

Supporting Information

Thiahelicenes with Long Persistent Phosphorescence

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Table of Contents

| | |
|---|----|
| 1. General | 3 |
| 2. Results And Discussions..... | 4 |
| 2.1. Synthesis Procedures | 4 |
| 2.1.1. Synthesis of 2 | 4 |
| 2.1.2. Synthesis of TB[4]H | 5 |
| 2.1.3. Synthesis of 5a | 6 |
| 2.1.4. Synthesis of 5b | 8 |
| 2.1.5. Synthesis of 5c | 9 |
| 2.2.6. Synthesis of 3c | 11 |
| 2.1.7. Synthesis of 7 | 12 |
| 2.1.8. Synthesis of 5d | 14 |
| 2.1.9. Synthesis of TB[5]H | 15 |
| 2.1.10. Synthesis of TB[6]H | 16 |
| 2.1.11. Synthesis of TB[7]H | 18 |
| 2.1.12. Synthesis of TB[8]H | 19 |
| 2.2. Single Crystal X-ray Structures | 21 |
| 2.2.1. X-ray Crystallographic Data of TB[4]H | 21 |
| 2.2.2. X-ray Crystallographic Data of TB[5]H | 22 |
| 2.2.3. X-ray Crystallographic Data of TB[6]H | 23 |
| 2.2.4. X-ray Crystallographic Data of TB[7]H | 24 |
| 2.3. Photophysical Properties..... | 25 |
| 2.3.1. UV-vis spectra of TB[n]H (n=3-8)..... | 25 |
| 2.3.2. Afterglow Photographs of Cryogenic Solid | 27 |
| 2.4. Computational Calculations..... | 28 |
| 2.4.1. TD-DFT Calculations of UV-Vis spectra | 28 |
| 2.4.2. Molecular Orbitals of TB[n]H (n = 3-8)..... | 29 |
| 2.4.3. Spin Density of TB[n]H (n = 3-8)..... | 29 |
| 2.4.4. Standard Orientation of Optimized Structures | 30 |
| 2.4.5. Illustration of the Transition Orbital Composition..... | 37 |
| 2.5. Chiral Resolutions and Chiroptical Spectra | 38 |
| 2.5.1. Chiral Resolution of Racemic TB[7]H | 38 |
| 2.5.2. Racemization Barrier and Simulated CD Spectra | 38 |
| 2.5.3. Comparison of Spectra between Chiral and Achiral Spectra | 39 |
| 3. References | 39 |

1. General

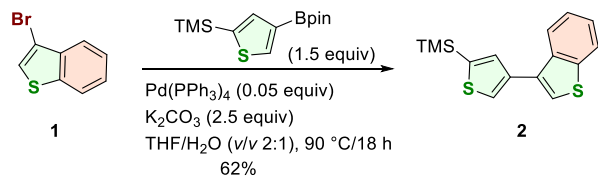
Ether and tetrahydrofuran (THF) used in the vacuum line were freshly distilled from sodium/ benzophenone prior to use. *n*-BuLi (in hexane) was acquired from Energy Chemical, and its concentration was titrated using *N*-pivaloyl-*o*-toluidine before use.¹ Other reagents, including CuCl₂, (iPr)₂NH, Ylide salts, iodine, Pd(PPh₃)₄, PPh₃, and so on, were purchased from Shanghai Haohong Scientific Co., Ltd. (I₂), Tianjin Kemiou Chemical Reagent Co. Ltd., etc. Column chromatography was conducted on silica gel (300–400 mesh), while analytical thin-layer chromatography was performed on glass plates coated with silica gel GF-254 and detected using UV light. Standard techniques for synthesis under an inert atmosphere were employed, using Schlenk glassware equipped with an 8 mm PTFE vacuum stopcock. All starting materials and reagents were commercially available. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE III 300 MHz, Bruker AVANCE III HD 400MHz, and Bruker AVANCE III HD 500MHz instruments, with CDCl₃ as the solvent. NMR chemical shifts were reported in ppm with reference to residual protons and carbons of CDCl₃ (δ 7.26 ppm in ¹H NMR, δ 77.16 ppm in ¹³C NMR). IR spectra were obtained using an FT-IR instrument (VERTEX 70). HRMS analysis was performed on a mass spectrometer (Waters Micromass Q-ToF MicroTM System) in various ionization modes, including ESI, DART positive, and MALDI. Melting point were determined using a Melt-Temp apparatus (TX4-100) and were uncorrected. X-ray crystallographic diffractions were conducted on a D8 Venture Bruker diffractometer using crystals of **TB[4]H**, **TB[5]H**, **TB[6]H**, and **TB[7]H** with the dimensions of 0.11 × 0.10 × 0.10 mm³, 0.15 × 0.12 × 0.07 mm³, 0.12 × 0.09 × 0.04 mm³, and 0.21 × 0.18 × 0.14 mm³, respectively. Intensity data was collected in the ω scan mode (296 K) on a diffractometer with a CCD detector using Mo K_α radiation (λ = 0.71073 Å). The data was corrected for Lorentz and polarization effects, and absorption corrections were performed using the SADABS program.² Crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares.³ Further details are described in deposited CIF files. Single crystals were grown by slow diffusion of methanol into chloroform solutions of **TB[4]H**, **TB[5]H**, **TB[6]H**, and **TB[7]H**. Ultraviolet-visible (UV-vis) absorption spectra were recorded using a PE Lambda 950 equipment. Fluorescence quantum yields (Φ_{FL}) of **TB[n]H** were determined in dichloromethane with quinine sulfate in 0.1 N H₂SO₄ as the control, and all data were recorded on a JY HORIBA FluoroLog-3 equipment. The calculation used the following formula: Φ_{FL} = (n_x / n_s)² • A_s / A_x • D_x / D_s • Φ_s (n: Refractive index of solvent, D: fluorescence emission area, A: absorbance, Φ_s: fluorescence quantum yield of standard substance, quinine sulfate, Φ_s = 0.54) with the slit fixed at 3/3 nm in all measurements.⁴ Photophysical data of steady-state emission, time-resolved emission and phosphorescence decay were collected on Edinburgh FLS980 Serial of Fluorescence Spectrometers. Circular dichroism (CD) was characterized using a Model 420SF CD spectrometer (Aviv Biomedical Inc.), while circular polarized luminescence was measured with a CPL-300 spectrophotometer (JASCO Inc.). DFT calculations were performed at the B3LYP/6-31G(d) and B3LYP/6-31G* level of theory using Gaussian 16 program. Spin-orbital coupling matrix elements were calculated using PySOC program combined with Gaussian 09 program.

2. Results and Discussion

2.1. Synthesis Procedures

Compounds **3a**, **3b**, **3c**, and **TB[3]H** were synthesized according to our previous work.^{5,6} **5c**⁷ and **7**⁸ were synthesized based on reports of literatures. All other compounds involved in this article are shown in following parts.

2.1.1. Synthesis of **2**



To an oven-dried Schlenk flask was added **1** (732.0 mg, 3.44 mmol, 1.0 equiv), 2-(trimethylsilyl)-4-Bpin-thiophene (1.45 g, 5.15 mmol, 1.5 equiv), tetrakis(triphenylphosphine)palladium (198.0 mg, 0.17 mmol, 0.05 equiv), and K₂CO₃ (1.19 g, 8.56 mmol, 2.5 equiv). The mixture was degassed under vacuum for 30 min, and then dry THF (60 mL) and deoxygenated H₂O (30 mL) were added sequentially under Ar flow. The solution was heated at 90 °C for 18 h. After cooled to ambient temperature, the separated water layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was washed with water (3 × 20 mL) and then dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether (60–90 °C) as eluent gave **2** (614.0 mg, 62%) as a colorless oil. IR (KBr): 3057, 2951, 1253, 838, 761 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.00-7.96 (m, 1H), 7.93-7.89 (m, 1H), 7.74 (d, *J* = 1.1 Hz, 1H), 7.48 (d, *J* = 1.1 Hz, 1H), 7.44 (s, 1H), 7.43-7.36 (m, 2H), 0.38 (s, 9H); ¹³C{¹H}NMR (100.6 MHz, CDCl₃) δ 141.3, 140.6, 138.1, 137.8, 134.9, 132.9, 127.5, 124.6, 124.5, 123.1, 123.1, 123.0, 0.1; HRMS (*m/z*) [M]⁺ calcd. for C₁₅H₁₆S₂Si, 288.0457; found, 288.0453.

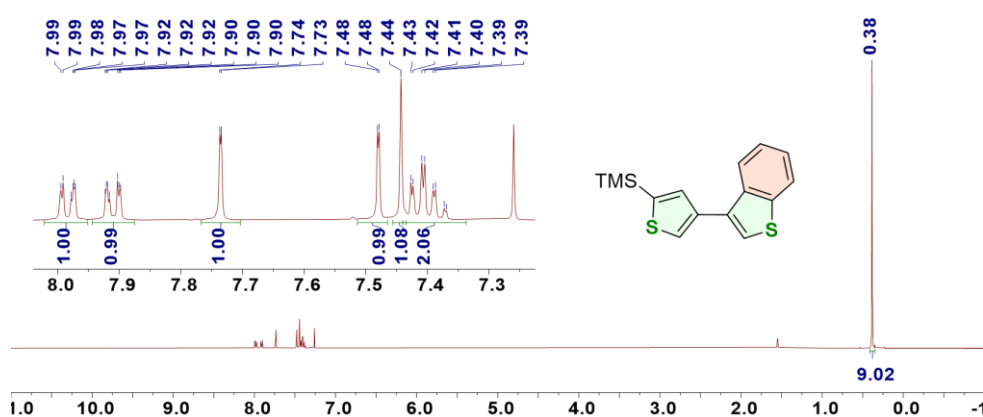


Fig. S1 | ¹H NMR (400 MHz, CDCl₃) spectra of **2**

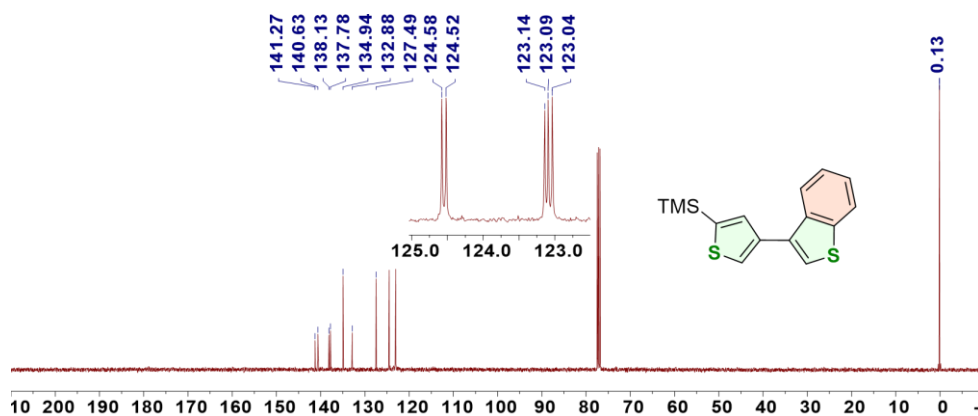


Fig. S2 | ¹³C NMR (100 MHz, CDCl₃) spectra of **2**.

| | | | |
|-----------------------|---------------------------|--------------------|------------|
| Instrument: | JEOL-AccuTOF-GCv4G-GCT MS | | |
| Operation Mode: | FI Positive Ion Mode | Counter Electrode: | 10000V |
| Card Serial Number: | GCT-FI-T22-09-OS-244 | | |
| Sample Serial Number: | HNU-TB4H-P | | |
| Operator: | Li | Date: | 2022/10/19 |

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|--|
| 288.0453 | 288.0451 | 0.76 | 10.0 | C ₁₅ H ₁₂ O ₄ S |
| | 288.0451 | 0.81 | 0.0 | C ₇ H ₂₀ O ₂ N ₂ S ₃ Si |
| | 288.0455 | -0.81 | 15.5 | C ₁₈ H ₇ O ₂ NF |
| | 288.0457 | -1.46 | 9.0 | C ₁₅ H ₁₆ S ₂ Si |
| | 288.0449 | 1.51 | 6.0 | C ₁₃ H ₁₄ O F ₂ S ₂ |

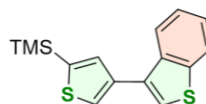
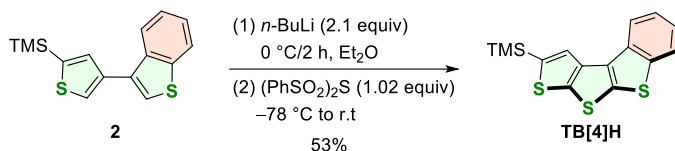


Fig. S3 | HRMS (FI positive ion mode) data of **2**.

2.1.2. Synthesis of TB[4]H



To an oven-dried Schlenk flask was added **2** (532.0 mg, 1.84 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry Et₂O (50 mL) was added under Ar flow. The solution was cooled down to $-78\text{ }^{\circ}\text{C}$ and *n*-BuLi (2.4 M in hexane, 1.60 mL, 3.87 mmol, 2.1 equiv) was added dropwisely. After warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 2 h, the solution was cooled down to $-78\text{ }^{\circ}\text{C}$. (PhSO₂)₂S (591.0 mg, 1.88 mmol, 1.02 equiv) was added into the solution quickly under Ar flow. Then the reaction mixture was warmed up slowly to ambient temperature and stirred overnight. The reaction was quenched with a drop of CH₃OH and then added water (20 mL). The separated water layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was washed with water (3 × 20 mL) and then dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether (60–90 °C) as eluent gave **TB[4]H** (311.0 mg, 53%) as a white solid. mp: 140–141 °C; IR (KBr): 3051, 2951, 1246, 842, 755 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 0.43 (s, 9H); ¹³C{¹H}NMR (100.6 MHz, CDCl₃) δ 145.2, 143.7, 143.3, 141.0, 140.4, 132.5, 132.4, 124.8, 124.4, 124.0, 123.3, 121.4, 0.1; HRMS (*m/z*) [M]⁺ calcd. for C₁₉H₁₄S₃Si, 318.0021; found, 318.0024.

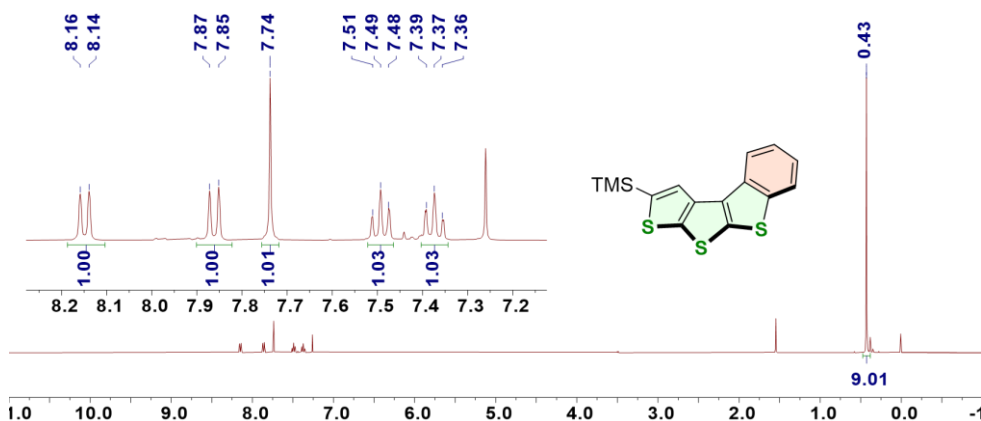


Fig. S4 | ¹H NMR (400 MHz, CDCl₃) spectra of **TB[4]H**.

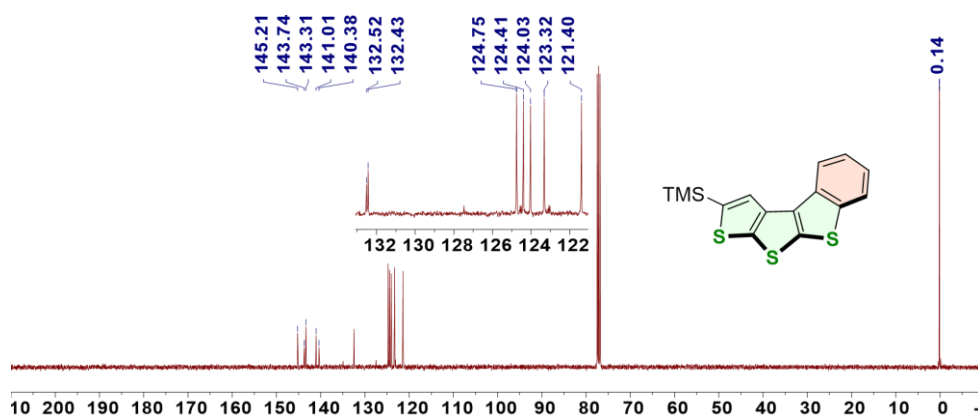


Fig. S5 | ^{13}C NMR (100 MHz, CDCl_3) spectra of **TB[4]H**.

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report



| | | | | |
|-----------------------|---------------------------|--------------------|------------|--|
| Instrument: | JEOL-AccuTOF-GCv4G-GCT MS | | | |
| Operation Mode: | FI Positive Ion Mode | Counter Electrode: | 10000V | |
| Card Serial Number: | GCT-FI-T22-09-OS-243 | | | |
| Sample Serial Number: | HNU-TB4H | | | |
| Operator: | Li | Date: | 2022/10/19 | |

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|--|
| 318.0024 | 318.0024 | -0.02 | 22.0 | $\text{C}_{21}\text{N}_2\text{F}_2$ |
| 318.0024 | 318.0024 | -0.09 | 3.0 | $\text{C}_{10}\text{H}_{13}\text{O}_2\text{F}_3\text{S}_3$ |
| 318.0022 | 318.0022 | 0.63 | 3.0 | $\text{C}_9\text{H}_{13}\text{O}_3\text{F}_3\text{S}_2\text{Si}$ |
| 318.0027 | 318.0027 | -0.79 | 8.5 | $\text{C}_{12}\text{H}_8\text{ONF}_4\text{S}_3\text{Si}$ |
| 318.0021 | 318.0021 | 0.82 | 10.0 | $\text{C}_{15}\text{H}_{14}\text{S}_3\text{Si}$ |

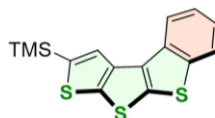
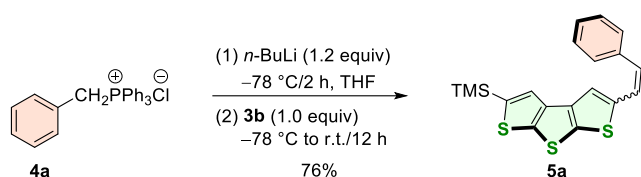


Fig. S6 | HRMS (FI ionization mode) data of **TB[4]H**.

2.1.3. Synthesis of **5a**



To an oven-dried Schlenk flask was added **4a** (160.0 mg, 0.42 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry THF (40 mL) was added under Ar flow. The solution was cooled down to $-78\text{ }^\circ\text{C}$ and *n*-BuLi (2.5 M in hexane, 0.17 mL, 0.42 mmol, 1.2 equiv) was added dropwisely. After stirring at $-78\text{ }^\circ\text{C}$ for 2 h, the THF (15 mL) solution of **3b** (100.0 mg, 0.35 mmol, 1.0 equiv) was added into the Schlenk flask dropwisely. The reaction mixture was warmed up slowly to ambient temperature and stirred overnight. The reaction was quenched with water. The separated water layer was extracted with CH_2Cl_2 ($3 \times 10\text{ mL}$). The combined organic layer was washed with water ($3 \times 10\text{ mL}$) and then dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether ($60\text{--}90\text{ }^\circ\text{C}$)/ CH_2Cl_2 (3:1, v/v) as eluent gave **5a** (70.0 mg, 75%) as a yellow solid. mp: $186\text{--}187\text{ }^\circ\text{C}$; IR (KBr): 3048, 2954, 1620, 1247, 951, 831 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.48 (d, $J = 7.2\text{ Hz}$, 2H), 7.44 (s, 1H), 7.36 (t, $J = 7.5\text{ Hz}$, 2H), 7.31 (s, 1H), 7.26 (d, $J = 16.0\text{ Hz}$, 1H), 6.91 (d, $J = 16.0\text{ Hz}$, 1H), 0.38 (s, 9H) (the multiplet (1H) of phenyl in ortho site was estimated to overlap with the signals in the region of 7.28-7.24 ppm; the signal of one olefin proton was estimated in the same region.); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 145.5, 144.7, 143.8, 140.8, 138.3, 137.8, 136.8, 128.8, 128.2, 127.8, 126.4, 125.1, 122.5, 118.0, 0.1; HRMS (m/z) $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{18}\text{S}_3\text{Si}$, 371.0413; found, 371.0410.

