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Interplay of Excited-States on Circularly Polarized Thermally Activated Delayed Fluorescent Chiral Exciplexes

Patthira Sumsalee, Ramar Arun Kumar, Fabien Lucas, Denis Tondelier, Jeanne Crassous, Grégory Pieters,* and Ludovic Favereau*

Molecular emitters that combined thermally activated delayed and circularly polarized fluorescence (CP-TADF) is of paramount importance for the next generation of displays. While most efforts have thus far focused on covalent donor and acceptor CP-TADF emitters, a novel strategy based on chiral exciplexes has recently emerged. In this context, we present the synthesis and chiroptical properties of four new CP-TADF exciplexes, involving two distinct C₂-symmetric bicarbazole systems and two terpyridine-based derivatives, which serve as the chiral donor and achiral acceptor units, respectively. These exciplexes exhibit CP-luminescence, with intensity dependent on both the chiral donor and achiral constituents, resulting in emission dissymmetry factors reaching up to 10⁻² in the thin-film solid state. Additionally, small singlet-triplet gaps ($\Delta E_{ST} \leq 0.1$ eV) have been measured, leading to TADF characteristics with a photoluminescence quantum yield of 20% for the most efficient emitter, which is also successfully used in non-optimized organic lightemitting diodes (OLEDs). Interestingly, these chiral exciplexes allow us to explore the impact of the locally-excited (LE) state of the chiral donor on overall exciplex emission, particularly in relation to the intensity of polarized emission—potentially highlighting a key factor in the design of this type of bimolecular CP-TADF emitter.

bioimaging.^[1-7] While chiral lanthanide complexes remain the archetype for obtaining high CPL intensity – thanks to their magnetically allowed and electrically forbidden transitions.^[1,8-10] chiral organic materials have recently aroused significant interest due to their readily tunable optoelectronic properties, better processability and often higher photoluminescence quantum yields (PLQYs). The latter aspect, combined with the high molar extinction coefficient of their related electric dipole-allowed transitions, gives organic chiral dyes the potential of high levels of CPL brightness.^[11,12] These features make them valuable candidates for CPL applications,^[13-20] such as the development of CP-OLEDs, which could enhance the efficiency of conventional non-polarized OLED displays, improving image brightness and reducing power consumption.

To achieve efficient CP-OLEDs based on a chiral emitter, the latter should ensure simultaneously high excitons conversion (both singlet and triplet) and a high degree of CPL. Among the explored research directions to meet these two objectives, the

design of CP-thermally activated delayed fluorescent (CP-TADF) molecules is currently of great interest, with the device's external quantum efficiency, EQE, reaching up to 30%.^[21-24] The crucial challenge in this research field remains combining a high degree of CPL to the TADF emission, usually involving a significant electronic dipole transition moment. Indeed, the latter aspect has an

1. Introduction

The design of chiral molecules displaying circularly polarized luminescence (CPL) has attracted renewed attention in the last decade, due to the potential applications of CP-light in various domains, ranging from optoelectronics to chiral sensing and

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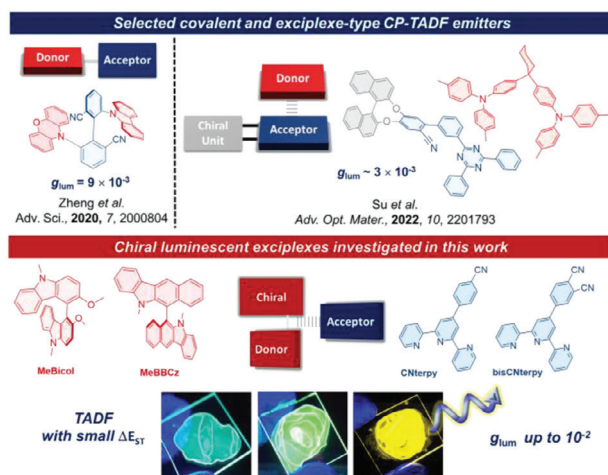


Figure 1. Top: Selected examples of reported chiral luminescent CP-TADF emitters based on covalent (left) and exciplex (right) approaches. Bottom: Chemical structures of the different chiral donors (in red) and achiral acceptors (in blue) used to form the new CPL exciplex emitters investigated in this study, and selected pictures of their emission colors in solid-state.

intrinsically negative effect on the intensity of CPL, characterized by the emission dissymmetry factor, g_{lum} , well approximated as $4|m|\cos\theta/(|\mu|)$ for an electric dipole-allowed transition (m and μ being the magnetic and electric transition dipole moments and θ the angle between the two latter).^[10] Despite the design of several types of CP-TADF emitters, in which the chiral element is either inherently involved in the charge-transfer photophysical process showing DF,^[21] or used as a chiral perturber of the latter (Figure 1), the obtained g_{lum} of the related TADF has hardly exceeded 9×10^{-3} , both in solution and thin-film solid state (Figure 1).^[25–27]

