Synthesis and structure of 4,4′-bis(2,3,4,5,6-pentafluorostyryl)stilbene, a self-assembling J aggregate based on aryl–fluoroaryl interactions

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Received (in Cambridge, UK) 2nd January 2001, Accepted 6th February 2001
First published as an Advance Article on the web 20th February 2001

The synthesis and characterisation of 4,4′-bis(2,3,4,5,6-pentafluorostyryl)stilbene is described; this molecule forms a J aggregate by self-assembly based on aryl–fluoroaryl interactions.

The molecular organisation of conjugated organic materials is important in relation to their potential for application as the active components of electronic and optoelectronic devices;[1] in particular, the structures of aggregates of organic materials can have profound effects on their optical properties.[2] Detailed studies of crystalline oligomers often aid understanding of the behaviour of polymeric materials; for example, distyrylbenzene (DSB) has been studied as a model for poly(phenylene vinylene) (PPV)[3] and self-assembling systems are particularly attractive since they have considerable processing advantages in device construction. Hydrogen bonding,[4] π-stacking[5] and arene–perfluoroarene interactions[6] have been used as organisational motifs in the design and synthesis of self-organising systems. The latter phenomenon was described by Patrick and Prosser in 1960 who demonstrated that benzene (mp 5.5 °C) and hexafluorobenzene (mp 4 °C) form a stable 1 : 1 complex (mp 24 °C),[7] consisting of a face-to-face stack of alternating benzene and hexafluorobenzene molecules. The origin for this stable arrangement has generally been thought to lie in the quadrupolar interaction between the two molecules, they both have large molecular quadrupole moments but of opposite sign;[8] however recent work suggests that the effect can be ascribed largely to van der Waals interactions.[9] Coates and Grubbs *et al.* have demonstrated that these non-covalent interactions can be used in substituted stilbenes and DSBs for self-assembly into structures aligned for photochemically induced [2+2] reactions in the solid state, while Bazan *et al.* have investigated the effect of different fluorine substitution patterns on the molecular packing of DSBs.[10]

We became interested in the possibility of making self-organising J aggregates of large aromatic chromophores suitable for optoelectronic applications using the directing effect of phenyl–pentafluorophenyl interactions. For this purpose the oligo-phenylenevinylene, distyrylstilbene, was the molecule of choice. J aggregates are characterised by a narrow and intense absorption band that shows a bathochromic shift relative to the single isolated molecule. This is a result of coherent excitonic coupling of the molecules in the solid state. Transitions to and from the bottom of the excitonic band are consequently allowed and fluorescence, as well as absorption, is expected to be intense and narrow. Jelley was one of the first to observe this strong absorption for the case of cyanine dyes (hence the name).[11] One possible arrangement for J aggregates is the simple ‘brickwall motif’ in which each ‘brick’, or molecule, is situated over the gap between the bricks in the row below (see Fig. 1a).[12] Here we report the synthesis and molecular packing of 4,4′-bis(2,3,4,5,6-pentafluorostyryl)stilbene **1**, which is accessible by the route summarised in Scheme 1 and can be processed by sublimation or from solution. The synthesis involves McMurry coupling of *p*-tolylaldehyde **2** to

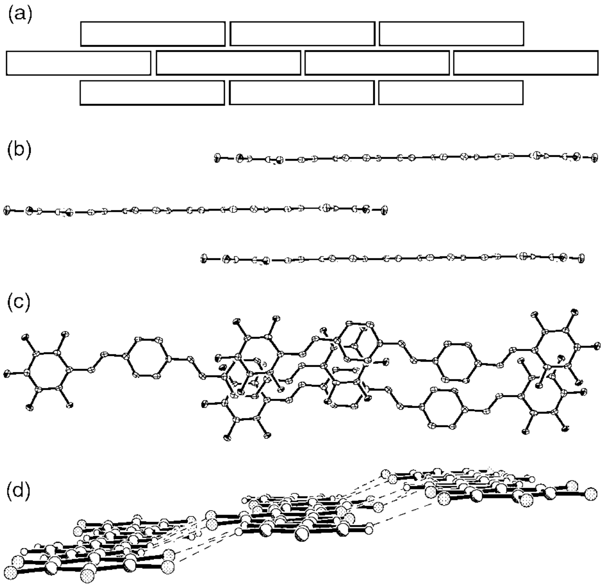
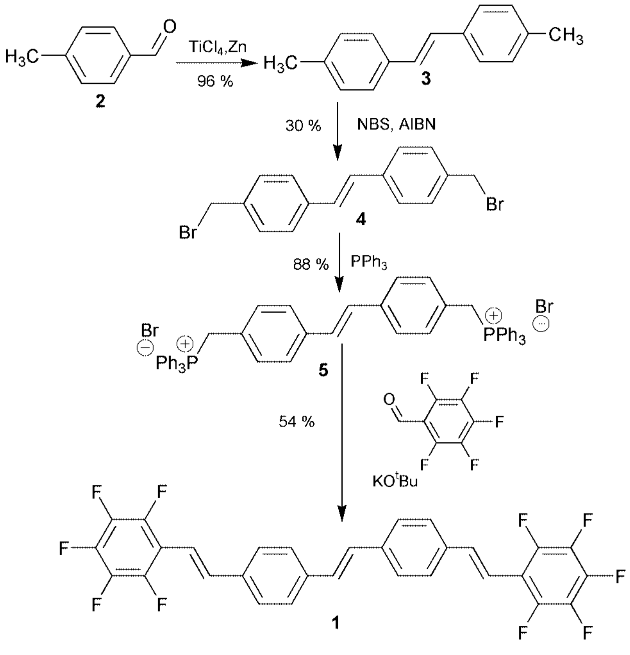


Fig. 1 a) ‘Brickwall’ motif, b) compound **1** side view, c) compound **1** top view, d) compound **1** edge on view.



