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Remarkable Improvement in Sensitizing Property of Tetraphenylporphyrincarboxylic Acids as Sensitizers for Dye-sensitized Solar Cells by the Introduction of Trimethylsilyl Groups as Substituents

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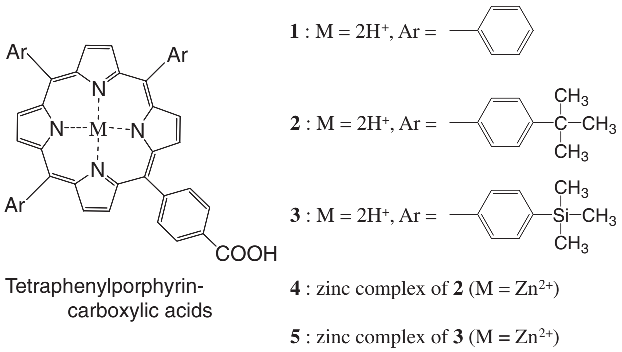
The effects of the introduction of alkylsilyl groups to porphyrin dyes on their sensitizing property in dye-sensitized solar cells were investigated by using a newly synthesized tetraphenylporphyrincarboxylic acid containing trimethylsilyl groups. The cell with the porphyrin showed higher photovoltaic performance than that with a *tert*-butyl-containing analog, and the zinc complex of the porphyrin exhibited remarkably high sensitizing performance comparable to N3 dye.

A dye-sensitized solar cell (DSSC) is a promising device as a practical solar cell of the next generation because of its high possibility for lowering energy costs, and the research and development task is now energetically pushed forward.[1] However, the light-to-electric energy conversion efficiencies of DSSCs have been limited to 11%,[2] and there is still room for a substantial improvement especially in the sensitizing dyes.[3] Porphyrins which are well-known light-harvesting moieties show strong absorptions with $\varepsilon > 10^4$ in the visible light region due to the conjugated macrocycle,[4] and can be controlled in oxidation and reduction potentials by changing central metal ions.[5] Therefore, porphyrincarboxylic acids have been actively studied as sensitizing dyes for DSSCs.[6] In the examination of porphyrincarboxylic acids as sensitizing dyes, the introduction of alkyl substituents such as *tert*-butyl (*t*-Bu) and methyl groups to the porphyrins has been performed to suppress intermolecular interaction producing rapid thermal relaxation of the light-excited porphyrin molecules and to increase the solubility of the porphyrins in the solvents used in their adsorption on TiO_2 electrodes.

Alkylsilyl groups are bulkier substituents than the corresponding alkyl groups and possess higher electron-donating properties resulting from the characteristics of Si.[7] By introducing alkylsilyl substituents to the porphyrins, therefore, the sensitizing ability of the porphyrins is expected to be improved and the DSSCs using them will show higher performance in light-to-electric energy conversion. However, porphyrins containing alkylsilyl substituents have never been examined as sensitizing dyes for DSSCs. In this work, we synthesized a derivative of tetraphenylporphyrincarboxylic acid possessing trimethylsilyl (TMS) groups as substituents in order to investigate the effects of the introduction of alkylsilyl groups to the sensitizing properties of the porphyrin. The TMS-containing porphyrin showed higher performance than the *t*-Bu-containing analog, and the zinc complex of the porphyrin exhibited remarkably high sensitization.



Scheme 1. Molecular structures of tetraphenylporphyrincarboxylic acids **1**–**5** used in this work as sensitizing dyes.

Tetraphenylporphyrincarboxylic acid (**1**), tetraphenylporphyrincarboxylic acid containing *t*-Bu groups (**2**), and tetraphenylporphyrincarboxylic acid containing TMS groups (**3**) (Scheme 1) were synthesized by the reaction of pyrrole with terephthalaldehydic acid and benzaldehyde, 4-*tert*-butylbenzaldehyde and 4-trimethylsilylbenzaldehyde, respectively. The zinc complexes of **2** and **3**, which correspond to **4** and **5** respectively, were obtained by the reactions of **2** and **3** with zinc acetate. The N3 dye of *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II), which was used as a reference sensitizing dye in this work, was purchased from SOLARONIX. The nanocrystalline TiO_2 film electrodes were prepared as reported previously.[8] The thickness of the porous TiO_2 film was estimated to be ca. 1.0 µm by SEM observation. Adsorptions of the porphyrin dyes and the N3 dye on the TiO_2 electrodes were performed by immersing the electrodes in 3.0×10^{-4} M toluene solutions of **1**–**5** at 95 °C for 15 h and an ethanol solution of N3 dye at 70 °C for 15 h, respectively. Photovoltaic measurements were carried out for electrochemical cells of an open sandwich type with an aperture area of 1.0 cm^2. The structure of the cell, the equipment for the measurements, and the measurement conditions were the same as reported in our previous paper.[9]

