CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

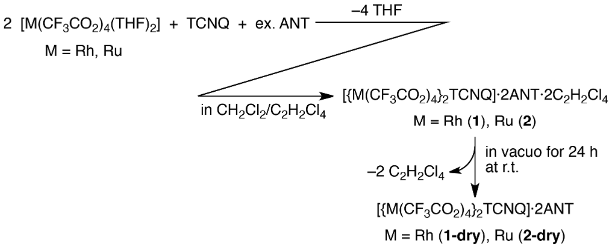
www.rsc.org/

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]

Fishnet-like layered compounds comprising trifluoroacetate-bridged paddlewheel dimetal(II, II) complexes and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) were crystalized with anthracene (ANT) molecules between their layers and crystallization solvents at their hexagonal columnar pores. These complexes undergo a solvent-release crystal-to-crystal transformation involving the migration of a portion of the ANT molecules from between the layers to the hexagonal pores, effectively locking slidable layers.

Crystal-to-crystal transformation is an intriguing phenomenon that possibly enables a drastic change or the switch of physical properties such as magnetic properties.[1,2] It often provides variable nanosized and mesosized pores, resulting in porous molecular materials involving the elimination/adsorption of small molecules such as crystallization solvents and common gas molecules.[3-6] From the viewpoint of dynamic structural transformations in host–guest chemistry, Kitagawa et al. have classified soft porous crystals into three categories: first-, second- and third-generation materials.[3] The first-generation materials undergo a guest-induced crystal-to-amorphous transformation, which enables a collapse of their framework on the removal of the guest molecules.[7] The second-generation materials consist of simple robust and rigid frameworks such as zeolite, which retain their crystallinity when the guests are not present in the pores. Finally, the third-generation materials undergo a structural transformation. Thus, the subject of crystal-to-crystal transformation is associated with the second- and third-generation materials; however, not many low-dimensional network compounds such as one-dimensional (1-D) chain and two-dimensional (2-D) layered compounds undergo crystal-to-crystal transformations with a stretching or breathing motion. Most undergo collapse induced by the elimination of crystallization solvents present between the frameworks, followed by the random piling up of frameworks due to their partial collapse; i.e., most 1-D chain and 2-D layered compounds are first-generation materials.



Scheme 1. Synthetic route for **1** and **2** and their desolvated compounds **1-dry** and **2-dry**.

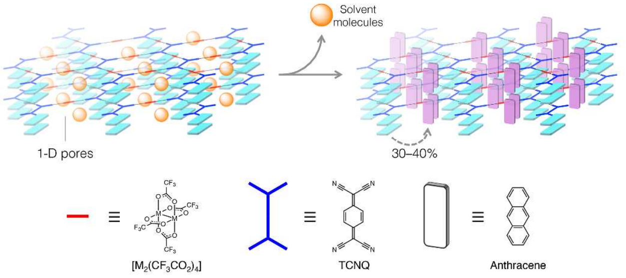
In the course of our research on the functional metal-organic frameworks (MOFs) composed of metal-complex donors and organic acceptors (the so-called D/A–MOFs),[1,8-10] we developed a family of unique 2-D layered porous materials with anthracene (ANT) intercalated between their layers and crystallization solvents (1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$)) in their pores, $[\{M_2^{II,II}(CF_3CO_2)_4\}_2TCNQ]\cdot 2ANT\cdot 2C_2H_2Cl_4$ (M = Rh, **1**; Ru, **2**; $CF_3CO_2^-$ = trifluoroacetate; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) (Scheme 1). These materials undergo a crystal-to-crystal transformation through the elimination of the solvent molecules from their micropores to yield a dried series—$[\{M_2^{II,II}(CF_3CO_2)_4\}_2TCNQ]\cdot 2ANT$ (M = Rh, **1-dry**; Ru, **2-dry**)—without a significant change in their unit cell (Scheme 1). Nevertheless, these materials are not categorized as simple second-generation materials, rather as combined second- and third-generation or combined second- and first-generation materials. This mixed classification stems from the interlayer-intercalated ANT molecules partially migrating into vacuum pores during the solvent-elimination process and consequently preventing the crashing and/or

---

[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

†Electronic Supplementary Information (ESI) available: the detail of X-ray crystallography, Table S1 and S2, and Fig. S1, S2 and S3. See DOI: 10.1039/x0xx00000x

sliding of layers that results in collapse, as generally observed in similar layered materials (Scheme 2).[1a,9] These materials are a unique case in which position-variable molecules prevent a collapse of frameworks.



