Chapter

Schiff Bases and Their Metal Complexes in Solar Cells

Mirjana M. Radanović and Marijana S. Kostić

Abstract

Schiff bases represent a large group of organic compounds interesting for many different profiles of researchers due to their easy synthesis, versatile coordination behavior, and structural properties of their metal complexes, but primarily due to different application possibilities. Besides the promising biological activities, Schiff bases and their metal complexes often show high photoluminescence, thus making good candidates for use in optical materials. Among these, the use of Schiff base metal complexes in different types of solar cells stands out. With the aim to make this more attractive for more coordination chemists, in this chapter, we highlight the main findings from this field to establish a better understanding of the structure-properties linkage and enable the design of new materials with enhanced characteristics.

Keywords: coordination compounds, structure, schiff bases, photovoltaics, DSSC, perovskite solar cells, organic solar cells

1. Introduction

Countless efforts are being made to achieve better substitutes for fossil fuels and suppress air pollution and climate change [1]. One of the roads to a greener future is undoubtedly the utilization of solar light instead of fossil fuels and its conversion into electrical energy through solar cells.

Dye-sensitized solar cells (DSSC) represent the third generation of solar cells. During the 3 decades since their introduction, different classes of compounds were investigated as photosensitizers to achieve better efficiency, stability, and improved production procedures. Research has revealed that metal complexes play a crucial role in enhancing the stability and photovoltaic performance of DSSC. Compounds featuring double carbon-nitrogen bonds emerge as promising candidates for investigating optical properties [2]. The conjugation and delocalization of such bonds and their complexation to metal ions, thus forming so-called push-pull molecules, offer an added boost to their optical activity, making them attractive for applications in photovoltaic cells.

Initially, ruthenium complexes with various ligands were explored for this purpose. However, the current thrust is toward discovering materials that leverage more cost-effective and readily available metals, considering ruthenium's rarity and price. Research has shown that complexes of 3d and 4d metals with N-heterocyclic ligands have broad absorption spectra and excellent light-harvesting properties [1], making them promising materials for enhancing the sensitivity of DSSC.

In addition to the DSSC, the usage of Schiff base derivatives in organic solar cells and perovskite solar cells (PSC) is currently being explored. The latter, being the most attractive type of solar cells for researchers nowadays, opens a new path of combining the advantages of both types of materials.

Hence, this chapter will present the main findings in using Schiff base metal complexes for various purposes in different kinds of solar cells.

2. Schiff bases and their complexes in DSSC

One of the main advantages of DSSC was using dyes as the absorbing layer instead of the semiconductor. With this aim, different classes of compounds were investigated, such as natural sensitizers, polymers, derivatives of anthracene, and metal complexes, the latter being among the most promising ones [2, 3]. Organic dyes were more efficient due to unlocalized electrons, but inorganic dyes were shown to be more durable and stable at higher temperatures [4]. This made metal-organic derivatives more interesting for research since they had both advantages. Also, the complexation of Schiff bases to metal ions could enhance their optoelectronic properties [5] and make them more suitable for this application.

The research has shown that metal complexes used as sensitizers should contain anchoring ligands (usually carboxylic or phosphorous acid) that bind to the surface of the semiconductor and ancillary ligands with π-donor properties to enable a "push-pull" design [6–8].

One of the first complexes used as light absorbers was the ruthenium complex with bipyridine $[Ru(bpy)]^{2+}$. Its application resulted in low-efficiency solar cells due to their low stability [2]. Later studies were made to obtain acceptable power conversion efficiency (PCE), and some ruthenium polypyridyl complexes were proved to possess many advantages, such as wide absorption due to metal-to-ligand charge transfer, longer excitation lifetime, and long-term chemical stability. However, issues like poor absorption in near-IR, low yields, complicated purification procedures, the toxicity of the Ru-based materials, high-cost fabrication, and limited resources remained. This motivated the scientists to search for sensitizers that contain less toxic and easily available metal center or metal-free sensitizers. The latter was shown to have lower PCE, shorter excitation lifetime, and aggregation-induced self-quenching, similar to natural dyes [9].

Numerous complexes with different metals were synthesized and tested for this application, but our attention is drawn to the Schiff bases and their metal complexes. These compounds could overcome the mentioned drawbacks due to their suitable optoelectronic features, better stability, and environment-friendly synthetic routes.

Two complexes of copper(II) (**Figure 1**) and cobalt(III) with the NO bidentate Schiff base salicylidene-ethanolamine, used as sensitizers of DSSC [10], gave PCEs of 3 and 3.84%, respectively.

The majority of the examined compounds are mononuclear, often homoleptic complexes. Polymeric complexes are not thoroughly investigated, probably due to more complicated preparation procedures [11]. One of the newest results in this field is the synthesis and characterization of copper(II) and cadmium(II) complexes (**Figure 2**) containing one of these two salicylaldehyde Schiff base derivatives with a "push-pull" structure [8].

