

Electronic Supplementary Information

**Non-Innocent Redox Behavior of Cu<sup>II</sup>-*p*-Dimethylaminophenolate  
Complexes: Formation and Characterization of the Cu<sup>I</sup>-Phenoxy  
Radical Species**

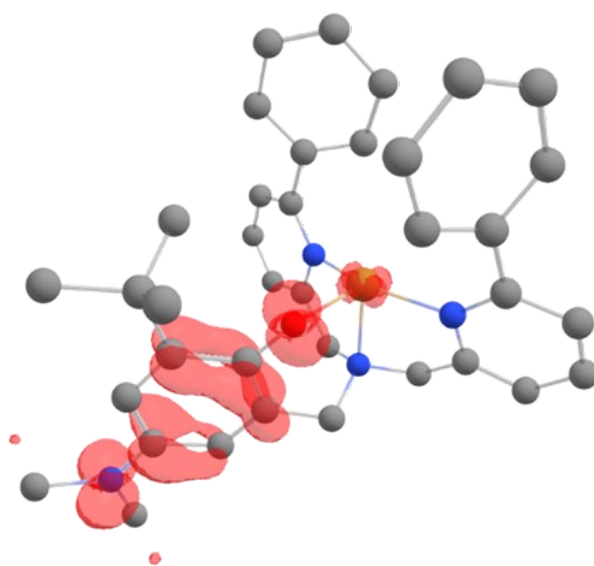
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Tatsuo Yajima, Seiji Mori and Yuichi Shimazaki\*

**Table S1.** Selected bond lengths (Å) of complexes **1**, **2**, **3** and **4**.

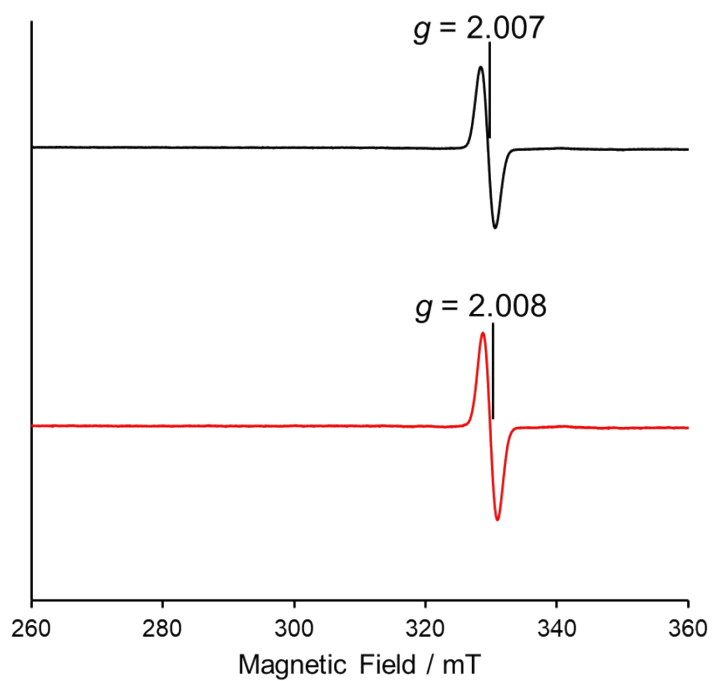
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Cu(1)–O(1)	1.951(2)	2.0669(13)	1.997(3)	-
Cu(1)–O(2)	2.000(2)	-	-	-
Cu(1)–O(3)	-	-	1.924(3)	-
Cu(2)–O(2)	-	-	1.997(3)	-
Cu(2)–O(3)	-	-	1.947(3)	-
Cu(1)–N(1)	2.056(3)	1.9863(14)	2.033(4)	2.064(4)
Cu(1)–N(2)	2.293(3)	1.9882(14)	2.279(4)	2.084(4)
Cu(1)–N(3)	2.044(3)	2.2057(14)	2.048(4)	2.195(4)
Cu(1)–N(4)	-	-	-	1.915(4)
Cu(2)–N(5)	-	-	2.039(4)	-
Cu(2)–N(6)	-	-	2.222(4)	-
Cu(2)–N(7)	-	-	2.054(4)	-

**Table S1.** Selected bond lengths (Å) of complexes **1**, **2**, **3** and **4** (continued).

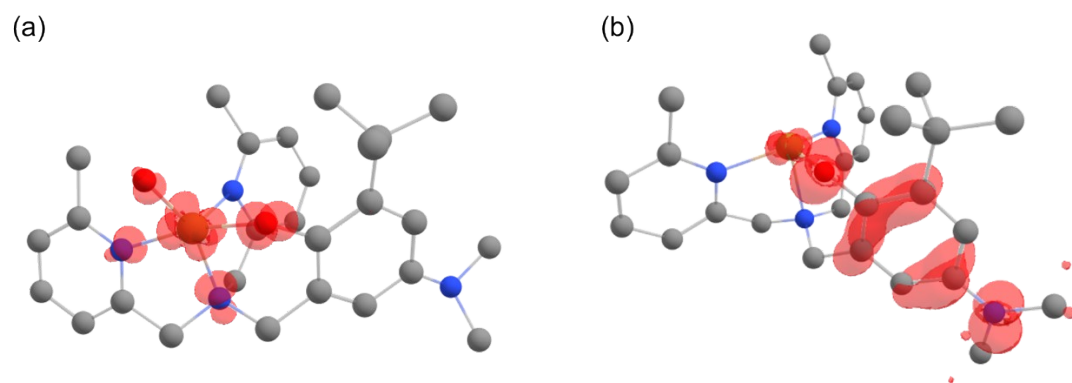
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	
	O–C(1)	1.360(3)	1.2724(19)	1.294(5), 1.290(6)	1.222(6)
	N–C(4)	1.424(4)	1.355(2)	1.350(6), 1.348(7)	1.304(4)
	C(1)–C(2)	1.420(4)	1.457(2)	1.452(7), 1.451(7)	1.512(7)
	C(2)–C(3)	1.403(4)	1.367(2)	1.373(7), 1.378(7)	1.343(7)
	C(3)–C(4)	1.393(5)	1.423(2)	1.426(7), 1.432(8)	1.461(6)
	C(4)–C(5)	1.392(5)	1.426(2)	1.419(7), 1.416(8)	1.459(7)
	C(5)–C(6)	1.390(4)	1.366(2)	1.370(6), 1.365(7)	1.338(7)
	C(6)–C(1)	1.413(5)	1.452(2)	1.444(6), 1.441(7)	1.489(6)



