The synthesis of mono- and diacetyl-9H-fluorenes. Reactivity and selectivity in the Lewis acid catalyzed Friedel-Crafts acetylation of 9H-fluorene

Salam J.J. Titinchi, Fadhil S. Kamounah, Hanna S. Abbo, and Ole Hammerich

Abstract
Friedel-Crafts acetylation of 9H-fluorene is an effective route for the preparation of mono- and diacetyl-9H-fluorenes. Using acetylchloride as the reagent and aluminum chloride as the Lewis acid catalyst the effect of the solvent polarity, the temperature, the reaction time and the mode of addition (Perrier or Bouveault) on the reactivity-selectivity pattern was investigated. The results showed that monoacetylation of 9H-fluorene in chloroalkanes and nitromethane gives mixtures of 2-acetyl- and 4-acetyl-9H-fluorene with the former dominating. In addition to these two isomers, 2,7-diacetyl-9H-fluorene was obtained in 5-11 % yield when carbon disulfide was used as the solvent. Acetylation of 9H-fluorene in dichloroethane and carbon disulfide, using an excess of acetyl chloride and aluminum chloride at reflux temperature, gives 2,7-diacetyl-9H-fluorene exclusively in high yields (> 97%). Attempts to carry out diacetylation in nitromethane on the other hand resulted in the formation of monoacetyl derivatives only. The ketones obtained were isolated and identified by various physico-chemical techniques. The 1H NMR spectrum of 4-acetyl-9H-fluorene is reported for the first time. Values of the total energies and the Gibbs free energies at 298K for 9H-fluorene, the five isomeric monoacetyl-9H-fluorenes and the four σ-complexes leading to 1-, 2-, 3- and 4-acetyl-9H-fluorene, respectively, were computed at the DFT B3LYP 6-31G** level of theory. The data serve as a basis for the discussion of the reactivity-selectivity pattern observed and it is concluded that the distribution of products is partly kinetically controlled.

Keywords: Friedel-Crafts acetylation; 9H-fluorene; 4-acetyl-9H-fluorene; reactivity and selectivity; kinetic and thermodynamic control; DFT B3LYP 6-31G** calculations
Introduction

Friedel-Crafts acylations are classic reactions in organic chemistry and are still of great importance in the synthesis of aromatic ketones. The reactions proceed generally with high selectivity and without rearrangements taking place although isomerizations have occasionally been observed.

Fluorene-based aromatic ketones are of increasing interest as building blocks for the production of drugs and pharmaceuticals and as fine chemicals of industrial relevance including applications in the production of thermosetting plastics and lubricating materials. In addition, fluorene-based polymers and copolymers are of interest owing to their unusual optical and electrical properties and are for that reason commonly used in organic light-emitting diodes, flat panel displays and in solar cells. The preparation of acetyl-9H-fluorenes by Friedel-Crafts acetylation is attractive in this type of work.

In the nineteen thirties Dziewonski and Schnayder reported that the Friedel-Crafts acetylation of 9H-fluorene (Fl) using acetylchloride (AcCl) and AlCl3 in carbon disulfide gave 2-acetyl-9H-fluorene (2-AcFl) and 2,7-diacetyl-9H-fluorene (2,7-DAcFl). The structures are shown in Scheme 1. Brown and Marino later found that acetylation using instead AlEt3 and AcCl in 1,2-dichloroethane (DCE) gave only 2-AcFl. Sulzberg and Cotter have reported that the acetylation of Fl using acetic anhydride and AlCl3 in DCE gives 2-AcFl and 2,7-DAcFl, while Hodson and Batchelor under similar conditions found the reaction to give only 2,7-DAcFl, which was subsequently oxidized to fluorenone-2,7-dicarboxylic acid. Acylation of Fl with different acylating agents in the presence of FeCl3 or ZnCl2 gave the 2-acyl-9H-fluorenes as the major products, in addition to the formation of small amounts of 4-acyl-, 2,7-diacyl-9H-fluorenes and 2-alkyl-9H-fluorenes, the latter being formed by elimination of CO. Acetylation of Fl with AcCl and AlCl3 at 0 °C, or with various carboxylic acids in trifluoroacetic acid, gave 2-acyl-9H-fluorenes in 34-96% yield.

