Supporting Information

A series of (*E*)-1,2-diaryldigermenes incorporating bulky Eind groups: structural characteristics and absorption properties

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(submitted to Dalton Trans.)

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1. NMR spectra

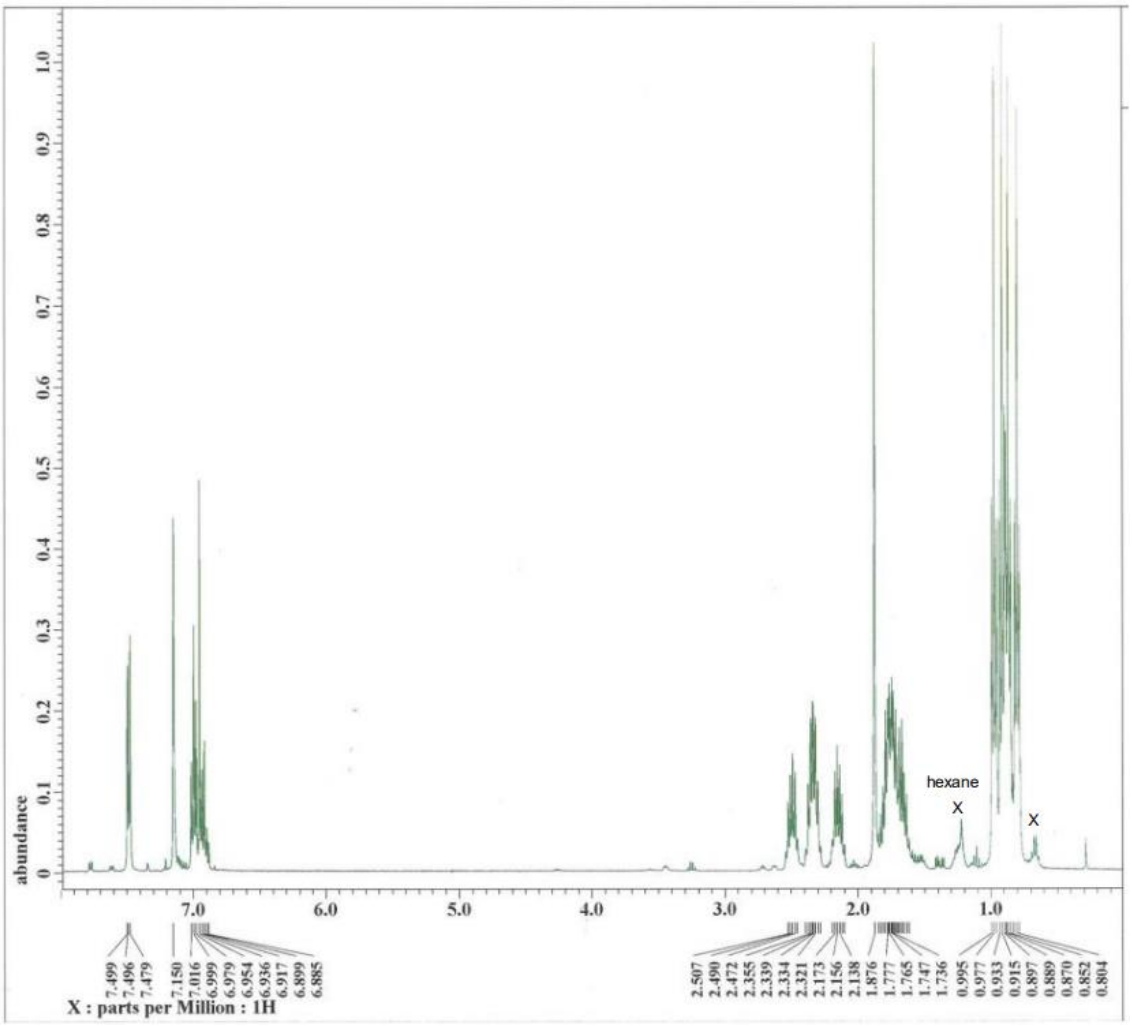

Fig. S1 ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

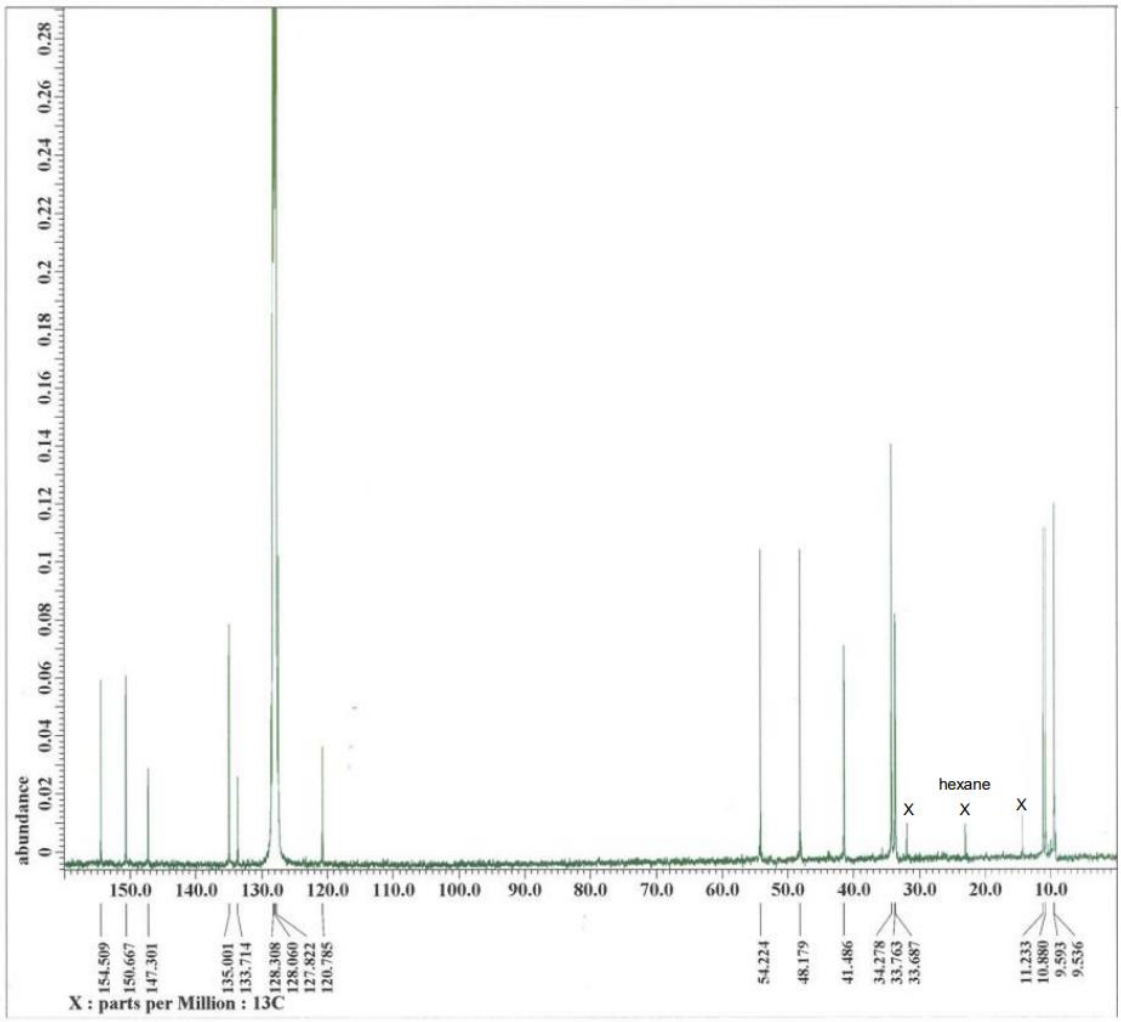

Fig. S2 ^{13}C NMR spectrum of **2** in C_6D_6 at room temperature.

