Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Modification of charge transfer in a two-dimensional donor/acceptor framework by the insertion of another donor-type molecule into electronegative interlayer pockets

Masaki Nishio,[a] Natsuko Motokawa,[b] Miho Takemura,[b] and Hitoshi Miyasaka*[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, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan*
[c] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

Correspondence*

Hitoshi Miyasaka

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan; TEL: +81-22-215-2030; FAX: +81-22-215-2031; email: miyasaka@imr.tohoku.ac.jp

Experimental Details

Syntheses

General procedures and chemicals. All synthetic procedures were performed under a N_2 atmosphere using standard Schlenk techniques and a commercial glovebox. All chemicals were purchased as reagent grade from commercial sources. Solvents used were distilled under a N_2 atmosphere using common drying agents. The starting material, $[Ru_2^{II,II}(O_2CCF_3)_4(THF)_2]$ was prepared by a literature method.[1]

Syntheses of $[\{Ru_2(O_2CCF_3)_4\}_2TCNQR_x]\cdot2$(pyrene) ($R_x$ = H_4, 1·pyrene; R_x = F_4, 2·pyrene). **1·pyrene** and **2·pyrene** were synthesized by a similar procedure used for the family of $[Ru_2]$/TCNQ compounds.[2] Only the method for **1·pyrene** is described: a 1,1,2,2-tetrachloroethane (TCE) solution (100 mL) of TCNQ (41 mg, 0.2 mmol) and pyrene (81 mg, 0.4 mmol) was separated into 2 mL portions and placed in narrow diameter sealed glass tubes (ϕ: 8 mm) (bottom layer). A mixed solvent of CH_2Cl_2 and TCE (1:1 v/v; 1 mL) was added carefully onto the bottom layer, and then a CH_2Cl_2 solution (100 mL) of $[Ru_2^{II,II}(O_2CCF_3)_4(THF)_2]$ (319 mg, 0.4 mmol) and pyrene (81 mg, 0.4 mmol) was placed in 2 mL portions onto the middle layer. The glass tubes were left undisturbed for one month or more to yield brown crystal of **1·pyrene** (26.7 mg, 5.5%) IR (KBr) for **1·pyrene**: ν(C≡N), 2239, 2196, 2140 cm^{-1}; ν(C=O), 1641, 1434 cm^{-1}; For **2·pyrene**: ν(C≡N), 2209, 2153 cm^{-1}; ν(C=O), 1639, 1493 cm^{-1}.

Physical measurements

Infrared spectra were measured using a KBr disk with a Jasco FT-IR 620 spectrophotometer. Powder reflection spectra were measured on pellets diluted with $BaSO_4$ with Shimadzu UV-3150 spectrometer. Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer (MPMS-XL). DC measurements were conducted over the temperature range 1.8–300 K and from −7 T to +7 T. The measurements were performed on polycrystalline samples restrained by Nujol. Diamagnetic contributions were corrected for the sample holder, Nujol, and for the sample using Pascal's constants.[3]

Crystallographic analyses

Single crystals of **1·pyrene** and **2·pyrene** were mounted on a thin Kapton film with Nujol and were cooled to 93(1) K or 103(1) K by a stream of cooled N_2 gas. Data collections were carried out on a Rigaku CCD diffractometer (Rigaku Saturn+VariMax) with graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å). The structures were solved using direct methods (SIR2008[4]) and expanded using Fourier techniques. The full-matrix least-squares refinement on F^2 was performed on the basis of observed reflections and variable parameters, and the refinement cycle was estimated from unweighted and weighted agreement factors of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($I > 2.00\sigma(I)$ and all data) and $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$ (all data). A Sheldrick weighting scheme was used. Neutral atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in F_c;[6] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure crystallographic software package,[9] except for refinement, which was performed using SHELXL-97.[10] The CIF data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-939182 and -939183 for **1·pyrene** and **2·pyrene**, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; email, deposit@ccdc.cam.ac.uk).