Scheme 2. Schematic of the crystal-to-crystal transformation observed in **1** and **2**.

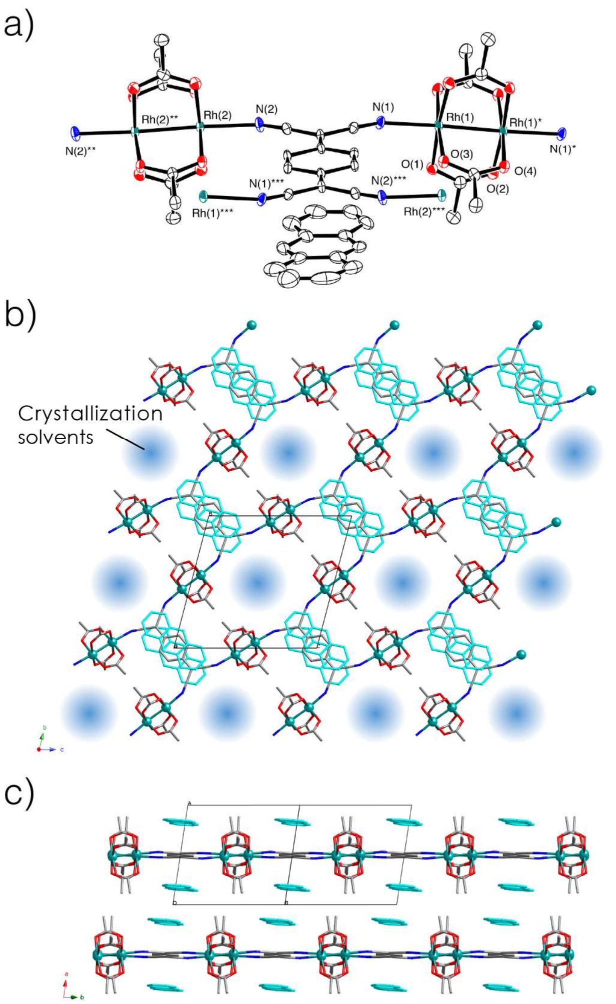


Fig. 1. Structure of **1** (H atoms, solvent molecules and F atoms of $[Rh_2(CF_3CO_2)_4]$ moieties are omitted for clarity). a) ORTEP drawings of the formula unit (30% probability ellipsoids), where one of two molar ANT units was omitted for clarity, and symmetry operations are *, $-x+1$, $-y$, $-z+1$; **, $-x+1$, $-y+1$, $-z+2$; and ***, $-x+1$, $-y$, $-z+2$. b) and c) Packing views projected along the *a* axis and along the (011) direction, respectively, where pale-blue-coloured molecules are intercalated anthracene molecules.

Compounds **1** and **2** were synthesized by the assembly reaction of trifluoroacetate-bridged paddlewheel-type dimetal(II, II) complexes ($[M_2^{II,II}(CF_3CO_2)_4]$, where M = Rh, Ru) and TCNQ in a reaction medium containing an excess amount of ANT. In general, for the assembly reactions in the reaction media composed of commonly used aromatic solvents such as toluene, *p*-xylene and 4-chlorotoluene, the aromatic solvent molecules (abbreviated as G) are automatically intercalated between the coordinating layers of $[\{M_2^{II,II}(CF_3CO_2)_4\}_2TCNQ]_\infty$ during the self-assembly process. These intercalated molecules form π–π stacking columns of $[\cdots TCNQ\cdots G\cdots G\cdots]_\infty$ along the stacking direction of layers, consequently stabilizing the crystallization of this type of neutral layered material.[9] Specifically, this type of assembly suggests that intercalated molecules are possibly replaced with other functional molecules if they form a similar stable π–π stacking mode.[11-13] In this vein, ANT, which possibly forms an alternating stacking fashion with TCNQ[14] and is solid under typical laboratory conditions, was chosen as a guest molecule, resulting in **1** and **2**. Notably, a non-aromatic solvent set—$CH_2Cl_2/C_2H_2Cl_4$—was used for this diffusion reaction to preclude the competing intercalation between the guest molecules and solvents.[‡] The ANT molecules and the crystallization solvents were separately located between layers and in a void space that forms pores through layers, respectively (Scheme 2; vide infra). A similar compound could nevertheless be isolated when 4-chlorotoluene (Cltoluene) was used as a reaction solvent: $[\{Ru_2^{II,II}(CF_3CO_2)_4\}_2TCNQ]\cdot 2ANT\cdot 2(Cltoluene)$. However, in many of the reaction batches, the obtained samples were a mixture of the original compound and the compound that contained 4-Cltoluene as stacked intercalated molecules.

