

Platinum Double Salts: Analyzing Fluorescence Spectra and Comparing Isonitrile Functionality

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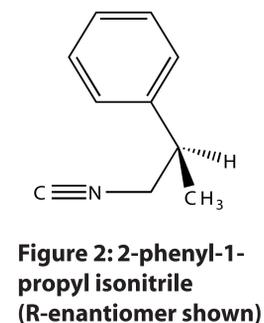
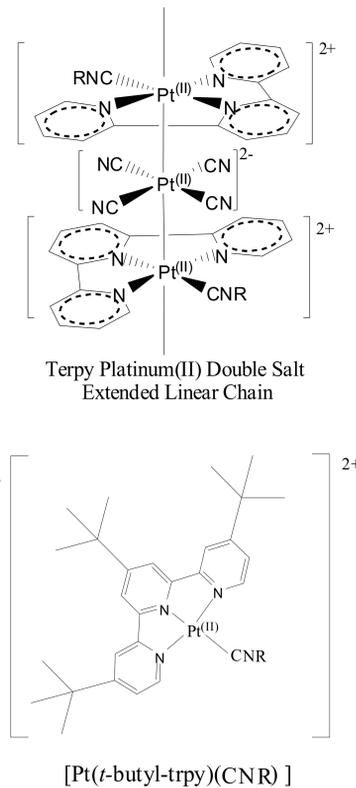
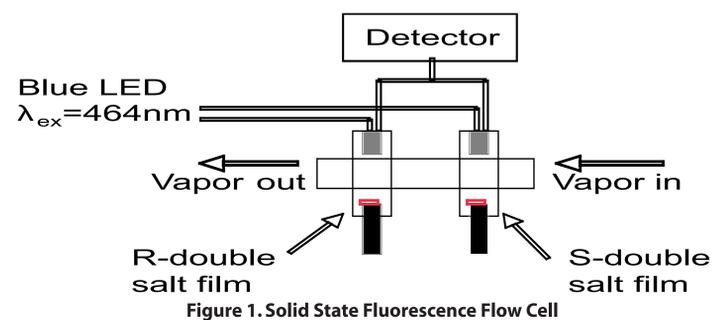
Introduction

Platinum(II) double salts consist of extended linear chains of alternating dications (+2 charge) and dianions (-2 charge). These double salts fluoresce and they possess vapochromic properties. The Platinum-Platinum bond will change in length in the presence of various volatile organic compounds (VOC's), which will in turn change the wavelengths of light that are emitted as fluorescence. The dianion always consists of a Platinum (II) with four square-planar oriented cyanide ligands. In our research, the ligands attached to the dication are varied to produce different Platinum-Platinum bond lengths with varying vapochromic capacities. Previous research has had four identical isonitriles attached to the dication, but this year three of the bonds were taken up by either a terpyridine (trpy) or tri-*tert*-butyl terpyridine (tri-*tert*-butyl trpy) while the fourth bond was available for the isonitrile. It has been observed in the past that certain chiral isonitriles showed enantiomeric selectivity in the presence of chiral vapors. Our goals this year were to determine whether or not a double salt with only one chiral isonitrile would still behave vapochromically, and to determine if enantiomeric selectivity is still present.

Experimental

Double salts were synthesized this year using the methods described on the poster by Ryan Martinez. Thin films of the R and S enantiomers of the double salt were prepared on the ends of small rods and placed in the apparatus (Figure 1), usually from a suspension in diethyl ether. N₂ was used as a carrier gas to move a saturated volatile organic compound (VOC) through a flow cell over double salt films. Fiber-optic probes above each double salt transmitted light from a blue LED (464nm) onto the sample. The reflected light, including the fluorescence, is carried through the fiber optics to an Ocean Optics VIS-Near IR detector. The sampling process was set up and monitored using LabVIEW.

