ and ethyl ether caused the precipitation of the desired complex, which was finally filtered and washed with diethyl ether.

[Co(phen)₃](PF₆)₂. Yield (85%). IR, KBr (cm⁻¹) ν_{B-F} = 834, 557. Anal. C₃₆H₂₄N₆CoF₁₂P₂ (%) Cal.: C 48.61; H 2.72; N 9.45 Exp.: C 48.88; H 3.56; N 9.52.

[Co(phen-NH₂)₃](PF₆)₂. Yield (93%). IR, KBr (cm⁻¹) ν_{N-H Alifatic} = 3223; ν_{p-F} = 842, 558. m/z 468 (M⁺-PF₆⁻); 322 (M⁺-2PF₆⁻); 224 (M⁺-(phen-NH₂)-2PF₆⁻).

[Co(phen-4Me)₃](PF₆)₂. Yield (96%). IR, KBr (cm⁻¹) ν_{C-H Alifatic} = 2927; ν_{p-F} = 841, 558. Anal. C₄₈H₄₈N₆CoF₁₂P₂ (%) Cal.: C 54.50; H 4.57; N 7.94. Exp.: C 54.35; H 4.87; N 7.89.

[Co(ppl)₃](PF₆)₂. Yield (62%). IR, KBr (cm⁻¹) ν_{p-F} = 840, 557. Anal. C₄₂H₂₄N₁₂CoF₁₂P₂ (%) Cal.: C 48.25; H 2.31; N 16.08 Exp.: C 48.56; H 3.04; N 16.01.

[Co(ppl-Me)₃](PF₆)₂. Yield (86%). IR, KBr (cm⁻¹) ν_{C-H Alifatic} = 2926; ν_{p-F} = 841, 557. Anal. C₅₄H₃₆N₁₂CoF₁₂P₂ (%) Cal.: C 49.69; H 2.87; N 15.45 Exp.: C 49.38; H 3.05; N 15.34.

[Co(dppz)₃](PF₆)₂. Yield (57%). IR, KBr (cm⁻¹) ν_{p-F} = 848, 558. Anal. C₅₄H₃₀N₁₂CoF₁₂P₂ (%) Cal.: C 54.24; H 2.53; N 14.06 Exp.: C 53.98; H 2.78; N 13.97.

[Co(dppz-Me)₃](PF₆)₂. Yield (53%). IR, KBr (cm⁻¹) ν_{C-H Alifatic} = 2930; ν_{p-F} = 840, 558. Anal. C₅₇H₃₆N₁₂CoF₁₂P₂ (%) Cal.: C 55.31; H 2.93; N 13.58 Exp.: C 55.09; H 3.14; N 13.37.

[Co(dppz-NH₂)₃](PF₆)₂. Yield (66%). IR, KBr (cm⁻¹) ν_{N-H Alifatic} = 3210; ν_{p-F} = 833, 559. Anal. C₅₄H₃₃N₁₅CoF₁₂P₂ (%) Cal.: C 52.27; H 2.68; N 16.93 Exp.: C 52.49; H 2.98; N 17.09.

Co(III) Complexes:

The oxidation of the corresponding Co(II) complex was done by the addition of an equivalent amount of nitrosonium tetrafluoroborate (NOBF₄) in

an acetonitrile solution. This mixture was stirred for 1 hour. The total volume was reduced to ca 70% with the use of rotary evaporation. Addition of NH₄PF₆ and ethyl ether caused the precipitation of the corresponding complex, although in some of them precipitation occurred with BF₄⁻ as counter ion. The presence of BF₄⁻ or PF₆⁻ as counterion was elucidated by IR. For Co(II) complexes with NH₂ substituents, the oxidation was performed bubbling air for 6 hour.