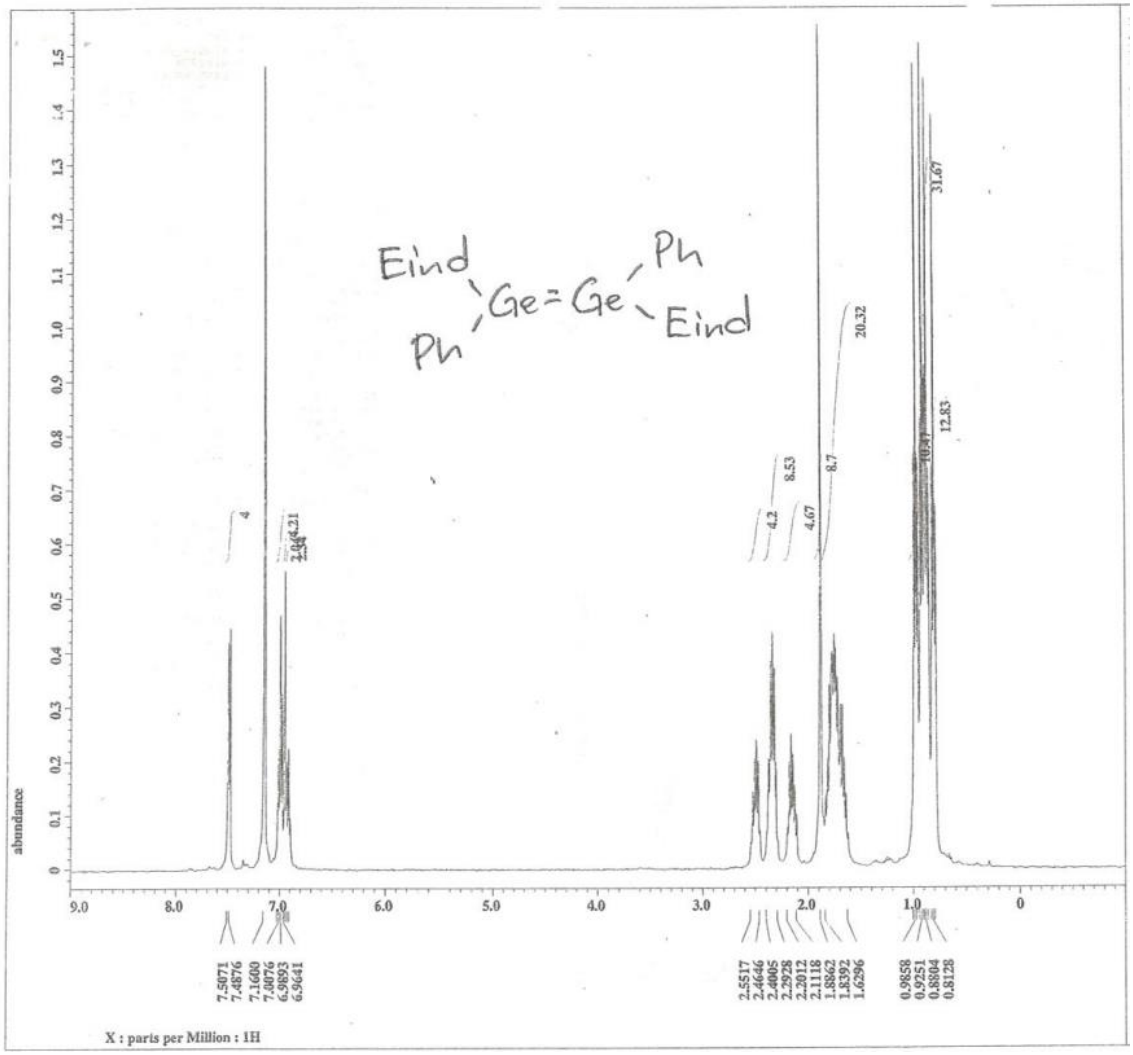

Fig. S3 ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

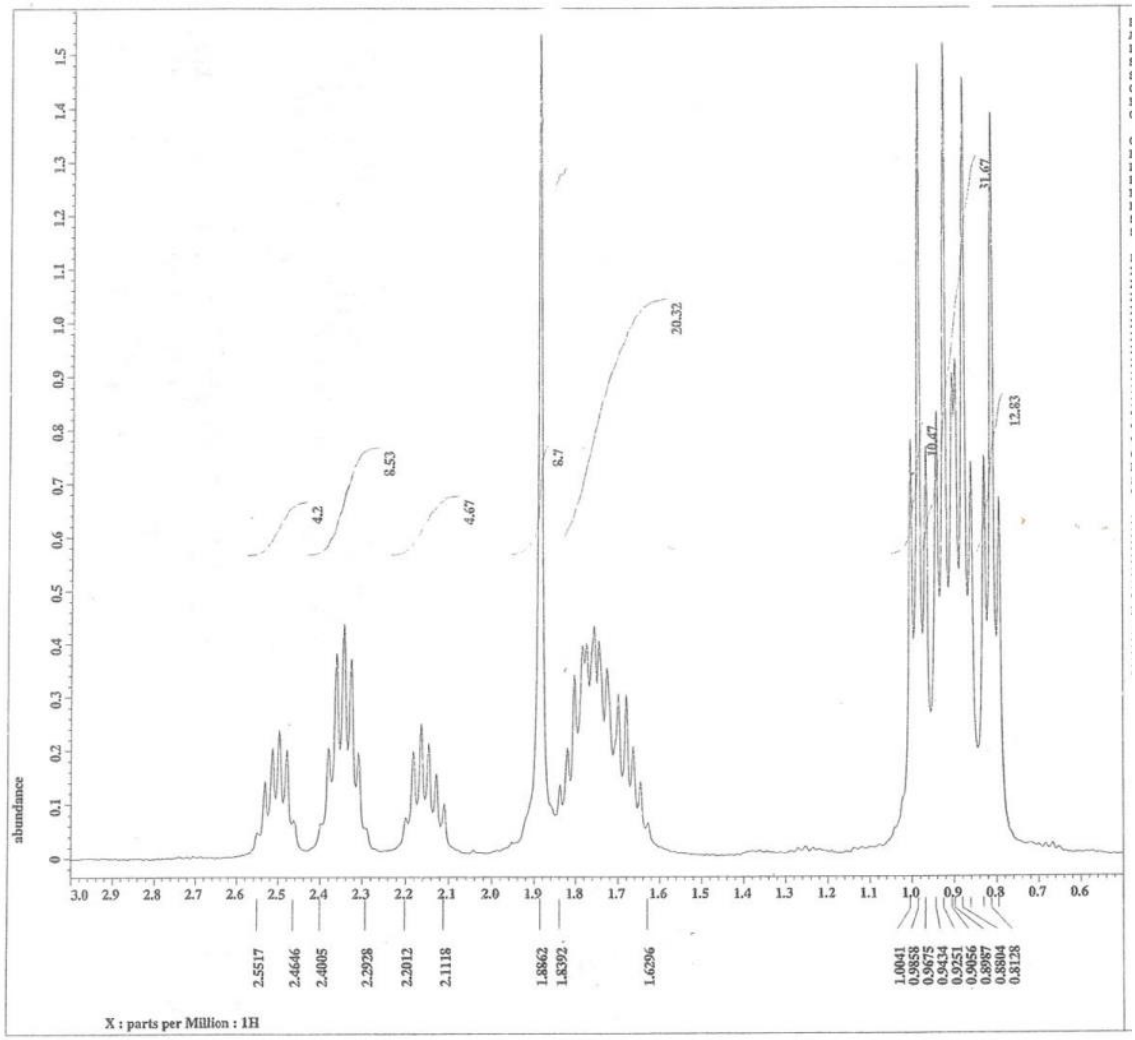

Fig. S4 ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

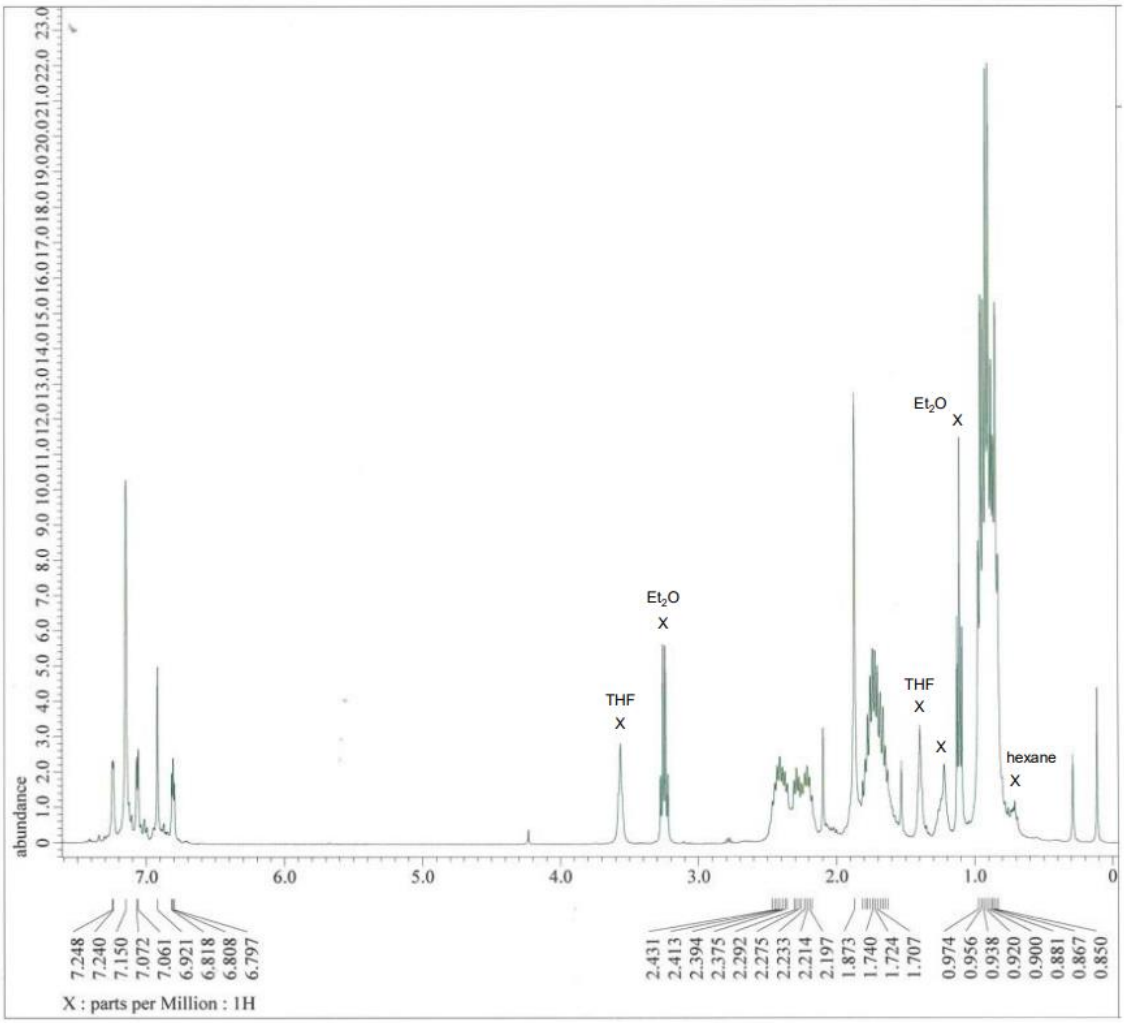

Fig. S5 ^{1}H NMR spectrum of **3** in C_6D_6 at room temperature.

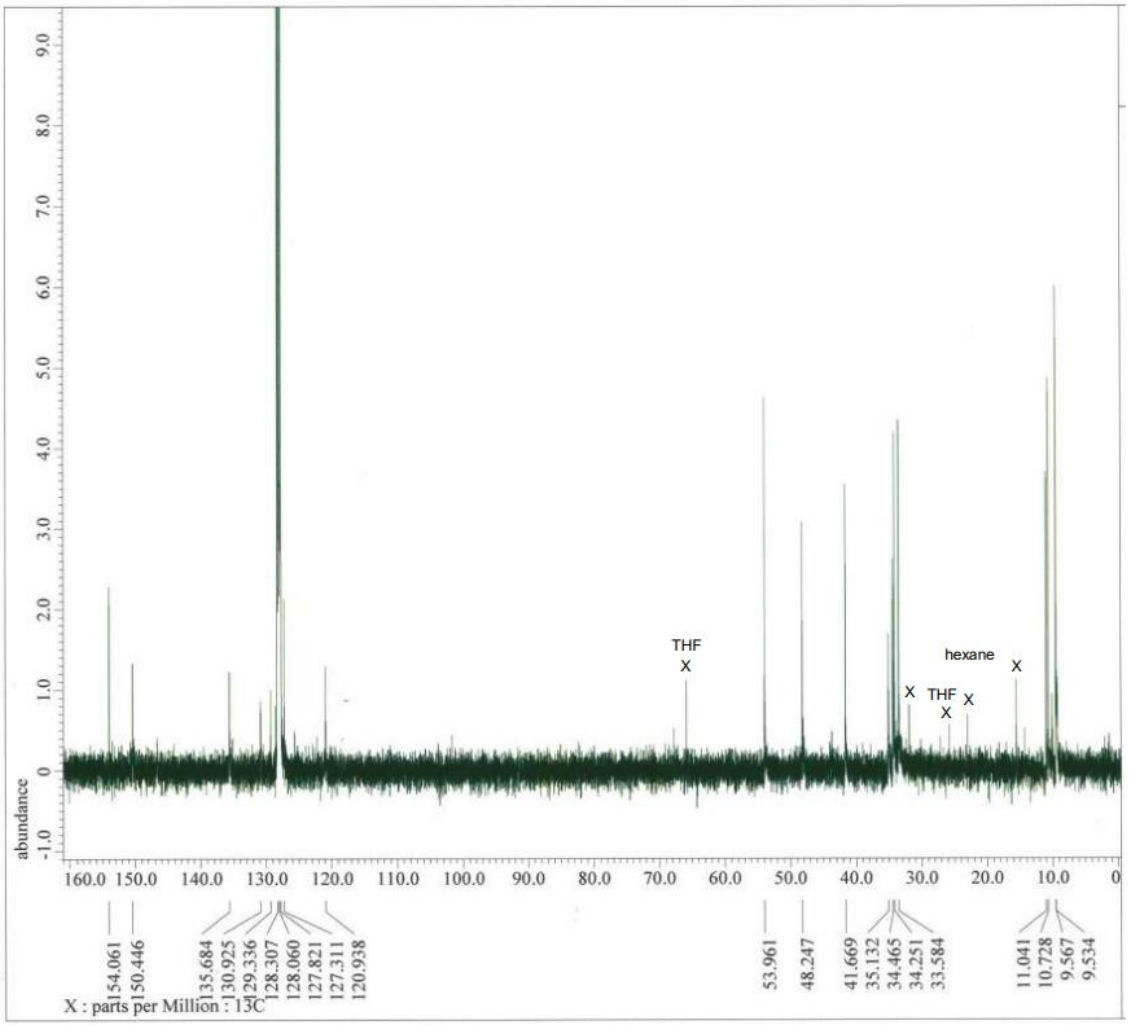

Fig. S6 ^{13}C NMR spectrum of **3** in C_6D_6 at room temperature.

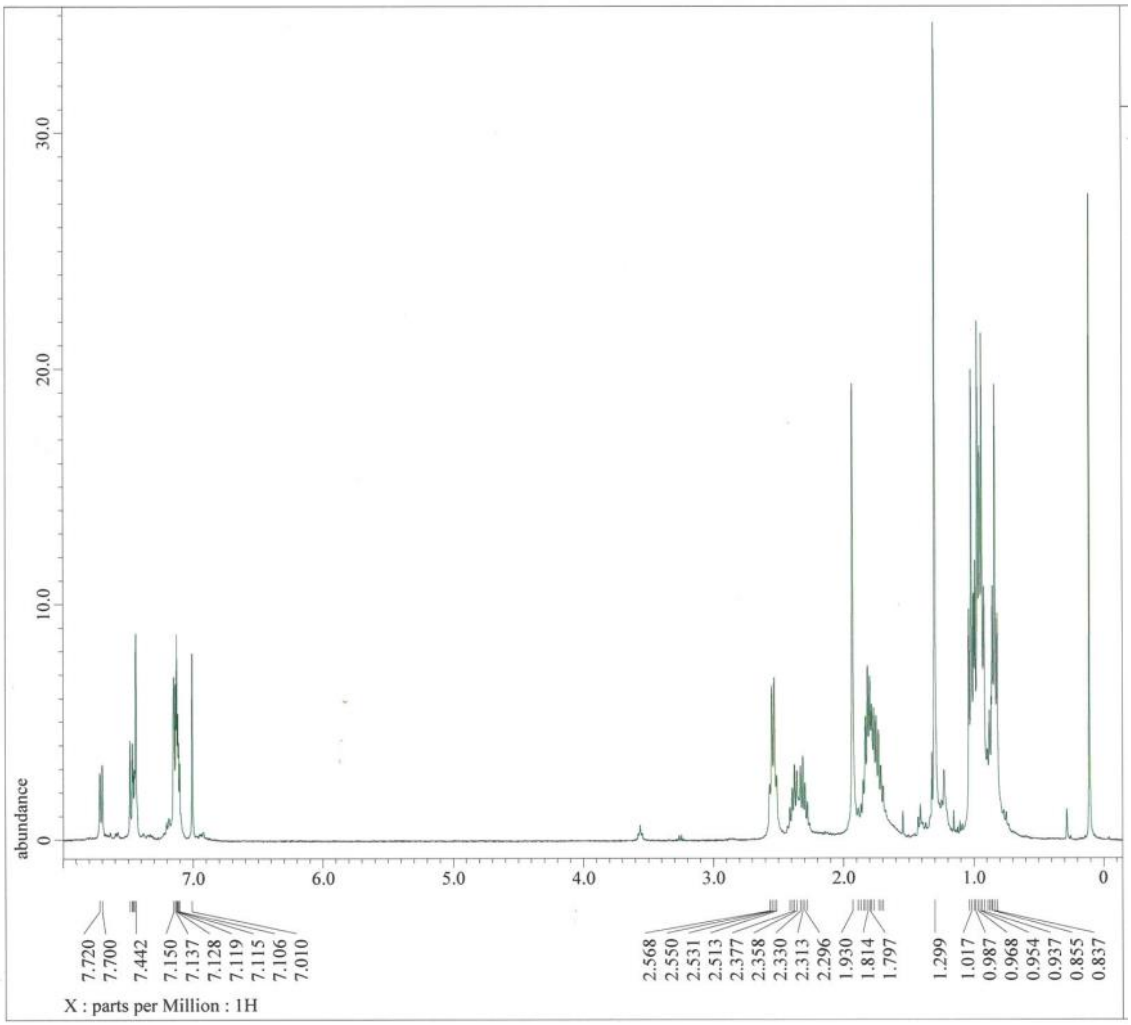

Fig. S7 ^{1}H NMR spectrum of **4** in C_6D_6 at room temperature.

