Synthesis and Characterization of Bipyridine-Based Platinum (II) Mesogens

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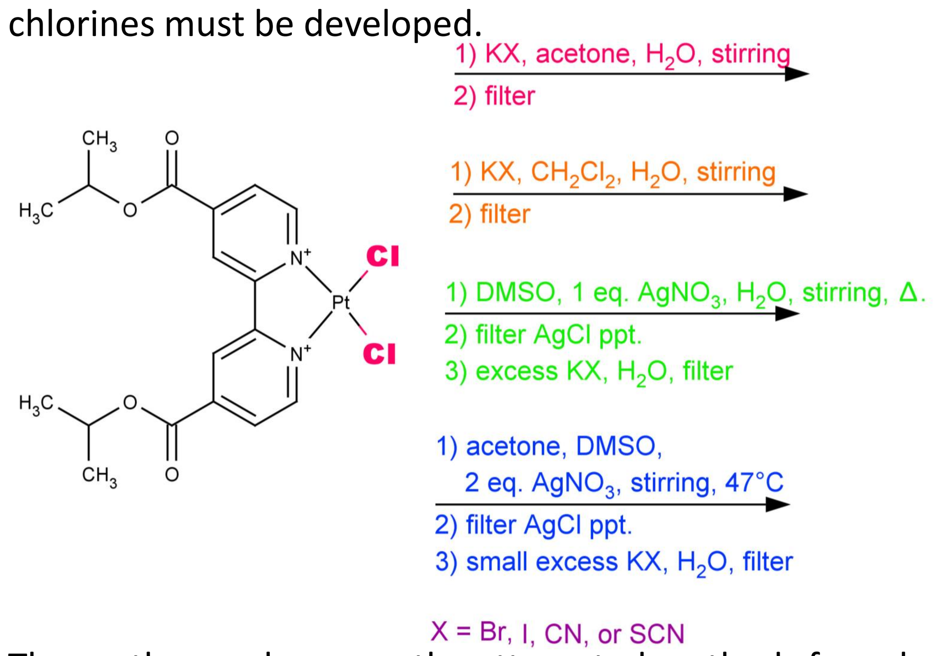
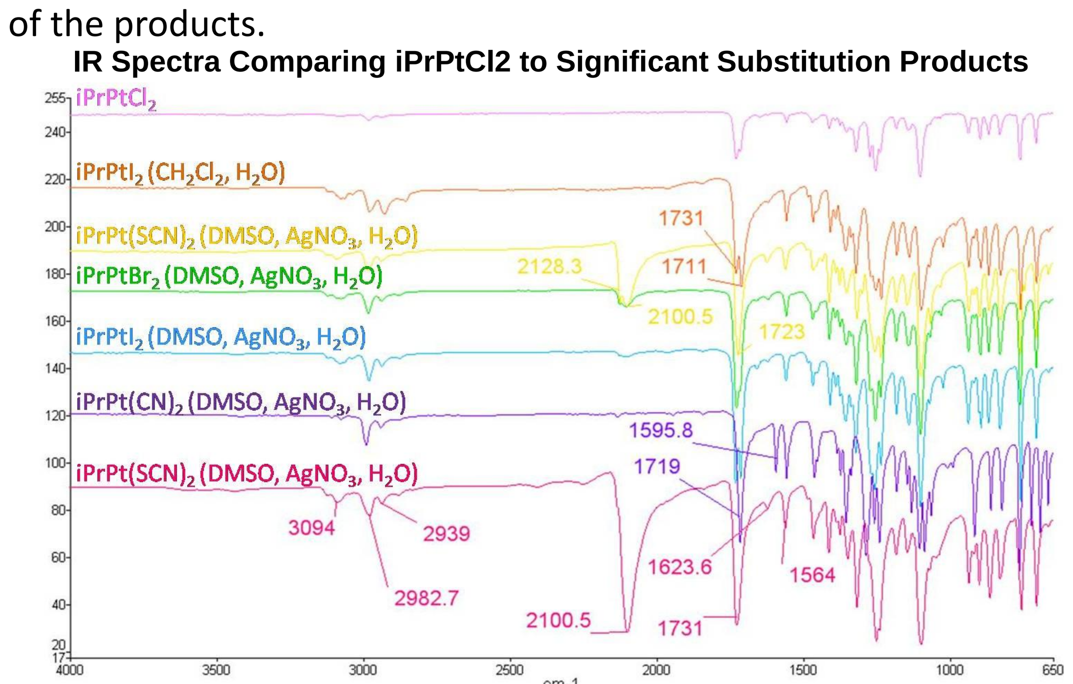
Abstract: Platinum (II) diimine complexes display a wide array of interesting physical properties, including luminescence, photoredox chemistry, polymorphism and polychromism. By coupling these chromophores to Guerbet alcohols we have prepared a new class of metal-containing liquid crystalline materials with very low transition temperatures and wide mesomorphic temperature ranges. These materials display unique physical properties, including thermo- and vapoluminescence. Ligand substitution reactions can be used to alter the spectral properties of these complexes and to construct supramolecular architectures. The relationships between structure, phase behavior and the luminescent properties of these materials will be explored.

Substitution of Chloride Ligands

Theoretically, the platinum metallomesogens' properties vary based on the identity of the anions attached to the platinum. Due to the difficulty of synthesizing $iPrPtCl_2$ via the Jones reaction, a reliable method for substituting other anions for the chlorines must be developed.



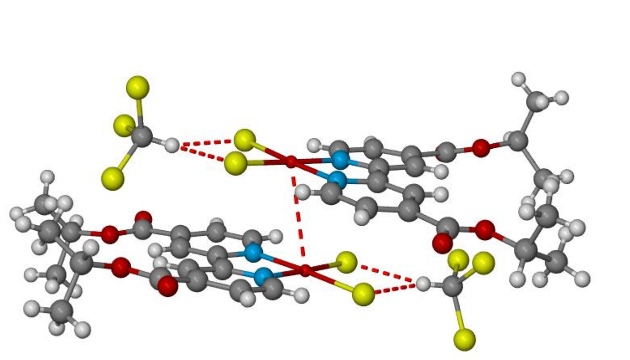
The syntheses above are the attempted methods for substituting the chlorine anions on the platinum (II) ligand ($iPrPtCl_2$) for bromine, iodine, cyanide, and thiocyanate anions. The DMSO/$AgNO_3$ reactions seem to be the most reliable method of substitution though more characterization must be done to determine the purity and identity of the products.



IR spectra of substitution products can theoretically be used to characterize them. IR spectra of $iPrPtI_2$ show double carbonyl peaks at 1710 and 1730 cm^{-1}, while the other compounds show only single peaks. This could indicate a mixture of $iPrPtI_2$ and $iPrPtCl_2$ in the compound. $iPrPt(SCN)_2$ shows the cyano peak at 2100 cm^{-1}, indicating a successful substitution. The $iPrPt(CN)_2$ does not show the cyano peak, so the excess cyanide may have removed the platinum, leaving the bare ligand. Melting point and ^1H NMR analysis will also be used to characterize the materials.

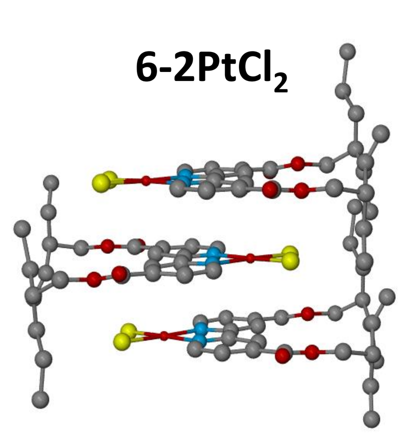
Crystal Structures:

$iPrPtCl_2$



Orange, emissive crystals. Note the presence of a short Pt-Pt interaction (3.490Å) and short H•••Cl contacts (2.74Å) involving the Cl atoms of the complex and the H atom of chloroform.

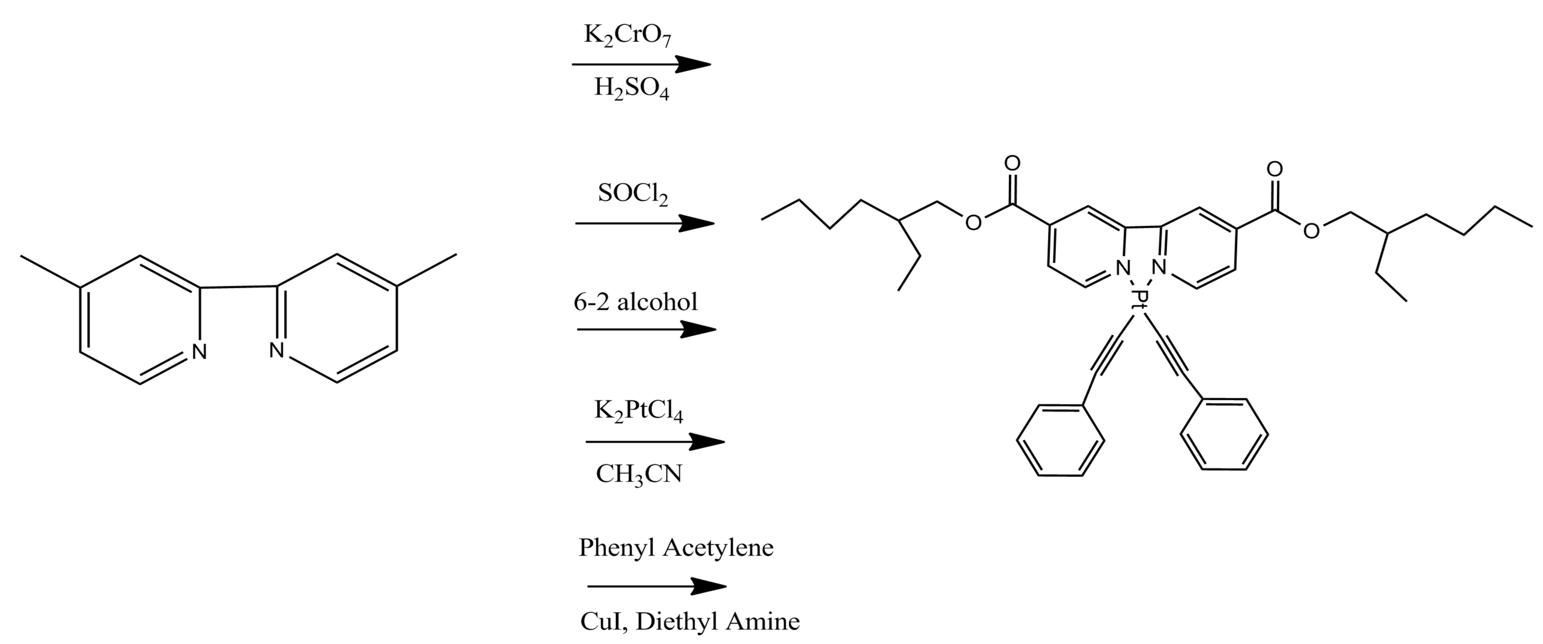
6-$2PtCl_2$



Yellow, non-emissive crystals. Note the absence of short Pt-Pt interactions; the nearest contact is 5.423Å (interplanar stacking distance is 3.36Å).

Synthesis of Bipyridine Platinum Supermolecular Squares

The synthesis of the supermolecular bipyridine platinum squares is of interest because of the interesting conductive properties that these compounds may have, as well as their possible fluorescence and use in electronic devices.

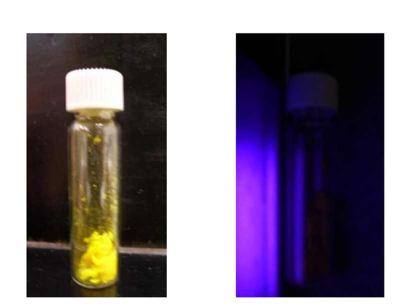


Completed Synthesis:
•Bipyridine platinum chloride complex has been successfully synthesized and acetylides have been attached.
•The first carbazole reaction has been started.

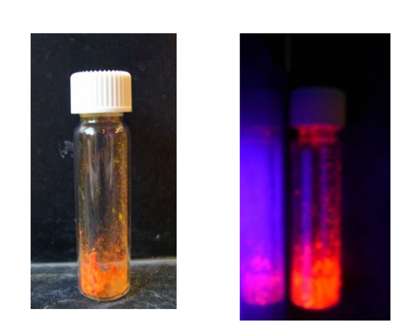
Goals:
• Need to successfully purify the platinum half of the square
•Need to synthesize the carbazole fragment necessary for another class of squares to be built.
•Need to run a full fluorescence study on each compound, as well as a full study on the electronic properties of each synthesized compound .

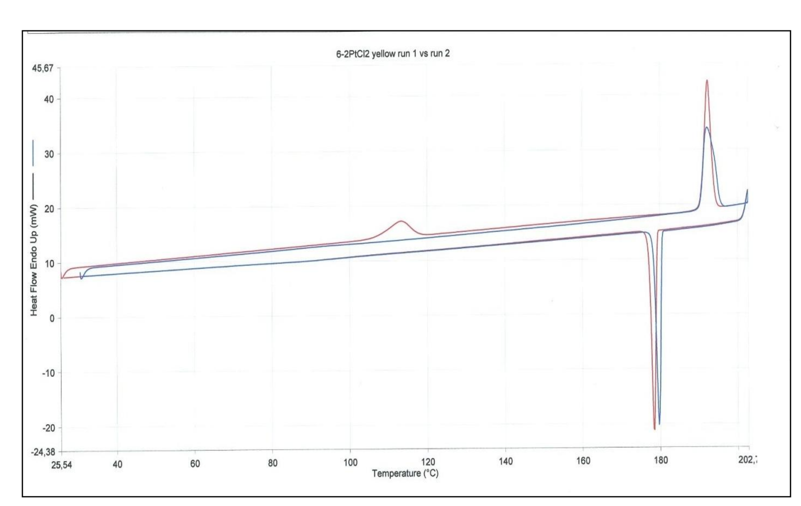
Thermotropic Polychromism & Luminescence of 6-$2PtCl_2$

