Recent Investigations on Thiocyanate-Free Ruthenium(II) 2,2'-Bipyridyl Complexes for Dye-Sensitized Solar Cells

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Abstract: Three decades ago, dye-sensitized solar cells (DSSCs) emerged as a method for harnessing the energy of the sun and for converting it into electricity. Since then, a lot of work has been devoted to create better global photovoltaic efficiencies and long term stability. Among photosensitizers for DSSCs, thiocyanate-free ruthenium(II) complexes have gained increasing interest due to their better stability compared to conventional thiocyanate-based complexes, such as benchmark dyes N719 and Z907. In this mini-review, two classes of thiocyanate-free Ru(II) complexes are presented: (a) bis-bipyridyl compounds bearing an ancillary cyclometalating bidentate ligand; (b) bipyridyl compounds bearing non-cyclometalating ancillary ligands. The coverage, mainly from 2014 up to now, is not exhaustive, but illustrates the most recent design strategies and photovoltaic properties of these two families of ruthenium(II) dyes.

Keywords: dye-sensitized solar cells; photosensitizers; thiocyanate-free ruthenium dyes; bipyridine ruthenium complexes

1. Introduction

Among the different types of photovoltaic devices developed in recent decades, dye-sensitized solar cells (DSSCs) have attracted growing interest, reaching remarkable improvements of their performances. This has been possible since all the components of such cells have been deeply studied, trying to optimize the sensitizer, the electrolytic mixture and the fabrication method.

The first examples of these solar cells were fabricated, tested and published by Grätzel and O’Regan in 1991 [1], reaching, in the following years, record efficiencies of 12% [2].

A DSSC is generally based on a dye molecule (a purely organic or an organometallic compound) adsorbed on a semiconductor layer, such as titanium dioxide, deposited on a photoanode made of a conductive oxide, such as fluoride-doped tin oxide (FTO). Between the anode and the cathode, the filling of the device is composed by an electrolytic mixture of a redox couple (more commonly the I$_3^-$/$I^-$/I$_2^-$ one, but recently an important series of earth-abundant metal complexes has been tested [3–10] together with some organic or inorganic additives [11]).

When the cell is irradiated by sunlight, the dye molecule is excited to a higher energy level, from which it loses an electron; the electron is injected into the titania layer, reaches the photoanode and then arrives at the cathode by means of an external circuit.

Thanks to a catalyst (e.g., platinum or graphite) present on the cathode, the electron recombines with the oxidized species of the redox couple, forming the reduced one. The reduced species then reacts with the cationic form of the dye, regenerating it and completing the cycle.

Up to now, one of the most used and best-performing dyes is the Ru(II) complex N719, having two ancillary NCS ligands and two anchoring 2,2'-bipyridine-4,4'-dicarboxylic acid...
(de bpy) ligands, in which two of the four carboxylic groups are present as tetrabutylammonium (TBA) salts (structure in Figure 1).

![Figure 1. Structure of the reference dyes Z907, N719, N3, P1, and YE05.](image)

One of the main problems coming from the presence of the thiocyanate ancillary ligand is its ambidentate nature, since it can coordinate to the metal through the nitrogen or the sulfur atom; moreover, it is quite labile and can be easily replaced by other species contained in the device, such as 4-tert-butylpyridine (TBP) often included as additive in the redox mixture.

To overcome the mentioned problems with thiocyanates, many research groups have investigated new bidentate or polydentate chelating ligands to replace the NCS ligands.

This review aims to illustrate some of the papers published in the last seven years in the field of NCS-free bipyridine ruthenium(II) complexes employed as dyes in DSSCs, as an update of the review of Dragonetti, Abbulto et al. of 2014 [12]. It is worth mentioning that other important reviews on this topic have been published in the last few years, providing a wide overview on the progresses made in the field of the dye design and synthesis, presenting both metal-based sensitizers, purely organic compounds, and natural derivatives [13–15].

A good laboratory practice is to report the photoelectrochemical performance of the DSSC employing the dye under investigation with that of a control cell with N719 as standard dye, in order to allow for an easier comparison of results obtained for cells fabricated in different laboratories. Therefore, when possible, we report in the Tables the photoconversion efficiencies of devices based on the investigated photosensitizer relative to N719 set at 100% (ηrel); this comparison has been made only in the case of devices fabricated with the exact same composition and formulation of both the dye and the electrolyte solution. When two N719-based devices, prepared in the same conditions, were presented (Table 1, entries 20–21), we considered the average value of the efficiency.

Table 1. Photovoltaic data of solar cells produced with Ru(II) dyes 1a–1b, 2a–2c, 3a–3d, 4a–4e, and 5a–5c.

| Entry | Dye | Redox Couple | V_{oc}/V | J_{sc}/(mA cm^{-2}) | FF | η (η_{rel})/% | CE | Ref. |
|-------|-----|--------------|----------|---------------------|----|--------------|----|------|
| 1     | 1a  | Γ−/I_{3}−    | 0.63     | 8.15                | 0.71 | 3.64 (38.8) | Pt | [16] |
| 2     | 1b  | Γ−/I_{3}−    | 0.63     | 9.45                | 0.71 | 4.22 (45.0) | Pt | [16] |
| 3     | N719| Γ−/I_{3}−    | 0.78     | 17.03               | 0.7 | 9.37         | Pt | [16] |
| 4     | 2a  | Co^{2+}/Co^{3+} | 0.44     | 3.26                | 0.68 | 0.98         | Pt | [17] |
| 5     | 2b  | Co^{2+}/Co^{3+} | 0.39     | 1.96                | 0.58 | 0.45         | Pt | [17] |
| 6     | 2c  | Co^{2+}/Co^{3+} | 0.38     | 1.75                | 0.55 | 0.38         | Pt | [17] |
| 7     | Z907| Co^{2+}/Co^{3+} | 0.4      | 4.86                | 0.72 | 1.33         | Pt | [17] |
| 8     | 2a  | Co^{2+}/Co^{3+} | 0.57     | 7.44                | 0.68 | 2.86         | Pt | [17] |
| 9     | 2b  | Co^{2+}/Co^{3+} | 0.51     | 5.53                | 0.69 | 1.94         | Pt | [17] |
| 10    | 2c  | Co^{2+}/Co^{3+} | 0.51     | 5.33                | 0.71 | 1.91         | Pt | [17] |
| 11    | Z907| Co^{2+}/Co^{3+} | 0.59     | 9.73                | 0.65 | 3.76         | Pt | [17] |
| 12    | 3a  | Γ−/I_{3}−    | 0.63     | 20.454              | 0.686 | 8.83         | Pt | [18] |
| 13    | 3a  | Γ−/I_{3}−    | 0.63     | 20.454              | 0.686 | 8.83         | Pt | [18] |
| 14    | 3b  | Γ−/I_{3}−    | 0.66     | 20.585              | 0.715 | 9.71         | Pt | [18] |
| 15    | 3b  | Γ−/I_{3}−    | 0.676    | 19.872              | 0.716 | 9.62 (104.3) | Pt | [18] |
2. Ruthenium Complexes with Bipyridine Ligands as Sensitizers in DSSCs

When considering ruthenium complexes as dyes for DSSC applications, 2,2'-bipyridine (generally abbreviated as bipy) is certainly one of the most employed chelating ligands for solar light harvesting; its functionalization with carboxylic or phosphonic groups allows the anchoring of the dye on the semiconductor surface.

2.1. Ruthenium Compounds with Cyclometalating Ligands

One of the first to realize the usefulness of cyclometalating 2-phenylpyridines as ligands in DSSC dyes was Berlinguette, with many important works in this field [21–25].

More recently, a wide range of this type of ligands have been obtained and tested in Ru-based sensitizers, providing interesting results.

In 2014, two thiophene-incorporated ruthenium complexes (1a and 1b, structure in Figure 2) were published by Li, Su, Wang et al. [16]. These dyes had two dcibpy ligands and a cyclometalated N'C ligand based on 2-thienylpyridine. In particular, complex 1a had a 2-(4-methyl-5-phenyl-thiophen-2-yl)pyridine ligand, whereas 1b a 2-(4-fluorobenzo[b]thiophene-2-yl)pyridine.

These dyes showed broader absorption spectra and higher molar extinction coefficients if compared to the reference sensitizer N719 when absorbed on TiO2 layers. The replacement of the two thiocyanate ligands with the cyclometalating 2-phenylpyridines provided slightly higher HOMO and LUMO levels (0.01–0.03 eV), but a comparable HOMO-LUMO gap (~1.60 eV), hence both 1a and 1b were suitable sensitizers for DSSCs.

