Achieving high circularly polarized luminescence with push–pull helicenic systems: from rationalized design to top-emission CP-OLED applications†‡†

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While the development of chiral molecules displaying circularly polarized luminescence (CPL) has received considerable attention, the corresponding CPL intensity, $g_{\text{CPL}}$, hardly exceeds $10^{-2}$ at the molecular level owing to the difficulty in optimizing the key parameters governing such a luminescence process. To address this challenge, we report here the synthesis and chiroptical properties of a new family of π-helicene push–pull systems based on carbo[6]helicene, where the latter acts as either a chiral electron acceptor or a donor unit. This comprehensive experimental and theoretical investigation shows that the magnitude and relative orientation of the electric ($\mu_e$) and magnetic ($\mu_m$) dipole transition moments can be tuned efficiently with regard to the molecular chiroptical properties, which results in high $g_{\text{CPL}}$ values, i.e. up to $3-4 \times 10^{-2}$. Our investigations revealed that the optimized mutual orientation of the electric and magnetic dipoles in the excited state is a crucial parameter to achieve intense helicene-mediated exciton coupling, which is a major contributor to the obtained strong CPL. Finally, top-emission CP-OLEDs were fabricated through vapor deposition, which afforded a promising $g_{\text{CPL}}$ of around $8 \times 10^{-2}$. These results bring about further molecular design guidelines to reach high CPL intensity and offer new insights into the development of innovative CP-OLED architectures.
is of crucial importance to design luminescent molecules with high $g_{\text{lum}}$ values,\textsuperscript{3,5,8} in order to reach strong CP electroluminescence when going to practical devices. However, structural and electronic factors that govern the CPL of chiral compounds are still poorly understood even if a few studies have recently tried to rationalize and establish molecular guidelines to obtain high $g_{\text{lum}}$ values.\textsuperscript{6}

Our team has contributed to the research in this area by developing extended $\pi$-helical molecular architectures resulting from the association of carbo[6]helicene and achiral dyes,\textsuperscript{7} which afforded enhanced chiroptical properties, with notably a $g_{\text{lum}}$ up to $10^{-2}$, owing to an uncommon chiral exciton coupling process mediated by the chiral helicenic unit.\textsuperscript{8} In addition, we also described an unusual solvent effect on the intensity of CPL of $\pi$-helical push–pull helicene–naphthalimide derivatives,\textsuperscript{7b} which showed a decrease of $g_{\text{lum}}$ from $10^{-2}$ to $10^{-3}$ upon increasing the polarity of solvent.\textsuperscript{7b} This solvatochromism effect was shown to be related to a symmetry breaking of the chiral excited state before emission,\textsuperscript{9} which modifies the relative intensity of the magnetic ($\mu_{\text{m}}$) and electric ($\mu_{\text{e}}$) dipole transition moments, and the angle, $\theta$, between them (Fig. 1), ultimately impacting $g_{\text{lum}}$. The latter is well approximated as $4|\mu|\cos \theta/|\mu_{\text{e}}|$ for an electric dipole-allowed transition.\textsuperscript{10}

While these results highlight interesting aspects regarding the key parameters influencing the CPL of organic emitters, this type of “helical push–pull design” remains limited to only one example, which render the systematic rationalization of these findings difficult. Accordingly, we decided to develop a complete family of new chiral push–pull compounds to explore the structural and electronic impact of the grafted substituents on the helical $\pi$-conjugated system. In addition, we went a step further and incorporated the designed chiral emitter into proof-of-concept CP-OLEDs using a top-emission architecture,\textsuperscript{11} which remains scarcely explored for CP-light generation despite its considerable potential for micro-display applications. To the best of our knowledge, only one example of such type of electroluminescent device has been reported, using a CP-TADF emitter, affording a modest $g_{\text{El}}$ of $10^{-3}$.\textsuperscript{11a}

Herein, we report the synthesis and chiroptical properties of a new family of $\pi$-helical push–pull systems based on chiral carbo[6]helicene, functionalized by either electron donor or acceptor units. Interestingly, the chiral $\pi$-conjugated system of the helicene may act as either an electron acceptor or a donor, depending on the nature of the attached substituents, thereby impacting the chiroptical properties, notably the resulting CPL. By optimizing the chiral exciton coupling process through the modulation of the magnitude and relative orientation of the electric ($\mu$) and magnetic ($m$) dipoles, the chiroptical properties of classical carbo[6]helicene-based emitters can be dramatically enhanced and reach high $g_{\text{lum}}$ values at the molecular level, i.e. up to $3-4 \times 10^{-2}$. Experimental and theoretical investigations revealed that the mutual orientation of the electric and magnetic dipoles in the excited-state is a crucial parameter and is optimal when the substituents attached to the helicene core possess a rather weak electron withdrawing or donating ability. Finally, proof of concept top-emission CP-OLEDs were fabricated through vapor deposition of $\pi$-helical push–pull derivatives and afforded a $g_{\text{lum}}$ of around $8 \times 10^{-3}$, which represents a significant improvement for the polarization of electroluminescence emitted using this device architecture.

