

SUPPORTING INFORMATION

Liquid State and Zombie Dye Sensitized Solar Cells with Copper Bipyridine Complexes Functionalized with Alkoxy Groups

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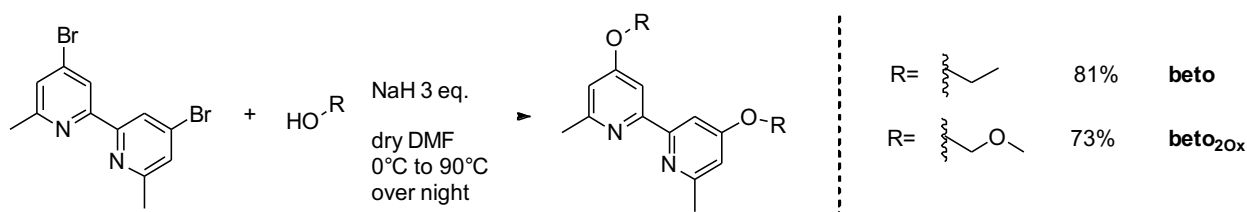
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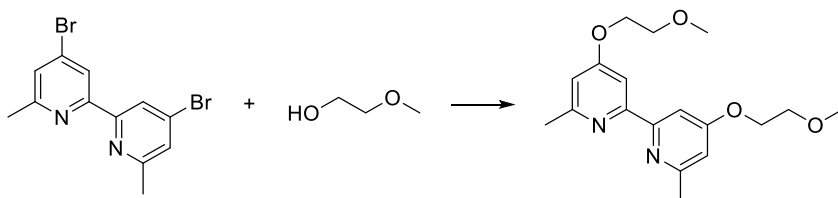
1. Synthesis of the Ligands

General information: Commercially available chemicals were used without any additional purification step. N,N-dimethylformamide (DMF) was purchased over Molecular Sieves from ACROS Organics™, Sodium Hydride (NaH) was purchased as a moistened oil (55-65% wt) from Sigma Aldrich™. ¹H and ¹³C NMR spectra were recorded on Bruker AvanceIII-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ) and referenced to tetramethylsilane (0 ppm) or solvent residual peak (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as internal standard. Mass spectra were collected on a HITACHI-80 mass spectrometer.



Scheme S1: Synthesis of beto and beto_{2Ox} ligands.

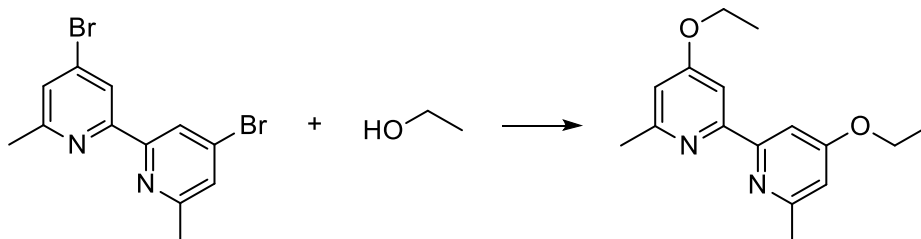
4,4'-bis(2-methoxyethoxy)-6,6'-dimethyl-2,2'-bipyridine (beto_{2Ox})



