Electronic Supplementary Material (ESI) for ChemComm.
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Direct light-induced polymerization of cobalt-based redox shuttles: an ultrafast way towards stable dye-sensitized solar cells

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SUPPORTING INFORMATION

Synthesis of Cobalt Complexes. All chemicals were purchased from Sigma-Aldrich unless otherwise mentioned. $Co(bpy)_3(PF_6)_2$ and $Co(bpy)_3(PF_6)_3$ were synthesized according to a modified procedure published by our group [1]. In particular, 1 equiv of $CoCl_2 \cdot 6H_2O$ and 3.3 equiv of the (2,2′-bipyridyl) ligand were dissolved in a minimal amount of methanol to give a brown-yellow solution. The solution was left to stir at reflux for 2 h; then, an excess of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was added to the solution to precipitate the compound. Afterwards, the product was filtered, washed with methanol, ethanol and diethylether, dried under vacuum, and used without further purification. Oxidation of the cobalt(II) to cobalt(III) complex was performed by adding H_2O_2 (30%) dropwise to an acetonitrile solution of the metal complex. The solution was left to stir. Subsequently, a large amount of saturated $TBAPF_6$ in distilled water was added to the solution in order to precipitate the compound. The final product was washed with water, filtered, dried under vacuum, and used without further purification.

Synthesis of quasi-solid polymer electrolytes. All chemicals were purchased from Sigma-Aldrich unless otherwise mentioned. Bisphenol A ethoxylate dimethacrylate (BEMA, average M_n: 1700) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, average M_n: 700) were mixed at 1:1 weight ratio (namely, 0.5 g : 0.5 g). Then, 0.5 g of such formulation were mixed with 0.5 g of an acetonitrile-based solution containing $Co(II)(bpy)_3(PF_6)_2$ 0.22 M, $Co(III)(bpy)_3(PF_6)_3$ 50 mM and 4-*tert*-butylpyridine 0.2 M. The resulting formulation was thoroughly mixed with a magnetic stirrer and, after the addition of a free-radical photoinitiator (Irgacure® 1173, 3 wt%), it was introduced in a pre-sealed DSSC *via* vacuum back-filling. Afterwards, each cell was UV-irradiated from the counter electrode side for 1 min by using a medium vapour pressure Hg lamp (Helios Italquartz, Italy), with a radiation intensity on the surface of 30 mW cm^{-2}, allowing the methacrylic double bond conversion through photoinduced radical polymerization.

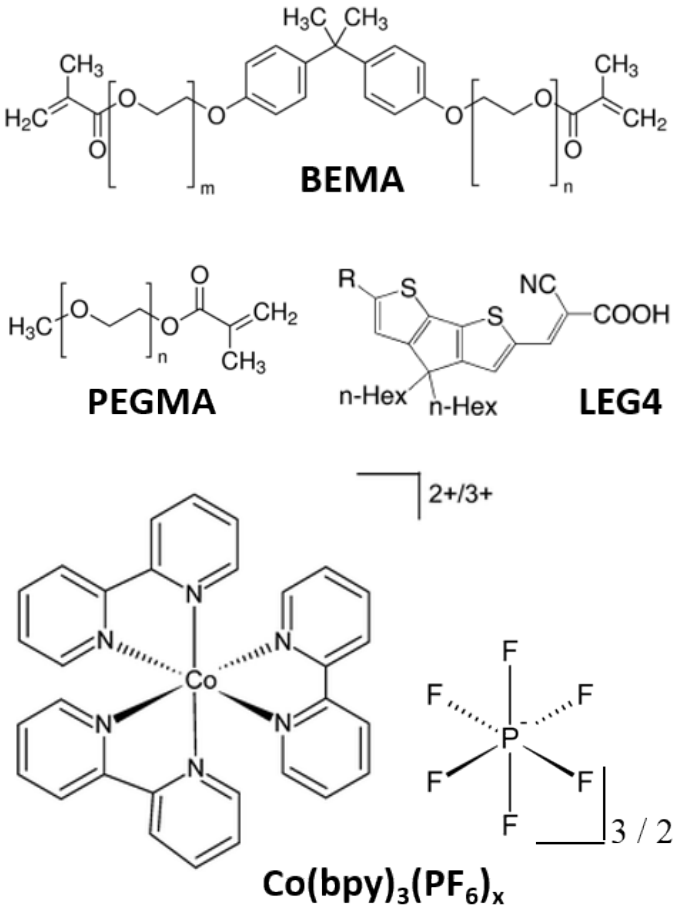
Fabrication of Dye-Sensitized Solar Cells. FTO-coated glass substrates (TEC15 and TEC8, Pilkington) were cleaned in an ultrasonic bath for 1 h in the following media: detergent (RBS 25 from Fluka analytical), deionized water and ethanol.

