Linking of N3 dye with C_{60} through diaminohydrocarbons for enhanced performance of dye-sensitized TiO_2 solar cells

Min Ki Lim [a], Song-Rim Jang [a], R. Vittal [a], Jiwon Lee [b], Kang-Jin Kim [a,*]

[a] *Department of Chemistry, Korea University, Seoul 136-713, Republic of Korea*
[b] *Samsung SDI Co. Ltd., Gyeonggi-do 449-577, Republic of Korea*

Abstract

In a novel approach, fullerene, C_{60} was attached to N3 dye (*cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanato ruthenium(II)) via diaminohydrocarbon linkers (L) with different carbon chain lengths. The resulting complexes (each designated as N3-L-C_{60}) were characterized by FT-IR spectra, FE-SEM images, and EDX analysis. The short-circuit photocurrent density (J_{sc}) of the dye-sensitized solar cells (DSSCs) using the fullerene-attached sensitizers varied markedly depending on the chain length of the linker. In the case of the linker 1,6-diaminohexane, the J_{sc}, V_{oc} and conversion efficiency of the pertaining cell were found to be 11.75 mA/cm^2, 0.70 V and 4.5%, respectively, as against the values of 10.55 mA/cm^2, 0.68 V and 4.0%, respectively, for a DSSC with ordinary N3 dye. The J_{sc} variations are discussed on the basis of effective dye adsorptions on TiO_2 films. The possible favorable effects for V_{oc} enhancement, caused by hydrophobic atmosphere around the TiO_2 particles due to diaminohydrocarbon chains and by the negative shift of the flat band potential of TiO_2 by NH groups, are offset by the mediation of back electron transfer by C_{60}; this phenomenon is seen as the reason for minimal V_{oc} changes.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Fullerene (C_{60}); Diaminohydrocarbon; Dye-sensitized solar cell; Back electron transfer; Short-circuit photocurrent; Open-circuit voltage

1. Introduction

It is well-known that recombination between conduction band electrons of TiO_2 and triiodide ions, I_3^-, of the electrolyte decreases the open-circuit voltage (V_{oc}) of a dye-sensitized solar cell (DSSC). Attempts have been made to reduce this recombination by using metal oxide blocking layers on TiO_2 surface [1], by using composite semiconductor oxide films [2], by forming an insulating film of poly(methylsiloxane) on parts of TiO_2 that may not be covered with dye [3], and by attaching long alkyl chains to the bipyridine rings of ruthenium dyes [4]. Aiming at reducing recombination of conduction band electrons with I_3^- ions, we have coated the TiO_2 film with the N3 dye (*cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanato ruthenium(II)) which was linked with fullerene (C_{60}) through diaminohydrocarbon linkers (L) of various chain lengths. The composite of diaminohydrocarbon-C_{60},

attached to the pyridine ring of N3, was considered to create a hydrophobic layer at the TiO_2/electrolyte interface, as per the schematic representation by Lagref et al. in their work [4].

The introduction of C_{60} at the TiO_2/electrolyte interface was based on the recent report that a layer of fullerene can form an energy barrier against the electron transfer from the conduction band to the electrolyte, as well as a diffusion barrier to the movement of anions toward the photoanode [5]; in our case the anions are I_3^- ions. In this context it is to be mentioned that Kamat et al. have reported that C_{60} clusters can act as electron shuttles which effectively regenerate the sensitizer but at the same time minimize direct interaction between the excited sensitizer and redox couple [6]. As we could not foresee the probable interactions between C_{60} and TiO_2 in our planned work, we desired some type of compatibility between fullerene and TiO_2. Fullerene is compatible with TiO_2, because there exists a delicate balance between intermolecular interactions of C_{60} and its interactions with TiO_2, and fullerene has a high association equilibrium with TiO_2 [7,8]. Diaminohydrocarbon linkers were selected because they can be connected to N3 and C_{60} through the formation of amide and C–N bonds, respectively.

* Corresponding author. Tel.: +82 2 3290 3127; fax: +82 2 3290 3121.
E-mail address: kjkim@korea.ac.kr (K.-J. Kim).

Although there have been several reports on the use of fullerene in plastic or organic solar cells [9–12], very few reports were made on the use of fullerenes in DSSCs [6,13]. Maggini et al. have simply synthesized a fullerene derivative covalently linked to a Ru(II) tris(bipyridine) complex [14]. New organic solar cells have been made by Hasobe et al., based on composite nanoclusters of dye-modified TiO_2 nanoparticles and fullerene using two different types of dyes (porphyrin and fluorescein derivatives) [15]. Very recently a report appeared [13] on the preparation of counter electrodes for DSSCs using ITO conducting glass coated with fullerene or functionalized fullerene. Bustos et al. have prepared TiO_2 silanized electrodes and modified them further with one, two and three layers of fullerene [16].

