Optical Properties of Benzylpiperazine/CuI (111) system

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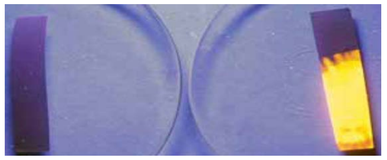
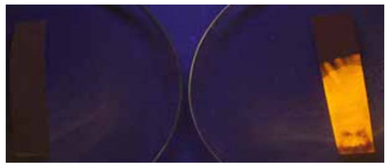
Motivation

- Cuprous iodide (CuI) films are promising ingredients for different optical applications, due to surface states and surface reactivity with adsorbed molecules.
- The electronic and optical properties of CuI film with different surface defects can be used for a prototype system (e.g. BZP-CuI) in molecular-conjugated fluorescence devices.
- The orange emission from Benzylpiperazine (BZP) molecule-conjugated with CuI film [1] can be used in photo-detectors, like drug detectors, which is of great interest for forensic and other optical technologies.
- In non-conjugated CuI film, there is a blue fluorescence [1] due to Iodine vapor atoms adsorbed at the CuI surface.
- The conjugated BZP-CuI system demonstrates the strong orange emission (~2.1eV) [1], which is the problem of interest for our study.

Long-wavelength – bright orange



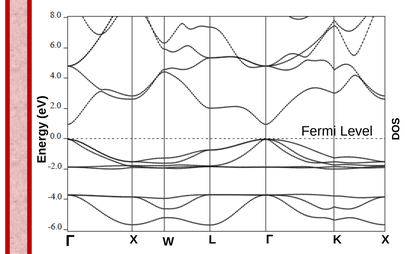
Short-wavelength – orange

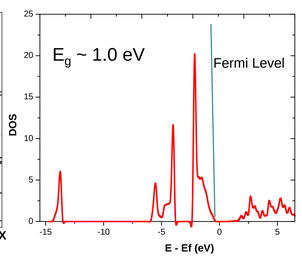


Experimental Results from Reference[1]

Electronic properties of CuI and BZP molecule

Band structure and DOS of bulk CuI (GGA)

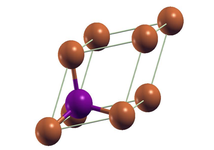




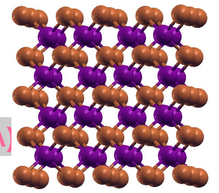
VB maximum Cu d-like & CB minimum Cu s-like

Band gap underestimated by 68 %

γ-CuI bulk structure

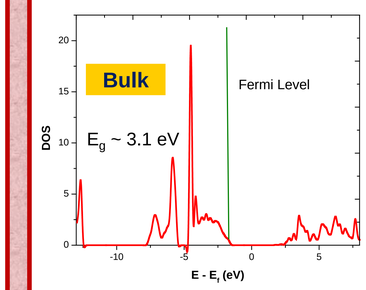


Unit Cell



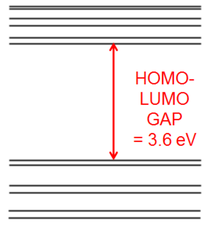
Bulk (a = 6.054) Å

DOS of CuI (GGA+U)

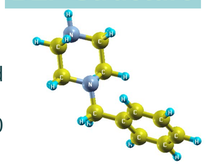


Energy gap corrected with Hubbard Parameters:
U(1) = 8.0 eV for Cu and U(2) = 5.0 eV for I

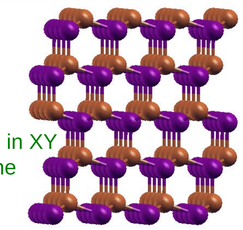
Energy levels of BZP (GGA)



BZP Structure



γ-CuI (111) surface Structure



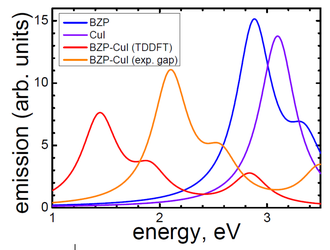
Periodic in XY plane

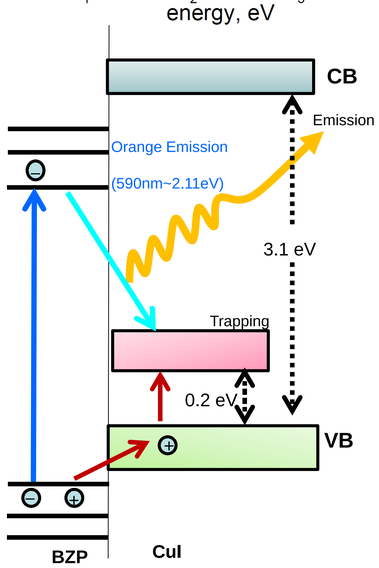
CuI(111) Most Stable Configuration [3]

