

Supporting Information

Crystal-to-crystal transformation of a fishnet-like layered compound: a self-Locking structure with position-variable intercalated molecules

Masaki Nishio,^a Natsuko Motokawa^b and Hitoshi Miyasaka^{*,b,c}

^a Department of Chemistry, Division of Material Sciences, Graduate School of Natural Science and Technology,
Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^b Department of Chemistry, Graduate School of Science, Tohoku University, 1-1 Aramaki-Aza-Aoba, Aoba-ku,
Sendai 980-8577, Japan

^c Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

E-mail: miyasaka@imr.tohoku.ac.jp

X-ray Crystallography

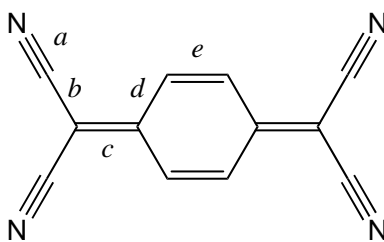
Single crystals with dimensions of $0.253 \times 0.018 \times 0.009 \text{ mm}^3$ for **1**, $0.120 \times 0.080 \times 0.060 \text{ mm}^3$ for **2**, $0.233 \times 0.140 \times 0.052 \text{ mm}^3$ for **1-dry**, and $0.196 \times 0.145 \times 0.048 \text{ mm}^3$ for **2-dry** were mounted on a thin Kapton film with Nujol and cooled in an N_2 gas stream. All measurements were made using a Rigaku Mercury70 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$) for **1**, a Rigaku Saturn70 diffractometer with multi-layer mirror monochromated Mo $K\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$) for **1-dry**, or a Rigaku Saturn70 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$) for **2** and **2-dry**. Crystal Data was collected at 123 K for **1**, 100 K for **1-dry**, and 93 K for **2** and **2-dry**. The structures were solved using direct methods (SIR97¹ for **1** and **2-dry**, SIR92² for **2** and SHELXS97³ for **1-dry**) and expanded using

Fourier techniques. All non-hydrogen atoms were refined anisotropically except for **1-dry** (carbon atoms in disordered anthracene moiety were refined isotropically, while the rest were refined anisotropically). Hydrogen atoms were only introduced for non-disordered carbon atoms at fixed positions, because H atoms on disordered atoms seem to be not accurate in their position. Hydrogen atoms were refined using the riding model. The position-disordered C and Cl atoms of solvent molecule in **2** and C atoms of anthracene in **1-dry** and **2-dry** were first calculated with free occupancies to find subequal proportions of temperature factor between possible sites, and then adequate occupancies, which come to 1, were determined to places of decimals. Full-matrix least-squares refinements on F^2 were based on observed reflections and variable parameters and converged with the unweighted and weighted agreement factors of $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ($I > 2.00\sigma(I)$ and all data), and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ (all data). The crystallization solvent molecules (probably dichloromethane and 1,1,2,2-tetrachloroethane) for **1** could not be determined perfectly, so the crystallographic data were finally treated by PLATON SQUEEZE program.⁴ All calculations were performed using the CrystalStructure crystallographic software package⁵ except for refinement, which was performed using SHELXL2013³.

Table S1. Selected bond lengths around metal dimer in compound **1**, **2**, **1-dry** and **2-dry** (M = Rh, Ru)

	1	2	1-dry	2-dry
M(1)–M(1)	2.4106(7)	2.2911(7)	2.416(2)	2.333(2)
M(2)–M(2)	2.4102(7)	2.2908(7)	2.419(2)	2.335(2)
M(1)–O(1)	2.042(4)	2.071(4)	2.028(7)	2.101(7)
M(1)–O(2)	2.038(4)	2.063(4)	2.054(8)	2.120(6)
M(1)–O(3)	2.036(4)	2.079(4)	2.048(8)	2.118(7)
M(1)–O(4)	2.037(4)	2.060(4)	2.023(8)	2.094(6)
M(2)–O(5)	2.028(4)	2.069(4)	2.023(8)	2.100(7)
M(2)–O(6)	2.037(4)	2.071(3)	2.037(8)	2.108(6)
M(2)–O(7)	2.037(4)	2.064(4)	2.038(8)	2.112(7)
M(2)–O(8)	2.033(4)	2.082(4)	2.022(8)	2.116(7)
M(1)–N(1)	2.188(5)	2.257(5)	2.241(13)	2.316(12)
M(2)–N(2)	2.195(5)	2.255(5)	2.254(13)	2.322(12)

