NMHU PREM: Light Matter Interactions: Theory and Applications

Partners: Georgia Institute of Technology and Morehouse College

- **Two-Photon Absorbing Materials**
- **Crystalline Nonlinear Optical and Electro-Optical Materials**
- **Conductive Organic Polymers for Solar Cells**

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Tatiana V. Timofeeva
New Mexico Highlands University

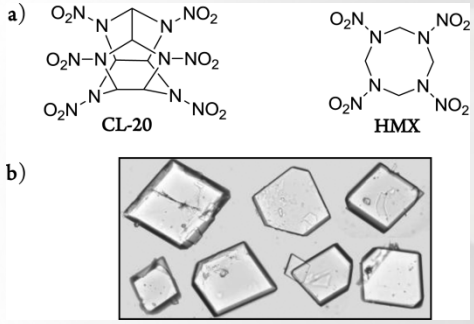
Crystal engineering of nonlinear optical and charge transfer materials

PREM Directors Meeting, May 20, 2013

PREM LMITA

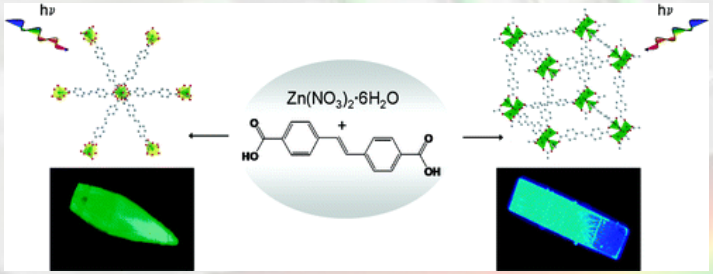
Crystal Engineering

Crystal engineering is the design and synthesis of molecular solid-state structures with desired properties, based on an understanding and exploitation of intermolecular interactions. The main strategies currently in use for crystal engineering are based on hydrogen bonding, search for polymorphs, co-crystallization and coordination complexation. These may be understood with key concepts such as the supramolecular synthon and the secondary building unit.

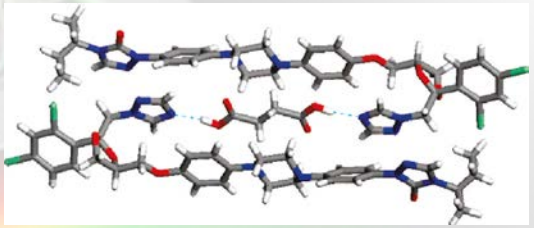


Onas Bolton, Leah R. Simke, Philip F. Pagoria, and Adam J. Matzger,
Cryst. Growth Des. **2012**, 12, 4311−4314

David I. A. Millar,* Helen E. Maynard-Casely, David R. Allan, Adam S. Cumming, Alistair R. Lennie, Alexandra J. Mackay, Iain D. H. Oswald, and Chiu C. Tangb and Colin R. Pulhama
CrystEngComm, **2012**,14, 3742-3749



Christina A. Bauer, Tatiana V. Timofeeva , Thomas B. Settersten , Brian D. Patterson , Vincent H. Liu , Blake A. Simmons , and Mark D. Allendorf *,
J. Am. Chem. Soc., **2007**, 129 (22), pp 7136–7144
> 200 citations



Single crystal X-ray structure of itraconazole succinic acid (2:1).
Remenar, J. F.; Morissette, S. L.; Peterson, M. L.; Moulton, B.; MacPhee, J. M.; Guzman, H. R.; Almarsson, €O. Crystal engineering of novel cocrystals of a triazole drug with 1,4-dicarboxylic acids. J. Am. Chem. Soc. **2003,** 125, 8456–8457

