Volume 23 Issue 1 2022 *CENTRAL ASIA AND THE CAUCASUS* *English Edition*

Insightful Discussion of Copper (I) Complexes As Promising Sensitizers for Dye-Sensitized Solar Cells

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DOI: https://doi.org/10.37178/ca-c.21.5.081

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Abstract

Energy production must evolve from heavily depending on fossil fuels to renewable resources in order to cease the depletion of those resources. Solar energy development is an alternative to reduce our reliance on fossil fuels which also helps to offset global warming by reducing greenhouse gas emissions. Generally, photovoltaic (PV) cells are classified based on the generation (GEN) or category. Dye-sensitized solar cells (DSSCs) which from the third GEN are still one of the best alternatives over the silicon-devices due to its sustainability and rapid improvement in conversion efficiency. However, there are several factors hampering dependency on DSSCs such as cost and environmental concerns. Therefore, we conducted this systematic *literature review based on the Scopus database to find out possible answers for those questions. To the present time, transition metal complexes based on ruthenium (Ru) are the most prevailing sensitizers. However, these noble metal-based devices are not sustainable due to the toxicity and scarcity of Ru metal. Thus, designing alternatives that transcend these drawbacks is worthwhile in the long run. In this context, copper (Cu) complexes become the prominent choice. Other than the economic benefits, Cu complexes mainly Cu(I) polypyridyl-based compounds display numerous photophysical similarities with* $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ *such as strong metal-ligand charge transfer (MLCT) absorption in the visible region and a relatively long excited-state lifetime. In summary, qualities possessed by Cu complexes are excellent as sensitizers and ideal to be the replacement for Ru complexes.*

Keywords: *Copper complexes, dye-sensitized solar cells, photovoltaic, polypyridyl-based compounds, sensitizers, solar energy.*

Introduction

Year after year, the global energy market grows at a breakneck rate due to population and economic growth, infrastructure development and demographic changes[1, 2]. Therefore, production of electricity has to be moved to renewable energy (RE) sources from conventional energy sources. In the energy sector, the RE such as solar, geothermal, biomass waste, wind, hydropower and biofuel [3] are preferred to replace the depletion of fossil fuels and gas sources. Acknowledging that sunlight is clean, generous and readily available in most zones on the Earth's surface, the direct conversion of solar radiation into electricity emerges as an engaging sustainable and green solution regarding energy in South East Asia, especially in Malaysia[4].

Since the introduction of DSSCs by Gratzel and O' Reagen, DSSC has become the most favourable system for less pricey production of PV energy[5]. Although PV is commonly used for converting solar energy to electricity, the price of PV cells is quite expensive. Thus, development of low cost and superior DSSCs over well-known silicon devices are utterly needed[6]. Generally, DSSCs consist of five important components as shown in Figure 1 which are a layer of transparent conductive oxide (TCO) on the glass surface[6, 7], semiconductor film with wide bandgap, light harvested dyes, redox mediator and the counter electrode[8-11]. The researcher always generalized a layer of TCO, semiconductor film with wide bandgap and light harvested dyes as a photoanode.

In developing efficient photoanode, factors such as rate of electron injection, recombination of charge carriers and production rate of photo-electron need to be considered[9]. The light absorption can be maximised if the photoanodes have wide surface area which can boost dye fill up. Photoanodes with high transparency also can improve light absorption by reducing wasting of incident photons. In addition, the conduction band of the photoanode must be fair under the lowest unoccupied molecular orbitals (LUMOs) of the dye in order to allow the injection of electrons to take place when reaction occurs. When photons from the light spectrum are struck on photoanode, the dye sensitizers in its ground state absorb the photons from the sunlight and get excited from the ground state to a higher energy state. The excited dye molecule is oxidized and an electron is injected into the conduction band of the semiconductor. The excited electrons from metal oxide are diffused to the TCO and reach at the counter electrode through an external circuit. The oxidized dye molecule is again regenerated by electron donation from the redox electrolyte. Therefore, the materials also must not be noxious to the redox electrolyte to lessen electron recombination rate[10]. The electrolyte is regenerated at the counter electrode when the circuit is complete by external circuit.

Dye sensitizers are very important in DSSC because it can harvest large intensity of light spectrum in the range from visible and up to the infrared (IR) region besides controlling the charge collection and passage of the photo-excited electrons from dye to external circuit[12]. Good dye sensitizers must be economical, practical, biocompatible and stable to be used for a longer period of time[9, 10, 13]. Some functional groups such as carboxyl, hydroxyl and so forth usually incorporate in dye's structure which can act as the anchor between dyes and the surface of semiconductor oxide for facile electron injection. The efficiency of absorption and conversion of incident photons to electron-hole pairs and charge transfer process will directly affect the cell performance. Thus, dyes must have more positive HOMO than the electrolyte's redox potential and more negative LUMO than the semiconductor's conduction band in order to increase the efficiency of the DSSCs[14].

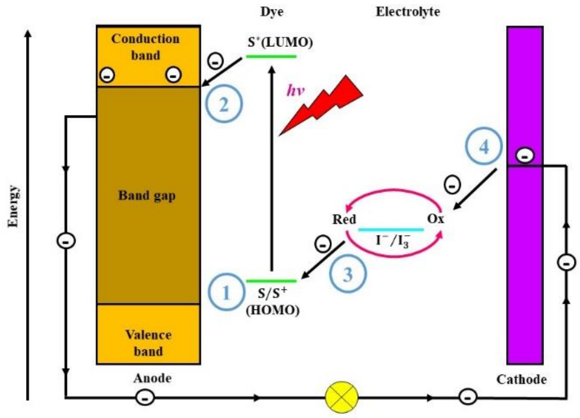


Figure 1: Basic working principle of a DSSC [8]

The engagement of the first row of transition metals in the periodic table such as copper (Cu) and iron (Fe) coincides with the 7th United Nations Sustainable Development Goal (SDG) that aims for clean and affordable energy sources [15]. SDG 7 focuses on three main objectives which are to ensure efficient, secure, and universal access to modern energy services by increasing the share of renewable energy in the global energy mix [16]. The United Nations General Assembly (UNGA) adopted the Sustainable Development Goals (SDGs) in 2015, which provide a powerful basis for international collaboration to achieve a sustainable future for the world. At the heart of "Agenda 2030," the 17 SDGs and their 169 objectives identify a roadmap to end extreme poverty, combat inequality and injustice, and protect the planet's climate whereby sustainable energy is the key to Agenda 2030's progress.

