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Efficient iodine-free dye-sensitized solar cells employing truxene-based organic dyes

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Two new truxene-based organic sensitizers (M15 and M16) featuring high extinction coefficients were synthesized for dye-sensitized solar cells in cobalt electrolyte. M16-sensitized device displays a 7.6% efficiency at an irradiation of AM1.5 ¹⁰ full sunlight.

Research on replacing the conventional iodide/triiodide electrolyte system in dye-sensitized solar cells (DSCs) with Co-complex based redox couples has recently received great attention because of their low corrosiveness, low visible light 15 absorption, and especially high redox potential, which enables attainment of high photovoltages.¹⁻³ Recently studies have shown that cobalt redox couples can give impressively high efficiencies comparable to iodide/triiodide electrolyte by using organic dyes. By employing a combination of an zinc 20 porphyrin dye (YD2-o-C8) and an organic dye (Y123) in conjunction with tris(2,2'-bipyridine)cobalt(II/III) redox couple, Grätzel et al. showed a 12.3%–efficiency DSC.¹ The efficiency exceeds those obtained with today's best ruthenium Wang al. explored sensitizers. et tris(1.10-25 phenanthroline)cobalt(II/III) redox shuttles in conjunction with the triphenylamine-based organic dyes to fabricate DSCs displaying power conversion efficiency of 5.8~9.4%² Boschloo and Hagfeldt et al. reported triphenylamine-based DSCs dye-sensitized employing tris(2.2'organic 30 bipyridine)cobalt(II/III) redox shuttles displaying the best efficiency of 6.7%.³ An advantage of the cobalt electrolyte over the iodide/triiodide redox couple is that very high opencircuit voltages can be realized but without sacrificing short circuit photocurrent or fill factor. However, simply 35 replacing the iodide/triiodide couple in the DSCs by cobalt redox couples may led to poorly performing devices with low photovoltages and photocurrents, which has been attributed to slow mass transport and increased recombination of

- photoinjected electrons with oxidized redox species in the ⁴⁰ electrolyte.^{3b,4} To overcome the mass transport limitation associated with the polypyridyl cobalt redox shuttles, a relatively thin titania film is always needed. Additionally, to meet the requirements of effective light harvesting and retards the rate of interfacial back electron transfer from the ⁴⁵ conduction band of the nanocrystalline titanium dioxide film
- to the Co(III) ions, developing new class of photosensitizers with high extinction coefficients, suitable proper electronic structures and steric properties is warranted.

In our previous study, we have explored triarylamine ⁵⁰ organic dyes containing functionalized-truxene unit for DSCs based on iodine electrolyte.⁵ The hexapropyltruxene group on the dyes retards the rate of interfacial back electron transfer from the conduction band of the nanocrystalline titanium dioxide film to the I_3^- ions, which enables attainment of high ⁵⁵ photovoltages approaching 800 mV. In addition, these truxene-based dyes pose high extinction coefficients apart from their ability of retarding charge recombination. It is expected that these truxene-based dyes could show interesting performance in the cobalt redox couple system.

⁶⁰ In this work, two new truxene–based organic sensitizers (M15 and M16) bearing binary π -conjugated linker were designed, synthesized and characterized. To tune both the electronic structures and steric properties of linker, benzene ring and 3-methylthieno[3,2-b]thiophene (MTT) were ⁶⁵ introducted, bringing on an opportunity to understand the dye structure–performance relationship of iodine–free dye– sensitized solar cells. Syntheses of dyes M15 and M16 in detail are described in the ESI (Scheme S1 and S2†).



Fig. 1 The molecular structures of M15 and M16.

Both the dyes have a relatively broad and strong absorption in the ultraviolet and visible region (Fig. 2a). The absorption spectrum of M15 shows an absorption maximum (λ_{max}) centered at 498 nm ($\varepsilon = 7.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which is 75 assigned to the π - π * transition. M16 shows a broad absorption spectrum covering a wide range of the visible region with a superior light-harvesting efficiency to M15 ($\lambda_{max} = 500 \text{ nm}$, ε

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- = $8.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) due to the stronger electron-donating nature of MTT and relatively smaller torsion angles between the plane of the donor and that of the acceptor (Fig. S11[†]), which is desirable for harvesting more solar light. It is noted 5 that both the dyes have high extinction coefficients compared to ruthenium-based dyes (e.g. N719,⁶ $1.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),
- which is desirable for thin-layer DSCs.



