Fluorescent and Phosphorescent Study of Germanium-Acetylene Polymers and Germa[N]pericyclynes

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Synthesis and optical properties of skipped polyynes comprising germanium-acetylene units are presented. The prepared germanium polymers were investigated by UV-vis, fluorescence, and phosphorescence spectroscopies and DFT calculations. The optical properties were compared to those of cyclic compounds, germa[*N*]pericyclynes. Unique fluorescence and phosphorescence behaviours of acyclic polymers were observed.

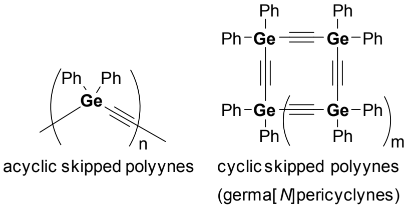

Fig 1 Germylene-ethynylene materials in this study.

With the growing importance of "element blocks" for electronic and optical materials,[1] polyacetylene research is receiving increasing attention.[2] Among polyacetylene materials, skipped polyynes ($[–R_2X–C{\equiv}C–]_n$) are of particular interest (Fig 1).[3] They consist of non-conjugated alkyne units interrupted by linker atoms (X). However, silicon (Si), which shows lower ionization energy than carbon (C), is expected to enhance the through-bond and through-space interactions when employed as the linker atom.[4] For these reasons, skipped polyynes are good candidates for functional materials[5] such as semiconductors, ceramic precursors, and hole-transporting materials. Si-tethered skipped polyynes,[6] including hypervalent Si-engaged materials[7] and platinum (Pt)-acetylene polymers,[8] have been well studied. Moreover, the linker sp^3-atom site of skipped polyynes, which limits the degree of conjugation, leads to phosphorescence emissions.[9] In this context, the use of a heavy atom as a linker unit is expected to produce unique optical organic-inorganic polymers for functional element-block materials.[1] The conductivity of (germylene)butadiyne polymers[10] and the phosphorescent properties of Pt-linked poly(silylacetylenes) and poly(fluorenylgermylenes)[8] have been reported. Because high thermal and air stabilities are required for functional materials, tetravalent group 14 atoms would be a preferable sp^3 unit due to the hypercoodination abilities of heavy atoms and strong covalent bonds between the sp-carbon atom units.

Of the group 14 atoms, Ge is known to show lower ionization energy than Si, and the sp-carbon–germanium bond is more stable than that of tin atom. For these reasons, Ge has also been used as a component of polymers containing such as alkynes, aromatic rings, or carbodiimides.[11,12] However, little is understood of the optical performance, particularly the light-emission properties, of skipped acetylene polymers composed exclusively of Ge atoms as the tethering species. Therefore, their properties should be explored. We recently developed cyclic poly(germylene-ethynylene) compounds, germa[*N*]pericyclynes, aimed at producing new element-block materials.[13] Herein, we disclose the synthesis and photoluminescent behaviours of novel Ge-acetylene monomers, oligomers, and polymers. Their properties are also discussed with comparison to our cyclic compounds, germa[*N*]pericyclynes.

The syntheses of acyclic Ge-acetylene materials are shown in Scheme 1. The terminal alkynes of monomer **1**[13] were substituted with trimethylsilyl groups to afford **2a**. We also prepared *tert*-butyl group-capped diyne **2a** with *tert*-butylacetylene from commercially available diphenylgermanium dichloride (Ph_2GeCl_2). Dimeric compound **3** was obtained by redistributing dimerization of **1**.[14] Heptameric compound **5** was prepared by disubstitution of Ph_2GeCl_2 with trimer **4**.[13b] Ge-acetylene polymer **6** was

