Materials Advances

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Lingamallu, S. Prasanthkumar and K. S. Vishnu, Mater. Adv., 2021, DOI: 10.1039/D0MA01023E.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Cu(II/I) Redox Couples: Potential Alternatives to Traditional Electrolytes for Dye-Sensitized Solar Cells

K. S. Srivishnu, a,b Seelam Prasanthkumar, a,b Lingamallu Giribabu* a,b

The redox shuttle is one of the essential ingredients of Dye-Sensitized Solar Cell devices. Though I/I₃ redox couple dominates the last couple of decades but due to loss of open-circuit potential, complementary absorption with sensitizer and volatile nature restricts module development. Metal complexes with variable oxidation states have the probable alternative candidates as redox shuttles due to change its redox potentials with varying ligands in order to suite different sensitizers. Co(II/III) redox couples using polypyridyl ligands have widely used in DSSC and crossed device efficiency of 14%. Due to mass transport constrains and health hazards effects on commercialization of the technology. Inspired from biological electron transfer reactions Cu(II/II) redox shuttles have gained much attention as reodx couples for DSSC applications in recent years. Particularly in low light conditions it minimizes mass transport and crossed device efficiency of 32%, potential to Internet of Things (IoT) applications. In this review, recent advancements in the use of Cu(II/II) redox shuttles using polypyridyl ligands for DSSC applications are presented.

1. Introduction

As a consequence of profusely increasing global energy demands and environmental worries dye-sensitized solar cells (DSSCs) are becoming alternative to existing photovoltaic technologies. 1-5 As both the first (silicon photovoltaic technologies) and second generation solar cells (thin film solar cells such as CdTe, GaAs etc.,) have their own limitations in aspects such as purity requirement, cost, scarcity, and toxicity of the required materials. For this reason, excitonic solar cells establish to be the dominant energy alternative to the photovoltaic technologies, where excitonic devices belonging to the third generation solar cells. Among third generation solar cells, DSSCs are in paramount position due to the verge of commercialization of technology. 6 The priority of DSSC over other conventional solar cells most importantly due to its own advantages such as cost effective, easy fabrication technique, depleted environmental hazards and good temperature performance over other photovoltaic technologies. Moreover low light performance can be achieved through DSSC which is not possible in conventional Silicon solar cells. 7 The hypothesis of DSSC was first accomplished by Grätzel and co-workers in 1991 with device efficiency of 7.1% using Ru(II) polypyridyl complex as sensitizer and I/I₃ as redox mediator. 8 Since then number of academicians and industries have paid attention to improve the certified device efficiency of up to 11.9% and device efficiency of 14.3%. 9-11 The enhanced device efficiency was possible through re-designing of various components of the device that includes photoanode, transparent conducting substrate, sensitizer, redox electrolyte, counter electrode and also by adopting new fabrication techniques. Among all these components of the device, the redox electrolyte acts as a pivotal position in attaining high efficiency and durability of the device. 12,13

Electrolyte is the most critical component of the device as it is accountable for the inner charge carrier transport between electrodes and continuously restores the dye and itself during DSSC process. 14-17 The three parameters in which power conversion efficiency (PCE) is determined in DSSC are photocurrent density (Jₒ), photovoltage (Vₒ) and fill factor (ff). Electrolyte plays an important role in all three parameters. Like transport of redox couple components can affect photocurrent density, of charge carrier in electrolyte can affect the fill factor and more important the redox potential of electrolyte can drastically affect photovoltage. Keeping all these points in consideration electrolyte should be optimized in view of device efficiency and durability. DSSC was all started with the redox couple I/I₃ in volatile acetonitrile solvent. 18-20 The liquid electrolyte was used for many years before the emerging of new electrolyte and many cases even at present scenario it’s been used. The iodide redox couple has its own disadvantages such as reduced long term stability, performance control, and inappropriateness with several...
metal compounds. The redox shuttle shows slight loss in open circuit voltage ($V_{OC}$) and significant loss in short circuit current density ($J_{sc}$). Since complimentary absorption in visible region with sensitizers, the redox shuttle $1/1^+$ leads to photocurrent loss. Moreover, Iodine can also doing as oxidizing agent and it corrodes the precious noble metals used in the device fabrication such as platinum, silver etc. Therefore one has to investigate alternative redox couples keeping the technical drawbacks of $1/1^+$ in mind and also large scale mini-module production of DSSC devices for commercialization.

A great variety of redox couples have been used in DSSCs that includes inorganic redox couples for instance Br/Br$_2$, SeCN/SeCN$_2$, SCN/SCN$_2$, and S$_2$/S also known as sulphide/polylysulfide (S$_2^+/S_2^-$). All these inorganic redox couples execute two or multi-electrons transfer system and the mass transport of these redox couples are insignificant in organic solvents. Like $1/1^+$ redox couple, their redox potential is almost fixed, choose and use of photosensitizers turn into much more imperative. In addition to this, an alternative important and interesting redox mediator ancestors is the pure organic compounds such as 2,2,6,6-tetramethyl-1-piperidinolxy, phenothiazine, tetraphenylidiamine, quinones, and thiolate/disulfide redox mediators have also been exhaustively probed as iodine-free substitutes redox couples for DSSCs. Besides, to inorganic and organic class of redox mediators, metal complexes are found to be alternative candidates to replace $1/1^+$ redox couple because of their reversible electrochemical properties. Moreover, the properties of metal complexes based redox reactions i.e., redox potentials can be certainly adjusted by varying the central metal atoms and/or the ligands in order to suit the energy levels of sensitizers and conduction band of semiconductor metal oxide. The transition metal complexes based redox mediators that used for DSSC applications include V(V/IV), [Mn(acac)_3]$^{3+/2+}$, Fe(III/II), Co(III/II), Ni(IV/III), Cu(I/II), Os(III/II) and etc. Despite to overcome many technical problems that associated with $1/1^+$, the metal complexes typically have sluggish mass transport concern in solution because of the large molecular size and even pronounced in the porous semiconductor. Hence, majority of the metal complex-based DSSCs be able to accomplish an improved efficiency under low light condition (indoor lighting) than that under full light (AM 1.5G, 100 mW cm$^{-2}$) showing an immense prospective towards power supplies of device for portable electronics and wireless sensor network or Internet of Things (IoTs). Of various metal complexes based redox couples available, Co(III/II) complexes based redox shuttles are very fascinating in recent years due to their marked advantages such as non-corrosiveness, non-volatility, achieve a variable electrical potential window when suitably alerting the ligands, and light coloration for less absorption. By using Co(III/II) redox shuttles, device efficiency has gone up to 13% and 14.3% using porphyrin and metal-free organic dye as sensitizers, respectively. Though Co(III/II) redox couple has many advantages over traditional $1/1^+$ but main concern are recombination losses and mass transport restrictions because of bulky nature of Co(III/II) complex. Recombination kinetics of various cobalt complexes suggest that electron lifetimes are low in [Co(dtb-bpy)$_3$]$^{3+/2+}$, slightly lower for [Co(dm-bpy)$_3$]$^{3+/2+}$, and the lowest in [Co(bpy)$_3$]$^{3+/2+}$. On the other hand, their recombination rate constants reduced in the contradictory order, whereby [Co(bpy)$_3$]$^{3+/2+}$ established the smallest constant [Co(dm-bpy)$_3$]$^{3+/2+}$ and [Co(dtb-bpy)$_3$]$^{3+/2+}$ the uppermost constant. This indicates that the structure of the cobalt electrolytes plays ultimate significance in attaining the accomplishment of the DSSCs. The other main drawback of these electrolytes is not human friendly as cobalt has its health effects on human beings. Cobalt causes breathing problems and severe effects on the lungs, including pneumonia, asthma, and wheezing. By scrutinizing in animals insinuate that contact of higher amounts of nonradioactive cobalt during pregnancy might influence the health of the embryonic foetus. Birth defects, however, have not been found in children born to mothers who were treated with cobalt for anaemia during pregnancy. Any trace amount of radioactive cobalt if present it can create consequential disorders and can damage tissues, ultimately leading to cancer. So there is a requirement to overcome these drawbacks and need for the new redox shuttle is important for DSSC.

2. Criteria of Selection of New Redox Couples

The redox potential of a redox couple should be match to that of highest occupied molecular orbital (HOMO) of the sensitizer. The minimal driving force required for regeneration is approximated at around 0.1 eV. This means that more positive redox potential of a redox couple with respective to the HOMO level of a sensitizer. The minimal driving force required for regeneration is approximated at around 0.1 eV. This means that more positive redox potential of a redox couple with respective to the HOMO level of a sensitizer so that less energy lost during regeneration of oxidized dye and larger photovoltage would be established (Figure 1).