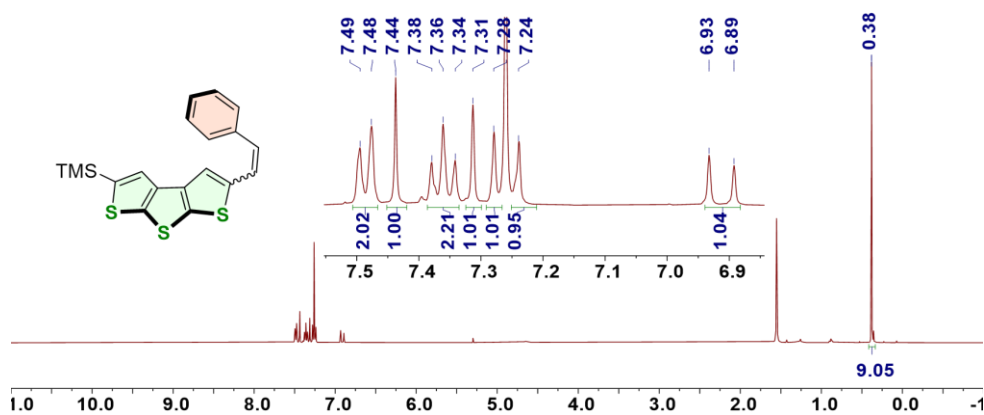


Fig. S7 | ^1H NMR (400 MHz, CDCl_3) spectra of **5a**.

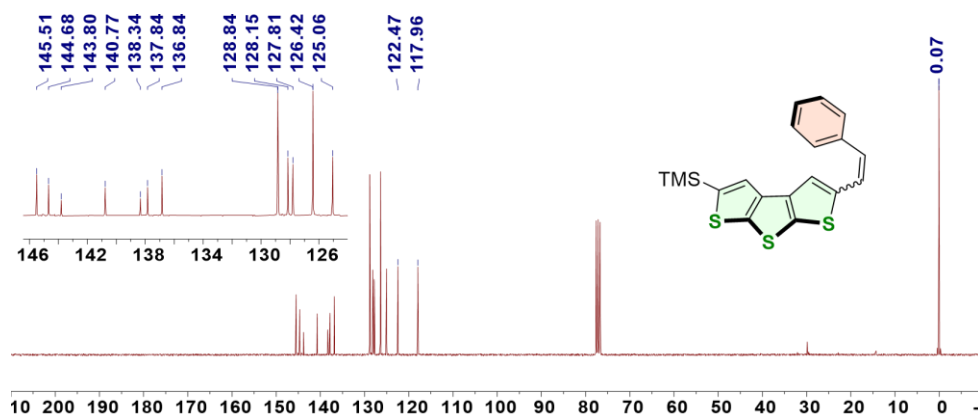


Fig. S8 | ^{13}C NMR (75 MHz, CDCl_3) spectra of **5a**.

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20220095

Sample Serial Number: SZ-2-88

Operator : DONG Date: 2021/12/03

Operation Mode: DART POSITIVE

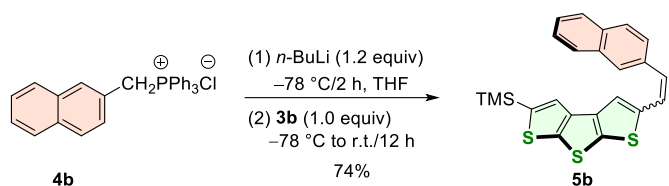
Elemental composition search on mass 371.0410

m/z= 366.0410-376.0410

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|---|
| 371.0410 | 371.0411 | -0.23 | 18.5 | $\text{C}_{19}\text{H}_7\text{O}_5\text{N}_4$ |
| | 371.0411 | -0.28 | 8.0 | $\text{C}_{16}\text{H}_{18}\text{O}_3\text{NClS}_2$ |
| | 371.0409 | 0.34 | 8.0 | $\text{C}_{15}\text{H}_{18}\text{O}_4\text{NClSSi}$ |
| | 371.0408 | 0.45 | 2.5 | $\text{C}_{12}\text{H}_{23}\text{ON}_2\text{S}_5$ |
| | 371.0413 | -0.69 | 11.5 | $\text{C}_{19}\text{H}_{19}\text{S}_3\text{Si}$ |
| | 371.0406 | 1.03 | 12.5 | $\text{C}_{19}\text{H}_{15}\text{O}_4\text{S}_2$ |
| | 371.0406 | 1.07 | 2.5 | $\text{C}_{11}\text{H}_{23}\text{O}_2\text{N}_2\text{S}_4\text{Si}$ |
| | 371.0405 | 1.48 | -1.0 | $\text{C}_8\text{H}_{22}\text{O}_5\text{N}_3\text{ClS}_3$ |
| | 371.0416 | -1.54 | 14.0 | $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_5\text{Cl}$ |
| | 371.0404 | 1.58 | 17.5 | $\text{C}_{22}\text{H}_{12}\text{N}_2\text{ClS}$ |

Fig. S9 | HRMS (DART Positive ion mode) data of **5a**.

2.1.4. Synthesis of 5b



To an oven-dried Schlenk flask was added **4b** (120.0 mg, 0.25 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry THF (40 mL) was added under Ar flow. The solution was cooled down to $-78\text{ }^{\circ}\text{C}$ and *n*-BuLi (2.5 M in hexane, 0.11 mL, 0.25 mmol, 1.2 equiv) was added dropwisely. After stirring at $-78\text{ }^{\circ}\text{C}$ for 2 h, the THF (15 mL) solution of **3b** (100.0 mg, 0.35 mmol, 1.0 equiv) was added into the Schlenk flask dropwisely. The reaction mixture was warmed up slowly to ambient temperature and stirred overnight. The reaction was quenched with water. The separated water layer was extracted with CH_2Cl_2 ($3 \times 10\text{ mL}$). The combined organic layer was washed with water ($3 \times 10\text{ mL}$) and then dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether ($60\text{--}90\text{ }^{\circ}\text{C}$)/ CH_2Cl_2 (5:1, v/v) as eluent gave **5b** (60.0 mg, 70%) as a yellow solid. mp: $> 300\text{ }^{\circ}\text{C}$; IR (KBr): 3048, 2948, 1634, 1249, 952, 836 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.86–7.79 (m, 4H), 7.70 (dd, $J = 8.7, 1.8\text{ Hz}$, 1H), 7.51–7.43 (m, 3H), 7.39 (d, $J = 16.0\text{ Hz}$, 1H), 7.35 (s, 1H), 7.08 (d, $J = 16.0\text{ Hz}$, 1H), 0.39 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 145.7, 144.9, 143.9, 140.9, 138.5, 138.0, 134.5, 133.9, 133.2, 128.6, 128.4, 128.2, 127.9, 126.7, 126.6, 126.2, 125.1, 123.4, 122.9, 118.0, 0.1; HRMS (m/z) [M] $^+$ calcd. for $\text{C}_{23}\text{H}_{20}\text{S}_3\text{Si}$, 420.0491; found, 420.0507.

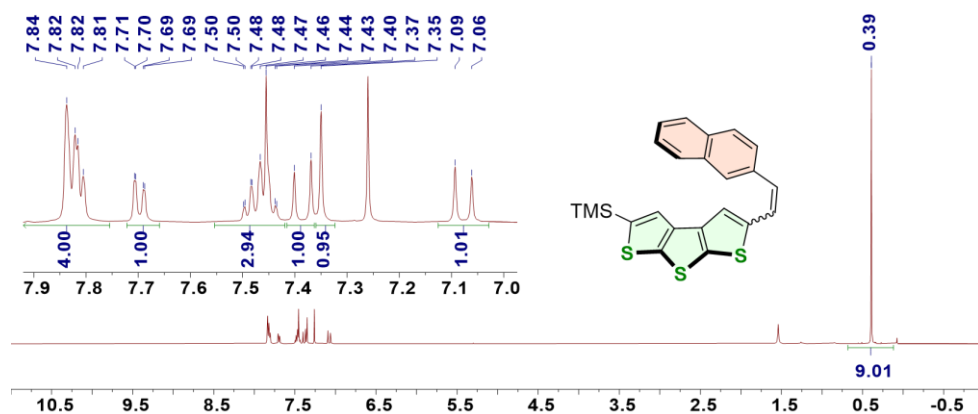


Fig. S10 | ^1H NMR (400 MHz, CDCl_3) spectra of **5b**.

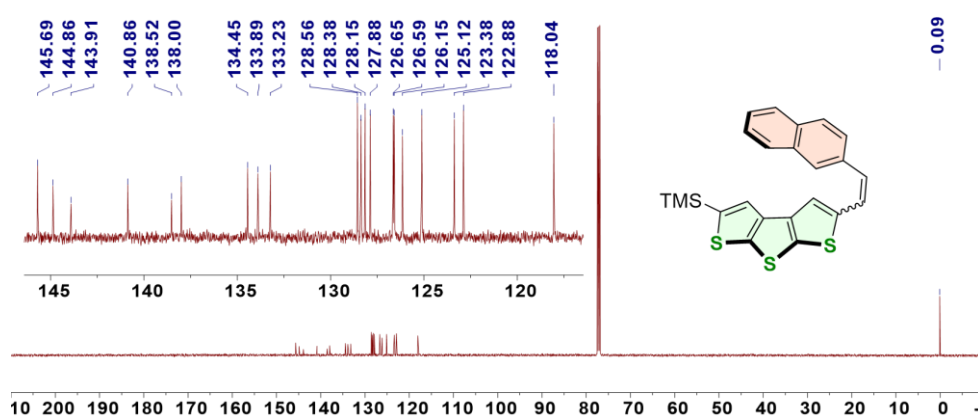


Fig. S11 | ^{13}C NMR (125 MHz, CDCl_3) spectra of **5b**.

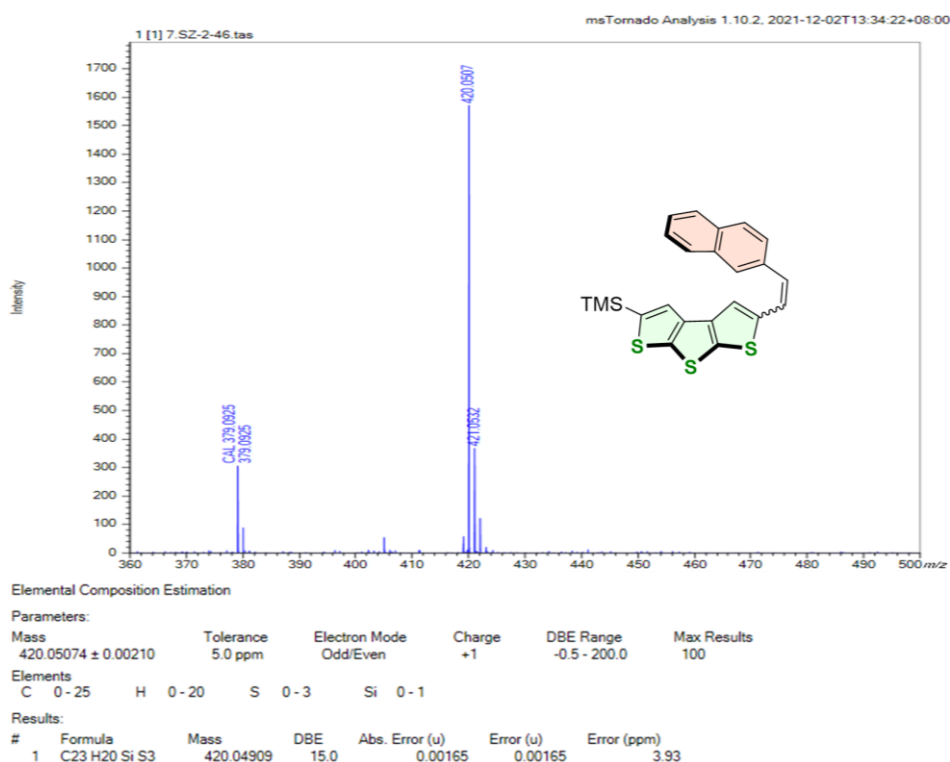
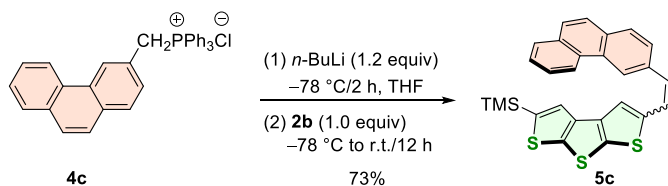


Fig. S12 | HRMS (MALDI-TOF) data of **5b**.

2.1.5. Synthesis of **5c**



To an oven-dried Schlenk flask was added **4c** (40.0 mg, 0.08 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry THF (10 mL) was added under Ar flow. The solution was cooled down to $-78\text{ }^\circ\text{C}$ and *n*-BuLi (2.5 M in hexane, 0.03 mL, 0.08 mmol, 1.2 equiv) was added dropwisely. After stirring at $-78\text{ }^\circ\text{C}$ for 2 h, the THF (5 mL) solution of **3b** (20.0 mg, 0.07 mmol, 1.0 equiv) was added into the Schlenk flask dropwisely. The reaction mixture was warmed up slowly to ambient temperature and stirred overnight. The reaction was quenched with water. The separated water layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layer was washed with water (3×5 mL) and then dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether ($60\text{--}90\text{ }^\circ\text{C}$)/ CH_2Cl_2 (5:1, v/v) as eluent gave **5c** (20.0 mg, 69%) as a yellow solid. mp: $263.7\text{--}265.3\text{ }^\circ\text{C}$; IR (KBr): 3046, 2954, 2385, 1615, 1248, 944, 837 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 8.74 (d, $J = 8.3$ Hz, 1H), 8.69 (d, $J = 1.0$ Hz, 1H), 7.90 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.87 (d, $J = 8.3$, 1H), 7.79 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.72 (s, 2H), 7.69 (dt, $J = 7.5, 1.5$ Hz, 1H), 7.62 (dt, $J = 7.5, 1.5$ Hz, 1H), 7.47 (s, 1H), 7.46 (d, $J = 15.0$ Hz, 1H), 7.37 (s, 1H), 7.18 (d, $J = 15.0$ Hz, 1H), 0.40 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 145.7, 144.9, 143.9, 140.9, 138.6, 138.0, 135.1, 132.5, 131.8, 130.7, 130.4, 129.2, 128.8, 128.6, 127.2, 126.9, 126.8, 126.8, 125.1, 124.0, 123.0, 122.8, 121.6, 118.1, 0.1; HRMS (m/z) [$\text{M}+\text{H}$]⁺ calcd. for $\text{C}_{27}\text{H}_{23}\text{S}_3\text{Si}$, 471.0726; found, 471.0723.

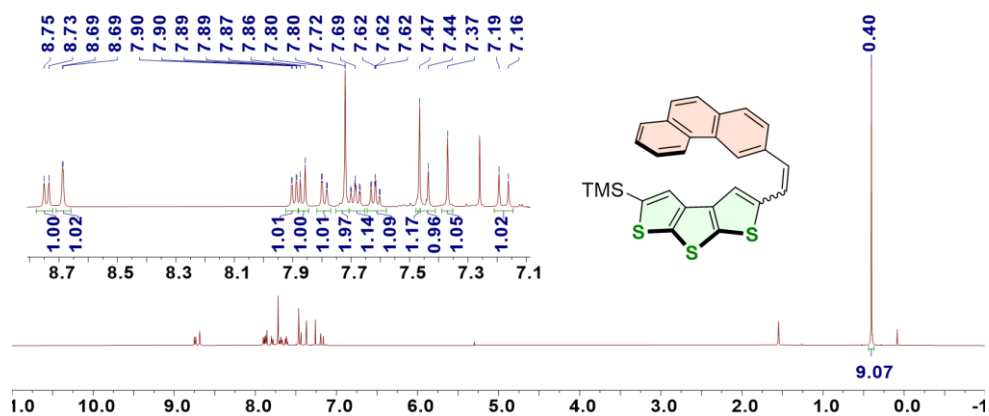


Fig. S13 | ^1H NMR (500 MHz, CDCl_3) spectra of 5c.

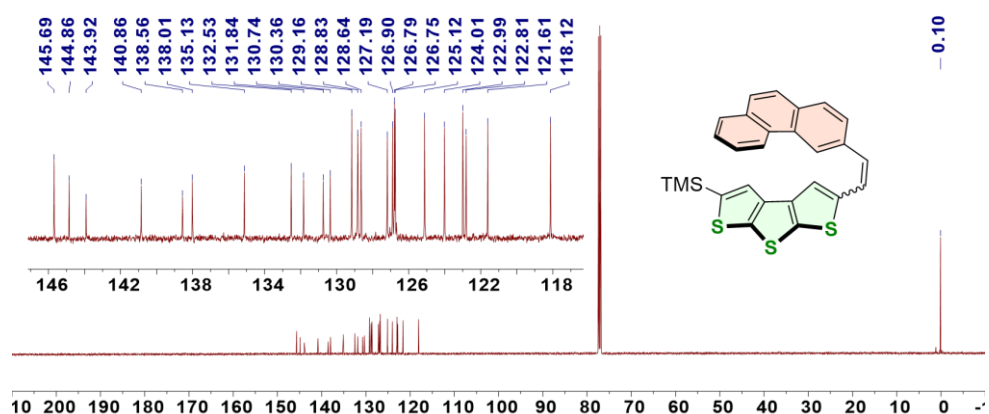


Fig. S14 | ^{13}C NMR (125 MHz, CDCl_3) spectra of 5c.

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Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20220097

Sample Serial Number: SZ-2-75

Operator : DONG Date: 2021/12/03

Operation Mode: DART POSITIVE

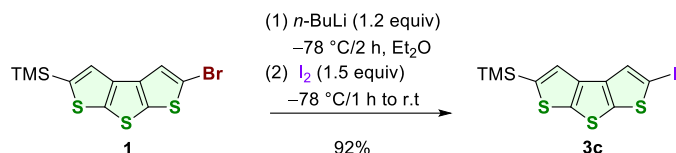
Elemental composition search on mass 471.0723

m/z= 466.0723-476.0723

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|---|
| 471.0723 | 471.0722 | 0.22 | 14.0 | C ₂₃ H ₂₂ O ₄ NClS ₅ Si |
| | 471.0724 | -0.22 | 24.5 | C ₂₇ H ₁₁ O ₅ N ₄ |
| | 471.0724 | -0.24 | 4.0 | C ₁₆ H ₃₀ ON ₃ ClS ₄ Si |
| | 471.0724 | -0.26 | 14.0 | C ₂₄ H ₂₂ O ₃ NClS ₂ |
| | 471.0721 | 0.31 | 8.5 | C ₂₀ H ₂₇ ON ₂ S ₅ |
| | 471.0726 | -0.59 | 17.5 | C ₂₇ H ₂₃ S ₃ Si |
| | 471.0726 | -0.67 | -1.0 | C ₁₃ H ₃₃ O ₅ N ₅ S ₅ Si |
| | 471.0726 | -0.72 | 4.0 | C ₁₇ H ₃₀ N ₃ ClS ₅ |
| | 471.0719 | 0.77 | 18.5 | C ₂₇ H ₁₉ O ₄ S ₂ |
| | 471.0719 | 0.80 | 8.5 | C ₁₉ H ₂₇ O ₂ N ₂ S ₄ Si |

Fig. S15 | HRMS (DART Positive ion mode) data of 5c.

2.2.6. Synthesis of 3c



To an oven-dried Schlenk flask was added **1** (100.0 mg, 0.29 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry Et₂O (40 mL) was added under Ar flow. The solution was cooled down to -78 °C and *n*-BuLi (2.5 M in hexane, 0.13 mL, 0.32 mmol, 1.2 equiv) was added dropwisely. After stirring at -78 °C for 1 h, iodine (87.7 mg, 0.35 mmol, 1.5 equiv) was added into the Schlenk flask, and then the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction was quenched with saturated aqueous sodium thiosulfate. The separated water layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layer was washed with water (3 × 10 mL) and then dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether (60–90 °C) as eluent gave **3c** (103.9 mg, 92%) as a yellow solid. mp: 91–92 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.55 (s, 1H), 7.40 (s, 1H), 0.37 (s, 9H); ¹³C{¹H}NMR (125.8 MHz, CDCl₃) δ 145.1, 144.2, 142.4, 139.7, 139.0, 128.8, 125.0, 73.5, -0.1; IR (KBr): 3048, 2955, 1633, 1255, 961, 836 cm⁻¹; HRMS (*m/z*): [M+H]⁺ calcd. for C₁₁H₁₂IS₃Si, 394.8874; found, 394.8910.