Table 1. Cont.

| Entry | Dye 2 | Redox Couple | V_{oc}/V | J_{sc}/(mA cm^{-2}) | FF | η (nrel)/% | CE 3 | Ref. |
|-------|-------|--------------|----------|----------------------|----|------------|------|------|
| 16    | 3c 9  | Γ−/I3− 12    | 0.492    | 16.999               | 0.642 | 5.37 | Pt [18] |
| 17    | 3c 9  | Γ−/I3− 10    | 0.584    | 12.832               | 0.647 | 4.85 | Pt [18] |
| 18    | 3d 9  | Γ−/I3− 12    | 0.497    | 14.68                | 0.614 | 4.48 | Pt [18] |
| 19    | 3d 9  | Γ−/I3− 10    | 0.575    | 10.787               | 0.682 | 4.23 | Pt [18] |
| 20    | N719 9| Γ−/I3− 11    | 0.733    | 17.16                | 0.725 | 9.12 | Pt [18] |
| 21    | N719 9| Γ−/I3− 11    | 0.749    | 16.85                | 0.739 | 9.32 | Pt [18] |
| 22    | 4a 13 | Γ−/I3− 12    | 0.62     | 8.06                 | 0.68  | 3.39 | Pt [19] |
| 23    | 4b 13 | Γ−/I3− 12    | 0.58     | 4.41                 | 0.69  | 1.77 | Pt [19] |
| 24    | 4c 13 | Γ−/I3− 12    | 0.57     | 3.54                 | 0.69  | 1.4  | Pt [19] |
| 25    | 4d 13 | Γ−/I3− 12    | 0.56     | 3.88                 | 0.69  | 1.5  | Pt [19] |
| 26    | 4e 13 | Γ−/I3− 12    | 0.55     | 4.67                 | 0.66  | 1.69 | Pt [19] |
| 27    | 5a 14 | Γ−/I3− 15    | 0.4      | 7.41                 | 0.67  | 2.00 | Pt [20] |
| 28    | 5b 14 | Γ−/I3− 15    | 0.468    | 15.24                | 0.65  | 4.64 | Pt [20] |
| 29    | 5c 14 | Γ−/I3− 15    | 0.408    | 8.02                 | 0.67  | 2.18 | Pt [20] |
| 30    | N719 16| Γ−/I3− 15   | 0.619    | 18.5                 | 0.64  | 7.41 | Pt [20] |
| 31    | 5a 14 | Γ−/I3− 17    | 0.39     | 16.46                | 0.99  | 3.81 | Pt [20] |
| 32    | 5b 14 | Γ−/I3− 17    | 0.468    | 21.16                | 0.56  | 5.53 | Pt [20] |
| 33    | 5c 14 | Γ−/I3− 17    | 0.346    | 18.18                | 0.55  | 3.43 | Pt [20] |
| 34    | N719 16| Γ−/I3− 17   | 0.502    | 18.23                | 0.61  | 5.56 | Pt [20] |

1 AM 1.5 simulated light source; input intensity of 100 mW cm^{-2} if not differently indicated. 2 having TiO2 as semiconductor if not differently indicated. 3 CE: counterelectrode. 4 0.3 mM dye in CH2CN:tBuOH 1:1. 5 0.5 M LiI + 0.05 M I2 + 0.5 M DMPII + 0.5 M TBP in CH2CN (DMPII = 1,2-dimethyl-3-propylimidazolium iodide). 6 0.3 mM dye + 0.3 mM CDCA in EtOH (CDCA = chenodeoxycholic acid). 7 0.2 M [Co(dmbpy)3][TFSI]2 + 0.02 M [Co(dmbpy)3][TFSI]1 + 0.1 M LiTFSI + 10.0 mM CDCA in CH2CN (TFSI = bis(trifluoromethane)sulfonylimide). 8 having an ultra-thin layer of Al2O3 on the TiO2 semiconductor. 9 0.02 M dye in 1:1:1 CH2CN:tBuOH:DMSO. 10 0.6 M DMPII + 0.1 M LiI + 0.05 M I2 + 0.3 M TBP in CH2CN. 11 0.6 M DMPII + 0.1 M LiI + 0.05 M I2 + 0.5 M TBP in CH2CN. 12 0.6 M DMPII + 0.1 M LiI + 0.05 M I2 in CH2CN. 13 0.2 mM dye + CDCA in 1:1 CH2CN:tBuOH. 14 0.1 mM dye + 10.0 mM DCA in EtOH (DCA = deoxycholic acid). 15 0.6 M DMPII + 0.1 M LiI + 0.05 M I2 in CH2CN. 16 0.3 mM dye in EtOH. 17 0.0 M LiI + 0.05 M I2 in CH2CN.
The photovoltaic performances were tested working with the \( \Gamma / I_3^- \) redox couple under AM 1.5G conditions (100 mW cm\(^{-2}\)). The performance data are listed in Table 1 (entries 1–2): with an efficiency of 4.22%, 1b was the most promising dye, but not yet able to compete with the standard dye N719 (\( \eta = 9.37\% \), entry 3). Additionally, the IPCE values followed the trend N719 > 1b > 1a. In order to explain these results, the electrochemical impedance spectroscopy (EIS) technique was used; with respect to N719, compounds 1a and 1b gave lower electron-transport resistances and higher electrochemical impedances, indicating a more efficient electron recombination of TiO₂ electrons with acceptor species in the electrolyte. This was also supported by the shorter electron lifetimes and the lower electron effective diffusion coefficients: 17.8 ms and \( 2.36 \times 10^{-4} \) cm\(^2\)/s for 1b, 31.6 ms and \( 2.69 \times 10^{-4} \) cm\(^2\)/s for 1a, and 3.12 ms and \( 3.90 \times 10^{-4} \) cm\(^2\)/s for N719.

In the same year, Hamann and coworkers published the two new Ru(II) complexes 2a and 2b (Figure 2) [17], having two bipy ligands and a cyclometalating 2-phenylpyridine. Both complexes had a dbipy and a 4,4′-dinonyl-2,2′-bipyridine (dnbipy); the aim of the nonyl chains was to provide a sufficient steric hindrance to avoid the ease of access of the redox mediators to the titania surface. In 2a, the third ligand was a 2-(2,4-difluorophenyl)pyridine, whereas in 2b a simple 2-phenylpyridine. The properties of these new compounds were compared with those of the previously known sensitizers 2c (the same structure as 2b but without the nonyl chains) and Z907 (see Figure 1: same bipyridines of the new complexes but with two NCS ligands instead of the phenylpyridine).

All ruthenium complexes were tested working with [Co(dmbipy)₃]²⁺/³⁺ as redox couple (dmbipy = 4,4′-dimethyl-2,2′-bipyridine) and under AM 1.5G conditions (100 mW cm\(^{-2}\)). Compound 2b presented very similar results with respect to the reference 2c, despite the introduction of the nonyl chains on the bipy ligand; better values were obtained with 2a, whose \( J_{sc} \) value was remarkably higher than that of 2b (3.26 vs. 1.96 mA cm\(^{-2}\); Table 1, entries 4 and 6). However, the best data were still those of the benchmark dye Z907, which showed an efficiency of 1.33% and a photocurrent of 4.86 mA cm\(^{-2}\) (entry 7).

In order to further hamper the recombination of the oxidized redox species, other devices were produced by adding an ultra-thin layer of alumina on the TiO₂, by means of atomic layer deposition (ALD) technique; the presence of the additional coating was beneficial to the measured values, with an important increase in all parameters. Additionally, in this case, Z907 was the best performing sensitizer (entry 11), followed by 2a, 2b, and 2c, in the same order as shown before in the absence of the alumina layer (entries 8–11).

In the same year Islam, El-Shafei, and coworkers presented four new sensitizers having a dbipy and a bithiophene- or terthiophene-based bipyridinic ligand [18]. The
remaining coordination centers were occupied by two NCS ligands in the case of 3a and 3b, and by a 2-(4-trifluoromethylphenyl)pyridine in 3c and 3d (Figure 2). The substitution of the thiocyanates with a cyclometalated ligand provided a smaller HOMO-LUMO gap (resulting in a red shift of the absorption), while the addition of a third thiophene ring in the light-harvesting bipyridine ligand increased the extinction coefficient of the sensitizers, giving the possibility of a lower dye loading and thinner TiO₂ layers in the devices.

The photovoltaic properties of the four complexes were compared with those of the classical N719 dye, also testing the effect of different amounts of TBP as an additive in the electrolytic mixture. The most promising compound was the NCS-based 3b, with a Jsc of 20.585 mA cm⁻², a Voc of 0.660 V and a conversion efficiency of 9.71% (Table 1, entry 14). Despite the lower efficiency (8.83 vs. 9.12%), also the photocurrent density of 3a was higher than that of N719 (20.454 vs. 17.160 mA cm⁻²; entries 12 and 20); in this case, such results could be explained considering a poorer charge separation and/or higher recombination reactions at the dye/titania/electrolyte interface. For all the parameters, dyes 3c and 3d registered worse results (entries 16–19), due to a slower dye regeneration (electron lifetimes of 13 and 18 µs, respectively, much longer than the 6 and 4 µs obtained with 3a and 3b) and a lower driving force, under the minimum required threshold of 0.25 eV. Table 1 resumes data for the mentioned solar cells.

Other five Ru(II) complexes were synthesized and published in the year 2014 by Ho, Chen, Wong et al. [19]. These cationic dyes had two dcbipy and a cyclometalated N°C ligand with the base structure of a 2-phenylpyridine with a CF₃ group in position 5. Compounds 4a, 4b, and 4c had an N-substituted pyridyl-carbazole, where the substituents were a p-tolyl, a phenyl and a n-butyl, respectively; 4d presented a diphenylamino group on the phenylpyridine ligand, while 4e had a diphenylamino-pyridyl-fluorene scaffold. The structure of the dyes is shown in Figure 3.

