Anomalous circularly polarized light emission in organic light-emitting diodes caused by orbital–momentum locking

Li Wan, Yizhou Liu, Matthew J. Fuchter & Binghai Yan

Chiral circularly polarized (CP) light is central to many photonic technologies, from the optical communication of spin information to novel display and imaging technologies. As such, there has been significant effort in the development of chiral emissive materials that enable the emission of strongly dissymmetric CP light from organic light-emitting diodes (OLEDs). It has been widely accepted that the molecular chirality of the active layer determines the favoured light handedness of the CP emission in such devices, regardless of the light-emitting direction. Here we discover that, unconventionally, oppositely propagating CP light exhibits opposite handedness, and reversing the current flow in OLEDs also switches the handedness of the emitted CP light. This direction-dependent CP emission boosts the net polarization rate by orders of magnitude by resolving an established issue in CP-OLEDs, where the CP light reflected by the back electrode typically erodes the measured dissymmetry. Through detailed theoretical analysis, we assign this anomalous CP emission to a ubiquitous topological electronic property in chiral materials, namely orbital–momentum locking. Our work paves the way to design new chiroptoelectronic devices and probes the close connections between chiral materials, topological electrons and CP light in the quantum regime.

Chirality characterizes parity-symmetry breaking where a molecule cannot be superposed on its mirror image in chemistry and biology. Chiral enantiomers exhibit opposite chiroptical activity when coupling to light. In physics, chirality usually refers to the spin–momentum locking of particles such as Weyl fermions and CP light. Chiral organics have recently been reported to exhibit a topological feature, in which the electronic orbital and momentum are locked together, to rationalize the intriguing spin selectivity in DNA-type molecules. Hence, given the intimate relationship between electronic states and light–matter interactions, we were inspired to raise a question: can topological electronic properties (that is, orbital–momentum locking) enhance the chiroptical activity and therefore advance the rapidly developing (chiro)optoelectronic technology?

A future industrial application of organic chiral emissive materials is in circularly polarized organic light-emitting diodes (CP-OLEDs), which should eliminate the ~50% internal light loss caused by the contrast-enhancing circular polarizer in OLED displays. Such efficiency gains occur via direct circularly polarized electroluminescence (CP-EL) from the CP-OLED, which can pass through the contrast-enhancing polarizer unhindered. The effectiveness of this strategy depends on...
the degree of circular polarization of the electroluminescence (EL), where a higher polarization gives a better efficiency for the display in the presence of such polarizers. Since the first CP-OLED reported in 1977, the CP-EL of a material was also assumed to be identical to the circular polarization measured in the absorption and the photoluminescence (PL) (that is, cases without current flow) from the same electronic transition. In other words, CP-EL was considered to be nearly the same process as circularly polarized photoluminescence (CP-PL) [or the inverse process of optical circular dichroism (CD)] due to a shared electronic transition, and the magnitude of the CP emission was determined as the product of the electric and magnetic transition dipole moments. Thus, most efforts in this field have been made in developing more twisted chiral emitters with stronger magnetic transition dipoles to improve the optical chirality, without taking current flow in an OLED device into consideration.

More importantly, in terms of device engineering, the reflective back electrode in an OLED device is another key issue. In all previous studies of chiral emissive materials, CP emission is conventionally expected to exhibit the same handedness in each emission direction (forward and back) from the point of recombination, thus any back reflection within the device will invert the handedness of the CP emission travelling backwards and cancel out the forward CP emission, reducing the net EL circular polarization that exits the device through the transparent electrode. Consequently, the magnitude of EL circular polarization from devices is much smaller than the corresponding CP-PL measured in transmittance geometry, which does not suffer issues of reflection (Fig. 1a). Even though constructing semi-transparent OLEDs can, to some extent, mitigate the problem of reflection, such a strategy reduces the overall device performance in displays, negating the original intention of energy saving at the polarizer.

Among all CP-OLEDs reported and many other chiral optoelectronic devices based on two-dimensional and perovskite materials, chiral polymeric materials demonstrate significant circular polarization in their PL and EL that is several orders of magnitude stronger than other chiral emissive systems (see Fig. 2a). Despite the analysis above, when constructing optoelectronic devices from such materials, their CP-EL remains equal, or sometimes is even enhanced compared to CP-PL or CD. Although previous theoretical and experimental work attributed the strong optical CD to a predominately excitonic origin, these analyses cannot account for the comparable or enhanced circular polarization in EL devices, given the expected detrimental effect of back-electrode reflection.