Cu is economical and has more abundance in nature compared to Ru [17]. Cu shows common function in electron transfer which displays vibration in the electromagnetic spectrum from vis to IR region [18,19] besides stable in two oxidation states whereby +1 is more favourable [20]. Cu(I) complexes generally form tetrahedral structures whereas Cu (II) complexes are more commonly present in the shape of square planar. Bis(diimine)copper(I) [21], copper(I)-polypyridyl complexes [22], copper(I)-bisphenanthroline complexes [23], copper(I)-bipyridine complexes [23], copper(I) biquinoline complexes [24], bis(2,9-diphenyl-1,10-phenanthroline)copper(I) complex [25], oligopyridine copper(I) based-complexes [26], 6,6'-bis{2-[4-(N,N'-diphenylamino)ethenyl}-2,2'-bipyridine)copper(I) complex [27], 12-membered tetra-imine macrocycle Cu(II) complex [28], copper(II) phenanthroline complexes [29] and copper(II)-rhodamine B complex [30] were the few examples of outstanding sensitizers from Cu. Cu(I) complexes are labile thus able to swap ligands rapidly. Although d-subshell of Cu(I) are filled completely, coordination between d-block metal complexes with bidentate heterocyclic nitrogenous bases such as polypyridyl ligands known to formed reliable complexes that display excellent photophysical and redox properties which suitable to be employed in fabrication of DSSC [31,32]. For instance, to form stable Cu(I) complexes, the ligands are substituents with carboxylic or phosphonic acids and must be at the position 6 to stabilize the Cu(I) state [28,33]. Cu(I) complexes also exhibit intrinsic long-lived triplet excited states which can prolong the exciton diffusion length and reduce the chance of charge recombination [34]. Since the photophysical properties of Cu(I) are similar with Ru(II) complexes, therefore Cu(I) can be a good alternative to replace the dependency upon Ru(II) complexes [35–37]. Notably, this paper aims to study types of Cu(I) complexes been engaged in fabrication of DSSC, the need to find replacement of Ru(II) complexes and the performance of DSSC based on Cu(I) complexes.

Research Method

A systematic literature review (SLR) is a process of reviewing research that is suitable to a certain subject or argument [38]. In this SLR, we focus on the roles of Cu complexes as dye in DSSCs. The review's research questions, search strategy, searched database, search keywords, inclusion/exclusion criteria, and SLR grade criteria are presented in the subsections below.

Planning the review

The study is organized by suggesting the suitable research question to the research objective. Then, the planning of search, search keywords and inclusion/exclusion guidelines are determined.

Research questions

The main goal of this work is to find out which and why Cu(I) complexes are suitable to replace Ru(II) as dye sensitizers in fabrication of DSSCs. To accomplish the research objective, we have worked out on the research question (RQs).

RQ1: What types of Cu complexes are used in DSSCs?

The aim of this research question is to study various types of Cu complexes being used as alternatives to Ru metal. The results will be able to give some insights in developing new types of complexes for DSSCs. Several complexes such as bis(diimine)Cu(I) complexes [19,39–42], copper(I)-polypyridyl complexes [22], copper(I)-bisphenanthroline complexes [23], copper(I)-bipyridine complexes [23], copper(I) biquinoline complexes [24], bis(2,9-diphenyl-1,10-phenanthroline)copper(I) complex [25], oligopyridine copper(I) based-complexes [26], 6,6’-bis{2-[4-(N,N’-diphenylamino)ethenyl}-2,2’-bipyridine)copper(I) complex [27], 12-membered tetra-imine macrocycle Cu(II) complex [28], copper(II) phenanthroline complexes [29] and copper(II)-rhodamine B complex [30] were successfully synthesised and employed as sensitizers in DSSCs.

RQ2: Why Ru metal needs to be replaced by Cu metal?

The aim of this research question is to understand the importance of replacing Ru metal with Cu metal in fabrication of synthesizer for DSSCs. The benefit and limitation of Cu complexes as sensitizers will be discussed. The result will bring cognizance to using non-toxic material sources such as Cu, Zn and Fe(II) [43].

RQ3: How good is the performance of Cu(I)- based DSSCs?

The aim of this research question is to compare the efficiency of Cu(I)-based DSSCs. The findings will help to recognise emerging trends and provide a potential solution to overcome the obstacles in engaging Cu complexes as DSSC sensitizers.

Search strategy

The SLR is carried out by referring to the guidelines of Kitchenham [44]. Formal search strategy was initially used and intense search for suitable articles to our research objective and research question were conducted. The publications were retrieved by tailored to Scopus database and irrelevant studies were filtered out. Next, thoroughly inclusion and exclusion criteria were exercised as explained in Figure 1.

Search string

In the first step, we identified a combination of keywords as follows: (“copper*”) AND (“sensitizer” OR “dye”) AND (“dye-sensitized solar cell” OR “dye sensitized solar cell" OR "DSSC"). This set of keywords was searched in the abstracts, titles, and keywords of the publications from 2011 to 2020, yielding 566 publications in the Scopus database. In addition, we also included the term dye-sensitized solar cell and its acronym DSSC because dye-sensitized solar cells are the alternative PV devices.

Inclusion and exclusion criteria

The selection criteria were based on the PRISMA Statement [45]. We widened our time frame to 2011–2020 instead of 2015–2020. Therefore, the total number of publications were 566 respectively. Then, the subject areas narrowed to material science and chemistry and subsequently the number of publications was reduced to 455. Since we intend to present state-of-the-art results, our focus is only on the most recent and original research articles. By doing this, discussion and finding about replacing Ru complexes for fabrication of DSSC will be more significant and impactful. There were 396 publications extracted at this stage. All records were checked and duplications were omitted in order to maintain the quality of this review. Abstracts were carefully scrutinised and each research paper was given a thorough review at the later stage. The next exclusion criterion resulted in only 391 articles when only English language was selected. Additionally, after filtration of duplicate records, no article was removed from the study. We selected 391 records after assessing each article on the aforementioned inclusion and exclusion criteria. Figure 2 shows the literature inclusion and exclusion at every stage.

In the second step, we assessed each publication to find the discussion about Cu complexes as dye based on the abstracts, titles, and keywords and resulted in 73 full texts. If the publication is relevant, it will count for inclusion in the third step. Then, the full texts were analysed in depth for the relevancy to the *all research questions* to ensure none suitable information will be overlooked. If the research involves some kind of Cu complexes, it will be analyzed in the next step. Total 36 full texts were retrieved. In the end, we analysed the performance of DSSCs from Cu complexes in four dimensions—*short circuit current, open circuit current, fill factor, and efficiency* with some supplementary references from prior research for insightful discussion.

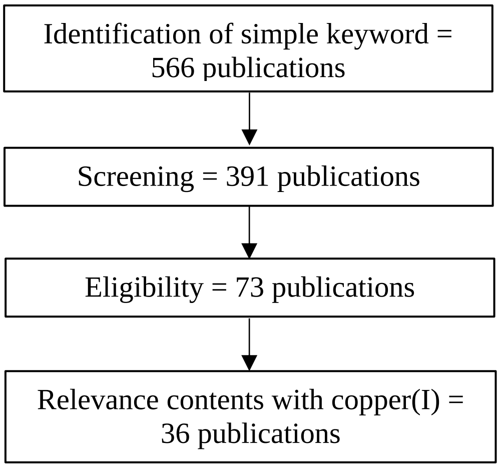


Figure 2: The flowchart of the PRISMA framework

Results and Discussions

The results of the SLR are highlighted in this section based on three research questions. The proposed research questions were as followed:

RQ1: What types of Cu complexes are used in DSSCs?

