## **Supporting Information for**

# A Double Hetero[4]helicene Composed of Two Phenothiazines: Synthesis, Structural Properties, and its Cationic States

Daisuke Sakamaki,\*,<sup>†</sup> Daisuke Kumano,<sup>‡</sup> Eiji Yashima,<sup>‡</sup> and Shu Seki<sup>\*,†</sup>

<sup>†</sup>Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

<sup>‡</sup>Department of Molecular Design and Engineering, Graduate School of Engineering,

Nagoya University, Nagoya, Aichi, 464-8603, Japan

# **Contents:**

General Information
Synthetic Details
MALDI MS spectra
NMR spectra of 1 and 2
X-ray Crystallography
Optical resolution of 1
DFT calculations
Electrochemistry
Crystal structure of $2^{2+}$ [SbCl <sub>6</sub> -] <sub>2</sub> .
Electronic Properties of $1^{+}$ and $2^{2+}$
Simulation of Circular Dichroism Spectrum of $\boldsymbol{1}$

#### **General Information**

All the purchased reagents were of standard quality, and used without further purification. All the reactions were carried out under argon atmosphere. Column chromatography was performed with silica gel (Fuji Silysia, PSQ 60N, spherical neutral). 3,7-di-*tert*-butylphenothiazine (3) was synthesized according to the literature.<sup>S1</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by a JEOL JNM-AL400 FT-NMR spectrometer. Chemical shifts of NMR spectra are determined relative to internal tetramethylsilane (TMS) standard ( $\delta$ ), and are given in parts per million (ppm). Low and high resolution matrix-assisted-laser-desorption/ionization (MALDI) mass spectra (MS) were obtained on a Bruker ultraflex mass spectrometer with dithranol as a matrix. UV-Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 19 spectrometer. The redox properties were evaluated by cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K with 0.1 M tetra-n-butylammonium tetrafluoroborate (TBABF4) as supporting electrolyte (scan rate 100 mV s<sup>-1</sup>) using an ALS/chi Electrochemical Analyzer model 612A. A three-electrode assembly was used, which was equipped with platinum disk (2 mm<sup>2</sup>), a platinum wire, and Ag/0.01 M AgNO<sub>3</sub> (acetonitrile) as the working electrode, the counter electrode, and the reference electrode, respectively. The redox potential were referenced against a ferrocene/ferrocenium ( $Fc^{0/+}$ ) redox potential measured in the same electrolytic solution. Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh, a platinum coil, and a silver wire as the working electrode, the counter electrode, and the pseudo-reference electrode, respectively. The potential was applied with an ALS/chi Electrochemical Analyzer

model 612A. ESR spectra at 298 K were recorded with JEOL JES-FA-200 X-band spectrometers. Low temperature ESR spectra were recorded with JEOL JES-RE-200 X-band spectrometers equipped with an analog plotter. The temperature was controlled with a JEOL DVT2 variable-temperature unit.

[S1] Kormos, A.; Móczár, I.; Sveiczer, A.; Baranyai, P.; Párkányi, L.; Tóth, K.; Huszthy,P.; *Tetrahedron*, **2012**, *68*, 7063-7069.