Fig. 2 Absorption spectra in dichloromethane (a) and IPCEs action spectra (b) of DSCs with electrolytes containing 0.5 M TBP

To obtain and understand the molecular orbital energy levels, cyclic voltammetry (CV) was carried out in a typical three-electrode electrochemical cell with TiO₂ film (5.5 μ m) stained with sensitizer as the working electrode (Fig. S4[†]). 15 The HOMO levels of M15 and M16 are calculated to be 0.91 and 0.90 V (vs. NHE), respectively, which are more positive than the $[Co(II/III)(phen)_3]^{n+}$ (phen = 1,10-phenanthroline) and I^{-}/I_{3}^{-} redox couples (0.62 V^{3b} and 0.4 V vs NHE, respectively). In this work, the driving forces for dye 20 regeneration of the dyes are around 0.5 eV for the iodine control cells, indicating the driving forces for dye regeneration are sufficient for the iodine control cells.⁸ Recently, Wenger et al. has proved that efficient regeneration of sensitizers with as little as a 0.15 eV driving force between 25 the oxidation potential of the sensitizer and the redox potential of the mediator is possible.9 In the cobalt control cells, the calculated driving forces for dye regeneration of M15 and M16 are 0.29 and 0.28 eV, respectively. Considering

30 values related to that of iodine control cells (see next section). It can be said that the driving forces in the cobalt control cells were sufficient to regenerate most of these dyes. On the other hand, the LUMO of M15 and M16 (-1.28 and -1.26 V vs NHE, respectively) are more negative than the conduction

the fact that cobalt control cells presented comparable J_{SC}

- 35 band of TiO₂ (-0.5 V vs NHE). Assuming that energy gap of 0.2 eV is necessary for efficient electron injection,¹⁰ these driving forces are sufficiently large for effective electron injection.
- Using the dyes as sensitizers, we compared the photovoltaic 40 performances of DSCs employing a cobalt electrolyte with those employing an iodine electrolyte. A relatively thin titania film (5.5 μ m) is employed so as to avoid the mass transport limitation of cobalt redox couple and to minimize interfacial charge recombination. The cobalt electrolyte is composed of
- 45 0.25 M [Co(II)(phen)₃](PF₆)₂, 0.05 M [Co(III) (phen)₃](PF₆)₃,

0.5 M 4-tertpyridine (TBP) and 0.1 M Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile. For comparison, the iodine electrolyte consisting of 0.25 M 1,2dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M 50 LiTFSI, 0.05 M I₂, and 0.5 M TBP in acetonitrile was formulated.



Figure 3. J-V characteristics of DSCs with the EL-Cobalt and EL-Iodide electrolytes.

The photocurrent density-voltage (J-V) curves of the 55 devices measured under AM 1.5 irradiation (100 mW cm⁻²) are shown in Fig. 3 and the detailed photovoltaic parameters are summarized in Table 1. The short-circuit photocurrent density (J_{SC}) , open-circuit photovoltage (V_{OC}) and fill factor 60 (FF) of a M16-sensitized cell with the cobalt electrolyte are 11.9 mA cm⁻², 830 mV and 0.70, respectively, affording an overall power conversion efficiency (PCE) of 6.9%. Whereas the M16-sensitized cell with the iodide electrolyte exhibits an slightly increased J_{SC} of 12.2 mA cm⁻² and a remarkably 65 decreased V_{OC} of 675 mV, leading to a relatively lower PCE of 5.6%. For the M15-sensitized solar cells based on the cobalt electrolyte, we again observe an obviously improvement of V_{OC} to 810 mV, but significant decreased J_{SC} to 9.8 mA cm^{-2} , leading to an attenuated PCE compared to 70 corresponding iodine-based cells. This discrepancy of J_{SC} is well consistent with the IPCEs measurements (Fig. 2b).

Table 1. Photovoltaic performance of DSCs using a 5.5 µm film

Dyes	$J_{SC}/~{ m mA~cm}^{-2}$	Voc/mV	FF	PCE%	TBP
M15/Iodine	11.8	756	0.68	6.1	0.5 M
M15/Cobalt	9.8	810	0.69	5.5	0.5 M
M15/Cobalt	9.6	870	0.70	5.8	0.8 M
M16/Iodine	12.2	675	0.68	5.6	0.5 M
M16/Cobalt	11.9	830	0.70	6.9	0.5 M
M16/Cobalt	11.9	900	0.71	7.6	0.8 M

Measurements were performed under AM 1.5 irradiation on the DSC devices with 0.16 cm² active surface area defined by a metal mask. The 75 amount of the dyes adsorbed on the TiO2 surface for M15 and M16 were determined to be 1.86×10^{-7} and 1.65×10^{-7} mol cm⁻², respectively.

