Highlight Review

A Key Role of Orbital Interaction in the Main Group Element-containing π-Electron Systems

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(Received July 20, 2004; CL-048010)

Abstract

Various types of main group element-containing π-electron systems have been synthesized using silole, dibenzoborole, or bis-silicon-bridged stilbene as the key building units. In these π-electron systems, the orbital interaction between the main group element moiety and the π-conjugated framework, such as p_{π}–π^* and σ^*–π^* conjugation, plays a crucial role in determining their characteristic electronic structures and makes them promising materials for applications in organic electronics and optoelectronics.

◆ Introduction

The progress in organic electronics and optoelectronics, such as organic thin film transistors and light emitting diodes (LEDs), highly relies on the development of new π-conjugated oligomeric and polymeric materials. One crucial issue in their molecular designs is how to tune their electronic structures in order to produce desirable photophysical and electronic properties. In this regard, increasing attention has recently been paid to the main group element-containing π-electron systems,[1] wherein the orbital interaction between the main group element moiety with the π-conjugated framework plays a crucial role in producing varied electronic structures.[2–5] For example, as shown in Figure 1, in the boron-containing 5-membered cyclic diene, the borole skeleton, the orbital interaction between the vacant p orbital of the boron atom with the π^* orbital of the butadiene moiety effectively occurs, giving rise to a significant low-lying LUMO. Similarly, in its silicon analogue, the silole skeleton, the σ^*–π^* conjugation between the σ^* orbital of the exocyclic two σ bonds on the silicon atom with the π^* orbital of the butadiene moiety decreases its LUMO energy level.[2] These element effects can also be seen in the extended π-conjugated systems. Figure 2 shows the calculation results, reported by Saltzner and co-workers, about polyheteroles having various main group elements.[3] The calculations suggest that their electronic structures are highly dependent on the main group element to be incorporated. In particular, polyborole and polysilole have significantly low-lying LUMOs. Thus, these electronic perturbations by the main group elements are a very powerful way to modulate the nature of the π-conjugated systems. Exploiting these orbital interactions as the guiding principles in the molecular designs, we have synthesized various types of main group element-containing π-conjugated systems. This short account describes our recent progress in this field, focusing attention on the development of new synthetic methodologies for them as well

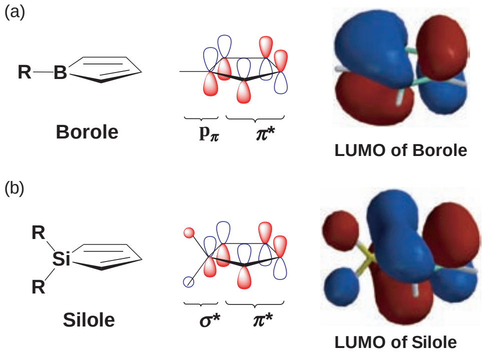

Figure 1. Schematic and graphical drawings of the orbital interaction in the LUMOs of (a) borole and (b) silole rings. The graphical drawings are based on the calculations at the HF/6-31G(d) level of theory.

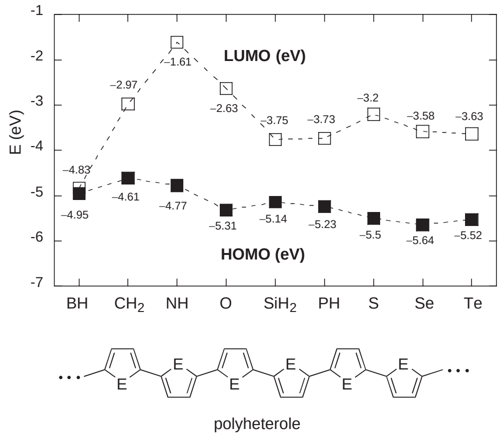

Figure 2. Calculated electronic structures of parent polyheteroles: the data taken from U. Salzner, J. B. Lagowski, P. G. Pickup, and R. A. Poirier, *Synth. Met.*, **96**, 177 (1998).

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as the effects of the main group elements on their photophyiscal properties.