#### **Synthetic Details**

**2** (oxidation with Ac<sub>2</sub>O/DMSO): 3,7-di-*tert*-butylphenothiazine (**3**) (9.368 g, 30.08 mmol) was dissolved in a mixed solution of acetic anhydride (20 ml) and dimethylsulfoxide (40 ml) and stirred for 7 days at rt. The reaction mixture was quenched by adding water, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was chromatographed on silica gel (hexane/ CH<sub>2</sub>Cl<sub>2</sub> = 4:1 as eluent) to afford **2** (6.037 g, 65%) as a white powder. <sup>1</sup>HNMR(400MHz, acetone-*d*<sub>6</sub>);  $\delta$  = 1.23 (s, 9H), 1.24 (s, 18H), 1.32 (s, 9H), 6.23 (d, *J* = 8.54, 2H), 6.59 (d, *J* = 8.54, 1H), 6.94-6.97 (m, 3H), 7.02 (d, *J* = 2.44, 1H), 7.06 (d, *J* = 2.44, 2H), 7.15 (d, *J* = 2.20, 1H), 7.19 (d, *J* = 2.20, 1H), 7.33 (s, 1H); <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>)  $\delta$  = 32.08, 32.13, 35.20, 35.26, 35.52, 116.78, 116.90, 118.84, 121.32, 121.37, 124.60, 124.96, 125.05, 125.64, 125.84, 127.19, 128.11, 139.99, 140.38, 141.87, 147.00, 147.03, 147.83; MALDI HRMS (dithranol): m/z calcd for C<sub>40</sub>H<sub>48</sub>N<sub>2</sub>S<sub>2</sub>: 620.3253 [M]<sup>+</sup>; found 620.3236.

**2** (oxidation with DDQ): A mixture of **3** (0.314 g, 1.01 mmol), DDQ (0.142 g, 0.63 mmol) in CHCl<sub>3</sub> (30 ml) was stirred for 7 h. The reaction was quenched by adding hydrazine hydrate (2 ml) and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by rotary evaporation. The crude product was chromatographed on silica gel (hexane/ CH<sub>2</sub>Cl<sub>2</sub> = 9:1 as eluent) to afford **2** (244.8 mg, 78%) as a white powder.

**1** (from **2**) A mixture of **2** (0.315 g, 0.507 mmol), DDQ (0.140 g, 0.617 mmol) and Sc(OTf)<sub>3</sub> (0.301 g, 0.611 mmol) in CHCl<sub>3</sub> (50 ml) was refluxed for 23 h. The reaction was quenched by adding hydrazine hydrate (4 ml) and washed with water. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by rotary evaporation. The crude product was chromatographed on silica gel (hexane as eluent) to afford **1** (0.078 g, 25%) as a yellow powder; <sup>1</sup>HNMR(400MHz, cyclohexane-*d*<sub>12</sub>);  $\delta = 1.21$  (s, 18H), 1.27 (s, 18H), 6.75 (d, *J* = 1.95 Hz, 2H), 6.96 (d, *J* = 1.95 Hz, 2H), 6.98 (dd, *J* = 2.20, 8.54 Hz, 2H), 7.12 (d, *J* = 8.54 Hz, 2H), 7.16 (d, *J* = 1.95 Hz, 2H); <sup>13</sup>C NMR (100 MHz, cyclohexane-*d*<sub>12</sub>)  $\delta = 31.59$ , 31.74, 34.78, 34.90, 115.64, 116.86, 119.32, 119.56, 124.00, 126.10, 126.84, 134.19, 134.86, 141.32, 147.27, 147.90; MALDI HRMS (dithranol): m/z calcd for C<sub>40</sub>H<sub>46</sub>N<sub>2</sub>S<sub>2</sub>: 618.3097 [M]<sup>+</sup>; found 618.3089.

**1** (from **3**): A mixture of **3** (0.328 g, 1.05 mmol) and DDQ (0.117 g, 0.51 mmol) in  $CH_2Cl_2$  (50 ml) was stirred for 2 h at rt. The reaction was monitored by TLC and MALDI-MS, and the generation of **2** was observed. To the reaction solution, DDQ (0.132 g, 0.58 mmol) and Sc(OTf)<sub>3</sub> (0.279 g, 0.57 mmol) was added, and the reaction

solution was refluxed. After 18 h, the reaction was quenched by adding hydrazine hydrate (2 ml) and washed with water. The organic layer was dried over  $Na_2SO_4$  and the solvent was removed by rotary evaporation. The crude product was chromatographed on silica gel (hexane as eluent) to afford **1** (0.070 g, 22% from **3**) as a yellow powder.



Fig. S1. MALDI mass spectrum of the reaction solution of the oxidation reaction of **3** with  $Ac_2O/DMSO$  as oxidant (reaction time = 7 days).



