

Supporting Information

Synthesis of aza[5]helicene-incorporated macrocyclic heteroarene via oxidation of o-phenylene-pyrrole-thiophene icosamer

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1. Instrumentation and Materials

Synthesis

Commercially available solvents and reagents were used without further purification unless otherwise noted. 1,2-Bis(5-bromothiophen-2-yl)benzene,^[S1] 2,5-bis(2-(1*H*-pyrrol-2-yl)phenyl)thiophene,^[S1] and 2,5-bis(2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrol-2-yl)phenyl)-1*H*-pyrrole^[S2] were prepared according to the reported procedures. Dry toluene and dichloromethane were used after distillation. Dry THF and dioxane were obtained by passing through alumina under N₂ in a solvent purification system. The spectroscopic grade solvents were used as solvents for all spectroscopic studies. Silica gel column chromatography was performed on Wako gel C-400. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (Merck 5554).

NMR and mass spectra

¹H and ¹³C NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600 MHz for ¹H and 151 MHz for ¹³C) and chemical shifts were reported as the δ scale in ppm relative to internal standards CHCl₃ (δ = 7.26 ppm for ¹H, 77.16 ppm for ¹³C), DMSO (δ = 2.50 ppm for ¹H, 39.52 ppm for ¹³C), and acetone (δ = 2.05 ppm for ¹H, δ = 29.84 ppm for ¹³C). HR-APCI-TOF-MS was recorded on a BRUKER micrOTOF model or Thermo Fisher Scientific LTQ orbitrap XL model using positive mode.

Optical properties

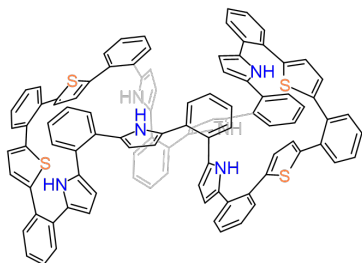
UV-visible absorption spectra were recorded on a Shimadzu UV-3600. Fluorescence spectra were recorded on a JASCO FP-8500 spectrometer. Absolute fluorescence quantum yields were determined on a HAMAMATSU C9920-02S. Fluorescence lifetime was recorded on a Hamamatsu Photonics QuantaTaurus-Tau C11367.

X-Ray crystallography

Single-crystal diffraction analysis data were collected at -180 °C with a Rigaku XtaLAB P200 by using graphite monochromated Cu-*K* α radiation (λ = 1.54187 Å) or with a Rigaku Saturn724+ CCD diffractometer with a graphite-monochromated Mo *K* α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXT-2014/5) and refined with full-matrix least squares technique (SHELXT-2014/7).^[S3]

2. Experimental Section

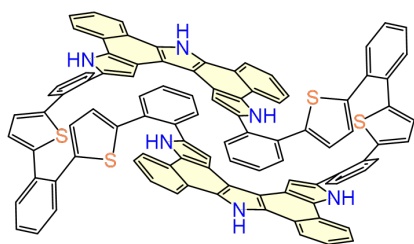
Compound 4



Procedure: A 2 L three-neck round-bottom flask was charged with XPhos Pd G2 (365 mg, 0.47 mmol, 5.0 mol%), **1** (5.12 g, 9.3 mmol), and **2** (6.13 g, 10.2 mmol, 1.1 eq.). The reaction flask was evacuated and purged with argon three times. After the mixture was dissolved in dry THF (720 mL) and 0.5 M tripotassium phosphate solution (200 mL, 100 mmol, 11 eq.), the reaction mixture was stirred at room

temperature for 24 h. After quenched with saturated aqueous ammonium chloride solution, the mixture was extracted with dichloromethane three times and the combined organic layers were washed with water and brine, and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, the residue was purified by column chromatography on silica with dichloromethane/*n*-hexane (*v/v* = 1/3) as eluent gave **3** (396 mg, yield: 6%) as pale yellow solids. **m.p.** 186.5–203.0 °C. ^1H NMR (600 MHz, acetone-*d*₆, room temperature) δ = 9.07 (s, 4H, pyrrole), 8.98 (s, 2H, pyrrole), 7.36–7.35 (m, 4H, phenyl), 7.30–7.29 (m, 12H, phenyl), 7.24–7.16 (m, 16H, phenyl), 7.06–7.03 (m, 8H, phenyl), 6.65 (d, *J* = 3.7 Hz, 4H, thiophene), 6.57 (d, *J* = 3.7 Hz, 4H, thiophene), 5.99 (d, *J* = 2.3 Hz, 4H, pyrrole), 5.95 (dd, *J* = 6.0, 3.0 Hz, 4H, pyrrole), and 5.87 (dd, *J* = 6.0, 3.0 Hz, 4H, pyrrole) ppm. ^{13}C NMR (101 MHz, acetone-*d*₆, room temperature) δ = 144.52, 143.38, 134.23, 133.22, 132.73, 132.58, 132.44, 131.89, 131.80, 131.69, 131.55, 131.54, 130.18, 130.01, 129.78, 128.95, 128.92, 128.20, 127.74, 127.59, 127.53, 127.41, 110.88, 110.02, and 109.91 ppm. **HR-APCI-TOF-MS** Found: *m/z* = 1479.4320 [*M*]⁺, calcd for C₁₀₀H₆₆N₆S₄: *m/z* = 1479.4305. **UV/vis** (THF, room temperature): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹) = 292 (4.6 × 10⁴). **Fluorescence** (THF, λ_{ex} = 300 nm) λ_{max} = 511 nm (Φ_{F} = 0.110).

