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## COMMUNICATION

# Luminescent Chiral Exciplexes with Sky-Blue and Green Circularly Polarized-Thermally Activated Delayed Fluorescence

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Dedication ((optional))

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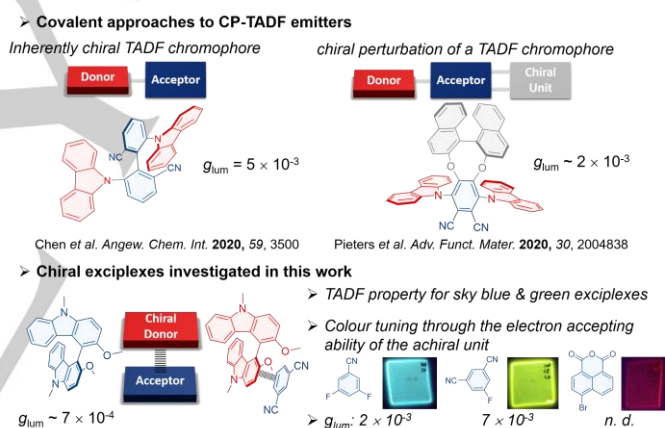
**Abstract:** Luminescent exciplexes based on a chiral electron donor molecule and achiral acceptor ones are reported as a new approach to design circularly polarized (CP) and thermally activated delayed fluorescence (TADF) emitters. This innovative strategy results in rather high CP luminescence values with  $g_{lum}$  up to  $7 \times 10^{-3}$ , one order of magnitude higher in comparison to the CPL signal recorded for the chiral donor alone ( $g_{lum} \sim 7 \times 10^{-4}$ ). This increase occurs concomitantly to a CPL sign inversion, as a result of the strong charge-transfer emission character, as experimentally and theoretically rationalized using a covalent chiral Donor-Acceptor model. Interestingly, blue, green-yellow and red chiral luminescent exciplexes can be obtained by playing with the electron accepting character of the achiral unit while keeping the same chiral donor unit. These results bring new (inter)molecular guidelines to obtain simply and efficiently multi-color CP-TADF emitters.

Designing Circularly Polarized Luminescence (CPL) materials has recently received considerable attention owing to the potential of CP-light in a broad range of applications ranging from chiroptoelectronics (Organic Light-Emitting Diodes (OLEDs), optical information processing, etc.) to bio-imaging or chiral sensing.<sup>[1]</sup> In this context, the development of CP-OLEDs appears particularly relevant for increasing both the energy efficiency and contrast performances of current display devices,<sup>[2]</sup> as well as an innovative approach to develop future CP-light photonic applications. Currently, CP-OLEDs rely mainly on the doping of the device's emitting layer by a CPL emitter, which should ensure simultaneously high exciton conversion and a high degree of circular polarization. Chiral lanthanide complexes and chiral polymeric materials embedded in CP-OLED architectures have efficiently afforded high degree of circularly polarized electroluminescence (CPEL),<sup>[2a]</sup> with corresponding dissymmetry factor,  $g_{El}$ , up to 1.<sup>[3]</sup> However, their overall devices performances remain rather low due to either poor luminescence quantum yields or non-utilization of triplet states generated upon excitons formation within the OLED emitting layer. To overcome this aspect, CP-thermally activated delayed fluorescence (TADF) emitters have recently emerged since they represent a valuable approach to simultaneously combine the use of both singlet and triplet excitons conversion for high devices efficiency, and a circularly polarized light emission.<sup>[4]</sup> In this regard, two main strategies have been developed to design emitters combining CPL and TADF properties based on either *i)* inherently chiral TADF chromophore, *i.e.* where the chiral element is electronically involved in the charge-transfer photophysical process showing DF<sup>[5]</sup> or *ii)*, on the chiral perturbation of a TADF unit, *i.e.* the chirality element is not taking part of the TADF process but is essential to induce CPL (Figure 1).<sup>[6]</sup>

