Importance of \( \mathbf{\mu} \mathbf{\mu} \) Bond for Long-range Antiferromagnetic Coupling in Directly Linked Cu(II)- and Ag(II)-Diporphyrins

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1. General

\(^1\text{H}\) NMR spectra were recorded on a JEOL delta-600 spectrometer, where chemical
shifts were determined with respect to undeuterated solvents as internal references. EPR spectra were recorded on a Bruker E500 spectrometer operating at X band and equipped with an Oxford helium cryostat. To determine the \( g \) values, the observed EPR spectrum was simulated by Bruker WIN-EPR Sim Fonia program using Gaussian line function. The solid-state magnetic susceptibilities were measured between 2 and 300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-5 and Quantum Design MPMS-1). UV-Vis absorption spectra were recorded on a ShimadzuUV-3100 spectrometer. MALDI-TOF-MS spectra were recorded using dithranol as a matrix on a SHIMADZU KOMPACT MALDI 4 mass spectrometer. FAB-MS spectra were recorded on a JEOL HX-110 spectrometer, using a positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzyl alcohol matrix.

2. Synthesis

2-1. Bis-copper(II) complexes 1Cu–5Cu.

A saturated solution of Cu(OAc)\(_2\) in CH\(_3\)OH (3 mL) was added to the diporphyrins 1–5 (0.10 mmol) in CHCl\(_3\) (100 mL) and the resulting mixture was stirred for 2 h at 60°C. After usual work-up, the organic extract was washed with water, dried over anhydrous Na\(_2\)SO\(_4\) and evaporated. The solid was taken up in CH\(_2\)Cl\(_2\) and purified by silica gel chromatography by CH\(_2\)Cl\(_2\). 1Cu: Yield, 91%. MS (FAB) found \( m/z \) 1756.89, calcd for C\(_{116}\)H\(_{122}\)N\(_8\)Cu\(_2\), \( m/z \) 1756.89; UV/vis (CHCl\(_3\)) \( \lambda_{\text{max}} (\varepsilon) = 416 \) (247000), 451 (244000), and 551 (65000) nm. 2Cu: Yield, 92%. MS (TOF) found 1498.5, calcd for C\(_{96}\)H\(_{102}\)N\(_8\)Cu\(_2\), 1498.7; UV/vis (CHCl\(_3\)) \( \lambda_{\text{max}} (\varepsilon) = 411 \) (293000), 434 (214000), and 543 (54000) nm. 3Cu: Yield, 86%. MS (TOF) found 1492.1, calcd for C\(_{96}\)H\(_{100}\)Cu\(_2\)N\(_8\), 1493.0; UV/vis (CHCl\(_3\)) \( \lambda_{\text{max}} (\varepsilon) = 414 \) (131000), 541 (99000), and 958 (68000) nm. 4Cu: Yield, 92%. MS (TOF) found 1755.4, calcd for C\(_{116}\)H\(_{122}\)N\(_8\)Cu\(_2\) 1754.9; UV/vis (CHCl\(_3\)) \( \lambda_{\text{max}} (\varepsilon) = 411 \) (153000), 573 (124000), and 995 (33000) nm. 5Cu: Yield, 88%. MS (TOF) found 1498.2, calcd for C\(_{96}\)H\(_{102}\)N\(_8\)Cu\(_2\) 1498.6; UV/vis (CHCl\(_3\)) \( \lambda_{\text{max}} (\varepsilon) = 407 \) (419000) and 537
2-2. Bis-silver(II) complexes 1Ag–5Ag.