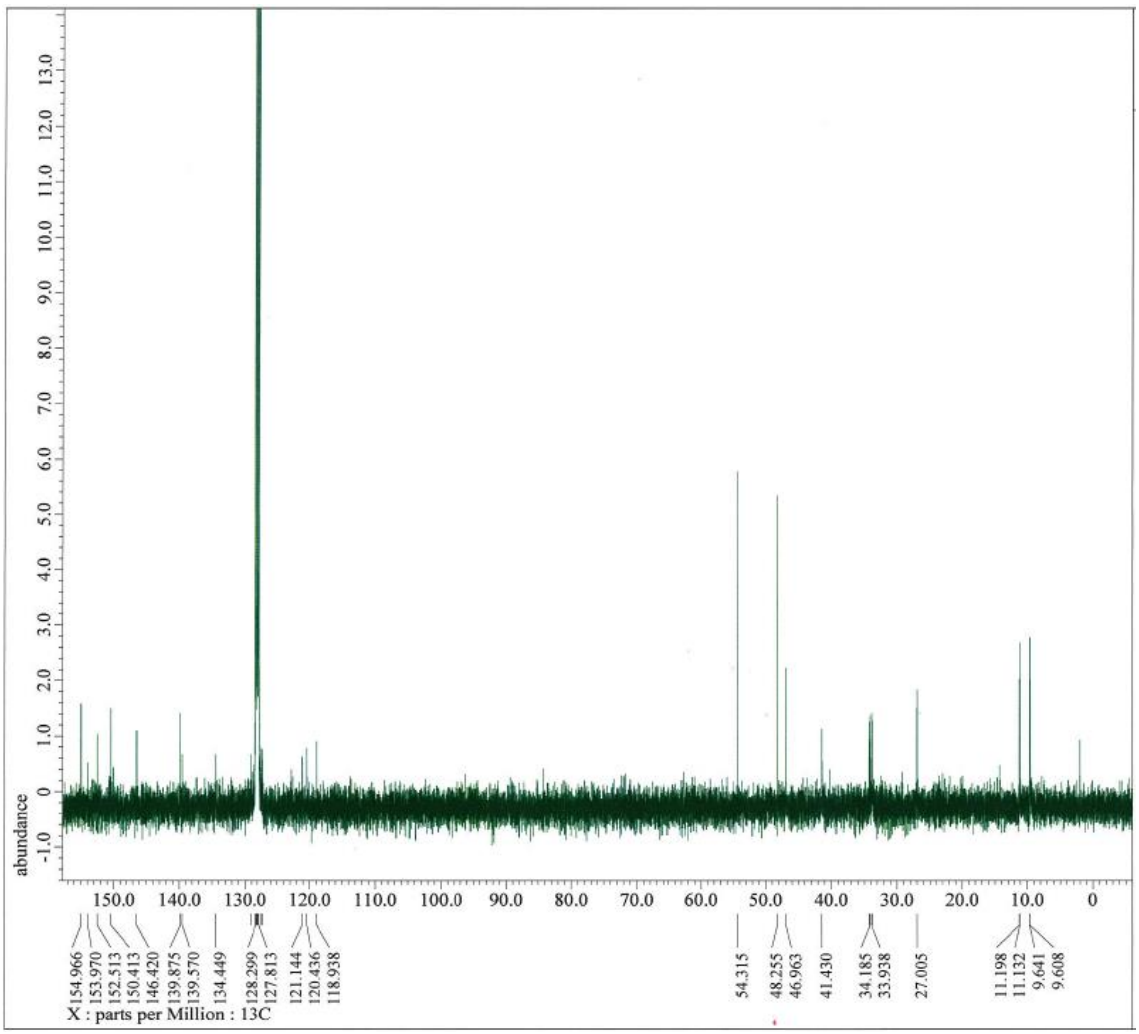

Fig. S8 ^{13}C NMR spectrum of **4** in C_6D_6 at room temperature.

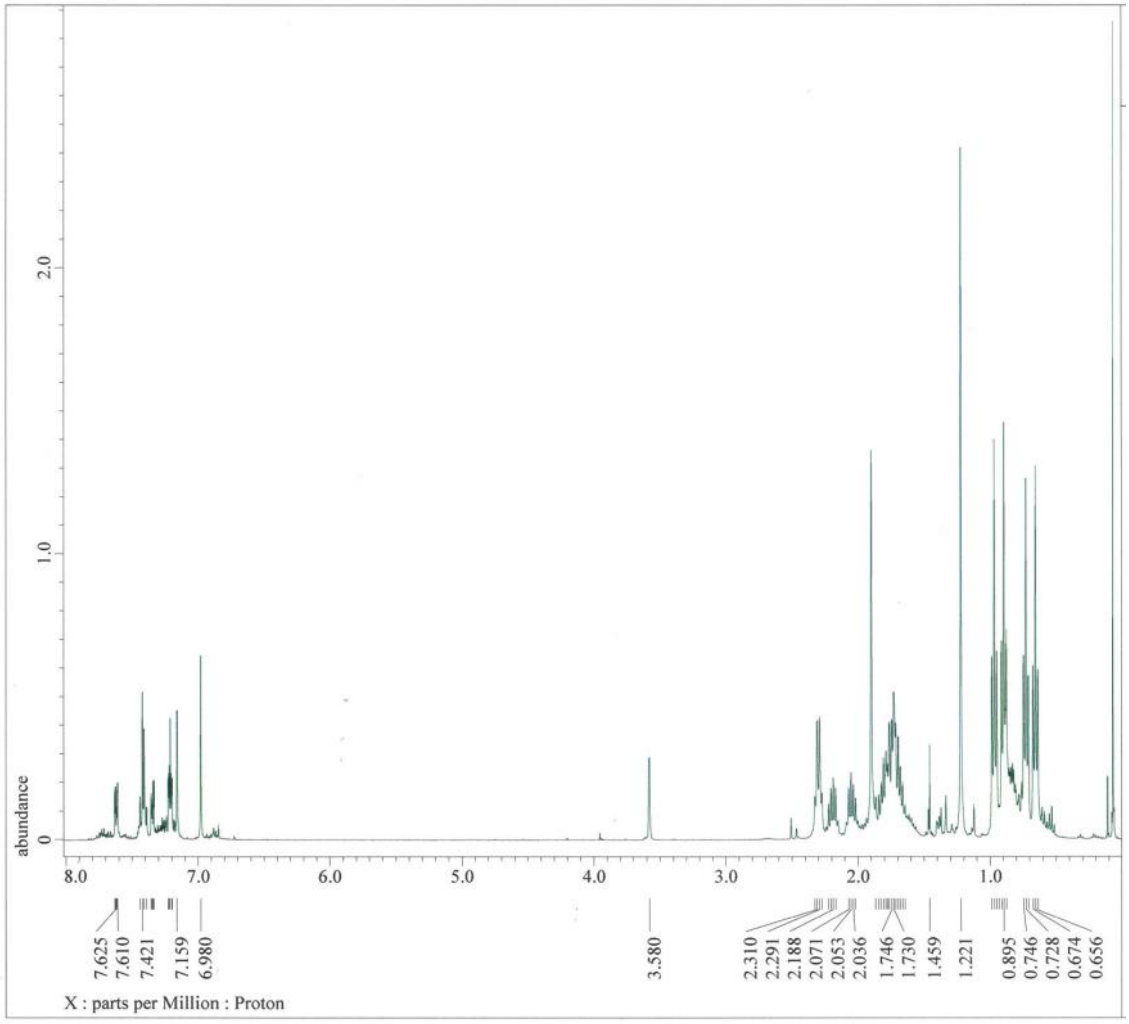

Fig. S9 ^{1}H NMR spectrum of **4** in THF-d_8 at room temperature.

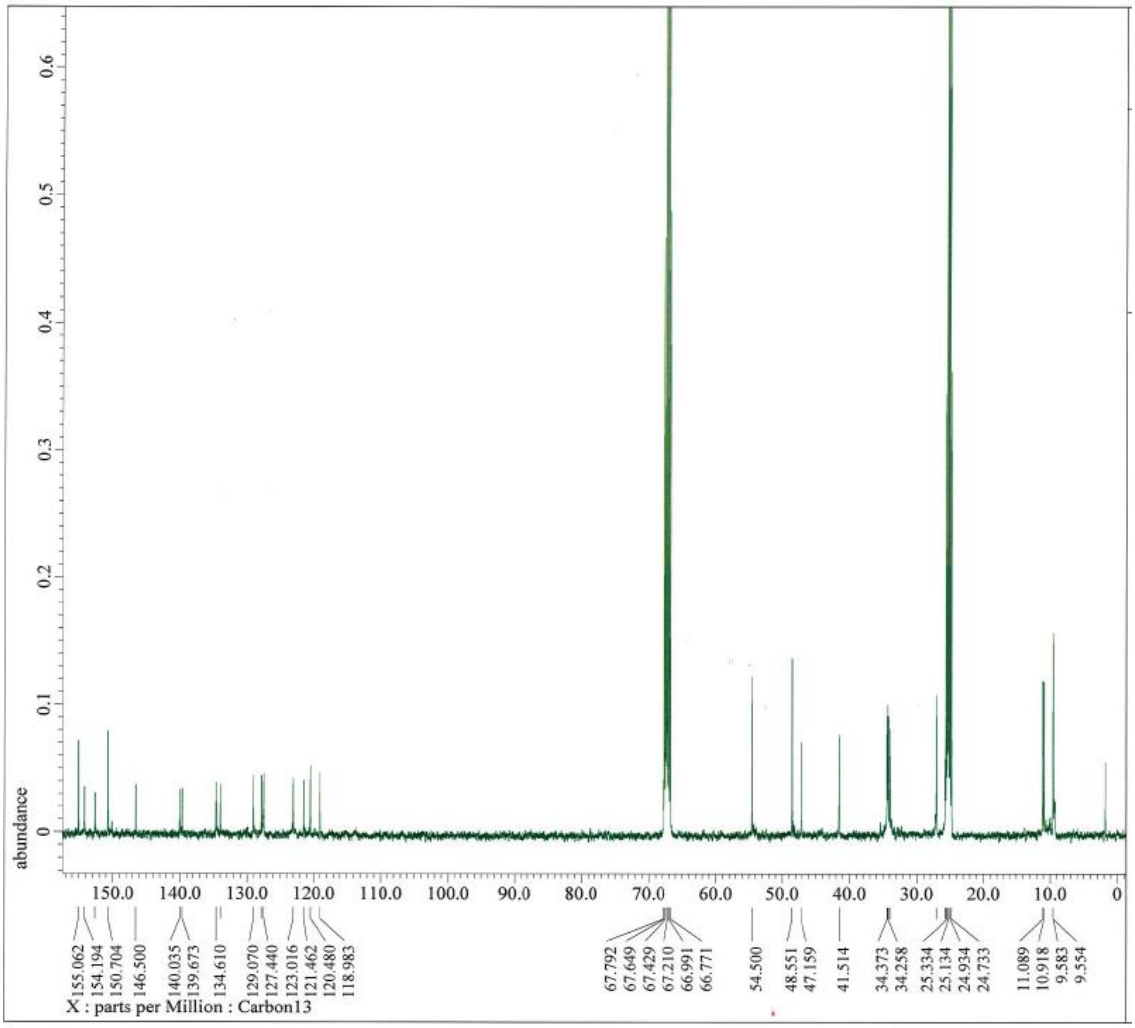

Fig. S10 ^{13}C NMR spectrum of **4** in THF-d_8 at room temperature.

