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Supporting Information

Stepwise Synthesis and characterization of Germa[4], [5], [8], and [10]pericyclynes

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General information

¹H and ¹³C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ¹H NMR and 126 MHz for ¹³C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak (CDCl₃, δ 7.26 for ¹H NMR and δ 77.00 for ¹³C NMR) or tetramethylsilane (δ 0 for ¹H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), g (quartet), sept (septet), br (broad peak), and m (complex multiplet). 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), CI, FAB, and ESI]. X-ray crystal analyses were performed using a Rigaku R-AXIS RAPID/S imaging plate diffractometer. Raman spectra were obtained using a JASCO laser Raman spectrophotometer, NRS-2100. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing *n*-Bu₄NPF₆ 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/AgNO₃ and normalized with respect to Fc/Fc⁺. 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 F254) with iodine/silica gel stain. The purification of the mixture of germapericyclynes was performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC) 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 Nakalai Tesque. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical, which was further dehydrated over activated molecular sieves 4A. Density functional theory (DFT) calculations were performed using the Gaussian09, 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.

•UV-visible and fluorescence emission spectra



Fig S1. UV-visible [(a): 0.1 mM in CH₂Cl₂], and fluorescence emission spectra [(b): 0.1 mM in CH₂Cl₂, λ_{ex} = 260 nm: solid lines, λ_{ex} = 273.5 nm: dashed lines, (c) normalized differential spectra based on **1a**, λ_{ex} = 260 nm, (d) excitation spectra, **5a**: λ_{ex} = 321.5 nm, **7a**: λ_{ex} = 320 nm] of phenyl compounds

Compounds	Absorption maxima / nm (ε)	Emission maxima / nm
7a	261 (5060)	$\lambda_{ex} = 260 \text{ nm}$: 281, 288, 320
		λ _{ex} = 273.5 nm : 310, 318
5 a ¹	261 (4240)	$\lambda_{ex} = 260 \text{ nm}$: 281, 288, 320
		λ _{ex} = 273.5 nm : 310, 318
9 a ¹	261 (3000)	$\lambda_{ex} = 260 \text{ nm}$: 282, 288
		λ _{ex} = 273.5 nm : 282, 288
6a	261 (2540)	λ _{ex} = 260 nm :282, 288
		λ_{ex} = 273.5 nm : 282, 288
4a ¹	261 (2110)	$\lambda_{ex} = 260 \text{ nm}$: 282, 287
		λ _{ex} = 273.5 nm : 282, 287
8a	261 (492)	λ_{ex} = 260 nm :283, 288
1 a ¹	261 (530)	λ _{ex} = 260 nm :281

Table S1. Absorption and emission maxima of phenyl compounds



Fig S2. UV-visible spectra of isopropyl germanium materials (0.1 mM in hexane)

Compounds	Absorption maxima / nm (ε)
7b	205 (28900), 212 (23200)
5b ¹	205 (22400), 213 (17800)
9b ¹	205 (18700), 213 (13900)
6b	205 (14500), 212 (10600)
8b	203 (4330), 210 (2994)
1b ¹	—

 Table S2.
 Absorption maxima of isopropyl compounds

•Raman Spectra

Table S3. Absorption maxima of isopropyl compounds

Germa[N]pericyclynes	Compounds	Absorption maxima / cm ⁻¹	
[40] a aria ya kwa a	7a	2113	_
[lo]pencyclynes	7b	_	2098
[8]pericyclynes ¹	5a	2112	_
	5b	_	2098
[6]pericyclynes ¹	9a	2114	_
	9b	-	2099
[5]pericyclynes	6a	2110	_
	6b	_	2103
[4]pericyclynes ¹	4a	2107	_
	4b	_	_

•Reference

1) H. Tanimoto, T. Nagao, Y. Nishiyama, T. Morimoto, F. Iseda, Y. Nagato, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans*. 2014, **43**, 8338–8373.

•Cyclic voltammetry (CV) and differential pulse voltammetry (DPV)



Fig S4. Cyclic and differential pulse voltammograms of germa[5], and [10]pericyclynes (1.0 mM in 0.1 M n-Bu₄NPF₆/CH₂Cl₂ solution; Scan rate = 0.1 V/s)

•DFT calculations of germa[5]pericyclynes' orbitals and levels [Gaussian 09, B3LYP/6-31G(d,p); Conformations based on cif files from X-ray analyses]

orbitals	decaphenyl germa[5]peryclyclyne (6a)		decaisopropyl germa[5]peryclyclyne (6b)	
LUMO+2		-0.393 eV		0.223 eV
LUMO+1		-0.485 eV		0.0664 eV
LUMO		-0.559 eV		0.0365 eV
НОМО		-6.48 eV		-6.39 eV
HOMO-1		-6.54 eV		-6.45 eV
HOMO-2		-6.56 eV		-6.49 eV





































DFILE













