

Research Advances in Helicene Structure-Based Chiral Luminescent Materials and Their Circularly Polarized Electroluminescence

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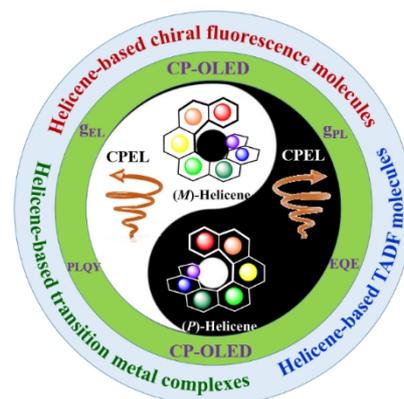
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ABSTRACT Benefited from direct generation of circularly polarized (CP) emission with tunable colors, high efficiencies and facile device architectures, CP organic light-emitting diodes (CP-OLEDs) have attracted great attention and are expected to meet industrial applications. Particularly, CP electroluminescence (CPEL) originated from CP-OLEDs has wide potential applications in 3D displays, optical information storage, quantum communication, and biological sensors. The diverse design strategies of chiral luminescent materials for CP-OLEDs, including small organic emitters, lanthanide and transition-metal complexes and conjugated polymers, have been extensively explored. Helicene with twisted extended π -conjugated molecular structure could exhibit special helical chirality and excellent circularly polarized luminescence properties, which has been employed as the ingenious chirality core for constructing efficient chiral luminescent materials. In addition, significant improvements have been made in terms of CP photoluminescence research, however, the development of CPEL with more application prospects in optoelectronic technology still lags behind. In this review, we systematically summarize the recent advances in chiral luminescent materials based on helicene structure and their CPEL

properties, including helicene-based chiral fluorescence molecules, transition metal complexes and thermally activated delayed fluorescence molecules, and discuss current challenges and future perspectives for this hot research field. We believe this progress report will provide a promising perspective of OLEDs based on helicene emitters with CPEL properties for extensive researchers, including chemical, physical and material scientists in different disciplinary fields and attract them to this rapidly developing field.

Keywords: helicene, circularly polarized luminescence, circularly polarized electroluminescence, chiral luminescent material, thermally activated delayed fluorescence



1 INTRODUCTION

Circularly polarized luminescence (CPL) displays potential applications in optical information storage, quantum communication, bioimaging, liquid crystal displays, and backlights in 3D displays.^[1-5] Generally, CP light can be obtained from non-polarized light continuously utilizing a linear polarizer and quarter-wave plate, however, this method suffers from efficiency and brightness loss with complicated device architecture (Figure 1a). Apart from this physical approach, CP light could also be directly obtained from chiral luminescent materials, which are featured of optical rotation characteristics and circular dichroism (CD) enabling to directly emit right- and left-CP light.^[6-17] Due to the different intrinsic excitation mechanisms, CP light can be classified into CP photoluminescence (CPPL) and CPEL. So far, although significant improvements have been made in terms of CPPL research, the development of CPEL with more application prospects in optoelectronic technology still lags behind.^[5,18-22] Therefore, it is of urgency to develop efficient chiral emitters and devices with excellent CPEL properties to meet practical application.

Since the first investigation to obtain direct CP light from organic electroluminescent displays by Meijer et al. in 1997,^[23] tremendous efforts have been devoted to develop chiral emitters-based OLEDs. CP-OLEDs, which are favorable for generating CP light directly, in terms of facile device architectures,

tunable emission colors and high efficiencies, have become a significant and prospective research field (Figure 1b).^[5] Device performance and CPEL activity are the key to determine CP-OLEDs performances. Similar to traditional OLEDs, the performance evaluation of CP-OLEDs mainly starts from low turn-on voltage, high brightness, high efficiency with low roll-off, and long device lifetime. While the chiroptical performances of CP-OLEDs are mainly evaluated by the asymmetry factor (g) value, which is measured by a CPL spectrometer and defined by formula (1).

$$g = 2(I_L - I_R)/(I_L + I_R) \quad (1)$$

where I_L and I_R denote the intensities of left- and right-handed CP component of the emitting light, respectively. A g value of zero indicates that the emitting light has no circular polarization, and +2 or -2 shows completely left- or right-handed CP light, respectively. According to the different excitation mechanisms, g_{PL} represents the CPPL intensity of the chiral luminescent materials from photo excitation while g_{EL} indicates the CPEL activity of chiral luminescent materials-based CP-OLEDs from electric excitation. Therefore, it is urgent and significant to develop CP-OLEDs based on chiral emitters with both high device performances and large g_{EL} values of CPEL.

The core of CP-OLEDs is the chiral luminescent material, which is responsible for generating CPEL. In general, chiral emitters from three categories are used in fabricating CP-OLEDs, including chiral conjugated polymers, chiral metal complexes (Eu,

