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### Introduction

Dye sensitized solar cells (DSSCs)<sup>1</sup> are hybrid nanostructured organic/inorganic cells that have attracted great attention so far from both the academic field and industry, due to the use of abundant, cheap materials and simple, low cost fabrication processes that can be applied to both rigid (glass) and flexible (plastics, metals) substrates<sup>2</sup> and easily scaled up.<sup>3</sup>

In its simplest assembly, a DSSC is an electrochemical cell with two electrodes and an electrolyte filled in the space between them. The highest efficiency reported for a small area DSSC based on ruthenium dye and an iodide/triiodide electrolyte

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# Triarylamine-based hydrido-carboxylate rhenium(ı) complexes as photosensitizers for dye-sensitized solar cells†

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Two new dyes based on a dinuclear rhenium complex and (E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (namely D35) have been investigated as sensitizers for dye sensitized solar cells (DSSCs). Two different pyridazine ligands have been used, namely 4-pyridazinecarboxylic acid for dye 2 ( $[Re_2(\mu-H)(-D35)(CO)_6(\mu-pyridazine-4-COOH)]$ ) and 4-pyridazinyl-butanoic acid for dye 3 ( $[\text{Re}_2(\mu-H)(-D35)(\text{CO})_6(\mu-pyridazine-4-C_3H_6-\text{COOH})]$ ). The performances of these new dyes have been compared with those of the dye containing the bare 4-diphenylaminobenzoic acid, namely TPA, as the ancillary ligand (dye 1). Compared to dye 1, dyes 2 and 3 show an impressive tenfold increase in the absorption intensity in the range of 487–493 nm on TiO<sub>2</sub> films, with great improvement of the light harvesting. Cyclic voltammetry experiments, performed on derivatives containing the methyl ester of the pyridazine ligands, show narrow electrochemical band gaps in the range of 1.36–1.84 eV. Solar cells with each dye have been prepared, using both iodide/triiodide and cobalt redox couples as the electrolytes, platinum or carbon as the counter electrodes, and  $TiO_2$  or  $SnO_2$  as the metal oxide photoelectrodes, respectively. The best DSSC results have been obtained using dye 3, with an overall solar-to-electric conversion efficiency of 3.5%, which greatly overcomes the previous result of 1.0% obtained for dye 1 in a not-optimized setup of the device. The performances of dye 3 are due to the presence of D35 ligand, which further suppresses the recombination of the injected electron with the electrolyte and with the oxidized state of the dye.

is 12.1%<sup>4</sup> with long-term stability,<sup>5</sup> while an efficiency as high as 13% was achieved using a molecularly engineered porphyrin dye in combination with a cobalt-based electrolyte.<sup>6</sup>

The most commonly used dyes in DSSCs are complexes of ruthenium, containing organic ligands functionalized with carboxylic substituents as anchoring groups to the TiO2.<sup>7</sup> These poly-pyridine complexes are characterized by intense and broad absorption bands due to metal-to-ligand charge transfer (MLCT) transitions, longer excited state lifetimes, and longterm chemical stability.8 Alternative dyes based on different metal complexes, such as iron,<sup>9</sup> copper<sup>10</sup> and platinum<sup>11</sup> mainly containing bipyridine ligands, have been investigated so far,<sup>12</sup> while no example of rhenium complexes used as a dye in operating solar cells has been reported in the literature. In order to cover this gap and following some preliminary studies concerning the electron transfer from Re-polypyridyl complexes to nano-crystalline  $TiO_2$ ,<sup>13</sup> we recently reported the first example of hydrido rhenium complexes employed in an operating DSSC.<sup>14</sup> The best results have been obtained for the hydridocarboxylato complex containing a triarylamine moiety (1, see Chart 1), which suppresses the recombination of the injected electron with the oxidized state of the complex, thus improving



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the charge separation on  $\text{TiO}_2$ . Moreover, the bulky triarylamine moiety also reduces the back reaction of the injected electron with the electrolyte. Even if the maximum power conversion efficiency is about 1%, these results have provided a sufficiently clear picture of the critical factors and of the lines to follow to improve the performances.

Therefore, in order to follow these lines, we report here on the design and preparation, based on a novel and versatile three-step procedure, of two new hydrido-carboxylate dinuclear organometallic rhenium complexes, namely 2 and 3 (see Chart 1) with the more conjugated TPA linker (E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid a.k.a. DN-F04 dye (from now on D35, see Chart 1). Interest in organic molecules, characterized by a D- $\pi$ -A electronic structure, as dyes in DSSCs has been growing quickly in the past decade, due to their unlimited availability from feedstock, improved prerequisites for scalability, recycling issues and economy on a large scale. The absorption spectrum of D35 makes it a reference organic dye for DSSCs. Excellent device stability has been obtained both under light and after at least 1000 h of storage in the dark at a temperature of 85 °C.<sup>15,16</sup> It is also interesting for indoor applications due to its good match with fluorescent light and its attractive orange color. Therefore, we linked D35 as a bridging ligand to the dinuclear rhenium complexes, to extend the light harvesting capacity and to allow their usage in cobalt-based electrolytes.

Looking at the anchoring group, one of the reasons for the observed low efficiency of the previously reported complexes is the excessive stabilization of the  $\pi^*$  orbitals of the 4-carboxy-pyridazine, which partially hampers the electron injection into TiO<sub>2</sub>.<sup>14</sup> In order to overcome this problem, we report here a new dye (3 in Chart 1) containing a diazine ligand endowed with an alkyl chain. In fact, the presence of electron-donor substituents in the  $\beta$  positions of the diazine ligand raises the LUMO level of the dye<sup>17</sup> and then fosters the electron injection into the semiconductor.

