

Influence of the peripheral alkyl chains length on the mesomorphic properties of electron acceptor π -extended HAT derivatives



Rafael Juárez^{a,b,1,2}, Mar Ramos^{b,2}, Matthias Lehmann^{c,**}, José L. Segura^{a,*}

^a Departamento de Química Orgánica, Facultad de Química, Universidad Complutense de Madrid, E-28040 Madrid, Spain

^b Department of Environmental and Technological Chemistry, Universidad Rey Juan Carlos, Madrid 28933, Spain

^c Institute of Organic Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

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ABSTRACT

Two 2D π -extended hexaazatriphenylene (HAT) derivatives with different alkyl chain peripheries are synthesized and electrochemically characterized showing their good electron acceptor ability. We highlight the influence of the peripheral alkyl chains in the liquid crystal properties of both HAT derivatives.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been widely studied in part because of their semiconducting properties that make them potentially useful for applications in organic electronics [1]. Anthony's and Wudl's syntheses of soluble and well-characterized higher acene derivatives (hexacene/heptacene) now lead the way to materials with even more promising properties [2]. Because of their excellent hole-conducting properties and advantageous crystalline packing, the higher acenes are currently receiving a lot of attention [3].

One of the most known and studied PAHs is pentacene (1) because of its high hole mobility. This high mobility results from a combination of different elements: (i) like many of its derivatives, pentacene packs in a herringbone pattern that allows for excellent π - π overlap in the solid state; (ii) it has a facile and reversible oxidation to its radical cation in the solid state; (iii) there is a good transfer integral (t) and correct nodal overlap of the highest occupied molecular orbitals (HOMOs) of adjacent molecules and (iv) it presents a small reorganization energy of the radical cation (λ_+) when going from the neutral molecule to the radi-

cation [4]. However, pentacene has some shortcomings when applied in devices, such as poor solubility and limited stability in ambient conditions [4,5]. Several approaches have been used to improve the stability and processability of acenes including the synthesis of alkynylated or halogenated derivatives. It has been observed that the substituents have a profound effect on the electronic properties of the material and even changes in the "polarity" of the molecule are observed. Thus, perfluoropentacene is a good example of this effect, as it has been described as a n -type material [6]. Another strategy to tune the properties of acenes is to introduce heteroatoms in the fused-ring system to construct more stable ladder-type fused molecules. These acene derivatives where a carbocyclic ring or rings have been replaced by a heteroaromatic ring, the so-called "heteroacenes" constitute one of the most common classes of small-molecule semiconducting materials [1]. Examples include fused oligothiophene [7], benzothiophenes [8], benzobisthiazole [9], thiazolothiazole [10], indolocarbazole [11], bisindenocarbazole [12], thienopyrrole [13] and indolothiophene [14] derivatives. Most of these systems involve electron rich heterocyclic moieties such as thiophene, pyrrole, indole or carbazole and therefore this strategy has proven fruitful to obtain p -type materials. In contrast, fewer examples have been reported of electron deficient heteroacenes. The replacement of C and H atoms by N atoms in acenes to yield the corresponding azaacenes or N-heteroacenes [15] not only stabilizes the molecules towards oxidation but also lowers their LUMO level, converting them into n -type materials. Recently some theoretical studies on azapentacenes have been performed and conclude that a high number of nitrogen atoms in the azaacene are necessary to obtain n -type

* Corresponding author. Tel.: +34 91 3945142; fax: +34 91 3944103.

** Corresponding author. Tel.: +49 0931 31 83708; fax: +49 0931 31 87350.

E-mail addresses: mariammar.ramos@urjc.es (M. Ramos),

Matthias.Lehmann@uni-wuerzburg.de (M. Lehmann), segura@quim.ucm.es (J.L. Segura).

¹ Tel.: +34 91 6647461.

² Tel.: +34 91 6647465.

organic materials. Thus, some of these theoretical studies claim that at least 5 [16] or even 7 or 8 nitrogen atoms (as in the case of compound **2**) are needed to obtain a *n*-type behaviour [17].

1,4,5,8,9,12-Hexaazatriphenylene (HAT, **3**) can be considered as a nitrogen rich 2D acene analogue containing six nitrogen atoms. Since its first synthesis in 1981 [18], HAT and its derivatives have been mainly investigated as metal ligands specially with applications in the synthesis of metal-organic frameworks (MOFs) [19]. More recently Ru²⁺ complexes with HAT-based systems have received attention for their implication in photoinduced electron transfer processes in combination with biomolecules [20]. Only very recently HAT derivatives have been explored as functional materials in the absence of metals. Because of (i) their discotic structure which provides them the ability to form discotic liquid crystals [21], and (ii) their low reorganization energy between their anionic and neutral forms [4,22], these systems are interesting organic semiconductors which may find application in organic field effect transistors (OFETs) or in organic photovoltaic devices (OPVs). Due to its electron deficient nature HAT derivatives are *n*-type organic materials. Derivatives endowed with long alkyl chains such as **4** [21b] are organized in columnar mesophases exhibiting modest *n*-type charge carrier mobilities while better performances have been reported for π -extended analogues such as hexaazatrinaphthylene (HATNA, **5**) [21a,c].

