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Raman spectroscopy of fluorene oligomers in the α -, β - and γ -phases

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Abstract

We present Raman spectroscopy measurements on a series of fluorene oligomers, and compare them with those of the polymer poly(9,9-dioctylfluorene) [PF8]. We show that such measurements can be used as evidence for the formation of the so-called β -phase in an oligofluorene, and confirm the picture in which the β -phase is stabilized by the adoption of an anti-gauche–gauche side chain conformation. We also demonstrate that Raman spectroscopy can be used to identify the formation of the so-called γ -phase (crystalline phase) in oligofluorene thin films. Our measurements suggest that the rich phase morphology observed in PF8 can often be replicated in thin films of its model oligomers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conjugated polymers are an important class of electronic materials, having a wide variety of possible applications including the active material in light-emitting diodes and displays [1, 2], low-cost photovoltaics [3, 4] and printable electronics [5, 6]. The conjugated polymer poly(9,9-dioctylfluorene) (PF8) can be viewed as model system for studying the effect of molecular conformation and morphology of a conjugated polymer on its electronic properties. Such studies are made possible by the fact that PF8 can be prepared in a number of distinct morphological phases including an amorphous phase [7, 8], a nematic liquid crystal-phase, a crystalline phase [9] and a phase with extended chain conformation termed the β -phase [10–12]. Recent studies have applied a clear nomenclature to the various phases of PF8 and demonstrate that there are three distinguishable classes of conformational isomers with different average backbone chain torsional angles (ϕ) [13, 14]. These classes have been termed the α -phase (the amorphous phase) where $\phi = 135^\circ$, the γ -phase (crystalline phase) where $\phi = 150^\circ$, and a single unique conformational isomer termed the β -phase in which $\phi = 160^\circ$. Films in the α -phase can be prepared simply from spin-coating from a solution of PF8 from toluene/THF [7, 13]. The γ -phase is most readily formed by thermal cycling above the melting point (430 K) [13], with the β -phase generated by

spin-casting from relatively poor solvents [8, 13] or by thermal cycling [15, 16] or exposure to solvent vapor [7, 17]. This rich phase morphology thus offers a ready method for studying the influence of film structure on the photophysics of conjugated polymers without the need for chemical modification [18].

Recent work has shown that the morphology adopted by the side chains of PF8 is closely linked to the structure of the molecular backbone [9, 13, 19]. For example, calculations show that the β -phase backbone conformation is stabilized when its side chains adopt an anti-gauche–gauche (agg) conformation [13]. In the γ -phase it has been shown using both experimental and theoretical calculations of Raman spectra of fluorene monomers that the side chains of PF8 in the γ -phase adopt an all-anti (aaa) side chain conformation [9, 19]. Following [19], the aaa, aag and agg side chain conformations of a fluorene monomer are shown in figure 1.

In order to elucidate the optical and electronic properties of (macromolecular) conjugated polymers, many groups have turned to model oligomers, in which a chemically identical material can be prepared having a well-defined structure and a defined conjugation length. We have followed this approach, and have recently demonstrated the formation of the β -phase in two short chain fluorene oligomers, permitting us to confirm that the effective conjugation length of the polyfluorene β -phase is ~ 30 monomer units [20].

In this paper, we continue our study of oligofluorenes, and give structural evidence for the formation of the β -phase in

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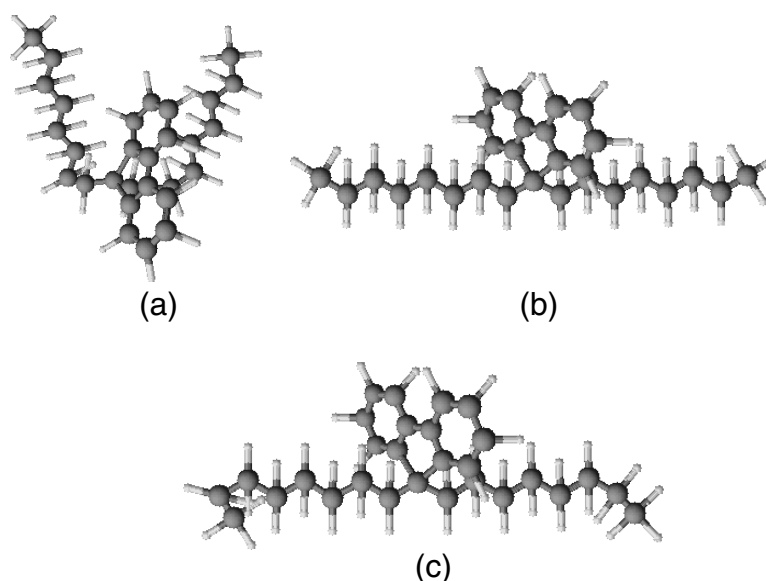


Figure 1. A fluorene monomer with (a) agg, (b) aaa and (c) aag side chain conformation.