Key Molecular Designs

A key point of our molecular design is to employ the main group element-containing 5-membered cyclic diene (heterole) as the basic skeleton. In the LUMO of the ring skeleton, the orbital of the main group element moiety, such as the above mentioned vacant p orbital of the boron atom or σ^* orbital of the silicon moiety, is fixed parallel to the π^* orbital of the butadiene framework with orbital symmetry in-phase to each other.[7] This perfect structural demand causes an effective interaction between each other, resulting in a decrease of the LUMO level. Notably, the tuning of the LUMO level is a currently important issue in the designs of electron-accepting n-type organic semiconductors.[6] On the basis of this consideration, we employed three types of 5-membered ring frameworks as the building units. They include the heterole itself, dibenzoheterole, and element-bridged stilbene, as shown in Figure 3.

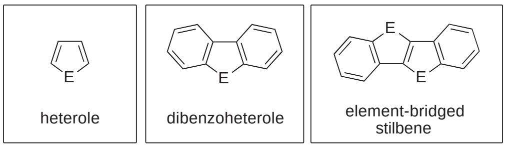
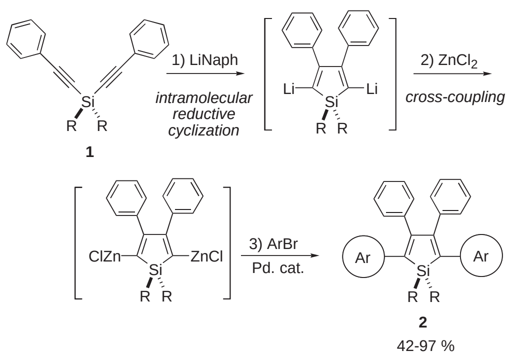


Figure 3. Key building units consisting of 5-membered cyclic diene skeletons.

Silole-based π-Electron Systems

As the heterole ring system, we have so far devoted considerable efforts to the synthesis of various types of silole-based π-electron systems, represented by the 2,5-diarylsiloles,[7] oligo- and poly(2,5-silole)s,[8] silole-containing cooligomers, and copolymers with other types of monomer units,[9] and silicon-catenating poly(1,1-silole)s.[10] While the details of this chemistry have been covered in previously published reviews,[11] it may be emphasized here that the synthesis of all these systems has been achieved based on an intramolecular reductive cyclization of the bis(phenylethynyl)silanes **1**,[8a] as shown in Scheme 1. For example, the combination of the cyclization with the cross-coupling reaction allows us to synthesize a series of 2,5-diarylsilole derivatives **2** in one pot from **1**.[7]

The silole-based π-electron systems have currently attracted significant attention as new materials for the organic LEDs. In 1996, we showed the utilization of 2,5-diarylsiloles in organic LEDs for the first time.[12] While several silole derivatives were examined, 2,5-dipyridylsilole **3** (Figure 4) exhibited an extremely high performance as an electron-transporting material. Its performance exceeds that of the aluminum-quinorinol complex Alq_3, which is one of the most widely used electron-transporting materials.[12] We further optimized the structure and found that its bipyridyl derivative **4** has a superior performance to that of **3** in terms of both the electron-transporting ability and the stability of the device.[13] Recently, Murata and co-workers indeed demonstrated its high electron mobility of $2.0 \times 10^{-4}\,cm^2V^{-1}s^{-1}$, which is two orders of magnitude higher than that of Alq_3.[14] The elucidation of the origin of the high performance of **4** is still a continuous topic in this chemistry,[15] together with the synthesis of new silole derivatives[16–19] as well as their unique photophysical properties such as strong fluorescence in the solid state.[20]



Scheme 1.

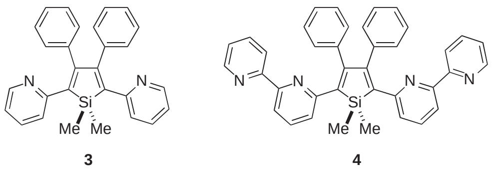


Figure 4. Silole-based excellent electron-transporting materials.

