

Effects of plant carotenoid spacers on the performance of a dye-sensitized solar cell using a chlorophyll derivative: Enhancement of photocurrent determined by one electron-oxidation potential of each carotenoid

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Abstract

Plant carotenoids (Cars) with 8–10 conjugated double bonds, having higher singlet energies than those of bacterial Cars with 9–13 conjugated double bonds, were added (by 20%) as redox spacers to a titania-based Grätzel-type solar cell using a chlorophyll derivative (PPB *a*) as the sensitizer. No clear indication of singlet-energy transfer from Car to PPB *a* was seen, but clear enhancement of photocurrent with the decreasing one electron-oxidation potential of Car was observed. An empirical equation correlating the increase in photocurrent to difference in one electron-oxidation potentials (PPB *a* minus Car) and the oscillator strength of Car is proposed.

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1. Introduction

This is in a series of investigations to develop new Grätzel-type dye-sensitized solar cells (DSSCs) [1], of high-performance, low-cost and free from environmental pollution, based on the principles and materials of photosynthesis.

In addition to the light-harvesting function, which includes the absorption of photon by Car followed by singlet-energy transfer to BChl, Cars in photosynthetic systems play the photo-protective function, which include the quenching of the triplet state of special-pair BChls (Refs. [2,3 for reviews) or the neutralization of chlorophyll (Chl) or BChl radical cation (Ref. [4] for a review). The former photo-protective function takes place in the bacterial RCs, whereas the latter, in the RC of spinach photosystem

II and in the bacterial LH2 antenna complexes. Thus, the light-harvesting and the redox functions of Cars can be introduced into a DSSC using a Chl derivative as the sensitizer.

The light-harvesting function of Cars consisting of a linear conjugated chain stems from their energies of the singlet-excited states relative to those of BChls and Chls: The singlet-state energies of polyenes lower with the increasing number of conjugated double bonds, *n* [5,6]. Therefore, in the bacterial photosynthetic systems, shorter-chain Cars mainly play the light-harvesting function that includes the Car → BChl singlet-energy transfer. The singlet energies of BChls are lower than those of Chls, and therefore, the bacterial Cars have conjugated chains with *n* = 9–13, whereas the plant Cars have those with *n* = 8–10. In each set of Cars, the shorter-chain Cars play the light-harvesting function by the use of the down-hill singlet-energy transfer.

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The redox function of Cars stems from their low one-electron-oxidation potential, which also decrease with increasing n . Therefore, longer-chain Cars tend to eject electron more efficiently, i.e., they have stronger reducing power.

In a previous investigation [7], we found that the addition of bacterial Cars as redox spacers can enhance the incident photon-to-current conversion efficiency (IPCE) and the solar energy-to-electricity conversion efficiency (hereafter abbreviated as ‘conversion efficiency η ’) of a DSSC using a Chl *a* derivative (methyl 3-devinyl-3-carboxy-pyropheophorbide *a* abbreviated as ‘PPB *a*’) as the sensitizer. The idea underlying this attempt was to add an additional redox component (Cars) between the sensitizer (PPB *a*) and the I^-/I_3^- redox couple to facilitate cascade electron transfer. The performance of the DSSC was enhanced with the increasing n (as a result, the decreasing one electron-oxidation potential), which was explained in terms of the electron-transfer mechanism. In a follow-up investigation [8], the electron transfer from each Car to PPB *a* radical cation (PPB *a* $^+$) was evidenced by picosecond time-resolved absorption spectroscopy using the singular-value decomposition and global fitting analysis. The transient absorptions originating from PPB *a* $^+$ and each Car $^+$ were clearly assigned, and it was shown that the decay of the former and the rise of the latter have the same time constant. However, no signs of singlet-energy transfer from bacterial Car to PPB *a* were seen due to the possible mismatching of singlet energies between the two components.

In the present investigation, we have attempted a combination of a Chl *a* derivative and a set of *plant* Cars to facilitate the Car-to-PPB *a* singlet-energy transfer in DSSCs. We have addressed the following two closely related questions: (1) Which mechanism, i.e., the energy-transfer mechanism or the electron-transfer mechanism, plays the major role in the enhancement of photocurrent? (2) Which physical parameter of Car, i.e., the oscillator strength or the redox potential, plays a major role in the enhancement of performance?