Figure 3. Structure of dyes 4a–4e.

These sensitizers showed a higher extinction coefficient when compared to the standard N719 dye and, as already mentioned, this could allow for a thinner layer of titania in the DSSC and for a lower possibility of recombination between the species. All data are presented in Table 1. The highest solar conversion was obtained by 4a, that reached a maximum IPCE value of 56% at 560 nm; the same dye also achieved the best Jsc (8.06 mA cm⁻², Table 1, entry 22) and η (3.39%), much higher than that of the other four complexes (entries 23–26). It can be observed that these performances came from the use of carbazole as electron-donating moiety in the N°C ligand, the best performance being reached with the p-tolyl group on the nitrogen atom.

Up to now all the presented works had COOH-substituted bipyridines as anchoring ligands, while in the paper of Funaki, Sugihara and coworkers from 2014 [20] two phenylquinolines were employed. The cyclometalating ligands of these compounds were a simple 2-phenylpyridine for 5a, a 2-(4-methoxyphenyl)pyridine for 5b and a 2-(2-thienyl)pyridine for 5c. In all cases the complex was cationic and had a PF₆⁻ counteranion (see Figure 4 for the structure of the compounds).
In order to have a proper adsorption of the dye onto the TiO₂, the presence of deoxycholic acid as co-adsorbent was necessary; moreover, different sensitizer concentrations were tested and the measurements were carried out under AM 1.5 irradiation (100 mW cm⁻²), employing two different electrolytic solutions in acetonitrile: the former containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide + 0.05 M I₂ + 0.1 M LiI, the latter having 0.05 M I₂ + 2.0 M LiI; also the benchmark dye N719 was used as a reference. Compound 5b gave the best results for all parameters, originating a J_sc of 15.24 mA cm⁻², a V_oc of 468 mV and an efficiency of 4.64% (Table 1, entry 28) when the first electrolytic solution was used; this efficiency largely overcame the values of both 5a and 5c (entries 27 and 29), due to higher photocurrent and voltage. Table 1 lists all photovoltaic data.

A dramatic improvement of the measured parameters was achieved with the second solution, containing a much larger amount of LiI, which was thought to positively shift the conduction-band edge of the titania. When compared to N719, 5b showed a better photo-response (entry 32) in the longer wavelengths, reaching an IPCE of 76% and having a panchromatic sensitization not only in the visible region but also in the NIR, up to 1020 nm. As stated by the authors, this was the best result for a cyclometalated Ru(II) complex in the NIR region. This red-shift was due to the use of a strong electron-donating N^C ligand and of a more π-extended anchoring ligand.

In 2016, Housecroft and coworkers published a paper in which two derivatives of complex [Ru(bipy)₂(Cl-ppy)][PF₆] (Cl-ppy = 4-chloro-2-phenylpyridine) were explored [26]. In the first compound (6a) the N^C ligand was expanded through a 4-PO₃H-phenyl moiety to form a zwitterionic dye of Ru²⁺, while in the second (6b) via a 4-COOH-phenyl ring (Figure 4). These phosphonic and carboxylic substituents aimed at the introduction of anchoring groups to link the sensitizers to the semiconductor, since the other ligands on the metal were simple bipyridines and not dcbipy as often presented before.

Then, 6a was tested in DSSCs together with the organic reference sensitizer P1 (depicted in Figure 1), adsorbed on one or two layers of NiO. Independently on the number of NiO layers, the photovoltaic performances of 6a were better than those of the standard P1 dye, reaching a J_sc of 2.18 mA cm⁻² in the case of a single layer and of 3.38 mA cm⁻² in the presence of two layers (Table 2, entries 1–8). The efficiency of these devices had a maximum value of 0.116% (entry 7).

Table 2. Photovoltaic data of solar cells produced with Ru(II) dyes 6a, 7a–7f, 7a–7f, 8a–8c, 9c–9d, 10a–10f, 11a–11d, 12f–12j.

| Entry | Dye ² | Redox Couple | V_oc/V | J_sc/(mA cm⁻²) | FF | η (ηrel)/% | CE ³ | Ref. |
|-------|-------|--------------|--------|----------------|----|------------|------|------|
| 1     | P1 ⁴,⁵ | I⁻ /I₃⁻ ⁶   | 0.091  | 1.54           | 0.35 | 0.049     | Pt   | [26] |
| 2     | P1 ⁴,⁵ | I⁻ /I₃⁻ ⁶   | 0.095  | 1.26           | 0.35 | 0.042     | Pt   | [26] |
| 3     | P1 ⁴,⁷ | I⁻ /I₃⁻ ⁶   | 0.088  | 1.84           | 0.35 | 0.057     | Pt   | [26] |
| 4     | P1 ⁴,⁷ | I⁻ /I₃⁻ ⁶   | 0.082  | 1.96           | 0.35 | 0.051     | Pt   | [26] |
| 5     | 6a ⁵,⁸ | I⁻ /I₃⁻ ⁶   | 0.093  | 2.18           | 0.39 | 0.079     | Pt   | [26] |
| 6     | 6a ⁵,⁸ | I⁻ /I₃⁻ ⁶   | 0.094  | 2.00           | 0.41 | 0.077     | Pt   | [26] |
| 7     | 6a ⁷,⁸ | I⁻ /I₃⁻ ⁶   | 0.095  | 3.38           | 0.36 | 0.116     | Pt   | [26] |
| 8     | 6a ⁷,⁸ | I⁻ /I₃⁻ ⁶   | 0.095  | 3.34           | 0.34 | 0.109     | Pt   | [26] |

Figure 4. Structure of dyes 5a–5c and 6a–6b.
In 2016, Nazeeruddin et al. developed a series of new tris-heteroleptic cyclometalated Ru(II) complexes [27] having a dcbipy molecule as anchoring ligand, a bipyridine with aromatic substituents in the 4 and 4’ positions as main light-harvesting moiety, and a...
2,6-didodecyloxy-3,2′-bipyridine as ancillary C=N ligand; the long alkyl chains prevented the access of the redox mediators to the semiconductor surface. The structures of the six new dyes 7a–7f and of the investigated substituents are shown in Figure 5.

In order to test the performances of these sensitizers, some DSSCs were produced, employing [Co(Phen)$_3$]$^{2+/3+}$ (Phen = 1,10-phenanthroline) as redox couple. Surprisingly, the best results came from compound 7c (Table 2, entry 11), with a short-circuit photocurrent of 14.55 mA cm$^{-2}$ and a $\eta$ of 9.4% under AM 1.5 conditions and a power of 100 mW cm$^{-2}$; this was not attended because of the limited absorption range of this dye, but desorption studies showed that the amount of sensitizer loaded onto the titania layer was much higher with respect to the other five compounds. Additionally, 6f provided a large loading, but its inefficiency in the dye regeneration made it produce a lower IPCE. It can be concluded that the higher dye loading of 7c was responsible for an increased J$_{sc}$, hence for a higher efficiency, despite its low extinction coefficient and its narrow absorption range. Table 2 contains all data for the discussed sensitizers.

Another useful take-home message is that the proper compromise between the various parameters is crucial to achieve the best cell performance, even if it is not easy to take into account all the factors which play a role in the complex processes occurring in a DSSC.

Four of the aforementioned ruthenium(II) sensitizers (7b, 7c, 7d, and 7f) were published by the same group and in the same year in another paper [28], this time focusing the attention on the role of sulfur atoms in the aromatic substituents of the light-harvesting bipyridine. These moieties were different in the number of the thiophene rings and in the way they were connected: 7d had no sulfur but a fluorene-based group, 6c presented a thienothiophene, while 7b and 7f a cyclopentadieno-dithiophene unit with methyl or hexyl chains. These ligands were designed in order to prove if the presence of sulfur in the dye...
structure had a positive or negative effect on the cell properties when the classical $\text{I}^-/\text{I}_3^-$ redox couple is chosen for the electrolytic solution.

Differently from the previous work, this time the best results were given by sensitizer 7d, (Table 2, entry 23), with the highest $V_{\text{OC}}$ (0.694 V) and the best efficiency (7.2%, under 1 Sun simulated conditions), even if with the lowest $J_{\text{SC}}$ (13.84 mA cm$^{-2}$). Complete data of the produced solar cells can be found in Table 2. Based on these data and on the in-depth absorption, electrochemical, and theoretical studies made by the authors, it can be concluded that the presence of sulfur in iodine-containing DSSCs is detrimental for the cell performances, due to the interaction between sulfur- and iodine-based species. In fact, sulfur-free dye 7d was characterized by an increased electron recombination efficiency, despite the lower dye regeneration yield.

In 2017, Aghazada, Ren, Wang et al. [29] described three tris-heteroleptic cyclometalated Ru(II) complexes ($8a$–$8c$) bearing different donor groups on the bipyridinic ligand. The complexes were based on a dcbipy anchoring ligand, a 4-(tert-butyl)-2',6'-bis(dodecyloxy)-2,3'-bipyridine N'C ligand, and a 4,4'-substituted bipy. The structure of the mentioned compounds are shown in Figure 5.