Fig. S2. MALDI mass spectrum of the reaction solution of the oxidation reaction of **3** with DDQ as oxidant (reaction time = 6 hours).



Fig. S3. <sup>1</sup>H NMR of **2** in acetone- $d_6$  at 298 K.



Fig. S4. <sup>1</sup>H NMR of **1** in cyclohexane- $d_{12}$  at 298 K.



Fig. S5. <sup>13</sup>C NMR of **1** in cyclohexane- $d_{12}$  at 298 K.

### X-ray Crystallography

The single crystals were obtained by the slow evaporation of a solution (CH<sub>2</sub>Cl<sub>2</sub>:MeOH for **2** and **1**; CH<sub>2</sub>Cl<sub>2</sub>:*n*-hexane for **1**<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> and **2**<sup>2+</sup>[SbCl<sub>6</sub><sup>-</sup>]). Data collections were performed on a Rigaku R-AXIS-RAPID diffractometer with Cu-K $\alpha$  radiation ( $\lambda =$ 1.54187 Å) for **2** and **1** and with Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å) for **1**<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> and **2**<sup>2+</sup>[SbCl<sub>6</sub><sup>-</sup>]<sub>2</sub>. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. All the calculations were performed by using CrystalStructure crystallographic software package,<sup>S2</sup> except for refinement, which was performed by using SHELXL-97.<sup>S3</sup>

<sup>[</sup>S2] CrystalStructure 4.0, Crystal Structure Analysis Package, Rigaku Corporation (2000–2011). Tokyo 196-8666, Japan.

<sup>[</sup>S3] Sheldrick, G. M. Acta Cryst. A 2008, 64, 112.

empirical formula	$C_{41}H_{52}N_2OS_2$
	[ <b>2</b> · CH <sub>3</sub> OH]
formula weight	652.99
<i>T</i> [°C]	-150
λ[Å]	1.54187
crystal system	monoclinic
space group	C 1 2/c 1 (#15)
Ζ	16
<i>a</i> [Å]	23.0126(5)
<i>b</i> [Å]	29.0068(6)
<i>c</i> [Å]	22.0641(4)
$\alpha$ [°]	90.0000
$\beta[\degree]$	104.7159(7)
γ[°]	90.0000
V[Å <sup>3</sup> ]	14245.1(5)
$ ho_{ m calcd} [ m g \  m cm^{-3}]$	1.218
collected data	123850
unique data / R <sub>int</sub>	13775/ 0.0396
no. of parameters	806
goodness-of-fit <sup>[a]</sup>	1.050
<i>R</i> 1 ( $I > 2\sigma$ ), <i>wR</i> 2 (all reflections) <sup>[b]</sup>	0.1064, 0.3091
residual density [e Å <sup>-3</sup> ]	2.380/-1.980

[a] GOF =  $\left\{ \sum \left[ w (F_0^2 - F_c^2)^2 \right] / (n - p) \right\}^2$ , where *n* and *p* denote the number of data and parameters. [b] R1 =  $\sum \left( \|F_0\| - \|F_c\| \right) / \sum \|F_0\|$  and  $wR2 = \left\{ \sum \left[ w (F_0^2 - F_c^2)^2 \right] / \sum \left[ w (F_0^2)^2 \right] \right\}^2$  where  $w = 1 / \left[ \sigma^2 (F_0^2) + (a \cdot P)^2 + b \cdot P \right]$  and  $P = \left[ (Max; 0, F_0^2) + 2 \cdot F_c^2 \right] / 3$ .

