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Electronic Supplementary Information to:

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

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Experimental

Materials and film samples preparation. T3 was available from previous work from the Skabara group.[1] Analytical data of the sample are found in the supporting information to ref. 1. Fluorene (TCI) was purified by recrystallization with methanol. Film samples were made from a toluene solution containing T3 and fluorene at a ratio of fluorene to unit residue in T3 ([fluorene]/[T3]) of 0.4 or 3.2 or 4.8 or 28.9 corresponding to a weight ratio of fluorene to T3 of 0.19 or 1.7 or 2.5 or 15 and a molar ratio of fluorene to T3 of 4.3 or 38.5 or 57.7 or 346.6. T3 (3.0 mg) was dissolved in 1 mL toluene ("T3 stock solution") and fluorene (5.0 mg) was dissolved in 1 mL toluene ("fluorene stock solution"). The mixtures at [fluorene]/[T3] = 0.4, 3.2, 4.8, and 28.9 were made by mixing 0.9 mL of the T3 stock solution and 0.1 mL of the fluorene stock solution, 0.5 mL of the T3 stock solution and 0.5 mL of the fluorene stock solution, 0.4 mL of the T3 stock solution and 0.6 mL of the fluorene stock solution, and 0.1 mL of the T3 stock solution and 0.9 mL of the fluorene stock solution, respectively. The film samples were prepared by drop casting on to a quartz plate (1 cm x 2 cm x 0.1 cm). The film thickness was *ca*. 70 nm as measured using a Keyence VK8700 confocal laser microscope.

Measurements. Circular dichroism (CD) and linear dichroism (LD) spectra were taken with a JASCO-820 spectrometer. UV-vis absorption spectra were measured on a JASCO V-570 spectrophotometer. Emission spectra were taken using a JASCO FP-8500 fluorescence spectrophotometer. FT-IR spectra were measured with a Thermo Fischer Scientific Nexus 870 spectrometer. Differential scanning calorimetry (DSC) and thermal gravity analysis (TGA) were performed on a Rigaku Thermo Plus DSC8230 and a TG8120 analyser at a heating rate of 10 K/min under nitrogen atmosphere. Film temperature was measured using a Yokogawa non-contact emission thermometer 53002. Polarized optical micrographs were taken using a Nikon Eclipse E600 POL microscope.

CPL irradiation. CPL was generated by passing light from an Ushio Optical Modulex SX-UID500MAMQQ 500-W Hg-Xe lamp through a Gran-Taylor prism and a glass-construction Fresnel Rhomb (50 mW ($Jsec^{-1}$)). Irradiation experiments were conducted under N_2 atmosphere at ambient temperature (*ca*. 23 °C). Film surface temperature measured using a non-contact emission thermometer did not change on irradiation and stayed at *ca.* 23 ^{o}C.

CD and LD spectra measurements. CD and LD spectra were obtained by averaging those recorded at eight (45° interval) or two (horizontal and perpendicular) different film orientations (angles) with the film face positioned vertically to the incident light beam for measurement. Linear dichroism contributions were thus minimized to afford true CD spectra.

Attempted chirality induction to pure T3

A film made only from T3 was irradiated for 180 min with L-CPL, however, no clear Cotton effects were observed (Fig. S1).

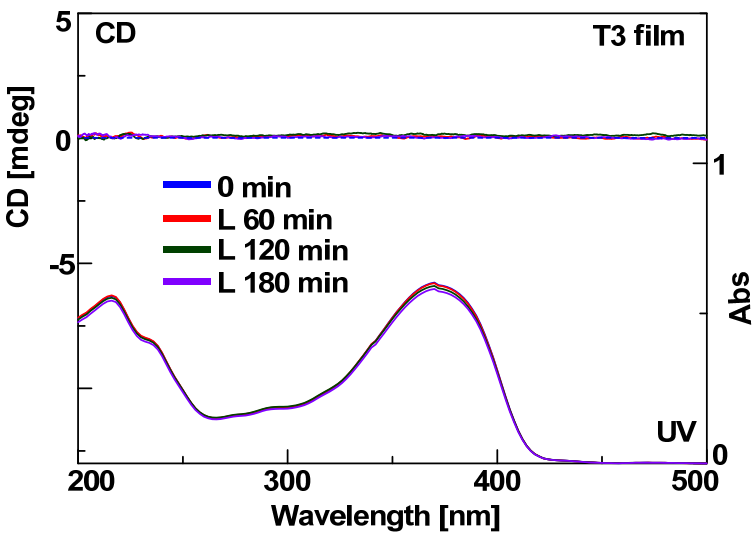


Fig. S1. CD and UV spectra of T3 film before and after irradiation using L-CPL during 0-180 min every 60 min.

