Supporting Information

A Genuine Stannylone with a Monoatomic Two-Coordinate Tin(0) Atom Supported by a Bis(silylene) Ligand

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A. Experimental Procedures

A1. General Considerations

All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or MBraun glove box fitted with a gas purification and recirculation unit. Solvents were dried by standard methods and freshly distilled prior to use. Potassium graphite (KGr) was prepared by reacting potassium with previously dried graphite in a 1:8 molar ratio at 160 °C for 2 h under dry nitrogen. Bis(NH3)Sxaxathene Si3(Xant)Si3+1 [Si3(Xant)Si3+ = PhC(N(Bu)3)Si(Xant)Si(N(Bu)3)CPH and K2Fe(CO)5] were synthesized according to reported procedures. The solution NMR spectra were recorded on Bruker Spectrometers AV 200, 400 or 500 with residual solvent signals as internal reference (1H NMR: D8-Benzene, 7.16 ppm; 13C([2]H) NMR: D6-Benzene, 128.06 ppm) or external standards (195Si([2]H) NMR: SiMe4, 0.0 ppm; 197Sn([2]H) NMR: SnMe5, 0.0 ppm). The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Elemental analyses were performed by the analytical labor service in the Institute of Chemistry, Technical University of Berlin, Germany. High-resolution ESI-MS were measured on a Thermo Scientific LTQ orbitrap XL. UV/Vis spectra were recorded on an Analytik Jena Specord S600 diode array spectrometer. IR spectra were measured with a Nicolet IS5 FT-IR-Spectrometer from the company Thermo.

A2. Single-Crystal X-ray Structure Determination

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N2 flow. The data of all compounds were collected on an Oxford Diffraction SuperNova, Single source at offset, Atlas at 150 K (Cu-Kα radiation, λ = 1.5418 Å). The structures were solved by direct methods and refined on F2 with the SHELX-97 software package.[3] For the crystal of compound 4, the strongly disordered C4H11 molecules are treated using Solvent Masking in Olex2. In the molecular structure of compound 5 which contains two independent molecules a and b, one of the tert-butyl groups in molecule a is disordered over two orientations with an approximate occupancy ratio of 0.75:0.25; two of the tert-butyl groups in molecule b are disordered over two orientations with an approximate occupancy ratio of 0.75:0.25 and 0.72:0.28, respectively. CCDC: 2110196 (2), 2110197 (3), 2110198 (4) and 2110199 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/

A3. Synthesis and Characterization

Synthesis of Compound 2.

To a mixture of bis(NH3)xanthen 1 (728 mg, 1 mmol) and SnCl2(dioxane) (277 mg, 1 mmol) in a 50 mL Schlenk flask was added 25 mL Et2O at room temperature under stirring. A bright yellow precipitate formed slowly. After stirring overnight, the bright yellow precipitate was separated by filtration and dried under vacuum affording compound 2 as a yellow solid (780 mg, 85% isolated yields). Yellow crystals suitable for X-ray analysis were obtained from a concentrated toluene solution at -30 °C.

2: M.p. 271 °C (decomp.). 1H NMR (200 MHz, D8-Benzene, 298 K): δ = 7.82 (dd, J = 6.9, 1.9 Hz, 2 H, Ar(Xant)-H), 7.44 – 7.36 (m, 4 H, Ar(Ph)-H), 7.40 – 7.35 (m, 2 H, Ar(Xant)-H), 7.10 – 7.05 (m, 2 H, Ar(Xant)-H), 6.85 – 6.93 (m, 6 H, Ar(Ph)-H), 1.48 (s, 6 H, C(CH3)3), 1.36 ppm (s, 36 H, NC(CH3)3). 13C([2]H) NMR (50 MHz, D8-Benzene, 298 K): δ = 173.01 (s, NCN), 158.25, 132.31, 131.81, 131.05, 130.59, 129.95, 129.16, 128.34, 125.06, 124.05, 123.66 (s, Ar-C) [A signal for Ar-C is covered by those of C6D6]. 55.40 (s, C(N(CH3))3), 31.72 (s, C(CH3)3), 31.57 (s, NC(CH3)3), 29.92 ppm (s, C(CH3)2). 195Sn([2]H) NMR (149 MHz, D8-Benzene, 298 K): δ = -348.13 ppm. 29Si([2]H) NMR (79 MHz, D8-Benzene, 298 K): δ = 29.36 ppm. 1H NMR (300 MHz, D8-Benzene, 298 K): δ = 1334 Hz. HRMS(EI): (m/z) calcd for [C11H43Cl2N2O6Si2]: 881.2854 [M+Cl]-; found: 881.2852. Elemental analysis calcd for C11H43Cl2N2O6Si2: C, 53.74; H, 5.81; N, 5.57; found: C, 53.74; H, 5.81; N, 5.57; C: 56.85; H, 6.34; N, 5.65 [Consistently low C analysis may be due to the formation of silicon carbide]. IR (cm⁻¹): 2969, 1472, 1445, 1395, 1388, 1274, 1239, 1200, 1120, 1089, 1020, 801, 780(m), 763(m), 746(m), 726(w), 717, 709(m), 630(m).

Synthesis of Compound 3.

To a mixture of bis(NH3)xanthen 1 (728 mg, 1 mmol) and SnBr2(dioxane) (467 mg, 1 mmol) in a 50 mL Schlenk flask was added 25 mL Et2O at room temperature under stirring. A bright yellow precipitate formed slowly. After stirring overnight, the bright yellow precipitate was separated by filtration and dried under vacuum affording compound 3 as yellow solid (734 mg, 72% isolated yields). Yellow crystals suitable for X-ray analysis were obtained from a concentrated Et2O solution at -30 °C.