Compounds **1** and **2** are essentially isostructural; they crystallize in the triclinic space group $P-1$ (#2);[§] half of the formula unit was determined as an asymmetrical unit with $Z = 1$, where two types of $[M_2]$ units, assigned as $[M(1)_2]$ and $[M(2)_2]$, and one TCNQ unit have an inversion centre at the midpoint of their respective units (Fig. 1a and Fig. S1a for **1** and **2**, respectively). Selected bond lengths around metal dimers and in the TCNQ moiety of **1** and **2** are summarized in Table S1 and S2, respectively, together with those for dried compounds **1-dry** and **2-dry** (vide infra). Four cyano groups of TCNQ coordinate to the axial sites of respective $[M_2]$ units to form the hexagonal fishnet-like network typically found in this type of 2-D layered compound (Fig. 1b and Fig. S1b for **1** and **2**, respectively).[9] Two ANT molecules are located between the layers, forming a π–π stacking column of $[\cdots TCNQ\cdots ANT\cdots ANT\cdots]_\infty$ along the stacking direction of layers (Fig. 1b and 1c and Fig. S1b and 1c for **1** and **2**, respectively). This in-phase stacking motif also provides one-dimensional pores with hexagonal void spaces perpendicular to the layers; these spaces are occupied by some crystallization solvent molecules (in the case of **1**, void spaces occupied by crystallization solvents were treated using the SQUEEZE program[15]). This structural motif was similarly observed in $[\{M_2(CF_3CO_2)_4\}_2TCNQ]\cdot 3(toluene)$ (M = Rh and Ru),[9a] where two toluene molecules form the stacking column in a $[\cdots TCNQ\cdots G\cdots G\cdots]_\infty$ manner and another toluene molecule occupies the one-dimensional pores. Importantly, this layered structure collapses, probably via a process involving the sliding and crushing of layers when the toluene molecules are gradually eliminated. Moreover, **1** and **2** undergo the desolvation of crystallization solvents (e.g., $C_2H_2Cl_4$) located at the one-dimensional pores even at such a mild condition as room temperature, yielding a series of solvent-free dried compounds, **1-dry** and **2-dry** involving a crystal-to-crystal transformation.[‡] Interestingly, **1-dry** and **2-dry** are sufficiently crystalline to be analysed by single-crystal X-ray crystallography.

