Research on Chemical Intermediates
https://doi.org/10.1007/s11164-020-04086-y

Synthesis and characterization of 5,5′-bis-silylated dithienylethene as a new building block of novel photochromic periodic mesoporous organosilicas

Mohamed Abboud[1]

Received: 27 October 2019 / Accepted: 9 January 2020

Abstract

Pure bis-silylated dithienylethene (DTE) 3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(triethoxysilyl)thiophen-3-yl)cyclopent-1-enyl)-2-methyl-5-(triethoxysilyl)thiophene was prepared from 3-(3,3,4,4,5,5-hexafluoro-2-(5-iodo-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-iodo-2-methylthiophene by iodine–lithium exchange. The synthesis and purification method were optimized after many attempts of different coupling methods and purification techniques to ovoid the hydrolysis and self-condensation reaction and to obtain a pure product. The obtained bis-silylated dithienylethene (BS-DTE) is a versatile building block for potential applications, such as synthesis of new photochromic periodic mesoporous organosilica (PPMO). The structure of the obtained precursor was characterized by ^{1}H, ^{13}C and ^{29}Si liquid NMR. Many attempts have been performed to prepare DTE-PMO but, the C–Si bond in the final material was fragile and could not resist to the hydrothermal treatment during the synthesis. The thermal stability of DTE-PMO will be studied in a future work.

Keywords Bis-silylated dithienylethene · Photochromic precursor · Periodic mesoporous organosilicas · Iodine–lithium exchange

Introduction

The mainstream of twenty-first century nanotechnology focuses on the control of matter at the nanoscale [1–3]. The ability to control the function and structure of some promising nanosystems using an external stimulus is an attractive research area for developing programmable and reconfigurable nanomaterials for multifunctional and smart devices [4]. Due to its particular advantages of temporal resolution, high spatial and digital controllability, light represents the most preferred external

---

✉ Mohamed Abboud
abboud_med@yahoo.fr

[1] Present Address: Catalysis Research Group, Chemistry Department, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

stimulus as a chemical and physical tool for in situ manipulation of the function and structure of some photochromic nanosystems.

Photochromism is the property of some moieties to undergo a reversible transformation between two or more different states, with distinct properties. Photochromic molecules have been extensively incorporated into several functional nanosystems such as nanoparticles, nanomachines, nanoelectronics, biological nanosystems, sensors, memory storage, and supramolecular nanoassemblies [5–8]. There are many organic photochromic molecules that exhibit isomerization upon light irradiation, such as DTE, azobenzene, stilbene, and spiropyrans [5, 9–11]. However, the application of these photochromic molecules is limited to a certain type of structure and properties. Both isomers have to be thermally stable, with low photofatigue and fast reversible response. Among the most promising organic photochromic molecules that employed until now, the DTE derivatives containing a perfluorocyclopentene have been demonstrated to exhibit excellent photochromic behaviour with low photofatigue [8]. There are only few examples in the literature of dithienylthene containing mesoporous silica materials. The dithienylthene derivatives in these materials were immobilized in the surface of the silica using organic linkers [12, 13]. However, surface-immobilized or physically impregnated photochromic molecules might aggregate, leading to a reduced photoisomerization, and might block material nanopores. The introduction of DET in the silica wall will prevent its packing and suppress the self-quenching. Therefore, to defeat this limitation, periodic mesoporous organosilicas (PMOs) [14–17] offer a great alternative for high loading of the photochromic molecules into silica wall framework, and show also a high quantum performance. Photochromic periodic mesoporous organosilica (PPMO) are new category of mesoporous organosilica materials that can be considered as smart nanomaterials. Pores diameter and shape and permeability can be controlled by applying an external stimulus such as UV light [18–20]. DTE exhibits a remarkable reversible change of structure upon UV irradiation, when it transforms from the colourless ring-open form to the purple ring-closed form (Fig. 1). This reversible process is thermally stable and can be only driven by visible light irradiation [5, 21]. If DTE is incorporated in a PMO, this drastic structure change will be observed in the PMO pore size, pore volume, surface area and morphology. However, the preparation of pure, rigid and ordered DTE-PMO requires the synthesis of a pure bis-silylated DTE (BS-DTE) precursor, without any linker between thiophene ring and silicon atom, because, the presence of this linker will make DTE-PMO less ordered and soft.