A dark current was taken before each series of tests. Typical sampling procedure was to average 10 scans at a 1 second integration period. The achiral vapors used were: water, dichloromethane, 1-propanol, 2-propanol, ethanol, ethyl acetate, acetonitrile, and acetone. R- and S-2-butanol were used as the chiral vapor. Nitrogen was normally used to purge the lines of vapors. Each run varied in length from 4 to 8 minutes, being sure to allow the emission spectrum to attain equilibrium before ending the exposure. Often it was difficult to get fluorescence peaks of R and S double salts under nitrogen to line up from one exposure to the next due to VOCs leaving the crystalline matrix slowly. With the 2-butanol exposures for the tri-*tert*-butyl trpy double salts it was found that acetonitrile vapor functioned better as a purge than nitrogen and gave more consistent results.



Results/Discussion

The only double salt with a trpy in the dication, made with a 1,2,3,4-tetrahydro-1-naphthyl isonitrile, showed no vapochromic effects with any VOC (Figure 3). This is most likely due to a very compact stacking with Pt-Pt bonds so short that the VOCs cannot even enter the crystal matrix to change the color of fluorescence.

The tri-*tert*-butyl-trpy versions of the double salts were all vapochromic and showed shifts in wavelength for many different VOCs (Figure 4). Last year it was observed that the double salts made with four S- or four R- 2-phenyl-1-propyl isonitriles (structure in Figure 2) in the dication were enantiomerically selective for S- and R-2-butanol (Figure 5). However, when the 2-phenyl-1-propyl double salt was tested for enantiomeric selectivity with 2-butanol, none was shown (Figure 6). The advantage of these trpy double salts is increased stability at higher temperatures and no degradation to thermodynamically stable neutral products like the previous double salts. It appears that either one chiral center per dication is not sufficient, or some other factor is involved.

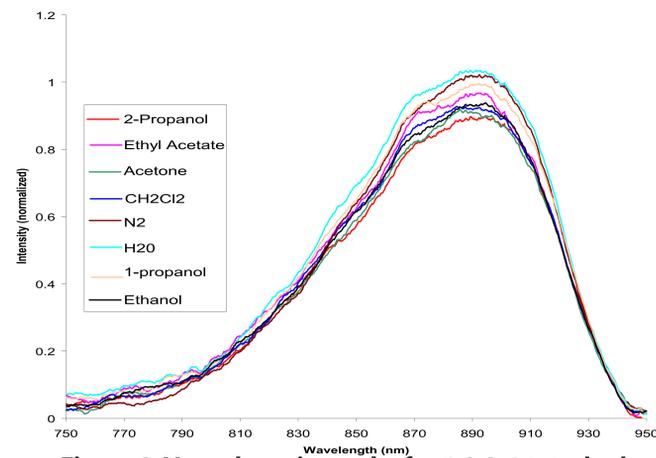


Figure 3: Vapochromic results for 1,2,3,4-tetrahydro-1-naphthyl with trpy double salt. Yellow LED was used (about 580 nm) because there was no fluorescence with the blue LED.

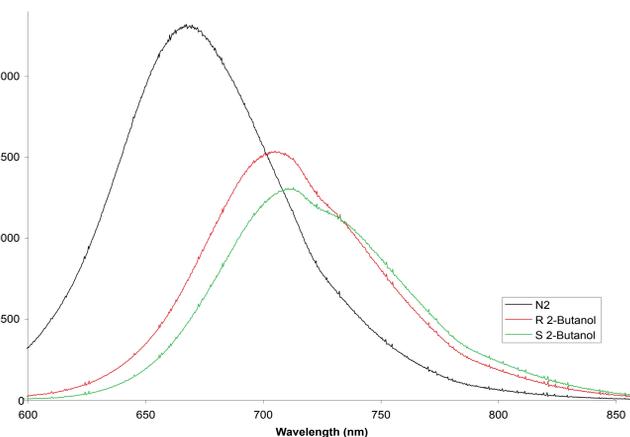
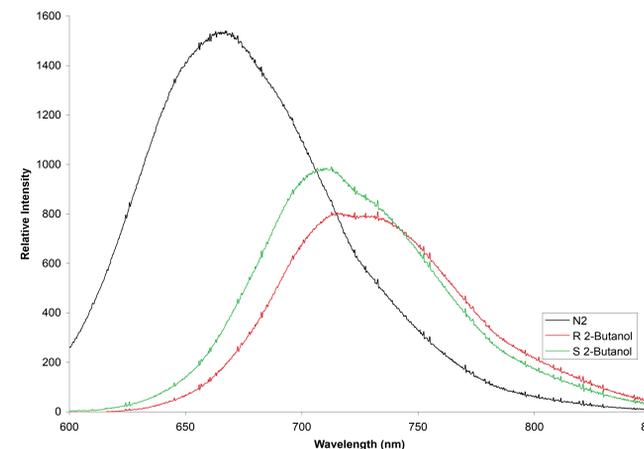