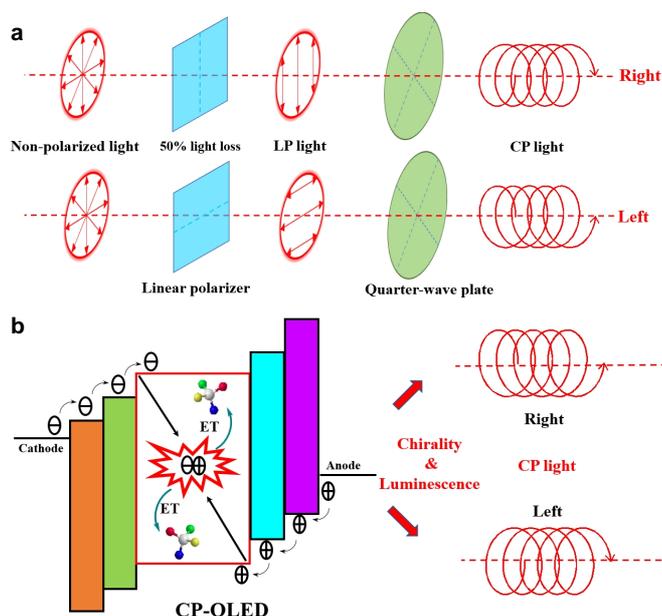


Figure 1. (a) The schematic diagram of the physical method versus (b) CP-OLEDs for obtaining CP light.

Ir, Pt, Zn, et al.), chiral simple organic molecules (SOMs), especially thermally activated delayed fluorescence (TADF) materials^[24-30] which are regarded as promising for their high-performance CP-OLEDs with producing metal-free and low-cost. Alternatively, based on different chirality sources, chiral luminescent materials with CPL properties are classified into four types of central chirality, axial chirality, planar chirality, and helical chirality (Figure 2).^[31-40] Notably, helicene derivatives featured of helical structures are a type of aromatic ortho-fused polycyclic compounds. Due to terminal aromatic rings' spatial hindrance, helicene molecular skeletons can be distorted for forming a spiral structure. Although such molecules do not have any asymmetric carbon centers, their twisted non-planar skeleton and extended π -conjugated molecular structures endow them with the characteristic of special helical chirality and exhibit excellent CPL properties,^[41-47] which has been employed as the ingenious chirality core for constructing efficient chiral luminescent materials. Although significant improvements have been made in the research of CPPL from helicene compounds, it is still a big gap in the practical application of optoelectronic technology.

In this review, we concisely discuss the recent advance, current challenge and outlook of helicene structure-based chiral

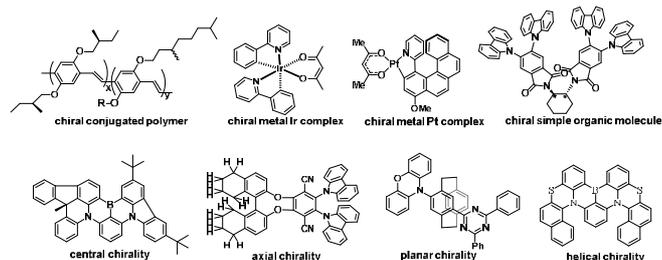


Figure 2. Categories of chiral luminescent materials.

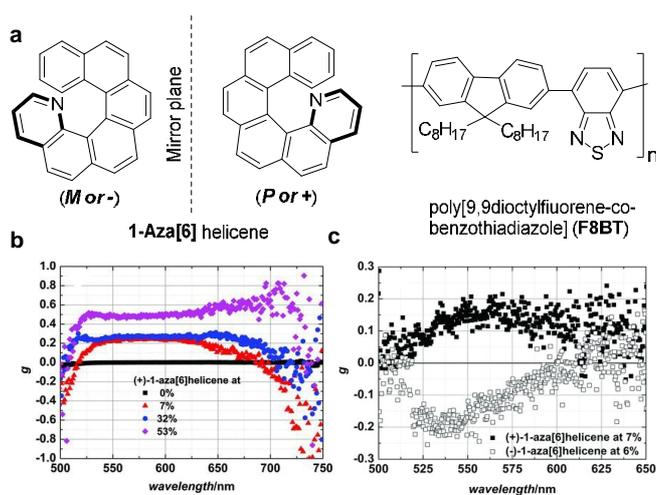


Figure 3. Molecular structures of (*M/P*)-1-Aza[6] helicene and light-emitting polymer **F8BT**. (b) CPPL spectra of **F8BT** doped with (+)-1-Aza[6] helicene. (c) CPEL spectra.^[48] Copyright 2013, WILEY-VCH.

luminescent materials and their CP-OLEDs with circularly polarized electroluminescence performances, which will not only be helpful for developing CPL/CPEL materials but also be beneficial for investigating optoelectronic devices.

n CLASSIFICATION AND PERFORMANCE

Helicene Structure-Based Chiral Fluorescence Molecules.

The first attempt to obtain CP light from helicene-based OLEDs was made by Fuchter laboratory in 2013.^[48] A pair of chiral SOMs (*M*) or (*P*)-1-Aza[6] helicene was successfully doped in a conventional achiral light-emitting polymer (LEP) **F8BT** to directly generate high levels of CPL activity (Figure 3a). A small amount of enantiopure 1-Aza[6] helicene (7 wt%) was doped into LEP, leading to a big CPPL signal of the **F8BT** film with the g_{PL} over 0.2. With the increase of 1-Aza[6] helicene blending ratio, the g_{PL} factor was improved to a significantly high value of 0.5 for the 53% helicene blend (Figure 3b). Notably, the CP-OLED was successfully fabricated by using **F8BT**: enantiopure 1-Aza[6] helicene (7% wt) as the emitter to directly emit CPEL with brightness up to 3000 cd/m² and power efficiency of 1.1 lm/W with a g_{EL} value of 0.27 (Figure 3c). This work successfully demonstrated an effective strategy to directly generate efficient CPEL based on doping a conventional achiral polymer with a chiral helicene emitter. After that, the blend ratio, film thickness, device architecture, material category, and so on were also systematically investigated by Fuchter group for achieving both good efficiency and large g_{EL} value of CP-OLEDs.^[49-51]