2. Experimental

Neoxanthin, violaxanthin and lutein were isolated as described in Supplementary information. The HPLC analysis (detected at the absorption maxima) showed that the purities of neoxanthin, violaxanthin and lutein were 97, 96 and 98%, respectively. β -Carotene purchased from Wako Chemicals showed a purity of $\approx 100\%$.

Each DSSC consisted of the optically transparent electrode (OTE), the counter electrode of Pt-sputtered, fluorine-doped tin oxide (FTO) glass (Nippon sheet Glass $10 \Omega \text{ cm}^{-2}$), and a methoxyacetonitrile solution containing 0.1 M LiI, 0.05 M I_2 and 0.6 M 1,2-dimethyl-3-propyl-imidazolium iodide. The OTE was fabricated by deposition of two layers of TiO_2 particles on an FTO glass; one layer (8- μm thick) consisted of 13-nm TiO_2 particles (Ti nanooxide T, Solarnix) for adsorbing the dye molecules, and the other

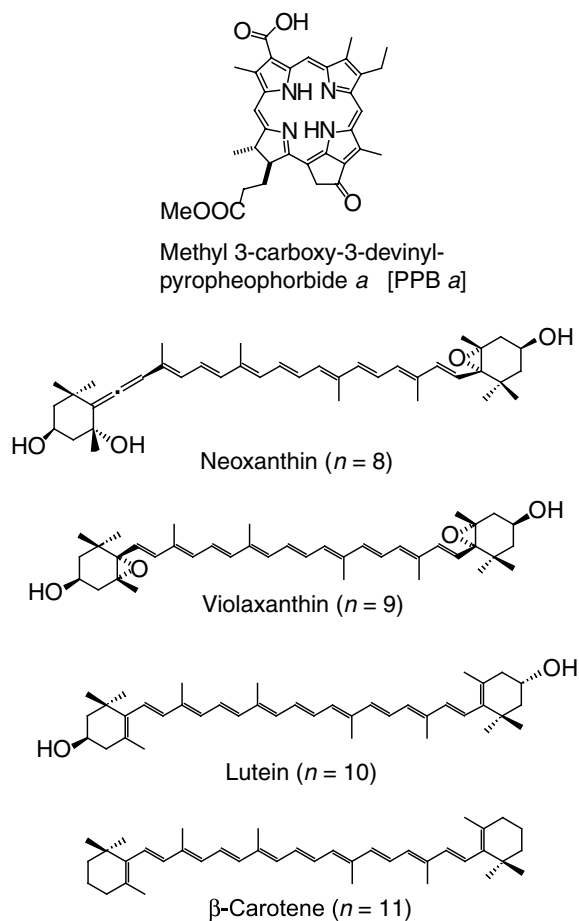
(2- μm thick) consisted of 300-nm TiO_2 particles (CR-EL, Ishihara Sangyo) for scattering the incident light. Then, the TiO_2 deposited FTO glass was soaked overnight in THF solution, which contained PPB *a* and one of the Cars with a molar ratio of 4:1, to form the OTE. The IPCE profiles and I - V curves of DSSCs were recorded as described previously [7].

The coverage of the PPB *a* and Car molecules, on the surface of TiO_2 layer, could not be determined experimentally due to their instability in the oxidizing conditions with no supply of electrons.

3. Results and discussion

3.1. Characterization of the dye and spacer molecules

The structures of the dye sensitizer (PPB *a*) and a set of redox spacers (Cars) can be characterized as follows (see Scheme 1): (1) We used exactly the same sensitizer as in a previous investigation [7]. It is methyl 3-devinyl-3-carboxy-pyropheophorbide *a*, abbreviated as ‘PPB *a*’. It has a chlorin macrocycle of pheophytin-type and a carboxyl group is directly attached to it to facilitate the binding as well as electron injection to TiO_2 . (2) The set of Cars has an extended, all-*trans* conjugated chain with different



Scheme 1.

numbers of conjugated double bonds, $n = 8, 9, 10$ and 11 , respectively. (3) Neoxanthin is an asymmetric allenic Car having cyclohexane rings at both ends, to which the hydroxyl and epoxide groups are attached. (4) Violaxanthin, lutein and β -carotene are symmetric Cars. At each end of those Cars attached are, respectively, a cyclohexane ring with the hydroxyl and epoxide groups, a β -ionone ring with the hydroxyl group, and a β -ionone ring.