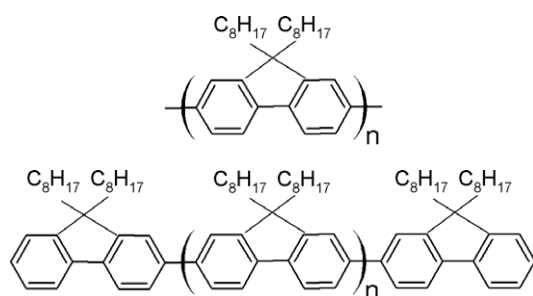


Figure 2. Chemical structure of PF8 (top) and fluorene oligomers.

an oligofluorene using Raman spectroscopy. In particular, we show that the agg conformation of the side chains expected in the full polymer is also present in a β -phase oligofluorene. Furthermore we use Raman spectroscopy to study the γ -phase in oligofluorenes, and demonstrate that in this phase the alkyl side chains of a fluorene pentamer adopt an aaa conformation. This work further highlights the importance of the relative interactions between the side chains and the polymer backbone in determining the overall conformation of the molecule.

2. Experimental details

Figure 2 shows the chemical structure of PF8 and the oligomers that we have studied. These oligomers included a fluorene trimer (3F8), a pentamer (5F8) and a fluorene heptamer (7F6). 3F8 and 5F8 have the same monomer unit as PF8 while 7F6 has solubilizing side chains of C_6H_{13} . The PF8 polymer was synthesized by Sumitomo Chemical Ltd. The 3F8, 5F8 and 7F6 oligomers were purchased from American Dye Source Inc and used without further purification.

Materials were characterized in thin-film form, where the α -phase was created either by spin-casting or drop-casting materials dissolved in chloroform solution. The drop-cast 3F8,

5F8 and 7F6 films had a thickness between 1 and 5 μm , whilst the spin-cast PF8 had a thickness of ~ 100 nm. We have also studied thin films of 5F8 doped at 80% by weight in a PMMA film where the total film thickness was less than 50 nm. For completeness, we have also performed studies on such materials dissolved in chloroform solution. To create the β -phase in PF8, thin films of the polymer were placed in toluene vapor for 18 h. Our spectroscopic studies [20] have demonstrated, however, that the β -phase of 5F8 can only be generated by dispersing the oligomer in a PMMA matrix at a concentration of between 50 and 80% by weight, and then cooling to liquid nitrogen temperature in a cryostat and slowly returning to room temperature. The γ -phase of PF8 was created by heating a thin film to 200 $^{\circ}\text{C}$ under nitrogen after which it was cooled to room temperature at a rate of 0.1 $^{\circ}\text{C min}^{-1}$. As discussed in the text, the γ -phases of 3F8 and 5F8 films were created by simply aging drop-cast films for a period of several days at room temperature in air. Our previous studies [20] have shown that in both the oligofluorene and the PF8 polymer films, only a fraction ($\leq 10\%$) of molecules are in fact converted to the β -phase. We believe that it is also likely that there is incomplete crystallization of the thin films that we have studied, pointing to an incomplete α - to γ -phase transition. In the following text we refer to β -phase or γ -phase films; however, this is meant to signify films containing a fraction of molecules that adopt the β -phase and γ -phase.

Raman spectroscopy was used to study the structure of the oligomers and polymer in the different morphological phases using a Renishaw Raman Imaging Microscope, with excitation provided using the 632.8 nm line of a HeNe laser. This system works in a backscattering configuration, where a 50 \times objective lens is used to focus the light from the HeNe laser onto the sample surface. Raman scattered light is then collected using the same lens and passed through a holographic notch filter to remove stray laser light. The remaining Raman scattered radiation is then delivered to a

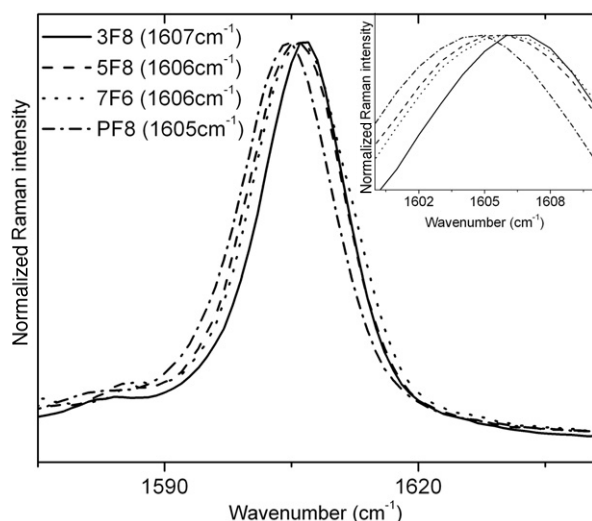


Figure 3. Raman spectrum of drop-cast (α -phase) F8 oligomers and spin-cast (α -phase) polymer around the peak of their Raman emission. The number shown in the legend indicates the peak Raman frequency of each material. The inset shows a magnified view of the 1605 cm^{-1} peak for each material.