[Co(phen)₃](BF₄)₃. Yield (80%). IR, KBr (cm⁻¹) ν_{B-F} = 1083, 1055, 1034. ¹H-NMR (CD₃CN) δ (ppm) 9.00 (dd, 6H, H1), 8.45 (s, 6H, H4), 7.88 (dd, 6H, H2), 7.50 (d, 6H, 3H). Anal. C₃₆H₂₄N₆CoF₁₂B₃ (%) Cal.: C 50.28; H 2.81; N 9.77 Exp.: C 50.49; H 2.98; N 9.85.

[Co(phen-NH₂)₃](PF₆)₃. Yield (75%). IR, KBr (cm⁻¹) ν_{N-H Alifatic} = 3229; ν_{p-F} = 840, 557. ¹H-NMR (CD₃CN) δ (ppm) 8.99 (dd, 3H, H1), 8.56 (dd, 3H, H1'), 7.93-7.81 (m, 3H, H3), 7.66-7.42 (m, 6H, H3', H2), 7.32 (s, 3H, H4), 7.19-7.02 (m, 3H, H2'), 5.94 (s, 6H, NH₂). Anal. C₃₆H₂₂N₉CoF₁₈P₃ (%) Cal.: C 40.05; H 2.52; N 11.68 Exp.: C 40.23; H 2.59; N 11.79.

[Co(phen-4Me)₃](BF₄)₃. Yield (96%). IR, KBr (cm⁻¹) ν_{C-H Alifatic} = 2930; ν_{B-F} = 1083, 1055, 1036. ¹H-NMR (CD₃CN) δ (ppm) 8.48 (s, 6H, H1), 7.01 (s, 6H, H4), 2.86 (s, 18H, CH₃), 2.27 (s, 18H, CH₃). Anal. C₄₈H₄₈N₆CoF₁₂B₃ (%) Cal.: C 56.07; H 4.71; N 8.17 Exp.: C 56.43; H 4.79; N 8.26.

[Co(ppl)₃](BF₄)₃. Yield (85%). IR, KBr (cm⁻¹) ν_{B-F} = 1083, 1055, 1033. ¹H-NMR (CD₃CN) δ (ppm) 9.88 (dd, 6H, H1), 9.36 (s, 6H, H4), 8.08 (dd, 6H, H2), 7.78 (dd, 6H, H1). Anal. C₄₂H₂₄N₁₂CoF₁₂B₃ (%) Cal.: C 49.65; H 2.38; N 16.54 Exp.: C 49.93; H 2.41; N 16.71.

[Co(ppl-Me)₃](BF₄)₃. Yield (82%). IR, KBr (cm⁻¹) ν_{C-H Alifatic} = 2923; ν_{B-F} = 1083, 1061, 1033. ¹H-NMR (CD₃CN) δ (ppm) 9.90-9.82 (m, 6H, H3 H3'), 9.23 (s, 3H, H4), 8.12-8.03 (m, 6H, H2 H2'), 7.80-7.75 (m, 6H, H1 H1'), 2.98 (s, 9H, CH₃). Anal. C₄₅H₃₀N₁₂CoF₁₂B₃ (%) Cal.: C 51.08; H 2.86; N 15.88 Exp.: C 51.53; H 2.90; N 15.97.

[Co(dppz)₃](BF₄)₃. Yield (51%). IR, KBr (cm⁻¹) ν_{B-F} = 1083, 1054, 1034. ¹H-NMR ((CD₃)₂SO) δ (ppm) 9.97 (d, 6H, H3), 8.61-8.59 (m, 6H, H4), 8.30-8.27 (m, 6H, H5), 8.22-8.17 (m, 6H, H2), 7.95-7.93 (m, 6H, H1). Anal. C₅₄H₃₀N₁₂CoF₁₂B₃ (%) Cal.: C 55.61; H 2.59; N 14.41 Exp.: C 56.02; H 2.62; N 14.52.

