

## Supporting Information

### First exfoliated Ru-Ru-Au organometallic polymer with layered structure.

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#### General considerations

All chemicals were of reagent grade and, unless otherwise stated, were used as received from commercial suppliers. Likewise, all reactions were carried out in a pure argon atmosphere by using standard Schlenk-tube techniques. Water was deoxygenated prior to use and organic solvents were dried through standard methods. The complex  $[\text{RuCp}(\text{PTA})_2-\mu\text{-CN}-1\kappa\text{C}:2\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$  was prepared as described in the literature.<sup>[1]</sup> NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.13 MHz ( $^1\text{H}$ ) and 121.49 and 282.40 MHz ( $^{31}\text{P}$ ). Chemical shifts of  $^1\text{H}$  spectra are relative to tetramethylsilane and were calibrated against the residual solvent resonance, while for  $^{31}\text{P}\{^1\text{H}\}$  the calibration is against external 85%  $\text{H}_3\text{PO}_4$ . All NMR spectra were obtained at 23 °C. Infrared spectra were recorded as KBr disks using a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA1108 elemental analyser.

#### Synthesis of 1

Complex **1** was obtained as yellow powder by reaction of  $[\text{RuCp}(\text{PTA})_2\text{-CN-1C:22N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$  (0.1 g, 0.088 mmol) in 5 mL of water with a solution of  $\text{K}[\text{Au}(\text{CN})_4]$ , previously prepared by reacting  $\text{Na}[\text{AuCl}_4]\cdot x\text{H}_2\text{O}$  (Au 50%) (175 mg, 0.440 mmol) and KCN (115 mg, 1.76 mmol) in 1 mL of  $\text{H}_2\text{O}$ . The resulting solution was kept at 90 °C during 5 min, cooled at room temperature and filtered. The solvent was removed under vacuum, giving rise to a yellow powder which was further dissolved in 1 mL of water/DMSO (1:1). Yellow crystals obtained after 2 weeks were suitable for X-ray analysis. Yield: 0.070 g, 57%;  $S_{25}(\text{mg}/\text{cm}^3)$ : 2.5. Elemental analysis for  $\text{C}_{39}\text{H}_{66}\text{AuN}_{17}\text{O}_4\text{P}_4\text{Ru}_2$  (1361.22): Found C, 33.95; H, 5.23; N, 17.03; calcd. C, 34.38; H, 4.89; N, 17.49. IR (KBr):  $\nu = 2183\text{ cm}^{-1}$  ( $\text{RuC}\equiv\text{N}$ );  $\nu = 2094\text{ cm}^{-1}$  ( $\text{AuC}\equiv\text{N}$ ).  $^1\text{H}$  NMR (300,13 MHz, 23 °C, TMS,  $\text{D}_2\text{O}$ ):  $\delta = 3.86, 3.97$  (m,  $\text{NCH}_2\text{P}$ ); 4.48 (m,  $\text{NCH}_2\text{N}$ ); 4.80, 4.95 ppm (s, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 Mz, 23 °C, 85 %  $\text{H}_3\text{PO}_4$ ,  $\text{D}_2\text{O}$ ):  $\delta = -19.33$  (s, PTA), -21.95 ppm (s, PTA).

#### Exfoliation of 1

Polymer **1** (1.5 mg) was suspended in 1 mL of water and sonicated in an ultrasonic bath during 15 min. The mixture was then centrifuged (500 rpm, 1 min) and the supernatant was extracted and sonicated again during 15 min. After the centrifugation of the resulting suspension (5000 rpm, 5 min), the supernatant was used for TEM analysis.

#### Electron microscopy

The electron microscopy analysis was conducted with a JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) with a point resolution of 0.194 nm. The exfoliated Ru-Ru-Au polymer was deposited on Formvar and dried at 40 °C for 12 hours before sample imaging. Micrographs were taken through the perpendicular direction to the layered structure of the sample.

