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Synthesis and Optoelectronic Properties of Completely Carbazole-substituted Double-decker-shaped Silsesquioxane

Michinari Kohri,† Jun Matsui, Akira Watanabe, and Tokuji Miyashita*
Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577

(Received August 10, 2010; CL-100692; E-mail: miya@tagen.tohoku.ac.jp)

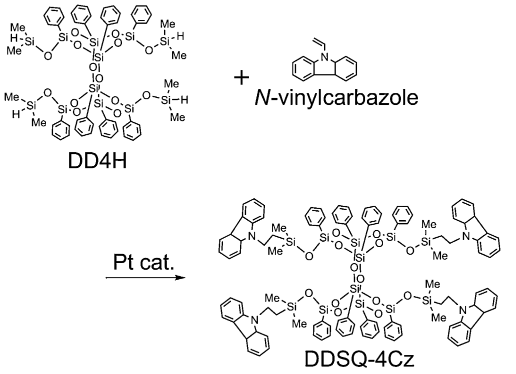
An organic–inorganic hybrid amorphous molecular material; carbazole-substituted double-decker-shaped silsesquioxane (DDSQ-4Cz) was synthesized, and an organic light-emitting diode was fabricated using the spin-coated DDSQ-4Cz film as a hole transport layer.

Organic–inorganic hybrid materials are expected to be useful in materials chemistry.[1] Double-decker-shaped silsesquioxanes (DDSQs) are one of the building blocks to prepare an organic-hybrid material with several functions.[2] Previously, we reported the synthesis of organic–inorganic hybrid films using a photoreactive sol–gel system with four silanol-containing DDSQ.[3] Kakimoto and co-workers reported the synthesis of linear polymers of two hydrosilane-containing DDSQ with diynes.[4] Very recently, we have succeeded in the fabrication of DDSQ-based organic–inorganic hybrid polymer film (Sila-DEC™) in collaboration with Chisso Co. The resulting polymer showed many exciting properties such as high thermal stability, good mechanical properties, low dielectric constant, excellent transparency, and excellent flexibility.[5] Developing a new organic–inorganic hybrid architecture based on the DDSQ is of interest both for scientific knowledge and applications.

Amorphous molecular materials, which are small organic molecules that readily form stable amorphous glass, have been applied successfully in organic light-emitting diodes (OLEDs) and photovoltaic, photochromic, and photoresist materials.[6] Amorphous molecular materials offer numerous features including high glass transition temperature, low polydispersity, high solubility, and high purity. Recently, an approach to prepare a new class of amorphous molecular materials based on a polyhedral oligomeric silsesquioxane (POSS) core has attracted much interest.[7] However, no report describes the application of DDSQ-based amorphous molecular materials.

Herein, we report the synthesis and characterization of a new amorphous molecular material based on DDSQ. Four hydrosilane-containing DDSQ (DD4H) was selected as a core material to react with *N*-vinylcarbazole. Carbazole has been widely used in OLED, photoconductor, and photorefractive devices. The carbazole-substituted DD4H (DDSQ-4Cz) formed a uniform film by spin-coating because of the amorphous nature of DDSQ-4Cz. We prepare an OLED using DDSQ-4Cz as a hole-transport layer.

DD4H was kindly donated by Chisso Co. *N*-Vinylcarbazole was introduced into the periphery of DD4H, which has an open-cage structure, by hydrosilylation reaction (Scheme 1). A reaction was conducted at reflux in toluene, using platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst: 50 ppm) as a catalyst. On completion, the reaction mixture was reprecipitated twice from chloroform/hexane to afford purified DDSQ-4Cz in 65% yield. The product was soluble in common organic solvents such as toluene, acetone, chloroform, and THF. The ^{1}H NMR spectrum of the product indicated the presence of $-Si-CH_2-CH_2-$ (3.92 ppm), $-Si-CH_2-$ (1.01 ppm), and $-Si-(CH_3)_2-$ (0.14 ppm) groups (Figure S1).[8] The structure of DDSQ-4Cz was also supported by ^{13}C NMR and ^{29}Si NMR (Figures S2 and S3).[8] The FT-IR spectra of DD4H, *N*-vinylcarbazole, and DDSQ-4Cz are shown in Figure 1. The disappearance of the Si–H absorption band at 2148 and 902 cm^{-1} shown in the spectrum of DDSQ-4Cz indicates the successful introduction of carbazole into the DD4H core. Moreover, the Si–O–Si absorption band at 1130 cm^{-1} shown in the spectrum of DDSQ-4Cz also suggests retention of the cage structure in the synthesized compound.[9]



Scheme 1. Synthesis of DDSQ-4Cz.