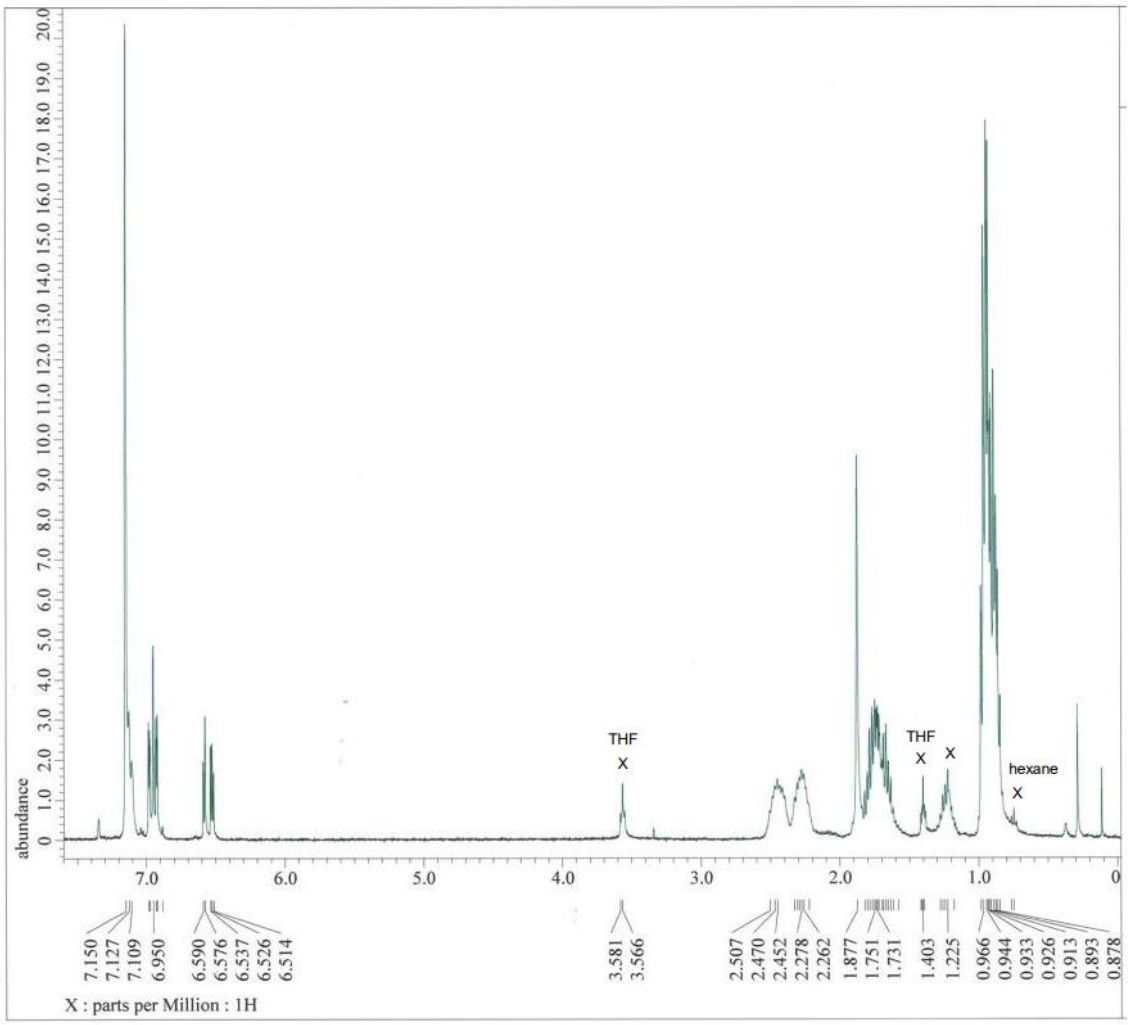

Fig. S11 ^{1}H NMR spectrum of **5** in C_6D_6 at room temperature.

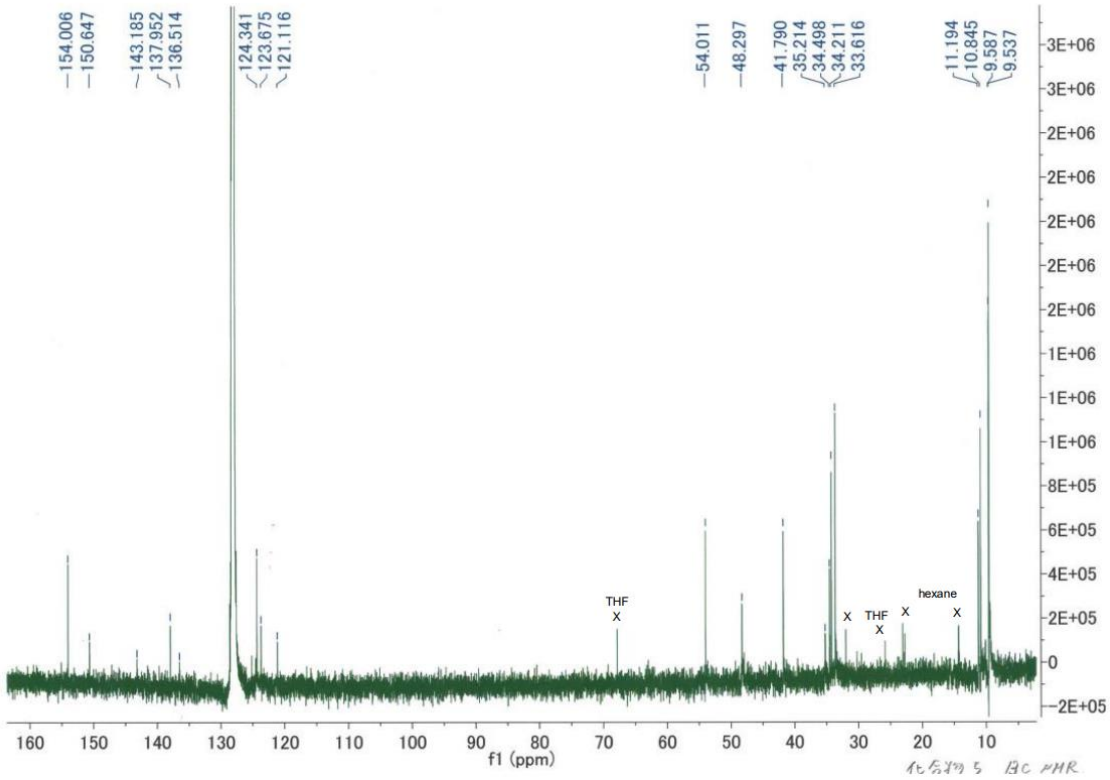

Fig. S12 ^{13}C NMR spectrum of **5** in C_6D_6 at room temperature.

2. X-Ray Crystallographic Analysis

Table S1 Crystallographic data for **2**

formula	$C_{68}H_{100}Ge_2$
FM	1062.65
T / K	200
wavelength / Å	0.71073 (Mo-$K\alpha$)
color	yellow
crystal size / mm	0.098 × 0.091 × 0.068
crystal system	triclinic
space group	P_{1-} (# 2)
a / Å	9.7901(13)
b / Å	10.5043(12)
c / Å	16.1645(17)
α / º	108.141(7)
β / º	100.768(7)
γ / º	98.913(9)
V / Å^3	1510.9(3)
Z	1
D_x / g cm^{-3}	1.168
μ (Mo-$K\alpha$) / mm^{-1}	1.033
reflections collected	38970
unique reflections	8831
refined parameters	354
GOF on F^2	1.103
$R(F)$ [$I > 2\sigma(I)$][a]	0.0569
$wR(F^2)$ (all data)[b]	0.1467
$\Delta\rho_{min,\ max}$ /e Å^{-3}	–0.65, 0.93

[a] $R(F) = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR(F^2) = [\Sigma\ (w(Fo^2 – Fc^2)^2 / \Sigma\ w(Fo^2)^2)^{1/2}$

Table S2 Crystallographic data for **3**

formula	$C_{64}H_{96}Ge_2S_2 \cdot 0.5\ C_4H_8O$
FM	1110.75
T / K	100
wavelength / Å	0.71073 (Mo-$K\alpha$)
color	yellow
crystal size / mm	0.161 × 0.118 × 0.061
crystal system	triclinic
space group	P_1– (# 2)
a / Å	11.3963(5)
b / Å	16.3240(6)
c / Å	18.0362(7)
α / º	103.576(3)
β / º	105.459(3)
γ / º	95.039(3)
V / Å^3	3102.8(2)
Z	2
D_x / g cm^{-3}	1.189
μ (Mo-$K\alpha$) / mm^{-1}	1.074
reflections collected	27050
unique reflections	10696
refined parameters	736
GOF on F^2	1.046
$R(F)$ [$I > 2\sigma(I)$][a]	0.0867
$wR(F^2)$ (all data)[b]	0.2553
$\Delta\rho_{min,\ max}$ /e Å^{-3}	–1.70, 1.67

[a] $R(F) = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR(F^2) = [\Sigma\ (w(Fo^2 – Fc^2)^2 / \Sigma\ w(Fo^2)^2)^{1/2}$

Table S3 Crystallographic data for **4**

formula	$C_{86}H_{116}Ge_2$
FM	1294.96
T / K	100
wavelength / Å	0.71073 (Mo-$K\alpha$)
color	orange
crystal size / mm	0.082 × 0.061 × 0.049
crystal system	triclinic
space group	P_1– (# 2)
a / Å	10.9234(3)
b / Å	11.2224(3)
c / Å	15.1362(5)
α / º	82.149(3)
β / º	78.332(3)
γ / º	86.759(2)
V / Å^3	1799.32(9)
Z	1
D_x / g cm^{-3}	1.195
μ (Mo-$K\alpha$) / mm^{-1}	0.879
reflections collected	43348
unique reflections	11459
refined parameters	578
GOF on F^2	1.014
$R(F)$ [$I > 2\sigma(I)$][a]	0.0627
$wR(F^2)$ (all data)[b]	0.1411
$\Delta\rho_{min,\ max}$ /e Å^{-3}	–0.45, 0.52

[a] $R(F) = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR(F^2) = [\Sigma\ (w(Fo^2 – Fc^2)^2 / \Sigma\ w(Fo^2)^2)^{1/2}$

Table S4 Crystallographic data for **5**

formula	$C_{72}H_{100}Ge_2O_{0.43}S_4$
FM	1245.85
T / K	100
wavelength / Å	0.71073 (Mo-$K\alpha$)
color	orange
crystal size / mm	0.182 × 0.090 × 0.079
crystal system	monoclinic
space group	$P2_1/c$ (# 14)
a / Å	11.2966(2)
b / Å	27.7798(6)
c / Å	10.3380(2)
α / º	90
β / º	91.415(2)
γ / º	90
V / Å^3	3243.25(11)
Z	2
D_x / g cm^{-3}	1.276
μ (Mo-$K\alpha$) / mm^{-1}	1.097
reflections collected	78615
unique reflections	10719
refined parameters	473
GOF on F^2	1.105
$R(F)$ [$I > 2\sigma(I)$][a]	0.0644
$wR(F^2)$ (all data)[b]	0.1612
$\Delta\rho_{min,\ max}$ /e Å^{-3}	–0.57, 0.92

[a] $R(F) = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR(F^2) = [\Sigma\ (w(Fo^2 – Fc^2)^2 / \Sigma\ w(Fo^2)^2)^{1/2}$

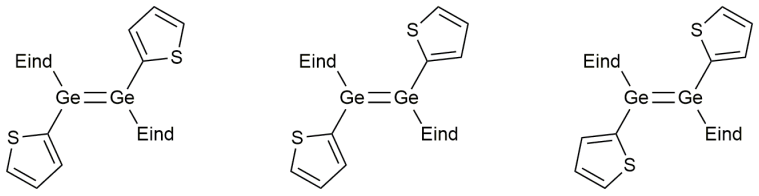

Fig. S13 Rotational isomers of **3**.

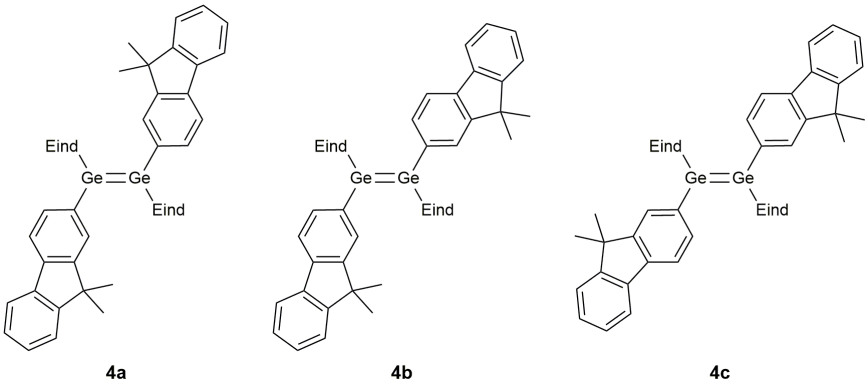

Fig. S14 Rotational isomers of **4**.

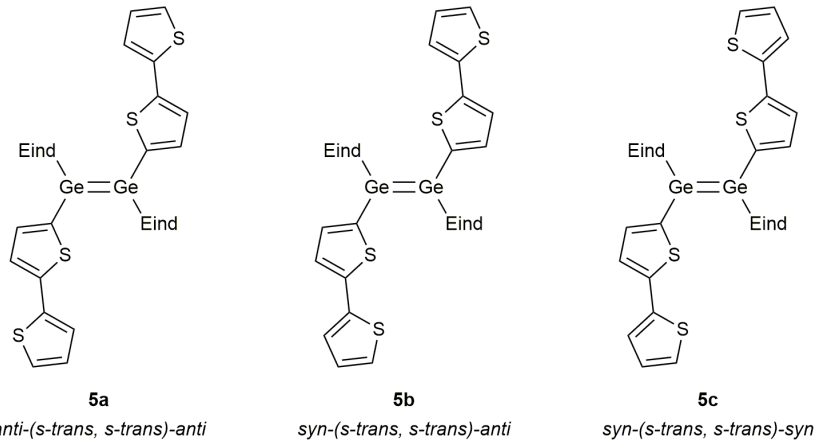

Fig. S15 Rotational isomers of **5**.