CCD detector via a monochromator, with individual Raman peaks being detected with a resolution of $\sim 1\text{ cm}^{-1}$. Our system is routinely calibrated against the 520 cm^{-1} peak of silicon, with Raman scattered light being detected at $(520 \pm 0.3)\text{ cm}^{-1}$. In all cases, the power of the laser light incident on the sample surface (focused into a $1\text{ }\mu\text{m}$ spot) was $\sim 1\text{ mW}$ (equivalent to a power density of 1.3 GWm^{-2}). To enhance the Raman scattered intensity, samples were prepared on silver-coated frosted-glass substrates [21]. To confirm the presence of the different morphological phases, we also performed UV/vis absorption measurements using a Unicam UV 500 UV-vis spectrophotometer and measured photoluminescence (PL) emission following excitation using a HeCd laser ($\lambda = 325\text{ nm}$). Here, the PL was collected using an optical fiber coupled to a monochromator with a CCD detector.

3. Results and discussion

3.1. Amorphous (α) phase

Figure 3 shows the most dominant peak of the Raman spectrum recorded from the drop-cast oligofluorenes and spin-cast PF8 polymer. This peak has been assigned to a symmetric ring stretching mode [10] by comparison with the Raman spectrum of fluorene (1616 cm^{-1}) [22], biphenyl (1612 cm^{-1}) [23] and poly(paraphenylenes) (1595 cm^{-1}) [24]. It can be seen that there is a small frequency shift of around 2 cm^{-1} going from the 3F8 oligomer to the PF8 polymer. This small shift is in contrast to the considerable energy difference between absorption and PL of the same two materials, which we have previously shown to be 0.32 eV and 0.16 eV , respectively [20]. This relative insensitivity of Raman modes to conjugation length is in accord with similar measurements on derivatives of paraphenylenes, phenylene-vinylenes and thiophenes and in contrast to the relatively large Raman

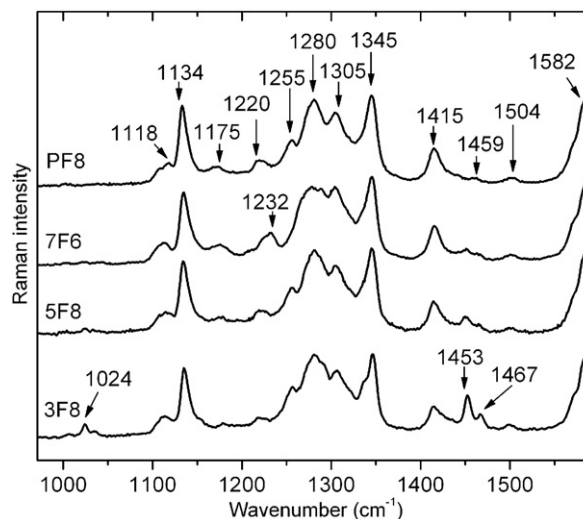


Figure 4. Raman spectrum of drop-cast (α -phase) F8 oligomers and spin-cast (α -phase) polymer between 975 and 1600 cm^{-1} .

dispersion (50 – 100 cm^{-1}) observed in polyenes, pyrroles and furan derivatives [25]. The small Raman shifts observed here may be attributable to the fact that the π -electrons experience strong confinement within the structural units [25]. Alternately, work on thiophene oligomers has suggested that such small Raman dispersions with molecular length result from competition between increasing conjugation (which tends to shift Raman modes to lower wavenumber) and an increase in intermolecular interaction (which shifts modes to a higher wavenumber) [26]. Indeed, measurements on sexithiophene confirm that an increase in pressure (equivalent to an increase in intermolecular interaction) causes an upward frequency shift [27].

Figure 4 plots Raman spectra recorded from 975 to 1600 cm^{-1} normalized to the peak of the Raman mode observed around 1605 cm^{-1} for the as-spun PF8 polymer and oligofluorenes. Here, the peaks at 1255 , 1280 , 1305 and 1345 cm^{-1} have been mainly assigned to C–C stretching modes between phenylene rings [10]. It can be seen that the positions of most of the Raman features between 1000 and 1600 cm^{-1} are very similar for both the oligofluorenes and the PF8. Indeed, it is clear that most of the Raman modes observed from the 7F6 oligomer have the same energy as the other oligomers and the polymer, even though it has shorter side chains (hexyl compared with octyl). This result is in accord with previous studies where it has been shown that the shift of Raman modes in polyfluorene based materials becomes small when the length of the side chains is longer than an ethyl group [28]. We note, however, that in the 7F6 the 1280 cm^{-1} mode is split, the feature around 1220 cm^{-1} is hardened (shifted to higher wavenumber) and the 1255 cm^{-1} peak is absent. As the main difference between 7F6 and 3F8, 5F8 and PF8 is the length of side chain this suggests that the Raman features around 1250 – 1300 cm^{-1} do have some sensitivity to side chain modes. In general, it is apparent that there are additional features in the oligomers (1024 , 1453 and 1467 cm^{-1}) that become weaker as the molecular length increases and are either very weak or absent in the PF8.

