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Robust Angular Anisotropy of Circularly Polarized Luminescence from a Single Twisted-Bipolar Polymeric Microsphere

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ABSTRACT: It has long been surmised that the circular polarization of luminescence (CPL) emitted by a chiral molecule or a molecular assembly should vary with the direction in which the photon is emitted. Despite its potential utility, this anisotropic CPL has not yet been demonstrated at the level of single molecules or supramolecular assemblies. Here we show that conjugated polymers bearing chiral side chains self-assemble into solid microspheres with a twisted bipolar interior, which are formed via liquid–liquid phase separation and subsequent condensation into a cholesteric lyotropic liquid crystalline mesophase. The resultant microspheres, when dispersed in methanol, exhibit CPL with a g_{lum} value as high as 0.23. The microspheres are mechanically robust enough to be handled with a microneedle under ambient conditions, allowing comprehensive examination of the angular anisotropy of CPL. The single microsphere is found to exhibit distinct angularly anisotropic birefringence and CPL with g_{lum} up to ~ 0.5 in the equatorial plane, which is 2.5-fold greater than that along the polar axis. Such optically anisotropic solid materials are important for the application to next-generation microlight-emitting and visualizing devices as well as for fundamental optics studies of chiral light–matter interaction.

INTRODUCTION

Anisotropic light emitters display orientation-dependent optical and optoelectronic properties, which are valuable for applications such as liquid crystal displays,^{1,2} autostereoscopy,^{3,4} and low-threshold lasers.^{5,6} Supramolecular assemblies are typically inherently anisotropic at the nano- to micrometer scale due to their ordered molecular arrangement,^{7–9} which is appropriate for anisotropic materials. Helically assembled organic chromophores are representatives of chiroptical materials that show circular dichroisms (CD) and circularly polarized luminescence (CPL).^{10–12} Anisotropic circular dichroism (ACD) is well attested^{13–15} and has recently been applied to the study of supramolecular assemblies such as the light-harvesting complex.¹⁶ Compared to their isotropically averaged counterparts, ACD holds much more intrinsic information on the electronic states of molecules. This may be gleaned from the simple fact that even achiral molecules may display ACD under anisotropic conditions, which should cancel out when taking the orientational average.¹⁷

In contrast to CD, anisotropic CPL has not yet been demonstrated at the level of single molecules or supramolecular assemblies, though it has long been surmised. It is well known that chiral molecular assemblies display CPL with extremely high dissymmetry factors (g_{lum}), in some cases even as large as a half of pure circular polarized light.^{18–20} These giant dissymmetry factors have been attributed to long-range

helical order associated with cholesteric-like molecular arrangement,^{18–21} although this view has recently been contested.²² The reason that anisotropic CPL has seldom been addressed is plausibly because most of the reported CPL emitters were evaluated in either dispersions or thin-film states, which lack macroscopic order. Very recently, Tang et al. reported handedness-switching of CPL from a film of luminogen-doped disc-like chiral spherulite by a simple tilting with g_{lum} on the order of 10^{-2} .²³ However, it is in principle difficult to evaluate CPL with full-angle resolution from helical supramolecular assemblies lying in a film. Provided the anisotropy of CPL from a high g_{lum} emitter is correctly evaluated, we can draw out the full potential of the materials.^{24–26}

In this context, pixelated supramolecular CPL emitters, being micrometer-scaled self-standing objects, that radiate anisotropic, high- g CPL are highly desirable. Liquid crystals (LCs) are representatives of optically anisotropic and miniaturizable organic materials.^{8,27–34} LCs, dispersed in an immiscible medium, form a droplet with characteristic molecular orders

