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Review

Transition Metal Coordination Compounds as Novel Materials for Dye-Sensitized Solar Cells

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Abstract: Dye-sensitized solar cells (DSSCs) are a novel solar cell alternative characterized by lower toxicity by using coordination transition metal compounds while providing high performance benchmarks, such as power conversion efficiency. Particular attention should be paid to compounds containing Cu, which can act both as dyes and as redox mediators, even though compounds relying on other transition metals are also frequently reported. In this paper, examples of compounds containing transition metals in combination with several ligands are presented, and their basic photovoltaic parameters are given.

Keywords: dye-sensitized solar cell; DSSC; coordination compound; transition metal; power conversion efficiency

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1. Introduction

Dye-sensitized solar cells (DSSC) are one of the most recently developed types of solar cells, alleviating the harsh material purity and processing requirements associated with traditional inorganic semiconductor-based solar cells, as well as avoiding the use of highly toxic substances, such as compounds of cadmium [1]. Initially, DSSCs relied on iodine-based electrolytes and charge transfer dyes based on the coordination compounds of ruthenium, reaching power conversion efficiency values of up to 10% [2]. Currently, the development of DSSCs is attracting great research interest, focused on improving their design and constituents. Significant attention has been given to the development of electrolytes [3] and dyes [4] for DSSCs, as well as to optimizing their performance by extending the range of harvested electromagnetic radiation [5] and demonstrating new avenues of their application [6]. Such advances have allowed DSSCs to operate in different external conditions (e.g., temperature) with unchanging efficiency and to operate consistently under different brightness levels or with color selectivity [7].

A particularly important issue in the design of DSSCs is the matter of selecting the material to be used as the charge transfer dye, as it determines both the ability of the DSSC to harvest electromagnetic radiation and the efficiency of charge separation. Although ruthenium-based dyes afford high power conversion efficiencies in DSSCs, such dyes typically have relatively low molar absorption coefficients. The drawbacks of such dyes are not limited to the above, as both ruthenium and its compounds are expensive, have limited availability and are often toxic or environmentally harmful [8].

Due to those issues, significant attention has been given to alternative, Ru-free dyes. Among such alternatives, however, the majority of proposed dyes also suffer from the key drawbacks of ruthenium-based dyes, that is, the use of expensive, limited-availability and environmentally problematic materials, including heavy metals such as osmium, platinum and rhenium [9]. Cu-based dyes may be one of the few exceptions to the above, which explains the research attention given to those materials as the search for high-performance, low-risk and cost-efficient dyes for DSSCs continues [10–12].

The aim of this work is to summarize the most recent (approx. 1–2 year old) and relevant developments concerning Cu-based charge transfer dyes for DSSCs. The main focus of our review is to showcase ligands that yield coordination compounds, which may become material alternatives to heavy metal-based dyes, both affording a high performance and limiting the environmental impact of producing DSSCs on the environment.

2. Characterization and Principle of Operation of Dye-Sensitized Solar Cells

There are two types of dye-sensitized solar cells based on the physical state of the electrolyte used in the solar cell: liquid state and solid state. In the case of DSSCs with liquid electrolytes, a redox couple (e.g., I^-/I^{3-}, Fc/Fc^+, or Cu^+/Cu^{2+}, Co^{2+}/Co^{3+}) is typically dissolved in the electrolyte [1].

The redox couple is one of the most important components of DSSCs due to it acting as a redox mediator, facilitating charge transports from the surface of the dye to the counter electrode of the DSSC. The redox couple also affects the electrochemical potential of the TiO_2 electrode through the kinetics of recombination among the electrons in the TiO_2 and the oxidised redox species [13]. This couple, as a result of metal reduction, is capable of regenerating the dye, and the solution is transferred to the cathode by diffusion. To seal a system consisting of an anode, cathode, spacer and electrolyte, thermoplastic films are often employed. For solid-state systems, the electrolyte is replaced by a solid transport material (HTM), and transport, in exchange for diffusion, occurs by inter-molecular charge jumps from the oxidized species to the nearest reduced species [14].

The principle of operation of dye-sensitized solar cells is based on the separation of n-type (electron selective layer) and p-type (hole selective layer) charges at the semiconductor junction under the influence of energy from electromagnetic radiation. The dye forms the outer layer of the system, and the supplied energy triggers the excitation of electrons from the valence band to the conduction band due to photon absorption. As a result of charge separation, some of the electrons are transported deep into the material (into the n layer) towards the anode, while the holes are transported towards the cathode (into the p layer). As a consequence of this process, a voltage appears in the conductive layer, and a closed circuit causes an electric current to flow [14].

An important parameter characterizing cells is the photopotential (V_{OC}), which is the maximum voltage value that can be reached with an open circuit when the current is 0 A. This quantity is also defined as the difference of the Fermi levels of electrons in TiO_2 (E_{Fn}) and the electrochemical Nernst potential of the redox mediator (E_{redox}). The efficiency of a working system is associated primarily with V_{OC}. As the V_{OC} decreases, the efficiency decreases, which is related, for instance, to the low regeneration of the dye used (Figure 1). Moreover, the V_{OC} value depends on the material and surface area of the counter electrode [15]. As a result, the highest possible solar cell efficiencies are currently being pursued, and the use of complex compounds as dyes promotes this process. The efficiency of photoelectric conversion depends primarily on the absorption capacity of the photo-sensitizing dyes of solar energy, i.e., as the intensity of solar energy absorption increases, the efficiency increases [16].

An issue relevant to the proper design and prediction of compound properties is to study the effect of the ligand on the redox potential, e.g., in the case of copper compounds. The density functional theory (DFT) method is used to calculate the energetic properties. The paper [17] presents how redox potentials will affect the catalytic properties of bis(β-diketonato)copper(II) compounds, especially compounds containing **1** and **2** (Figure 2).

The work indicates that, depending on the reduction potential of the copper-containing compound, the properties of the dyes can be modified. The estimation of the reduction potential is derived from the dependence of E_{LUMO} and the experimentally determined reduction potential E_{pc}, thereby making it possible to determine the effect of the ligand on the redox potential of above-mentioned compounds (as E_{pc} decreases, the calculated value of E_{LUMO} increases). Furthermore, the copper redox pair Cu^{2+}/Cu^+ can provide an alternative electrolyte for DSSCs. By affecting the reduction potential, the resulting dyes

used in solar cells may exhibit varied properties, thus affecting the cell performance and lifetime [17]. This paper reports the determined value of the reduction potential E_{pc} (V), the values of which were varied depending on the solvent used during the measurements. For the compound **1** (Figure 2) in dimethyl sulfoxide, the values ranged from −1.06 to −1.05 (carbon fiber working electrode), for acetonitrile from −0.91 to 0.27 (carbon fiber working electrode) and for acetonitrile from −1.624 to −0.473 (glassy carbon working electrode). On the other hand, the value of E_{LUMO} (eV) ranged from −4.14 to −2.31. For the compound **2** (Figure 2), the value of the reduction potential E_{pc} (V) was determined using dimethyl sulfoxide as solvent with carbon fiber working electrode with values from −0.73 to −0.16 and E_{LUMO} from −7.07 to −5.99 [17].