These new dyes have been characterized from the spectroscopic and electrochemical points of view. Solar cells with each dye have been prepared and their performances have also been reported, using both iodide/triiodide and cobalt redox couples as the electrolytes, platinum or carbon as the counter electrodes, and  $TiO_2$  (and partially  $SnO_2$ ) as the metal oxide photoelectrode. The performances have been compared to those obtained for **D35** and discussed in relation to the molecular structure of the dyes and the previous results obtained for dye **1** in a notoptimized setup of the device.

### Results and discussion

#### Synthesis of the dyes

The hydrido-carboxylato derivatives 2 and 3 have been prepared by exploiting the same three-step synthetic procedure already developed for the synthesis of the TPA-based derivative 1.<sup>14</sup> This procedure, shown in Scheme 1, is based on the peculiar reactivity of the tetrahedral hydrido-carbonyl cluster  $[Re_4(\mu_3-H)_4(CO)_{12}]$  with bridging donor ligands such as 2,5-diphenyl-1,3,4-oxadiazole (ppd), a sterically hindered heterocycle which contains two aromatic substituents in the  $\alpha$  positions of the oxadiazole ring.<sup>18</sup> In the first step, the  $[Re_2(\mu-H)_2(CO)_6(\mu-ppd)]$  intermediate has been obtained in high yields by reacting  $[Re_4(\mu_3-H)_4(CO)_{12}]$  with two equivalents of ppd at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>18</sup> Then, the mixed hydridocarboxylato complexes [Re<sub>2</sub>(µ-H)(µ-OOCR)(CO)<sub>6</sub>(µ-ppd)] (Scheme 1) have been obtained by reaction (1), which exploits the reactivity of the hydride ligands towards the acidic proton of any carboxylic acid. Through a simple acid-base reaction, one of the two hydrides is removed as H<sub>2</sub> and the carboxylate anion takes its place, bridging the two metal centers.<sup>14,19</sup> Three different carboxylic acids have been used for the synthesis of the dyes and, in particular, 4(diphenylamino)benzoic acid



Scheme 1 Synthetic pathways for the preparation of the rhenium hydrido-carboxylato dyes 1-3

(TPA-COOH) for dye 1 and the carboxylic acid of D35 for dyes 2 and 3.

$$[\text{Re}_{2}(\mu-\text{H})(\mu-\text{OOCR})(\text{CO})_{6}(\mu-\text{ppd})] + \text{RCOOH} [\text{Re}_{2}(\mu-\text{H})(\mu-\text{OOCR})(\text{CO})_{6}(\mu-\text{ppd})] + \text{H}_{2}$$
(1)

Finally, substitution of the oxadiazole with properly functionalized diazine ligands (namely the pyridazinyl-carboxylic acid for dyes **1** and **2** and the pyridazinyl-4-butanoic acid for dye **3**, respectively) afforded the desired products.

#### **Electrochemical characterization**

Cyclic voltammetry analysis has been performed on all the derivatives **1-COOMe**, **2-COOMe** and **3-COOMe** containing the methyl ester of the corresponding diazine ligand, in order to avoid the reduction of the acidic proton and  $H_2$  evolution. The cyclic voltammetry behavior in acetonitrile, at 298 K, is shown in Fig. 1 and the peak potentials, together with the related HOMO and LUMO energy values, are reported in Table 1. In the cathodic region, dye 2, containing the same diazine ligand of 1, displays the same behavior as that reported previously: namely one monoelectronic reduction peak at about -0.9 V (*vs.* Fc<sup>+</sup>|Fc),

which is centered on the diazine ligand and whose chemical reversibility is confirmed by the presence of its anodic counterpart. In contrast, for dye 3, the reduction peak is observed at -1.47 V, *i.e.* at the same reduction potential of the complex  $[\text{Re}_2(\mu\text{-Cl})_2(\text{CO})_6(\mu\text{-}4\text{-}n\text{-hexylpydz})] (-1.46 V)^{20}$  containing a pyridazine ligand functionalized at one of the  $\beta$  positions with a similar aliphatic chain. Also, in this case, the reduction is chemically and electrochemically reversible. It is interesting to note that the peak potential is slightly modulated by the different nature of the ancillary ligand, in agreement with the different localization of the ground-state energy levels.

All these features are in agreement with the localization of the reduction process on the diazine ring, as also indicated by the description of the LUMO provided by the DFT computations.<sup>17,20</sup> Therefore, the LUMO level results stabilized, and partially delocalized, due to the presence of the carboxylic group at the  $\beta$  position, as in the dyes **1** and **2**. On the other hand, a partial destabilization of the LUMO is observed in the presence of the electron-donor alkyl chain, as in the case of **3**.

In the anodic part, dyes 1–3 display a close sequence of three monoelectronic oxidation peaks. The two oxidation processes, observed at the highest potentials, are clearly localized on the metal core. This attribution is confirmed both by the computational analysis and by comparison with the electrochemical



Fig. 1 Normalized CV features of the methyl–ester derivatives of dyes  $\rm 1-3$  on GC electrodes, in ACN + 0.1 M TBAPF\_6 solution, at 0.2 V s^{-1} with ohmic drop compensation.

behavior already observed in the derivatives containing alcoholate, phenolate<sup>21</sup> and benzoate<sup>14</sup> anions as ancillary ligands. Moreover, these oxidation potentials are lower for dyes 2 and 3 than for dye 1 (+0.75 V vs. +1.07, see Table 1), and this is due to the presence of the strong electron-withdrawing acrylonitrile moiety bound to the coordinating carboxylate group. These data still confirm that the oxidation process is markedly different in the case of the oxygen-bridged derivatives compared to that observed for halide<sup>17</sup> or chalcogenide ones.<sup>22</sup> This behaviour could be related to the hard–soft nature of the bridging ancillary ligands. Indeed, the softer halides or chalcogenides anions can better stabilize the cationic products, favoring the simultaneous loss of two electrons instead of two mono-electronic oxidations, as observed in the case of the harder oxygen-based anions.