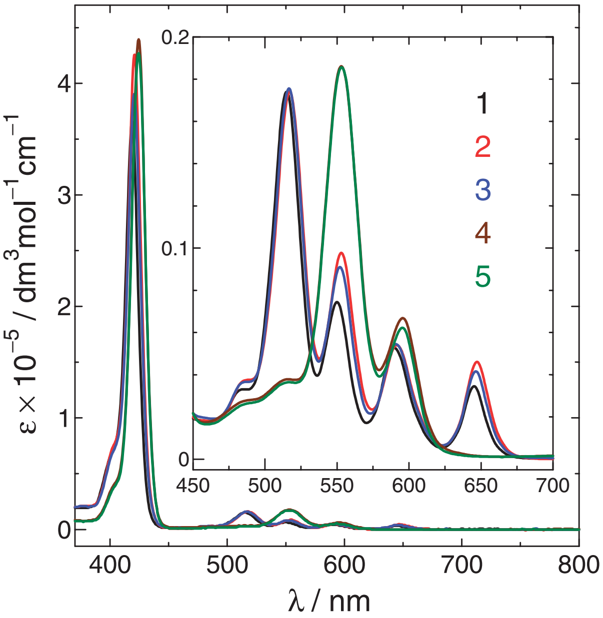


Figure 1. UV–visible absorption spectra of **1**–**5** in chloroform solutions. Inset shows the enlarged spectra in the Q-band region.

Figure 1 shows the UV–visible absorption spectra of **1**–**5** in chloroform solutions. The spectra of **1**–**5** exhibited a series of absorption bands due to the π–π^* transition in the conjugated macrocycle between 380 and 680 nm: The absorption at around 420 nm is assignable to the Soret band and that from 460 to 680 nm to the Q-bands.[4] The *t*-Bu-containing dye **2** and the TMS-containing dye **3** showed spectra similar to that of tetraphenylporphyrincarboxylic acid (**1**) and the difference of the maximum molar absorption coefficients in the Q-band did not exceed 1% of the magnitude among them, while in the zinc complexes **4** and **5** a red shift of the absorption maximum in the Q-band by 36 nm and a slight increase of the maximum molar absorption coefficient by 6% were observed.

Figure 2 shows the absorption spectra in the visible region of **1**–**5** adsorbed on the TiO_2 electrodes which were used in the cells for photovoltaic measurements. The spectra were obtained by subtracting the absorption due to the TiO_2 electrode from those of dye-adsorbed TiO_2 electrodes. Since the molar absorption coefficients of **1**–**3** at around 515 nm are similar to each other as shown in Figure 1, the maximum absorbances observed here are considered to be an index of the amount of dye molecules adsorbed on the electrodes. The amounts were estimated thus to be 0.95 for **2** and 0.86 for **3** in comparison with the case of **1** in the order of **1** > **2** > **3**. This result shows that the adsorption of the porphyrin dyes on the TiO_2 electrodes would be slightly hindered sterically by the bulkiness of the substituents (TMS > *t*-Bu > H). The amounts of **4** and **5** adsorbed on the TiO_2 electrodes were also estimated from the maximum absorbances and confirmed to be almost the same as **2** and **3**, respectively.

In order to compare the sensitizing properties between the porphyrin dyes containing TMS groups and *t*-Bu groups, we measured *I*–*V* properties of the cells using **1**–**3** as sensitizing dyes under simulated sunlight irradiation (AM-1.5G, 100 mW cm^{-2}). The results of the *I*–*V* measurements are shown in Figure 3, and characteristic parameters are listed in Table 1. The cell with *t*-Bu-containing dye **2** exhibited higher short-circuit photocurrent density (J_{sc}) and higher open-circuit photovoltage (V_{oc}) than the cell with **1**, showing higher photocurrent density in the measured photovoltage region. The enhancements of photocurrent density and photovoltage were more significant in the cell with TMS-containing dye **3**. Although the amount of dye molecules of **3** adsorbed on the TiO_2 electrode was smaller than in the cases of **1** and **2** as mentioned above, the cell with **3**

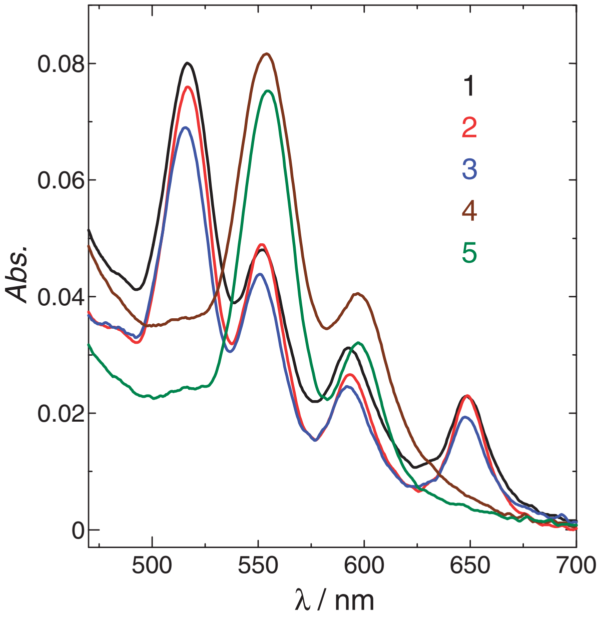


Figure 2. Absorption spectra in the visible region of **1**–**5** adsorbed on the TiO_2 electrodes.

