# Photovoltage enhancement from cyanobiphenyl liquid crystals and 4-*tert*-butylpyridine in Co(II/III) mediated dye-sensitized solar cells

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## Synthesis of sensitizers

Sensitizers L102<sup>1</sup> and C218<sup>2</sup> were synthesized according to reported literatures.

# Synthesis of Co(bpy)<sub>3</sub>(TFSI)<sub>2</sub>

The cobalt complex was synthesized by using a modified literature method<sup>3</sup>. Briefly, 1 equivalent of  $CoCl_2 \cdot 6H_2O$  (Sigma Aldrich) was dissolved in methanol and another methanolic solution containing 3.2 equivalents of 2,2'-bipyridyl (Sigma Aldrich) ligand was added. The solution was heated with stirring at 60 °C for 1 hr. The solution was cooled to room temperature and 10-fold excess of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma Aldrich) was added into the solution. The solution was stirred for another 30 min at room temperature. Water was added to precipitate the desired products. The yellowish brown solid formed was collected by filtration and washed with water and diethyl ether. The solid was dried under vacuum and used without further purification.

## Synthesis of Co(bpy)<sub>3</sub>(TFSI)<sub>3</sub>

1 equivalent of  $Co(bpy)_3(TFSI)_2$  was dissolved in a minimal amount of acetonitrile and an excess (2.5 equivalents) of NOBF<sub>4</sub> (Sigma Aldrich) was added to the solution. The solution was stirred for 15 min at room temperature. A 3-fold excess of LiTFSI salt was added into the solution and stirred for another 15 min. Water was added to precipitate the desired products. The light yellow solid formed was collected by filtration and washed with water and diethyl ether. The solid was dried under vacuum and used without further purification.

#### **Preparation of PEDOT counter electrodes**

Electropolymerization of PEDOT on FTO was performed by a modified literature method<sup>4</sup>. The PEDOT counter electrode was prepared by electropolymerization in a three-electrode configuration cell. The working electrode, a cleaned flourine-doped tin oxide (FTO) substrate, was immersed into the cell containing 0.01 M of EDOT (Sigma Aldrich) in 0.1 M aqueous sodium dodecyl sulphate (SDS, Sigma Aldrich) solution. Stainless steel grid and a leak-free Ag/AgCl electrode were used as counter and reference electrodes, respectively. The PEDOT film was deposited potentiostatically using a DC potential of 1.2 V for 30 s. The PEDOT counter electrode was subsequently rinsed with deionized water and ethanol.

#### Solar cell fabrication

Flourine-doped tin oxide (FTO) glass substrates (Pilkington, TEC15) were cleaned with Decon90 solution in ultrasonic bath for 30 min, followed by washing with water and ethanol. Pre-TiCl<sub>4</sub> treatment was performed by dipping the cleaned glass substrates in a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min. The substrates were then washed with water and ethanol. Mesoporous TiO<sub>2</sub> films (0.16 cm<sup>2</sup>) were prepared by screen printing colloidal TiO<sub>2</sub> paste (Dyesol DSL 18 NR-T) and drying at 125 °C between deposition steps. Two layers of scattering TiO<sub>2</sub> layer (Dyesol WER2-O) were deposited on top of the mesoporous TiO<sub>2</sub> film. The electrodes with total thickness of 9.5  $\mu$ m were subsequently heated to 500 °C for 15 min with programmed temperature ramping. After sintering, the electrodes were treated again with 40 mM TiCl<sub>4</sub> at 70 °C for 30 min.

Once cooled, the electrodes were immersed in 0.25 mM of L102 in THF:*t*-butanol (4:1) for 15 hours. Solar cells were assembled with PEDOT counter electrode using 25 µm thick hotmelt spacer (Surlyn, Dupont). Cobalt electrolyte was injected via two holes predrilled in the counter electrode and sealed with Surlyn cover and a glass coverslip.

