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Towards efficient sustainable full-copper dye-sensitized solar cells

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Two new heteroleptic copper(I) sensitizers bearing 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid, to anchor the dye on the titania surface, and a π -delocalized 2-(R-phenyl)-1H-phenanthro[9,10-d]imidazole (R = NPh₂ or OHexyl) ancillary ligand were prepared and well characterized. Their performance as dyes in DSSCs is quite similar to that of the related complex bearing 2,9-dimesityl-1,10-phenanthroline as ancillary ligand, when using the common I⁻/I₃⁻ redox couple or homoleptic copper complexes as electron shuttles. The experimental results along with theoretical calculations confirm the great potential of full-copper DSSCs.

Introduction

To have enough clean and low cost energy for the future is one of the world's most important challenges. The sun could be the answer to our energy needs, since more energy from sunlight strikes the earth in one hour than all the energy consumed on the planet in one year.

Following the discovery of Grätzel-type Dye sensitized solar cells (DSSCs) as a cheap and convenient way for harnessing the energy of the sun and converting it into electricity [1], there has been a lot of effort to improve the photo-conversion efficiency (PCE), trying to optimize every components of the device. In particular, an impressive amount of work has been devoted to optimize the sensitizer [2-7] and the redox mediators [7-12].

Coordination compounds based on Ru with bipyridine ligands such as *cis*-di(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylate)Ru(II) (N3) and the related doubly deprotonated

complex (N719) [13] are amongst the most performing photosensitizers with the iodide/triiodide couple (I⁻/I₃⁻) as electrolyte [14,15]. Cyclometalated ruthenium complexes, characterized by a better stability, represent good alternatives for application in DSSCs [16-23]. However, these sensitizers are not ideal because ruthenium is one of the rarest and most expensive metal. For this reason, there is currently significant interest in the use of earth-abundant metals [5-7, 24]. Sauvage and co-workers [25] were the first to use copper(I) complexes as sensitizers. The rationale for their application is based on similarities between the photophysical properties of copper(I) and ruthenium(II) complexes [26-27].

In the last few years, an exponential amount of work has been dedicated to the use of cheap and environmental-friendly copper(I) complexes as sensitizers in DSSCs with the I⁻/I₃⁻ redox couple as electrolyte [5-7, 24, 28-32]. The actual 4.66% record efficiency, corresponding to a remarkable 63% relative efficiency (η_{rel} [33]) respect to a N719-sensitized control cell set at 100%, was obtained with a copper(I) complex having as anchoring ligand a 4,4'-dicarboxylic acid-6,6'-dimesityl-2,2'-bipyridine and, as ancillary ligand, a 4,4'-bis(N,N diethylaminestyryl)-6,6'-dimethyl-2,2'-bipyridine [34]. A lower efficiency (1.46%) was reached by substitution of the latter ligand with 4,4'-dimethyl-6,6'-dimethyl-2,2'-bipyridine due to a lower light harvesting efficiency [34].

Recently, the observed long term incompatibility of copper complexes with I⁻/I₃⁻, due to the low solubility of CuI [35,36], and the fact that iodine is a non-abundant element [37] led to

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the preparation of iodine-free copper(I) solar cells. The use of $[\text{Co}(2,2'\text{-bipyridine})_3]^{2+/3+}$, as redox couple, and a copper(I) complex bearing (6,6'-dimethyl-[2,2'-bipyridine]-4,4'-diyl)bis(4,1-phenylene)bis(phosphonic acid) and a 2-(diphenylaminophenyl)-1*H*-phenanthro[9,10-*d*]imidazole derivative, as dye, afforded a DSSC with a 1.73% efficiency (25% η_{rel}) similar to that obtained with the reference I^-/I_3^- electrolyte [36]. This was an important step towards the development of stable iodide-free copper(I) solar cells [38].

Besides, it was found that $\text{Cu}^{+/2+}$ mediators can outperform both iodine-based [39-42] and Co-based [43-44] electrolytes in combination with ruthenium(II) dyes, Zn^{2+} porphyrin or organic sensitizers. Fast dye regeneration and tunability of both redox potential and electron transfer rate make Cu mediators able to solve the thermodynamic and kinetic dichotomies of the device operation [45-47].

These observations were the springboard for the development of full-copper DSSCs in which a copper(I) dye is coupled with a copper(I/II) electron shuttle [48, 49]. Thus, with the aim of achieving sustainable energy conversion by solar cells with earth-abundant components, Housecroft et al have investigated the performances of DSSCs based on heteroleptic bis(diimine)copper(I) sensitizers coupled with homoleptic bis(diimine)copper(I/II) complexes; the best photoconversion efficiency (2.06% corresponding to 38.1% relative to N719 set at 100%) was achieved by using a phosphonic acid anchor, and 4,4'-dimethoxy-6,6'-dimethyl-2,2'-bipyridine as the ancillary ligand in the dye and in the electrolyte [49]. In parallel we found that the use of a simple heteroleptic copper dye (**D1**, Chart 1), bearing one 2,9-dimesityl-1,10-phenanthroline and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid anchoring ligand, in combination with an homoleptic copper(I/II) complex bearing two 2-*n*-butyl-1,10-phenanthrolines (**E3/E4**, Chart 1) as electron shuttle allows to reach a good photoconversion efficiency (*ca* 2.0 % corresponding to *ca* 22% η_{rel}) although lower than that obtained with the conventional I^-/I_3^- couple as electrolyte [48]. The use of the same copper dye with a copper electron shuttle bearing two 2,9-dimethyl-1,10-phenanthroline ligands (**E1/E2**) led to a lower efficiency [48].

These first examples of full-copper solar cells [48,49] open a new route for cheap and environmentally friendly DSSCs. Now work should be devoted to improve the photoconversion efficiency by tuning the photophysical and redox properties of the copper complexes. In the present work, we focus the attention on the nature of the heteroleptic copper(I) sensitizer.

In the design of such complexes, one keeps in mind that one ligand should carry a group suitable for anchoring to TiO_2 and the second ligand be electronically and structurally tuned to harvest light, to support efficient electron transfer from electrolyte to dye and to provide directionality for electron injection in the TiO_2 conduction band. The LUMO should reside on the ligand anchored on the TiO_2 surface so that the electron is localized on this domain in the excited state (ideal for injection into the semiconductor) whereas the HOMO of the excited state should be localized on the ancillary ligand to minimize back-migration of an electron from the

semiconductor to the dye and to enhance electron transfer from the electrolyte [5-7]

In the present work we study DSSCs based on two novel Cu(I) photosensitizers, **D2** and **D3**, having the anchoring ligand of the previously studied **D1** [48] but more π -delocalized ancillary ligands in order to increase light harvesting. To define a relationship between the structure and the electronic/optical properties of the investigated copper-based dyes, calculations have been performed on **D1-D3** sensitizers by employing Density Functional Theory (DFT) and Time Dependent DFT methods.

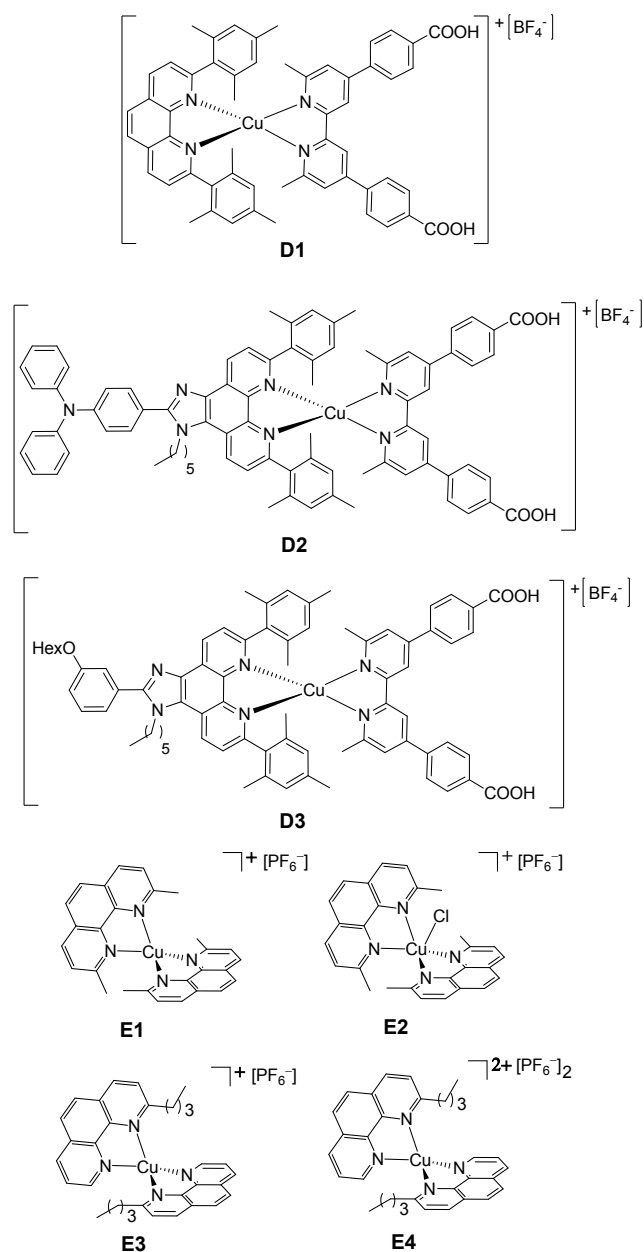


Chart 1. Chemical structures of the investigated dyes (**D1**, **D2**, **D3**) and of the two couples of copper-based redox mediators (**E1/E2** and **E3/E4**).

Experimental

General comments

Solvents for the syntheses were dried by standard procedures: *N,N*-dimethylformamide (DMF) was dried over activated molecular sieves and toluene was distilled over Na/benzophenone. All reagents were purchased from Sigma-Aldrich and were used without further purification. Reactions requiring anhydrous conditions were performed under argon or nitrogen. Thin layer chromatography (TLC) was carried out with pre-coated Merck F254 silica gel plates. Flash chromatography (FC) was carried out with Macherey-Nagel silica gel 60 (230-400 mesh).

Synthesis of new ligands (Scheme 1).

The synthesis of ligand **L2** and **L3** was performed by reaction of the known 2,9-dimesityl-1,10-phenanthroline-5,6-dione [36, 50, 51] with the suitable aldehyde affording the imidazole ring (**I2** and **I3**) which was then alkylated to afford in good yields **L2** and **L3**. The 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid was obtained as previously reported [29].

Synthesis of I2

A solution of 2,9-dimesityl-1,10-phenanthroline-5,6-dione (34 mg, 0.076 mmol), 4-(diphenylamino)benzaldehyde (27.0 mg, 0.098 mmol) and NH_4OAc (147 mg, 1.9 mmol) in 6 mL of glacial acetic acid was stirred at reflux overnight. After cooling to room temperature, water was added (15 mL) and the pale yellow precipitate was collected by filtration and washed with water. The crude product was dissolved in dichloromethane (20 mL) and washed twice with water (2x30mL). The organic phase was dried on Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH} = 99 : 1$) affording the pure product as a yellow solid (34 mg, 64%). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ ppm 13.64 (s broad, 1H), 8.98 (d, $J = 8.4$ Hz, 2H), 8.21 (d, $J = 8.4$ Hz, 2H), 7.73 (s, 2H), 7.39 (t, $J = 7.8$ Hz, 4H), 7.22–7.08 (m, 8H), 6.97 (s, 4H), 2.30 (s, 6H), 2.03 (s, 12H).