In this work, we discover an anomalous light-emission phenomenon from chiral polymeric CP-OLEDs. For the chiral polymeric materials under study, CP-EL exhibits opposite handedness in the forward and backward emission directions, which is counterintuitive to that usually expected in EL or PL (Fig. 1b). With such direction-dependent CP emission, the back-reflected light exhibits the same handedness as the forward emission, avoiding the polarization cancellation that occurs in devices using other materials and boosting the net CP-EL that exits the device. Furthermore, we explain the effect of current flow on CP-EL, where its handedness can also be switched by reversing the current flow in an OLED. We propose that the directionality of CP-EL observed is caused by the topological nature of the electronic wavefunctions in chiral polymers. Because of orbital–momentum locking, the current flow induces non-equilibrium orbital polarization in the electron and hole carriers. Therefore, finite angular momentum transfers from the electron/hole orbital to the photon spin in the optical transition. When they have the same spin, the counterpropagating CP light emissions exhibit opposite handedness. This orbital polarization effect rationalizes the fact that
handedness of CP light is determined by both the current direction and the emission direction. Furthermore, this model reveals an exotic CP-EL mechanism caused by current-induced time-reversal breaking. Our work paves the way to design novel chiroptoelectronic devices with strong circular polarization.

Results

A chiral polymer blend consisting of an achiral light-emitting polymer (that is, FSBT (poly(9,9-diocetylfluorene-alt-benzothiadiazole))) and a non-emissive chiral additive (that is, [P]-aza[6] helicene (see Fig. 1c, d insets)) was selected for investigating the CP-EL. Upon thermal annealing of spin-coat thin films, the chiral additive (10 wt%) induces a strong and robust chiral structure and optical CD to the originally achiral polymer with an absorption dissymmetry factor (\(g_{\text{abs}}\)) of -0.6 (see Supplementary Fig. 1), calculated in the following way:

\[
g_{\text{abs}} = \frac{A_L - A_R}{A} = \frac{\Delta A}{A},
\]

where the subscripts L and R stand for left- and right-handed CP light, respectively, and \(A\) refers to the absorbance. To investigate how the emission direction affects the CP-EL, CP-OLEDs were fabricated using both conventional and inverted device structures (Fig. 1c, d), where the transparent electrode indium tin oxide (ITO) serves as the anode and cathode, respectively.

With a fixed direction of current flow (Fig. 1c, d), when measuring the EL through transparent ITO, left-handed CP light is observed in a conventional device where the light emits in the same direction as the electron injection. A positive EL dissymmetry factor (\(g_{\text{EL}}\)) of +0.54 can be calculated following:

\[
ge_{\text{EL}} = \frac{k_L - k_R}{(k_L + k_R)/2},
\]

where \(k_L\) and \(k_R\) denote the irradiance recorded from the CP-OLEDs. However, despite a fixed absolute stereochemistry of the chiral material in the emissive layer of both devices, the sign of the CP-EL signals was found to be dependent on the device structure. When the emission direction relative to the current direction is switched, the inverted CP-OLED emits right-handed CP light through ITO with a \(g_{\text{EL}}\) of -0.33. Apart from the emission-direction-dependent CP-EL signals in conventional versus inverted devices, we detected no evidence of the erosion of \(g_{\text{EL}}\) by the reflective electrodes. Compared with other reported CP-OLEDs, the polyfluorene-based CP-OLEDs we developed exhibit one of the highest known \(g_{\text{EL}}\) values (Fig. 2a). By contrast, lanthanide complexes exhibit intrinsically high PL dissymmetry factor (\(g_{\text{PL}}\)) values, but the \(g_{\text{EL}}\) recorded from the transparent electrode of lanthanide-based CP-OLEDs decreases dramatically when increasing the thickness of the reflective metal electrode. This is similarly observed in other small-molecule CP-OLEDs (Fig. 2b).

To compare our results with other previously reported CP-OLEDs, we performed CP-EL measurements on semi-transparent OLEDs with both conventional and inverted device structures (Fig. 2c). Surprisingly, emission-direction-dependent CP-EL behaviour was observed in both device structures, where the CP-EL from forward and backward emission (that is, through a semi-reflective electrode) exhibits opposite
handedness. Considering that this emission-direction-dependent dissymmetry factor is only observable in EL but not for the CP-PL or CD of chiral thin films (Supplementary Fig. 2), we speculate that this behaviour is associated with the flow of charge carriers within the devices. To unambiguously describe and compare the emission-direction-dependent CP-EL signals in the two device architectures, we define the emission direction relative to the charge-carrier flow direction (Fig. 2c). Specifically, emission from the transparent ITO in the conventional device and the emission from semi-transparent Au in the inverted device are defined as being directionally aligned with the electron flow. Conversely, emission from the opposite electrodes in conventional and inverted devices is defined as being directionally aligned with the hole flow. In contrast to other chiral emitters in OLED devices,20,23,24 we find that the $g_{\text{EL}}$ value of net emission from the transparent electrode increases when increasing the thickness of the reflective electrode (Fig. 2b,d) for our chiral polymeric materials. As summarized in Fig. 2d, regardless of the device structure used, F8BT:[P]-aza6 helicene-based CP-OLEDs demonstrate a positive $g_{\text{EL}}$ when emission occurs along the direction of electron flow, and switch to negative $g_{\text{EL}}$ when emission occurs along the direction of hole flow. This indicates that the previously observed inversion of the CP-EL sign from conventional versus inverted devices (see Fig. 1) is due to emission-direction-dependent CP-EL relative to the direction of electron flow. Given this outcome, the reflective electrode in our system results in reflected light with an identical sign to the forward emission, resulting in a comparable or boosted net CP-EL signal (Fig. 2b).