Li et al. designed and synthesized a pair of helicene enantiomers, (*P*)-HAI and (*M*)-HAI (Figure 4a).^[52] The helicene enantiomers with the rigid helical π -skeleton showed excellent photophysical properties, especially intense mirror-image CPL activities with large g_{PL} value of about 6×10^{-3} . Importantly, the CP-OLEDs with helicene enantiomers as emitters and a TADF molecule as sensitizer not only exhibited better performance of lower turn-on voltage of 2.6 V, four-fold maximum external quantum efficiency (EQE_{max}) of 5.3%, and lower efficiency roll-off

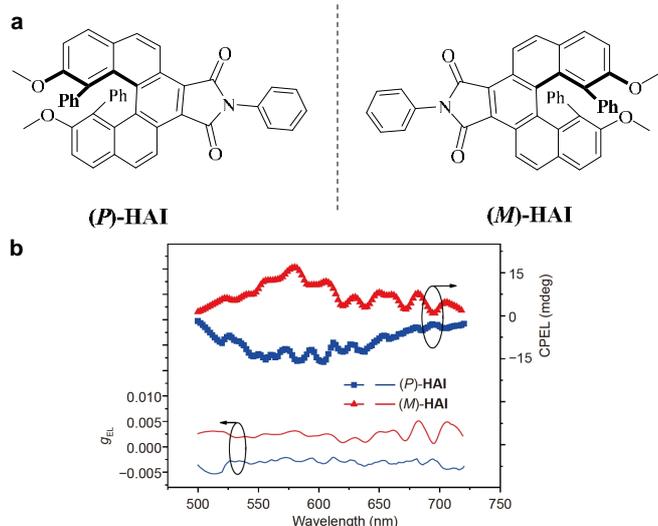


Figure 4. Molecular structures of the helicene enantiomers (*P*)-HAI and (*M*)-HAI. (b) CPEL spectra and g_{EL} versus wavelength curves of the CP-OLEDs.^[52] Copyright 2020, Science China Press.

than the devices without TADF sensitizer, but also exhibited intense CPEL signals with g_{EL} values of -2.3×10^{-3} and $+3.0 \times 10^{-3}$ (Figure 4b). This research leads to the development of thermally activated sensitized fluorescent CP-OLEDs with markedly enhanced efficiencies and intense CPEL.

Dhbaibi et al. developed novel twisted helical push-pull chiral emitters (Figure 5a),^[53] which show strong CD and CPL activities with g_{PL} values up to 3×10^{-2} , among the highest CPL intensities at the molecular level reported so far. Due to their strong CPL and high racemization barrier, these chiral derivatives were then doped in proof of concept top-emission CP-OLEDs and afforded a promising CPEL signal with the g_{EL} of around 8×10^{-3} (Figure 5b), which represents a significant result for CP-OLEDs using top-emission device architecture.

Though the CP-OLEDs with helicene structure-based chiral fluorescence molecules illustrated relatively large g_{EL} value, the EL efficiency is low due to the only 25% utilization of excitons. Notably, a novel strategy for TADF-sensitized helicene enantiomer-based OLEDs opens up a novel research direction towards achieving efficient CP-OLEDs with improved EL efficiency and large g value.

Helicene Structure-Based Transition Metal Complexes. As fluorescent material can only use singlet luminescence, its maximum internal quantum efficiency is only 25%. Phosphorescent materials, such as iridium and platinum complexes, can introduce heavy metal atoms to the spin-orbit coupling, leading to the quantum efficiency of 100%. Though helicene compounds have larger g value and the transition phosphorescent metal complexes own sufficient photoluminescence quantum efficiency (PLQY), the research on helicene structure-based chiral metal complexes, especially their CP-OLEDs, is rare due to the difficulties in their synthesis and device fabrication.

Crassous group developed an iridium complex **A²** with fused π -helical *N*-heterocyclic carbene (NHC) structure (Figure 6).^[54] The enantiomers exhibit green emission with unusually long