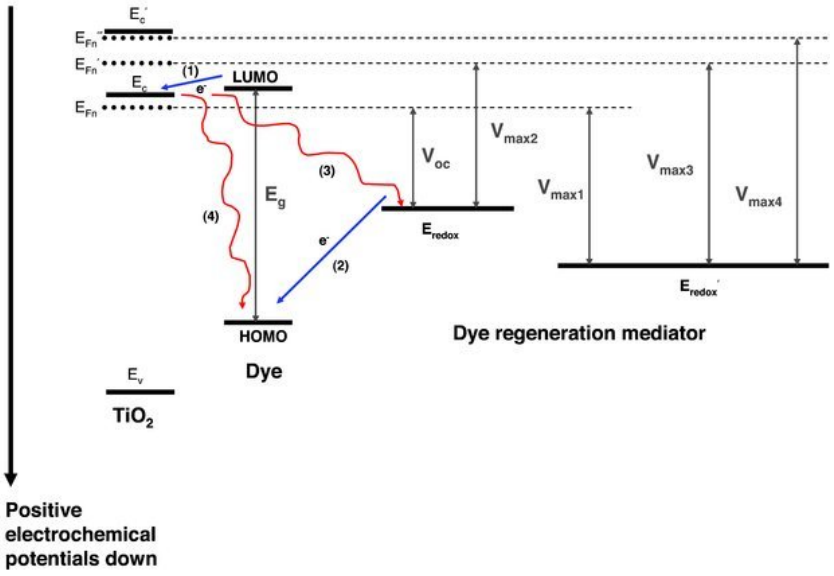


Figure 1. Processes occurring in DSSC: (1) electron injection, (2) dye regeneration, (3) recombination by electrolyte and (4) dye. Reprinted from [1] with permission from John Wiley and Sons.

2.1. Compounds Used as Dyes

In a dye-sensitized solar cell, the dye is absorbed in the semiconductor layer. The dye in the cell has a crucial function due to its enhancement of the ability to generate electrons and holes enabling charge transport [18]. In order to do so, the dyes used in solar cells should [19]:

- Absorb electromagnetic radiation in the visible light range to the greatest possible extent;
- Have energy levels matching the energy levels of the redox mediator and the conduction band edge of TiO_2, so as to ensure efficient electron transport;
- Be chemically accessible and (photo)chemically stable.

Currently, copper compounds in DSSCs are widely employed as dyes. Depending on its oxidation level from 0 to +4, a copper atom can coordinate different amounts of ligands, with the resultant coordination compounds exhibiting various geometries. Most commonly, coordination compounds of Cu^{+} and Cu^{2+} are encountered, exhibiting tetrahedral and linear, trigonal or tetragonal geometries, respectively. Among such coordination compounds, polymeric species formed on the framework of cuprous iodide with organic ligands, such as methyl nicotinate [20], have been reported to have potential application in solar cells as down-shifters alternative to lanthanides [21].

A recent study on copper compounds with 2,9-disubstituted-1,10-phenanthroline ligands—**3–7** (Figure 2) used in DSSCs indicated that high conversion efficiencies ranging from 6 to 11% with high V_{OC} approaching above 1 V could be achieved [22]. Particularly, complexes based on Cu_2I_2 and **39** posses double chains such as CuI-**39** and Cu_2I_2-**39**. Selected photovoltaic parameters of the DSSC compounds are shown in the Table (Table 1). The examples of Cu-based complexes were shown in the figure below (Figure 2):

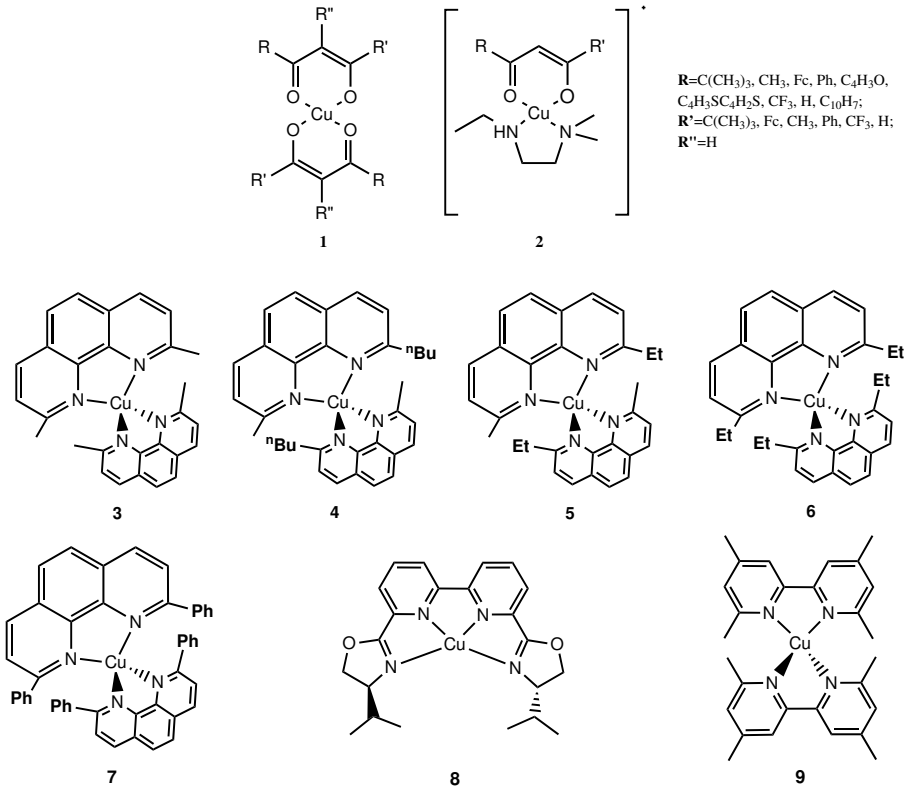


Figure 2. Examples of Cu coordination compounds envisioned for application in DSSCs. Reprinted from [17] under a Creative Commons CC-BY license and from [23] with the permission of the Royal Society of Chemistry.

Table 1. Selected photovoltaic parameters of DSSCs of electrolyte/dye compositions. Reprinted from [23] with the permission of the Royal Society of Chemistry.

Electrolyte	Dye	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
3	LEG4	10.00	1.03	60.9	6.29
4	LEG4	10.06	0.84	66.4	5.90
5	LEG4	7.52	0.82	52.6	3.25
6	LEG4	6.77	0.81	46.4	2.56
7	LEG4	4.18	0.85	62.4	2.21
8	Y123	9.75	0.92	69	6.20
9	D203	6.12	0.92	82	4.60
9	D205Si	6.40	0.95	78	4.75
9	WS-72	13.8	1.07	79	11.7

One interesting example of dye-sensitized solar cells is the use of alizarin yellow GG-$CuCl_2$ mixed with polyvinyl alcohol/ITO as a thin film. The main advantage of this type of cells is their low cost of fabrication by low-temperature processes, and they can be used in various types of sensors such as NO_2 sensors or temperature sensors. The use of polyvinyl alcohol with azo dyes improves the physical properties with good flexibility of the film, providing it with electrical and dielectric properties in an organic cell. The work [24] shows the basic properties of an alizarin yellow GG-$CuCl_2$ cell blended with polyvinyl alcohol that changes depending on the light color used. The reported cell shows the highest efficiency (Table 2) when exposed to green light. Furthermore, it appears that the electrical resistivity of the film is not temperature-dependent [24].

The low efficiency of this type of photocells may be explained by the formation of a limited number of holes and electrons as a result of exception splitting at the phase boundary or as a consequence of excitons encountering impurities in the sample and, as a

consequence, shortening their lifetime [24]. Another example of a copper-containing dye is C218 (including tris(1,10-phenanthroline)) with a 6.5 µm TiO_2 layer. Its efficiency is 7.0% at V_{OC} 0.93 V [25].

