CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Reversible Conversion of Electronic Structures in Cyclic Octacopper Complex

Tatsuya Kawamoto,* Masato Nishiwaki, Makiko Nishijima, Koichi Nozaki,
Asako Igashira-Kamiyama, and Takumi Konno

Department of Chemistry, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560-0043, Japan
Department of Chemistry, Graduate School of Science and Engineering,
University of Toyama, Toyama, Toyama 930-8555, Japan

Experimental Section

General Procedures. Synthetic reactions except [**1**]$(ClO_4)_2$ were carried out using standard Schlenk techniques under a nitrogen atmosphere; the solvents were thoroughly degassed by nitrogen purge. All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise.

Infrared spectra were obtained on a JASCO FT/IR-5000 spectrophotometer using the nujol mulls, NMR spectra on a JEOL JNM-A500 instrument using tetramethylsilane as internal standard (*d* = 0). The UV/Vis/NIR absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical studies were performed by a CV-600A apparatus (BAS) with a glassy carbon working electrode, Ag/Ag^+ reference electrode, and a Pt-wire auxiliary electrode. Voltammetric measurements were conducted in $ClCH_2CH_2Cl$ with 0.1 M $[Bu_4N]BF_4$ as a supporting electrolyte and complex concentration of 1.0 mM. Spectroelectrochemical measurements were performed under same conditions except for the use of a thin-layer quartz cell with a Pt-mesh as a working electrode. X-Band EPR spectra were recorded on a JEOL EPR spectrometer JM-FE1. Elemental analysis of all compounds was performed at Osaka University.

Preparation of $[Cu_8\{S(C_6H_4)N{=}CH(C_6H_4NMe_2)\}_8](CuCl_2)$ ([1]$(CuCl_2)$). To a solution of 2-(4-dimethylaminophenyl)benzothiazoline (0.42 g, 1.6 mmol) in 1,2-dichloroethane (10 mL) was added copper(II) acetate monohydrate (0.16 g, 0.82 mmol). The reaction solution was refluxed for 2 h and diethyl ether (10 mL) was added to it. Precipitated dark brown powder was collected by filtration. Yield: 31 mg (11% based on Cu). Anal. Calcd for $(C_{15}H_{15}CuN_2S)_8CuCl_2.3ClCH_2CH_2Cl$: C, 50.74; H, 4.46; N, 7.51%. Found: C, 50.77; H, 4.59; N, 7.81%. IR (Nujol mull, cm^{-1}): $\nu_{C=N}$ = 1607. l_{max}/nm (e/dm^3 mol^{-1} cm^{-1}) 385 (1.84×10^5), 1768 (2.56×10^4). Crystals suitable for an X-ray crystallographic study were grown from the slow diffusion of diethyl ether into a 1,2-dichloroethane solution of dark brown powder.

Preparation of $[Cu_8\{S(C_6H_4)N{=}CH(C_6H_4NMe_2)\}_8](ClO_4)_2$ ([1]$(ClO_4)_2$). $[Cu_8\{S(C_6H_4)N{=}CH(C_6H_4NMe_2)\}_8](CuCl_2)$ ([**1**]$(CuCl_2)$) (104 mg, 0.035 mmol) was dissolved in methanol (50 mL) and the suspension was then filtered through Celite. To a dark brown filtrate was added sodium perchlorate (90 mg, 0.74 mmol) in methanol (5 mL). Precipitated brown powder was collected by filtration. Yield: 63 mg (62%). Anal. Calcd for $(C_{15}H_{15}CuN_2S)_8(ClO_4)_2.(NaClO_4)_{1.5}$: C, 49.13; H, 4.12; N, 7.64%. Found: C, 48.93; H, 4.13; N, 7.41%. ^{1}H NMR (500 MHz, $ClCD_2CD_2Cl$, 323 K): *d* 7.58 (br s, 2H), 7.45 (s, 1H), 7.02 (d, 1H), 6.80 (t, 1H), 6.57 (d, 2H), 6.55 (d, 1H), 6.42 (t, 1H), 3.16 (s, 6H). IR (Nujol mull, cm^{-1}): $\nu_{C=N}$ = 1609, $\nu_{Cl\text{-}O}$ = 1096. l_{max}/nm (*e*/dm^3 mol^{-1} cm^{-1}) 392 (1.87 × 10^5), 1221 (8.45 × 10^4). Crystals suitable for an X-ray crystallographic study were grown from the slow diffusion of diethyl ether into a 1,2-dichloroethane solution of very fine brown powder which was obtained by using ammonium hexafluorophosphate instead of sodium perchlorate.

