Supporting information for

Linking metal-organic cages pairwise as a design approach for assembling multivariate crystalline materials

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1. Experimental section

1.1. Materials and measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Infrared spectra were collected on a Perkin-Elmer Spectrum 100 using a UATR sampling accessory. Thermal gravimetric analysis (TGA) was performed on a Netzsch STA 449 F5 Jupiter.

Powder X-ray diffraction data were collected on a Bruker Advance D8 diffractometer (capillary stage) using Cu K α radiation (λ = 1.5418 Å, 50 kW/40mA). 0.8 mm or 1.0 mm capillaries were filled with the respective solvent before loading crystals of the samples. This was done to avoid any possible desolvation of the crystalline sample. Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 2020.3.0. Gas sorption isotherm measurements were performed on a Micromeritics 3Flex Surface Characterisation Analyser. UHP grade (99.999 %) N₂ was used for all measurements. Temperatures were maintained at 77 K using a cryo-cooler. The isotherms were then analysed to determine the Brunauer Emmett-Teller (BET) surface area and pore-size distribution using the MicroActive software (Version 3.00, Micromeritics Instrument Corp. 2013). Ligands L¹, L² and **1-Cu** were prepared according to previously published procedures.^{1,2}

1.2. Synthesis of pyridyl-functionalised ligand 8

In order to examine whether pyridine functionalized MOCs can be assembled, we synthesized compound 8 (Scheme 1)



Scheme 1

1.2.1. dimethyl 3,3'-(pyridine-3,5-diylbis(ethyne-2,1-diyl))dibenzoate (7)

3,5-dibromopyridine **5** (0.25 g, 1.06 mmol), alkyne **6** (0.43 g, 2.68 mmol), THF (15 mL), and diisopropylamine (8 mL) were added to a Schlenk flask and the resulting mixture was degassed with Ar for 30 minutes. Pd(PPh₃)₂Cl₂ (75 mg, 0.107 mmol) and Cul (20 mg, 0.105 mmol) was added in one portion, and the reaction mixture was heated at 40 °C for 48 h. The reaction mixture was filtered and the precipitate was washed with EtOAc (2 x 20 mL). The filtrate was reduced *in vacuo* to give a black crude gum, which was diluted with Et₂O (100 mL) and filtered. The crude precipitate was washed with Et₂O (2 x 50 mL) and was purified via flash column chromatography (1% Et₃N in CH₂Cl₂) to afford X as a pale-yellow solid (0.16 g, 38 %). ¹H NMR (500 MHz, CDCl₃) δ 8.71 (2H, s), 8.24 (2H, s), 8.06 (2H, d, J = 7.2 Hz), 7.96 (1H, s), 7.73 (2H, d, J = 7.8 Hz), 7.48 (2H, dd, J = 7.8, J = 7.8 Hz), 3.95 (6H, s). ¹³C NMR (126 MHz, CDCl₃) δ 166.4, 151.2, 140.9, 135.9, 133.1, 130.8, 130.1, 128.8, 122.9, 120.0, 92.4, 86.1, 52.5. v_{max} (neat, cm⁻¹): 3032 (w), 1726 (s, HC=O), 1435 (m), 1292 (s), 1245 (s), 746 (s).



Figure S1. ¹H NMR spectrum (500 MHz/CDCl₃) of compound 7.

1.2.2. 3,3'-(pyridine-3,5-diylbis(ethyne-2,1-diyl))dibenzoic acid (8)