Cu is an element in first row transition metal complexes that has d10 electronic configuration which possess two oxidation states; +1 and +2. Whereby +1 is the most stable oxidation state. Cu complexes can be distinguished based on the geometry shape in which the Cu(I) complexes are tetrahedral while Cu(II) complexes are square-planar arrangements [46]. Cu(I) complexes easily displace in solution and undergo interchange ligands rapidly. Perfect pack of d orbitals contribute to uniform localization of the electronic configuration which promotes tetrahedral disposition of ligands around the Cu(I) metal core by placing the coordination sites distant from one another and subsequently reducing electrostatic repulsions. These complexes have small wavelength value because of their tetrahedral geometry [47] and show profuse luminescence with long-lived photoexcited state due to the $[Ar]3d^{10}$ electron configuration [48]. The engagement of ligands such as 6,6'- position of bipyridine (bpy) or 2,9-substituents of 1,10-phenanthroline (phen) will reduce the electron transfer rate and this can minimize the conformational change if Cu(I) oxidise to Cu(II) [22,40]. Cu(I) complexes also display wide MLCT transition bands in the visible region which maximize the light harvesting efficiency (LHE) [46]. For instance, the bis-diimine copper(I) complex shows MLCT excited-state attribute in the visible spectrum and long lifetime of the triplet condition [49]. MLCT of bis(diimine) Cu(I) complexes which undergo significant Jahn-Teller structural reorganisation will show low oxidation potentials and display structure-dependent energetics [50]. Therefore, the coordination sphere around Cu(I) is sufficiently limited to avoid flattening distortions during excitation.

Bis(diimine) copper(I) complexes consist of homoleptic and heteroleptic species which the homoleptic bis(diimine) copper(I) generally will lack of "push-pull" feature. Whilst for the heteroleptic species, it will consist of two ligands which one ligand conveys an appropriate group that can perform as anchor and the other ligand structurally and electronically adjusted to receive light. Hence, it can boost electron transfer from electrolyte to dye. As dye gets excited, dye will unleash an electron and the electron will diffuse to the conduction band of transparent conductive oxide [51]. The heteroleptic bis-diimine copper(I) complexes have its downsides as sensitizers for DSSC due to the complexity of separating them as steady species. Nevertheless, this issue has been successfully resolved by the introduction of HETPHEN [52].

The HETPHEN approach is an acronym for HETeroleptic PHENanthroline which depends on huge ligands to obstruct ligand interchange between the demanding groups in 2,9-positions in a 1,10-phenanthroline or 6,6'-position of a 2,2'-bipyridine (bpy) ligand to stabilize the heteroleptic complex. The Cu(I)-polypyridyl complexes are easily synthesized using SALSAC and HETPHEN approaches. SALSAC is the acronym of "surfaces-as-ligands, surfaces as complexes" offers an adaptable strategy in which the heteroleptic dye is stepwisely assembled on the electrode. On the other hand, the HETPHEN approach was utilized the bulky groups in the 6,6'-positions of a 2,2'-bipyridine (bpy) ligand stabilize the heteroleptic $[Cu(L^1)(L^2)]^+$ with respect to ligand redistribution [43,46]. Besides Cu(I)-polypyridyl complexes [22], other examples of Cu(I) complexes which suitables to be synthesize using these methods are Cu(I)-bisphenanthroline complexes [23], Cu(I)-bipyridine complexes [23], Cu(I) biquinoline complexes [24], bis(2,9-diphenyl-1,10-phenanthroline)Cu(I) complex [25], oligopyridine Cu(I) based-complexes [26], 6,6'-bis{2-[4-(N,N'-diphenylamino)ethenyl]-2,2'-bipyridine)Cu(I) complex [27], 12-membered tetra-imine macrocycle Cu(II) complex [28], Cu(II) phenanthroline complexes [29] and Cu(II)-rhodamine B complex [30].

RQ2: Why Ru metal needs to be replaced by Cu metal?

DSSC is the only PV device that mimics the photosynthesis process as in plants which separates light absorption and charge transportation during the photoelectric conversion [53]. Thus, dye has an important role in DSSC by absorbing the light spectrum. Heavy and noble transition metals such as ruthenium (II), iridium (III), copper (I), platinum (II), silver (I), iron (II) [54] and zinc (II) [55] are used in fabricating dyes and these transition metals also widely use in different types of energy applications due to their distinctive attributes of the metals centre dissimilar geometries [56]. Ru(II) is widely used as dyes in DSSC because the photoconversion efficiency (PCE) can reach as far as 14% [57]. However, Ru(II) is highly toxic and not environmentally-friendly. Moreover, Ru metal is classified as a rare element which exists about 0.001 ppm and overpriced compared to other metal salts [58]. In addition, Ru-based complexes face many problems in the synthesis and purification procedures [59]. Hence, the similarities between these two elements on its photophysical tracts make Cu(I) complexes being the prominent candidate to replace dependency on Ru(II) complex [60].

Cu is selected as the alternative to Ru because of the abundance on earth crust [61], reasonable price tag [62], environmental friendly [63] and highly conducting element. Cu is also known to boost the visible light absorption by their peculiar localized surface plasmon resonance (LSPR) [64]. For instance, Cu-doped ZnO has been established as photoanode material in DSSCs. ZnO is benefited mostly in the UV-region due to the wide band gap energy. However, doping by precious metals such as Cu surprisingly enhanced the visible light absorption by the unique LSPR [65,66]. When the LSPRs are illuminated on the nanostructure surfaces, they create confined electromagnetic fields, which the sensitizer molecules use as a secondary light source. A large number of electron-hole pairs are formed, enhancing electron transfer from excited dye molecules to the metal oxide's CB. Furthermore, Cu-doped nanostructures can improve the light-harvesting efficiency of the sensitizing dye by increasing far-field scattering.

RQ3: How good are Cu(I)-based DSSCs in terms of performance?

It is important to recognize the maturity of Ru(II) complexes which have been established for decades as dyes in DSSCs, whilst the development of Cu(I)-dye complexes are still in early stage [28,42,67]. The conversion efficiency of solar energy is directly proportional to the intensity of photon absorption by dye complexes [68]. The performance of DSSCs are calculated based on the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), power conversion efficiency (PCE), and fill factor (FF) [69]. The V_{OC} in a DSSC is determined by the energy dissimilar between the redox potential of the electrolyte and the quasi-Fermi level of the TiO_2. Whereby, the J_{SC} is affected by the rate of transfer of redox couple components in the electrolyte. Numerous factors such as remerge of sensitizer, band gap of semiconductor or redox mediator, charge transfer resistance on the electrolyte to the electrode and transmission of charge carrier in an electrolyte are majorly affecting the value of FF [70].

High efficiency in DSSCs can be achieved by increasing the open-circuit voltage (V_{OC}). For instance, the coordination copper complexes with 1,10-phenanthroline or 2,2’-bipyridyl based ligands showed high V_{OC} over 1.0V [47] which resulting good PCE ranging from 6%-11%. Bis(2,9-diphenyl-1,10-phenanthroline) Cu(I) complex (**1**, Table 1) that altered at the para positions of the phenyl rings with sodium carboxylate groups was first used in DSSC and recorded 0.6V V_{OC} and 0.6 mA/cm^2 J_{SC}. As the carboxylic groups are bound to the phenyl substituents instead of direct to the phenanthroline scaffold, it shows complex **1** a deficient photocurrent. It causes an abundance of steric drawbacks and conflicting electrons to the conduction band of TiO_2. In addition, the anchoring to the mesoporous TiO_2 surface is restricted by the existence of four deprotonated carboxylic groups [71].

Recently, the trigonal planar of copper(I) complex dye (**2**, Table 1), $[Cu(L)(CH_3CN)]$ was introduced and 6,6’-dimethyl-4,4’-bis(phenylethynyl)-2,2’-bipyridine ligand is labelled as L. The highest PCE about 0.08%, 0.48 mA/cm^2 of J_{SC} and 477 mV of V_{OC} is achieved by this dye. Nonetheless, poor light harvesting process and charge injection due to the deficiency of an anchor group of the dye become the restriction issue on this copper(I) complex dye. Thus, to boost the effectiveness, the anchor group must be added [25].