Sodium hydride (0.150 g, 6.14 mmol, 3 eq.) was added to 20 mL of anhydrous DMF at 0°C. The resulting suspension was stirred for 10 minutes after which 2-methoxyethanol (0.620 g, 8.19 mmol, 4 eq.) was added dropwise to afford the formation of hydrogen gas. The solution was then left at 0°C for 2 hours. 4,4'-dibromo-6,6'-dimethyl-2,2'-bipyridine (0.7 g, 2.05 mmol, 1 eq.) was added to the opaque mixture and the ice bath was removed to allow the reaction mixture to slowly warm up to room temperature. The beige opaque suspension was then heated at 90°C overnight. The dark green solution was then cooled down to RT, quenched with a saturated solution of ammonium chloride (200 mL). And the organics were extracted with DCM (3x100 mL). DCM was then removed and the residue dissolved in diethyl ether (100 mL). The organic phase was washed with deionized water (3x100 mL) and a saturated solution of sodium chloride (100 mL). The obtained yellow solution was dried over magnesium sulfate followed by evaporation of the diethyl ether. The product was obtained as a yellow solid 0.5 g (73% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.3 Hz, 2H), 6.75 (d, *J* = 2.3 Hz, 2H), 4.30 (t, *J* = 4.7 Hz, 5H), 3.81 (t, *J* = 4.7 Hz, 5H), 3.49 (s, 6H), 2.58 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.03, 159.23, 157.56, 110.22, 104.32, 70.71, 67.07, 59.26, 24.71; MS (APPI, *m/z*): [M+H]⁺ calculated: 333.1809 found: 333.1809

4,4'-diethoxy-6,6'-dimethyl-2,2'-bipyridine(**beto**)



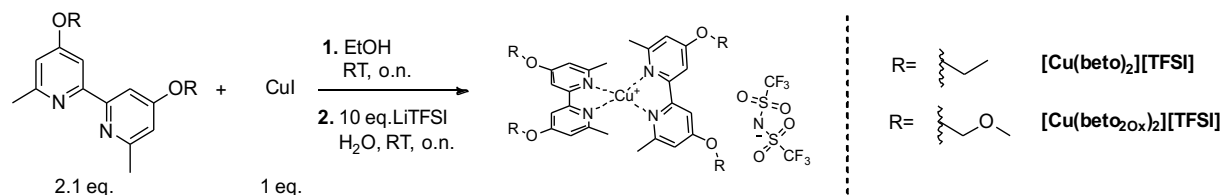
Sodium hydride (0.250 g, 10.53 mmol, 3 eq.) was added to 20 mL of anhydrous DMF at 0°C. The resulting suspension was stirred for 10 minutes after which 5 mL of Ethanol was added dropwise under vigorous stirring to afford the formation of hydrogen gas. The solution was then left at 0°C for 2 hours. 4,4'-dibromo-6,6'-dimethyl-2,2'-bipyridine (1.2 g, 3.51 mmol, 1 eq.) was added to the opaque mixture and the ice bath was removed to allow the reaction mixture to slowly warm up to room temperature. The beige opaque suspension was then heat at 65°C overnight. The dark green solution was then cooled down to RT, quenched with a saturated solution of ammonium chloride until neutral pH and diluted with deionized water. The organics were collected by extraction with Ether followed by drying over magnesium sulfate. The product was obtained as a beige crystalline solid: 0.671 g (70% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.3 Hz, 2H), 6.69 (d, *J* = 2.4 Hz, 2H), 4.21 (q, *J* = 7.0 Hz, 4H), 2.58 (s, 6H), 1.47 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.20, 159.16, 157.64, 109.89, 104.52, 63.44, 24.73, 14.63; MS (APPI⁺, *m/z*): [M+H]⁺ calculated: 273.1598 found: 273.1600

2. Synthesis of the Cu(I) complexes

For [Cu(beto)₂][TFSI] and [Cu(beto_{2Ox})₂][TFSI], one equivalent of CuI (35 mg, 0.175 mmol) was mixed with 3 equivalents of 4,4'-diethoxy-6,6'-dimethyl-2,2'-bipyridine (190mg, 0.7 mmol) or 4,4'-bis(2-methoxyethoxy)-6,6'-dimethyl-2,2'-bipyridine (232 mg, 0.7 mmol) in 20 ml ethanol, under nitrogen atmosphere, at room temperature for 2 hours. The resulted complex was obtained as intense orange/red, crystalline powder. The product was filtered and redissolved by addition of 5 ml of deionized water followed by an addition of 10 equivalents of LiTFSI (37 mg, 0.65 mmol). The solution was further stirred for 2 hours at room temperature and under nitrogen atmosphere resulting in orange/red precipitation. The