When used as sensitizers, cadmium(II) complexes were more efficient than copper(II) complexes with the same ligand, most probably due to the larger radius of the cadmium ion. The range of PCEs was from 4.77 to 8.59% [8].

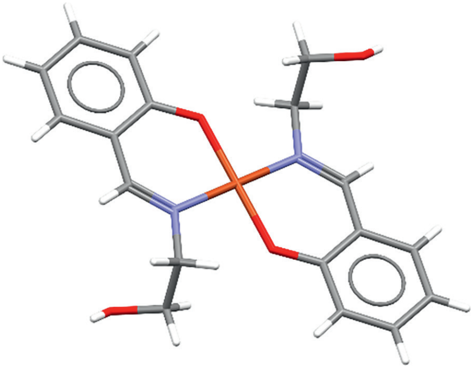


Figure 1.
Molecular structure of the copper(II) complex with Schiff base of salicylaldehyde and ethanolamine (refcode HESLCU10).

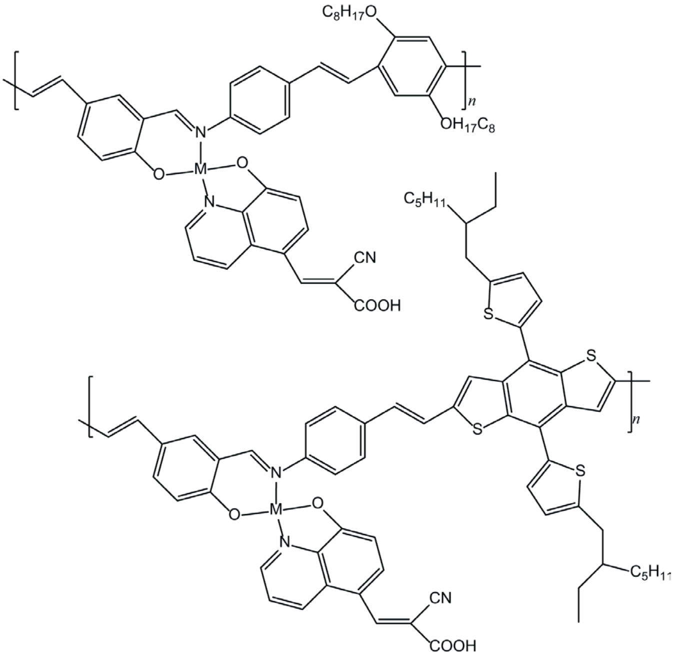
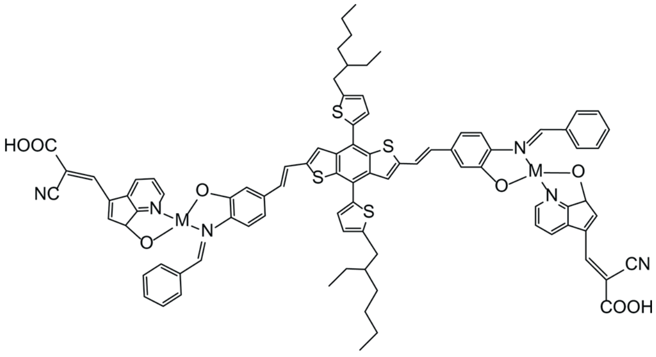


Figure 2.
Structural formulas of the complexes with salicylaldehyde derivative (M = Cu, Cd).

Other four complexes of d-metals were synthesized and characterized, and their efficiency as dyes was examined (**Figure 3**) [12]. Cobalt(II) and copper(II) complexes were less effective than zinc and cadmium ones, meaning the impact of central ion is one of the crucial factors for obtaining higher efficiency.

Copper complexes are among the most promising ones since they could be used not only as photosensitizers but also as redox shuttles (**Figure 4**) [13]. Namely, the commonly used triiodide/iodide redox couple, aside from good performance, could cause various problems due to its volatile nature, corrosive effect, and dark red color of the triiodide ion. These obstacles could be vanquished by using metal complexes with variable oxidation states.



M = Cd, Zn, Cu, Co

Figure 3.
The structural formula of complexes with thienylbenzo[1,2-b,4,5-b′]dithiophene and the 8-quinolinol derivative [12].

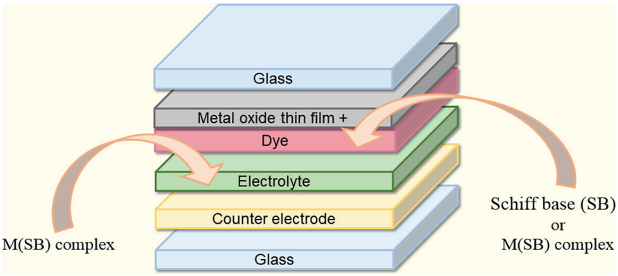


Figure 4.
Strategies to enhance DSSCs using Schiff bases or their metal complexes.