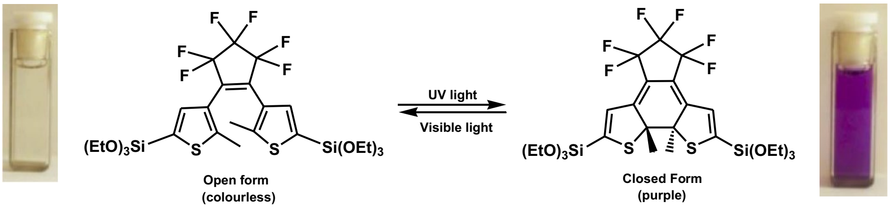


Fig. 1 Photoisomerization process of bis-silylated dithienylethene

Herein, I report the successful synthesis, purification and characterization of BS-DTE as a building block of novel PPMO. The synthesis of this new precursor was based on the iodine–lithium exchange, and its structure was investigated by liquid ^{1}H, ^{13}C and ^{29}Si liquid NMR. This precursor was used as 100% organosilica source, in combination with CTAB as a structure directing agents to prepare DTE-PMO, but unfortunately, the C–Si bond in the final material was fragile and could not resist to the hydrothermal treatment. The thermal stability of DTE-PMO will be investigated in a future work.

Results and discussion

Synthesis

Figure 2 describes the synthetic pathway employed for the preparation of diiodinated DTE **6**.

Synthon **6** was prepared from bis(5-trimethylsilyl) derivative of 1,2-bis(29-methylthien-39-yl)perfluorocyclopentene (**5**), using a procedure described by Irie et al. [22, 23]. The trimethylsilyl (TMS) was substituted smoothly by iodine using ICl as iodinating agent to afford the diiodo derivative **6** in a good yield.

The resulting 5,5′-diiodo-DTE **6** were subjected to different silylation conditions used in the literature to access to BS-DTE precursors **8**, namely the palladium and rhodium-catalyzed carbon–silicon bond-forming reactions between aryl halides and trialkoxysilanes $HSi(OR)_3$ (R = Me, Et) [24–28].

Since its discovery in the late 1990s, this σ-bond metathesis-type reaction [27] was further developed by Manoso and De-Shong [28] as well as by Masuda et al. [29, 30], who also presented a rhodium-mediated version. The main reason for the comparatively minor attention this reaction has received up to now might be its rather limited scope of starting materials, comprising only several aryl iodides and electron-rich aryl bromides, and its tendency to give considerable amounts of

