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Introduction

Circularly polarized (CP) luminescence, traditionally obtained from unpolarized light through a filter, has attracted considerable attention due to the wide potential applications in optical data storage, optical recognition sensors, quantum computing, optical communication, and 3D displays.^{1–3} It becomes even more attractive when CP light can be directly generated in organic light emitting diodes (OLEDs) using chiral materials.^{4,5} Pioneering work can be dated back to 1997, when Meijer and co-workers firstly observed circularly polarized electroluminescence (CPEL) from a chiral conjugated polymer.⁶ Since then, significant efforts have been devoted to developing chiral illuminants to prepare efficient CP-OLEDs with strong CPEL.^{7–9} The CPEL signal, which is characterized by the electroluminescence dissymmetry factor ($g_{\rm FL}$), can be enhanced by many molecular

Thermally activated delayed fluorescence enantiomers for solution-processed circularly polarized electroluminescence[†]

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Circularly polarized organic light-emitting diodes (CP-OLEDs) with thermally activated delayed fluorescence (TADF) characteristics are receiving increasing interest, as they have shown improving efficiencies of circularly polarized electroluminescence (CPEL). Here, we developed a series of TADF enantiomers based on chiral binaphthalene, an acceptor (A) of cyanopyridine, and donors (D) of carbazoles in a chiral–A–D architecture. Good solubility, high luminescence yields, and excellent chiral stability with a photoluminescence dissymmetry factor (g_{PL}) up to 5.8 × 10⁻⁴ were achieved. Efficient CP-OLEDs using these chiral TADF molecules as dopants were successfully fabricated, exhibiting high external quantum efficiencies (EQEs) up to 12.4% and opposite CPEL signals with g_{EL} of 6 × 10⁻⁴/–8.6 × 10⁻⁴ in vacuum-deposited devices. More impressively, the solution-processed TADF CP-OLEDs result in much larger g_{EL} values (3.5 × 10⁻³/–3.9 × 10⁻³) with EQEs up to 10.6%. This discovery is encouraging and instructive, which could stimulate the development of high-performance CP-OLEDs using chiral TADF molecules through solution-processing approaches.

design strategies, typically including using light-emitting polymers modified with chiral sidechains¹⁴ or dopants¹⁰ and developing novel chiral emissive molecules or complexes.¹¹⁻¹³ Nevertheless, although CP-OLEDs with strong CPEL and high $g_{\rm EL}$ up to 1.13¹⁴ have been fabricated, they are mainly based on chiral transition metal complexes or polymers, and the device efficiencies are generally low.^{15,16}

To improve the efficiencies of OLEDs, thermally activated delayed fluorescence (TADF) has been introduced to harvest both singlet and triplet excitons for electroluminance with theoretically 100% internal quantum efficiency by the up-conversion of excitons from the lowest triplet (T_1) to singlet (S_1) excited states through efficient reverse intersystem crossing (RISC) under small singlettriplet splitting energy $(\Delta E_{\rm ST})$.^{17–21} Pieters *et al.* constructed the first CP TADF molecule using a chiral binaphthol moiety, a donor of carbazole and an acceptor of dicyanobenzene; an external quantum efficiency (EQE) of 9.1% and a CP photoluminance dissymmetry factor (g_{PL}) of 1.3×10^{-3} were observed in solution, but no CPEL was obtained.²² With the same building blocks of the chiral perturbation group, and donor and acceptor units, Tang et al. improved the EQE to 9.3% and $g_{\rm EL}$ up to +0.026/-0.021 with the aid of asymmetric molecular structure and aggregation-induced emission behaviour.²³ Recently, Chen et al. achieved both high EQE up to 19.8% and an intense CPEL signal of 2.3 \times 10⁻³ by introducing chiral 1,2-diaminocyclohexane into the achiral TADF unit.²⁴ Zheng et al. further