With this aim, cobalt complexes (**Figure 5**) were investigated, and some improvements were observed [14].

Still, because of limitations and potential health problems cobalt complexes could cause, copper(I/II) compounds of distorted tetragonal geometry were suggested as suitable. In addition to copper and cobalt complexes, iron, nickel, manganese, and vanadium complexes were also investigated as replacements for the triiodide/iodide redox couple [15].

In [16], an oxovanadium(IV/V) redox coupled with a well-known salen ligand (symmetric Schiff base of salicylaldehyde and ethylenediamine in molar ratio 2:1)

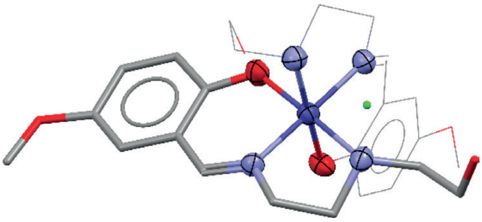


Figure 5.
Molecular structure of the bis(ligand) cobalt(III) complex (refcode YIWCAK). Hydrogen atoms are omitted for clarity; metal center and ligator atoms are represented as ellipsoids.

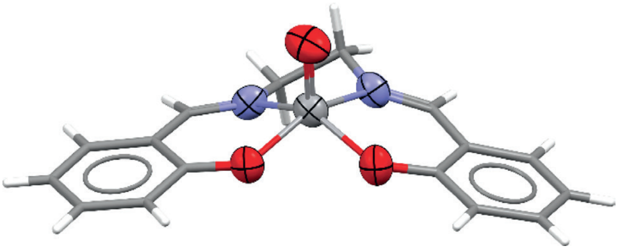


Figure 6.
Molecular structure of VO(salen) complex (refcode DOGSOH). Metal center and ligator atoms are represented as ellipsoids.

was used as a redox mediator in DSSC (**Figure 6**). The results showed the efficiency of back then satisfying more than 5%.

Until now, studies for optimal sensitizers have been much broader and more thorough than the search for alternatives to common redox shuttles. Still, this area represents a field in which much progress could be made in the following years.

3. Schiff bases and their metal complexes in perovskite solar cells

As said earlier, PSCs are currently the most attractive type of solar cells due to their tunable properties, high sensitivity, and high tolerance to structure defects, imperfections, and impurities. Besides, PSCs are simpler to fabricate and cost less than the most widely used and commercialized crystalline solar cells. The researchers' great interest in PSCs led to fast progress in the field—in 10 years, the PCE was enlarged almost seven times (from 3.8 to 25.8%) [17]!

Even though PSCs seem the best for now, they are far from ideal. One strategy for improvement consists of changing the hole-transport materials (HTM). Different compounds have been tested as HTMs, some purely organic—different small molecules, as well as polymers, some hybrid organic-inorganic and pure inorganic compounds such as different metal oxides, copper(I)-iodide, and copper(I)-thiocyanate. However, the PSCs with the best performances are produced using the spirobifluorene derivative Spiro-OMeTAD (**Figure 7**) as HTM.

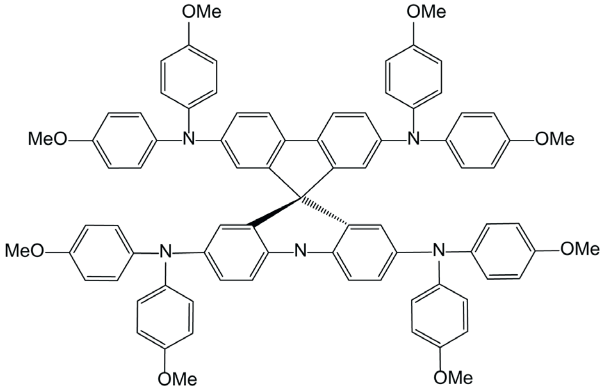


Figure 7.
The structural formula of the most effective HTM in PSCs.

The most commonly used HTMs involve complicated reaction routes with an inert atmosphere, high-cost catalysts, and a purification process. For this purpose, Schiff bases were suggested as a good replacement [18]. They are obtained in excellent yields in a simple one-pot condensation reaction, with water as the only by-product. This makes their synthesis easy, cost-effective, environment-friendly, and easy to scale up, while their purification process is straightforward. When applied as HTMs, the solar cell's performance is comparable to those with the usually used materials.

