

Thiophene–nitroxide radical as a novel combination of sensitizer–redox mediator for dye-sensitized solar cells

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Abstract We report a novel combination of organic sensitizer and redox mediator in the electrolyte for dye-sensitized solar cells (DSSCs): a thiophene dye and nitroxide radicals. Nitroxide radicals and their oxidized counterparts of oxoammonium cations show robust reversible redox reactions, thus supporting robust DSSC operations. Moreover, their redox potentials ($E_{1/2}$) and thus open-circuit voltages (V_{OC}) can be tuned further by attached functional groups. Optical and electrochemical characterization reveal that these new combinations exhibit enhanced V_{OC} and power conversion efficiencies compared to the existing iodine mediator (I^-/I_3^-) due to the increased V_{OC} . Also, the selection of the sensitizer–redox mediator turns out to be critical in the overall cell performance. Indeed, the typical ruthenium dye loses its light absorption capability when it is operated in conjunction with the nitroxide radicals.

Keywords Nitroxide · Thiophene dye · Redox mediator · Open-circuit voltage · Dye-sensitized solar cell

Introduction

Dye-sensitized solar cells (DSSCs) have been intensively investigated and developed since their original invention by the Grätzel group in 1991 due to a variety of advantages such as high efficiency, simple fabrication process, and low cost [1, 2]. So far the most well-established system consists of a titanium oxide (TiO_2) nanoparticle anode, a platinum cathode, a ruthenium-based dye called N719, and an electrolyte containing I^-/I_3^- redox couples. This system has made a remarkable progress in improving efficiency reaching ~11% and has also been routinely reproduced by a number of research groups [3]. Still, DSSCs have room for

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further improvement, and in fact, each component of the cell such as anode [4–6], cathode [7–9], sensitizer [10–13], and redox electrolyte [14–18] has continuously attracted research toward novel materials and concepts. Also, it is noteworthy that all the components are coupled to each other, and thus, we need to consider all of the components as a single system.

In a typical DSSC, the dye molecules adsorbed on the nanostructured TiO_2 electrode are excited under illumination, and the excited electrons are injected to the conduction band of TiO_2 (Fig. 1). The oxidized dye molecules are regenerated by being reduced by the iodine redox couple (I^-/I_3^-) in the electrolyte: during the dye reduction, I^- is oxidized to I_3^- , and then I_3^- diffuses to the counter electrode for its reduction back to I^- . Therefore, the most efficient redox couple would be the one that allows fast charge transfer as well as a redox potential close to the ground state of the dye for a large open-circuit voltage (V_{OC}) [19].

Although the system has shown good performance, the I^-/I_3^- couple has its own disadvantages:

1. The low redox potential of the I_3^- with regard to the normal hydrogen electrode (NHE) limits the V_{OC} available due to the large gap between its redox

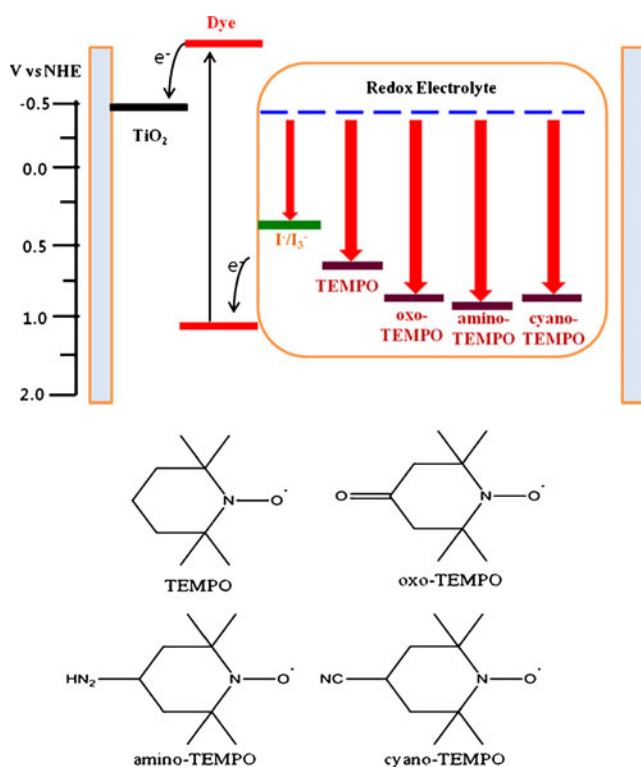


Fig. 1 A diagram of energy levels of all DSSC components including TiO_2 photoanode, a new thiophene dye, and various nitroxide redox couples used in this study. The chemical structure of each nitroxide (TEMPO, oxo-TEMPO, amino-TEMPO, cyano-TEMPO) is also presented

potential (0.4 V vs. NHE) and the valence bands of most dyes (ca. 1.0 V vs. NHE; Fig. 1).