Based on other findings, V_{OC} of a DSSC can be enhanced by employing an electrolyte with a more positive redox potential than iodide/triiodide (I^-/I_3^-) [72]. The photoconversion efficiency also can improve tremendously if the photophysical and redox properties of the Cu complexes are successfully altered by making the MLCT band in the range between 430 nm to 570 nm [73]. Sakaki and co-workers had studied a Cu(I) complex bipyridine-based ligand (**3**, Table 1) and this complex shown wide MLCT band around 450 nm. DSSC fabricated using this complex showed efficiency about 2.5% whereas the J_{SC} and V_{OC} were 4 mA/cm^2 and 630 mV [26]. The synthesis of this Cu(I) complex in which the 1,10-phenanthroline is changed with a 4,4',6,6'-tetramethyl-2,2'-bipyridine substituted in 5,5' positions with two carboxylic groups [51].

The use of Cu(I) complexes with substituted 2,2'-bipyridine (**4** and **5**, Table 1) as dyes in DSSCs is reported by Constable et al. in 2008. To assure a fast injection of the electron from the dye to the conduction band of TiO_2 and methyl groups in the α positions of the coordinating nitrogen atoms, they utilize carboxylic acids. It can also create long-lived excited states. PCE relative of 20% and 24%, corresponding to N719 set at 100%, were achieved by the complexes **4** and **5**, respectively, during tested using light shading masks [33]. The better performance of complex **5** can be attributed to the more extended π- conjugated than in **4** which leads to a better light harvesting.

Then, the natural effects and position of the anchoring groups on the bipyridine ligand are studied at the next step by the same author. The methyl groups in the complexes are replaced with phenyl groups at the 6,6' positions and their effectiveness are also studied (**6–8**, Table 1). However, their DSSC efficiencies were lower compared to the previous studies due to the non-optimized cell fabrication. Complex **6** achieved η_{rel} = 9.0% and its shown the excellent performance that can be gained by carboxylic groups at the 4,4' or 5,5' positions due to strongly bind at the TiO_2 nanoparticles. Besides, the complex **7** with the furan moiety has recorded lower efficiency of η_{rel} = 2.8% because of its less potential of anchoring groups. Next, complex **8** reached the efficiency of about η_{rel} = 4.2% when the methyl groups in the complexes are replaced with phenyl groups. The efficiency is not good because of less dye-loading on the photoanode and low absorption of the complex [74].

The homoleptic complex **9** (Table 1) is used as a sensitizer in DSSC and boost the photoreduction of CO_2 under visible light. In addition, the methyl groups are attached at the 6- and 6'-position of the 2,2'-bipyridine (bpy) to give the shield around the labile metal copper(I) and also can increase the excited-state lifetime of the copper complex. The cyanoacetic acid moieties at the end of the complex acted as anchoring groups to bind on the semiconductor surface. The photovoltaic performance of solar cells that used complex **9** as a sensitizer was measured under standard AM 1.5G and overall energy conversion efficiency of 2.2%. The result was lower than the previous value reported for the copper(I)-based DSSCs which is 2.3% with a higher short-circuit current, 5.9 mA/cm^2. Moreover, complex **9** was also fabricated similar to N719 under the same conditions and achieved an efficiency value of 7.8%. So, the result has clearly shown that complex **9** can be used as a sensitizer in the DSSC and can transfer the injected electron effectively [75].

The homoleptic copper(I) complex bears two 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid ligands (complex **10**, Table 1) and also have higher efficiency as a sensitizer in DSSC of 2.5% [48]. This photosensitizer has higher efficiency compared to heteroleptic copper(I) complexes bearing one 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid ligand and one 2,2'-bipyridine ligand that replaced in the 6-position by a furyl, thienyl, N-methylpyrrolyl, selenophenyl, methyl or phenyl group (η = 1.07 – 1.31%) [76].

The copper(I) complex bearing two 2,2'-biquinoline-4,4'-dicarboxylic acid ligands (complex **11**, Table 1) is using as a sensitizer in DSSC. This complex has a higher molar extinction coefficient and strong adsorbing effects. However, it has low efficiency because the dye does not have enough energy to inject the excited electron properly into the TiO_2 conduction band. So, the modification on the ligands was required to increase DSSC performance [24].

Then, the two heteroleptic bis(diimine) copper(I) complexes (**12** and **13**, Table 1) are the first stable complexes as sensitizers in DSSC that synthesis using the HETPHEN technique. The 2,2'-biquinoline-4,4'-dicarboxylic acid as an anchoring ligand to absorb broader wavelengths and two different mesityl-substituted phenanthrolines as an electron-rich group also used to complete the copper(I) coordination sphere. The electron-rich group are used to increase electron transfer and repel the photogenerated hole away from the TiO_2 surface thus reducing the charge recombination experience. The UV-Vis spectra for both complexes are very similar. The UV region in the spectrum is dominated by the strong ligand centred (LC) transitions that involve anchoring ligand and ancillary ligand which the broader MLCT transitions are presented in the visible region at the maximum of about 560nm and extended low intensity until 700nm. However, both complexes have low photovoltaic performance (η_{rel} = 7.5 and 3.4% for complexes **12** and **13**) due to the weak injection driving force and a short lifetime of the MLCT excited state [46].

Heteroleptic Cu(I)-polypyridine complex (**14-17**, Table 1) which applied the HETPHEN approach achieved the highest PCE around 4.66% with chenodeoxycholic acid (CDCA) that relative to 7.36% for reference dye, di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II), N719 as reported by Odobel and coworkers. These complexes are used 4,4'-dicarboxylic acid bipyridine as anchoring ligand and two mesityl groups in 6,6' positions to provide the capable steric bulk to avoid the formation of homoleptic complexes. The electronic absorption spectra of these complexes show MLCT transitions at ca. 500 nm. Complexes **16** and **17** show higher light-harvesting efficiency in the visible range because of an intense additional intraligand charge transfer transition (ILCT) that was discovered around 420 nm which can be assigned to a shift of the electron density from the electron-rich amine moieties to the electron-poor pyridine rings. Moreover, complexes **14** and **15** have low photocurrents due to their lower solar spectrum coverage. Furthermore, 4.66% is the highest PCE reported for heteroleptic copper(I)-polypyridine complex based cell, compared to numerous types of Cu(I) complexes that has been developed [77].

The two Cu(I) diimine heteroleptic complexes (**18** and **19**, Table 1) with a catenane chain are introduced by Chen et al. [50]. These complexes are designed to explain the modification of structure that occurred between excited and ground state, gain the stability of photogenerated Cu(II) species and study the effectiveness of charge injection in TiO_2. In this research, the carboxylic acid that acts as anchoring groups are on the 2,9 positions of the phenanthrolines and separated by one (complex **18**) or two spacer-rings (complex **19**). In addition, the phenyl rings are added near the copper centre and lead to flattening of the complex shape that showing in a broader and red-shifted absorption band and shielding of the copper by solvent access showing in a long-life excited state. The effectiveness of the interfacial electron transfer process was not affected by the length between the phenanthroline and TiO_2 [51].