**Discussions**

**Experimental summary**

Our CP-EL data exhibit profound features, which are distinct from those obtained using other chiral emitters in OLEDs (Fig. 2b). Besides the extremely large $g_{\text{EL}}$, the CP-EL handedness can be switched by both the current-flow direction and the light-emission direction. By carefully examining the optical elements in our blend thin films,19, the sign inversion observed here is not caused by either linear effects (that is, linear dichroism and/or linear birefringence) or CP scattering. There are negligible morphological changes when the film is cast on the poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or ZnO layer, which suggests that the active-layer morphology is identical between the conventional and inverted devices (Supplementary Fig. 5). Previously, for CP-OLEDs constructed from other materials, the position of the recombination has been reported to affect the magnitude of the CP-EL.20,27 In our conventional devices, using an electron-transport layer of TBPb (2,2′-bithiophene-5,5′-diyl) (TPB), which has a lowest unoccupied molecular orbital (LUMO) of −2.7 eV, we generate a larger electron-injection barrier from Ca (≈ 2.9 eV) than would be the case when directly depositing Ca onto F8BT (LUMO = 3.3 eV). We observe the TPB emission in our EL spectra, which indicates that the recombination zone in our conventional devices occurs at the F8BT/TPB interface, away from the ITO electrode. Similarly, in our inverted OLEDS, TCTA (4,4′,4″-triphenylamine) was used to shift the recombination to the F8BT/TCTA interface until the observation of the interface recombination (Supplementary Fig. 6). Therefore, through careful selection of the contact and transport layers, the recombination zones in both devices were pinned physically at the far interface of F8BT, away from ITO electrode. This ensures that the CP-EL sign inversion investigated here is not caused by the previously reported active-layer thickness/recombination zone25,27 but instead by the current direction (see the sign-unchanged data in Supplementary Fig. 7).

By ruling out other origins, we demonstrate that the CP-EL handedness inversion is sensitive to both the current-flow direction and the light-emission direction. In other words, the emitted photon seems to retain a memory of the propagating direction of recombining electrons and holes, despite the fact that the initial carrier velocities are usually ignored to understand the light-emission process.28 Such an outcome indicates the salient current-flow-induced breaking of time-reversal symmetry (TRS) in the system. The exciton-coupling model22,23 is based on quantum states with TRS and cannot explain such CP-EL that is dependent on the current and emission directions.

**Theoretical model**

It is known that the helicene additive promotes the F8BT polymer to form chiral assemblies in solid-state thin films23,24. The chiral polymer blend is the real-space channel for both current flow and light emission. In the following, we will discuss the light emission in the presence of TRS breaking due to the current flow.

We will first revisit the general theory that describes the CP emission effect and interpret our experiments from an anomalous term. According to Fermi’s golden rule, the emission rate of CP light is

$\tilde{I}_{\text{L/R}} = \frac{2e^2}{h} |\langle 0 | H | 1 \rangle|^2 \delta(\epsilon_1 - \epsilon_0 - \hbar \omega), \tag{3}$

where $|0\rangle$ ($|1\rangle$) represents the ground (excited) state with energy $\epsilon_0$ ($\epsilon_1$), $\hbar \omega$ is the photon energy (where $\hbar$ is Planck’s constant/2π), $\delta$ is the Dirac delta distribution, and $H$ is the light–interaction Hamiltonian (where $H = -eE \cdot \mathbf{r} - m \mathbf{B}$, with $m$ being the magnetic moment, $e$ being the electron charge, $\mathbf{r}$ being the position, and $\mathbf{E}$ and $\mathbf{B}$ being the light electric and magnetic fields, respectively). For right-/left-handed light traveling along the $z$ axis, the electric and magnetic fields are $\mathbf{E} = E_0(\mathbf{1}, \pm i\mathbf{1}, 0)/\sqrt{2}$ and $\mathbf{B} = E_0(c \mathbf{1}, \pm i\mathbf{1}, 0)/\sqrt{2}$, respectively. Therefore, the leading term of CP light emission can be derived as

$\tilde{I}_l - \tilde{I}_h = -\frac{2e^2}{h} I_0 \text{Im}(x^{01} x^{10}) \delta - \frac{2e^2}{hc} I_0 \text{Im}(m_1^{01} x^{10} + m_1^{10} x^{01}) \delta, \tag{4}$

where $x^{ij}$ is the transition $\Delta \epsilon_i$.

