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Mini review

Cross-coupling reactions in the chemistry of silole-containing π-conjugated oligomers and polymers

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Abstract

Various types of silole-containing π-conjugated oligomers and polymers, including the silole–pyrrole cooligomers, silole–diethynylarene copolymers, silole–arene alternating copolymers such as the silole–thiophene copolymer, and 2,5-diarylsiloles, have been synthesized by the combination of the new intramolecular reductive cyclization of bis(phenylethynyl)silanes with the well-established transition metal complex-catalyzed cross-coupling reactions. The silole-based π-electron systems thus prepared have unique photophysical properties due to the unusual electronic structure of the silole ring. Some of them have been applied as new materials for organic electroluminescent devices. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silole; Cross-coupling reaction; Reductive cyclization; UV–vis absorption spectra; Fluorescence spectra; Organic electroluminescent devices

1. Introduction

Silole (silacyclopentadiene) is an attractive building unit for new π-electron systems aimed at electronic and optoelectronic devices [1,2], because of its significantly low-lying LUMO due to the σ*–π* conjugation in the ring [3]. Considerable efforts have so far been devoted to the development of new silole-containing oligomers and polymers experimentally [4–8] as well as theoretically [9–14]. In the synthesis of silole-based π-electron systems, the most straightforward route to them may be the transition metal complex-catalyzed cross-coupling reactions using 2,5-difunctionalized siloles as the key precursors. However, only a few synthetic methodologies for the preparation of the functionalized siloles had been available in the literature before we started this chemistry [15]. In 1994, we developed a new and general synthetic route to the 2,5-difunctionalized siloles, which is the intramolecular reductive cyclization of the bis(phenylethynyl)silanes (**1**) using lithium naphthalenide, as shown in Scheme 1 [16]. This cyclization efficiently proceeds in the *endo–endo* mode to form 2,5-dilithiosilole (**2**), which can be further converted into a series of 2,5-difunctionalized siloles (**3**). By combination of this new cyclization method with the well-established cross-coupling reactions, we have developed several types of new silole-based π-electron systems [17]. This account describes our recent progress in this chemistry from a synthetic viewpoint.

2. The Kosugi–Migita–Stille coupling using 2,5-dibromosiloles

Among the 2,5-difuntionalized siloles prepared according to Scheme 1, while the 2,5-distannylated siloles (**3b**) exhibit no reactivity toward the Kosugi–Migita–Stille coupling [18] probably due to the steric hindrance by the phenyl groups at the 3,4-positions of the silole ring [16], the 2,5-dibomosiloles (**3a**) serve as good starting materials for this coupling reaction with arylstannanes. Based on the Kosugi–Migita–Stille coupling using **3a**, several types of silole π-electron systems such as silole–pyrrole cooligomers [19] and silole–diethynylarene copolymers [20] have been synthesized.

2.1. Silole–pyrrole cooligomers

The silole–pyrrole cooligomers are of interest as the π-conjugated systems consisting of the electron-accept-