2. The dye regeneration process involves the formation of thermodynamically unfavorable I^*/I^- couple and thus takes an excessive driving force [20]. This is one of the main factors limiting the performance of DSSCs [21].
3. It absorbs a significant portion of the visible light when employed in a high concentration.
4. It has poor compatibility with other substrates.

For example, upon contact with iodine, stainless steel substrates used for replacing high cost fluorine-doped tin oxide (FTO) glass are vulnerable to corrosion causing poor long-term stability [22, 23]. For these reasons, the search for alternative redox couples is a current research topic of high priority.

As possible alternatives to the I^-/I_3^- couple, nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinyl-oxo (TEMPO) and its derivatives ($\text{R}'\text{-TEMPO}$) have been tested with other dyes than the existing ruthenium-based ones. The Grätzel group initially demonstrated TEMPO as a novel redox mediator [17], and the Nishide group improved the system further by introducing TEMPO derivatives [18] that increase V_{OC} . However, to the best of our knowledge, only these two groups have reported the use of these new mediators and also only limited ranges of TEMPO derivatives and dyes excluding most commonly used ruthenium dyes such as N3, N719 have been tested. Moreover, the power conversion efficiency varies significantly (1–5%) depending on dyes and TEMPO derivatives.

As an effort to expand a materials pool and improve the cell performance, in this study we developed a novel thiophene dye and tested it in conjunction with nitroxide radicals with various functional groups. By electrochemical and spectroscopic measurements, we found that nitroxide mediators improve V_{OC} significantly compared to the existing iodine counterpart, and this property can be tuned even further by the attached functional groups. After testing different TEMPO derivatives, we also found only certain TEMPO derivatives function with this new thiophene dye, which indicates that the selection of sensitizer–redox mediator pair plays a critical role in operating DSSCs. In fact, we found that light absorption of the existing ruthenium-based dye becomes deteriorated significantly in the presence of the TEMPO family.

Experimental

Materials

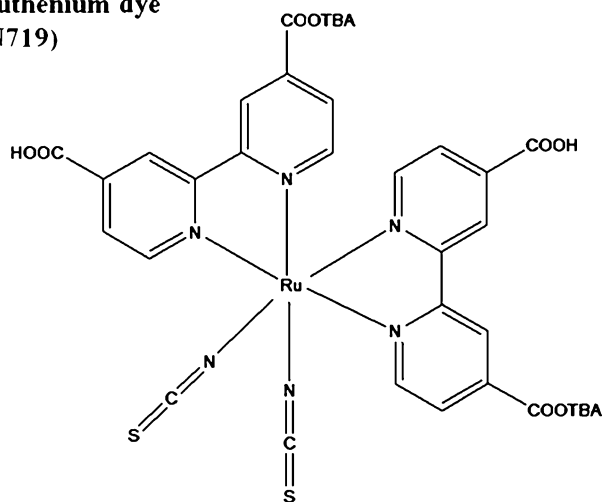
TEMPO and its derivatives (oxy-TEMPO, amino-TEMPO, cyano-TEMPO) were obtained from Aldrich. Acetonitrile

(Merck) and tert-butanol (Aldrich) were dehydrated using 4 Å molecular sieves. For electrolytes, tetrabutylammonium hexafluorophosphate (TBAPF₆; Aldrich), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI; 3 M), nitronium tetrafluoroborate (NOBF₄; Aldrich), 1-methyl-3-propylimidazolium iodide (Aldrich), lithium iodide (LiI; Aldrich), and iodine (I₂; Aldrich) were used as received. For dyes, *cis*-bis(isothiocyanato) bis(2, 2'-bipyridyl-4, 4'-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium dye was received from Solaronix, and thiophene organic dye (DCSC 5.13 M) was synthesized by Dongjin Semichem Co. Ltd. (Fig. 2) [24].