3: M.p. 284 °C (decomp.). 1H NMR (200 MHz, D8-Benzene, 298 K): δ = 7.79 (dd, J = 7.1, 1.7 Hz, 2H, Ar(Xant)-H), 7.68 (d, J = 8.3 Hz, 2H, Ar(Xant)-H), 7.41 (m, 2H, Ar(Ph)-H), 7.33 – 7.24 (m, 2H, Ar(Xant)-H), 7.03 – 6.81 (m, 8H, Ar(Ph)-H), 1.48 (s, 6H, C(CH3)3), 1.37 ppm (s, 36H, NC(CH3)3). 13C([2]H) NMR (50 MHz, D8-Benzene, 298 K): δ = 173.34 (s, NCN), 158.09, 131.83, 131.75, 130.93, 130.58, 130.51, 128.81, 128.35, 127.86, 123.76, 122.95 (s, Ar-C) [A signal for Ar-C is covered by those of C6D6]. 55.46 (s, C(N(CH3))3), 35.65 (s, C(CH3)3), 31.95 (s, NC(CH3)3), 30.36 ppm (s, C(CH3)2). 195Sn([2]H) NMR (75 MHz, D8-Benzene, 298 K): δ = -391.95ppm. 29Si([2]H) NMR (99 MHz, D8-Benzene, 298 K): δ = 30.27 ppm. HRMS(EI): (m/z) calcd for [C11H43BrN2O6Si2]: 925.2349 [M+Br]-; found: 925.2316. Elemental analysis calcd for C11H43BrN2O6Si2: C, 53.74; H, 5.81; N, 5.57; found: C, 54.82; H, 5.37; N, 4.70 [Consistently low C analysis may be due to the formation of silicon carbide]. IR (cm⁻¹): 2969, 1471, 1395, 1362, 1272, 1235, 1199, 1118, 1105, 1089, 1079, 1021, 860, 801, 780(m), 763(m), 745(m), 726(w), 715, 709(m), 630(m), 614(w), 574(w), 563(w).
Synthesis of Compound 4.

**Reduction of 2:** To a mixture of compound 2 (917 mg, 0.1 mmol) and K$_2$Fe(CO)$_4$ (295.2 mg, 1.2 mmol) in a 100 mL Schlenk flask was added 60 mL THF at room temperature under stirring. The color of the mixture changed to red immediately. After stirring overnight, the red mixture was filtered and the residue was washed with THF (10 mL x 2). Volatiles were removed under vacuum and the residue was washed with Et$_2$O (10 mL) to afford compound 4 as a red powder after dried under vacuum (496 mg, 42% isolated yield). Red crystals suitable for X-ray analysis were obtained from a concentrated benzene solution at room temperature.

**Reduction of 3:** To a mixture of compound 3 (100.7 mg, 0.1 mmol) and K$_2$Fe(CO)$_4$ (29.52 mg, 0.12 mmol) in a 25 mL Schlenk flask was added 10 mL THF at room temperature under stirring. The color of the mixture changed to red immediately. After stirring overnight, the red mixture was filtered and the residue was washed with THF (2 mL x 2). Volatiles were removed under vacuum and the residue was washed with Et$_2$O (3 mL) to afford compound 4 as a red powder after dried under vacuum (47 mg, 40% isolated yield).

**Synthesis of Compound 5.** To a mixture of compound 4 (591.5 mg, 0.5 mmol) and KC$_8$ (276.75 mg, 2.05 mmol) in a 100 mL Schlenk flask was added 50 mL THF at room temperature under stirring. The color of the mixture from red changed to dark blue slowly. After stirring 6 h, the dark blue mixture was filtered and the black residue of graphite was washed with THF (10 mL x 3). The volatiles were removed under vacuum from the combined filtrate to give blue residue. Then hexane (80 mL) was introduced to the residue, the resulting solution was separated from the precipitates by filtration. The volatiles were removed under vacuum to afford almost pure compound 5 as a dark blue powder (474.32 mg, 56% isolated yields). Dark blue crystal suitable for X-ray analysis was obtained from a saturated isopropyl ether solution at 20°C more than 5 days.

**Synthesis of Compound 6.** To a mixture of compound 5 (424 mg, 0.05 mmol) and Fe$_2$(CO)$_9$ (18.2 mg, 0.05 mmol) was added 20 mL THF at room temperature under stirring. The color of the mixture changed to red immediately. After stirring overnight, volatiles were removed under vacuum and the residue was washed with Et$_2$O (10 mL) to afford compound 4 (47.3 mg, 80% isolated yields).
A4. NMR Spectra

Figure S1. $^1$H NMR spectrum of 2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S2. $^{13}$C($^1$H) NMR spectrum of 2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S3. $^{119}$Sn[$^1$H] NMR spectrum of 2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S4. $^{29}$Si[$^1$H] NMR spectrum of 2 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S5. $^1$H NMR spectrum of 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S6. $^{13}$C($^1$H) NMR spectrum of 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S7. $^{119}$Sn[$^{1}$H] NMR spectrum of 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S8. $^{29}$Si[$^{1}$H] NMR spectrum of 3 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S9. $^1$H NMR spectrum of 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S10. $^{13}$C[$^1$H] NMR spectrum of 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S11. $^{119}$Sn[$^1$H] NMR spectrum of 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S12(a). $^{29}$Si[$^1$H] NMR spectrum of 4 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S12(b). $^{29}$Si[$^1$H] NMR spectrum of 4 in THF-$d_8$ under 1 bar N$_2$ at 298 K.

Figure S13. $^1$H NMR spectrum of 5 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S10. $^{13}$C$[^1]$H) NMR spectrum of 5 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.

Figure S15. $^{119}$Sn$[^1]$H) NMR spectrum of 5 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
Figure S16. $^{29}$Si($^1$H) NMR spectrum of 5 in C$_6$D$_6$ under 1 bar N$_2$ at 298 K.
A5. IR Spectra

Figure S17. IR spectrum of 2

Figure S18. IR spectrum of 3
Figure S19. IR spectrum of 4

Figure S20. IR spectrum of 5
A6. UV/Vis Spectra

![UV/Vis Spectrum of Compound 4](image)

**Figure S21.** UV/Vis spectrum of compound 4 (RT, toluene, 1.4 x 10^{-4} M).

![UV/Vis Spectrum of Compound 5](image)

