Three-metal-center spin interactions through the intercalation of metal azaporphines and porphines into an organic pillared coordination box†

Kosuke Ono,[a] Michito Yoshizawa,*[ab] Tatsuhisa Kato*[c] and Makoto Fujita*[a]

Received (in Cambridge, UK) 31st January 2008, Accepted 7th March 2008
First published as an Advance Article on the web 11th April 2008
DOI: 10.1039/b801701h

Discrete homo Cu–Cu–Cu and hetero Cu–Pd–Cu or Cu–Co–Cu metal arrays are prepared within an organic-pillared coordination box by inserting M(II)-azaporphine/porphine cartridges (M = Cu(II), Pd(II) or Co(II)), where the metal arrays show unique spin interactions in ESR: in particular, $\Delta m_s = 3$ for the Cu–Cu–Cu array.

The strict control of quantity and order in one-dimensional arrays of metal ions promises the development of new class of molecular-based materials.[1] For example, right ordering of spin-active metal ions is expected to lead to data storage at the molecular level. However, ordering metal ions precisely is technically difficult and there are only a few principal strategies for the control: (1) the rational design of multidentate ligands with linearly arrayed donor sites, typically oligo-amidopyridyls,[2] oligo-phosphines,[3] polyenes,[4] helicated strands[5] or even DNA;[6] (2) the array of metal complexes *via* electrostatic interactions with or without templates.[7] Herein we report a unique approach to form linear Cu(II)–M–Cu(II) arrays (M = Cu(II), Pd(II), and Co(II)) through the intercalation of metal azaporphines and porphines into an organic pillared coordination box **1** (Fig. 1a).[8] Box **1** self-assembles from two panels (**2**), three pillars (**3**) and six Pd(II) hinges (**4**). In this strategy, the metal porphine/azaporphine is a cartridge of metal ions and, in principle, any metals can be arrayed in the box by selecting the cartridge. When three Cu(II)-azaporphine cartridges are intercalated, a quartet state of the interacting three Cu(II) centers is observed despite the absence of any covalent or non-covalent bonds among the azaporphine cores. Box **1** also selectively encapsulates alternating azaporphine/porphine triple stacks, allowing the successful generation of hetero-arrays containing Cu(II)–M–Cu(II), where M = Pd(II) or Co(II).

Box **1** has an ideal interplane distance in the cavity to accommodate three aromatic molecules in layers. Our attempt to bind three porphine molecules (**5**) in the box was, however, unsuccessful because the D–D–D stacking of the electron-rich porphine cores is unfavorable. Instead, we observed a hetero triple stacking where two porphine molecules sandwiched the electron deficient free ligand (**2**), forming a favorable D–A–D stacking.[9] We then employed the relatively electron deficient azaporphine (**6**),[10] which has a polarized (–C=N–C=N–)$_4$ periphery that is expected to induce quadrupole interaction when the nuclei are stacked in layers. When panel **2**, pillar **3**, and Pd(II) hinge **4** were combined in a 2 : 3 : 6 ratio in D_2O in the presence of an excess amount of azaporphine and stirred for 2 h at 100 °C, the triple homo- inclusion complex $\mathbf{1}\supset(\mathbf{6a})_3$ was formed (Fig. 1b). As expected, the three guest molecules are differentiated in a 2 : 1 ratio by NMR (Fig. 2). CSI-MS revealed a series of signals $[\text{M-}n(\text{NO}_3)]^{n+}$ for $\mathbf{1}\supset(\mathbf{6a})_3$.