As can be seen from the references, and to the best of our knowledge, no report has been made on the use of fullerene in a DSSC with a ruthenium dye as the sensitizer. In this paper we report the linking of N3 dye to C_{60} through diaminohydrocarbon linkers with different carbon chain lengths, subsequent anchoring of the resulting complexes (each designated as N3-L-C_{60}) to TiO_2 films and the performances of the pertinent DSSCs using such TiO_2 film electrodes.

2. Experimental

As it is not easy to dissolve N3 dye and C_{60} together in a common solvent [14], we used a diaminohydrocarbon linker to functionalize the fullerene first and then attached this composite to the dye. Six solutions of 0.2 mM C_{60} were prepared, each by dissolving 7.2 mg of C_{60} in 50 mL of toluene (1×10^{-5} mol). Each solution was reacted with 2 mL of a diaminohydrocarbon linker (3×10^{-2} mol in the case of 1,2-diaminoethane) at 110 °C for 3d to attach the linker to C_{60} [17]. The linkers were 1,2-diaminoethane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane, 1,10-diaminodecane, and 1,12-diaminododecane. The reaction product was filtered by using a membrane filter of pore size 0.2 μm, and thoroughly washed with toluene and anhydrous ethanol. The product was then dispersed in an anhydrous ethanol solution of 0.3 mM N3, and the mixture was sonicated for 5 min. The sonicated mixture was then kept at 70–80 °C for 3d to produce the complex of interest, N3-L-C_{60} (Fig. 1). The resulting complex was

Fig. 1. Chemical structure of the N3-L-C_{60} complex.

washed several times with anhydrous ethanol and characterized by energy dispersive X-ray (EDX), field emission-scanning electron micrograms (FE-SEM) and FT-IR spectroscopy. It was dispersed in anhydrous ethanol by sonication. A TiO_2 film of 15 μm thickness, which was prepared as described elsewhere [18], was then dipped into the solution containing N3-L-C_{60} and kept at room temperature for 3d. The substrate of the TiO_2 film electrode was an FTO glass, purchased from Libbey-Owens-Ford (TEC 8, 75% transmittance in the visible). Finally, the N3-L-C_{60} coated TiO_2 film (hereafter (N3-L-C_{60})/TiO_2) was dipped into a 0.3 mM N3 ethanol solution at room temperature for 24 h to coat the (N3-L-C_{60})/TiO_2 additionally with N3; this process also ensures the enhanced dye-coverage of TiO_2 sites that might not have been covered with the N3-L-C_{60} complex. The resulting TiO_2 film coated with both the complex N3-L-C_{60} and N3 (hereafter (N3,N3-L-C_{60})/TiO_2 film) was removed, washed thoroughly with anhydrous ethanol and used to fabricate a DSSC, according to the procedure given elsewhere [18]. It is to be mentioned here that N3-L-C_{60} could not be coated on an N3 pre-coated TiO_2 film.

Each DSSC had an active area of 0.4 cm × 0.4 cm, unless otherwise specified. The redox electrolyte consisted of 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethy-l,3-hexylimidazolium iodide and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile. A reference DSSC was prepared under identical conditions using only N3.

EDX spectra and FE-SEM were recorded with a Hitachi S-4300 microscope. FT-IR spectra were obtained using a Bowman, Harman & Braun MB series. An HP 8453A diode array spectrophotometer was used for estimating the amount of dye adsorbed on to a TiO_2 film. Photocurrent–voltage (*J–V*) curves were obtained using a Keithley M 236 source measure unit. A 300 W Xe arc lamp (Oriel), with an AM 1.5 solar simulating filter for spectral correction was used to illuminate the working electrode and its light intensity was adjusted to 100 mW/cm^2 using a Si solar cell.

