

Towards Sustainable Dyes for Dye-Sensitized Solar Cells

Ana Hernandez Rendondo[§], Edwin C. Constable^{*}, and Catherine E. Housecroft

[§]SCS Poster Prize Winner

Abstract: Dye-sensitized solar cells (DSCs) are an emerging technology for the conversion of solar photons to electrical energy. Typical DSCs are based upon ruthenium complexes which act as photosensitizers for a wide band-gap semiconductor such as titanium dioxide. The low abundance of ruthenium raises issues about the sustainability of such devices. We now present promising prototype DSCs based upon copper(I) complexes.

Keywords: Copper(I) complexes · Dye-sensitized solar cells

Dye-sensitized solar cells (DSCs) are intensively investigated devices for the conversion of solar-derived photons into electrical energy. The nanostructured DSC introduced by Graetzel and O'Regan^[1] consists of a thin film of nanoparticles of a wide-band gap semiconductor (usually TiO_2) functionalized with a coloured material that has a ground state below, and an excited state above, the conduction band (Fig. 1). It is thus possible to inject photons into the conduction band of the semiconductor with photons of an energy corresponding to the absorption of the dye sensitizer rather than that of the semiconductor band-gap. Following the first report of dye-sensitisation of a semiconductor,^[2] the most common dyes have been ruthenium(II) oligopyridine complexes.^[3] After injection of an electron into the semiconductor, the oxidized dye molecule is returned to the ground state by reaction with a reducing agent (most commonly iodide). The oxidized form of the reducing agent (triiodide ion in the case of iodide as reductant) is then reduced at the counter-electrode by an electron previously released by the dye and coming through the outer circuit, thus closing the circuit.

The dye sensitizer has a number of critical features:

- i) the HOMO-LUMO gap must span the lower level of the conduction band of the semi-conductor;

- ii) the absorption should allow collection of as many solar photons as possible across the entire spectrum;
- iii) the molecule should have some functionality for covalent attachment to the semi-conductor to optimise electron-injection efficiency;
- iv) the molecule should be stable in contact with the chosen redox couple and
- v) the dye and redox couple should be chosen to optimise the open-circuit voltage V_{oc} .

Although ruthenium(II) oligopyridine complexes exhibit many of the desired properties, there are a number of significant disadvantages. Ruthenium is certainly an expensive metal (3,000 US\$ kg^{-1} as of 13.01.2009) but more importantly, it is relatively rare (approximately

1 ppb by weight in the Earth's crust). In view of these constraints, we have been involved in the search for alternative dye-sensitizers which have either lower cost or greater sustainability. Although organic dye-sensitizers are beginning to emerge as candidates, in many cases metal-containing species have advantages in terms of long-term and thermal stability under the typical operating conditions of a DSC.

It has been known since the pioneering work of McMillin,^[4] that the photo-physical properties of copper(I) $[\text{CuL}_2]^+$ species, where L are bpy (2,2'-bipyridine) or phen (1,10-phenanthroline) derivatives (Fig. 2), are similar to those of the archetypal $[\text{Ru}(\text{bpy})_3]^{2+}$ dye sensitizers.^[5] Copper-based dyes have a number of ad-

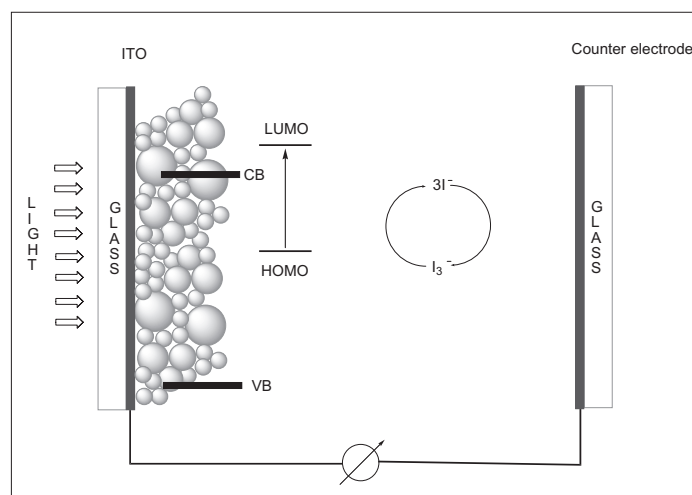


Fig. 1. Schematic representation of the DSC. The semiconductor nanoparticles surface-functionalised with a dye-sensitizer form a layer at a conducting glass electrode (in this case indium tin oxide, ITO). The dye has a HOMO-LUMO gap that straddles the conduction band lower edge of the semiconductor. After absorption of light, the oxidised dye molecule is reduced by iodide, and the resultant triiodide is subsequently reduced at the counter electrode after work has been taken out of the system.

