Electronic Supporting Information

Merging of Inner and Outer Ruthenium Organometallic Coordination within an Azuliporphyrin Framework

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Detailed experimental procedures

All chemicals used in the synthesis were readily available from commercial sources and were used as received unless otherwise stated. *Infrared absorption spectra* of solids were measured on a Bruker FT-IR VERTEX70 spectrophotometer in KBr discs. All *NMR spectra* were recorded with high-field spectrometers [Bruker Avance (500.13 MHz for ¹H) and Bruker Avance III (600.15 MHz for ¹H)]. Spectra were referenced to the residual solvent signal (for chloroform-d, 7.24 ppm, 77.14 ppm). High resolution and accurate *mass spectra* were recorded using Bruker MicrOTOF-Q with electrospray ionization. *Electronic spectra* were recorded on a diode-array spectrophotometer Varian Carry-50 Bio.

[Ru(TPAP)(CO)] (2)

meso-tetraphenylazuliporphyrin **1** (20 mg, 2.96 mmol) and $[Ru_3(CO)_{12}]$ (10.0 mg, 1.56 mmol) were added to degased toluene (25 mL) and the mixture was refluxed for 1.5 h under nitrogen. Product was subjected to chromatography (basic Al₂O₃, III° grade). At the beginning, a green-brown fraction of $[Ru_3(CO)_{12}]$ and reacted **3** was eluted with dichloromethane. Next, a brown fraction of a product was eluted in a gradient from DCM : ethyl acetate 100:1 to 10:1 (v/v).

Yield = 8.3 mg (35 %), ¹**H** NMR (600 MHz, CDCl₃ + Py-d₅, 270 K) δ 7.90 (d, J = 7.1 Hz, 2H, 5,20 *o*Ph), 7.84 (d, J = 7.3 Hz, 2H, 5,20-*o*Ph), 7.73 (t, J = 6.3 Hz, 4H, 5,20-*m*Ph), 7.70 (d, J = 5.0 Hz, 2H, 8,17/7,18), 7.69 (s, 2H, 12,13), 7.62 (d, J = 4.9 Hz, 2H, 8,17/7,18), 7.57 – 7.48 (m, 12H, 5,20-*p*Ph, 10,15-*o*,*m*,*p*Ph), 6.80 (d, J = 10.3 Hz, 2H, 2¹,3¹), 6.64 (t, J = 9.4 Hz, 1H, 2³), 6.38 (t, J = 9.9 Hz, 2H, 2²,3²), ¹³C NMR (151 MHz, CDCl₃ + Py-d₅, 300 K) δ 181.0 (CO), 160.5, 151.5, 147.3, 146.3, 143.6, 142.8, 136.9 (2²,3²), 135.1 (2³), 133.6 (5,20-*o*Ph), 133.4 (5,20-*o*Ph), 133.1 (8,17/7,18), 132.8 (5,20 *m*Ph), 132.7 (5,20-*m*Ph), 132.6 (12,13), 131.5 (2¹,3¹), 129.0, 128.9 (8,17/7,18), {127.2, 127.0, 126.9, 126.7, 126.6, 126.3, (5,20-*p*Ph, 10,15-*o*,*o*,*m*,*m*,*P*Ph)}, 118.3. **HRMS** (ESI) calcd for C₅₁H₃₁N₃ORu (M⁺): 803.1519; found: 803.1501 (m/z). **IR** (v_{CO}) 1922 cm⁻¹. **UV-Vis** (CHCl₃) λ_{max} (log ε) 391.0 (4.76), 467.4 (4.60), 577.9 (4.20), 619.0 (4.11), 796.0 (3.42) nm.

