

## Tuning of the electronic levels of oligothiophene-naphthalimide semiconductors: in the search of ambipolar behaviour.

Iratxe Arrechea Marcos,<sup>1</sup> A. de la Peña,<sup>2</sup> M.J. Mancheño,<sup>2</sup> M.C. Ruiz Delgado,<sup>1</sup> J.L. Segura,<sup>\*2</sup> J.T. López Navarrete,<sup>\*1</sup> R. Ponce Ortiz,<sup>\*1</sup>

<sup>1</sup> Department of Physical Chemistry, University of Malaga

<sup>2</sup> Department of Organic Chemistry, Complutense University of Madrid

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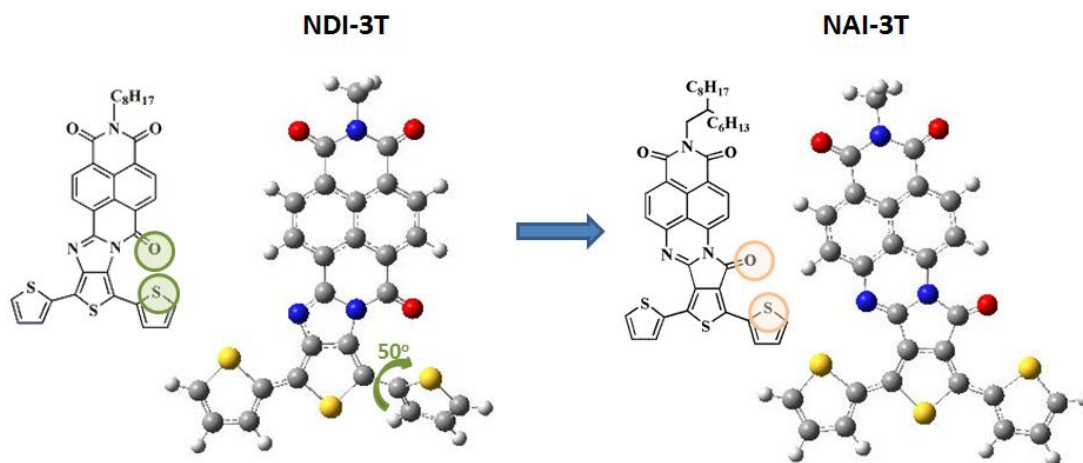
Ambipolar organic field-effect transistors (OFETs), which can efficiently transport both holes and electrons,<sup>[1]</sup> using a single type of electrode, are currently of great interest due to their possible applications in complementary metal oxide semiconductor (CMOS)-like circuits, sensors, and in light-emitting transistors.<sup>[2]</sup> Several theoretical and experimental studies have argued that most organic semiconductors should be able to transport both types of carrier,<sup>[3]</sup> although typically unipolar behavior is observed.

One factor that can compromise ambipolar transport in organic semiconductors is poor solid state overlap between the HOMO (p-type) or LUMO (n-type) orbitals of neighboring molecules in the semiconductor thin film. In the search of low-bandgap ambipolar materials, where the absence of skeletal distortions allows closer intermolecular  $\pi$ - $\pi$  stacking and enhanced intramolecular  $\pi$ -conjugation, a new family of oligothiophene-naphthalimide assemblies have been synthesized and characterized, in which both donor and acceptor moieties are directly conjugated through rigid linkers.

In previous works<sup>[4]</sup> we found that oligothiophene-naphthalimide assemblies connected through amidine linkers (NDI derivatives) exhibit skeletal distortions (50-60°) arising from steric hindrance between the carbonyl group of the arylene core and the sulphur atom of the neighbored thiophene ring (see Figure 1).

In the present work we report novel oligo- and polythiophene-naphthalimide analogues NAI-3T, NAI-5T and poly-NAI-8C-3T, in which the connections of the amidine linkage have been inverted in order to prevent steric interactions. Thus, the nitrogen atoms are directly connected to the naphthalene moiety in NAI derivatives while they were attached directly to the thiophene moiety in the previously investigated NDI-3T and NDI-5T. In Figure 1 is depicted the calculated molecular structure of NAI-3T together with that of NDI-3T showing how the steric interactions are not present in the novel

NAI derivative. The planar skeletons in these new family induce higher degree of crystallinity and the carrier charge transport can be switched from n-type to ambipolar behaviour.



The highest FET performance is achieved for vapor-deposited films of NAI-3T with mobilities of  $1.95 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  and  $2.00 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for electrons and holes, respectively. Finally, these planar semiconductors are compared with their NDI derivatives analogues, which exhibit only n-type mobility, in order to understand the origin of the ambipolarity in this new series of molecular semiconductors.

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