- Redox couple must be capable to transport the charge carriers between photoanode and photocathode. The oxidized dye should be quickly reduced to the ground state, once the dye injects electron to the conduction band of TiO$_2$. Hence, this aspect should be addressed while designing a new redox couple.
- The redox couples should be designed in such a way where it processes chemical, optical, thermal, electrochemical and interfacial consistency. It should be having a long term stability and do not make happen desorption and mortification of the sensitizer.
- Redox couple must assure higher conductivity (10$^{-3}$ S cm$^{-1}$) at ambient temperatures and produce excellent contact with semiconductor layer and counter electrode.
For liquid redox couples, care has to be taken such as the solvent has minimal leakage and evaporation of liquid electrolyte.

Since the dye has to absorb maximum photons in visible range, redox couple should be in such a way it has no absorption or a minimal absorption in visible region. Where \( I^-/I^3^- \) drawback are it absorption lies in visible region. If the redox couple has absorption in visible region its concentration should be optimized.

By and large, electrolytes are present in all forms of physical state i.e., liquid, quasi-solid or gel and solid form. Efficiencies of up to 14.3% have been accomplished in DSSC by means of liquid electrolytes (either \( I^-/I^3^- \) or \( Co^{3+/2+} \) redox couples). On the whole, the redox couple is formulated with the combination of parts of a chemical species accessible in various oxidation states. In a photoelectrochemical cell the redox couple can perform as a reducing or oxidizing agent. Redox couple, additive, and an organic solvent or ionic liquid constitute liquid electrolyte. The low viscous solvents such as acetonitrile, valeronitrile, 3-methoxy propionitrile etc., have better interfacial contacts that yield higher efficiency of the device in comparison with gel or solid-state redox electrolytes.

3. \( Cu(II/I) \) Redox Couples

Though several redox mediators have used for DSSC applications with device efficiency even crossed 14% but each redox mediator have its own merits and demerits. To overcome the disadvantages of redox couples particularly in terms of photovoltaic accomplishments and health issues, Fukuzumi and co-workers have first attempted \( Cu(II/I) \) redox couples for DSSC applications. Copper is one of the low-cost metals which abundantly available in earth’s crust. Application of \( Cu(II/I) \) redox couple to DSSC was inspired from the electron transfer reactions take place in copper complexes in which copper oscillate between +2 and +1 oxidation states in biological systems.

Copper complexes present in natural systems are identified as blue copper proteins that serve as an electron transfer mediators. In the electron transfer process among Photosystems I and II of natural photosynthesis it involves Plastocyanine a copper system, whereas the electron transfer of the respiratory chain between cytochrome c551 and cytochrome c oxidase involves Azulin copper systems. According to the Franck Condon theory, the transfer of electron is recognized to advance via transition state structures, the transition of reactant and product. Hence, for the effective transfer of electron, the metal centre should be vibrationally stimulated to match the geometry of the product complex. The electron transfer reactions involve significant reorganizational energies, because of electron density and orbital configuration there will be internal changes in bond length and bond angles. But in copper such alteration in bond lengths in the geometry typically needs a significant energy due to Copper (I) prefers tetrahedral and Copper (II)
prefers tetragonal.\textsuperscript{53-55} Whereas in case of natural system due to protein system present minimizes the disparity in bond lengths and geometries which makes the copper site optimized for quick electron transfer. Cu(II) which possess d-9 system tend to attain a six coordinate tetragonal (distorted octahedral) geometry or a five coordinate (square pyramidal or trigonal bipyramidal) geometry and Cu(I) which has d-10 system it tends to achieve four coordinate (tetrahedral) geometry (Figure 2). When the electron transfer occur in Cu(II/I) system it is assumed that rupturing of one or two coordinate bonds and twisting of remaining bonds occur. So the internal reorganizational energies are of mainly important in the behaviour of copper in electron transfer.\textsuperscript{56,57}

![Fig. 2 Orbital splitting pattern of Cu(I) and Cu(II) complexes.](image)

Even Jahn-Tellar distortion plays a significant role in Cu(II) complex which is a dynamic process and it suggests Cu(II) have plastic geometry (Figure 3). It is evident in Plastocyanin which has distorted tetrahedral geometry, an intermediate geometry between Cu(I) and Cu(II) states, which has unusual copper-methionine contact found in each oxidation state.\textsuperscript{58-61} Plastocyanin belongs to type-1 blue proteins, which has an intense absorption band at 600 nm whereas that band is not usually found in other octahedral copper complexes; it has distinct electron spin resonance spectra and more importantly high redox potentials. Keeping this in mind many copper complexes have been designed and synthesised for DSSC to mimic it for higher redox potentials in achieving high open circuit voltages ($V_{OC}$) of the cell and high photon conversion efficiency (PCE).\textsuperscript{32} Similar to the cobalt complexes, by choosing different ligands on copper the redox potentials of the complex can be tuned, in turn $V_{OC}$ will also increase. Many copper complexes with bipyridyl, phenanthroline and other ligands have been reported and used as redox shuttles using different dyes for DSSC and significant improvement has been observed in $V_{OC}$ and PCE. Copper complexes not only possess high redox potentials, they also consent to minimal driving force (\(-0.1\) V) for the regeneration of dye which reduces the

![Fig. 3 Jahn-Tellar distortion in Cu(II) complexes.](image)

![Fig. 4 Molecular structure of metal complex based sensitizers.](image)

3.1 Bipyridyl Ligands
Fig. 5 Molecular structure of metal-free organic sensitizers.
2,2'-bipyridine ligand has been comprehensively studied in coordination chemistry of the complexation of metal ions since its discovery at the end of nineteenth century. The ligand has been used in a variety of approaches that includes structural coordination chemistry mainly as dyes and redox shuttles for DSSC applications. Of these in this section discussed about the 2,2'-bipyridine ligand Cu(II/I) redox mediators for DSSC applications (Figure 6).

For the regenerative photoelectrochemical cells, Bignozzi and co-workers first reported Cu(II/I) redox mediators using a series of bipyridine and pyridyl-quinoline ligands. Due to decrease in dark current, it showed that the copper redox couples achieved higher $V_{OC}$ when compared to $I_{LS}$ redox couple. It was evidenced from photo electrochemical studies that maximum incident photon-to-current conversion efficiencies (IPCE) of the order of 35-40%, but it was quite low to consider in a realistic aspect for substituting the traditional $I_{LS}$ electrolyte. Because of slower dye reduction, which resulted in lower $J_{sc}$ value is the prime reason for the lower efficiencies. To suppress the parasitic electron re-collect by Cu(II) acceptors, nature of the dye also play a prominent role. The exact information regarding the electron transfer processes concerning Cu(II)/(I) species could be identified by further the electron transfer processes involving Cu(II)/(I) species containing these electrode. In designing the novel efficient redox couples, understanding the relationship between redox properties, mediator structure and electron transfer kinetics is an important task.

Lars Kloo and co-workers have designed and synthesized a novel copper redox couple [Cu(bpye)$_2$]$^{3+/2+}$ (bpye = 1,1-bis(2-pyridyl)ethane) and employed in DSSC in amalgamation with a metal-free organic dye (LEG 4). The photovoltaic measurements in which both IPCE and $I-V$ were measured at various light intensities and compared with the cobalt redox couple, [Co(bpy)$_2$]$^{3+/2+}$ (bpy = 2,2'-bipyridine). The copper complex is highly stable under electrochemical stress. Higher power conversion efficiencies were obtained, when evaluated to cobalt redox couple under similar test cell conditions in all three light intensities of 1.0, 0.5, 0.1 sun. At 1 sun using copper redox couple gave a PCE of 9.0% whereas cobalt gave 7.7%. Similarly all other photovoltaic parameters recorded for copper complex were higher compared to cobalt complex. The higher value of $V_{OC}$ may be attributed for couple of reasons; the change in electrolyte redox potential and another one is the recombination loss reactions at the interface. The difference in redox potential of [Cu(bpy)$_2$]$^{3+/2+}$ over [Co(bpy)$_3$]$^{3+/2+}$ by 30 mV also contributes to the better $V_{OC}$. The higher $J_{sc}$ may be attributed to better electrolyte charge transport and quicker dye regeneration by Cu complex. Long term stability studies suggests that the device looses efficiency from 9% to 6% within 20-40 h after that the device stable photochemically up to 700 h. These results suggest that the copper complex based devices are potential for the indoor applications.

