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Versatile Synthesis of Blue Luminescent Siloles and Germoles and Hydrogen-Bond-Assisted Color Alteration

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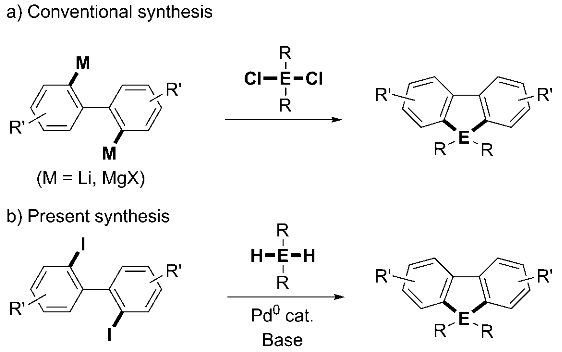
Group 14 metalloles are an interesting class of Si-, Ge-, or Sn-based annulated π-conjugated molecules.[1] The silole ring system contains a σ* orbital on the silicon atom, which effectively interacts with the π* orbital of the butadiene unit, producing a low-lying LUMO. Although a variety of sophisticated silole derivatives have been prepared, the preparation of these well-designed compounds depends heavily on classical Si–C bond-formation methods by using highly reactive organometallic reagents (Scheme 1a).[2,3] This procedure is not always simple, nor is it safe to implement, from the perspective of its applications.



Scheme 1. Strategy for the preparation of Group 14 metalloles (E = Si, Ge).

Recently, a transition-metal-catalyzed process has been developed to overcome these problems. The groups of Murakami[4] and Shimizu[5] independently reported the pioneering construction of a silole moiety in the presence of a metal catalyst. These protocols were limited by high reaction temperatures and multistep procedures for the preparation of the starting materials. Thus, the development of mild and general methods for the preparation of silole derivatives has remained an important goal. During development of organosilicon compounds containing an aromatic ring, we identified a new methodology based on transition-metal-catalyzed arylation of hydrosilanes with aryl halides.[6] Herein, we report a novel method for constructing the skeletons of Group 14 metalloles from the corresponding dihydrosilanes or dihydrogermanes using Pd-catalyzed E–C (E = Si, Ge) bond formation (Scheme 1b). The effects of the substituents on the physical properties of these materials will be discussed in detail.

We examined the cyclic double intramolecular arylation of a 2,2′-diiodobiaryl with a secondary silane in the presence of the base $(i\mathrm{Pr})_2\mathrm{EtN}$, using $[\mathrm{Pd}(\mathrm{P}(t\mathrm{Bu})_3)_2]$ as the catalyst.[7,8] The results are shown in Scheme 2. The reaction proceeded smoothly to produce the desired dibenzosiloles or -germoles as colorless solids in good to high yields (**1**–**16**). The reaction described herein provides a unique method for the preparation of Group 14 metalloles containing a reactive functional group on the aromatic rings, some of which (**13**–**16**) are difficult to synthesize when using conventional synthetic methods. 2,2′-Diiodobithiophene gave an inferior yield for product **17**; the reduced product was favored. Unfortunately, the intramolecular cyclization of 1-NpPhSiH$_2$ (Np = naphthyl) or $(t\mathrm{Bu})_2\mathrm{SiH}_2$ with 2,2′-diiodobiphenyl did not occur at all under the present conditions due to the steric crowding of the secondary silanes.

The photophysical properties of compounds **1**–**17** were determined by UV-visible and fluorescence spectroscopies, collected in dichloromethane or in the corresponding crystalline state. These results are summarized in Table 1. The UV-visible absorption spectra showed that the position of the

