

Emergent non-reciprocal circularly polarized emission from an organic thin film

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Abstract

Controlling circularly polarized (CP) emission is key for both fundamental understanding and applications in the field of chiral photonics and electronics. Here, a completely new way to achieve this goal is presented. A luminescent thin film, made from a chiral conjugated phenylene bis-thiophenylpropynone able to self-assemble into ordered structures, emits highly circularly polarized light with opposite handedness from its two opposite faces. Such emergent non-reciprocal behaviour in CP emission, so far unprecedented, represents a fundamental advance, opening new opportunities in design, preparation and applications of CP emitting materials.

Main text

Harnessing circularly polarized (CP) emission from molecular systems opens the way to new opportunities in chirality sensing,^[1] chiral templating,^[2] CP-electrochemiluminescence^[3] and CP-OLEDs.^[4] In the flourishing field of chiral photonics and electronics, new ways for more thorough control of CP light generation are desirable.^[5] To widen the scope of applications of CP emitting systems, a material capable of CP emission with opposite handedness depending of the direction of the emitted light would have major implications. This would require an apparent breaking of CP emission reciprocity, that is inverting the handedness of CP light upon reversal of the emitted light wavevector.^[6] So far, organic materials featuring non-reciprocal CP emission have never been explored. Here we show that upon thin film deposition, a designed chiral molecule self-assembles in aggregates displaying a very high degree of emergent non-reciprocal CP absorption and emission, making it possible to achieve a new type of CP emitting functional material.

Recently, we showed that some relatively rigid π -conjugated systems (such as benzo[1,2-*b*:4,5-*b'*]dithiophene-based^[7] or 1,4-phenylene-based^[8] oligothiophenes) bearing chiral side-chains can form thin films displaying non-reciprocal CP absorption^[7-9] that is an almost complete inversion of the handedness of the CP component preferentially transmitted by the two opposite faces of the sample. This is practically observed as an apparent electronic circular dichroism (ECD) signal which changes sign by flipping the film sample by 180° with respect to light propagation axis. This is due to a significant coupling between linear dichroism (*LD*) and linear birefringence (*LB*), while *emergent* LD or LB are negligible. Such phenomenon is made possible by the peculiar aggregates formed by the molecules upon film deposition and annealing, whereby their linear anisotropies average to zero on the large (from 1 mm on) scale, while their combination does not.^[6, 10] Thanks to this unique mechanism, relatively large absorption dissymmetry factors g_{abs} (defined as $2(A_L - A_R)/(A_L + A_R)$, A_L and A_R being the left

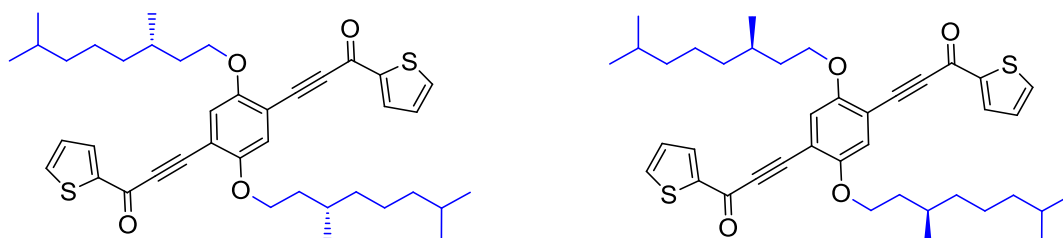
and right CP component of the absorption) in the emergent ECD spectrum can be obtained, typically falling in the 10^{-2} – 10^{-1} range.

On the other hand, non-reciprocal CP emission, although theoretically expected, was never observed, probably due to the lack of compounds able to self-assemble in suitably ordered structures and to display significant emission in aggregate form.^[11] This was also the case of the above-mentioned compounds, which were completely quenched in solid state and in thin films. Despite this lack of experimental evidence so far, such properties would be extremely useful in terms of dissymmetry factor enhancement thanks to its underlying mechanism, tunability and spatial and directional control of CP emission. This would provide a functional material capable of opposite handedness CP emission from the two opposite faces without resorting to stacking different layers such as additional chiral coatings,^[12] acting as opposite CP-sensitive band rejection filter. Indeed, CP generation and control is key to achieve the forecasted applications such as optical data storage,^[13] CP-laser^[14] and better performing CP-OLEDs^[15] furthering the emergent field of chiral electronics and photonics. The CP emission reported here is not related to the commonly reported CP luminescence (CPL), which stems directly from the intrinsic chirality of the system (molecules or their supramolecular structures).