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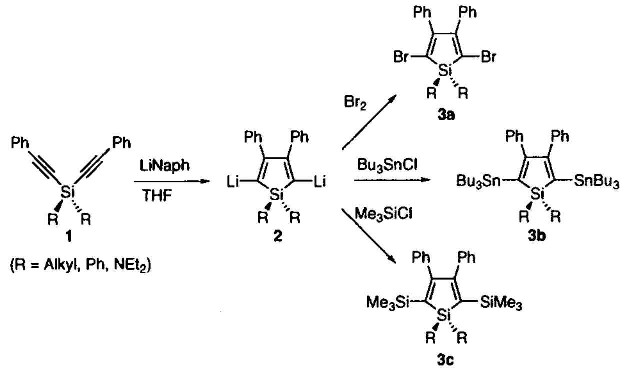
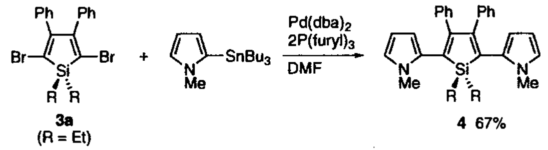
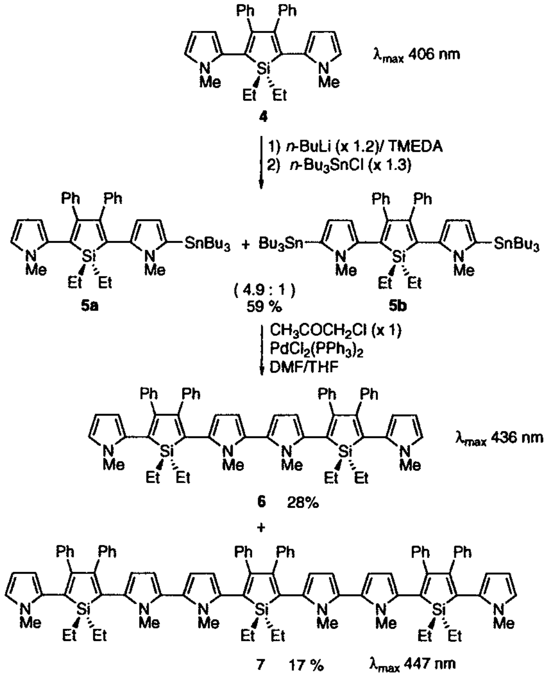
ing silole with the electron-donating pyrrole. As a prototype of this class of compounds, 2,5-dipyrrolylsilole (**4**) was prepared by the coupling reaction of 2,5-dibromosilole (**3a**) with *N*-methyl-2-tributylstannylpyrrole using the Pd(dba)$_2$–P(furyl)$_3$ catalyst system [21], as shown in Scheme 2 [19]. The more extended cooligomers, dimer **6** and trimer **7**, have been synthesized by the Pd(II)-catalyzed oxidative coupling of stannylated compounds **5** using chloroacetone as an oxidant [22], as shown in Scheme 3.



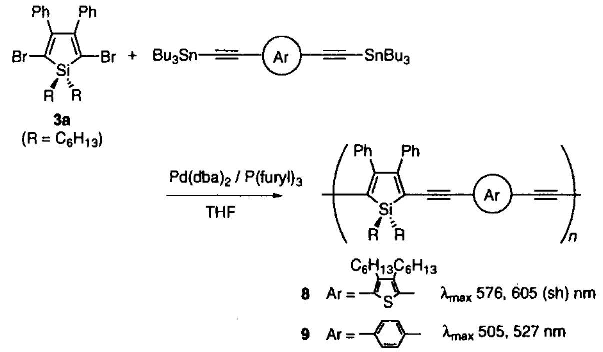
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

The X-ray crystallography has revealed that 2,5-dipyrrolylsilole (**4**) has a highly twisted conformation of the three pyrrole–silole–pyrrole rings (torsion angle, 51.7 and 55.7°) due to steric repulsion. Nevertheless, the absorption maximum of **4** (λ_{max}, 406 nm) is >130 nm longer than that of *N*,*N*′,*N*″-trimethylterpyrrole (λ_{max}, 271 nm) [23], suggesting its unusual electronic structure due to the combination of the silole with the pyrrole. However, the absorption maxima of the extended cooligomers **6** (λ_{max}, 436 nm) and **7** (λ_{max}, 447 nm) are only slightly longer than that of **4** due to the severe steric congestion along the main chain. According to the theoretical calculation, a coplanar silole–pyrrole alternating copolymer would have a low bandgap of 1.68 eV [13g].

2.2. *Silole–diethynylarene copolymers*

The silole–diethynylthiophene and silole–diethynylbenzene copolymers, **8** and **9**, have been synthesized by the coupling reaction of **3a** with the corresponding distannylated diethynylarenes, as shown in Scheme 4 [20]. Although acetylene-containing π-conjugated polymers generally have relatively large bandgaps [24], our polymers have their absorption maxima at significantly long wavelengths. For instance, the thiophene-containing polymer **8** has the longest absorption maximum (λ_{max} 576, 605(sh) nm) among the poly(ethynylenearylene)-type polymers reported to date. The bandgaps of **8** and **9** estimated from their absorption edges are 1.77 and 2.07 eV, respectively.

