Supplementary Information

An ionicity diagram for the family of $[\{Ru_2(CF_3CO_2)_4\}_2(TCNQR_x)]$ ($TCNQR_x$ = R-substituted 7,7,8,8-tetracyano-*p*-quinodimethane)

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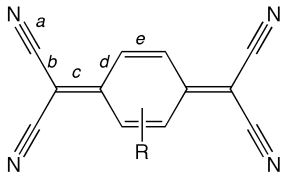
Table S1. Comparison of bond distances (Å) in $TCNQMe_2$ for **6** and **6-Rh** and $TCNQ(MeO)_2$ for **7** and **7-Rh**



Comp.	*a*	*b*	*c*	*d*	*e*	*c*/(*b*+*d*)	Calcd. ρ
TCNQ	1.140(1)	1.441(4)	1.374(3)	1.448(4)	1.346(3)	0.476	0 (fix)
RbTCNQ	1.153(7)	1.416(8)	1.420(1)	1.423(3)	1.373(1)	0.500	1 (fix)
6	1.142(6)	1.423(5)	1.393(8)	1.446(6)	1.345(5)	0.486	0.40
7	1.14(1)	1.433(9)	1.40(2)	1.433(8)	1.408(6)	0.488	0.52
6-Rh	1.09(2) 1.15(2) av. 1.12	1.42(2) 1.45(2) av. 1.435	1.39(2)	1.45(2) 1.46(2) av. 1.455	1.346(9)	0.481	0.21
7-Rh	1.111(8)	1.456(7)	1.38(1)	1.428(6)	1.383(5)	0.479	0.10

The calculated ρ value was estimated by using Kinstenmacher relationship, $\rho_{c/(b+d)} = -[A\{c/(b+d)\} + B]$ (A = -41.667, B = 19.833),[1] based on dimensions in TCNQ[2] and RbTCNQ.[3]

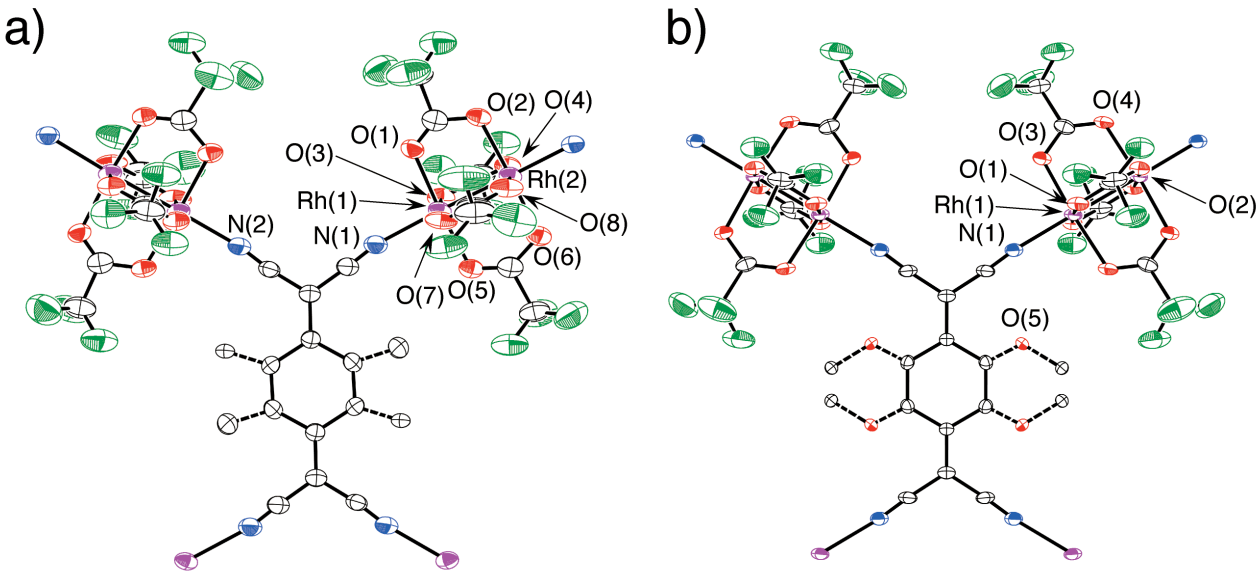


Fig. S1. ORTEP drawings of formula unit of **6-Rh** (a) and **7-Rh** (b) (30 % probability ellipsoids), where the dotted bonds represent disordered atoms. Hydrogen atoms and interstitial solvent molecules were omitted for clarity.

Powder reflection spectra of 6 and 7

Powder reflection spectra of **6** and **7** exhibited an intense CT band of $[Ru_2^{II,II}]\rightarrow TCNQR_x$ at ca. 1.0 and 1.1 eV, respectively, and no absorption below 1 eV (Fig. S2), being characteristic of neutral form.