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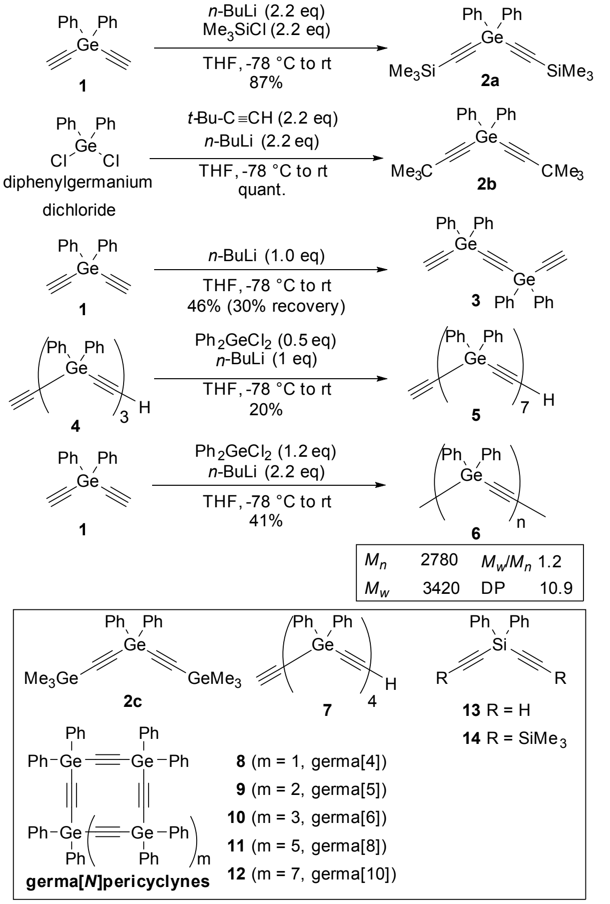
synthesized by the coupling of **1** with Ph_2GeCl_2, and its properties were determined by GPC analysis (M_n = 2,800, M_w = 3,400, M_w/M_n = 1.2, degree of polymerization (DP) = 10.9). For comparison with these acyclic compounds, bis(trimethylgermyl)-substituted monomer **2c**, acyclic tetramer **7**, and germa[4], [5], [6], [8], and [10]pericyclynes **8–12**, which were prepared in accordance with our reported methods,[13] were also analyzed by UV–vis absorption, fluorescence emission, and phosphorescence emission spectroscopies. Phosphorescence emission spectroscopy was also performed on Si derivatives, diethynyldiphenylsilane **13**[15a] and its silylated compound **14**,[15b] for comparison with Ge materials.



Scheme 1 Synthesis of germylene-ethynylene materials.

The optical properties of the prepared Ge-acetylene oligomers and polymers were investigated in dichloromethane (CH_2Cl_2), and were compared with those of our previously reported pericyclynes.[13] In the UV–vis absorption spectra (Fig 2a), all samples show absorption bands around 260 nm, and significant changes in the λ_{max} values are hardly observed. The ε values increase in accordance with the number of benzene rings (Fig 2b, see Supporting Information). From these results, it is clear that phenyl groups do not affect the peak positions in the absorption spectra, regardless if compounds are acyclic or cyclic, and Ph_2Ge or Ph_2Si although small red shifts are observed in Si monomers **13** and **14** (λ_{max} = 264 nm). This result means that slight electronic interaction could be obtained between the Ph_2Ge units at the ground state.

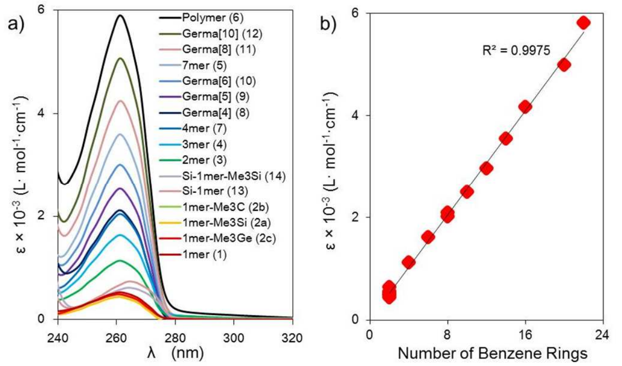


Fig 2 a) UV–vis absorption spectra of acyclic compounds compared to those of germapericyclynes (0.1 mM in CH_2Cl_2). ε values of **1**, **2c** and **8–12** are referred from our previous works,[13] b) Plot of ε values at 260 nm against the number of benzene rings.

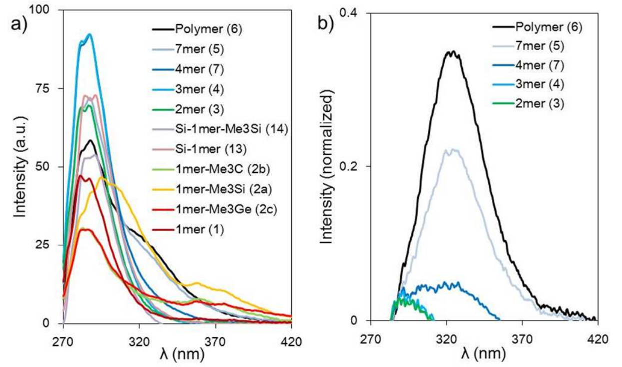


Fig 3 Fluorescence emission spectra (0.1 mM in CH_2Cl_2, λ_{ex} = 260 nm): a) polymers. **1** and **2c** are referred from our previous work,[13b] b) normalized differential spectra based on monomer **1**.

