

Final report for 2017-18 on the project

# **Copper-based Dye-sensitized Solar Cells: The Next Step**

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Project No. 43237-1

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## 1. Sammanfattning

Intensiv forskning inom alla fyra delprojekt beskrivna i ansökan har genomförts. Projektets resurser har omfattat två post-doktorer verksamma till 75% inom delprojekten under två år. Projektet har genererat nya grundläggande insikter rörande tillämpningen av koppar-baserade system i färgämnessensiterade solceller baserade på flytande såväl som fasta elektrolyter inom n-typ såväl som p-typ solceller. Projektet har resulterat i hela 10 vetenskapliga publikationer, där vid projektets slut majoriteten är publicerade i vetenskapliga tidskrifter av mycket hög kvalitet. Noterbart är att de allra flesta publikationerna utgör samarbeten mellan ingående forskargrupper, vilket påvisar det vetenskapliga mervärdet av det genomförda projektet.

## 2. Status of sub-projects

The project consists of four sub-projects:

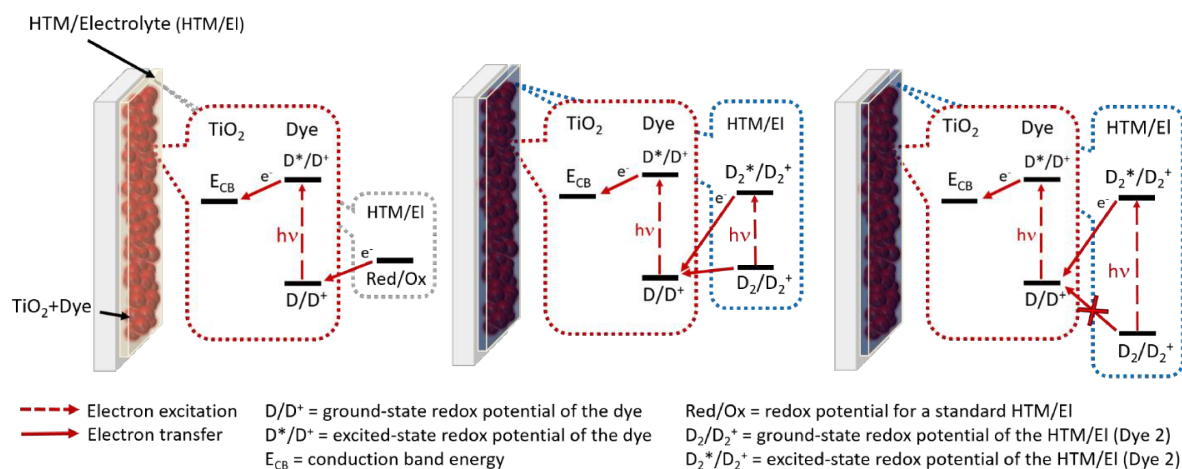
- (1) Effects of photoexcitation on Cu(I/II) complexes
- (2) p-type and tandem cells based on Cu redox systems
- (3) Ligand and self exchange in Cu redox systems
- (4) Charge transport in molecular Cu materials

These activities are described in detail in the corresponding four subsections. All projects are to be regarded as challenging because of scientific novelty and complexity.

### 2.1. Sub-project 1: Effects of photoexcitation on Cu(I/II) complexes

Hole-transporting materials in DSSC often are designed for being transparent to visible light and with ground-state redox properties that match the dye that will oxidize them. However, a tandem light solar cell could be created from hole-transporting materials that absorb light as well as transport charge. Such a scenario could dramatically increase solar cell efficiency. Our first attempts using copper coordination complexes in the role of light absorbing hole-transporting materials were not successful. To explore what the possible challenges were for improving upon our initial attempts Tris(2,2'-bipyridine) ruthenium(II) hexafluorophosphate,  $[\text{Ru}(\text{bpy})_3(\text{PF}_6)_2]$ , was selected as a hole transporting (HTM) material for the generation of tandem dye/HTM-sensitized solar cell (DHSSC) in which both the dye and the HTM function as light absorbers. In this design, the regeneration of the oxidized dye is expected to occur both from the HTM's ground state and excited-state, leading to improved photovoltaic performance. The positive redox potential of the ruthenium complex used in this study prevents regeneration of the oxidized dye from its ground state, therefore allowing us to prove excited-state regeneration. The organic dyes LEG4 and MKA253 were selected as sensitizers. A Stern-Volmer plot of LEG4 sensitized  $\text{TiO}_2$  substrates with a spin-coated ruthenium HTM layer on top shows considerable quenching of the emission of the latter. Time-resolved emission spectroscopy reveals the presence of a fast-decay time component ( $25 \pm 5$  ns), which we assign to a population of  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  in the excited-state undergoing electron transfer to regenerate the oxidized LEG4 molecules. Such a time component is absent when the anatase  $\text{TiO}_2$  semiconductor is replaced by  $\text{ZrO}_2$ . The photovoltaic devices employing MKA253 and LEG4 dyes exhibit 1.2% and 1.1% power conversion efficiency, respectively. This remarkable

result shows that excited-state regeneration from a light-absorbing HTM can be a valuable strategy to significantly boost the efficiency of a new generation of photovoltaic devices. This work was accepted in ChemPhysChem at the end of 2018.[Paper 1]



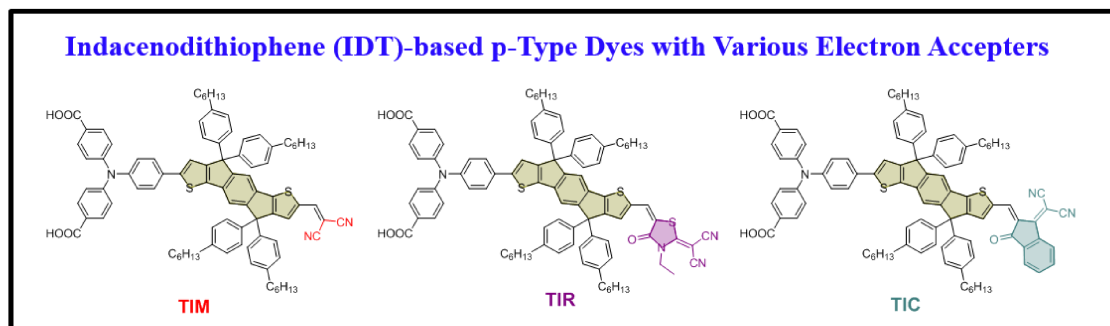
## 2.2. Sub-project 2: p-type and tandem cells based on Cu redox systems

A post-doctoral fellow, Dr. Bo Xu, was hired full time since July 2017 and the initial work in this sub-project is described below. Cu(II) complexes will be used as the electron transport materials/buffer layer to make p-type solid-state dye-sensitized solar cells (p-ssDSSCs) due to the low toxic and the abundance of the copper element in the earth. There are four main steps need to be done in this project, the design and synthesis of new p-type photosensitizers, characterization of the new p-type photosensitizers, preparation of the NiO electrodes and fabrication of solid-state p-type dye-sensitized solar cells [Paper 9]. The progress of the processes is described in the following paragraphs.