**Figure S22.** UV/Vis spectrum of compound 5 (RT, toluene, 1.65 x 10^{-4} M).

A7. X-ray Crystallographic Data
**Table S1. Crystallographic data and structure refinement for compound 2**

| Property                                    | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Empirical formula                           | C52 H66 Cl2 N4 O Si2 Sn                   |
| Formula weight                              | 1008.85                                    |
| Temperature                                 | 150.00(10) K                              |
| Wavelength                                  | 1.54184 Å                                  |
| Crystal system                              | Orthorhombic                               |
| Space group                                 | Pca2₁                                      |
| Unit cell dimensions                        | a = 18.6531(3) Å                           |
|                                            | b = 15.7277(2) Å                           |
|                                            | c = 17.5139(2) Å                           |
| Volume                                      | 5138.06(12) Å                             |
| Z                                           | 4                                          |
| Density (calculated)                        | 1.304 Mg/m³                                |
| Absorption coefficient                      | 5.662 mm⁻¹                                 |
| F(000)                                      | 2104                                       |
| Crystal size                                | 0.02 x 0.02 x 0.01 mm³                     |
| Theta range for data collection             | 2.810 to 72.607°.                          |
| Index ranges                                | -22<=h<=23, -19<=k<=17, -20<=l<=21          |
| Reflections collected                       | 21196                                      |
| Independent reflections                     | 8171 [R(int) = 0.0301]                     |
| Completeness to theta = 67.684°             | 100.0 %                                    |
| Absorption correction                       | Semi-empirical from equivalents           |
| Max. and min. transmission                  | 1.00000 and 0.53572                        |
| Refinement method                           | Full-matrix least-squares on F²            |
| Data / restraints / parameters              | 8171 / 1 / 574                             |
| Goodness-of-fit on F²                        | 1.063                                      |
| Final R indices [I>2sigma(I)]               | R1 = 0.0466, wR2 = 0.1180                  |
| R indices (all data)                        | R1 = 0.0498, wR2 = 0.1222                  |
| Absolute structure parameter                | -0.026(7)                                  |
| Extinction coefficient                      | n/a                                        |
| Largest diff. peak and hole                 | 1.059 and -1.553 eÅ⁻³                      |
Figure S23. Molecular structure of compound 2. Thermal ellipsoids are drawn at the 50% probability level. H atoms and solvent (toluene) molecules are omitted for clarity.

Table S2. Selected interatomic distances and angles of compound 2.

| Interatomic distances(Å) | Angles(°) |
|--------------------------|-----------|
| Si(1)−Sn(1)              | 2.6747(15) 99.62(5) |
| Si(2)−Sn(1)              | 2.6216(17) 91.85(5) |
| Sn(1)−Cl(1)              | 2.5486(17) 102.84(5) |
| Si(2)−Cl(2)              | 2.522(2) 73.39(5) |
| Si(1)−N(2)               | 1.839(5) 85.53(17) |
| Si(1)−N(1)               | 1.827(5) 134.01(19) |
| Si(2)−N(3)               | 1.886(5) 138.3(2) |
| Si(2)−N(4)               | 1.844(6) 71.6(2) |
| Si(1)−C(1)               | 1.884(6) 112.99(17) |
| Si(2)−C(15)              | 1.892(6) 110.64(17) |
| Si(1)−N(2)               | 1.839(5) 71.6(2) |
| Si(1)−N(1)               | 1.827(5) 134.01(19) |
| Si(2)−N(3)               | 1.886(5) 138.3(2) |
| Si(2)−N(4)               | 1.844(6) 71.6(2) |
| Si(1)−C(1)               | 1.884(6) 112.99(17) |
| Si(2)−C(15)              | 1.892(6) 110.64(17) |
| Si(1)−N(2)               | 1.839(5) 71.6(2) |
| Si(1)−N(1)               | 1.827(5) 134.01(19) |
| Si(2)−N(3)               | 1.886(5) 138.3(2) |
| Si(2)−N(4)               | 1.844(6) 71.6(2) |
| Si(1)−C(1)               | 1.884(6) 112.99(17) |
| Si(2)−C(15)              | 1.892(6) 110.64(17) |
**Table S3. Crystallographic data and structure refinement for compound 3**

- **Empirical formula:** C49 H68 Br2 N4 O2 Si2 Sn
- **Formula weight:** 1079.76
- **Temperature:** 150(2) K
- **Wavelength:** 1.54184 Å
- **Crystal system:** Monoclinic
- **Space group:** P2₁/n
- **Unit cell dimensions:**
  - a = 13.42660(10) Å, a = 90°.
  - b = 20.6091(2) Å, b = 97.1290(10)°.
  - c = 18.5970(2) Å, g = 90°.
- **Volume:** 5106.20(8) Å³
- **Z:** 4
- **Density (calculated):** 1.405 Mg/m³
- **Absorption coefficient:** 6.572 mm⁻¹
- **F(000):** 2216
- **Crystal size:** 0.050 x 0.030 x 0.030 mm³
- **Theta range for data collection:** 3.215 to 67.488°.
- **Index ranges:** -12<=h<=16, -24<=k<=23, -22<=l<=22
- **Reflections collected:** 21311
- **Independent reflections:** 9166 [R(int) = 0.0206]
- **Completeness to theta = 67.488°:** 99.6 %
- **Absorption correction:** Semi-empirical from equivalents
- **Max. and min. transmission:** 1.00000 and 0.37620
- **Refinement method:** Full-matrix least-squares on F²
- **Data / restraints / parameters:** 9166 / 0 / 557
- **Goodness-of-fit on F²:** 1.027
- **Final R indices [I>2sigma(I)]:** R1 = 0.0333, wR2 = 0.0846
- **R indices (all data):** R1 = 0.0371, wR2 = 0.0876
- **Extinction coefficient:** n/a
- **Largest diff. peak and hole:** 1.071 and -0.662 e.Å⁻³
Figure S24. Molecular structure of compound 3. Thermal ellipsoids are drawn at the 50% probability level. H atoms and solvent (Et₂O) molecules are omitted for clarity.

Table S4. Selected interatomic distances and angles of compound 3.

| Interatomic distances(Å) | Angles(°) |
|-------------------------|-----------|
| Si(1)−Sn(1) 2.7087(7) | Si(1)−Sn(1)−Si(2) 100.81(2) |
| Si(2)−Sn(1) 2.6707(7) | Br(1)−Sn(1)−Br(2) 165.794(13) |
| Sn(1)−Br(1) 2.8651(4) | Si(1)−Sn(1)−Br(1) 97.834(18) |
| Sn(1)−Br(2) 2.9434(4) | Si(1)−Sn(1)−Br(2) 80.894(17) |
| Si(1)−N(2) 1.829(2) | Si(2)−Sn(1)−Br(1) 85.381(17) |
| Si(1)−N(1) 1.847(2) | Si(2)−Sn(1)−Br(2) 80.995(17) |
| Si(1)−C(1) 1.878(3) | C(1)−Si(1)−Sn(1) 128.22(9) |
| Si(2)−N(3) 1.841(2) | C(7)−Si(2)−Sn(1) 127.20(9) |
| Si(2)−N(4) 1.825(2) | N(2)−Si(1)−N(1) 71.39(11) |
| Si(2)−C(7) 1.881(3) | N(1)−Si(1)−Sn(1) 109.18(8) |
|                       | N(2)−Si(1)−Sn(1) 119.63(8) |
|                       | N(4)−Si(2)−N(3) 71.42(10) |
|                       | N(3)−Si(2)−Sn(1) 107.60(8) |
|                       | N(4)−Si(2)−Sn(1) 122.30(8) |
Table S5. Crystallographic data and structure refinement for compound 4.5CeHs