Table 2. Selected photovoltaic performance of a solar cell using alizarin yellow GG-$CuCl_2$ blended with PVA)/ITO under illumination for white, blue, yellow and green. Reprinted from [24] with permission of Elsevier.

Light	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
White	0.021	0.37	0.47	3.96×10^{-3}
Yellow	0.020	0.39	0.44	3.44×10^{-3}
Green	0.051	0.40	0.43	8.67×10^{-3}
Blue	0.022	0.40	0.44	3.8×10^{-3}

According to most recent literature reports, there are substitutes for inorganic dyes employed in cells as sensitizers based on organic dyes, such as bixin **10** (Figure 3) [26].

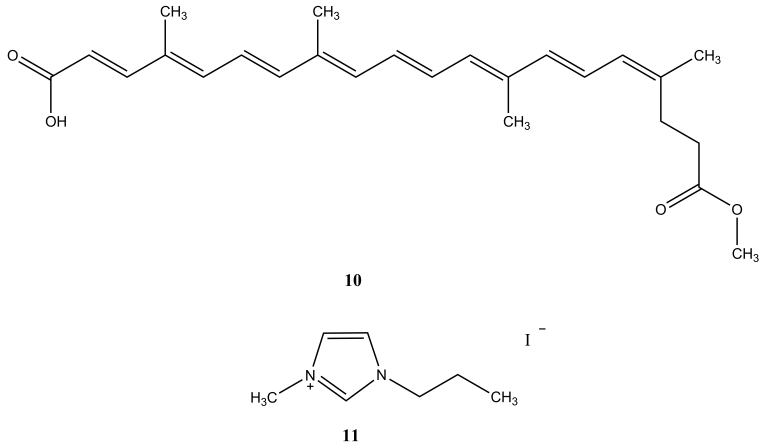


Figure 3. Structure of *cis*-bixin.

The use of bixin in combination with $ZnSO_4 \cdot H_2O$ and $CuSO_4 \cdot H_2O$ to obtain complexes with Zn(II)-ZnBx and Cu(II)-CuBx has also been reported [26]. The addition of **10** (MPII) (Figure 3 to the electrolyte system (containing I^-/I^{3-}) enabled increasing the performance of dye-sensitized solar cells simultaneously with increasing the conductivity and viscosity of the electrolyte [26]. However, the presence of conjugated double bonds in the structure may contribute to the decrease in bixin stability, which remains an unresolved issue [26].

Another group of compounds used in dye-sensitized solar cells are porphyrin zinc sensitizers ZnPi (i = 1–3) **11–13** (Figure 4) due to their ability to obtain high efficiency in cells.

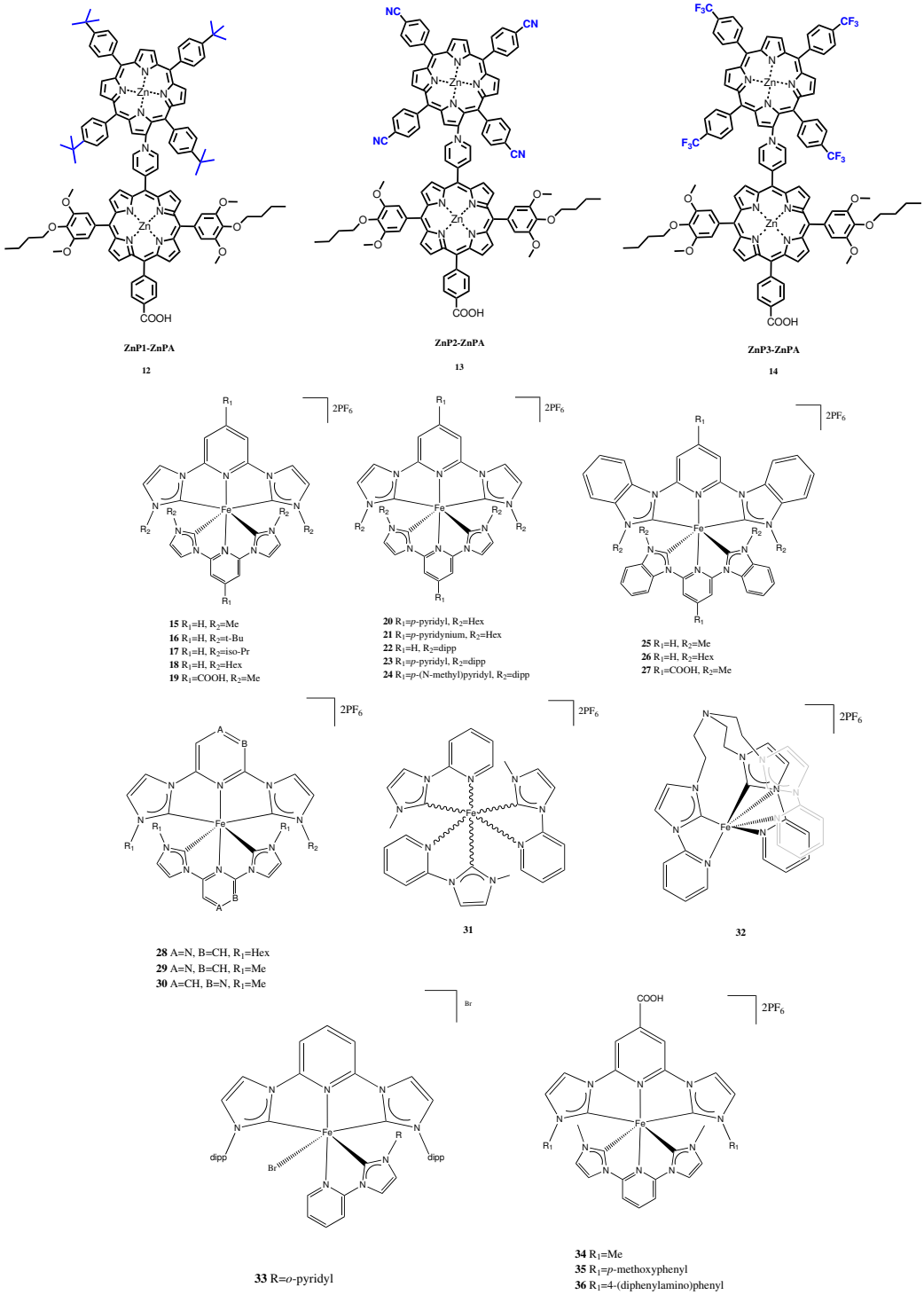


Figure 4. Examples of porphyrin zinc sensitizers (**12**–**14**) and photofunctional iron coordination compounds (**15**–**36**). Reprinted from [27] with permission of Elsevier and from [28] under a Creative Common CC BY license.

In contrast to ZnPA, these cells possess higher short-circuit current densities (J_{sc}) and lower V_{OC} due to the increase in the charge recombination rate in ZnPi cells at the electrode. As a result, ZnPi-based devices (i = 1–3) have higher photoelectric conversion efficiency (PCE) [27]. The high efficiency of porphyrin-based cells is attributed to the strong absorption of radiation in the visible and near-infrared light range [29]. The following table shows the selected photovoltaic parameters of ZnPi (i = 1–3)-ZnPA dyes (Table 3).

Table 3. Performance benchmarks for DSSCs utilizing selected compounds presented in Figures 4 and 5. Reprinted from [27,30] with permission of Elsevier and from [28] under a Creative Common CC BY license.

