

## Supporting Information for:

### Long-term stability for cobalt-based dye-sensitized solar cells obtained by electrolyte optimization

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### Experimental

#### Reagents

Acetonitrile (99.8%), 4-*tert*-butylpyridine (TBP, 96%) and LiClO<sub>4</sub> (99.99%) were purchased from Sigma-Aldrich. The dye D35 and tris(2, 2'-bipyridine-2N, N') cobalt(II) bis(tetracyanoborate) (Co(bpy)<sub>3</sub>[B(CN)<sub>4</sub>]<sub>2</sub>) and tris(2, 2'-bipyridine-2N, N') cobalt(III) tris(tetracyanoborate) (Co(bpy)<sub>3</sub>[B(CN)<sub>4</sub>]<sub>3</sub>) were purchased from Dyenamo AB, Sweden. TiO<sub>2</sub> pastes (DSL 18NR-T and WER2-O) were obtained from Dyesol Ltd. All chemicals were used without further purification.

#### Device fabrication

The details of fabrication of solar cell devices have been reported previously.<sup>S1</sup> A 2.0-2.5 μm thick layer of diluted TiO<sub>2</sub> paste (60 wt % TiO<sub>2</sub> paste [DSL 18NR-T, Dyesol] was mixed with 36 wt % terpineol and 4 wt % ethyl cellulose) was screen-printed with an active area of 0.5×0.5 cm<sup>2</sup> on a fluorine-doped tin oxide (FTO) glass substrate (Pilkington, TEC15), which was pre-treated by first immersing them into a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min, then washed with water and ethanol and finally sintered in an oven. Subsequently, a scattering layer [WER2-O, Dyesol] was screen-printed and a final film thickness of 5-5.5 μm was obtained. The sintering process was conducted in ambient atmosphere according to the temperature gradient program: heating to 325 °C in 25 min, left at that temperature for 30 min and then heated further to 500 °C in 25 min, and finally cooled after being kept at the highest temperature for 30 min. Afterwards, the electrodes were treated by an aqueous TiCl<sub>4</sub> solution and rinsed once again, as described above. In the cooling step, when the prepared working electrodes had reached 80 °C, they were immersed into a 0.25 mM D35/ethanol dye bath solution kept in the dark for around 15 hours. The platinized counter electrodes (Pilkington, TEC15) were prepared by depositing 20 μl of 4.8 mM H<sub>2</sub>PtCl<sub>6</sub> isopropanol solution to a pre-drilled FTO glass; the Pt films were sintered in air at 400 °C for 30 min. The sensitized electrodes and platinized counter electrodes were assembled into a sandwich-type structure using a 25 μm hot-melt Surlyn frame (Solaronix). The electrolyte was injected through a pre-drilled hole in the counter electrode

under air pressure, and the hole was afterwards sealed with a 50 μm thermoplastic sheet and a glass coverslip.

#### Photovoltaic characteristics

A Newport solar simulator (model 91160-1000) was used to give an irradiation of up to 100 mW cm<sup>-2</sup> with AM 1.5 spectral distribution, which was calibrated using a certified reference solar cell (Fraunhofer ISE) before use. The current-voltage diagrams and characteristics including the overall conversion efficiency ( $\eta$ ), short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ) and fill factor ( $ff$ ) of the solar cells were recorded using a computerized Keithley model 2400 source/meter unit. In order to reduce the scattered light from the edge of the glass electrodes of the dyed TiO<sub>2</sub> layer and to ensure light falling on the active area of the device, light-shading metal mask (0.7 × 0.7 cm<sup>2</sup>) was applied on the top of the cell.

#### Electrochemical impedance measurements

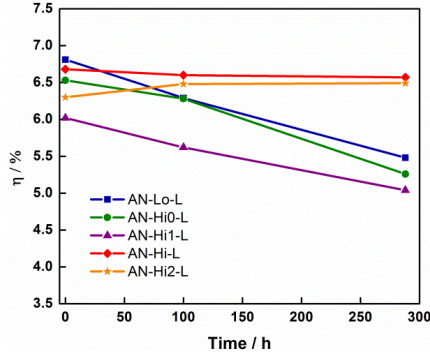
Impedance measurements were conducted with Autolab PGstat12 potentiostat with an impedance module. The frequency was swept from 10<sup>5</sup> Hz to 0.1 Hz using 20 mV AC amplitude, with illumination provided by a 5W white Luxeon LED. Impedance was recorded under dark conditions with a bias applied voltage. Resistances and capacitances were analyzed by the software Z-View using an equivalent circuit model as commonly used.