Preparation of [$Cu_8\{S(C_6H_4)N{=}CH(C_6H_4CF_3)\}_8$] ([1a]^0). To a solution of 2-(4-trifluoromethylphenyl)benzothiazoline (0.24 g, 0.84 mmol) in 1,2-dichloroethane (15 mL) was added copper(II) acetate monohydrate (0.082 g, 0.41 mmol). The reaction solution was refluxed for 2 h and *n*-pentane (30 mL) was added to it. Precipitated black powder was collected by filtration. Yield: 0.13 g (87% based on Cu). Anal. Calcd for $(C_{14}H_9CuF_3NS)_8 \cdot ClCH_2CH_2Cl$: C, 48.05; H, 2.69; N, 3.93%. Found: C, 48.01; H, 2.74; N, 3.95%. IR (Nujol mull, cm^{-1}): $n_{C=N}$ = 1614. l_{max}/nm (*e*/dm^3 mol^{-1} cm^{-1}) 297 (1.07 × 10^5), 481 (1.30 × 10^4), 625 (1.21 × 10^4), 1685 (6.84 × 10^2). Crystals suitable for an X-ray crystallographic study were obtained from a 1,2-dichloroethane solution of [**1a**]^0 layered with *n*-pentane.

X-ray Crystallography. X-ray crystallographic data for [**1**]($CuCl_2$) and [**1**](PF_6)$_2$ were collected on a Rigaku RAXIS-RAPID image plate diffractometer with Mo Kα (l = 0.71073 Å) radiation at 200 K. Empirical absorption corrections were applied. The structures of [**1**]($CuCl_2$) and [**1**](PF_6)$_2$ were respectively solved by direct methods with SIR 92 and the Patterson method with DIRDIF99 (PATTY)[1] and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[2] Hydrogen atoms were placed at calculated positions and refined isotropically. [**1a**]^0 was measured on a Bruker SMART CCD diffractometer with Mo Kα (l = 0.71073 Å) radiation at 100 K. Semiempirical absorption corrections with SADABS were applied. The structure was solved by direct methods with SIR 97 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[2] Hydrogen atoms were placed at calculated positions and refined isotropically.

References

[1] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF99 Program System, Technical Report of the Crystallography Laboratory*; University of Nijmegen, The Netherlands, 1999.

[2] G. M. Sheldrick, *SHELXL-97. A Program for Crystal Structure Refinement*; University of Göttingen, Germany, 1997.

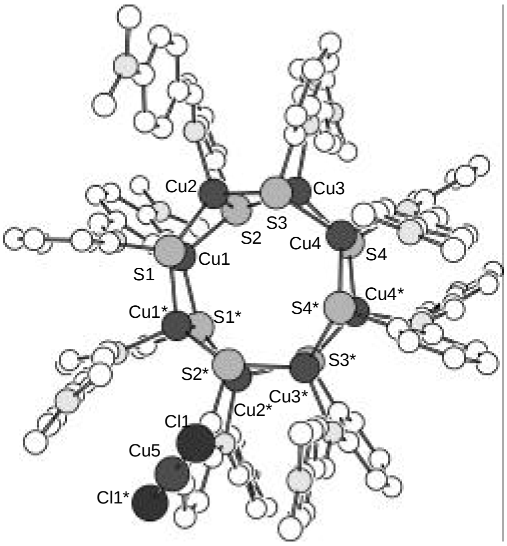


Figure S1. Structure of the monocation $[\mathbf{1}]^+$ and monoanion $CuCl_2^-$. Selected bond length [Å]: Cu1-S1 2.4285(15), Cu1-S1* 2.3323(17), Cu1-S2 2.3304(16), Cu1-N1 2.056(4), Cu2-S1 2.3085(17), Cu2-S2 2.4159(15), Cu2-S3 2.3457(15), Cu2-N2 2.051(5), Cu3-S2 2.3352(14), Cu3-S3 2.4305(16), Cu3-S4 2.3039(15), Cu3-N3 2.070(5), Cu4-S3 2.3399(15), Cu4-S4 2.4493(16), Cu4-S4* 2.3245(19), Cu4-N4 2.049(4), Cu1···Cu1* 2.6322(16), Cu1···Cu2 2.5709(10), Cu2···Cu3 2.6301(9), Cu3···Cu4 2.5689(11), C4···Cu4* 2.6709(15).