IR spectra: chemical structures before and after CPL irradiation

In order to assess the possibility of chemical structural transformation on irradiation, FT-IR spectra of a film made [fluorene]/[T3] = 3.2 on a NaCl plate were measured before and after irradiation with L-CPL for 60 min. No obvious changes are observed between (C) and (D), indicating the chemical structure and composition of the film was almost unchanged through irradiation. Neither chemical reactions of T3 or fluorene or sublimation of fluorene is likely.

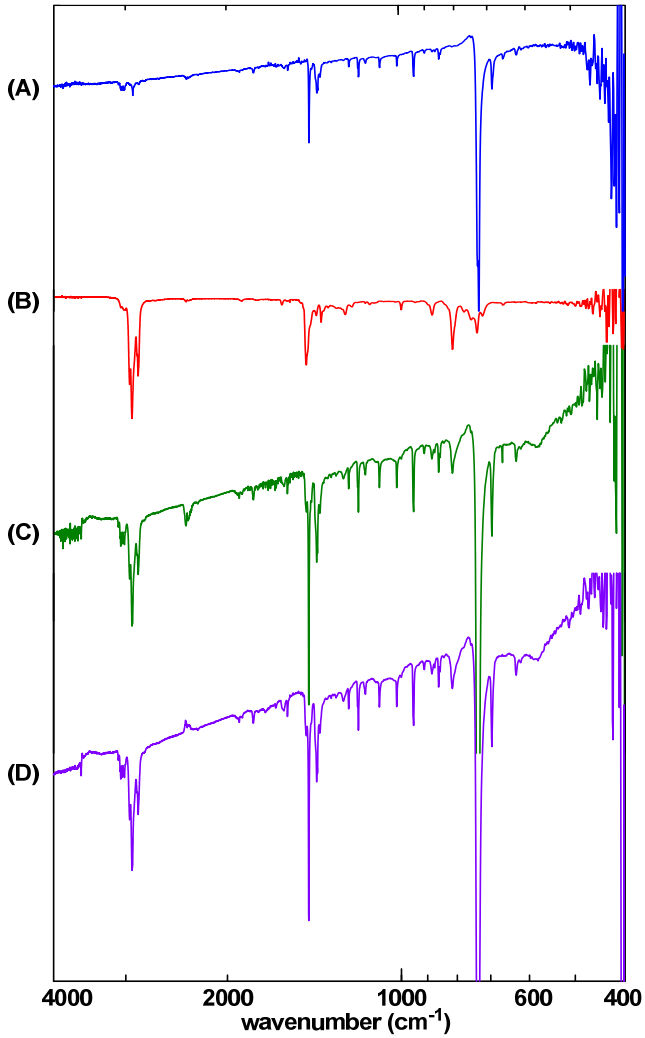


Fig. S2. FT-IR spectra of pure fluorene (A), pure T3 (B), a film at [fluorene]/[T3] = 3.2 before (C) and after irradiation using L-CPL for 60 min (D). [NaCl plate]

Chirality induction to fluorene-T3 film made on NaCl plate

The sample of (C) in Fig. S2 was subjected to chirality induction experiment. Clear CD spectra were observed on L-CPL irradiation, indicating that not only on quartz but also on NaCl chirality induction occurs.

