

Cite this: *Chem. Commun.*, 2011, **47**, 5025–5027

www.rsc.org/chemcomm

COMMUNICATION

Synthesis of a spirobifluorene-bridged allylsilane precursor for periodic mesoporous organosilica†

Natsuko Tanaka,^a Norihiro Mizoshita,^{bc} Yoshifumi Maegawa,^{bc} Takao Tani,^{bc} Shinji Inagaki,^{*bc} Yogesh R. Jorapur^{ac} and Toyoshi Shimada^{*ac}

Received 28th December 2010, Accepted 5th March 2011

DOI: 10.1039/c0cc05823h

A novel spirobifluorene-bridged allylsilane precursor, which can be easily purified by silica gel chromatography, was prepared by using a new molecular building block for allylsilane sol-gel precursors (MBAS) and successfully converted into a highly fluorescent periodic mesoporous organosilica film.

Among the various types of organic–inorganic hybrid materials, periodic mesoporous organosilicas (PMOs) have been established as some of the most promising materials.¹ Many PMOs have been synthesized from organic-bridged alkoxy silane precursors ($R[Si(OR')_3]_n$; $n \geq 2$, R: organic group, R': Me, Et *etc.*),^{2–6} which were typically prepared by halogen–lithium and –magnesium exchange reactions or rhodium-catalyzed silylations.^{7–9} However, as alkoxy silane is difficult to purify using silica gel chromatography owing to its high reactivity with silica, it is limited in its applicability to large organic-bridged alkoxy silanes with high boiling points which are not available for distillation. Besides, the conventional silylation approaches sometimes cause unfavorable side reactions. Recently, we reported an alternative class of sol-gel precursors, allylorganosilanes ($R[Si(CH_2CH=CH_2)_m(OEt)_{3-m}]_n$; $m = 1–3$), which behave as the synthetic equivalent of alkoxyorganosilane and have sufficiently low reactivity to allow purification using silica gel chromatography.¹⁰ Very recently, Jun *et al.* also reported organofunctionalization on silica gel and glass with methallylsilane in the presence of scandium triflate as a catalyst at room temperature.¹¹ Furthermore, we proposed a general synthetic route for allylorganosilanes using a series of molecular building blocks for allylsilane sol-gel precursors (MBAS) and their palladium-catalyzed coupling reactions (Fig. 1).¹² The building blocks and derived precursors with diallylethoxysilyl groups ($m = 2$) are especially versatile

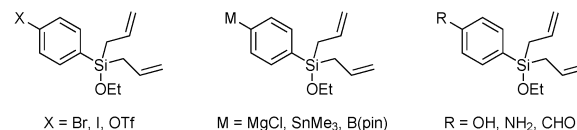
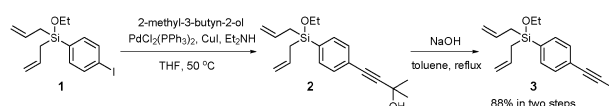


Fig. 1 Examples of molecular building blocks for allylsilane sol-gel precursors (MBAS).

because of the easiness in synthesis, sufficient stability in purification and applicability to sol-gel processes. These findings enable us to synthesize a variety of sol-gel precursors with large organic groups and a high purity, which are favorable for the synthesis of highly functional PMOs. However, the advanced utilization of the allylorganosilane precursor for the synthesis of PMOs has so far been limited to only a benzene-bridged allylsilane precursor.^{10c,d}

Here, we report the synthesis of a novel spirobifluorene-bridged allylsilane precursor **5** via the unique MBAS route and its conversion into a highly fluorescent PMO film using surfactant-directed self-assembly (Schemes 1 and 2). Spirobifluorene is a promising emitting phosphor owing to the unique spatial conformation of two fluorene units.^{13–20} The emissive PMO can be applied to highly luminescent films with tunable emission color²¹ because of its unique light-harvesting function.²² We designed a new ethynyl-MBAS **3** for the synthesis of the spirobifluorene derivative **5** (Scheme 1). The MBAS **3** can be widely utilized for the synthesis of various extended π -conjugated sol-gel precursors using the Sonogashira coupling reaction. The allylsilylated **5** has an advantage of being easily purifiable by silica gel chromatography, but conventional alkoxy silylated spirobifluorene cannot be purified by either chromatography or distillation.

