

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

Jochen R. Brandt,<sup>†</sup> Xuhua Wang,<sup>§</sup> Ying Yang,<sup>§</sup> Alasdair J. Campbell,<sup>§</sup> and Matthew J. Fuchter<sup>\*†</sup>

<sup>†</sup>Department of Chemistry, Imperial College London, South Kensington campus, London SW7 2AZ, UK

<sup>§</sup>Department of Physics, Imperial College London, South Kensington campus, London, SW7 2AZ, UK

<sup>†</sup>Centre for Plastic Electronics, Imperial College London, South Kensington campus, London, SW7 2AZ, UK

## Supporting Information Placeholder

**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 non-polarized emission, and paves the way towards chiral metal complex-based CP-PHOLED displays.

Circularly polarized (CP) luminescence<sup>1-3</sup> is of interest in quantum computing,<sup>4</sup> optical communication for spintronics,<sup>5</sup> bioresponsive imaging,<sup>6</sup> asymmetric synthesis,<sup>7,8</sup> three-dimensional displays,<sup>9</sup> and more efficient LCD<sup>10</sup> and OLED<sup>11</sup> screens. Currently, CP light is often produced from non-polarized light through the use of filters, which lead to a loss in brightness, and, in the case of light emitting devices, to more complex and bulky device architecture.<sup>12</sup> 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 bright-

ness compared to non-polarized OLEDs of comparable efficiency in a display using a common circular polarization anti-glare filter (see SI for a detailed explanation and a definition of the CP-light convention).<sup>11</sup>

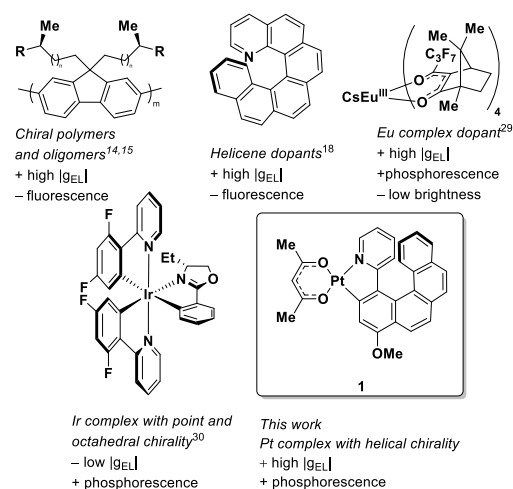


Figure 1. Examples of different chiral components used in the construction of CP-OLEDs (see SI for tabulated data).

Several approaches exist for the production of OLEDs that directly emit circularly polarized light (CP-OLEDs, see Figure 1). Until 2013, most examples<sup>13</sup> were based on the use of polymers and oligomers bearing chiral side chains.<sup>14</sup> OLEDs based on these chiral organic semiconducting materials can reach impressive  $|g_{EL}|$  factors of up to 0.35,<sup>15</sup> but their usage often involves complicated device fabrication (such as the use of alignment layers). Instead, our groups employed an operationally simpler approach, whereby a non-emissive, chiral helicene<sup>16,17</sup> dopant was blended with a standard non-chiral polyfluorene-based polymer, which induced CP electroluminescence from the polymer with a  $|g_{EL}|$  factor of 0.2.<sup>18,19</sup>

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.<sup>20,21</sup> Phosphorescent materials, on the other hand, can emit light

from triplet states (phosphorescence) and can therefore be used to fabricate much more efficient phosphorescent OLEDs (PHOLEDs)<sup>22-24</sup> that achieve internal quantum efficiencies of nearly 100 %<sup>25</sup> and external quantum efficiencies of 30 %.<sup>26</sup> The desired phosphorescence is most commonly achieved by exploiting the strong spin-orbit coupling of iridium or platinum complexes, which are used as luminescent dopants in OLEDs.<sup>27,28</sup> Thus, we were interested in using *chiral* complexes of these metals as dopants to produce phosphorescent CP emission in the presence of a non-chiral semiconductive polymer host.

