Electronic Supplementary Material

Barrier effect of dendrons on TiO_2 particles in dye sensitized solar cells

Bongha Shin[a], Jongok Won[a*], Taewook Son[b] , Yong Soo Kang[b] and Chan Kyung Kim[c]
[a,] *Department of Chemistry, Sejong University, 98 Gunja, Gwangjin, Seoul, 143-747,Korea*
[b,]*Department of Energy Engineering, Hanyang University, 1 Haengdang, Seongdong, Seoul,133-791, Korea*
[c,] *Department of Chemistry, Inha University, Yonghyun, Nam, Incheon 402-751, Korea*

Cell fabrication and characterization

A photoelectrode was fabricated by spin-coating Ti(IV) bis(ethyl acetoacetato)-diisopropoxide solution (2 wt.% in n-butanol) onto to the conductive fluorine-doped tin oxide (FTO) glass (TEC8, 8Ω/□, Pilkington), followed by heating at 450 °C for 30 min. The TiO_2 layer of 12 μm thickness was then deposited over the FTO glass by a doctor blade and successive sintering at 450 °C for 30 min using TiO_2 paste (13 nm, Ti-Nanoxide D/SP Solaronix). The thin film of TiO_2 was dipped in a 0.3 mM N719 dye (Solaronix) solution (1:1 acetonitrile and *tert*-butanol) for 18 hours at 30 °C. The residual dye solution was rinsed with acetonitrile and dried with N_2 gas. Then, an appropriate amount of dendron solution (Aldrich) was dropped onto the top of the dye-dipped cell and dried at room temperature for one day. The Pt counter electrodes were prepared by spin coating a H_2PtCl_6 solution (0.01 M in isopropanol) onto the conductive FTO glass and successive sintering at 450 °C for 30 min. Liquid electrolyte solution was prepared with 1-methyl-3-propyl imidazolium iodide (PMII) and I_2 (0.6 M:0.025 M) in acetonitrile. For assembling cells, two electrodes were sealed together by surlyn (SX1170-25, thickness of 25 μm, Solaronix) heated in a press at 90 °C. The active area of DSSC was 0.16 cm^2. The photovoltaic parameters were measured using a 300 W xenon light source to give an irradiance of 100 mW cm^{-2} (the equivalent of one sun at AM 1.5) using a mask with an aperture area of 0.25 cm^2. IPCEs (PV Measurement Inc.) were measured using a halogen source for monochromatic light and a broadband bias light for approximating 1 sun light intensity. The work function of the film is measured by a photon electron spectrometer (AC-2, Riken Keiki Co., Ltd)