3. The Suzuki–Miyaura coupling using silolediboronic acids

3.1. *Synthesis of silole-2,5-diboronic acids*

For the development of the general synthetic route to the silole–arene alternating copolymers, it is essential to prepare an isolable but still reactive 2,5-difunctional ized silole as a key precursor. From this viewpoint, the 2,5-silolediboronic acid (**10**) has been newly prepared based on our cyclization reaction, as shown in Scheme 5 [25]. Thus, the 2,5-dilithiosilole (**2**) was allowed to react with $(Et_2N)_2BCl$ to produce the diborylsilole **11**, which was subsequently hydrolyzed to give the diboronic acid **10**. The diboronic acid exhibits high reactivity to the Suzuki–Miyaura coupling [26] and serve as a useful precursor for the silole–arene alternating copolymers as described below.

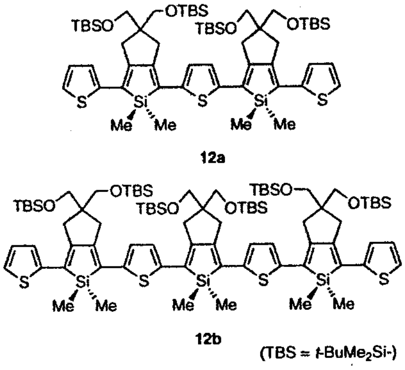
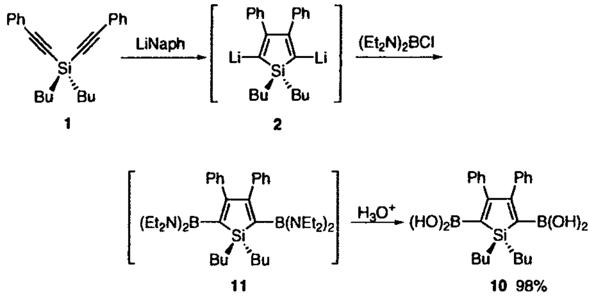


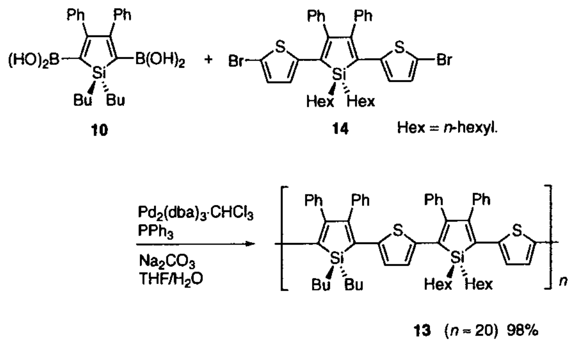
Chart 1.

3.2. Silole–thiophene alternating copolymers

We previously prepared a series of silole–thiophene copolymers with varying silole:thiophene ratios from 1:2 to 1:4 based on the Ni(0)-catalyzed cyclization of the corresponding diyne precursors with hydrodisilanes [27]. The 1:1 alternating cooligomers 12 up to only the 7-ring system (Chart 1) were similarly synthesized [27b]. With the 2,5-silolediboronic acid (**10**) available, the synthesis of the 1:1 alternating copolymer **13** has been achieved for the first time by the Suzuki–Miyaura coupling with 2,5-bis(bromothienyl)silole (**14**), as shown in Scheme 6 [25]. The use of the tri-ring compound **14** as a counter part was effective for obtaining the high molecular-weight polymer. This is a versatile method for the synthesis of a series of silole–arene alternating copolymers, such as the silole–phenylene, silole–pyridine, and silole–thiazole 1:1 alternating copolymers [28].

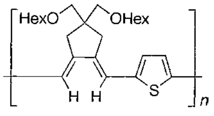


Scheme 5.



Scheme 6.