Synthesis of L2

A solution of **I2** (58 mg, 0.083 mmol) and Cs_2CO_3 (173 mg, 0.53 mmol) in 17.5 mL of dry DMF was heated at 100 °C under argon for 30 minutes, and then *n*-hexyl iodide (0.038 mL, 3.1 mmol) was injected into the flask and the mixture was further stirred at 100 °C for 4 hours. After cooling to room temperature the solvent was removed and the crude product was purified by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 99.5/0.5$) to give **L2** (46 mg, 71%). $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ ppm 9.07 (d, $J = 8.2$ Hz, 1H), 8.70 (d, $J = 8.6$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.38 (t, $J = 7.8$ Hz, 4H), 7.26 (t, $J = 6.7$ Hz, 6H), 7.18 (t, $J = 7.3$ Hz, 2H), 7.01 (s, 2H), 6.99 (s, 2H), 4.75 (t, $J = 7.4$ Hz, 2H), 2.37 (s, 6H), 2.14 (s, 6 H), 2.11 (s, 6H), 2.05 (t, $J = 7.4$ Hz, 2H), 1.34–1.28 (m, 6H), 0.87–0.84 (m, 3H). $^{13}\text{C-NMR}$ (75 MHz, DMSO) δ 158.69, 157.45, 154.21, 149.57, 147.66, 145.05, 144.63, 138.87, 138.37, 137.74, 137.53, 136.36, 136.29, 131.06, 130.37, 129.86, 128.69, 128.59, 128.52, 125.58, 125.15, 124.29, 124.16, 124.08, 122.54, 118.88, 47.20, 31.37, 30.53, 26.27, 22.80, 21.21, 20.52, 20.47, 14.05. Elemental Analysis: Calcd. for $\text{C}_{55}\text{H}_{53}\text{N}_5$: C 84.25, H 6.81, N 8.93. Found. C 84.30, H 6.82, N 8.91.

Synthesis of I3

First the 3-(hexyloxy)benzaldehyde was prepared as follows. In a flask under argon were dissolved 3-hydroxybenzaldehyde (500 mg,

4.09 mmol) and K_2CO_3 (5.7g, 10 mmol) in dry acetonitrile (15 mL). After 5 min, *n*-hexylbromide was added and the mixture was heated at reflux and stirred overnight. After cooling to r.t. the solvent was removed and the residue dissolved in dichloromethane and washed with water. The organic phase was dried on Na_2SO_4 , filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (Hex/Acetate/ CH_2Cl_2 7/2/1) to give the desired product in 67% yield (564 mg). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 10.00 (s, 1H) 7.47 (d, $J = 0.8$ Hz, 1H), 7.46–7.44 (m, 1H), 7.42–7.39 (m, 1H), 7.22–1.17 (m, 1H), 4.04 (t, $J = 6.6$ Hz, 2H), 1.89–1.73 (m, 2H), 1.55–1.43 (m, 2H), 1.37 (td, $J_1 = 7.1$ $J_2 = 3.6$, 5H), 0.93 (t, $J = 7.0$ Hz, 3H).

The precursor **I3** was then prepared as follows: A solution of 2,9-dimesityl-1,10-phenanthroline-5,6-dione (37 mg, 0.083 mmol), 3-(hexyloxy)benzaldehyde (29.5 mg, 0.108 mmol) and NH_4OAc (160 mg, 2.07 mmol) in 6 mL of glacial acetic acid was stirred under reflux overnight. After cooling to room temperature, water was added (15 mL) and the pale yellow precipitate was collected by filtration and washed with water. The crude product was dissolved in dichloromethane (30 mL) and washed twice with water (2x40mL). The organic phase was dried on Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 99 : 1$) affording the pure product as a yellow solid (30 mg, 50%). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6): δ ppm 13.96 (s broad, 1H), 9.01 (d, $J = 8.3$ Hz, 2H), 7.92 (d, $J = 7.8$ Hz, 1H), 7.85 (s, 1H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.96 (s, 4H), 4.08 (t, $J = 6.4$ Hz, 2H), 2.54 – 2.46 (m, 3H), 2.28 (s, 6H), 2.00 (s, 12H), 1.85 – 1.71 (m, 2H), 1.40 – 1.28 (m, 3H). $^{13}\text{C-NMR}$ (75 MHz, DMSO) δ 160.04, 157.83, 151.33, 144.26, 138.86, 137.51, 136.15, 132.35, 131.11, 130.87, 128.98, 125.34, 119.40, 116.20, 113.04, 68.49, 31.91, 29.85, 29.58, 26.13, 22.98, 21.60, 20.94, 14.81.

Synthesis of L3

A solution of **I3** (33.7 mg, 0.0532 mmol) and Cs_2CO_3 (110 mg, 0.340 mmol) in 4.8 mL of dry DMF was heated at 100 °C under argon for 30 minutes, and then *n*-hexyl iodide (0.024 mL, 0.165 mmol) was injected into the flask and the mixture was further stirred at 100 °C for 4 hours. After cooling to room temperature the solvent was removed and the crude product was purified by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 99.5/0.5$) to give **L3** (29.4 mg, 76%). $^1\text{H-NMR}$ (300 MHz, CD_2Cl_2): δ ppm 9.10 (d, $J = 8.2$ Hz, 1H), 8.69 (d, $J = 8.4$ Hz, 1H), 7.69–7.64 (m, 2H), 7.58 – 7.47 (m, 1H), 7.39 – 7.29 (m, 2H), 7.20 – 7.07 (m, 1H), 6.90 (s, 4H) 4.72 (t, $J = 7.4$ Hz, 2H), 4.12 (t, $J = 6.5$ Hz, 2H), 2.28 (s, 6H), 2.18 – 1.97 (m, 15H), 1.95 – 1.77 (m, 2H), 1.52–1.50 (m, 2H), 1.46 – 1.35 (m, 4H), 1.31–1.25 (m, 6H), 0.95 (t, $J = 6.9$ Hz, 3H), 0.86 (t, $J = 6.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 159.88, 158.93, 157.73, 154.11, 145.13, 144.65, 138.68, 138.17, 137.71, 137.52, 137.10, 136.20, 136.16, 132.39, 130.54, 130.16, 128.72, 128.56, 128.48, 125.49, 125.30, 124.42, 122.93, 122.22, 118.92, 116.43, 116.26, 68.73, 47.22, 31.98, 31.93, 31.42, 30.58, 29.62, 26.35, 26.10, 26.03, 23.01, 22.81, 21.14, 20.51, 20.46, 14.22, 14.19, 14.01. Elemental Analysis: Calcd. for $\text{C}_{49}\text{H}_{56}\text{N}_4\text{O}$: C, 82.08; H, 7.87; N, 7.81 Found. C, 82.20; H, 7.89; N, 7.80

Synthesis of copper complexes

The copper precursor $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ was obtained as described by Kubas G. et al [52] whereas the redox mediators (**E1/E2** and **E3/E4**) and **D1** were prepared as we previously reported [48]. The

new copper complexes **D2** and **D3** were synthesized as **D1**, introducing initially on copper the sterically hindered ligand.

Synthesis of **D2**

The 2,9-dimesityl-1,10-phenanthroline derivative **L2** (23 mg, 0.029 mmol) in 5 mL of dry DMF was added under argon to a solution of the Cu(I) precursor $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ (9.2 mg, 0.029 mmol) in dry DMF (5 mL). The mixture was stirred for 1 h at room temperature and then 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid (12.4 mg, 0.029 mmol) in dry DMF (3 mL) was added. The obtained red mixture was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure affording the desired product which was crystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (v/v 7/3) to give a red complex which was dried under vacuum (37 mg, 93% yield).

$^1\text{H-NMR}$ (400 MHz; MeOD): δ ppm 9.38 (d, $J = 8.2$ Hz, 1H), 9.23 (d, $J = 8.5$ Hz, 1H), 8.49 (s, 2H), 8.11-8.04 (m, 8H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.68 (s, 2H), 7.40 (t, $J = 7.7$ Hz, 5H), 7.32 – 7.13 (m, 9H), 6.45 (s, 2H), 6.43 (s, 2H), 4.96-4.94 (m, 2H), 3.01 (s, 2H), 2.87 (s, 2H), 2.21 – 2.01 (m, 8H), 1.86 (s, 3H), 1.85 (s, 3H), 1.43 – 1.17 (m, 11H), 0.98 – 0.78 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.89, 157.23, 156.95, 152.34, 150.13, 148.77, 146.98, 142.17, 141.88, 138.14, 138.05, 137.26, 136.97, 135.83, 134.81, 131.44, 130.78, 130.44, 129.41, 127.30, 126.85, 125.34, 124.13, 123.27, 123.09, 121.63, 121.23, 119.71, 116.97, 53.56, 53.29, 53.02, 52.75, 52.47, 48.34, 48.13, 47.92, 47.70, 47.49, 47.28, 47.06, 46.58, 31.34, 30.65, 29.65, 25.42, 25.10, 22.09, 19.76, 19.22, 12.9. Elemental Analysis: Calcd. for $\text{C}_{81}\text{H}_{73}\text{BCuF}_4\text{N}_7\text{O}_4$: C 71.60, H 5.41, N 7.22. Found: C 71.77, H 5.41, N 7.29. MS (ESI+FTICR) $\text{C}_{81}\text{H}_{73}\text{CuN}_7\text{O}_4^+$ m/z: 1270.5052

Synthesis of **D3**

The 2,9-dimesityl-1,10-phenanthroline derivative **L3** (20.5 mg, 0.028 mmol) in 5 mL of dry DMF was added under argon to a solution of Cu(I) precursor $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ (9.3 mg, 0.028 mmol) in dry DMF (5 mL). The mixture was stirred for 1 h at room temperature and then 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid (12.2 mg, 0.028 mmol) in dry DMF (8 mL) was added. The obtained red mixture was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure affording the desired product which was crystallized from DCM/MeOH (v/v 7/3) to give a red complex which was dried under vacuum (36 mg, 98% yield). $^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 9.43 (d, $J = 8.2$ Hz, 1H), 9.01 (d, $J = 8.6$ Hz, 1H), 8.14 (s, 2H), 8.06 – 7.86 (m, 6H), 7.63-7.54 (m, 4H), 7.39 (s, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 6.44 (d, $J = 4.4$ Hz, 4H), 4.84 (s, 2H), 4.14 (t, $J = 6.3$ Hz, 2H), 2.96-2.95 (m, 2H), 2.16 (s 6H), 1.89 (s, 6H), 1.77 (s, 9H), 1.63 – 1.20 (m, 17H), 1.06 – 0.67 (m, 8H). $^{13}\text{C-NMR}$ (100 MHz; CD_2Cl_2): δ 200.41, 160.02, 158.06, 157.80, 157.04, 155.59, 152.37, 148.92, 142.72, 142.25, 138.62, 138.48, 137.70, 137.31, 136.98, 135.36, 132.29, 131.43, 130.48, 130.37, 129.35, 127.83, 127.13, 125.64, 124.30, 123.70, 122.15, 120.24, 117.17, 116.79, 116.51, 68.82, 54.53, 54.17, 53.81, 53.45, 53.09, 51.22, 50.38, 47.41, 37.24, 36.76, 32.30, 31.98, 31.39, 30.61, 30.06, 29.60, 26.37, 26.20, 26.10, 25.07, 23.02, 22.83, 20.98, 20.29, 14.20, 14.02. Elemental Analysis: Calcd. for $\text{C}_{75}\text{H}_{76}\text{BCuF}_4\text{N}_6\text{O}_5$: C 69.73, H 5.93, N 6.51 Found: C 69.78, H 5.95, N 6.52. MS (ESI+FTICR) $\text{C}_{75}\text{H}_{76}\text{CuN}_6\text{O}_5^+$ m/z: 1203.5185

