



# Synthesis, optical properties and lamellar self-organization of new $N,N',N''$ -trialkyl-triazatriangulenium tetrafluoroborate salts



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## ABSTRACT

Here we report the synthesis of six new  $N,N',N''$ -trialkyl-triazatriangulenium ( $R_3$ -TATA<sup>+</sup>) tetrafluoroborate salts with ether functions in their side chains. Solution and solid-state optical properties of the  $R_3$ -TATA<sup>+</sup> salts were investigated to elucidate the influence of the side chain heteroatoms on the electronic structure of the chromophore. Structural studies of spin-cast thin films of nine different  $R_3$ -TATA<sup>+</sup> BF<sub>4</sub><sup>-</sup> salts showed, for all derivatives, formation of a rare structure with homeotropic aligned discotic dyes in a lamellar structure. In the lamellar structure, layers of the charged discotic TATA<sup>+</sup> dyes and their counter ions are separated by the perpendicularly oriented alkyl chains. In all cases, it was found that simple spin-casting gave films with macroscopic alignment of the lamellar structure parallel to the substrate. Formation of the lamellar structure, for all the  $R_3$ -TATA<sup>+</sup> BF<sub>4</sub><sup>-</sup> salts, both with branched and linear side chains, highlight the robustness of this self-organizing motif.

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## 1. Introduction

Molecular self-assembly is an integral part of the bottom up approach in materials science and nanotechnology [1–12]. The optical and electronic properties of molecular thin films and materials are to a large extent governed by the supramolecular organization in the materials. Consequently, a large degree of structural control is needed to make efficient devices such as OFETs and OLEDs [13–16]. Yet, the detailed structure of a material is very difficult to predict, as it is a result of a complex balance of forces and energies: the individual molecule's covalent structure and conformation is perturbed by the nearest neighbour interactions and the necessity of the individual units to be part of larger macroscopic aggregates or domains. One class of materials, where a large degree of control over molecular and macroscopic structure is possible, is liquid crystals [5,7]. A large number of columnar liquid crystals have been used as anisotropic semiconductors [17,18]. In the columnar liquid crystals, discotic molecules are arranged in 1D aggregates. We recently reported a molecular material based on tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) salts of the fluorescent  $N,N',N''$ -trialkyl-triazatriangulenium ( $R_3$ -TATA<sup>+</sup>) dye, where the discotic cations are arranged in a 2D

lattice, rather than in the typical 1D stack [19,20]. This motif had previously only been achieved by Ohta et al. [21], and Faul et al., who used ionic self-assembly (ISA) to create similar structures [11,22–24]. We further showed that this spatial arrangement of the TATA<sup>+</sup> dyes provides a new material with promising exciton transport properties [20]. Recently, other trialkyl-TATA<sup>+</sup> salts have been used by Maeda and co-workers to form novel 1D columnar structures [25–27].

The triazatriangulenium salts belong to the family triangulenium dyes [19,28–34]. The triangulenium compounds are exceptionally stable carbocations and good fluorescent dyes. The high cation stability of TATA<sup>+</sup> ( $pK_{R_3} = 23.7$ ) is a result of a high degree of charge delocalization in the cation. This allows a segregated packing of cations and anions in the solid-state of several TATA<sup>+</sup> salts, with a full overlap of two cationic  $\pi$ -surfaces. The resulting dimer is the building block of the rare self-assembling lamellar structure in  $R_3$ -TATA<sup>+</sup>·BF<sub>4</sub><sup>-</sup> thin films form upon spin-casting, see in Fig. 1 [20]. The structure can be rationalized by the molecular structure, shape and a close to perfect matching between the surface of the TATA<sup>+</sup> core in its lattice with the BF<sub>4</sub><sup>-</sup> counter ions and six alkyl side chains (approx. 135 Å<sup>2</sup>).