From a theoretical point of view it has been reported that by increasing the size of the aromatic core the charge hopping rate should also increase [23]. Thus, the extension of π conjugation has proven to be effective to enhance the charge carrier mobility in *p*-type organic semiconductors. As an example, the charge-carrier mobility in acene OFETs increased in one order of magnitude when pentacene [24] instead of anthracene [25] was used. Concerning with *n*-type molecules the rylene family has been the most extensively investigated due to their high electron mobility [26]. In this kind of arylene-based semiconductors extension of conjugation has allowed even to obtain ambipolar semiconductors [27]. In this regard, there are very few reports concerning with the extension of conjugation in HAT derivatives. Lehn and co-workers reported the synthesis of derivative **6** (Fig. 1) as a metal ligand for polymetallic molecular architectures [28], and Ishi-i and co-workers investigated the ability of HAT derivative **7** (Fig. 1) to self-assemble in solution and in the solid state [29]. We have recently reported a theoretical and experimental joint study based on the 2D π -extended system **8** (Fig. 1) having three fused HAT moieties showing that this molecule is a good electron acceptor with self-assembling properties in solution and low reorganization energies [30].

In this article we investigate two 2D π -extended tri-HAT derivatives **8** and **9**, that have been designed with three remarkable characteristics: (i) a planar discotic core in order to favour the π -stacking of the molecules; (ii) the presence of 18 sp^2 nitrogen atoms to improve the electron acceptor ability in comparison with HAT which only contains six sp^2 nitrogen atoms; and (iii) a periphery with 12 *n*-alkyl chains to favour their solubility and liquid crystalline behaviour. The electron acceptor ability of the tri-HAT derivatives **8** and **9** in comparison with that of the parent HAT reference **3** is investigated and the influence of the peripheral alkyl chains in the liquid crystal properties of the tri-HAT molecules is highlighted.

2. Experimental

Solvents were dried using common methods: THF was distilled over a sodium benzophenone mixture, dichloromethane was distilled over P₂O₅. All commercial chemicals were purchased from commercial sources and used as received. Hexaaminobenzene

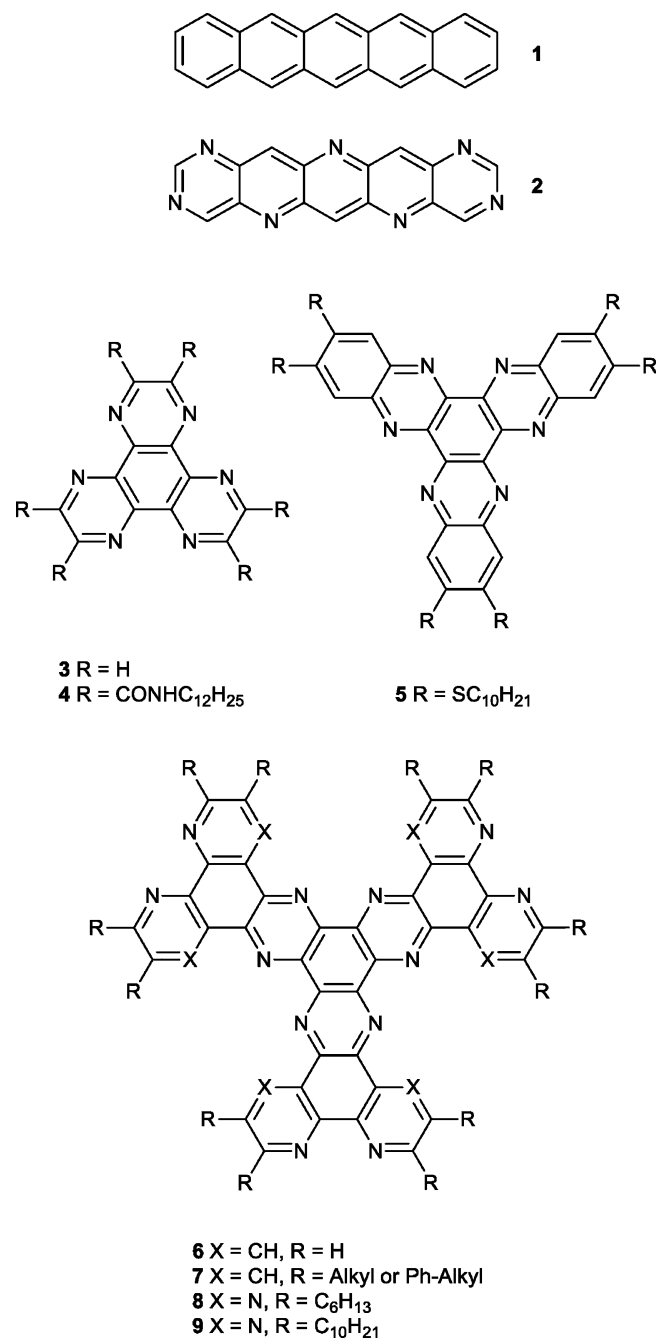


Fig. 1. HAT derivatives 1–5 and the tri-HAT molecules (6 and 7).

[31], hexaketocyclohexane octahydrate [32] and tri-HAT derivative **8** [30] were synthesized by following previously described synthetic procedures. Electrochemical measurements were carried out in an Autolab potentiostat using dry solvents and degassing the samples bubbling argon for 10 min prior to the measure. UV–vis spectra were obtained in a Varian Cary 50 spectrometer. NMR spectra were recorded in a Varian Gemini 400 MHz and a Bruker Avance III 700 MHz. Solvent signals were used as internal references (CDCl₃: 7.26 ppm and 77.0 ppm), coupling constants are given in Hz. FTIR measurements were recorded in a Bruker Tensor equip. Mass experiments were carried out in a Bruker Ultraflex. Elemental analysis was carried out in a Elementar Vario EL III analyzer. The temperature dependent SAXS X-ray investigations were performed on extruded fibres on a Bruker Nanostar (Detector Vantec2000,

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