Dibenzoborole-containing π-Electron Systems

Among the dibenzoheterole ring systems, we focused our attention on the dibenzoborole skeleton, which is a group 13 boron analogue of fluorene and carbazole. While both the fluorene and carbazole currently represent core building units for highly fluorescent emitting materials[21] and hole-transporting materials,[22] respectively, there has been no example to employ the dibenzoborole skeleton as a building unit for the extended π-electron systems, when we started this chemsitry. From the viewpoint of application of the dibenzoborole skeleton in organic electronics, worthy of note is its charactristic electronic structure, which is quite different from those of fluorene and carbazole. Our preliminary calculations (Figure 5) suggest that, while the HOMO level of the dibenzoborole is comparable to that of fluorene or slightly lower than carbazole, its LUMO level is significantly lower than those of fluorene and carbazole by more than 1.2 eV. This is apparently attributable to the contribution of the p_π–π^* conjugation in the dibenzoborole skeleton between the vacant p orbital of the boron atom and the π^* orbital of the biphenyl moiety. This unique electronic structure of the dibenzoborole skeleton makes it a promising candidate as a new building unit for electron-transporting materials. A recent calculation of the polydibenzoborole, reported by Brière and Côté, also suggests an interesting electronic structure such as a low-lying LUMO energy level and thus a low bandgap for the polymeric conjugated systems.[23]

Experimentally, we have recently achieved the first synthesis of a series of dibenzoborole-based π-conjugated systems using 3,7-dihalogenated dibenzoboroles **6** as the key precursor.[24] Our molecular design relied on the following two points. First, in order to overcome the inherent instability of the boron com-

Published on the web (Advance View) November 27, 2004; DOI 10.1246/cl.2005.2

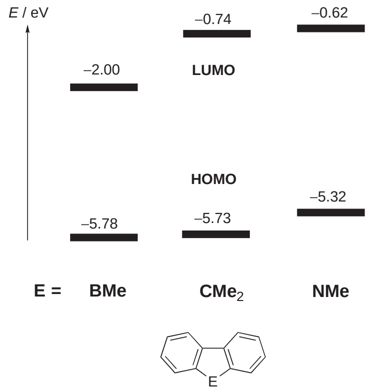
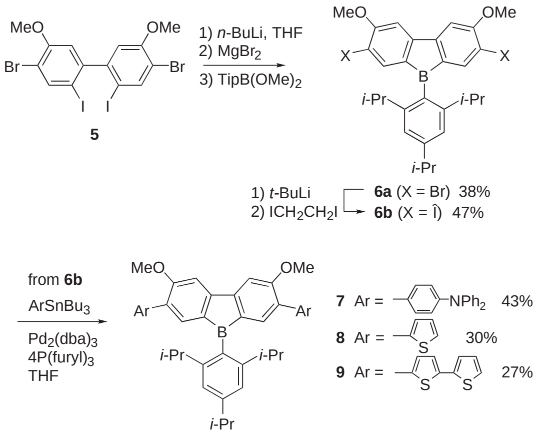
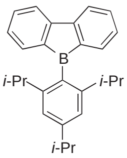


Figure 5. Kohn–Sham HOMO and LUMO energy levels of the dibenzoheteroles calculated at the B3LYP/6-31G(d) level of theory.



Scheme 2.

pounds, we introduced a bulky 2,4,6-triisopropylphenyl (Tip) group onto the boron atom. Second, we incorporated methoxy groups at the 2,8 positions of the skeleton for the facile introduction of functional groups onto the 3,7 positions. As shown in Scheme 2, compound **6a** was synthesized by the dimetalation of 4,4′-dibromo-2,2′-diiodobiphenyl **5**, prepared by the bromination of the corresponding 2,2′-diiodobiphenyl, followed by the reaction with $TipB(OMe)_2$. After the transformation from **6a** to **6b** via *ortho*-lithiation with *t*-BuLi, the Kosugi–Migita–Stille coupling of **6b** with various arylstannanes produced a series of extended dibenzoborole π-electron systems **7**–**9**. All the produced dibenzoborole derivatives have a substantial stability in air due to the kinetic stabilization by the bulky Tip group and can be handled without special care.



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The elucidation of the fundamental properties of the parent dibenzoborole is important to understand the intrinsic nature of this skeleton. In THF, compound **10** shows a characteristic weak shoulder absorption band at 410 nm (log ε, 2.39) in the UV–vis spectrum and exhibits a green fluorescence at 514 nm with a low quantum yield of 0.09. The large Stokes shift (≈100 nm) and the significantly longer emission maximum compared to those of fluorene (λ_{em} 314 nm) and carbazole (λ_{em} 349 nm)[25] are particularly noteworthy, suggesting the significant contribution of the boron vacant p orbital to the electronic structure. Actually, the shoulder absorption band of **10** can be ascribed to the transition from the HOMO delocalized over the biphenyl moiety to the LUMO delocalized over the dibenzoborole skeleton through the p_π–π^* conjugation.