empirical formula	$C_{40}H_{46}N_2S_2$
formula weight	618.94
T [°C]	-60
λ[Å]	1.54187
crystal system	triclinic
space group	P -1 (#2)
Ζ	2
<i>a</i> [Å]	9.4905(3)
<i>b</i> [Å]	13.4085(4)
<i>c</i> [Å]	15.1433(5)
<i>α</i> [°]	77.1900(17)
$\beta[\degree]$	87.7430(19)
γ[°]	74.9540(18)
V[Å <sup>3</sup> ]	1814.32(10)
$ ho_{ m calcd} [ m g  cm^{-3}]$	1.133
collected data	28881
unique data / R <sub>int</sub>	5343 / 0.1360
no. of parameters	581
goodness-of-fit <sup>[a]</sup>	1.001
<i>R</i> 1 ( $I > 2\sigma$ ), <i>wR</i> 2 (all reflections) <sup>[b]</sup>	0.1141, 0.3942
residual density [e Å <sup>-3</sup> ]	0.450 / -0.420

[a] GOF = 
$$\left\{ \sum \left[ w \left( F_0^2 - F_c^2 \right)^2 \right] / (n - p) \right\}^2$$
, where *n* and *p* denote the number of data and parameters.  
[b]  $R1 = \sum \left( \|F_0\| - \|F_c\| \right) / \sum \|F_0\|$  and  $wR2 = \left\{ \sum \left[ w \left( F_0^2 - F_c^2 \right)^2 \right] / \sum \left[ w \left( F_0^2 \right)^2 \right] \right\}^2$  where  $w = 1 / \left[ \sigma^2 \left( F_0^2 \right) + (a \cdot P)^2 + b \cdot P \right]$  and  $P = \left[ \left( Max; 0, F_0^2 \right) + 2 \cdot F_c^2 \right] / 3$ .

empirical formula	$C_{41}H_{48}Cl_8N_2O_2Sb$
	$[1^{+}SbCl_{6}^{-}\bullet CH_{2}Cl_{2}]$
formula weight	1038.34
T [°C]	-150
λ[Å]	0.71075
crystal system	monoclinic
space group	P 1 21/c 1 (#14)
Ζ	4
<i>a</i> [Å]	11.982(4)
<i>b</i> [Å]	15.925(6)
<i>c</i> [Å]	24.598(9)
$\alpha$ [°]	90.0000
$\beta[\degree]$	90.150(6)
$\gamma[^{\circ}]$	90.0000
V[Å <sup>3</sup> ]	4694(3)
$ ho_{ m calcd} [ m g  cm^{-3}]$	1.469
collected data	27131
unique data / <i>R</i> <sub>int</sub>	6718/ 0.0697
no. of parameters	487
goodness-of-fit <sup>[a]</sup>	1.058
<i>R</i> 1 ( $I > 2\sigma$ ), <i>wR</i> 2 (all reflections) <sup>[b]</sup>	0.1013, 0.3008
residual density [e Å <sup>-3</sup> ]	9.060/-1.190

Table S3: X-ray crystallographic data for 1<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>.

[a] GOF =  $\left\{ \sum \left[ w (F_0^2 - F_c^2)^2 \right] / (n - p) \right\}^2$ , where *n* and *p* denote the number of data and parameters. [b]  $R1 = \sum \left( \|F_0\| - \|F_c\| \right) / \sum \|F_0\|$  and  $wR2 = \left\{ \sum \left[ w (F_0^2 - F_c^2)^2 \right] / \sum \left[ w (F_0^2)^2 \right] \right\}^2$  where  $w = 1 / \left[ \sigma^2 (F_0^2) + (a \cdot P)^2 + b \cdot P \right]$  and  $P = \left[ \left( \text{Max}; 0, F_0^2 \right) + 2 \cdot F_c^2 \right] / 3$ .

empirical formula	$C_{46}H_{62}Cl_{12}N_2S_2Sb_2$
	$[2^{2+}[SbCl_6^-]_2 \bullet n$ -hexane]
formula weight	1376.07
T [°C]	-150
λ[Å]	0.71075
crystal system	triclinic
space group	P -1 (#2)
Ζ	4
<i>a</i> [Å]	16.3370(12)
<i>b</i> [Å]	20.1317(13)
<i>c</i> [Å]	20.3767(14)
$\alpha$ [°]	103.1816(19)
$\beta$ [°]	91.496(2)
γ[°]	112.2261(18)
V [Å <sup>3</sup> ]	5993.2(7)
$ ho_{ m calcd} [ m g  cm^{-3}]$	1.525
collected data	53692
unique data / R <sub>int</sub>	25930/ 0.2003
no. of parameters	1070
goodness-of-fit <sup>[a]</sup>	1.015
<i>R</i> 1 ( $I > 2\sigma$ ), <i>wR</i> 2 (all reflections) <sup>[b]</sup>	0.1484, 0.3957
residual density [e Å <sup>-3</sup> ]	3.97 / -1.68

