CHEMISTRY
A European Journal

A Journal of
ChemPubSoc
Europe

Accepted Article

Title: Arene-inserted Extended Germa[N]pericyclynes: Synthesis, Structure, and Phosphorescence Properties

Authors: Hiroki Tanimoto, Junta Mori, Shunichiro Ito, Yasuhiro Nishiyama, Tsumoru Morimoto, Kazuo Tanaka, Yoshiki Chujo, and Kiyomi Kakiuchi

To be cited as: *Chem. Eur. J.* 10.1002/chem.201701359

Link to VoR: http://dx.doi.org/10.1002/chem.201701359

Arene-inserted Extended Germa[*N*]pericyclynes: Synthesis, Structure, and Phosphorescence Properties

Hiroki Tanimoto,*[a] Junta Mori,[a] Shunichiro Ito,[b] Yasuhiro Nishiyama,[a] Tsumoru Morimoto,[a] Kazuo Tanaka,[b] Yoshiki Chujo,[b] and Kiyomi Kakiuchi*[a]

Dedication ((optional))

Abstract: This report describes the synthesis and characterization of arene-inserted type extended (ArEx) germa[*N*]pericyclynes composed of germanium and 1,4-diethynylbenzene units. These novel cyclic germanium-π unit materials were synthesized with diethynylbenzene and germanium dichloride. X-ray crystallographic analysis revealed their structures and the planar conformation of ArEx germa[4]pericyclyne along with the regulated aromatic rings. UV-vis absorption spectra and fluorescence emission spectra showed considerably unique and highly improved characters compared to previous germapericyclynes. Even in the absence of transition metal components, phosphorescence emissions were observed, and the emission lifetimes were dramatically improved. ArEx germapericyclynes showed high photoluminescence quantum yields, while that of acyclic compound was low. Density functional theory calculations show delocalized orbitals between skipped alkyne units through a germanium tether and an increase in the HOMO energy level leading small HOMO-LUMO energy gap.

Introduction

Polyene and polyyne materials have been of interest of industry and emerging high performance devices. Among them, skipped polyyne compounds ($[-M-C\equiv C-]_n$) consisting of conjugation-interrupted alkyne units by linker atoms (M) are of particular interest for novel optical materials.[1] Although the conjugation degree of these compounds are limited, the use of heavy linker atoms which influence the d orbital can afford specific characteristics to the materials compared to carbon (C) linkers.[2] And to date, silicon (Si) and other main-group elements heavier than C have been employed as linker atoms in skipped polyynes to enhance hyperconjugation through bond and space interactions.[3] With these backgrounds, the importance of the "element-blocks" concept[4] has specifically increased, resulting in novel organic-inorganic hybrid polymer functionalities by use of various elements for applications including electronic and optical materials.

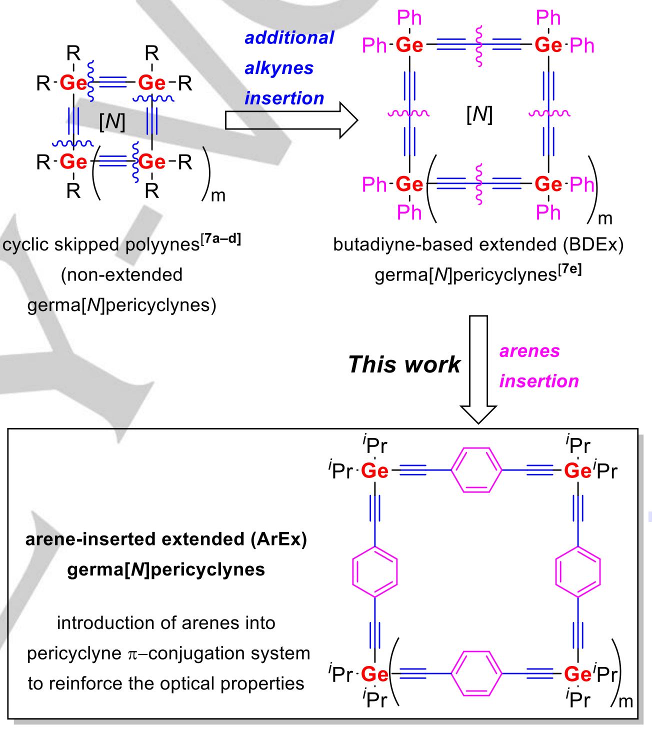


Figure 1. Structure and performance improvement of germa[*N*]pericyclynes by π-conjugation extension.

To improve optical properties of the skipped polyynes, cyclic skipped polyynes, known as pericyclynes, are promising candidates for use in functional materials such as ceramic precursors and hole-transporting materials.[1,5] As well as controlling the polymerization degree precisely, cyclic structures of skipped polyynes are expected to stabilize their structures by fixing the conformation, which could reduce thermal deactivation of excited states. Additionally, the use of hetero or heavy linker atoms could reinforce through-space interactions between the skipped alkyne moieties through the double propargylic tether units.[3,5,6] Of the group 14 atoms available for use in such systems, we have focused on the use of germanium (Ge), which has lower ionization energy than Si and C. By using a C(sp)–Ge σ bond which is more stable than the C(sp)–Sn (tin) σ bond, we have developed cyclic poly(germylene-ethynylene) compounds of novel element-block materials which are called (extended)

---

[a] Dr. Hiroki Tanimoto, Junta Mori, Dr. Yasuhiro Nishiyama, Prof. Dr. Tsumoru Morimoto, and Prof. Dr. Kiyomi Kakiuchi
Graduate School of Materials Science
Nara Institute of Science and Technology (NAIST)
8916-5 Takayamacho, Ikoma, Nara 630-0192, Japan
E-mail: tanimoto@ms.naist.jp; kakiuchi@ms.naist.jp
[b] Shunichiro Ito, Prof. Dr. Kazuo Tanaka, and Prof. Dr. Yoshiki Chujo
Department of Polymer Chemistry
Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