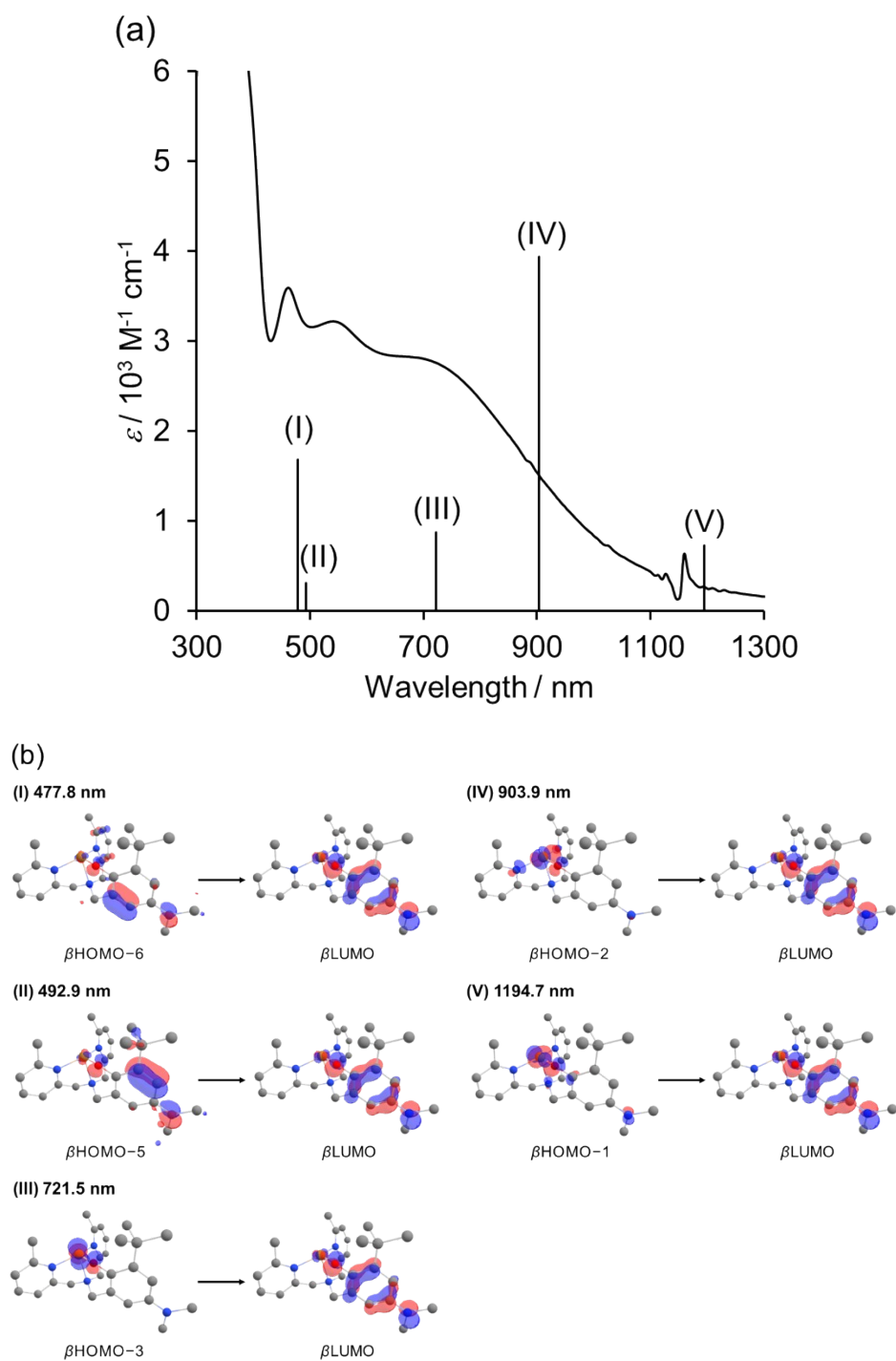
**Figure S1.** Spin density plot of complex **2**.



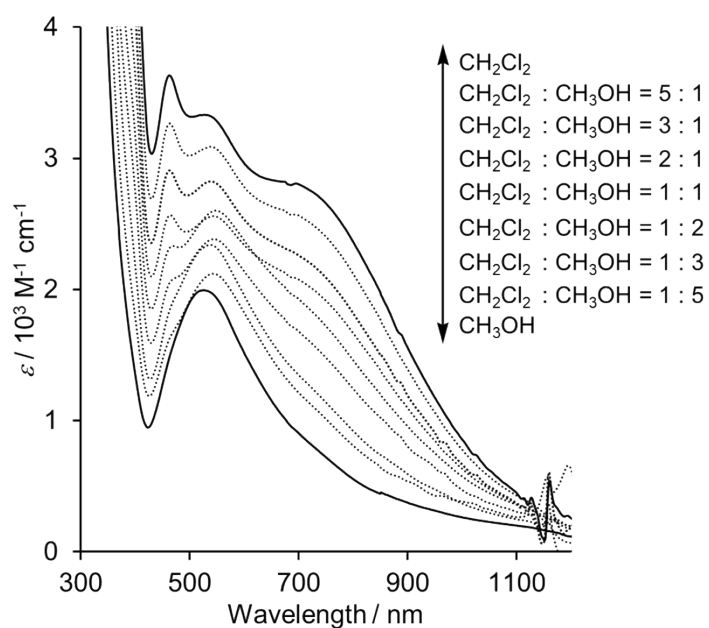
**Figure S2.** EPR spectra of complexes **1** (black line) and **2** (red line) in  $\text{CH}_2\text{Cl}_2$  solutions at 293 K.