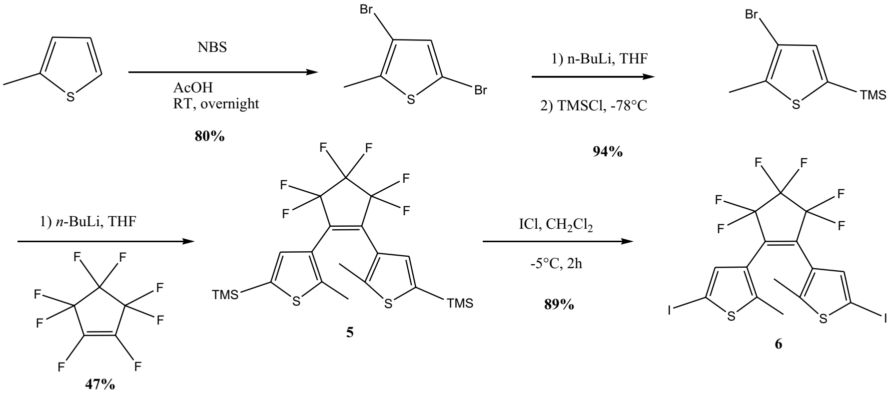


Fig. 2 Synthesis of the diiodinated synthon **6**

undesired by-products, especially by reductive proto-dehalogenation. Furthermore, the reaction products are very moisture sensitive and can be purified only to a very limited extent. The low solubility and the high molecular weight of 5,5′-diiodo-DTE **6** make it even more difficult to pursue common purification methods, for example, bulb-to-bulb distillation. To develop a suitable condition for the coupling of **6** with triethoxysilane or trimethoxysilane I tried many methods. I based my initial screening on the protocol of Manoso and DeShong, employing N-methyl-2-pyrrolidone (NMP) as a polar aprotic solvent and $Pd(dba)_2$/Johnphos (di-tert-butylphosphanylbiphenyl) as catalyst [28]. In contrast to the literature, aqueous workup of the obtained solutions was not feasible, because extraction with pentane and washing with deionized water yielded only inseparable mixtures of polymerized material including dehalogenated starting materials. Using the conditions improved by Thiel et al. [31] by changing the solvent to DMF and replacing triethoxysilane with trimethoxysilane showed no beneficial effect. After all these attempts, I was convinced that the access to pure BS-DTE precursors **8** is not possible via metal-catalyzed cross-coupling reactions. Therefore, I searched for an alternative method to substitute iodine by $Si(OEt)_3$ group. After an exhaustive literature search about this kind of cleavage, I found only few examples about the creation of C–$Si(OR)_3$ bond on thiophene or phenyl ring with Si attached directly to the ring without linker. The iodine–lithium exchange [32–36] was among the methods used to create Si–C bond. In this process, the iodine was exchanged to lithium at low temperature (− 105 °C) using *n*-BuLi, then Li–C bond was converted to C–Si after transmetallation with chlorotrithoxysilane $ClSi(OEt)_3$. Using this method with some modifications, and developing a new purification process, using bulb-to-bulb distillation, I was able to obtain the desired BS-DTE precursor with high purity and acceptable yield. Indeed, 1 equivalent of *n*-BuLi and $ClSi(OEt)_3$ was not sufficient to convert totally diiodo-DTE **6** to dilithio-DTE **7** (Fig. 3). Thus, an excess of *n*-BuLi and $ClSi(OEt)_3$ was necessary to