### *Design and synthesis of new p-type photosensitizers*

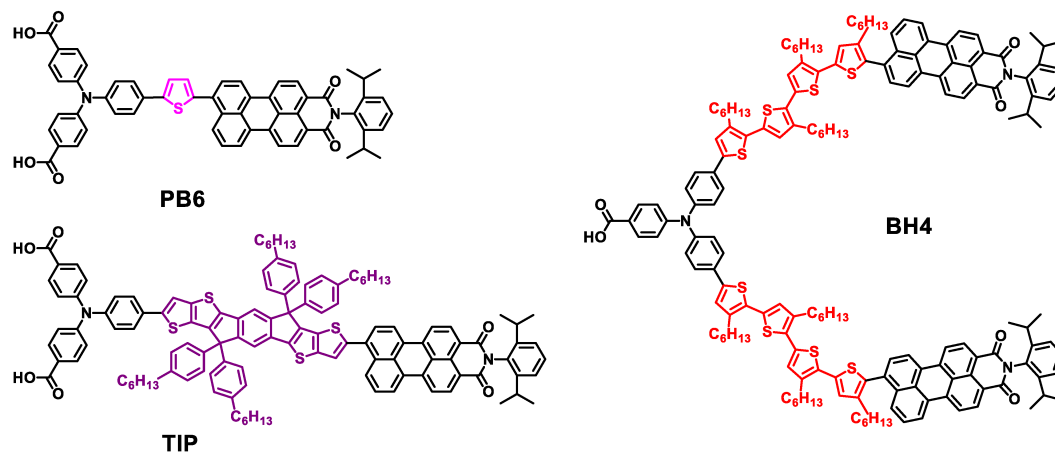
#### *Photosensitizers with different acceptors*

A series of new p-type photosensitizers, named **TIM**, **TIR** and **TIC** (the chemical structures are listed below), were designed and synthesized. We used the Indacenodithiophene (IDT) as the  $\pi$ -conjugation link and different electron-withdrawing group as the acceptors to construct the push-pull organic p-type photosensitizers. This work is to study the effect of electron acceptors on photophysical properties and photovoltaic performance in p-ssDSSCs.



### Photosensitizers with different linkers

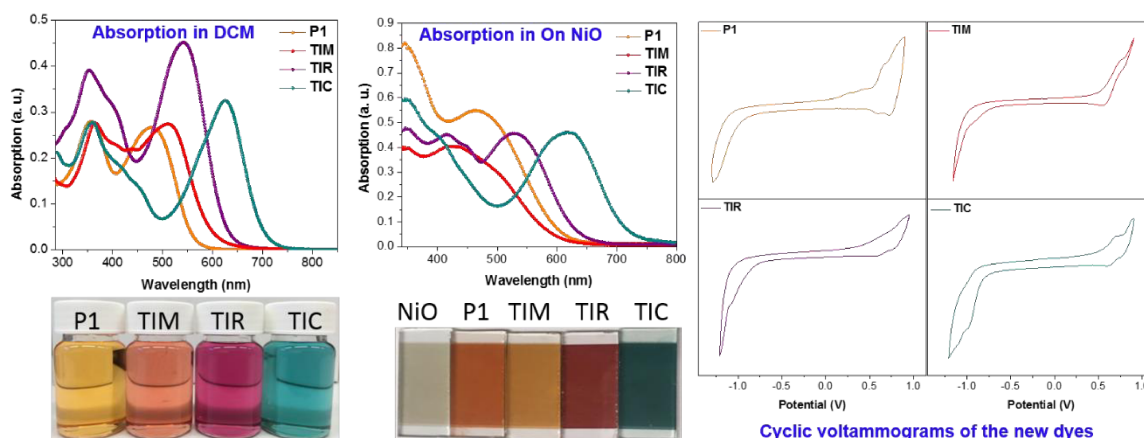
In this work, we designed and synthesized a indacenodithieno[3,2-b]thiophene (IDTT) linker-based dye (**TIP**. See figure below). Two reported dyes, **PB6** and **BH4**, are used as references to compare with the **TIP** dye. This work is to study the effect of linkers on photophysical properties and photovoltaic performance in p-ssDSSCs.



### Characterization of the new p-type photosensitizers

#### Photosensitizers with different acceptors

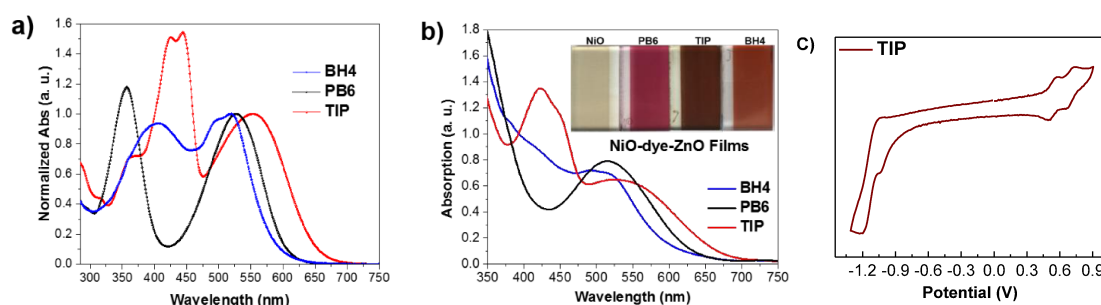
The absorption spectra (both in solution and on NiO film) and the oxidation potentials of the new p-type photosensitizers were recorded by ultraviolet-visible spectrophotometer and cyclic voltammetry (CV) at the electrochemical workstation, respectively. The corresponding curves and parameters are listed below. The TIC dye shows the most red-shifted absorption spectrum among three dyes due to its strong electron acceptor. None of three dyes have reversible reduction peak from CV measurements due to the instability of the acceptors under reduction condition, causing from cyano units in the dyes.



### Photosensitizers with different linkers

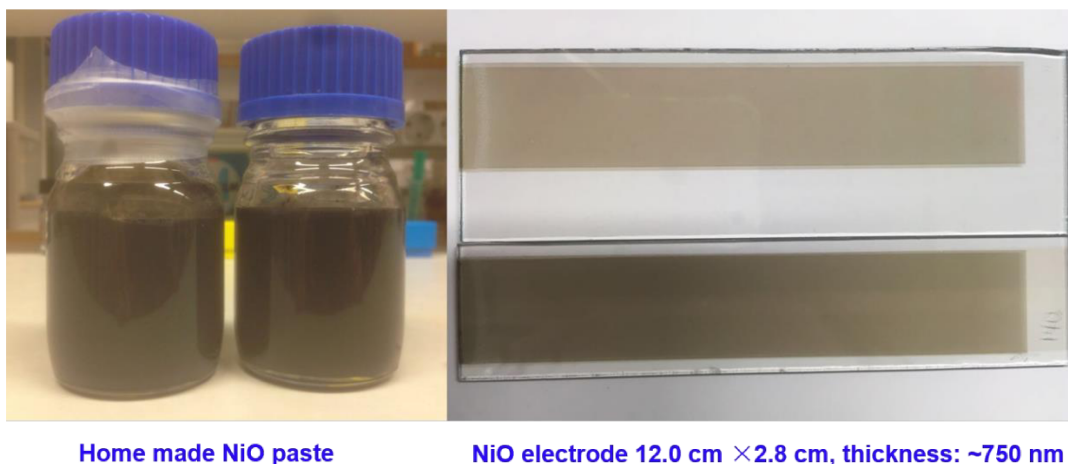
The absorption spectra of dyes in solution and on NiO film are shown in following Figure. **TIP** dye shows maximum absorption at 554 nm and 550 nm in solution and on NiO film, respectively, which are red-shifted as compared to **PB6** and **BH4** dyes due to large  $\pi$  conjugated system and planar structure of the IDTT unit in **TIP** dye. After sensitizing NiO, all dyes showed slightly blue-shifted absorption as compared to that in solution due to

