Supporting Information

Charge-disproportionate ordered state with $\delta = 0.75$ in a chemically sensitive donor/acceptor $D^{\delta+}{}_{2}A^{2\delta-}$ layered framework

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Experimental

General procedures and materials

All synthetic procedures were carried out under anaerobic conditions using standard Schlenk-line techniques and a commercial glove box. Solvents were distilled under a N₂ atmosphere using common drying agents. The starting materials, $[Ru_2(x-FPhCO_2)_4(THF)_2]$ (x = o-, m-, p-)¹ and TCNQ(OMe)₂,² were prepared by following the respective literature procedures.

Syntheses of 1 – 3

Compounds 1 - 3 were synthesized by a similar procedure, so only the method used for 1 is provided as a representative example: A solution of $[Ru_2(o-FPhCO_2)_4(THF)_2]$ (45.1mg, 0.05 mmol) in CH₂Cl₂ (20 mL) was separated into 2 mL portions and placed in narrow diameter glass tubes ($\phi =$ 8 mm), respectively (bottom layer). After this time, a mixed solvent of CH₂Cl₂/PhNO₂ 1:1 v/v (0.5 mL) was added onto the bottom layer as a means to slow the rate of diffusion (middle layer). Finally, a solution (2 mL) of TCNQ(OMe)₂ (6.6 mg, 0.025 mmol) in PhNO₂ (20 mL) was carefully added onto the middle layer of each batch (top layer). The glass tubes were left undisturbed for 3 week or more to obtain rose-like or block-type black crystals of 1. Yield: 9.6%. Elemental analysis (%) calcd for the dried sample of **1** prepared in vacuum for 12 h at room temperature (four CH₂Cl₂) molecules of **1** were removed); C₇₀H₄₀F₈N₄O₁₈Ru₄: C 47.20, H 2.25, N 3.14. Found: C 47.19, H 2.32, N 3.11. IR (Single crystal): v(C=N), 2202, 2158, 2109 cm⁻¹. For **2**, yield: 14.0%. Elemental analysis (%) calcd for 2 with 1.5CH₂Cl₂ (2.5CH₂Cl₂ molecules were partially removed from 2 even at room temperature just before the elemental analysis); C_{71.5}H₄₃F₈N₄O₁₈Ru₄Cl₃: C 45.00, H 2.25, N 2.93. Found: C 45.02, H 2.34, N 3.40. IR (Single crystal): v(C=N), 2190, 2154, 2098(br) cm⁻¹ (br = broad). For **3**, yield: 7.4%. Elemental analysis (%) calcd for **3** with one PhNO₂ molecule prepared in vacuum for 12 h at 100°C (three CH2Cl2 molecules of **3** were removed in this pre-treatment); C₇₆H₄₅F₈N₅O₂₀Ru₄: C 47.93, H 2.38, N 3.68. Found: C 47.92, H 2.38, N 4.18. IR (Single crystal): v(C=N), 2202, 2191(sh), 2167, 2113(br) cm⁻¹ (br = broad; sh = shoulder).

Physical measurements

Infrared (IR) absorption spectra were measured for single crystal at room temperature on a JASCO FTIR 620 spectrophotometer attached to an IRT-5000 infrared microscope. TG-DTA data were collected using aluminum-pan on a SHIMADZU DTG-60H. Powder reflection spectra were measured on pellets diluted with BaSO₄ with a SHIMADZU UV-3150 spectrometer. Magnetic susceptibility measurements were conducted on a SQUID magnetometer (Quantum Design MPMS-XL) in the temperature range of 1.8 to 300 K applied 1 or 0.1 T. Magnetic measurements of the ac type were performed at various frequencies ranging from 1 to 1488 Hz with an ac field

amplitude of 3 Oe. Polycrystalline samples of **1** and **3** embedded in liquid paraffin were measured. Polycrystalline samples of **2** soaked with the solvents were coated by two portions of liquid paraffin and then measured. The χ value of **2** was estimated by dry phase of **2**. Experimental data were corrected for the sample holder and liquid paraffin and for the diamagnetic contribution calculated from Pascal constants.³