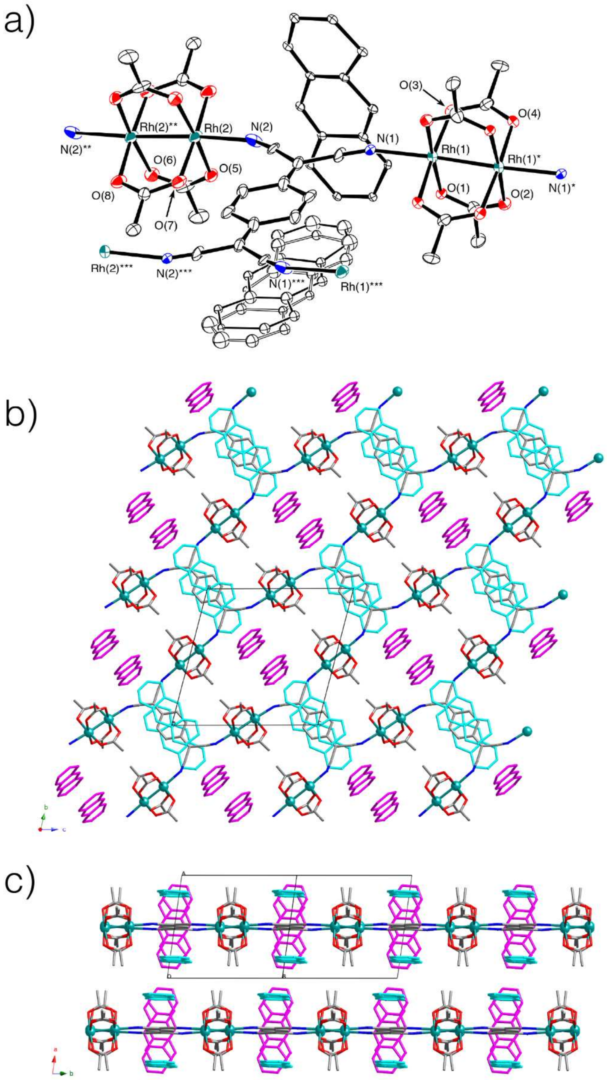


Fig. 2. Structure of **1-dry (**H atoms, solvent molecules and F atoms of $[Rh_2(CF_3CO_2)_4]$ moieties are omitted for clarity). a) ORTEP drawings of the formula unit (30% probability ellipsoids), where one of two molar ANT units was omitted for clarity, and symmetry operations are *, $-x+1$, $-y$, $-z+1$; **, $-x+1$, $-y+1$, $-z+2$; and ***, $-x+1$, $-y$, $-z+2$. b) and c) Packing views projected along the *a* axis and along the (011) direction, where pale-blue- and pink-coloured molecules indicate intercalated anthracene molecules that remained between layers and anthracene molecules that migrated to occupy the void space of hexagonal columns.

Compounds **1-dry** and **2-dry** crystallize in *P*–1 (#2), as do their original compounds **1** and **2** with a very similar unit cell ($Z = 1$).[§] The hexagonal network structure composed of two $[M_2]$ units and TCNQ is maintained in **1-dry** and **2-dry**, which exhibit frameworks very similar to those of **1** and **2** (see Fig. 2 and Fig. S2 for their respective structures; XRPD patterns of **1**, **2**, **1-dry** and **2-dry** in Fig. S3; their bond lengths are summarized in Tables S1 and S2). A main change from **1** and **2** is provided by ANT, which newly occupies the one-dimensional pores formed by hexagonal void spaces instead of crystallization solvent molecules in **1-dry** and **2-dry** (Fig. 2 and Fig. S2, respectively), indicating that the ANT molecule migrated from the interlayer position concomitantly with the elimination of crystallization solvent molecules. In addition, not all ANT molecules, but only about 30-40 % of ANT molecules at the interlayer position move to the one-dimensional pores, as if locking the layers to prevent crashing and/or sliding, and ~60 % of ANT molecules remain between layers with two disordered positions (about 50:50% of occupancy; Fig. 2a and Fig. S2a for **1-dry** and **2-dry**, respectively). Thus, this position transition of ANT molecules resulted in a crystal-to-crystal transformation without the decomposition of frameworks generally observed in this type of layered compound.[9a,b,d,e]

Notably, the layered compounds, $[\{Ru_2^{II,II}(CF_3CO_2)_4\}_2TCNQR_x]\cdot 2(\text{pyrene})$ ($TCNQR_x$ = TCNQ and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$)), in which pyrene molecules are intercalated between layers, exhibited a structure similar to those of **1** and **2**, but did not exhibit a crystal-to-crystal transformation involving the moving of pyrene molecules.[12]

In conclusion, fishnet-like layered compounds comprising trifluoroacetate-bridged paddlewheel dimetal(II, II) complexes with M = Rh and Ru and TCNQ were obtained as crystals stabilized by ANT molecules intercalated between layers. Layered compounds with aromatic solvent molecules intercalated between layers and at hexagonal columnar pores typically exhibit a collapse of their crystallinity caused by the loss of solvents, probably due to the sliding/crushing of layers. In contrast, the present compounds underwent a crystal-to-crystal transformation involving the elimination of crystallization solvents located at hexagonal columnar pores, followed by the partial migration of ANT molecules from between layers to the hexagonal pores. This quasi-dynamical feature of ANT molecules effectively locks slidable layers.

