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## Chemistry of ternary monocarboxyterpyridine-bipyridinetrimercaptotriazine ruthenium complexes and application in dye sensitized solar cells

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The synthesis of the [Ru<sup>II</sup>(Hmctpy)(H<sub>2</sub>O)(Cl<sub>2</sub>)], [Ru<sup>II</sup>(Hmctpy)(dmbpy)Cl]Cl and [Ru<sup>II</sup>(Hmctpy)(dmbpy)  $(H_3 tmt)](PF_6)_2$  complexes (mctpy = monocarboxyterpyridine, dmbpy = dimethylbipyridine, tmt = trimercaptotriazine) was carried out based on a vectorial design for energy transfer in dye sensitized solar cells (DSSC). The [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>x</sub>tmt)]<sup>n</sup> complexes were fully characterized and the electrochemical and absorption/emission properties corroborated their potentially as TiO<sub>2</sub> photosensitizing agents. However, the observed current density and open circuit voltage were rather small, imparting a low efficiency for the assembled DSSCs. The results indicated a unexpected contribution of the charge recombination effects at the electrode surface. Such effects increased with the number of deprotonated groups in the tmt ligand as they interact with the nanocrystalline TiO<sub>2</sub> surface, capturing electrons from the conduction band.

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#### 1. Introduction

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The synthesis of heteroleptic or ternary ruthenium complexes encompassing mixed ligands [1-5] has been pursued aiming new applications in chemistry, including alternative routes for improving the photoelectrochemical response of TiO<sub>2</sub> dye solar cells (DSSC) inspired on the  $[Ru(dcbpy)_2(SCN)_2]^{n-}$  and [Ru(tctpy) $(SCN)_3$ <sup>*n*-</sup> complexes. Such complexes have also been referred as N719 and black dyes, (dcbpy = dicarboxybipyridine, tctpy = tricarboxyterpyridine), respectively [6], and are in the top list of photoinjecting complexes [7]. In their design, the carboxypolypyridine ligands promote the binding and photoelectron injection to the TiO<sub>2</sub> nanoparticles, while the thiocyanate ancillary ligands help improving the cell efficiency, by increasing light harvesting from the red shift of the absorption maxima in the visible and also increasing the optical oscillator strength. In addition, steric hindrance and electrostatic repulsion diminish the dark current, precluding recombination from the  $I_3^-$  species in the electrolyte media. Ancillary ligands [8] have also been employed to improve the electron-hole charge separation distance from the TiO<sub>2</sub> surface and the oxidized dye, and increase the DSSC efficiency [9–11].

Considering the current efforts to improve the DSSC yields, alternative photoinjecting complexes can be devised, for instance, by replacing the thiocyanate ligands by trimercaptotriazine (tmt). This particular ligand is a trimeric species from thiocyanate, (SCN)<sub>3</sub>, exhibiting an aromatic triazine ring and three thiol ligands to bind metal ions. As a matter of fact, the  $[Ru(dcbpy)_2(H_2tmt)]^{3-1}$ complex has already been investigated in our laboratory [12] exhibiting a significant performance in DSSC, with quantum yields comparable to those observed for the N3 and N719 thiocyanate dyes. Along this line, we are directing efforts to obtain the ternary complex [Ru(tctpy)(tmt)(SCN)]<sup>2-</sup>, inspired on the black dye complex. Unfortunately, however, its synthesis has proved rather cumbersome and has not yet been successful in our Laboratory. For this reason, we are investigating the best routes for obtaining this type of complex, and in a particular attempt we have replaced the tricarboxyterpyridine ligand by the less expensive monocarboxyterpyridine (mctpy) analogue. This ligand can be synthesized with good yields, allowing to generate new ruthenium-tmt mixed complexes capable of anchoring onto TiO<sub>2</sub> surfaces and promoting excited electron transfer in DSSC devices.

Accordingly, in this work we focused our attention on the ternary  $[Ru(mctpy)(dmbpy)(H_xtmt)]^n$  complexes (Fig. 1), encompassing the Ru(mctpy) moiety and two ancillary ligands: dmbpy and tmt. The tmt ligand exhibits suitable HOMO-LUMO levels for promoting vectorial energy transfer into the central ruthenium(II) ion. Similarly, the 4,4'-dimethylbipyridine ligand was also selected

ABSTRACT





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Fig. 1. Structural representation of the [Ru(Hmctpy)(dmbpy)(H<sub>2</sub>tmt)]<sup>+</sup> complex.

according to a vectorial planning, in order to achieve efficient energy transfer to the ruthenium(II) center.

