Supporting information for:

Ternary self-assemblies in water: forming a pentanuclear $ReLn_4$ assembly by association of binuclear lanthanide binding pockets with *fac*-Re $(CO)_3$(dinicotinate)$_2$Cl

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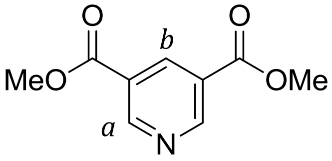
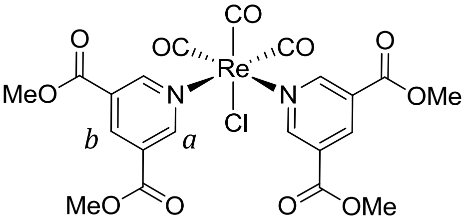
SYNTHESIS:

DIMETHYL PYRIDINE-3,5-DICARBOXYLATE



Thionyl chloride (0.54 mL, 7.5 mmol) was added dropwise to dinicotinic acid (500 mg, 3.0 mmol) suspended in methanol (25 mL) at 0°C. The reaction mixture was refluxed overnight under nitrogen. The reaction was quenched with drops of water, then extracted with dichloromethane and washed with saturated sodium bicarbonate solution. The white suspension became a solution. Further extractions with ethyl acetate and washings with sodium bicarbonate solution were performed, and the organic layers combined, dried over sodium sulphate, filtered and concentrated under reduced pressure. Yield: δ_H/ppm (300 MHz, $CDCl_3$) = 9.38 (2H, d, J=2.6 Hz, *a*), 8.89 (1H, t, J=2.6 Hz, *b*), 4.00 (6H, s, CH_3).
ES+ (*m/z*) 196 ($[M + H]^+$), ES- (*m/z*) 180 ($[M - CH_3]^-$).

RHENIUM TRICARBONYL BIS(DIMETHYL PYRIDINE-3,5-DICARBOXYLATE) CHLORIDE[1] *(1)*



Rhenium pentacarbonyl chloride (100 mg, 0.28 mmol) and dimethyl pyridine-3,5-dicarboxylate (108 mg, 0.55 mmol) were dissolved in 1:1 tetrahydrofuran:toluene (50 mL) and heated to reflux for 3 days. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The solid was redissolved in THF:toluene (5 mL), filtered, washed with petroleum ether (5 mL) and the residue collected. The filtrate was concentrated under reduced pressure, redissolved in THF:toluene (1 mL), washed with petroleum ether (5 mL), filtered, and the residue collected. The residues were dried under reduced pressure. Yield: 121 mg, 63%. δ_H/ppm (300 MHz, $CDCl_3$) = 9.53 (2H, d, J=1.8 Hz, *a*), 9.05 (1H, t, J=1.8 Hz, *b*), 4.00 (6H, s, CH_3). ES+ (*m/z*) 718.99 ($[M + Na]^+$). Accurate mass MICROTOF+ (*m/z*) predicted: 717.0021, 718.0054, 719.0049, 720.0081, 721.0021, 722.0053 ($[M + Na]^+$); measured: 717.0027, 718.0068, 719.0050, 720.0086, 721.0049 ($[M + Na]^+$). IR ν(CO) 2030, 1940, 1870 cm^{-1}. X-ray data: crystal system: triclinic; space group: P-1; colour: yellow; size (nm): 0.20 × 0.20 × 0.38.

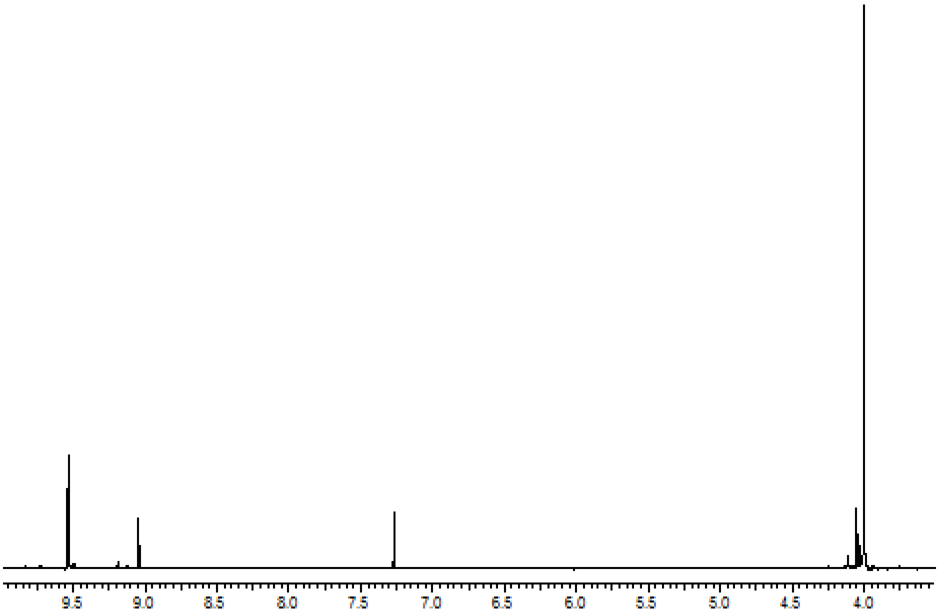


Figure S1. ^{1}H NMR of **1**

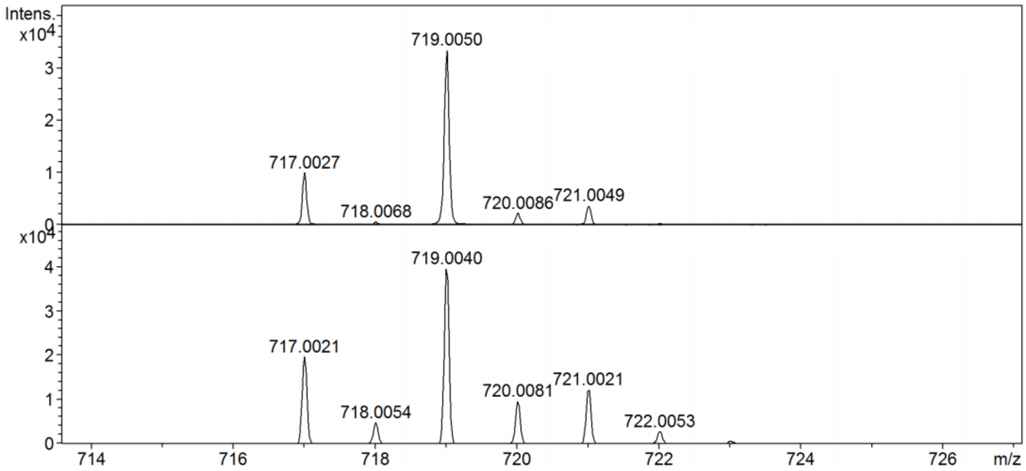
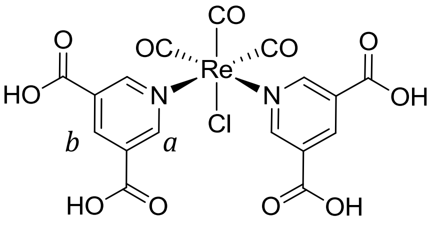


Figure S2. Predicted (top) and measured (bottom) high-resolution ESI-TOF mass spectrum for **1**.

