

Polypyridyl copper complexes as dye sensitizer and redox mediator for dye-sensitized solar cells

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ABSTRACT

Developments on the application of polypyridyl-based copper complexes in dye-sensitized solar cells (DSSCs) are briefly discussed in this mini review. Copper complexes in solar cells are special in that they can be used either as dye sensitizer and/or as redox mediator (redox couple) in dye-sensitized solar cells (DSSCs). Both the abundance and low cost of copper motivates research on the use of copper complexes, as cheaper and non-toxic alternative to the mostly used iodide/triiodide (I^-/I_3^-) electrolyte redox couple, and the expensive and rare ruthenium-based dyes of good performance, which currently are best known.

1. Introduction

Dye-Sensitized Solar Cell (DSSC), invented in 1988 by O'Regan and Grätzel [1], is a low-cost solar cell working under a wide range of light conditions, including low light conditions. DSSCs convert light energy into electricity. The name originated from the fact that a dye is the component of the solar cell responsible for the maximum absorption of the incident light. The three basic components of a DSSC are the dye-sensitized conducting photoanode, the redox electrolyte and counter electrode or cathode. The functionality of a DSSC is based on the following steps: light absorption by the dye, electron injection from the electronically excited dye into the conduction band (CB) of the photoanode (e.g. semi-conductor TiO_2), the collection of charge, flow of electrons through the external circuit to the counter electrode (cathode) and into the redox electrolyte (e.g. I^-/I_3^-). The redox system of the electrolyte transports the electrons back to the dye molecules and regenerates the oxidized dye by reducing the dye-molecule, see Fig. 1.

The role of the redox mediator (electrolyte) is to transport charges between the electrodes and to regenerate the oxidized dye. Electrolytes used in DSSCs can be in the liquid, quasi-solid or solid states. The use of liquid electrolytes, such as the I^-/I_3^- redox couple, leads to leakage and corrosion of the solar cells and degradation of the dyes. Metal complexes as replacement of the liquid I^-/I_3^- redox couple, have been found to be a good alternative, due to their reversible one-step oxidation and reduction processes [2]. Studies on copper(II/I) complexes as redox mediators and hole conductors have shown surprisingly high performance under

low light conditions [3]. In Section 2 the development of polypyridyl-based copper redox mediators is discussed.

The role of the dye sensitizer at the photoanode is for light harvesting and charge injection. The dye molecules are adsorbed onto a mesoporous TiO_2 film on the anode. Both organic and inorganic-based dyes are used as dye sensitizer. Ruthenium and osmium complex sensitizers have been well tested in the past and are best known [4]. The rarity and high cost of ruthenium has led to the development of many novel cheaper dyes. Copper, as an abundant and nontoxic non-noble metal, is now considered as a good substitute for the expensive ruthenium in DSSCs [5]. In Section 3 the development of polypyridyl-based copper dye sensitizers is discussed.

In DSSCs the driving force of electron injection (ΔG_{inject}) and dye regeneration ($\Delta G_{\text{regenerate}}$) is evaluated by comparing the computed highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) of the dyes with the potential of the CB of the TiO_2 semi-conductor ($E_{\text{CB}} = -4.0$ eV vs vacuum, or -0.5 eV vs NHE [6]) and with the potential of the most widely used electrolyte redox couple I^-/I_3^- (-4.8 eV vs vacuum, or 0.3 eV vs NHE [7]), respectively. More negative HOMO energies than the I^-/I_3^- redox couple imply a fast regeneration of the oxidized dyes. More positive LUMO energies than the E_{CB} of TiO_2 could ensure an effective injection of excited electrons [8], see Fig. 2. The application of the ΔG_{inject} and $\Delta G_{\text{regenerate}}$ driving force is important in both experimental and theoretical studies of redox mediators and dye sensitizers, in determining possible candidates for DSSCs.

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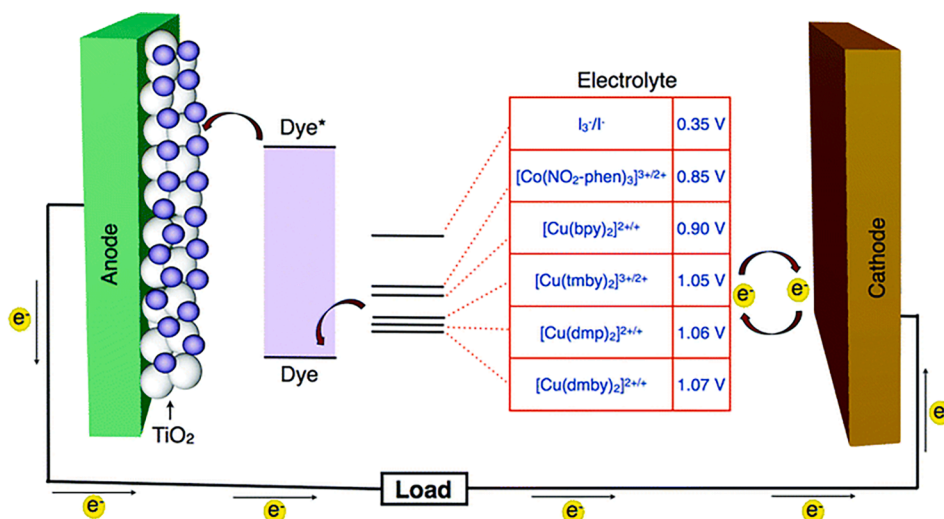


Fig. 1. Schematic energy level diagram of a DSSC, showing the basic operation of a Grätzel cell. The voltage output generated by different redox couples or electrolytes is listed. Reproduced from Ref. [2] with permission from the Royal Society of Chemistry.