![Scheme 1](image)

**Scheme 1**

9H-Fl : \( R_2 = R_4 = R_7 = H \)

2-AcFl : \( R_2 = Ac, R_4 = R_7 = H \)

4-AcFl : \( R_2 = R_7 = H, R_4 = Ac \)

2,7-DAcFl : \( R_2 = R_7 = Ac, R_4 = H \)
Although the reaction has previously been studied in some detail as it appears above it is not clear to which extent parameters, such as the solvent polarity, the temperature, the reaction time and the mode of addition (Perrier or Bouveault), affect the yields and the selectivity of the reaction. For that reason and in view of the importance of the reaction we have undertaken a study in which these parameters were varied systematically with the aim of finding the best possible conditions for the direct synthesis of 9H-fluorene mono- and diketones (Scheme 2). We also report the $^1$H NMR spectrum of 4-AcFl, which to the best of our knowledge is presently not available through the literature.

Scheme 2

Results and Discussion

The effect of the solvent
To investigate the solvent dependence, a variety of solvents with different polarities were used as detailed below (Figure 1 and Table 1). In terms of reactivity, the results show that DCE is the best solvent for acetylations carried out to a high conversion (>95 %) independent of other reaction details. On the other hand, using a polar solvent, here nitromethane, the conversion was only low to moderate (~9 - 38 %) owing to the additional formation of dark polymeric materials. In the polar solvent the solutions are considered to be homogeneous and the solvent dissolves and solvates not only the AlCl$_3$, but also the [CH$_3$CO$^+$·AlCl$_3$X$^-$] complex and usually also the AlCl$_3$ complex of the resulting ketones. In chloroform, the reaction was slow owing to the low ability of this solvent to dissolve AlCl$_3$. However, the [CH$_3$CO$^+$·AlCl$_3$X$^-$] complex is soluble and this causes the formation of polymeric material in high yield, which in turn affects the yield of the ketones.$^{15}$ As a result of this, polymerization is the dominating reaction in chloroform under the conditions of the experiments in agreement with previous reports that polymerization of 9H-fluorene occurs readily in solution in the presence of free AlCl$_3$.$^{16,17}$ When acetylation was carried out in the non-polar carbon disulfide the conversion was moderate to high depending on the temperature and reaction time without notable formation of polymeric materials.
Figure 1. The effect of solvent on the conversion and selectivity of the Friedel-Crafts acetylation of Fl at 25°C. The reaction time was 3 hours.

In terms of the selectivity, 2-AcFl was the predominant isomer resulting from monoacetylation in most solvents except carbon disulfide, where also 2,7-DAcFl was detected in appreciable amounts (~5-13 %). In the non-polar solvents, neither Fl nor AlCl₃, or the [CH₃CO⁺·AlCl₃X⁻] complex, are appreciably soluble and the reaction is largely heterogeneous. This facilitates the second acetylation step owing to the free AlCl₃. The results clearly show that polarity of the solvents influences both the reactivity and the positional selectivity.
**Table 1. Results of the Friedel-Crafts acetylation of Fl using the Perrier addition procedure**

