Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Metamagnetism with T_N = 97 K in a Layered Assembly of Paddlewheel [Ru_2] Units and TCNQ: An Empirical Rule for Interlayer Distances Determining the Magnetic Ground State

Wataru Kosaka,[a,b] Masahisa Itoh,[b] and Hitoshi Miyasaka*[a,b]

[a] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

[b] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

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

Corresponding author*

Prof. Dr. Hitoshi Miyasaka

Institute for Materials Research, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

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

Tel: +81-22-215-2030

FAX: +81-22-215-2031

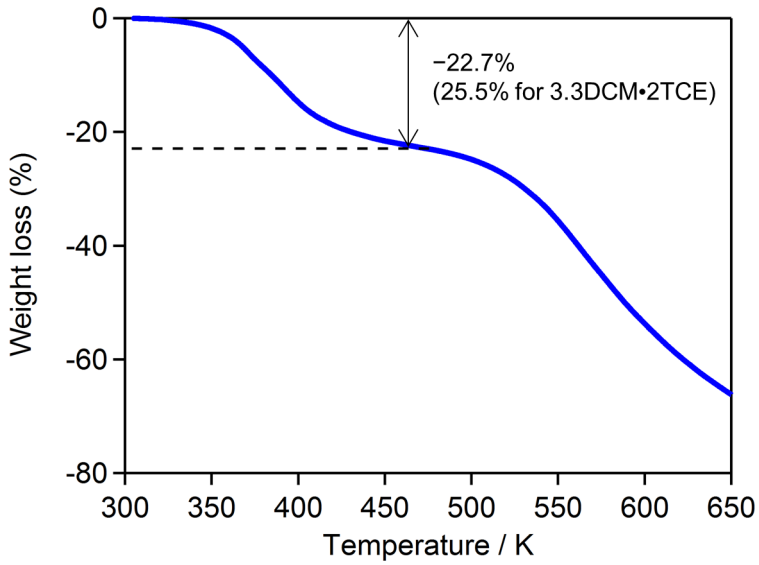


Fig. S1 Thermal gravimetric analysis (TGA) profiles of **1** with a heating rate of 5 K min^{-1} under N_2 atmosphere.

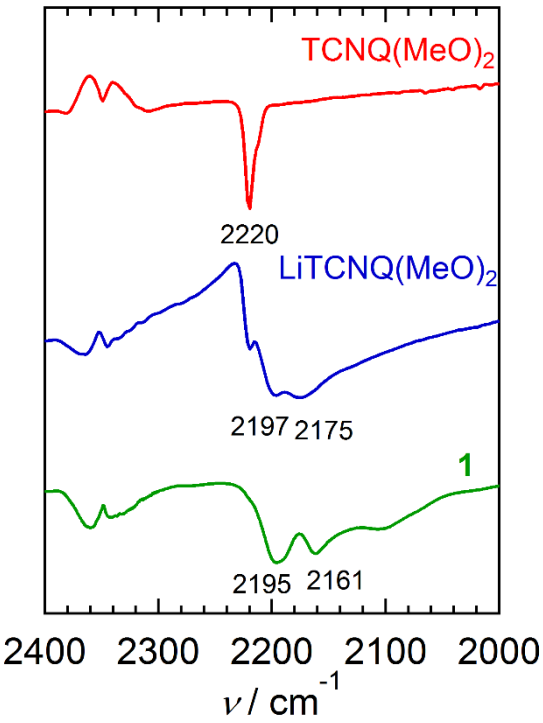


Fig. S2 Infrared spectra in the range of 2000−2400 cm^{-1} for **1**, $TCNQ(MeO)_2^0$, and $Li^+TCNQ(MeO)_2^{\bullet-}$ measured on KBr pellets at room temperature.