**Results and discussion**

**Synthesis and structural characterization**

The $\pi$-helical systems were prepared by functionalizing the alkynyl groups of racemic 2,15-bis-ethynyl-carbo[6]helicene H6(H)\textsubscript{2} with electron-donating and electron-accepting units of different strengths (Scheme 1). These push–pull systems were designed in order to modulate the resulting electric and magnetic intramolecular dipole moments and investigate their impact on their photophysical and chiroptical properties. In this way, five novel chiral helicenic compounds (H6(CN)\textsubscript{2}, H6(Py)\textsubscript{2}, H6(NO\textsubscript{3})\textsubscript{2}, H6(NMe\textsubscript{2})\textsubscript{2} and H6(NH\textsubscript{2})\textsubscript{2}) were synthetized by Sonogashira coupling reactions between rac-H6(H)\textsubscript{2} and the corresponding halogenoaryles (Scheme 1). The different helicene derivatives were obtained in enantiopure forms by HPLC separations over chiral stationary phases (ee’s > 99%, see the ESI\textsuperscript{†}). P- and M-H6(NMe\textsubscript{2})\textsubscript{2} were prepared under modified Eschweiler–Clarke conditions from P- and M-H6(NH\textsubscript{2})\textsubscript{2} (see the ESI\textsuperscript{†} for details).\textsuperscript{12}

![Configure diagram](image-url)
The structures of M-H6(CN)$_2$, rac-H6(NH$_2$)$_2$, and rac-H6(NO$_2$)$_2$ molecules were solved by X-ray crystallography (Fig. 2). They displayed helicities (dihedral angles between the terminal helicenic rings) of 42.47, 42.13, and 47.53°, which are slightly lower compared to classical carbo[6]helicene (58.5°), as it was previously observed for derivatives with substituents in the overlapping region of the helix. For H6(CN)$_2$ the coplanarity of the bis-4-cyano-phenyl-ethynyl group with the connected terminal phenyl rings of the helicene moiety is illustrated by angles values of 176.71 and 174.03° for Cd-Cc-Cb and Cc-Cb-Ca, respectively, and an angle of 14.88° between the benzonitrile and the terminal helicene phenylethynyl rings. This efficient electronic coupling between the helicene core and the para-ligand is also confirmed for both rac-H6(NH$_2$)$_2$ and rac-H6(NO$_2$)$_2$ by analyzing their crystal structures (see ESI†).

Computational details

Kohn–Sham density functional theory (DFT) as implemented in the Gaussian (G16) package was used for the computations utilizing the CAM-B3LYP functional and the def2-SV(P) basis. Excited state structures, excited state vibrational normal modes, and absorption and emission spectra were computed via time-dependent DFT (TD-DFT) response theory.

Absorption and electronic circular dichroism (ECD) spectra were simulated from the lowest 200 vertical singlet electronic excitations. The spectra were Gaussian broadened with σ = 0.20 eV. Solvent effects on the spectra were considered by means of the polarizable continuum model (PCM) for dichloromethane but found to be negligible. For overviews of the theoretical approach to model natural optical activity by quantum chemical calculations, esp. TD-DFT, see, for example, available reviews.

Electronic emission and CPL spectra were Gaussian broadened with σ = 0.0248 eV for the vibronic transitions. The Franck–Condon–Herzberg–Teller (FCHT) approximation was employed for the vibronic intensities, with the optimized structures and harmonic force fields of the ground state and first excited state used as input. Additional computational details, along with the full set of theoretical results, are provided in the ESI‡.

**Photophysical and chiroptical properties of H6 and H6(H)$_2$ precursors**

In line with our recent study on helicene-organic dyes, we detail here the crucial parameters influencing the photophysical and chiroptical properties of these new chiral compounds, namely (1) the extended conjugation of the π-helical system and the alignment between the electric and magnetic transition dipole moments for excitation and emission processes and (2) the magnitude of charge transfer and the exciton coupling between the two push–pull type branches of the helical system. In this study, depending on the electron acceptor or donor substituent ability, the helical π-conjugated core adopts a complementary electron donating or accepting character (vide infra), thus forming two branches with modest to strong electric dipole moments which interact through space in a chiral environment and result in a chiral exciton coupling.

Prior to investigating the photophysical and chiroptical properties of the synthesized chiral systems, we revisited those of carbo[6]helicene (H6) and its 2,15-bis-ethynyl (H6(H)$_2$) derivative. We and others empirically observed that the latter exhibits enhanced chiroptical properties, namely optical rotation, electronic circular dichroism (ECD) and CPL, compared to its unsubstituted hexahelicene precursor, the mono-substituted 2-ethynylcarbo[6]helicene and other isomers of bis-ethynyl carbo[6]helicene derivatives (see Fig. S7†). Despite these experimental findings, a complete rationalization of the key parameters responsible for enhanced optical activity remains unknown and appears of strong interest to bring about new molecular design directions for reaching higher chiroptical properties. Accordingly, the unpolarized (absorption and fluorescence) and polarized (ECD and CPL) optical properties of H6 and H6(H)$_2$ were recorded in dichloromethane solutions (Fig. 3 and S1–S5†). H6 and H6(H)$_2$ display very similar UV-vis absorption spectra with one intense absorption band below 300 nm (~50 × 10$^3$ M$^{-1}$ cm$^{-1}$) and a second one with a vibronic pattern between 300 and 375 nm (~20 × 10$^3$ M$^{-1}$ cm$^{-1}$). The main difference comes from the 15–20 nm red shift of both bands for H6(H)$_2$, owing to the extension of the π-conjugated helical system by the presence of the additional triple bonds. Both compounds show structured blue luminescence dominated by two maxima at 425 and 450 nm and additional shoulders at around 460 nm and 500 nm, affording a rather low quantum yield of fluorescence ($\phi = 2–3\%$) owing to a relatively large spin–orbit coupling often found in distorted aromatic cores. The two ethynyl units do not induce a significant red shift of the luminescence spectrum but clearly impact the vibronic transition frequencies, separated by ~1000 and 1300 cm$^{-1}$ for H6 and H6(H)$_2$, respectively. In comparison to the optical properties, the presence of the two triple bonds at the 2 and 15 positions of the helicene core significantly modifies the chiroptical features of the helicene. Indeed, the typical $\pi \rightarrow \pi^*$ polarized transitions perpendicular to the $C_2$ axis of $P$-H6 for...
the positive ECD band at 325 nm (232 M⁻¹ cm⁻¹) and polarized along the C₂ axis for the negative ECD band at higher energy (246 nm, −238 M⁻¹ cm⁻¹), of the respective B and A symmetry, are red-shifted and show a much higher intensity for both the 1Ba and 1Bb bands, in P-H⁶(H)₂, with D₃ magnitudes of up to 300 and 400 M⁻¹ cm⁻¹ at 270 and 340 nm, respectively. Such an increase of ECD response is also clearly evidenced by plotting their corresponding absorption dissymmetry factor, gₐₐ₅ (Fig. S5), which afforded a maximum value of 2.1 × 10⁻² at 360 nm for P-H⁶(H)₂, twice more intense than for P-H⁶ (~10⁻² at 360 nm). The calculated spectra for both compounds reproduce the experimental spectra well, including, importantly, the ECD intensity increase upon the introduction of the ethynyl fragments (Fig. 3). For P-H⁶(H)₂, the increased ECD intensity is due to contributions of the ethynyl groups in the transitions.