| Solvent         | Temp. (°C) | Reaction time (h) | Overall yield (%) | Product distribution (%) |
|-----------------|------------|-------------------|-------------------|--------------------------|
|                 |            |                   |                   | 2-AcFl 4-AcFl 2,7-DAcFl |
| CHCl₃           | 25         | 1.5               | 0.9               | 100.0 --- --- |
|                 | 25         | 3                 | 1.1               | 100.0 --- --- |
|                 | 45         | 1.5               | 0.2               | 100.0 --- --- |
|                 | reflux     | 23                | 5.8               | 100.0 --- --- |
| ClCH₂CH₂Cl      | 25         | 1.5               | 55.8              | 98.2 1.8 --- |
|                 | 25         | 6                 | 68.4              | 99.1 0.9 --- |
|                 | 25         | 12                | 79.4              | 99.2 0.8 --- |
|                 | 25         | 24                | 82.1              | 99.0 1.0 --- |
|                 | 0          | 3                 | 58.2              | 98.6 1.4 --- |
|                 | 25         | 3                 | 61.7              | 98.5 1.5 --- |
|                 | 45         | 3                 | 56.7              | 99.3 0.7 --- |
|                 | reflux     | 3                 | 81.6              | 98.7 1.3 --- |
|                 | reflux     | 23                | 96.1              | 99.0 1.0 --- |
|                 | reflux     | 23ᵇ               | 92.1              | --- 100.0 |
| Cl₂CHCHCl₂      | 25         | 3                 | 56.4              | 98.8 1.2 --- |
|                 | 45         | 3                 | 60.5              | 98.8 1.2 --- |
|                 | reflux     | 3                 | 71.5              | 99.3 0.8 --- |
|                 | reflux     | 23                | 77.8              | 99.2 0.8 --- |
| CS₂             | 25         | 3                 | 49.4              | 94.2 0.7 5.1 |
|                 | 45         | 3                 | 63.4              | 87.6 1.0 12.5 |
|                 | reflux     | 23                | 61.1              | 90.7 0.9 8.8 |
|                 | reflux     | 48                | 86.9              | 88.1 0.7 11.2 |
|                 | reflux     | 23ᵇ               | 67.2              | 2.9  --- 97.2 |
| CH₃NO₂          | 0          | 1.5               | 38.3              | 99.6 0.4 --- |
|                 | 25         | 3                 | 21.2              | 100.0 --- --- |
|                 | 45         | 3                 | 19.8              | 100.0 --- --- |
|                 | reflux     | 3                 | 8.9               | 97.7 2.3 --- |
|                 | reflux     | 23                | 8.7               | 98.0 2.5 --- |
|                 | reflux     | 23ᵇ               | 10.8              | 99.3 0.7 --- |

ᵃThe Fl:AcCl:AlCl₃ molar ratio was 1:1:1.ᵇThe Fl:AcCl:AlCl₃ molar ratio was 1:4:4.
The effect of the temperature
To examine the role of the temperature on monoacetylation, four experiments were carried out using DCE as the solvent at $t = 0, 25, 45$ °C and at the boiling point of the solvent, 83 °C. The reaction time was 3 hours. The reactivity and product selectivity were unaffected by a temperature rise from 0 to 45 °C as seen in Fig. 2. However, the reactivity increased significantly when the temperature was raised to 83 °C without affecting the selectivity. The same pattern was found when the reaction was carried out in 1,1,2,2-tetrachloroethane. In carbon disulfide and chloroform it was observed that the reactivity increased by increasing the reaction temperature, whereas the reactivity decreased on increasing the reaction temperature in nitromethane. This may be caused by the formation of polymeric material at low temperature (0 °C) compared with the higher temperatures. On the other hand, the selectivity was not affected by varying the reaction temperature.

![Bar Chart](image)

**Figure 2.** The effect of temperature on the conversion and selectivity of Friedel-Crafts acetylation of Fl in DCE. The reaction time was 3 hours.

The effect of the mode of addition
Perrier and Bouveault modes of addition were used to study the effect of addition on the reactivity and selectivity in two different solvents, DCE and nitromethane. In the Perrier addition
procedure the substrate was added to the preformed \([\text{CH}_3\text{CO}^+\cdot\text{AlCl}_3\text{X}^-]\) complex, whereas the Bouveault addition procedure involves addition of AcCl to a premixed solution of AlCl\(_3\) and the substrate. It was found that the mode of addition had no significant effect on either the conversion, the selectivity or the isomer distribution (Table 2).

