



Structure-directed functional properties of symmetrical and unsymmetrical Br-substituted Schiff-bases



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HIGHLIGHTS

- Very similar low molecular Schiff bases show different solution and solid state optical, electrochemical and thermic properties.
- The presence of a CH₃ group on the aromatic increase the energy gap which hinder the electronic transitions.
- The introduction of a methyl unit as a bulky group induce large intermolecular distances in the crystal packing.

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ABSTRACT

This study deals with the investigation of two low molecular weight Schiff base compounds with bromine end groups, differing only by the presence or absence of one methyl group, with the aim of better understanding the solution and the solid state optical, electrochemical and thermic properties generated by the small structural features. The compounds were structurally characterized by ¹H NMR, ¹³C NMR and FTIR spectroscopies, single-crystal X-ray diffraction and gas chromatography analysis. Their thermal behavior was evidenced by polarized light microscopy and differential scanning calorimetry. The single crystal structure of the compounds reveals the versatility of bromine substituents which can adopt an attractive or repulsive electron effect, driven by the structural environment. A comparison of the structures shows that the introduction of a methyl unit as a bulky group hinders completely the π - π stacking interaction within the structural rows, inducing larger intermolecular distances resulting in quite different functional physical and chemical properties.

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1. Introduction

Schiff-bases compounds containing one or more CH=N imine bonds are intensely studied due to their large spectrum of physico-chemical properties: ability to form various coordination complexes, high thermal stability, semiconducting, liquid crystal, optical, therapeutic properties. As a consequence of their well-organized structures, all these features make them useful as thermo resistant materials, pharmaceutical products, or organic substrates in electronic and opto-electronic devices [1–5]. The easily processable imine bonds [6] provide a direct access to complex systems like double helices [7], grids [8], borromean rings [9], dynamic polymers [10], capsules [11], polygons [12], etc. The self-organization of constitutional systems [13] resulting from reversible connectivity (molecular level) [14] and self-assembly (supramolecular level) [15] of subcomponents under the pressure of internal and external

structural factors, is also endowing dynamic features for this type of compounds. Moreover, Schiff bases can give rise to extended conjugated platforms with unique optical, electronic and thermic properties. Depending on their molecular structure and composition, they can exist in various crystalline phases and only slight structural modifications can induce interesting modulation of functional properties.

On the other hand, recent studies reveal the benefit of the halogen bonding in the crystal state which lead to impressive electronic performances that is amplifying triplet generation and activating triplet emission [16]. The Br atom is almost inert from an electronic point of view due to two antagonistic electronic effects: a donor electronic effect due to the lone pair donor 4p orbital and a withdrawing effect due to a vacant 4d orbital acting as a weak electron acceptor [17]. Moreover, the Br moieties can be easily used as anchoring sites for further Suzuki coupling reactions [18,19].

In this context, we present here two examples of Schiff-bases prepared under mild reactional conditions, containing two bromo-phenyl moieties connected via an imine bond, combined with

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