Besides the two oxidation peaks centered on the metal core, another chemically reversible oxidation peak at a lower

potential is observed (see Table 1 and Fig. 1). This peak is clearly attributed to the formation of a radical cation on the triarylamine (TPA) moiety, as indicated by the comparison with the electrochemical behavior of the free 4-diphenylaminobenzoic acid  $(E_{p,a} = 0.70 \text{ V})^{14}$  and by the modulation of the peak potential by the substituents on the TPA core. Indeed, dyes 2 and 3, containing a more conjugated TPA moiety, display a lower oxidation potential than dye 1 (+0.66 V *vs.* +0.41 V, see Table 1).

#### Spectroscopic characterization

The UV-Vis absorption maxima and molar absorptivities are reported in Table 2 both in solution and upon adsorption on  $TiO_2$ , while Fig. 2 shows all the spectra in toluene solution. In solution, all the dyes exhibit two broad and featureless absorption bands extending in a conspicuous part of the visible spectrum between 300 nm and 600 nm.

The low energy absorption band is ascribable to the metalto-ligand  $d\pi(\text{Re}) \rightarrow \pi(\text{diazine})$  charge transfer transition (<sup>1</sup>MLCT), in agreement with the DFT computations and by comparison with the analogous complexes of this family.<sup>17</sup> This broad MLCT band arises from the convolution of multiple transitions, as testified by the more-or-less pronounced shoulders observed at longer wavelengths. This attribution is supported by their solvatochromic behavior and by the presence of the predicted red-shift in the absorption maximum for the D35-based dyes 2 and 3, compared to the bare TPA-based dye 1. In addition, dyes 2 and 3 show an impressive tenfold increase in the value of  $\varepsilon$  compared to 1, therefore, greatly improving the light harvesting. This is due to a partial superposition between the MLCT band and the absorption band of the D35 ligand, which displays an absorption band at 500 nm in CH<sub>2</sub>Cl<sub>2</sub> solution with a high molar extinction coefficient  $(31\,300\,\text{M}^{-1}\,\text{cm}^{-1})$ .<sup>16</sup>

All the dyes also display another higher energy absorption band around 335–350 nm, whose position is completely independent of the polarity of the solvent. In agreement with the electrochemical and computational data already reported for

Table 2  $\;$  UV-Vis MLCT absorption data of the dyes in solution and on  $\text{TiO}_2$  films

Complex	$\lambda_{\max}^{a}/nm$	$\varepsilon/M^{-1} \mathrm{~cm}^{-1}$	$\lambda_{\max}^{b}/nm$	$\lambda_{\max}^{c}/nm$
1	483	$5.2 imes10^3$	425	443
2	493	$3.1 imes10^4$	486	487
3	486	$3.5 imes10^4$	487	493

 $^a$  Toluene solution (2  $\times$  10 $^{-5}$  M).  $^b$  EtOH solution (2  $\times$  10 $^{-5}$  M).  $^c$  TiO<sub>2</sub> film. Absorption data for D35: 31 300 M<sup>-1</sup> cm<sup>-1</sup> at 500 nm.

**Table 1** The first reduction and oxidation peak potentials  $(E_{p,c} \text{ and } E_{p,a})$  and electrochemical  $(\Delta E_e)$  and spectroscopic  $(\Delta E_S)^a$  energy gaps of the dyes. Potentials are referred to the Fc<sup>+</sup>|Fc couple<sup>b</sup> in the operating medium (ACN, 0.1 M TBAPF<sub>6</sub>). Scan rate: 0.2 V s<sup>-1</sup>

Complex	$E_{\rm p,c} \left[ {\rm V} \right]$	$E_{\rm p,a} \left[ {\rm V}  ight]$	$\Delta E_{\rm e}  [{\rm eV}]$	$\Delta E_{\rm s}  [{\rm eV}]$	$E_{\rm LUMO} [eV]$	$E_{\mathrm{HOMO}}\left[\mathrm{eV}\right]$
1-COOMe	-0.97	0.66, 1.07, 1.32	1.64	2.56	-3.81	-5.45
2-COOMe	-0.94	0.41, 0.74, 1.10	1.36	2.52	-3.85	-5.21
3-COOMe	-1.42	0.42, 0.75, 1.10	1.84	2.55	-3.37	-5.21

<sup>*a*</sup> The spectroscopic ( $\Delta E_s$ ) energy gap is the energy associated with the electronic transition determined from the maximum of the <sup>1</sup>MLCT absorption band. <sup>*b*</sup> Fc<sup>+</sup>|Fc potential is 0.385 V vs. SCE in ACN solution.





dye 1,<sup>14</sup> this band is attributed to the  $\pi$ - $\pi$ \* transition involving the triarylamine moiety. Noticeably, for dves 2 and 3, containing the more conjugated D35 ligand, this band is moderately blue-shifted, as a consequence of the presence of two butoxyphenyl electron donating units on the TPA moiety of D35.