Each dye had a high molar absorption coefficient almost over the entire visible spectrum. For what concerned the electrochemical properties, the three sensitizers showed two oxidations; the first one was attributed to the $\text{Ru}^{3+/2+}$ redox reaction, the second one to the oxidation of the donor groups on the ancillary ligands; while the first oxidation was found to be completely reversible, the second one was not. However, the authors observed that only the first oxidation occurred in a DSSC; since the dye was present in a reducing environment, the second oxidation could not take place and did not represent an issue for the performances of the photovoltaic device.

Moving to the photovoltaic performances, the synthesized dyes were tested using the redox couple [Co(Phen)$_3$]$^{3+/2+}$ under AM 1.5G irradiation. Except for the FF, the order of the $V_{\text{OC}}$, the $J_{\text{SC}}$ and the efficiency was the following: $8b > 8a > 8c$, Table 2 entries 25–27.

In the same year, four new cycloruthenated complexes ($9a$, $9b$, $9c$, and $9d$, structure in Figure 5) containing ortho-metalated thiophenes were published by Medved’ko, Ivanov et al. [27]. The complexes were based on two dcbipy, which carboxyl groups were present as ethyl esters in compounds $9a$ and $9b$, while they were free carboxyl groups in compounds $9c$ and $9d$. Complexes $9a$ and $9c$ had a N-(thiophen-2-ylmethyliden)aniline ligand, whereas complexes $9b$ and $9d$ had a 2-(thiophen-2-yl)pyridine.

All dyes showed intense and broad absorption bands with high molar absorption coefficients, and absorption spectra almost over the entire visible spectrum. All the complexes were found to be redox-active with completely reversible oxidations.

The photovoltaic performances of DSSCs fabricated with the dyes $9c$ and $9d$ were tested using the method of photopotential and photocurrent transient to study the dye regeneration process, under AM 1.5G illumination conditions and compared to those of the reference dye $\text{N3}$ (Figure 1) and of the dyes $1a$ and $1b$ previously published by Li et al. [16]. The dye $9c$ showed a $J_{\text{SC}}$ and a $V_{\text{OC}}$ that exceed those of dye $9d$, but not those of the standard dye. The same trend was observed for the efficiency. However, the dyes $9c$ and $9d$ represented an improvement respect to the previously published dyes $1a$ and $1b$ both in terms of $J_{\text{SC}}$, $V_{\text{OC}}$ and efficiency. The experimental results are listed in Table 2 (entries 28–30).

A further example of an interesting family of NCS-free ruthenium(II) dyes was published in 2017 by Wu’s group [31]. The new complexes shared a cyclometalating 2-phenylpyridine with a different location of CF$_3$ substituents, and two anchoring bipy ligands with a different number of carboxylic and/or EDOTSR moieties (where EDOTSR stands for 5-hexylthio-3,4-ethylendioxythiophen-2-yl, whose structure is shown in Figure 6).
In compounds 10a, 10c, and 10e the trifluoromethyl groups were in the *ortho* and *para* positions with respect to the Ru-bound carbon atom of the phenyl ring, while in the case of 10b, 10d, and 10f they were in the *meta* positions. Additionally, 10a and 10b contained two dcbipy ligands, while 10c and 10d had one dcbipy and one EDOTSR-bearing bipy; finally, 10e and 10f had two EDOTSR-substituted bipy.

This work aimed at understanding how the photovoltaic properties of the mentioned Ru$^{2+}$ dyes were influenced by the presence and position of the electron-withdrawing CF$_3$ groups on the N$^+$C ligand. It was observed that the *meta*-substitution reduced the electron density on the metal less than that in the *ortho* and *para* positions, and also provided a better interaction between the I$^−$ and the oxidized sensitizer, due to less steric hindrance. As a result, the best efficiency value (9.03%) was achieved by 10b (Table 2, entry 32) which also had the highest $J_{sc}$ of 18.40 mA cm$^{-2}$; these performances overcame those of the devices produced with the classical N719 dye (entry 37), in the same fabrication conditions. Table 2 lists all detailed data for these dyes.

Another paper with four new dyes was published in 2018 by the same group [32], this time choosing as only anchoring ligands the tetrabutylammonium salts of dcbipy and as N$^+$C ligand a thiienyl- or thienothiienyl-pyridine, bearing a 5-Hex-thienyl moiety in the 4 position of the pyridine and different alkyl chains on the cyclometalating ring. Figure 6 shows the structures of the novel compounds 11a–11d, through which the authors explored the effect of having a simple thiophene or a thienothiophene on the pyridine, and also the influence of the presence of a sulfur atom between the ring and the hexyl chain.

As expected, the highest dye loading onto the titania layer was achieved by complexes 11a and 11b (8.76 × 10$^{-8}$ and 14.5 × 10$^{-8}$ mol cm$^{-2}$, respectively), being the less sterically hindered molecules.

The short-circuit current was in the range 14.9 to 16.5 mA cm$^{-2}$ (Table 2, entries 38–57), in all cases higher than the value achieved using N719 (entry 42) in reference DSSCs; on the contrary, this standard dye still had the best $V_{oc}$ (0.67 V), FF (0.73) and $\eta$ (7.26%). Moreover, the new dyes showed an open-circuit voltage, Fill Factor and efficiency very close to each other. Data are presented in Table 2.

As stated by the authors, an important feature of sulfur-containing sensitizers was represented by the positive interaction between the soft sulfur atom and the soft iodide anion, producing a good dye regeneration.
In 2020, Lavrova, Mishurinskiy et al. [33] published five new ruthenium-based dyes having two anchoring dcmBipy ligands and a N-phenyl-2-arylbenzimidazole cyclometalating ligand bearing different substituents (complexes 12a–12e; Figure 6). The main difference among the different dyes was represented by the substituents on the phenyl ring in position 2, being both electron-withdrawing (-NO2 and -Cl) and electron-donating (-OMe and -NMe2) groups. Complex 12c was characterized by an unsubstituted phenyl ring.

Compounds 12a–12e showed fully reversible redox properties. By comparing the substituted dyes with the unsubstituted 12c, it emerged that electron-withdrawing groups caused an increase in the redox potential (+50 mV for 12a and +60 mV for 12b) whereas the electron-donating groups caused the opposite effect, but in a more pronounced way (−180 mV and −190 mV for 12d and 12e, respectively). The effect of the different substitution was also observed in the absorption spectra, since an increase in the electron-donor properties of the benzimidazole ligand was associated with a red-shift of the longest absorption maxima of the complexes, up to 40 nm. Moreover, each dye had higher molar absorption coefficients with respect to N719, except in the region between 500 and 550 nm, due to both the stronger electron-donating ability and the extended π-system of cyclometalating benzimidazoles compared to isothiocyanates.

The photovoltaic performances were not measured using the dyes 12a–12e, but the corresponding carboxylic acids 12f–12h, obtained through basic hydrolysis using tetra-n-butylammonium hydroxide followed by protonation with HCl. The absorption spectra of the carboxylic acids were identical to those of the esters 12a–12e. The determination of the photovoltaic properties was carried out using I−/I3− redox couple, under AM 1.5G conditions. The dye 12f showed the poorest performances because the efficient non-radiative decay of the excited state of the dye prevented the electron injection in the TiO2 layer. On the other hand, the other dyes demonstrated similar photovoltaic properties, and the best ones were those with the electron-donating moieties, namely complexes 12i and 12j. Additionally, in this case, the reference dye N719 still gave the best results. The transit time (τtr, i.e., the time necessary to cross the TiO2 layer and reach the FTO surface) and the lifetime of electrons (τ) were determined through intensity modulated photocurrent (IMPS) and photovoltage spectroscopy (IMVS), finding that the lifetimes of electrons were 3–4.5 times longer than the injection times (12g: τtr = 4.0 ms, τ = 12.6 ms, 12h: τtr = 3.1 ms, τ = 10.7 ms, 12i: τtr = 2.5 ms, τ = 9.3 ms, 12j: τtr = 2.0 ms, τ = 9.3 ms). From the transit time and the lifetime of electrons it was possible to determine the charge collection efficiency (hcc). Each dye allowed for a high hcc (12g: 0.68, 12h: 0.71, 12i: 0.73, 12j: 0.78), making them promising candidates for applications in DSSCs.

2.2. Ruthenium Compounds with non Cyclometalating Ligands

Although many research groups have exploited the presence of N-C cyclometalating ligands for the ruthenium sensitizers, others have focused their attention on the use of N-based ligands; such ligands can belong to the family of N=N- or N=O-type ligands (chelating the metal via at least one anionic nitrogen atom) or can be monodentate. In this paragraph the different solutions proposed in this field will be presented and discussed.