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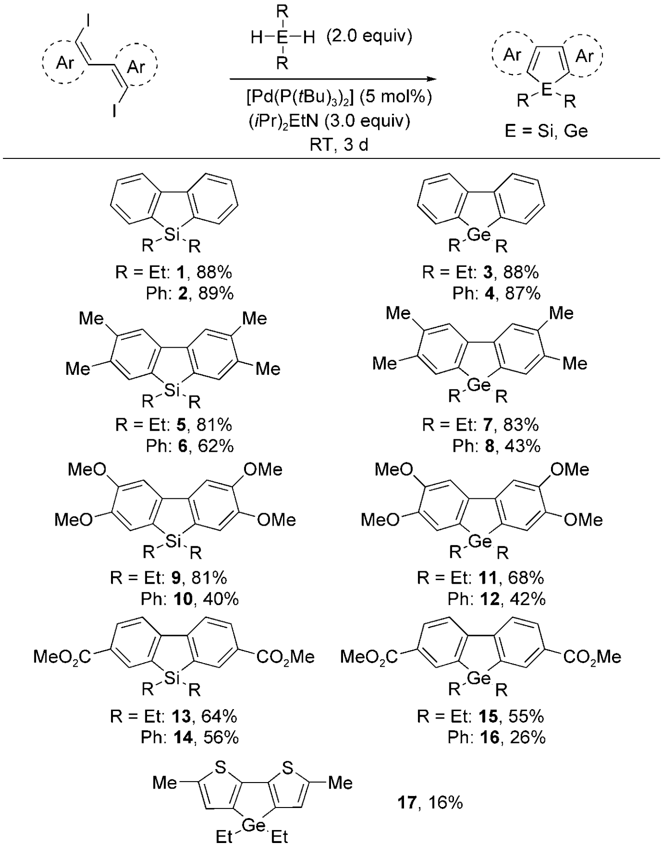

Scheme 2. Palladium-catalyzed one-pot synthesis of dibenzosiloles and dibenzogermoles.

Table 1. Photophysical properties of Group 14 metalloles **1**–**17**.[a]

Compound	UV/Vis λ_{abs} [nm][b]	log ε	Fluorescence λ_{em} [nm]	Φ_F[e]	λ_{em} [nm][d]	Φ_F[f]
1	289	4.06	352	0.03	352	0.14
2	292	3.80	355	0.04	355	0.16
3	285	3.97	345	<0.01	349	0.02
4	288	4.16	346	0.01	350	0.03
5	299	3.99	362	0.01	367	0.23
6	302	4.12	369	0.02	369	0.13
7	290	4.25	354	<0.01	362	<0.01
8	297	4.18	360	<0.01	363	<0.01
9	331	4.14	391	0.07	382	0.17
10	333	4.08	404	0.08	400	0.11
11	330	4.09	357	0.01	363	0.01
12	332	3.99	389	<0.01	392	<0.01
13	325	4.38	353	0.32	363	0.33
14	327	4.34	351	0.32	392	0.59
15	324	4.43	354	0.02	363	0.07
16	323	4.35	356	0.05	394	0.18
17	340	4.07	420	0.34	[g]	[g]

[a] All measurements were carried out in dichloromethane at room temperature. [b] Absorption maximum of the longest wavelength. [c] Excited at 250 nm. [d] Crystalline solid-state fluorescence. [e] Determined with respect to anthracene in EtOH ($\Phi_F = 0.27$). [f] Absolute quantum yield measurement. [g] Fluorescence in the solid state could not be measured because the compound was an oil.

absorption maximum (ca. 290–340 nm), ascribed to the π–π* transition of the silole ring, depended on the identity of substituent of the aromatic ring. The siloles exhibited fluorescence maxima at 350–410 nm under the irradiation at 250 nm.

The fluorescence quantum yields depended significantly on the aromatic substituent groups. Dibenzosiloles with electron-neutral or -releasing groups on their aromatic rings were weakly fluorescent ($\Phi_F = <0.01$–0.08). This was in a sharp contrast to the high fluorescence efficiencies observed with an electron-accepting group (**13** and **14**, $\Phi_F = 0.32$). The Stokes shift was also found to depend on the identity of the substituent. Dibenzosiloles and -germoles **13**–**16** exhibited smaller Stokes shifts than did other Group 14 metalloles. These results suggested smaller structural differences between the ground and excited states.

