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Solvent polarity driven helicity inversion and circularly polarized luminescence in chiral aggregation induced emission fluorophores†

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Development of functional materials capable of exhibiting chirality tunable circularly polarized luminescence (CPL) is currently in high demand for potential technological applications. Herein we demonstrate the formation of both left- and right-handed fluorescent helical superstructures from each enantiomer of a chiral tetraphenylethylene derivative through judicious choice of the solution processing conditions. Interestingly, both the aggregation induced emission active enantiomers exhibit handedness inversion of their supramolecular helical assemblies just by varying the solution polarity without any change in their molecular chirality. The resulting helical supramolecular aggregates from each enantiomer are capable of emitting circularly polarized light, thus enabling both right- and left-handed CPL from a single chiral material. The left- and right-handed supramolecular helical aggregates in the dried films have been characterized using spectroscopy, scanning electron microscopy, and transmission electron microscopy techniques. These new chiral aggregation induced emission compounds could find applications in devices where CPL of opposite handedness is required from the same material and would facilitate our understanding of the formation of helical assemblies with switchable supramolecular chirality.

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Introduction

Controlling handedness is a fascinating challenge that has attracted much attention over several decades worldwide.¹ Thus, much effort has been made to precisely control the chirality inversion of self-assemblies as well as to gain an understanding of the inversion mechanisms.² Primarily, scientists focused on handedness inversion originating from the breaking of the molecular chiral balance and simultaneous reestablishment of a new chiral balance with preferred handedness upon the action of stimuli such as heat,³ solvent,⁴ electrons,⁵ and redox.⁶ Adding an ionic⁷ or achiral matrix⁸ was also observed to induce chirality inversion of constructions.

Afterwards, researchers found that light driving *cis-trans* isomerization,⁹ open-closed cyclization,¹⁰ *etc.* can induce chirality inversion as well. So far most reported studies on chirality inversion, which originated from configurational transformation, have application prospects in life science,¹¹ nonlinear optics,¹² asymmetric catalysis,¹³ photoelectric devices,¹⁴ and so on.

It is known that the chiral supermolecules resulting from molecular or bulky group asymmetric stacking are among the most promising chiral materials due to their dynamic,¹⁵ stimuli-responsive¹⁶ and amplified chiroptical properties.¹⁷ In recent reports, supramolecular helicity inversion was found in chiral molecules with *cis-trans* configuration¹⁸ or multiple chiral centers.¹⁹ However, it is a challenge to control the handedness of the self-assembled supramolecular structures by regulating the molecular packing model especially from single chiral center molecules, for example, by modulating external parameters without changing the molecular chirality. In addition, chiroptical properties from chiral supramolecular assemblies are much stronger and more stable.²⁰ To induce or enhance the chiroptical properties, especially the circularly polarized luminescence (CPL), constructing a helical supramolecular assembly from fluorescent molecules is an attractive and efficient strategy.²¹

Here we disclose the formation of both left- and right-handed fluorescent helical superstructures from each enantiomer of a chiral tetraphenylethylene (TPE) derivative just by

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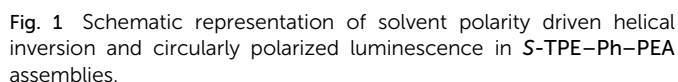
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Results and discussion

Scanning electron microscopy (SEM) was employed to obtain more detailed information on the morphologies of the