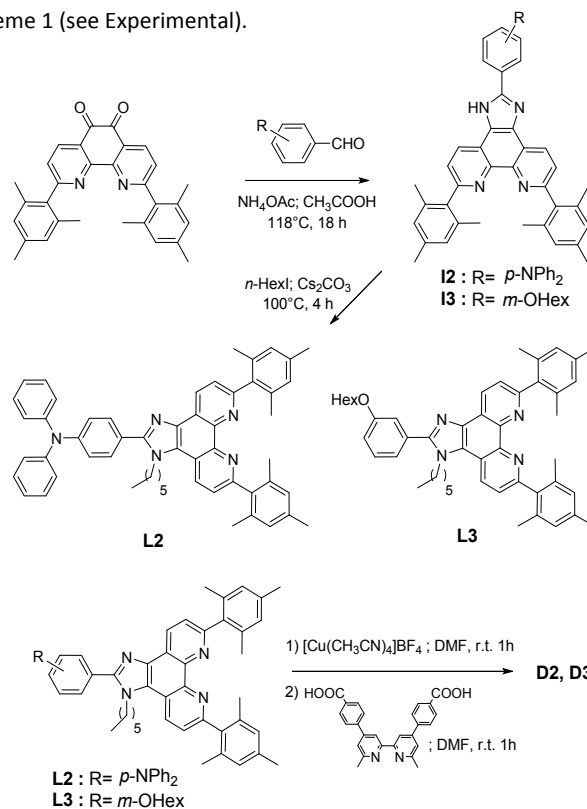
DFT modeling

All the calculations were performed with Gaussian09 (G09), without any symmetry constraints [53]. The molecular geometry of **D1-D3** dyes has been optimized by using a 6-311G** basis set [54] and the PBE0 exchange–correlation (xc) functional [55] integrated with the

D3-BJ model to include the dispersion interactions [56]. We optimized the geometries in dichloromethane solution including solvation effects by means of the conductor-like polarizable continuum model (C-PCM) as implemented in G09 [57]. TDDFT calculations of the lowest singlet-singlet excitations were performed in dichloromethane solution using the PBE0 xc functional and the 6311g** basis set. The non equilibrium version of C-PCM was employed for TDDFT calculations, as implemented in G09 [58]. To simulate the optical spectra, the 40 lowest spin-allowed singlet-singlet transitions were computed on the ground state geometry. Transition energies and oscillator strengths were interpolated by a Gaussian convolution with a σ value of 0.12 eV.

Results and discussion

We prepared, with the HETPHEN synthetic method [59], the new copper(I) dyes **D2** and **D3** (Chart 1) bearing one π -delocalized 2,9-dimesityl-1,10-phenanthroline (**L2** and **L3**), where the mesityl groups provide enough steric hindrance to avoid the formation of homoleptic complexes and prevent geometric changes, and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid, chosen as anchoring ligand because the related homoleptic copper complex had a high efficiency as dye [29]. The alkylation of the imidazole is important to improve the solubility and to avoid the easy deprotonation of the NH group; in addition, the presence of a long alkyl chain inhibits the dye aggregation on the semiconductor surface [24] and protects the surface of the semi-conductor preventing the reaction between the oxidized form of the redox mediator and the electrons injected in the TiO_2 conduction band. The new ligands and related copper(I) dyes can be easily prepared following the pathways shown in Scheme 1 (see Experimental).



Scheme 1: Synthesis of ligands **L2-L3** and related complexes **D2-D3**.

The performance of **D1**, **D2** and **D3** in DSSCs was investigated in the presence of three different electrolytes, namely the common I^-/I_3^- electrolyte and two couples of copper electron shuttles (**E1/E2** and **E3/E4**, Chart 1), prepared as previously reported [48].

The UV-visible absorption spectrum of **D1**, **D2** and **D3** in CH_2Cl_2 are shown in Figure 1 along with that of **E3**, for comparison.

As expected for the increase of the π -conjugation of the ancillary ligands, the band at 478 nm of **D1** becomes more intense and is red-shifted on going to **D2** and **D3** (Table 1), justifying their use in the design of dyes for DSSCs.

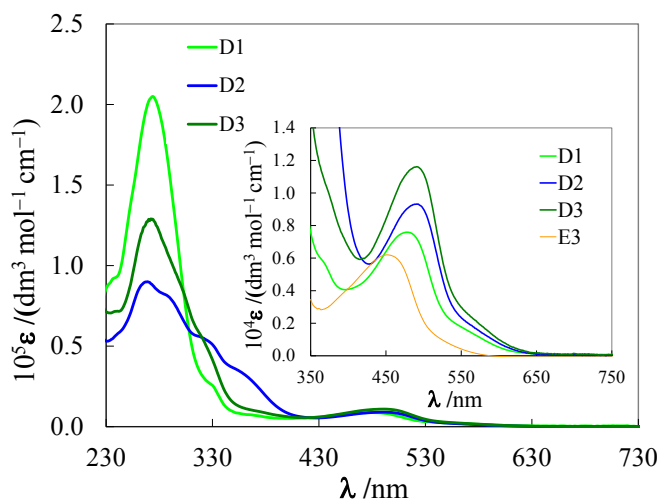


Figure 1. UV-Vis absorption spectra for **D1-D3** Cu(I) dyes in CH_2Cl_2 . Inset: magnification of the visible window with, for sake of comparison, absorption spectrum of Cu(I)-based redox mediator **E3**.

To understand the effect of different ligands in **D1-D3** dyes, we investigated the structural, electronic and optical properties of the experimentally characterized complexes by means of DFT. The optimized molecular geometry of **D1-D3** complexes core is quite similar (Figure 2), with Cu-N distances in between 2.04-2.05 Å. The Cu centre shows a distorted octahedral coordination related to the presence of the mesityl substituents of the phenanthroline, that are oriented in such a way to π -stack to the bipyridyl rings, thus inducing a strain in the bipyridine. We analysed the frontier molecular orbitals in terms of energy levels and electron density delocalization. In Figure 2 the energy level of frontier molecular orbitals and the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) isodensity surface plots are reported. The HOMO-LUMO gap energy is almost coincident in the three dyes (**D1**=2.94 eV, **D2**=2.98 eV; **D3**=2.99 eV).

The HOMO/HOMO-2 of **D1** and **D3** are mainly d-states of the Cu centre, while in **D2**, the triphenylamino substituent orbital insert as HOMO-2 among the d-type Cu orbitals. In **D1-D3** the LUMO is delocalized on the bipyridine ligand, while the LUMO+1 is a π^* orbital of the phenanthroline ligand. The LUMOs of the three dyes show substantial contribution from the COOH groups which is a

prerequisite for an effective charge injection from the dye excited state to the TiO_2 conduction band.

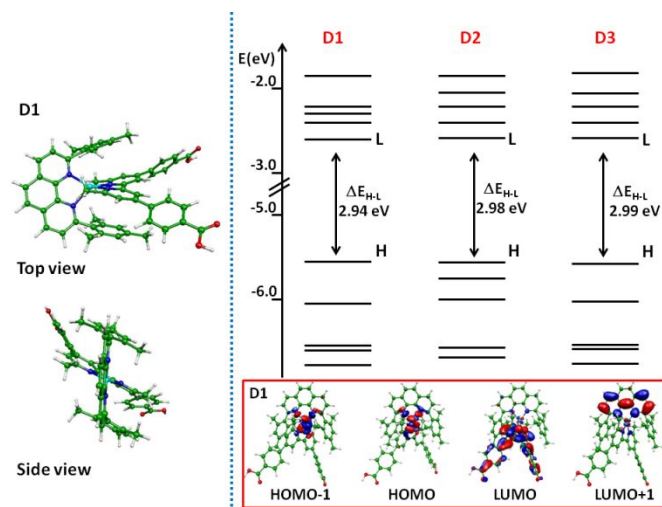


Figure 2. Left: top and side views of **D1** optimized geometry. Right: schematic representation of the energy levels of the frontier molecular orbitals of **D1-D3** dyes along with the isodensity surface plots of **D1** HOMO-1, HOMO, LUMO and LUMO+1 (isodensity contour=0.3).

The absorption spectra of **D1-D3** sensitizers have been simulated to assign the lowest absorption bands in the visible region. In Figure 3 the simulated absorption spectra for the **D1-D3** dyes are reported. The computed spectra satisfactorily reproduce the main visible absorption band of the experimental spectra. The maxima of the simulated spectra have been computed at 495 nm, 508 nm and 501 nm from **D1** to **D3**, in good agreement with the experimental λ_{max} , see Table 1. Also the experimental shoulder at lower energies is well reproduced even though this feature is slightly red shifted and its intensity partly overestimated. In the three dyes the main absorption band is originated by an electronic transition having as starting state HOMO-1 (Cu d orbital) and as final states both LUMO and LUMO+1 (delocalized on bipyridine and phenanthroline, respectively). This intense transition has a MLL'CT transition from Cu to bipyridine and phenanthroline. Also the shoulder shows a MLL'CT character involving the same final state of the main absorption band but having as starting state the HOMO of Cu character.

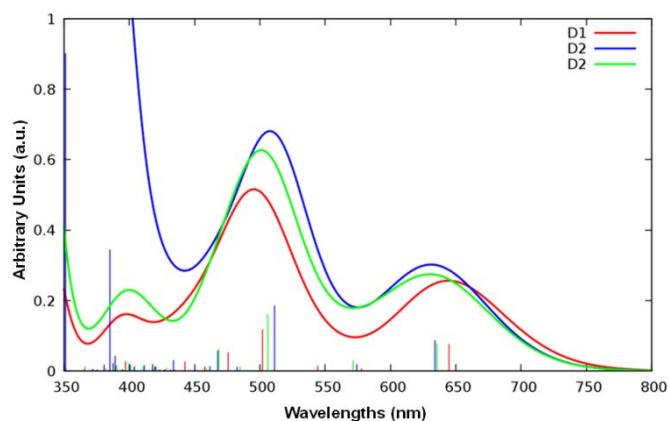


Figure 3. TDDFT computed absorption spectra and computed energy and oscillator strengths excitations of **D1** (red), **D2** (blue) and **D3** (green).

A cyclic voltammetry study (CV) on glassy carbon electrode (GC) was performed to clarify the electrochemical behaviour of the dyes and the redox couples (Table 1). Clearly the nature of the ancillary ligand in the investigated dyes has a negligible effect on the oxidation potential of the copper(I) center.

Table 1. Key optical absorption and cyclovoltammetric data for the investigated complexes.