RHENIUM TRICARBONYL BIS(PYRIDINE-3,5-DICARBOXYLIC ACID) CHLORIDE[2] *(2)*



1 (48 mg, 0.069 mmol) and lithium hydroxide (17 mg, 0.041 mmol) were dissolved in ethanol (5 mL) and the brown solution was refluxed and monitored by TLC. After two days a suspension had formed, and on the third day the reaction mixture was centrifuged and the residue was found to contain the product. Yield: 14 mg (0.023 mmol, 33%) δ_H/ppm (300 MHz, $CDCl_3$) = 8.97 (2H, d, J=2.1 Hz, *a*), 8.54 (1H, t, J=2.1 Hz, *b*). ESI-TOF MS m/z = 662.25 ($M+Na^+$).

ABSORPTION, EMISSION AND EXCITATION SPECTRA

Absorption and emission spectra were recorded in TRIS at pH 9, the concentration was kept below 10^{-4} M (due to the low solubility of **1** a 1:4 TRIS/MeCN solvent mixture was used). The point of excitation was 260 nm for the emission spectra. The point of observation was 425 nm for the excitation spectra. The resolution is 2 nm.

The luminescence spectra were recorded on a Horiba Fluorolog 3. The absorption spectra were recorded on a conventional single beam spectrometer and are baseline and dark corrected.

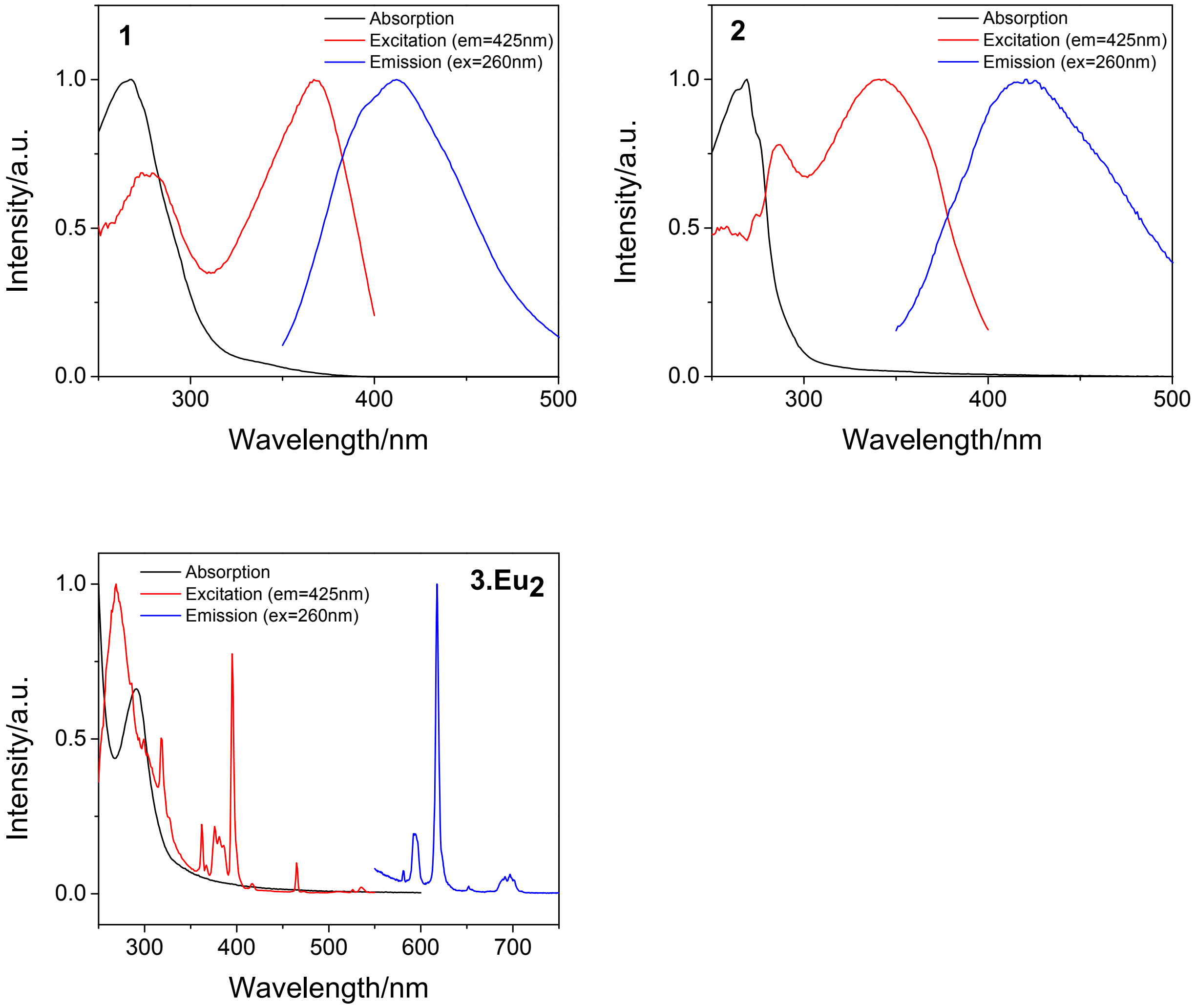


Figure S3. Absorption, emission and excitation spectra of **1**, **2** **3**. Eu$_2$.

LUMINESCENCE LIFETIMES

Absorption and emission spectra were recorded in TRIS at pH 9, the concentration was kept below 10^{-4} M (due to the low solubility of **1** a 1:4 TRIS/MeCN solvent mixture was used). The point of excitation was for the europium centred emission 260 nm, and for the rhenium centred emission at 375 nm.

The measurements were performed on a Horiba Fluorolog 3, modified to allow for excitation using Edinburgh Instruments pulsed solid-state lasers as excitation source. A TSCPC card from EI was used to record the time resolved emission profiles for the rhenium centred emission.

