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Anil Reddy Marri, Edoardo Marchini, Valentin Diez-Cabanes, Roberto Argazzi, Mariachiara Pastore, et al.. Panchromatic light harvesting and record power conversion efficiency for carboxylic/cyanoacrylic Fe(II) NHC co-sensitized FeSSCs.. *Chemical Science*, 2023, 16, pp.4288-4301. 10.1039/D2SC05971A . hal-04049604

**HAL Id: hal-04049604**

**<https://hal.science/hal-04049604v1>**

Submitted on 20 Oct 2023

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## ARTICLE

# Panchromatic light harvesting and record power conversion efficiency for carboxylic/cyanoacrylic Fe(II) NHC co-sensitized FeSSCs.

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Fe(II) pyridyl-NHC sensitizers bearing thienylcyanoacrylic anchoring groups (ThCA) have been designed and characterized with the aim of enhancing the metal to surface charge separation and the light harvesting window in iron-sensitized DSSCs (FeSSCs). In these new Fe(II) dyes, the introduction of the ThCA moiety remarkably extended the spectral response and the photocurrent by comparison with their carboxylic analogues. The co-sensitization based on a mixture of a carboxylic and a ThCA-iron complex produced a panchromatic absorption, up to 800 nm and the best photocurrent and efficiency ( $J_{sc}$ : 9 mA.cm<sup>-2</sup>, PCE: 2%) ever reported for a FeSSC.

## 1. Introduction

Dye sensitized solar cells (DSSCs) are a credible contender in the course for cost-effective alternative to conventional silicon based solar cells.<sup>1–4</sup> Some of the best efficiencies have been achieved using Ru(II) complexes as sensitizers (up to 11%).<sup>5</sup> The reason of such a success results from the combination of long-lived metal-to-ligand charge transfer (MLCT) states (ns regime) responsible for the electron transfer into the semiconductor conduction band (CB) and efficient electron-hole separation preventing the parasitic charge recombination processes at the dye/semiconductor interface.<sup>6–8</sup> However, modern research is intended to integrate holistic approaches taking into account the availability, cost and strategic nature of raw materials. In this context, ruthenium complexes are not the best candidates due to the scarcity of ruthenium, their high cost, tricky purifications, and environmental issues precluding potential large-scale applications.

Thus, researchers have focussed their attention on more cost-effective alternative sensitizers such as earth abundant first row transition metal complexes<sup>9,10</sup> or metal-free organic conjugated compounds.<sup>11–14</sup> Since the pioneering works by Ferrere,<sup>15,16</sup> first investigating Fe(dcbpy)<sub>2</sub>(CN)<sub>2</sub> as sensitizer and despite the recent improvements achieved by McCusker,<sup>17</sup> the maximum efficiency attained with iron (II) polypyridyl sensitizers is 0.35%. The origin of such a poor performance lies in the fact that, in contrast with ruthenium (II) polypyridyl complexes possessing long-lived MLCT states,<sup>18</sup> ultrafast relaxation to metal centred (MC) states and subsequent ground-state recovery is observed for the iron analogues<sup>19–22</sup> precluding their successful application in photochemical applications requiring stabilized MLCT states, such as DSSCs.<sup>23</sup> The introduction of *N*-heterocyclic carbenes (NHC) in the ligands surrounding the iron centre has been decisive in the quest for long-lived MLCTs. Especially tridentate pyridyl-*N*-heterocyclic carbenes (pyridylNHC), due to their marked  $\sigma$ -donating strength, promoted an unprecedented stabilization of the MLCT states with respect to the MC ones.<sup>24–28</sup> This strategy opened the way to the preparation of iron(II) complexes with MLCT state lifetimes up to the picosecond.<sup>27,29–31</sup> Complex **C1** (Figure 1) which combines  $\sigma$ -donating NHCs ligands (showing MLCT lifetimes up to 16 ps) with  $\pi$ -accepting carboxylic groups for grafting to the TiO<sub>2</sub> surface was the first Fe(II)NHC prototype to be employed in an operating DSSC (FeSSC), albeit with poor photovoltaic performances.<sup>25</sup> Very recently, some of us reported that this efficiency could be boosted up to 1% with a photocurrent reaching 3.3 mA/cm<sup>2</sup> by introducing Mg<sup>2+</sup> cations in the electrolyte composition.<sup>32</sup> Mg<sup>2+</sup> cations are capable to adsorb at the sensitizer/semiconductor interface and to improve the interfacial electron transfer kinetics (regeneration and/or electron injection), thus resulting in higher measured

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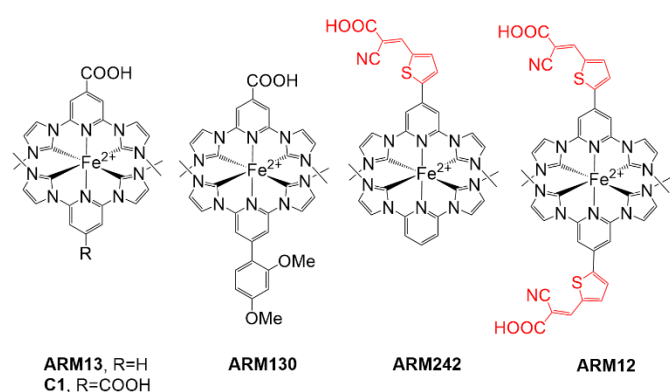
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Electronic Supplementary Information (ESI) available: Synthetic procedures, NMR spectra, additional computational details, electrochemical and photovoltaic data. See DOI: 10.1039/x0xx00000x

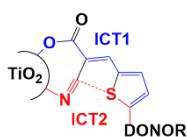
photocurrents.<sup>33</sup> This result was very recently further improved by our group up to reach the best efficiencies ever reported of 1.44 % ( $J_{sc} = 4.8 \text{ mA/cm}^2$ ) and 1.83% ( $J_{sc} = 4.8 \text{ mA/cm}^2$ ) by sensitizing FeSSCs respectively, with the heteroleptic complexes **ARM13**<sup>33</sup> and **ARM130**<sup>34</sup> (Figure 1). The heteroleptic approach was also recently applied by Warnmark that reported the introduction of diarylamino substituents on the central pyridine of the ancillary ligand resulting in 1.31% efficiency and  $J_{sc} = 3.5 \text{ mA/cm}^2$ .<sup>35</sup>

Besides the stereoelectronic tuning of the ancillary ligand, to our knowledge, the modification of the anchoring functionality has not been investigated yet in this series of sensitizers. Indeed, the nature and strength of the anchoring group's interaction with the surface of the DSSC's photoanode is critical to ensure an efficient injection and to prevent back electron transfer (recombination) processes.



**Figure 1.** Iron sensitizers reported and complexes studied in this work, counterion is  $\text{PF}_6^-$  in every case

When compared with the carboxylic function, the cyanoacrylic group, which has been used extensively with organic dyes<sup>11</sup>, exhibits a bifunctionality in terms of enhanced  $\pi$ -conjugation via the acrylate double bond. Cole has reported that the coordination of CN with the titanium atoms of the  $\text{TiO}_2$  surface ensured the necessary electron withdrawal from the oxidized sensitizer, while the carboxylate group acts as an efficient anchor.<sup>36,37</sup> The same group also disclosed a very interesting property of the cyanoacrylic function when linked to a thiophene unit in organic dyes. Indeed, a synchrotron-based x-ray analysis highlighted the creation of a very strong intramolecular interaction with an energy similar to a chemical bond between the thiophene's sulfur atom and the cyano group.<sup>37</sup> The study revealed that this robust S...CN bond led to two intramolecular charge transfer (ICT) processes (Figure 2), ICT1 (blue path) and ICT2 (red path). The summed contribution of these two ICTs greatly enhanced the cell performance.



**Figure 2.** The S...CN bonding reported by Cole<sup>37</sup>

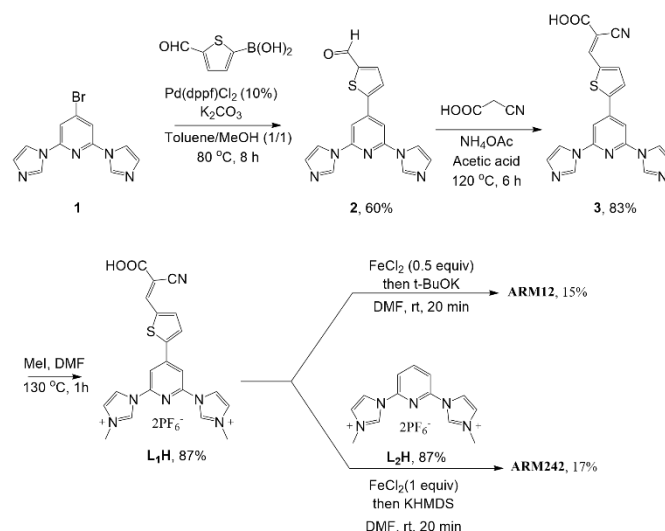
These remarkable properties drew us to investigate the impact of thienylcyanoacrylic anchoring (ThCA) groups on the electronic properties of Fe(II) NHC complexes and on the performance of DSSC sensitized by the same.

Herein we report the synthesis and characterization of the new iron sensitizers **ARM12** and **ARM242** decorated with ThCAs (Figure 1); and the investigation of their photovoltaic properties. The homoleptic **ARM12** promoted a remarkable improvement of the photocurrent compared to **C1** bearing carboxylic groups, whereas a co-sensitization of **C1** and **ARM12** outperformed the best efficiency and photocurrent ever reported for a FeSSC.

