Triazatrinaphthylene, a three-fold symmetry planar conjugated system with two-dimensional self-assembly properties[†]

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A novel threefold symmetry planar system based on a π -conjugated triazatrinaphthylene core has been synthesized and deposited on atomically flat surfaces of highly oriented pyrolytic graphite (HOPG). Scanning tunnelling microscopy (STM) of 2,8,14-trimethyl-5,11,17-triazatrinaphthylene (denoted TrisK by analogy with the Triskele Celtic symbol) deposited at the *n*-tetradecane/HOPG interface reveals the spontaneous formation of self-assembled monolayers with a hexagonal close-packed arrangement extending over several tens of nanometers. Surprisingly, sub-molecular STM resolution reveals an extremely bright contrast spot on one of the three symmetrical branches of the triangular-shaped molecule TrisK. This non-equivalent adsorption site can be interpreted as originating from a local specific molecule–HOPG interaction. Besides, *ab-initio* calculations show that a purely molecular contribution may also be involved.

Introduction

Extended planar aromatic systems represent attractive targets as active materials in electronic devices.¹ Some of them are also commonly used in biology to achieve structure-specific recognition of DNA through π - π overlapping of nucleic bases.² This class of compounds thus represents key motifs at the crossroads between materials and bioorganic chemistry and this duplicity is illustrated by numerous recent studies making use of polynuclear aromatics for studying the ability of DNA to transport electrical charges.³ In order to achieve their self-organization in solution or the solid state it is therefore essential to tailor them properly.⁴ From this viewpoint, planar conjugated molecules having threefold symmetry and bearing long alkyl chains such as hexa-peri-hexabenzocoronenes⁵ or hexaazatrinaphthylenes⁶ are of particular interest because they behave as liquid crystals. It has also been reported recently that alkoxy-triphenylenes⁷⁻⁹ and conjugated {C}3-oligothiophenes¹⁰ form two-dimensional (2D) self-assemblies on highly oriented pyrolytic graphite (HOPG) as revealed by scanning tunnelling microscopy (STM).

We report here on the synthesis and 2D self-assembly on graphite of 2,8,14-trimethyl-5,11,17-triazatrinaphthylene, a novel C_{3h} -symmetry conjugated compound denoted TrisK by analogy with the Celtic symbol Triskele meaning "threelegged". The molecule of TrisK consists of a central benzene ring with three peripheral branches made of quinoline moieties, each of them terminated by a methyl group. The relative positions of the three nitrogen atoms and of the three methyl groups on the same side of each branch (clockwise and counter-clockwise respectively) make TrisK a prochiral molecule exhibiting two enantiotopic faces. As pointed out above, the large aromatic surface of triazatrinaphthylenes makes them potentially interesting as neutral precursors of nucleic acid binders¹¹ as well as liquid crystals by substituting the methyl group by longer alkyl chains. Following the description of its chemical synthesis, we show here that compound TrisK forms long range self-assembled monolayers (SAMs) with hexagonal packing on HOPG and that high resolution STM reveals the presence of a high contrast adsorption site on one of its three branches. This intramolecular non-equivalent adsorption site is very surprising for a symmetrical molecule and is interpreted in terms of a strong local electronic interaction between certain atoms of the molecule and those of graphite.



TrisK

Results and discussion

Synthesis

In general, fused aromatic systems containing heteroatoms, in particular the aza-series, are more easily accessible than their all-carbon counterparts. The synthesis of polyazaaromatic compounds mainly proceeds *via* three well-established

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procedures, namely the condensation of an aromatic *o*-aminoaldehyde with an enolizable ketone (Friedländer method),^{12,13} the condensation of *o*-phenylene diamines with quinones (Skraup reaction)^{14,15} and the amination of aryl halides (Ullmann–Goldberg type)¹⁶ followed by an intra-molecular cyclization. However, the two former methods are often limited by the availability and the stability of the starting materials.¹⁷

Accordingly, we successfully synthesized compound TrisK *via* a three-step process based on *N*-arylation of 1,3,5-tribromobenzene. *N*-Arylation allows in principle the use of a variety of substrates, but it often leads to poor yields and low reproducibilities when copper catalysis is carried out.¹⁶ However, during the past decade, considerable improvements of this synthetic process have been performed through the development of novel palladium catalytic systems.¹⁸ In respect of these advances and to our previous works in the synthesis of various acridine and quinacridine series,¹⁹ we selected Pd-catalyzed *N*-arylation as the key step of our synthetic approach to TrisK.