In another study, Freitag and co-workers, to keep the driving force sufficiently less for dye regeneration and quicker electron back transfer to the oxidized dye with the redox couple synthesized couple of Cu bipyridyl complexes i.e., [Cu(dmby)$_2$]TFSI$_{2+}$ (dmby = 6,6'-dimethyl-2,2'-bipyridine) and [Cu(tmby)$_2$]TFSI$_{2+}$ (tmby = 4,4',6,6'-tetramethyl-2,2'-bipyridine) as a promising redox couples in DSSC. They evaluated with the previously accounted copper complex of [Cu(dpmp)$_2$]TFSI$_{2+}$ (dpmp = bis(2,9-dimethyl-1,10-phenanthroline). Using Y123 as a sensitizer and [Cu(tmby)$_2$]$^{3+/2+}$, [Cu(dmby)$_2$]$^{2+/+}$ and [Cu(dpmp)$_2$]$^{2+/+}$ as electrolites relatively higher solar to power conversion efficiencies were obtained i.e., 10.3%, 10% and 10.3% correspondingly under 1000 W m$^{-2}$ AM1.5G illumination. The reasons for present copper redox mediators were showed higher efficiencies might be due to that the sufficient regeneration of oxidized dye almost to the unit yield by driving force as low as 0.1 V, this is because of lesser reorganisation energy between Cu(I) and Cu(II) species. Higher photovoltages of above 1.0 V were attained in the series of copper complexes without negotiating the photocurrent densities. Though the driving forces were small but fast regeneration of dye i.e., 2-3 µs were examined for both complexes. With the evidence of longer lifetimes observed for [Cu(tmby)$_2$]TFSI$_{2+}$ the electron back transfer rates were much slower, this would be the added advantage. It was predicted for Cu complexes very low inner-sphere reorganisation energies were obtained when compared to Co complexes. For Co(II) complexes inner-sphere reorganisation energy ($\lambda_{oa}$) values lies between 0.52–0.63 eV (when Co(II) is considered as low spin) and Co(II) lies in 1.39–1.78 eV when considered in high spin sate. Since inner sphere reorganisation energy has proven to limit the dye regeneration process in Co complexes as redox mediators, this group reported for the same in Cu complexes. The low reorganisation energy arises because these copper complexes originate from very small changes in ligand-copper distance upon oxidation, which are only ~2% for Cu ligand (against ~10% for Co-ligand complexes). The spherically symmetric Cu(I) 3d$^{10}$ configuration is very much less sensitive than Co(II) for the structural
deformations in the ligand coordination sphere. Since the reorganizational energies for these complexes are less the driving force for the dye regeneration could be kept small to attain superior photo voltages. Also anticipate these copper complexes based DSSC to be pleasant for indoor applications since photovoltages are as high as 1V with 0.2 Sun illumination. Also they suggested further improvement of device efficiency could be possible through improving fill factor by better counter electrode materials.

![Chemical structure of [Cu(dmbp)]2+/2-](image)

**Fig. 7** (a) Chemical structure of [Cu(dmbp)]2+/2-. (b) Single crystal structure of Cu(dmbp)2+ and (c) Cu(dmbp)2++. (Ref. 66)

In the seminal time, Li et al., have also applied [Cu(dmbpy)]2+BF4 2- redox couple in combination with Y123 as a sensitizer. The single crystal XRD studies suggest that Cu(I) complex has distorted tetrahedral geometry with dihedral angle of angle of 80.9° and Cu(II) complex crystal having a distorted tetrahedral geometry with dihedral angle of 62.6° (Figure 7). The device has demonstrated a considerable increase in VOC of 1048 mV, short circuit photocurrent density of Jsc 14.4 mA cm⁻² with a high power conversion efficiency of 10.3% under AM 1.5G condition. They also compared the device with I/II and Co(III/II) redox mediators under similar test cell conditions. The study suggested that as driving force reduced from I/II to Cu(II)/I) redox mediators, VOC has enhanced from 724 to 1048 mV while reducing the Jsc from 15.8 to 14.4 mA cm⁻². The small driving force of 0.11 eV is sufficient to regenerate the oxidized dye with minimal energy loss (Figure 8). Very rapid electron self-exchange between Cu(I) and Cu(II) complexes is noticed because of stacking interactions between the neighbouring aromatic ligands which tends to a small alteration in structure of the complex. They also noticed reduction process was relatively slower when compared to oxidation. The redox potential of the copper complex was found to be 0.97 V vs. NHE that is far more positive than 1/I3- and cobalt(III/II) redox couple. The corresponding increment in VOC can be explained by the synergy of recombination and shifts of the conduction band. They observed a comparatively low reduction rate for [Cu(dmbpy)]2+/2- system and incompetent catalytic activity between platinum and the copper complex shuttle at the counter electrode which is responsible for the low FF.

The addition of additives such as 4-tert-butyl pyridine (TBP) in redox couples is to decrease the dark current and enhance the device efficiency. Wang et al. have studied the role of TBP additive in [Cu(dmbpy)]2+/2- redox couple and reported higher efficiencies in combination with Y123 sensitizer both in liquid and solid-state.\(^6^9\) The addition of 0.6 M concentration of TBP to [Cu(dmbpy)]2+/2- couple there is hasty ligand substitution reaction that results [Cu(TBP)]2+/2+[Cu(dmbpy)]2+ redox species in solution. This has been confirmed by the absorption, electrochemical and \(^1\)H NMR studies. Previous reports of [Cu(dmbpy)]2+ species shows quantitative regeneration of dyes with minimal driving force, which is important for getting better efficiencies. The presence of [Cu(TBP)]2+ and free TBP in redox electrolyte both influence the Jsc and VOC. The losses in VOC are due to –Ve shift of the solution potential due to ligand exchange reaction by 270 mV. The enhanced short-circuit current by the addition of TBP due to the reduced recombination (Figure 9). By suitable tuning of ligand substitution it allows further to improve the photovoltage without marked loss in photocurrent.

![Schematic energy levels of Y123 sensitized TiO2 film with different redox systems](image)

**Fig. 8** (a) Schematic energy levels of Y123 sensitized TiO2 film with different redox systems. (b) Chemical structure of the Y123 sensitizer. (c) Cyclic voltammograms of Cu(dmbp)2+ complex and Y123 adsorbed on the TiO2 film. (Ref. 66)

![J–V characteristics of DSSCs devices using various concentrations of TBP](image)

**Fig. 9** (a) J–V characteristics of DSSCs devices using various concentrations of TBP. (b) Plots of the charge transfer resistance (RCT) vs. the chemical capacitance (Cm) of devices to demonstrate the effect of TBP on recombination kinetics [0 M (black), 0.1 M (gray), 0.2 M (green), 0.3 M (dark yellow), 0.4 M (orange) and 0.5 M (red)]. (Ref. 69)

In an another study by Freitag and co-workers have examined the recombination of injected electrons with oxidized redox species and regeneration behaviour of copper electrolytes using D5, D35 and D45 metal-free organic sensitizers which have various degrees of blocking factor.\(^7^0\)
The CuII/I redox couples that they are used [Cu(dmby)]^{2+/+}, [Cu(tmby)]^{2+/+}, [Cu(eto)]^{2+/+} (eto = 4-ethoxy-6,6'-dimethyl-2,2'-bipyridine), and [Cu(dmmp)]^{2+/+} (dmmp = bis(2,9-dimethyl-1,10-phenanthroline) for this study. The driving forces were as low as 0.1 eV which allows efficient regeneration of oxidized dye, in which low reorganization energy of (λ = 0.31−0.34 eV) supports to this fact and the electron transfer regeneration reaction lies in Marcus normal regime (Figure 10). Whereas, due to the presence of TBP for CuII species in electrolyte medium will have an altered charge recombination kinetics due to penta-coordinated complex (λ = 1.23−1.40 eV).

From the large driving force for the electrons it could have been expected that charge recombination in Marcus inverted regime, instead it has Marcus normal regime due to higher reorganisation energies. When compared to reference cobalt electrolyte, copper electrolyte had a better recombination resistance and electron lifetime values. When compared to reference cobalt electrolyte, copper electrolyte had a better recombination resistance and electron lifetime values. When D35 was coupled with [Cu(dmmp)]^{2+/+} without compromising with the short circuit current density, a record open circuit voltage of 1.14 V was reached. While D5 sensitizer which doesn’t have recombination preventing steric units, when coupled with [Cu(dmmp)]^{2+/+}, [Cu(dmby)]^{2+/+} it could reach efficiency of 7.5% with 1.5G full sun illumination with 1.13 V as open circuit voltage. On the other hand the intermediate degree of blocking factor i.e., D45 has observed only 1.02 V under similar test cell conditions.

**Fig. 10** (a) Schematic Energy diagram represents the highest occupied molecular orbitals (HOMO) of D5, D35, and D45 dyes with the formal redox potentials of the CuI species and (b-d) Current density vs applied potential curves under dark and 100W/cm² AM1.5G illumination for DSSCs devices measured with a mask aperture of 0.158 cm². ([(Cu(dmby)]^{2+/+}, blue; [Cu(tmby)]^{2+/+}, red; [Cu(eto)]^{2+/+}, purple; [Cu(dmmp)]^{2+/+}, green; [Cu(bpy)]^{2+/+}, black). (Ref. 70)

Ladislav Kavan and co-workers have studied performance of 3 copper complexes i.e., [Cu(dmmp)]^{2+/+}, [Cu(dmby)]^{2+/+} and [Cu(tmby)]^{2+/+} as redox mediators on diverse electrodes and different electrolyte solutions using impedance spectroscopy and cyclic voltammetry using dummy cells. When compared to the activity of platinum, Graphene based catalyst showed higher activity to PEDOT and both outperformed that of platinum. In presence of TBP, the diffusion rate and charge transfer kinetics slows down significantly and this effect is not observed in Cobalt electrolytes and it can be seen only in copper based mediators because of coordination sphere of CuII species to structural and substitutional changes. From PEDOT/PEDOT symmetrical devices they prepared Zombie cells which showed improved charge transfer rate and improved diffusion resistance. As a result of electrochemical oxidation of parent CuI complex, they prepared electrochemically clean CuII bipyridine for the first time. These results suggests that the electrochemically-grown clean CuII-bipyridine complex is demonstrated on practical dye-sensitized solar cells.