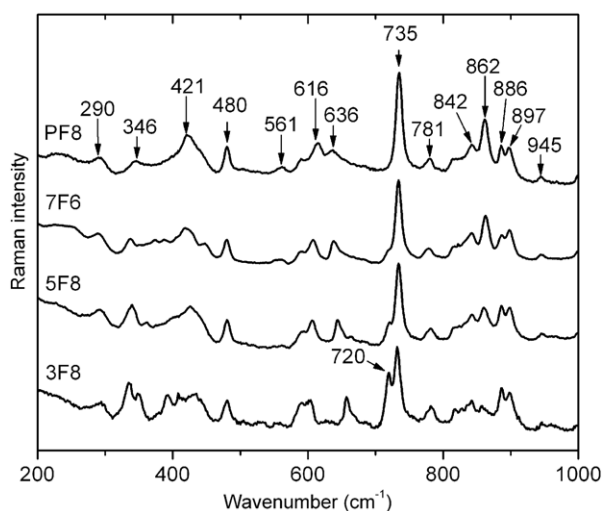


Figure 5. Raman spectrum of drop-cast (α -phase) F8 oligomers and spin-cast (α -phase) PF8 polymer between 200 and 1000 cm^{-1} .

In figure 5, we present the Raman modes of the oligofluorenes and polymer between 200 and 1000 cm^{-1} (in figure 5, we have normalized all spectra to the peak at $\sim 735 \text{ cm}^{-1}$). It is known that the intensity and position of Raman modes in the spectral region between 800 and 1000 cm^{-1} are most sensitive to different conformations of the alkane side chains arising from end gauche defects (aag side chain conformation) and other non-planar conformations [19]. The modes observed at 421 cm^{-1} , 480 cm^{-1} , 735 cm^{-1} and 862 cm^{-1} have been previously assigned as ring torsion (inter-ring), ring torsion (out of plane)/C–H bend, ring breathing and C–C stretch (bridging C) modes, respectively [19]. A new mode is also observed at 720 cm^{-1} in the 3F8 that becomes progressively weaker as the length of the oligomer increases.

In summary, we find that the Raman spectra for the as-spun cast polymer and drop-cast oligomers between 200 and 1600 cm^{-1} are alike, implying that these materials have a similar molecular morphology; a result which (apart from a differences in conjugation length) is consistent with the similarities in their absorption and PL spectra [20]. For completeness, we have also measured Raman spectra of 3F8, 5F8, 7F6 and PF8 in chloroform solution (not shown). Here, we find that the Raman spectra in solution are also very similar to those in films over the range 1000–2000 cm^{-1} , implying that the chain conformation of the oligofluorenes and polymer in solution and film adopt an amorphous (α) phase.

3.2. β -phase

Figure 6 plots Raman spectra for the PF8 and 5F8 films that have been exposed to solvent vapor or thermally treated (respectively) to induce the β -phase (embedded in an α -phase matrix) along with a regular α -phase spectrum. Note that to form the β -phase in the 5F8, it was necessary to first disperse the 5F8 in a PMMA matrix at a concentration of 80% by mass. At present, the exact function of the PMMA in forming the β -phase in the 5F8 is unclear; however, it is possible that the PMMA matrix exerts a stretching force on the oligomer during

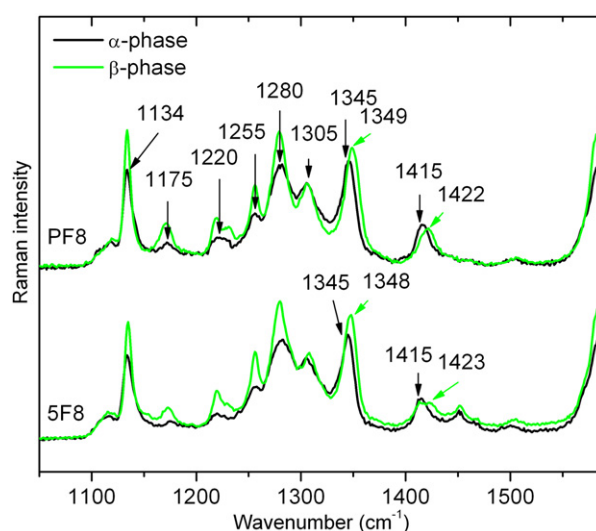


Figure 6. Raman spectrum of as-spun (α -phase) and treated film (β -phase) PF8 and 5F8 (80 wt% in PMMA) between 1050 and 1600 cm^{-1} .

the thermal treatment that facilitates the formation of the β -phase morphology. Extensive experiments have shown that it is not possible to form the β -phase unless the PMMA is present. We emphasize that control measurements on PMMA thin films identified two main modes at 811 and 1449 cm^{-1} that are either absent from, or appear only weakly in, the 5F8 β -phase spectra. Previous PL and absorption measurements have shown that both the PF8 and 5F8 films can adopt the β -phase; however, the β -phase is not supported in 3F8 or 7F6 [20]. We have speculated that 3F8 cannot form the β -phase as its chain-length is not sufficiently long to stabilize the planar molecular structure. Other work has shown, using molecular modeling, that fluorene polymers having alkyl side chains that are shorter than eight carbon atoms also cannot support the β -phase [13], also explaining our failure to generate the β -phase in 7F6.

