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Xingzhu Wang, Jing Yang, Hao Yu, Feng Li, Li Fan, Wen Sun, Yeru Liu, Zhen Yu Koh, Jia Hong Pan, Wai-Leung Yim, Lei Yan* and Qing Wang*

1 Department of Materials Science and Engineering, NUSNNI-NanoCore, National University of Singapore, 9 Engineering Drive 1, Singapore, 117576. Fax: (+)(65) 6776-3604, E-mail: qing.wang@nus.edu.sg

2 College of Chemistry and Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Xiangtan University, Xiangtan 411105, Hunan Province, P. R. China, E-mail: yanlei@xtu.edu.cn

3 Institute of High Performance Computing, Agency for Science, Technology, and Research, 1 Fusionopolis Way, No. 16-16 Connexis, Singapore 138632

Scheme S1. Synthetic route of D2. Reagents and conditions: i) Pd(PPh3)2Cl2, THF, reflux; ii) DMF, POCl3, 1,2-dichloroethane, 25°C; iii) 4,4,5,5-tetramethyl-2-{4-[N, N–bis (4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, Pd(PPh3)4, K2CO3, toluene /H2O (5/1, v/v), 25°C; iv) cyanoacetic acid, piperidine, CHCl3, reflux.

Experimental Details
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1. Materials

4,7-dibromobenzo[c][1,2,5]thiadiazole,\textsuperscript{S1} 4,4,5,5-tetramethyl-2-{4-[N, N-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, \textsuperscript{S2} tributyl (4,4-dihexyl-4H-cyclopenta[2,1-b:3, 4-b']dithiophene) stannane\textsuperscript{S3} 2-cyano-3-{6-[N,N-bis(4-hexyloxyphenyl)amino]phenyl}-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl}acrylic acid \textsuperscript{S4} were synthesized according to the literature procedures. Electrode preparation and cell fabrication followed previous reports.\textsuperscript{S5} Optimized devices employed double layer TiO2 films comprising of 4.8 μm transparent layers (Dyesol, DSL 18-NR) and 2 μm light scattering layers (WER-O paste, Dyesol). The cobalt complexes [Co(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}, [Co(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{3} (bpy=2,2'-bipyridine) were synthesized according to a previously reported procedure \textsuperscript{S6} and other chemicals were used as received from Sigma-Aldrich.

2. Synthesis

2.1 Synthesis of compound 1.

In a 100 ml two-neck reaction flask, 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.88 g, 3 mmol), tributyl (4,4-dihexyl-4H-cyclopenta[2,1-b:3, 4-b']dithiophene) stannane (2.23 g, 3.5 mmol) were degassed for three times with N\textsubscript{2} followed by the addition of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (60.0 mg, 0.086 mmol), and then dry THF (40.0 ml) was injected into the mixture. After the mixture refluxed for 18 h, the solvent was removed under a reduced pressure, the residue was loaded onto a silica gel column for purification with dichloromethane/petroleumether (1/5, v/v) as eluent to afford 2 (0.81g, 48%) as a red solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, ppm) δ: 8.03 (s, 1H, Ar) 7.84 (d, J = 8, 1H, Ar), 7.72 (d, J = 8.4, 1H, Ar), 6.98 (d, J = 4.4, 1H, Ar), 1.91 (t, J = 8.0 Hz, 4H, alkyl), 1.01-1.16 (m, 16H, alkyl), 0.81 (s, 6H, alkyl). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, ppm) δ: 159.1, 153.8, 151.5, 139.3, 138.4, 136.5, 132.3, 128.0, 126.3, 123.9, 122.9, 121.8, 110.9(Ar), 53.9, 37.9, 31.7, 29.8, 24.7, 22.7, 14.1(alkyl). FAB-MS: m/z 558 (M\textsuperscript{+}). C\textsubscript{28}H\textsubscript{31}BrN\textsubscript{2}OS\textsubscript{3} (559.65): Calcd. C 57.95, H 5.58, N 5.01; Found C 57.94, H 5.59, N 5.0.
2.2 Synthesis of compound 2.