Single-crystal X-ray crystallography for 1, 2, and 3

Crystal data were collected on a Rigaku CCD diffractometer (Saturn70) with graphite-monochromated Mo K α radiation (l = 0.71070 Å). A single crystal of size of $0.31 \times 0.14 \times 0.14$ 0.03 mm for $1, 0.54 \times 0.22 \times 0.14$ mm for 2 and $0.08 \times 0.06 \times 0.03$ mm for 3 (3' in Table S1) was mounted on a thin-kapton film with Paratone-N (HAMPTON Research Inc.) and cooled in an N₂ gas stream. The structure of 1 was solved using Patterson methods (SHELX97⁴) and the others were solved using direct methods (SIR 2008⁵). The non-hydrogen atoms were refined anisotropically, except for some disordered solvent atoms which were refined isotropically; hydrogen atoms were introduced as fixed contributors. The crystal-solvents in 3 (3') were disordered and could not be satisfactorily localized. Therefore, after all of the framework atoms were refined, the SOUEEZE function was used to determine the contribution of the disordered solvent molecules that could not be refined to the structure factors.⁶ The contribution of these species was removed from the final structure factor calculations. Full-matrix least squares refinements on F^2 converged with unweighted and weighted agreement factors of $R1 = \Sigma ||F_0| - |F_0|| / \Sigma |F_0|$ ($I > 2\sigma(I)$ and all data), and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ (all data). All calculations were performed using CrystalStructure crystallographic software package.⁷ The crystallographic analysis for **3** was finally done with a superlattice with Z = 2, details of which were noted in the next paragraph.

Single-crystal X-ray crystallography for 3 (superlattice)

Crystal data were collected on a Bruker CCD diffractometer (SMART APEX) with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 100 K. Single crystal sample with a dimension of 0.4 × 0.4 × 0.8 mm³ was used. An absorption correction was performed using semi-empirical methods (SADABS⁸). All nonhydrogen atoms were refined anisotropically and hydrogen atoms were introduced as fixed contributors using SHELXL-97. Other procedures were identical to those for other crystallographic analyses described in the previous paragraph.

	1	2	3 ^a	3 ^{2a}
Formula	$C_{74}H_{48}N_4O_{18}F_8Cl_8Ru_4\\$	$C_{74}H_{48}N_4O_{18}F_8Cl_8Ru_4\\$	$C_{70}H_{40}N_4O_{18}F_8Ru_4\\$	$C_{70}H_{40}N_4O_{18}F_8Ru_4$
Formula weight	2121	2121	1781	1781
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Crystal Dimensions / mm	0.314 × 0.139 × 0.033	$0.540 \times 0.220 \times 0.140$	$0.80\times0.40\times0.40$	$0.080 \times 0.060 \times 0.030$
Space group	P -1	<i>P</i> –1	<i>P</i> –1	P-1
<i>a</i> / Å	9.994(3)	10.641(3)	10.551(3)	10.533(3)
<i>b</i> / Å	14.265(5)	14.224(4)	13.573(4)	13.540(4)
<i>c</i> / Å	14.433(4)	15.449(4)	30.865(5)	15.467(5)
lpha / °	82.602(9)	91.028(2)	80.126(11)	80.095(11)
β/°	79.222(8)	110.013(3)	79.263(11)	79.281(11)
γ/°	82.472(8)	109.772(4)	74.635(10)	74.543(10)
V / Å ³	1992.5(10)	2043.7(10)	4152.6(18)	2071.3(11)
<i>T /</i> K	103(1)	98(1)	100(2)	93(1)
Ζ	1	1	2	1
$ ho_{ m calcd}$ / g cm $^{-3}$	1.768	1.723	1.425	1.428
GOF	1.098	1.085	1.103	1.074
$R_1 (I > 2.00\sigma(I))^{\rm b}$	0.0518	0.0569	0.0363	0.0373
R_1 (all data) ^b	0.0623	0.0610	0.0445	0.0446
wR_2 (all data) ^b	0.1611	0.1604	0.1180	0.1041
CCDC No.	1050724	1050723	1050725	_