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Empirical formula             | C53 H58 Fe2 N4 O9 Si2 Sn                  |
| Formula weight                | 1181.60                                    |
| Temperature                   | 150.00(10) K                               |
| Wavelength                    | 1.54184 Å                                  |
| Crystal system                | Triclinic                                  |
| Space group                   | P-1                                        |
| Unit cell dimensions          | a = 13.3362(3) Å                           |
|                              | b = 13.4474(3) Å                           |
|                              | c = 19.2279(5) Å                           |
|                              | a= 100.683(2)°.                            |
|                              | b= 107.806(2)°.                            |
|                              | g = 96.738(2)°.                            |
| Volume                        | 3169.90(14) Å³                             |
| Z                             | 2                                          |
| Density (calculated)          | 1.238 Mg/m³                                |
| Absorption coefficient        | 7.494 mm⁻¹                                 |
| F(000)                        | 1212                                       |
| Crystal size                  | 0.02 x 0.02 x 0.01 mm³                     |
| Theta range for data collection| 3.404 to 72.659°.                         |
| Index ranges                  | -16<=h<=16, -16<=k<=13, -22<=l<=23         |
| Reflections collected         | 23962                                      |
| Independent reflections       | 12252 [R(int) = 0.0529]                    |
| Completeness to theta = 67.684°| 99.8 %                                    |
| Absorption correction         | Semi-empirical from equivalents            |
| Max. and min. transmission    | 1.00000 and 0.51619                        |
| Refinement method             | Full-matrix least-squares on F²            |
| Data / restraints / parameters| 12252 / 0 / 654                            |
| Goodness-of-fit on F²         | 1.019                                      |
| Final R indices [I>2sigma(I)] | R1 = 0.0613, wR2 = 0.1642                  |
| R indices (all data)          | R1 = 0.0638, wR2 = 0.1666                  |
| Extinction coefficient        | n/a                                        |
| Largest diff. peak and hole   | 2.056 and -2.065 eÅ⁻³                      |
Figure S25. Molecular structure of compound 4. C\textsubscript{6}H\textsubscript{6}. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The strongly disordered C\textsubscript{6}H\textsubscript{6} molecules are treated using Solvent Masking in Olex2.

Table S6. Selected interatomic distances and angles of compound 4.

| Interatomic distances(Å) | Angles(°) |
|--------------------------|-----------|
| Si(1)−Sn(1)              | 2.6956(12) |
| Si(2)−Sn(1)              | 2.6797(11) |
| Sn(1)−Fe(1)              | 2.6488(9)  |
| Sn(1)−Fe(2)              | 2.6031(7)  |
| Si(1)−C(1)               | 1.891(4)   |
| Si(2)−C(15)              | 1.867(5)   |
| Si(1)−N(1)               | 1.833(4)   |
| Si(1)−N(2)               | 1.833(4)   |
| Si(2)−N(3)               | 1.844(4)   |
| Si(2)−N(4)               | 1.816(4)   |
| Fe(2)−Sn(1)−Fe(1)        | 120.56(3)  |
| Fe(2)−Sn(1)−Si(2)        | 110.25(3)  |
| Fe(2)−Sn(1)−Si(1)        | 107.47(3)  |
| Fe(2)−Sn(1)−Si(1)        | 106.61(3)  |
| N(1)−Si(1)−N(2)          | 71.63(17)  |
| N(1)−Si(1)−N(2)          | 71.70(17)  |
| N(1)−Si(1)−Sn(1)         | 101.09(4)  |
| N(2)−Si(1)−Sn(1)         | 118.69(12) |
| N(1)−Si(1)−Sn(1)         | 129.84(13) |
| N(1)−Si(1)−Sn(1)         | 124.36(13) |
| N(1)−Si(1)−Sn(1)         | 118.15(12) |
| C(1)−Si(1)−Sn(1)         | 122.33(14) |
| C(1)−Si(1)−Sn(1)         | 116.93(16) |

Table S7. Crystallographic data and structure refinement for compound 5

Empirical formula

C\textsubscript{45}H\textsubscript{58}N\textsubscript{4}O\textsubscript{2}SiSn
| **Formula weight**       | 845.82                                      |
|-------------------------|---------------------------------------------|
| **Temperature**         | 150(2) K                                    |
| **Wavelength**          | 1.54184 Å                                   |
| **Crystal system**       | Monoclinic                                  |
| **Space group**          | P2₁/c                                       |
| **Unit cell dimensions**|                                            |
| a                       | 19.1331(12) Å                              |
| b                       | 27.5473(13) Å                              |
| c                       | 18.1070(12) Å                              |
| a= 90°                  |                                            |
| b= 110.956(7)°          |                                            |
| g = 90°                 |                                            |
| **Volume**              | 8912.3(10) Å³                              |
| **Z**                   | 8                                            |
| **Density (calculated)**| 1.261 Mg/m³                                 |
| **Absorption coefficient**| 5.352 mm⁻¹                                 |
| F(000)                  | 3536                                         |
| **Crystal size**        | 0.110 x 0.050 x 0.040 mm³                   |
| **Theta range for data collection** | 4.140 to 67.500°.                           |
| **Index ranges**        |                                            |
| h                       | -16<=h<=22                                  |
| k                       | -31<=k<=32                                  |
| l                       | -21<=l<=21                                  |
| **Reflections collected**| 36635                                       |
| **Independent reflections** | 15972 [R(int) = 0.1643]                    |
| **Completeness to theta** | 99.4 %                                      |
| **Absorption correction** | Semi-empirical from equivalents             |
| **Max. and min. transmission** | 1.00000 and 0.38202                        |
| **Refinement method**   | Full-matrix least-squares on F²             |
| **Data / restraints / parameters** | 15972 / 153 / 1032                      |
| **Goodness-of-fit on F²**| 0.898                                       |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0863, wR2 = 0.1645                |
| **R indices (all data)** | R1 = 0.2096, wR2 = 0.2208                  |
| **Extinction coefficient** | n/a                                         |
| **Largest diff. peak and hole** | 0.888 and -0.800 e.Å⁻³                    |
Figure S26. Molecular structure of compound 5. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (Two independent molecules a and b, one of the tert-butyl groups of molecule a is disordered over two orientations with an approximate occupancy ratio of 0.75:0.25; two of the tert-butyl groups of molecule b are disordered over two orientations with an approximate occupancy ratio of 0.75:0.25 and 0.72:0.28, respectively.)

