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Solid state structures of fluorine-rich fluoranthenes†

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The solid state structures of seven substituted fluoranthenes were determined by single-crystal X-ray diffraction. All compounds bear electron withdrawing substituents in various positions, giving rise to an excellent opportunity to compare the solid state packing influences of the trifluoromethyl substituent and other electron withdrawing groups (pentafluorophenyl and nitrile groups). It was found that, depending on the substituent and the position of the substituent, the most commonly observed molecular packing motifs in crystals, such as herringbone packing with or without π - π overlap, 1D π -stacking and lamellar 2D π -stacking can be realized.

Introduction

Extended π -conjugated systems are of major scientific and industrial interest due to the ability to control the band gap, and their applications in molecular (opto)electronic materials as organic thin-film transistors (OTFTs), organic photovoltaic cells (OPVs) and light-emitting diodes.¹ Therefore, electron withdrawing substituents, especially the fluorine atom itself and fluorinated substituents such as the trifluoromethyl group are commonly used to lower the HOMO and the LUMO energy levels because of their negative inductive effect in a conjugated electronic system.² Additionally, lowering the electron density of a conjugated system *via* fluorination is a viable method to convert a p-type semiconductor parent structure to an n-type semiconductor.^{1a,3}

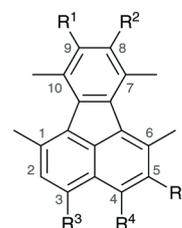
Attempts in the field of crystal engineering to improve the material properties for applications where electron mobilities are important usually aim for close packing with short intermolecular π - π -stacking distances, an overall dense packing to prevent oxidation, or hydrolysis by a kinetic barrier and a sufficient short-range order.^{1c}

To gain a greater understanding about the intermolecular forces that govern crystal packing, we present a structural study by single-crystal X-ray analysis of rigid fluorene derivatives bearing several electron withdrawing substituents (trifluoromethyl, pentafluorophenyl, and nitrile) in the same

position. Furthermore we investigated different substitution patterns using the trifluoromethyl group, giving insight into the dependence of the solid state packing compared to the substitution pattern. In the past, non-symmetrically substituted fluoranthenes were shown to inherit useful properties such as a wide band gap with blue emission⁴ or sensitive fluorescent chemosensors.⁵ Recently, several imide derivatives of fluoranthenes⁶ and also their dimers⁷ were synthesized and studied with regards to their morphology and optoelectronic properties.

All fluoranthenes employed in this study are shown below (Fig. 1). In general, the substituted 1,6,7,10-tetramethylfluoranthenes show both excellent solubility in common organic solvents and crystallinity. They can be classically synthesized by condensation of 2,7-dimethyl-acenaphthenequinone with 3-pentanone, followed by Diels-Alder reaction with acetylenes and subsequent decarbonylation.⁸

We employed the potent dienophile hexafluoro-2-butyne to gain access to *ortho*-bis(trifluoromethylated) fluorene 2.⁹ Direct trifluoromethylation¹⁰ of 2 gives access to 3, which



- 1 R¹ = CF₃, R² = R³ = R⁴ = R⁵ = H 5 R¹ = R² = R³ = R⁵ = CF₃, R⁴ = H
 2 R¹ = R² = CF₃, R³ = R⁴ = R⁵ = H 6 R¹ = R² = C₆F₅, R³ = R⁴ = R⁵ = H
 3 R¹ = R² = R³ = CF₃, R⁴ = R⁵ = H 7 R¹ = R² = CN, R³ = R⁴ = R⁵ = H
 4 R¹ = R² = R³ = R⁴ = CF₃, R⁵ = H

Fig. 1 Substituted fluoranthenes used in this work.

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can be reacted one more time yielding a mixture 4 and 5.¹¹ Likewise, 6 and 7 can be obtained by using bis(pentafluorophenyl)acetylene¹² and dicyanoacetylene,¹³ respectively.

Experimental section

General information

Full experimental details for previously unreported compound 1 and 7, as well as general information are given in the ESI.† Compounds 2,⁹ and 3–6,¹¹ were obtained as described previously. In all cases, solvent-free crystals suitable for X-ray analysis were obtained by slow cooling, or by evaporation of a dichloromethane/*n*-pentane solution of the fluoranthene.