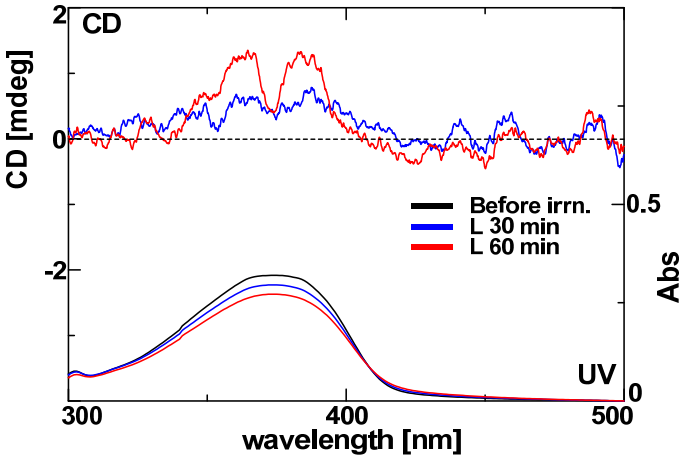


Fig. S3. The traces in CD and UV spectra of [fluorene]/[T3] = 3.2 film before and after irradiation using L-CPL for 60 min taken every 30 min.(NaCl plate)

LD spectra

No clear LD is observed in the region corresponding to the lowest-energy UV band before and after irradiation, indicating that the CD spectra observed after irradiation are not contributed by LD and reflects molecular chirality.

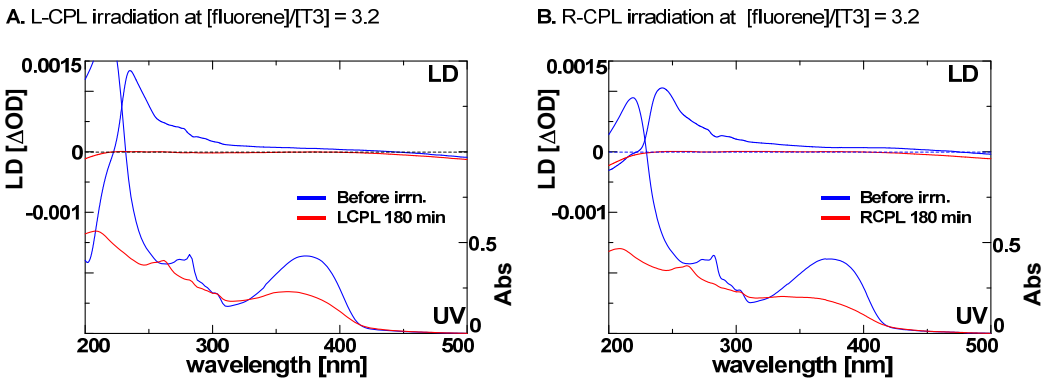


Fig. S4. LD and UV spectra of fluorene-T3 films made at [fluorene]/[T3] = 3.2 recorded before and after L-CPL (A) and R-CPL (B) irraditaion.

Switchable chirality induction to fluorene-T3 film at [fluorene]/[T3] = 3.2

A film made at [fluorene]/[T3] = 3.2 was completely CD-silent before irradiation. It indicated a positive CD band at around 380 nm after L-CPL irradiation for 30~60 min whose intensity increased with an increase in irradiation time, and this CD spectrum was inverted to a spectrum with a negative sign on irradiation by R-CPL for 60~90 min; the former and latter CD spectra were almost mirror images. The negative CD spectrum almost disappeared on further irradiation on L-irradiation for 60 min. These results indicate that chirality induction to fluorene-T3 film is reversible, and chirality of the film can be switched by changing handedness of CPL.

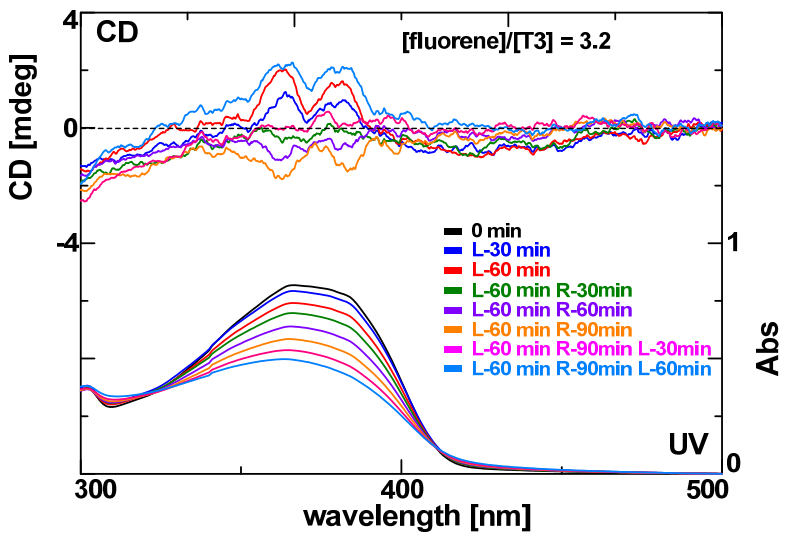


Fig. S5. Switchable chirality induction by CPL to [fluorene]/[T3] = 3.2 in film.