To the best of our knowledge, there are only two previous attempts at using chiral, non-racemic 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 non-emissive 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<sup>2</sup>.<sup>29</sup> 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.<sup>30</sup> Based on the high dissymmetry factors achieved using non-emissive helicene dopants,<sup>18</sup> 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,<sup>31</sup> 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.<sup>32-37</sup> For this proof of concept device, we chose phosphorescent platinahelicene complex **1**, on the basis of its high solution  $|g_{PL}|$  value ( $\approx 10^{-2}$ ).<sup>32,36</sup>

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).<sup>38</sup> The optical band gap of 2.7 eV was extracted from the UV absorption edge of **1**.<sup>32</sup> 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  $\pi$ -system<sup>39</sup> but lies below those of less conjugated 2-phenylpyridine derivatives.<sup>40,41</sup>

To construct CP-PHOLEDs using **1**, we chose the single-layer solution-processed device architecture previously demonstrated by Tsutsui.<sup>42</sup> Such an architecture can be used in large-area solution processed devices (eg. LCD backlights) and allows rapid assessment of soluble emissive materials. Based on the HOMO and LUMO level of **1**, PVK (HOMO:  $-5.8$  eV)<sup>43</sup> and OXD-7 (LUMO:  $-1.3$  eV)<sup>44</sup> 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 ( $\pm$ )-**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). Blend films of enan-

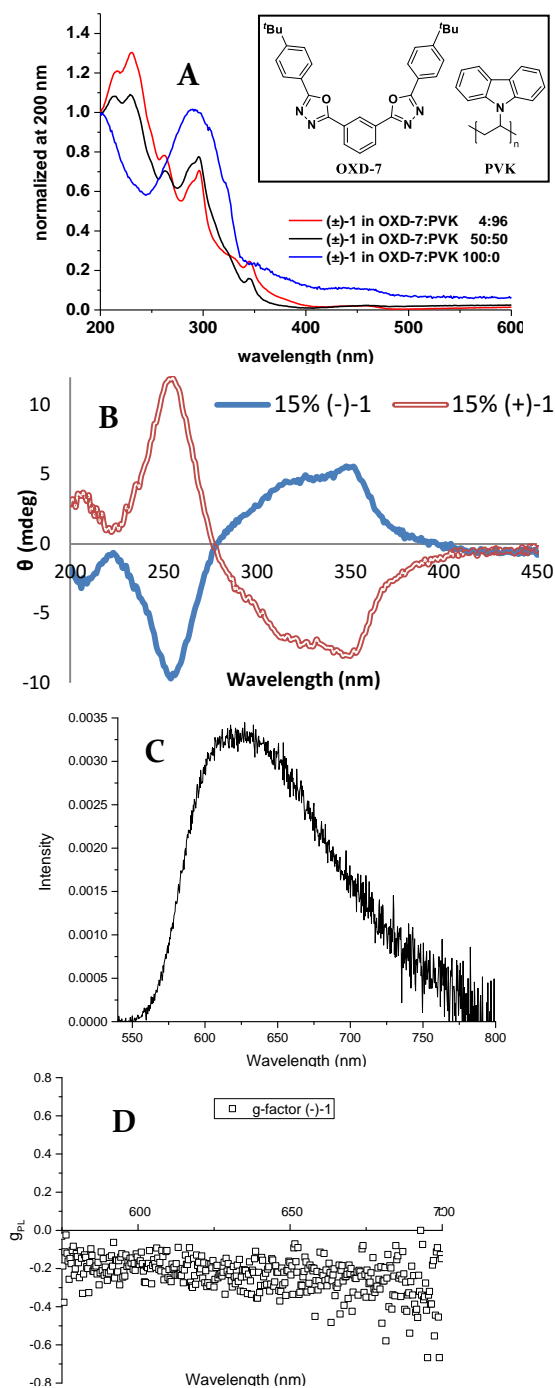


Figure 2. A) Absorption spectra of 12–13 wt% racemic ( $\pm$ )-**1** in a mixture of OXD-7 and PVK. Inset: molecular structures of OXD-7 and PVK; B) CD spectra of 15 wt% ( $-$ )-**1** (blue, solid line) and ( $+$ )-**1** (red, hollow line) in a mixture of OXD-7 and PVK (1:1). C) PL spectrum of 15 wt% ( $-$ )-**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).