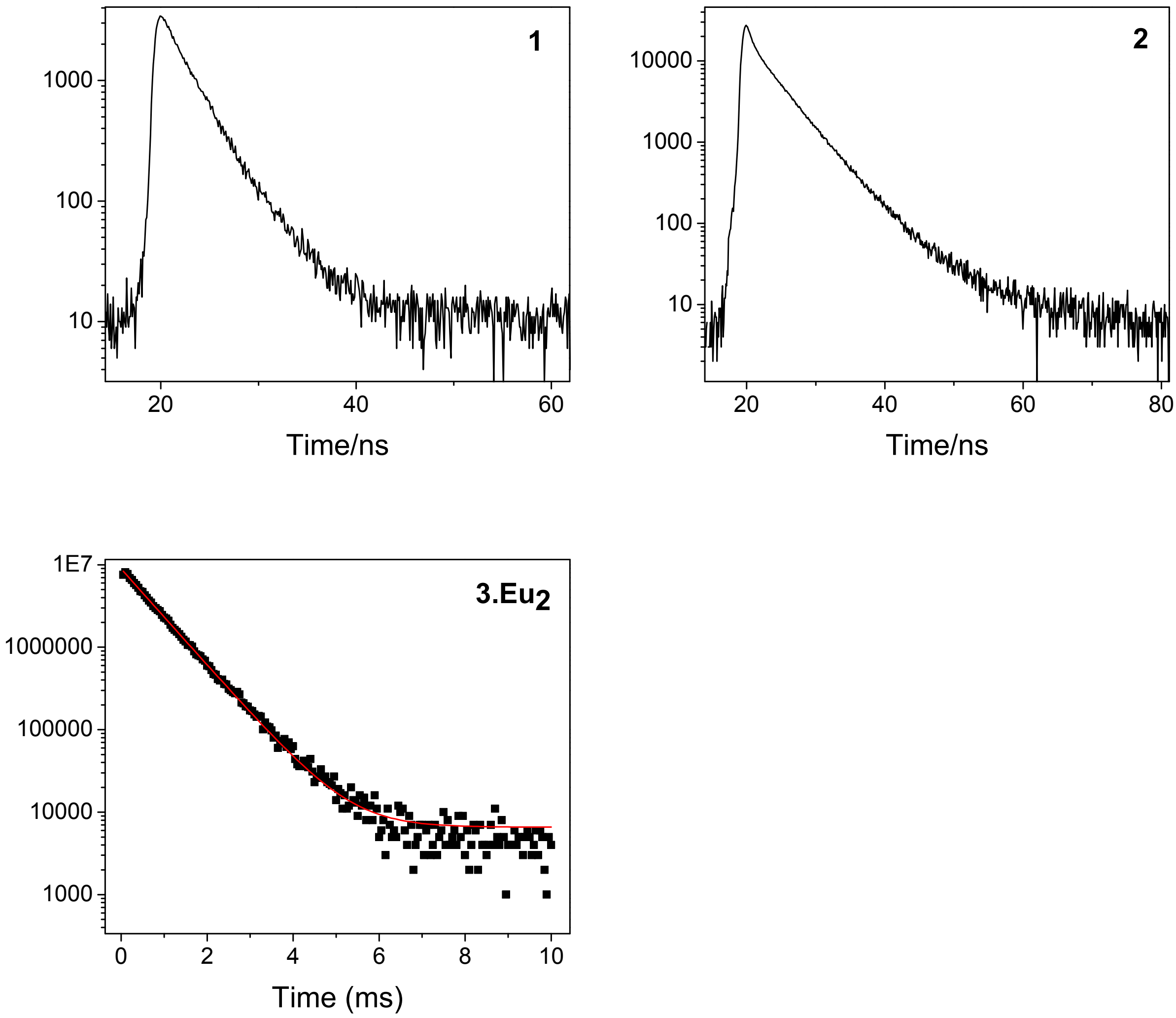


Figure S4. Time-resolved emission profiles of **1**, **2** **3**. Eu_2. The unit of the y-axis is in counts.

TITRATIONS WHERE THE CONCENTRATION OF THE RHENIUM SPECIES **2** IS KEPT CONSTANT:

The concentration of **2** was kept at $5{\cdot}10^5$ M. To 2 mL of this solution a solution containing a high concentration of **3**.Eu$_2$ and $5{\cdot}10^5$ M of **2** was added in microliter increments. After each addition the total emission spectrum was recorded on a Perkin Elmer LS55 or the emission spectrum was recorded using the phosphorescence mode on a Horiba Fluorolog 3. The spectra contain a rhenium emission band and europium emission bands, each generating a separate data series. The intensity ratios cannot be used as the tail of the rhenium bands perturbs the europium emission spectrum. The titration monitored using the emission following 260 nm excitation. The first titration, in phosphorescence mode, resulted in 7 data series with 19 data points each. The second titration was conducted in total emission mode and resulted in 8 data series of 16 points.

Titrations where the concentration of the europium complex (**3**.Eu$_2$) is kept constant:

The concentration of **3**.Eu$_2$ was kept at $5{\cdot}10^5$ M. To 2 mL of this solution a solution containing a high concentration of **2** and $5{\cdot}10^5$ M of **3**.Eu$_2$ was added in microliter increments. After each addition the emission spectrum was recorded using the phosphorescence mode on a Horiba Fluorolog 3. The spectra contain seven distinct europium bands which each constitute a data series. The intensity ratio of the $\Delta J=2$ band at 613 nm and the four most intense bands were generated and each constitute an independent measure with regards to the association of **2** and **3**.Eu$_2$; as such each can be used as a data series. The two titrations yielded 14 data series with 18 data points from the each titration. A high concentration of **2** was used in the latter titration allowing for it to continue into the regime where Stern-Volmer quenching dominates the binding isotherm.

TITRATING **2** WITH **3**.EU$_2$

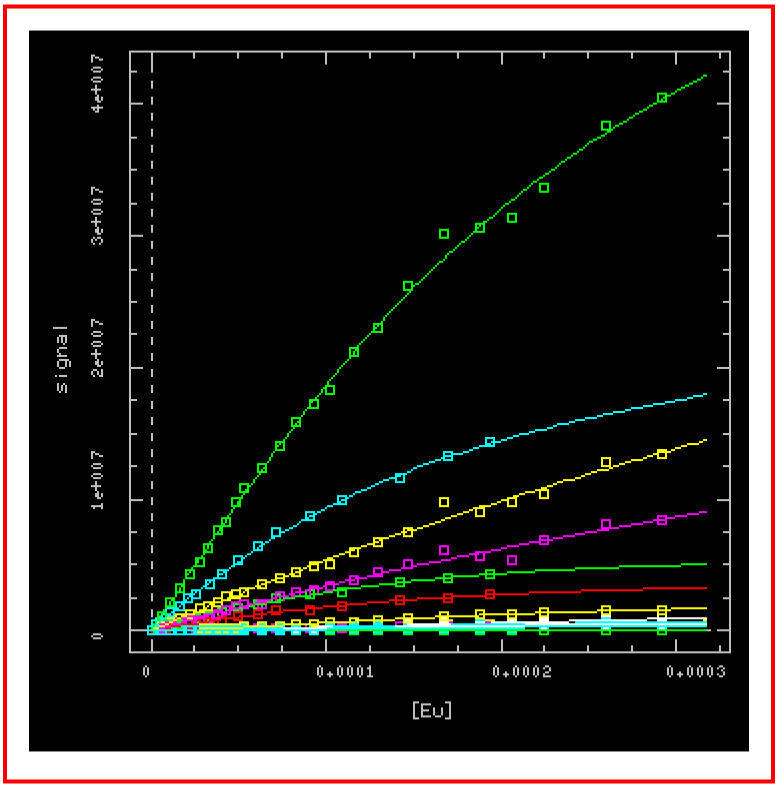
Model discrimination is performed using DynaFit and are all conducted as global fits.

MODEL: SEQUENTIAL, IDENTICAL K:

2 + 3 = 2:3 ; K1

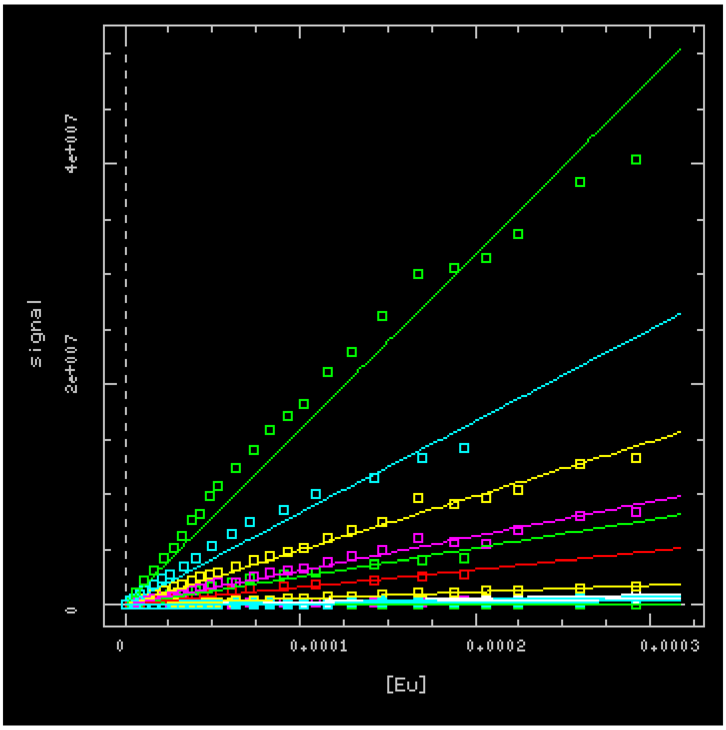
2:3 + 3 = 3:2:3 ; K2

K1 = K2



MODEL: COOPERATIVE:

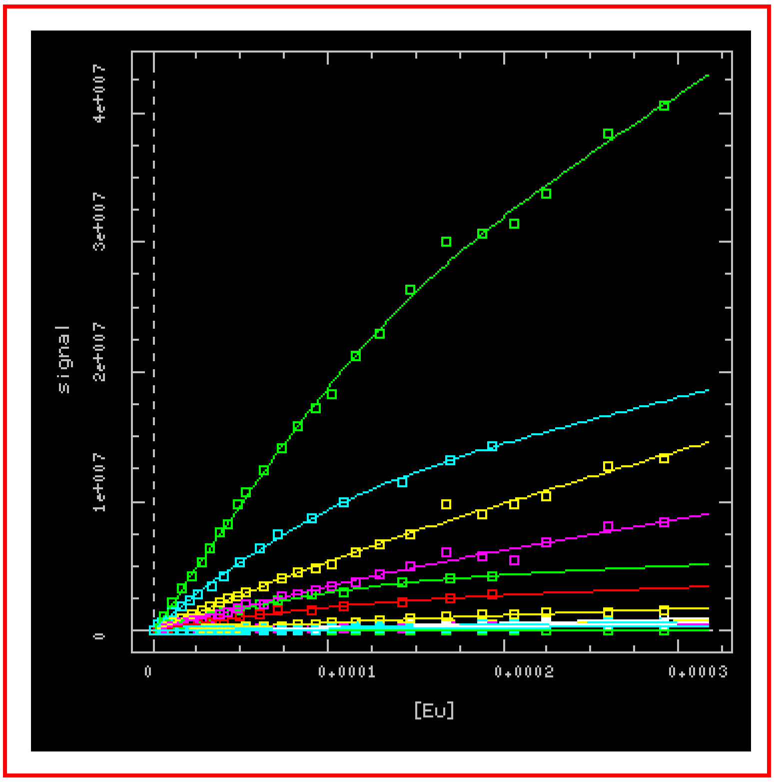
2 + 3 + 3 = 3:2:3 ; K



MODEL: SEQUENTIAL:

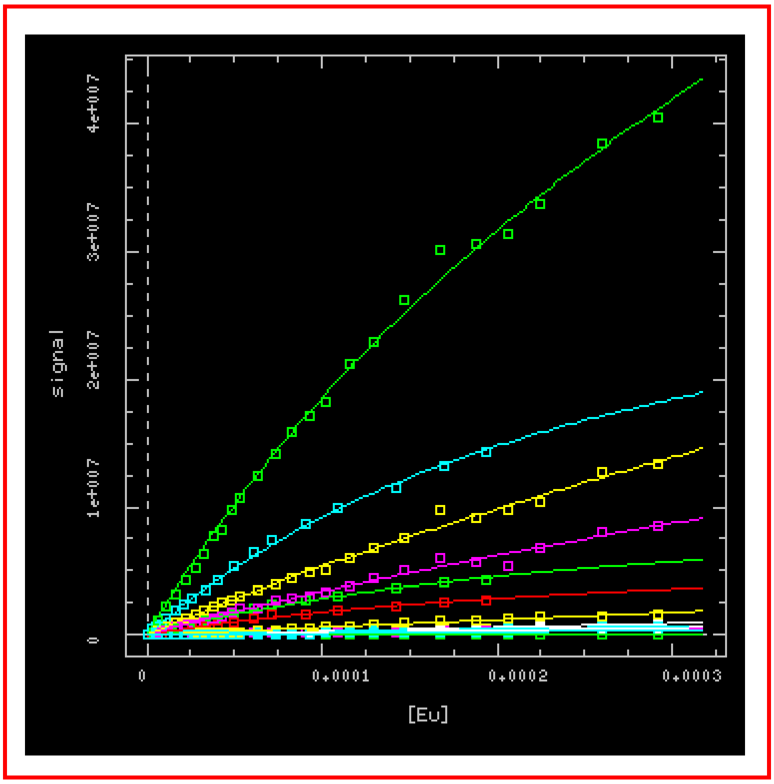
2 + **3** = **2**:**3** ; **K1**

2:**3** + **3** = **3**:**2**:**3** ; **K2**

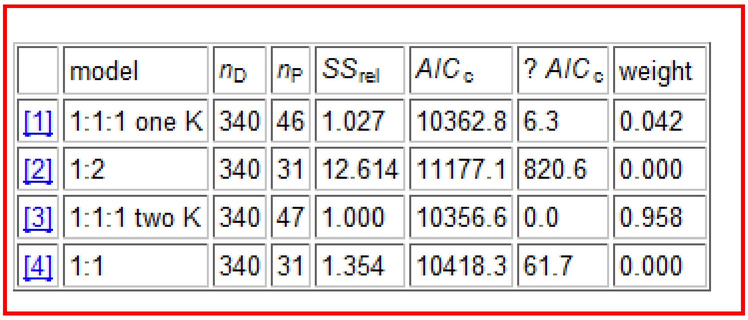


MODEL: 1 TO 1:

2 + **3** = **2**:**3** ; **K**

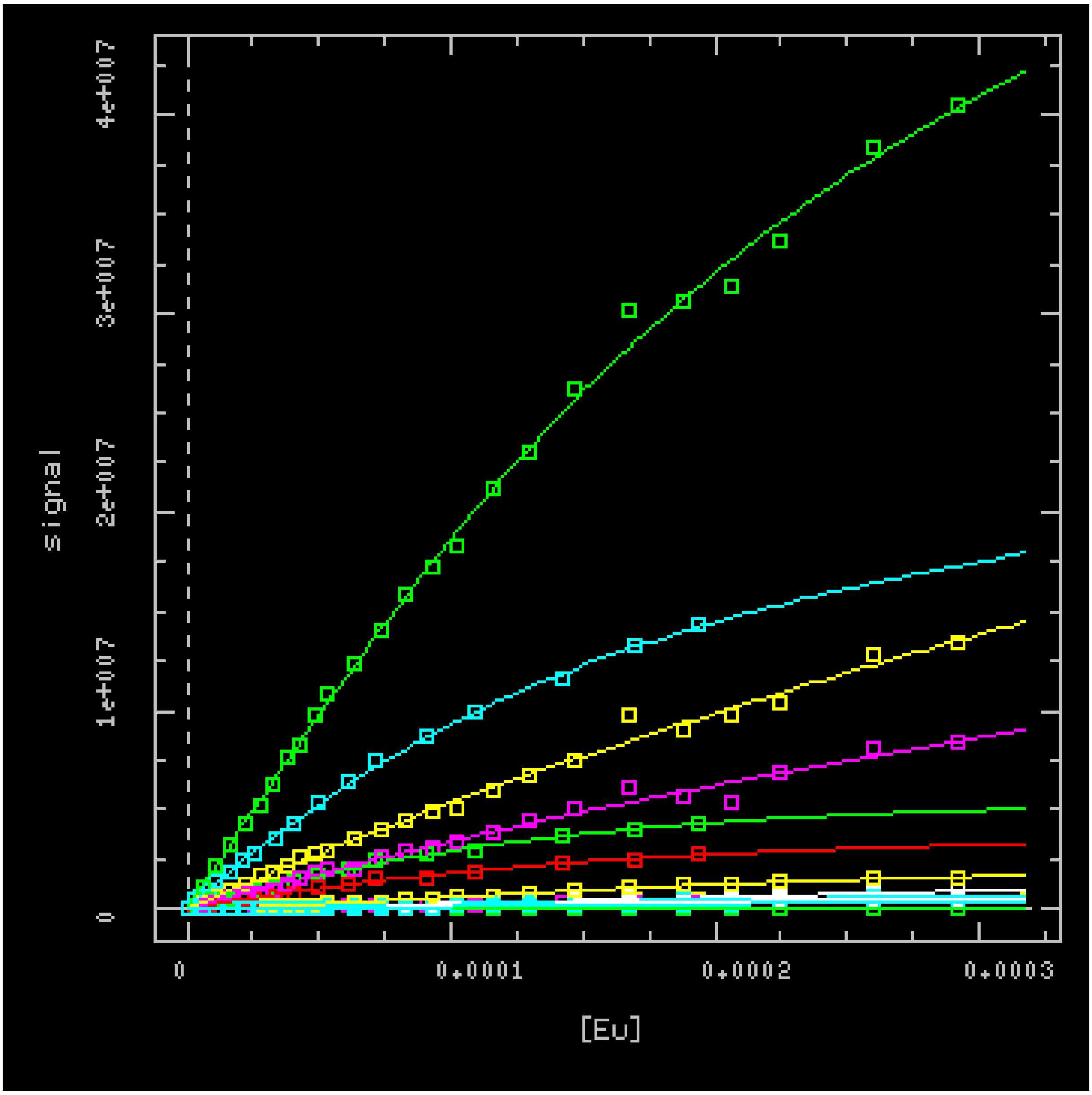


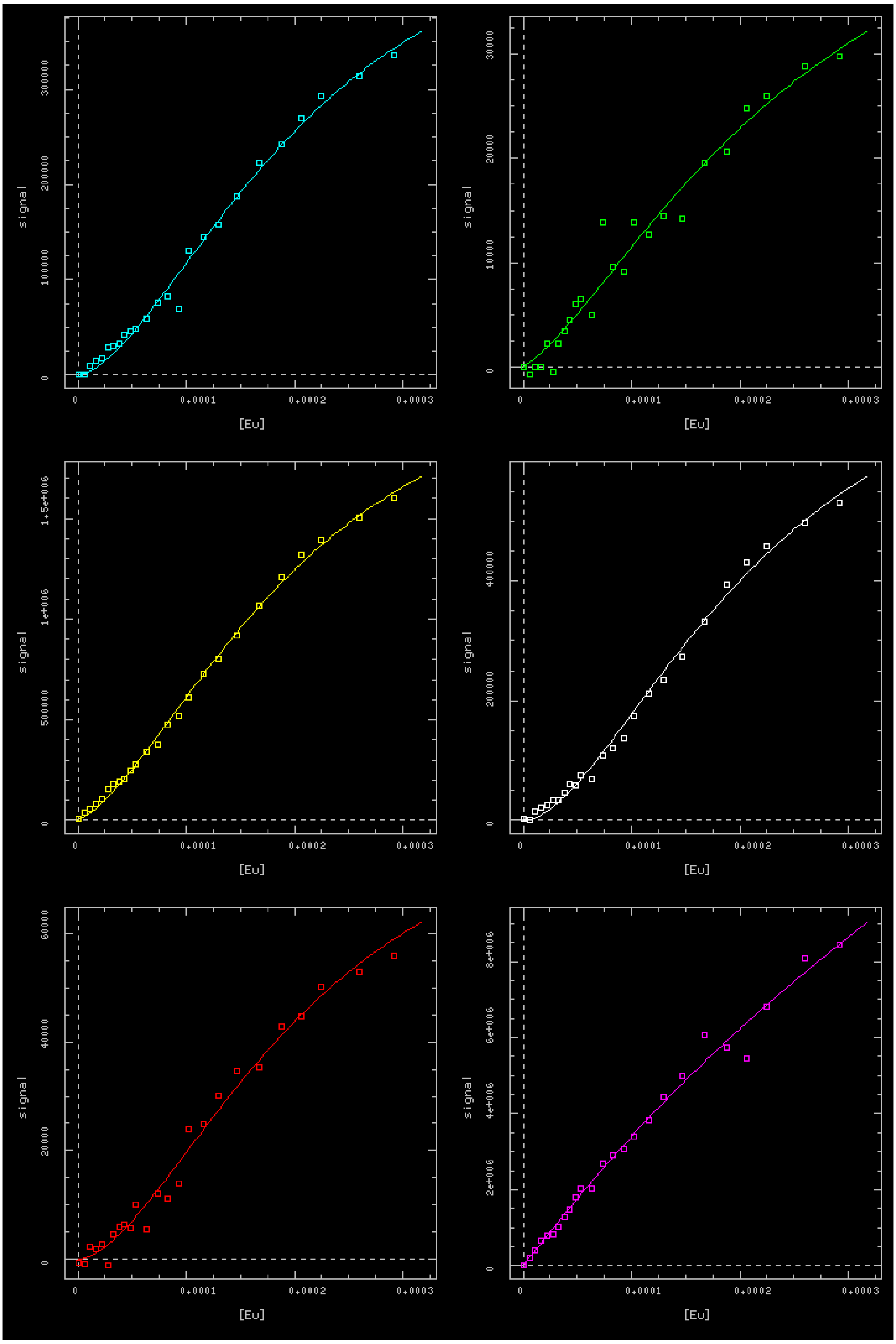
RESULT FROM MODELDISCRIMINATION:



	model	n_D	n_P	SS_{rel}	AIC_c	? AIC_c	weight
[1]	1:1:1 one K	340	46	1.027	10362.8	6.3	0.042
[2]	1:2	340	31	12.614	11177.1	820.6	0.000
[3]	1:1:1 two K	340	47	1.000	10356.6	0.0	0.958
[4]	1:1	340	31	1.354	10418.3	61.7	0.000