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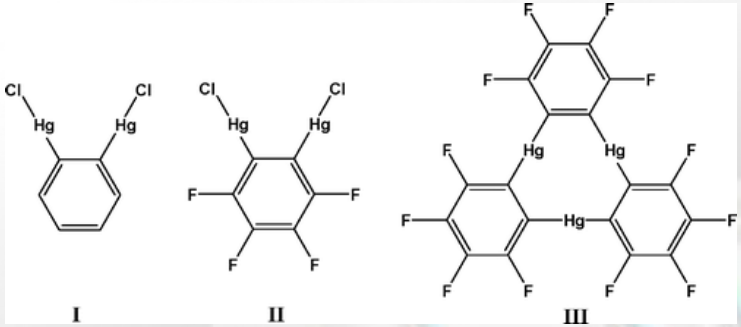
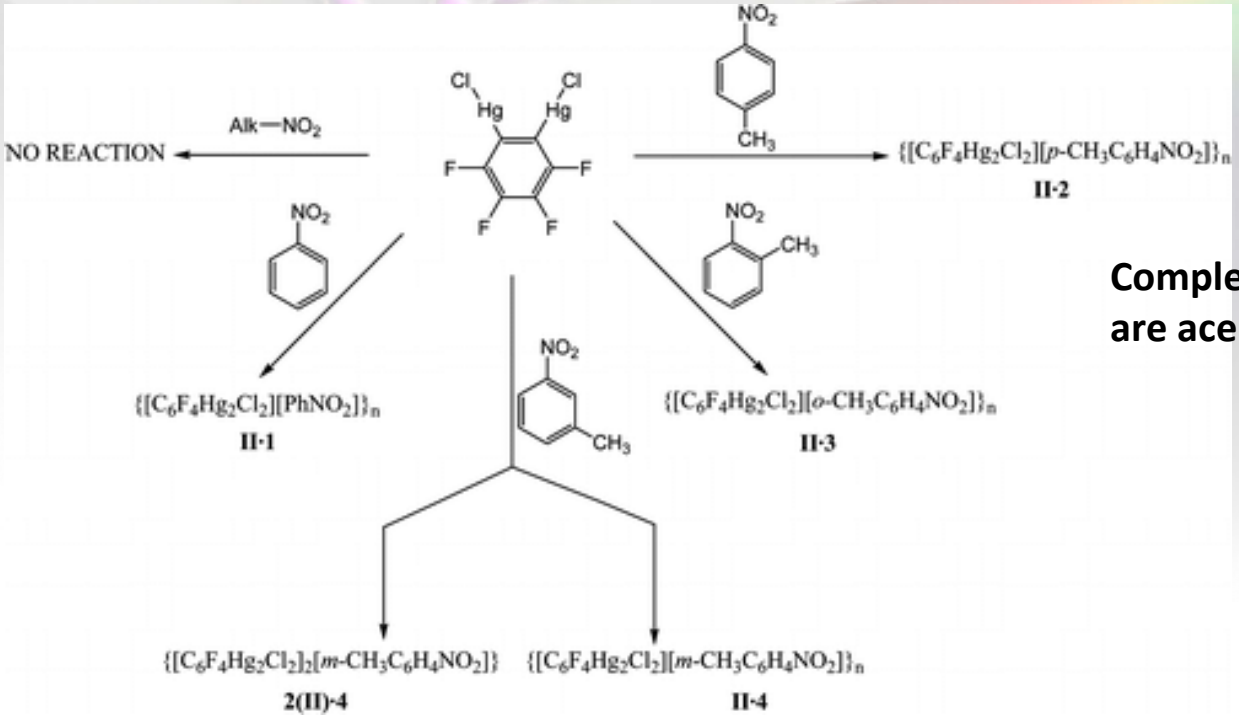
Co-crystallization of nitro benzenes with o-$(C_6F_4)(HgCl)_2$



Scheme 1

Bidentate 1,2-bis(chloromercurio)benzene, o-$(C_6H_4)(HgCl)_2$ (I), and 1,2-bis(chloromercurio)-tetrafluorobenzene, o-$(C_6F_4)(HgCl)_2$ (II) or cyclic tridentate perfluoro-o-phenylmercury, o-$(C_6F_4Hg)_3$ (III), Lewis acids (LA) presented in Scheme 1 easily form adducts (molecular complexes, guest–host structures, co-crystals) with organic ionic and neutral electron-reach compounds.



Complexes II-1 and II-4 are acentric.

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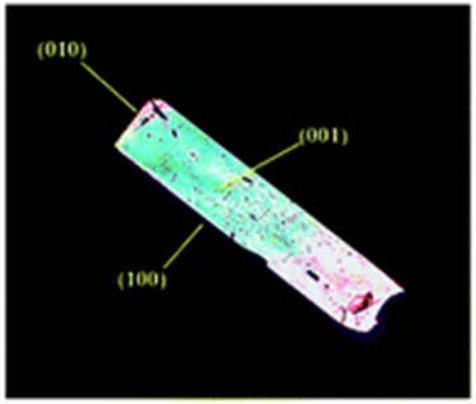
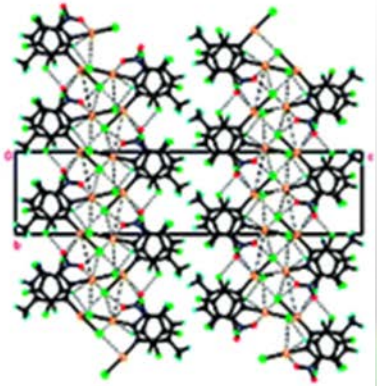
Co-crystallization of nitro benzenes with o-$(C_6F_4)(HgCl)_2$