Closer inspection of the low-energy positive ECD excitation (no. 3, Fig. 3), indicates that the higher rotatory strength for P-H⁶(H)₂ may be related to a more favorable angle between the electric and magnetic transition dipole moments (μₑ and μₚ). Indeed, the calculated θ values of 69.2° and 48.6° were respectively determined for P-H⁶ and P-H⁶(H)₂, ultimately resulting in an absorption dissymmetry factor, gₐ₅, twice as high for the latter (Fig. 3). In addition, the presence of two intense electronic excitations (no. 3, 5) implying partial charge-
transfer between the helicene and the ethynyl substituents with opposite signs and small LUMO and LUMO+1 energetic splitting for $P$-$H6(H)_2$, $0.154$ eV, Fig. $S25^\dagger$ seems to indicate the presence of a weak exciton coupling between each $\pi$-conjugated arm of the helicene. As mentioned, we recently reported several examples of intramolecular chiral exciton coupling within $[6]$ helicene derivatives and showed their contributions in the enhancement of chiroptical properties.$^7$ In the specific case of $H6(H)_2$, this process may also occur to a lesser extent, in addition to the classical ECD of carbo$[6]$/helicene.

These emitters in dichloromethane solution show the expected mirror-image structured CPL spectra with maxima of intensity corresponding to the ones of their respective unpolarized fluorescence. The measured $g_{\text{sum}}$ values are $+1.0 \times 10^{-3}$ at $420$ nm and $+9.4 \times 10^{-3}$ at $421$ nm for $P$-$H6$ and $P$-$H6(H)_2$, respectively, thus highlighting an order of magnitude increase when simply adding two triple bonds at the 2 and 15 positions. As mentioned above, this high intensity of CPL has also been observed by other groups for similar derivatives,$^a$ notably highlighting the importance of the helicene functionalization at the 2,15 positions in comparison to the 4 and 13 positions.$^{2,3}$ The obtained $g_{\text{sum}}$ values for $P$-$H6$ and $P$-$H6(H)_2$ reveal higher differences of chiroptical properties in emission than in absorption, as also indicated by their corresponding $g_{\text{sum}}/g_{\text{abs}}$ ratios of 0.1 and 0.4, respectively.$^a$ These values indicate that both emitters experience a different organization of their electric and magnetic transition dipoles between light absorption and emission processes, as the excited state geometries of $P$-$H6$ and $P$-$H6(H)_2$ are similar to the ground state geometries (see Fig. $S39^\dagger$).

Theoretical analyses of the electronic emission and circularly polarized luminescence spectra were performed to gain insight into the observed difference of CPL intensity. The computed normalized emission and CPL spectra of $H6$ and $H6(H)_2$ presented in Fig. 3 correctly reproduce the vibronic structure seen in the experimental spectra, except that the emission peaks are presented in Fig. 3 correctly reproduce the vibronic structure seen in the experimental spectra, except that the emission peaks are