FINAL RESULTS OF TITRATING **2** WITH **3**.EU$_2$




signal
300000
200000
100000
0
0
0.0001
0.0002
0.0003
[Eu]
signal
30000
20000
10000
0
0
0.0001
0.0002
0.0003
[Eu]
signal
1.5e+006
1e+006
500000
0
0
0.0001
0.0002
0.0003
[Eu]
signal
400000
200000
0
0
0.0001
0.0002
0.0003
[Eu]
signal
60000
40000
20000
0
0
0.0001
0.0002
0.0003
[Eu]
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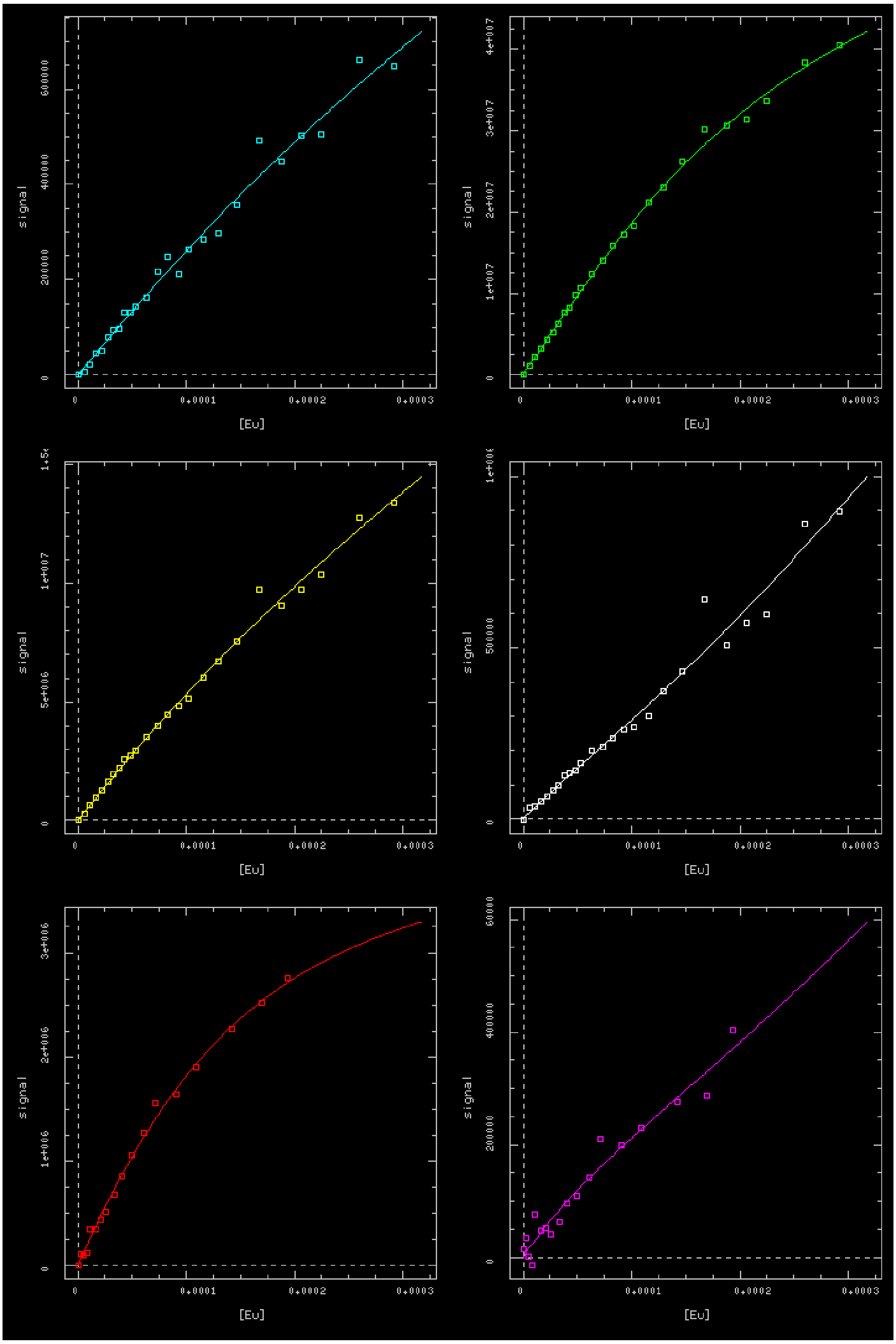
8e+006
6e+006
4e+006
2e+006
0
0
0.0001
0.0002
0.0003
[Eu]


signal
0
200000
400000
600000
0
0.0001
0.0002
0.0003
[Eu]
signal
0
1e+007
2e+007
3e+007
4e+007
0
0.0001
0.0002
0.0003
[Eu]
signal
0
5e+006
1e+007
1.5e
0
0.0001
0.0002
0.0003
[Eu]
signal
0
500000
1e+00
0
0.0001
0.0002
0.0003
[Eu]
signal
0
1e+006
2e+006
3e+006
0
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0.0002
0.0003
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400000
600000
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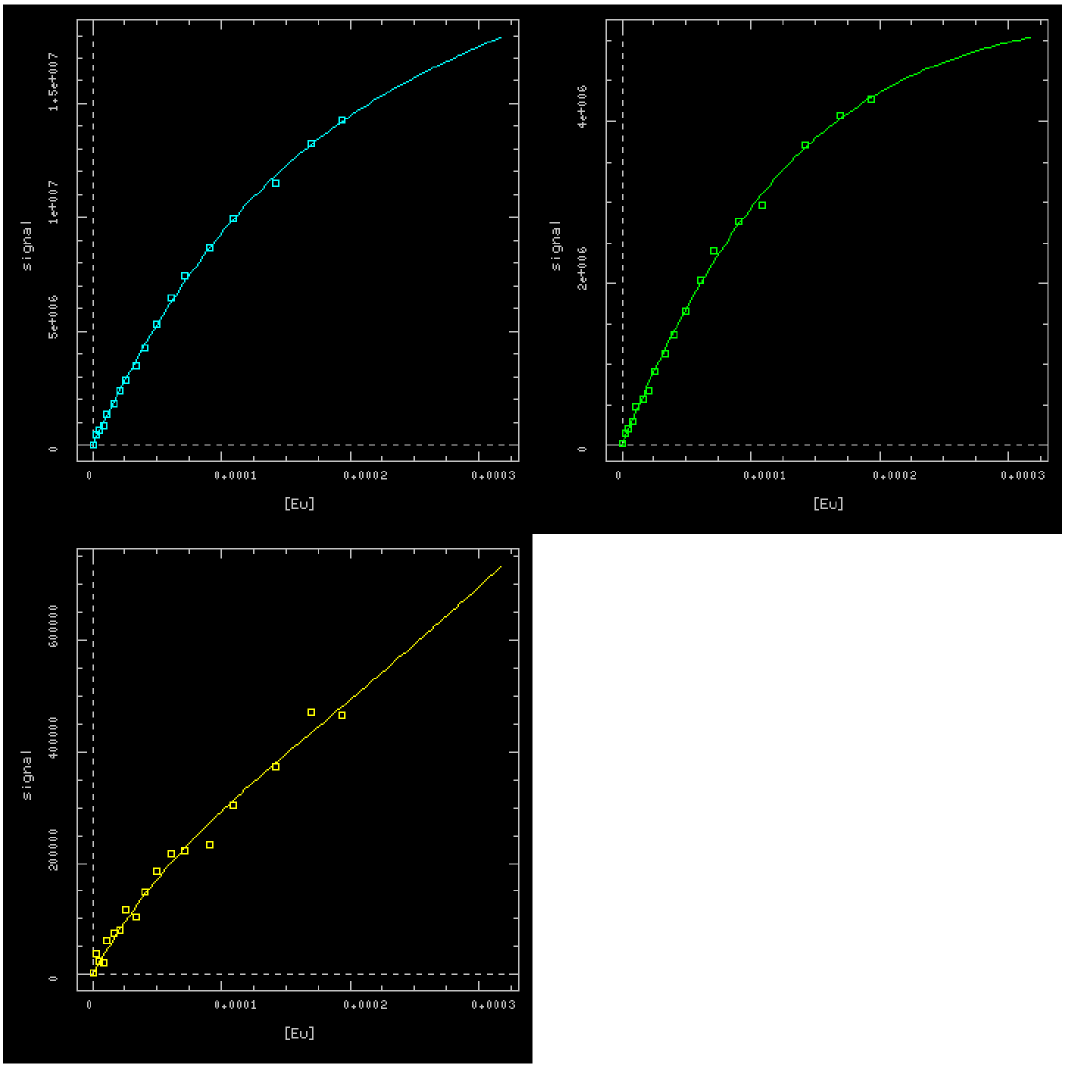
0.0001
0.0002
0.0003
[Eu]


