From thiophene building blocks to conjugated molecular systems for OLEDs: an investigation by synchrotron spectroscopies

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Conjugated molecular systems are of growing interest in the field of organic molecular electronics [1], due to the possibility to combine building block molecules to form more complex structures tuned to the desired device efficiency and performance in OLEDs [2]. In a typical device, the photoactive material is made by donor–acceptor (D−A) counterparts designed by combining their electron donor and acceptor properties on two sites of the same molecule usually connected by covalent bonds through π-bridge linkers (D−π−A) [3]. Thiophene-containing molecules [4] are well-know electron donors which are considered suitable donors/π-bridges in D−π−A molecular systems, capable to improve the light harvesting efficiency and charge transport properties, facilitating the electron migration from the donor to the acceptor counterparts. Moreover, the introduction of π-conjugated ring-annulated moieties, such as benzene, simultaneously extends the π-conjugation and improves the stability of the resulting electron-donors and π-bridges for the assembling of organic electronic materials.

The present study focused on the gas phase electronic structure characterization of building block molecules such as: Thiophene (T) [5, 6], benzo[b]thiophene (BBT) and dibenzothiophene (DBT) [7]. The final goal is the comprehensive gas phase electronic structure characterization of the 2,8-bis(diphenylphosphoryl)dibenzothiophene (PPT), a promising ambipolar host-guest layer recently introduced in OLEDs. This molecular system is formed by two diphosphate oxide moieties functionalizing the small dibenzothiophene (DBT) core. It is characterized by high triplet energy and is known as good vacuum sublimable electron transporting host material for blue OLEDs. The phosphine oxide groups act as breaking points of π-conjugation between the core and the outer groups, leaving the electronic structures of the compound practically matching those of the central DBT moiety. For this reason, we have also characterized the Triphenyl Phosphine oxide (TPPO) as model compound of the phosphine oxide groups in PPT acting usually as π-conjugation breaking points (see Figure 1 for all the chemical structures).

For this purpose, in this work we present a combined experimental and theoretical study of the electronic structure in the gas phase of T, BBT, DBT, PPT and TPPO by means of X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy based on assignments resulting from density functional theory (DFT) calculations and its time-dependent generalization (TDDFT) in the linear response regime. The acquired knowledge about the building blocks is useful to predict, control and manipulate their behavior when introduced in bigger molecular systems like in PPT.

![Molecular sketches of: Thiophene (T), benzo[b]thiophene (BBT), Triphenylphosphine oxide (TPPO), dibenzothiophene (DBT) and 2,8-bis-diphenylphosphoryl-dibenzothiophene (PPT).](image)

Figure 1. Molecular sketches of: Thiophene (T), benzo[b]thiophene (BBT), Triphenylphosphine oxide (TPPO), dibenzothiophene (DBT) and 2,8-bis-diphenylphosphoryl-dibenzothiophene (PPT).