However, designing such chiral TADF molecular emitters is a highly challenging task because of the difficulty to efficiently combine TADF process and intense degree of CPL at the same time (and high racemization barrier). While the property of TADF is rather well-mastered in the above mentioned two approaches, presumably owing to the accumulate expertise during the last decade on achiral TADF emitters, the reported values of CPL remains rather modest, with dissymmetry factor,  $g_{lum}$ , often below  $3 \times 10^{-3}$ . In fact only limited examples of CP-TADF emitters have displayed  $g_{lum}$  equal or superior to  $5 \times 10^{-3}$ , owing presumably to the involvement of a through-space charge transfer transition within a chiral environment.<sup>[5c, 5d]</sup> However, maximizing one of the two properties (TADF/CPL) without disturbing the other seems a challenging task and only compromises have been reached up to now.<sup>[4a]</sup> Moreover, the resulting color tuning and facile preparation

of CP-TADF remain also a delicate aspect due to the covalent link between the donor and acceptor units within a chiral environment. Recently, intermolecular approaches such as energy transfer, charge transfer and excimer involving chiral molecules have resulted in promising to impressive CPL values,<sup>[7]</sup> with  $g_{lum}$  up to 0.15,<sup>[8]</sup> opening new opportunities to combine such strategies with the TADF property.

Herein, we report a new approach to design multi-colored CP-TADF materials based on exciplexes emitters. Such unexplored strategy involves an intermolecular charge-transfer (CT) transition between a chiral donor molecule and an achiral acceptor unit, which results in an efficient and tuneable CP-TADF property. Interestingly, the obtained chiral exciplexes lead to rather high CPL values, with  $g_{lum}$  up to  $7 \times 10^{-3}$ , *i.e.* one order of magnitude higher in comparison to the CPL signal recorded for the chiral donor alone ( $g_{lum} \sim 7 \times 10^{-4}$ ). This significant improvement occurs concomitantly with a CPL sign inversion, which results from the formation of a CT transition within the chiral exciplex, as experimentally and theoretically investigated using a covalent chiral donor-acceptor model compound. Finally, the color of the emitted CP-TADF can be readily tuned by playing with the LUMO energy level of the achiral acceptor while keeping the same chiral donor unit. Following this strategy, blue, green and red emissions have been obtained, highlighting the versatility and the straightforward character of this unprecedented intermolecular chiral exciplex concept (Figure 1).



**Figure 1.** Top: Current molecular designs of CP-TADF emitters. Bottom: chiral luminescent exciplex approach investigated in this report (n.d.: not detected).

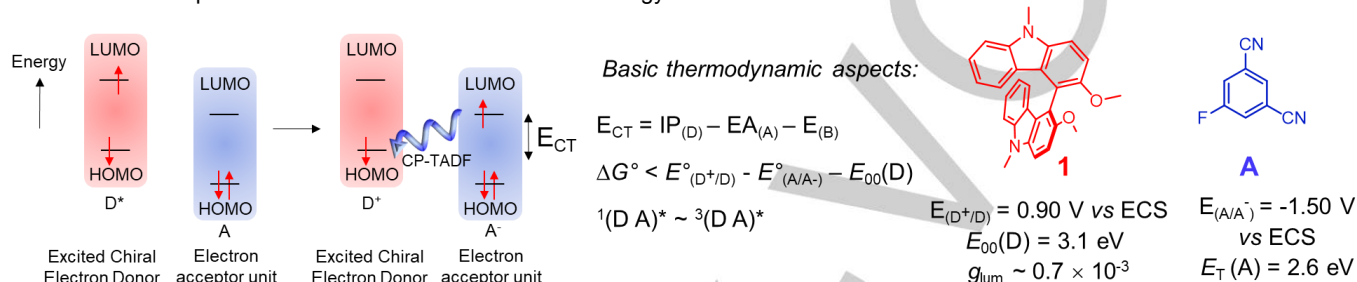
Exciplexes are defined as excited-state complexes formed between an excited electron donor (or acceptor) molecule and an unexcited electron acceptor (or donor) one, and are often observed at relatively high concentration of the involved partners.<sup>[9]</sup> We illustrate the various electron attachment/ detachment/ excitation steps using the orbitals of the neutral donor/acceptor moieties (Figure 2). The intermolecular charge-transfer can occur under both electrical and photo-excitation and results in a radiative recombination of charges, owing to an electron transfer from the LUMO of the acceptor molecule to the HOMO of the donor counterpart (Figure 2).<sup>[10]</sup> Interestingly, such photophysical process often involves a small energy gap between the lowest excited singlet and triplet states ( $\Delta E_{ST}$ ) due to the spatial localization of the frontier orbitals on each partner, and may give rise to TADF luminescent materials. Such approach has been indeed successfully used in conventional unpolarized OLEDs with External Quantum Efficiency up to 18%.<sup>[11]</sup>