Yellow, Non-Luminescent Form



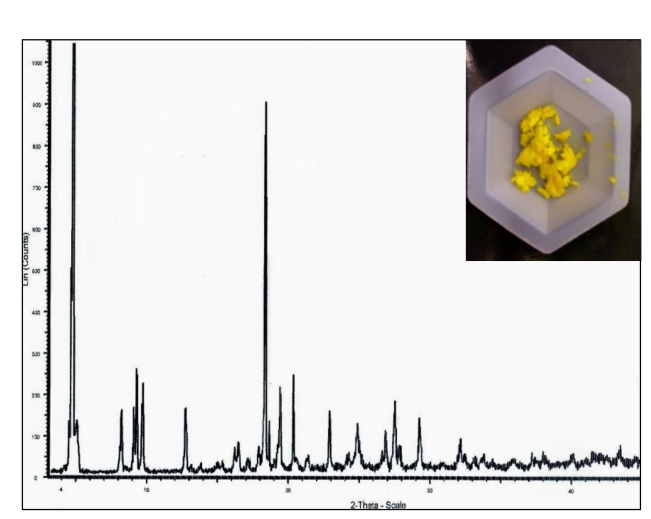
Orange, Luminescent Form

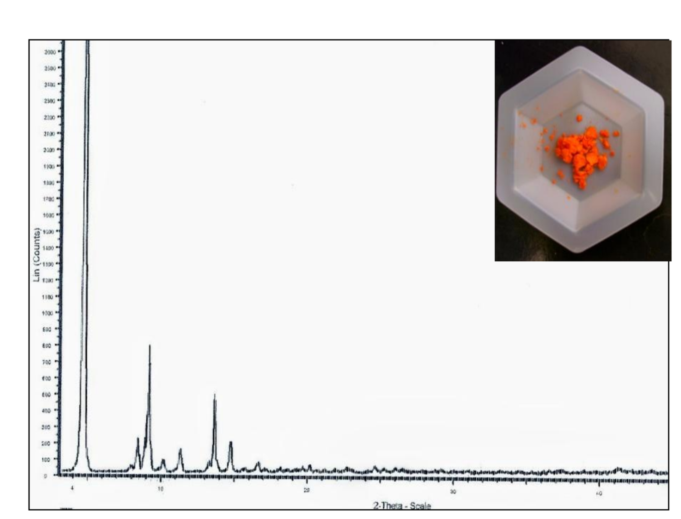




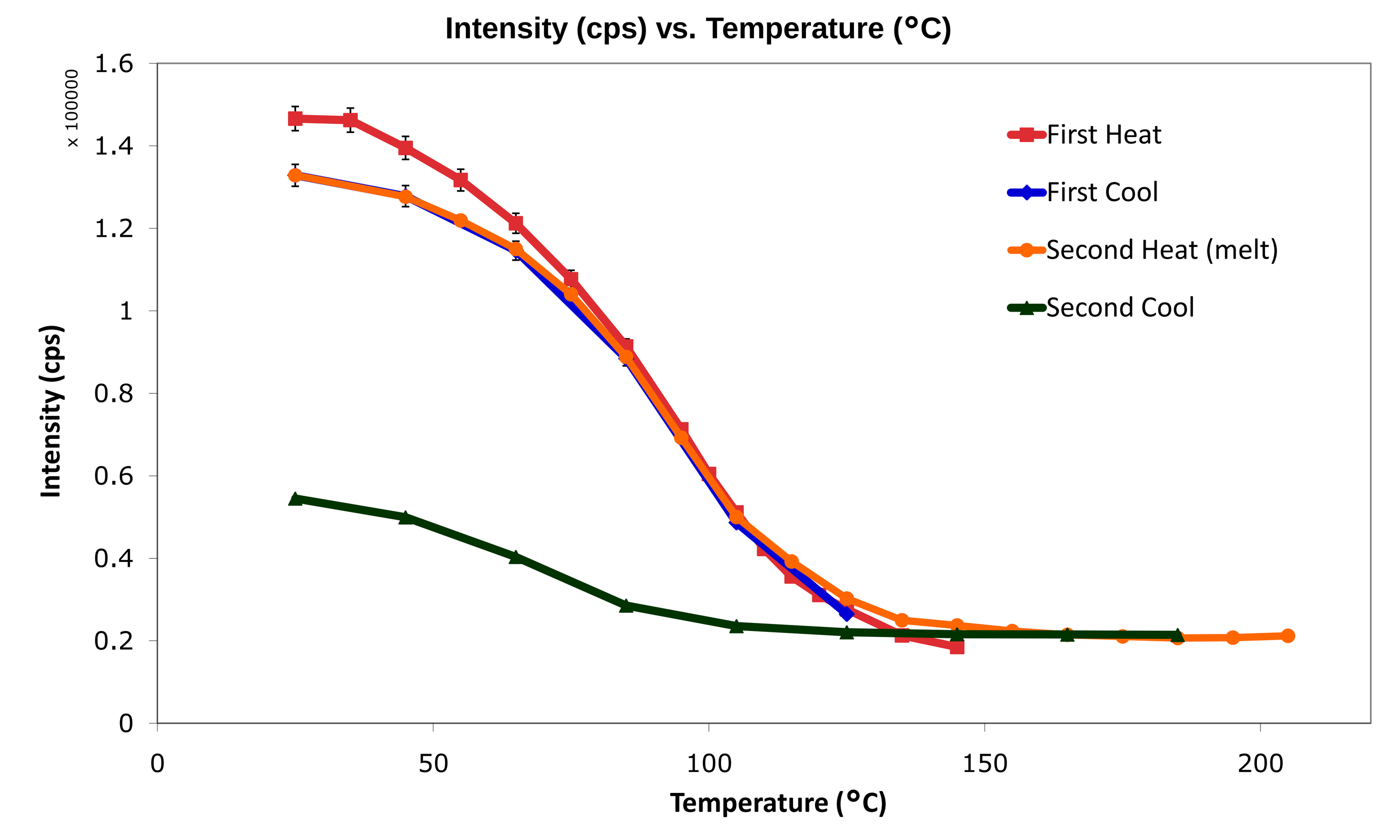
DSC shows an endothermic transition from the yellow, non-emissive to the orange, emissive at 110 °C. TGA shows no weight loss until well above the melting point; hence the change is not associated with the gaining or loss of solvent molecules.

Powder X-Ray Diffraction clearly shows that the change in photophysical properties is the result of a solid-state phase change.





