Dye-sensitized solar cells are a promising alternative to traditional inorganic semiconductor-based solar cells. Here we report an open-circuit voltage of over 1,000 mV in mesoscopic dye-sensitized solar cells incorporating a molecularly engineered cobalt complex as redox mediator. Cobalt complexes have negligible absorption in the visible region of the solar spectrum, and their redox properties can be tuned in a controlled fashion by selecting suitable donor/acceptor substituents on the ligand. This approach offers an attractive alternate to the traditional I₃⁻/I⁻ redox shuttle used in dye-sensitized solar cells. A cobalt complex using tridentate ligands [Co(bpy-pz)₂]³⁺/²⁺(PF₆)³/² as redox mediator in combination with a cyclopentadithiophene-bridged donor-acceptor dye (Y123), adsorbed on TiO₂, yielded a power conversion efficiency of over 10% at 100 mW cm⁻². This result indicates that the molecularly engineered cobalt redox shuttle is a legitimate alternative to the commonly used I₃⁻/I⁻ redox shuttle.
The dye-sensitized solar cell (DSC) is a promising alternative to traditional inorganic semiconductor-based solar cells because of favourable ecological and economical features. Sun light is absorbed by a dye monolayer located at the junction between a nanostructured electron transporting (n-type) and hole-transporting (p-type) phase. The former is a wide bandgap semiconductor oxide (typically TiO₂, anatase), and the latter is typically the triiodide/iodide (I⁻²/I⁻) redox electrolyte. On photo-excitation, the dye injects an electron into the n-type material and the hole is captured by the electrolyte. The electrons then travel through the nanostructure to be collected as current at the external contact, while the holes are transported to the cathode by the redox shuttle.

The main drawback of the commonly used triiodide/iodide redox (I⁻²/I⁻) system is a large mismatch between its oxidation potential (E⁰(I⁻²/I⁻) = 0.35 V versus the normal hydrogen electrode (NHE)) and the dye oxidation potential (E⁰(π-π*) = ~1.0 V versus NHE), which limits the open circuit voltage (Voc) to 0.7–0.8 V (ref. 4). The large expenditure needed for efficient dye regeneration is due to the complex regeneration kinetics with the I⁻²⁻ redox couple involving formation of intermediates that is, the I⁻⁻ radical. Additionally, this redox couple is very corrosive towards metals such as Ag, Au and Cu, so excluding the use of such materials as current collectors in DSC modules requiring long-term stability. Therefore, the development of non-corrosive redox mediators, with reduced mismatch between the oxidation potential of the dye and the redox couple, is paramount to enhancing open circuit potential.

Previous studies to replace the I⁻²⁻ redox system by cobalt polypyridine complexes have drawn attention because of their low visible light absorption, the higher redox potential and the reduced corrosiveness towards metallic conductors offered by these redox couples. However, the overall efficiency obtained with these cobalt electrolytes was inferior compared with the I⁻²⁻ redox couple, especially under full sunlight. This has been attributed to slow mass transport and faster back reaction of photo-injected electrons with the oxidized redox species coupled with the slow regeneration of the Co(II) species at the cathode. Recently, cobalt redox shuttles have attracted renewed attention after Feldt et al. increased the power conversion efficiency (PCE) by 6.7% by employing a newly designed D–π–A organic sensitizer, coded D35, in conjunction with the cobalt (III/II) tris-bipyridyl complex, [Co(III)(bpy)₃][PF₆]₃/ [Co(II)(bpy)₃](PF₆)₂ couple. Most recently, S. M. Feldt et al. have achieved over 1,000 mV with cells based on cobalt phenan-throline redox shuttles but the power conversion efficiencies were below 3.6% (ref. 16).