Table S2. Selected bond lengths in TCNQ moiety and degree of charge transfer estimated from the Kistenmacher relationship⁶



compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>b + d</i>	<i>c / (b + d)</i>	ρ^c
I ^d	1.140(1)	1.441(4)	1.374(3)	1.448(4)	1.346(3)	2.889	0.476	0
II ^e	1.153(7)	1.416(8)	1.420(1)	1.423(3)	1.373(1)	2.839	0.500	-1
III ^f	1.1316	1.426	1.366	1.455	1.366	2.881	0.474	0.08
IV ^g	1.131(6)	1.436(5)	1.409(9)	1.432(5)	1.358(8)	2.868	0.491	-0.63
V ^h	1.139(4)	1.428(4)	1.393(6)	1.440(3)	1.351(4)	2.868	0.486	-0.42
VI ⁱ	1.132(4)	1.431(4)	1.393(6)	1.435(4)	1.349(6)	2.866	0.486	-0.42
VII ^j	1.140(3)	1.433(3)	1.393(5)	1.444(3)	1.359(3)	2.877	0.484	-0.33
VIII ^k	1.13(1)	1.44(1)	1.38(1)	1.44(1)	1.35(1)	2.875 ^b	0.480 ^b	-0.13 ^b
	1.14(1)	1.42(1)		1.45(1)				
	1.14 ^a	1.43 ^a		1.45 ^a				
1	1.119(7)	1.434(7)	1.385(6)	1.454(8)	1.330(7)	2.869 ^b	0.483 ^b	-0.28 ^b
	1.128(8)	1.440(7)		1.410(7)				
	1.124 ^a	1.437 ⁱ		1.432 ^a				
2	1.137(8)	1.430(9)	1.378(7)	1.450(9)	1.331(7)	2.882 ^b	0.478 ^b	-0.09 ^b
	1.147(8)	1.423(8)		1.460(8)				
	1.142 ^a	1.427 ^a		1.455 ^a				
1-dry	1.07(2)	1.49(3)	1.35(2)	1.46(2)	1.39(2)	2.98 ^b	0.454 ^b	0.93 ^b
	1.04(2)	1.53(2)		1.47(2)				
	1.06 ^a	1.51 ^a		1.47 ^a				
2-dry	1.15(2)	1.51(2)	1.37(2)	1.45(2)	1.42(2)	2.97 ^b	0.461 ^b	0.61 ^b
	1.14(2)	1.51(2)		1.47(2)				
	1.15 ^a	1.51 ^a		1.46 ^a				

^a average value. ^b calculated from average values. ^c $\rho = A[c / (b + d)] + B$ with $A = -41.667$ and $B = 19.833$. ^d **I**: TCNQ; ref. 7. ^e **II**: RbTCNQ; ref. 8. ^f **III**: (anthracene)TCNQ; ref. 9. ^g **IV**: $[\{\text{Rh}_2(\text{CF}_3\text{CO}_2)_4\}_2\text{TCNQ}] \cdot 3(\text{toluene})$; ref. 10. ^h **V**: $[\{\text{Rh}_2(\text{CF}_3\text{CO}_2)_4\}_2\text{TCNQ}] \cdot 3(p\text{-xylene})$; ref. 11. ⁱ **VI**: $[\{\text{Ru}_2(\text{CF}_3\text{CO}_2)_4\}_2\text{TCNQ}] \cdot 3(\text{toluene})$; ref. 10. ^j **VII**: $[\{\text{Ru}_2(\text{CF}_3\text{CO}_2)_4\}_2\text{TCNQ}] \cdot 3(p\text{-xylene})$; ref. 11. ^k **VIII**: $[\{\text{Ru}_2(\text{CF}_3\text{CO}_2)_4\}_2\text{TCNQ}] \cdot 2(\text{pyrene}) \cdot n(\text{solv.})$; ref. 12.