The dibenzosilole molecule **14** yielded an emission maximum at 351 nm in solution and this emission peak was shifted to 392 nm in the crystalline bulk solid with a concomitant increase in the emission quantum yield (Figure 1).[9] The redshift in the emission maximum and enhancement of luminescence efficiency can be explained as follows: The solid-state structure of **14**, derived from single-crystal X-ray analysis, revealed that variations in the molecular packing played a major role in the crystalline-state fluorescence behavior (Figure 2).[10] In the packed model of **14**, hydrogen bonding between the carbonyl and the aromatic hydrogen (C=O···H–C: 2.40 Å), along with the C=O···C=O interaction (which forms a motif parallel to the weak carbon–oxygen interaction, 3.20 Å) (Figure 2c), produce a compact aggregation structure in the crystalline state with a J-type staggered intermolecular π–π overlapping (3.40 Å) geometry throughout the crystal.[11] A similar redshift was observed for dibenzogermole **16**, and the X-ray structure was very similar to that of **14** and contained dimer units π stacked with the aid of C=O···H–C (2.38 Å) and C=O···C=O (3.22 Å) interactions.[12] These interactions produced a redshift in the photoluminescent emission in the crystalline state relative to the emission spectrum in solution. The influence of the ester substituent can also be illustrated in a comparison of the X-ray structures of **10**.[13] No strong interactions were present-

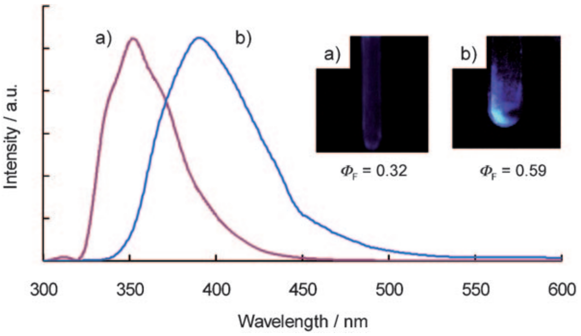

Figure 1. Fluorescence spectra and photographs (excited at 250 nm) of **14** at room temperature a) in dichloromethane and b) in the solid state.

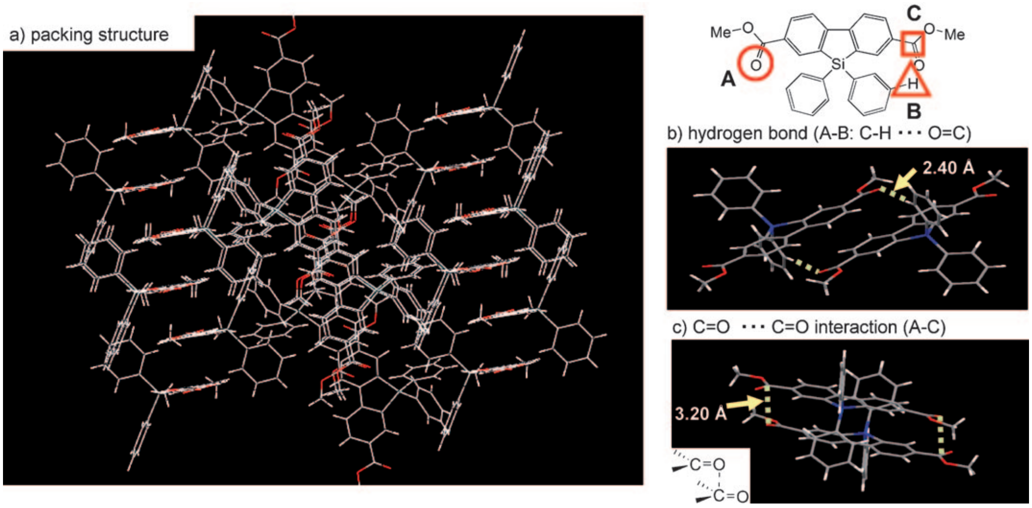

Figure 2. Packing arrangement in the crystal structure of **14**. a) Packing structure, b) hydrogen bond (A–B), and c) carbonyl interactions (A–C).

ed between the dibenzosilole molecules in the molecular packing of **10**. Accordingly, the small redshift observed for other dibenzosiloles may have been the result of a lack of aggregation in the crystalline state. This is the first example of siloles that show a hydrogen-bond-assisted luminescent color change.[14]

Finally, we investigated systematically the effects of substituents on phosphorescence of dibenzosiloles for the first time. All dibenzosiloles **1**, **2**, **5**, **6**, **9**, **10**, **13**, and **14** exhibited long-lived phosphorescence ($\tau_p = 1$–4 s) in the region 450–650 nm (Table 2 and Figure 3) at 77 K in glassy 2-methyltetrahydrofuran. The phosphorescence quantum yields were low ($\Phi_P = 0.01$–0.11), but were somewhat higher than that of tetraphenylsilane ($\Phi_P < 0.01$) due to a more extensively conjugated electronic structure. The substituents on the dibenzosilole ring influenced the phosphorescent quantum yield.[15] The electron-neutral and -donating substituted dibenzosilole derivatives showed higher quantum efficiencies relative to the electron-withdrawing substituted derivatives.