For the 5F8 and PF8 materials in the β -phase, we find that the mode around 1605 cm^{-1} appears at a similar wavenumber to that in the α -phase. This apparent frequency insensitivity to chain-length (electronic conjugation) is consistent with observations made for the amorphous phase described above. It is clear, however, that there are differences between the α -phase Raman spectra and β -phase spectra for both materials. In particular it can be seen that the Raman features around 1125–1350 cm^{-1} are narrower and more intense in the β -phase; a result consistent with earlier studies [10, 28]. Here, such enhancements in Raman scattering efficiency have been attributed to the increase in electronic polarizability caused by an increase of conjugation length [29]. This dependence results from the fact that polarizability can be a function of the number of bonding electrons [30], which is itself sensitive to electron delocalization. It can also be seen for both 5F8 and PF8 that there is a hardening of the modes at 1345 and 1415 cm^{-1} in the β -phase. Such hardening has been attributed to a general increase in intermolecular interaction [29]. We believe that the close similarity in the behavior of PF8 and 5F8 suggests that 5F8 can indeed be prepared in the β -phase, a conclusion

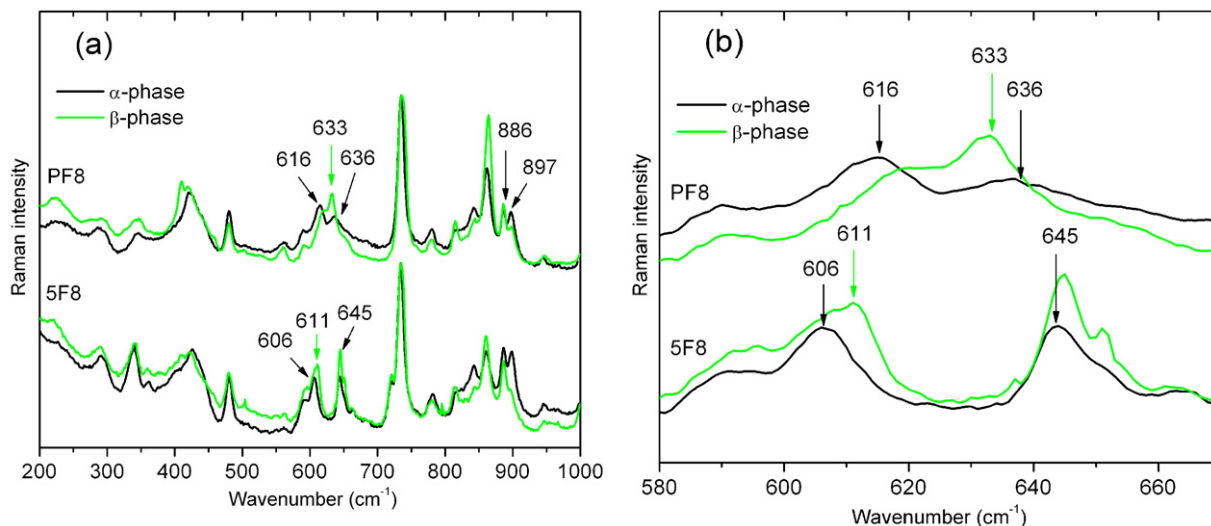


Figure 7. (a) Raman spectrum of as-spun (α -phase) and treated film (β -phase) PF8 and 5F8 (80 wt% in PMMA) between 200 and 1000 cm^{-1} and (b) the Raman spectrum between 580 and 670 cm^{-1} .

consistent with our early assignment on the basis of absorption and PL [20].

We can gain further confirmation for our assignment of the β -phase in 5F8 from Raman spectra covering the wavenumber range 200–1000 cm^{-1} as shown in figure 7(a). As discussed above, Raman modes at these low frequencies are mainly characterized by side chain modes and hence provide information about the conformation of the side chains in each phase. It can be seen that there are differences between the α - and β -phases for both the oligomer and the polymer; in particular we observe changes in the relative magnitude of the doublet of peaks at around 625 and 900 cm^{-1} which is believed to be a key indicator of the formation of the β -phase [19]. In figure 7(a) and in the expanded region of the Raman spectra shown in figure 7(b), it can be seen that the α -phase of the PF8 polymer is characterized by two modes at 616 and 636 cm^{-1} . On being driven into the β -phase, the 636 cm^{-1} mode softens to 633 cm^{-1} and grows in intensity relative to that at 616 cm^{-1} (which hardens to 620 cm^{-1}). This result is consistent with that reported by Volz *et al* [19] who observed a similar increase in intensity of the 633 cm^{-1} mode relative to that at 620 cm^{-1} and argued that the ratio of these modes is a guide to the formation of β -phase/agg side chain conformation [9].

In the Raman spectra of 5F8 shown in figure 7(b), it can be seen that there are two modes in the α -phase at 606 and 645 cm^{-1} that we associate with the modes observed at 616 and 636 cm^{-1} of the α -phase of PF8. This assignment is supported using the α -phase spectra presented in figure 5 for the different oligofluorenes and the polymer. Here it can be seen that as the length of the molecule is reduced, the modes seen at 616 and 636 cm^{-1} in the polymer move apart in energy. In the 5F8 β -phase, it can be seen that the mode observed at 606 cm^{-1} has hardened to 611 cm^{-1} . This is accompanied by a relative increase in the intensity of the mode observed at 645 cm^{-1} (which is more intense than that at 611 cm^{-1}), replicating the trend of the 633 and 620 cm^{-1} modes observed in β -phase PF8. This further suggests that 5F8 can be driven into the β -phase and that its side chains adopt an agg side chain conformation.