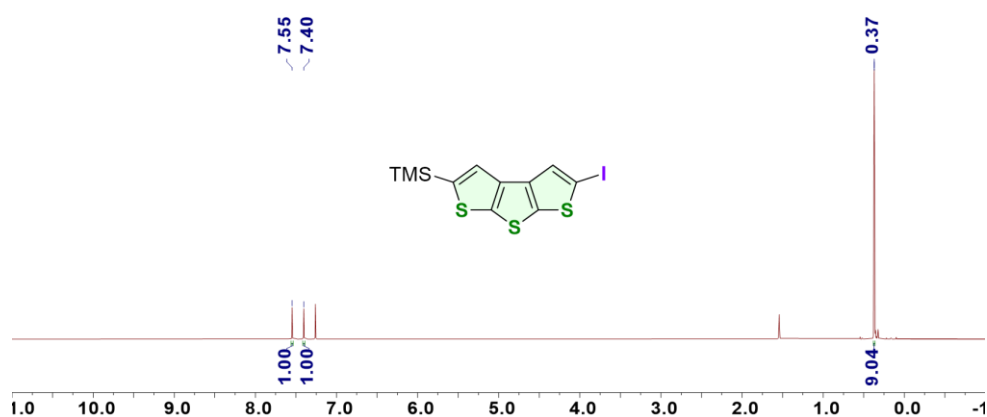


Fig. S16 | ¹H NMR (400 MHz, CDCl₃) spectrum of **3c**.

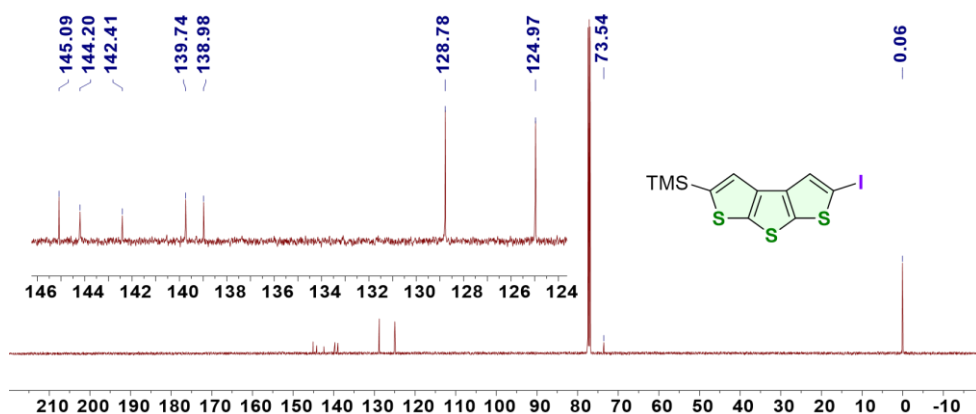


Fig. S17 | ¹³C NMR (125 MHz, CDCl₃) spectra of **3c**.

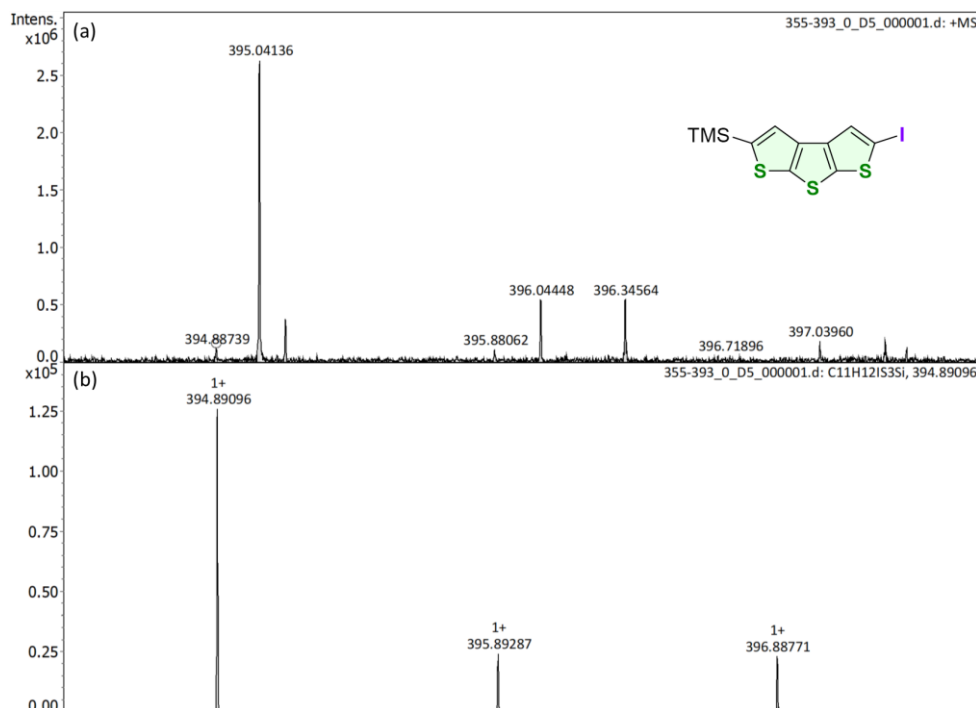
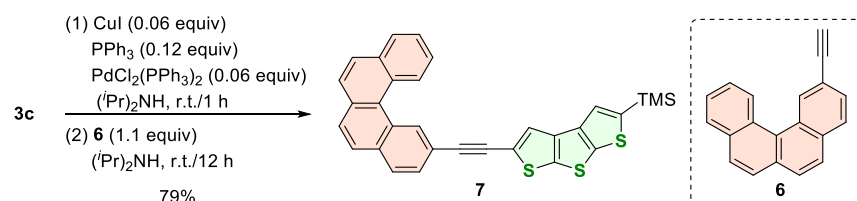


Fig. S18 | HRMS (MALDI-FT) spectra of **3c**: (a) experimental spectrum; (b) calculated spectrum.

2.1.7. Synthesis of **7**



To an oven-dried Schlenk flask was added **3c** (514.8 mg, 1.32 mmol, 1.1 equiv), PdCl₂(PPh₃)₂ (50.1 mg, 0.07 mmol, 0.06 equiv), CuI (13.2 mg, 0.07 mmol, 0.06 equiv), and PPh₃ (37.2 mg, 0.12 mmol, 0.12 equiv). After degassed under vacuum for 30 min, dry diisopropylamine (40 mL) was added under Ar flow. The solution was allowed to stir at room temperature for 1 h. A solution of **6** (300.0 mg, 1.2 mmol, 1.0 equiv) in diisopropylamine (20 mL) was transferred by cannula to the reaction mixture over 20 min, and the mixture was stirred for 12 h. The reaction mixture was quenched with water. The separated water layer was extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layer was washed with water (3 × 15 mL) and then dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether (60–90 °C) as eluent gave **7** (485.1 mg, 79%) as a yellow solid. mp: 132.5–134.9 °C; IR (KBr): 3054, 2951, 2379, 1610, 1250, 939, 832 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (ppm) 9.31 (d, *J* = 1.5 Hz, 1H), 9.14 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.78 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.74 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.62 (s, 1H), 7.47 (s, 1H), 0.41 (s, 9H); ¹³C{¹H}NMR (125 MHz, CDCl₃) δ 145.2, 144.5, 140.6, 140.5, 137.1, 133.8, 133.3, 131.5, 131.4, 130.3, 130.2, 128.9, 128.8, 128.4, 128.1, 128.1, 128.0, 127.2, 127.1, 126.8, 126.8, 126.3, 125.5, 125.2, 123.7, 120.5, 94.9, 83.9, 0.1; HRMS (*m/z*) [M+H]⁺ calcd. for C₃₁H₂₃S₃Si, 519.0726; found, 519.0723.

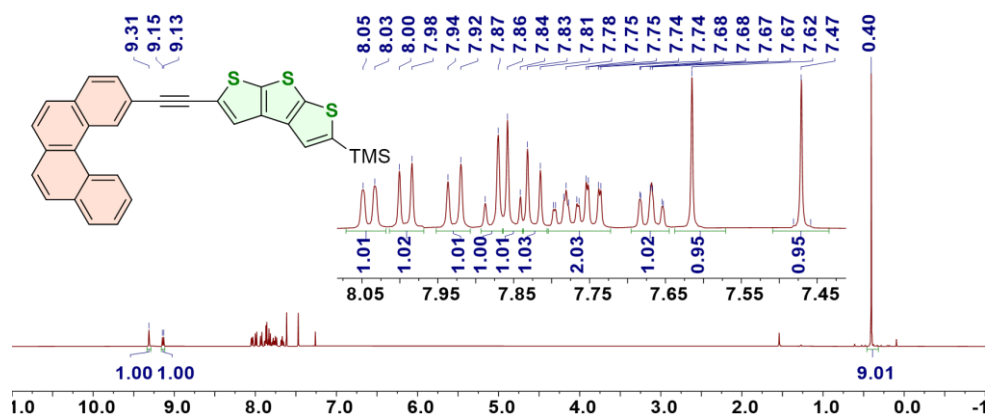


Fig. S19 | ^1H NMR (500 MHz, CDCl_3) spectra of 7.

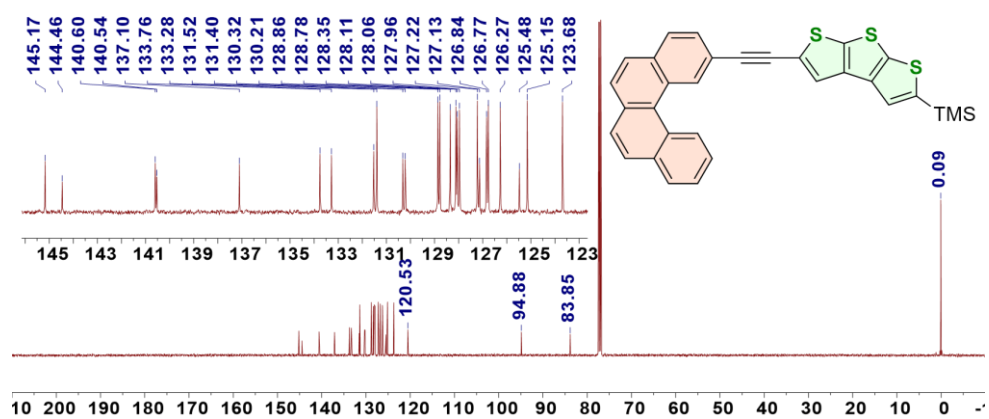


Fig. S20 | ^{13}C NMR (125 MHz, CDCl_3) spectra of 7.

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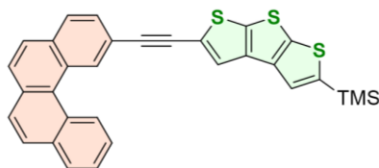
Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20220023

Sample Serial Number: SZ-3-65

Operator : DONG Date: 2021/12/02

Operation Mode: DART POSITIVE



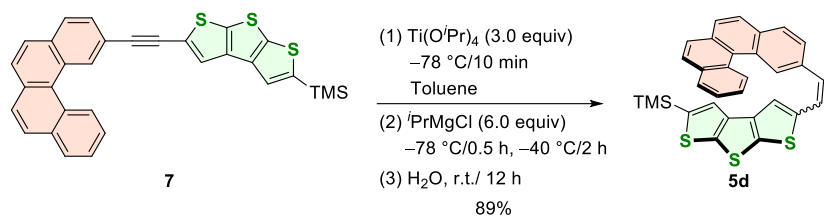
Elemental composition search on mass 519.0723

m/z= 514.0723-524.0723

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|---|
| 519.0723 | 519.0723 | 0.05 | 17.0 | $\text{C}_{25}\text{H}_{22}\text{O}_5\text{N}_5\text{BrS}$ |
| 519.0723 | 519.0723 | 0.06 | 1.5 | $\text{C}_{18}\text{H}_{36}\text{O}_4\text{BrS}_3\text{Si}$ |
| 519.0724 | 519.0724 | -0.15 | 28.5 | $\text{C}_{31}\text{H}_{11}\text{O}_5\text{N}_4$ |
| 519.0721 | 519.0721 | 0.34 | 12.5 | $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}_2\text{S}_5$ |
| 519.0725 | 519.0725 | -0.38 | 1.5 | $\text{C}_{19}\text{H}_{36}\text{O}_3\text{BrS}_4$ |
| 519.0726 | 519.0726 | -0.47 | 21.5 | $\text{C}_{31}\text{H}_{23}\text{S}_3\text{Si}$ |
| 519.0721 | 519.0721 | 0.49 | 17.0 | $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_5\text{BrSi}$ |
| 519.0726 | 519.0726 | -0.55 | 3.0 | $\text{C}_{17}\text{H}_{33}\text{O}_5\text{N}_5\text{S}_5\text{Si}$ |
| 519.0719 | 519.0719 | 0.76 | 22.5 | $\text{C}_{31}\text{H}_{19}\text{O}_4\text{S}_2$ |
| 519.0719 | 519.0719 | 0.78 | 12.5 | $\text{C}_{23}\text{H}_{27}\text{O}_2\text{N}_2\text{S}_4\text{Si}$ |

Fig. S21 | HRMS (DART positive ion mode) data of 7.

2.1.8. Synthesis of 5d



To an oven-dried Schlenk flask was added **7** (250.0 mg, 0.5 mmol, 1.0 equiv). After degassed under vacuum for 30 min, dry toluene (40 mL), titanium isopropoxide (0.40 mL, 1.45 mmol, 3.0 equiv), and *i*-propylmagnesium chloride (2 M in Et_2O , 1.45 mL, 2.9 mmol, 6.0 equiv) were added sequentially under Ar flow. The reaction was stirred at -78 °C for 30 min and then warmed to -40 °C for 2 h. Water (2.5 mL) was added and then warmed to room temperature for 18 h. The reaction mixture was quenched with water. The separated water layer was extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was washed with water (3×15 mL) and then dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether (60–90 °C) / CH_2Cl_2 (5:1, *v/v*) as eluent gave **5d** (222.0 mg, 89%) as a yellow solid. mp: 229.5–231.9 °C; IR (KBr): 3046, 2956, 2911, 1615, 1250, 832 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 9.15 (d, $J = 8.4$ Hz, 1H), 9.11 (s, 1H), 8.04 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.99 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.84–7.79 (m, 3H), 7.76 (dt, $J = 7.6, 1.7$ Hz, 1H), 7.67 (dt, $J = 7.6, 1.7$ Hz, 1H), 7.46 (s, 1H), 7.44 (dd, $J = 15.9, 2.2$ Hz, 1H), 7.37 (d, $J = 2.2$ Hz, 1H), 7.18 (d, $J = 15.9$ Hz, 1H), 0.40 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 145.7, 144.9, 143.9, 140.9, 138.6, 138.0, 134.8, 133.7, 133.2, 131.6, 130.8, 130.5, 129.2, 128.8, 128.8, 128.0, 127.8, 127.5, 127.3, 127.1, 127.0, 127.0, 126.5, 126.1, 125.1, 123.2, 123.0, 118.1, 0.1; HRMS (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{31}\text{H}_{25}\text{S}_3\text{Si}$, 521.0882; found, 521.0883.

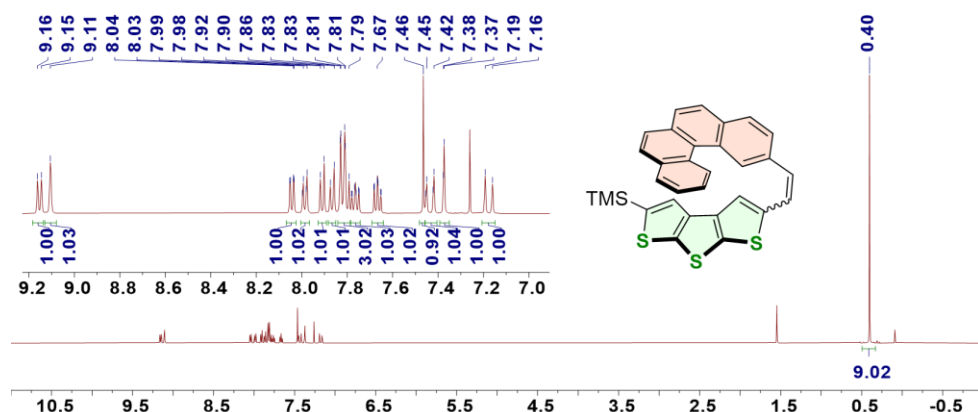


Fig. S22 | ^1H NMR (500 MHz, CDCl_3) spectra of **5d**.

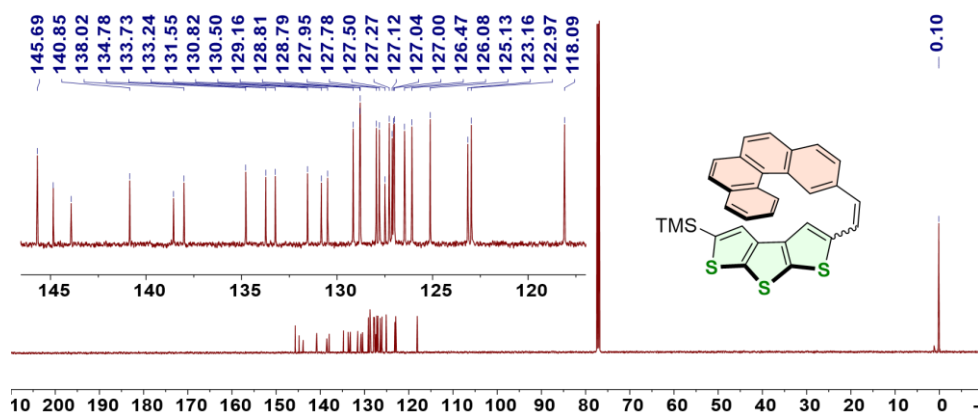


Fig. S23 | ^{13}C NMR (125 MHz, CDCl_3) spectra of **5d**.

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20220099

Sample Serial Number: SZ-4-19

Operator : DONG Date: 2021/12/03

Operation Mode: DART POSITIVE



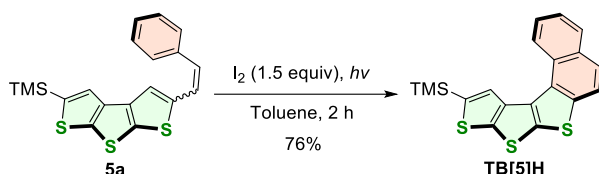
Elemental composition search on mass 521.0883

m/z = 516.0883-526.0883

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|--|
| 521.0883 | 521.0883 | -0.01 | 2.0 | C ₁₇ H ₃₅ O ₅ N ₅ S ₅ Si |
| 521.0883 | 521.0883 | -0.06 | 7.0 | C ₂₁ H ₃₂ N ₃ Cl ₁ S ₅ |
| 521.0882 | 521.0882 | 0.07 | 20.5 | C ₃₁ H ₂₅ S ₃ Si |
| 521.0881 | 521.0881 | 0.36 | 17.0 | C ₂₉ H ₂₄ O ₃ N ₁ Cl ₁ S ₂ |
| 521.0881 | 521.0881 | 0.38 | 7.0 | C ₂₀ H ₃₂ ON ₃ Cl ₁ S ₄ Si |
| 521.0880 | 521.0880 | 0.39 | 27.5 | C ₃₁ H ₁₃ O ₅ N ₄ |
| 521.0885 | 521.0885 | -0.54 | 23.0 | C ₂₈ H ₁₆ O ₄ N ₅ Cl ₁ |
| 521.0878 | 521.0878 | 0.80 | 17.0 | C ₂₇ H ₂₄ O ₄ N ₁ Cl ₁ S ₁ |
| 521.0887 | 521.0887 | -0.83 | 26.5 | C ₃₁ H ₁₇ ON ₄ S ₁ |
| 521.0878 | 521.0878 | 0.88 | 11.5 | C ₂₄ H ₂₅ ON ₂ S ₅ |

Fig. S24 | HRMS (DART Positive ion mode) data of **5d**.

2.1.9. Synthesis of TB[5]H



To a photochemical reaction tube was added **5a** (22.6 mg, 0.06 mmol, 1.0 equiv), dry toluene (10 mL), iodine (23.1 mg, 0.09 mmol, 1.5 equiv), and catalytic amount of propylene oxide. After bubbled with Ar gas for 20 min, the solution was irradiated for 2 h under an argon using a photochemical reactor fitted with a 500-watt mercury lamps. The reaction mixture was washed by aqueous Na₂S₂O₃, water and then dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether as eluent gave **TB[5]H** (12.4 mg, 76%) as a white solid. mp: 174.5–175.6 °C; IR (KBr): 3049, 2928, 2380, 1634, 1105, 793 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (ppm) 9.09 (d, *J* = 8.4 Hz, 1H), 8.17 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.79–7.71 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 0.47 (s, 9H); ¹³C {¹H}NMR (125 MHz, CDCl₃) δ 144.8, 143.7, 141.3, 141.1, 140.8, 133.6, 131.9, 129.3, 129.0, 127.7, 126.0, 125.3, 125.2, 125.0, 121.5, 0.1; HRMS (*m/z*) [M]⁺ calcd. for C₁₉H₁₆S₃Si, 368.0166; found, 368.0178.