Measurements

The absorption spectra were measured by an Optizen 3220 (Mecasys) UV/VIS spectrometer, and fluorescence emission spectra were measured using fluorospectroscopy (ISS PC1 Photon Counter Meter; Fig. 3). To evaluate redox

Ruthenium dye (N719)



Thiophene dye (DCSC 5.13M)

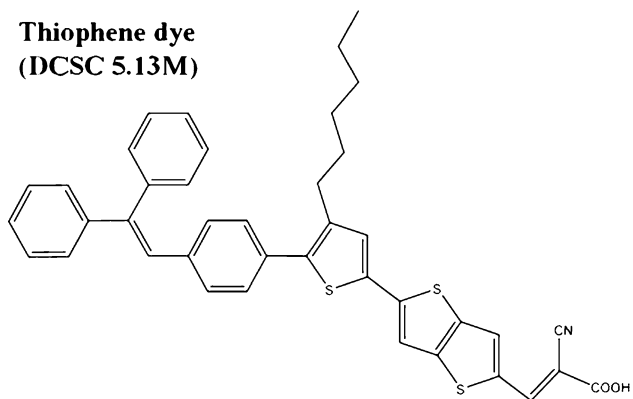
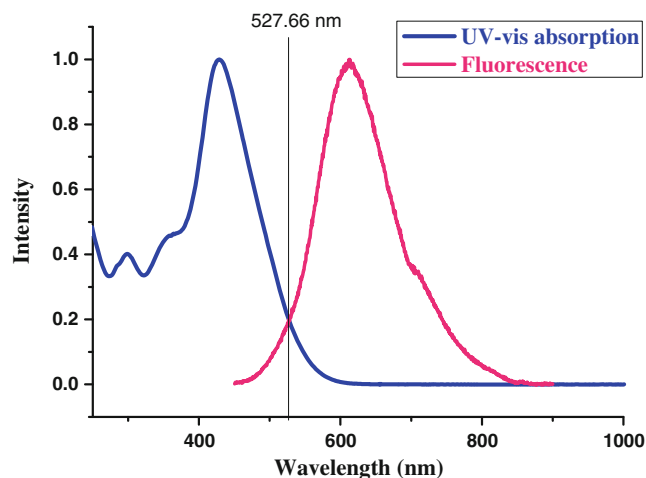


Fig. 2 Chemical structures of dyes—**a** ruthenium dye (N719), **b** thiophene dye (DCSC 5.13 M)



	λ_{\max}/nm	F_{\max}/nm	E_g/eV	HOMO /eV	LUMO /eV
DCSC 5.13M	429	614	2.36	-5.71	-3.35

Fig. 3 UV–VIS normalized absorption and fluorescence emission spectra of thiophene organic dye in acetonitrile (DCSC 5.13 M)

potentials and diffusion coefficients of these mediators, cyclic voltammetry (CV) experiments were performed in sealed, three-electrode glass cells using a Solartron 1,470 potentiostat/galvanostat. Platinum wires and gold disks were used as counter and working electrodes, respectively. The reference electrode was Ag/AgCl, calibrated using the ferrocene/ferrocenium redox couple. The concentration of TEMPO derivatives was 1 mM. The supporting electrolyte was 0.1 M TBAPF₆. The CV data were collected at scanning rates of 0.005, 0.01, 0.02, 0.05, and 0.1 Vs⁻¹. FT-IR spectra were recorded in the attenuated total reflectance (ATR) mode on a Bruker Tensor 27 spectrometer with the resolution of 4 cm⁻¹ in the vibrational frequency range of 600–4,000 cm⁻¹.

Fabrication of DSSC devices

Conducting glass sheets (Pilkington TEC-8, 8 Ωcm⁻²) coated with FTO were used as substrates. Before use, the glass substrates were cleaned by sonication for 30 min in isopropanol and for another 30 min in acetone, followed by rinsing with deionized water and drying in air. For the TiO₂ electrode layer, a very thin layer of dilute (2 wt.% solution in 1-butanol) titanium (IV)-bis (acetylaceto) diisopropoxide (Merck) was first spin-coated over the FTO layer and then sintered at 300 °C. The nanosized TiO₂ layer was obtained over it by doctor blading the TiO₂ paste (DSL 18NR-T, Dyesol). The thickness of this layer was controlled by scotch tape. The film was first dried at room temperature and then sintered at 500 °C for 30 min [25]. After the photoelectrodes were cooled to 150 °C, they were