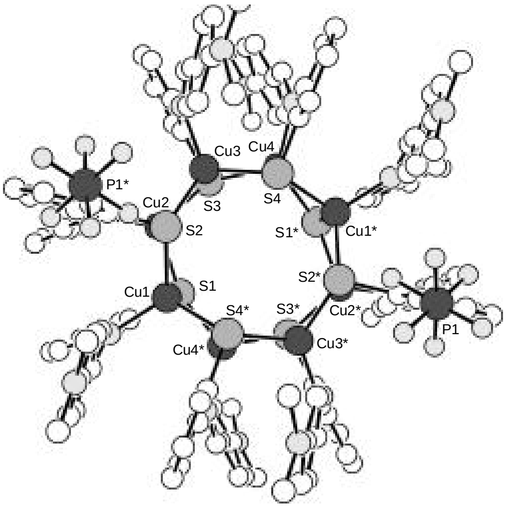


Figure S2. Structure of the dication $[\mathbf{1}]^{2+}$ and two PF_6^- anion. Selected bond length [Å]: Cu1-S1 2.4196(18), Cu1-S2 2.2939(16), Cu1-S4* 2.3238(16), Cu1-N1 2.061(5), Cu2-S1 2.3450(16), Cu2-S2 2.4165(18), Cu2-S3 2.3018(15), Cu2-N2 2.057(5), Cu3-S2 2.3101(15), Cu3-S3 2.4222(18), Cu3-S4 2.3305(16), Cu3-N3 2.035(5), Cu4-S1* 2.3028(16), Cu4-S3 2.3056(16), Cu4-S4 2.3922(18), Cu4-N4 2.050(5), Cu1···Cu2 2.5845(10), Cu1···Cu4* 2.5627(10), Cu2···Cu3 2.5619(10), Cu3···Cu4 2.6165(11).