Table 2. The effect of the mode of addition on the conversion and selectivity of the acetylation of Fl at 0°C

| Solvent   | Reaction time | Mode of addition | Conversion (%) | Product distribution (%) |
|-----------|---------------|------------------|---------------|-------------------------|
|           |               |                  |               | 2-AcFl | 4-AcFl |
| ClCH\(_2\)CH\(_2\)Cl | 3 h          | Perrier          | 58.2          | 98.6   | 1.4    |
|           | 3 h          | Bouveault        | 58.6          | 97.7   | 2.2    |
| CH\(_3\)NO\(_2\) | 1.5 h        | Perrier          | 38.3          | 99.6   | 0.4    |
|           | 1.5 h        | Bouveault        | 41.6          | 99.8   | 0.2    |

The effect of the molar ratio of the reactants, Fl:AcCl:AlCl\(_3\)
A 1:1:1 molar ratio results as a rule in the formation of 2-AcFl mainly in all solvent with a small amount of 4-AcFl being detected as well. As mentioned in the previous section 2,7-DAcFl was formed only in carbon disulfide. When the reaction was performed in DCE and carbon disulfide with a large excess of AcCl and AlCl\(_3\) (1:4:4 molar ratio) at the reflux temperature, 2,7-DAcFl was formed as the main product and in a good yield, while in nitromethane under the same conditions only 2-AcFl and 4-AcFl were formed, and in low yields as mentioned above. However the yield and the selectivity did not differ significantly from the results obtained when a 1:1:1 molar ratio was used (see Table 1).

The effect of the reaction time
The reaction time was found to affect the conversion, not unexpectedly, but not the selectivity. A representative example (DCE, 25 °C) is shown in Fig. 3. It is seen that the conversion increased from 56 to 68 % as the reaction time increased from 1.5 to 6 hours. A further increase in conversion (~79 %) was achieved after 12 hours reaction time after which no real effect was observed. A similar effect of the reaction time was observed for the other solvents except for nitromethane (see Table 1).
Reactivity and selectivity
Some insight into the reactivity-selectivity pattern of the reaction was gained through a series of DFT calculations carried out at the B3LYP 6-31G** level of theory. The calculations included Fl, the five monoacetyl-9H-fluorene isomers and the four σ-complexes leading eventually to 1-, 2-, 3- and 4-acetyl-9H-fluorene, respectively. The results are shown in Table 3 (monoacetyl-9H-fluorenes) and Table 4 (σ-complexes) and include models of the fully optimized structures together with selected characteristic geometric properties and values of the total energies, $E$, and the Gibbs free energies at 298 K, $G_{298}$. Only structures and data for the conformers with the most favorable orientation of the acetyl group are included in the Table.

Inspection of the data in Table 3 immediately reveals that the major product of acetylation, 2-AcFl, is indeed also the most stable of the five isomers the stability of which decreases in the order 2 > 3 > 1 > 4 > 9. The relatively low stability of 4-AcFl is caused by steric interactions between the acetyl substituent and the C-5 proton which forces the carbonyl group out of the plane defined by the benzene ring to which it is attached. The dihedral C=C-C=O angle for this isomer is 20.4° in comparison to the 0° characteristic for the all-planar geometries of the 1-, 2- and 3-isomers. For completeness, it should be noticed also that the acetyl group in 9-AcFl was found to be almost perpendicular to the fluorene ring, in agreement with infrared studies and single crystal structures of analogous compounds.\textsuperscript{18,19}
### Table 3. Total energies, $E$, and Gibbs free energies at 298K, $G_{298}$, for 9H-fluorene and the five isomeric monoacetyl-9H-fluorenes

| Optimized structure (DFT B3LYP 6-31G**) | Total energy $E$ (a.u.) | $G_{298}$ (a.u.) | $G_{298}$ relative to 2-AcFl (kJ mol$^{-1}$) | C=C-C=O dihedral angle$^a$ (degrees) |
|----------------------------------------|------------------------|-----------------|---------------------------------|----------------------------------|
| 9H-Fl                                  | -501.43868             | -501.28463      | –                               | –                                |
| 1-AcFl                                 | -654.08860             | -653.90208      | 3.3                             | 0                                |
| 2-AcFl                                 | -654.08970             | -653.90335      | 0                               | 0                                |
| 3-AcFl                                 | -654.08892             | -653.90265      | 1.8                             | 0                                |
| 4-AcFl                                 | -654.08126             | -653.89493      | 22.1                            | 20.4                             |
| 9-AcFl                                 | -654.080716            | -653.885349     | 47.3                            | –                                |