Here, we report the synthesis, optical properties and structural investigation of a diverse series of new  $R_3$ -TATA<sup>+</sup>·BF<sub>4</sub><sup>-</sup> salts with ether linkages in the 3 or 4 positions of the side chains (compounds **4** and **5** respectively, Fig. 2). The effect of the ether bridges and their position on the spectroscopic properties of the dyes is investigated,

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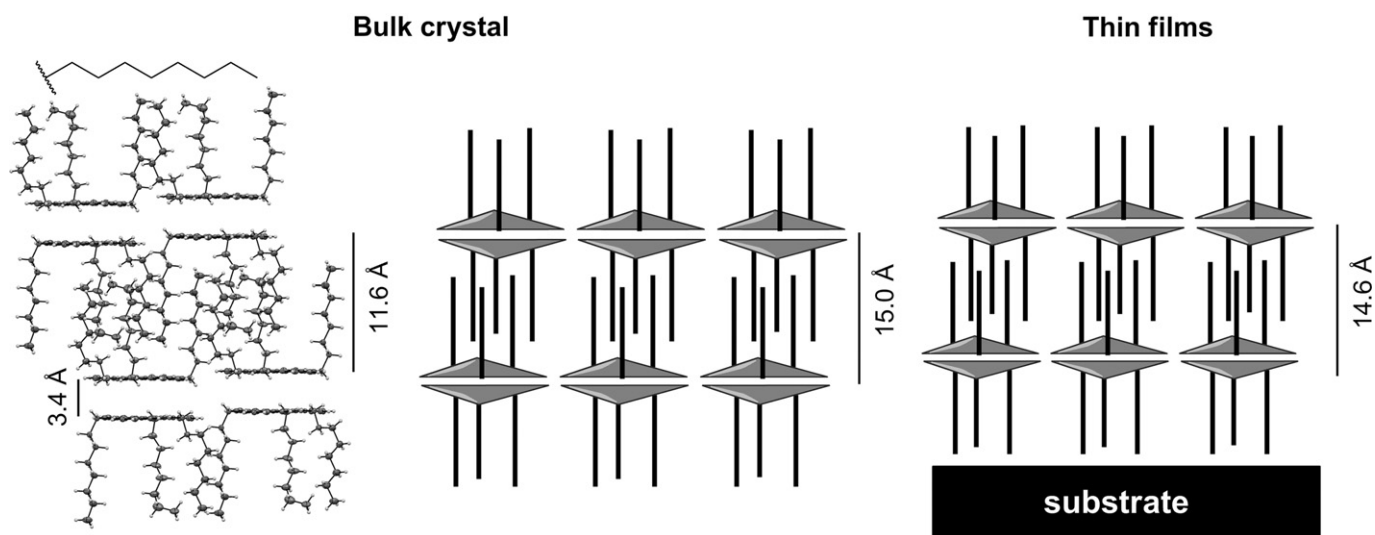


Fig. 1. The packing motif of  $N,N',N''$ -trialkyl-triazatriangulenium tetrafluoroborate crystals and thin films. The repeat distance or layer separation is shown on the two models [20].

and the supramolecular structure of nine different  $R_3$ -TATA· $BF_4$  salts in spin-cast thin films was investigated using spectroscopy and X-ray reflectometry. We find that variation of the side-chains does not prohibit the special lamellar structure of the thin films, but gives a precise control of interlayer separation. Thus, we document that the lamellar structure with perfect homeotropic orientation of the discotic chromophore is a robust self-organizing motif, for the  $R_3$ -TATA· $BF_4$  dyes in thin films.

## 2. Methods and materials

Chemicals, materials and solvents were used as received. Solvents were HPLC grade. Hexamethoxy-triphenylmethylum tetrafluoroborate and **1** were synthesized as previously reported [19,35].

