Novel Heteroleptic Ruthenium(II) Complexes with 2,2′-Bipyridines Containing a Series of Electron-Donor and Electron-Acceptor Substituents in 4,4′-Positions: Syntheses, Characterization, and Application as Sensitizers for ZnO Nanowire-Based Solar Cells

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ABSTRACT: A novel series of complexes of the formula \([\text{Ru}(4,4′-X_2\text{-bpy})_2(\text{Mebpy-CN})](\text{PF}_6)_2\) (X = −CH₃, −OCH₃, −N(CH₃)₂; Mebpy-CN = 4-methyl-2,2′-bipyridine-4′-carbonitrile) have been synthesized and characterized by spectroscopic, electrochemical, and photophysical techniques. Inclusion of the electron-withdrawing substituent −CN at one bpy ligand and different electron-donor groups −X at the 4,4′-positions of the other two bpy ligands produce a fine tuning of physicochemical properties. Redox potentials, electronic absorption maxima, and emission maxima correlate well with Hammett’s σᵢ parameters of X. Quantum mechanical calculations are consistent with experimental data. All the complexes can be anchored through the nitrile moiety of Mebpy-CN over ZnO nanowires in dye-sensitized solar cells that exhibit an improvement of light to electrical energy conversion efficiency as the electronic asymmetry increases in the series.

INTRODUCTION

Developing new materials for conversion of solar into electrical or chemical energy is a relevant area of research for the substitution of fossil fuels and mitigation of climate change. Dye-sensitized solar cells (DSCs) using n-type semiconductor materials such as TiO₂ and sensitizers such as ruthenium complexes are promising low-cost devices based on the discovery of the Grätzel cell. Polypyridylruthenium(II) complexes have been extensively studied since their photosensitive and redox properties are suitable for using them as sensitizers in optoelectronic devices and DSCs. The commercial dye N719⁵ and the black dye⁶ are examples of efficient sensitizers that absorb a wide range of wavenumbers of visible light. Although they are very efficient converters, chemical stability problems arise when considering the possibility of decomposition of the −NCS group, as suggested before.⁷

Tris-substituted bipyridineruthenium(II) complexes are highly stable and a large variety of chemical transformations in the bipyridine rings can be accomplished. It is well known that addition of electron-donor or electron-acceptor groups to the 4- and 4′-positions of bpy (bpy = 2,2′-bipyridine) alter the physicochemical properties of trisbipyridineruthenium complexes. Byps with electron-donor substituent groups have π orbitals suitable to mix with d orbitals of Ru(II), the net effect being the destabilization of the highest occupied molecular orbital (HOMO). On the other hand, the lowest unoccupied molecular orbital (LUMO) is a π* orbital centered in the byps and it can be stabilized by introducing electron-acceptor substituents in the bpy rings. The usual procedure to obtain red-emitting Ru(II) complexes is the addition of better π-accepting substituents, such as −CN, −CH₃, and −OCH₃.
acceptor ligands than bpy in order to decrease the energy of the LUMO and better σ-donor ligands than bpy in order to increase the energy of the HOMO, such as those complexes described by Hanan et al.\textsuperscript{3} The overall result of combining both trends is a decrease of the HOMO–LUMO gap and a shift of light absorption and emission maxima to the near-infrared (NIR) spectrum region, among other physicochemical property changes.

With these modifications, the sensitization of a wide band gap semiconductor at longer wavelengths of the solar spectrum led to the creation of new electrodes in DSC devices, as already reported for TiO\textsubscript{2}-nanostructured electrodes.\textsuperscript{5,10} In recent years, ZnO have become very common in semiconductor devices\textsuperscript{11} due to its unique optical, chemical, electrical, and piezoelectrical properties,\textsuperscript{11–16} being also a material easy to obtain in different morphologies (films, nanoparticles, and nanowires)\textsuperscript{17–19} and having the added possibility of making core–shell structures with other materials to change their optical and electrical properties.\textsuperscript{20,21} In the broad spectrum of challenges related to this issue, we address in this work the possibility of improving electron injection efficiency in ruthenium complex DSCs by a careful selection of coligands and using ZnO as a semiconductor, since its sensitization with Ru complexes has received much less attention. ZnO is currently considered as one of the most promising materials to replace the TiO\textsubscript{2} semiconductor\textsuperscript{22} in solar energy conversion technology. In particular, ZnO nanowires (NWs) in a DSC create direct electron pathways, which lead to an increase of electron diffusion length and lifetime.\textsuperscript{22,23} In some of our previous studies, very efficient charge transfer between Ru complexes and ZnO nanowires\textsuperscript{24,25} was evidenced, indicating the possibility of exploring new Ru complex/ZnO nanowire structures to develop better DSCs.