## 2. Results and discussion

### 3.1. Synthesis of ligand precursors and complexes

The synthesis of the target complexes first required the preparation of the pyridylimidazolium salts **L1H** and **L2H**, precursors of the pyridyl-NHC ligands to be coordinated to iron (Scheme 1). **L1H** was obtained in good yield by quaternization of the pyridylimidazole **3** with methyl iodide. **3** was the result of a palladium-catalyzed Suzuki coupling of the bromo derivative **1**<sup>33</sup> with 5-formyl-2-thienylboronic acid followed by a condensation reaction with cyanoacetic acid to generate the cyanoacrylic function. **L2H** was prepared according to previously reported works.<sup>24</sup> With the ligands in hand we turned to the preparation of the homoleptic and heteroleptic complexes respectively **ARM12** and **ARM242**. **ARM12** was prepared by first reacting 2 equiv of **L1H** with  $\text{FeCl}_2$  followed by addition of *t*-BuOK as the base to generate the NHC. The heteroleptic **ARM242** was obtained using a statistical synthesis that we reported previously, consisting in reacting  $\text{FeCl}_2$  with an equimolar mixture of **L1H** and **L2H** ending with KHMDS addition.<sup>33</sup> KHMDS was found to be more efficient than *t*-BuOK in this case. **ARM242** was further cleanly separated by column chromatography from a mixture containing both the homoleptic complexes coming from each ligand concomitantly formed during the process.



**Scheme 1.** Synthesis of **L1H** and complexes **ARM12** and **ARM242**

### 3.2. Spectroscopic properties of complexes

The UV-Vis spectra recorded in methanol solution are shown in Figure 3 and the corresponding absorption maxima gathered in Table 1.

As already reported, **C1** displayed three distinct absorption bands in this energy region.<sup>25</sup> The band at higher energy (250–350 nm) is assigned to  $\pi-\pi^*$  transitions, while the two lower-energy bands correspond to the Fe-NHC MLCT transitions (340–420 nm) and Fe-Pyridine MLCT transitions (410–650 nm).

On overall, introduction of ThCA as an anchoring moiety induces a significant red shift of the Fe-Pyridine MLCT bands, whose extent is directly proportional to the number of ThCA units in the complex, namely 0.22/0.11 eV for **ARM12/ARM242** (Table 1). In **ARM12** and **ARM242**, the Fe-NHC MLCT band was masked by the very broad  $\pi-\pi^*$  character absorption band.

Focusing on the lowest-energy portion of the spectrum, the MLCT Fe-Pyridine band, **ARM12** and **ARM242** present a broad absorption, ranging from 450 to 650 nm. Among all, the homoleptic **ARM12** showed the broadest, most intense and largest red shifted absorption ( $\lambda_{\text{max}}$ : 555 nm,  $\epsilon$ : 25900 M<sup>-1</sup>.cm<sup>-1</sup>). Similar absorption features were observed in the computed TD-DFT spectra which, indeed, were able to fairly reproduce the red-shift and intensity increase prompted by the ThCA units (Table 1 and Figure S11). The estimated red shifts for **ARM12** and **ARM242** are 0.37 and 0.31 eV, respectively, being slightly overestimated with respect to the experimental one as a consequence of the small blue shift of the calculated **C1** MLCT band maximum when using the B3LYP\* functional employed in our previous works (see SI for details).<sup>33</sup>

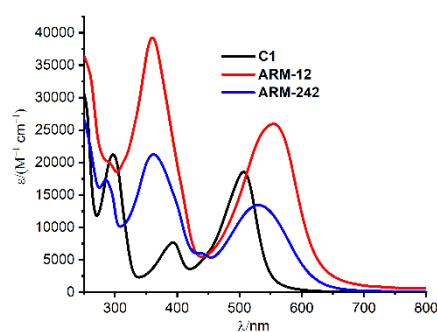


Figure 3. UV-VIS spectra of **C1**, **ARM12** and **ARM242** in methanol.

As is apparent, on the other hand, B3LYP very accurately (within 0.1 eV) predicts the energy of the new complexes that, due to the larger electron withdrawing effect of the cyanoacrylic functionality are characterized by a greater extent of intramolecular CT (0.8 for **C1** and 0.9 for **ARM242** and **ARM12**, as CT index ( $0 < \text{CT} < 1$ ),<sup>38</sup> requiring the use of a slightly larger fraction of non-local exchange to be properly treated (20% in B3LYP vs. 15% in B3LYP\*). Regarding the nature of the MLCT bands, they are mainly composed by transitions between molecular orbitals (MOs) in the vicinity of the Highest Occupied MO (HOMO), such as HOMO-1 and HOMO-2 levels, and the

degenerate lowest unoccupied MO (LUMO) levels of the dyes, in a similar way as it has been reported for other Fe-NHC complexes.<sup>33,34</sup> Figure S12 displays the isosurfaces of the MOs involved in the main transitions composing the MLCT bands of the studied dyes. As expected, the nature of the frontier occupied MOs is barely influenced by the introduction of the ThCA moiety, whereas the degenerated LUMO levels of **ARM242/ARM12** more largely delocalize over the ligands and toward the anchoring unit, resulting in a larger stabilization with respect to those of **ARM13/C1** (see Tables S3 and S4), and in the red-shift of the MLCT bands.

Table 1. Experimental absorption maxima (in MeOH and on TiO<sub>2</sub>) and calculated vertical excitation energies with relative oscillator strengths and nature of the main single particle excitations contributing to these excited states (percentage for each transition).

Dye	Experiments		Theory <sup>a</sup>	
	$\lambda_{\text{max}}$ (10 <sup>4</sup> . $\epsilon$ (M <sup>-1</sup> .cm <sup>-1</sup> ))	$\lambda_{\text{max}}$ (TiO <sub>2</sub> )	E <sub>max</sub> (Osc. Str.)	Transition (%)
<b>C1</b>	506 (1.85)	504	464 (0.324)	H-2→L+1 (45.4%) H-1→L (45.1%)
<b>ARM12</b>	555 (2.59)	553	538 (1.193)	H-2→L+1 (49.8%)
<b>ARM242</b>	531 (1.34)	556	524 (0.566)	H-1→L (68.9%)

a) All energy values are in nm. Calculated vertical excitation properties for **C1**, **ARM242** and **ARM12** computed at the TD-B3LYP\* and TD-B3LYP levels of theory, respectively, within a 6-311G(d) basis set in their corresponding ground state (GS) geometries.

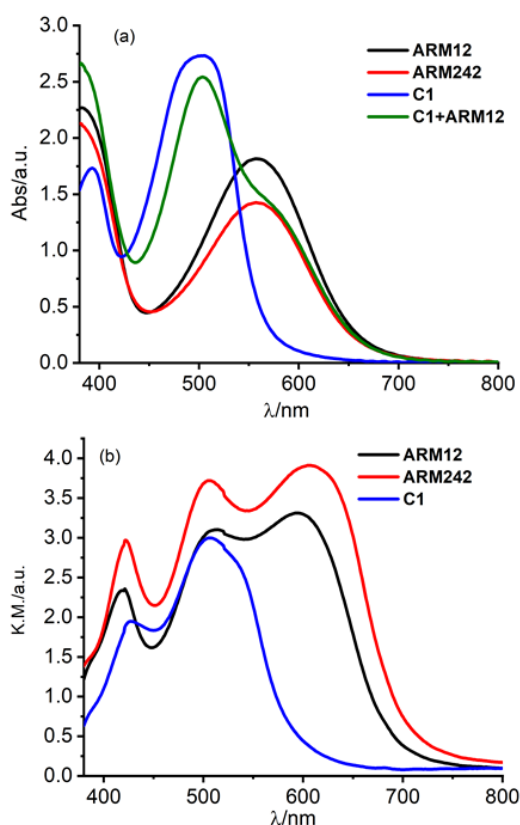
### 3.3. Spectroscopic and electrochemical properties of FeNHC-sensitized films

In order to gain information about the spectroscopic features of the new Fe(II)NHC series grafted onto TiO<sub>2</sub>, relatively thick 13  $\mu\text{m}$  electrodes sensitized with **ARM12**, **ARM242** and **C1** have been prepared. Their relative absorption spectra are depicted in Figure 4a and  $\lambda_{\text{max}}$  values reported in Table 1. The dyes bearing the ThCA functions are characterized by a broad and intense symmetric MLCT band, spanning the 500–700 nm interval with  $\lambda_{\text{max}} \approx 550$  nm, while **C1** exhibits a narrower and blue shifted main band ( $\lambda_{\text{max}} \approx 500$  nm).

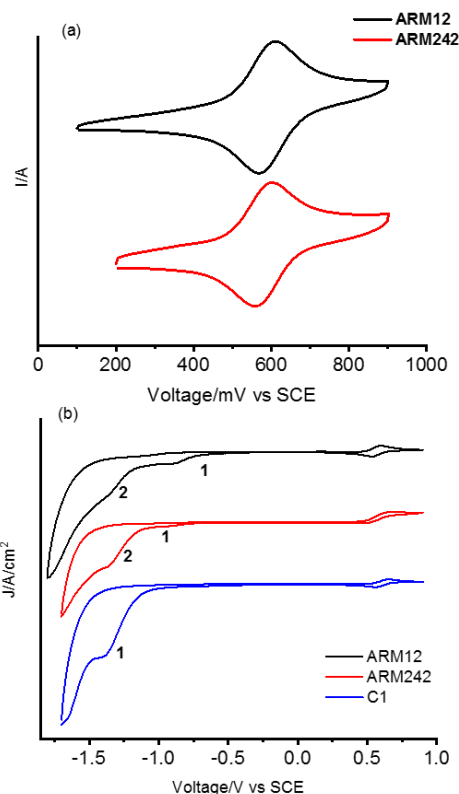
The red shifted MLCT bands, with a strong Fe(II)-pyridine character are consistent with the reduced electrochemical gap that we measured by cyclic voltammetry on the dyed TiO<sub>2</sub> or ZrO<sub>2</sub> thin films in contact with 0.1 M LiClO<sub>4</sub> in acetonitrile solution (Figure 5 and Table 2). ZrO<sub>2</sub> was used as an electrochemically inert porous support allowing to explore the energetics of dye reduction.<sup>39–41</sup>