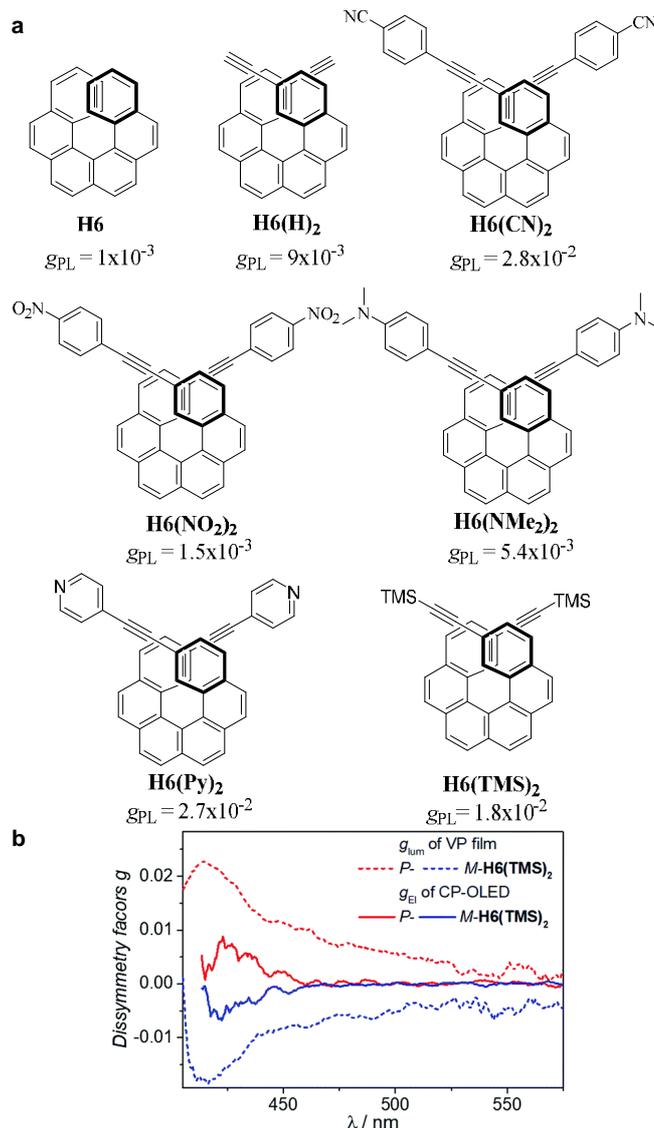


Figure 5. (a) Molecular structures and g values for each compound. (b) g_{PL} and g_{EL} based on (*P*) or (*M*)-H6(TMS)₂.^[53] Copyright 2021, Royal Society of Chemistry.

lifetimes and circular polarization with g_{PL} value around 10^{-3} . This novel diversification in organometallic helicene chemistry endows molecules with distinctive features and opens a new field, namely Ir-NHC-helicene complexes. However, there is no

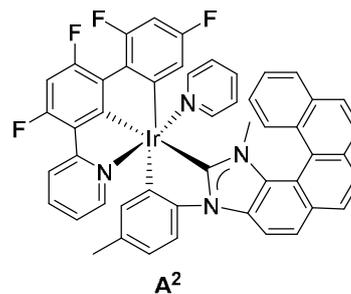


Figure 6. Molecular structure of the helicene iridium complex **A²**.

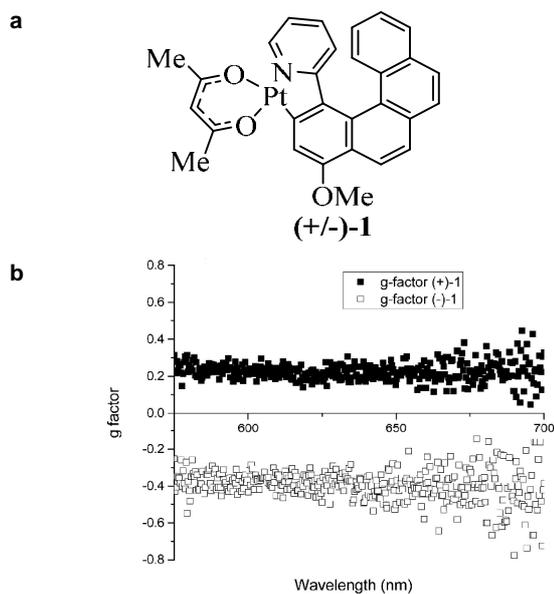


Figure 7. (a) Molecular structure of platinum-helicene complex (+/-)-1. (b) g_{EL} as a function of emission wavelength.^[55] Copyright 2016, American Chemical Society.

research on CPEL from these Ir-NHC-helicene complexes.

Fuchter group developed a pair of platinum-helicene complexes (+/-)-1^[55] to construct a solution-processed circularly polarized phosphorescent organic light-emitting diode (CP-PhOLED) that achieves a very high g_{EL} value of up to 0.38, which is the best result among the platinum complexes-based CP-OLEDs. Unfortunately, the device performances of current efficiency of 0.25 cd/A and maximum luminance of 222 cd/m² are insufficient for practical application (Figure 7). Notably, the dissymmetry of CP emission from this helicene-based device efficiently provides real-world advantages compared to nonpolarized emission, and will pave the way to chiral metal complex-based CP-PhOLED displays.

Zheng group designed and synthesized a pair of platinum-helicene enantiomers (*M*)-Pt and (*P*)-Pt (Figure 8a) by decorating the pyridinyl-helicene ligands with -CF₃ and -F groups,^[56] which are featured of superior configurational stability, high sublimation yield (> 90%) and obvious CPPL properties with g_{PL} of approximately 3.7×10^{-3} in solution and about 4.1×10^{-3} in doped film. Notably, the evaporated CP-PhOLEDs with enantiomers as emitters exhibited symmetric CPEL signals with g_{EL} value of 1.1 - 1.6×10^{-3} (Figure 8b) and decent device performances with a maximum brightness of 11590 cd/m² and an EQE_{max} up to 18.81%, which are the best results among the reported devices from chiral phosphorescent Pt(II) complexes. To suppress the effect of reverse CPEL signal from the cathode reflection, the further fabrication of semitransparent aluminum/ silver cathode-based CP-OLED successfully boosts up the g_{EL} by over three times to 5.1×10^{-3} (Figure 8c).

