

Review

Recent Developments of Ruthenium Complexes for Dye-Sensitized Solar Cells

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Abstract: Almost forty years ago, dye-sensitized solar cells (DSSCs) appeared as a promising route for harnessing the energy of the sun and for converting it into electricity. In the following years, a huge number of studies have been dedicated to increase the global photovoltaic efficiencies and stability of DSSCs. Thiocyanate ruthenium complexes bearing chelating nitrogen donor ligands turned out to be among the best performing photosensitizers. In the last 15 years, a lot of work has also been dedicated to the preparation of efficient thiocyanate-free Ru dyes. In this review, these two families of ruthenium(II) complexes are presented: (a) dyes presenting thiocyanate ligands and (b) thiocyanate-free dyes. The coverage, mainly from 2021, is not exhaustive, but exemplifies the most recent design approaches and photovoltaic properties of these two classes of Ru(II) photosensitizers.

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



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1. Introduction

One of the major challenges in the world is replacing fossil fuels with renewable and low-cost energy sources necessary for the growing global energy request while minimizing harmful climate and environmental impacts. Sunlight offers a clean and convenient energy spring that could play a key role in forthcoming energy solutions [1].

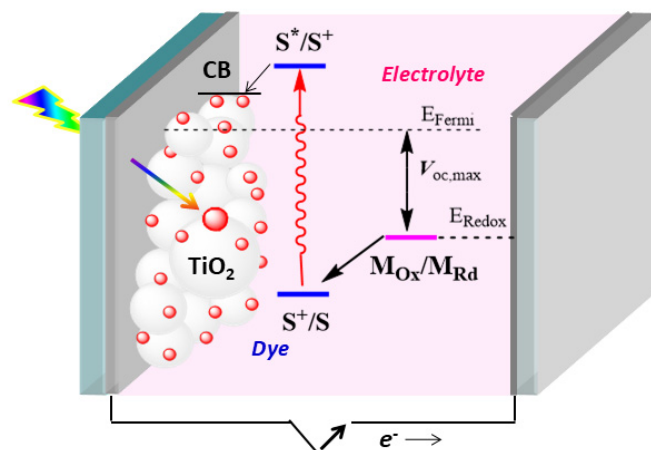
Among the various kinds of photovoltaic devices, dye-sensitized solar cells (DSSCs) [2–4] have attracted growing interest and are seen as a practical option for capturing sunlight and converting it into electricity. A DSSC consists of the following key components: a substrate coated with a transparent conductive oxide; a semiconductor film; a dye adsorbed onto the surface of the semiconductor; an electrolyte containing a redox mediator; and a counter electrode that regenerates the redox mediator. The dye absorbs sunlight, generating an exciton; charge separation and generation then occur at the semiconductor–dye interface. Finally, the semiconductor and electrolyte function as charge transport materials that collect charges at the electrodes. As such, the photosensitizer is critical to DSSC technology.

Scheme 1 shows the general structure and working mechanism of a DSSC.

The efficiency of the DSSC depends on the suitable choice of all the components of the cell, in order to optimize the kinetics and the energetics of all the involved processes [2–4]. The global conversion efficiency (η , which represents the fraction of incident power that is converted into electric energy) depends on various parameters [2–7]:

- (a) The short-circuit current density (J_{sc} , which is the maximum current density in the DSSC when the applied voltage is zero);

- (b) The open-circuit potential (V_{oc} , which represents the maximum voltage available from the DSSC when there is no current);
- (c) The fill factor (FF, which is the ratio between the maximum power of the DSSC and the product of V_{oc} and J_{sc} ; having values between 0 and 1, it reflects electrical and electrochemical losses during operation of the cell);
- (d) The intensity of the incident light (I_s , commonly set to 100 mW cm^{-2} , under air mass 1.5 global illumination, AM1.5 G).



Scheme 1. General structure and working mechanism of a dye-sensitized solar cell.

The efficiency value can be obtained with the following equation:

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{I_s}$$

Ruthenium complexes with bipyridine ligands like *cis*-di (thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylate)Ru(II) (**N3**) and the parent doubly deprotonated compound (**N719**) are amongst the most efficient photosensitizers with the iodide/triiodide couple (I^-/I_3^-) as the electrolyte (Figure 1) [5–7].

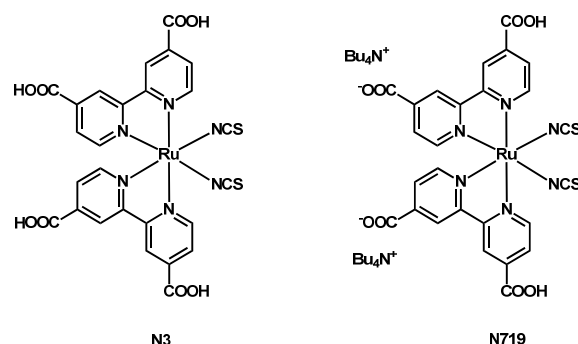


Figure 1. Structure of the reference dyes **N719** and **N3**.

Besides the mentioned dyes **N3** and **N719**, commonly considered reference compounds when testing new sensitizers, in recent decades many other Ru-based complexes belonging to that family have been proposed and applied, with various substituents on the bipyridine ligands in order to tune the electronic properties by expanding the aromatic system and introducing heteroaromatic rings [8–12].

A drawback of Ru thiocyanato sensitizers is their vulnerability to long-term chemical degradation, due to the substitution of the thiocyanate ligands with other molecules, resulting in less efficient dyes, with a significant loss in device performances. Thiocyanate

acts as an ambidentate ligand, capable of coordinating either at the sulfur or nitrogen atom, and as a monodentate ligand, and it can be readily displaced by other molecules, such as 4-*tert*-butylpyridine, used to improve the cell efficiency (η) [13–15]. Thus, it was shown that the substitution of one thiocyanate ligand by 4-*tert*-butylpyridine leads to a drastic cell efficiency reduction (ca 50%) due to a lower light harvesting efficiency (caused by a ca. 30 nm blue shift in the absorption spectrum of the dye), a shorter electron diffusion length, and a lower charge separation efficiency [16].

To address these limitations, in 2007, Van Koten et al. presented the first example of a thiocyanate-free Ru sensitizer with chelating tetradentate ligands, although with a moderate cell efficiency [16]. This work opened the door to a novel class of ruthenium dyes: the thiocyanate-free photosensitizers.

Thus, following this pioneering work, many researchers have substituted thiocyanate ligands with other chelating ligands, such as bi-, tri-, or tetradentate ligands, which may be cyclometalated or not [17–33].

Researchers are continuing to work from an experimental point of view on both ruthenium complexes with thiocyanate and without thiocyanate. Some reviews cover the results achieved up to 2021 [34–36].

In the present review, we will illustrate the latest developments, obtained experimentally since 2021, on these two families of ruthenium(II) compounds: (a) dyes presenting thiocyanate ligands and (b) thiocyanate-free dyes.

2. Dyes Presenting Thiocyanate Ligands

Concerning the photosensitizers with the thiocyanate group, the papers reported in the literature are different from each other, but it is possible to divide the complexes in three groups.

The first group includes ruthenium complexes that have a substituted terpyridine bearing the anchoring group, the second group involves several ruthenium complexes with a bipyridine bearing the anchoring groups, and the third group involves a co-sensitization between N719 and various organic chromophores.