deprotonation of the carboxylic acid units. **TIP** dye exhibits a reversible one-electron reduction ( $E_{S/S^-}$ ) at  $-0.68$  V vs. the Normal Hydrogen Electrode (NHE). With fluorescence spectra and absorption spectrum of TIP dye, one can determine the zero-zero transition energy ( $E_{0-0}$ ) of TIP dye to be 2.02 eV. Therefore, an estimate of its excited state energies ( $E_{S^*/S^-}$ ), 1.34 V vs. NHE is obtained through the combination of  $E_{0-0}$  and the reduction potential. The energy levels of the reference dyes **PB6** and **BH4** are also suitable for fabrication solid state p-type dye sensitized solar cells.



### Preparation of NiO electrodes

The NiO electrode is a very important component for fabrication of the p-type solid-state dye-sensitized solar cells. Instead of the doctor-blading past, we have successfully prepared NiO paste for screen-printing, which accelerates the fabrication, reproducibility and optimization of the devices.



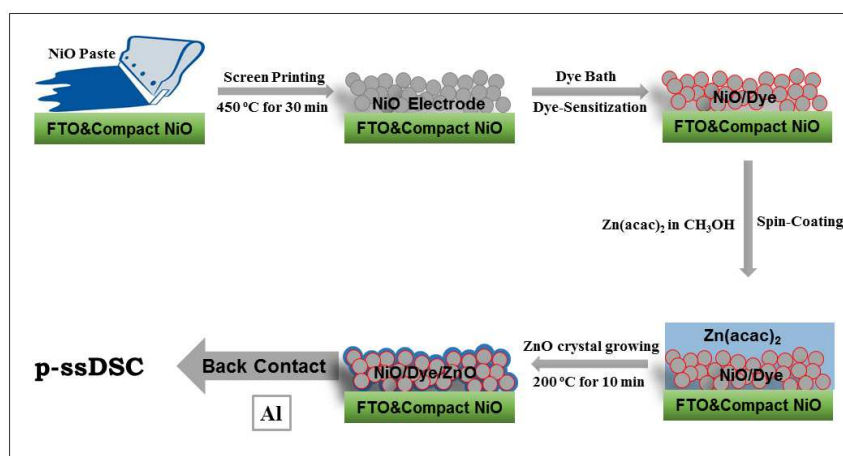
### Fabrication and optimization of p-type solid-state dye-sensitized solar cells

In the final step, we developed for new method to fabricate device, investigated our newly designed dyes in the devices and used copper hexadecafluorophthalocyanine as electron transport material in the device as proposed in the project.

### Development of a new method for device fabrication

In our previous method, we used atomic layer deposition to prepare  $\text{TiO}_2$  as electron transport materials (ETM). Unfortunately, the photocurrent density of the device is very low of the device based on ALD electrodes, ca.  $20 \mu\text{A}\cdot\text{cm}^{-2}$ , making it one of the main challenges in these photocathodes. Possible explanations for the low photocurrent in the photocathodes with  $\text{TiO}_2$  as the ETM; first, the uncompleted penetration of  $\text{TiO}_2$  into the NiO nanoporous layer could

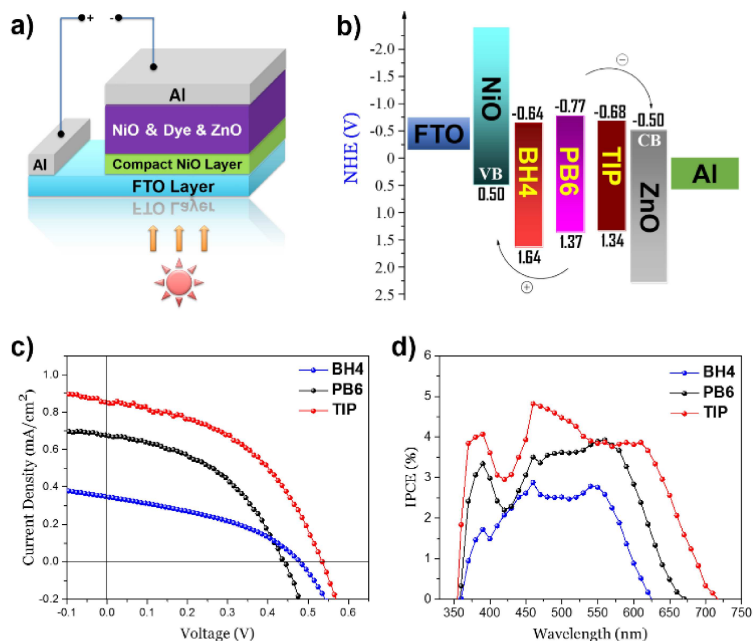
result in low  $J_{sc}$ . Additionally, the low electron mobility of the amorphous  $\text{TiO}_2$ , having been deposited by atomic layer deposition (ALD) technique at low temperature, could also lower the  $J_{sc}$ . Challenges in these devices include finding an easily crystallized inorganic ETM and improving the pore filling of the ETM into the nanoporous  $\text{NiO}$  layer *via* a facile preparation method. In order to develop new and low-cost method, we employed a facile solution-processed method to *in-situ* grow  $\text{ZnO}$  materials in a nanoporous dye-sensitized  $\text{NiO}$  photoelectrode to construct  $\text{NiO}$ -dye- $\text{ZnO}$  photocathode for fabrication of p-ssDSCs. The method is shown in the following figure. With **PB6** dye as photosensitizer, we were able to obtain an efficiency of 0.135% which is higher than that of the liquid device, 0.106%. This work has been published in [Paper 4].