Compound 5



Procedure: A 200 mL three-necked round bottom flask was charged with **3** (74.0 mg, 0.050 mmol) and dry dichloromethane (120 mL) under argon, which was cooled to -78 °C. PIFA (323 mg, 0.75 mmol, 15 eq.) was then added, and the reaction mixture was kept at -78 °C for 3 h. Then, the reaction system was allowed to

warm to ambient temperature. Next, excess amount of sodium borohydride and methanol were added, and the reaction was kept for 10 min. The mixture was extracted with dichloromethane three times and the combined organic layers were washed with water and brine, and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, recrystallization from THF gave **5** (42.9 mg, yield: 58%) as pale yellow solids. **m.p.** >350 °C

(decomp.). **¹H NMR** (600 MHz, DMSO-*d*₆, 100 °C) δ = 12.02 (s, 2H, pyrrole), 11.54 (s, 4H, pyrrole), 8.81 (d, *J* = 7.8 Hz, 4H, phenyl), 8.47 (d, *J* = 7.8 Hz, 4H, phenyl), 7.59 (d, *J* = 7.8 Hz, 4H, phenyl), 7.52 (t, *J* = 7.6 Hz, 4H, phenyl), 7.47 (t, *J* = 7.3 Hz, 4H, phenyl), 7.30 (t, *J* = 7.3 Hz, 4H, phenyl), 7.19 (d, *J* = 7.3 Hz, 4H phenyl), 7.15 (t, *J* = 7.6 Hz, 4H, phenyl), 6.97 (d, *J* = 2.4 Hz, 4H, pyrrole), 6.84–6.82 (m, 8H, phenyl), 6.26 (d, *J* = 3.7 Hz, 4H, thiophene), and 5.94 (d, *J* = 3.7 Hz, 4H, thiophene) ppm. **¹³C NMR** (151 MHz, DMSO-*d*₆, 100°C) δ = 142.31, 141.04, 133.53, 132.89, 132.20, 131.91, 130.30, 129.38, 129.36, 128.80, 126.85, 126.79, 126.71, 126.50, 126.20, 125.83, 123.38, 122.47, 121.78, 120.90, 120.54, 119.47, 118.45, 112.78, and 104.35 ppm. **HR-APCI-TOF-MS** Found: *m/z* = 1471.3682 [*M*]⁺, calcd for C₁₀₀H₅₈N₆S₄: *m/z* = 1471.3679. **UV/vis** (THF, room temperature): λ_{max} / nm (ϵ / M⁻¹ cm⁻¹) = 313 (1.2 × 10⁵) and 399 (2.8 × 10⁴). **Fluorescence** (THF, λ_{ex} = 400 nm) λ_{max} = 528 nm (Φ_{F} = 0.072).

3. NMR Spectra

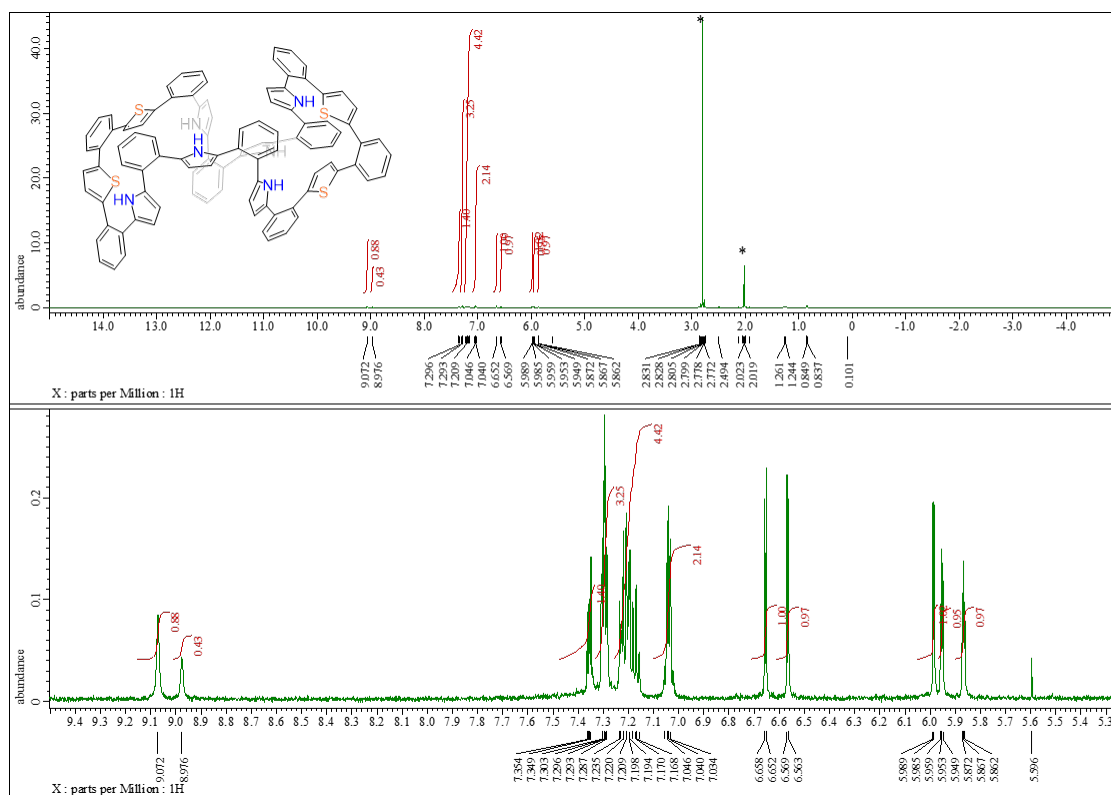


Figure S3-1. ^1H NMR spectrum of **4** in acetone- d_6 at room temperature. Peaks with * are due to the residual solvents.

