Understanding the effect of rigid linkers on the optoelectronic properties of naphthalimide-oligothiophene semiconductors

Alexandra Harbuzaru,[a] Matias J. Alonso-Navarro,[b] José L. Segura,[b] Rocio Ponce Ortiz*[a]
a) Department of Organic Chemistry, Complutense University of Madrid, Faculty of Chemistry, Madrid 28040, Spain; Department of Physical Chemistry, University of Málaga, Málaga, 29071, Spain.
b) Chemical and Environmental Technology Department. Univ. Rey Juan Carlos, Móstoles, 28933, Spain.

π-conjugated small molecules and polymers are extensively used in organic electronics because of their low-cost manufacturing, light weight, good processability and capability to be deposited on flexible substrates in comparison with conventional inorganic semiconductors. In order to efficiently tune the charge transport abilities and electronic performances of π-conjugated materials in optoelectronic devices, an in depth understanding of their molecular structures, supramolecular organization and film morphology are required.[1-3] Naphthalenediimides (NDI) are among the most extensively investigated electron accepting organic materials, and stand out because of their good electron-withdrawing abilities and their low-lying LUMO levels, which properly stabilize multiple negative charges. On the other hand, thiophene-based π-conjugated oligomers and polymers are efficient electron-donor systems with tunable HOMO levels, suitable to stabilize multiple positive charges. For these reasons, donor-acceptor assemblies based on oligothiophene and naphthalimide moieties have received a great deal of attention in organic electronics[1–4].

In this study we analyse the electronic and molecular characteristics of some π-conjugated naphthalimide-oligothiophene systems in order to evaluate their potential as semiconducting materials for organic electronics. For this purpose, we focus on the study of (i) the effect of different rigid linkers on the electronic and molecular characteristics of these systems and (ii) the effect of different lateral substituents at the oligothiophene units on the materials electrical properties. To achieve this goal, we use a combined experimental and theoretical approach that includes electronic spectroscopies (absorption), vibrational Raman spectroscopy and DFT calculations. The different rigid linkers as well as the different lateral substituents on the terthiophene moieties are found to provoke a strong impact on the HOMO and LUMO levels and the molecular morphology, and, consequently, on their suitability as semiconductors in organic electronic applications.

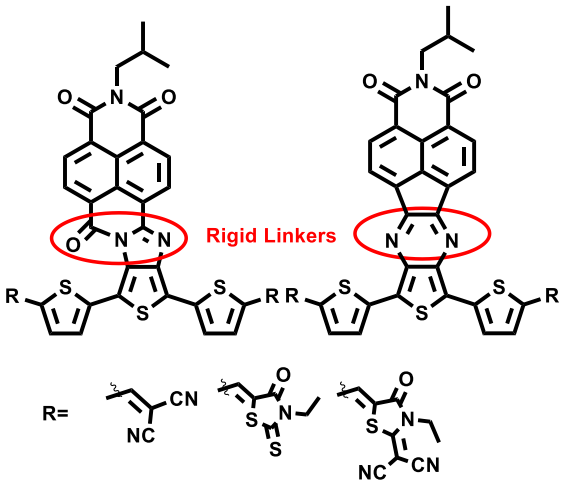

Figure 1. Chemical structures of oligothiophene-naphthalimide assemblies connected through different linkers.

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