#### *New dyes for the devices*

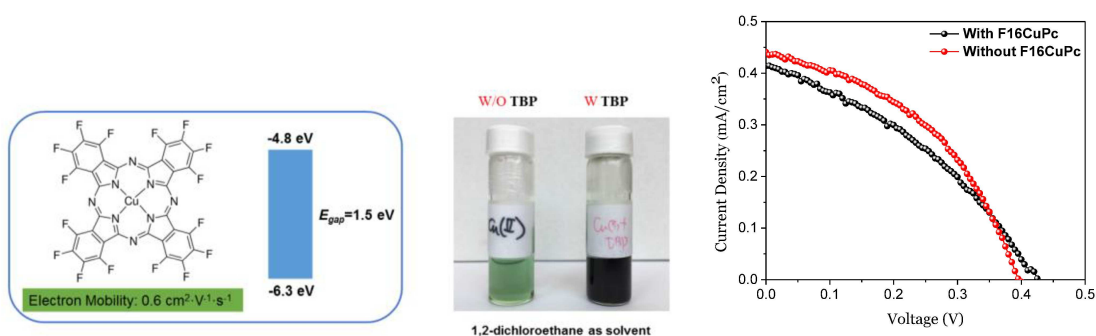
With the new method of device fabrication, we further optimized the device from dyes. As the first series of dye are not stability, we only focused on optimization of the TIP dye and two reference dyes PB6 and BH4 in the devices. From the photovoltaic measurements (see the following figure), TIP dye gave an efficiency of 0.18% with a  $J_{sc}$  of  $0.86 \text{ mA}\cdot\text{cm}^{-2}$ , a  $V_{oc}$  of 535 mV and an  $ff$  of 0.4 under AM 1.5G,  $100 \text{ mW}\cdot\text{cm}^{-2}$ , simulated sunlight illumination. Under the same condition, **PB6** and **BH4** rendered efficiencies of 0.13% and 0.07%, respectively. **TIP** dye obtained the highest short-circuit photocurrent density ( $J_{sc}$ ) of  $0.86 \text{ mA}\cdot\text{cm}^{-2}$  among three dyes due to its broad IPCE spectrum. Notably, **TIP**-based device has a concave shape of IPCE spectrum around 420 nm, although the dye has strong absorption at that wavelength. It could imply that not all dyes in the film contribute to generation of photocurrent due to discontinuity of  $\text{ZnO}$  layer or unsatisfied pore filling of  $\text{ZnO}$  in  $\text{NiO}$  film. Some dyes, in particular for dyes at the bottom of the  $\text{NiO}$  film (near FTO), only work as light filter. Therefore, there is still a big room to improve the photocurrent by developing new ETMs or optimizing preparation method of ETM layer. The work has been formulated as a manuscript and will be submitted to Chem. Commun. soon [Paper 8].





### Copper hexadecafluorophthalocyanine as electron transport material buffer layer

Copper hexadecafluorophthalocyanine (F<sub>16</sub>CuPc) is a promising ETM with high electron mobility (0.6 cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup>) and excellent stability as well as suitable energy levels. It is also a commercial available product in *Sigma-Aldrich*. We have tried to fabricate the p-ssDSCs by using the homemade NiO electrodes, the newly designed p-type photosensitizers and the electron transport material-F<sub>16</sub>CuPc. Due to insolubility of F<sub>16</sub>CuPc in any organic solvent, we have to use evaporation method to prepare the ETM layer. We were not able to get enough ETM loading in our NiO film. With addition of 4-tert-butylpyridine (TBP), we can improve the solubility of F<sub>16</sub>CuPc in organic solvent; we used the F<sub>16</sub>CuPc as a ETM buffer layer prepared from solution process before ZnO layer. Due to the limited loading of F<sub>16</sub>CuPc, the performance of the device did not get significant improvement, but we indeed observed enhanced photovoltage in the presence of F<sub>16</sub>CuPc in the device. This work is still on-going and more optimization work and study need to be done before satisfied performance obtained.

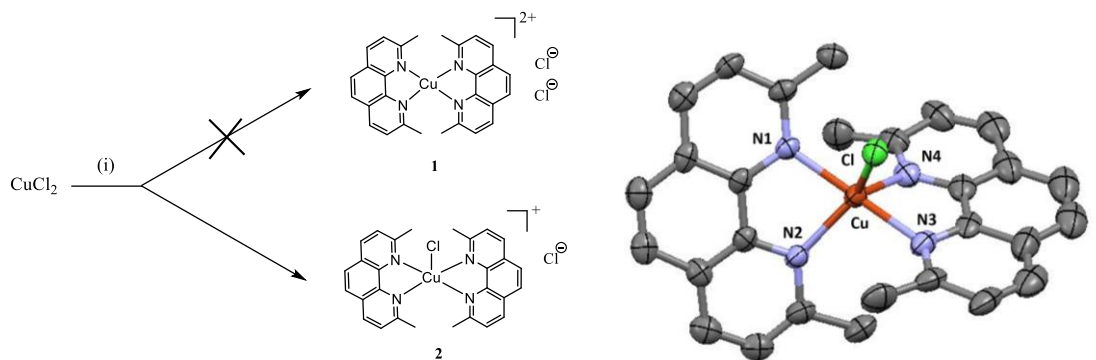


### 2.3. Sub-project 3: Ligand and self exchange in Cu redox systems

Copper coordination complexes have shown great promise as hole transporting materials in DSSC. We have explored details for how the redox couple functions and how to improve it. The work will soon be submitted to the journal *Inorganic Chemistry*.

#### *The synthesis of Cu-based redox systems*

Reaction of  $\text{CuCl}_2$  with 2,9-dimethyl-1,10-phenanthroline (dmp) does not lead to the formation of  $[\text{Cu}(\text{dmp})_2](\text{Cl})_2$  but instead to  $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl}$ , a 5-coordinated complex, in which one chloride is directly coordinated to the metal center. Attempts at removing the coordinated chloride by changing the counter ion by metathesis were unsuccessful and resulted only in the exchange of the non-coordinated chloride, as confirmed from a crystal structure analysis. Complex  $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{PF}_6$  exhibits a reversible cyclic voltammogram characterized by a significant peak splitting between the reductive and oxidative waves (0.85 and 0.60 V vs NHE, respectively), with a half-wave potential  $E_{1/2} = 0.73$  V vs NHE. When reduced electrochemically, the complex does not convert into  $[\text{Cu}(\text{dmp})_2]^+$ , as one may expect. Instead,  $[\text{Cu}(\text{dmp})_2]^+$  is isolated as a product when the reduction of  $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{PF}_6$  is performed with L-ascorbic acid, as confirmed by electrochemistry, NMR spectroscopy, and diffractometry.  $[\text{Cu}(\text{dmp})_2]^{2+}$  complexes can be synthesized starting from Cu(II) salts with weakly coordinating counter ions, such as perchlorate. Growth of  $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)_2$  crystals in acetonitrile results in a 5-coordinated complex,  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})(\text{ClO}_4)_2$ , in which a solvent molecule is coordinated to the metal center. However, solvent coordination is associated with a dynamic decoordination–coordination behaviour upon reduction and oxidation. Hence, the cyclic voltammogram of  $[\text{Cu}(\text{dmp})_2(\text{CH}_3\text{CN})]^{2+}$  is identical to the one of  $[\text{Cu}(\text{dmp})_2]^+$ , if the measurements are performed in acetonitrile. The current results show that halide ions in precursors to Cu(II) metal-organic coordination compound synthesis, and most likely also other multivalent coordination centers, are not readily exchanged when exposed to presumed strongly binding and chelating ligand, and thus special care needs to be taken with respect to product characterization.