$[Ru(TPAP)(CO){Ru_4(CO)_9}] (\mathbf{3})$

meso-tetraphenylazuliporphyrin **1** (15.0 mg, 0.0222 mmol) and $[Ru_3(CO)_{12}]$ (100.0 mg, 0.156 mmol) were added to degased chlorobenzene (20 mL) and the mixture was refluxed for 2 h under nitrogen atmosphere. After that, solvent was evaporated under reduced pressure and a crude product was subjected to chromatography (neutral Al₂O₃, I^o grade)¹. At the beginning, a small yellow fraction of $[Ru_3(CO)_{12}]$ was eluted with hexanes : DCM (1:1). Next, a light brown band of the desired product was eluted with DCM.

Yield = 17.2 mg (53 %), ¹**H NMR** (600 MHz, CD₂Cl₂, 250 K) δ 7.81 (d, *J* = 7.5 Hz, 2H, 5,20-*o*Ph), 7.70 – 7.65 (m, 2H, 10,15-*o*Ph), 7.66 – 7.61 (m, 2H, 10,15-*o*Ph), 7.60 (t, *J* = 7.5 Hz, 2H, 5,20-*m*Ph), 7.57 (s, 2H, 12,13), 7.58 – 7.52 (m, 8H, 5,20-*p*Ph, 10,15-*m*,*p*Ph), 7.47 (t, *J* = 7.4 Hz, 2H, 5,20-*m*Ph), 7.34 (d, *J* = 5.3 Hz, 2H, 7,18), 7.30 (d, *J* = 7.5 Hz, 2H, 5,20-*o*Ph), 7.16 (d, *J* = 5.3 Hz, 2H, 8,17), 4.84 (dd, *J* = 7.7, 6.6 Hz, 2H, 2²,3²), 3.74 (dd, *J* = 6.5, 1.2 Hz, 2H, 2¹,3¹), 1.84 (tt, *J* = 7.7, 1.3 Hz, 1H, 2³). ¹³C NMR (151 MHz, CD₂Cl₂, 250 K) δ 197.4 (very broad, CO, Ru cluster), 183.8 (CO, Ru core), 160.8, 152.1, 152.0, 139.5, 137.3, 135.5 (12,13), 134.5 (7,18), 133.5, 133.1 (5,20-*o*Ph, 10,15-*o*Ph), 132.9 (8,17), 132.8 (10,15-*o*Ph), 131.1 (5,20-*o*Ph), 129.0, 128.6 (5,20-*m*Ph), 128.3 (5,20-*m*Ph), 128.1, 127.9 (10,15-*m*Ph), 127.8 (10,15-*m*Ph), 121.5, 121.1, 104.2 (1,4), 88.9 (21), 74.1 (2,3), 66.7 (2², 3²), 63.2 (2¹, 3¹), 32.3 (2³). **HRMS** (ESI) calcd for C₆₀H₃₂N₃O₁₀Ru₅ (M+H⁺): 1460.7256; found: 1460.7228

¹ The effect of chromatography depends on activity of alumina. Deactivated alumina induces secondary reactivity of cluster compounds but too active alumina (depends on the batch of alumina) causes stopping of the product and need of more polar solvents use. Not-too-active basic alumina was also used in chromatography of clusters.

(*m/z*). **IR** (ν_{CO}) 2074, 2049, 2022, 1994, 1928 cm⁻¹. **UV-Vis** (CHCl₃) λ_{max} (log ε) 361.6 (4.54), 459.9 (4.49), 665.2 (3.72), 814.2 (3.70) nm.

$[Ni(TPAP){Ru_4(CO)_9}](4)$

[Ni(TPAP)] (15.0mg, 0.0205 mmol) and [Ru₃(CO)₁₂] (100.0 mg, 0.157 mmol) were added to degased chlorobenzene (20 mL) and the mixture was refluxed for 2 h under nitrogen atmosphere. After that, solvent was evaporated under reduced pressure and a crude product was subjected to chromatography (neutral Al₂O₃, I^o grade). At the beginning, a small amount of a [Ru₃(CO)₁₂] yellow fraction was eluted with hexanes : DCM (1:1). Next, a light brown band of the desired product was eluted with hexane system what provided pure compound **4**.