Table S8. Selected interatomic distances and angles of compound 5.

| Interatomic distances(Å) | Angles(°) |
|--------------------------|-----------|
| molecule a               |           |
| Sn(1)-Si(1)              | 2.520(3)  | Si(1)-Sn(1)-Si(2) | 99.34(10) |
| Sn(1)-Si(2)              | 2.506(3)  | C(3)-Si(1)-Sn(1)  | 134.7(4)  |
| Si(2)-N(4)               | 1.877(9)  | C(10)-Si(2)-Sn(1) | 133.3(4)  |
| Si(2)-N(3)               | 1.904(9)  | N(1)-Si(1)-N(2)   | 70.3(4)   |
| Si(1)-N(1)               | 1.849(9)  | N(4)-Si(2)-N(3)   | 68.7(4)   |
| Si(1)-N(2)               | 1.855(8)  | N(3)-Si(2)-Sn(1)  | 122.4(3)  |
| Si(2)-C(10)              | 1.879(10) | N(4)-Si(2)-Sn(1)  | 110.7(3)  |
| Si(1)-C(3)               | 1.901(12) | N(1)-Si(1)-Sn(1)  | 120.7(3)  |
|                         |           | N(2)-Si(1)-Sn(1)  | 110.6(3)  |

molecule b:

| Interatomic distances(Å) | Angles(°) |
|--------------------------|-----------|
| Sn(2)-Si(3)              | 2.540(3)  | Si(3)-Sn(2)-Si(4) | 100.10(9) |
| Sn(2)-Si(4)              | 2.535(3)  | C(55)-Si(4)-Sn(2) | 131.5(3)  |
| Si(4)-N(7)               | 1.840(8)  | C(47)-Si(3)-Sn(2) | 106.6(5)  |
| Si(4)-N(8)               | 1.884(8)  | N(7)-Si(4)-N(8)   | 70.2(3)   |
| Si(3)-N(5)               | 1.865(8)  | N(5)-Si(3)-N(6)   | 70.1(4)   |
| Si(3)-N(6)               | 1.870(8)  | N(7)-Si(4)-Sn(2)  | 111.0(3)  |
| Si(4)-C(55)              | 1.892(9)  | N(8)-Si(4)-Sn(2)  | 123.9(3)  |
| Si(3)-C(47)              | 1.851(11) | N(5)-Si(3)-Sn(2)  | 108.1(3)  |
|                         |           | N(6)-Si(3)-Sn(2)  | 121.4(3)  |
B. DFT Calculations

Computational details. All the DFT calculations were performed with Gaussian 16 (Revision A.03) program. All structures were optimized at the PEB0-D3BJ/Def2-SVP level of theory in the gas phase due to the smallest relative mean deviation (RD) of structural parameters in comparison with the experimental structure. No imaginary frequency was obtained at the same level, confirming a local minima. All presented principal interacting orbital (PIO) analyses were performed by NBO 7.0 program at the same level based on the optimized structure. Natural adaptive orbital (NAdO) analyses were carried out by the Multiwfn program. All orbitals were plotted with the help of Multiwfn and VMD programs.

Gauge-Independent Atomic Orbital (GIAO) calculation. The B97-2/Def2-TZVP (for all toms except Sn atom)−Sapporo-DKH3-DZP-2012-diffuse (for Sn atom) method is used to calculate the $^{119}$Sn chemical shifts of compound 5, where the solvent effect (solvent = benzene) is taken into accounts by the PCM model. The calculated $^{119}$Sn absolute shielding constants are converted to $^{119}$Sn NMR chemical shift, with SnMe$_4$ calculated at the same level as reference. 5: $^{119}$Sn NMR: $\delta_{\text{cal.}}$ = -1325.49 ppm, $\delta_{\text{ex.}}$ = -1147.24 ppm.

Table S9. Key distances (Å) of experimental and DFT-optimized structures of 4.

| Functional | Exp. | B3PW91 | PBE0 | TPSS |
|------------|------|--------|------|------|
| Sn-Si1     | 2.696| 2.647  | 2.679| 2.681|
| Sn-Si2     | 2.68 | 2.635  | 2.665| 2.584|
| Sn-Fe1     | 2.603| 2.550  | 2.559| 2.558|
| Sn-Fe2     | 2.649| 2.575  | 2.586| 2.691|
| $\angle$Si1-Sn-Si2 | 101.1| 101.0 | 100.5| 100.5|
| $\angle$Si1-Sn-Fe1 | 107.5| 107.5 | 107.8| 107.7|
| $\angle$Fe1-Sn-Fe2 | 120.6| 124.6 | 124.3| 125.4|
| $\angle$Fe2-Sn-Si2 | 109.0| 108.4 | 108.8| 108.5|
| RD(%)$^b$   | 0    | 1.5    | 1.2  | 1.6  |

$^a$ The basis set is Def2-SVP–ma-TZVP. ma-TZVP is the abbreviation of def2-TZVP with minimal augmentation, proposed by Truhlar and co-workers.

$^b$ RD = $\frac{\sum_{|\text{BL(Exp.)-BL(DFT)}|\times100}}{\text{BL(Exp.)}}$ BL means bond length.

Table S10. The relative electronic energy of 4 (Si$_2$SnFe$_2$) in the two states. Here S$_0$ means the lowest singlet state, T$_1$ means the lowest triplet state.

| State | 4 (Si$_2$SnFe$_2$) |
|-------|--------------------|
| S$_0$ | 0                  |
| T$_1$ | 25.6               |
Figure S27. Frontier molecular orbital of compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The isosurfaces 0.030 au are plotted.

Figure S28. Four key bonding NAdOs of Sn-Si and Sn-Fe in 4. Hydrogen atoms in 3D structures are omitted for clarity. The strength of the interaction is quantified by the eigenvalue labeled by blue. The eigenvalue sum of two Sn-Si and two Sn-Fe bonds is 3.764. The isosurface 0.050 au is plotted.

