Electronic supplementary information

Towards efficient sustainable full-copper dye-sensitized solar cells

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



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



 $^{13}\text{C-NMR}$ (75MHz) in DMSO-d₆ of the Ligand L2



¹³C-NMR (75 MHz) in DMSO-d₆ of the precursor I3



 $^{13}\text{C-NMR}$ (75 MHz) in CDCl₃ of the ligand L3

2. NMR and mass spectra of complexes D2 and D3



¹³C-NMR (100MHz) in CD₃OD of complex **D2**



MS (ESI+FTICR) of complex D2



 $^{13}\text{C-NMR}$ (100MHz) in CD₂Cl₂ of complex **D3**



MS (ESI+FTICR) of complex D3



3. Cyclovoltammetric CV pattern of D2 and D3

CV patterns of **D2** (first oxdation process "blue line" and complete "thin blue line") 3.7×10^{-4} M in CH₃CN/CH₂Cl₂ 2.4:1 and **D3** (red line) 4.5×10^{-4} M in CH₃CN.

4. 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/cm^2) 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.