Photophysical and chiroptical properties of push–pull systems

Considering the CPL enhancement when going from $H6$ to $H6(H)_2$, and then to $H6(TMS)_2$, it was then decided to study the photophysical and chiroptical properties of helicene-bis-ethynyl systems functionalized by both electron donor and acceptor groups of different strengths. Owing to the high similarity in the UV-vis and ECD spectra of $H6(Py)_2$ and $H6(CN)_2$, on one side and $H6(NO_2)_2$ and $H6(NMe_2)_2$, on the other side, we only discuss the properties of $H6(CN)_2$ and $H6(NMe_2)_2$ in the manuscript (further details can be found in the ESI†). As depicted in Fig. 5 and in comparison to $H6(H)_2$, the extension of the helical $\pi$-conjugated system in $H6(CN)_2$ and $H6(NMe_2)_2$ induces an expected red-shift of the UV-vis absorption spectra with maxima at $305$ ($\epsilon = 76800$ M$^{-1}$ cm$^{-1}$) and $323$ nm ($63000$ M$^{-1}$ cm$^{-1}$), respectively. For both compounds, this main band is accompanied by a broad and intense shoulder at $350$–$370$ nm (30–40 000 M$^{-1}$ cm$^{-1}$) involving intramolecular charge transfer (ICT) transitions, namely from the $\pi$-helical core to the alkynyl Ph-CN group for $H6(CN)_2$ and from the alkynyl Ph-NMe$_2$ group to the helical core for $H6(NMe_2)_2$ (see excitations no. 1–2, Fig. 5). $H6(CN)_2$ presents distinct $\pi$-orbitals of the helicene electronic structure.
system among the HOMO−1 and HOMO, whereas the LUMO and LUMO+1 with a small energetic splitting (0.084 eV) come from an in-phase and out-of-phase linear combination of the lowest unoccupied substituent (Ph-CN) frontier molecular fragment orbitals (FOs). The situation is opposite for H6(NMe2)2, where the HOMO−1 and HOMO are mainly centered on the ethynyl-phenyl amino fragments while the LUMO and LUMO+1 spread over the helicene core. For this push–pull configuration, the HOMO and HOMO−1 show a weak energetic splitting, arising also from in-phase and out-of-phase linear combinations of the donor FOs (0.094 eV).

Overall, the direct electronic interaction between the two ethynyl-Ph-CN and -Ph-NMe2 substituents within the helix in the ground state appears even weaker than for the ethynyl ones in H6(H)2, suggesting a stronger exciton coupling for both H6(CN)2 and H6(NMe2)2. The observed differences between the UV-vis spectra of these two latter compounds and their common precursor H6(H)2 are also found in their corresponding ECD spectra, as illustrated in Fig. 5.

Concomitant to the global ECD red-shift, a less energetic splitting is observed between the most intense positive and negative peaks in the low-energy region for both P-H6(CN)2 and P-H6(NMe2)2 (ca. 50 nm), in comparison to P-H6(H)2 (ca. 70 nm). The calculations assign these bands as follows: the lowest-energy #1 and #2 excitations for P-H6(CN)2 and P-H6(NMe2)2 contribute to the first intense positive ECD band (350–380 nm), involving ICT transitions among HOMO−1, HOMO, and LUMO, LUMO+1, LUMO+2 (Fig. 5c), between the helicenic π system and the respective Ph-CN and Ph-NMe2 groups; the observed complementary negative ECD bands at shorter wavelengths (280–330 nm), from excitations #3 to #7, are also assigned to π/π* and ICT transitions. In line with our recent studies,7,8 the high intensity of these positive and negative transitions, together with the sign inversion and the already mentioned frontier orbital electronic configuration, indicates the presence of an intramolecular chiral exciton coupling between the electric transition dipoles of the ethynyl-Ph-CN and -Ph-NMe2 fragments within the helical environment. To confirm the existence of this process, an exciton coupling model calculation,7,11 based on the electric transition dipole moments (TDMs) of a mono-substituted helicene-Ph-CN H6(CN), was performed, and the obtained ECD spectra were compared to the

Fig. 5 (a) Top: UV−vis absorption (solid lines) and bottom: ECD spectra of H6(H)2 (grey), H6(CN)2 (blue) and H6(NMe2)2 (red) in dichloromethane at 298 K (| | T0 = 10−5 M); (b) calculated (Calc.) absorption (top) and ECD (bottom) of P-H6(H)2 (grey), P-H6(CN)2 (blue) and P-H6(NMe2)2 (red), selected transitions and oscillator and rotatory strengths indicated as ‘stick bars’. (c) Details for the selected transitions and oscillator and rotatory strengths; (d and e) isosurfaces (±0.04 au) of the frontier molecular orbitals (MOs) with the corresponding electric (green) and magnetic (red) dipole moment vectors corresponding to excitation #2 (S0 → S1 transition), and the experimental (Expt.) and calculated (Theo.) absorption dissymmetry factor (g) and θ angle (in degrees) for H6(CN)2 and H6(NMe2)2, respectively.