**Fig. 11** (a) Stability evaluation of semi-transparent devices. a) Colour coordinate of 4 µm thick HY64- sensitized TiO₂ film in permutation with copper electrolyte-[Cu(tmby)]^{2+/2} on CIE 1931 XY chromaticity diagram. The inner photograph represents the film state device. b) Current density (J) – voltage (V) curves of DSSCs with dye HY64 adsorbed on scattering layer of free TiO₂ film employing [Cu(tmby)]^{2+/2} as a redox shuttle under various light intensities. c) Evaluation of Voc, Jsc, FF and PCE of the dye HY64 based DSSCs under AM1.5 sunlight (100 mW cm⁻²) while continuous light soaking at 60°C for 500 h. (Ref. 73)

In another study, Ladislav Kavan and co-workers developed an innovative synthetic procedure to made electrochemically and optically clean [Cu(tmby)]^{2+/2}TFSI and [Cu(tmby)]^{2+/2}TFSI in a mixture (tmby = 4,4,6,6-tetramethyl-2,2'-bipyridine; TFSI = trifluoromethylsulfonilimide). Faster diffusion transport rate in solution and better charge transfer rate is observed with this copper electrolyte at the counter electrode (PEDOT). They have examined with 4 pyridine bases as electrolyte additives i.e., 4-tert-butylypyridine, 2,6-bis-tert-butylypyridine, 4-methoxyprpyridine and 4-(5-onyl)pyridine. It was found that in [Cu(tmby)]^{2+/2} base specific electrochemical properties were observed where as in cobalt complexes as electrolyte it wasn’t. 2,6-bis-tert-butylypyridine shows smallest consequence on mediators electrochemistry because of stearic hindrance and also ineffective Voc enhancement. Basicity of the used pyridine derivatives has the direct influence on charge transfer rates and diffusion resistance. Solar cells are fabricated with dye Y-123 and power conversion efficiency is evaluated in presence of different bases. Coordination ability dependence on basicity can be tuned by optimizing the pyridine bases Cu mediated solar cells. This further allows tuning the charge transfer rate at the counter electrode and...
the mass transport in electrolyte solution. 4-(5-nonyl)pyridine outperformed other bases in the photovoltaical properties, where 9.4% efficiency could be achieved.

The enhanced device efficiency using CuI/II redox shuttles due to the higher $V_{OC}$ values but major bottleneck for further improvement of PCE is that the $J_{SC}$ values are moderate. In order to improve the $J_{SC}$ values, the sensitizer should have absorption till red or NIR region. Grätzel and co-workers have modified Y123 dye by introducing either benzothiadiazole (BTZ) or phenanthrene-fused-quinoxaline (PFQ) HY64 as auxiliary acceptor to push absorption to near-IR region. The spectral response of both HY63 and HY64 sensitizers have improved in red region of spectra in comparison with Y123 sensitizer. The photovoltaical properties of both dyes along with standard Y123 were compared using $[\text{Cu}(\text{tmby})]_{2}^{2+/+}$ (TFSI)$_{12}$ redox couple under similar test conditions (Figure 11). The device studies suggest that the sensitizer HY64 outperforms over its counterparts with a PCE of 12.5% that is highest efficiency, reported by Cu(II/I) redox couple under one sun condition. The energy levels and absorption onset are identical but high efficiency of PFQ over BTZ due to decreasing spectral response of both HY63 and HY64 sensitizers have improved in red region of spectra in comparison with Y123 sensitizer. The photovoltaical properties of both dyes along with standard Y123 were compared using $[\text{Cu}(\text{tmby})]_{2}^{2+/+}$ (TFSI)$_{12}$ redox couple under similar test cell conditions (Figure 11). The device studies suggest that the sensitizer HY64 outperforms over its counterparts with a PCE of 12.5% that is highest efficiency, reported by Cu(II/I) redox couple under one sun condition. The energy levels and absorption onset are identical but high efficiency of PFQ over BTZ due to decreasing charge recombination ensuing in the near quantitative collection of photogenerated charge carriers. In addition to this, the sensitizer HY64 has showed greater stability under continues light soaking at 60°C. Furthermore, see-through devices attain a PCE of 11.2%, demonstrating for semi-transparent photovoltaics.

Recently, Robertson and co-workers have mixed a less expensive 5T dye with better performing XY1 dye to engineer the co-sensitized devices using $[\text{Cu}(\text{tmby})]_{2}^{2+/+}$ redox mediator (Figure 12). At 1 sun condition co-sensitised device showed a comparable power conversion efficiency of XY1 (avg. 9.1%), but exhibit higher conversion at 0.1 sun perhaps attributed to the drift in equilibrium between charge recombination and mass transport in the electrolyte and the interface. Cao et. al. have reported a different device architecture in which the PEDOT acting as counter electrode dye-impregnated mesoporous TiO$_{2}$ electrode are directly contacted without using any spacer. The novel architecture diminishes the diffusion channel of redox mediator to purely the TiO$_{2}$ film satisfying the Warburg resistance. Co-sensitization of metal-free organic dyes Y123 reaches to 11.3%, a new record for a system based on a copper electrolyte using co-sensitization concept. Once again in the present co-sensitization system also the driving force necessitated to regenerate the oxidized dyes is only a 0.1-0.2 eV. With the help of artificial fluorescent lighting by using Osram 930 warm-white fluorescent light tube accomplishes power generation of 15.6 and 88.5 $\mu W$ cm$^{-2}$ at 200 and 1,000 lux, correspondingly, and translates the PCE of 28.9%.

![Fig. 12](image1.png) **Fig. 12** IPCE curves of XY1 (black), 5T (red) and XY1 + 5T (blue)-sensitized DSSCs. The dotted lines are the integrated current density values. (Ref. 75)

Co-sensitization of different sensitizers having absorption in harmonizing spectral region is another way to enhance the device efficiency. Freitag et al. have combined two thoughtfully designed sensitizers D35 and XY1 with $[\text{Cu}(\text{tmby})]_{2}^{2+/+}$ redox couple. The devices made out in combination of D35 and XY1 dyes in 4:1 ratio has given best performance as external quantum efficiency surpass 90% across the whole visible area from 400 to 650 nm with PCE

![Fig. 13](image2.png) **Fig. 13** (a) The pictorial representation of new generation of DSSCs to prevent electrical shunts. The redox couple has to diffuse in both mesoporous film and the bulk phase of electrolyte. b) J-V chartersics curves. Inset figure represents the impedance analysis of contacted and separated TiO$_{2}$/PEDOT. c) J-V spectra of co-sensitization of mesoscopic TiO$_{2}$ by XY1b/Y123 and a Cu(II)/Cu(I)-based electrolyte and emitted power density spectrum using White fluorescent tube light. Inset picture of two DSSCs with different photoactive areas of 2.80 and 20.25 cm$^{2}$ respectively. (Ref. 76)
and XY1b with liquid [Cu(tmby)]_{2/3} redox mediator has reached an efficiency of 13.1% using the advanced device architecture under standard conditions (J_{SC} 15.74 mA cm^{-2}, V_{OC} 1.050 mV, and FF of 0.79). The efficiency further enhanced to 32% under artificial indoor lighting at 1,000 lux with output power density of 101.2 mW cm^{-2}, which is highest reported DSSC device efficiency till date (Figure 13). Overall, the sensitization concept using Cu(I/II) redox mediators that function well under indoor lighting are of potential practical curiosity as they can operate as electric power supplies for devices for portable electronics and wireless sensor network or Internet of Things.

The fancy efficiencies of DSSC devices were obtained using a liquid redox electrolyte but durability of the device is not sufficient mainly due to utilization of volatile acetonitrile solvent. Either polymer gel or solid-state hole conductors may give probable solution towards this direction. The low efficiency of DSSC devices using solid-state hole conductors are due to inadequate nanopore filling, crystallization of hole-transport materials penetrated in the nanocrystalline TiO_{2} and low conductivity at ambient temperatures. Boschool and co-workers have used a hole transport material composed of a blend of [Cu(tmby)]_{2} (TFSI), using metal-free organic dye Y123 and reported with a record efficiency of 11%.\textsuperscript{74,78} In contrast, using 0.06M [Cu(tmby)]_{2} (TFSI), 0.2M [Cu(tmby)]_{2} (TFSI), 0.1M LiTFSI and 0.6M 4-tert-butylpyridine (TBP) in acetonitrile with PEDOT on FTO as counter electrode obtained only 9.3±0.3% efficiency under standard AM1.5G conditions (Figure 14). The high efficiency of solid-state device over liquid based redox mediator that the slow evaporation of the solvent acetonitrile of electrolyte in ambient air persuades the solidification of [Cu(tmby)]_{2/3} and provide better interfacial contact, which is not possible in rapid evaporation. The time-resolved laser photolysis studies indicates that electron injection from excited state of dye into the TiO_{2} conduction band is 25 ps against dye regeneration by taking electron from redox mediator was 3.2 ms.