The electronic-absorption spectra of the PPB *a* sensitizer and the Car redox spacers are presented in Fig. 1. The relevant optical parameters derived from the spectra, including the state energies, molar extinction coefficients, oscillator strengths and transition-dipole moments, are listed in Tables 1 and 2. They can be characterized as follows: (1) The PPB *a* molecule exhibits a pair of split absorption peaks that are ascribable to transitions, from the ground state, to the Soret, Q_x and Q_y states. (2) Each

Car molecule exhibits a progression ascribable to transitions from the ground $1A_g^-(0)$ state to the $1B_u^+(v = 0 - 3)$ vibronic states. Most importantly, the $1B_u^+$ absorption maximum systematically shifts and increases in intensity with increasing n , in the order, neoxanthin ($n = 8$) < violaxanthin ($n = 9$) < lutein ($n = 10$) < β -carotene ($n = 11$). (3) Correspondingly, the oscillator strength as well as the transition-dipole moment increases in the same order (see Table 2). In other words, a Car molecule having a longer conjugated chain efficiently absorbs photon, and gives rise to a larger change in the dipole moment upon photo-excitation.

Since we used a PPB *a*: Car molar ratio of 4:1, the photons absorbed by Car is much smaller than those absorbed by PPB *a*, although the molar extinction coefficient of Car is approximately twice larger than that of PPB *a*, when the relevant molecules are in the monomeric form.

The values of one electron-oxidation potential (E_{ox}) for PPB *a* and Cars are also listed in Tables 1 and 2, respectively. The E_{ox} value of each Car is smaller than that of PPB *a*, which indicates that electron can be transferred from each Car to PPB *a*⁺. Among the set of Cars, the E_{ox} value decreases in the order, violaxanthin ($n = 9$) > neoxanthin ($n = 8$) > lutein ($n = 10$) > β -carotene ($n = 11$), indicating that the efficiency of the Car \rightarrow PPB *a*⁺ electron transfer should increase in the order, violaxanthin < neoxanthin < lutein < β -carotene.

3.2. Possibility of Car to PPB *a* singlet-energy transfer

We have first examined the possibility if the singlet energy-transfer reaction can take place from each Car to PPB *a* based on an energy diagram shown in Fig. 2: the stretched all-*trans* conjugated chain of Cars, having

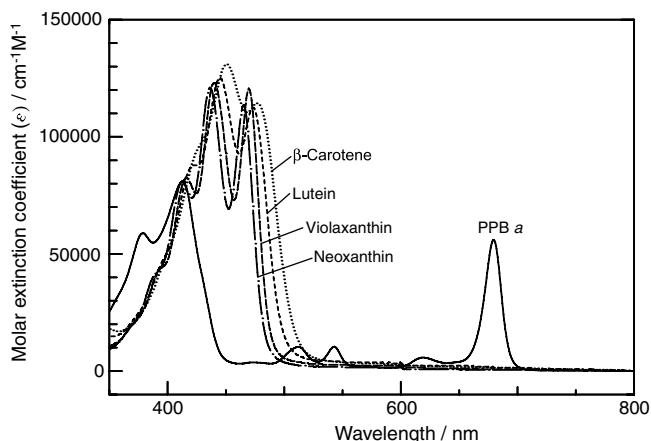


Fig. 1. Electronic absorption spectra of PPB *a*, and Cars including neoxanthin, violaxanthin, lutein and β -carotene.

