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Synthesis and spectroscopic study of silacyclyne-substituted phenyleneethynylenes

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ABSTRACT

A series of 1,1-dimethyl-4,5:8,9-dibenzo-1-silacycloundeca-4,8-diene-2,6,10-triyne (DST)-substituted phenyleneethynylenes were successfully synthesized by reaction of Me_2SiCl_2 with dimagnesium dianions which had been prepared from 2,2′-diethynyl(diphenylethyne) derivatives by treatment with 2 equiv of MeMgBr. All the products were white-to-pale yellow powder stable enough to handle in the air, and their photoluminescence spectra were recorded both in solution and in solid state.

Great attention has been focused on dehydrobenzoannulene derivatives[1] because of their unique electronic[2] and optical properties[3] as well as key building blocks for two-dimensional carbon networks.[4] Although aromatic compounds having highly conjugated π-system are promising as emission materials of OLED (organic light-emitting diode)[5] because of their small HOMO-LUMO band gaps, dehydrobenzo[12]annulenes emitted only weak fluorescence in solution when UV light was irradiated.[6] In our continuing study on syntheses of acetylene derivatives and their optical properties,[7] we disclosed that the π-conjugated system in ethynylsilane is expanded through σ*(C–Si)-π (C≡C) interaction to enhance fluorescence emission.[8] We envisaged that introduction of dimethylsilylbis(ethynylene) group(s) to phenyleneethynylene array could achieve expansion of two-dimensional π-conjugated system in terms of σ*(C–Si)-π (C≡C) interaction and/or enhanced planarity of phenyleneethynylene array induced by restricted rotation of benzene rings[9] to effect facile control of fluorescence wavelength keeping a high quantum yield. We have already established a double elimination protocol of β-substituted sulfones for synthesis of functionalized diarylethynes.[7] Herein are described syntheses of a series of 1,1-dimethyl-4,5:8,9-dibenzo-1-silacycloundeca-4,8-diene-2,6,10-triyne (DST)-substituted phenyleneethynylenes by taking advantage of the double elimination protocol in combination with Sonogashira coupling.[10] We also reveal their optical properties in solution and in the solid state,[11] and bathochromic shifts in UV–vis absorption spectra in comparison with the corresponding unsubstituted linear phenyleneethynylenes.

Firstly, we synthesized 1,1-dimethyl-4,5:8,9-dibenzo-1-silacycloundeca-4,8-diene-2,6,10-triyne (DST, **1a**) by using 2,2′-dibromodiphenylethyne as starting compound which can be easily obtained from the one-shot double elimination reaction between 2-bromobenzyl sulfone **2** and 2-bromobenzaldehyde **3** (Scheme 1). Addition of an excess amount of lithium hexamethyldisilazide (LiHMDS) to a THF solution of **2**, **3** and diethyl chlorophosphate afforded **4** in 75% yield. Dibromide **4** was transformed into **5** by Sonogashira coupling with trimethylsilylethyne. The TMS-protected acetylene **5** underwent desilylation by treatment with K_2CO_3/MeOH to give **6**. Treatment of **6** with methyl magnesium bromide and dichlorodimethylsilane at 50–60 °C provided **1a** in 58% yield. Column chromatography on silica gel enabled facile separation of DST (**1a**) from the remaining starting compound **6** and other byproducts to achieve satisfactory results of elemental analysis. DST (**1a**) is air-stable white powder with mp 210–212 °C, and its ^{13}C NMR in $CDCl_3$ indicated three acetylenic carbons at 92.3, 98.5 and 107.2 ppm.

Secondly, fused DST derivative **1b** was prepared from commercially available 2,6-dibromoaniline (**7**) (Scheme 2). The aniline **7** was transformed to 1,3-dibromo-2-iodobenzene (**8**) by Sandmeyer iodination. Sonogashira coupling of **8** with 2-methyl-3-butyn-2-ol