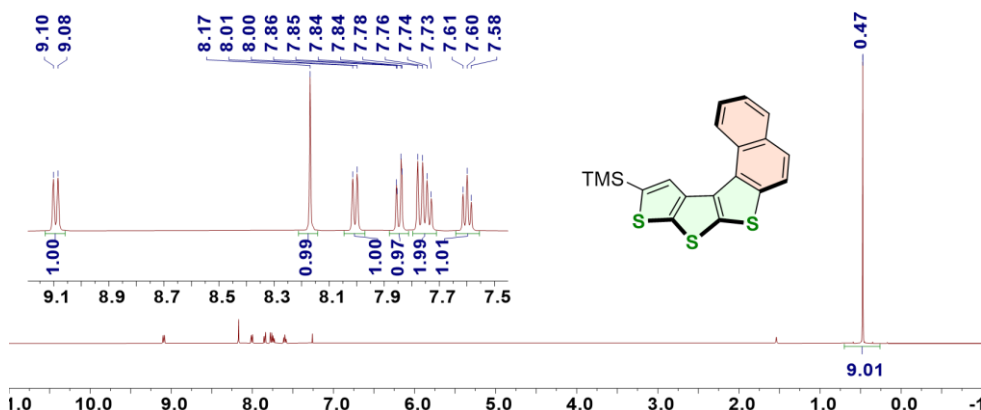


Fig. S25 | ¹H NMR (500 MHz, CDCl₃) spectra of **TB[5]H**.

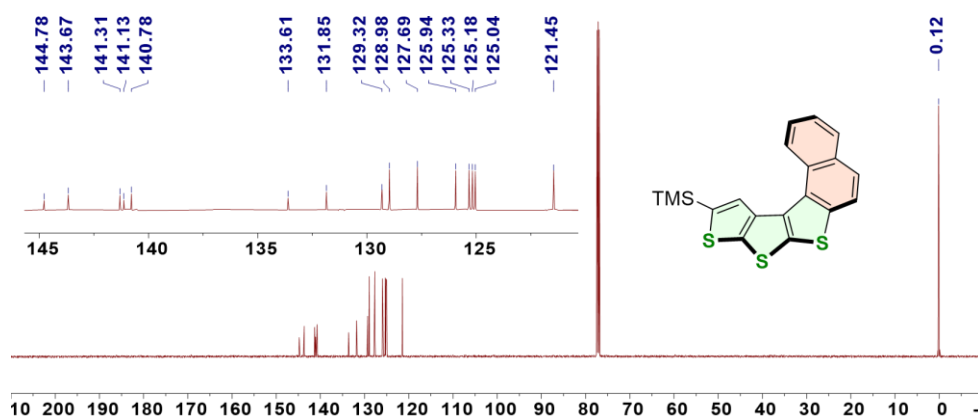


Fig. S26 | ^{13}C NMR (125 MHz, CDCl_3) spectra of **TB[5]H**.

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Instrument: JMS-S3000 MALDI-TOFMS

Sample Serial Number: SZ-TM-1

Operator: Zhang, Li

Date: 2021/03/25

Operation Mode: MALDI-Positive

Elemental Composition Estimation

Parameters:

| Mass | Tolerance | Electron Mode | Charge | DBE Range | Max Results |
|---------------------|-----------|---------------|--------|--------------|-------------|
| 368.01662 ± 0.00184 | 5.0 ppm | Odd/Even | +1 | -0.5 - 200.0 | 100 |

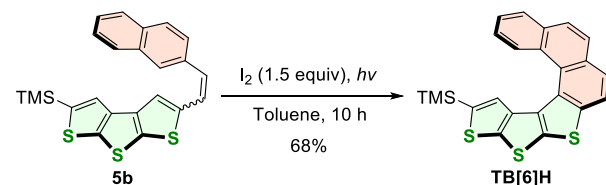
| Elements | C | H | O | Si | S | F | Na |
|----------|------|-------|-----|-----|-----|-----|-----|
| | 0-19 | 0-200 | 0-0 | 0-1 | 0-3 | 0-0 | 0-0 |

Results:

| # | Formula | Mass | DBE | Abs. Error (u) | Error (u) | Error (ppm) |
|---|--|-----------|------|----------------|-----------|-------------|
| 1 | C ₁₉ H ₁₆ SiS ₃ | 368.01779 | 13.0 | 0.00117 | -0.00117 | -3.17 |

Fig. S27 | HRMS (MALDI positive ion mode) data of **TB[5]H**.

2.1.10. Synthesis of **TB[6]H**



To a photochemical reaction tube was added **5b** (49.5 mg, 0.12 mmol, 1.0 equiv), dry toluene (15 mL), iodine (44.8 mg, 0.18 mmol, 1.5 equiv), and catalytic amount of propylene oxide. After bubbled with Ar gas for 20 min, the solution was irradiated for 10 h under an argon using a photochemical reactor fitted with a 500-watt mercury lamps. The reaction mixture was washed by aqueous $\text{Na}_2\text{S}_2\text{O}_3$, water and then dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether as eluent gave **TB[6]H** (33.3 mg, 67%) as a light yellow solid. mp: 174.8–176.4 °C; IR (KBr): 3048, 2957, 2376, 1626, 1250, 836 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 8.59 (d, $J = 8.3$ Hz, 1H), 8.02 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 8.7$ Hz, 1H), 7.86 (d, $J = 8.7$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.66 (dt, $J = 7.5, 1.7$ Hz, 1H), 7.48 (dt, $J = 7.5, 1.7$ Hz, 1H), 6.78 (s, 1H), 0.24 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 143.3, 143.2, 142.4, 142.1, 141.4, 135.1, 132.9, 131.1, 130.6, 129.8, 129.5, 127.6, 127.5, 126.9, 126.8, 126.6, 126.5, 125.4, 124.6, 121.6, -0.2; HRMS (m/z) $[\text{M}]^+$ calcd. for $\text{C}_{23}\text{H}_{18}\text{S}_3\text{Si}$, 418.0335; found, 418.0334.

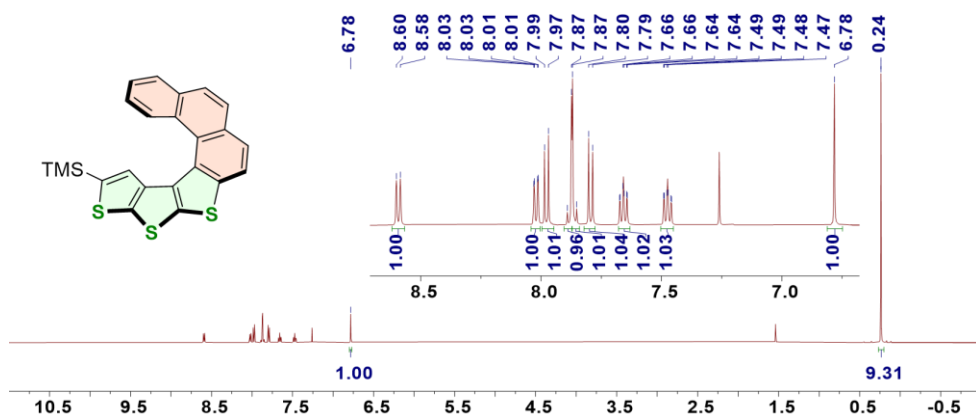


Fig. S28 | ^1H NMR (500 MHz, CDCl_3) spectra of TB[6]H.

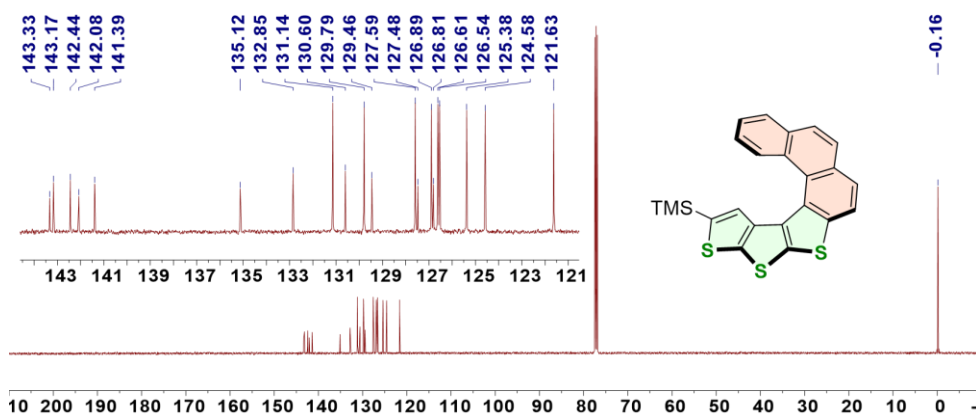


Fig. S29 | ^{13}C NMR (125 MHz, CDCl_3) spectra of TB[6]H.

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HIGH RESOLUTION MS REPORT



Instrument: JMS-S3000 MALDI-TOFMS

Sample Serial Number: SZ-TM-2

Operator: Zhang, Li

Date: 2021/03/25

Operation Mode: MALDI-Positive

Elemental Composition Estimation

Parameters:

| Mass | Tolerance | Electron Mode | Charge | DBE Range | Max Results |
|---------------------|-----------|---------------|--------|--------------|-------------|
| 418.03351 ± 0.00209 | 5.0 ppm | Odd/Even | +1 | -0.5 - 200.0 | 100 |

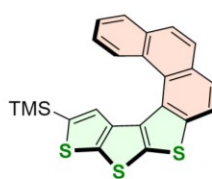
Elements

| C | H | O | Si | S | F | Na |
|------|-------|-----|-----|-----|-----|-----|
| 0-23 | 0-200 | 0-0 | 0-1 | 0-3 | 0-0 | 0-0 |

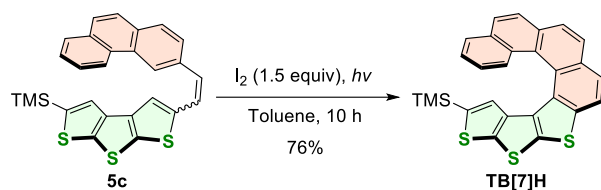
Results:

| # | Formula | Mass | DBE | Abs. Error (u) | Error (u) | Error (ppm) |
|---|--|-----------|------|----------------|-----------|-------------|
| 1 | C ₂₃ H ₁₈ SiS ₃ | 418.03344 | 16.0 | 0.00007 | 0.00007 | 0.17 |

Fig. S30 | HRMS (MALDI Positive ion mode) data of TB[6]H.



2.1.11. Synthesis of TB[7]H



To a photochemical reaction tube was added **5c** (11.0 mg, 0.02 mmol, 1.0 equiv), dry toluene (15 mL), iodine (8.9 mg, 0.03 mmol, 1.5 equiv), and catalytic amount of propylene oxide. After bubbled with Ar gas for 20 min, the solution was irradiated for 10 h under an argon using a photochemical reactor fitted with a 500-watt mercury lamps. The reaction mixture was washed by aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and water, and dried over MgSO_4 . Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether as eluent gave **TB[7]H** (8.0 mg, 73%) as a light yellow solid. mp: 226.8–228.9 °C; IR (KBr): 3046, 2939, 2385, 1619, 1250, 836 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.11–8.06 (m, 2H), 8.06–7.99 (m, 3H), 7.97–7.87 (m, 3H), 7.31–7.26 (m, 1H), 6.89 (dt, $J = 8.7, 1.6$ Hz, 1H), 5.26 (s, 1H), 0.07 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 142.5, 142.4, 141.3, 139.6, 135.5, 132.1, 131.8, 131.7, 131.1, 129.7, 128.0, 127.9, 127.3, 127.2, 127.1, 126.6, 126.3, 126.2, 126.1, 125.4, 124.2, 124.2, 121.7, –0.2; HRMS (m/z) [M] $^+$ calcd. for $\text{C}_{27}\text{H}_{20}\text{S}_3\text{Si}$, 468.0473; found, 468.0491.

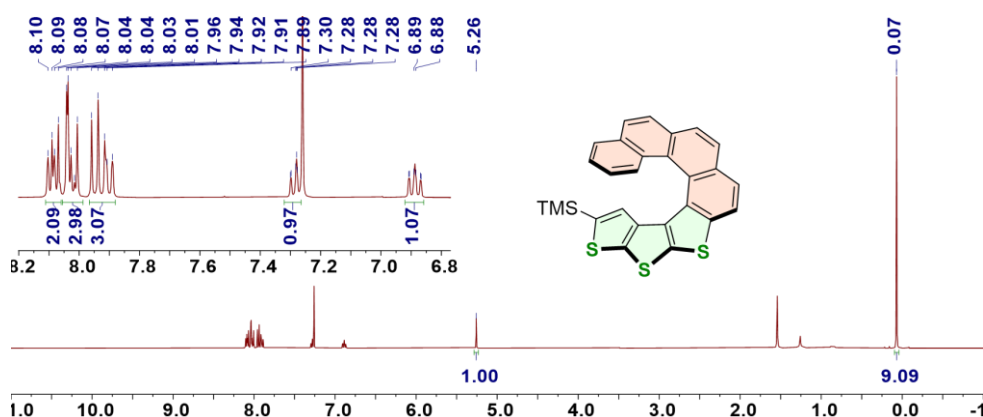


Fig. S31 | ^1H NMR (400 MHz, CDCl_3) spectra of **TB[7]H**.

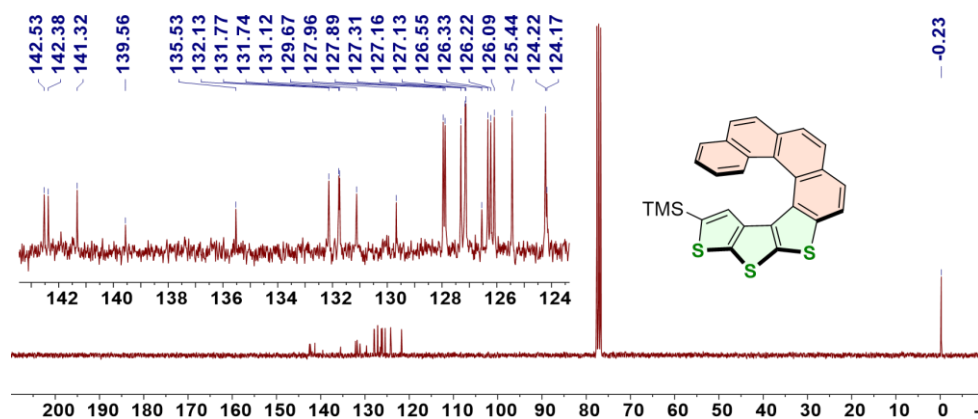


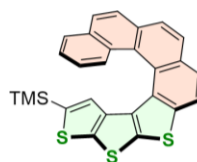
Fig. S32 | ^{13}C NMR (75 MHz, CDCl_3) spectra of **TB[7]H**.

Instrument: JMS-S3000 MALDI-TOFMS

Sample Serial Number: SZ-TM-3

Operator: Zhang, Li

Date: 2021/03/25



Operation Mode: MALDI-Positive

Elemental Composition Estimation

Parameters:

| Mass | Tolerance | Electron Mode | Charge | DBE Range | Max Results |
|---------------------|-----------|---------------|--------|--------------|-------------|
| 468.04728 ± 0.00234 | 5.0 ppm | Odd/Even | +1 | -0.5 - 200.0 | 100 |

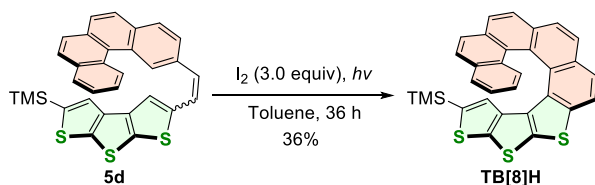
| Elements | C | H | O | Si | S | F | Na |
|----------|------|-------|-----|-----|-----|-----|-----|
| | 0-27 | 0-200 | 0-0 | 0-1 | 0-3 | 0-0 | 0-0 |

Results:

| # | Formula | Mass | DBE | Abs. Error (u) | Error (u) | Error (ppm) |
|---|--|-----------|------|----------------|-----------|-------------|
| 1 | C ₂₇ H ₂₀ SiS ₃ | 468.04909 | 19.0 | 0.00181 | -0.00181 | -3.86 |

Fig. S33 | HRMS (MALDI Positive ion mode) data of TB[7]H.

2.1.12. Synthesis of TB[8]H



To a photochemical reaction tube was added **5d** (50.0 mg, 0.10 mmol, 1.0 equiv), dry toluene (15 mL), iodine (72.9 mg, 0.29 mmol, 3.0 equiv), and catalytic amount of propylene oxide. After bubbled with Ar gas for 20 min, the solution was irradiated for 36 h under an argon using a photochemical reactor fitted with a 500-watt mercury lamps. The reaction mixture was washed by aqueous Na₂S₂O₃ and water, and dried over MgSO₄. Then the mixture was filtered, and the solvent was removed by rotary evaporation giving crude product. Purification using column chromatography on silica gel with petrol ether as eluent gave **TB[8]H** (17.8 mg, 36%) as a light yellow solid. mp: 229.5–231.9 °C; IR (KBr): 3046, 2938, 2385, 1619, 1249, 836 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.17 (d, *J* = 8.2 Hz, 1H), 8.12–8.04 (m, 4H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.03 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.63 (dt, *J* = 7.7, 2.0 Hz, 1H), 5.04 (s, 1H), 0.20 (s, 9H); ¹³C{¹H}NMR (75 MHz, CDCl₃) δ 141.6, 141.3, 141.2, 140.0, 135.4, 132.6, 132.2, 131.8, 131.0, 129.8, 129.6, 128.3, 128.0, 127.5, 127.2, 126.8, 126.8, 126.4, 126.3, 126.1, 125.4, 125.2, 125.1, 124.1, 124.0, 123.2, 121.9, 0.0; HRMS (*m/z*) [*M*+*H*]⁺ calcd. for C₃₁H₂₃S₃Si, 519.0726; found, 519.0725.

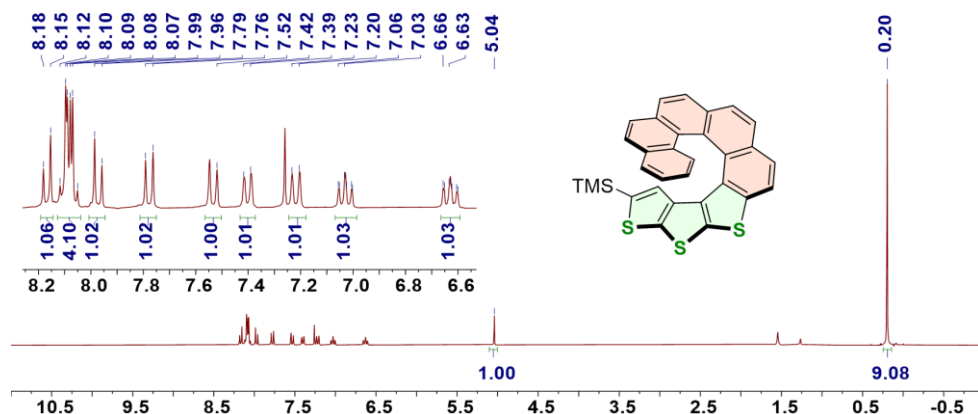


Fig. S34 | ¹H NMR (400 MHz, CDCl₃) spectra of TB[8]H.

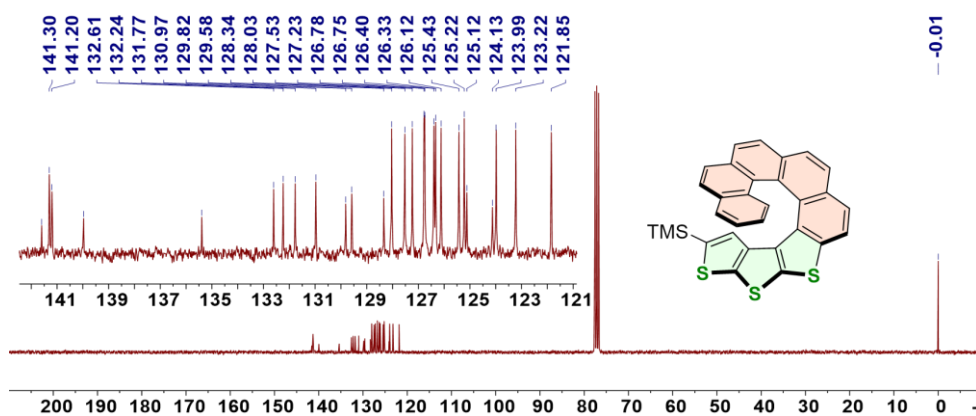


Fig. S35 | ^{13}C NMR (75 MHz, CDCl_3) spectra of TB[8]H.