$^a$Angle between the carbonyl group and the benzene ring to which it is attached.
Table 4. Total energies, $E$, and Gibbs free energies at 298K, $G_{298}$, for the four $\sigma$-complexes leading to the 1-, 2-, 3- and 4-acetyl-9H-fluorene

| Optimized structure (DFT B3LYP 6-31G**) | Total energy $E$ (a.u.) | $G_{298}$ (a.u.) | $G_{298}$ relative to $\sigma$-2-AcFl (kJ mol$^{-1}$) | $\theta^a$ (degrees) |
|----------------------------------------|------------------------|-----------------|-------------------------------------|--------------------|
| $\sigma$-1-AcFl                         | -654.40310             | -654.20836      | 41.4                                 | 149.6              |
| $\sigma$-2-AcFl                         | -654.41977             | -654.22413      | 0                                    | 126.0              |
| $\sigma$-3-AcFl                         | -654.40517             | -654.21072      | 35.2                                 | 146.4              |
| $\sigma$-4-AcFl                         | -654.41676             | -654.22080      | 8.7                                  | 139.8              |

$^a$The angle between the H-atom at the position of attack and the carbon para to this position (see Scheme 3, left).

The fact that 4-AcFl is less stable than the 1- and 3-isomers is of particular interest in the present context and from the relative stabilities of these three acetyl derivatives alone it might have been expected that the 1- and 3-isomers would have been present in the product mixtures, in addition to the 2- and 4-isomers, in yields exceeding that of 4-AcFl. This, however, was not the case as the 1- and 3-isomers were not detected. In other words, from a thermodynamic point of view, there is an over-representation of 4-AcFl in the product mixtures.

The trend observed for the intermediate $\sigma$-complexes is different. It is seen from Table 4 that the stability decreases in the order $2 > 4 > 3 > 1$ reflecting that in the $\sigma$-complexes, in which the acetyl group is bound to a non-aromatic carbon, the steric interactions that is the origin of the
relatively low stability of 4-AcFl are absent. The decreasing stability in passing from \( \sigma\-2\-\text{AcFl} \) to \( \sigma\-1\-\text{AcFl} \) is paralleled by an increase in the angle, \( \theta \), between the H-atom at the position of attack and the carbon \textit{para} to this position (Scheme 3, left). The lower limit of \( \theta \) is close to the value for a hypothetical structure including a tetrahedral aliphatic carbon for which \( \theta \) equals \( 180^\circ - 109.47/2 = 125.3^\circ \). In comparison, the value of \( \theta \) resulting from a DFT B3LYP 6-31G** calculation for a model compound, 1-cyclohexa-2,5-dienyl-ethanone, is 130.0° (Scheme 3, middle). The higher limit of \( \theta \) obviously corresponds to an H-atom attached to an unperturbed benzene ring, that is \( 180^\circ \). (Scheme 3, right). The \( \theta \)-values in Table 4 for the \( \sigma \)-complexes range from 126.0° for \( \sigma\-2\-\text{AcFl} \) to 149.6° for \( \sigma\-1\-\text{AcFl} \) and thus, the theoretical data are in agreement with the expectation that the structure of the \( \sigma \)-complex becomes more transition-state-like the less stable it is. It should be noticed also that the \( \theta \)-value for the most stable \( \sigma \)-complex, \( \sigma\-2\-\text{AcFl} \), is close to that for a fully relaxed saturated aliphatic carbon.

Scheme 3

The relative energies of the \( \sigma \)-complexes agree well with the observed product distribution as the observed yields were found to decrease in the same order \( 2 > 4 >> 3 \) and 1) indicating that the acetylation process is, at least partly, under kinetic control.