In this paper, three new ruthenium(II) polypyridyl complexes of the formula \([\text{Ru}(4,4′-\text{X}_2\text{bpy})_2\text{Mbpyn-CN}]\cdot(\text{PF}_6)_2\), where \(\text{X} = \text{-CH}_3, \text{OCH}_3, \text{-N(CH}_3)_2\) and \text{Mbpyn-CN} = 4-methyl-2,2′-bipyridine-4′-carbonitrile, have been synthesized (Scheme 1). Electrochemical, spectroscopic, and photophysical studies have been carried out and the electronic properties can be rationalized by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Finally, we demonstrate that ZnO nanowires, grown in fluoride tin oxide (FTO) substrates using a hydrothermal technique, can be sensitized by these complexes anchored to the semiconductor surface through a nitrile group and used as working electrodes in DSCs that perform at low efficiencies but could be improved by increasing the number of anchoring nitrile groups.

**RESULTS AND DISCUSSION**

**Syntheses, IR, and NMR Spectra.** The precursors Ru(4,4′-X\textsubscript{2}-bpy\textsubscript{2})Cl\textsubscript{2} were prepared by using procedures similar to those previously reported.\textsuperscript{26,27} As described by Pannwitz et al.,\textsuperscript{27} \([\text{Ru}(4,4′-\{\text{N(CH}_3)_2\}_2\text{bpy})_2\text{Cl}]\)Cl was obtained first as a Ru(III) precursor due to the stabilization of higher oxidation states induced by a strong electron-donor group in the bpy ring such as dimethylamine. For this particular complex, trimethylamine was added in the next preparative step in order to reduce Ru(III) to Ru(II). The new complexes 1–3 were prepared by protocols already known.\textsuperscript{26}

Fourier transform infrared (FTIR) spectra of complexes 1–3 exhibit a very weak band at 2235 cm\textsuperscript{-1}, which is characteristic of \(\nu_{\text{CN}}\) of the stretching vibration of the C\equivN group of Mebpy-CN. Typical bands corresponding to the vibrational modes of the polypyridyl moieties (4,4′-(X)\textsubscript{2}-bpy and Mebpy-CN) are observed between 1600 and 1400 cm\textsuperscript{-1}.

Figure S2 shows the FTIR spectrum of complex 3 as a representative example. The values of \(\nu_{\text{CN}}\) are obtained using the Raman spectra of complexes 1–3 are identical with those measured by FTIR and almost equal to that of the free ligand, indicating that Mebpy-CN is not coordinated to the metal through the nitrile group.

Complexes 1–3 possess C\textsubscript{3} symmetry and all the signals of the atoms of the substituted bpy ligands in the NMR spectra are therefore inequivalent. For this reason, signals of \(^1\text{H}\) and \(^13\text{C}\) for the 4,4′-X\textsubscript{2}-bpy ligands are reported as broad bands.

On the other hand, signals for the Mebpy-CN ligand can be assigned straightforwardly by comparison with data previously reported for similar complexes with this ligand.\textsuperscript{22} Detailed assignments of \(^1\text{H}\)-NMR, \(^13\text{C}\)-NMR, and \(^15\text{N}\)-NMR signals of complexes 1–3 as well as mass spectroscopy (MS) data can be found in the Syntheses Section. Figures S3–S9 show all the NMR spectra of complex 3 as a representative example and the complete assignments are shown in Figure S10. NMR and MS results confirm the proposed structures depicted in Scheme 1.

**Electrochemistry.** Redox potentials of complexes 1–3 in CH\textsubscript{3}CN with 0.1 M TBAH are shown in Table 1. The first two reduction potentials were measured by CV, while the following ones were measured by DPV. The values for the reference complex \([\text{Ru(bpy)}_2\text{(Mebpy-CN)}](\text{PF}_6)_2\)\textsuperscript{25} were measured again under the same conditions. Cyclic and differential pulse voltammograms of complex 3 as a representative example are shown in Figures S11 and S12, respectively.

