## **Supplementary Information**

# A stable free tetragermacyclobutadiene incorporating fused-ring bulky EMind groups

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#### 1. Experimental

#### **General Procedures**

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a glove box under an inert atmosphere of argon. Anhydrous hexane, benzene, toluene, and tetrahydrofuran (THF) were dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Anhydrous pentane was purchased from Kanto Chemical Co., Inc. and used without further purification. Hexamethyldisiloxane (HMDSO) and deuterated benzene (benzene- $d_6$ , C<sub>6</sub>D<sub>6</sub>) was dried and degassed over a potassium mirror in vacuo prior to use. 4-Bromo-1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacene, (EMind)Br,<sup>S1</sup> and dibromogermylene dioxane complex, GeBr<sub>2</sub>•dioxane,<sup>S2</sup> were prepared by the literature procedures. Other chemicals and gases were used as received.

The nuclear magnetic resonance (NMR) measurements were carried out on JEOL ECS-400 spectrometer (399.8 MHz for <sup>1</sup>H and 100.5 MHz for <sup>13</sup>C). Chemical shifts ( $\delta$ ) are given by definition as dimensionless numbers and relative to <sup>1</sup>H or <sup>13</sup>C NMR chemical shifts of the solvent (residual C<sub>6</sub>D<sub>5</sub>H in C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H( $\delta$ ) = 7.15 and <sup>13</sup>C( $\delta$ ) = 128.0). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

The UV-visible spectra were obtained using a Shimadzu UV-3101(PC)S spectrometer. The elemental analyses (C and H) were performed at the Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science. Melting points (mp) were determined by a Stanford Research Systems OptiMelt instrument and a Yazawa BY-2 instrument. We were unable to obtain a satisfactory elemental analysis for several compounds. For example, diffraction-quality single crystals afforded a rather lower-than-expected carbon analysis, even when combustion aids were used. On the basis of the NMR spectra (Figs. S1–S8) and the X-ray crystal structures, we believe that these compounds are authentic and analytically pure but that its lability on heating or incomplete combustion is responsible for the disappointing elemental analysis.

#### Synthesis of (EMind)<sub>2</sub>Ge: (4)

To a solution of (EMind)Br (2.64 g, 6.52 mmol) in THF (30 mL) was dropwise added "BuLi (2.69 M in hexane, 4.8 mL, 13.2 mmol) at -78 °C. The resulting pale yellow solution was allowed to 0 °C to give a yellow solution. This yellow solution was dropwise added to a colorless solution of GeCl<sub>2</sub>•dioxane (751 mg, 3.24 mmol) in THF (15 mL) in 30 min to give a deep purple solution. After stirring for overnight at room temperature, the solvents were removed under reduced pressure to provide a deep purple solid. To the residue was added hexane (40 mL) and the resulting mixture was centrifuged to remove insoluble materials. The supernatant was concentrated to dryness and recrystallized from HMDSO at -30 °C to afford **4** as purple crystals, which were isolated by filtration in 41% yield (949 mg, 1.31 mmol). mp (argon atmosphere in a sealed tube) 109–110 °C (dec.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.86 (t, *J* = 7.3 Hz, 24 H, CH<sub>2</sub>CH<sub>3</sub>), 1.48 (s, 24 H, CH<sub>3</sub>), 1.60–1.72 (m, 16 H, CH<sub>2</sub>CH<sub>3</sub>), 1.76 (s, 8 H, CH<sub>2</sub>), 6.77 (s, 2 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  9.5, 33.8, 36.2, 46.2, 49.8, 52.3, 121.4, 147.7, 155.1, 169.2. UV-vis (hexane)  $\lambda_{max}$  ( $\varepsilon$ ) = 566 nm (940).

