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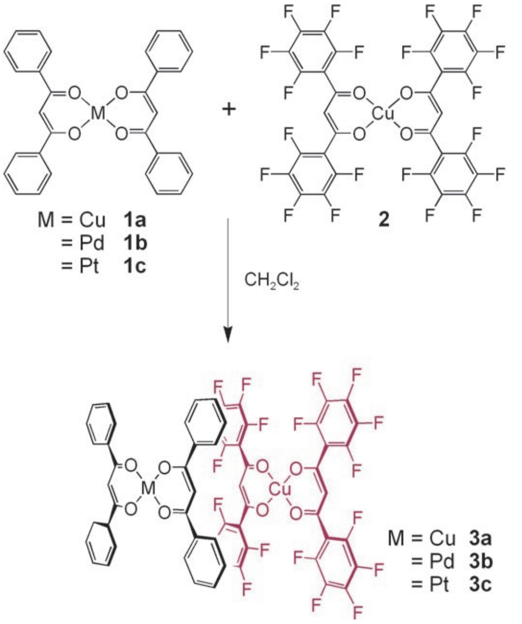
Metal Arrays

1:1 Cross-Assembly of Two β-Diketonate Complexes through Arene–Perfluoroarene Interactions**

Akiko Hori, Ayaka Shinohe, Mikio Yamasaki, Eiji Nishibori, Shinobu Aoyagi, and Makoto Sakata*

Closely arranged metal–metal systems[1,2] have been investigated in efforts to obtain new magnetic[3] and conductive[4] materials of nanometer size to exploit innovative functions. How to construct the systems in order to make use of the metal–metal interactions is a crucial issue for many chemists. The most popular strategy for this purpose is direct construction of coordination compounds from metals and organic frames through coordination bonds.[5,6] On the other hand, in an example of an indirect method, hydrogen bonds were used to arrange discrete metal complexes.[7] Electrostatic interactions are also frequently used to control the systems as they are weaker,[8,9] though it is difficult to control the directionality of the self-assembled system in many cases. The arene–perfluoroarene interaction[10] as an example of electrostatic interactions is a promising approach to control the direction and position of intermolecular interactions by quadrupole moments.[11] For example, two different organic molecules are regularly arranged by such interactions between arene- and perfluoroarene-functionalized moieties.[10,12,13] This idea prompted us to cross-assemble different metal complexes through arene–perfluoroarene interactions. Here, we demonstrate the one-dimensional arrangement of metal complexes, namely, the arene-functionalized Cu^{II} complex[14] **1a** and the perfluoroarene-functionalized Cu^{II} complex[15,16] **2** (Scheme 1). The metal–metal distance is close to that of the van der Waals contact. This is the first application of the simple and unique construction strategy through arene–perfluoroarene interactions between different complexes to obtain a metal–metal arrangement.[17] Furthermore, the analogous cross-assembled architectures have also been achieved with Pd^{II} and Pt^{II} complexes,[18] which suggests a great utility of this method for obtaining metal cross-assemblies.



Scheme 1. Arene complexes **1a–1c**, perfluoroarene complex **2**, and the 1:1 mixed complexes **3a–3c**.

Complexes **1a** and **2**, prepared independently as previously described,[14,16] were combined in an organic solvent to promote the cross-assembly. Typically, a solution of arene complex **1a** (20.4 mg, 0.04 mmol) in CH_2Cl_2 (10 mL) and a solution of perfluoroarene complex **2** (34.8 mg, 0.04 mmol) in CH_2Cl_2 (2 mL) were combined at ambient temperature to give slowly a cocrystal, **3a**, as fiber-like pale green microcrystals (48% yield). After slow evaporation of the remaining solvent, pure **3a** was obtained as crystals in almost quantitative yield. Elemental (C,H) and atomic absorption (Cu) analyses were consistent with the formula $C_{60}H_{24}Cu_2F_{20}O_8$ for **3a** (calcd (%) for $C_{60}H_{24}Cu_2F_{20}O_8$: C 52.22, H 1.75, Cu 9.21; found: C 52.26, H 1.86, Cu 9.58).