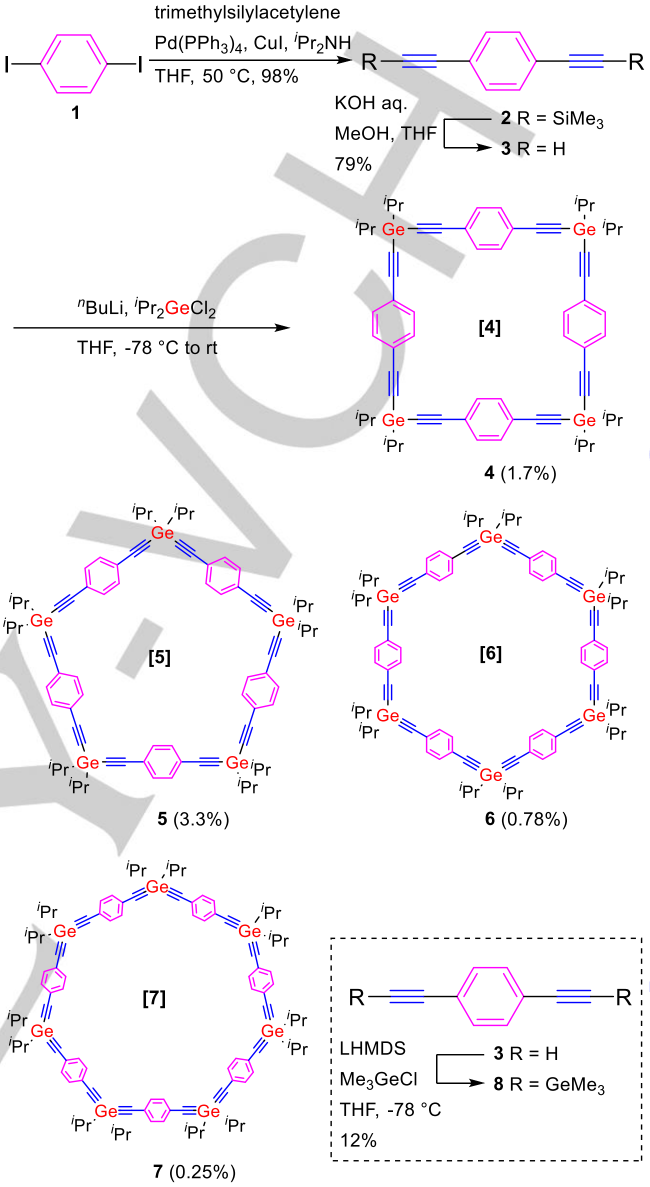
Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201701359

germa[*N*]pericyclynes (Figure 1).[7] Structural modification of germapericyclynes by way of expanding the alkyne unit π-conjugation from acetylene-based (non-extended) to butadiyne-based extended (BDEx) materials changed their various characteristics (e.g. UV-vis, phosphorescence emission spectra and HOMO-LUMO energy gaps) changed dramatically.[7e] This suggests that modification of sp/sp^2 conjugation units in pericyclynes can further improve the potential of germapericyclynes. With this background, we designed new extended germa[*N*]pericyclynes, of which arene groups are inserted in the ring system. With the aromatic groups inside of the ring systems, further extension of π-conjugation should improve the optical characters of the pericyclynes. Moreover, in contrast to the previous (extended) germa[*N*]pericyclynes, the arene moiety of the pericyclyne circuits can be a good potential scaffold for fabrication of polymeric pericyclyne materials[7d] by cross coupling reactions, and for future performance modification by functionalization of the arene group. In this report, we describe the synthesis of arene-inserted extended germa[*N*]pericyclynes (ArEx germa[*N*]pericyclynes), which are characterized by X-ray crystallographic structures and optical performances with comparison to those of previously synthesized (extended) germa[*N*]pericyclynes.

Results and Discussion

We previously researched BDEx germapericlycnes with peripheral phenyl groups (Figure 1).[7e] To discuss the effect of the aryl group position (peripheral or ring component), we chose isopropyl of alkyl group as peripheral substituents. The initial attempt was examined by Sonogashira coupling reaction with diethynyl germane[7a,b] and commercially available 1,4-diiodobenzene **1** to construct ArEx pericyclyne structures.[8] Although double cross coupling with simple iodobenzene and diethynyl germane was successful, oligomerization/cyclization with **1** failed to obtain the desired cyclic compounds. We believe this was due to the difficulty of the macrocyclization between the sp^2 and the sp carbon centers. Thus, we adopted an alternative synthetic strategy for macrocyclization by nucleophilic substitution on Ge centers. 1,4-diethynylbenzene **3** prepared through two steps from **1**[8b] was treated with *n*-butyllithium and diisopropylgermanium dichloride[7a,b] to successfully afford the desired ArEx germa[4], [5], [6], and [7]pericyclynes **4**–**7**. ArEx compounds **5** and **7** of odd Ge numbers would also be afforded by distributing substitution reaction of group 14 elements.[7c,7e,9] Although ArEx germa[8] and [10]pericyclynes could be found from mass spectroscopy, **4**–**7** were chosen for the characterization because of the available quantity of the products for various analyses. The desired products were purified by silica gel column chromatography followed by recycling gel permeation chromatography (GPC) and recrystallization. For comparison with these cyclic compounds and acyclic monomer units **2** and **3**, we also prepared 1,4-bis(trimethylgermylethynyl)benzene **8**.