On the titania substrates (Figure 5a), both the new complexes, **ARM12** and **ARM242**, revealed a reversible Fe(II)/(III) oxidation potential ( $\Delta E \approx 59$  mV) with E<sub>ox</sub> of 0.59 V and 0.58 V respectively, more cathodic ( $\approx 70$  mV) than that recorded for our standard **C1** (0.67 V vs SCE<sup>32</sup>). All these complexes are characterized by irreversible cathodic waves. The complexes

bearing the ThCA, **ARM12** and **ARM242** highlight a first irreversible process (wave at -0.88 V and -0.94 V respectively), which is absent in **C1**. The same complexes display a second more intense polyelectronic wave peaking at -1.34 and -1.36 V vs SCE, similar to that recorded in the case of **C1** at -1.39 V. The estimation of the HOMO-LUMO gap, based on these potentials, provide values ranging between 650 and 833 nm, which embraces the onset of the absorption spectrum found around 700 nm, confirming the MLCT character of the lowest energy transition. Indeed, on average, the manifold of electron acceptor states lying at the midpoint between the redox waves (-1.12 V) provides a gap value (732 nm) in excellent agreement with the onset of the experimental absorption spectrum of the thin film sensitized by these new dyes. Thus, both stabilization of the LUMOs and destabilization of the Fe(II) centered HOMO are responsible for the substantial red shift in the spectra response of the Fe complexes bearing the cyanoacrylic moieties (ThCA). The data obtained on ZrO<sub>2</sub> could be safely extended to TiO<sub>2</sub>, where a marginal anodic shift (10-20 mV) of the Fe(II)/III wave is observed. Clearly, on TiO<sub>2</sub>, the observation of the cathodic features of the Fe(II) sensitizers is precluded by the interception of its CB states.



**Figure 4.** Absorption spectra (recorded against an identical undyed electrode as a reference) of the Fe(II)NHC series together with **ARM12** + **C1** loaded (a) on 13 μm TiO<sub>2</sub> and (b) on 20 μm + top scattering layer. In the latter case the **C1+ARM12** system saturated the spectrophotometer response at absorbance higher than 4.



**Figure 5.** Cyclic voltammetry recorded for Fe(II)NHC on (a) TiO<sub>2</sub> and on (b) ZrO<sub>2</sub> (full scan) in 0.1 M LiClO<sub>4</sub>/ACN solution.

**Table 2:** Electrochemical and spectroscopic parameters for the Fe(II)NHC sensitized TiO<sub>2</sub> and ZrO<sub>2</sub>.

Dye	E <sub>ox</sub> (TiO <sub>2</sub> ) (V vs SCE)	E <sub>ox</sub> (ZrO <sub>2</sub> ) (V vs SCE)	E <sub>(peak)red</sub> (ZrO <sub>2</sub> ) (V vs SCE)	ΔE <sub>redox</sub> <sup>b</sup> (ZrO <sub>2</sub> ) (eV)	E <sup>00</sup> <sub>(TiO<sub>2</sub>)<sup>c</sup> (eV)</sub>	E <sup>00</sup> -E <sub>ox</sub>	E <sub>ox</sub> <sup>*</sup> (V) <sup>d</sup>
<b>C1</b>	0.67 <sup>a</sup>	0.61	-1.39	2.00	2.10	1.49	-1.41
<b>ARM12</b>	0.59	0.57	-0.88 -1.34	1.85	1.81	1.24	-1.22
<b>ARM242</b>	0.58	0.57	-0.94 -1.36	1.93	1.81	1.24	-1.23

Data taken from ref <sup>32</sup>

b) Calculated according to: |E<sub>ox</sub>(ZrO<sub>2</sub>)| + |E<sub>red</sub>(ZrO<sub>2</sub>)|

c) The E<sup>00</sup><sub>(TiO<sub>2</sub>)</sub> energy was estimated from the onset of the absorption spectrum, by taking the 5% absorbance relative to the MLCT maximum on TiO<sub>2</sub>

d) Calculated according to: E<sub>ox</sub>(TiO<sub>2</sub>) - E<sup>00</sup><sub>Abs-TiO<sub>2</sub></sub>

As for the excited state energetics, as expected,<sup>27</sup> the iron(II) complexes did not emit in fluid solution nor loaded on the semiconductor, thus the spectroscopic E<sup>00</sup> was estimated from the onset of the absorption spectra at ca. 5% of the maximum absorption. E<sup>00</sup> was 1.81 eV for both chemisorbed ThCA substituted complexes, this value was smaller than the energy calculated in the case of our standard **C1** (2.10 eV). Such an

estimate appears to be in acceptable agreement with the electrochemical gap discussed before, if consideration is made for the irreversible nature of the cathodic processes which precludes a rigorous thermodynamic information. The excited state potential  $E^*_{ox}$  ( $E^*_{ox} = E_{ox} - E^{00}$ ) where  $E_{ox}$  is the Fe(III)/(II) ground state potential affords values around -1.2 V for **ARM12** and **ARM242** and -1.4 V for **C1**. Thus, injection in the TiO<sub>2</sub> semiconductor is an exergonic process whose driving force can be calculated according to  $\Delta G_{inj} = -e(|E_{ox}| - |E_{FB}|)$  where  $E_{FB}$  represents the flat band potential of the TiO<sub>2</sub>. Considering the flat band potential of the TiO<sub>2</sub> in an organic medium in the presence of lithium cations at ca. -0.7 V vs SCE,<sup>42</sup> we obtained  $\Delta G_{inj} \approx 500$  meV for **ARM12** and **ARM242** and around 700 meV for **C1**. The ground state potential also indicates that regeneration of the Fe(II) species by the iodide/triiodide-based electrolyte is an exergonic process by at least 200 meV.

From Figure 4a, it can be seen that the enhanced red sensitivity of **ARM12**, **ARM242** leaves a "valley" in the absorption spectrum between 400 and 500 nm, where, in contrast with **C1**, their extinction coefficient is small. Thus, to further increase the spectral sensitivity of the thin films, we have realized the co-sensitization of **C1** and **ARM12** to obtain a panchromatic profile to collect both the relative blue (450 – 500 nm) and green-red (500 - 650 nm) energy portions of the visible region. Due to the stronger stability of the -CNCOO-Ti linkage<sup>36</sup> of **ARM12** with respect to the COO-Ti binding of **C1**, we first dipped the TiO<sub>2</sub> electrodes for 1h in **ARM12** until a ca. 1 of maximum MLCT absorbance was reached, followed by 6h of immersion in the **C1** solution to complete the saturation of the remaining available adsorption sites of the TiO<sub>2</sub> film. Figure S20 shows the evolution of the absorption spectrum of the TiO<sub>2</sub> film after 1h of immersion in **ARM12** and after treatment with **C1**. This co-sensitized electrode clearly exhibits both the spectroscopic fingerprints of the COOH- and ThCA-based complexes with the first band around 500 nm and the second shoulder at 570 nm that, coherently with the presence of **ARM12**, collects photons up to 700 nm in the transparent film. The difference in the spectrum shows that spectral fingerprints of **C1** are maintained in the **C1+ARM12** system, and that the interaction between both Fe(II) sensitizers is ostensibly weak. The average surface loading was estimated according to eq. 1:

$$\Gamma = \frac{A(\lambda)}{1000\varepsilon(\lambda)} \quad (\text{eq.1})$$

where  $A$  and  $\varepsilon$  are the maximum visible absorbance and the molar extinction coefficient respectively of each dye. Probably due to the higher steric hindrance of the homoleptic **ARM12**, its surface coverage was the lowest among the series (70 nmol.cm<sup>-2</sup>). An intermediate loading of 107 nmol.cm<sup>-2</sup> was found in the case of **ARM242** and the highest value of 147 nmol.cm<sup>-2</sup> was obtained with **C1**. As for the co-sensitized electrode, the estimated loading was 51 and 91 nmol.cm<sup>-2</sup> for **ARM12** and **C1** respectively.

We have further improved the light harvesting capability of the sensitized TiO<sub>2</sub> films by preparing ca. 20  $\mu\text{m}$  transparent TiO<sub>2</sub> equipped with a top scattering layer characterized by >100 nm

nanoparticles. The increased optical path obtained with the scattering layer broadens notably the spectral features of the sensitized films (Figure 4b): in particular **C1** collects photons up to  $\lambda > 600$  nm and **ARM12** and **ARM242** up to 750 nm. Under these conditions, **C1+ARM12** saturated the spectrophotometer response at absorbance higher than 4.