As an alternative strategy for obtaining CP-TADF emitters, we recently pioneered the design of chiral luminescent exciplexes involving a chiral electron donor and achiral electron acceptor units.^[28] In condensed phase, these two components interact through electron transfer upon light excitation, resulting in CP-TADF emission with g_{lum} values up to 6×10^{-3} , which appears much higher than that of the chiral donor unit alone (6×10^{-4}). Beyond these results, this chiral exciplex approach affords distinct advantages such as: 1) a small energy difference between singlet and triplet excited states, ΔE_{ST} , because of the spatially separated lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) of the acceptor and donor molecules, respectively; and 2) the possibility to tune the CP emission color by simply playing with the electron accepting ability of the achiral units, without requiring any chemical reactions. Following our work,^[28] Shi-Jian Su et al. reported chiral exciplexes with TADF and g_{lum} up to 3×10^{-3} in thin-film solid state, using an achiral electron donor and a chiral electron acceptor (Figure 1), and

showed that efficient CP-OLED based on that emissive system could be obtained, with an EQE of ca. 13%.^[29] Interestingly, intermolecular approaches such as energy transfer, charge transfer, and excimer formation involving chiral molecules have resulted in promising impressive CPL values,^[30–36] with g_{lum} up to 0.15,^[37] opening new opportunities to combine such strategies with the TADF property.^[38]

While these results bring a new direction for designing more efficient CP-TADF emitters, this type of chiral exciplex remains limited to a few examples, which render challenging the rationalization of this approach and the identification of the key parameters influencing the synergy between TADF and the degree of CP emission. In particular, obtaining more information on the link between the nature of the chiral molecular components, their supramolecular interaction, and the resulting intensity of CPL remain to be fully established.

To explore deeper this luminescent chiral exciplex approach, it appears crucial to investigate new combinations of chiral electron donating and electron accepting units in order to gain insights into the structural and electronic factors that impact notably the intensity of the CP-TADF emission. Herein, we report the synthesis and properties of four new chiral luminescent exciplexes, involving two different C_2 -symmetric donors and two terpyridine-based acceptors. The formation of these chiral complexes is obtained in condensed phase, and affords CP-TADF emitters with PLQYs up to 20%. In addition, all these exciplexes display CPL, being dependent of the nature of both chiral donor and the achiral units, with g_{lum} values going up to 10^{-2} in thin film state. Proof-of-concept OLEDs based on the reported chiral exciplexes afforded a promising EQE of ca. 1.24%. More than affording one of the highest intensities of CPL for molecular TADF emitters, these findings bring important aspects regarding the chiral exciplex approach and the parameters governing the underlying process at play in these luminescent bimolecular systems.

2. Results and Discussion

To design the new chiral luminescent exciplexes, we selected two different chiral electron donor (Figure 1), the 3,3'-dimethoxy-9,9'-dimethyl-9H,9'H-4,4'-bicarbazole system (MeBicol) and 5,5'-dimethyl-5H,5'H-6,6'-bibenzo[b]carbazole (MeBBCz),^[39] based on their suitable optical and electronic intrinsic properties to promote photoinduced electron transfer reaction with different electron acceptor units.^[40,41] Indeed, these chiral systems are configurationally stable, possess oxidation potentials ≈ 0.8 – 0.9 V versus SCE, relatively high absorption optical gap, ca. ~ 3.0 eV, and high energy of the first singlet and triplet excited states, as estimated from their photophysical and electrochemical properties measured in solution (Figure 2; Figure S11, Supporting Information). The additional fused phenyl ring in MeBBCz slightly stabilizes the energy of its HOMO, which impact the resulting color of the exciplex emission, as well as its thermodynamic characteristics (vide supra). Regarding the acceptor components, two terpyridine derivatives have been chosen as electron acceptors based on recent results reporting their potential use to efficiently generate luminescent achiral exciplexes.^[42] In the present study, the terpyridine backbone was functionalized by either a mono- or a biscyanophenyl ring (Figure 1), named CNterpy and BisCNterpy, respectively, in order to also modulate the optoelectronic