As shown in Scheme 1, the condensation of 1,3,5-tribromobenzene with the 5-methyl derivative of anthranilic acid catalyzed by Pd(OAc)/BINAP affords the tris-condensation product 1 in good yield under mild conditions. This intermediate is then submitted to ring closure by treatment in P(O)Cl₃,²⁰ which leads to the tris-chloro derivative. Finally, compound TrisK is obtained from the reduction of the trischloro intermediate 2 by LiAlH₄. These conditions allow the tris-amination to go to completion in good conversion yield (>60%), whereas copper catalysis (Cu/CuI) only affords a mixture of mono- and di-substituted products in low yield (<15%).

Scanning tunnelling microscopy

Fig. 1a is a large scale STM image of a self-assembled monolayer of TrisK physisorbed at the *n*-tetradecane/HOPG



Fig. 1 STM images of a self-assembled monolayer of TrisK recorded at the interface between graphite HOPG and *n*-tetradecane. (a) 61.1 × 61.1 nm², $U_t = 138$ mV, $I_t = 15$ pA; (b) 20.2 × 20.2 nm², $U_t = 177$ mV, $I_t = 12$ pA; (c) high resolution image (4.4 × 4.4 nm², $U_t = 177$ mV, $I_t = 15$ pA) revealing a hexagonal arrangement of high contrast spots; (d) one possible arrangement of molecule TrisK on HOPG as deduced from (c).

interface. The monolayer consists of highly ordered domains extending over a few tens of nanometers and delineated by linear dislocations generated by the misfit between the graphite and organic 2D lattices. These dislocations form a triangular pattern with angles of 60° which reflect the underlying geometry of the graphite substrate. Higher resolution (Fig. 1b) reveals that molecules of TrisK self-assemble as a hexagonal



Scheme 1 Synthetic pathway to compound TrisK. *Reagents and conditions*: i) Pd(OAc)₂/BINAP/Cs₂CO₃/dioxane; ii) P(O)Cl₃, reflux; iii) LiAlH₄, THF, reflux, then FeCl₃/NH₄OH.

lattice having a unit cell with $a = b = 16.1 \pm 0.2$ Å. The triangular shape of TrisK is already visible but becomes even more apparent in Fig. 1c where intramolecular details also appear. The corresponding molecular 2D-arrangement of TrisK is given in Fig. 1d as a superposition of its carbon backbone onto the STM image. However, at this point it remains impossible to locate precisely either the nitrogen atoms or the terminal methyl groups which can be on either side of the three branches of the molecule because of its prochiral nature. Note that the dark contrast regions appearing between molecules of TrisK in Fig. 1c,d correspond to graphite areas only covered by *n*-tetradecane.

Surprisingly, a hexagonal arrangement of extremely bright spots is clearly visible in Fig. 1c, each of them being located on the side-end of one of the three branches of TrisK. Such bright spots correspond to high tunnelling currents and are *a priori* not compatible with the ternary symmetry of TrisK where the three branches are supposed to be equivalent towards adsorption. This non-equivalent adsorption site is dominated either by molecule–substrate interactions or by a hypothetical asymmetry of molecular orbitals (MOs).

A first way to address this question consists of building a model packing of the adlayer of TrisK on graphite. It is well known that the graphite surface is constituted of two types of carbons marked as small black and white dots in Fig. 2. Two adjacent graphite layers are shifted so that their respective carbon atoms are located either at the apex of each other (white dots) or at the apex of the center of a hexagon (black dots). Therefore, prominent tunnelling sites of bare graphite (carbons in white) correspond to each second carbon atom of the hexagonal lattice.²¹ The main consequence is that atoms (or groups of atoms) of each individual molecule of an organic adlayer will have different graphite environments and different STM contrasts. For example, a number of studies have shown that consecutive CH₂ groups of long rod-like n-alkanes selfassembled on graphite are alternately close to either of the two types of carbon and only one CH2 group of every two is visible