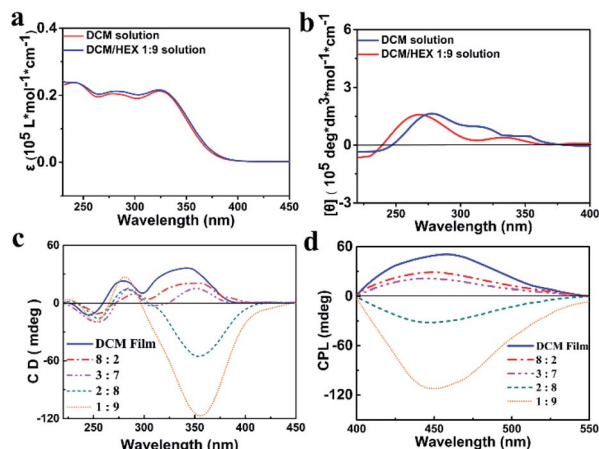


Fig. 2 Absorption spectra (5×10^{-6} M) (a); CD spectra in solution (b). CD spectra from solid films (c) and circularly polarized luminescence spectra (d) of *S*-TPE-Ph-PEA assemblies obtained from different solutions: DCM (blue); DCM/HEX 3 : 7 (cyan); DCM/HEX 2 : 8 (pink) and DCM/HEX 1 : 9 (red).

assemblies. Interestingly, increasing the hexane composition in the DCM solutions of *S*-TPE-Ph-PEA with a concentration of 1×10^{-4} M resulted in a morphological change from plate to disordered film and to helical fibers (Fig. 3). In DCM, the relatively hydrophobic *S*- and *R*-TPE-Ph-PEA molecules would already aggregate due to extended π -conjugation of TPE moieties (Fig. S1†).²² Upon increasing the hexane content in DCM to 20%, right-handed helical assemblies were found as shown in Fig. 3b. Moreover, after further increasing the hexane content to 80% and more, distinct left-handed helical fibers were observed (Fig. 3d and e) which would possibly form from the delicate balance between multiple noncovalent interactions such as hydrogen-bonding interactions, hydrophobic and hydrophilic interactions in DCM/HEX mixtures. Confirmed by SEM, *S*-assemblies in DCM/HEX (2 : 8 and 1 : 9) systems revealed distinct left-handed fibers. These supramolecular helical fibers are highly luminescent and emit circularly polarized light (Fig. 3f). Similar results were found for *R*-assemblies; left-handed helical assemblies were found in films obtained from a solution containing 20% hexane while right-handed helical fibers were formed in DCM/HEX (2 : 8 and 1 : 9) systems (Fig. S7†). For self-assembly from the DCM/HEX 1 : 9 system, a homogeneous screw pitch was determined to be *ca.* 140 nm with a width of about 30 nm for *S*-assembly, and around 190 nm with a width of *ca.* 40 nm for *R*-assembly.

The transmission electron microscope (TEM) studies presented sufficient evidence for the self-assembly process and the growth of helical fibers with inversed helicity in DCM/HEX (1 : 9) for both *S*-assemblies (Fig. 4) and *R*-assemblies (Fig. S6†). At the beginning (*ca.* 1 min), only slender fibers without a helical structure were observed. With the ongoing assembly process, obvious helical fibers with left-handed chirality were formed as shown in Fig. 4a (2 min). It was worth noting that smaller helical fibers assembled into larger helical fibers through entanglement with each other (Fig. 4b). Helical fibers for *R*-assemblies observed by TEM are shown in