Single crystals of **3a**, composed of **1a** and **2**, were obtained from CH_2Cl_2-benzene and were suitable for X-ray crystallography studies (Figure 1).[19] The geometries around the two Cu centers are essentially planar. In the part corresponding to **1a**, the Cu1–O1 and Cu1–O2 bond lengths are 1.9078(10) and

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[*] Dr. A. Hori, A. Shinohe
Department of Chemistry, School of Science
Kitasato University
1-15-1 Kitasato, Sagamihara-shi, Kanagawa 228-8555 (Japan)
Fax: (+81) 42-778-9953
E-mail: hori@kitasato-u.ac.jp

Dr. M. Yamasaki
Rigaku Corporation
Matsubara-cho, Akishima-shi, Tokyo 196-8666 (Japan)

Prof. Dr. E. Nishibori, Dr. S. Aoyagi, Prof. Dr. M. Sakata
Department of Applied Physics, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603 (Japan)

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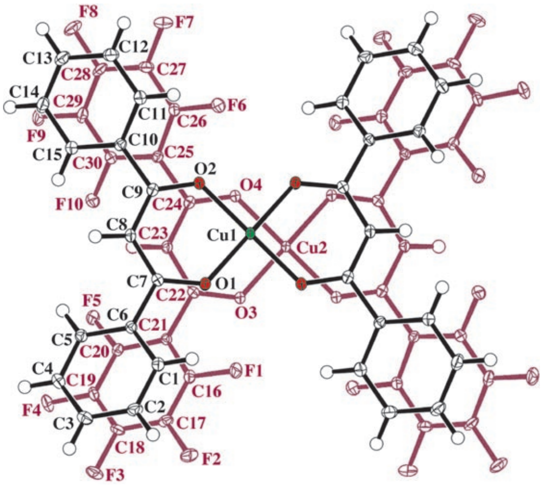

Figure 1. ORTEP drawing of the crystal structure of **3a** with 50% probability thermal ellipsoids.

1.9148(10) Å, respectively, and the O1–C7 and O2–C9 bond lengths are 1.2817(17) and 1.2769(17) Å, respectively. In the part corresponding to **2**, the Cu2–O3 and Cu2–O4 bond lengths are 1.9032 (10) and 1.9095(10) Å, respectively, and the O3–C22 and O4–C24 bond lengths are 1.2724(16) and 1.2709(17) Å, respectively. The phenyl rings of **1a** have twisted conformations with respect to the coordination plane with torsion angles C5-C6-C7-C8 and C8-C9-C10-C15 of 28.0(2) and 35.1(2)°, respectively, while the pentafluorophenyl rings of **2** have more twisted conformations with respect to the coordination plane with torsion angles C20-C21-C22-C23 and C23-C24-C25-C30 of 38.0(2) and 45.5(2)°, respectively.

The two complexes are alternately aligned as columnar stacks (Figure 2). The Cu1···Cu2 distance is 3.612 Å. The average distances between phenyl and pentafluorophenyl rings are also short: 3.610 Å between C1-C2-C3-C4-C5-C6 and C16-C17-C18-C19-C20-C21, and 3.618 Å between C10-C11-C12-C13-C14-C15 and C25-C26-C27-C28-C29-C30. The torsion angles are quite different in **3a** as compared to the individual crystals of **1a** and **2**: for example, from 0.6–10.5° in pure **1a**[14] to 28.0–35.1° in **3a**, and from 60.4–61.0° in pure **2**[16] to 38.0–45.4° in the crystal of **3a**, as mentioned above. Thus, the torsion angles of the phenyl and pentafluorophenyl rings are forced closer for close packing of the planes. Accordingly, the arene–perfluoroarene interaction is observed in the columnar stacking along the *a* axis through alternatively aligned **1a** and **2**. Note that the interaction does not depend on the aryl rings being coplanar. It is pointed out that the direction of the stacking is along the direction of the needle crystal growth. C–H···F interactions are also observed as intermolecular interactions between **1a** and **2** in this alignment; the shortest C–H···F distances between hydrogen and fluorine atoms is 2.42 Å (H1(**1a**)···F6(**2**)).[16,20]