#### Tool-box measurements

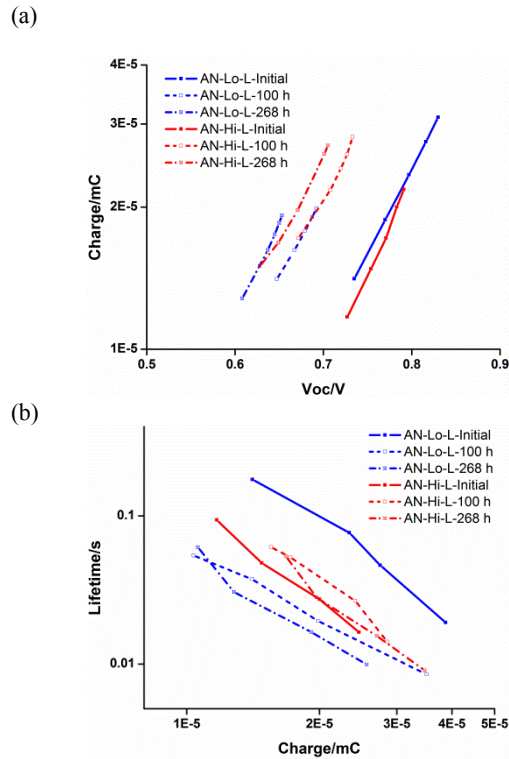
Extracted charge ( $Q_{oc}$ ), electron lifetime ( $\tau_e$ ) and transport time measurements were performed using a white LED (Luxeon Star 1W) as the light source. The methods of measurement have been reported previously.<sup>S2, 3</sup> Voltage and current traces were recorded using a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic switches. Transport time and lifetime were determined by monitoring the photocurrent and the photovoltage transients at different light intensities upon applying a small square-wave modulation to the base light intensity. The photocurrent and photovoltaic responses were fitted using first-order kinetics in order to obtain the time constants. Extracted charge measurements were performed by illuminating the cell for 10 seconds under open-circuit conditions and then turning off the lamp to let the voltage decay to a certain value  $V$ . The cell was then short-circuited, and the current was measured under 0.1 s and integrated to obtain  $Q_{oc}$ .

#### Stability tests

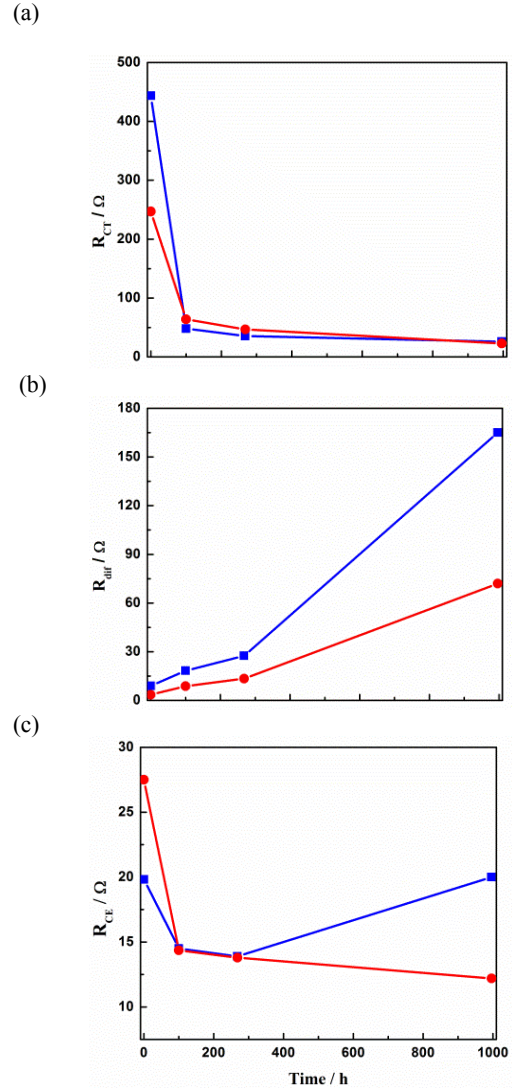
Long-term stability tests were performed under continuous illumination (ATLAS Suntest XLS) at approximately 100 mW cm<sup>-2</sup> using a 400 nm UV cut-off filter with a temperature of 60°C in the sample compartment. Photovoltaic characteristics of the cells were determined out of the compartment at selected intervals in order to obtain the trend of changes over time.