Table S1. Crystallographic Data of 1–3, where two types of unit cell were taken for 3: 3' was analyzed in a minimal unit cell with Z = 1

^a Crystal solvents in **3** and **3'** were removed by SQUEEZE. b $R1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ ($I > 2.00\sigma(I)$ and all data), and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ (all data).

Table S2. Relevant bond lengths around Ru centers in 1

	•		
Ru(1)–Ru(1)*	2.2810(8)	Ru(1)-O(1)	2.028(4)
Ru(1)–O(2)*	2.026(4)	Ru(1)-O(3)	2.020(4)
Ru(1)–O(4)*	2.034(5)	Ru(1) - N(1)	2.223(5)
Ru(2)–Ru(2)**	2.2813(7)	Ru(2)-O(5)	2.065(4)
Ru(2)–O(6)**	2.060(4)	Ru(2)-O(7)	2.066(4)
Ru(2)–O(8)**	2.081(4)	Ru(2) - N(2)	2.276(4)

Symmetry operation: *, -x+1, -y+1, -z; **, -x, -y, -z+1

 Table S3. Relevant bond lengths around Ru centers in 2

Ru(1)–Ru(1)*	2.2896(7)	Ru(1)-O(1)	2.019(4)
Ru(1)–O(2)*	2.022(4)	Ru(1)–O(3)	2.025(4)
Ru(1)–O(4)*	2.026(4)	Ru(1) - N(1)	2.230(5)
Ru(2)–Ru(2)**	2.2940(6)	Ru(2) - O(5)	2.020(4)
Ru(2)–O(6)**	2.039(4)	Ru(2)-O(7)	2.019(4)
Ru(2)–O(8)**	2.024(4)	Ru(2) - N(2)	2.231(4)

Symmetry operation: *, -x, -y+2, -z+1; **, -x, -y+1, -z

Table S4. Charge estimation from Kistenmacher relationship.



Comp.	a	b	С	d	е	c/(b+d)	Calcd. ρ^{a}	Ref.
TCNQ	1.140(1)	1.441(4)	1.374(3)	1.448(4)	1.346(3)	0.476	0 (fix)	9
RbTCNQ	1.153(7)	1.416(8)	1.420(1)	1.423(3)	1.373(1)	0.500	1 (fix)	10
1	1.153(7)	1.404(7)	1.435(7)	1.432(7)	1.362(7)	0.508°	1.31°	This work
	1.156(6)	1.407(7)		1.410(7)				
	1.155 ^b	1.406 ^b		1.421 ^b				
2	1.156(8)	1.396(8)	1.478(7)	1.396(8)	1.387(7)	0.528°	2.18 ^c	This work
	1.160(8)	1.397(8)		1.403(8)				
	1.158 ^b	1.397 ^b		1.400 ^b				
3 (unit1) ^d	1.143(6)	1.410(7)	1.428(7)	1.436(6)	1.371(8)	0.503°	1.13 ^c	
	1.152(6)	1.416(6)		1.413(7)				
	1.148 ^b	1.413 ^b		1.425 ^b				This work
3 (unit2) ^d	1.147(6)	1.401(6)	1.471(6)	1.400(6)	1.386(7)	0.526°	2.08°	THIS WOLK
	1.158(6)	1.390(6)		1.402(7)				
	1.153ª	1.396 ^a		1.401ª				
3' e	1.157(5)	1.400(5)	1.453(5)	1.413(5)	1.387(6)	0.517°	1.71°	This work
	1.150(5)	1.402(5)		1.404(5)				
	1.154ª	1.401 ^a		1.409 ^a				