Table S11. Key distances (Å) of experimental and DFT-optimized structures of 5 (Si₂Sn). *

| Functional | Exp. | TPSS |
|------------|------|------|
| ∠Sn-Si1    | 2.506| 2.531|
| ∠Sn-Si2    | 2.520| 2.531|
| ∠Si1-Sn-Si2| 99.3 | 97.0 |
| RD(%)*      | 0    | 1.3  |

* The basis set is Def2-SVP~ma-TZVP. ma-TZVP is the abbreviation of def2-TZVP with minimal.

RD = \[ \frac{\sum_{i=1}^{n} |BL(DFT) - BL(Exp.)|}{n} \times 100\%

BL means bond length.

Table S12. The relative electronic energy of 5 (Si₂Sn) in the two states. Here S₀ means the lowest singlet state, T₁ means the lowest triplet state.

| State | 5 |
|-------|---|
| S₀    | 0 |
| T₁    | 19.1 |
Figure S29. Frontier molecular orbital of compound 5. Hydrogen atoms in 3D structures are omitted for clarity. The isosurfaces 0.030 au are plotted.

Figure S30. Three main bonding NAdOs of Sn-Si in compound 5. Hydrogen atoms in 3D structures are omitted for clarity. The strength of the interaction is quantified by the eigenvalue labeled by blue. The eigenvalue sum of two Sn-Si is 2.570. The isosurface 0.050 au is plotted.

Cartesian Coordinates

Si$_2$SnFe$_2$Se$_6$

PBE0-D3BJ/Def2-SVP--ma-TZVP

E = -6265.493436 a.u.

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Sn   | 0.07358100 | -0.50781500| 1.12851700 |
| Fe   | 0.05436900 | -3.06235500| 0.98452600 |
| Fe   | 0.57912400 | 0.82513400 | 3.28551500 |
| Si   | -2.18826000| 0.41226800 | 0.05976500 |
| Si   | 1.85685800 | 0.39986800 | -0.65228900|
| O    | -0.38324200| 2.36924900 | -0.54879400|
| O    | 2.95949200 | -2.86281600| 0.90149500 |
| N    | 2.68337600 | -0.69682800| -1.89953200|
| N    | -3.01333400| 0.26681000 | -1.57500100|
| O    | -1.09220500| -3.01500090| 3.67519900 |
| N    | 3.66024700 | 0.23549000 | -0.23002300|
| N    | -3.74256100| -0.52460800| 0.37210000 |
| O    | -1.59846100| -2.77719000| -1.39626000|
| C    | 3.84920900 | -0.59012000| -1.25120800|
| O    | 0.02894700 | -5.95969500| 0.78279600 |
| C    | 0.66840400 | 2.96619400 | -1.15338700|
| C    | 1.75399200 | 2.12207900 | -1.42992900|
| C    | 5.11828100 | -1.26862700| -1.62843600|
| O    | 2.37086000 | -1.43458700| 3.76366800 |
| C    | -1.50187100| 3.06214700 | -0.21070600|
| C    | 5.50133100 | -2.46197100| -1.00719800|
| H    | 4.85641500 | -2.90183600| -0.24547300|
| O    | 0.70324100 | 3.34968800 | 1.83152300 |
| C    | 0.64743400 | 4.32874700 | -1.46847400|
| O    | 1.92687800 | 2.21797900 | 5.43921200 |
| C    | -3.97270600| -0.64320700| -0.93861400|
| C    | -2.53946300| 2.24751500 | 0.28053000 |
| C    | 2.82327700 | 2.66470900 | -2.15060500|
| H    | 3.68196600 | 2.03359500 | -2.39525000|
| C    | -5.08208500| -1.40503500| -1.55986800|
| C    | 1.74407100 | 4.82055500 | -2.17339600|
| H    | 1.77891500 | 5.87907100 | -2.44244700|
| C    | 7.13182900 | -1.31024000| 2.96403500 |
| H    | 7.76867100 | -0.85715500| -3.72643800|
| C    | 7.51353700 | -2.50326700| -2.34836800|
| H    | 8.45176700 | -2.98692500| -2.62976400|
| O    | -1.88031800| 0.54991100 | 4.82455500 |
\[
\begin{align*}
\text{Si}_2\text{SnFe}_2\text{S}_5 & \\
\text{TPSS-D3BJ/Def2-SVP~ma-TZVP} & \\
\text{E} = -6270.384458 \text{ a.u.} & \\
\text{Sn} & 0.07647700 -0.47992900 1.15743900 \\
\text{Fe} & 0.05871000 -3.03708900 1.08272200 \\
\text{Fe} & 0.57972800 0.95178400 3.24897700 \\
\text{Si} & -2.19899500 0.40417900 0.04894300 \\
\text{Si} & 1.86972600 0.37716800 -0.65672400 \\
\text{O} & -0.39435700 2.33718700 -0.89411000 \\
\text{O} & 2.99848800 -2.65554800 0.98473700 \\
\text{N} & 2.69296300 -0.74565100 -1.90085200 \\
\text{N} & -3.03432000 -0.00581500 -1.58935400 \\
\text{O} & -1.08275700 -2.90567400 3.80964300 \\
\text{N} & 3.68562800 0.20738200 -0.23267200 \\
\text{N} & -3.75971900 -0.53872100 0.38297500 \\
\text{O} & -1.59387900 -2.78889800 -1.34455400 \\
\text{C} & 3.87474100 -0.64954400 -1.25276200 \\
\text{O} & 0.00971900 -5.97309800 0.96181600 \\
\text{C} & 0.67481300 2.93993100 -1.21954100 \\
\text{C} & 1.77206200 2.06878500 -1.46749000 \\
\text{C} & 5.14167400 -1.33669600 -1.62446700 \\
\text{O} & 2.38743200 -1.31365200 3.82859800 \\
\text{C} & -1.51521300 3.05594200 -0.26006700 \\
\text{C} & 5.53075800 -2.52302800 0.97475700 \\
\text{H} & 4.89091500 -2.94106400 -0.19435200 \\
\text{O} & 0.77932000 3.44739200 1.69430900 \\
\text{C} & 0.65049400 4.30501000 -1.55609700 \\
\text{C} & 1.90387400 2.42718900 5.40930400 \\
\text{C} & -4.00023000 -0.68115800 -0.93841600 \\
\text{C} & -2.55311100 2.24495000 0.23772600 \\
\text{C} & 2.85406700 2.62739400 -2.19081600 \\
\text{H} & 3.71857700 1.99279900 -2.41534200 \\
\text{C} & -5.10912300 -1.46422700 -1.54702200 \\
\text{C} & 1.76498400 4.79223200 -2.26111400 \\
\text{H} & 1.79295200 5.84878200 -2.54802200 \\
\text{C} & 7.15166000 -1.42445100 -2.99297900 \\
\text{H} & 7.78254700 -0.99259300 -3.77850600 \\
\text{C} & 7.53841500 -2.60867000 -2.34680900 \\
\text{H} & 8.47332400 -3.10475900 -2.62729400 \\
\text{O} & -1.93427800 0.78117600 4.77822000 \\
\text{C} & -0.49537600 5.23677000 -1.12930900 \\
\text{C} & -2.98186000 0.40929300 -3.01574200 \\
\text{C} & 2.84642000 3.96520700 -2.60154100 \\
\text{H} & 3.69142600 4.37672000 -3.16264200 \\
\text{C} & 6.72707900 -3.15462600 -1.34252200 \\
\text{H} & 7.02405900 -0.47900100 -0.83696400 \\
\text{C} & 2.24571500 -1.66027700 -2.97873600 \\
\text{C} & 5.87374200 1.39170600 0.02497900 \\
\text{H} & 5.54904800 2.10029500 -0.80607500 \\
\text{H} & 6.49570700 0.60941500 -0.48509000 \\
\text{H} & 6.50200400 1.94239100 0.69544100 \\
\text{C} & 5.95582100 -0.79074700 -0.36383900 \\
\text{C} & 5.65150400 0.13336800 -3.13754300 \\
\text{C} & -1.61143300 4.43747200 -0.44723100 \\
\text{C} & 1.82563400 -2.89810800 1.03556000 \\
\text{C} & -4.86038900 -2.76702800 -2.02120200 
\end{align*}
\]
Sn\textsubscript{2}Sn\textsubscript{3}