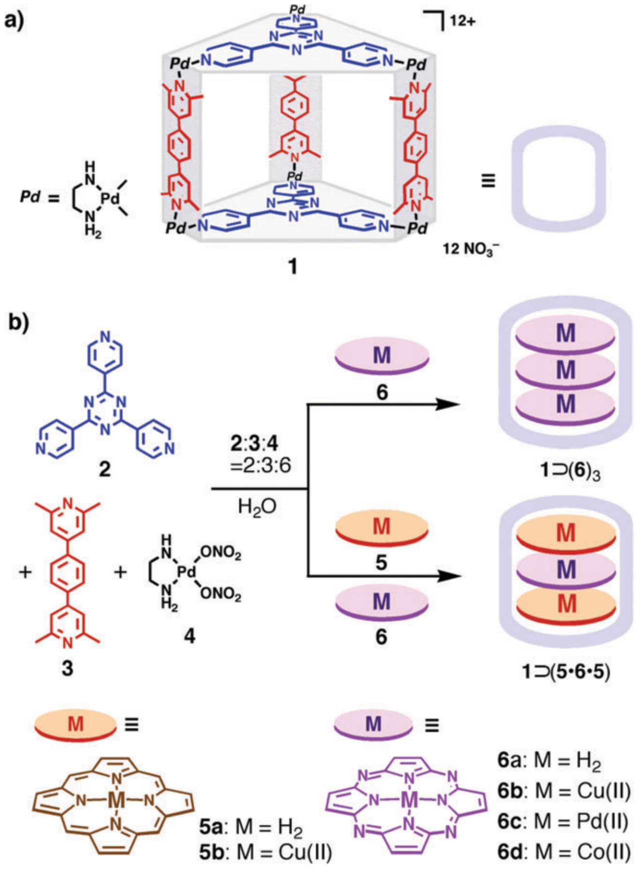

Fig. 1 (a) Chemical structure of coordination box **1**. (b) Self-assembly of $\mathbf{1}\supset(\mathbf{6})_3$ and $1\supset(\mathbf{5{\cdot}6{\cdot}5})$ complexes.

---

[a] *Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan. E-mail: mfujita@appchem.t.u-tokyo.ac.jp; Fax: +81 3-5841-7257; Tel: +81 3-5841-7259*
[b] *PRESTO, Japan Science and Technology Agency (JST). E-mail: myoshiza@appchem.t.u-tokyo.ac.jp*
[c] *Department of Chemistry, Faculty of Science Josai University, 1-1 Keyakidai, Sakado, Saitama, 350-0295, Japan. E-mail: rik@josai.ac.jp; Fax: +81 49-271-7985; Tel: +81 49-271-7295*

† Electronic supplementary information (ESI) available: Experimental, physical data for the complexes and crystallographic data in CIF or other electronic format for CCDC 666139. See DOI: 10.1039/b801701h

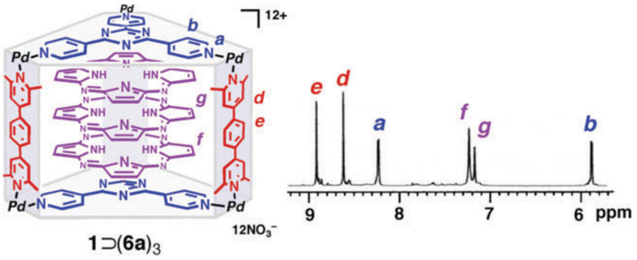

Fig. 2 ^{1}H NMR (500 MHz, D$_2$O, RT, aromatic region) spectrum of $\mathbf{1}\supset(\mathbf{6a})_3$ complex.

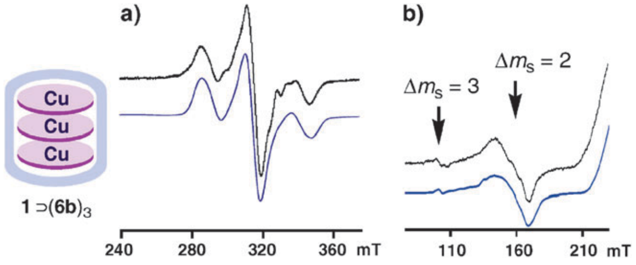

Fig. 4 ESR spectra (H$_2$O, 113 K) of $\mathbf{1}\supset(\mathbf{6b})_3$ around (a) $\Delta m_s = 1$ and (b) $\Delta m_s = 2$ and 3 regions (blue lines: simulated spectra).