^{*}Correspondence: Prof. Dr. E. C. Constable
University of Basel
Department of Chemistry
Spitalstrasse 51
CH-4056 Basel
Tel.: +41 61 267 1001
Fax: +41 61 267 1005
E-mail: edwin.constable@unibas.ch

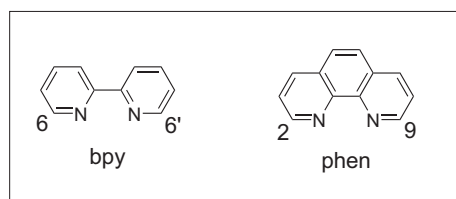


Fig. 2.

vantages in terms of price (3 US\$ kg⁻¹ as of 13.01.2009) and sustainability (approximately 68,000 ppb by weight in the Earth's crust). Accordingly, we have commenced a programme assessing copper(I) complexes as dye-sensitizers. A number of structural constraints need to be applied to the ligands. Firstly, it is usually necessary to incorporate substituents at the 6- and 6'-positions of the bpy (or the 2- and 9-positions of the phen) ligands to confer long-term stability in aerobic conditions.^[6] Our initial ligands of choice possess methyl substituents at these positions and the space-filling representation of the [Cu(6,6'-Me₂bpy)₂]⁺ cation in [Cu(6,6'-Me₂bpy)₂][PF₆]⁻ (Fig. 3a) demonstrates how efficiently the metal centre is screened from the environment.^[7]

The second chemical constraint is the need to introduce substituents to bind the complex to the semiconductor surface. A number of such anchoring groups have been developed for the ruthenium dyes, including carboxylic or phosphonic acids, and we selected carboxylic acids for our prototype dyes. Taking these structural constraints into consideration, we selected ligands **1** and **2** as our initial targets. These would allow us to test the concept of DSCs containing copper dyes and also to investigate the ease of tuning the absorption and device characteristics through ligand design, as the extended conjugation in **2** is expected to result in a red-shifting of the absorption, allowing the collection of lower energy photons. Ligand **1** was prepared using standard methods (Scheme) and the vinylogous analogue **2** was obtained from **1** by esterification, followed by sequential reduction to the alcohol, oxidation to the aldehyde and Wittig reaction with Ph₃P=CHCO₂Me to give the methyl ester of **2**, which was finally hydrolysed to the desired acid with LiOH.

The copper(I) complexes of **1** and **2** were prepared as deep red solids by the addition of copper(II) sulfate to aqueous solutions of the sodium salts of the acids, followed by reduction with ascorbic acid, using a method reported in the literature.^[8] The solid-state structure of the ester complex [Cu(6,6'-Me₂-4,4'-(CO₂Me)₂bpy][PF₆]⁻ was determined to confirm that the introduction of the carboxylate functionality had no unexpected effects upon the complex geometry and the [Cu(6,6'-Me₂-4,4'-(CO₂Me)₂bpy]⁺ cation is presented in Fig.