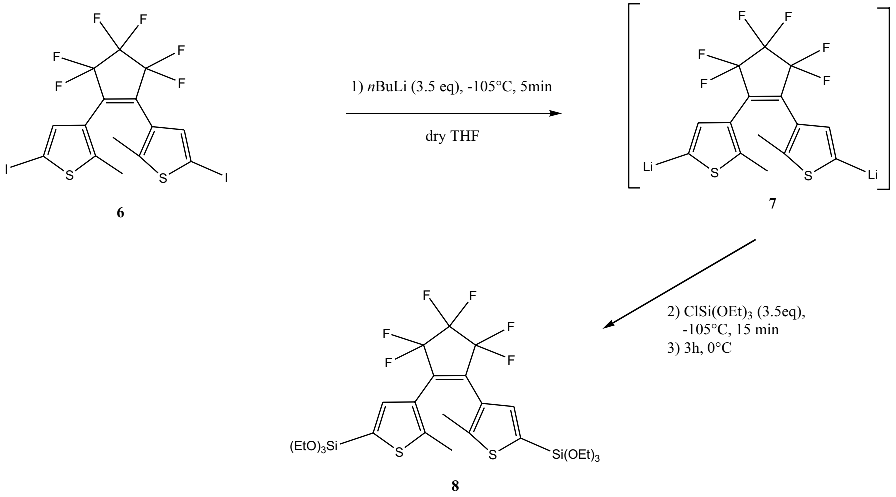


Fig. 3 Synthesis of the precursor **8** by iodine–lithium exchange

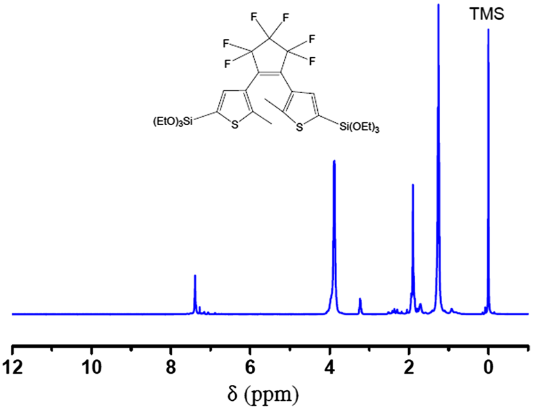


Fig. 4 H NMR of 5,5′-bis-silylated dithienylethene

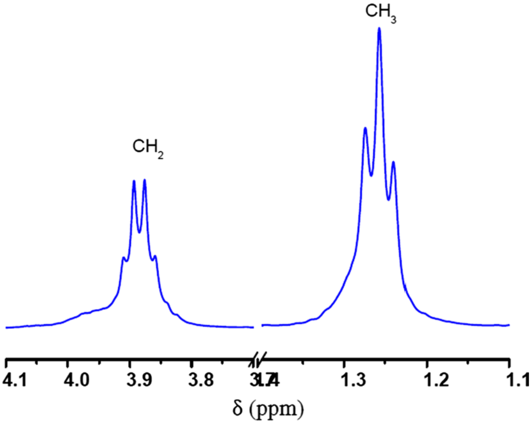


Fig. 5 Zoom from Fig. 4 shows H NMR peaks of Si–O-CH_2-CH_3

perform a total iodine–lithium exchange and to avoid the formation of the undesired mono-iodo-DTE.

Liquid ^1H, ^{13}C and ^{29}Si liquid NMR spectra confirmed the structure and purity of the obtained precursor. These analyses confirmed also the preservation of both, DTE moiety and C–Si bonds. The liquid ^1H NMR spectra (Figs. 4 and 5) displayed clearly the tree protons of CH_3 (1.25 ppm) and two protons of CH_2 (3.88 ppm) in Si–O–CH_2–CH_3, the methyl group attached to the thiophene ring (1.9 ppm), and the single proton of thiophene rings (7.39 ppm).

The liquid ^{13}C NMR spectrum (Figs. 6 and 7) showed the two carbons of the ethoxy groups (21.2 ppm and 59.1 ppm), the 4 carbons of thiophene rings (130.0, 133.0, 134.4, 142.6 ppm), the carbon of methyl group attached to thiophene (18.0 ppm), and the tree carbons of hexafluorocyclopentene (126.1, 128.6, and 142.8 ppm).

The liquid ^{29}Si NMR spectrum (Fig. 8) exhibited a singlet at around -62.7 ppm which correspond to silicon atom in –Si$(OEt)_3$ groups, which confirm the purity of bis-silylated precursor, preservation of C–Si bond, and the absence of hydrolysis and self-condensation reaction of triethoxysilane groups.

Fig. 6 ^{13}C NMR spectrum of precursor **8**

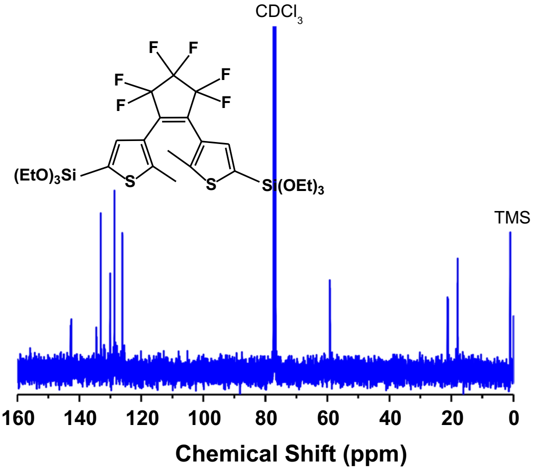


Fig. 7 Zoom from Fig. 5 shows ^{13}C NMR peaks of the aromatic carbons in precursor **8**