#### Neutron scattering

The polymer dynamics was studied through incoherent quasielastic neutron-scattering (QENS). Measurements were carried out using the IRIS time-of-flight backscattering spectrometer at the ISIS Pulsed Neutron and Muon Source (UK). IRIS can access a Q-range of 0.4 to 1.85  $\text{\AA}^{-1}$  and has an energy resolution of 17.5  $\mu\text{eV}$ . The technique probes signal close to the elastic line, giving access to low energy modes like translational and rotational modes, and slower segmental relaxations. For polymer **1**, the ratio of the incoherent neutron scattering cross-section  $\sigma_{\text{inc}}(\text{H})/\sigma_{\text{inc}}(\text{total polymer})$  is about 0.997. As a consequence, the scattering is dominated

by the incoherent radiation from H atoms and thus we can measure the dynamics of the polymeric chains to which the H atoms are attached. The temperature of the sample was controlled using a top-loading closed cycle refrigerator.

## Single crystal x-ray diffraction

Light orange single crystals of polymer **1** were obtained as indicated in the synthetic procedure. Single crystal x-ray diffraction was performed with a Bruker APEX-II CCD diffractometer at 100K. Data was integrated (SAINT, Bruker) and scaled (SADABS, Bruker), and finally the structure was solved with SHELXT<sup>[2]</sup> using intrinsic phasing and refined with SHELXL<sup>[3]</sup> by least squares. Solution and refinement procedures were accomplished by Olex2 software.<sup>[4]</sup> The VMD software were used to process the graphics.<sup>[5]</sup> The crystal structure have been deposited at CSD with CCDC number CCDC 2002761. Crystallographic and structural data are given in tables S1-S3.

**Table S1.** Crystal data and structure refinement for **1**.

Empirical formula	C <sub>43</sub> H <sub>66</sub> Au <sub>2</sub> N <sub>21</sub> O <sub>4</sub> P <sub>4</sub> RU <sub>2</sub>
Formula weight	1661.12
Temperature [K]	100
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a [Å]	13.3590(11)
b [Å]	13.2038(11)
c [Å]	17.1923(14)
α [°]	90
β [°]	108.9750(10)
γ [°]	90
Volume [Å <sup>3</sup> ]	2867.8(4)
Z	2
ρ <sub>calc</sub> [g/cm <sup>3</sup> ]	1.924
μ [mm <sup>-1</sup> ]	5.788
Radiation	MoKα (λ = 0.71073)
Index ranges	-10 ≤ h ≤ 16, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	17591
Independent reflections	6045 [R <sub>int</sub> = 0.0190, R <sub>sigma</sub> = 0.0221]
Data/restraints/parameters	6045/1/353
Goodness-of-fit on F <sup>2</sup>	1.039
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0209, wR <sub>2</sub> = 0.0482
Final R indexes [all data]	R <sub>1</sub> = 0.0226, wR <sub>2</sub> = 0.0491
Largest diff. peak/hole [e Å <sup>-3</sup> ]	1.63/-0.55

**Table S2.** Bond Lengths for 1.

Atom 1	Atom 2	Length [Å]	Atom 1	Atom	Length [Å]
Au1	N1	2.952(2)	N2	C6	1.465(4)
Au1	C3G	2.006(3)	N2	C5	1.464(4)
Au1	N6 <sup>a</sup>	3.193(3)	NCN	NCN <sup>b</sup>	1.151(5)
Au1	C4G	1.995(3)	N4	C11	1.498(4)
Au1	C1G	2.005(3)	N4	C7	1.501(4)
Au1	C2G	2.003(3)	N4	C10	1.494(4)
Ru1	P1	2.2689(7)	N3	C4	1.463(4)
Ru1	P2	2.2610(7)	N3	C6	1.474(4)
Ru1	NCN	2.012(3)	N3	C3	1.475(3)
Ru1	C16	2.196(3)	C3G	N3G	1.140(4)
Ru1	C15	2.209(3)	N5	C8	1.466(4)
Ru1	C14	2.236(3)	N5	C11	1.446(4)
Ru1	C13	2.218(3)	N5	C12	1.464(4)
Ru1	C17	2.216(3)	N1G	C1G	1.147(4)
Ru1	CCN	2.012(3)	N6	C9	1.471(4)
P1	C1	1.855(3)	N6	C12	1.469(4)
P1	C2	1.845(3)	N6	C10	1.452(4)
P1	C3	1.847(3)	C16	C15	1.401(5)
P2	C8	1.846(3)	C16	C17	1.428(4)
P2	C9	1.841(3)	N2G	C2G	1.140(4)
P2	C7	1.845(3)	N4G	C4G	1.141(4)
N1	C1	1.478(4)	C15	C14	1.427(5)
N1	C4	1.476(4)	C14	C13	1.413(4)
N1	C5	1.479(4)	C13	C17	1.409(4)
N2	C2	1.479(4)			