One of the drawbacks of Schiff bases is the hydrolysis azomethine bond is prone to. Nevertheless, this phenomenon is more noticeable in aliphatic derivatives, whereas in aromatic, highly conjugated ones, the imine group exhibits greater resistance to hydrolysis [19].

Some azomethines and diimines (**Figure 8**) were examined regarding acid-base discoloration and optoelectronic properties [20] and suggested as promising candidates for HTMs in PSCs but not competitive with Spiro-OMeTAD.

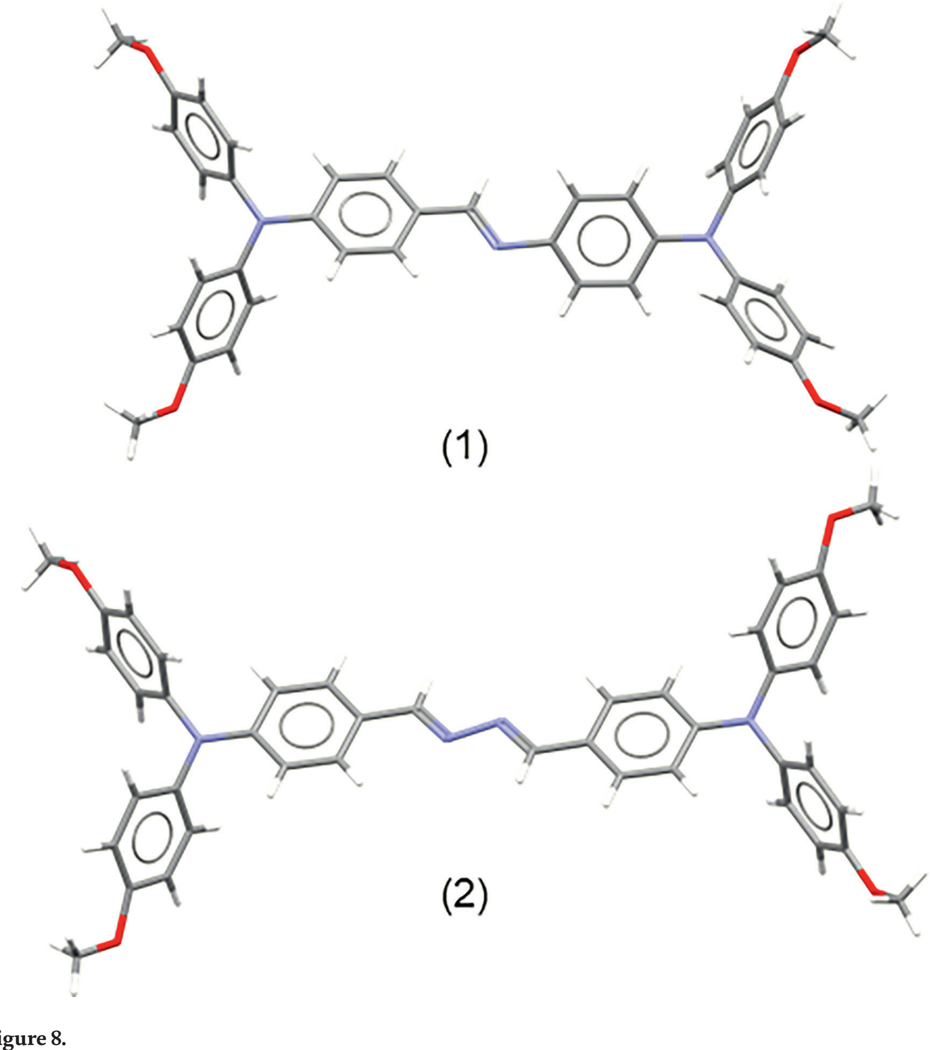


Figure 8.
Molecular structures of Schiff base derivative examined for use in PSCs (refcodes CUHXUA (1) and CUHXOU (2)).

Another series of Schiff bases as possible HTMs were synthesized, in which the core and direction of the azomethine bond were varied to examine their influence on the performance of PSCs [19]. The best ones showed to be those containing heterocyclic rings, most probably due to the stronger dipole and close molecular packing. Unlike Spiro-OMeTAD, all Schiff base derivatives used as HTMs were good against degradation due to moisture.

To overcome the disadvantages of state-of-the-art PSCs, some phenothiazines were also examined as potential HTMs (**Figure 9**). Namely, the existing method for HTM preparation typically relies on using predominantly chlorinated toxic solvents [21, 22]. These Schiff bases were synthesized in a procedure designed to minimize health and environmental hazards. Among these, AZO-II showed the best performance, with a PCE of 14%, excellent stability, and a low production price. While the results have not demonstrated a significant enhancement in efficiency, adopting a procedure nearly ten times cheaper and utilizing green solvents leads the authors to believe that this represents a promising approach for developing improved PSCs.