Yield = 15.6 mg (55 %), ¹H NMR (600 MHz, CDCl₃, 270 K) δ 7.54 – 7.47 (m, 16H, 5,20-Ph, 10,15-Ph), 7.45 (s, 2H, 12,13), 7.41 – 7.35 (m, 2H, 5,20-Ph), 7.18 (d, J = 7.7 Hz, 2H, 5,20-*o*Ph), 7.10 (d, J = 5.3 Hz, 2H, 7,18), 6.87 (d, J = 5.2 Hz, 2H, 8,17), 4.68 (t, J = 7.1 Hz, 2H, 2²,3²), 3.68 (d, J = 6.5 Hz, 2H, 2¹,3¹), 1.96 (t, J = 7.7 Hz, 1H, 2³).¹³C NMR (151 MHz, CDCl₃, 270 K) δ 197.8 (CO, Ru cluster), 159.2, 154.3, 153.0, 138.3, 136.9, 134.8 (12,13-pyrr), 134.7 (7,18-pyrr), 132.8 (two Ph atoms and third 5,20-*o*Ph), 132.0 (8,17-pyrr), 130.2 (Ph), 129.6, 128.9 (Ph), 128.2, 128.1, 128.1 (5,20-Ph), 127.9 (two Ph atoms), 119.5, 103.9 (1,4), 77.3 (2,3), 74.1 (21), 64.5 (2², 3²), 62.0 (2¹, 3¹), 32.6 (2³). HRMS (ESI) calcd for C₅₉H₃₂N₃NiO₉Ru₄ (M+H⁺): 1390.7694; found: 1390.7671 (*m*/*z*). IR (ν_{CO}) 2043, 1991, 1940, 1912 cm⁻¹. UV-Vis (CHCl₃) λ_{max} (log ε) 373.0 (4.63), 460.4 (4.69), 705.1 (3.91), 828.1 (3.87) nm.

$[Pd(TPAP){Ru_4(CO)_9}]$ (5)

[Pd(TPAP)] (17.5 mg, 0.0224 mmol) and [Ru₃(CO)₁₂] (100.0 mg, 0.157 mmol) were added to degased chlorobenzene (25 mL) and the mixture was refluxed for 2 h under nitrogen atmosphere. After that, solvent was evaporated under reduced pressure and a crude product was subjected to chromatography (neutral Al₂O₃, I^{\circ} grade). At the beginning, an yellow fraction of [Ru₃(CO)₁₂] was eluted with hexanes : DCM (1:1). Next, a light brown band of the desired product was eluted with hexanes : DCM (1:3). The product was crystallized from a dichloromethane/hexane system what provided pure compound 5. Yield = 17.7 mg (55 %), ¹H NMR (600 MHz, CDCl₃, 240 K) δ 7.61 – 7.59 (m, 2H, 10,15-*o*Ph), 7.57 – 7.55 (m, 2H, 10,15-*o*Ph), 7.53 – 7.46 (m, *J* = 13.4, 5.7, 4.6 Hz, 12H, 10,15-*m*,*m*,*p*Ph, 5,20-*o*,*m*,*p*Ph), 7.43 (t, J = 7.3, 2H, 5,20-mPh), 7.35 (s, 2H, 12,13), 7.33 (d, J = 7.5 Hz, 2H, 5,20-oPh), 7.13 (d, J = 5.4 Hz, 2H, 7,18), 7.02 (d, J = 5.4 Hz, 2H, 8,17), 4.73 (t, J = 7.2 Hz, 2H, 2^2 , 3^2), 3.67 (d, J = 6.6 Hz, 2H, 2^{1} , 3^{1}), 2.00 (t, J = 7.7 Hz, 1H, 2^{3}). ¹³C NMR (151 MHz, CDCl₃, 240 K) δ 198.0 (CO, Ru cluster), 156.1, 152.8, 150.5, 138. 9, 137.2, 134.4 (12,13), 134.2 (7,18), 132.9 (10,15-oPh), 132.7 (10,15-oPh), 132.6 (5,20-oPh), 132.2 (8,17), 132.1, 130.6, 128.9, 128.1, 128.0, 127.9 (5,20-mPh), 127.8, 127.7, 120.4, 100.6 (1,4), 81.7 (21), 78.2 (2, 3), 65.0 (2², 3²), 62.4 (2¹, 3¹), 32.0 (2³). **HRMS** (ESI) calcd for C59H32N3O9PdRu4 (M+H⁺): 1437.7398; found: 1437.7369 (*m/z*). **IR** (v_{CO})2043, 1994, 1941, 1911 cm⁻¹. UV-Vis (CHCl₃) λ_{max} (log ϵ) 332.0 (4.48), 457.0 (4.64), 723.1 (3.87) nm.