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corresponding spectra of the bis-substituted helicene, \( \text{H}_6(\text{CN})_2 \) (Fig. S33 and Table S11). The model strongly supports the presence of an exciton coupling ECD for \( \text{P-H}_6(\text{CN})_2 \) and likely also in the case of \( \text{P-H}_6(\text{Py})_2 \), \( \text{P-H}_6(\text{NO}_2)_2 \) and \( \text{P-H}_6(\text{NMe}_2)_2 \) given their comparable chiroptical properties with \( \text{P-H}_6(\text{CN})_2 \). For these four \( P \)-enantiomers, a positive exciton coupling signature is present, in line with the sense of the helical arrangement of the electrostatically coupled transition dipole moments.\(^{74-77}\) Further inspections of the electric and magnetic transition dipole moments for the first ECD-intense excitation of each compound reveal a nearly parallel orientation of the corresponding vectors with angles of 5.9° for \( \text{H}_6(\text{CN})_2 \) and 7.4° for \( \text{H}_6(\text{NMe}_2)_2 \) (Fig. 5), resulting in high chiroptical properties in absorption, with a \( \gamma_{\text{abs}} \) of 3.2 \( \times \) 10\(^{-2} \) and 2.2 \( \times \) 10\(^{-2} \) in dichloromethane, respectively. These close values also indicate a small impact of the gauche conformations for the two former ones (with Franck-Condon sums for the S\(_0\) transitions of 6.6 \( \times \) 10\(^{-2} \) and 5.2 \( \times \) 10\(^{-2} \) for \( \text{P-H}_6(\text{Py})_2 \) and \( \text{P-H}_6(\text{CN})_2 \), respectively. As in the case of the ECD spectrum, a helicene-mediated exciton coupling of \( \pi \)-system transitions involving the substituents is also present in the emission and appears to be a major contributor to the strong CPL of \( \text{P-H}_6(\text{Py})_2 \) and \( \text{P-H}_6(\text{CN})_2 \). Surprisingly and despite a higher rotational strength for the \( S_1 \rightarrow S_0 \) transition, such an exciton coupling process appears to be less efficient in promoting high CPL intensity for \( \text{P-H}_6(\text{NMe}_2)_2 \) and \( \text{P-H}_6(\text{NO}_2)_2 \), albeit being almost as important as for \( \text{P-H}_6(\text{Py})_2 \) and \( \text{P-H}_6(\text{CN})_2 \) in the related ECD spectra. In fact, the calculated electric and magnetic transition dipole moments at the \( S_1 \) geometries of \( \text{P-H}_6(\text{NMe}_2)_2 \) and \( \text{P-H}_6(\text{NO}_2)_2 \) afford a higher angle between them (48°, Fig. 6) than for \( \text{P-H}_6(\text{Py})_2 \) and \( \text{P-H}_6(\text{CN})_2 \), ultimately resulting in a lower intensity of the emission process and an overall decrease of the calculated \( \gamma_{\text{Lum}} \) values at ca. 2.5 \( \times \) 10\(^{-2} \).

Interestingly, moving to a less electron-donating group on the phenyl substituents such as \( \text{NH}_2 \) in \( \text{P-H}_6(\text{NH})_2 \), the synthetic precursor of \( \text{P-H}_6(\text{NMe}_2)_2 \) also results in an intense structured blue CPL with a \( \gamma_{\text{Lum}} \) of +2.1 \( \times \) 10\(^{-2} \) associated to a promising fluorescence quantum yield of 16%, clearly highlighting the crucial role of the substituent electron donating and accepting character in reaching high emission and polarisation degrees of luminescence in 2,15-bis-ethyl helicene derivatives. The investigation of the CPL solvatochromism of \( \text{P-H}_6(\text{NMe}_2)_2 \) helps us gain more insight into this dipole effect. As depicted in Fig. 7, the intensity of the CPL appears to be significantly dependent on the solvent polarity since \( \text{P-H}_6(\text{NMe}_2)_2 \) displays a \( \gamma_{\text{Lum}} \) value of +2.1 \( \times \) 10\(^{-2} \) in apolar cyclohexane, which dramatically drops to +3.0 \( \times \) 10\(^{-3} \) in polar dimethylformamide. In analogy to our previous study on chiral acceptor–donor–acceptor structures,\(^{78}\) such a dramatic decrease may be related to a symmetry breaking of the emitting excited state and a loss of the exciton coupling between each individual \( \text{Ph(NMe}_2)_2 \rightarrow \text{helicene ICT transitions on the CPL signal} \) (Fig. 7). In an apolar solvent, the emission of \( \text{P-H}_6(\text{NMe}_2)_2 \) is highly structured owing to a weak molecular reorganization,
which indicates a small intramolecular charge-transfer character of the emitting excited state. For such configurations, the electron density difference between the excited and ground states is almost equally distributed between each Ph(NMe₂)₂/helicene arm, which favors an intense exciton coupling process as in the case of P-H₆(Py)₂ and P-H₆(CN)₂ and ultimately a high degree of CPL. Conversely, the more intense electrostatic field imposed by the polar dimethylformamide solvent induces a localization of the excited state on one Ph(NMe₂)₂/helicene branch and, as a consequence, a loss of the exciton coupling mechanism.

Given the high CPL intensity of the reported helical emitters and particularly for H₆(CN)₂, we confirmed the obtained results by recording their CPL using different spectrometers.⁹

**CP-OLED devices**

Having these unprecedented chiral luminophores available, we decided to investigate their performances as CPL emissive dopants in top-emission OLEDs, which represent a highly relevant and emergent OLED architecture for micro-display applications such as in cameras, near-eye displays and medical analysis. Surprisingly, this type of electroluminescent device remains almost unexplored in the context of CP-OLEDs and may afford a new approach to investigate the impact of the device architecture on the propagation of CP light and its possible depolarization through reflection at the metallic electrode.

The investigated top-emission CP-OLED architecture in this study included notably a silicon wafer, covered with an Al–Cu bottom cathode, a thin passivation layer (TiN), a thin layer of calcium (Ca), different electron and hole injection, transport and blocking layers (EIL/ETL, HTL/HBL), the chiral emissive layer composed of enantiopure P- or M-helicene derivative as a dopant (~15–20%) in a 1,3-bis[N-carbazolyl]benzene, m-CP, a matrix and a top ultra-thin silver (Ag) anode, all being encapsulated using a SiO/Al₂O₃ bilayer (see Fig. 8 and the ESI‡ for details). We first tried to use P- and M-H₆(CN)₂ as the emitter, since they afford the highest CPL intensity among the helicene derivatives reported herein. However, despite several attempts, vapor deposition of H₆(CN)₂ was not efficient,