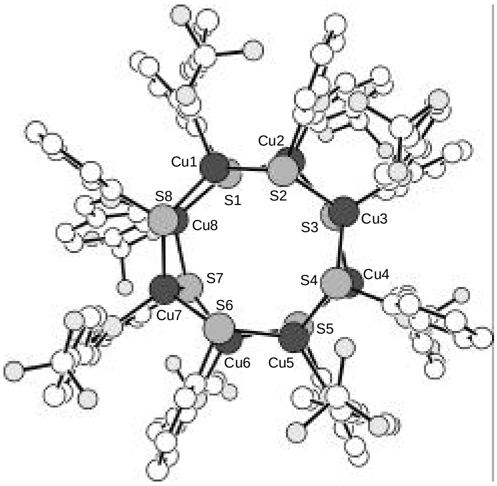
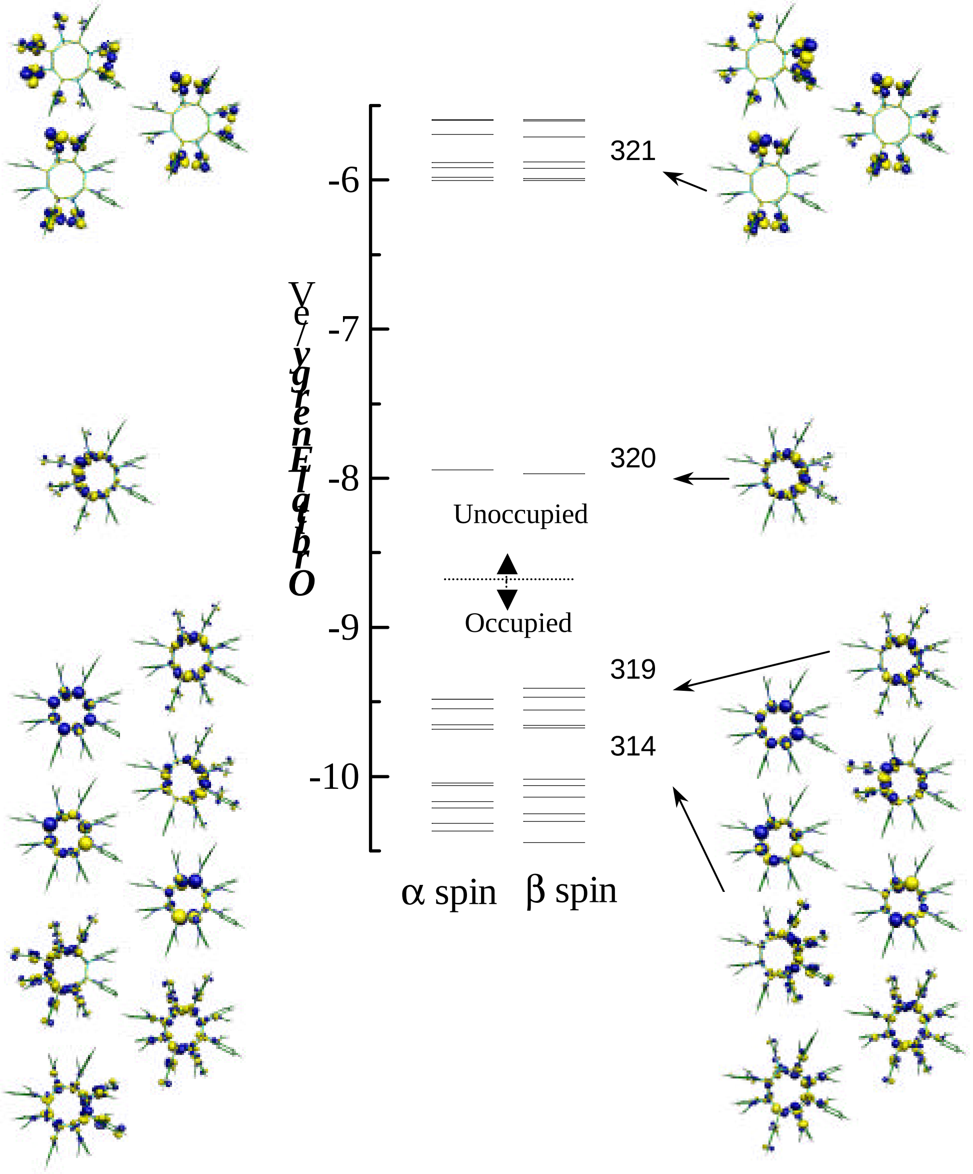


Figure S3. Molecular structure of [**1a**]^0. Selected bond length [Å]: Cu1-S1 2.4599(12), Cu1-S2 2.3405(12), Cu1-S8 2.3155(12), Cu1-N1 2.060(4), Cu2-S1 2.3235(12), Cu2-S2 2.3941(12), Cu2-S3 2.3522(12), Cu2-N2 2.056(4), Cu3-S2 2.3490(12), Cu3-S3 2.3832(12), Cu3-S4 2.3518(12), Cu3-N3 2.052(4), Cu4-S3 2.3406(11), Cu4-S4 2.4185(13), Cu4-S5 2.3480(13), Cu4-N4 2.066(4), Cu5-S4 2.3424(13), Cu5-S5 2.4139(12), Cu5-S6 2.3518(11), Cu5-N5 2.076(4), Cu6-S5 2.3502(12), Cu6-S6 2.3759(12), Cu6-S7 2.3402(12), Cu6-N6 2.054(4), Cu7-S6 2.3580(12), Cu7-S7 2.3998(12), Cu7-S8 2.3162(12), Cu7-N7 2.045(4), Cu8-S1 2.3091(12), Cu8-S7 2.3318(12), Cu8-S8 2.4734(12), Cu8-N8 2.055(4), Cu1···Cu2 2.5607(7), Cu1···Cu8 2.6691(8), Cu2···Cu3 2.6691(8), Cu3···Cu4 2.5590(8), Cu4···Cu5 2.6528(8), Cu5···Cu6 2.5560(8), Cu6···Cu7 2.6816(8), Cu7···Cu8 2.5563(7).



MOs for α spin
(No312~No323)

MOs for β spin
(No312~No323)

Figure S4. Energy level of molecular orbital calculated using unrestricted DFT for [**1b**]$^{2+}$, a model molecule for [**1**]$^{2+}$, obtained by replacing dimethylamino group in **1** by hydrogen. Gaussian keyword for density functional used was UPBE1PBE and the basis set employed were LANL2DZ for Cu and S, D95 for C, N, H atoms.