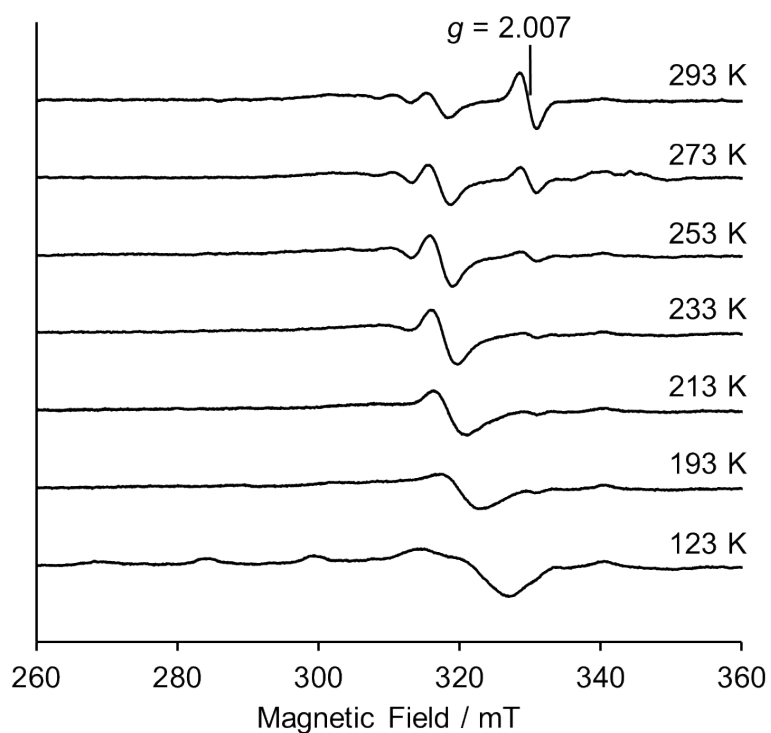
**Figure S3.** Spin density plots of complexes **1** (a) and **1** without the water molecule coordination species (b).



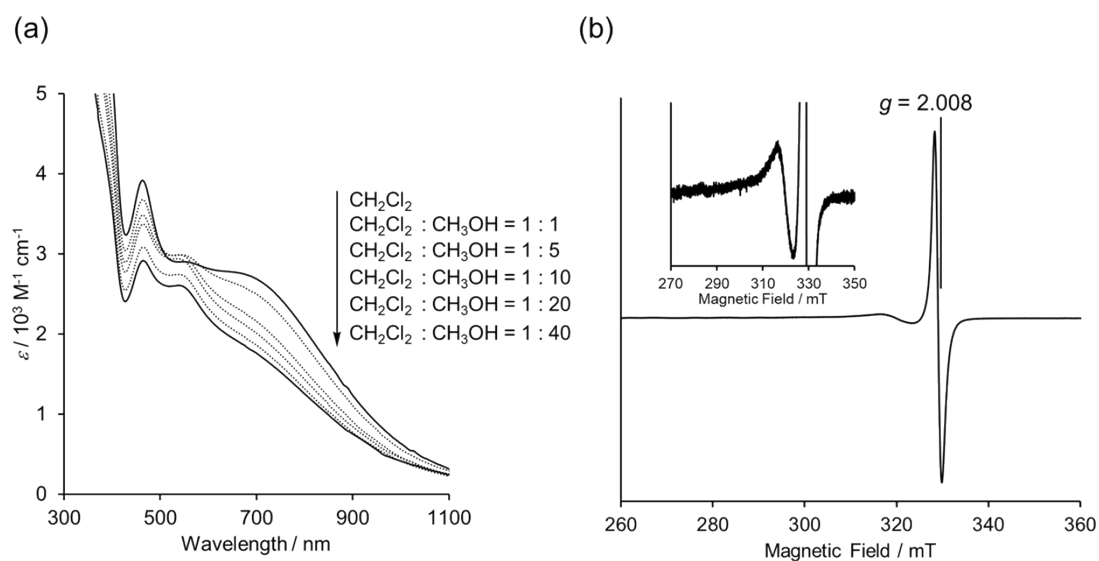
**Figure S4.** (a) Absorption spectrum of **1** in  $\text{CH}_2\text{Cl}_2$  at 293 K and predicted band positions and intensities of the TD-DFT calculation of **1** (vertical lines). (b) TD-DFT assignments of the calculated energy transitions for **1** predicted at 477.8 (I), 492.9 (II), 721.5 (III), 903.9 (IV) and 1194.7 nm (V), respectively.



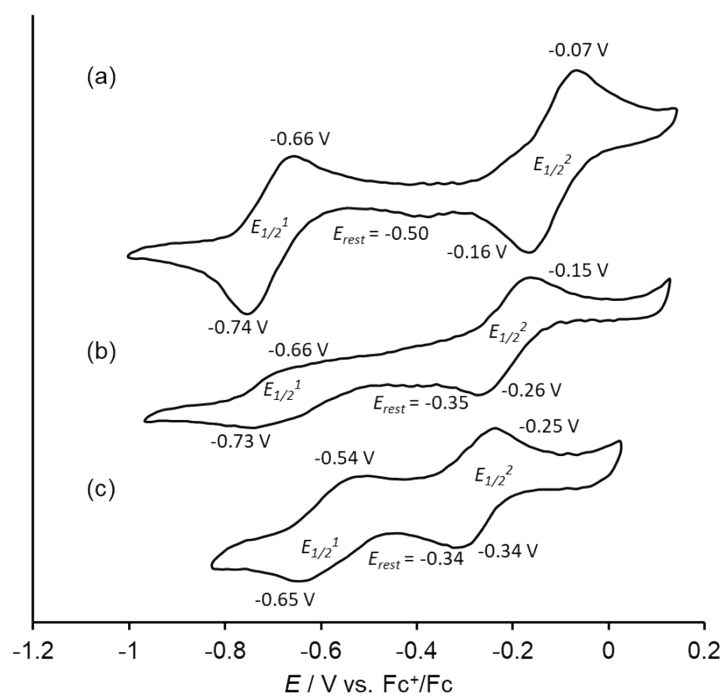
**Figure S5.** Absorption spectral change by titration of  $\text{CH}_3\text{OH}$  to the  $\text{CH}_2\text{Cl}_2$  solution of complex **1** at 293 K.



**Figure S6** Temperature dependent EPR spectral changes of complex **1** in  $\text{CH}_3\text{OH}$ .



**Figure S7.** (a) Absorption spectral change by titration of  $\text{CH}_3\text{OH}$  to the  $\text{CH}_2\text{Cl}_2$  solution of complex **2** at 293 K. (b) EPR spectrum of the  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  solution (1:40 v/v) of complex **2** at 123 K. Inset: an expanded view of the  $\text{Cu}^{\text{II}}$  signal.

