Supporting Information for:

High Efficiency Stable Dve-Sensitized Solar Cells Based on a **Cobalt Polymer Gel Electrolyte**

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Experimental

Materials and reagents

25 All the reagents, chemicals and solvents were purchased from Sigma-Aldrich or Merck Specialty Chemicals unless otherwise specified. The TiO₂ paste was purchased from JGC Catalysts and Chemicals Ltd.

Synthesis of cobalt complex

- The [Co(bpy)₃](TFSI)₂ complex was synthesized with slight modifications to a literature method.^{S1} One equivalent of CoCl₂.6H₂O and 3.3 equivalents of 2,2'-bipyridine were dissolved in a minimum amount of methanol, the solution was stirred at
- 35 reflux for 1 h. An excess of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was then added to the solution to precipitate the cobalt complex. The solid was filtered, washed with water and diethyl ether and dried under vacuum for 24 h. Oxidation of the Co^{II} complex was achieved by adding slightly
- 40 more than one molar equivalent of NOBF₄ to an acetonitrile solution of the complex. The solvent was removed by rotary evaporation. The complex was redissolved in acetonitrile and a 10 fold excess of LiTFSI was added to precipitate the product which was then filtered, washed with diethyl ether and water and
- 45 dried under vacuum for 24 h. These two compounds were used without further purification.

Device fabrication

The glass substrate used was 4 mm thick 10 Ω^{-1} conductive 50 FTO (fluorine doped tin oxide) glass with high transparency in the visible range purchased from Nippon sheet glass. Mesoporous 4x4 mm TiO₂ films were printed using a commercial semi automatic screen printer and commercial 30 nm TiO2 screen printing paste (PST-30NR, JGC Catalysts and Chemicals). The

- 55 scattering paste was prepared from 400 nm particles mixed 5 to 1 by weight with 30 nm particles and addition of 3.5 parts ethyl cellulose and 30.5 parts terpineol. After a first sintering process (500 °C), a TiCl₄ treatment was applied by immersing the films in a 30 mM aqueous TiCl₄ solution at 70 °C for 30 min in a water
- 60 saturated atmosphere. Prior to device assembly, the films were sintered again (500 °C), cooled to approximately 80 °C and immersed in MK2 solution with a mixture of acetonitrile, toluene and isobutanol (v:v:v=1:1:1) for 6 h. The dyed films were rinsed with absolute ethanol to remove non-attached dye from the films.
- 65 Counter electrodes were prepared from 3 mm thick 15 Ω^{-1} conductive FTO (fluorine doped tin oxide) glass purchased from Nippon glass. A solution of chloroplatinic acid hexahydrate (10 mM) in ethanol was doctor bladed onto the pre-drilled substrate and pyrolyzed for 15 min at 450 °C. All electrolytes were
- 70 prepared using anhydrous solvents, deoxygenated by freezedrying and stored in a nitrogen glove box. The dried working electrode and counter electrode were assembled using a 25 µm thick Surlyn gasket (Solaronix) of the dimensions 5x6 mm. A pneumatic finger was used to apply pressure while heating
- 75 through the counter electrode. The cells were then vacuum backfilled by warm electrolyte through a predrilled hole in the counter electrode. The backfilling hole was sealed at 150 °C using a square of aluminium backed Surlyn prepared by melting 25 µm Surlyn onto aluminium foil at 100 °C. The devices were
- 80 soaked under one sun simulater light illumination for 40 min and left for at least 5 h at room temperature before characterizations. The electrolyte compositions were as follows: 0.20 M tris(2,2'bipyridine)cobalt(II) bis(trifluoromethanesulfonyl)imide ([Co(bpy)₃](TFSI)₂), 0.07 M Co(bpy)₃(TFSI)₃, 1.0 M tert-85 butylpyridine (tBP), 0.05 M LiTFSI in acetonitrile and 4-10% of a PVDF-HFP mixture.

Rheology characterization

The ARES Rheometer was employed to determine the 90 rheological performance of PVDF-HFP content electrolytes via dynamic shear method. The temperature was kept at the room temperature (25°C) for all the measurements. The dynamic test was conducted by cone-and plate geometry with 0.01 rad in angle, 25 mm in diameter and 0.05 mm in gap.

IV and IPCE

IV characterization was carried out on a sun simulator (Oriel) fitted with a filtered 1,000 W xenon lamp as simulated solar ¹⁰⁰ irradiation (AM1.5, 1,000 Wm⁻²). Current–voltage curves were recorded using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (Peccell Technologies). The photodiode was fitted with a color filter provided by the supplier, to minimize the optical mismatch 105 between the calibration diode and the dye-sensitized solar cells. The light intensity was adjusted by using a filter wheel equipped with a series of mesh filters. IPCE was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260) as a monochromatic light source. The illumination spot size ¹¹⁰ was chosen to be slightly smaller than the active area of the DSC test cells. IPCE photocurrents were recorded under short circuit conditions using a Keithley 2400 source meter. The

monochromatic photon flux was quantified by means of a calibrated silicon photodiode (Peccell Technologies).