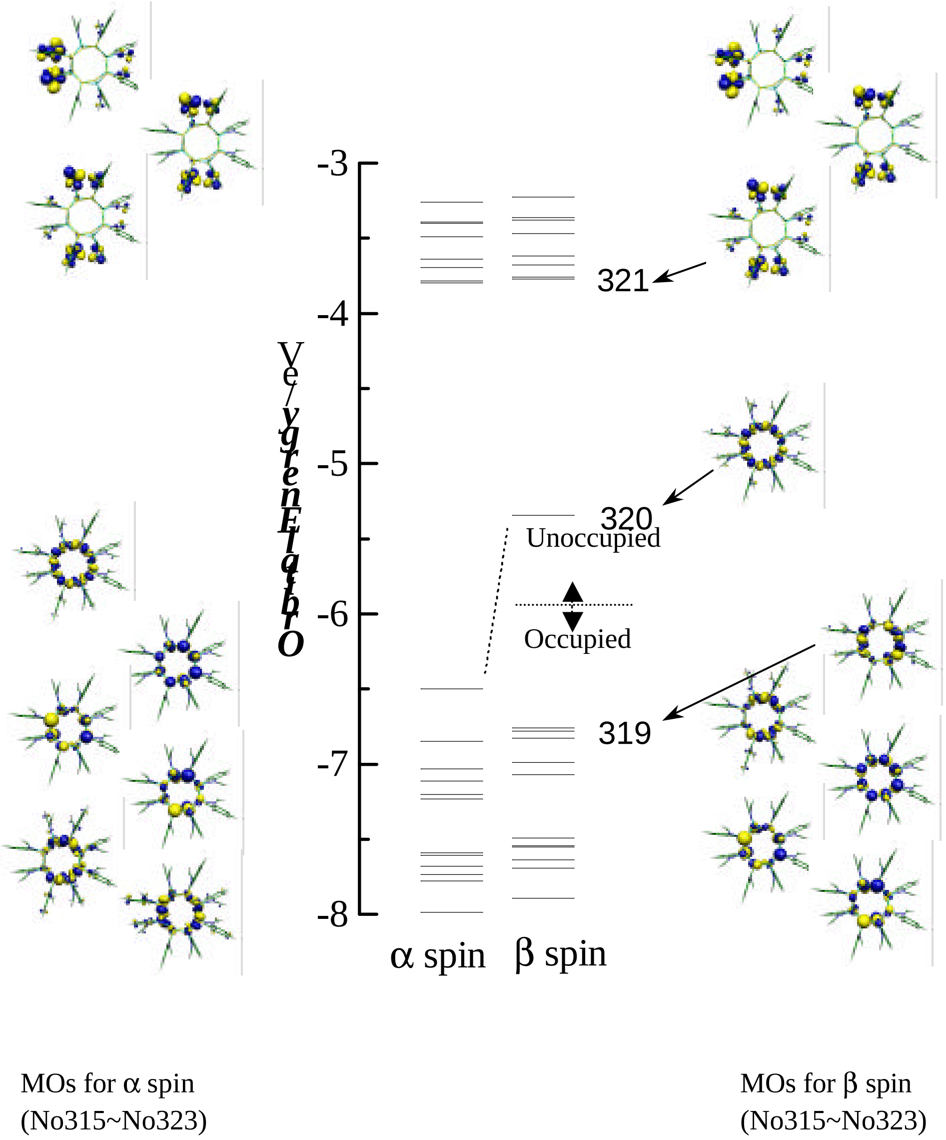


Figure S5. Energy level of molecular orbital calculated using unrestricted DFT for $[\mathbf{1b}]^{+}$.