taken out of the furnace and immersed into a 0.5 mM solution of dye dissolved in a mixture of acetonitrile and tert-butanol (1:1 by vol.) to prevent cracking of TiO₂ and the substrate. All samples were sensitized for 24 h. Counter electrodes were prepared by spin coating H₂PtCl₆ solution (Aldrich, 5 mM in isopropyl alcohol) onto the FTO conductive glass and then sintering it at 400 °C for 30 min. The dye-sensitized TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich type cell by heating at 80 °C with a hot melt film (Surlyn, Solaronix) as a spacer between both electrodes. A drop of redox electrolyte was placed on the drilled hole in the counter electrode of the cell and was driven into the cell via vacuum backfilling. Two types of electrolytes were used for device evaluation. The first one was prepared with 0.5 M TEMPO and its derivatives, 0.05 M NOBF₄ and 1.5 M LiTFSI, in acetonitrile. The other one was a control electrolyte containing the I⁻/I₃⁻ redox couple that consists of 0.6 M 1-methyl-3-propylimidazolium iodine, 0.1 M LiI, and 0.06 M I₂ in acetonitrile.

Characterization of DSSC

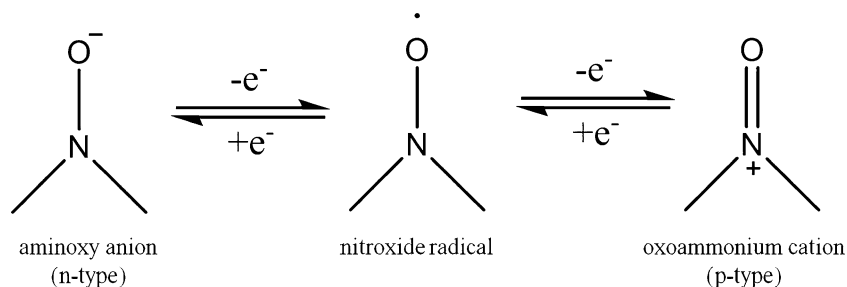
The current density–voltage (J – V) characteristics of the DSSCs were recorded with a computer controlled digital parameter analyzer (Solartron 1470 potentiostat/galvanostat) by applying external potential bias to the cell and measuring the photocurrent generated under 1.5 AM condition (LS-150, ABET technologies) which was calibrated prior to use.

Results and discussion

An efficient redox mediator in DSSCs should satisfy the following requirements [26]:

1. The redox potential should be such that it is as negative as possible for large V_{OC} but positive enough to avoid unnecessary loss of usable energy.
2. The solubility should be high enough to ensure sufficient supply of the redox mediator.
3. The diffusion coefficient should be high for efficient mass transport.

Fig. 4 The mechanism of the redox reaction of nitroxide radical



4. It should absorb the least light in the visible region.
5. Both reduced and oxidized forms need to be stable for efficient redox reactions and the redox reactions need to be highly reversible.

As an effort to find novel redox mediators that meet the above requirements and thus improve the cell performance compared to the existing iodine redox couple, nitroxide radicals R₂NO[•] were tested in this study. These radicals have been well-known for their stability in air and water as well as against dimerization and other radical-based reactions. Also, these radical reactions hold a long and rich history such that a variety of derivatives have been developed based on simple chemical processes [27]. Moreover, nitroxide radicals exhibit fully reversible redox reactions and their reduced or oxidized compounds form stable counterparts. As shown in Fig. 4, nitroxide radicals show two redox couples: Nitroxide radicals are oxidized to oxoammonium cations (p-type doping) or reduced to aminoxy anions (n-type doping). The stability of the doping state differs by the substituent unit.