Fig. 2 Two geometrical model positions of molecule TrisK with respect to the HOPG substrate. (a) Carbon atoms of TrisK are positioned as if it were a graphite layer. All adsorption sites are equivalent such as for example that of the terminal methyl groups inside the black circles. (b) Position obtained by shifting TrisK by a few tenths of angströms along the (110) direction of graphite. Adsorption sites of two of the methyl groups remain equivalent (black circles) while the third one becomes non-equivalent (red circle).

in STM.^{22–24} The same concept also applies to large polycyclic aromatic hydrocarbons as recently reported by Samori *et al.*^{25,26} Given this, if we position all carbon atoms of molecule TrisK as if it were a graphite layer (Fig. 2a), adsorption sites of each of the three branches of TrisK (denoted α , β and γ in Fig. 2) are equivalent. The identical positions of the three methyl groups with respect to HOPG (large black circles) provide a clear example of such a symmetrical situation. This model graphite-like position of TrisK on HOPG cannot in itself account for the observed non-equivalent STM contrast feature. Since molecule TrisK contains a number of noncarbon atoms (in particular three nitrogen atoms), it is very likely that its position on a graphite surface is slightly shifted compared to the model position.

Starting from the graphite-like position and by sliding molecule TrisK only by a few tenths of angströms, it appears that adsorption sites remain equivalent in two branches while that of the third branch becomes non-equivalent. One example of such a situation is represented in Fig. 2b where TrisK has been shifted along the (110) direction of graphite. In this new geometry, methyl groups of branches α and β have similar graphite environments (black circles) while the methyl group of branch γ becomes non-equivalent due to a different graphite environment (red circle). This is also clearly the case for the nitrogen atoms (represented by blue spots in Fig. 2) which adopt equivalent graphite environments in branches α and γ and a non-equivalent one in branch β (Fig. 2b). Note that various similar molecule-substrate positions leading to one non-equivalent intramolecular adsorption site can be obtained by shifting TrisK along other directions starting from the graphite-like position of Fig. 2a. The geometrical situation shown in Fig. 2b illustrates our interpretation and may indeed explain the non-equivalent STM contrast observed on one branch of the TrisK molecule. It is well known that a subangström scale displacement of a molecular adlayer may induce a pronounced tunnelling contrast change.

An alternative origin for the dissymmetrical intramolecular contrast of TrisK when physisorbed on graphite could be the loss of planarity of the molecule. Such an explanation has been recently proposed for phenylene-alkyl substituted hexabenzocoronenes to account for different tunnelling contrasts of the single aromatic cores within a monolayer.²⁵ In this case, the loss of planarity was attributed to steric interactions between the aromatic core and the phenylene substituents and was homogeneously distributed over the entire molecule. In contrast, here compound TrisK does not contain any bulky substituent susceptible to distortion of its planar conformation. Furthermore, non-planarity should be inhomogeneous from one molecular branch to the other resulting in an intramolecular contrast peculiarity.

Ab-initio calculations

However, a purely molecular contribution cannot be excluded given the particular ternary symmetry of molecule TrisK. In STM images, the contrast is mainly due to the electronic interaction between the tip and the adlayer–substrate system, more specifically through the HOMO and LUMO levels. In order to check this assumption, we performed *ab initio* calculations of charge density distribution in TrisK. *Ab-initio* molecular orbital (MO) calculations have been performed on an isolated molecule TrisK using the Gaussian 03W package,²⁷ with geometry optimization at the HF/STO-3G level. Further optimization is obtained with the local density approximation (LDA) using the spin-density functional of Vosko *et al.*²⁸ (SVWN) and the 6-31G** basis set, which is comparable to the double numerical basis sets with polarization functions used in other studies.¹⁰ MOs are visualized with the program Molden 4.0²⁹ and a contour value of 0.01.