The structure of the inclusion complex $\mathbf{1'}\supset(\mathbf{6a})_3$ (**1′**: an analogue of **1** where 1,4-bis(2,6-dimethyl-4-pyridyl)benzene and ethylenediamine are replaced by 1,4-bis(4-pyridyl)benzene and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, respectively) was unambiguously determined by X-ray crystallography (Fig. 3).‡ Three azaporphine centers are arrayed in a roughly linear fashion, but the three azaporphine rings are slightly offset to enhance quadrupole interaction arising from the C(δ+)–N(δ−) polarization at the periphery. Efficient π-stacking is observed not only among the three guests but also between **6** and the host (panel **2**) to form a stable quintuple **2**–**6**–**6**–**6**–**2** aromatic stacking. The interplane distances for **2**–**6** and **6**–**6** are 3.32 Å and 3.40 Å, respectively.

In the presence of excess Cu(II)-azaporphine **6b**, box **1** was assembled to give complex $\mathbf{1}\supset(\mathbf{6b})_3$, in which a Cu–Cu–Cu array was selectively formed. The formation of complex $\mathbf{1}\supset(\mathbf{6b})_3$ was evidenced by CSI-MS measurement.† Exciton coupling between the three stacked Cu(II)-azaporphine nuclei was clearly visible in the UV-vis absorption spectrum of inclusion complex $\mathbf{1}\supset(\mathbf{6b})_3$. The Q-band, appearing at $\lambda_{\max} = 555$ nm ($\varepsilon = 1.9 \times 10^4$), was both broadened ($\Delta\lambda_{1/2} = 88$ nm) and blue-shifted ($\Delta\lambda = -21$ nm) in comparison with that of free **6b**.

It is noteworthy that ESR analysis of complex $\mathbf{1}\supset(\mathbf{6b})_3$ revealed the quartet state of the three intercalated Cu(II) centers despite the absence of any covalent or non-covalent bonds between the stacking azaporphine nuclei (Fig. 4).[11] The ESR spectrum at 113 K showed a three-line $\Delta m_s = 1$ transition signal around 320 mT and $\Delta m_s = 2$ forbidden transition signal around 160 mT that was overlapping two transitions between $m_s = -3/2 \rightarrow m_s = +1/2$ and $m_s = -1/2 \rightarrow m_s = +3/2$ broadened by nuclear hyperfine interactions among three Cu ($I = 3/2$) nuclei. More significantly, a single-line $\Delta m_s = 3$ forbidden transition signal was observed around 100 mT at 113 K. In inorganic systems, a $\Delta m_s = 3$ forbidden transition *via* the interaction of three spin centers has never been observed.[12] These features are well reproduced by simulation.§ Therefore, it is clearly proved that three molecules of Cu(II)-azaporphine couple ferromagnetically, resulting in the quartet state ($S = 3/2$) within coordination box **1**. It should be noted that the $\Delta m_s = 3$ signal can be simulated only by nonzero value of E (1.5 mT), which shows the distortion from the axial symmetry of the stacking formation among three Cu(II).

Expecting the alternative D–A–D stacking of electron-rich porphine and electron-defficient azaporphine cores, we examined the complexation of **1** with a mixture of porphine **5a** and azaporphine **6a**. Substrates **5a** and **6a** (2.5 : 1 ratio) were combined with panel **2**, pillar **3**, and Pd(II) hinge **4** (2 : 3 : 6 ratio) in D$_2$O, and the mixture was stirred at 100 °C for 2 h. The expected $\mathbf{1}\supset(\mathbf{5a\cdot6a\cdot5a})$ complex with alternating porphine/azaporphine stacking was formed as a dark red–purple precipitate in 31% yield. The precipitate was collected and dissolved in D$_2$O to give a red-purple solution, whose ^{1}H NMR, UV-vis, and CSI-MS spectra revealed the selective formation of the $\mathbf{1}\supset(\mathbf{5a\cdot6a\cdot5a})$ complex. The NMR signals of **5a** and **6a** were observed in a 2 : 1 integral ratio at 7.53 and 7.31 ppm (for **5a**), and 6.65 ppm (for **6a**). An NOE was observed between **6a** and the pillar (H_e) of **1** by NOESY. The UV-vis spectrum also suggested the alternating **5a**–**6a**–**5a** arrangement as the Soret-bands characteristic to the **5a**–**5a** homo stack were absent.[9] These data strongly indicate an alternating **5a**–**6a**–**5a** stacking structure without disorder.