PBE0-D3BJ/Def2-SVP–ma-TZVP

\[ E = -2833.247451 \text{ a.u.} \]

Sn

-0.00018500  -1.44674900  -1.07278000

Si

1.89528600  0.08702100  -0.39260500

-1.89531400  0.08724500  -0.39208100

O

0.00038400  2.18377300  0.43261900

N

-3.50741000  -0.57831000  -1.08996100

N

3.05548600  -0.49530800  1.00329400

N

3.05719400  -0.57919800  -1.09025100

N

-3.05547100  -0.49527500  1.00357400

C

2.20483700  1.95789000  -0.32609700

C

1.16026900  2.79831300  0.05524100

C

0.00046700  6.40648500  0.08536600

H

0.88253000  6.93920000  0.48684700

H

-0.88124500  6.93929000  0.46932900

H

0.00045000  6.47770400  -1.01239300

C

3.52231100  3.96683000  -0.69618600

H

4.46310700  4.43554900  -0.99490100

C

-3.97465600  -0.93652300  -2.43296500

C

3.40940000  2.57783000  -0.68612800

H

4.26082200  1.95947300  -0.98274700

C

1.22759400  4.19382100  0.05921500

C

-3.92313100  -0.95077400  1.24010000

H

3.93197100  -0.96102400  0.12389800

C

2.43689400  4.76896000  -0.33763700

C

2.54249800  5.85498700  -0.36166000

C

-1.22689400  4.19394300  0.06013500

C

-1.15969900  2.79842400  0.05604800

C

0.00057400  4.95489900  0.55298400
E = \sum_{i} E_{i}

\begin{align*}
\text{Sn} & : -0.02352400, -1.22064400, -1.26237500 \\
\text{Si} & : 1.96372700, 0.19083300, -0.36339000 \\
\text{O} & : 0.01884300, 2.22462800, 0.45989000 \\
\text{N} & : -3.67972200, -0.35845900, -1.08663100 \\
\text{C} & : 2.94724800, -0.65149300, 0.98551800 \\
\text{N} & : 3.56244500, -0.47117300, -1.05878200 \\
\text{C} & : -2.91692000, -0.63905200, 0.95032000 \\
\text{C} & : 2.27877700, 2.03289000, -0.13165400 \\
\text{C} & : 1.20086500, 2.85267700, 0.20976900 \\
\text{H} & : 0.75153000, 6.46771200, 0.32496400 \\
\text{H} & : 0.93422000, 6.97626300, 0.78539500 \\
\text{H} & : -0.82387900, 6.99525000, 0.67315900 \\
\text{H} & : 0.14494500, 6.58219900, -0.76691700 \\
\text{H} & : 3.63396400, 4.04089500, -0.28083900 \\
\text{H} & : 4.59735200, 4.51896700, -0.47229300 \\
\text{C} & : -3.94208000, -0.84793300, -2.45015500 \\
\text{C} & : 3.51405000, 2.65073000, -0.35753600 \\
\text{H} & : 4.38274400, 2.04568400, -0.61791700 \\
\text{C} & : 1.28056200, 4.24643100, 0.29311500 \\
\text{C} & : -3.98026000, -1.01752600, 0.12543200 \\
\text{C} & : 3.86461600, -1.04897500, 0.10967400 \\
\text{C} & : 2.52223500, 4.82703100, 0.03002800 \\
\text{H} & : 2.63316000, 5.91168400, 0.07689700 \\
\text{C} & : -1.17140700, 4.27095500, 0.14186900 \\
\text{C} & : -1.12819000, 2.87537400, 0.09269000 \\
\text{C} & : 0.03141400, 4.99374700, 0.73393800 \\
\text{C} & : -3.44962800, 4.12697500, -0.68374500 \\
\text{H} & : -4.37063900, 4.62789600, -0.99095300 \\
\text{C} & : -4.74874500, -3.12843200, 1.17409600 \\
\text{H} & : -3.71951500, -3.34301400, 1.46350100 \\
\text{C} & : -3.37269800, 2.73589900, -0.70271600 \\
\text{C} & : -4.22714700, 2.13143700, -1.01821300 \\
\text{C} & : 2.70665300, -0.95600400, 2.39546500 \\
\text{C} & : 4.08853400, -0.68150100, -2.41276300 \\
\text{C} & : -2.19482300, 2.07574300, -0.32696500 \\
\text{C} & : -7.36121900, -2.64891700, 0.33879100 \\
\text{H} & : -8.39084100, -2.43970900, 0.03439900 \\
\text{C} & : 5.59287800, -0.40921400, -2.46622800 \\
\text{H} & : 5.82431200, 0.59172800, -2.07273200 \\
\text{H} & : 5.93753200, -0.45241600, -3.51004800 \\
\text{H} & : 6.16538400, -1.15257300, -1.89480300 \\
\text{C} & : -2.35689900, 4.88667000, -0.26656800 \\
\text{C} & : -2.43840100, 5.97478400, -0.24696600 \\
\text{C} & : -3.57094800, -2.32671100, -2.59700900 \\
\text{C} & : -2.50444700, -2.48837200, -2.37264800 \\
\text{C} & : -3.75814700, -2.67335400, -3.62533300 \\
\text{C} & : -4.16283000, -2.94801300, -1.90524000 \\
\text{C} & : 3.99353900, -0.87617700, 3.21644200 \\
\text{C} & : 4.49665600, 0.08794100, 3.05937900 \\
\text{H} & : 4.69505600, -1.88488000, 2.96547200 \\
\text{H} & : 3.74875100, -0.96721700, 4.28523300 \\
\text{C} & : 4.97662500, -1.99196900, 0.37608800 \\
\text{C} & : 3.36370400, 0.32243700, -3.30960000 \\
\text{H} & : 2.27502600, 0.15359900, -3.28409600 \\