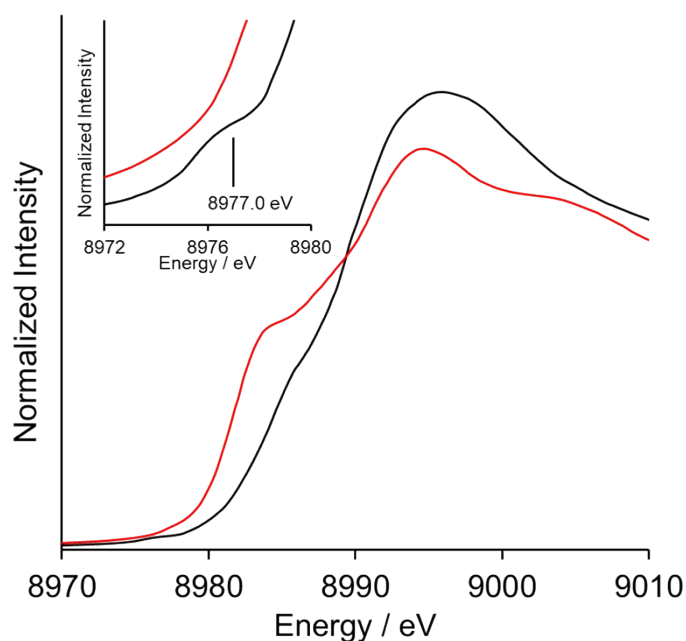


**Figure S8.** Cyclic voltammograms of the 1 mM solutions of complex **2** in  $\text{CH}_2\text{Cl}_2$  (a), **1** in  $\text{CH}_2\text{Cl}_2$  (b) and **1** in  $\text{CH}_3\text{OH}$  (c). Scan rate:  $0.05 \text{ V s}^{-1}$ ,  $T = 233 \text{ K}$ . The potentials are

referenced versus the Fc<sup>+</sup>/Fc couple. The wave at  $E_{1/2}^1 = -0.70$  V in the lower range from the rest potential in (a) was assigned to the redox of the phenoxy radical, and that at  $E_{1/2}^2 = -0.11$  V was assignable to the redox of Cu<sup>I</sup> ion, while the CH<sub>3</sub>OH solution of **1** at -40 °C existing mainly in the Cu<sup>II</sup>-phenolate state (c) also showed two quasi-reversible redox waves at  $E_{1/2}^1 = -0.59$  V and  $E_{1/2}^2 = -0.29$  V, assigned to the redox potential of Cu<sup>I</sup> ion and the phenoxy radical, respectively.

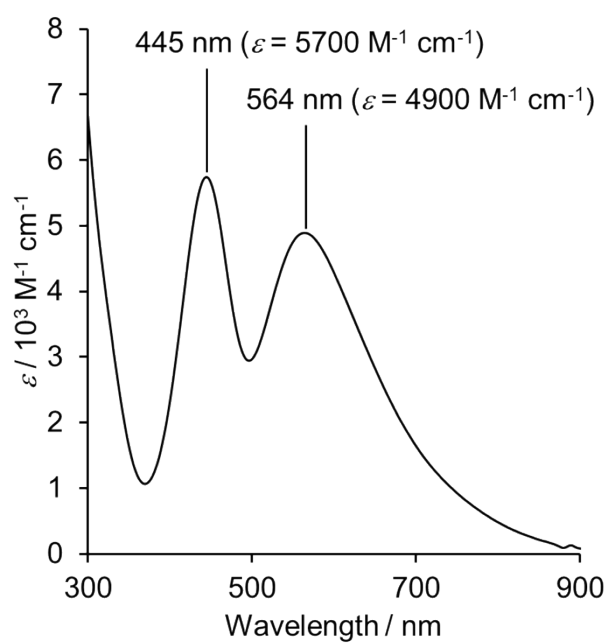
**Table S2.** CV data of **2** in CH<sub>2</sub>Cl<sub>2</sub>, **1** in CH<sub>2</sub>Cl<sub>2</sub> and **1** in CH<sub>3</sub>OH

Complex	$E_{\text{rest}} / \text{V}$	$E_{1/2}^1 / \text{V}$	$E_{1/2}^2 / \text{V}$
<b>2</b> in CH <sub>2</sub> Cl <sub>2</sub>	-0.50	-0.70	-0.11
<b>1</b> in CH <sub>2</sub> Cl <sub>2</sub>	-0.35	-0.69	-0.21
<b>1</b> in CH <sub>3</sub> OH	-0.34	-0.59	-0.29



**Figure S9.** Cu K-edge XAFS of **3** (black line) and **4** (red line). Inset; an expanded view of the pre-edge region.





**Figure S10.** Absorption spectrum of the isolated complex **4** in CH<sub>2</sub>Cl<sub>2</sub>.

## Materials

All chemicals used for syntheses and analyses were of the highest grade available.

Solvents were purified before use according to the standard methods.<sup>1</sup>

## Synthesis

### **2-*tert*-butyl-4-dimethylamino-6-{bis[(6-methyl-2-**

**pyridyl)methyl]aminomethyl}phenol (HL<sup>Mepy</sup>):** 3-*tert*-Butyl-5-(*N,N*-dimethylamino)salicylaldehyde<sup>2</sup> (1.1 g, 5.0 mmol) in CH<sub>3</sub>OH (80 mL) was added to a solution of bis(6-methyl-2-pyridylmethyl)amine (1.1 g, 5.0 mmol) in CH<sub>3</sub>OH (20 mL). The reaction mixture was stirred for 30 min at 333 K. A few drops of acetic acid and sodium cyanotrihydroborate (0.32 g, 5.0 mmol) were added to the resulting solution with stirring. The reaction mixture was stirred for 12 h at room temperature. Then, it was acidified by adding concentrated HCl and evaporated almost to dryness under reduced pressure. The residue was dissolved in saturated aqueous K<sub>2</sub>CO<sub>3</sub> (50 mL) and extracted with CHCl<sub>3</sub> (3 × 50 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated almost to dryness under reduced pressure to give a brown oil, which was purified by silica gel column chromatography (chloroform/methanol 100:1 v/v) to give the ligand, HL<sup>Mepy</sup>. Yield: 1.31 g (62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 1.46 (s, 9H), 2.56 (s, 6H), 2.81 (s, 6H), 3.74 (s, 2H), 3.82 (s, 4H), 6.42 (d, 1H), 6.75 (d, 1H), 6.98 (d, 2H), 7.16 (d, 2H), 7.49 (t, 2H), 10.26 (br s, 1H) ppm.