This study was supported by a Grant-in-Aid for Scientific Research (No. 15K13652) and on Innovative Areas ('π-System Figuration' Area 2601, No. 15H00983) from the MEXT of Japan, the ICC-IMR project, the LC-IMR project, the E-IMR project, the Asahi Glass Foundation and the Mitsubishi Foundation.

Notes and references

‡ **Synthesis.** All synthesis procedures were performed under an inert atmosphere using standard Schlenk techniques and a commercial glove box. All chemicals were purchased as reagent grade from commercial sources. Solvents were distilled under N_2 atmosphere using common drying agents. $[Rh_2(CF_3CO_2)_4(THF)_2]$[16] and $[Ru_2(CF_3CO_2)_4(THF)_2]$[17] were prepared according to the methods reported in the literature.

[{$Rh_2(CF_3CO_2)_4$}$_2$TCNQ]·2(anthracene)·2TCE (1). A 1,1,2,2-tetrachloroethane (TCE) solution (20 ml) of TCNQ (8.2 mg, 0.04 mmol) and anthracene (24 mg, 0.135 mmol) was separated into 2-ml portions (bottom layer) and placed in narrow-diameter sealed glass tubes (ϕ: 8 mm). A mixture of CH_2Cl_2 and TCE (1:1 v/v; 1 ml) was added (middle layer). A CH_2Cl_2 solution (20 ml) of [$Ru_2(CF_3CO_2)_4(THF)_2$] (64.2 mg, 0.08 mmol) and ANT (24 mg, 0.135 mmol) was carefully added in 2-ml portions to the middle layer. The glass tubes were left undisturbed for 2 week or more to yield needle-like crystals of **1**. Yield: 33.5 mg (39.3%). Notably, the TCE molecules as crystallization solvents partially eliminate even at room temperature. Elemental analysis (%) calcd for [{$Rh_2(CF_3CO_2)_4$}$_2$TCNQ]·2(anthracene)·1.2TCE, $C_{58.4}H_{26.4}Cl_{4.8}F_{24}N_4O_{16}Rh_4$: C, 33.76; H, 1.28; N, 2.70. Found: C, 33.70; H, 1.02; N, 2.64. FT-IR (KBr): ν(C≡N), 2245, 2220 cm^{-1}. ν(C=O), 1659, 1443 cm^{-1}.

[{$Ru_2(CF_3CO_2)_4$}$_2$TCNQ]·2(anthracene)·2TCE (2). This compound was synthesized in a manner similar to that use to prepare **1**, except that [$Ru_2(CF_3CO_2)_4(THF)_2$] (63.9 mg, 0.08 mmol) was used instead of [$Rh_2(CF_3CO_2)_4(THF)_2$]. Rectangular-shaped crystals of **2** of sufficient quality for single-crystal X-ray crystallography were obtained; however, their yield was extremely low. Hence, the elemental analysis for **2** was not conducted. FT-IR (KBr): ν(C≡N), 2243, 2201, 2142 cm^{-1}. ν(C=O), 1643, 1444 cm^{-1}.

Preparation of dried samples. Samples **1-dry** and **2-dry** were prepared by drying the fresh samples *in vacuo* for 24 h at room temperature. FT-IR (KBr): for **1-dry**, ν(C≡N), 2245, 2220 cm^{-1}. ν(C=O), 1659, 1443 cm^{-1}; for **2-dry**, ν(C≡N), 2243, 2201, 2142 cm^{-1}. ν(C=O), 1643, 1444 cm^{-1}.

§ Crystal data for **1**: $C_{56}H_{24}F_{24}N_4O_{16}Rh_4$, $M = 1876.41$, triclinic, $a = 10.1283(14)$ Å, $b = 13.8996(13)$ Å, $c = 14.2922(18)$ Å, $\alpha = 74.962(8)°$, $\beta = 87.263(9)°$, $\gamma = 79.420(8)°$, $V = 1910.1(4)$ Å^3, $T = 123$ K, space group P–1, $Z = 1$, μ(Mo-Kα) = 9.640 cm^{-1}, 20757 reflections measured, 9610 independent reflections ($R_{int} = 0.0496$). The final R_1 values were 0.0533 ($I > 2\sigma(I)$) and 0.0657 (all data), and the final $wR_2(F^2)$ value was 0.1900 (all data) after PLATON SQUEEZE treatment.[15] The goodness of fit on F^2 was 1.058. CCDC number CCDC 1409054.