In 2014, Robertson, Chi et al. reported the synthesis and study of two couples of ruthenium(II) complexes [34], whose anchoring ligand was a dcbpy, while the ancillary ligands were a hexylthienyl-substituted pyrazolyl-pyridine for 13a and 13b, and a pyrazolyl-isoquinoline for 13c and 13d; moreover, the pyrazole ring carried a CF3 group, whereas the isoquinoline a tert-butyl. The structure of the complexes is shown in Figure 7.
The effect of the molecular isomerism was studied by employing the aforementioned complexes as sensitizers in DSSCs, together with two electrolyte solutions: the former consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) + 0.05 M I₂ + 0.5 M TBP in a 15:85 (v/v) mixture of valeronitrile and acetonitrile, while the latter of a mixture of 0.6 M 1-methyl-3-propylimidazolium iodide (PMII) + 0.03 M I₂ + 0.5 M TBP + 0.1 M guanidinium thiocyanate + 0.05 M LiI in the same solvents. The best performing dye with the first electrolyte mixture was 13c, giving a \( J_{sc} \) of 15.23 mA cm\(^{-2} \) and a \( \eta \) of 9.90\%, (Table 3, entry 3), followed by 13a, with a photocurrent of 13.81 mA cm\(^{-2} \) and an efficiency of 8.87\% (entry 1). The lower values provided by sensitizers 13b and 13d (entries 2 and 4) were attributable to the lower loading on the semiconductor and to the asymmetry of their structure, which did not allow for a uniform coverage of the TiO\(_2\) surface, causing an easier access to it for the I\(_3^-\) species.

Table 3. Photovoltaic data of solar cells produced with Ru(II) dyes 13a–13d, 14a–14c, and 15.

| Entry | Dye \(^2\) | Redox Couple | \( V_{oc}/V \) | \( J_{sc}/(\text{mA cm}^{-2}) \) | FF | \( \eta \) (\text{\%})/\( \eta \) (\text{\%}) | CE \(^3\) | Ref. |
|-------|------------|--------------|----------------|-----------------|----|----------------|-------------|-----|
| 1     | 13a \(^4\) | \( I^-/I_3^- \) | 0.89 | 12.93 | 0.727 | 8.37 | Pt | [34] |
| 2     | 13b \(^4\) | \( I^-/I_3^- \) | 0.78 | 9.81 | 0.725 | 5.55 | Pt | [34] |
| 3     | 13c \(^4\) | \( I^-/I_3^- \) | 0.78 | 12.41 | 0.756 | 8.26 | Pt | [34] |
| 4     | 13d \(^4\) | \( I^-/I_3^- \) | 0.78 | 13.12 | 0.731 | 8.34 | Pt | [34] |
| 5     | 13a \(^4\) | \( I^-/I_3^- \) | 0.72 | 14.49 | 0.668 | 7.55 | Pt | [34] |
| 6     | 13b \(^4\) | \( I^-/I_3^- \) | 0.68 | 10.39 | 0.681 | 4.80 | Pt | [34] |
| 7     | 13c \(^4\) | \( I^-/I_3^- \) | 0.73 | 14.84 | 0.651 | 7.06 | Pt | [34] |
| 8     | 13d \(^4\) | \( I^-/I_3^- \) | 0.84 | 13.30 | 0.766 | 8.36 | Pt | [34] |
| 9     | 14a \(^7,8\) | \( I^-/I_3^- \) | 0.84 | 14.32 | 0.754 | 9.06 | Pt | [34] |
| 10    | 14b \(^7,8\) | \( I^-/I_3^- \) | 0.72 | 0.9 | 0.50 | 0.4 | PEDOT-FTO | [36] |
| 11    | 14c \(^7,8\) | \( I^-/I_3^- \) | 0.71 | 2.4 | 0.58 | 0.9 | PEDOT-FTO | [36] |
| 12    | 14a+c \(^7,8\) | \( I^-/I_3^- \) | 0.60 | 2.0 | 0.64 | 0.9 | PEDOT-FTO | [36] |
| 13    | 14b \(^7,8\) | \( I^-/I_3^- \) | 0.55 | 2.7 | 0.49 | 0.8 | PEDOT-FTO | [36] |
| 14    | 14c \(^7,8\) | \( I^-/I_3^- \) | 0.51 | 4.0 | 0.51 | 1.2 | PEDOT-FTO | [36] |
| 15    | 14a \(^7,8\) | \( I^-/I_3^- \) | 0.62 | 1.7 | 0.69 | 0.8 | PEDOT-FTO | [36] |
| 16    | 14b \(^7,8\) | \( I^-/I_3^- \) | 0.67 | 1.3 | 0.50 | 0.5 | PEDOT-FTO | [36] |
| 17    | 14c \(^7,8\) | \( I^-/I_3^- \) | 0.60 | 3.8 | 0.66 | 1.7 | PEDOT-FTO | [36] |
| 18    | 14a \(^7,8\) | \( I^-/I_3^- \) | 0.55 | 2.4 | 0.66 | 1.0 | PEDOT-FTO | [36] |
Table 3. Cont.

| Entry | Dye 2 | Redox Couple | Voc/V | Jsc/(mA cm⁻²) | FF | η (η_rel) % | CE 3 | Ref. |
|-------|-------|--------------|-------|----------------|----|-------------|------|------|
| 30    | 15    | Cu⁺/Cu²⁺     | 0.56  | 2.4            | 0.64| 1.0         | PEDOT-FTO [36] |
| 31    | 15    | Cu⁺/Cu²⁺     | 0.57  | 2.4            | 0.61| 0.9         | PEDOT-FTO [36] |
| 32    | 15    | Cu⁺/Cu²⁺     | 0.59  | 2.2            | 0.66| 0.9         | PEDOT-FTO [36] |
| 33    | 15    | Cu⁺/Cu²⁺     | 0.57  | 1.8            | 0.65| 0.7         | PEDOT-FTO [36] |
| 34    | 15    | Cu⁺/Cu²⁺     | 0.59  | 2.4            | 0.64| 1.0         | PEDOT-FTO [36] |
| 35    | 15    | Cu⁺/Cu²⁺     | 0.61  | 2.1            | 0.65| 0.9         | PEDOT-FTO [36] |
| 36    | 15    | Cu⁺/Cu²⁺     | 0.61  | 2.1            | 0.66| 0.9         | PEDOT-FTO [36] |
| 37    | 15    | Cu⁺/Cu²⁺     | 0.62  | 2.2            | 0.65| 1.0         | PEDOT-FTO [36] |

1 AM 1.5 simulated light source; input intensity of 100 mW cm⁻² for dyes 9a–9d and 10a–10c; input intensity of 90 mW cm⁻² for dye 11.
2 having TiO₂ as semiconductor if not differently indicated. 3 CE: counter electrode; PEDOT = poly(3,4-ethylenedioxythiophene).
4 0.3 mM dye + 0.6 mM TBADCl in EtOH-DMSO 4:1 (TBADCl = Tetrabutylammonium deoxycholate). 5 0.6 M DMPII + 0.05 M I2 + 0.5 M TBP in 85:15 CH₂CN:Bu-CN. 6 0.6 M PMII + 0.1 M LiI + 0.03 M I2 + 0.5 M TBP + 0.1 M GNCS in 85:15 CH₂CN:Bu-CN. 7 having two layers of TiO₂ as semiconductor. 8 0.3 mM dye + 0.6 mM TBADCl in EtOH-DMSO 9:1. 9 0.6 M DMPII + 0.05 M I2 + 0.5 M TBP in CH₃CN. 10 0.45 M DMPII + 0.15 M LiI + 0.05 M I2 + 0.8 M TBP in CH₃CN. 11 0.45 M [Co(Phen)₂][TFSI]₂ + 0.15 M [Co(Phen)₃][TFSI]₃ + 0.15 M LiFSl + 0.8 M TBP in CH₃CN. 12 0.1 mM dye, then 0.1% APTES in toluene (APTES = (3-aminopropyl)triethoxysilane). 13 0.15 M Cu1 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 14 0.10 M Cu1 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 15 0.15 M Cu2 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 16 0.15 M Cu2 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 17 0.10 M Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 18 0.10 M Cu3 + NOBF₄ + 0.1 M LiClO₄ + 0.01 M FeI in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 19 0.10 M Cu3 + NOBF₄ + 0.1 M LiClO₄ + 0.01 M FeI in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 20 0.10 M Cu3 + NOBF₄ + 0.1 M LiClO₄ + 0.01 M TBP + 0.01 M FeI in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 21 0.10 M Cu3 + NOBF₄ + 0.1 M LiClO₄ + 0.01 M FeI in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 22 0.1 M FeI in CH₃CN. 23 0.20 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.15. 24 0.20 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.10. 25 0.20 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 26 0.15 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.15. 27 0.15 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.10. 28 0.15 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05. 29 0.10 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.15. 30 0.10 Cu3 + NOBF₄ + 0.1 M LiClO₄ in CH₃CN, Cu²⁺/(Cu²⁺ + Cu⁺) = 0.05.

Considering the second electrolyte, the best performances were those achieved with 13a, with a photocurrent and an efficiency of 18.23 mA cm⁻² and 9.11%, respectively (entry 5). Data are summarized in Table 3.

