



Synthesis of pentamethyldisilanyl-substituted starlike molecule with triazine core and its application to dye-sensitized solar cells



Akinobu Naka^{a,*}, Kiyoshi Fujishima^a, Erika Okada^a, Mao Noguchi^a, Joji Ohshita^b, Yohei Adachi^b, Yousuke Ooyama^b, Mitsuo Ishikawa^a

^a Department of Life Science, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan

^b Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:

Received 23 July 2016

Received in revised form

24 September 2016

Accepted 15 October 2016

Available online 15 October 2016

Keywords:

Starlike molecule

Triazine

Pentamethyldisilanyl

UV absorption

Photoluminescence

Dye-sensitized solar cell

ABSTRACT

Two-dimensional starlike molecule **7** consisting of benzothiadiazole-thiophenylphenyltriazine groups and pentamethyldisilanyl substituted thienylene units that extend to three directions was synthesized by the reactions of 2,4,6-tris[4-(4-hexyl-5-(7-(3-hexyl-5-iodothiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl]-1,3,5-triazine (**5**) with the pentamethyldisilanylthienyl substituted stannyl derivative (**6**). UV-visible absorption and fluorescence properties of starlike molecules **4** and **7** have been investigated in dioxane and in the solid state. The application of TiO₂-electrode coated on the surface with the use of **7** to dye-sensitized solar cells has been discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Three-dimensional organosilicon dendrimers containing π -conjugated units have attracted a great deal of attention to their potential application in organic photo- and electroluminescent materials [1–13]. We have reported synthesis and optical properties of various types of three-dimensional starlike silicon compounds [14,15], and also two-dimensional ones, whose arms extended to three or four directions [16,17] (see Chart 1). They show interesting properties, depending on their unique molecular structure, and may be used as functionality materials. For example, the compounds bearing the arms consisting of a regular alternating arrangement of a silicon-silicon bond and bithienylene unit, which extend to three directions reveal high fluorescence quantum yields and long lifetimes of the excited state [15–17].

Recently, a considerable attention has been focused on low-band gap materials as active layer in photovoltaic cells for light absorption [18,19]. The alternating arrangements of electron-donating and electron-accepting moieties in the materials give

rise to mutual interaction between HOMO of the donor and LUMO of the acceptor, and reduction of the band gap in these systems. Recently, Ohshita et al. prepared disilanylene polymers with conjugated donor–acceptor systems and used them as sensitizing dyes [20–24]. In this paper we report synthesis of a new donor-acceptor type of the disilanyl substituted starlike molecule bearing a triazine core, and its application to dye-sensitized solar cells (DSSCs).

2. Results and discussion

The synthesis of the arms having benzothiadiazole and pentamethyldisilanyl substituted thienylene units were carried out as shown in Schemes 1–3. Treatment of the lithio derivative prepared by the reaction of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (**1**) and *n*-butyllithium, with 2-isopropyl-4,4,5,5-tetramethyl-1,3-dioxaborolane afforded compound **2** in 18% yield (Scheme 1) [25].

Suzuki-Miyaura cross coupling reaction of **2** with 4-(5-bromo-3-hexylthiophen-2-yl)-7-(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol (**3**) in THF afforded 2,4,6-tris(4-(4-hexyl-5-(7-(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl)-1,3,5-triazine (**4**) in 24% yield.

Compound **5** was prepared by treating **4** with 3 equiv. of *N*-iodosuccinimide (NIS) in chloroform in 47% yield. The starlike

* Corresponding author.

E-mail address: anaka@chem.kusa.ac.jp (A. Naka).