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improved the EQE to 32.6% using chiral octahydro-binaphtholbased TADF molecules.²⁵ However, all the TADF CP-OLEDs reported so far were fabricated by vacuum deposition technology. This is due to the relatively high requirements in designing TADF materials with both high photoluminescence quantum yields (PLQYs) and efficient RISC,²⁶ and the solubility and chirality issues would make it even more challenging to develop chiral TADF molecules for solution processing.²⁷ But it is worth noting that solution-processed OLEDs have been widely considered to be fundamentally important for low-cost and large-area displays and lighting.^{28–30}

Here, we developed a series of solution-processible TADF enantiomers with strong CPEL based on chiral binaphthol, cyanopyridine, and carbazoles for CP-OLEDs. The binaphthol unit has good solubility, strong conjugation effects, high stability upon electro/photo-excitation against racemization, and an excellent ability to induce CP emission through chiral perturbation.^{31,32} Cyanopyridine acts as an acceptor (A) unit of the TADF materials to modulate the degree of intra-molecular charge transfer (ICT) for TADF emission and, more importantly, to acquire high solution processability of the resulting materials.³³ Carbazole and 3,6-di-*tert*-butyl-9*H*-carbazole with high triplet energy $(E_T)^{23}$ are donor (D) moieties of the chiral TADF molecules for sky-blue emission (Fig. 1a). These newly designed TADF enantiomers in a chiral-A-D architecture can be prepared facilely through a scalable one-pot sequential synthetic procedure at room temperature in high yields (>80%). Excellent TADF characteristics were observed along with excellent solubility and strong sky-blue photo-luminance with high chiral stability and



Fig. 1 (a) Molecular design, chemical structures and (b) frontier molecular orbital distributions of the chiral TADF materials.

mirror-image circular dichroism (CD) and circularly polarized luminescence (CPL) activities ($g_{\rm PL}$ up to 5.8 × 10⁻⁴). The CP-OLEDs based on these facilely prepared TADF enantiomers demonstrate not only high EQEs up to 12.4% in vacuumdeposited TADF OLEDs and 10.6% in solution-processed devices, but also decent CPEL signals with $g_{\rm EL}$ of 6 × 10⁻⁴/ -8.6 × 10⁻⁴ in vacuum-deposited devices and higher $g_{\rm EL}$ of 3.5 × 10⁻³/-3.9 × 10⁻³ in solution-processed TADF devices. The amplified chirality and high EQEs of the solutionprocessed TADF OLEDs illustrate large progress of CP-OLEDs, which should initiate the investigation of highly soluble CP TADF molecules in chiral–A–D architectures for solution-processed chiral devices.

Results and discussion

Synthesis and characterization

The enantiomerically pure TADF emitters S-CPDCz, R-CPDCz, S-CPDCB and R-CPDCB were conveniently prepared on the gram scale by an optimized one-pot sequential procedure starting from commercially available compounds (Scheme S1, ESI⁺).²³ Tetrafluoro cyanopyridine with enantiopure 1,1'-bi-2-naphthol (BINOL) and carbazoles and K₂CO₃ as a base were added into N,N-dimethylformamide (DMF) to produce the target molecules at room temperature with overall yields over 80% after purification by silica gel column chromatography. These easily prepared chiral compounds through the above straightforward and costeffective procedure were fully characterized (Fig. S1-S18, ESI†). Benefiting from the stable central chirality of enantiomerically pure **BINOL**,³⁴ no racemization of the chiral TADF emitters occurs during the synthesis and post treatments of the target TADF enantiomers with high enantiomeric excess (>99%, according to chiral HPLC, see Fig. S19 and S20, ESI[†]).