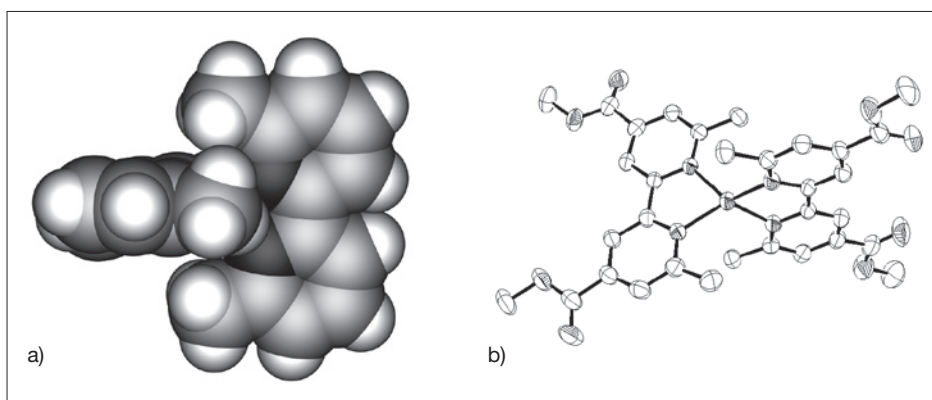
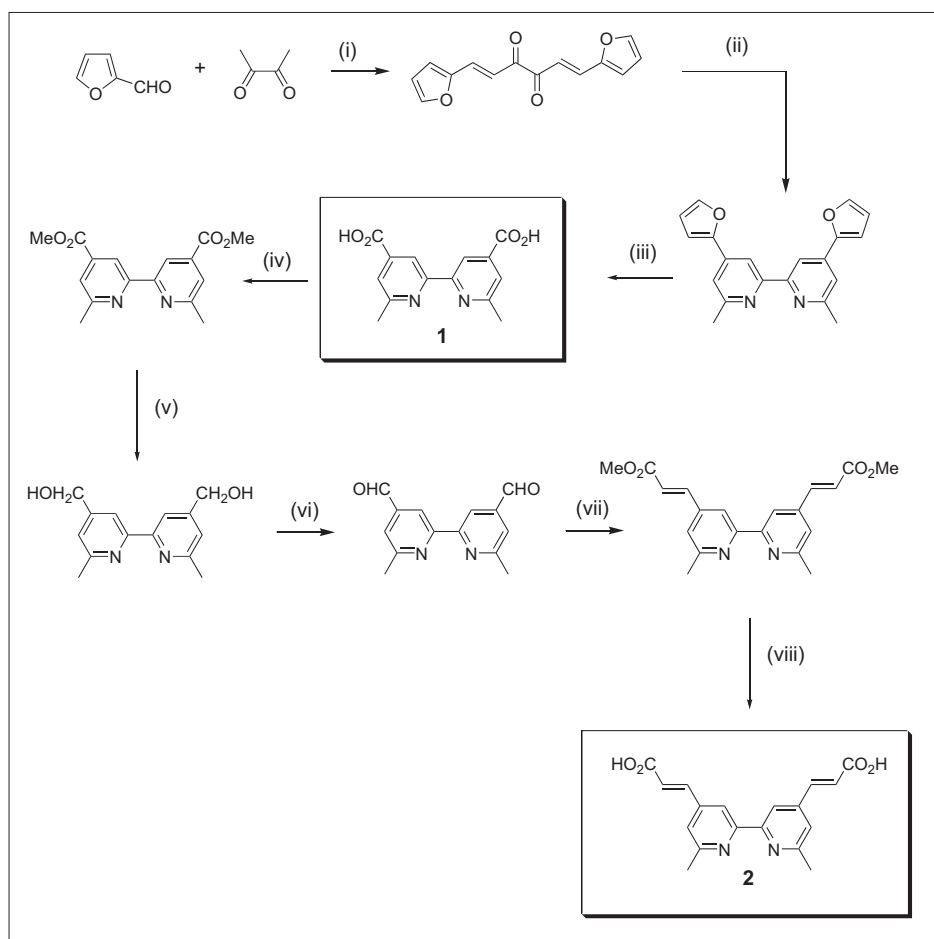


Fig. 3. (a) The [Cu(6,6'-Me₂bpy)₂]⁺ cation in [Cu(6,6'-Me₂bpy)₂][PF₆]⁻ with carbon atoms in grey and nitrogen in black demonstrating the role of the substituents in protecting the metal centre from the environment.^[7] (b) The [Cu(**1**)₂]⁺ cation in [Cu(**1**)₂][PF₆]⁻ demonstrating that the introduction of the carboxylate substituents has no gross geometrical consequences for the complex. Thermal ellipsoids are depicted at the 50% level and hydrogen atoms are omitted for clarity.



