# Supporting Information

## Honeycomb frameworks with a very large mesh of 39 × 29 Å diameters stabilized by π-stacked coronene molecules

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## Experimental Section

### Syntheses

All synthetic procedures were performed under an anaerobic condition using standard Schlenk-line techniques and a commercial glovebox. The $[Ru_2^{II,II}]$ and $[Rh_2^{II,II}]$ complexes with axial ligands of THF were prepared according to the literature methods.[1,2,3]

**Synthesis of Ru-1.** A 1,1,2,2-tetrachloroethane (TCE) solution (60 mL) of TPT (46.8 mg, 0.15 mmol) and coronene (22.5 mg, 0.075 mmol) was prepared in a Schlenk tube. After a mixture of TCE/acetonitrile (MeCN) (1:1 v/v; 10 mL) was added on the previous solution as a middle layer, an acetonitrile solution (30 mL) of $[Ru_2(PhCO_2)_4(THF)_2]$ (125 mg, 0.15 mmol) was put onto the layer. The tube was left undisturbed for one week to yield dark-purple hexagonal platelet crystals of **Ru-1**. Yield: 2.0 %. Elemental analysis calcd for $[\{Ru_2(PhCO_2)_4\}_3(TPT)_2]\cdot$coronene$\cdot 10.6TCE\cdot 2CH_3CN$ $C_{169.2}H_{123.2}N_{14}O_{24}Ru_6$: C 41.94, H 2.56, N 4.05, found: C 42.41, H 2.81, N 3.73. IR (KBr): $\nu$(C=O), 1406, 1550 $cm^{-1}$; $\nu$(C=N), 1517 $cm^{-1}$; $\nu$(C=C), 1374 $cm^{-1}$.

**Synthesis of Ru-2.** A TCE solution (40 mL) of TPT (31.2 mg, 0.10 mmol) and coronene (15.0 mg, 0.05 mmol) was separated into 4 mL portions and placed in test tubes ($\phi$: 13 mm). A mixture of TCE/MeCN (1:1 v/v; 1 mL) was added. Then, a MeCN solution (20 mL) of $[Ru_2(o\text{-}FPhCO_2)_4(THF)_2]$ (90 mg, 0.1 mmol) was carefully placed in 2 mL portions on the middle layer. The tube was left undisturbed for two weeks to yield dark-purple hexagonal platelet crystals of **Ru-2**. IR (KBr): $\nu$(C=O), 1402, 1558 $cm^{-1}$; $\nu$(C=N), 1517 $cm^{-1}$; $\nu$(C=C), 1374 $cm^{-1}$.

**Synthesis of Ru-3.** A TCE solution (40 mL) of TPT (31.2 mg, 0.10 mmol) and coronene (15.0 mg, 0.05 mmol) was separated into 3 mL portions and placed in test tubes ($\phi$: 13 mm). A mixture of TCE/MeCN (1:1 v/v; 1 mL) was added. Then, a MeCN solution (40 mL) of $[Ru_2(m\text{-}FPhCO_2)_4(THF)_2]$ (90 mg, 0.1 mmol) was carefully placed in 3 mL portions on the middle layer. The tube was left undisturbed for two weeks to yield dark-purple hexagonal platelet crystals of **Ru-3**. IR (KBr): $\nu$(C=O), 1395, 1558 $cm^{-1}$; $\nu$(C=N), 1517 $cm^{-1}$; $\nu$(C=C), 1374 $cm^{-1}$.

**Synthesis of Rh-1.** A TCE solution (40 mL) of TPT (31.2 mg, 0.10 mmol) and coronene (15.0 mg, 0.05 mmol) was separated into 4 mL portions and placed in test tubes ($\phi$: 13 mm). A mixture of TCE/MeCN (1:1 v/v; 1 mL) was added. Then, a MeCN solution (20 mL) of $[Rh_2(PhCO_2)_4(THF)_2]$ (80 mg, 0.1 mmol) was carefully placed in 2 mL portions on the middle layer. The tube was left undisturbed for two weeks to yield reddish-orange hexagonal platelet crystals of **Rh-1**. IR (KBr): $\nu$(C=O), 1398, 1565, 1601 $cm^{-1}$; $\nu$(C=N), 1517 $cm^{-1}$; $\nu$(C=C), 1314, 1373 $cm^{-1}$.