Additionally, in 2014, the same group published a paper on three new isomeric Ru(II) complexes [35] having the same three ligands, namely a simple anchoring dcbipy and two pyrazolyl-isouquinolines (structure in Figure 8). Although the ligands were the same, the compounds were different because of the relative disposition of the N’N ligands: while 14a and 14c were symmetrical, compound 14b was not. The isomers were identified by NMR spectroscopy, especially through 19F spectra to distinguish them.

Figure 8. Structure of dyes 14a–14c and 15.

The chosen ligand was an evolution of those employed in the previous work for dyes 13a–13d; the thienyl moiety on the isouquinoline system was introduced to expand the π conjugation of the ligand, whereas the function of the dihexyloxy-phenyl ring was to prevent aggregation of the molecules, providing larger steric hindrance.
The dyes were tested together with three different electrolytic solutions in acetonitrile: the first having 0.6 M DMPII + 0.05 M I₂ + 0.5 M TBP; the second 0.45 M [Co(Phen)]₃[TFSI]₂ (TFSI = trifluoromethanesulfonyl)imide + 0.15 M [Co(Phen)]₃[TFSI]₁ + 0.15 M LiTFSI + 0.8 M TBP, while the third 0.45 M DMPII + 0.05 M I₂ + 0.15 M LiI + 0.8 M TBP. Considering the first solution, compounds 14a and 14c gave the best results, with a J_sc of 12.93 and 12.41 mA cm⁻², respectively (Table 3, entries 9 and 11), versus the 9.81 mA cm⁻² of 14b (entry 10). The efficiency followed also this trend, with values of 8.37%, 5.55%, and 8.26% for dyes 14a-c (entries 9–11).

The same relationship was observed for the other iodine-based solution (i.e., the third one), with photocurrents of 14.49 and 14.84 vs. 10.39 mA cm⁻² (entries 13–15). A quite different situation appeared when employing the Co²⁺/³⁺ redox couple (entries 16–18), since dyes 14a and 14b had very close values of J_sc (13.44 and 13.30 mA cm⁻²), V_oc (0.84 and 0.82 V), Fill Factor (0.757 and 0.766), and η (8.55 and 8.36%), while 14c was the best performing, with a J_sc of 14.32 mA cm⁻² and an efficiency of 9.06% (entry 18). This phenomenon was attributed to the structure of complex 14c, having the dialkylxy-phenyl moieties oriented towards the titania layer, thus hampering the reduction in Co(III) species with the electrons injected in the semiconductor by the sensitizer. Table 3 reports all data.

In the same year Colombo, Magni, Caramori et al. tested three copper-based redox couples with the ruthenium dye 15, having two dbipy anchoring ligands and a dnbipy [36]. The chosen redox mediators were [Cu(2,9-dimethyl-1,10-phenanthroline)₂]¹⁺/²⁺ (Cu1), [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)₂]¹⁺/²⁺ (Cu2), and [Cu(2-mesityl-4,7-dimethyl-1,10-phenanthroline)₂]¹⁺/²⁺ (Cu3), all obtained as hexafluorophosphate salts.

In addition, the mentioned copper(I)/(II) compounds and the typical I⁻/I₃⁻ reference, the sensitizer was tested with an electrolytic mixture containing the iron-based co-mediators Fe1 and Fe2, where Fe1 was [Fe(dmo-bipy)₃]²⁺ and Fe2 was [Fe(dtb-bipy)₃]²⁺ (dmo-bipy = 4,4’-dimethoxy-2,2’-bipyridine and dtb-bipy = 4,4’-di-tert-butyl-2,2’-bipyridine).

The structure of 15 is shown in Figure 8, while that of the copper and iron shuttles is in Figure 9.

![Figure 9. Structure of the redox mediators Cu1-Cu3 and co-mediators Fe1-Fe2.](image-url)
Figure 10. Structure of dyes 16, 17a–17b, and 18a–18c.

The formation of the host-guest structure was confirmed by luminescence measurements, since a shift and a broadening of the fluorescence spectrum were observed. Some solar cells were fabricated using 16 with and without the presence of CM-β-CD; the best results were achieved by the 16-cyclodextrine aggregate under an excitation wavelength of 490 nm, reaching an IPCE of 3.33%, a FF of 0.81 and an open-circuit voltage of 0.54 V (Table 4, entry 3). These data showed a remarkable improvement if compared with the device having only the Ru complex, due to the more difficult recombination of triiodide and electrons on the less accessible titania surface.

Table 4. Photovoltaic data of solar cells produced with Ru(II) dyes 16, 17a–17b, 18a–18c, 19a–19d, 20a–20b, 21a–21b, 22, 23a–23d, 24a–24b, and 25.

| Entry | Dye | Redox Couple | Voc/V | Jsc/(mA cm⁻²) | FF | η (η_rel)/% | CE | Ref. |
|-------|-----|--------------|-------|---------------|----|------------|-----|------|
| 1     | 16  | I⁺/I⁻³⁻⁷     | 0.28  | 0.012         | 0.49| 0.77       | Pt-FTO | [37] |
| 2     | 16  | I⁺/I⁻³⁻⁷     | 0.52  | 0.035         | 0.78| 2.35       | Pt-FTO | [37] |
| 3     | 16  | I⁺/I⁻³⁻⁷     | 0.54  | 0.062         | 0.81| 3.33       | Pt-FTO | [37] |
| 4     | 17a | I⁺/I⁻³⁻¹¹    | 0.435 | 9.767         | 0.651| 2.79      | Pt-FTO | [40] |
| 5     | 17b | I⁺/I⁻³⁻¹¹    | 0.320 | 4.275         | 0.619| 0.85      | Pt-FTO | [40] |
| 6     | 18a | I⁺/I⁻³⁻¹³    | 0.718 | 15.31         | 0.746| 8.20      | FTO  | [41] |
| 7     | 18b | I⁺/I⁻³⁻¹³    | 0.727 | 14.17         | 0.743| 7.66      | FTO  | [41] |
| 8     | 18c | I⁺/I⁻³⁻¹³    | 0.740 | 13.53         | 0.749| 7.50      | FTO  | [41] |
| 9     | 18a | Co²⁺/Co³⁺₋₁₄ | 0.840 | 12.78         | 0.764| 8.22      | FTO  | [41] |
| 10    | 18b | Co²⁺/Co³⁺₋₁₄ | 0.844 | 13.56         | 0.742| 8.49      | FTO  | [41] |
| 11    | 18c | Co²⁺/Co³⁺₋₁₄ | 0.853 | 13.36         | 0.750| 8.55      | FTO  | [41] |
| 12    | 18a | Co²⁺/Co³⁺₋₁₅ | 0.842 | 12.17         | 0.750| 7.69      | FTO  | [41] |
| 13    | 18b | Co²⁺/Co³⁺₋₁₅ | 0.898 | 12.32         | 0.754| 8.34      | FTO  | [41] |
| 14    | 18c | Co²⁺/Co³⁺₋₁₅ | 0.900 | 13.89         | 0.762| 9.53      | FTO  | [41] |
| 15    | 19a | I⁺/I⁻³⁻¹⁷    | 0.45  | 1.18          | 0.64| 0.34      | Pt-FTO | [42] |
| 16    | 19b | I⁺/I⁻³⁻¹⁷    | 0.43  | 1.35          | 0.60| 0.35      | Pt-FTO | [42] |
| 17    | 19c | I⁺/I⁻³⁻¹⁷    | 0.56  | 5.93          | 0.69| 2.23      | Pt-FTO | [42] |
| 18    | 19d | I⁺/I⁻³⁻¹⁷    | 0.57  | 7.25          | 0.74| 3.06      | Pt-FTO | [42] |
| 19    | YE05| I⁺/I⁻³⁻¹⁷    | 0.56  | 9.42          | 0.69| 3.64      | Pt-FTO | [42] |
| 20    | N3  | I⁺/I⁻³⁻¹⁷    | 0.62  | 15.40         | 0.60| 5.72      | Pt-FTO | [42] |
Two dipirrinato ruthenium(II) complexes were published in the same year by Singh and coworkers [40]. These compounds had two dipieryl ligands and a dipirrin anionic ligand, with a 4-tolyl substituent in the case of 17a, having NiO as semiconductor. In addition, in 17b, due to unfavorable position of the HOMO level, thus limiting the application in solar cells even if having superior panchromatic light-harvesting features.

In 2016, Chi, Nazeeruddin and coworkers published other three isocyanate-free ruthenium compounds [41], whose ancillary ligands had the basic structure of a substituted pyrazolyl-isoquinoline, as for sensitizers 13c-d and 14a-c previously discussed, while the anchoring ligand was still a simple dipieryl.

As can be seen in Figure 10, complex 18a presented a CF$_3$ group on the pyrazole and a hexylthiophene on the isoquinoline, while 18b had the same ligand but with an additional Hex-thiophene on the isoquinoline. In addition, in 18e the trifluoromethyl group was substituted with a perfluorinated n-butyl chain.

These dyes were tested with three different electrolyte mixtures in acetonitrile: the first was iodine-based and contained 0.45 M PMII + 0.15 M I$_2$ + 0.15 M LiI + 0.8 M DCA in 1:1 CH$_2$CN:MeOH.