In a 100 ml two-neck reaction flask, phosphorus chloride oxide (0.18 g, 1.2 mmol) was added into the cold solution of 1 (0.56 g, 1.0 mmol) and N,N-dimethylformide (0.09 g, 1.2 mmol) in 1,2-dichloroethane (15 ml) at 0 °C. The reaction solution was heated to 90 °C, stirred for 12 h, and then saturated sodium acetate aqueous solution (20.0 ml) was added. The mixture was further stirred at room temperature for 30 min. The crude product was extracted into dichloromethane, and the organic layer was washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/petroleumether 60-90 °C, 3/1, v/v) on silica gel to yield compound 3 (0.53 g, 90%) as a red solid. \( \text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz, ppm) \delta: 9.87 \text{ (s, 1H, CHO), 8.04 (s, 1H, Ar), 7.89 (d, J=6.8, 1H, Ar), 7.78 (d, J=8.0, 1H, Ar), 7.61 (s, 1H, Ar), 1.95 (t, J=7.4 Hz, 4H, alkyl), 1.01-1.16 (m, 16H, alkyl), 0.81 (s, 6H, alkyl).} \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz, ppm) \delta: 182.5 \text{ (CHO), 162.9, 158.7, 153.9, 151.5, 147.1, 144.3, 143.0, 137.7, 132.3, 129.80, 127.30, 125.2, 122.5, 112.6 (Ar), 54.4, 37.7, 31.6, 29.6, 24.66, 22.6, 14.0 (alkyl).} \text{FAB-MS: } m/z 856 (M^+). \text{C}_{28}\text{H}_{31}\text{BrN}_2\text{OS}_3 (587.66): \text{Calcd. C 57.23, H 5.32, N 4.77; Found C 57.22, H 5.31, N 4.78.}

2.3 Synthesis of compound 3.

Into a 50 ml two-neck flask were added 4,4,5,5-tetramethyl-2-{4-[N, N -bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2 -dioxaborolane (0.35 g, 0.61 mmol) and (0.30 g, 0.51 mmol) of compound 2 in 15 ml of anhydrous toluene. 25.0 mg Pd(0) tetrakis(triphenylphosphine) palladium, was transferred into the mixture. Subsequently, 2.0 M aqueous sodium carbonate which was deaerated for 30 min in toluene purged under Ar for 1 h was transferred via cannula. The reaction mixture was stirred at 100 °C for 24 h. The reaction mixture is cooled to room temperature and the crude product was extracted into dichloromethane, and the organic layer was washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/petroleumether 60-
90 °C, 1/2, v/v) on silica gel to yield a dark red solid. (0.37 g, 76 %). \(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm) \(\delta\): 9.85 (s, 1H, CHO), 8.04 (s, 1H, Ar), 7.97 (d, J = 7.4 Hz, 1H, Ar), 7.83 (d, J = 7.8 Hz, 2H, Ar), 7.69 (d, J = 7.2 Hz, 1H, Ar), 7.60 (s, 1H, Ar), 7.13 (d, J = 8.1 Hz, 4H, Ar), 7.05 (d, J = 7.6 Hz, 2H, Ar), 6.86 (d, J = 8.2 Hz, 4H, Ar), 3.95 (t, J = 8.0 Hz, 4H, alkyl), 1.96 (t, J = 8.0 Hz, 4H, alkyl), 1.79 (s, 4H, alkyl), 1.47-1.02 (m, 28H, alkyl), 1.02 (m, 6H, alkyl), 0.91 (m, 6H, alkyl), 0.80 (t, 6H, alkyl). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm) \(\delta\): 182.4 (CHO), 163.1, 158.4, 155.9, 154.0, 152.6, 149.3, 147.7, 144.6, 143.8, 140.3, 136.8, 133.0, 129.8, 128.9, 128.3, 127.2, 126.5, 125.6, 125.32, 121.5, 119.5, 115.5 (Ar), 68.3, 65.6, 54.3, 37.8, 31.6, 30.7, 29.7, 29.4, 25.8, 24.7, 22.6, 19.2, 14.1, 13.8 (alkyl). MALDI-TOF MS: \(m/z\) 952. \(C_{58}H_{69}N_{3}O_{3}S_{3}\) (952.38): Calcd. C 73.15, H 7.30, N 4.41; Found C 73.16, H 7.29, N 4.43.

