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Circularly Polarized Phosphorescent Electroluminescence with a High Dissymmetry Factor from PHOLEDs Based on a Platinahelicene

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S *Supporting Information*

ABSTRACT: Circularly polarized (CP) light is of interest in areas such as quantum optical computing, optical spintronics, biomedicine, and high efficiency displays. Direct emission of CP light from organic light-emitting diodes (OLEDs) has been a focus of research as it has the immediate application of increasing efficiency and simplifying device architecture in OLED based displays. High dissymmetry (g_{EL}) factor values have been reported for devices employing fluorescent polymers, but these CP-OLEDs are limited in their ultimate efficiencies by the type of emissive electronic transitions involved. In contrast, phosphorescent OLEDs (PHOLEDs) can emit light from triplet excited states and can therefore achieve very high efficiencies. However, CP-PHOLEDs are significantly understudied, and the two previous reports suffered from very low brightness or g_{EL} values. Here, we use a platinahelicene complex to construct a CP-PHOLED that achieves both a display level brightness and a high g_{EL} factor. The dissymmetry of CP emission reached with this proof-of-concept single-layer helicene-based device is sufficient to provide real-world benefits over nonpolarized emission and paves the way toward chiral metal complex-based CP-PHOLED displays.

Circularly polarized (CP) luminescence[1−3] is of interest in quantum computing,[4] optical communication for spintronics,[5] bioresponsive imaging,[6] asymmetric synthesis,[7,8] three-dimensional displays,[9] and more efficient LCD[10] and OLED[11] screens. Currently, CP light is often produced from non-polarized light through the use of filters, which leads to a loss in brightness, and, in the case of light emitting devices, to more complex and bulky device architectures.[12] Instead, it would be desirable to have organic light-emitting diodes (OLEDs) that can directly emit CP light.

The relationship between the left- and right-handed components of the circularly polarized electroluminescence (EL) or photoluminescence (PL) is given by the dissymmetry factor (*g* factor), which is defined as $g = 2\frac{I_L - I_R}{I_L + I_R}$. A *g* factor of zero corresponds to light with no circular polarization, while +2 and −2 correspond to fully left- or right-handed CP light, respectively. The maximum dissymmetry factor $|g_{EL}|$ of 0.38 reported here is sufficient to afford a 19% increased brightness compared to nonpolarized OLEDs of comparable efficiency in a display using a common circular polarization antiglare filter (see

SI for a detailed explanation and a definition of the CP-light convention).[11]

Several approaches exist for the production of OLEDs that directly emit circularly polarized light (CP-OLEDs, see Figure 1). Until 2013, most examples[13] were based on the use of
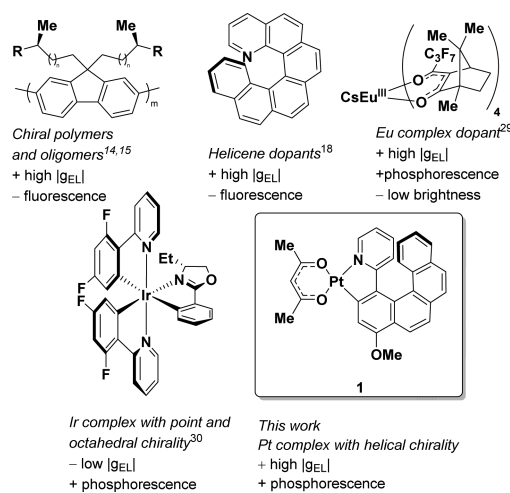

Figure 1. Examples of different chiral components used in the construction of CP-OLEDs (see SI for tabulated data).

polymers and oligomers bearing chiral side chains.[14] OLEDs based on these chiral organic semiconducting materials can reach impressive $|g_{EL}|$ factors of up to 0.35,[15] but their usage often involves complicated device fabrication (such as the use of alignment layers). Instead, our group employed an operationally simpler approach, whereby a nonemissive, chiral helicene[16,17] dopant was blended with a standard nonchiral polyfluorene-based polymer, which induced CP electroluminescence from the polymer with a $|g_{EL}|$ factor of 0.2.[18,19]

Fluorescent materials, like the emissive polymers described above, cannot emit light from triplet states and are therefore limited to a maximum of 25% internal quantum efficiency from consideration of exciton spin statistics.[20,21] Phosphorescent materials, however, can emit light from triplet states (phosphorescence) and can therefore be used to fabricate much more efficient phosphorescent OLEDs (PHOLEDs)[22−24] that achieve internal quantum efficiencies of nearly 100%[25] and external quantum efficiencies of 30%.[26] The desired phosphor-

escence is most commonly achieved by exploiting the strong spin−orbit coupling of iridium or platinum complexes, which are used as luminescent dopants in OLEDs.[27,28] Thus, we were interested in using *chiral* complexes of these metals as dopants to produce phosphorescent CP emission in the presence of a nonchiral semiconductive polymer host.