Table 2. Phosphorescence of dibenzosiloles.[a]

Compound	Phosphorescence λ_{em} [nm][b]	τ_p [s]	Φ_p[c]
1	490	2.87	0.11
2	491	2.91	0.11
5	505	3.05	0.06
6	505	3.69	0.09
9	545	1.26	0.04
10	547	0.98	0.08
13	526	1.71	0.01
14	526	1.56	0.02

[a] Measured in 2-methyltetrahydrofuran at 77 K. [b] Excited at λ_{abs}. [c] Absolute quantum yield measurement.

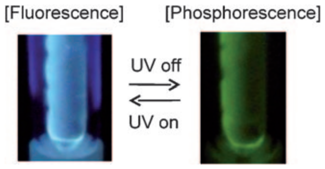

Figure 3. Phosphorescence of **10** in 0.1 mM 2-methyltetrahydrofuran at 77 K (UV lamp, 254 nm).

In summary, the synthesis of dibenzosiloles and -germoles obtained through an intramolecular Pd-catalyzed cyclization pathway is described. Compared with the conventional synthetic strategies for achieving siloles and germoles, the present cyclization has several advantages in terms of functional group tolerances. The luminescence properties could be tuned through the molecular structure, particularly the electronic effects of the substituents.[16–18] The remarkably high efficiency of the solid-state fluorescence, with a longer emission shift observed for **14**, was achieved through the formation of a J-type aggregation structure. The structure–property relationships described herein will be valuable for the future design and synthesis of new organic electroluminescent materials containing Group 14 metalloles as a key building unit.

Experimental Section

General: All experiments were carried out under an argon atmosphere in oven-dried glassware. See the Supporting Information for details of characterization of individual compounds.

Typical experimental procedure for palladium-catalyzed intramolecular cyclization of 2,2′-diiodobiaryl with a secondary silane: The procedure for palladium-catalyzed cyclization is illustrated by the synthesis of 9,9-diethylsilafluorene (**1**). *N,N*-diisopropylethylamine (270 μL, 1.51 mmol) and diethylsilane (130 μL, 1.00 mmol) were added to a solution of 2,2′-diiodobiphenyl (204 mg, 0.503 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (12.4 mg, 0.024 mmol) in THF (1.0 mL) under a nitrogen atmosphere. After stirring for 3 d at room temperature, the reaction mixture was quenched with water, extracted with CH_2Cl_2 three times, and dried with Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel to give **1** (105 mg, 88 %).[2a] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.83$ (d, 2H, $J = 7.8$ Hz), 7.62 (d, 2H, $J = 7.1$ Hz), 7.43 (dt, 2H, $J = 1.3$, 7.6 Hz), 7.26 (t, 2H, $J = 7.3$ Hz), 0.91–1.01 ppm (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.5$ (C_q), 137.3 (C_q), 133.2 (CH), 130.1 (CH), 127.1 (CH), 120.8 (CH), 7.6 (CH_3), 3.8 ppm (CH_2); EIMS: m/z: 238 [M^+].

Photochemical measurements: The solutions were degassed by three freeze–pump–thaw cycles prior to measurements. Photoluminescent quantum yields were measured by using the optically dilute method ($A = \approx 0.1$). Fluorescence quantum yields were determined in dichloromethane relative to anthracene ($\Phi_F = 0.27$ in EtOH) at RT.[19] Fluorescent quantum yields of **1**–**16** in the solid state and phosphorescent quantum yields of **1**, **2**, **5**, **6**, **9**, **10**, **13**, and **14** at 77 K were recorded with a Hamamatsu Photonics C9920-02G Absolute PL Quantum Yield Measurement System.