Dye	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
12	5.63 ± 0.30	0.76 ± 0.01	0.66 ± 0.1	2.83 ± 0.12
13	6.59 ± 0.28	0.74 ± 0.02	0.65 ± 0.1	3.17 ± 0.12
14	8.02 ± 0.21	0.71 ± 0.02	0.60 ± 0.2	3.44 ± 0.11
19	3.30	**0.44**	0.63	0.92
27	0.12	**0.37**	0.71	0.03
34	0.33	**0.40**	0.73	0.10
35	0.36	**0.44**	0.73	0.11
36	0.36	**0.39**	0.71	0.10
42	14.50	1.02	70.50	10.50
43	14.40	1.03	69.30	10.30

Literature reports indicate that coordination compounds containing $Fe^{2+/3+}$ with N-donors with a pyridine ring may also be useful. However, the performance of such solar cells was found to be rather limited, as seen by the reported power conversion efficiency (PCE) values on the order of 2% [31,32].

On the other hand, the use of transition metal coordination compounds with special emphasis on iron (Fe) is a new development trend of DSSCs due to its widespread occurrence on Earth. The previous use of this metal in polypyridyl complexes did not work, as these compounds were difficult to maintain in the excited state. By the subsequent introduction of iron carbene, the photocatalytic and photophysical properties were improved, making this group of compounds promising in terms of achieving longer excited state lifetimes (Figure 4). These compounds utilize N-heterocyclic carbene ligands, which can be further tailored, e.g., by replacing the central pyridyl group by a diazinyl moiety surrounded by benzimidazolium and imidazolium carbenes [28].

In the following table, the basic parameters for iron-containing DSSCs are presented (Table 3).

Some Fe^{3+} complexes have an unfilled d sub-shell with a high-spin ground state (sextet), which are more commonly used nowadays. When some Fe^{3+} complexes of hexacarbene were formed, low-spin ground states were formed (doublet) [33].

Coordination compounds of silver, such as $[Ag(L)_{0.5}]_n$ (L = azobenzene-4,4′-dicarboxylate) have been reported to enhance the absorption of DSSCs cells in the ultraviolet region. In the case of this compound, the enhancement stems from the co-sensitization of the compound and a Ru-bipyridine dye (N719), allowing the $Ag(L)_{0.5}]_n$/N719/TiO_2 system to achieve a PCE of 3.14% [34]. Zn-based coordination compounds use similar ligands, such as 4-[(8-hydroxy-5-quinolinyl)azo]-benzenesulfonic acid, with the resulting coordination compound, augmented with N719 dye, achieving a PCE of approx. 8% [35].

Recent literature reports indicate the use of bile acids and bile salts (e.g., sodium cholate and sodium deoxycholate), both of which are naturally occurring anionic biosurfactants, in dye-sensitized solar cells. On the other hand, in the synthesis of inorganic as well as organic materials, they enable charge compensation. The use of bile acids, capable of acting as coadsorbates, influences the efficiency of the cell, among others, by blocking the current leakage (related to the generation of energy losses) or by the solubilization of dyes in solutions, thus facilitating the formation of DSSCs. For example, the use of deoxycholic acid as a coadsorbate with the dye N749 attains a cell conversion coefficient of 8.4%, NKX-2700—7.8%—or N719—6.4% [18].

2.2. Compounds Used as Redox Mediators

Recent literature reports indicate that electrolytes containing copper or cobalt ions together with a suitable dye, e.g., N3 or N719, can be used in addition to the previously dis-

cussed electrolytes used in DSSCs devices. It seems important to select the appropriate ligand together with the metal considering their effect on the redox potential. Some examples of electrolytes can be compounds 1-substituted with 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole ligands, such as in **37**–**38** (Figure 5).

By simplified alkylation of the NH_2-(2-pyridyl)benzimidazole group, this group may be capable of attaching various substituents to the metal-diimine core. The paper [36] provides information about the use of copper-based compounds in liquid DSSCs with ruthenium dyes, allowing conversion efficiencies of about 5% (4.99 and 4.82%)—complexes of 4-nitro-benzyl-substituted 2-(pyridin-2-yl)-1*H*-benzo[*d*]-imidazole ligands [36].

Coordination compounds of copper can serve as redox mediators. An example of copper-containing coordination compounds are those involving bipyridine-bearing ligands, such as in **40**–**43** (Figure 5) [37].

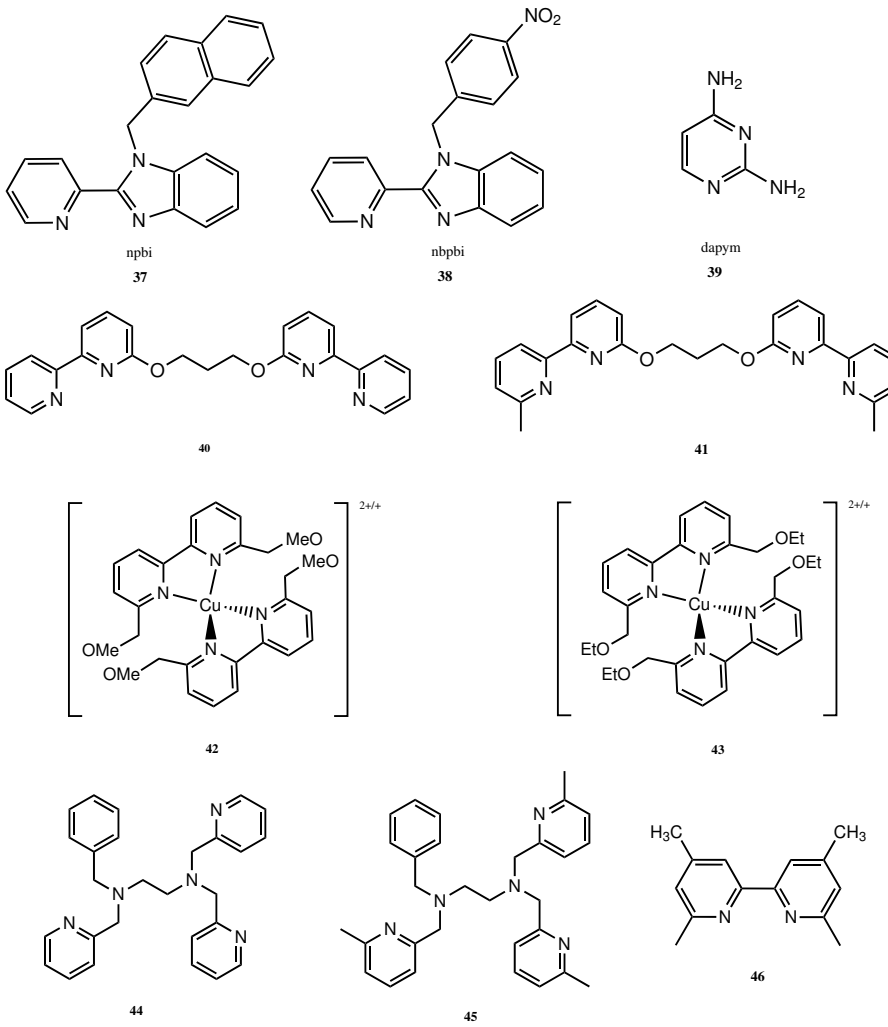


Figure 5. Structures of ligands and coordination compounds used in DSSCs. Reprinted from [30] with permission of Elsevier.