### **2-*tert*-butyl-4-dimethylamino-6-{bis[(6-phenyl-2-**

**pyridyl)methyl]aminomethyl}phenol (HL<sup>Phpy</sup>):** This ligand was prepared in a similar

manner to described in 2-*tert*-Butyl-4-dimethylamino-6-{bis[(6-methyl-2-pyridyl)methyl]aminomethyl}phenol (HL<sup>Mepy</sup>) by used of bis(6-phenyl-2-pyridylmethyl)amine<sup>3</sup> instead of bis(6-methyl-2-pyridylmethyl)amine, and isolated in 52% yield purified by silica gel column chromatography (CHCl<sub>3</sub> as a eluent.). Yield: 1.44 g (52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 1.47 (s, 9H), 2.82 (s, 6H), 3.96 (s, 2H), 4.00 (s, 4H), 6.44 (d, 1H), 6.77 (d, 1H), 7.28 (d, 2H), 7.41 (t, 2H), 7.47 (t, 4H), 7.57 (d, 2H), 7.64 (t, 2H), 8.09 (d, 4H), 10.57 (br s, 1H) ppm.

**[Cu(L<sup>Mepy</sup>)(H<sub>2</sub>O)]CF<sub>3</sub>SO<sub>3</sub> (1)** Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (0.045 g, 0.125 mmol) in CH<sub>3</sub>OH (1.0 ml) was added to a mixture of HL<sup>Mepy</sup> (0.054 g, 0.125 mmol) and triethylamine (17  $\mu$ l, 0.125 mmol) in CH<sub>3</sub>OH (1.0 ml) under N<sub>2</sub> atmosphere at 243 K. The reaction mixture was kept stand at 243 K under N<sub>2</sub> atmosphere for 24 h to give complex **1** as blue crystals. Yield: 39.7 mg (48%). Elemental analysis (%) calcd for (C<sub>28</sub>H<sub>37</sub>CuF<sub>3</sub>N<sub>4</sub>O<sub>5</sub>S·0.5CH<sub>2</sub>Cl<sub>2</sub>) C: 48.58, H: 5.44, N: 7.95; found: C: 48.76, H: 5.77, N: 7.78.

**[Cu(L<sup>Phpy</sup>)]BPh<sub>4</sub> (2)** Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (0.045 g, 0.125 mmol) in acetone (0.3 ml) was added to a mixture of HL<sup>Phpy</sup> (0.068 g, 0.125 mmol) and triethylamine (17  $\mu$ l, 0.125 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 ml) under N<sub>2</sub> atmosphere at 243 K. NaBPh<sub>4</sub> (0.042 g, 0.125 mmol) in acetone (0.3 ml) was added to the mixture solution. The reaction mixture was kept stand at 243 K under N<sub>2</sub> atmosphere for 24 h to give complex **2** as black crystals. Yield: 69.2 mg (59%). Elemental analysis (%) calcd for (C<sub>61</sub>H<sub>59</sub>BCuN<sub>4</sub>O·0.75CH<sub>2</sub>Cl<sub>2</sub>) C: 74.00, H: 6.08, N: 5.59; found: C: 73.88, H: 6.23, N: 5.58.

**[Cu<sub>2</sub>(L<sup>Mepy</sup>)<sub>2</sub>( $\mu$ -OH)](BF<sub>4</sub>)<sub>3</sub> (3)** Cu(BF<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O (0.042 g, 0.125 mmol) in CH<sub>3</sub>OH (1.2

ml) was added to a mixture of HL<sup>Mepy</sup> (0.054 g, 0.125 mmol) and triethylamine (17  $\mu$ l, 0.125 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 ml), and the reaction mixture was stirred for 1 h at 233 K. The solvent was concentrated by N<sub>2</sub> gas-flow at 233K, and then the reaction mixture was kept stand under the aerobic condition for 24 h at 233K to give complex **3**, as purple crystals. Yield: 38.2 mg (48%). Elemental analysis (%) calcd for (C<sub>54</sub>H<sub>71</sub>B<sub>3</sub>Cu<sub>2</sub>F<sub>12</sub>N<sub>8</sub>O<sub>3</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>) C: 49.96, H: 5.54, N: 8.55; found: C: 49.78, H: 5.59, N: 8.63.

**Cu<sup>I</sup>-iminoquinone complex, [Cu<sub>2</sub>(LQ<sup>Mepy</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**4**)** Cu(BF<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O (0.042 g, 0.125 mmol) in CH<sub>3</sub>OH (0.5 ml) was added to a mixture of HL<sup>Mepy</sup> (0.054 g, 0.125 mmol) and triethylamine (17  $\mu$ l, 0.125 mmol) in CH<sub>3</sub>OH (0.5 ml) under N<sub>2</sub> atmosphere at room temperature. The reaction mixture was kept stand under N<sub>2</sub> for 24 h at room temperature to give complex **4**, as black crystals. Yield: 12.3 mg (18 %). Elemental analysis (%) calcd for (C<sub>25</sub>H<sub>30</sub>BCuF<sub>4</sub>N<sub>4</sub>O·0.25CH<sub>3</sub>OH) C: 54.07, H: 5.57, N: 9.99; Found: C: 53.23, H: 5.41, N: 9.97. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  = 0.79 (s, 9H), 2.73 (s, 6H), 3.64 (s, 2H), 3.77 (s, 4H), 6.70 (s, 1H), 7.21 (s, 1H), 7.24 (d, 2H), 7.38 (d, 2H), 7.77 (t, 2H), 10.21 (s, 1H) ppm.