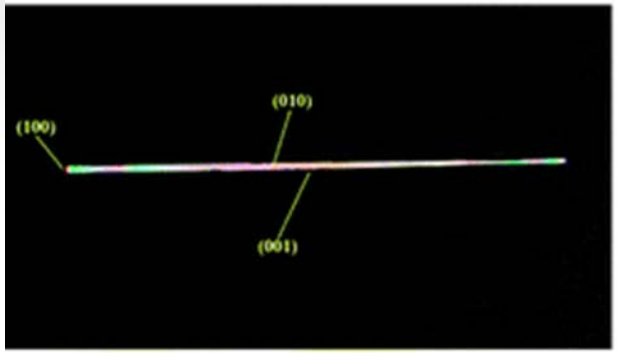
plate crystal



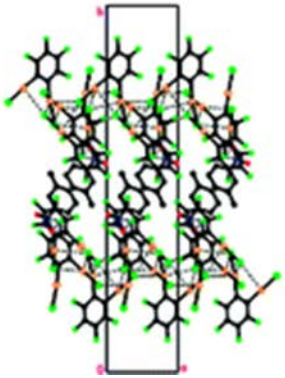
layers



needle crystal



chains



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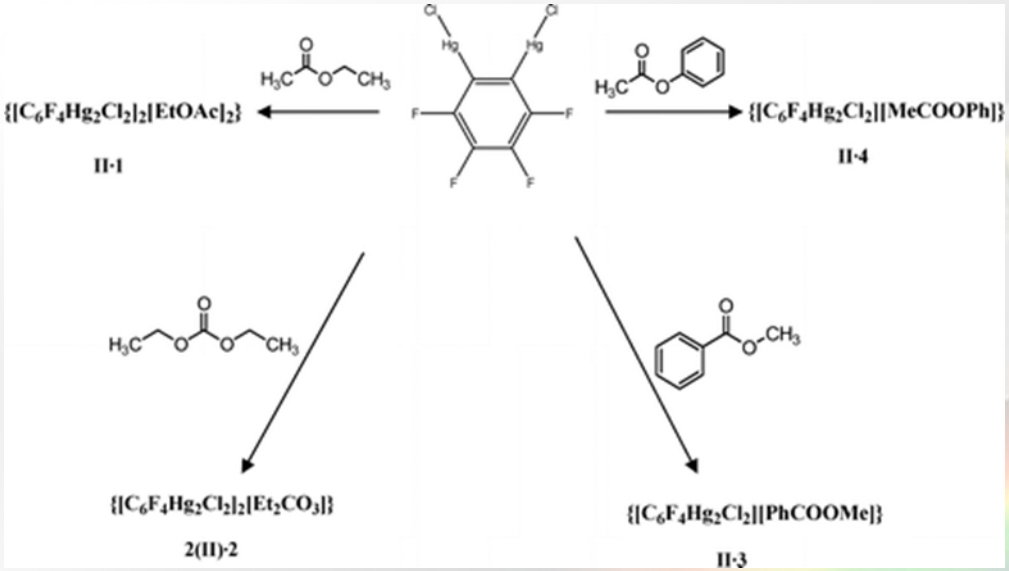
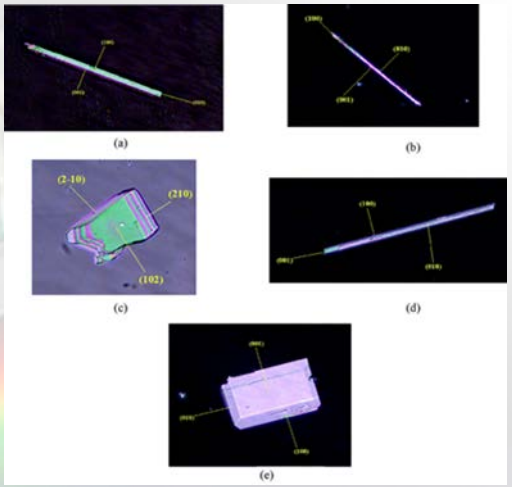
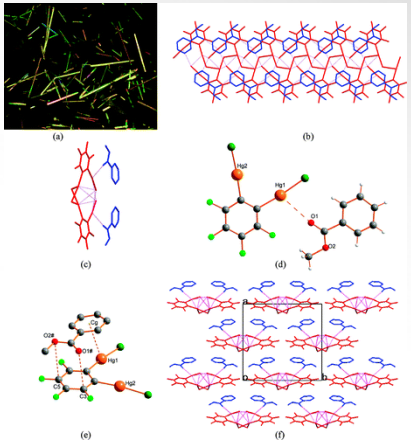
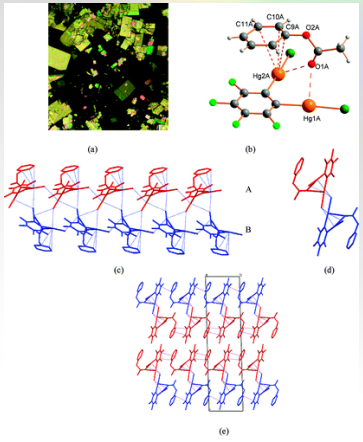
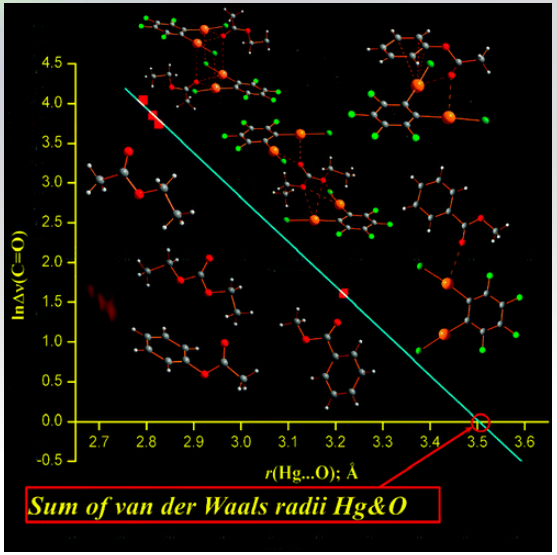
Crystal Morphology as an Evidence of Supramolecular Organization in Adducts of o-$(C_6F_4)(HgCl)_2$ with Organic Esters