Crystal structure determination

Crystallographic data and structure refinement parameters for all compounds are summarized in the ESI.† Single-crystal X-ray structure determination was performed on a Bruker-AXS SMART 1000 fitted with a CCD (2, 3, 6, 7) and a Bruker D8 VENTURE fitted with a CMOS-detector (1). Data collection, reduction and empirical absorption correction were performed using the APEX2, SMART, SAINT and SADABS programs, respectively.¹⁴ Single crystals of 4 and 5 were collected by using CrystalClear software (Rigaku)¹⁵ and a Rigaku Mercury-CCD diffractometer. The structure were solved using direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-2014/7).¹⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. Figures are obtained using Mercury 3.8.¹⁷

Results and discussion

Seven substituted fluoranthenes have been synthesized and their structures characterized *via* single-crystal X-ray diffraction. In the paragraphs below, we describe the structures in detail.

In general, the introduction of four methyl groups and additional substituents in the *peri* and bay regions causes steric overcrowding, and splaying/twisting distortions of the framework become apparent.⁸

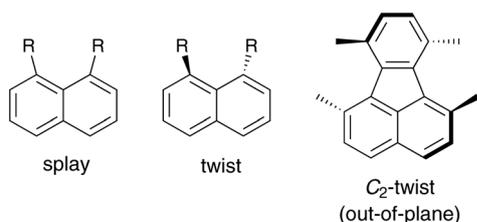


Fig. 2 Distortion modes relevant for the fluoranthenes are presented. Left: Molecular distortions of the *peri* region. Right: Methyl groups in the *bay* region induce twisting of the fluoranthene framework.

In accordance with the literature,^{1a} the nomenclature for the classification of the observed structures presented in Fig. 3 is used.

These molecular packing motifs can be further classified into face-to-face, or face-to-edge motifs with, or without, π - π overlap.

Observed trends

To the best of our knowledge, we present one of the most comprehensive solid state study of electron-poor fluoranthenes described so far (Fig. 4). Nevertheless, some important crystal structures of previously reported systems should be mentioned. Importantly, the structure of the parent fluoranthene was elucidated in 1977 by X-ray and neutron diffraction,¹⁸ suggesting a lamellar 1D π -stacking arrangement. Not much later, the perfluorinated fluoranthene was examined, which seemed to retain the overall alignment.¹⁹ We reported two similar structures in the past,²⁰ as the compounds serve as precursors for the corresponding corannulene compounds.^{11b} The group of Siegel published a study on eighteen diazafluoranthenes which were intended as synthetic precursors for diazacorannulenes.²¹ For the seven fluoranthenes studied herein, all common molecular packing motifs in crystals (Fig. 3) are observed (Fig. 4).

The reason for the formation of each distinct packing motif being favoured over another remains to speculation of course; however it seems, that the induced dipole on the molecule by the substituents has only a weak influence on the overall packing obtained. This follows the recently introduced Wheeler–Houk model,²³ in contrast to the classic Hunter–Sanders picture, where the tuning of the π -density leads to an attractive interaction (π -acid/ π -base attractions). For example, although 7 inherits the strongest dipole of all fluoranthenes studied herein (in the gas phase, see the ESI†), followed closely by 2, both fluoranthenes neither show close π - π overlap nor a head-to-tail arrangement. In the case of 2, both electron-depleted parts even interact closely in an unfavourable head-to-head array (Fig. 6) facilitating π -stacking of the electron-richer parts.

Instead, the sum of the weak interactions such as C–H \cdots F,²² C–H \cdots π ²⁴ and π - π contacts seem to largely contribute to the overall obtained energetic minimum in the solid state, (as they are additive). Since the periodicity in crystals is a product of the sum of all the short-ranged

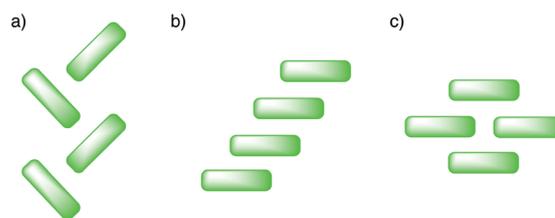


Fig. 3 Molecular packing motifs in crystals. a) Herringbone packing (face-to-edge); b) lamellar motif, 1D π -stacking; c) lamellar motif, 2D π -stacking.