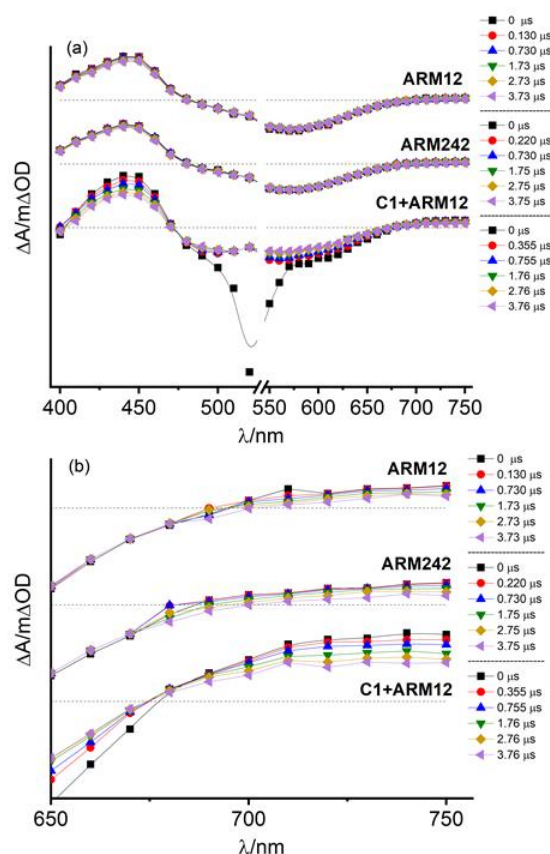
### 3.3. Transient absorption spectroscopy

Regeneration and recombination dynamics were evaluated by means of Transient Absorption Spectroscopy (TAS) in the  $\mu\text{s}$  to  $\text{s}$  timescale on dyed-TiO<sub>2</sub> thin films in contact with 0.1 M LiClO<sub>4</sub>/ACN solutions. The absorption spectra of **ARM12** and **ARM242** are characterized by similar features with a strong band mirroring the MLCT manifold if consideration is made for the small bathochromic shift of the ground state spectrum occurring in the presence of small high-density cations such as Li<sup>+</sup> and Mg<sup>2+</sup> (Figure S21) interacting with the TiO<sub>2</sub> film.<sup>33</sup> The transient absorption spectra of **ARM12** and **ARM242** (Figure 6) exhibited a bleach centred around 575 nm with a small shoulder around 500 nm, a comparatively intense absorption band peaking at ca. 430 nm, and weaker and featureless broad absorption starting at ca. 670 nm and extending into the NIR. These transient features are very long lived, showing a minor evolution during the first 4  $\mu\text{s}$  after the laser pulse. The extremely long lived state and the bleaching of the ground state absorption is consistent with the photoinduced formation of Fe(III) following electron injection. The high (450 nm) and low energy absorption bands (> 700 nm), whose time evolution parallels that of the bleaching are assigned to LMCT transitions, with the weaker low energy contributions by photoinjected electrons trapped inside TiO<sub>2</sub>. To confirm the interpretation of the TA spectra, we have performed spectroelectrochemical (SE) measurements on TiO<sub>2</sub> (Figure S22). In general, we observed a remarkable agreement with the transient difference spectra on the same substrate, confirming the assignment we made to the photoinduced formation of the oxidized state of the iron complex following visible excitation (Figures 6 and S23). In detail, spectra in Figure S22 exhibited the deep bleach of the charge transfer bands at 500 nm in the case of **C1** and around 570 nm and 490 nm in the case of the ThCA-based systems. Consistent with the TAS analysis, the oxidized forms of **ARM12** and **ARM242** show distinctively the higher energy (450 nm) and lower energy (> 700 nm) absorption due to LMCT transitions further corroborating our results from the TA spectra. It is interesting to observe that the SE changes for **C1**, upon electrochemical oxidation are quantitatively more significant ( $\Delta A_{\text{min}} = -0.2$ ) than those found with the cyanoacrylic dyes ( $\Delta A_{\text{min}} \approx -0.04$ ), while during TAS measurements all complexes exhibit similar  $\Delta A$  amplitudes in correspondence of their main MLCT band. Considering that the electrochemical oxidation on TiO<sub>2</sub> proceeds through charge hopping from molecules in proximity of the FTO back contact, this suggests that **C1** is able to sensitize deeper layers of TiO<sub>2</sub>, closer to the FTO collector, than **ARM12** or **ARM 242**. This could be due to a better

permeation of the TiO<sub>2</sub> by **C1**, due to its less hydrophobic and less sterically hindered structure. It is also interesting to note that the SE variations in the co-sensitized system are the most significant within the explored series, achieving a much more considerable bleaching of the **ARM12** signature, i.e. more than 1 order of magnitude compared to **ARM12@TiO<sub>2</sub>** ( $\Delta A_{580} = -0.5$ , Figure S22d) This is indicative of an oxidation of **ARM12** proceeding through hopping from oxidized **C1** states. Notably, since the co-sensitized electrode was prepared by first dipping the TiO<sub>2</sub> electrode in the **ARM12** solution, the distribution of **ARM12** within the co-sensitized TiO<sub>2</sub> mesoporous substrate should be identical to that of **ARM12@TiO<sub>2</sub>** case.

The TAS spectrum of **C1+ARM12** exhibited the clear fingerprints of both components. While the formation of the charge separated state Fe(III)/e-(TiO<sub>2</sub>) is almost completely convolved with the instrumental time resolution of our apparatus (100 ns FWHM with 350  $\Omega$  impedance), we observed with our highest time resolution (50  $\Omega$  impedance and FWHM  $\approx$  7 ns), in agreement with a previous work,<sup>32</sup> the residual of a very fast dynamic (relatively to the time scale of our apparatus) involving **C1**, which consists in the narrowing and a weak hypsochromic shift of the MLCT bleach, due to relaxation of the lowest triplet state (T<sub>1</sub>) which may also inject (Figure S23a), resulting in the rise of weak absorption bands for  $\lambda > 570$  nm and  $\lambda \approx 430$  nm. A spectral evolution during the first 15 ns is clearly observed in the case of **ARM12** (Figure S23b), where the rise of a well-defined absorption band centred at 450 nm occurs. After 100 ns changes to the spectral shape almost completely ceased, and no further evolution in the spectral fingerprints reported in Figure 6, are observed in the following hundreds of ms during which the amplitude of the transient signals simply decays by recombination according to a non-monoexponential kinetics. Charge separated state recombination was probed at 500 nm in the case of **C1**, whereas the ground state recovery of **ARM12** and **ARM242** were both monitored at 570 nm. The transient spectrum of **C1+ARM12** (Figure 6 and Figure S23) contains the contribution of the charge separated states of both **C1** and **ARM12**, meaning that each dye is able to inject independently of each other, as indicated by the coexistence of two bleaching bands centred at 500 nm (**C1**) and at 570 nm (**ARM12**), which are well defined already at time scales convolved with the laser pulse (4-10 ns delay, Figure S23c). Note that in order to avoid the interference of the 532 nm laser excitation with the ground state bleaching of the respective dyes, we performed experiments at short time scales by using the 355 nm excitation. Similar to what is reported for **ARM12** alone, we observe the formation of the 450 nm absorption band, assigned to the oxidized state of **ARM12**, within the first 40 ns after the excitation pulse. We confirmed that this latter spectral feature is absent on ZrO<sub>2</sub> (Figure S23d) where, due to the lack of injection we could observe the spectral contribution of the excited states of both **ARM12** and **C1**, where the sharp and intense bleaching of **C1** overlapped with the broader ground

state bleaching of **ARM12**, extending up to 700 nm. This also confirmed that energy transfer from surface bound **C1** to **ARM12** was not a significant excited state deactivation process, at least compared to charge injection into TiO<sub>2</sub>. Regardless to the excitation wavelength, the shape of the transient spectrum of **C1+ARM12** after the first 100 ns, is very similar to that observed, with a lower time resolution, at longer time scales (up to 3.2  $\mu$ s delay (Figure S24)), where we only observe the recovery of the charge separated state by recombination.



**Figure 6.** (a) Transient absorption spectra recorded for **ARM12**, **ARM242** and **C1+ARM12** in contact with 0.1 M LiClO<sub>4</sub>/ACN solution. (b) Magnification of low energy flat absorption. Laser source: 532 nm. Laser power: 7 mJ/cm<sup>2</sup>/pulse. Input impedance: 350  $\Omega$ .

In order to investigate in more detail the recombination processes underlying the solar cell device operation in relevant conditions, recombination kinetics were explored under a relatively low excitation power (480  $\mu$ J/cm<sup>2</sup>/pulse) to avoid an excess of localized electron-hole pairs that could lead to an underestimation of the recombination lifetime. Fe(II) recovery was ca. 100 % complete within a time window of 500 ms. Figure 7 summarizes the evolution of the photoinduced bleaching of the dyed thin films in contact with the I<sup>-</sup>/I<sub>2</sub> free electrolyte (0.1 M LiOTf, 0.6 M PMOTf, 0.1 M GuNCS, 0.1 M TBAPF<sub>6</sub>, 0.1 Mg(OTf)<sub>2</sub>). The decay was fitted by the combination of a power law function (eq. 2),<sup>43</sup> owing to the fast bimolecular electron-hole recombination which contributes to ca. 50% of the decay of the initial amplitude, with a stretched exponential function

(Kohlrausch-Williams-Watts (KWW), eq. 3) accounting for the distribution of recombination rate constants motivated by the inherent inhomogeneity of the nanocrystalline titania film:<sup>44,45</sup>

$$\Delta A_{t < 2 \text{ ms}} = A + bt^{-c} \quad (\text{eq. 2})$$

$$\Delta A_{t > 2 \text{ ms}} = A' + b'e\left(\frac{t}{\tau_0}\right)^\beta \quad (\text{eq. 3})$$

In eq. 3, where  $\beta$  represents the stretch exponential parameter which was set to 0.25 in all cases. The weighted lifetime is defined from  $\tau_0$  and  $\beta$  according to eq. 4:

$$\langle \tau \rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (\text{eq. 4})$$

where  $\Gamma$  is the gamma function.<sup>46</sup>

All the complexes exhibited  $\langle \tau \rangle$  values in the ms range (Table 3), in particular 6 ms was obtained in the case of **ARM12** and **C1** and a shorter value of 1 ms in the case of the heteroleptic complex **ARM242**. Quite similar time constants values (1.6 and 2.9 ms probed at 500 and 570 nm) were also found in the **C1+ARM12** system. Nevertheless, considering that at 500 nm the spectral contribution of **C1** is dominant, the shorter Fe(III) lifetime at 500 nm might be due to hole transfer to **C1** from **ARM12**, consistent with the lower oxidation potential of the latter and with the observations from the steady state spectrochemistry discussed above. We note that the hole transfer from **C1** to **ARM12**, even assuming a slow kinetics, should be feasible, since the dyes' oxidized state on the surface is extremely long lived. This contrasts with the excited state lifetime, which, besides being short lived is further quenched by electron transfer to the semiconductor, making energy transfer unlikely to occur.