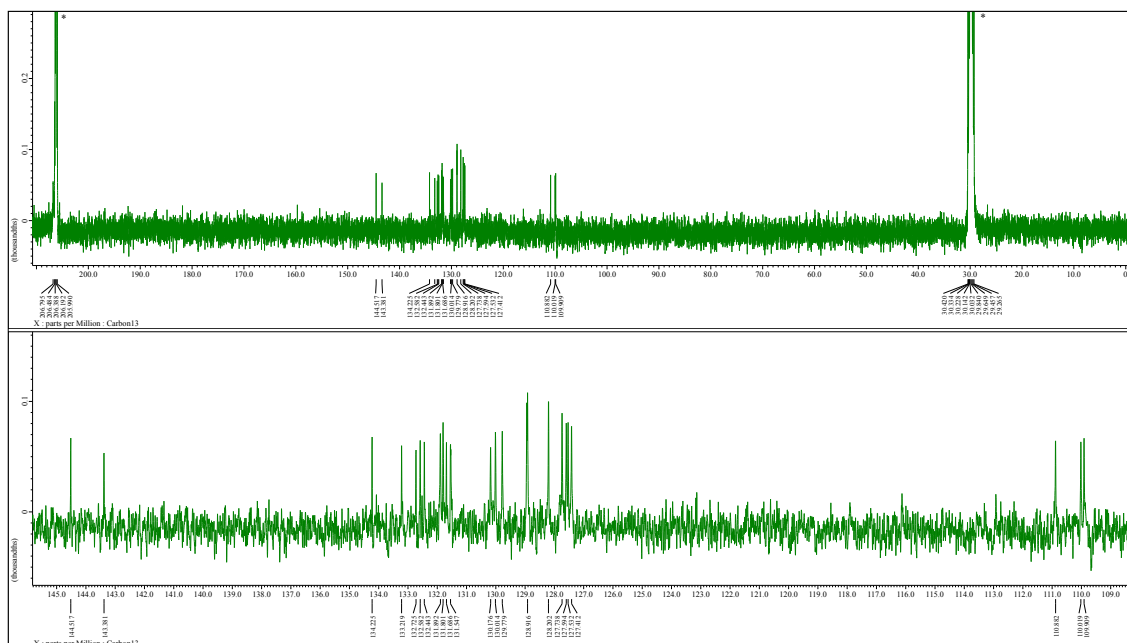


Figure S3-2. ^{13}C NMR spectrum of **4** in acetone- d_6 at room temperature. Peaks with * are due to the residual solvents.

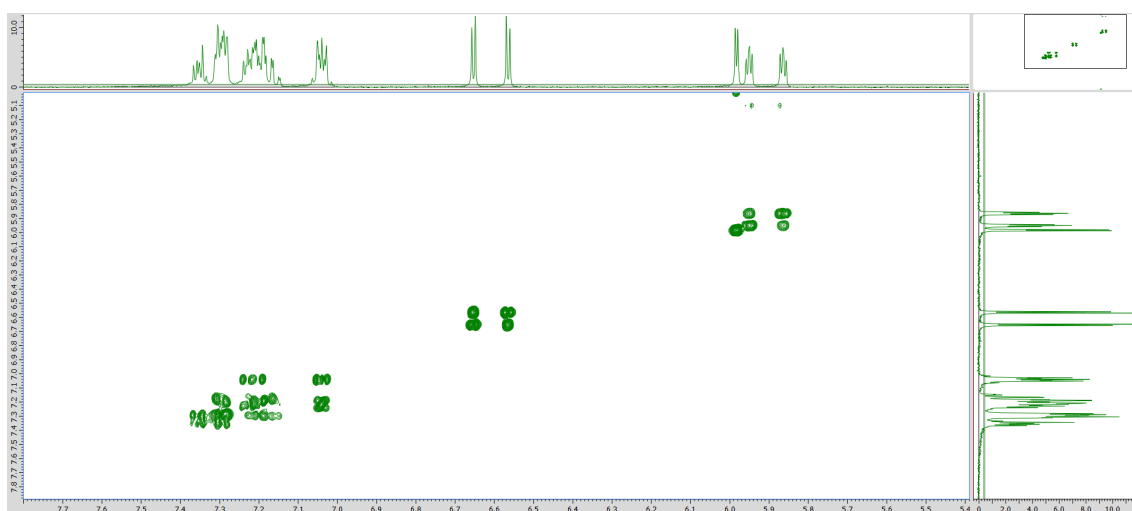
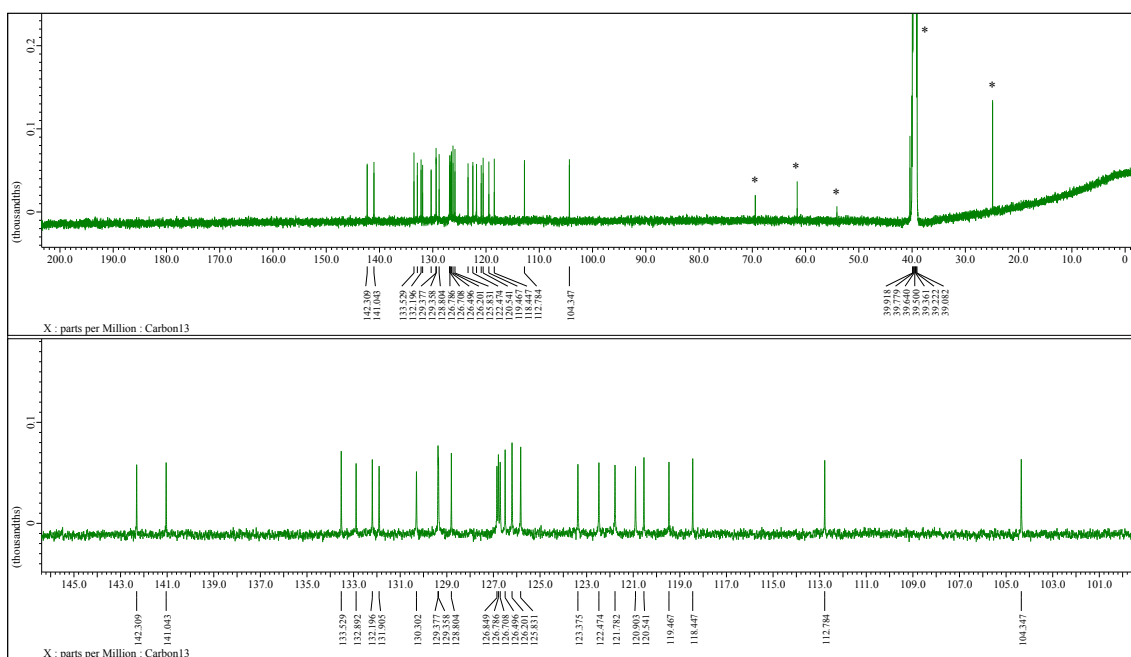
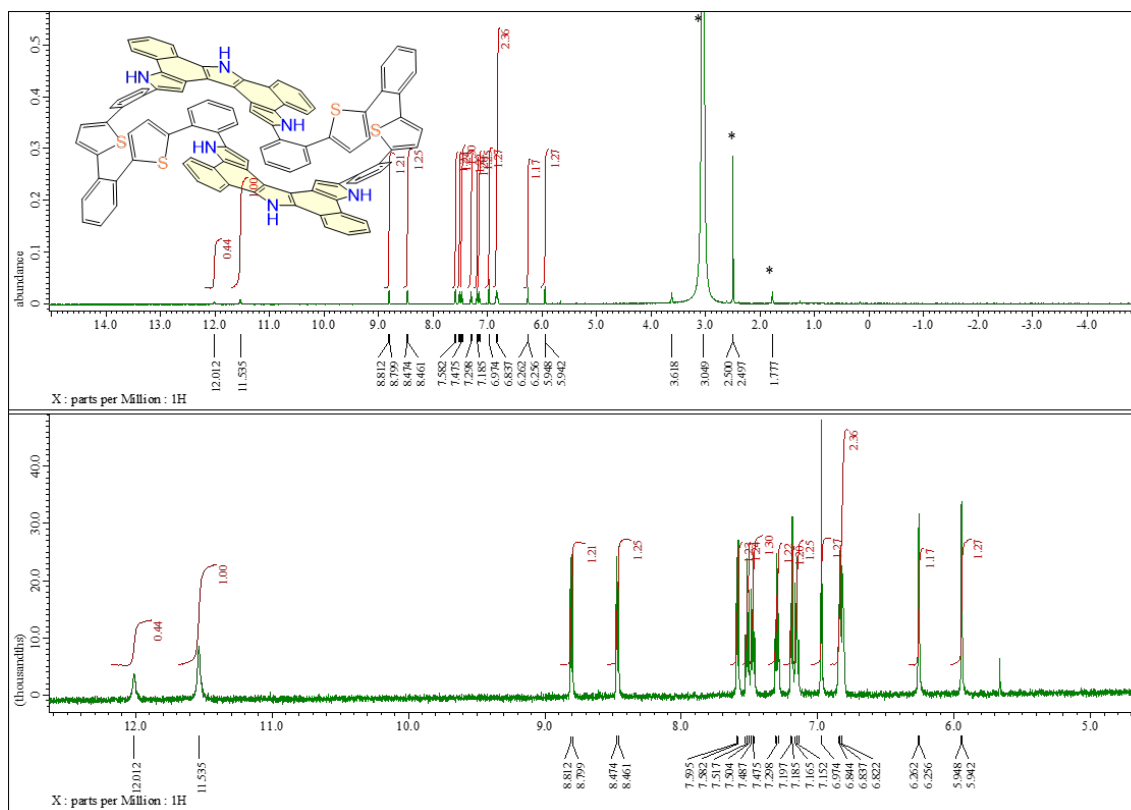