Changes in UV spectra through fluorene-T3 interactions in film

Peak maxima of pure T3 film and fluorene-T3 films at [fluorene]/[T3] = 0.4 and 3.2 were 370 nm, 372 nm, and 374 nm, respectively, suggesting that fluorene and T3 are well dispersed into each other and are interacting in the ground state.

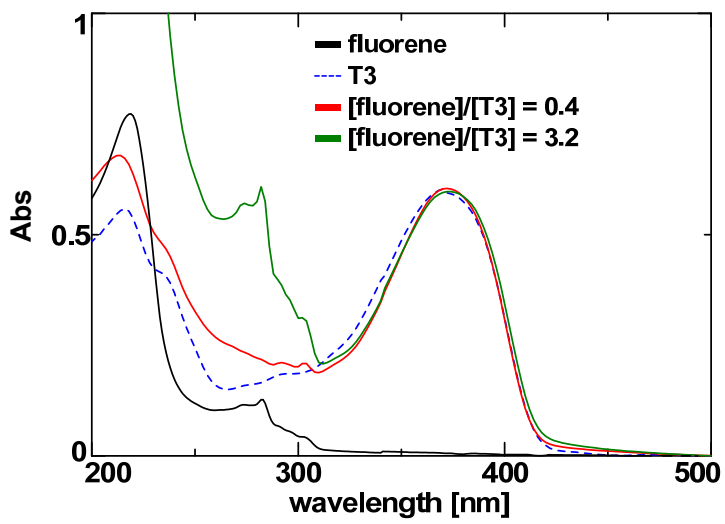


Fig. S6. UV spectra of pure T3 film, pure fluorene film, and fluorene-T3 film prepared at [fluorene]/[T3] = 0.4 and 3.2 taken before irradiation.

Changes in UV spectra through fluorene-T3 interactions in solution and suspension

In order to further confirm the interactions between fluorene and T3, UV spectra of pure T3 (Fig. S7A) and a fluorene-T3 mixture (Fig. S7B) were measured in a mixture of toluene and MeOH.

Pure T3 in toluene-MeOH:

A T3 stock solution at [T3] = 1.95 x 10^{-5} M was prepared by first dissolving T3 (3.0 mg) in 10 mL of toluene ([T3] = 7.81 x 10^{-5} M) and then diluting 1 mL of this solution by adding 3 mL of toluene. To 0.2 mL of the T3 stock solution, a total of 0.4 mL of MeOH was added stepwise where the amount of MeOH was increased by 0.05 mL per time. While no clear change was observed at the early stages of MeOH addition (0-0.25 mL), absorption largely decreased when the total amount of MeOH reached 0.3 ml and greater, suggesting that large aggregates formed due to insolubility. Evidentially, a new broad band appeared in the range of 400-500 nm. *The peak top of the T3's lowest energy band stayed at almost the same wavelength (370-371 nm).*

Fluorene-T3 in toluene-MeOH:

A stock solution of T3 at [T3] = 3.91 x 10^{-5} M was prepared by first dissolving T3 (3.0 mg) in 10 mL of toluene ([T3] = 7.81 x 10^{-5} M) and then diluting 1 mL of this solution by adding 1 mL toluene. A stock solution of fluorene at [fluorene] = 1.50 x 10^{-3} M by first dissolving fluorene (5.0 mg) in 10 mL of toluene ([fluorene] = 3.00 x 10^{-3} M) and then diluting 1 mL of this solution by adding 1 mL of toluene. A mixed solution at [fluorene]/[T3] = 3.2 was prepared by adding 0.1 mL of the fluorene stock solution to 0.1 mL of the T3 stock solution. A total of 0.4 mL of MeOH was added to this mixed solution stepwise where the amount of MeOH was increased by 0.05 mL per time. When the total amount of MeOH reached 0.3 mL, the system became opaque and absorption suddenly dropped, suggesting the formation of aggregates. *The peak top of the T3's lowest energy band shifted from 370 nm to 374 nm.*