tiopure **1** displayed circular dichroism (CD) spectra with strong similarity to the solution phase data of **1** (see Figure 2B).<sup>32</sup> The PL maximum at 625 nm indicates that **1** is the emissive species (see Figure 2C, cf.  $\lambda_{max} = 644$  nm for **1** in solution<sup>32</sup>). The  $g_{PL}$  value obtained at 625 nm was  $-0.22$  (see Figure 2D).

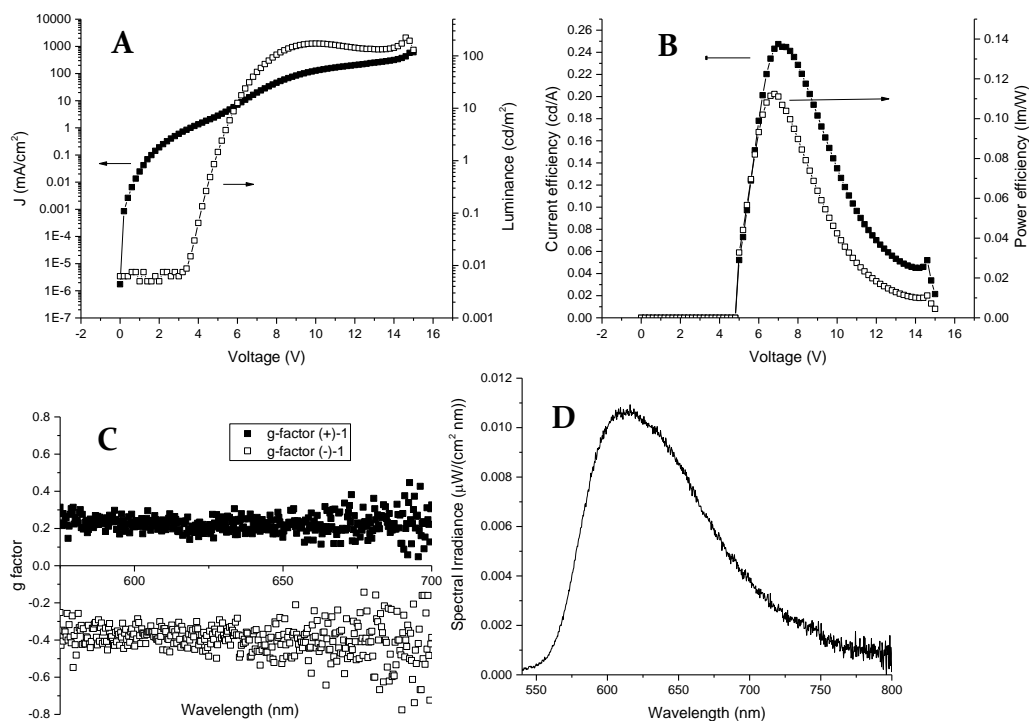


Figure 3 Device performance of CP-PHOLED using 15 wt% (–)-**1** in OXD-7:PVK 70:30 matrix. A) J-V-L graph; B) power and current efficiency as a function of potential; C)  $g_{EL}$  of (–)-**1** and (+)-**1** as a function of emission wavelength; D) EL spectrum.