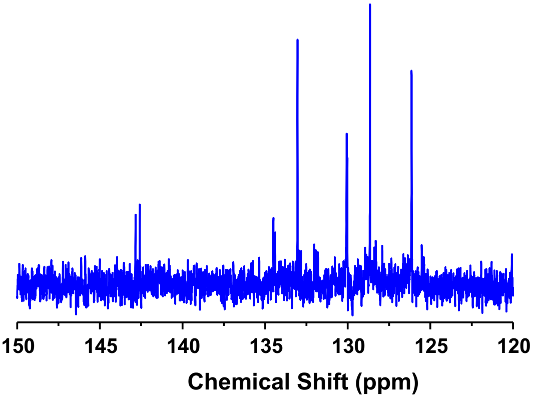
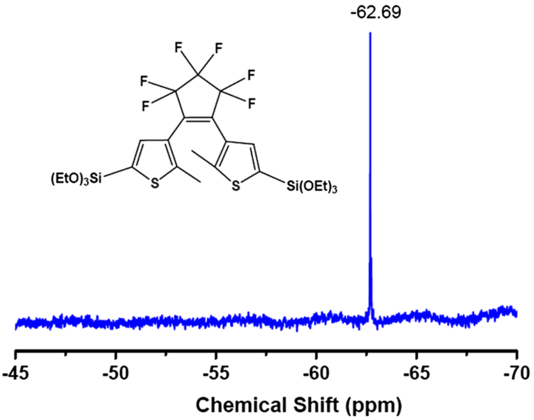


Fig. 8 Liquid ^{29}Si NMR spectrum of 5,5′-bi-silylated dithienylethene



Using a method reported by Inagaki et al. [37] this new bis-silylated precursor was involved then in the hydrolysis and polycondensation reaction under basic conditions in the presence of C_{18}TMACl as a structure directing agent. Unfortunately, after the hydrothermal treatment at 97 °C in autoclave, and the characterization of the final product by ^{13}C, and ^{29}Si solid NMR I discovered that the PMO was not pure and C–Si bond was broken during the hydrothermal treatment.

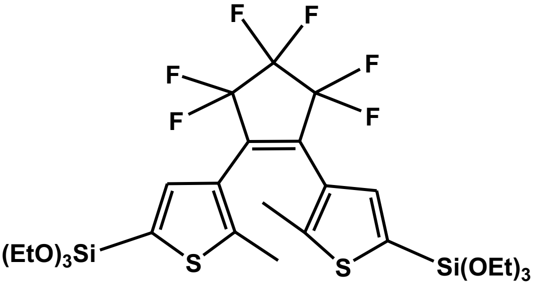
Experimental section

Materials and methods

All reactions were carried out under nitrogen using standard high-vacuum and Schlenk-line techniques. Unless otherwise noted, all chemicals were purchased from commercial suppliers (TC America, Sigma-Aldrich, Acros Organics, Alfa aesar and Gelest), and used without further purification. Tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) used in synthesis were distilled before use, according to standard procedures. Liquid-state ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 spectrometer operating at 400 MHz and 100 Hz, respectively. Liquid-state ^{29}Si NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz equipped with the one NMR 5 mm probe and without sample-spinning. Chemical shifts are reported in δ parts per million (ppm) referenced to tetramethylsilane (TMS) or residual protonated solvent as an internal standard, using deuterated chloroform ($CDCl_3$) as solvent.

Synthesis of 3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(triethoxysilyl)thiophen-3-yl)cyclopent-1-enyl)-2-methyl-5-(triethoxysilyl)thiophene (8)

The precursor was prepared according to procedure adapted from the literature [33, 35, 38]. To a THF solution (130 mL) of the compound **6** (620 mg, 1 mmol) at − 105 °C, 3.5 equivalents of *n*-BuLi (1.60 M in hexane, 2.2 mL, 3.5 mmol) was added rapidly. After the reaction solution was stirred further at − 105 °C for 5 min then, 3.5 equivalents of chlorotriethoxysilane (0.7 mL, 3.5 mmol) was added dropwise at − 105 °C. The mixture was stirred at − 105 °C for 15 min and then at 0 °C for 3 h, evaporated, and extracted with CH_2Cl_2. The crude product was separated by a chromatograph (CH_2Cl_2, Silica Gel 230–400 Mesh). The eluted main component was purified by distillation with a glass tube oven (0.07 mmHg, 125 °C) to give **4c** as colourless oil (311 mg, 45%).