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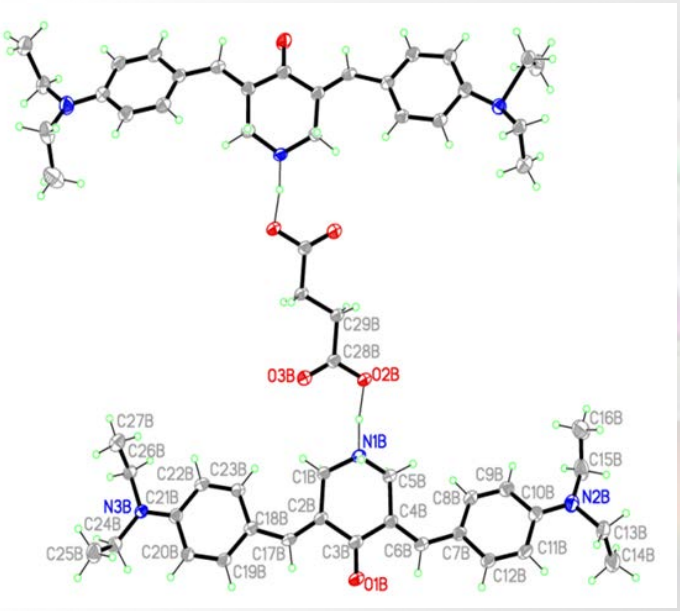
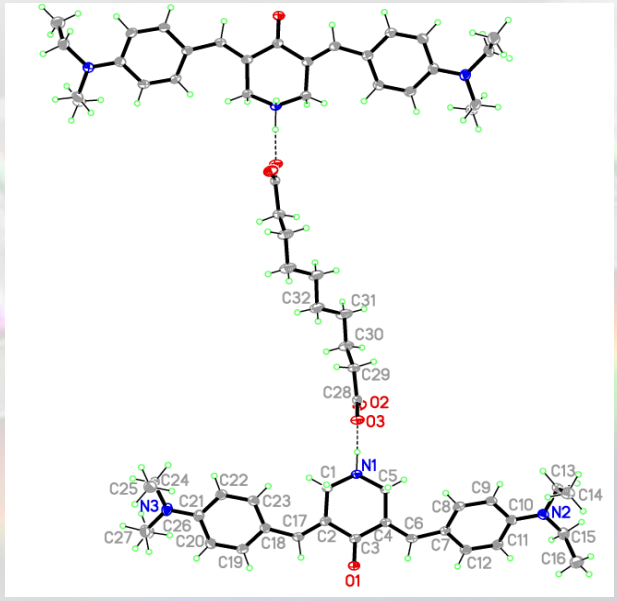
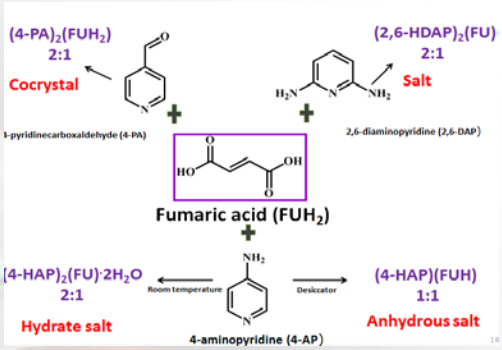
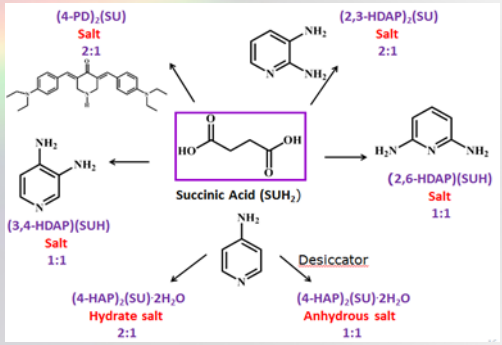
Crystal Engineering for Pharmaceutical Applications
Mixed Crystals, Adducts, Co-crystals, Salts