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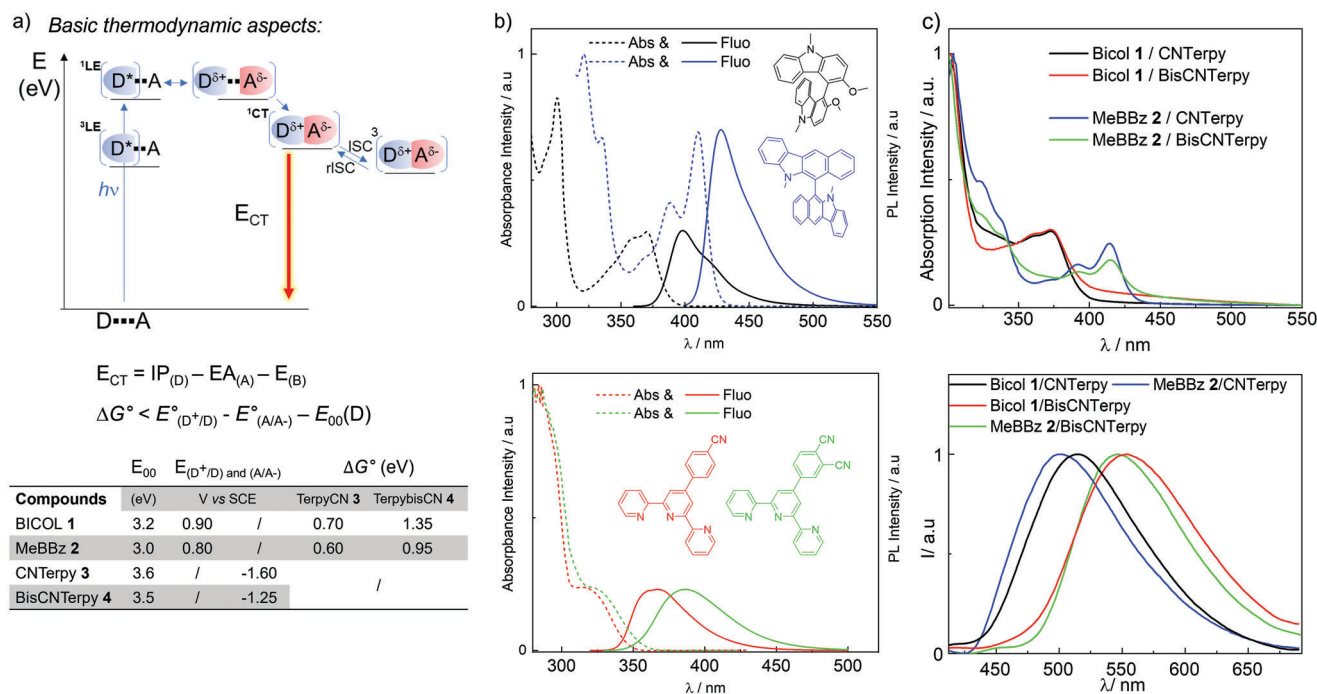


Figure 2. a) Top: Energy-level scheme for the luminescence process of a donor-acceptor pair upon photoexcitation, with basic thermodynamic considerations: E_{CT} , the energy of the charge-transfer process with IP = ionization potential, EA = electron affinity and E_B , the binding energy of the charge-transfer state.^[40] ΔG° is the driving force for the photoinduced electron transfer between the donor and the acceptor implying the oxidation and reduction potentials of the donor and acceptor, respectively, and E_{00} the optical gap of the donor molecule, with experimental data for the donor and acceptor units investigated in this study (SCE = saturated calomel electrode). b) Absorption and emission spectra of bicarbazole systems (top) and terpyridine derivatives (bottom) in dichloromethane at 298 K ($[c] \approx 10^{-5}$ M), c) Absorption spectra (top) of spin-coated films involving one bicarbazole donor and one terpyridine acceptor and their corresponding exciplex luminescence spectra recorded at 298 K (bottom).

properties of the resulting exciplexes. The terpyridine derivatives and **MeBicol** were obtained following established synthetic procedures and the corresponding enantiomers were prepared by HPLC separations over chiral stationary phases (ee's > 99%, see Supporting Information, SI). The synthesis of **MeBBCz** was revisited with the objective of obtaining both enantiomers starting from commercially available (*R*)- and (*S*)-3,3'-Dimethyl-[1,1'-binaphthalene]-2,2'-diamine (BINAM) with high ee and overall yields. The developed three-step synthetic procedure (see Supporting Information page 3) involves a Buchwald–Hartwig coupling between commercially available (*R*)- or (*S*)-BINAM and 2-bromiodobenzene, followed by a palladocatalyzed C-H annulation to construct the **BBCz** scaffold, and finally, a methylation using iodomethane.

Characterizations of the donor/acceptor mixtures were firstly conducted in DCM solution ($[c]$ up to $\approx 10^{-3}$ M), and the results were compared to those obtained for the two chiral donors and achiral acceptors alone. As detailed in the SI, similar absorption and emission responses were obtained for solutions of **MeBicol**/CNTerpy and **MeBBCz**/CNTerpy mixtures than for solutions of **MeBicol**, **MeBBCz** or CNTerpy alone (Figure 2; Figure S1–S4, Supporting Information) at both low and high concentration ($[c]$ up to $\approx 10^{-3}$ M), evidencing a lack of electronic interaction between the donor and acceptor units. A similar result was also obtained for the other **MeBicol**/BisCNTerpy and **MeBBCz**/BisCNTerpy mixtures upon comparison with solutions of **MeBicol**, **MeBBCz** and **BisCNTerpy** alone. The only difference comes from

the emission of the latter electron acceptor molecule, which is slightly red-shifted by about ≈ 10 nm in comparison to **CNTerpy** because of the presence of the additional cyano group.

2.1. Ground and Excited States Photophysical and Chiroptical Properties

The chiroptical and photophysical properties of the D/A mixtures were further investigated in the solid state, on spin-coated films using a 2/1 molecular ratio.^[28] The UV–vis and ECD spectra of the obtained blends display responses very close to the one recorded for neat film of the bicarbazole derivatives alone (Figure 2; Figure S5, Supporting Information), which also indicates a very weak electronic interaction between the donor and acceptor units within the film. In contrast, all films display a broad unstructured emission band between 450 and 650 nm which does not correspond to the photoluminescence of the isolated units neither in solution, nor in the solid state. Accordingly, we attributed these new signals to an exciplex emission arising from an intermolecular radiative charges recombination from the LUMO of the acceptor to the HOMO of the donor units (Figure 2b,c).