## Methods

### Physicochemical measurements

Cyclic voltammetry (CV) was performed with a HOKUTO DENKO HZ-5000 automatic polarization system. A glassy-carbon electrode and a platinum wire were used as a working and a counter electrode, respectively, with a Ag/Ag<sup>+</sup> reference electrode. All samples were prepared as a 1 mM solution with tetra-*n*-butylammonium perchlorate (0.1

M) as the electrolyte. The measurements were carried out at 233 K. The correction of the reference electrode was made by standard procedures and referenced against the ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) redox couple. UV-vis-NIR spectra were obtained with a JASCO V-670 spectrophotometer in a 10 mm cell equipped with a liquid nitrogen cooled cryostat (UNISOKU CoolSpeK UV USP-203-A). Electron paramagnetic resonance (EPR) spectra were obtained using a JES-X320 equipped with standard variable temperature control apparatus. The spectra were recorded using quartz tubes with a 5 mm inner diameter. The magnetic field was standardized against a  $\text{Mn}^{\text{II}}$  marker.  $^1\text{H-NMR}$  spectra were performed with a BRUKER AVANCE III 500 (500 MHz) NMR spectrometers. Cu K-edge XAS spectra were obtained at BL-9A of the Photon Factory (PF) at the Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. PF is operated under the ring condition of 2.5 GeV and 450 mA. BL-9A has a Si (111) double-crystal monochromator. All complexes were measured in transmission mode.

### **X-ray crystal structure determination**

X-ray diffraction measurements of all complexes were carried out at  $-140\text{ }^\circ\text{C}$  using a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71075\text{ \AA}$ ). The crystals were mounted on a loop. The cell constants and the orientation matrix were determined from three oscillation photographs taken for each frame. Intensity data were collected by taking oscillation photographs. Diffraction data were corrected for both Lorentz and polarization effects. All structures were solved by direct methods and refined anisotropically for non-hydrogen atoms. The hydrogen atoms except for water,  $\text{CH}_3\text{OH}$  and the NH group of the iminoquinone moiety in **4** were located

at the calculated positions in the last cycle of refinement. These hydrogen atoms were determined using a difference Fourier map. All the calculations were performed using the Crystal Structure crystallographic software program package.<sup>4</sup> Summaries of the fundamental crystal data and experimental parameters for the structure determination of the complexes are given in Table S3. CCDC 2153817–2153820 for complexes **1–4** respectively, contain the supplementary crystallographic data for this paper.

### Theoretical calculation

Density functional theory (DFT) calculations were performed by Gaussian 16 program (Revision B.01)<sup>5</sup> for characterization of the electronic structures of the Cu complexes,  $[\text{Cu}(\text{L}^{\text{Mepy}})(\text{H}_2\text{O})]^+$ ,  $[\text{Cu}(\text{L}^{\text{Mepy}})]^+$  and  $[\text{Cu}(\text{L}^{\text{Phpy}})]^+$ . The initial structures of  $[\text{Cu}(\text{L}^{\text{Mepy}})(\text{H}_2\text{O})]^+$  and  $[\text{Cu}(\text{L}^{\text{Phpy}})]^+$  were drawn by X-ray crystal structures of **1** and **2**, and were optimized. In the case of  $[\text{Cu}(\text{L}^{\text{Mepy}})]^+$ , the initial structure was drawn based on X-ray crystal structure of **1** without a coordinated water molecule.

The Unrestricted B3LYP+D3BJ<sup>6</sup> functional was employed for all Cu complexes. A double zeta valence polarization basis set, def2-SVP,<sup>7</sup> was employed for geometry optimizations and normal coordinate analyses. For the single-point energy calculations of more accurate electronic structures, a triple zeta valence polarization basis set, def2-TZVP<sup>8</sup> was employed.

The intensities of the 30 lowest-energy electronic transitions in the UV/Vis/NIR spectra of  $[\text{Cu}(\text{L}^{\text{Mepy}})]^+$  and  $[\text{Cu}(\text{L}^{\text{Phpy}})]^+$  were calculated by TD-B3LYP+D3BJ (denoted as TD-DFT)<sup>9</sup> with a polarized continuum model by using the integral equation formalism variant (IEF-PCM) with a dielectric constant of  $\epsilon = 8.94$  was used to estimate the  $\text{CH}_2\text{Cl}_2$  solvent effects.<sup>10,11</sup> The spin densities and molecular orbitals were visualized by

ChemCraft 1.8.<sup>12</sup>

## References

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**Table S3.** Crystallographic Data for complexes 1-4.

	1	2	3
Formula	C <sub>29</sub> H <sub>41</sub> CuF <sub>3</sub> N <sub>4</sub> O <sub>6</sub> S	C <sub>61</sub> H <sub>59</sub> BCuN <sub>4</sub> O	C <sub>59</sub> H <sub>81</sub> B <sub>3</sub> Cl <sub>10</sub> Cu <sub>2</sub> F <sub>12</sub> N <sub>8</sub> O <sub>3</sub>
Formula weight	694.27	938.52	1692.37
Color	Blue	Black	Purple
Crystal size / mm	0.15 x 0.03 x 0.02	0.23 x 0.10 x 0.05	0.24 x 0.18 x 0.07
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	10.1539(3)	11.7542(9)	11.9251(13)
<i>b</i> (Å)	12.0599(4)	15.1892(15)	14.574(3)
<i>c</i> (Å)	13.1132(5)	16.2630(14)	23.160(5)
$\alpha$ (°)	80.675(6)	115.095(8)	79.492(10)
$\beta$ (°)	84.497(6)	102.698(7)	75.784(9)
$\gamma$ (°)	87.330(6)	96.747(7)	70.683(9)
<i>V</i> (Å <sup>3</sup> )	1576.46(11)	2491.1(4)	3659.6(11)
<i>Z</i>	2	2	2
$\mu$ (cm <sup>-1</sup> )	8.24	4.85	10.25
<i>F</i> (000)	726.00	990.00	1732.00
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.462	1.251	1.536
$2\theta_{\max}$ (°)	55.0	55.0	55.0
No. reflections obsd.	15410	24218	35032
No. reflections used.	7157	11312	16499
No. variables	421	613	874
<i>R</i> <sub><i>I</i></sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0562	0.0380	0.0769
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1314	0.1033	0.1891

<sup>a</sup> $R_I = \sum ||F_o| - |F_c|| / \sum |F_o|$  for  $I > 2\sigma(I)$  data. <sup>b</sup> $R_w = \{\sum \omega (|F_o| - |F_c|)^2 / \sum \omega F_o^2\}^{1/2}$ ;  $\omega = 1 / \sigma^2(F_o)$   
 $= \{\sigma_c^2(F_o) + p^2 / 4 - F_o^2\}^{-1}$