The primary advantage of the established chemistry of nitroxide radicals with diverse derivatives is to tune the redox potentials. To validate this opportunity, the redox potentials of the nitroxide/ammonium cation couple were determined for TEMPO, oxo-TEMPO, amino-TEMPO, and cyano-TEMPO. CV data for TEMPO and other derivatives are shown in Fig. 5 and Electronic Supplementary Material (ESM)—Fig. S1, respectively. From the CV data, it is noteworthy that the anodic (i_{pa}) and cathodic (i_{pc}) peak current densities for all the derivatives are the same ($i_{pa}/i_{pc} \approx 1$) independent of scan rate. This indicates that the redox reactions of nitroxides are highly reversible, thus satisfying the aforementioned requirement #5. $E_{1/2}$ values obtained by equation $E_{1/2} = (E_{pa} + E_{pc})/2$ are listed in Table 1 for all the derivatives. $E_{1/2}$ values shift quite a bit depending on the substituent groups, thus validating that the replacement of substituent group is a feasible tool to tune the electrochemical properties of the cell. In all the cases, $E_{1/2}$ values are much higher than that of I⁻/I₃⁻ couple so that V_{OC} could be enhanced in DSSC operation.

Diffusion coefficients of TEMPO and TEMPO derivatives were obtained by employing various scan rates in the CV measurements. The peak currents (i_p) for all the

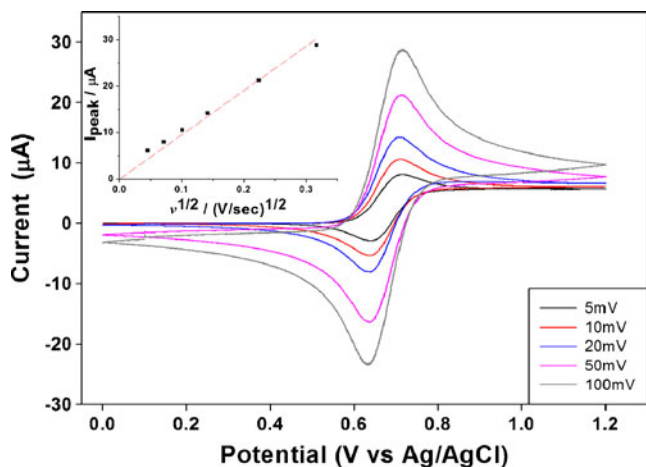


Fig. 5 Cyclic voltammetry for TEMPO in an acetonitrile solution. The scan rates were 0.005, 0.01, 0.02, 0.05, and 0.1 V s^{-1} . *Inset*: a plot of anodic current as a function of the square root of the scan rate exhibits linear dependence

compounds increase with scan rates (ν) as indicated from linear plots of i_p versus $\nu^{1/2}$ (Fig. 5 inset and ESM—Fig. S1). The diffusion coefficients D values were calculated from the slope of the plot of i_p versus $\nu^{1/2}$ using the Randles–Sevcik equation

$$i_p = 0.4463 (F^3/RT)^{1/2} n^{3/2} AD^{1/2} C\nu^{1/2}$$

where i_p is the peak current, F is the Faraday’s constant, R is the gas constant, T is the absolute temperature, n is the number of electrons, A is the electrode area, C is the concentration, ν is the scan rate, and D is the diffusion coefficient.

The obtained values of D (10^{-6} – 10^{-5} $\text{cm}^2 \text{s}^{-1}$) are comparable to that of iodine as listed in Table 1 and therefore must be large enough for decent DSSC operation. Moreover, TEMPO and TEMPO derivatives absorb negligible light in the visible wavelength range as indicated by their UV–VIS absorption data in Fig. 6. The negligible absorption is in a clear contrast to the Γ/I_3^- electrolyte which partially absorbed visible light around 430 nm by the I_3^- [28]. Although nitroxide redox electrolytes absorb the

Table 1 The redox potentials ($E_{1/2}$) and diffusion coefficients of nitroxides

	E_{redox} (V)	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
Iodine	0.4	1.80×10^{-5a}
TEMPO	0.68	1.95×10^{-5}
Oxo-TEMPO	0.86	8.02×10^{-6}
Amino-TEMPO	0.87	1.98×10^{-5}
Cyano-TEMPO	0.85	3.22×10^{-6}

^a [33]

