



# Study of bulk polymorphism of NDI derivatives

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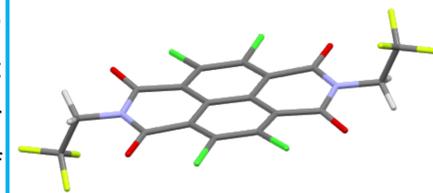


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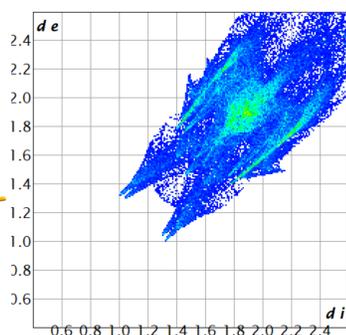
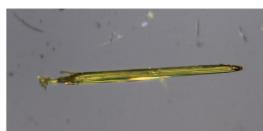
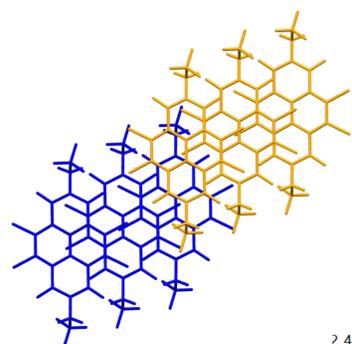
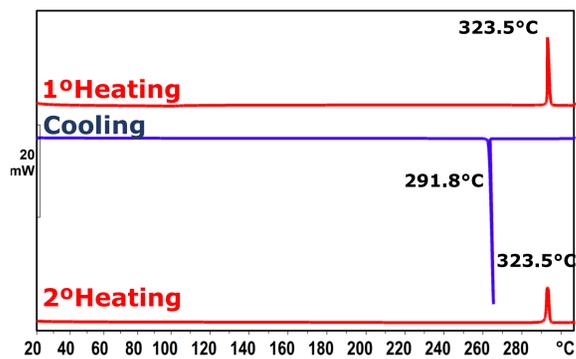


## Introduction

Organic field-effect transistors (OFETs) are very promising components as they allow to process and fabricate low-cost, large-area, and flexible electronics. Although much progress has been made in p-type organic semiconductors, the development of organic n-type semiconductors significantly falls behind. The main reason can be attributed to the difficulty in finding n-type semiconductors with high charge-carrier mobility and air stability. NDI derivatives without core substitution suffer by the lack of stability under ambient conditions. To improve the air-stability, two molecular designs of NDI were commonly employed: introduction of fluorinated substituents at the imide nitrogen and addition of strong electron-withdrawing groups at the NDI core. In this work we studied the polymorphism of C<sub>2</sub>F<sub>3</sub>-Cl<sub>4</sub>NDI, a core-chlorinated naphthalene tetracarboxylic diimide (NDI) with fluoroalkyl chains and it was possible to identify and solve the crystal structure of two polymorphs and a solvate.



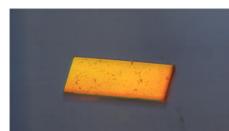
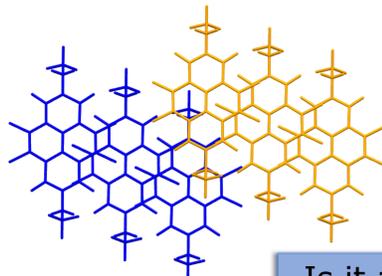
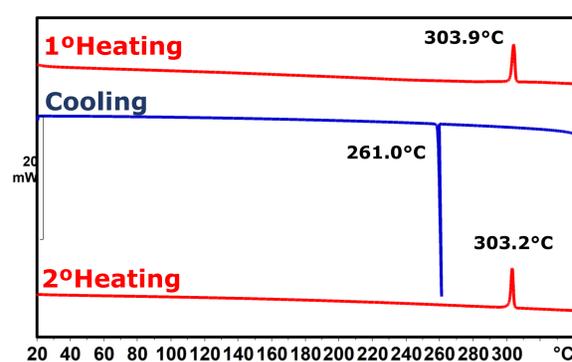
Form 1



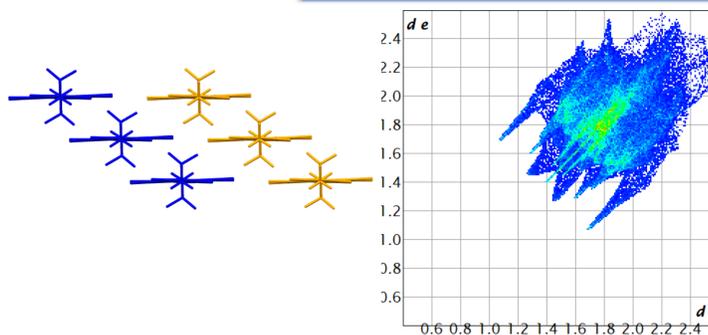
**Space Group** P-1  
**a** 4.866(2)Å **b** 8.836(2)Å **c** 11.604(4)Å  
**α** 74.41(3)° **β** 87.21(3)° **γ** 83.14(3)°  
**Volume** 477.036 Å<sup>3</sup>  
**Z/Z'** 1,0.5

**R<sub>1</sub> (on F, I>2σ(I)) R<sub>ex</sub> 0.0929**  
**WR<sub>2</sub> (F<sup>2</sup> all data) R<sub>wp</sub> 0.2623**