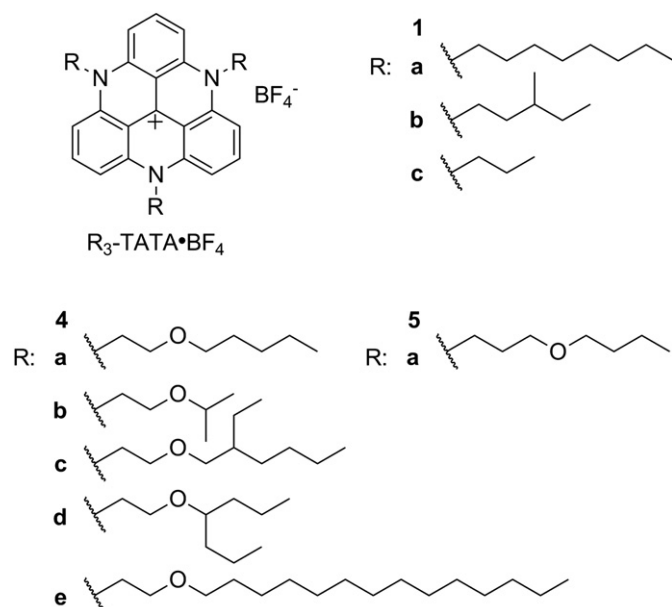


Fig. 2. The molecular structure of the nine different  $N,N',N''$ -trialkyl-triazatriangulenium tetrafluoroborate salts under investigation.

### 2.1. Synthesis

#### 2.1.1. General procedure to **2** and **3**

Hexamethoxy-triphenylmethylum tetrafluoroborate (1 g = 2 mmol) was dissolved in 5 ml NMP and 10 equivalents of the appropriate hydroxylamine (10 equivalents per reaction site, 30 equivalents in total) was added and the reaction was heated to reflux overnight (approx. 160 °C). When the reaction had cooled to room temperature the reaction mixture was poured into 200 ml 0.1 M aqueous  $NaBF_4$  and the crude product collected by filtration.

**2.1.1.1.  $N,N',N''$ -tris(2-hydroxyethyl)-triazatriangulenium hexafluorophosphate (**2**).** Yield after precipitation with methanol from hot DMSO 0.40 g (34%).  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  ppm 3.84 (d, 6H) 4.37 (br. s., 6H) 5.08 (t, 6H) 7.31 (d, 6H) 7.94 (t, 3H)  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  ppm 49.04, 56.77, 105.57, 109.50, 137.11, 139.54, 140.18. ESI High Resolution Mass Spectrometry: Calculated for  $C_{25}H_{24}N_3O_3^+$ :  $m/z = 414.1818$ ; Found  $m/z = 414.1834$ , deviation 3.8 ppm. Elemental Analysis: Calculated for  $C_{25}H_{24}N_3O_3 \cdot PF_6^-$ : C: 53.67, H: 4.32, N: 7.51; Found: C: 53.63, H: 4.33, N: 7.50. Melting point: no melting observed, decomposition at 300 °C.

**2.1.1.2.  $N,N',N''$ -tris(3-hydroxypropyl)-triazatriangulenium tetrafluoroborate (**3**).** Yield after precipitation with ether from acetonitrile 0.54 g (46%).  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  ppm 1.98 (br. s., 6H), 3.69 (d, 6H), 4.48 (br. s., 6H), 4.97 (br. s., 6H), 7.45 (d, 6H), 8.08 (t, 3H).  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  ppm 27.66, 44.58, 57.80, 104.84, 109.62, 137.49, 139.31, 139.72.

ESI High Resolution Mass Spectrometry: Calculated for  $C_{28}H_{30}N_3O_3^+$ :  $m/z = 456.2287$ ; Found  $m/z = 456.2284$ , deviation -0.8 ppm. Elemental Analysis: Calculated for  $C_{28}H_{30}N_3O_3 \cdot BF_4^- \cdot H_2O$ : C: 59.91, H: 5.75, N: 7.49; Found: C: 59.61, H: 5.65, N: 7.00. Melting point: no melting observed, decomposition at 300 °C.

#### 2.1.2. General procedure to **4** and **5**

1 equivalent of starting material (**2** or **3**) (0.2 mmol) was dissolved in 5 ml DMF and 30 mol equivalents of sodium hydride (60% in mineral oil) was added with vigorous stirring. After 10 min 30 mol equivalents of the alkyl bromide is added neat. The reaction was followed using MALDI-TOF MS and when complete conversion was observed the reaction was poured onto 20 ml 50%

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