National Center for Organic Mass Spectrometry in Shanghai
 Shanghai Institute of Organic Chemistry
 Chinese Academic of Sciences
 High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20220025

Sample Serial Number: SZ-4-21

Operator : DONG Date: 2021/12/02

Operation Mode: DART POSITIVE

Elemental composition search on mass 519.0725

m/z= 514.0725-524.0725

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|----------|------------|-------------|------------|---|
| 519.0725 | 519.0724 | 0.10 | 28.5 | $\text{C}_{31}\text{H}_{11}\text{O}_5\text{N}_4$ |
| | 519.0726 | -0.22 | 21.5 | $\text{C}_{31}\text{H}_{23}\text{S}_3\text{Si}$ |
| | 519.0726 | -0.30 | 3.0 | $\text{C}_{17}\text{H}_{33}\text{O}_5\text{N}_5\text{S}_5\text{Si}$ |
| | 519.0721 | 0.59 | 12.5 | $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}_2\text{S}_5$ |
| | 519.0719 | 1.01 | 22.5 | $\text{C}_{31}\text{H}_{19}\text{O}_4\text{S}_2$ |
| | 519.0719 | 1.03 | 12.5 | $\text{C}_{23}\text{H}_{27}\text{O}_2\text{N}_2\text{S}_4\text{Si}$ |
| | 519.0730 | -1.13 | 27.5 | $\text{C}_{31}\text{H}_{15}\text{O}_4\text{N}_4\text{S}_5\text{Si}$ |
| | 519.0717 | 1.45 | 22.5 | $\text{C}_{30}\text{H}_{19}\text{O}_5\text{S}_5\text{Si}$ |
| | 519.0733 | -1.57 | 27.5 | $\text{C}_{32}\text{H}_{15}\text{N}_4\text{S}_2$ |
| | 519.0733 | -1.64 | 9.0 | $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}_5\text{S}_4$ |

Fig. S36 | HRMS (DART Positive ion mode) data of TB[8]H.

2.2. Single Crystal X-ray Structures

2.2.1. X-ray Crystallographic Data of TB[4]H

Table S1 | Crystal data and structure refinement for TB[4]H

| | |
|-----------------------------------|---|
| Identification code | TB[4]H |
| Empirical formula | C ₁₅ H ₁₄ S ₃ Si |
| Formula weight | 318.53 |
| Temperature | 150.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | <i>P</i> -1 |
| Unit cell dimensions | <i>a</i> = 7.3326(15) Å α = 94.479(7)°. <i>b</i> = 8.0726(19) Å β = 99.553(7)°. <i>c</i> = 14.315(3) Å γ = 115.167(7)°. |
| Volume | 745.7(3) Å ³ |
| Z | 2 |
| Density (calculated) | 1.419 Mg/m ³ |
| Absorption coefficient | 0.560 mm ⁻¹ |
| F(000) | 332 |
| Crystal size | 0.11 × 0.1 × 0.1 mm ³ |
| Theta range for data collection | 2.827 to 25.249°. |
| Index ranges | -8 ≤ <i>h</i> ≤ 7, -9 ≤ <i>k</i> ≤ 9, -17 ≤ <i>l</i> ≤ 17 |
| Reflections collected | 18627 |
| Independent reflections | 2682 [R(int) = 0.0935] |
| Completeness to theta = 25.242° | 99.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.2627 and 0.1719 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 2682 / 0 / 175 |
| Goodness-of-fit on F ² | 1.329 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.1102, wR ₂ = 0.2979 |
| R indices (all data) | R ₁ = 0.1224, wR ₂ = 0.3102 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.944 and -0.603 e.Å ⁻³ |

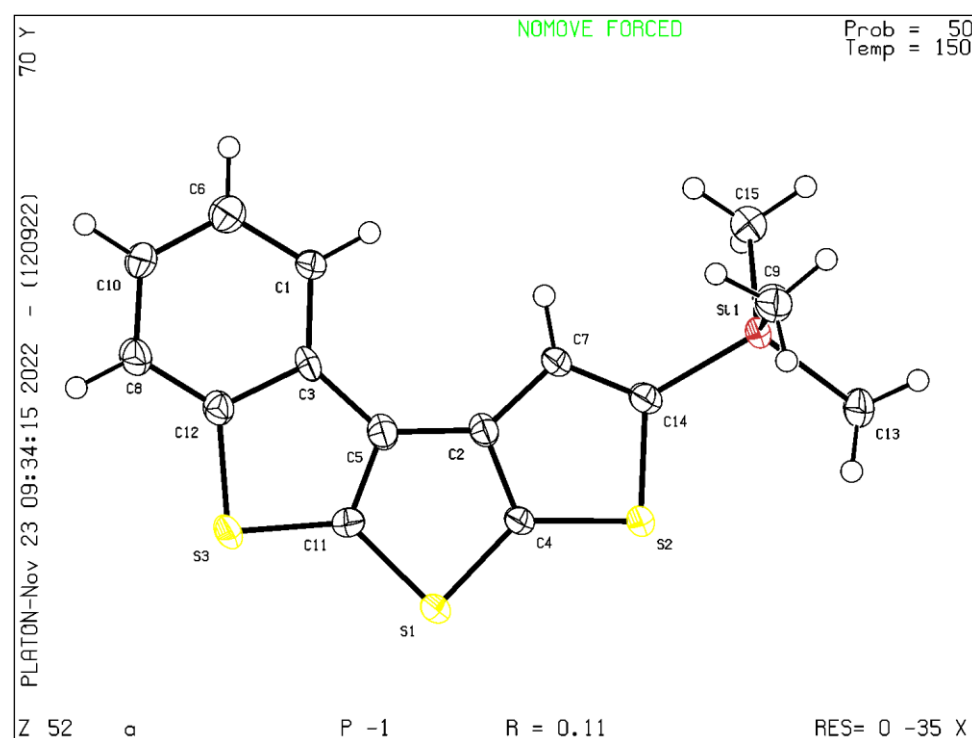


Fig. S37 | Molecular structure for compound TB[4]H with thermal ellipsoids of 50% probability level (CCDC number: 2292750).

2.2.2. X-ray Crystallographic Data of TB[5]H

Table S2 | Crystal data and structure refinement for **TB[5]H**

| | |
|-----------------------------------|--|
| Identification code | TB[5]H |
| Empirical formula | C ₁₉ H ₁₆ S ₃ Si |
| Formula weight | 368.59 |
| Temperature | 150.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | <i>Pbca</i> |
| Unit cell dimensions | a = 12.8509(2) Å α = 90° b = 12.4040(2) Å β = 90° c = 21.8020(4) Å γ = 90° |
| Volume | 3475.29(10) Å ³ |
| Z | 8 |
| Density (calculated) | 1.409 Mg/m ³ |
| Absorption coefficient | 0.491 mm ⁻¹ |
| F(000) | 1536 |
| Crystal size | 0.15 × 0.12 × 0.07 mm ³ |
| Theta range for data collection | 2.450 to 28.313° |
| Index ranges | -17 ≤ h ≤ 16, -15 ≤ k ≤ 16, -28 ≤ l ≤ 29 |
| Reflections collected | 26331 |
| Independent reflections | 4321 [R(int) = 0.0393] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.6855 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4321 / 0 / 211 |
| Goodness-of-fit on F ² | 1.042 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0304, wR ₂ = 0.0714 |
| R indices (all data) | R ₁ = 0.0401, wR ₂ = 0.0774 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.320 and -0.234 e.Å ⁻³ |

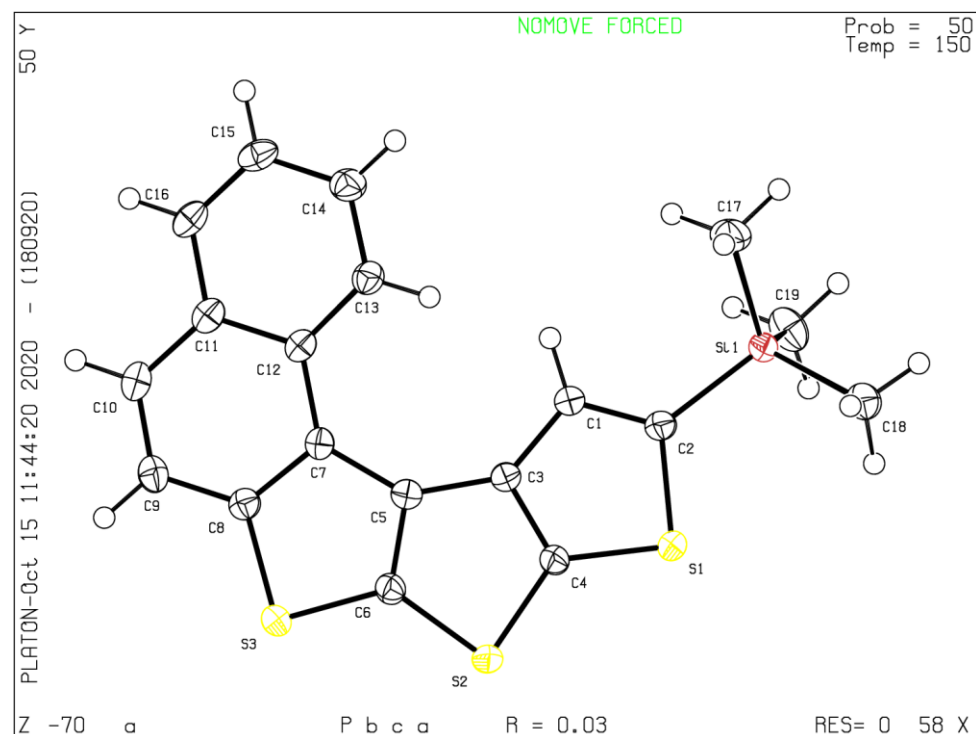


Fig. S38 | Molecular structure for compound **TB[5]H** with thermal ellipsoids of 50% probability level (CCDC number: 2225686).

2.2.3. X-ray Crystallographic Data of TB[6]H

Table S3 | Crystal data and structure refinement for **TB[6]H**

| | |
|-----------------------------------|---|
| Identification code | TB[6]H |
| Empirical formula | C ₂₃ H ₁₈ S ₃ Si |
| Formula weight | 418.64 |
| Temperature | 149.97 K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | <i>Pbca</i> |
| Unit cell dimensions | a = 21.1138(8) Å α = 90° b = 7.7627(2) Å β = 90° c = 24.2285(8) Å γ = 90° |
| Volume | 3971.1(2) Å ³ |
| Z | 8 |
| Density (calculated) | 1.400 Mg/m ³ |
| Absorption coefficient | 0.440 mm ⁻¹ |
| F(000) | 1744 |
| Crystal size | 0.12 × 0.09 × 0.04 mm ³ |
| Theta range for data collection | 2.559 to 28.291° |
| Index ranges | -24 ≤ h ≤ 28, -10 ≤ k ≤ 10, -32 ≤ l ≤ 31 |
| Reflections collected | 32514 |
| Independent reflections | 4925 [R(int) = 0.0791] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.3950 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4925 / 0 / 247 |
| Goodness-of-fit on F ² | 1.038 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0450, wR ₂ = 0.1133 |
| R indices (all data) | R ₁ = 0.0590, wR ₂ = 0.1254 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.549 and -0.417 e.Å ⁻³ |

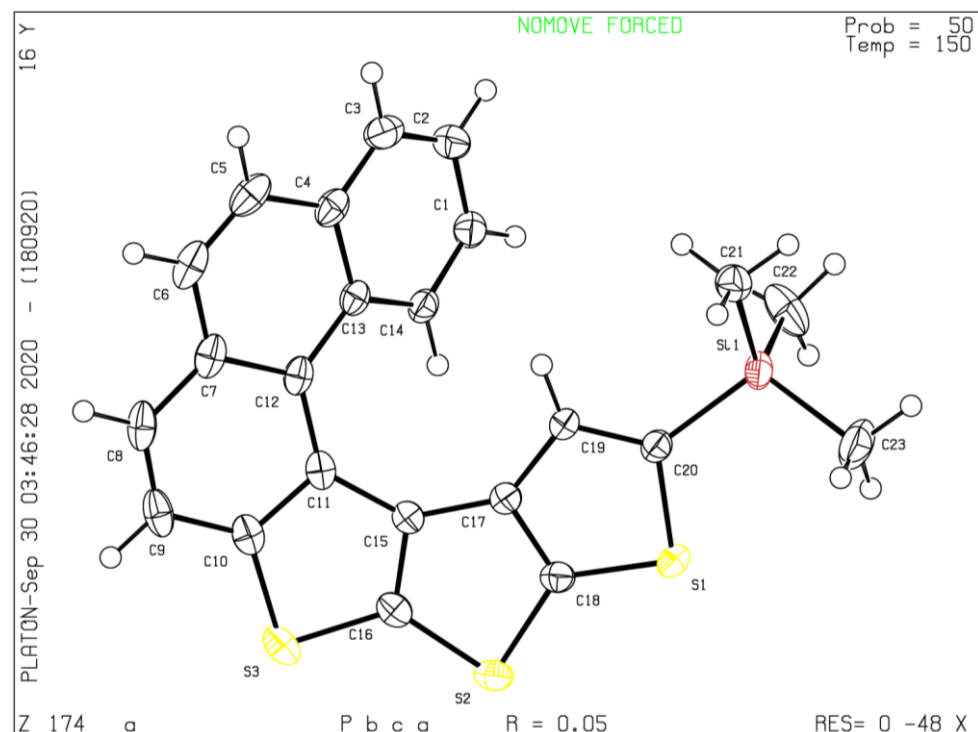


Fig. S39 | Molecular structure for compound **TB[6]H** with thermal ellipsoids of 50% probability level (CCDC number: 2225687).

2.2.4. X-ray Crystallographic Data of TB[7]H

Table S4 | Crystal data and structure refinement for TB[7]H

| | |
|-----------------------------------|---|
| Identification code | TB[7]H |
| Empirical formula | C ₂₇ H ₂₀ S ₃ Si |
| Formula weight | 468.70 |
| Temperature | 149.98 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| Unit cell dimensions | a = 14.2989(3) Å α = 90° b = 12.2575(2) Å β = 96.9100(10)° c = 12.9384(2) Å γ = 90° |
| Volume | 2251.23(7) Å ³ |
| Z | 4 |
| Density (calculated) | 1.383 Mg/m ³ |
| Absorption coefficient | 0.396 mm ⁻¹ |
| F(000) | 976 |
| Crystal size | 0.21 × 0.18 × 0.14 mm ³ |
| Theta range for data collection | 2.195 to 28.308° |
| Index ranges | -19 ≤ h ≤ 19, -14 ≤ k ≤ 16, -17 ≤ l ≤ 16 |
| Reflections collected | 25550 |
| Independent reflections | 5583 [R(int) = 0.0287] |
| Completeness to theta = 25.242° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.6602 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5583 / 0 / 283 |
| Goodness-of-fit on F ² | 1.036 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0293, wR ₂ = 0.0759 |
| R indices (all data) | R ₁ = 0.0353, wR ₂ = 0.0805 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.363 and -0.28 e.Å ⁻³ |

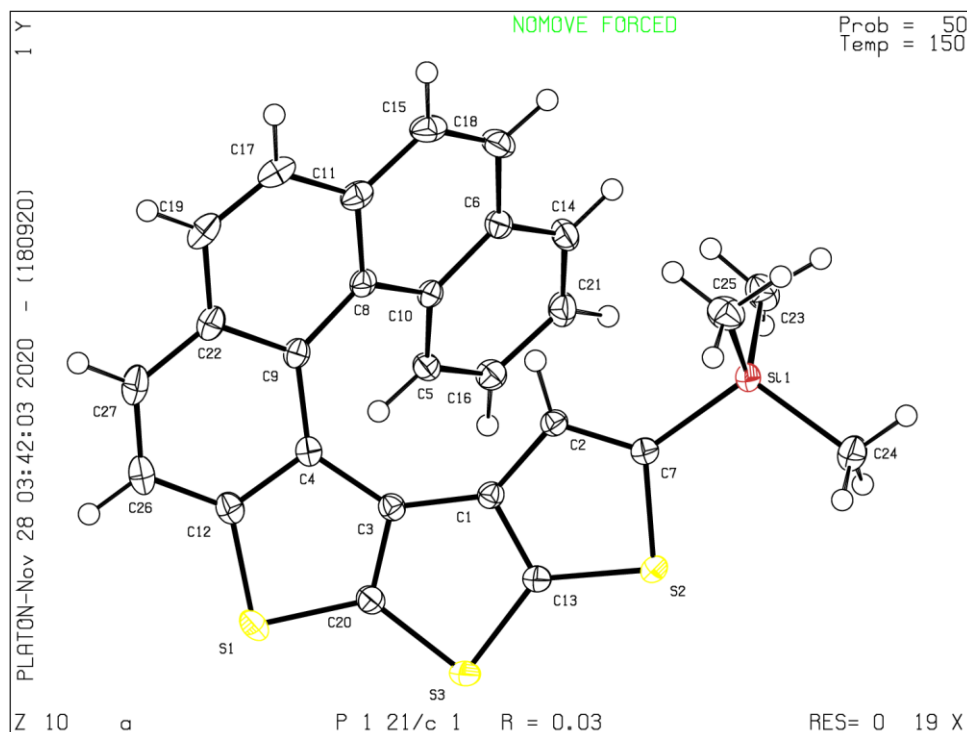


Fig. S40 | Molecular structure for compound TB[7]H with thermal ellipsoids of 50% probability level (CCDC number: 2225691).

2.2.5. Crystal Structures and Crystal Packings

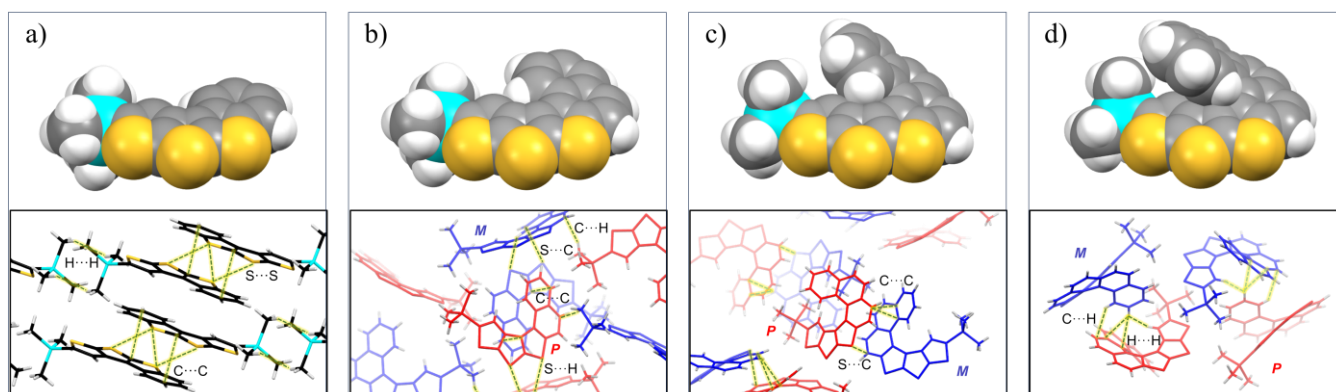


Fig. S41 | Supplemental X-ray single crystal structures. Crystal structures under space-filling mode and crystal packings of: a TB[4]H; b TB[5]H; c TB[6]H, and d TB[7]H.

2.3. Photophysical Properties

2.3.1. UV-vis spectra of TB[n]H (n=3-8)

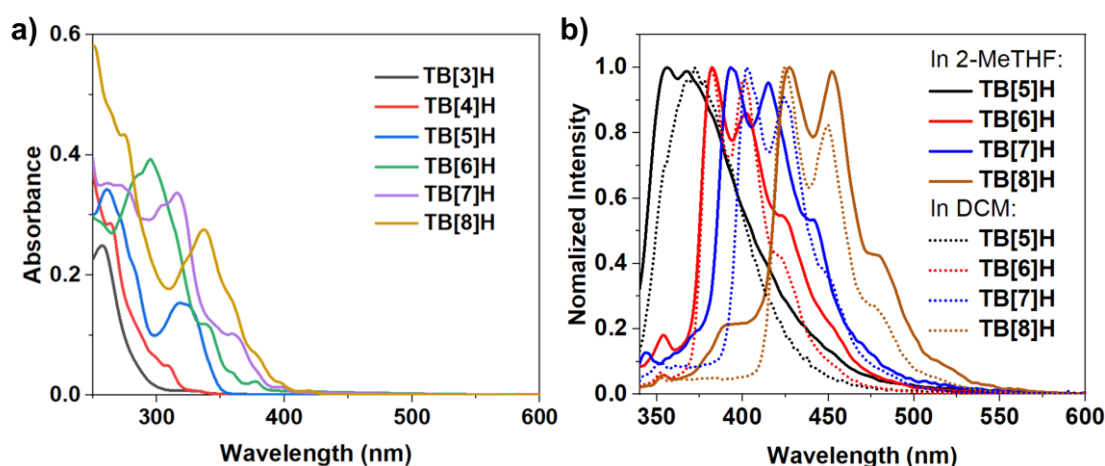


Fig. S42 | Comparison of UV-vis and fluorescence spectra. a UV-vis spectra (DCM, 1×10^{-5} M). b Fluorescence spectra in 2-MeTHF and DCM (1×10^{-5} M).