**Table S3.** Crystallographic data (continued).

4	
Formula	C <sub>25</sub> H <sub>30</sub> BCuF <sub>4</sub> N <sub>4</sub> O
Formula weight	552.89
Color	Black
Crystal size / mm	0.10 x 0.10 x 0.10
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	9.7190(8)
<i>b</i> (Å)	22.498(2)
<i>c</i> (Å)	12.1552(10)
$\alpha$ (°)	-
$\beta$ (°)	105.257(7)
$\gamma$ (°)	-
<i>V</i> (Å <sup>3</sup> )	2564.2(4)
<i>Z</i>	4
$\mu$ (cm <sup>-1</sup> )	9.06
<i>F</i> (000)	1144.00
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.432
2 $\theta$ <sub>max</sub> (°)	55.0
No. reflections obsd.	23747
No. reflections used.	5836
No. variables	329
<i>R</i> <sub><i>I</i></sub> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0728
<i>R</i> <sub>w</sub> <sup>b</sup>	0.2140

<sup>a</sup> $R_I = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  for  $I > 2\sigma(I)$  data. <sup>b</sup> $R_w = \{\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2\}^{1/2}$ ;  $\omega = 1 / \sigma^2(F_o)$   
 $= \{\sigma_c^2(F_o) + p^2 / 4 - F_o^2\}^{-1}$

**Table S4.** Total electronic energies of Cu complexes at the B3LYP+D3BJ/def2-TZVP//B3LYP+D3BJ/def2-SVP level.

	[Cu(L <sup>Mepy</sup> )(H <sub>2</sub> O)] <sup>+</sup>	[Cu(L <sup>Mepy</sup> )] <sup>+</sup>	[Cu(L <sup>Phpy</sup> )] <sup>+</sup>
$E(E_h)$	-3061.8436	-2985.3706	-3369.0373

**Table S5.** Cartesian coordinates of Cu complexes

[Cu(L<sup>Mepy</sup>)(H<sub>2</sub>O)]<sup>+</sup> ( $\langle S^2 \rangle = 0.7500$ )

Cu	1.513610	0.386520	-0.726174
O	-0.227551	0.772655	-1.516061
O	2.218083	1.981511	-1.705893
H	2.916402	1.801960	-2.359635
H	1.462230	2.335375	-2.210649
N	3.402132	-0.289810	-0.274215
N	0.742855	0.427153	1.432551
N	1.099936	-1.606805	-0.552045
N	-4.672785	-2.100779	0.375025
C	-1.345213	0.134812	-1.075288
C	-2.544674	0.818923	-0.743447
C	-3.618842	0.049880	-0.270845
H	-4.538756	0.564769	-0.010715
C	-3.587653	-1.335332	-0.140772
C	-2.418194	-1.989406	-0.516864
H	-2.343861	-3.075009	-0.421786
C	-1.318591	-1.274470	-0.975700
C	-0.079947	-1.998691	-1.380440
H	0.182748	-1.755618	-2.421957
H	-0.224865	-3.088925	-1.304296
C	4.307456	1.851617	0.515460
H	5.152537	2.216276	1.114047
H	4.247194	2.456737	-0.401385

H	3.374967	2.018773	1.069916
C	4.474370	0.398849	0.201067
C	5.694606	-0.240467	0.385617
H	6.538672	0.346135	0.752698
C	5.822544	-1.578475	0.150825
H	6.777133	-2.083852	0.315475
C	4.714498	-2.298944	-0.296809
H	4.761429	-3.372689	-0.482648
C	3.531919	-1.608568	-0.503059
C	2.305016	-2.298082	-1.046715
H	2.310631	-2.225513	-2.146143
H	2.300692	-3.369065	-0.785650
C	0.945627	2.785783	2.006379
H	0.277740	3.604410	2.306109
H	1.851796	2.846445	2.633209
H	1.252807	2.933266	0.963048
C	0.290510	1.442779	2.188742
C	-0.718458	1.263061	3.121448
H	-1.066532	2.118011	3.704008
C	-1.276566	0.011006	3.297374
H	-2.086918	-0.140243	4.014336
C	-0.793790	-1.041834	2.551148
H	-1.202638	-2.047991	2.657055
C	0.218150	-0.808319	1.639088
C	0.861273	-1.937541	0.892897
H	0.265282	-2.857993	0.975488
H	1.839947	-2.131209	1.357356
C	-5.751998	-1.348315	1.003081
H	-6.435606	-2.052925	1.500864
H	-5.350740	-0.664170	1.765115
H	-6.352272	-0.751888	0.283386
C	-5.199629	-3.101534	-0.543439
H	-5.892847	-3.769371	-0.007894
H	-5.752579	-2.644497	-1.392281
H	-4.394528	-3.721253	-0.960265

C	-2.703100	2.337479	-0.945443
C	-4.115564	2.827294	-0.580159
H	-4.894455	2.355748	-1.199301
H	-4.357464	2.641955	0.477824
H	-4.175476	3.914686	-0.745547
C	-1.708664	3.094891	-0.056153
H	-1.909300	2.900540	1.007803
H	-0.682306	2.778929	-0.275735
H	-1.786959	4.181813	-0.225499
C	-2.442692	2.696436	-2.414161
H	-3.171037	2.200010	-3.076666
H	-2.536138	3.784630	-2.566491
H	-1.435217	2.384031	-2.720716

[Cu(L<sup>Mepy</sup>)]<sup>+</sup> (<S<sup>2</sup>> = 0.7501)

Cu	-1.471716	0.325725	0.403704
O	0.150822	-0.485379	1.302610
N	-2.928233	-1.108874	0.346100
N	-1.211453	1.972485	-0.742259
N	-0.871878	-0.703026	-1.556538
N	4.956684	-1.305770	-1.239745
C	1.266840	-0.616251	0.695034
C	2.503840	-0.084423	1.249619
C	3.691531	-0.333810	0.591295
H	4.616333	0.045041	1.014034
C	3.762208	-1.068189	-0.631447
C	2.539828	-1.526676	-1.203218
H	2.543879	-2.052189	-2.157034
C	1.331686	-1.306965	-0.578762
C	0.055606	-1.791078	-1.222078
C	-0.328661	0.359673	-2.385077
H	-0.496228	0.190230	-3.465477
H	0.763490	0.375537	-2.245007