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Figure 1. (a, f) Molecular structures of (S,S)-PFBT (a) and (R,R)-PFBT (f). (b–e, g–j) SEM micrographs (b, g), optical micrographs (c, h), and POM micrographs (d, i) of μ -(S,S)-PFBT and μ -(R,R)-PFBT, respectively. Insets in (b) and (g) show histograms of the diameter d . Counterclockwise- and clockwise-spiral POM texture of μ -(S,S)-PFBT (e) and μ -(R,R)-PFBT (j), respectively. (k–o) Schematic representation of proposed molecular configuration in a self-assembled chiral microsphere (k) and its cross-section views at the x - z plane (l) and x - y plane (o). (m, p) TEM micrographs of a 80 nm thick slice of μ -(S,S)-PFBT, showing ellipsoidal (m) and circular black (p) stripes, overlapping with schematic molecular arrangements. Because of the slicing process, the disks are elongated toward the slicing direction. (n, q) POM micrographs of a 300 nm thick slice of μ -(S,S)-PFBT, showing ellipsoidal (n) and circular stripes with a Maltese cross (q) images. In the POM images, A and P indicate analyzer and polarizer, respectively.

such as angularly isotropic radial spherical phases (spherulites)^{35–38} and angularly anisotropic bipolar phases.^{39,40} However, these droplets are fluidic and, thus, difficult to handle in air without a supporting medium. From a materials point of view, mechanically stiff supramolecular materials with discrete, self-standing morphology are preferable.

In this article, for the first time, we present highly anisotropic novel CPL emitters from self-assembled polymeric microspheres. The solid microspheres are formed by a slow precipitation of π -conjugated polymers bearing chiral side chains through liquid droplet and lyotropic LC phases. Unlike typical polymer microspheres with isotropic internal structure, the resultant microspheres involve structurally anisotropic twisted-bipolar topology, where the polymer chains helically stack with one another to form cholesteric helicoids. The helical axis is mostly parallel to the equatorial plane, and the bipolar topological defect appears at the opposite points of the sphere surface. The suspension of the microspheres displays CPL with the average $|g_{\text{lum}}|$ value as high as 0.23. At a single-particle scale, the twisted-bipolar microspheres show clear

angularly anisotropic CPL with the $|g_{\text{lum}}|$ value of 0.50 toward the equatorial direction, which is 2.5-fold greater than that along the polar axis. The micrometer-scale chiral molecular objects with anisotropic CPL will be beneficial for applications to microchiroptical tools.

RESULTS AND DISCUSSION

Self-Assembly of Chiral π -Conjugated Copolymer. A π -conjugated polymer bearing chiral side chains, poly(9,9-bis((S)-3,7-dimethyloctyl)-2,7-fluorene-*alt*-benzothiadiazole), (S,S)-PFBT (Figure 1a), and its enantiomeric counterpart, (R,R)-PFBT (Figure 1f), were synthesized according to our previous reports^{19,41,42} and as detailed in this study, respectively (see Supporting Information and Figures S1–S3). The enantiomerically pure chiral PFBTs (c-PFBTs) display intense fluorescence bands at 538 nm in CHCl_3 and 553 nm in its film state (Figure S4), which is consistent with their achiral version (a-PFBT). We applied the previously reported versatile method to c-PFBTs for the formation microspherical particles (μ -c-PFBT).^{43,44} Typically, a small

Figure 2. (a) Optical micrograph of a μ -(S,S)-PFBT with a spiral texture (POM in the inset), picked up by a thin tungsten needle. (b, c) Schematic representations of angle-dependent POM analysis for in-plane (ϕ) rotation (b) and out-of-plane (θ) rotation (c). (d, e) Micrographs of angle-dependent POM textures of a μ -(S,S)-PFBT operated at in-plane rotation (d) and out-of-plane rotation (e). POM micrographs taken at $\theta = 0^\circ$, 40° , and 90° represent three simplistic kinds of POM features of μ -(S,S)-PFBT, namely, spiral texture (pink box), eclipse texture (green box), and ellipsoidal texture (blue box), respectively.

uncapped glass vial containing 500 μL of CHCl_3 solution of c-PFBT (initial concentration, $C_0 = 0.5 \text{ mg mL}^{-1}$) was set in a glass container that contained 2.5 mL of MeOH. The container was then sealed and stood at 25°C to allow the MeOH vapor to diffuse into the CHCl_3 solution of c-PFBT (Figure S5). In 48 h, c-PFBT precipitated to form a yellowish powder at the bottom of the small vial.