\text{C} & : 3.70026300, 0.21142400, -4.35027200 \\
\text{C} & : 3.56083100, 1.35957000, -2.98886100 \\
\text{C} & : -3.08203700, 0.00517200, -3.38720100 \\
\text{C} & : -3.34635500, 1.07008200, -3.29810700 \\
\text{H} & : -3.23968000, -0.30346900, -4.43201600 \\
\text{H} & : -2.00811400, -0.10147400, -3.16343700
\end{align*}
C 4.74845100 -3.37084300 0.32689400
H 3.75502400 -3.74675100 0.07171800
C -5.01480300 -1.95024300 0.69841100
H 6.42090300 -0.42957000 0.74104500
C 1.72911200 0.11329500 2.88144700
H 2.17964800 1.11517600 2.82216400
H 1.43072700 -0.07939000 3.92167000
H 0.81710300 0.11010300 2.26492800
C -6.36594200 -1.74064700 0.01710800
H -6.62886700 -0.81154100 -0.48811200
C -5.40245500 -0.64508500 -2.86927100
H -6.07133500 -1.36247600 -2.38020500
H -5.49891300 -0.78653300 -3.95666100
H -5.73562500 0.37476700 -2.62394000
C -5.75377500 -4.02875500 1.48616900
H -5.50367700 -4.93315400 2.04841100
C -7.07478700 -3.80871900 1.07231500
H -7.86413000 -4.52056900 1.32191400
C -0.06510000 4.89949800 2.27131300
H -0.10091900 3.84948100 2.59693200
H -0.98019800 5.39730300 2.62789300
H 0.80668900 5.37785600 2.74341200
C -2.86096600 -0.48421600 2.40485100
C 5.70883300 -4.25712600 0.59764200
H 5.60719200 -5.33327900 0.55683900
C 2.06506600 -2.34017000 2.52385200
H 1.76974800 -2.53152100 3.56644700
H 2.76637800 -3.12994000 2.21872900
H 1.16820600 -2.40645600 1.88902600
C 3.78223900 -2.10409000 -2.88783300
H 4.32080700 -2.85019400 -2.28626500
H 4.09160300 -2.22981100 -3.93640000
H 2.70220700 -2.30647400 -2.81741700
C 7.05497500 -3.77221300 0.92150200
H 7.86836000 -4.46903000 1.13605300
C 7.28319700 -2.39699700 0.97177000
H 8.27391600 -2.01444900 1.22682300
C -2.13453800 0.82972300 2.70961800
H -1.15695300 0.87095200 2.20490800
H -1.95564500 0.92817200 3.79109900
H -2.72452500 1.69451300 2.37401400
C -2.05255800 -1.63159200 3.02545500
H -1.05649400 -1.68460600 2.56070700
H -2.54975500 -2.59839700 2.87393700
H -1.92504600 -1.48188100 4.10935400
C -4.25456500 -0.40988900 3.03165300
H -4.85608500 0.36929600 2.54056300
H -4.15886600 -0.15390700 4.09817800
H -4.80006300 -1.35847200 2.95392100
C. TD-DFT Calculations

**Computational details.** Time dependent density functional theory (TD-DFT) were performed to calculate UV-vis spectra, under TD-B3LYP-D3BJ/Def2-SVP~ma-TZVP level including solvent effect in a SMD continuum model (solvent= toluene), due to the good agreement with experimental UV-vis spectra.

**Results of UV-vis calculation:** According to the TD-DFT calculation, the observed peak ($\lambda_{\text{ex.}}=674$ nm, $\lambda_{\text{TD-DFT}}=672$ nm, Figure S31) is mainly assigned to the $S_1$ state (Table S13), which corresponds to the $\pi-\pi^*$ excitation from HOMO to LUMO orbital (Table S13).

![Figure S31. TD-DFT absorption spectra for 5.](image)

**Table S13.** Main contributions of individual transitions to the peak ($\lambda_{\text{TD-DFT}} = 672$ nm).

| Transition | Contribution |
|------------|--------------|
| $S_1$      | 54.2%        |
| $S_7$      | 15.2%        |
| $S_2$      | 13.5%        |
| $S_3$      | 10.6%        |

**Table S14.** Oscillator strengths and transitions in different states of the compound 5 by TD-DFT calculations.

| state | Main transition     | Wavelength (nm) | Oscillator strength |
|-------|---------------------|-----------------|---------------------|
| $S_1$ | HOMO→LUMO (96.8%)   | 726.5           | 0.154               |
| $S_7$ | HOMO→LUMO+6 (89.3%) | 567.8           | 0.055               |
|       | HOMO→LUMO (9.2%)    |                 |                     |
| $S_2$ | HOMO→LUMO+1 (82.3%) | 685.8           | 0.036               |
|       | HOMO→LUMO+2 (14.1%) |                 |                     |
| $S_3$ | HOMO→LUMO+2 (73.1%) | 669.2           | 0.028               |
|       | HOMO→LUMO+1 (17.2%) |                 |                     |
|       | HOMO→LUMO+6 (7.8%)  |                 |                     |
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