MeBicol/CNTerpy and **MeBBCz**/CNTerpy films exhibit a maximum of emission wavelength ≈ 500 –510 nm while **MeBicol**/BisCNTerpy and **MeBBCz**/BisCNTerpy blends show a maximum of ≈ 550 –560 nm. The observed red-shift ≈ 50 nm can be

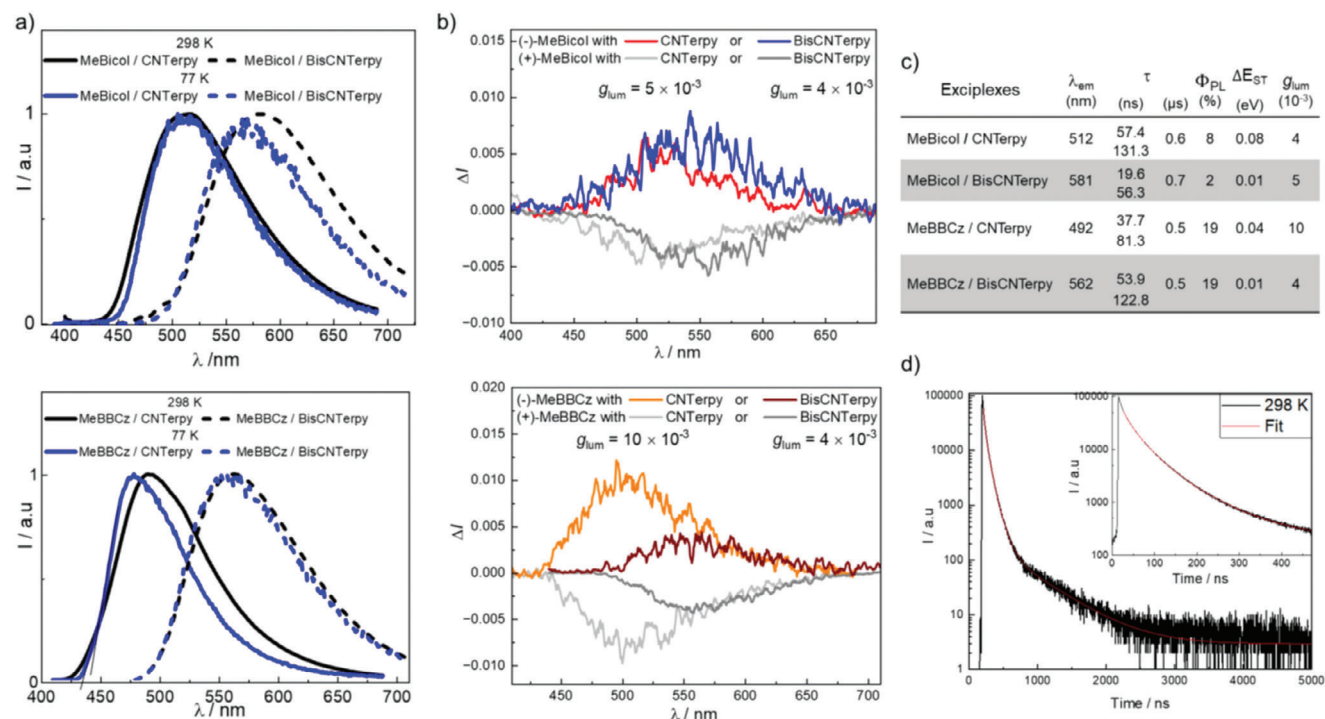


Figure 3. a) Luminescence spectra of spin-coated films involving **MeBicol** (top) or **MeBBCz** (bottom) with either **CNTerpy** (solid line) or **BisCNTerpy** (dotted line) recorded at 298 K (black) and 77 K (blue); b) CPL spectra of spin-coated films involving **MeBicol** (top) or **MeBBCz** (bottom) with either **CNTerpy** or **BisCNTerpy** recorded at 298 K; c) Photophysical properties of the luminescent exciplexes; and d) Luminescence decays of exciplex **MeBBCz/CNTerpy** recorded at 298 K (black solid line) and its corresponding fit (red line) with an inset focusing on the short lifetime decays.

related to the presence of the additional cyano group on the acceptor unit (**CNTerpy** vs **BisCNTerpy**). Cyclic voltammetry experiments further confirm this aspect since comparable oxidation potentials were recorded for chiral donors **MeBicol** and **MeBBCz** ($\Delta E_{ox} \approx 0.1$ V between their first oxidation events, Figure 1; Figure S11, Supporting Information), while a difference of 0.35 V is observed between the first reduction events for mono- and biscyano terpyridine derivatives ($E_{red} = -1.25$ and -1.60 V vs SCE for **CN-Terpy** and **BisCNTerpy**, respectively). HOMO levels were calculated to be -5.34 and -5.24 for **MeBicol** and **MeBBCz**, respectively, and LUMO levels -2.84 and -3.9 eV for **CN-Terpy** and **BisCN-Terpy**, respectively.