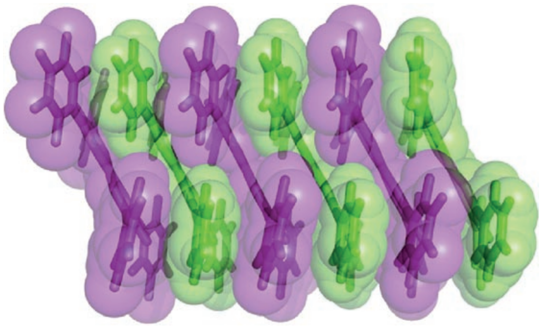

Figure 2. Crystal packing of **3a**: view approximately along the *c* axis showing the formation of one-dimensional columns through arene–perfluoroarene interactions (complex **1a**, green; complex **2**, purple).

Surprisingly, the cross-assembly through arene–perfluoroarene interactions also proceeded easily when the central metal was changed to Pd (**1b**) and Pt (**1c**). The 1:1 cocrystals **3b** and **3c** were prepared as fiber-like microcrystals. The results of elemental (C,H) and atomic absorption (Cu) analyses clearly showed the 1:1 cross-assemblies for **3b** (calcd (%) for $C_{60}H_{24}CuF_{20}O_8Pd$: C 50.65, H 1.70, Cu 4.47; found: C 50.70, H 1.75, Cu 4.69) and for **3c** (calcd (%) for $C_{60}H_{24}CuF_{20}O_8Pt$: C 47.68, H 1.60, Cu 4.20; found: C 47.62, H 1.64, Cu 4.54).[21] The melting points of complexes **3** (284 °C (**3a**), 290 °C (**3b**), and 309 °C (**3c**)) were sufficiently different from those of the starting materials (321 °C (**1a**), 270 °C dec. (**1b**), 287 °C dec. (**1c**), and 216 °C (**2**)). The thermal stability of the resultant complexes **3a**–**3c** was higher than those of the starting materials, except for **1a**.

As the crystals of **3b** and **3c** were very small, synchrotron radiation (SR) X-ray powder experiments were performed to obtain structural information.[22,23] SR powder patterns of **3a**, **3b**, and **3c** are shown in Figure 3. The peak positions of **3a**–**3c** are very similar in this 2θ range. No peak splits indicating existence of other phases were observed in these data, which suggests that the same manner of alignment was achieved through arene–perfluoroarene interactions. The lattice parameters determined by the LeBail method for **3a**–**3c** are listed in Table 1. The differences in the length and angle are as low as less than 0.1 Å and 1.0°, respectively. The metal–metal distances were estimated from the lattice parameters, and at

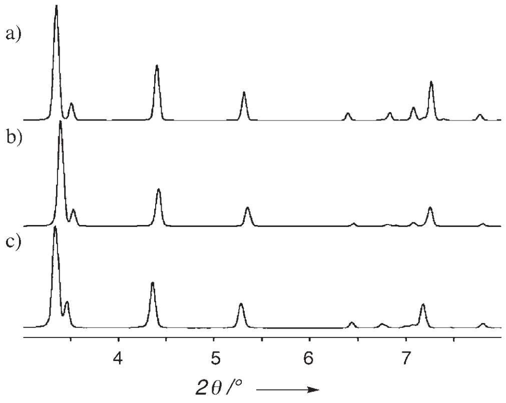

Figure 3. The powder X-ray analyses show very similar patterns: a) CuCu of **3a**, b) CuPd of **3b**, and c) CuPt of **3c** at 100 K (the full region 0–75° (2θ) is provided in the Supporting Information).

Table 1: Crystal parameters for **3a** (single-crystal analysis) and **3a**–**3c** (powder X-ray analysis).