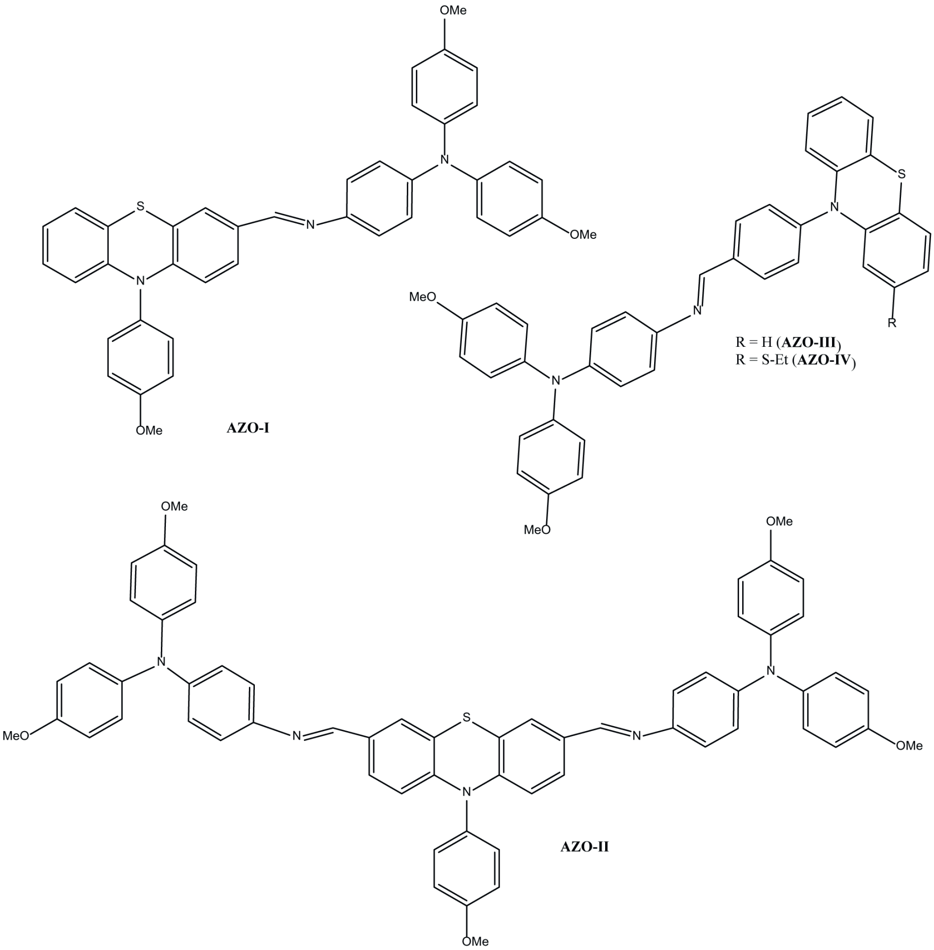


Figure 9.
Molecular structures of Schiff base derivative examined for use in PSCs.

A few years ago, interest in implementing Schiff base metal complexes to enhance the properties of perovskite solar cells arose. Namely, since the energy levels could be refined by changing the central metal ion, better alignment with the PSC absorber, lower surface roughness, and higher crystallinity could be achieved. All of this could lead to higher conversion efficiencies. Ones of the first to explore were complexes of platinum, palladium, and copper (**Figure 10**) [23]. These results open a new path to enhancing PSCs and solar cells in general.

Some earlier synthesized and characterized Co(II) complexes with the Schiff base of ninhydrin and glycin, obtained by template reaction (**Figure 11**), were evaluated as possible sensitizers for TiO_2 and ZnO layers [24]. The preliminary research has shown the enhanced efficiency of sensitized PSCs for a few percentiles.

One of the newest studies examined the use of Cu(II) complex with Schiff base derivative of 3,5-dichlorosalicylaldehyde and 3,4-diaminobenzoic acid as HTM [25] in all-inorganic PSCs, such as $CsBrBr_3$. Inorganic-organic hybrid PSCs (e.g., $CH_3NH_3PbX_3$ ($MAPbX_3$), $HC(NH_2)$ BbX_3($FAPbX_3$), and X = Cl, Br or I)) are more prone to moisture and oxygen invasion; thus, apart from reaching the highest efficiency, improved stability is necessary. This could be achieved by the enlargement of the inorganic portion of the hybrid and the use of Schiff base derivatives as HTMs. The outcome was the efficiencies comparable to those of carbon-based $CsBrBr_3$ cells, with the hint for future research to deal with using other transition metals and tuning the properties of materials by varying the Schiff base derivatives.

Generally, two approaches for utilizing Schiff bases and their metal complexes to improve PSCs are known so far: using these compounds as HTMs or as sensitizers for the electron transport layer, as summarized in **Figure 12**.