The morphology of the resultant powder is visualized by optical and scanning electron microscopies (OM and SEM, respectively). OM and SEM images of the air-dried precipitate show discrete microparticles with a smooth spherical morphology (μ -(S,S)-PFBT, Figure 1b and c). The average diameter (d_{av}) of the microspheres is $3.8 \mu\text{m}$ with a standard deviation (σ) of $0.65 \mu\text{m}$ (Figure 1b, inset). Similarly, precipitates obtained from (R,R)-PFBT feature microspherical morphology (μ -(R,R)-PFBT) with a d_{av} and σ of 3.2 and $0.42 \mu\text{m}$, respectively (Figure 1g and h).

Twisted-Bipolar Arrangement of c-PFBT in the Microspheres. Noncrystalline polymers tend to form amorphous aggregates upon precipitation and thus exhibit no birefringent texture in the polarized optical microscopy (POM) (Figure S6). In contrast, the prepared μ -c-PFBTs display apparent birefringent textures, as shown in Figure 1d and i, which indicate pronounced molecular order inside μ -c-PFBTs. To assign the internal molecular order, the μ -(S,S)-PFBT was sliced into thin sections with a microtome and observed by transmission electron microscopy (TEM) and POM. Prior to the slicing, μ -(S,S)-PFBTs were embedded in an epoxy resin at 25°C and stood for 72 h for curing.⁴⁵ The hardened resin was then cut into several thin slices with thicknesses of ~ 80 and $\sim 300 \text{ nm}$ for TEM and POM measurements, respectively.

TEM images of the sliced μ -(S,S)-PFBTs show either ellipsoidal or circular black stripes depending on the slicing orientation (Figure S7a,b). POM images of the sliced μ -(S,S)-

PFBTs show analogous texture with a Maltese cross (Figure 1n and q). The position of the Maltese cross and the stripes in the circular pattern does not change upon in-plane rotation of the specimens (Figure S8), while the ellipsoidal stripes alter their brightness periodically depending on the rotation angle (Figure S9). This indicates that the slices that show a Maltese cross have a microscopic structure with rotational symmetry and the slice plane is parallel to the equatorial plane (Figure 1o). On the contrary, the slices that show ellipsoidal stripes with rotational angle-dependent brightness are most likely cut along the longitudinal plane including the bipole (Figure 1l).

These textures are common with cholesteric LC droplets and have been assigned to a twisted-bipolar phase (Figure 1k).²⁷ Therein, the polymer chains helically stack with one another, and the helical axes radially direct from the core to the surface of the microsphere. Unlike a spherulite, where all polymer chains are along the radial direction, the helical axis of the bipolar phase is mostly parallel to the equatorial plane, and the bipole appears as structural defects at the opposite sides of the sphere surface (Figure 1l,o and 1m,p). The POM images of the μ -c-PFBTs, viewed from the polar direction, clearly display characteristic spiral textures with opposite handedness. Namely, the point chirality in the repeating unit of the polymer dictates the mesoscopic structural chirality (Figure 1e and j).^{10,11} To the best of our knowledge, this is the first example of self-assembled solid microspheres with twisted bipolar molecular order without an intricate solidification process such as thermosetting and photocuring.

In order to further confirm the bipolar arrangement, a single microparticle was picked up with a sharp and rotatable tungsten needle equipped on a micromanipulation apparatus (Figure 2a). The microsphere was directly subjected to POM observation with its spiral axis pointing toward the objective lens (Figure 2b). As shown in Figure 2d, the appearance of the spiral texture is virtually kept intact upon in-plane rotation,

Figure 3. (a–d) Schematic representation of the formation process of a twisted bipolar microsphere (d) from an isotropic solution (a) through a liquid droplet (b) and cholesteric lyotropic liquid crystalline mesophase (c).

which corresponds to the azimuthally rotated sphere viewed along the bipolar axis. On the other hand, the POM textures of the sphere, upon out-of-plane rotation (Figure 2c), turn from a spiral ($\theta = 0^\circ$, Figure 2e pink box) into an ellipsoidal texture ($\theta = 90^\circ$, Figure 2e blue box) via an eclipse texture ($\theta = 40^\circ$, Figure 2e, green box). The POM textures observed from the other directions feature intermediate textures (Figure S10). Altogether, the birefringence of individual μ -(S,S)-PFBTs is angularly anisotropic despite its spherical morphology. Consistently, μ -(R,R)-PFBTs display mirror-image textures (Figure S11).