In terms of luminescence efficiency, the solid state PLQY of the exciplexes afforded rather modest values, ranging from 0.05 to 0.2 under inert atmosphere, in the range of what is often obtained for this type of luminescent emitters.^[43] Interestingly, the exciplexes based on **MeBBCz** with either **CN-Terpy** and **BisCN-Terpy** afforded brighter emission than the exciplexes based on **MeBicol** (Figure 3), suggesting an important influence of the donor nature on this property. Further photophysical investigations show that the intensity of the emission decreases in presence of oxygen for all of the exciplex (Figure S15, Supporting Information). Evaluation of the solid-state photoluminescence lifetimes of the films under inert atmosphere affords a multi-exponential decay with a long component in the microsecond timescale (Figure 3), which decreases under air condition, suggesting the presence of TADF for these exciplexes.

As the temperature is cooled to 77 K, the lifetime attributed to the delayed component increases (Figure S19, Supporting

Information). This indicates that the reverse intersystem crossing (rISC) process occurring from triplet to singlet excited states becomes less favored at low temperature while remaining not completely quenched because of the probably low ΔE_{ST} , as usually observed for exciplex-type TADF emitters.^[40,44–46]

To gain further insights, the S_1 and T_1 energy levels of each exciplexes have been estimated from the onset of the fluorescence and phosphorescence emissions of the films recorded at room temperature and 77 K, respectively and using a time-gated mode for isolating the later signal (Figures S13 and S14, Supporting Information). From these values, ΔE_{ST} values of the exciplexes have been estimated to be less than 0.1 eV for all the D/A combinations, as it is usually observed for that type of bimolecular exciplexes displaying a net spatial separation of the HOMO (located on the donor unit) and LUMO (located on the acceptor unit).^[43,41,47]

The potential CP-TADF of the reported exciplexes has been investigated in the solid state and compared with the signals obtained for the isolated chiral donors alone, which show a g_{lum} of $4\text{--}7 \times 10^{-4}$ in solution for both systems (Figures S6–S10, Supporting Information). As depicted in Figure 3, all the exciplexes emit CPL with clear mirror-image spectra for both enantiomers of each donor, and with maxima corresponding to the unpolarized luminescence spectra. In line with our previous report and the different nature of the emitting transition,^[28,48] all the exciplexes show CPL sign inversion when compared with the CPL of the chiral donor alone. In addition, the obtained exciplex CPL exhibit also higher polarization than the isolated chiral units, with g_{lum} values ranging from 4 to 10×10^{-3} , the highest g_{lum} being

obtained by the exciplex composed of MeBBCz and CNterpy. These levels of polarization are among the highest measured for molecular CP-TADF emitters,^[26,27,49] and further highlight the potential of chiral exciplexes for reaching efficiently CP-TADF.

2.2. Electroluminescence of Chiral Exciplexes

To get further insights into the chiral exciplex systems developed in this study, multilayer OLED based on (*R*) or (*S*)-MeBBCz/CNterpy emissive layers were prepared through vapor deposition technique with a weight ratio 2:1 using the following architecture: ITO/HATCN (10 nm)/TAPC (45 nm)/TcTa (8 nm)/ (*R*) or (*S*)-MeBBCz/CNterpy (1:2) (20 nm)/TmPyPB (55 nm)/LiF (1.2 nm)/Al (100 nm), where HATCN, TAPC, TcTa, TmPyPB, and LiF are respectively hole injection, hole transport, electron blocking, electron transport and electron injection layers. The chemical structures of these compounds and the energy diagram of the device stack are shown in Figure S19 (Supporting Information). This non-optimized device architecture exhibited a greenish-blue electroluminescence close to the emission of the exciplex in thin film (Figure 4), with maximal external quantum efficiency (EQE_{max}), current efficiency (CE_{max}) and power efficiency (PE_{max}) of 1.24%, 2.28 Cd A⁻¹ and 1.05 lm W⁻¹, respectively, Figure 4. The EQE of the OLED can be calculated according to the following formula:

$$\text{EQE} = \eta_{\text{int}} \times \eta_{\text{out}} = \gamma \times \eta_r \times \Phi_{\text{PL}} \times \eta_{\text{out}} \quad (1)$$

where η_{int} is the internal quantum efficiency, η_{out} is the light extraction efficiency, γ is the charged carrier balance factor, η_r is the radiative exciton generation ratio, and Φ_{PL} is the photoluminescence quantum yield. From this formula, and by considering that the charge transport is balanced ($\gamma = 1$), η_r is 100%, η_{out} is 20% and an Φ_{PL} of 0.20, EQE can be estimated to be $\approx 4\%$. While being promising for exciplexes-based devices,^[43,50,51] the obtained electroluminescence performances do not show any circular polarization, presumably because of the non-optimized OLED architecture involving notably a highly reflective counter electrode (Al, 100 nm), which could strongly decrease the output light circular polarization. By looking closer at the electroluminescent spectrum, one can note a shoulder at ≈ 430 nm.