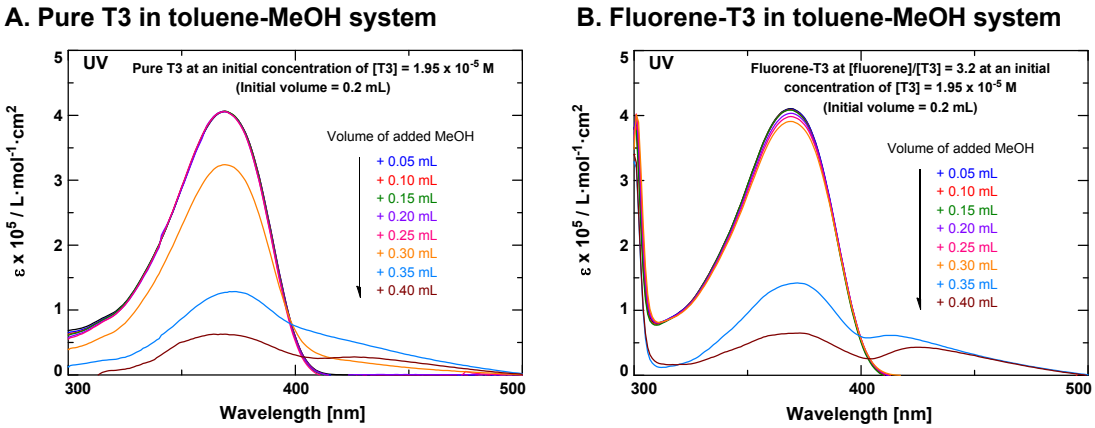
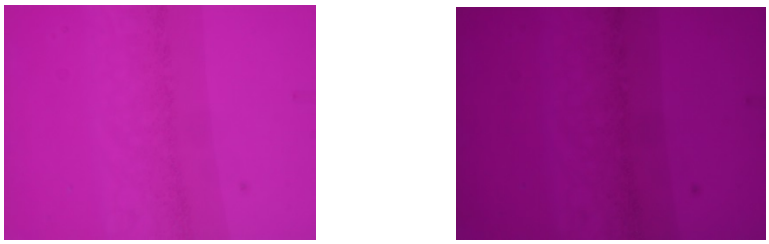


Fig. S7. Changes in UV spectra of pure T3 (A) and a fluorene-T3 mixture at [fluorene]/[T3] = 3.2 (B) in toluene-MeOH system where MeOH was added to toluene solution.

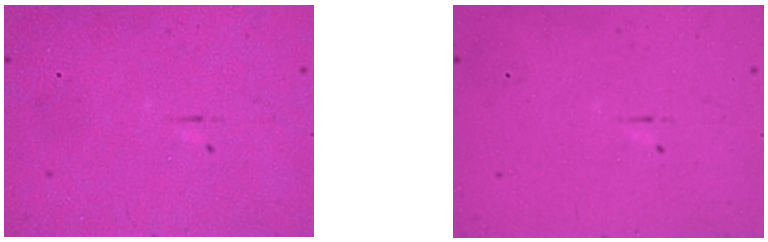
Polarized optical microscopic pictures of film samples

No clear crystal particles are observed in **A** and **B** while crystalline textures are indicated in **C**, **D**, and **E**.