The newly obtained chiral TADF molecules possess good solubility in commonly used organic solvents, which is important for the solution-processing of the devices. Very high decomposition temperatures (T_d) over 420 °C were observed for the carbazole-based TADF molecules, while those of the *tert*-butylcarbazole-based ones show even higher values up to 439 °C, according to thermogravimetric analysis. Differential scanning calorimetry also reveals high glass transition temperatures (T_g) of these chiral compounds, which are 329 °C/326 °C and 248 °C/244 °C for *R*- and *S*-CPDCz and *R*- and *S*-CPDCB, respectively (Fig. S21, ESI†). These excellent thermal stability properties are due to the highly rigid and twisted molecular structures, endowing these enantiomers with high thermal and morphological stability of films for high-performance device applications.³⁵

Theoretical investigations

Time-dependent density-functional-theory (TD-DFT) calculations show that the highest occupied molecular orbital (HOMO) is dominated by the donor of carbazoles, while the acceptor of the central cyanopyridine determines the lowest unoccupied molecular orbital (LUMO) and the chiral perturbation group of BINOL has limited contribution to both the HOMO and

LUMO (Fig. 1b). This clear spatial electronic separation of the HOMO and LUMO is a key feature of TADF molecules in realizing a small $\Delta E_{\rm ST}$ for efficient RISC.²¹ It should be also noted that a small spatial overlap of the HOMO and LUMO on the cyanopyridine moiety with an overlap extent $(I_{H/L})$ of about 33% can be observed, which is important for high luminescence efficiency of TADF emitters.²¹ Therefore, their absolute PLQYs measured using an integrating sphere are up to 37% in dilute tetrahydrofuran (THF) solution and 55% in the doped (10 wt%) film of 1,3-bis(carbazol-9-yl) benzene (mCP). Moreover, good morphology of the spin-coated thin films on ITO was also observed by atomic force microscopy (Fig. S22, ESI[†]) with a surface roughness lower than 0.4 nm, demonstrating clearly their great potential in solution-processed devices.³⁹

Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of the TADF enantiomers were studied in both dilute solutions and thin films. As illustrated in Fig. 2a, almost identical spectra of the enantiomers were observed in THF solutions, exhibiting a strong absorption band around 320 nm assigned to the BINOL absorption,²³ a weak absorption peak at about 410 nm associated with the intramolecular charge transfer (ICT) process derived from the chiral-A-D electronic structures of these TADF

> ntensity (a.u.) rbance (a.u.)

0.6

0.4

0.0

10

10

10

10⁰

10

10

300

350

(f)

CD (mdeg)

ice (a.u.)

Ah 0.0

1.0

-0.5

(d) 10⁴ 300 400

-0.6

0.4

R-CPDCz S-CPDCE

R-CPDCE

700 800

Fluo. 77K

S-CPDC

750

In THF

I-CPDUZ S-CPDCZ R-CPDCB

450

500 600 Wavelength (nm)

600

Wavelength (nm)

S-CPDCz R-CPDCz S-CPDCB R-CPDCB

500 600 700 Wavelength (nm)

40

In neat film

0.5 0.1

-0.0 P

500

20 30

Time (µs)

400 450 Wavelength (nm) 450 -0. -0. -0. 7. -0. -0. -0. intensity (a.u.)

-0.2 d

-0.0

800

350 400 4 Wavelength (nm) Fig. 2 (a and b) UV-vis absorption and PL spectra of the chiral TADF molecules in (a) dilute THF solutions ($\sim 10^{-5}$ mol L⁻¹) and (b) thin films at room temperature (RT). (c) Fluorescence and phosphorescence spectra of S-CPDCz in THF at 77 K. (d) Transient decays of the emission peaks (excited at 315 nm), photographs (inset left) and fluorescence decay curves (inset right) of the chiral TADF molecules doped in mCP films (10 wt%). (e and f) CD spectra of the chiral TADF molecules in (e) THF and (f) neat films at RT.