**Table 3:** Recombination lifetime for the Fe(II)NHC complexes and the co-sensitized system extrapolated by eq. 3 and eq. 4

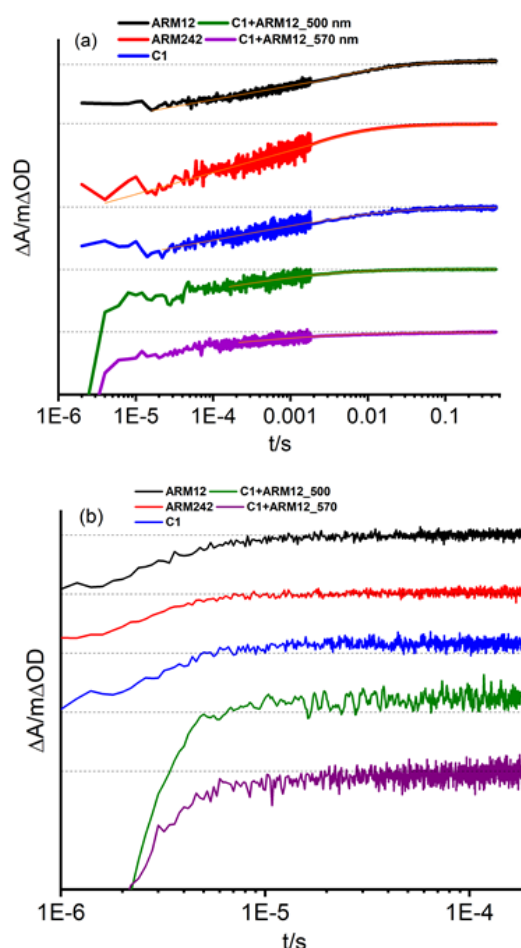
Dye	$\tau_0$ (s)	$\langle \tau \rangle$ (ms)
<b>ARM12</b>	$2.7 \times 10^{-4}$	6.5
<b>ARM242</b>	$5.9 \times 10^{-5}$	1.4
<b>C1</b>	$2.6 \times 10^{-4}$	6.1
<b>C1+ARM12</b> (500 nm)	$6.7 \times 10^{-5}$	1.6
<b>C1+ARM12</b> (570 nm)	$1.2 \times 10^{-4}$	2.9

To better gain insight into the injection quantum yield in a shorter time scale, we have carried out a comparative actinometry<sup>47</sup> 50 ns after the 355 nm laser excitation and probed at the bleach of their respective MLCT states, to evaluate the injection of **ARM12** relative to that one of **C1** according to eq.5:

$$\frac{\phi_{inj}^{ARM12}}{\phi_{inj}^{C1}} = \left( \frac{\Delta A_{ARM12}(590 \text{ nm})}{\Delta A_{C1}(506 \text{ nm})} \times \frac{\Delta \epsilon_{C1}(506 \text{ nm})}{\Delta \epsilon_{ARM12}(590 \text{ nm})} \times \frac{LHE_{C1}(\lambda_{exc-355 \text{ nm}})}{LHE_{ARM12}(\lambda_{exc-355 \text{ nm}})} \right) \quad (\text{eq.5})$$

where  $\Delta A$  represents the difference of the absorbance between the oxidized and the ground state of the dye extrapolated by the TAS data (Figure S23),  $\Delta \epsilon$  the difference in the extinction molar coefficient determined by the SE data (Figure S22) and LHE, the light

harvesting efficiency at the considered excitation wavelength. We have selected a delay of 50 ns to ensure the signal are not convolved with the laser pulse (FWHM  $\approx$  7 ns). The ratio between  $\Phi_{inj}$  (**ARM12**) and  $\Phi_{inj}$  (**C1**) was 0.92 and 0.98 either when **ARM12** is alone or in the co-sensitized TiO<sub>2</sub> film (**C1+ARM12**), in good agreement with the ratio obtained from the APCE measurements (0.87) (Figure S25b). This corroborates the indication of a similar injection kinetics in the two iron NHC sensitizers and that the injection efficiencies are preserved in the co-sensitized electrode.



**Figure 7.** (a) Recombination dynamics of the dyed TiO<sub>2</sub> thin films in contact with the blank electrolyte 3 (0.1 M LiOTf, 0.6 M PMIOtf, 0.1 M GuNCS, 0.1 M TBAPF<sub>6</sub>, 0.1 MgOTf). The kinetics were obtained by joining traces sampled with 10 k $\Omega$  and 1 M $\Omega$  input impedance. The orange lines represent the fit of the decay. (b) Regeneration kinetics where the same films as in (a) are in contact with the reduced form of the electrolyte (deprived of I<sub>2</sub>). Laser excitation: 532 nm Input impedance: 10 k $\Omega$ . Laser power for curve recorded in (a) and in (b): 480  $\mu\text{J}/\text{cm}^2/\text{pulse}$ .

When iodide was introduced in the electrolyte (electrolyte without I<sub>2</sub>), the bleach recovery of all Fe(III) was largely confined inside the instrumental response function of our spectrometer (10 k $\Omega$  input impedance), suggesting a regeneration process with nearly unitary efficiency  $\eta_{reg}$  expressed by eq. 6:

$$\eta_{reg} = \frac{k_{reg}}{k_{reg} + k_{rec}} \quad (\text{eq. 6})$$

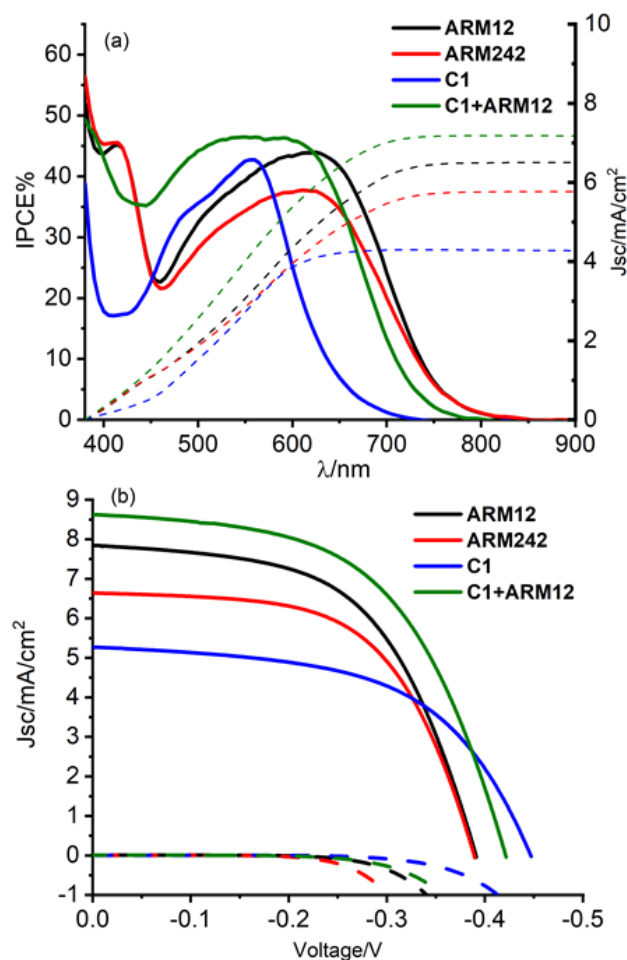


where  $k_{\text{reg}}$  represents the pseudo first order rate constant associated to the regeneration of the oxidized dye by the reduced form of the redox mediator in the order of  $10^6 \text{ s}^{-1}$ ; and  $k_{\text{rec}}$  is the recombination rate constant on the order of  $10^3 \text{ s}^{-1}$ . Being  $k_{\text{rec}}$  three order of magnitudes smaller than  $k_{\text{reg}}$  we can assume that  $\eta_{\text{reg}} \approx 1$ .

### 3.4. Photovoltaic properties

The photovoltaic properties of the new Fe(II)NHC series have been evaluated in the presence of our previously reported customized electrolyte.<sup>33</sup> The electrolyte contains  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ , TBAI and GuNCS. The role of the small high-density cations, able to interact with the titania surface, enhances the directionality of the excited state, via formation of a favorable surface dipole, leading to improved charge injection; TBAI contributes to decrease the overall cell resistance helping to increase the concentration of iodide without further decreasing the open circuit photovoltage ( $V_{\text{oc}}$ ) as it would happen with potential determining ion containing salts like LiI; the mild base GuNCS, also adsorbs on the titania surface, and partially screens recombination with  $\text{I}_3^-$ , bringing a small improvement in  $V_{\text{oc}}$  and Fill Factor (FF). Unfortunately, the addition of stronger bases, like  $^t\text{BuPy}$  proved detrimental in the case of all the Fe(II)NHC sensitizers explored so far causing a large drop in the resulting photocurrent.<sup>32,48</sup> On transparent thin films (13  $\mu\text{m}$  thick active layer), the Incident Photon to Current Conversion Efficiency (IPCE) spectra (Figure S25a) clearly highlight the extended light harvesting capability provided by the introduction of the ThCA moieties generating photoconversion at the threshold of 800 nm. This is an unprecedented result for Fe(II) sensitizers, whose commonly narrow MLCT bands normally limit the conversion to the green/orange region of the Vis spectrum. Among the series, **C1** resulted in the highest IPCE value of 45 % probably due to its higher injection driving force, but **C1** was closely matched by **ARM12** (max. 40%), which was superior to **ARM242** (max. 35%). The integrated short circuit photocurrent density extracted from the IPCE spectra afforded maximum photocurrents of the order of 6  $\text{mA}/\text{cm}^2$  with the ThCA-based dyes, in good agreement with the data obtained under AM 1.5 white light illumination: **ARM12** exhibited indeed the best  $J_{\text{sc}}$  of 6.23  $\text{mA}/\text{cm}^2$ , a  $V_{\text{oc}}$  of 0.37 V, a FF of 56% and the highest Power Conversion Efficiency (PCE) among the series (1.28%); **ARM242** exhibited a PCE of 1.14% owing to the lower photocurrent density of 5.30  $\text{mA}/\text{cm}^2$  (Figure S26 and Table S11). In agreement with its narrowest spectral response, the standard **C1** generates the lowest  $J_{\text{sc}}$  of 4.64  $\text{mA}/\text{cm}^2$  but the highest  $V_{\text{oc}}$  leading to a PCE of 1.11%. The computed Absorbed Photon to Current conversion Efficiency (APCE%) spectra confirms a slightly higher injection in the case of **ARM12** compared to its heteroleptic analogue, providing a value of 40%, where the light harvesting efficiency is essentially unitary (Figure S25b). The panchromatic sensitization provided by the co-adsorption of **C1** and **ARM12** brought a further increase in photocurrent leading to ca.  $J_{\text{sc}}=7 \text{ mA}/\text{cm}^2$  a  $V_{\text{oc}} = 0.42 \text{ V}$  and PCE of 1.56%. The favorable competition between dye regeneration and charge