Considering these concepts, we envisioned to develop a chiral luminescent exciplex with CP-TADF property based on a

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judiciously selected chiral donor molecule, *i.e.* the  $C_2$ -symmetric bicarbazole system, **1**.<sup>[12]</sup> This system presents a suitable donor ability, as indicated by its oxidation potential of 0.9 V vs SCE and its high optical gap ( $E_{00} = 3.1$  eV), to induce photoinduced electron transfer reaction with different electron acceptor units.<sup>[10-11]</sup> Moreover, such chiral electron donor shows a high tendency to aggregate in solid state, as indicated by the appearance of a broad excimer emission band between 450 and 600 nm in addition to the monomer fluorescence at 400 nm, suggesting a promising predisposition for obtaining chiral luminescent exciplexes (Figure 3 a).<sup>[13]</sup>

We firstly investigated the use of 5-fluoroisophthalonitrile (**A**) as an ideal electron acceptor candidate because of its suitable energy



**Figure 2.** Illustration of the circularly polarized luminescence process obtained in the reported chiral exciplexes with basic thermodynamic considerations regarding the HOMO and LUMO of the respective donor and acceptor neutral ground-states, respectively.  $E_{CT}$ , 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.<sup>[10]</sup>  $\Delta G^\circ$  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. Chemical structures of the chiral electron donor and the achiral electron acceptor investigated as luminescent exciplexes.

transfer process occurring between the two units in the condensed phase. The fact that similar UV-vis responses were obtained between neat **1** and **1:A** blend films further indicates no electronic interaction between the donor and acceptor units in their ground states, and strongly suggests the presence of an exciplex formation. In addition, the energy of the resulting lowest unoccupied exciplex excited state, ( $E_{CT}^1(1:A)$ ), of 2.76 eV can be correlated to the difference between the ionization potential (IP) of the donor fragment **1**, and the electron affinity (EA) of the electron acceptor **A**, estimated from their oxidation and reduction potentials, respectively, and assuming a binding energy of the CT state of  $\sim 0.4$  eV.<sup>[10]</sup> These results bring strong evidences of an exciplex process and allow us to determine the driving force,  $\Delta G^\circ$ , for the photoinduced electron transfer between **1** and **A**, to  $-0.70$  eV (Figure 2), which confirms the thermodynamic feasibility of the luminescence exciplex. The obtained photoluminescence quantum yield (PLQY) measured in the solid state affords a modest value of 19% under inert atmosphere.

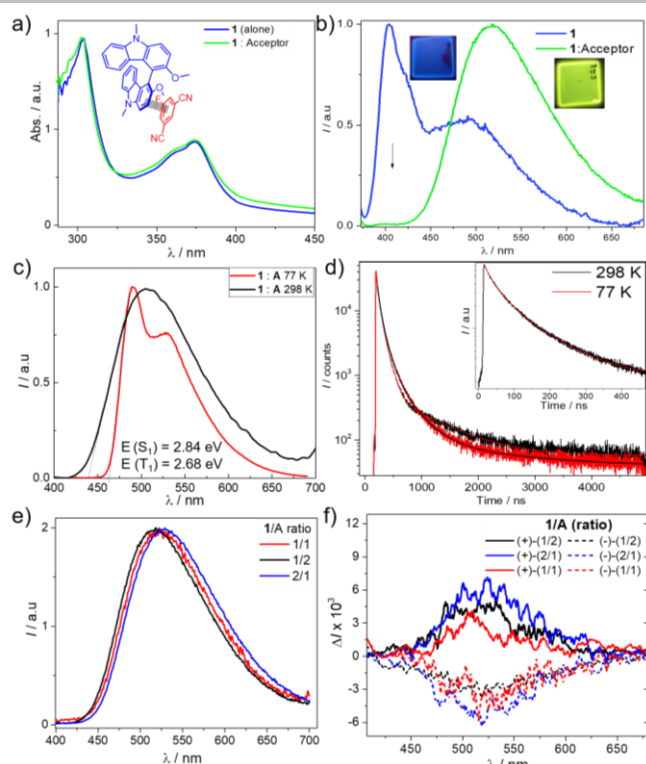
Further photophysical characterizations of the exciplex emission show a decrease of its intensity in the presence of oxygen (Figure S9), suggesting an active TADF process. Careful evaluation of the solid state photoluminescence lifetime in the absence of oxygen reveals a multi-exponential decay with a long component reaching 0.7  $\mu$ s. The delayed emission component decreases upon cooling the temperature down to 77 K, as expected for a TADF emitter for which the reverse intersystem crossing (RISC) process becomes less favored at low temperature. The appearance of a longer decay at 77 K (1.7  $\mu$ s) may be attributed to a phosphorescence emission (Figure 3). We therefore evaluate the  $\Delta E_{ST}$  of the **1:A** blend by comparing its photoluminescence (PL) at 298 K and 77 K. The  $S_1$  and  $T_1$  energy levels of 2.84 and 2.68 eV have been estimated from