As cobalt is a first row transition metal, dissociation and exchange of ligands may occur rapidly in the case of Co(II). Tridentate ligands are expected to improve significantly the stability of the cobalt complex compared with bidentate ligands. Another advantage of tridentate ligands over bidentate ligands is the absence of isomers. Thus, in the case of disymmetric bidentate ligands, useful for fine tuning of the redox properties, facial and meridional isomers coexist. One particular attractive feature of cobalt complexes is the facile tuning of their redox potential, which can be adjusted to match the oxidation potential of the sensitizer minimizing energy loss in the dye regeneration step. We report a redox relay that can generate a high potential and, thus, highly efficient DSCs with [Co(III/II)(bpy-pz)₂](PF₆)₃/₂ (denoted hereafter as [Co(bpy-pz)₂]⁺²+/²⁻) [bpy-pz = 6-(1H-pyrazol-1-yl)-2,2′-bipyridine]). The tridentate cobalt [Co(bpy-pz)₂]⁺²⁻/²⁻ complex, used as a redox mediator, achieved an unprecedented output voltage exceeding 1,000 mV owing to its high oxidation potential of 0.86 V versus NHE. The designed complex [Co(bpy-pz)₂]⁺²⁻ (Fig. 1), whose redox potential is offset by only 230 mV from that of the 3-[6-[(bis(2′,4′-dihexyloxybiphenyl)4-yl)amino-2-naphthalen]-2-cyanoacrylic acid (Y123) dye gave a PCE of over 10%, under different solar intensities from 10 to 100 mW cm⁻².

**Results**

**Electrochemical data.** The standard redox potential of the [Co(bpy-pz)₂]⁺²⁻ couple was determined as 0.22 V versus ferrocenium/ferrocene (Fc⁺/Fc) (0.86 V versus NHE using E⁰(Fc⁺/Fc) = 0.64 V versus NHE) by cyclic voltammetry (Supplementary Fig. S1). The higher oxidation potential compared with [Co(bpy)₃]⁺²⁻/²⁻ is attributed to the presence of pyrazoles, which stabilize the highest occupied molecular orbital (HOMO) of the complex more than the bipyridine ligand. For the [Co(bpy-pz)₂]⁺²⁻ containing 0.22 M of Co(II) and 0.05 M Co(III), the calculated redox potential is 0.82 V versus NHE whereas, for the I⁻⁻/²⁻ -based electrolyte, the value is 0.37 V versus NHE. The absorption spectra of the oxidized species [Co(bpy-pz)₂]⁺²⁻ show maxima: λmax(4) = 265 (28,300), 320 nm (24,400), and, for reduced species [Co(bpy-pz)₂]²⁻ λmax

![Figure 1](https://example.com/figure1.png)

**Figure 1** | Schematic energy diagram for dye-sensitized solar cell. (a) TiO₂ sensitized with Y123 dye. (b) Molecular structures of tris bipyridyl cobalt complex. (c) Molecular structures of bis bipyridine-pyrazole cobalt complex. (d) Molecular structures of Y123 dye.
\( (\epsilon) = 240 \, (35,500), \, 276 \, \text{nm} \, (20,500) \) (Supplementary Fig. S2). Strong \( \pi \) accepting nature of pyrazoles increased HOMO–LUMO (lowest unoccupied molecular orbital) gap, hence reduced its absorption in the visible spectrum compared with \([\text{Co(bpy)}]^{3+/2+}\) systems. It is worthy to note that triiodide has a molar extinction coefficient of 25,500 at 360 nm \(^{17}\). The additional photocurrent generated by the sensitizer in the blue part of the spectrum is expected with the use of the cobalt electrolyte system compared with the \( (I_3^-/I^-) \) due to the lower extinction coefficient of the cobalt complexes.

**Dye sensitized solar cell.** The redox reactions of dye sensitized solar cells (DSCs) under illumination will be briefly presented. Details can be found elsewhere \(^{18-20}\). The photo-excitation of the adsorbed sensitizer on nanocrystalline semiconductor (equation (1)) leads to injection of electrons into the conduction band of the semiconductor (equation (2)). The oxidized dye is subsequently reduced by electron donation from an electrolyte containing the redox system (equation (3)). The injected electron flows through the semiconductor network to arrive at the back contact of the anode and then through the external load to the counter electrode. At the counter electrode, reduction of oxidized component of the redox couple in turn generates the reduced form (equation (4)), which completes the circuit. With a closed external circuit and under illumination, the device then constitutes a photovoltaic regenerative energy conversion system. However, there are undesirable loss reactions, such as the injected electrons may recombine either with the oxidized sensitizer (equation (5)) or with the oxidized form of the redox couple at the TiO\(_2\) surface (equation (6)), resulting in a loss of cell efficiency.