According to the PL measurements depicted in Figure 2, this undesirable emission could arise from the donor unit alone within the blend, presumably because of the difficulty to control the optimum ratio of the donor and acceptor units during the evaporation. Furthermore, it is also reasonable to think that the charge transport is not correctly balanced which in turn could also affect the EQE. Such optimizations and other factors (thickness of the different layer and weight ratio within the emissive layer) are currently being investigated to afford better device performances.

3. Discussion

Although OLED performance is an important consideration when designing new organic emitters, the primary focus of this work is on exploring previously unexamined electronic factors

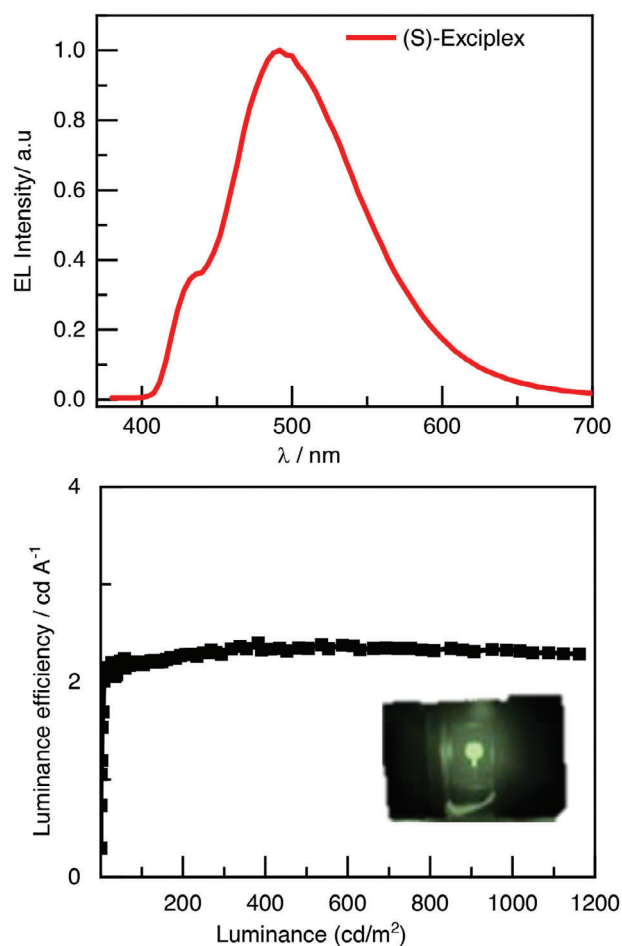


Figure 4. Top: Electroluminescence spectra of (*S*)-MeBBCz/CNterpy exciplex and bottom: Plot of external efficiency versus luminance and in insert a picture of the device.

that could enhance the intensity of CP light in chiral exciplexes. While this type of emitter is now well-established in the field of non-polarized OLEDs, its application in the generation of CP-light remains much less explored. Although previous reports have demonstrated the potential of the exciplex strategy for designing efficient CP-TADF emitters, the understanding of the electronic parameters involved in the molecular design of chiral exciplexes is still largely based on their achiral counterparts, without fully considering the factors that influence CP light emission intensity. For instance, in a previous study, we used a chiral electron donor in combination with various achiral electron acceptor units, achieving a g_{lum} barely exceeding to 5×10^{-3} .^[28] Using a complementary approach, Shi-Jian Su et al. used an achiral electron donor with chirally perturbed electron acceptor units and obtained CP-TADF with a g_{lum} of ca. 3×10^{-3} in the solid-state.^[29] Interestingly, they also showed that such type of emitters could lead to efficient CP-OLED, achieving an EQE of ca. 13% and a g_{EL} of ca. 10^{-2} . These two studies have greatly contributed to laying the foundations for the molecular design of chiral luminescent exciplexes, albeit remaining mainly based on the photophysical aspects found in achiral exciplexes (ionization potential and

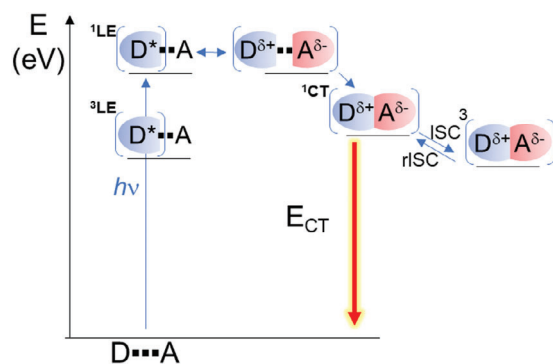


Figure 5. Energy-level scheme for the luminescence process of a donor-acceptor pair upon photoexcitation involving a (reverse) intersystem crossing ((r)ISC) event, with photo-excitation on the locally excited (LE) state of the donor and photoemission from a charge-transfer (CT) state between donor and acceptor units.

reduction of units, singlet and triplet state levels, donor/acceptor ratio, rigidity of the molecular systems used).