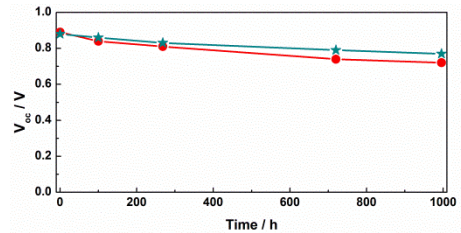
**Fig. S1** Efficiency variation of DSCs during a stability test under light-soaking conditions (1 sun illumination, 60 °C). Acetonitrile-based electrolytes with different concentrations of  $\text{Co}(\text{bpy})_3^{2+}/\text{Co}(\text{bpy})_3^{3+}$ : **AN-Lo-L**, 0.22 M/0.05 M (blue, square); **AN-Hi0-L**, 0.30 M/0.05 M (green, circle); **AN-Hi1-L**, 0.40 M/0.05 M (pink, triangle); **AN-Hi-L**, 0.30 M/0.15 M (red, diamond); **AN-Hi2-L**, 0.30 M/0.20M (orange, star).

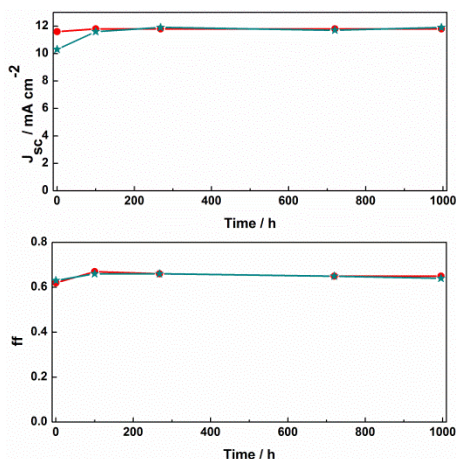


**Fig. S2** (a) Extracted charge under open-circuit conditions against  $V_{oc}$  and (b) electron lifetime in the  $\text{TiO}_2$  conduction band against extracted charge of DSCs fabricated with the electrolytes **AN-Lo-L** (blue) and **AN-Hi-L** (red); recorded immediately (solid), 100 hours (dash) and 268 hours (dash dot) after fabrication during the stability test.

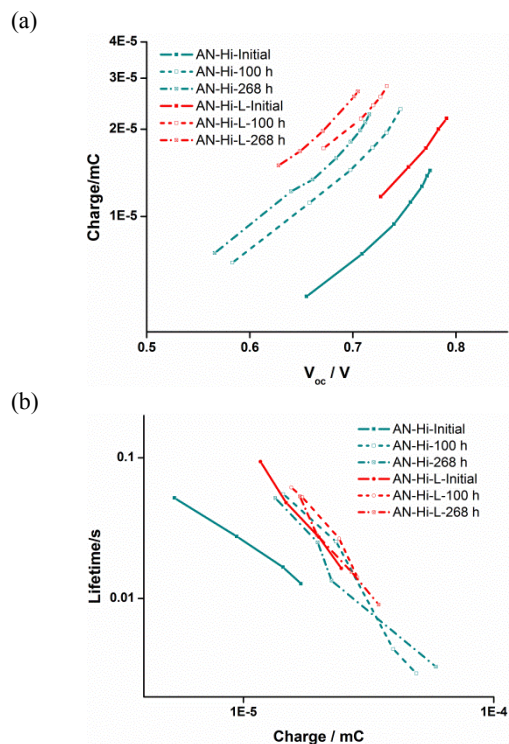


**Fig. S3** The changes over time of (a) the charge-transfer resistance,  $R_{CT}$ , (b) diffusion resistance,  $R_{diff}$  and (c) charge-transfer resistance at the counter electrode,  $R_{CE}$  extracted from EIS data for DSCs based on the electrolytes **AN-Lo-L** (blue) and **AN-Hi-L** (red) measured during the stability test.