LUMO level ( $-2.23$  eV), its rather high localized triplet state (2.6 eV), and its well-known use for the design of conventional covalent achiral TADF emitters.<sup>[14]</sup> In high concentrated solution, mixing a 1:2 ratio in weight of **1** and **A** does not result in any intermolecular interaction since only the luminescence and the CPL of **1** are observed (Figure S7-S8). In strike contrast, the spin-coated films obtained from the same solution display a bright green-yellow emission under photoexcitation (Figure 3). In comparison to neat film of **1**, the **1:A** blend affords a broad unstructured emission profile that can be attributed to an intermolecular luminescent charge-

the onset of the fluorescence and phosphorescence bands of the film, the former appearing as a shoulder in the blue region of the emission spectra recorded at 77 K (Figure 3), which results on a  $\Delta E_{ST}$  value of 0.160 eV, in the classical range found for TADF emitters.

We then focused our investigation on the CPL property of these innovative chiral TADF emitters. The efficient intermolecular charge transfer between the excited states of the chiral electron donor and achiral acceptor units prompted us to study the potential CPL of the **1:A** blend made with each enantiomer of **1**. Gratifyingly, mirror-image CPL spectra were obtained for (+)-**1:A** and (-)-**1:A** with positive signals for the (+)-enantiomer based blend with maxima corresponding to the unpolarized luminescence spectra. Playing with the ratio of the chiral donor vs. the achiral unit in the blend affects the intensity of CPL to some extent, but not the overall luminescence profile (the small observed shifts between each ratio may arise from intermolecular arrangement differences between the donor and the acceptor in the solid state).

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**Figure 3.** a) and b) UV-vis absorption and luminescence spectra, respectively, of **1** alone (blue solid line) and **1** blended (exciplex) with 5-fluoroisophthalonitrile (green solid line) from spin-coated film substrate excited at 370 nm; c) Exciplex luminescence spectra recorded at 77 K (recorded with a 10 ms delayed time, red solid line) and 298 K (black solid line), with estimated values of the singlet and triplet excited-states; d) Corresponding luminescence decays of exciplex recording at 77 K (red solid line) and 298 K (black solid line) with an inset focusing on the short lifetime decays (see details in Figure S10); e) and f) luminescence and CPL spectra, respectively, of exciplexes involving different ratios of Donor and Acceptor compounds.

These findings suggest that CPL emission is closely related to a limited number of intermolecular interactions, involving one (or two) Donor-Acceptor through space charge transfer transitions. Finally, a 2:1 ratio between **1** and **A** units seems the optimal one in term of CPL intensity, resulting in a  $g_{\text{lum}}$  of  $7 \times 10^{-3}$ , among the highest measured for molecular CP-TADF emitters.<sup>[4b, 5d, 15]</sup> Importantly, this value is one order of magnitude higher than the one measured for the chiral donor unit in solution ( $g_{\text{lum}} \sim 7 \times 10^{-4}$ ), highlighting an interesting CPL amplification effect through the exciplex process, while giving rise to TADF.