Figure S3-3. ^1H - ^1H COSY chart of **4** in acetone- d_6 at room temperature.



4. Mass Spectra

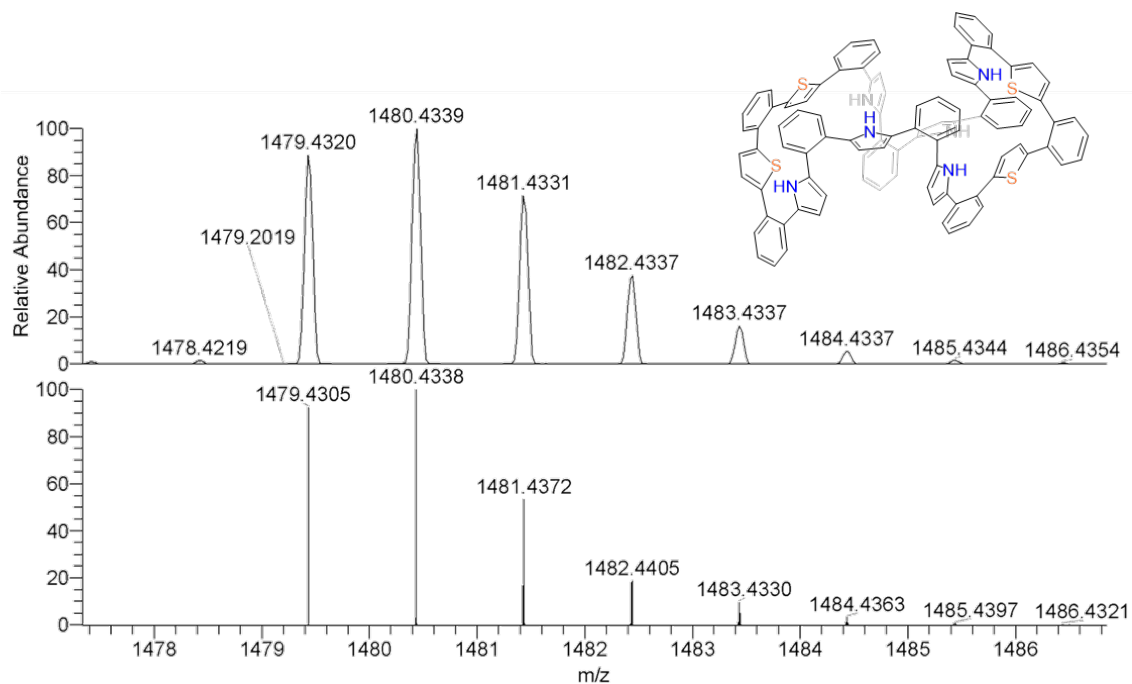


Figure S4-1 APCI-TOF-mass spectra of **4**. (Top; observed. Middle; calculated $[M]^+$. Bottom; calculated $[M+H]^+$.)