When the electron-donor strength of the substituent X of 4,4′-(X)\textsubscript{2}-bpy was increased, a cathodic shift of redox potential of the Ru\textsubscript{III}/\textsubscript{II} couple, \(E_{\text{1/2}}\text{ox}\) was observed. Less pronounced cathodic shifts are also observed for the redox potentials of the ligand reductions \(E_{\text{1/2}}\text{red}^1\) and \(E_{\text{1/2}}\text{red}^2\) and \(E_{\text{1/2}}\text{red}^3\). In polypyridylruthenium(II) complexes, when the metal center

![Scheme 1. Molecular Structures of the New Trisbipyridine Ruthenium(II) Complexes](image-url)
is oxidized to Ru(III), electron-donor groups in the bpy rings stabilize this latter state by sharing more electron density with the metal. The one-electron reduction process is expected to be centered in the best electron-accepting bpy, Mebpy-CN in this case. Increasing the electron-donor strength of the substituent X in the bpy rings changes the amount of metal-to-ligand π-backbonding, making their reduction more difficult.

The one-electron oxidation process involves removal of an electron from the HOMO, which is a dπ(Ru) orbital. On the other hand, the one-electron reduction process involves addition of an electron to the LUMO, which is centered in the best electron-accepting bpy, Mebpy-CN, as discussed in the Calculations Section. A plot of the difference of potentials of the oxidative and the first reductive processes, ΔE1/2, as a function of Hammett’s σp parameter shown in Figure 1, is linear and evidences that increasing the donor strength of the substituent group −X destabilizes the HOMO more than the LUMO. This was already reported by Maestri et al. for a series of electron-donor-substituted terpyridines.29 The net effect is a reduction of the HOMO–LUMO energy gap with the increase of the electron-donor strength of −X, as discussed below.

**UV–Vis Spectra.** The electronic absorption spectra of complexes 1–3 are displayed in Figure 2. The absorption maxima and molar extinction data are summarized in Table S1. For comparative purposes, data for [Ru(bpy)3](PF6)2 and [Ru(bpy)2(Mebpy-CN)](PF6)2 have also been included in the table. All the complexes show intense absorption bands in the visible region, which can be assigned to metal-to-ligand charge transfer (MLCT) transitions.3 As shown in Table S1, coordination of a 4,4'-X2-bpy ligand diminishes the wavelength of the lowest-energy MLCT band in the order of increasing donor strength of −X:

\[
-H < -\text{CH}_3 < -\text{O}(\text{CH}_3)_2 < -\text{N}(\text{CH}_3)_2
\]

Besides, the asymmetry within the coordination sphere increases in the same order, resulting in splitting of all the visible absorption bands, as compared to [Ru(bpy)3](PF6)2 and [Ru(bpy)2(Mebpy-CN)](PF6)2. The splitting goes from 0.20 eV in complex 1 (λmax = 478 and 444 nm) to 0.24 eV in complex 2 (λmax = 488 and 446 nm) and to 0.44 eV in complex 3 (λmax = 532 and 448 nm). As explained in the Calculations section, the least energetic band can be assigned to a dπ(Ru) → π*(Mebpy-CN) MLCT transition, while the following band can be assigned to a dπ(Ru) → π*(4,4'-X2-bpy) MLCT transition. Absorption of visible light is thus extended to a broader range when increasing the donor strength of −X, making complex 3—with X = −N(\text{CH}_3)_2—almost black in color. The area below the two split bands is almost the same as that of the MLCT bands of [Ru(bpy)3](PF6)2. The maximum frequency of the lowest-lying MLCT band, νMLCT, and the electrochemical energy gap, ΔE1/2 (see Table 1), are correlated linearly, as expected since both values depend on the HOMO–LUMO gap.30

**Spectroelectrochemistry.** UV–vis–NIR spectroelectrochemical measurements for complexes 1–3 are shown in Figure 3. One-electron oxidation, MLCT bands for all these complexes decrease in intensity, as expected upon changing the metal configuration from d6 to d5. Also, new bands arise at λmax between 300 and 400 nm, which can be assigned to intraligand charge transfer (ILCT) transitions in the oxidized species. Complex 3 exhibits a wide band at λmax from 600 to 1000 nm, which is not present in the other complexes. TD-DFT calculations of 3 show a set of ligand-to-metal charge transfer (LMCT) transitions from a π(4,4'-DMA-bpy) to a dπ-Ru(III) orbital, as explained below in the Calculations Section. On the other hand, upon one-electron reduction, two new bands appear at λmax around 350 to 370 and 530 to 550 nm. Both are typical of bpy radical formation.31