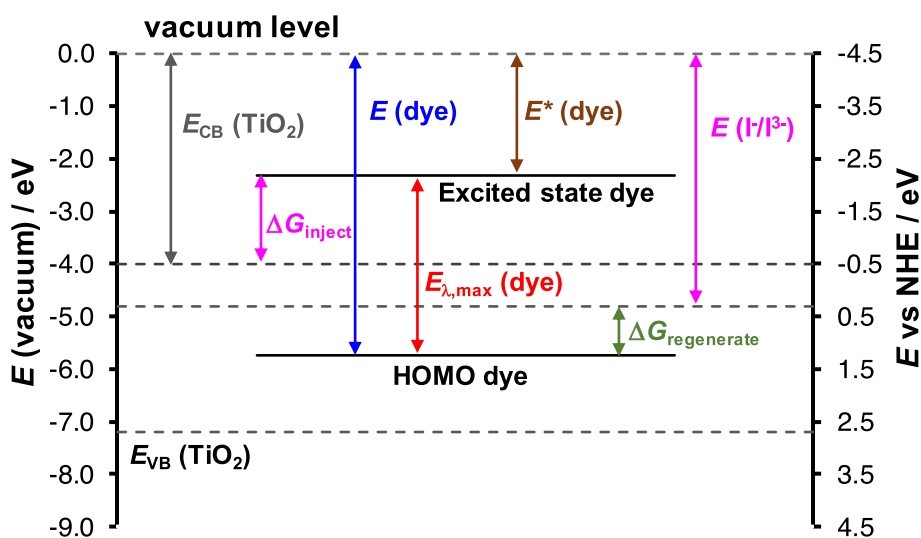


Fig. 2. Energy levels of a dye-sensitized solar cell, DSSC [9], where E_{CB} is the conduction band potential and E_{VB} the valence band potential of the TiO_2 semiconductor, ΔG_{inject} is the driving force of electron injection, and $\Delta G_{\text{regenerate}}$ of dye regeneration.

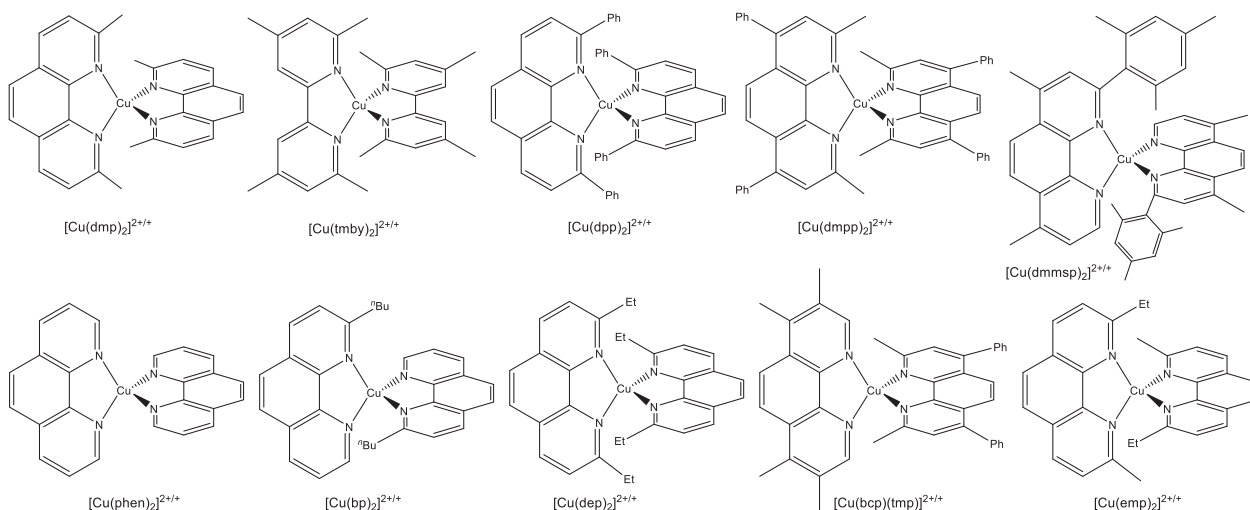


Fig. 3. Structures of selected homoleptic Cu-polypyridyl complexes reported in literature [10,16,17,20–22], used as redox mediators (electrolytes) in DSSCs.