By introducing alkoxy groups into them, it was possible to reach power conversion efficiency of more than 10% [30]. Currently, bidentate ligands, i.e., pyridine and phenanthroline derivatives, are a major group of investigated redox mediator [38]. These compounds serving as a redox mediator in DSSCs (in combination with Y123 dye), due to their higher solubility, lead to a rise in concentration in the solar cells up to 0.3 M, causing an increase in the photocurrent. The following table shows the basic photovoltaic parameters of the above-mentioned redox mediators (Table 3).

The work [38] shows further examples of copper-containing complex compounds with applications as redox mediators are compounds with diamino-tripyridine ligands **44** and **45**. The chemical structure of the ligands is presented in the following graph (Figure 5).

The systems based on **46** depending on the DSSCs liquid or solid state attained maximum efficiencies of 13.5% and 11% [38]. The work of [39] reports the use of Cu compounds with the phenanthroline ligand and LEG4 dye as redox mediators in electrolyte solution, enabling them to achieve a conversion rate of 8.3% (Voc = 1020 mV, Jsc = 12.6 mA^{-2}, CE-PEDOT) [39].

Regarding the available redox pairs, transition metal coordination compounds are often used as cobalt-based redox pairs due to their several advantages. These complexes are non-corrosive, and in addition, they exhibit more positive potentials than the I^-/I^{3-} redox pair, which can increase the value of the Voc potential [40]. Such compounds are used for DSSCs, and the literature reports that the efficiency of solar cells using cobalt compounds increased up to 13% ($Co^{2+/3+}$ redox couple). These cobalt compounds can be divided based on the type of ligand. These are [41]:

1. $Co^{2+/3+}$ tris(bipyridine) complexes;
2. $Co^{2+/3+}$ bis(terpyridine) complexes;
3. $Co^{2+/3+}$ (tris)phenanthroline complexes;
4. $Co^{2+/3+}$ bis(benzimidazole-2-yl)pyridine complexes;
5. $Co^{2+/3+}$ pyrazole-based complexes;
6. $Co^{2+/3+}$ complexes with pentadentate ligands;
7. $Co^{2+/3+}$ complexes with non-pyridyl ligands.

Examples of transition metal coordination compounds containing cobalt are shown in the figure below (Figure 6). One example is the cobalt tris(bipyridine) redox pair $[Co^{2+}(bpy)_3]$, showing a redox potential of 0.56 V with respect to NHE.

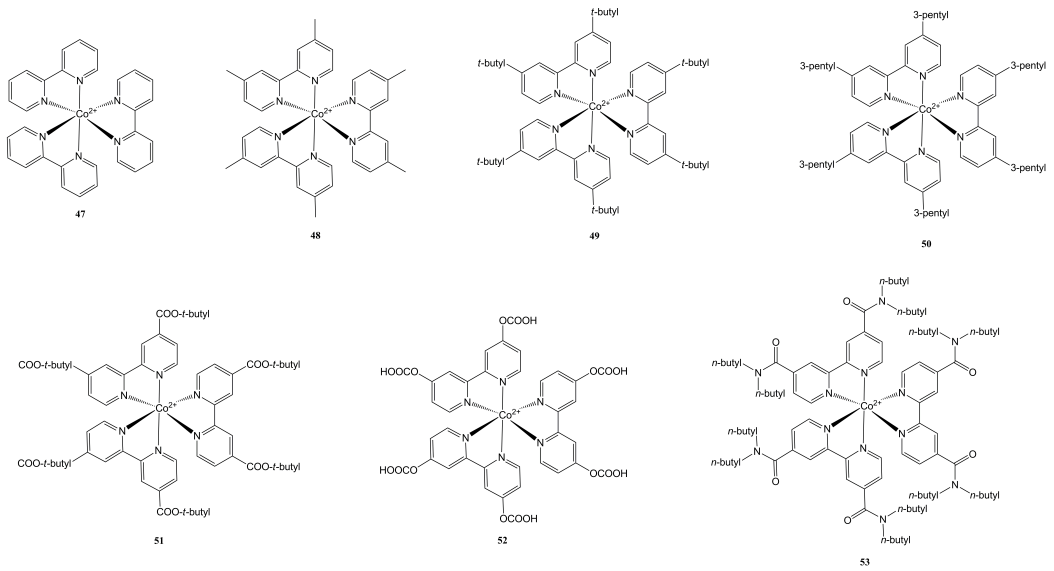


Figure 6. Examples of DSSCs containing $Co^{2+/3+}$ redox shuttles used in DSSCs. Reprinted from [41] with permission of John Wiley and Sons.

2.3. Alternative Electrodes

In terms of their commercial application, one of the key objectives of DSSCs is to replace the counter electrode (CE) constituting Pt with any other electrode to achieve as high electrocatalytic activity or high conductivity [15]. Literature sources report the use of carbide materials based on WC, W_2C [42] or W_xC [43] forms (W-based carbides); transition metal compounds (TMCs); or metal–organic frameworks (MOFs). For instance, complex com-

pounds based on polyoxotungstate ($H_3PW_{12}O_{40}$), which contained varied amounts of pyrrole (W_2C@C composites), were reported to PCE values above 7% and open circuit voltages (V_{OC}) above 0.77 V [15]. Another example to replace the Pt electrode (energy conversion efficiency of 7.67%) is the use of a Cu-MOF/PEDOT (poly(3,4-ethylenedioxythiophene)) composite electrode, which, under sunlight illumination, achieved a solar cell conversion efficiency of 9.45% [44]. The following table indicates the selected photovoltaic characteristics with the use of different electrodes (compared to the platinum electrode (Table 4):

Table 4. Selected photovoltaic parameters using different electrodes. Reprinted with permission from [44]. Copyright 2021 American Chemical Society.

Counter Electrode	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
Pt [a]	16.08 ± 0.13	748 ± 2	0.64 ± 0.01	7.67 ± 0.04
Cu-MOF [a]	0.88 ± 0.88	618 ± 166	0.10 ± 0.03	0.04 ± 0.04
PEDOT [a]	15.49 ± 0.48	769 ± 7	0.64 ± 0.01	7.58 ± 0.25
Cu-MOF/PEDOT [a]	16.36 ± 0.27	777 ± 3	0.65 ± 0.02	8.26 ± 0.06
Cu-MOF/PEDOT [b]	17.48 ± 0.92	786 ± 9	0.69 ± 0.01	9.45 ± 0.35

[a] CEs substrate—fluorine-doped tin oxide; [b] CEs substrate—Carbon cloth (CC).

The paper of [44] confirms that the used Cu-MOF/PEDOT composite electrodes with appropriate redox pairs of I^-/I^{3-}, Co-phen^{2+}/Co-phen^{3+} and Cu-dmp$^+$/Cu-dmp^{2+} exhibit high electrochemical capabilities, which may be applicable to electrochemical process devices. The presence of Cu-MOF (the main electrocatalyst) in the composite electrode provides a conductive character, while PEDOT functions as an auxiliary electrocatalyst [44]. Another advantage of replacing Pt as CEs by PEDOT is the achievement of stability and high conductivity at room temperature [45]. PEDOT-based material should exhibit good electrocatalytic behavior used for dye regeneration. The authors of [45] report that the use of unmodified PEDOT allowed a cell conversion efficiency of 0.1%, while platinized FTOs and a counter electrode containing PEDOT allowed a conversion efficiency of over 4%. The following table shows the basic photovoltaic performance of dye-sensitized solar cells, including CEs with PEDOT (Table 5) [45]:

Table 5. Selected photovoltaic performance of PEDOT-based DSSCs with differing redox mediators and dyes. Reprinted from [45] under a Creative Common CC BY license.