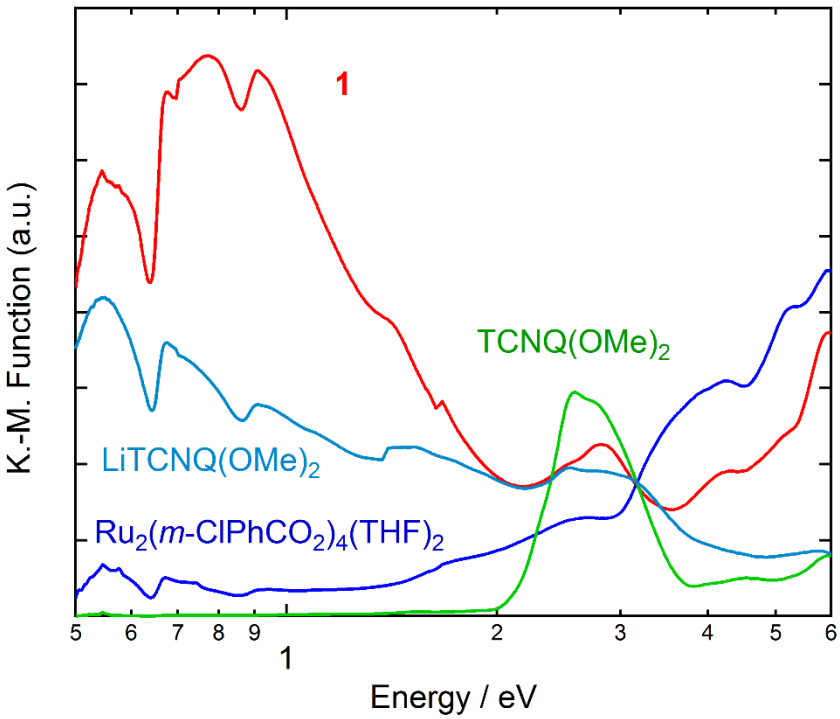


Fig. S3 Powder reflection spectra of **1**, $Ru_2(m\text{-}ClPhCO_2)_4(THF)_2$, $TCNQ(MeO)_2^0$, and $Li^+TCNQ(MeO)_2^{\bullet-}$ measured on pellets diluted with $BaSO_4$.