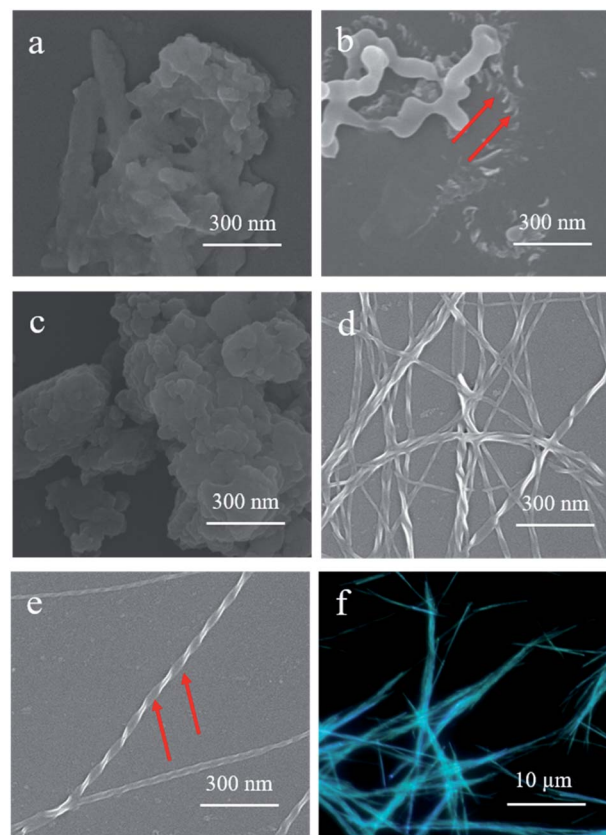


Fig. 3 SEM images of *S*-TPE-Ph-PEA assemblies in DCM/HEX with different ratios: (a) DCM, (b) 8 : 2, (c) 3 : 7, (d) 2 : 8 and (e) 1 : 9. (f) Confocal fluorescence microscope image of *S*-TPE-Ph-PEA assemblies in DCM/HEX with a ratio of 1 : 9.

Fig. S8.† At the end of the assembly process, larger nano-helical fibers were dramatically generated with a homogeneous width of about 27 nm and pitches to be *ca.* 130 nm for *S*-assembly, and about 35 nm and pitches around 160 nm for *R*-assembly. It was noted that the obvious helix structure was found only in fibers large enough because the surface tension interaction of solvent restricted the surface morphology.

Preliminary computational studies were carried out to understand the assembly of the compounds under different polarity conditions. As shown in Fig. S11–S21,† the rotation of two dihedral angles ϕ_1 and ϕ_2 would bring different conformations to both *S*- and *R*-TPE-Ph-PEA molecules. In view of

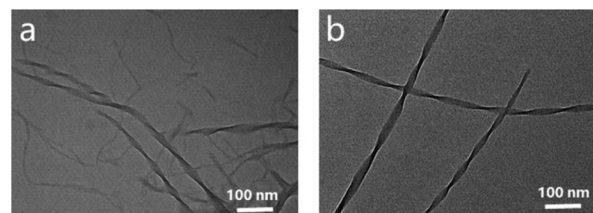


Fig. 4 TEM images of *S*-TPE-Ph-PEA assemblies from the DCM/HEX 1 : 9 system after self-assembling for 2 min (a) and 4 min (b), illustrating the formation and growth of helical fibers of *S*-TPE-Ph-PEA assemblies from solutions with a concentration of 1×10^{-4} M.



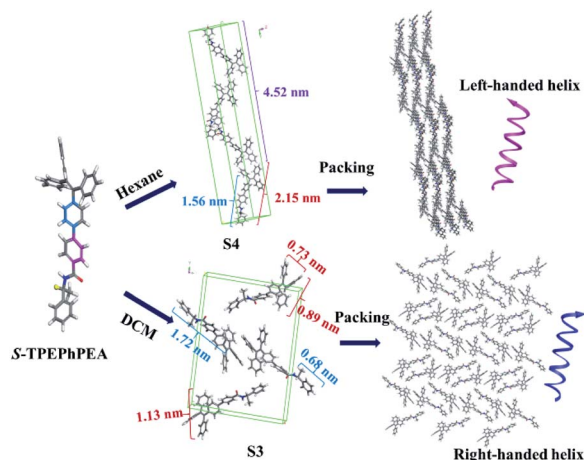


Fig. 5 Possible molecular assemblies computationally determined for *S*-TPE-Ph-PEA in DCM and hexane.