### Synthesis of (EMind)ClGe=GeCl(EMind) (3)

A mixture of **4** (1.15 g, 1.59 mmol) and GeCl<sub>2</sub>•dioxane (389 mg, 1.68 mmol) was dissolved in toluene (40 mL). The reaction mixture was stirred at for 1 day. After the solvent was removed in vacuo, the residue was dissolved with THF and filtered to remove insoluble materials. The filtrate was concentrated and recrystallized from a mixture of THF and pentane at -30 °C to afford **3** as yellow crystals, which were isolated by filtration in 54% yield (791 mg, 0.912 mmol). mp (argon atmosphere in a sealed tube) 170–172 °C (dec.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.79 (t, *J* = 7.3 Hz, 24 H, CH<sub>2</sub>CH<sub>3</sub>), 1.40 (s, 24 H, CH<sub>3</sub>), 1.48–1.67 (m, 24 H, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>), 6.78 (s, 2 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  9.3, 33.1, 35.1, 45.1, 50.8, 51.3, 121.5, 147.3, 157.1 (one peak of the aromatic carbon, *ipso* position to the germanium, was not observed). Anal. Calcd for C<sub>48</sub>H<sub>74</sub>Cl<sub>2</sub>Ge<sub>2</sub>: C, 66.48; H, 8.60. Found: C, 64.95; H, 8.69. UV-vis (hexane)  $\lambda_{max}$  ( $\varepsilon$ ) = 402 nm (2000).

#### Synthesis of (EMind)BrGe=GeBr(EMind)

To a suspension of activated magnesium (Mg\*)<sup>S3</sup> in THF, which was prepared from

MgCl<sub>2</sub> (978 mg, 10.3 mmol), potassium (790 mg, 20.2 mmol), and KI (677 mg, 4.08 mmol) in THF (10 mL), was added (EMind)Br<sup>S1</sup> (2.04 g, 5.03 mmol) at room temperature. The suspension was warmed to 60 °C and stirred at 60 °C for 3.5 h. The resulting suspension was dropwise added GeBr<sub>2</sub>•dioxane<sup>S2</sup> (1.28 g, 3.99 mmol) in THF (40 mL) at room temperature and stirred overnight. After the mixture was concentrated in vacuo, to the residual solid was added benzene and the resulting suspension was centrifuged to remove any insoluble materials. The supernatant was evaporated to residue recrystallized dryness, and the was from toluene give to (EMind)BrGe=GeBr(EMind) as yellow crystals (629 mg, 0.658 mmol, 33 %): mp (argon atmosphere in a sealed tube) 213–215 °C (dec.); <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  0.79 (t, J = 7.4 Hz, 24 H, CH<sub>2</sub>CH<sub>3</sub>), 1.44–1.67 (m, 40 H, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>), 1.68 (s, 8 H, CH<sub>2</sub>), 6.79 (s, 2 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 9.3, 33.1, 34.0, 45.4, 50.8, 51.1, 121.8, 147.8, 156.5 (one peak of the aromatic carbon, *ipso* position to the germanium, was not observed). UV-vis (hexane)  $\lambda_{max}$  ( $\varepsilon$ ) = 418 nm (1100).

#### Synthesis of Ge<sub>4</sub>(EMind)<sub>4</sub> (2) from 3

To a solution of **3** (502 mg, 0.579 mmol) in THF (30 mL) was dropwise added a solution of lithium naphthalenide (LiNaph) (Li, 9.0 mg, 1.30 mmol, naphthalene, 187 mg, 1.46 mmol) in THF (2.0 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min and allowed to warm to room temperature. The solvents were removed under reduced pressure to provide a dark red solid. To the residue was added benzene (30 mL), and the resulting suspension was centrifuged to remove any insoluble materials. The residual solid was washed with hexane (10 mL) to remove naphthalene. The residue was recrystallized from a mixture of hexane and toluene to afford **2** as dark red crystals (97 mg, 61.4 µmol, 21%): mp 343–345 °C (dec.) (argon atmosphere in a sealed tube). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 0.79 (t, *J* = 7.3 Hz, 48 H, CH<sub>2</sub>CH<sub>3</sub>), 1.52–1.68 (m, 56 H, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>), 1.77 (br.s, 8 H, CH<sub>2</sub>), 1.84 (br.s, 8 H, CH<sub>2</sub>), 2.08 (br.s, 24 H, CH<sub>3</sub>), 6.67 (s, 4 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 9.4, 33.6 (br), 33.9, 34.4 (br), 45.7, 48.8, 52.7, 120.6, 147.7, 154.0 (one peak of the aromatic carbon, *ipso* position to the germanium, was not observed). Anal. Calcd for C<sub>96</sub>H<sub>148</sub>Ge<sub>4</sub>: C, 72.39; H, 9.37. Found: C, 72.15; H, 9.44. UV-vis-NIR (hexane)  $\lambda_{max}$  ( $\varepsilon$ ) = 458 nm (15000), 510 nm (sh, 7400), 836 nm (150).