Examples of salt formation of (a) (E,E)-3,5-bis[4-(diethylamino) benzylidene]-4-oxopiperidinium butanedioate (b) (E,E)-3,5-bis[4-(diethylamino)benzylidene]-4-oxopiperidinium decanedioate

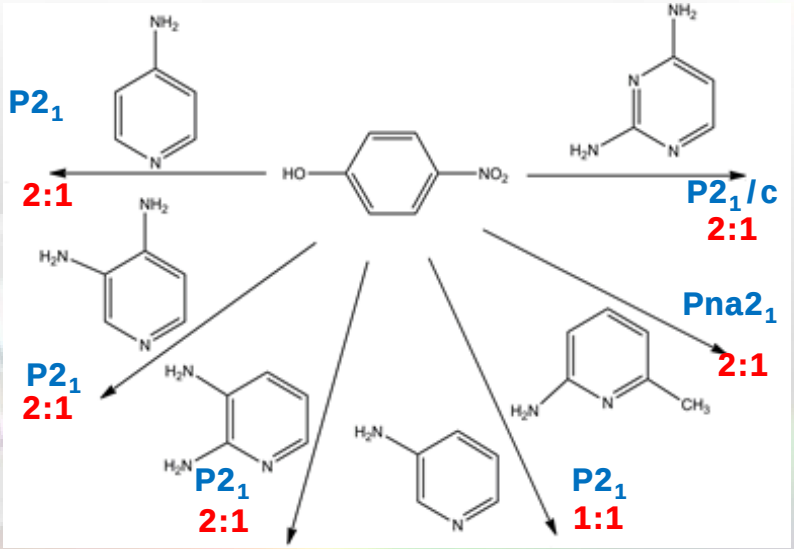




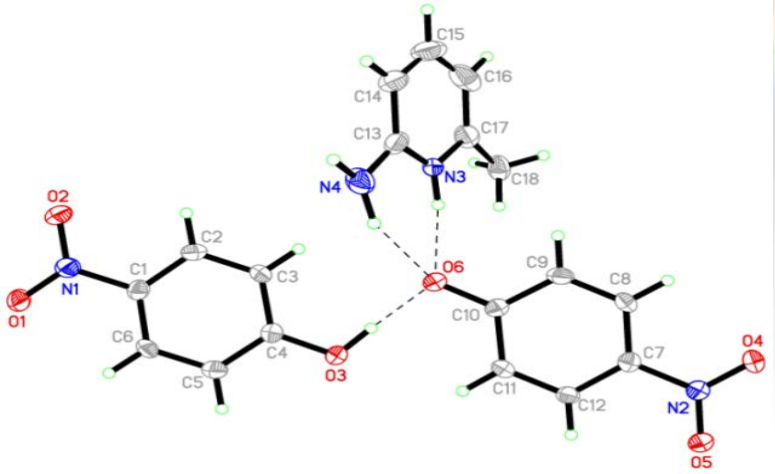
Schematic diagram of Crystals obtained with (I) Fumaric acid, (II) Succinic acid

LMITA PREM
New acentric materials constructed from aminopyridines and 4-nitrophenol

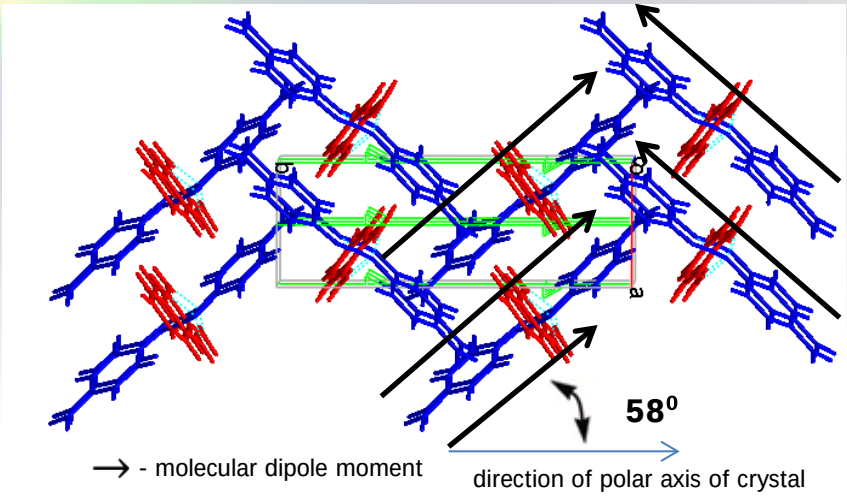
To make organic crystals useful for TeraHerz Generation and Non-Linear Optical applications crystal structure of materials should be acentric. To obtain materials with acentric structure crystal engineering approach was applied. Mixture of two individual organic compounds crystallize in new acentric material which acentricity controlled by specific “twisting agent .