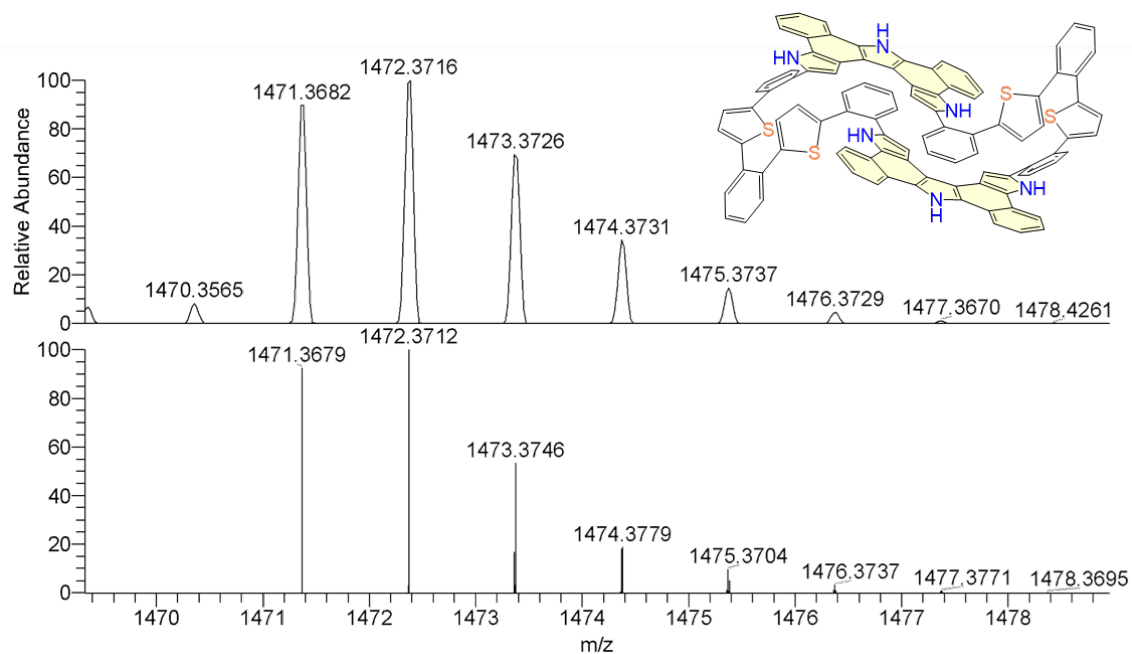


Figure S4-2 APCI-TOF-mass spectra of **5**. (Top; observed. Middle; calculated $[M]^+$. Bottom; calculated $[M+H]^+$.)

5. X-Ray Crystallographic Details

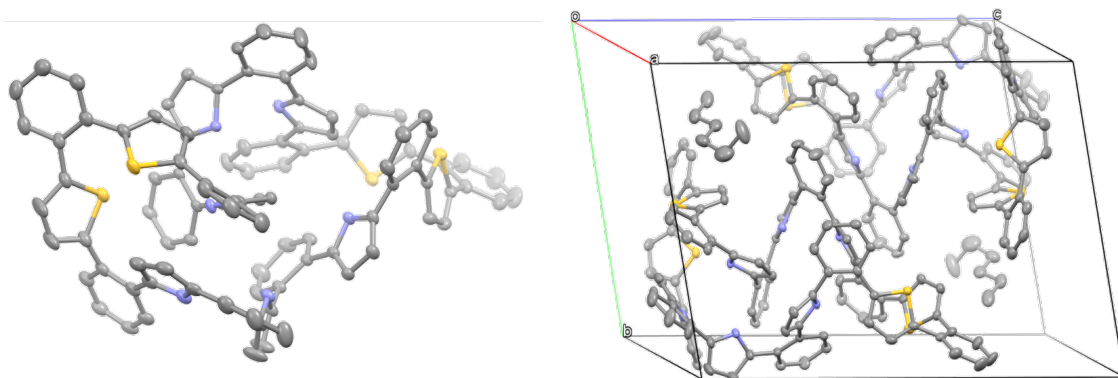


Figure S5-1 X-Ray crystal structure of **4**. Thermal ellipsoids were scaled to 50% probability. (left) Top view and side view. (right) Packing structure. Hydrogen atoms are omitted for clarity.

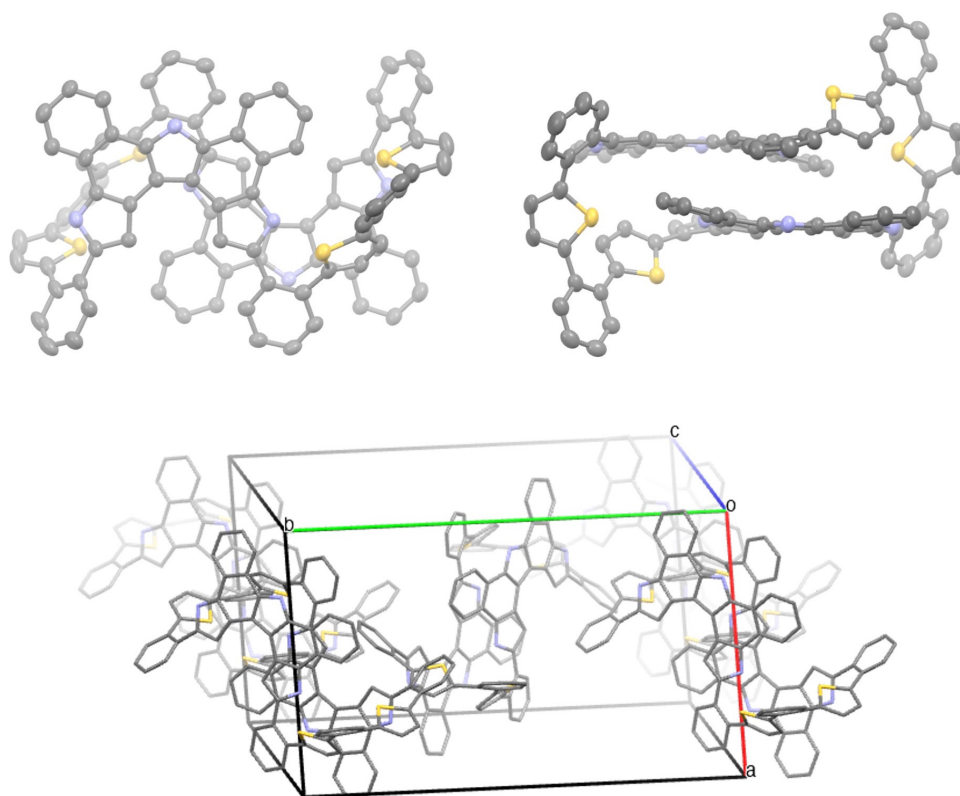


Figure S5-2 X-Ray crystal structure of **5**. Thermal ellipsoids were scaled to 50% probability. (Top) Top view and side view. (Bottom) Packing structure. Solvent molecules (DMSO) and hydrogen atoms are omitted for clarity.