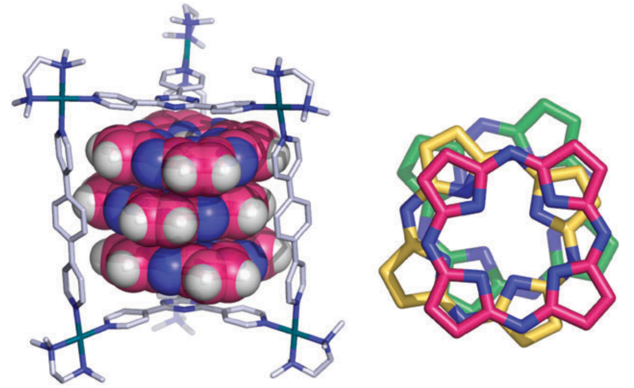

Fig. 3 X-Ray structure of $\mathbf{1'}\supset(\mathbf{6a})_3$ (left) and the top view of the three guest molecules (right).

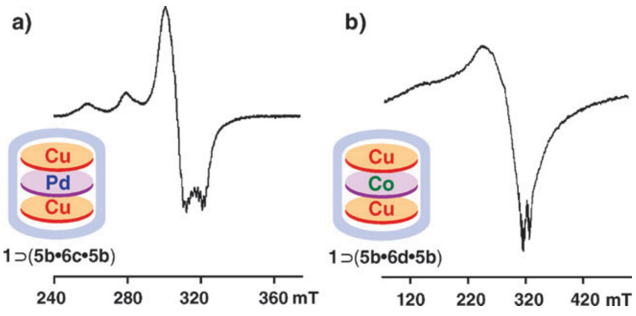

Fig. 5 ESR spectra (H$_2$O, 113 K) of (a) $\mathbf{1}\supset(\mathbf{5b\cdot6c\cdot5b})$ and (b) $\mathbf{1}\supset(\mathbf{5b\cdot6d\cdot5b})$.

The alternating porphine/azaporphine stacking was applied to the arrangement of three hetero metal nuclei, Cu–M–Cu (M = Pd and Co). Inclusion complex **1**⊃(**5b**·**6c**·**5b**) and **1**⊃(**5b**·**6d**·**5b**) were prepared and characterized by CSI-MS and UV-vis spectra. ESR spectrum of **1**⊃(**5b**·**6c**·**5b**) (Cu–Pd–Cu) complex showed a broad doublet signal of **5b** (Fig. 5). The spectrum is heavily distorted from that of **1**⊃(**5b**·**6a**·**5b**) (Cu–H_2–Cu) due to the insertion of the Pd(II) ion between the two Cu(II).† Moreover, the ESR spectrum of **1**⊃(**5b**·**6d**·**5b**) (Cu–Co–Cu) was very broad in wide range from *ca.* 50 mT to *ca.* 400 mT, being very different from that of **1**⊃(**5b**·**6a**·**5b**) (Cu–H_2–Cu) or **1**⊃(**5a**·**6c**·**5a**) (H_2–Co–H_2). The hyperfine structures of Cu and Co nuclear spins are smeared out by interaction among the three Cu–Co–Cu spin centers.

Notes and references

‡ Crystal data for **1**′⊃(**6a**)$_3$: The diffraction data were measured at 80 K [wavelength (λ) = 0.71073 Å]. $C_{168}H_{186}N_{64.75}O_{104.5}Pd_6$, M_r = 5404.12, triclinic, $P\bar{1}$, a = 20.025(3) Å, b = 26.094(4) Å, c = 26.215(4) Å, α = 107.593(2)°, β = 102.779(2)°, γ = 95.762(2)°, V = 125 26(3) Å, Z = 2, T = 80(2) K, ρ_{calcd} = 1.438 g cm^{-3}; 99 554 reflections were measured, of which 50 850 were unique (R_{int} = 0.0302) and were used in all calculations. The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F with 3085 parameters. R_1 = 0.0752 ($I > 2\sigma(I)$) and wR_2 = 0.2556, GOF = 1.023, max/min residual density 1.762/–0.995 eÅ^{-3}. CCDC 666139.†

§ ESR simulation parameters for **1**⊃(**6b**)$_3$: Spin quantum number: $S = 3/2$, g tensor: g = (2.01, 2.01, 2.147), hyperfine coupling tensor of Cu nuclear spin: A_{Cu} = (1.03, 1.03, 7.17)/mT, spin–spin dipole interaction parameters: D = 27.3/mT, E = 1.5/mT.