2.1. Ru–Thiocyanate Dyes with Terpyridines Bearing the Anchoring Group

Naziruddin et al. [37] presented Ru(II) complexes 1–4, bearing an *N*-heterocyclic carbenic chelating ligand, an NCS, and a COOH-functionalized terpyridine to anchor the compound to the TiO₂ layer. The last synthetic steps caused the formation of distinct isomeric forms of the dye, with different electronic properties due to the ligands' arrangement around the metal center; the structure of the obtained sensitizers is reported in Figure 2.

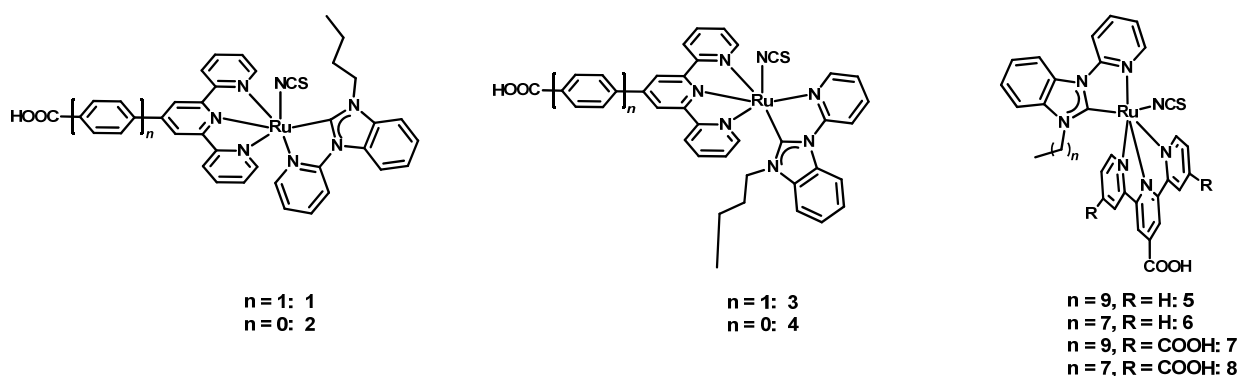


Figure 2. Structure of dyes 1–8.

The results indicate that complexes lacking the phenylene bridge between the acid anchor and the terpyridine absorb visible light more efficiently. When visible light is

absorbed, the electron density is transferred from the Ru, NHC, and NCS donors to the terpyridine acceptor.

In complexes where the NHC and terpyridine ligands are oriented oppositely, the stronger Ru–ligand σ -bonds facilitate easier oxidation of the ruthenium center. In contrast, oxidation of the metal center in complexes with trans-oriented NHC and NCS ligands is more challenging. Despite this, the compounds exhibit a better photon conversion efficiency in dye-sensitized solar cells.

One of these complexes (**4**) has an η of 3.44%, that is ~70% of the **N3** standard dye under the same conditions, this representing a relevant result. Complete data are reported in Table 1.

Table 1. Photovoltaic values of DSSCs fabricated with terpy-Ru(II) sensitizers **1–10**¹.

	Dye	$\lambda_{\max, \text{abs}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	$J_{\text{sc}} (\text{mA cm}^{-2})$	Voc (V)	FF	η (%)	Refs.
1	1 ²	283 [14.227] 316 [7.878] 486 [1.615] 233 [25.945]	0.525	0.577	63	0.191	[37]
2	2 ²	280 [23.143] 321 [17.292] 482 [4.180] 281 [25.352]	2.245	0.598	73	0.980	
3	3 ²	318 [14.852] 485 [3.466] 233 [53.720]	0.786	0.574	65	0.294	
4	4 ²	277 [47.545] 320 [36.568] 479 [8.971]	7.982	0.643	67	3.440	
5	N3 ²	-	16.832	0.559	53	4.977	[38]
6	5 ²	279 [48.4] 324 [21.1] 496 [4.7] 281 [84.5]	6.70	0.64	54	2.32	
7	6 ²	322 [50.5] 497 [11.0] 283 [55.3]	3.10	0.65	75	1.51	
8	7 ²	324 [32.0] 507 [6.1] 280 [73.7]	1.21	0.47	73	0.42	
9	8 ²	323 [46.1] 505 [8.9]	3.55	0.54	54	1.04	[39]
10	N3 ²	-	12.0	0.67	58	4.66	
11	9 ²	283 [109.120] 318 [52.080] 499 [14.600] 280 [75.960]	1.602	0.648	44.0	0.460	
12	10 ²	321 [50.920] 492 [10.760]	3.792	0.678	55.1	1.410	
13	N3 ²	-	16.832	0.559	52.9	4.980	

¹ Under AM 1.5 simulated light source; having TiO₂ as a semiconductor, Pt as a counter electrode, and 0.1 M LiI + 0.06 M I₂ + 0.5 M 1-butyl-3-methylimidazolium iodide in ACN as an electrolytic mixture. Absorption spectra registered in ACN. ² 0.6 mM in 1:1 ACN:tBuOH.

Some of the authors of reference [37] along with some colleagues [38] presented various heteroleptic Ru(II) compounds with N-heterocyclic carbene (NHC)-based C⁺N donor sets,

functionalized with long lipophilic chains (*n*-octyl and *n*-decyl) and thiocyanate ligands (5–8), as shown in Figure 2. These compounds employ monocarboxy or tricarboxy terpyridine ligands as anchoring groups to attach TiO₂. The preparative strategy predominantly led to the formation of compounds with NCS and NHC ligands in a *trans* configuration. These compounds display a broader visible light absorption extending up to 750 nm. Enhanced electron donation from the NCS ligand and the C⁺N moiety drives metal–ligand-to-ligand charge transfer excitations, which shift the electron density towards the anchoring carboxylate groups. Complex 5 demonstrated the best power conversion efficiency, which is approximately half that of N3 (2.32 vs. 4.66%, all data in Table 1).

In 2022, Naziruddin et al. proposed two new Ru(II) dyes (9–10, see Figure 3) bearing a terpyridine ligand together with a chelating carbenic bis-imidazole-2-ylidene and a thiocyanate completing the octahedral coordination sphere [39]; the authors also investigated the influence of the linker between the terpyridine scaffold and its COOH anchoring group: in 9 a phenylene spacer linked the two moieties, while in 10 the carboxylic group was bound directly to the central pyridine ring.

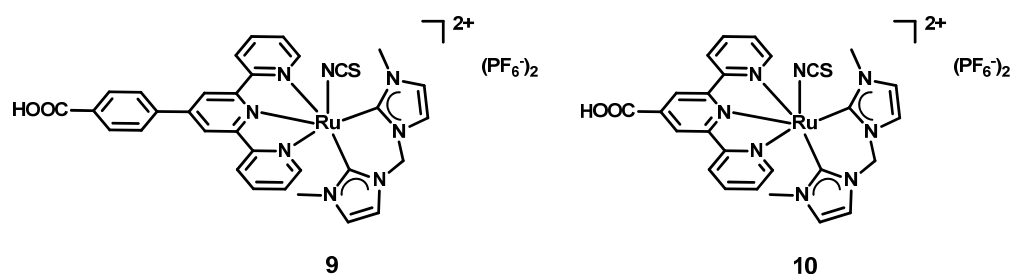


Figure 3. Structure of dyes 9–10.

Complexes 9–10 were tested as dyes in DSSCs together with iodine-based redox mediators, with the best results ($J_{SC} = 3.792 \text{ mA cm}^{-2}$, $V_{OC} = 678 \text{ mV}$, $\eta = 1.41\%$) being achieved with 10, i.e., the dye having no spacer between the COOH group and the terpyridine. Furthermore, the presence of the thiocyanate allowed for a wider absorption range, reaching 800 nm and causing a better overall result of the sensitized device.