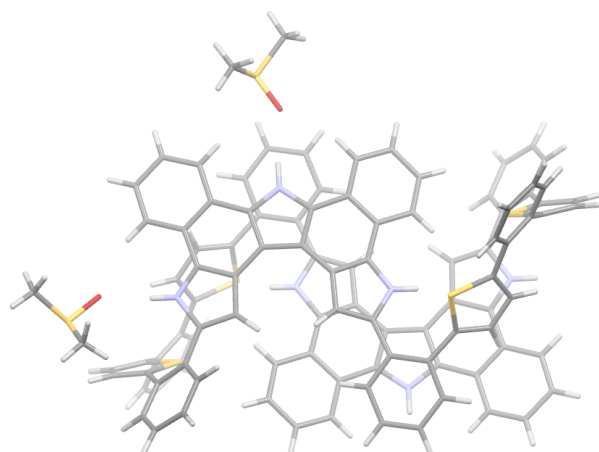


Figure S5-3 X-Ray crystal structure of **5** with DMSO molecules coordinated to the NH sites.

Table S5. Crystal data and structure refinements for **4** and **5**.

Compound	4	5
Empirical Formula	C ₁₀₀ H ₆₆ N ₆ S ₄ , 0.666(C ₆ H ₁₄), 0.668(C ₃ H ₆ O)	C ₅₀ H ₂₉ N ₃ S ₂ , 4(C ₂ H ₆ OS)
<i>M</i> _w	1576.01	1048.39
Crystal System	Triclinic	Monoclinic
Space Group	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> [Å]	12.9137(5)	15.0226(5)
<i>b</i> [Å]	15.6940(5)	25.1556(5)
<i>c</i> [Å]	20.8461(7)	15.0221(4)
α [deg]	80.038(3)	90
β [deg]	81.684(3)	113.837(4)
γ [deg]	85.216(3)	90
Volume [Å ³]	4110.0(3)	5192.6(3)
<i>Z</i>	2	4
Density [g/cm ³]	1.273	1.341
Completeness	0.968	0.996
Goodness-of-fit	1.007	1.243
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0914	0.1008
<i>wR</i> ₂ (all data)	0.2591	0.3095
Solvent System	acetone/ <i>n</i> -hexane	DMSO/THF/H ₂ O
CCDC No.	2455171	2455172

6. UV/Vis Absorption and Fluorescence Spectra

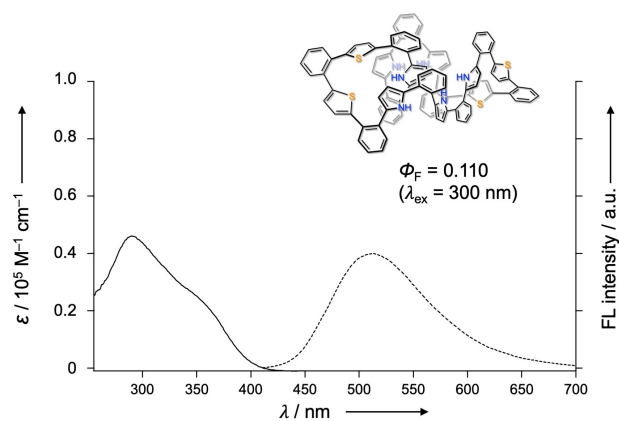


Figure S6-1. UV/Vis absorption and fluorescence spectra of **4** in THF at room temperature.

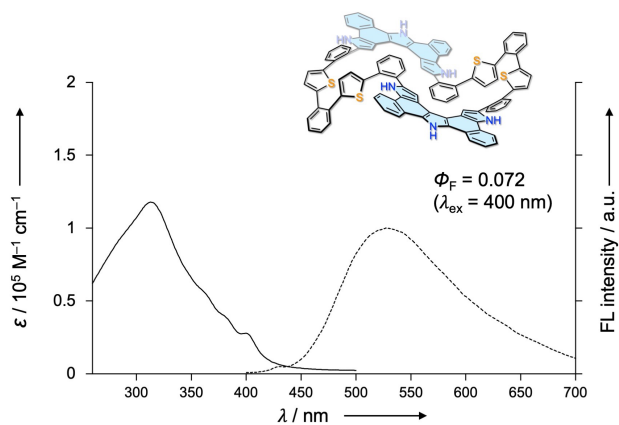


Figure S6-2. UV/Vis absorption and fluorescence spectra of **5** in DMSO at room temperature.

7. DFT Calculations

All calculations were carried out using the Gaussian 16 program.^[S4] All structures were fully optimized without any symmetry restriction based on the structures obtained by single-crystal X-ray diffraction analysis. The calculations were performed at B3LYP-GD3BJ/def2SVP for all atoms.^[S5]

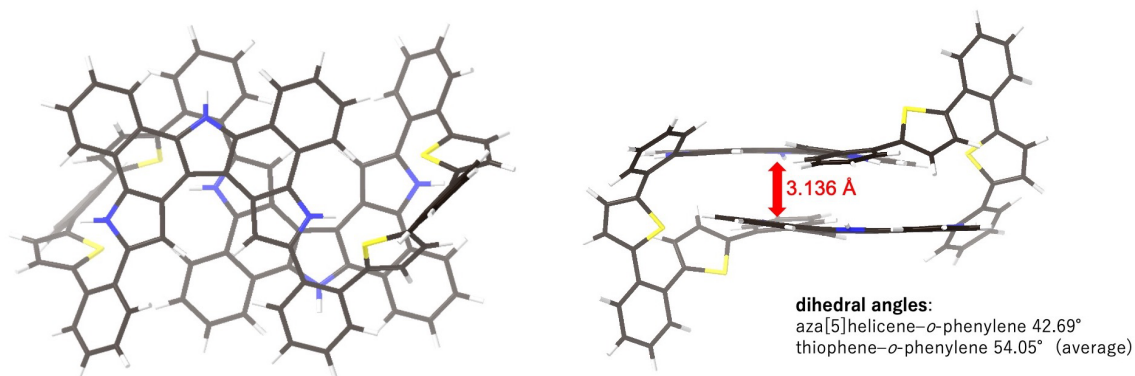


Figure S7-1. DFT optimized structure of **5**.