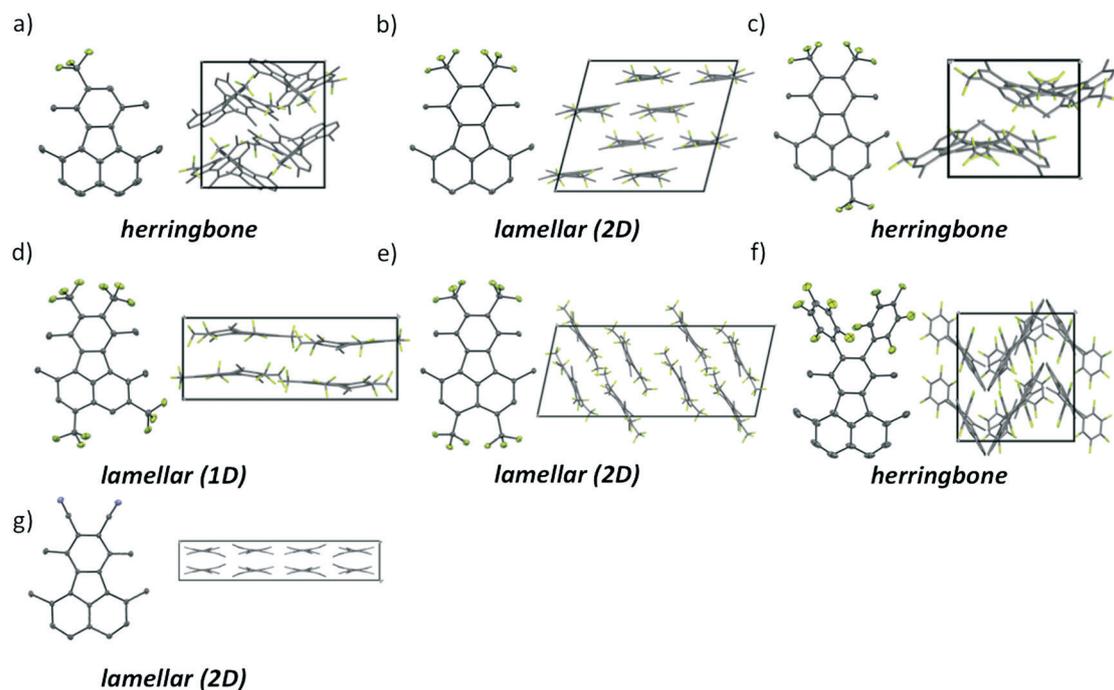


Fig. 4 Substituted fluoranthenes crystallized in this work. a) 1,6,7,10-Tetramethyl-8-(trifluoromethyl)fluoranthene (1); b) 1,6,7,10-tetramethyl-8,9-bis(trifluoromethyl)fluoranthene (2); c) 1,6,7,10-tetramethyl-3,8,9-tris(trifluoromethyl)fluoranthene (3); d) 1,6,7,10-tetramethyl-2,4,8,9-tetrakis(trifluoromethyl)fluoranthene (5); e) 1,6,7,10-tetramethyl-3,4,8,9-tetrakis(trifluoromethyl)fluoranthene (4); f) 1,6,7,10-tetramethyl-8,9-bis(perfluorophenyl)fluoranthene (6); g) 1,6,7,10-tetramethylfluoranthene-8,9-dicarbonitrile (7); accompanied by the view of the unit cell along the crystallographic *a* axis (1, 5, 6 and 7), *b* axis (2 and 4) and *c* axis (3), respectively.

intermolecular interactions, it is well worth investigating and discussing the molecular interactions specifically, as follows.^{24c}

Crystal structure of 1

1 crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit. Both molecules show short intermolecular C–H \cdots F contacts, the shortest being 2.32 Å for the *ortho*-H atom to one of the fluorine atoms of the trifluoromethyl group (Fig. 5). Two independent molecules of **1** form loosely stacked dimers (3.90–3.93 Å), engaging in an overall herringbone type arrangement. The structure is

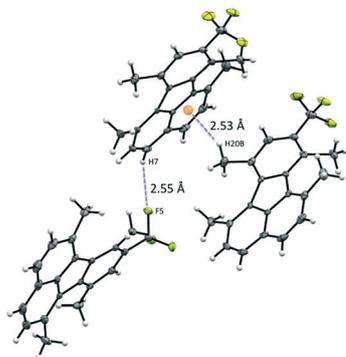


Fig. 5 Excerpt of the structure of **1** showing the shortest intermolecular C–H \cdots F contact and the shortest C–H \cdots π contact.

supported by around ten C–H \cdots F contacts in the range from 2.55–2.99 Å, most of them originating from the methyl groups of the naphthalene unit, and rather few C–H \cdots π contacts from the methyl groups of the six-membered ring in the short range of down to 2.53–3.04 Å.