Fig. S1

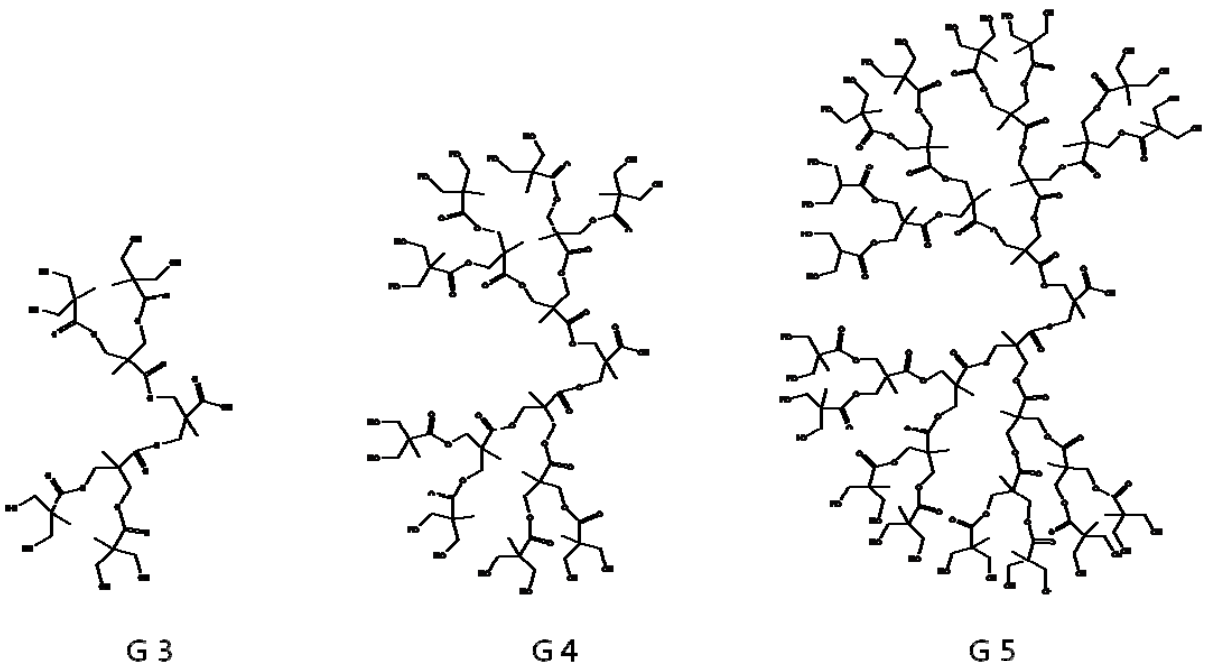


Fig. S1 Chemical structure of generation 3-5 polyester hydroxyl acetylene bis(hydroxymethyl) propanoic acid dendrons.

Fig. S2

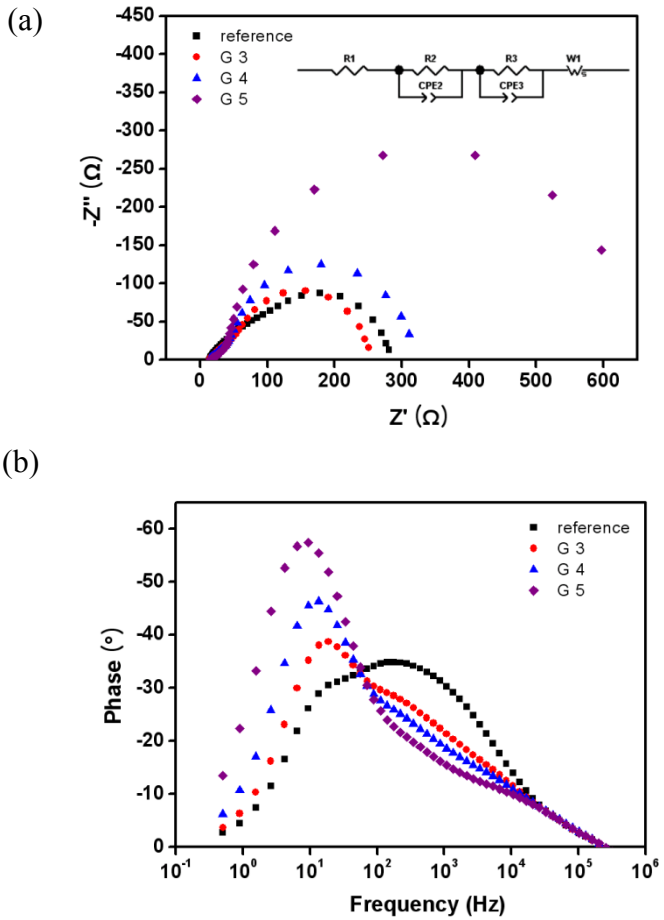


Fig. S2 Electrochemical impedance spectra of DSSCs based on different generations of dendrons measured at an external potential of V_{oc} in the dark; (a) Nyquist plot and (b) Bode plot. The equivalent circuit of this study is shown in the insert.

Fig. S3

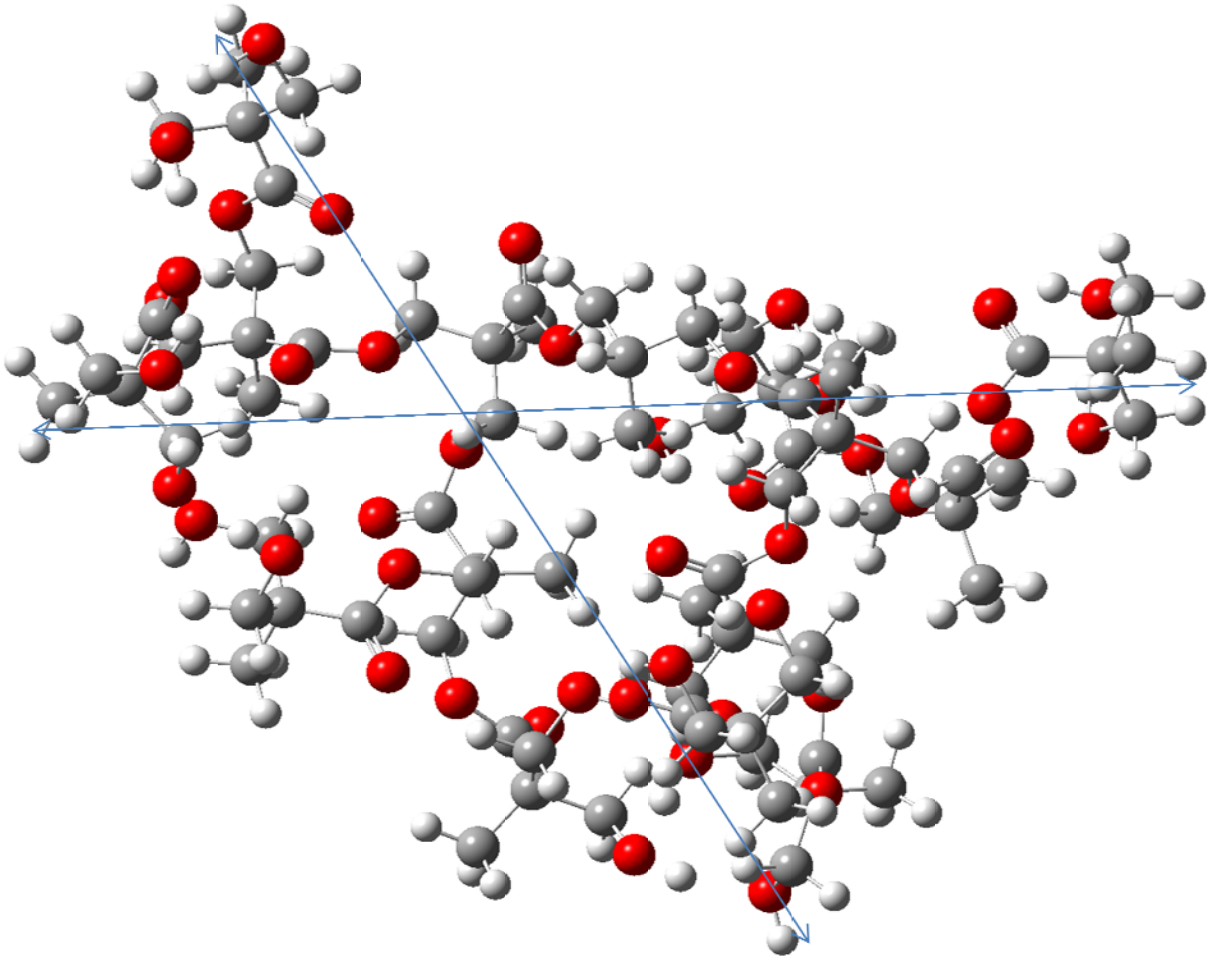


Fig. S3 Energy-optimised structure of G4 dendron optimised by Gaussian 03 program, using using density functional theory of the B3LYP hybrid exchange functional with a 3-21G basis set.

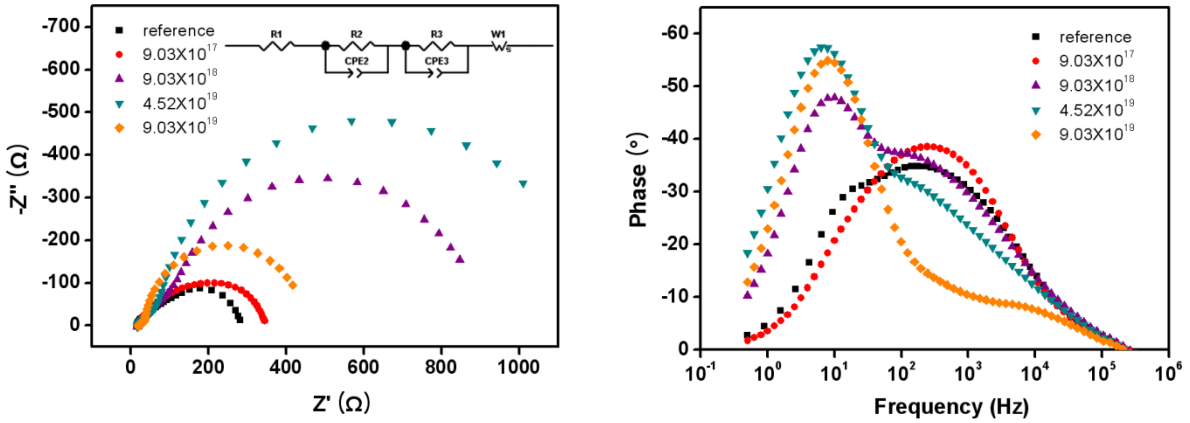
The surface coverage of the TiO_2 particle was roughly estimated under the homogeneous adsorption of dendrons in TiO_2 without sensitizers. The coverage of dendron was estimated under the assumption that at least half of the hemispherical dendron adsorbed on the surface of TiO_2 particle. Although the actual coverage value of a TiO_2 nanoparticle could not be determined exactly due to the rough estimation of the size of the dendron and the ignorance of the presence of the sensitisers, it is clear that the cell efficiency increased with an increase in the surface coverage and reached the maximum value when the surface of the TiO_2 particles were covered completely enough.

Fig. S4

Analysing EIS measured in the dark with an appropriate equivalent circuit model yields parameters of charge-transfer resistance R_2 corresponding to the recombination current across the TiO_2/electrolyte interface. The results are shown in Fig. S4 in the form of (a) Nyquist plots and (b) Bode plots.

In the dark, electrons are transported through the mesoporous TiO_2 network and react with I_3^-. At the same time, I^- is oxidised to I_3^- at the counter electrode. The impedance due to the electron transfer from the conduction band of the mesoscopic film to I_3^- ions in the electrolyte presented by the semi-circle in an intermediate frequency regime. The parameters analysed EIS measurement with an equivalent circuit model are summarised in Table 2. In figure S4 (a), the values of R_2 for the reference increased with the addition of G5 dendrons and continued to increase, and then the values decreased. The significantly high R_2 values suggest that charge recombination between the injected electrons and electron accepters in the redox electrolyte, I_3^-, was remarkably retarded.

The characteristic frequency peak obtained from the Bode phase plots shifted to a lower frequency when the amount of dendrons increased, implying that the electron lifetime in the TiO_2 film increased with the effective barrier amount of the dendrons. That is, the large amount of dendrons may effectively cover the barrier layer that blocks the recapture of the photo-injected electrons by the I_3^-, resulting in a higher open-circuit voltage and higher short circuit current.



(a) (b)

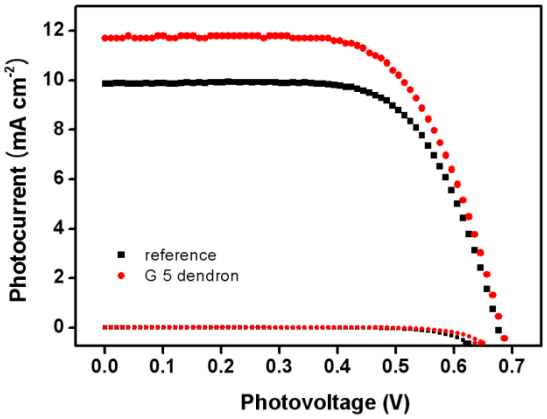
Fig. S4 Electrochemical impedance spectra of DSSCs based on different amounts of G5 dendrons measured at an external potential of V_{oc} in the dark; (a) Nyquist plot and (b) Bode plot. The equivalent circuit of this study is shown in the insert.

Table S1. The barrier effect of dendrons in different electrolyte matrices based on PEGDME.

Electrolyte matrix	co-adsorbent	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
PEGDME	none	9.85	0.68	66.95	4.46
	G5 dendron	11.72	0.68	64.70	5.17
PEGDME/fumed silica	none	10.20	0.68	69.03	4.77
	G5 dendron	11.34	0.68	67.90	5.26

The mole number of dendrons was fixed at 9.03×10^{18} mole g^{-1} (TiO_2).

(a)



(b)

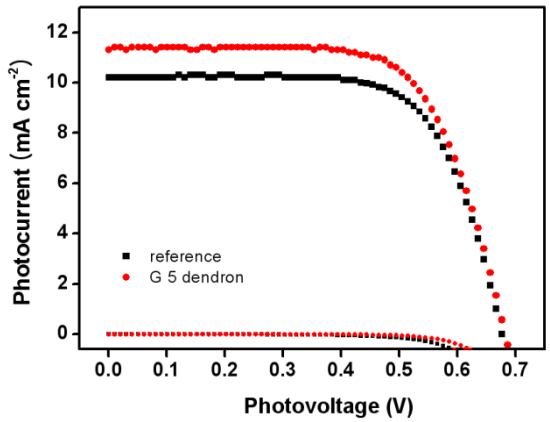


Fig. S5 Photocurrent density-potential characteristics of DSSCs employing (a) PEGDME (M_w = 500 $gmol^{-1}$, Aldrich) and (b) PEGDME/fumed silica (14 nm, Sigma) with and without G5 dendron co-adsorbent under simulated illumination. The mole number of dendrons was fixed at $9.03x10^{18}$ mole/g of TiO_2. The redox electrolyte comprised PEGDME, PMII and I_2. The mole ratio of oxygen atoms in the oligomer to iodide was fixed at 10:1 (PMII/I_2=10:1 w/w)[17]. The content of the silica nanoparticles was fixed at 9wt % of the total polymer electrolyte.