Formation Process of the Twisted-Bipolar Microsphere. In order to gain insight into the formation process of the twisted-bipolar microspheres, we investigate the time-course of sphere formation.⁴⁶ An aliquot of (R,R)-PFBT solution was collected from the vial repeatedly in the course of the vapor diffusion and was subjected to observation by OM, POM, and SEM. Until 12 h of vapor diffusion ($t_{VD} = 12$ h), the solution is isotropic without any apparent precipitation (Figures 3a and S13a). In the meantime, the volume fraction of CHCl_3 (F_{CHCl_3}) in the polymer solution, which is calculated based on its ^1H NMR spectra, decreases to 0.53 due to the diffusion of MeOH.

At $t_{VD} = 13$ h ($F_{\text{CHCl}_3} = 0.48$), the solution gets turbid, and the optical density of the supernatant decreases drastically. This is caused by the liquid–liquid phase separation (binodal decomposition, Figure S14).⁴⁷ Before drying up, d_{av} of the spherical droplets is $1.6 \mu\text{m}$ (Figure S15). These particles are in the liquid state containing condensed polymer. The particles are isotropic and display no birefringence in POM images. The spherical morphology collapses when the liquid droplet was cast on a substrate and air-dried (Figures 3b and S13b,e).

At $t_{VD} = 14$ h ($F_{\text{CHCl}_3} = 0.43$), the droplets become semifluidic lyotropic liquid crystals. The POM image shows clear birefringence with twisted-bipolar character with a d_{av} of $3.4 \mu\text{m}$ (Figure S13f). These microparticles are spherical in the presence of the mother solvent but are irregularly distorted in the drying process on a substrate (Figures 3c and S13c,g). At $t_{VD} = 23$ h ($F_{\text{CHCl}_3} = 0.11$), the particles get hardened. The particles maintain their spherical morphology and the birefringent texture even after drying (Figure S13d), demonstrating the mechanical robustness of the particles (Figure 3d).

We conduct self-assembly of (R,R)-PFBT with various C_0 , in order to know the threshold of the initial concentration for the formation of twisted-bipolar microspheres (Figure S16). When C_0 is reduced from 0.5 mg mL^{-1} to 0.05 mg mL^{-1} , d_{av} of the

resultant microsphere decreases from $3.8 \mu\text{m}$ to $2.3 \mu\text{m}$, while the twisted-bipolar structure is still observed by POM. A further decrease of C_0 to 0.005 mg mL^{-1} reduces d_{av} to $0.64 \mu\text{m}$, and the POM image of the resultant spheres is too elusive to define the twisted-bipolar structure. Upon further reduction of C_0 to $0.0005 \text{ mg mL}^{-1}$, the spherical morphology is hardly observed after 27 h of vapor diffusion. Therefore, the threshold concentration to form a twisted-bipolar structure is in between 0.05 and 0.005 mg mL^{-1} .

In the course of the study on the size dependency of the molecular arrangement, we occasionally observe a radial spherical arrangement for microspheres with a d greater than $6 \mu\text{m}$. As confirmed by TEM and POM of the sliced μ -(R,R)-PFBT, the concentric spiral ring pattern and corresponding spiral texture are observed, which are characteristic of a radial spherical configuration (Figure S17). Generally in LC, radial spherical droplets tend to form when the radius of the droplet is greater than the helical pitch of the cholesteric mesogen.^{39,40}

Note that a kinetic self-assembly of (S,S)-PFBT, prepared by a mini-emulsion method, does not display a POM texture characteristic of a twisted-bipolar arrangement but shows polycrystalline textures (Figure S18). This result indicates that a slow assembly process is essential for the formation of the twisted-bipolar arrangement in the microsphere as a thermodynamic product.