\[
\begin{align*}
S/\text{TiO}_2 + h\nu & \rightarrow S^*/\text{TiO}_2 \quad (1) \\
S^*/\text{TiO}_2 & \rightarrow S^+/\text{TiO}_2 + e_{cb}(\text{TiO}_2) \quad (2) \\
S^+/\text{TiO}_2 + R & \rightarrow S/\text{TiO}_2 + R^+ \quad (3) \\
R^+ + e^- (\text{cathode}) & \rightarrow R (\text{cathode}) \quad (4) \\
e_{cb}(\text{TiO}_2) + S^+/\text{TiO}_2 & \rightarrow S/\text{TiO}_2 \quad (5) \\
e_{cb}(\text{TiO}_2) + R^+ & \rightarrow R (\text{anode}) \quad (6)
\end{align*}
\]

**Charge transfer dynamics.** To gain insight into dye regeneration rate, time-resolved nanosecond laser transient absorbance measurements were performed on both the cobalt and the \( I_3^-/I^- \) redox systems. The dye regeneration yield, \( \eta_r \), is defined by equation (7):

\[
\eta_r = k_r / (k_r + k_b)
\]

where \( k_r \) is the first-order rate constant of the dye regeneration (equation (3)) occurring in the presence of a redox couple \( (R^+/R^-) \). And \( k_b \) is the rate constant of the recombination reaction (equation (5)) that takes place between the oxidized state of the dye \( (S^+) \) and electrons injected into the conduction band following the primary ultrafast photoinduced charge separation process (equations (1) and (2)). The dynamics of the oxidized state of the dye after its initial generation was monitored by measuring transient changes of its optical absorption at the wavelength \( \lambda = 715 \) nm. In the absence of a redox mediator, that is, in pure acetonitrile solvent, the decay of the absorption signal recorded at 715 nm reflects the dynamics of the recombination of injected electrons with \( S^- \). Figure 2, in the black curve shows that the transient absorbance of the oxidized state of the Y123 dye decays with a typical half-reaction time \( t_{1/2} = 1.1 \) ms.

Data fitted by a single exponential yielded a rate constant of \( k_b = 6.4 \times 10^2 \) s\(^{-1}\). In the presence of the redox couple, the decay of the oxidized dye signal was significantly accelerated and the half-reaction time decreased to \( t_{1/2} = 80 \) ms for \([\text{Co(bpy-pz)}]^{3+/2+}\) and to 16 ms for \( I_3^-/I^- \). The rate constants extracted by fitting with a single exponential are \( k_r = 9.1 \times 10^4 \) s\(^{-1}\) and \( 5.3 \times 10^4 \) s\(^{-1}\) for the regeneration of the dye by \([\text{Co(bpy-pz)}]^{3+/2+}\) and \( I_3^-/I^- \) redox systems, respectively \(^9\). Despite the dissimilar rate constants in the cobalt and the \( I_3^-/I^- \) system, \( k_r \) remains much larger than \( k_b \) indicating that electron recombination with the oxidized dye is indeed intercepted efficiently by the mediator, corresponding to a dye regeneration yield of \( \eta_r = 0.93 \) by the \([\text{Co(bpy-pz)}]^{3+/2+}\) redox system, whereas the dye regeneration yield by \( I_3^-/I^- \) is \( \eta_r > 0.98 \). This efficient dye regeneration yield observed with the \([\text{Co(bpy-pz)}]^{3+/2+}\) redox system is particularly noteworthy as the difference in the oxidation potential between the dye and the redox couple is only 230 mV. Larger energy expenditure is usually required for the effective regeneration of the dye \(^6,16,21,22\).

