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Chirality Induction Using Circularly Polarized Light to a Branched Oligofluorene Derivative in the Presence of Achiral Aid Molecule

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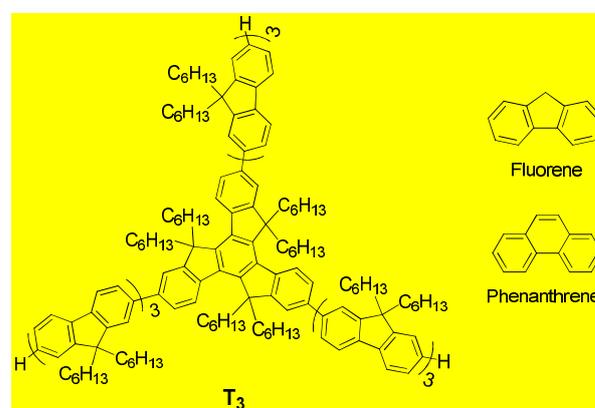
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Chirality induction to a uniform, star-shaped fluorene oligomer with a central truxene moiety (T3) was achieved using circularly polarised light in the presence of achiral fluorene or phenanthrene. Induction to T3 alone was difficult, suggesting that close chain packing realised through interactions of T3 with small molecules plays a role in chirality induction.

Circularly polarised light (CPL) was proposed to be a source of chirality for the synthesis of asymmetric organic molecules for the first time in 1874,^{1,2} and various experimental examples of CPL-based chiral synthesis have been reported thereafter.^{3,4} Target materials include small molecules, polymers and supramolecular ensembles. Since chiral polymers find a wide range of applications, facile methods of synthesis using CPL are important.⁵ As for CPL-based chiral polymer preparation, a polymethacrylate bearing a side chain containing an azobenzene moiety was for the first time made optically active using CPL;⁶ polymers having azobenzene moieties buried in the main-chain have also been studied.⁷ We have recently reported a preferred-handed helix formation of linear poly(9,9-di-*n*-octylfluorene-2,7-diyl) (PDOF) using CPL as a chirality source, where the twist bias around the single bonds connecting the aromatic groups was controlled by chirality of light.^{8,9a} PDOF became optically active in a thin film form on CPL irradiation and exhibited intense circular dichroism (CD) bands. The optical activity of PDOF arises from a 5/1-helical conformation of the polymer generated from a random conformation as disclosed through metadynamics simulation of stereomutation of the polymer chain.⁹ Through the

simulations, inter-chain interactions as well as chain-to-substrate interactions were found to be important in chirality induction. The conformational transformation is triggered by a “twist-coplanar” transition of the Ar-Ar unit on photoexcitation.¹⁰ Selective photoexcitation of a right- or left-handed twist modifies a chiral twist into an achiral coplanar conformation which can be deactivated into both right- and left-handed twists, leading to a decrease in population of the selectively excited twist where a preferred-handed twist (helix) is formed.^{8,9a,11}

Herein, we report chirality induction to a monodisperse, well-defined, star-shaped oligofluorene with a central truxene core and terfluorene arms (T3, Scheme 1).¹² T3 has a higher luminescence quantum yield than linear polymer systems and also has a high nonlinear absorption coefficient.^{12b} On the basis of these characters, T3 is a promising candidate for photoelectronic material, and addition of chirality would widen its range of application. Chirality induction to T3, however, is a challenge since the solid-state form of T3 does not have close packing of chains due to its branched structure, while chain-to-chain interactions have been found to be important in chirality induction to linear PDOF^{8,9a}.



Scheme 1. Structures of compounds used in this work.