$[Pt(TPAP){Ru_4(CO)_9}]$ (6)

[Pt(TPAP)] (18.0 mg, 0.0207 mmol) and [Ru₃(CO)₁₂] (110.0 mg, 0.172 mmol) were added to degased chlorobenzene (25 mL) and the mixture was refluxed for 2 h under nitrogen atmosphere. After that, solvent was evaporated under reduced pressure and a crude product was subjected to chromatography (neutral Al₂O₃, I° grade). At the beginning, an yellow-orange fraction of [Ru₃(CO)₁₂] was eluted with hexanes : DCM (1:1). Next, a light brown band of the desired product was eluted with hexanes : DCM (1:3). The product was crystallized from a dichloromethane/hexane system what provided pure compound **6**.

Yield = 19.0 mg (60 %), ¹**H** NMR (600 MHz, CDCl₃, 270 K) δ 7.64 – 7.61 (m, 2H, 10,15-*o*Ph), 7.61 – 7.58 (m, 2H, 10,15-*o*Ph), 7.56 – 7.45 (m, 10H, 10,15-*m*Ph, 10,15-*p*Ph, 5,20-*o*Ph, 12,13), 7.49 (tt, J = 7.1, 1.4 Hz, 2H, 5,20-*p*Ph), 7.47 (td, J = 7.4, 1.6 Hz, 2H, 5,20-*m*Ph), 7.43 (td, J = 7.4, 1.8 Hz, 2H, 5,20-*m*Ph), 7.36 (d, J = 7.5 Hz, 2H, 5,20-*o*Ph), 7.22 (d, J = 5.5 Hz, 2H, 7,18), 7.08 (d, J = 5.4 Hz, 2H, 8,17), 4.75 (t, J = 7.2 Hz, 2H, 2²,3²), 3.72 (d, J = 6.8 Hz, 2H, 2¹,3¹), 2.05 (t, J = 7.6 Hz, 1H, 2³). ¹³C NMR (151 MHz, CDCl₃, 270 K) δ 198.3 (CO, Ru cluster), 156.0, 151.6, 148.4, 138.9, 137.1, 135.2 (7,18-pyrr), 134.7, 134.4, 133.0 (5,20-*o*Ph), 132.8 (10,15-*o*Ph), 132.6 (10,15-*o*Ph), 130.9 (5,20-*o*Ph), 130.4 (8,17-pyrr), 129.0 (5,20-*p*Ph), 128.2, 128.1 (5,20-*m*Ph), 127.9, 127.8 (5,20-*m*Ph), 127.7, 119.8, 99.4 (1,4), 79.2 (2, 3), 75.1 (21), 64.8 (2², 3²), 62.6 (2¹, 3¹), 32.9 (2³). **HRMS** (ESI) calcd for C₅₉H₃₂N₃O₉PtRu₄ (M+H⁺): 1526.7998; found: 1526.8020 (*m*/*z*). **IR** (v_{CO}) 2046, 1991, 1933 cm⁻¹. **UV-Vis** (CHCl₃) λ_{max} (log ε) 361.0 (4.54), 466.0 (4.61), 704.0 (3.90) nm.