2M aqueous KOH solution (2.0 mL, 4.0 mmol) was slowly added dropwise (over 30 minutes) to a solution of **7** (0.16 g, 0.41 mmol) in CH₂Cl₂ (10 mL) and MeOH (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 h, and the solvent was reduced to 5 mL under a stream of N₂. The residue was acidified to pH 4 with 3M HCl and the resulting precipitate was isolated under reduced pressure, followed by washing with water and dried under reduced pressure to afford L² as an off-white solid (93 mg, 63 %). Due to the poor solubility of this compound in all common solvents, the tetrabutylammonium salt was prepared for characterisation: Compound 8 was dissolved in DMSO containing 2-3 molar equivalents of 1M tetrabutylammonium hydroxide solution in THF and the solvent was evaporated. ¹H NMR (500 MHz, DMSO) δ 8.74 (2H, s), 8.17 (1H, s), 8.05 (2H, s), 7.90 (2H, d, J = 7.65 Hz), 7.50 (2H, d, J = 7.5 Hz), 7.34 (2H, dd, J = 7.6, 7.6 Hz), 3.36 (16H, m), 1.56 (16H, m), 1.30 (16H, m), 0.93 (24H, t, J = 7.3 Hz). ¹³C NMR (126 MHz, DMSO) δ 172.1, 166.6, 151.1, 140.9, 135.3, 132.4, 130.2, 129.3, 121.9, 119.3, 92.3, 86.0. v_{max} (neat, cm⁻¹): 3029 (br, w) 1677 (s, HC=O), 1576 (m, C=C), 1432 (m), 752 (s), 678 (s).



Figure S2. ¹H NMR spectrum (500 MHz/DMSO) of the tetrabutylammonium (TBA) salt compound 8.

In order to examine MOC formation with compound **8**, we sought to also trial the potassium salt. **8** (20 mg, 0.054 mmol) was dissolved in a 0.1M aqueous KOH (1.05 mL, 0.105 mmol) solution at room temperature. Ethanol (10 mL) was added to the resulting aqueous solution and the solvent was removed *in vacuo*. This drying process to remove water as an azeotrope with ethanol was repeated twice more until a white salt was observed. ¹H NMR (500 MHz, DMSO) δ 8.72 (2H, s), 8.17 (1H, s), 8.03 (2H, s), 7.89 (2H, d, J = 7.7 Hz), 7.55 (2H, d, J = 7.6 Hz), 7.37 (2H, dd, J = 7.7, 7.6 Hz). ¹³C NMR (126 MHz, DMSO) δ 168.8, 151.0, 141.0, 132.7, 132.4, 130.5, 128.4, 120.7, 120.1, 85.0. *v*_{max} (neat, cm⁻¹): 3174 (br), 2981 (w), 1584 (m, C=C), 1551 (s, C=C), 1386 (s), 762 (m). Both TBA and potassium salts of compound **8** had significantly improved solubility in DMSO, DMF and DMA.

1.3. Synthesis of MOCs

1.3.1. Attempted synthesis of $[Cu_4(\mathbf{8})_4]$

In a screw-cap vial the potassium salt of compound **8** (10 mg, 0.02 mmol) was combined with $Cu(OAc)_2 \cdot H_2O$ (4.5 mg, 0.02 mmol) in DMF (3.5 mL). The suspension was sonicated for 10 seconds. The precipitation of an amorphous blue solid was observed immediately. The precipitate was completely insoluble in all common laboratory solvents. The same outcome was observed for DMA as the solvent, or when attempting the reaction with the TBA salt of **8**.



Figure S3. A scheme showing the attempted synthesis of $[Cu_4(8)_4]$. The instantaneous precipitation indicates that the pyridyl donor of **8** interferes with Cu-mediated self-assembly resulting in coordination by both carboxylate and pyridyl donors.³

1.3.2. [Rh₄L²₄] (2-Rh)

In a screw-cap vial L² (90 mg, 0.23 mmol) was combined with Rh₂(OAc)₄ (50 mg, 0.11 mmol) and anhydrous Na₂CO₃ (24 mg, 0.23 mmol) in 8.5 mL of dry and degassed DMA. The vial was placed on a temperature-controlled heating block pre-set to 85 °C and left to stand for 40 h. After allowing to cool to room temperature, the resulting blue-green solution was separated from the solids by centrifugation, and the supernatant combined with 24 mL of MeOH, causing a precipitate to form immediately. The precipitate was isolated by centrifugation and the supernatant was discarded. The solid was washed by re-suspending in fresh MeOH, followed by consecutive centrifugation (4 x 6 mL). After removing residual solvent under high-vacuum, **2-Rh** was dissolved in DMF and recrystallised by slow-vapour diffusion of acetonitrile (48 mg, 42% yield). ¹H NMR (500 MHz, DMF-*d*₇): δ 10.10 (s, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 8.24 (d, *J* = 1.7 Hz, 2H), 8.08 (d, *J* = 1.6 Hz, 2H), 8.03 (s, 13H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H). *v*_{max} (neat, cm⁻¹): 1698.5 (m, C=O), 1682.8 (m, C=O), 1588.7 (m), 1563.0 (s), 1427.5 (s), 1394.8 (s).