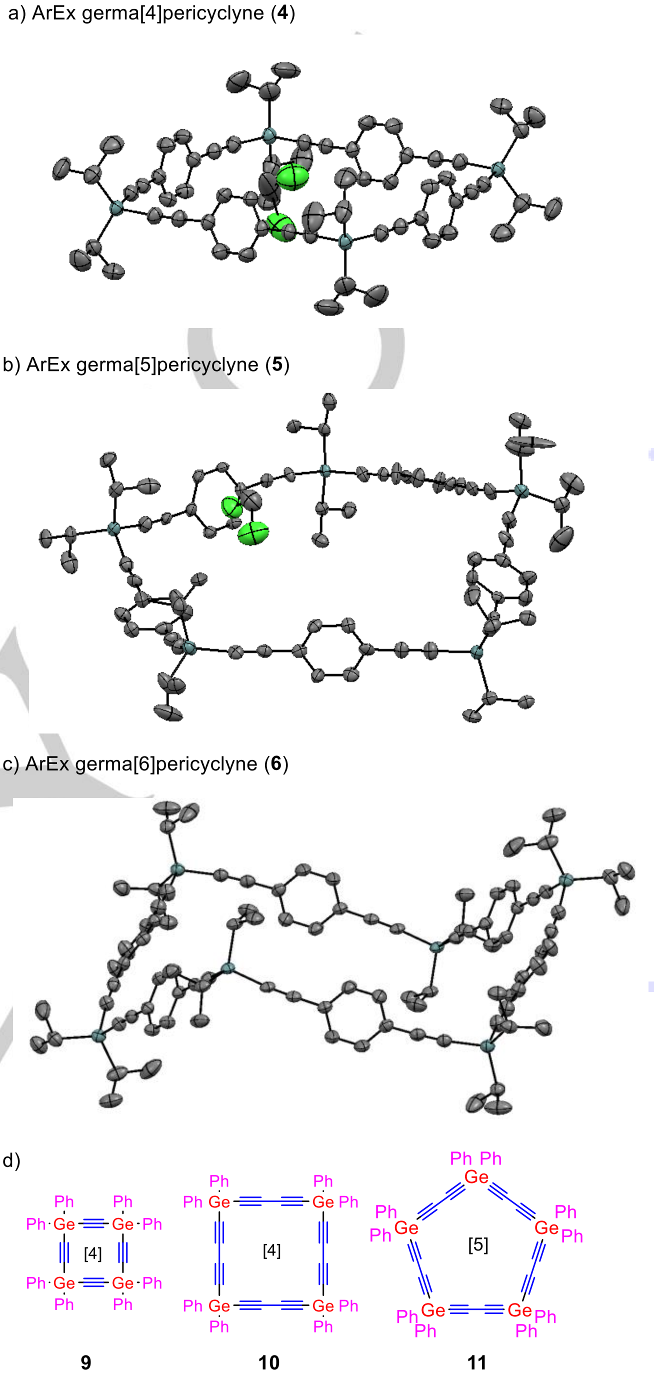


Scheme 1. Synthesis of arene-inserted extended (ArEx) germa[*N*]pericyclynes.

The afforded ArEx germapericyclynes were crystalline compounds, and the single crystal-obtained **4**–**6** were analyzed by X-ray crystallography.[10] As shown in Figure 2, ArEx germa[4]pericyclyne **4** exhibited a planar conformation. ArEx germa[5]pericyclyne **5** adopted a slightly loose envelope conformation compared to the other previous perphenyl germa[5]pericyclynes like **9**.[7b,e] Similar to the previous phenyl-substituted acetylene-based and BDEx germa[6]periclynes,[7a,e] Perisopropyl ArEx germa[6]pericyclyne **6** was in the chair conformation, whereas isopropyl-substituted acetylene-based germa[6]pericyclyne was in a nearly planar conformation.[7a,e] Because the steric bulkiness of isopropyl group accounts for the planar structure of the acetylene-based compound,[7a] ring expansion should result in allowing chair conformation of **6**.

10.1002/chem.201701359

Interestingly, the benzene rings of **4** in the obtained crystal were vertical to the pericyclyne rings, while those of **5** and **6** were directed irregularly. In the cavities of **4** and **5**, recrystallization solvent molecules (CH_2Cl_2) were found. Due to the enlarged cavity sizes from the previous molecules (for hole diagonal distance of [4]pericyclynes, **9**: 7.1 Å, **10**: 10.7 Å, **4**: 16.9 Å),[7] the fixing ability by coordination seemed to be poor. The C≡C lengths of the ArEx, BDEx, and acetylene-based germapericyclynes were comparable (average length **4**: 1.20 Å, **5**: 1.19 Å, **6**: 1.20 Å).[11] The C–Ge–C angles of **4** (104.14(14)° and 103.13(14)°) were comparable to the non-extended and BDEx [4]pericyclynes. While those of BDEx [5]pericyclyne **11** were squeezed (102.9° average), those of **5** were close to the non-extended compound (106° average). In the case of **6**, the C–Ge–C angles (105.6° average) were close to the butadiyne-type compound (104.8 ° average) and were narrower than that of acetylene-type non-extended germa[6]pericyclyne (109° average). Ge-C≡C bonds (average angle **4**: 174°, **5**: 171°, **6**: 175°) were flatter than non-extended compounds, but more bent than BDEx molecules,[11] while the Ar-C≡C bond (average angle **4**: 177°, **5**: 177°, **6**: 178°) are flatter than Ge-C≡C bonds.


a) ArEx germa[4]pericyclyne (**4**)

b) ArEx germa[5]pericyclyne (**5**)

c) ArEx germa[6]pericyclyne (**6**)

d)

Figure 2. ORTEP drawings of ArEx germa[*N*]pericyclynes with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity; (a) ArEx germa[4]pericyclyne **4** with dichloromethane; (b) ArEx germa[5]pericyclyne **5** with dichloromethane; (c) ArEx germa[6]pericyclyne **6**; (d) Structure of acetylene-based germa[4]pericylcyne **9**, BDEx germa[4], and [5]pericyclynes **10**, **11**.