Crystal data for **2**: $C_{60}H_{28}Cl_8F_{24}N_4O_{16}Ru_4$, $M = 2204.76$, triclinic, $a = 10.0773(17)$ Å, $b = 13.935(2)$ Å, $c = 14.259(2)$ Å, $\alpha = 74.988(5)°$, $\beta = 86.579(6)°$, $\gamma = 79.096(6)°$, $V = 1899.0(5)$ Å^3, $T = 93$ K, space group P–1, $Z = 1$, μ(Mo-Kα) = 11.859 cm^{-1}, 15221 reflections measured, 7995 independent reflections ($R_{int} = 0.0445$). The final R_1 values were 0.0543 ($I > 2\sigma(I)$) and 0.0848 (all data), and the final $wR_2(F^2)$ value was 0.1577 (all data). The goodness of fit on F^2 was 1.008. CCDC number CCDC 1409056.

Crystal data for **1-dry**: $C_{56}H_{24}F_{24}N_4O_{16}Rh_4$, $M = 1876.41$, triclinic, $a = 10.214(3)$ Å, $b = 14.064(3)$ Å, $c = 14.282(4)$ Å, $\alpha = 75.127(11)°$, $\beta = 87.917(12)°$, $\gamma = 79.520(13)°$, $V = 1949.7(9)$ Å^3, $T = 100$ K, space group P–1, $Z = 1$, μ(Mo-Kα) = 9.445 cm^{-1}, 15554 reflections measured, 8196 independent reflections ($R_{int} = 0.1109$). The final R_1 values were 0.1064 ($I > 2\sigma(I)$) and 0.1847 (all data), and the final $wR_2(F^2)$ value was 0.3529 (all data). The goodness of fit on F^2 was 1.035. CCDC number CCDC 1409053.

Crystal data for **2-dry**: $C_{56}H_{24}F_{24}N_4O_{16}Ru_4$, $M = 1869.06$, triclinic, $a = 10.406(10)$ Å, $b = 14.261(13)$ Å, $c = 14.520(15)$ Å, $\alpha = 74.70(3)°$, $\beta = 88.45(4)°$, $\gamma = 79.38(4)°$, $V = 2042(3)$ Å^3, $T = 93$ K, space group P–1, $Z = 1$, μ(Mo-Kα) = 8.352 cm^{-1}, 14055 reflections measured, 7723 independent reflections ($R_{int} = 0.0579$). The final R_1 values were 0.1069 ($I > 2\sigma(I)$) and 0.1579 (all data), and the final $wR_2(F^2)$ value was 0.353 (all data). The goodness of fit on F^2 was 1.041. CCDC number CCDC 1409055.

1 (*a*) N. Motokawa, S. Matsunaga, S. Takaishi, H. Miyasaka, M. Yamashita and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 11943; (*b*) M. Nishio and H. Miyasaka, *Inorg. Chem.*, 2014, **53**, 4716.