Pursuing this idea, we here report the sequential synthesis and characterization of the monocarboxyterpyridine ligand (mctpy) and the corresponding [Ru(mctpy)Cl<sub>3</sub>], [Ru(mctpy)(H<sub>2</sub>O)<sub>2</sub>Cl], [Ru (mtcpy)(dmbpy)Cl]Cl (dmbpy = 4,4'dimethyl,2,2'bipyridine) and [Ru(mctpy)(dmbpy)(H<sub>x</sub>tmt)]<sup>n</sup> complexes. The photoelectrochemistry of the target complex, [Ru(mctpy)(dmbpy)(H<sub>2</sub>tmt)] (Fig. 1) has been investigated in detail, exhibiting significant photoinjection response in TiO<sub>2/</sub>DSSCs while providing important clues for understanding the limitations and for improving the efficiency of this type of dye.

### 2. Materials and methods

All reagents were obtained from commercial sources including Sigma-Aldrich and Synth, and used as supplied, unless stated otherwise.

#### 2.1. Synthesis of [2,2':6',2''-terpyridine]-4'-carboxylic acid (Hmctpy)

The monocarboxyterpyridine ligand was obtained by adapting a literature procedure [13]: in a 125 mL round bottom reaction flask equipped with a magnetic bar 3.44 mL of furfural (0.042 mol) and 9.44 mL of 2-acetylpyridine (0.084 mol) were poured together. Then, 5.2 g of KOH and 60 mL of NH<sub>4</sub>OH (28-30%) were added and the reaction was left to proceed for 19 h under reflux. The dark brown solid was collected on a filter, and recrystallized from an ethanol-water mixture giving a white solid with about 50% yield. The white 4'-(2-furyl)-2,2':6',2''-terpyridine (futpy) product was filtered and washed with water, diethyl ether and dried under vacuum. In the next step, 1.0 g of futpy (3.3  $\times$  10<sup>-3</sup> mol) were suspended in 100 mL of deionized water and the pH was adjusted to 13 using NaOH. Then, 2.12 g of  $KMnO_4$  (1.34  $\times$  10<sup>-2</sup> mol) were added to the slurry and let to reflux for four hours. After this time, 1.66 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> were added to reduce unreacted permanganate and the MnO<sub>2</sub> was filtered off. The supernatant pH was adjusted to 4 with HCl (36%) to precipitate the [2,2':6',2''-terpyridine]-4'-carboxylic acid which was centrifuged and washed three times with pH 4-5 deionized water. The white solid was dried under vacuum, yielding 0.61 g (67%) of product. <sup>1</sup>H NMR (300 MHz,  $D_2O$  /NaOD)  $\delta$ ppm 7.41 (2H, ddd, J = 7.62, 4.91, 1.25 Hz) 7.87 (2H, td, J = 7.76, 1.76 Hz) 8.09 (2H, d, J = 7.91 Hz) 8.22 (2H, s) 8.50 (2H, d, I = 4.98 Hz).

#### 2.2. Synthesis of [Ru<sup>II</sup>(Hmctpy)(H<sub>2</sub>O)Cl<sub>2</sub>].H<sub>2</sub>O

This complex was synthesized by dissolving 1.10 g of RuCl<sub>3</sub>- $3H_2O$  (4.23 × 10<sup>-3</sup> mol) in dinitrogen purged ethanol, in a 125 mL reaction flask equipped with a magnetic bar. Under a stream of dinitrogen, 1.17 g of mctpy (4.24 × 10<sup>-3</sup> mol) were added and the reaction mixture was let to reflux for 4 h. Upon cooling down to room temperature, a red-brown solid precipitated. This solid was centrifuged and washed three times with cold ethanol, yielding 1.95 g of product (82% yield). Analysis: Exp(Calc) C 39.56(39.60); H 3.19(3.12);, N 7.91(8.66). <sup>1</sup>H NMR (500 MHz, dmso-*d*<sub>6</sub>)  $\delta$  ppm 7.58 (2H, ddd, *J* = 7.40, 5.72, 1.22 Hz) 8.00 (2H, td, *J* = 7.78, 1.53 Hz) 8.79 (2H, d, *J* = 7.32 Hz) 8.98 (2H, s) 9.34 (2H, dd, *J* = 5.49, 0.92 Hz). Mass spectra of [Ru<sup>II</sup>(mctpy)Cl<sub>2</sub>(H<sup>+</sup>)]<sup>+</sup> ion (449.93 *m/z*) exhibited 449.2 *m/z* signal.