Silole–thiophene alternating copolymer **13** thus prepared shows an unusual UV–vis absorption spectrum with a considerably long absorption maximum [25]. The λ_{max} of the copolymer **13** (648 nm at 298 K) is >100 nm longer than that of a butadiene analog **15** (λ_{max} 538 nm) [29], suggesting the significant contribution of the silicon atoms to the π-conjugation of the polymer backbone. The bandgap of **13** determined from the λ_{0-0} bandedge is 1.55 eV, which is significantly small as a neutral and linear π-conjugated polymer consisting of 5-membered heteroarenes and well coincides with the theoretically predicted value [13f].



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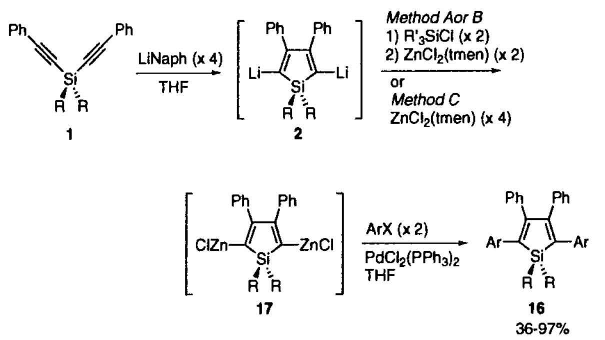
4. The Negishi coupling with 2,5-dizincated siloles

4.1. One-pot synthesis of 2,5-diarylsiloles

The combination of our cyclization method with the cross-coupling reaction is also very effective for the synthesis of the 2,5-diarylsilole derivatives. A series of 2,5-diarylsiloles (**16**) bearing various aryl groups as well as heteroaryl groups have been synthesized in one pot from the bis(phenylethynyl)silanes (**1**), as shown in Scheme 7 [30,31]. Thus, the intramolecular reductive cyclization of **1** followed by quenching of the remaining lithium naphthalenide with bulky chlorosilanes and/or direct treatment with $ZnCl_2(tmen)$ (tmen: N,N,N',N''-tetramethylethylenediamine) afforded the 2,5-dizincated siloles (**17**). The subsequent Negishi coupling [32] with the appropriate aryl bromides in the presence of a Pd catalyst gave the corresponding 2,5-diarylsiloles (**16**) in high yields. These results are summarized in Table 1. Although the 3,4-diphenyl groups are present as essential substituents, this is the first general synthetic route to the 2,5-diarylsilole derivatives. On the basis of this



Scheme 7.

Table 1
Results of the one-pot synthesis of 2,5-diarylsiloles

Compound	2,5-Aryl groups	Method [a]	Yield (%) [b]
16a	p-$(Me_2N)C_6H_4$	A	53
		C	97
16b	p-$MeOC_6H_4$	A	68
16c	p-MeC_6H_4	A	75
16d	C_6H_5	A	70
16e	p-$CF_3C_6H_4$	A	67
16f [c]	p-$(NO_2)C_6H_4$	A	36
		C	87
16g	m-MeC_6H_4	B	82
16h	m-FC_6H_4	A	81
16i	m-$CF_3C_6H_4$	B	67
16j	1-naphthyl	A	42
16k	2-styryl	A	82
16l	Biphenyl	A	74
16m	2-thienyl	A	82
		C	92
16n	Bithienyl	A	81
16o	2-thiazolyl	A	54
16p	2-pyridyl	B	62
16q [d]	3-pyridyl	A	58

Substituents at the 1,1-positions are methyl groups and the corresponding aryl bromides were used as an aryl halide for the coupling reaction, unless otherwise stated.

[a] The method for quenching of the remaining LiNaph and the subsequent transmetalation: A, (1) Ph_3SiCl (2 mol. amount); (2) $ZnCl_2(tmen)$ (2 mol. amount): B, (1) Bu^tPh_2SiCl (2 mol. amount); (2) $ZnCl_2(tmen)$ (2 mol. amount): C, $ZnCl_2(tmen)$ (4 mol. amount).

[b] Isolated yields.

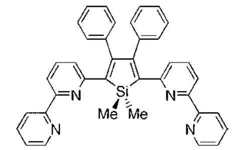
[c] p-$(NO_2)C_6H_4I$ was used.