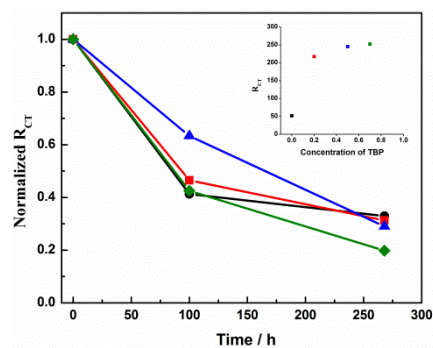




**Fig. S4** Variations of  $V_{oc}$ ,  $J_{sc}$ ,  $ff$  for DSCs based on the electrolytes: AN-Hi-L (red, circle), AN-Hi (cyan, star) during the stability test under light-soaking conditions (1 sun illumination, 60 °C).



**Fig. S5** (a) Extracted charge under open-circuit conditions against  $V_{oc}$  and (b) electron lifetime in the  $TiO_2$  conduction band against extracted charge of DSCs fabricated with the electrolytes AN-Hi (cyan) and AN-Hi-L (red) recorded immediately (solid), 100 hours (dash) and 268 hours (dash dot) after fabrication during the stability test.



**Fig. S6** Variation of the charge-transfer resistance,  $R_{CT}$ , extracted from EIS data of DSCs based on the AN-Hi-type electrolytes containing TBP of different concentration: 0 M (black, circle), 0.2 M (red, square), 0.5 M (blue, triangle), 0.7 M (green, diamond) measured during the stability test (Inset: Initial  $R_{CT}$  with various TBP concentrations.)

**Table S1** Initial  $J$ - $V$  characteristics of DSCs assembled with various electrolytes containing different concentrations of TBP and measured under simulated sunlight (AM 1.5 G, 1000 W/m<sup>2</sup>)

Electrolytes	AN-Hi	AN-Hi-type <sup>a</sup>	AN-Hi-L	AN-Lo-L		
TBP concentration (mol/L)	0.2	0	0.5	0.7	0.2	0.2
$J_{sc}$ (mA cm <sup>-2</sup> )	10.3	2.2	9.5	9.7	11.6	10.8
$V_{oc}$ (V)	0.88	0.61	0.90	0.91	0.89	0.91
$ff$	0.63	0.52	0.62	0.63	0.62	0.59
$\eta$ (%)	5.7	0.7	5.3	5.5	6.4	5.8

<sup>a</sup> AN-Hi and AN-Hi-type electrolytes only differ in the concentration of TBP. Other components are the same.

**Table S2**  $J$ - $V$  characteristics of DSC device containing TBP-free AN-Hi-type electrolyte measured at different stages of stability test.

	0 h	100 h	268 h	720 h	1000 h
$J_{sc}$ (mA cm <sup>-2</sup> )	2.2	5.7	6.9	9.3	9.5
$V_{oc}$ (V)	0.61	0.64	0.62	0.61	0.59
$ff$	0.52	0.62	0.61	0.61	0.62
$\eta$ (%)	0.7	2.2	2.6	3.5	3.5

## References

- S1 M. Bhagavathi Achari, V. Elumalai, N. Vlachopoulos, M. Safdari, J. Gao, J. M. Gardner and L. Kloo, *Physical Chemistry Chemical Physics*, 2013, **15**, 17419-17425.

- S2 S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, *Journal of the American Chemical Society*, 2010, **132**, 16714-16724.
- S3 J. Nissfolk, K. Fredin, A. Hagfeldt and G. Boschloo, *The Journal of Physical Chemistry B*, 2006, **110**, 17715-17718.