	λ_{\max} /nm ($10^3 \epsilon$ /M ⁻¹ cm ⁻¹)	$E_{1/2,ox}$ /V vs Fc ⁺ /Fc ^a	HOMO /eV ^b
D1 ^c	478 (7.6) ^d	0.39 ^f	-5.19
D2	491 (9.3) ^d	0.39 ^g	-5.19
D3	490 (12) ^d	0.39 ^h	-5.19
E1 ^c	455 (8.0) ^e	0.30 ^h	-5.10
E2 ^c	741 (0.23) ^e	0.04 ^h	-4.84
E3 ^c	452 (6.2) ^e	0.11 ^h	-4.91
E4 ^c	756 (0.096) ^e	0.11 ^h	-4.91

^aWith [NBu₄][PF₆] 0.1 M, on GC electrode at 0.2 V s⁻¹. ^bHOMO = -e[E_{1/2,ox}+4.8]. e=unitary charge; 4.8 = potential of Fc⁺/Fc couple versus vacuum [60]. ^cReference 48. ^dIn CH₂Cl₂. ^eIn CH₃CN. ^fIn CH₃CN/CH₂Cl₂ 25/1, E_{1/2} Fc⁺/Fc = 0.40 V vs SCE. ^gIn CH₃CN/CH₂Cl₂ 2.4:1, E_{1/2}(Fc⁺/Fc)=0.427V vs SCE; there is a second oxidation process at 0.62 V probably associated with oxidation of the Ph₂N unit, as previously reported for a similar complex [36]. ^hIn CH₃CN, E_{1/2} Fc⁺/Fc = 0.39 V vs SCE.

The level energy matching between all the investigated dyes and the Cu-based redox mediators is promising, being the driving force for dye regeneration 0.09 eV and 0.28 eV for **E1/E2** and **E3/E4**, respectively (Table 1).

Dye-sensitized solar cells were fabricated using FTO glass coated TiO₂ sensitized with **D1**, **D2** or **D3** as photoanode, a platinized FTO as counter electrode and an electrolyte solution containing I⁻/I₃⁻, **E1/E2** or **E3/E4** as redox couple (see ESI). They were fully masked [61]. Results of the investigated thin film DSSCs are presented in Table 2 together with those obtained with the Ru(II) benchmark **N719**. In addition to the absolute photo-conversion efficiency (η), Table 2 reports the efficiency relative to a cell based on N719 dye and I⁻/I₃⁻ electrolyte set at 100% (η_{rel}).

Table 2. Main PV parameters of the DSSCs based on copper dyes **D1** – **D3** in comparison with the benchmark **N719**.^a

Dye	Electrolyte	j_{sc} /mA cm ⁻²	V_{oc} /mV	FF	$\eta\%$	$\eta_{rel}\%b$
N719	I ⁻ /I ₃ ⁻ ^c	15.4 ^d	802	71	8.9	100 %
D1	I ⁻ /I ₃ ⁻ ^c	6.1 (4.7) ^d	592 (571)	71 (74)	2.5 (2.0)	28 % (22 %)
D2	I ⁻ /I ₃ ⁻ ^c	5.6 (5.2) ^d	602 (607)	75 (75)	2.5 (2.3)	28 % (26 %)
D3	I ⁻ /I ₃ ⁻ ^c	5.8 (5.6) ^d	597 (599)	74 (72)	2.6 (2.4)	29 % (27 %)
D1	E1/E2 ^e	2.9	694	36	0.7	8.0 %
D2	E1/E2 ^e	2.6	647	35	0.6	6.5 %
D3	E1/E2 ^e	0.9	370	37	0.1	1.3 %
D1	E3/E4 ^e	3.8	593	61	1.4	16 %
D2	E3/E4 ^e	3.2	570	67	1.2	13 %
D3	E3/E4 ^e	2.8	573	62	1.0	11 %

^a In the presence of a 16mm² black mask. ^bRelative efficiency respect to a N719-sensitized control cell set at 100%. ^c0.28M *tert*-butylpyridine in 15/85 (v/v) mixture of valeronitrile/acetonitrile; 0.65M *N*-methyl-*N*-butylimidazolium iodide, 0.025M LiI, 0.04M iodine. ^d0.05M guanidinium thiocyanate is present. ^e0.17M Cu(I) : 0.017M Cu(II) + 0.1M LiTFSI in CH₃CN.

It turned out that the dye-sensitized solar cells containing I⁻/I₃⁻ as redox shuttle and the novel heteroleptic copper complexes **D2** and **D3** as dyes have a photo-conversion efficiency similar to that reached with **D1** despite the higher π -delocalization of their ancillary ligand. Their slightly larger fill factor (FF) is counterbalanced by a slightly lower photocurrent density (j_{sc}) whereas their V_{oc} is similar (Table 2). When guanidinium thiocyanate was added in the electrolyte solution, the photo-conversion efficiency decreases slightly due to a lower j_{sc} , especially in the case of **D1** (Table 2), confirming its negative effect in the optimization of the electrolyte solution for efficient Cu(I) based DSSCs [29]. Interestingly, the three dyes are much more performing than the related heteroleptic complex bearing 2,2'-biquinoline-4,4'-dicarboxylic acid as anchoring ligand and the same ancillary ligand of **D1** (2,9-dimesityl-1,10-phenanthroline) (η = 0.49%; η_{rel} = 7.5%) or an ancillary ligand quite similar to that of **D2** but with a dianisylamino group instead of the diphenylamino substituent (η = 0.22%; η_{rel} = 3.4%) [24], mainly due to a much higher j_{sc} , confirming the particular goodness of 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid to anchor the dye on the titania surface [29, 48]. Substitution of the common I⁻/I₃⁻ redox couple by the **E1/E2** couple leads to a significant drop of the DSSCs performance efficiency, the effect being more pronounced for **D3** (Table 2). However, the use of the **E3/E4** couple gives good efficiencies for the three dyes (1.0-1.4 %; η_{rel} = 11-16 %) due to much better j_{sc} and FF . The lower short-circuit photocurrent observed with the **E1/E2** couple can be attributed to a more competitive light harvesting with the dyes, as indicated by a higher molar extinction coefficient of the absorption band around 450 nm (Table 1) [48].

The incident monochromatic photon-to-current conversion

efficiency of some investigated DSSCs are shown in Figure 4. The IPCE data agree with the current/voltage measurements (Table 2).

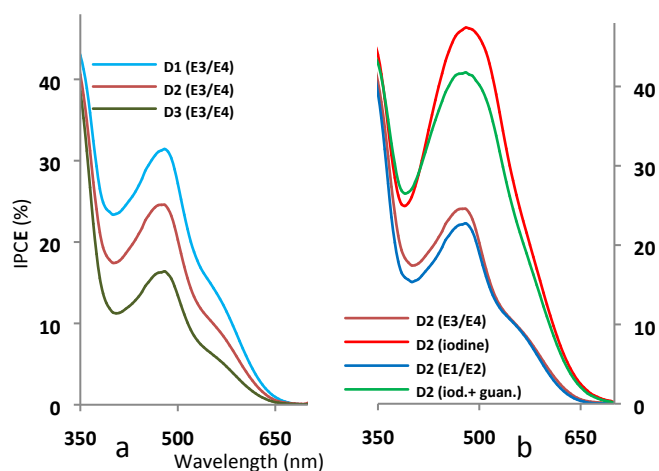


Figure 4. IPCE of DSSCs: a) sensitized by dyes **D1** – **D3** in the presence of copper based electrolyte **E3/E4**; b) sensitized by **D2** in the presence of different electrolytes.

The **D1** based device showed the most intense external quantum efficiency (~30% in the 450 – 500 nm region), when the copper based redox couple **E3/E4** was employed (Figure 4a). In these conditions the IPCE results do not reproduce the trend of the UV spectra (Figure 1) suggesting that when copper based electrolytes are used the light harvesting capability of the dye is not the most important feature in order to improve the photo-current. Regarding the **D2** based devices (Figure 4b), the best IPCE was reached in the presence of a classic I^-/I_3^- redox shuttle, with a maximum value of ~50% in the 450 – 500 nm region. All the other electrolytes tested produced a significant decrease of the performances.

Conclusions

In this work two new heteroleptic copper(I) sensitizers bearing a π -delocalized 2-(R-phenyl)-1*H*-phenanthro[9,10-*d*]imidazole (R = NPh₂ or OHexyl) ancillary ligand were prepared and well characterized. Both of them, like the related complex bearing 2,9-dimesityl-1,10-phenanthroline as ancillary ligand, can be coupled with the common I^-/I_3^- redox couple to prepare DSSCs with a good efficiency. They can also be combined with homoleptic copper redox couples to afford full-copper DSSCs with fair to good performance, depending on the nature of the electron shuttle.

It appears that, in copper(I) dyes, the use of π -delocalized ancillary ligands is not sufficient to improve drastically light harvesting, electron transfer enhancement from electrolyte to dye and directionality for electron injection in the TiO₂ conduction band.

TDDFT calculations assign the main absorption band as a MLCT involving not only the bipyridine but also the phenanthroline ligand which upon TiO₂ sensitization should point in the opposite way of the TiO₂ surface. Such phenanthroline involvement in the excited state originating visible light absorption becomes therefore detrimental implying a reduction in the charge transfer directionality. Further investigation on the tuning of this class of

compounds should point to up-shift the phenanthroline-based LUMOs by electron donating ligands, for instance, to avoid interfere on the low-lying MLCT transitions.

Nevertheless, this study confirms the potential of full-copper DSSCs, consolidating the way to DSSCs with earth-abundant components. Future work should be devoted also to increase the solar light harvesting of the copper(I)-based DSSCs, may be by co-sensitization [62], and to check the effect of the concentration of the copper-based electrolytes and of additives such as *tert*-butylpyridine.

