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New mixed ligand Co(II) complexes as possible electrolytes for dye-sensitized solar cells – A combined experimental and computational approach

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Abstract: We report the synthesis and characterization of a new series of mixed ligand Co(II) complexes, $[\text{Co}(\text{AA})(\text{BB})_2]\text{X}_2$, where AA and BB are derivatives of 1,10-phenanthroline and 2,2'-bipyridil, $\text{X}=\text{Cl}^-$, TFSI⁻ (TFSI= bis(trifluoromethanesulfonyl) imide), as possible redox electrolytes for dye-sensitized solar cells. Compared to the I_3^-/I^- system, the cobalt(III/II) polypyridyl complex redox shuttles have low visible light absorption, and the ease of tuning their redox potentials is a very significant aspect for accomplishing a photovoltage enhancement. The compounds were characterized by spectral (IR and UV-VIS spectroscopy) and theoretical modeling, via Density Functional Theory calculations.

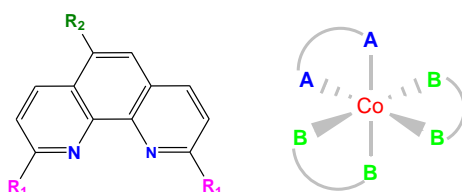
Keywords: cobalt (II) complexes; mixed ligands; DFT calculations; redox electrolyte; dye sensitized solar cells

1. Introduction

In the quest for higher performance dye-sensitized solar cells (DSCs), [1,2] an important role, belongs to the electrolyte, which ensures the electron transport and the regeneration of the dye. Aside to the initially chosen iodide based couple, a distinct series of cobalt complexes emerged, consisting in $[\text{Co}^{\text{II,III}}(\text{AA})_3]$ couples, where AA= 1,10 phenanthroline (phen), 2,2'-bipyridine (bipy), have been investigated [3]. The DSCs employing cobalt redox mediators are promising for indoor applications, the efficiency and the open-circuit voltage remaining high even at low light intensities. Moreover, related terpyridine congeners, $\text{Co}^{\text{II/III}}(\text{terpy})_2$ were relatively recently reported [4], enlarging the landscape of the systems based on cobalt complexes with aromatic amine ligands.

We advance here the idea of using mixed ligand complexes, presenting data placed at the beginning of such a way, emphasizing methodological aspects of synthesis and characterization. We have obtained and characterized a new series of heteroleptic cobalt complexes, $[\text{Co}(\text{AA})(\text{BB})_2]\text{X}_2$, where AA are derivatives of 1,10-phenanthroline (Scheme 1), 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen), 5-methyl-1,10-phenanthroline (5-mphen) and BB, 1,10-phenanthroline (phen) or 2,2'-bipyridil (bipy), X^- are chloride (Cl) or bis(trifluoromethanesulfonyl)imide (TFSI) anions. The quantum chemical calculations (performed with the GAUSSIAN03 package [5]) in the frame of Density Functional Theory (DFT) [6] were used as complement in the characterization.

Scheme 1.



2. Results and Discussion

2.1. Synthesis and experimental spectroscopical characterization.

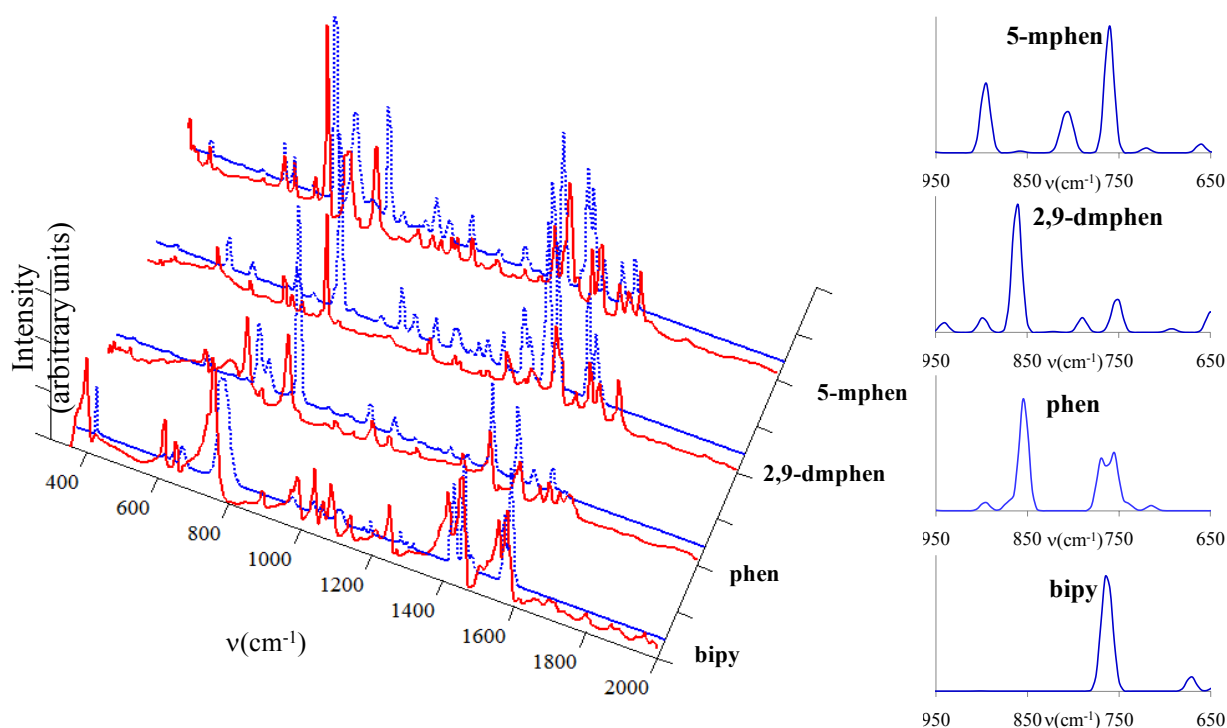
We synthesized four new mixed ligand Co(II) complexes, $[\text{Co}(2,9\text{-dmphen})(\text{phen})_2](\text{TFSI})_2$ (**1**), $[\text{Co}(2,9\text{-dmphen})(\text{bipy})_2](\text{TFSI})_2$ (**2**), $[\text{Co}(5\text{-mphen})(\text{phen})_2](\text{TFSI})_2$ (**3**), $[\text{Co}(5\text{-mphen})(\text{bipy})_2](\text{TFSI})_2$ (**4**) by a stepwise synthesis, avoiding the tendency to form homoleptic tris-chelates compounds. In the first step we synthesized $[\text{Co}(\text{AA})\text{Cl}_2]$ complexes, where AA=2,9-dmphen, 5-mphen and in the second, the corresponding $[\text{Co}(\text{AA})(\text{BB})_2]\text{Cl}_2$, where BB=phen, bipy. The counter ion was exchanged in the third step by TFSI⁻ anion, to obtain more soluble complexes.

The IR spectrum of 1,10-phenanthroline present intense lines at 738, 853, 1421 and 1503 cm^{-1} . In the case of complexes (**1**) and (**3**) we found this peaks at near 726, 846, 1428 and 1519 cm^{-1} pointing out the presence of phen in these complexes. Similarly, 2,2'-bipyridil has strong peaks at 760 (wagging mode of the periferal H atoms) and 1454 cm^{-1} (scissoring mode, δCCH), which are also found at about 767 and 1444 cm^{-1} in the infrared spectra of complexes (**2**) and (**4**). The spectrum of K(TFSI) shows strong peaks at 1055, 1143, 1198 and 1332 cm^{-1} .

The analysis of experimental vibration spectra benefits from the help of the nowadays available tools of molecular modeling. Since the spectra of mixed ligand complexes are rather complicated, we

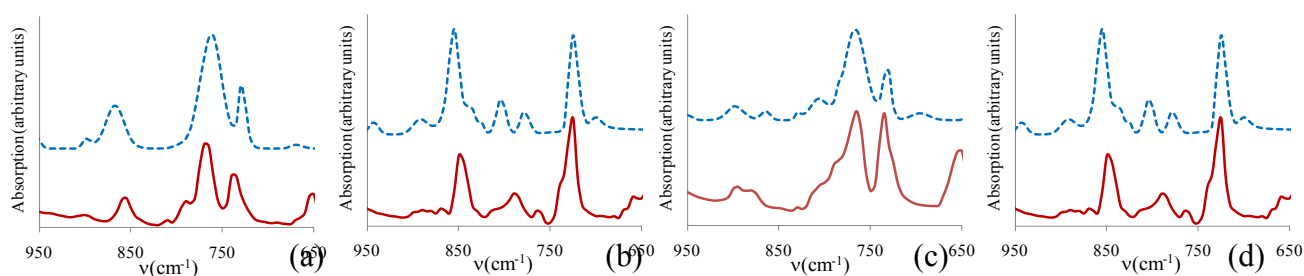
systematically start with a methodological preamble, illustrating that the computational data are reproducing well the vibration pattern of each diamine ligand (see Figure 1. left). Based on this premise, we employ the molecular modeling in the further, understanding of coordination compound molecular vibration spectra. We selected as spectral interval ($650\text{-}950\text{ cm}^{-1}$) as characteristic fingerprint for identifying the different diamines, which, as illustrated in the Figure 1 (right side), shows distinct features for the each ligand. The vibrations in this mode are assigned to wagging modes of peripheral C-H bonds, the overall patterns being therefore characteristic to the ligand skeleton.

Figure 1. Left side: The experimental (red continuous line) vs. computed (blue dotted line) vibration spectra of the used diamine ligands. Right side: the simulated patterns in the interval $650\text{-}950\text{ cm}^{-1}$ considered as fingerprint zone for the different diamine ligands.



After the above assessment, we use the comparison between the experiment and the computational simulation on the complex coordination units. The structures of all complexes with tris-chelates and a pseudo-octahedral geometry were optimized for the quartet spin state by unrestricted DFT calculations. Based on optimized geometries, the IR spectra were simulated using the B3LYP/ECP-LANL2-DZ setting in the DFT method. Using the above discussed fingerprint window, we compare in the Figure 2 the pattern of experimental vs. computed spectra. With an overall adjusting factor of the 0.96-0.98 of the computed frequencies, in accordance with customary practice [7], we find a good match of the computed vs. experimental profiles. In the inherent complexity of the coordination unit, as a whole, the denominated finger zone cannot be simply characterized as the sum of ligand frequencies. The frequencies are slightly affected by coordination and the intensity mechanisms can be entirely changed in the global charge distribution. The resembling of the computed pattern with the experimental one is considered as a validation of the mixed ligand structure, in each specific case.

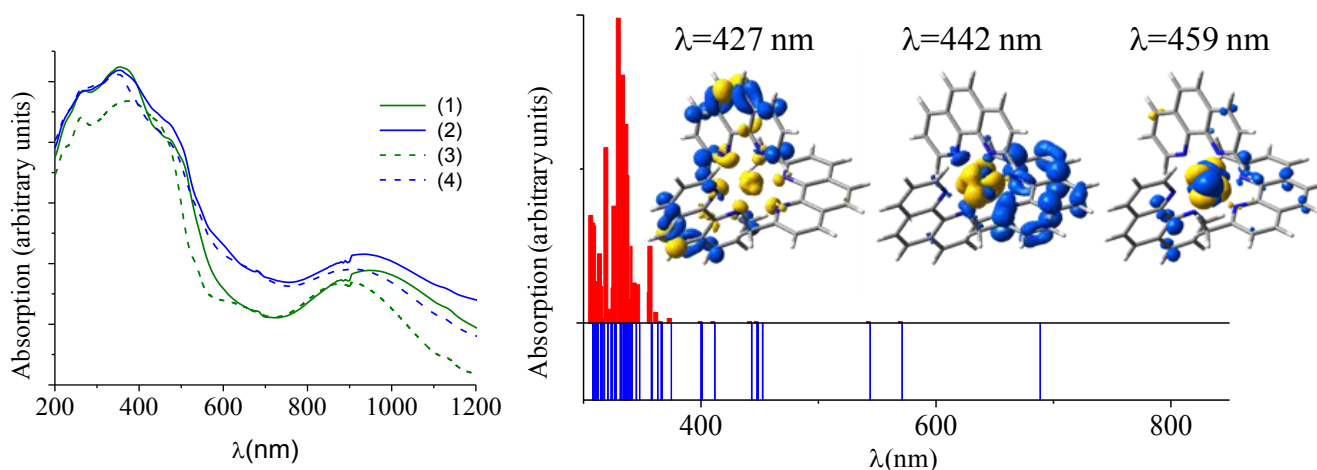
Figure 2. The experimental (continuous line) vs. simulated (dashed line) vibration bands in the interval 650-950 cm^{-1} for the mixed ligand complexes, as follows: (a) $[\text{Co}(2,9\text{-dmphen})(\text{bipy})_2]^{2+}$; (b) $[\text{Co}(2,9\text{-dmphen})(\text{phen})_2]^{2+}$; (c) $[\text{Co}(5\text{-mphen})(\text{bipy})_2]^{2+}$; (d) $[\text{Co}(5\text{-mphen})(\text{phen})_2]^{2+}$.



In the following we will consider the electronic spectra. The experimental curves shown in Figure 3 have the shape known from the general textbooks of inorganic electronic spectroscopy [8]. The Co(II) octahedral chromophore shows three bands, ν_1 , ν_2 , ν_3 as transitions from ${}^4T_{1g}$ groundstate to the respective ${}^4T_{2g}$, ${}^4A_{2g}$, and ${}^4T_{1g}$ excited levels. The ν_1 band is assignable to the maxima visible, in all the cases, between 900-1000 nm. The ν_2 transition is usually not visible, while the ν_3 is assignable to the peaks and shoulders between 400-500 nm, the split aspect being possibly due to the mixed nature of the coordination spheres.

Optical absorption spectra of all complexes were simulated using the Time Dependent (TD)-DFT method [9]. In contrast to the IR spectra, the computed optical transitions and intensities cannot reproduce well the experimental profile. A cause is in the intensity part, since the d-d transitions acquire intensity by vibronic mechanisms, [10] that are not accounted by TD-DFT.

Figure 3. Left side: experimental UV-VIS electronic spectra for the compounds 1-4. Right side: TD-DFT data for $[\text{Co}(2,9\text{-dmphen})(\text{phen})_2]^{2+}$ unit (energy levels and intensities). Inset: density difference maps (excited states minus groundstate) for selected transitions.



We characterize the TD transitions, in a very picturesque manner, performing the difference between the density in a given excited state and those of the groundstate, the corresponding map revealing the molecular zones where the density is depleted vs. those where it is accumulated, in the

given transition. Selected transitions are shown in Figure 3. For $\lambda = 459$ nm, the lobes of the charge displacement are concentrated around the metal, suggesting a d-d transition. The $\lambda = 442$ nm is a metal-to-ligand charge transfer, identified as a $d \rightarrow \pi^*(2,9\text{-dmphen})$ process, while a $d \rightarrow \pi^*(\text{phen})$ band is identified at 427 nm. The other bands are of various other $d \rightarrow \pi^*$, $\pi \rightarrow d$ and $\pi \rightarrow \pi^*$ nature.

3. Experimental Section

3.1. Synthesis

All chemicals and solvents were used as received (Sigma Aldrich). The synthesis of $[\text{Co}(\text{AA})\text{Cl}_2]$ complexes started from ethanolic solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2 mmol, 10mL EtOH) and aromatic diamine (AA, 2 mmol, 10mL EtOH), stirring 1 hour and gently refluxing at 60°C , until a crystalline product was deposited. The suspension was filtered and dried. The second step consists in the adding of the other aromatic diamine BB (4 mmol, 10mL EtOH), over the solution in acetonitrile of $[\text{Co}(\text{AA})\text{Cl}_2]$, gently refluxing at 60°C for 30 minutes. The $[\text{Co}(\text{AA})(\text{BB})_2]\text{Cl}_2$ complexes are obtained concentrating the yellow solution on the rotaevaporator. In the last step we replaced the Cl^- with TFSI⁻ anions, by adding KTFSI to the acetonitrile/ethanol solution containing the $[\text{Co}(\text{AA})(\text{BB})_2]\text{Cl}_2$ complex. The suspension was filtered to eliminate KCl and the solution was concentrated on the rotaevaporator. Yellow-brown crystalline powders were filtered and dried.

3.2. Physical Measurements

Fourier transform infrared spectroscopy was performed using a JASCO FT/IR-4200 instrument with KBr pellets in the $400\text{--}4000\text{ cm}^{-1}$ region. Electronic spectra of the solids were obtained by diffuse reflectance, using MgO as standard, on a JASCO V670 spectrometer.

3.3. Computational details

The geometry optimization, IR and Raman optical activity spectra, electronic structure and transitions in acetonitrile solvent were calculated with the GAUSSIAN03 package [5] using unrestricted DFT methods based on the hybrid B3LYP exchange-correlation functional. The Los Alamos Effective Core Potential (ECP) and double- ζ quality functions for valence electrons were used by employing the LANL2DZ basis set.

4. Conclusions

With the aim to obtain new redox couples designed to increase the open-circuit voltage of dye-sensitized solar cells, new cobalt polypyridine complexes were synthesized and characterized spectroscopically. The systems are individualized by characteristic fingerprints of the vibration spectrum in the $650\text{--}950\text{ cm}^{-1}$. The different patterns in the series $[\text{Co}(\text{AA})(\text{BB})_2]^{2+}$ are indicative of mixed ligand nature of the obtained systems.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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