**Photovoltaic data.** Table 1 summarizes the photocurrent-voltage characteristics of the DSCs employing a 5.6-μm thin transparent nanoporous TiO\(_2\) (anatase) film, the Y123 sensitizer, and the redox electrolytes under simulated sunlight at various intensities: 9.5, 51 and 100 mW cm\(^{-2}\). The \([\text{Co(bpy-pz)}]^{3+/2+}\) redox system gave a photocurrent density of \( J_{sc} \) \( 12.54 \) mA cm\(^{-2}\), an open-circuit potentials \( V_{oc} \) of 1,020 mV and a fill factor \( FF \) of 0.69, yielding a PCE \( (\eta) \) of 8.87%, as derived from equation (8):

\[
\eta = J_{sc} \times V_{oc} \times FF / I_0
\]
Table 1 | J-V characterization of the DSCs employing 5.6-µm thin thick TiO₂ films.

| Redox          | Incident light intensity I₀ (mW cm⁻²) | J₀C (mA cm⁻²) | V₀C (mV) | FF (%) | η (%) |
|----------------|--------------------------------------|---------------|----------|--------|-------|
| [Co(bpy-pz)₃]³⁺/²⁺ | 100                                  | 12.54         | 1020     | 69.4   | 8.87  |
|                | 51                                   | 6.52          | 998      | 73.7   | 9.40  |
|                | 9.5                                  | 1.23          | 933      | 77.0   | 9.30  |
| I₃⁻/I⁻         | 100                                  | 13.01         | 754      | 66.7   | 6.57  |
|                | 51                                   | 6.70          | 743      | 70.0   | 6.84  |
|                | 9.5                                  | 1.27          | 713      | 73.7   | 7.03  |

Figure 3 | Photovoltaic characteristics using cobalt and iodide redox systems. (a) Comparison of J-V curve for the [Co(bpy-pz)₃]³⁺/²⁺ (red lines) and I₃⁻/I⁻ (black lines). (b) Photo-current dynamics as a function of light intensity for the [Co(bpy-pz)₃]³⁺/²⁺ (red lines) and I₃⁻/I⁻ (black lines). (c) Comparison of IPCE spectra using TiO₂ film thickness is 5.6μm and [Co(bpy-pz)₃]³⁺/²⁺ (red lines) and I₃⁻/I⁻ (black lines) redox systems.

Electrochemical impedance spectroscopy. To clarify the origin of our observation, we performed electrochemical impedance spectroscopy (EIS) measurements. Figure 4a shows the recombination and the transport resistance as well as the chemical capacitance for the cells based on [Co(bpy-pz)₃]³⁺/²⁺ and I₃⁻/I⁻ redox electrolyte in the dark. As implied by the dark current near 0 V, the recombination resistance is lower for the [Co(bpy-pz)₃]³⁺/²⁺ than the I₃⁻/I⁻ redox electrolyte. The chemical capacitance is shifted by ~430 mV, which is due to the differences of the two redox potentials associated with a higher recombination for the cobalt redox system and a small shift in the conduction band (Ecb) of the TiO₂.

Effect of TiO₂ film thickness on photovoltaic properties. To fully characterize the DSC performance with the [Co(bpy-pz)₃]³⁺/²⁺ system, the transparent TiO₂ film thickness was varied between 2.8 and 5.6 µm onto which a 5-µm scattering layer was deposited (Table 2; all averaged J-V characterization are summarized in...
Figure 4 | EIS results of \( I_{3^−}/I^{−} \) and [Co(bpy-pz)\(_2\)\(^{3+}/2^+\)] system-based DSCs. Transport resistance (\( R_{\text{trans}} \)) (dashed lines), recombination resistance (\( R_{\text{rec}} \)) (solid lines), and chemical capacitance (dotted lines) of the [Co(bpy-pz)\(_2\)\(^{3+}/2^+\)] (red lines and markers) and \( I_{3^−}/I^{−} \) (black lines and markers) system-based DSCs (a) in the dark and (b) at 1 sun by light-emitting diode. (c) Charge collection efficiency of \( I_{3^−}/I^{−} \) (black solid line with open squares) and [Co(bpy-pz)\(_2\)\(^{3+}/2^+\)] (red dashed line with closed circles)-based DSCs as function of applied potential. Inset shows the electron lifetime and the transport time for [Co(bpy-pz)\(_2\)\(^{3+}/2^+\)] and the \( I_{3^−}/I^{−} \) plotted against DOS.