[d] 1,1-Diisopropyl.

synthesis, the structure-photophysical property relationship for the 2,5-diarylsilole has been elucidated in detail for the first time [31].

4.2. Application to organic electroluminescent devices

The 2,5-diarylsiloles thus prepared have a great potential as new materials for organic electroluminescent (EL) devices, due to the unique electronic structure of the silole ring. In particular, 2,5-di(2-pyridyl)silole (**16p**) showed a very high performance as an electron-transporting (ET) material in our device with the ITO/TPD/Alq/**16p**/Mg:Ag configuration, where the triphenylamine dimer (TPD) and tris(8-quinolinolato)aluminum (Alq) were employed as the hole-transporting material and the emissive material, respectively, as shown in Fig. 1 [30]. The device emitted a greenish–yellow light from the Alq layer. The threshold applied voltage was about 3 V and the maximum luminance reached 12 000 cd m^{-2} at 10 V. The luminous efficiency at 100 cd m^{-2} was 1.9 lm W^{-1}. The electron-transporting ability of the dipyridylsilole **16p** exceeded that of Alq which was one of the best ET materials reported so far. Recently, further structural optimization has revealed that a bis(bipyridyl) analog **18** has a better performance in terms of the power efficiency as well as the longevity [33,34].



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2,5-Diarylsiloles can also be applied as efficient emissive materials and the wavelengths of their luminescence are widely tunable by changing the 2,5-aryl groups, as shown in Fig. 2 [30]. Thus, in the devices having the ITO/TPD/2,5-diarylsilole/Mg:Ag configuration, three types of silole derivatives, the m-tolyl derivative **16g**, the thienyl derivative **19**, and the bithienyl derivative **16n** worked as emissive ET materials, emitting greenish–blue, yellowish–green, and reddish–orange light, respectively. Notably, a significant red shift in the emission wavelength about 100 nm from the m-tolyl derivative **16g** to the bithienyl derivative **16n** suggests widely tunable emission colors, from blue to

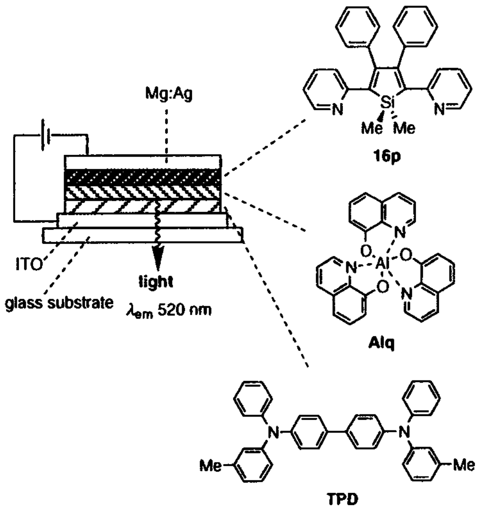


Fig. 1. Organic EL device using 2,5-di(2-pyridyl)silole (**16p**), Alq, and TPD as electron-transporting, emissive, and hole-transporting materials, respectively.

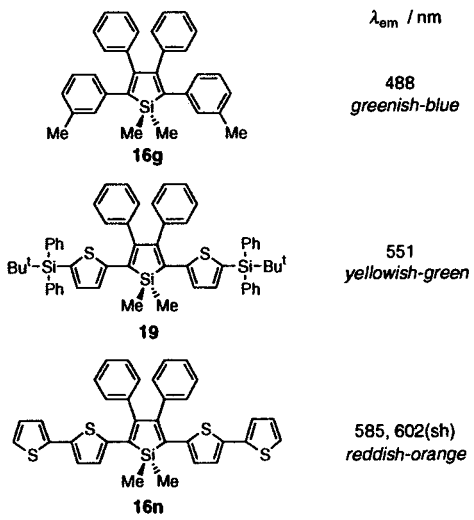
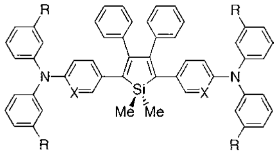


Fig. 2. Emission wavelengths of organic EL devices using 2,5-diarylsiloles as emissive electron-transporting materials: device configuration; ITO/TPD/2,5-diarylsilole/Mg:Ag.

red, only by modification of the 2,5-aryl groups on the silole ring. Advantageously, this structural modification can be readily achieved by our one-pot synthesis shown in Scheme 7. Recently, a new series of 2,5-diarylsiloles (**20**) with triphenylamine moieties have also been synthesized based on the present synthetic methodology for application to single-layer organic EL devices [35].