signal
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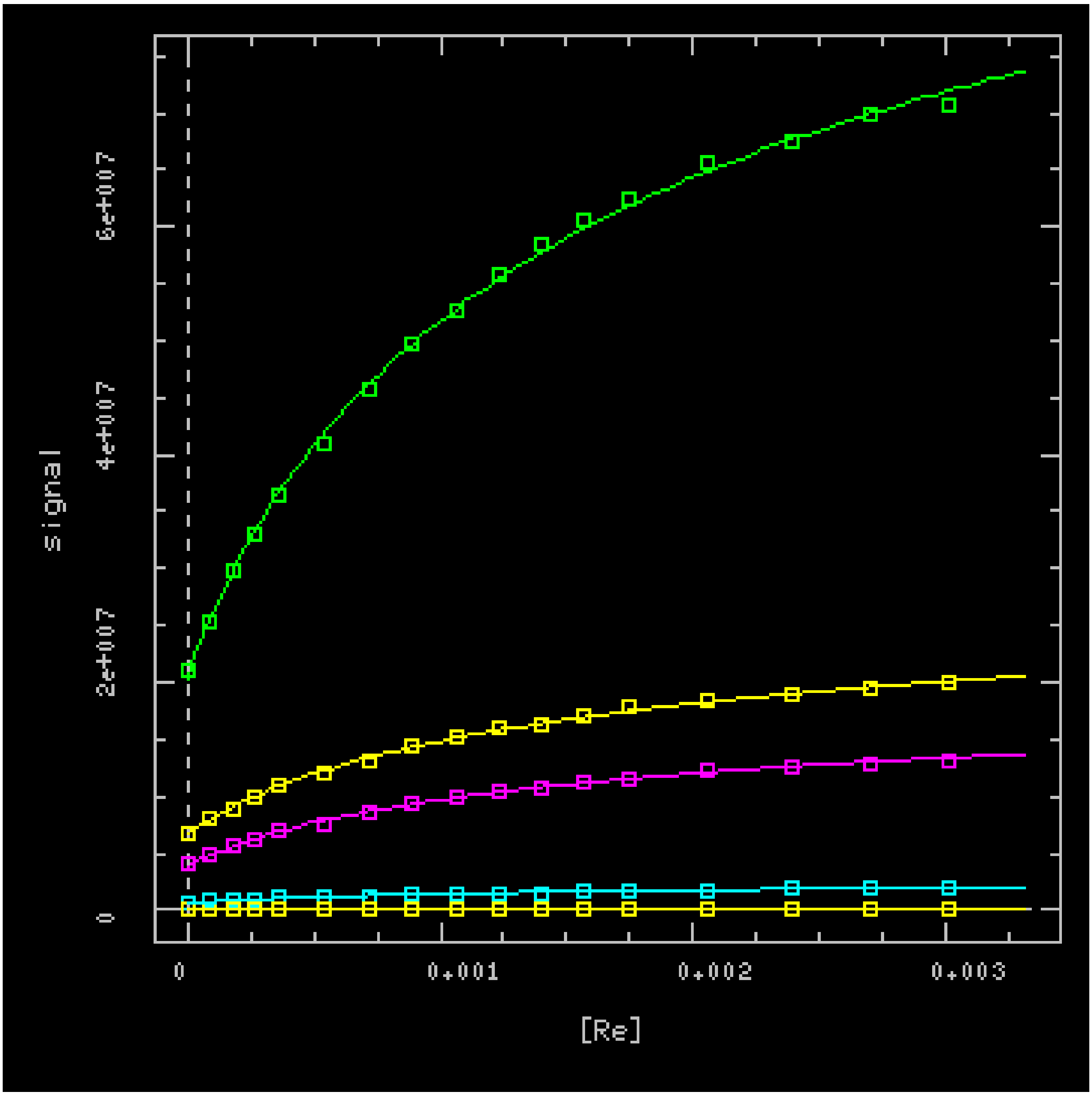
1e+007
5e+006
0
0
0.0001
0.0002
0.0003
[Eu]
signal
4e+006
2e+006
0
0
0.0001
0.0002
0.0003
[Eu]
signal
600000
400000
200000
0
0
0.0001
0.0002
0.0003
[Eu]

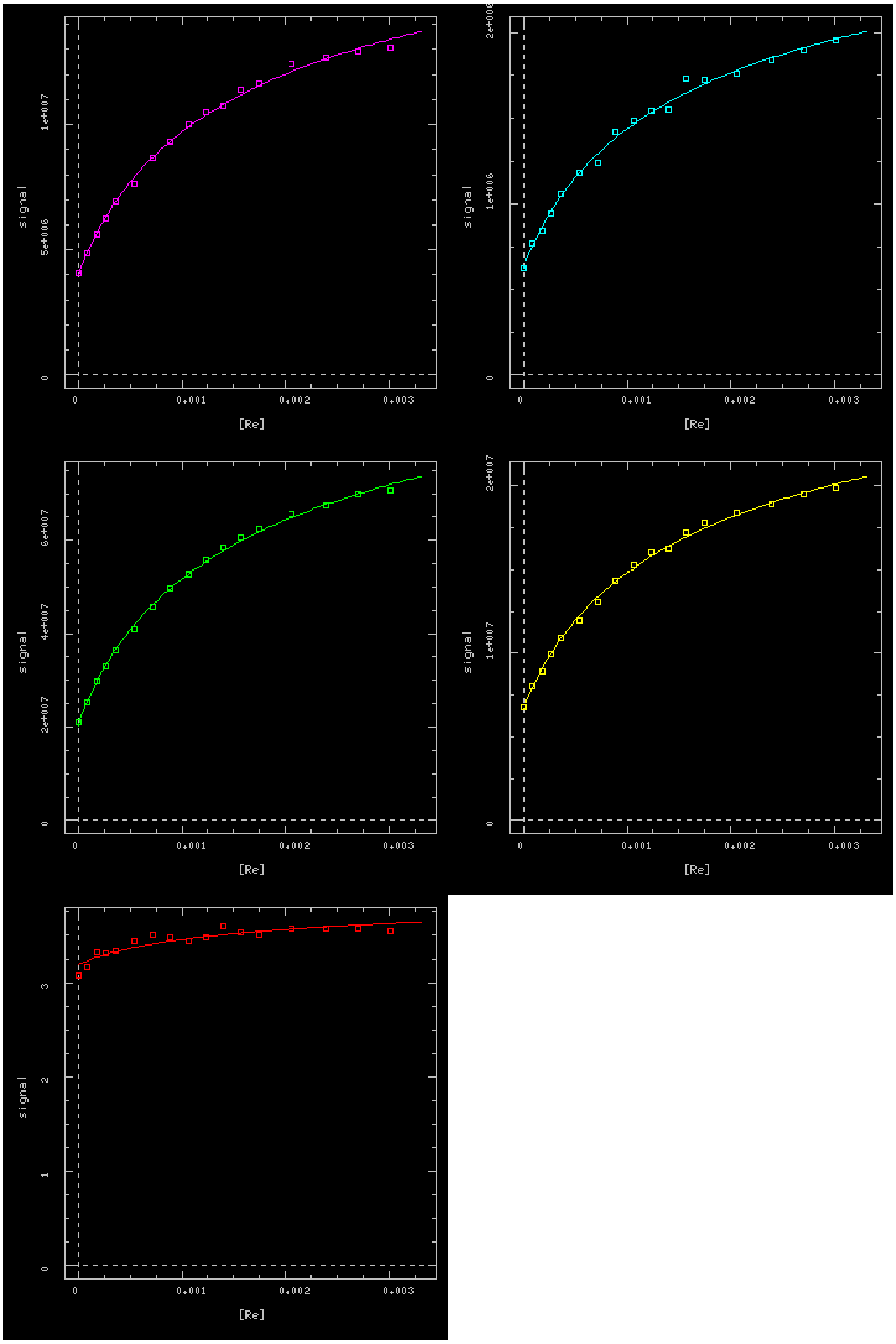
FINAL RESULTS OF TITRATING **3**.EU_2 WITH **2**