**Fig. 3 | Illustration of orbital–momentum locking and the ACPE.** a. The wavefunction $\langle \psi |$ of the electron confined in an achiral box can be regarded as a superposition of counterpropagating plane waves, $\langle \psi | = e^{ik\mathbf{r}}$. b. The wavefunction in a chiral box can be regarded as a superposition of counterpropagating chiral plane waves, $\langle \psi | = e^{ik\mathbf{r}} \epsilon^l$. Here, $\epsilon^l$ carry opposite OAM values ($\pm \hbar$), that is, $\psi^l$ share the same electronic chirality induced by the box chirality. Black arrows represent the propagating direction ($\mathbf{k}$) and the helix-like trajectories indicate the circular polarization emitted from the excited state |1⟩ to the ground state |0⟩, where |0⟩ carry zero OAM. The angular momentum transfer in the transition $\Delta l = 0$, thus the zero net spin of light leads to the same handedness in the emitted light along two directions. Subscripts ‘e’ and ‘h’ denote electron and hole, respectively. d. Anomalous circular polarized emission from |1⟩ to |0⟩, where |0⟩, |1⟩ carry finite OAM. Because $\Delta l$ is finite, oppositely emitted lights carry the same spin and exhibit opposite handedness. e. Reversing the current flow with respect to d switches the handedness of the CP light.
where \( x^{\text{el}} = (0, x | 1 \rangle \) and \( m^{\text{m}} = (0, m_y | 1 \rangle \) represent the electric and magnetic transition dipoles, respectively, and \( l_c = |E_c|^2 \). We note \( m = (m_x, m_y, m_z) \), \( r = (x, y, z) \) and \( \delta \) for the same \( \delta \)-function in equation (3).

The second term in equation (4) is routinely employed to understand CD, CP-PL or CP-EL for organic/inorganic systems and has been called natural chiroptical activity. Because it corresponds to an interaction with the electric and magnetic fields of light, this term involves both electric and magnetic transition dipoles. We call it the normal circular polarization effect (NCPE) in the following. In chiral organic molecules, the orbital angular momentum (OAM) change in the transition is zero because TRS forces the net OAM of \([0, 1] \) to be zero. Due to the conservation of angular momentum, the total spin angular momenta of all emitted photons sum to zero. Because counterpropagating photons emitted are equal in probability, they carry opposite momenta of all emitted photons sum to zero. Because counterpropagation, the OAM relaxation time should be much longer than the momentum relaxation time. [11]

Orbital–magnetic locking in chiral molecules

We discuss the TRS breaking of \([0, 1] \) in the presence of current flow. Although the average momentum is zero for electrons in a molecule, the simultaneous momentum \((k) \) can be significant. For example, we can approximate the molecule as a box in which electrons are confined (see Fig. 3a, b). The electrons move back and forth due to boundary scattering and form a standing wave \(|\psi\rangle\). The standing wave is a superposition of a forward-moving state \(|\psi^+\rangle\) and a backward-moving state \(|\psi^-\rangle\), where we choose \(|\psi^+\rangle = |\psi^-\rangle^*\) (\(\ast\) represents the complex conjugate) because TRS allows \(|\psi\rangle\) to be real valued. If an electron picks up a velocity along \(\pm z\) caused by the current flow, its wavefunction reduces from \(|\psi\rangle\) to \(|\psi^+\rangle\).

We point out that \(|\psi^-\rangle\) itself violates TRS, although \(|\psi^-\rangle\) does not.

Next, \(|\psi^-\rangle\) carries opposite OAM (\(\pm l\)) in a chiral molecule. As illustrated in Fig. 3b, electrons that travel along a chiral pathway pick up a self-rotation, that is, the OAM, analogous to the spinning bullet out of a rifled barrel. Mathematically, we can generally describe a positive-moving plane wave using \(|\psi\rangle = A(p, z) e^{i\rho x e^{ikz}}\), where \(A(p, z)\) is a general coefficient depending on \(z\) and the radial distance \(p\), \(\psi\) is the azimuth angle, \(k\) is the momentum and \(l = 0, \pm 1, \pm 2, \ldots\) represents the OAM. \(|\psi^-\rangle\) is a chiral plane wave if \(l \neq 0\) and reduces to a normal plane wave for \(l = 0\). Because both the inversion symmetry and mirror symmetry (either of which forces \(l = 0\)) are broken, \(l \neq 0\) generically holds in a chiral system. It is obvious that \(|\psi^-\rangle\) with \(-l \neq k\) carries opposite OAM of \(-l\) because \(|\psi^-\rangle = |\psi^+\rangle^*\). Such orbital–magnetic locking \((l \neq k)\) locking represents the wavefunction topology in which the parallel and antiparallel \(l \neq k\) relation depends on the molecular chirality and chemical potential. This is similar to the monopole–spin–magnetic pathlocking in the topological Weyl fermion.

Angular momentum transfer from electrons to light

The injected electrons and holes carry finite OAM because of the polymer chirality in the OLED. Given the low mobility in the organic semiconductor, the linear momentum is quickly relaxed, for instance, by interface scattering between neighbouring aggregate clusters. But the OAM relaxation time should be much longer than the momentum relaxation time because neighbouring clusters share the same chirality. Owing to the same chirality protection, we also expect that OAM is robust against electron–electron interactions. Therefore, electrons and holes can preserve the OAM polarization when they form excitons for light emission. In the following, we discuss the OAM transfer from carriers to CP light in the electron–hole recombination.