### Table 4. Cont.

| Entry | Dye | Redox Couple | $V_{oc}$/V | $J_{sc}$/mA cm$^{-2}$ | FF | $\eta$ (n$_{rel}$)/% | CE | Ref. |
|-------|-----|--------------|-----------|------------------|----|----------------|----|-----|
| 21    | 20a | 1$^-$ /I$_3$$^-$$^19$ | 0.58      | 10.20            | 0.56 | 3.32            | Pt | [43] |
| 22    | 20b | 1$^-$ /I$_3$$^-$$^19$ | 0.52      | 3.52             | 0.58 | 1.06            | Pt | [43] |
| 23    | 21a | 1$^-$ /I$_3$$^-$$^21$ | 0.56      | 8.1              | 0.610 | 2.8 (49.1)     | Pt-FTO | [44] |
| 24    | 21b | 1$^-$ /I$_3$$^-$$^21$ | 0.55      | 7.1              | 0.624 | 2.5 (43.8)     | Pt-FTO | [44] |
| 25    | 21c | 1$^-$ /I$_3$$^-$$^21$ | 0.60      | 6.5              | 0.665 | 2.6 (45.6)     | Pt-FTO | [44] |
| 26    | 21d | 1$^-$ /I$_3$$^-$$^21$ | 0.61      | 6.2              | 0.670 | 2.5 (43.8)     | Pt-FTO | [44] |
| 27    | N719| 1$^-$ /I$_3$$^-$$^21$ | 0.67      | 13.3             | 0.642 | 5.7            | Pt-FTO | [44] |
| 28    | 22  | 1$^-$ /I$_3$$^-$$^23$ | 0.79      | 7.12             | 0.61 | 3.42           | Pt-FTO | [45] |
| 29    | 23a | 1$^-$ /I$_3$$^-$$^25$ | 0.548     | 1.30             | 0.72 | 0.50 (86.2)    | FTO | [46] |
| 30    | 23b | 1$^-$ /I$_3$$^-$$^25$ | 0.564     | 2.15             | 0.70 | 0.87 (15.0)    | FTO | [46] |
| 31    | 23c | 1$^-$ /I$_3$$^-$$^25$ | 0.546     | 1.35             | 0.68 | 0.52 (8.96)    | FTO | [46] |
| 32    | 23d | 1$^-$ /I$_3$$^-$$^25$ | 0.592     | 2.55             | 0.73 | 1.10 (18.96)   | FTO | [46] |
| 33    | N719| 1$^-$ /I$_3$$^-$$^25$ | 0.693     | 11.70            | 0.71 | 5.80           | FTO | [46] |
| 34    | 24a | 1$^-$ /I$_3$$^-$$^30$ | 0.064     | 1.6              | 0.31 | 0.040          | Pt  | [47] |
| 35    | 24b | 1$^-$ /I$_3$$^-$$^30$ | 0.081     | 1.1              | 0.23 | 0.026          | Pt  | [47] |
| 36    | 25  | 1$^-$ /I$_3$$^-$$^33$ | 0.6       | 5.82             | 0.52 | 1.82           | Pt  | [48] |
| 37    | 25  | Spiro-OMeTAD 33      | 0.68      | 3.04             | 0.6  | 1.26           | Au  | [48] |

1 AM 1.5 simulated light source; input intensity of 100 mW cm$^{-2}$. 2 having TiO$_2$ as semiconductor if not differently indicated. 3 CE: counter electrode. 4 0.03 M dye in EtOH. 5 Power intensity non specified. 6 Excitation wavelength of 450 nm. 7 Electrolyte formulation non specified. 8 With cyclodextrin solution (0.029 g/mL in water). 9 Excitation wavelength of 490 nm. 10 0.3 mM dye + 0.02 M DCA in 1:1 CH$_2$CN:nBuOH. 11 DMPII (unspecified concentration) + 0.1 M Li+ + 0.05 M I$_2$ in CH$_2$CN. 12 0.3 mM dye in 4:1 EtOH:DMSO. 13 0.45 M PMII + 0.15 M LiI + 0.15 M I$_2$ + 0.8 M TBP in CH$_2$CN. 14 0.6 M [Co(bipy)$_2$][TFSI]$_2$ + 0.15 M [Co(bipy)$_3$][TFSI]$_2$ + 0.15 M LiTFSI + 0.8 M TBP in CH$_2$CN. 15 0.6 M [Co(Phen)$_2$][TFSI]$_2$ + 0.15 M LiTFSI + 0.8 M TBP in CH$_2$CN. 16 0.25 mM dye in MeOH. 17 0.6 M DBII + 0.05 M Li+ + 0.03 M I$_2$ in 85:15 CH$_2$CN:nBuCN (DBII = 1,3-dibutylimidazolium iodide). 18 0.3 mM dye + 0.04 M DCA in 1:1 CH$_2$CN:BuOH:DMSO. 19 Solaronix Iodolyte AN-50. 20 0.12 mM dye in 3:1 CH$_2$CN:nBuOH. 21 0.6 M TBAI + 0.1 M LiI + 0.1 M I$_2$ + 0.5 M TBP in 3-methoxypropionitrile (TBAI = tetrabutylammonium iodide). 22 0.3 mM dye in MeOH. 23 0.6 M DMPII + 0.1 M LiI + 0.05 M I$_2$ + 1.0 M TBP in CH$_2$CN. 24 0.3 mM dye in EtOH. 25 0.6 M PMII + 0.1 M LiI + 0.05 M MgI$_2$ + 0.1 M I$_2$ in CH$_2$CN. 26 Not specified if with Pt or PEDOT. 27 Having NiO as semiconductor. 28 450 nm light, power not specified. 29 0.5 mM dye in MeOH. 30 0.1 M TBAI + 0.1 M LiI + 0.05 M I$_2$ + 0.4 M TBP in CH$_2$CN. 31 0.5 mM dye in CH$_2$CN or DCM. 32 0.3 mM dye in CH$_2$CN:BuOH:1:1. 33 solutions A (97 mg/mL of Spiro-OMeTAD in chlorobenzene), B (175 mg/mL of LiTFSI in CH$_2$CN) and C (46.6% v/v solution of TBP in CH$_2$CN) were prepared separately. 1200 $\mu$L of solution A + 36.24 $\mu$L of solution B + 11.7 $\mu$L of solution C were mixed and deposited over the substrate through spin coating; the substrate was then sintered under nitrogen.
TBP; the second contained 0.6 M [Co(bipy)]_2[TFSI]_2 + 0.15 M [Co(bipy)]_3[TFSI]_3 + 0.15 M LiTFSI + 0.8 M TBP, while the third 0.6 M [Co(Phen)]_2[TFSI]_2 + 0.15 M [Co(bipy)]_3[TFSI]_3 + 0.15 M LiTFSI + 0.8 M TBP.

Coupled with the cobalt-phenanthroline redox mediators, 18c gave the best results, with a J_sc of 13.89 mA cm^{-2}, a V_oc of 900 mV, a FF of 0.762 and an efficiency of 9.53% (Table 4, entry 14). On the contrary, sensitizers 18a and 18b reached the highest photocurrents (15.31 and 14.17 mA cm^{-2}, respectively, entries 6 and 7) with the I^-/I_3^- electrolytes, even if with lower efficiencies (8.20 and 7.66%). All data are listed in Table 4.

Rochford and coworkers published in 2017 an extensive study on four new 8-oxoquinolate-based Ru(II) dyes [42], whose performances were compared to those of the known sensitizers N3 and YE05 (structure of both compounds in Figure 1).

Compound 19a had two dcbpy ligands and a simple 8-oxoquinolate, while dyes 19b-19d presented more electron-withdrawing substituents on the quinoline, aiming at the reduction in the electron-donating strength of this ancillary ligand, hence improving its redox properties without limiting its light-harvesting ability. In 19b a fluorine atom was present in position 5 of the quinoline, while in 19c two pentafluoro-phenyl rings in positions 5 and 7. Finally, in compound 19d the N^O ligand was replaced with a N^N one, having an amidic nitrogen donor-atom in position 8, as shown in Figure 11.

![Figure 11. Structure of dyes 19a–19d and 20a–20b.](image)

The redox properties of these complexes came from the fact that the ancillary ligands were non-innocent, since a mixing of the metal-dπ and ligand-π orbitals occurred, generating hybrid metal–ligand frontier orbitals.

The novel dyes and the two reference sensitizers were tested under 1 sun conditions (100 mW cm^{-2}) using iodine-based electrolyte solutions containing 0.60 M 1,3-dimethylimidazolium iodide + 0.03 M I_2 + 0.10 M guanidinium thiocyanate + 0.50 M TBP in a 85:15 mixture of acetonitrile and valeronitrile. Among the new dyes, 19a and 19b showed very poor results (Table 4, entries 15–16) when applied in solar cells, while 19d gave the best results, with a J_sc of 7.25 mA cm^{-2}, a V_oc of 0.57 V and an efficiency of 3.06% (entry 18), so approaching the values obtained by YE05 (entry 19), but still being much less performing than N3 (entry 20).