[a] GOF = 
$$\left\{ \sum \left[ w \left( F_0^2 - F_c^2 \right)^2 \right] / (n-p) \right\}^2$$
, where *n* and *p* denote the number of data and parameters.  
[b] R1 =  $\sum \left( \|F_0\| - \|F_c\| \right) / \sum \|F_0\|$  and  $wR2 = \left\{ \sum \left[ w \left( F_0^2 - F_c^2 \right)^2 \right] / \sum \left[ w \left( F_0^2 \right)^2 \right] \right\}^2$  where  $w = 1 / \left[ \sigma^2 \left( F_0^2 \right) + (a \cdot P)^2 + b \cdot P \right]$  and  $P = \left[ \left( \text{Max}; 0, F_0^2 \right) + 2 \cdot F_c^2 \right] / 3$ .

**Optical resolution of 1** 



Fig. S6. Chromatograms for the resolution of **1** using UV (254 nm) and CD detectors (324 nm) in *n*-hexane/CHCl<sub>3</sub> (90/10, v/v) at the flow rate of 1.0 mL/min. Optical resolution was carried out with a DAICEL CHIRALPAK-IB column (0.46(i.d.)  $\times$ 25 cm).



Fig. S7. (a) Racemization kinetics of **1** in 1,4-dioxane. Changes in CD intensity at 257 nm were followed in a 1.0-mm cell at 60, 50, 40, and 30 °C. (b) CD and absorption spectral changes of **1** before and after the heating process of (a). (c) First order plots of  $\ln(CD/CD_{t=0})$  versus time at 60, 50, 40, and 30 °C. (d) Arrhenius plot of *k* at 60, 50, 40, and 30 °C.

temperature (°C)	$k \times 10^4 ({\rm sec}^{-1})$	ln k
60	5.55	-7.496
50	1.61	-8.736
40	0.418	-10.08
30	0.0985	-11.53

Table S5: Racemization kinetics data for **1** in 1,4-dioxane.

## **DFT calculations**



Fig. S8. Potential energy diagram for the isomerization of 1' calculated at  $B3LYP/6-31G^*$  level (kJ mol<sup>-1</sup>).



Fig. S9. Potential energy diagram for the isomerization of dibenzo[a,j]perylene calculated at  $B3LYP/6-31G^*$  level (kJ mol<sup>-1</sup>).



Fig. S10. Potential energy diagram for the isomerization of phenoxazine dimer 4 calculated at B3LYP/6-31G\* level (kJ mol<sup>-1</sup>).



Fig. S11. Potential energy diagram for the isomerization of phenoxazine dimer 5 calculated at  $B3LYP/6-31G^*$  level (kJ mol<sup>-1</sup>).



Fig. S12. Spin density of the radical cation of  $1^{,+}$  (UB3LYP/6-31G\*).

Electrochemistry



Fig. S13. Cyclic voltammograms of (a) **2** and (b) **1** measured in  $CH_2Cl_2$  containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> at 298 K (scan rate 100 m V s<sup>-1</sup>).



Fig. S14. X-ray structure of  $2^{2+}$ [SbCl<sub>6</sub>-]<sub>2</sub>. (a) The structure of  $2^{2+}$  and (b) a unit cell. Thermal ellipsoids are set at 50% probability. The *t*Bu groups, hydrogen atoms and solvent molecules were omitted for clarity.