¹H and ¹³C NMR spectra



Figure S1. ¹H NMR spectra of regular complex **2**: a) 500 MHz, CDCl₃, 300 K; b) 600 MHz, CDCl₃, 270 K, saturation of the sample with pyridine-d₅.



Figure S2. A ¹H NMR spectrum of cluster complex **3**; 500 MHz, CDCl₃, 300 K, and an inset showing a phenyl region much better resolved due to temperature lowering: 600 MHz, CD₂Cl₂, 250 K.



Figure S3. A set of ¹H NMR spectra for 2-6. One can easily observe significant azulene shifts.



Figure S4. The ¹³C NMR spectrum of **2** (151 MHz, CDCl₃+Py-d₅, 300 K)





High resolution mass spectra



Figure S9. Experimental (upper) and simulated (lower) [Ru(TPAP)(CO)] HRMS spectra.



 $\label{eq:Figure S10.} Figure \ S10. \ Experimental \ (upper) \ and \ simulated \ (lower) \ [Ru(TPAP)(CO) \{Ru_4(CO)_9\}] \ HRMS \ spectra.$



Figure S11. Experimental (upper) and simulated (lower) [Ni(TPAP){Ru₄(CO)₉}] HRMS spectra.



Figure S12. Experimental (upper) and simulated (lower) [Pd(TPAP){Ru₄(CO)₉}] HRMS spectra.



Figure S13. Experimental (upper) and simulated (lower) $[Pt(TPAP){Ru_4(CO)_9}]$ HRMS spectra.

UV-Vis spectra



Figure S14. An electronic spectrum of regular complex [Ru(TPAP)(CO)] (in chloroform).



Figure S15. An electronic spectrum of $[Ru(TPAP)(CO){Ru_4(CO)_9}]$ (in chloroform).



Figure S16. An electronic spectrum of $[Ni(TPAP){Ru_4(CO)_9}]$ (in chloroform).



Figure S17. An electronic spectrum of [Pd(TPAP){Ru₄(CO)₉}] (in chloroform).



Figure S18. An electronic spectrum of $[Pt(TPAP){Ru_4(CO)_9}]$ (in chloroform).