3. Results and discussion

The complexes, N3-L-C_{60} (Fig. 1) were identified with FT-IR. The FT-IR spectra of C_{60}, N3, and N3-L-C_{60} are comparatively shown in Fig. 2 to illustrate the formation of the complex. The spectrum of N3-L-C_{60} shows the characteristic band due to the NCS group of N3 at 2101 cm^{-1}, the band due to C=O of the amide at 1610 cm^{-1} which is well distinguishable, owing to its high intensity, from the band at 1740 cm^{-1} due to C=O of the dye. The fundamental peaks of fullerene are discernible at 1419, 1301, 1182, 573 and 528 cm^{-1}, and they are slightly shifted to higher frequencies, relative to those peaks in the spectrum of C_{60}. The broad band near 3424 cm^{-1} of N3-L-C_{60} indicates the overlapping of OH of N3 with NH of amide groups. These results indicate the formation of the complex N3-L-C_{60}. An NH addition to C_{60} presumably occurs at one of the C=C bonds in C_{60} which fuses two six-membered rings; this is the proposed site of the reactivity for C_{60} with primary and secondary amines in solution [19].
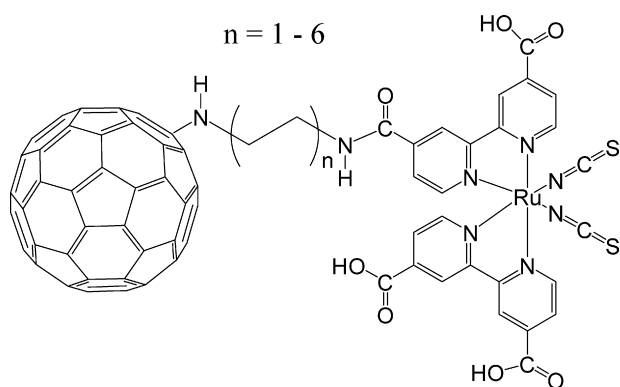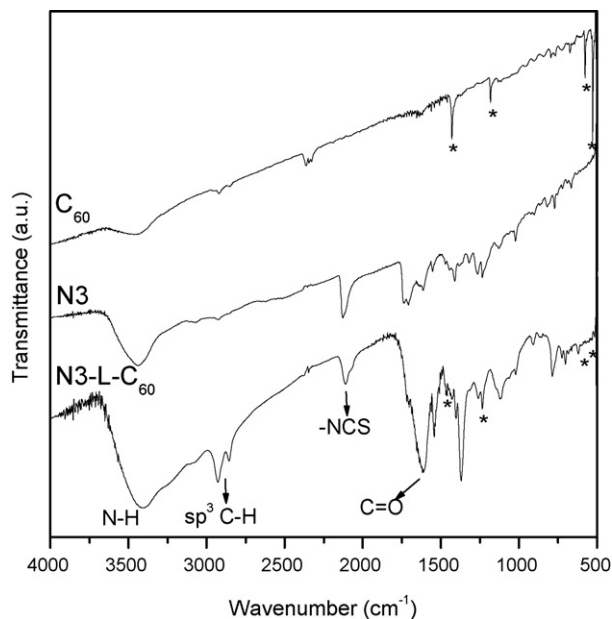
Fig. 2. FT-IR spectra of C_{60}, N3 dye and N3-L-C_{60}, where L is 1,6-diaminohexane. Peaks with asterisks are the fundamental peaks of C_{60}.
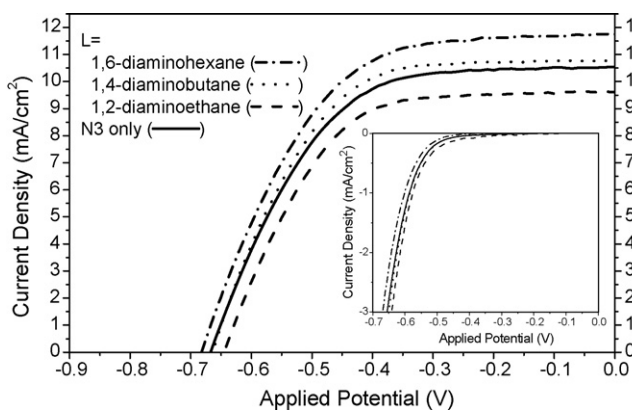

Fig. 3. J–V curves of DSSCs fabricated with (N3,N3-L-C_{60})/TiO$_2$ and N3/TiO$_2$ film electrodes with L being 1,2-diaminoethane, 1,4-diaminobutane and 1,6-diaminohexane. Inset shows the corresponding dark current–potential curves. Curves related to the other three linkers are omitted in the figure for clarity. Light intensity was 100 mW/cm^2.

Fig. 4. J_{sc}, V_{oc}, η and relative amount of total sensitizer (RTS) of DSSCs sensitized with both N3 and N3-L-C_{60}, each parameter as a function of number of carbon atoms in the linker. RTS is the relative amount of total sensitizer desorbed from the (N3,N3-L-C_{60})/TiO$_2$ film with respect to the amount of N3 desorbed from the N3/TiO$_2$ film, latter being taken arbitrarily as 100.