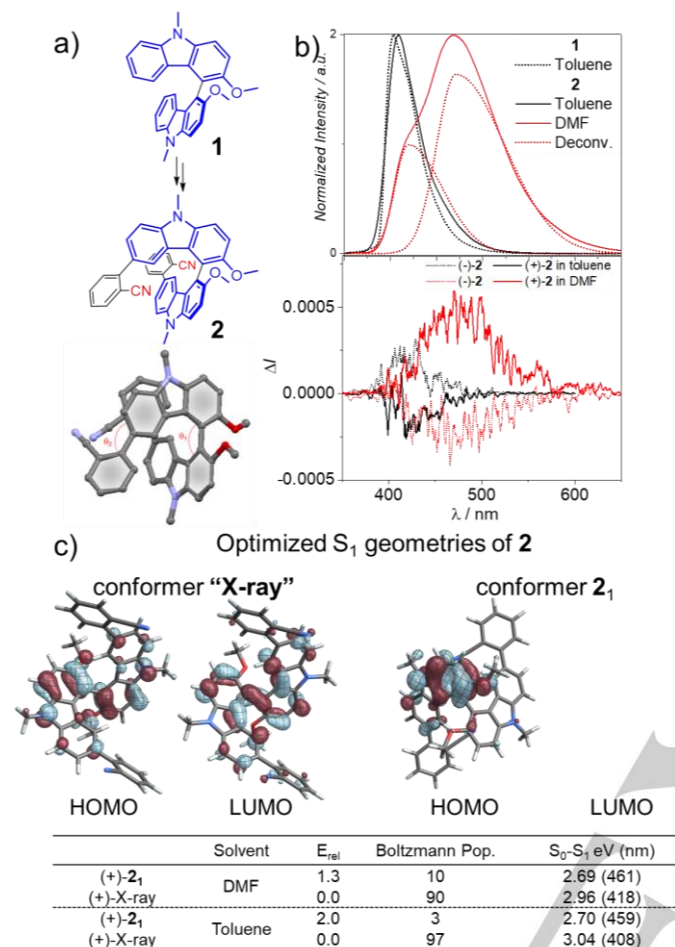
While it is rather difficult to clearly rationalize the obtained CPL signal and the underlying process at play, it is interesting to note that the signs of the CPL for the blend do not follow the ones recorded for the chiral donor in solution, *i.e.* (-)- and (+)-**1** give positive and negative CPL, respectively (Figure S2). Because theoretical investigations of the D-A intermolecular interaction in the solid state would be a daunting task, we attempted to gain more insight regarding this intriguing aspect by measuring CPL of the exciplexes in concentrated solutions in different solvents; however, all these attempts failed. Therefore, as an alternative, we synthesized a covalent chiral donor-acceptor compound, (**2**, Figure 4), based on bicarbazole and 2-cyanophenyl units, designed to mimic the chiral exciplex discussed previously and rationalize the observed CPL sign inversion (Figure 4, see SI for the detailed

synthesis procedure). The design of the compound implies an *ortho*-substituted cyano group on the phenyl linked to the carbazole donor unit in order to induce through-space charge transfer interactions with the second carbazole unit of the molecule. X-ray structure analyses of *rac*-**2**, which crystallized in the *P*-1 space group, provide further structural insights. As expected, a dihedral angle of 89.2° between the carbazole units was measured ( $\theta_1$ , Figure 4), which indicates a weak electronic coupling between them. A second torsion angle of 50.2° is also measured between the carbazole and the 2-cyanophenyl substituents ( $\theta_2$ , Figure 4), which does not point towards the opposite carbazole system. The measured absorption and ECD spectra of **2** are reported in the SI.

The luminescence and CPL of this new chiral push-pull derivative was fully characterized, including its solvatochromism and potential TADF characteristics. In toluene, emission of **2** displays a sharp signal with a maximum at 410 nm, close to the one recorded for the bicarbazole precursor **1**, involving mainly a carbazole-centered  $\pi$ - $\pi^*$  radiative process. In more polar solvents, such as chloroform and dimethylformamide (DMF), the luminescence profile becomes much broader and red-shifted, with maxima at 470 and 475 nm, respectively, owing to a stronger charge-transfer emission character from the carbazole donors to the cyano phenyl acceptors (Figures 4 and S15). In line with this observation, the associated PLQY of **2** increases from 20 % in toluene solution to *ca.* 40 % in DMF. Its luminescence intensity is not affected by the presence of oxygen, suggesting the absence of TADF property for this covalent D-A, in accordance with its significant  $\Delta E_{\text{ST}}$  of 0.50 eV (Figure S14). This high value further highlights the benefit of the exciplex strategy to reach low  $\Delta E_{\text{ST}}$  (0.18 eV for exciplex), and therefore TADF. Interestingly, the associated mirror-image CPL responses measured in toluene and DMF solution display a clear sign inversion along with increasing polarity. In toluene, (+)-**2** shows a negative CPL signal associated to a  $g_{\text{lum}}$  value of  $2 \times 10^{-4}$ , which becomes positive and higher in intensity in DMF ( $g_{\text{lum}} \sim -5 \times 10^{-4}$ ). Being rare in the literature,<sup>[16]</sup> such switch of CPL induced by the polarity of the medium has been previously rationalized in terms of either a dual-fluorescence behavior or a modulation of the intramolecular charge-transfer strength of the emission transition.<sup>[17]</sup> In the case of compound **2**, a complete explanation of the obtained results is beyond the scope of this communication. However, it is interesting to note that (+)-**2** has a similar luminescence profile and CPL sign than its corresponding precursor (+)-**1** in toluene (Figure 4), indicating that the involved emission transition is mainly centered on the bicarbazole part of the compound for both emitters. Nevertheless, the CPL intensity of (+)-**2** is three times lower than for (+)-**1**, suggesting also some other contributions to the overall emission process in the case of (+)-**2**. Indeed, the clear shoulder observed at 420 nm in the emission spectrum of the latter in DMF may lead us to propose a dual emission behavior (the deconvolution of the DMF spectrum is depicted in Figure 4), as reported in a previous example of chiral D/A binaphthyl derivative.<sup>[17a]</sup> In chloroform solution, a solvent of medium polarity between toluene and DMF, two bands of emission are unambiguously observed at 415 and 460 nm for (+)-**2**, associated to a weak bisignate CPL response, with positive and negative signals at 415 and 460 nm, respectively (Figure S18). Overall, these findings are consistent with a dual luminescence behavior, implying different magnetic and electric dipole transition