X-ray crystallography

Table S1.	Crystal	and	structure	refinement	data
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symbol of the structure	DMAP (2-1)	MeCN (2-2)	Ru-Ru CLUSTER (3)	Ni-Ru CLUSTER (4)	Pd-Ru CLUSTER (5)	Pt-Ru CLUSTER (6)	Pt (7)
empirical formula	$C_{60}H_{44}N_6ORu$	$C_{53}H_{34}N_4ORu$	$C_{67}H_{39}N_3O_{10}Ru_5$	$C_{59}H_{31}N_3NiO_9Ru_4$	$C_{59}H_{31}N_3O_9PdRu_4$	$C_{59}H_{31}N_3O_9PtRu_4$	$C_{50}H_{31}N_3Pt$
formula weight	966.08	843.91	1551.36	1388.86	1436.55	1525.24	868.87
crystal size [mm ³]	0.19 x 0.04 x 0.03	0.16 x 0.08 x 0.03	0.44 x 0.16 x 0.08	0.66 x 0.23 x 0.16	0.69 x 0.20 x 0.15	0.20 x 0.06 x 0.03	0.22 x 0.08 x 0.05
crystal system	triclinic						
space group	PĪ						
a [Å]	12.840(3)	10.203(5)	10.468(3)	9.461(3)	9.344(2)	10.192(4)	10.315(3)
b [Å]	13.714(4)	13.884(6)	13.376(4)	12.465(3)	12.595(3)	13.967(5)	11.935(3)
c [Å]	16.694(5)	14.858(6)	22.516(7)	22.653(5)	22.998(4)	20.939(7)	14.841(4)
α [°]	110.48(4)	77.68(5)	96.81(5)	98.26(3)	76.21(2)	80.13(3)	103.07(4)
β [°]	92.56(4)	70.21(5)	100.38(5)	100.04(3)	79.06(3)	86.41(4)	97.56(3)
γ [°]	113.89(5)	87.94(5)	112.03(6)	105.21(4)	73.79(2)	68.98(4)	102.32(4)
V [Å ³]	2457.6(19)	1933.3(15)	2814(2)	2487.5(13)	2501.9(10)	2741.2(19)	1707.4(9)
Z	2	2	2	2	2	2	2
density (calcd) [Mg·m ⁻³]	1.305	1.450	1.831	1.854	1.907	1.848	1.690
F(000)	996	864	1524	1364	1400	1464	860
coeff, µ [mm ⁻¹]	2.951	3.650	1.377	1.622	1.596	3.678	8.016
abs. correction	analytical						
T _{min.} /T _{max.}	0.75/0.93	0.70/0.91	0.70/0.92	0.53/0.81	0.50/0.84	0.63/0.93	0.46/0.77
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	120(2)
λ [Å]	1.5418	1.5418	0.71073	0.71073	0.71073	0.71073	1.5418
reflections coll., independ., obs.	18841, 8720, 5380	15999, 6879, 2348	23250, 10996, 6906	22724, 9759, 8976	26833, 9836, 8050	18240, 10152, 7730	12842, 6010, 5043
R _{int}	0.0943	0.1753	0.0694	0.0259	0.0500	0.0412	0.0915
data/parameter s	8720/616	6879/533	10996/771	9759/685	9836/685	10152/681	6010/476
final R indices $(I > 2\sigma(I))$	$R_1 = 0.0630,$ wR = 0.1501	$R_1 = 0.0855,$ wR = 0.0843	$R_1 = 0.0746,$ wR = 0.1877	$R_1 = 0.0320,$ wR = 0.0844	$R_1 = 0.0590,$ wR = 0.1319	$R_1 = 0.0418,$ wR = 0.0649	$R_1 = 0.0749,$ wR = 0.1837
R indices (all data)	$R_1 = 0.0896,$ wR = 0.1570	$R_1 = 0.1863,$ wR = 0.0982	$R_1 = 0.1201,$ wR = 0.2158	$R_1 = 0.0352,$ wR = 0.0873	$R_1 = 0.0753,$ wR = 0.1397	$R_1 = 0.0687,$ wR = 0.0742	$R_1 = 0.0836,$ wR = 0.1953
GOF on F ²	0.866	0.873	1.022	1.039	1.128	0.983	0.959
Completness	0.984	0.976	0.994	0.997	0.998	0.994	0.988
peak, hole [e∙Å ⁻ ³]	1.34, -1.11	1.04, -1.20	2.38, -1.23	0.71, -0.67	2.22, -1.09	0.74, -0.77	3.82/-3.07
CCDC number	1006123	1006124	1006125	1006126	1006127	1006128	1006129

Crystal preparations

Single crystals for all complexes were obtained in following solvent/antisolvent systems:

- 2-1 dichloromethane/acetonitrile, DMAP dissolved in CH₃CN (layering in a narrow tube),
- 2-2 ethyl acetate/acetonitrile (vapour diffusion),
- 3 to 7 toluene/heptane (layering in a narrow tube; low temperature).

X-ray data collection

Data were collected on a four-circle diffractometer (KM4 or XCALIBUR) equipped with a twodimensional CCD area detector. Graphite monochromatized Mo or Cu K_a radiation and the ω -scan technique ($\Delta \omega = 1^{\circ}$) were also used for data collection, while additional data collection and reduction, along with analytical absorption correction, were performed using the *CrysAlis* software package.