Crystallographic data for 1·pyrene

Formula: $C_{62.6}H_{29.2}Cl_{5.2}F_{24}N_4O_{16}Ru_4$, M_r = 2137.93, triclinic, P-1 (#2), a = 10.108(3) Å, b = 13.897(4) Å, c = 15.301(4) Å, α = 98.591(4), β = 104.313(4), γ = 97.696(3), V = 2026.2(10) Å^3, T = 93 K, Z = 1, D_{calc} = 1.752 g cm^{-3}, F_{000} = 1041.20, λ = 0.71070 Å, μ(Mo-Kα) = 10.194 cm^{-1}, 20309 measured reflections, 7072 unique (R_{int} = 0.0178). R_1 = 0.0881 ($I > 2\sigma(I)$), R_1 = 0.0952 (all data), and wR_2 = 0.2515 (all data) with GOF = 1.087. CCDC-939182.

Crystallographic data for 2·pyrene

Formula: $C_{65}H_{26}Cl_{10}F_{28}N_4O_{16}Ru_4$, M_r = 2409.70, monoclinic, $P2_1/m$ (#11), a = 9.895(4) Å, b = 21.386(7) Å, c = 20.452(7) Å, β = 99.418(7), V = 4270(3) Å^3, T = 103 K, Z = 2, D_{calc} = 1.874 g cm^{-3}, F_{000} = 2340.00, λ = 0.71070 Å, μ(Mo-Kα) = 11.306 cm^{-1}, 27868 measured reflections, 7633 unique (R_{int} = 0.0641). R_1 = 0.0945 ($I > 2\sigma(I)$), R_1 = 0.1237 (all data), and wR_2 = 0.2739 (all data) with GOF = 1.064. CCDC-939183.