Finally, the phenylene spacer caused torsional issues which were detrimental for the solar cells, with lower short-circuit current densities ($1.602 \text{ vs. } 3.792 \text{ mA cm}^{-2}$ in 9 and 10, respectively) and efficiencies (0.460 vs. 1.410% in 9 and 10). For data, see Table 1.

2.2. Ru–Thiocyanate Dyes with Bipyridines Bearing the Anchoring Groups

El-Shafei et al. [40] introduced two novel heteroleptic polypyridyl ruthenium(II) complexes incorporating heteroaromatic electron-donor *N*-alkyl-2-phenylindole units into the ancillary ligand (Figure 4). The main goal was to assess the electron-donor influence of the indole groups on the photoresponsive properties and how the length of the alkyl chains attached to *N*-indole affects charge recombination resistance. The photovoltaic performance of 12 overcame that of N719, achieving a very high overall efficiency of 8.14%, compared to N719 at 7.74%. The improved performance of complex 12 can be attributed to the long alkyl chains, which reduced dye aggregation and minimized charge recombination. Additionally, the incorporation of indole groups with long alkyl chains further improved the photovoltaic efficiency relative to N719 with bi-anchoring ligands. See Table 2 for complete data.

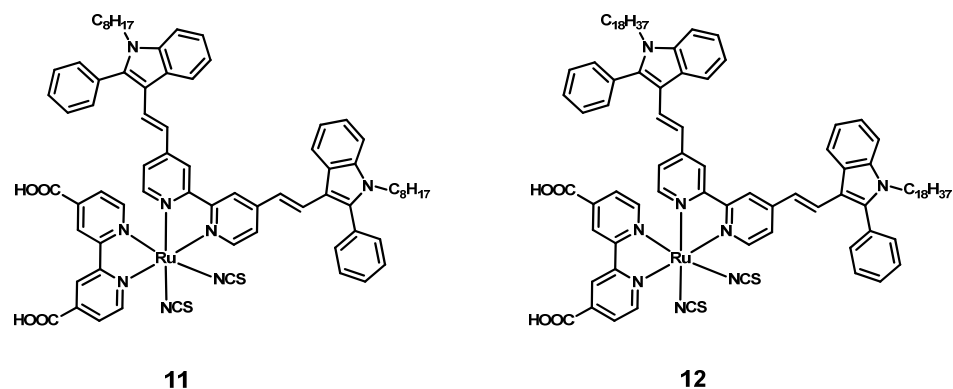


Figure 4. Structure of dyes **11–12**.

Table 2. Photovoltaic values of DSSCs fabricated with bpy-Ru(II) sensitizers **11–12** and **17–19** ¹.

Entry	Dye	$\lambda_{\max, \text{abs}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	Redox Couple	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	Refs.
1	11 ²	297 [63.1] 372 [15.3] 516 [10.1]	I^-/I_3^- ³	13.94	0.594	60.3	4.99	[40]
2	12 ²	297 [66.6] 371 [15.3] 525 [14.6]		19.21	0.675	62.7	8.14	
3	N719 ²	-		19.11	0.693	58.5	7.74	
4	17 ⁴	377 [66.9] 569 [33.4]	I^-/I_3^- ⁵	17.13	0.714	70.57	8.63	[41]
5	18 ⁴	352 [49.4] 563 [27.6]		14.08	0.646	73.05	6.64	
6	19 ⁴	353 [54.5] 563 [28.6]		16.32	0.722	71.11	8.38	
7	N719 ⁴	-		13.34	0.787	74.37	7.75	

¹ Under AM 1.5 simulated light source; having TiO_2 as a semiconductor and Pt as a counter electrode. Absorption spectra registered in DMF. ² 0.3 mM in 1:1:1 ACN:tBuOH:DMSO, in the presence of deoxycholic acid. ³ 0.1 M LiI + 0.05 M I_2 + 0.6 M 1-propyl-2,3-dimethylimidazolium iodide + 0.5 M TBP in ACN. ⁴ 0.1 mM in ACN:tBuOH:DMSO. ⁵ 0.1 M LiI + 0.03 M I_2 + 0.6 M 1-butyl-3-methylimidazolium iodide + 0.5 M TBP + 0.1 M guanidinium thiocyanate.

In 2023, Sidrah, Zafar et al. [42] introduced four new ruthenium(II) dyes with a core structure based on 2-(2-pyridyl) benzimidazole, incorporating both electron-donor and electron-acceptor groups (**13–16**, see Figure 5). To gain a deeper understanding of the property–structure relationships of these sensitizers, density functional theory (DFT) and time-dependent DFT were applied. The results revealed an excellent correlation between theoretical and experimental findings. The sensitizers demonstrated low singlet excitation energies and narrow band gaps, suggesting strong light-harvesting capabilities in dye-sensitized solar cells (DSSCs). While the potential of these sensitizers was highlighted, DSSC performance data were not provided.

In 2024, Chia-Yuan Chen et al. obtained excellent new results [41], proposing three new heteroleptic Ru complexes (**17–19**, Figure 6) as dyes for coadsorbent-free, panchromatic, and efficient DSSCs. They are functionalized with conjugated ligands to investigate the steric and electronic effects on their photovoltaic efficiency. The coadsorbent-free device fabricated with complex **17** reached the best power conversion performance (8.63%) and a wide panchromatic answer extending to 850 nm. They also studied different stereoisomers, concerning the absorption properties and the related cell efficiency and stability (data in Table 2). Their investigation on the steric effects caused by the highly conjugated and unsymmetrical anchoring ligand on the adsorption geometry and photovoltaic performance

of the dyes opens a new way for advancing the molecular design of polypyridyl metal complex sensitizers.

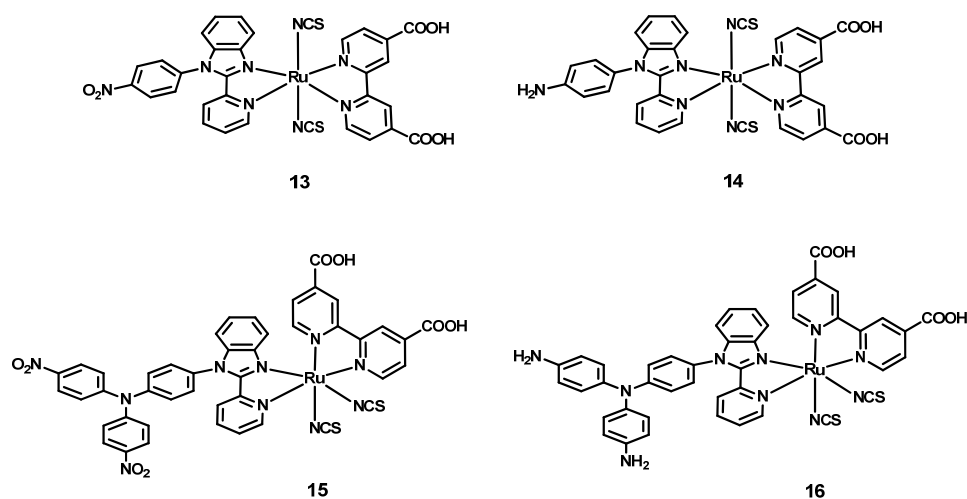


Figure 5. Structure of dyes 13–16.