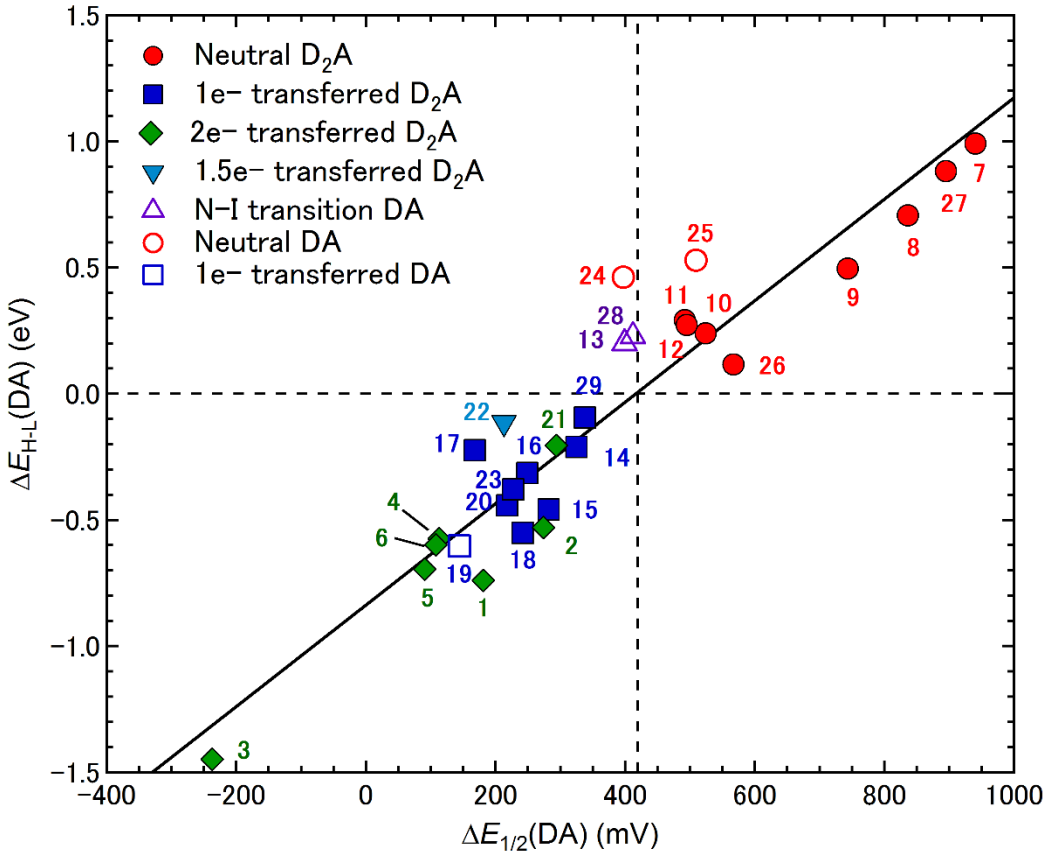


Fig. S4 Plot of $\Delta E_{H\text{-}L}$(DA) vs $\Delta E_{1/2}$(DA) for D_2A and DA materials of $[Ru_2^{II,II}]$/TCNQR$_x$, DCNQIR$_x$ sets reported until now, where red circle, blue square, green diamond and cyan triangle plots represent N, 1e-I, 2e-I and 1.5e-I, respectively. Open and close plots correspond to D_2A and DA compound, respectively. Purple triangle corresponds to the DA compound exhibits temperature and pressure-induced N-I phase transition. **1**: [{Ru$_2$(*o*-CF$_3$PhCO$_2$)$_4$}(TCNQ)],[1] **2**: [{Ru$_2$(*o*-CF$_3$PhCO$_2$)$_4$}{TCNQ(Me)$_2$}],[1] **3**: [{Ru$_2$(*o*-CF$_3$PhCO$_2$)$_4$}(TCNQF$_4$)],[1] **4**: [{Ru$_2$(*o*-CH$_3$PhCO$_2$)$_4$}(BTDA-TCNQ)],[1] **5**: [{Ru$_2$(*p*-CH$_3$PhCO$_2$)$_4$}(BTDA-TCNQ)],[1] **6**: [{Ru$_2$(*m*-CH$_3$PhCO$_2$)$_4$}(BTDA-TCNQ)],[2,3] **7**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}{TCNQ(MeO)$_2$}],[4] **8**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}{TCNQ(Me)$_2$}],[4] **9**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(TCNQ)],[4,5,6] **10**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(TCNQBr$_2$)],[4,6] **11**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(TCNQF$_2$)],[4,6] **12**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(TCNQCl$_2$)],[4,6] **13**: [{Ru$_2$(2,3,5,6-F$_4$PhCO$_2$)$_4$}{DCNQI(Me)$_2$}],[7,8,9] **14**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(TCNQF$_4$)],[4,6,10] **15**: [{Ru$_2$(*o*-ClPhCO$_2$)$_4$}{TCNQ(MeO)$_2$}],[11] **16**: [{Ru$_2$(*m*-FPhCO$_2$)$_4$}(BTDA-TCNQ)],[3,12,13] **17**: [{Ru$_2$(*p*-FPhCO$_2$)$_4$}(BTDA-TCNQ)],[14] **18**: [{Ru$_2$(*o*-FPhCO$_2$)$_4$}(BTDA-TCNQ)],[14] **19**: [{Ru$_2$(4-Cl-2-MeOPhCO$_2$)$_4$}(BTDA-TCNQ)],[15,16] **20**: [{Ru$_2$(*o*-FPhCO$_2$)$_4$}{TCNQ(MeO)$_2$}],[17] **21**: [{Ru$_2$(*m*-FPhCO$_2$)$_4$}{TCNQ(MeO)$_2$}],[17] **22**: [{Ru$_2$(*p*-FPhCO$_2$)$_4$}{TCNQ(MeO)$_2$}],[17] **23**: [{Ru$_2$(2,4,6-F$_3$PhCO$_2$)$_4$}(TCNQ)],[18] **24**: [{Ru$_2$(F$_5$PhCO$_2$)$_4$}{DCNQI(Me)$_2$}],[8] **25**: [{Ru$_2$(2,3,5,6-F$_4$PhCO$_2$)$_4$}{DCNQI(MeO)$_2$}],[9] **26**: [{Ru$_2$(2,3,5,6-F$_4$PhCO$_2$)$_4$}(BTDA-TCNQ)],[19] **27**: [{Ru$_2$(CF$_3$CO$_2$)$_4$}(BTDA-TCNQ)],[20] **28**: [{Ru$_2$(3,4-Cl$_2$PhCO$_2$)$_4$}{TCNQ(EtO)$_2$}],[21] **29**: [{Ru$_2$(*m*-ClPhCO$_2$)$_4$}{TCNQ(MeO)$_2$}].