Table 1

Optical and redox parameters of PPB *a* including the state energies, molar extinction coefficient at absorption maximum (ϵ_{max}), oscillator strength (f), transition dipole moment (μ) and one-electron-oxidation potential (E_{ox} vs. NHE)

| State energies/cm ⁻¹ | | | | | | ϵ_{max} (cm ⁻¹ M ⁻¹) |
|---------------------------------|-------|-------|---------|-------|-------|--|
| Soret | Q_x | | Q_y | | | |
| 24213 | 26385 | 18416 | 19550 | 14705 | 16155 | 83000 |
| f^a | | | μ^a | | | E_{ox} (V) |
| Soret | Q_x | Q_y | Soret | Q_x | Q_y | |
| 1.8 | 0.18 | 0.99 | 12.6 | 4.6 | 12.0 | 1.18 |

^a Integrated throughout the absorption peaks.

Table 2

Optical and redox parameters of the Cars including the $1B_u^+$ energy ($1B_u^+(0)$), molar extinction coefficient (ϵ), oscillator strength (f), transition-dipole moment (μ) and one-electron-oxidation potential (E_{ox} vs. NHE)

| n | Car | $1B_u^+(0)$ (cm ⁻¹) | ϵ (cm ⁻¹ M ⁻¹) | f^a | μ^a (Debye) | E_{ox} (V) |
|-----|-------------------|---------------------------------|--|-------|-----------------|--------------|
| 8 | Neoxanthin | 21482 | 121000 | 2.56 | 15.9 | 0.69 |
| 9 | Violaxanthin | 21299 | 123000 | 2.70 | 16.5 | 0.73 |
| 10 | Lutein | 21097 | 125000 | 3.07 | 17.6 | 0.67 |
| 11 | β -Carotene | 20942 | 131000 | 3.23 | 18.6 | 0.61 |

^a Integrated throughout the $1B_u^+$ absorption.

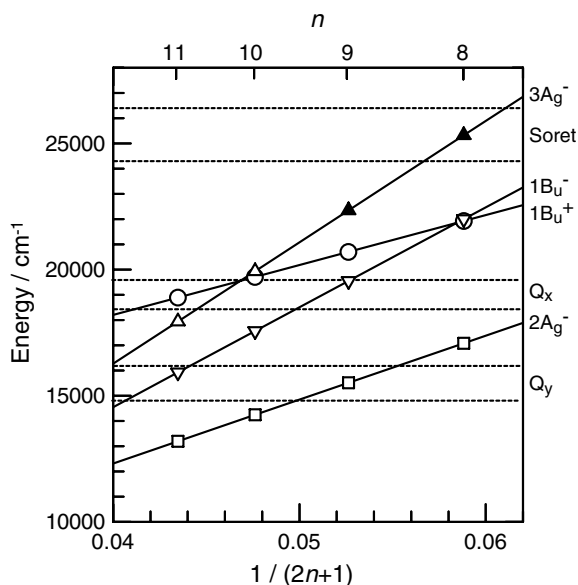


Fig. 2. Comparison of the energies of the $3A_g^-$, $1B_u^-$, $1B_u^+$ and $2A_g^-$ singlet states of Cars having different number of conjugated double bonds (n) with those of the Soret, Q_x and Q_y singlet states of PPB *a*. The former is based on the linear relations, as functions of $1/(2n+1)$, that were determined by resonance-Raman excitation profiles of crystalline bacterial carotenoids [6], whereas the latter was determined by conventional electronic-absorption spectroscopy (Fig. 1).

approximate C_{2h} symmetry like a polyene, gives rise to low-lying singlet states that can be classified into the ionic $1B_u^+$ state and the covalent $2A_g^-$, $1B_u^-$ and $3A_g^-$ states [5,6,9]. Upon absorption of photons, a transition from the ground $1A_g^-$ state to the ionic state is allowed, but those to the covalent states are forbidden, based on the selection rule concerning the symmetry of relevant states and the electronic configurations [10,11]. Therefore, the $1B_u^+$ state can be easily identified by conventional electronic-absorption spectroscopy, but the $2A_g^-$, $1B_u^-$ and $3A_g^-$ states can not (therefore, they are called 'dark states'). In Fig. 2, we transferred those state energies, expressed as linear functions of $1/(2n+1)$, that were determined in bacterial Cars by measurement of resonance-Raman excitation profiles [6]. Those excited states of Cars are compared with the Soret, Q_x and Q_y states of PPB *a* that were directly determined by absorption spectroscopy (see Fig. 1 and Table 1).