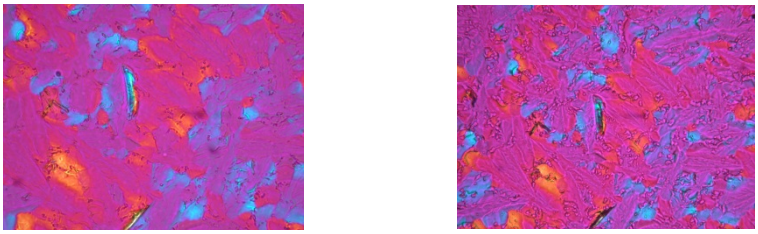
A. Pure T3, before (left) and after (right) L-CPL irradiation for 120 min



B. [fluorene]/[T3] = 0.4, before (left) and after (right) L-CPL irradiation for 180 min



C. [fluorene]/[T3] = 3.2, before (left) and after (right) L-CPL 180 min irradiation



D. [fluorene]/[T3] = 4.8, before (left) and after (right) L-CPL 120 min irradiation

E. [fluorene]/[T3] = 28.9, before (left) and after (right) L-CPL 180 min irradiation.

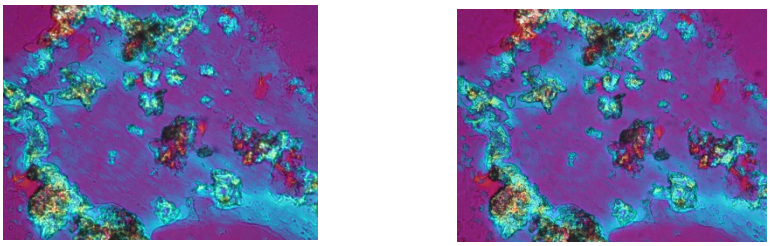


Fig. S8. Polarized microscopic photographs of films made at different [fluorene]/[T3] ratios taken with an objective lens of 20 magnifications using a 546-nm l/4 filter.

Chirality induction to fluorene-T3 film at [fluorene]/[T3] = 4.8

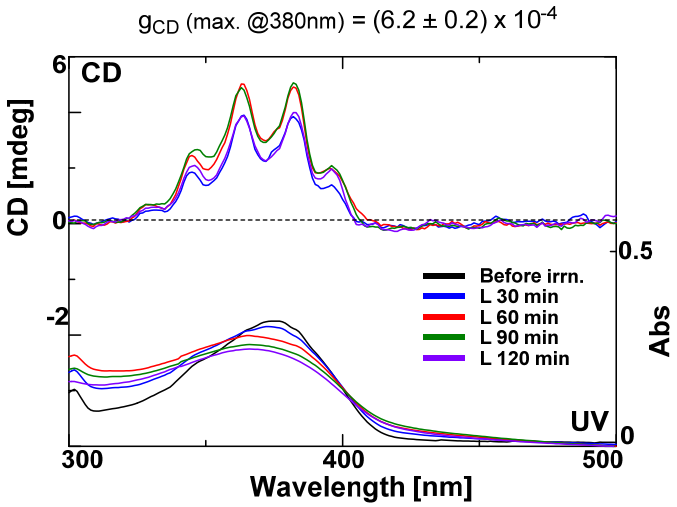


Fig. S9. CD and UV spectra of fluorene-T3 film prepared at [fluorene]/[T3] = 4.8 observed on L-CPL irradiation. The error range of g_{CD} value was estimated on the basis of the average noise level in the range of 495-500 nm.

Thermal properties (full results for all fluorene-T3 samples)