To the best of our knowledge, there are only two previous attempts at using chiral, nonracemic organometallic complexes as phosphorescent dopants in a CP-PHOLED. In the first study, the Di Bari group reported that an emissive chiral europium complex dopant in a nonemissive semiconducting polymer possesses narrow emission bands with remarkable $|g_{EL}|$ factors of 0.09−0.15 and 0.73−0.79, but a very low total luminance of less than 3 cd/m^2.[29] In an alternative approach, a small series of iridium complexes with octahedral and point chirality were found to possess very low $|g_{EL}|$ factors of up to 0.0026.[30] Based on the high dissymmetry factors achieved using nonemissive helicene dopants,[18] we hoped that metal complexes featuring helical chirality could combine bright phosphorescence with significantly improved $|g_{EL}|$ values. While many different transition metal complexes with helicene ligands have been reported,[31] we focused on the group of platinahelicene complexes developed by the groups of Crassous, Autschbach, and Réau, due to their structural similarity to common platinum phosphors and their excellent chiroptical characterization.[32−37] For this proof of concept device, we chose phosphorescent platinahelicene complex **1**, on the basis of its high solution $|g_{PL}|$ value ($\sim10^{-2}$).[32,36]

The absolute HOMO energy of complex **1** was determined by electrochemical measurements. Cyclic voltammetry (CV) showed irreversible oxidation and reduction of **1**. Therefore, only the oxidative wave was recorded in a fresh experiment and the HOMO calculated as −5.3 eV (see SI for more details).[38] The optical band gap of 2.7 eV was extracted from the UV absorption edge of **1**.[32] Adding this band gap to the HOMO energy affords a LUMO level of −2.6 eV. The HOMO of **1** is similar to that of a related complex possessing an extended carbacyclic π-system[39] but lies below those of less conjugated 2-phenylpyridine derivatives.[40,41]

To construct CP-PHOLEDs using **1**, we chose the single-layer solution-processed device architecture previously demonstrated by Tsutsui.[42] Such an architecture can be used in large-area solution processed devices (e.g., LCD backlights) and allows rapid assessment of soluble emissive materials. Based on the HOMO and LUMO level of **1**, PVK (HOMO: − 5.8 eV)[43] and OXD-7 (LUMO: − 1.3 eV)[44] were selected to act as hole and electron transport materials, respectively. For initial tests on the optical properties of these materials, blend films of racemic (±)-**1**, PVK, and OXD-7 in varying ratios were spin coated onto a glass substrate. The UV-absorption spectra of the thin films correspond to the features of the individual components (see Figure 2A). Blended films of enantiopure **1** displayed circular dichroism (CD) spectra with strong similarity to the solution phase data of **1** (see Figure 2B).[32] The PL maximum at 625 nm indicates that **1** is the emissive species (see Figure 2C, cf. λ_{max} = 644 nm for **1** in solution[32]). The g_{PL} value obtained at 625 nm was −0.22 (see Figure 2D).