Fig. 3 shows the interesting influence of anchorage of both N3-L-C_{60} and N3 to TiO$_2$ films on the J–V curves of respective solar cells. The corresponding photovoltaic parameters are summarized in Table 1. Fig. 4 depicts the significance of the data of Table 1. Fig. 4 and Table 1 reveal that the short-circuit photocurrent density (J_{sc}) of the cell fabricated with the film electrode, (N3,N3-L-C_{60})/TiO$_2$ is the highest, being 11.75 mA/cm,^{2} when L = 1,6-diaminohexane, relative to the reference J_{sc} value of 10.55 mA/cm^2 of the cell with the N3/TiO$_2$ film electrode. The open-circuit voltages (V_{oc}s) show a trend, albeit small, of increase and decrease similar to the behavior of J_{sc}s, with respect to the V_{oc} and J_{sc} of the cell with 1,6-diaminohexane. The V_{oc} has increased by about 20 mV when L is 1,6-diaminohexane, relative to the V_{oc} value of the cell prepared with N3 only. Fill factors (FFs) of the cells with (N3,N3-L-C_{60})/TiO$_2$ film electrodes in general show an increasing tendency, regardless of the length of the linker, with respect to the FF value of the reference cell (Table 1). As a result of these changes, the solar-to-electricity conversion efficiency (η) has consistently increased with the increase of carbon chain length from 4.0% of the reference cell to 4.5% of the modified cell with N3-1,6-diaminohexane-C_{60}. This shows that the photovoltaic parameters of a DSSC can

Table 1

Photovoltaic parameters of DSSCs sensitized using both N3-L-C_{60} and N3[a,b]

L of N3-L-C_{60}	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	RTS[c]	N3-L-C_{60}[d] (%)
N3 only	10.55	0.68	0.56	4.0	100	0
1,2-Diaminoethane	9.61	0.66	0.58	3.7	95	19
1,4-Diaminobutane	10.77	0.68	0.58	4.2	110	42
1,6-Diaminohexane	11.75	0.70	0.55	4.5	130	47
1,8-Diaminooctane	10.46	0.65	0.59	4.0	99	56
1,10-Diaminodecane	10.91	0.67	0.58	4.3	101	46
1,12-Diaminododecane	9.87	0.65	0.59	3.8	106	16

[a] Electrolyte consisted of 0.05 M I$_2$, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-hexylimidazolium iodide and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile.

[b] Measured under illumination of AM 1.5 solar light (100 mW/cm^2).

[c] Relative amount of total sensitizer desorbed from the (N3,N3-L-C_{60})/TiO$_2$ film with respect to the amount of N3 desorbed from the N3/TiO$_2$ film, latter being taken arbitrarily as 100.

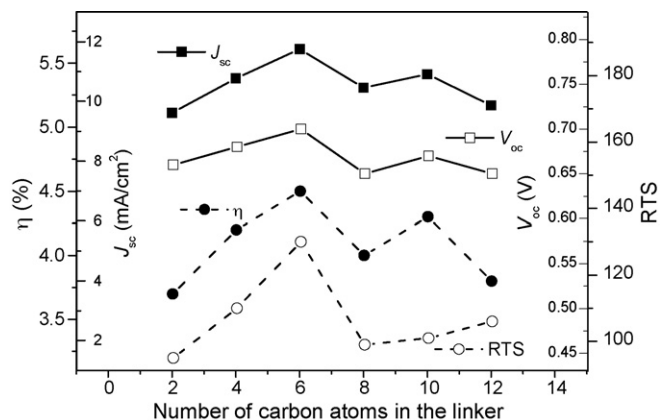[d] Percentage of N3-L-C_{60} in the total adsorbed sensitizer.

be influenced beneficially with the linking of fullerene to N3 through a diaminohydrocarbon linker, provided the linker has an appropriate chain length.

First, we explore reasons for the small V_{oc} change as a result of the fullerene linkage to N3 through diaminohydrocarbons. There are some possible causes that increase the V_{oc}. Firstly, the NH groups of diaminohydrocarbon moiety in an N3-L-C_{60} complex can take up protons released from N3 and present at the TiO_2/electrolyte interface, causing the flat band potential of the TiO_2 to shift negatively and thereby increasing the pertinent V_{oc}. The presence of N3-L-C_{60} complex on the TiO_2 surface can increase the basicity of the TiO_2 surface owing to the NH groups of diaminohydrocarbon moiety and retard the movement of triiodide ions into and out of the film. The increase in the surface basicity also leads to a negative shift of flat band potential of TiO_2, which in turn contributes for a V_{oc} increase. Secondly, C_{60}-linked diaminohydrocarbons can create a hydrophobic atmosphere around the TiO_2 particles. Our supposition of the hydrophobic atmosphere is based on the reports from Lagref et al. and Schmidt-Mende et al. that Ru(II) sensitizers, attached with long alkyl chains such as C_6H_{13} and $C_{13}H_{27}$ have shown large enhancements of V_{oc} relative to the V_{oc} obtainable with N3 [4,20] and that additional presence of an amide bond can induce self-organization of Ru(II) sensitizer on the surface of TiO_2 nanocrystals through hydrogen bond formation [4]. Each N3-L-C_{60} contains an amide bond and an alkyl chain bearing C_{60}. Furthermore, C_{60}^- can separate N3 and I_3^-/I^- redox couple, thereby minimizing their interaction [6]. The formation of the hydrophobic atmosphere around the TiO_2 particles and the separation of N3 from I_3^-/I^- redox couple reduce the rate of the back electron transfer from TiO_2 conduction band to I_3^- ions. This suppression of the I_3^- reduction by conduction band electrons should lead to an increase in V_{oc} based on the relationship [21]:

$$V_{oc} = \left(\frac{kT}{e} \right) \ln \left(\frac{I_{inj}}{n_{cb} k_{ct} [I_3^-]} \right),$$

where I_{inj} is the charge flux from sensitized injection, n_{cb} the surface electron concentration at the TiO_2 surface, and k_{ct} is the rate constant of the I_3^- reduction.

Contrary to the expectation, the above-mentioned causes for V_{oc} increase appear to have been largely offset by the adverse role of C_{60}, as can be seen from the fact that V_{oc} decreases in all the cases except those of the cells with 1,4-diaminobutane and 1,6-diaminohexane (Table 1). The V_{oc} values suggest the possibility of electron transfer from the conduction band of TiO_2 to C_{60}, which apparently dominates over the phenomena of the shift of flat band potential and the formation of hydrophobic atmosphere. This is explained schematically in Fig. 5. The figure shows that the conduction band edge of TiO_2 lies about 0.3 eV above the one-electron reduction potential of C_{60}, E (C_{60}/C_{60}^-), being -0.2 V versus NHE [8], which in turn exists above the redox potential of I_3^-/I^- at 0.5 V versus NHE. These energetics appear to be favorable for the transfer of electrons from the conduction band of TiO_2 to I_3^- ions through C_{60}, facilitating the back electron transfer and thereby decreasing the V_{oc}. Neverthe-
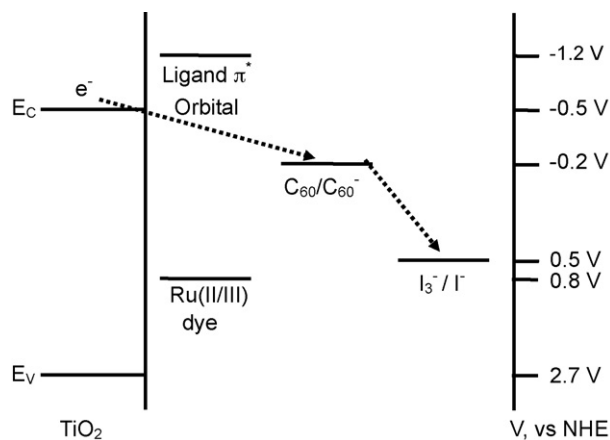

Fig. 5. Schematic representation of energy levels of TiO_2, sensitizer and C_{60}, showing possible electron transfer from the conduction band of TiO_2 to I_3^- ions through C_{60}.

less, it can be seen in Table 1 that the V_{oc}s decrease when the linker lengths become shorter or longer than the linker length of 1,6-diaminohexane. This behavior can be explained in terms of rate of the back electron transfer to I_3^- ions through C_{60}, depending on the linker length. As the linker length becomes shorter toward 1,2-diaminoethane, C_{60} can directly accept the conduction band electrons due to its proximity to TiO_2, increasing the back electron transfer. As the linker length becomes longer toward 1,12-diaminododecane, C_{60} can come again closer to TiO_2 particles as a result of the bending of the flexible longer alkyl chain, thereby making the conduction band electron transfer to C_{60} again feasible. In the case of linkers with intermediate chain lengths, e.g., 1,6-diaminohexane, the pertaining fullerenes stay far enough from the TiO_2 surfaces, minimizing the back electron transfer to I_3^- ions, as is rationalized by the highest V_{oc} value for the cell with 1,6-diaminohexane. In any case, the V_{oc} variation is in agreement with the dark current change, which is shown with the help of an inset in Fig. 3.