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moments, and resulting in a different CPL signature in function of the type of transitions involved in the emission process.



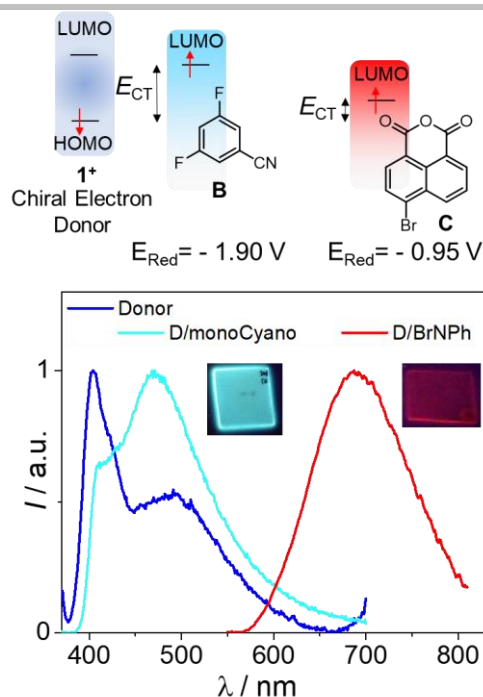
**Figure 4.** a) XRD structure of **2** and precursor **1** and b), emission (only the emission of (+)-**2** is shown) and CPL spectra of (+)- and (-)-**2** in toluene (black lines) and DMF (red lines) at 298 K (the normalization is done to **2** to have a direct lecture of the g<sub>lum</sub> value at the emission maxima of **2**). Deconvolution (Deconv.) of the emission of compound **2** in DMF (red dotted lines), with bands found at 418 and 478 nm; c) Isosurfaces ( $\pm 0.035$  au) of the frontier molecular orbitals (HOMO/LUMO classification according to the ground state) for optimized structures of conformers of (+)-**2** (X-ray and **2**<sub>1</sub>) in DMF (see SI for details), relative conformer energy (in kcal·mol<sup>-1</sup>) in toluene and DMF solvents, Boltzmann weight at 298 K (in %) and first electronic transition in the excited state optimization in solution in eV (nm), all obtained using the TD-DFT/PBE0/def2-SV(P)/D3 method.

Theoretical investigations using Kohn-Sham Density functional theory (DFT) and time-dependent DFT (TD-DFT) as implemented in Gaussian (G16) package,<sup>[18]</sup> the PBE0 functional<sup>[19]</sup> and the def2-SV(P) basis<sup>[20]</sup> (see further details in the SI), bring further insight into the photophysical properties of **2** and reveal that the observed luminescence (involving HOMO and LUMO) may arise from two different conformers the  $S_1$  excited state. Calculations predicted two conformers for the ground state that are close in energy, with one of them corresponding to the experimental X-ray diffraction structure, and the other one (**2**<sub>1</sub>) having both cyano groups pointing at the carbazole (see SI for details). Optimizations of the  $S_1$  state likewise located two local minima close in energy (Figure 4) with structures that are similar to the ground state minima. Hence, we adopt the same labelling. In toluene, the X-ray