On the basis of the unique nature of the dibenzoborole skeleton, the extended systems **7**–**9** also show characteristic absorption and emission spectra (Figure 6a). In THF, while these compounds have weak absorption bands around 480–505 nm, they show yellow to orange emissions around 550–575 nm with low quantum yields of 0.02–0.04. The large red shifts in their absorption and emission maxima relative to that of **10** suggest the effective extension of the π-conjugation.

Notably, the fluorescence properties of these compounds are highly dependent on the solvent. Thus, in donor solvents such as DMF, the emission bands observed in THF completely disappear and new intense blue emission bands appear around 420–480 nm, whose quantum yields are dramatically increased to about 0.5–0.9. Thus, about 100–140 nm blue shifts and 20–30 fold increments in the quantum yields are observed by changing the solvent from THF to DMF. Figure 6b shows the visual changes in their fluorescence depending on the solvents. This significant solvatochromism can be rationalized owing to the coordination of the donor solvent to the boron atom, which turns off the p_π–π^* conjugation in the LUMO and increases the HOMO–LUMO gap, resulting in the blue shift of the emission. On the basis of these observations, we have applied this class of compounds as new chemosensors for the fluoride ion, wherein the binding event of the fluoride ion by the formation of the corresponding borate complex induces a similar change in the fluorescence spectra.[26]

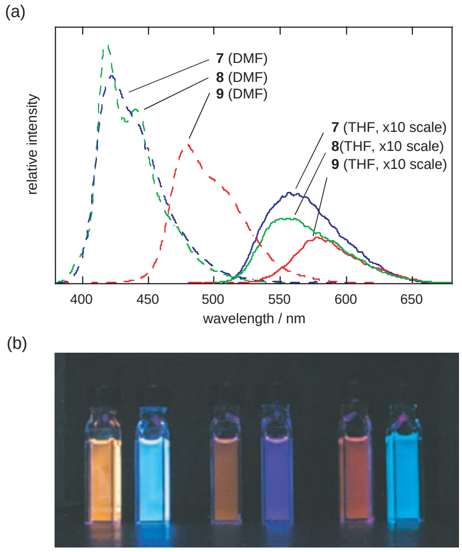


Figure 6. Solvent-dependent fluorescence of **7**–**9**: (a) fluorescence spectra and (b) a photo of their solutions under irradiation of 365-nm black light: from left to right, **7** in THF and DMF, **8** in THF and DMF, **9**, in THF and DMF (ca. 1 mM).

The fact that the donor solvent or the fluoride ion can coordinate to the boron atom may suggest the incomplete steric protection of the ring boron atom by the 2,4,6-triisopropylphenyl group. However, it is important to note that this steric protection is effective enough to stabilize the reduced state. Thus, in the cyclic voltammetry measurements, we found that compound **10** showed a nice reversible redox process with a reduction potential at $-2.10\,\mathrm{V}$ (vs Ferrocene/Ferrocene$^+$). The high stability of the reduced state as well as the low reduction potential are the primary requisites for the electron-transporting materials. The present preliminary result indicates the significant potential of the dibenzoborole skeleton as the key building unit for electron-transporting materials. The application of the series of dibenzoborole compounds to organic LEDs is now under investigation.

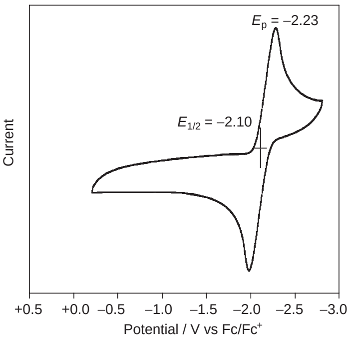
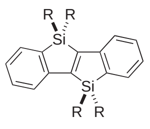


Figure 7. Cyclic voltammogram of compound **10** (1 mM) in THF containing $Bu_4N^+ClO_4^-$ (0.1 M) with scan rate of $100\,\mathrm{mV\,s^{-1}}$.