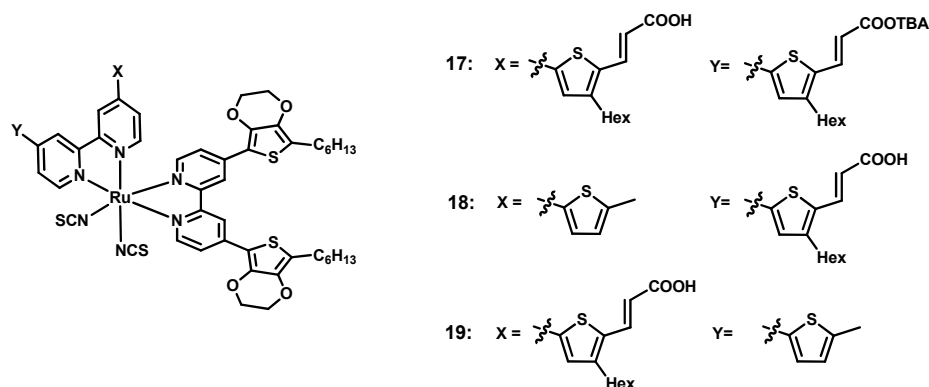


Figure 6. Structure of dyes 17–19.

2.3. Co-Sensitization Between N719 and Organic Chromophores

Co-sensitization is another important topic. Aldusi et al., in 2022 [43], reported a comprehensive photovoltaic investigation of eight organic, low-cost 2-cyano-*N*-thiazolyacrylamide co-sensitizers for dye-sensitized solar cells with the standard Ru(II) sensitizer **N719**.

The co-sensitization, achieved through the absorption of the organic co-sensitizers **O1–O8** (structure in Figure 7), results in a broader light-harvesting range and boosts photovoltaic efficiency, with values ranging from 6.08% to 9.30%. In particular, the device incorporating the bis(2-cyanoacetamide) co-sensitizer achieved the highest power conversion efficiency (9.30%), surpassing the performance of the standard dye **N719** (7.30%). The significant enhancement due to the co-sensitizer **O7** on the **N719**'s performance can be attributed to improvements in both the short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}). The higher J_{SC} value is linked to the maximum dye loading capacity on the TiO_2 surface, due to the introduction of two anchoring groups in the sensitizer. The intensification in V_{OC} is explained by the superior recombination resistance, which is a result of multi-anchoring moieties, as evidenced by electrochemical impedance spectroscopy.

Very recently, in 2024, Badawy and coworkers [44] reported the preparation and characterization of 2-acetonitrile-benzoxazole sensitizers **O9–O11** (structure reported in Figure 8), bearing various donor groups. Computational simulations were conducted to assess their efficiency as dyes or co-dyes for photovoltaic devices. The simulations revealed a clear separation of charges between the acceptor and the donor moieties. Among the

tested dyes, **O12** exhibited the highest performance, outperforming the reference compound **O13**. Furthermore, **O11** was co-sensitized with the standard **N719**, enhancing light absorption across a broader spectral range and thus boosting efficiency. The co-sensitizer combination **O11** + **N719** achieved an efficiency of 10.20%, surpassing the performance of a DSSC with **N719** alone as the sensitizer, which was characterized by an efficiency of 7.50%. The optimal dye loading of **O11** + **N719** facilitated an effective harvesting of light and allowed to maximize photoexcitation, resulting in improved solar cell performance. For complete data see Table 3.

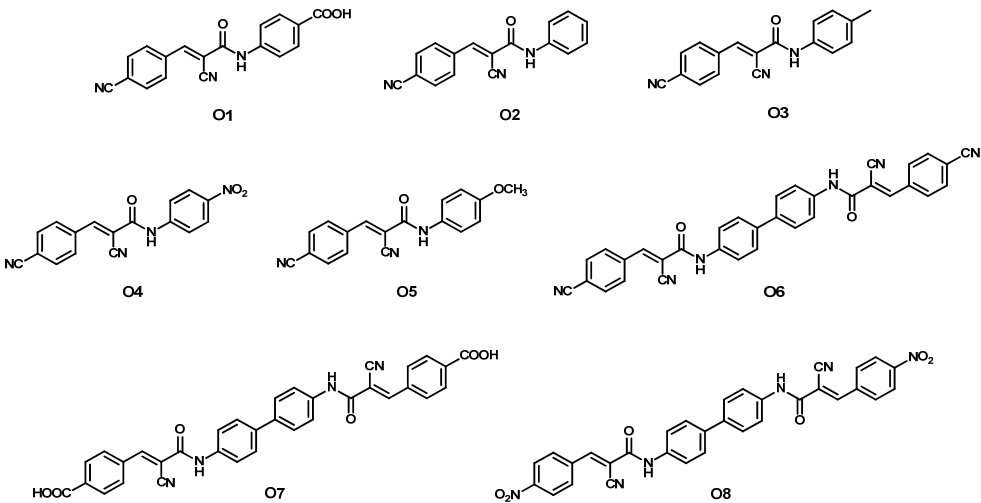


Figure 7. Structure of organic dyes **O1–O8**.

Table 3. Photovoltaic values of DSSCs fabricated by co-sensitizing **N719** with organic dyes **O1–O13** ¹.

Entry	Dye	$\lambda_{\text{max, abs}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	$J_{\text{sc}} \text{ (mA cm}^{-2}\text{)}$	$V_{\text{oc}} \text{ (V)}$	FF	$\eta \text{ (%)}$	Refs.
1	O1 + N719 ²	-	19.17	0.62	65.40	7.78	[43]
2	O2 + N719 ²	-	16.09	0.60	63.01	6.08	
3	O3 + N719 ²	-	17.25	0.60	63.56	6.57	
4	O4 + N719 ²	-	18.49	0.65	60.32	7.25	
5	O5 + N719 ²	-	17.95	0.61	65.03	7.12	
6	O6 + N719 ²	-	20.29	0.69	62.14	8.70	
7	O7 + N719 ²	-	20.96	0.73	60.78	9.30	
8	O8 + N719 ²	-	19.68	0.66	64.99	8.38	
9	N719 ³	-	18.68	0.64	61.00	7.30	[44]
10	O9 ³	321 [21.6] 460 [50.9]	10.49	0.575	52.02	3.13	
11	O10 ³	324 [23.3] 480 [56.8]	11.17	0.625	54.85	3.82	
12	O11 ³	322 [23.5] 495 [63.4]	11.65	0.610	57.43	4.08	
13	O12 ³	325 [26.2] 546 [79.2]	13.60	0.651	70.82	6.27	
14	O13 ³	-	12.68	0.632	74.10	5.93	
15	N719 ³	-	19.13	0.771	50.85	7.50	
16	O11 + N719 ²	-	21.96	0.791	58.72	10.20	

¹ Under AM 1.5 simulated light source; having TiO_2 as a semiconductor, Pt as a counter electrode, and 0.1 M LiI + 0.05 M I_2 + 0.6 M 1-propyl-2,3-dimethylimidazolium iodide + 0.5 M TBP in ACN as an electrolytic mixture. ² 0.2 mM dye + 0.2 mM **N719** in 1:1:1 ACN:*t*BuOH:DMSO. ³ 0.2 mM **N719** in 1:1:1 ACN:*t*BuOH:DMSO.

