Supporting Information

Engineering Non-Covalent Spin-Spin Interactions in an Organic-Pillared Spin Cage

Yusuke Ozaki, Masaki Kawano, Makoto Fujita*

Supporting Information (8 pages)

---

[*] Yusuke Ozaki, Prof. Dr. M. Kawano, and Prof. Dr. M. Fujita

Department of Applied Chemistry, School of Engineering,

The University of Tokyo,

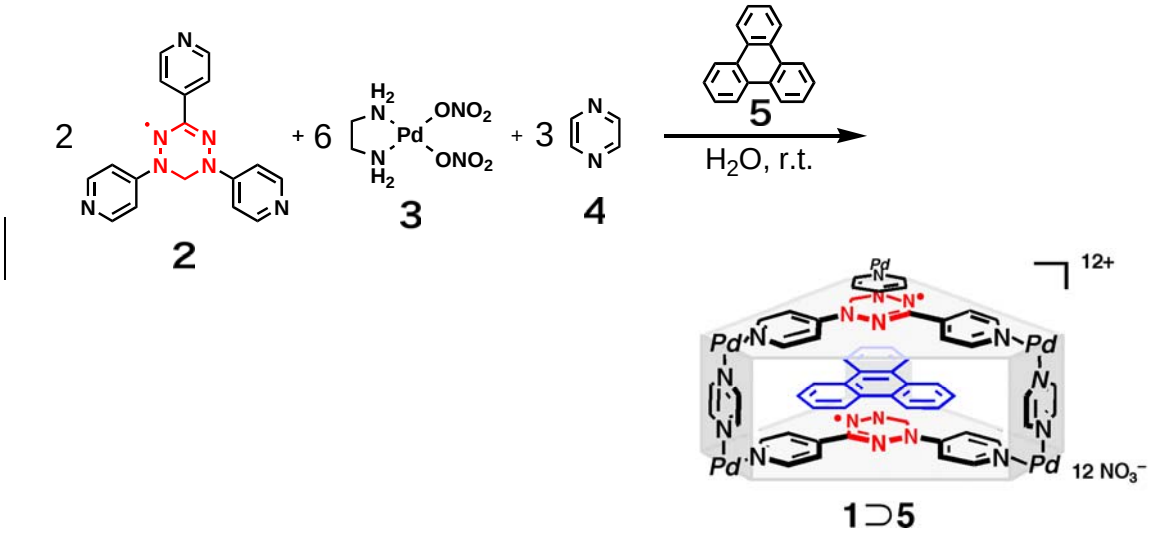
and CREST, Japan Science and Technology Agency (JST),

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

FAX: +81-3-5841-7257

E-mail: mkawano@appchem.t.u-tokyo.ac.jp, mfujita@appchem.t.u-tokyo.ac.jp

1. Preparation of prism-shaped spin cage **1**



Prism-shaped spin cage **1**: *cis*-(Ethylenediamine)dinitratopalladium(II) (104.6 mg, 0.36 mmol), 1,3,5-tris(4-pyridyl)verdazyl (38.1 mg, 0.12 mmol), 1,4-pyradine (14.4 mg, 0.18 mmol) and triphenylene (56 mg, 24.6 mmol) were mixed in distilled water (3 mL), stirred for 36 h at room temperature. Suspended solution was filtrated to remove excess amount of triphenylene and crystallized by slow evaporation of solution at 10 °C to give **1**⊃**5** in 74 %.

Elemental analysis calcd for $C_{58}H_{88}N_{44}O_{36}Pd_6\cdot(C_{18}H_{12})_{0.74}\cdot13H_2O$: C 28.37, H 4.10, N 20.41; found: C 28.52, H 4.09, N 20.14.