[Co(dppz-Me)₃](BF₄)₃. Yield (52%). IR, KBr (cm⁻¹) ν_{B-F} = 1083, 1055, 1033. ¹H-NMR ((CD₃)₂SO) δ (ppm) 9.93 (d, 6H, H3 H3'), 8.49 (s, 3H, H4), 8.37 (s, 3H, H4'), 8.20-8.15 (m, 6H, H2 H2'), 8.12 (d, 3H, H5), 7.93 (d, 6H, H1 H1'), 2.76 (s, 9H, CH₃). Anal. C₅₈H₄₀N₁₂CoF₁₂B₃ (%) Cal.: C 56.90; H 3.29; N 13.73 Exp.: C 57.22; H 3.35; N 13.81.

[Co(dppz-NH₂)₃](PF₆)₃. Yield (50%). IR, KBr (cm⁻¹) ν_{N-H Alifatic} = 3330; 3204 ν_{p-F} = 835, 559. ¹H-NMR ((CD₃)₂SO) δ (ppm) 9.53 (d, 3H, H3), 9.45 (d, 3H, H3'), 9.18 (d, 3H, H1), 9.12 (d, 3H, H1'), 8.05 (s, 3H, H4), 7.96-7.91 (m, 6H, H2 H2'), 7.50 (d, 3H, H5), 7.13 (s, 3H, H4'). Anal. C₅₄H₃₃N₉CoF₁₈P₃ (%) Cal.: C 46.80; H 2.40; N 15.16 Exp.: C 47.06; H 2.44; N 15.28.

Characterization

The synthesis of the Co(II) and Co(III) complexes described in this work was attained with reasonable good yields, over 50 %. The microanalytical results were in satisfactory agreement with the predicted values for the corresponding *tris* homoleptic complexes. The [Co(phen-NH₂)₃](PF₆)₂ complex was additionally characterized by Mass Spectroscopy. The IR spectra of the series of cationic complexes under study showed the presence of the PF₆⁻ bands at 840 and 558 cm⁻¹. For compounds [Co(phen-NH₂)₃](PF₆)₂ and [Co(dppz-NH₂)₃](PF₆)₂, bands assignable to the NH₂ groups at 3223 and 3210 cm⁻¹ are also observed, while for complexes [Co(phen-4Me)₃](PF₆)₂, [Co(ppl-Me)₃](PF₆)₂ and [Co(dppz-Me)₃](PF₆)₂, the corresponding methyl C-H signals at 2927, 2926 y 2930 cm⁻¹ are present. The ¹H-NMR spectra for the Co(III)⁹ low spin complexes permit to unambiguously assure the presence of the corresponding *tris* homoleptic complex. As an example, Figure 1 shows the ¹H-NMR spectrum for [Co(phen-NH₂)₃]³⁺ in CD₃CN; the assignment of the signals is also shown. Given the paramagnetic nature of the Co(II) complexes, no ¹H-NMR spectra is reported.

Figure 1. ^1H -NMR spectrum for $[\text{Co}(\text{phen-NH}_2)_3]^{3+}$ in CD_3CN . Proton numbering is shown in the inset.

RESULTS AND DISCUSSION

UV-Vis.

All the Co(II) and Co(III) complexes dissolved in acetonitrile show a common absorption pattern, with two distinct regions, one between 220 to 350 nm with high intensity absorption bands ($\epsilon = 90,000$ to $240,000 \text{ M}^{-1} \text{ cm}^{-1}$) and a second lower intensity region, from 350 to 460 nm ($\epsilon = 20,000$ to $40,000 \text{ M}^{-1} \text{ cm}^{-1}$). Both can be assigned to ligand centered bands, mostly of $\pi\text{-}\pi^*$ origin.^{7b} The main exception to this assignment appears in the case where NH_2 appears as substituent in the ligand, where intraligand charge transfer bands are to be expected. Figure 2 shows the spectra corresponding to $[\text{Co}(\text{ppl-Me})_3]^{2+}$ and $[\text{Co}(\text{ppl-Me})_3]^{3+}$. When comparing the spectra of a given Co^{2+} complex with its analogue of Co^{3+} , for example $[\text{Co}(\text{ppl-Me})_3]^{2+}$ and $[\text{Co}(\text{ppl-Me})_3]^{3+}$ in Figure 2, a similar pattern is observed, with displacements of the band maxima. For example, as shown in Table 1, $[\text{Co}(\text{phen})_3]^{2+}$ presents absorption bands at 267 and 280 nm, while for its oxidized equivalent, $[\text{Co}(\text{phen})_3]^{3+}$, these bands appear at 280 and 303 nm. This effect can be ascribed to the stronger Lewis acid character of Co^{3+} in regard to Co^{2+} , which would decrease the electron density on the π type orbitals of the ligand.