#### 2.3. Synthesis of [Ru<sup>II</sup>(Hmctpy)(dmbpy)Cl]Cl

In a 50 mL round bottom flask equipped with a magnetic bar, 174.9 mg (4.1 mmol) LiCl, 200 mg (0.41 mmol) [Ru<sup>II</sup>(Hmctpy) (H<sub>2</sub>O)Cl<sub>2</sub>].H<sub>2</sub>O and 0.5 mL 4-ethylmorpholine were dissolved in 15 mL of methanol/water 5:1 mixture. 76 mg (0.41 mmol) dmbpy were added to the stirred solution, and brought to reflux for three hours in the dark. The solution was let to cool down to room temperature and the crude sample was dried in a rotary evaporator. The purple solid was dissolved and loaded into a silica gel column and eluted with acetone/methanol/water (3:1:1) saturated with LiCl. The purple fraction was collected and concentrated in the rotary evaporator and 3 mL of concentrated HCl were added. The purple solid precipitated was centrifuged and washed three times with 1 mol L<sup>-1</sup>HCl. The solid was left to dry under vacuum. Yield 45%. <sup>1</sup>H NMR (500 MHz, methanol *d*<sub>4</sub>) δ ppm 2.37 (s, 3H) 2.81 (s, 3H) 6.86 (d, J = 7.05 Hz, 1H) 7.09 (d, J = 5.76 Hz, 1H) 7.33-7.37 (m, 2H) 7.70 (d, J = 5.55 Hz, 2H) 7.86 (d, J = 6.83 Hz, 1H) 7.94 (t, J = 8.43 Hz, 2H) 8.37 (s, 1H) 8.57 (d, J = 7.90 Hz, 2H) 8.66 (s, 1H) 9.03 (s, 2H) 9.99 (d, J = 5.76 Hz, 1H).

#### 2.4. Synthesis of $[Ru^{II}(Hmctpy)(dmbpy)(H_2O)](PF_6)_2$

150 mg (0.24 mmol) of  $[Ru^{II}(Hmctpy)(dmbpy)CI]CI$  were dissolved in deionized water and 81.5 mg (0.48 mmol) of AgNO<sub>3</sub> were added slowly over the course of four hours under reflux. AgCl formed was centrifuged and discarded after cooling down the reaction mixture. Supernatant was concentrated and the complex precipitated with the addition of  $NH_4PF_6$ . The solid was filtered out, washed carefully with cold water and dried under vacuum overnight. This complex was used without further characterization.

#### 2.5. Synthesis of [Ru<sup>II</sup>(Hmctpy)(dmbpy)(H<sub>3</sub>tmt)](PF<sub>6</sub>)<sub>2</sub>

100 mg (0.12 mmol) of  $[Ru^{II}(Hmctpy)(dmbpy)(H_2O)](PF_6)_2$ were dissolved in 15 mL ethanol and 21.3 mg (0.12 mmol) of H<sub>3</sub>tmt were added to the stirred solution and refluxed for 4 h in the dark. After cooling down, the solvent was removed in the rotary evaporator and the solid dissolved in the minimum amount of DMF. This solution was added dropwise to a concentrated NH<sub>4</sub>-PF<sub>6</sub> aqueous solution, and the precipitated solid was filtered off and washed carefully with cold water and ether and dried under vacuum. Further purification was carried out using Sephadex LH-20 column chromatography using methanol as eluent. The solid was loaded and four fractions were eluted from the column; the last one containing the desired complex. Such fraction was dried under reduced pressure in a rotary evaporator and the hygroscopic solid kept overnight under high vacuum. <sup>1</sup>H NMR (500 MHz, methanol  $d_4$ )  $\delta$  ppm 2.38 (s, 3H) 2.79 (s, 3H) 6.94 (dd, I = 5.95, 1.07 Hz, 1H) 6.98–7.00 (m, 1H) 7.34 (ddd, J = 7.32, 5.80, 1.22 Hz, 2H) 7.80 (dd, J = 5.80, 1.22 Hz, 1H) 7.86 (dd, J = 5.65, 0.76 Hz, 2H) 7.91 (td, J = 7.78, 1.53 Hz, 2H) 8.39 (s, 1H) 8.57 (d, J = 7.93 Hz, 2H) 8.63 (s, 1H) 9.04 (s, 2H) 9.79 (d, J = 5.80 Hz, 1H). Calcd(Found) for [Ru(Hmctpy)(dmbpy)(H<sub>3</sub> tmt)](PF6)<sub>2</sub>·12H<sub>2</sub>O, C<sub>31</sub>H<sub>50</sub>F<sub>12</sub>N<sub>8</sub>O<sub>14</sub>P<sub>2</sub>-RuS<sub>3</sub>: C 29.88 (29.43); H 4.05 (3.87); N 8.99 (9.02).

#### 2.6. Spectrophotometric titration

The complex  $[Ru^{II}(Hmctpy)(dmbpy)(H_3tmt)](PF_6)_2 \cdot 12H_2O$  was spectrophotometric titrated employing a H<sub>2</sub>O/MeOH 20:1 solution containing 0.5 mol L<sup>-1</sup> of NaCl supporting electrolyte in order to maintain and control the ionic force. All of the spectra were collected at room temperature (25 °C) by starting at pH 13 and acidifying stepwise with HCl (3 mol L<sup>-1</sup>) solution until pH 2.