**Syntheses of Rh-2 and Rh-3. Rh-2** and **Rh-3** were synthesized according to the same procedure for **Rh-1** using $[Rh_2(x\text{-}PhCO_2)_4(THF)_2]$ ($x$ = $o$-F, $m$-F) instead of $[Rh_2(PhCO_2)_4(THF)_2]$. For **Rh-2**, IR(KBr): $\nu$(C=O), 1397, 1604 $cm^{-1}$; $\nu$(C=N), 1517 $cm^{-1}$; $\nu$(C=C), 1314, 1375 $cm^{-1}$. For **Rh-3**, IR (KBr): $\nu$(C=O), 1393, 1442, 1608 $cm^{-1}$; $\nu$(C=N), 1520 $cm^{-1}$; $\nu$(C=C), 1312, 1373 $cm^{-1}$.

**DFT calculations**

Molecular orbital calculations for $[Ru_2^{II,II}(x\text{-}PhCO_2)_4(THF)_2]$ ($x$ = H, $o$-F, $m$-F) and TPT were carried out using the density functional theory (DFT) formalism, as implemented in the Gaussian09 software, with B3LYP (UB3LYP) using basic functions LANL2TZ(f) for Ru and 6-31+G* for other atoms, where the atomic coordinates determined from X-ray crystallography for $[Ru_2^{II,II}(x\text{-}PhCO_2)_4(THF)_2]$ and computer-optimized for TPT were used, an $S_z$ = 1 (spin multiplicity of 3) spin state for $[Ru_2]$ was assumed, and the charge of molecules was zero.

**Crystallographic analyses**

Crystal data for **Ru-1** – **3** and **Rh-1** and **Rh-3** were collected on a Rigaku CCD diffractometer (Saturn70-VariMax) with graphite-monochromated Mo Ka radiation ($\lambda$ = 0.71070 Å). The structures were solved using direct methods (SIR97 or SHELX97).[4,5] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were only introduced for non-disordered carbon atoms at fixed positions, because H atoms on disordered atoms seem to be not accurate in their position (in addition, electron density with less than $1e^-$ is inconsequential for the accuracy of other atoms). The position-disordered C and F atoms in **Ru-2**, **Ru-3**, **Rh-1**, and **Rh-3** were first calculated with free occupancies to find subequal proportions of temperature factor between possible two sites, and then adequate occupancies, which come to 1, were determined to two places of decimals. One phenyl ring (C(26)–C(31) on the $[Ru(2)_2]$ unit) has a heavily disorder probably in swing and flip modes, and this situation can be seen in all compounds. Full-matrix least-squares refinements on $F^2$ converged with unweighted and weighted agreement factors of $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ ($I > 2.00\sigma(I)$ and all data), and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (all data), respectively. A Sheldrick weighting scheme was used, where the $f'$ and $f''$ scattering factor values were refined in four places of decimals (the values were rounded in CIF). The crystallization solvent molecules (probably TCE and MeCN) for all compounds could not determined perfectly, so the crystallographic data were finally treated by PLATON SQUEEZE program.[6] All calculations were performed using the CrystalStructure crystallographic software package.[7]

CCDC for respective compounds contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