2. Thermal ellipsoid plots of **1**⊃**5**

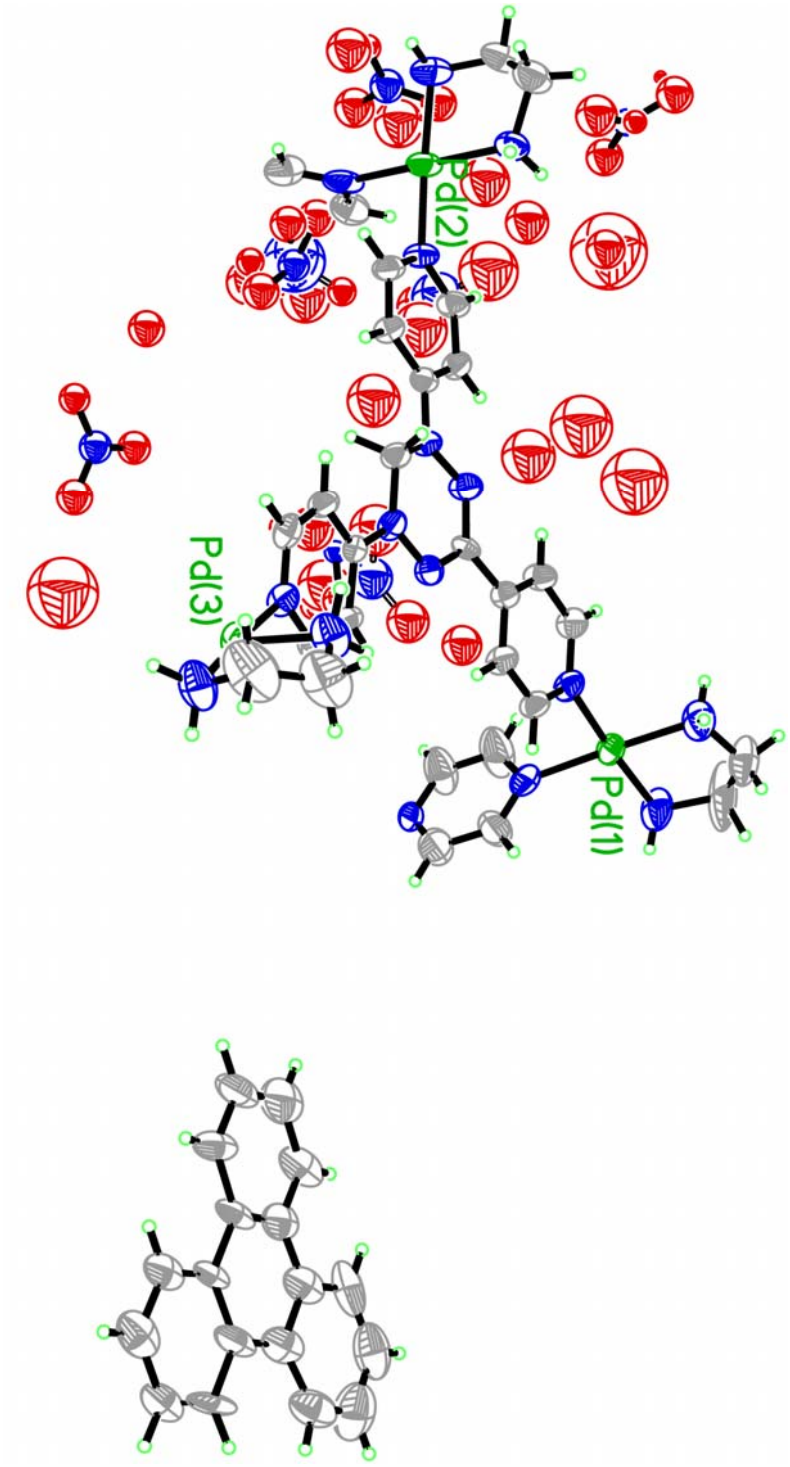


Figure S1. Thermal ellipsoid plots (50% probability level) of the molecular structure of prism-shaped spin cage **1**⊃**5**.

All independent atoms including water and nitrate ions are shown. Hydrogen atoms are omitted for clarity.

3. Encapsulation of planar aromatic molecules

General procedure: *cis*-(Ethylenediamine)dinitratopalladium(II) (0.36 mmol), 1,3,5-tris(4-pyridyl)verdazyl (0.12 mmol) and 1,4-pyradine (0.18 mmol) were mixed in distilled water (2 mL), in the presence of excess amount (ca. 3 equivalent) of planar aromatic guest molecule (shown below), stirred for 36 h at room temperature. The suspended solution was filtrated to remove surplus guest. Guest in 2.5 μL of the aqueous solution was extracted by 1 mL of chloroform. And UV-vis absorption of the resulting organic layer was measured and compared to that of as-prepared 0.05 mM chloroform solution of the guest (which corresponds to the concentration for one-molecule-encapsulation).