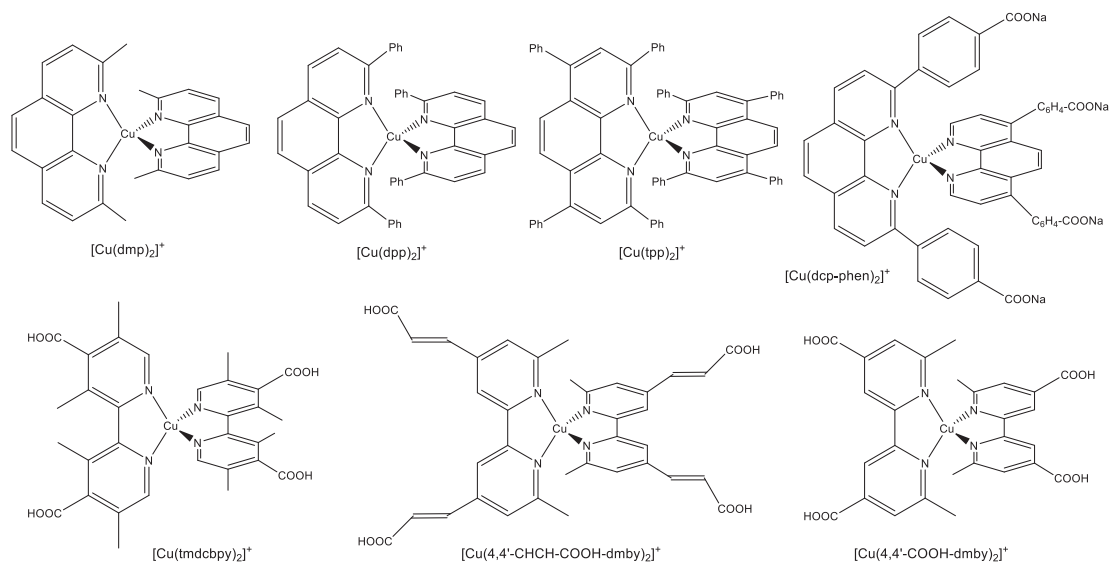


Fig. 4. Structures of selected homoleptic Cu-polypyridyl complexes reported [23–27] as dyes in DSSCs.

2. Polypyridyl copper complexes as redox mediator – Experimental results

The first experimental report on using polypyridyl copper complexes as redox mediator to replace the conventional I^-/I_3^- redox couple in DSSC, was a study by Fukuzumi et al. [10] in 2005, on redox couples $[Cu(dmp)_2]^{2+/+}$ and $[Cu(phen)_2]^{2+/+}$ (see Fig. 3 for structures). Although a lower power conversion efficiency (PCE) was obtained compared to the I^-/I_3^- electrolyte, a higher open-circuit voltage (V_{oc}) of the cell has been attained than compared to I^-/I_3^- . Complexes with a smaller structural change between the copper(I) and copper(II) molecules, result in better electron-transport since less energy is dissipated by geometry rearrangement. The coordination geometry of the molecule is dependent on the oxidation state of the metal. Copper(I) is generally characterized by

a pseudo tetrahedral coordination, while oxidation to copper(II) leads to a flattening of the geometry to compressed (flattened) tetrahedral, nearing a square planar geometry [11,12]. The change in oxidation state during redox reactions leads to loss of efficiency of the whole DSSC system, since a certain amount of energy is required for the reorganization of the coordination sphere of copper(I) [13]. It has been found that bulky ortho substituents on the polypyridyl ligands, fix the geometry in an intermediate situation between tetrahedral and tetragonal, leading to less dissipation and better efficiency of the DSSC [10,13,14].

Since the first report, the application of different polypyridyl copper complexes as redox mediator have been studied (Fig. 3 for selected structures) by different groups: for excellent reviews, see [2,4,13].

In 2015, researchers Freitag et al. were the first group to publish a study on solid-state dye-sensitized solar cells (ssDSSC), using electrolyte

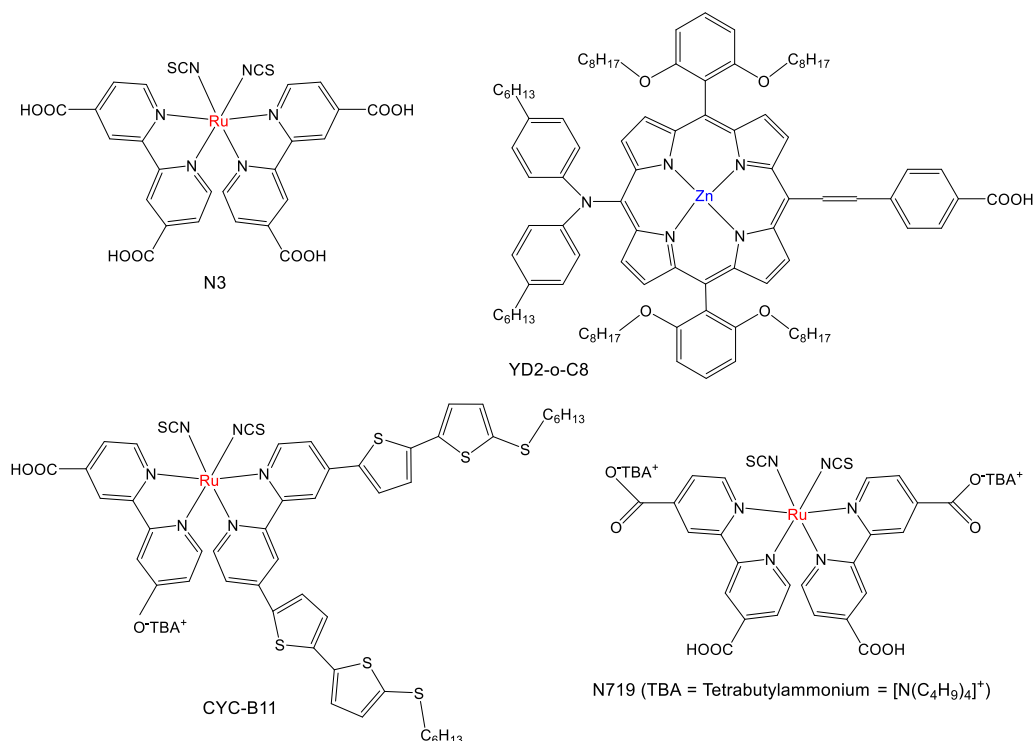


Fig. 5. Structures of well-known efficient Ru [45–47] and Zn [48,49] dyes used in DSSCs.