Crystal structure of 2

2 crystallizes in monoclinic space group $I2/a$ and has an asymmetric unit that contains one independent molecule. **2** is distorted (C_2 -twist) while the trifluoromethyl groups in 8,9 position are slightly splayed. A look at the unit cell reveals a lamellar motif with 2D π -stacking, where adjacent molecules

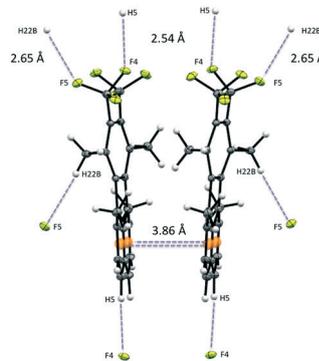


Fig. 6 Excerpt of the structure of **2** showing the shortest intermolecular C–H \cdots F contacts and π -stacking between dimers.

of 2 undergo π -stacking in a distance of 3.86 Å (centroid-to-centroid distance of the naphthalene units) by forming head-to-head dimers.

Geometrically, the lamellar π -stacking hampers the formation of C–H \cdots π contacts, only one short contact within a fluoranthene dimer, as a short contact within two dimers can be observed, ranging from 2.97–3.23 Å. Short inter- and intramolecular C–H \cdots F contacts are in the range of 2.41–2.65 Å, the shortest being the intermolecular C–H \cdots F contact from a methyl to a trifluoromethyl group (H22A–F5).

Crystal structure of 3

3 crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The additional trifluoromethyl group of C_1 -symmetric 3 is disordered at both possible *peri*-positions (3- and 4-position), due to symmetry with equal occupancy. The overall solid state packing is largely herringbone-like, which is supported by π -stacking (distance of 3.83 Å) of only one of the six-membered rings to the next ring of a neighbouring molecule. Various intramolecular C–H \cdots F contacts are present (2.35–2.76 Å), as well as intermolecular C–H \cdots F contacts (2.60–3.10 Å), which are longer on average and are almost exclusively originate from the two trifluoromethyl groups in *ortho* position, highlighting the importance of this motif for intermolecular and interlayer connectivity (Fig. 7).

The structure might be the most complex structure in this study and appears to be a “transition state” between herringbone packing and the formation of a layered, lamellar packing. Several probably slightly elongated C–H \cdots π contacts in the range of 2.9 Å are also observed.

Crystal structure of 4

The crystal system and space group of 4 are monoclinic and $P2_1/c$, respectively, with two independent molecules of 4 in the asymmetric unit. Like 2, 4 the unit cell reveals a lamellar motif with 2D π -stacking. However due to the shift in the arrangement, no significant short π -stacking interactions could be observed. Again this might be caused by the increased

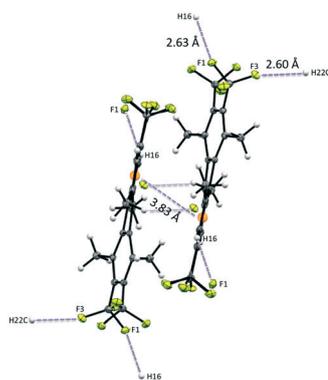


Fig. 7 Excerpt of the structure of 3 showing the shortest interlayer C–H \cdots F contacts and π -stacking between shifted dimers.

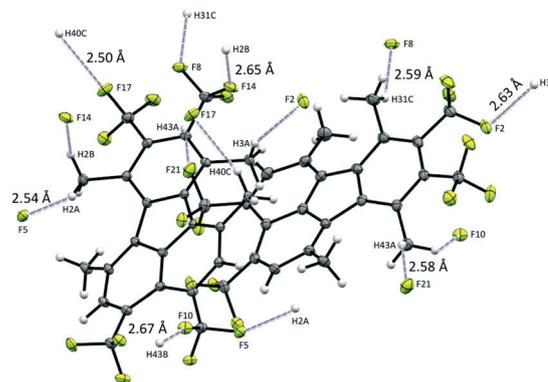


Fig. 8 Excerpt of the structure of 4, showing the C–H \cdots F contacts of the two independent molecules of the asymmetric unit.

sterical bulk of the substituents, prohibiting close encounters. Within the layers, more than ten short and unique intermolecular C–H \cdots F contacts (2.48–2.91 Å) are observed, almost all of them origination from the methyl groups of the naphthalene or benzene unit of the fluoranthene (Fig. 8).