Single layer PHOLED devices were fabricated by spin-coating a solution of (±)-**1**, PVK, and OXD-7 onto PEDOT:PSS-coated ITO substrates. The photoemissive layer (PEL) was then capped with a Ca/Al cathode (see SI for more details). For racemic **1**, the best overall OLED performance was obtained with a 1:1 ratio of OXD-7 and PVK, yielding a turn-on
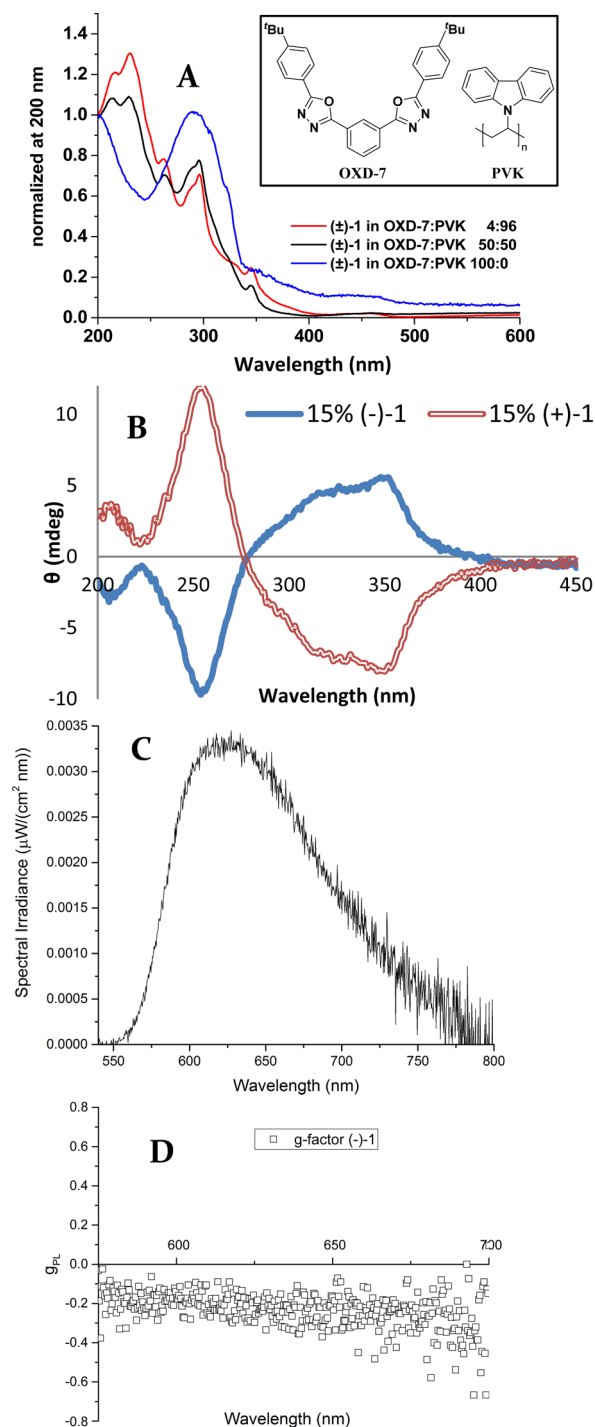

Figure 2. (A) Absorption spectra of 12−13 wt % racemic (±)-**1** in a mixture of OXD-7 and PVK. Inset: molecular structures of OXD-7 and PVK. (B) CD spectra of 15 wt % (−)-**1** (blue, solid line) and (+)-**1** (red, hollow line) in a mixture of OXD-7 and PVK (1:1). (C) PL spectrum of 15 wt % (−)-**1** in a mixture of OXD-7 and PVK (1:1). (D) g_{PL} as a function of emission wavelength for 15 wt % (−)-**1** in a mixture of OXD-7 and PVK (1:1).

voltage of 5.7 V, maximum luminance of 230 cd/m^2, and a maximum power efficiency and current efficiency of 0.16 lm/W and 0.52 cd/A, respectively (see Figures S11 and S12). Increasing the ratio of OXD-7 led to phase separation and poor film quality.[45]
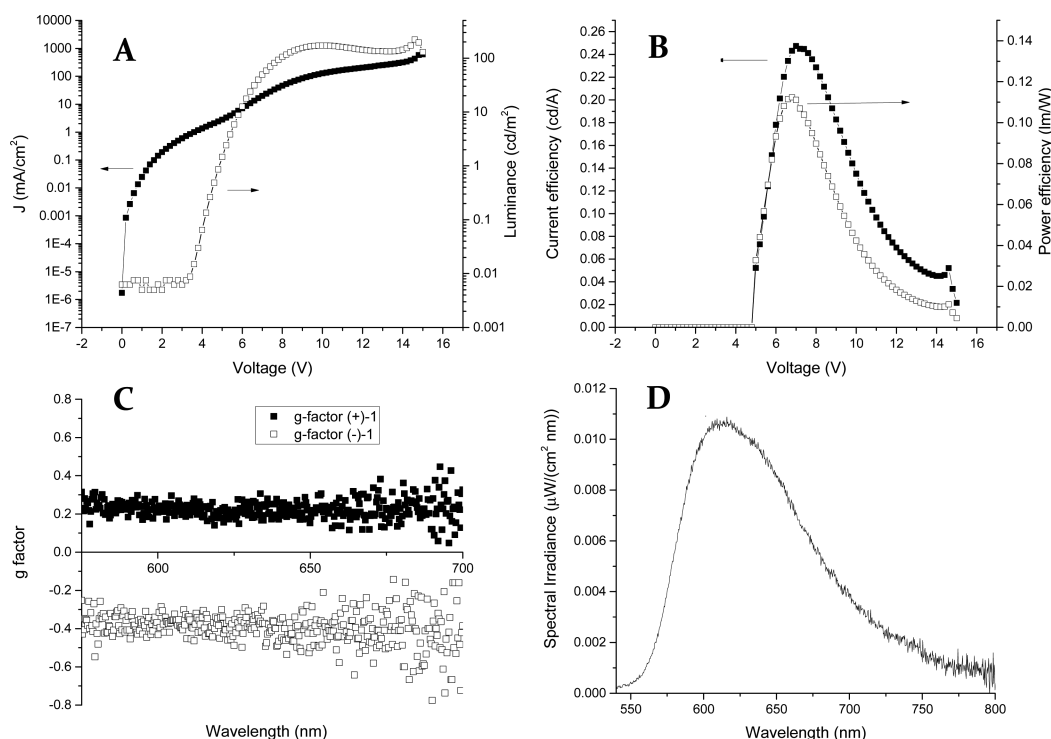
Figure 3. Device performance of CP-PHOLED using 15 wt % (−)-**1** in OXD-7/PVK 70:30 matrix. (A) $J-V-L$ graph. (B) Power and current efficiency as a function of potential. (C) g_{EL} of (−)-**1** and (+)-**1** as a function of emission wavelength. (D) EL spectrum.