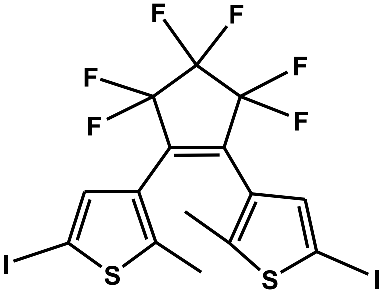
8

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (*t*, $J = 6.9$ Hz, 18H, CH_3 of $Si(OEt)_3$), 1.9 (*s*, 6H, CH_3), 3.88 (*q*, $J = 6.8$ Hz, 12H, CH_2 of $Si(OEt)_3$), 7.39 (*s*, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 21.2, 59.1, 126.1, 128.6, 130.0, 133.0, 134.4, 142.6, 142.8.

Synthesis of 3-(3,3,4,4,5,5-hexafluoro-2-(5-iodo-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-iodo-2-methylthiophene 6

The procedure was adapted from the literature [39]. Iodine monochloride (570 mg, 3.5 mmol) was added to a solution of **5** (450 mg, 0.87 mmol) in CH_2Cl_2 (30 mL), and the solution was stirred at − 5 °C for 2 h. After the evaporation of CH_2Cl_2, the final product was purified by column chromatography (basic alumina, pentane) to afford 490 mg of **9** as a waxy solid with 89% yield. Mp. 95 °C.



6

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.9 (*s*, 6H, CH_3), 7.2 (*s*, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 111.8, 115.6, 119.8, 126.6, 135.4, 136.1, 147.8.

Conclusion

Herein, I report the successful synthesis of pure 5,5′-bis-silylated dithienylethene as a new building block of novel photochromic PMO. This precursor was successfully synthesized for the first time from 5,5′-diiododithienylethene trough iodine–lithium exchange method. Triethoxysilane—$Si(OEt)_3$—groups are attached directly to thiophene ring without any linker. Despite, the product is very moisture sensitive and can be purified only to a very limited extent using traditional purification techniques, the synthesis conditions and purification method were optimized after many attempts of different coupling methods and purification techniques to ovoid the formation of undesired by-products and to obtain a pure bi-silylated precursor. The structure of the obtained precursor was investigated by ^{1}H, ^{13}C and ^{29}Si liquid NMR. Many attempts have been made to prepare the photochromic PMO of 5,5′-bis-silylated dithienylethene (DTE-PMO), but the C–Si bond was fragile and could not resist to the hydrothermal treatment during the synthesis of PMO. The thermal stability of this precursor in the preparation process of DTE-PMO will be studied in a future work.

Acknowledgement The author extend its appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through General Research Project under Grant Number (G.R.P-255). The author would like to express its gratitude to King Khalid University, Abha, Saudi Arabia for providing administrative and technical support.