#### Devices

Photovoltaic measurements have been carried out to evaluate the potential of the new rhenium complexes as dyes in DSSC devices. The main photovoltaic parameter performances of the solar cells under AM 1.5 G at 1 sun (1000 W m<sup>2</sup>) illumination are presented in Table 3 and the current-voltage (J-V) curves are displayed in Fig. 3.

Sets of cells have been prepared and measured, changing one parameter at a time, in order to find the best operating conditions for each of these parameters. Dye 1, already tested in an optimized device,<sup>14</sup> has also been re-tested after the engineering of optimized cells. In particular, different semiconductor oxides (TiO<sub>2</sub>, SnO<sub>2</sub>)<sup>23</sup> have been tried in single or stackedlayer architecture, along with their relative thickness. The dyes were adsorbed on the semiconductors in different media to find out the best solvent and the adsorption time. At the same time, various counter electrode glasses with different sheet resistances have been tested with our dyes. The nature of the electrolytes has also been intensively investigated and the behavior of each dye has been tested in two different types of

Table 3 Photovoltaic parameters for optimized and solid-state cells sensitized by 1-3 compared to D35 using homemade iodine based (IE) and cobalt (CE) electrolytes

CELL	$J_{ m SC}/ m mA~cm^{-2}$	$V_{\rm OC}/{ m V}$	FF	η/%
1 IE/Pt	-4.5	0.51	78	1.8
1 CE/C	-1.4	0.47	72	0.5
1 SSD	-0.5	0.52	57	0.15
2 IE/Pt	-7.9	0.52	51	2.05
2  CE/C	-9.1	0.54	64	3.0
2 SSD	-0.4	0.46	53	0.35
3 IE/Pt	-8.8	0.54	67	3.15
3 CE/C	-7.6	0.65	71	3.5
3 SSD	-1.1	0.48	63	0.32
D35 CE/C	-11	0.88	72	7



Fig. 3 Current-voltage curves for the optimized devices sensitized by rhenium-based dyes 1-3 under 1 Sun illumination, AM 1.5.

electrolyte: one based on the iodide/triiodide redox shuttle, and the other employing  $Co^{2+/3+}$  metal complexes. Each electrolyte has been coupled with a suitable counter electrode: platinum for iodine and carbon for cobalt. Both the electrolytes have been developed in-house, the first one was labeled IE and the latter one CE.

The compositions of both iodine-based and cobalt-based electrolytes have been varied to obtain the best current-voltage compromise. We have used cells with pure D35 as photosensitizers as a reference for this comparison. Solid-state devices (SSDs) have also been prepared to investigate if these dyes may hold potential for this kind of devices. However, the generally low efficiencies detected prevented us from carrying out further investigations.

The values related to the performances of the cells, reported in Table 3, clearly indicate that a careful engineering of the cells has afforded a new maximum performance of 1.8% for dye 1, nearly doubling the previous value obtained for such a dye.<sup>14</sup>

A substantial increase in the photogenerated currents can be observed (see Table 3) for dyes 2 and 3 compared to dye 1, due to the presence of the highly light-absorbing D35 moiety. This is also confirmed by the incident photon-to-current conversion efficiency (IPCE) plots. Indeed, the monochromatic IPCE spectra, displayed in Fig. 4, show that the highest IPCE is obtained



Fig. 4 IPCE spectra for optimized devices sensitized by rhenium-based dyes 1-3

from the solar cell sensitized by 3 which, however, is not as red as 2.

Due to the introduction of D35, the new dyes appear to work best under CE/C conditions, while dye 1, with a simple triarylamine remains more efficient under the IE/Pt condition. The performances of dye 2 is only slightly better than those of 1 under IE conditions, affording 2%, while, under CE conditions, a value of 3% in efficiency can be achieved. The best performing cells are sensitized by dye 3, giving an overall power conversion efficiency of 3.15% (IE) and 3.5% (CE). The recombination between the electrons in TiO<sub>2</sub> and the oxidized dye or between the electrons in TiO<sub>2</sub> and the electrolyte are crucial factors for the performances of the cells. Introduction of the D35 moiety in dyes 2 and 3 clearly contributes to further suppression of the former recombination, thus improving the charge separation on TiO<sub>2</sub>. Moreover, the higher steric hindrance of D35 also reduces the back reaction between the injected electron and the electrolyte. The recombination process with the oxidized dye is further suppressed in dye 3, in which the presence of the less electron-withdrawing diazine affords a gain both in  $J_{SC}$  and  $V_{OC}$ , leading to an efficiency of 3.5%. Indeed, by replacing the direct carboxylic moiety with the 4-butanoic acid derivative, the electron injection into the conduction band of TiO<sub>2</sub> becomes retarded, as proved by Durrant, et al.,<sup>24</sup> to minimize the kinetic redundancy. This adjustment prolongs the electron lifetime in the photoelectrode before recombining with the oxidized dye and/or cation in the electrolyte.

The external efficiency values, however, remain well below those obtained under similar conditions by cells assembled using the conventional **D35** dye, reaching 7% (CE).

Even though dyes 2 and 3 have a similar or even wider light absorption compared to D35, this superior property is not reflected in the device efficiency. This is the case for dye 2 that has the smallest energy gap (see Table 1). Dye 2 can harvest the photons the most among the tested dyes. However, due to several reasons (discussed below), dye 2 did not show the best properties, even for photocurrent. This can be explained by the desorption of the dye and it is also confirmed by electrochemical impedance spectroscopy (EIS) results.