Scheme 1 Route for the synthesis of 4,4′-bis(2,3,4,5,6-pentafluorostyryl)-stilbene.

give (*E*)-4,4′-dimethylstilbene **3**. The methyl groups were brominated with NBS and the bromine substituted with triphenylphosphine yielding the bis(phosphonium) salt **5**. A Wittig reaction with two equivalents of pentafluorobenzaldehyde afforded **1**, which was purified by sublimation.

The ^{1}H NMR spectrum shows three resonances for olefinic protons; a singlet at δ 7.17 and two doublets at δ 7.00 and 7.43 with coupling constants of 16.5 Hz typical for a *trans* vinylene configuration. The ^{19}F NMR spectrum confirms that only one isomer was formed since only one set of three resonances was observed (δ −143.81, −157.47, −163.75).[13] Identical crystals of **1** were grown by sublimation and from solution in stilbene at 170 °C indicating that there is one predominant form of aggregation. The crystal structure† shows that all double bonds are *trans*. The centre of each molecule is an inversion centre so that only half the molecule is crystallographically unique. The fluorinated and the non-fluorinated rings are twisted very slightly with respect to each other (2.2°) and the two central rings are twisted with an angle of 3°. This almost planar arrangement allows strong π–π interactions.

The molecules aggregate in a simple brickwall motif in which each molecule overlaps with two halves of neighbouring molecules in the row below and above it (Fig. 1a and b). Thereby, each central aromatic ring is sandwiched between two terminal fluorinated aromatic rings of neighbouring molecules and *vice versa*. The distance between the mean planes of all the atoms in the molecules is 3.41Å. However, the situation is further complicated by the fact that there is some lateral slippage between the aromatic rings which results in successive rows of the ‘brickwall’ being slightly offset with respect to each other; analogous structures have been reported and described as ‘molecular staircases’.[14] This slippage is not equally distributed between all aromatic rings but the molecules are paired in the sense that one ring overlaps more with its fluorinated counterpart above than the one below or *vice versa* (Fig. 1c). As a consequence of this the two olefinic carbons of the central molecule in Fig. 1c are closer to their counterparts below (3.659 Å) than the one above (3.869 Å).

In addition to the face-to-face π-stacking the molecular packing is associated with intermolecular C–F···H–C interactions.[13] Four such interactions are observed on each ring resulting in 16 per molecule. H···F distances derived from this X-ray study are 2.390, 2.467, 2.480 and 2.595 Å, derived using the neutron normalised C–H distance of 1.083 Å. The corresponding C–H···F angles are 159.4°, 157.6°, 132.1° and 122.9°. The distance between the terminal fluorine atoms in the 4 positions of edge-to-edge neighbours is short (2.676 Å).

The packing of **1** is analogous to that of 2,3,4,5,6-pentafluorostilbene (PFS); the densities are very similar (1.635 g cm^{-3} for **1**; 1.641 g cm^{-3} for PFS). Molecules of PFS in crystals are also paired, but the pairing is less obvious than in the present case since the distance between olefinic carbons of neighbouring PFS molecules is quoted as 3.700 Å for one side and 3.707 Å for the other. Grubbs and Coates have shown photochemically induced [2+2] reactions in crystals of PFS.[10] We expected a similar topochemical reaction for the olefinic bonds in **1** which are separated by 3.659 Å and observed that UV irradiation of a thin film of **1** resulted in a colour change from yellow to almost colourless consistent with the loss of conjugation. ^{1}H NMR spectroscopy shows a new signal at δ 4.88 for cyclobutane hydrogens and the ^{19}F NMR spectrum shows three new resonances at δ −142.11, −156.11 and −162.98 with concomitant reduction in the intensity of the initial signals at δ −143.81, −157.47, −163.75.

The work reported here provides strong evidence for the value and power of fluoroaryl–aryl face-to-face interactions as a design motif for self-assembling systems. The electronic and optical properties of **1** in the solid state are the subject of ongoing investigations.

We thank the European Commission HPRT Network LAMINATE (Contract No HPRN-CT-2000-00135) for financial support and Professor T. B. Marder (Durham) for his interest and helpful comments.

Notes and references

† *Crystallographic data for* **1**. $C_{30}H_{14}F_{10}$, M_r = 564, space group $P\bar{1}$, a = 6.0624, b = 7.4468, c = 13.0565 Å, α = 78.442, β = 82.972, γ = 85.693°, U = 572.378 Å^3, T = 100 K, Z = 1, μ(Mo-Kα) = 0.152 mm^{-1}, 2604 reflections measured, 2604 unique (R_{int} = 0.0797) which were used in all calculations and 1486 greater than $2\sigma(I)$. The final $R(F)$ was 0.0853 ($I > 2\sigma(I)$ data) and the $wR(F^2)$ was 0.1885 (all data). The relatively large R factor is due to the small crystals available, 0.20 × 0.10 × 0.05 mm^3. CCDC 156709. See http://www.rsc.org/suppdata/cc/b1/b100002k/ for crystallographic files in .cif formats.

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Typeset and printed by Black Bear Press Limited, Cambridge, England