A solution of AgOAc (1.0 mmol) in CH$_3$OH (3 mL) was added to the diporphyrins 1–5 (0.10 mmol) in CHCl$_3$ (100 mL) and the resulting mixture was stirred for 2 h at 60°C. After usual work-up, the organic extract was washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated. The solid was taken up in CH$_2$Cl$_2$ and purified by silica gel chromatography by CH$_2$Cl$_2$. Ag(I)-porphyrins were spontaneously oxidized to Ag(II)-porphyrins 1Ag–5Ag. 1Ag: Yield, 93%. MS (TOF) found 1847.4, calcd for C$_{116}$H$_{126}$N$_8$Ag$_2$, 1847.4; UV/vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$) = 423 (288000), 457 (221000), and 554 (42000) nm. 2Ag: Yield, 90%. MS (TOF) found 1583.4, calcd for C$_{96}$H$_{102}$N$_8$Ag$_2$, 1583.6; UV/vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$) = 427 (174000), 437 (231000), and 541 (41000) nm. 3Ag: Yield, 86%. MS (TOF) found, 1583.2, calcd for C$_{96}$H$_{100}$N$_8$Ag$_2$, 1581.6; UV/vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$) = 426 (128000), 542 (87000), and 775 (59000) nm. 4Ag: Yield, 87%. MS (TOF) found 1842.3, calcd for C$_{116}$H$_{122}$N$_8$Ag$_2$, 1844.0; UV/vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$) = 421 (117000), 572 (122000), 914 (17000), and 1045 (18000) nm. 5Ag: Yield, 92%. MS (TOF) found 1583.2 calcd for C$_{96}$H$_{102}$N$_8$Ag$_2$, 1583.6, UV/vis (CHCl$_3$) $\lambda_{\text{max}}$ ($\varepsilon$) = 420 (381000), 539 (59000), and 576 (27000) nm.

3. Magnetic Susceptibility

The magnetic susceptibility was measured for powder samples of the complexes 1M–5M in the temperature range from 2 to 300 K at 0.1 T magnetic field by using Quantum Design MPMS-5. Spin Hamiltonian for the two spin systems is expressed by $H = -2J \mathbf{S}_A \cdot \mathbf{S}_B$, where the $\mathbf{S}_A$, $\mathbf{S}_B$ and $J$ denote the spin operator for the spin A and B and the exchange coupling constant, respectively. In the two spin systems, the magnetic susceptibility $\chi$ are displayed by the extended Bleaney-Bowers equation,\textsuperscript{[1]}
\[
\chi_p = \frac{2Ng^2\mu_0^2}{3k_B(T-\theta)}\left(\frac{1}{1 + \frac{1}{3}\exp\left(-\frac{2J}{k_BT}\right)}\right),
\]

where \(N, g, \mu_0, k_B, T\) and \(\theta\) denote the Avogadro number, the mean value of the principal values of the \(g\) tensor, the Bohr magneton, the Boltzmann factor, the temperature and the Weiss constant. In this equation, the inter-molecular magnetic interaction is introduced as the mean-field. Figures S1 show the \(\chi_p T\) v.s. \(T\) plots for the complexes 1M and 2M. Open circles and the solid line stands for the observed and the calculated values obtained by eq. (1), respectively. The obtained parameters for the 1Cu-5Cu and the 1Ag-5Ag are summarized in table S1 and S2. In the calculation the averaged \(g\) value of \(g\) tensor are used, which are determined by the simulation of the ESR spectra. In the cases of 1Cu-2Cu and 1Ag-2Ag, the \(\chi_p T\) values are observed independent to temperature. The spin structures of 1Cu-2Cu and 1Ag-2Ag are assigned doublet ground states, in which the individual spins in the porphyrin dimer are isolated. In the case of 3Cu-5Cu and 3Ag-5Ag, the \(\chi_p T\) values are decreased with decreasing temperature. In the case of 4Cu-5Cu and 4Ag-5Ag, the magnetic susceptibility is quenched at 0 K. This suggests that these systems are described by the singlet ground state, which results from the intramolecular antiferromagnetic interaction. On the other hand, it should be noted that the \(\chi_p T\) value of 3Cu and 3Ag is not zero at 0 K. This suggests that the decreasing of the \(\chi_p T\) value is not originated from the intra-molecular coupling but from the intermolecular antiferromagnetic coupling. Therefore, the ground spin states of 3Cu and 3Ag are concluded to be double doublet states, which are non-interacting spin structure.
**Figure S1.** Variable temperature magnetic susceptibility measurements in the range of 2—300 K; (1) 1Cu and 1Ag and (2) 2Cu and 2Ag. Solid lines represent the fitting curves based on the Bleaney-Bowers equation.