Counter Electrode	Redox Mediator	Dye	PCE (%)
PEDOT-TsO	I_3^-/I^-	N719	4.60
PEDOT-PSS	I_3^-/I^-	N719	7.60
PEDOT-ClO_4	T^-/T_2	TH305	6.00
PEDOT-TFSI	I_3^-/I^-	C106	9.80
PEDOT-Cl	I_3^-/I^-	N719	8.42
PEDOT-FAP	$[Co(phen)_3]^{3+/2+}$	Y123	10.30
PEDOT-SDS	$[Cu(tmby)_2]^{1+/2+}$	Y123/XY1b	13.10

An interesting literature report in DSSCs appears to be the employment of carbon nanotubes (CNTs) as counter electrodes (CEs) in exchange for platinum. The use of graphene in the form of single and multi-walled carbon tubes (MWCNTs) allows for comparable catalytic activity or conversion efficiency and possibly better conductivity than those based on Pt/TCO [46]. In addition to carbon nanotubes or graphene, conductive polymers and also semiconductors made of metal oxides can be employed [47]. Carbon is a commonly found raw material on Earth, and its lower price compared to platinum, as well as its good chemical resistance, enables it to be classified as a good candidate for the production of DSSCs. For example, the use of Cu-based electrolytes with Pt can achieve solar-to-electric

conversion efficiencies of 1.4% [48], while the use of Pt/carbon black in DSSCs has achieved conversion rates in the order of 7% [25].

2.4. Application of Coordination Compounds in DSSCs

The development of DSSCs is mainly focused on improving the performance of the utilised dyes. The most recent reports are dedicated to the use of coordination compounds of transition metals, focusing on dyes based on non-heavy metal elements, so as to serve as alternatives to dyes based on highly toxic heavy metals, such as Pt^{2+}, Ir^{3+} and Ru^{2+} [40]. Developments regarding such alternative dyes focus on compounds that are environmentally friendly and originate from transition metals that are most commonly present in the natural environment, such as from copper [14]. Due to advances in photophysical and photoelectrochemical research using copper compounds as catalysts or photosensitizers, applications were found, for example, in energy conversion or storage.

Copper in complex compounds contained in DSSCs can serve not only as a dye but also as a redox mediator. Copper mediators as redox couples have found applications in electronic devices despite the sparse presence of solar cells in the device [23]. This is due to their high ability to regenerate the dye in the cell using merely 100 mV of driving force [49], providing and supporting a large cell output voltage of up to 1 V. Compared to previously mentioned redox mediators, such as I^-/I^{3-}, copper compounds do not pose a threat in terms of corrosivity [23]. Moreover, their longer diffusion length in systems with similar properties can provide higher photocurrents and higher fill factors [50]. Compared to iodine/iodide or cobalt-based complex compounds, the copper-containing compounds provide less energy loss arising from the transition from the reduced to the oxidized state [51].

An application of Cu-based compounds as dyes in solar cells is possible by improving the lifetime or degradation of some cell components caused by photoinduced oxidation under UV light (UV absorption capacity) [52,53]. These compounds exhibit luminescent properties [54]. The use of copper compounds in dye-sensitized solar cells, as recently reported in the literature, has achieved power conversion efficiencies up to 32%, under 1000 lux fluorescent illumination [23]. Copper compounds are also used in OLED devices, batteries or systems responsible for water oxidation using electrocatalysts [39].

3. Conclusions

The conversion of solar radiation to electricity, achieved with the use of solar cells, such as dye-sensitised solar cells (DSSCs) is one of the most abundant and effectively inexhaustible sources of energy. Despite this abundance, practical considerations, such as availability of space and materials used to produce solar cells, necessitate the development and use of increasingly efficient and inexpensive solar cell designs for harvesting the available solar energy.

The key advantage of DSSCs in comparison with other solar cell types (e.g., bulk heterojunction, multijunction, crystalline silicon) is that of cost-efficiency, as even though the PCE values achieved for DSSCs may not be considered particularly high among solar cells, DSSCs are fabricated from materials that can be considered relatively inexpensive when compared with the extremely pure raw materials required for producing other types of solar cells.

The initial works on DSSCs were strongly focused on heavy-metal-based materials, such as the coordination compounds of ruthenium, which are becoming increasingly expensive and are hazardous to both the environment and human health. Even though such materials remain in use, the number of annually reported DSSCs utilizing such materials is rapidly dwindling as alternative materials are discovered. Coordination compounds of copper should be mentioned with particular emphasis as one of the most promising alternatives to heavy-metal-based DSSC materials. The reported coordination compounds of copper can be used in DSSCs as dyes, as redox mediators in liquid electrolytes and as hole-transporting materials due to their available electronic energy levels. Although copper-based com-

pounds appear most prominently in recent works, zinc, iron and cobalt coordination compounds have also recently been reported as promising for DSSC applications.