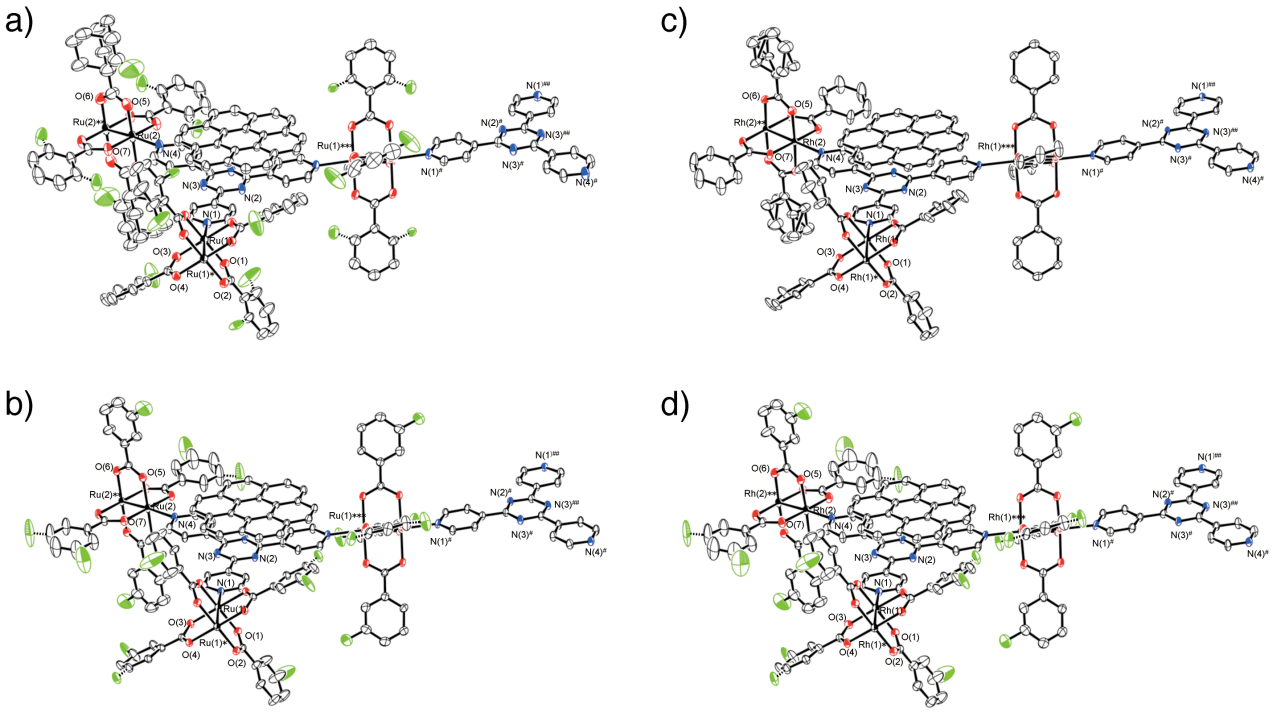


**Fig. S1.** Structure of the formula unit of **Ru-2** (a), **Ru-3** (b), **Rh-1** (c), and **Rh-3** (d) (30 % probability ellipsoid), where hydrogen atoms and crystallization solvents were omitted for clarity. Symmetry operation: *, -*x*-1/2, -*y*+1/2, -*z*; **, -*x*+1, -*y*, -*z*+1; ***, *x*, -*y*+1, *z*; #, -*x*-1/2, *y*+1/2, -*z*; ##, -*x*-1/2, -*y*+3/2, -*z*.

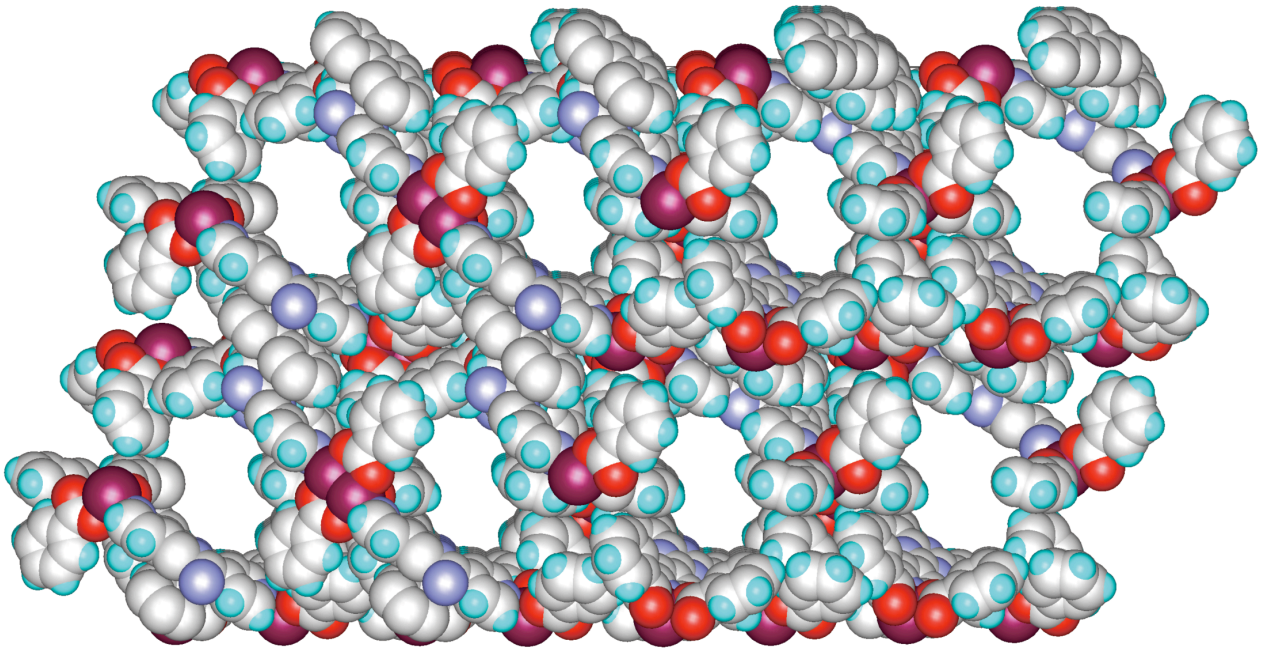

**Fig. S2.** CPK-model representation of the packing of **Ru-1** projected along the (-110) direction, where C, light-gray; H, light-blue; N, blue; O, red; Ru, win-red.