# 2.7. Preparation of $[Ru^{ll}(mctpy)(dmbpy)(H_xtmt)]^n$ deprotonated species

Spectrophotometric titration afforded three pKa values in the pH window employed. In this way, the deprotonated species,  $[Ru^{II}(mctpy)(dmbpy)(H_xtmt)]^n$  were prepared by adjusting the pH with (Bu<sub>4</sub>N)OH and precipitated upon addition of diethyl ether.

#### 3. DSSC assembly

DSSCs were assembled by employing a sandwich format. In the anode, TiO<sub>2</sub> nanoparticles paste were deposited by spin coating forming working areas averaging 0.25  $\text{cm}^2$  onto FTO/glass optically transparent electrode and then sintered at 450 °C for 30 min. The dyes were adsorbed on TiO<sub>2</sub> surface by immersing the anode in dye solution for 24 h before mounting the cells. The FTO/glass counter electrode was coated with Pt by treating with H<sub>2</sub>PtCl<sub>6</sub> solution and heating at 450 °C for 30 min. The cells were put together using Surlyn<sup>®</sup> as spacer and gluer, and sealed at 110 °C for ten minutes. Through a predrilled hole in the counter electrode, the I<sup>-</sup>/I<sub>3</sub> based electrolyte (0.5 M *tert*-butylpyridine, 0.6 M tetrabutylammonium iodide, 0.1 M LiI, 0.1 M I<sub>2</sub> in methoxypropionitrile) was injected after applying vacuum, and then the hole was sealed with a coverslip glass using Surlyn<sup>®</sup> as glue. The electrolyte was let to accommodate on the DSSC unity for 24 h before making the measurements.

The quantification of the loaded complexes on the DSSC anode was performed by treating with 0.1 mol L<sup>-1</sup> NaOH aqueous solution, and monitored spectrophotometrically after diluting with deionized water. Based on the absorption spectra of the complex, the surface coverage was estimated as  $9.3 \times 10^{16}$  molecules cm<sup>-2</sup>.

#### 4. Instrumentation

The electronic spectra of the complexes were obtained using a Hewlett-Packard, model HP-8453-A diode array spectrophotometer in the 200–1100 nm range. <sup>1</sup>H NMR spectra were recorded on a Bruker AIII 500 MHz equipment. Low resolution mass spectra were obtained using a Esquire 3000 Plus Bruker Daltonics, and high resolution spectra were collected on a MicroTof Bruker Daltonics spectrometer. Cyclic voltammetry was carried out with an Autolab PGStat30 instrument, using a glassy carbon working electrode. An Oriel Spectral Luminator, whose power at cell position was controlled (1 and 2 mW cm<sup>-2</sup>) with a standard Si photodiode (1830-C Newport Optical Power Meter), was used for the IPCE measurements. The I-V curves were registered using an ABB class Oriel solar simulator (AM 1.5, IEC, JIS, ASTM) calibrated with a Si cell (VLSI standards, Oriel P/N 91150 V), interfaced to a computer-controlled Keithley 2400 instrument.

#### 5. Theoretical calculations

Theoretical calculations were carried out on a preliminary basis. for help understanding of the electronic structure and spectra. Although DFT and TDTFD theoretical calculations were initially performed using the ORCA software, the molecular complexity of the complexes demanded more than 10 days of computational processing, and were frequently aborted for technical problems after such a long computational time. For this reason, the ZINDO-S semiempirical method from the Hyperchem 8.05 computational package was here preferred.<sup>13</sup> As demonstrated by Gorelski and Lever [14] and according to our own experience, there is a reasonable agreement between the two methods; however, the last one requires only few seconds to perform on a lap top computer. As a normal procedure, atomic dipoles were initially used to start the MM<sup>+</sup> geometry optimization, and then replaced by the atomic charges obtained from the ZINDO-S method, with a convergence limit of about  $10^{-5}$  kcal Å<sup>-1</sup> mol<sup>-1</sup>. The electronic distribution was generated from single CI excitations in an active space involving 20 frontier molecular orbitals (10 highest occupied and 10 lowest unoccupied MOs). After many cycles of MM<sup>+</sup>/ZINDO-S geometry optimization up to the convergence point, the final electronic spectra and the molecular orbitals involved were plotted as 2D energy contours.

#### 6. Results and discussion

#### 6.1. NMR spectra

The first hint about the low spin Ru(II) center in [Ru(mctpy)Cl<sub>2</sub>-H<sub>2</sub>O] was given by its <sup>1</sup>H NMR spectrum (Fig. 2 top). Five well-defined, symmetric signals can be observed, and the lack of broadening is typical of a diamagnetic metal center, exhibiting slower nuclear relaxation times in contrast with the paramagnetic species [15]. This supported the assignment of a highly symmetrical Ru(II) complex and the singlet in 8.98 ppm enabled the integration of every signal acting as reference. The coupling constants permitted the correlation between nuclei thanks to the *-orto*, *-meta* and *-para* values.