## Synthesis of Ge<sub>4</sub>(EMind)<sub>4</sub> (2) from (EMind)BrGe=GeBr(EMind)

To a solution of (EMind)BrGe=GeBr(EMind) (383 mg, 0.401 mmol) in THF (20 mL) was dropwise added a solution of LiNaph (0.909 mmol) in THF (1.0 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min and allowed to warm to room temperature. After the mixture was concentrated in vacuo, the residual solid was washed with hexane (20 mL) to remove naphthalene. To the residue was added benzene (80 mL), and the resulting suspension was centrifuged to remove any insoluble materials. The supernatant was evaporated to dryness, and the residue was recrystallized from a mixture of hexane and toluene to give **2** as dark red crystals (101 mg, 63.4  $\mu$ mol, 32%).



**Fig. S1** <sup>1</sup>H NMR Spectrum of  $(EMind)_2Ge: (4)$  in  $C_6D_6$ .



**Fig. S2** <sup>13</sup>C NMR Spectrum of (EMind)<sub>2</sub>Ge: (4) in  $C_6D_6$ .



**Fig. S3** <sup>1</sup>H NMR Spectrum of (EMind)ClGe=GeCl(EMind) (3) in  $C_6D_6$ .



**Fig. S4** <sup>13</sup>C NMR Spectrum of (EMind)ClGe=GeCl(EMind) (3) in  $C_6D_6$ .



**Fig. S5** <sup>1</sup>H NMR Spectrum of (EMind)BrGe=GeBr(EMind) in C<sub>6</sub>D<sub>6</sub>.



**Fig. S6** <sup>13</sup>C NMR Spectrum of (EMind)BrGe=GeBr(EMind) in  $C_6D_6$ .



**Fig. S7** <sup>1</sup>H NMR Spectrum of  $Ge_4(EMind)_4$  (2) in  $C_6D_6$ .



**Fig. S8**  $^{13}$ C NMR Spectrum of Ge<sub>4</sub>(EMind)<sub>4</sub> (**2**) in C<sub>6</sub>D<sub>6</sub>.

## 2. X-ray Crystallographic Analysis

Crystallographic data are summarized in Table S1. Single crystals suitable for X-ray diffraction measurements were obtained from a mixture of hexane and toluene for  $2 \cdot 0.5$  C<sub>6</sub>H<sub>14</sub> as orange blocks and from a mixture of THF and pentane for **3** as yellow blocks.

The single crystals were immersed in oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and mounted on a Rigaku AFC-8 diffractometer with a Saturn70 CCD detector for **2**•0.5 C<sub>6</sub>H<sub>14</sub> and a Rigaku XtaLAB P200 with a PILATUS200 K detector for **3**. The diffraction data were collected using MoK $\alpha$ radiation ( $\lambda = 0.71073$  Å), which was monochromated by a multi-layered confocal mirror. The specimens were cooled at 90 K for **2**•0.5 C<sub>6</sub>H<sub>14</sub> and 100 K for **3** in a cold nitrogen stream during the measurements. Bragg spots were integrated and scaled with the programs of HKL2000<sup>S4</sup> for **2**•0.5 C<sub>6</sub>H<sub>14</sub> and CrysAlisPro<sup>S5</sup> for **3**. Then, intensities of the equivalent reflections merged for structure analysis.

The structure was solved by a direct method with the program of SIR2004<sup>S6</sup> for **2**•0.5  $C_6H_{14}$  and SIR2008<sup>S7</sup> for **3**, and refined on  $F^2$  by a full-matrix least-squares method using the program of SHELXL-2013<sup>S8</sup> for **2**•0.5  $C_6H_{14}$  and SHELXL-2017/1 for **3**.<sup>S9</sup> The anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1505261 (**2**•0.5  $C_6H_{14}$ ) and 1580780 (**3**). A copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data–request.

The molecular structures of **2** are shown in Fig. S9. The space-filling models of **2** are depicted in Fig. S10. The molecular structure of **3** is shown in Fig. S11.