^a The calculated ρ value was estimated by Kinstenmacher relationship, $\rho_{c/(b+d)} = -[A\{c/(b+d)\} + B]$ (A = -41.667, B = 19.833),¹¹ based on dimensions in TCNQ⁹ and RbTCNQ¹⁰. ^b Average values. ^c Estimated from the average values. ^d Compound **3** was analyzed in a superlattice with Z = 2 (see Table S1). ^e Compound **3**' means compound **3** analyzed in a minimal unit cell with Z = 1 (see Table S1).

Table S5. Relevant bond lengths around Ru centers in **3** in the minimum cell with Z = 1 (**3'**)

Ru(1)–Ru(1)*	2.2914(6)	Ru(1)–O(1)	2.046(3)
Ru(1)–O(2)*	2.042(3)	Ru(1)-O(3)	2.042(3)
Ru(1)–O(4)*	2.040(3)	Ru(1) - N(1)	2.227(3)
Ru(2)–Ru(2)**	2.2934(8)	Ru(2)-O(5)	2.023(3)
Ru(2)–O(6)**	2.017(3)	Ru(2)-O(7)	2.022(3)
Ru(2)–O(8)**	2.026(3)	Ru(2)–N(2)	2.234(3)

Symmetry operation: *, -x+2, -y, -z+1; **, -x+1, -y+1, -z

	e	-	
Ru(1)-Ru(1)*	2.2889(8)	Ru(1)–O(1)	2.070(3)
Ru(1)–O(2)*	2.061(3)	Ru(1)-O(3)	2.059(4)
Ru(1)–O(4)*	2.066(4)	Ru(1)-N(1)	2.265(5)
Ru(2)-Ru(3)	2.2906(6)	Ru(2)–O(6)	2.027(3)
Ru(2)–O(15)	2.033(3)	Ru(2)–O(8)	2.031(3)
Ru(2)–O(17)	2.014(3)	Ru(2)-N(2)	2.256(4)
Ru(3)–O(7)	2.030(3)	Ru(3)–O(16)	2.020(3)
Ru(3)–O(9)	2.019(3)	Ru(3)–O(18)	2.027(3)
Ru(3)-N(3)	2.211(4)		
Ru(4) - Ru(4) **	2.2961(8)	Ru(4)–O(10)	2.030(3)
Ru(4)–O(11)**	2.024(3)	Ru(4)–O(12)	2.026(3)
Ru(4)-O(13)**	2.025(3)	Ru(4) - N(4)	2.214(5)

Table S6. Relevant bond lengths around Ru centers in **3** in the superlattice with Z = 2

Symmetry operation: *, -x+2, -y, -z+1; **, -x, -y+2, -z



Fig. S1. Schematic diagrams defining the neutral (N) and ionic (I) phases for the $[Ru_2]/TCNQ$, DCNQI system. (a) A plot of $\Delta E_{H-L}(DA)$ and $\Delta E_{1/2}(DA)$, where $\Delta E_{H-L}(DA)$ is an energy gap between HOMO level of D and LUMO level of A: $\Delta E_{H-L}(DA) = E_{LUMO/A} - E_{HOMO/D}$ and $\Delta E_{1/2}(DA)$ is the difference in first-redox potentials between D and A ($\Delta E_{1/2}(DA) = {}^{1}E_{1/2}(D) - {}^{1}E_{1/2}(A)$). The red and blue lines represent ideal plot lines for the neutral and ionic D/A combinations, respectively. The D/A combinations located near at the boundary between N and I phases (orange circle) are candidates for the N–I transition materials. (b) A plot of $\Delta E_{H-L}(DA)$ and ${}^{2}E_{1/2}(A) - {}^{1}E_{1/2}(A)|$, where ${}^{1}E_{1/2}(A) - {}^{1}E_{1/2}(A)|$ is the potential difference between the 1st and 2nd redox potentials of TCNQR_x. The red, blue, and green regions represent potential windows (arbitrary scale) where respective species of $D_{2}^{0}A^{0}$, $D_{-2}^{0.5+}A^{-}$, and $D_{-2}^{+}A^{-}$ in a $D_{2}A$ type are capable of existence.