Solution and refinement

The structures were solved by direct methods using *SHELXS-97*, revealing the positions of all or almost all non-hydrogen atoms. The remaining atoms were located as a result of subsequent difference Fourier syntheses. The structures were refined using *SHELXL-97* or *SHELXL-2013* with *ShelXle* or *Shelxtl* interfaces. All non-hydrogen atoms were refined with anisotropic displacement parameters except one atom in platinum complexes **6** and **7**. A few others were restrained with DELU/SIMU command. The SQUEEZE procedure was applied for severely disordered acetonitrile molecule in **2**-1 and disordered toluene molecule in **6**. Hydrogen atoms were constrained and refined as a riding model. The H2C (2^3) atom in cluster complexes was found on residual density map, a C-H distance was normalized with DFIX and then the H atom was constrained in a proper geometry with AFIX 3. Details of the data collection parameters, crystallographic data and final agreement parameters are listed in Table S1, while selected geometrical parameters can be found in Table S2 and S3. Visualization of the structures was conducted using the *Diamond* program, while the Hirshfeld surface calculations were performed using the *Crystal Explorer* package.



Figure S19. The asymmetric unit of [Ru(TPAP)(CO)(DMAP)] 2-1. Displacement ellipsoids are drawn at 30% probability.



Figure S20. The asymmetric unit of [Ru(TPAP)(CH₃CN)(CO)] 2-2. Displacement ellipsoids are drawn at 30% probability.



Figure S21. The asymmetric unit of [Ru(TPAP)(CO){Ru₄(CO)₉}] 3. Displacement ellipsoids are drawn at 30% probability.





4. Displacement ellipsoids are drawn at 30% probability.

Figure S22. The asymmetric unit of [Ni(TPAP){Ru₄(CO)₉}] Figure S23. The asymmetric unit of [Pd(TPAP){Ru₄(CO)₉}] 5. Displacement ellipsoids are drawn at 30% probability.



Figure S24. The asymmetric unit of [Pt(TPAP){Ru₄(CO)₉}] **6.** Displacement ellipsoids are drawn at 30% probability.



Figure S25. The asymmetric unit of [Pt(TPAP)] 7. Displacement ellipsoids are drawn at 30% probability.



Figure S26. Presentation of the Hirshfeld surface of structure 2-2. This surface around the complex molecule mapped with a d_{norm} function indicates contacts with environment closer than the sum of vdW radii as red spots (white areas come from contacts with a distance equals the vdW sum). One can see a series of C-H… π contacts around the azulene unit. One, especially strong, derives from an interaction with π density of a coordinated acetonitrile C=N bond (a marked red spot).



Figure S27. Porphyrin skeletons lying on a plane defined by C21-N22-N23-N24 atoms. Out-of-plane deformations have been clearly identified (darkened atoms are bellow the plane, those above cast shadows).



Figure S28. Presentation of the cluster-azulene connectivity (structure 3). Carbonyl groups from cluster removed to preserve clarity. Ruthenium cluster tetrahedron darkened. One ruthenium atom binds to the cyclopentadiene ring. Two ruthenium atoms bind to the tropylium ring (each with the η^4 coordination mode).

Table S2. Selected distances [Å].

