Supporting Information

Observation of Long-Range f-f Interactions between Two f-Electronic Systems in Quadruple-Decker Phthalocyanines

Takamitsu Fukuda, Wakako Kuroda and Naoto Ishikawa**

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, 560-0043, Japan.

Preparation of 2a diluted with the [Y-Y] complex

A mixture of either **1a** (100 mg) or **1d** (735 mg) and $Cd(OAc)_2·2H_2O$ (50 or 366 mg, respectively) was refluxed individually in TCB (2 or 4 mL, respectively) for 2 h under argon. After cooling to room temperature, the reactants were mixed and the TCB was distilled off at 60 °C *in vacuo*. The residue was chromatographed (silica, CH_2Cl_2) to remove the first green fraction containing a neutral form of the double-decker Pc. The eluent was changed to $CHCl_3$, and the blue fraction was collected, which was added excess amounts of hydrazine monohydrate. After the rigorous stirring overnight, chromatography (silica, $CHCl_3$) followed by recrystallization from $CHCl_3$/toluene gave a desired sample as a blue powder. The molar ratio of the complexes was estimated to be [Y-Y] : [Tb-Tb] = 92.8 : 7.2 by the MALDI mass (Figure S1).

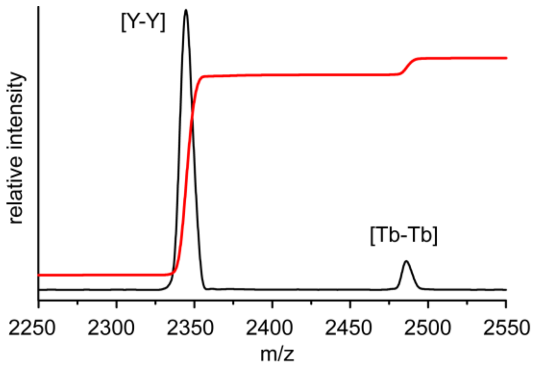

Figure S1 MALDI mass spectrum of the mixture of [Tb-Tb] and [Y-Y] complexes.

Measurements.

Mass spectra were obtained by using a Shimazu AXIMA-CFR MALDI-TOF-MS spectrometer using dithranol as a matrix. Magnetic susceptibility measurements were carried out on a Quantum Design MPMS LX7AC SQUID (superconducting quantum interference device) magnetometer. To correct for the diamagnetic susceptibility contributions, the data for metal-free H_2Pc were used.

Geometry optimization calculations.

The GAUSSIAN 09 program[1] was used to perform geometry optimizations by employing the combination of the B3LYP hybrid functional and LanL2DZ basis set.

Estimation of LF parameters.

The LF term for C_4 point group symmetry is written as:

$$\mathbf{F} = A_2^0\langle r^2\rangle\alpha\mathbf{O}_2^0 + A_4^0\langle r^4\rangle\beta\mathbf{O}_4^0 + A_4^4\langle r^4\rangle\beta\mathbf{O}_4^4 + A_6^0\langle r^6\rangle\gamma\mathbf{O}_6^0 + A_6^4\langle r^6\rangle\gamma\mathbf{O}_6^4$$

Although the five coefficients $A_k^q\langle r^k\rangle$ are the parameters to be determined, off-diagonal components (i.e. $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$) arising from the lower cite symmetry of the quadruple deckers than D_{4d} were neglected due to the limited number of the experimental data. The $\mathbf{O}_k^q$ matrices are polynomials of the total angular momentum matrices $\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{J}_-$, and $\mathbf{J}_+$.[2] The α, β and γ coefficients are the constants tabulated by Stevens.[3] Each parameter is assumed to be expressed as a linear function of the number of f-electron (n), and as a consequence, defined as

$$A_k^q\langle r^k\rangle(n) = a_k^q + b_k^q(n-8)$$

, where n = 8, 9 and 11 for Tb, Dy, and Er complexes, respectively. The estimated parameters are summarized in Table S1.

Table S1 Estimated LF parameters, a_k^0 and b_k^0 in cm^{-1} by using the experimental data of **2a-2c**.

LF parameters	
a_2^0	140
b_2^0	-30
a_4^0	-135
b_4^0	30
a_6^0	14
b_6^0	7

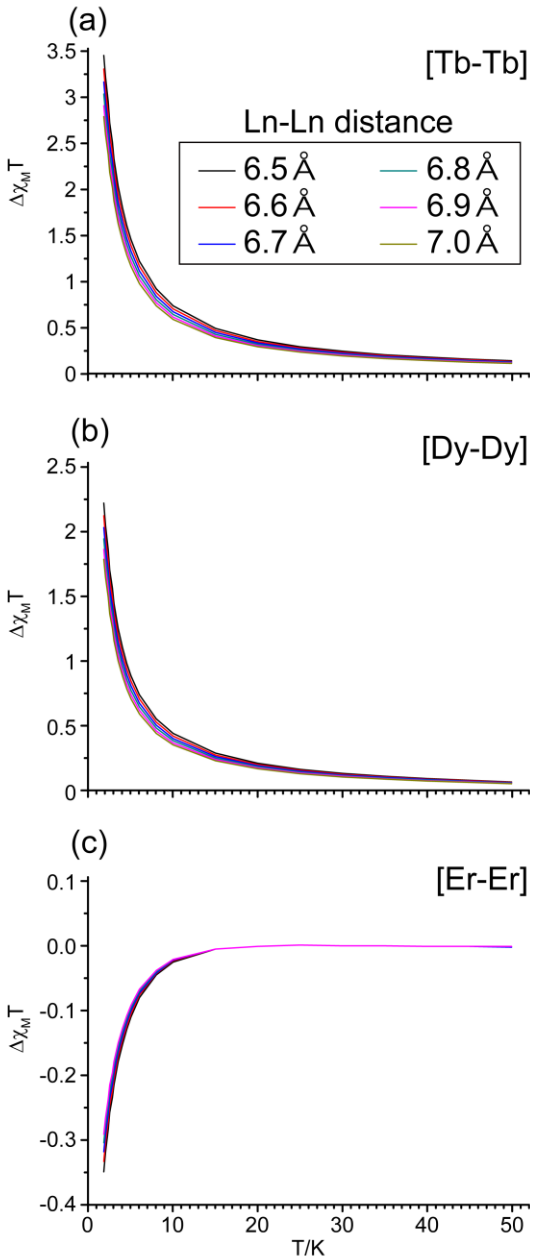

Figure S2 Distance dependency of the calculated $\Delta\chi_M T$ values with the Ln-Ln distance ranging from 6.5–7.0 Å

Reference

1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
2. A. Abragam, B. Blendy, *Electron Paramagnetic Resonance*, Clarendon Press, Oxford, 1970.
3. K. W. H. Stevens, *Proc. Phys. Soc. A*, 1952, **65**, 209.