Next, the dependence of J_{sc} on the chain length of a diaminohydrocarbon linker may be correlated with the amount of total sensitizer adsorbed on the surface of the TiO_2 film, which was determined by absorption spectra for each TiO_2 film with a relatively large area of 1.0 cm $\times$ 1.0 cm. Fig. 6a and b quantitatively show the absorption spectra of sensitizers desorbed from (N3-L-C_{60})/TiO_2 and (N3,N3-L-C_{60})/TiO_2 films, respectively, into 0.1 M KOH. It was observed that the sensitizers on the TiO_2 films were completely desorbed into the KOH solutions. Fig. 6a indicates that the complexes adsorb to the TiO_2 films to different extents, with the amount of adsorption of any complex being less than that of N3. Furthermore, Fig. 6b, with reference to Fig. 6a, shows that the total amount of the sensitizers in each case exceeds that of the corresponding complex, indicating that the complexes remain adsorbed onto the respective films during the additional coating with N3. Fig. 6b, with reference to Fig. 6a, also clearly shows enhancement of dye-coverage on TiO_2 in each case of the complexes, owing to the additional coverage of dye from co-adsorbed N3 dye. It is known that even N3 molecules do not adsorb on all of the available sites of TiO_2, and N3-L-C60 complexes cannot be expected to do so, due to steric hindrance
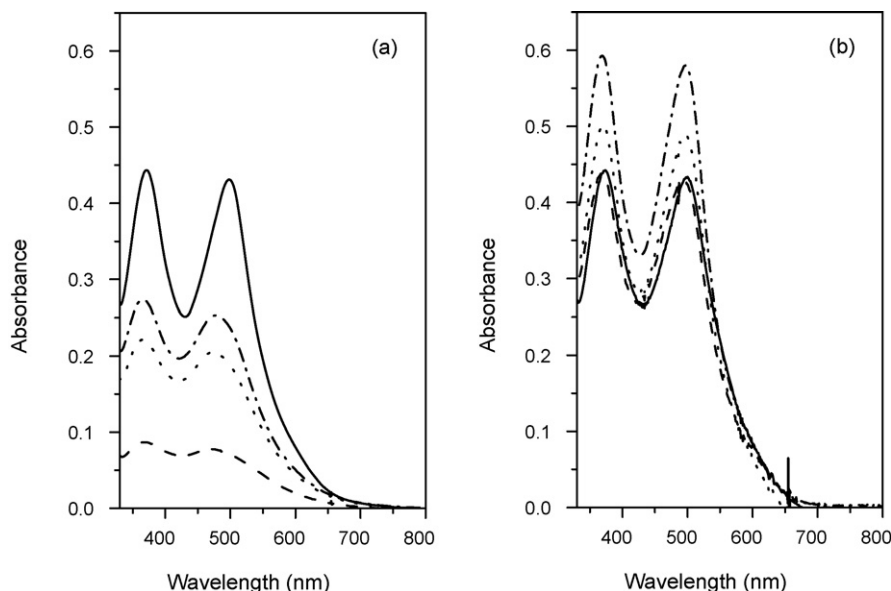
Fig. 6. Absorption spectra of sensitizers desorbed into 1 mM KOH from the films of (a) N3-L-C_{60}/TiO$_2$ and (b) (N3,N3-L-C_{60})/TiO$_2$, with L being 1,2-diaminoethane (dash), 1,4-diaminobutane (dot) and 1,6-diaminohexane (dash dot). The spectrum of N3 (solid line) from N3/TiO$_2$ film is included as a reference in both (a) and (b). Data for other linkers are omitted for clarity of the viewing.

from the diaminohydrocarbon chains. Additionally co-adsorbed N3 enhances the dye-coverage of TiO$_2$ sites that might not have been covered with the N3-L-C_{60} complex.

The amount of adsorbed N3 in each case of the complexes can be calculated from the respective difference in the absorbances of Fig. 6a and b, assuming that the molar absorptivities of the complexes at the respective maxima are the same as that of N3 and that the adsorbed complexes are not exchanged with the N3 molecules during the additional coating with N3. The latter assumption is based on the fact that the mode of adsorption of both N3 and N3-L-C_{60} on TiO$_2$ film is the same, because the adsorption involving the N3 sensitizer occurs through covalent bond formation between the COOH groups of the sensitizer and the hydroxyl groups of TiO$_2$. The absorption maxima of the complexes shift differently toward the blue compared to that of N3, possibly due to differences in the linkers [22]. Table 1 lists the calculated relative amounts of total sensitizers (RTS) desorbed from the (N3,N3-L-C_{60})/TiO$_2$ films, with respect to the amount of N3 desorbed from the N3/TiO$_2$ film, latter being taken arbitrarily as 100. From Table 1 and Fig. 4, it can be concluded that the J_{sc} values are well correlated with the RTS values (or the amounts of total dye adsorbed). In addition, it is interesting to find in Table 1 that in the case of 1,6-diaminohexane, the corresponding total dye adsorption exceeds that of N3 by 30%, but the corresponding J_{sc} enhancement is only 11%. This discrepancy may be attributed to the self-organization of N3 of the complex on the TiO$_2$ surface to produce needle-shaped structures as shown in Fig. 7. In the case of variation of molar absorption coefficients of N3 dye in its N3-L-C_{60} form, relative to those of its discrete form, its light harvesting efficiency (LHE) also varies and this can be another reason for this discrepancy, because J_{sc} depends strongly on the LHE of a dye.