◆ Bis-silicon-bridged Stilbenes

Our third key building unit is the bis-silicon-bridged stilbene (5,10-dihydro-5,10-disilaindeno[2,1-*a*]indene) skeleton **11**, which is a silicon analogue of the methylene-bridged stilbene **12**. In general, the annelation of the π-conjugated framework with certain bridging moieties is an effective way to enhance the π-conjugation, which provides a rigid planar structure without conformational disorder, leading to a set of desirable properties such as a strong luminescent property and a high charge career mobility. One typical example is that of **12**. While *trans*-stilbene only shows a weak fluorescence ($\Phi_F \approx 0.05$) at ambient temperature, the fluorescence quantum yield of **12** (R = H) approaches almost unity.[27] In the bis-silicon-bridged stilbene, it is expected that the silicon-bridges would not only stiffen the coplanar structure but also contribute to the electronic structure through an orbital interaction, as seen in the silole chemistry.



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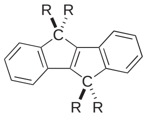
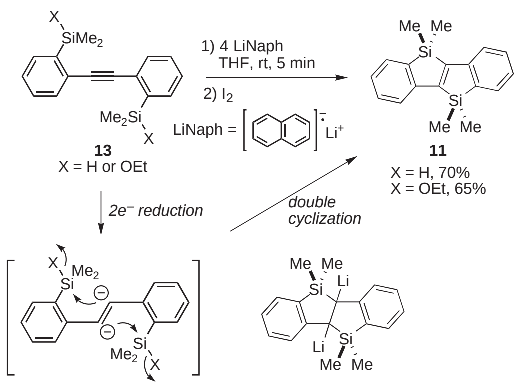


12

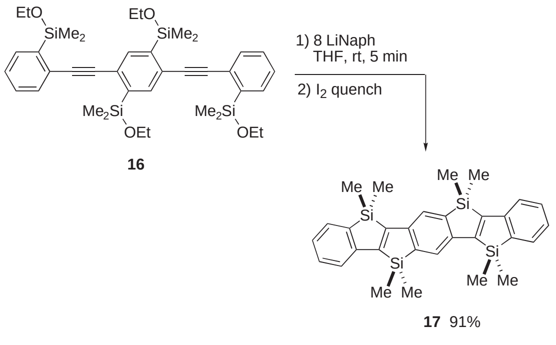


Scheme 3.

One of the challenges in this chemistry is how to efficiently produce this skeleton. While the carbon analogues **12** are known compounds, the lack of generality in their conventional synthesis limits their utility as a building unit.[28] For the silicon analogue, the first synthesis of compound **11** (R = Me) was achieved by Barton and co-workers on the basis of the thermal or photo rearrangement of the 5,6-disiladibenzo[*c*,*g*]cyclooctynes.[29] They also synthesized some attractive polymeric systems bearing this skeleton as a pendant group.[30] We independently investigated the synthetic method of this skeleton and have recently developed a new efficient intramolecular reductive double cyclization, as shown in Scheme 3.[31]

Our reaction is based on a very simple procedure, that is, the treatment of bis(*o*-silylphenyl)acetylene derivatives **13** with a reducing agent such as lithium naphthalenide (LiNaph). Under this condition, the two-electron reduction on the acetylene moiety formally produces a dianionic intermediate **14**, which undergoes a subsequent double cyclization to give the desired product **11**. The key point of this procedure is the quenching of the reaction mixture with iodine. The over-reduction of the produced stilbene derivatives **11** is an inevitable side reaction for the present reaction, because the stilbene derivatives have lower reduction potentials than those of the starting acetylene compounds. In this regard, the use of iodine efficiently reoxidizes the over-reduced dilithiated product **15** to regenerate the desired stilbene products. The choice of the leaving group on the silicon atom is another important point in this reaction. The Si–H or Si–OR functionalities are our choice, because these groups are generally inert toward LiNaph which we used as a reducing agent.

Notably, the present cyclization is more effective for the preparation of the extended homologue **17**, as shown in Scheme 4. Thus, upon treatment of the diacetylenic compound **16** with excess LiNaph at room temperature, the intramolecular reductive double cyclization proceeded at the two acetylene moieties to afford the *tetrakis-silicon-bridged* derivative **17** in



Scheme 4.