Fig. S2. Infrared spectra of 1–3 together with the neutral TCNQ(MeO)₂ and LiTCNQ(MeO)₂ in the wavenumber range of 2000–2250 cm⁻¹ showing the vibrational mode of C=N groups of the TCNQR_x moiety.



Fig. S3. ORTEP drawing of the formula unit of **1** (a) and **2** (b) (50 % probability ellipsoids are shown and hydrogen atoms are omitted for clarity), where some F atoms and benzoate moieties have position disorders. Symmetry operations: *) -x+1, -y+1, -z; **) -x, -y, -z+1; #) -x, -y+1, -z+1 for **1**; *) -x, -y+2, -z+1; **) -x, -y+1, -z; #) -x, -y+1, -z+1 for **2**.



Fig. S4. Packing views of layers of **1** (a) and **2** (b) projected along the (101) plane for **1** and the (100) plane for **2**, respectively, where the aromatic group (*x*-FPh) of $[Ru_2]$ units, hydrogen atoms, and crystallization solvent molecules are omitted for clarity.



Fig. S5. Structure of **3** (**3'**) analyzed in a unit cell of the triclinic P-1 space group (Z = 1) with cell parameters shown in Table S1, in which two kinds of $[Ru_2]$ units ($[Ru(1)_2]$ and $[Ru(2)_2]$) and one TCNQ(MeO)₂ unit with respective inversion centers were determined as an asymmetric unit.



Fig. S6. A packing view of layers of **3** (superlattice) projected along the (101) plane, where the aromatic group (*p*-FPh) of $[Ru_2]$ units, hydrogen atoms, and crystallization solvent molecules are omitted for clarity.



Fig. S7. Temperature dependence of the magnetic susceptibility (χ) and χT product of **1** measured at 1 kOe.



Fig. S8. An H-T phase diagram for **1**, where AF and P indicate antiferromagnetic and paramagnetic phases, respectively. The data were taken from the M-H curves (red dots) shown in Fig. S9 and the FCM curves (blue dots) shown in Fig. 3b.



Fig. S9. Field dependence of the magnetization of 1 measured at several temperatures.



Fig. S10. Magnetic properties of **2**. a) Temperature dependence of χ and χT of **2** measured from 180 K to 1.8 K at 1 kOe (1st cooling process), for which the sample was supercooled to 180 K to avoid the desolvation in the process of measurements. b) The variation of χ in the process of temperature sweeping in the range of 1.8–300 K (in-situ magnetic measurements with 1st cooling from 180 K to 1.8 K; 1st heating from 1.8 K to 300 K; 2nd cooling from 300 K to 1.8 K; 3rd cooling from 300 K to 1.8 K after keeping the sample for 8 hours at 300 K in vacuo (MPMS level)).



Fig. S11. Magnetic properties of the dried sample of **2** prepared in vacuum at 100°C for 12 hours. a) Temperature dependence of dc susceptibility (χ) and the χT product measured applying a 1 kOe dc field. b) Temperature dependence of ac susceptibilities (χ ', in-phase; χ '', out-of-phase) at zero dc field and 3 Oe oscillating field.



Fig. S12. Field-cooled magnetization curves of **3** measured at several external magnetic fields from 3 Oe to 1 kOe.



Fig. S13. Field dependence of the magnetization of **3** measured at several temperatures (a), and the variations of the coercive field (H_c) and the remnant magnetization (*RM*) (b) found from Fig S11a.

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