UV-vis spectra of ArEx pericyclynes were recorded in dichloromethane (Figure 3a). ε values of **4**–**7** were much larger than those of previous BDEx germa[*N*]pericyclynes such as **11** due to the presence of alkyne-conjugated aromatic group. Compared to the cyclic and acyclic compounds, the spectral figures of ArEx pericyclynes seem to be similar to the end-capped diethynylbenzene compounds **2** and **8**. Although replacing the Ge with Si did not affect the UV-vis spectra, the absorption maxima of **4**–**7** (268 (sh), 282, and 298 nm) are slightly red-shifted from those of the acyclic materials **2** and **8** (265, 278 and 293 nm). This is probably due to the orbital interaction between neighbouring π conjugation units through Ge tethers (See also LUMO in Figure 6). From the plot of ε values of **4**–**7** against the number of diethynylbenzene units, linear correlation was observed (Figure 3b), and the degree of the increase at 298 nm is higher than those at 282 nm. From the ORTEP figures of **4** showing vetically lying benzene rings of **4** and irregularly lying those of **5** and **6** (Figure 2), this would be due to the increasing conjugation to enhance σ*–π* interaction between diethynylbenzenes and Ge tethers by ring expansion allowing rotation of benzene rings in the parallel direction to the pericyclyne rings.

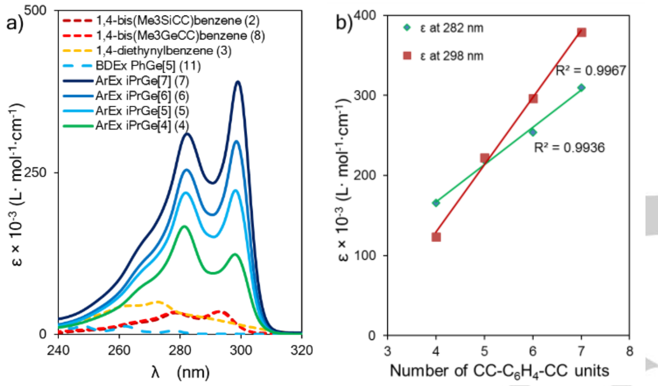


Figure 3. (a) UV-Vis spectra of the various compounds of interest in dichloromethane. The absorption spectrum of **11** was taken from our previous works.[7e] (b) Plot of ε values of each absorption maxima against the number of CC-C_6H_4-CC units.

We next examined the fluorescence emission spectroscopy (Figure 4). Although previous BDEx compounds like **5** only showed very weak emission,[7e] three absorption maxima were observed from ArEx germapericyclynes **4**–**7** (Figure 4a). Acyclic compound **8** showed a considerably different emission spectrum from other cyclic materials. Although previous germapericyclynes consisted with acetylenes or butadiynes did not show the largely different emission spectra from their monomeric π-components,[7] compounds **4**–**7** containing arene units in the ring systems could affect the emission spectra by interaction between skipped diethynylbenzene units through tethering Ge moiety (See LUMO in Figure 6 and Supporting Information). On comparing ArEx germa[4]pericyclyne **4** to other ArEx materials **5**–**7**, it can be seen that emission intensity of **4** around 310 nm is relatively weak against that around 320 nm, and the character observed from UV-vis spectra (Figure 3a) enhanced the increasing intensity of emission by around 310 nm compared to other emission areas.

Even in the absence of transition metal components, phosphorescence emissions of **4**–**7** as well as acyclic **8** were observed around 462 nm, although the intensities were lower than those of the previous germapericyclnes (Figure 4b).[7c–e] The relative intensity trend between **4**–**8** was similar to that of the fluorescence emission around 310 nm (Figure 4a). While phosphorescence emission results of previous BDEx and acetylene-based germapericyclynes were obtained by excitation of the germylbenzene (PhGe) group, excited diethynylarenes in ArEx compounds, from which Ge atoms were placed relatively far, can show sufficient phosphorescence emission. To our surprise, the phosphorescence emission lifetimes of **4**–**7** were over 100 ms (**4**: 200 ms, **5**: 190 ms, **6**: 130 ms, **7**: 180 ms), and were much longer than those of BDEx (ca. 0.7 ms) and acetylene-based materials (ca. 20 μs).[7c,11] The emission of Ge-capped diethynylbenzene **8** was slightly shorter than those of cyclic compounds (97 ms). The absolute photoluminescence quantum yields Φ_{PL} were also recorded, and **4**–**7** showed higher values than **8** (Φ_{PL} at room temperature **4**: 0.13, **5**: 0.24, **6**: 0.19, **7**: 0.14, **8**: 0.043; Φ_{PL} at 77K **4**: 0.53, **5**: 0.71, **6**: 0.55, **7**: 0.63, **8**: 0.21). Unfortunately, due to the low intensity, it was hard to observe these phosphorescence emissions by the naked eyes. However, These results could give us significant suggestions for the molecular design of organic-inorganic hybrid element-block materials with photoluminescence of a long duration.[4]

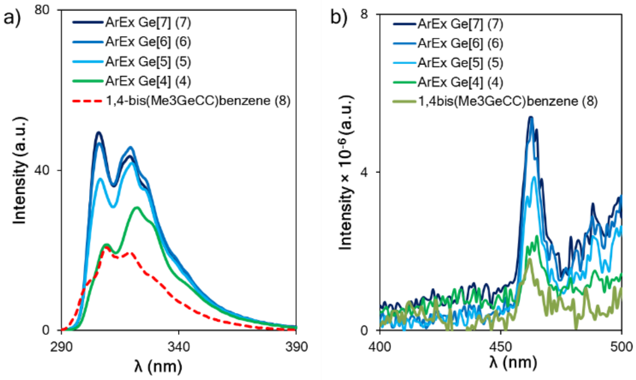


Figure 4. (a) Fluorescence emission spectra of ArEx germapericyclynes **4**–**7** and bis(trimethylgermylethynyl)benzene **8** ($1{\times}10^{-6}$ M in CH_2Cl_2, λ_{ex} = 282 nm for **4**–**7**, λ_{ex} = 278 nm for **8**). (b) Phosphorescence emission spectra ($1{\times}10^{-6}$ M in 2-methyltetrahydrofuran at 77 K, λ_{ex} = 298 mn for **4**–**7**, λ_{ex} = 293 mn for **8**, background cut off).

