

MOLECULAR STRUCTURES OF FLUORENE DERIVATIVES

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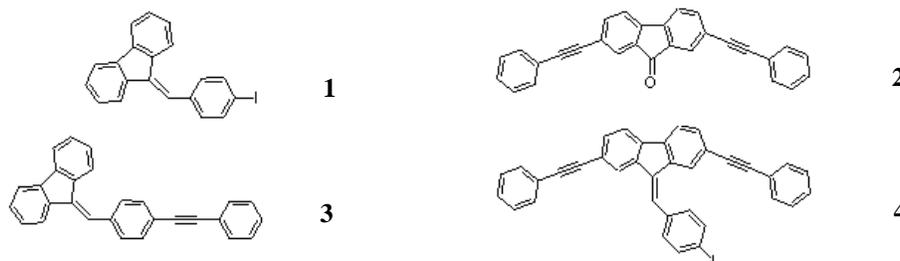
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ABSTRACT

π -Conjugated polymers and oligomers, based on fluorene structure, have achieved significance as the active materials in diverse organic optoelectronic devices, mainly as organic light-emitting diodes and organic photovoltaic cells. Lately new applications of this kind of materials appeared. They have proven to be useful as chemical sensors and imaging agents. The optical and electronic properties of fluorene-based materials highly depend on both their chemical structures and their supramolecular organization. The choice of appropriated substituent allows tuning their absorption or emission colors capability. In this work we address the study four of fluorene derivatives C-2, C-7 and/or C-9 substituted, which present diverse response to the UV-Vis radiation. Single crystal x-ray diffraction data collection and structure elucidation has been performed for 9-(*p*-iodo-benzylidene)-9H-fluorene (1), bis-(phenylethynyl)-9-fluorenone (2), 9-(*p*-phenylethynyl-benzylidene)-9H-fluorene (3), 9-(*p*-iodo-benzylidene)-2,7-bis-phenylethynyl-9H-fluorene (4). A scheme of the studied molecules is shown below.



Compounds 1, 2 and 3 crystallize with two molecules for asymmetric unit. All the 3D structures are stabilized by C – H \cdots π (aryl/fluorene) interactions. In 1 they help to build helicoidally arranged chains along *c*, which organize in layers parallel to (011) plane. The later are linked by C–H \cdots I contacts. In 2 C – H \cdots C \equiv C, and π (arom) \cdots π (arom) contacts are also observed and help molecules to build chains perpendicular to the (100) plane forming herringbone interactions. In 3, in spite of some degree of disorder it could be determined that the substituent in 9 is twisted out of the fluorene plane and that inequivalent molecules are arranged in planes perpendicular to *a*. In (4) we also found contacts I \cdots π (C – C \equiv C – C) and C – H \cdots I originating an helix along *b*, which organize in infinite chains along this axis. Adjacent chains are linked by the C – H \cdots π (arom) forming layers perpendicular to *c* and connected by C–H \cdots π and C–H \cdots C–H contacts. Fluorescence spectra of all the samples were obtained exciting different concentration solutions at their UV-Vis absorption maximum (within the range 330-350 nm). Though emission of blue light was observed, bands centered in the range 410- 450 nm, are quite broad; 2 also shows emission of green light. The influence of molecular conformation and intermolecular interactions as observed in the crystal on optical properties are discussed.

Keywords: single crystal X-Ray, intermolecular interactions, UV-Visible, Fluorescence

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