We initially attempted to synthesize a spirobifluorene-based precursor by rhodium-catalyzed triethoxysilylation of 2,2',7,7'-tetraiodo-9,9'-spirobifluorene **4**. However, the reaction afforded a complex mixture containing no target compound (Scheme 2). Eventually, the Sonogashira coupling reaction with MBAS **3** successfully yielded the sol-gel precursor **5**.



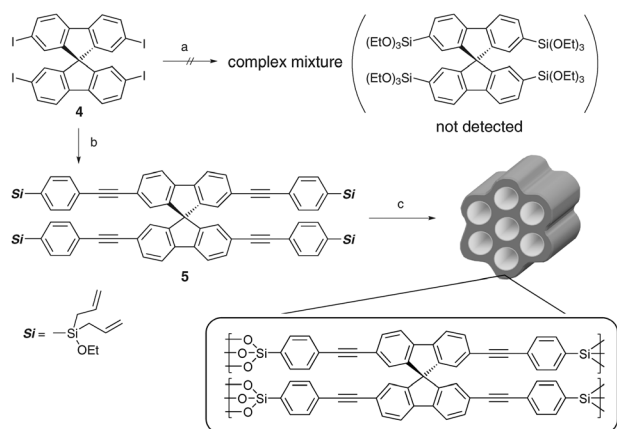
Scheme 1 Preparation of ethynyl-MBAS **3**.

^a Department of Chemical Engineering, Nara National College of Technology, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan. E-mail: shimada@chem.nara-k.ac.jp; Fax: +81-743-55-6154; Tel: +81-743-55-6154

^b Toyota Central R&D Laboratories Inc., Nagakute, Aichi 480-1192, Japan. E-mail: inagaki@mosk.tytlabs.co.jp; Fax: +81-561-63-6507; Tel: +81-561-71-7393

^c Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

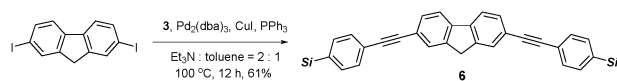
† Electronic supplementary information (ESI) available: Experimental details and spectroscopic data. See DOI: 10.1039/c0cc05823h



Scheme 2 Synthesis of the spirobifluorene precursor **5** and mesostructured organosilica. (a) $[\text{Rh}(\text{cod})(\text{CH}_3\text{CN})_2]\text{BF}_4$, $\text{HSi}(\text{OEt})_3$, Et_3N , $n\text{-Bu}_4\text{NI}$, $\text{DMF} : \text{toluene} = 1 : 1$; (b) **3**, $\text{Pd}_2(\text{dba})_3$, CuI , PPh_3 , $\text{Et}_3\text{N} : \text{toluene} = 2 : 1$, 100°C , 24 h, 56%; (c) Brij76, HCl aq. , THF.

The ethynyl-MBAS **3** was synthesized by the Sonogashira coupling reaction of **1** with 2-methyl-3-butyn-2-ol followed by deprotection with sodium hydroxide in 88% yield without affecting the diallylethoxysilyl group (Scheme 1).²³ The coupling reaction of **3** with 2,2',7,7'-tetraiodo-9,9'-spirobifluorene **4** in the presence of $\text{Pd}_2(\text{dba})_3$ as catalyst in triethylamine/toluene = 2/1 at 100°C for 24 h followed by purification with silica gel column chromatography afforded the desired 2,2',7,7'-tetrakis(diallylethoxysilylphenylethynyl)-9,9'-spirobifluorene **5** in 56% yield (Scheme 2). 2,7-Bis(diallylethoxysilylphenylethynyl)-fluorene **6** without the spirocarbon was also synthesized by the coupling reaction of **3** with 2,7-diiodofluorene for comparison (Scheme 3).²³

Acidic sol-gel polycondensation of **5** in the presence of the nonionic template surfactant Brij76 ($\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$) gave organosilica hybrid films with a meso-scale periodic structure.²³ Fig. 2a shows an X-ray diffraction (XRD) pattern of the organosilica (**5**-Brij76) film. The film showed a single intense peak at $d = 5.52$ nm and no higher-order diffraction peaks were observed, which implies the formation of a wormhole-like array of mesochannels. The periodic mesostructure was retained after extraction of the template



Scheme 3 Synthesis of the bis(phenylethynyl)fluorene derivative **6**.