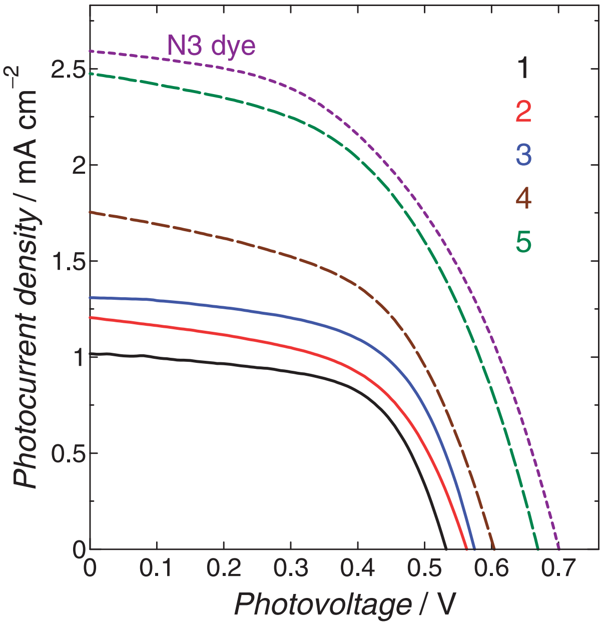


Figure 3. *I*–*V* properties of the cells using **1**–**5** and N3 dye as sensitizing dyes under simulated sunlight irradiation of AM-1.5G with the intensity of 100 mW cm^{-2}.

Table 1. Photovoltaic performances of cells with an aperture area of 1.0 cm^2 using **1**–**5** and N3 dye as sensitizing dyes under simulated sunlight irradiation (AM-1.5G, 100 mW cm^{-2}): short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (*FF*), and conversion efficiency (η)

Dyes	J_{sc}/mA cm^{-2}	V_{oc}/V	*FF*	η/%
1	1.02	0.53	0.61	0.33
2	1.21	0.56	0.54	0.37
3	1.32	0.57	0.59	0.44
4	1.76	0.60	0.52	0.55
5	2.47	0.67	0.50	0.83
N3	2.59	0.70	0.49	0.89

showed a higher light-to-electric energy conversion efficiency (η) than the cells with **1** and **2** by factors of 1.3 and 1.2, respectively, under the present test conditions.

These results exhibit clearly that the introduction of TMS groups to tetraphenylporphyrincarboxylic acid is more effective in the improvement of the sensitizing ability than that of *t*-Bu groups. The improvement is thought to be due to the bulkiness of TMS group which prevents the quenching of light-excited porphyrin molecules resulting from intermolecular interaction, and also due to electron donation producing the increment of electron-injection efficiency from the light-excited porphyrin molecule to the TiO_2 electrode.

The *I*–*V* properties of the cells with **4** and **5**, which are the zinc complexes of the *t*-Bu-containing and TMS-containing porphyrins **2** and **3** respectively, were also examined in this study. The results of the *I*–*V* measurements are shown in Figure 3 along with that for the cell using N3 dye, and characteristic parameters are listed in Table 1. The cells with **4** and **5** showed higher photovoltaic performances than those with **2** and **3**, and the remarkable performance of the cell with **5** was close to that with N3 dye which is known as one of the most effective sensitizers for DSSCs. Such a high sensitizing ability of **5** is thought to originate in the higher energy level of the LUMO of **5** than that of **3**,[5] and also in the bulkiness and the electron-donating property of TMS group, which would bring higher efficiency in the electron-injection from the light-excited dye to the TiO_2 electrode in the cell.

In this study, we examined for the first time the applicability of dyes containing alkylsilyl groups as sensitizers for DSSCs, and successfully revealed the effectiveness of the introduction of TMS groups to the tetraphenylporphyrincarboxylic acid for improving the photosensitizing ability. The results indicate that such an improvement is also possible for sensitizing dyes possessing π-electron systems by introducing alkylsilyl substituents, and show the high potential of organosilicon compounds as sensitizing dyes for DSSCs.