1 (*a*) M. C. Böhn, *One-Dimensional Organometallic Materials*, Springer, New York, 1987; (*b*) F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*. Clarendon Press, Oxford, UK, 2nd edn., 1993; (*c*) J. K. Bera and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2002, **41**, 4453–4457.

2 E.-C. Yang, M.-C. Cheng, S.-M. Tsai and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, 1994, 2377–2378.

3 (*a*) K. Mashima, H. Nakano and A. Nakamura, *J. Am. Chem. Soc.*, 1993, **115**, 11632–11633; (*b*) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li and Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639–7651; (*c*) E. Goto, R. A. Begum, S. Zhan, T. Tanase, K. Tanigaki and K. Sakai, *Angew. Chem., Int. Ed.*, 2004, **43**, 5029–5032.

4 T. Murahashi, E. Mochizuki, Y. Kai and H. Kurosawa, *J. Am. Chem. Soc.*, 1999, **121**, 10600–10661.

5 (*a*) R. Krämer, J.-M. Lehn and A. Marquis-Rigault, *Proc. Natl. Acad. Sci. U. S. A.*, 1993, **90**, 5394–5398; (*b*) S. Floquet, N. Ouali, B. Bocquet, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner and C. Piguet, *Chem. Eur. J.*, 2003, **9**, 1860–1875.

6 K. Tanaka, A. Tengeiji, T. Kato, N. Toyama and M. Shionoya, *Science*, 2003, **299**, 1212–1213.

7 (*a*) J. F. Lipskier and T. H. Tran-Thi, *Inorg. Chem.*, 1993, **32**, 722–731; (*b*) L. Di. Costanzo, S. Geremia, L. Randaccio, R. Purrello, R. Lauceri, D. Sciotto, F. G. Gulino and V. Pavone, *Angew. Chem., Int. Ed.*, 2001, **40**, 4245–4247; (*c*) A. J. Goshe, I. M. Steele and B. Bosnich, *J. Am. Chem. Soc.*, 2003, **125**, 444–451; (*d*) A. Tsuda, E. Hirahara, Y.-S. Kim, H. Tanaka, T. Kawai and T. Aida, *Angew. Chem., Int. Ed.*, 2004, **43**, 6327–6331.

8 (*a*) M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 1810–1813; (*b*) C. J. Kuehl, Y. K. Kryschenko, U. Radhakrishnan, S. R. Seidel, S. D. Huang and P. J. Stang, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4932–4936.

9 K. Ono, M. Yoshizawa, T. Kato and M. Fujita, *Angew. Chem., Int. Ed.*, 2007, **46**, 1803–1806.

10 N. Kobayashi, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2000, ch. 13, vol. 2.

11 C. P. Casey, J. M. O'Connor and K. J. Haller, *J. Am. Chem. Soc.*, 1985, **107**, 3172–3177.

12 In organic systems, there are several examples for the observation of Δm_s = 3 transition. See: (*a*) S. I. Weissman and G. Kothe, *J. Am. Chem. Soc.*, 1975, **97**, 2537–2538; (*b*) A. Rajca and S. Utamapanya, *J. Am. Chem. Soc.*, 1993, **115**, 2396–2401; (*c*) A. Rajca, S. Rajca and S. R. Desai, *J. Am. Chem. Soc.*, 1995, **117**, 806–816; (*d*) U. Mller and M. Baumgrten, *J. Am. Chem. Soc.*, 1995, **117**, 5840–5850; (*e*) M. Baumgarten, *Mol. Cryst. Liq. Cryst.*, 1995, **272**, 109; (*f*) M. M. Wienk and R. A. Janssen, *J. Am. Chem. Soc.*, 1997, **119**, 5398–5403.