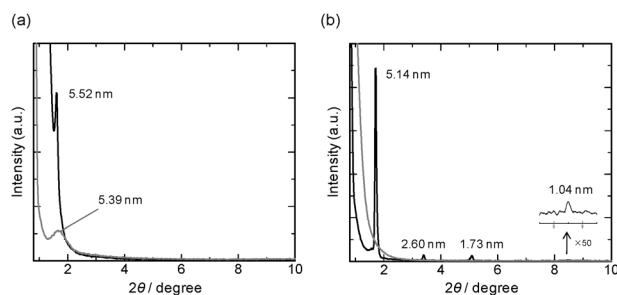


Fig. 2 XRD patterns of (a) **5**-Brij76 and (b) **6**-Brij76 films before (black) and after (gray) extraction of the template surfactant.

surfactant. The XRD pattern of the extracted film showed a broad diffraction peak at $d = 5.39$ nm (Fig. 2a). Nitrogen adsorption-desorption isotherms of the extracted film (peeling off the substrate) after reinforcing the framework indicated the formation of a mesoporous structure with a pore diameter of *ca.* 4.1 nm although it seems to partially collapse (see ESI†). These results show that **5** is suitable for the preparation of mesostructured organosilica films. According to the molecular geometry of **5**, the hydrophobic spirobifluorene core is surrounded by four silyl groups. These silyl groups can facilitate the interaction of the precursor with hydrophilic surfaces of the template surfactant micelles. Moreover, the four spatially distributed silyl groups in **5** are more conducive to the formation of a three-dimensionally crosslinked network, resulting in a structurally stable organosilica framework after the removal of the template. In contrast, the rod-like precursor **6** was not suitable for the preparation of mesoporous organosilicas. The polycondensed organosilica **6**-Brij76 film showed XRD peaks at $d = 5.14$, 2.60, 1.73, and 1.04 nm (Fig. 2b). These peaks with a d -spacing ratio of $1 : 1/2 : 1/3 : 1/5$ strongly suggested the formation of a lamellar structure. After extraction of Brij76, the XRD peaks completely disappeared, which indicates that the **6**-based organosilica does not form a three-dimensionally crosslinked structure. In the sol-gel polycondensation process, the hydrophobic rigid rod-like core of **6** likely forms side-by-side aggregates, while the terminal silyl groups of **6** can interact with the hydrophilic chain of Brij76, which leads to the formation of the lamellar structure consisting of organosilica layers and surfactant assemblies, rather than a three-dimensional network. The side-by-side aggregation of **6** is also supported by a 9 nm blue shift of the absorption maximum wavelength of the **6**-Brij76 film (343 nm) in comparison with a solution of **6** in 2-propanol (352 nm) (see ESI†).

The introduction of a spirobifluorene group into mesostructured organosilica films has positive effects on the fluorescence properties. Fig. 3 shows fluorescence spectra of the organosilica films (**5**-Brij76 and **6**-Brij76). The **5**-Brij76 film showed a strong fluorescence emission with a quantum yield (QY) of 0.59 upon excitation at $\lambda = 360$ nm (QY of a solution of **5** in 2-propanol: 0.92). The fluorescence spectrum has a vibronic structure, which suggests that the organic chromophore is fixed by the silica-based robust framework