Similar to the previous germapericyclynes, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analysis of ArEx materials **4**–**7** indicated their oxidation potentials (Figure 5). Those of previous BDEx germapericyclynes were found at +1.36V and acetylene-based germapericyclynes were from +1.31 to +1.38 V. In contrast, the ArEx germapericyclynes **4**–**7** had oxidation potentials at 1.50–1.69 V (**4**: +1.69 V, **5**: +1.64 V, **6**: +1.50 V, **7**: +1.61 V). Although correlation between the potential level and the ring size was not found, these new pericyclynes showed higher oxidation potentials than previous materials, probably due to the presence of an alkyne-conjugated arene moiety.

10.1002/chem.201701359

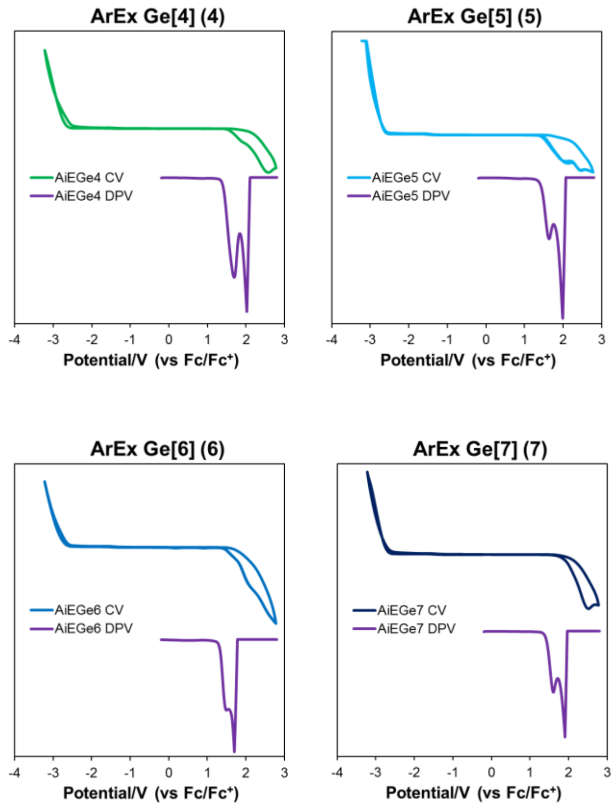


Figure 5. Cyclic and differential pulse voltammetry curves for ArEx germa[4]–[7]pericyclynes **4**–**7** (0.1 mM in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 solution).

To understand the molecular orbitals, and the energy levels of these compounds and the related previous germapericyclyne series, density functional theory (DFT) calculations were performed (Figure 6). As observed in the previous molecules, **4** shows orbital delocalization in the LUMO between adjacent non-conjugated alkyne moieties through the Ge vertices. This delocalization and the presence of arene group would support the spectral change from **8** to ArEx pericyclynes (Figure 4). Although the LUMO energy levels are similar to **10**, HOMO level of **4** is observed at higher level than other two types of germapericyclynes, and these follows the results from the CV. Based on the energy level comparison of acyclic model compounds, the small gap of **4** would be mainly derived from the diethynylbenzene moiety. Slightly low LUMO level of **4** compared to **12** would be one of the reasons for bathochromic shifts in UV-vis spectra (Figure 3a). Although the energy levels and energy gap of **12** were close to **4**, low quantum yields of **8** compared to other ArEx compounds could be attributed to a lack of Ge-(C≡C)$_2$ structures producing a delocalized orbital through the Ge tether moiety. Overall, in our study of germapericyclynes starting from **9**[7a–d] to **10**[7e] to this ArEx compound **4**, we successfully reduced the energy gaps, and these ArEx germapericyclynes are presumably promising candidates of element-block optical materials[4] which improve the performances of the previous germapericyclynes.