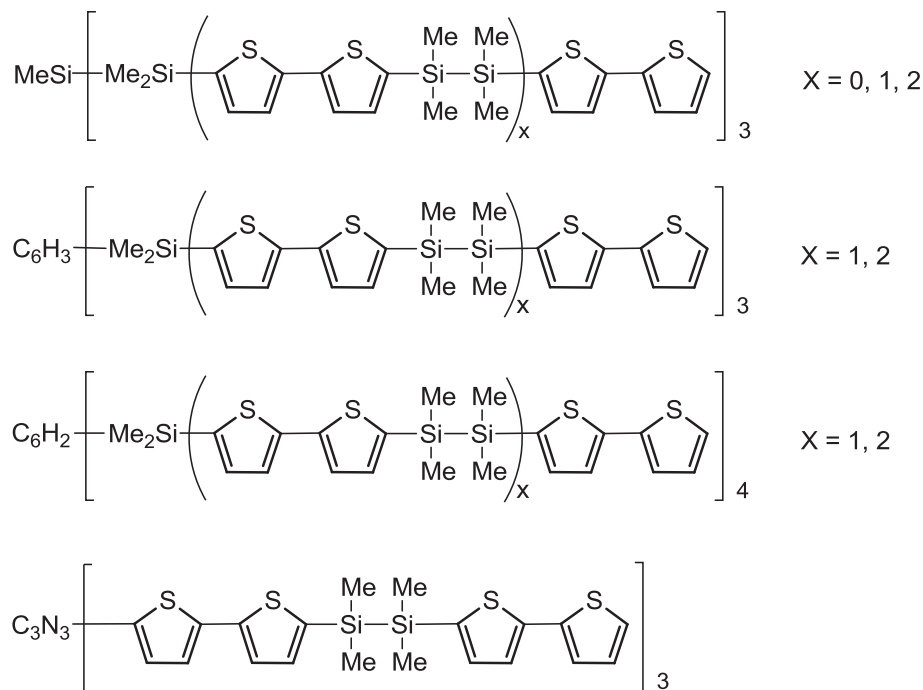
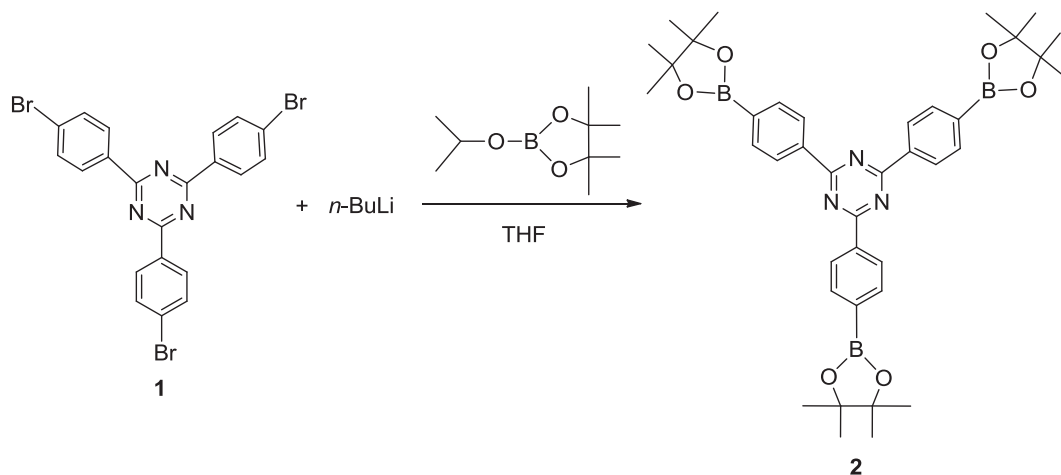


Chart 1. Various types of three-dimensional starlike silicon compounds.



Scheme 1. Synthesis of compound 2.

molecule, 2,4,6-tris(4-(4-hexyl-5-(7-(4-hexyl-5'-(1,1,2,2,2-pentamethyldisilyl)-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl-1,3,5-triazine (**7**) was prepared by Stille coupling reaction of 1,1,2,2,2-pentamethyl-2-(5-(tributylstannyl)thiophen-2-yl)disilane (**6**) with **5**. The product **7** was isolated from the resulting reaction mixture, using a silica gel column in 24% yield.

The structure of **7** was verified by mass and ^1H , ^{13}C , and ^{29}Si NMR spectrometric analysis (see [Experimental Section](#)).

In fact, mass spectrometric analysis for **7** indicates the presence of a parent ion at m/z 2343, which is consistent with the calculated value for $\text{C}_{126}\text{H}_{153}\text{N}_9\text{Si}_6\text{S}_{12}$. The ^1H NMR spectrum of **7** shows two signals at 0.13, 0.40 ppm due to the methylsilyl protons, and the signals at 7.10, 7.21, 7.31, 7.52 ppm attributed to thienyl ring protons, along with hexyl protons and phenylene protons. The ^{13}C NMR spectrum of **7** reveals two signals at -2.9 and -2.4 ppm attributed

to the methylsilyl carbons, and twenty three signals due to the aromatic carbons, as well as the signals due to the hexyl carbons. The ^{29}Si NMR spectrum reveals three signals at -23.5 and -18.8 ppm, due to two different kinds of the silicon atoms. These results are wholly consistent with the structure proposed for **7**.

2.1. Optical properties of starlike molecules **4** and **7**

The UV–visible absorption spectra and fluorescence spectra of compounds **4** and **7** are shown in [Figs. 1 and 2](#), respectively, and their spectral data are summarized in [Table 1](#). Compound **4** in dioxane exhibits two bands at 373 nm ($\epsilon = 74000 \text{ M}^{-1} \text{ cm}^{-1}$) and 414 nm ($\epsilon = 56000 \text{ M}^{-1} \text{ cm}^{-1}$). The fluorescence spectrum of **4** excited at 373 nm displays the emission maximum at 560 nm. In the case of excitation at 373 nm, the fluorescence quantum yield of

Download English Version:

<https://daneshyari.com/en/article/5153137>

Download Persian Version:

<https://daneshyari.com/article/5153137>

[Daneshyari.com](https://daneshyari.com)