molecules, and a broad emission band owing to the ICT effects with typical emission peaks around 510-520 nm, which can be red-shifted by increasing the solvent polarity from CHCl₃ to cyclohexane (Fig. S23, ESI⁺). Similar photophysical behaviours of these chiral TADF molecules were observed in films (Fig. 2b); the small red-shifts (<11 nm) of the spectra in the solid state indicate weak intermolecular interactions due to the twisted molecular structure caused by the chiral BINOL units. It should be noted that the ICT absorption bands of the spin-coated films are relatively stronger than those of vacuum-deposited films (Fig. S24, ESI[†]). The higher ICT due to stronger D-A interactions of the solution-processed films may lead to a higher dissymmetry factor of the luminescence. The introduction of the bulky tert-butyl groups further reduces the intermolecular interactions, leading to a very small red-shift (<2 nm) in the solid film state.³⁵ In addition, due to the introduction of four electron-donating tert-butyl groups, which results in stronger ICT effects for smaller energy bandgaps, the absorption and PL spectra of *R*- and *S*-CPDCB undergo a red-shift of 30 nm in both solution and film states (Table S1, ESI†).³⁶ The low-temperature emission properties of the enantiomers were studied to explore their TADF properties (Fig. S25, ESI[†]). Taking S-CPDCz as an example (Fig. 2c), the fluorescence band of S-CPDCz in THF solution at 77 K is centered at 467 nm, which indicates an S1 energy of 2.65 eV. Meanwhile, the phosphorescence band of S-CPDCz at 484 nm suggests a T_1 energy of 2.57 eV. Thus, $\Delta E_{\rm ST}$ of *S*-CPDCz was measured to be 0.08 eV in THF solution. From their small ΔE_{ST} values (<0.08 eV) (Table S2, ESI[†]), TADF features should be successfully established in these chiral molecules in the chiral-A-D architecture. Further, the transient PL decay profiles exhibit two distinct lifetimes; the fast one in several nanoseconds presents the prompt fluorescent emission, while the slow one in several microseconds is related to the delayed fluorescent emission through RISC, giving direct evidence of the TADF characteristic (Fig. 2d).²⁰ Also, significantly reduced PL lifetimes were observed at low temperatures (Fig. S26, ESI[†]), indicating again the TADF emission feature, which is sensitive to temperature.²⁴

Chiroptical properties

The chiroptical properties of these optically stable TADF enantiomers were investigated using CD and CPL spectra in both THF solution and neat films. From Fig. 2e and f, the CD spectra of the chiral TADF molecules display an obvious mirrorimage relationship with the maximum band centred around 320 nm, which matches well the corresponding BINOL absorption band.²³ These results indicate that the chiral unit in the TADF enantiomers has successfully induced the TADF molecules to produce chirality in the ground state. Consequently, almost mirror-image CPL spectra of the TADF emission were recorded with g_{PL} of $3.4 \times 10^{-4}/-3.0 \times 10^{-4}$ for *R*-/*S*-CPDCz and $3.2 \times 10^{-4}/-2.1 \times 10^{-4}$ for *R*-/*S*-CPDCB in THF, respectively (Fig. 3a and b), which further confirms the chiroptical properties of the enantiomers in the excited state. More interestingly, when the neat films of these chiral molecules were fabricated by spin-coating, larger average $g_{
m PL}$ values of $3.7 imes 10^{-4}/-3.3 imes 10^{-4}$

(a)

ŝ

0.8

0.6

0.4

0.2

0.0

10

0.8

(a.u.)

0.4

0.2

0.0

20

(e)

CD (mdeg) 15 450

300

ntensitv

(c)

300 400





Fig. 3 (a and c) CPL spectra and (b and d) g_{PL} values of the chiral TADF molecules in (a and b) dilute THF solutions ($\sim 10^{-5}$ mol L⁻¹) and (c and d) neat films at RT.

and $5.8 \times 10^{-4}/-4.0 \times 10^{-4}$ were detected (Fig. 3c and d). Possibly, this is because the chiral molecules exist in an isolated state in solution, whereas in the neat film state formed by spincoating, chiral aggregates could be slight oriented, leading to chiroptical amplification in spin-coated films.⁴⁰ All in all, our strategy of incorporating a chiral unit into TADF architectures in a chiral–A–D structure is efficient in producing chiral TADF molecules with CD and CPL properties, which should be instructive to develop high-performance CP-OLEDs with intense CPEL.