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Journal Name

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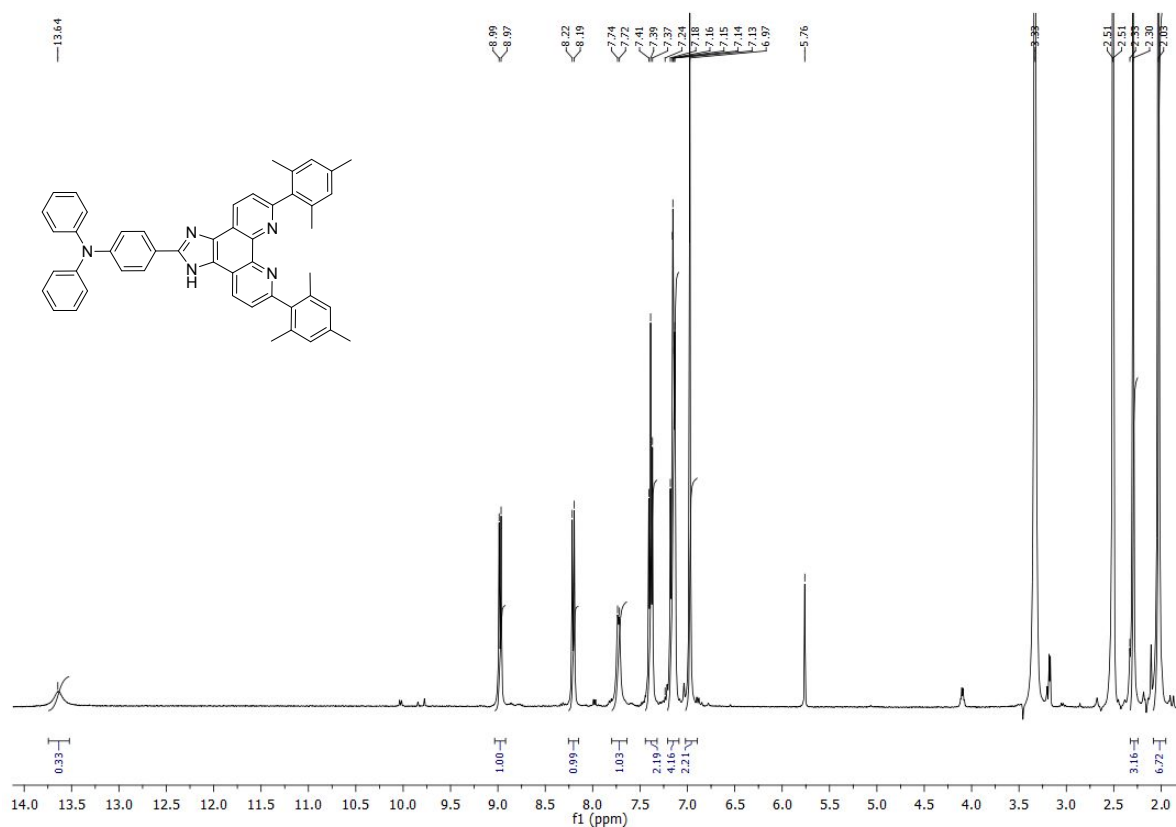
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Electronic supplementary information

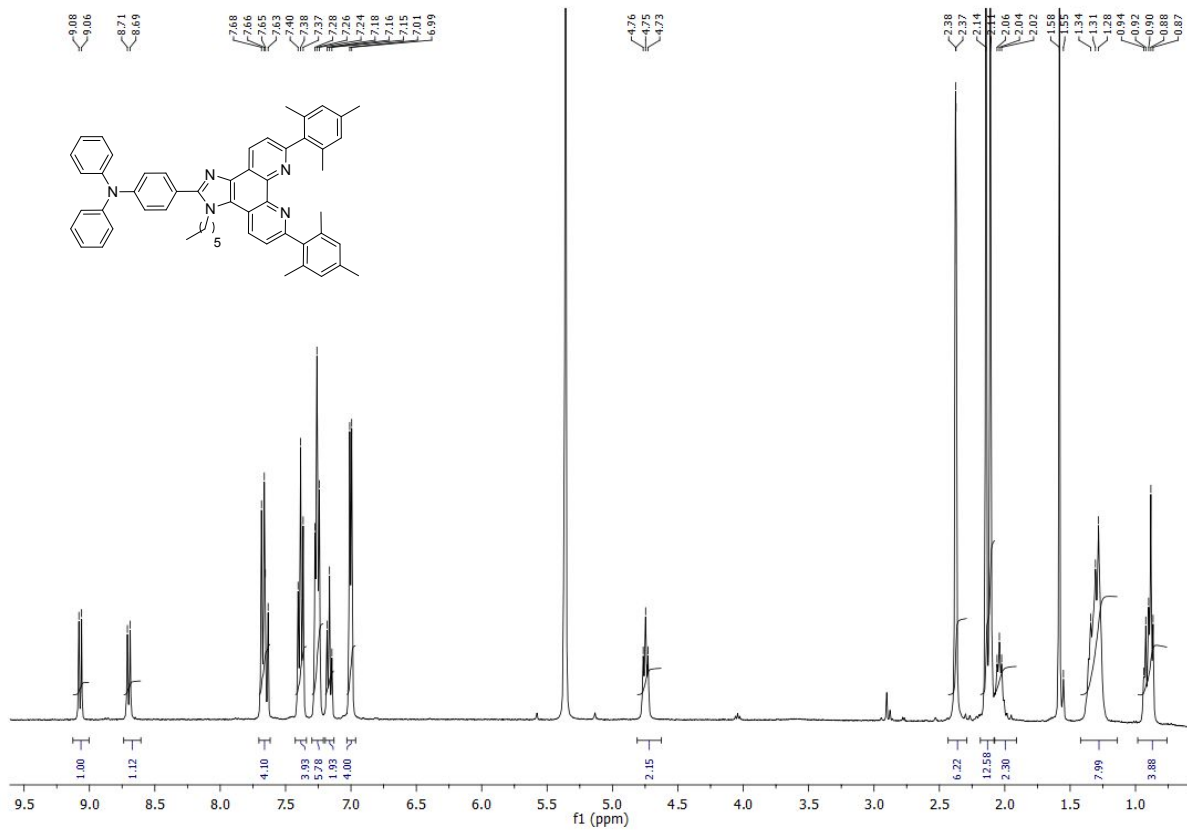
Towards efficient sustainable full-copper dye-sensitized solar cells

Claudia Dragonetti, Mirko Magni, Alessia Colombo, Francesco Fagnani, Dominique Roberto, Fabio Melchiorre, Paolo Biagini and Simona Fantacci

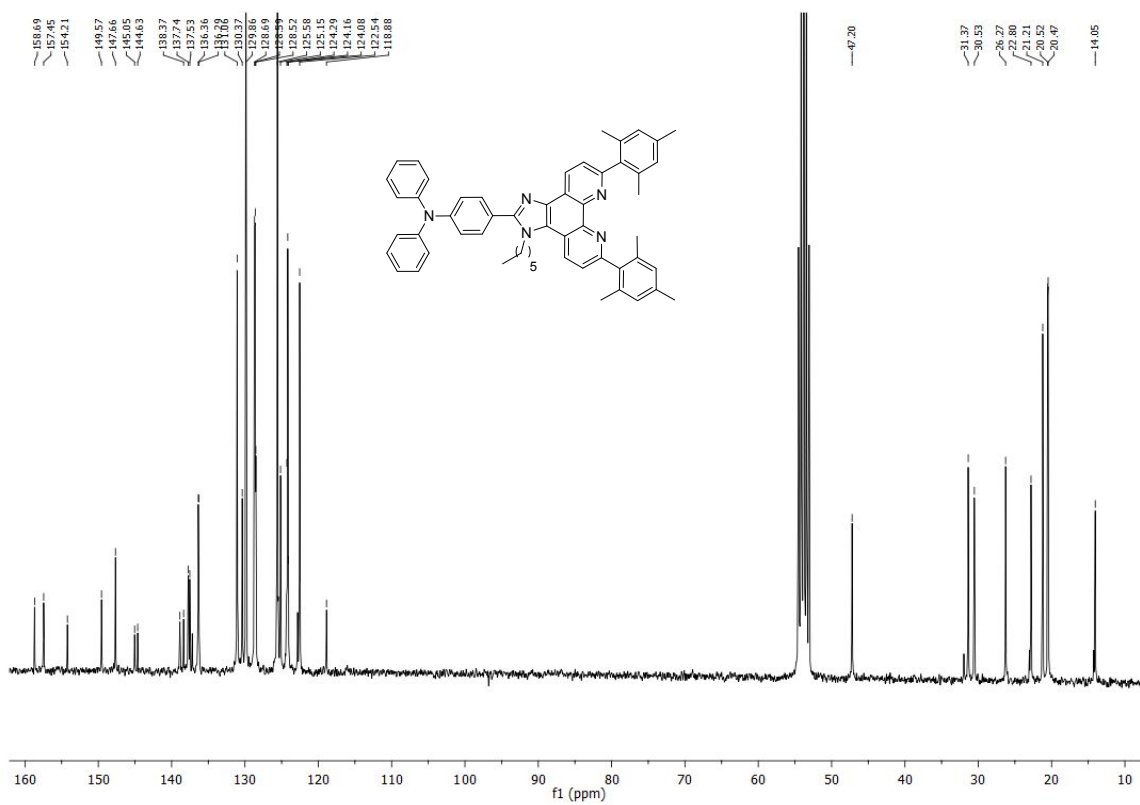
1. NMR of precursors (**I2**, **I3**) and ligands (**L2**, **L3**)

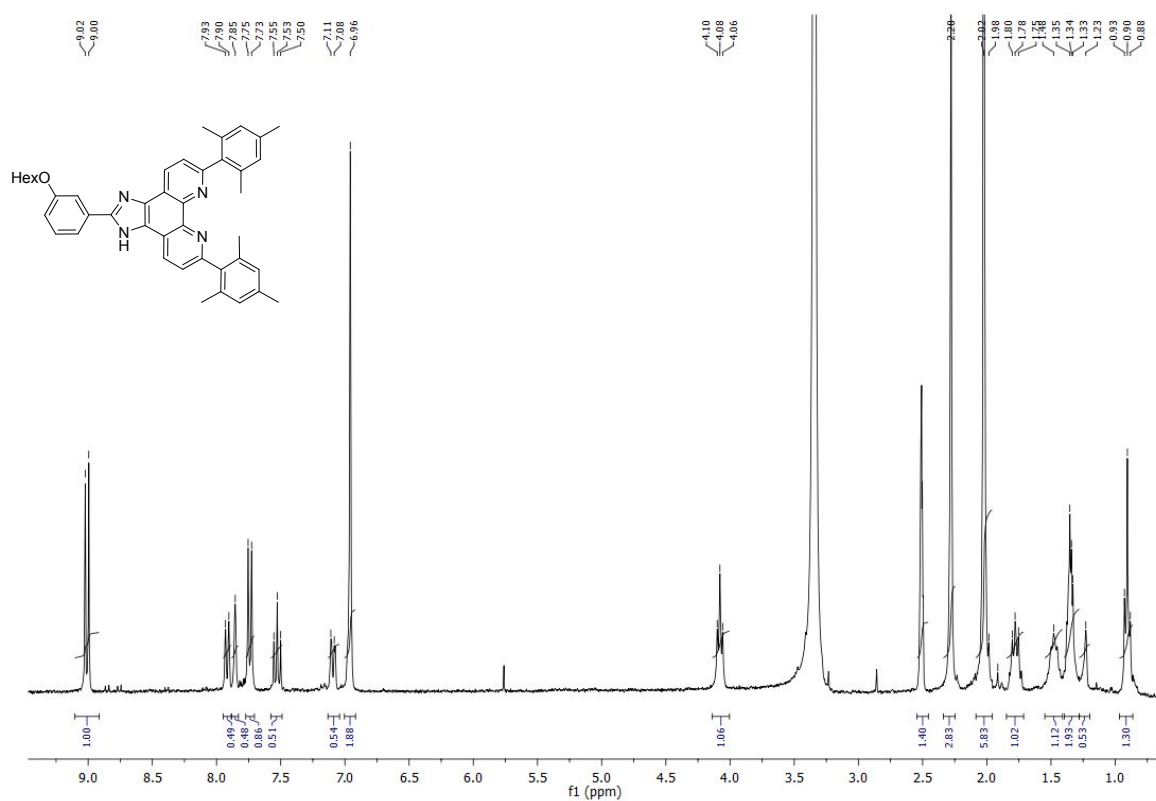
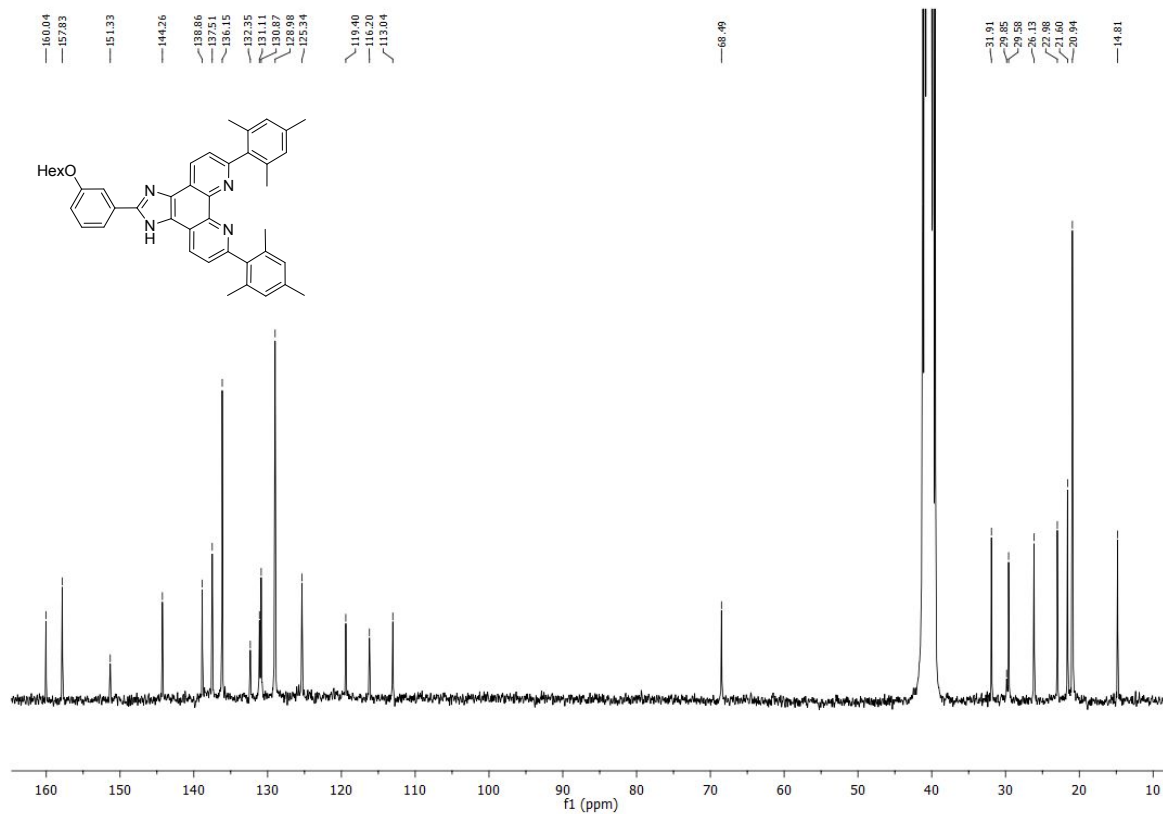