Figure S4. ¹H NMR spectrum (500 MHz/DMF-*d*₇) of L² (bottom) and re-crystallised [Rh₄L²₄] (2-Rh) (top).

1.4. Synthesis of $\{[1-Cu] \cdot [2-Rh]_m\}_n$

General procedure: 4 mM solutions of **1-Cu** and **2-Rh** were prepared in dry DMA. The solution of **1-Cu** was prepared by combining appropriate quantities of L¹ and Cu(OAc)₂*in-situ*, whilst for **2-Rh**, the solution was prepared by dissolution of the dry cage powder in DMA.

1.4.1. Synthesis of $\{[1-Cu] \cdot [2-Rh]_2\}_n$ (3)

400 µL of **1-Cu** (4 mM in DMA) and 800 µL of **2-Rh** (4 mM in DMA) were combined in a 2 mL glass vial. Slow vapour diffusion of ethyl acetate into the DMA mixture over a period of 5 days resulted in deep blue crystals with a square plate appearance. The mother liquor was removed and the crystals were successively washed with acetone (4 x 3 mL) and stored in acetone for further use. v_{max} (neat, cm⁻¹): 1698.5 (m, C=O), 1629.4 (NH₂, w), 1588.68 (m), 1563.0 (m), 1427.5(m), 1386.2 (s).



Figure S5. ¹H NMR spectrum (500 MHz/DMF- d_7) of a dissolved sample **3** (dissolution achieved by heating the solid in DMF- d_7 at 70 °C for 10 mins). The integration of resonance *c* from **2-Rh** (1H each) and *b*' from **1-Cu** (2H each) is ~1:1 respectively, indicating the ratio a 2:1 ratio of **2-Rh** and **1-Cu**.

1.4.2. Synthesis of $\{[1-Cu] \cdot [2-Rh]\}_n$ (4)

500 µL of **1-Cu** (4 mM in DMA) and 500 µL of **2-Rh** (4 mM in DMA) were combined and mixed in a 2 mL glass vial. A 500 µL portion of DMA was added to the mixture. Slow vapour diffusion of disopropyl ether into the DMA mixture over a period of 6 days resulted in deep blue block crystals. The mother liquor was removed and the crystals were successively washed with acetone (4 x 3 mL) and stored in acetone for further use: v_{max} (neat, cm⁻¹): 1699.5 (m, C=O), 1628.0 (NH₂, w), 1590.1 (m), 1564.4 (m), 1427.5 (m), 1386.1 (s).



Figure S6. ¹H NMR spectrum (500 MHz/DMF- d_7) of a dissolved sample of **4** (dissolution achieved by heating the solid in DMF- d_7 at 70 °C for 10 mins). The integration of resonance *c* from **2-Rh** (1H each) and *b*' from **1-Cu** (2H each) is ~1:2 respectively, indicating the ratio a 1:1 ratio of **2-Rh** and **1-Cu**.



Figure S7. IR spectra of $\{[1-Cu] \cdot [2-Rh]_2\}_n$ (3) and $\{[1-Cu] \cdot [2-Rh]\}_n$ (4); a) Full IR spectrum of 1-Cu, 2-Rh and 3; b) full IR spectrum of 1-Cu, 2-Rh and 4; c) comparison of 1-Cu, 2-Rh and 3 showing key NH₂ scissoring and C-N stretches; d) comparison of 1-Cu, 2-Rh and 4 showing key NH₂ scissoring and C-N stretches.