2.4 Synthesis of \(\text{D2}\).

To a stirred solution of compound 3 (0.047 g, 0.5 mmol) and cyanoacetic acid (0.022 g, 0.25 mmol) in chloroform (10.0 ml), piperidine (0.043 g, 0.5 mmol) was added. The reaction mixture was refluxed under argon for 18 h and then acidified with 2.0 M hydrochloric acid aqueous solution (10.0 ml). The crude product was extracted into chloroform, washed with water, and dried over anhydrous sodium sulfate. After solvent was removed under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/10, v/v) in turn as the eluent to yield a purple-black powder (0.047 g, 90%). \(^1\)H NMR (DMSO\(_6\), 400 MHz, ppm) \(\delta\): 8.36 (s, 1H, Ar), 8.26 (s, 1H, Ar), 8.22 (d, J = 7.5 Hz, 1H, Ar), 7.93 (m, 3H, Ar), 7.87 (d, J = 7.6 Hz, 1H, Ar), 7.10 (d, J = 8.6 Hz, 4H, Ar), 6.95 (d, J = 8.7 Hz, 4H, Ar), 6.90 (d, J = 8.5 Hz, 2H, Ar), 3.97 (t, J = 6.2 Hz, 4H, alkyl), 3.07 (t, J = 7.2, 2H, alkyl), 1.97 (t, J = 7.4, 4H, alkyl), 1.82-1.61 (m, 4H, alkyl), 1.45-1.33 (m, 10H, alkyl), 1.19 (m, 12H, alkyl), 0.93 (m, 10H, alkyl), 0.77 (t, J = 6.7 Hz, 6H, alkyl). MALDI-TOF MS: \(m/z\) 1019. \(C_{61}H_{70}N_{4}O_{3}S_{3}\) (1019.43): Calcd. C 71.87, H 6.92, N 5.50; Found C 71.86, H 6.9, N 5.48.

3. Instruments and characterization
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$^1$H NMR and $^{13}$C NMR spectra were measured with a Bruker AV400 spectrometer at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Absorption spectra were taken with a Varian Cary 50 ultraviolet-visible spectrometer. Photoluminescence (PL) spectra were measured on a Perkin–Elmer LS-55 fluorescence spectrometer at room temperature. The cyclic voltammetry (CV) was conducted with an Autolab Electrochemical Station. Ag/AgNO$_3$ and platinum wire electrodes were used as reference and counter electrodes, respectively. The electrolyte solution was 0.1 M LiClO$_4$ in anhydrous acetonitrile. The potential scan rate was 50 mVs$^{-1}$.

4. Computation

The electron distributions in HOMO and LUMO levels were predicted at B3LYP/6-311G (d, p) level using the Gaussian 09 program$^{87}$. To study the interaction between the dye and the TiO$_2$, a two-dimensional slab model with 40 TiO$_2$ in one supercell cell was applied to simulate the most stable anatase TiO$_2$ (1 0 1) surface. Calculations on the Γ-point crystalline orbitals and the electron injection time of the dye/TiO$_2$ systems were performed by using the plane-wave technique implemented in Vienna ab initio simulation package (VASP)$^{88}$. The generalized gradient approximation (GGA) with the PBE functional has been employed to describe the exchange-correction potential in all calculations.$^{89}$ The projector-augmented wave (PAW) method has been applied to describe the electron-ion interaction, and a cut-off energy was set to 400 eV.$^{810}$ All atomic positions were optimized by the conjugated gradient method and the results were converged with all atomic force components less than 0.02 eV Å$^{-1}$. The electron injection time, $\tau$ (in fs), from the dye to the substrate was estimated using the Newns-Anderson model, where

$$\tau = \frac{658}{\Delta}$$

$\tau$ is estimated from the broadening parameter $\Delta$ (in meV) of the donor orbital of the dye.
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upon adsorption. Such a model, which has already been applied to numerous dye/TiO$_2$
-systems, typically provides estimates that are about one-half of the experimental ones in
line with more sophisticated models.$^{511}$

5. Device fabrication
Nanocrystalline and transparent TiO$_2$ (20 nm particle size) layers were deposited by
successive screen printing using a TiO$_2$ paste (Dyesol, DSL 18-NR). Where applicable,
a layer of larger (400 nm particle size) TiO$_2$ particles (WER-O paste, Dyesol) was then
deposited on top of the transparent layer to increase light scattering in the TiO$_2$ layer.
Electrodes were then soaked in a 40 mM solution of TiCl$_4$ in distilled water for 30 min at
75$^\circ$C. The prepared electrodes were immersed into sensitizer solution in 1:4 EtOH/DCM
overnight, before removing and rinsing in acetonitrile immediately prior to cell assembly.
Platinized counter electrodes were fabricated on identical pieces of fluorine-doped tin
oxide (FTO) with small holes drilled into one corner. After cleaning, a thin layer of
platinum was deposited onto the FTO by thermal decomposition of hexachloroplatinic
acid. The electrolyte solution was 0.20 M [Co(bpy)$_3$](PF$_6$)$_2$, 0.02 M [Co(bpy)$_3$](PF$_6$)$_3$,
0.10 M LiClO$_4$ and 0.50 M 4-tert-butylpyridine in acetonitrile. The dye solutions were
prepared by dissolving 0.30 mM organic dye in the mixture of EtOH:DCM (1:4) with 8
mM deoxycholic acid (DCA) as co-adsorbent. More detailed electrode-preparation and
device-fabrication procedures can be found in previous reports.$^{56}$