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[1] For representative reviews, see: a) J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* **1990**, *90*, 215; b) E. Colomer, R. J. P. Corriu, M. Lheureux, *Chem. Rev.* **1990**, *90*, 265; c) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1; d) S. Yamaguchi, K. Tamao, *J. Chem. Soc. Dalton Trans.* **1998**, 3693; e) S. Yamaguchi, K. Tamao, *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 500; f) S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, *34*, 2; g) S. Yamaguchi, K. Tamao, *J. Organomet. Chem.* **2002**, *653*, 223; h) M. Saito, M. Yoshioka, *Coord. Chem. Rev.* **2005**, *249*, 765; i) A. Fukazawa, S. Yamaguchi, *Chem. Asian J.* **2009**, *4*, 1386; j) X. Zhan, S. Barlow, S. R. Marder, *Chem. Commun.* **2009**, 1948.

[2] For selected examples, see: a) Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 49; b) S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, *Chem. Eur. J.* **2000**, *6*, 1683; c) B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu, D. L. J. Zhu, *Mater. Chem.* **2001**, *11*, 2974; d) 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* **1999**, *18*, 1453; e) L. Li, J. Xiang, C. Xu, *Org. Lett.* **2007**, *9*, 4877; f) K. Tamao, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1994**, *116*, 11715; g) K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974; h) S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327; i) S. Yamaguchi, C. Xu, K. Tamao, *J. Am. Chem. Soc.* **2003**, *125*, 13662; j) H. Gilman, R. D. Gorsich, *J. Am. Chem. Soc.* **1955**, *77*, 6380; k) S. Choi, P. Boudjouk, *Tetrahedron Lett.* **2000**, *41*, 6685; l) M. Shimizu, H. Tatsumi, K. Mochida, K. Oda, T. Hiyama, *Chem. Asian J.* **2008**, *3*, 1238; m) K. L. Chan, M. J. McKierman, C. R. Towns, A. B. Holmes, *J. Am. Chem. Soc.* **2005**, *127*, 7662; n) L. Ilies, H. Tsuji, Y. Sato, E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 4240; o) K. L. Chan, S. E. Watkins, C. S. K. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascu, A. B. Holmes, *Chem. Commun.* **2005**, 5766; p) Y. Mo, R. Tian, W. Shi, Y. Cao, *Chem. Commun.* **2005**, 4925; q) C. Xu, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2004**, *6*, 3707; r) S. Yamaguchi, C. Xu, H. Yamada, A. Wakamiya, *J. Organomet. Chem.* **2005**, *690*, 5365.

[3] Recently, the development of an intramolecular sila-Friedel–Crafts reaction as a novel synthetic method for dibenzosilole derivatives was reported, see: S. Furukawa, J. Kobayashi, T. Kawashima, *J. Am. Chem. Soc.* **2009**, *131*, 14192.

[4] The synthesis of silole skeletons through the iridium-catalyzed [2+2+2] cycloaddition of silicon-bridged 1,6-diynes with alkynes, ruthenium-catalyzed double *trans*-hydrosilylation of 1,4-diarylbuta-1,3-diynes, and ring-closing metathesis of silicon-tethered dienes or trienes has been reported, see: a) T. Matsuda, S. Kadowaki, T. Goya, M. Murakami, *Org. Lett.* **2007**, *9*, 133; b) T. Matsuda, S. Kadowaki, M. Murakami, *Chem. Commun.* **2007**, 2627; c) T. Matsuda, Y. Yamaguchi, M. Murakami, *Synlett* **2008**, 561.

[5] The palladium-catalyzed intermolecular coupling of 2-(arylsilyl)aryl triflates has been reported, see: a) K. Mochida, M. Shimizu, T. Hiyama, *J. Am. Chem. Soc.* **2009**, *131*, 8350; b) M. Shimizu, K. Mochida, T. Hiyama, *Angew. Chem.* **2008**, *120*, 9906; *Angew. Chem. Int. Ed.* **2008**, *47*, 9760.

[6] a) Y. Yamanoi, *J. Org. Chem.* **2005**, *70*, 9607; b) Y. Yamanoi, H. Nishihara, *Tetrahedron Lett.* **2006**, *47*, 7157; c) Y. Yamanoi, T. Taira, J.-I. Sato, I. Nakamula, H. Nishihara, *Org. Lett.* **2007**, *9*, 4543; d) Y. Yamanoi, H. Nishihara, *J. Org. Chem.* **2008**, *73*, 6671; e) Y. Yamanoi, H. Nishihara, *J. Synth. Org. Chem. Jpn.* **2009**, *67*, 778.