Table 1. Raman peak of α -phase (R_α), γ -phase (R_γ) and linewidth (full width at half maximum) at the peaks (Γ_α and Γ_γ) of 3F8, 5F8 and PF8. ΔR is the Raman shift from the α -phase to the γ -phase (i.e. $R_\gamma - R_\alpha$). The units of the Raman peak, Raman shift and FWHM are all in cm^{-1} .

| | R_α | R_γ | ΔR | Γ_α | Γ_γ |
|-----|------------|------------|------------|-----------------|-----------------|
| 3F8 | 1607 | 1603 | -4 | 11 | 11 |
| 5F8 | 1606 | 1603 | -3 | 14 | 16 |
| PF8 | 1605 | 1603 | -2 | 19 | 25 |

3.3. Crystalline (γ) phase

When studying oligofluorene thin films, we have noticed that there is, in some cases, a gradual evolution in the Raman spectra as a function of time after the film is cast. This is particularly pronounced in drop-cast 3F8 films which show changes within 1 day of being prepared. Similar changes occur for 5F8 films within 2 days; however, the Raman spectrum of 7F6 does not change within 18 days. We assume that such differences in Raman spectra that we discuss below result from slow crystallization at room temperature. Clearly, such crystallization is most favored in low mass molecules due to their higher intrinsic mobility in a thin film. In figure 8, we compare the Raman mode around 1605 cm^{-1} for 3F8 and 5F8 drop-cast films that have been allowed to form the γ -phase in air, with a γ -phase film of PF8 (presumably embedded in an α -phase matrix). At present, however, it is very difficult to distinguish whether such partial crystallization points to structural defects at the molecular level or whether the films are inherently quasicrystalline. More work is needed to address this issue. For comparison, we also present a Raman spectrum recorded for a freshly cast amorphous film (α -phase) of each material. In table 1, we tabulate (for each material) the wavenumber of the peak Raman mode (in the α and γ -phases), the difference in wavenumber between α - and γ -phases along with their linewidth (full width at half maximum).

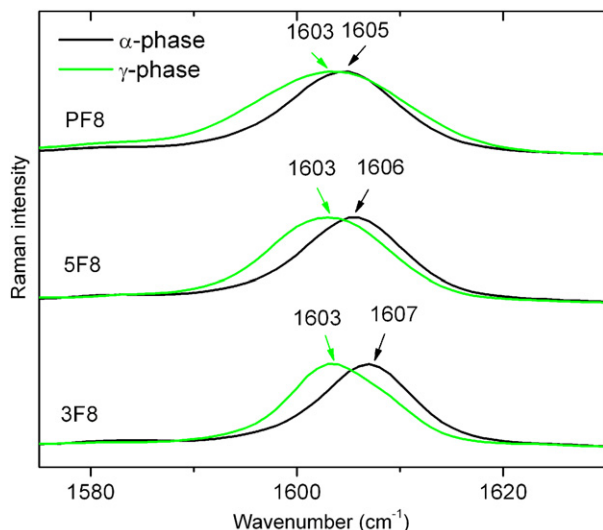


Figure 8. Raman spectrum of α -phase and crystalline phase (γ -phase) PF8, aged 5F8 and aged 3F8 at around their Raman peak position.

As it can be seen in figure 8 and table 1, the Raman peak in PF8 softens and broadens as the α -phase is driven into the γ -phase; an observation consistent with previous findings [10, 28]. Note that such effects are not apparently connected with the thickness of the films. Indeed, we find that the linewidth of the 1603 cm^{-1} feature observed in γ -phase-containing 3F8 and 5F8 films is very similar whether they have been prepared by drop-casting or spin-casting (data not shown). Considering the significant difference between the thickness of drop-cast and spin-cast films ($5\text{ }\mu\text{m}$ and $\sim 100\text{ nm}$, respectively), we conclude that the linewidth broadening of the γ -phase oligomers is not a function of film thickness. The observed shift to lower wavenumbers is clearly suggestive of a reduction in the polymer stiffness in the γ -phase. It can be seen that a similar softening of this mode is evident in 3F8 and 5F8 films that have been aged at room temperature, also suggesting that they too adopt a γ -phase morphology. As it can be seen from table 1, the 3F8 apparently undergoes a slightly larger Raman shift between the α -phase and γ -phase than does the PF8 polymer. It has been reported that the relative broadening of the γ -phase observed in the PF8 results from compositional inhomogeneity in the film occurring from the coexistence of the α -phase and the γ -phases (i.e. pointing to incomplete crystallization) [28]. This coexistence of phases would clearly result in inhomogeneous broadening of selected Raman modes, and thus such features can be interpreted as corresponding to superposition of contributions from the α - and γ -phases. However, it is also possible that other effects may result in an energy shift and an apparent mode broadening. For example, increases in conjugation length can result in a general softening of Raman modes [25]; however, this seems an unlikely explanation in this case, as no shift in this mode is observed when the PF8 polymer or the oligofluorene are driven from the α -phase into the β -phase. Furthermore, as shown in figure 3, the energy of this mode is only weakly sensitive to the length of the