recombination leading to nearly unitary collection efficiency prompted us to further enhance the light harvesting capability of our series by increasing the thickness of the transparent  $\text{TiO}_2$  tasked with dye adsorption (up to ca. 20  $\mu\text{m}$ ) and by introducing a top scattering layer made of ca. 100 nm anatase nanoparticles. Under these conditions, the photocurrent current reached 8  $\text{mA}/\text{cm}^2$  for **ARM12**, ca. 7  $\text{mA}/\text{cm}^2$  for **ARM242** and 5  $\text{mA}/\text{cm}^2$  to **C1** associated to a PCE of 1.71%, 1.52% and 1.30% respectively (Figure 8 and Table 4). These are, to the best of our knowledge, the highest photocurrent densities ever reported for an iron sensitized solar cell. The lower performances obtained from **ARM242** compared to **ARM12** can be attributable both to the slightly lower injection quantum yield as shown by the APCE and by a faster recombination rate with  $\text{I}_3^-$  as pointed out by the less negative threshold of the dark current well visible in Figure 8b. Finally, the **C1+ARM12** system generated  $J_{\text{sc}} \approx 9 \text{ mA}/\text{cm}^2$ ,  $V_{\text{oc}} = 0.42 \text{ V}$  and an average PCE of 2% that at the moment represents the best efficiency ever reported for n-type sensitization by Fe(II) dyes. **ARM12** and **ARM242** exhibited a lower  $V_{\text{oc}}$  than the standard **C1** by at least 30-60 mV.



**Figure 8:** (a) IPCE spectra for the Fe(II)NHC complexes and their relative integrated photocurrent density. (b) J/V curves for the dyed 20  $\mu\text{m}$  + scattering layer  $\text{TiO}_2$  electrodes.

Often a reduced  $V_{oc}$  is obtained by metal complex-based sensitizers endowed with an increased red sensitivity, that is usually obtained by lowering the energy of the lowest unoccupied orbitals of the chromophoric ligands, in agreement with works by Sayama<sup>49</sup> in the case of Ru(II) complexes bearing biquinoline ligands.

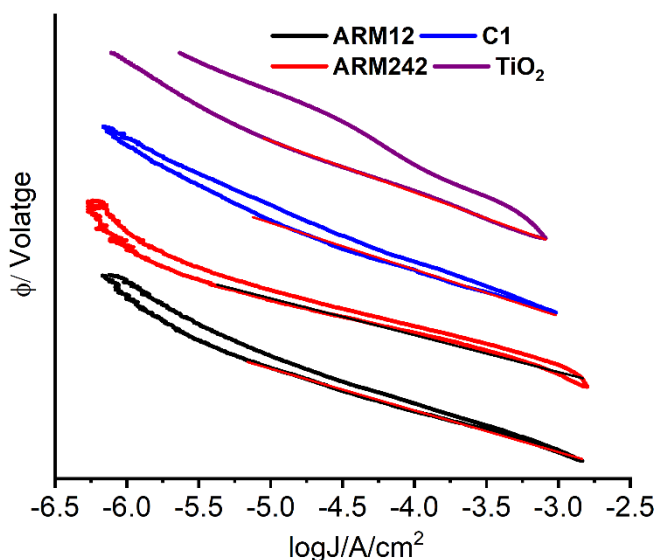
**Table 4:** Power conversion parameters for the Fe(II)NHC complexes loaded on 20  $\mu\text{m}$   $\text{TiO}_2$  + scattering layer. The values reported in brackets for the co-sensitized electrode represent the parameters associated to the best cell.

Dye	$J_{sc}/(\text{mA}/\text{cm}^2)$	$V_{oc}/\text{V}$	FF%	$\eta\%$
ARM12	7.84 $\pm$ 0.38	0.39 $\pm$ 0.01	56 $\pm$ 1	1.71 $\pm$ 0.15
ARM242	6.64 $\pm$ 0.12	0.39 $\pm$ 0.01	59 $\pm$ 1	1.52 $\pm$ 0.10
C1	5.27 $\pm$ 0.14	0.45 $\pm$ 0.01	55 $\pm$ 1	1.30 $\pm$ 0.07
C1+ARM12	8.63 $\pm$ 0.24 (8.74)	0.42 $\pm$ 0.01 (0.43)	55 $\pm$ 1 (55)	1.98 $\pm$ 0.10 (2.06)

This phenomenon was explained by the back-electron recombination of photoinjected electrons with the oxidized form of the electrolyte mediated through  $\pi$  delocalized ligands. The dark current related to the recombination of the photoinjected electrons with the  $\text{I}_3^-$  species ( $\text{I}_3^- + 2e-(\text{CB}(\text{TiO}_2) \rightarrow 3\text{I}^-)$ ) influences the  $V_{oc}$  that can be written according to eq. 7, a simplified form of the Diode equation:<sup>50</sup>

$$V_{oc} = \frac{kT}{e} \ln \left( \frac{I_{ph}}{n_{CB} k_{et} [I_3^-]} \right) \quad (\text{eq. 7})$$

where  $k$  represents the Boltzmann's constant,  $T$  the absolute temperature,  $I_{ph}$  the short circuit photocurrent,  $n_{CB}$  the electron density in the semiconductor, and  $k_{et}$  is the apparent rate constant of the reduction of  $\text{I}_3^-$  to  $\text{I}^-$ .



**Figure 9:** Tafel plots of the dark current of the Fe(II)NHC sensitized  $\text{TiO}_2$  films in contact with  $10^{-2} \text{ M I}^-/10^{-2} \text{ I}_3^-/\text{CH}_3\text{CN}$  solution. Tafel slopes extrapolated by the plots are 126, 112, 99 and 139  $\text{mV}\cdot\text{dec}^{-1}$  for C1, ARM12, ARM242 and bare  $\text{TiO}_2$  respectively.

According to eq.7, the  $V_{oc}$  logarithmically decreases with the increase of the back- recombination rate. To better quantify the

recombination kinetics involving the electron transfer from ARM12 and ARM242 modified  $\text{TiO}_2$  films to  $\text{I}_3^-$  electron acceptors in the electrolyte, we have carried out a Tafel analysis on the polarization curves obtained from the dyed  $\text{TiO}_2$  films in contact with a simplified electrolyte where only  $10^{-2} \text{ M LiI}$  ( $10^{-2} \text{ M LiI} + 10^{-2} \text{ M I}_2$ ) was present. Figure 9 reports the Tafel plots and their relative slopes obtained by linear fit on a current interval of ca. 2.5 decades.

In general, we found Tafel slopes in the proximity of  $120 \text{ mV}\cdot\text{dec}^{-1}$ , typical of an electrochemical process kinetically limited by the electron transfer kinetics, as it would be expected in the case of the generation of the  $\text{I}_2(-)$  radical anion by a poorly electrocatalytic electrode, like  $\text{TiO}_2$ . In general, the Tafel slope can be expressed as eq.8:

$$\frac{\partial \phi}{\partial J} = \frac{2.3RT}{\alpha nF} \quad (\text{eq. 8})$$

where  $R$  represents the gas constant,  $T$  the absolute temperature,  $n$  the number of electrons involved in the process,  $F$  the Faraday's constant and  $\alpha$  the transfer coefficient which accounts for the mechanistic details in a given multi-step electrochemical reaction. The Tafel slope is thus proportional to  $1/\alpha$  which, in the case of the new complexes was higher than for C1 and bare  $\text{TiO}_2$ , indicating that the recombination reaction involving electrons injected into  $\text{TiO}_2$  and  $\text{I}_3^-$  requires a proportionally larger overvoltage in the order  $\text{TiO}_2$  ( $139 \text{ mV}\cdot\text{dec}^{-1}$ ) > C1 ( $126 \text{ mV}\cdot\text{dec}^{-1}$ ) > ARM12 ( $112 \text{ mV}\cdot\text{dec}^{-1}$ ) > ARM242 ( $99 \text{ mV}\cdot\text{dec}^{-1}$ ), thus contributing to explain the lower performance of ARM242 compared to ARM12.

### 3.5. Computational analysis

Herein we discuss the results of DFT/TD-DFT calculations performed with the aim of shining light on the photovoltaic behaviour and the interfacial charge separation processes observed experimentally for the distinct Fe(II)NHC dye sensitizers. The TAS experiments in the  $\mu\text{s}$  to  $\text{s}$  timescale, discussed in section 3.3, do not provide us with information on the ultrafast electron injection rates and thus on the relative efficiency of the interfacial charge separation. By calculating the electronic structure of the dye@ $\text{TiO}_2$  interface and the electronic coupling between the dye and the metal oxide we can quantify the impact of the introduction of the ThCA anchoring group in terms of electron injection efficiency. Note that in this section we also considered the results of the unsubstituted heteroleptic Fe(II)NHC dye (ARM13) with the objective of having a reference system for ARM242.