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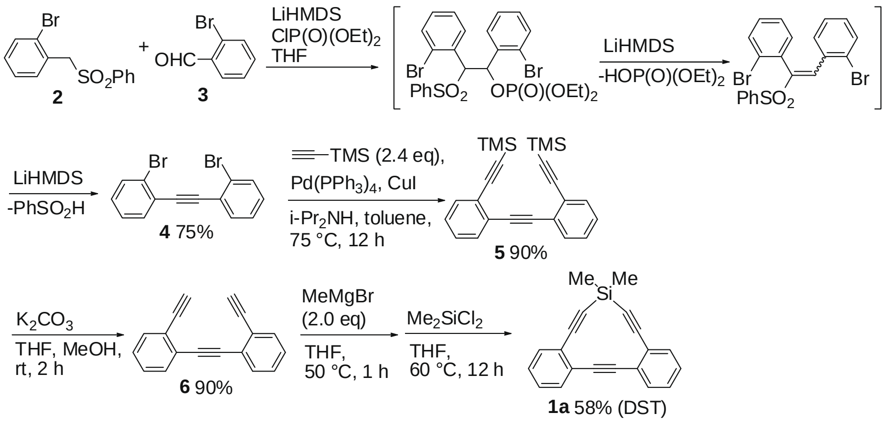
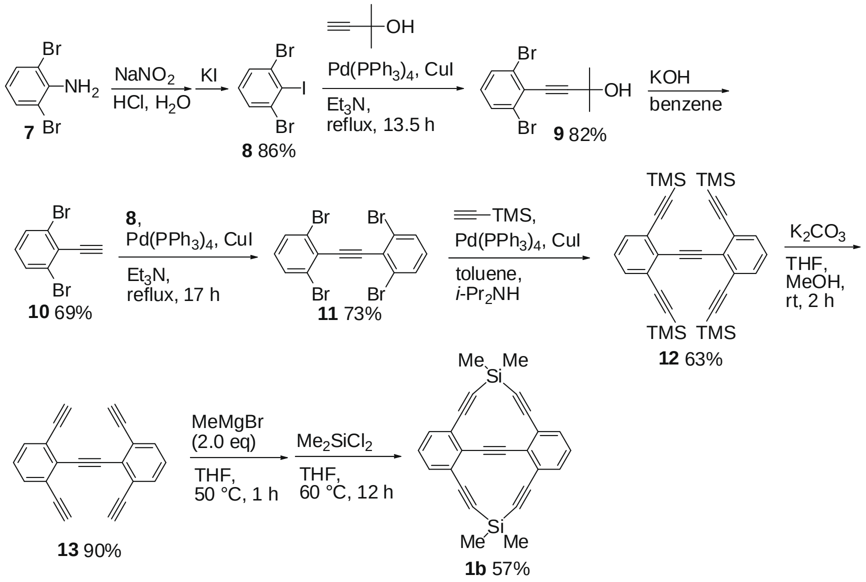


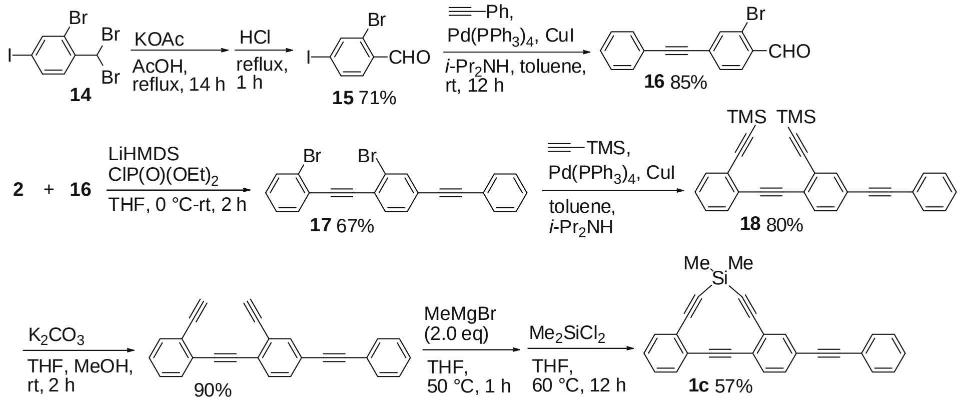
Scheme 1.



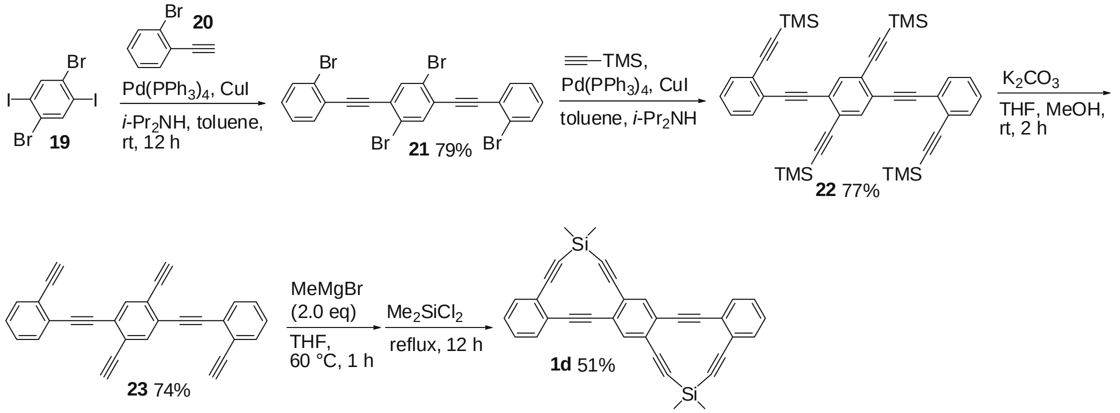
Scheme 2.