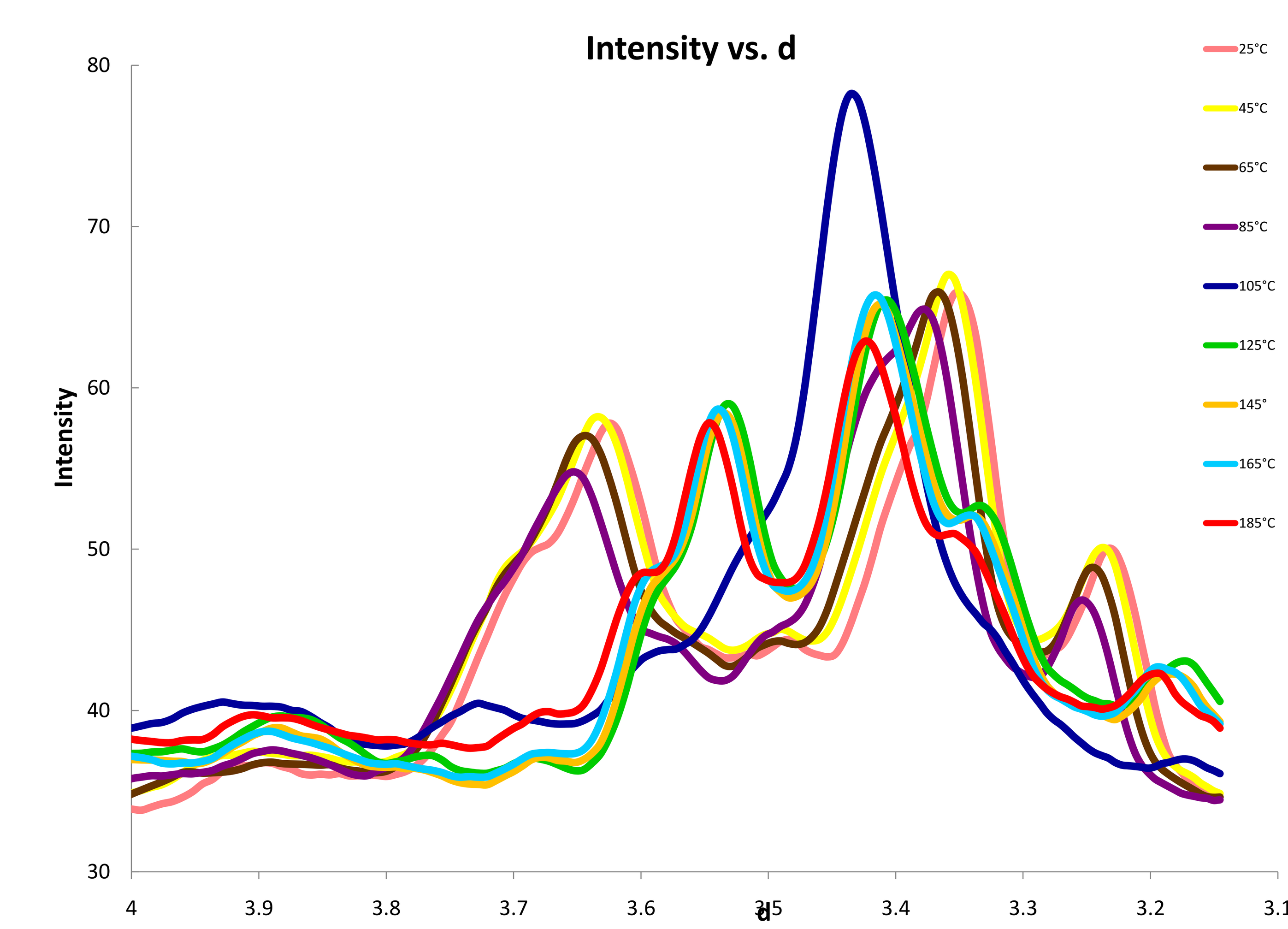
Variable Temperature Luminescence of 6-$2PtCl_2$



Hypothesis: As 6-$2PtCl_2$ heats the spacing between platinums changes as a function of the temperature. An increase in the temperature leads to an increase in the spacing between the platinums.

Variable Temperature X-Ray Data of the yellow polymorph of 6-$2PtCl_2$

The 6-$2PtCl_2$ changes from the yellow to the orange polymorph at 105°C (blue line below).



Conclusions

• Single crystal and powder X-ray diffraction show that dimerization and aggregation of $PtCl_2$ complexes lead to red/orange luminescent and yellow non-luminescent forms of the same compound.
• Vapoluminescent studies show that films of these complexes respond to vapors of chlorinated solvents by switching photophysical behavior.

Future Work

• Work on making better, more uniform films for these studies.
•Determine structurally why some solvents work better than others.
•Use the powder x-ray diffraction variable temperature data of the 6-$2PtCl_2$ to determine any structural changes.

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