



Benzodifuroxazinones, a new class of heteroacene molecules for possible applications in organic electronics: Synthesis, electronic properties and crystal structure

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ABSTRACT

A novel class of heteroacene molecules, benzodifuroxazin-4-ones, has been effectively synthesized by means of a thermally activated double cyclization reaction starting from amidic precursors. The new molecules were thermally and optically characterized, revealing an outstanding thermal stability to oxidation and an uncommon enhancement of fluorescent properties in solid state as compared to solution. As shown by single-crystal XRD analysis, the molecules crystallize in a face-to-face (π -stack) arrangement instead of the herringbone structure typical of the most acene derivatives. The electronic properties of both molecules and crystals have been investigated by means of a detailed Density Functional Theory computational analysis: very stable HOMO energies have been calculated and, from the band structure analysis, it is possible to suggest a preferential direction of charge transport along the π -stacking direction. All the reported properties indicate this new class of heteroacene derivatives as interesting candidates for a possible application in organic electronics.

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1. Introduction

Organic semiconductors has received a great deal of attention for their possible use as active layers in thin film electronic devices such as transistors [1–3], light emitting devices (OLED) [4–6] or solar cells [7–9]. As compared to the inorganic semiconductors typically used in electronics, the unique mechanical properties of organic molecules and polymers may allow the fabrication of flexible electronic devices, while their easier processability might open the way to low-cost manufacturing techniques such as spin-coating, ink-jet printing, and roll-to-roll printing processes [10]; this technological aspect is particularly striking in a field like electronics where manufacturing costs weight much more than the cost of the material itself. Another important factor justifying the huge interest in organic semiconductors is the possibility to design or modify π -conjugated chemical structures in ways that could directly impact the properties of the material.

Most of the investigated organic semiconductors could be roughly divided into two classes, conjugated polycyclic compounds with low molecular weight [11–15] and polyheterocycles [11,16,17]. As far as the former are concerned, oligoacenes are one of the most intensively investigated class of materials in the literature: organic transistors endowed with outstanding mobility have been fabricated by using pentacene and its derivatives as active layer. However, acene-type molecules show a number of drawbacks for practical applications like for instance a high-energy-lying HOMO and a narrow bandgap that make them extremely sensitive to photo-oxidation [18]. A possible synthetic approach for improving the oxidative stability is to insert, within the fused ring system, more electronegative heteroatoms [19,20].

The typical crystalline structure presented by heteroacene compounds is characterized by a herringbone pattern, in which the molecules are packed edge-to-face in 2D layers (with the highest charge mobility in this plane) [21]. However, theoretical works have shown that charge mobility in organic semiconductors is intrinsically related to the overlap of π molecular orbitals of adjacent conjugated molecules [22]; in this respect, the herringbone

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structure is not the most suitable one and it could be argued that, in principle, higher mobility could be obtained by designing new molecules that crystallize in a face-to-face (π -stack) arrangement. Indeed, proper synthetic modifications of the molecules can turn the crystal packing from herringbone to π -stacked, for example through functionalization of the acene core with halogens [23,24] or bulky substituents in the peripositions of the oligoacenes [24,25].

In a recent paper dealing with the amino-benzodifurane reactivity, we hypothesized the formation of the **B-OXA** compound (see Fig. 1) based on an unprecedented penta-atomic fused heterocycle, a benzodifuroxazinone prepared through a cyclization reaction thermally initiated in the bulk [26]. While in the mentioned paper only preliminary results were reported, a later single-crystal X-Ray Diffraction (XRD) analysis confirmed the structure of the **B-OXA**.

Here, we report (for the first time) the optimized synthesis of **B-OXA** and of two new fluorinated derivatives, **FB-OXA** and **DFB-OXA**. The molecular structure of these molecules, presented in Fig. 1, shows several elements of interest: the core structure is composed of five fused rings, as in pentacene, and should allow a high degree of planarity that, in turn, could lead to high electrical performance. Moreover, because of the presence of more electronegative heteroatoms, it can be argued a higher stability of benzodifuroxazinone derivatives against oxidation, compared to that of pentacene. Finally, the versatility of the synthetic strategy to prepare this class of compounds could easily give access to a wide number of derivatives with tailored features.

The chemical physical properties of the three benzodifuroxazinones derivatives and their intermediates have been fully characterized. A peculiar feature of all three compounds is revealed in fluorescence experiments: they are good green emitters in solid state while they show very weak fluorescence when excited in solution. This phenomenon (also referred to in the literature as “aggregate induced emission, AIE” [27,28]) makes them interesting candidates in OLED technology.

The structures of **FB-OXA** and **DFB-OXA** have been resolved by means of single-crystal XRD. The obtained crystal structures and crystallographic coordinates have been used as the basis for a detailed computational analysis that will be extensively described in the next sections.