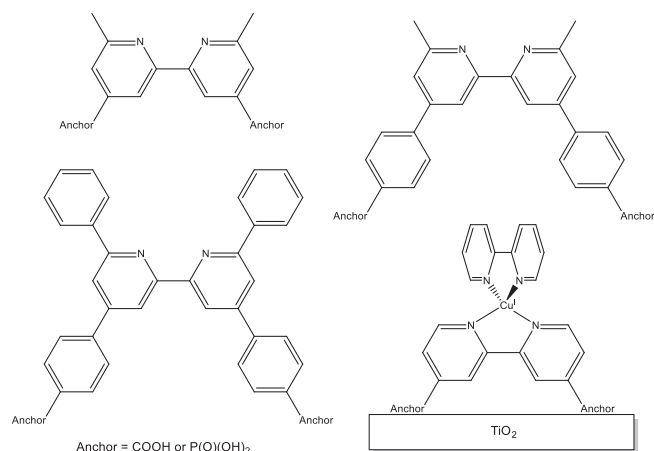


Fig. 6. Structures of three selected anchoring ligands, as well as complex $[\text{Cu}(\text{L})(\text{L}_{\text{anchor}})]^+$ anchored onto semi-conductor TiO_2 in DSSCs [29,31].

$\text{Cu}(\text{dmp})_2$ as hole transport material (HTM) between the photoanode and cathode [15]. To make a ssDSSC initially was like liquid-injecting a DSSC with HTM, but instead of sealing the cell after electrolyte injection, the solvent was evaporated into the air and new injections were performed, until the space between the photoanode and the counter electrode was filled with solid HTM. Development of very high performing ssDSSCs followed, based on research using $\text{Cu}(\text{tmby})_2$ as HTM [16,17]. That study has found that by using Cu complexes, a driving force of about 0.1 eV is sufficient for efficient dye regeneration by the HTM [18]. Enhanced efficiency has been obtained by co-sensitization of different sensitizers [19]. The introduction of bulky groups either at position C2 and/or C9 of the phenanthroline ligand, such as in electrolytes $\text{Cu}(\text{dmp})_2$, $\text{Cu}(\text{dmp})_2$ and $\text{Cu}(\text{dmmp})_2$, is effective in reducing dark current (residual electric current flowing when there is no incident light) by minimizing the recombination process, leading to higher efficiencies [20]. Complexes with groups exhibiting larger steric hindrance, such as electrolytes $\text{Cu}(\text{emp})_2$ and $\text{Cu}(\text{dep})_2$, showed more positive redox potentials, when compared to $\text{Cu}(\text{dmp})_2$ and $\text{Cu}(\text{bp})_2$ [21]. The redox potential of a redox couple should be higher than E_{HOMO} of the sensitizer,