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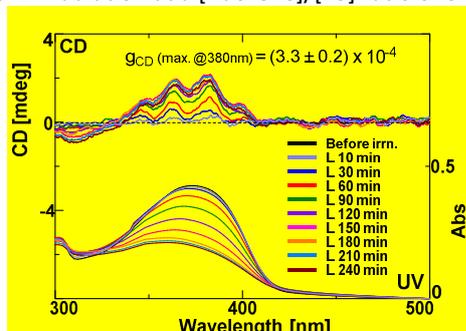
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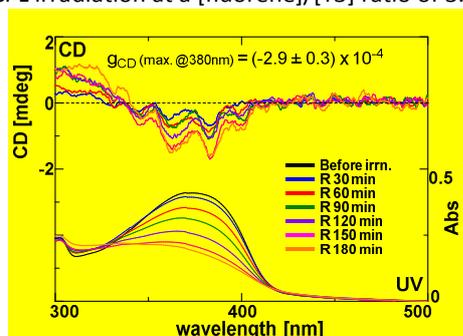
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Pure T3 film cast on a quartz plate from a toluene solution indeed did not give rise to any detectable circular dichroism spectra on irradiation with CPL when the experimental conditions were identical to those applied for the linear PDOF (ESI, Fig. S1). This result can reasonably be ascribed to the lack of strong intermolecular interactions, because the T3 molecule is known to form an amorphous bulk material where crystalline domains are absent.

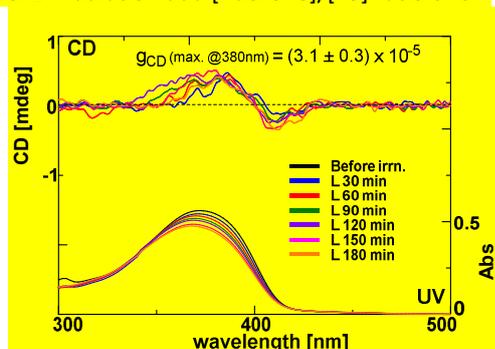
A. L-CPL irradiation at a [fluorene]/[T3] ratio of 3.2



B. R-CPL irradiation at a [fluorene]/[T3] ratio of 3.2



C. L-CPL irradiation at a [fluorene]/[T3] ratio of 0.4



D. g_{CD} -vs.-relative irradiation energy sum plot at a [fluorene]/[T3] ratio of 3.2

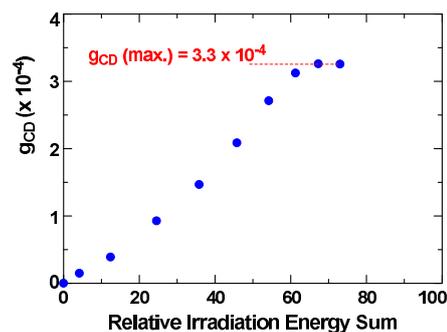


Fig. 1. CD (top) and UV (bottom) spectra of fluorene-T3 films prepared at [fluorene]/[T3] = 3.2 observed on L-CPL (A) and R-CPL (B) irradiation; those of a fluorene-T3 film prepared at [fluorene]/[T3] = 0.4 observed on L-CPL irradiation (C) and a g_{CD} -vs.-relative irradiation energy sum plot at [fluorene]/[T3] = 3.2 on CPL-irradiation (D). Error ranges of g_{CD} values were estimated on the basis of average noise level in the range of 495-500 nm.

In order to circumvent this problem, we elaborated a way to enhance intermolecular interactions with the aid of an achiral small molecule. Fluorene was first investigated as an aid molecule since π - π interactions between T3 and fluorene are expected on the basis of structural similarity. A film was made on a quartz plate by casting a toluene solution containing T3 and fluorene at [fluorene]/[T3] = 0.4 or 3.2 or 4.8 or 28.9 (a ratio of fluorene to unit residue in T3). Whilst the film made at a ratio of [fluorene]/[T3] = 28.9 appeared to consist mostly of fluorene crystals and was not suited for CD spectral measurements due to low transparency, those made at the lower ratios appeared transparent enough and were subjected to the CPL experiments where those at [fluorene]/[T3] = 0.4 or 3.2 were mainly analysed.

It was confirmed by IR spectra (ESI, Fig. S2) that the chemical structures of T3 and the small molecules were intact through the irradiation experiments discussed hereafter. Confirming the stability is important, since monomeric units in polyfluorene derivatives can be transformed to 9-fluorenone (the so-called keto defect) upon electronic excitation (ESI, Fig. S2). It is also worth noting that sublimation of fluorene was negligible under the current experimental conditions, as confirmed by the IR spectra.