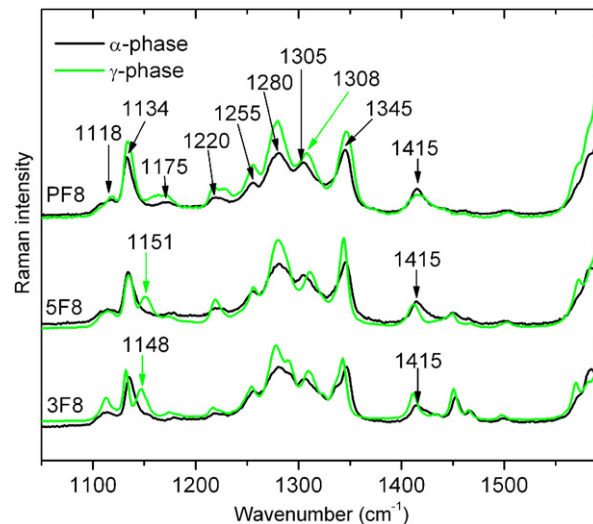


Figure 9. Raman spectrum of α -phase and crystalline phase (γ -phase) PF8, aged 5F8 and aged 3F8 between 1050 and 1600 cm^{-1} .

molecule. Mode softening can also result from a reduction in intermolecular interactions [26]; however, this also seems unlikely in a polycrystalline solid. It is therefore possible that the effects that we observe result from Davydov splitting of internal molecular vibrations (as has been observed in PTCDA molecular crystals [31]) which act to shift and broaden the 1605 cm^{-1} Raman peak. Clearly more work is required to address this issue.

For completeness, we have tried to induce the γ -phase in the oligofluorenes by annealing thin films at 100°C (for 3F8) and 200°C (for 5F8) and then slowly cooling them at $\sim 0.1^\circ\text{C min}^{-1}$. This process, however, does not create a γ -phase as it does for the polymer, but simply creates the α -phase. The reason for this is that it is very likely that crystallization of short oligomers occurs at a considerably lower temperature than that of the polymer. Indeed the optimum crystallization temperature may well be below room temperature, hence any thermal treatment applied to the oligofluorene thin films at a temperature above room temperature has no significant effect on crystal growth.

We can gain further evidence for crystallization of the oligofluorenes by studying the Raman spectra between 1050 and 1600 cm^{-1} , as shown in figure 9. Again, normalizing to the mode at 1605 cm^{-1} , we find that the intensity of the Raman modes in the region between 1000 and 1400 cm^{-1} for the PF8 and the 3F8 and 5F8 oligomers is relatively enhanced. It can also be seen that in PF8, the peak at 1415 cm^{-1} broadens, consistent with earlier observations [10, 28]; however, in γ -phase 5F8 and 3F8 this mode is narrower. Further support for the identification of crystallization in the oligofluorenes comes from the fact that the Raman peak observed in β -phase PF8 at 1305 cm^{-1} hardens to 1308 cm^{-1} in the γ -phase film. Importantly we also observe that a similar peak at 1308 cm^{-1} in β -phase 5F8 also hardens to 1311 cm^{-1} in the aged film; an observation consistent with the calculations by Arif *et al* using short oligomers without side chains [9].

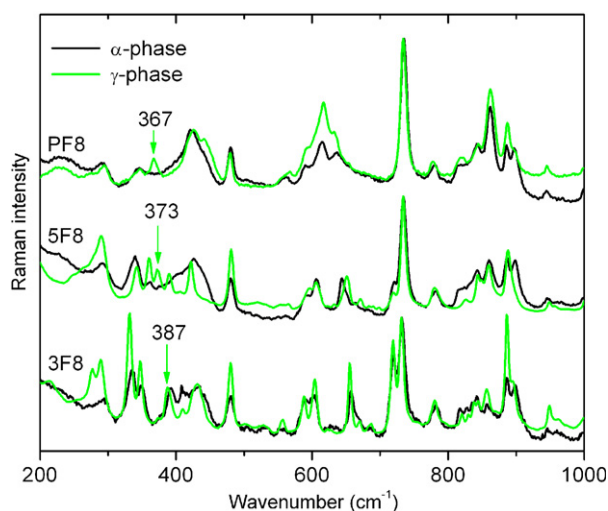


Figure 10. Raman spectrum of α -phase and crystalline phase (γ -phase) PF8, aged 5F8 and aged 3F8 between 200 and 1000 cm^{-1} .

Figure 10 shows Raman spectra for 3F8, 5F8 and PF8 over the wavenumber range 200–1000 cm^{-1} for both γ -phase and α -phase. Again, many of the peaks appear better resolved in the γ -phase films. It is apparent that in the PF8 γ -phase we observe an additional peak at 367 cm^{-1} (attributed to an aaa side chain conformation); a result consistent with those of Arif *et al* [9] and Volz *et al* [19]. In the oligofluorenes, we observe a new peak at 373 cm^{-1} for the aged 5F8. On the basis that Raman modes tend to harden in shorter chain-length molecules, we believe that this further suggests that the γ -phase of 5F8 adopts an aaa side chain conformation. For 3F8, a new mode is observed at 387 cm^{-1} , but it is much less clear whether we can firmly associate this mode with the aaa side chain conformation.