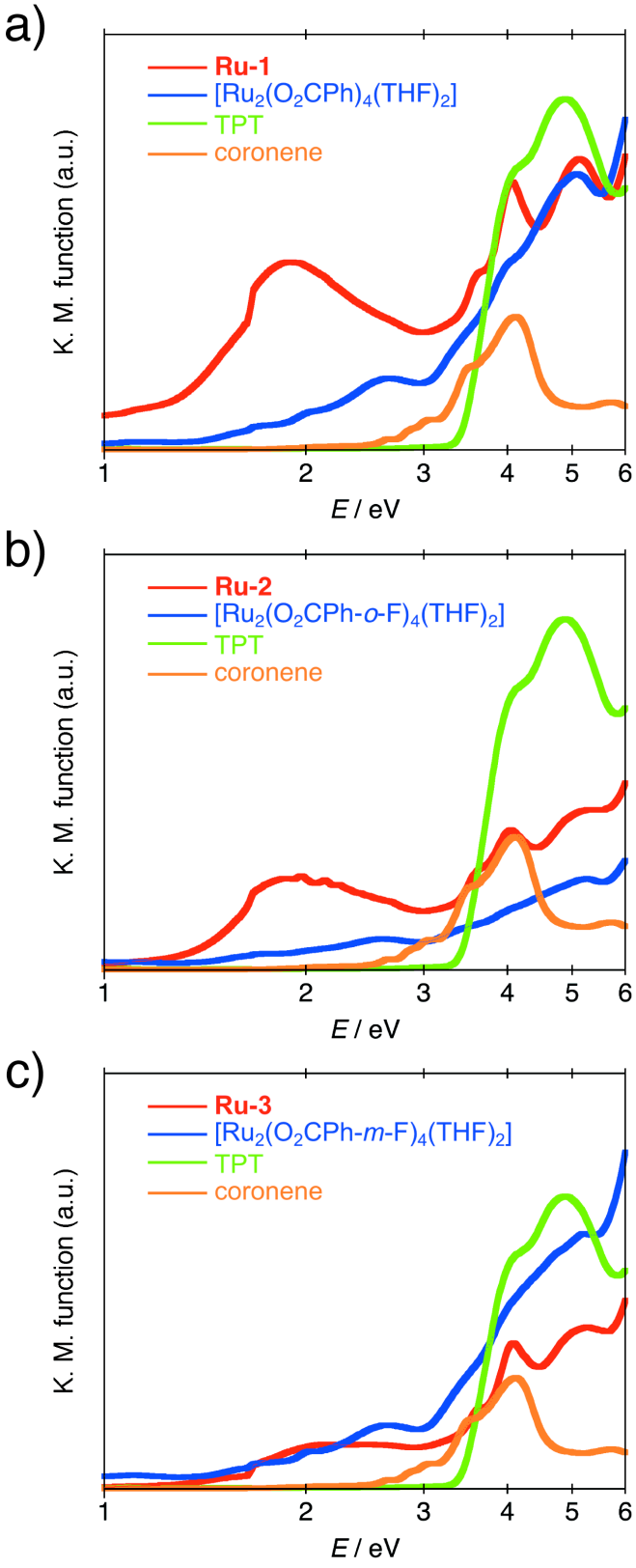


**Fig. S3.** Powder reflection spectra of the Ru series together with the starting materials measured on powder pellets diluted with $BaSO_4$.