As shown in Fig. 1A and B, on irradiation with L- and R-CPL, the films made at [fluorene]/[T3] = 3.2 indicated clear Cotton bands in the lowest-energy absorbance range of T3, and L- and R-CPL induced mirror image CD spectra. CD intensity increased with irradiation time and reached a plateau showing the maximum anisotropy factor ($g_{CD} = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)$, where ϵ_L and ϵ_R are molar absorptivities for L- and R-CPL, respectively)¹³ of 3.3×10^{-4} after 210 min (Fig. 1D corresponding to Fig. 1A). In addition, linear dichroism was not detected in the same wavelength region (ESI, Fig. S4). These results indicate that the preferred handed twist was induced to T3 by CPL. It is noticeable that the absorbance peak became weaker (hypochromism) and blue-shifted on CPL irradiation.

Hypochromism and a blue shift of UV bands were also observed for PDOF and were ascribed to an increase in the dihedral angle between fluorene units that occurred when a helical conformation was induced.^{9a} Further, the CPL-based chirality induction was confirmed to be reversible where a film made at $[\text{fluorene}]/[\text{T3}] = 3.2$ indicated positive Cotton effects at around 380 nm on L-CPL irradiation for 60 min and the sign of the cotton effects changed to negative on extended irradiation using R-CPL for 60 min (ESI, Fig. S5). Also, chirality induction was possible not only for the films made on quartz but also for a film made on NaCl plate (ESI, Fig. S3). Further, a thinner film made at $[\text{fluorene}]/[\text{T3}] = 3.2$ showing UV absorbance of 0.104 at 380 nm indicated on CPL irradiation a maximum g_{CD} of $(3.6 \pm 0.4) \times 10^{-4}$ which is similar to that of the film in Fig. 1A.

Fig. 1D indicates a plot of g_{CD} against the sum of irradiation time multiplied by absorbance which corresponds to the relative irradiation energy sum.¹⁴ A clear increase in slope of the plot is confirmed until g_{CD} reached a plateau. This strongly suggests that chirality is amplified in the film structure upon irradiation.

In addition, the film prepared at $[\text{fluorene}]/[\text{T3}] = 0.4$ also gave CD spectra on L-CPL irradiation; however, the intensity was much less than that of the film made at $[\text{fluorene}]/[\text{T3}] = 3.2$ (Fig. 1C). Also, the CD spectral patterns $[\text{fluorene}]/[\text{T3}] = 0.4$ are slightly different from those at $[\text{fluorene}]/[\text{T3}] = 3.2$, suggesting that induced chiral conformation varies depending on the ratio.

The observed CD bands are ascribed mainly to T3 chirality since fluorene does not absorb in the corresponding wavelength region; however, fluorene-T3 interactions are indicated by the fact that T3's lowest-energy band peak in the film was slightly red-shifted in the presence of fluorene and observed at 372 nm ($[\text{fluorene}]/[\text{T3}] = 0.4$) and at 374 nm ($[\text{fluorene}]/[\text{T3}] = 3.2$) while that of pure T3 was at 370 nm (ESI, Fig. S6). A similar red shift of T3 in the presence of fluorene was observed also in a toluene-MeOH solution at several ratios of the two solvents (ESI, Fig. S7). These results suggest that interactions between T3 and fluorene play a role in chirality induction to T3 by CPL.

Further information on the structure of fluorene-T3 films and intermolecular interactions in excited states was obtained from fluorescence spectra (Fig. 2). A pure fluorene sample cast on a quartz plate from a toluene solution indicated an emission spectrum with clear vibronic structure with peaks at 387 nm, 409 nm, 433 nm, and 460 nm, which agree with the reported fluorescence bands of crystalline fluorene (Fig. 2A).¹⁵ Pure T3 film gave a structured band with peaks at 415 nm, 438 nm and 467 nm (shoulder) and a broad band centred at 520 nm, which may be assigned to monomer and excimer emissions, respectively (Fig. 2B). The excimer band of pure T3 became more intense after L-CPL irradiation, suggesting irradiation enhanced molecular alignment of T3 through the activation of single bond rotation between monomeric units, although chirality induction was not observed.