	<b>2•</b> 0.5 C <sub>6</sub> H <sub>14</sub>	3
formula	$C_{99}H_{155}Ge_4$	$C_{48}H_{74}Cl_2Ge_2$
М	1635.58	867.15
$T / \mathbf{K}$	90	100
colour	orange	yellow
size, mm	0.14 x 0.13 x 0.05	0.18 x 0.12 x 0.11
crystal system	triclinic	triclinic
space group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)
<i>a</i> / Å	10.3376(1)	10.9924(4)
b / Å	17.8421(2)	11.3428(4)
<i>c</i> / Å	25.5819(3)	11.8084(5)
lpha / deg.	84.4742(5)	118.544(4)
$\beta$ / deg.	83.1749(6)	92.150(3)
$\gamma$ / deg.	87.3583(8)	113.282(3)
V / Å <sup>3</sup>	4660.37(9)	1140.33(9)
Ζ	2	1
$D_{\rm x}$ / g cm <sup>-3</sup>	1.166	1.263
reflections collected	264416	18211
unique reflections	35880	5213
refined parameters	967	258
GOF on $F^2$	1.029	1.133
$R1 \left[I > 2\sigma(I)\right]^{a}$	0.0377	0.0438
wR2 (all data) <sup>b</sup>	0.1036	0.1150
$\Delta ho_{ m min,\ max}$ / e Å $^{-3}$	-0.567, 0.994	-0.468, 0.783

**Table S1**Crystallographic Data for  $2 \cdot 0.5 C_6 H_{14}$  and 3.

<sup>a</sup> R1 =  $\Sigma ||Fo| - |Fc|| / \Sigma |Fo|$ , <sup>b</sup> wR2 =  $[\Sigma \{w(Fo^2 - Fc^2)^2 / \Sigma w(Fo^2)^2\}]^{1/2}$ 



**Fig. S9** Molecular structures of **2**; (a) top view, (b) front view. The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms, disordered carbon atoms of the ethyl groups, and hexane molecule are omitted for clarity. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg): Ge1–Ge2 = 2.4283(2), Ge1–Ge4 = 2.4606(2), Ge2–Ge3 = 2.4014(2), Ge3–Ge4 = 2.4294(2), Ge1–Ge3 = 3.0175(5), Ge2–Ge4 = 3.8089(6), Ge1–C1 = 1.9953(13), Ge2–C25 = 2.0241(14), Ge3–C49 = 1.9825(14), Ge4–C73 = 2.0368(15), Ge2–Ge1–Ge4 = 102.354(8), Ge2–Ge1–C1 = 128.22(4), Ge4–Ge1–C1 = 129.42(4), Ge1–Ge2–Ge3 = 77.329(7), Ge1–Ge2–C25 = 133.17(4), Ge3–Ge2–C25 = 123.54(4), Ge2–Ge3–Ge4 = 104.083(8), Ge2–Ge3–C49 = 127.10(4), Ge4–Ge3–C49 = 128.82(4), Ge1–Ge4–Ge3 = 76.202(7), Ge1–Ge4–C73 = 131.33(5), Ge3–Ge4–C73 = 120.18(4), Ge2–Ge1–Ge4/Ge1–C1 = 0.71(4), Ge1–Ge2–Ge3/Ge2–C25 = 37.85(5), Ge2–Ge3–Ge4/Ge3–C49 = 0.59(4), Ge1–Ge4–Ge3/Ge4–C73 = 40.57(5), Ge1–Ge2–Ge3–Ge4 = 1.42(2).



**Fig. S10** Space filling models of **2**; (a) top view, (b) front view: purple, germanium; gray, carbon; white, hydrogen.



**Fig. S11** Molecular structure of **3**. The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms, disordered chlorine and germanium atoms, and disordered carbon atoms of the ethyl groups are omitted for clarity. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg):  $Ge1-Ge1^* = 2.3853(7)$ , Ge1-Cl1 = 2.1980(13), Ge1-Cl = 1.981(3),  $C1-Ge1-Ge1^* = 124.24(9)$ ,  $Cl1-Ge1-Ge1^* = 104.89(4)$ , C1-Ge1-Cl1 = 107.57(10),  $C1-Ge1-Cl1/Ge1-Ge1^* = 44.02(12)^\circ$ .

## 3. Photophysical Data

The UV-visible-NIR absorption spectra of **2** was recorded on Shimadzu UV-3101(PC)S spectrometer with a resolution of 0.2 nm.  $3.09 \times 10^{-5}$  M and  $3.65 \times 10^{-4}$  M of sample solutions in a 1.0 cm square quartz cell were used for the measurement. Dry hexane (purchased from Kanto Chemical Co., Inc.) was used for the sample solution. The UV-vis-NIR absorption spectra of **2** are shown in Fig. S12.