6. Device characterization
Device characterization was performed using equipment and procedures described
in detail elsewhere.$^{56}$ Incident photon-to-current efficiency (IPCE) spectra were
measured with a spectral resolution of approximately 5 nm using a 300 W xenon lamp
and a grating monochromator equipped with order sorting filters (Newport/Oriel). The
incident-photon flux was determined by using a calibrated silicon photodiode
(Newport/Oriel). Photocurrents were measured by using an auto-ranging current
amplifier (Newport/Oriel). Control of the monochromator and recording of photocurrent
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spectra were performed by means of a PC running the TRACQ Basic software (Newport). Current-voltage characteristics under simulated AM 1.5G illumination were measured by using a Keithley source meter and the PVIV software package (Newport). Simulated AM 1.5G illumination was provided by a Newport class A solar simulator, and light intensity was measured by using a calibrated silicon reference cell. Cells were masked during measurements and the active working area was 0.120 cm².

TA decay and TAS measurements were performed with a home-built system. Both regular and inert cells were excited with laser pulses from a Nd:YAG Q-switched laser (Continuum Minilite II, 532 nm, 5 ns pulse width, 5 Hz repetition rate, ca. 20 μJ cm⁻² per pulse). A near-infrared LED with emission spectra centered at 850 nm (M850L2, ca. 100 nm emission width, Thorlabs) was used as probe light for TA measurements due to its perfect stability on millisecond and longer timescales. While for TAS measurements spanning from 10⁻⁷ to 10⁻³ s, a 300 W xenon lamp combined with a monochromator (Newport/Oriel) was used as probe light. Either an 830 nm bandpass filter (10 nm pass band) or another monochromator (Newport/Oriel) were mounted in front of the photodiode to reject stray light for TA decay and TAS measurements, respectively. The overall bandwidth of the system is 35 MHz limited by the photodiode (FDS100, Thorlabs) and all equipments were controlled by Labview. During all measurements, the front/rear surfaces of the sample were covered with a shallow mask slightly larger/smaller than the active area.

The probe light for TA decay measurements was chosen to be 830 nm, where both D⁺ and e⁻ absorb. Thus the TA of regular cells with DCA is fitted to the following equation:

\[
\Delta OD(t) = \Delta OD_{0,D^+} \exp \left[ -\left( \frac{t}{\tau_{WW,D^+}} \right)^{\beta_{D^+}} \right] + \Delta OD_{0,e^-}
\]  

(1)

Where \( \Delta OD_0 \) is the optical density at \( t = 0 \) induced by the laser pulse, \( \beta \) is the stretch parameter, \( \tau_{WW} \) is the characteristic stretched exponential lifetime and the subscripts D⁺ and e⁻ denote parameters of each species. While the TA of the redox inactive “inert” cells is fitted to:
The rationale of Eq. 1 lies in two facts: i) the regeneration of D\(^+\) is very efficient by comparing the TA of regular and inert cells; ii) by the end of the D\(^+\) decay at ca. 10\(^{-4}\) s, electron electrolyte recombination (EER) has barely started. Thus tiny amount of electrons are removed by EDR and EER in the fast timescale and \(\Delta \text{OD}_{e}\) is taken to be identical to the \(\Delta \text{OD}_{0,e}\) in Eq. 1.