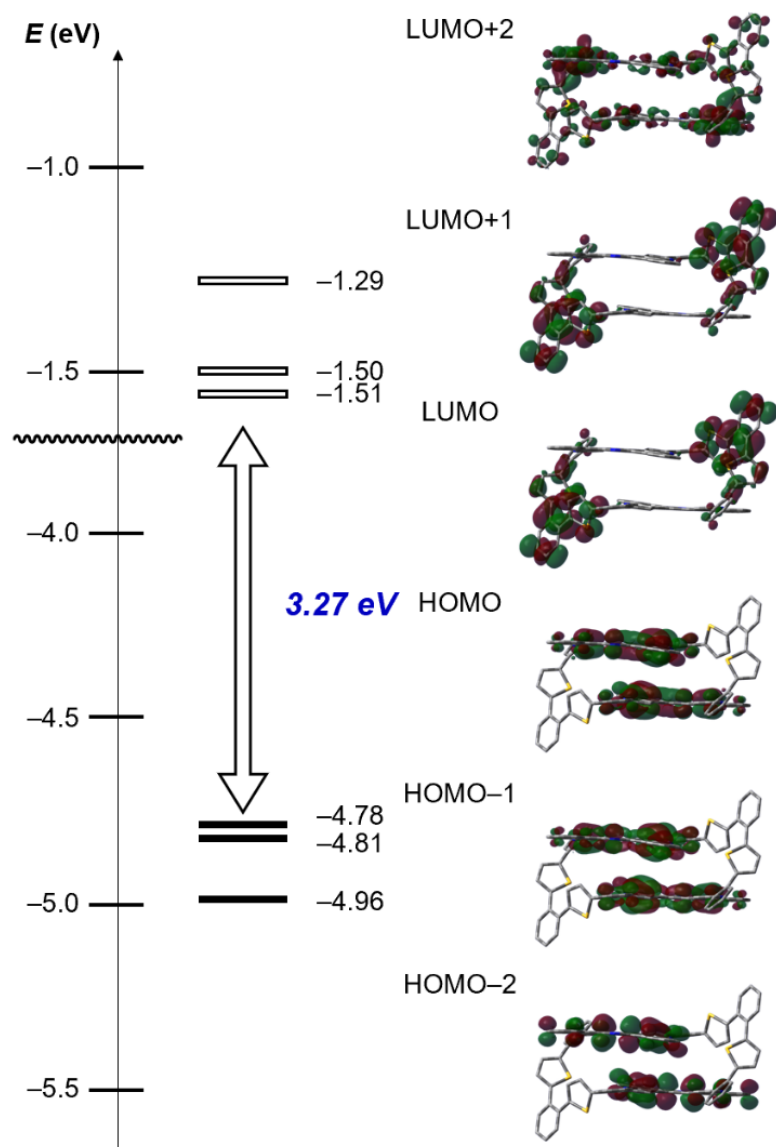


Figure S7-2. Kohn-Sham MO representation and energy diagrams of **5**. (Hydrogen atoms are omitted for clarity.)

Table S7. Cartesian coordinates of the optimized geometry of **5**.

Symbol	X	Y	Z	C	1.3200190	-1.8110650	1.2076410
S	4.6175110	-1.9598200	2.4165150	C	1.7155130	-3.1925370	0.9293940
S	6.5763980	1.3502810	0.4046300	C	0.6740140	-4.1366470	0.7949460
N	-5.4330800	-0.3686700	2.6786600	H	-0.3529360	-3.8067840	0.9371020
H	-6.4368570	-0.3330490	2.7913780	C	0.9059220	-5.4515220	0.4132400
N	-1.3725470	3.2827130	2.3655040	H	0.0632440	-6.1383170	0.3091420
H	-1.3660800	4.2801600	2.2010270	C	2.2119230	-5.8723840	0.1389300
N	2.1059780	-0.7033490	0.9626160	H	2.4160610	-6.8986300	-0.1752650
H	3.0085110	-0.7355520	0.5072490	C	3.2611550	-4.9751160	0.3138960
C	-4.7287820	-1.5259170	2.4189800	H	4.2873250	-5.3095060	0.1579300
C	-3.3868990	-1.1892760	2.2840510	C	3.0515170	-3.6434140	0.7291260
H	-2.6033850	-1.8921320	2.0336060	C	4.2760220	-2.8452000	0.9408100
C	-3.2703900	0.2223220	2.4544340	C	5.3928940	-2.8532490	0.1281540
C	-4.5775310	0.7071100	2.7126920	H	5.4180360	-3.3815320	-0.8191460
C	-4.8959210	2.0768210	2.9598840	C	6.4961870	-2.1383930	0.6572470
C	-6.2005790	2.5401710	3.2459630	H	7.4551300	-2.0370560	0.1499000
H	-7.0229180	1.8239690	3.3196840	C	6.2524500	-1.6050940	1.9054220
C	-6.4588490	3.8906020	3.4164790	C	7.2114530	-0.9329950	2.7942990
H	-7.4749590	4.2296410	3.6298270	C	7.2796480	-1.3173590	4.1464880
C	-5.4097030	4.8280990	3.3150700	H	6.5680860	-2.0593740	4.5146640
H	-5.6146430	5.8924470	3.4496950	C	8.2572410	-0.8115140	5.0003380
C	-4.1186670	4.4004410	3.0498590	H	8.2880060	-1.1342370	6.0434630
H	-3.3154950	5.1363500	2.9756060	C	9.2040030	0.0911640	4.5099170
C	-3.8246640	3.0293930	2.8656610	H	9.9825240	0.4885280	5.1650710
C	-2.5185630	2.5380360	2.5523550	C	9.1327040	0.5088370	3.1822570
C	-2.1985700	1.1719860	2.3762920	H	9.8316530	1.2602130	2.8097950
C	-0.7942650	1.1096620	2.0629760	C	8.1384380	0.0276470	2.3102390
C	-0.3272450	2.4423880	2.0373980	C	8.0638400	0.6342560	0.9672590
C	1.0035780	2.8254890	1.6776540	C	9.0932890	0.9224610	0.0958270
C	1.4695110	4.1605030	1.7017100	H	10.1131420	0.5697210	0.2555970
H	0.8051380	4.9540050	2.0497200	C	8.6928070	1.7323760	-1.0082270
C	2.7525570	4.4796290	1.2874840	H	9.3718050	2.0797520	-1.7885720
H	3.0910240	5.5180960	1.3085070	C	7.3546940	2.0680110	-0.9860460
C	3.6274590	3.4628560	0.8517950	C	6.6398360	3.0707550	-1.8017430
H	4.6410820	3.7109050	0.5310540	C	7.2140910	4.3520550	-1.9020960
C	3.2060050	2.1440970	0.8473430	H	8.1889830	4.5220750	-1.4408080
H	3.8925370	1.3614780	0.5309210	C	6.5420910	5.4052680	-2.5192900
C	1.8996270	1.7911030	1.2490560	H	7.0086740	6.3913450	-2.5753880
C	1.4224290	0.4443650	1.2807020	C	5.2603540	5.1960930	-3.0373260
C	0.1321220	0.0677910	1.7256710	H	4.7138720	6.0165580	-3.5079830
C	0.0925300	-1.3526870	1.6889170	C	4.6875860	3.9288460	-2.9728960
H	-0.7243620	-1.9883670	2.0031700	H	3.7084380	3.7481890	-3.4196800