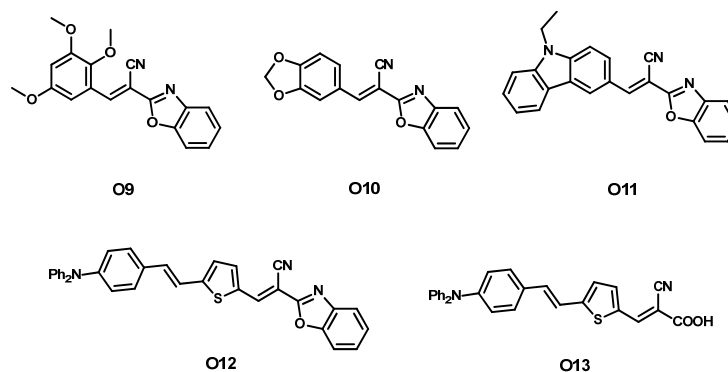


Figure 8. Structure of organic dyes O9–O13.

3. Thiocyanate-Free Dyes

Thiocyanate ruthenium complexes featuring chelating nitrogen donor ligands have proven to be very efficient photosensitizers. However, they are subjected to chemical transformation by substitution of the thiocyanate in the ruthenium coordination sphere with molecules within the cell, leading to a notable decrease in photovoltaic efficiency. Consequently, considerable effort has been focused on developing thiocyanate-free Ru dyes.

3.1. Thiocyanate-Free Ru Dyes with Terpyridines Bearing the Anchoring Group

In 2022, Naziruddin and coworkers proposed ruthenium(II) complexes **20** and **21** (structure in Figure 9) presents two terdentate ligands, the first being a 4-COOH-phenyl-terpyridine (aimed at anchoring the dye to the titania surface), while the second is a C^NC carbene-based ligand [45]. Moreover, in **20** the carbenic ligand was a symmetric 2,6-bis(imidazolyl)pyridine, and in **21** was an asymmetric 2-benzimidazolyl-6-benzimidazolylmethyl pyridine. Since, in general, terpyridine ligands exhibit small bite angles to the metal center, causing a distorted octahedral coordination and enhancing the thermal depopulation of the excited states, shortening their lifetimes, the introduction of a methylene bridge between the pyridine and a benzimidazole in **21** aimed at prolonging the excited-state lifetimes.

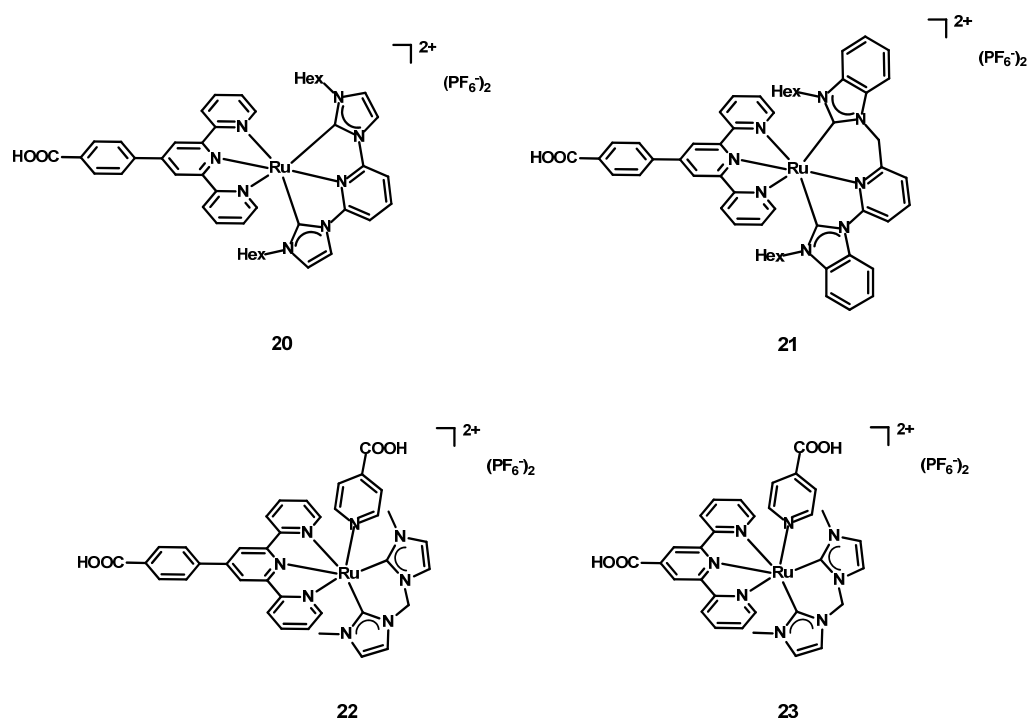


Figure 9. Structure of dyes 20–23.

The discussed sensitizers were tested in solar cells together with the traditional I^-/I_3^- redox mediator, and the performances were compared to those given by standard dye **N3**. In all cases, the results provided by the new dyes were much lower than those given by **N3**, with **21** reaching a J_{SC} of 0.167 mA cm^{-2} , a V_{OC} of 352 mV, and an efficiency of 0.28%, while the DSSC sensitized with **N3** presented a short-circuit current density of 2.49 mA cm^{-2} , an open-circuit voltage of 516 mV, and a η of 8.04%.

The low J_{SC} of **20** can explain the low efficiency of the corresponding DSSC, since the short lifetime of 4.11 ns could be disadvantageous to the electron injection into the titania layer. Concerning **21**, the longer excited-state lifetime (16.57 ns) gave better efficiency (0.28% vs. 0.06%).

The same research group already mentioned in paragraph 2.1 proposed also two Ru(II) dyes differing from complexes **22** and **23** (see Figure 9) for the ancillary ligand, this being a 4-COOH-pyridine instead of the standard thiocyanate [39]. Also, for these sensitizers the effect of the linker between the terpyridine scaffold and its COOH anchoring group was investigated: in **22**, a phenylene spacer linked the two moieties, while in **23** the carboxylic group was bound directly to the terpyridine.

It is interesting to point out that the presence of the pyridine acting as an additional anchoring ligand did not bring about improvements of the cell performance, since theoretical calculations showed that such a ligand did not participate in the LUMO of the dye, thus was not useful for the electron transfer process.

As shown previously for the corresponding thiocyanate-based dyes, the presence of the spacer caused torsional issues which reduced the performance of the DSSCs, with a lower J_{SC} and η (1.040 vs. 2.380 mA cm^{-2} and 0.380 vs. 1.000% in **22** and **23**, respectively, complete data in Table 4).

The same terpyridine directly bearing an anchoring COOH moiety in *para* of the central pyridine was employed by Naziruddin and coworkers in 2023 in complexes **28–30** [46]. These heteroleptic compounds presented a second terpyridine with a variable number of OMe substituents on the phenyl ring on the terpy scaffold (Figure 10). The goal of this study was to explore the influence of an increasing number of electron-donating groups (and consequently of an increasing electron density on the metal) on the electron injection towards the semiconductor layer in DSSCs. The efficiency of the obtained devices was compared to the results provided by previously published analogous dyes **24–27**, presenting a variable number of phenylene bridge linking the terpy core and the COOH anchoring moiety, and different methyl and/or methoxy substituents on the second terdentate ligand (see Figure 10 for their structure). The discussed complexes were applied as dyes in DSSCs, having I^-/I_3^- as the redox couple, and the results were compared to those given by the known **28–30**. In the case of **30** and **27**, the absence of the phenylene spacer was beneficial for the photovoltaic efficiency due to the lower torsional angle: 0.130% vs. 0.087% for **30** and **25**, respectively, and 0.713% vs. 0.441% for **27** and **26**. The only exception was represented by dyes **28** ($\eta = 0.131\%$) and **24** ($\eta = 0.321\%$), this being explained through the lower loading measured for **28** with respect to **24**. When considering the number of methoxy groups in complexes **28–30**, the authors pointed out that the calculated torsion angles in the case of **28** and **30** were very similar and larger than that obtained for **29** (with two OMe groups), this being consistent with the higher efficiency measured for the cell sensitized with **29** (0.164 vs. 0.131 and 1.130% for **29**, **28**, and **30**, respectively). All photovoltaic results are collected in Table 4.