Although the <sup>1</sup>H NMR spectra gave us a hint about the oxidation state of the ruthenium center, spin delocalization across the whole complex may be poor enough to enable a good NMR signal [16]. The complex formed by the coordination of the tridentate ligand terpy and its analogues is commonly reported as being Ru<sup>III</sup>(tpy) Cl<sub>3</sub>. It is assumed that due to the lack of a reducing agent in the reaction media, the ruthenium center does not undergo a redox process during the complex formation [17–20]. However, EPR measurement provided no signals of unpaired electrons as expected for 4d<sup>5</sup> Ru(III) [21], indicating a low spin Ru(II) center

<sup>1</sup>H NMR spectrum of the [Ru<sup>II</sup>(Hmctpy)(dmbpy)CI]CI complex afforded 13 signals between 2.37 and 9.99 ppm expected for a symmetric terpy with 5 signals and a unsymmetrical dmbpy ligand due to the electronic *trans* influence of the chloride to one of the pyridyl rings, making them magnetically distinct. Therefore, every ring in dmbpy gives rise to four signals each, as shown in Fig. 2 middle. In the figure, the labeling has been kept for mctpy for comparison purposes and another labeling was adopted for dmbpy hydrogens.

The spectrum of the  $[Ru^{II}(Hmctpy)(dmbpy)(H_3tmt)](PF_6)_2$  complex is shown in Fig. 2 bottom. Due to the use of a protic solvent (MeOD-d<sub>4</sub>), isotopic exchange takes place with the thiol residues making the hydrogens non visible in the spectrum. Nevertheless, chemical shifts for the eleven signals found between 6.94 and 9.79 ppm differ substantially from those found for the  $[Ru^{II}(Hmctpy)(dmbpy)CI]^+$  precursor as observed in Fig. 2, allowing



Fig. 2. <sup>1</sup>H NMR spectra of the synthesized ruthenium complexes in DMSO d<sub>6</sub> (top) and MeOD-d4 (middle and bottom).

us to infer the coordination of the tmt is exerting a magnetic effect, which is more pronounced in the nearest hydrogens although more analyses were performed to confirm this hypothesis.

#### 6.2. Electronic spectra

The electronic spectra of the  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$ complex and its precursor species can be seen in Fig. 3. The bands at 275 and 326 nm for the  $[Ru^{II}(mctpy)(H_2O)Cl_2]^-$  complex (black line) are assigned to IL  $(p\pi \rightarrow p\pi^*)$  from the mctpy ligand and the band located at 396 and 489 nm are ascribed to charge transfer (MLCT) from the Ru(II) center to the terpy ligand  $(d\pi \rightarrow p\pi^*)$ . The electronic absorption spectrum of  $[Ru^{II}(mctpy)(dmbpy)Cl]$  (red



Fig. 3. UV-vis spectra in MeOH of the synthesized ruthenium species (1.3  $\times$   $10^{-5}$  mol  $L^{-1}).$ 

line) exhibits two absorption bands of  $p\pi \rightarrow p\pi^*$  nature at 285 and 325 nm with a sharper and simpler profile than that of the  $[Ru^{II}(mctpy)(H_2O)Cl_2]^-$  complex due to the contribution of both polypyridine ligands. On the other hand, the MLCT ( $d\pi \rightarrow p\pi^*$ ) transitions afforded a notorious change upon dmbpy coordination with a broader band centered in 523 nm displaying a stronger absorption when compared with the  $[Ru^{II}(mctpy)(H_2O)Cl_2]^-$  spectrum, indicating the influence of low lying  $\pi^*$  orbitals from dmbpy.

The electronic spectrum of the [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] complex (blue line) exhibits typical IL transitions in the region below 400 nm. At 281 nm is located an intense band with a shoulder in 317 nm which are ascribed to both dmbpy and mctpy IL transitions ( $p\pi \rightarrow p\pi^*$ ). However, the bands profile differs notably from those in the precursors, indicating a major influence or presence of underlying absorptions from the tmt ligand. In the visible region there are located two MLCT bands at 435 and 497 nm and a shoulder at 630.

According to the theoretical calculations, the highest occupied molecular orbitals (MO110, 111, 112) in Fig. 4 have a major contribution of the ruthenium center, in addition to the mctpy and dmbpy ligands. The tmt ligand has a predominant participation in MO107. On the other hand, the lowest unoccupied molecular orbitals, MO111, 112, exhibited a majori contribution from the mctpy ligand, while MO113 seems mainly localized on the dmbpy ligand. MO 114 involves contributions of both ligands. It seems that tmt has little participation in the accessible LUMO levels.