Based on the assumption that the arrangement and decay time constants of the low-lying singlet states of the present set of Cars were not very different from those of bacterial Cars, the internal conversion within Car and the Car-to-PPB *a* singlet-energy transfer are expected to take place as follows: (1) Upon absorption of photon, each Car molecule is excited to the optically allowed $1B_u^+$ state, and the subsequent internal conversion populates the dark $3A_g^-$, $1B_u^-$ and $2A_g^-$ states according to the state ordering. The lifetimes of the $1B_u^+$, $3A_g^-$ ($1B_u^-$) and $2A_g^-$ states are on the order of 10 fs, 10–100 fs and 1–10 ps, respectively [9]. Thus, the long-lived $2A_g^-$ state may play the most important role. (2) Upon excitation to the $1B_u^+$ state, the $1B_u^+ \rightarrow Q_x$ energy transfer from Car to PPB *a* can take

place for all the set of Cars. However, the $1B_u^- \rightarrow Q_x$ as well as the $2A_g^- \rightarrow Q_y$ energy transfer channels can be open for Cars with $n = 8$ and 9, but they should be closed for Cars with $n = 10$ and 11.

In summary, efficient singlet-energy transfer can take place not in lutein or β -carotene ($n = 10$ and 11), but in neoxanthin or violaxanthin ($n = 8$ and 9).

3.3. Effect of Car spacers on the performance of PPB *a*-sensitized DSSC

Next, we have examined experimentally the effects of adding the Car spacers on the photocurrent and conversion efficiency of the DSSC using the PPB *a* sensitizer, and found that addition of 20% each of Cars gave rise to the highest enhancement of those values. Therefore, we will confine ourselves to describing the results and to proposing the mechanism of enhancement under this particular concentration.

The IPCE profiles and the $I-V$ curves in the absence and presence of the set of Cars are shown in Fig. 3. All of the IPCE profiles are similar to one another, and no signs of absorption of photons by Cars are seen in the IPCE profile

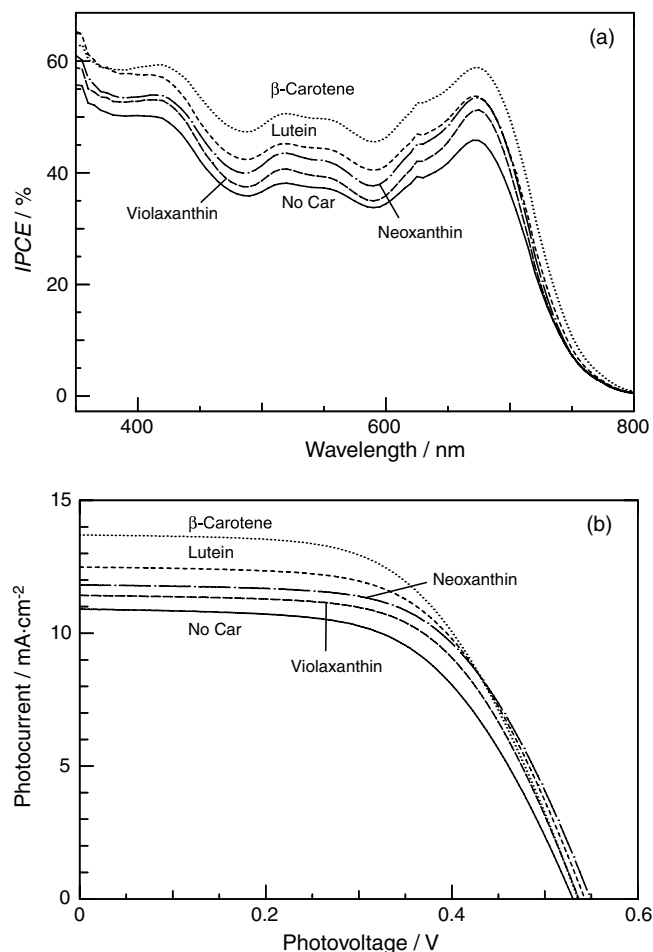


Fig. 3. The IPCE profiles (a) and the $I-V$ curves (b) for the PPB *a*-sensitized solar cells without Car and with a 20% each of Cars including neoxanthin, violaxanthin, lutein and β -carotene.