The fluorene-T3 film at $[\text{fluorene}]/[\text{T3}] = 0.4$ gave an emission pattern similar to that of pure T3 before CPL irradiation with

almost no emission band due to pure fluorene at 387 nm, implying that the two molecules are dispersed well into each other on the molecular level and that energy transfer from fluorene to T3 effectively occurred (Fig. 2C). After irradiation with L-CPL, the intensity of the lowest-energy band became much greater than before irradiation. In addition, the peak position of this band was red-shifted compared with the lowest-energy band of pure T3 (531 nm). These results suggest that an exciplex between T3 and fluorene contributes to the lowest-energy band.

As indicated in Fig. 2D, the emission pattern of fluorene-T3 film at $[\text{fluorene}]/[\text{T3}] = 3.2$ was similar to that of fluorene-T3 mixture at $[\text{fluorene}]/[\text{T3}] = 0.4$ before irradiation. However, after CPL irradiation, a clear emission band at 387 nm developed, probably due to pure fluorene crystal, suggesting that crystallisation of fluorene was enhanced through molecular motion induced by light. Further, the intensity of the lowest-energy emission band at 535 nm, which may be due mainly to the fluorene-T3 exciplex, was greater than that at $[\text{fluorene}]/[\text{T3}] = 0.4$ after irradiation. The results in Figs. 2C and D support that T3 and fluorene are effectively interacting in excited states.

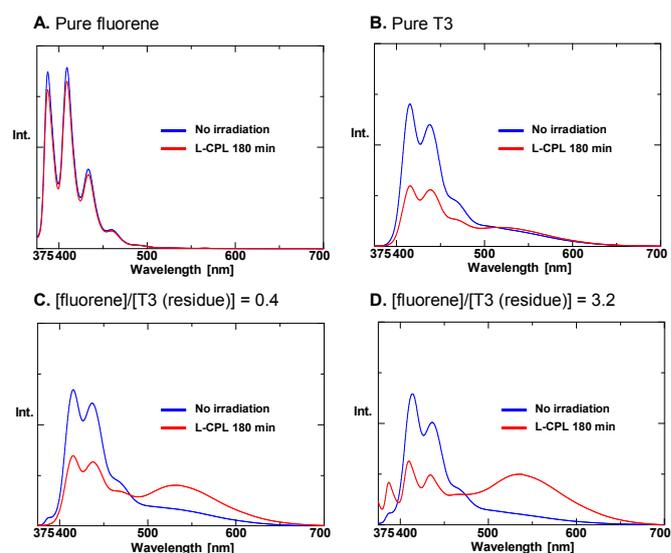


Fig. 2. Fluorescence spectra of pure fluorene film (A), pure T3 film (B), and fluorene-T3 mixture at $[\text{fluorene}]/[\text{T3}] = 0.4$ (C) and 3.2 (D). Excitation wavelengths (λ_{ex}) were 282 nm in A and 380 nm in B-D.

In order to obtain information of film morphology and to obtain an insight into the role of fluorene, thermal properties of the samples were measured. Fig. 3 indicates differential scanning calorimetry (DSC) curves of pure T3, pure fluorene and fluorene-T3 mixtures. T3 alone does not show any thermal transitions as it is an amorphous material. Conversely, pure fluorene indicated a sharp endothermic transition of -68 J/g at 123 °C corresponding to melting. No clear melting was observed for the fluorene-T3 mixture at $[\text{fluorene}]/[\text{T3}] = 0.4$ and a broader endothermic signal of -35 J/g (per weight of fluorene) appeared at 118 °C for the fluorene-T3 mixture at

[fluorene]/[T3] = 3.2. These results indicate that crystallisation of fluorene is hampered in the presence of T3. In the fluorene-T3 mixture at [fluorene]/[T3] = 0.4, fluorene and T3 molecules seem to be homogeneously dispersed into each other while, at [fluorene]/[T3] = 3.2, about 52% of the fluorene molecules form less ordered crystals than pure fluorene crystals and the rest is molecularly dispersed into T3.