Accordingly, the main electronic band observed at 497 nm in the [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] complex, is consistent with the theoretical band calculated at 495 nm, corresponding to a predominant Ru(II)  $\rightarrow$  mctpy charge-transfer transition (MO108  $\rightarrow$  MO111). On the other hand the second band at 435 nm is compatible with the theoretical band at 477 nm, predominantly of Ru(II)  $\rightarrow$  dcbpy charge transfer nature (MO110  $\rightarrow$  MO113). The shoulder around 630 nm corresponds to



Fig. 4. 2D contour orbital plots for the HOMO and LUMO levels in the  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$  complex and the corresponding theoretical electronic transitions indicated by the dotted arrows.

the theoretical band expected at 636 nm involving a Ru (II)  $\rightarrow$  mctpy charge-transfer transition (MO110  $\rightarrow$  MO112). It is interesting to note that the theoretical transition from the occupied tmt level (MO107) to the empty mctpy level (MO111) only occurs at 302 nm, and does not contribute to the electronic spectrum in the visible.

The mctpy ligand provides not only the anchoring groups to  $TiO_2$  but also the injecting levels (MO 111) to the conducting band (Fig. 4). It should be noted that the charge-transfer transition to the dmbpy ligand (MO 113) occurs at a higher energy in relation to mctpy, and in this sense it can promote vectorial energy transfer to the electrode. Although the tmt LUMO level seems not accessible, this ligand can have a significant role as a donor species through the HOMO level, MO 107. Therefore, both dmbpy and tmt ligands can contribute for energy transfer to the injecting orbitals of the dye, as expected from the vectorial design.

#### 6.3. Acid-base titration

The  $[Ru^{ll}(mctpy)(dmbpy)(H_2tmt)]$  complex exhibits several functional groups displaying acid-base equilibria. Determining their pK<sub>a</sub> values is quite important, since the coordination chemistry (for anchoring onto TiO<sub>2</sub> nanoparticles), electronic properties (HOMO/LUMO energies) and electrostatic interactions depend on the degree of protonation in the complex, as previously shown by Guimarães et al. [12].

In Fig. 5A it is shown a collection of spectra in the 13–7 pH window. It is noteworthy the bathochromic shift of the  $p\pi \rightarrow p\pi^*$  transitions, due to the stabilization of the  $\pi^*$  molecular orbital of the tmt ligand upon protonation, whereas the MLCT bands in the visible range exhibit minimum variation. Fig. 5B shows the spectra collected between pH 7–2 and once again the main and most noticeable variations are in the  $p\pi \rightarrow p\pi^*$  transitions, with a bathochromic shift owed to the stabilization of the  $\pi^*$  mctpy orbital upon protonation.

In order to interpret the acid-base equilibria, a plot of the absorbance at 302 nm (which was the band with the greater variation along the experiment) *versus* pH is presented in Fig. 5C. It displays three distinguishable regions at pH 2–7, 7–10 and 11–13, which can be fitted by a sigmoidal function with  $r^2 = 0.99979$ , providing the pK<sub>a</sub> values shown in Table 1, in comparison with the reported pK<sub>a</sub> for the free tmt ligand. Presumably the first pK<sub>a</sub> of 5.35 encompasses the protonated Hmctpy and H<sub>3</sub>tmt ligands, while the pK<sub>a</sub> of 8.49 and 12.32 belongs to the coordinated H<sub>2</sub>tmt and Htmt ligands.

#### 6.4. Electrochemistry

Cyclic voltammetry for the [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] complex was carried out as shown in Fig. 6, exhibiting five redox processes in the range of -2 to +1.5 V vs SHE. The anodic region presents one monoelectronic process assigned to the Ru<sup>II</sup>/Ru<sup>III</sup> oxidation at E<sub>1/2</sub> = 1.03 V. The cathodic region is much richer since it displays all of the electrochemical processes of the ligands. The E<sub>pc</sub> = -0.98 V can be ascribed to the reduction of the mctpy ligand, and the voltammogram is followed by the reduction of tmt at E<sub>pc</sub> = -1.31 V and the stepwise reduction of the dmbpy rings at E<sub>pc</sub> = -1.51 and -1.77 V, these four processes match their current intensities for a one electron process each in agreement with previously reported ruthenium complexes [23–25].

#### 6.5. Spectroelectrochemistry

The spectroelectrochemical behavior illustrated in Fig. 7 is consistent with the Ru(III)/(II) process observed at 1.07 V in the cyclic



Fig. 5. Spectrophotometric titration of  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$  complex  $(1 \times 10^{-5} \text{ mol } L^{-1})$  in basic (A) and acid (B) pH window. Absorbance at 302 nm vs pH (C).

Table 1			
pK <sub>as</sub> for [Ru <sup>II</sup> (mctpy)(dmbpy)(H <sub>2</sub> tmt	)] complex in com	parison with i	free tmt ligand.
Compound	nV	nV	nV

Compound	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>
TMT	5.71 <sup>b</sup>	8.36 <sup>b</sup>	11.38 <sup>b</sup>
[Ru <sup>ll</sup> (Hmctpy)(dmbpy)(H <sub>3</sub> tmt)] <sup>2+</sup>	5.35 <sup>a</sup>	8.49	12.32

a) Average value for the protonated mctpy and tmt ligands, b) pKas extracted from ref. [22].