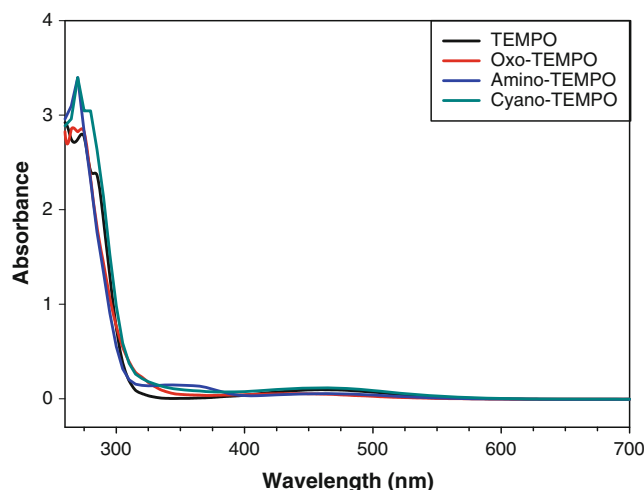


Fig. 6 UV–VIS spectra of nitroxide redox electrolytes (concentration 0.01 M in acetonitrile for all of the electrolyte cases)

light below wavelength of 300 nm, FTO glass substrates usually cut the region [29].

DSSCs were fabricated to evaluate the photovoltaic performance of the nitroxide-based electrolytes. For these cell measurements, both a ruthenium dye (N719) and the novel thiophene organic dye (DCSC 5.13 M) were tested. Interestingly, J – V curves of the solar cells with N719 dye do not show the typical S-type nature, that is, the cells do not operate in A.M. 1.5 condition (ESM—Fig. S2). To figure out the reason for the damaged cell function, FT-IR technique (ATR mode) was used to check the peak intensity of the ruthenium dye after contact with the electrolyte (Fig. 7). The sharp peak at $2,100 \text{ cm}^{-1}$ is characteristic of the thiocyanato group ($-\text{NCS}$) of the dye. After the dye is adsorbed into the TiO_2 film, this peak remains, thus indicating that the basic structure of the N719 dye is not altered when it contacts TiO_2 electrodes. However, a

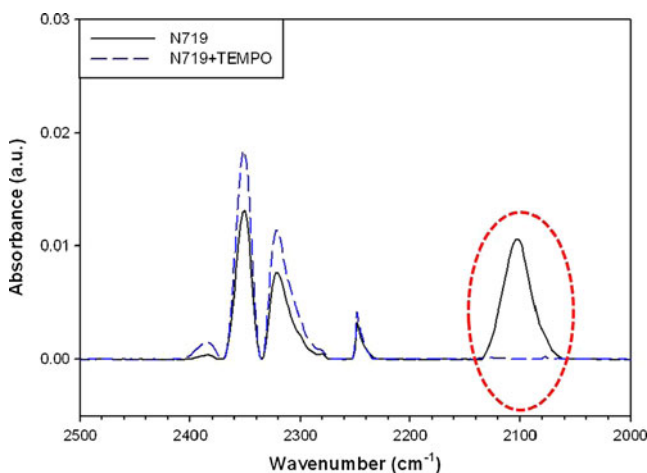


Fig. 7 FT-IR spectra of TiO_2 films after N719 dye adsorption (black solid line) as well as after N719 dye adsorption and nitroxide electrolyte treatment (blue dash line)

control sample in which the dye is first loaded on the TiO₂ film and then immersed in a nitroxide redox electrolyte solution for 5 min loses the peak, which implies that the ruthenium dye loses its light absorption capability significantly. It might be that the oxoammonium cation attacks the sulfur atom of the NCS group in the ruthenium dye and decomposes it to a cyanide byproduct [30]. Due to that reason, ruthenium dyes such as N3, N719 are not suitable for the operation of DSSCs containing nitroxide electrolytes.

The photocurrent density–photovoltage (J – V) characteristics of DSSCs using our new thiophene dye with nitroxide redox electrolytes are shown in Fig. 8. Table 2 summarizes J – V parameters for both nitroxide radicals and iodine redox electrolytes when they were tested with our thiophene (DCSC 5.13 M) dye. From these data, the following points are noticeable: First, TEMPO and oxo-TEMPO exhibit increased V_{OC} compared to the prepared Γ/I_3^- redox couple electrolytes. Considering that the V_{OC} corresponds to the difference between the quasi-Fermi level of the electrons in the TiO₂ film and the redox potential of the electrolyte, the increased V_{OC} verifies that the tuning of the redox energy levels by attached functional groups is reflected in the real cell operation. The V_{OC} increases from 0.61 to ~0.7 V as the redox mediator changes from iodine to TEMPO or oxo-TEMPO. It must be noted that no additional additives such as 4-*tert*-butylpyridine (tBP) and *N*-methylbenzimidazole (NMBI) [31, 32] that are known for intensifying V_{OC} was used in these measurements to directly compare the redox mediator effect. Second, the J – V plots prove that our novel thiophene dye functions well as a novel organic thiophene dye in conjunction with TEMPO and TEMPO derivatives. The development of organic dyes is meaningful because

