Stepwise synthesis of mixed-metal assemblies using pre-formed Ru(II) ‘complex ligands’ as building blocks

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SUPPORTING INFORMATION
Characterisation data for [Ru(Lth)$_3$](PF$_6$)$_2$

Fig. S1. Electrospray mass spectrum of [Ru(Lth)$_3$](PF$_6$)$_2$ showing the [RuL$_3$H]$^{3+}$ and [RuL$_3$]$^{2+}$ peaks (left); expansion of the [RuL$_3$]$^{2+}$ peak (right), blue = experimental, red = predicted.

Fig. S2. UV vis spectrum (MeCN) of [Ru(Lth)$_3$](PF$_6$)$_2$
Fig. S3: COSY spectrum (in CD$_3$CN, 400 MHz) of [Ru(L$^{th}$)$_3$][PF$_6$]$_2$ – note 4 pairs of thiophene doublets, and 4 of the CH$_2$ pairs.

Characterisation data for [Ru$_2$Co$_2$(L$^{th}$)$_6$](BF$_4$)$_4$(PF$_6$)$_4$.

Fig. S4. UV vis spectrum (MeCN) of [Ru$_2$Co$_2$(L$^{th}$)$_6$](BF$_4$)$_4$(PF$_6$)$_4$.  

Fig. S5. DOSY spectrum (400 MHz, CD$_2$CN) of the diamagnetic region of

$[\text{Ru}_2\text{Co}_2(L^{th})_6](\text{BF}_4)_4(\text{PF}_6)_4$.

Fig. S6. Electrospray mass spectrum of $[\text{Ru}_2\text{Co}_2(L^{th})_6](\text{BF}_4)_4(\text{PF}_6)_4$ showing the series of $\{[\text{Ru}_2\text{Co}_2(L^{th})_6]X_3\}^{3+}$ peaks (left); expansion of the $\{[\text{Ru}_2\text{Co}_2(L^{th})_6](\text{BF}_4)_4(\text{PF}_6)\}^{3+}$ peak (right), black = experimental, red = predicted.
Characterisation data for $\{[\text{CdRu}(L^{n})_3](\text{ClO}_4)_2(\text{PF}_6)_2\}_\infty$.

Fig. S7. UV vis spectrum (MeCN) of $\{[\text{CdRu}(L^{n})_3](\text{ClO}_4)_2(\text{PF}_6)_2\}_\infty$.

Fig. S8. Expansion of the ESMS of $\{[\text{CdRu}(L^{n})_3](\text{ClO}_4)_2(\text{PF}_6)_2\}_\infty$ showing the $\{[\text{RuCd}(L^{n})_3](\text{ClO}_4)_2\}_{2^+}$ peak at 804, black = experimental, red = predicted.
Fig. S9. Overlay of UV vis spectra of: [Ru(L\text{th})\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} (black), [{CdRu(L\text{th})\textsubscript{3}}(ClO\textsubscript{4})\textsubscript{2}(PF\textsubscript{6})\textsubscript{2}]\textsubscript{∞} (blue) and [Ru\textsubscript{2}Co\textsubscript{2}(L\text{th})\textsubscript{6}](BF\textsubscript{4})\textsubscript{4}(PF\textsubscript{6})\textsubscript{4} (red), all in MeCN

**Synthesis of 4:1-Ru(L\text{ph})\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}**

A solution of L\text{ph} (0.24 g, 0.62 mmol, 5.9 eq) was stirred rapidly in refluxing ethylene glycol (25 cm\textsuperscript{3}) until dissolved. To this was added a solution of RuCl\textsubscript{2}(dms)\textsubscript{4} (0.05 g, 0.11 mmol) in H\textsubscript{2}O / ethylene glycol (1 : 12, 65 cm\textsuperscript{3}) by dropping funnel over 3 hours, and then the orange mixture was stirred at reflux for 40 h. The solution was cooled to 25 °C and excess saturated KPF\textsubscript{6} (aq) was added. The product was extracted with dichloromethane, dried over MgSO\textsubscript{4} and evaporated to dryness.

The product was purified by repeated column chromatography on silica. Elution with MeCN–water–saturated aqueous KNO\textsubscript{3} (100 : 10 : 1) resulted in two yellow bands moving down the column – the second major band was collected, and purified further by another column. After removing acetonitrile by rotary evaporation, excess saturated aqueous KPF\textsubscript{6} was added and the product was extracted from the suspension into dichloromethane. The organic layer was separated, dried over MgSO\textsubscript{4}, and the solvent removed in vacuo to yield [Ru(L\text{ph})\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}, 4 : 1 mer:fac isomers, as a yellow solid. Yield: 0.10 g, 61 %. ESMS m/z 1423 (M – PF\textsubscript{6})\textsuperscript{+}, 639 (M – 2PF\textsubscript{6})\textsuperscript{2+}, 426 (M + H – 2PF\textsubscript{6})\textsuperscript{3+}. UV/Vis in MeCN [\lambda_{\text{max/nm}}(10\textsuperscript{-3} \epsilon/M^{-1} cm^{-1})]: 397 (14.6), 282 (79.2), 248 (76.3).
Fig. S10. UV vis spectrum (MeCN) of [Ru(Lph)₃](PF₆)₂, 4 : 1 mer:fac isomers.

Fig. S11. Electrospray mass spectrum of [Ru(Lph)₃](PF₆)₂, 4 : 1 mer:fac isomers.
Fig. S12. COSY spectrum (400 MHz, CD$_3$CN) of [Ru(L$_{ph}$)$_3$](PF$_6$)$_2$, 4 : 1 mer:fac isomers.

[Ru$_3$Co$_3$(L$_{ph}$)$_9$](BF$_4$)$_8$(PF$_6$)$_8$
Fig. S13. Expansions of the electrospray mass spectrum of [Ru₃Co₃(L₉)₉](BF₄)₁₂ showing the {[Ru₃Co₃(L₉)₉](BF₄)}₅⁺ and {[Ru₃Co₃(L₉)₉](BF₄)}₄⁺ peaks (m/z = 924 and 1177, respectively), black = experimental, red = predicted.

Fig. S14. UV vis spectrum (MeCN) of [Ru₃Co₃(L₉)₉](BF₄)₁₂ (black) compared to RuL₉ (red)
Fig. S15. Paramagnetic $^1$H NMR spectrum (400MHz, CD$_3$CN) of redissolved crystals of [Ru$_3$Co$_3$(L$_{ph}$)$_3$](BF$_4$)$_{12}$.

[Ru$_4$Co$_4$(L$_{ph}$)$_{12}$](BF$_4$)$_8$(PF$_6$)$_8$

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**Table 1.** Table summarising the key crystallographic information for correct* and deliberate mis-assignment** of the different metal sites.

*Correct assignment of metals gives sensible thermal parameters.
**Deliberate mis-assignment of metals with physically unreasonable thermal parameters.