We first investigated the optoelectronic properties of the standalone dye sensitizers by focusing on i) the efficiency of the intramolecular charge separation in the MLCT state, and ii) the improvement of light harvesting capabilities in terms of generated photocurrent. To quantify the hole/electron spatial delocalization in the MLCT excited state along the different molecular fragments conforming the dyes (see Figure S13 for

the fragment definitions), we used the transition density matrix analysis tools as implemented in the TheoDORÉ package.<sup>38</sup> The fragment delocalization percentages for the heteroleptic and homoleptic dyes are summarized in Tables S5 and S6, respectively. As it is apparent in Figure 10, when introducing the ThCA unit, the electron density is largely moving from the Fe-NHC core towards the carboxylic group, resulting in a larger electron delocalization around the anchoring moieties (almost 16% increase) for **ARM242** with respect to **ARM13**, as spatially represented by the electron Natural Transition Orbitals (NTOs).<sup>51</sup> It is important to stress here that the effect of the CA group in increasing the electron localization on the anchoring moiety is even larger than the one shown in Figure 10 (about 24%), since we should compare with the value of 8% calculated for the heteroleptic COOH-substituted dye bearing a thiophene bridge (**ARM7** see ref<sup>33</sup>). On the other hand, the spatial delocalization of the hole density remained almost unaffected upon the chemical functionalization of the ThCA groups (Tables S5 and S6). Identical results were, clearly, obtained for the homoleptic dye, but in this case the amount of delocalization on the fragments was halved due to the split of the charge density into the two symmetric branches.

Then, we evaluated the impact on the photogenerated current of the red-shift absorption prompted by the inclusion of the ThCA group, by following the methodology used in ref.<sup>52</sup>, where the photocurrent ( $J_{sc}$ ) generated by the dye's lowest energy absorption MLCT band was calculated by integrating the simulated absorption spectra against the ASTM G173 solar spectrum ( $P_{in}$ ) applying eq.9:

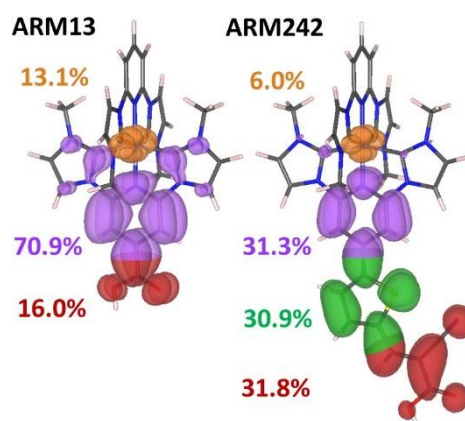
$$J_{sc}(\text{mA/cm}^2) = \int P_{in}(\text{mW/cm}^2) * \frac{\lambda}{1240} * IPCE(\lambda) d\lambda \quad (\text{eq. 9})$$

Where IPCE is defined here as the product of the quantum yield of electron injection ( $\phi_{inj}$ ), the electron collection efficiency ( $\phi_{coll}$ ), and the light harvesting efficiency (LHE). We set up a value of  $\phi_{inj}$  equal to 0.5, as it can be obtained from the experimental APCE measurements, whereas no losses in the electron collection were considered ( $\phi_{coll}=1$ ). Then the LHE has been calculated applying eq.10:

$$LHE(\lambda) = 1 - 10^{A(\lambda)} \quad (\text{eq. 10})$$

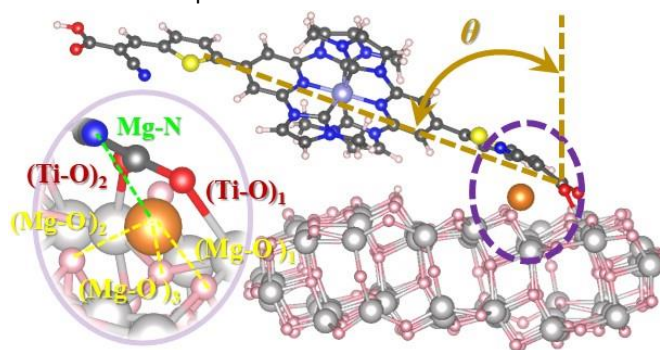
Being  $A(\lambda)$  the reciprocal absorption of the electrode, given by the product of the molar extinction coefficients ( $\epsilon$ ) and the surface concentration ( $\Gamma$ ) of the sensitizer. The values of  $\Gamma$  were extracted from the experimental absorption spectra (see section 3.2), and amounted to 147, 107 and 70 nmol/cm<sup>2</sup> for **C1**, **ARM242** and **ARM12**; while for **ARM13** we used a surface coverage of 120 nmol/cm<sup>2</sup> as it was obtained in our previous work.<sup>33</sup> Finally, in order to get consistent results which are not biased by the errors introduced by our theoretical models, the excited state vertical energies used to compute the simulated spectra have been rigidly shifted to make coincide the main MLCT transitions energies with the experimental absorption maximum wavelengths, as they are reported in Table 1. The calculated  $J_{sc}$  curves as a function of the absorption in the VIS region are represented in Figure S14.

Notably, the computed current intensities achieved by **ARM242/ARM12** are about 1.8 and 1.5 higher than their previous heteroleptic/homoleptic homologues, respectively, which is in good qualitative agreement with respect to experiments ( $(J_{sc})_{\text{ARM242}}/(J_{sc})_{\text{ARM13}}$  and  $(J_{sc})_{\text{ARM12}}/(J_{sc})_{\text{C1}}$  ratios amounting to 1.2 and 1.4, respectively). This result confirms that the increase of the current intensities induced by the light harvesting enhancement, is originated by the effect of the acceptor ThCA moiety, even though the surface coverage of by **ARM242/ARM12** is lower with respect to the reference dyes.



**Figure 10:** Electron Natural Transition Orbitals (NTOs) in ARM13 and ARM242 with the percentages of delocalization for each fragment. The colors employed to plot the isodensities correspond to the unbound pyridyl NHC ligand and iron (orange), anchoring ligand: pyridyl NHC (purple), thiophene spacer (green) and carboxylic group (red) moieties. The isovalue used for this plot was 0.02 a.u.

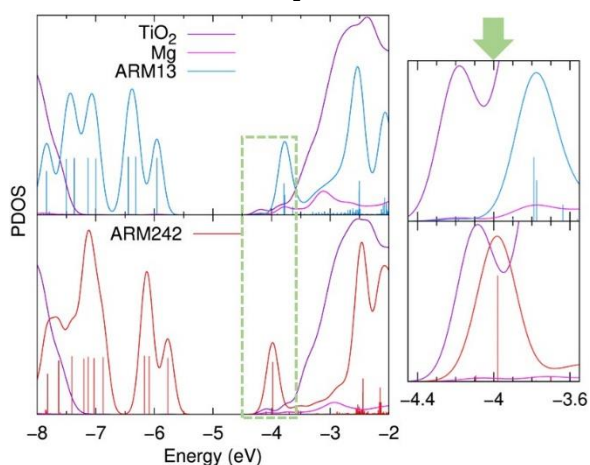
Overall, based on the results discussed so far, the ThCA dyes should show high photocurrents and higher values of PCEs with respect to the reference **ARM13/C1** by virtue of their red-shifted absorption and higher electron localization on the anchoring group. Till here, we are, however, neglecting the impact of the energetics, that is the relative position between the donor (LUMO) dye's state and the acceptors CB states, and we already know from experiments that introduction of ThCA translates into a reduction of the driving force for electron injection, estimated from experiments to be of about 0.2 eV.



**Figure 11.** Optimized structure of the ARM12@Mg-TiO<sub>2</sub> system representing tilted angles ( $\theta$ ) formed by the normal surface vector and the dye; whereas a zoomed image of the Mg<sup>2+</sup> cation (orange color atom) and its closest O neighbor atoms of the TiO<sub>2</sub> surface and the N atom of the ThCA moiety; is displayed in the onset of lateral view as well.

Thus, with the goal of extracting a more quantitative picture of the electron injection efficiency when the dyes are grafted to the TiO<sub>2</sub> surface, we modelled the dye@TiO<sub>2</sub>-Mg interfaces as described in the Computational methods section of the SI (Figure 11).

A first comment concerns the geometry of the dye@TiO<sub>2</sub>-Mg system: although all dyes exhibited similar O-Ti bond lengths (in the order of 2-2.3 Å) when attached to the surface, those bearing the ThCA units (**ARM242/ARM12**) resulted to be more bent toward the semiconductor surface by about 10° with respect to the **C1/ARM13** dyes, see the relevant optimized structural parameters listed in Table S7; this is the consequence of the extension of the  $\pi$ -electronic conjugation on the whole molecular skeleton, which results in the increase of the Van der Waals interactions with the TiO<sub>2</sub> surface.



**Figure 12.** Projected Density of States (PDOS) of dye@TiO<sub>2</sub>-Mg systems along the **ARM13** (bright blue) and **ARM242** (red) dyes, TiO<sub>2</sub> surface (purple) and Mg<sup>2+</sup> cation (magenta), as calculated by Mulliken population analysis. Furthermore, a caption of the graph in the energy region where the dye's LUMO and TiO<sub>2</sub> CB are located and delimited by the green dotted line, is also displayed on the right part. For visualization purposes, only the vertical bars of the dye's PDOS are represented here. On the same vein, the TiO<sub>2</sub> DOS intensity has been divided by a factor of 14 in the main plot, whereas for the zoomed graph no DOS intensity renormalizations have been applied. The rest of PDOS plots are presented in Figure S15.