By regulating the position of CF₃ group, another pair of platinum-helicene enantiomers with deep red emission was also developed by Zheng group (Figure 9a).^[57] Compared with the plat-

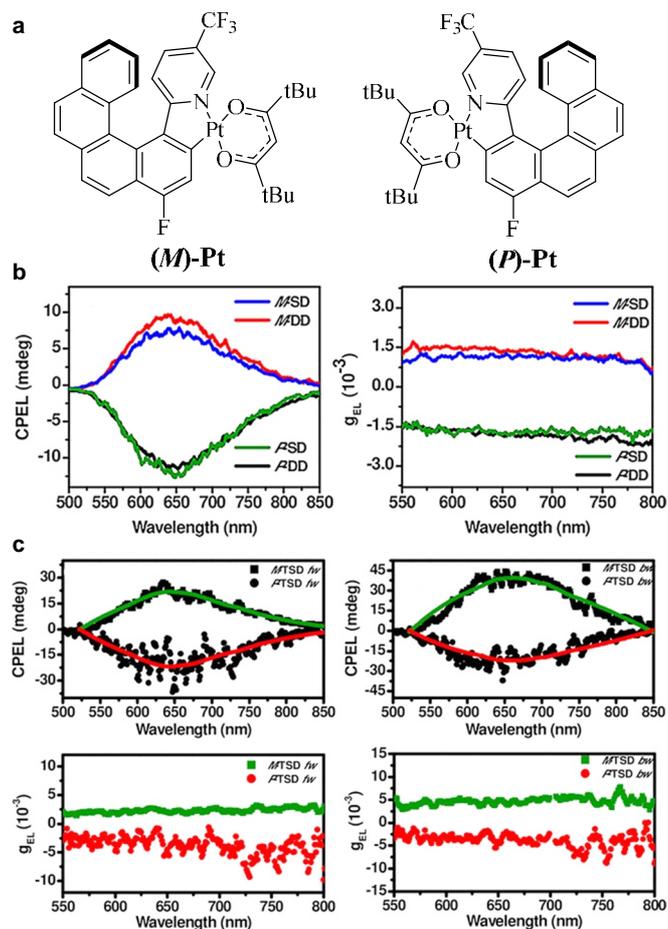


Figure 8. (a) Molecular structures of platinum-helicene enantiomers (*M*)-Pt and (*P*)-Pt. (b) CPEL spectra and g_{EL} versus wavelength curves. (c) CPEL spectra and g_{EL} versus the wavelength curves of semitransparent electrode devices.^[56] Copyright 2019, WILEY-VCH.

ina helicene reported by Crassous and Fuchter, (*M/P*)-Pt

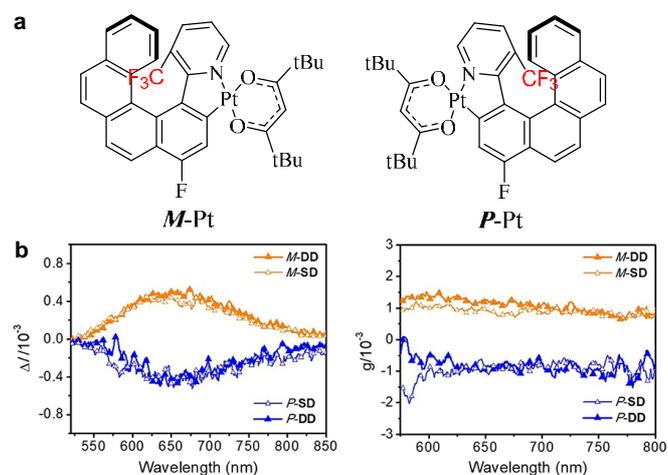


Figure 9. (a) Molecular structures of (*M/P*)-Pt. (b) CPEL spectra and g_{EL} versus wavelength curves.^[57] Copyright 2020, Yan, Luo, Liao, Zheng and Zuo.

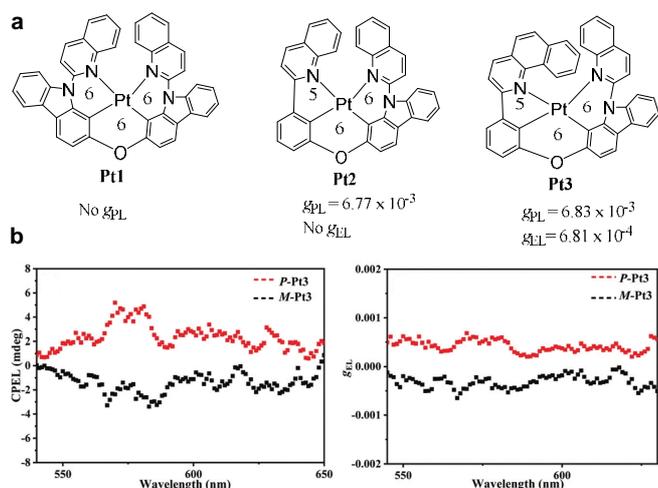


Figure 10. (a) Molecular structures of the chiral Pt(II) complexes. (b) CPEL spectra and g_{EL} versus wavelength curves.^[58] Copyright 2021, Royal Society of Chemistry.

displays excellent thermal stability and could be easily sublimated because of the introduction of peripheral hindered groups (CF_3 , tBu). Additionally, the special substitution position of the groups not only endows the helicene structure with more configurationally stable, but also enables (*MP*)-Pt better CPL performance with g_{PL} value of 6×10^{-3} due to the more twisted structures. The platinahelicene enantiomers-based evaporated CP-OLEDs displayed the deep-red emission with the peak at 653 nm and obvious CPEL signals with the g_{EL} in 10^{-3} order (Figure 9b). Therefore, the design strategy affords an efficient way to enhance the CPL performances of platinahelicene to realize the future application in CP-OLEDs.