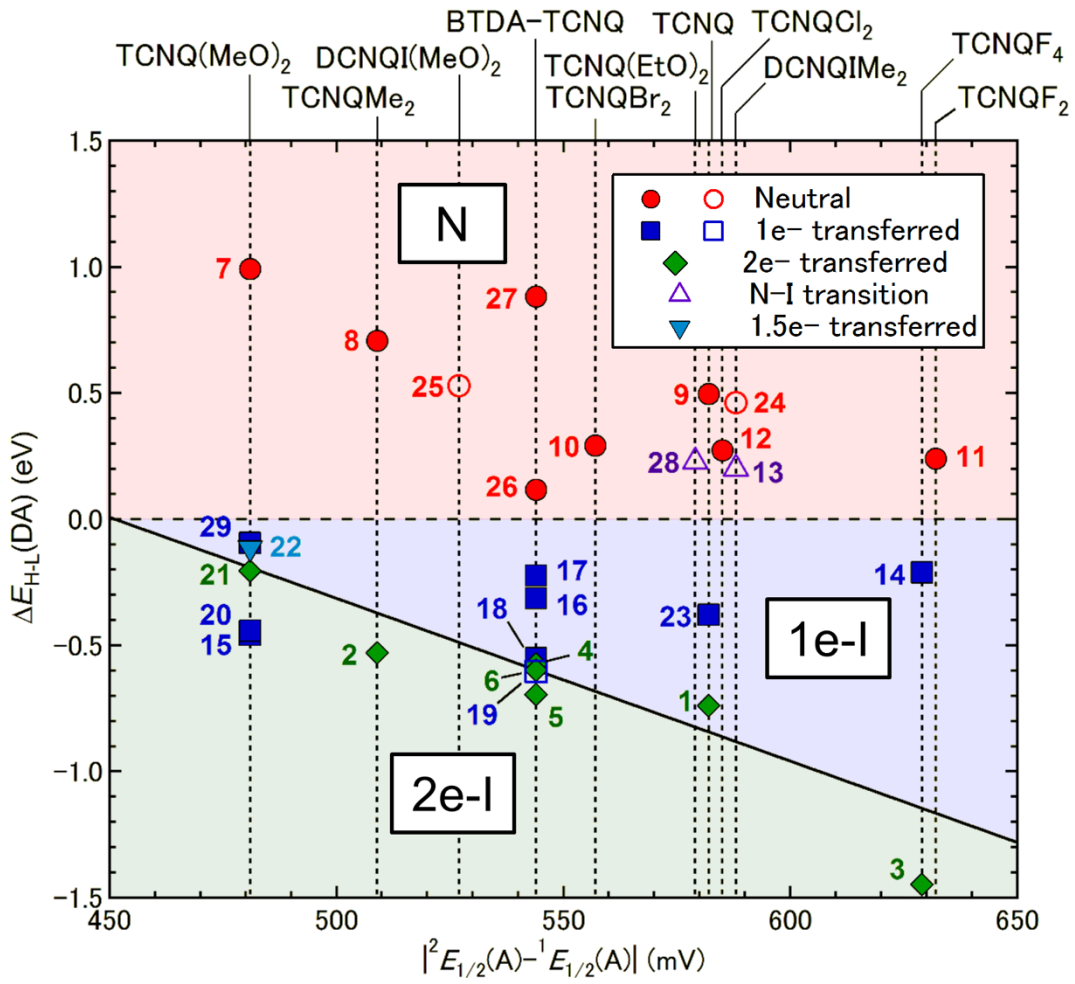
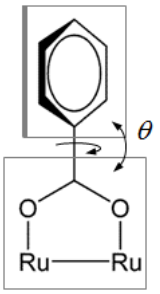


Fig. S5 Plots of $\Delta E_{\text{H-L}}$(DA) vs $|^2E_{1/2}(\text{A}) - {}^1E_{1/2}(\text{A})|$. Numberings of compounds were given in the caption of Fig. S3.