As regards photoanodes, the TEC15 glass substrates were pretreated in a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and then rinsed with ethanol and water. Subsequently, substrates were screen-printed (active area 0.25 cm^2) with a diluted Dyesol DSL 18 NR-T paste. The paste was prepared by adding a 40 wt% mixture containing 90 wt% terpineol and 10 wt% ethyl cellulose to 60 wt% of Dyesol paste. After drying at 125 °C for 10 min, the substrates were printed with a second layer of a 20 wt% terpineol-diluted TiO_2 light-scattering paste (JGC C&C Ltd. PST-400C, kindly provided by JGC Catalysts and Chemical Ltd.). Afterwards, the samples were heat-treated according to the following temperature *vs.* time ramp: 180 °C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (60 min) in an oven (Nabertherm Controller P320) under air. After sintering, the samples were once again treated in 40 mM aqueous $TiCl_4$ by the aforementioned procedure. Finally, a heating step (500 °C for 60 min) was performed. The final thickness of the TiO_2 films obtained by this procedure was 8.5 μm. In order to tune the photoanode thickness as required by the experiments shown in Fig. 1D, the amount of Dyesol paste in the first screen-printing step was varied between 45 and 75 wt%. Finally, electrodes (kept at 90 °C) were immersed in a LEG4-based solution (Scheme S1) having a concentration of 0.2 mM in ethanol. LEG4 dye was synthesized as previously reported by Gabrielsson *et al.* [2]. The R group of LEG4 molecular structure shown in Scheme S1 is depicted in Scheme S2. The TiO_2 films were left in the dye bath overnight (15 h) before being rinsed with acetonitrile and sandwich-structured.

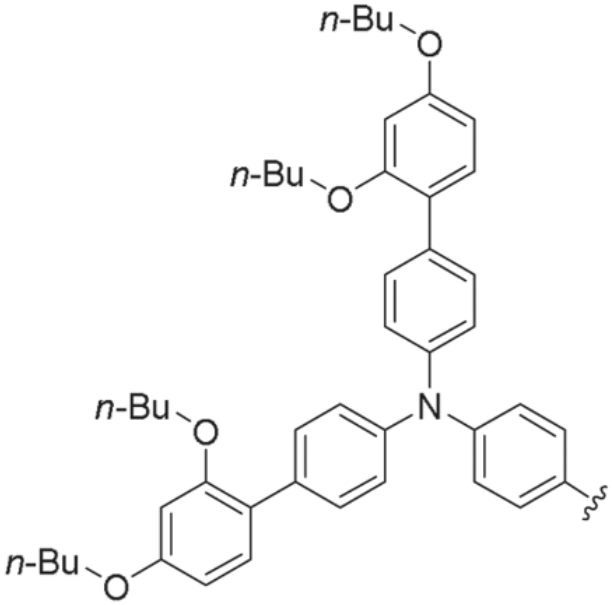
Solar cells were assembled, using a 60 μm-thick thermoplastic Meltonix 1170-60 frame, with a platinized counter electrode (TEC8). The latter was prepared by depositing 10 μL cm^{-2} of a 4.8 mM H_2PtCl_6 solution in ethanol to the glass substrate, followed by heating in air at 400 °C for 30 min.