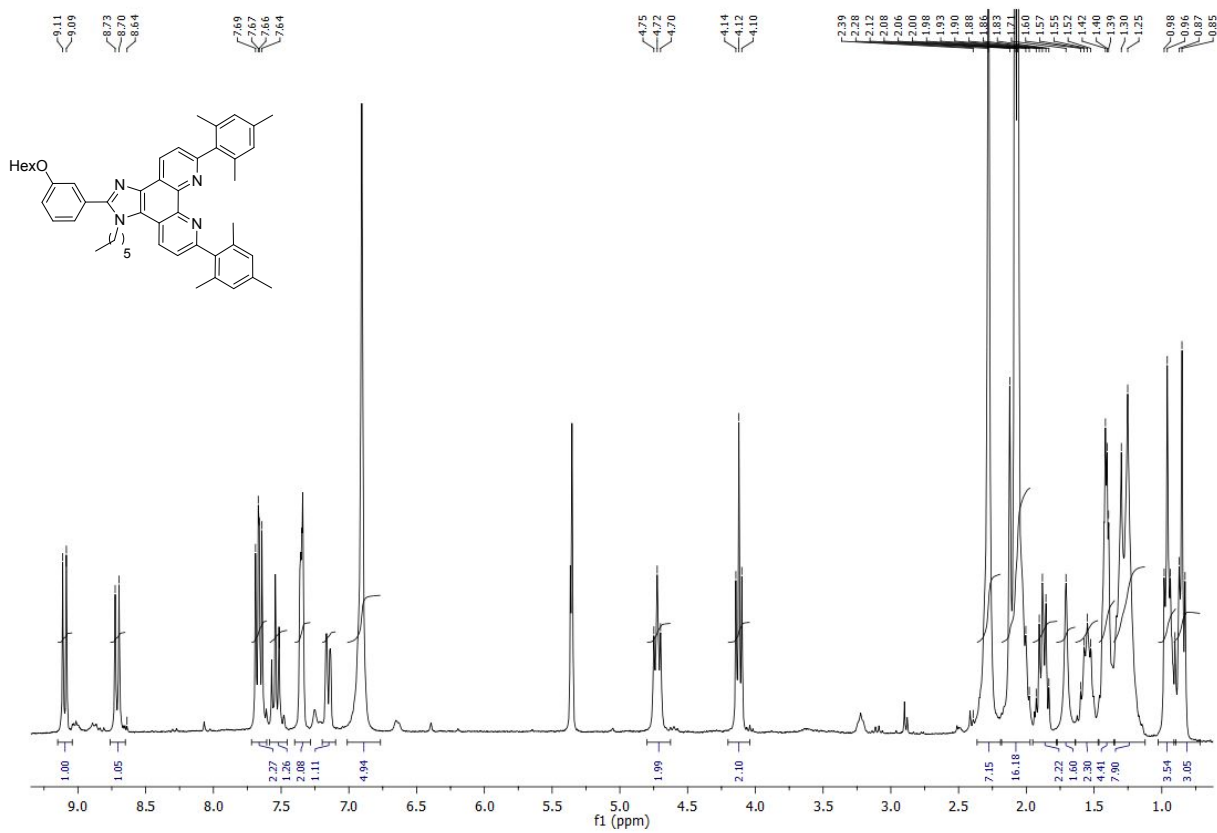
¹H-NMR (400 MHz, DMSO-d₆) of the precursor **I2**

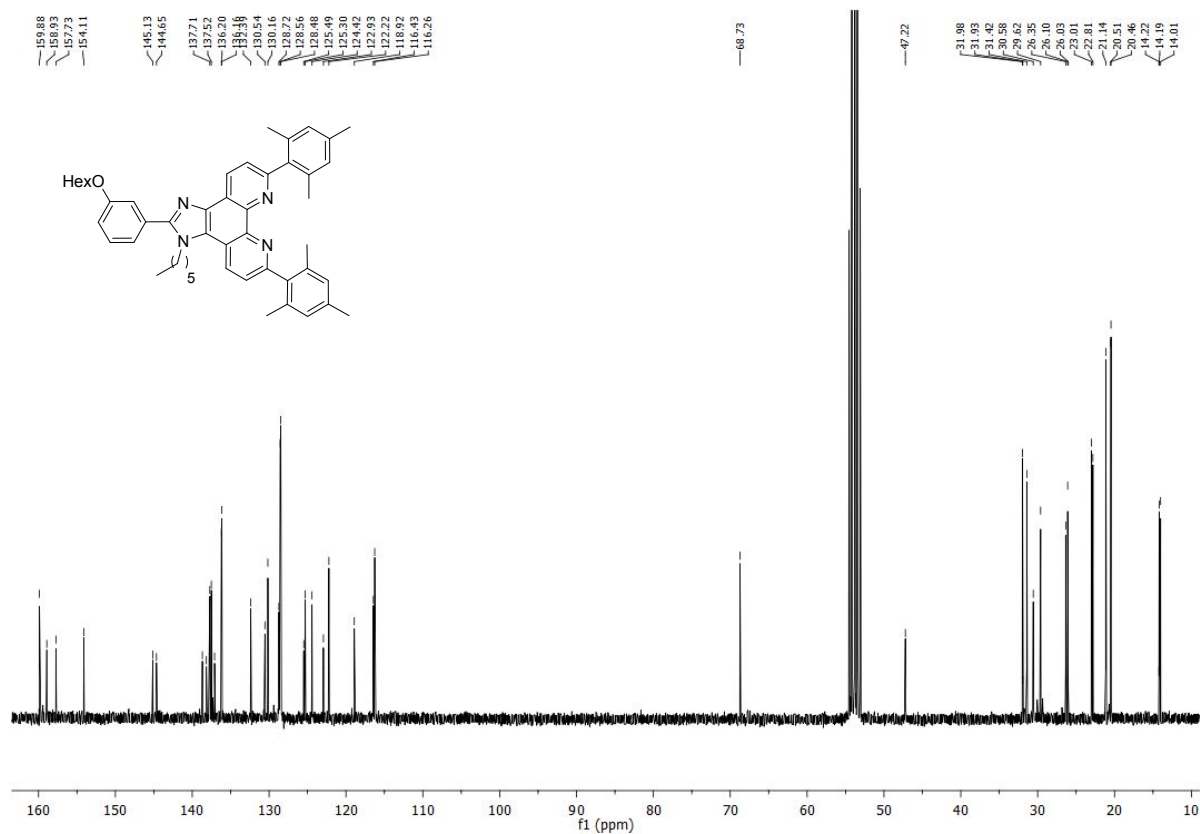


¹H-NMR (400MHz) in CD₂Cl₂ of the ligand L2



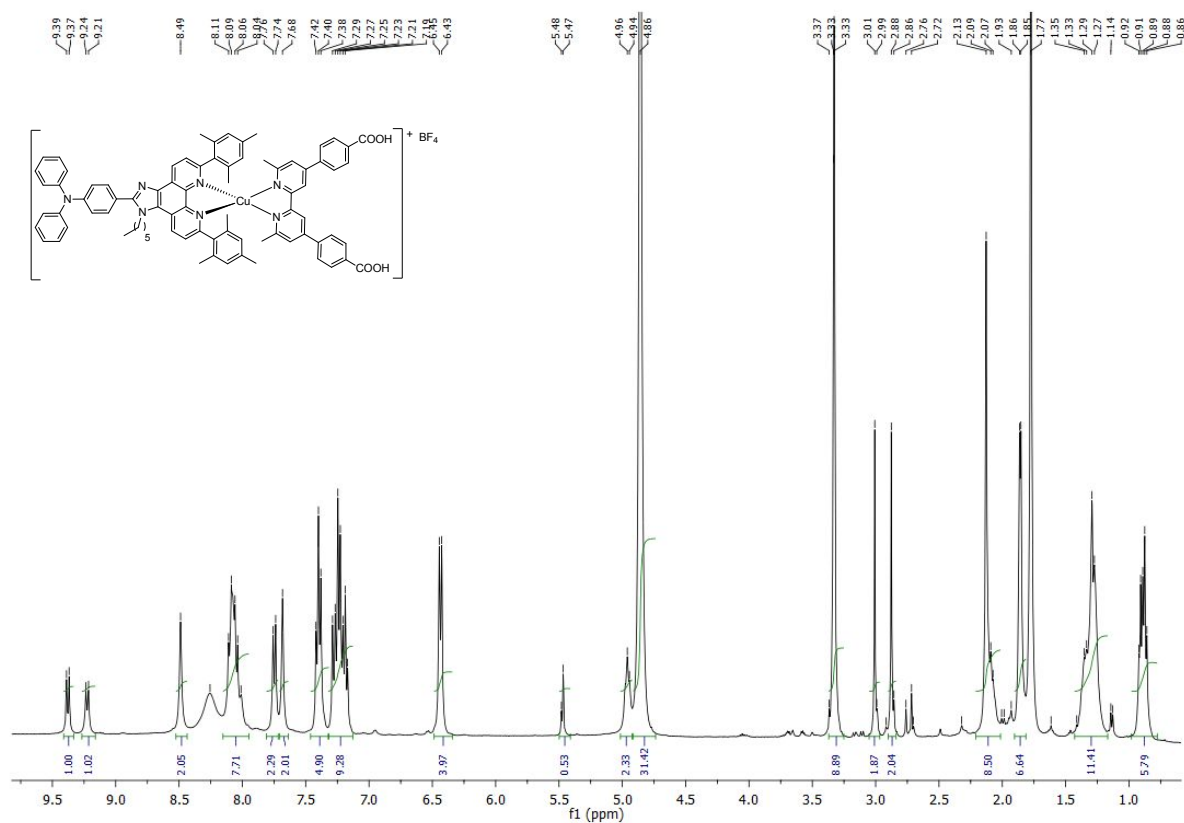
$^{13}\text{C-NMR}$ (75MHz) in DMSO of the Ligand **L2** $^1\text{H-NMR}$ (300MHz) in DMSO of the precursor **I3**