C	5.3634920	2.8453620	-2.3803250	C	-1.7155230	3.1922520	-0.9292350
S	-4.6176710	1.9597440	-2.4163730	C	-0.6740250	4.1363790	-0.7948220
S	-6.5765640	-1.3500540	-0.4050430	H	0.3529220	3.8065400	-0.9370670
N	5.4331500	0.3686700	-2.6787450	C	-0.9058990	5.4512420	-0.4130570
H	6.4369230	0.3330890	-2.7914990	H	-0.0632290	6.1380560	-0.3090480
N	1.3727770	-3.2828420	-2.3653210	C	-2.2118850	5.8720730	-0.1386080
H	1.3661630	-4.2803930	-2.2015870	H	-2.4160250	6.8982880	0.1756910
N	-2.1060050	0.7030530	-0.9626570	C	-3.2611120	4.9748040	-0.3135430
H	-3.0085570	0.7352170	-0.5073280	H	-4.2872550	5.3092350	-0.1575310
C	4.7287920	1.5259360	-2.4192690	C	-3.0515290	3.6431200	-0.7288680
C	3.3869360	1.1892390	-2.2842400	C	-4.2760510	2.8450110	-0.9406140
H	2.6034040	1.8920900	-2.0338450	C	-5.3929970	2.8532550	-0.1280330
C	3.2704700	-0.2223840	-2.4544600	H	-5.4181100	3.3814280	0.8193280
C	4.5776390	-0.7071460	-2.7126590	C	-6.4963930	2.1386460	-0.6571970
C	4.8960780	-2.0768670	-2.9597400	H	-7.4553850	2.0374840	-0.1499120
C	6.2007530	-2.5401800	-3.2457890	C	-6.2526870	1.6053430	-1.9053750
H	7.0230290	-1.8239280	-3.3197070	C	-7.2117400	0.9334470	-2.7943410
C	6.4591220	-3.8906300	-3.4160370	C	-7.2799930	1.3179770	-4.1464660
H	7.4752480	-4.2296380	-3.6293550	H	-6.5684090	2.0600000	-4.5145940
C	5.4100570	-4.8281830	-3.3143540	C	-8.2576700	0.8122590	-5.0003120
H	5.6150780	-5.8925530	-3.4486830	H	-8.2884940	1.1350750	-6.0434060
C	4.1189920	-4.4005550	-3.0492230	C	-9.2044400	-0.0904230	-4.5099320
H	3.3158990	-5.1365300	-2.9746610	H	-9.9830390	-0.4876430	-5.1650810
C	3.8248840	-3.0294880	-2.8653810	C	-9.1330870	-0.5082540	-3.1823140
C	2.5187410	-2.5381500	-2.5522410	H	-9.8320650	-1.2596240	-2.8098860
C	2.1986720	-1.1720880	-2.3762940	C	-8.1387540	-0.0272050	-2.3103230
C	0.7943630	-1.1098230	-2.0629920	C	-8.0640300	-0.6338920	-0.9673860
C	0.3274230	-2.4425810	-2.0373140	C	-9.0933570	-0.9219360	-0.0957590
C	-1.0033850	-2.8257490	-1.6775900	H	-10.1131900	-0.5690480	-0.2553360
C	-1.4692180	-4.1607980	-1.7016120	C	-8.6927450	-1.7318990	1.0082250
H	-0.8047880	-4.9542710	-2.0495770	H	-9.3716300	-2.0792440	1.7886880
C	-2.7522500	-4.4800010	-1.2873890	C	-7.3546800	-2.0676900	0.9857870
H	-3.0906480	-5.5184890	-1.3083980	C	-6.6398840	-3.0706270	1.8013290
C	-3.6272260	-3.4632740	-0.8517340	C	-7.2141280	-4.3519320	1.9014340
H	-4.6408150	-3.7114030	-0.5309570	H	-8.1890210	-4.5218550	1.4401090
C	-3.2058760	-2.1444800	-0.8473310	C	-6.5421280	-5.4052370	2.5184760
H	-3.8924480	-1.3619080	-0.5308930	H	-7.0086740	-6.3913420	2.5743790
C	-1.8995140	-1.7914070	-1.2490410	C	-5.2604250	-5.1961370	3.0366010
C	-1.4223770	-0.4446440	-1.2806680	H	-4.7139840	-6.0166940	3.5071460
C	-0.1320720	-0.0680100	-1.7256280	C	-4.6876350	-3.9288840	2.9723890
C	-0.0925260	1.3524480	-1.6888100	H	-3.7084950	-3.7482970	3.4192140
H	0.7244120	1.9881410	-2.0029000	C	-5.3635330	-2.8453220	2.3799630
C	-1.3200450	1.8108000	-1.2075740				

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