Table 2 | J-V characterization of the DSCs.

| TiO\(_2\) thickness (\( \mu \)m) | \( I_0 \) (mW cm\(^{-2}\)) | \( J_{sc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (mV) | \( FF \) (%) | \( \eta \) (%) |
|-----------------|--------------|--------------|--------------|-------------|-------------|
| 2.8             | 100          | 10.80        | 1031         | 67.5        | 7.52        |
| 5.6 + 5         | 100          | 13.45        | 1015         | 69.7        | 8.21        |
| 4.0 + 4.5 with PProDOT | 100          | 13.06        | 998          | 77.4        | 10.08       |

The short-circuit current, open-circuit potential and fill-factor data were obtained employing [Co(bpy-pz)\(_2\)\(^{3+}/2^+\)] redox system with various TiO\(_2\) film thickness under different incident light intensity conditions.
Supplementary Table S2). The 2.8-μm transparent layer gave a $J_{sc}$ of 10.80 mA cm$^{-2}$, a $V_{oc}$ of 1.03 mV and a $FF$ of 0.68, corresponding to a PCE of 7.52% at full sun, 100 mW cm$^{-2}$. The light harvesting efficiency (LHE), defined as

$$\text{LHE} = 1 - 10^{-\epsilon \Gamma} = 1 - 10^{-A} \quad (9)$$

where $\epsilon$ is the molar extinction coefficient of the dye, $\Gamma$ is the dye molar concentration per projected surface area of the film, and $A$ is the absorbance of the dye-sensitized film (equal to the product of $\epsilon$ and $\Gamma$) is estimated to be already over 98% at maximum with the 2.8-μm TiO$_2$ film, which indicates the impact of high molar extinction coefficient dyes. So the photocurrent of 10.80 mA cm$^{-2}$ was decreased only by 16% when decreasing the TiO$_2$ film thickness by 50%. At low intensities, 51 and 9.5 mW cm$^{-2}$, the devices exhibited dramatically high $V_{oc}$, 1.013 and 960 mV leading to a PCE of 8.21% and 8.51%, respectively. The introduction of optical elements, that is, layers composed of large particles enhanced the photocurrent owing to incident light scattering towards nanocrystalline mesoporous TiO$_2$ film. A dye-sensitized solar cell incorporating a 5-μm thick scattering layer on 5.6-μm transparent layer exhibited an enhanced photocurrent of 13.45 mA cm$^{-2}$, which is an increase of 7% while retaining $V_{oc}$ and $FF$ when compared with the DSC with 5.6-μm transparent layer. The respective PCE were 9.52, 10.29 and 9.93% at 100, 51 and 9.5 mW cm$^{-2}$ (see $J$–$V$ curves in Fig. 5a). Figure 5b shows the IPCE of the cell based on the [Co(bpy-pz)$_2$]$_{3+}/^{2+}$ system with a TiO$_2$ double layer. The IPCE spectrum exhibits very high values, that is, 70–90% between excitation wavelengths of 430 and 620 nm. Assuming a 10% optical loss in the conducting glass, the internal quantum efficiency ranged from 80–100% (ref. 29). These overall PCEs with the dramatically high $V_{oc}$ is, to the best of our knowledge, an unprecedented result. Given the high $V_{oc}$ this new cobalt redox relay–based DSC will be also very attractive for use as photovoltaic devices in water cleavage, as the required photovoltage can be reached by merely two cells connected in series to a water electrolyzer, or with just one cell in tandem with a water oxidizing photoanode. A device kept at ambient conditions showed no loss in the conversion efficiency after 1 month, which is a promising result. Further work on stability of this new redox system is ongoing.