![Figure 14](image)

**Fig. 14** (a) Cross-sectional SEM image without counter electrode. b) J–V curves of a champion ssDSSCs under standard illumination of AM1.5G at 1,000 (royal blue), 500 (red) and 100Wm^{-2} (olive). (Ref. 78)

| Electrolyte | Dye | J_{SC} \text{mA cm}^{-2} | V_{OC} \text{mV} | FF | \eta (%) | Ref. |
|-------------|-----|--------------------------|-----------------|----|---------|-----|
| [Cu(bpye)]_{2/3} | LEG4 | 13.8 | 0.90 | 0.71 | 9.0 | 64 |
| [Cu(tmby)]_{2/3} | Y123 | 7.3 | 0.89 | 0.76 | 9.9\textsuperscript{a} | 65 |
| [Cu(dmby)]_{2/3} | Y123 | 15.5 | 1.04 | 0.64 | 10.3 | 65 |
| [Cu(dmby)]_{2/3} | Y123 | 14.1 | 1.07 | 0.68 | 10.0 | 65 |
| [Cu(dmby)]_{2/3} | D5 | 10.12 | 0.83 | 0.72 | 6.0 | 70 |
| [Cu(eto)]_{2/3} | D5 | 12.59 | 0.98 | 0.67 | 8.21 | 70 |
| [Cu(eto)]_{2/3} | D5 | 11.93 | 1.12 | 0.66 | 8.84 | 70 |
| [Cu(tmby)]_{2/3} | D5 | 10.79 | 0.98 | 0.67 | 6.61 | 70 |
| [Cu(tmby)]_{2/3} | D5 | 12.52 | 0.98 | 0.67 | 8.3 | 70 |
| [Cu(tmby)]_{2/3} | D5 | 12.81 | 1.11 | 0.66 | 9.44 | 70 |
| [Cu(dmby)]_{2/3} | D5 | 9.85 | 1.07 | 0.71 | 7.53 | 70 |
| [Cu(dmby)]_{2/3} | D45 | 11.85 | 0.96 | 0.68 | 7.71 | 70 |
| [Cu(dmby)]_{2/3} | D35 | 11.53 | 1.13 | 0.60 | 7.84 | 70 |
| [Cu(tmby)]_{2/3} | Y123 | 13.33 | 1.03 | 0.75 | 10.03 | 73 |
| [Cu(tmby)]_{2/3} | HY63 | 13.71 | 0.99 | 0.76 | 10.3 | 73 |
| [Cu(tmby)]_{2/3} | HY64 | 15.76 | 1.03 | 0.77 | 12.5 | 73 |
| [Cu(tmby)]_{2/3} | D35+XY1 | 16.20 | 1.10 | 0.68 | 11.3 | 74 |
| [Cu(tmby)]_{2/3} | (4:1 ratio) | 0.14 | 0.80 | 0.80 | 28.9\textsuperscript{a} | 74 |
| [Cu(tmby)]_{2/3} | XY1 | 11.4 | 1.05 | 0.76 | 9.1 | 75 |
| [Cu(tmby)]_{2/3} | ST | 9.90 | 0.97 | 0.77 | 7.5 | 75 |
| [Cu(tmby)]_{2/3} | XY1+ST | 11.80 | 1.04 | 0.74 | 9.1 | 75 |
| [Cu(tmby)]_{2/3} | XY1+ST | 0.13 | 0.86 | 0.78 | 29.2\textsuperscript{a} | 75 |
| [Cu(tmby)]_{2/3} | Y123+XY1 | 15.74 | 1.05 | 0.79 | 13.1 | 76 |
| [Cu(tmby)]_{2/3} | b | 0.004 | 0.88 | 0.77 | 31.8\textsuperscript{a} | 76 |
| [Cu(tmby)]_{2/3} | Y123 | 13.87 | 1.08 | 0.68 | 11.0 | 777 |
| [Cu(tmby)]_{2/3} | D205multi capping | 6.33 | 0.89 | 0.81 | 4.51 | 79 |
| [Cu(tmby)]_{2/3} | D205-CB7 | 5.86 | 0.92 | 0.82 | 4.38 | 79 |
| [Cu(tmby)]_{2/3} | D205-Si | 5.76 | 0.89 | 0.77 | 3.92 | 79 |
| [Cu(tmby)]_{2/3} | D205-Si multicappi | 6.22 | 0.88 | 0.80 | 4.37 | 79 |
has showed better device performance of 5.07% over LG5 sensitizer (4.36%), which is highest efficiency of a porphyrin based sensitizer with copper redox mediators till date.

3.2 Phenanthroline Ligands

![Molecular structure of 1,10-phenanthroline ligand based copper complexes.](image)

Like 2,2′-bipyridine ligands another interesting ligand in coordination chemistry is 1,10-phenanthroline (Phen) used in different fields of chemistry. Indeed, a great variety of Cu(II) derivatives using substituted phenanthroline ligands and applied DNA binding and photocleavage studies. However, Cu(II) complexes of phenanthroline ligand derivatives have not much explored in the literature. The copper complexes of both I and II oxidation states using phenanthroline ligand derivatives as redox couples were also studied for DSSC applications (Figure 15).

Shunichi Fukuzumi and group reported the copper complex [Cu(dmp)]^{2+/2} [dmp = bis(2,9-dimethyl-1,10-phenanthroline)] as redox shuttle to DSSC for the first time to replace I$_3$/I$_2$ redox couple. This has great advantage since dmp ligands are commercially available and copper complex of dmp can be easily made in one step. The structural modification between the copper- (I) and copper(II) complexes is minimized, giving a capable approach for developing to DSSC. Along with [Cu(dmp)]^{2+/2} another two copper complexes were reported i.e., [Cu(SP)(mmt)]^{0/+} [SP(mmt) = (-)-sparteine-
N,N’][maleonitriledithiolato-S,S’) and ([Cu(phen)]^{2+/+} [phen = bis(1,10-phenanthroline)]. Under the solar simulated illumination (100 mW/cm²) the power conversion efficiency of DSSC was found to 0.1%, 1.4%, and 1.3% for [Cu(phen)]^{2+/+}, [Cu(dmp)]^{2+/+}, and [Cu(SP)(mmt)]^{0/-}, respectively. For [Cu(dmp)]^{2+/+} redox couple it realized the maximum efficiency of 2.2% under low light intensity of 20 mW/cm², higher V_Oc were observed when compared to that I/I_0 redox couple. Low photovoltaic properties for [Cu(phen)]^{1+/2+} redox couple may be attributed to the lowest self-exchange rate and of lowest redox potential of -0.10 V. Whereas in case of [Cu(SP)(mmt)]^{0/-} redox couple both J_sc and V_Oc are improved probable because of faster self-exchange rate of electron and higher redox potential of 0.29 V. But in case of [Cu(dmp)]^{2+/+} J_sc value is smaller than [Cu(SP)(mmt)]^{0/-} even though the electron self exchange rate was much faster than [Cu(SP)(mmt)]^{0/-} perhaps due to the considerably lesser driving force of electron transfer from [Cu(dmp)]^{2+/+} to the dye cation compared to [Cu(SP)(mmt)]^{0/-}. But that difficulty of lower J_sc is remunerated by the V_Oc which is of highest among three complexes which is of 0.66 V.

Using [Cu(dmp)]^{2+/+} redox couple and a mesoporous titania thin-film coated with metal-free organic sensitizer, C218, Peng Wang and his group reported DSSC device of PCE 7% at 100 mW cm⁻². The low efficiency of DSSC device with copper electrolyte had a low electron transfer rates on numerous noble metals, conducting oxides and carbon black which resulted in poor fill factor which is evident in their work. The copper device showed even of 7.8% efficiency when illuminated with weaker light. This demonstrates the nonlinear reliance of photocurrent on light intensity further it can be outlined that photocurrent under full sunlight would be still imperfect by the mass transport of Cu(II) ions to some extent. When cell was constructed with iodine based electrolyte they obtained 6.5% PCE which is lower than that of copper based one, the improved efficiency in copper may to credited to the imperfect by the mass transport of Cu(II) ions to some extent.

In another study Freitag et al., have used [Cu(dmp)]^{2+/+} with LEG-4, a metal-free organic sensitizer and achieved high photovoltaic performance of 8.3% with high V_Oc of over 1.0 V at 1000 W m⁻² under AM1.5G conditions. The high voltage is due to that it requires driving force of 0.2 V for dye regeneration that guides to higher efficiencies of the device (Figure 16). The diffusion coefficient of copper complexes is high in comparison to cobalt redox mediators and hence oxidized dye gets reduced faster. In DSSC, the excited dye quenched by the components of the electrolyte which effects on the efficiency of the device. By using steady state emission measurements and time correlated single photon counting, propose that the excited state of sensitizer quenched by [Cu(dmp)]^{2+/+} species contributes with electron injection and lowers the overall device accomplishment. These results suggests that [Cu-(dmp)]^{2+/+} redox couple with LEG-4 dye have higher recombination when evaluated to [Co(bpy)]^{3+/2+} redox mediator as a result multiple recombination pathways such as reductive quenching of excited dye and with TiO₂ layer. By structural modifications of phenanthroline ligands or creation of steric hindrance at dye that leads to minimization of unwanted process and increase overall performance of the device.

