Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary Information

Supramolecular aggregates of metalloacids with stilbazoles. Formation of columnar mesophases and Langmuir films.

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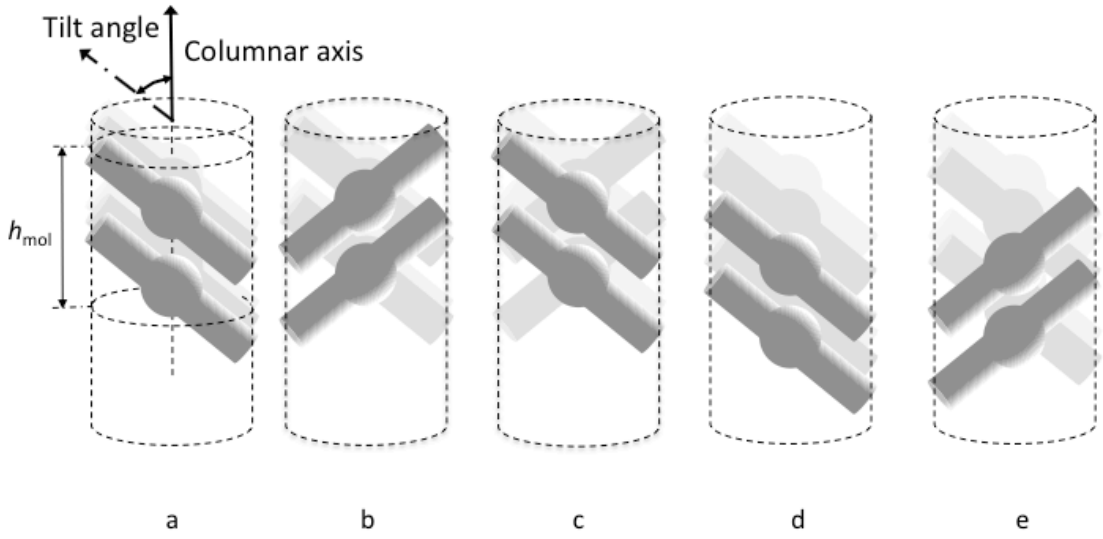
Additional information on molecular arrangement within columns

Various alternative possibilities for the supramolecular packing of the adducts within the cylindrical column, all in agreement with the data:



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a) the bundles made of three side-by-side adducts stack with a tilt with respect to the columnar axis (the metallic centres of each bundle lie in the 2D phase symmetry plane); b) and c) the adducts associate but with no tilt correlation (the metallic centres of one row lie in the 2D phase symmetry plane); d) the bundles made of three side-by-side adducts stack with two tilts with respect to the columnar axis have two tilts (the metallic centres of each bundle do not lie in the same plane as the phase symmetry plane, but are tilted with respect to this plane); e) combination of b) and e).

Figure SI1. BAM images (620 x 500 μm) obtained during the compression of the Langmuir film of: (c) **S6** at A = 306 Å^2, and (d) **S7** at A = 220 Å^2.

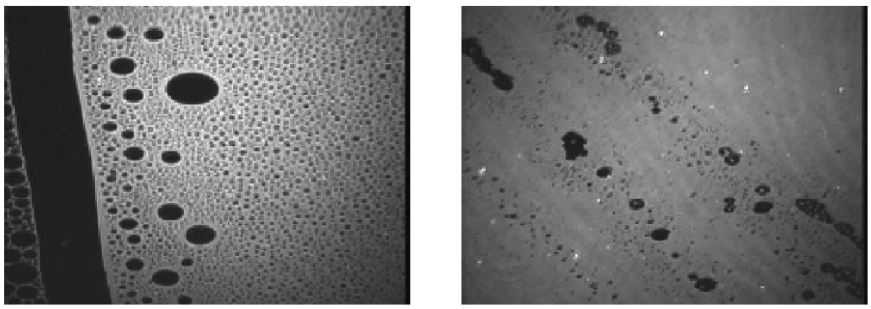

Figure SI2. BAM images (620 x 500 μm) obtained during the collapse of the Langmuir film of **S4** at: (a) A = 95 Å^2, and (b) A = 90 Å^2.

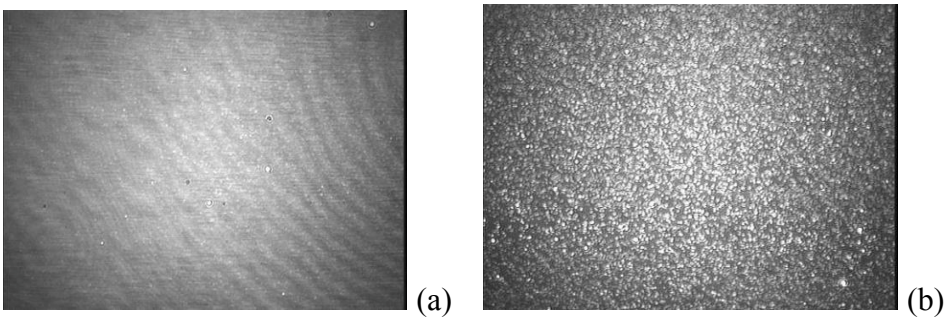

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Figure SI3. BAM images (620 x 500 μm) obtained during the compression-decompression cycles of the Langmuir film of [Au($C_6F_4OC_{10}H_{21}$)(CNC_6H_4COOH)-4-decyloxystilbazole] at ($Å^2$/molecule): (a) 150, (b) 109, (c) 76, (d) 56, (e) 56, (f) 35, (g) 60, (h) 60.

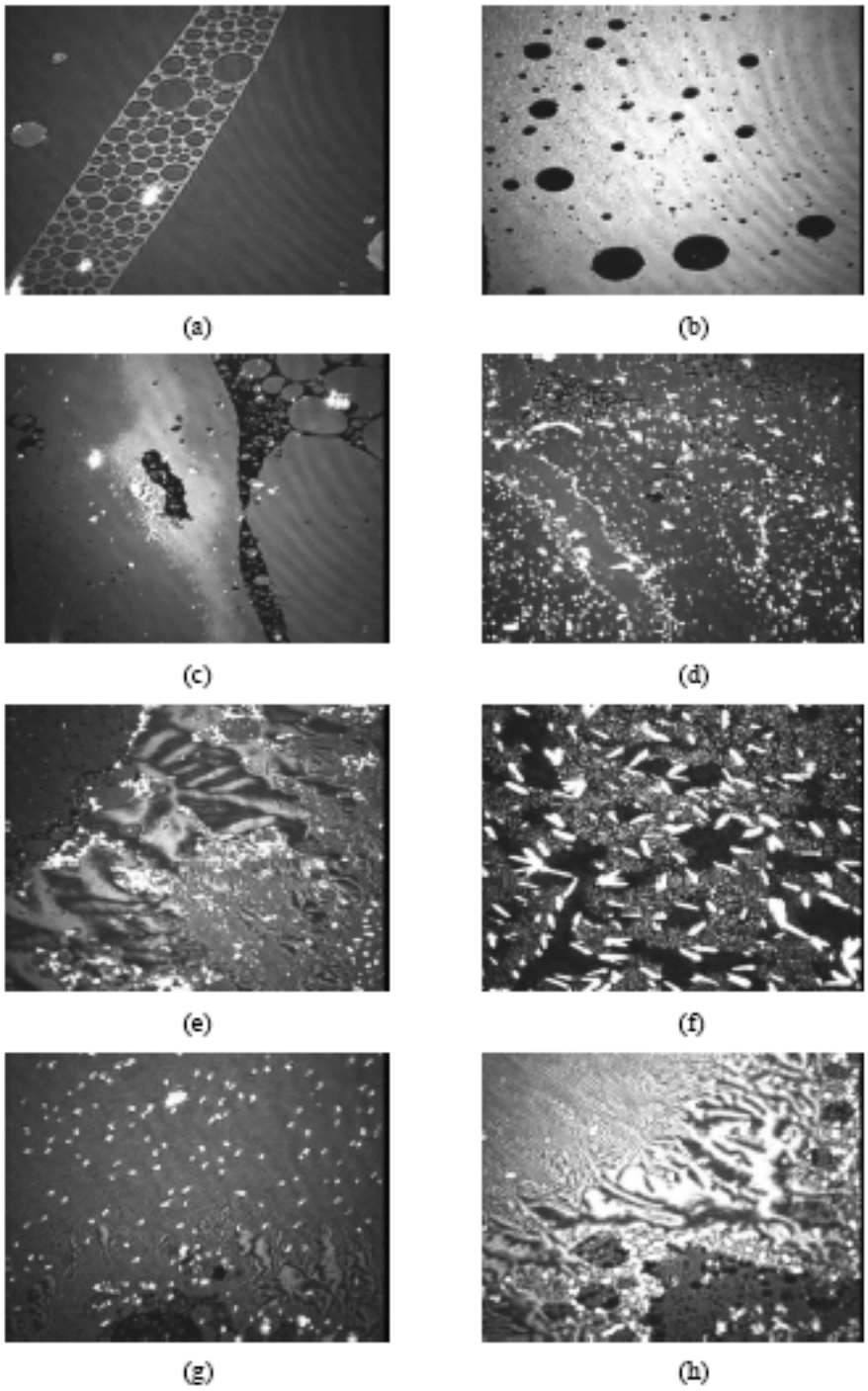

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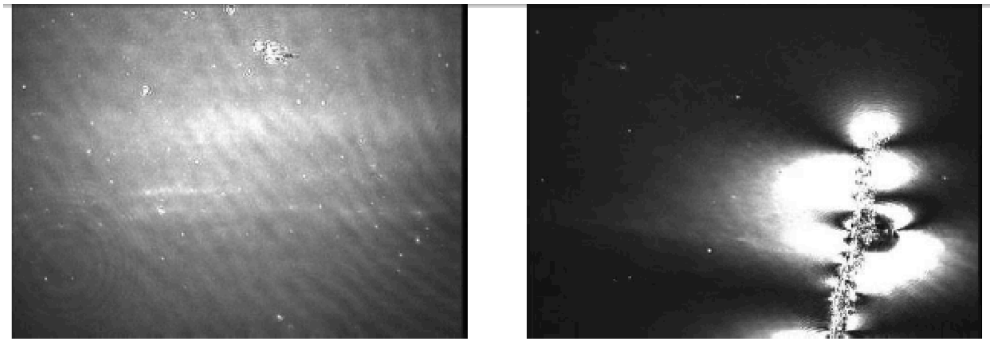
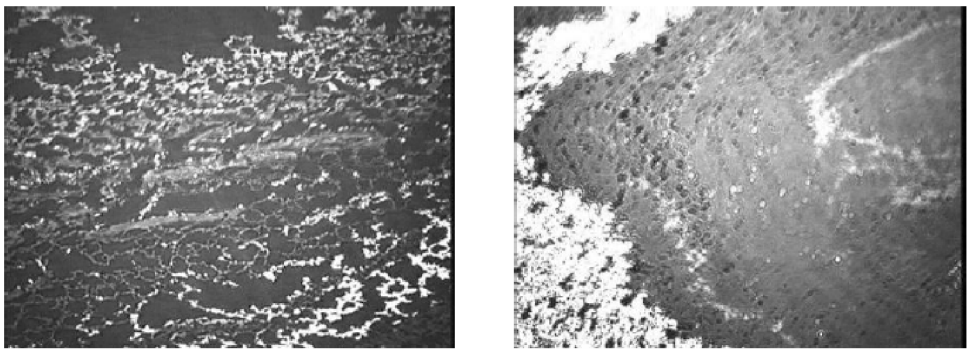
Figure SI4. BAM images (620 x 500 μm) of **S6** obtained during collapse of film at 90 $Å^2$.



(a) (b)

Figure SI5. BAM images (620 x 500 μm) obtained for *trans*-$[PdI_2(CNC_6H_4CO_2H)_2]$.



Elemental Microanalysis for the aggregates

[$CNC_6H_4CO_2H$---S] (S1): Anal. Calcd for $C_{51}H_{76}N_2O_5$: C, 76.84; H, 9.60; N, 3.51 %. Found: C, 76.91; H, 9.65; N, 3.54%.

[$Au(C_6F_5)(CNC_6H_4CO_2H$---S)] (S3): Anal. Calcd for $C_{57}H_{76}AuF_5N_2O_5$: C, 58.95; H, 6.59; N, 2.41 %. Found: C, 59.12; H, 6.72; N, 2.64%.

[$Au(C_6F_4OC_{10}H_{21})(CNC_6H_4CO_2H$---S)] (S4): Anal. Calcd for $C_{67}H_{97}AuF_4N_2O_6$: C, 61.92; H, 7.52; N, 2.15 %. Found: C, 62.08; H, 7.55; N, 2.30%.

[$PdI_2(CNC_6H_4COOH\text{---}S)_2$] S6): Anal. Calcd for $C_{102}H_{152}PdI_2N_4O_{10}$: C, 62.67; H, 7.83; N, 2.86 %. Found: C, 62.75; H, 8.01; N, 2.98%.

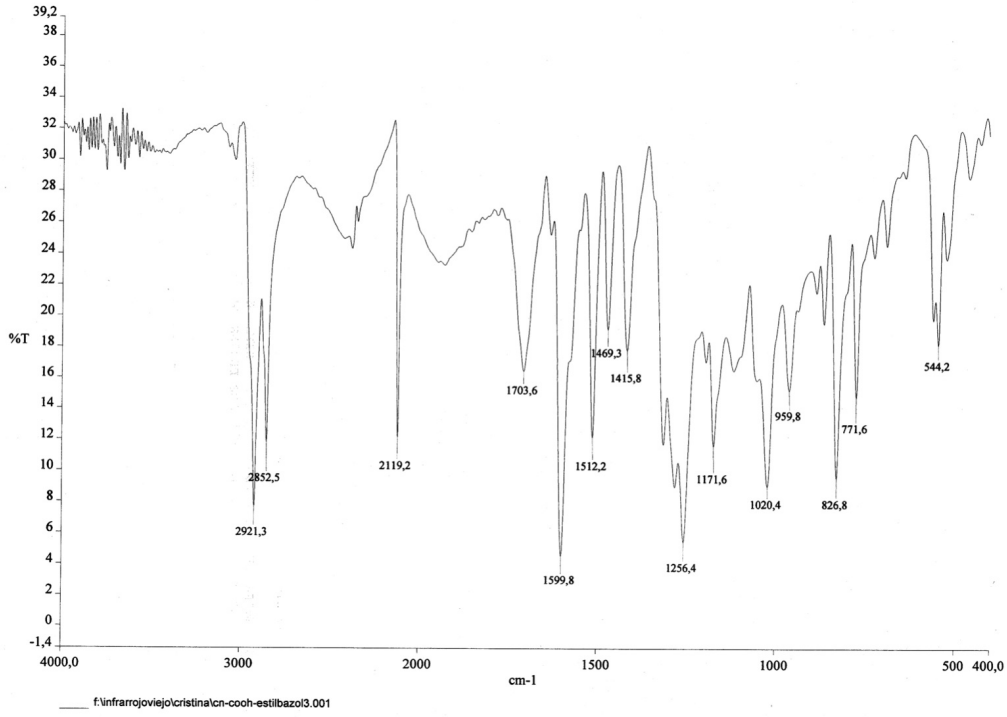
[$PtI_2(CNC_6H_4COOH\text{---}S)_2$] (S7): Anal. Calcd for $C_{102}H_{152}PtI_2N_4O_{10}$: C, 59.95; H, 7.49; N, 2.74 %. Found: C, 60.15; H, 7.61; N, 2.85%.

[$PdCl_2(CNC_6H_4COOH\text{---}S)_2$] ((S8): Anal. Calcd for $C_{102}H_{152}PdCl_2N_4O_{10}$: C, 69.15; H, 8.64; N, 3.13 %. Found: C, 69.25; H, 8.81; N, 3.27%.

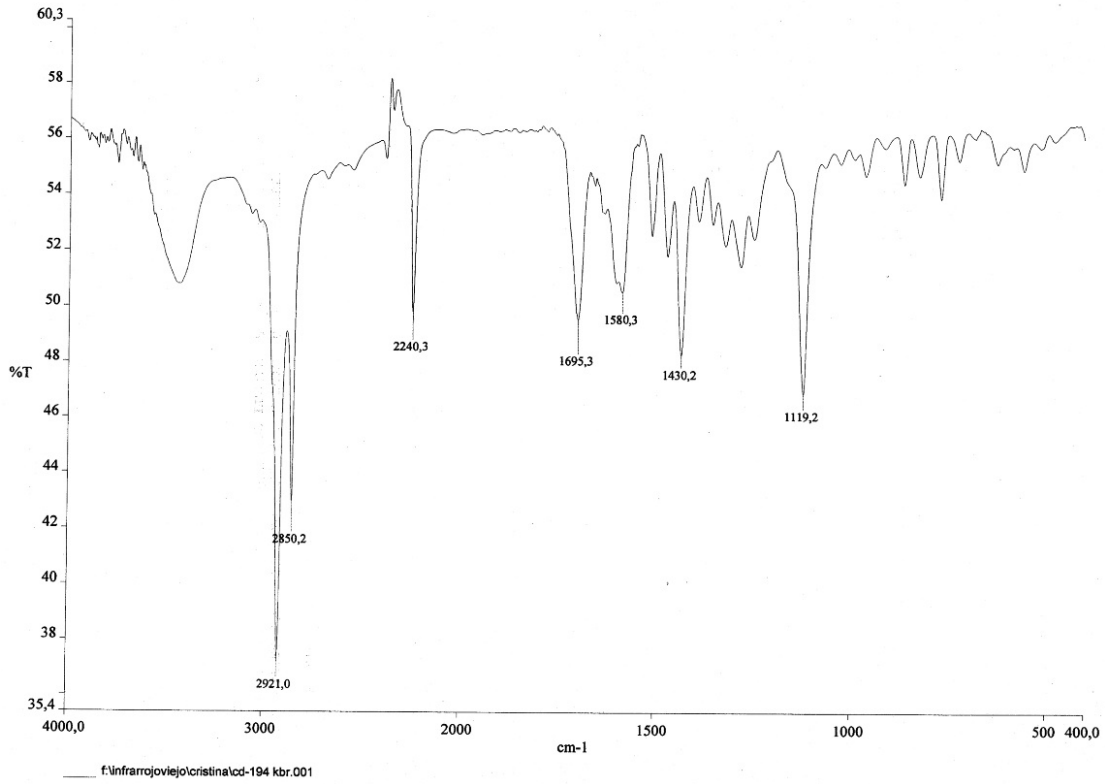
[$PtCl_2(CNC_6H_4COOH\text{---}S)_2$] ((S9): Anal. Calcd for $C_{102}H_{152}PtCl_2N_4O_{10}$: C, 65.85; H, 8.23; N, 3.01 %. Found: C, 65.89; H, 8.32; N, 3.16%.

IR spectra (KBr)

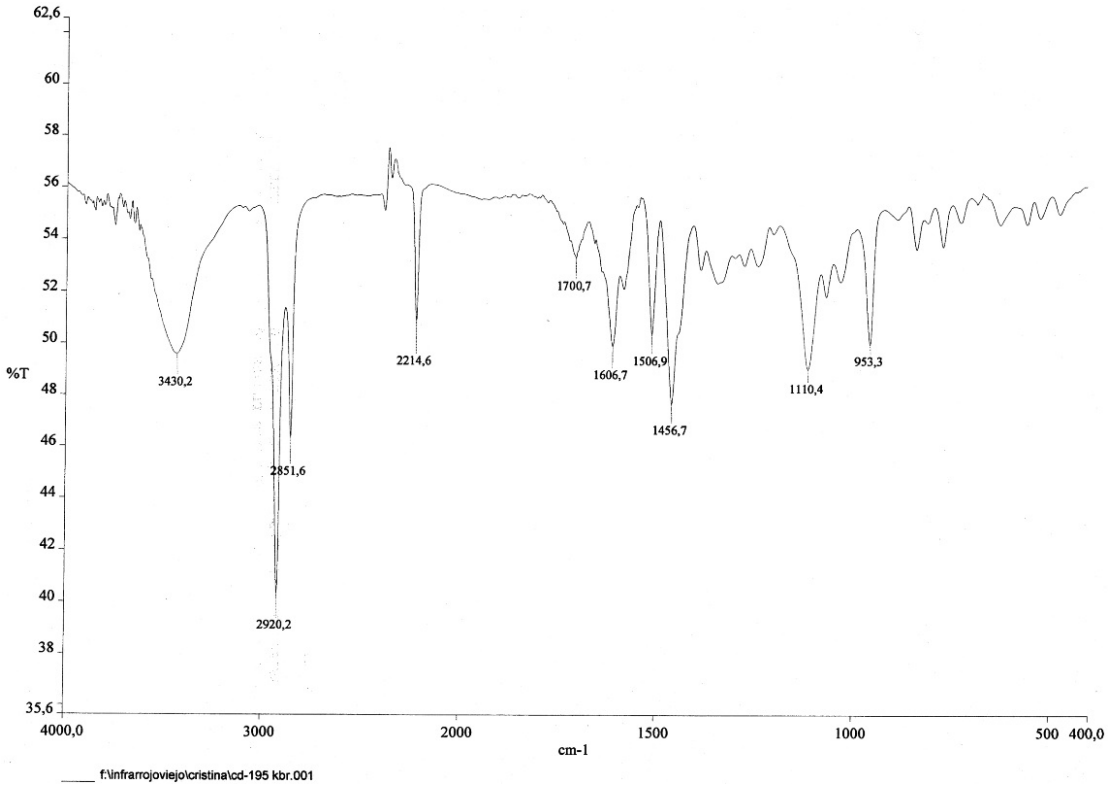
Aggregate S1



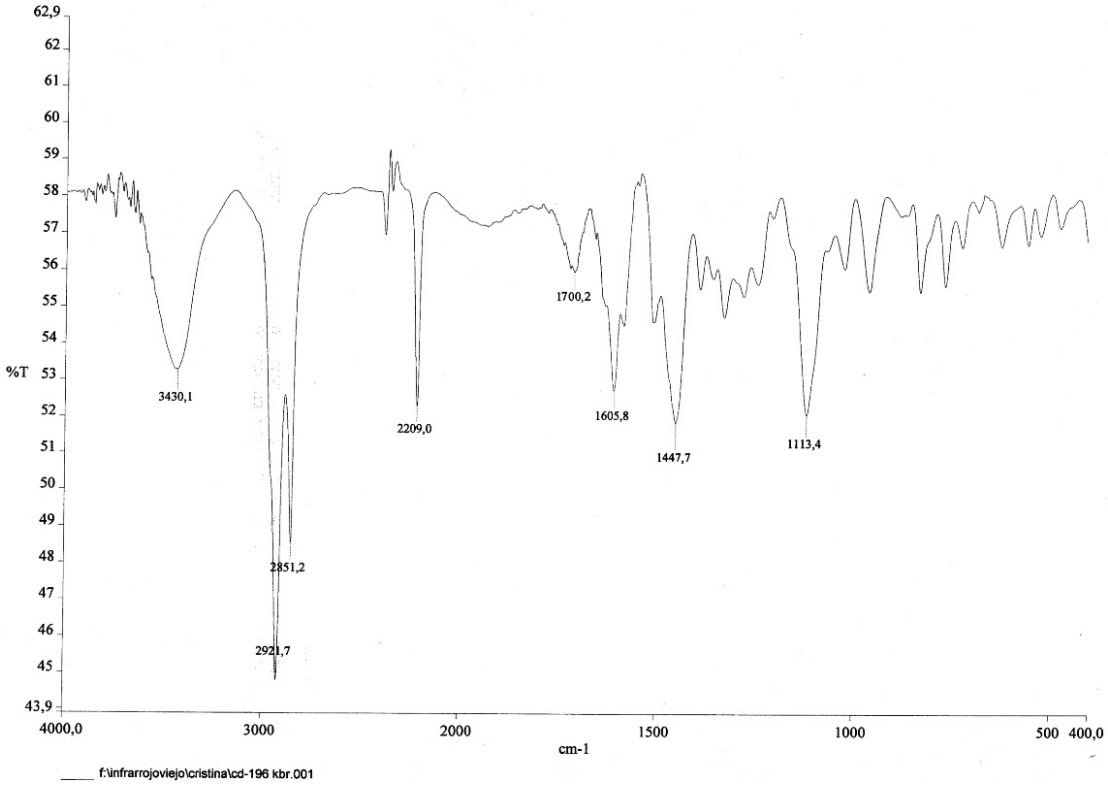
AuCl(CNC6H4COOH) (2) + stilbazole



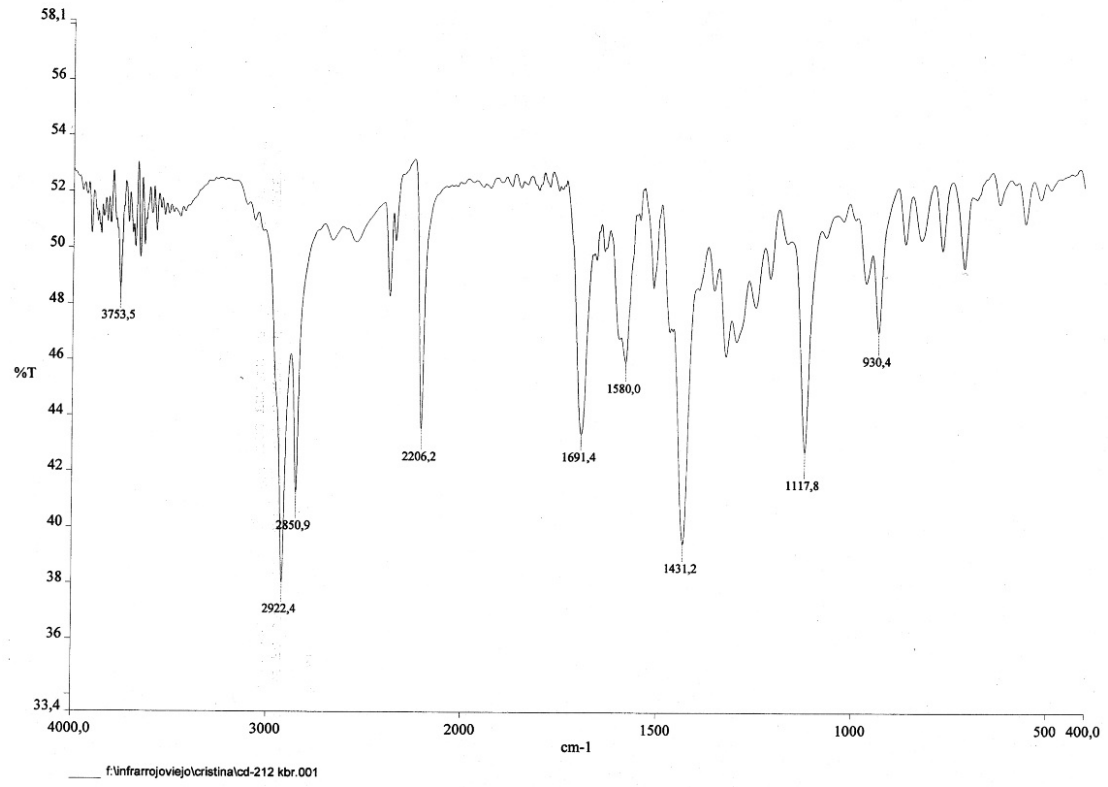
Aggregate S3



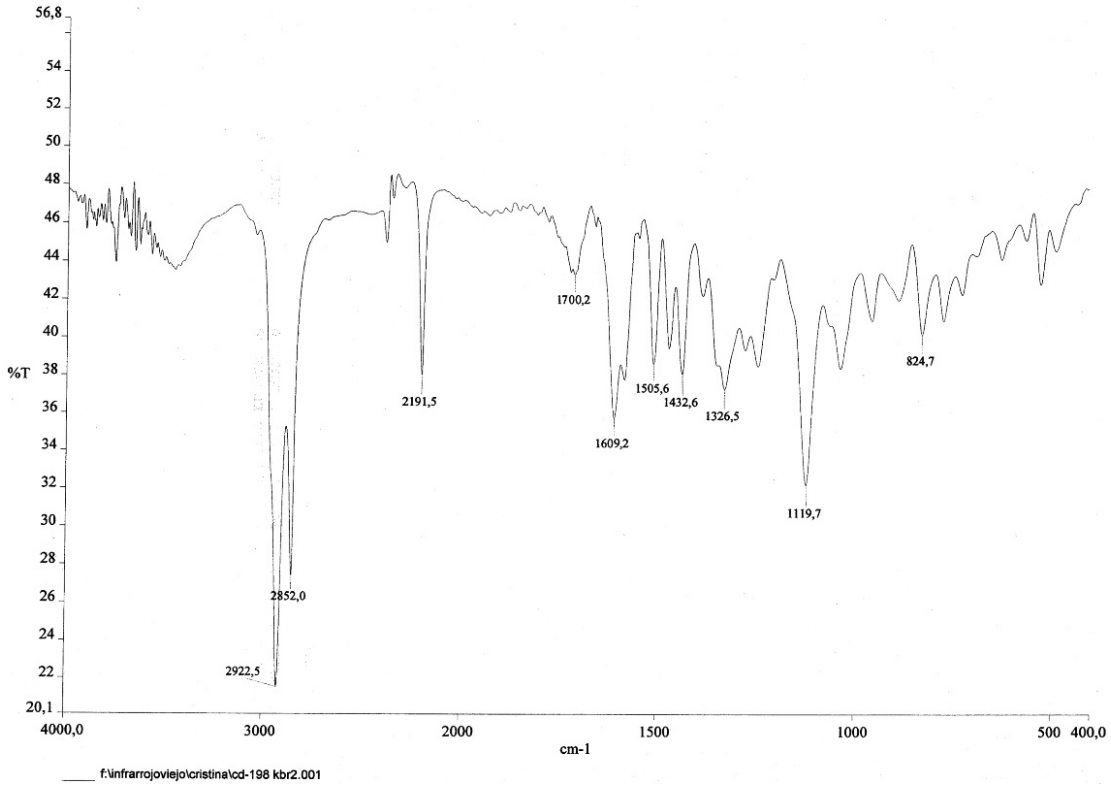
Aggregate S4



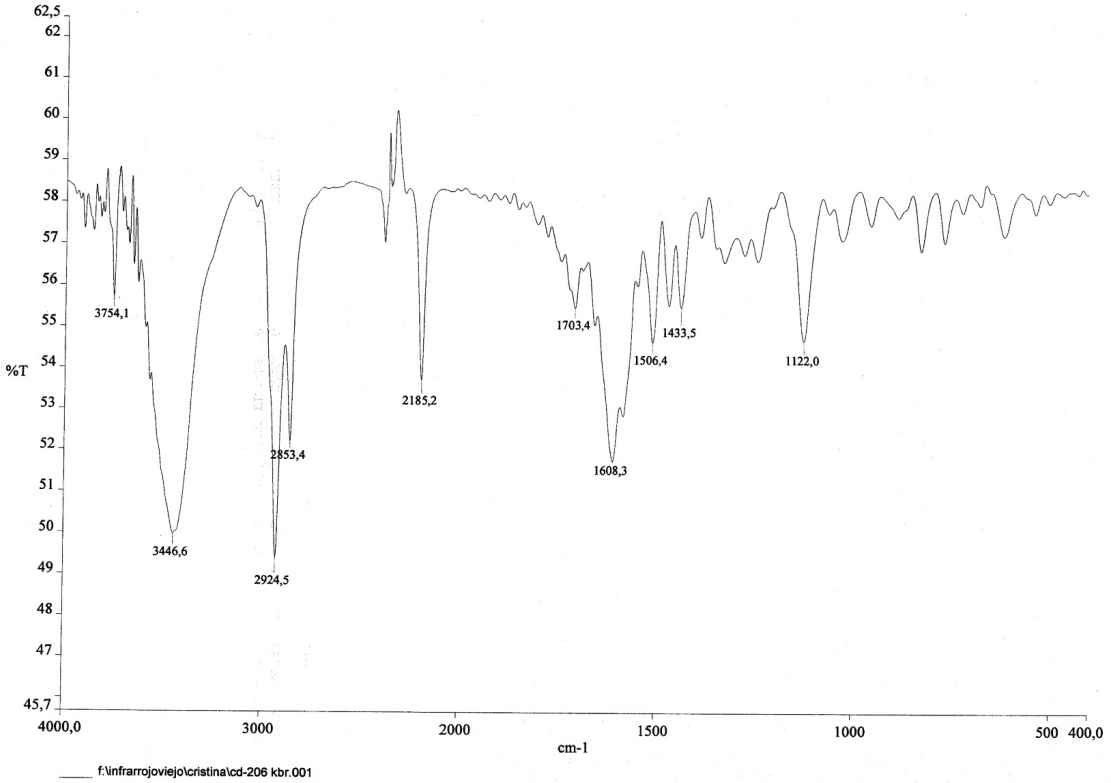
[μ-$C_6F_4C_6F_4$-{$AuCNC_6H_4CO_2H$}$_2$] (5) + stilbazole



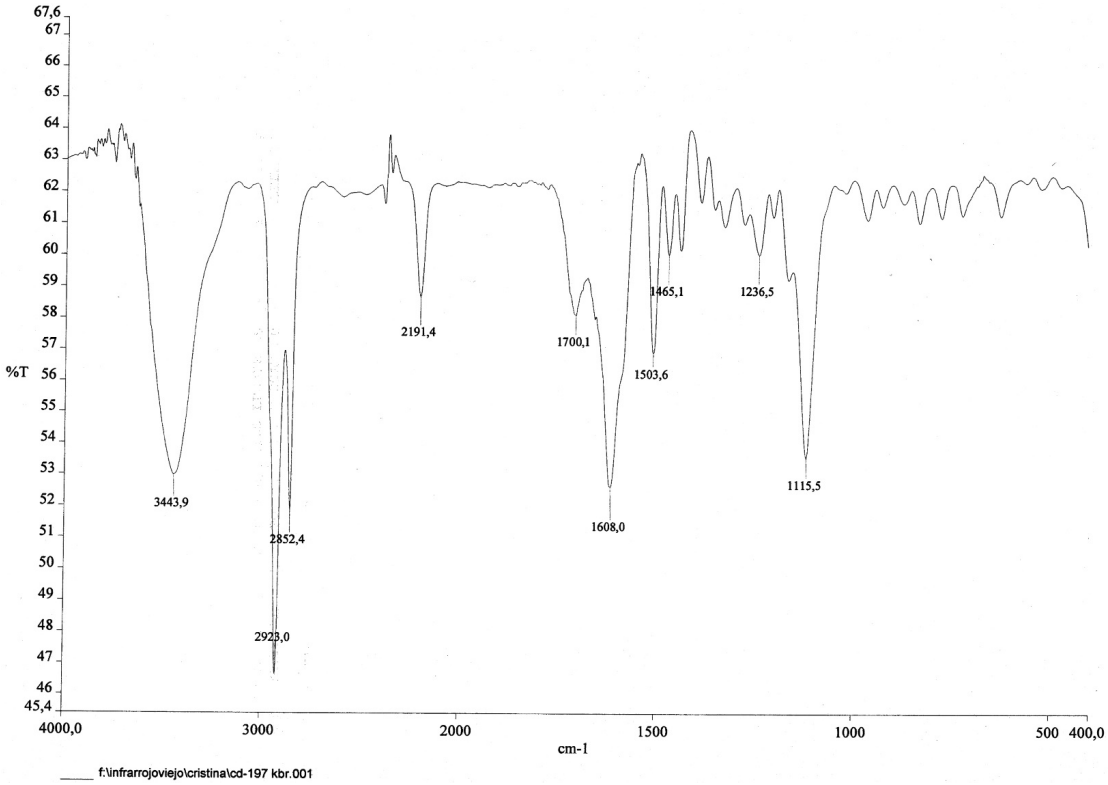
Aggregate S6



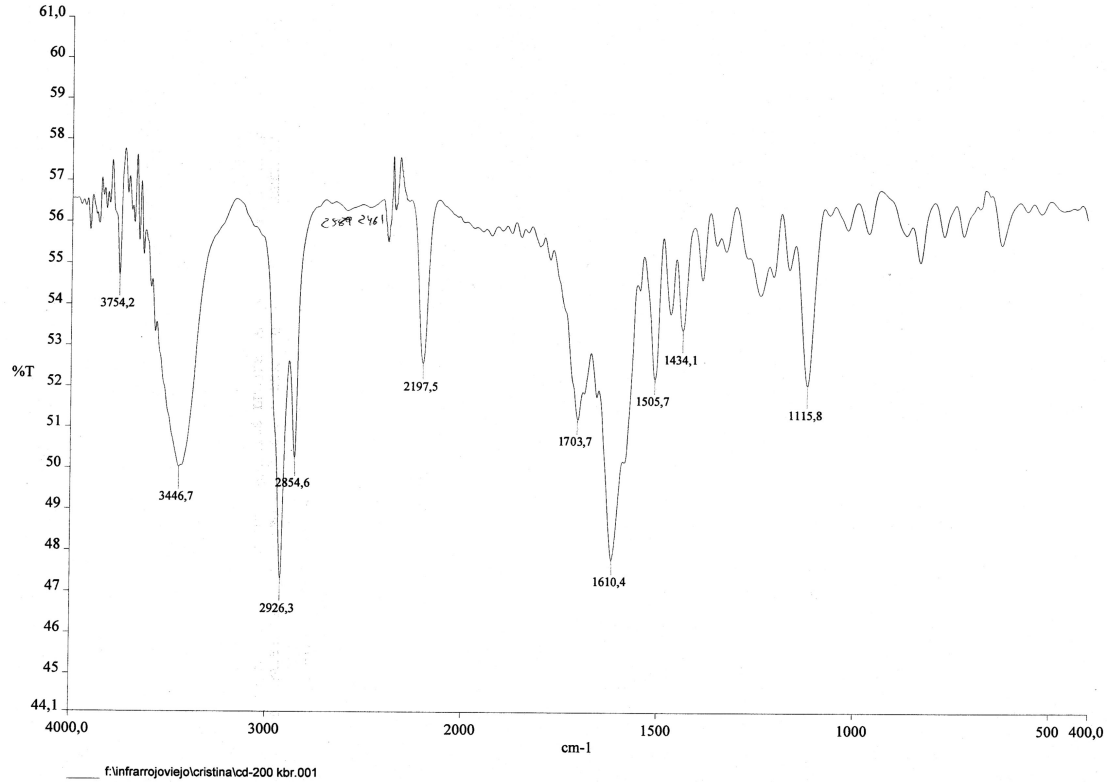
Aggregate S7



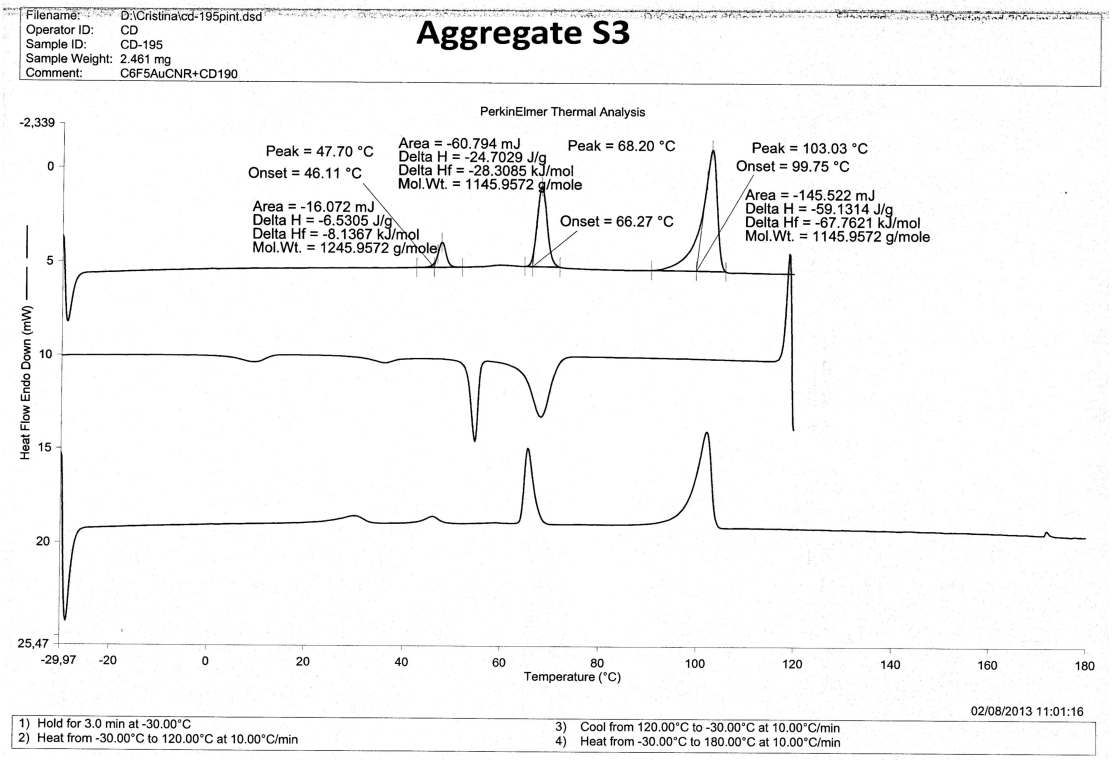
Aggregate S8

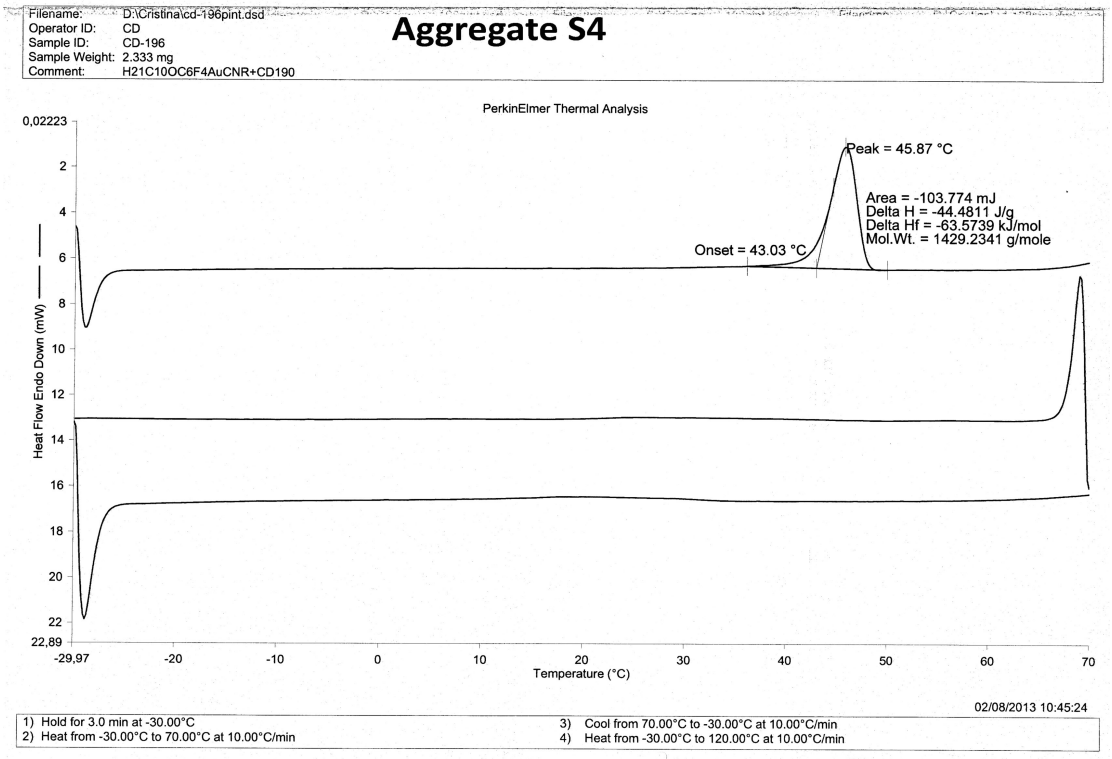


Aggregate S9

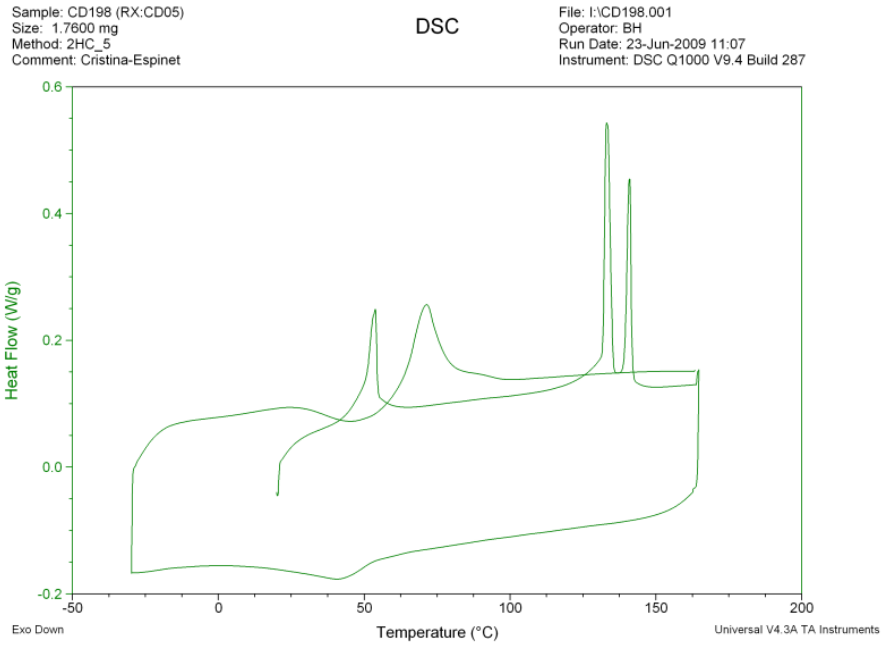


DCS scans

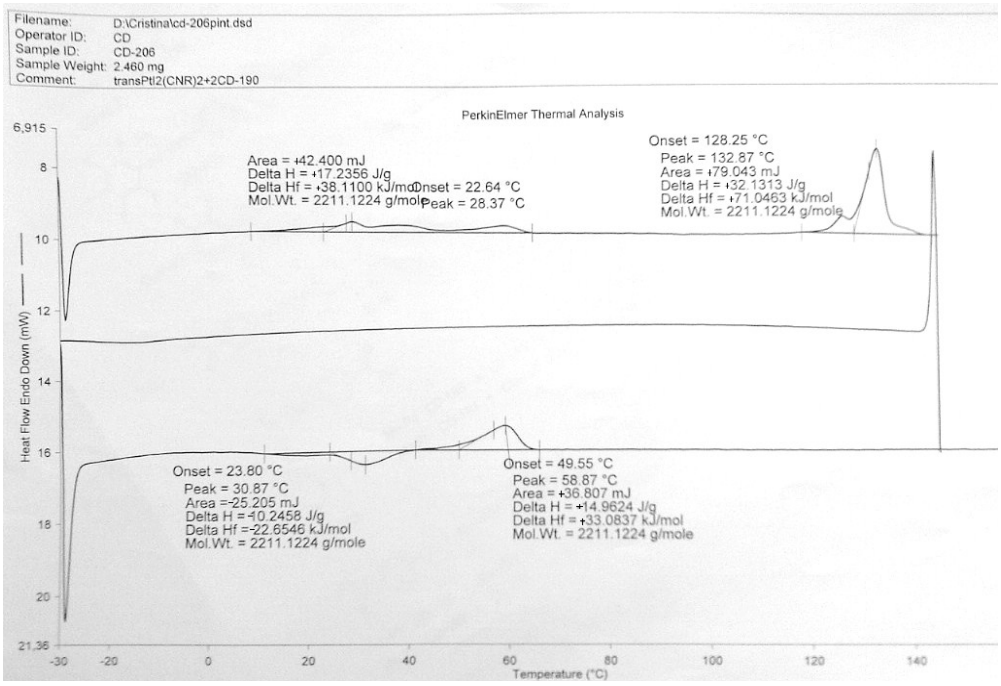

Filename: D:\Cristina\cd-195pint.dsd
Operator ID: CD
Sample ID: CD-195
Sample Weight: 2.461 mg
Comment: C6F5AuCNR+CD190
Aggregate S3
PerkinElmer Thermal Analysis
Peak = 47.70 °C
Onset = 46.11 °C
Area = -60.794 mJ
Delta H = -24.7029 J/g
Delta Hf = -28.3085 kJ/mol
Mol.Wt. = 1145.9572 g/mole
Peak = 68.20 °C
Onset = 66.27 °C
Peak = 103.03 °C
Onset = 99.75 °C
Area = -145.522 mJ
Delta H = -59.1314 J/g
Delta Hf = -67.7621 kJ/mol
Mol.Wt. = 1145.9572 g/mole
Area = -16.072 mJ
Delta H = -6.5305 J/g
Delta Hf = -8.1367 kJ/mol
Mol.Wt. = 1245.9572 g/mole
Heat Flow Endo Down (mW)
Temperature (°C)
02/08/2013 11:01:16
1) Hold for 3.0 min at -30.00°C
2) Heat from -30.00°C to 120.00°C at 10.00°C/min
3) Cool from 120.00°C to -30.00°C at 10.00°C/min
4) Heat from -30.00°C to 180.00°C at 10.00°C/min

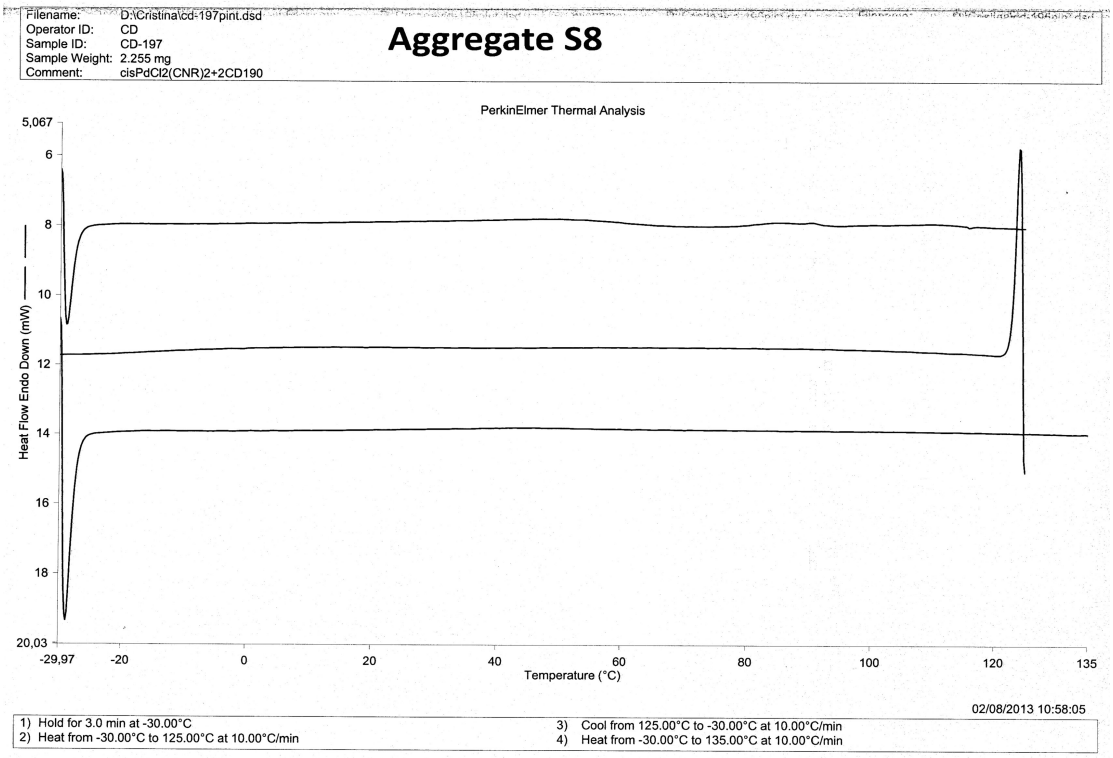

Filename: D:\Cristina\cd-196pint.dsd
Operator ID: CD
Sample ID: CD-196
Sample Weight: 2.333 mg
Comment: H21C10OC6F4AuCNR+CD190
Aggregate S4
PerkinElmer Thermal Analysis
Peak = 45.87 °C
Onset = 43.03 °C
Area = -103.774 mJ
Delta H = -44.4811 J/g
Delta Hf = -63.5739 kJ/mol
Mol.Wt. = 1429.2341 g/mole
Heat Flow Endo Down (mW)
Temperature (°C)
02/08/2013 10:45:24
1) Hold for 3.0 min at -30.00°C
2) Heat from -30.00°C to 70.00°C at 10.00°C/min
3) Cool from 70.00°C to -30.00°C at 10.00°C/min
4) Heat from -30.00°C to 120.00°C at 10.00°C/min

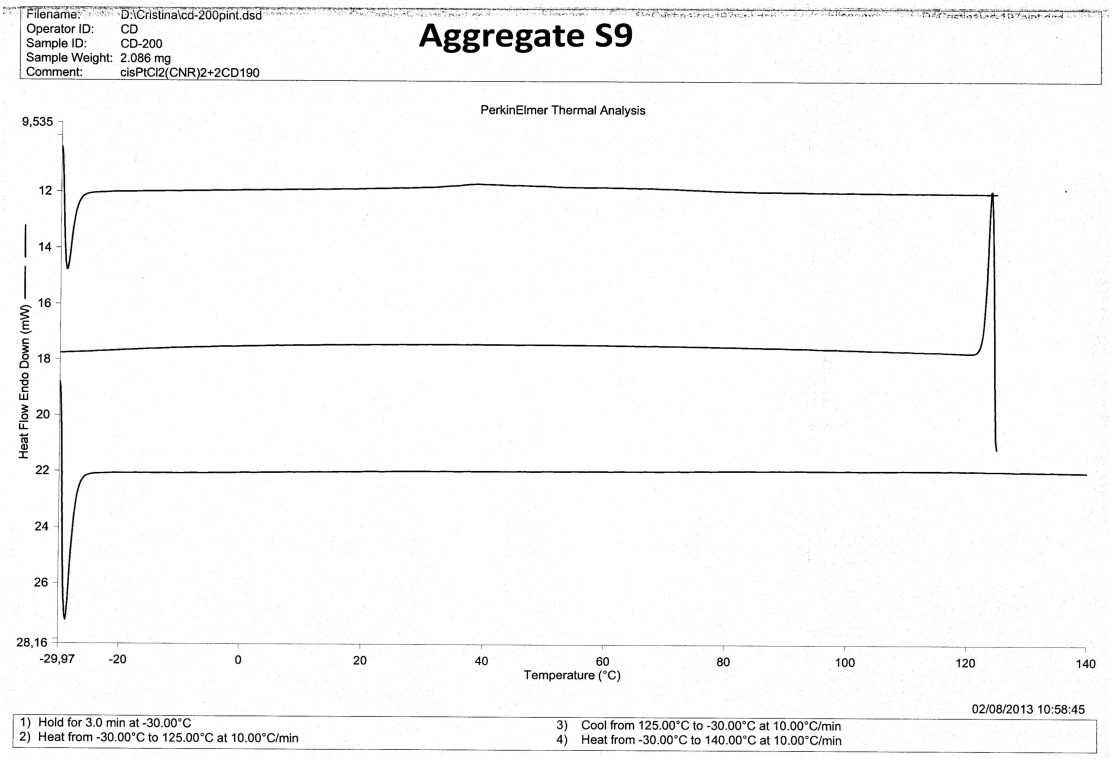
Aggregate S6



Aggregate S7




Filename: D:\Cristina\cd-197pint.dsd
Operator ID: CD
Sample ID: CD-197
Sample Weight: 2.255 mg
Comment: cisPdCl2(CNR)2+2CD190
Aggregate S8
PerkinElmer Thermal Analysis
5,067
6
8
10
12
14
16
18
20,03
Heat Flow Endo Down (mW)
-29,97
-20
0
20
40
60
80
100
120
135
Temperature (°C)
02/08/2013 10:58:05
1) Hold for 3.0 min at -30.00°C
2) Heat from -30.00°C to 125.00°C at 10.00°C/min
3) Cool from 125.00°C to -30.00°C at 10.00°C/min
4) Heat from -30.00°C to 135.00°C at 10.00°C/min


Filename: D:\Cristina\cd-200pint.dsd
Operator ID: CD
Sample ID: CD-200
Sample Weight: 2.086 mg
Comment: cisPtCl2(CNR)2+2CD190
Aggregate S9
PerkinElmer Thermal Analysis
9,535
12
14
16
18
20
22
24
26
28,16
Heat Flow Endo Down (mW)
-29,97
-20
0
20
40
60
80
100
120
140
Temperature (°C)
02/08/2013 10:58:45
1) Hold for 3.0 min at -30.00°C
2) Heat from -30.00°C to 125.00°C at 10.00°C/min
3) Cool from 125.00°C to -30.00°C at 10.00°C/min
4) Heat from -30.00°C to 140.00°C at 10.00°C/min

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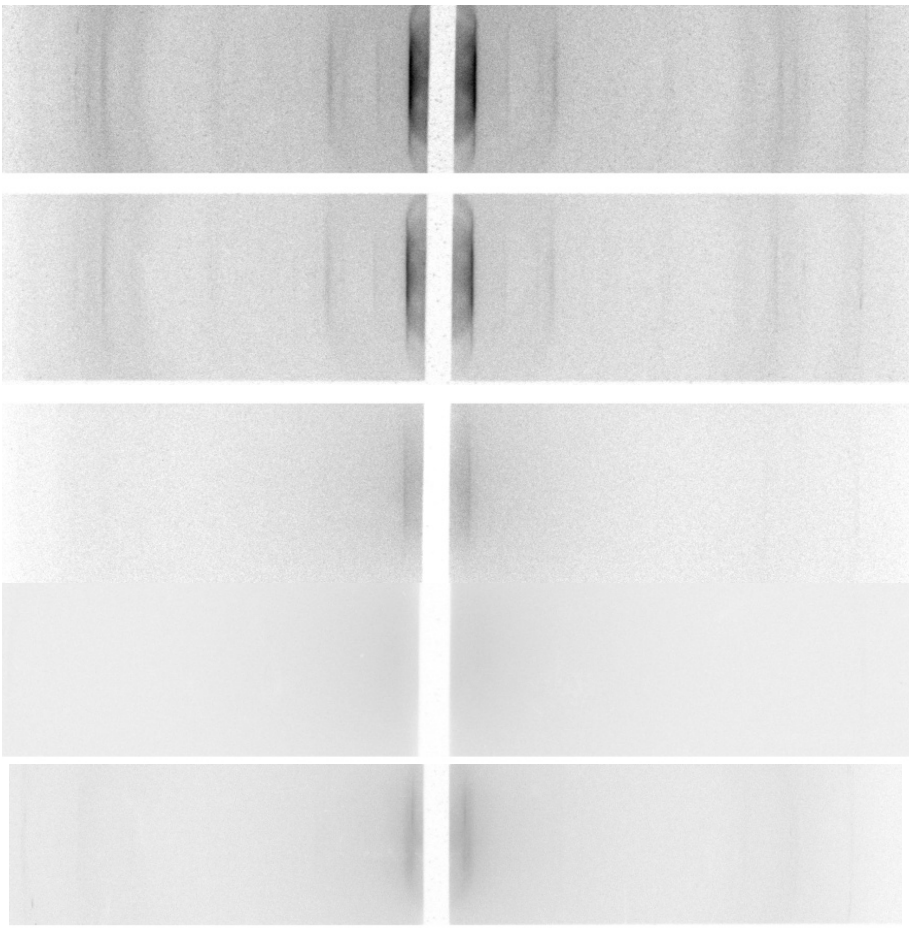
X-Ray Diffractograms

$PdI_2[CN(C_6H_4)CO_2H\cdots Stilbazole]_2$ (S6)

In the pristine state, at 40°C, numerous reflections are registered in the diffractogram, in both the small- and wide-angle range. A careful observation reveals that the first four reflections are in the ratio 1:2:3:√12, in perfect agreement with a hexagonal two-dimensionnal lattice. However, the presence of several sharp reflections in the large-angle range indicates that the chains are crystallized. At T = 80°C all the reflections, except that at the smallest angle, have less intensity, and at T = 120°C, only the small-angle reflection subsits. This reflection corresponds to the periodicity of the Col_h phase. At T = 135°C, all the reflections have disappeared (isotropic liquid), and at 40°C, the only reflection observed corresponds to the fundamental periodicity to the columnar phase; the weak halo embedding the sharp reflection likely is due to the fact that the mesophase is frozen in the glassy state. Thus, is seems that hexagonal phase is present at room temperature, but the chains are not molten.

First heating and cooling (from top to bottom : T = 40°C, 80°C, 120°C, 135°C, 40°C)



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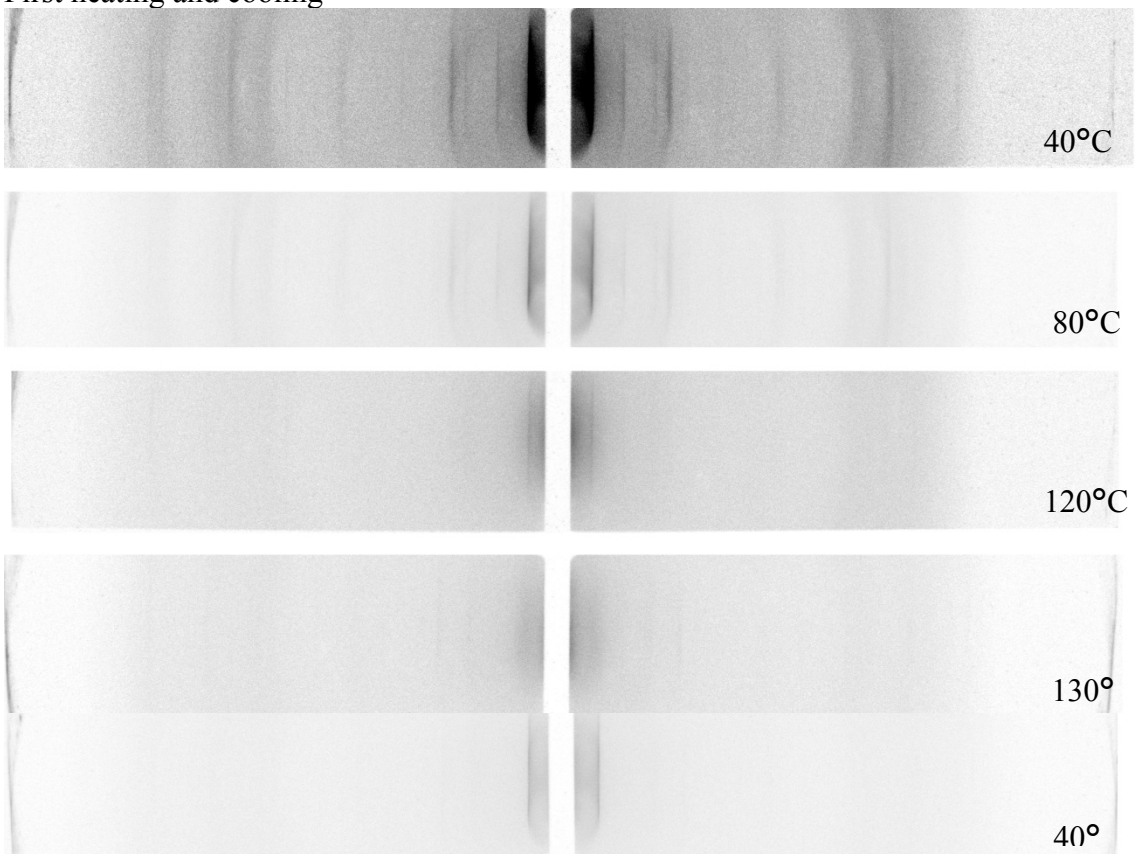
$PtI_2[CN(C_6H_4)CO_2H\cdots stilbazole]_2$ (S7)

Exactly the same observations were made for the homologous X-ray patterns recorded for the platinum homologous compounds.

First heating and cooling



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$PdCl_2[CN(C_6H_4)CO_2H\cdots stilbazole]_2$ (S8)

For both the chloro compounds, the mesophase is detected right at room temperature, but is frozen in the glassy state.

First heating and cooling, second heating

$PtCl_2[CN(C_6H_4)CO_2H\cdots stilbazole]_2$ (S9)

First heating and cooling, and second heating