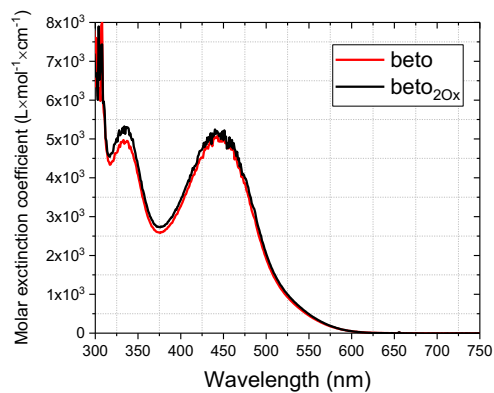
complex was collected by filtration and washed with water. The yield of the products over 80 % (mol).



Scheme S2: Synthesis of [Cu(beto)₂][TFSI] and [Cu(beto_{2Ox})₂][TFSI].

3. UV-visible measurements.

a.



b.

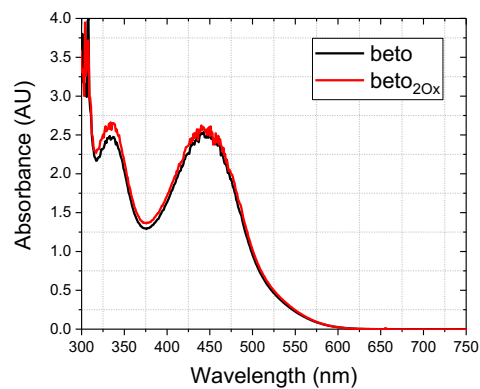


Figure S1: a) Molar extinction coefficient of [Cu(beto)₂][TFSI] (red) and [Cu(beto_{2Ox})₂][TFSI] (black). b) Absorption of [Cu(beto)₂][TFSI] (red) and [Cu(beto_{2Ox})₂][TFSI] (black). Measured in 0.5 mM MeCN solution.

4. Electrochemical measurements

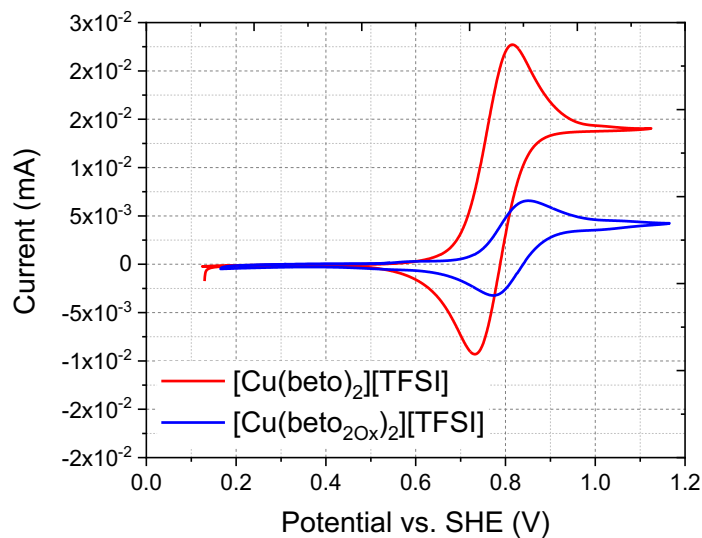


Figure S2: Cyclic voltammograms of [Cu(beto)₂][TFSI] (red) and [Cu(beto_{2Ox})₂][TFSI] (blue). (Measured in MeCN solution containing 0.1 M of LiTFSI as supporting electrolyte. The complexes concentrations were respectively 0.2 mM for [Cu(beto)₂][TFSI] and 0.5 mM for [Cu(beto_{2Ox})₂][TFSI]. The electrodes consisted in a Pt disk working electrode, a Pt wire counter electrode and a Ag/AgCl in saturated sodium chloride electrode.)