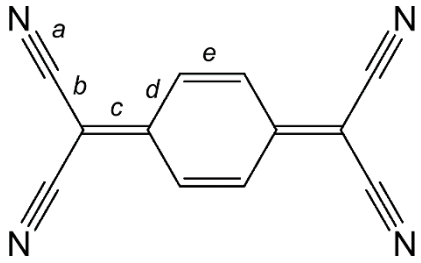
Table S1 Selected bond lengths (Å) and angles (˚) in **1**, where θ represents dihedral angle between least-squares planes defined by phenyl ring of benzoate ligand and carboxylate-bridging mode (atom set of Ru_2O_2C).



	1
Ru1–O1	2.026(4)
Ru1–O2a	2.006(4)
Ru1–O3	2.030(4)
Ru1–O4a	2.010(4)
Ru2–O5	2.053(3)
Ru2–O6b	2.064(4)
Ru2–O7	2.056(4)
Ru2–O8b	2.060(4)
Ru1–N1	2.219(5)
Ru2–N2	2.253(5)
Ru1–Ru1a	2.2814(7)
Ru2–Ru2b	2.2830(7)
Ru1a–Ru1–N1	178.56(13)
Ru2b–Ru2–N2	178.48(12)
Ru1–N1–C29	167.9(4)
Ru2 –N2–C31	166.7(4)
θ	
benzoate set-1	17.31
benzoate set-2	5.54
benzoate set-3	10.63
benzoate set-4	4.79

Symmetry codes: (a) $-x + 1, -y + 2, -z + 1$, (b) $-x + 1, -y + 1, -z$.
Benzoate set-1 to -4: the phenyl group of C2−C8, C10−C16, C18−C24 and C26−C32, respectively.

Table S2 Comparison of bond lengths (Å) in TCNQ moiety and a charge of TCNQ (ρ) estimated based on the Kistenmacher' relationship.[22]



	charge	*a*	*b*	*c*	*d*	*e*	ρ^b	Ref
I	0	1.140(1)	1.441(1)	1.374(3)	1.448(4)	1.346(3)	0	23
II	−1	1.153(7)	1.416(8)	1.420(1)	1.423(3)	1.373(1)	−1	24
1		1.146(7)	1.401(7)	1.419(8)	1.432(7)	1.373(8)	−1.08[c]	This work
		1.158(7)	1.413(7)		1.409(7)			
		1.152[a]	1.407[a]		1.442[a]			

I: TCNQ, **II**: RbTCNQ. [a]average value, [b]estimated from average values, [c]$\rho = A_H[c/(b + d)] + B_H$ with $A_H = -41.667$ and $B_H = 19.833$.