Our results show that TrisK is a planar molecule belonging to the C_{3h} symmetry point group. It has a two-fold degenerate HOMO level (two components denoted HOMO 1 and HOMO 2) but only one LUMO. The separation between the HOMO and the LUMO levels is found to be 2.14 eV. Interestingly, Fig. 3 clearly shows that the three branches of molecule TrisK have different MO contours in both HOMOs whereas they are perfectly identical in the LUMO. Such a HOMO picture has already been reported for other conjugated molecules with ternary symmetry.¹⁰ In addition, a prominent feature in the HOMO is the difference in the coefficients on the terminal methyl groups. For both HOMO 1 and HOMO 2, the contribution of the carbon $2p_z$ orbital is predominantly located on two methyl groups (see values of coefficients in the ESI[†]). Although these calculations are performed on a non-interacting molecule, they suggest that the HOMO of TrisK may contribute to the non-equivalent adsorption sites observed on HOPG. They also suggest that the methyl group could play a role in the intense contrast spot of the STM images.

(а) HOMO 1 HOMO 2 Image: Constraint of the second secon

Fig. 3 *Ab-initio* calculation of the charge density distribution of the frontier orbitals of 2,8,14-trimethyl-5,11,17-triazatrinaphthylene TrisK. (a) The two components of its degenerate HOMO orbital (symmetry E", eigenvalue -0.215690 a.u.) and (b) the non-degenerate LUMO orbital (symmetry A", eigenvalue -0.119220 a.u.). Note that the three branches of TrisK have different MO contours in both components of the HOMO whereas they are perfectly identical in the LUMO.

Conclusion

In summary, we have synthesized 2,8,14-trimethyl-5,11,17triazatrinaphthylene TrisK, the first member of a new class of planar conjugated molecules with ternary symmetry. Compound TrisK physisorbs on the basal plane of graphite HOPG to form self-assembled domains extending over several tens of nanometers. Sub-molecular STM resolution reveals a high contrast spot located on one of the three branches of TrisK. We interpret this peculiar local contrast in terms of a non-equivalent intramolecular adsorption site due to a strong local interaction with HOPG. If the precise identification of the responsible atoms is premature, the terminal part of one of the three branches of TrisK plays an important role due to its coincidence with the bright spot on the STM images. As a first argument, we show that a slight shift of TrisK on the graphite lattice away from a model graphite-like position may induce non-equivalent intramolecular substrate environments. Furthermore, ab-initio MO calculations lead to two degenerate HOMOs with slightly different contributions of the methyl-2p_z coefficients in the overall molecular orbital, thus suggesting that it may also contribute to the non-equivalent adsorption sites of TrisK on graphite. We are presently modifying the chemical structure of molecule TrisK, in particular by substituting the terminal methyl group by a longer alkyl chain in view of investigating potential liquid crystal properties and tuning the possibility of a stereochemical morphology of the monolayers.³⁰

Experimental

Synthesis

5,5',5"-Trimethyl-2,2',2"-(1,3,5-phenylenetriamino)tribenzoic acid (1). 1.79 g (5.7 mmol) of 1,3,5-tribromobenzene, 3 g (19.8 mmol, 3.5 eq.) of 2-amino-5-methylbenzoic acid, 0.32 g (0.5 mmol, 0.09 eq.) of BINAP, 0.08 g (0.3 mmol, 0.06 eq.) of Pd(OAc)₂ and 9.22 g (28.3 mmol, 5 eq.) of Cs₂CO₃ are introduced into an argon-purged round-bottom flask with 20 mL freshly distilled 1,4-dioxane on sodium and refluxed during 24 h under an argon stream. After cooling, the dioxane is evaporated and the residue is dissolved in 80 mL methanolwater 1 : 1. The solution is acidified with concentrated HCl until the pH drops significantly (pH \sim 4.5). The green precipitate is filtered and extracted with hot ether. The filtrate is evaporated and methanol is added; the resulting precipitate is filtered and dried, yielding 1 as a pale yellow solid (1.08 g, isolated yield 36%). ¹H NMR (DMSO): 9.52 (br s, 3 COOH), 7.82 (s, 3H), 7.41 (m, 6H), 6.74 (s, 3H), 2.35 (s, 9H). ¹³C NMR (DMSO): 170.1, 144.3, 143.7, 135.2, 132.0, 127.3, 116.2, 114.1, 105.4, 20.4. ESI-MS (H₂O-MeOH) m/z: 526.28 $(MH^{+}); mp > 260 \, ^{\circ}C.$