Yuan et al. synthesized three pairs of tetradentate Pt(II) enantiomers^[58] with a helical structure by adjusting a six-membered to a five-membered metalocycle and replacing quinoline by benzo[h]quinoline with greater steric hindrance, and the configurational stability of the Pt(II) complex is gradually improved (Figure 10a). Compared with **Pt1** enantiomer with fused 6/6/6 metalocycles, which is easy to racemize at room temperature, the **Pt2** enantiomer with 5/6/6 metalocycles shows phosphorescent CPL properties with g_{PL} of $+6.77/-5.22 \times 10^{-3}$ in CH_2Cl_2 solutions at room temperature. By using a benzo[h]quinoline group to replace a quinoline unit, the larger overlap between the second quinoline and benzo[h]quinoline leads to good configurational stability of **Pt3** enantiomers at evaporation temperature. The evaporated OLEDs with **Pt1** and **Pt2** emitters show good device performances with an EQE_{max} of 14.2% and a maximum luminance of 39072 cd/m^2 . Based on the good configurational stability of **Pt3** enantiomers, the evaporated CP-OLEDs with **Pt3** enantiomers show symmetrical CPEL signals with g_{EL} value of $+6.81/-6.49 \times 10^{-4}$, as well as an EQE_{max} of 12.6% (Figure 10b).

The author also synthesized a pair of helicene Pt(II) enantiomers, (*RR*)-*P-QPt* and (*SS*)-*M-QPt*.^[59] The intrinsic *P*- and *M*-configurations were effectively induced from intrinsic chiral carbon centers (*R* or *S*), ingeniously avoiding the racemic mix-

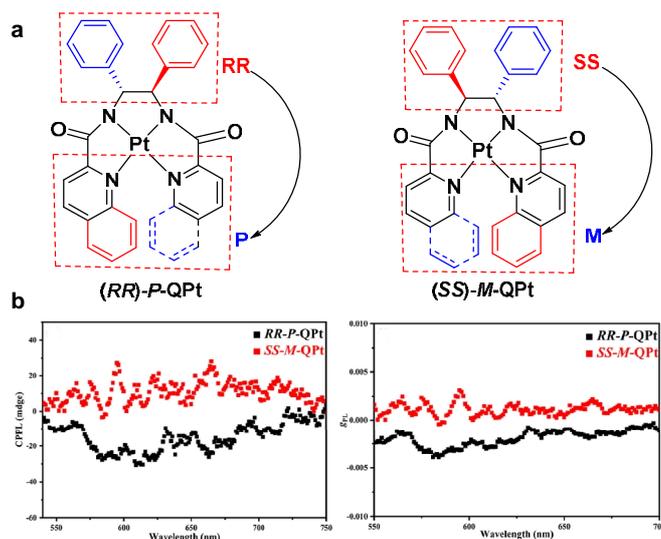


Figure 11. (a) Design strategy and molecular structures of chiral tetradentate Pt(II) complexes. (b) CPPL spectra and g_{PL} versus wavelength curves.^[59] Copyright 2022, Elsevier.

ture formation and chiral separation (Figure 11a). Notably, the chirality originating from both chiral carbon centers and helicene-like structure enhances the g factor greatly (Figure 11b). Though no CPEL was reported, this study brings new inspiration for the design of chiral Pt(II) enantiomers with good CPL properties.

The research on CP-OLEDs based on helicene phosphorescent metal complexes is scarce, and high g factors and satisfactory device performances seem to be incompatible currently.

Helicene Structure-Based TADF Molecules. Merging CPL functions into TADF structures is an effective strategy for directly constructing circularly polarized thermally activated delayed fluorescence (CP-TADF) materials. The high quantum efficiency and nearly 100% exciton utilization of CP-TADF molecules could effectively overcome the inherent shortcomings of traditional chiral fluorescent molecules and chiral lanthanide complexes, while helicenes often show strong chiral optical performance due to their inherent spiral chirality and π -conjugate electronic structures. Combining the superiority of these two molecules, the design and development of helicene structure-based TADF chiral molecule will promote the overlap of luminescence center and chiral core, thus achieving the organic unity of high efficiency and large g factor for realizing highly efficient CP-OLEDs.

Integrated CP-TADF and MR-TADF (CPMR-TADF) molecules are constructed from Zhu group by strategic design and synthesis of asymmetrical peripherally locked enantiomers, which are separated and named as (*+/-*)-**BN4** and (*+/-*)-**BN5** with TADF and CPL properties (Figure 12a).^[60] Because of the entire molecular frame coverage in the frontier orbitals, (*+/-*)-**BN4**- and (*+/-*)-**BN5**-based solution processed organic light-emitting diodes (OLEDs) achieved narrow full width at half maximum (FWHMs) of 49/49 and 48/48 nm and a high EQE_{max} of 20.6%/19.0% and 22.0%/ 26.5%, respectively. Importantly, un-