Circularly Polarized Luminescence from PFBT Microspheres. We previously reported that thermal annealing of a spin-cast film of c-PFBT at 240°C results in the formation of cholesteric order, which shows circularly polarized electroluminescence with a $|g_{\text{lum}}|$ value of ~ 0.8 .¹⁹ Taking this result into account, we investigate the CPL properties of μ -c-PFBTs. As shown in Figure 4, the MeOH suspension of μ -(S,S)-PFBT shows remarkable CPL in the visible region (see the Supporting Information and Figure S19) with a negative g_{lum} value of -0.22 at 541 nm , while the suspension of μ -(R,R)-PFBT shows a mirror-image spectrum with a positive g_{lum} value of $+0.23$ at 541 nm . As a control, a suspension of μ -a-PFBT, prepared according to the reported method,⁴⁸ shows negligible g_{lum} values. On the basis of these results, we conclude that the left- and right-handed helical cholesteric orders emerge in μ -(S,S)-PFBT and μ -(R,R)-PFBT, respectively, even without thermal annealing treatments.

CPL spectra from individual microspheres (μ -CPL) are measured with a homemade microscopy setup (Figure 5a). Mechanically robust μ -c-PFBTs are manipulated with a sharp tungsten needle for further optical measurements. A single μ -c-PFBT is mounted on a quartz substrate and excited with a

Figure 4. Plots of the g_{lum} versus λ of a MeOH suspensions of μ -(S,S)-PFBT (red solid circles), μ -(R,R)-PFBT (red open circles), and μ -a-PFBT (blue triangles).

depolarized cw laser ($\lambda = 405$ nm). The emission from a μ -c-PFBT is collected through an objective lens (50 $\times$, NA = 0.42) at the opposite side of the incident laser and detected through a quarter wave plate and linear polarizer in a straight-line pass. Left- and right-handed CPL (I_L and I_R) are collected by adjusting the relative angle of the polarizer to $+45^\circ$ and -45° , respectively (see the Supporting Information and Figure 5b). Each CPL spectrum and CPL intensity are the average of five measurements with the polarizer angle of $+45^\circ$ and -45° .

Figure 5c and e show I_L (purple) and I_R (orange) profiles of μ -(S,S)-PFBT and μ -(R,R)-PFBT, respectively. The μ -(S,S)-PFBT displays stronger right-handed CPL than left-handed CPL with a g_{lum} value of -0.41 at 546 nm (Figure 5d).

Conversely, μ -(R,R)-PFBT emits left-handed CPL with a g_{lum} value of $+0.37$ at 546 nm (Figure 5f). CPL measurements of more than 20 particles show that μ -(S,S)-PFBT and μ -(R,R)-PFBT display mirror g_{lum} spectra with the average g_{lum} at 546 nm of -0.38 and $+0.39$, respectively (Figures S20 and S21). While the signs of g_{lum} values coincide with those obtained from their MeOH suspensions, the $|g_{lum}|$ values detected with the μ -CPL system are larger than those observed from the MeOH suspension of the microspheres. We note that the excitation geometries are different (in-line vs right angle) and that photoselection effects and perhaps selective scattering may contribute to the suspension measurements. Also note that LP light affects the $|g|$ values in the range of 0.0015–0.034 (Figure S22), which is virtually negligible in comparison with the $|g_{lum}|$ value from a single twisted-bipolar microsphere (0.18–0.55).

We then conducted angular-dependent CPL measurements by putting a single μ -c-PFBT on a microneedle and rotating it around an axis perpendicular to the bipolar axis (θ -direction, Figure 6a). As shown in Figure 6c, the altitudinal polar coordinate of $|g_{lum}|$ values plotted against θ (altitudinal angle from the bipolar axis) shows a highly anisotropic profile, where the highest $|g_{lum}|$ value of ~ 0.49 was obtained at a θ of 90° and 270° (orthogonal to the bipolar axis). On the other hand, the minimum $|g_{lum}|$ value of ~ 0.18 is observed at $\theta = 0^\circ$ and 180° (parallel to the bipolar axis). Analogously, the angular-dependent CPL profile in the equatorial plane is measured by rotating a microsphere around the bipolar axis (ϕ -direction, Figure 6b). The $|g_{lum}|$ values are kept virtually constant upon rotation in the range from 0.40 to 0.51 with an average value of 0.47 (Figure 6d). This value coincides well with the maxima in the meridional profile (Figure 6c).