Finally, we present absorption and fluorescence measurements of 3F8, 5F8 and PF8 in the γ -phase and α -phase in figure 11. As reported previously [20], there is a noticeable shift in absorption and PL of the α -phase to higher energies as the length of the molecule is reduced. It can be seen that for all materials there is a distinct difference between the absorption of the α -phase and the γ -phase, with a new low-energy shoulder or peak appearing in the absorption spectrum of the γ -phase material that is accompanied by substantial broadening of the entire absorption spectrum. In table 2, we tabulate (for each material) the energy of the α -phase absorption maxima and the energy of the new low-energy peak/shoulder that is observed in the γ -phase absorption. We also record the energy shift between the α -phase peak and the γ -phase shoulder/peak, together with the overall linewidth of the transition (full width at half maximum). We find that the absorption peak of the 5F8 γ -phase appears at around 3.17 eV; an energy in between that of the α -phase (3.36 eV) and the β -phase (2.96 eV) [20]. Previous studies have modeled the α -, β - and γ -phase absorption spectra of PF8 on the basis of differing conjugation length, and have shown that the low-energy absorption component of the PF8 γ -phase is expected to lie in between that of the α -phase and β -phase [13]; it is clear, however, that intermolecular interactions (such as Davydov splitting) may well be important

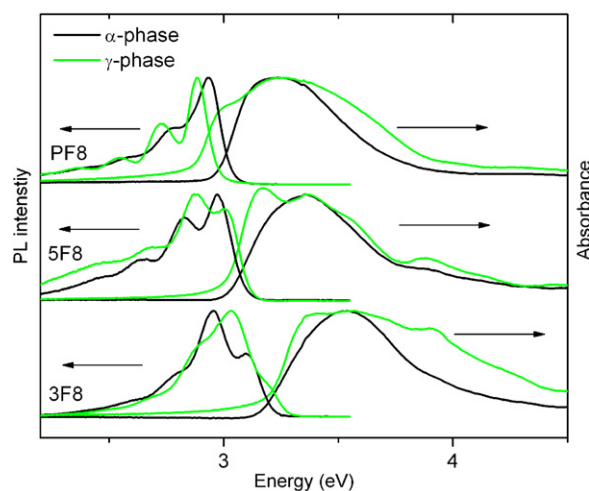


Figure 11. Normalized absorption spectrum and PL spectrum of α -phase, and γ -phase PF8, aged 5F8 and aged 3F8, respectively.

Table 2. Energy of the absorption peak of α -phase (A_α), the energy of the shoulder of the γ -phase (A_γ) and the linewidth of the absorption band (full width at half maximum) in the α - and γ -phases (Γ_α and Γ_γ respectively) of 3F8, 5F8 and PF8. ΔA is the absorption shift from α -phase to γ -phase (i.e. $A_\gamma - A_\alpha$). The units of the absorption peak/shoulder, absorption shift and FWHM are all in eV.

| | A_α | A_γ | ΔA | Γ_α | Γ_γ |
|-----|------------|------------|------------|-----------------|-----------------|
| 3F8 | 3.53 | 3.34 | -0.19 | 0.53 | 0.89 |
| 5F8 | 3.36 | 3.17 | -0.19 | 0.53 | 0.61 |
| PF8 | 3.21 | 2.98 | -0.23 | 0.52 | 0.79 |

in determining both the energy and linewidth of the electronic transitions observed in the absorption spectra, as has been reported in aggregates of thienylene vinylene oligomers [32] and sexithiophenes [33].

4. Conclusions

Raman spectroscopy was used to study three short polyfluorene oligomers of different chain-length, with such materials being compared to the full poly(9,9-dioctylfluorene) [PF8] polymer. In particular, such measurements were able to confirm our previous spectroscopic measurements demonstrating that the so-called β -phase (having an extended electronic conjugation) can be formed in a short oligomer composed of five fluorene monomers. This assignment was made by comparison of the relative intensity of two characteristic Raman modes observed in the PF8 polymer associated with the octyl side chains (at 616 and 636 cm^{-1}), whose behavior was mirrored by that of two similar modes identified in the fluorene pentamer. We then demonstrated that thin films of short chain oligomers (a trimer and a pentamer) underwent crystallization within a couple of days of being cast into a thin film from solution. Our identification of the formation of the so-called γ -phase (crystalline phase) was made on the basis of the softening of the dominant mode at $\sim 1605 \text{ cm}^{-1}$ and the appearance of a Raman mode at 367 cm^{-1} associated with an aaa side chain conformation in the crystalline PF8 polymer which was

also observed at a slightly higher frequency in the crystalline pentamer. We also observed that the mode at 1605 cm^{-1} in the γ -phase-containing films underwent an energy shift that was also accompanied by broadening; an effect that was particularly pronounced in the PF8 polymer. The origin of energy shifts and broadening of this mode observed in the γ -phase is unclear, but it may either result from incomplete crystallization (resulting in coexistence of the α - and γ -phases), or it may be originate from interactions between different molecular vibrational modes. In general, our work confirms that much of the phase morphology previously identified for PF8 can also be observed in model fluorene oligomers, thus presenting a rich field for study of the link between structure and optical and electronic properties in materials having a well-defined conjugation length.

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