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References

1. Stergiopoulos, T.; Falaras, P. Minimizing Energy Losses in Dye-Sensitized Solar Cells Using Coordination Compounds as Alternative Redox Mediators Coupled with Appropriate Organic Dyes. *Adv. Energy Mater.* **2012**, *2*, 616–627. [CrossRef]
2. Schlichthörl, G.; Park, N.; Frank, A.J. Evaluation of the charge-collection efficiency of dye-sensitized nanocrystalline TiO_2 solar cells. *J. Phys. Chem.* **1999**, *103*, 782–791. [CrossRef]
3. Teo, L.P.; Buraidah, M.H.; Arof, A.K. Development on Solid Polymer Electrolytes for Electrochemical Devices. *Molecules* **2021**, *26*, 6499. [CrossRef]
4. Castillo-Robles, J.A.; Rocha-Rangel, E.; Ramírez-de León, J.A.; Caballero-Rico, F.C.; Armendáriz-Mireles, E.N. Advances on Dye-Sensitized Solar Cells (DSSCs) Nanostructures and Natural Colorants: A Review. *J. Compos. Sci.* **2021**, *5*, 288. [CrossRef]
5. Grifoni, F.; Bonomo, M.; Naim, W.; Barbero, N.; Alnasser, T.; Dzeba, I.; Giordano, M.; Tsaturyan, A.; Urbani, M.; Torres, T.; et al. Toward Sustainable, Colorless, and Transparent Photovoltaics: State of the Art and Perspectives for the Development of Selective Near-Infrared Dye-Sensitized Solar Cells. *Adv. Energy Mater.* **2021**, *11*, 2101598. [CrossRef]
6. Saeed, M.A.; Yoo, K.; Kang, H.C.; Shim, J.W.; Lee, J.J. Recent developments in dye-sensitized photovoltaic cells under ambient illumination. *Dyes Pigments* **2021**, *194*, 109626. [CrossRef]
7. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. *Chem. Rev.* **2010**, *110*, 6595–6663. [CrossRef]
8. Yahya, M.; Bouziani, A.; Ocak, C.; Seferoğlu, Z.; Sillanpää, M. Organic/Metal-organic photosensitizers for dye-sensitized solar cells (DSSC): Recent developments, new trends, and future perceptions. *Dyes Pigments* **2021**, *192*, 109227. [CrossRef]
9. Inomata, T.; Hatano, M.; Kawai, Y.; Matsunaga, A.; Kitagawa, T.; Wasada-Tsutsui, Y.; Ozawa, T.; Masuda, H. Synthesis and Physico-Chemical Properties of Homoleptic Copper(I) Complexes with Asymmetric Ligands as a DSSC Dye. *Molecules* **2021**, *26*, 6835. [CrossRef]
10. Sauve, G.; Cass, M.E.; Coia, G.; Doig, S.J.; Lauermann, I.; Pomykal, K.E.; Lewis, N.S. Dye sensitization of nanocrystalline titanium dioxide with osmium and ruthenium polypyridyl complexes. *J. Phys. Chem.* **2000**, *104*, 6821–6836. [CrossRef]
11. Wong, H.L.; Mak, C.S.; Chan, W.K.; Djurišić, A.B. Efficient photovoltaic cells with wide photosensitization range fabricated from rhenium benzathiazole complexes. *Appl. Phys. Lett.* **2007**, *90*, 081107. [CrossRef]
12. Islam, A.; Sugihara, H.; Hara, K.; Singh, L.P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H. New platinum(II) polypyridyl photosensitizers for TiO_2 solar cells. *New J. Chem.* **2000**, *24*, 343–345. [CrossRef]
13. Boschloo, G.; Hagfeldt, A. Characteristics of the iodide/triiodide redox mediator in dye-sensitized solar cells. *Accounts Chem. Res.* **2009**, *42*, 1819–1826. [CrossRef] [PubMed]
14. Benesperi, I.; Singh, R.; Freitag, M. Copper coordination complexes for energy-relevant applications. *Energies* **2020**, *13*, 2198. [CrossRef]
15. Wu, K.; Liu, S.; Wang, Z.; Qi, X.; Chen, R.; Wu, M. The modified W2C@C composites derived from the polyoxotungstate-based organic complexes assisted by pyrrole for efficient counter electrode in dye-sensitized solar cells. *Surf. Interfaces* **2022**, *28*, 101628. [CrossRef]
16. Zhang, H.; Wu, X.; Tang, S.; Wang, K.; Tian, Y.; Zhong, C. Novel metal complexes for D-(A-π-A) 2 motif dye sensitizer: Synthesis and photovoltaic application. *Appl. Organomet. Chem.* **2021**, *35*, e6220. [CrossRef]
17. Conradie, M.M.; Langner, E.H.; Conradie, J. DFT data to relate calculated LUMO energy with experimental reduction potentials of Cu(II)-β-diketonato complexes. *Data Brief* **2021**, *38*, 107331. [CrossRef]
18. Baker, K.; Sikkema, R.; Liang, W.; Zhitomirsky, I. Multifunctional Properties of Commercial Bile Salts for Advanced Materials Engineering. *Adv. Eng. Mater.* **2021**, *23*, 2001261. [CrossRef]
19. Stojanović, M.; Flores-Diaz, N.; Ren, Y.; Vlachopoulos, N.; Pfeifer, L.; Shen, Z.; Liu, Y.; Zakeeruddin, S.M.; Milić, J.V.; Hagfeldt, A. The Rise of Dye-Sensitized Solar Cells: From Molecular Photovoltaics to Emerging Solid-State Photovoltaic Technologies. *Helv. Chim. Acta* **2021**, *104*, e2000230. [CrossRef]