Table 4. Photovoltaic values of DSSCs fabricated with terpy-Ru(II) sensitizers **20–30** ¹.

Entry	Dye	$\lambda_{\text{max, abs}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	J_{sc} (mA cm ^{−2})	V_{oc} (V)	FF	η (%)	Refs.
1	20 ²	280 [17.78] 469 [0.85]	0.075	0.28864	27	0.06	[45]
2	21 ²	281 [4.49] 464 [1.27]	0.167	0.35254	44	0.28	
3	N3 ²	-	2.49	0.51610	56	8.04	
4	22 ³	283 [108.160] 319 [50.402] 490 [13.320]	1.040	1.040	1.040	1.040	[39]
5	23 ³	280 [77.960] 319 [42.600] 479 [7.920]	0.615	0.615	0.615	0.615	
6	24 ³	282 [25.77] 310 [18.72] 492 [10.75]	1.397	0.479	48.0	0.321	
7	25 ³	281 [13.74] 307 [13.74] 491 [6.41]	0.225	0.535	72.0	0.087	[46]
8	26 ³	285 [18.36] 310 [18.72] 490 [8.02]	1.542	0.512	56.3	0.441	
9	27 ³	281 [23.21] 310 [25.18] 491 [8.02]	1.750	0.565	72.1	0.713	
10	28 ³	274 [45.8] 313 [52.6] 493 [24.5]	0.375	0.603	57.1	0.131	
11	29 ³	275 [25.7] 309 [28.3] 494 [14.1]	0.379	0.632	69.3	0.164	
12	30 ³	274 [14.0] 310 [16.6] 494 [6.9]	0.358	0.597	61.1	0.130	
13	N3 ³	-	7.725	0.804	68.1	4.065	

¹ Under AM 1.5 simulated light source; having TiO₂ as a semiconductor, Pt as a counter electrode, and 0.1 M LiI + 0.06 M I₂ + 0.5 M 1-butyl-3-methylimidazolium iodide in ACN as an electrolytic mixture. Absorption spectra registered in ACN. ² 0.6 mM in acetone. ³ 0.6 mM in 1:1 ACN:tBuOH.

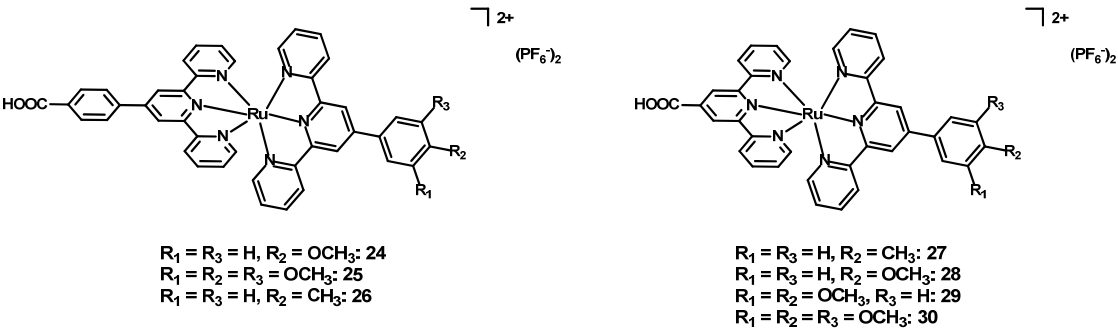


Figure 10. Structure of dyes **24–30**.

3.2. Thiocyanate-Free Ru Dyes with Bipyridines Bearing the Anchoring Groups

In 2024, Vega, Fagalde, and coworkers [47] published five novel ruthenium(II) compounds with differently substituted bipyridines (Figure 11) and presenting nitrile anchoring groups. While dyes **31–33** had a single 4-methy-2,2'-bipyridine-4'-carbonitrile (Me-bpy-CN) and two bipyridines with methyl, methoxy, and dimethylamino groups in positions 4 and

4', respectively, in the other two compounds two Me-bpy-CN ligands were bound to the metal together with a 4,4'-dimethoxy-bpy (**34**) or a 4,4'-bis(dimethylamino)-bpy (**35**).

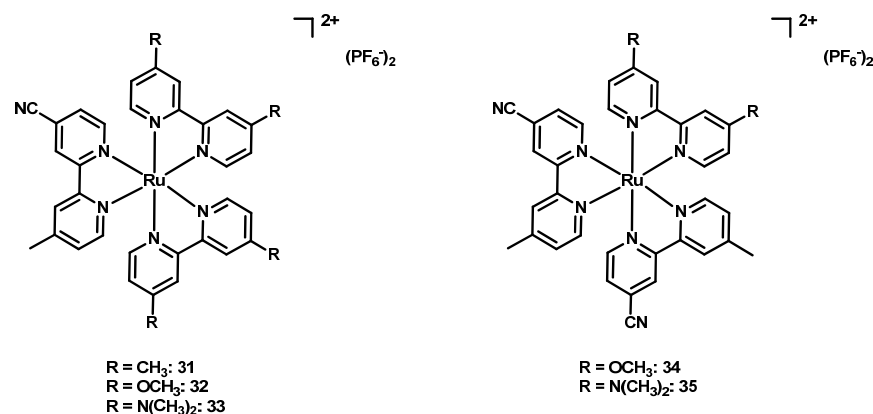


Figure 11. Structure of dyes **31–35**.

These complexes were tested in DSSCs in association with the typical I^-/I_3^- electrolytic solution and in both groups of dyes it appeared that the presence of the NMe_2 group provided the best photovoltaic performances, reaching a V_{OC} of 332 mV and 344 mV for **33** and **35**, respectively, with an efficiency of 0.054% and 0.065%. Among the discussed sensitizers, the highest values were achieved in the presence of a higher number of nitriles, coupled with the high electron-donating ability of the dimethylamino substituent, which allows for an extension of the absorption towards lower energies (Table 5).

Table 5. Photovoltaic values of DSSCs fabricated with bpy-Ru(II) sensitizers **31–39**¹.