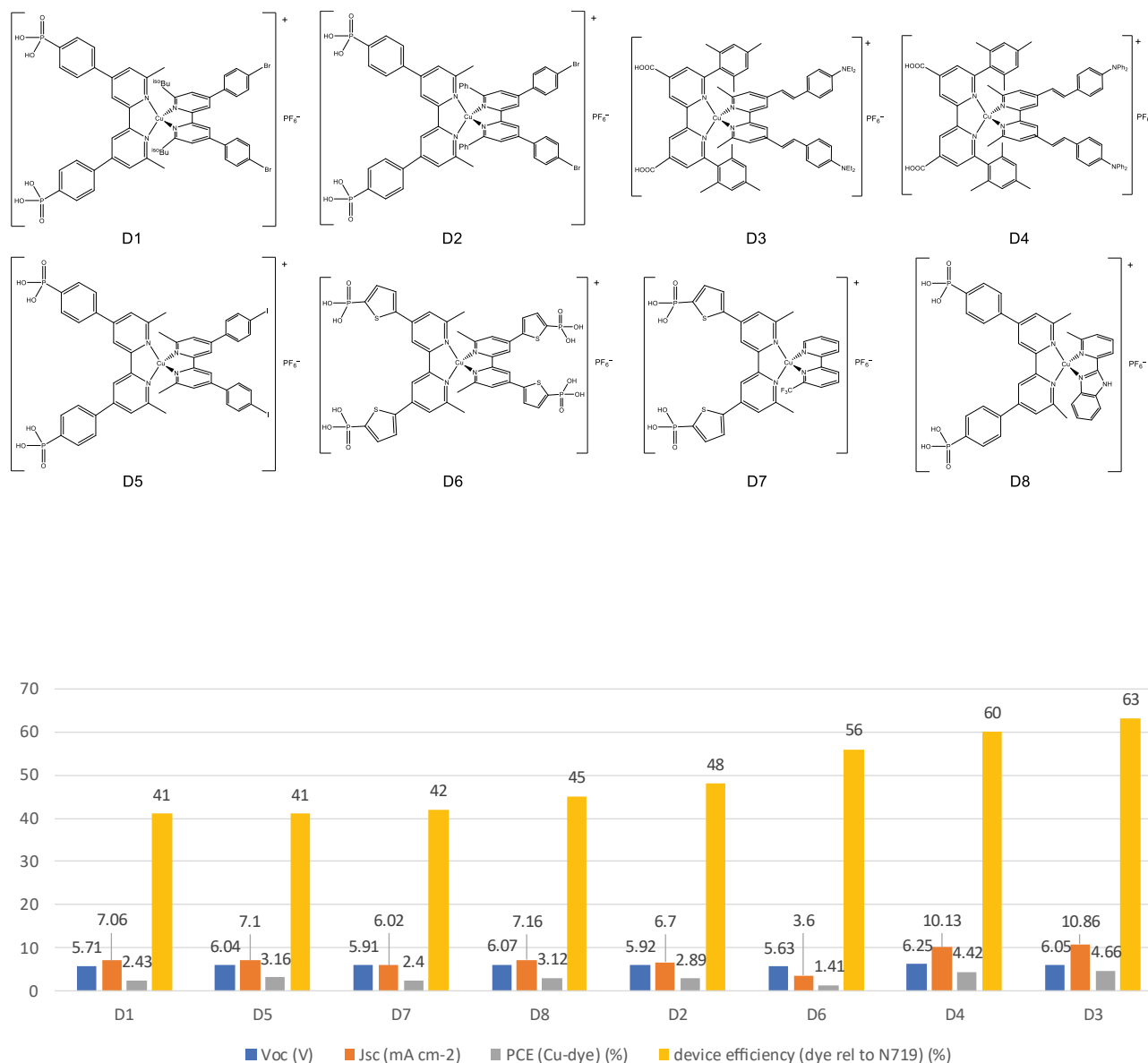


Fig. 7. Selected complexes reported as dye sensitizers in literature, with device efficiency $\eta_{\text{rel}} > 40\%$: namely homoleptic dye D6 [37], and heteroleptic dyes D1, D2 [31], D3, D4 [32], D5 [36], D7 [38] and D8 [39].

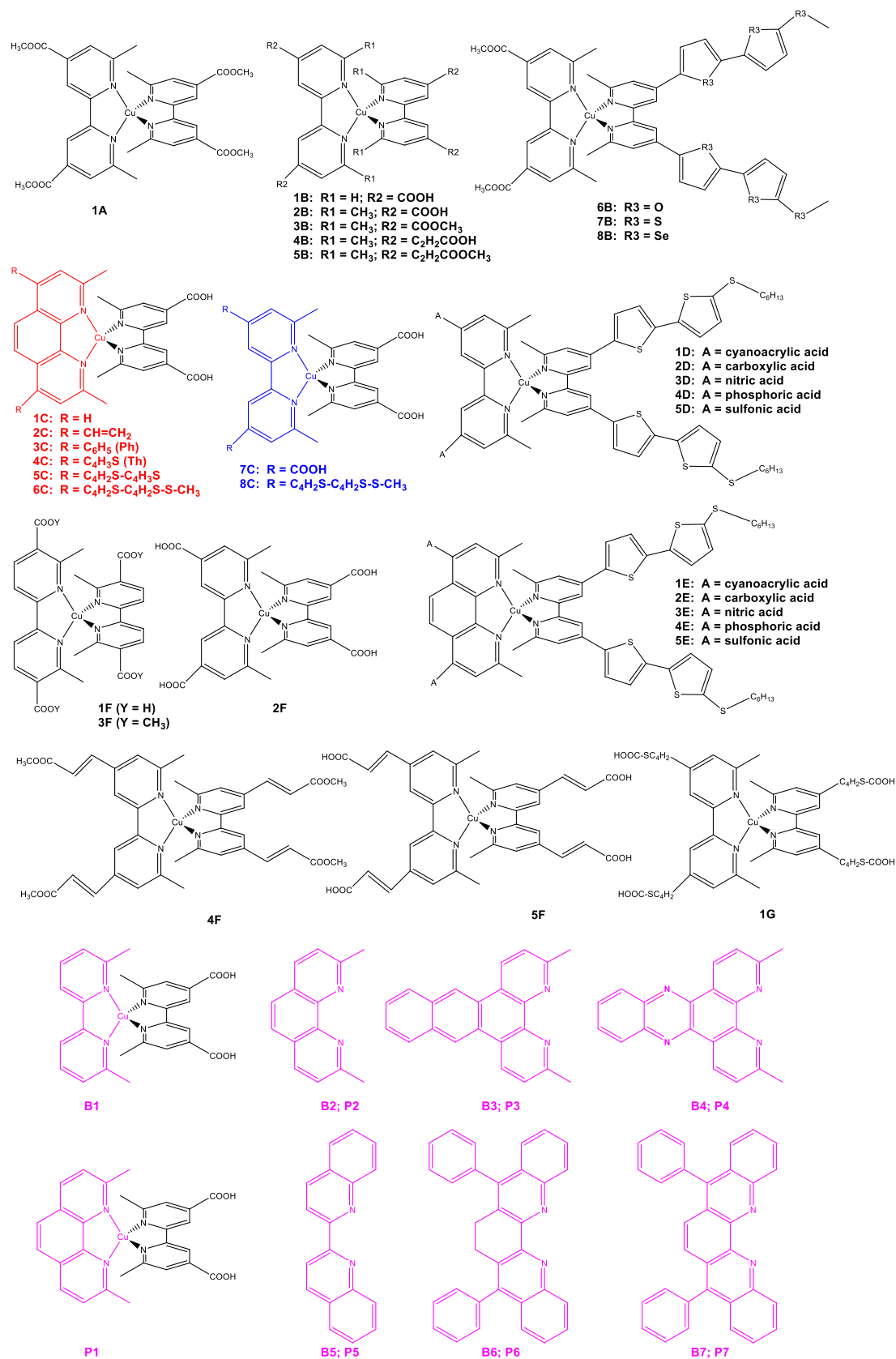


Fig. 8. Structures of various Cu(I)-polypyridyl complexes used as dye sensitizers [5,37,54–58], as studied theoretically by DFT computations.

in order to provide the required driving force for dye regeneration (Fig. 2). A more positive redox potential of a redox couple with respect to the E_{HOMO} level of the sensitizer, will lead to less energy loss during dye regeneration [2].