The ACPE in equation (4) is equivalent to the OAM shift in the optical transition

\[
\Delta l = \langle F_z \rangle_{0, -1} = x^{\text{el}} p_y^{10} - y^{\text{el}} p_x^{10},
\]

where \(F_z = x p_y - y p_x\) is the OAM operator (more details in the Supplementary Information). In the presence of current along \(-z\), we need replace \([0] \langle 1 \rangle\) for \([0] \langle 1 \rangle\) to evaluate the ACPE in equation (4).
In this case, $\Delta$ is non-zero in the optical transition from $|1\rangle$ to $|0\rangle$, both of which carry finite OAM, as illustrated in Fig. 3d. In addition, reversing the current leads to $-\Delta f$ (Fig. 3c). We note that $\Delta$ is gauge invariant, although $f$ of a given band depends on the specific gauge.

For a photon with a positive spin angular momentum, it is defined as right-handed CP light if it travels along $+\mathbf{z}$ and as left-handed CP light if it travels along $-\mathbf{z}$. Therefore, the finite angular momentum, which is transferred from the OAM of electrons/holes to the spin of photons ($S = +\Delta l$), forces that the handedness of CP light relies on the emission direction. Overall, the orbital–momentum locking eventually leads to the current-direction and emission-direction dependencies of CP-EL, which is fully consistent with our experiments.

To summarize the ACPE mechanism, it includes two parts. (1) In a chiral molecule/chiral aggregate, the OAM is locked parallel or antiparallel to the intrinsic momentum (see more discussion on its difference from the mobility-related drift velocity in the Supplementary Information). Opposite momenta with opposite OAM coexist and cancel each other at equilibrium. (2) When the current flows, one momentum is enhanced while the opposite one is suppressed, as with the OAM. Therefore, conducting electrons/holes are OAM-polarized in the non-equilibrium phase. Direct electron–hole recombination leads to finite OAM transfer from charge carriers to the CP light, leading to the ACPE.

Ab initio calculations

Furthermore, we quantitatively estimate the ACPE and NCPE for the chiral F8BT polymer assembly via ab initio calculations. It is challenging to refine the accurate atomic structure of such chiral aggregates. Without losing generality, we simulate the chiral stacking of F8BT molecules and focus on the intermolecular chirality that is associated with the dominant charge-transport direction along the layered packing structure (noted as the $x$ axis here)\textsuperscript{44}. Although $|0,\, 1\rangle$ can generally be many-body wavefunctions, in our calculations we use the highest occupied molecular orbital (HOMO) and the LUMO to represent $|0\rangle$ and $|1\rangle$, respectively, by ignoring higher-order corrections (like the distortion in excited states). As shown in Fig. 4, two-layer stacking with a counterlockwise twist angle of 30\textdegree reshares the HOMO and LUMO wavefunctions dramatically compared with a single molecular layer. By calculating the ACPE involving the $+\mathbf{z}$ moving HOMO and LUMO, we obtain a large disymmetry factor $|g_{zz}|$ of 0.48 (0.44) for the stacking of two (three) layers, which is of the same order of magnitude as the experimental $g_{zz}$. The OAM can be evaluated from the phase winding number in the $x$–$y$ plane (see Fig. 4c and the Methods section), verifying the orbital–momentum locking in $|0\rangle$ and $|1\rangle$. Because $|0,\, 1\rangle$ are usually comprised of many plane waves, the total value of $l$ is unnecessarily an integer. Better knowledge of the molecular arrangement of chiral polymer assemblies will help to improve the prediction power of calculations in future work.

In addition, the current-induced magnetization in our experiments is relevant to the orbital rather than the spin of electronic states. If electron-spin polarization matters, it would require substantial spin–orbit coupling (SOC) in the device. We know that these organic polymers made of light elements exhibit negligible SOC. Despite that metal electrodes may include heavy elements, the circular polarization rate remains the same for Al, Ag and Au electrodes with largely varied SOC (Supplementary Fig. 8). Thus, the role of electron spin may be negligible in ACPE, although ACPE may also appear in systems with strong SOC. The ACPE is caused by the chirality-induced orbital polarization, which is different from the chirality-induced spin selectivity effect discussed in the literature\textsuperscript{7}. Our experiment demonstrates a significant consequence of the electron orbital effect in chiral materials. Here, the electron OAM is indicated by the shift in emission direction of CP light (the spin flip of light) upon reversing the current flow (for example, see Fig. 1c,d).

Summary

In summary, we report an anomalous phenomenon where the handedness of the CP light emission depends on the emission direction. This effect enables us to design unconventional CP-OLED devices with a large $g_{zz}$ and without erosion from the back-electrode reflection. We highlight that the orbit–momentum locking causing ACPE is strongly associated with the charge-transport mode in the polymer systems and therefore suggest the following design principles for further development of CP-OLEDs with strong CP-EL. To ensure that the entire stack of molecular assemblies exhibit strong ACPE, it is necessary that the emissive sites should strongly couple with chiral transport sites, or ideally within the same sites to ensure strong orbital–momentum locking in conduction electrons. In this case, the origin of CP-EL can no longer be considered to be the same as CP-PL and CD where no charge transport and current flows exist. If charge carriers are independently transported, such as in host materials, then they are scattered to random adjacent chiral emissive sites, the net momentum and OAM will be quenched, and only the NCPE will appear.