[7] The intramolecular cyclization in the presence of $(i\mathrm{Pr})_2\mathrm{EtN}$ was slightly superior to that in the presence of Et_3N.

[8] The coupling reaction of 2,2′-dibromobipheyl with diethylsilane gave the corresponding dibenzosilole **1** in 26 % yield. The reduced product, biphenyl, was obtained as a major product by the observation of GC–MS.

[9] For reports on the redshift of emission spectra and enhancement in emission yields in the solid state, see: a) R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. Das, *J. Phys. Chem. C* **2008**, *112*, 2137; b) K. Itami, Y. Ohashi, J.-I. Yoshida, *J. Org. Chem.* **2005**, *70*, 2778; c) K. Ono, K. Yoshikawa, Y. Tsuji, H. Yamaguchi, R. Uozumi, M. Tomura, K. Taga, K. Saito, *Tetrahedron* **2007**, *63*, 9354; d) Y. Ooyama, S. Nagano, M. Okumura, K. Yoshida, *Eur. J. Org. Chem.* **2008**, 5899; see also reference [5b].

[10] CCDC-741424 contains the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For detailed crystallographic data for **14**, see the Supporting Information.

[11] Generally, crystal-packing structures with intermolecular electronic interactions, such as π–π stacking, lead to luminescence quenching. However, the formation of J-type aggregation resulted in a strongly emissive system, see: a) N. S. S. Kumar, S. Varghese, N. P. Rath, S. Das, *J. Phys. Chem. C* **2008**, *112*, 8429; b) E. Da Como, M. A. Loi, M. Murgia, R. Zamboni, M. Muccini, *J. Am. Chem. Soc.* **2006**, *128*, 4277; c) W.-L. Jia, Q.-D. Liu, D. Song, S. Wang, *Organometallics* **2003**, *22*, 321; d) F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.* **2001**, *7*, 2245; e) D. Möbius, *Adv. Mater.* **1995**, *7*, 437.

[12] CCDC-756872 contains the crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For crystallographic data and molecular packing structure of **16**, see the Supporting Information.

[13] CCDC-741425 contains the crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For crystallographic data and molecular packing structure of **10**, see the Supporting Information.

[14] Recently, the aggregation-induced emission of 2,5-bis(trialkylsilylethynyl)-3,4-diphenylsiloles in the solid state was reported, see: Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Ma, B. Z. Tang, *Angew. Chem.* **2009**, *121*, 7744; *Angew. Chem. Int. Ed.* **2009**, *48*, 7608.

[15] The phosphorescence of diphenyldibenzosilole in a 3:1 mixture of methylcyclohexane and isopentane at 77 K has been reported. The lifetime and quantum yield were 3.2 s and 0.13, respectively, see: S. N. Davydov, A. N. Rodionov, D. N. Shigorin, O. P. Syutkina, T. L. Krasnova, *Russ. J. Phys. Chem.* **1981**, *55*, 444.

[16] The fluorescence and phosphorescence studies of Group 14 elemental derivatives of fluorene has been reported. An increase of atomic number ($C < Si < Ge < Sn$) entails a sharp decrease of fluorescence quantum yields (Φ_F), an increase of the ratio Φ_P/Φ_F, and a decrease of the lifetime of the phosphorescent state τ_p, see reference [15].

[17] The fluorescence of 4*H*-cyclopenta[2,1-b;3,4-b′]dithiophene (CPDT) has been reported, see: M. Fujitsuka, T. Sato, F. Sezaki, K. Tanaka, A. Watanabe, O. Ito, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 3331.

[18] The fluorescence of 4,4-dialkyldithieno[3,2-b;2′,3′-d]silole has been reported. Comparison of absorption spectra between silole and CPDT was also discussed, see: a) J. Ohshita, M. Nodono, T. Watanabe, Y. Ueno, A. Kunai, Y. Harima, K. Yamashita, M. Ishikawa, *J. Organomet. Chem.* **1998**, *553*, 487; see also reference [2d].

[19] a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991; b) D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107; c) W. H. Melhuish, *J. Phys. Chem.* **1961**, *65*, 229; d) W. R. Dawson, M. W. Windsor, *J. Phys. Chem.* **1968**, *72*, 3251.

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