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precluding device engineering. To circumvent this aspect, we turned our attention to $P$- and $M$-$\text{H}_6(\text{TMS})_2$ since these compounds show also intense CPL ($\gamma_{\text{lum}} = 1.8 \times 10^{-2}$), in addition to the fact that the silyl groups may help the vaporization process by decreasing intermolecular interactions in the solid state. Gratifyingly, the deposition of $P$- and $M$-$\text{H}_6(\text{TMS})_2$ occurred smoothly with no racemization during the thermal vaporization, as indicated by the similar CPL intensity between films obtained either from solution spin-coated processes or vacuum deposition on glass substrates, and the value measured in diluted solution (Fig. S47‡). Following these control experiments, proof-of-concept CP-OLEDs were obtained and their optoelectronic characteristics investigated (Fig. 8). Similar electroluminescence spectra were recorded for both enantiomers of $\text{H}_6(\text{TMS})_2$, showing a structured profile with a maximum of intensity at 480 nm. This response is red-shifted in comparison to the luminescence obtained for the chiral emitter thin film (Fig. 8), which can be explained by the specific architecture of the top-emission configuration. The presence of two reflective metallic electrodes provides the OLED with an optical cavity behavior, namely a selective optical band pass filter, whose central wavelength depends on the thickness of the organic stack. In the present CP-OLED, the resulting architecture results in a transmission of photons of around 500 nm wavelength and therefore does not match perfectly the luminescence maximum of the chiral emitter dopant (see the ESI‡ for further explanations). The voltage ($V$–luminance ($L$) characteristics of these non-optimized obtained OLED devices show a clear rectifier diode behavior, low leakage current ($\approx 1 \mu\text{A cm}^{-2}$) and luminance performances of up to 1000 cd

![Fig. 7](image_url) Top: CPL spectra of $P$-$\text{H}_6(\text{NMe}_2)_2$ in cyclohexane (dark red), dichloromethane (red) and dimethylformamide (light red) at 298 K and of $P$-$\text{H}_6(\text{NH}_2)_2$ (blue) in dichloromethane with the corresponding $\gamma_{\text{lum}}$ values, along with bottom: illustration of the solvent polarity effect underlying the observed decrease of $\gamma_{\text{lum}}$ for $P$-$\text{H}_6(\text{NMe}_2)_2$.

![Fig. 8](image_url) (a) Illustration of the top-emission OLED architecture with the optical cavity effect resulting in a wavelength selectivity related to the thickness of the organic stack (see the ESI‡); (b) luminescence (from vapor deposition film) and electroluminescence spectra (CP-OLED under 7.5 V) of $P$-$\text{H}_6(\text{TMS})_2$ and (c), ($V$–$L$ characteristics of the CP-OLED including $P$-$\text{H}_6(\text{TMS})_2$, (d) a picture of an operating CP-OLED; (e) circularly polarized electroluminescence ($\Delta E$) of devices recorded under different operation voltages with $P$-$\text{H}_6(\text{TMS})_2$ emitter dopants (see the ESI‡ for the corresponding spectra for $M$-$\text{H}_6(\text{TMS})_2$) and (f) corresponding plots of the luminescence (from the vapor deposition film) and electroluminescence dissymmetry factor, $\gamma_{\text{lum}}$ and $\gamma_{\text{El}}$, respectively.
m$^{-2}$ under 13 V, which remains a rather modest value compared to standard blue-green top-emission devices. The resulting external quantum efficiency is 0.2%, a modest value that can be explained by the rather low fluorescence quantum yield of this helical emitter (6%). Improved performances should be reached by developing more efficient chiral fluorophores, phosphors or CPL-TADF emitters. Finally, the polarization of the electroluminescence was measured by placing CP-OLEDs in the sample holder of an in-house built CPL spectrometer. The recorded difference of circularly polarized electroluminescence (ΔE) is respectively positive and negative for $P$- and $M$-H6(TMS)$_2$ based CP-OLEDs, in agreement with the CPL sign measured in solution, and increases with the applied voltage. Importantly, significant ΔE signals are clearly recorded between 400 and 450 nm, corresponding to the maxima of CPL intensity for $P$- and $M$-H6(TMS)$_2$ and suggesting that the circular polarization is effectively induced by the chiral dopant (Fig. 8). In fact, plots of the electroluminescence dissymmetry factors $g_{sl}$ agreed well with the $g_{sl}$ in films (Fig. 8), confirming the origin of the polarized electroluminescence. Finally, $g_{sl}$ values of $+8.0 \times 10^{-3}$ and $-7.0 \times 10^{-3}$ were determined for $P$- and $M$-H6(TMS)$_2$ emissive dopants, indicating that 56% of the CPL measured in film ($g_{sl} = 1.8 \times 10^{-2}$) is lost upon integrating the emitter into the CP-OLED architecture. This presumably comes from light reflection and polarization inversion at the counter electrode (accounting for 28% of the electrogenerated CPL signal, which then cancels another 28% of the initial degree of circular polarization). While further optimizations regarding the optical cavity, wavelength selectivity and the organic stack are needed, these promising results clearly represent a strong increase in terms of CPEL for top-emission based CP-OLEDs and may open new opportunities for CP-light display applications.