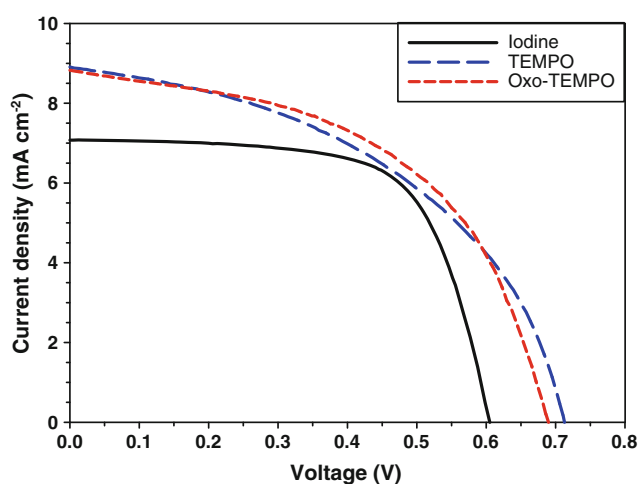


Fig. 8 J – V characteristics of DSSCs based on the thiophene dye with various redox couples in the electrolyte including iodine (black solid line), TEMPO (blue long dash line), and oxo-TEMPO (red short dash line)

Table 2 Photocurrent density–voltage (J – V) characteristics of thiophene dye-sensitized solar cells that include nitroxide and iodine redox electrolytes

	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	η (%)
Iodine	7.09	0.61	0.66	2.85
TEMPO	8.90	0.71	0.47	2.94
Oxo-TEMPO	8.83	0.69	0.51	3.12

organic dyes have many advantages such as large molar extinction coefficients, control of absorption wavelengths, facile design and synthesis, and lower cost than ruthenium complexes. Especially, thiophene-based π -conjugated materials have been known for good properties—chemical and environmental stability as well as their electronic tunability. Third, the DSSCs based on the nitroxide radical electrolytes exhibit higher short-circuit currents (J_{SC}) than the iodine couple. Considering other conditions being identical, the increased value might reflect that the dye regeneration with nitroxide redox couples involve more thermodynamically favorable reaction steps, unlike the iodine case that generates Γ/Γ^- couple in the intermediate step [20]. Finally, the function of the thiophene dye is sensitive to the selection of redox mediator. All the TEMPO derivatives tested show the increased $E_{1/2}$ from CV measurements in Table 1. However, the increased $E_{1/2}$ is not always reflected in the V_{OC} . Indeed, cyano- and amino-TEMPOs show impaired cell performance such that the power conversion efficiencies are below 1%. The detailed failure mechanism is currently under investigation. However, this inconsistent trend indicates that the interaction between the dye and redox mediator in the electrolyte is very critical in DSSC operation, and thus, the dye–redox mediator pair must be chosen with caution.

Conclusions

Thiophene dye–nitroxide radicals are demonstrated as novel pairs of organic dye–redox mediators for DSSCs. Compared to the existing iodine redox mediator, these nitroxide radicals show improved properties such as negligible light absorption in the visible wavelength range and increased V_{OC} and power conversion efficiencies. The efficiency ranges between 2.9% and 3.1%. Moreover, the redox potential and thus V_{OC} can be tuned further by attaching different functional groups in the nitroxide radicals. While the nitroxide radicals show improved performance compared to the iodine mediator, further study is still required to understand more detailed mechanisms on the new dye–redox mediator interaction and its effect on the overall cell performance. The selection of dye–redox

mediator in the electrolyte turns out to be very critical in determining the cell performance. In fact, the conventional ruthenium dye fails in operating the cell in the presence of these nitroxide radicals in the electrolyte. The research utilizing nitroxide radicals in DSSCs is expected to be very significant because nitroxide radicals are well-established chemicals in diverse applications such as lithium rechargeable batteries, electrochromic cells, and OLEDs owing to their excellent stabilities in ambient conditions.