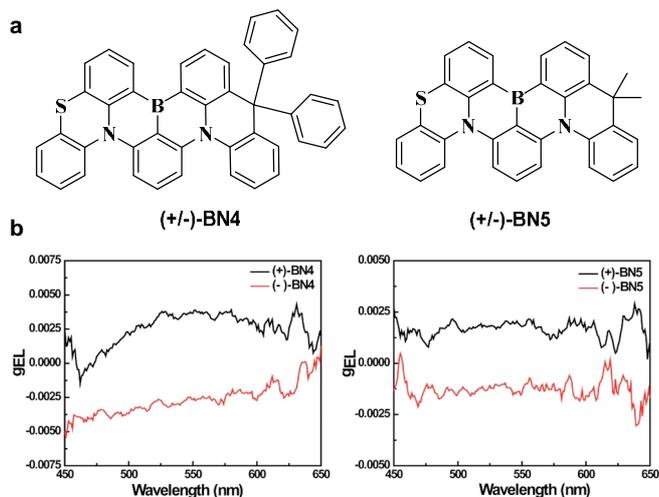


Figure 12. (a) Molecular structures of B/N nanographenes. (b) g_{EL} versus wavelength curves.^[60] Copyright 2021, WILEY-VCH.

ambiguous CPEL signals with g_{EL} values of $+3.7\text{--}3.1 \times 10^{-3}$ (**BN4**) and $+1.9\text{--}1.6 \times 10^{-3}$ (**BN5**) are obtained (Figure 12b). This research provides a facile and general concept for developing CPMR-TADF materials simultaneously with high efficiency, high color purity, and large luminescence dissymmetry factor, promoting the CP-TADF materials for practical applications in optoelectronics.

Yang group reported a helical M-shaped double hetero [5]helicene,^[61] (**P/M**)-helicene-BN, featured of the B/N/S embedded polycyclic fused aromatic skeleton, which was conveniently synthesized by a two-step method. These enantiomers-based CP-OLEDs achieved very high EQE_{max} over 30% and high brightness over 70,000 cd/m^2 , as well as pure-green emission with a narrow FWHM of 49 nm. Importantly, the CP-OLED based on helicene-BN enantiomer exhibited strong CPEL signals with g_{EL} value up to 2.2×10^{-3} (Figure 13).

A novel strategy for designing narrowband CP-TADF emitters with a triarylamine-based helicene framework was proposed by Jiang group. This design adopts carbonyl/nitrogen (C=O/N) or (C=O/N/O=S=O) system^[62,63] as a MR-TADF framework and introduces 9-phenyl-9H-carbazole (PhCz) at the ortho position of the central nitrogen to construct a helical structure, illustrating the origin of molecular chirality (Figure 14a). (**M**)-**QAO-PhCz** or

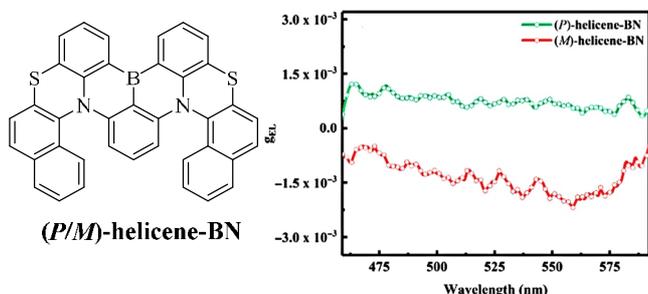


Figure 13. Molecular structure of (**P/M**)-helicene-BN and g_{EL} values versus wavelength curves of (**P/M**)-helicene-BN based CP-OLEDs.^[61] Copyright 2022, Chinese Chemical Society.

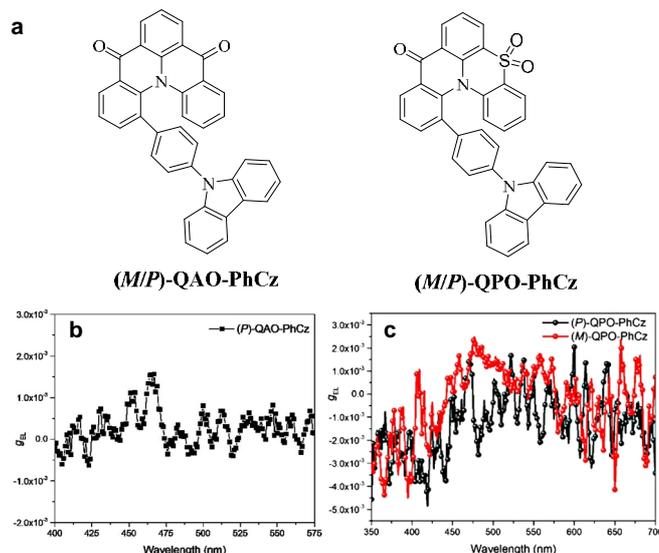


Figure 14. (a) Molecular structures. (b) and (c) g_{EL} versus wavelength curves.^[62,63] Copyright 2021, Royal Society of Chemistry.

(**P**)-**QAO-PhCz** presents CPL activity with g_{PL} as high as 1.1×10^{-3} in toluene. The offered OLEDs utilizing **QAO-PhCz** as guest show blue electroluminescence (467 nm) with a narrow FWHM of 36 nm and an EQE_{max} of 14.0%. Finally, the CP-OLEDs display distinct CPEL signal with g_{EL} of 1.5×10^{-3} for (**P**)-**QAO-PhCz** (Figure 14b). Due to the similar helicene structure, the performances of **QPO-PhCz** enantiomers can match that of **QAO-PhCz**, with g_{PL} of 1.2×10^{-3} in solution, EQE_{max} of 10.6%, g_{EL} of $+1.6 \times 10^{-3}$ and 1.1×10^{-3} for (**M**)-**QPO-PhCz** and (**P**)-**QPO-PhCz**, respectively (Figure 14c). These results demonstrate a new route to develop efficient CPL/CPEL materials from heterohelical structures and may enlighten related optoelectronic areas.