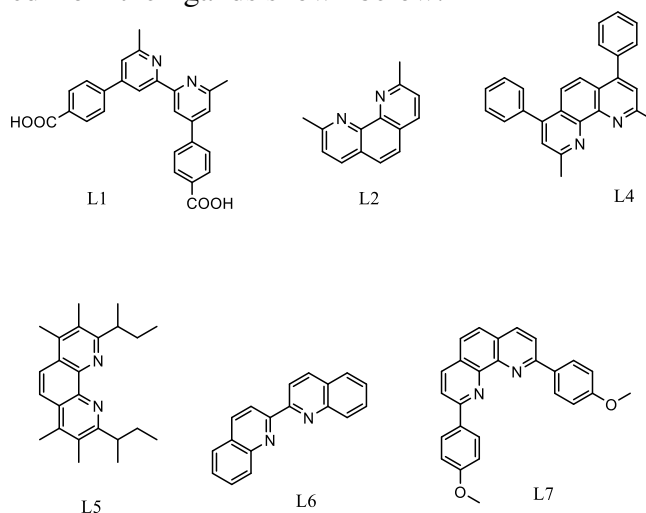


#### *Lepticity effects on properties*

A well-known characteristic of Cu(I) complexes is their lability which is due to a dynamic and reversible ligand coordination-decoordination mechanism which we have also shown in our previous manuscript. This aspect makes the synthesis and study of the properties of heteroleptic complexes (complexes with mixed-type ligands) very challenging. The Nobel laureate in Chemistry 2016 Jean-Pierre Sauvage introduced and extensively studied stable Cu(I) complexes using catenates ligands, interlocked ring systems able to completely suppress

ligand scrambling. Nevertheless, heteroleptic Cu(I) catenates are difficult to synthesize and purify. A second approach to the synthesis of stable heteroleptic Cu(I) complexes relies on the use of particularly bulky ligands which are too sterically hindered to form the corresponding homoleptic Cu(I) complex, thus pushing the equilibrium in favor of the heteroleptic complex. Based on this strategy, mixed 1,10-phenanthroline derivatives and bulky phosphine ligand POP (POP = bis[2-(diphenylphosphino)phenyl]ether) Cu(I) complexes have been synthesized. Diimine ligands with particularly bulky substituents used for the same purpose have been first introduced by Schmittel and colleagues, and have successfully led to the preparation of several heteroleptic Cu(I) complexes. However, this particular design poses some limitations on the type of heteroleptic complexes that can be studied. An elegant alternative which allows for more structural variety in the realization of surface-immobilized heteroleptic Cu(I) complexes was adopted by C. E. Housecroft and E. C. Constable. The method consists of a step-by-step self-assembly of the heteroleptic complexes on the surface of TiO<sub>2</sub>. In this work, we use the same approach for the synthesis and the study of the electronic and electrochemical properties of a series of heteroleptic Cu(I) complexes and we compare them to those of the corresponding homoleptic ones.

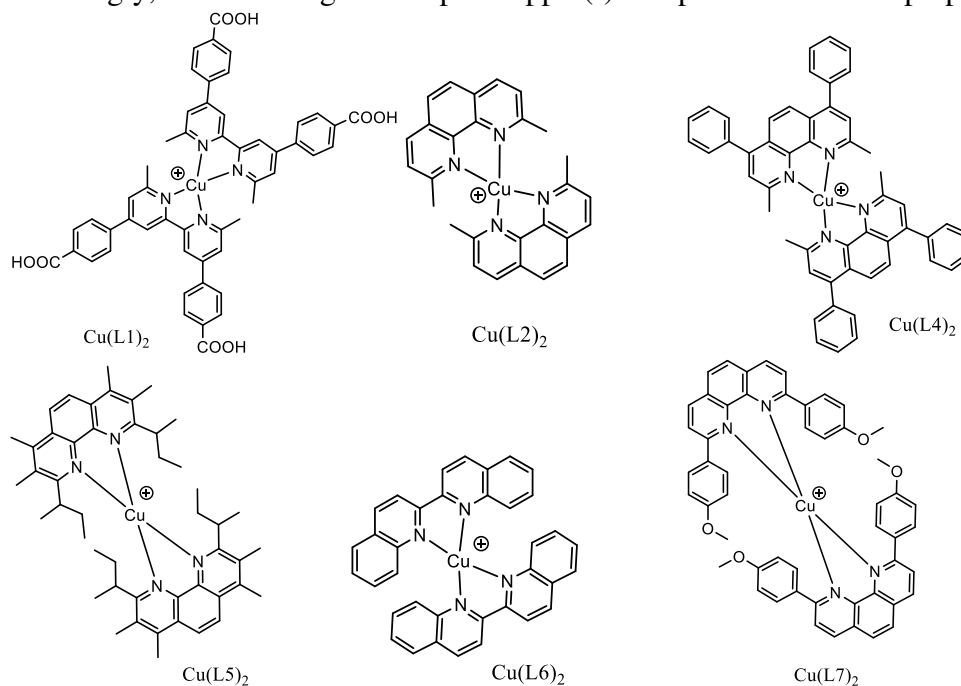
We have investigated the properties of a series of homoleptic and heteroleptic copper complexes synthesized from the ligands shown below:



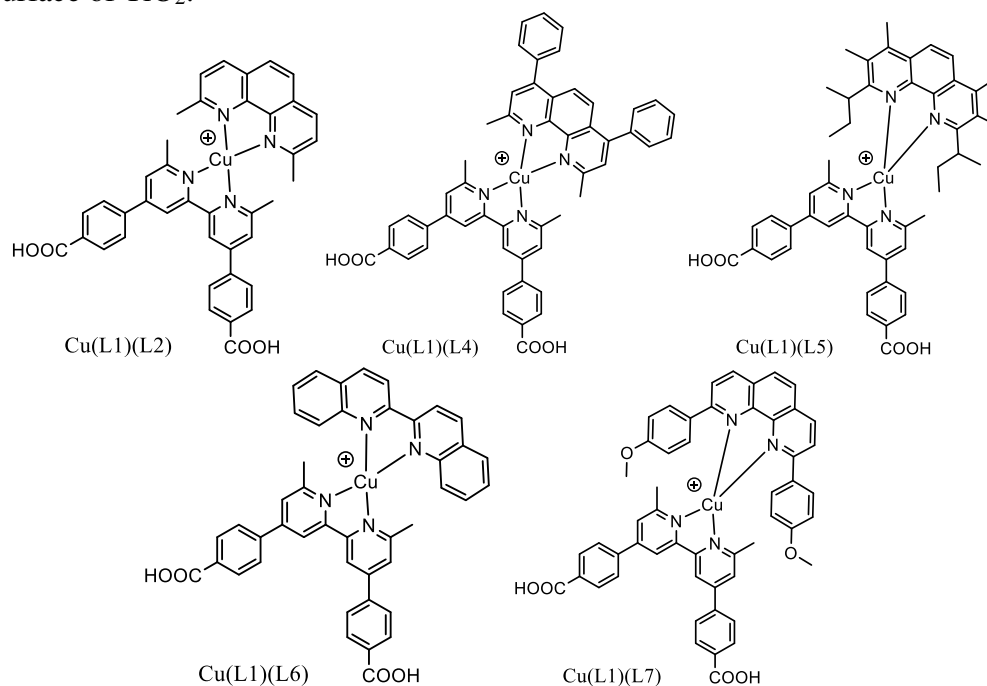
The 2,2'-bipyridine derivative (L1) was selected as anchoring ligand as it is able to bind to the surface of TiO<sub>2</sub> through the carboxylic acid moieties. The ancillary ligands (L2-L7) were chosen with the scope of having a reasonable variability of their different sterical, electrical and redox properties deriving from the different nature and position of the substituents, and from the rigidity or flexibility of the structure. The ligand L2, 2,9-Dimethyl-1,10-phenanthroline (dmp), or neocuproine, is one of the most basic and studied building blocks for the synthesis of sterically hindered copper(I) complexes due to the presence of the methyl groups in position 2,9 of the phenanthroline. Ligand L4, bathocuproine (bcp), has been investigated as well and it can be regarded as a slightly modified version of L2 in which additional phenyl groups are present in the 4,7 positions of the phenanthroline. Ligand L5, 2,9-di(*sec*-butyl)-3,4,7,8-tetra-methyl-1,10-phenanthroline (dsbtmp) was selected on grounds of its ability to screen more efficiently the metal center from solvent interactions, giving reversible redox chemistry, impressive thermodynamic and photochemical stability in solution. The 2,2'-Biquinoline (biq) framework (L6) was chosen in order to introduce a