Parameter	**3a** (single crystal)	**3a**	**3b**	**3c**
a [Å]	7.2240(11)	7.2210(6)	7.2095(1)	7.1833(1)
b [Å]	13.294(3)	13.2670(2)	13.3598(3)	13.4353(3)
c [Å]	13.766(3)	13.7478(2)	13.7666(3)	13.7648(3)
α [°]	78.841(5)	78.810(10)	78.417(2)	78.434(2)
β [°]	85.387(6)	85.351(10)	84.392(2)	84.320(3)
γ [°]	80.713(7)	80.657(10)	80.722(2)	80.088(3)

100 K they correspond to 3.611 Å for **3a** (Cu···Cu), 3.605 Å for **3b** (Cu···Pd), and 3.592 Å for **3c** (Cu···Pt).

The constitution of the crystals **3** was independent of the starting ratios of **1** and **2**. When a mixed solution of **1** and **2** in different ratios was completely dried by natural evaporation, two kinds of crystals crystallized separately, corresponding to **3** and the excess starting material **1** or **2**.[24] In other words, a 1:1 assembly is exclusively obtained and any random mixture was not observed. The solubility of complexes **3** in CH_2Cl_2 decreases in the order **3a**$\gg$**3b**$>$**3c**, appearing to depend on the metals present, and it is probably due to the different rigidities of the complexes **1a**–**1c**. Thus, in a competitive experiment in which a combination of **1a**, **1b**, and **2** (1:1:1 stoichiometry) was employed, **3b** was obtained exclusively and as a pure product. Similarly, compounds **1a**, **1c**, and **2** (1:1:1 stoichiometry) gave **3c**, while **1b**, **1c**, and **2** (1:1:1 stoichiometry) gave a mixture ($\approx$1:2) of **3b**:**3c**.[21] This is the selectivity induced by the crystallization process of the differently soluble complexes.

Furthermore, non-radiative decay was observed in the Cu···Pt mixed complex **3c** in studies of solid-state luminescence and UV/Vis spectroscopy (with $BaSO_4$), while the Pt complex **1c** showed luminescence around 540 nm (irradiation at 440 nm). It is suggested that energy transfer occurs between the closely arranged Pt and Cu complexes. A detailed investigation of the metal···metal properties with the indirect interaction is of further interest.

In conclusion, we have reported a 1:1 cross-assembly by combining arene- and perfluoroarene-functionalized complexes in an organic solvent. The two different metals in these complexes are highly ordered to give striped one-dimensional structures through arene–perfluoroarene interactions. This strategy may open the door to next-generation nanometer-sized metal-wire synthesis.

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[19] Crystal data for **3a** ($C_{60}H_{24}Cu_2F_{20}O_8$: M_r 1379.90): triclinic, $P\bar{1}$, $T=93$ K, $a=7.2240(11)$ Å, $b=13.294(3)$ Å, $c=13.766(3)$ Å, $\alpha=78.841(5)°$, $\beta=85.387(6)°$, $\gamma=80.713(7)°$, $V=1278.4(4)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.792$ g cm^{-3}, $F(000)=686$, $\lambda=0.71070$ Å, GOF = 1.019, $R1(I>2\sigma(I))=0.0268$, $wR2(F_o^2)=0.0817$. X-ray data were collected using a Rigaku CCD detector (Saturn 724) mounted on a Rigaku rotating anode X-ray generator (Micro Max-007HF) and Mo Kα radiation from a corresponding confocal optics.

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CCDC-650334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] Detailed results of elemental (C,H) and atomic absorption (Cu) analyses are summarized in the Supporting Information. Components **1a**–**1c** and **2** are expected to give the following results: calcd (%) for **1a**: C 70.65, H 4.35; **1b**: C 65.17, H 4.01; **1c**: C 56.16, H 3.46; **2**: C 41.42, H 0.23.

[22] The synchrotron powder diffraction experiment was carried out at BL02B2 Spring-8 with a large Debye–Scherrer type diffractometer.[23] The wavelength of the incident X-rays was 0.80 Å. The powder samples were loaded into a lindeman glass capillary with 0.4 mm inner diameter. The temperature was controlled by using a low-temperature nitrogen gas blower. The powder patterns were measured at 100 K. The exposure time of each sample was 75 min for **3a**, 60 min for **3b**, and 55 min for **3c**.

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[24] The order of crystallization was determined by the relative solubilities: for example, in the case of **3a**, the starting material **1** crystallized first on the condition of **1a**/**2** ≥ 2; in the case of **3b** and **3c**, only mixed complex **3** was crystallized in high yields in the condition of **1**:**2** = 1:5–5:1 at 2 mM. See Supporting Information.

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