20a (X = CH, R = Me)
20b (X = N, R = H)

5. Conclusion

The combination of our new silole cyclization method with the well-established various types of cross-coupling reactions has proven to be very powerful. In fact, based on these methodologies, we have succeeded in the synthesis of a variety of silole-containing π-conjugated oligomers and polymers. The silole π-electron systems thus prepared have unique photophysical properties due to the unusual electronic structure of the silole ring. In addition, some silole π-electron systems show great potential as new materials for optoelectronics such as organic EL devices.

Acknowledgements

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References

[1] (a) S. Yamaguchi, K. Tamao, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Vol. 3, John Wiley & Sons, Chichester, 2001, pp, 647–694;
(b) S. Yamaguchi, K. Tamao, in: D. Jones, W. Ando, J. Chojnowski (Eds.), Silicon-containing Polymers: The Science and Technology of their Synthesis and Applications, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000, pp. 461–498.

[2] Recent Reviews for the Silole Chemistry: (a) J. Dubac, A. Laporterie, G. Manuel, Chem. Rev. 90 (1990) 215.
(b) E. Colomer, R.J.P. Corriu, M. Lheureux, Chem. Rev. 90 (1990) 265.
(c) J. Hermanns, B. Schmidt, J. Chem. Soc. Perkin Trans. 1 (1998) 2209.
(d) J. Dubac, C. Guerin, P. Meunier, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Vol. 2, John Wiley & Sons, 1999, Chapter 34.

[3] S. Yamaguchi, K. Tamao, Bull. Chem. Soc. Jpn. 69 (1996) 2327.

[4] (a) J. Shinar, S. Ijadi-Maghsoodi, Q.-X. Ni, Y. Pang, T.J. Barton, Synth. Met. 28 (1989) C593;
(b) T.J. Barton, S. Ijadi-Maghsoodi, Y. Pang, Macromolecules 24 (1991) 1257.

[5] W. Chen, S. Ijadi-Maghsoodi, T.J. Barton, Polym. Prepr. 38 (1997) 189.

[6] (a) E. Toyoda, A. Kunai, M. Ishikawa, Organometallics 14 (1995) 1089;
(b) A. Kunai, T. Ueda, K. Horata, E. Toyoda, J. Ohshita, M. Ishikawa, K. Tanaka, Organometallics 15 (1996) 2000;
(c) J. Ohshita, N. Mimura, H. Arase, M. Nodono, A. Kunai, K. Komaguchi, M. Shiotani, Macromolecules 31 (1998) 7985;
(d) J. Ohshita, M. Nodono, T. Watanabe, Y. Ueno, A. Kunai, Y. Harima, K. Yamashita, M. Ishikawa, J. Organomet. Chem. 553 (1998) 487;
(e) A. Adachi, J. Ohshita, A. Kunai, J. Kido, K. Okita, Chem. Lett. (1998) 1233;
(f) J. Ohshita, T. Hamaguchi, E. Toyoda, A. Kunai, K. Komaguchi, M. Shiotani, M. Ishikawa, A. Naka, Organometallics 18 (1999) 1717;
(g) J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita, M. Ishikawa, Organometallics 18 (1999) 1453.