Fig. S15. UV-Vis-NIR absorption spectrum of  $1^{+}$ SbCl<sub>6</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



Fig. S16. The electronic transitions of  $1^{,+}$  based on the TD-DFT calculations at UB3LYP/6-31G\* level (blue bars). The black line represents the UV-Vis-NIR absorption spectrum of  $1^{,+}$ SbCl<sub>6</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



Fig. S17. UV-Vis-NIR absorption spectrum of  $CH_2Cl_2$  solutions of  $1^{+}SbCl_6^{-}$  at 298 K. (a) as prepared (blue) and (b) after 2 weeks under ambient conditions (red).



Fig. S18. UV-Vis-NIR absorption spectrum of 2<sup>2+</sup>[SbCl<sub>6</sub>-]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



Fig. S19. ESR spectrum of  $\mathbf{1}^{+}$  in CH<sub>2</sub>Cl<sub>2</sub> at 123 K.

#### Simulation of Circular Dichroism Spectrum of 1'

The excitation energies of **1**' were calculated by the TD-DFT method at B3LYP/6-31G\* level for the optimized structure at the same level. The fifty lowest transitions were calculated. The CD spectrum was simulated by using the Gauss function:

$$\Delta \varepsilon(E) = N \frac{1}{\sqrt{2\pi\sigma}} \sum_{i}^{n} \Delta E_{i} R_{i} e^{\left[-\frac{(E-\Delta E_{i})^{2}}{2\sigma^{2}}\right]}$$

where *N* is the normalization factor,  $\sigma$  is the standard deviation,  $\Delta E_i$  and  $\Delta R_i$  are the excitation energies and rotatory strengths for the *i*th transition. The  $\sigma$  value of 0.15 eV and *R* in the length form were used.



Fig. S20. Simulated CD spectra of (P,P')-1' and (M,M')-1' based on TD-DFT calculations at B3LYP/6-31G\* level.

Excitation energy f		<i>R</i> (10 <sup>-40</sup> cgs)
(eV)		
3.2941	0.0185	-155.554
3.4836	0.0005	11.6475
3.5011	0.0144	64.2878
3.757	0.1885	-30.6507
3.8625	0.0126	148.8448
3.973	0.0045	3.8385
4.1462	0.0819	-117.906
4.1673	0.0028	79.0578
4.2593	0.1871	104.8254
4.4043	0.0081	-3.8414
4.5502	0.0113	26.9221
4.5964	0.0948	-36.2509
4.6456	0.0197	92.5823
4.7103	0.0053	6.9568
4.7621	0.0107	19.0649
4.8236	0.0060	37.6998
4.832	0.1635	-147.394
4.9688	0.0007	-20.6364
4.9712	0.0371	-20.7711
4.9981	0.0163	60.0371
5.1495	0.0414	-54.2784
5.1689	0.0230	17.0378
5.2429	0.0660	-93.6555
5.2953	0.0003	-0.2099
5.3635	0.0083	-0.0936
5.4684	0.0046	17.7672
5.4727	0.0387	-13.5382
5.5258	0.0053	44.0917
5.5447	0.0264	-1.1165
5.6036	0.0013	7.3686
5.6088	0.0888	-46.8408
5.6995	0.0067	35.6576

Table S6: TD-DFT calculated transition energies and oscillator and rotatory strengths of (P,P')-1' (B3LYP/6-31G\* level, Nstate = 50).

5.7035	0.0170	-2.4309
5.741	0.0081	48.0624
5.7656	0.0025	15.3511
5.8891	0.0237	-0.3763
5.8992	0.0077	32.0774
5.903	0.0059	1.9496
5.9379	0.0272	12.9783
5.9617	0.0033	-3.7327
5.967	0.0000	0.4853
6.0162	0.0712	38.9506
6.0245	0.0277	11.0718
6.0344	0.0091	-0.2333
6.0592	0.0186	70.1807
6.0963	0.0903	14.2366
6.1141	0.0741	29.1225
6.1539	0.0003	-6.1177
6.1827	0.0914	-23.5817
6.1836	0.0016	-46.0095