C	-0.831714	1.746426	-2.014595
C	-0.825807	2.773429	-2.961743
H	-0.529412	2.559742	-3.990417
C	-1.196594	4.058383	-2.569155
H	-1.196529	4.879359	-3.290050
C	-1.573958	4.281409	-1.244635
H	-1.871464	5.274114	-0.902977
C	-1.580255	3.209614	-0.346826
C	-1.991884	3.363543	1.085762
H	-2.319268	4.388777	1.305532
H	-2.814870	2.668576	1.320669
H	-1.152586	3.111531	1.753582
C	-2.184797	-1.179643	-1.975498
H	-2.120414	-1.920387	-2.796020
H	-2.747965	-0.316343	-2.367370
C	-2.984879	-1.766247	-0.828097
C	-3.770620	-2.908286	-0.983103
H	-3.790416	-3.429673	-1.941773
C	-4.515528	-3.363963	0.106440
H	-5.138947	-4.256449	0.014659
C	-4.443906	-2.675572	1.316937
H	-5.005631	-3.012394	2.189744
C	-3.628218	-1.541343	1.411484
C	-3.478814	-0.750513	2.676648
H	-4.019514	-1.212783	3.513642
H	-2.412641	-0.664814	2.941383
H	-3.862709	0.273613	2.534226
C	2.463124	0.741355	2.543775
C	1.546954	1.967589	2.331798
H	0.529392	1.659983	2.064429
H	1.501099	2.570104	3.253569

H	1.935351	2.611387	1.525803
C	1.926169	-0.125558	3.703800
H	0.911628	-0.486004	3.493714
H	2.578598	-0.997969	3.871291
H	1.905390	0.463761	4.635261
C	3.853601	1.257567	2.945982
H	4.557745	0.435931	3.150624
H	4.294855	1.904698	2.171689
H	3.767157	1.854613	3.866959
C	6.193123	-0.785613	-0.674254
H	7.028530	-1.056264	-1.329094
H	6.163549	0.312847	-0.587393
H	6.385533	-1.204675	0.327381
C	5.017624	-2.073403	-2.475003
H	6.065875	-2.209326	-2.762497
H	4.562033	-3.068807	-2.349086
H	4.495324	-1.557463	-3.298531
H	0.304162	-2.394365	-2.117480
H	-0.472942	-2.455386	-0.519673

**[Cu(L<sup>Phpy</sup>)]<sup>+</sup> (<S<sup>2</sup>> = 0.7500)**

Cu	0.801688	0.693904	0.524228
O	-0.434854	0.080004	-1.01394
N	1.976194	2.146658	-0.15088
N	0.007267	-0.17642	2.125456
N	-0.595433	2.330099	1.010157
N	-5.892597	0.457113	-0.94297
C	-1.704216	0.142412	-0.95125
C	-2.535861	-0.97514	-1.37821
C	-3.895083	-0.83049	-1.35267
H	-4.515571	-1.66136	-1.67299

C	-4.540748	0.361182	-0.91788
C	-3.722166	1.441694	-0.47465
H	-4.185353	2.37554	-0.15576
C	-2.359758	1.350516	-0.48274
C	-1.518936	2.554987	-0.11778
H	-0.895266	2.818356	-0.98776
H	-2.181020	3.418751	0.08858
C	4.899963	0.392401	-1.3096
H	5.613871	1.086388	-0.86041
C	5.331927	-0.84125	-1.77405
H	6.388467	-1.10863	-1.69614
C	4.434865	-1.71973	-2.34889
H	4.781373	-2.6829	-2.73097
C	3.087528	-1.38307	-2.43888
H	2.375283	-2.0764	-2.89136
C	2.638990	-0.17013	-1.93975
H	1.582774	0.091618	-2.00439
C	3.545978	0.73122	-1.37752
C	3.097034	2.067574	-0.91259
C	3.818550	3.202482	-1.27873
H	4.707021	3.094511	-1.90047
C	3.369653	4.445556	-0.881
H	3.912939	5.348348	-1.16942
C	2.209884	4.535968	-0.1372
H	1.818372	5.504724	0.179627
C	1.538563	3.374158	0.223523
C	0.346348	3.451937	1.150954
H	0.742462	3.428499	2.179301
H	-0.152126	4.432653	1.028212
C	2.560431	-1.55153	1.585254
H	2.681510	-0.48269	1.776515



C	3.592388	-2.2698	1.003846
H	4.514179	-1.75907	0.723844
C	3.448788	-3.6305	0.769541
H	4.261849	-4.19068	0.301935
C	2.275721	-4.27925	1.130093
H	2.157240	-5.34866	0.94249
C	1.243113	-3.56334	1.720619
H	0.312731	-4.07126	1.982325
C	1.372859	-2.18908	1.951981
C	0.275080	-1.42437	2.594197
C	-0.440561	-1.96616	3.656916
H	-0.173104	-2.95462	4.030413
C	-1.460214	-1.23762	4.241928
H	-2.027273	-1.65176	5.078549
C	-1.740774	0.02001	3.75435
H	-2.538213	0.627137	4.188909
C	-0.989628	0.531003	2.705615
C	-1.265573	1.953064	2.251494
H	-2.357073	2.077586	2.161202
H	-0.956247	2.625805	3.068823
C	-6.718964	-0.56016	-1.58084
H	-7.752369	-0.20287	-1.6383
H	-6.371811	-0.77164	-2.60456
H	-6.712391	-1.50679	-1.01411
C	-6.589070	1.630677	-0.43274
H	-7.655546	1.403602	-0.32784
H	-6.207539	1.915512	0.559212
H	-6.482376	2.499673	-1.10649
C	-1.863940	-2.26244	-1.86774
C	-1.061805	-1.95804	-3.14108
H	-1.717263	-1.57542	-3.93934

H	-0.277178	-1.21603	-2.95263
H	-0.586392	-2.88015	-3.51241
C	-0.930392	-2.81789	-0.78854
H	-0.475128	-3.75995	-1.13151
H	-0.122675	-2.12024	-0.54658
H	-1.485263	-3.03561	0.138646
C	-2.889364	-3.35724	-2.20351
H	-3.567609	-3.05879	-3.01812
H	-2.359650	-4.26137	-2.53725
H	-3.497424	-3.63511	-1.32812