2.3.2. Comparison of Fluorescence Spectra of Thia[n]helicenes (n=5-8) in 2-MeTHF and DCM

The variation in fluorescence of thiahelicenes **TB[n]H** (n=5-8) in 2-methyltetrahydrofuran (2-MeTHF) and dichloromethane (DCM) were roughly explored. As depicted in Fig. S42b, **TB[5]H** and **TB[7]H** exhibited differences of 12 nm and 9 nm, respectively, in their maximum emissions between the two solvents. The emission wavelengths of even-numbered-ring thiahelicenes, on the other hand, remained relatively constant. Although the small spectral difference were observed, they did not significantly influence the emission characteristics due to the overall similarity in emission profiles. Consequently, 2-MeTHF was selected as the solvent in photophysical research. In the frozen state, 2-MeTHF would form a glass-state solid, which is more suitable for cryogenic photophysical studies. In contrast, DCM crystallized automatically in the frozen state, which could affect the spectral profiles.

The radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated based on the following functions⁹:

$$\Phi_{FL} = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

$$\tau_f = \frac{1}{k_r + k_{nr}} \quad (2)$$

2.3.3. Comparison of Fluorescence of Room and Cryogenic Temperature

Normalized spectra based on fluorescence were generated to illustrate the difference in emission between room and cryogenic temperature. Given that **TB[3]H** exhibits no emission at room temperature, the primary focus of the discussion is on **TB[n]H** (n = 4-8). As shown in Fig. S43, there is a gradual decrease in the relative strength of the emission in the short-wavelength region (corresponding to fluorescence) at 77 K, while the emission in the long-wavelength region (corresponding to phosphorescence) becomes more pronounced. The opposing trend suggests a progressive opening of the intersystem crossing process. Notably, **TB[7]H** exhibits the most significant transition from fluorescence to phosphorescence, aligning

with its highly efficient phosphorescence and longest PL lifetime, as discussed in the maintext. Furthermore, the fluorescence observed at cryogenic temperature displays more fine structures than that at room temperature, and all cryogenic FL spectra exhibit a hypochromatic shift towards the high-energy region. These phenomena can be attributed to suppresses some of nonradiative emission in the frozen state.

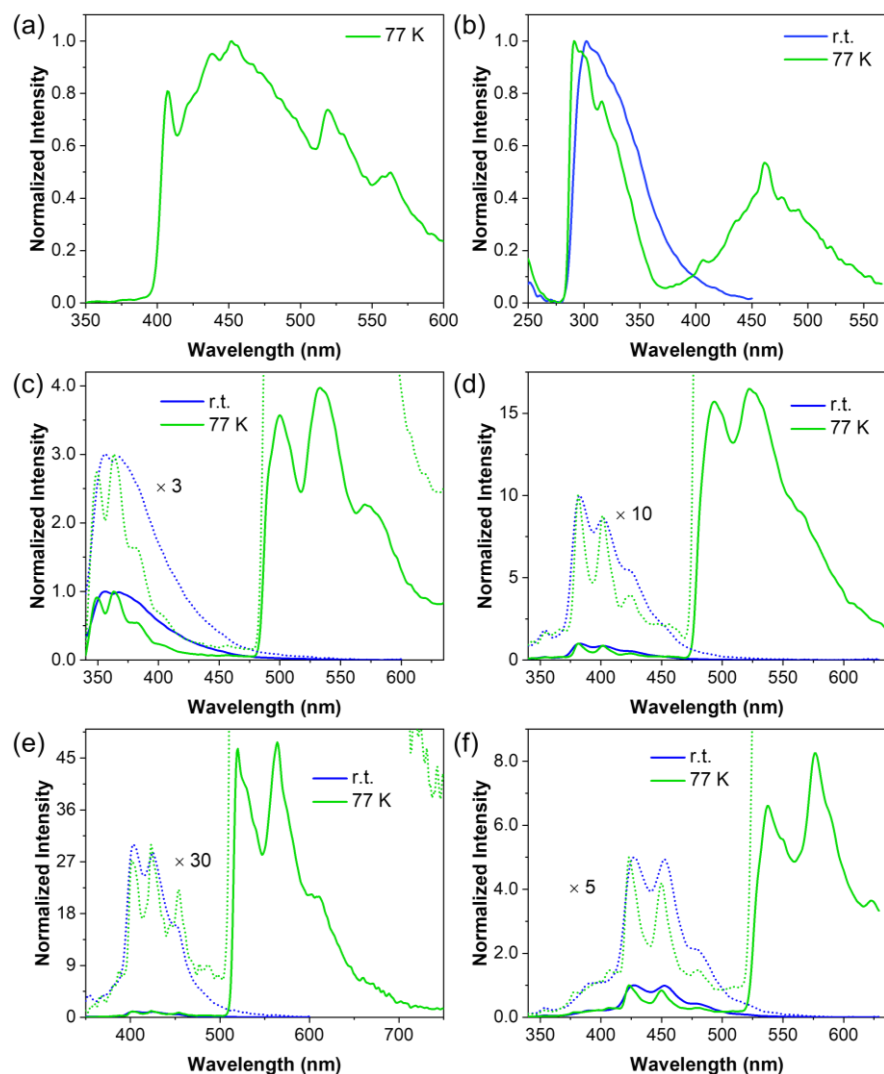


Fig. S43 | Emission spectra of a TB[3]H, b TB[4]H, c TB[5]H, d TB[6]H, e TB[7]H, and f TB[8]H. All spectra were normalized based on the fluorescent emission to compare the fluorescence difference at room and cryogenic temperature (77 K, 5×10^{-5} M in 2-MeTHF. Due to the high melting point and the heavy-atom effect of DCM, all emission spectra were recorded in 2-MeTHF.). The spectra of TB[5]H, TB[6]H, TB[7]H, and TB[8]H were simultaneously amplified (dash line) to show the fluorescence clearly.

2.3.2. Afterglow Photographs of Cryogenic Solid

The investigation of solid-state emission was conducted to explore the aggregating luminescent properties of the compounds. At room temperature, none of the compounds exhibited emission under UV light (365 nm) irradiation. This phenomenon can primarily be attributed to aggregation-induced fluorescence quenching. However, all compounds displayed luminescence under irradiation at cryogenic conditions (77 K), with the emission color shifting from light yellow to orange. Notably, **TB[6]H** and **TB[7]H** exhibited higher brightness than the others. Upon discontinuing the irradiation, delayed luminescence appeared and was captured using a cell phone, which was then transferred into images (Fig. S44). The duration of the afterglow in **TB[n]H** compounds did not follow the same trend observed in their solution state. Small molecules like **TB[3]H**, **TB[4]H**, and **TB[5]H** exhibited relatively short afterglow durations of less than 1.1 s, while other helicenes, namely **TB[6]H**, **TB[7]H**, and **TB[8]H**, displayed longer persistent phosphorescence lasting over 1.7 s. **TB[7]H** exhibited the longest duration of 3.2 s, suggesting its potential as a candidate for persistent phosphors in both solution and solid states.

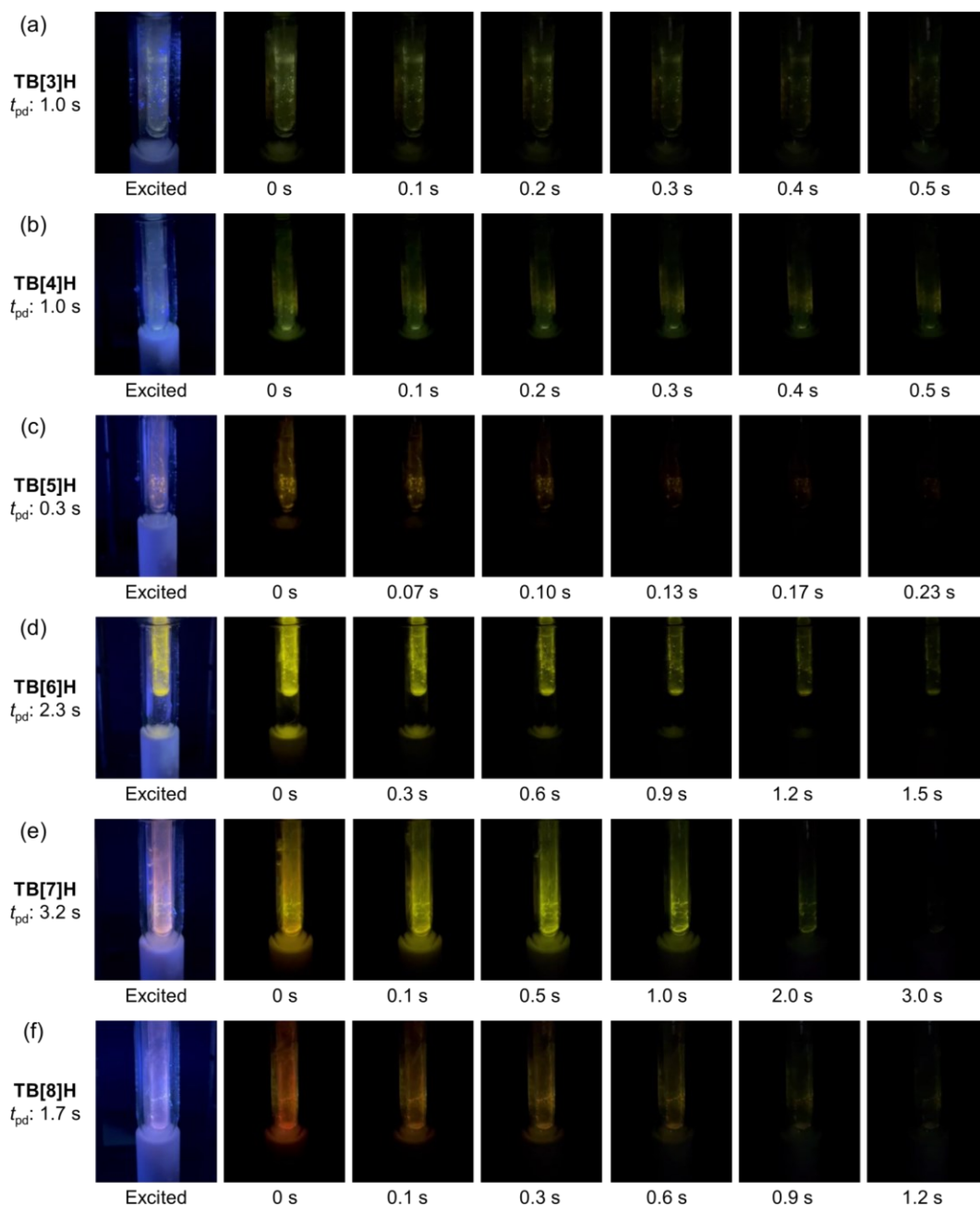


Fig. S44 | Photographs of solid-state phosphorescence of **TB[n]H at 77 K. a **TB[3]H**, b **TB[4]H**, c **TB[5]H**, d **TB[6]H**, e **TB[7]H**, and f **TB[8]H**.** During the graph capture course, the quartz tube was kept in a Dewar flask which was filled with liquid nitrogen, and the sample was frozen for 10 min before excited. The phosphorescence duration (t_{pd}) of all compounds were also recorded and shown in the figure.

2.4. Computational Calculations

2.4.1. TD-DFT Calculations of UV-Vis spectra

The absorption behaviors of TB[n]H ($n = 3-8$) can indeed be explained by the elongated conjugation due to the increasing number of benzene rings, but the underlying reasons for this alteration trend were further elucidated through TD-DFT calculations at the B3LYP/6-31G(d) level of theory. In these calculations, we considered 20 types of states, and transitions triggering absorption beyond 250 nm were recorded (Figure S45). The simulated results revealed that the number of transition paths increased with the accumulation of benzene rings, leading to a gradual reduction in transition energies. This indicates that extended conjugation facilitates low-energy electronic transitions, resulting in bathochromic (red) absorption bands. Moreover, the presence of multiple transition paths gives rise to broader and non-normal absorption bands in higher thia[n]helicenes. Since some of these transitions have lower oscillator strength and are located close to the strong absorption band, complex shoulder bands appear alongside the major absorptions, especially in higher thia[n]helicenes. The alteration in transition behavior is attributable to the expanded π orbitals and, in part, to spatial configuration-induced π -orbital overlap between the terminal rings of thia[n]helicenes.

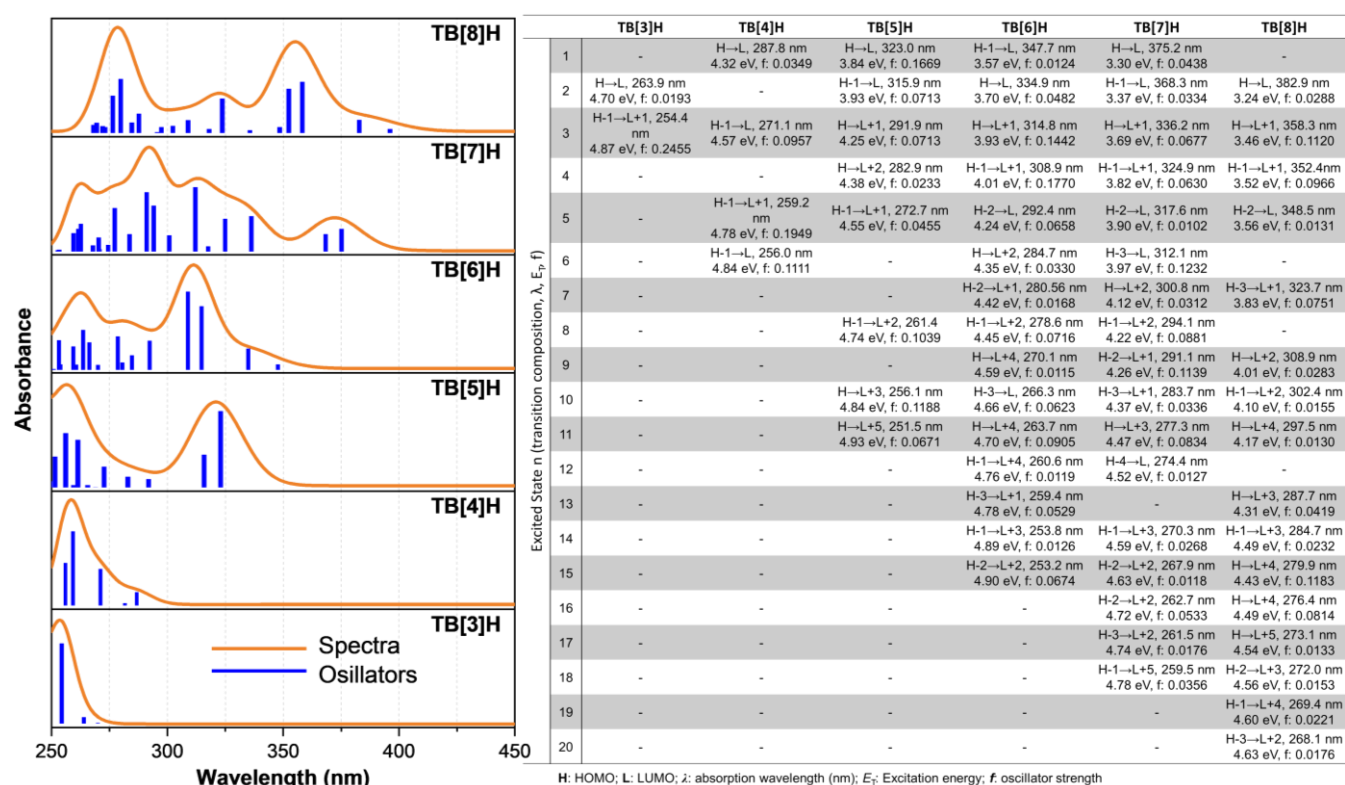


Fig. S45 | TD-DFT calculations (B3LYP/6-31G(d)) of UV-vis absorption spectra of TB[3]H, TB[4]H, TB[5]H, TB[6]H, TB[7]H, and TB[8]H. Transition modes, molecular orbital composition, absorption wavelength, and oscillator strength were summarized in the right table. In all calculations, 20 types of states ($N_{state} = 20$) for each molecule were solved, and the data with the wavelength range larger than 250 nm were concluded in table for the purpose of comparison with experimental data. The oscillator strength lower than 0.01 were not listed in the table owing to the negligible influence on absorption, i.e., forbidden transitions.

2.4.2. Molecular Orbitals of TB[n]H (n = 3-8)

The Highest Occupied Molecular Orbitals (HOMOs) and Lowest Unoccupied Molecular Orbitals (LUMOs) of TB[n]H (n = 3-8) were simulated using DFT calculations at the B3LYP/6-31G* level of theory (Figure S44). The HOMOs are primarily located on the molecular backbone, while the LUMOs show deviations toward the angular acene moieties with increasing ring number. This observation suggests that the fused benzene rings have stronger electron-withdrawing abilities compared to the DTT unit. Looking from a side-view perspective, it's apparent that as the ring number increases, the HOMOs between terminal rings become more obstructive. This may induce some through-space interactions between orbitals, leading to changes in electronic structures and excited states. These changes could partially contribute to the alterations observed in absorption and emission properties.

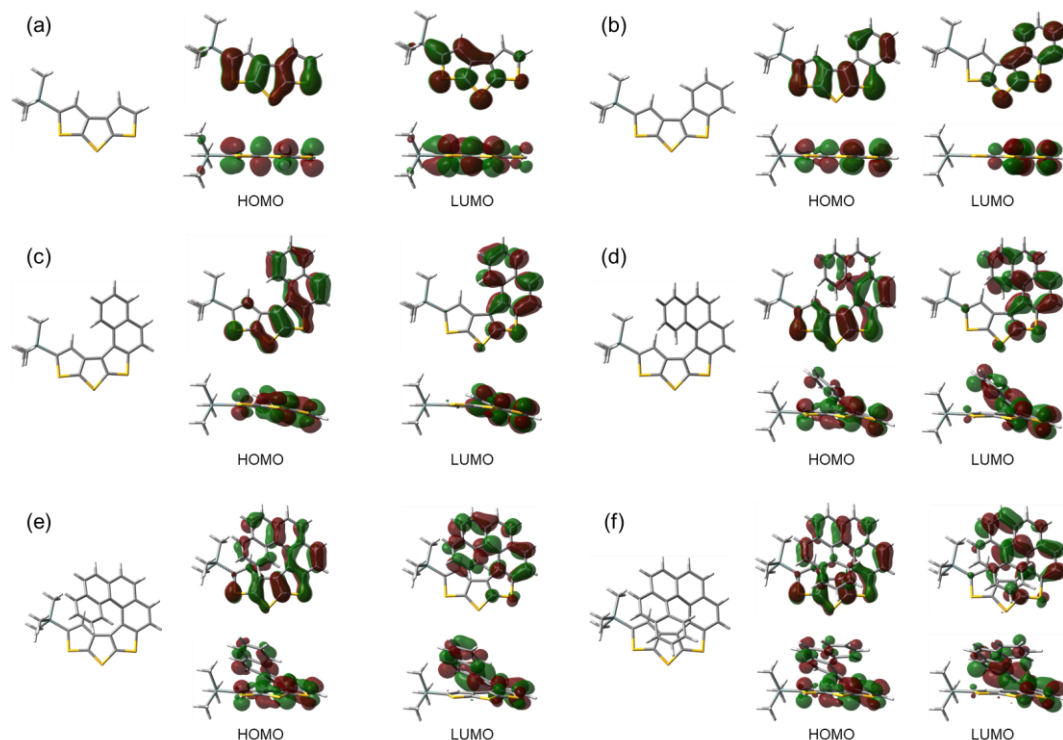


Fig. S46 | Frontier molecular orbitals, HOMOs and LUMOs. a TB[3]H, b TB[4]H, c TB[5]H, d TB[6]H, e TB[7]H, and f TB[8]H. DFT calculations were performed at the B3LYP/6-31G* level of theory (isosurface value = 0.04). Every molecular orbital was two modes, namely top view and side view.

2.4.3. Spin Density of TB[n]H (n = 3-8)

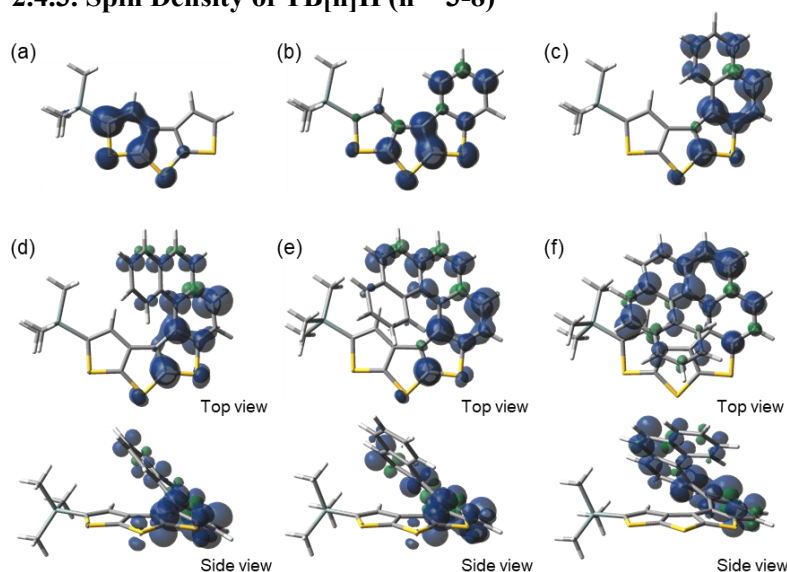
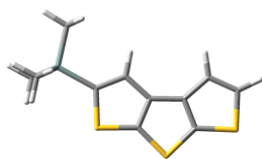


Fig. S47 | Spin density distribution of triplet for a TB[3]H, b TB[4]H, c TB[5]H, d TB[6]H, e TB[7]H, and f TB[8]H. DFT calculations were performed at the B3LYP/6-31G* level of theory (isosurface value = 0.004). Both top views and side view of TB[6]H, TB[7]H, and TB[8]H are shown for more clear observation.