From the analysis after electrochemical impedance spectroscopy, it was found that the charge transfer resistance at the counter electrode for dye 2 is higher than that for other samples (data not shown). This implies the desorption of dye 2 from the surface of TiO<sub>2</sub> and then, their adsorption on the surface of the counter electrode. Such phenomena can explain one of the reasons for the lower fill factor for the sample with dye 2. Moreover, the desorption of dye molecules from the surface of TiO<sub>2</sub> causes a negative influence on the solar cell properties, such as reduction in light harvesting and an increase of the TiO<sub>2</sub> surface area that is exposed to the electrolyte (Fig. 5).

Together with the desorption of the dye, the presence of considerable amounts of  $Li^+$  in the electrolyte should also be taken into account. Indeed, the presence of  $Li^+$  shifts the



Fig. 5 Left: Resistance vs. potential (solid curves:  $R_{ct}$ ; solid straight lines:  $R_{trans}$ : dotted curves: C) and right: electron lifetimes vs. capacitance (solid lines: lifetime; dotted lines: transport time) plots for devices sensitized by dyes **1** (orange line), **2** (brown line) and **3** (red line) under IE/Pt conditions.



Fig. 6 Left: Resistance vs. potential (solid line:  $R_{ct}$ ; dotted line: C) and right: electron lifetimes vs. capacitance plots for devices sensitized by dyes 1 (orange line), 2 (brown line) and 3 (red line) under CE/C conditions.

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conduction band of TiO<sub>2</sub> more for devices with Co as the electrolyte than those with iodide. This feature also affects the open current voltage ( $V_{OC}$ ) which is calculated by the difference between the Fermi level of the TiO<sub>2</sub> and the redox potential of the electrolyte. For the cells with the Co redox couple, the  $V_{OC}$  increases on going from 1 to 3 and the difference in the  $V_{OC}$  of the cells with iodide is the smallest for complex 2. This is in agreement with the desorption of dye 2, which leaves a larger surface area exposed to the electrolyte allowing, therefore, the Li<sup>+</sup> to come to the surface of TiO<sub>2</sub>. The lowering of the conduction band of TiO<sub>2</sub> for the sample with dye 2 improves the electron lifetimes since the driving force between the conduction band of TiO<sub>2</sub> and the electrolyte is reduced and hence the transport efficiency, which are the best for dye 2.

In the case of the cobalt-based electrolyte, the EIS shows a similar tendency (Fig. 6). The conduction band of **2** is once again the lowest among all the complexes, while **3** exhibits a slightly higher one compared to **1**, as expected after the introduction of a non-conjugated chain. The lifetimes are, in the case of the cobalt electrolytes, relatively similar between the three different dyes, but also in this case, complex **2** shows the longest one.

### Conclusions

In our previous work, quantomechanical calculations using density functional theory (DFT) and time-dependent density functional theory (TDDFT) have been coupled with UV/vis absorption spectroscopy and preliminary photovoltaic device testing. Based on these results, herein we have designed and synthesized new dirhenium complexed dyes. We have analyzed their electronic/optical properties and characterized the nature of their interaction with the TiO<sub>2</sub> substrate. Dye-sensitized solar cells were prepared and tested in operating solar cells. Light-tocurrent conversion, which greatly overcomes the previous result of 1.0% obtained for dye 1 in a not-optimized setup of the device, has been observed for all the dyes here investigated. These interesting results are mainly due to the introduction of the triarylamine-based D35 as a carboxylate ligand, which further suppresses the recombination of the injected electron with the oxidized state of the dye. This wider light-harvesting and bulkier triarylamine moiety also reduces the back-reaction of the injected electron with the electrolyte. The best results have been obtained for the hydrido-carboxylato dye 3, with a power conversion efficiency of 3.5%. This feature resulted by combining molecular design with optimization of the cell. Indeed, the problems concerning the lower efficiency of the other two dyes, 1 and 2, have been represented by the excessive stabilization of the  $\pi^*$  orbitals of the diazine and by the desorption of the dye. These critical factors have been overcome by the use of a more electron-rich diazine ligand, contained in dye 3, which provides a higher LUMO level and a better anchoring group on the TiO<sub>2</sub> surface. In summary, the presence of the bulkier triphenylamine moiety and the use of a more electronrich ligand successfully improved the photovoltaic efficiency due to the reduced recombination and an optimization of the kinetic retardation. However, there are still challenges, such as dyeaggregation, thus requiring further tuning of the HOMO–LUMO energy level for realizing high-efficiency dye-sensitized solar cells.

As the last notable point, the three-step synthetic procedure developed here has a wider scope than the preparation procedure for the compounds described here and opens the way for a large number of dinuclear complexes of this family, tailored for specific applications.

### Experimental

#### Materials and methods

All the reactions are performed under a nitrogen atmosphere unless specified otherwise. The reagents are purchased from Aldrich, Fluka and Lancaster and used as received. D35 is purchased from Dyenamo, washed with H<sub>2</sub>O and then dried under vacuum before use. All the solvents are deoxygenated and dried by standard methods before use; toluene is distilled on Na(s) and CH<sub>2</sub>Cl<sub>2</sub> on P<sub>2</sub>O<sub>5</sub>, both under a N<sub>2</sub> atmosphere. Commercial deuterated solvents are used as received. Column chromatography is performed using Alfa Aesar silica gel 60  $(0.032-0.063 \text{ mm}). [\text{Re}_4(\mu_3-\text{H})_4(\text{CO})_{12}](\text{C}_6\text{H}_6)_2, ^{25} [\text{Re}_2(\mu-\text{H})_2(\text{CO})_6 (\mu$ -ppd)] (ppd = 2,5-diphenyl-1,3,4-oxadiazole)<sup>18</sup> and  $[Re_2(\mu-H) (\mu$ -4-OOC-TPA)(CO)<sub>6</sub>( $\mu$ -pydz-4-COOH)] (1) (4-OOC-TPA = 4-(diphenylamino)benzoate anion pydz-4-COOH = pyridazine-4-carboxylic acid)14 are synthesized according to literature procedures. The IR spectra in solution are acquired using a Bruker Vector 22 FT spectrophotometer. The solution and thin-film UV/Vis absorption spectra are obtained using an Agilent 8453 spectrophotometer, fused quartz cuvettes (10 mm optical path), and CHROMASOL V grade solvents.