In a complementary and innovative way, we obtained g_{lum} of up to 10^{-2} for a chiral exciplex investigated in this study. Although fully rationalizing the underlying processes responsible for these high intensities of CPL remains challenging, it is important to highlight some potential molecular design guidelines for developing efficient chiral luminescent exciplexes. Exciplex emission is often described as a radiative electron transfer from the LUMO of the acceptor to the HOMO of the donor (Figure 2). While this is a widely accepted description, this process is actually more complex. Indeed, it is more accurate to consider the electron transfer as occurring within a partial charge-transfer (CT) state, mixed with locally excited (LE) state from the donor and acceptor units (Figure 5).^[52,53]

The ratio between the CT and LE states is strongly correlated with the electronic interaction between the molecular components and their mutual orientation. As a result, a qualitative description of the exciplex wave function, $\psi([DA]^*)$, considering the weak influence of the donor and acceptor ground states, can be expressed as a linear combination of the LE and CT state wave functions as follows:^[54]

$$\Psi([DA]^*) \approx c_1 \Psi(D^+A^-) + c_2 \Psi(DA^*) + c_3 \Psi(D^*A) \quad (2)$$

with the $c_{1,3}$ coefficients being related to the proportion of the CT and LE states wave functions from the charge-separated state, and the acceptor and donor excited-states, respectively. According to this equation, as c_1 increases, the luminescent spectrum of the exciplex becomes more and more red-shifted, broader and unstructured.^[55–57,40,41,58,59] In the context of chiral luminescent exciplexes, it appears crucial to better understand how the relative distribution of the $c_{1,3}$ coefficients impacts the CP exciplex emission, and more specifically, if the coefficient related to the chiral excited-state partner (c_3 for chiral donor in this case) is a key parameter for increasing the resulting intensity of polarization of this radiative process.

While all chiral exciplexes exhibit TADF with a promising level of CP emission, the g_{lum} value for **MeBBCz/CNTerpy** appears particularly high in comparison to the others. Following

the aforementioned equation, the exciplex wavefunction can be expressed as the mixed state of pure LE and CT states, depending on the electronic properties of each partner and their interaction in condensed phases. In fact, while the luminescence responses for the chiral exciplexes **MeBicol/CNTerpy**, **MeBicol/BisCNTerpy** and **MeBBCz/BisCNTerpy** have a broad and featureless profile, the one corresponding to the **MeBBCz/CNTerpy** exciplex is narrower (full width at half maximum, FWHM, ≈ 70 nm versus 110 nm for **MeBBCz/CNTerpy** and **MeBicol/CNTerpy**, respectively) and appears less broad, starting to be even structured at both 298 and 77 K (Figures 3 and 6). Moreover, the maximum emission wavelength is blue-shifted by ca. 0.1 eV in comparison to that of **MeBicol/CNTerpy** despite the lower oxidation potential of the chiral donor **MeBBCz** ($E_{\text{ox}} = 0.9$ and 0.8 V vs SCE for **MeBicol** and **MeBBCz** respectively). These experimental evidences suggest that the CT fraction, c_1 (Equation 1), is lower for the exciplex wave function of **MeBBCz/CNTerpy** than for **MeBicol/CNTerpy**. This becomes even clearer when comparing the emission of pure films of the bicarbazole compounds alone with the luminescence from the corresponding exciplexes. As depicted in Figure 6, the fluorescence signal of **MeBBCz** largely overlaps with that of **MeBBCz/CNTerpy** at both 77 and 298 K, while a weaker overlap is observed between the fluorescence signal of **MeBicol** and **MeBicol/CNTerpy** exciplex (despite the presence of a broad excimer emission band between 450 and 600 nm for **MeBicol**).^[60] These results suggest that the radiative CP emission of **MeBBCz/CNTerpy** exciplex possesses a higher proportion of chiral LE states of **MeBBCz** compared to the remaining LE state proportion of **MeBicol** in the **MeBicol/CNTerpy** exciplex. Following this reasoning, the proportion of chiral LE state of **MeBicol** and **MeBBCz** appears less important into the emission of **MeBicol/BisCNTerpy** and **MeBBCz/BisCNTerpy** exciplexes, respectively. For the systems investigated here, increasing the proportion of chiral LE state within the overall exciplex wave function appears beneficial for enhancing the emission dissymmetry factor value, as illustrated for **MeBBCz/CNTerpy**. (while the other exciplexes lead to almost similar g_{lum} of $4 - 5 \times 10^{-3}$, remaining still of interest in comparison to other CP-TADF emitters).