**Table S1.** Magnetic data of 1Cu–5Cu.

<table>
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<tr>
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<th>1Cu</th>
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<th>3Cu</th>
<th>4Cu</th>
<th>5Cu</th>
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<td>$\xi_{\text{mean}}$</td>
<td>2.1014</td>
<td>2.1170</td>
<td>2.1270</td>
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<tr>
<td>$J$ (cm$^{-1}$)</td>
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<tr>
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**Table S2.** Magnetic data of 1Ag–5Ag.

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<td>2.065</td>
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<td>2.058</td>
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<td>$J$ (cm$^{-1}$)</td>
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<td>-1.73</td>
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<td>0.0</td>
<td>-0.20</td>
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</tr>
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4. ESR Spectra

The ESR spectra were recorded by a Bruker E500 spectrometer equipped with a OXFORD ESR910 cryostat. The temperature was controlled by an OXFORD ITC500 temperature controller. The ESR measurements were performed on 0.1 mM toluene solutions at 4 K. The observed ESR spectra for 1M-5M are shown in Figure S2 and S3. In the case of the magnetically coupled systems 4M-5M, the spin Hamiltonian is expressed by

$$H = \mu_B (S^A \cdot g^A + S^B \cdot g^B) \cdot B_0 + S^A \cdot D^{AB} \cdot S^B + \sum_i S^{tot} \cdot A_i^N \cdot I_i^N - 2J S^A \cdot S^B,$$

(2)

where $g^k$ ($k = A$ and $B$), $A_i^N$, $I_i^N$ and $J$ denote the $g$-tensor of the electron spin for the site $A$ and $B$, the hyperfine structure tensor between the total spin $S^{tot}$ ($= S^A + S^B$) and the nucleus spins, the nucleus spin operator, and the exchange coupling constant. $D^{AB}$ stands for the fine structure tensor, whose principal values are expressed as $(-D/3 + E$, $-D/3 - E, 2D/3)$. The $D$ and $E$ terms are indicated the deviation from the spherical symmetry and the axial symmetry. In the case of the two-spin system, the $E$-term disappears, since the fine structure interaction is brought by the dipole-dipole interaction. In the cases of 4M and 5M, the long metal-metal distance results in the negligible D value, as mentioned below. In the case of the two-spin system, the $E$ term disappears, since the fine structure interaction is brought by the dipole-dipole interaction. In the bis-copper complexes 1Cu-3Cu with the doublet ground state, the ESR spectra were simulated as a simple sum of isolated Cu(II)-porphyrin. The simulated spectra for 1M-5M are shown in figures S2 and S3. In all cases, the simulated spectra are in good agreement with the observed ones. The obtained spin Hamiltonian parameters are summarized in tables S3 and S4. The spectral
simulations based on the perturbation theory were performed. The hyperfine splitting of the N and Ag nuclei merges into the linewidth. We assumed that the axial components of the hyperfine splitting between the Cu(II) nuclei and the electron spin $A_{\text{Cu axial}}$ is 0.0 cm$^{-1}$, since the splitting for $A_{\text{Cu axial}}$ merge into the line width in the 2Cu-5Cu.