Further, in addition to the mentioned homoleptic polypyridyl copper complexes, where all ligands are identical, it has been found that both the absorption and redox properties of many heteroleptic complexes (e. g. $\text{Cu}(\text{bcp})(\text{tmp})$) are also very attractive for DSSC applications [22].

3. Polypyridyl copper complexes as dye sensitizer – Experimental results

Probably the first mentioning of the sensitization effect of polypyridyl copper(I) complexes in photochemical systems, was in 1983 on $[\text{Cu}(\text{dmp})_2]^+$, $[\text{Cu}(\text{dpp})_2]^+$ and $[\text{Cu}(\text{tpp})_2]^+$ complexes (see Fig. 4 for structures) [23], covering a large fraction of the solar spectrum. Then in 1994 Sauvage and co-workers investigated $[\text{Cu}(\text{dcp-phen})_2]^+$ as dye in a TiO_2 solar cell, although the obtained photocurrents and photovoltages were much smaller than those of the Grätzel cell itself [24]. The dye is the component of DSSCs responsible for the maximum absorption of the incident light. Therefore, in 2002 a new copper(I) dye $[\text{Cu}(\text{tmdcbpy})_2]^+$ with higher photoresponse was successfully used in a DSSC, with 30% IPCE (incident monochromatic photon-to-current conversion efficiency) [25]. Further, introduction of anchoring ligands, by adding carboxylate groups in the $[\text{Cu}(4,4'\text{-COOH-dmby})_2]^+$ and $[\text{Cu}(4,4'\text{-CHCH-COOH-dmby})_2]^+$ dyes, has led to effective bonding or anchoring of these homoleptic dyes to the TiO_2 nanoparticles of the semi-conductor. However, the efficiency of these homoleptic Cu(I) dyes (IPCE values 38.6 and 50.1%) were over 4 times lower than that of the N719 ruthenium sensitizer (Fig. 5), although the cost of copper(I) sensitizers is an order of magnitude lower than Ru [26,27]. Due to the rarity of ruthenium, research on the application of copper(I)-polypyridyl as dyes in DSSCs has continued [28].

Subsequently, ligand exchange reactions between various $[\text{CuL}_2]^+$ complexes (L = substituted bipyridine) and TiO_2 -anchored bipyridine-based ligands, containing CO_2H or $\text{PO}(\text{OH})_2$ anchoring groups, were applied to the dyes. This produced surface-anchored heteroleptic copper(I) complexes, $[\text{Cu}(\text{L})(\text{L}_{\text{anchor}})]^+$ (Fig. 6), with increased efficiencies [29–32] compared to homoleptic Cu(I) dyes. In heteroleptic dyes, one ligand (L_{anchor}) carries a group effective for anchoring the dye to the TiO_2 semiconductor, while the second ligand (L) can be electronically and structurally tuned to enhance electron transfer from electrolyte to dye, by adding appropriate substituents [33]. Incorporation of extended π -conjugation in substituted bipyridine as ligand (L), enhances dye performance of $[\text{Cu}(\text{L})(\text{L}_{\text{anchor}})]^+$ [29,30,34]. Introduction of an aromatic spacer into the phosphonic acid anchoring ligand, has led to increased photon-to-current conversion of the heteroleptic dyes, with IPCE up to 48.5%, compared to the standard high performance ruthenium dye N719 (100%) [31]. An advantage of heteroleptic complexes is the possibility to finely adjust their opto-electronic properties more accurately than for homoleptic complexes [35]. Heteroleptic dyes (such as D1 – D5, D7 – D8 in Fig. 7, as obtained from literature) generally lead to enhanced conversion efficiencies compared to homoleptic dyes (D6).

Some important measurements used to characterize the effectiveness of dyes used as sensitizers in DSSCs, include the PCE, short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), device efficiency (η_{ext}) and percentage device efficiency ($\eta_{\text{rel}} = \text{PCE}/\text{PCE}_{\text{ref}} \times 100\%$). Fig. 7 shows selected polypyridyl-based copper complexes from literature, with $\eta_{\text{N719}} > 40\%$ [31,32,36–39], where device efficiency is measured relative to the standard ruthenium dye molecule. More data on these heteroleptic dyes is found in references [26,35,40–43]. The synthesis and characterization of these different dye complexes are described in the references provided. The DSSC fabrication (for testing of solar cell application) is generally based on the method of Grätzel and co-workers [44].

4. Copper(I) dye coupled with a copper(I)/(II) electron shuttle – Experimental results

The combination of copper(I)-based dyes and $[\text{Cu}(\text{bpy})_3]^{2+/3+}$ type electrolytes, called electron shuttles, has been an important step towards the development of stable iodide-free copper(I) solar cells [34,50,51]. High power conversion efficiencies have been obtained with full-copper DSSCs, in which a heteroleptic copper(I) dye (bearing one 2,9-dimesityl-1,10-phenanthroline ligand, together with a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid as anchoring ligand, to anchor the dye onto the TiO_2 semi-conductor surface) was coupled with a copper(I)/(II) electron shuttle [52]. Electron shuttles are redox mediators that can reversibly be oxidized and reduced, thereby repeatedly serving as electron carriers. By using heteroleptic bis(diimine)copper(I) dyes, coupled with homoleptic bis(diimine)copper(I)/(II) redox shuttles, photoconversion efficiencies up to 2.06% (38.1% relative to the standard ruthenium N719 dye, set at 100%) have been obtained. The best efficiency was obtained when using phosphonic acid as anchor ligand and 4,4'-dimethoxy-6,6'-dimethyl-2,2'-bipyridine as the ancillary ligand in the dye, together with two 4,4'-dimethoxy-6,6'-dimethyl-2,2'-bipyridine ligands in the electrolyte [53].

