Supporting information

Light-induced electrolyte improvement in cobalt tris(bipyridine)mediated dye-sensitized solar cells

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Experiment section

Raman scattering spectroscopy measurements of electrolyte solutions were conducted using a BioRad FTS 6000 spectrometer equipped with a Raman accessory. An exciting wavelength of 1064 nm (Nd:YAG laser), a quartz beamsplitter and a resolution of 4 cm⁻¹ were employed. The scattered radiation was detected by a nitrogen-cooled solid state germanium detector. The FT-IR spectra were recorded over a range of 4000-700 cm⁻¹ using a Nicolet Avatar 370 spectrometer equipped with a DTGS detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. 16 scans were averaged for each spectrum. The samples were prepared from the dried solid powers by mixing either of electrolytes, i.e. fresh and light-exposed electrolyte, with non-sensitized, sintered TiO₂ nanoparticles, respectively.



Scheme S1 The equivalent circuit model used for fitting impedance curves. Parameters include series resistance (R_s), charge transfer resistance (R_{ct}) and capacitance (C_{ct}) at Pt/electrolyte interface, recombination resistance (R_{rec}) and chemical capacitance (C_{μ}) at TiO2/electrolyte interface and Warburg impedance (W_s).



Fig. S1 Molecular structures of dyes D35 (left) and LEG4 (right).



Fig. S2 Efficiency (η) and short circuit current density (J_{sc}) for DSSCs containing electrolytes without (Normal) and with light exposure (*) based on different combinations of electrolyte components as labelled, and that after device-based light exposure (**Device***).

| Dyes | Electrolytes* | $V_{\rm oc}/{ m mV}$ | $J_{ m sc}/ m mA$ cm ⁻² | FF | η/% |
|-------|-----------------------|----------------------|------------------------------------|------|-----|
| I ECA | Α | 845 | 11.4 | 0.67 | 6.5 |
| LEU4 | A* | 860 | 12.5 | 0.70 | 7.5 |
| | A-Li ⁺ | 830 | 13.0 | 0.68 | 7.3 |
| | | | | | |
| D35 | A(PF ₆ -) | 925 | 10.0 | 0.62 | 5.8 |
| | A*(PF ₆ -) | 955 | 11.6 | 0.68 | 7.5 |
| | A-0.2TBP | 925 | 10.2 | 0.62 | 5.9 |
| | A*-0.2TBP | 905 | 11.2 | 0.64 | 6.5 |
| | A-0.2bpy | 915 | 9.2 | 0.64 | 5.4 |
| | A*-0.2bpy | 915 | 11.6 | 0.66 | 7.0 |

Table S1 *J-V* characteristics data for DSSCs based on various cobalt-based electrolytes under different treatments.

^a All electrolytes were composed of the same recipe: 0.3 $M/0.15 M Co(bpy)_3^{2+/3+}$ and 0.2 M TBP in acetonitrile except for additional 0.1 M LiClO₄ in A-Li⁺, extra 0.2 M TBP (totally 0.4 M TBP)in A-0.2TBP, A*-0.2TBP and additional 0.2 M bipyridine in A-0.2bpy, A*-0.2bpy. A* represents electrolytes containing the Co(III)/Lewis base component subject to full sun/60°C exposure before formulated. A and A(PF₆⁻) differs in the anion of the cobalt complexes: the former, B(CN)₄⁻ and the latter, PF₆⁻.



Fig. S3 Incident photo-to-current conversion efficiency (IPCE) spectra (solid lines) for LEG4-sensitized DSCs assembled with various cobalt-based electrolytes under different treatments: **A**, blue, normal; **A***, red, the Co(III)/TBP acetonitrile solution was exposed under full sun irradiation before preparing the electrolyte; **A-Li**⁺, green, co-added with 0.1 M LiClO₄.



Fig. S4: The normalized Kinetics at 5000 nm for electron injection and electron recombination processes of the adsorbed D35 on TiO₂ surface in contact with cobalt electrolytes with (**A***) and without (**A**) $Co(bpy)_3^{3+}/TBP$ -based light exposure. The dye was excited at 520 nm with a power of ~150-200 μ W.

