Hydrogen bonded networks with variable functionalized netpoints: A probe of mesophase stability

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Wiegel Research: Careening from catastrophe to catastrophe since 2000

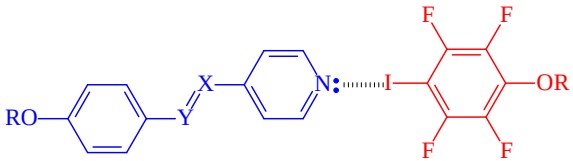
Background

Liquid Crystals

- Materials that exhibit long-range and some short-range directional ordering in a fluid state.
- Composed of mesogens (shaped molecules) and flexible spacers
- Different types of mesogens based on molecular shape (calamitic: rod-shaped)

Molecular Self-assembly Through Halogen Bonding

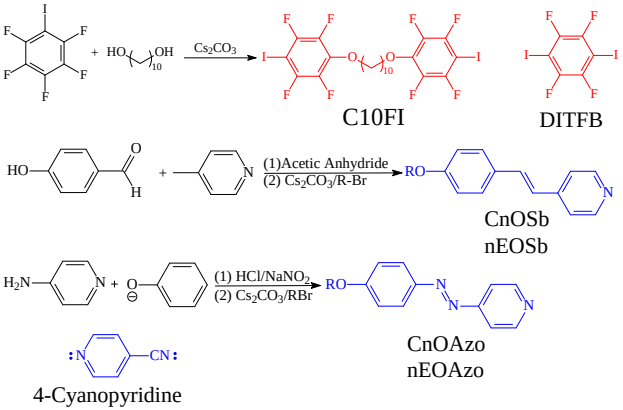
- Non-covalent interaction between an electron deficient halogen (iodine or bromine) and a strong electron donor (pyridine and nitrile)



X= N, C
Y=C, N

- Specific and directional associations
- Thermodynamically weaker than hydrogen bonds
- Preliminary work from several groups show the capability of forming liquid crystalline assemblies from non-mesogenic precursors through halogen bonding.

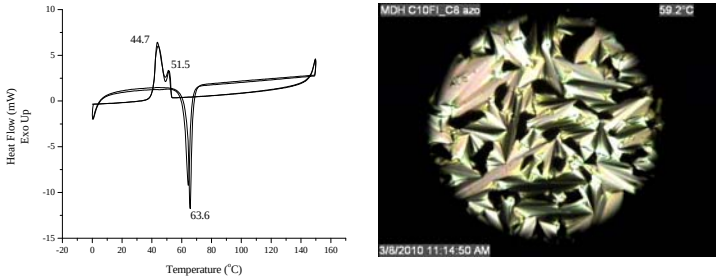
Materials Used/Synthetic Methodologies



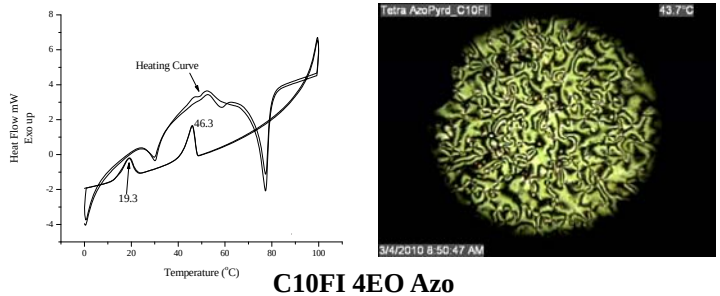
Thermal Analysis

- Complexes synthesized through solution-complex methodology
- Components stoichiometrically weighed and mixed in a common solvent (methylene chloride or THF)
- The solvent was allowed to evaporate in a covered flask
- DSC data determined on a Mettler-Toledo STAR e1 DSC at 10˚C/Min heating rate unless otherwise noted
- Optical micrographs were measured using a Mettler-Toledo FP82 Hotstage Mounted on an Olympus BHT polarizing light microscope at a 10˚C/Min heating.

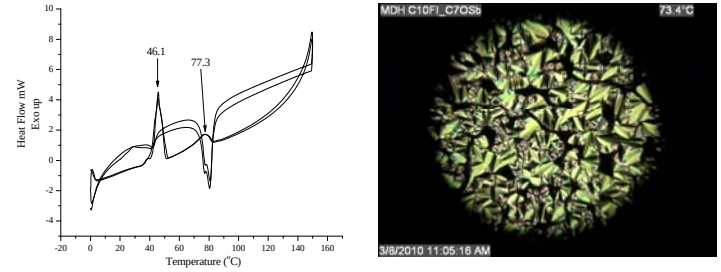
Results/Observations



C10FI C8OAzo

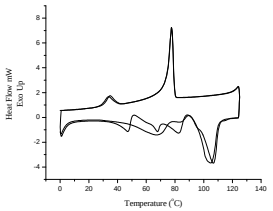


C10FI 4EO Azo

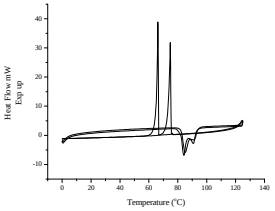


C10FI 7OSb

Results/Observations



DITFB 5Eo Sb



DITFB 4-cyano pyridine

Results

- Nitriles failed to produce any liquid crystalline phases when used as a donor
  - Electron density on the nitrile may be insufficient to form a stable halogen bond
  - Changing the electron density in the ring could drive halogen bond formation
- 1,4-diiodotetrafluorobenzene failed to produce any liquid crystalline phases when used as an acceptor
  - Initial calculations showed no significant electron density difference between the iodine atoms on C10FI and DITFB
  - The crystallization enthalpy on DITFB may have been too strong to form a mesogen
- Stilbazole species provided more ordered smectic species
- The azo donors produced more nematic phases
- Azo donors also provided liquid crystalline phases that existed at sub ambient temperatures.

Observations/Conclusions

- Halogen bonds form liquid crystalline assemblies from non-mesogenic components
- Azo-based halogen bond donors provide liquid crystalline phases at markedly lower temperatures than analogous stilbazole species

Acknowledgements

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