Fig. 16 Pictographic representation of Cu(I) and Cu(II) in situ and structure of the LEG4 sensitizer. (Ref. 87)

To facilitate further boost the device efficiency using Cu(I/II) redox mediators particularly using phenanthroline ligands, one has to introduce bulky groups either at 2ⁿ or at 9ᵗʰ positions of phenanthroline ligand so that the dark current reduces by minimizing recombination process and leads to higher efficiencies. Colombo et al., have systematically designed and synthesized by three different Cu(II/I) redox mediators [i.e., [Cu(2,9-dimethyl-1,10-phenanthroline)]PF₆, [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)]PF₆, and [Cu(2-mesityl-4,7-dimethyl-1,10-phenanthroline)]PF₆]. The occurrence of bulky mesityl group at the position 2 but only H at position 9 of phenanthroline causes the steric effect, keeping the mesityl groups on contradictory sides of the copper center. The complex [Cu(dmp)₃]PF₆ involves in an outer sphere electron transfer reactions. These consequences, however, could be accomplished only after a meticulous alternative of the dye and suitable TiO₂ passivation approaches, based on the co-adsorption of alkyl-siloxanes. When [Ru(4,4′-dicarboxy-2,2′-bipyridine)]PF₆ and [Ru(4,4′-dinonyl-2,2′-bipyridine)](PF₆)₂ sensitizers is combined with the copper electrolyte [Cu(dmmsp)₃]PF₆ along with co-mediator Fe(II), it was noticed that performance of the cell increased with higher J_sc values of 4.0 mA cm⁻² when compared to I/I₇ where it was recorded 3.8 mA cm⁻². When [Ru(4,4′-dicarboxy-2,2′-bipyridine)]PF₆ dyed combined with copper complex attractive advances were revealed, compared to [Cu(dmnp)₃]PF₆ where photocurrent and overall efficiency were doubled. The recovery kinetic studies of Ru (II) showed the main limitation of these copper complexes was about slow dye regeneration but when co-mediator was added in form of 10% poly pyridine Fe(II), there was a considerable increase in photocurrent.
Imahori and co-workers have designed and synthesized a series of copper complexes systematically and applied as redox shuttles in DSSC using Zn(II) metal-free organic photosensitizer. They reported that copper phenanthroline complexes were synthesized as sensitizers at 2,9-positions of phenanthroline to check the light-to-electric conversion efficiency of these complexes. Further, the device efficiency has risen to 10.3% using Y123 as sensitizer.

Fig. 17 Energy level diagram comprising of LEG4 dye with different copper redox couples. (Ref. 89)
Dye sensitizers are combined in DSSC with moderate efficiency. Based on characteristics in DSSC by processing 2,9-dimesityl-1,10-phenanthroline as an ancillary ligand, their performance in DSSC as dyes were much similar when homoleptic copper complexes or iodide/triiodide electrolytes were used. But in full copper complexes from both experimental results and theoretical calculations it was found to be having better potential. Since the compounds prepared are similar processing 2,9-dimesityl-1,10-phenanthroline as an ancillary ligand, they could be coupled with iodide/triiodide electrolyte to prepare DSSC with moderate efficiency. Based on electron shuttle, they can also be coupled with homoleptic copper electrolyte to provide full-copper DSSCs with adequate to good performance. It was noticed that, in copper dyes, the use of n-delocalized ancillary ligands was to electron transfer augmentation from the electrolyte to dye and directionality for electron injection into the TiO₂ conduction band and was not adequate to enhance light harvesting drastically. Main absorption was assigned to MLL’CT from TDDFT calculations, in which phenanthroline was also involved not only the bipyridyl ligand which upon TiO₂ sensitization should point in the opposite way of the TiO₂ surface. Due to phenanthroline participation there was reduction in charge transfer directionality in which the excited state originating visible light absorption becomes therefore detrimental. To avoid interference on the low-lying MLCT transitions, this class of compounds should be tuned to up-shift the phenanthroline-based LUMOs by electron donating ligands. Keeping earth

Table 2. Photovoltaic data of copper(II/I) redox shuttles using phenanthroline ligands.

| Electrolyte | Dye        | $k_\text{cat}$ | $k_\text{sc}$ | FF (%) | $\eta$ (%) | Ref. |
|-------------|------------|---------------|---------------|--------|------------|------|
| [Cu(dmp)],PF₆ | N719       | 3.2           | 0.79          | 0.55   | 1.4        | 47   |
| [Cu(phen)],PF₆ | N719       | 0.48          | 0.57          | 0.43   | 0.12       | 47   |
| [Cu(dmp)],PF₆ | C218       | 11.29         | 0.93          | 0.66   | 7.0        | 86   |
| [Cu(dmp)],PF₆ | LEG4       | 12.6          | 1.02          | 0.62   | 8.3        | 87   |
| [Cu(dmp)],PF₆ | [Ru(dcbpy)]PF₆ | 1.10          | 0.73          | 0.50   | 0.4        | 88   |
| [Cu(dmp)],PF₆ | [Ru(bpy)]PF₆ | 1.10          | 0.71          | 0.49   | 0.4        | 88   |
### 2.2 Materials Advances

| Journal Name | ARTICLE |
|--------------|---------|
| [Cu(dnbp)]₂⁺⁺ | D1 3.8 0.59 0.61 |
| [Cu(n-butyl-dmp)]₂⁺⁺ | D2 3.2 0.57 0.67 |
| [Cu(dnbp)]₂⁺⁺ | D3 2.8 0.57 0.62 |

*Error limits: J_{SC} = ±0.20 mA cm⁻², V_{OC} = ±0.30 mV, FF = ±0.03, and η = ±0.1.*

abundant components in view, this study shows copper complexes are potential for DSSC.

Lennert et al., have designed and synthesized a series of phenanthroline based homoleptic and heteroleptic Cu(II/I) redox shuttles, tested in DSSC using D35 organic dye. Initially from a homoleptic copper complex containing bathocuproine ligands, \([\text{Cu(bcp)}]^{2+}\) [bcp = 9,9-dimethyl-4,7-diphenyl-1,10-phenanthroline] \([\text{Cu(bcp)}]_{2}\) and substitute one of them by another N- or a P-coordinating ligand. They are \([\text{Cu(bcp)}(tmp)]^{2+}\), \([\text{Cu(bcp)}(dppm)]^{2+}\) (dppm = diphenylphosphino) methane), \([\text{Cu(bcp)}(dppx)]^{2+}\) (dppx = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) and \([\text{Cu(dnbp)}]^{2+}\). The absorption and redox properties of these complexes are very attractive for DSSC applications. The electrochemical properties of P containing ligands i.e., complex D and E were not stable. The Electrochemical Impedance Studies suggests was observed the A and E homoleptic complexes were having highest diffusion coefficients and maximum current density. For B, C and D heteroleptic complexes it was found that performance depended on the size of the appropriate ligand. Also noticed in heteroleptic complexes charge transport resistance exceeding 200 Ω, where as it was noted a reasonably low transport resistance of 100 Ω for homoleptic complexes. The change in efficiency was dependent on lesser resistance against the recombination of A relative with the reference E, homoleptic complexes obtained the best PCE in terms of DSSC. With and without copper complexes, compliment transient absorption studies they noted that start effects, charge injection, long lived fingerprints of dye cation, geminate recombination and non-recombination. Marked variations were noticed in terms of long lived fingerprints of the one-electron oxidised form of D35 when electrolyte were present the implied a better dye regeneration. The recombination process in geminate and non-geminate, in presence of electrolyte were largely unaffected.

### 3.3 Tetradentate Ligands

In addition to bidentate and tridentate polypyridyl ligands that include both bipyridine and phenanthroline, there are other ligands having either P- or O- as coordinating atoms or beyond tridentate ligands i.e., tetradentate ligands in which all four coordination sites into one ligand molecule considerably decreases geometry rearrangements (Figure 20). Freitag and...
co-workers have designed and synthesized a Cu(oxabpy)$^{2+/+}$TFSI$_{1/2}$ (oxabpy = 6,6’-bis(4-(S)-isopropyl-2-oxazolinyl)-2,2’-bipyridine) for DSSC application using Y123 as photosensitizer. In this complex, copper is present in square planar geometry it possesses low reorganizational energies and in turn has smaller losses in photovoltage. Exceptionally long electron lifetime was achieved due to sluggish recombination kinetics of excited electron between TiO$_2$ and Cu(II) species. A 6.2% of PCE was obtained with high photovoltage of 920 mV and photocurrents of 1.0 mA cm$^{-2}$. Despite the square planar complex obtained in high viscous gel, the charge transport performance was obtained with Cu(oxabpy) was comparable with previously reported Cu(tmby)$^{2+/+}$ redox mediator. The improvement of the charge transport in the gel like electrolyte originates from charge hopping mechanism on the top of diffusive transport.