In the literature, various ways are reported to control the chirality of an emitting system and therefore the handedness of regular CPL, e.g. interaction with cations,^[16] light irradiation^[17] or upon pH^[18] or solvent change.^[19] Moreover, in other thin film materials, optical phenomena, such as circular scattering, result in changes in the handedness of CPL,^[20] even though the precise mechanism remains to be fully determined. On the other hand a direction-dependent circular polarization in the emitted light is unprecedented.

Given the context, in order to experimentally demonstrate emergent non-reciprocal CP emission, we synthesised a π -conjugated molecule, PTPO (phenylene bis-thiophenylpropynone, Scheme 1), decorated with chiral aliphatic side-chains deriving from naturally occurring β -

citronello^[21] (see Supporting Information for synthetic details). Such compound displays an extended electronic conjugation together with a relatively rigid structure of the conjugated core. The intrinsic chirality of the compound alone is not sufficient to give rise to any significant chiroptical property of the isolated (solvated) molecules, in absorption (ECD) or in emission (CPL), but it is necessary to lead the aggregation into ordered dissymmetric structures upon thin film deposition, where ECD and possibly CP emission may become relevant.^[22]



Scheme 1. Structures of (*S,S*)-PTPO (left) and (*R,R*)-PTPO (right).

With such compound in hand, we prepared spin-coated films of PTPO, deposited onto a transparent glass substrate, under optimized conditions (Figure S1 and Table S1, Supporting Information). Then the films underwent thermal annealing at 80 °C (compound melting point 95-97 °C), to allow for the necessary molecular mobility. This treatment spontaneously leads to a thermodynamically favourable arrangement of the molecules in the thin film,^[23] which is responsible for all the chiroptical properties herein described. The films appeared homogeneous and semi-transparent (OD around 0.36, T ~40% at 444 nm, and T>90% above 500 nm, thickness 300 nm).

Firstly, we noticed that PTPO thin films displayed a bright emission in the green region (λ_{max} 512 nm, Figure S2), making them good candidates for CP emission measurements. Then, in order to prove non-reciprocal CP emission, the following experiment was designed: the film

was excited using a non-polarized 0° illumination between excitation and emission and the luminescence was collected from the same face of the film (Figure S4). The excitation beam (365 nm) size was sufficiently large to illuminate the thin film almost completely (around 5 cm^2). In this way, it is possible to reliably measure independently the luminescence circular polarization stemming from the two faces of the film: with the coated side facing the excitation source/detector (*forward* configuration) or, oppositely, with the uncoated face oriented towards the excitation source/detector (*backward* configuration). Therefore, in these two configurations, the wavevector of the emitted light propagates in opposite directions with respect to the film surface (Figure 1d). Indeed, when (S,S)-PTPO films were placed facing the detector (forward), an intense negative CP emission signal (λ_{max} 505 nm) was detected throughout the emission spectrum.

Interestingly, when the circular polarization of the emission was measured in the backward configuration (with the uncoated side of the film facing the detector), an opposite (positive), signal was obtained. The signal was mirror-like with respect to the forward CP emission, that is it displayed the same shape and the same maximum wavelength (Figure 1b).