Figure 5: Vapochromic results for S(top) and R(bottom)-2-phenyl-1-propyl double salt. Enantiomeric selectivity is observed in the shift in wavelength of maximum fluorescence for the R- and S-2-butanol.

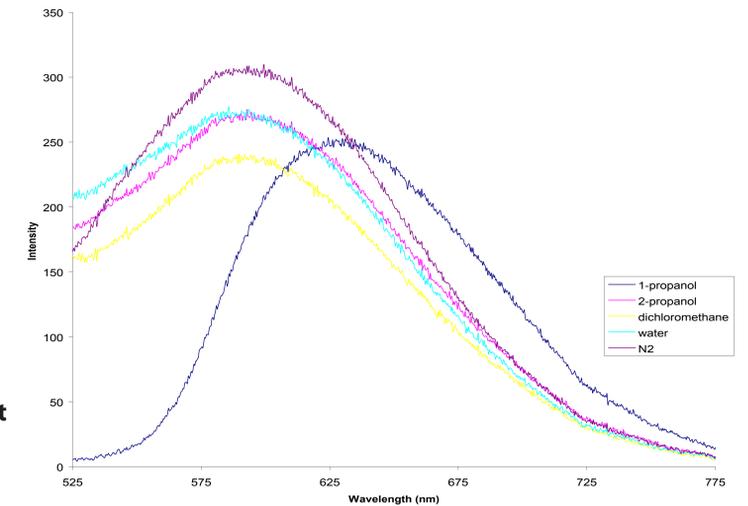


Figure 4: 2-phenyl-1-propyl isonitrile with tri-*tert*-butyl trpy double salt. Fluorescence shifts are seen with various VOCs.

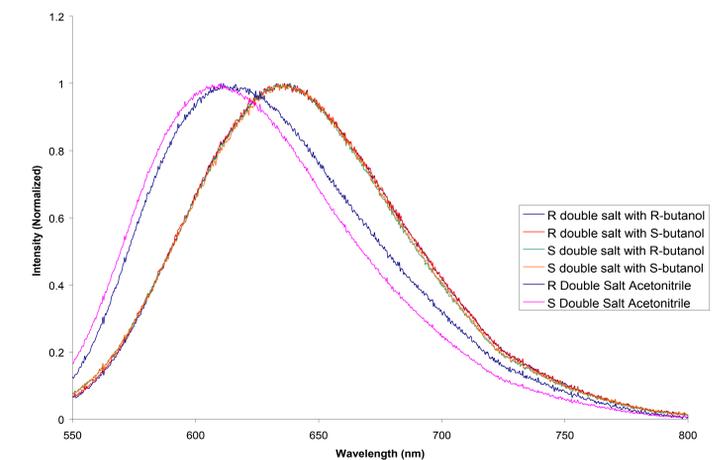


Figure 6: Vapochromic results for R- and S- 2-phenyl-1-propyl/ t-butyl trpy double salts. No enantiomeric selectivity is observed.

Future Work

Future research for this project will determine if a bipyridine ligand, which allows two isonitriles on each dication, will retain some of the best qualities of all previous double salts with improved stability and enantiomeric selectivity.

Acknowledgements

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