5. Polypyridyl copper complexes – Theoretical studies

The suitability and performance of dyes for effective DSSC application can also be computed by theoretical density functional theory (DFT) calculations. During such theoretical studies, computed properties of the dyes, such as frontier orbitals, UV-vis absorbance spectrum, charge transfer characteristics, the driving force of electron injection (ΔG_{inject}) and dye regeneration ($\Delta G_{\text{regenerate}}$), light harvesting efficiency (LHE) and the excited-state lifetime (τ), are reported [5,54–58]. E_{HOMO} and E_{LUMO} are of importance, see Fig. 2. DFT studies have found that different oxidation states of the redox mediator result in different geometries: for example the geometry of reduced $[\text{Cu}(\text{bpy})_2]^{1+}$ is four-coordinate pseudo tetrahedral, while the geometry of oxidized $[\text{Cu}(\text{bpy})_2]^{2+}$ is four-coordinate compressed (flattened) tetrahedral [12].

In 2010, a comprehensive DFT study on the polypyridyl copper(I) complexes $[\text{CuL}_2]^+$ and $[\text{CuL}_2][\text{PF}_6]$ (with L = 6,6'-dimethyl-2,2'-bipyridine-4,4'-dimethylformate) was published (see structures 1A and 1A[PF₆] in Fig. 8). The electronic structures and spectral properties of these homoleptic Cu(I) complexes, both in the gas phase and in methyl cyanide (MeCN) solution, were investigated on the B3LYP/6-31G(d) and B3LYP/DZVP levels of theory [54]. Results indicate that the five HOMOs are Cu-3d based orbitals, whereas the four LUMOs are the bipyridine ligand π^* orbitals. The maxima of the UV/vis spectra in the range of 400–600 nm have been found to originate from metal-to-ligand charge-transfer (MLCT) transitions. These results indicate that the copper-based complexes might be effective sensitizers for a next-generation dye-sensitized solar cell. In 2011 the same authors followed up on this study by a DFT computational study (at B3LYP/6-31G* level of theory), on a series of eight polypyridyl Cu(I)-based complexes with general formula $[\text{CuLL}']^+$ (where L and L' represent heteroleptic bipyridyl ligands) (see structures 1B – 8B in Fig. 8), as well as on two experimentally well-known Ru(II) sensitizers, N3 and CYC-B11 (see structures in Fig. 5). Compared with the efficient well-known Ru(II) sensitizers, these heteroleptic polypyridyl Cu(I)-based complexes under study exhibited similar optical properties, but an improving trend of photoresponse and DSSC performance [55].

The same group of authors continued to publish further theoretical studies on a variety of polypyridyl Cu(I)-based dye-sensitizer complexes, namely: Cu(I)-based sensitizers, containing 6,6'-dimethyl-4,4'-dicarboxylate-2,2'-bipyridine with functionalized 2,9-dimethyl-1,10-phenanthroline ligands (at B3LYP/DZVP level, in CH_2Cl_2 solution) (see structures 1C – 8C in Fig. 8) [56]; a series of 14 heteroleptic Cu(I) complexes integrating dicarboxylic acid dimethyl bipyridine/phenanthroline with functionalized chromophores (B3LYP/6-31G(d) + DZVP basis set, in CH_2Cl_2 solution) (see structures B1–B7 and P1–P7 in Fig. 8)