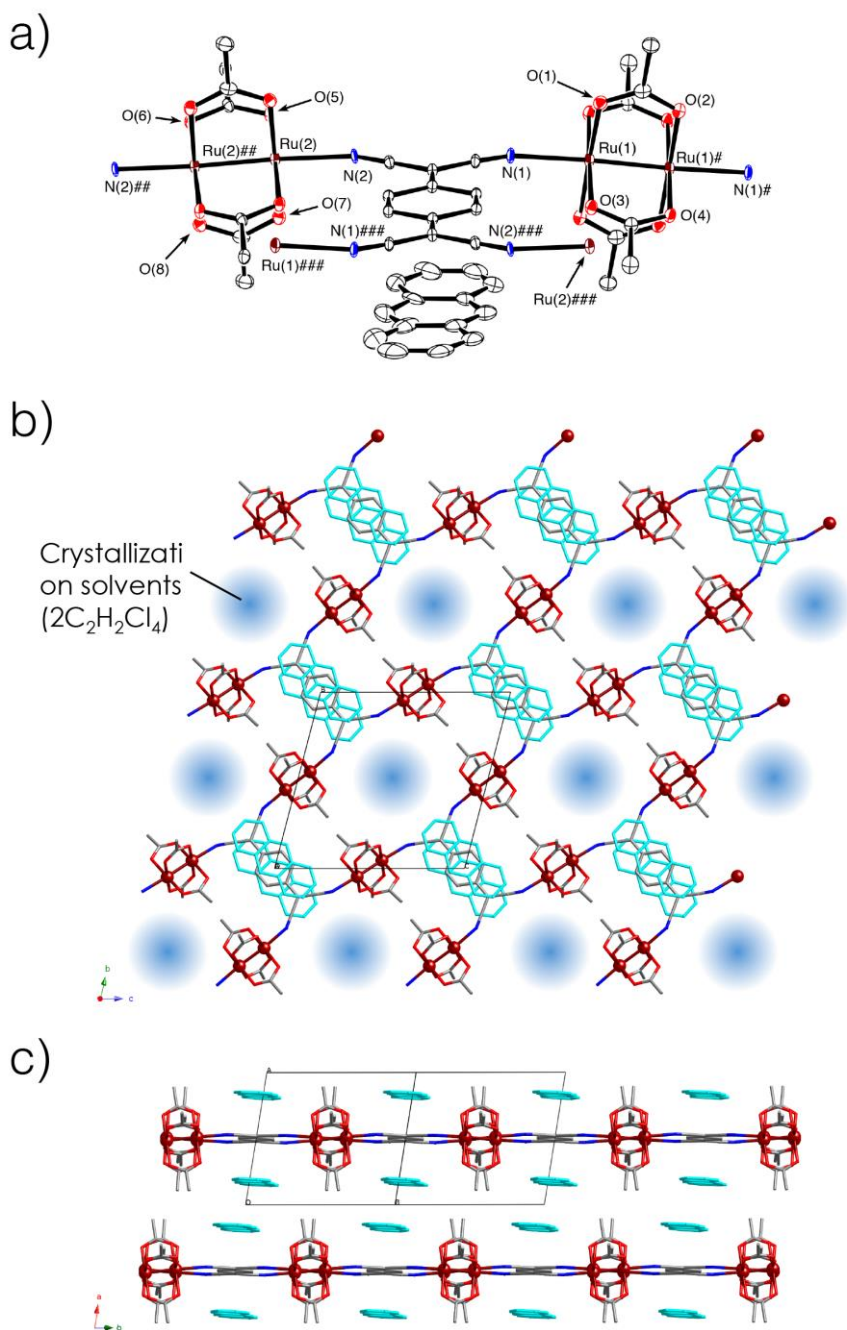


Fig. S1. Structure of **2** (H atoms, solvent molecules, and F atoms of $[\text{Ru}_2(\text{CF}_3\text{CO}_2)_4]$ moieties were omitted for clarity). a) ORTEP drawings of the formula unit (30% probability ellipsoids), where one of two molar ANT units was omitted for clarity, and symmetry operations are #, $-x+1, -y, -z+1$; ##, $-x+1, -y+1, -z+2$; ###, $-x+1, -y, -z+2$. b) and c) Packing views projected along the a axis and along the (011) direction, respectively, where pale-blue-colored molecules are intercalated anthracene molecules.