^{13}C -NMR (75 MHz) DMSO of the precursor **I3** ^1H -NMR (300MHz, CD_2Cl_2) of the ligand **L3**

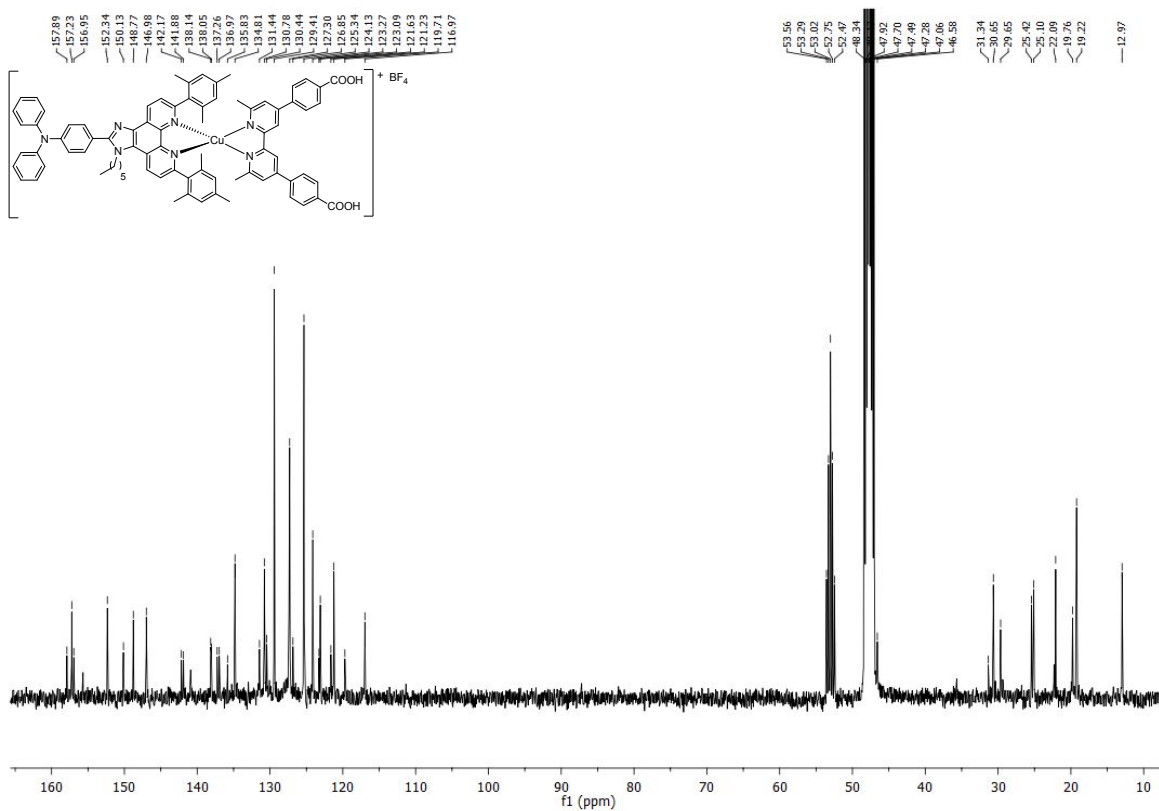


¹³C-NMR (75 MHz) CDCl₃ of the ligand **L3**

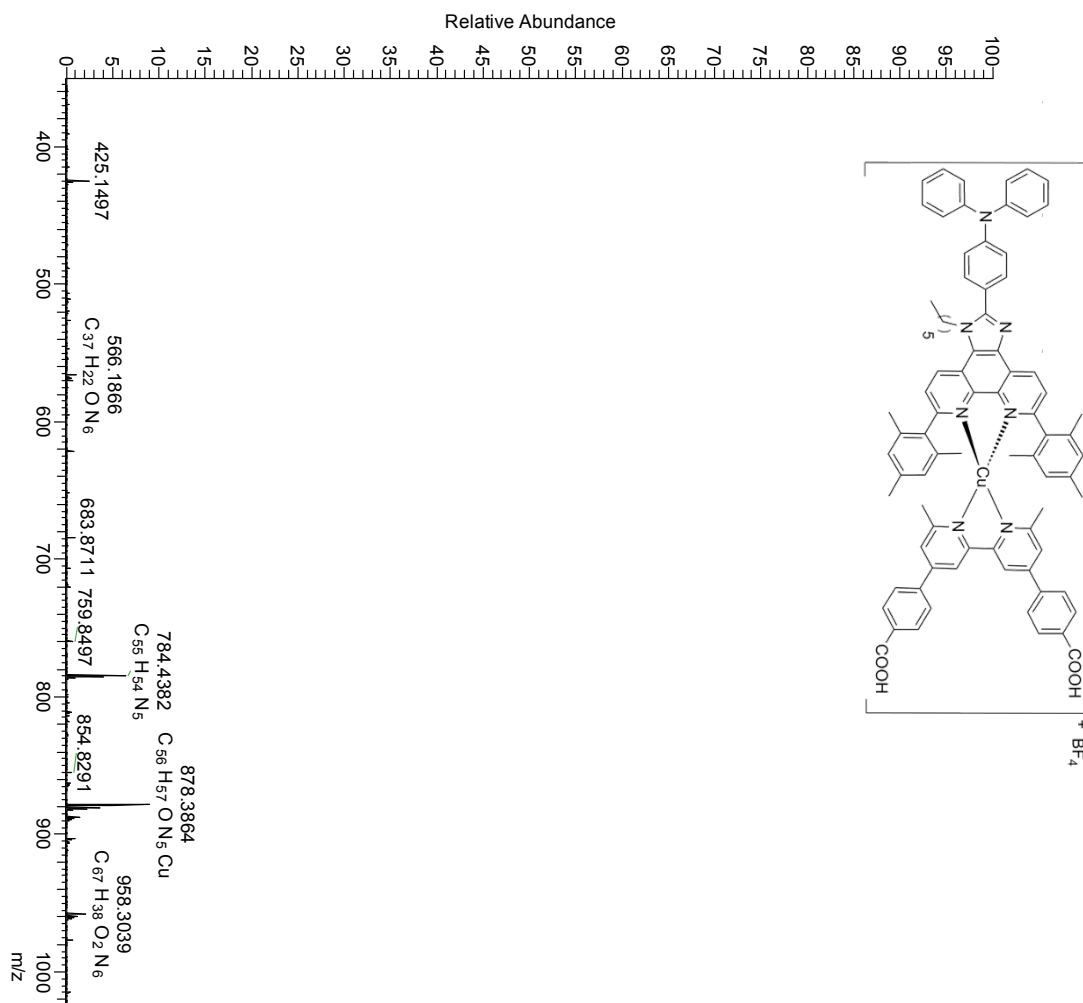
2. NMR and mass spectra of complexes **D2** and **D3**



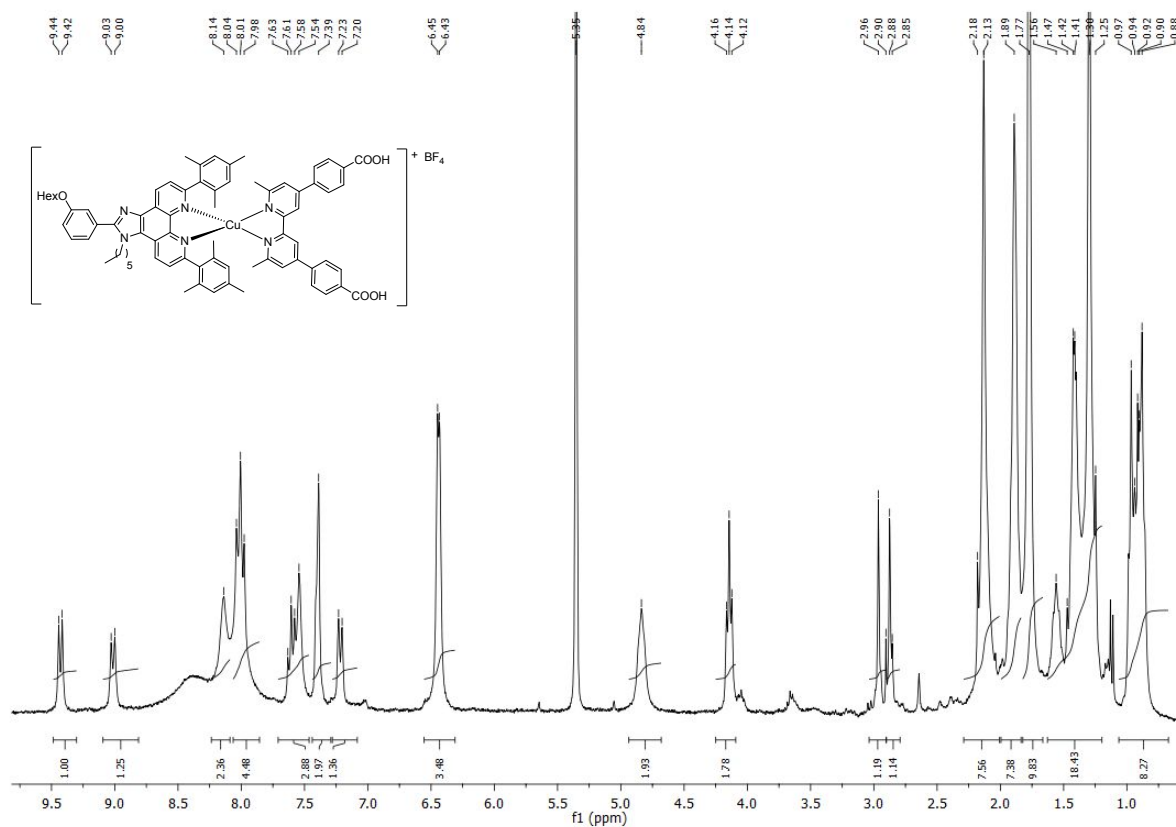
¹H-NMR (400MHz) in CD₃OD of complex **D2**