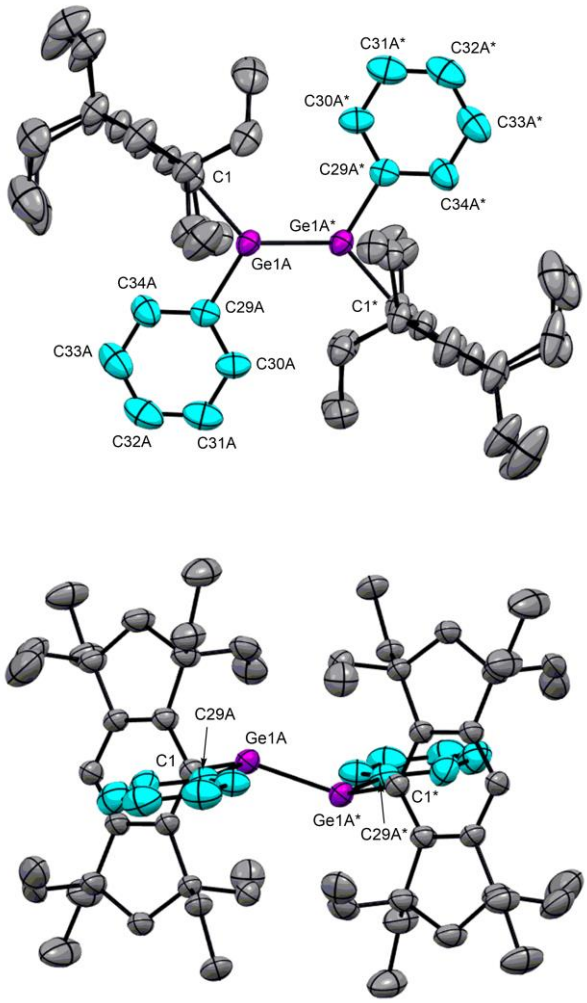

Fig. S16 Molecular structures of **2**: top view (top) and side view (bottom). The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms and disordered atoms are omitted for clarity. Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1A–Ge1A* = 2.2954(5), Ge1A–C1 = 1.983(2), Ge1A–C29A = 1.959(3); C1–Ge1A–C29A = 105.35(11), C1–Ge1A–Ge1A* = 125.52(7), C29A–Ge1A–Ge1A* = 114.60(9), ΣGe1A = 345.47, Ge1A–Ge1A*/ C1–Ge1A–C29A (θ) = 34.04(12).

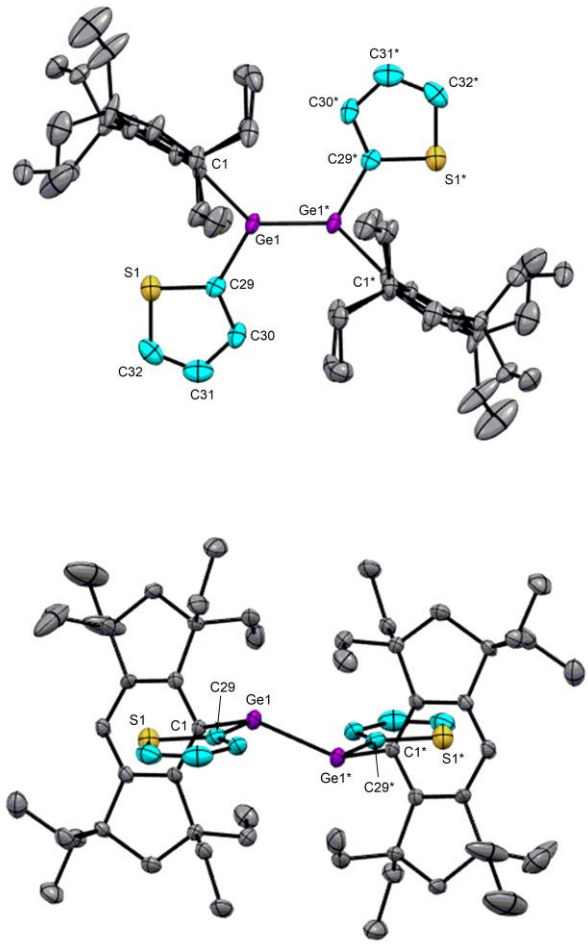

Fig. S17 Molecular structures of **3a** (Molecule A): top view (top) and side view (bottom). The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge1* = 2.3392(12), Ge1–C1 = 1.994(5), Ge1–C29 = 1.967(6); C1–Ge1–C29 = 103.2(2), C1–Ge1–Ge1* = 126.23(17), C29–Ge1–Ge1* = 111.52(18), ΣGe1 = 340.95, Ge1–Ge1*/C1–Ge1–C29 (θ) = 38.3(3).

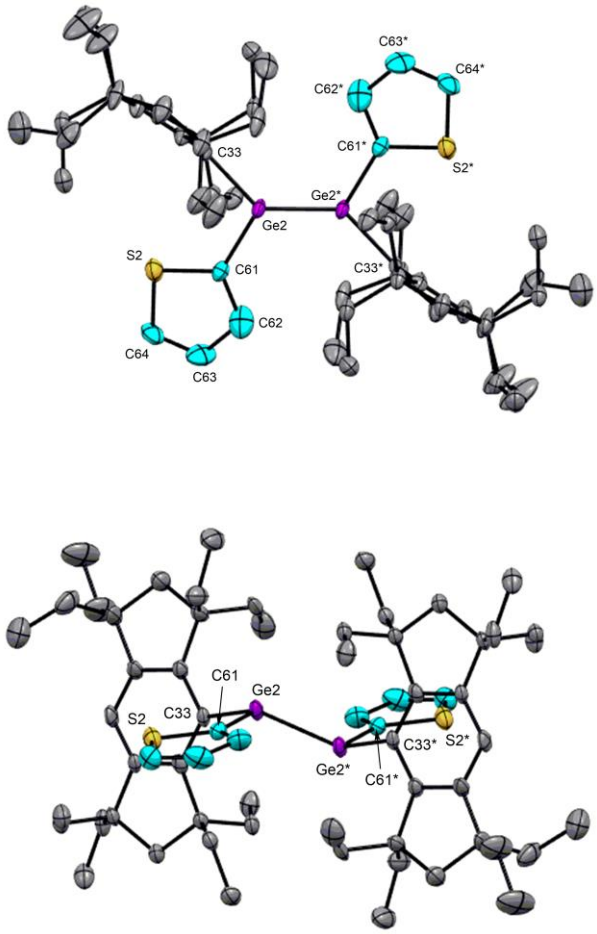

Fig. S18 Molecular structures of **3a** (Molecule B): top view (top) and side view (bottom). The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms, disordered atoms, and solvent molecules are omitted for clarity. Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge2–Ge2* = 2.3478(12), Ge2–C33 = 1.999(5), Ge2–C61 = 1.958(6); C33–Ge2–C61 = 103.3(3), C33–Ge2–Ge2* = 126.36(17), C61–Ge2–Ge2* = 110.0(3), ΣGe2 = 339.66, Ge2–Ge2*/C33–Ge2–C61 (θ) = 38.3(3).

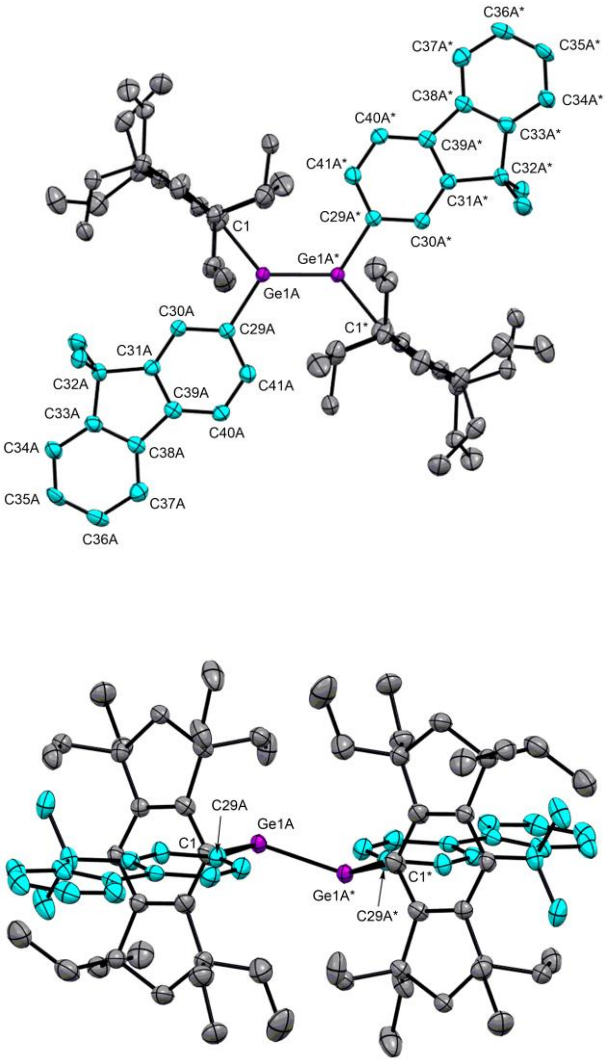

Fig. S19 Molecular structures of **4c**: top view (top) and side view (bottom). The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms and disordered atoms are omitted for clarity. Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1A–Ge1A* = 2.2830(7), Ge1A–C1 = 1.995(2), Ge1A–C29A = 1.953(3); C1–Ge1A–C29A = 106.48(12), C1–Ge1A–Ge1A* = 123.35(8), C29A–Ge1A–Ge1A* = 116.30(10), ΣGe1A = 346.13, Ge1A–Ge1A*/C1–Ge1A–C29A (θ) = 33.69(12).

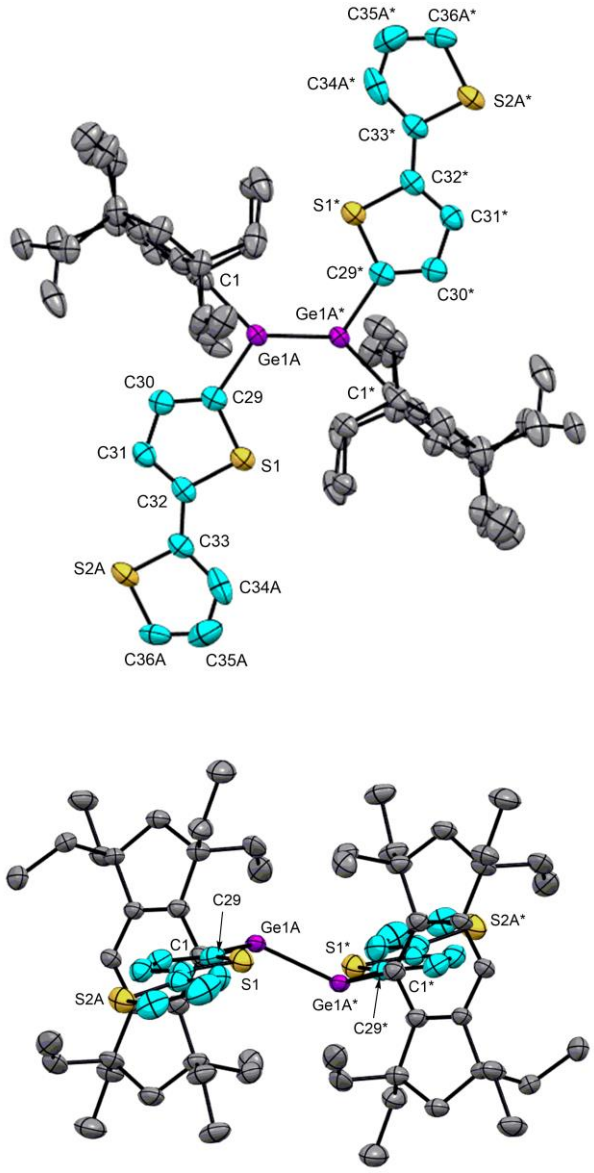

Fig. S20 Molecular structures of **5a**: top view (top) and side view (bottom). The thermal ellipsoids are shown in the 50% probability level. All hydrogen atoms and disordered atoms are omitted for clarity. Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1A–Ge1A* = 2.3443(9), Ge1A–C1 = 2.022(3), Ge1A–C29 = 1.985(3); C1–Ge1A–C29 = 100.55(12), C1–Ge1A–Ge1* = 124.73(9), C29–Ge1A–Ge1A* = 114.25(9), SGe1A = 339.53, Ge1–Ge1*/C1–Ge1–C29 (θ) = 39.30(13).