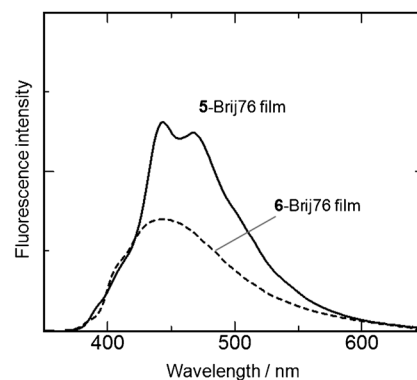


Fig. 3 Fluorescence emission spectra of **5**-Brij76 (solid line) and **6**-Brij76 (dashed line) films.

without strong aggregation. Compared with spirobifluorene-based molecular solid films,²⁴ the 5-Brij76 film showed a shift of the emission band to a longer wavelength exhibiting blue owing to the extension of the π -conjugation length with phenylethynyl substituents, which can be appropriate for luminescence applications. On the other hand, the 6-Brij76 film showed a broad fluorescence spectrum attributable to excimer-band emission with a QY of 0.38 (QY of a solution of 6 in 2-propanol: 0.96). The lower QY of the 6-based organosilica is probably due to self-quenching by the side-by-side aggregation of the chromophore. Although solid-state quenching is often observed in fluorescent polymer materials including polyfluorene-based films,^{17–20,25} the bulky molecular scaffold of 5 was effective in suppressing a large decrease in QY during the polycondensation. The highly emissive PMO film has potential for various luminescence applications including white-LEDs and fluorescence sensing owing to its unique light-harvesting properties.

In conclusion, a novel spirobifluorene-bridged allylsilane precursor, which could be purified by silica gel chromatography, was successfully synthesized *via* a recently developed new route using MBAS. Acidic sol–gel polycondensation of the allylsilane precursors yielded mesostructured organosilica films. The spirocarbon was effective in forming a structurally stable organosilica framework and exhibiting efficient fluorescence. These results demonstrate the suitability of MBAS for use in designing various functional organosilane precursors intended for the preparation of highly functional PMOs.