Fig. S12 UV-vis-NIR absorption spectra of 2 in hexane at ambient temperature.

#### 4. Theoretical Calculations

The geometry optimization of the planar rhombic singlet 2 and the twisted rectangular singlet 2(re) were performed at the B3LYP/6-31G(d,p) level of theory using Gaussian 09 program package.<sup>S10</sup> The geometry optimization of the twisted square triplet of **2(sq)** was performed at the UB3LYP/6-31G(d,p) level. The geometry optimization of 2 was also performed at the B3LYP-D3/6-31G(d,p) level. The optimized structures and selected structural parameters of 2 ( $C_1$  symmetry), 2(re) ( $C_1$  symmetry), and 2(sq) ( $C_1$ symmetry) are shown in Figs. S13–S16. The relative energy diagram is shown in Fig. S17. Selected molecular orbitals (MOs) and their energy levels of 2 are shown in Figs. S18 and S19. The Wiberg bond index (WBI)<sup>S11</sup> and natural population analysis (NPA)<sup>S12</sup> charge distribution of 2, 2(re), and 2(sq) were calculated by natural bond orbital method (Figs. S20-S23). The absorption wavelength of 2 was calculated at the ground-state geometry using TD-B3LYP/6-31G(d,p) and TD-B3LYP-D3/6-31G(d,p) methods (Figs. S24 and S25). Figs. S24 and S25 were drawn by using GaussView software.<sup>S13</sup> The <sup>73</sup>Ge chemical shifts were calculated for the optimized geometry of **2** (GIAO) using the gauge-independent atomic orbital method at the B3LYP/6-311+G(d,p) level ( $\delta = 0.0$  ppm for GeMe<sub>4</sub>) (Fig. S26). The nucleus-independent chemical shift (NICS)-scan analysis was performed for the optimized geometry of **2** using Stanger's method<sup>S14</sup> at the B3LYP/6-311+G(d,p) level (Fig. S27). The electron occupation numbers of 2 in terms of the natural orbitals (NOs) were obtained by the complete active space self consistent field (CASSCF) (4,4)/6-31G(d,p) level using GAMESS program package (Fig. S28).<sup>S15</sup>



**Fig. S13** Optimized structures of **2** ( $C_1$  symmetry) (B3LYP/6-31G(d,p) level); (a) top view, (b) front view. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg): Ge1–Ge2 = 2.3723, Ge1–Ge4 = 2.3708, Ge2–Ge3 = 2.3730, Ge3–Ge4 = 2.3720, Ge1····Ge3 = 2.9926, Ge2····Ge4 = 3.6810, Ge2–Ge1–Ge4 = 101.81, Ge1–Ge2–Ge3 = 78.20, Ge2–Ge3–Ge4 = 101.75, Ge1–Ge4–Ge3 = 78.20, Ge2–Ge1–Ge4 = 0.33, Ge1–Ge2–Ge3/Ge2–C25 = 40.09, Ge2–Ge3–Ge4/Ge3–C49 = 0.34, Ge1–Ge4–Ge3/Ge4–C73 = 39.93, Ge1–Ge2–Ge3–Ge4 = -0.08.



**Fig. S14** Optimized structures of **2(re)** ( $C_1$  symmetry) (B3LYP/6-31G(d,p) level); (a) top view, (b) front view. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg): Ge1–Ge2 = 2.2852, Ge1–Ge4 = 2.4741, Ge2–Ge3 = 2.4782, Ge3–Ge4 = 2.2796, Ge1…Ge3 = 3.2724, Ge2…Ge4 = 3.2581, Ge2–Ge1–Ge4 = 86.31, Ge1–Ge2–Ge3 = 86.68, Ge2–Ge3–Ge4 = 86.33, Ge1–Ge4–Ge3 = 86.90, Ge2–Ge1–Ge4/Ge1–C1 = 11.97, Ge1–Ge2–Ge3/Ge2–C25 = 11.79, Ge2–Ge3–Ge4/Ge3–C49 = 11.76, Ge1–Ge4–Ge3/Ge4–C73 = 12.11, Ge1–Ge2–Ge3–Ge4 = -28.76.