We propose an ACPE that involves the transfer of finite angular momentum in the optical transition. Because the ACPE and NCPE may come from the first- and second-order optical transitions in equation (4), ACPE is often much larger than NCPE when TRS is broken. We highlight that the unusual TRS breaking in the ACPE is driven by the non-equilibrium orbital magnetization that originates in the chiral orbital nature in wavefunctions. In CP-OLEDs, such orbital magnetization is caused by the current flow (rather than static magnetization or a magnetic field), the impact of which has rarely been recognized in previous studies on chiral materials\textsuperscript{34}. Our work reveals an intriguing unification of chirality in the seemingly unrelated aspects of the structure geometry, the electronic topology and the handedness of light. The chirality information can be transferred from the material geometry to the electronic wavefunction and further to the spin light.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41566-022-01113-9.

References

1. Siegel, J. S. Homochiral imperative of molecular evolution. Chirality 10, 24–27 (1998).
2. Barron, L. D. Symmetry and chirality: where physics shakes hands with chemistry and biology. Isr. J. Chem. 61, 517–529 (2021).
3. Kuball, H.-G., Höfer, T. & Kiesewalter, S. in Encyclopedia of Spectroscopy and Spectrometry 217–231 (Elsevier, 2017); https://linkinghub.elsevier.com/retrieve/pii/089780124095472049805
4. Barron, L. Symmetry and molecular chirality. Chem. Soc. Rev. 15, 189–223 (1986).
5. Armitage, N. P., Mele, E. J. & Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. Rev. Mod. Phys. 90, 015001 (2018).
6. Yan, B. & Felser, C. Topological materials: Weyl semimetals. Annu. Rev. Condens. Matter Phys. 8, 337–354 (2017).
7. Liu, Y., Xiao, J., Koo, J. & Yan, B. Chirality-driven topological electronic structure of DNA-like materials. Nat. Mater. 6, 638–644 (2021).
8. Naaman, R., Paltiel, Y. & Waldeck, D. H. Chiral molecules and the electron spin. Nat. Rev. Chem. 3, 250–260 (2019).
9. Evers, F. et al. Theory of chirality induced spin selectivity: progress and challenges. Adv. Mater. 34, 2106629 (2022).
10. Brandt, J. R., Salerno, F. & Fuchter, M. J. The added value of small-molecule chirality in technological applications. Nat. Rev. Chem. 1, 0045 (2017).
11. Shang, X., Wan, L., Wang, L., Gao, F. & Li, H. Emerging materials for circularly polarized light detection. J. Mater. Chem. C 10, 2400–2410 (2022).
12. Zhang, D.-W., Li, M. & Chen, C.-F. Recent advances in circularly polarized electroluminescence based on organic light-emitting diodes. Chem. Soc. Rev. 49, 1331–1343 (2020).
13. Yang, Y., da Costa, R. C., Smilgies, D.-M., Campbell, A. J. & Fuchter, M. J. Induction of circularly polarized electroluminescence from an achiral light-emitting polymer via a chiral small-molecule dopant. Adv. Mater. 25, 2624–2628 (2013).
14. Wan, L. et al. Highly efficient inverted circularly polarized organic light-emitting diodes. ACS Appl. Mater. Interfaces 12, 39471–39478 (2020).
15. Peeters, E. et al. Circularly polarized electroluminescence from a polymer light-emitting diode. J. Am. Chem. Soc. 119, 9909–9910 (1997).
16. Craig, D. P. & Thirunamachandran, T. Molecular Quantum Electrodynamics: An Introduction to Radiation–Molecule Interactions (Academic, 1984).
17. Greenfield, J. L. et al. Pathways to increase the dissymmetry in the interaction of chiral light and chiral molecules. Chem. Sci. 12, 8589–8602 (2021).
18. Yan, Z.-P. et al. Configurationally stable platinahelicene enantiomers for efficient circularly polarized phosphorescent organic light-emitting diodes. Chem. Eur. J. 25, 5672–5676 (2019).
19. Frédéric, L., Desmarchelier, A., Favereau, L. & Pieters, G. Designs and applications of circularly polarized thermally activated delayed fluorescence molecules. Adv. Funct. Mater. 31, 2010281 (2021).
20. Zinna, F. et al. Design of lanthanide-based OLEDs with remarkable circularly polarized electroluminescence. Adv. Funct. Mater. 27, 1603719 (2017).