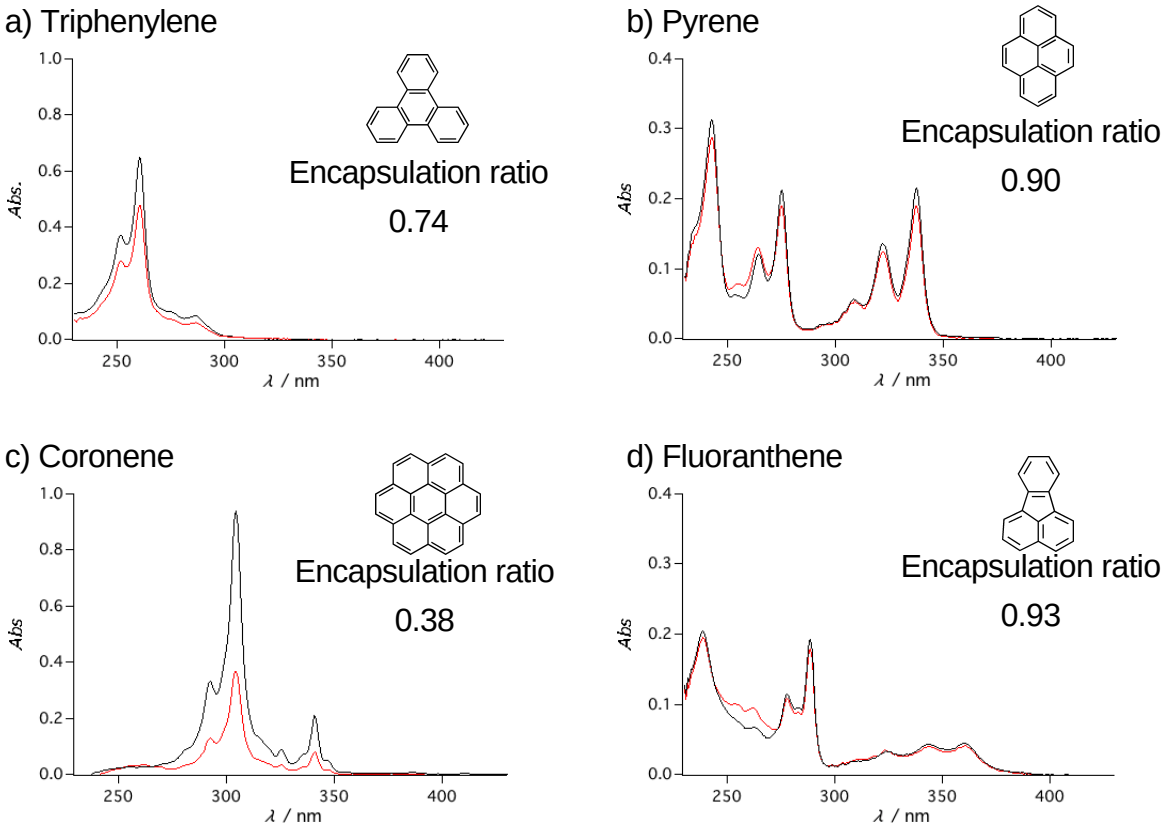


Figure S2. Quantification of encapsulated guest molecules

Red lines and black lines show spectra of extracted guest solution and as-prepared guest solution, respectively.