**Table S3.** Bond Angles for 1.

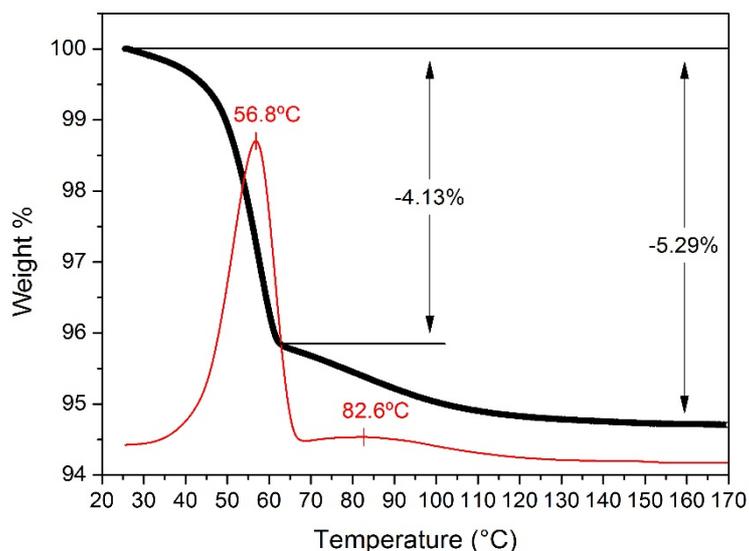
Atom1	Atom2	Atom3	Angle [°]	Atom1	Atom2	Atom3	Angle [°]
N1	Au1	N6 <sup>a</sup>	167.29(7)	C9	P2	C8	98.17(14)
C3G	Au1	N1	91.04(10)	C9	P2	C7	96.69(14)
C3G	Au1	N6 <sup>a</sup>	98.95(10)	C7	P2	Ru1	117.02(10)
C4G	Au1	N1	91.75(10)	C7	P2	C8	97.54(13)
C4G	Au1	C3G	91.24(13)	C1	N1	Au1	112.93(17)
C4G	Au1	N6 <sup>a</sup>	80.27(10)	C1	N1	C5	110.4(2)
C4G	Au1	C1G	89.49(13)	C4	N1	Au1	104.11(15)
C4G	Au1	C2G	176.27(13)	C4	N1	C1	111.5(2)
C1G	Au1	N1	90.42(10)	C4	N1	C5	107.9(2)
C1G	Au1	C3G	178.35(12)	C5	N1	Au1	109.65(16)
C1G	Au1	N6 <sup>a</sup>	79.72(10)	C6	N2	C2	111.0(2)
C2G	Au1	N1	91.96(10)	C5	N2	C2	111.5(2)
C2G	Au1	C3G	88.33(12)	C5	N2	C6	108.6(2)
C2G	Au1	N6A	96.14(10)	NCN <sup>b</sup>	NCN	Ru1	177.4(3)
C2G	Au1	C1G	90.84(12)	C11	N4	C7	111.0(2)
P2	Ru1	P1	97.26(3)	C10	N4	C11	108.6(2)
NCN	Ru1	P1	88.29(7)	C10	N4	C7	111.3(2)
NCN	Ru1	P2	85.40(8)	C4	N3	C6	108.4(2)
NCN	Ru1	C16	150.17(11)	C4	N3	C3	111.1(2)
NCN	Ru1	C15	145.96(12)	C6	N3	C3	111.5(2)
NCN	Ru1	C14	108.81(12)	N3G	C3G	Au1	175.4(3)
NCN	Ru1	C13	93.07(11)	C11	N5	C8	112.4(2)
NCN	Ru1	C17	112.42(11)	C11	N5	C12	110.3(2)
C16	Ru1	P1	120.91(9)	C12	N5	C8	110.7(2)
C16	Ru1	P2	95.80(9)	N1	C1	P1	113.0(2)
C16	Ru1	C15	37.07(12)	N3	C4	N1	114.1(2)
C16	Ru1	C14	62.53(12)	N5	C8	P2	112.57(19)
C16	Ru1	C13	62.44(11)	C12	N6	C9	111.8(2)
C16	Ru1	C17	37.76(12)	C10	N6	C9	111.2(2)
C15	Ru1	P1	94.46(9)	C10	N6	C12	109.1(2)
C15	Ru1	P2	127.62(10)	C15	C16	Ru1	71.98(17)
C15	Ru1	C14	37.44(13)	C15	C16	C17	107.8(3)
C15	Ru1	C13	61.97(12)	C17	C16	Ru1	71.87(16)
C15	Ru1	C17	62.17(12)	C16	C15	Ru1	70.95(17)
C14	Ru1	P1	101.57(8)	C16	C15	C14	108.9(3)
C14	Ru1	P2	156.59(8)	C14	C15	Ru1	72.30(17)