An electrolyte precursor solution was then introduced through two holes pre-drilled in the counter electrode and the cell was sealed with thermoplastic Meltonix covers and a glass coverslip. The electrolyte precursor contained bisphenol A ethoxylate dimethacrylate (BEMA, average M_n: 1700, Scheme S1) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, average M_n: 700, Scheme S1), mixed at 1:1 ratio with an acetonitrile-based solution containing $Co(II)(bpy)_3(PF_6)_2$ 0.22 M, $Co(III)(bpy)_3(PF_6)_3$ 50 mM (Scheme S1) and 4-*tert*-butylpyridine 0.2 M. After magnetic mixing, the photoinitiator Irgacure® 1173 (3 wt% with respect to the BEMA:PEGMA amount) was added. *In-situ* photopolymerized electrolytes were obtained by UV-irradiating the mixtures for 1 min using a medium vapour pressure Hg lamp (Helios Italquartz, Italy), with an irradiation intensity on the surface of 30 mW cm^{-2}, measured with a Powerpuck II radiometer (EIT).

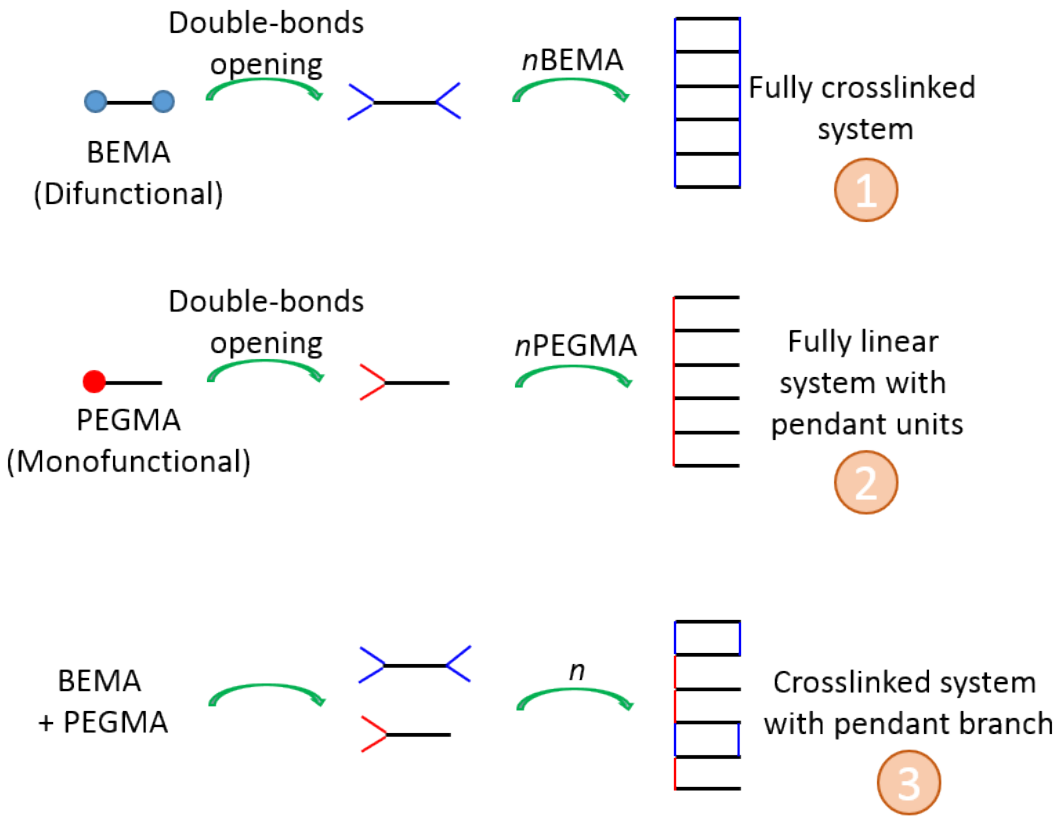
For comparison purposes, cells were also sealed with the bare cobalt-based liquid electrolyte: $Co(II)(bpy)_3(PF_6)_2$ 0.22 M, $Co(III)(bpy)_3(PF_6)_3$ 50 mM and 4-*tert*-butylpyridine 0.2 M in acetonitrile solvent.