In general, in the triplet state, the transition corresponding to $|\Delta m_s| = 2$, i.e. “forbidden transition”, should be observed at the half field (around $g = 4.0$). Although the ESR spectra of the systems $4\text{M}$ and $5\text{M}$ are assigned to the triplet states, no signal was observed at the half field. The origin of the forbidden transition is the quantum mixing by the fine-structure interaction $|D|$ that can be estimated from the metal-metal distance under the point-dipole approximation.[1] Figure S4 shows the $|D|$ value as a function of the meta-metal distance and the transition probability of the forbidden transition, which is expressed by $\langle M'_s|H_1|M_s\rangle$, where $\langle M'_s\rangle$ and $|M_s\rangle$ stand for the eigen-vectors at the half field.[1] $H_1$ indicated the Zeeman term of the alternating field. The transition probability decreases with decreasing the $|D|$ value. Therefore, “forbidden transition” is hardly observed in the case of the triplet state with small fine-structure interaction $|D|$. The calculated $|D|$ values from the metal-metal distance (8.42 Å in $4\text{M}$, 9.63 Å in $5\text{M}$) are 0.005 cm$^{-1}$ in $4\text{M}$ and 0.003 cm$^{-1}$ in $5\text{M}$, respectively. In both cases, the transition probability become only $\sim 1 \times 10^{-4}$. On the other hand, in typical Cu(II) dimers such as bis(salicylaldehydato)Cu(II) with a metal-metal distance of 4.05 Å, the $|D|$ value and the transition probability are 0.043 cm$^{-1}$ and $\sim 9.5 \times 10^{-3}$.[2] Compared with these typical Cu(II) dimers, the transition probability of the porphyrin dimers $4\text{M}$ and $5\text{M}$ is negligibly small, leading to a prediction that the transition at the half field disappears even if the spin structure is attributed to the triplet states.
Figure S2. EPR Spectra of (1) 1Cu, (2) 2Cu, (3) 3Cu, (4) 4Cu, and (5) 5Cu. Upper; spectra observed in frozen toluene at 4 K. Lower; simulated spectra.

Table S3. EPR data of 1Cu–5Cu in frozen toluene at 4 K.

<table>
<thead>
<tr>
<th></th>
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<th>3Cu</th>
<th>4Cu</th>
<th>5Cu</th>
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<tr>
<td>$g_{\text{mean}}$</td>
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<td>0.0157</td>
<td>0.0157</td>
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Figure S3. EPR Spectra of (1) 1Ag, (2) 2Ag, (3) 3Ag, (4) 4Ag, and (5) 5Ag. Upper; spectra observed in frozen toluene at 4 K. Lower; simulated spectra.

Table S4. EPR data of 1Ag–5Ag in frozen toluene at 4 K.

<table>
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<tr>
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</table>
Figure S4. Metal-metal distance dependence of transition probability (red line) and $|D|$ value (blue line).


5. Absorption Spectra
Figure S5. Absorption spectra of 1Cu-5Cu (upper) and 1Ag-5Ag (lower) in CHCl₃.

6. DFT calculation

Calculations were conducted on Cu(II)-porphine, Ag(II)-porphine, and a model
compound for $4\text{Cu}$, in which all meso-substituents were replaced with hydrogen. All calculations were carried out using the *Gaussian 03* program.$^{[1]}$ All structures were fully optimized with Becke’s three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)$^{[2]}$ with a basis set consisting of the Stuttgart effective core potential (SDD)$^{[3]}$ for Cu and Ag and 6-31G(d) for the rest. Unrestricted open-shell wavefunctions were used for each calculation. Spin densities of Cu(II)- and Ag(II)-porphines were depicted below (Figure S5). The $J$ value was calculated according to the following equation where $^X E$ and $^X <S^2>$ denote the total energy and total spin angular momentum of the spin state $X$, respectively (Figure S6).$^{[4]}

$$J = \frac{\text{LS} E - \text{HS} E}{\text{HS} \langle S^2 \rangle - \text{LS} \langle S^2 \rangle}$$

Figure S5. Spin densities of Cu(II)- and Ag(II)-porphines.
Calculation of Bis Cu(II)-Triply Linked Porphyrin Dimer
UB3LYP/631SDD (6-31G* for C, H, and N + SDD for Cu)

\[ S = 0 \quad \text{LUMO} \quad E = -2367.904281 \]

47.6 kcal/mol

\[ S = 1 \quad \text{SOMO} \quad E = -2367.980144 \quad \langle S^2 \rangle = 2.005996 \]

\[ S = 0 \quad \text{SOMO} \quad E = -2367.980153 \quad \langle S^2 \rangle = 1.006082 \]

0.0053 kcal/mol

Figure S6. Summary of calculation on the model compound for 4Cu (molecular orbitals, total energy, and total spin angular momentums for each state).

1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.


7. Relation of \(-J\) values of 4Cu, 5Cu, 4Ag, and 5Ag with the long-range limit of antiferromagnetic coupling (Coffman–Buettner equation).

**Figure S7.** A Coffman-Buettner plot of \(-J\) values for 4Cu, 4Ag, 5Cu, and 5Ag.