2.4.4. Standard Orientation of Optimized Structures

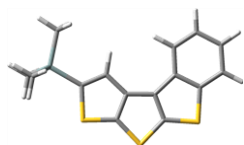
Table S5 | Optimized structure of **TB[3]H** (B3LYP/6-31G*).



Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | 1.66919 | 0.020409 | -0.000006 |
| 2 | 6 | 0 | 0.626954 | 0.917599 | -0.000006 |
| 3 | 6 | 0 | -0.66936 | 0.31327 | -0.000001 |
| 4 | 6 | 0 | -0.58493 | -1.07383 | 0.000003 |
| 5 | 16 | 0 | 1.051559 | -1.6403 | -0.000002 |
| 6 | 6 | 0 | -2.04362 | 0.754957 | -0.000002 |
| 7 | 6 | 0 | -2.91853 | -0.32391 | 0.000001 |
| 8 | 16 | 0 | -2.13518 | -1.89423 | 0.000005 |
| 9 | 6 | 0 | -2.74426 | 2.005272 | -0.000004 |
| 10 | 6 | 0 | -4.09853 | 1.843271 | -0.000002 |
| 11 | 16 | 0 | -4.58537 | 0.158811 | 0.000002 |
| 12 | 14 | 0 | 3.518656 | 0.388907 | 0 |
| 13 | 6 | 0 | 3.726289 | 2.268855 | -0.000072 |
| 14 | 6 | 0 | 4.314218 | -0.35657 | -1.546159 |
| 15 | 6 | 0 | 4.314201 | -0.35643 | 1.546235 |
| 16 | 1 | 0 | 0.784282 | 1.991426 | -0.00001 |
| 17 | 1 | 0 | -2.26224 | 2.976706 | -0.000006 |
| 18 | 1 | 0 | -4.86426 | 2.607448 | -0.000003 |
| 19 | 1 | 0 | 3.273994 | 2.728057 | 0.886501 |
| 20 | 1 | 0 | 4.790948 | 2.532475 | -0.000008 |
| 21 | 1 | 0 | 3.273995 | 2.727988 | -0.886668 |
| 22 | 1 | 0 | 4.178569 | -1.44393 | -1.585054 |
| 23 | 1 | 0 | 5.392818 | -0.15702 | -1.567812 |
| 24 | 1 | 0 | 3.87672 | 0.063334 | -2.459163 |
| 25 | 1 | 0 | 3.876692 | 0.063559 | 2.459194 |
| 26 | 1 | 0 | 4.178555 | -1.44379 | 1.585229 |
| 27 | 1 | 0 | 5.3928 | -0.15687 | 1.567881 |

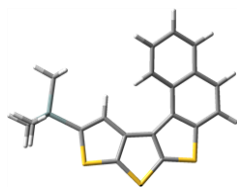
The total electronic energy was calculated to be -1910.4796612 Hartree.

Table S6 | Optimized structure of **TB[4]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | 2.334849 | 0.002648 | -0.000002 |
| 2 | 6 | 0 | 1.102801 | 0.613387 | -0.000002 |
| 3 | 6 | 0 | -0.00467 | -0.293534 | -0.000001 |
| 4 | 6 | 0 | 0.424903 | -1.616198 | 0 |
| 5 | 16 | 0 | 2.150005 | -1.758526 | -0.000001 |
| 6 | 6 | 0 | -1.4453 | -0.212498 | 0 |
| 7 | 6 | 0 | -2.02044 | -1.469268 | 0 |
| 8 | 16 | 0 | -0.87315 | -2.792719 | 0 |
| 9 | 6 | 0 | -2.44047 | 0.835517 | 0 |
| 10 | 6 | 0 | -3.75538 | 0.302591 | 0 |
| 11 | 16 | 0 | -3.76896 | -1.471198 | 0.000001 |
| 12 | 14 | 0 | -2.28288 | 2.231695 | -0.000001 |
| 13 | 6 | 0 | -3.40394 | 3.053295 | -0.000001 |
| 14 | 6 | 0 | -4.69667 | 2.505637 | 0 |
| 15 | 6 | 0 | -4.88253 | 1.125591 | 0 |
| 16 | 1 | 0 | 4.035324 | 0.819511 | 0 |
| 17 | 1 | 0 | 3.768985 | 2.691937 | -0.000008 |
| 18 | 1 | 0 | 4.989955 | 0.294588 | -1.546514 |
| 19 | 1 | 0 | 4.989943 | 0.294601 | 1.546526 |
| 20 | 1 | 0 | 0.993626 | 1.692651 | -0.000002 |
| 21 | 1 | 0 | -1.28714 | 2.665327 | -0.000001 |
| 22 | 1 | 0 | -3.27817 | 4.13238 | -0.000001 |
| 23 | 1 | 0 | -5.56213 | 3.16211 | 0 |
| 24 | 1 | 0 | -5.88211 | 0.700494 | 0.000001 |
| 25 | 1 | 0 | 3.217156 | 3.02456 | 0.886736 |
| 26 | 1 | 0 | 4.734886 | 3.211572 | -0.000004 |
| 27 | 1 | 0 | 3.217167 | 3.024554 | -0.88676 |
| 28 | 1 | 0 | 5.12889 | -0.792355 | -1.585336 |
| 29 | 1 | 0 | 5.985094 | 0.755948 | -1.568662 |
| 30 | 1 | 0 | 4.461462 | 0.592554 | -2.45931 |
| 31 | 1 | 0 | 5.985085 | 0.755957 | 1.568675 |
| 32 | 1 | 0 | 4.461445 | 0.592582 | 2.459314 |
| 33 | 1 | 0 | 5.128873 | -0.792341 | 1.585364 |

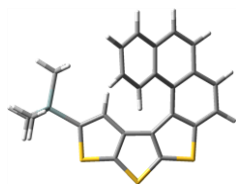
The total electronic energy was calculated to be -2064.1322527 Hartree.

Table S7 | Optimized structure of **TB[5]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|----------|
| | | | X | Y | Z |
| 1 | 16 | 0 | 2.86079 | -1.77643 | -0.15904 |
| 2 | 16 | 0 | 0.126582 | -3.38105 | -0.20121 |
| 3 | 16 | 0 | -2.94451 | -2.73702 | 0.089911 |
| 4 | 14 | 0 | 4.197795 | 1.093203 | 0.163147 |
| 5 | 6 | 0 | 1.376486 | 0.339406 | 0.038904 |
| 6 | 1 | 0 | 1.084795 | 1.36915 | 0.190355 |
| 7 | 6 | 0 | 2.700251 | -0.02788 | 0.0156 |
| 8 | 6 | 0 | 0.450716 | -0.74921 | -0.09766 |
| 9 | 6 | 0 | 1.141072 | -1.95928 | -0.1862 |
| 10 | 6 | 0 | -0.98641 | -0.96713 | -0.09049 |
| 11 | 6 | 0 | -1.26511 | -2.33021 | -0.09607 |
| 12 | 6 | 0 | -2.20958 | -0.18815 | -0.00596 |
| 13 | 6 | 0 | -3.33224 | -1.01913 | 0.157998 |
| 14 | 6 | 0 | -4.6362 | -0.52204 | 0.368528 |
| 15 | 1 | 0 | -5.46538 | -1.20743 | 0.514283 |
| 16 | 6 | 0 | -4.8252 | 0.835221 | 0.404865 |
| 17 | 1 | 0 | -5.81399 | 1.245497 | 0.589798 |
| 18 | 6 | 0 | -3.7481 | 1.734684 | 0.158284 |
| 19 | 6 | 0 | -2.43054 | 1.228493 | -0.09682 |
| 20 | 6 | 0 | -1.42952 | 2.148993 | -0.48987 |
| 21 | 1 | 0 | -0.46833 | 1.772773 | -0.80703 |
| 22 | 6 | 0 | -1.68114 | 3.503925 | -0.54617 |
| 23 | 1 | 0 | -0.89528 | 4.18468 | -0.86103 |
| 24 | 6 | 0 | -2.95699 | 4.007664 | -0.21657 |
| 25 | 1 | 0 | -3.1454 | 5.076674 | -0.25177 |
| 26 | 6 | 0 | -3.96937 | 3.134079 | 0.113662 |
| 27 | 1 | 0 | -4.9683 | 3.505804 | 0.327755 |
| 28 | 6 | 0 | 3.558121 | 2.864259 | 0.269213 |
| 29 | 1 | 0 | 4.393401 | 3.56794 | 0.364336 |
| 30 | 1 | 0 | 2.991588 | 3.140488 | -0.6272 |
| 31 | 1 | 0 | 2.90623 | 3.005069 | 1.138764 |
| 32 | 6 | 0 | 5.290007 | 0.868329 | -1.35826 |
| 33 | 1 | 0 | 5.632259 | -0.16901 | -1.45173 |
| 34 | 1 | 0 | 4.745157 | 1.121261 | -2.2746 |
| 35 | 1 | 0 | 6.178752 | 1.508465 | -1.30446 |
| 36 | 6 | 0 | 5.165142 | 0.640225 | 1.717654 |
| 37 | 1 | 0 | 6.054928 | 1.271604 | 1.829223 |
| 38 | 1 | 0 | 4.547663 | 0.764129 | 2.614263 |
| 39 | 1 | 0 | 5.498721 | -0.40355 | 1.686617 |

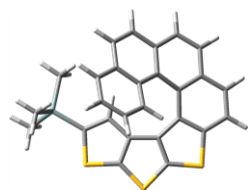
The total electronic energy was calculated to be -2217.7701188 Hartree.

Table S8 | Optimized structure of **TB[6]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|----------|
| | | | X | Y | Z |
| 1 | 16 | 0 | 2.979209 | -3.11426 | 0.142752 |
| 2 | 16 | 0 | -2.84347 | -2.21293 | 0.08627 |
| 3 | 16 | 0 | -0.09379 | -3.7795 | 0.451164 |
| 4 | 14 | 0 | -4.13916 | 0.646376 | -0.52651 |
| 5 | 6 | 0 | -0.44033 | -1.18502 | 0.046654 |
| 6 | 6 | 0 | -1.34663 | -0.12226 | -0.27037 |
| 7 | 1 | 0 | -1.02984 | 0.886034 | -0.49229 |
| 8 | 6 | 0 | 0.992446 | -1.37231 | 0.156944 |
| 9 | 6 | 0 | 2.195536 | -0.57346 | -0.00741 |
| 10 | 6 | 0 | -0.38799 | 2.493026 | 1.873953 |
| 11 | 6 | 0 | -2.66931 | -0.49053 | -0.27499 |
| 12 | 6 | 0 | 1.462359 | 1.832702 | 0.428025 |
| 13 | 6 | 0 | 2.390643 | 0.842852 | -0.08781 |
| 14 | 6 | 0 | 0.476348 | 1.52596 | 1.393861 |
| 15 | 6 | 0 | 1.624996 | 3.202592 | 0.056127 |
| 16 | 6 | 0 | 3.328925 | -1.40723 | -0.14701 |
| 17 | 6 | 0 | -1.12619 | -2.38434 | 0.228335 |
| 18 | 6 | 0 | 0.702821 | 4.164884 | 0.525249 |
| 19 | 1 | 0 | 0.822833 | 5.19715 | 0.206302 |
| 20 | 6 | 0 | 2.773454 | 3.593969 | -0.70405 |
| 21 | 1 | 0 | 2.878765 | 4.637834 | -0.98728 |
| 22 | 6 | 0 | -0.30098 | 3.818191 | 1.409123 |
| 23 | 1 | 0 | -0.99274 | 4.571476 | 1.774962 |
| 24 | 6 | 0 | 3.758137 | 2.695881 | -0.97655 |
| 25 | 1 | 0 | 4.674277 | 3.012454 | -1.46821 |
| 26 | 6 | 0 | 1.292045 | -2.72055 | 0.310601 |
| 27 | 6 | 0 | 3.616686 | 1.307739 | -0.64644 |
| 28 | 6 | 0 | -5.10184 | 0.766111 | 1.092502 |
| 29 | 1 | 0 | -4.47079 | 1.172947 | 1.890744 |
| 30 | 1 | 0 | -5.45431 | -0.21939 | 1.418347 |
| 31 | 1 | 0 | -5.97807 | 1.41742 | 0.98851 |
| 32 | 6 | 0 | -5.25157 | -0.04768 | -1.88263 |
| 33 | 1 | 0 | -6.1255 | 0.594374 | -2.0457 |
| 34 | 1 | 0 | -5.61824 | -1.04806 | -1.6238 |
| 35 | 1 | 0 | -4.7095 | -0.1287 | -2.83138 |
| 36 | 6 | 0 | -3.45041 | 2.333099 | -1.01186 |
| 37 | 1 | 0 | -4.26314 | 3.058158 | -1.13842 |
| 38 | 1 | 0 | -2.90003 | 2.281898 | -1.95799 |
| 39 | 1 | 0 | -2.76788 | 2.724487 | -0.24892 |
| 40 | 6 | 0 | 4.582916 | -0.92514 | -0.55363 |
| 41 | 1 | 0 | 5.424106 | -1.601 | -0.67099 |
| 42 | 6 | 0 | 4.692233 | 0.410714 | -0.86842 |
| 43 | 1 | 0 | 5.624207 | 0.803777 | -1.26472 |
| 44 | 1 | 0 | -1.1323 | 2.224632 | 2.617973 |
| 45 | 1 | 0 | 0.409336 | 0.517106 | 1.779771 |

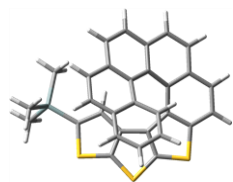
The total electronic energy was calculated to be -2371.405684 Hartree.

Table S9 | Optimized structure of **TB[7]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|----------|
| | | | X | Y | Z |
| 1 | 16 | 0 | 3.393285 | -2.92286 | 0.143171 |
| 2 | 16 | 0 | -2.48391 | -2.57256 | -0.25405 |
| 3 | 16 | 0 | 0.378239 | -3.87483 | 0.253228 |
| 4 | 14 | 0 | -4.02149 | 0.130092 | -0.95235 |
| 5 | 6 | 0 | -0.18277 | -1.33431 | -0.2488 |
| 6 | 6 | 0 | -1.16836 | -0.36362 | -0.61766 |
| 7 | 1 | 0 | -0.93583 | 0.664181 | -0.85396 |
| 8 | 6 | 0 | 1.252326 | -1.38983 | -0.07211 |
| 9 | 6 | 0 | 2.379231 | -0.4771 | -0.1411 |
| 10 | 6 | 0 | 0.472505 | 0.550874 | 2.061311 |
| 11 | 6 | 0 | -0.76316 | 2.475466 | 1.232468 |
| 12 | 6 | 0 | -2.45151 | -0.84862 | -0.65092 |
| 13 | 6 | 0 | 1.365865 | 1.868216 | 0.101781 |
| 14 | 6 | 0 | 2.431718 | 0.95407 | -0.25363 |
| 15 | 6 | 0 | 0.361947 | 1.598979 | 1.114816 |
| 16 | 6 | 0 | 1.36559 | 3.153978 | -0.49928 |
| 17 | 6 | 0 | 3.59678 | -1.19334 | -0.15339 |
| 18 | 6 | 0 | -0.76403 | -2.58604 | -0.05911 |
| 19 | 6 | 0 | -1.78549 | 2.182745 | 2.165129 |
| 20 | 1 | 0 | -2.64442 | 2.847234 | 2.216876 |
| 21 | 6 | 0 | 0.23419 | 4.013366 | -0.34948 |
| 22 | 1 | 0 | 0.235228 | 4.960226 | -0.88287 |
| 23 | 6 | 0 | -0.52561 | 0.301339 | 2.980791 |
| 24 | 6 | 0 | 2.517259 | 3.6141 | -1.20384 |
| 25 | 1 | 0 | 2.497751 | 4.611708 | -1.63403 |
| 26 | 6 | 0 | -0.81897 | 3.662219 | 0.441204 |
| 27 | 1 | 0 | -1.68609 | 4.310858 | 0.534073 |
| 28 | 6 | 0 | 3.649805 | 2.856119 | -1.24701 |
| 29 | 1 | 0 | 4.564117 | 3.245352 | -1.68671 |
| 30 | 6 | 0 | 1.666812 | -2.69748 | 0.143686 |
| 31 | 6 | 0 | -1.68535 | 1.099568 | 3.012693 |
| 32 | 1 | 0 | -2.4763 | 0.885021 | 3.725269 |
| 33 | 6 | 0 | 3.64421 | 1.510461 | -0.77279 |
| 34 | 6 | 0 | -4.93565 | 0.342207 | 0.684775 |
| 35 | 1 | 0 | -4.29029 | 0.837253 | 1.417824 |
| 36 | 1 | 0 | -5.22825 | -0.62873 | 1.101103 |
| 37 | 1 | 0 | -5.84505 | 0.942902 | 0.561846 |
| 38 | 6 | 0 | -5.11144 | -0.80617 | -2.17558 |
| 39 | 1 | 0 | -6.049 | -0.26874 | -2.36195 |
| 40 | 1 | 0 | -5.37082 | -1.80217 | -1.79719 |
| 41 | 1 | 0 | -4.60107 | -0.93919 | -3.13599 |
| 42 | 6 | 0 | -3.5126 | 1.80532 | -1.65062 |
| 43 | 1 | 0 | -4.39345 | 2.436689 | -1.81761 |
| 44 | 1 | 0 | -2.99301 | 1.695501 | -2.609 |
| 45 | 1 | 0 | -2.84303 | 2.337292 | -0.96673 |
| 46 | 6 | 0 | 4.829029 | -0.5967 | -0.46952 |
| 47 | 1 | 0 | 5.741598 | -1.18413 | -0.48403 |
| 48 | 6 | 0 | 4.825047 | 0.725783 | -0.84627 |
| 49 | 1 | 0 | 5.73843 | 1.197247 | -1.1977 |
| 50 | 1 | 0 | -0.41021 | -0.51511 | 3.687335 |
| 51 | 1 | 0 | 1.364341 | -0.06033 | 2.073375 |

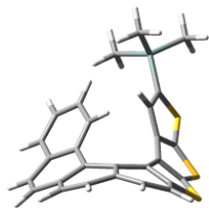
The total electronic energy was calculated to be -2525.2009422 Hartree.