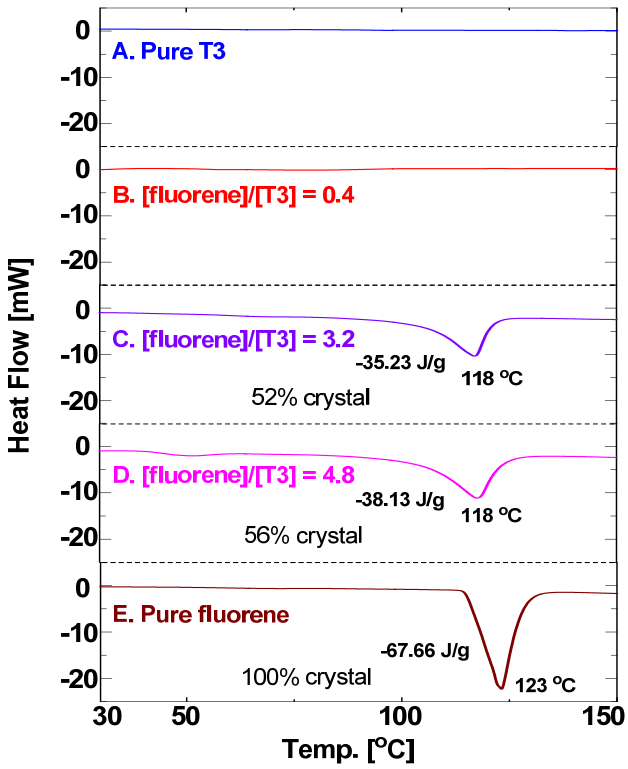


Fig. S10. DSC profiles of pure T3 (A), fluorene-T3 mixtures at [fluorene]/[T3] = 0.4 (B), 3.2 (C) and 4.8 (D), and pure fluorene (E) obtained in the first heating scan at 10 °C/min.

Chirality induction to T3 with phenanthrene as aid molecule

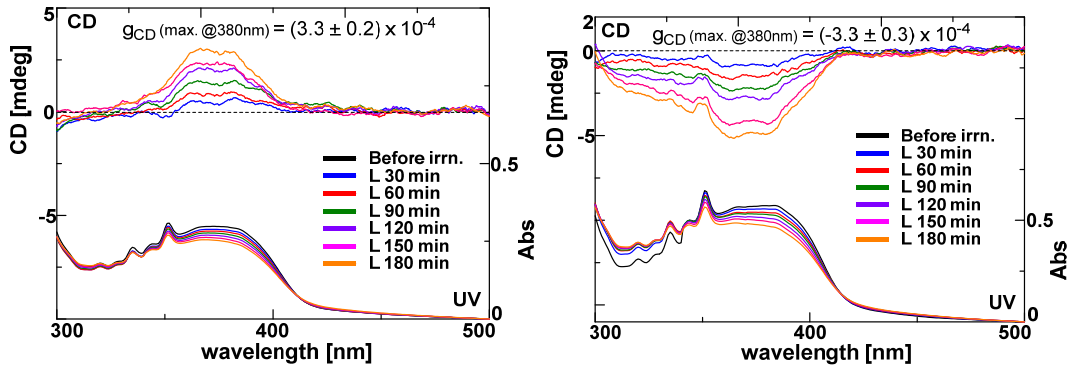


Fig. S11. CD and UV spectra of phenanthrene-T3 films prepared at [phenanthrene]/[T3] = 3.0 observed on L-CPL (left) and R-CPL (right) irradiation for up to a 180 min duration.

Thermal properties of phenanthrene-T3 mixture and related systems

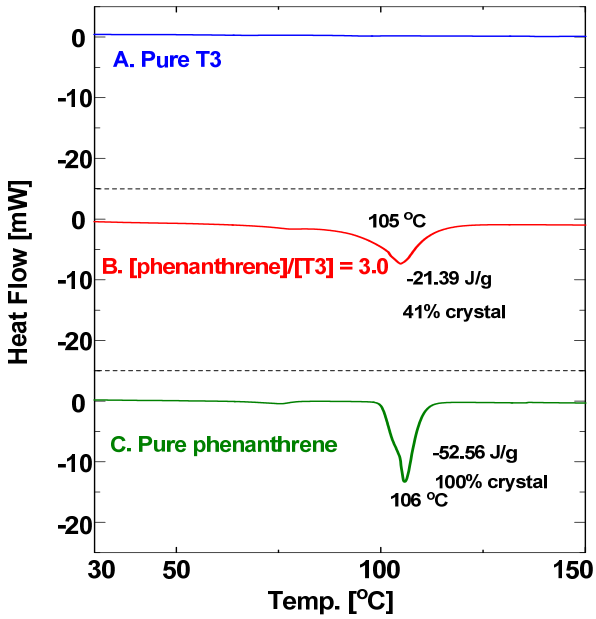


Fig. S12. DSC profiles of pure T3 (A), a phenanthrene-T3 mixtures at [phenanthrene]/[T3] = 3.0 (B), and pure phenanthrene (C) obtained in the first heating scan at 10 °C/min.

Reference

(1) A. L. Kanibolotsky, R. Berridge, P. J. Skabara, I. F. Perepichka, D. D. C. Bradley, M. Koeberg, *J. Am. Chem. Soc.*, 2004, **126**, 13695-13702.