[7] Silole σ-Conjugated Systems: (a) S. Yamaguchi, R.-Z. Jin, K. Tamao, M. Shiro, Organometallics 16 (1997) 2486.
(b) K. Kanno, M. Ichinohe, C. Kabuto, M. Kira, Chem. Lett. (1998) 99.
(c) H. Sohn, R. Huddleston, D.R. Powell, R. West, K. Oka, X. Yonghua, J. Am. Chem. Soc. 121 (1999) 2935.
(d) S. Yamaguchi, R.-Z. Jin, K. Tamao, J. Am. Chem. Soc. 121 (1999) 2937.
(e) Y. Xu, T. Fujino, H. Naito, T. Dohmaru, K. Oka, H. Sohn, R. West, Jpn. J. Appl. Phys. 38 (1999) 6915.
(f) B.P.S. Chauhan, T. Shimizu, M. Tanaka, Chem. Lett. (1997) 785.
(g) T. Sanji, T. Sakai, C. Kabuto, H. Sakurai, J. Am. Chem. Soc. 120 (1998) 4552.

[8] (a) J.L. Bréfort, R.J.P. Corriu, P. Gerbier, C. Guérin, B.J.L. Henner, A. Jean, T. Kuhlmann, F. Garnier, A. Yassar, Organometallics 11 (1992) 2500;
(b) R.J.P. Corriu, N. Devylder, C. Guérin, B. Henner, A. Jean, Organometallics 13 (1994) 3194;
(c) R.J.P. Corriu, W.E. Douglas, Z.-X Yang, F. Garnier, A. Yassar, J. Organomet. Chem. 417 (1991) C50;
(d) R.J.P. Corriu, W.E. Douglas, Z.-X. Yang, J. Organomet. Chem. 456 (1993) 35.

[9] (a) G. Frapper, M. Kertész, Organometallics 11 (1992) 3178;
(b) G. Frapper, M. Kertész, Synth. Met. 55–57 (1993) 4255;
(c) J. Kürti, P.R. Surján, M. Kertész, G. Frapper, Synth. Met. 55–57 (1993) 4338.

[10] (a) K.S. Wong, S.G. Han, Z.V. Vardeny, J. Shinar, Y. Pang, S. Ijadi-Maghsoodi, T.J. Barton, S. Grigoras, B. Parbhoo, Appl. Phys. Lett. 58 (1991) 1695;
(b) X. Wei, S.G. Han, K.S. Wong, B.C. Hess, L.X. Zheng, Z.V. Vardeny, Q.-X. Ni, J. Shinar, Y. Pang, S. Ijadi-Maghsoodi, T.J. Barton, S. Grigoras, Synth. Met. 41–43 (1991) 1583;
(c) S. Grigoras, G.C. Lie, T.J. Barton, S. Ijadi-Maghsoodi, Y. Pang, J. Shinar, Z.V. Vardeny, K.S. Wong, S.G. Han, Synth. Met. 49–50 (1992) 293;
(d) M. Liess, S. Jeglinski, P.A. Lane, Z.V. Vardeny, Synth. Met. 84 (1997) 891;
(e) M. Liess, S. Jeglinski, Z.V. Vardeny, M. Ozaki, K. Yoshino, Y. Ding, T. Barton, Phys. Rev. B 56 (1997) 15712.

[11] (a) Y. Yamaguchi, J. Shioya, Mol. Eng. 2 (1993) 339;
(b) Y. Yamaguchi, Mol. Eng. 3 (1994) 311;
(c) Y. Yamaguchi, T. Yamabe, Int. J. Quantum Chem. 57 (1996) 73;
(d) Y. Yamaguchi, Synth. Met. 82 (1996) 149.

[12] (a) Y. Matsuzaki, M. Nakano, K. Yamaguchi, K. Tanaka, T. Yamabe, Synth. Met. 71 (1995) 1737;
(b) Y. Matsuzaki, M. Nakano, K. Yamaguchi, K. Tanaka, T. Yamabe, Chem. Phys. Lett. 263 (1996) 119.

[13] (a) S.Y. Hong, D.S. Marynick, Macromolecules 28 (1995) 4991;
(b) S.Y. Hong, S.J. Kwon, S.C. Kim, J. Chem. Phys. 103 (1995) 1871;
(c) S.Y. Hong, Bull. Korean. Chem. Soc. 16 (1995) 845;
(d) S.Y. Hong, S.J. Kwon, S.C. Kim, D.S. Marynick, Synth. Met. 69 (1995) 701;
(e) S.Y. Hong, S.J. Kwon, S.C. Kim, J. Chem. Phys. 104 (1996) 1140;
(f) S.Y. Hong, J.M. Song, Synth. Met. 85 (1997) 1113;
(g) S.Y. Hong, J.M. Song, Chem. Mater. 9 (1997) 297.