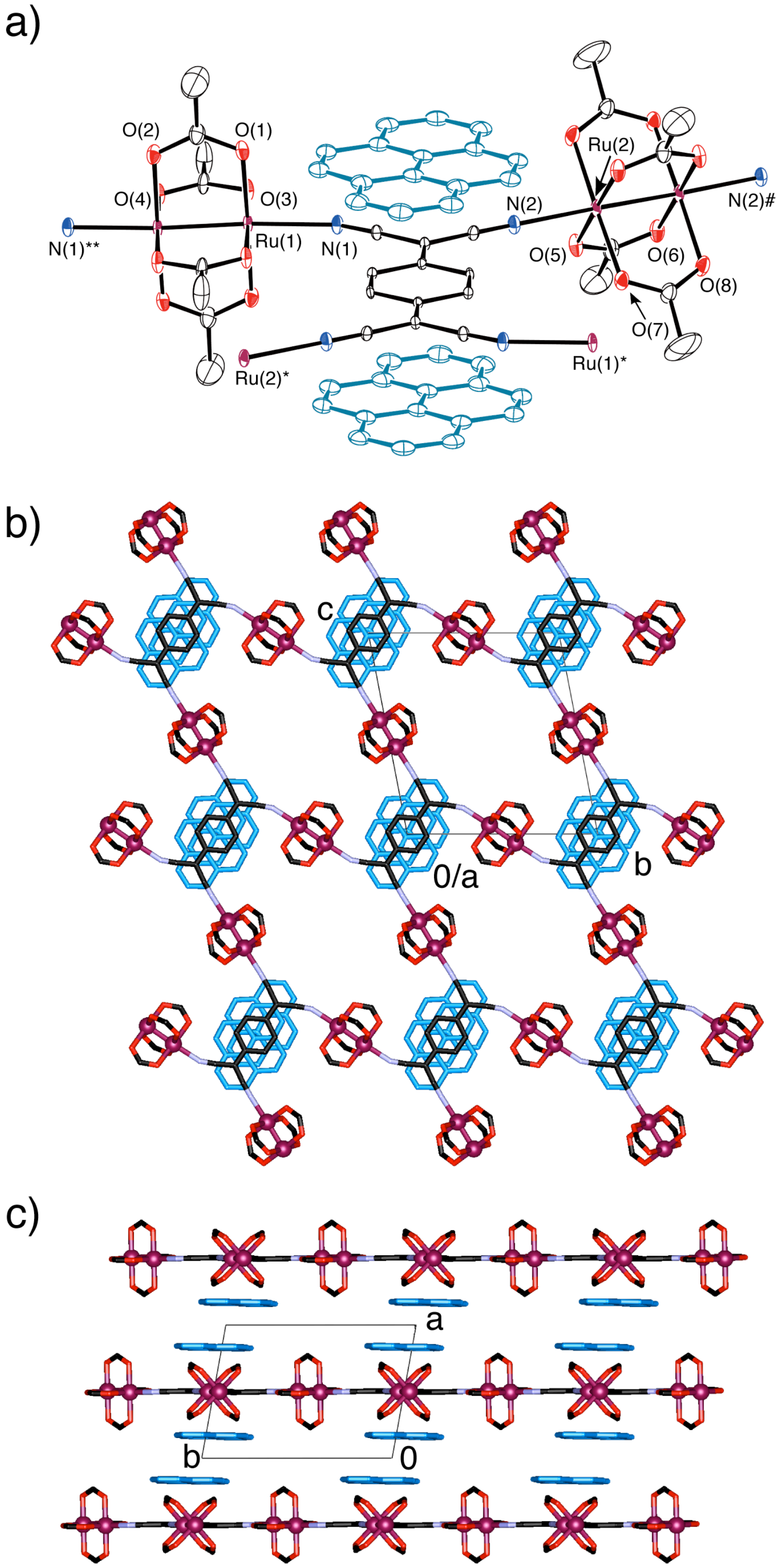

Fig. S1. Thermal ellipsoid drawings (a; 30 % probability; H atoms, and solvent molecules, and F atoms of [$Ru_2(CF_3CO_2)_4$] moieties were omitted for clarity) and packing diagrams of **1·pyrene** (b and c; H atoms, solvent molecules, and CF_3 groups were omitted for clarity). Symmetry operations: * $-x+1, -y, -z$; ** $-x+1, -y+1, -z$; $^{\#}$ $-x+1, -y, -z+1$.