However, still, many issues remain to be addressed. One of them is the toxicity of the used PSCs, mostly because of the lead presence [17]. The global use of these solar cells could cause the contamination of the ecosystem with lead, which will eventually be present in the air, soil, and water in higher concentrations. Also, the higher stability of PSCs under high temperatures and humidity is of great interest. Considering the positive effect of Schiff bases and their metal complexes on improving the material's resilience to corrosion [26–28] and the fact that the application of metal complexes in PSCs is not thoroughly examined, this path could be one of the solutions for the mentioned issues.

Besides, some novel paths in designing the structure of the complexes might be attractive based on the results of the assessment of optoelectronic properties of some Schiff bases of aminoguanidine [29–31].

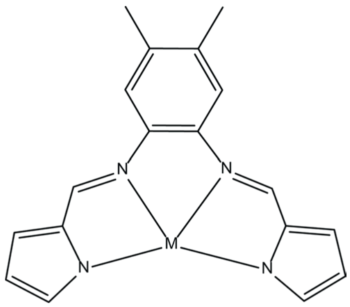


Figure 10.
Structural formula of the complexes (M = Pt, Pd, Cu).

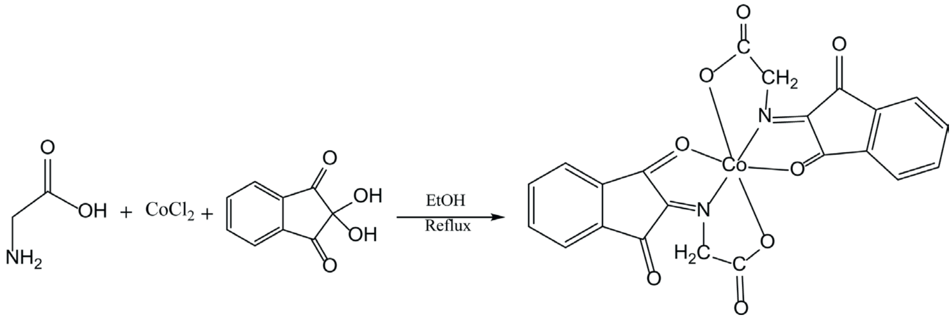


Figure 11.
Reaction route for the synthesis of Co(II) complex with Schiff base of ninhydrin and glycin.

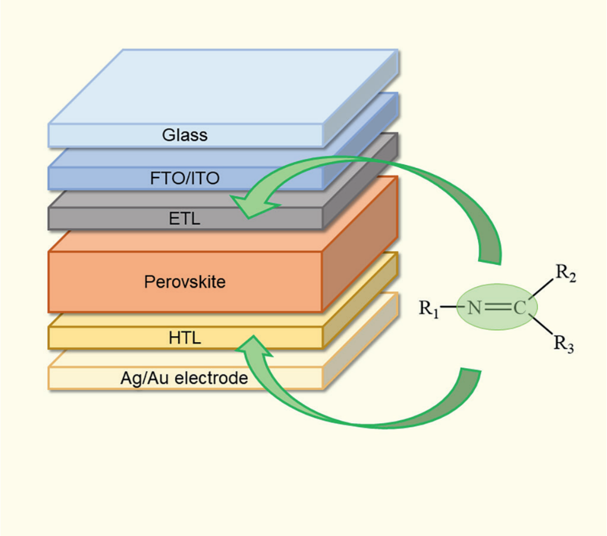


Figure 12.
Examined possibilities of enhancement of PSCs by using Schiff bases and their metal complexes. FTO = fluoride doped tin oxide; ITO = indium tin oxide; ETL = electron transport layer, HTL = hole transport layer.

Also, it should be noted that detailed structural characterization of these materials would lead to better insight into structure-properties linkage, which could enable the design of environment-friendly stable solar products with optimal efficacy and lifetime, as well as manufacturing costs.

4. Conclusions

Utilizing Schiff bases and their metal complexes in solar cells offers promising potential for advancing photovoltaic technology. Exploring these materials in dye-sensitized solar cells and perovskite solar cells revealed they provide notable advantages like adjustable electronic properties, high light absorption, and easy manufacturing processes. Additionally, exploring novel Schiff base ligands and metal complexes holds promise for enhancing device efficiency, stability, and cost-effectiveness while considering major environmental challenges. Nevertheless, more detailed studies are needed to understand and optimize their performance in solar cell applications fully. In both dye-sensitized solar cells and perovskite solar cells, the interaction between the Schiff base ligands and metal ions impacts the device's efficiency and stability. Thus, the design of novel Schiff bases and their complexes should be highly interesting. Future research should focus on comprehensive structural characterization by X-ray crystallography and the comparative analysis of the structures and performances of numerous compounds to gain better insight into the structure-property relationships governing their performance.