Coordination environment								
	2 -1	2 -2	3	4	5	6	7	
M-C21	2.017(6)	1.973(12)	2.037(9)	1.921(3)	1.986(8)	2.000(6)	1.989(9)	
M-N22	2.053(5)	2.102(8)	2.053(8)	1.921(3)	2.017(6)	1.997(5)	2.065(9)	
M-N23	2.105(4)	2.029(10)	2.080(8)	1.955(3)	2.046(7)	2.065(5)	2.063(8)	
M-N24	2.054(5)	2.132(8)	2.047(8)	1.922(3)	2.020(7)	2.001(5)	2.066(9)	
			Rutheniur	n cluster ²				
M _{centr} -			2 1509(19)	22112(5)	2,4074(12)	25002(16)		
Ru _{cluster}	-	-	5.1596(16)	5.5115(5)	3.4074(12)	5.5665(10)	-	
Ru1-Ru2	-	-	2.8824(16)	2.8833(11)	2.8646(12)	2.8080(12)	-	
Ru1-Ru3	-	-	2.897(2)	2.8477(7)	2.8602(11)	2.9014(16)	-	
Ru2-Ru3	-	-	2.898(2)	2.8786(12)	2.8740(12)	2.8796(16)	-	
Ru1-Ru4	-	-	2.8749(15)	2.8792(10)	2.8782(11)	2.8606(13)	-	
Ru2-Ru4	-	-	2.714(2)	2.6952(9)	2.6954(11)	2.7141(16)	-	
Ru3-Ru4	-	-	2.6857(16)	2.6845(13)	2.6883(12)	2.7141(13)	-	
Ru1-								
Azulene(5)	-	-	1.9670(12)	1.9128(7)	1.9076(9)	1.922(1)	-	
centroid								
Ru2-C2C	-	-	2.432(11)	2.422(3)	2.431(9)	2.522(6)	-	
Ru3-C2C	-	-	2.436(11)	2.480(3)	2.481(8)	2.449(6)	-	

Table S3. Selected angles [°]. Azulene(n) means a plane built on n azulene atoms (5-cyclopentadienyl, 7-tropyl). Atoms separated with commas produce the second plane between which the angle is measured. The label C2A corresponds to the 2^1 carbon atom, C2B to 2^2 etc. One can see significant tropylium distortion upon coordination of a cluster (angles: azulene(7) - M1,C21,N22,N23,N24 and C2B,C2C,C3B - C2,C2A,C3A,C3). Increased porphyrin framework deformation for **3-6** is also noticeable (C5-M1-C15 and C10-M1-C20 angles).

Azulene curvedness									
an angle between:	2 -1	2 -2	3	4	5	6	[Pd(T(pCl)PAP)] ³	7	
azulene(10)- M1,N22,N23,N24	11.08(14)	26.1(3)	42.9(3)	33.08(9)	28.0(2)	19.33(16)	12.90(8)	17.2(2)	
azulene(7)- M1,C21,N22,N23,N24	15.73(13)	28.0(3)	43.3(3)	36.19(9)	32.8(2)	24.69(15)	16.85(8)	21.8(3)	
azulene(5)- M1,C21,N22,N23,N24	7.22(17)	10.3(5)	22.9(4)	20.13(13)	17.8(3)	11.20 (18)	6.49(9)	5.7(3)	
azulene(5)- C2A,C2B,C3B,C3A	12.1(2)	15.0(6)	15.5(4)	14.91(13)	14.5(4)	14.2 (2)	12.58(12)	17.9(3)	
C2B,C2C,C3B- C2,C2A,C3A,C3	4.4(3)	2.4(12)	61.7(11)	55.4(3)	54.5(10)	48.0(7)	5.35(16)	8.2(10)	
Porphyrin curvedness									
C5-M1-C15	177.49(18)	179.4(3)	174.3(2)	167.28(8)	171.0(2)	178.50(15)	178.19(6)	178.4(3)	
C10-M1-C20	175.16(15)	174.7(3)	171.3(2)	168.24(9)	171.9(2)	176.17(16)	176.90(6)	178.4(2)	

² For Ru-Ru complex **3** ruthenium atoms numeration is one unit higher, *i.e.* Ru1 in other structures is equivalent to Ru2 in **3**, Ru2 \rightarrow Ru3, *etc.* as the central ruthenium(II) cation is labeled Ru1.

³ Lash T.D., Colby D.A., Graham S.R., Ferrence G.M., Szczepura L.F., *Inorg. Chem.* 2003, 42, 7326–7338



Figure S29. A histogram based on the Cambridge Structural Database search with a Ru-Ru distance query. Distances present in structure 3 are marked.