afforded **9**, and base-catalyzed deprotection of **9** furnished terminal acetylene **10** (Scheme 2). Sonogashira coupling of **10** with **8** afforded bis(1,3-dibromophenyl)ethyne (**11**) in 73% yield. Sonogashira coupling of **11** with trimethylsilylethyne was rather sluggish to require subjection of the crude products to the same coupling reaction again for completion. Otherwise, an inseparable mixture of bis-, tri- and tetra-adducts was obtained. The fused DST derivative **1b** was obtained by desilylation of tetra-adduct **12** followed by treatment of MeMgBr/Me$_2$SiCl$_2$.

DST-substituted phenyleneethynylenes **1c–f** were prepared successfully by virtue of the double elimination reaction and Sonogashira coupling as shown in Schemes 3–5.[12]



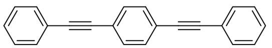
Scheme 3.



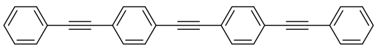
Scheme 4.

In order to evaluate electronic effect of silacyclyne on phenyleneethynylenes, UV–vis absorption spectra were recorded for **1a** and **1b** in CH_2Cl_2 (1.0×10^{-5} mol/L) (Fig. 1). Silacyclynes are stable enough, and no decomposition of **1a** nor **1b** was observed in measurement of UV–vis absorption spectra. While **1a** showed a sharp vibronic spectrum, **1b** recorded 20 nm red-shifted absorption bands at 250–300 nm and 310–360 nm indicative of a larger expanded π system.

Figure 2 illustrates three profiles of UV–vis absorption of 1,4-di(phenylethynyl)benzene (**32**), **1c** and **1d** in CH_2Cl_2. While **32** exhibited a broad vibronic absorption in the region of 270–350 nm, incorporation of the DST moiety/moieties induced bathochromic shift of absorption maxima of the longest wavelength by 21 nm (341–362 nm) and 39 nm (341–380 nm) in **1c** and **1d**, respectively. Such bathochromic shift supports again that introduction of DST component enables efficient π-system expansion of phenyleneethynylenes.