Form 2



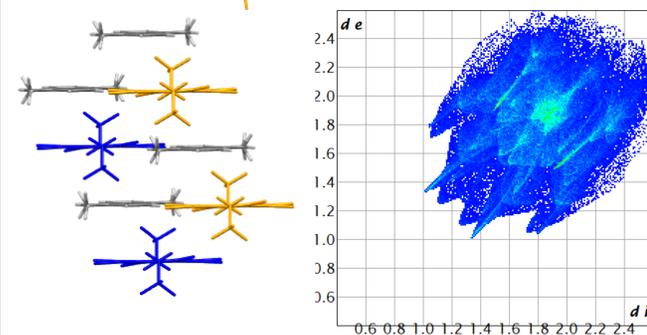
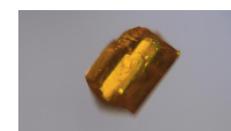
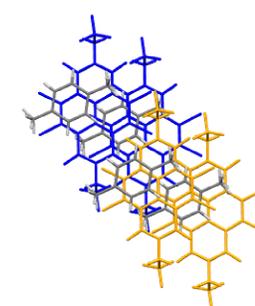
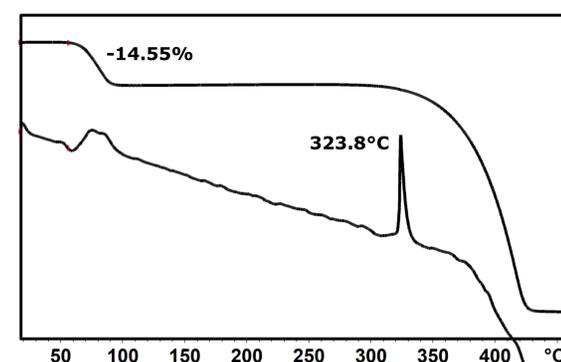
Is it a new polymorph?



**Space Group** P-1  
**a** 5.8401(5)Å **b** 8.1526(5)Å **c** 9.8378(7)Å  
**α** 97.384(5)° **β** 95.304(6)° **γ** 101.711(6)°  
**Volume** 451.443 Å<sup>3</sup>  
**Z/Z'** 1,0.5

**R<sub>1</sub> (on F, I>2σ(I)) R<sub>ex</sub> 0.1523**  
**WR<sub>2</sub> (F<sup>2</sup> all data) R<sub>wp</sub> 0.4854**

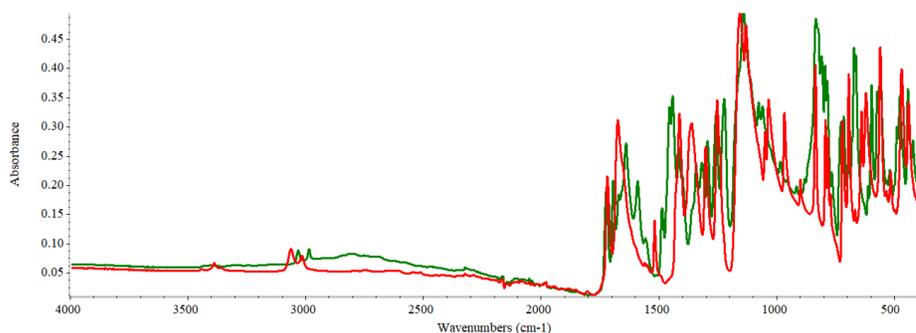
Form 3 (solvate)



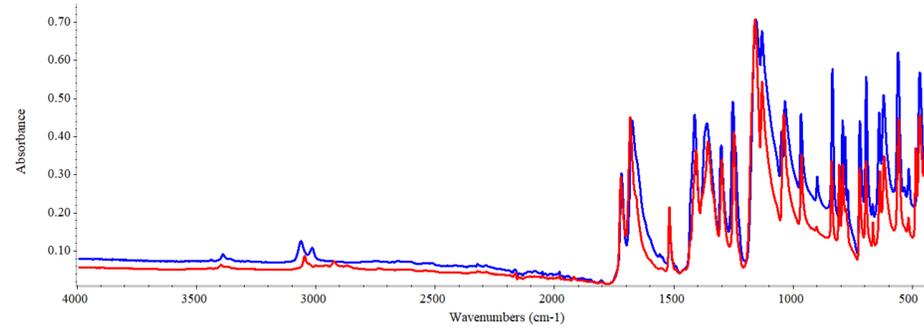
**Space Group** P-1  
**a** 7.7798(7)Å **b** 8.1543(9)Å **c** 10.6415(7)Å  
**α** 91.60(7)° **β** 101.96(7)° **γ** 90.58(8)°  
**Volume** 660.079 Å<sup>3</sup>  
**Z/Z'** 1,0.5

**R<sub>1</sub> (on F, I>2σ(I)) R<sub>ex</sub> 0.0516**  
**WR<sub>2</sub> (F<sup>2</sup> all data) R<sub>wp</sub> 0.1410**

Form 1 and Form 2



Form 1 and Form 3



## Conclusions

Form 1 is the most stable phase without any transition observed on DSC. All the three different phases have very distinct two-dimensional fingerprint plots for all intermolecular contacts. Even the dominant interaction is different for the all the phases; in Form 1 Cl-F surface contacts are dominant, in Form 2 the dominant interaction is Cl-C, while for Form 3 the main interaction is H-F.

From the single crystal XRD it was possible to conclude that Cl-atoms are not occupied 100% by Cl, the reason for the high R-factor, what suggests that the compound is not pure C<sub>2</sub>F<sub>3</sub>-Cl<sub>4</sub>NDI, but possibly a mixture of two or more compounds that have a variety of substituents at the sites assumed to be always Cl. For this reason, the FTIR spectrum of Form 1 and Form 2 present massive differences.

The formation of solvates is very uncommon in organic semiconductors. Nonetheless, a p-xylene solvate was obtained and the way the solvent molecules are arranged in the crystal packing: interlayering in the π-π stacking of the NDI molecules, opened the discussion of possible co-crystals formation.