Notes and references

- (a) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611–9614; (b) B. J. Melde, B. T. Holland, C. F. Blanford and A. Stein, *Chem. Mater.*, 1999, **11**, 3302–3308; (c) T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867–871; (d) A. Stein, B. J. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403–1419; (e) F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216–3251; (f) M. P. Kapoor and S. Inagaki, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 1463–1475; (g) S. Fujita and S. Inagaki, *Chem. Mater.*, 2008, **20**, 891–908; (h) T. Tani, N. Mizoshita and S. Inagaki, *J. Mater. Chem.*, 2009, **19**, 4451–4456.
- S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, **416**, 304–307.
- M. P. Kapoor, Q. Yang and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 15176–15177.
- N. Mizoshita, Y. Goto, M. P. Kapoor, T. Shimada, T. Tani and S. Inagaki, *Chem.–Eur. J.*, 2009, **15**, 219–226.
- H. Takeda, Y. Goto, Y. Maegawa, T. Ohsuna, T. Tani, K. Matsumoto, T. Shimada and S. Inagaki, *Chem. Commun.*, 2009, 6032–6034.
- N. Mizoshita, M. Ikai, T. Tani and S. Inagaki, *J. Am. Chem. Soc.*, 2009, **131**, 14225–14227.
- Y. Goto, K. Nakajima, N. Mizoshita, M. Suda, N. Tanaka, T. Hasegawa, T. Shimada, T. Tani and S. Inagaki, *Microporous Mesoporous Mater.*, 2009, **117**, 535–540.
- Y. Maegawa, Y. Goto, S. Inagaki and T. Shimada, *Tetrahedron Lett.*, 2006, **47**, 6957–6960.
- J. Morell, G. Wolter and M. Fröba, *Chem. Mater.*, 2005, **17**, 804–808.
- (a) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki and T. Hayashi, *J. Am. Chem. Soc.*, 2003, **125**, 4688–4689; (b) K. Aoki, T. Shimada and T. Hayashi, *Tetrahedron: Asymmetry*, 2004, **15**, 1771–1777; (c) M. P. Kapoor, S. Inagaki, S. Ikeda, K. Kakiuchi, M. Suda and T. Shimada, *J. Am. Chem. Soc.*, 2005, **127**, 8174–8178; (d) M. P. Kapoor, M. Yanagi, Y. Kasama, T. Yokoyama, S. Inagaki, T. Shimada, H. Nanbu and L. R. Juneja, *J. Mater. Chem.*, 2006, **16**, 3305–3311; (e) Y. Wang, S. Hu and W. J. Brittain, *Macromolecules*, 2006, **39**, 5675–5678; (f) N. Fukaya, S. Onozawa, M. Ueda, K. Saitou, Y. Takagi, T. Sakakura and H. Yasuda, *Chem. Lett.*, 2010, 402–403; (g) N. Fukaya, H. Yamashita, H. Haga, T. Tsuchimoto, S. Onozawa, T. Sakakura and H. Yasuda, *J. Organomet. Chem.*, 2011, **696**, 825–828.
- Y.-R. Yeon, Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang and C.-H. Jun, *Angew. Chem., Int. Ed.*, 2008, **47**, 109–112.
- Y. Maegawa, T. Nagano, T. Yabuno, H. Nakagawa and T. Shimada, *Tetrahedron*, 2007, **63**, 11467–11474.
- (a) D. Katsis, Y. H. Geng, J. J. Ou, S. W. Culligan, A. Trajkovska, S. H. Chen and L. J. Rothberg, *Chem. Mater.*, 2002, **14**, 1332–1339; (b) X.-M. Liu, J. Xu, X. Lu and C. He, *Macromolecules*, 2006, **39**, 1397–1402.
- R. Wu, J. S. Schumm, D. L. Pearson and J. Tour, *J. Org. Chem.*, 1996, **61**, 6906–6921.
- A. Wakamiya, T. Ide and S. Yamaguchi, *J. Am. Chem. Soc.*, 2005, **127**, 14859–14866.
- G. Zeng, W.-L. Yu, S.-J. Chua and W. Huang, *Macromolecules*, 2002, **35**, 6907–6914.
- H.-J. Su, F.-I. Wu and C.-F. Shu, *Macromolecules*, 2004, **37**, 7197–7202.
- J. Lee, H.-J. Cho, B.-J. Jung, N. S. Cho and H.-K. Shim, *Macromolecules*, 2004, **37**, 8523–8529.
- (a) X.-M. Liu, T. Lin, J. Huang, X.-T. Hao, K. S. Ong and C. He, *Macromolecules*, 2005, **38**, 4157–4168; (b) X.-M. Liu, J. Xu, X. Lu and C. Hu, *Macromolecules*, 2006, **39**, 1397–1402.
- C.-L. Chiang, C.-F. Shu and C.-T. Chen, *Org. Lett.*, 2005, **7**, 3717–3720.
- (a) N. Mizoshita, Y. Goto, T. Tani and S. Inagaki, *Adv. Mater.*, 2009, **21**, 4798–4801; (b) N. Mizoshita, Y. Goto, Y. Maegawa, T. Tani and S. Inagaki, *Chem. Mater.*, 2010, **22**, 2548–2554.
- S. Inagaki, O. Ohtani, Y. Goto, K. Okamoto, M. Ikai, K. Yamanaka, T. Tani and T. Okada, *Angew. Chem., Int. Ed.*, 2009, **48**, 4042–4046.
- For detailed experimental procedures for the synthesis of ethynyl-MBAS 3, precursors 5 and 6, and for the preparation of mesostructured organosilica *via* acidic sol–gel polycondensation, see ESI†.
- N. Johansson, J. Salbeck, J. Bauer, F. Weissörtel, P. Bröms, A. Andersson and W. R. Salaneck, *Adv. Mater.*, 1998, **10**, 1136–1141.
- S. M. King, I. I. Perepichka, I. F. Perepichka, F. B. Dias, M. R. Bryce and A. P. Monkman, *Adv. Funct. Mater.*, 2009, **19**, 586–591.