When comparing complexes with the metal in the same oxidation state but with different ligands, the general trend is that the more aromatic ligands as ppl and dppz, tend to present bands at lower energy when compared to phen, as expected for the stabilization of their π^* levels. Finally, the donor properties of substituents on the ligands, as in dppz-Me and dppz- NH_2 , compared to dppz, are also reflected in a displacement to the red, with bands at 280 and 316 nm, respectively, for the formers, and at 268 nm for the latter.

It is relevant to point out that, with the sole exception of $[\text{Co}(\text{dppz-NH}_2)_3]^{2+}$ that presents a band at 457 nm with ϵ of $21,000 \text{ M}^{-1} \text{ cm}^{-1}$, that can be assigned to an intraligand (IL) transition,¹⁵ the Cobalt complexes under study do not noticeably absorb in the visible region. In some cases, very low intensity ligand field bands can be observed. For example, for $[\text{Co}(\text{phen})_3]^{2+}$ these bands appear at bands at 440 and 930 nm of $\epsilon = 90$ and $10 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.

Figure 2. Absorption spectra in CH_3CN . (a) $[\text{Co}(\text{ppl-Me})_3]^{2+}$ (—) and $[\text{Co}(\text{ppl-Me})_3]^{3+}$ (---). (b) $[\text{Co}(\text{dppz-NH}_2)_3]^{2+}$ (—) and $[\text{Co}(\text{dppz-NH}_2)_3]^{3+}$ (---).

Table 1. Absorption spectra in CH_3CN for the complexes $[\text{Co}(\text{L-L})_3]^{2+}$ and $[\text{Co}(\text{L-L})_3]^{3+}$

L-L	$[\text{Co}(\text{L-L})_3]^{2+}$ Abs ,nm				$[\text{Co}(\text{L-L})_3]^{3+}$ Abs ,nm			
	227	267	290(sh)	346	220	280	303	348
phen	227	267	290(sh)	346	220	280	303	348
phen-4Me	240	274	310(sh)	318(sh) 333(sh)	225	289	313	334(sh) 352
phen- NH_2	241	261	288	353 436(sh)	241	261	290	355
ppl	220	256	288	323(sh) 339	268	299(sh)	318(sh)	340
ppl-Me	222	260	293(sh)	325(sh) 342	216	272	302(sh)	320(sh) 345
dppz	242(sh)	268	291(sh)	359 377	275	292	345(sh)	377
dppz-Me	228(sh)	280	297(sh)	364 384	232(sh)	291	366	384
dppz- NH_2	263	316	355(sh)	457	250	302	443	

Electrochemical Properties

The redox properties of the Co(II) complexes under study were studied by cyclic voltammetry. As an example, Figure 3 shows the CV for $[\text{Co}(\text{phen-4Me})_3]^{2+}$ and $[\text{Co}(\text{ppl-Me})_3]^{2+}$ in CH_3CN . In Table 2 the half wave potentials vs. NHE for all the Co(II)/Co(III) redox couples is shown. The existence of reversible

monoelectronic processes in all the cases was verified with an internal ferrocene standard. As should be expected, the redox potential of the different couples is sensible to the electronic nature of the substituent. Specifically, incorporation of donor groups to the polypyridinic ligands makes the metal oxidation easier. For example, $E_{1/2} = 638$ mV for $[\text{Co}(\text{phen})_3]^{2+/3+}$ while $E_{1/2} = 384$ mV for $[\text{Co}(\text{phen-4Me})_3]^{2+/3+}$. Conversely, an enhanced ligand aromaticity in regard to phen, as in ppl and dppz, reflects in a more difficult oxidation process in the corresponding complexes, showing the electronic acceptor nature of this type of ligands.¹¹