**Figure S1.** The UV-vis spectra of the two dyes loaded on 2.5 \(\mu\)m transparent TiO\(_2\) films.
Figure S2. Optimized structures of D1 and D2 and their corresponding HOMOs and LUMOs. The electronic band gap (in eV) results are listed in both vacuum (without parentheses) and DCM solution condition (with parentheses). The electronic structure analyses were performed based on the ground state geometries at the B3LYP/6-311G (d, p) level of theory.
Figure S3. Typical IPCE spectra a) and j-V characteristics b) of DSCs sensitized with D1 and D2.
Table S1. UV–Vis absorption and electrochemical properties of D1 and D2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;(a)&lt;/sup&gt; (nm)</th>
<th>ε at λ&lt;sub&gt;max&lt;/sub&gt; (M&lt;sup&gt;-1&lt;/sup&gt;·cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;(b)&lt;/sup&gt; on TiO&lt;sub&gt;2&lt;/sub&gt; (nm)</th>
<th>E&lt;sub&gt;0–0&lt;/sub&gt; (eV)&lt;sup&gt;(c)&lt;/sup&gt;</th>
<th>E&lt;sub&gt;D/D&lt;/sub&gt;+(V)&lt;sup&gt;(d)&lt;/sup&gt; (vs. NHE)</th>
<th>E&lt;sub&gt;D*/D&lt;/sub&gt;+(V)&lt;sup&gt;(e)&lt;/sup&gt; (vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>292</td>
<td>19380</td>
<td>363</td>
<td>512</td>
<td>2.03</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>307</td>
<td>30600</td>
<td>466</td>
<td>556</td>
<td>1.95</td>
<td>1.09</td>
</tr>
<tr>
<td>D2</td>
<td>307</td>
<td>30600</td>
<td>466</td>
<td>556</td>
<td>1.95</td>
<td>1.09</td>
</tr>
</tbody>
</table>

(a) Absorption spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> solution (2×10<sup>-5</sup> M). (b) Absorption spectra on TiO<sub>2</sub> film were measured with dye–loaded TiO<sub>2</sub> films immerged in CH<sub>2</sub>Cl<sub>2</sub> solutions. (c) Zero-zero excitation energy (E<sub>0–0</sub>) determined from the intersection of normalized the absorption and emission spectra in CH<sub>2</sub>Cl<sub>2</sub>. (d) The oxidation potentials (E<sub>D/D</sub>+) of the dyes were measured in CH<sub>2</sub>Cl<sub>2</sub> solutions with 0.1 M LiClO<sub>4</sub> as electrolyte, ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal reference and converted to NHE by addition of 630 mV, (e) The excited state potentials (E<sub>D*/D</sub>+) were calculated by E<sub>D*/D</sub>+ – E<sub>0–0</sub>.

Table S2 Typical photovoltaic parameters of DSCs with D1 and D2 as the sensitizer<sup>(a)</sup>.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Electrolyte</th>
<th>j&lt;sub&gt;sc&lt;/sub&gt;/mA cm&lt;sup&gt;-2&lt;/sup&gt;</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;/ mV</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>[Co(bpy)&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;2+/3+&lt;/sup&gt;</td>
<td>11.81</td>
<td>768</td>
<td>0.72</td>
<td>6.53</td>
</tr>
<tr>
<td>D2</td>
<td>[Co(bpy)&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;2+/3+&lt;/sup&gt;</td>
<td>15.24</td>
<td>786</td>
<td>0.67</td>
<td>7.99</td>
</tr>
</tbody>
</table>

<sup>(a)</sup>The cell employed 7.0 μm TiO<sub>2</sub> transparent without light scattering layers, the electrolyte solution was 0.2 M [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 0.02 M [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 0.1 M LiClO<sub>4</sub> and 0.5 M 4-tert-butylpyridine in acetonitrile. j–V measurements were performed under simulated AM 1.5G 1 Sun illumination.
Table. S3 Optimized photovoltaic parameters of DSCs based on D2 (a).

<table>
<thead>
<tr>
<th>Condition</th>
<th>$P_{in}$ / mW cm$^{-2}$</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/ mV</th>
<th>FF</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh cell</td>
<td>100.00</td>
<td>16.97</td>
<td>749</td>
<td>0.71</td>
<td>9.01</td>
</tr>
<tr>
<td>Aging for 20 days</td>
<td>50.00</td>
<td>8.52</td>
<td>730</td>
<td>0.748</td>
<td>9.30</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>17.2</td>
<td>752</td>
<td>0.72</td>
<td>9.31</td>
</tr>
</tbody>
</table>

(a) The cell employed 4.8 $\mu$m transparent and 2.0 $\mu$m scattering TiO$_2$ layers, the electrolyte solution was 0.2 M [Co(bpy)$_3$](PF$_6$)$_2$, 0.02 M [Co(bpy)$_3$](PF$_6$)$_3$, 0.1 M LiClO$_4$ and 0.5 M 4-tert-butylpyridine in acetonitrile. $j$-$V$ measurements were performed under simulated AM 1.5G 1 sun illumination. The size of the electrode was 0.120 cm$^2$.

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