Single layer PHOLED devices were fabricated by spin-coating a solution of ( $\pm$ )-**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 voltage of 5.7 V, maximum luminance of 230  $\text{cd}/\text{m}^2$  and a maximum power efficiency and current efficiency of 0.16  $\text{lm}/\text{W}$  and 0.52  $\text{cd}/\text{A}$ , respectively (see Figures S11, S12). Increasing the ratio of OXD-7 led to phase separation and poor film quality.<sup>45</sup>

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  $\text{cd}/\text{m}^2$ , 0.13  $\text{lm}/\text{W}$ , 0.33  $\text{cd}/\text{A}$  for (–)-**1**, see Figures S19, S20). The enantiopure helicene complex displayed a notably improved solubility compared to racemic ( $\pm$ )-**1**.<sup>46</sup> Thus, the OXD-7:PVK ratio could be increased from 50:50 without resulting in the phase separation observed for racemic ( $\pm$ )-**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  $\text{cd}/\text{m}^2$ , 0.23  $\text{lm}/\text{W}$ , 0.49  $\text{cd}/\text{A}$  for (–)-**1**, see Figures S21, S22). We note the maximum luminance observed exceeds that which would be required (200  $\text{cd}/\text{m}^2$ ) 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  $\text{cd}/\text{m}^2$ , 0.11  $\text{lm}/\text{W}$ , 0.25  $\text{cd}/\text{A}$ , for (–)-**1**, see Figure 3A and 3B) 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 non-polarized emission when used in an OLED display employing a common circular polarization anti-glare filter (see SI for a detailed explanation).<sup>11</sup> This brightness increase could reduce power consumption by even more than 19%, as the device could be operated at lower voltage in a more efficient regime due to PHOLED efficiency roll-off.<sup>47</sup> The high  $|g_{EL}|$  value displayed by this device is comparable to those recorded for the emission maxima of previous fluorescent or phosphorescent OLEDs,<sup>15,18,29</sup> more than 140-fold larger than the only previous transition metal CP-PHOLED<sup>30</sup> and one order of magnitude higher than the values recorded for **1** in solution.<sup>36</sup>

Although the  $|g_{EL}|$  factor of our devices is sufficiently large to provide real-world benefits over non-polarized emission, the luminance and power efficiency of this simple proof-of-concept device are below the current state of the art,<sup>26</sup> possibly due to the small quantum yield of **1** (10%).<sup>32</sup> 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<sup>2,3,18,48</sup> and the high  $|g_{EL}|$  factor obtained in this and our previous CP-OLED study<sup>18</sup> we propose that helically chi-

ral 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:

Detailed experimental procedures, device fabrication, device performance, electrochemical, chiral resolution, AFM, synthetic and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*m.fuchter@imperial.ac.uk

### Notes

The authors declare no competing financial interests.

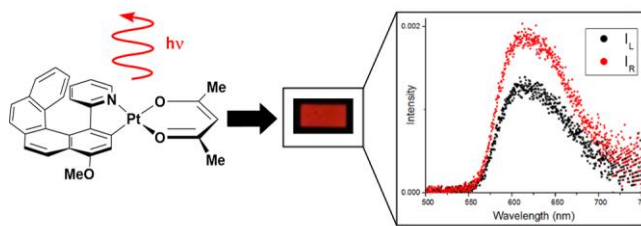
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## REFERENCES