The theoretical data in Table 3 do not include contributions from solvation or from the presence of counter ions and are for that reason not directly applicable in a detailed discussion of the reaction pathway. Still the data indicate, as consequence of the relatively low stability of 4-AcFl, that the back reaction leading to the re-formation of the starting materials is likely to proceed at an appreciable rate and therefore that the formation of 4-AcFl is a reversible process. The question of the reversibility of the acetylation of aromatic hydrocarbons has been addressed recently by Agranat and co-workers\(^{20}\) in a study of the acetylation of phenanthrene in polyphosphoric acid (PPA). It was found, for instance, that both the 2- and the 9-isomer when treated with PPA were converted to a mixture of isomers showing that the acetylation in those cases is indeed a reversible process. Similarly, it might be expected that 1-AcFl, 3-AcFl and 4-AcFl would be converted to mixtures of isomers with 2-AcFl dominating if subjected to the conditions of our experiments. These and other kinetic and mechanistic aspects of the acetylation of 9\( H \)-fluorene are now under investigation.

Discussions of reactivity-selectivity often include the charge density of the substrate as an important parameter. The charge densities obtained for Fl by the DFT calculations are shown in Scheme 4 and are seen to decrease (numerically) in the order C-9 > C-1 > C-4 > C-3 > C-2.
Thus, by comparison of the data for the four aromatic carbons with the relative yields obtained it is obvious that the charge densities at the aromatic carbons alone cannot be used to predict the selectivity of the acetylation of Fl. However, the relatively high charge density observed at C-4 (-0.128) may contribute to stabilizing the transition-state leading to $\sigma$-4-AcFl and hence to a rate enhancement that may explain the presence of 4-AcFl in the reaction mixtures.

Scheme 4

Experimental Section

General Procedures. The identity of each component of an acetylation product mixture was established by comparison the GLC retention time of each component with that of an authentic pure material recorded under identical conditions. All the synthesized acetyl-9H-fluorenes showed satisfactory elemental analyses.

Apparatus. GLC analyses were carried out with a Pye Unicam 204 chromatograph equipped with flame ionization detector. A stainless steel column was used and packed with SE30(10) on acid-washed Chromosorb W (80-100 mesh) (2m x 2.2mm i.d.). Nitrogen (flow rate 15 lb in$^2$/min) was used as carrier gas at 250 °C. Mass response towards the different compounds was determined and appropriate corrections were applied. Elemental analyses were carried out in Alfred Bernhard Mikroanalytisches Laboratorium, Germany. IR spectra were measured as KBr discs on a Pye Unicam SP3-300 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker 100 MHz for solutions in deuterated chloroform using tetramethylsilane as an internal standard.

Materials. 9H-Fluorene (99%), aluminum chloride anhydrous, acetyl chloride were from Aldrich, chloroform, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane, hydrochloric acid from Merck, carbon disulphide and nitromethane from Fluka. Silica gel used for column chromatography was of type 230-400 mesh ASTM and the preparative T.L.C (silica gel P.L.C) size 20 x 40 cm thickness 2.0 mm from Merck. Petroleum ether and benzene were from RDH.
Sodium hydroxide was from BDH. All solvents used were of analytical purity and were dried over anhydrous calcium chloride or sodium sulfate prior to use in the acetylation reactions.

**General acetylation procedure**

The Friedel-Crafts acetylations were carried out in a three-necked round-bottomed flask placed in oil bath fitted with a dropping funnel, a thermometer and a reflux condenser attached with a calcium chloride absorption trap. Equimolar quantities of the acetyl chloride and anhydrous aluminum chloride in the dry solvent (20 ml) were brought together under the Perrier addition (final addition of the hydrocarbon to the acetylation agent). A stoichiometric amount of 9H-fluorene in the same solvent (20 ml) was added drop wise over a period of 5 min to the stirred reaction mixture at the desired temperature. Stirring was continued at the same temperature for the total time shown in the Tables. The mixture was then added to an excess of crushed ice and 3M HCl. The organic phase was separated and the water phase was washed with the organic solvent. The combined organic phases were then washed with water (5 x 50 ml), dried with anhydrous sodium sulfate and finally the solvent was removed at reduced pressure using a rotary evaporator. When nitromethane was used as the solvent, the organic layer was washed with (2 x 100 ml) of 3M NaOH instead of water. The viscous residue was dissolved in benzene and passed through a short column of silica gel to remove any polymeric material. The benzene was removed at reduced pressure and the residue analyzed quantitatively by GLC.