Table 2. Electrochemical properties of Cobalt $[\text{Co}(\text{L-L})_3]^{2+}$ type complexes.

L	$E_{1/2}$, mV ^a	ΔE , mV	$E_{\text{pa}}(\text{NH}_2)$, mV
phen	638	162	---
phen-4Me	384	78	---
phen-NH ₂	494	90	1803
ppl	758	121	---
ppl-Me	740	124	---
dppz	754	60	---
dppz-NH ₂	680	85	1620

^a $E_{1/2} = 1/2(E_{\text{pa}} + E_{\text{pc}})$ v/s NHE for the Co(II/III) process.

Figure 3. Cyclic voltammograms for: a) $[\text{Co}(\text{phen-4Me})_3]^{2+}$ and b) $[\text{Co}(\text{ppl-Me})_3]^{2+}$ in CH_3CN . The concentration of the complexes was 10^{-4} M, scan rate 100 mV s^{-1} and NHE as reference electrode.

Figure 4 shows the redox potentials for the different complexes, compared to other known redox couples. As can be seen, the series of Co couples offer potentials in the 0.38 to 0.75 V range, permitting to select the most suitable for a specific dye in a given cell, according to the potential needed for its regeneration. This permits alternatives to iodine, specially in cases where the potential of the latter, (0.93 V),¹⁴ may not be suitable to regenerate the dye, e.g., for cyclometallated Ru complexes, with Ru(II/III) redox potentials of the order of 0.5 – 0.6 V.¹⁶ According to Figure 4, and given the donor nature of its substituents, the $[\text{Co}(\text{phen-4Me})_3]^{3+}/[\text{Co}(\text{phen-4Me})_3]^{2+}$ and $[\text{Co}(\text{phen-NH}_2)_3]^{3+}/[\text{Co}(\text{phen-NH}_2)_3]^{2+}$ couples seem to be the best candidates to replace iodine in these cases. Finally, the visible absorption observed in the case of where NH_2 substituents are present, makes the $[\text{Co}(\text{phen-4Me})_3]^{3+}/[\text{Co}(\text{phen-4Me})_3]^{2+}$ to be the best choice for the cases where the iodine potential is not sufficient for the dye regeneration.

Figure 4: Electrochemical redox potentials vs. NHE for a series of Cobalt polypyridine couples of general type $[\text{Co}(\text{L-L})_3]^{3+}/[\text{Co}(\text{L-L})_3]^{2+}$. Values for Fc/Fc^+ and the iodine mediator are included for comparison reasons.

CONCLUSION

The use of varied polypyridinic ligands to synthesize different Co(II) *tris* homoleptic complexes has permitted to obtain compounds with an ample range of Co(II)/Co(III) redox potentials, and that at the same time are transparent in the visible region. As mentioned in the introduction, this is a necessary condition if these systems are intended to be used as mediators in solar cells, as this is the region where the dye usually absorbs, through MLCT bands, which are efficient for the light to electricity conversion in the cell.¹⁰ In the case of the $[\text{Co}(\text{dppz-NH}_2)_3]^{2+/3+}$ couple, given that the reduced form absorbs in the visible region, its use as redox shuttle is less recommendable. The work here reported opens the possibility to have a battery of potential mediators for photoelectrochemical solar cells. Ultimately, the election of a determined couple as mediator will depend mainly on the electronic properties of the specific dye in a given cell.

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