The degree of CP emission was quantified using the dissymmetry factor $g_{\text{lum}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, where I_{L} and I_{R} are the left and right CP component of the emission respectively. Importantly, forward CP and backward CP emission displayed opposite but same order of magnitude g_{lum} factors: -0.15 ± 0.01 for forward configuration and $+0.09 \pm 0.02$ for backward one, calculated on the CPL maximum (505 nm, Figure 1b). Such figures, on the upper range for aggregated (non-cholesteric) films prepared from organic materials (see Table S2),^[11b, 24] are due to the peculiar mechanism generating the CP emission (see below). The g_{lum} factor is fairly constant throughout the emission region, but it shows a maximum around 475 nm (forward $g_{\text{lum}} = -0.23 \pm 0.03$, backward $g_{\text{lum}} = +0.12 \pm 0.03$) suggesting the presence of more than one contribution under the relatively simple emission spectrum (Figure 1b). Such properties were measured on

several samples from independent preparations to check for consistency and reproducibility (see error bars in Figure 1b). This confirmed the robustness of both film preparation and measurement techniques employed.

At this point, care was taken to demonstrate that such non-reciprocal CP effect in emission, was free from instrumental artefacts or spurious effects. Fluorescence linear anisotropy was measured and determined to be negligible with respect to the total measured signal (below 3%, see Figure S5). Such contribution would be reciprocal (i.e. invariant in forward and backward configuration) but sign-changing upon sample rotation around the optical axis. As a further confirmation, CP emission spectra were recorded at different film rotations to ensure that no significant variations were present (Figure S6).

The chiroptical analysis was then carried out in absorption. ECD spectra were recorded on the same films in forward (coated side facing the illumination) and backward (coated side facing the detector) configuration (see Figure 1c). Again, the direction of the irradiating wavevector is opposite in the two configurations. As expected, (*S,S*)-PTPO, showed predominantly negative bands in the forward configuration, while it was completely inverted (mainly positive bands) in backward configurations. In both configurations the emergent ECD signals recorded were particularly intense. In fact, the absorption dissymmetry factor g_{abs} was -0.19 ± 0.03 and $+0.17 \pm 0.03$ at 465 nm for forward and backward configuration respectively (Figure 1c). These values are relatively high in comparison with other π -conjugated systems displaying non-reciprocal CP absorption.^[7-9] Again, a rotation of the sample around its optical axis did not show any significant variation in the emergent ECD spectrum indicating no significant net contribution from linear components (Figure S8). This is consistent with the weak LD of the sample (Figure S9). Moreover, no significant trace of scattering is visible in the ECD or in the absorption spectra.

To further confirm the phenomenon, the enantiomer compound (*R,R*)-PTPO was synthesized (Scheme 1) and its films investigated in the same manner. As expected, ECD and CP emission measured in forward configuration were positive, that is opposite with respect to (*S,S*)-PTPO, while they were negative in backward configuration. On the other hand, no significant change in the spectral shape of ECD and CP emission was observed (Figure S10). Small differences in the magnitude of g_{abs} and g_{lum} obtained with the two enantiomers are due to a lower optical purity of the starting (*R*)- β -citronellol with respect to the (*S*) enantiomer.