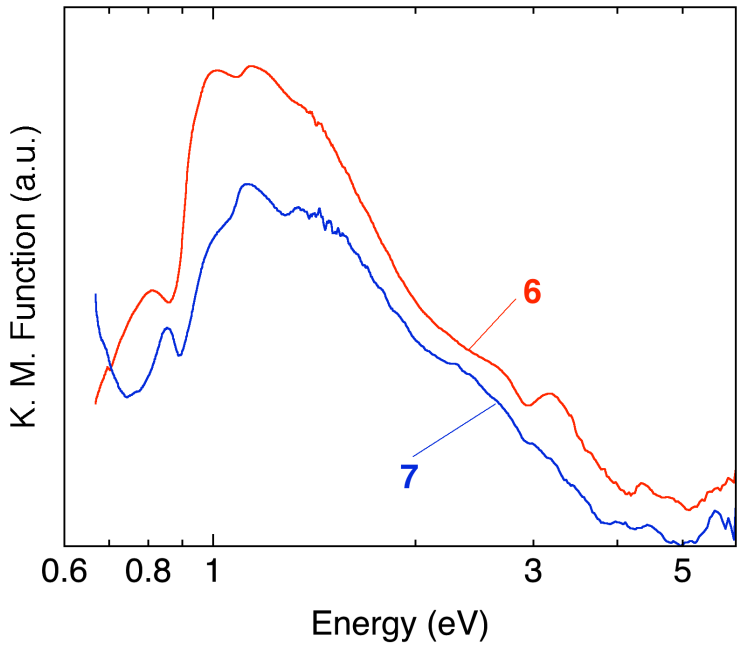


Fig. S2. Powder reflection spectra of **6** and **7** measured based on a $BaSO_4$ pellet.

Infrared Spectra of 6 and 7

In the infrared region, characteristic C=C and C≡N vibrational bands of neutral $TCNQR_x$ form were detected (Fig. S3 and S4).

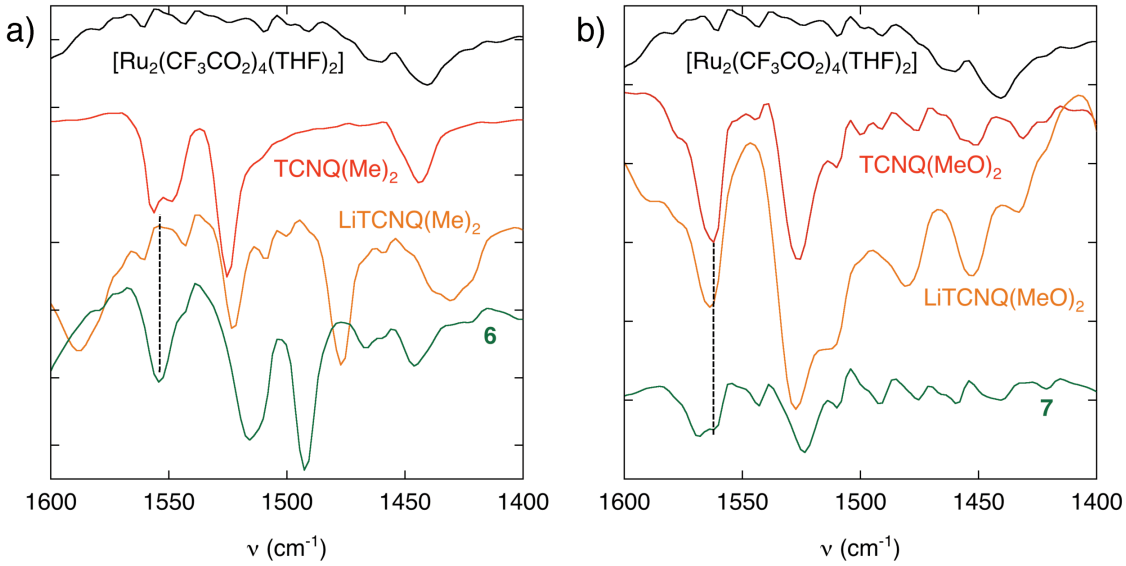


Fig. S3. Infrared spectra of **6** (a) and **7** (b) with those of $[Ru_2(CF_3CO_2)_4(THF)_2]$, $TCNQR_2$, and Li salts of $TCNQR_2$ (R = Me and MeO) for comparison, which indicate characteristic C=C vibrational bands for compounds in the range of 1400 – 1600 cm^{-1}.