3. Theoretical Calculations

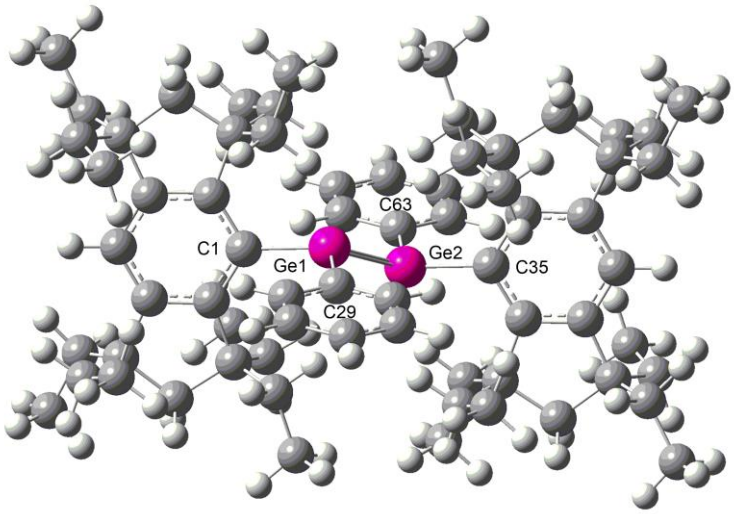

Fig. S21 Optimized structure of **2** (*trans*-bent) in the ground state (C_1 symmetry). Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge2 = 2.3088, Ge1–C1 =1.9956, Ge1–C29 = 1.9649, Ge2–C35 = 1.9956, Ge2–C63 = 1.9649, C1–Ge1–C29 = 106.63, C1–Ge1–Ge2 = 124.16, C29–Ge1–Ge2 = 115.57, C35–Ge2–C63 = 106.63, C35–Ge2–Ge1 = 124.16, C63–Ge2–Ge1 = 115.57, ΣGe1 = 346.35, ΣGe2 = 346.35, Ge1–Ge2/C1–Ge1–C29 = 33.34, Ge2–Ge1/C35–Ge2–C63 = 33.34.

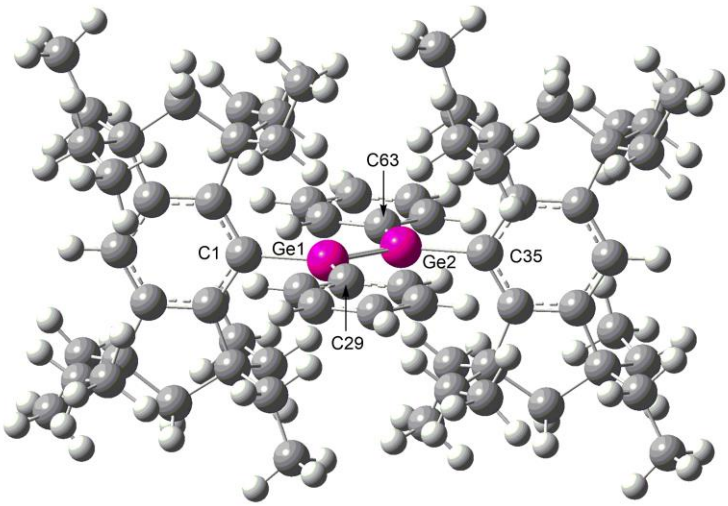

Fig. S22 Optimized structure of **2** (planar) in the ground state (C_1 symmetry). Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge2 = 2.1787, Ge1–C1 = 1.9311, Ge1–C29 = 1.9192, Ge2–C35 = 1.9311, Ge2–C63 = 1.9192, C1–Ge1–C29 = 112.24, C1–Ge1–Ge2 = 129.56, C29–Ge1–Ge2 = 118.20, C35–Ge2–C63 = 112.24, C35–Ge2–Ge1 = 129.56, C63–Ge2–Ge1 = 118.20, ΣGe1 = 360.00, ΣGe2 = 360.00, Ge1–Ge2/C1–Ge1–C29 = 0.00, Ge2–Ge1/C35–Ge2–C63 = 0.00.

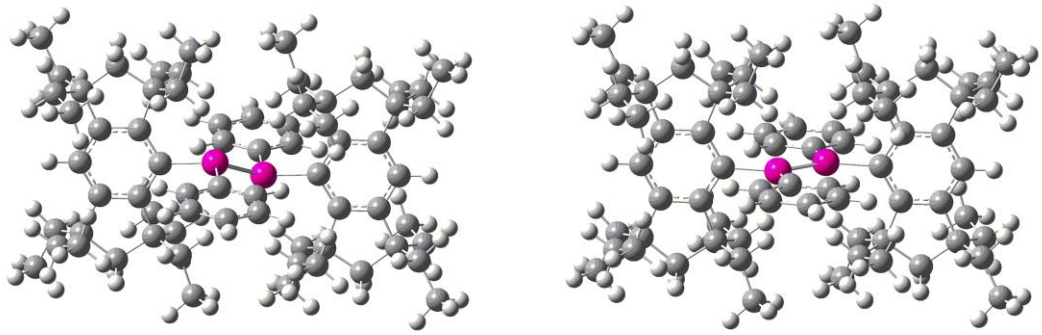

Fig. S23 Relative energies of **2** (*trans*-bent) and **2** (planar) (kcal mol^{-1}).

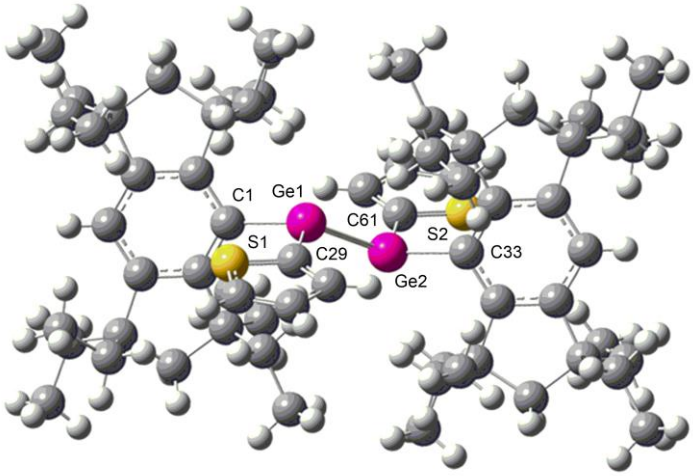

Fig. S24 Optimized structure of **3a** (*s-cis*, *s-cis*) in the ground state (C_1 symmetry). Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge2 = 2.3266, Ge1–C1 = 1.9848, Ge1–C29 = 1.9384, Ge2–C33 = 1.9839, Ge2–C61 = 1.9389, C1–Ge1–C29 = 101.29, C1–Ge1–Ge2 = 127.28, C29–Ge1–Ge2 = 112.07, C33–Ge2–C61 = 101.31, C33–Ge2–Ge1 = 127.27 C61–Ge2–Ge1 = 112.03, ΣGe1 = 340.64, ΣGe2 = 340.61, Ge1–Ge2/C1–Ge1–C29 = 38.01, Ge2–Ge1/C33–Ge2–C61 = 38.05.

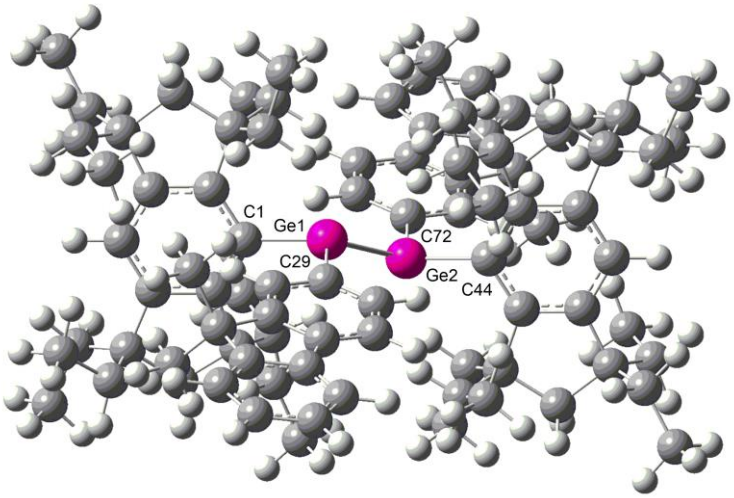

Fig. S25 Optimized structure of **4c** in the ground state (C_1 symmetry). Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge2 = 2.3176, Ge1–C1 = 1.9990, Ge1–C29 = 1.9623, Ge2–C44 = 1.9989, Ge2–C72 = 1.9630, C1–Ge1–C29 = 103.51, C1–Ge1–Ge2 = 125.49, C29–Ge1–Ge2 = 115.88, C44–Ge2–C72 = 103.51, C44–Ge2–Ge1 = 125.50 C72–Ge2–Ge1 = 115.88, ΣGe1 = 344.88, ΣGe2 = 344.88, Ge1–Ge2/C1–Ge1–C29 = 34.20, Ge2–Ge1/C44–Ge2–C72 = 34.21.

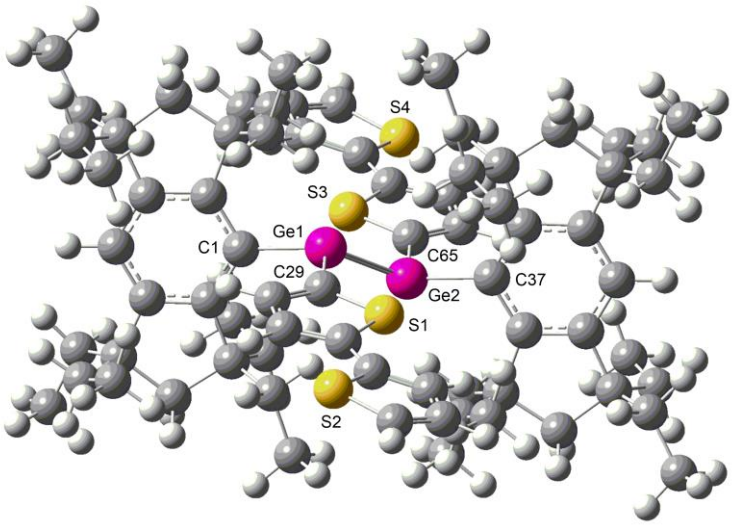

Fig. S26 Optimized structure of **5a** in the ground state (C_1 symmetry). Selected bond distances (Å), bond angles (°), sum of the bond angles at Ge atom (ΣGe) (°), and *trans*-bent angle (θ) (°): Ge1–Ge2 = 2.3552, Ge1–C1 = 2.0000, Ge1–C29 = 1.9531, Ge2–C37 = 1.9999, Ge2–C65 = 1.9530, C1–Ge1–C29 = 101.81, C1–Ge1–Ge2 = 125.73, C29–Ge1–Ge2 = 112.46, C37–Ge2–C65 = 101.81, C37–Ge2–Ge1 = 125.72 C65–Ge2–Ge1 = 112.47, ΣGe1 = 340.00, ΣGe2 = 339.40, Ge1–Ge2/C1–Ge1–C29 = 39.03, Ge2–Ge1/C37–Ge2–C65 = 39.77.

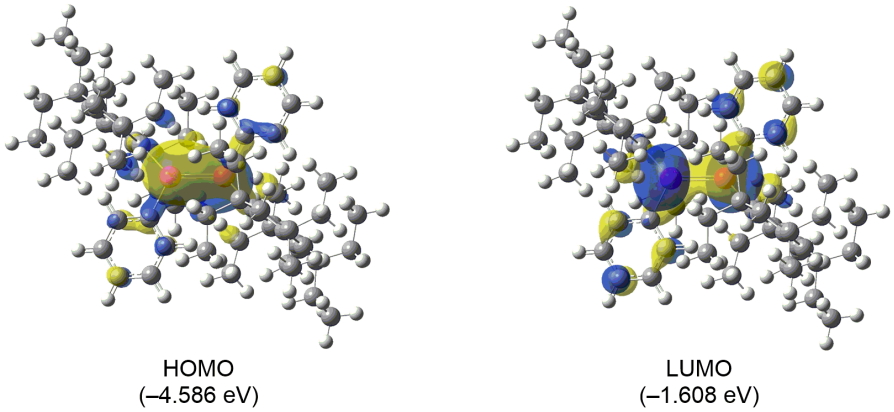

Fig. S27 Selected MOs of **2** (*trans*-bent) and their energy level (eV).

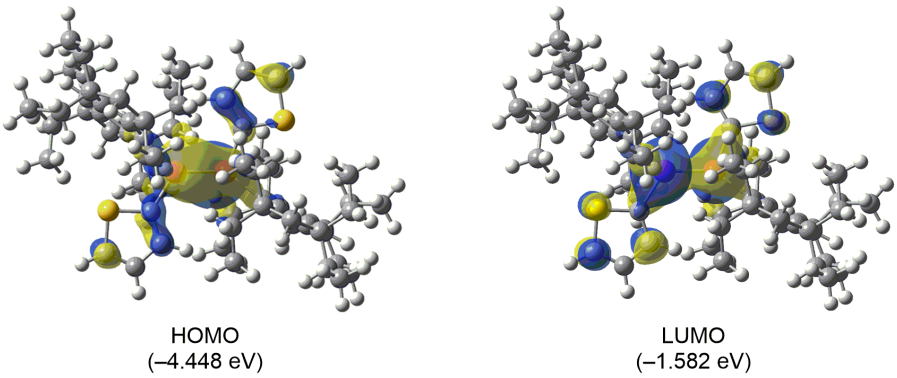

Fig. S28 Selected MOs of **3a** (*s-cis*, *s-cis*) and their energy level (eV).

