

Planar thiaheterocyclic compounds and chiral thiaheterohelicenes
as new systems with potential application in optoelectronics and photovoltaics.

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The research activities developed in our group have been focused on two main targets: benzodithiophene based materials and tetrathia[7]helicene based NLOphore.

Benzodithiophene based materials (Figure 1, compounds 1 and 2): the synthesis, characterization and the study of the optical and electronic properties of several thiophene-based polycyclic aromatic hydrocarbons of general formula 1 and 2, have been performed in view of their application as rigid, planar and stable, π -conjugated heteroaromatic framework which could constitute the core of electroluminescent dyes,¹ as well as organic semiconducting materials.² In our group we have developed general and efficient synthetic methods to functionalize, in regioselective manner, the positions 2 and 5 of the thiophene rings present in the benzodithiophene system.

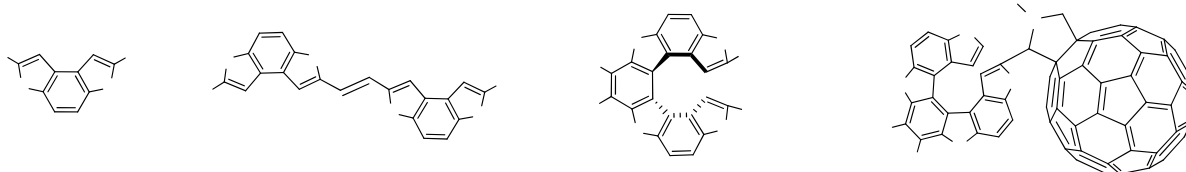


Figure 1

Tetrathia[7]helicene based NLOphore: tetrathiahelicenes **3** (Figure 1)³ have been recognized and developed as an extremely attractive class of polyconjugated chiral molecules, investigated for optoelectronic applications and second-order NLO phenomena.⁴ The absence of centrosymmetry at the supramolecular level is a requirement to achieve second order phenomena and therefore chirality is increasingly important in the design of π -conjugated materials. Thiahelicenes combine the electronic properties afforded by their extensive π -conjugated system with the chiroptical properties associated to their helical structure,^{5,6} resulting from the *ortho*-condensation of benzene and thiophene rings. In addition, the regioselective functionalization of **3** (e.g. positions 2, 7, 8, and 13, figure 1) could allow the tuning of both their electronic and structural (*i.e.* helical pitch) properties. Very recently, in collaboration with Prof. Maggini (Padova University), we undertook an investigation concerning the charge transfer phenomena in fulleropyrrolidine-helicene diades (Figure 1, **4**).

The main electronic properties of benzodithiophene and thiahelicene scaffolds **1** and **3**, (**2** can be regarded as the dimeric form of **1**), are reported in figure 2. Dashed lines indicate how, upon introduction of a strong electron donor and acceptor substituent, the property could be tuned.

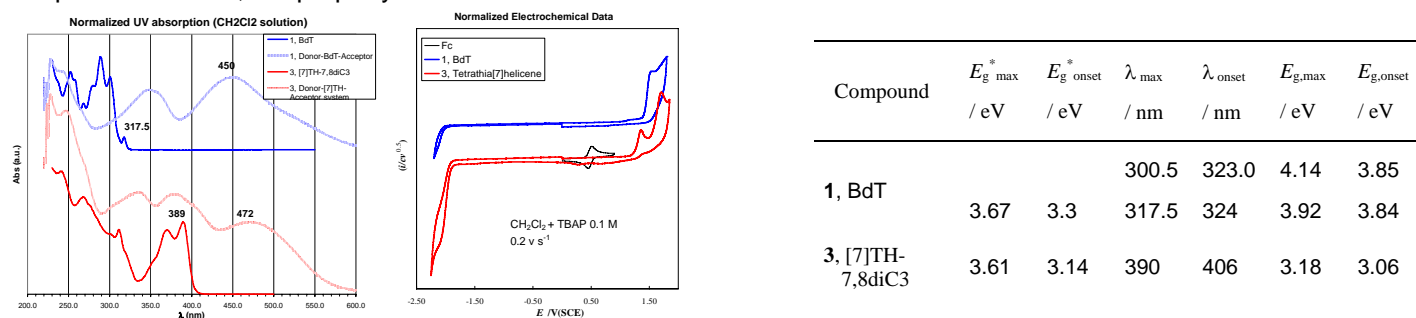


Figure 2. Optical and electrochemical properties of compound **1** and **3**.

In our research group we experienced both synthetic and analytical skills which could allow a deep understand of structure-property relationship. Moreover, none of the cited systems have been so far reported in the realization of chromophores or sensitizers for organic photovoltaic application.

¹ Giovannella U., Botta C., Bossi A., Licandro E., Maiorana S., *J. Appl. Phys.*, **2006**, 100, 083107

² Schiavo M., Bossi A., Facchetti A., Marks T. J., Licandro E., Maiorana S., Muccini M., *Manuscript in preparation*.

³ Maiorana, S.; Licandro, E.; Clays, K.; Persoons, A. *et al. Tetrahedron*, **2003**, 59, 6481; Bossi, A.; Licandro, E.; Maiorana, S.; et al. *Synlett*, **2005**, 1137; Licandro, E.; Rigamonti, C.; Maiorana, S., et al. *Synthesis*, **2006**, 21, 3670; Bossi, A.; Maiorana, S.; Licandro, E.; et al. *Eur. J. Org. Chem.*, **2007**, 27, 4499.; Rajca, A.; Miyasaka, M. "Synthesis and Characterization of Novel Chiral Conjugated Materials" in *Functional Organic Materials. Syntheses, Strategies, and Applications* (Miller, T.J.J.; Bunz, U.H.F. eds.), Wiley-VCH, Weinheim (2007), pp. 547–581.

⁴ Champagne, B.; et al. *J. Chem. Phys.* **2004**, 120, 2042; Champagne, B.; Licandro, E.; Maiorana, S.; Bossi, A.; Clays, K.; *CHEMPHYSICHEM* **2004**, 5, 1438; Bossi A., Licandro E., Maiorana S., Righetto S., Stephenson G.R., Champagne B., et al. *J. Phys Chem. C* **2008**, in press.

⁵ Collins, S. K.; Vachon, M. P. *Org. Biomol. Chem.* **2006**, 4, 2518.

⁶ Bossi, A.; Licandro, E.; Maiorana, S.; Mussini, P. R.; et al. *Chem. Eur. J.* **2007**, submitted.

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