Discussion on solvent dependence

Crystals of **3** and **4** can be obtained from DMF or DMA. Because these solvents coordinate at axial paddlewheel sites of Rh(II), they essentially compete for Rh-aniline coordination (which is the basis for MOC linking and structure formation). In DMF, **3** forms spontaneously after 2 h, whilst in DMA, the mixture of **1-Cu** and **2-Rh** remains soluble, and diffusion of a non-coordinating solvent is required for structure formation. This suggests that DMA is a stronger ligand (compared to DMF) and better competes for the Rh(II) axial paddlewheel site. Indeed, a study carried out by Alvarez et al. indicates that DMA is 2 x more likely to coordinate to transition metals compared to DMF, as determined by their criteria.⁴

Discussion on MOC stability and ligand exchange



Figure S8. ¹H NMR spectra (500 MHz/DMF- d_7) a) a dissolved sample of **3** (dissolution achieved by heating the solid in DMF- d_7 at 70 °C for 10 mins); **b**) the same sample after 5 days at room temperature (note: some recrystallisation of **3** was observed during this period). **2-Rh** is kinetically inert, and as expected, ligand shuffling between **1-Cu** and **2-Rh** is not observed under these conditions.

2. Powder X-ray diffraction



Figure S9. Rietveld refinement of the Powder X-ray diffraction pattern (PXRD) of $[Rh_4L_4^2]$ (**2-Rh**). Refinement cell parameters: *P*-1, *a* = 12.6; *b* = 14.7; *c* = 18.3; α = 74.5; β = 70.8; γ = 72.7. For comparison, the cell parameters of the X-ray structure are: *P*-1 *a* = 12.4; *b* = 14.2; *c* = 18.2; α = 74.5; β = 70.6; γ = 71.5.



Figure S10. Powder X-ray diffraction pattern (PXRD) of the activated sample of 2-Rh.



Figure S11. Rietveld refinement of the Powder X-ray diffraction pattern (PXRD) of $\{[1-Cu][2-Rh]_2\}_n$ (3). Refined parameters: Tetragonal *I*4/*m*, *a* = 33.7; *c* = 25.8.8. For comparison, the parameters of the X-ray structure are: *a* = 32.4; *c* = 25.6.



Figure S12. Rietveld refinement of the Powder X-ray diffraction pattern (PXRD) of $\{[1-Cu][2-Rh]\}_n$ (4). Refined cell parameters: *P*-1 *a* = 16.3; *b* = 16.1; *c* = 35.6; α = 92.9; β = 100.2; γ = 93.0. For comparison, the parameters of the X-ray structure are: *P*-1 *a* = 16.1; *b* = 16.2; *c* = 35.6; α = 93.9; β = 102.9; γ = 93.7



Figure S13. Powder X-ray diffraction patterns (PXRD) of **3**; as-synthesised, acetone exchanged, activated sample and recrystallised sample (obtained by redissolving the activated sample in DMF). The acetone exchanged sample shows minor peak shifts, most likely due to the impact of solvent exchange (and coordination) on the distance between the layers. The acetone-exchanged crystals did not diffract sufficiently to obtain a reasonable SCXRD data set, however, a reliable unit cell could be obtained from multiple data sets: Tetragonal I4, a = b = 34.83; c = 25.55 (*ca. a* = b = 32.4; *c* = 25.6 for the as-synthesised structure).



3. Thermal gravimetric analysis (TGA)

Figure S14. TGA trace of 2-Rh (acetone exchanged sample).



Figure S15. TGA trace of $\{[1-Cu] \cdot [2-Rh]_2\}_n$ (3) (acetone exchanged sample).