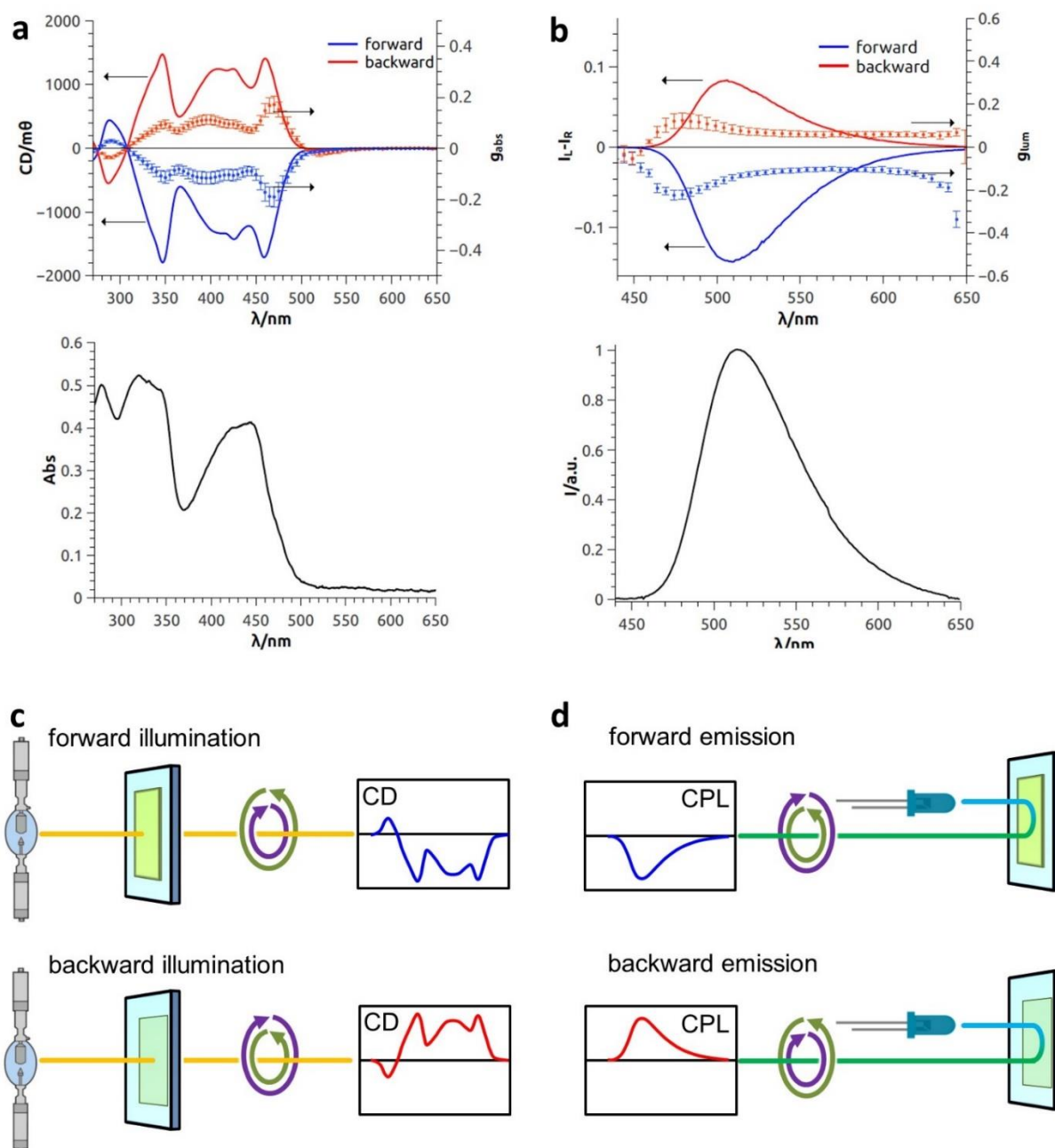


Figure 1. a: ECD, g_{abs} values and absorption spectrum of thermally annealed (*S,S*)-PTPO films in forward and backward configuration. **b:** CP emission, g_{lum} values and emission spectrum of the film in forward and backward configuration (excitation 365 nm). The error bars on g_{abs} and g_{lum} values represent one standard deviation calculated over 5 replicates. Bottom: cartoon illustrating forward/backward measuring conditions for ECD (**c**) and CP emission (**d**).

For completeness, the chiroptical behaviour and morphological characteristics of the non-annealed, as-cast films were studied as well. ECD spectra show almost identical shape and sign in forward and backward configurations at lower energies, while they show already some hint of non-reciprocal CP absorption below 350 nm (Figure S11 and S12). Similarly, a difference in

CP emission spectra between forward and backward configuration is observable: forward CP emission spectrum displays a negative band (for (*S,S*)-PTPO) with a g_{lum} around $-9 \cdot 10^{-2}$ at 503 nm, while in backward configuration no significant signal is recorded at 503 nm, but a small opposite band is visible at 470 nm ($+1 \cdot 10^{-2}$, see Figure S11 and S12). We note that the as-cast film (i.e. before annealing) has not reached yet the thermodynamic equilibrium and therefore the observed spectral features are due to kinetic/metastable aggregation modes.^[23]

The morphological characterisation confirms the effect of the thermal annealing. Non-annealed films display a surface entirely formed by needle-like crystals (100x500 nm), as visible in atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) images (Figure S13). Upon thermal annealing, such features completely disappear, giving rise to step-terrace structures (see discussion below).