In the work of El-Shafei and coworkers from 2017, two new heteroleptic Ru complexes were published [43], having an anchoring dcbpy, a tetramethyl bis-imidazole and a bipyridine bearing an electron-donating moiety, namely a diphenylamino-phenyl group in the case of 20a and a N-ethyl-carbazolyl moiety in 20b (Figure 11).

Considering the short-circuit current and the efficiency, the best results in the produced solar cells were given by 20a, with a J_sc of 10.20 mA cm^{-2} and a η of 3.32% (Table 4, entry 21), being around three times higher than the corresponding results of 20b (entry 22).

A different manner to reduce the recombination of the oxidized redox shuttle with the electrons on the titania surface was tested and published by Araki and coworkers in 2017 [44]; in this paper, they described a family of ruthenium(II) complexes (structure in Figure 12) having two dcbpy ligands and two benzotriazoles (btzH) ancillary ligands, whose degree of deprotonation was investigated by titration of an acidic solution of the dye by means of NaOH.
species, an opposite trend was observed, with the others had two monodentate 4-R-phenyl-tetrazole (R = CN for nate moiety improved the binding ability of the compounds.

In 2020, Sangiorgi, Caramori, Stagni et al. published three novel ruthenium(II) sensitizers, having in common two dcbipy ligands [46]; complex 21a, being dcbipyH the monoprotonated 2,2′-bipyridine-4,4′-dicarboxylic acid) at pH 2, the increase in pH up to a value of 4.2 gave complex 21b, i.e., [Ru(dcbipy)2(btzH)][TBA]2, then [Ru(dcbipy)2(btzH)(btz)][TBA]2 at pH = 9 (21c) and finally [Ru(dcbipyH)2(btzH) (btz)][TBA]4 (21d) at pH = 13. All these compounds were isolated and tested in DSSCs, in order to study the effect of a growing electron density around the metal complex, coming from a higher deprotonation of both the anchoring and the ancillary ligands.

According to impedance measurements, the concept of the electrostatic blocking barrier was successfully demonstrated by the result that the highest recombination resistance was provided by complex 21d; the trend of the resistance was the following: 21d > N719 > 21c > 21b > 21a, including also sensitizer N719 as reference dye.

Considering the performances of the solar cells sensitized with the mentioned Ru species, an opposite trend was observed, with 21a giving a $J_{sc}$ of 8.1 mA cm$^{-2}$ and an efficiency of 2.8% (Table 4, entry 23), while 21d a $J_{sc}$ of 6.2 mA cm$^{-2}$ and a $\eta$ of 2.5% (entry 26).

In 2019, a new heteroleptic complex was published by Swarnalatha and coworkers [45]. This compound (22, structure in Figure 13) had two bipy ligands and a neutral nitro-substituted N′N ligand binding the metal with an amine and an enamine group. The produced device had an efficiency of 3.42%, a $J_{sc}$ of 7.12 mA cm$^{-2}$, a $V_{oc}$ of 0.79 V and a Fill Factor of 0.61 (Table 4, entry 28).

In 2020, Sangiorgi, Caramori, Stagni et al. published three novel ruthenium(II) sensitizers, having in common two dcbipy ligands [46]; complex 23a had a tetrazolyl-pyrindine (similar to the previously published complex 23b, having a tetrazolyl-pyridine [49]), while the others had two monodentate 4-R-phenyl-tetrazole (R = CN for 23c and Br for 23d), bound to the metal through the deprotonated nitrogen atom (structure in Figure 13).

Table 4 lists photovoltaic data for the discussed compounds. When tested in solar cells, the best results were obtained by 23d, with a $J_{sc}$ of 2.55 mA cm$^{-2}$, a FF of 0.73 and an efficiency of 2.5% (entry 26).

In the same year Jacob, Rau and coworkers presented a Ru complex (24b) having a simple 2,2′-bipyridine and two bipyridines substituted in positions 4 and 4′ with CH$_2$P(=O)(OSiMe)$_3$$_2$ chains [47]; this was a development of the similar complex 24a, bearing -CH$_2$PO$_3^{2-}$ chains; the structure of the two compounds is shown in Figure 14.

![Figure 12. Structure of dyes 21a–21d.](image1)

![Figure 13. Structure of dyes 22 and 23a–23d.](image2)
The dyes were tested in DSSCs having a layer of NiO over the FTO semiconductor; in fact, the phosphonate groups were the best anchoring groups on such type of metal oxide and, moreover, the methylene spacer between the pyridine ring and the phosphonate moiety improved the binding ability of the compounds.

The best performances were reached by sensitizer 24a, with a Jsc of 1.6 mA cm$^{-2}$ and an efficiency of 0.040% (Table 4, entry 34).

In 2021, Pirashanthan, Thanhaichelvan, Mariappan et al. [48] described a simple ruthenium dye (25, Figure 14) having two unsubstituted 2,2$'$-bipyridine and a 4,4$'$-dicarboxy-2,2$'$-bipyridine ligands with two perchlorate counterions. The dye was tested in DSSCs fabricated with both a conventional liquid electrolyte and with a solid one.

The absorption spectra showed a strong absorption band in the near UV region and a decay tailing around 516 nm. When compared to the reference dyes N719, N3, and Z907, 25 showed a higher molar absorption coefficient.

The photovoltaic performances of 25 were tested in two different manners: in the former, by employing a liquid electrolyte based on the I$^-$/I$_3^-$ redox couple, in the latter having the solid electrolyte Spiro-OMeTAD. Differently from the device fabricated with the liquid electrolyte, the one containing the solid electrolyte showed a broader absorption spectrum, and the presence of the dye increased the gap between the conduction band of the TiO$_2$ layer and the HOMO of the Spiro-OMeTAD from 1.0 eV to 1.4 eV, hence reducing the electron recombination. The sensitizing of TiO$_2$ with 25 assisted the electron transport from Spiro-OMeTAD in the reduction in the oxidised dye to its reduced form, and acted as a hole-blocking layer. The measured J$_{SC}$ and V$_{OC}$ were higher in the device containing the solid electrolyte, but on the contrary the efficiency of this device was lower than that of the one fabricated with the liquid electrolyte (Table 4, entries 36–37).

3. Conclusions

Through this review we have shown the last developments in the research of novel thiocyanate-free bipyridine ruthenium(II) complexes to be employed as sensitizers in dye-sensitized solar cells. The compounds we have focused our attention on are characterized by a bipyridine ligand bearing or not an anchoring group such as a carboxylic moiety, through which the complex is bound to the semiconductor layer of the photoanode.

The presented bipyridine-based dyes can be divided into two categories depending on the ancillary and main light-harvesting ligand, being a N'C cyclometalating ligand in the first case and a N'N or N'O in the second one. The cyclometalated sensitizers usually share a 2-phenylpyridine or a 2-thienylpyridine, bearing different substituents or an extended aromatic system. On the other hand, the non-cyclometalated dyes often present anionic species binding the metal via nitrogen atoms, such as pyrazolyl- or tetrazolyl-pyridines, pyrazolyl-quinolines, dipyrrins, hydroxy-quinolines, bis-imidazoles, benzotriazoles.

Remarkably, efficiencies similar to that of N719 have been reached with well designed thiocyanate-free ruthenium(II) 2,2$'$-bipyridyl complexes with either a cyclometalating or non-cyclometalating bidentate ancillary ligand. Particularly efficient are tris-heteroleptic cyclometalated Ru(II) complexes having a 2,2$'$-bipyridine-4,4$'$-dicarboxylic acid molecule as anchoring ligand, a bipyridine with aromatic substituents in the 4 and 4$'$ positions as main...
light-harvesting moiety and a 2,6-didodecyloxy-3,2′-bipyridine as ancillary C=N ligand, where the long alkyl chains prevent the access of the redox mediators to the semiconductor surface. Another interesting sensitizer is a Ru(II) complex bearing two 2,2′-bipyridine-4,4′-dicarboxylic acid ligands and a cyclometalating 2-phenylpyridine substituted with two CF<sub>3</sub> groups on the phenyl ring, in meta positions with respect to the Ru-bound carbon atom, and with 5-hexylthio-3,4-ethylendioxythiophen-2-yl group in para position of the pyridine; its use in DSSCs led to better performances (9.03%) than those of devices produced with the classical N719 dye (8.63%) in the same fabrication conditions. Very appealing are also ruthenium complexes bearing two phenylquinolines and a cyclometalating 2-(4-methoxyphenyl)pyridine and ruthenium complexes bearing a 2,2′-bipyridine-4,4′-dicarboxylic acid ligand and two hexythienyl-substituted pyrazolyl-pyridines or pyrazolyl-isoquinolines, allowing efficiencies similar to that reached with N719.

The discussed works, which represent only a limited sample of the many families of compounds published about NCS-free ruthenium(II) dyes from the year 2014, not only demonstrate that a valid alternative to thiocyanate ligands in the aforementioned dyes is possible, but that the results can be even better than the usual reference sensitizers, paving the way to further investigations to improve the performances of the devices.

To conclude, it should be pointed out that a proper molecular design of the dye is surely essential, but it is not the only factor to be taken into account, since a suitable choice of the electrolyte mixture, of the additives and of the fabrication method is crucial to optimize the photovoltaic results and to reach in the future a wide application of such solar cells in everyday life.

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