Apparent diffusion coefficients

- s The apparent diffusion coefficient of $[Co(bpy_3)]^{3+}$ was measured on a potentiostat (BioLogic VSP) with symmetric cells. The symmetric cells were fabricated with a structure of Pt/electrolyte/Pt with a 25 µm thick Surlyn gasket (Solaronix) of the dimensions 8x8 mm. The current voltage scan range was set
- ¹⁰ between -1.3 V and 1.3 V and the scan rate is 20 mVs⁻¹. The limiting currents were obtained by reading the plateau of the diffusion curve.

Transient currents

- ¹⁵ Transient currents were measured using a solar simulator with EC lab software. The light intensity was adjusted by using a filter wheel equipped with a series of mesh filters. At each light intensity, the transient current was measured three times in order to obtain a stable current response. An on/off ratio of illumination
- 20 at 2 was fixed, which means that the cells were illuminated for 7 seconds following a 3.5 seconds period without illumination.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements on 25 the complete DSCs were made on a potentiostat (BioLogic VSP) with a frequency range of $0.5 - 10^5$ Hz. The magnitude of the alternative signal was 10 mV. The EIS measurements were carried out in the dark with different applied voltage bias from 500 mV to 900mV. Z-view software was used to fit the curves

Stability measurements

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For the stability testing, devices based on one of the best performing cobalt gel electrolyte (4wt% PVDF-HFP content) and the liquid electrolyte were chosen for study. Cool white light ³⁵ LEDs (Luxeon Star LEDs, part No. 263, spectrum profile

- between 400 nm and 750 nm) equipped with a polymer optics 7 cell cluster concentrator lens was used as the light source. The illumination intensity of the LED light source was adjusted, so that the test cells yielded the same photocurrent that was observed
- ⁴⁰ when simulated under AM 1.5 (1,000 Wm⁻²) illumination. Prior to light soaking, the devices were characterized under AM1.5 simulated sun light. Afterwards, each device was exposed to white LED. The devices were measured after a certain amount of time under AM1.5 simulated sun light. Efficiency measurements
- ⁴⁵ during the stability test were performed under AM 1.5 G simulated sun light.



70 Figure S1 The elastic and loss modulus variation as a function of the concentration of PVDF-HFP under dynamic frequency test at the constant strain of 1% and a frequency of 1 rad/s. For the 4wt% PVDF-HFP polymer content, the value of elastic modulus is almost identical to the loss modulus showing the viscous gel structure. When the concentration 75 of PVDF-HFP is increased to 10wt%, the elastic modulus becomes much higher than the loss modulus, indicating that this material has a gel-like structure.^{S2}



Figure S2. Photocurrent density - voltage characteristics for devices made ⁸⁰ with the organic sensitizer MK2 and $[Co(bpy)_3]^{2+/3+}$ electrolytes containing different amounts of PVDF-HFP in acetonitrile, (working electrode: 6 µm thick transparent TiO₂ + 6 µm thick scattering TiO₂ layer, irradiation: simulated AM 1.5G (1,000 Wm⁻²)



85 Figure S3 IV curves for devices made with MK2 dye and different thickness transparent TiO₂ working electrode, tested under simulated AM 1.5 solar irradiation (1,000 Wm⁻²)

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Figure S4. IPCE characteristics for devices made with MK2 dye and tested under simulated AM 1.5 solar irradiation $(1,000 \text{ Wm}^{-2})$ for the $(Co(bpy)_3)^{2+/3+}$ electrolyte system containing different amount of PVDF-HFP in acetonitrile. Working electrode: 6 µm thick transparent TiO₂ + 6 µm thick scattering TiO₂ layer.



Figure S5. Dependence of the diffusion coefficient of $[Co(bpy)_3]^{2+}$ ¹⁰ (black) and $[Co(bpy)_3]^{3+}$ (red) on the ratio of the $[Co(bpy)_3]^{2+}/Co(bpy)_3]^{3+}$ concentration in electrolytes with 4% PVDF-HFP content. The concentration of $[Co(bpy)_3]^{2+}$ was kept at 0.05 M while that of $[Co(bpy)_3]^{3+}$ was varied from 0.017 M to 0.5 M. A lower limiting current density is generated at lower ratios (lower Co(III) present), which is ¹⁵ considered to be the current-determining species.



- 20 Figure S6 (a) Chemical capacitance and (b) charge transfer resistance between gel electrolyte and working electrode fitted from the EIS curves measured with different applied voltages.
- **Table S1** Parameters of DSCs made with different thickness transparent ²⁵ TiO₂ working electrodes and a 4% polymer containing gel electrolyte at 1 sun irradiation (same electrolyte as for devices in Table 1 was used).

TiO ₂ thickness	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	η (%)
2 µm	900 ± 1	10.4 ± 0.3	0.75 ± 0.01	7.0 ± 0.1
4 µm	880± 5	10.8 ± 0.2	0.75 ± 0.01	7.1 ± 0.1
6 µm	880 ± 1	11.1 ± 0.2	0.75 ± 0.01	7.4 ± 0.1

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