- (1) Zinna, F.; Di Bari, L. *Chirality* **2015**, *27*, 1–13.
- (2) Sánchez-Carnerero, E. M.; Agarrabeitia, A. R.; Moreno, F.; Maroto, B. L.; Muller, G.; Ortiz, M. J.; de la Moya, S. *Chem. - A Eur. J.* **2015**, *21*, 13488–13500.
- (3) Kumar, J.; Nakashima, T.; Kawai, T. *J. Phys. Chem. Lett.* **2015**, *6*, 3445–3452.
- (4) Wagenknecht, C.; Li, C.-M.; Reingruber, A.; Bao, X.-H.; Goebel, A.; Chen, Y.-A.; Zhang, Q.; Chen, K.; Pan, J.-W. *Nat. Photonics* **2010**, *4*, 549–552.
- (5) Farshchi, R.; Ramsteiner, M.; Herfort, J.; Tahraoui, A.; Grahn, H. T. *Appl. Phys. Lett.* **2011**, *98*, 162508.
- (6) Heffern, M. C.; Matosziuk, L. M.; Meade, T. J. *Chem. Rev.* **2014**, *114*, 4496–4539.
- (7) Inoue, Y. *Chem. Rev.* **1992**, *92*, 741–770.
- (8) Richardson, R. D.; Baud, M. G. J.; Weston, C. E.; Rzepa, H. S.; Kuimova, M. K.; Fuchter, M. J. *Chem. Sci.* **2015**, *6*, 3853–3862.
- (9) Kim, D.-Y. *J. Korean Phys. Soc.* **2006**, *49*, S505–S508.
- (10) Schadt, M. *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379.
- (11) Singh, R.; Unni, K. N. N.; Solanki, A.; Deepak. *Opt. Mater. (Amst).* **2012**, *34*, 716–723.
- (12) Grell, M.; Oda, M.; Whitehead, K. S.; Asimakis, A.; Neher, D.; Bradley, D. D. C. *Adv. Mater.* **2001**, *13*, 577–580.
- (13) For a rare example of CP emission by spin injection into an OLED, see: Shikoh, E.; Fujiwara, A.; Ando, Y.; Miyazaki, T. *Jpn. J. Appl. Phys.* **2006**, *45*, 6897–6901.
- (14) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119*, 9909–9910.
- (15) Geng, Y.; Trajkovska, A.; Culligan, S. W.; Ou, J. J.; Chen, H. M. P.; Katsis, D.; Chen, S. H. *J. Am. Chem. Soc.* **2003**, *125*, 14032–14038.
- (16) Shen, Y.; Chen, C.-F. *Chem. Rev.* **2012**, *112*, 1463–1535.
- (17) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051–1095.
- (18) Yang, Y.; da Costa, R. C.; Smilgies, D.-M.; Campbell, A. J.; Fuchter, M. J. *Adv. Mater.* **2013**, *25*, 2624–2628.
- (19) Chiral helicenes have also been successfully applied to the detection of CP-light: Yang, Y.; da Costa, R. C.; Fuchter, M. J.; Campbell, A. J. *Nat. Photonics* **2013**, *7*, 634–638.
- (20) Baldo, M. A.; O'Brien, D. F.; Thompson, M. E.; Forrest, S. R. *Phys. Rev. B* **1999**, *60*, 14422–14428.
- (21) Please see this review on thermally activated delayed fluorescence (TDAF) for an elegant way to improve fluorescence quantum yields: Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. *Adv. Mater.* **2014**, *26*, 7931–7958.
- (22) Sasabe, H.; Kido, J. *European J. Org. Chem.* **2013**, *2013*, 7653–7663.
- (23) Minaev, B.; Baryshnikov, G.; Agren, H. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1719–1758.
- (24) Nguyen, C.; Ingram, G.; Lu, Z.-H. In *SPIE Photonics West 2014-OPTO: Optoelectronic Devices and Materials*; Tabor, C. E., Kajzar, F., Kaino, T., Koike, Y., Eds.; 2014; Vol. 8983, p 89830C.
- (25) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048.
- (26) Lee, C. W.; Lee, J. Y. *Adv. Mater.* **2013**, *25*, 5450–5454.
- (27) Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 638–655.
- (28) Kalinowski, J.; Fattori, V.; Cocchi, M.; Williams, J. A. G. *Coord. Chem. Rev.* **2011**, *255*, 2401–2425.