A smaller number of longer interlayer C–H \cdots F contacts (2.53–2.95 Å) is noted as well in addition to few interlayer C–H \cdots π interactions in the range of (2.82–3.10 Å) originating from the hydrogen atoms of the methyl groups.

Crystal structure of 5

5 crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. 5 suffers from the increasing sterical demand of the four trifluoromethyl groups in addition to the four methyl groups at the scaffold, resulting in a severely twisted fluoranthene (*cf.* Fig. 2). Because of the alternating methyl and trifluoromethyl groups, a variability in intramolecular C–H \cdots F contacts must be present (2.29–2.66 Å).

The unit cell is consequently formed from four molecules of 5 engaging in two strands, giving rise to intermolecular C–H \cdots F contacts within the strands (2.59–2.82 Å) and between the strands (2.53–2.89 Å) (Fig. 9).

In contrast to the crystal structure of 3, all trifluoromethyl groups participate equally in hydrogen bonding. Interlayer π -stacking distances are greater than 4 Å (centroid-to-centroid distances), suggesting that neither π -stacking nor C–H \cdots π

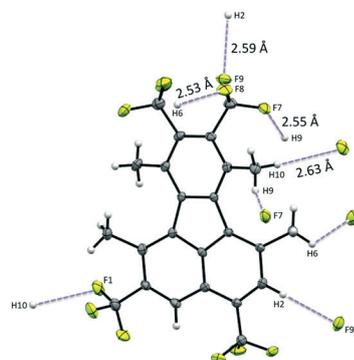


Fig. 9 Asymmetric unit of 5, showing the shortest C–H \cdots F contacts.

contacts account for the obtained solid state structure. It is possible, that both are inhibited by the sum of the rather large substituents along the rim of the fluoranthene 5.

Crystal structure of 6

6 is the only compound in this study that crystallizes in the orthorhombic space group *Pccn*. The asymmetric unit consists of one fluoranthene 6 with a significant C_2 -twist, while the pentafluorophenyl groups in 8,9 position are splayed. As expected the pentafluorophenyl rings are perpendicular to the mean fluoranthene plane. One pentafluorophenyl of the two exhibits a rotational disorder, which was treated accordingly and will be therefore excluded from the following discussion. Overall, the assembly forms a classic herringbone structure, where the fluorocarbon and hydrocarbon moieties are separate. The hydrocarbon part forms the predominant herringbone patterns C–H $\cdots\pi$ contacts of around 3 Å. Additionally C–H \cdots F contacts in the range of 2.40–3.06 Å can be observed, connecting the sections.

Crystal structure of 7

One of the fluoranthenes in this study that is twisted the most (besides the sterically highly congested 5) is 7 with an angle of 18 degrees (angle between the plane of the naphthalene subunit and the plane of the benzene subunit). 7 crystallizes, like 2, in the monoclinic space group *I2/a* with one molecule in the asymmetric unit. The unit cell clearly reveals a lamellar 2D π -stacking arrangement. The structure appears loosely packed by weak π - π interactions in the range 4.04–4.07 Å and few C–H $\cdots\pi$ contacts within a layer.

Conclusions

We could show that depending on the substituent and the pattern of substitution, solid state structures of the fluoranthene scaffold can be potentially engineered precisely, if it would be possible to take all of the additive interactions observed herein into account. A variety of accessible motifs were presented, depending on the position of the trifluoromethyl group or depending on the chosen substituent in the 8,9 position. We achieved this using fluorinated (and non-fluorinated) strong electron withdrawing groups, most importantly the trifluoromethyl group, which had a larger influence on the overall crystal packing. This is of special importance, since increasing electron affinities is the most common approach to obtain strong performance and potentially air stable materials for high performance n-type and ambipolar materials and devices. Such devices rely on close and extensive intermolecular overlap of the molecules, which is on the other hand directly hampered by the introduction of substituents as shown in this study. Besides the material-oriented engineering aspect, the absence of strong directional interactions in the crystals of the compounds permitted us to observe and discuss weak interactions, such as C–H $\cdots\pi$ and C–H \cdots F interactions that apparently govern the

solid-state alignment of these systems to an extent and will contribute to the unravelling of the structure property relationship in these systems.

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