References

1. G.A. Mansoori, T.F. George, G. Zhang, L. Assoufid, *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications* (Springer, Berlin, 2007), p. 1
2. K.E. Drexler, *Engines of Creation-The Coming Era of Nanotechnology* (Anchor Press, New York, 1986), p. 1
3. B. Bhushan, *Springer Handbook of Nanotechnology* (Springer, Berlin, 2010), p. 1
4. Z. Pianowski, Chem. Eur. J. **25**, 5128 (2019)
5. L. Wang, Q. Li, Chem. Soc. Rev. **47**, 1044 (2018)
6. Z. Li, Y. Dai, Z. Lu, Y. Pei, Y. Song, L. Zhang, H. Guo, Eur. J. Org. Chem. **2019**, 3614 (2019)
7. Z. Li, Y. Wang, M. Li, H. Zhang, H. Guo, H. Ya, J. Yin, Org. Biomol. Chem. **16**, 6988 (2018)
8. J.C.-H. Chan, W.H. Lam, V.W.-W. Yam, J. Am. Chem. Soc. **136**, 16994 (2014)
9. M. Irie, Proc. Jpn. Acad. Ser. B **86**, 472 (2010)
10. M. Abboud, A. Sayari, Microporous Mesoporous Mater. **249**, 157 (2017)
11. M. Abboud, R. Bel-Hadj-Tahar, N. Fakhri, A. Sayari, Microporous Mesoporous Mater. **265**, 179 (2018)
12. J. Fölling, S. Polyakova, V. Belov, A. van Blaaderen, M.L. Bossi, S.W. Hell, Small **4**, 134 (2008)
13. K. Uchida, Y. Yamanoi, T. Yonezawa, H. Nishihara, J. Am. Chem. Soc. **133**, 9239 (2011)
14. C.-S. Ha, S.S. Park, *Periodic Mesoporous Organosilicas Preparation, Properties and Applications* (Springer, Berlin, 2019), p. 1
15. N. Yao, J. Tan, X. Liu, Y. Liu, Y.L. Hu, J. Saudi. Chem. Soc. **23**, 740 (2019)
16. J. Tan, D. Fang, Y. Liu, Y.L. Hu, New. J. Chem. **43**, 2583 (2019)
17. N. Yao, Y.P. Wu, K.B. Zheng, Y.L. Hu, Curr. Org. Chem. **22**, 462 (2018)
18. G.A. Ozin, A. Kuperman, A. Stein, Angew. Chem. **101**, 373 (1989)
19. K. Weh, M. Noack, in *Host-Guest-Systems Based on Nanoporous Crystals*, ed. by F. Laeri, F. Schüth, U. Simon, M. Wark (Wiley, New York, 2003), p. 484
20. Y. Kim, P.K. Dutta, Res. Chem. Intermed. **30**, 147 (2004)
21. M. Irie, Chem. Rev. **100**, 1685 (2000)

22. T. Saika, M. Irie, T. Shimidzu, J. Chem. Soc. Chem. Commun. **18**, 2123 (1994)
23. K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, Angew. Chem. Int. Ed. **45**, 6470 (2006)
24. A. Kunai, T. Sakurai, E. Toyoda, M. Ishikawa, Y. Yamamoto, Organometallics **13**, 3233 (1994)
25. A.S. Manoso, P. DeShong, J. Org. Chem. **66**, 7449 (2001)
26. M. Murata, K. Suzuki, S. Watanabe, Y. Masuda, J. Org. Chem. **62**, 8569 (1997)
27. M. Murata, M. Ishikura, M. Nagata, S. Watanabe, Y. Masuda, Org. Lett. **4**, 1843 (2002)
28. M. Hemgesberg, D.M. Ohlmann, Y. Schmitt, M.R. Wolfe, M.K. Müller, B. Erb, Y. Sun, L.J. Gooßen, M. Gerhards, W.R. Thiel, Eur. J. Org. Chem. **2012**, 2142 (2012)
29. N. Kano, F. Komatsu, M. Yamamura, T. Kawashima, J. Am. Chem. Soc. **128**, 7097 (2006)
30. M. Unno, K. Kakiage, M. Yamamura, T. Kogure, T. Kyomen, M. Hanaya, Appl. Organomet. Chem. **24**, 247 (2010)
31. M. Yamamura, N. Kano, T. Kawashima, Inorg. Chem. **45**, 6497 (2006)
32. S.R. Zhai, I. Kim, C.S. Ha, J. Solid State Chem. **181**, 67 (2008)
33. M. Yamamura, N. Kano, T. Kawashima, J. Organomet. Chem. **692**, 313 (2007)
34. D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* (Academic Press, Cambridge, 1991), p. 197
35. H. Rau, S. Yu-Qua, J. Photochem. Photobiol. A Chem. **42**, 321 (1988)
36. A. Schaate, S. Dühnen, G. Platz, S. Lilienthal, A.M. Schneider, P. Behrens, Eur. J. Inorg. Chem. **2012**, 790 (2012)
37. M. Waki, N. Mizoshita, T. Tani, S. Inagaki, Angew. Chem. Int. Ed. **50**, 11667 (2011)
38. M. Alvaro, M. Benitez, D. Das, G. Garcia, E. Peris, Chem. Mater. **17**, 4958 (2005)
39. S. Fraysse, C. Coudret, J.-P. Launay, Eur. J. Inorg. Chem. **2000**, 1581 (2000)