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References

1. O'Regan B, Grätzel M (1991) *Nature* 353:737
2. Grätzel M (2005) *Inorg Chem* 44:6841
3. Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M (2005) *J Am Chem Soc* 127:16835
4. Law M, Greene LE, Johnson JC, Saykally R, Yang P (2005) *Nat Mater* 4:455
5. Quintana M, Edvinsson T, Hagfeldt A, Boschloo G (2007) *J Phys Chem C* 111:1035
6. Sayama K, Sugihara H, Arakawa H (1998) *Chem Mater* 10:3825
7. Wang M, Anghel AM, Marsan B, Ha N, Pootrakulchote N, Zakeeruddin SM, Grätzel M (2009) *J Am Chem Soc* 131:15976
8. Lee WJ, Ramasamy E, Lee DY, Song JS (2009) *ACS Appl Mater Interf* 1:1145
9. Xia J, Yuan C, Yanagida S (2010) *ACS Appl Mater Interf* 2:2136
10. Hagfeldt A, Grätzel M (2000) *Acc Chem Res* 33:269
11. Chen C, Wang M, Li J, Pootrakulchote N, Alibabaei L, Ngoc-le C, Decoppet J, Tsai J, Grätzel C, Wu C, Zakeeruddin SM, Grätzel M (2009) *ACS Nano* 3:3103
12. Miyashita M, Sunahara K, Nishikawa T, Uemura Y, Koumura N, Hara K, Mori A, Abe T, Suzuki E, Mori S (2008) *J Am Chem Soc* 130:17874
13. Qin H, Wenger S, Xu M, Gao F, Jing X, Wang P, Zakeeruddin SM, Grätzel M (2008) *J Am Chem Soc* 130:9202
14. Oskam G, Bergeron BV, Meyer GJ, Searson PC (2001) *J Phys Chem B* 105:6867
15. Nusbaumer H, Moser J, Zakeeruddin SM, Nazeeruddin MK, Grätzel M (2001) *J Phys Chem B* 105:10461
16. Wang Z, Sayama K, Sugihara H (2005) *J Phys Chem B* 109:22449
17. Zhang Z, Chen P, Murakami TN, Zakeeruddin SM, Grätzel M (2008) *Adv Funct Mater* 18:341
18. Kato F, Hayashi N, Murakami T, Okumura C, Oyaizu K, Nishide H (2010) *Chem Lett* 39:464
19. Rutkowska IA, Skunik M, Miecznikowski K, Kulesza PJ (2008) *ECS Trans* 13:185
20. Clifford JN, Palomares E, Nazeeruddin MK, Grätzel M, Durrant JR (2007) *J Phys Chem C* 111:6561
21. Teng C, Yang X, Yuan C, Li C, Chen R, Tian H, Li S, Hagfeldt A, Sun L (2009) *Org Lett* 11:5542
22. Park JH, Jun Y, Yun HG, Lee SY, Kang MG (2008) *J Electrochem Soc* 155:F145
23. Li D, Li H, Luo Y, Li K, Meng Q, Armand M, Chen L (2010) *Adv Funct Mater* 20:3358
24. Bae HG, Lee CC, Kim JB, Park TJ, Moon HD, Baek JH, An HC, Yang HT (2008) KR Patent appl. No. 2008-0100967
25. Lee JY, Bhattacharya B, Kim DW, Park JK (2008) *J Phys Chem C* 112:12576
26. Wolfbauer G, Bond AM, Eklund JC, MacFarlane DR (2001) *Sol Energy Mater Sol Cells* 70:85
27. Hicks RG (2007) *Org Biomol Chem* 5:1321
28. Wang M, Chamberland N, Breau L, Moser J, Humphry-Baker R, Marsan B, Zakeeruddin SM, Grätzel M (2010) *Nat Chem* 2:385
29. Lee H, Bae S, Jo Y, Kim K, Jun Y, Han C (2010) *Electrochim Acta* 55:7159
30. Zhang Z (2008) Ph.D. thesis, Swiss Federal Institute of Technology, Lausanne, Switzerland
31. Schlichthorl G, Huang SY, Sprague J, Frank AJ (1997) *J Phys Chem B* 101:8141
32. Park JH, Choi KJ, Kim J, Kang YS, Lee SS (2007) *J Power Sources* 173:1029
33. Nelson JJ, Amick TJ, Elliott CM (2008) *J Phys Chem C* 112:18255