variation in terms of both electronic properties and geometrical flexibility from the rest of the series which is based on a rigid phenanthroline building block. Finally, we wanted to include a ligand bearing bulkier substituents in the phenanthroline 2,9- positions, so L7 (dap), with anisyl substituents, was chosen.

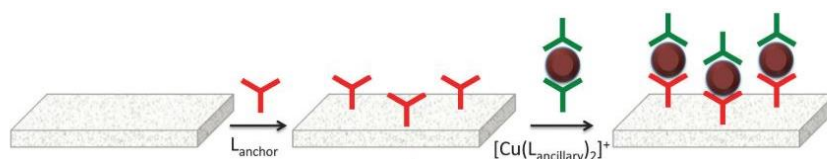
Accordingly, the following homoleptic copper(I) complexes have been prepared:



As well as the following heteroleptic complexes, obtained by a self-assembly technique on the surface of TiO<sub>2</sub>:

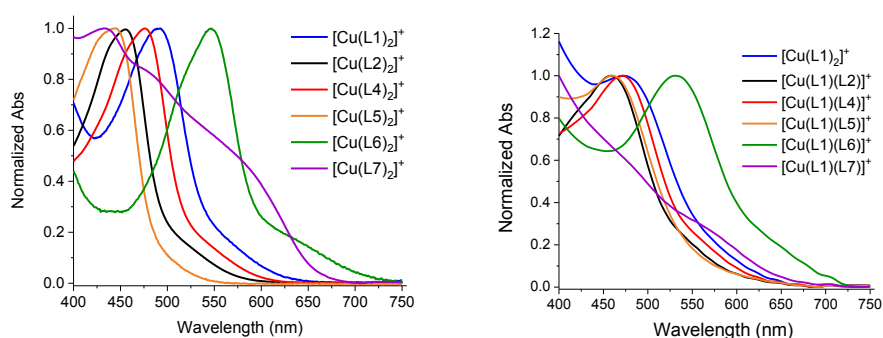


A schematic representation of the self-assembly process on  $\text{TiO}_2$  can be found below:

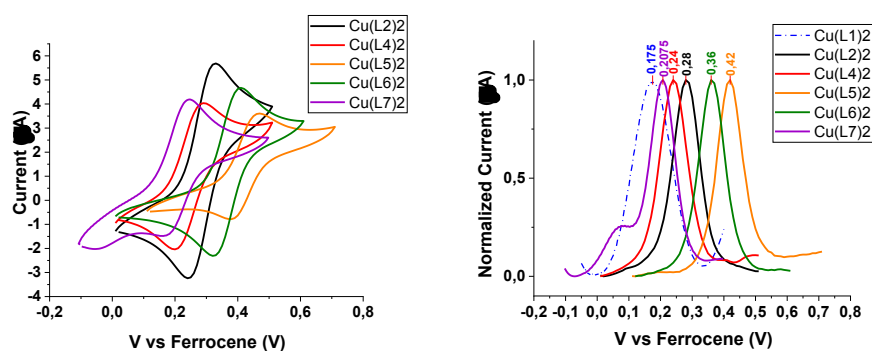


The approach consists in a stepwise, on-surface assembly of  $[\text{Cu}(\text{L}_{\text{anchor}})(\text{L}_{\text{ancillary}})]^+$  complexes by soaking a  $\text{TiO}_2$  substrate in a solution of  $\text{L}_{\text{anchor}}$ , and then in a solution containing either  $[\text{Cu}(\text{L}_{\text{ancillary}})_2]^+$  or a mixture of  $[\text{Cu}(\text{NCMe})_4]^+$  and  $\text{L}_{\text{ancillary}}$ . The method relies on ligand exchange between surface-anchored  $\text{L}_{\text{anchor}}$  and  $[\text{Cu}(\text{L}_{\text{ancillary}})_2]^+$  for the formation of the desired heteroleptic complex.

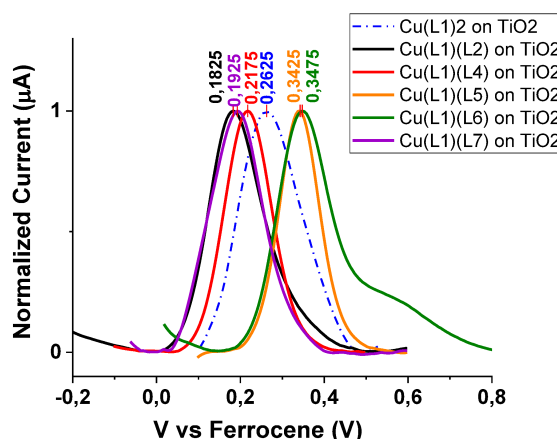
The absorption spectra of the homoleptic and heteroleptic complexes, the latter on the surface of  $\text{TiO}_2$ , are shown below:



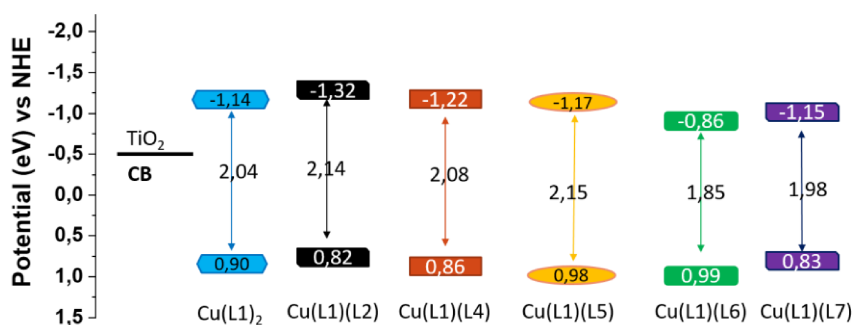
We have then characterized the homoleptic complexes by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), respectively:



The characterization of the heteroleptic complexes in solution is not possible due to ligand scrambling. However, we measured the DPVs of the complexes adsorbed on the surface of  $\text{TiO}_2$ :



Combining the information obtained by the optical characterization and the CVs/DPVs we have determined the HOMO and LUMO energetic levels of the complexes:



Few last measurements are still in progress but for this part of this particular sub-project, a manuscript entitled “*Exploring the properties of heteroleptic vs homoleptic diimine copper complexes*” is currently in preparation. [Paper 6]

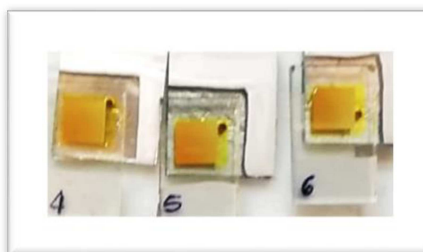
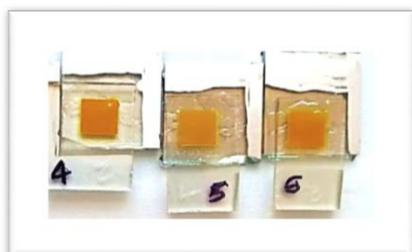
### **Heteroleptic light absorbers**

In this study, we investigate how the properties of the heteroleptic complexes studied in the preceding sub-project affect their performance as dyes in liquid dye-sensitized solar cells. For simplicity, initial experiments directed at finding optimal operating conditions of the dyes in the solar cells have been carried out using the heteroleptic complex Cu(L1)(L4) as a reference. We chose this complex due to the commercial availability of the ancillary ligand L4 and due to the ease of formation and relative stability of the heteroleptic complex.

We have investigated the impact of the thickness of the TiO<sub>2</sub> substrates (from 9 to 12 micrometers) as well as the type of electrolyte used (cobalt-based or iodide-based) on the efficiency of the solar cells. The table below shows the results of a part of the performed experiments:

Cu(L1)(L4)	$\eta$ (%)	$V_{oc}$ (mV)	$J_{sc}$ ( $mA\ cm^{-2}$ )	FF
Cobalt Electrolyte_Standard (9,3 $\mu m$ )	0,06	500	0,233	0,514
Cobalt Electrolyte_No TBP (9,3 $\mu m$ )	0,011	130	0,133	0,610
Iodide/Triiodide (9,3 $\mu m$ ), 3-methoxypropionitrile	0,140	510	0,419	0,654
Iodide/Triiodide (12 $\mu m$ ), 3-methoxypropionitrile	0,723	540	1,937	0,691
Iodide/Triiodide (12 $\mu m$ ) + Cu(L4)2 complex, 3-methoxypropionitrile	0,657	535	1,666	0,737

Thicker TiO<sub>2</sub> layers gave higher efficiency. Furthermore, the iodide/triiodide electrolyte performed better than the cobalt-based one which caused dye desorption when injected in the devices. For this reason, we have decided to further investigate two iodide-based electrolyte compositions:

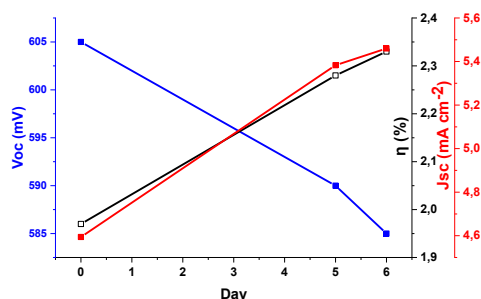


Electrolyte 1	
ACN/valeronitrile	85/15 v/v
N-methyl-N-butylimidazole	0,65 M
LiI	0,025 M
I <sub>2</sub>	0,04 M
TBP	0,28 M

Electrolyte 2	
ACN/valeronitrile	85/15 v/v
N-methyl-N-butylimidazole	1 M
LiI	0,1 M
I <sub>2</sub>	0,05 M
TBP	0,5 M

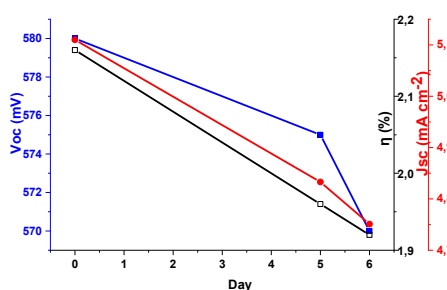
We have assembled devices with optimal TiO<sub>2</sub> thickness, injected the different electrolytes and measured the efficiency of the devices over time:

### Electrolyte 1



Day	$\eta$ (%)	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF
0	1,97	605	4,594	0,71
5	2,28	590	5,383	0,72
6	2,33	585	5,460	0,73

### Electrolyte 2



Day	$\eta$ (%)	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF
0	2,16	580	5,110	0,73
5	1,96	575	4,833	0,71
6	1,92	570	4,751	0,71

Optimal devices have reached up to 2.4% of efficiency and we are currently testing the performances of all the heteroleptic complexes previously shown as well as of a benchmark dye (N719). For each dye-based solar cells we are investigating the following parameters: photovoltaic parameters, efficiency at different light intensities, IPCE, dark current, lifetime and stability over time.

We are collecting all the findings from this sub-project in a separate manuscript, which will be solely focused on the performance of the heteroleptic complexes in the solar cells as a function of their properties. [Paper 7]

## 2.4. Sub-project 4: Charge transport in molecular Cu materials

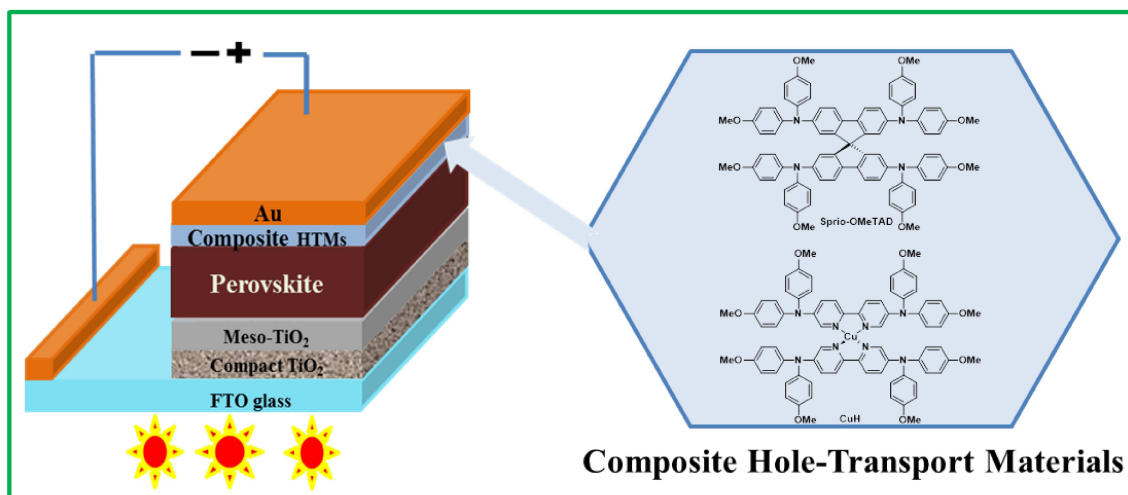
Copper-based materials have been studied in two separate project as hole-transport materials in perovskite solar cells (PSCs). Spiro-OMeTAD has been the most commonly used hole-transport material in perovskite solar cells, but it suffers from several drawbacks, of which the most important are high cost/complex route of synthesis, aggregation tendency preventing defect-free film formation and surprisingly bad charge-transport properties. Thus it is natural to seek alternatives or composites as replace replacement or complement.