Scheme S1. Structural formula of BEMA (n = 22), PEGMA (n = 9), LEG4 dye (R group is shown in Scheme S2) and Co(II)/Co(III) complexes (bpy is 2,2′-bipyridine).



Scheme S2 R group of LEG4 dye shown in Scheme S1.



Scheme S3 Polymers obtained by UV-irradiating BEMA, PEGMA and their mixtures in the presence of a free-radical photoinitiator. The system proposed in this work is (3), where a cross-linked matrix is obtained; in our present case, the crosslinking density is lowered by the introduction of a monofunctional monomer (PEGMA).

Characterization Techniques. The kinetics of the photopolymerization was followed by real-time Fourier transform infrared (RT-FTIR) spectroscopy, employing a Thermo-Nicolet 5700 instrument. Typically, a thin layer of reactive mixture was deposited onto a silicon wafer and concurrently exposed to the UV beam (which induced the polymerization) and to the IR beam (which analysed *in situ* the extent of the conversion reaction). The conversion of the methacrylate double bonds at any time was calculated by monitoring the peak area under the 1634 cm^{-1} band (methacrylate C=C signal), normalized by a constant signal in the spectra (C=O peak at 1726 cm^{-1}).

The viscoelasticity was investigated by dynamic mechanical thermal analyses (DMTA) on a TTDMA instrument (Triton Technology Ltd), at a frequency of 1 Hz and a heating rate of 2 °C min^{-1} in the tensile configuration. The maximum of the *tanδ* trend was taken as the glass transition temperature (T_g) value.

The thermal stability of the UV-cured polymer membranes was tested by thermo-gravimetric analysis (TGA), with a TG 209 F1 Libra® instrument from Netzsch, over a temperature range of 25-700 °C under N_2 flux at a heating rate of 10 °C min^{-1}.

A PARSTAT 2273 potentiostat/galvanostat equipped with a frequency response analyser (Princeton Applied Research, US) was used to apply a sinusoidal signal with an amplitude of 10 mV and a frequency variable in the range of 10^{-2} - 10^4 Hz, and to measure the current signal. Such a protocol was used for the electrochemical impedance spectroscopy (EIS) measurements shown in Fig. 1D. Moreover, the apparent diffusion coefficient of $[Co(bpy_3)]^{3+}$ was measured with symmetric cells. The symmetric cells were fabricated with a structure of Pt/electrolyte/Pt, where the two electrodes were separated by means of a 60 μm-thick thermoplastic Meltonix 1170-60 frame. The current potential scan range was set between –1.3 and 1.3 V and the scan rate was set at 20 mV s^{-1}. The limiting currents were obtained by reading the plateau of the diffusion curve. The diffusion coefficient value was calculated with the equation:

$$D_{app} = \frac{J_{lim} \cdot d}{2 \cdot n \cdot F \cdot C}$$

where J_{lim} is the limiting current density, d is the distance between the two electrodes, F is the Faraday constant, C is the bulk concentration of the diffusion-limiting species and n = 1, the number of electrons transferred for the cobalt-based redox couple.

Current-voltage (I-V) characteristics of the solar cells were investigated by a Keithley 2400 source/meter and a Newport solar simulator (model 91160). The light intensity was calibrated using a certified reference solar cell (Fraunhofer ISE), to an intensity of 1000 W m^{-2}. When performing the I-V measurements, a black mask of 0.4 × 0.4 cm^2 was used in order to avoid significant additional contribution from light impinging on the device outside the active area. I-V

measurements were also performed at light intensities in the range of 0.2-1.0 sun, by using neutral density filters purchased from Newport. All the measurements were carried out on at least four different fresh cells in order to verify the reproducibility of the obtained results.

The measurements of the incident photon-to-current conversion efficiency (IPCE) were performed by means of a computer-controlled setup consisting of a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM 110), and a Keithley 2700 multimeter. The same certified reference solar cell previously mentioned was used for IPCE calibration. IPCE curves were recorded under bias light.