6,12,18-Trichloro-2,8,14-trimethyl-5,11,17-triazatrinaphthylene (2). 0.51 g (0.97 mmol) of **1** and 8 mL of POCl₃ are introduced into an argon-purged round-bottom flask and refluxed for 3 h with a CaCl₂ guard. After evaporation of POCl₃, the residue is dissolved in 50 mL of chloroform and slowly poured onto 15 mL of ice-cooled 15% NH₄OH. The organic layer is decanted and the aqueous layer is further extracted with chloroform. The organic phase is dried over Na₂SO₄, and concentrated almost to precipitation. Methanol is added to form a precipitate, which after filtration gives **2** as a brown solid (0.18 g, 35%).¹H NMR (CDCl₃): 8.475 (s, 3H), 8.26 (d, 3H, ⁵*J* = 8.7 Hz), 7.75 (dd, 3H, ³*J* = 1.8 Hz, ⁵*J* = 8.7 Hz), 2.72 (s, 9H). (CI-MS) *m*/*z*: 526 (MH⁺). UV-vis (CHCl₃) λ_{max}/nm (M⁻¹ cm⁻¹) = 294 (40526) 307(48421), 323(37526); Mp m260 °C.

2,8,14-Trimethyl-5,11,17-triazatrinaphthylene (TrisK). To a suspension of 0.10 g LiAlH₄ (2.6 mmol.) in 8 mL freshly distilled THF under argon is slowly added 0.18 g of 2 (0.32 mmol.) in 8 mL THF. After refluxing overnight, the mixture is cooled to 0 °C and 0.2 mL water, 0.2 mL 15% NaOH and 0.6 mL water are added successively. After stirring for 20 min the mixture is filtered and the solid residue washed with CHCl₃ until decoloration. The filtrate is decanted and the aqueous phase is extracted with CHCl₃. The organic phase, containing TrisK along with hemireduced products, is treated as follows: after evaporation, the residue is taken up in 12 mL EtOH and a solution of 0.44 g of FeCl₃·6H₂O (1.62 mmol.) in 2 mL water is added and refluxed overnight. After cooling to 0 °C, 0.6 mL of 15% NH₄OH is added and the mixture is filtered. The precipitate is washed with CH₂Cl₂ and the filtrate is decanted and further extracted with CH₂Cl₂. After drying over Na_2SO_4 and evaporation, the residue is taken up in a 1 : 3 mixture of CH₂Cl₂-MeOH. The formed precipitate is filtered and dried, yielding TrisK as an orange solid (30 mg, 22%). ¹H NMR (CDCl₃): 9.96 (s, 3H), 8.25 (d, 3H, ${}^{5}J = 8.4$ Hz), 7.952 (s, 3H), 7.71 (d, 3H, ${}^{5}J = 8.4$ Hz), 2.67 (s, 9H). (CI-MS) m/z: 424 (MH⁺); UV-vis (CHCl₃) λ_{max}/nm (M⁻¹ cm⁻¹) = 288 (62457) 298 (73898), 311 (53237), 368 (14237); 386 (14151); fluorescence (CHCl₃, $\lambda_{\text{exc}} = 298 \text{ nm}$) $\lambda_{\text{em}}/\text{nm} = 390, 413, 437$; mp >260 °C.

Scanning tunnelling microscopy (STM)

STM is performed using a PicoSPM (Molecular Imaging) equipped with a home-built liquid cell. Samples (5 × 5 mm²) of highly oriented pyrolytic graphite (HOPG) are cleaved just prior to sample deposition. A small quantity of purified 2,8,14-trimethyl-5,11,17-triazatrinaphthylene TrisK is solubilized in *n*-tetradecane $C_{14}H_{30}$ (99+% purity, Aldrich). The STM tips are mechanically cut from a 250 µm Pt–Ir (80 : 20) wire and tested on cleaved HOPG. STM images are recorded at room temperature at the HOPG/*n*-tetradecane interface in the constant-current mode. Typical imaging conditions are 100–300 mV for the tip voltage and 10–20 pA for the tunnelling current.

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