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Heteroleptic copper(I)-polypyridine complexes as efficient sensitizers for dye sensitized solar cells

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The synthesis and the physical-chemical characterizations of HETPHEN based heteroleptic copper(I)-bis(diimine) complexes are reported. In TiO2 based dye sensitized solar cells (DSCs), the latter display impressive photoconversion efficiencies (PCEs), unprecedented for first row transition metal coordination complexes.

Since 1991, and the discovery of DSC (Grätzel cells), many attempts to replace the costly and toxic (albeit remarkably efficient) ruthenium-polypyridine complexes have been reported. Copper(I)-bis(diimine) complexes have early shown promising results in this field. Laterly, the use of heteroleptic copper(I) complexes has afforded significant PCEs, unprecedented for first row transition metal coordination complexes.

Three complexes C2, C3 and C4, bearing respectively alkoxy, N,N-diethylamine and N,N-diphenylamine moieties were thus isolated. For the sake of comparison, a fourth model complex [CuL3+] was synthesized, with L3 = 2,2',4,4'-tetrakis(dimethyl)pyridine. The syntheses of all ligands are reported in ESI. The HETPHEN modus operandi was used to isolate CuL3+ and started with the synthesis of the CuL3+ intermediate in DMF. An equivalent of L3 was subsequently added dropwise, entailing an immediate colour change of the medium towards deep red. Impurities were removed by size exclusion chromatography. A similar protocol was used to isolate the dimethyl-ester forms of each complex (named hereafter  CuN, n=1-4, synthesis given in ESI). The electronic absorption spectra of the complexes were recorded in solution and on nanocrystalline TiO2 films (Figures 2 and S3). All the complexes featured the classical MLCT absorption band at ca. 500 nm (Table 1 and Figure 2). The increased conjugation of the π system on both L and L (n = 2-4) induces a stabilization of the π* orbitals, explaining the red-shift of this transition compared to the benchmark bis-neocuproine Cu(I) complex C5 (Figure S7). One notices that the MLCT bands are more intense as well, because of the increased ground state dipolar moment generated by the combination of electron poor L and electron rich L. The complexes C3 and C4 present higher light harvesting efficiency in the visible than C1 and C2 because of an intense additional intraligand charge transfer transition (ILCT), located at the edge of the visible around 420 nm.

This very intense ILCT transition corresponds to a shift of the electron density from the electron rich amine moieties to the electron poor pyridine. Such band does exist for C2 too, but is significantly blue-shifted compared to C3 and C4 because of the poorer electron donating power of L. Spectra recorded on TiO2 transparent electrodes (Figure S3) feature the same patterns than those recorded in solution phase (Figure 2). Overall, the complexes displayed a rather broad and intense absorption over a large wavelength frame (λmax~620 nm), revealing their potentials

% Table 1. UV-Visible and electrochemical data for C1-4. *data collected with the methyl ester forms of C1-4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ (nm) [ε (M⁻¹·cm⁻¹)]</th>
<th>E (V)* [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>477 [4.7·10⁴]</td>
<td>0.94 [96]</td>
</tr>
<tr>
<td>C2</td>
<td>500 [9.8·10⁴]</td>
<td>0.91 [96]</td>
</tr>
<tr>
<td>C3</td>
<td>504 [1.3·10⁵]</td>
<td>1.08 [-]</td>
</tr>
<tr>
<td>C4</td>
<td>502 [1.4·10⁵]</td>
<td>1.03 [-]</td>
</tr>
</tbody>
</table>

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as wide band gap semi-conductors sensitzers.

Figure 2. UV-Visible spectra of complexes C1 (dash-dot), C2 (plain), C3 (dot) and C4 (dash) recorded in dichloromethane.

No luminescence was detected upon excitation in the MLCT band, regardless the conditions. This could be due to cis-trans isomerization of the vinyl double bond or the lesser rigidity of the Cu-bpy coordination cage compared to Cu-Phen, facilitating the deleterious exciplex quenching.

To record better resolved cyclic and pulsed voltammograms (no adsorption of the dye on the electrode), these measurements were performed on the diester forms of complexes. The latter featured the expected, reversible copper-centred oxidation around 1 V vs. SCE (Table 1). The voltammograms of \( C_\text{ester} \) and \( C_4 \text{ester} \) displayed an additional oxidation wave at 0.95 and 0.80 V vs. SCE respectively, corresponding to the removal of one electron from the NR2 (R = ethyl or phenyl) amine moieties. Only differential pulse voltammetry allowed discriminating the two close oxidation steps for complex \( C_4 \text{ester} \). The higher Cu/N=C potentials displayed by \( C_3 \text{ester} \) and \( C_4 \text{ester} \) likely originate in the coulombic repulsion between the copper cation and the electrogenerated hole on the amine fragment.

The combination of electrochemical and UV-Vis data allowed evaluating the Gibbs energies associated to the various charge transfer processes. In all cases, both charge injection and dye regeneration are exergonic (ca. 300 meV, see Table S1 in SI). Energy-wise, C1-4 feature roughly the same behaviours. TiO2 electrodes were dipped while still hot for two days in anhelic solutions of C1-4 and the photovoltaic devices were then assembled with a platinum counter-electrode, sealed with a hotmelt polymer frame and their performances along those of the reference benchmark N719 were evaluated under AM 1.5 calibrated artificial sunlight (Table 2 and SI for details).