Table S2 The resulted lifetimes from the models of the kinetics extracted at 5000 nm. Lifetimes are in ps, and the amplitudes are shown in percent between parentheses.

| Condition | Electron injection | Electron recombination | | recombination Long lifetime (> 5 ns) | |
|-------------------|--------------------|------------------------|----------|--|-----------|
| Dry | 0.38 | 3.7 (22) | 75 (35) | $\tau_{3}(43)$ | 23.5 (57) |
| Aged electrolyte | 0.66 | 34 (40) | 427 (20) | $\tau_{3}(40)$ | 79 (60) |
| Fresh electrolyte | 0.29 | 26 (31) | 400 (21) | $\tau_{3}(48)$ | 78 (52) |



Fig. S5 Kinetics of the absorption changes at 760 nm for solar cells with aged (light-exposed) and fresh electrolyte. Excitation wavelength: 560 nm, ~ 0.1 - 0.2 mJ/pulse. Note: Three samples were investigated for each electrolyte. The statistical half-time was summarized in Table S3. The figure illustrates the kinetic traces of the samples with biggest difference. The solid line was obtained from KWW models.

Table S3. Summary of the statistical half-time ($\tau_{1/2}$) of the regeneration processes in DSSCs fabricated with aged (light-exposed) and fresh electrolyte.

| | Aged electrolyte | Fresh electrolyte |
|-------------------|------------------|-------------------|
| $	au_{1/2},\mu s$ | 0.39±0.10 | 0.58 ± 0.08 |



Fig. S6 (a) Photovoltaic parameters of DSSCs as function of the light-exposure time of the Co(III)/TBP component in the electrolyte. (b) Trap state distribution in D35-sensitized TiO₂ films and (c) the electron transport time in TiO₂ as function of the short-circuit current density for DSSCs containing electrolytes without (A) and with (A*) Co(III)/TBP solutions pre-exposed to the light for different times as labelled. Inset in (a): the energy-level difference of E_c - E_{redox} obtained from models as function of light-exposure time.

The distribution of band-gap trap states was modeled using an exponential function according to:1

$$N_t(qV_{oc}) = \frac{N_t}{kT_c} exp^{(to)} (\frac{qV_{oc} - E_c}{kT_c})$$
S1

where T_c , E_c and N_t respectively represent the characteristic temperature indicating the depth of trap states, the conduction band energy and the total volume density of trap states in the TiO₂ film. Therefore,

$$qV_{\rm oc} = kT_{\rm c} ln N_{\rm t} (qV_{\rm oc}) + A,$$

herein,

$$A = (E_c - E_{redox}) - kT_c ln \frac{N_t}{kT_c}$$
S3



Fig. S7 Cyclic voltammetry curves (Inset: DPV) for fresh (blue) and exposed (red) $Co(bpy)_3^{3+}/TBP$ acetonitrile solution to the light.

| Table S4. | Rest potentials | of electrolytes A | A and A* |
|-----------|-----------------|-------------------|----------|
| | 1 | 2 | |

| | A* | Α |
|---------------|-------------|-------------|
| E,V (vs. NHE) | 0.506±0.001 | 0.508±0.003 |



Fig. S8 Trap states distribution in D35-sensitized TiO_2 films for DSSCs based on cobalt electrolytes containing 0.2M TBP without (red) and with extra 0.2 M TBP (blue) and 0.2 M bipyridine (green) added before (solid) and after (hollow) Co(III)/TBP-based light exposure. Inset: E_c , E_c^* are the calculated energy level of TiO₂ conduction band versus the redox potential of the electrolyte after models of the curves.

| Electrolytes | C _{Co3+} | $V_{\rm oc}/{ m mV}$ | $J_{\rm sc}/$ mA cm ⁻² | FF | η/% |
|------------------------------|-------------------|----------------------|---|------|-----|
| $\mathbf{A}_{\mathbf{low}}$ | 0.10 M | 895 | 9.7 | 0.63 | 5.4 |
| Α | 0.15 M | 915 | 10.1 | 0.64 | 5.9 |
| $\mathbf{A}_{\mathbf{high}}$ | 0.20 M | 900 | 10.3 | 0.64 | 5.9 |

Table S5 *J-V* characteristics of DSCs assembled with electrolytes containing different concentrations of $Co(bpy)_3^{3+}$.