#### Synthesis

Synthesis of [Re2(µ-H)(µ-D35)(CO)6(µ-ppd)]. 40 mg (0.046 mmol) of solid D35 are added to a solution of 32 mg (0.042 mmol) of  $[\operatorname{Re}_2(\mu-H)_2(\operatorname{CO})_6(\mu-ppd)]$  previously dissolved in 5 mL of anhydrous toluene. The reaction mixture is left stirring under reflux overnight; then, the solution is evaporated to dryness under vacuum. The obtained solid is purified by column chromatography (eluent  $CH_2Cl_2$ /hexane 75:25), then dried under vacuum, yielding 30 mg (0.018 mmol) of a brick-red powder (yield 44%). IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO): 2042 (s), 2024 (vs), 1937 (vs), 1917 (s) cm  $^{-1}$ .  $^1\mathrm{H}$  NMR: (CD\_2Cl\_2, 300 K, 400 MHz)  $\delta_{\rm H}$  (ppm) 8.18 (d, J = 7.5 Hz, 4H, H<sub>ortho</sub> ppd), 7.90 (m, 2H, H<sub>para</sub> ppd), 7.79 (m, 4H, H<sub>meta</sub> ppd), 8.16 (s, 1H), 7.75 (d, J = 4.2 Hz, 1H), 7.60 (d, J = 8.88 Hz, 2H), 7.52 (d, J = 8.47 Hz, 4H), 7.37 (d, J = 4.2 Hz, 2H), 7.29 (d, J = 9.3 Hz, 2H), 7.21 (d, J = 8.47 Hz, 4H), 7.17 (d, J = 8.88 Hz, 2H), 6.59 (s, 2H), 6.58 (m, 2H), 4.02 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 4.01 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 1.79 (m, 8H, CH<sub>2</sub>) 1.57 (m, 4H, CH<sub>2</sub>), 1.50 (m, 4H, CH<sub>2</sub>), 1.03 (m, 6H, CH<sub>3</sub>), 0.97 (m, 6H, CH<sub>3</sub>), -7.14 (s, 1H, hydride). Elemental anal. calcd for C<sub>74</sub>H<sub>68</sub>N<sub>4</sub>O<sub>12</sub>SRe<sub>2</sub>: C, 54.67; H, 4.22; N, 3.45. Found: C 55.31, H 4.83, N 3.27.

Synthesis of  $[\text{Re}_2(\mu-H)(\mu-D35)(\text{CO})_6(\mu-\text{pydz-4-COOH})]$  (2). Once 15 mg (0.009 mmol) of  $[\text{Re}_2(\mu-H)(\mu-D35)(\text{CO})_6(\mu-\text{ppd})]$  are dissolved in 5 mL of freshly distilled and degassed THF, 1.5 mg (0.01 mmol) of 4-pyridazine-carboxylic acid are added to the reaction mixture. The reaction is set at 85 °C for 2 hours. The solution is evaporated to dryness under vacuum and the crude product dissolved in CH<sub>2</sub>Cl<sub>2</sub> and re-precipitated with n-hexane. The supernatant solution is removed and the remaining powder is washed with hexane (3 mL) five times and dried under vacuum affording 11 mg (0.072 mmol) of the desired product (yield 80%). IR (CH<sub>2</sub>Cl<sub>2</sub>) v(CO): 2040 (m), 2020 (s), 1938 (s), 1920 (m) cm<sup>-1</sup>, <sup>1</sup>H NMR: (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, 400 MHz)  $\delta_{\rm H}$  (ppm) 9.75 (s, 1H,  $H_{3pydz-4-COOH}$ ), 9.51 (d, J = 5.6 Hz, 1H,  $H_{6pydz-4-COOH}$ ), 8.39 (dd, J = 4.7, 2.9 Hz, 1H, H<sub>5pydz-4-COOH</sub>), 8.13 (s, 1H), 7.73 (m, 1H), 7.62 (m, 2H), 7.51 (m, 4H), 7.36 (m, 2H), 7.27 (m, 2H), 7.22 (m, 4H), 7.18 (m, 2H), 6.59 (s, 2H), 6.57 (m, 2H), 4.02 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 4.01 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 1.79 (m, 8H, CH<sub>2</sub>) 1.53 (m, 4H, CH<sub>2</sub>), 1.49 (m, 4H, CH<sub>2</sub>), 1.03 (t, J = 7.4 Hz, 6H, CH<sub>3</sub>), 0.97 (t, J = 7.4 Hz, 6H, CH<sub>3</sub>), -6.75 (s, 1H, hydride). Elemental anal. calcd for C<sub>65</sub>H<sub>62</sub>N<sub>4</sub>O<sub>14</sub>SRe<sub>2</sub>: C, 51.10; H, 4.09; N, 3.67. Found: C 52.09, H 4.42, N 3.19.