Table S10 | Optimized structure of **TB[8]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|----------|
| | | | X | Y | Z |
| 1 | 16 | 0 | 3.306282 | -2.67917 | -0.88004 |
| 2 | 16 | 0 | -2.57689 | -2.32624 | -0.72979 |
| 3 | 16 | 0 | 0.310915 | -3.66252 | -0.64004 |
| 4 | 14 | 0 | -4.16458 | 0.403915 | -1.08951 |
| 5 | 6 | 0 | -0.28126 | -1.08237 | -0.74328 |
| 6 | 6 | 0 | -1.28766 | -0.08023 | -0.91893 |
| 7 | 1 | 0 | -1.06829 | 0.969859 | -1.0477 |
| 8 | 6 | 0 | 1.162081 | -1.1503 | -0.70058 |
| 9 | 6 | 0 | 2.280646 | -0.23035 | -0.70478 |
| 10 | 6 | 0 | 0.48439 | 0.313452 | 1.8919 |
| 11 | 6 | 0 | -0.82638 | 2.306131 | 1.316788 |
| 12 | 6 | 0 | -2.57147 | -0.56758 | -0.92037 |
| 13 | 6 | 0 | 1.311673 | 1.997646 | 0.134977 |
| 14 | 6 | 0 | 2.343235 | 1.188342 | -0.49625 |
| 15 | 6 | 0 | 0.337903 | 1.519125 | 1.091672 |
| 16 | 6 | 0 | 1.287188 | 3.385917 | -0.19438 |
| 17 | 6 | 0 | 3.492934 | -0.92407 | -0.91835 |
| 18 | 6 | 0 | -0.8486 | -2.35241 | -0.66905 |
| 19 | 6 | 0 | -1.93251 | 1.762662 | 2.041031 |
| 20 | 1 | 0 | -2.82723 | 2.371659 | 2.140267 |
| 21 | 6 | 0 | 0.157673 | 4.179279 | 0.143528 |
| 22 | 1 | 0 | 0.146278 | 5.222141 | -0.16144 |
| 23 | 6 | 0 | -0.66531 | -0.23708 | 2.536091 |
| 24 | 6 | 0 | 2.411794 | 3.99235 | -0.83056 |
| 25 | 1 | 0 | 2.376416 | 5.059567 | -1.03175 |
| 26 | 6 | 0 | -0.9021 | 3.631617 | 0.809739 |
| 27 | 1 | 0 | -1.79483 | 4.216835 | 1.013794 |
| 28 | 6 | 0 | 3.531873 | 3.266252 | -1.10063 |
| 29 | 1 | 0 | 4.426551 | 3.743743 | -1.49083 |
| 30 | 6 | 0 | 1.587303 | -2.47196 | -0.71918 |
| 31 | 6 | 0 | -1.88685 | 0.502836 | 2.554146 |
| 32 | 1 | 0 | -2.75088 | 0.070093 | 3.050657 |
| 33 | 6 | 0 | 3.530937 | 1.846938 | -0.94636 |
| 34 | 6 | 0 | -5.16373 | 0.271657 | 0.506591 |
| 35 | 1 | 0 | -4.60535 | 0.68895 | 1.350053 |
| 36 | 1 | 0 | -5.39065 | -0.77464 | 0.742575 |
| 37 | 1 | 0 | -6.11584 | 0.809667 | 0.424352 |
| 38 | 6 | 0 | -5.17379 | -0.31562 | -2.51317 |
| 39 | 1 | 0 | -6.11865 | 0.225863 | -2.64296 |
| 40 | 1 | 0 | -5.41676 | -1.36992 | -2.33539 |
| 41 | 1 | 0 | -4.6185 | -0.25868 | -3.45603 |
| 42 | 6 | 0 | -3.6979 | 2.194693 | -1.44658 |
| 43 | 1 | 0 | -4.5952 | 2.821366 | -1.51282 |
| 44 | 1 | 0 | -3.15982 | 2.28111 | -2.39722 |
| 45 | 1 | 0 | -3.05512 | 2.606321 | -0.66226 |
| 46 | 6 | 0 | 4.709956 | -0.27179 | -1.17579 |
| 47 | 1 | 0 | 5.616589 | -0.84028 | -1.35736 |
| 48 | 6 | 0 | 4.696448 | 1.100532 | -1.26366 |
| 49 | 1 | 0 | 5.592452 | 1.640217 | -1.5567 |
| 50 | 6 | 0 | 1.72909 | -0.31357 | 2.135869 |
| 51 | 6 | 0 | -0.56213 | -1.47096 | 3.218975 |
| 52 | 6 | 0 | 0.65289 | -2.10992 | 3.350321 |
| 53 | 1 | 0 | 0.721527 | -3.05665 | 3.877957 |
| 54 | 6 | 0 | 1.814121 | -1.49724 | 2.84128 |
| 55 | 1 | 0 | 2.785529 | -1.955 | 3.003162 |
| 56 | 1 | 0 | -1.45942 | -1.8922 | 3.664794 |
| 57 | 1 | 0 | 2.635693 | 0.148112 | 1.769749 |

The total electronic energy was calculated to be -2678.8614708 Hartree.

Table S11 | Optimized structure of transition-state **TB[7]H** (B3LYP/6-31G*).

Standard orientation

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|----------|----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | -4.24247 | -1.5402 | 1.881124 |
| 2 | 6 | 0 | -3.62071 | -2.63628 | 1.376571 |
| 3 | 6 | 0 | -3.85174 | -0.25218 | 1.43269 |
| 4 | 6 | 0 | -2.47805 | -2.42652 | 0.590171 |
| 5 | 6 | 0 | -2.61696 | -0.01281 | 0.755584 |
| 6 | 6 | 0 | -1.79587 | -1.19905 | 0.468999 |
| 7 | 6 | 0 | -4.90135 | 0.714121 | 1.450354 |
| 8 | 6 | 0 | -4.87645 | 1.748929 | 0.581095 |
| 9 | 6 | 0 | -3.68892 | 2.017975 | -0.14817 |
| 10 | 6 | 0 | -2.50486 | 1.302629 | 0.120735 |
| 11 | 1 | 0 | -5.14623 | -1.63609 | 2.473519 |
| 12 | 1 | 0 | -4.00422 | -3.63841 | 1.534859 |
| 13 | 1 | 0 | -5.78666 | 0.499325 | 2.040031 |
| 14 | 1 | 0 | -5.73769 | 2.394793 | 0.441642 |
| 15 | 6 | 0 | -3.70724 | 3.04665 | -1.14634 |
| 16 | 6 | 0 | -1.29037 | 1.993248 | -0.26241 |
| 17 | 6 | 0 | -1.31782 | 3.008548 | -1.25624 |
| 18 | 6 | 0 | -2.57633 | 3.449066 | -1.76865 |
| 19 | 1 | 0 | -4.67019 | 3.476516 | -1.40551 |
| 20 | 1 | 0 | -2.59799 | 4.197521 | -2.55466 |
| 21 | 6 | 0 | -0.56931 | -2.67301 | -0.89415 |
| 22 | 6 | 0 | -0.50814 | -1.46582 | -0.22179 |
| 23 | 6 | 0 | 1.632595 | -1.73231 | -1.18227 |
| 24 | 6 | 0 | 0.888791 | -1.01047 | -0.26193 |
| 25 | 6 | 0 | 1.785648 | -0.26501 | 0.57847 |
| 26 | 6 | 0 | -0.12765 | 1.874332 | 0.508807 |
| 27 | 6 | 0 | -0.13347 | 3.697294 | -1.58098 |
| 28 | 6 | 0 | 3.101336 | -0.32867 | 0.221509 |
| 29 | 6 | 0 | 0.993063 | 2.630408 | 0.245768 |
| 30 | 6 | 0 | 1.012671 | 3.510863 | -0.8434 |
| 31 | 1 | 0 | 1.482109 | 0.258831 | 1.469511 |
| 32 | 1 | 0 | -0.17202 | 1.227076 | 1.374545 |
| 33 | 1 | 0 | 1.8629 | 2.552143 | 0.886784 |
| 34 | 1 | 0 | 1.908963 | 4.080274 | -1.06797 |
| 35 | 1 | 0 | -0.1637 | 4.437259 | -2.37548 |
| 36 | 16 | 0 | 3.318631 | -1.38303 | -1.15853 |
| 37 | 16 | 0 | 0.807545 | -3.09969 | -1.86277 |
| 38 | 16 | 0 | -1.87437 | -3.70298 | -0.44055 |
| 39 | 14 | 0 | 4.538461 | 0.58595 | 1.006474 |
| 40 | 6 | 0 | 6.007535 | -0.578 | 1.124751 |
| 41 | 1 | 0 | 6.313045 | -0.94163 | 0.137902 |
| 42 | 1 | 0 | 6.870086 | -0.07166 | 1.570778 |
| 43 | 1 | 0 | 5.771829 | -1.44999 | 1.742722 |
| 44 | 6 | 0 | 3.995287 | 1.134763 | 2.71942 |
| 45 | 1 | 0 | 3.153983 | 1.834289 | 2.688399 |
| 46 | 1 | 0 | 3.697285 | 0.279259 | 3.333484 |
| 47 | 1 | 0 | 4.820762 | 1.641046 | 3.230851 |
| 48 | 6 | 0 | 4.987565 | 2.071667 | -0.05433 |
| 49 | 1 | 0 | 4.137433 | 2.750951 | -0.17079 |
| 50 | 1 | 0 | 5.812882 | 2.636822 | 0.391891 |
| 51 | 1 | 0 | 5.299392 | 1.758582 | -1.05593 |

The total electronic energy was calculated to be -2525.1323306 Hartree.

2.4.5. Illustration of the Transition Orbital Composition

The orbital transition composition (or transition configuration) refers to the transition between different occupied and unoccupied orbitals. In the primary content, having the same orbital transition composition for the T_n state as the S_1 state indicates that the T_n states share a common transition path from occupied to unoccupied orbitals, such as HOMO \rightarrow LUMO (H \rightarrow L), HOMO-1 \rightarrow LUMO (H-1 \rightarrow L), HOMO \rightarrow LUMO+1 (H \rightarrow L+1). In this study, we computed the orbital transition compositions of S_1 and T_n states for TB[n]H (n=3-8). Taking TB[3]H as an example, the orbital transition composition of the S_1 state involves three transition configurations: H \rightarrow L, H-1 \rightarrow L, and H \rightarrow L+1. The intersystem crossing (ISC) process necessitates that the triplets have these transition configurations. Upon analyzing the triplet states, we observed that T_1 , T_2 , T_3 , T_4 , and T_6 states contain the same transition configurations as the S_1 state, albeit with different contributions (Fig. S51). Similarly, we applied this analysis to the other molecules in this study.

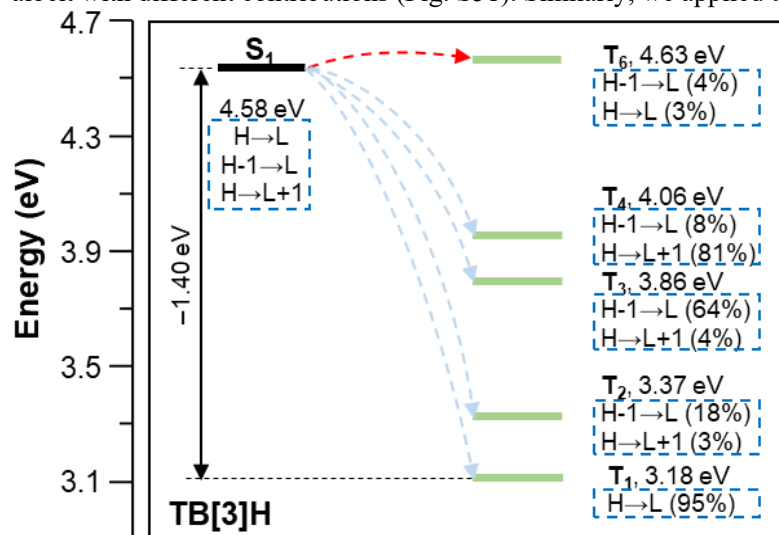


Fig. S48 | The diagram of transition from the first excited singlet (S_1) to triplets (T_n) for TB[3]H. The transition orbital compositions of S_1 state and triplet states are highlighted with blue dashed frame with the related contribution in each bracket.

2.5. Chiral Resolutions and Chiroptical Spectra

2.5.1. Chiral Resolution of Racemic TB[7]H

The racemic mixture of TB[7]H was subjected to chiral resolution through preparative high-performance liquid chromatography (HPLC) using a supercritical fluid chromatographic technique with a CO₂/isopropanol mixture (65:35, v/v) as the mobile phase. A chiral chromatographic column coated with polysaccharide derivatives in the normal phase (EnantioPak®Y1, Guangzhou Research & Creativity Biotechnology, Co., Ltd) was employed for the separation. The HPLC chromatograms are displayed in Fig. S48. The first eluted enantiomer ((*P*)-TB[7]H) had a retention time (Rt) of approximately 6.5 minutes, while the second eluted enantiomer ((*M*)-TB[7]H) had an Rt of approximately 7.8 minutes. This significant difference in Rt facilitated their successful separation, resulting in (*P*)-TB[7]H and (*M*)-TB[7]H with purities of 99.795% and 99.10%, respectively.

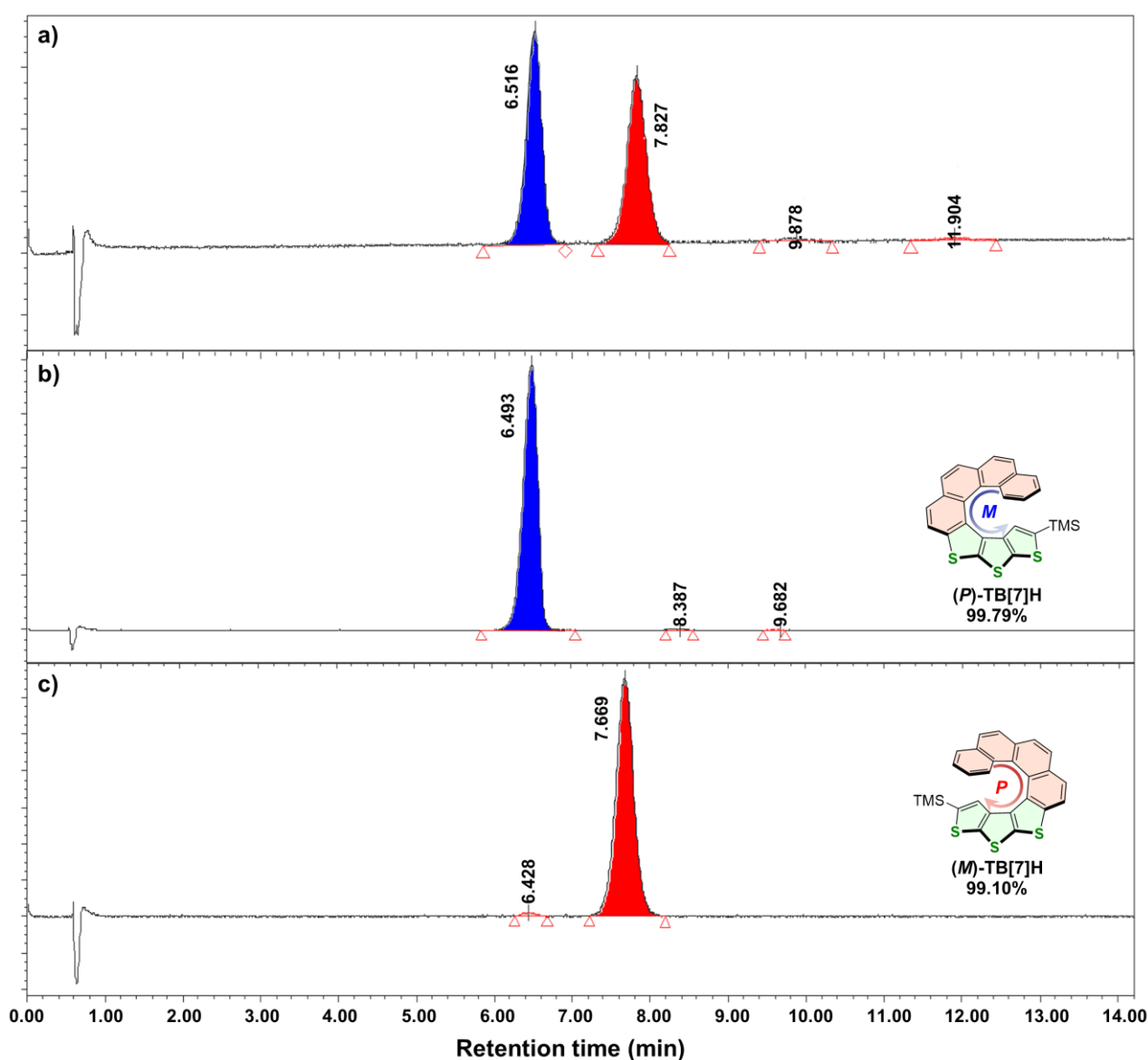


Fig. S49 | HPLC spectra of TB[7]H. **a** before separation, **b** the first eluted enantiomer, i.e. (*M*)-TB[7]H; **c** the second eluted enantiomer, i.e. (*P*)-TB[7]H.

2.5.2. Racemization Barrier and Simulated CD Spectra

The racemization barrier was calculated at the B3LYP/6-31G* level of theory. The transition state exhibited a saddle-shaped configuration, which is similar to the currently accepted transition structure in literature. The

racemization barrier was determined as 43.2 kcal/mol, coinciding with the majority of [7]helicenes (Fig. S49a).¹⁰ The higher interconversion energy indicated that the two conformers are stable enough to be separated, stored, and chiroptical studies.¹¹

The CD spectra of both enantiomers of **TB[7]H** were simulated through TD-DFT calculations at the B3LYP/6-31G(d) level of theory. These enantiomers displayed mirror-image CD profiles. Specifically, (*P*)-**TB[7]H** exhibited positive signals in the wavelength range of 270-330 nm and 360-420 nm, while (*M*)-**TB[7]H** exhibited negative signals in the same regions. Based on the agreement between the simulated and experimental CD spectra, the absolute configurations of the two HPLC-eluted fractions can be confidently assigned as follows: the first eluted fraction (Rt: 6.493 min) corresponds to the (*M*)-enantiomer, which exhibits a left-handed helix configuration; the second eluted fraction (Rt: 7.669 min) corresponds to the (*P*)-enantiomer, presenting a right-handed helix configuration (Fig. S49b).

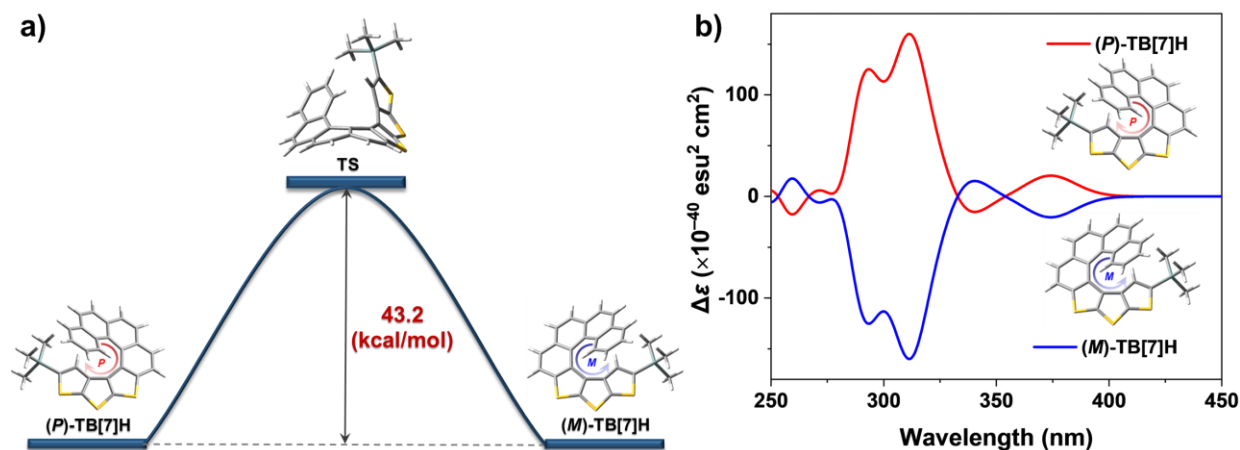


Fig. S50 | Calculations of *P* and *M* conformers of TBH. **a** Interconversion barrier of *P* and *M* conformers (B3LYP/6-31G*). **b** Simulated CD spectra and optimized structures of (*P*)-**TB[7]H** and (*M*)-**TB[7]H** at the theory level of B3LYP/6-31G(d).

2.5.3. Comparison of Spectra between Chiral and Achiral Spectra

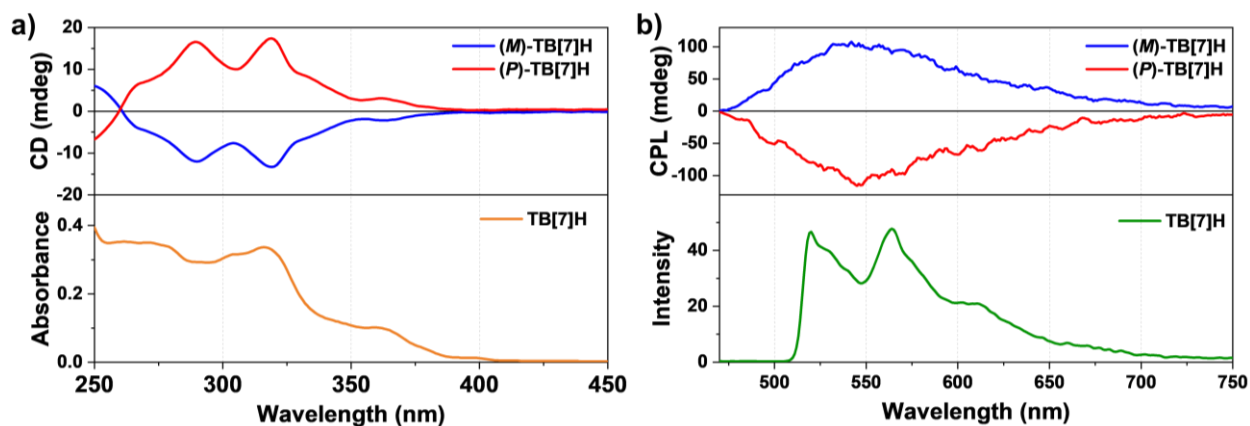


Fig. S51 | Spectra Comparison of racemic **TB[7]H and enantiomers ((*M*)-**TB[7]H** and (*P*)-**TB[7]H**):** **a** UV-vis and CD spectra; **b** phosphorescent and CPL spectra (77 K).

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