Supplementary Information

Self-assembly of a hydrogen bonded framework from a gold phosphine complex with a pendant uracil group.

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1. General Considerations.

The synthesis of $AuCl(SC_4H_8)$ was performed according to the literature procedure.[1] PPh_2Ur was prepared according to a method developed in our laboratory.[2] The preparation of **3**.2thf was performed under an atmosphere of dry nitrogen: the CH_2Cl_2 used in this reaction was purified with an Innovative Technology anhydrous solvent engineering system. Unless otherwise stated, the remaining manipulations were performed under ambient conditions using reagent grade solvents.

NMR spectra were recorded on a Bruker AVANCE 300 Spectrometer (Operating frequencies ^1H 300.13 MHz; ^{31}P 129.49 MHz, ^{13}C 75.47). ^{31}P and ^{13}C NMR spectra were acquired with proton decoupling.

Thermogravimetric analysis (TGA) was performed on a Stanton Redcroft STA-780 series thermal analyser. All samples were analysed in an alumina sample cup (~15 mg sample). The sample was exposed to an inert atmosphere using a gas flow of 20 ml min^{-1} He. A temperature ramp was programmed for 20 °C min^{-1} up to 1000 °C. Differential Thermal Analysis (DTA) data and mass loss (from TGA/TPO) data were collected.

Details of X-ray Diffraction Analysis

Single crystal X-ray diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using “SMART”.[3] Frame integration and unit-cell refinement software was carried out with “SAINT+”.[4] Absorption corrections were applied by SADABS (v2.03, Sheldrick).[5] Structures were solved by direct methods using SHELXS-97[6] and refined by full-matrix least squares using SHELXL-97.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions. In the structure of **3.thf$_2$** the C-O and C-C bond distances with the thf molecules were restrained to 1.44 Å and 1.54 Å respectively. The toluene molecule in the structure of **3.tol** was restrained to be planar using the FLAT 0.02 command in SHELXL and the C_{ipso}-CH_3 bond length restrained to 1.52 Å.

Powder X-ray data was collected at room temperature on a Bruker DB8 diffractometer with Cu-K_α radiation. Data were generally collected between 2θ 5 and 60 using a step size of 0.02 °. Predicted patterns were calculated using the “Powder” routine in the Mercury programme.[8]

The powder patter for elemental gold was generated from structure ICSD 64701 from on the CDC database.[9] We wish to acknowledge the use of the Chemical Database Service at Daresbury for these data.

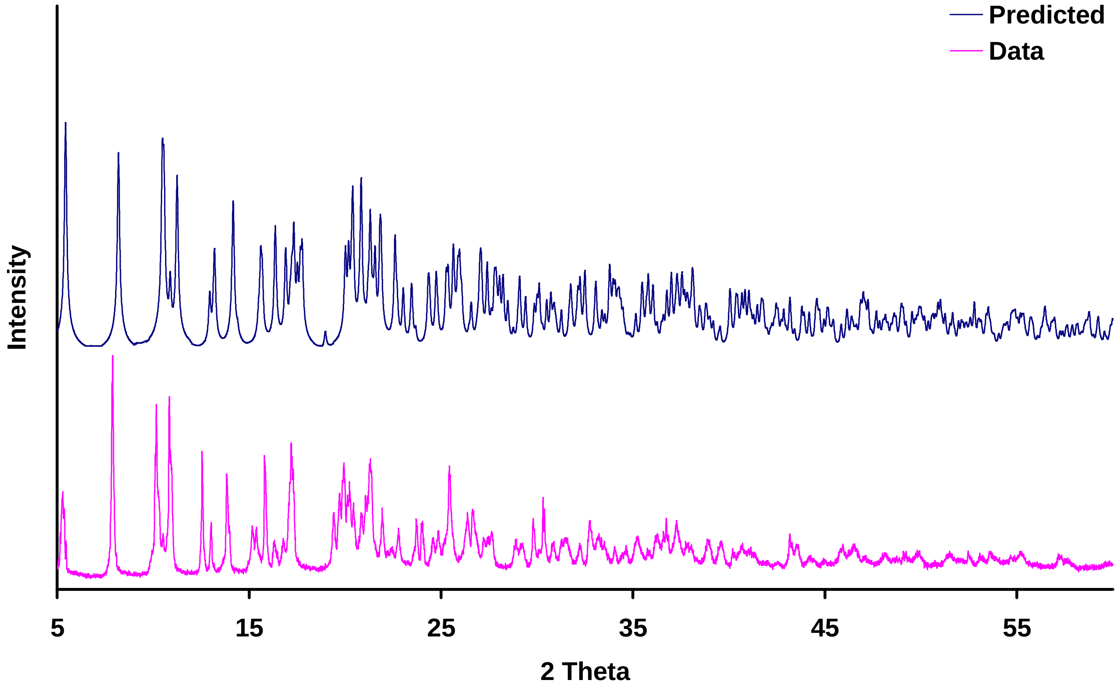
2. Synthesis of 3.thf$_2$

A Schlenk tube was charged with AuCl(SC_4H_8) (700 mg, 1.67 mmol) and PPh_2Ur (500 mg, 1.69 mmol) under argon and CH_2Cl_2 (65 ml) was added *via* cannula. After 1 hr of stirring a white ppt had formed, the solvent was removed *in vacuo* and the resulting colourless solid washed with hexane (4 x 30 ml). The white solid was then dissolved in warm methanol then layered with thf to afford colourless needle-like crystals. Alternatively, crystalisation may be performed by slow diffusion of hexane into a thf solution of **3**. ^{1}H NMR (d_6-DMSO) δ 11.63 (br s, 2H, N**H**), 7.49 (m, 4 H, ***Ph***), δ 7.34 (m, 6 H, ***Ph***), δ 7.13 (d, 1 H, $^{3}J_{\mathrm{PH}}$ = 11.3 Hz, uracil C6-***H***) δ 3.61 (m, 6.7 H, thf) δ 1.77 (m, 6.7 H, thf); ^{31}P{^{1}H} (d_6-DMSO) δ 24.4 (s); ^{13}C{^{1}H} (d_6-DMSO) δ 168.0(s, C=O), δ 162.5(s, ***C***=O), δ 150.9 (s, Ur-$\boldsymbol{C_6}$), δ 133.6 (d, $^{2}J_{\mathrm{PC}}$ = 15.3 Hz, Ph-$\boldsymbol{C_2}$), δ 132.1 (s, Ph-$\boldsymbol{C_4}$) δ 129.3 (d, $^{3}J_{\mathrm{PC}}$ = 12.1 Hz, Ph-$\boldsymbol{C_3}$) δ 127.4 (d, $^{1}J_{\mathrm{PC}}$ = 65.8 Hz, Ph-$\boldsymbol{C_1}$), δ 98.5 (d, $^{1}J_{\mathrm{PC}}$ = 81.8 Hz, Ur-$\boldsymbol{C_5}$). Ratio of **3**:thf from ^{1}H NMR = 1:1.7. Yield 425 mg (66 %)

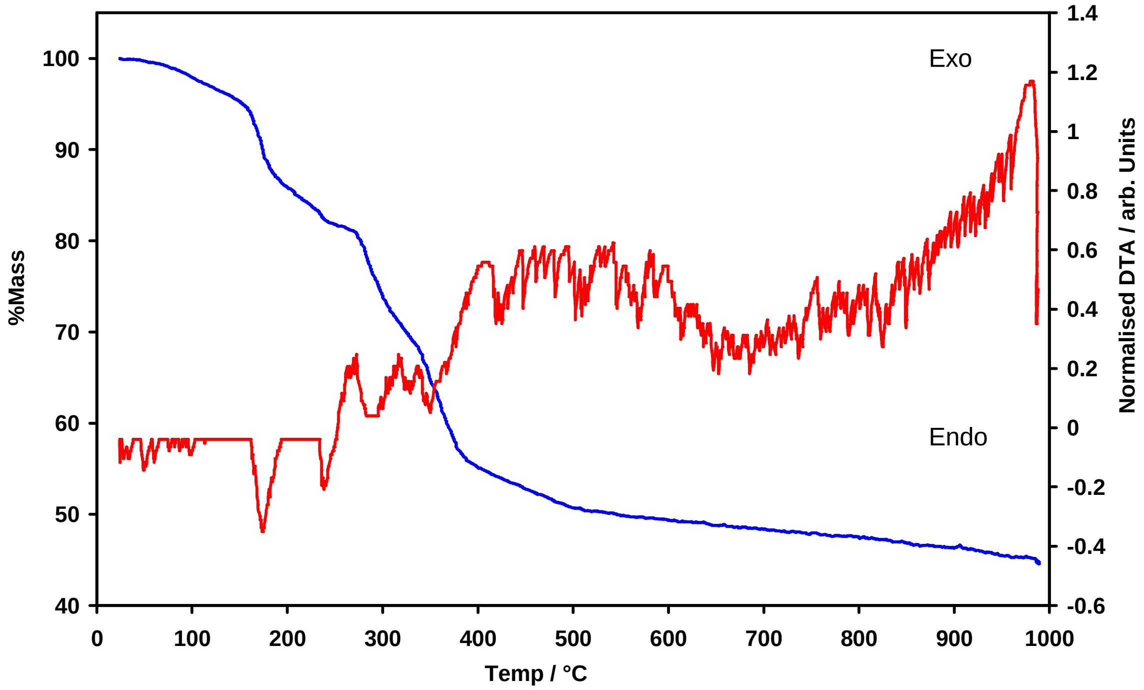
Aged samples of **3** (and **4)** take on a purple colouration possibly indicating the formation of elemental gold however pure **3.thf$_2$** can be reobtained by recrystallisation from thf/hexane.

Elemental Analysis	Expected for **3**.2thf (%)	C 42.84 H 4.34 N 4.16
	Expected for **3**.1.8thf (%)	C 42.32 H 4.19 N 4.25
	Found (%)	C 42.36 H 4.16 N 4.21

Powder X-ray diffraction Study on 3.thf$_2$



TGA/DSC study on 3.thf$_2$

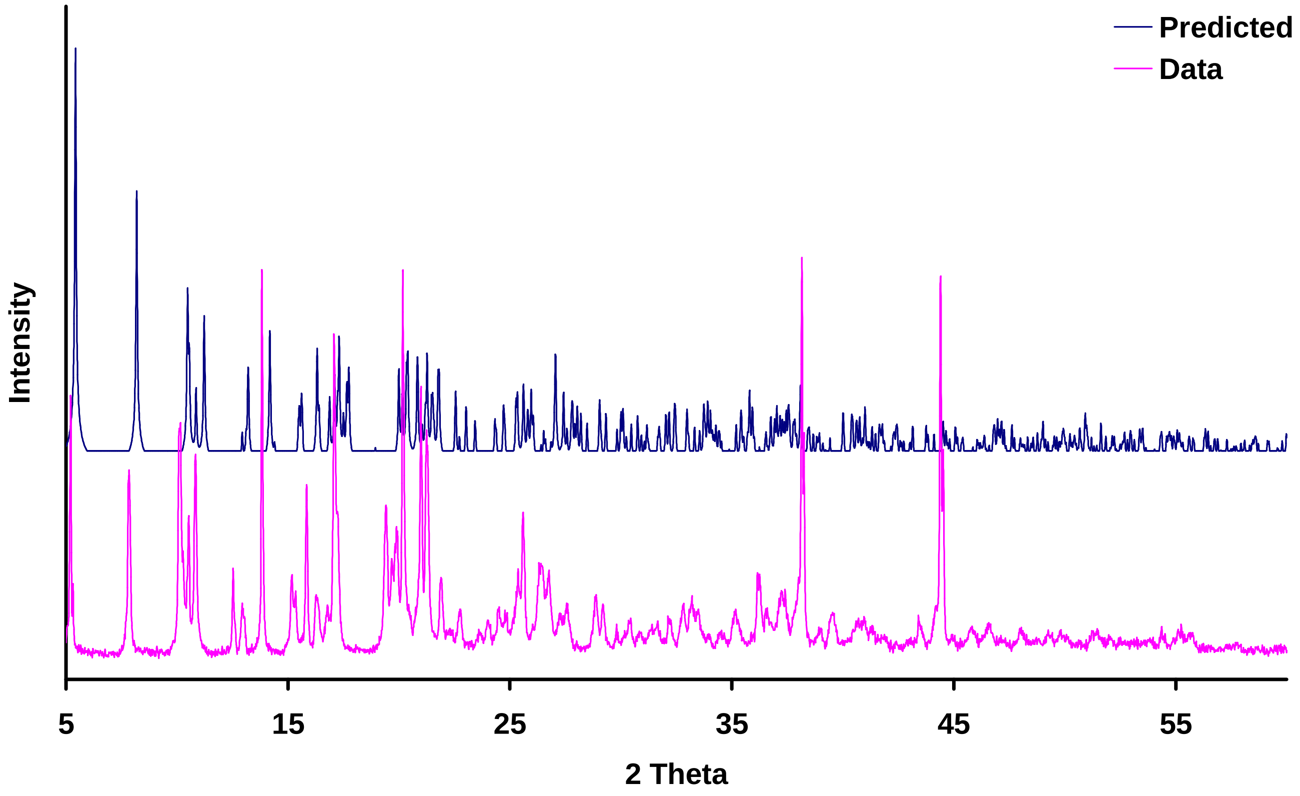


3. Preparation of 3vac

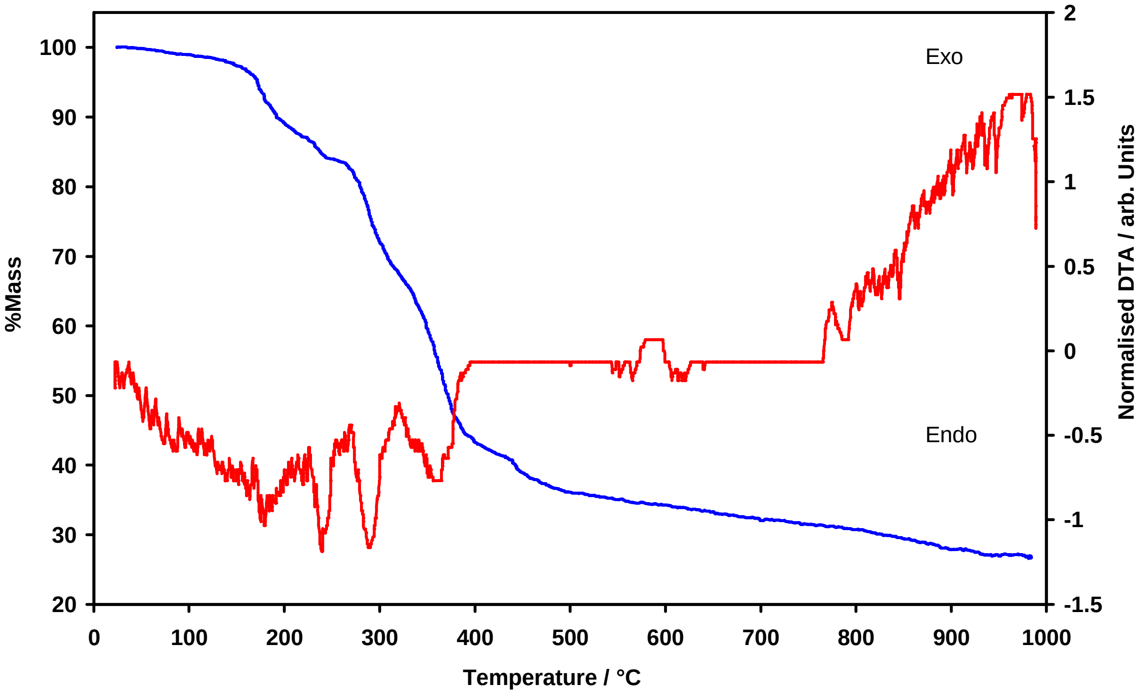
In a typical experiment, a sample vial was charged with 50 mg of **3.thf$_2$** and then placed in a Schlenk tube. The sample was then exposed to high vacuum (1 × 10^{-4} mbar) for 24 hours then sealed under an atmosphere of dry nitrogen. The ^{1}H and ^{31}P{^{1}H} NMR spectra of this material were essentially identical to **3.thf$_2$**, except that integration of the appropriate resonances in the ^{1}H NMR spectra demonstrated that 1.2 thf molecules were present per gold.

Elemental Analysis	Expected for **3.(thf)$_{1.2}$** (%)	C 40.61 H 3.70 N 4.55
	Expected for **3.(thf)$_{0.1}$** (%)	C 36.76 H 2.60 N 5.23
	Expected for **3** (%)	C 36.35 H 2.48 N 5.30
	Found (%)	C 36.61 H 2.63 N 5.63

Powder X-ray diffraction Study on 3vac



TGA/DSC study on 3.vac

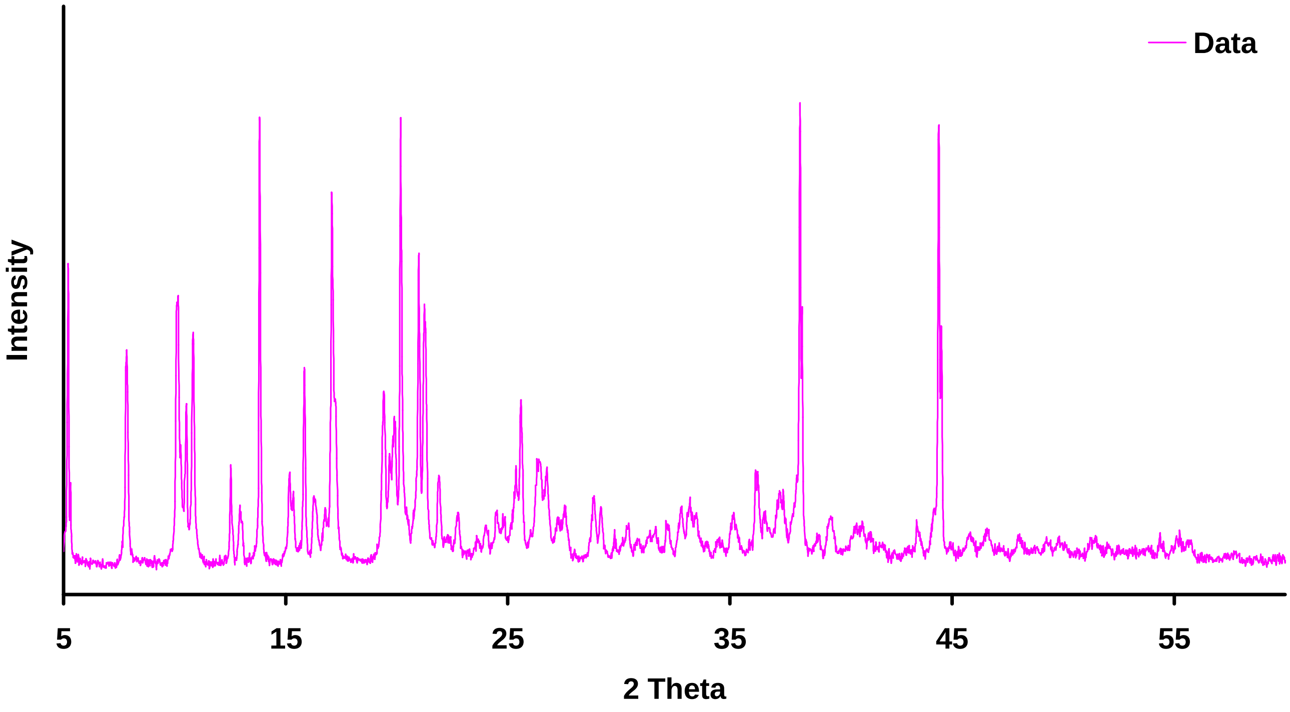

%Mass
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800
900
1000
Temperature / °C
2
1.5
1
0.5
0
-0.5
-1
-1.5
Normalised DTA / arb. Units
Exo
Endo

4. Preparation of 3resolv

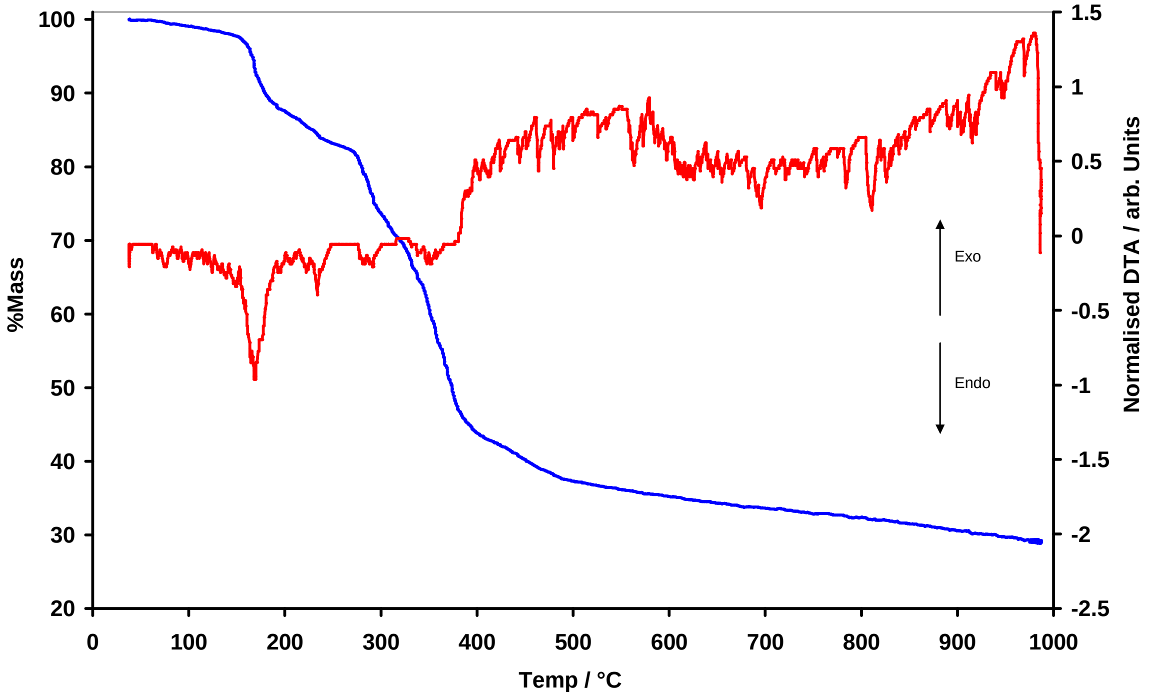
A sample of **3vac** was prepared as described in Section 3. The sample vial containing **3**vac was then transferred into a vessel containing *ca.* 3 ml of THF. The vessel was then tightly sealed and stored for a minimum of 24 hours before appropriate analysis. In some instances samples were stored under THF vapour for prolonged periods. The ^{1}H and ^{31}P{^{1}H} NMR spectra of this material were essentially identical to **3.thf$_2$**, except that integration of the resonances demonstrated that 1.8 thf molecules were present per gold.

Elemental Analysis	Expected for **3.(thf)**$_{1.8}$ (%)	C 42.32 H 4.19 N 4.25
	Expected for **3.thf** (%)	C 39.98 H 3.52 N 4.66
	Expected for **3.(thf)$_{0.8}$** (%)	C 39.33 H 3.33 N 4.78
	Found (%)	C 39.34 H 3.88 N 3.38

Powder X-ray diffraction Study on 3.vac treated with THF vapour



TGA/DSC study on 3.vac after treatment with THF vapour


100
90
80
70
60
50
40
30
20
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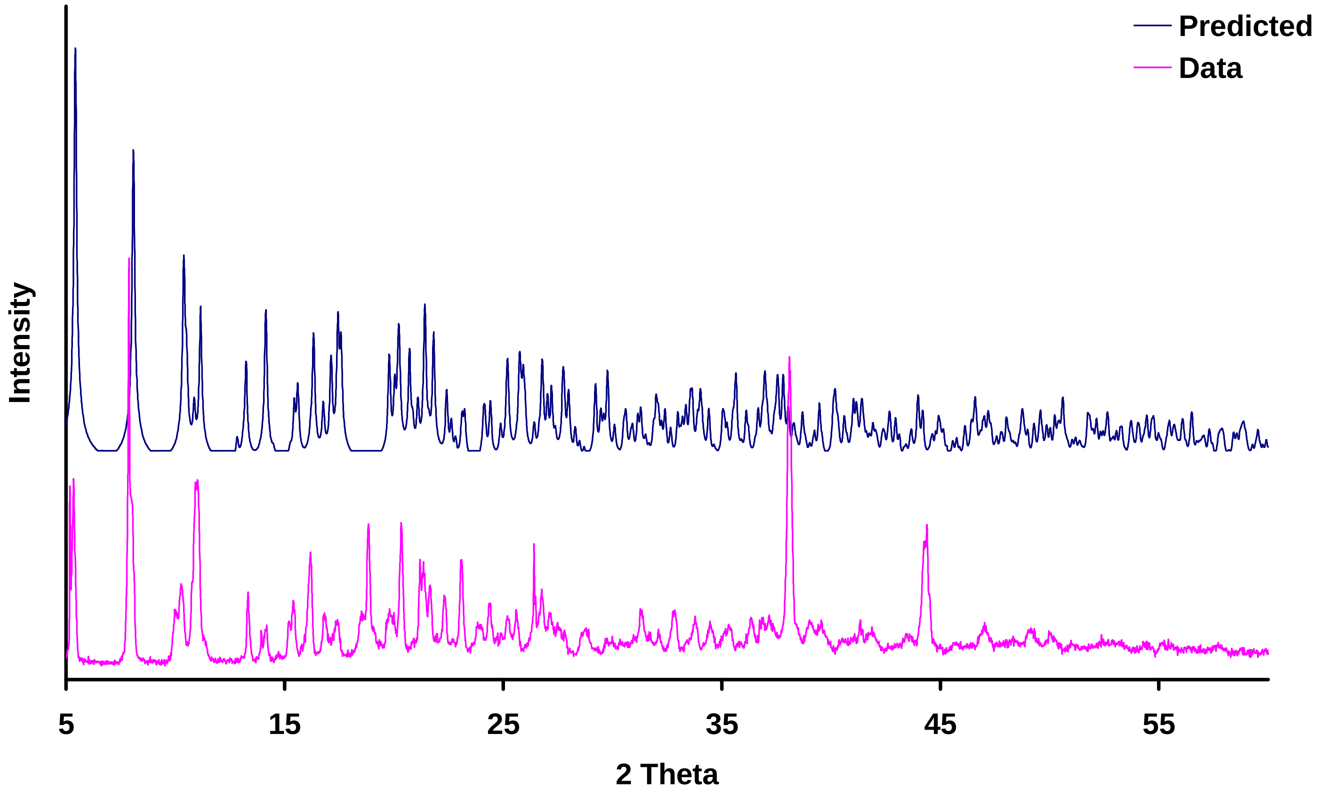
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
Normalised DTA / arb. Units
Exo
Endo
0
100
200
300
400
500
600
700
800
900
1000
Temp / °C

5. Synthesis of 3.toluene

In a typical experiment, a crystalline sample of ca. 50mg **3.thf$_2$** was prepared as described in Section 2 and placed in a sample vial. Toluene (3 mL) was then added to the solid material and the vial tightly sealed. The sample was stored for a minimum of 24 hours before any subsequent analysis. The ^{1}H and ^{31}P{^{1}H} NMR spectra of this material were essentially identical to **3**.**thf$_2$**, except that integration of the resonances demonstrated that 0.3 thf and 1.0 of toluene molecules were present per gold.

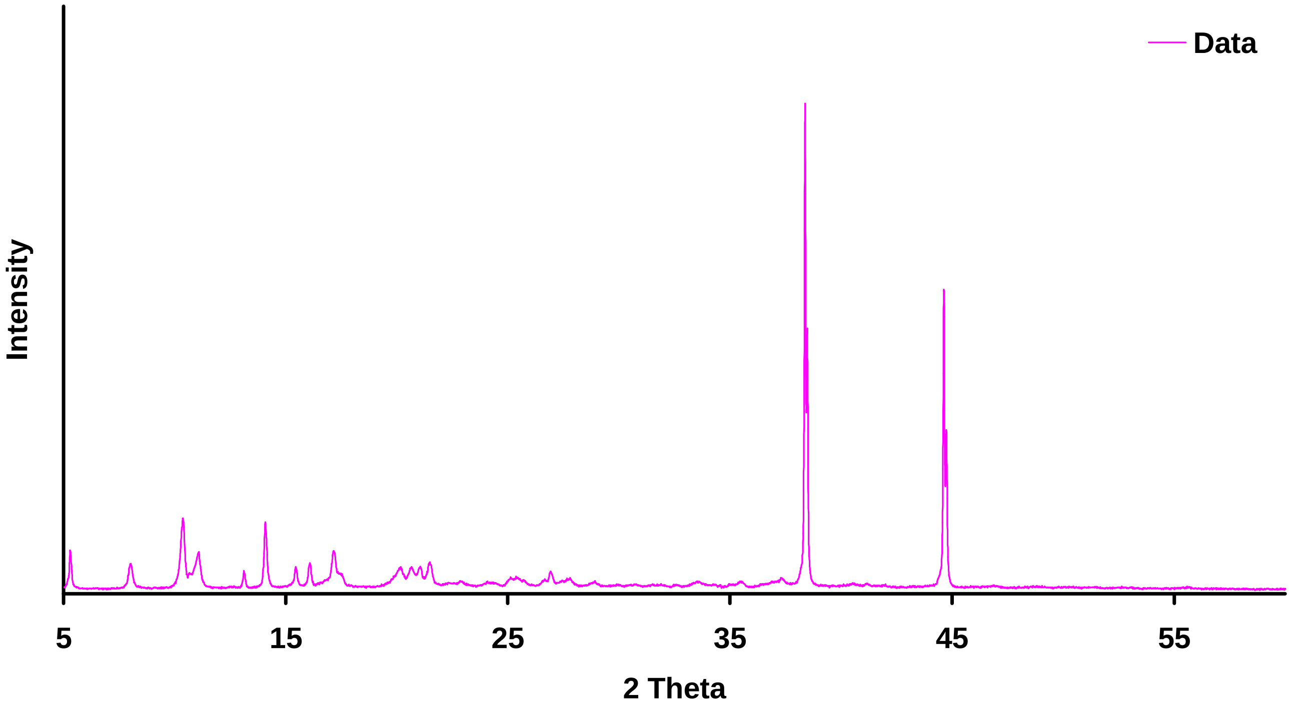
Elemental Analysis	Expected for **3**.toluene (%)	C 44.50 H 3.41 N4.51
	Expected for **3**.(toluene)$_{0.7}$ (%)	C 42.32 H 3.16 N 4.72
	Expected for **3**.(toluene)(thf)$_{0.3}$ (%)	C 45.24 H 3.67 N 4.36
	Found (%)	C 42.50 H 3.47 N 3.98



6. Heating Sample of 3 at 120 °C (3vac120)

A sample of **3.thf$_2$** (ca. 10 mg) was placed into a round bottomed flask and heated at 120 °C under high vaccum (1 × 10^{-4} mbar) for 24 hours before sealing under an atmosphere of dry nitrogen. The ^{1}H and ^{31}P{^{1}H} NMR spectra of this material were essentially identical to **3.thf$_2$**, except that integration of the resonances demonstrated that 0.6 thf molecules were present per gold.

Powder X-ray diffraction Study on 3.thf$_2$ heated at 120 °C for 24 hr.

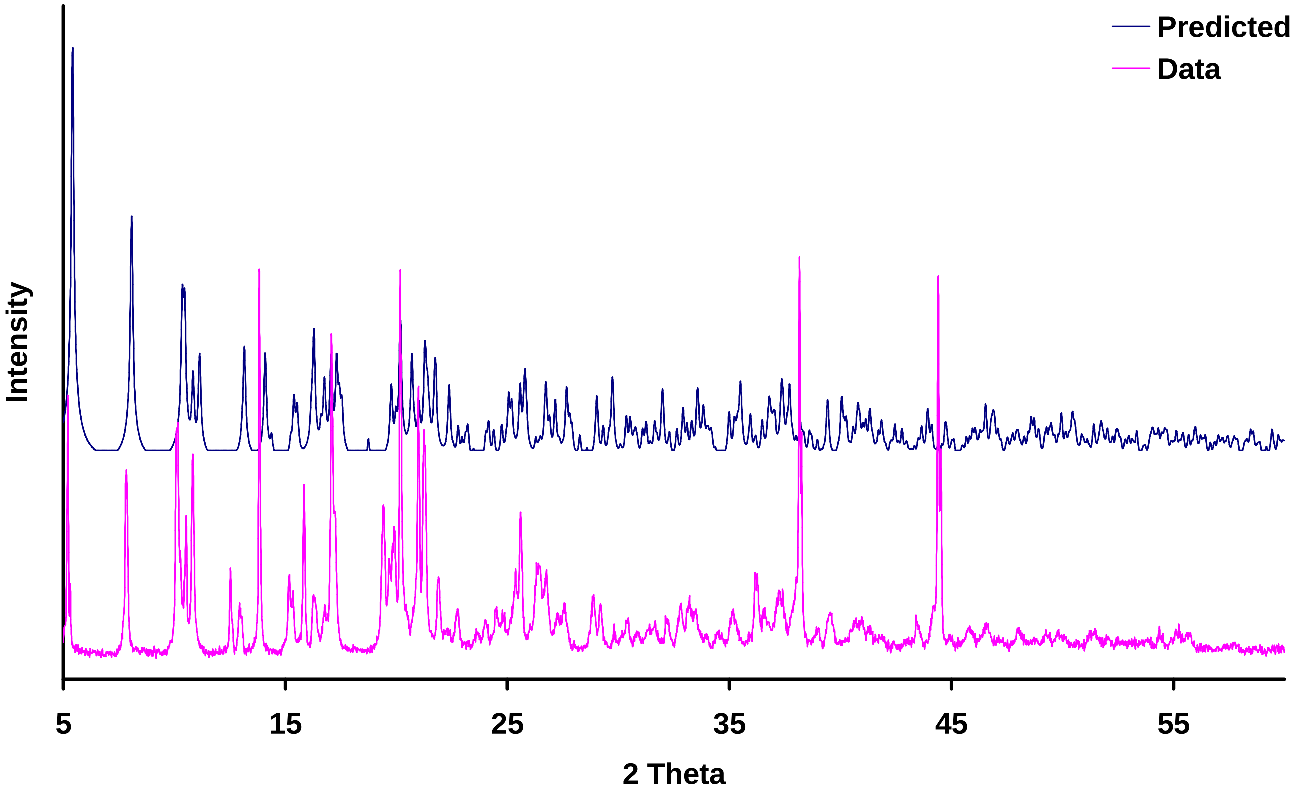


7. Synthesis of 4

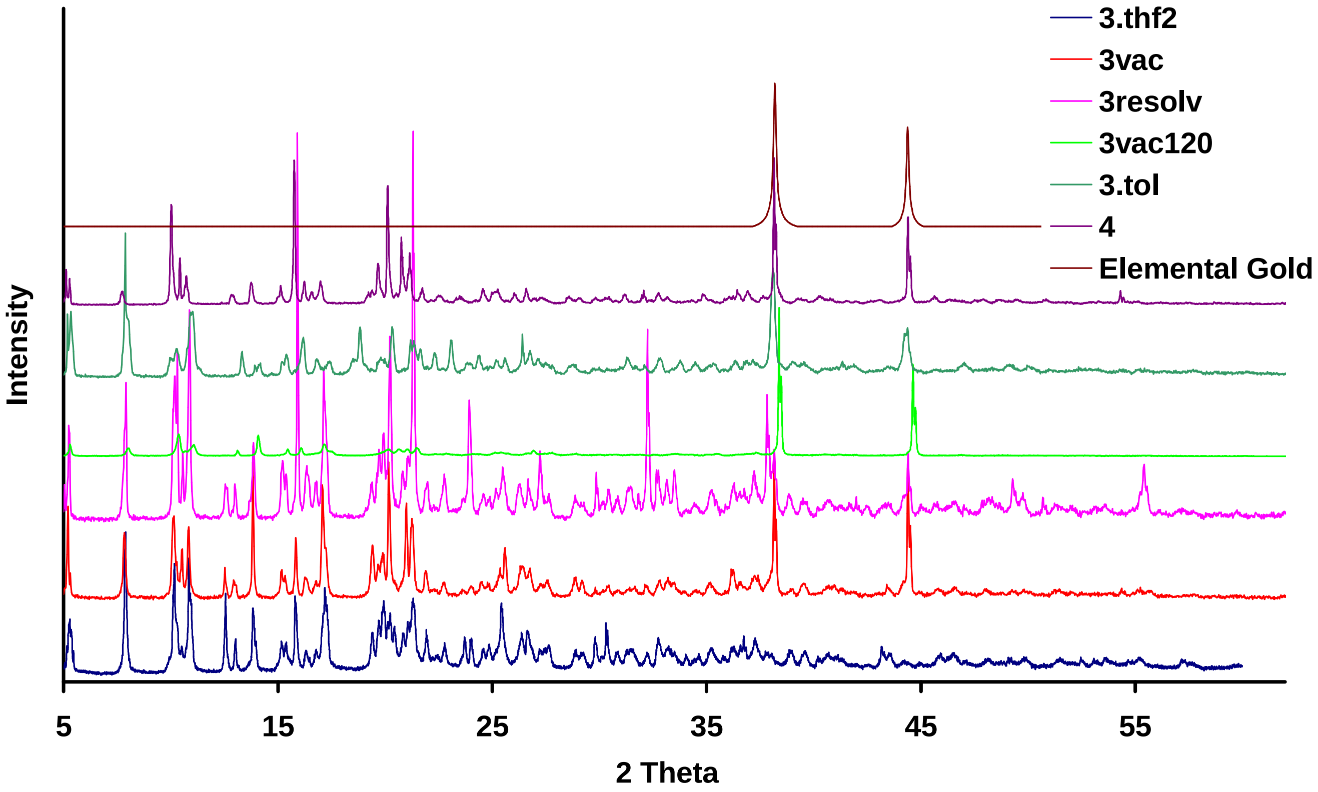
In a round bottomed flask fitted with a magnetic stirred bead **3.thf$_2$** (46 mg, 0.07 mmol) was dissolved in 10 mL of acetone. NaBr (700 mg, 7.0 mmol) was added and the resulting slurry stirred for 16 hr at room temperature. The sample was then filtered and the residue washed with 10 ml THF. The combined filtrates were combined and the solvent removed *in vacuo*. The resulting residue was dissolved in 3 ml THF. Slow diffusion of hexane into the THF solution of **4** resulted in the formation of colourless crystals suitable for study by X-ray diffraction. Yield 20 mg (41 %.)

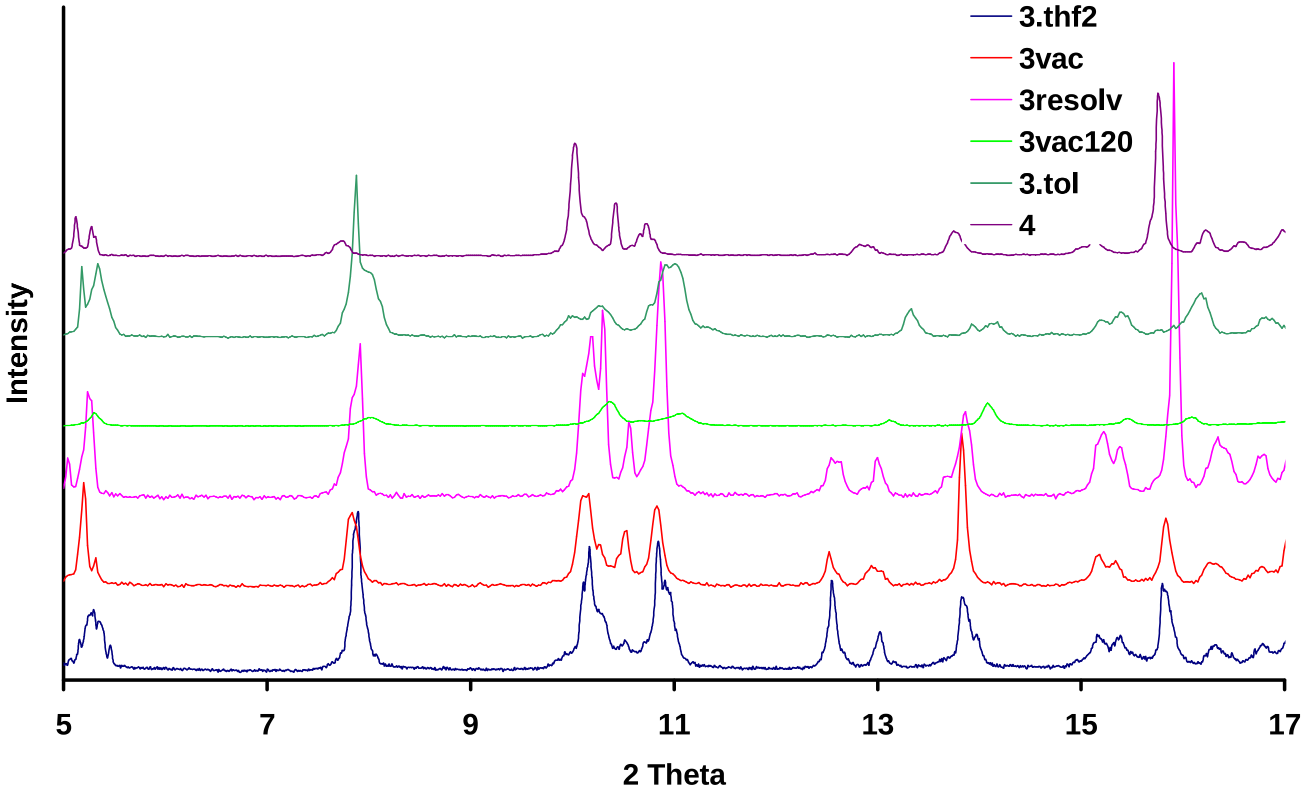
^{1}H NMR (d$_6$-DMSO) δ 11.63 (br s, 2H, N**H**), 7.64 (m, 10 H, ***Ph***), δ 7.14 (d, 1 H, $^3J_{PH}$ = 10.9 Hz, uracil C6-***H***), δ 3.61 (m, 6.2 H, thf) δ 1.77 (m, 6.1 H, thf); ^{31}P{^{1}H} (d$_6$-DMSO) δ 26.3 (s).
Ratio of **3**:thf from ^{1}H NMR = 1:1.5.

Powder X-ray diffraction Study on 4



8. Comparison of Powder X-ray Diffraction Patterns





9. References

[1] R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray, J. P. Fackler Jr., *Inorg. Synth*, 1989, **26**, 86.
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[9] D. A. Fletcher, R. F. McMeeking and D. *J. Chem. Inf. Comput. Sci.* 1996, **36**, 746.