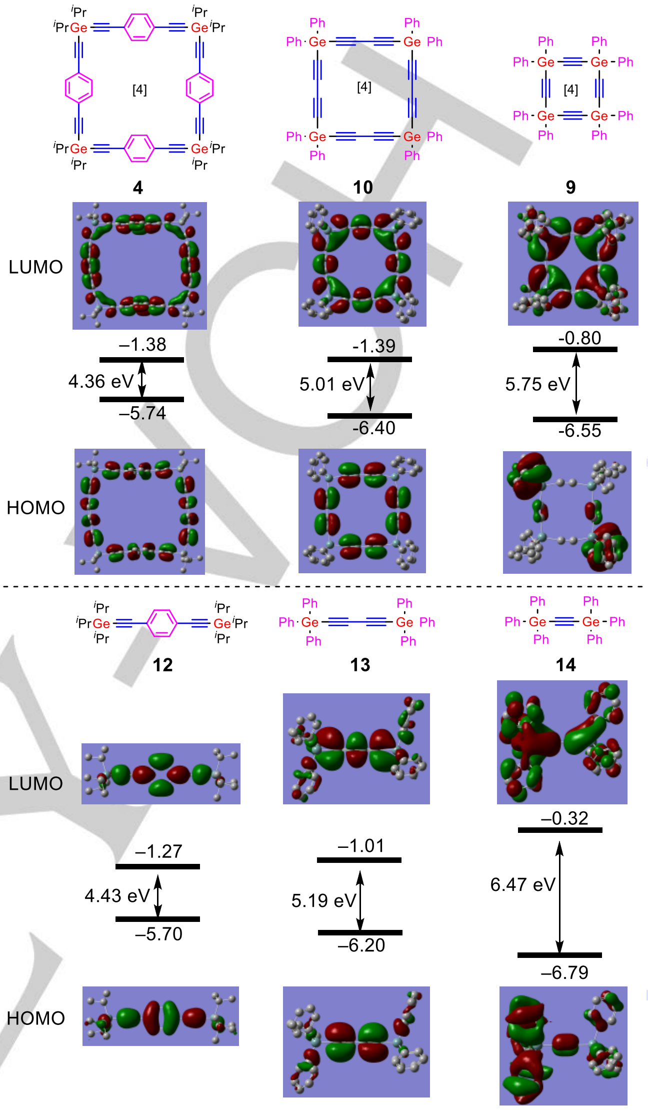


Figure 6. Comparisons of the molecular orbitals and energy levels of the (extended) germa[4]pericyclynes as determined by DFT calculations (Gaussian 09 B3LYP/6-31G(d,p)). Hydrogen atoms are omitted for clarity. The conformation of **4** is based on CIF files from X-ray analyses. The calculated results of **9** and **10** were obtained from our previous study. [7c,e].

Conclusions

Novel type of extended germapericyclynes, arene-inserted extended (ArEx) germa[4]–[7]pericyclynes composed of germylene-ethynylene-arene units were synthesized and were characterized. X-ray crystallography revealed their structures and the planar conformation of ArEx germa[4]pericyclyne along with its regulated aromatic rings. UV-vis absorption spectra and fluorescence emission spectra showed considerably unique and improved characteristics compared to butadiyne-based extended (BDEx) macrocycles. Phosphorescence emissions were clearly observed, and the emission lifetimes were dramatically improved over the previous germapericyclynes. Photoluminescence

10.1002/chem.201701359

quantum yields of ArEx germapericyclynes showed large improvement compared to the acyclic digermyldiethynylbenzene of the pericyclyne ring component. The molecular orbitals and their energy levels estimated by DFT calculations show an increase in the HOMO energy level leading to a small HOMO-LUMO energy gap, which follow the results obtained from cyclic and differential pulse voltammetry. These results revealed the potential of π-extended germylene-ethynylene molecules and provide efficient suggestions for the optical properties for further improvement of skipped polyyne-type materials. We hope our research leads to the optical materials of these cyclic organogermanium element-block materials.

Experimental Section

General Information

^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak ($CDCl_3$: δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR). The abbreviations used are as follows: s (singlet), d (doublet), sept (septet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStaion [EI (70 eV)], and Bruker Autoflex II (MALDI-TOF). UV-visible spectra were recorded using JASCO V-630. Fluorescence emission spectra were collected using JASCO FP-6500. Low temperature fluorescence and phosphorescence emission spectra were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. Photoluminescence quantum yields were measured using Hamamatsu Photonics Quantaurus-QY Plus C13534-01. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing n-Bu_4NPF_6 as the supporting electrolyte at 298 K (100 mV s^{-1}). The glassy carbon working electrode was polished using BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to $Ag/AgNO_3$ and normalized with respect to Fc/Fc^+. All measurements of single crystal X-ray diffraction analysis were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation. The data were usually collected at a temperature of -150 °C. Elemental analysis were performed using a Perkin Elmer 2400Ⅱ CHNS/O. Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F_{254}). Iodine on silica gel was used for the TLC stains, and TLC was also monitored with UV lamp. The further purifications of the crude materials were performed using a LC-908 recycling gel permeation chromatography (GPC) equipped with a JAIGEL 2H-40 column (chloroform elution) made by Japan Analytical Industry Co., Ltd. All the reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Merck. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical. Density Functional Theory (DFT) calculations were performed using the Gaussian 09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-31G(d,p) basis set in this series of calculations.

1,4-Bis(trimethylsilylethynyl)benzene (**2**). Under nitrogen atmosphere, 1,4-diodobenzene **1** (4.0 g, 12 mmol), copper(I) iodide (0.12 g, 0.63 mmol), and tetrakis(triphenylphosphine)palladium (0.7 g, 0.61 mmol) were dissolved in tetrahydrofuran (101 mL), and the stirred solution was heated at 50 °C for 21 h. The solution was filtered by Celite and was washed with dichloromethane. The crude material obtained after concentration of the filtrate *in vacuo* was purified by silica gel column chromatography (hexane elution) to afford **2** (3.2 g, 98%) as a white solid. R_f value 0.4 (hexane); m.p. 119–121 °C; IR (NaCl, neat) ν_{max} 2958, 2898, 2154, 1492, 1409, 1249, 1214, 848, 757 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 4H), 0.24 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 123.1, 104.5, 96.3, -0.12; HRMS (EI) calcd for $C_{16}H_{22}Si_2$ (M^+) 270.1260, found 270.1252.

1,4-diethynylbenzene (**3**). 1,4-bis(trimethylsilylethynyl)benzene **2** (3.2 g, 12 mmol) was added to a stirred mixture of 1M potassium hydroxide aqueous solution (36 mL), methanol (108 mL), and tetrahydrofuran (108 mL). Then, the reaction mixture was stirred for 3 h. The mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate. The concentration of the combined organic layer *in vacuo* was followed by silica gel column chromatography (hexane to hexane/CH_2Cl_2 = 5 / 1) to afford **3** (1.2 g, 79%) as a white solid. R_f value 0.57 (hexane / CH_2Cl_2 = 3 / 1); m.p. 92–95 °C; IR (NaCl, neat) ν_{max} 3301, 3262, 2102, 1918, 1795, 1675, 1492, 1400, 1371, 1257, 1105, 1016 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 4H), 3.17 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.0, 122.5, 83.0, 79.1; HRMS (EI) calcd for $C_{10}H_6$ (M^+) 126.0470, found 126.0481.