**Conclusion**

In conclusion, we described here the synthesis of new extended π-helical push–pull chiral emitters and investigated their chiroptical properties both experimentally and theoretically. These compounds display strong ECD and CPL, with $g_{sl}$ values of up to $3 \times 10^{-2}$, which are among the highest CPL intensities recorded so far at the molecular level. By careful investigation of the structure–property relationship of these chiral lumino-phores, we attributed these results to an optimized mutual orientation of the electric and magnetic dipoles in the excited state which facilitates an intense exciton coupling process mediated by the [6]helicene unit. Owing to their strong CPL and high racemization barrier, such chiral derivatives were then tested as emissive dopants in proof of concept top-emission CP-OLEDs and afforded a promising CP electroluminescence, $g_{sl}$ of around $8 \times 10^{-3}$, which represents a significant result for CP-OLEDs using this device architecture. These results further highlight the potential of helical π-conjugated molecules for chiral optoelectronic applications and may offer new opportunities to design innovative and efficient CPL emitters and directions to develop more efficient CP-OLEDs.

**Author contributions**

J. C. and L. F. conceived the project. K. D. synthesized the compounds and collected the spectral data. L. A. and J. A. performed theoretical calculations. S. M.-D.-G made the OLED devices and B. R., E. Q., G. P., J. C. and L. F. did the circularly polarized electroluminescence measurement and analysis. N.V. performed the chiral HPLC separation. T. R. did the X-ray analysis. All authors participated in the manuscript writing.

**Conflicts of interest**

There are no conflicts of interest to declare.

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**References**

1 (a) M. Lindemann, G. Xu, T. Pusch, R. Michalzik, M. R. Hofmann, I. Žutić and N. C. Gerhardt, Nature, 2019, 568, 212–215; (b) H. Wang, L. liu and C. Lu, Procedia Comput. Sci., 2018, 131, 511–519; (c) J. Han, S. Guo, H. Lu, S. Liu, Q. Zhao and W. Huang, Adv. Opt. Mater., 2018, 6, 1800538; (d) T. Novikova, A. Pierangelo, S. Manhas, A. Benali, P. Validire, B. Gayet and A. D. Martino, Appl. Phys. Lett., 2013, 102, 241103; (e) B. Kunnen, C. Macdonald, A. Doronin, S. Jacques, M. Eccles and I. Meglinski, J. Biophotonics, 2015, 8, 317–323; (f) R. Carr, N. H. Evans and D. Parker, Chem. Soc. Rev., 2012, 41, 7673–7686.

2 D. W. Zhang, M. Li and C. F. Chen, Chem. Soc. Rev., 2020, 49, 1331–1343.

3 J. R. Brandt, X. Wang, Y. Yang, A. J. Campbell and M. J. Fuchter, J. Am. Chem. Soc., 2016, 138, 9743–9746.

4 (a) T.-Y. Li, Y.-M. Jing, X. Liu, Y. Zhao, L. Shi, Z. Tang, Y.-X. Zheng and J.-L. Zuo, Sci. Rep., 2015, 5, 14912; (b) S. Feuillastre, M. Pauton, L. Gao, A. Desmarchelier, A. J. Riives, D. Prim, D. Tondelier, B. Geffroy, G. Muller, G. Clavier and G. Pieters, J. Am. Chem. Soc., 2016, 138, 3990–3993; (c) J. Han, S. Guo, J. Wang, L. Wei, Y. Zhuang,
(a) D. M. Lee, J. W. Song, Y. J. Lee, C. J. Yu and J. H. Kim, R. H. Friend, F. Tassinari, S. C. J. Meskers, R. Naaman, E. W. Meijer and F. Hernandez, J. Autschbach, Y. Trolez and J. Crassous, Chem. Soc. Engl., 2020, 14511–14516; (b) Y.-F. Wang, H.-Y. Lu, C. Chen, M. Li and C.-F. Chen, Org. Electron., 2019, 70, 71–77; (c) Z. G. Wu, H. B. Han, Z. P. Yan, X. F. Luo, Y. Wang, Y. X. Zheng, J. L. Zuo and Y. Pan, Adv. Mater., 2019, 31, e1900524; (d) Z.-P. Yan, K. Liao, H.-B. Han, J. Su, Y.-X. Zheng and J.-L. Zuo, Chem. Commun., 2019, 5, 8215–8218; (e) M. Li, Y. F. Wang, D. Zhang, L. Duan and C. F. Chen, Angew. Chem., Int. Ed. Engl., 2020, 59, 3500–3504; (f) Y. F. Wang, M. Li, W. L. Zhao, Y. F. Shen, H. Y. Lu and C. F. Chen, Chem. Commun., 2020, 56, 9380–9383; (g) S. Abbate, Funct. Mater., 2017, 27, 1791–1795; (h) D. Di Nuzzo, C. Kulkarni, B. Zhao, E. Smolinsky, F. Tassinari, S. C. J. Meskers, R. Naaman, E. W. Meijer and R. H. Friend, ACS Nano, 2017, 11, 12713–12722; (i) D. M. Lee, J. W. Song, Y. J. Lee, C. J. Yu and J. H. Kim, Adv. Mater., 2017, 29, 1700907; (j) F. Zinna, M. Pasini, F. Galeotti, C. Botta, L. Dari and U. Giovanella, Adv. Funct. Mater., 2017, 27, 1603719; (k) L. Wan, J. Wade, F. Salerno, O. Arteaga, B. Laidlaw, X. Wang, T. Penfold, M. J. Fuchter and A. J. Campbell, ACS Nano, 2019, 13, 8099–8105; (l) W. L. Zhao, Y. F. Shen, H. Y. Lu and C. F. Chen, J. Am. Chem. Soc., 2020, 142, 17756–17765.