In contrast, specific spectral changes are observed in the fluorescence emission spectra (Fig 3a, λ_{ex} = 260 nm). As previously reported, germa[8] and [10]pericyclynes (**11** and **12**) show specific emission at 320 nm, along with weaker emissions than the other three pericyclynes **8–10** at 281 and 288 nm.[13b] The emission around 320 nm could be assigned to excimer emission by intramolecular π-π interactions between phenyl groups of different Ph_2Ge units or to electron delocalization through the germylene-ethynylene repeats. For acyclic compounds from monomers and tetramers **1**, **2a**, **2c**, **3**, **4**, and **7** emission peaks are only observed at 281 and 288 nm. On the other hand, heptamer **5** and polymer **6** show broad emissions around 320 nm with a decrease in the emission intensity at 285 nm (Fig 3a). This result implies that the polymers might form folding conformations in CH_2Cl_2, in which case π-π interactions between phenyl groups such as pericyclynes **11** and **12** could be observed even in acyclic compounds. Differences in the emission behaviour are clearly observed by normalized differential spectra based on monomer **1**, with tetramer **7** showing weak emission around

320 nm (Fig 3c). Compared to the peak shapes of the germapericyclynes from the previous work,[13] broad peaks of **5**–**6** are obtained. These data could be the results of loose and random interactions due to their chain structures. Fluorescence emission quantum yields were not recorded because the emissions were observed at only short wavelength.

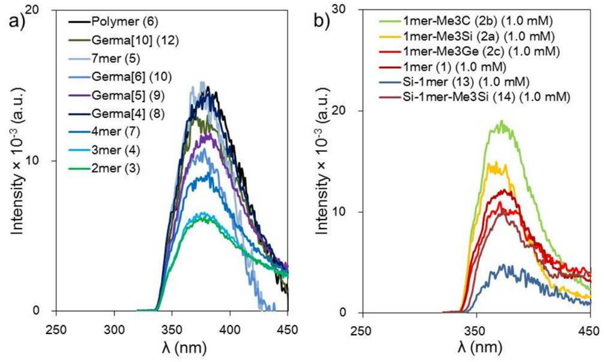


Fig 4 Phosphorescence emission spectra (λ_{ex} = 260 nm) in 2-methyltetrahydrofuran at 77 K: a) 0.1 mM, and b) 1.0 mM.

Next, we examined phosphorescence emissions of these compounds in 2-methyltetrahydrofuran at 77 K (λ_{ex} = 260 nm) (Fig 4).[16] Interestingly, without metal atoms, the phosphorescence properties were surely observed from these germylene-ethynylene compounds (Fig 4a). The emission maxima are found around 385 nm, and their lifetimes are obtained in the relatively longer time scale than those of the typical fluorescence emissions (15 μs, see Supporting Information). This result represents the phosphorescence property of Ge-containing compounds. The intensity seems to increase in accordance with the number of Ph_2Ge units. Although the emission from monomeric compound **1** (0.1 mM) is too weak to observe, it can be viewed under concentrated conditions (1.0 mM) (Fig 4b). Among the monomeric compounds, although the phosphorescence emission of Si compounds **13** and **14** were also observed, their intensities are less than those of Ge monomers **1** and **2a**–**c**. As noted, UV-vis absorption and fluorescence emission spectra of Ge materials are comparable to those of silicon compounds (Fig 1 and 2). However, these results demonstrate that, of the group 14 atoms, the use of a heavy atom tether (Ge) instead of Si can provide much more efficient phosphorescence abilities to the polymers. This means that polymerization could enhance the phosphorescence intensities.