Figure S16. TGA traces demonstrating the difference between aniline desolvation for Cu(II) vs. Rh(II) paddwheel complexes. Green line = $[Rh(CH_3COO)_4(PhNH_2)_2]$, blue line = $[Cu(CH_3COO)_4(PhNH_2)_2]$. The experimental weight loss % is in excellent agreement with the expected weight loss of two aniline molecules for each complex. For $[Rh(CH_3COO)_4(PhNH_2)_2]$, desolvation occurs from 111 °C, whilst for $[Cu(CH_3COO)_4(PhNH_2)_2]$, this occurs earlier from ~ 80 °C. (These paddlewheel complexes were prepared from their respective acetates by solvent exchange with aniline, according to literature procedures).⁵



Figure S17. DSC traces demonstrating the difference between aniline desolvation for Cu(II) vs. Rh(II) paddwheel complexes. Green line = $[Rh(CH_3COO)_4(PhNH_2)_2]$, blue line = $[Cu(CH_3COO)_4(PhNH_2)_2]$. The exothermic peaks ~150 °C and 275 °C relates to the desolvation and decomposition of the Rh(II) complex, respectively. The two exothermic peaks at ~100 °C for the Cu(II) complex indicate that desolvation is accompanied with a structural change. Cu(II) complexes of aniline are notorious for readily undergoing redox processes.⁶

4. Gas adsorption

Prior to activation, samples were repeatedly soaked in acetone (x 7) over a period of 24 h. The samples were then transferred into an autosamdri supercritical point dryer. After the activation process, samples were transferred directly into an adsorption measurement tube, where they were heated at 60 $^{\circ}$ C for 3 h prior to analysis.

Table S1: Surface areas (m^2/g) as calculated from the N₂ 77K and CO₂ 195 K isotherms

Samples	N ₂ 77 K SA _{BET} (Langmuir)	CO ₂ 195 K SA _{BET} (Langmuir)
[1-Cu]	-	$95.0 \pm 3.0^2 (172.2 \pm 2.2)$
[2-Rh]	-	282.5 ± 2.5 (595 ± 16.4)
3	422.4 ± 2.4 (722.1 ± 6.9)	358.9 ± 0.9 (666.2 ± 10.8)



Figure S18. N₂ 77K isotherm and pore-size distribution of $\{[1-Cu] \cdot [2-Rh]_2\}_n(3)$.



Figure S19. 195 K CO₂ isotherms of $\{[1-Cu] \cdot [2-Rh]_2\}_n$ (3, teal circles), 1-Cu (green triangles) and 2-Rh (blue squares).



Figure S20. Derivation of the BET surface area from the 77 K N_2 adsorption isotherms for 3.



Figure S21. Derivation of the BET surface area from the 195 K CO₂ adsorption isotherms for a) **3** and b) **2- Rh**.

5. Scanning electron microscopy

Scanning Electron Microscope (SEM) images were collected on a Phillips XL30/Quanta 450 scanning electron microscope in secondary electron mode, (spot size 3 and 10 KeV). Electron Dispersive X-ray Analysis was collected with an Oxford Instruments Ultim Max 170 EDX attachment on the Phillips XL30/Quanta 450 (spot size 4, 15 KeV). Samples for SEM analysis were loaded with solvent or dry loaded onto adhesive carbon tabs on aluminium stubs and carbon coated (5 nm) prior to analysis.



Figure S22. a) SEM image of **3**, with elemental mapping of Rh L α 1 (b) and c) Cu L α 1,2; of a selected area (d); e) optical microscope image of the crystals of **3**; f) EDX graph showing a ~1:2 ratio of Cu:Rh.



Figure S23. a) SEM image of **4**, with elemental mapping of Rh L α 1 (b) and Cu L α 1,2 (c) of a selected area; d) EDX graph showing a ~1:1 ratio of Rh:Cu.

6. Transmission electron microscopy (TEM)

TEM imaging was performed using a probe-corrected, low-base FEI Titan Themis 80-200 (FEI, Hillsboro, OR, USA) operated at 200 kV with an X-FEG Schottky source. EDS elemental mapping was acquired in STEM mode using the Super-X EDS detectors which provide a combined 0.8 Sr collection angle.



Figure S24. a) HAADF image of a ~500 nm crystal of **3**, with EDS elemental mapping of Rh, Cu, O, N and F (the latter originating from **1-Cu**); b) EDS graph of the elemental distribution from the sample.