Fig. 7 shows a top view FE-SEM image of N3-L-C_{60} coated TiO$_2$ film, with L being 1,6-diaminohexane. The figure shows

several needle-shaped structures. One such structure is shown as a magnified image. A comparison of the elemental compositions obtained by EDX with those obtained by calculation for N3 (Table 2) reveals that the needle-shaped structure is essentially the aggregate of N3-L-C_{60}. Similar needle-shaped structures were observed in the cases of 1,4-diaminobutane, 1,8-diaminooctane and 1,10-diaminodecane, but not in the cases of 1,2-diaminoethane and 1,12-diaminododecane (the two extremes in the sense of chain length). These FE-SEM and EDX results indicate that N3-L-C_{60} complexes in each case of 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,10-diaminodecane can strongly interact laterally with their neighboring N3-L-C_{60} complexes through hydrogen bonding between the amide bonds. The lateral interactions between the amide bonds near the respective TiO$_2$ surfaces apparently induce self-organization of the linked N3 molecules to result in needle-shaped aggregated structures. On the other hand, in the case
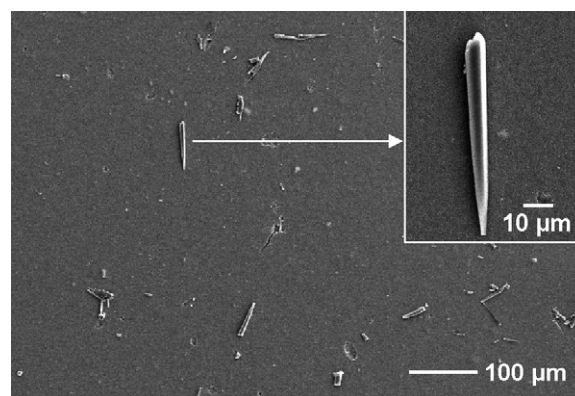

Fig. 7. Top view FE-SEM image of N3-L-C_{60} coated TiO$_2$ film with L being 1,6-diaminohexane. Inset shows the magnified image of a needle-shaped structure of the N3-L-C_{60} complex.

Table 2
Comparison of elemental compositions of the needle-shaped aggregate with those of N3

Element[a]	Composition in wt%	
	Observed by EDX[b]	Calculated for N3
Ru	14.6	14.3
S	8.2	9.1
O	16.0	18.2
C	41.2	44.2
N	20.0[c]	11.9

[a] Hydrogen is not included.
[b] Measured for the sample shown in Fig. 7.
[c] A large uncertainty is envisaged with the use of nitrogen gas in the EDX measurement.

of 1,2-diaminoethane linker, such self-organization is difficult due to its short length in the presence of relatively large N3 and C_{60} at its ends, and in the case of 1,12-diaminododecane it remains probably bent, owing to its long chain length which also makes the self-organization difficult. Some of the N3-L-C_{60} complexes in the self-organized aggregates are not expected to attach themselves to the TiO_2 particles through their N3 parts; this reduces the effective amount of the sensitizers in the film and thereby the J_{sc}. From this point of view, it can be said that such self-organization in general is detrimental to the photovoltaic performance of a DSSC.

Finally, the percentage of N3-L-C_{60} in the total adsorbed dye (Table 1) is analyzed as a function of the chain length of the linker. In the cases of linkers having intermediate chain lengths, i.e., from 1,4- to 1,10-diaminohydrocarbons, it can be noted from Table 1 that about one half of the total dye adsorbed to the TiO_2 film comes from N3-L-C_{60}. This observation suggests that N3-L-C_{60} adsorbs on only about half of the available sites on a TiO_2 film, owing to the steric hindrance from the long chains of the complexes, while the other half sites are covered by N3 from additional coating of TiO_2 by pure N3. On the other hand, in the cases of 1,2-diaminoethane and 1,12-diaminododecane, one-fifth or slightly less than one-sixth, respectively, of the total adsorbed dye comes from the respective N3-L-C_{60} complex. It is surprising to observe low adsorption of the complex of 1,2-diaminoethane. It is uncertain, but a multiple linkage of N3-L to C_{60}, such as (N3-L)$_2$-C_{60} appears to be possible, as the complex was synthesized with a reaction mixture with a large excess of 1,2-diaminoethane relative to C_{60}. The formation of bulky (N3-L)$_2$-C_{60} complex would reduce its adsorption capabilities on TiO_2. In the case of 1,12-diaminododecane, however, the adsorption of its complex is expected to be small due to the long hydrocarbon chain that can result in bending and/or entanglement of it.