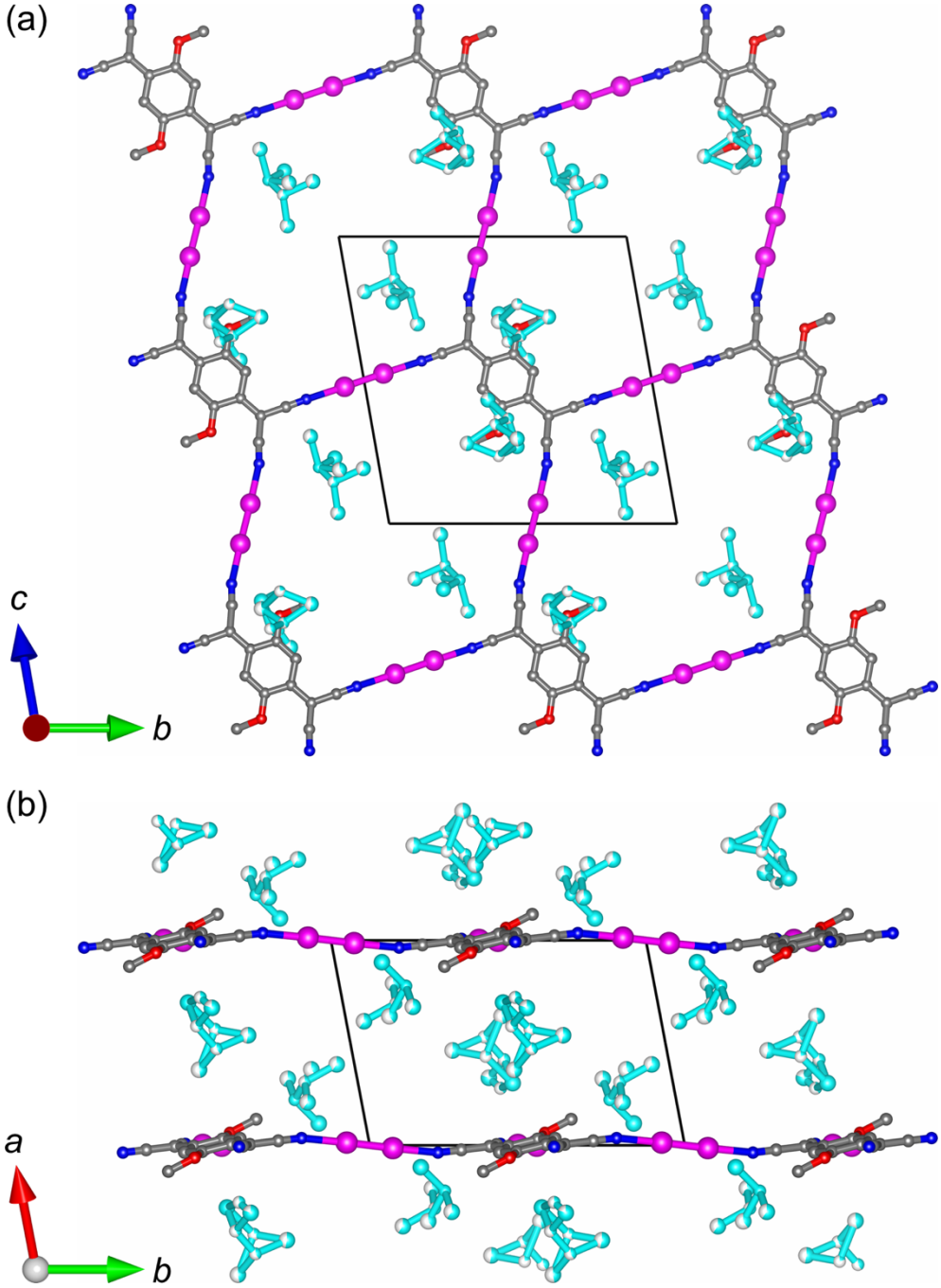


Fig. S6 Packing diagrams of **1**. A view along *a*-axis (a) and *c*-axis (b), where atoms C, N, O, and Ru are represented in gray, blue, red, and purple, respectively. Crystallization solvents are depicted in cyan. The equatorial carboxylate ligands are located around the [Ru_2] units. Hydrogen atoms are omitted for clarity.

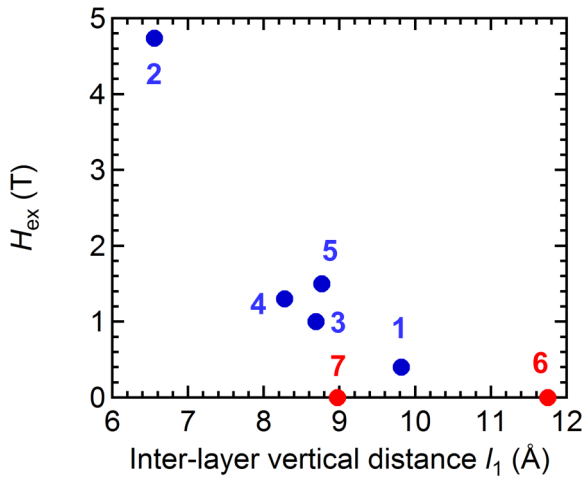


Fig. S7 Spin-flipping field at 1.8 K (H_{ex}) vs. inter-layer vertical distance (l_1, Fig. 2b) plots for **1** and relevant $[Ru_2]/TCNQR_x$ layered magnets reported previously, where the compound with ferromagnetic and antiferromagnetic ground states are colored in red and blue, respectively: **1**, $[\{Ru_2(m\text{-}ClPhCO_2)_4\}_2\{TCNQ(MeO)_2\}]\cdot 3.3DCM\cdot 2TCE$; **2**, $[\{Ru_2(CF_3CO_2)_4\}_2(TCNQF_4)]\cdot 3(p\text{-xylene})$;[6,10] **3**, $[\{Ru_2(o\text{-}FPhCO_2)_4\}_2(BTDA\text{-}TCNQ)]\cdot 4DCM$;[14] **4**, $[\{Ru_2(o\text{-}ClPhCO_2)_4\}\{TCNQ(MeO)_2\}]\cdot DCM$;[11] **5**, $[\{Ru_2(o\text{-}FPhCO_2)_4\}\{TCNQ(MeO)_2\}]\cdot 4DCM$;[17] **6**, $[\{Ru_2(2,4,6\text{-}F_3PhCO_2)_4\}(TCNQ)]\cdot 2DCM\cdot 2(p\text{-xylene})$;[18] **7**, $[\{Ru_2(p\text{-}FPhCO_2)_4\}(BTDA\text{-}TCNQ)]\cdot 2DCM\cdot 2(p\text{-chlorotoluene})$.[14]