4. The magnetic susceptibility measurement of **1**⊃**5**

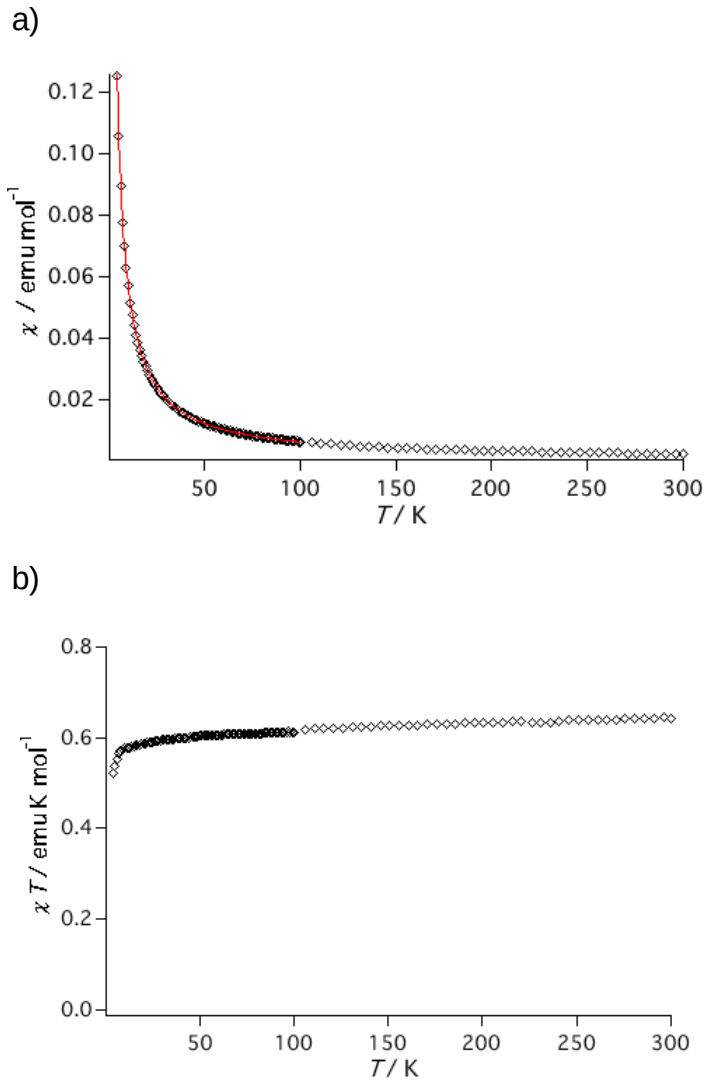


Figure S3. a) χ versus *T* plot, and b) χT versus *T* plot of **1**⊃**5**

A fitting curve of Curie-Weiss law from 4 K to 100 K (the red line) is superimposed on χ versus *T* plot. The Weiss constant θ was calculated to be -0.6 K.

5. The ESR spectrum of **1**⊃**7**

Sample preparation

Suspending excessive amount of $Cu(bzac)_2$ **7** (bzac = benzoylacetonate) in an aqueous solution of cage **1** (20 mM) was stirred for 2 h at room temperature to give, after filtration of surplus guest, clathrate compound **1**⊃**7** in ca. 30% yield. Elemental analysis calcd for $C_{58}H_{88}N_{44}O_{36}Pd_6\cdot(C_{20}H_{18}O_4Cu)_{0.3}\cdot14H_2O$: C 25.76, H 4.10, N 20.65; found: C 25.65, H 3.89, N 20.63.