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Notes/thanks/other declarations

Molecular structures presented throughout the text are visualized using Mercury software.

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References

[1] Colombo A, Dragonetti C, Roberto D, Fagnani F. Copper complexes as alternative redox mediators in dye-sensitized solar cells. Molecules. 2021;**26**:194. DOI: 10.3390/molecules26010194

[2] Polo AS, Itokazu MK, Murakami Iha NY. Metal complex sensitizers in dye-sensitized solar cells. Coordination Chemistry Reviews. 2004;**248**:1343-1361. DOI: 10.1016/j.ccr.2004.04.013

[3] Kalyanasundaram K, Grätzel M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. Coordination Chemistry Reviews. 1998;**177**:347-414. DOI: 10.1016/S0010-8545(98)00189-1

[4] Arjmand F, Rashidi Ranjbar Z, Fatemi EGH. Effect of dye complex structure on performance in DSSCs; An Experimental and Theoretical Study. Heliyon. 2022;**8**:e11692. DOI: 10.1016/j.heliyon.2022.e11692

[5] Chouk R, Aguir C, Haouanoh D, Bergaoui M, Tala-Ighil R, Stathatos E, et al. A first-principles computational and experimental investigation on Schiff base cobalt complex towards designing solar cells. Journal of Molecular Structure. 2019;**1196**:676-684. DOI: 10.1016/J.MOLSTRUC.2019.07.026

[6] Cantón-Díaz AM, Muñoz-Flores BM, Moggio I, Arias E, De León A, García-López MC, et al. One-pot microwave-assisted synthesis of organotin Schiff bases: An optical and electrochemical study towards their effects in organic solar cells. New Journal of Chemistry. 2018;**42**:14586-14596. DOI: 10.1039/C8NJ02998A

[7] Lüthi E, Cortés PAF, Prescimone A, Constable EC, Housecroft CE. Schiff base ancillary ligands in bis(diimine) copper(I) dye-sensitized solar cells. International Journal of Molecular Sciences. 2020;**21**:1735. DOI: 10.3390/IJMS21051735

[8] Tian Y, Wang K, Zhang H, Wu X, Zhong C. Novel polymeric metal complexes of salicylaldehyde Schiff base derivative being used for dye sensitizer. Tetrahedron. 2022;**113**:132756. DOI: 10.1016/J.TET.2022.132756

[9] Mahadevi P, Sumathi S. Mini review on the performance of Schiff base and their metal complexes as photosensitizers in dye-sensitized solar cells. Synthetic Communications. 2020;**50**:2237-2249. DOI: 10.1080/00397911.2020.1748200

[10] Gautam C, Srivastava D, Kociok-Köhn G, Gosavi SW, Sharma VK, Chauhan R, et al. Copper(II) and cobalt(III) Schiff base complexes with hydroxy anchors as sensitizers in dye-sensitized solar cells (DSSCs). RSC Advances. 2023;**13**:9046-9054. DOI: 10.1039/D3RA00344B

[11] Okubo T, Tanaka N, Anma H, Kim KH, Maekawa M, Kuroda-Sowa T. Dye-sensitized solar cells with new one-dimensional halide-bridged Cu(I)–Ni(II) heterometal coordination polymers containing hexamethylene dithiocarbamate ligand. Polymers. 2012;**4**:1613-1626. DOI: 10.3390/POLYM4031613

[12] 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. Applied Organometallic Chemistry. 2021;**35**:e6220. DOI: 10.1002/AOC.6220

[13] Fagnani F, Colombo A, Dragonetti C, Roberto D. Recent investigations on the

use of copper complexes as molecular materials for dye-sensitized solar cells. Molecules. 2024;**29**:6. DOI: 10.3390/MOLECULES29010006

[14] Nasr-Esfahani M, Zendehdel M, Yaghoobi Nia N, Jafari B, Khosravi BM. Fabrication and characterization of a new dye sensitized solar cell with a new Schiff base cobalt complex as a redox mediator. RSC Advances. 2014;**4**:15961-15967. DOI: 10.1039/C3RA46531D

[15] Muñoz-García AB, Benesperi I, Boschloo G, Concepcion JJ, Delcamp JH, Gibson EA, et al. Dye-sensitized solar cells strike back. Chemical Society Reviews. 2021;**50**:12450-12550. DOI: 10.1039/D0CS01336F

[16] Oyaizu K, Hayo N, Sasada Y, Kato F, Nishide H. Enhanced bimolecular exchange reaction through programmed coordination of a five-coordinate oxovanadium complex for efficient redox mediation in dye-sensitized solar cells. Dalton Transactions. 2013;**42**:16090-16095. DOI: 10.1039/C3DT51698A