2. Materials and methods

2.1. Chemical and characterization

All solvents and reagent were purchased by Aldrich and used without further purification. The thermal behaviour of the compounds was studied by differential scanning calorimetry (Perkin–Elmer Pyris 1, nitrogen atmosphere, scanning rate 10 K/min), temperature controlled polarizing microscopy (Zeiss microscope, Mettler FP5 microfurnace) and thermo-gravimetric analysis

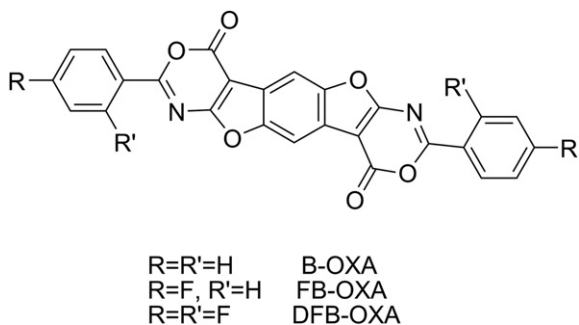


Fig. 1. Molecular structure of the prepared chromophores.

(TA SDT 2960, air, 20 K/min). ^1H and ^{13}C NMR spectra were recorded with a Varian XL 200-MHz apparatus. UV/Vis absorption and fluorescence spectra of the prepared chromophores, both in solution and as thin films, were recorded respectively with a Jasco V560 spectrophotometer and a Jasco spectrofluorimeter FP750. PL-efficiency measurements on thin film (thickness of about 50 nm) were conducted using a conventional setup that consists of a 376 nm solid state laser as a light source and an integrating sphere coupled to photospectrometer (Black Comet) by Stellarnet. The experiment was controlled by an LABVIEW script that also calculated the efficiency. The setup and the calculation algorithm is the same as the one outlined in de Mello paper [29]. Maldi mass spectra were recorded in positive ion mode on a Maldi Voyager STR Applied Biosystems.

Single crystals of **B-OXA**, **FB-OXA** and **DFB-OXA** suitable for XRD analysis were obtained by sublimation. One crystal of **B-OXA** (red, $0.60 \times 0.25 \times 0.10$), one crystal of **FB-OXA** (yellow, $0.50 \times 0.05 \times 0.01$ mm) and one crystal of **DFB-OXA** (yellow, $0.60 \times 0.20 \times 0.01$ mm) were mounted at 296 K on a Bruker-Nonius KappaCCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å, CCD rotation images, thick slices, φ and ω scans to fill asymmetric unit). Semiempirical absorption correction (SADABS) was applied. The structures were solved by direct methods (SIR97 package [30]) and refined by the full matrix least-squares method on F^2 against all independent measured reflections (SHELXL program of SHELX97 package [31]). All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were introduced in calculated positions and refined according to a riding model, except for H atoms on benzodifurane ring system that were found in difference Fourier maps. The final refinement converged to $R_1 = 0.0891$, $wR_2 = 0.224$ for **B-OXA**, $R_1 = 0.0613$, $wR_2 = 0.0875$ for **FB-OXA** and $R_1 = 0.0501$, $wR_2 = 0.0950$ for **DFB-OXA**. Evidences of twinning by 180° rotation around the **a** axis (twin law $1\ 0\ 0\ 0\ -1\ 0\ 0\ 0\ -1$) were found in **B-OXA**, data were not merged and refined using HKLF 5 instruction of SHELXL program. In **DFB-OXA** the Fourier maps showed a static disorder of fluorine F2 atom in two positions related by 180° rotation around C4–C7 bond (occupancy factor refined to 0.63).

CCDC-830737 (**B-OXA**), CCDC-830738 (**FB-OXA**) and CCDC-830739 (**DFB-OXA**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44 1223/336 033.

2.2. Synthesis

2,6-Diamino-benzo[1,2-b:4,5-b']difuran-3,7-dicarboxylic acid, dibutyl ester (**C4**) was prepared as previously described. Amide precursors were prepared by reacting **C4** with the correspondent acyl chlorides with the same procedure and the details of synthesis are reported only for the synthesis of **C4-DFB**. The benzodifuroxazinone chromophores were obtained by means of a double thermal cyclization with the reaction parameters (time and temperature) suggested by a previously performed thermo-gravimetric analysis.

2.2.1. Dibutyl 2,6-bis(2,4-difluorobenzamido)-4,8-dihydrobenzofuro[5,6-b]furan-3,7-dicarboxylate (**C4-DFB**)

C4 (0.775 g, 2 mmol) were suspended in 10 mL of dry pyridine and the system was kept under stirring at room temperature; then, 2,4-difluorobenzoylchloride (1.045 g, 5.92 mmol) was added dropwise and the previous suspension turned to a dark solution. The solution was then warmed and kept at a gentle boiling for 45 min until the formation of some precipitate was observed.

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