Entry	Dye	$\lambda_{\text{max, abs}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	Redox Couple	J_{sc} (mA cm ⁻²)	Voc (V)	FF	η (%)	Refs.
1	31 ²	444, 478	I ⁻ /I ₃ ⁻³	0.0404	0.171	28	0.00194	[47]
2	32 ²	446, 488		0.123	0.068	30	0.00252	
3	33 ²	448, 530		0.325	0.332	47	0.054	
4	34 ²	453, 489		0.0142	0.038	25	0.00013	
5	35 ²	454, 509		0.427	0.344	45	0.0656	
6	36 ^{4,5,6}	564 [9.437]	Cu(I)/Cu(II) ⁷	2.74	0.57	62.22	0.98	[48]
7	36 ^{4,5,8}			3.34	0.56	61.93	1.16	
8	36 ^{4,5,9}			2.93	0.55	62.63	1.02	
9	36 ^{4,5,10}			2.93	0.54	62.62	1.00	
10	37 ^{4,5,8}			513 [13.688]	0.76	0.44	51.2	
11	38 ^{4,5,8}	562 [11.120]	Co(II)/Co(III) ¹¹	1.75	0.49	51.2	0.43	[49]
12	36 ^{4,5,8}	564 [9.437]		1.62	0.21	37.0	0.13	
		246 [17.650]						
13	39 ¹²	307 [29.550] 371 [7.050] 492 [6.750]	I ⁻ /I ₃ ⁻¹³	6.670	0.6004	77.29	3.09	
14	N3 ^{12,14}	-		17.813	0.675	60.73	7.3	
15	N3 ^{12,15}	-		11.2	0.650	68.06	5	

¹ Under AM 1.5 simulated light source; having TiO_2 as a semiconductor and Pt as a counter electrode, if not differently indicated. Absorption spectra registered in ACN in the case of complexes **31–35**, in MeOH in the case of **36–38**, and in EtOH for **39**. No ϵ values provided for **31–35**. ² 1.3 mM in ACN. ³ 0.5 M KI + 0.005 M I_2 in ACN. ⁴ using PEDOT as a counter electrode. ⁵ 0.03 mM in 1:1 MeOH:EtOH. ⁶ 1 active layer (3 μm). ⁷ 0.2 M $[\text{Cu}(\text{bpy})_2](\text{TFSI}) + 0.04 \text{ M } [\text{Cu}(\text{bpy})_2](\text{TFSI})_2 + 0.6 \text{ M TBP} + 0.1 \text{ M LiTFSI}$ in ACN. ⁸ 1 active layer + 1 scattering layer (8 μm). ⁹ Two active layers (6 μm). ¹⁰ Two active layers + one scattering layer (10 μm). ¹¹ Formulation of the $[\text{Co}(\text{bpy})_3]^{2+/3+}(\text{PF}_6^-)_{2/3}$ electrolytic mixture not provided. ¹² 10^{-5} M in EtOH. ¹³ 0.5 M LiI + 0.05 M I_2 + 0.5 M TBP in 3-methoxypropionitrile. ¹⁴ Commercial. ¹⁵ Synthesized by the authors.

In the same year, Sruthi et al. presented complexes **36** and **37** [\[48\]](#), in which the Ru(II) center was bound to two dcbipy (dcbipy = bipyridine-4,4'-dicarboxylic acid, acting as

anchoring ligands) and a $N^{\wedge}C$ cyclometalating ligand, being a 1-phenylisoquinoline in the first case and a 4-(3,5-bis(trifluoromethyl)phenyl)quinazoline in the second one. The aim of introducing such ligands on the structure of the already known dye **38** (presenting a simple 2-phenylpyridine as cyclometalating ligand) was to enhance the light harvesting capability of the dye by extending its aromatic system. Moreover, in the case of **37**, electron acceptor CF_3 substituents were added to shift the ground state to more positive potentials, thus providing a suitable driving force for dye regeneration, to make it compatible with alternate metal complex redox systems.

The aim of the authors was to investigate the discussed Ru(II) dyes together with metal-based redox couples such as $[Cu(bpye)_2]^{+/2+}$ (where bpye is 1,1-bis(2-pyridyl)ethane) and $[Co(bpy)_3]^{2+/3+}$ (where bpy is bipyridine) (Figure 12). At first, DSSCs had **36** as the sensitizer and the presented copper(I/II) compounds as redox shuttles were prepared with a different thickness of the TiO_2 layer to explore the optimal structure able to allow for enough dye loading while minimizing the mass transport limitations. The best result was achieved in the case of an 8 μm layer characterized by an additional scattering layer over the transparent titania one.

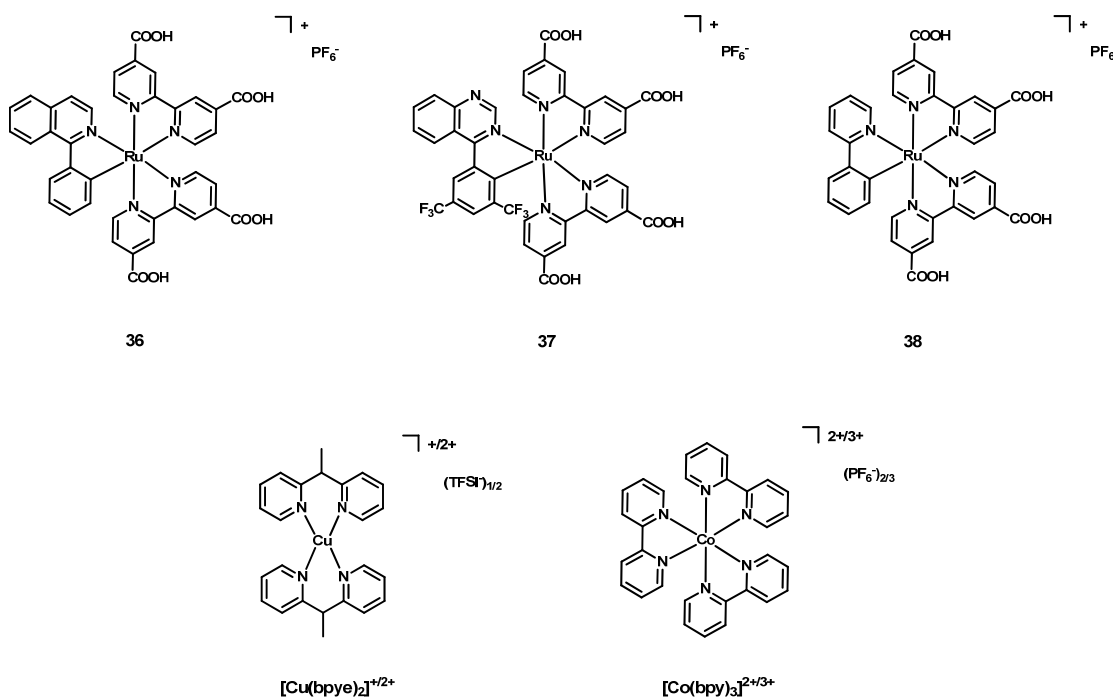


Figure 12. Structure of dyes **36–38** and of redox couples $[Cu(bpye)_2]^{+/2+}$ and $[Co(bpy)_3]^{2+/3+}$.

Then, this device architecture was employed for the cells sensitized with **38**, **36**, and **37**, with the best performances given by **36** (J_{SC} of 3.34 mA cm^{-2} and $\eta = 1.16\%$); this result has been explained by a higher dye loading and a shorter electron transport time, allowing this dye to clearly overcome the other two as sensitizer in DSSCs. Finally, **36**, namely the best thiocyanate-free complex discussed in the paper, was tested together with the redox couple $[Co(bpy)_3]^{2+/3+}$, resulting in minor performances when compared to the copper-based redox mediators, with a V_{OC} of 210 mV, a J_{SC} of 1.62 mA cm^{-2} , and an η of 0.13%. This behavior was mainly attributed to a higher recombination of charges at the TiO_2 -electrolyte interface, as highlighted by the short lifetime measured for the cobalt(II/III) mediators. Table 5 reports all data about the discussed sensitizers.

In 2024, Fetouh and Fathy investigated the effect of replacing the thiocyanate ligand of the traditional dye **N3** with the corresponding selenium-based NCSe ligand (complex **39**,

Figure 13) to point out the electrochemical, photophysical, and photovoltaic features of the two Ru(II) sensitizers [49].