Later, the effect of increasing the π-conjugation of the ancillary ligand are studied and compared the DSSC performance of heteroleptic complexes with 6,6'-dimethyl-2,2'-bipyridine or 6,6'-bis{2-[4-(N,N'-diphenylamino)phenyl]ethenyl}-2,2'-bipyridine and a bipyridine with carboxylate (**20** and **21**, Table 1) or phosphonate (**22** and **23**, Table 1) anchoring groups. Surprisingly, the relative efficiency of complexes **21** and **23** are increased from 23% and 27% (2 days after sealing of cell) to the same values of about 32% (7 days after sealing of cell). However, complexes **20** and **22** are low efficiencies with time due to the less π-delocalized ancillary bipyridine. These excellent results show that the combination of an extended π- conjugation in the ancillary 2,2'-bipyridine can boost the dye performance. the formation of sensitizer's aggregates on the TiO_2 surface causes a photovoltaic performance improvement after a few days of sealing of the cell [27].

Besides, the complexes **24-28** (Table 1) that used the simplest phosphonate anchoring ligand have achieved higher energy conversion efficiency values after 4 days of sealing cells (η_{rel} = 20-28% with fully masked cells). The highest efficiency was achieved for the complex with methyl groups at 6 and 6' positions of the 2,2'-bipyridine. In addition, the complexes with an aromatic spacer at the anchoring ligand (**29-33**,

Table 1) can increase the photovoltaic performance by about η_{rel} = 30-49% with fully masked cells. It is because complexes **29** and **33** have the methyl and phenyl groups in the 6 and 6' positions of the ancillary ligand [60]. Complex **29** also study the effect of replacing the bromo atoms by F, Cl and I maintaining the 6,6'-dimethyl-[2,2'-bipyridine]-4,4'-diyl)bi(4,1-phenylene)bis(phosphonic acid) [78]. The performance of photovoltaic for these complexes relies on the halo-atom. For example, I, F, Br and Cl. The best relative efficiency value recorded is 41% for complex **34** (Table 1) that bears the iodo atom with fully masked devices.

In 2013, the first and second generations of hole-transport triphenylamino-dendrons have been selected as ancillary ligand in the Cu(I) complexes for DSSC. The highest performance was achieved by using a phosphonate anchoring ligand (**35-36**, Table 1). These complexes have measured the performance for first, third, sixth and 47 days after sealing of cell unmasked. The complexes **35** and **36** were recorded the highest relative efficiency performance about 19.6% (6 days after sealing of cell unmasked) and 23.9% (6 and 47 days after sealing of cell unmasked). It showed that phosphonate anchoring ligand enhances efficiency better than carboxylate anchors. In this research, the incorporation between hole-transport substituents onto ancillary ligands in Cu(I) complexes is successful and get the best efficiency of about 3.77% [79].

The effectiveness of the solvent applied in the dye-bath of the heteroleptic complex and the presence of a co-adsorbent on the DSSC achievement has been studied by Constable, Housecroft et al. To acquire high PCE, chenodeoxycholic acid (cheno or CDCA), which is the co-adsorbent, is extensively used. Even though the CDCA are well known to boosts the V_{OC} of the ruthenium(II)-containing dyes like N719 and zinc(II) porphyrin dyes, it is unexpected that the co-adsorbents also affect Cu(I) dyes, as proved in few studies. Additionally, the co-adsorbents could perform to anchor to the surface and be able to spatially unbind the dye molecules. For instance, the CDCA is added to complex **37** (Table 1) and sealed the cells after using dichloromethane as a solvent in the dye dipping cycle. The relative efficiency performance boosts from 25.3% to 30.0% for 22 days. When measured the DSSC performance, the co-adsorbent also raised the V_{OC} and J_{SC} of complex **37**. Nonetheless, the addition of CDCA to the same complex that using acetone as a solvent in the dye dipping cycle shows the contradict result which the efficiency is slightly low [80]. Indeed, the concentration of the solution of the homoleptic copper(I) bis(diimine) complex used during the stepwise assembly of the dye on the semiconductor surface become a crucial aspect that affects the performance of heteroleptic copper(I) bis(diimine) dyes in DSSC [21].

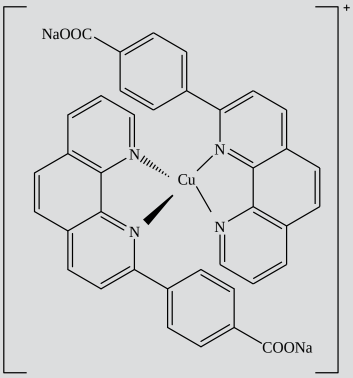
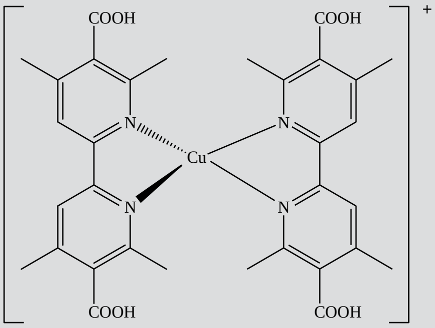
Impressively, on the day of sealing cell, in masked configuration, the photoconversion efficiency of 30-35% relative to N719 is achieved by the copper(I) complexes bearing 6,6'-dimethyl-[2,2'-bipyridine]-4,4'-diyl)bi(4,1-phenylene)bis(phosphonic acid) as anchoring ligand and either 6,6'-bis(trifluoromethyl)-2,2'-bipyridine or 6-trifluoromethyl-2,2'-bipyridine (complex **38**, Table 1) as ancillary ligand. It is an enhancement concerning DSSC based on the complex with 6,6'-dimethyl-2,2'-bipyridine as an ancillary ligand (η_{rel} = 23-25%) [81]. This finding shows that the significant performance can be seen for the design of simple copper sensitizers while using simple halo- or halogenated alkyl substituents.

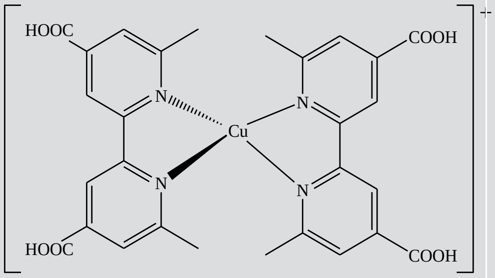
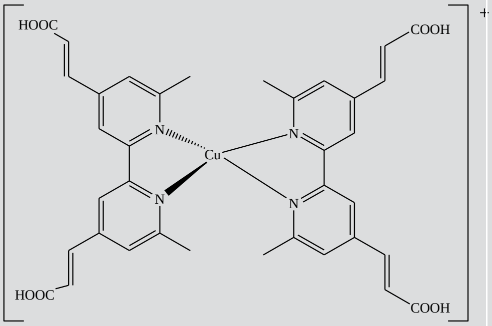
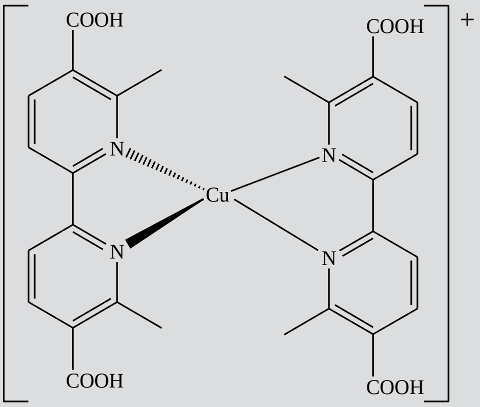
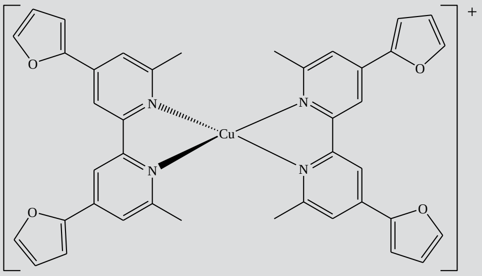
The different π-delocalized dipyrrins as ancillary ligands for neutral heteroleptic copper(I) complexes, prepared in situ on the TiO_2 surface. The light-harvesting attribute promoted efficiency by raising the conjugation of the dipyrrin ligand. The dipyrrin contains CF_3 groups in complex **39** (Table 1) show the highest efficiency of 0.41% (J_{SC} = 1.21 mA cm^{-2}, V_{OC} = 0.520 V, FF = 0.64) [22]. Dye regeneration can be improved by the increased driving force as the complex has higher oxidation potential when the HOMO energy level is reduced by the addition of these electron-withdrawing groups.