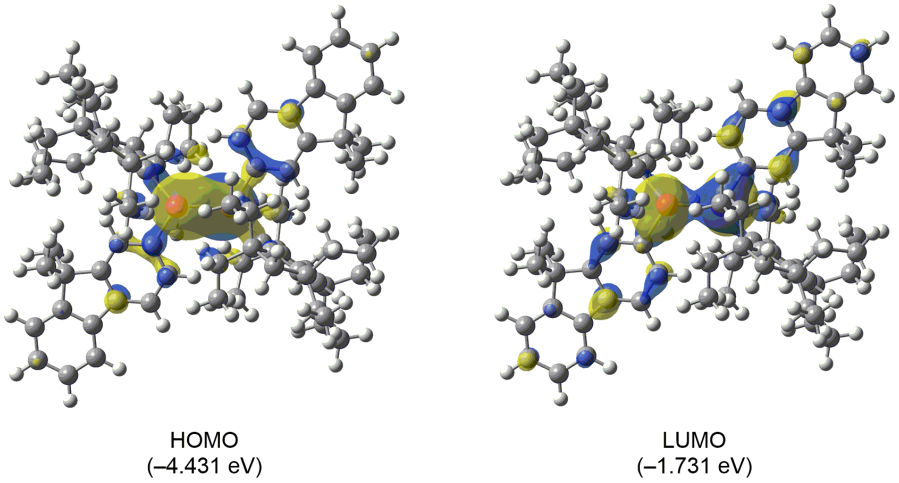

Fig. S29 Selected MOs of **4c** and their energy level (eV).

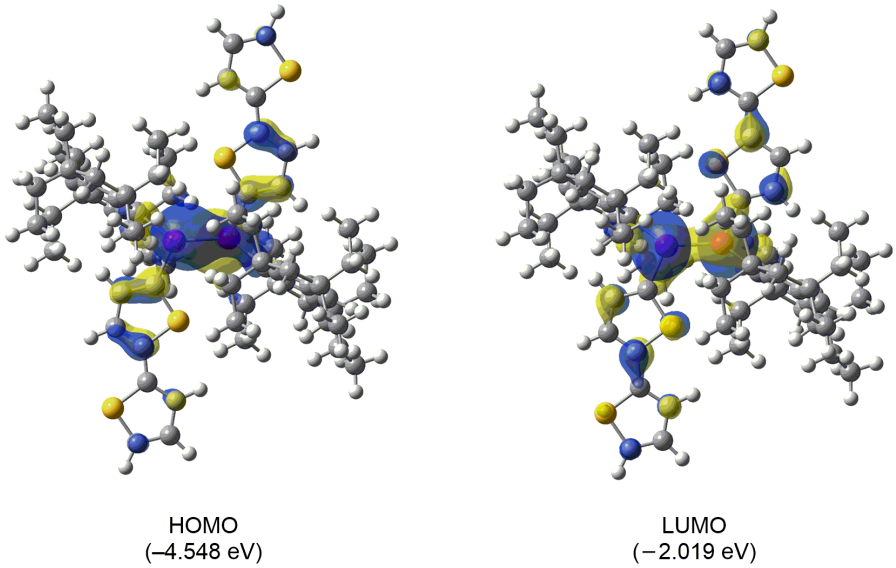

Fig. S30 Selected MOs of **5a** (*anti-(s-trans, s-trans)-anti*) and their energy level (eV).

Table S5 Excitation energies and oscillator strengths for **2** (*trans*-bent) (The 286th orbital is HOMO in Figure S27).

Excited State 1: Singlet-A 2.7007 eV 459.08 nm f=0.3001 <S**2>=0.000
286 -> 287 0.70362
286 <- 287 -0.10249
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -6806.35875524
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1463 eV 394.06 nm f=0.0000 <S**2>=0.000
286 -> 288 0.70420

Excited State 3: Singlet-A 3.3560 eV 369.44 nm f=0.0045 <S**2>=0.000
286 -> 289 0.70580

Excited State 4: Singlet-A 3.6649 eV 338.30 nm f=0.0000 <S**2>=0.000
286 -> 290 0.68451
286 -> 292 -0.15049

Excited State 5: Singlet-A 3.7153 eV 333.71 nm f=0.0095 <S**2>=0.000
284 -> 287 0.16484
286 -> 291 0.68279

Excited State 6: Singlet-A 3.7221 eV 333.10 nm f=0.0000 <S**2>=0.000
285 -> 287 0.60523
286 -> 292 -0.35555

Excited State 7: Singlet-A 3.7359 eV 331.88 nm f=0.0033 <S**2>=0.000
284 -> 287 0.68667
286 -> 291 -0.16362

Excited State 8: Singlet-A 3.7434 eV 331.21 nm f=0.0000 <S**2>=0.000
285 -> 287 0.36279
286 -> 290 0.13653
286 -> 292 0.58265

Excited State 9: Singlet-A 3.8736 eV 320.07 nm f=0.0000 <S**2>=0.000
283 -> 287 0.69850

Excited State 10: Singlet-A 4.1053 eV 302.01 nm f=0.0006 <S**2>=0.000
286 -> 293 0.70433

Excited State 11: Singlet-A 4.1187 eV 301.03 nm f=0.0000 <S**2>=0.000
286 -> 294 0.69991

Excited State 12: Singlet-A 4.2007 eV 295.15 nm f=0.0040 <S**2>=0.000
282 -> 287 0.70327

Excited State 13: Singlet-A 4.3018 eV 288.21 nm f=0.0666 <S**2>=0.000
278 -> 287 0.25300
286 -> 295 0.65020

Excited State 14: Singlet-A 4.4324 eV 279.72 nm f=0.0000 <S**2>=0.000
279 -> 287 -0.12818
281 -> 287 -0.13630
286 -> 296 0.64087
286 -> 297 0.19378

Excited State 15: Singlet-A 4.4664 eV 277.59 nm f=0.0000 <S**2>=0.000
281 -> 287 0.66711
286 -> 296 0.16089

Excited State 16: Singlet-A 4.4742 eV 277.11 nm f=0.0160 <S**2>=0.000
280 -> 287 0.68897

Excited State 17: Singlet-A 4.5717 eV 271.20 nm f=0.0000 <S**2>=0.000
279 -> 287 0.53518
286 -> 297 0.42310

```
      286 -> 303         0.10533

Excited State   18:      Singlet-A      4.6245 eV  268.10 nm  f=0.0000  <S**2>=0.000
      279 -> 287        -0.41595
      281 -> 287         0.10768
      286 -> 296        -0.20780
      286 -> 297         0.48254
      286 -> 303         0.11791

Excited State   19:      Singlet-A      4.6526 eV  266.48 nm  f=0.0938  <S**2>=0.000
      278 -> 287         0.52826
      284 -> 289        -0.20910
      285 -> 288         0.33143
      286 -> 295        -0.17314

Excited State   20:      Singlet-A      4.6679 eV  265.61 nm  f=0.0000  <S**2>=0.000
      277 -> 287        -0.12382
      282 -> 294         0.13414
      283 -> 293         0.16235
      284 -> 288         0.54335
      285 -> 289        -0.35140
SavETr:  write IOETrn=     770 NScale= 10 NData=   16 NLR=1 NState=     20 LETran=        370.
Leave Link  914 at Tue Oct 17 07:12:00 2017, MaxMem= 14763950080 cpu:       59092.0
(Enter C:¥G09W¥l601.exe)
Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.
```

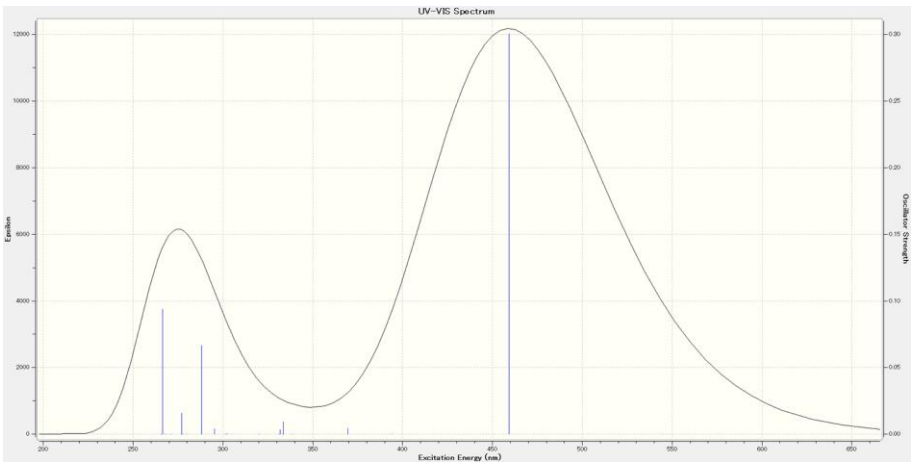

Fig. S31 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of **2** (*trans*-bent).

Table S6 Excitation energies and oscillator strengths for **3a** (*s-cis, s-cis*) (The 288th orbital is HOMO in Figure S28).

Excited State 1: Singlet-A 2.7267 eV 454.71 nm f=0.3418 <S**2>=0.000
288 -> 289 0.70597
288 <- 289 -0.11745
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -7442.38567182
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4115 eV 363.43 nm f=0.0000 <S**2>=0.000
287 -> 289 0.65262
288 -> 290 -0.26084

Excited State 3: Singlet-A 3.4203 eV 362.49 nm f=0.0020 <S**2>=0.000
286 -> 289 0.70157

Excited State 4: Singlet-A 3.4233 eV 362.18 nm f=0.0000 <S**2>=0.000
287 -> 289 0.26029
288 -> 290 0.64777

Excited State 5: Singlet-A 3.5713 eV 347.17 nm f=0.0050 <S**2>=0.000
288 -> 291 0.70477

Excited State 6: Singlet-A 3.6685 eV 337.97 nm f=0.0000 <S**2>=0.000
285 -> 289 0.68990
288 -> 292 -0.11862

Excited State 7: Singlet-A 3.7944 eV 326.76 nm f=0.0000 <S**2>=0.000
284 -> 289 -0.25652
288 -> 292 0.64410

Excited State 8: Singlet-A 4.0016 eV 309.84 nm f=0.0143 <S**2>=0.000
282 -> 289 -0.26054
283 -> 289 0.63945
288 -> 293 -0.12363

Excited State 9: Singlet-A 4.0676 eV 304.81 nm f=0.0000 <S**2>=0.000
284 -> 289 0.63853
288 -> 292 0.22869
288 -> 296 -0.13437

Excited State 10: Singlet-A 4.0896 eV 303.17 nm f=0.0067 <S**2>=0.000
282 -> 289 0.55008
283 -> 289 0.13834
288 -> 293 -0.40100
288 -> 295 -0.10677

Excited State 11: Singlet-A 4.2331 eV 292.89 nm f=0.0575 <S**2>=0.000
280 -> 289 -0.15127
282 -> 289 0.31762
283 -> 289 0.21153
288 -> 293 0.54177
288 -> 295 -0.17185

Excited State 12: Singlet-A 4.2863 eV 289.26 nm f=0.0000 <S**2>=0.000
288 -> 294 0.69975

Excited State 13: Singlet-A 4.3670 eV 283.91 nm f=0.0000 <S**2>=0.000
281 -> 289 0.56703
288 -> 296 -0.41370

Excited State 14: Singlet-A 4.3901 eV 282.41 nm f=0.0173 <S**2>=0.000
280 -> 289 0.65011
288 -> 293 0.11301
288 -> 295 -0.23839