21. Grell, M. et al. A compact device for the efficient, electrically driven generation of highly circularly polarized light. Adv. Mater. 13, 577–580 (2001).
22. Zinna, F. et al. Modular chiral Eu(III) complexes for efficient circularly polarized OLEDs. J. Mater. Chem. C 10, 463–468 (2022).
23. Zhang, Y. J., Oka, T., Suzuki, R., Ye, J. T. & Iwasa, Y. Electrically switchable chiral light-emitting transistor. Science 344, 725–728 (2014).
24. Kim, Y.-H. et al. Chiral-induced spin selectivity enables a room-temperature spin light-emitting diode. Science 371, 1129–1133 (2021).
25. Wan, L. et al. Inverting the handedness of circularly polarized luminescence from light-emitting polymers using film thickness. ACS Nano 13, 8099–8105 (2019).
26. Wan, L., Shi, X., Wade, J., Campbell, A. J. & Fuchter, M. J. Strongly circularly polarized crystalline and β-phase emission from poly(9,9-diocetylfluorene)-based deep-blue light-emitting diodes. Adv. Opt. Mater. 9, 2100066 (2021).
27. Lee, D.-M., Song, J.-W., Lee, Y.-J., Yu, C.-J. & Kim, J.-H. Control of circularly polarized electroluminescence in induced twist structure of conjugate polymer. Adv. Mater. 29, 1700907 (2017).
28. Di Nuzzo, D. et al. High circular polarization of electroluminescence achieved via self-assembly of a light-emitting chiral conjugated polymer into multidomain cholesteric films. ACS Nano 11, 12713–12722 (2017).
29. Li, M., Wang, Y.-F., Zhang, D., Duan, L. & Chen, C.-F. Axially chiral TADF-active enantiomers designed for efficient blue circularly polarized electroluminescence. Angew. Chem. 132, 3528–3532 (2020).
30. Li, M., Wang, M. Y., Wang, Y. F., Feng, L. & Chen, C. F. High-efficiency circularly polarized electroluminescence from TADF-sensitized fluorescent enantiomers. Angew. Chem. Int. Ed. 60, 20728–20733 (2021).
31. Li, M. et al. Stable enantiomers displaying thermally activated delayed fluorescence: efficient OLEDs with circularly polarized electroluminescence. Angew. Chem. Int. Ed. 57, 2889–2893 (2018).
32. Laidlaw, B. et al. On the factors influencing the chiroptical response of conjugated polymer thin films. Chem. Commun. 57, 9914–9917 (2021).
33. Swathi, K., Sissa, C., Painelli, A. & Thomas, K. G. Supramolecular chirality: a caveat in assigning the handedness of chiral aggregates. Chem. Commun. 56, 8281–8284 (2020).
34. Wade, J. et al. Natural optical activity as the origin of the large chiroptical properties in n-conjugated polymer thin films. Nat. Commun. 11, 6137 (2020).
35. Jesuraj, P. J. et al. Recombination zone control without sensing layer and the exciton confinement in green phosphorescent OLEDs by excluding interface energy transfer. J. Phys. Chem. C 122, 2951–2958 (2018).
36. Geffroy, B., le Roy, P. & Prat, C. Organic light-emitting diode (OLED) technology: materials, devices and display technologies. Polym. Int. 55, 572–582 (2006).
37. Riehl, J. P. in Encyclopedia of Spectroscopy and Spectrometry 243–249 (Elsevier,1999).
38. Gaspar, D. J. & Polikarpov, E. (eds) OLED Fundamentals: Materials, Devices, and Processing of Organic Light-Emitting Diodes (CRC, 2015).
39. Xiao, D., Chang, M.-C. & Niu, Q. Berry phase effects on electronic properties. Rev. Mod. Phys. 82, 1959–2007 (2010).
40. Nagaosa, N., Sinova, J., Onoda, S., MacDonald, A. H. & Ong, N. P. Anomalous Hall effect. Rev. Mod. Phys. 82, 1539–1592 (2010).
41. Souza, I. & Vanderbilt, D. Dichroic f-sum rule and the orbital magnetization of crystals. Phys. Rev. B 77, 054438 (2008).
42. Yao, W., Xiao, D. & Niu, Q. Valley-dependent optoelectronics from inversion symmetry breaking. Phys. Rev. B 77, 235406 (2008).
43. Oppeneer, P. Magneto-optical spectroscopy in the valence-band energy regime: relationship to the magnetocrystalline anisotropy. J. Magn. Magn. Mater. 188, 275–285 (1998).
44. Donley, C. L. et al. Effects of packing structure on the optoelectronic and charge transport properties in poly(9,9-di-octylfluorene-alt-benzothiadiazole). J. Am. Chem. Soc. 127, 12890–12899 (2005).
45. Barron, L. D. Compliments from Lord Kelvin. Nature 446, 505–506 (2007).
Methods