[17] Diouf B, Muley A, Pode R. Issues, challenges, and future perspectives of perovskites for energy conversion applications. Energies. 2023;**16**:6498. DOI: 10.3390/EN16186498

[18] Petrus ML, Bein T, Dingemans TJ, Docampo P. A low cost azomethine-based hole transporting material for perovskite photovoltaics. Journal of Materials Chemistry A. 2015;**3**:12159-12162. DOI: 10.1039/C5TA03046C

[19] Petrus ML, Music A, Closs AC, Bijleveld JC, Sirtl MT, Hu Y, et al. Design rules for the preparation of low-cost hole transporting materials for perovskite solar cells with moisture barrier properties. Journal of Materials Chemistry A. 2017;**5**:25200-25210. DOI: 10.1039/C7TA06452G

[20] Ma BB, Zhang H, Wang Y, Peng YX, Huang W, Wang MK, et al. Visualized acid–base discoloration and optoelectronic investigations of azines and azomethines having double 4-[N,N-di(4-methoxyphenyl)amino] phenyl terminals. Journal of Materials Chemistry C. 2015;**3**:7748-7755. DOI: 10.1039/C5TC00909J

[21] Salunke J, Guo X, Lin Z, Vale JR, Candeias NR, Nyman M, et al. Phenothiazine-based hole-transporting materials toward eco-friendly perovskite solar cells. ACS Applied Energy Materials. 2019;**2**:3021-3027. DOI: 10.1021/ACSAEM.9B00408

[22] Salunke J, Guo X, Liu M, Lin Z, Candeias NR, Priimagi A, et al. N-substituted phenothiazines as environmentally friendly hole-transporting materials for low-cost and highly stable halide perovskite solar cells. ACS Omega. 2020;**5**:23334-23342. DOI: 10.1021/acsomega.0c03184

[23] Wang Y, Ye W, Yang X, Rezaee E, Shan H, Yang S, et al. Hole transport layers based on metal Schiff base complexes in perovskite solar cells. Synthetic Metals. 2020;**259**:116248. DOI: 10.1016/J.SYNTHMET.2019.116248

[24] Chouk R, Haouanoh D, Bergaoui M, Aguir C, Tala-Ighil R, Khalfaoui M. Efficient planar perovskite solar cells using Schiff base complex as sensitizer for TiO2 and ZnO layers. In: 6th IEEE International Energy Conference (ENERGYCon 2020); 28 September 2020; Gammarth, Tunisia. New York, USA: IEEE; 2020. pp. 7-10

[25] Zheng L, Jackson E, Warren N, Owor R, Li Z. Perovskite CsPbBr3 solar cells with novel hole-transporting layer of metal complexes. Georgia Journal of Science. 2023;**81**:15

[26] Verma C, Quraishi MA. Recent progresses in Schiff bases as aqueous phase corrosion inhibitors: Design and applications. Coordination Chemistry Reviews. 2021;**446**:214105. DOI: 10.1016/J.CCR.2021.214105

[27] Afshari F, Ghomi ER, Dinari M, Ramakrishna S. Recent advances on the corrosion inhibition behavior of Schiff base compounds on mild steel in acidic media. ChemistrySelect. 2023;**8**:e202203231. DOI: 10.1002/slct.202203231

[28] Boulechfar C, Ferkous H, Delimi A, Berredjem M, Kahlouche A, Madaci A, et al. Corrosion inhibition of Schiff base and their metal complexes with [Mn (II), Co (II) and Zn (II)]: Experimental and quantum chemical studies. Journal of Molecular Liquids. 2023;**378**:121637. DOI: 10.1016/J.MOLLIQ.2023.121637

[29] Jelić MG, Georgiadou DG, Radanović MM, Romčević N, Giannakopoulos KP, Leovac VM, et al. Efficient electron injecting layer for PLEDs based on (PLAGH)2[ZnCl4]. Optical and Quantum Electronics. 2016;**48**:1-10. DOI: 10.1007/s11082-016-0547-5

[30] Radanović MM, Vojinović-Ješić LS, Jelić MG, Sakellis E, Barta Holló B, Leovac VM, et al. Synthesis, structures, and photoluminescence of two novel zinc(II) compounds containing 2-acetylpyridine-aminoguanidine. Inorganics. 2022;**10**:147. DOI: 10.3390/INORGANICS10100147

[31] Babic B, Romcevic M, Gilic M, Trajic J, Radanović MM, Vojinović-Ješić LS, et al. Phonon assisted charge transfer in complexes of Zn(II) and Cd(II) with 2-acetylpyridine-aminoguanidine. Optical Materials. 2023;**136**:113445. DOI: 10.1016/J.OPTMAT.2023.113445