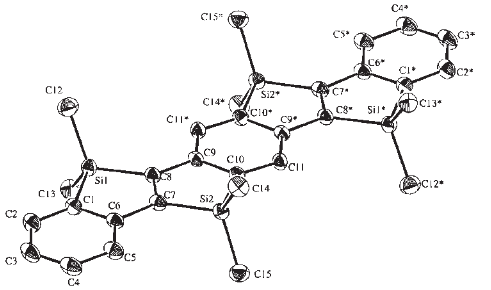
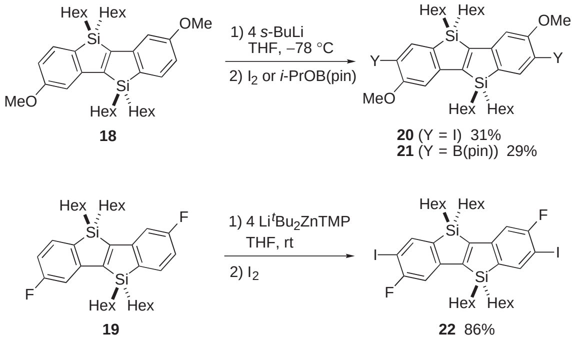


Figure 8. ORTEP drawing of **17** (50% probability for thermal ellipsoids).



Scheme 5.

91% yield as a bright yellow solid. The X-ray crystallographic analysis of **17** proved its nearly coplanar structure due to the tetrakis-silicon bridges, as shown in Figure 8.

In order to employ the bis-silicon-bridged stilbene as a building unit, it is essential to introduce certain functional groups such as halogens or metal functionalities required for the further cross-coupling reactions. By incorporation of *ortho*-directing groups, such as OMe or F, on the 3,8 positions of the skeleton, a variety of functional groups can be introduced onto the 2,7 positions via the *ortho*-metalation.[32] Advantageously, the present cyclization readily affords the 3,8-dimethoxy or difluoro derivatives, **18** and **19**, respectively. After the screening of bases, we found that the *ortho*-metalation of **18** with *sec*-BuLi, or of **19** with Li^{t}Bu$_2$ZnTMP (TMP: tetramethylpiperidine),[33] followed by treatment with appropriate electrophiles successfully gave the corresponding diiodides and diboronic esters **20**–**22**, as shown in Scheme 5. With these functionalized derivatives in hand, various types of polymeric materials, including the stilbene homopolymer **23** and copolymers **24**–**26**, have been synthesized by the cross-coupling methodologies (Figure 9).[32]

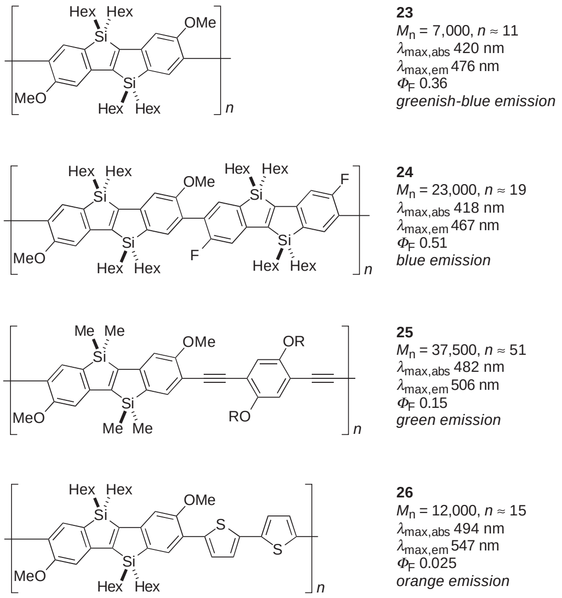


Figure 9. The structures of the synthesized bis-silicon-bridged stilbene-containing homopolymers and copolymers and their photopysical properties in THF.

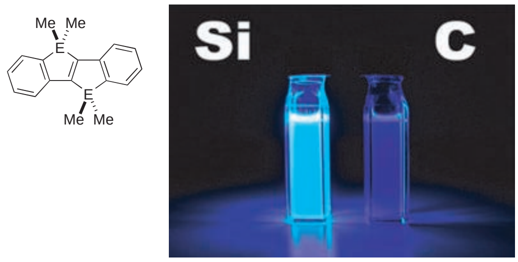


Figure 10. Photo of the THF solutions of **11** (left) and **12** (right) under the irradiation of black light (365 nm).