Synthesis of  $[Re_2(\mu-H)(\mu-D35)(CO)_6(\mu-4-pyridazinyl-butanoic$ acid)] (3). 15 mg (0.009 mmol) of [Re<sub>2</sub>(µ-H)(µ-D35)(CO)<sub>6</sub>(µ-ppd)] are dissolved in 5 mL of freshly distilled and degassed THF; 2 mg (0.012 mmol) of 4-pyridazinyl-butanoic acid are added to the reaction mixture. The reaction is maintained under reflux for 2 hours. The solution is evaporated to dryness under vacuum, the crude product dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and re-precipitated with *n*-hexane. The supernatant solution is removed and the remaining powder is washed with hexane (3 mL) five times, then dried under vacuum affording 11 mg (0.007 mmol) of a red powder (yield 78%). IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO): 2042 (m), 2024 (s), 1943 (s), 1921 (m) cm<sup>-1</sup>, <sup>1</sup>H NMR: (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, 400 MHz)  $\delta_{\rm H}$  (ppm) 9.22 (d, J = 5.9 Hz, 2H, H<sub>64-pydz-BuCOOH</sub>), 9.21 (d, J = 5.9 Hz, 2H, H<sub>34-pydz-BuCOOH</sub>), 8.12 (s, 1H), 7.78 (d, *J* = 2.0 Hz, 1H, H<sub>54-pydz-BuCOOH</sub>), 7.74 (d, J = 4.1 Hz, 1H), 7.60 (d, J = 8.88 Hz, 2H), 7.52 (d, J = 8.6 Hz, 4H), 7.36 (d, J = 4.1 Hz, 2H), 7.28 (m, 2H), 7.21 (d, J = 8.8 Hz, 4H), 7.17 (d, J = 7.4 Hz, 2H), 6.59 (s, 2H), 6.58 (d, J = 6.8 Hz, 2H), 4.02 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 4.01 (t, J = 6.98 Hz, 4H, CH<sub>2</sub>), 1.79 (m, 8H, CH<sub>2</sub>) 1.56 (m, 4H, CH<sub>2</sub>), 1.47 (m, 4H, CH<sub>2</sub>), 1.03 (m, 6H, CH<sub>3</sub>), 0.97 (m, 6H, CH<sub>3</sub>), -6.65 (s, 1H, hydride). Elemental anal. calcd for C68H68N4O14SRe2: C, 52.02; H, 4.37; N, 3.57. Found: C 53.64, H 4.95, N 3.10.

Synthesis of the methyl ester of pydz-4-COOMe and complexes (1-3)-COOMe. A sample of pyridazine-4-carboxylic acid (100 mg, 0.805 mmol) (for 1 and 2) or pyridazine-4-butanoic acid (134 mg, 0.805 mmol) (for 3) was dissolved in MeOH (2 mL) and was treated with H<sub>2</sub>SO<sub>4</sub> (40 mL, 96% w/w) at room temperature. The reaction mixture was heated at reflux temperature and was stirred overnight. Then, the solution was cooled at room temperature and the reaction was quenched by the addition of a saturated solution of Na<sub>2</sub>CO<sub>3</sub> up to pH 8. The product was extracted with Et<sub>2</sub>O and the organic fractions were collected, washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness to afford a pale yellow solid (isolated yield 30%). <sup>1</sup>H NMR (DMSO, 300 K, 400 MHz)  $\delta_{\rm H}$  (ppm) 9.58 (s, 1H, Hortho), 9.51 (d, 1H, Hortho), 8.09 (dd, 1H, Hmeta), 3.94 (s, 3H, CH<sub>3</sub>). This pyridazine was used to synthesize the corresponding derivatives 1-COOMe, 2-COOMe and 3-COOMe according to the previous procedures.

Electrochemical measurements. A cyclic voltammetry study of the complexes has been performed at scan rates typically ranging from 0.02 to 10 V s<sup>-1</sup> in HPLC-grade acetonitrile (MeCN) solutions at 2.5  $\times$  10<sup>-4</sup> M concentration for each substrate, deaerated by  $N_2$  bubbling with 0.1 M TBAPF<sub>6</sub> (TBA = NBu<sub>4</sub>, Aldrich) as the supporting electrolyte, at 298 K. The ohmic drop was compensated by the positive feedback technique. The experiments were carried out using an AUTOLAB PGSTAT potentiostat (EcoChemie, The Netherlands) run by a PC with a GPES software. The working electrode was a glassy carbon one (AMEL, diameter 1.5 mm) cleaned with diamond powder (Aldrich, diameter 1 mm) on a wet cloth (STRUERS DP-NAP); the counter electrode was a platinum wire; the reference electrode was an aqueous saturated calomel electrode, with a difference of 0.385 V vs. the Fc<sup>+</sup>|Fc couple (the intersolvent redox potential reference currently recommended by IUPAC) in our working medium.