Having demonstrated the feasibility of using platinahelicene **1** as an emissive dopant in an OLED, we fabricated devices using enantiopure **1**. The resultant PHOLEDs had turn-on voltage, luminance, and efficiency values that were comparable to the devices obtained with racemic **1** (4.4 V, 122 cd/m², 0.13 lm/W, 0.33 cd/A for (−)-**1**, see Figures S19 and S20). The enantiopure helicene complex displayed a notably improved solubility compared to racemic (±)-**1**.[46] Thus, the OXD-7/PVK ratio could be increased from 50:50 without resulting in the phase separation observed for racemic (±)-**1**. Devices prepared with an OXD-7:PVK ratio of 70:30 displayed improved maximum luminance, current efficiency, and power efficiency (3.6 V, 374 cd/m², 0.23 lm/W, 0.49 cd/A for (−)-**1**, see Figures S21, S22). We note the maximum luminance observed exceeds that which would be required (200 cd/m²) in a display containing a CP filter.

To compare the g-factors of both enantiomers of **1**, devices with (+)-**1** and (−)-**1** were fabricated using the optimized OXD-7/PVK ratio. Due to batch-to-batch variability, the performance parameters were slightly smaller (3.6 V, 222 cd/m², 0.11 lm/W, 0.25 cd/A, for (−)-**1**, see Figure 3A,B) than devices from the previous device run. The Commission internationale de l'éclairage (CIE) coordinates are (0.58, 0.41). Importantly, the two different enantiomers resulted in CP emission with opposite g_{EL} signs (see Figure 3C), indicating the platinahelicene to be responsible for the observed CP effect. At the emission maximum of 615 nm, the g-factors of (+)-**1** and (−)-**1** correspond to +0.22 and −0.38, respectively (see Figure 3C).

The highest $|g_{EL}|$ value measured (0.38) means that one sign of circular polarization is 47% larger than the other. This dissymmetry would correspond to a 19% increased brightness over nonpolarized emission when used in an OLED display employing a common circular polarization antiglare filter (see SI for a detailed explanation).[11] This brightness increase could reduce power consumption by even more than 19%, as the device could be operated at a lower voltage in a more efficient regime due to PHOLED efficiency roll-off.[47] The high $|g_{EL}|$ value displayed by this device is comparable to those recorded for the emission maxima of previous fluorescent or phosphorescent OLEDs,[15,18,29] more than 140-fold larger than the only previous transition metal CP-PHOLED[30] and 1 order of magnitude higher than the values recorded for **1** in solution.[36]

Although the $|g_{EL}|$ factor of our devices is sufficiently large to provide real-world benefits over nonpolarized emission, the luminance and power efficiency of this simple proof-of-concept device are below the current state-of-the-art,[26] possibly due to the small quantum yield of **1** (10%).[32] By developing new helically chiral metal complexes, devices with different colors and higher efficiencies could be obtained. Additionally, the development of highly thermally stable complexes could allow the fabrication of vacuum sublimed devices. Such improvements, leading to bright and highly dissymmetric CP-PHOLEDS, are likely to have a large impact on future display technologies and other applications employing CP-light. Based on the strong chiral selection of helicenes[2,3,18,48] and the high $|g_{EL}|$ factor obtained in this and our previous CP-OLED study,[18] we propose that helically chiral materials should remain a focus of attention in the research for second-generation CP-PHOLEDs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02463.

Detailed experimental procedures, device fabrication, device performance, electrochemical, chiral resolution, AFM, synthetic and spectroscopic data (PDF)

Raw data files are openly available (DOI: 10.6084/m9.figshare.c.3290264)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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