First Principle Investigation of Novel Organic Cocrystals

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Abstract

Organic donor–acceptor (D–A) cocrystals have emerged as promising candidates for electronic materials due to their low cost, ease of processing, and excellent electronic properties. But the performance of cocrystal is far from optimized. To help close this gap, we analyzed the electronic structures of a novel organic cocrystal built from 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives and benzimidazole-hydride (BIH) based donors. First-principles DFT calculations were carried out on the molecular and crystalline scales using NYU HPC. The objective is to investigate the electronic properties of these novel cocrystals. HOMO-LUMO gaps were consistent in the range of 1.1 to 1.5 eV. Visualization suggests D–A charge transfer is limited in the isolated molecular scale. Crystalline calculations suggest most cocrystals having semiconductor traits with band gaps under 2 eV. The results provide preliminary insight into these novel cocrystals.

Background

The discovery of TTF-TCNQ cocrystal in 1973 demonstrated cocrystal achieving higher electrical conductivity than any previously known organic compound has prompted extensive research into cocrystals. The partial charge transfer (CT) and the formation of mixed-valence band due to interaction between frontier orbitals of constituent compounds (HOMO/LUMO) allows these insulators to inherit high conductivity. This electrical property has led TTF-TCNQ, and later other synthesized cocrystals, to the fabrication of electronic devices: transistors, LEDs, solar cells, memory devices, and sensors. However, the countless possible D–A combinations, stacking modes, and the unpredictable changes in property shows performance of cocrystal has yet to be optimized (Figure 1). To help close this gap, we analyzed the potential of novel BIH-TCNQ cocrystals through DFT computational calculations.

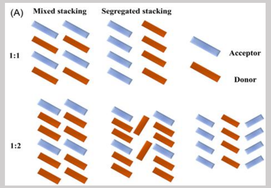


Figure 1: Different Stacking Mode

Methodology

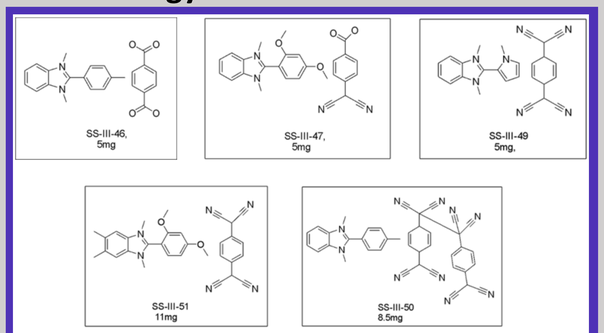
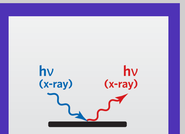


Figure 2: Co-crystal of BIH (Right) with TCNQ (Left)

X-Ray Diffraction (XRD)
- .CIF files
- Cell parameter
- Atomic Coordinate



Gaussian 16
- Molecular Simulations
- Three Basis Sets of B3LYP
- Confirming Frequencies
- Collecting HOMO/LUMO energies

Neutral D-A Pair
- Confident charge and multiplicity

Isolated Cat/anion
- Ambiguous charge and multiplicity
- undesirable

GAUSSVIEW
Visualization of HOMO/LUMO

MedeA 3.10/VASP
- Crystalline Simulations
- Band Structure
- Density of States (DOS)

VASP

Results

The HOMO/LUMO energies of the Neutral D–A including TTF-TCNQ for reference are plotted in eV. The energy gap is obtained (Figure 3).

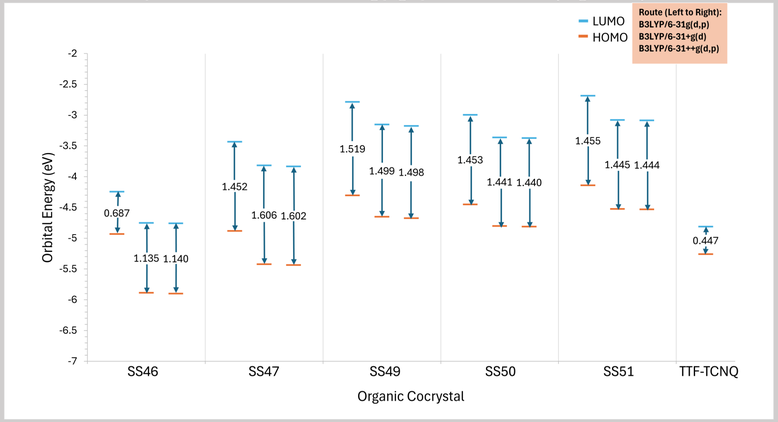
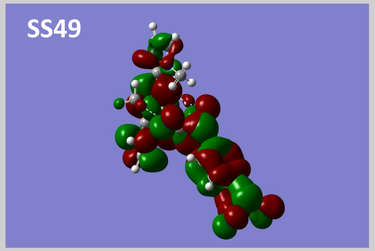
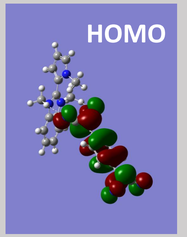


Figure 3: Energy Level of Cocrystal Calculated from Three Basis Sets of B3LYP





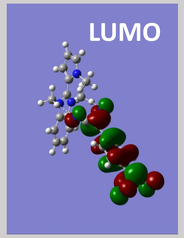


Figure 4:Visualizations of Frontier Orbitals

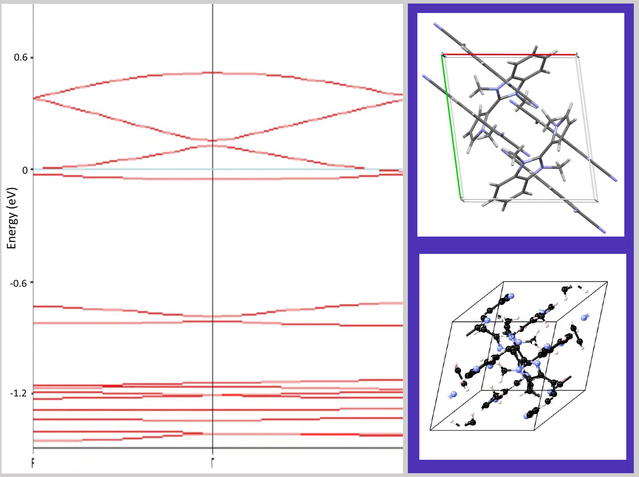


Figure 5:Band Structure (Right) and Crystalline Cell (Left) of Cocrystal SS49

Discussion

Using diffuse basis sets, molecular calculations give consistent HOMO–LUMO gaps of 1.1–1.5 eV (~0.4 eV for TTF–TCNQ under the same conditions). Orbital visualizations show that the frontier orbitals are confined on TCNQ, suggesting limited donor–acceptor coupling molecularly. On the crystalline level, most candidates demonstrate semiconducting properties (band gaps <2 eV), with SS49 showing the narrowest gap (0.066 eV) and therefore the highest expected conductivity. Our next step is to further analyze band structure and DOS on the crystalline scale, followed by charge-transport calculations.

Works Cited

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