C13	Ru1	P1	135.90(8)	N4G	C4G	Au1	174.9(3)
C13	Ru1	P2	126.81(8)	N2	C2	P1	112.43(19)
C13	Ru1	C14	36.99(11)	C15	C14	Ru1	70.26(17)
C17	Ru1	P1	156.46(8)	C13	C14	Ru1	70.82(17)
C17	Ru1	P2	95.52(8)	C13	C14	C15	106.8(3)
C17	Ru1	C14	62.16(11)	N2	C6	N3	114.2(2)
C17	Ru1	C13	37.06(11)	C14	C13	Ru1	72.19(17)
CCN	Ru1	P1	88.29(7)	C17	C13	Ru1	71.36(17)
CCN	Ru1	P2	85.40(8)	C17	C13	C14	109.0(3)
CCN	Ru1	C16	150.17(11)	N3	C3	P1	112.81(19)
CCN	Ru1	C15	145.96(12)	C16	C17	Ru1	70.38(16)
CCN	Ru1	C14	108.81(12)	C13	C17	Ru1	71.57(16)
CCN	Ru1	C13	93.07(11)	C13	C17	C16	107.5(3)
CCN	Ru1	C17	112.42(11)	N6	C9	P2	112.91(19)
C1	P1	Ru1	116.59(10)	N1G	C1G	Au1	177.5(3)
C2	P1	Ru1	120.87(9)	N2G	C2G	Au1	178.3(3)
C2	P1	C1	97.63(13)	N5	C11	N4	112.2(2)
C2	P1	C3	98.26(14)	N4	C7	P2	112.16(19)
C3	P1	Ru1	121.64(9)	N2	C5	N1	114.4(2)
C3	P1	C1	96.65(13)	N5	C12	N6	113.5(2)
C8	P2	Ru1	115.59(10)	N6	C10	N4	112.8(2)
C9	P2	Ru1	126.44(9)				