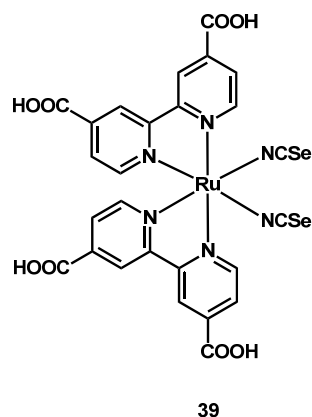


Figure 13. Structure of dye 39.

Considering the absorption spectra, both compounds showed the typical MLCT with maxima at 394 and 535 nm for **N3-S** (corresponding to the already known dye **N3**, but synthesized by the authors) and at 371 and 492 for **39**; both emissions were very similar and in the red region had peaks at 700 and 701 nm for **N3-S** and **39**, respectively.

Moving to the DSSCs with the proposed complexes, both synthesized and commercial **N3** were tested, together with the new analog **39**. The best results were given by commercial **N3**, achieving a J_{SC} of $17.813 \text{ mA cm}^{-2}$ and a η of 7.3%, these values being higher than those of prepared **N3** ($J_{SC} = 11.2 \text{ mA cm}^{-2}$, $\eta = 5\%$) and of **39** ($J_{SC} = 6.67 \text{ mA cm}^{-2}$, $\eta = 3.09\%$). All data are reported in Table 5.

The authors concluded that the lower performances of **39** were due to its longer lifetime when compared to the sulfur-based **N3**, and this could be solved by modifying the dye structure by inserting more electron-withdrawing substituents.

3.3. Co-Sensitization Between N719 and Thiocyanate-Free Ru Dyes

A different strategy, often employed in the attempt to achieve a better performance of solar cells, is to co-sensitize the cells by mixing dyes possessing different photophysical features in order to overcome the limitations of single sensitizers. One example of this procedure was proposed in 2022 by Sun, Pan, Zhou, and coworkers [50], who coupled the traditional dye **N719** with **40** (**40** being $[\text{Ru}(\text{bpy})_2(\text{dcbpy})][\text{PF}_6]_2$, bpy = bipyridine, dcbpy = bipyridine-4,4'-dicarboxylic acid, Figure 14). Compound **40** showed a strong light absorption in the 400–500 nm region, this corresponding to a spectral region in which **N719** lacks an efficient absorption. As highlighted in the paper, the absorption of the co-sensitizer also reduced the competitive absorption in the mentioned region by I_3^- ions.

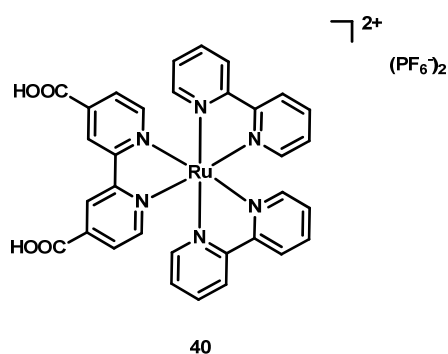


Figure 14. Structure of dye 40.

The authors applied the dyes' mixture together with iodine-based redox mediators, fixing the concentration of **N719** at 0.4 mM and varying that of **40** in the range 0.2–0.6 mM, to assess the best **N719:40** ratio to maximize their photovoltaic performance. At first, the increase in **40** in the mixture up to a concentration of 0.4 mM led to an enhancement of the J_{SC} from 11.5 to 12.8 mA cm^{−2} and of the efficiency from 5.8 to 6.3%, this representing an improvement of 19% with respect to **N719** alone. A further increase up to 0.6 mM brought about lower short-circuit current density (12.2 mA cm^{−2}) and η (5.5%), this behavior being explained by the authors as caused by an enhanced recombination of photogenerated carriers due to excessive amount of dye **40**.

Finally, if the DSSC sensitized with **40** alone is considered, the measured photovoltaic results are essentially low (J_{SC} = 2.5 mA cm^{−2}, V_{OC} = 585 mV, η = 0.94%); this has been mainly ascribed to the narrow absorption region of the complex, which allowed only for limited light harvesting (Table 6).

Table 6. Photovoltaic values of DSSCs fabricated by co-sensitizing **N719** with Ru(II) sensitizer **40**¹.

Entry	Dye	$\lambda_{max, abs}/nm$ [$\epsilon/10^3 M^{-1} cm^{-1}$]	J_{sc} (mA cm ^{−2})	V_{oc} (V)	FF	η (%)	Refs.
1	40 ²	475 [17.5]	2.5	0.585	63.35	0.94	
2	N719 ³	-	9.8	0.790	69.40	5.3	
3	40 + N719 ⁴	-	11.5	0.727	69.06	5.8	
4	40 + N719 ⁵	-	11.9	0.736	67.87	6.0	[50]
5	40 + N719 ⁶	-	12.8	0.733	65.02	6.3	
6	40 + N719 ⁷	-	11.5	0.737	64.11	5.6	
7	40 + N719 ⁸	-	12.2	0.723	63.39	5.5	

¹ Under AM 1.5 simulated light source; having TiO₂ as a semiconductor, Pt as a counter electrode, and 0.1 M LiI + 0.05 M I₂ + 0.6 M 1,2-dimethyl-3-propylimidazolium iodide + 0.5 M TBP in ACN as an electrolytic mixture. Absorption spectra registered in EtOH. ² Dye concentration not specified. ³ 0.4 mM in EtOH. ⁴ **N719** 0.4 mM + dye 0.2 mM in EtOH. ⁵ **N719** 0.4 mM + dye 0.3 mM in EtOH. ⁶ **N719** 0.4 mM + dye 0.4 mM in EtOH. ⁷ **N719** 0.4 mM + dye 0.5 mM in EtOH. ⁸ **N719** 0.4 mM + dye 0.6 mM in EtOH.

4. Conclusions

The focus of this minireview is on recent classes of Ru(II) DSSC sensitizers with or without thiocyanate groups, compared to routinely used benchmarks **N3** or **N719**. A collection of the recent literature reports on these important classes of novel Ru(II) DSSC sensitizers could be particularly useful to the researcher dealing with DSSCs. Interesting results have been recently obtained both on thiocyanate-based and thiocyanate-free ruthenium dyes. In particular, concerning thiocyanate ruthenium dyes, excellent results have been obtained in 2024 by Chia-Yuan Chen et al. [41] with the heteroleptic Ru complex **17** with substituted thiophenes, with a 8.63% efficiency, this resulting in better performance when compared to **N719**.

An aspect that deserves greater attention is that of the co-sensitization of the well-employed dye **N719** with both other Ru complexes and/or organic dyes: in the case of compound **40** [50], this strategy allowed for an interesting increase in the cell efficiency, as a consequence of the broader light absorption range provided by the presence of the new dye, harvesting light in the region in which **N719** has lower capacity. A similar improvement was achieved also by Aldusi and coworkers [43] by co-sensitizing **N719** with various members of a class of organic dyes presenting different extended aromatic systems and anchoring groups; in most cases, this was effective in overcoming the performances of **N719** alone.

In conclusion, this review shows how the field of DSSCs is always relevant and crucial in the perspective of a greener future, leaving large opportunities for advancement. For sure,

many researchers will continue to focus on new ruthenium dyes and on the development of novel DSSCs.

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Abbreviations

The following abbreviations are used in this manuscript:

ACN	Acetonitrile
AM1.5 G	Air mass 1.5 global illumination
bpy	2,2'-bipyridine
DSSC	Dye-sensitized solar cell
FF	Fill factor
J _{sc}	Short-circuit current density
LUMO	Lowest unoccupied molecular orbital
V _{oc}	Open-circuit voltage

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