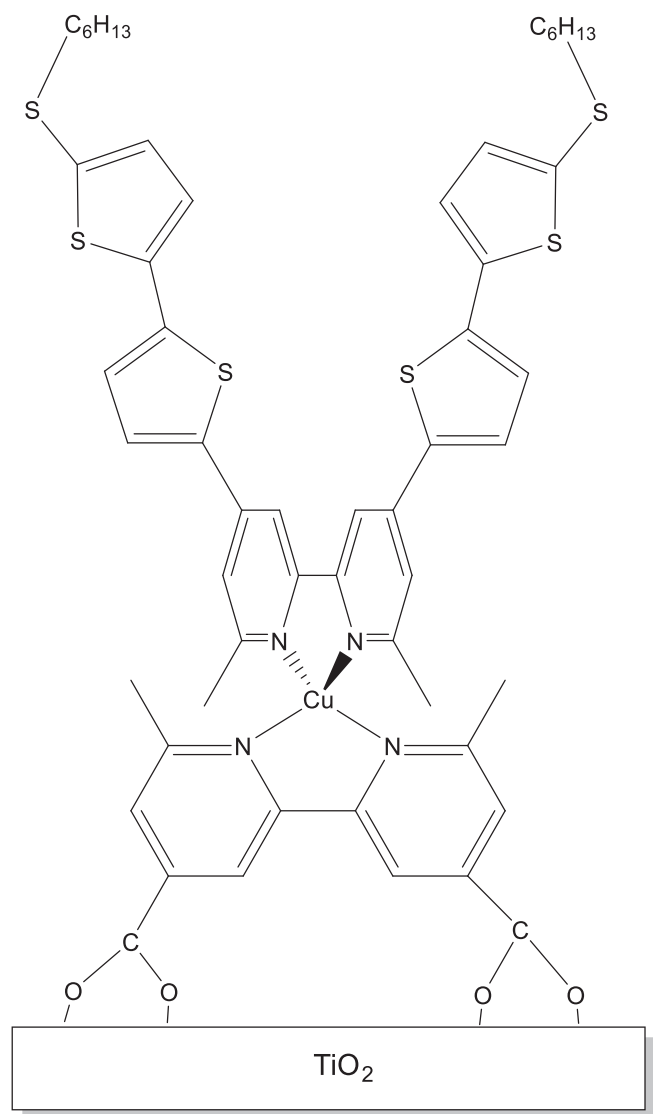


Fig. 9. Structure of the dye(B2)/(TiO₂)₃₈ system, anchored onto the anatase TiO₂ semi-conductor [5].

[57]; and two groups of heteroleptic Cu(I) based dyes with different anchoring groups, based on substituted bipyridine and 2,9-dimethyl-1,10-phenanthroline ligands (B3LYP/6-31G(d) + DZVP basis set, in CH₂Cl₂ solution) (see structures 1D–5D and 1E–5E in Fig. 8) [5]. The latter study included DFT calculations on the dyes, adsorbed onto the anatase mineral form of TiO₂ (101) surface, namely computations on dye/(TiO₂)₃₈ systems [5], see example in Fig. 9. A further study on five homoleptic molecular systems of the type [CuL₂]⁺, with differently substituted bipyridine ligands (computed at the M06/LANL2DZ + DZVP level of theory) (see structures 1F–5F in Fig. 8) [58], which are to be used as sensitizers in dye-sensitized solar cells, suggested potential applications for these copper complexes in photovoltaic devices.

These theoretical studies also produced simulated UV/vis spectra [58,59], with an analysis of the orbitals involved in the important electronic transitions relating to the absorbance maxima. These confirmed MLCT bands [43,58], ILCT (intra-ligand charge transfer) transitions [59], as well as whether ligand-based oxidation [59] or Cu(I/II) oxidation [37] occurs first. In the case of surface-anchored heteroleptic copper(I) complexes, for the sake of efficient electron injection, the LUMOs should be localized on the anchoring domain of the dye [32,36].

A combined experimental and theoretical DFT study demonstrated,

that incorporation of thiophene motifs into the ligands of these copper(I) complexes (structure 1G in Fig. 8) for use as dyes in DSSCs, has led to a bathochromic shift of the MLCT absorbance. Thiophene further also has led to an increase in the computed HOMO energy level and an increase in efficiency compared to the related complex lacking the thiophenes (structure 2F in Fig. 8) [37]. E_{HOMO} and E_{LUMO} of many of these polypyridyl copper complexes compared favourably with the potential of the TiO₂ semi-conductor CB and the potential of the electrolyte I[−]/I₃[−] redox couple [5,55–58] (Fig. 2).

Light harvesting efficiency (LHE), defined as the fraction of light intensity absorbed by the dye at a certain wavelength, was calculated in some of the above studies [55–57]. For a good PCE, the LHE of the dye should be as high as possible. The relative LHE (RLHE) of different copper(I) dyes, relative to the well-known N3 Ru(II) sensitizer, has varied as follows: Variation between 1.00 and 1.44 for the heteroleptic [CuLL']⁺ sensitizers (with L and L' = bipyridyl ligands, see structures 1B–8B in Fig. 8) [55], and variation of 1.00–1.79 for the Cu(I)-based sensitizers containing 6,6'-dimethyl-4,4'-dicarboxylate-2,2'-bipyridine, with functionalized 2,9-dimethyl-1,10-phenanthroline ligands (see structures 1C–8C in Fig. 8) [56].

A dye with longer lifetime in the excited state is expected to be more facile for electron injection into the CB of the semiconductor. The reported calculated excited state lifetime (τ) was computed for two groups of heteroleptic Cu(I) based dyes with different anchoring groups, based on substituted bipyridine and 2,9-dimethyl-1,10-phenanthroline ligands (structures 1D–5D and 1E–5E in Fig. 8). The excited lifetime (τ values) of these Cu(I) dyes were at the nanosecond timescale, between 2.5 and 6.5 ns [5]. This τ value is similar to $\tau = 11.7$ ns [8], calculated for the well-known Zn-based sensitizer YD2-o-C8 (Fig. 5), which is an experimentally efficient Zn-porphyrin based sensitizer [49].

6. Conclusions

A vast amount of experimental research has been done over the past 30 years in optimizing the different parts of DSSCs. The main importance has been to find cost-effective functional materials that can be produced economically under environmentally friendly conditions. Theoretical computational studies assisted in the interpretation of experimental results, as well as in the screening and prediction of new dyes and redox couples with improved performance, for implementation in the next-generation DSSCs. Experimental studies have shown that copper complexes are excellent alternative redox mediators to the currently used expensive iodide/triiodide redox couple. Copper complexes have shown good performance even at very low lighting conditions and can be combined with copper dyes to produce eco-sustainable, iodide-free, low-cost DSSCs soon.

CRediT authorship contribution statement

Jeanet Conradie: Conceptualization, Resources, Validation, Methodology, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Ethics statement

This work does not require any ethical statement.

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