5 (a) Yang, R. C. da Costa, D.-M. Smilgies, A. J. Campbell and M. J. Fuchter, Adv. Mater., 2013, 25, 2624–2628; (b) F. Zinna, U. Giovanella and L. D. Bari, Adv. Mater., 2015, 27, 1791–1795; (c) D. Di Nuzzo, C. Kulkarni, B. Zhao, E. Smolinsky, F. Tassinari, S. C. J. Meskers, R. Naaman, E. W. Meijer and R. H. Friend, Gaussian, Inc., Wallingford CT, 2009; (d) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, C. G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. J. J. Van Lysse, R.omperts, B. Mennucci, H. P. Hratchtian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidio, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuada, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, M. K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01, 2016. www.gaussian.com.

10 (a) B. Dereka, A. Rosspeintner, Z. Li, R. Liska and E. Vauthey, J. Am. Chem. Soc., 2016, 138, 4643–4649; (b) B. Dereka, M. Koch and E. Vauthey, Acc. Chem. Res., 2017, 50, 426–434; (c) B. Dereka, A. Rosspeintner, R. Stężycki, C. Ruckebusch, D. T. Gryko and E. Vauthey, J. Phys. Chem. Lett., 2017, 8, 6029–6034.

11 F. Zinna and L. Di Bari, Chirality, 2015, 27, 1–13.

14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, C. G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. J. J. Van Lysse, R.omperts, B. Mennucci, H. P. Hratchtian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidio, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuada, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, M. K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01, 2016. www.gaussian.com.

15 T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett., 2004, 391, 51–57.

16 (a) F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297–3305; (b) F. Weigend, Phys. Chem. Chem. Phys., 2006, 8, 1057–1065.

17 G. Scalmani and M. J. Frisch, J. Chem. Phys., 2010, 132, 114110.

18 (a) J. Autschbach, L. Nitsch-Velasquez and M. Rudolph, Top. Curr. Chem., 2011, 298, 1–98; (b) M. Srebro-Hooper and J. Autschbach, Annu. Rev. Phys. Chem., 2017, 68, 399–420.

19 F. Santoro, A. Lami, R. Improta, J. Bloino and V. Barone, J. Chem. Phys., 2008, 128, 224311.

20 K. Dhbai, C. Shen, M. Jean, N. Vanthuyne, T. Roisnel, M. Gorecki, B. Jamoussi, L. Favereau and J. Crassous, Front. Chem., 2020, 8, 237.
21 (a) C. Shen, F. Gan, G. Zhang, Y. Ding, J. Wang, R. Wang, J. Crassous and H. Qiu, Mater. Chem. Front., 2020, 4, 837–844; (b) M. Srebro, E. Anger, B. Moore II, N. Vanthuyne, C. Roussel, R. Réau, J. Autschbach and J. Crassous, Chem.–Eur. J., 2015, 21, 17100–17115.

22 (a) M. Sapir and E. V. Donckt, Chem. Phys. Lett., 1975, 36, 108–110; (b) N. I. Nijegorodov and W. S. Downey, J. Phys. Chem., 1994, 98, 5639–5643; (c) K. Nagarajan, A. R. Mallia, K. Muraleedharan and M. Hariharan, Chem. Sci., 2017, 8, 1776.

23 (a) F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle and S. Grimme, J. Am. Chem. Soc., 2000, 122, 1717–1724; (b) Y. Nakai, T. Mori and Y. Inoue, J. Phys. Chem. A, 2012, 116, 7372–7385; (c) Y. Nakai, T. Mori and Y. Inoue, J. Phys. Chem. A, 2013, 117, 83–93.

24 J. A. Schellman, Chem. Rev., 1975, 75, 323–331.

25 H. Tanaka, Y. Inoue and T. Mori, ChemPhotoChem, 2018, 2, 386–402.

26 M. Rudolph and J. Autschbach, J. Phys. Chem. A, 2011, 115, 2635–2649.

27 (a) N. Berova, L. D. Bari and G. Pescitelli, Chem. Soc. Rev., 2007, 36, 914–931; (b) G. Pescitelli, L. Di Bari and N. Berova, Chem. Soc. Rev., 2014, 43, 5211–5233.

28 (a) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi and K. Tanaka, J. Am. Chem. Soc., 2012, 134, 4080–4083; (b) C. Schaarack, L. Arrico, E. Sidler, M. Gorecki, L. D. Bari and F. Diederich, Chem. – Eur. J., 2019, 25, 8003–8007; (c) K. Dhbaibi, L. Favereau and J. Crassous, Chem. Rev., 2019, 119, 8846–8953; (d) W.-L. Zhao, M. Li, H.-Y. Lu and C.-F. Chen, Chem. Commun., 2019, 55, 13793–13803.

29 (a) P. Reine, A. G. Campana, L. Alvarez de Cienfuegos, V. Blanco, S. Abbate, A. J. Mota, G. Longhi, D. Miguel and J. M. Cuerva, Chem. Commun., 2019, 55, 10685–10688; (b) N. Chen and B. Yan, Molecules, 2018, 23, 3376.

30 In this regard, the CPL of P- and M-H6(CN)2 was also measured by the groups of Prof. Di Bari in Pisa and the one of Dr Pieters in Paris (see the ESI‡ for details on their CPL spectrometers) and afforded almost similar CPL spectra, both in terms of shape and intensity with glum values of 3.1 × 10–2 (CPL spectrometer in Paris) and 3.8 × 10–2 (CPL spectrometer in Pisa), confirming that our molecular design provides one of the most efficient CPL emitters based on carbo[6]helicene reported to date.