At this point an explanation for the observed non-reciprocal behaviour was looked for. Analogously to non-reciprocal CP transmission,^[6, 25] emergent non-reciprocal CP emission in the present sample may be rationalized taking into account the presence of a significant coupling between fluorescence linear anisotropy (f) and linear birefringence (LB) giving rise to an emergent CP emission.^[5b] Such contribution is odd by wavevector inversion and therefore the film displays CP emission with opposite polarization from its two faces. This is not in contrast with the absence of a net fluorescence linear anisotropy from the sample, as the film may consist of several domains, each of them with a random orientation, effectively averaging out to zero the overall linear contribution. On the other hand, coupling between f and LB does not vanish out as it depends only on the reciprocal position of f and LB vectors and not by their orientation on the film surface (see the mathematical modellization in the Supporting Information).

Such view is strongly corroborated by optical and electron microscopy images of the films. FE-SEM images show that the film bulk is made of distinct grain-like domains (50-100 μm size), clearly separated by boundaries (Figure 2a). Each domain displays a clear orientation on the film surface, as indicated by the regular and persistent parallel striping pattern within each grain (Figure 2a and S15), compatible with locally non-vanishing f and LB (Figure 2c). On the other hand, each grain is randomly oriented with respect to the other ones. As the grains are much smaller than the illuminated film surface from which emission is collected ($\sim 10^4$ grains contributing to the emission), no net linear contribution in the emission is observed. Moreover, a clear birefringence pattern compatible with the size of the grains ($\sim 100 \mu\text{m}$) is observed as well in cross polarized optical microscopy (Figure 2e), through which a relatively large area (around 2.5 cm^2) is investigated. This indicates that the grain-like structure is persistent over the whole film. FE-SEM images at higher magnification reveal that the parallel stripes are around $2.5 \mu\text{m}$ apart. Between the stripes, at an angle, the above-mentioned step-terrace structures emerge ($\sim 2 \mu\text{m}$ size) clearly visible in FE-SEM (Figure S15) and more in details in AFM images ($1 \times 1 \mu\text{m}$ portion of the film, see Figure 2b). Moreover, AFM profiling allows one to appreciate the stacking of such structures at around 2.5 nm (Figure S16). In Figure S17, we show the size relationship between images obtained from the different microscopies employed in this work. Finally, grazing incidence X-ray diffraction indicates long-range order at about 20.5 \AA (Figure S18), associated to lamellar-like structures stacked parallel to the film surface, which is compatible with the step-terrace structures observed by AFM.