(the action spectrum). However, the IPCE is enhanced in the presence of Car, in the order, violaxanthin ($n = 9$) < neoxanthin ($n = 8$) < lutein ($n = 10$) < β -carotene ($n = 11$). The I - V curves show that the J_{sc} value increases in the same order, whereas the V_{oc} values are similar to one another. As a result, the conversion efficiency η increases in the same order as shown in Table 3. The IPCE value that was integrated over the range of 350–800 nm ($12\,500$ – $28\,571\text{ cm}^{-1}$) also exhibits the same ranking. Most importantly, the increasing order of photocurrent parallels the decreasing order of one electron-oxidation potential (E_{ox}), i.e., the increasing potential of Car as an electron donor. The dependence of the $\int \text{IPCE} d\bar{\nu}$, J_{sc} and η values (all of them are relevant to the photocurrent) on the E_{ox} value is pictorially shown in Fig. 4.

As described in Section 3.2, we anticipated that the enhancement of performance due to the energy-transfer mechanism must decrease in the order, neoxanthin ($n = 8$) > violaxanthin ($n = 9$) > lutein ($n = 10$) > β -carotene ($n = 11$). This ranking sharply contrasts to the enhancement of performance due to the electron-transfer mechanism, increasing in the order, violaxanthin ($n = 9$) < neoxanthin ($n = 8$) < lutein ($n = 10$) < β -carotene ($n = 11$). Based on our observation (Fig. 4), we conclude that *not* the energy-transfer mechanism *but* the electron-transfer mechanism is taking the major role.

In order to find out the contributions of the electron-transfer and energy-transfer mechanisms, we have tried to correlate the photocurrent in the present DSSC (Table 3) to the redox and optical parameters of each Car molecule (Table 2). More specifically, we tried to correlate, by the use of an empirical equation, the photocurrent enhanced by each Car (ΔJ_{sc}) to the difference in the redox potential in V of PPB *a* minus Car ($1.18 - E_{ox}$) and the oscillator strength (f) of the relevant Car. In the equation, the first term is ascribable to the redox electron transfer from each Car to PPB *a*, and the second term, to the Car-to-PPB *a* singlet-energy transfer upon photo-excitation of the relevant Car. Least-squares fitting led us to the following empirical equation:

$$\Delta J_{sc} = 2.92(1.18 - E_{ox}) + 0.116f. \quad (1)$$

(Here, both coefficients, 1, 2.92 and 0.116 are supposed to have appropriate dimensions to make each term in the equation consistent.) Judging from the relative contribution, the former redox electron-transfer process, plays a predominant role under the present conditions. Justifica-