Starting materials, compositions and space groups for the products



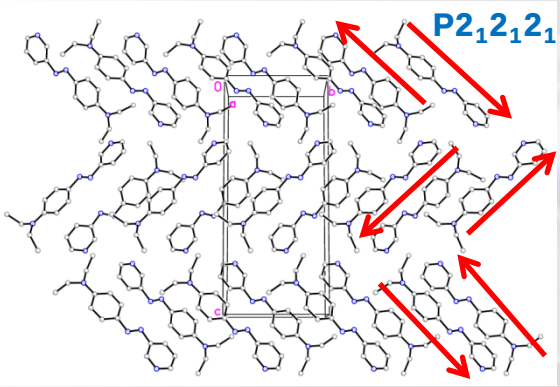
Example of asymmetric unit containing 4-nitrophenol-4-nitrophenolate dimer.



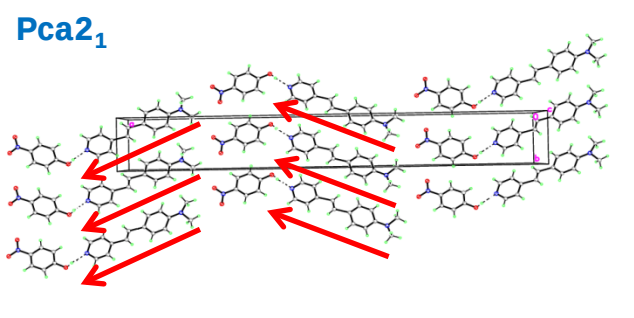
Molecular packing and orientation of molecular dipole moment for 3,4-diamino-pyridine and 4-nitrophenol adduct, 4-nitrophenol-4nitrophenolate dimer with blue

LMITA PREM
New Series of Acid-base Adducts for Nonlinear Optical Application

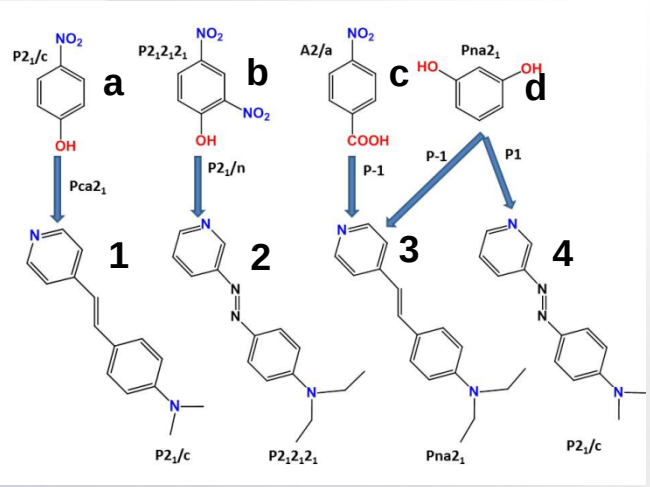
To enrich group of organic salts with such properties and elevate level of understanding of engineering of acentric crystalline materials for industrial applications, a series of co-crystals (or salts) containing polar stilbene-like molecules and small second component for formation of H-bonded systems was synthesized. Adducts of molecules with extended polar conjugated system prone to manifestation of second harmonic generation and small molecules that we used are predisposed to formation of chiral supramolecular associates.



Molecular packing and relative orientation of dipole moments for 2



Molecular packing and relative orientation of dipole moments for 1a



Starting material used and space groups for initial base and final adduct formed

Photos of single crystal for 1a, 2 and 4

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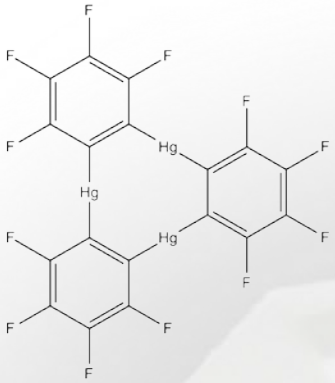
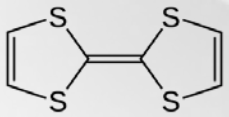
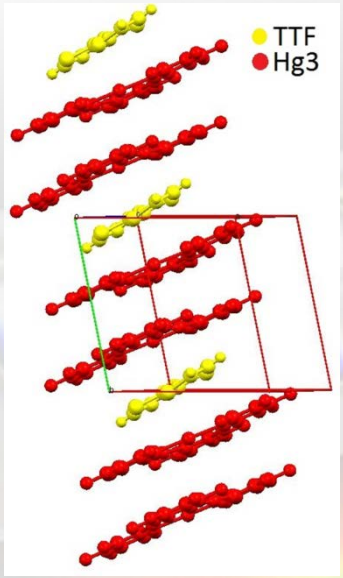
New Series of Adducts Charge Transfer Applications