In the photophysical properties, a comparison between the bis-silicon-bridged stilbene **11** (R = Me) and its carbon analogue **12** (R = Me) shows a clear-cut effect of the silicon bridges. Thus, in THF, the silicon-bridged one **11** has its absorption maximum at 360 nm and emission maximum at 428 nm, which are longer by 38 and 64 nm, respectively, than those of the carbon analogue **12** ($\lambda_{\rm max,abs}$ 322 nm, $\lambda_{\rm max,em}$ 367 nm), although the fluorescence quantum yield decreases from 0.92 for **12** to 0.58 for **11**. As the consequence of this substantial red shift, the silicon analogue shows an intense blue emission, whereas **12** does not show a fluorescence in the visible region, as shown in Figure 10. The molecular orbital calculations of these two compounds proved that the origin of their difference is due to the lower-lying LUMO of the silicon analogue. Thus, **11** has a 0.55 eV lower LUMO than that of the carbon analogue, and the orbital interaction with the silicon moieties and stilbene framework plays an important role to lower the LUMO level.

The π-conjugated polymers listed in Figure 9 also shows moderate to intense fluorescence in the visible region. Their emission colors vary from blue to orange, dependent on the nature of the π-conjugated frameworks, suggesting the readily accessible color tuning over a wide range.

◆ *Summary and Outlook*

Exploiting the orbital interaction between the main group element moiety and the π-conjugated framework in the heterole-based ring systems as a guiding principle in the molecular designs, we have developed a variety of new π-electron systems containing silole, dibenzoborole, and bis-silicon-bridged stilbene as the key building units. It is particularly noteworthy that some of the silole derivatives indeed show considerably high performances as electron-transporting materials for organic LEDs. In the dibenzoborole systems, not only the significant contribution of the p_π–π^* conjugation to the electronic structure but also their great potential as the building unit for the electron-transporting materials have been experimentally demonstrated. In the chemistry of the bis-silicon-bridged stilbene systems, the synthetic methodology for them has been well established based on the newly developed intramolecular reductive cyclization. Although we have not yet fully investigated their applicability to organic electronics, the fundamental studies of their photophysical properties reveal the substantial silicon effects on the electronic structures. All these results demonstrate the effectiveness of the present approach in the designs of new π-electron systems. We believe that further studies along this line will lead to the creation of truly excellent functional materials.

References and Notes

1 For recent reviews, see: a) C. D. Entwistle and T. B. Marder, *Angew. Chem., Int. Ed.*, **41**, 2927 (2002). b) S. Yamaguchi and K. Tamao, in "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, John Wiley & Sons, Chichester (2001), Vol. 3, Chap. 11, pp 641–694. c) M. Hissler, P. W. Dyer, and R. Réau, *Coord. Chem. Rev.*, **244**, 1 (2003).

2 S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, **69**, 2327 (1996).

3 U. Salzner, J. B. Lagowski, P. G. Pickup, and R. A. Poirier, *Synth. Met.*, **96**, 177 (1998).

4 J. Ma, S. Li, and Y. Jiang, *Macromolecules*, **35**, 1109 (2002).

5 A. Alparone, A. Millefiori, and S. Millefiori, *Chem. Phys.*, **298**, 75 (2004).

6 C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, **14**, 99 (2002).

7 S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, and K. Tamao, *Chem.—Eur. J.*, **6**, 1684 (2000).

8 a) K. Tamao, S. Yamaguchi, and M. Shiro, *J. Am. Chem. Soc.*, **116**, 11715 (1994). b) S. Yamaguchi, R.-Z. Jin, Y. Itami, T. Goto, and K. Tamao, *J. Am. Chem. Soc.*, **121**, 10420 (1999).

9 a) K. Tamao, S. Yamaguchi, M. Shiozaki, Y. Nakagawa, and Y. Ito, *J. Am. Chem. Soc.*, **114**, 5867 (1992). b) K. Tamao, S. Ohno, and S. Yamaguchi, *Chem. Commun.*, **1996**, 1873. c) S. Yamaguchi, T. Goto, and K. Tamao, *Angew. Chem., Int. Ed.*, **39**, 1695 (2000).