<sup>a</sup>-1/2+X,3/2-Y,-1/2+Z; <sup>b</sup>1-X,1-Y,1-Z

## Thermogravimetry

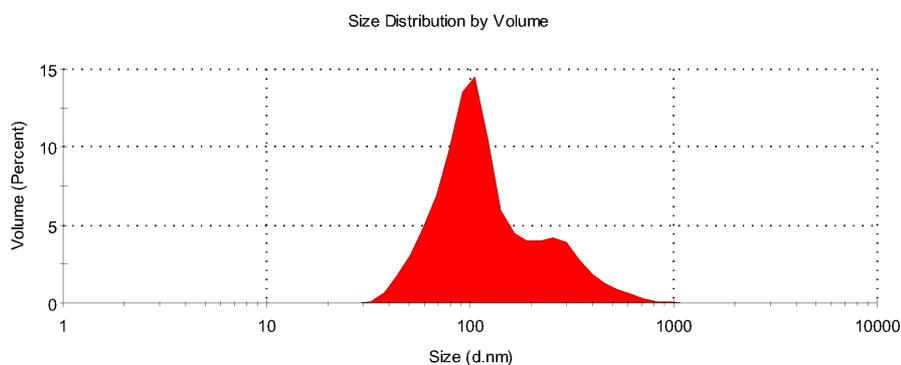
The thermo-gravimetric analysis was performed with a TGA Q50 analyzer (TA Instruments). The sample was loaded on a Pt pan and a temperature ramp of 2 °C/min was run from room temperature to 170 °C under N<sub>2</sub>. Figure S4 plots the mass loss for polymer **1** as a function of the temperature.



**Figure S1.** Thermo-gravimetric analysis of **1**. Black line: weight loss against temperature. Red line: first derivative of the weight loss against temperature.

## Dynamic light scattering

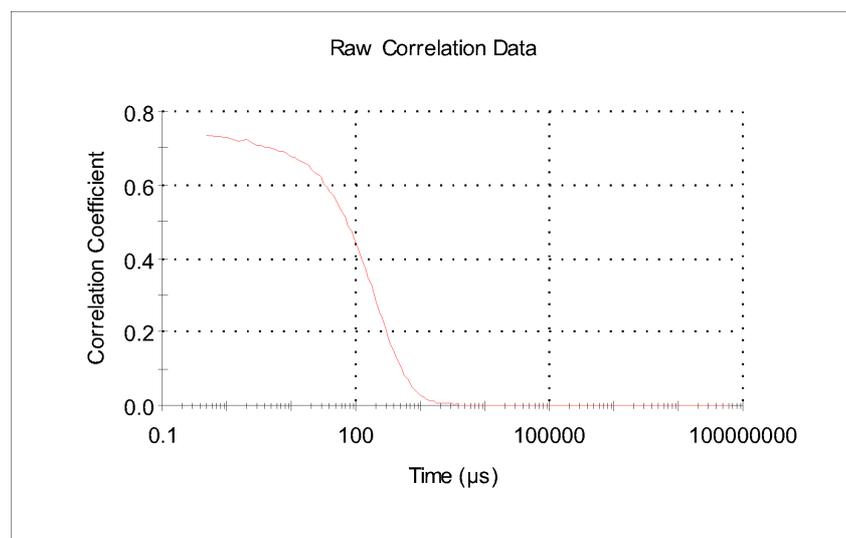
Dynamic Light Scattering (DLS) experiments were performed in a Zetasizer nano instrument (Malvern Instrument Ltd, United Kingdom) and the data were analyzed with Zetasizer software (Malvern Instrument Ltd, United Kingdom). A solution of **1** in H<sub>2</sub>O at a concentration of 0.5 mg/mL was filtered through a 0.22 µm PTFE filter and introduced in a 12 µL quartz thermostated sample cuvette (low-volume quartz batch cuvette, Malvern). The measurement was performed after 120 s to allow thermal equilibration at 25°C. After that, 10 runs of 20 s separated by 10 s delays were averaged.



**Figure S2.** Dynamic light scattering of **1** in H<sub>2</sub>O (25°C, 0.5 mg/mL): distribution of the microparticles by intensity.

**Table S4.** DLS results for 1.

	Size (d, nm)	% Volume	St. dev.
Peak 1	107.7	80.7	43.20
Peak 2	332.6	19.2	131.2
Peak 3	4098	0.1	1175



**Figure S3.** Raw correlation data for the DLS measurement.

## References

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