1,4-Bis(trimethylgermylethynyl)benzene (**8**). Lithium hexamethyldisilazide (0.48 mL, 0. 48 mmol, 1.0 M in THF) was added to a stirred solution of 1,4-diethynylbenzene **3** (0.14 g, 1.1 mmol) and trimethylgermanium chloride (0.38 g, 2.5 mmol) in tetrahydrofuran at -78 °C under nitrogen atmosphere, and then the mixture was warmed up to ambient temperature. After 4 days, the reaction was quenched with saturated ammonium chloride aqueous solution and was extracted with dichloromethane. The extract was washed with brine and the combined organic layer was dried over magnesium sulfate. The organic solvent was removed *in vacuo* and the obtained residue was purified by silica gel column chromatography (hexane/ dichloromethane = 5 / 1) followed by GPC to afford **8** (47 mg, 12%) as a white crystal. R_f value 0.11 (hexane); m.p. 92–95 °C; IR (NaCl, neat) ν_{max} 2975, 2912, 2154, 1495, 1414, 1236, 837, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 4H), 0.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.6, 123.1, 103.8, 96.7, -0.20; LRMS (EI, M = $C_{16}H_{22}Ge_2$) 262 (M^+).

Synthesis of arene-inserted extended (ArEx) germa[*N*]pericyclynes

n-Butyllithium (23 mL, 38 mmol, 1.64 M in hexane) was added dropwise at -78 °C to a stirred solution of 1,4-diethynylbenzene **3** (2.0 g, 15.9 mmol) in tetrahydrofuran (317 mL) under nitrogen atmosphere. After 2 h, diisopropylgermanium dichloride (3.65 g, 15.9 mmol), prepared in accordance with our work,[7a] was added to the mixture dropwise. The mixture was stirred at the same temperature for 24 h, and then warmed up to the ambient temperature. After stirring for 6 days, the reaction was quenched with saturated ammonium chloride aqueous solution and water at 0 °C. The mixture was extracted with dichloromethane and was washed with water and brine. The combined organic layer was dried over magnesium sulfate. The organic layer was concentrated *in vacuo* followed by silica gel column chromatography (hexane to hexane / CH_2Cl_2 = 10 / 1) to afford crude ArEx germapericyclynes. The obtained crude material was further purified by GPC and recrystallization to afford the ArEx germa[4], [5], [6] and [7]pericyclynes **4**–**7**, respectively. White crystals of the ArEx germapericyclynes were obtained in the following yields: **4** (78 mg, 1.7 %), **5** (150 mg, 3.3%), **6** (35 mg, 0.78%), and **7** (11 mg, 0.3%).

Arene-inserted extended octaisopropylgerma[4]pericyclyne (**4**, CCDC 1539470). Recrystallization for X-ray analysis was performed with dichloromethane and methanol. White solid; R_f value 0.52 (hexane /

CH_2Cl_2 = 3 / 1); m.p. 250–280 °C (decomposed / discolored); IR (NaCl, neat) $ν_{max}$ 2946, 2865, 2156, 1492, 1463, 1216, 1004, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 16H), 1.55 (sept, 8H, J = 7.5 Hz), 1.28 (d, 48H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9, 123.2, 106.3, 90.2, 19.0, 16.6; LRMS (MALDI-TOF, $[M+Na]^+$, M = $C_{60}H_{72}Ge_4Na$) 1155. Anal. Calcd: C. 67.92%; H. 6.41%, found: C. 67.52%, H. 6.36%.

Arene-inserted extended decaisopropylgerma[5]pericyclyne (**5**, CCDC 1539472). Recrystallization for X-ray analysis was performed with dichloromethane and methanol. White solid; R_f value 0.50 (hexane / CH_2Cl_2 = 3 / 1); m.p. 240–280 °C (decomposed / discolored); IR (NaCl, neat) $ν_{max}$ 2942, 2862, 2157, 1494, 836, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 20H), 1.55 (sept, 10H), 1.28 (d, 60H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9, 123.1, 106.1, 89.7, 19.0, 16.9; LRMS (MALDI-TOF, $[M+Na]^+$, M =$C_{80}H_{90}Ge_5$) 1438. Anal. Calcd: C. 67.92%; H. 6.41%, found: C. 67.58%, H. 6.19%.

Arene-inserted extended dodecaisopropylgerma[6]pericyclyne (**6**, CCDC 1539471). Recrystallization for X-ray analysis was performed with dichloromethane and methanol. White solid; R_f value 0.44 (hexane / CH_2Cl_2 = 3/1); m.p. 250–270 °C (decomposed / discolored); IR (NaCl, neat) $ν_{max}$ 2942, 2861, 2157, 1494, 1459, 1220, 1002, 836, 763 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 24H), 1.56 (sept, 12H, J = 7.5 Hz), 1.27 (d, 72H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9, 123.1, 106.1, 89.6, 19.0, 17.0; LRMS (MALDI-TOF, $[M+Na]^+$, M = $C_{96}H_{108}Ge_6$) 1721; Anal. Calcd C. 67.92, H. 6.41, found C. 67.77, H.6.27.

Arene-inserted extended tetradecaisopropylgerma[7]pericyclyne (**7**). White solid; R_f value 0.42 (hexane / CH_2Cl_2 = 3 / 1); m.p. 250–270 °C (decomposed / discolored); IR (NaCl, neat) $ν_{max}$ 2942, 2861, 2157, 1494, 1220, 1006, 836, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 28H), 1.56 (sept, 14H, J = 7.5 Hz), 1.27 (d, 84H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.0, 123.2, 106.3, 89.8, 19.2, 17.0; LRMS (MALDI-TOF, $[M+Na]^+$, M = $C_{112}H_{126}Ge_7$) 2003. Anal. Calcd: C. 67.92%; H. 6.41%, found: C. 67.65%, H. 6.16%.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas ‘New Polymeric Materials Based on Element-Blocks (No. 2401)’ of JSPS KAKENHI (JP15H00750 for H.T., JP15H00736 for K. T., JP24102013 and JP24102001 for Y.C.). We thank Profs. Naoki Aratani and Hiroko Yamada (CV and DPV), Mr. Shohei Katao (X-ray crystallographic analysis), Mr. Fumio Asanoma (elemental analysis), Ms. Yoshiko Nishikawa and Mr. Kazuo Fukuda (MS measurement) of NAIST.