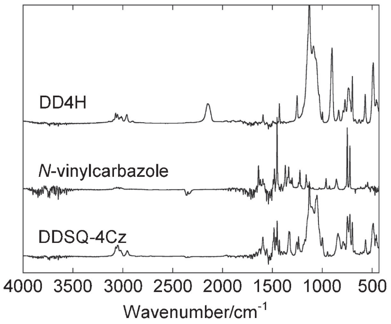


Figure 1. FT-IR spectra of DD4H, *N*-vinylcarbazole, and DDSQ-4Cz.

Thermal properties of DDSQ-4Cz were analyzed using thermogravimetric analysis (TGA) in air, revealing high thermal stability greater than 355 °C and a ceramic yield to SiO_2 of 24%, indicating an average substitution of 4 (Figure 2). This suggests that the hydrosilane groups of DD4H were completely substituted by a carbazole unit. Although several publications report the preparation of organic–inorganic hybrid materials using silsesquioxane as a core, these were related in the main to partially substituted compounds.

Figure 3 shows the UV–vis absorption and photoluminescence spectra of DDSQ-4Cz and *N*-vinylcarbazole in chloroform solution. The UV–vis absorption spectrum of DDSQ-4Cz showed two peaks attributable to the π–π^* absorption (B-band) of carbazole, which

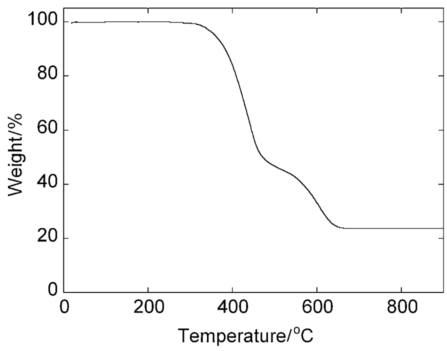


Figure 2. TGA curve of DDSQ-4Cz at a heating rate of 10 °C min^{-1} in air.

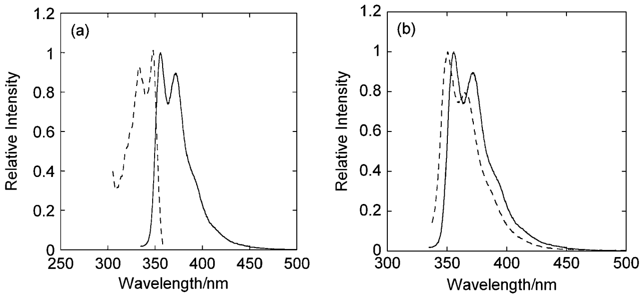


Figure 3. (a) Normalized UV–vis absorption (dash) and photoluminescence (solid) spectra of DDSQ-4Cz. (b) Photoluminescence spectra of *N*-vinylcarbazole (dash) and DDSQ-4Cz (solid).

closely resembles that of *N*-vinylcarbazole. It is particularly interesting that the photoluminescence spectrum of DDSQ-4Cz showed a similar emission spectrum to *N*-vinylcarbazole. This result indicates that the four carbazoles are isolated by the rigid DDSQ core, thereby preventing excimer formation. This result was similar to that of a fully carbazole-substituted POSS.[10]

The DDSQ-4Cz was spin-coated onto a quartz substrate, and baked at 100 °C for 60 min. The AFM analysis of the surface revealed that the resulting film is homogeneous and smooth with root-mean-square (RMS) roughness of 0.38 nm. The spin-coated film showed only a broad peak in X-ray diffraction (XRD) analysis, indicating it has an amorphous property (Figure S4).[8]

To demonstrate the potential of DDSQ-4Cz in organic electronic applications, an OLED was prepared using DDSQ-4Cz and (8-hydroxyquinolinato)aluminum (Alq_3) as a hole transport layer and an emissive layer, respectively. An OLED with the configuration ITO/DDSQ-4Cz (45 nm)/Alq_3 (55 nm)/Al (50 nm) was fabricated.[11] The DDSQ-4Cz was spin-coated onto an ITO substrate with 45-nm-thick film and baked at 100 °C for 60 min. The Alq_3 layer and Al were vacuum deposited onto the DDSQ-4Cz layer with film thickness of 55 and 50 nm, respectively. As shown in Figure 4, the OLED showed maximum brightness of 320 cd m^{-2} at 20 V drive voltage with 40 mA cm^{-2} current density. As far as we concerned, this is the first report of a OLED device fabricated using completely carbazole-substituted silsesquioxane.