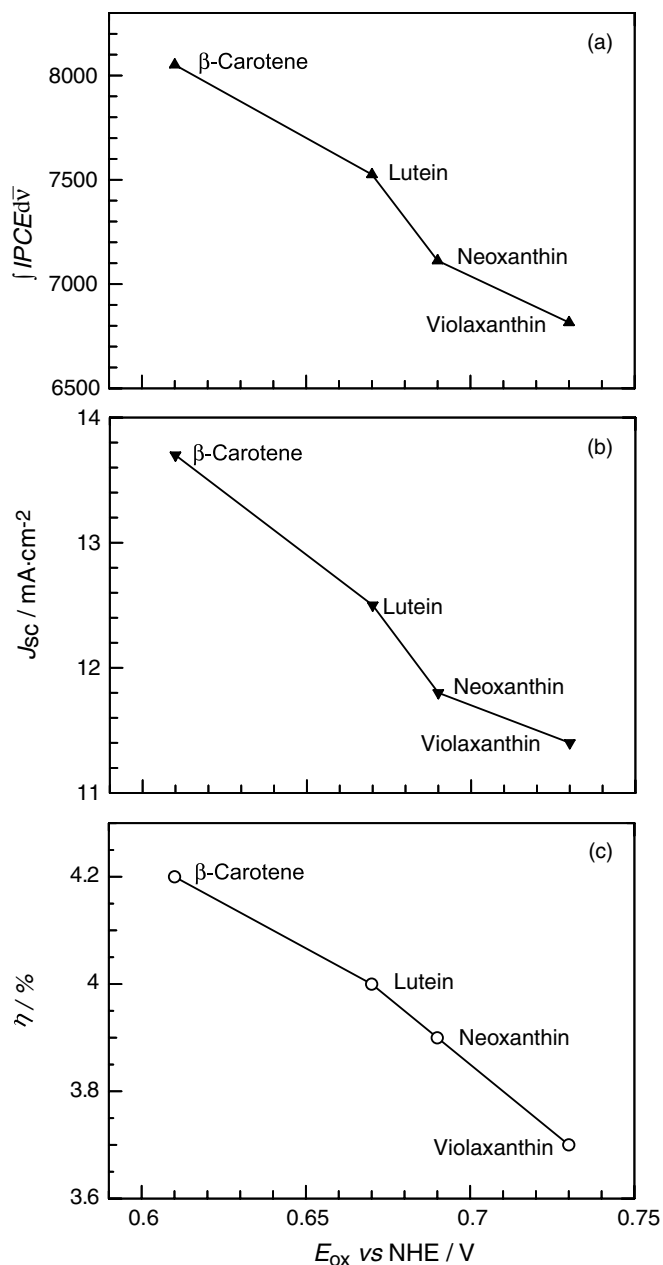


Fig. 4. Dependence of integrated IPCE over the $12\,500$ – $28\,571\text{ cm}^{-1}$ range ($\int \text{IPCE} d\bar{\nu}$), (a), short-circuit current density (J_{sc}) (b), and conversion efficiency (η) (c) on the one-electron-oxidation potentials of Cars (E_{ox}) including neoxanthin, violaxanthin, lutein and β -carotene.

tion of the linear expression of the first term, based on the Marcus theory, is presented in the Supplementary information.

Table 3

Performance of DSSCs using PPB *a* as the sensitizer and Cars as redox spacers; parameters include the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), Fill factor (FF), conversion efficiency (η) and integrated IPCE ($\int \text{IPCE} d\bar{\nu}$)

| n | PPB <i>a</i> /Car | J_{sc} (ΔJ_{sc}) (mA cm ⁻²) | V_{oc} (V) | FF | η (%) | $\int \text{IPCE} d\bar{\nu}$ / (cm ⁻¹) |
|-----|---------------------|---|--------------|------|------------|---|
| | No Car | 10.6 (0) | 0.54 | 0.60 | 3.4 | 6431 |
| 8 | +Neoxanthin | 11.8 (+1.2) | 0.55 | 0.60 | 3.9 | 7112 |
| 9 | +Violaxanthin | 11.4 (+0.8) | 0.54 | 0.61 | 3.7 | 6816 |
| 10 | +Lutein | 12.5 (+1.9) | 0.54 | 0.59 | 4.0 | 7525 |
| 11 | + β -Carotene | 13.7 (+3.1) | 0.53 | 0.58 | 4.2 | 8051 |

4. Conclusion

We have used a set of plant Cars as redox spacers in the PPB *a*-sensitized solar cell. An attempt to identify singlet-energy transfer from Cars to PPB *a* was not successful. However more definitive answers concerning the pair of questions addressed in Section 1 have been obtained: (1) the electron-transfer mechanism instead of the energy-transfer mechanism, or in other words and (2) the one electron-oxidation potential instead of the oscillator strength, plays a predominant role in the enhancement of the photocurrent and conversion efficiency of the PPB *a*-sensitized solar cell. Most importantly, an empirical equation has been proposed to evaluate the relative contributions of the two mechanisms.

Further investigation is necessary to establish the implication of the empirical equation proposed in the present investigation. Our recent results of investigation on PPB *a* and related compounds suggest the presence of two pathways of electron injection, i.e., one from the Q_y state of the PPB *a* to the conduction band of TiO_2 , and the other from the ground state of PPB *a* to the hole of valence band of TiO_2 that is generated by absorption of photons by TiO_2 itself. Selective photo-excitation of TiO_2 , PPB *a* and Car should reveal the relevance of the two terms in the absence and presence of Cars.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2006.04.008](https://doi.org/10.1016/j.cplett.2006.04.008).

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