Only a sub set of data sets shown; can only be fitted by:

COOPERATIVE:

2 + 3 + 3 = 3:2:3 ; K




signal
1e+007
5e+006
0
0.001
0.002
0.003
[Re]
signal
2e+006
1e+006
0
0.001
0.002
0.003
[Re]
signal
6e+007
4e+007
2e+007
0
0.001
0.002
0.003
[Re]
signal
2e+007
1e+007
0
0.001
0.002
0.003
[Re]
signal
3
2
1
0
0.001
0.002
0.003
[Re]

SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION

Single crystal X-ray diffraction data were obtained for compound **1**. In each case, a typical crystal was mounted using the oil drop technique, in perfluoropolyether oil at 150(2) K using a Cryostream N_2 open-flow cooling device.[1] Diffraction data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. For the data collections, a series of ω-scans was performed in such a way as to collect a complete data set to a maximum resolution of 0.77 Å. Data reduction including unit cell refinement and inter-frame scaling was carried out using DENZO-SMN/SCALEPACK.[2] Intensity data were processed and corrected for absorption effects by the multi-scan method, based on repeat measurements of identical and Laue equivalent reflections. Structure solution was carried out with direct methods using the programs SIR92[3] within the CRYSTALS software suite.[4] In general, coordinates and anisotropic displacement parameters of all non-hydrogen atoms were refined freely except where disorder necessitated the use of "same distance restraints" together with thermal similarity and vibrational restraints to maintain sensible geometry/displacement parameters. Hydrogen atoms were generally visible in the difference map and refined with soft restraints prior to inclusion in the final refinement using a riding model.[5] Tables summarising the X-ray crystallographic data follow.

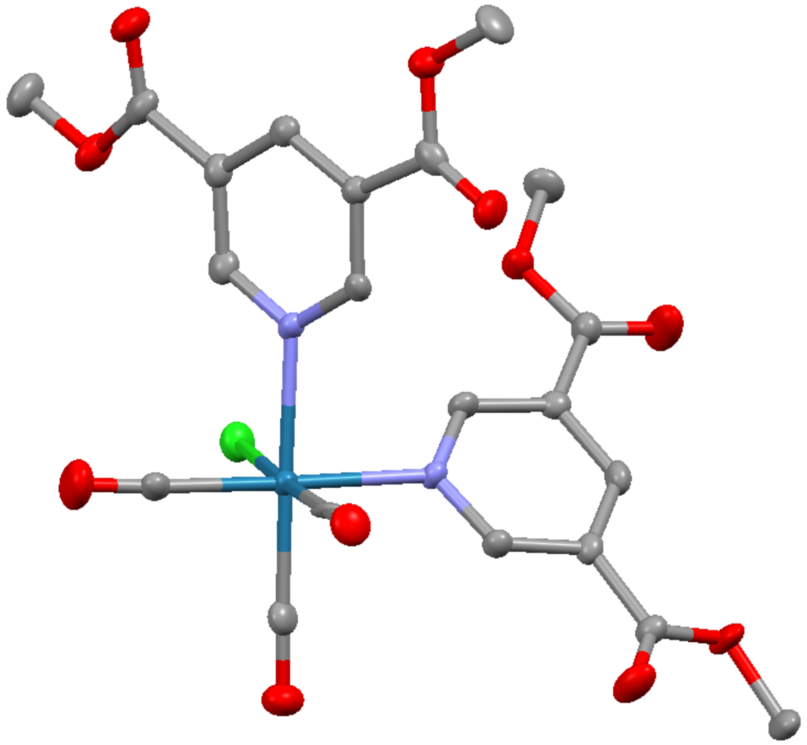


Figure 1. X-ray crystal structure of Rhenium complex (**1**) with thermal ellipsoids shown at 50% created in Mercury (3.1). Hydrogen atoms have been omitted for clarity.

Compound name	**1**
Chemical Formula	$C_{21}H_{18}ClN_2O_{11}Re$
FW	696.03
Crystal system	Triclinic
Space group	P-1
Crystal colour	Yellow
Crystal size (mm)	0.20 × 0.24 × 0.38
a (Å)	10.5500(2)
b (Å)	10.7458(2)
c (Å)	11.6084(2)
□□□□□	85.1863(9)
□□□□□	87.7739(9)
□□□□□	65.2832(8)
V (Å^3)	1191.23(4)
□	2
D_{calcd} (g/cm^3)	1.940
□ (mm^{-1})	5.276
F (000)	676
Reflections collected	48725
Unique reflections (R_{int})	5380 (0.056)
R_1 *(I>2□(I))*	0.073
wR'_2 (all data)	0.210

CRYSTALLOGRAPHIC DISTANCES OF RELEVANCE

Re1 . Cl2 . 2.464(4)
Re1 . N3 . 2.213(11)
Re1 . N12 . 2.213(12)
Re1 . C22 . 1.913(16)
Re1 . C24 . 1.894(17)
Re1 . C9 . 1.915(15)

CRYSTALLOGRAPHIC ANGLES OF RELEVANCE

Cl2 . Re1 . N3 . 85.5(3)
Cl2 . Re1 . N12 . 85.7(3)
N3 . Re1 . N12 . 88.2(4)
Cl2 . Re1 . C22 . 92.6(5)
N3 . Re1 . C22 . 90.2(5)
N12 . Re1 . C22 . 177.7(6)
Cl2 . Re1 . C24 . 177.4(4)
N3 . Re1 . C24 . 92.7(5)
N12 . Re1 . C24 . 92.4(5)
C22 . Re1 . C24 . 89.3(6)
Cl2 . Re1 . C9 . 92.4(5)
N3 . Re1 . C9 . 177.6(6)
N12 . Re1 . C9 . 90.7(5)
C22 . Re1 . C9 . 90.9(6)
C24 . Re1 . C9 . 89.4(6)
Re1 . N3 . C4 . 122.4(9)
Re1 . N3 . C6 . 119.5(9)
Re1 . N12 . C13 . 121.2(9)
Re1 . N12 . C21 . 121.4(10)
Re1 . C22 . O23 . 178.2(14)
Re1 . C24 . O25 . 178.4(13)
C18 . O3 . C25 . 116.2(13)
Re1 . C9 . O8 . 177.0(14)

H-Bonds/short contacts

C6 . H61 . O18 2_666 174.1(4) 0.929 2.583 3.51(2) yes
C10 . H101 . O25 1_565 163.9(4) 0.959 2.552 3.48(2) yes
C13 . H131 . O25 2_666 162.7(4) 0.930 2.511 3.41(2) yes
C19 . H191 . O28 2_665 144.9(4) 0.929 2.588 3.39(2)

References

1. Cosier, J.; Glazer, A. M., *Journal of Applied Crystallography* **1986,** *19*, 105-107.
2. Otwinowski, Z.; Minor, W., *Macromolecular Crystallography, Pt A* **1997,** *276*, 307-326.
3. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A., *Journal of Applied Crystallography* **1994,** *27*, 1045-1050.
4. Watkin, D.; Cooper, R.; Prout, C. K., *Zeitschrift Fur Kristallographie* **2002,** *217* (7-8), 429-430.
5. Cooper, R. I.; Thompson, A. L.; Watkin, D. J., *Journal of Applied Crystallography* **2010,** *43*, 1100-1107.