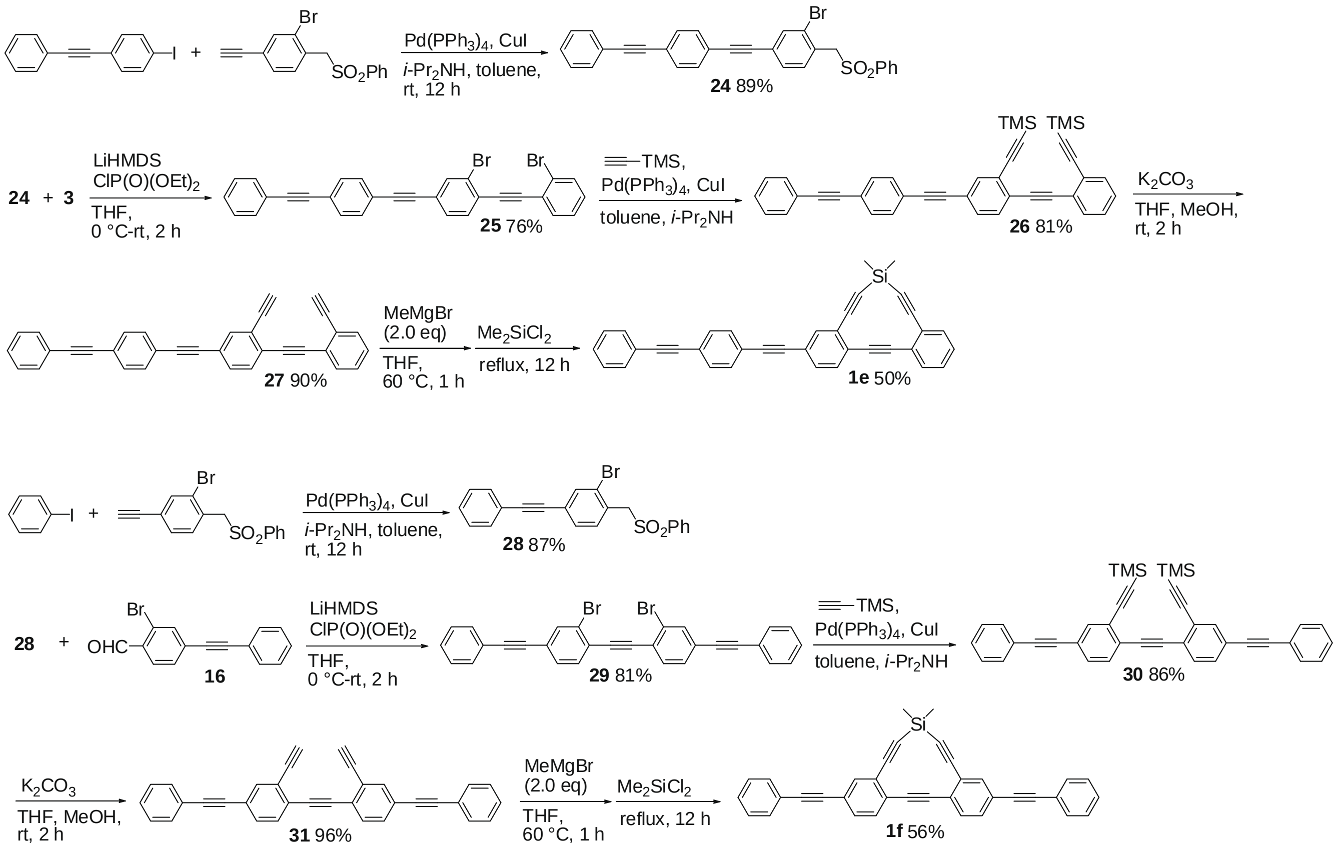


32



33

While bis(4-(phenylethynyl)phenyl)ethyne (**33**) showed an intense vibronic absorption band in the region of 270–380 nm, silacyclynes **1e** and **1f** exhibited strong absorption bands from 285 to 395 nm and from 300 to 400 nm, respectively (Fig. 3). It should



Scheme 5.

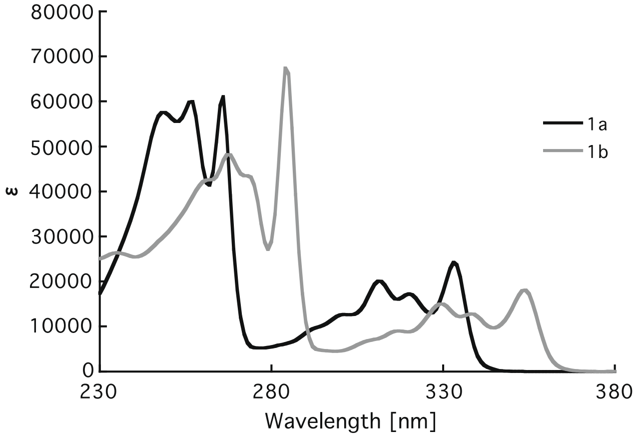


Figure 1. UV–vis absorption spectra of **1a** and **1b**.

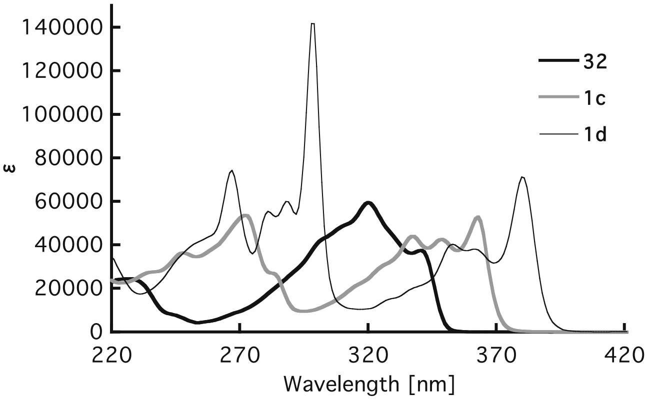


Figure 2. UV–vis absorption spectra of **1c**, **1b** and **32**.

be noted that introduction of silacyclyne to the central position (**1f**) gave rise to a larger bathochromic shift than introduction to the terminal position (**1e**).