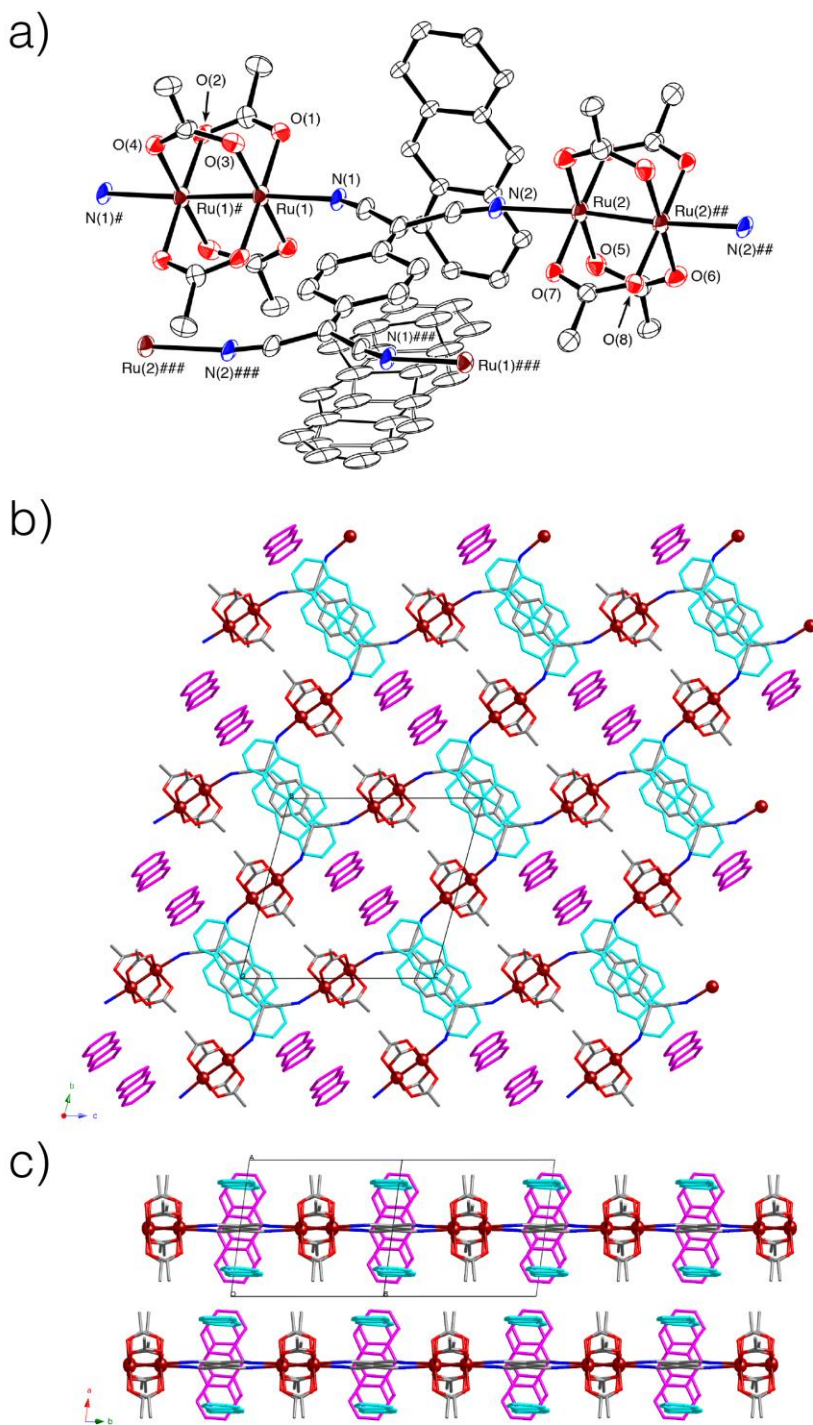


Fig. S2. Structure of **2-dry** (H atoms, solvent molecules, and F atoms of $[\text{Ru}_2(\text{CF}_3\text{CO}_2)_4]$ moieties were omitted for clarity). a) ORTEP drawings of the formula unit (30% probability ellipsoids), where one of two molar ANT units was omitted for clarity, and symmetry operations are #, $-x+1, -y, -z+1$; ##, $-x+1, -y+1, -z+2$; ###, $-x+1, -y, -z+2$. b) and c) Packing views projected along the *a* axis and along the (011) direction, where pale-blue- and pink-colored molecules indicate intercalated anthracene molecules that remained between layers and anthracene molecules that migrated to occupy the void space of hexagonal columns.