Figure 5. (a) Schematic representations of the experimental setup of CPL measurement from a single microsphere. A single microsphere was excited by a depolarized CW laser ($\lambda_{ex} = 405$ nm). PL from a single microsphere passes through a quarter wave plate (working range: 465–610 nm), a polarizer (working range: 400–700 nm), and a long-pass filter (working range: >450 nm) in a straight-line pass. (b) Schematic representations of the detection mechanism of left- and right-handed CPL (I_L and I_R) by adjusting a polarizer at $+45^\circ$ and -45° , respectively. (c, e) PL spectra of a single μ -(S,S)-PFBT (c) and μ -(R,R)-PFBT (e) with the direction of the polarizer at $+45^\circ$ (purple, I_L) and -45° (orange, I_R). (d, f) g_{lum} spectra of μ -(S,S)-PFBT (d) and μ -(R,R)-PFBT (f).

Figure 6. (a, b) Schematic representations of the experimental setup of CPL measurement from a single microsphere. A single microsphere was picked up at a tip of a microneedle orthogonal (a) and parallel (b) to the bipolar axis. (c, d) Altitudinal (c) and azimuthal (d) polar coordinates of $|g_{lum}|$ at 546 nm values of μ -(S,S)-PFBT.

The remarkable angular anisotropy of $|g_{lum}|$ in the meridional plane and isotropic profile in the equatorial plane are consistent with the twisted-bipolar molecular order in the microsphere, where the helical axis orients orthogonal to the bipolar axis. Emission that goes along these helical axes experiences the periodic modulation of the local linear birefringence characteristic of the cholesteric arrangement, leading to the typical chiroptical traits of this arrangement. The θ -angle dependency of g_{lum} fits well with a sine curve (Figures S23b, broken curve, and S23a), indicating that scattering efficiency of CPL by the chiral cholesteric helix is a function of the angle between the helical axis and the detection (Figure S23b). μ -(R,R)-PFBT displays a θ -angle-dependent g_{lum} plot that is substantially identical with that of μ -(S,S)-PFBT as a mirrored sine curve (Figure S23a and c). In contrast, with rotation around the bipolar axis (ϕ -angle dependency), no such modulation occurs and circular differentials will be less pronounced.^{19,42} As a result, the dissymmetry of CPL along the bipolar axis is rather small. This angle-resolved examination of the CPL allows us to confirm the ordered structure of the twisted bipolar molecular arrangement in the interior of the self-assembled microsphere. It is important to note that such comprehensive examination of the angular anisotropy of CPL is not possible without the high mechanical stiffness of the microspheres.

CONCLUSIONS

We demonstrate spontaneous precipitation of π -conjugated polymers bearing enantiopure chiral side chains into well-defined microspheres. They remain robust even after the complete removal of the mother solvents. Since the particle formation process involves a lyotropic liquid crystalline mesophase, the resultant solid sphere forms with a twisted-bipolar molecular arrangement in the interior. Photoluminescence from the spheres features circular polarization with g_{lum} as high as 0.23 in the suspension state due to the handedness-selective light scattering by the helically stacked polymer main chains. Despite its spherical morphology, the degree of circular

polarization is anisotropic due to the twisted-bipolar arrangement, where CPL toward the equatorial direction shows the maximum g_{lum} value of 0.5, which is 2.5-fold higher than that along the bipolar axis. The micrometer-scale particles with anisotropic chiroptical properties are attractive not only for applications as a minute CPL emitter but also for an object of fundamental optics studies of chiral light–chiral matter interaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c03185>.

Materials and methods, synthesis and characterization, spectroscopy, and microscopy data (PDF)

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Author Contributions

E.W.M. and Y.Y. conceived the idea; O.O., H.Y., and Y.Y. designed the experiments; C.K. prepared materials; O.O. performed self-assembly and characterizations; O.O., C.K., S.C.J.M., Z.H.L., and J.S.H. conducted the CPL experiments; O.O., H.Y., J.S.H., S.C.J.M., E.W.M., and Y.Y. prepared the manuscript.

Notes

The authors declare no competing financial interest.

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