Fig. S9 Electron lifetime in D35-sensitized TiO_2 films of DSSCs varying in the concentration of $[Co(bpy)_3]^{3+}$ as labelled.

Table S6 Fit parameters extracted from EIS measurements of D35-sensitized solar cells containing electrolytes without (A) and with (A*) Co(III)/TBP solutions pre-exposed to the light. The results were obtained from EIS measurements under dark and -0.9 V bias.

| Electrolytes | $R_{\rm CE}/\Omega$ | $R_{\rm CT}/\Omega$ | $R_{\rm dif}/\Omega$ |
|--------------|---------------------|---------------------|----------------------|
| Α | 3.6 | 52.3 | 10.1 |
| A* | 3.3 | 56.6 | 3.2 |



Fig. S10 Cyclic voltammograms of (a) fresh 0.15 M $[Co(bpy)_3]^{3+}$ and (b) 0.15 M/0.2 M $[Co(bpy)_3]^{3+}/TBP$ electrolytes in acetonitrile after light exposure and 0.3 M $[Co(bpy)_3]^{2+}$ added afterwards, investigated in a symmetrical cell with two platinized FTO glass as the electrode at scan rates from 25 mV/s to 250 mV/s, interspace 25 mV/s. The arrows show the direction of change with increasing scan rate.



Fig. S11 Peak current (i_p) measured for a symmetrical dummy cell containing the 0.15 M/0.3 M $[Co(bpy)_3]^{3+}/TBP$ electrolyte as function of the square root of the scan rate $(v^{1/2})$ by cyclic voltammetry from 0.4 V to -0.4 V. Points in the high scan rate range were modeled using a linear function.



Fig. S12 (a) Diffusion resistances (R_{dif}) and (b) diffusion times (τ_d) as a function of applied bias voltage obtained from a symmetrical dummy cell containing 0.15 M [Co(bpy)₃]³⁺ in the presence of TBP at different concentrations; fresh: 0 M, green; 0.05 M, cyan; 0.1 M, blue; 0.2 M, purple and at 0.2 M TBP after light exposure after different times: 0.5 h, orange; 2h, pink; 24h, red; 268h, brown. The data were extracted from EIS results and approximated with a linear model in the figure.



Fig. S13 a: UV-vis spectra of the $Co(bpy)_3^{3+}/TBP/acetonitrile solution with different initial concentration ratios; b: the decrease in the UV-vis absorbance at 450 nm of <math>Co(bpy)_3^{3+}/TBP$ in acetonitrile in low and high concentrations respectively as a function of light exposure time.



Fig. S14 UV-vis spectra of the 2 mM $Co(bpy)_3^{3+}$ before and after TBP (3 mM) and bpy added. The amount of bpy added is gradually increased from 3 mM to 9 mM.

Table S7. Characteristic chemical shifts of TBP ring protons (δ_{TBP-2H}) obtained from ¹H-NMR results of electrolytes containing different components before and after light ageing for different time as noted, and correspondingly the predicted fraction of free TBP concentration (χ_{tbp}) in the electrolyte.

| Components | C(Co ³⁺) | C(TBP) | C(bpy) | Ageing time | $\delta_{\text{TBP-2H}}$ | $\chi_{tbp}{}^{a}$ |
|---------------------------|----------------------|--------|--------|----------------|--------------------------|--------------------|
| TBP | - | - | - | 0 h | 7.39-7.37 | 100% |
| Co ³⁺ /TBP | 0.05 M | 0.05M | 0 M | 0 h | 7.40-7.39 | 95% |
| | | | | 0 h | 7.40-7.39 | 95% |
| | | | | 2 h | 7.48-7.47 | 70% |
| Co ³⁺ /TBP/bpy | 0.05 M | 0.008M | 0.05 M | 4 h | 7.51-7.49 | 62% |
| | | | | 24 h | 7.60-7.59 | 33% |

^a The crude estimation of χ_{tbp} relies on a few simple assumptions:

- The main process taking place in the solution is ligand exchange at the Co^{III} coordination centre and all other processes can be neglected.
- The chemical shift of the TBP-2H protons in non-coordinated TBP is 7.38 ppm
- The chemical shift of the TBP-2H protons in tbp coordinated to a Co^{III} complex is 7.70 ppm (taken from the previous publicaiton)²
- The general equilibrium upon mixing a solution containing the Co(bpy)₃³⁺ complex and TBP is as follows:

$$Co(bpy)_{3^{3+}} + TBP < - -> Co(bpy)_{2}(TBP)^{3+} + bpy,$$

The equilibrium constant,

$$K = [Co(bpy)_2(TBP)^{3+}] [bpy] / [Co(bpy)_3^{3+}] [TBP]$$

The NMR-shift relation for a fast (spin-state) exchange situation can be summarized in two equations:

$$\begin{bmatrix} \delta_{obs} = \chi_{tbp} \, \delta_{tbp} + \chi_{Co} \, \delta_{Co} \\ \chi_{tbp} + \chi_{Co} = 1 \end{bmatrix}$$

where δ_{obs} is the observed chemical shift, δ_{tbp} is the chemical shift of non-coordinated TBP, δ_{Co} is the chemical shift of TBP coordinated to the Co^{III} centre, χ_{tbp} is the fraction of total TBP concentration existing in the form of non-coordinated TBP, and χ_{Co} is the fraction of TBP existing in the form of Co-coordinated TBP.

Then,

 $\chi_{tbp} = (\delta_{obs} - \delta_{Co}) / (\delta_{tbp} - \delta_{Co})$



Fig. S15 ¹H NMR spectra of $[Co(bpy)_3]^{3+}/TBP$ in CD₃CN after light exposure for 0 min, 20 min, 60min and 120 min from bottom to top respectively. The characteristic peak of TBP at 7.4 ppm was labelled *a*. Inset: ¹H NMR spectra respectively showing the evolution of peak *a* (right) and the new peak at 14.5 ppm (left) with light exposure time.



Fig. S16 ¹H NMR spectra of 0.05 M/0.05 M $[Co(bpy)_3]^{3+}/TBP$ in CD₃CN after exposed to the light for 0.5 h, with (red) and without (green) 0.005 M bipyridine added afterwards.



Fig. S17 ¹H NMR spectra of $[Co(bpy)_3]^{3+}/TBP$ in CD₃CN before and after storage under dark/60°C for different time as labelled.





Fig. S18 (a) Raman spectra of TBP only (black, dashed), $[Co(bpy)_3]^{3+}$ only (green), $[Co(bpy)_3]^{3+}/TBP$ in acetonitrile before (blue) and after (red) light exposure. (b) FT-IR spectra of TiO₂ films spin-coated with $[Co(bpy)_3]^{3+}/TBP$ acetonitrile solutions before and after light exposure treatment and dried in air afterward.



Fig. S19 ¹H NMR spectra of (from top to bottom) $[Co(bpy)_3]^{3+}/Dpy$, $[Co(bpy)_3]^{3+}/TBP/bpy$ when fresh and after light exposure for 2 h, 24 h and 48 h. The initial component concentrations are: TBP 0.06 M, $[Co(bpy)_3]^{3+}$ 0.05 M and bpy 0.009 M.



Fig. S20 ¹H NMR spectra of $[Co(bpy)_3]^{3+}/TBP$ in CD₃CN measured at different temperature: (from top to bottom) -15°C, -5°C, 5°C, 15°C, 25°C, 35°C, 45°C.



Fig. S21 Mass spectrometry of the $[Co(bpy)_3]^{3+}/TBP/acetonitrile solution after light exposure.$



Fig. S22 ¹H NMR spectra of 0.05 M $[Co(bpy)_3]^{3+}/0.06$ M TBP without and with 0.025 M, 0.05 M, 0.1 M and 0.15 M $[Co(bpy)_3]^{2+}$ added (from bottom to top). The characteristic peak of TBP at 7.4 ppm was labelled *a*. Inset: ¹H NMR spectra showing the evolution of peak *a* with increasing the concentration of $[Co(bpy)_3]^{3+}$ added.



Fig. S23 UV-Vis absorption spectra of D35/acetonitrile saturated solution ($<2.5\times10-5$ M) containing (a) 0.005 M LiClO₄ and (b) low (0.005 M, upper) and high (0.01M, lower) concentrations of HCOOH before (dashed lines) and after exposure to full sun (390 nm cut-off)/60 °C conditions (Inset: dark/60 °C) for different times.

References

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