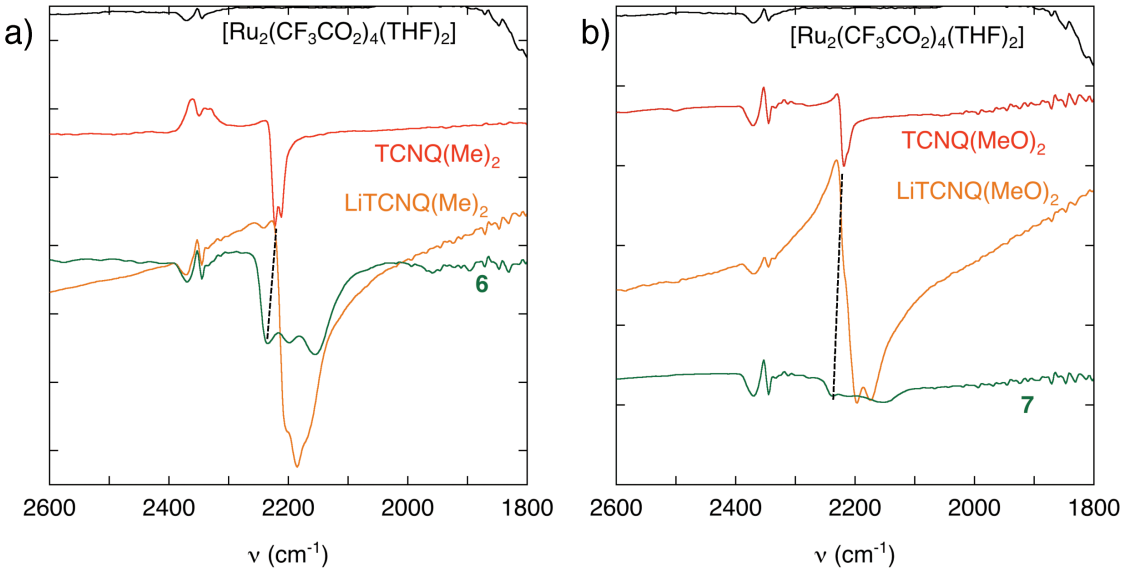


Fig. S4. Infrared spectra of **6** (a) and **7** (b) with those of $[Ru_2(CF_3CO_2)_4(THF)_2]$, $TCNQR_2$, and Li salts of $TCNQR_2$ (R = Me and MeO) for comparison, which indicate characteristic C≡N vibrational bands for compounds in the range of 1800 – 2600 cm^{-1}.

Magnetic Properties of 6 and 7

The magnetic behaviors of **6** and **7** are consistent with those for isolated [$Ru_2^{II,II}$] complexes with an $S = 1$ ground state affected by strong zero-field splitting (ZFS; $D \approx 230 - 320$ cm^{-1}) (Fig. S5). The χ and χT were simulated using a Curie paramagnetic model with $S = 1$ taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and impurity with $S = 3/2$ (ρ).[4] In an initial try, the contribution of intermolecular interactions (zJ) was taken into account in the frame of the mean-field approximation, but not required to obtain adequate fitting. So, all were done with $zJ = 0$. The best-fitting parameters were: $g = 2.0$ (fix), $D/k_B = 344(2)$ K, $\chi_{TIP} = 52(27)\times10^{-6}$ cm^3 mol^{-1}, and $\rho = 0.0410(4)$ for **6** and $g = 2.0$ (fix), $D/k_B = 364(1)$ K, $\chi_{TIP} = 175(16)\times10^{-6}$ cm^3 mol^{-1}, and $\rho = 0.00725(5)$ for **7**.

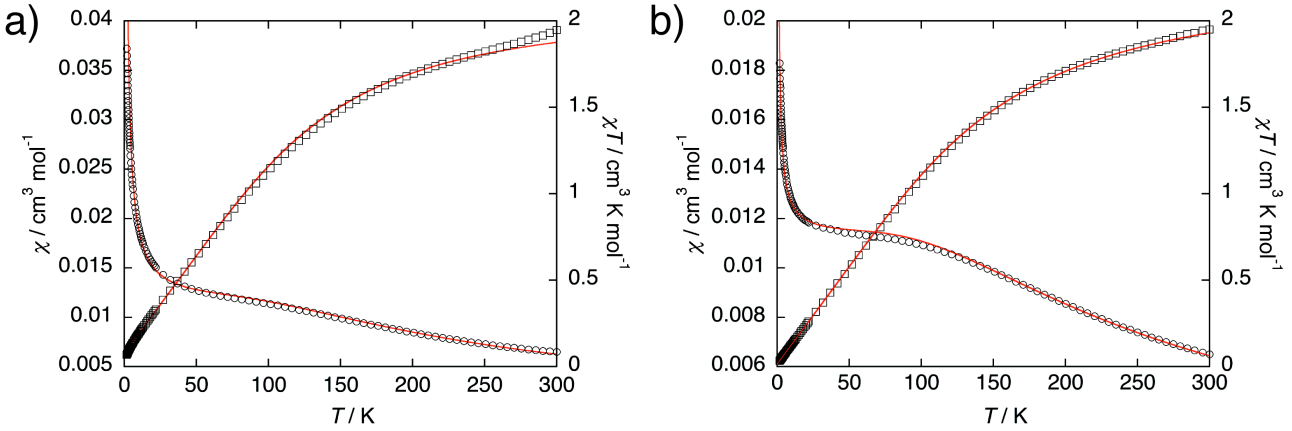


Fig. S5. Temperature dependence of χ and χT for **6** (a) and **7** (b), where the red solid lines represent simulated curves based on a Curie paramagnetic model with $S = 1$ taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and impurity with $S = 3/2$ (ρ).

Referneces

1 T. J. Kistenmacher, T. J. Emge, A. N. Bloch, D. O. Cowan, *Acta Crystallogr., Sect. B* 1982, **38**, 1193.
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