**Fig. S15** Optimized structures of **2(sq)** ( $C_1$  symmetry) (UB3LYP/6-31G(d,p) level); (a) top view, (b) front view. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg): Ge1–Ge2 = 2.3867, Ge1–Ge4 = 2.3744, Ge2–Ge3 = 2.3867, Ge3–Ge4 = 2.3789, Ge1···Ge3 = 3.2443, Ge2···Ge4 = 3.2322, Ge2–Ge1–Ge4 = 85.51, Ge1–Ge2–Ge3 = 85.77, Ge2–Ge3–Ge4 = 85.55, Ge1–Ge4–Ge3 = 86.09, Ge2–Ge1–Ge4/Ge1–C1 = 11.91, Ge1–Ge2–Ge3/Ge2–C25 = 12.38, Ge2–Ge3–Ge4/Ge3–C49 = 12.95, Ge1–Ge4–Ge3/Ge4–C73 = 12.46, Ge1–Ge2–Ge3–Ge4 = 30.45.



**Fig. S16** Optimized structures of **2** ( $C_1$  symmetry) (B3LYP-D3/6-31G(d,p) level); (a) top view, (b) front view. Selected atomic distances (Å), bond angles (deg), deviation angles (deg), and dihedral angle (deg): Ge1–Ge2 = 2.3469, Ge1–Ge4 = 2.3500, Ge2–Ge3 = 2.3425, Ge3–Ge4 = 2.3489, Ge1…Ge3 = 2.9576, Ge2…Ge4 = 3.6452, Ge2–Ge1–Ge4 = 101.81, Ge1–Ge2–Ge3 = 78.20, Ge2–Ge3–Ge4 = 101.97, Ge1–Ge4–Ge3 = 78.01, Ge2–Ge1–Ge4/Ge1–C1 = 1.00, Ge1–Ge2–Ge3/Ge2–C25 = 42.42, Ge2–Ge3–Ge4/Ge3–C49 = 0.63, Ge1–Ge4–Ge3/Ge4–C73 = 44.06, Ge1–Ge2–Ge3–Ge4 = 0.61.



**Fig. S17** Relative energy diagram for **2**, **2(re)**, and **2(sq)** ((U)B3LYP/6-31G(d,p) level).



**Fig. S18** Selected molecular orbitals and their energy levels of **2** (B3LYP/6-31G(d,p) level); top views (left), front views (right).



**Fig. S19** Selected molecular orbitals and their energy levels of **2** (B3LYP-D3/6-31G(d,p) level); top views (left), front views (right).



**Fig. S20** WBI (left) and NPA charge distribution (right) of **2** (B3LYP/6-31G(d,p) level).



**Fig. S21** WBI (left) and NPA charge distribution (right) of **2(re)** (B3LYP/6-31G(d,p) level).



**Fig. S22** WBI (left) and NPA charge distribution (right) of **2(sq)** (UB3LYP/6-31G(d,p) level).



**Fig. S23** WBI (left) and NPA charge distribution (right) of **2** (B3LYP-D3/6-31G(d,p) level).



Wavelength	Excitation Energy	Transition	Oscillator Strength
/nm	/ eV		
433.92	2.8573	HOMO→LUMO+1	0.1652
495.11	2.5041	HOMO-1→LUMO	0.1251
1007.72	1.2303	HOMO→LUMO	0.0002

**Fig. S24** Calculated transitions (vertical bars) and simulated UV-vis absorption spectrum of **2** (TD-B3LYP/6-31G(d,p) method).



Wavelength	Excitation Energy	Transition	Oscillator Strength
/nm	/ eV		
429.15	2.8890	HOMO→LUMO+1	0.2021
502.76	2.4661	HOMO-1→LUMO	0.1337
949.54	1.3057	HOMO→LUMO	0.0004

**Fig. S25** Calculated transitions (vertical bars) and simulated UV-vis absorption spectrum of **2** (TD-B3LYP-D3/6-31G(d,p) method).



**Fig. S26** The calculated <sup>73</sup>Ge chemical shifts (ppm) of **2** (B3LYP/6-311+G(2d,p) //B3LYP/6-31G(d,p) level)





NICS(+1)	-3.1216
NICS(0)	-4.5515
NICS(-1)	-3.1817

**Fig. S27** NICS-scan plots of out-of-plane components (red), in-plane components (green), and NICS values (blue) for **2** (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) level).



Fig. S28 Natural orbitals and their occupation numbers of 2.

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