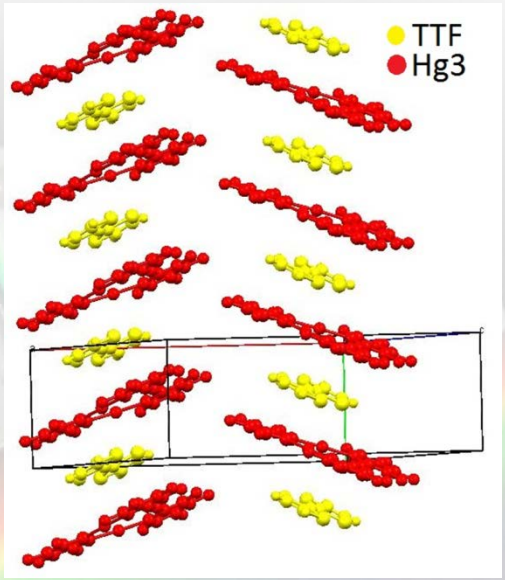


$o\text{-}(C_6F_4Hg)_3$

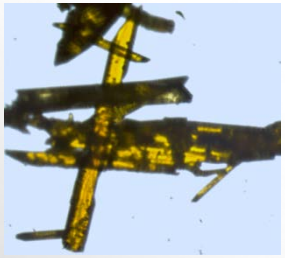


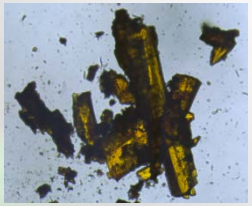
Tetrathiafulvalene (TTF)



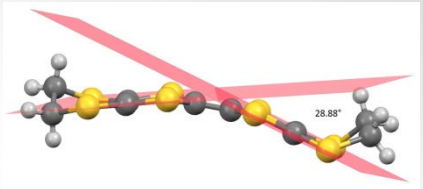


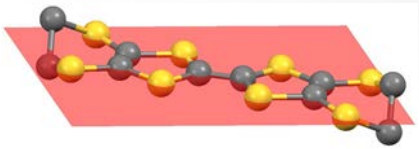
Molecular stacks in $[(Hg_3)\cdot TTF]$, $P2_1/c$ and $[(Hg_3)_2\cdot TTF]$ P-1