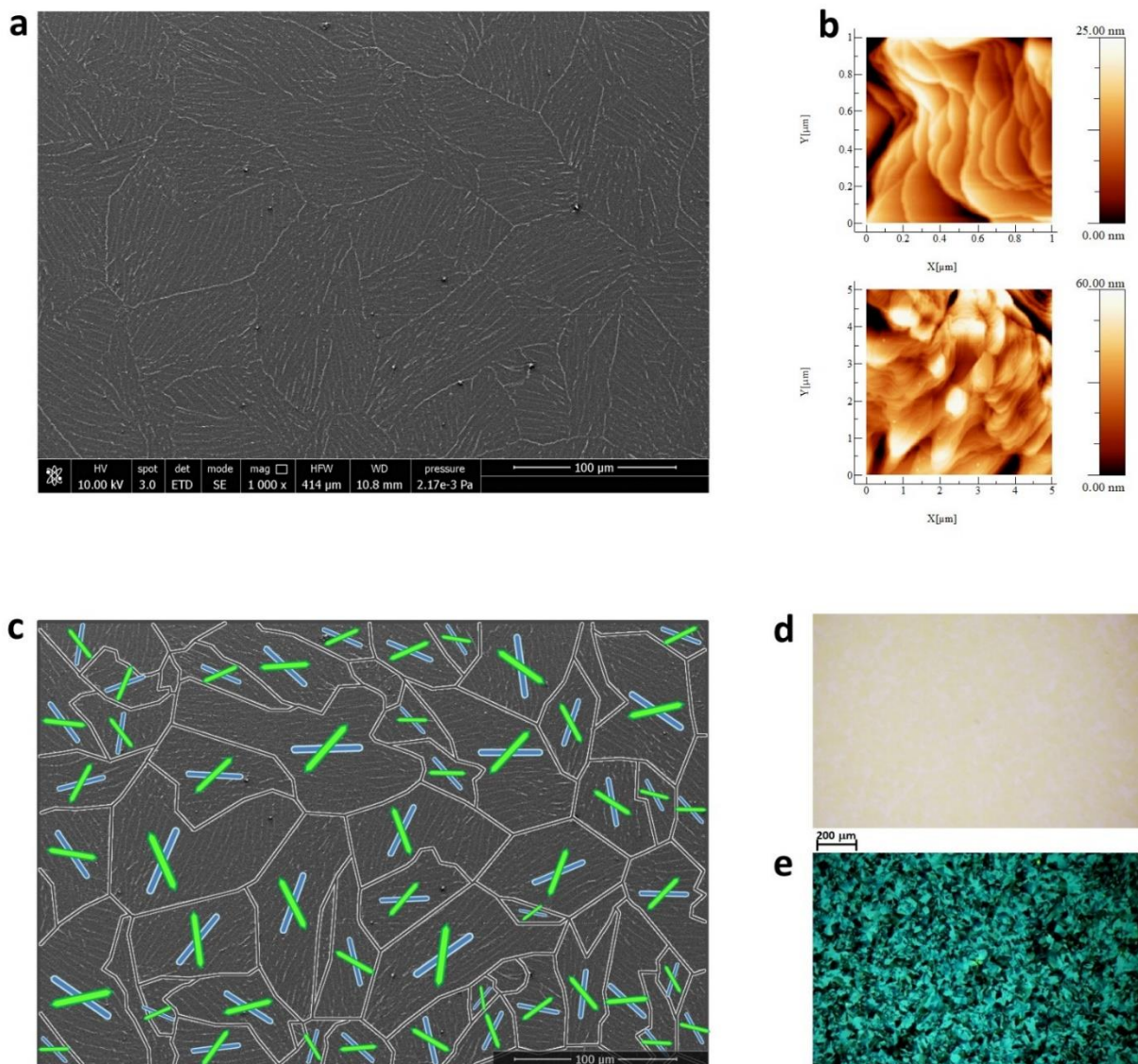


Figure 2. **a:** FE-SEM image of a thermally annealed film of (*S,S*)-PTPO. **b:** AFM images of portions of the film. **c:** cartoon showing an elaboration of the FE-SEM image, with grain boundaries highlighted and a pictorial representation of oriented *f* (green sticks) and *LB* (blue rods) within each grain; blue rods are oriented along the striping pattern, while the angle with green sticks chosen arbitrarily. Bottom right: bright field (**d**) and crossed polarized (**e**) optical microscopy images of the film.

We are not unaware that a possible application of materials displaying non-reciprocal CP emission may be in CP-OLEDs, where opposite forward and backward polarization may be beneficial in avoiding depolarization upon reflection on the device electrode (see discussion in Supporting Information).^[15, 26]

In conclusion, we have presented an unprecedented example of emergent non-reciprocal CP-emission thanks to a molecule able to self-aggregate in thin film forming peculiar structures. In the present example, front and back film surfaces display almost enantiomer-like behaviour in terms of circular polarization of emitted and absorbed light. This phenomenon is not related to commonly reported CP luminescence, but if carefully engineered and measured, it allows for control of optical activity in emission within the same thin film and we believe that materials displaying such properties will benefit the promising field of chiral electronics and photonics.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Emergent Non-Reciprocal Circularly Polarized Emission from an Organic Thin Film

The thin film of a chiral π -conjugated phenylene derivative emits circularly polarized (CP) light with high degree of dissymmetry and opposite handedness from the two opposite faces of the film. Non-reciprocal CP emission is unreported so far, and it offers unprecedented opportunities in the design of CP emitting materials.