5. X-ray diffraction

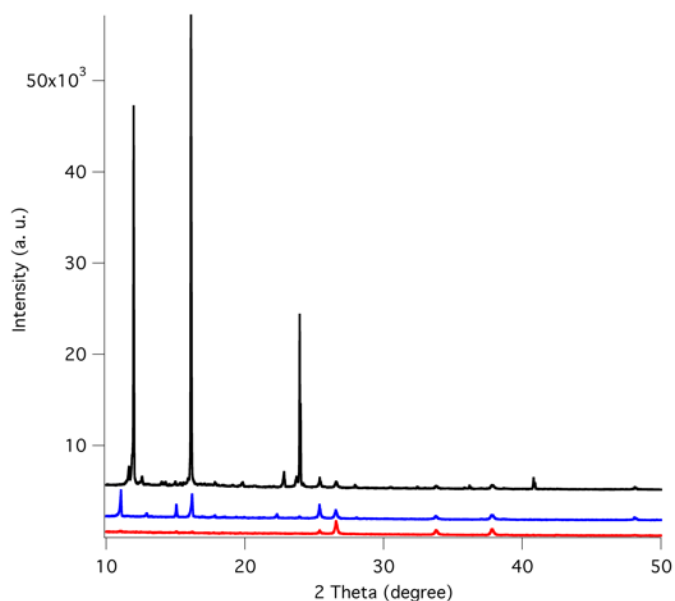


Figure S3: XRD data of the dried [Cu(beto)₂]^{2+/1+} (blue), [Cu(beto_{2Ox})₂]^{2+/1+} (red), and [Cu(tmby)₂]^{2+/1+} (black) electrolytes after drop-casting on top of a TiO₂ working electrode.

6. IV data

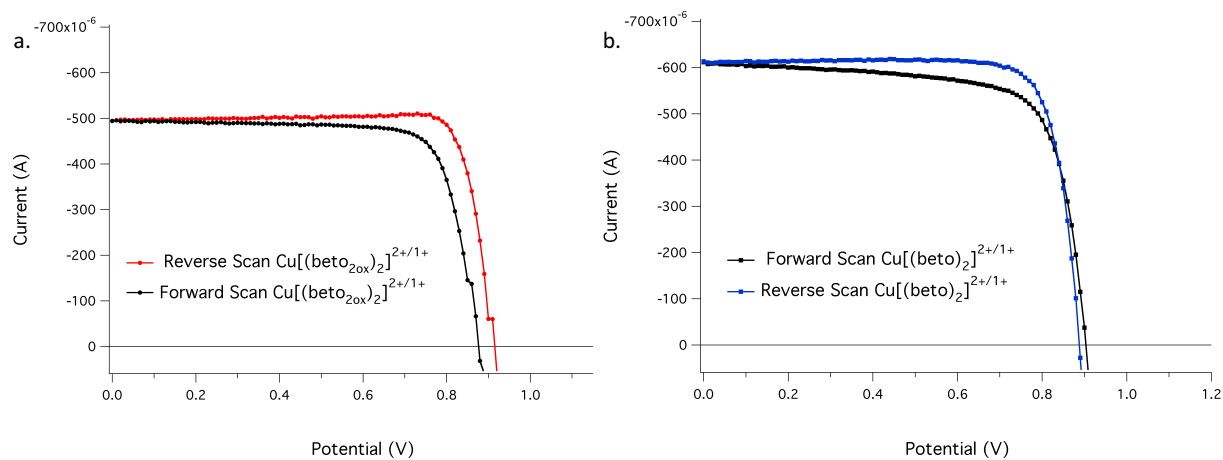
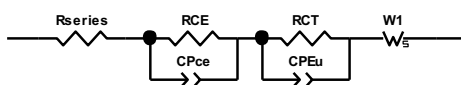


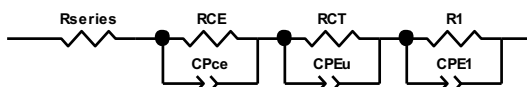
Figure S4: Hysteresis test for zombie devices employing a) $[\text{Cu}(\text{beto}_{2\text{ox}})_2]^{2+/1+}$ and b) $[\text{Cu}(\text{beto})_2]^{2+/1+}$ complexes. (The scan settling time is 0.08 with 10mV/s voltage steps, the measurements are carried out with, 0.16 cm^2 mask).