Excited State 15: Singlet-A 4.4134 eV 280.93 nm f=0.0000 <S**2>=0.000
281 -> 289 0.40347

```
      284 -> 289         0.11409
      288 -> 292         0.10023
      288 -> 296         0.53915

Excited State   16:      Singlet-A      4.6358 eV  267.45 nm  f=0.0966  <S**2>=0.000
      280 -> 289         0.20643
      282 -> 289         0.14167
      283 -> 289         0.13158
      288 -> 293         0.10000
      288 -> 295         0.62109

Excited State   17:      Singlet-A      4.6869 eV  264.53 nm  f=0.0001  <S**2>=0.000
      279 -> 289         0.45898
      286 -> 290        -0.39519
      287 -> 291         0.29849

Excited State   18:      Singlet-A      4.7215 eV  262.60 nm  f=0.1545  <S**2>=0.000
      285 -> 294         0.17264
      286 -> 291        -0.36997
      287 -> 290         0.52556

Excited State   19:      Singlet-A      4.7511 eV  260.96 nm  f=0.0001  <S**2>=0.000
      279 -> 289         0.52042
      285 -> 293         0.11203
      286 -> 290         0.34397
      287 -> 291        -0.23859

Excited State   20:      Singlet-A      4.9876 eV  248.58 nm  f=0.0058  <S**2>=0.000
      286 -> 290         0.36333
      286 -> 291        -0.26240
      286 -> 292        -0.31683
      287 -> 290        -0.14811
      287 -> 291         0.37831
      287 -> 292         0.13076
SavETr:  write IOETrn=     770 NScale= 10 NData=   16 NLR=1 NState=     20 LETran=          370.
Leave Link  914 at Wed Sep 09 19:54:25 2020, MaxMem= 17179869184 cpu:          8278.0
(Enter C:¥G09W¥l601.exe)
Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.
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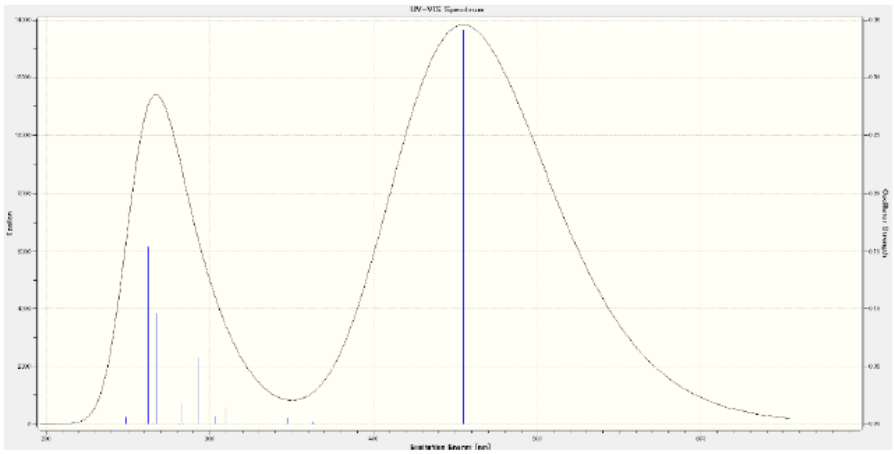

Fig. S32 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of **3a** (*s-cis*, *s-cis*).

Table S7 Excitation energies and oscillator strengths for **4c** (The 348th orbital is HOMO in Figure S29).

Excited State 1: Singlet-A 2.5215 eV 491.71 nm f=0.6161 <S**2>=0.000
348 -> 349 0.70191
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -7497.59589264
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.2071 eV 386.60 nm f=0.0000 <S**2>=0.000
347 -> 349 0.11161
348 -> 350 0.61808
348 -> 352 -0.31212

Excited State 3: Singlet-A 3.2818 eV 377.80 nm f=0.0000 <S**2>=0.000
347 -> 349 0.10416
348 -> 350 0.29791
348 -> 352 0.62854

Excited State 4: Singlet-A 3.3758 eV 367.28 nm f=0.0071 <S**2>=0.000
346 -> 349 -0.11847
348 -> 351 0.58205
348 -> 353 -0.36563

Excited State 5: Singlet-A 3.5388 eV 350.35 nm f=0.0157 <S**2>=0.000
346 -> 349 -0.38501
348 -> 351 0.24573
348 -> 353 0.52649

Excited State 6: Singlet-A 3.5549 eV 348.77 nm f=0.0000 <S**2>=0.000
345 -> 349 0.39399
347 -> 349 0.56515
348 -> 350 -0.10711

Excited State 7: Singlet-A 3.6099 eV 343.45 nm f=0.0301 <S**2>=0.000
344 -> 349 0.56485
346 -> 349 0.31161
348 -> 351 0.15823
348 -> 353 0.21669

Excited State 8: Singlet-A 3.6790 eV 337.01 nm f=0.0000 <S**2>=0.000
345 -> 349 0.56221
347 -> 349 -0.35674
348 -> 354 0.17338

Excited State 9: Singlet-A 3.7095 eV 334.24 nm f=0.2156 <S**2>=0.000
344 -> 349 -0.38664
346 -> 349 0.41703
348 -> 351 0.14016
348 -> 353 0.15378
348 -> 355 0.32606
348 -> 357 -0.10445

Excited State 10: Singlet-A 3.7106 eV 334.14 nm f=0.0000 <S**2>=0.000
345 -> 349 -0.15552
348 -> 354 0.65571
348 -> 356 -0.13243

Excited State 11: Singlet-A 3.7600 eV 329.74 nm f=0.0000 <S**2>=0.000
343 -> 349 0.68992
347 -> 349 0.11892

Excited State 12: Singlet-A 3.9380 eV 314.84 nm f=0.1212 <S**2>=0.000
342 -> 349 -0.16369
344 -> 349 0.14247
346 -> 349 -0.22818
348 -> 351 -0.19481
348 -> 355 0.57627

Excited State 13: Singlet-A 4.0802 eV 303.87 nm f=0.0000 <S**2>=0.000
348 -> 356 0.60129
348 -> 358 0.33635

Excited State 14: Singlet-A 4.0897 eV 303.16 nm f=0.0204 <S**2>=0.000
342 -> 349 0.67474
348 -> 355 0.13170

Excited State 15: Singlet-A 4.1394 eV 299.52 nm f=0.0104 <S**2>=0.000
348 -> 357 0.62444
348 -> 359 -0.29930

Excited State 16: Singlet-A 4.2072 eV 294.70 nm f=0.0000 <S**2>=0.000
339 -> 349 -0.20566
341 -> 349 0.57965
348 -> 354 0.14316
348 -> 356 0.16175
348 -> 358 -0.23372

Excited State 17: Singlet-A 4.2164 eV 294.06 nm f=0.0126 <S**2>=0.000
338 -> 349 0.23793
340 -> 349 0.58791
348 -> 355 0.12444
348 -> 357 0.11561
348 -> 359 0.20870

Excited State 18: Singlet-A 4.2689 eV 290.43 nm f=0.0000 <S**2>=0.000
339 -> 349 -0.16725
341 -> 349 0.19558
348 -> 356 -0.26331
348 -> 358 0.38205
348 -> 360 0.42500

Excited State 19: Singlet-A 4.3507 eV 284.97 nm f=0.0144 <S**2>=0.000
338 -> 349 -0.26467
340 -> 349 -0.14569
348 -> 357 0.23377
348 -> 359 0.56430

Excited State 20: Singlet-A 4.3916 eV 282.32 nm f=0.0000 <S**2>=0.000
339 -> 349 0.21904
348 -> 358 -0.37784
348 -> 360 0.51594

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(Enter C:¥G09W¥l601.exe)
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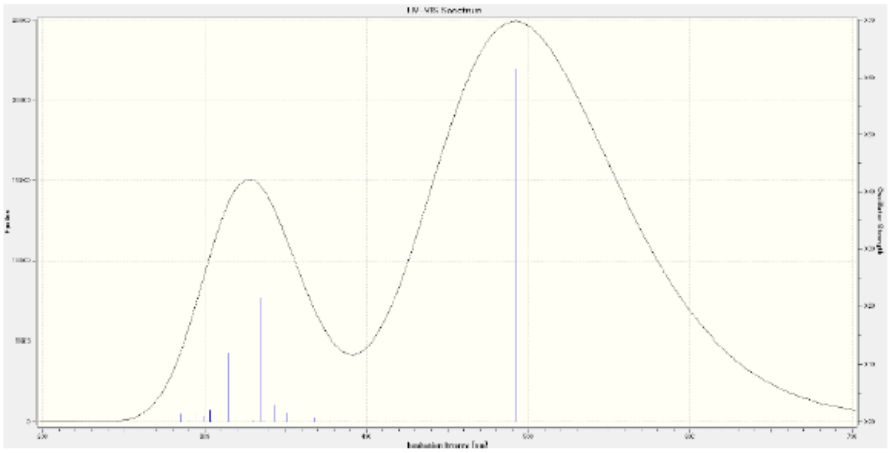

Fig. S33 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of **4c**.

Table S8 Excitation energies and oscillator strengths for **5a** (*anti-(s-trans, s-trans)-anti*) (The 330th orbital is HOMO in Figure S30).

Excited State 1:	Singlet-A	2.3099 eV	536.76 nm	f=0.4713	<S**2>=0.000	
330 -> 331	0.70166					
This state for optimization and/or second-order correction.						
Total Energy, E(TD-HF/TD-KS) = -8547.08096820						
Copying the excited state density for this state as the 1-particle RhoCI density.						
Excited State 2:	Singlet-A	2.8616 eV	433.26 nm	f=0.0000	<S**2>=0.000	
329 -> 331	0.30669					
330 -> 332	0.62668					
Excited State 3:	Singlet-A	3.0741 eV	403.31 nm	f=0.0000	<S**2>=0.000	
329 -> 331	0.62151					
330 -> 332	-0.28680					
330 -> 334	-0.14203					
Excited State 4:	Singlet-A	3.1017 eV	399.73 nm	f=0.0685	<S**2>=0.000	
328 -> 331	0.59138					
330 -> 333	0.38080					
Excited State 5:	Singlet-A	3.3065 eV	374.97 nm	f=0.0000	<S**2>=0.000	
327 -> 331	-0.11637					
330 -> 332	-0.12005					
330 -> 334	0.67412					
Excited State 6:	Singlet-A	3.3585 eV	369.17 nm	f=0.0279	<S**2>=0.000	
326 -> 331	0.61153					
328 -> 331	0.14773					
330 -> 333	-0.26989					
330 -> 335	0.16039					
Excited State 7:	Singlet-A	3.3754 eV	367.32 nm	f=0.0000	<S**2>=0.000	
327 -> 331	0.69247					
330 -> 334	0.10070					
Excited State 8:	Singlet-A	3.4087 eV	363.72 nm	f=0.1068	<S**2>=0.000	
326 -> 331	-0.34393					
328 -> 331	0.27116					
330 -> 333	-0.38167					
330 -> 335	0.38710					
Excited State 9:	Singlet-A	3.5849 eV	345.86 nm	f=0.0000	<S**2>=0.000	
325 -> 331	0.70007					
Excited State 10:	Singlet-A	3.6059 eV	343.84 nm	f=0.1560	<S**2>=0.000	
328 -> 331	-0.20222					
330 -> 333	0.33560					
330 -> 335	0.55919					
Excited State 11:	Singlet-A	3.8480 eV	322.21 nm	f=0.0155	<S**2>=0.000	
324 -> 331	0.69401					
Excited State 12:	Singlet-A	3.9490 eV	313.97 nm	f=0.5171	<S**2>=0.000	
322 -> 331	-0.11614					
329 -> 332	0.68003					
Excited State 13:	Singlet-A	4.0472 eV	306.34 nm	f=0.0000	<S**2>=0.000	
323 -> 331	-0.36797					
330 -> 336	0.54957					
330 -> 337	-0.16300					
330 -> 339	0.12082					
Excited State 14:	Singlet-A	4.0602 eV	305.37 nm	f=0.0000	<S**2>=0.000	
323 -> 331	0.26260					
328 -> 332	0.61270					
330 -> 336	0.16162					

```
Excited State   15:      Singlet-A      4.1033 eV  302.15 nm  f=0.0734  <S**2>=0.000
     320 -> 331            -0.12368
     322 -> 331             0.67240
     329 -> 332             0.10686

Excited State   16:      Singlet-A      4.1048 eV  302.04 nm  f=0.0002  <S**2>=0.000
     323 -> 331             0.50457
     328 -> 332            -0.32554
     329 -> 333             0.13591
     330 -> 336             0.29336

Excited State   17:      Singlet-A      4.2470 eV  291.93 nm  f=0.0000  <S**2>=0.000
     329 -> 333            -0.21378
     330 -> 336             0.22836
     330 -> 337             0.61921

Excited State   18:      Singlet-A      4.2584 eV  291.15 nm  f=0.0002  <S**2>=0.000
     330 -> 338             0.69670

Excited State   19:      Singlet-A      4.2736 eV  290.12 nm  f=0.0000  <S**2>=0.000
     323 -> 331            -0.11421
     329 -> 333             0.63543
     330 -> 337             0.22587

Excited State   20:      Singlet-A      4.3407 eV  285.63 nm  f=0.0104  <S**2>=0.000
     327 -> 332             0.70129
SavETr:  write IOETrn=    770 NScale= 10 NData=  16 NLR=1 NState=    20 LETran=        370.
Leave Link  914 at Wed Sep 23 12:11:25 2020, MaxMem= 17179869184 cpu:         9287.0
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Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.
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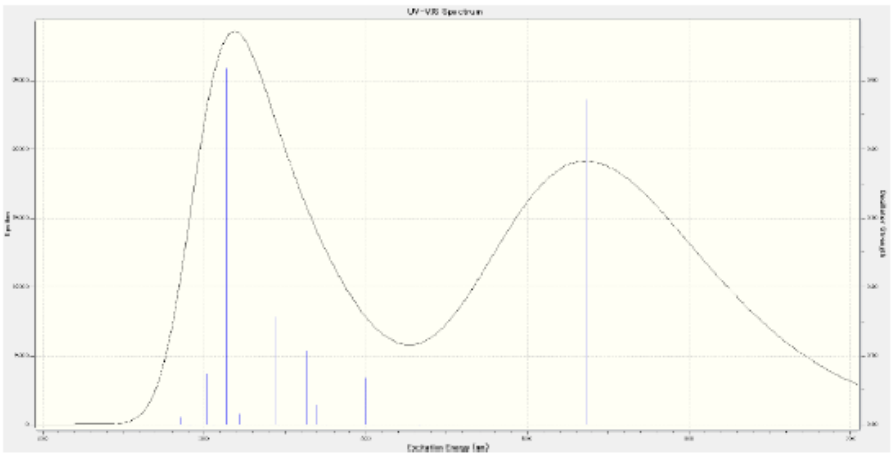

Fig. S34 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of **5a** (*anti-(s-trans, s-trans)-anti*).