In summary, completely carbazole-substituted DDSQ, i.e., DDSQ-4Cz, was synthesized and characterized for use in OLED. The product was isolated in high yield and high purity. This shows that each carbazole introduced into the DD4H core side was effectively isolated by steric effects. Our results clearly show that DDSQ is a promising building block material for the construction of organic–inorganic hybrid materials, which are useful for OLEDs. Further studies including applications of this methodology using other organic electronic functional groups are progressing at our laboratory.

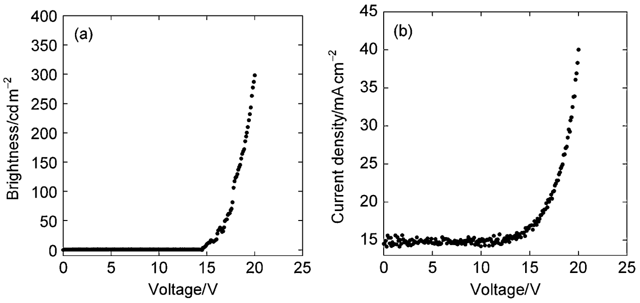


Figure 4. (a) Brightness and (b) current density with the driven voltage for the OLED based on the DDSQ-4Cz.

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References and Notes

† Present address: Division of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522

1 a) Y. Chujo, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 806. b) Y. Chujo, R. Tamaki, *MRS Bull.* **2001**, *26*, 389. c) A. B. Descalzo, R. Martínez-Máñez, F. Sancenón, K. Hoffmann, K. Rurack, *Angew. Chem., Int. Ed.* **2006**, *45*, 5924.

2 K. Yoshida, K. Ito, H. Oikawa, M. Yamahiro, Y. Moromoto, K. Ohguma, K. Watanabe, N. Ootake, U.S. Pat. Appl. 2004024903A1.

3 A. Watanabe, T. Miyashita, *Chem. Lett.* **2006**, *35*, 1130.

4 a) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe, H. Oikawa, *Macromolecules* **2006**, *39*, 3473. b) S. Wu, T. Hayakawa, R. Kikuchi, S. Grunzinger, M. Kakimoto, H. Oikawa, *Macromolecules* **2007**, *40*, 5698.

5 a) A. Watanabe, S. Tadenuma, T. Miyashita, *J. Photopolym. Sci. Technol.* **2008**, *21*, 317. b) M. Aminuzzaman, A. Watanabe, T. Miyashita, *J. Mater. Chem.* **2008**, *18*, 5092. c) M. Aminuzzaman, A. Watanabe, T. Miyashita, *Thin Solid Films* **2009**, *517*, 5935. d) A. Watanabe, S. Tadenuma, T. Miyashita, *J. Photopolym. Sci. Technol.* **2009**, *22*, 305.

6 a) Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1. b) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953. c) H. Nakano, T. Takahashi, T. Tanino, Y. Shirota, *Dyes Pigm.* **2010**, *84*, 102.

7 a) R. Tamaki, Y. Tanaka, M. Z. Asuncion, J. Choi, R. M. Laine, *J. Am. Chem. Soc.* **2001**, *123*, 12416. b) C. He, Y. Xiao, J. Huang, T. Lin, K. Mya, X. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 7792. c) A. Sellinger, R. Tamaki, R. M. Laine, K. Ueno, H. Tanabe, E. Williams, G. E. Jabbour, *Chem. Commun.* **2005**, 3700. d) M. Y. Lo, C. Zhen, M. Lauters, G. E. Jabbour, A. Sellinger, *J. Am. Chem. Soc.* **2007**, *129*, 5808.

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 W.-J. Lin, W.-C. Chen, W.-C. Wu, Y.-H. Niu, A. K.-Y. Jen, *Macromolecules* **2004**, *37*, 2335.

10 a) I. Imae, Y. Kawakami, *J. Mater. Chem.* **2005**, *15*, 4581. b) I. Imae, Y. Kawakami, Y. Ooyama, Y. Harima, *Macromol. Symp.* **2007**, *249–250*, 50.

11 Glass substrates coated with ITO were cleaned ultrasonically in sequential steps using acetone and isopropyl alcohol. Ozone cleaning of ITO surface was performed to remove organic contaminants. DDSQ-4Cz was spin coated from toluene 20 mg mL^{-1} to yield thickness of 45 nm. The substrates were then loaded into a vacuum chamber and the light-emitting layer of Alq_3 (55 nm) was deposited on top of the hole transport layer, followed by 50 nm Al.