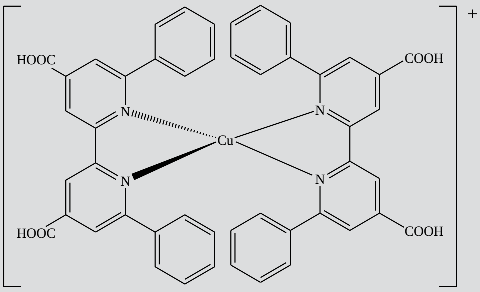
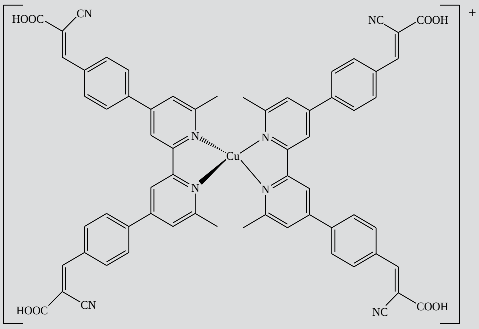
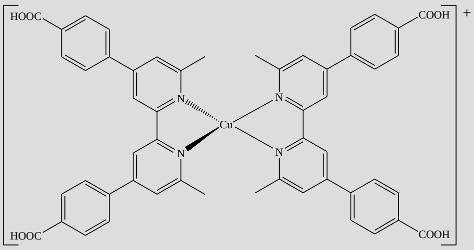
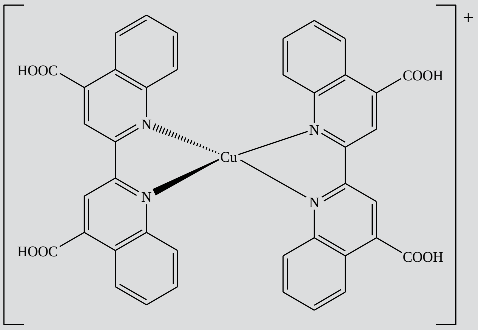
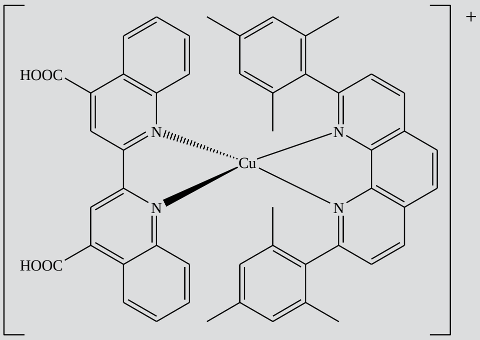
In addition, performance of a DSSC also can be affected by the choice of anchor ligands in the Cu-based dyes. The anchor ligands such as carboxylic and cyanoacrylic acids, pyridine groups, perylene dicarboxylic acid anhydride groups, catechol groups, sulfonic acid groups, nitro groups and so forth act as anchors for the dyes to immobilise onto the TCO surfaces which act as the working electrode in DSSCs. Immobilisation of the Cu-based dye is the fundamental step to initiate the electrical current upon the injection of electrons from the dye into the conduction band of the metal oxide. For instance, heteroleptic Cu(I) dyes coordinated with 2,2'-bipyridine or 1,10-phenanthroline-based ligands generally have phosphonic acid at 4-position of the thienyl ring acts as anchor will help improve electron injection instead of using carboxylic acid [58]. Moreover, the PCE for porphyrin of type copper chlorophyll is 2.6% [82]. The Ru-based dyes generally produce conversion efficiencies greater than 10%. However, Ru-based dyes have less molar extinction coefficients and limited near infra-red (NIR) absorption [83]. Based on data in 2017, the PCE of DSSC which used Cu(I) as dyes had achieved 65.6% compared to the N719 [43].

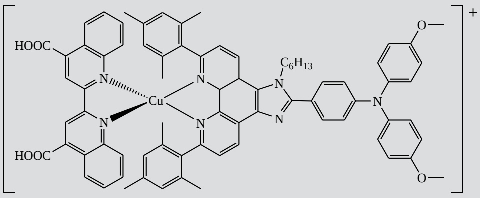
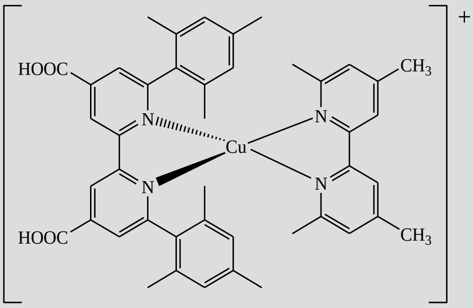
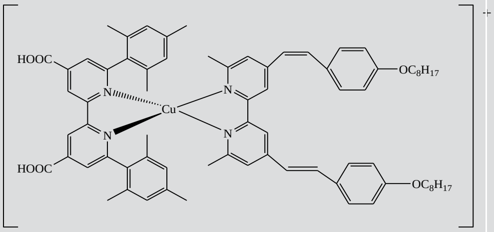
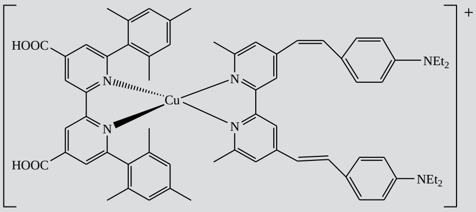
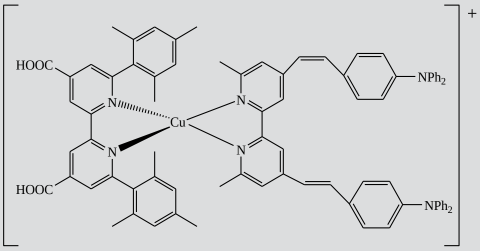
Table 1