10 S. Yamaguchi, R.-Z. Jin, and K. Tamao, *J. Am. Chem. Soc.*, **121**, 2937 (1999).

11 a) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, **1998**, 3693. b) S. Yamaguchi and K. Tamao, *J. Organomet. Chem.*, **653**, 223 (2002).

12 K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, and S. Yamaguchi, *J. Am. Chem. Soc.*, **118**, 11974 (1996).

13 M. Uchida, T. Izumizawa, T. Nakano, S. Yamaguchi, K. Tamao, and K. Furukawa, *Chem. Mater.*, **13**, 268 (2001).

14 a) H. Murata, G. G. Malliaras, M. Uchida, Y. Shen, and Z. H. Kafafi, *Chem. Phys. Lett.*, **339**, 161 (2001). b) H. Murata, Z. H. Kafafi, and M. Uchida, *Appl. Phys. Lett.*, **80**, 189 (2002).

15 a) L. C. Palilis, A. J. Makinen, M. Uchida, and Z. H. Kafafi, *Appl. Phys. Lett.*, **82**, 2209 (2003). b) A. J. Makinen, M. Uchida, and Z. H. Kafafi, *Appl. Phys. Lett.*, **82**, 3889 (2003). c) A. J. Makinen, M. Uchida, and Z. H. Kafafi, *J. Appl. Phys.*, **95**, 2832 (2004).

16 J. Lee, Q.-D. Liu, M. Motala, J. Dane, J. Gao, Y. Kang, and S. Wang, *Chem. Mater.*, **16**, 1869 (2004).

17 N. Roques, P. Gerbier, J.-P. Sutter, P. Guionneau, D. Luneau, and G. Guérin, *Organometallics*, **22**, 4833 (2003).

18 A. J. Boydston, Y. Yin, and B. L. Pagenkopf, *J. Am. Chem. Soc.*, **126**, 3724 (2004).

19 Y. Lee, S. Sadki, B. Tsuie, P. Schottland, and J. R. Reynolds, *Synth. Met.*, **119**, 77 (2001).

20 B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu, and D. Zhu, *J. Mater. Chem.*, **11**, 2974 (2001).

21 M. R. Craig, M. M. de Kok, J. W. Hofstraat, A. P. H. J. Schenning, and E. W. Meijer, *J. Mater. Chem.*, **13**, 2861 (2003) and references therein.

22 J. F. Morin and M. Leclerc, *Macromolecules*, **34**, 4680 (2001) and references therein.

23 J.-F. Brière and M. Côtè, *J. Phys. Chem. B*, **108**, 3123 (2004).

24 S. Yamaguchi, T. Shirasaka, S. Akiyama, and K. Tamao, *J. Am. Chem. Soc.*, **124**, 8816 (2002).

25 I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1971).

26 Recently, a similar phenomenon was observed for the dithienoborole-based compounds: S. Kin, K.-H. Song, S. O. Kang, and J. Ko, *Chem. Commun.*, **2004**, 68.

27 a) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *J. Am. Chem. Soc.*, **90**, 4759 (1968). b) J. Saltiel, A. Marinari, D. W. L. Chang, J. C. Mitchener, and E. D. Megarity, *J. Am. Chem. Soc.*, **101**, 2982 (1979).

28 D. Hellwinkel, H.-J. Hasselbach, and F. Lämmerzahl, *Angew. Chem., Int. Ed. Engl.*, **23**, 705 (1984).

29 M. Serby, S. Ijadi-Maghsoodi, and T. J. Barton, XXXIIIrd Symposium on Organosilicon Chemistry, Saginaw, Michigan, U.S.A., 2000, Abstr., No. PA-35.

30 Z. Ma, S. Ijadi-Maghsoodi, and T. J. Barton, *Polym. Prepr.*, **38**, 249 (1997).

31 S. Yamaguchi, C. Xu, and K. Tamao, *J. Am. Chem. Soc.*, **125**, 13662 (2003).

32 C. Xu, H. Yamada, A. Wakamiya, S. Yamaguchi, and K. Tamao, *Macromolecules*, in press.

33 Y. Kondo, M. Shilai, M. Uchiyama, and T. Sakamoto, *J. Am. Chem. Soc.*, **121**, 3539 (1999).