**Platinum-free counter electrode.** A comparatively high charge-transfer resistance, $R_{CT}$, at the Pt counter electrode with the cobalt redox system was observed despite the promising PCE. To further reduce the $R_{CT}$, a high surface area–cathode material (that is, nanoporous poly(3,4-propylenedioxythiophene) (PProDOT)) layers was exploited to replace the Pt. With the incorporation of the PProDOT as cathode material, the $FF$ was strongly improved owing to a lower $R_{CT}$ (Supplementary Table S3) and thus the PCE increased to 10.08% at 1 sun illumination (Table 2; Fig. 5c). The PProDOT layer showed a drastically lower $R_{CT}$, 2.5 ohms in comparison to the 50 ohms of the counter electrodes made with Pt. It is noted that the $R_{CT}$ of $I^-/I^-$ system is ~0.8 ohms with Pt counter electrode. The lower $V_{oc}$, which is plausibly ascribed to the downward shift of the TiO$_2$ band edge, was compensated by a higher fill factor. Our ongoing study concentrates to develop and analyse diverse alternative cathode materials.

**Discussion**

We have synthesized novel cobalt (III) and (II) complexes based on 6-beta-(1H-pyrrozol-1-yl)-2,2′-bipyridine tridentate ligand, and used them as a redox couple in mesoscopic dye-sensitized solar cells in conjunction with a high molar extinction coefficient organic donor-acceptor dye. Under 1 sun condition, a very high open-circuit voltage, ~1.000 mV, along with a short circuit current of 13.06 mA/cm$^2$, and $FF$, 0.77 were obtained, resulting in a PCE of above 10%. The high open-circuit voltage was obtained by stabilizing the HOMO level of the cobalt (II) complex to minimize the mismatch between the redox couple and the sensitizer HOMO level to just 230 mV. This resulted in higher PCE compared with the iodide/triiodide redox couple. Also, we found that the conventional Pt catalyst coated counter electrode is not optimum with the newly developed cobalt redox mediators; therefore, to overcome this issue, a series of polythiophene family members were exploited as a cathode material. PProDOT-based counter electrode in DSCs show optimum results owing to their ultrahigh surface area morphology and without the possibility of forming any passivation layer at electrolytes–electrode interface. These promising results not only confirm that the molecularly engineered cobalt redox shuttle is a legitimate alternative to the commonly used $I^-/I^-$ redox shuttle but also assures improved performance with low-cost materials as a cathode. Future work will focus on further improvements of this potential new redox system, and to increase the recombination resistance. As a possibility, the recombination process could be retarded by depositing a conformal insulating oxide blocking layer on the surface of the TiO$_2$ films by atomic layer deposition. We believe that the dye-sensitized solar cell described here is straightforward, which carries the promise of truly inexpensive and environment-friendly solar power.

**Materials synthesis.** The synthetic details of 3-(6-14-βis(2,4-dihexyloxybiphenyl-4-yl)aminophenyl)-4,4-dihexyl-cyclopenta [2,1-b:3,4-b]dithiophene-2-yl)-2-cyanoacrylic acid, coded Y123, were described in our previous study. The ligand bpy-pz has been prepared in a similar manner to ligands reported previously. Spectroscopic analysis gave similar results to that reported in literature. The preparation details of PProDOT-coated FTO as counter electrode has been described in our previous study. In this study, ~160-nm thick PProDOT on FTO was prepared and used as the cathode.

**Methods**
films were photoexcited by short light pulses (5 ns full-width at half-maximum duration) generated by an optical parametric oscillator pumped by a frequency-doubled Q-switched Nd:YAG laser (Ekspla NT-340). The excitation wavelength was tuned at λ = 580 nm. The excitation laser beam was attenuated by gray filters and expanded by plano-concave lens so as to reduce the light pulse fluence on the sample below 20 μJ cm⁻². These conditions ensure that, at most, one electron is injected per TiO₂ particle at a time. The probe light from a Xenon arc lamp was passed through filters, various optical elements, the sample, and a second grating monochromator, before being detected by a fast photomultiplier tube and recorded by a digital oscilloscope. The transient probe signal measured at λ = 715 nm corresponds to the time evolution of the absorbance of the oxidized state of the dye (S²−) as deduced from previously recorded transient absorption spectra. The transient decay observed corresponds to the lifetime of S¹ in the presence or absence of a redox electrolyte. The samples measured without any redox species were covered with an acetoni-trile film. Trails used to calculate the kinetics of S¹ decay were typically averaged over 3,000 consecutive laser shots.

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