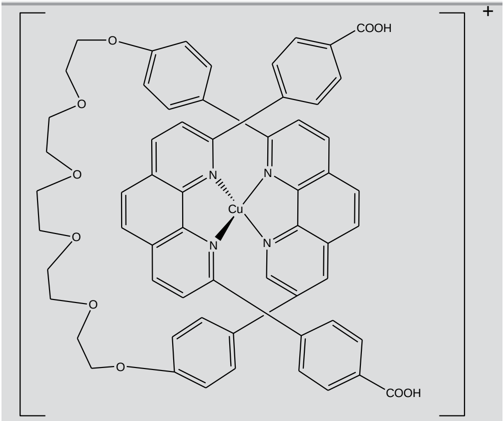
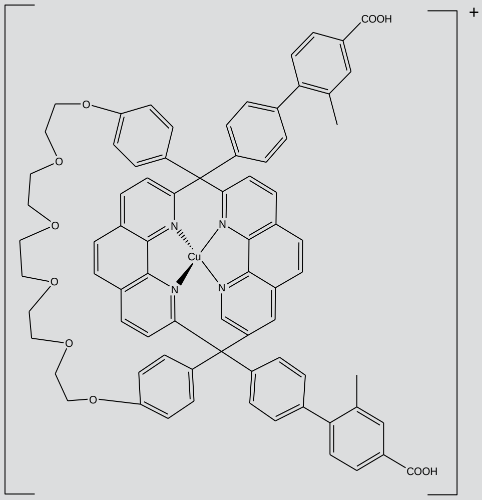
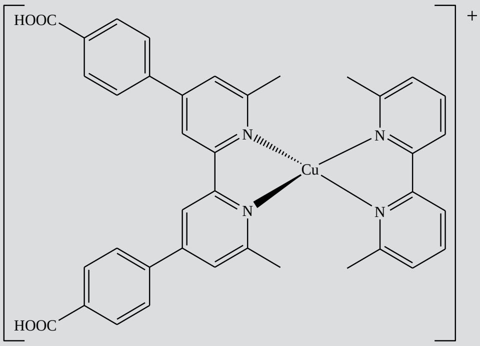
List of Cu(I) complexes-based cell

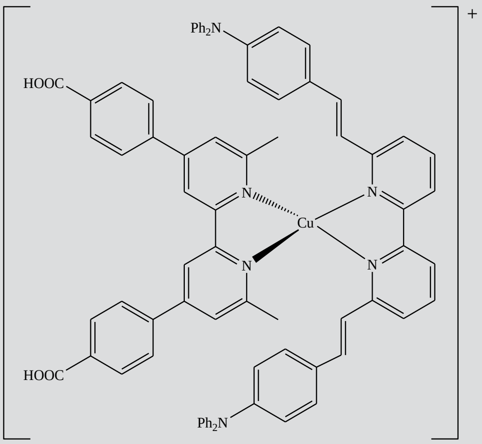
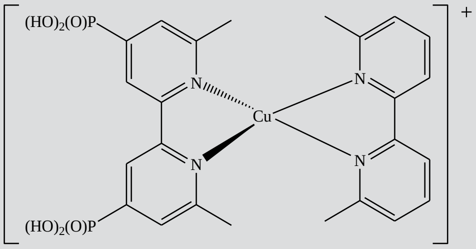
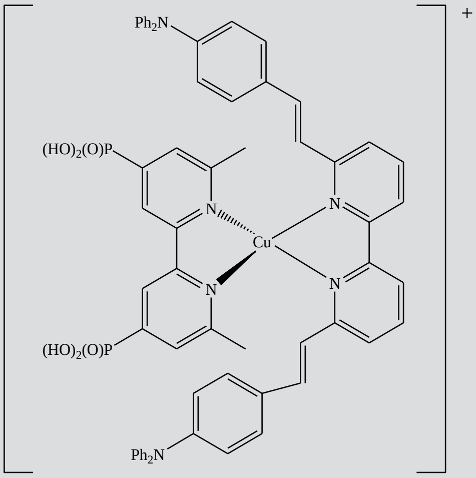
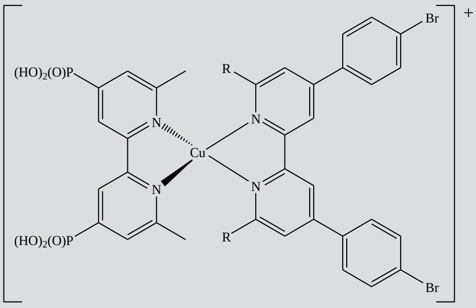
Complexes	Structure of complexes	J_{SC} (mA/cm^2)	V_{OC} (V)	η (%)	$η_{rel}$ (%)	Ref
1		0.6	0.6	0.1	-	[71]
2		0.48	0.477	0.08	-	[25]
3		4.0	0.630	2.5	-	[26]
4		5.25	0.566	1.9	20	[33]

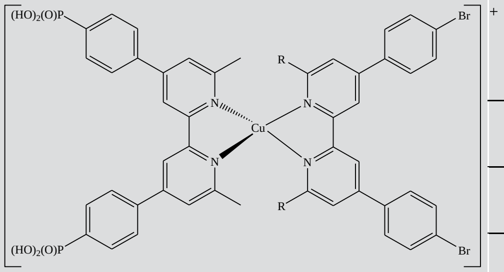
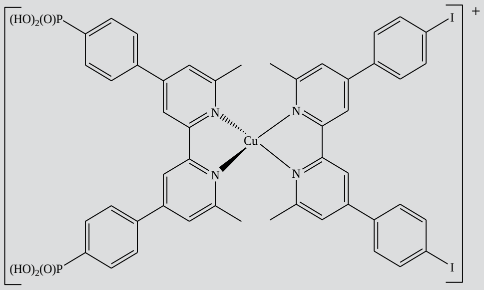
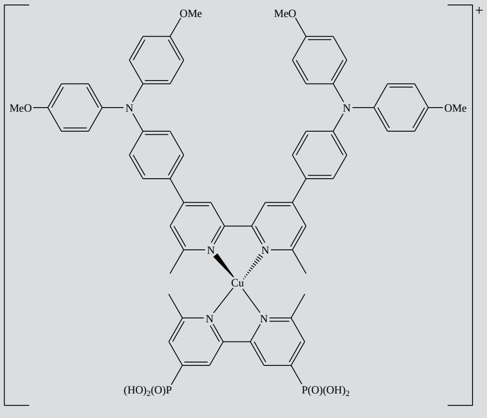
						
5		5.9	0.556	2.3	24	[33]
6		1.21	0.57	0.45	9.0	[74]
7		0.46	0.49	0.14	2.8	[74]
8		0.69	0.484	0.21	4.2	[74]

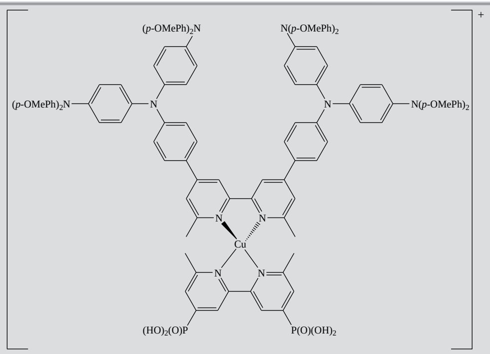
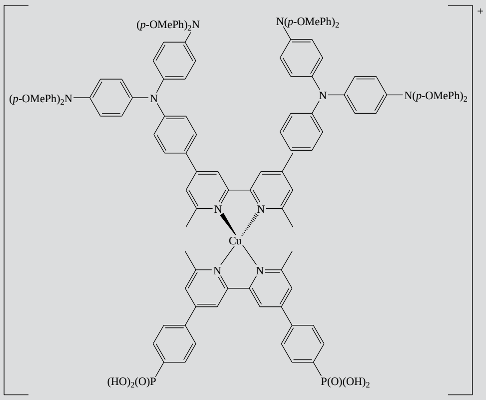
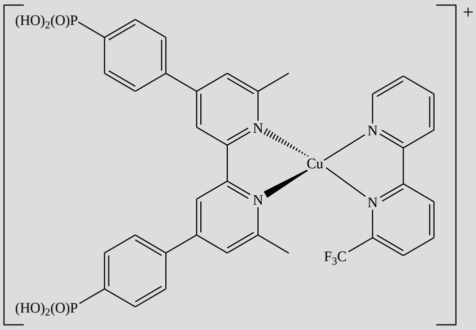
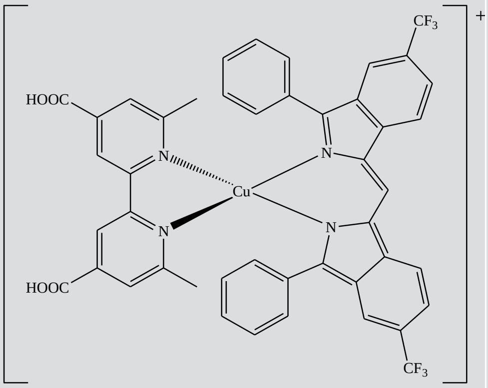
						