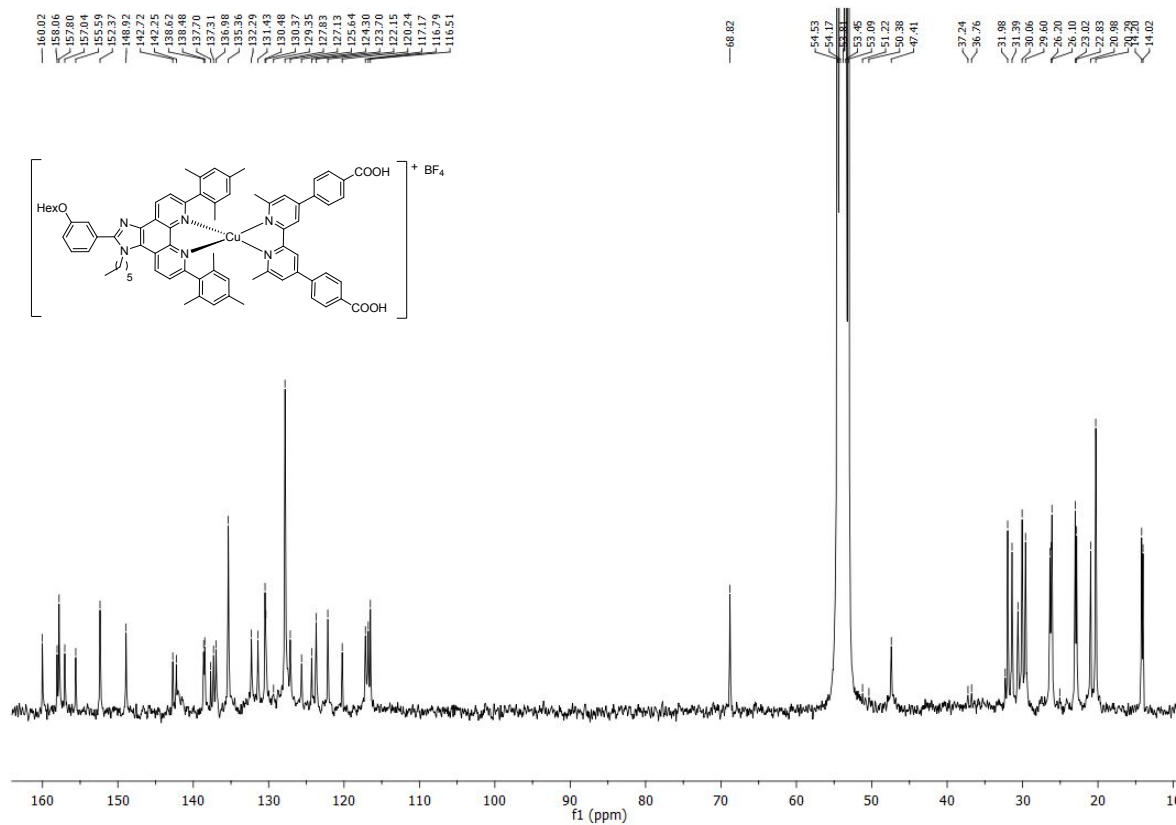
$^{13}\text{C-NMR}$ (100MHz) in CD_3OD of complex **D2**



MS (ESI+FTICR) of complex **D2**



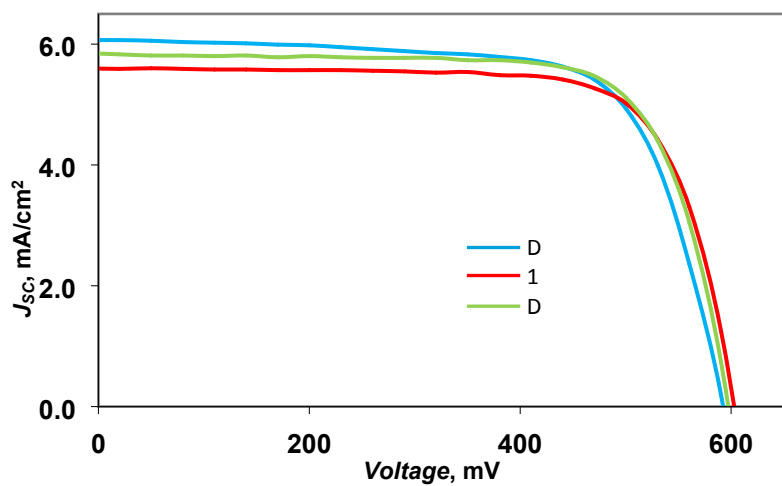
$^1\text{H-NMR}$ (400MHz) in CD_2Cl_2 of complex **D3**



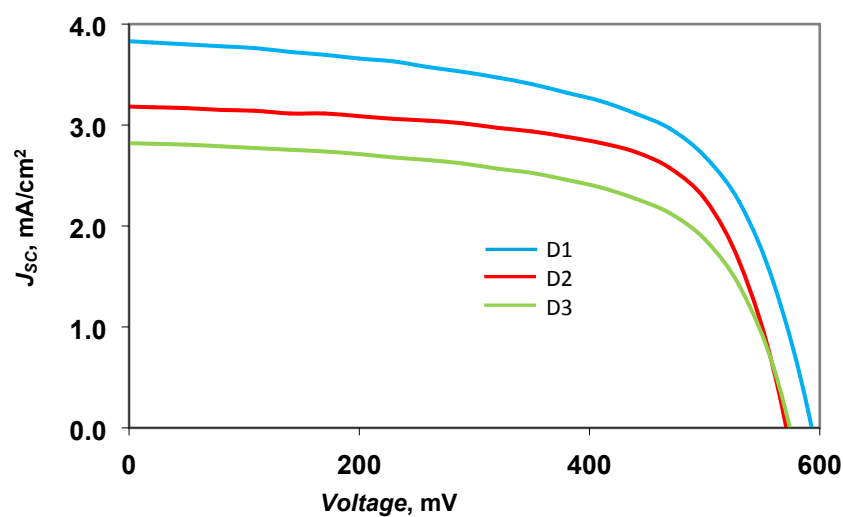
$^{13}\text{C-NMR}$ (100MHz) in CD_2Cl_2 of complex **D3**

3. Fabrication and evaluation of solar cells.¹

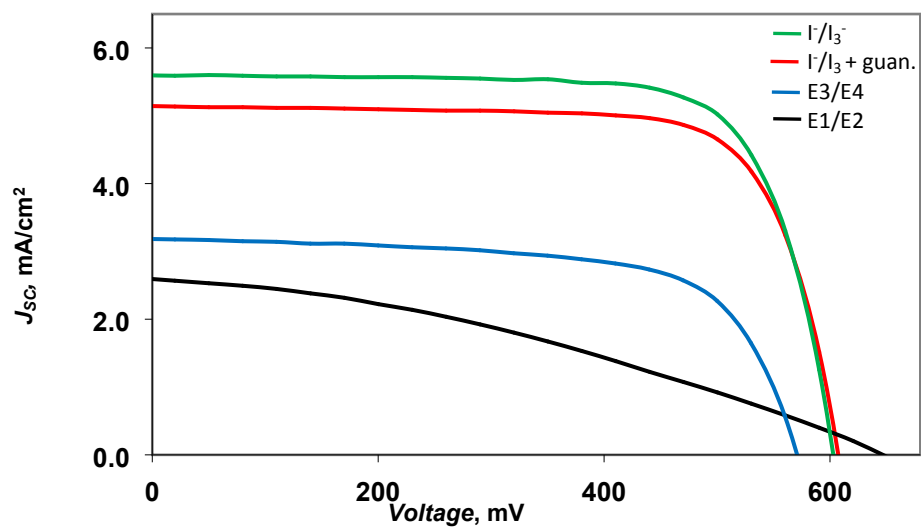
TiO₂ electrodes were prepared by spreading (doctor blading) a colloidal TiO₂ paste (20 nm sized; “Dyesol” DSL 18NR-T) onto a conducting glass slide (FTO, Hartford glass company, TEC 8, with a thickness of 2.3 mm and a sheet resistance in the range 6 - 9 Ω/cm²) that had been cleaned with water and EtOH, treated with a plasma cleaner at 100 W for 10 min, dipped in aqueous TiCl₄ solution (4.5 x 10⁻² M), at 70°C, for 30 minutes, and washed with ethanol. After a first drying at 125 °C for 15 min, a reflecting scattering layer containing >100 nm sized TiO₂ (“Solaronix” Ti-Nanoxide R/SP) was bladed over the first TiO₂ coat and sintered till 500 °C for 30 min. Then the glass coated TiO₂ was dipped again into a freshly prepared aqueous TiCl₄ solution (4.5 x 10⁻² M), at 70°C for 30 minutes, washed with ethanol and heated once more at 500 °C for 15 min. At the end of these operations the final thickness of the TiO₂ electrode was in the range 8–12 μm, as determined by SEM analysis. After the second sintering, the FTO glass coated TiO₂ was cooled at about 80 °C and immediately dipped into a methanol solution (1.5x10⁻³ M) of the dye at room temperature for 24 h. The dyed titania-glasses were washed with EtOH and dried at room temperature under a N₂ flux. Finally, the excess of TiO₂ was removed with a sharp teflon penknife and the exact active area of the dyed TiO₂ was calculated by means of a microphotography. A 50 μm thick Surlyn spacer (TPS 065093-50 from Dyesol) was used to seal the photoanode and a platinized FTO counter electrode. Then the cell was filled up with the desired electrolyte solution. The photovoltaic performance of the cells was measured with a solar simulator (Abet 2000) equipped with a 300 W Xenon light source; the light intensity was adjusted with a standard calibrated Si solar cell (“VLSI Standard” SRC-1000-RTD-KG5); the current-voltage characteristics were acquired by applying an external voltage to the cell and measuring the generated photocurrent with a “Keithley 2602A” (3A DC, 10A Pulse) digital source meter. For a given complex and configuration, at least four different devices were made and characterized in different days; the difference between the average and the highest or lowest efficiency values was usually lower than 5%.



Current density-Voltage characteristics of DSSCs sensitized with **D1** – **D3** in the presence of I^-/I_3^- based electrolyte



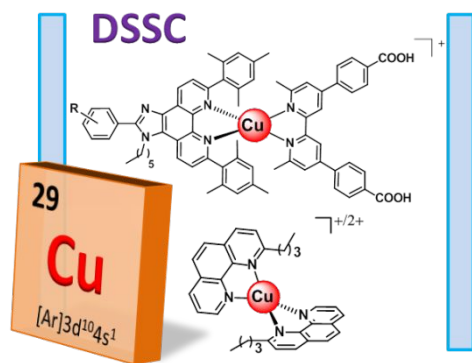
Current density-Voltage characteristics of DSSCs sensitized with **D1** – **D3** in the presence of **E3/E4** based electrolyte



Current density-Voltage characteristics of DSSCs sensitized with **D2** in the presence of different electrolytes

Reference

1. Colombo, A.; Dragonetti, C.; Roberto, D.; Valore, A.; Biagini, P.; Melchiorre, F. *Inorg. Chim. Acta* **2013**, *407*, 204.



Two new heteroleptic copper(I) sensitizers with π -delocalized ancillary ligands for full copper DSSCs