[14] U. Salzner, J.B. Lagowski, P.G. Pickup, R.A. Poirier, Synth. Met 96 (1998) 177.

[15] (a) B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (1986) 397;
(b) B. Wrackmeyer, J. Organomet. Chem. 310 (1986) 151;
(c) R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, Chem. Ber. 126 (1993) 1107;
(d) B. Wrackmeyer, G. Kehr, J. Süß, Chem. Ber. 126 (1993) 2221.

[16] K. Tamao, S. Yamaguchi, M. Shiro, J. Am. Chem. Soc. 116 (1994) 11715.

[17] (a) K. Tamao, S. Yamaguchi, M. Uchida, T. Izumizawa, K. Furukawa, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry IV. From Molecules to Materials, Wiley-VCH Verlag GmbH, Weinheim, 2000, pp. 245–251;
(b) S. Yamaguchi, K. Tamao, J. Chem. Soc. Dalton Trans. (1998) 3693;
(c) K. Tamao, S. Yamaguchi, Pure Appl. Chem. 68 (1996) 139;
(d) K. Tamao, S. Yamaguchi, J. Organomet. Chem. 611 (2000) 5.

[18] (a) M. Kosugi, Y. Shimizu, T. Migita, Chem. Lett. (1977) 1423;
(b) J.K. Stille, Angew. Chem. Int. Ed. Engl. 25 (1986) 508.

[19] K. Tamao, S. Ohno, S. Yamaguchi, Chem. Commun. (1996) 1873.

[20] S. Yamaguchi, K. Iimura, K. Tamao, Chem. Lett. (1998) 89.

[21] (a) V. Farina, B. Krishnan, J. Am. Chem. Soc. 113 (1991) 9585;
(b) N.G. Andersen, B.A. Keay, Chem. Rev. 101 (2001) 997.

[22] (a) Y. Shinya, A. Takata, K. Kawaguchi, K. Kikukawa, 65th Annual Meetings of the Chemical Society of Japan, Tokyo, March 1993, 1E441;
(b) S. Yamaguchi, S. Ohno, K. Tamao, Synlett (1997) 1199.

[23] T. Kauffmann, L. Hexy, Chem. Ber. 114 (1981) 3674.

[24] U.H.F. Bunz, Chem. Rev. 100 (2000) 1605.

[25] S. Yamaguchi, T. Goto, K. Tamao, Angew. Chem. Int. Ed. 39 (2000) 1695.

[26] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.

[27] (a) K. Tamao, S. Yamaguchi, M. Shiozaki, Y. Nakagawa, Y. Ito, J. Am. Chem. Soc. 114 (1992) 5867;
(b) K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, M. Fukushima, S. Mori, Macromolecules 28 (1995) 8668.

[28] S. Yamaguchi, T. Goto, K. Tamao, manuscript under preparation.

[29] B.L. Lucht, T.D. Tilley, Chem. Commun. (1998) 1645.

[30] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, J. Am. Chem. Soc. 118 (1996) 11974.

[31] S. Yamaguchi, T. Endo, K. Tamao, Chem. Eur. J. 6 (2000) 1684.

[32] (a) E. Negishi, F.T. Luo, R. Frisbee, H. Matsushita, Heterocycles 18 (1982) 117;
(b) A. Minato, K. Suzuki, K. Tamao, M. Kumada, J. Chem. Soc. Chem. Commun. (1984) 511.

[33] M. Uchida, T. Izumizawa, T. Nakano, S. Yamaguchi, K. Tamao, K. Furukawa, Chem. Mater. 13 (2001) 268.

[34] H. Murata, G.G. Malliaras, M. Uchida, Y. Shen, Z.H. Kafafi., Chem. Phys. Lett. (2001) 161.

[35] S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, Chem. Lett. (2001) 98.