### *Composite hole-transport materials containing Cu-based materials*

In order to address these issues, we designed a new type of composite hole-transport materials based on a new metal-organic copper complex (CuH) and Spiro-OMeTAD. The incorporation of the molecularly bulky HTM CuH into the Spiro-OMeTAD material efficiently improves the hole mobility and suppresses the aggregation in the Spiro-OMeTAD film. As a result, the conversion efficiencies obtained for perovskite solar cells based on the composite HTM

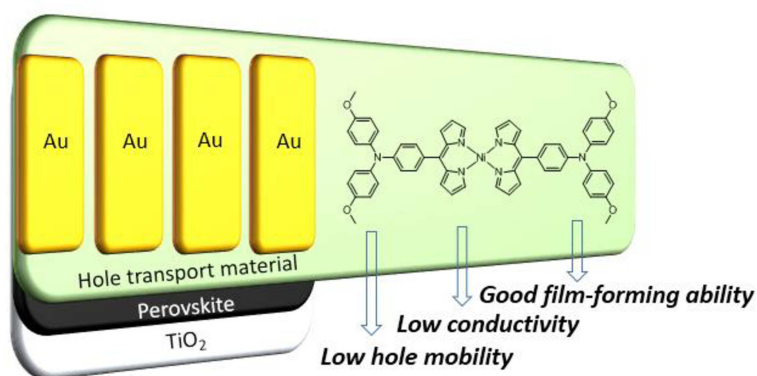


system reached as high as 18.83%, which is superior to solar cells based on the individual hole-transport materials CuH (15.75%) or Spiro-OMeTAD (14.47%) under the same working conditions. These results show that composite HTM systems may constitute an effective strategy to further improve the efficiency of perovskite solar cells. This work was published in the journal Solar RRL [Paper 3].



### *Triphenylamine-based metal complexes as hole-transport materials*

Triphenylamine (TPA) based metal complexes were designed and synthesized via coordination to Ni(II), Cu(II) and Zn(II) using their respective acetate salts as starting materials. The resulting metal complexes exhibit more negative energy levels (vs. vacuum) as compared to Spiro-OMeTAD, high hole extraction efficiency but low hole mobilities and conductivities. Application of dopants typically used for Spiro-OMeTAD was not successful, indicating a more complicated mechanism of partial oxidation besides the redox potential. However, utilization as hole transport material was successful, giving a highest efficiency of 11.1% under AM 1.5G solar illumination. This work has very recently been published in the open-access journal ACS Omega [Paper 4].



### 3. Objectives of the project

Below, a table describing the degree of project targets met is included.

Objectives	Status
1. Design and synthesis of Cu-based complexes with reversible redox chemistry and long lifetimes for DSSCs	On its way; this is conceptually completely new, and the inclusion of also Ru-based systems has allowed a proof-of-concept valuable for the ongoing efforts
2. Design and investigation of new Cu-based materials for p- and tandem-type DSSCs	Fulfilled
3. New insights regarding ligand exchange and self-exchange reactions as a base for the design of new photochemically stable systems	Fulfilled and exceeded in the design of very promising heteroleptic systems.
4. New insights regarding how the 3D molecular structure affects charge mobility and conductivity	Fulfilled, although efforts are continued in related projects also funded by the EM aiming at the development of a predictive theoretical tool for organic as well as metal-organic systems
5. Extra objective: LCA of Cu-based DSSCs	A collaboration has been initiated with Dr. Maria Laura Maria Parisi at Univ of Siena, Italy

### 4. Papers from the sub-projects 2017-18

Only manuscripts published, submitted or in a late stage of preparation are listed below.

1. V. Leandri, P. Liu, A. Sadollahkhani, M. Safdari, L. Kloo, J.M. Gardner, *Excited state dynamics of Ru(bpy)<sub>3</sub><sup>2+</sup> - Thin films on sensitized TiO<sub>2</sub> and ZrO<sub>2</sub>*, *ChemPhysChem*, **2019**, accepted for publication (DOI: 10.1002/cphc.201801010).
2. V. Leandri, Q. Daniel, H. Chen, L. Sun, J.M. Gardner, L. Kloo, *Electronic and structural effects of inner-sphere coordination of chloride to a homoleptic copper(II) diamine complex*, *Inorg. Chem.*, **2018**, 57, 4556-4562.
3. Y. Hua, P. Liu, Y. Li, L. Sun, L. Kloo, *Composite hole-transport materials based on a metal-organic copper complex and Spiro-OMeTAD for efficient perovskite solar cells*, *Solar RRL*, **2018**, 2, 1700073 (p. 1-7).
4. W. Zhang, P. Liu, A. Sadollahkhani, Y. Li, B. Zhang, F. Zhang, M. Safdari, Y. Hao, Y. Hua, L. Kloo, *Investigation of triphenylamine (TPA)-based metal complexes and their application in perovskite solar cells*, *ACS Omega*, **2017**, 2, 9231-9240.
5. B. Xu, B. Xu, L. Tian, A. Etman, J. Sun, H. Tian, *Solution-Processed Nanoporous NiO-Dye-ZnO Photocathodes: Toward Efficient and Stable Solid-State p-Type Dye-Sensitized Solar Cells and Dye-Sensitized Photoelectrosynthesis Cells*, *Nano Energy*, **2019**, 55, 59-64.
6. V. Leandri, R. Pizzichetti, B. Xu, H. Tian, L. Kloo, J.M. Gardner, "Exploring the properties of heteroleptic vs homoleptic diimine copper complexes" - *in preparation*.
7. V. Leandri, R. Pizzichetti, B. Xu, H. Tian, L. Kloo, J.M. Gardner, "Effect of the ancillary ligand on the performance of heteroleptic Cu(I) diimine complexes in dye-sensitized solar cells" - *in preparation*.
8. B. Xu., P. Pati, L. Kloo, Y. Wu, H. Tian, *Improving Performance of Solid-state p-Type Dye-sensitized Solar Cells by an Indacenodithieno[3,2-b]thiophene based Organic Dye*, *Chem. Commun.*, to be submitted.

9. H. Tian, *Solid State p-Type Dye Sensitized Solar Cells: Progresses, Potential Applications and Challenges*, *Sustainable Energy & Fuels*, **2019**, in revision (invited perspective)
10. H. Tian and L. Kloo, "Liquid Dye-Sensitized Solar Cells", in *Molecular Devices for Solar Energy Conversion and Storage*, Eds. H. Tian, G. Boschloo and A. Hagfeldt, Springer., **2018**, Chapter 3, pp. 109-150
11. H. Tian, J. Gardner, T. Edvinsson, P. B. Pati, J. Cong, B. Xu, M. Abrahamsson, U. B. Cappel, E. M. Barea , "Dye-sensitized Solar Cells", in *Solar Energy Capture Materials*, Ed. Elizabeth Gibson, Royal Society of Chemistry, UK, **2018** (in Press)