Using helicene structure-based TADF molecules for CP-OLED is an effective strategy for achieving high EL efficiency, however, the CPEL intensity and g_{EL} value are hardly satisfactory at present. The development of efficient helicene TADF materials for practical CP-OLEDs merging high efficiency and intense CPEL is urgent.

n CONCLUSION AND PERSPECTIVE

This review systematically summarizes the latest progress on helicene structure-based chiral luminescent materials and their circularly polarized electroluminescence performances of CP-OLEDs. Generally, the CP-OLEDs fabricated with helicene fluorescence molecules show large g_{EL} value, but poor device performances due to the 25% utilization of excitations. While helicene phosphorescent metal complexes usually exhibit decent EL efficiency with EQE over 18%, but the g_{EL} value is low at the 10^{-3} level, except for platinum complex (**+/-**)-**1**-based solution process devices with g_{EL} of up to 0.38. As for helicene structure-based TADF materials, excellent photophysical properties made them become promising materials for producing metal-free, low-cost, and high-performance CP-OLEDs. Although the EL efficiency of CP-OLEDs is fascinating with EQE over 30%, the low g_{EL} is difficult for practical applications at present.

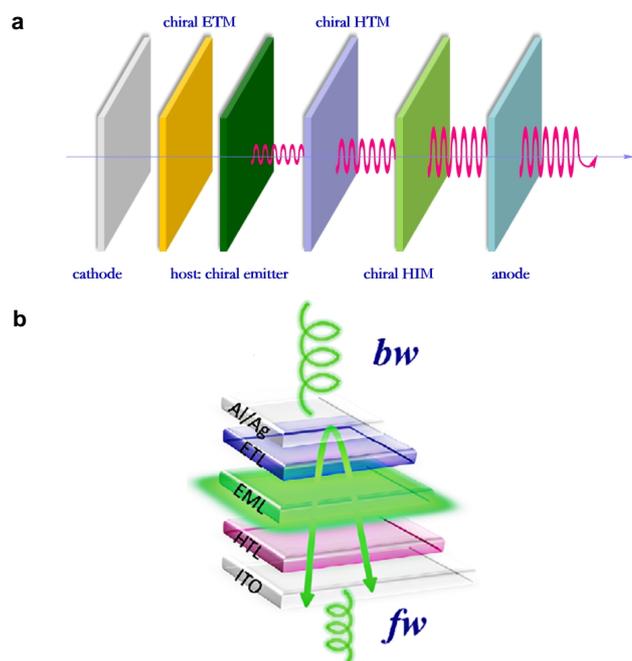


Figure 15. (a) The schematic diagram of CP-OLEDs with the architecture of full chiral layers (FCLs). (b) CP-OLEDs with a semi- or fully transparent cathode.^[64] Copyright 2021, WILEY-VCH.

The systematic studies on helicene chiral materials for CPEL are relatively few, which is in its infancy, but the present results offer the direction and hope for developing efficient helicene structure-based chiral luminescent materials for fabricating CP-OLEDs. Achieving large g_{EL} values and high efficiency simultaneously through technical means such as new molecular structure design and ingenious device fabrication technique of CP-OLEDs based on helicene chiral emitters remains a huge challenge.

At the molecule level, the development of new chiral emitters with both high PLQYs and large g_{PL} values will always be the primary goal of this research area, especially for designing novel helicene phosphorescent metal complexes and TADF molecules, which are of great significance because high PLQY and nearly 100% utilization of excitons are important for the high efficiency of device. As CPEL performance mainly depends on emissive layers rather than single molecules, the formation of supramolecular spiral structure through annealing or affixing of the external layer becomes effective means to greatly amplify the g factor for meeting the industrial requirements. Besides, the properties of other materials such as hole injection material (HIM), hole transport material (HTM), host and electron transport material (ETM) in OLEDs may also influence the CPEL activity and g_{EL} . The CP-OLEDs with the architecture of full chiral layers (FCLs) with chiral ETM, chiral host:chiral emitter, chiral HTM and chiral HIM materials may improve the g_{EL} value due to the amplification and superposition of CPEL signals (Figure 15a). Furthermore, as we know, g_{EL} values are usually lower than the g_{PL} ones, which may be attributed to light reflection in the OLED stack, such as cathode reflection of aluminum, thus leading to depolarization

and consumption of CPEL intensity. Through suitable device engineering, we believe that semi- or fully transparent devices would be enabled to achieve desirable g_{EL} values (Figure 15b).^[64]

Importantly, due to the complexity behind the CPEL phenomenon, a close collaboration between organic chemists and physicists appears essential to thoroughly understand and control the different aspects of molecular structure design and device engineering allowing the construction of applicable CP-OLEDs simultaneously displaying high EQE and g_{EL} factors. Owing to the wide potential applications of CPEL in 3D displays, optical information storage, quantum communication, and biological sensors, we believe that with the rapid development of chiral emitting materials and device architectures, CPEL based on OLEDs will attract more interest and become a research hotspot of luminescent materials in the future.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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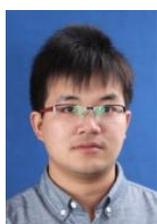
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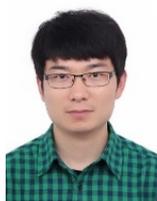
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