**Photophysical Properties.** Table 2 shows the photophysical properties of complexes 1–3 in CH3CN at room temperature, together with the previously studied complex with X = −H.28 The room-temperature emission spectra of complexes 1–3 are depicted in Figure S13. Time-resolved differential absorption spectra of complexes 1–3, obtained by LFP, are shown in Figure 4. In all cases, bleaching of the MLCT bands and appearance of new bands at λmax = 370 nm are detected. This latter band is associated with ILCT transitions of the Mebpy-CN− radical and is unaffected by the electron-donor ability of −X in the substituted bpy's. The spectroelectrochemical measurements described above show that upon one-electron oxidation and reduction of complexes 1–3, similar bands are detected; therefore, the lowest-lying MLCT excited state can be formulated as [Ru3+(4,4'-X2-bpy)2(Mebpy-CN−)]2+. As the electron-donor ability of X increases, the excited state is stabilized and the
emission band shifts to longer wavelengths reaching the near-infrared region (see Table 2 and Figure S13). The emission wavenumbers correlate with the MLCT absorption wavenumbers.

As predicted by the energy gap law,32 lowering of the energy gap between the excited and ground state is accompanied by an increase in the nonradiative kinetic constant, $k_{nr}$, and consequently a decrease of the excited state lifetime.

**Calculations.** DFT and TD-DFT calculations allowed us to explain the experimental results that depend on electronic structures. Geometries were assumed to be the same as those of a similar complex determined by crystal structure studies.25 The molecular orbital energy levels of complexes 1–3 and

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**Figure 3.** (a) Oxidative difference spectra acquired at an applied potential 100 mV higher than the oxidative potential of the metallic center of complexes 1–3, respectively, in CH$_3$CN solutions. (b) Reductive difference spectra acquired at an applied potential 100 mV lower than the first reductive potential of complexes 1–3, respectively, in CH$_3$CN solutions.

**Table 2. Photophysical Properties of Complexes 1–3 and [Ru(Bpy)$_2$(Mebpy-CN)](PF$_6$)$_2$ in CH$_3$CN at rt**

| complex                  | $\lambda_{em}$ [nm] | $\Phi_{em}$ | $\tau$ [µs] | $k_{obs} \times 10^{-5}$ [s$^{-1}$] | $k_r \times 10^{-5}$ [s$^{-1}$] | $k_{nr} \times 10^{-5}$ [s$^{-1}$] |
|-------------------------|---------------------|-------------|-------------|----------------------------------|------------------|-------------------|
| [Ru(bpy)$_2$(Mebpy-CN)](PF$_6$)$_2$ | 623                 | 0.120       | 0.76        | 13.2                             | 1.58             | 11.6              |
| 1                       | 666                 | 0.024       | 0.67        | 14.9                             | 0.36             | 14.5              |
| 2                       | 709                 | 9.3 x 10^{-3}| 0.32        | 31.3                             | 0.29             | 31.0              |
| 3                       | 798                 | 2.0 x 10^{-4}| 0.02        | 465                              | 0.093            | 465               |
[Ru(bpy)$_2$(Mebp-CN)](PF$_6$)$_2$, calculated by DFT, are shown in Figure 5. For all complexes (see Figure 5 and Table S2), the HOMOs are d$_{\pi}$-Ru(II)-type orbitals close in energy with some contribution of $\pi$ orbitals of 4,4$'$-$(X)$2-bpy that increases with increasing electron-donor strength of X. LUMOs for all complexes are delocalized over the Mebpy-CN ligand. A small destabilization of the LUMO with an increase of the electron-donor strength of X is observed due to some mixing with $\pi$(4,4$'$-$(X)$2-bpy) orbitals. The overall effect of increasing the electron-donor strength of X is a decrease in the HOMO−LUMO gap (see Figure 5). Orbital pictures of HOMOs and LUMOs for complexes 1−3 are displayed in Figure 6. For example, the HOMO of complex 3 has a larger contribution of orbitals localized at the bpy ligand with dimethylamino substituents, indicating higher delocalization between electron-donor-substituted byps and metal orbitals than that observed for the other two complexes. This is also reflected in Table S2, where participation of X2bpy in the HOMO increases from 10% in [Ru(bpy)$_2$(Mebp-CN)]$^{2+}$ to 12% in 1, to 15% in 2, and to 40% in 3.

Figure 4. Time-resolved differential absorption spectra of 1(top), 2 (middle), and 3 (bottom) in CH$_3$CN solutions at different times ($\lambda_{exc} = 370$ nm) (left) and the absorbance decay at $\lambda = 370$ nm and mono-exponential fitting (right).

Figure 5. Molecular orbital (MO) diagrams calculated by DFT for complexes 1−3 and [Ru(bpy)$_2$(Mebp-CN)](PF$_6$)$_2$. Different contributions of the groups are marked in different colors: ruthenium in black, 4,4$'$-$(X)$2-bpy in red, and Mebpy-CN in blue. The HOMO−LUMO energy gaps are also depicted.

Figure 6. Orbital representations of LUMOs (top) and HOMOs (bottom) of complexes 1–3.
Raman spectra of FTO/ZnO NW electrodes sensitized by complexes 1–3 are shown in Figure S17. In all cases, two bands are detected in the nitrile stretching frequency region, $\nu_{\text{CN}}$: one at 2240 cm$^{-1}$, which is identical with those measured in the FTIR spectra of the solid complexes, as described before, corresponding to free nitriles, and one at 2333 cm$^{-1}$, which can be assigned to nitrile groups bound to the ZnO surface, indicating chemical adsorption of the complex on the semiconductor. This shift has been observed before when the complex with $X = H$ was adhered to TiO$_2$.33 The appearance of an unbound dye can be attributed to the presence of only one anchoring nitrile group in all the complexes studied here. Ongoing work on the series [Ru($4,4'$-X$_2$-bpy)($\text{Mebpy-CN}$)$_2$](PF$_6$)$_2$ containing two anchoring nitrile groups will hopefully improve the quantity of sensitizers adsorbed on the surface and consequently the solar cell efficiency. It must be noted that the highest efficiency was detected in our previously studied Ru systems with two nitrile groups adsorbed on TiO$_2$.33

The QE spectra of the solar cells, Figure 9a, were acquired under ambient temperature (25 ± 1 °C). The higher efficiencies were observed for incident radiation with the wavelength ranging from 450 to 600 nm, consistent with the UV–visible spectra of sensitized FTO/ZnO NW electrodes (Figure S16). A red shift in the QE band of the electrode is detected when going from 1 to 3, showing that the sample sensitized with complex 3 presents a higher value of efficiency than the other complexes for identical times of immersion and a better response to lower wavelengths. In Figure 9b, $I$–$V$ curves for all the solar cells are presented: they were obtained under irradiation with a solar simulator (linear sweep voltammetry, 5 mV s$^{-1}$) at 28 ± 1 °C. Table 3 shows the parameters obtained for these DSCs: under polychromatic irradiation, they all show an overall efficiency, $\eta$, of 0.03–0.017 %, open circuit voltages ($V_{oc}$) in a 0.38–0.26 V range and short circuit current values between 0.17 and 0.14 mA/cm$^2$.

Considering these data, the best photoresponse was that of the cell sensitized by complex 3, according to its higher absorption in the NIR region. When comparing these data with the reference N719, the efficiencies were found to be lower by a factor of 10 for our complexes in the same conditions, as expected because of lower adsorption of the dyes, as discussed before. Although the efficiencies obtained are low, our data support the fact that panchromatic shifts in absorption lead to increasing photocurrent generation by modulating the electronic asymmetry by small structural changes in the sensitizer. We hope to improve the cell performances using complexes with two anchoring nitrile groups.

It has already been reported that very low efficiencies are obtained when loading ruthenium polypyridyl complexes onto ZnO surfaces with anchoring carboxylate groups.34 We demonstrate in this work that anchoring similar complexes with nitrile groups onto ZnO nanowires is a promising approach when combined with the occurrence of panchromatic shifting induced by small structural variations in the bipyridine rings as described in this work.

### CONCLUSIONS

Changing the electron-donor ability of substituent $-X$ in heteroleptic complexes of the formula [Ru($4,4'$-$X$$_2$-bpy)($\text{Mebpy-CN}$)$_2$](PF$_6$)$_2$, with $X = -\text{CH}_3$, $-\text{OCH}_3$, and $-\text{N}$(CH$_3$)$_2$, allows us to obtain a fine tuning of the electronic properties of this series of new complexes. Enhancing

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**Figure 7.** TD-DFT calculated (straight line) and experimental (dashed line) UV–vis spectra of complexes 1–3.

**Application as Sensitizers for ZnO Nanowire-Based Solar Cells.** Figure 8a,b shows the side and front SEM images, respectively, corresponding to a FTO/ZnO NW sample grown by the hydrothermal technique; both images prove that nanowires are formed. Besides, the morphology of the ZnO NWs shows the expected hexagonal wurtzite structure in agreement with the XRD results, shown in Figure 8c, with a mean diameter of 100 nm.

Electrodes of FTO/ZnO NWs were characterized by EDAX, UV–vis, and Raman spectra. The EDAX spectrum, shown in Figure S15, indicates only the presence of ZnO, evidencing the purity of this semiconductor. As shown in Figure 8c, the XRD patterns of ZnO NWs, as compared with those of a standard ZnO polycrystalline powder sample, indicate that the NWs grew with a preferential orientation normal to the (002) plane, corresponding to the c axis of the wurtzite structure. Secondary peaks, corresponding to (101) and (102) planes, are not present in the NW structure. The normalized UV–vis spectra of ZnO NWs sensitized with complexes 1–3 are displayed in Figure S16; they present bands in the visible region, which correspond to those previously measured in CH$_3$CN solutions of complexes 1–3, as shown in Figure 2, which are somewhat masked by bands in the UV region due to the ZnO NWs.
asymmetry induces absorption over all visible wavelengths and emission with appreciable quantum yields in the NIR region. The observed changes in redox potentials, MLCT absorption and emission maxima, and excited state dynamics can be rationalized using Hammett $\sigma_p$ parameters of X, consistent with the important contribution of $-X$ in modulating electron densities and orbital energies in these complexes, which can be used as dyes in DSCs over Zn NWs by anchoring the nitrile group of Mebpy-CN to the semiconductor surface. Enlarging the electron density asymmetry in these molecules by increasing the donor strength of $-X$ gives more pronounced panchromatic shifting and higher photocurrent generation, a concept that may be useful for the development of more efficient DSCs.

![Figure 8](image_url)

**Figure 8.** (a) Side and (b) front view SEM images of ZnO NWs grown using the hydrothermal technique. (c) XRD data of FTO/ZnO NWs compared with those of a bulk sample of the ZnO (commercial powder) spectrum.

![Figure 9](image_url)

**Figure 9.** Performance of solar cells assembled with the sensitized FTO/ZnO NWs, Pt counter electrodes, and a liquid electrolyte: (a) quantum efficiency spectra and (b) current–potential ($I$–$V$) curves under polychromatic irradiation.

| dye | $V_{oc}$ (V) | $I_{sc}$ (mA/cm²) | $P_{max}$ (mW/cm²) | $P_{theo}$ (mW/cm²) | $ff$ | $\eta$ (%) |
|-----|--------------|-------------------|--------------------|---------------------|------|------------|
| (1) | 0.26         | 0.14              | 3.7                | 2.1                 | 0.58 | 0.016      |
| (2) | 0.22         | 0.15              | 3.4                | 2.2                 | 0.64 | 0.018      |
| (3) | 0.38         | 0.17              | 6.6                | 3.9                 | 0.59 | 0.030      |

$P_{theo} = V_{oc} \times I_{sc}$. $P_{max} = I_{max} \times V_{max}$. $ff = (P_{max}/P_{theo})$. $\eta = overall efficiency$.  

Table 3. Parameters Obtained from $I$–$V$ Curves for the Dye-Sensitized ZnO Solar Cells under Polychromatic Irradiation

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### EXPERIMENTAL SECTION

**Materials and Instrumentation.** All the chemicals used in this work were of analytical reagent grade and were used as purchased. CH$_3$CN was freshly distilled over KMnO$_4$. Infrared spectra (4000–400 cm$^{-1}$) of the solids were obtained using...
KBr pellets with a Perkin-Elmer FTIR RX-I spectrometer. Characterization of the new complexes was carried out in CH3CN solutions by spectroscopic, electrochemical, and photophysical techniques. Construction and instruments used for characterizing the dye-sensitized ZnO nanowire-based solar cells are described below. NMR spectra were obtained in CD3CN with a Bruker 500 MHz device operating at a frequency of 500.13 MHz for 1H NMR, 125.75 MHz for 13C NMR, and 100.67 MHz for 15N NMR. Electron spray ionization (ESI) mass spectra were recorded on a Bruker Esquire 6000 MS. Chemical analyses were performed at INQUIMAE, University of Buenos Aires, Buenos Aires, Argentina, with an estimated error of ±0.5%. Electrochemical measurements were performed with BAS Epsilon EC equipment, using 0.1 M tetraethylammonium hexafluorophosphate (TBAH) as the reference electrode. For reversible electrochemical processes, reported E1/2 values were calculated from cyclic voltammetry (CV) measurements as the averages between the peak values corresponding to the cathodic (Ec) and anodic (Ea) waves: E1/2 = (Ea + Ec)/2. In cases where redox processes were quasi-reversible, potentials were obtained by differential pulse voltammetry (DPV). UV–vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer using 1 cm quartz cells. Absorption spectra of solid films were measured in the same instrument using a solid sample holder for Cary 50/60. Raman spectra were obtained with a DXR spectrometer from Thermo Scientific equipped with a binocular Olympus microscope. Steady-state emission measurements were made at room temperature on a Shimadzu RF-5301 PC spectrophotometer. Relative radiative quantum yields were calculated by eq 1

\[
\Phi_r = \Phi_l \left( \frac{I_r}{I_l} \right) \left( \frac{\eta_l}{\eta_r} \right)^2
\]

where \(\Phi_l\) is the quantum yield of a reference \([Ru(bpy)_3]^2+\) (PF6)2 in acetonitrile \((\Phi_l = 0.995)\). UV–vis spectrophotometric and electrochemical experiments were performed in CH3CN (0.1 M TBAH) using a Honeycomb spectrophotocatalytic cell (Pine Research) with Pt as the working and counter electrode and Ag/AgCl as the reference electrode. Lifetime and transient spectra of the lowest-lying MLCT excited states were obtained with the laser flash photolysis (LFP) setup described previously. Luminescence lifetimes were also determined by the time-correlated single photon counting (TCSPC) technique with a Temporo-01 apparatus from HORIBA Jobin Yvon (Glasgow, U.K.) using as the excitation pulse source an ultrafast 450±15 nm Nanoleo operating at 250 kHz. Fluorescence intensity decay was fitted with the fluorescence decay analysis software DAS6 of HORIBA Jobin Yvon. The obtained fluorescence lifetimes were determined and TD-DFT calculations were made. The contribution of the different groups of molecules to orbitals and electronic transitions were obtained using version 3.0 of the GaussSum software package.

**Syntheses.** The precursors \([Ru(4,4′-X_2-bpy)_2Cl_2]\) were prepared following previously published methods. Mebpy-CN was prepared as reported previously. A mixture of 26 mg of Mebpy-CN (0.13 mmol) and 72 mg of \([Ru(4,4′-(OCH_3)_2-bpy)_2Cl_2]\) (0.13 mmol) was added to 30 mL of deaerated methanol and heated at reflux under Ar for 4 h. The obtained orange solution was rotaevaporated to dryness, dissolved in a minimum amount of water, and passed through a CM Sephadex C-25 column. The complex was eluted with 1 M HCl, and the collected fractions were rotaevaporated to dryness, dissolved in a minimum amount of water, and precipitated with a concentrated aqueous solution of KPF6 (1 g in 5 mL of water). The mixture was kept in the refrigerator overnight and filtered; the obtained orange powder was stored in vacuum over P2O5 for 1 day. Yield: 68 mg (54%). Chemical analyses and NMR were coherent with the formula \([Ru(4,4′-(OCH_3)_2-bpy)_2(Mebpy-CN)](PF_6)_2\) (1). A mixture of 26 mg of Mebpy-CN (0.10 mmol) and 60 mg of \([Ru(4,4′-(OCH_3)_2-bpy)_2Cl_2]\) (0.10 mmol) was added to 30 mL of deaerated methanol and heated at reflux under Ar for 4 h. The obtained reddish-orange solution was rotaevaporated to dryness, dissolved in a minimum amount of water, and passed through a CM Sephadex C-25 column. The complex was eluted with 1 M HCl, and the collected fractions were rotaevaporated to dryness, dissolved in a minimum amount of water, and precipitated with a concentrated aqueous solution of KPF6 (1 g in 5 mL of water). The mixture was kept in the refrigerator overnight and filtered; the obtained orange powder was stored in vacuum over P2O5 for 1 day. Yield: 46 mg (45%). Chemical analyses and NMR were coherent with the formula \([Ru(4,4′-(OCH_3)_2-bpy)_2(Mebpy-CN)](PF_6)_2\) (2). A mixture of 20 mg of Mebpy-CN (0.10 mmol) and 60 mg of \([Ru(4,4′-(OCH_3)_2-bpy)_2Cl_2]\) (0.10 mmol) was added to 30 mL of deaerated methanol and heated at reflux under Ar for 4 h. The obtained reddish-orange solution was rotaevaporated to dryness, dissolved in a minimum amount of water, and passed through a CM Sephadex C-25 column. The complex was eluted with 1 M HCl, and the collected fractions were rotaevaporated to dryness, dissolved in a minimum amount of water, and precipitated with a concentrated aqueous solution of KPF6 (1 g in 5 mL of water). The mixture was kept in the refrigerator overnight and filtered; the obtained dark orange powder was stored in vacuum over P2O5 for 1 day. Yield: 46 mg (45%). Chemical analyses and NMR were coherent with the formula \([Ru(4,4′-(OCH_3)_2-bpy)_2(Mebpy-CN)](PF_6)_2\) (2).
(iii) [Ru(4,4′-N(CH3)_2-bpy)_(Mebpy-CN)](PF_6)_2 (3). A mixture of 47 mg of [Ru(4,4′-N(CH3)_2-bpy)_(Mebpy-CN)]Cl (0.067 mmol), 14 mg of Mebpy-CN (0.071 mmol), and 0.2 mL of triethylamine was added to 10 mL of deaerated ethanol and heated to reflux under Ar for 4 h. The obtained dark red solution was rotaevaporated to a minimum volume, recrystallized with ether, and filtered. The solid was dissolved in 5 mL of water and precipitated with a concentrated aqueous solution of NH_4PF_6 (1 g in 5 mL of water). The mixture was kept in a refrigerator overnight and filtered; the obtained dark red powder was stored in vacuum over P_2O_5 for 1 day. Yield: 26 mg (36%). Chemical analyses and NMR were coherent with 3 (125.75 MHz, CD3CN): 20.1, 39.1, 105.8, 109.3, 121.1, 124.0, 44.1 (44.1); H, 4.3 (4.2); N, 13.4 (14.1). 1H-NMR (500.13 MHz, CD3CN): 2.56 (s, 3H), 3.13 (s, 12H), 3.17 (s, 12H), 3.46 (s, 12H), 3.69 (br, 2H), 3.82 (br, 2H), 4.10 (d, 1H), 4.12 (d, 1H), 4.73 (d, 1H), 7.37 (d, 1H), 7.66 (d, 1H), 8.10 (d, 1H), 8.47 (s, 1H). 13C-NMR (125.75 MHz, CD3CN): 20.1, 39.1, 105.8, 109.3, 121.1, 124.0, 124.9, 128.0, 145.0, 149.5, 150.6, 152.9, 156.6, 226.6, 244.1, 269.4. Positive ESI-MS ion clusters at m/z 925.9, 973.9, 1301.9, 1349.9, 1411.9, 1567.9, 1617.9, 1753.9, 1873.9, 2079.9, 2191.9, 2409.9, 2577.9, 2695.9, 2843.9, 2955.9, 3107.9, 3219.9.

**FOTO iZnO NWs.** For ZnO NW growth, glass-FTO substrates (Sigma-Aldrich) of 2 × 1.5 cm were used. They were initially cleaned in ultrasonic baths of ethanol and acetone for 3 min. Then, seeds of ZnO were made on glass/FTO substrates (Sigma-Aldrich) of 2 cm × 1.5 cm. The substrates were put in 25 mL polytetrafluoroethylene (PTFE) vessels, which were then filled with a solution of distilled water (DW), hexamethylenetetramine (HMTA), and zinc nitrate dihydrate (0.5 M, aqueous solutions). The vessels were placed inside a stainless steel autoclave and heated to 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs were synthesized by a solvothermal method: ZnO-seeded substrates were rinsed with DW and dried in air. The substrates were heated at 125 °C for 4 h to improve the seed adherence. In a second step, ZnO NWs, and Raman spectra of sensitized FTO iZnO NWs (PDF).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00243.

Construction of DSCs, FTIR spectrum of complex 3, 1D and 2D NMR spectra and assignments of complex 3, UV–vis absorption data of complexes 1–3, CV and DPV curves of complex 3, emission spectra of complexes 1–3, TD-DFT calculations and assignments of complexes 1–3 and 3′, EDAX of ZnO NWs, UV–vis absorption spectra of bare and sensitized FTO iZnO NWs, and Raman spectra of sensitized FTO iZnO NWs (PDF).

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