Film morphology was assessed also by polarized optical microscopic observations; the mixture [fluorene]/[T3] = 0.4 indicated no presence of crystals while those at higher ratios exhibited crystalline particles (ESI, Fig. S8). These observations are consistent with the results of thermal analysis.

The DSC results along with the facts that T3 alone does not become optically active and that induced CD intensity was greater at [fluorene]/[T3] = 3.2 than at 0.4 imply that intermolecular interactions between fluorene and T3 are indispensable in chirality induction and that crystalline fluorene also is important in achieving a high anisotropy. We recently reported the importance of molecular scaffold effects of a solid substrate surface in the chirality induction of PDOF.^{9a} The crystal surface of fluorene may be acting as a scaffold in chirality induction to T3.

This assumption was supported by the fact that a film at [fluorene]/[T3] = 4.8 indicated more intense CD spectra (max. $g_{CD} = (6.2 \pm 0.2) \times 10^{-4}$) than that at [fluorene]/[T3] = 3.2 (ESI, Fig. S9). The mixture at [fluorene]/[T3] = 4.8 indicated an endothermic signal of -38 J/g (per weight of fluorene) at 123 °C which suggests 56% of fluorene formed crystal (ESI, Fig. S10).

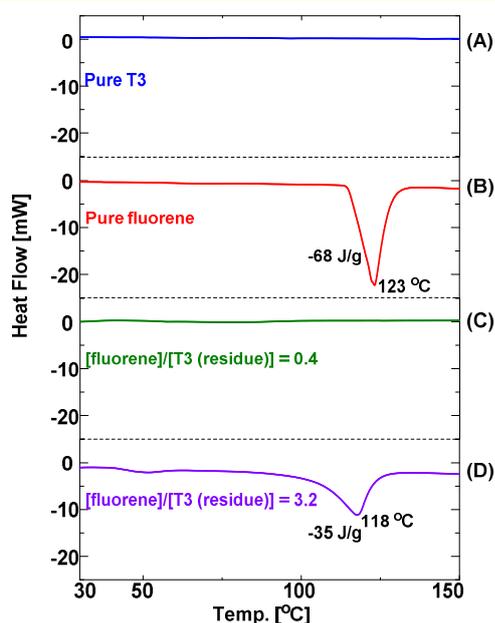


Fig. 3. DSC profiles of pure T3 (A), pure fluorene (B) and fluorene-T3 mixture at [fluorene]/[T3] = 0.4 (C) and 3.2 (D) obtained in the first heating scan at 10 °C/min.

It is noteworthy that the CD spectra of the fluorene-T3 film at [fluorene]/[T3] = 3.2 have clear vibronic structure which is absent in the CD spectra of PDOF.⁸ This observation implies

that T3 molecules in the presence of fluorene molecules and crystals are in a more rigid environment compared with PDOF. It is not yet clear and under investigation why only the CD spectra indicate vibronic structure and the UV spectra do not. A similar phenomenon with less clear vibronic structure has been reported for CD spectra of camphor.¹⁶

In addition to fluorene, phenanthrene was also found to be effective as an aid molecule in inducing chirality to T3 by CPL at [phenanthrene]/[T3] = 3.0 where phenanthrene was present partially in crystalline form (ESI, Figs. S11 and S12). This fact suggests that the aid-molecule method found in this work may be based on a variety of achiral, aromatic molecules.

In conclusion, chirality induction to T3 by CPL was successfully achieved in the presence of fluorene or phenanthrene as an achiral aromatic molecule. Although T3 alone could not be made optically active using CPL, probably due to the lack of strong intermolecular interactions, this point was circumvented by the use of fluorene or phenanthrene present in the mixed film samples in both amorphous and crystalline forms. In the case of fluorene, the amorphous molecules may enhance intermolecular π - π stacking interactions by occupying the gaps between T3 molecules, whilst the fluorene crystalline surface may act as a scaffold^{9a} to support the formation of a chiral structure of T3. The methodology presented here will expand the scope of properties and functions of polymeric materials through controlled interchain interactions.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Relative irradiation energy sum = $\sum_{i=0}^n \Delta t_i \times Abs_i$.
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