The concentration of TBP was found to be very crucial in the cobalt cells. The cobalt electrolytes with different concentration of TBP were prepared for DSCs application. The corresponding 80 experimental results are shown in the Fig. S5⁺. Under the optimized condition, cells containing 0.8 M TBP gave the best efficiency among all the cobalt electrolytes. As presented in Fig. 3, the lower rate of electron recapture by $[Co(III) (phen)_3]$ for

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M16-sensitized nanocrystalline TiO₂ film allows very high V_{OC} to be realized, with this sensitizer reaching a value of 900 mV in full sunlight without sacrificing short circuit photocurrent or fill factor. The advantage in voltage of M16 over M15 is maintained

5 at lower light levels, down to 10 mW cm⁻² solar intensity (Fig. S8[†]). The cumulative increases of V_{OC} and FF give rise to an efficiency of 7.6% at AM 1.5 global full sun. M15-sensitized cells also display similar features. This phenomenon has also been observed by Yella et al.¹ These results confirm that for M16, ¹⁰ the Co(II/III)tris(phen) redox couple outperforms the I^{-}/I_{3}^{-} redox couple for thin-film DSCs.

It is noteworthy that the dye alteration from M15 to M16 in the iodine cells (with 0.5 M TBP) have caused a V_{OC} attenuation of 81 mV (756 mV versus 675 mV), sharply contrasting a 20 mV 15 enhancement (810 mV versus 830 mV) in the cobalt cells (with 0.5 M TBP). The opposite V_{OC} variation for the iodine and cobalt cells from M15 to M16 is intriguing. To clarify the origin of our observation, the charge recombination resistance at the interface TiO₂/electrolyte (R_{CT}) was modelled from 20 electrochemical impedance spectroscopy (EIS) as a function of

 $E_{F,n}$ level, as shown in Fig. 4.



Fig. 4. Plots of *Rct versus* E_{Fn} level of the cobalt cells and the iodine cells.

- The charge recombination resistance is related to the charge 25 recombination rate, such that a smaller R_{CT} means the larger charge recombination rate. For the cobalt cells, R_{CT} increases in the order of M15 < M16, indicating a same order of decreased charge recombination rate. In iodine cells, an opposite result was observed. It is known that the halogen bonding between iodine 30 and some electron-rich segments of dye molecules could cause a
- larger charge recombination rate at the titania/electrolyte interface.¹¹ It is suspected that the R_{CT} variation of the dyes in different electrolytes is probably related to the adverse impact of possible halogen bonding on interfacial charge recombination in
- 35 DSCs. M16 containing MTT with more interaction sites (sulfur atom) prefers formation of dye-iodine complexes in comparison with M15. Thereby, the increasing I_3^- concentration at the vicinity of the TiO₂ decreases the electron lifetimes (τ , extracted from the C_{μ} and R_{CT} using $\tau = C_{\mu} \times R_{CT}^{-12}$, Fig. S10†), leading to a ⁴⁰ lower V_{OC} for M16–sensitized cells. In cobalt cells, the V_{OC} of
- M16-sensitized cells higher than those of M15 can be partially 45 DSCs.

To summarize, the feasibility of employing the truxene-based organic dyes for high efficiency dye-sensitized solar cell free of a corrosive iodine electrolyte has been demonstrated. The hexapropyltruxene group on the dyes retards the rate of ⁵⁰ interfacial back electron transfer from the conduction band of the

- nanocrystalline titanium dioxide film to the Co(III) ions, which enables attainment of high photovoltage up to 900 mV. The photovoltaic performance of the cobalt redox couple was superior to that of I⁻/I₃⁻ redox couple for thin-film DSCs sensitized with
- 55 M16. Our results strongly indicate that the application of truxenebased organic dyes as photosensitizers in DSCs employing cobalt electrolyte is promising.

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60 Notes and references

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ascribed to the absence of this non-covalent interaction between the dyes and electrolytes. These results suggest that organic dyes with thiophene derivates as linkers are suitable for iodine-free

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