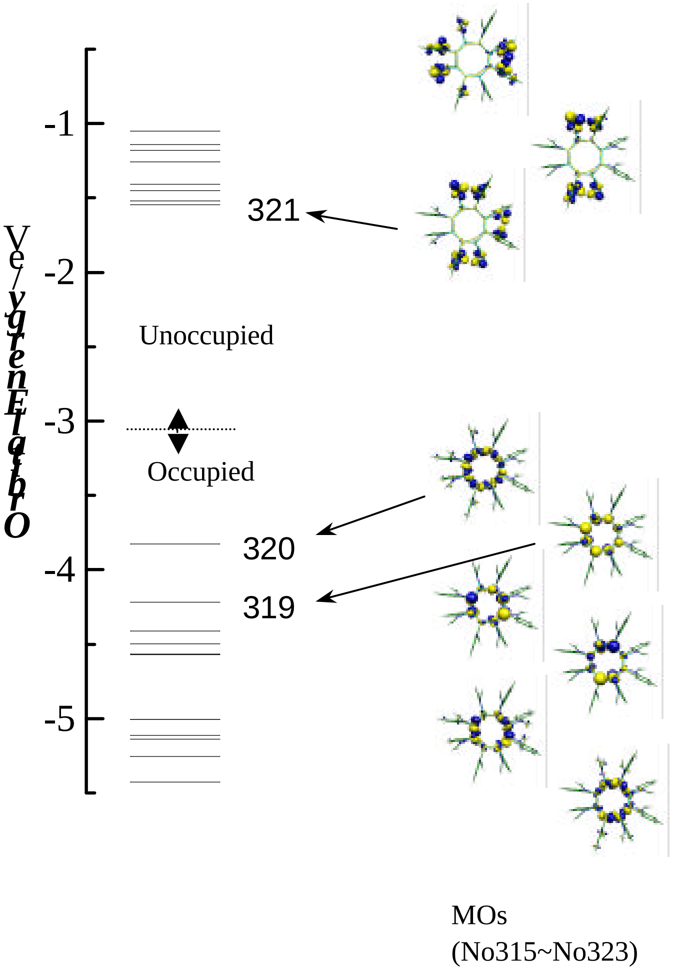


Figure S6. Energy level of molecular orbital calculated using unrestricted DFT for [**1b**]^0.

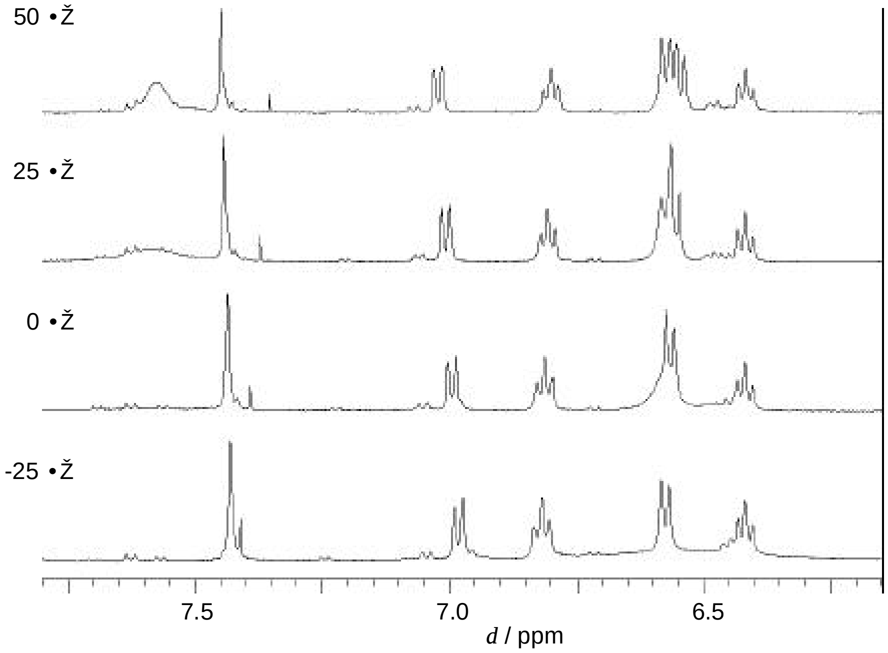


Figure S7. The variable-temperature ^{1}H NMR spectra of [**1**]$^{2+}$ in $ClCD_2CD_2Cl$.