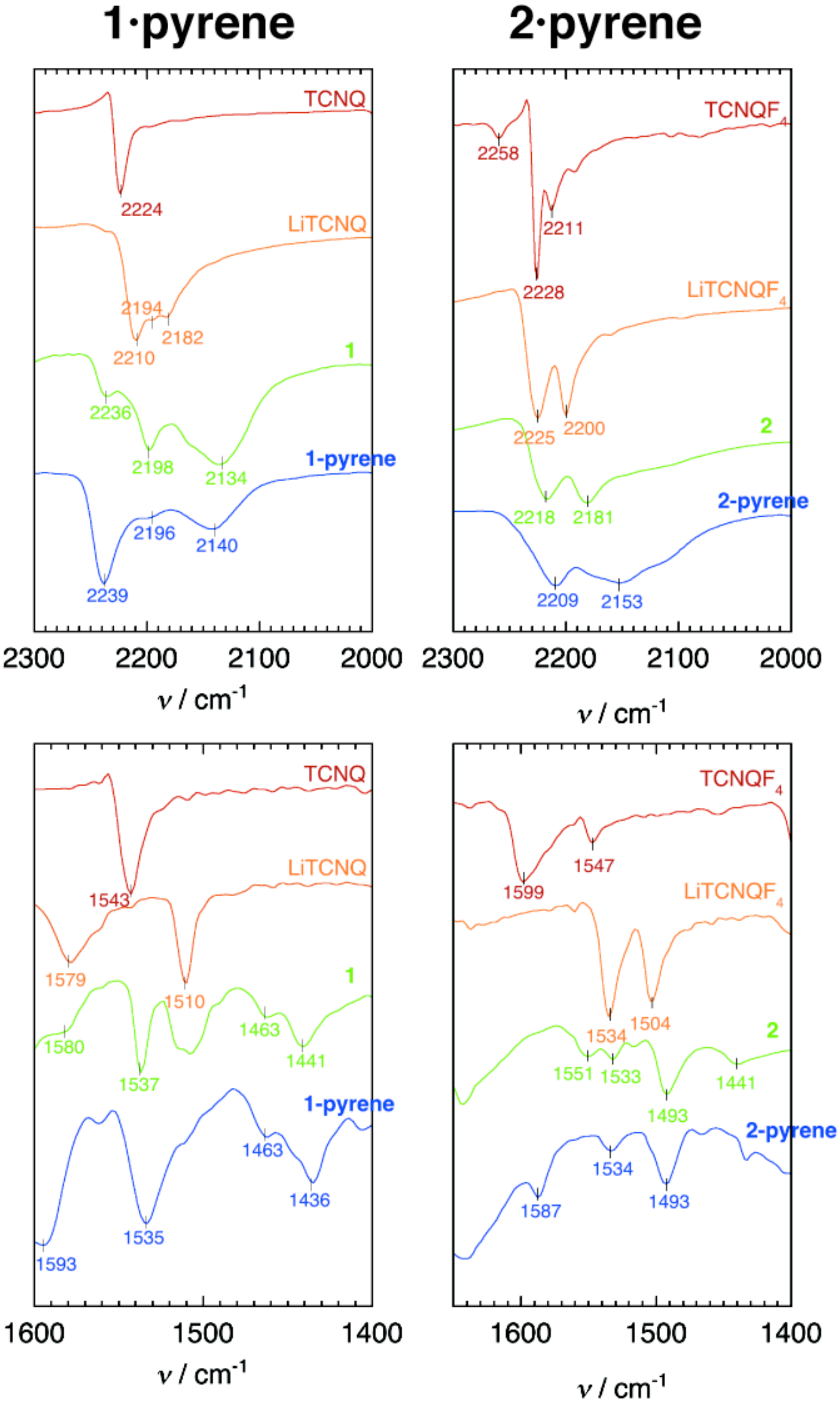

Fig. S2. IR spectra of **1·pyrene** (left side; blue) and **2·pyrene** (right side; blue) together with references on TCNQR$_x$ (red), LiTCNQR$_x$ (orange), and **1** and **2** (light green), where peaks in the range 2000–2300 cm^{-1} and 1400–1600 cm–1 include vibrational modes of $\nu_{C\equiv N}$ and $\nu_{C=C}$, respectively.

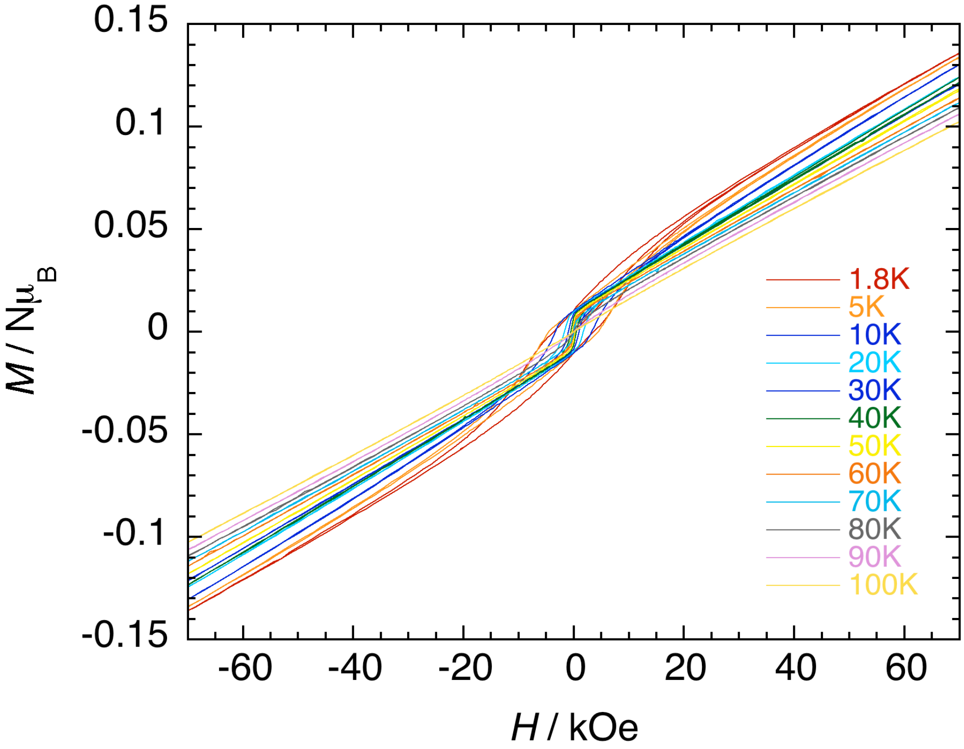

Fig. S3. Field dependence of the magnetization of **2·pyrene** measured at several temperatures in the range 1.8 – 100 K.

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