**Synthesis of 2-Acetyl-9H-fluorene (2-AcFl).** To a stirred solution of AcCl (0.392 g; 0.005 mol) and AlCl$_3$ (0.666 g; 0.005 mol) in DCE (20 ml), 9H-fluorene (0.83 g; 0.005 mol) in the same solvent (20 ml) was added drop wise over 5 min and the mixture was stirred at r.t. for 1 h and then refluxed for another 23 h. At the end of the reaction time, the resulting mixture was cooled and added to a mixture of conc. HCl and ice. The dark brown-yellow solid obtained was chromatographed over a short column of silica gel and eluted first with petroleum ether to remove any unreacted hydrocarbon and then with benzene which upon concentration gave the white needle-like crystals of 2-acetyl-9H-fluorene (0.96 g, 92.3% yield), m.p. 131-132°C (Lit.$^{14}$ m.p.: 132 °C). $\nu_{\text{max}}$ (neat) 1676 (C=O) cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 2.65 (s, 3H, CH$_3$CO), 3.88, 2H, CH$_2$), 8.08 (m, 1H, H-1), 7.22-7.88 (m, 6H, aromatic H).

**Synthesis of 4-Acetyl-9H-fluorene (4-AcFl).** To a stirred solution of AcCl (0.785 g; 0.01 mol) and AlCl$_3$ (1.33 g; 0.01 mol) in DCE (20 ml), 9H-fluorene (1.66 g; 0.01 mol) in the same solvent (20 ml) was added drop wise over 5 minutes. The mixture was stirred at 0 °C for 3 h. The dark brown oil obtained was chromatographed over silica gel/petroleum ether first to remove the remaining starting hydrocarbon. The pale brown solid obtained was subjected to preparative TLC (silica gel) using benzene/petroleum ether (1:1) as eluent. Two bands were isolated, the early one ($R_f = 0.83$) was shown to be 4-acetyl-9H-fluorene and the latter 2-acetyl-9H-fluorene ($R_f = 0.62$). The pure 4-acetyl-9H-fluorene was obtained as a dark creamy solid (0.04 g; 1.9 % yield), m.p. 62-64 °C (Lit.$^{21}$ m.p.: 62-63 °C), $\nu_{\text{max}}$ (KBr) 1676 (C=O) cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 2.59 (s, 3H, CH$_3$CO), 3.96 (s, 2H, 2CH$_2$), 7.93 (m, 1H, H-3), 7.26-7.77 (m, 7H, aromatic H).
2,7-diacetyl-9H-fluorene (2,7-DAcF). To a stirred solution of AcCl (1.568 g; 0.02 mol) and AlCl₃ (2.664 g; 0.02 mol) in DCE (20 ml), 9H-fluorene (0.83 g; 0.005 mol, in 1:4:4 molar ratio) in the same solvent (20 ml) was added drop wise over 5 min at r.t. and left stirring for 1 h, then the mixture was refluxed for 23 h. At the end of the reaction time the resulting mixture was cooled and added to a mixture of conc. HCl and ice. The dark brown solid obtained was chromatographed over a silica gel column, eluting with benzene to remove any colored polymeric materials. On evaporation of the benzene in vacuum, a pale brown solid was obtained, which was re-crystallized from benzene to give dark creamy needle-like crystals of 2,7-diacetyl-9H-fluorene (1.14 g, 91.2 % yield), m.p. 181-182 °C (Lit. m.p.:180-182 °C), νmax (KBr) 1678 (C=O) cm⁻¹; ¹H NMR δ(CDCl₃) 2.68 (s, 6H, 2,7-CH₃CO), 3.97 (s, 2H, CH₂), 8.13 (m, 2H, H-1 and H-8), 7.77-7.97 (m, 4H, aromatic H).

DFT calculations. The DFT calculations were carried out at the B3LYP 6-31G** level of theory using the Gaussian 03 W collection of programs. All structures were optimized at the ‘opt=tight’ level and converged normally, except for 9-AcFl, which did not converge using this criterion. Instead the G03W default optimization criterion was used. The calculations were all carried out at a standard desktop PC.

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