From cyclic voltammetry and differential pulse voltammetry (DPV) (Fig. 5), only oxidation potentials were obtained as same as germapericyclynes.[13] Heptamer **5** and polymer **6** showed same oxidation potentials (E_{OX}^{DPV} = 1.31 V), and these potentials were found to be found to be comparable to or slightly lower than those of phenylated germapericyclynes ((E_{OX}^{DPV} = 1.31–1.38 V)).[13]

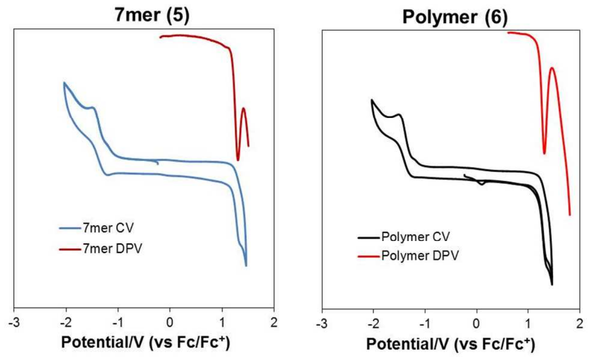


Fig 5 Cyclic and differential pulse voltammograms of heptamer **5** and polymer **6** (1.0 mM in 0.1 M n-Bu_4NPF_6–CH_2Cl_2 solution; scan rate = 0.1 or 0.05 V s^{-1}).

To improve the understanding of the electronic structures of Ge-containing compounds, density functional theory (DFT) calculations were performed (Fig 6). To compare the results in the point of view of the polymer chain length, number of Ge atoms, and cyclic/acyclic structures, we chose monomers, trimers and germapericyclynes for calculation. The HOMO-LUMO orbitals of **1**, **4**, **8**, and **10** are shown in Fig 5 (for detailed orbital levels and those of other compounds, see Supporting Information).[13b] Delocalized orbitals between Ge centres and π-carbon atoms are demonstrated in the LUMOs of all tested molecules. Strong in-plane orbitals are found in **8**. These data support the generation of new emission bands in the longer-wavelength region observed in the fluorescence spectra of the polymer, heptamer, and relatively larger cyclic compounds. In addition, electronic interactions involving the Ge atom could contribute to the phosphorescence of the germylene-ethynylene compounds via the internal heavy-atom effect. The phosphorescence emissions of the Ge compounds were greater than those of Si compound **13**. This implies that the greater heavy-atom effect of Ge than that Si might enhance the phosphorescence properties.

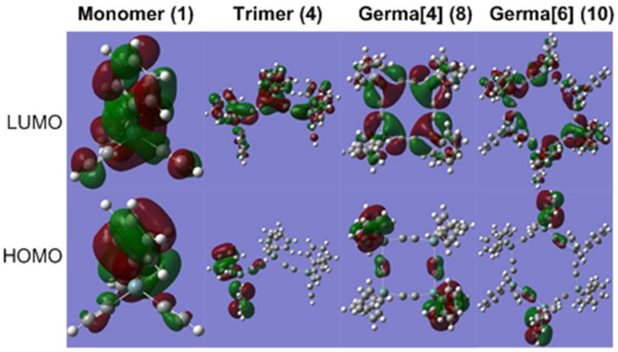


Fig 6 HOMO-LUMO orbitals calculated by Gaussian09 (B3LYP/6-31G(d,p)).

In summary, the optical properties of synthesized Ge-acetylene-composed polymers and pericyclynes were investigated using UV–vis absorption, fluorescence emission, and phosphorescence emission spectra. Acyclic materials as well as germa[*N*]pericyclynes showed new fluorescence emission peaks, probably by electronic interaction through the germylene-ethynylene tandem repeats. Phosphorescence emissions of germylene-ethynylene compounds were satisfactorily observed, even in the absence of transition metal atoms. DFT calculations suggest delocalized orbitals between the phenyl rings and alkynes through Ge atoms, which have the possibility to enhance the phosphorescent emission by excitation of the benzene rings. Our work, especially on the phosphorescence abilities of germylene-ethynylene polymers, should provide new aspects of skipped polyynes towards organic-inorganic hybrid materials of element blocks for optoelectronics.

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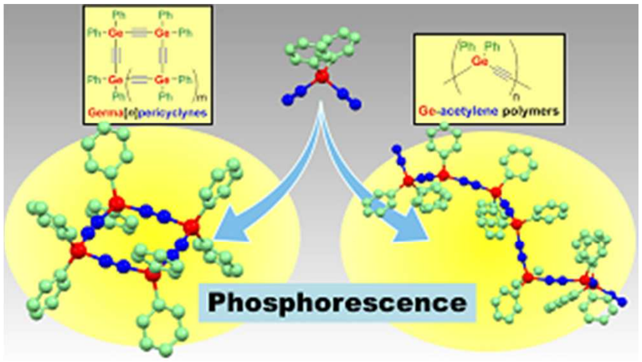
16 Phosphorescence emission spectrum of germa[8]pericyclynes **11** was not majored because it did not dissolve in 2-methyltetrahydropyran.



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