OLED performance

These TADF enantiomers were then used as the emissive dopants (10 wt%) in multilayer OLEDs to investigate their electroluminescence (EL) properties. The HOMO and LUMO energy levels of *R*- and *S*-CPDCz were found to be at -5.8 and -2.9 eV, while these of R- and S-CPDCB were identified to be -5.7 and -2.9 eV, as measured by the oxidation onsets of cyclic voltammetry curves (Fig. S27, ESI[†]) and optical bandgaps from the absorption edges of thin films (Fig. 2b).³⁷ The higher HOMO levels of *R*- and S-CPDCB are due to the electron-donating effects of the tert-butyl groups. With the frontier orbital energy levels, mCP was chosen as the host material of these chiral TADF emitters, poly(3,4ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) and LiF as the hole- and electron-injecting materials, and 4,4'cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) and 1,3,5-tri(*m*-pyrid-3-yl-phenyl)-benzene (TmPyPB) as hole- and electrontransporting materials, respectively, in the vacuum-deposited



Fig. 4 (a and b) Energy level diagrams of the related materials, and (c and d) current density–luminance–voltage, and (e and f) efficiency–luminance curves in (a, c and e) vacuum-deposited and (b, d and f) solution-processed CP-OLEDs based on TADF emitters of **S-CPDCz** and **S-CPDCB**. Inset: EL spectra and device structures.

CP-OLEDs (Fig. S28, ESI[†]) under the following device configuration: ITO/PEDOT:PSS (30 nm)/TAPC (20 nm)/mCP:TADF dopants (10 wt%, 20 nm)/TmPyPB (30 nm)/LiF (1 nm)/Al (100 nm).³⁸ Almost identical spectra of the PL and electroluminescence (EL) of the TADF molecules were observed, exhibiting excellent energy transfer from the host to the guest material for the sky-blue EL peaks at 492 and 515 nm of the R-/S-CPDCz and R-/S-CPDCB based devices, respectively (Table 1). Due to the higher HOMO energy levels and larger PLQYs of R-/S-CPDCB, superior device performance with a maximum current efficiency (CE) of 39.5 cd A^{-1} , power efficiency (PE) of 30.3 lm W^{-1} , and EQE of 12.4% resulted (Fig. 4c–e). More impressively, when these TADF emitters were used in solutionprocessed OLEDs with the simplified device configuration (Fig. S29, ESI[†]): ITO/PEDOT:PSS (30 nm)/mCP:TADF dopants (10 wt%, 40 nm)/DPEPO (10 nm)/TmPyPB (50 nm)/Liq (1 nm)/Al (100 nm),³⁹ high device performances were also observed (Fig. 4d-f). The EQEs of both the S-CPDCz and S-CPDCB based OLEDs are over 10% with identical EL spectra to those of the solution-processed devices (Fig. S30 and S31, ESI⁺). It should be noted that this is the first report of solution-processed

Table 1 Device performance of the sky-blue TADF CP-OLEDs based on S-CPDCz and S-CPDCB

Compound	Method	$\mathbf{V}^{a}\left(\mathbf{V}\right)$	λ_{\max}^{b} (nm)	$L_{\max}^{c} (\mathrm{cd} \ \mathrm{m}^{-2})$	$\operatorname{CE}^{d}(\operatorname{cd} \operatorname{A}^{-1})$	$\mathrm{PE}^{d} \left(\mathrm{lm} \ \mathrm{W}^{-1} \right)$	EQE^{d} (%)	$g_{ m EL}$
S-CPDCz	Vacuum	3.80	492	3700	21.4	15.7	8.4	$-5.5 imes10^{-4}$
S-CPDCB	Vacuum	3.70	515	7700	39.5	30.3	12.4	$-8.6 imes10^{-4}$
S-CPDCz	Solution	3.60	496	923	24.6	19.3	10.1	$-3.7 imes10^{-3}$
S-CPDCB	Solution	3.60	516	1785	33.3	26.1	10.6	$-3.9 imes10^{-3}$

^a Turn-on voltage at a brightness of 1 cd m⁻². ^b EL peak wavelength at 1000 cd m⁻². ^c Maximum luminance. ^d Maximum efficiencies.