DSSC and SSD preparation. The solution-processed and the solid-state devices were made using 18 NR-T and 30 NR-D titanium oxide (TiO<sub>2</sub>) paste, respectively, obtained from Dyesol. Lithium iodide (LiI), lithium bis(trifluoromethane)sulfonimide (LiTFSI), iodine, tert-butyl pyridine (TBP), and guanidinium thiocyanate (GuSCN) were purchased from Aldrich, and 2,2',7,7'tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) was obtained from Solaronix. [Co(bpy)<sub>3</sub>(B(CN)<sub>4</sub>)<sub>2</sub>] and  $[Co(bpy)_3(B(CN)_4)_3]$  were synthesized at EPFL. The homemade substrates for liquid-containing cells have a size of approximately 1.4 cm  $\times$  1.6 cm, with an active area of 0.159 cm<sup>2</sup>. The device structure consists of a transparent fluorine doped tin oxide (FTO) layer as the bottom electrode, supported on an NSG TEC C10 glass substrate. After being cleaned and having undergone UV-O3 treatment for 15 minutes, the FTO glass plates were immersed in a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 35 min and then washed with water and ethanol. Two screen-printed layers of nanocrystalline TiO<sub>2</sub> particles were used as the photoelectrode. The transparent mesoporous layer (tl), made of 18 nm sized  $TiO_2$ particles (Dyesol DSL18NR-T), was printed on the FTO conducting glass, and the plates were then heated at 150 °C for 7 min. To obtain a high PCE, an ~5 µm scattering layer (sl, 400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd (CCIC), HPW-400) was deposited on the transparent layer. A total film thickness of 7(tl) + 5(sl) µm was used. Sintering was carried out following a 4-step temperature ramp from 175 to 500 °C, with a residence time of 30 min. The sintered glass plates were immersed again in 20 mM aqueous TiCl<sub>4</sub> solution at 70  $^\circ$ C for 35 min and washed with water and ethanol. The films were heated again at 500 °C for 30 min using a heat blower followed by cooling to 90 °C and dipping into 0.3 mM toluene solution of the dyes overnight at room temperature. To prepare the counter-electrode, the Pt catalyst was deposited on a cleaned TEC 15 FTO glass by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (5 mM in 2-PrOH solution) with subsequent rapid thermal treatment at 400 °C for 15 min. For carbon counter-electrodes the same procedure was followed using a graphite/acetone solution. For the assembly of DSSCs containing a liquid electrolyte, the dye-containing TiO<sub>2</sub> electrode and the counter-electrode were assembled into a sandwich-type cell and

#### PCCP

sealed with a hot-melt gasket with 25 µm thickness made of the ionomer Surlyn 1702 (Dupont). The redox electrolyte was driven into the cells through two holes previously drilled in the counterelectrode. The iodine-based type of electrolyte used for rheniumbased dyes consists of 0.7 M LiI, 0.025 M  $I_2$  and 0.2 M TBP in ACN. The cobalt-based type of electrolyte contained instead 1 M LiTFSI, 0.33 M [Co(bpy)<sub>3</sub>(B(CN)<sub>4</sub>)<sub>2</sub>], 0.06 M [Co(bpy)<sub>3</sub>(B(CN)<sub>4</sub>)<sub>3</sub>] and 0.2 M TBP in ACN. Finally, the hole was sealed using Surlyn and a cover glass (0.1 mm thickness). Solid state devices (SSDs) were prepared following a similar procedure. An FTO glass plate with 1.4  $\times$  2.3 cm was laser etched to create a non-conductive zone for the separation of the contacts, then it was cleaned and UV/O3 treated before undergoing flame spray pyrolysis. A solution containing 0.6 mL of titanium isopropoxide acetylacetonate [Ti(OiPr)<sub>2</sub>(acac)<sub>2</sub>], 0.4 mL of acetylacetone and 9 mL of ethanol was then sprayed (gas carrier:  $O_2$ , 0.8 bar) on the glass plates at 450 °C, creating a non-porous transparent TiO<sub>2</sub> layer. The transparent mesoporous layer, in this case made of 30 nm sized TiO<sub>2</sub> particles (Dyesol DSL30NR-D), was printed with a different mesh on the FTO conducting glass, followed by a no scattering layer. Sintering was carried out as described above. The titania films were then dipped into 0.3 mM toluene solution of the dyes overnight at room temperature, then dried, and transferred into a glove box. A solution of the hole transporting material (HTM), Spiro-OMeTAD, was spin coated onto the adsorbed dye. The final thickness of the whole cell was measured to be around 2 µm. The counter-electrode, metallic gold, was deposed via physical vapor deposition, without sealing the cell before measurements.

DSSC and SSD characterization. All measurements were carried out in air directly after the fabrication of the cells. A black shadow mask with a fixed aperture was used on DSSCs and SSDs, so that the active area was set to be  $0.16 \text{ cm}^2$ . The current-voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent using a digital source meter (Keithley model 2400) connected to a pc. The light source was a 450 W xenon lamp (Oriel) equipped with a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH) to match the emission spectrum of the lamp with the AM 1.5 G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cutoff filter (Schott KG-3). The incident photon to collected electron conversion efficiency (IPCE) measurement was plotted as a function of wavelength by using light from a 300 W xenon lamp (ILC Technology), which was focused through a Gemini-180 double monochromator (Jobin Yvon) onto the photovoltaic cell under test. A computer-controlled monochromator equipped with automatic grating and wavelength selection and operating in the spectral range (300-800 nm) generates a photocurrent action spectrum with a sampling interval of 10 nm and a current sampling time of 4 s to reduce scattered light from the edge of the glass electrodes of the dyed TiO<sub>2</sub> layer. Electrochemical impedance spectroscopy (10 mV steps in the  $10^{-1}\text{--}10^{-6}~\text{Hz}$ range) was carried out only on the transparent layer-only version of the already assembled DSSC cells, using a BioLogic SP-300

potentiostat with a Zview software, at open circuit, both in the dark and under illumination. Spectra were analyzed with a Zview equivalent circuit modeling software, including the distributed element DX11 (transmission line model). All the measurements were performed one day after cell preparation.

### Conflicts of interest

There are no conflicts to declare.

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