7. Electrochemical Impedance Spectroscopy

Liquid state DSC



Quasi-solid state DSC



Dummy cells

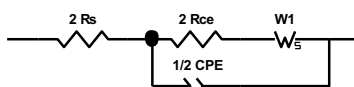


Figure S5: The equivalent circuits representing the liquid state devices, solid state devices and symmetrical dummy cells.

Table S1: Electrochemical parameters of the studied DSC devices with $[\text{Cu}(\text{beto})_2]^{2+/1+}$ and $[\text{Cu}(\text{beto}_{2\text{Ox}})_2]^{2+/1+}$ electrolytes.

	$[\text{Cu}(\text{beto})_2]^{2+/1+}$		$[\text{Cu}(\text{beto}_{2\text{Ox}})_2]^{2+/1+}$	
Device type	Liquid state	Zombie	Liquid state	Zombie
Rseries (Ω)	9.249	10.32	9.415	53.33
R _{CE} (Ω)	4.44	4.567	3.145	21.08
CPce-T	0.00010928	0.0000186	0.00003619	0.00032693
CPce-P	0.9	0.9	0.9	0.9
R _{ct} (Ω)	79.26	30.59	181.6	32.51
CPEu-T	0.00027246	0.00011806	0.0001783	0.0000355
CPEu-P	0.84864	0.76275	0.96491	0.75102
W1-R (R1 for zombie)	95.99	287	69.6	1541
W1-T(CPEu-T for zombie)	0.022155	0.0000999	0.027274	0.0001082
W1_P(CPEu-P for zombie)	0.5	0.93188	0.5	0.91442

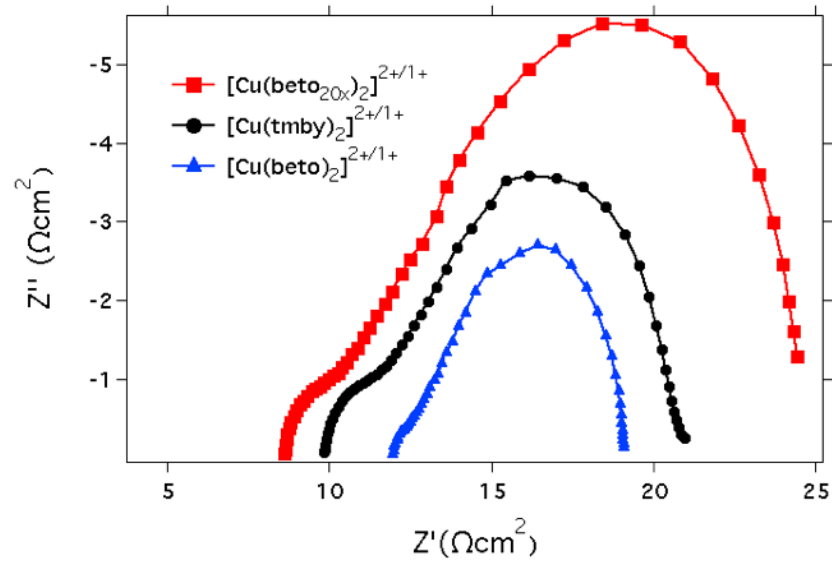


Figure S6: Nyquist plots of electrochemical impedance spectra measured at 0 V for the PEDOT/PEDOT symmetrical dummy cells. In order to avoid crossing of the curves, impedance spectra of the $[\text{Cu}(\text{beto})_2]^{2+/1+}$ offset $4\Omega\text{cm}^2$ in the bottom axis.