Samples

[1]-aza[6]helicene was synthesized as previously reported and separated using preparative chiral HPLC.

Thin-film and device fabrication

The cleaning process for all substrates (fused silica and prepatterned ITO glass (20 ohms per square; Thin Film Devices)) involved rinsing in an ultrasonic bath with acetone, isopropyl alcohol, Hellmanex III (Sigma-Aldrich) and deionized water for 30 min. The substrates were transferred to a plasma ash for 3 min at 80 W and 50 W before spin-coating for fused silica and prepatterned ITO, respectively. F8BT and [1]-aza[6]helicene were dissolved in toluene to a concentration of 30 mg ml\(^{-1}\) and blended to form a 10% [1]-aza[6]helicene solution. An emissive layer of about 130 nm thick can be achieved by dynamically spin-coating at 2,300 revolutions per minute for 1 min. Chiral samples were annealed for 10 min in a nitrogen atmosphere (glovebox, <0.1 ppm H\(_2\)O, <0.1 ppm O\(_2\)). Dynamic coating ensures that strong chirpial activity is achieved without giving films that are too thick, as compared with previous studies. The organic film thickness was monitored using a Dektak 150 surface profiler, and the metal thickness was used as displayed using a quartz crystal microbalance monitor.

Photophysical characterization

CD measurements were performed using a Chirascan (Applied Photophysics) spectrophotometer. The CP-PL was measured in a transmittance geometry using a CPL-300 JASCO spectrometer. The CP-EL was recorded using an Ocean Optics USB 2000 charge-coupled photodiode detector. The charge density is \(\rho_0 = |\langle 0 | \uparrow \rangle\rangle\). Besides \(G_z\), the phase of the \(G\) propagating wave in Fig. 4 is \(\arg \phi_G(G)\). Under an electrical current along \(z\), the CP electric dipole transition amplitudes are calculated as:

\[
\begin{align*}
\langle G_z | \rho_0 | 0 \rangle &= \sum_{G_0} \sum_{G_1} \phi_0(G_1)|G_0, G_1, 0\rangle \langle G_1, G_0, 0|, \\
|0\rangle &= \sum_{G_0} \phi_0(G_0)|G_0, G_0, 0\rangle, \\
|0^\mp\rangle &= \sum_{G_0 > G_1, G_0 > 0} \phi_0(G_1)|G_0, G_1, 0\rangle.
\end{align*}
\]

where \(\phi_0(G) = \sum_{G_0, G_1} \phi_0(G_0)|G_0, G_1, 0\rangle\) and \(c_0\) is the plane wave coefficient extracted directly from density functional theory wavefunctions. The charge density is \(\rho_0 = |\langle 0 | \uparrow \rangle\rangle\).

Inverted devices

ZnO was deposited onto a cleaned ITO substrate via a sol–gel method, which has been described elsewhere, followed by a rinsing step with PEIE (polyethylenimine ethoxylated, 30 wt% in water; Sigma-Aldrich). Then, the [1]-aza[6]helicene-blended F8BT was dynamically spin-coated onto the ZnO/PEIE. Afterward, 25 nm TCTA (97% Sigma-Aldrich), MoO\(_3\) (99.97%, Sigma-Aldrich) and Au (99.99%, Kurt J. Lesker Company) up to 120 nm thick were thermally evaporated onto the organic layer under a vacuum of 1 × 10\(^{-7}\) mbar. Inverted device structure: ITO/ZnO/PEIE/F8BT:[1]-aza[6]helicene/TCTA/MoO\(_3)/Au.

Ab initio calculations

The electronic wavefunctions and charge densities of the F8BT chiral assemblies were calculated using density functional theory as implemented in the Vienna ab initio simulation package. The generalized gradient approximation was used for the exchange–correlation functionals. F8BT molecules were stacked along the \(z\) axis in a twisted manner. The molecular cluster model included at least 10 Å vacuum distances along all directions. An energy cutoff of 400 eV was used for the plane wave basis. The total number of plane waves is about 4 × 10\(^5\). We note the plane wave by the wave vector \(\mathbf{G}\) along the \(z\) axis in a twisted manner.

Data availability

The main data supporting the findings of this study are available within this Article and its Supplementary Information. Further data are available from the corresponding author on reasonable request. Source data are provided with this paper.
References
46. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).
47. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
48. Nakahara, M. Geometry, Topology and Physics (Taylor & Francis, 2017).

Acknowledgements
We dedicate this paper to the memory of Professor Alasdair James Campbell (1961–2021). L.W. would like to thank Alasdair James Campbell and J. Nelson for useful discussions at Imperial College London. L.W. would like to thank K. Stjerne (Biolab A/S, Denmark) and T. Brock-Nannestad (University of Copenhagen, Denmark) for access to the CPL-300 spectrometer. L.W. would like to thank R. Zhang (Linköping University) for help with processing the GIWAXS data. B.Y. acknowledges the financial support of the MINERVA Stiftung with the funds from the BMBF of the Federal Republic of Germany and the European Research Council (ERC Consolidator Grant ‘NonlinearTopo’, number 815869). L.W. and M.J.F. would like to thank Cambridge Display Technology Limited (company number 02672530) for providing the F8BT polymers. L.W. and M.J.F. would like to acknowledge EPSRC research grants EP/P000525/1, EP/LO16702/1 and EP/R00188X/1. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising.

Author contributions
L.W. and B.Y. conceived the project. L.W. collected the spectroscopy and device data. L.W. and M.J.F. analysed the experimental data. Y.L. and B.Y. wrote the theory and performed theoreteical calculations. L.W., Y.L. and B.Y wrote the manuscript. All authors contribute to the discussion and the revision of the manuscript.

Competing interests
M.J.F. is an inventor on a patent concerning chiral blend materials (WO2014016611). The remaining authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41566-022-01113-9.

Correspondence and requests for materials should be addressed to Li Wan or Binghai Yan.

Peer review information Nature Photonics thanks Lorenzo Di Bari and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.