20. Conesa-Egea, J.; Nogal, N.; Martínez, J.I.; Fernández-Moreira, V.; Rodríguez-Mendoza, U.R.; González-Platas, J.; Gómez-García, C.J.; Delgado, S.; Zamora, F.; Amo-Ochoa, P. Smart composite films of nanometric thickness based on copper–iodine coordination polymers. Toward sensors. *Chem. Sci.* **2018**, *9*, 8000–8010. [CrossRef]
21. López-Molina, J.; Hernández-Rodríguez, C.; Guerrero-Lemus, R.; Cantelar, E.; Lifante, G.; Muñoz, M.; Amo-Ochoa, P. Cu(i)–I coordination polymers as the possible substitutes of lanthanides as downshifters for increasing the conversion efficiency of solar cells. *Dalton Trans.* **2020**, *49*, 4315–4322. [CrossRef] [PubMed]
22. Higashino, T.; Iiyama, H.; Nimura, S.; Kurumisawa, Y.; Imahori, H. Effect of Ligand Structures of Copper Redox Shuttles on Photovoltaic Performance of Dye-Sensitized Solar Cells. *Inorg. Chem.* **2019**, *59*, 452–459. [CrossRef] [PubMed]
23. Vlachopoulos, N.; Hagfeldt, A.; Benesperi, I.; Freitag, M.; Hashmi, G.; Jia, G.; Wahyuono, R.A.; Plentz, J.; Dietzek, B. New approaches in component design for dye-sensitized solar cells. *Sustain. Energy Fuels* **2021**, *5*, 367–383. [CrossRef]
24. Khalil, M.M.; El-Sayed, A.H.; Masaoud, M.; Hamad, M.A. Dielectric properties and potential applications of alizarin yellow GG-Cu(II) complex film blended with polyvinyl alcohol. *J. Mater. Res. Technol.* **2021**, *11*, 1799–1805. [CrossRef]
25. Bai, Y.; Yu, Q.; Cai, N.; Wang, Y.; Zhang, M.; Wang, P. High-efficiency organic dye-sensitized mesoscopic solar cells with a copper redox shuttle. *Chem. Commun.* **2011**, *47*, 4376–4378. [CrossRef] [PubMed]
26. Rahmalia, W.; Septiani, S.; Naselia, U.; Usman, T.; Silalahi, I.; Mouloungui, Z. Performance improvements of bixin and metal-bixin complexes sensitized solar cells by 1-methyl-3-propylimidazolium iodide in electrolyte system. *Indones. J. Chem.* **2021**, *21*, 669–678. [CrossRef]
27. Li, Y.; Wang, G.; Feng, X.; Jia, Q.; Li, Y.; Liu, J.; Cao, J.; Liu, J. Double-layer novel zinc porphyrin based on axial coordination self-assembly for dye-sensitized solar cells. *J. Mol. Struct.* **2021**, *1242*, 130819. [CrossRef]
28. Lindh, L.; Chábera, P.; Rosemann, N.W.; Uhlig, J.; Wärnmark, K.; Yartsev, A.; Sundström, V.; Persson, P. Photophysics and photochemistry of iron carbene complexes for solar energy conversion and photocatalysis. *Catalysts* **2020**, *10*, 315. [CrossRef]
29. Xiang, N.; Huang, X.; Feng, X.; Liu, Y.; Zhao, B.; Deng, L.; Shen, P.; Fei, J.; Tan, S. The structural modification of thiophene-linked porphyrin sensitizers for dye-sensitized solar cells. *Dyes Pigments* **2011**, *88*, 75–83. [CrossRef]
30. Yang, K.; Yang, X.; Zhang, L.; An, J.; Wang, H.; Deng, Z. Copper redox mediators with alkoxy groups suppressing recombination for dye-sensitized solar cells. *Electrochim. Acta* **2021**, *368*, 137564. [CrossRef]
31. Kashif, M.K.; Benesperi, I.; Milhuisen, R.A.; Meyer, S.; Hellerstedt, J.; Zee, D.; Duffy, N.W.; Halstead, B.; Fuhrer, M.S.; Cashion, J.; et al. Polypyridyl Iron Complex as a Hole-Transporting Material for Formamidinium Lead Bromide Perovskite Solar Cells. *ACS Energy Lett.* **2017**, *2*, 1855–1859. [CrossRef]
32. Lin, L.; Lian, C.; Jones, T.W.; Bennett, R.D.; Mihaylov, B.; Yang, T.C.J.; Wang, J.T.W.; Chi, B.; Duffy, N.W.; Li, J.; et al. Tunable transition metal complexes as hole transport materials for stable perovskite solar cells. *Chem. Commun.* **2021**, *57*, 2093–2096. [CrossRef] [PubMed]
33. Fränkel, R.; Kernbach, U.; Bakola-Christianopoulou, M.; Plaia, U.; Suter, M.; Ponikwar, W.; Nöth, H.; Moinet, C.; Fehlhammer, W.P. Homoleptic carbene complexes: Part VIII. Hexacarbene complexes. *J. Organomet. Chem.* **2001**, *617*, 530–545. [CrossRef]
34. Luo, Y.N.; Kong, M.; Lu, Y.H.; Gao, Y.W.; Ren, H.; Yu, X.Y. A new (3, 6)-connected silver(I) coordination polymer with photovoltaic performance. *Inorg. Chem. Commun.* **2020**, *120*, 108079. [CrossRef]
35. Luo, Y.; Jiang, H.; Yu, L.; Liu, Z.; Yu, X. Synthesis, crystal structure, and photoelectrical property of a new (3, 6) connected 3D Zn(II) coordination polymer. *Inorg. Chem. Commun.* **2017**, *86*, 304–307. [CrossRef]
36. Selvaraj, B.; Shanmugam, G.; Kamaraj, S.; Gunasekeran, A.; Sambandam, A. Effect of 1-Substituted 2-(Pyridin-2-yl)-1*H*-Benzo[*d*] imidazole Ligand-Coordinated Copper and Cobalt Complex Redox Electrolytes on Performance of Ru(II) Dye-Based Dye-Sensitized Solar Cells. *Inorg. Chem.* **2021**, *60*, 1937–1947. [CrossRef]
37. Deng, Z.; Yang, X.; Yang, K.; Zhang, L.; Wang, H.; Wang, X.; Sun, L. Helical Copper Redox Mediator with Low Electron Recombination for Dye-Sensitized Solar Cells. *ACS Sustain. Chem. Eng.* **2021**, *9*, 5252–5259. [CrossRef]
38. Rui, H.; Shen, J.; Yu, Z.; Li, L.; Han, H.; Sun, L. Stable Dye-Sensitized Solar Cells Based on Copper(II/I) Redox Mediators Bearing a Pentadentate Ligand. *Angew. Chem.* **2021**, *133*, 16292–16299. [CrossRef]
39. Colombo, A.; Dragonetti, C.; Roberto, D.; Fagnani, F. Copper Complexes as Alternative Redox Mediators in Dye-Sensitized Solar Cells. *Molecules* **2021**, *26*, 194. [CrossRef]
40. Bella, F.; Galliano, S.; Gerbaldi, C.; Viscardi, G. Cobalt-based electrolytes for dye-sensitized solar cells: Recent advances towards stable devices. *Energies* **2016**, *9*, 384. [CrossRef]
41. Giribabu, L.; Bolligarla, R.; Panigrahi, M. Recent Advances of Cobalt(II/III) Redox Couples for Dye-Sensitized Solar Cell Applications. *Chem. Rec.* **2015**, *15*, 760–788. [CrossRef] [PubMed]
42. Yuan, X.; Huang, W.; Kong, L.; Guo, S.; Cheng, Y. Ditungsten Carbide Nanoparticles Homogeneously Embedded in Carbon Nanofibers for Efficient Hydrogen Production. *Chem. Eng. J.* **2021**, *420*, 130480. [CrossRef]
43. Fan, J.; Dou, Y.; Jiang, R.; Du, K.; Deng, B.; Wang, D. Electro-synthesis of tungsten carbide containing catalysts in molten salt for efficiently electrolytic hydrogen generation assisted by urea oxidation. *Int. J. Hydrog. Energy* **2021**, *46*, 14932–14943. [CrossRef]
44. Yang, A.N.; Lin, J.T.; Li, C.T. Electroactive and Sustainable Cu-MOF/PEDOT Composite Electrocatalysts for Multiple Redox Mediators and for High-Performance Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* **2021**, *13*, 8435–8444. [CrossRef] [PubMed]
45. Marchini, E.; Caramori, S.; Bignozzi, C.A.; Carli, S. On the Use of PEDOT as a Catalytic Counter Electrode Material in Dye-Sensitized Solar Cells. *Appl. Sci.* **2021**, *11*, 3795. [CrossRef]

46. Yun, S.; Hagfeldt, A.; Ma, T. Pt-free counter electrode for dye-sensitized solar cells with high efficiency. *Adv. Mater.* **2014**, *26*, 6210–6237. [CrossRef] [PubMed]
47. Kaur, K.; Patyal, M.; Gupta, N. A review on the use of carbon matrix incorporated with macrocyclic metal complexes as counter electrodes for platinum free dye sensitized solar cells. *J. Coord. Chem.* **2021**, *74*, 543–562. [CrossRef]
48. Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. Blue copper model complexes with distorted tetragonal geometry acting as effective electron-transfer mediators in dye-sensitized solar cells. *J. Am. Chem. Soc.* **2005**, *127*, 9648–9654. [CrossRef]
49. Freitag, M.; Giordano, F.; Yang, W.; Pazoki, M.; Hao, Y.; Zietz, B.; Gratzel, M.; Hagfeldt, A.; Boschloo, G. Copper phenanthroline as a fast and high-performance redox mediator for dye-sensitized solar cells. *J. Phys. Chem. C* **2016**, *120*, 9595–9603. [CrossRef]
50. Pradhan, S.C.; Hagfeldt, A.; Soman, S. Resurgence of DSCs with copper electrolyte: A detailed investigation of interfacial charge dynamics with cobalt and iodine based electrolytes. *J. Mater. Chem. A* **2018**, *6*, 22204–22214. [CrossRef]
51. Zhang, J.; Vlachopoulos, N.; Jouini, M.; Johansson, M.B.; Zhang, X.; Nazeeruddin, M.K.; Boschloo, G.; Johansson, E.M.; Hagfeldt, A. Efficient solid-state dye sensitized solar cells: The influence of dye molecular structures for the in-situ photoelectrochemically polymerized PEDOT as hole transporting material. *Nano Energy* **2016**, *19*, 455–470. [CrossRef]
52. Day, J.; Senthilarasu, S.; Mallick, T.K. Improving spectral modification for applications in solar cells: A review. *Renew. Energy* **2019**, *132*, 186–205. [CrossRef]
53. López, J.; Platas, J.G.; Rodríguez-Mendoza, U.R.; Martínez, J.I.; Delgado, S.; Lifante-Pedrola, G.; Cantelar, E.; Guerrero-Lemus, R.; Hernández-Rodríguez, C.; Amo-Ochoa, P. Cu(I)–I-2,4-diaminopyrimidine Coordination Polymers with Optoelectronic Properties as a Proof of Concept for Solar Cells. *Inorg. Chem.* **2020**, *60*, 1208–1219. [CrossRef] [PubMed]
54. Hu, L.X.; Gao, M.; Wen, T.; Kang, Y.; Chen, S. Synthesis of halide-modulated cuprous(I) coordination polymers with mechanochromic and photocatalytic properties. *Inorg. Chem.* **2017**, *56*, 6507–6511. [CrossRef] [PubMed]