Figure S25. a) TEM image of **3**.We also collected HAADF images of **3** at higher magnification - b) and c) - however, the best contrast for the crystalline lattice was observed in the TEM image (a).

7. X-ray crystallography

7.1. General methods

Single crystals were mounted in paratone-N oil on a plastic loop. X-ray diffraction data for **2-Rh, 3** and **4** were collected at 100(2) K on the MX-1 or MX-2 beamlines of the Australian Synchrotron.^{7,8} Structures were solved by direct methods using SHELXT⁹ and refined with SHELXL¹⁰ and ShelXle¹¹ as a graphical user interface. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. X-ray experimental data is given in Table S2.

7.1.2. Specific refinement details for 3

All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was aided by similarity restraints (SIMU).¹² The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE¹³ routine in PLATON,¹⁴ which strongly improved all figures of merit (FOM).

7.1.1. Specific refinement details for 4

Stereochemical restraints for L¹, L² and DMA solvent molecules were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). This help to produce a stable model of the DMA solvent and aided in developing a model for the ligand components with more precise C-C bonds. All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was enabled by a combination of similarity restraints (SIMU).¹² The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE¹³ routine in PLATON,¹⁴ which strongly improved all figures of merit (FOM).

Compound	2-Rh	{[1-Cu]·[2-Rh] ₂ } _n (3)	{[1-Cu]·[2-Rh]} _n (4)	_
CCDC number	2106776	2106778	2106777	
Empirical formula	$C_{108}H_{60}N_4O_{20}Rh_4$	$C_{74}H_{36}CuFNO_{16}Rh_2$	$C_{110}H_{75}Cu_2F_2N_5O_{24}Rh_2$	
Formula weight	2145.24	1483.40	2221.65	
Crystal system	Triclinic	Tetragonal	Triclinic	
Space group	<i>P</i> -1	l4/m	<i>P</i> -1	
a (Å)	12.446(3)	32.444(5)	16.053(3)	
b (Å)	14.231(3)	32.444(5)	16.197(3)	
<i>c</i> (Å)	18.240(4)	25.626(5)	35.627(7)	
α (°)	74.52(3)	90	93.94(3)	
β (°)	70.59(3)	90	102.90(3)	
γ (°)	71.55(3)	90	93.78(3)	
Volume (Å ³)	2842.8(13)	26974(9)	8977(3)	
Z	1	8	2	
Density (calc.) (Mg/m³)	1.253	0.731	0.822	
Absorption coefficient (mm ⁻¹)	0.632	0.434	0.460	
F(000)	1076	5944	2256	
Crystal size (mm ³)	0.15 x 0.07 x 0.05	0.15 x 0.14 x 0.03	0.10 x 0.04 x 0.03	
$\boldsymbol{\theta}$ range for data collection (°)	1.534 to 27.103	0.888 to 20.333	1.177 to 18.847	
Reflections collected	48055	108604	46753	
Observed reflections [R(int)]	11628 [0.0369]	6779 [0.0567]	12645 [0.0363]	
Goodness-of-fit on F ²	1.052	1.375	1.225	

Table S2: X-ray experimental data for

R ₁ [l>2σ(I)]	0.0794	0.1164	0.0938
wR ₂ (all data)	0.2656	0.3710	0.3252
Largest diff. peak and hole (e.Å-3)	2.545 and -0.644	1.500 and -0.431	0.481 and -0.531
Data / restraints / parameters	11628 / 412 / 615	6779 / 306 / 442	12645 / 1413 / 1329

7.1. X-ray structure of 2-Rh



Figure S26. X-ray structure of $[Rh_4L^2_4(CH_3CN)_4]$ (2-Rh).



Figure S27. X-ray structures of the extended crystal packing of solvatomorphs of $[Cu_4L_4^2]^1$ as well as the isolated solvatomoph of $[Rh_4L_4^2]$ (**2-Rh**). The crystallization of **2-Rh** and **1a** are both carried out from DMF/MeCN.

7.2. Thermal ellipsoid plots



Figure S28. The asymmetric unit of the X-ray structures of **2-Rh** with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.