References in ESI

1 W. Kosaka, T. Morita, T. Yokoyama, J. Zhang and H. Miyasaka, *Inorg. Chem.*, 2015, **54**, 1518−1527.
2 H. Miyasaka, T. Morita and M. Yamashita, *Chem. Commun.*, 2011, **47**, 271–273.
3 H. Fukunaga, W. Kosaka and H. Miyasaka, *Chem. Lett.*, 2014, **43**, 541−543.
4 K. Nakabayashi, M. Nishio, K. Kubo, W. Kosaka and H. Miyasaka, *Dalton Trans.*, 2012, **41**, 6072–6074.
5 H. Miyasaka, C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2000, **39**, 3831–3835.
6 H. Miyasaka, N. Motokawa, S. Matsunaga, M. Yamashita, K. Sugimoto, T. Mori, N. Toyota and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 1532–1544.
7 H. Miyasaka, N. Motokawa, T. Chiyo, M. Takemura, M. Yamashita, H. Sagayama and T. Arima, *J. Am. Chem. Soc.*, 2011, **133**, 5338–5345.
8 K. Nakabayashi and H. Miyasaka, *Chem. Eur. J.*, 2014, **20**, 5121–5131.
9 K. Nakabayashi, M. Nishio and H. Miyasaka, *Inorg. Chem.*, 2016, **55**, 2473–2480.
10 H. Miyasaka, T. Izawa, N. Takahashi, M. Yamashita and K. R. Dunbar, *J. Am. Chem. Soc.*, 2006, **128**, 11358–11359.
11 N. Motokawa, S. Matsunaga, S. Takaishi, H. Miyasaka, M. Yamashita and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 11943–11951.
12 N. Motokawa, H. Miyasaka, M. Yamashita and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2008, **47**, 7760–7763.
13 N. Motokawa, H. Miyasaka and M. Yamashita, *Dalton Trans.*, 2010, **39**, 4724−4726.
14 N. Motokawa, T. Oyama, S. Matsunaga, H. Miyasaka, M. Yamashita and K. R. Dunbar, *CrystEngComm*, 2009, **11**, 2121–2130.
15 M. Nishio, N. Hoshino, W. Kosaka, T. Akutagawa and H. Miyasaka, *J. Am. Chem. Soc.*, 2013, **135**, 17715–17718.
16 M. Nishio and H. Miyasaka, *Inorg. Chem.*, 2014, **53**, 4716–4723.
17 H. Fukunaga, T. Yoshino, H. Sagayama, J. Yamaura, T. Arima, W. Kosaka, H. Miyasaka, *Chem. Commun.*, 2015, **51**, 7795−7798.
18 W. Kosaka, H. Fukunaga and H. Miyasaka, *Inorg. Chem.*, 2015, **54**, 10001−10006.
19 K. Taniguchi, K. Narushima, J. Mahin, W. Kosaka and H. Miyasaka, *Angew. Chem. Int. Ed.*, 2016, **55**, 5238−5242.
20 K. Taniguchi, K. Narushima, H. Sagayama, W. Kosaka, N. Shito and H. Miyasaka, *Adv. Func. Mater.*, 2017, **27**, 1604990.
21 W. Kosaka, Y. Takahashi, M. Nishio, K. Narushima, H. Fukunaga and H. Miyasaka, *Adv. Sci.*, 2017, in press, DOI: 10.1002/advs.201700526.
22 T. J. Kistenmacher, T. J. Emge, A. N. Bloch, D. O. Cowan, *Acta Crystallogr., Sect. B*, 1982, **38**, 1193−1199.
23 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 932−939.
24 C. J. Fritche and P. Arthur, *Acta Cryst.*, 1966, **21**, 139−145.