![Molecular structure of tetradentate ligands.](image)

**Fig. 20** Molecular structure of tetradentate ligands.

Rodrigues et al. have designed and synthesized three copper complexes featuring tetradentate ligands and they are [Cu(bpyph)$_2$]$^{2+/+}$ (bpyph = 2,2’-di(2,2’-bipyrinid-6-yl)-1,10-biphenyl), [Cu(mbptb)$_2$]$^{2+/+}$ (mbptb = 2,2’-Bis(methyltriazole-pyridine)-biphene), and [Cu(mcptb)$_2$]$^{2+/+}$ (mcptb = 2,2’-Bis(methyltriazole-4-trifluoromethylpyridine)-biphene). All these three tetradentated copper complexes were evaluated in DSSC using Y123 as photosensitizer and compared their performance with [Cu(bpy)$_2$]$^{2+/+}$. To improve power conversion efficiency a new strategy have been adopted by introducing neutral polyaromatic ligands with partial flexibility thereby reducing voltage losses affiliated to redox couple. Quantum mechanical calculations were used for inner sphere electron transfer reorganization energies ($\lambda$) calculations and evaluated to commonly used [Cu(bpy)$_2$]$^{2+/+}$ complex which has a reported $\lambda$ of 0.61eV. The triazole group in [Cu(mbptb)$_2$]$^{2+/+}$ and [Cu(mcptb)$_2$]$^{2+/+}$ slight increase in reorganisation energies but when compared to traditional copper bidentate complexes their reorganizational energies are lower. The lower reorganization energies (0.34-0.053 eV) of tetradentated copper complexes are due to geometrically constrained and they could activate with low driving forces for dye regeneration. Because of this it allows better electron transfer reactions primarily to enhance $J_{sc}$. By using PEDOT counter electrode with [Cu(mbptb)$_2$]$^{2+/+}$ redox shuttle showed a PCE of 4.7% where as with Pt counter electrode observed a PCE of 4.4%.

**Table 3.** Photovoltaic data of copper(I/II) redox shuttles using tetradenate ligands.

| Electrolyte | Dye | $J_{sc}$ a | $V_{oc}$ b | FF c | $\eta$ (%) | Ref. |
|-------------|-----|-----------|------------|------|------------|------|
| [Cu(SP)(nml)$_3$]$^{2+/+}$ | N719 | 4.4 | 0.66 | 0.44 | 1.3 | 47 |
| [Cu(oxabpy)$_2$]$^{2+/+}$ | Y123 | 9.75 | 0.92 | 0.69 | 6.2 | 96 |
| [Cu(bpyph)$_2$]$^{2+/+}$ | Y123 | 1.32 | 0.86 | 0.79 | 8.9 | 97 |
| [Cu(mbptb)$_2$]$^{2+/+}$ | Y123 | 5.7 | 0.69 | 0.77 | 3.1 | 97 |
| [Cu(mcptb)$_2$]$^{2+/+}$ | Y123 | 10.2 | 0.69 | 0.72 | 4.7 | 97 |
| (N,N’-Dibenzyl-N,N’-bis(6-methylpyridin-2-ylmethyl)ethylendiamine) | Y123 | 7.9 | 0.79 | 0.75 | 4.3 | 97 |

$\text{Δ}$Error limits: $J_{sc} = \pm 0.20$ mA cm$^{-2}$, $V_{oc} = \pm 0.30$ mV, $\text{FF} = \pm 0.03$, and $\eta = \pm 0.1$.

The efficiencies that obtained by tetradenate copper complexes are not sufficient to commercialize the technology. To further enhancement of PCE of tetradenate copper complexes Hu et al., have designed and synthesized two complexes and they are [Cu(dadp)$_2$]$^{2+/+}$ (dadp = N,N,N’,N’-dibenzyl-N,N’-bis-(pyridin-2-ylmethyl)ethylenediamine) and [Cu(dmddp$_2$)$^{2+/+}$ (dmddp = N,N,N’,N’-dibenzyl-N,N’-bis-(pyridin-2-ylmethyl)ethylenediamine). The redox potential of [Cu(dmddp)$_2$]$^{2+/+}$ shifts positively by 300 mV by introduction of methyl group because of the steric-hindrance effect of L2 that manages to a 180 mV increase in $V_{oc}$. In addition to this the methyl group on tetradentate ligand diminishes the internal reorganization energy that upshot in a high dye regeneration yield and as a result a much improved PCE of 9.2%. More importantly the complexes have good air, phot and electrochemical stability thus resulting in longer durability of whole DSSC. The present study for the sensible design of the coordination sphere of the copper complexes as an efficient tactic to tune the redox potentials of redox couple, which helps to design the redox couples in future.

Majority of oxidation potentials of Cu complexes are more positive and the dyes are having with higher oxidation potentials are suitable combination for DSSC applications. In general, such type of oxidation potentials can be easily tuned by metal-free organic dyes as well as pigment based dyes (porphyrins, phthalocyanines, corroles etc.,) are more compatible for Cu(I/II) redox couples. In addition to this that the Cu complexes have higher diffusion coefficients compared...
to the Co-based alternatives. Therefore, the Cu-based systems considered exhibit less mass transport limitations compared to Co-based systems and it has showed better device efficiency under low-light conditions.

4. Conclusions

In conclusion the redox shuttle dictates the efficiency and durability of the device. Though the certified efficiencies have crossed 11% using traditional I/II redox mediator but their module development hindered mainly due to its volatile nature and complementary absorption with sensitizer. To conquer these boundaries, an immense deal of attempt has dedicated towards alternative redox shuttles for past couple of decades particularly the transition metals having variable oxidation states. The tuning redox potential of redox shuttle will help in controlling over potential that ultimately leads to improving efficiency of the device. Co(II/III) redox mediators using polypyridyl ligands have successfully tuned the redox potential to suit for various sensitzers and achieved the device efficiency more than 14% recently. But, major bottle neck for Co(II/III) redox shuttles are mass transport and health hazards hampered the commercialization of the technology. Inspired from biological electron transport systems that involved copper complexes might be the alternative choice as redox mediators for DSSC applications. The main advantage of Cu(II/I) redox shuttles that their redox potentials are positive than Co(III/II) so that the regeneration potential of oxidized dye ~0.1 V. This will not only control the recombination of oxidized dye with electrons in TiO₂ conduction band but also improve \( \Phi_{oc} \) of the device. Another drawback in Co(III/II) redox mediators are mass transport due to bulky nature, remarkably at high incident light intensities, reducing overall device accomplishments. Several sensitizers using Cu(II/I) redox mediators have crossed device efficiency of 10% under 1 sun irradiation and in case of co-sensitization the device efficiency even crossed 13%. Like in Co(III/II) redox mediators, the copper mediators also suffer about mass transport and it will worked excellently in case of Cu(II/I) redox mediators particularly in co-sensitization of metal-free organic dyes it reached to 31.8% at 1000 lux intensity. Also in one of the bipyridyl copper complex using organic dye has shown better efficiency of 11% in solid-state rather than in liquid state. All these results are encouraging to researchers in which copper electrolytes are particularly interested under low light conditions and potential for commercialization of technology precisely for Internet of Things (IoT) applications.

Acknowledgements

The authors would like to thank Department of Science and Technology, Indo-Israel bilateral programme for financial support. The authors thank the Director, CSIR-IICT (Manuscript No. IICT/Pubs./2020/349).