Scheme. Synthesis of ligands **1** and **2**. (i) EtOH, piperidine, room temp., 7 d, 12% (ii) MeOH, [CH₃COCH₂py]Cl, NH₄OAc, 12 h, reflux, 55% (iii) KMnO₄, *t*-BuOH, H₂O, 36% (iv) H₂SO₄, MeOH, 12 h, reflux, 70% (v) LiAlH₄, THF, -40°C to RT, 86% (vi) ClCOCOCl, CH₂Cl₂, DMSO, Et₃N, -60 °C to 0°C, 89% (vii) Ph₃P=CHCO₂Me, PhMe, 74% (viii) LiOH, THF, H₂O, 92%.

3b. As expected, the molar extinction coefficients for the more conjugated [Cu(**2**)₂]⁺ complexes are higher than for [Cu(**1**)₂]⁺, suggesting that the former dyes might be more efficient sensitizers.

DSCs were prepared using conventional methods on glass-ITO substrates modified with a TiO₂ nanoparticle surface. Full details are presented in the communication

reporting this work.^[9] The DSCs prepared using the prototype copper(I) dyes were surprisingly effective and Fig. 4 presents the I-V curves characterising these devices. The global efficiencies of the devices with **1** and **2** were 1.9 and 2.35% respectively. These should be compared to an efficiency for the state-of-the-art optimized dye N719 of 9.7% under the same conditions: we

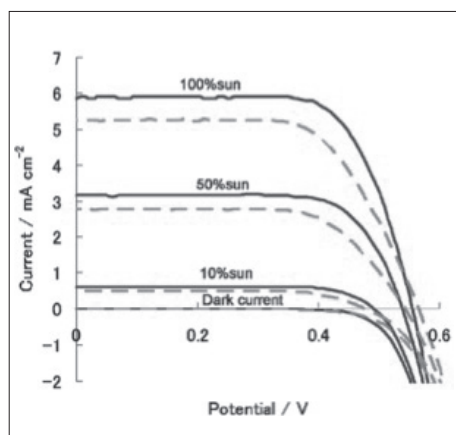


Fig. 4. Current-voltage curves for DSCs prepared using $[\text{Cu}(\mathbf{1})_2]^+$ (broken curves) and $[\text{Cu}(\mathbf{2})_2]^+$ (solid curves).^[9]

consider that these results are extremely optimistic for non-optimized prototype systems, bearing in mind that the first ruthenium dyes employed had similar efficiencies.^[1,3] The maximum incident photon to current efficiencies (IPCE) for the devices with $[\text{Cu}(\mathbf{1})_2]^+$ and $[\text{Cu}(\mathbf{2})_2]^+$ were 39 and 50% respectively, confirming the expectation that the extended conjugation would result in improved electron injection.

The devices are not as long-lived as those with ruthenium dyes, which we attribute to slow reaction with the electrolyte leading to the formation of copper(I) iodide. Further optimisation of the system will involve the replacement of the iodide/triiodide redox couple with a more benign redox couple. However, in parallel studies we can investigate the effect of the substituents and anchoring groups on the efficiency of the devices. In the final part of this report, we describe preliminary studies making use of the fundamentally different properties of ruthenium and copper(I) centres. Copper(I) complexes are labile and the exchange of ligands is rapid, in contrast to ruthenium(II) and ruthenium(III) complexes where the exchange is relatively to very slow. How can this be turned to an advantage?

To the best of our knowledge, there have been no studies of the exchange of ligands between copper(I) oligopyridine complexes, however, a simple example establishes its rapidity: Fig. 5 shows the methyl signals in the ^1H NMR spectrum of a CD_3CN solution of equimolar amounts of the complexes $[\text{Cu}(\mathbf{6,6'}\text{-Me}_2\text{bpy})_2][\text{PF}_6]$ and $[\text{Cu}(\mathbf{2,9}\text{-Me}_2\text{phen})_2][\text{PF}_6]$. Each of the individual complexes exhibits a single methyl signal, but within the time of mixing the observed equilibrium mixture exhibiting four methyl signals is observed, with the additional two signals arising from the heteroleptic species $[\text{Cu}(\mathbf{6,6'}\text{-Me}_2\text{bpy})(\mathbf{2,9}\text{-Me}_2\text{phen})]^+$.