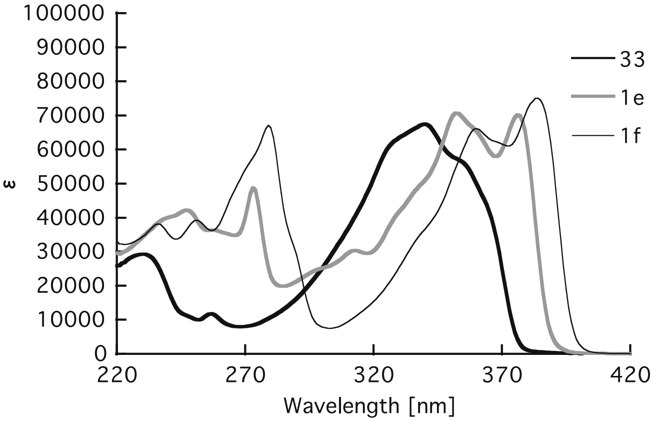


Figure 3. UV–vis absorption spectra of **1e**, **1f** and **33**.

Table 1
Fluorescence properties of **1a**–**f**, diphenylethyne, **32** and **33**

	Emission in CH_2Cl_2 (nm) (9.4×10^{-7} M)	Excitation wavelength (nm)	Φ_F in CH_2Cl_2[a]	Emission in the solid state (nm)	Φ_F in the solid state[a]
Diphenylethyne	Weak emission	288	—	359	0.41
1a	342	265	0.52	375	0.14
1b	362	284	0.35	397	0.24
32	353	319	0.86	394	0.59
1c	371	272	0.67	451	0.37
1d	390	299	0.85	451	0.41
33	375	340	0.99	444	1.00
1e	388	377	0.86	471	0.18
1f	396	384	0.88	473	0.17

[a] Absolute quantum yields were recorded by an integration sphere (Hamamatsu photonics C9920-02).

Emission spectra of **1a–f**, diphenylethyne, **32** and **33** were recorded in CH_2Cl_2 solution (9.4×10^{-7} M) and in the solid state at room temperature. All the fluorescence properties of these compounds are summarized in Table 1. The excitation profiles of **1a**–**f** are compatible with those of UV–vis absorption. Although the monocyclyne **1a** showed higher quantum yield than fused silacyclyne **1b** in solution (Φ_{PL} in CH_2Cl_2, **1a** 0.52, **1b** 0.35), **1b** showed longer wavelength of emission maximum than **1a**. In **1a** and **1b**, introduction of dimethylsilylbis(ethynylene) group to innately non-emissive diphenylethyne brought about efficient expansion of π-conjugated system inducing effective emission of **1a** and **1b**. Such expansion of π-conjugated system was observed in other cyclic derivatives **1c–f**. Silacyclynes **1c** and **1d** showed emission maxima at 371 and 390 nm, respectively, and these emission maxima were red shifted by 18 and 37 nm in comparison with emission maximum of **32**. Fluorescence quantum yield of **1d** ($\Phi_F = 0.85$) is larger than that of **1c** ($\Phi_F = 0.67$). Silacyclynes (**1e**, **1f**) exhibited strong emission as well, and the internal silacyclyne **1f** showed larger red shift of emission maximum (396 nm) than the terminal silacyclyne **1e** (388 nm). This larger red shift of **1f** would be induced by larger bathochromic shift in UV–vis absorption spectra. Notably, in sharp contrast to dehydrobenzo[12]annulenes, silacyclynes **1a–f** enables tuning of wavelengths in photoluminescence with high fluorescence quantum yields.

When UV-light was irradiated, the silacyclynes **1a–f** emitted strong fluorescence in the solid state. Although fluorescence quantum yields of **1a–f** were smaller than those of the corresponding parent linear phenyleneethynylenes, the wavelengths of emission maxima of **1a–f** underwent bathochromic shift.[13]

We succeeded in preparation of a variety of silacyclynes by reaction of dichlorodimethylsilane with 2,2′-bis(magnesioethynyl)diphenylethynes which had been derived by treatment of 2,2′-di(ethynyl)diphenylethynes with MeMgBr. These silacyclynes exhibited intense absorption bands in UV–vis spectroscopy, and the absorption maxima of the longest wavelength showed bathochromic shift in proportion to the lengths of π-conjugated system in phenyleneethynylene arrays. When irradiated by UV light, a set of silacyclynes emitted strong fluorescence in moderate to high fluorescence quantum yields both in CH_2Cl_2 and in the solid state. Application of the silacyclynes to emission material of electroluminescence device is under investigation.

Acknowledgements

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Supplementary data

Full synthetic details for the preparation of **1a–f** and PL profiles of **1a–f** and their precursors **5**, **12**, **18**, **26** and **30** are provided.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.163.

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