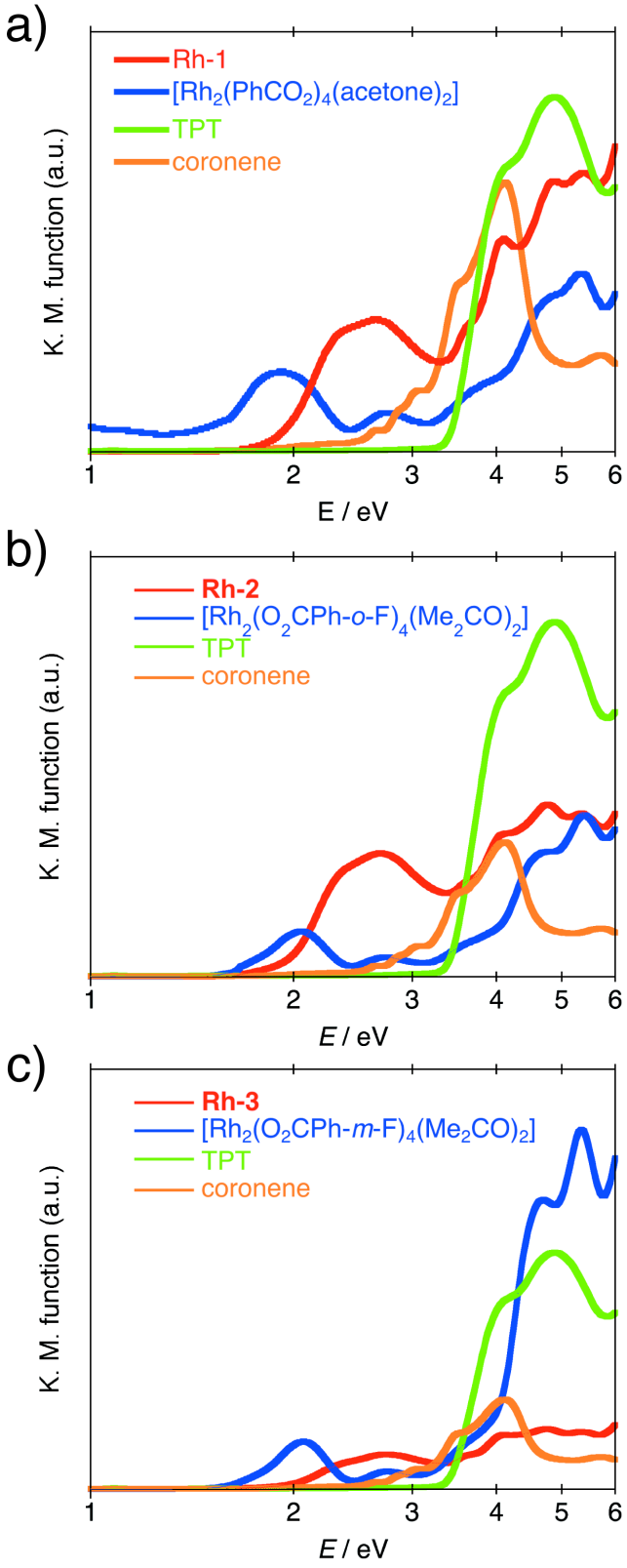


**Fig. S4.** Powder reflection spectra of the Rh series together with the starting materials measured on powder pellets diluted with $BaSO_4$.

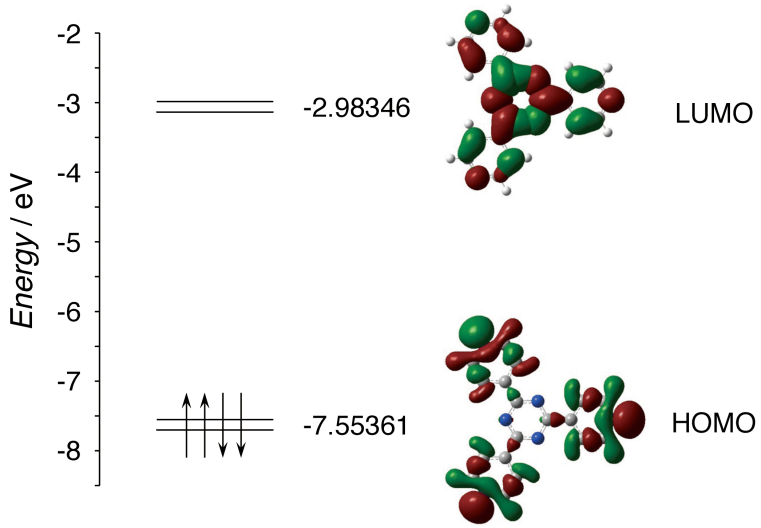


**Fig. S5.** HOMO and LUMO plots (0.02 isosurface contour) and their energy levels for TPT calculated on the computer-optimized model. Note that HOMO and LUMO are doubly degenerated and the isosurface contour representations are for the degenerated orbitals.

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