Notes and references

1. M. Nicole, B. Matteo, F. Lucia, B. Nadia, G. Claudio, B. Federico, B. Claudia, Green Chem., 2020, 22, 7168-7218.
2. A. M. Hisham, B. Vikas, K. B. Sanjay, Renewable & Sustainable Energy Reviews 2020, 121, 109678.
3. M. Mrinalini, N. Islavath, S. Prasanthkumar, L. Giribabu, Chem. Rec. 2019, 19, 661-674.
4. G. Jiawei, K. Sumathy, Q. Qiquano, Z. Zhengping, Renewable & Sustainable Energy Reviews 2017, 68, 234-246.
5. L. Giribabu, R. K. Kanaparthi, V. Velkannan, Chem. Rec. 2012, 12, 306-328.
6. S. Mozaffari, M. R. Nateghi, M. B. Zarandi, Renewable & Sustainable Energy Reviews 2017, 71, 675-686.
7. N.H. Reich, W. G. J. H. M. van Sark, E.A. Alsema, R. W. Lof, R. E. I. Schropp, W. C. Sinke, W.C. Turkenburg, Solar Energy Mater. Solar Cells 2009, 93, 1471-1481.
8. B. O’Regan, M. Grätzel, Nature 1991, 353, 737-740.
9. K. Kakigae, Y. Aoyama, T. Yano, K. Oya, J. –J. Fujisawa, M. Hanaya, Chem. Commun., 2015, 51, 15894-15897.
10. www.nrel.gov/pv, National Renewable Energy Laboratory (NREL)
11. S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. A. Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Gratzel, Nature Chem., 2014, 6, 242-247.
12. J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, Chem. Rev., 2015, 115, 2136-2173.
13. A. Mohammad, J. Eng. Chem. 2015, 24, 686-692.
14. N. C. D. Nath, J. –J. Lee, J. Ind. Eng. Chem., 2019, 78, 53-65.
15. L. Giribabu, R. Bolligarla, M. Panigrahi, Chem. Rec., 2015, 15, 760-788.
16. J. W. Ondersma, T. W. Hamann, Coord. Chem. Rev., 2013, 257, 1533-1543.
17. T. W. Hamann, O. K. Farah, J. T. Hupp, J. Phys. Chem. C, 2008, 112, 19756-19764.
18. M. Wang, C. Grätzel, S. M. Zakeeruddin, M. Gratzel, Energy Environ., Sci., 2012, 5, 9394-9405.
19. P. J. Cameron, L. M. Peter, S. M. Zakeeruddin, M. Grätzel, Coord. Chem. Rev., 2004, 284, 1447-1453.
20. G. Boschloo, A. Hegfeldt, Acc. Chem. Res. 2009, 42, 1819-1826.
21. H. Kusama, J. Photochem. Photobiol. A, Chem, 2019, 376, 255-262.
22. V. Chakrapani, D. Baker, P. V. Kamat, J. Am. Chem. Soc., 2011, 133, 9607-9615.
23. C. Teng, X. Yang, C. Yuan, C. Li, R. Chen, H. Tian, S. Li, A. Hagfeldt, L. Sun, Org. Lett. 2009, 11, 5542-5545.
24. Z.-S. Wang, K. Sayama, H. Sugihara, J. Phys. Chem. B 2005, 109, 22449-22455.
25. B. V. Bergeron, A. Marton, G. Oskam, G. J. Meyer, J. Phys. Chem. B 2005, 109, 937–943.
26. F. Pichot, B. A. Gregg, J. Phys. Chem. B 1999, 104, 6–10.
27. Z. Yu, S. You, C. Wang, C. Bu, S. Bai, Z. Zhou, Q. Tai, W. Liu, S. Guo, X. Zhao, J. Mater. Chem. A 2014, 2, 9007–9010.
28. Y. Zhang, Z. Sun, C. Shi, F. Yan, RSC Adv., 2016, 6, 70460-70467.
29. W. Zhang, L. Qiu, X. Chen, F. Yan, Electrochim. Acta 2014, 117, 48–54.
30. M. Cheng, X. Yang, F. Zhang, J. Zhao, L. Sun, Angew. Chem. Int. Ed. 2012, 51, 9896–9899.
31. H. Iftikhar, G. G. Sonai, S. G. Hashmi, A. F. Nogueira, P. D. Lund, Materials 2019, 12, 1998.
32. Y. Liu, S., –C. Yu, C. –L. Ho, W. –Y. Wong, Coord. Chem. Rev., 2018, 375, 514-557.
33. S. Carli, E. Benazzi, L. Casarin, T. Bernardi, V. Bertolasi, R. Argazzi, S. Caramoria, C. A. Bignozzi, Phys. Chem. Chem. Phys. 2016, 18, 5949-5956.
34. F. Bella, S. Galliano, G. Gerbaldi, G. Viscardi, Energies 2016, 9, 384.
35. A. Apostolopoulou, M. Vlasiou, P. A. Tziouris, C. Tsiafoulis, A. C. Tsipis, D. Rehder, T. A. Kabanos, A. D. Keramidas, E. Stathatos, Inorg. Chem. 2015, 54, 3979-3988.
36. H. Tian, L. Sun, J. Mater. Chem. 2011, 21, 10592-10601.
37. T. Li, A. M. Spokony, C. She, O. K. Farha, C. A. Mirkin, T. J. Marks, J. T. Hupp, J. Am. Chem. Soc., 2010, 132, 4580-4582.
38. S. C. Pradhan, A. Hegfeldt, S. Soman, J. Mater. Chem. A 2018, 6, 22204-22214.
39. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. —I. Fujisawa, M. Hanaya, Chem. Commun., 2015, 51, 15894-15897.
40. S. Mathew, A. Yella, P. Gao, R. Humphrey-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Grätzel, Nature Chem., 2014, 6, 242-247.
41. B. Pashaie, H. Shahroosvand, P. Abbasi, RSC Adv., 2015, 5, 94814-94848.
42. I. Leyssens, B. Vinck, C. Vanderstraeten, F. Wuyts, L. Maes, Toxicology 2017, 387, 43-56.
43. J. Fritzsche, C. Borisch, Ch. Schaefer, Clin. Ortho-rop. Relat. Res., 2012, 470, 2325-2331.
44. D. V. Brusselen, T. K. Kitenge, S/ Mbuyi-Musanzayi, T. L. Kasole, L. K.Ngombe, P. M. Obadia, D. K. wa Mukoma, K. V. Herck, D. Avonts, K. Devriendt, E. Smolders C. B. L. Nkulu, B. Nemery, Lancet Planetary Health, 2020, 4, e158-e167.
45. L. Giribabu, T. Bessho, M. Srinivasu, Ch. V. Kumar, Y. Soujanya, V. G. Reddy, P. Y. Reddy, J. —H. Hum, M. Grätzel, M. K. Nazeeruddin, Dalton Trans., 2011, 40, 4497-4504.
46. L. Giribabu, Ch. V. Kumar, Ch. S. Rao, V. G. Reddy, P. Y. Reddy, M. Chandrasekharam, Y. Soujanya, Energy Environ., Sci., 2009, 2, 770-773.
47. S. Hattori, Y. Wada, S. Yanagida, S. Fukuzumi, J. Am. Chem. Soc., 2005, 127, 9648-9654.
48. E. L. Gross, Photosynth. Res. 1993, 37, 103-116.
49. A. G. Sykes, Adv. Inorg. Chem. 1991, 107, 377-408.
50. C. M. Groeneveld, S. Dahlin, B. Reinhammar, G. W. Canters, J. Am. Chem. Soc., 1987, 109, 3247-3250.
51. R. A. Marcus, H. Eyring, Annu. Rev. Phys. Chem., 1964, 15, 155-196.
52. R. A. Marcus, N. Sutin, Biochim. Biophys. Acta 1985, 811, 265-322.
53. D. B. Rorabacher, Chem. Rev., 2004, 104, 651-698.
54. B. J. Hathaway, Coord. Chem. Rev., 1981, 35, 211-252.
55. B. J. Hathaway, D. E. Billing, Coord. Chem. Rev., 1970, 5, 143-207.
56. J. M. Guss, H. D. Bartunik, H. C. Freemann, Acta Crystallogr. B 1992, 48, 790-811.
57. E. T. Adman, Adv. Protein Chem. 1991, 42, 145-197.
58. E. I. Solmon, R. G. Hadt, Coord. Chem. Rev., 2011, 255, 774-789.
59. E. I. Solmon, R. K. Szilgyi, S. D. George, L. Basumallick, Chem. Rev., 2004, 104, 419-458.
60. E. I. Solmon, L. B. LaCorix, D. W. Randal, Pure & Appl. Chem. 1998, 70, 799-808.
61. L. B. LaCroix, S. E. Shadle, Y. Wang, B. A. Averill, B. Hedeman, K. O. Hodgson, E. I. Solmon, J. Am. Chem. Soc., 1996, 118, 7755-7768.
62. F. Balu, Monatsh. Chem. 1889, 10, 375-388.
63. M. Brugnati, S. Caramori, S. Cazzanti, L. Marchini, R. Argazzi, C. A. Bignozzi, Int. J. Photo Eng., 2007 Article ID. 80756.
64. J. Cong, D. Kinschel, Q. Daniel, M. Safdar, E. Gabrielsson, H. Chen, P. H. Svensson, L. Sunce, L. Kloo, J. Mater. Chem. A, 2016, 4, 14550-14554.
65. Y. Saygili, M. Söderberg, N. Pellet, F. Giordano, M. L. Giribabu, M. Chandrasekharam, M. Grätzel, Nature Chemistry, 2014, 6, 242-247.
66. B. J. Hathaway, D. E. Billing, Coord. Chem. Rev., 1970, 5, 143-207.
67. J. V. S. Krishna, J. V. S. Krishna, S. P. Singh, L. Giribabu, M. Chandrasekharam, M. Grätzel, Nature Chemistry, 2014, 6, 242-247.
68. N. V. Krishna, J. V. S. Krishna, S. P. Singh, L. Giribabu, M. Chandrasekharam, M. Grätzel, Nature Chemistry, 2014, 6, 242-247.
69. Y. Wang, T. W. Hamann, Chem. Commun., 2018, 54, 12361-12364.
70. Y. Saygili, M. Stojanovic, H. Michaels, J. Tiepel, J. Teuscher, A. Massaro, M. Pavone, F. Giordano, S. M.