We have not focused on the optimization of the cell for higher efficiency, in view of the nature of this fundamental study to understand the influence of fullerene attachment to N3 dye on the photovoltaic parameters of DSSCs and the related effects of various carbon chain lengths of diaminohydrocarbon linkers that connect N3 with fullerene. The performance of the cell with 1,6-diaminohexane could be improved by using additionally a

scattering layer of large TiO_2 particles of about 400 nm, treating the TiO_2 surface with $TiCl_4$ before it is coated with the dye, and by covering the cell surface with antireflection film.

4. Conclusions

A new synthetic route is developed to attach fullerene to the N3 dye through diaminohydrocarbons (L) of various chain lengths. FT-IR spectra have identified the complexes, N3-L-C_{60}, that consists of N3 and fullerene connected by various diamino-hydrocarbons. The (N3,N3-L-C_{60})/TiO_2 film electrodes when used in DSSCs have shown considerable influence on the photovoltaic parameters of the cells, depending on the carbon chain lengths of diaminohydrocarbon linkers. Linkage of fullerene to the N3 dye through 1,6-diaminohexane has rendered improved photovoltaic performance for the pertinent DSSC, mainly owing to the enhanced dye adsorption on to its TiO_2 film electrode. The adsorption of N3-L-C_{60} complex is found to depend on the chain length of the diaminohydrocarbon linker. A critical carbon chain length appears to be important for obtaining the optimum photovoltaic performance of a DSSC.

Acknowledgment

References

[1] E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, J.R. Durrant, J. Am. Chem. Soc. 125 (2003) 475–482.
[2] K. Tennkone, G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera, Chem. Commun. 1 (1999) 15–16.
[3] B.A. Gregg, F. Pichot, S. Ferrere, C.L. Fieldes, J. Phys. Chem. B 105 (2001) 1422–1429.
[4] J.-J. Lagref, M.K. Nazeeruddin, M. Grätzel, Synth. Met. 138 (2003) 333–339.
[5] S.-Y. Oh, S.-H. Han, Synth. Met. 121 (2001) 1369–1370.
[6] P.V. Kamat, M. Haria, S. Hotchandani, J. Phys. Chem. B 108 (2004) 5166–5170.
[7] P.W. Murray, J.K. Gimzewski, R.R. Schlittler, G. Thornton, Surf. Sci. 367 (1996) L79–L84.
[8] P.V. Kamat, I. Bedja, S. Hotchandani, J. Phys. Chem. 98 (1994) 9137–9142.
[9] G. Yu, J. Gao, J.C. Hummelen, F. Wudi, A.J. Heeger, Science 270 (1995) 1789–1791.
[10] C.J. Brabec, H. Johannson, F. Padinger, H. Neugebauer, J.C. Hummelen, N.S. Sariciftci, Sol. Energy Mater. Sol. Cells 61 (2000) 19–33.
[11] A. Fujii, A.A. Zakhidov, V.V. Borovkov, Y. Ohmori, K. Yoshino, Jpn. J. Appl. Phys. 35 (1996) L1438–L1441.
[12] Y.J. Ahn, G.W. Kang, C.H. Lee, I.S. Yeom, S.H. Jin, Synth. Met. 137 (2003) 1447–1448.
[13] T. Hino, Y. Ogawa, N. Kuramoto, Carbon 44 (2006) 880–887.
[14] M. Maggini, A. Dono, G. Scorrano, M. Prato, J. Chem. Soc., Chem. Commun. 8 (1995) 845–846.
[15] T. Hasobe, S. Hattori, P.V. Kamat, Y. Urano, N. Umezawa, T. Nagano, S. Fukuzumi, Chem. Phys. 319 (2005) 243–252.
[16] E. Bustos, J. Manríquez, L. Echegoyen, L.A. Godínez, Chem. Commun. 12 (2005) 1613–1615.
[17] K. Chen, W.B. Caldwell, C.A. Mirkin, J. Am. Chem. Soc. 115 (1993) 1193–1194.

[18] N.-G. Park, S.-H. Chang, J. van de Lagemaat, K.-J. Kim, A.J. Frank, Bull. Korean Chem. Soc. 21 (2000) 985–988.

[19] A. Hirsh, Q. Li, F. Wudl, Angew. Chem. Int. Ed. Engl. 30 (1991) 1309–1310.

[20] L. Schmidt-Mende, J.E. Kroeze, J.R. Durrant, M.K. Nazeeruddin, M. Grätzel, Nano Lett. 5 (2005) 1315–1320.

[21] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382–6390.

[22] C.G. Garcia, N.Y. Murakami Iha, R. Argazzi, C.A. Bignozzi, J. Photochem. Photobiol. A: Chem. 115 (1998) 239–242.