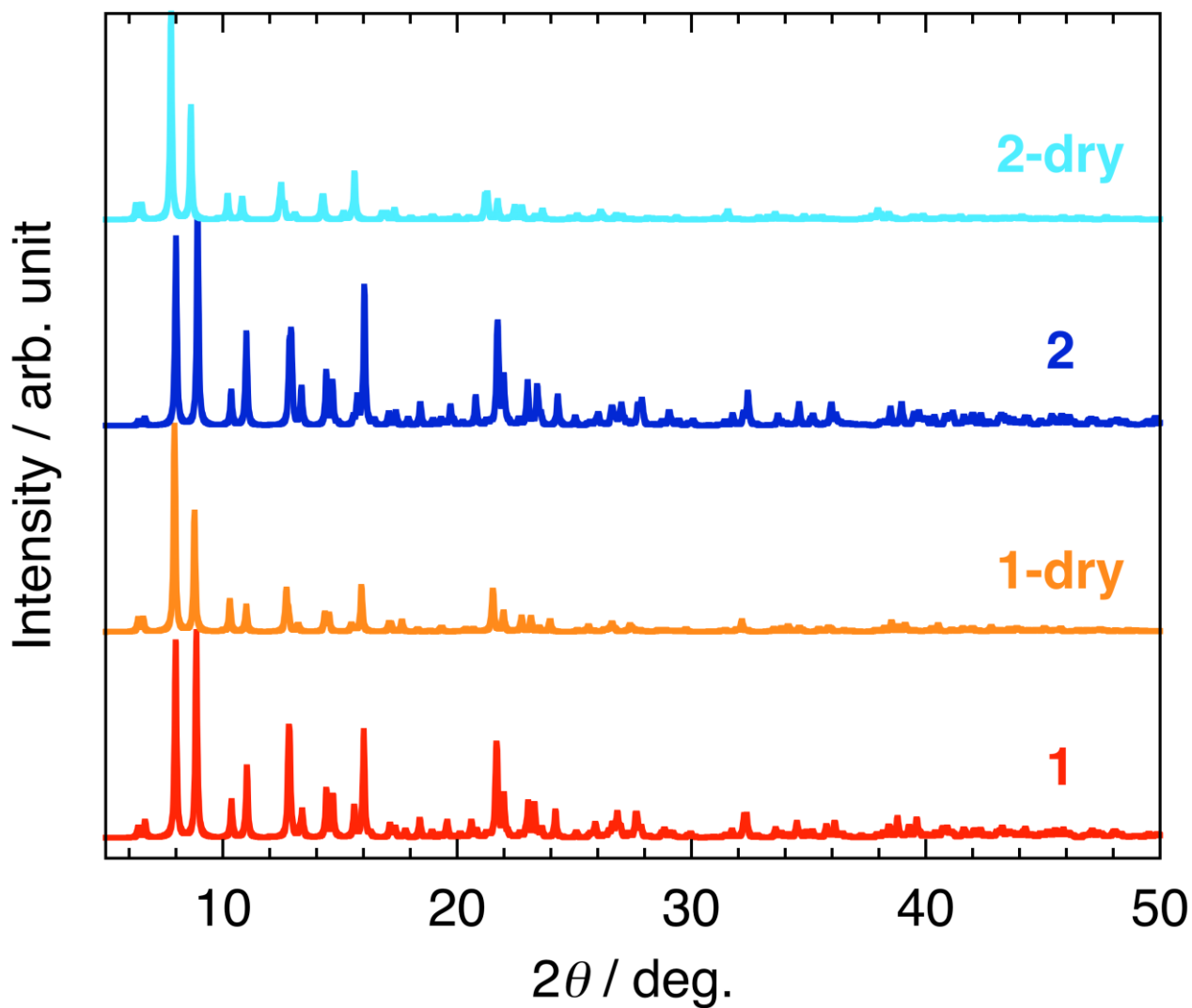


Fig. S3. X-ray powder diffraction patterns of **1**, **2**, **1-dry** and **2-dry**, which were simulated from single-crystal X-ray crystallographic data.

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