conformer is lower in energy (97% Boltzmann weight) and displays vertical emission at 3.04 eV (408 nm) with a process exclusively localized on the biscarbazole unit, similarly to the experimental luminescence found for **2**. In DMF, the two ground and excited states conformers are closer in energy than they are in toluene, and it appears that emission occurs simultaneously from the corresponding excited-state structures, causing the shoulder seen in the experimental emission spectrum. The calculated vertical emission energies are in good agreement with the shoulder and peak positions in the measured spectrum: One emission corresponds to the X-ray conformer at 2.96 eV (418 nm) and the other emission corresponds to conformer **2**<sub>1</sub> at 2.69 eV (461 nm). Interestingly, the latter displays through-space charge-transfer character from one carbazole to the opposite 2-cyanophenyl units, as it may happen for the reported exciplexes. From these findings, we hypothesize that the change of the transition nature of the emission process when going to  $\pi-\pi^*$  in pure **1** compound to intermolecular CT in the exciplex configuration may also invert the obtained CPL signals, as it is the case for **2**.

To demonstrate the general nature of this exciplex approach and its ability to generate different CP-TADF colors by solely playing with the achiral electron accepting unit, we repeated the measurements using 3,5-difluorobenzonitrile **B** and 4-bromonaphthalene monoanhydride **C** units in place of the 5-fluoroisophthalonitrile compound (Figure 5). For non-optimized D/A ratios, the results depicted in Figure 5 show that in both cases chiral luminescent exciplexes are formed in films, giving rises to a bright blue (using **B**) and red (using **C**) luminescence. As with the isophthalonitrile acceptor **A**, the broad unresolved structure emission of the blends indicate that the photoluminescence is dominated by an intermolecular charge transfer process between the chiral donor and the achiral acceptor. As expected, the energy of the resulting lowest unoccupied exciplex excited state follows the trend in the reduction potential of the accepting units, which afford many possibilities to further optimize both the CPL and TADF efficiency. Interestingly, blue CPL response of the exciplex involving **B** were obtained, with  $g_{lum} \sim 2 \times 10^{-3}$  (Figure S13), while the CPL of the red chiral exciplex cannot be accurately detected in our conditions, probably due to its low photoluminescence quantum yield (PLQY, 1%).

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**Figure 5.** Top: Chemical structures of the different electron acceptors screened in this study to obtain multi-colored chiral exciplex luminescence with the associated reduction potentials, and bottom: exciplex luminescence spectra recorded at 298 K of spin-coated films involving chiral **1** as the donor and 3,5-difluorobenzonitrile (**B**, sky blue), and 4-bromonaphthalene monoanhydride (**C**, red) electron acceptor units, with associated pictures.

In conclusion, we have reported a new approach to design multi-color chiral luminescent exciplexes, with the most efficient ones (sky blue and green exciplexes) displaying CP-TADF characteristics. By combining a chiral electron donor unit and several achiral electron acceptor molecules, blue, green and red luminescence are obtained in solid-state, with PLQY and CPL intensity up to 10% and  $7 \times 10^{-3}$ , respectively. Interestingly, the CPL response of the exciplexes shows a strong intensity enhancement in comparison to the chiral donor alone, owing to the formation of intense intermolecular charge-transfer transition. Such behavior was experimentally and theoretically rationalized with the help of a covalent chiral donor-acceptor emitter, which brings interesting aspects regarding the conception of future switchable CPL materials. Finally, we hope that such unprecedented study opens-up new perspectives for development of new classes CP-TADF materials and their use in CP-OLEDs.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** Circularly polarized luminescence, chiral luminescent exciplexes, thermally activated delayed fluorescence, multi-colored emission

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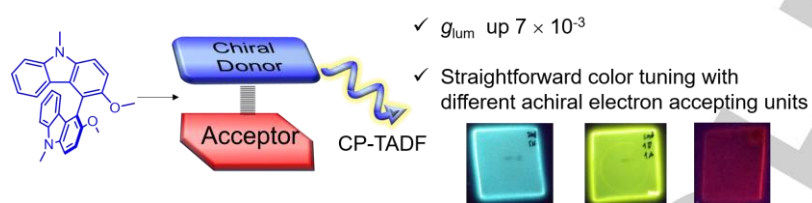
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