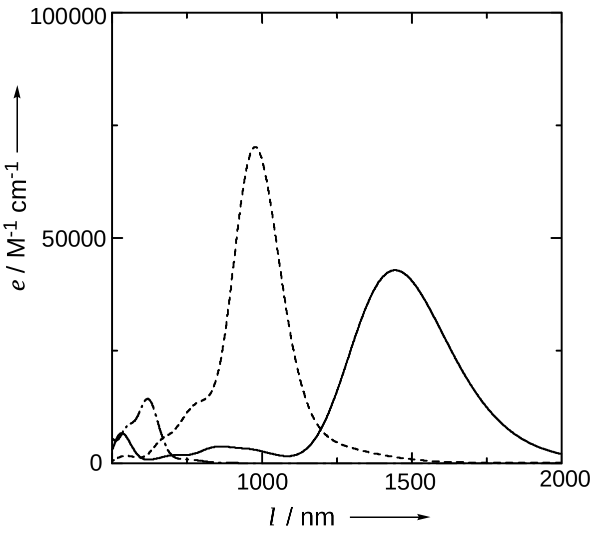


Figure S8. Simulated electronic absorption spectra for [**1b**]$^{2+}$ (dashed line), [**1b**]$^{+}$ (solid line), and [**1b**]^{0} (dashed-dotted line).

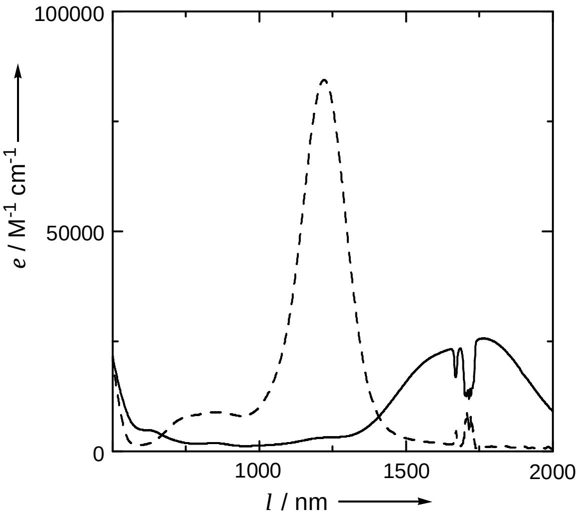


Figure S9. Electronic absorption spectra of [**1**]$^{2+}$ (dashed line) and [**1**]$^{+}$ (solid line) in $ClCH_2CH_2Cl$.

Table S1. Excitation wavelengths, oscillator strength (*f*), and major electronic configurations obtained by time-dependent DFT calculations for **1b**.

Excitation Index	Wavelength /nm	*f*	major contribution (coeff)
[**1b**]$^{2+}$			
9:	1277	0.0205	312B? 320B(0.72) 314B? 320B(0.51)
14:	997	0.2122	319A? 320A(0.44) 311B? 320B(0.46) 319B? 320B(0.38)
15:	974	0.2373	317A ? 320A(0.53) 317B? 320B(-0.49)
16:	958	0.0550	311A ? 320A(0.42) 314B? 320B(0.49)
17:	952	0.0761	310B? 320B(0.74)
19:	871	0.0260	309A? 320A(-0.49) 311B? 320B(0.64)
20:	816	0.0277	309A? 320A(0.48) 314A? 320A(0.41)
21:	798	0.0352	311A? 320A(-0.45) 312A? 320A(0.56) 309B? 320B(-0.46)
22:	758	0.0428	309A? 320A(-0.43) 307B? 320B(0.61)
28:	665	0.0250	296A? 320A(-0.38) 306B? 320B(0.63)
[**1b**]$^{+}$			
4:	1446	0.1741	318B? 320B(0.91)
5:	1442	0.1803	317B? 320B(0.39) 319B? 320B(0.81)
8:	975	0.0205	311B? 320B(-0.46) 312B? 320B(0.66) 313B? 320B(-0.54)
10:	850	0.0258	311B? 320B(0.74) 313B? 320B(-0.64)
46:	520	0.0243	319A? 323A(0.39) 317B? 323B(0.43)
[**1b**]^{0}			
9:	621	0.0305	320? 326(0.57)
10:	617	0.0333	318? 323(0.29) 319? 324(0.39)
11:	614	0.0227	320? 327(0.60)
15:	555	0.0423	318? 321(-0.32) 319? 326(0.42)
38:	466	0.0388	313? 323(0.20) 313? 324(0.36) 317? 327(-0.20)
45:	456	0.0251	315? 326(0.28) 316? 325(-0.26) 319? 328(-0.26)