- (29) Zinna, F.; Giovanella, U.; Di Bari, L. *Adv. Mater.* **2015**, *27*, 1791–1795.
- (30) Li, T.-Y.; Jing, Y.-M.; Liu, X.; Zhao, Y.; Shi, L.; Tang, Z.; Zheng, Y.-X.; Zuo, J.-L. *Sci. Rep.* **2015**, *5*, 14912.
- (31) Saleh, N.; Shen, C.; Crassous, J. *Chem. Sci.* **2014**, *5*, 3680–3694.
- (32) Norel, L.; Rudolph, M.; Vanthuyne, N.; Williams, J. A. G.; Lescop, C.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R. *Angew. Chemie Int. Ed.* **2010**, *49*, 99–102.
- (33) Anger, E.; Rudolph, M.; Norel, L.; Zrig, S.; Shen, C.; Vanthuyne, N.; Toupet, L.; Williams, J. A. G.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R. *Chem. - A Eur. J.* **2011**, *17*, 14178–14198.
- (34) Anger, E.; Rudolph, M.; Shen, C.; Vanthuyne, N.; Toupet, L.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R. *J. Am. Chem. Soc.* **2011**, *133*, 3800–3803.
- (35) Shen, C.; Anger, E.; Srebro, M.; Vanthuyne, N.; Toupet, L.; Roussel, C.; Autschbach, J.; Réau, R.; Crassous, J. *Chem. - A Eur. J.* **2013**, *19*, 16722–16728.
- (36) Shen, C.; Anger, E.; Srebro, M.; Vanthuyne, N.; Deol, K. K.; Jefferson, T. D.; Muller, G.; Williams, J. A. G.; Toupet, L.; Roussel, C.; Autschbach, J.; Réau, R.; Crassous, J. *Chem. Sci.* **2014**, *5*, 1915–1927.
- (37) Saleh, N.; Moore, B.; Srebro, M.; Vanthuyne, N.; Toupet, L.; Williams, J. A. G.; Roussel, C.; Deol, K. K.; Muller, G.; Autschbach, J.; Crassous, J. *Chem. - A Eur. J.* **2015**, *21*, 1673–1681.
- (38) D'Andrade, B. W.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. *Org. Electron.* **2005**, *6*, 11–20.
- (39) Facendola, J. W.; Seifrid, M.; Siegel, J.; Djurovich, P. I.; Thompson, M. E. *Dalt. Trans.* **2015**, *44*, 8456–8466.
- (40) Choi, W. J.; Choi, S.; Ohkubo, K.; Fukuzumi, S.; Cho, E. J.; You, Y. *Chem. Sci.* **2015**, *6*, 1454–1464.
- (41) Xing, Y.; Liu, C.; Xiu, J.-H.; Li, J.-Y. *Inorg. Chem.* **2015**, *54*, 7783–7790.
- (42) Lin, C. P.; Tsutsui, T.; Saito, S. *Nippon Kagaku Kaishi* **1995**, No. 8, 649–655.
- (43) Suzuki, H. *Thin Solid Films* **2001**, *393*, 352–357.
- (44) Wang, C.; Jung, G.-Y.; Batsanov, A. S.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **2002**, *12*, 173–180.
- (45) The solubility of racemic platinum complexes was improved by substituting the acac ligand with other O,O' or O,N ligands. Although the higher solubility improved the film quality, devices produced from these other complexes displayed lower PHOLED luminance and efficiency.
- (46) Mendola, D.; Saleh, N.; Hellou, N.; Vanthuyne, N.; Roussel, C.; Toupet, L.; Castiglione, F.; Melone, F.; Caronna, T.; Fontana, F.; Marti-Rujas, J.; Parisini, E.; Malpezzi, L.; Mele, A.; Crassous, J. *Inorg. Chem.* **2016**, *55*, 2009–2017.
- (47) Murawski, C.; Leo, K.; Gather, M. C. *Adv. Mater.* **2013**, *25*, 6801–6827.
- (48) Kiran, V.; Mathew, S. P.; Cohen, S. R.; Hernández Delgado, I.; Lacour, J.; Naaman, R. *Adv. Mater.* **2016**, *28*, 1957–1962.

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*Circularly Polarized  
Phosphorescence*

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Electroluminescence*