Fig. 6. Cyclic voltammetry of  $[Ru^{II}(mctpy)(dmbpy)(H_{2}tmt)]$  in CH\_3CN, at room temperature, 50 mV  $s^{-1}.$ 

voltammogram. The major changes reflect the predominant contribution of the ruthenium center to the electronic structure of the complex, since all of the absorption's intensities in the visible are diminished when the potential sweep is set between 0.89 and 1.15 V. The MLCT bands in 400–600 nm interval are replaced by a new band at 425 nm, consistent with a LMCT from the sulfur in the tmt ligand to the Ru(III) center, as previously reported by Guimaraes et al. [12].



Fig. 7. Spectroelectrochemistry response of  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$  associated with the Ru(III)/(II) process in DMF.

#### 6.6. Emission and excitation studies

In Fig. 8 one can compare the electronic spectrum (blue) for the  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$  complex and its fluorescence spectrum (red) in methanol. Upon excitation in the MLCT band at 496 nm, a composite emission profile has been detected at 583 nm. The energy gap between HOMO and LUMO orbitals (E<sub>0-0</sub>) was calculated in the point where the two spectra practically cross, at 516 nm, affording a 2.39 eV difference.

#### 7. Photoaction performance

After obtaining the energy gap it is necessary to calculate either HOMO or LUMO energy for comparison with the energy levels of the conduction band (CB) in nanocrystalline anatase TiO<sub>2</sub> and redox potential of the  $I^-/I_3$  couple found in literature [26]. According to the CV experiments the first oxidation potential is related to the ionization potential ( $I_p$ ) for the Ru<sup>II</sup>/Ru<sup>III</sup> process, and the



**Fig. 8.** (A) Absorption (blue) and (B) emission spectra (red) of [Ru<sup>II</sup>(mctpy)(dmbpy) (H<sub>2</sub>tmt)] in MeOH. ((Colour online.))



Fig. 9. Energy diagram comparison for TiO<sub>2</sub> (anatase), [Ru<sup>II</sup>(mctpy)(dmbpy) (H<sub>2</sub>tmt)] and  $I^-/I_3^-$  redox couple.

energy of the HOMO orbital can be expressed by equation (1) [27,28].

$$I_p = -(E_{ox} + 4.44)eV$$
 (1)

where  $E_{ox}$  is the onset potential for the Ru<sup>II</sup>/Ru<sup>III</sup> process *versus* an SHE reference electrode and the value 4.44 is the vacuum level potential of the normal hydrogen electrode. The calculated values shown in Fig. 9 indicate that the HOMO energy in the complex is in good position with respect to the  $I^-/I_3^-$  redox potential for the proper regeneration of the oxidized dye after the photoelectron injection into the TiO<sub>2</sub> CB. Furthermore, the energy of the LUMO is placed well above the TiO<sub>2</sub> CB, thus favoring the electron injection.

The energy profiles support a correct planning of the electronic structure for the [Ru<sup>II</sup>(mctpy)(dmbpy)(tmt)] complex as a photosensitizer for DSSCs.

### 7.1. Incident photon-to-current efficiency (IPCE) measurements

Three DSSCs were assembled for the series of deprotonated ruthenium complexes, [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)], [Ru<sup>II</sup>(mctpy)  $(dmbpy)(Htmt)]^{-}$ ,  $[Ru^{II}(mctpy)(dmbpy)(tmt)]^{2-}$  and a reference cell was also mounted with the classical N719 sensitizer for comparison purposes. Fig. 10 exhibits the monochromatic photo injection properties of the three ruthenium species prepared. It can be observed that all three species exhibit IPCE profiles consistent with the shape of their absorption spectra, with an injection efficiency peak around 490 nm where the MLCT  $d\pi \rightarrow p\pi^*$  bands are located. Light harvesting seems not particularly improved by the presence of the tmt ligand in the complex, in contrast to a previous paper [12], but in agreement with the theoretical calculations indicating the tmt  $\rightarrow$  Ru(mctpy)\* band only at 302 nm (Fig. 4). It should be noticed that in the previous paper the tmt ligand was bidentate, and the tmt  $\rightarrow$  Ru(dcbpy)\* transition was indeed observed at 465 nm. In the series, the [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] complex exhibited the most efficient photoaction response, but with a maximum IPCE of only 23%. The efficiency decreased systematically with the proton removal from the H<sub>x</sub>tmt ligand in the (N-Bu<sub>4</sub>) ([Ru<sup>II</sup>(mctpy)(dmbpy)(Htmt)] and (N-Bu<sub>4</sub>)<sub>2</sub>[Ru<sup>II</sup>(mctpy)(dmbpy) (tmt)] complexes.