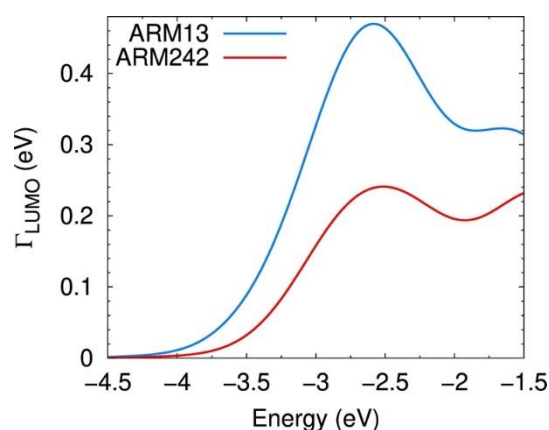
Note that the “almost flat” adsorption configuration predicted by structural optimization of the dye@TiO<sub>2</sub> surface slab is in line with the decreased surface coverage experimentally estimated for the two ThCA complexes. As one can expect, this particular adsorption configuration, leading to the breaking of the electronic conjugation between the dye and the surface, is, in principle, detrimental for the LUMO-CB states electronic coupling, despite the larger fraction of charge localized upon excitation on the anchoring group (Figure 10).

Looking at the dye@TiO<sub>2</sub>-Mg electronic structure and energetic alignment at the interface, the projected density of states (PDOS) over the dye and the TiO<sub>2</sub> components (Figure 12) and the corresponding occupied/unoccupied dye and TiO<sub>2</sub> Kohn-Sham (KS) levels listed in Table S9, indicate that when

introducing the ThCA group, the predicted stabilization of the dye's LUMO amounts to about 0.15-0.2 eV (from -3.79/-3.83 for **ARM13/C1** to -3.98 eV for **ARM242**), in perfect agreement with the experimentally estimated value of 0.2 eV.

In addition, in our simulations the LUMO vs CB driving force is further reduced by a 0.1 eV upshift of the TiO<sub>2</sub> CB states (Table S9) driven by the presence of a larger interfacial dipole (Table S8).<sup>53</sup> As it is apparent in Figure 12, this change in the relative dye/TiO<sub>2</sub> energetics places the dye LUMO at the edge of the semiconductor CB, in a lower density of states region, being thus detrimental for the electron injection process. Since, as we discussed before, the two families of dyes require different DFT functionals if one want to accurately predict their optical properties, we checked if the larger extent of Hartree Fock exchange going from B3LYP\* to B3LYP may affect to some extent the dye/TiO<sub>2</sub> relative energy lining up. Data listed in Table S10, in line with previous results on organic sensitizers,<sup>54</sup> show that the TiO<sub>2</sub> and dye occupied/unoccupied levels are downshifted/upshifted of a comparable extent resulting in a similar LUMO vs. CBM alignment.

The bent adsorption configuration showed in Figure 11 and the reduction in the electron injection driving force discussed so far qualitatively explain the similar maximum IPCEs values with respect to **C1**, partially affecting the PCEs measured for the new ThCA-substituted dyes (Figure 8a). By explicitly calculating the electronic coupling between the dye's LUMO and the TiO<sub>2</sub> CB states as detailed in the Computational details section of the Supporting Information, we can quantitatively estimate the electron injection probability ( $\Gamma_{inj}$ ) over the semiconductor manifold of unoccupied levels, as shown in Figure 13. Evidently, the  $\Gamma_{inj}$  values estimated for the ThCA dye, **ARM242**, regardless of the LUMO position (driving force), are always lower with respect to the ones displayed by the COOH reference dye, indicating that the reduction in the electronic coupling due to the breaking of the dye-TiO<sub>2</sub> electronic conjugation has a quite sizable impact on the injection efficiency.



**Figure 13.** Probability distribution  $\Gamma(e)$  for electron injection from the LUMO of **ARM13** (bright blue) and **ARM242** (red) dyes to the TiO<sub>2</sub>-Mg states within the energy region of the TiO<sub>2</sub> CB edge. The probability distributions for all systems analysed here are plotted in Figure S19.

Although these results nicely account for the measured PCEs curves reported in Figure 8a (note that the  $\Gamma(\varepsilon)$  curves for **ARM13** and **C1** are similar, as it is showed in Figure S19), the picture we are providing, based on the optimized bidentate adsorption configuration via the COO<sup>-</sup> deprotonated group, might only partially represent the actual working conditions.

Previous investigations have, indeed, evidenced the formation of bonds between the N atoms of the cyano (CN) groups with the Ti surface atoms (as schematised in Figure 2), which can be indeed stabilized under certain conditions.<sup>55,56</sup> In this regard, with the objective of evaluating the impact of the formation of such bonds in the interfacial electron injection properties, we carried out the diabatic analysis on **ARM242** and **ARM12** grafted in a bidentate mode to the surface by one Ti-N bond from the cyano moiety, and by one Ti-O bond from the carboxylic group (called in the following **ARM242-CN** and **ARM12-CN**), as it represented in Figure S18. At this stage, it is important to stress that we relied on a bidentate CN/COO<sup>-</sup> mode to assess the modification of the interfacial electronic structure when changing one COO<sup>-</sup> by another CN-based bond, even though this configuration is less stable than the previous considered bidentate COO<sup>-</sup> type of anchoring, which is in line with the findings of previous theoretical works.<sup>56</sup> On the same footing, we are aware that to properly tackle the relative stability of the different anchoring groups that these dyes can form with the surface, one should rely on Molecular Dynamics (MD) simulations for all possible bidentate/tridentate and CN/COO<sup>-</sup>-based bonds conformations. However, since this type of analysis has been already established for other organic dyes bearing similar anchoring groups,<sup>56</sup> these stability issues are out of the scope of the present paper. Interestingly, the transition density matrix analysis of the isolated **ARM242** revealed a high electron delocalization around the N atom of the CN moiety (4%) compared with the O atoms of the COOH group (2.8 and 0.6%), suggesting a strong coupling between the dye's LUMO and the TiO<sub>2</sub> CB edge states for both **ARM12-CN** and **ARM242-CN** (see Figures S16 and S17). On the top of that, the anchoring geometries achieved with CN/COO<sup>-</sup> moieties clearly enhance the electron injection due to a higher conjugation between the  $\pi$ -electrons of the dye and the surface, if one compares with the bent geometries displayed by the bidentate COO<sup>-</sup> binding modes, (see the comparison between Figures 11 and S18). As a result, the calculated injection probability,  $\Gamma_{inj}$ , over the TiO<sub>2</sub> CB states is always higher with respect to the one calculated for both **ARM242** and **ARM12** in the COO<sup>-</sup> bidentate configurations (Figure S19). Notably, such an improvement in the electron injection rates driven by the formation of CN-based bonds has been already observed for other dyes containing CA anchoring groups.<sup>56</sup> It is noteworthy to emphasize that the two considered systems correspond to the extreme scenario where only one type of anchoring group is formed, whereas in the experimental conditions both binding modes probably exist. Nonetheless, our calculations provided an interval for the injection probability values  $\Gamma_{inj}$  achieved by **ARM242/ARM12** which, indeed, systematically underperformed those ones calculated for **ARM13/C1**. To sum up, based on the results of our atomistic

simulations, we can conclude that the measured photocurrents come from a balance between the notable improvement of the light harvesting properties (Figure 10) and the detrimental lowering of the driving force for electron injection, with a different extent depending on the type of binding mode formed with the TiO<sub>2</sub> surface.

## 4. Conclusions

Two new Fe(II) pyridylNHC sensitizers **ARM242** and **ARM12** bearing respectively one and two thienylcyanoacrylic anchoring groups (ThCA) have been prepared with the aim of promoting the metal to surface charge separation and the light harvesting window in iron-sensitized solar cells (FeSSCs). The complexes have been fully characterized in both solution and chemisorbed on titanium dioxide photoanodes by means of electrochemistry, transient absorption spectroscopy and TD-DFT calculations. Charge injection resulted in extremely long-lived charge separated states on TiO<sub>2</sub> photoanodes which could be used to intercept with nearly quantitative efficiency the redox couple. The introduction of the ThCA moiety remarkably improved the photocurrent by comparison with the carboxylic analogue (**C1**) thanks to the unprecedented extension of the spectral sensitization for the case of Fe(II) sensitizers. The use of a co-sensitizing mixture of a carboxylic and a ThCA-iron complex (**C1+ARM12**) produced a panchromatic absorption covering intensely the 450-700 nm range and extending up to 800 nm. The co-sensitization allowed to further improve the photocurrent and efficiency of the FeSSC ( $J_{sc}$ : 9 mA.cm<sup>-2</sup>, PCE: 2%) to the best values reported so far. At this time, however, it has been impossible to obtain both reasonably high current density and high photovoltage which can only be obtained by using basic additives to shift the Fermi level of TiO<sub>2</sub>. A comparative ultrafast investigation to address the role of the electrolyte's composition on the excited state dynamics of these Fe(II) sensitizers grafted on TiO<sub>2</sub> and ZrO<sub>2</sub> semiconductors is currently in progress.

## Author Contributions

A.R.M performed the synthesis and ground state characterizations of ligands and complexes. E.M. assembled the DSSCs, characterized them and analysed the results with S.C. V.D.-C. performed DFT calculations and analysed the results with M.P. P.C.G. conceived the project and wrote the manuscript with S.C. and M.P.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The L2CM thanks the French Agence Nationale de Recherche (ANR-16-CE07-0013-02), Lorraine Université d'Excellence (IMPACT N4S) and the European Regional Development Funds (Programme opérationnel FEDER-FSE Lorraine et

Massif des Vosges 2014-2020/"Fire Light" project: "Photo-bio-active molecules and nanoparticles" for financial support and grants to A.R.M. The L2CM laboratory is also grateful to F. Dupire for mass spectrometry of the complexes. University of Ferrara acknowledges financial support from Emilia Romagna Region. The LPCT thanks the European Regional Development Funds (Programme opérationnel FEDER-FSE Lorraine et Massif des Vosges 2014-2020/ COMETE (COncEption in silico de Matériaux pour l'Environnement et l'Energie) and Fire Light projects for financial support to V. D-C.

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