ESR measurement

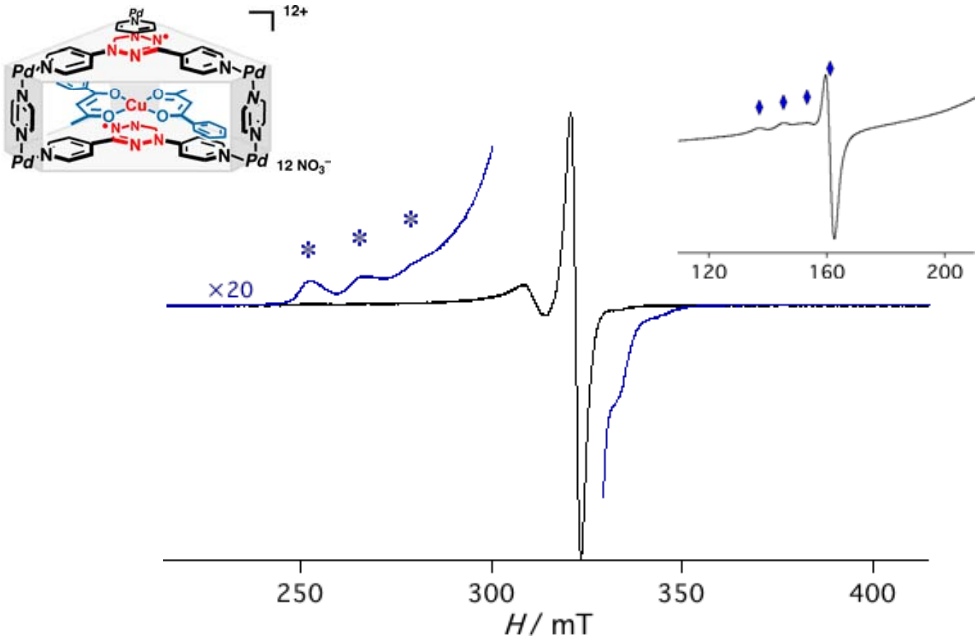
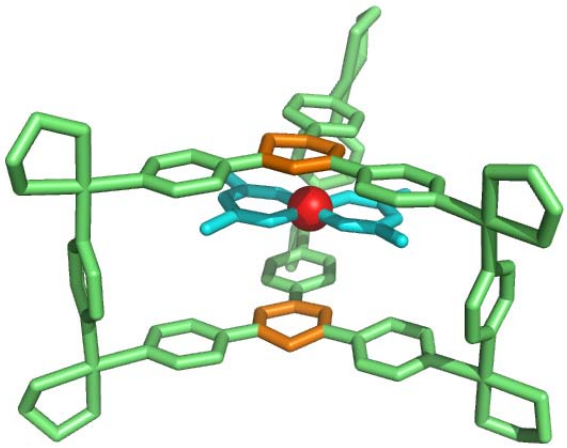


Figure S4. ESR spectrum of **1**⊃**7** at 11K (g = 2.006, inset: ΔM_s = 2 at 6 K)

Split peaks in lower field (g = 2.311) with average separation of 12.6 mT (marked with ∗) can be attributed to the hyperfine structure due to the copper nucleus (I = 3/2). The signal on ΔM_s = 2 transition also showed hyperfine structure into four lines with an average separation of 8.1 mT (marked with ♦). The presence of the splitting on ΔM_s = 2 indicates that radical ligand and copper ion had through-space spin-spin interaction.

6. Molecular models of **1**⊃**6** and **1**⊃**7**

a)



b)

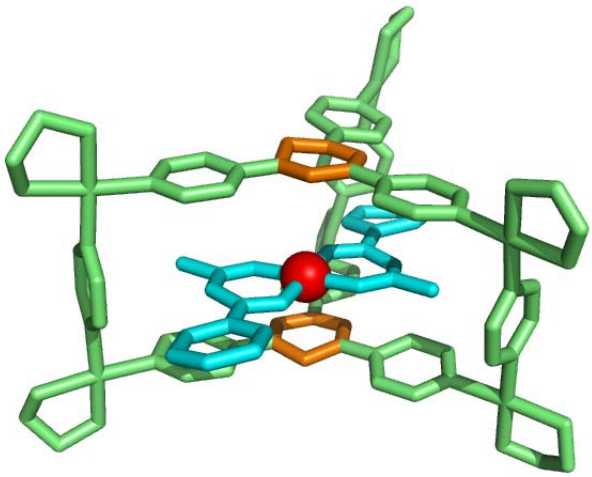


Figure S5. Molecular models of a) **1**⊃**6**, and b) **1**⊃**7**.

The geometry of each guest **6** and **7** was optimized using a force-field calculation on Materials Studio 4.3. The coordinates of spin cage **1** were used from the crystallographic data. Spin centers of radical ligands and copper are colored by orange and red, respectively.

7. Instrumentation and materials

All ESR spectra were recoded on a JEOL JES-RE1X spectrometer. Modulation frequency was 100 kHz. ESR spectra in solution were measured using a LABOTEC capillary tube. The magnetic susceptibility was measured by SQUID (MPMS-5S, Quantum Design). UV-vis spectra were recorded on a SHIMADZU UV-3150. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich Chemical, Ltd.