<table>
<thead>
<tr>
<th>( V_{OC} ) (mV)</th>
<th>( J_{SC} ) (mA.cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1' 475</td>
<td>2.20</td>
<td>72.80</td>
<td>0.76</td>
</tr>
<tr>
<td>C2' 535</td>
<td>2.89</td>
<td>72.54</td>
<td>1.12</td>
</tr>
<tr>
<td>C3' 545</td>
<td>7.51</td>
<td>71.52</td>
<td>2.93</td>
</tr>
<tr>
<td>C4' 565</td>
<td>6.70</td>
<td>73.32</td>
<td>2.77</td>
</tr>
<tr>
<td>N719</td>
<td>635</td>
<td>16.87</td>
<td>68.69</td>
</tr>
</tbody>
</table>

Table 2. Photovoltaic data for DSCs based on TiO2 sensitization by C1-4

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Table 2. Photovoltaic data for DSCs based on TiO2 sensitization by C1-4 without (a) and with (b) CDCA. \( V_{OC} \): open circuit voltage; \( J_{SC} \): short circuit current density; \( \text{FF} \): fill factor.

The weakest PCE is afforded by C1 based DSCs, grounded in low photocurrent and photovoltage. The latter is assigned to a lower light harvesting efficiency (LHE) and probably an exacerbated charge recombination with the electrolyte. Indeed, the positive charge of C1 recorded a coulombic repulsion between them on the surface of TiO2, increasing the number of unoccupied adsorption sites and thus recombination centres. C3, C4 and C2 are a lot bulkier than C1, and thus passive more the surface of the semi-conductor, yielding a higher Voc. This is further confirmed by the higher dark current displayed by C1-based DSCs (see SI). Besides, both C1 and C2 yield poor photocurrents, likely because of their less intense absorption coversions of the solar spectrum, leading to an overall weaker LHE (see Figures 3 & S4).

The short circuit currents of C3 and C4 based DSCs are by far the highest of the series, in part because of the presence of ILCT bands in the visible domain, increasing the LHE. This is confirmed by the incident photon to current efficiency (IPCE) recorded on each DSC, where a current generation is indeed monitored between 400 and 460 nm for C3 and C4 (around 43% at 410 nm). C1 and C2 based DSCs, being deprived of such ILCT above 400 nm consequently display lesser LHE and IPCE.

Spin coating a 0.1M CDCA (chenedexochyclic acid) ethanol solution onto the photo-electrodes prior to the final sealing is anticipated to eliminate the deleterious self-quenching process induced by aggregation. Rewardingly, unprecedented improvements in the power conversion efficiencies (PCEs) of all DSCs were observed upon such CDCA-surface treatment. First of all, an increase of the photopotential was observed for all DSCs. C1-4 based devices exhibited a 50-60 mV rise of the Voc, together with a decrease of the dark current. This improvement was therefore assigned to the higher electron concentration in the CB and to a passivation of recombination sites by the co-adsorbed molecules. In the case of C2, the octyl chains may provide a built-in, efficient protection of titanium dioxide’s surface, thus explaining the lesser increase of the Voc (ca. 30 mV). The electron lifetime (\( \tau_e \)) and mean transit time (\( \tau_m \)) of photoinjected charge carriers were then recorded by intensity-modulated photovoltage spectroscopy (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS). However, these measurements reveal that no significant improvement of both \( \tau_e \) and \( \tau_m \) was observed when CDCA was added in the preparation of the series of solar cells (see SI). As a result, the charge collection efficiency \( \eta \) measured as a function of the illumination intensity is quite similar for all the dyes (see SI).

Figure 3. IPCE for DSCs sensitized with C1 (dash-dot), C2 (dot), C3 (plain), and C4 (dash) recorded with CDCA.

The most spectacular improvement of the PCE originates in the rise of
the Jsc for all devices. One calculates a 70% increase of the photocurrent for C1 and C4 and 45 and 50% for C2 and C3 based photovoltaic devices, respectively. For a better understanding, IPCES of DSCs with and without CDCA treatment were compared (Figure S5). A significant increase of the IPCE is observed for CDCA-treated cells, regardless the dye (Figure 3), together with a broadening of the signals. Several reasons can be invoked to rationalize this important result. First, CDCA molecules release protons and this bends the conduction band downwards, increasing thus the driving force of the electron injection into the semi-conductor, and consequently improving the electron injection yield.13 Second, a noticeable increase of the absorbance of C1-4 based photo-electrodes was monitored upon CDCA treatment, along with a slightly broadened MLCT transition (Figure S4). These subtle changes in the absorption spectra of the chemisorbed complexes are in line with the IPCE, and are probably grounded in a reorganization of the dye monolayer upon CDCA adsorption. The role of CDCA is often associated with the disruption of dye aggregates and certainly comes into play here, especially due to the presence of organic styryl branches on the complexes C2-4. Based on the effect of CDCA on both IPCE measurements and on the Jsc enhancement, we conclude that the main role of CDCA with these complexes is certainly to decrease the aggregation on TiO2 surface leading to higher LHE and injection quantum yield. In these conditions, DSCs provided a maximum PCE of 4.66% for complexes, absorption spectra on TiO2 and electron lifetime (τe) and ηcoll measured by IMVS and IMPS. See DOE: 10.1039/b000000x/

Graphical abstract for entry

\[ \eta = 4.66\% \]

\[ \lambda (\text{nm}) \]

\[ \text{IPCE} \]