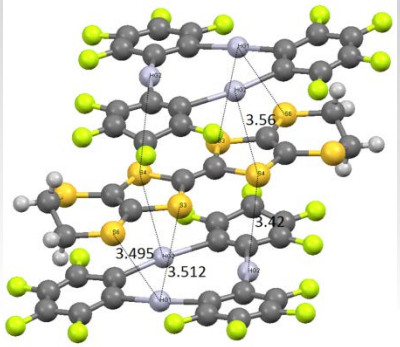




Crystal shape of
a) $[(Hg_3)\cdot TTF]$ $P2_1/c$
b) $[(Hg_3)_2\cdot TTF]$ P -1







BEDT-TTF forms 1:1 stack complex with Hg_3

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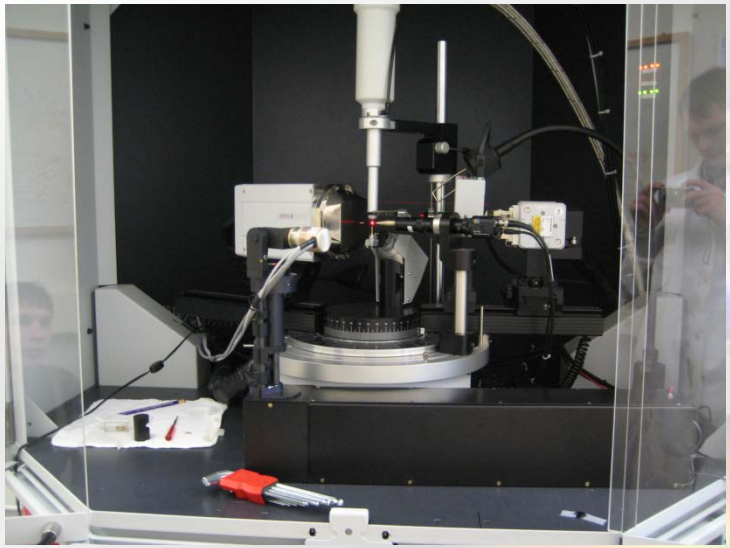
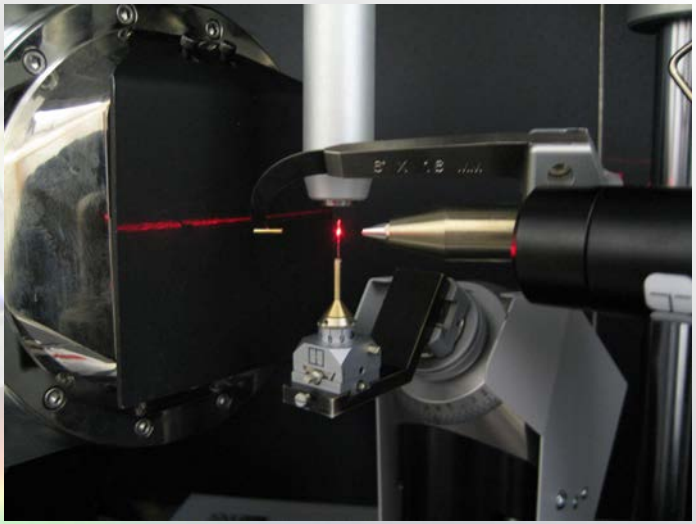
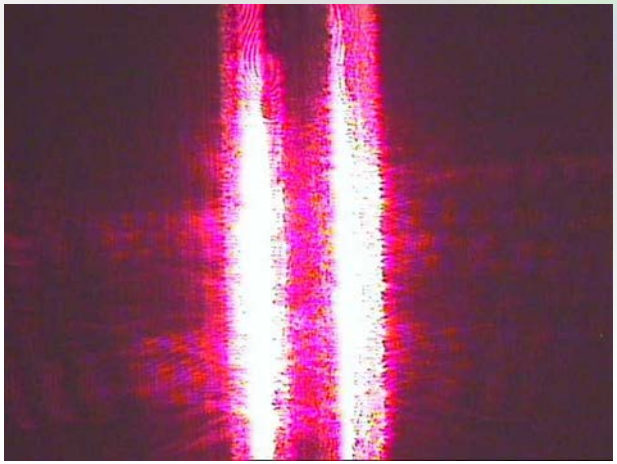
X-ray Diffraction and Laser Instrumentation for Crystal Grows in capillary

Laser System



Laser System, close-up





Capillary with Liquid

- Crystals are grown from liquids at room temperature
- Zone Melting technique

Undergraduate Students

Jose Gallegos 2009 MS Student @ NM Tech

Joseph Torres 2011 MS Student @ U. of Oregon

Jose Herrera 2012 IT specialist @ Bank

Deanna Montoya 2012 Employed @ Bank

Isaiah Otero 2012 MS Student @ NM Tech

Moses Kirui 2012 MS Student @ Florida Tech

Kayla Sawyer 2012 Chemist @ Hospira

Bhupinder Sandhu 2013 PhD Student @ Kansas State U.

Joel Zazueta 2013

Carlos Ordonez 2013 MS Student @ NMHU

Rachael Lucero 2013

Graduate Students

Ekaterina Badaeva 2005 Postdoc @ U. of Washington; Engineer at Boeing

Boris Averkiev 2005 PhD @ U. of Utah, Postdoc @ Washington State U.

Ilya Kosilkin 2005 PhD Student @ U. of Washington; Engineer at Boeing

Tiffany Kinnibrugh 2005 PhD @ Texas A&M U.; Argon National Lab

Andrey Yakovenko 2008 PhD @ Texas A&M U.; Argon National Lab

Ernest Asani 2008 Corporate vendor auditor at Leprino Foods Company, Denver, CO

Geetha Bhagavana 2008 INVAGEN pharmaceuticals, Hauppauge, NY

Joseph Mulroy 2009 UNM School of Pharmacy

Kamal Devis 2010 NMHU Business School

Scott Valdez 2010 Employed @ LANL

Nagakeerthi Dasari 2010 Florida

Renuka Tammisetti 2010 Employed @ Pharmacy Store, CA

Graduate Students

Shravana Lakshmi Nayani
2010
Employed at Pharmacy Store, TX

Alexander Romanov
2011
PhD
Russian Academy of Sciences

Alexandr Fonari
2011
PhD Student @ GATech

Praveen Pandi
2011
Neumeric Technologies Corp., OH

Paul Tongwa
2011
PhD Student @ Missouri U. of Science and Technology

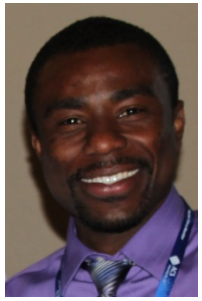
Crystal Ulibarri
2012
Medical Office

Galina Skinner
2012
IT manager, High School, Arizona

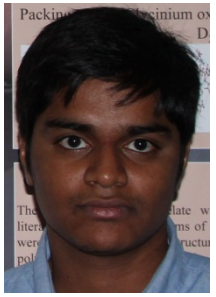
Peter Demianov
2012
IT Self employed

Samuel Bentum
2013
SABIC Innovative Plastics, Mt. Vernon

Gary Angles
2013
PhD Student @ NM Tech



Rene Ebule
2013
PhD Student @ U. Kentucky



Gnaneswar Elaprolu
2013