2 (*a*) J. Larionova, S. A. Chavan, J. V. Yakhmi, A. G. Frøystein, J. Sletten, C. Sourisseau and O. Kahn, *Inorg. Chem.*, 1997, **36**, 6374; (*b*) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190; (*c*) M. Kurmoo, H. Kumagai, S. M. Hughes and C. J. Kepert, *Inorg. Chem.*, 2003, **42**, 6709; (*d*) M. Kurmoo, H. Kumagai, K. W. Chapman and C. J. Kepert, *Chem. Commun.*, 2005, 3012; (*e*) N. Yanai, W. Kaneko, K. Yoneda, M. Ohba and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 3496; (*f*) J. Milon, M.-C. Daniel, A. Kaiba, P. Guionneau, S. Brandès and J.-P. Sutter, *J. Am. Chem. Soc.*, 2007, **129**, 13872; (*g*) N. Lopez, H. Zhao, A. V. Prosvirin, A. Chouai, M. Shatruk and K. R. Dunbar, *Chem. Commun.*, 2007, 4611; (*h*) X.-N. Cheng, W.-X. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 15738; (*i*) S. Ohkoshi, Y. Tsunobuchi, H. Takahashi, T. Hozumi, M. Shiro and K. Hashimoto, *J. Am. Chem. Soc.*, 2007, **129,** 3084; (*j*) S. K. Ghosh, W. Kaneko, D. Kiriya, M. Ohba and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2008, **47**, 8843; (*k*) Y.-J. Zhang, T. Liu, S. Kanegawa and O. Sato, *J. Am. Chem. Soc.*, 2009, **131**, 7942; (*l*) Z. Duan, Y. Zhang, B. Zhang and D. Zhu, *J. Am. Chem. Soc.*, 2009, **131**, 6934; (*m*) W.-X. Zhang, W. Xue and X.-M. Chen, *Inorg. Chem.*, 2011, **50**, 309; (*n*) Q.–L. Wang, H. Southerland, J.–R. Li, A. V. Prosvirin, H. Zhao and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2012, **51**, 9321; (*o*) M. Wriedt, A. A. Yakovenko, G. J. Halder, A. V. Prosvirin and K. R. Dunbar, *J. Am. Chem. Soc*., 2013, **135**, 4040.

3 (*a*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334; (*b*) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695.

4 (*a*) O. M. Yaghi, M. O´Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and H. Kim, *Nature,* 2003, **423**, 705; (*b*) G. Férey, *Chem. Soc. Rev.,* 2008, **37**, 191.

5 J. -R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.,* 2012, **112**, 869.

6 Y.–C. He, J. Yang, Y.–Y. Liu and J.–F. Ma, *Inorg. Chem.*, 2014, **53**, 7527.

7 Some cases may also make a recovery of frameworks from the amorphous phase under the initial conditions. These are categorized to the 3rd-generation.

8 H. Miyasaka, *Acc. Chem. Res.,* 2013, **46**, 248.

9 (*a*) H. Miyasaka, C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2000, **39**, 3831; (*b*) H. Miyasaka, T. Izawa, N. Takahashi, M. Yamashita and K. R. Dunbar, *J. Am. Chem. Soc.*, 2006, **128**, 11358; (*c*) N. Motokawa, T. Oyama, S. Matsunaga, H. Miyasaka, M. Yamashita and K. R. Dunbar, *CrystEngComm*, 2009, **11**, 2121; (*d*) H. Miyasaka, N. Motokawa, S. Matsunaga, M. Yamashita, K. Sugimoto, T. Mori, N. Toyota and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 1532; (*e*) K. Nakabayashi, M. Nishio, K. Kubo, W. Kosaka and H. Miyasaka, *Dalton Trans.*, 2012, **41**, 6072.

10 (*a*) J.–J. Liu, Y. Wang, Y.–J. Hong, M.–J. Lin, C.–C. Huang and W.–X. Dai, *Dalton Trans.*, 2014, **43**, 17908; (*b*) J.–J. Liu, Y. Wang, M.–J. Lin, C.–C. Huang and W.–X. Dai, *Dalton Trans.*, 2015, **44**, 484.

11 T. Nozaki, W. Kosaka and H. Miyasaka, *CrystEngComm*, 2012, **14**, 5398.

12 M. Nishio, N. Motokawa, M. Takemura and H. Miyasaka, *Dalton Trans.*, 2013, **42**, 15898.

13 H. Fukunaga and H. Miyasaka, *Angew. Chem. Int. Ed.*, 2015, **54**, 569.

14 R. M. Williams and S. C. Wallwork, *Acta Crystallogr.*, *Sect. B*, 1968, **24**, 168.

15 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

16 J. Telser, R. S. Drago, *Inorg. Chem.*, 1984, **23**, 2599.

17 A. J. Lindsay, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 2723.

Figure for Contents

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

Masaki Nishio, Natsuko Motokawa and Hitoshi Miyasaka*

Graphite-like layered compounds crystalized with anthracene (ANT) molecules between their layers and crystallization solvents at their hexagonal columnar pores; these complexes undergo a solvent-release crystal-to-crystal transformation involving the migration of a portion of the ANT molecules from between the layers to the hexagonal pores.