this, a computational study was carried out to determine the most stable conformers in different solvents. We carried out a potential energy scan (PES) on the **TPE-Ph-PEA** molecules by varying the degree of ϕ_1 and ϕ_2 (Fig. S12 and S13[†]). Considering all possibilities, four possible conformations for each enantiomer were found. These conformers were then optimized in solvation models with hexane and DCM and are summarized in Fig. S14 and S15.[†] From frequency analysis, the relative Gibbs free energies of each conformer were calculated and are summarized in Table S1.[†] When using DCM as a solvation model, **S3** and **R3** conformers were found to have the lowest energy for *S*-TPE-Ph-PEA and *R*-TPE-Ph-PEA, respectively, in which the dihedral angle ϕ_1 was found to twist by about 35° , while ϕ_2 twisted by about 90° . On the other hand, in the hexane solvation model, one conformer with the lowest energy was located, **S4** for *S*-TPE-Ph-PEA and **R4** for *R*-TPE-Ph-PEA, in which the dihedral angle ϕ_1 was found to twist by about -140° , while ϕ_2 twisted by about 90° . Since ϕ_1 , resulting from the C-C rotation between two phenyl rings, can lead to the formation of both *cis*-like and *trans*-like conformations of the chiral building blocks (Fig. S14[†]), it is believed to play a significant role in molecular packing in the helical assemblies during solvent drying which could induce the handedness inversion in such self-assembly systems. The non-covalent bonding interactions like intermolecular hydrogen bonding between the amide groups, π - π interaction, and C-H- π interaction could provide additional stability to these handedness invertible helical luminescent aggregates.

We envisioned that we could predict the possible packing models of *S*- and *R*-TPE-Ph-PEA molecules according to the experimental PXRD patterns, and thereby gain insight into the molecular packing of the assemblies. Computational models for the most stable conformer of *S*-TPE-Ph-PEA in hexane, **S4**, were minimized using the COMPASSII force field in different space groups, and the corresponding simulated XRD patterns were generated (Fig. S16[†]). It is shown in Fig. S17[†] that the simulated packing model for **S4** has a head-to-tail arrangement in a unit cell (b), and the molecules are packed to form a chain-

like structure with a left-handed helix (c). Similar simulations were performed to predict the possible packing models for compounds in DCM based on their experimental powder XRD patterns. The simulated XRD pattern is shown in Fig. S19.[†] It corresponds to the predicted packing model as shown in Fig. S20,[†] where the most stable conformer **S3** in DCM assembles into a right-handed form structure. Combining X-ray diffraction experiments of *S*-TPE-Ph-PEA assemblies (Fig. S9[†]) and a computational study in DCM and hexane, the possible mechanisms of molecular packing models of *S*-TPE-Ph-PEA were proposed to illustrate handedness inversion (Fig. 5) during assembly processes in different solutions. Interestingly, the lowest energy conformers **S3** and **R3** in DCM solution have *cis*-like conformation, while the lowest energy conformers **S4** and **R4** in hexane have *trans*-like conformation. Both **S3** and **S4** or **R3** and **R4** showed the same chirality as their corresponding molecular chirality in solution; however, the corresponding assemblies show handedness inversion after properly assembling during solvent evaporation due to different spatial structures of conformers. This exciting result gives a broad view to fabricate helical inversion systems that simply design one configuration chiral molecule with *cis*-like and *trans*-like conformations just by regulating their packing structures.

Conclusions

In summary, the realization of both left- and right-handed fluorescent helical assemblies from each enantiomer of a chiral aggregation induced emission active tetraphenylethylene derivative has been demonstrated by modulating the polarity of the processing solution without changing the molecular chirality. The *S*-enantiomer forms right-handed helical assemblies in more polar solution while left-handed helical assemblies are obtained from less polar solution for this enantiomer. Thus, the inversion of supramolecular chirality has been achieved in the system. The *R*-enantiomer exhibits a similar behavior. The driving force for such supramolecular assembly has been attributed to the rotation of the C-C bond between two phenyl rings and different types of molecular packing induced by different non-covalent interactions in assemblies. Moreover, the switching and enhancement of CPL emission were achieved by helicity inversion of the assemblies which is a challenging task but is highly desirable for device applications involving chirality switchable CPL. These results would provide new insights into preparing both left- and right-handed helical structures through building block conformation-controlled *cis*-like and *trans*-like components from the same chiral molecules, thus presenting broad potential applications in chemistry, materials science and life science.

Conflicts of interest

There are no conflicts to declare.

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