Figure S29. The asymmetric unit of the X-ray structures of **3** with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.



Figure S30. The asymmetric unit of the X-ray structure of **4** with all non-hydrogen atoms shown as ellipsoids at the 50% probability level. **Figure S31.**

8. DFT calculations

8.1. Computational details

All presented electronic structure calculations were conducted with the ORCA quantum chemistry package in its version 4.2.¹⁵ During both geometry optimizations and single point energy calculations the TPSSh functional was utilized.^{16,17} Scalar relativistic effects were taken into account by the zero'th order regular approximation (ZORA) while solvation effects in DMF were modeled implicitly via a conductor-like polarizable continuum model (C-PCM).^{18–20} The scalar relativistic recontraction of the def2-TZVP basis set (SARC-ZORA-TZVP for Rh and ZORA-def2-TZVP for all other elements) was used throughout all calculations.^{21,22} Coulomb and exchange integral calculations during the Fock matrix construction were accelerated by means of the resolution-of-the-identity (RIJ) and chainof- spheres exchange (COSX) approximation, respectively.²³⁻²⁷ The former employed the scalar set.^{28,29} relativistically recontracted SARC/J auxiliarv basis Dispersion effects were accounted for within the framework of Grimme's D3 correction using Becke-Johnson damping (D3BJ).³⁰ The minimum nature of all optimized structures was verified by numerical frequency calculations ignoring negative eigenvalues of the electronic hessian below 20 cm⁻¹ which were attributed to numerical noise.

8.2. Computational results

To gain additional insight into the observed distribution of axial ligands in **3** and **4**, a simplified ligand exchange reaction in DMF was investigated by means of electronic structure calculations (equation 1). Our computational results confirm the established picture that the two unpaired electrons in $[Cu_2(PhCOO)_4(PhNH_2)_2]$ and $[Cu_2(PhCOO)_4(DMF)_2]$ are antiferromagnetically coupled leading to an open-shell singlet state while both Rh paddlewheel complexes feature a closed-shell ground state with a Rh-Rh bond. Both, DMF and aniline appear to bind stronger to Cu than to Rh, as is reflected by slightly larger bond orders (see Table S3). Most importantly, the calculated reaction energy for equation (1) amounts to $\Delta E = -7.6$ kcal mol⁻¹ which supports a thermodynamic argument in favour of a preferred coordination of Rh paddlewheel complexes as compared to their Cu counterparts. Whether this result is caused by or merely coincides with the predicted tilt in the core unit of $[Cu_2(PhCOO)_4(PhNH_2)_2]$ (as discussed in the main manuscript) cannot be revealed on the basis of the current data.

$$[\operatorname{Cu}_{2}(\operatorname{PhCOO})_{4}(\operatorname{PhNH}_{2})_{2}] + [\operatorname{Rh}_{2}(\operatorname{PhCOO})_{4}(\operatorname{DMF})_{2}] \xleftarrow{\operatorname{DMF}} [\operatorname{Rh}_{2}(\operatorname{PhCOO})_{4}(\operatorname{PhNH}_{2})_{2}] + [\operatorname{Cu}_{2}(\operatorname{PhCOO})_{4}(\operatorname{DMF})_{2}] \tag{1}$$

Table S3: Calculated bond orders and M-L bond distances together with M-L axial paddlwheel distances from X-ray crystallography

Compound	M-L Bond Order	d ^{calc} (M-L) Å	d ^{exp} (M-L) Å
[Cu ₂ (PhCOO) ₄ (PhNH ₂) ₂]	0.33	2.24	-
[Rh ₂ (PhCOO) ₄ (PhNH ₂) ₂]	0.23	2.32	-
[Cu ₂ (PhCOO) ₄ (DMF) ₂]	0.30	2.21	-
[Rh ₂ (PhCOO) ₄ (DMF) ₂]	0.23	2.32	-
{[1-Cu]} _n	-	-	2.19 ²
3	-	-	2.23
4	-	-	2.22



Figure S32. DFT calculated structures of the Cu and Rh paddlewheel complexes.

9. References

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