Keywords: germanium • pericyclynes • fluorescence emission • phosphorescence emission • X-ray crystallographic analysis

[1] *Acetylene Chemistry: Chemistry, Biology, and Material Science*, (Eds: F. Diederich, P. J. Stang and R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**.

[2] a) M. Birot, J.-P. Pillot, J. Dunoguès, *Chem. Rev.* **1995**, *95*, 1443–1477; b) N. J. Long, C. K. Williams, *Angew. Chem., Int. Ed.* **2003**, *42*, 2586–2617; c) W.-Y. Wong, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 197–219; d) W.-Y. Wong, *Dalton Trans.* **2007**, 4495–4510; e) W.-Y. Wong, S.-Y. Poon, J.-X. Shi, K.-W. Cheah, *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 189–200; f) R. Gleiter, D. B. Werz, *Chem. Rev.* **2010**, *110*, 4447–4488.

[3] a) H. Sakurai, H. Sugiyama, M. Kira, *J. Phys. Chem.* **1990**, *94*, 1837–1843; b) R. Gleiter, W. Schäfer, H. Sakurai, *J. Am. Chem. Soc.* **1985**, *107*, 3046–3050; c) R. Emanuelsson, A. Wallner, E. A. M. Ng, J. R. Smith, D. Nauroozi, S. Ott, H. Ottosson, *Angew. Chem. Int. Ed.* **2013**, *52*, 983–987; d) E. Göransson, R. Emanuelsson, K. Jorner, T. F. Markle, L. Hammarström, H. Ottosson, *Chem. Sci.* **2013**, *4*, 3522–3532; e) S. Yamaguchi, Y. Itami, K. Tamao, *Organometallics* **1998**, *17*, 4910–4916; e) S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn*. **1996**, *69*, 2327–2334.

[4] Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jpn*. **2015**, *88*, 633–643.

[5] For reviews of pericyclynes, see: a) L. T. Scott, K. J. M. Cooney, in: *Modern Acetylene Chemistry,* (Eds: P. J. Stang and F. Diederich), VCH, Weinheim, **1995**, pp 321–351; b) A. de Meijere, S. I. Kozhushkov, in: *Carbon Rich Compounds II. Topics in Current Chemistry vol 201*, (Ed. A. de Meijere), Springer, **1999**, pp 1–42; c) V. Maraval, R. Chauvin, *Chem. Rev.* **2006**, *106*, 5317–5343.

[6] G. Märkl, T. Zollitsch, P. Kreimeier, M. Prinzhorn, S. Reithinger, E. Eibler, *Chem.–Eur. J.* **2000**, *6*, 3806–3820.

[7] a) H. Tanimoto, T. Nagao, Y. Nishiyama, T. Morimoto, F. Iseda, Y. Nagato, T. Suzuka, K. Tsutsumi, K. Kakiuchi, *Dalton Trans.* **2014**, *43*, 8338–8343; b) H. Tanimoto, T. Nagao, T. Fujiwara, Y. Nishiyama, T. Morimoto, T. Suzuka, K. Tsutsumi, K. Kakiuchi, *Dalton Trans*. **2015**, *44*, 11811–11818; c) H. Tanimoto, T. Nagao, T. Fujiwara, T. Kakuta, K. Tanaka, Y. Chujo, K. Kakiuchi, *Polymer Chem*. **2015**, *6*, 7495–7499; d) H. Tanimoto, T. Nagao, S. Hosokawa, T. Fujiwara, Y. Nishiyama, T. Morimoto, K. Tsutsumi, T. Kakuta, K. Tanaka, Y. Chujo, K. Kakiuchi, *Chem. Lett*. **2016**, *45*, 782–784; e) H. Tanimoto, T. Fujiwara, J. Mori, T. Nagao, Y. Nishiyama, T. Morimoto, S. Ito, K. Tanaka, Y. Chujo, K. Kakiuchi, *Dalton Trans.* **2017**, *46*, 2281–2288.

[8] a) J. Ohshita, D. Nada, Y. Tada, Y. Kimura, H. Yoshida, A. Kunai, Y. Kunugi, *J. Organomet. Chem.* **2005**, *690*, 3951–3956; b) K. Yoosaf, A. Llanes-Pallas, T. Marangoni, A. Belbakra, R. Marega, E. Botek, B. Champagne, D. Bonifazi, N. Armaroli, *Chem. Eur. J*. **2011**, *17*, 3262–3273.

[9] R. Bortolin, B. Parbhoo S. S. D. Brown, *J. Chem. Soc., Chem. Commun.* **1988**, 1079–1081

[10] CCDC-1539470 (**4**), CCDC-1539472 (**5**), and CCDC-1539471 (**6**) contain the corresponding supplementary crystallographic data. These data can be obtained free of charge from: The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] For detailed summary and comparison of values to the previous compounds, see Supporting Information.

10.1002/chem.201701359

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

This report describes the syntheses of arene-inserted type extended (ArEx) germa[*N*]pericyclynes composed of germanium-1,4-diethynylbenzene units, and their characterization. These novel cyclic germanium-π unit materials were characterized by X-ray crystallography, UV-Vis spectroscopy, fluorescence and phosphorescence emission spectroscopy, which showed characteristic optical properties, and large emission lifetimes compared to previous derivatives.

Hiroki Tanimoto, Junta Mori, Shunichiro Ito, Yasuhiro Nishiyama, Tsumoru Morimoto, Kazuo Tanaka, Yoshiki Chujo, and Kiyomi Kakiuchi**

Page No. – Page No.

Arene-inserted Extended Germa[*N*]pericyclynes: Synthesis, Structure, and Phosphorescence Properties

Layout 2:

FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents