Condensed Phase Engineering: From Molecular Structure to Physical Properties
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Abstract: The observed physical properties of all materials are tied intimately to the underlying molecular and supramolecular structures—that is the arrangement of atoms into molecules and the arrangement of molecules into bulk materials. Consequently, control of these relationships is central to our ability to engineer new materials with enhanced properties. One interesting facet of this problem is the observation that a single compound can exhibit different properties based on differences in supramolecular aggregation in the condensed phase, i.e. polymorphism. Our research has focused on the synthesis and characterization of alkylated derivatives of the 2,2-bipyridineplatinum(II) fragment (A). Complexes synthesized in our lab have been shown to be capable of exhibiting a wide array of novel properties—polymorphism, polychromism, vapochromism, luminescence, vapoluminescence, and liquid crystallinity. We will present representative examples of these behaviors and discuss our preliminary work to uncover the structural basis for this wide array of novel and potentially useful properties. These preliminary studies suggest that strong non-covalent interactions between platinum atoms play a key role in determining the observed properties.

Synthesis:

Aggregation in Solution and the Condensed Phase

Hypothesis: Polychromism and other photophysical properties in the condensed phase are the result of aggregation of dimers in solution via formation of a Pt-Pt interaction. At low solution concentrations, the crystal building blocks are monomeric units, leading to yellow crystals. At high solution concentration the crystal building block is the dimeric unit leading to orange or red crystals.

Testing Effect of Concentration on Properties:

1) High concentration of 6-2 PtCl2 compound dissolved in chloroform was layered with ethanol.
2) Red/orange crystals grew as ethanol diffused into chloroform.
3) More ethanol was layered on top of ethanol/chloroform solution.
4) Yellow crystals grew above the red crystals in the now dilute solution.

Crystal Structures

Thermotropic Polychromism and Luminescence of 6-2PtCl2

Yellow, Non-Luminescent Form

Orange, Luminescent Form

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

Vapoluminescence Behavior

Thin films of these complexes show responsive behavior toward chlorinated solvent vapors. For the complex with isopropyl alkyl groups (shown below), the behavior can be characterized as "on"—the film becomes luminescent in the presence of the solvent vapor. In other complexes, such as 6-2PtCl2, the situation is reversed and the film shows "off" behavior.

Conclusions

• Single crystal and powder X-ray diffraction show that dimerization and aggregation of PtCl2 complexes leads 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

• Determination of equilibrium constant for dimerization (Kd) of 6-2 compound using UV-Vis spectra and compare to values determined from NMR shifts (work done by Audrea Buckley).
• Apply structural knowledge to the construction of functional devices—vapor sensors, new emissive display materials, etc.

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