#### **Characterization techniques**

For the photovoltaic measurements, the solar cells having  $0.16 \text{ cm}^2$  active area were measured with  $0.25 \text{ cm}^2$  metal mask using solar simulator (San-EI Electric, XEC-301S) under AM 1.5G standard. *J-V* characteristics were recorded by applying external potential bias while measuring the current response with a Keithley 2612A SourceMeter. For light intensity dependence studies, the light intensity was controlled by using UV Fused Silica Metallic

Neutral Density Filters (Newport Corporation). Incident photon to current efficiency (IPCE) was performed using PVE300 (Bentham), with dual Xenon/quartz halogen light source, measured in DC mode and no bias light is used. For electrochemical impedance spectroscopy study, measurements were carried out using AutoLab PGSTAT302N under illumination condition and different bias potentials were applied and frequencies between 1 MHz and 0.1 Hz. Considering the internal potential drop at series resistance, chemical capacitance (C) is plotted against Fermi level voltage (V<sub>f</sub>). To eliminate the effect of conduction band position, recombination resistance (R<sub>rec</sub>) is plotted against the common equivalent conduction band potential (V<sub>ecb</sub>)<sup>5</sup>. PEDOT electropolymerization was performed using a CHI-660D Electrochemical Workstation (CH Instrument, USA). Cyclic voltammetry was carried out using a three-electrode setup where platinum was used as working electrode, glassy carbon as counter electrode and aqueous Ag/AgCl as reference electrode. The redox solution was 10 mM of Co(bpy)<sub>3</sub>(TFSI)<sub>2</sub>, 0.1 M of TBAPF<sub>6</sub> and 10 mM of 5CB/8CB while the scan rate is 100 mVs<sup>-1</sup>.



Fig. S1 Cyclic voltammogram of Co(bpy)<sub>3</sub>(TFSI)<sub>2</sub> and in the presence of 5CB and 8CB.



**Fig. S2** Chemical capacitance as a function of corrected potential in DSCs using E1-E4. Left: fresh cell; Right: 1 day after fabrication.

**Table S1** *J-V* characteristics of fresh prepared DSCs using various Co(II/III) electrolyte containing different concentration of TBP, 5CB and 8CB as additives.

Electrolyte*	E1	E2	E3	E4	E5	E6	E7	E8
TBP (M)	-	0.2	-	-	0.2	0.2	0.2	0.2
5CB (M)	-	-	0.2	-	0.1	0.2	-	-
8CB (M)	-	-	-	0.2	-	-	0.1	0.2
$J_{sc}$ (mAcm <sup>-2</sup> )	9.70	9.08	8.91	8.99	9.92	9.44	9.47	8.83
$V_{oc} (mV)$	703	809	725	805	823	841	821	856
FF	0.72	0.74	0.72	0.66	0.72	0.72	0.72	0.70
η (%)	4.94	5.44	4.62	4.78	5.88	5.69	5.58	5.29

\*All electrolytes consisted of 0.22 M Co(bpy)<sub>3</sub>(TFSI)<sub>2</sub>, 0.05 M Co(bpy)<sub>3</sub>(TFSI)<sub>3</sub> and 0.1 M LiTFSI in MeCN.



Fig. S3 (Top) EIS spectra of devices using E2, E3 and E4 electrolytes measured under illumination at  $V_{oc}$ . Symbols represent experimental data and solid lines show the fits and (bottom) complete equivalent circuit model for fitting.

**E1** 

E2

0 L

0

E3

Electrolyte

$R_{CE}$ ( $\Omega cm^2$ )	1.38	1.89	1.19	1.15	1.19	1.56	2.29	1.42
	n (%) EE V/oc (m/V) Icc (m Acm <sup>-2</sup> )			8-8-8-8 8-3-8-8				

Table S2 Charge transfer resistance of DSCs measured at open-circuit potential using different Co(II/III) electrolytes

**E4** 

E5

**E6** 

E7

**E8** 

Fig. S4 Stability testing (stored in dark) of DSCs with E8 electrolyte.

Time (h)

100

150

50



Fig. S5 Reproducibility of the study among 3 batches of devices.



Fig. S6 Optimization of Co-based electrolyte for varying ratio of Co(II) to Co(III) in electrolyte.

### References

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