Synthesis of Molecular and Polymeric Benzimidazoline-based N-Type Dopants

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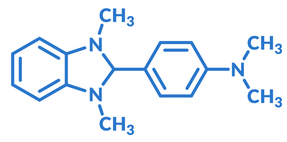
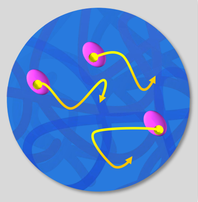
Introduction

Benzimidazoline-based dopants, which are derived from 4-(2,3-Dihydro-1,3-Dimethyl-1H-Benzimidazol-2-Yl)-N,N-Dimethylbenzenamine (N-DMBI-H), are used as **precursors** that can be thermally activated in situ to inject a negative charge into N-type Organic Semiconductors (OSCs) [1]. These dopants are preferred over actual n-dopants due to their higher stability under ambient conditions. The doping triggered by N-DMBI-H and DMBI derivatives involves **three thermally promoted contemporary process:**

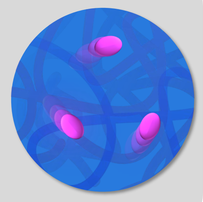


N-DMBI-H

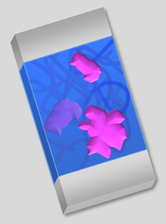
Activation
The activation of the dopant involves a **charge transfer** with the semiconductor, leading to the formation of an ion-pair.



Diffusion
Molecular dopants diffuse through the OSC matrix, facilitating donor-acceptor proximity but at the same time enhancing phase segregation.



Phase segregation
The dopant tends to segregate, **reducing** the interfacial area with the semiconductor and thus the **doping efficiency**.

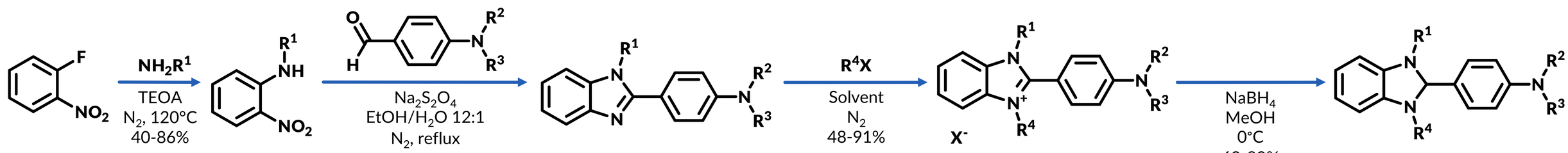


By introducing different functional groups on DMBI, it is possible to control doping energetics, kinetics, miscibility in the OSC phase, and diffusion. However, t**he variety of benzimidazoline-based dopants** reported in literature remains **limited** despite their potential.

Goal

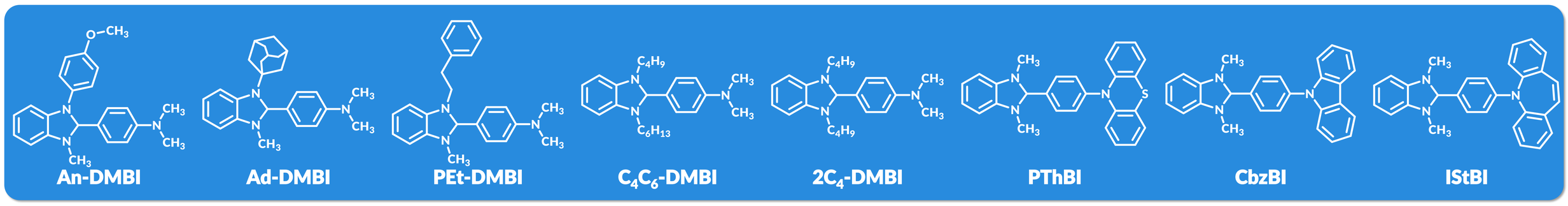
This research seeks to expand the dopant repertoire by engineering innovative benzimidazoline-based derivatives, encompassing both species with one doping unit (***monofunctional n-dopants***) and species constituted by multiple doping units (***multifunctional n-dopants***), to achieve superior doping efficiency. The selected designs are intended to ensure not only optimal activation but also **controlled diffusion** and **minimized phase segregation**, pushing the boundaries of current doping technologies.