In Fig. 11 it is shown the I-V curves obtained for the  $[Ru^{II}(mctpy)(dmbpy)(H_2tmt)]$  (left) and N719 (right) DSSCs. The H<sub>2</sub>tmt complex exhibited much lower values of V<sub>oc</sub> and J<sub>sc</sub> in relation to N719, reflecting undesired recombination processes in the



Fig. 10. IPCE measurements of [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] (a), (N-But<sub>4</sub>) [Ru<sup>II</sup>(mctpy)(dmbpy)(Htmt)] (b) and (N-But<sub>4</sub>)<sub>2</sub>[Ru<sup>II</sup>(mctpy)(dmbpy)(tmt)](c) complexes.



Fig. 11. I-V curves for [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] (left) and N719 (right) assembled DSSCs.



Fig. 12. Vectorial electron transfer and recombination effects in the  $TiO_2$  /Ru (mctpy)(dmbpy)(H\_xtmt))^{n-} DSSC.

DSSC device. This may be due to a) the smaller number of anchoring groups in the tmtH<sub>2</sub> complex, decreasing the electron photoinjection in TiO<sub>2</sub> and also J<sub>sc</sub> and b) the possible interaction of the monodentate H<sub>2</sub>tmt ligand (see Fig. 12) with the nanocrystalline TiO<sub>2</sub> surface, facilitating the electron transfer from the CB to the adsorbed photooxidized complex, thus significantly reducing V<sub>oc</sub>. Such interaction would be facilitated in the deprotonated complexes, because as the sulfur atoms become more available for interacting with the titanium ions, the energy transfer from the conducting band is facilitated, leading to the decay of efficiency and voltage parameters observed along the series. This conclusion is also consistent with our previous report [12] for a bidentate tmt ligand exhibiting a much better photoaction response in relation to the monodentate complex.

FF and efficiency  $(\eta)$  were calculated employing equations (2) and (3) and the results for all of the three dyes and the reference (N719) appear in Table 2.

$$FF = \frac{J_{pmax} * V_{pmax}}{J_{sc} * V_{oc}}$$
(2)

$$\gamma = \frac{P_{dssc}}{P_{lamp} * A} * 100 \tag{3}$$

From Table 2, it is noticeable the low values for the current density and the open circuit voltage, responding for the low power and efficiency of the assembled DSSCs. In relation to the reference N719 dye, the poor performance of the  $[Ru^{II}(mctpy)(dmbpy)(H_x-tmt)^n$  complexes should be ascribed to their smaller light harvesting properties and the large recombination effects at the electrode surface. On the other hand, the monocarboxyterpyridine ligand has only an anchoring group to the TiO<sub>2</sub> surface, and this might also decrease its photoinjecting efficiency in relation to the reference N719 and tricarboxyterpyridine black dyes.

#### 8. Conclusions

Vectorial planning has been successfully applied for the synthesis of the new [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>2</sub>tmt)] complex, pursuing suitable properties for performing as a DSSC dye. Its electrochemical and spectroscopic properties confirmed a good potentially for DSSC application, while the determination of the pKa's of the acid-base processes allowed to test the behavior of the deprotonated species in the IPCE response and cell performance. In comparison with the N719 DSSC, rather low values for current density and open circuit voltage have been observed, accounting for low power and efficiency of the assembled DSSCs. Such results reflected their smaller light harvesting properties and large recombination effects occurring at the electrode surface. The recombination effects increased with the number of deprotonated groups in the tmt ligand, facilitating the interactions with the nanocrystalline TiO<sub>2</sub> surface and promoting back-electron transfer from its CB level.

Table 2

Comparative performance of [Ru<sup>II</sup>(mctpy)(dmbpy)(H<sub>x</sub>tmt)]<sup>n</sup> complexes in their assembled DSSCs.

Compound	Power (mW)	FF	$J_{sc}$ (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	η (%)
[Ru <sup>II</sup> (mctpy)(dmbpy)(H <sub>2</sub> tmt)] [Ru <sup>II</sup> (mctpy)(dmbpy)(Htmt)] <sup>-</sup> [Ru <sup>II</sup> (mctpy)(dmbpy)(tmt)] <sup>2-</sup>	0.175 8.59 x10 <sup>-2</sup> 4.79 x10 <sup>-2</sup>	0.49 0.58 0.50	3.12 1.71 1.33	0.44 0.36 0.33	0.7 0.35 0.19
N719	1.32	0.60	14.14	0.69	5.28

#### Author contributions

Juan S. Aguirre-Araque has performed the investigation as part of his PhD thesis. Robson R. Guimaraes has also performed the investigation, focusing on dye solar cells, Henrique E. Toma has been involved in conceptualization, supervision and writing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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