Having established the rapid exchange of oligopyridine ligands at copper(I) centres, a new strategy emerges for the preparation of DSCs that cannot easily be

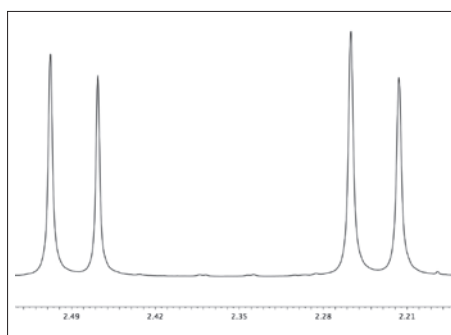


Fig. 5. The methyl signals in the 250 MHz ^1H NMR spectrum of a CD_3CN solution of equimolar amounts of $[\text{Cu}(\mathbf{6,6'}\text{-Me}_2\text{bpy})_2][\text{PF}_6]$ and $[\text{Cu}(\mathbf{2,9}\text{-Me}_2\text{phen})_2][\text{PF}_6]$. The four signals arise from a 1:2:1 statistical equilibrium mixture of the starting complexes and the heteroleptic species $[\text{Cu}(\mathbf{6,6'}\text{-Me}_2\text{bpy})(\mathbf{2,9}\text{-Me}_2\text{phen})]^+$.^[7]

achieved with kinetically inert ruthenium centres, namely the stepwise synthesis of the complex on the semiconductor surface. This strategy is illustrated in Fig. 6. The first step is the functionalisation of the surface with ligand **1** or **2** alone, followed by washing with a $[\text{CuL}_2]^+$ complex lacking anchoring groups. The surface-bound ligand behaves as an N_2 donor in exactly the same way as a solution species and equilibrates with the solution $[\text{CuL}_2]^+$ complex through ligand exchange. As the new surface bound complex is removed from the equilibrium, the process proceeds to complete surface coverage with the copper, as shown by the red colour observed at the surface. Naturally, the surface-bound species is now a heteroleptic complex, being anchored to the semiconductor by the carboxylate groups of **1** or **2** with the remaining coordination sites occupied by ligand **L**. Logically, **L** may be varied at will to optimise absorption or redox characteristics. Preliminary studies on solar cells constructed using this approach indicate that the tuning concept is indeed successful, but that the complexes only anchored through a single ligand are more sensitive

to attack by iodide, as shown in the long terms stability of the DSC. The ability to switch the ancillary ligands at will opens the intriguing possibility of constructing bespoke libraries of copper(I) dyes or of building self-regenerating DSCs.

The design of new types of DSC involves a close collaboration of inorganic, organic, materials and physical chemistry together with microengineers. In this short report, we have described how simple concepts in coordination chemistry have been used to develop prototype DSC devices based upon dye-sensitizers that are more sustainable than state-of-the-art ruthenium compounds.

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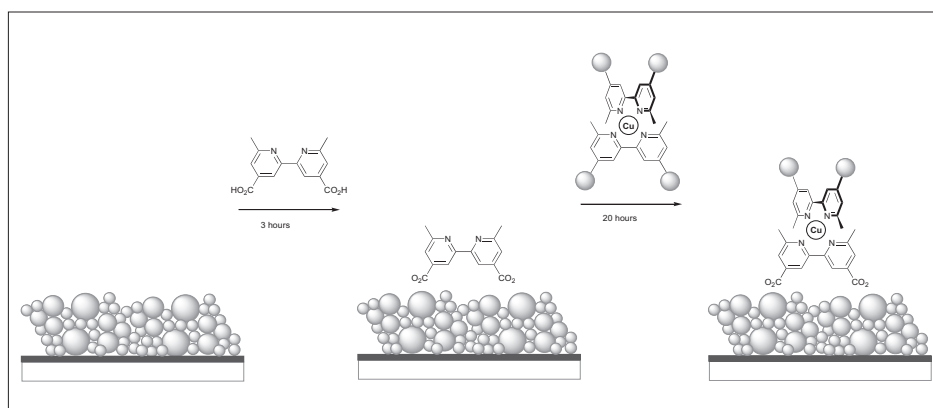


Fig. 6. The stepwise construction of a DSC involving the initial binding of a carboxylic acid ligand to the semiconductor surface to give a colourless device, followed by ligand exchange with a $[\text{CuL}_2]^+$ complex to give a surface-bound red heteroleptic species.