Fluorescence Mechanism

- Adsorbed Iodine creates the surface trapping sites nearly 0.2 eV above the valence band edge of CuI.
- The absorption mainly takes place on the molecular part of the system.
- The holes from BZP molecules migrate to the CuI valence band and consequently get trapped by one of the trapping surface iodine sites.
- The recombination of the excited electrons- and trapped holes causes the emission at 590 nm.

Emission Spectrum





Computational Details

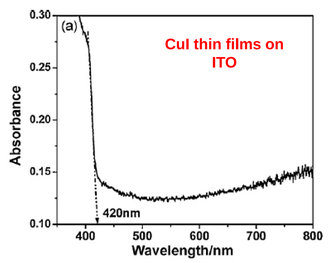
- **Calculation of total energy for BZP-CuI**
  - Quantum Espresso: 4.3.1 Package
  - PAW(Projected-augmented wave method)
  - Ultrasoft Pseudopotential GGA(Perdew-Burke-Ernzerhof) for the exchange correlation [5]
  - Optimization of BZP and CuI(111) slab: GGA (PBE)
  - Optimization of CuI bulk: GGA+U
  - Energy Cut-off for the plane wave basis set – 476 eV
  - Charge density cut off – 5714 eV
  - K-Points sampling : 7×7×7 (bulk) and 7×7×1 (surface)
- **Periodic boundary condition supercell**
  - CuI (111) : 4×4 5 layers
  - About 30 Å vacuum
- **Calculation of Optical Properties**
- TDDFT, PBE, Ultrasoft PP, Abinit code [6]

Acknowledgment

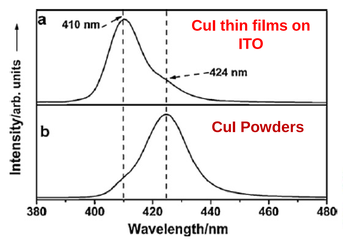
- Work supported in part by DOE Grant No.:
- Computational resource supported by Stokes and Discovery at UCF
- Thankful to Duy Le for the valuable help and suggestion

Optical properties of BZP- CuI(111) system

Absorption spectrum

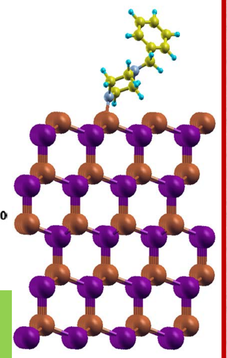


Photoluminescence Spectra

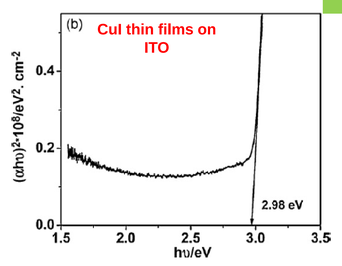


Experimental results Ref. from [4]

BZP-CuI (111) Structure

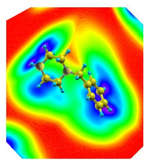


Band gap

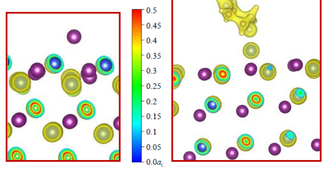


Charge Distribution (GGA)

BZP



CuI+I



BZP-CuI

Conclusion

1. We have studied the electronic and the optical properties of BZP-CuI(111) system.
2. The energy gap (3.1 eV) of CuI has been reproduced using Hubbard parameters within GGA approximation.
3. In conjugated BZP-CuI film, we found the strong orange fluorescence due to recombination of excited BZP electrons and trapped holes, trapped by Iodine vapor atoms on CuI surface.
4. The effect can have many application in forensic sciences and different optical technologies.

References

[1] R. Blair, unpublished;
[2] V. P. S. Perera, 79, 249 (2003);
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[6] X. Gonze et al, Computational Material Science 25, 478 (2002)