Synthetic procedure



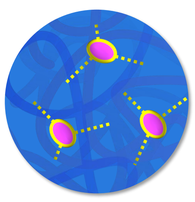
Results

a. Monofunctional n-dopants



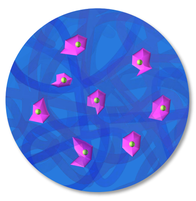
b. Multifunctional n-dopants

To achieve greater **control over blend morphology**, we have pinpointed three key features that significantly enhance the stability of the dopant-semiconductor interface. Guided by these insights, we synthesized and isolated a **dimeric form of DMBI-H**, distinguished by the incorporation of two carbamate groups.

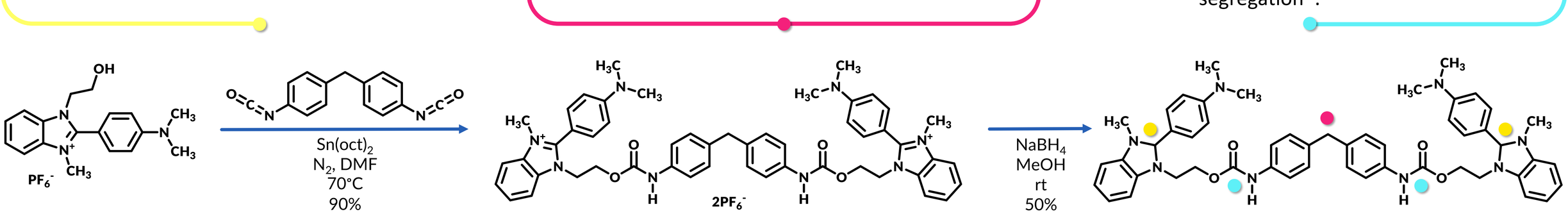


Post-activation, **multifunctional dopants** form ionic crosslinks with the semiconductor, stabilizing the morphology of the interface [2].

In a generic matrix, larger molecules like DMBI derivatives with **significant steric hindrance** have limited mobility.

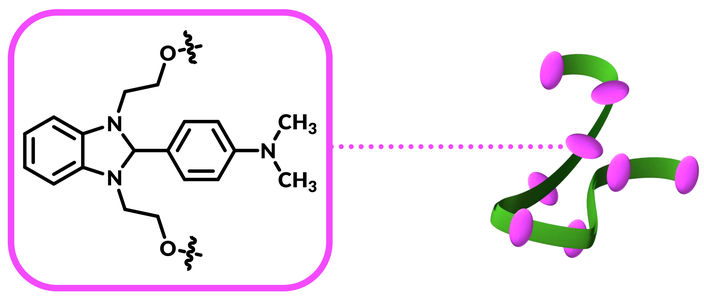


Nucleating agents promote small dopant cluster formation, enhancing interaction with the semiconductor and positively impacting dopant phase segregation [3].



Conclusions and Outlooks

We have optimized a synthetic procedure that has proven to be both versatile and effective for the synthesis of various benzimidazoline-based n-dopants. Currently, we are leveraging this method to produce polymerizable DMBI derivatives. Our goal is to synthesize **polyurethane oligomeric n-dopants** starting from **di-hydroxyl DMBI derivatives**.



References

1. Scaccabarozzi, A. D. *et al*. *Chem. Rev.* (2022), 122, 4420–4492.
2. Saeedifard, F. et al. *ACS Appl. Mater. Interfaces* (2022), 14, 33598–33605.
3. Pallini, F. et al. *ACS Appl. Energy Mater.* (2022), 5, 2, 2421–2429.