9		4.69	0.570	2.2	28	[75]
10		6.0	0.59	2.5	-	[48]
11		0.206	0.515	0.075	-	[24]
12		1.61	0.455	0.49	7.5	[46]

13		0.78	0.445	0.22	3.4	[46]
14		3.76	0.525	1.47	20	[77]
15		4.99	0.565	2.04	28	[77]
16		10.86	0.605	4.66	63	[77]
17		10.13	0.625	4.42	60	[77]
18		-	-	-	-	[50]

						
19		-	-	-	-	[50]
20		6.0	0.595	1.69	23	[27]
21		7.0	0.579	2.33	32	[27]

						
22		5.0	0.643	1.30	18	[27]
23		6.0	0.627	2.35	32	[27]
24-28	 R = Me (Complex 24) ^{n}Bu (Complex 25) ^{iso}Bu (Complex 26)	4 days after sealing the cell				[60]
		24 = 4.53	24 = 0.507	24 = 1.65	24 = 27.7	
		25 = 3.56	25 = 0.502	25 = 1.18	25 = 19.8	
		26 = 4.44	26 = 0.549	26 = 1.61	26 = 27.0	
		27 = 4.21	27 = 0.514	27 = 1.50	27 = 25.2	
		28 = 3.53	28 = 0.536	28 = 1.29	28 = 21.6	

	^{n}Hexyl (Complex 27) Ph (Complex 28)					
		4 days after sealing the cell				
29-33	 R = Me (Complex 29) ^{n}Bu (Complex 30) ^{iso}Bu (Complex 31) ^{n}Hexyl (Complex 32) Ph (Complex 33)	29 = 6.01	29 = 0.527	29 = 2.30	29 = 39	[60]
		30 = 5.30	30 = 0.525	30 = 1.80	30 = 30.2	
		31 = 7.06	31 = 0.571	31 = 2.43	31 = 40.8	
		32 = 6.07	32 = 0.520	32 = 1.90	32 = 31.9	
		33 = 6.70	33 = 0.592	33 = 2.89	33 = 49	
34		7.10	0.604	3.16	41	[78]
		6 days after sealing of cell unmasked				
35		5.49	5.51	2.14	19.6	[79]
36		47 days after sealing of cell unmasked				[79]
		5.51	0.610	2.37	23.9	

						
		22 days after sealing the cells				
37		6.18	0.572	2.47	30.0	[80]
38		5.35	0.530	2.08	34.8	[81]
39		1.21	0.520	0.41	-	[22]

Concluding Remarks and Outlook

One of the indicators for SDG 7 is to assist developing countries in terms of financial support for renewable energy production and clean energy research and development.

The target of the 7th SDG can only be achieved if all the industry players are willing to invest and aid the development of sustainable energy resources. RE is an environmentally friendly type of energy generated from naturally abundant sources that emit zero to very low levels of CO_2. For instance, the Sun is an excellent resource for producing clean and long-lasting energy which does not pollute the environment or contribute to global warming. A separate policy or mechanism for routine monitoring of climatic changes and CO_2 emissions and a committee to regulate RE contributions to greenhouse emission reduction must be developed. Solar PV systems are one of the most sustainable technologies to counter the effect of global warming. Energy-related CO_2 emissions account for two-thirds of all greenhouse gas emissions, therefore making a shift away from fossil fuels to low-carbon solutions is critically needed. Latest advancements in solar photovoltaic (PV) systems have resulted in remarkable growth in Malaysia and throughout the world. With the aid of PV technology, the cost of energy-reduced is not only becoming more available to the public.

Furthermore, solar power generation emits no greenhouse gases, allowing the planet to move towards greener and cleaner energy. PV cells are generally classified based on generation (GEN) or category. The first and second GENs mainly covered current market needs. Gallium arsenide and mono/polycrystalline silicon cells [84] are the first GEN, while thin-film technologies are the second GEN [85]. Even though the cost production of these two GENs is generally lower, these PV cells are not favourable due to lower efficiency. The introduction of novel materials and delicate designs as third GEN successfully increased the efficiency of PV cells, albeit the price more expensive [86]. Combining flexible polymer thin films with metal oxides and metal nanoparticles with organic-based nanomaterials such as graphene is known as the fourth GEN or “inorganics-in-organics.” Even with the introduction of the fourth GEN, DSSCs are still one of the best alternatives over silicon devices due to their sustainability and rapid improvement in conversion efficiency [87]. The benefit of thriving DSSC is that they are hustle-free to produce and uncomplicated to exploit. Even under low light density and at high temperature, they could perform better in contrast to other solar cell technologies. Eventually, the introduction of environmental friendly sensitizers such as Cu(I) complexes creating the new path for DSSCs to thriving as sustainable PV cells compare to others GENs. Despite the lack of “push-pull” feature in homoleptic Cu(I) complexes such as in bis(diimine) compounds, the introduction of heteroleptic bis(diimine) Cu(I) complexes have successfully overcome these issues by engaging the HETPEN strategy. The HETPEN strategy is proven to increase the DSSC efficiency since huge ligands are employed to obstruct ligand interchange between demanding groups in 2,9-positions in a 1,10-phenanthroline or 6,6’-position of a 2,2’-bipyridine (bpy) ligand in order to stabilize the heteroleptic complex. Interestingly, complexes **16** and **17** are achieved best DSSC efficiency in the visible range about 4.66 and 4.42%. In addition, the homoleptic Cu(I) complexes (**3** and **10**) were recorded to achieved maximum light harvesting efficiency about 2.5%. Recently, polymer substrate has been introduced [88] as the substitution for the DSSC glass substrate since polymer substrates permit roll-to-roll production, which allows a massive volume of production. For example, ITO/polyethylene naphthalate (PEN) and ITO/polyethylene terephthalate (PET) are the latest technologies found for conductive polymer substrates. These become common due to low cost, high clarity, less sheet resistance [89], flexibility and low weight [89,90]. Therefore, environmental awareness can be led in the future by the potential use of DSSC.

The RE pathways demonstrate that improving energy supply, air quality, and energy security while preventing dangerous climate change is theoretically feasible. In reality, a variety of alternative resources, technology, and policy combinations can achieve these goals [91].

Acknowledgements

The authors would like to extend their gratitude to the Ministry of Higher Education Malaysia for the Fundamental Research Grant Scheme for Research Acculturation of Early Career Researchers-FRGS-RACER (code: 2019-0162-103-62 (RACER/1/2019/STG01/UPSI//4) and Research Management and Innovation Centre (RMIC), Universiti Pendidikan Sultan Idris (UPSI) for the University Research Grants-GPU (code: 2018-0143-101-01) and University Research Grants-GGPU (code: 2018-0080-106-01).

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