References

1 B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737; M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382; M. Grätzel, *Chem. Lett.* **2005**, *34*, 8; T. Miyasaka, N. Ikeda, T. N. Murakami, K. Teshima, *Chem. Lett.* **2007**, *36*, 480; A. Mishra, M. K. R. Fischer, P. Bäuerle, *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.

2 M. Grätzel, *J. Photochem. Photobiol., A* **2004**, *164*, 3; M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 16835; Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Han, *Jpn. J. Appl. Phys.* **2006**, *45*, L638; F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2008**, *130*, 10720; M. Grätzel, *Acc. Chem. Res.* **2009**, *42*, 1788.

3 M. Grätzel, J. R. Durrant, in *Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion*, ed. by M. D. Archer, A. J. Nozik, Imperial College Press, London, **2008**, Chap. 8, pp. 503–536; M. K. Nazeeruddin, M. Grätzel, *Struct. Bond.* **2007**, *123*, 113; S. Mori, S. Yanagida, in *Nanostructured Materials for Solar Energy Conversion*, ed. by T. Soga, Elsevier, Amsterdam, **2006**, Chap. 7, pp. 193–225; K. Hara, H. Arakawa, in *Handbook of Photovoltaic Science and Engineering*, ed. by A. Luque, S. Hegedus, John Wiley & Sons, Chichester, **2003**, Chap. 15, pp. 663–700; M. Grätzel, *J. Photochem. Photobiol., C* **2003**, *4*, 145.

4 M. Gouterman, *J. Mol. Spectrosc.* **1961**, *6*, 138; M. Gouterman, G. H. Wagnière, L. C. Snyder, *J. Mol. Spectrosc.* **1963**, *11*, 108; *The Porphyrins*, ed. by D. Dolphin, Academic Press, New York, **1978**; H. Horiuchi, T. Tanaka, K. Yoshimura, K. Sato, S. Kyushin, H. Matsumoto, H. Hiratsuka, *Chem. Lett.* **2006**, *35*, 662; S. Kyushin, K. Yoshimura, K. Sato, H. Matsumoto, *Chem. Lett.* **2009**, *38*, 324.

5 *The Porphyrin Handbook*, ed. by K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego, **2000**; F. J. Kampas, K. Yamashita, J. Fajer, *Nature* **1980**, *284*, 40; K. Takahashi, M. Asano, K. Imoto, T. Yamaguchi, T. Komura, J. Nakamura, K. Murata, *J. Phys. Chem. B* **2003**, *107*, 1646; M. Gervaldo, F. Fungo, E. N. Durantini, J. J. Silber, L. Sereno, L. Otero, *J. Phys. Chem. B* **2005**, *109*, 20953.

6 W. M. Campbell, A. K. Burrell, D. L. Officer, K. W. Jolley, *Coord. Chem. Rev.* **2004**, *248*, 1363; M. K. Nazeeruddin, R. Humphry-Baker, D. L. Officer, W. M. Campbell, A. K. Burrell, M. Grätzel, *Langmuir* **2004**, *20*, 6514; W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, M. K. Nazeeruddin, Q. Wang, M. Grätzel, D. L. Officer, *J. Phys. Chem. C* **2007**, *111*, 11760; A. J. Mozer, P. Wagner, D. L. Officer, G. G. Wallace, W. M. Campbell, M. Miyashita, K. Sunahara, S. Mori, *Chem. Commun.* **2008**, 4741; *Data Book on Dye-Sensitized Solar Cells*, ed. by T. Horiuchi, J. Fujisawa, S. Uchida, M. Grätzel, CMC Publishing, Tokyo, **2009**; J. T. Dy, K. Tamaki, Y. Sanehira, J. Nakazaki, S. Uchida, T. Kubo, H. Segawa, *Electrochemistry* **2009**, *77*, 206; H. Imahori, T. Umeyama, S. Ito, *Acc. Chem. Res.* **2009**, *42*, 1809.

7 *Organosilicon Chemistry I-VI: From Molecules to Materials*, ed. by N. Auner, J. Weis, Wiley-VCH, Weinheim, **1993–2005**; *The Chemistry of Organic Silicon Compounds*, ed. by S. Patai, Z. Rappoport, Y. Apeloig, John Wiley & Sons, Chichester, **1989–2001**, Vol. 1–3; S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka, H. Matsumoto, *Organometallics* **1996**, *15*, 1067.

8 K. Kakiage, Y. Nakada, T. Kogure, M. Yamamura, T. Kyomen, M. Unno, M. Hanaya, *Silicon Chem.* **2008**, *3*, 303.

9 K. Kakiage, M. Yamamura, E. Fujimura, T. Kyomen, M. Unno, M. Hanaya, *Chem. Lett.* **2010**, *39*, 260; M. Unno, K. Kakiage, M. Yamamura, T. Kogure, T. Kyomen, M. Hanaya, *Appl. Organomet. Chem.* **2010**, *24*, 247.