Fig. 5 (a and b) g_{EL} spectra of *R***-/S-CPDCz** as a function of emission wavelength in (a) vacuum-deposited and (b) solution-processed devices. (c and d) g_{EL} values at the maximum emission wavelength of (c) *R*- and (d) *S*-enantiomers.

TADF CP-OLEDs by overcoming the intrinsic difficulties to simultaneously achieve good solubility, chiroptical properties, TADF features, and matched frontier orbital energy levels of the materials.

Owing to the high conformational stability of the BINOLbased enantiomers, these high-performance TADF OLEDs show intense CPEL, even after the thermal evaporation for the vacuum deposition of the emitting layer during the device fabrication (Fig. S32-S35, ESI[†]). As shown in Fig. 5, the two different chiral TADF molecules of *R*/*S*-CPDCz and *R*/*S*-CPDCB result in typical CPEL of their OLEDs with opposite $g_{\rm EL}$ signals, and the $g_{\rm EL}$ values are slightly higher than the corresponding $g_{\rm PL}$, reaching up to 4.0 \times $10^{-4}\!/\!-\!5.5$ \times 10^{-4} and 6.0 \times $10^{-4}\!/\!-\!8.6$ \times 10^{-4} in the vacuum-deposited devices, respectively. More interestingly, these $g_{\rm EL}$ values further increase to $2.5 \times 10^{-3}/-3.7 \times 10^{-3}$ and 3.5 \times $10^{-3}/{-3.9}$ \times 10^{-3} in the solution-processed devices. It should be noted that the $g_{\rm EL}$ values of the solution-processed CP-OLEDs are almost an order of magnitude higher than those of the vacuum-deposited devices. The higher $g_{\rm EL}$ in the spincoated emitting layers are coincident with the higher $g_{\rm PL}$ of the spin-coated films (Fig. S32, S33 and Table S3, ESI[†]), which could be ascribed to the oriented chiral molecules by the centrifugal force during the spin-coating.⁴⁰ To the best of our knowledge, these $g_{\rm EL}$ values and device efficiencies are comparable to the best results of CP-OLEDs (Table S4 and Fig. S36, ESI[†]). This discovery is encouraging, since the solution-processing of TADF enantiomers can significantly increase the $g_{\rm EL}$ of CP-OLEDs.

Conclusions

In summary, we succeed in developing two couples of **BINOL**based TADF enantiomers using a typical donor of carbazoles, acceptor of cyanopyridine, and chiral unit of **BINOL** in a chiral– A–D architecture for the first solution-processible CP-OLEDs

with amplified chirality. Owing to the effective separation but slight overlap of their HOMO/LUMO distributions for small $\Delta E_{\rm ST}$ and high PLQY, excellent TADF properties of these enantiomers were achieved, along with good solubility, excellent optical stability, mirror-image CD and CPL activities. Sky-blue CP-OLEDs using these chiral TADF molecules as dopants exhibit not only high EQEs of up to 12.4% in vacuum-deposited TADF OLEDs and 10.6% in solution-processed devices, but also intense opposite CPEL signals with $g_{\rm EL}$ values of 6 \times 10⁻⁴/-8.6 \times 10⁻⁴ (vacuumdeposited devices) and $3.5 \times 10^{-3}/-3.9 \times 10^{-3}$ (solution-processed OLEDs). These promising device performances, which are among the best results of CP-OLEDs and BINOL-based TADF OLEDs reported so far, are encouraging. The amplified chirality of the TADF CP-OLEDs through solution-processing using chiral-A-D molecules is fundamentally important and conceptually instructive, which should promote significantly the investigations of solutionprocessible TADF enantiomers for CP-OLEDs.

Conflicts of interest

There are no conflicts to declare.

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