OCVD measurements

Open circuit voltage decay (OCVD) curves were acquired using an electrochemical workstation (CH Instruments 760D) with a time resolution of 100 ms.

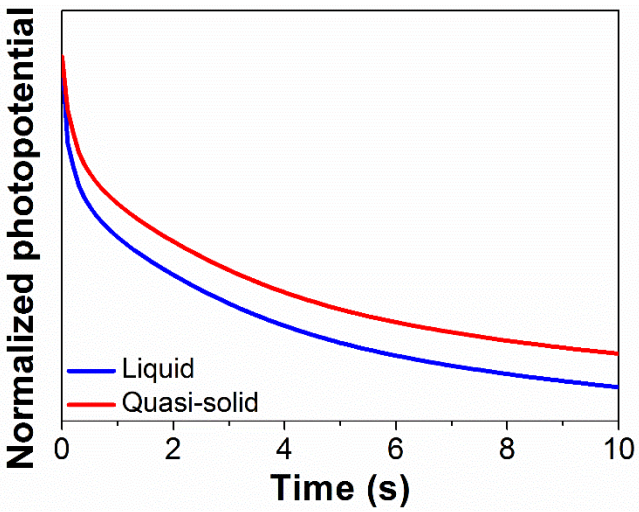


Fig. S1. OCVD curves for DSSCs assembled with Co(II)/Co(III) complex-based liquid or quasi-solid electrolytes.

R_{CE} measurements

Impedance spectroscopy measurements were also performed on DSSCs in order to evaluate the electrolyte/counter electrode interfacial charge transfer properties. To this purpose, the same potentiostat used for the measurements on the dummy cell in Fig. 1D was employed. The impedance of DSSCs was measured at the open circuit voltage, while the amplitude of the AC signal was 10 mV and the frequency range 10^{-1} - 10^{4} Hz. Data were fitted with an equivalent circuit described in [3]. The values of the impedance of charge transfer at the counter electrode (R_{CE}) upon aging are shown below for the two electrolytes under study. For the liquid cell, an initial 44% increase in R_{CE} was recorded, while it remained constant for the rest of the experiment. On the other hand, the cell assembled with the quasi-solid electrolyte showed a stable electrolyte/counter electrode interface upon the whole aging test.

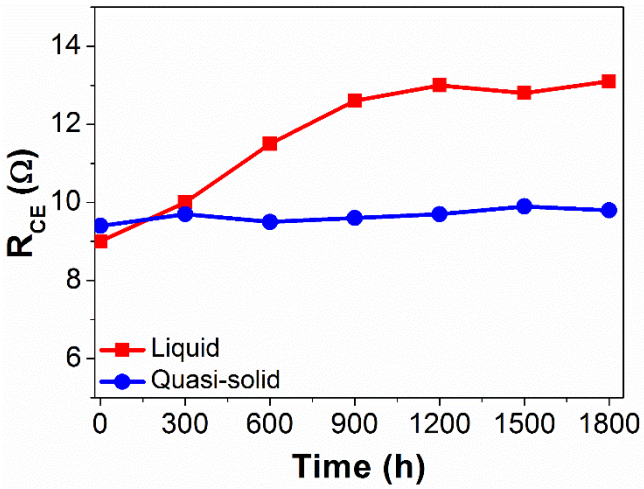


Fig. S2. Variation of R_{CE} during long-term stability test for DSSCs assembled with Co(II)/Co(III) complex-based liquid or quasi-solid electrolytes.

[1] S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, *J. Am. Chem. Soc.*, 2010, **132**, 16714.

[2] E. Gabrielsson, H. Ellis, S. Feldt, H. Tian, G. Boschloo, A. Hagfeldt and L. Sun, *Adv. Energy Mater.*, 2013, **3**, 1647.

[3] F. Bella, A. Lamberti, A. Sacco, S. Bianco, A. Chiodoni and R. Bongiovanni, *J. Membr. Sci.*, 2014, **470**, 125.