While this intensity of polarized emission is of fundamental interest for the development of efficient CP-OLEDs, it also important to link this parameter to the PLQY of the emitter. Since CPL exciplexes are relatively rare in the literature, the CPL brightness (B_{CPL}) of the exciplexes was also calculated. B_{CPL} values range from 0.6 to 9.5 $\text{m}^{-1} \text{cm}^{-1}$ in the solid state, with the highest value corresponding to the **MeBBCz/CNTerpy** system due to its higher g_{lum} . These values fall into the lower end of what it is usually obtained for organic CPL emitters.^[11] It is worth noting that higher B_{CPL} could be achieved by increasing the PLQY of such exciplex emitters. The spatial separation of the frontier orbitals (HOMO and LUMO) results in a low transition dipole and hence a small radiative rate constant (k_r) of the emission compared to non-radiative decays. Therefore, further progress requires a deeper understanding of the exciplex structure and its relationship with thermodynamics and photophysics, which remains a significant challenge. Recent advances in this area have been made by Wong, Pi-Tai Chou et al.,^[61] who designed a TADF exciplex involving an electron deficient cage that can encapsulate electron donor compounds. This design resulted in an exciplex PLQY of 56%, affording an interesting research direction

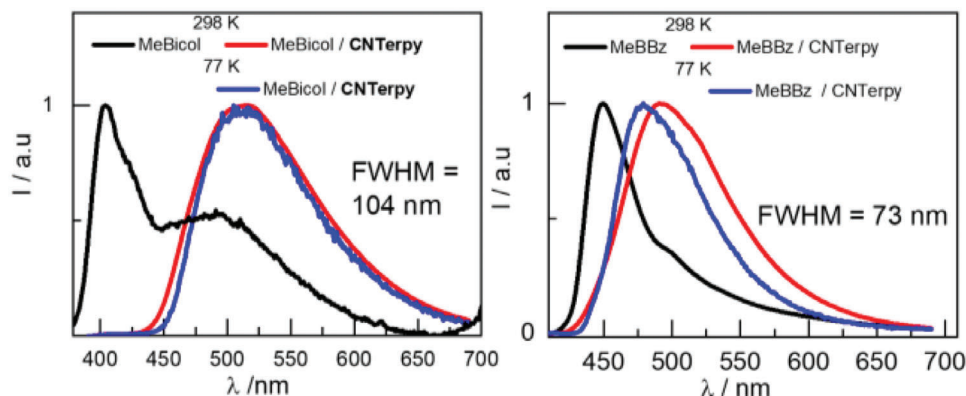


Figure 6. Left: Emission spectra of spin-coated films of **MeBicol** (black) and its corresponding exciplex luminescence spectra with **CNterpy** recorded at 77 K (blue) and 298 K (red); Right: Emission spectra of spin-coated films of **MeBBCz** (black) and its corresponding exciplex luminescence spectra with **CNterpy** recorded at 77 K (blue) and 298 K (red).

for such type of emitters. In a complementary approach, Adachi, Mathevet, Zhang et al. recently designed a chiral donor–acceptor cage displaying efficient CP-TADF with $|g_{lum}|$ values up to 2.1×10^{-3} and a PLQY of 32%, based on through-space charge transfer emission.^[62] They notably demonstrated that this type of design can provide a small ΔE_{ST} of 0.051 eV and quasi-parallel ($\theta = 6^\circ$) transition electric and magnetic dipole moments, which is a key parameter to reach high CPL intensity when considering the simplified equation $g_{lum} = 4(|\mu|/|\sim\mu|) \times \cos \theta$. These aspects are crucial for developing chiral exciplexes with intense CP-TADF.

4. Conclusion

In this paper, we present a comprehensive study of four chiral TADF exciplexes involving two distinct types of chiral donors: 3'-dimethoxy-9,9'-dimethyl-9H,9'H-4,4'-bicarbazole (**MeBicol**) and bibenzo[b]carbazole (**MeBBCz**), along with two different achiral acceptors based on terpyridine scaffolds (**CNterpy** and **bisCNterpy**). All combinations of these donors and acceptors resulted in TADF-active exciplexes in the condensed phase, exhibiting minimal singlet-triplet gaps (ranging from 0.01 to 0.08 eV) and photoluminescence quantum yields (PLQYs) up to 20% under inert atmosphere. Notably, the chiroptical properties of these exciplexes were significantly influenced by the chiral donor, and, more unexpectedly, by the nature of the achiral acceptor, particularly when using **MeBBCz** as the chiral donor. The pairing of **MeBBCz** with **CNterpy** yielded the highest dissymmetry factors (10^{-2}) reported to date for CP-TADF molecular systems. Experimental data suggest that the enhancement of CPL properties can be attributed to a larger proportion of chiral LE states from **MeBBCz** when combined with **CNterpy**, compared to the other exciplexes studied.

Proof-of-concept OLEDs were successfully fabricated using a vapor deposition technique, with **MeBBCz/CNterpy** as the emissive layer. Beyond demonstrating the potential of the chiral exciplex strategy in designing TADF-active materials with high emission dissymmetry factors, this study provides valuable insights into the key factors governing the underlying processes in these luminescent bimolecular systems. These findings pave the way for advancements in CPL emissive materials, offering promising enhancements in performance levels.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

L.F., G.P., and P.S. conceived the project. P.S. and R.A.K. synthesized the compounds, collected, and interpreted the spectral data with the help of J.C., G.P., and L.F., F.L., and D.T. fabricated OLEDs. All authors participated in the writing process.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

circularly polarized light emission, exciplexes, organic emitters, thermally activated delayed fluorescence

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