

Cite this: *J. Mater. Chem. C*, 2022, 10, 15491

# Green light-emitting electrochemical cells based on platinum(II) complexes with a carbazole-appended carbene ligand†‡

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Platinum(II) complexes bearing new carbazole-appended cyclometallated N-heterocyclic carbenes such as [Pt(Cbz-C<sup>∧</sup>C\*)Cl(NCCH<sub>3</sub>)](**3**), [Pt(Cbz-C<sup>∧</sup>C\*)Cl(PPh<sub>3</sub>)](**4**), [Pt(Cbz-C<sup>∧</sup>C\*)(PPh<sub>3</sub>)(py)]PF<sub>6</sub> (py = pyridine, **5**), [Pt(Cbz-C<sup>∧</sup>C\*)(P<sup>∧</sup>N)]PF<sub>6</sub> (P<sup>∧</sup>N = 2-(2-(diphenylphosphino) ethyl) pyridine, **6**), and [Pt(Cbz-C<sup>∧</sup>C\*)(P<sup>∧</sup>P)]PF<sub>6</sub> (P<sup>∧</sup>P: 1,1-bis(diphenylphosphino)methane, dppm **7**; 1,2-bis(diphenylphosphino)ethane, dppe, **8**, 1,2-bis(diphenylphosphino) benzene, dppbz, **9**) have been prepared using a stepwise procedure from 9-(4-bromophenyl)-9H-carbazole, imidazole, [(Pt(μ-Cl)(η<sup>3</sup>-2-Me-C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>)] and the corresponding ancillary ligands. They have been fully characterized. Also, single-crystal X-ray structures, theoretical calculations and photophysical studies have been performed. These complexes have been employed as emitters in simple solution-processed light-emitting electrochemical cells (LECs). When driven under a pulsed current of 50 A m<sup>-2</sup>, devices based on **7–9** exhibited green emission, a luminance of 265 cd m<sup>-2</sup> and a current efficiency of 5.7 cd A<sup>-1</sup> (for the best performing emitter, **7**). As far as we know, these are the first examples of green-emitting Pt(II)-based LECs.

Received 17th June 2022,  
Accepted 16th September 2022

DOI: 10.1039/d2tc02539f

rsc.li/materials-c

## Introduction

Light-emitting electrochemical cells (LECs) celebrated their 25th anniversary in 2020.<sup>1,2</sup> Since the LEC technology was first discovered by Pei *et al.*,<sup>3</sup> it has become an excellent candidate and a viable alternative to traditional solid state light sources.<sup>4–7</sup> In its simplest form, it consists of a single layer of an ionic luminescent material sandwiched between two air-stable contact electrodes.<sup>8</sup> Generally, this material consists of either a conjugated light-emitting polymer (CP)<sup>9–12</sup> or an ionic transition-metal complex (iTMC).<sup>13</sup> The latter presents some advantages since the ionic metal complex can perform all the necessary roles for light generation: (a) charge injection

promoted by the mobile counterions, (b) transport of electrons and holes, and (c) generation of photons from triplet excited states.<sup>13–16</sup> In this context, iTMCs have been largely investigated,<sup>13,17–19</sup> in particular those based on Ir(III) complexes;<sup>18,20–22</sup> however, platinum-based LECs have seldom been explored, with just a few examples found in the literature.<sup>23–26</sup> Most of them are polynuclear complexes of Pt(II) with cyclometallated C<sup>∧</sup>N or N<sup>∧</sup>C<sup>∧</sup>N/N<sup>∧</sup>N<sup>∧</sup>C pincer ligands. All the cited materials exhibit emission in the red region of the visible spectrum with no examples of green or blue emitting Pt(II)-based LECs reported to date. In this regard, Pt(II) complexes with cyclometallated N-heterocyclic carbenes (NHCs; C<sup>∧</sup>C\*) have been proved to emit light in different colours (blue,<sup>27–32</sup> green-yellow,<sup>33,34</sup> and orange-red<sup>29,30,35,36</sup>) with elevated quantum efficiencies. The cycloplatinated C<sup>∧</sup>C\* ligands surpass the donor capability of C<sup>∧</sup>N-cyclometallated imines, increasing the energy of the empty d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals and preventing their photo- or thermal population, which would lead to severe distortions resulting in non-emissive deactivation.<sup>37</sup> In line with this, when designing a Pt(II) emitter, it is important to minimize the structural distortions upon excitation. These promote non-emissive decays due to the electron-vibrational coupling of the excited and ground states.<sup>38</sup> Thus, rigid or semi-rigid scaffolds with chelating coordination and strong donor atoms are desired structural features to improve emission quantum yields.

With this in mind, the 9H-carbazol-9-yl (Cbz) group possesses several advantages: an intrinsic rigid molecular structure, strong

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† Dedicated to Paul R. Raithby, celebrating a career in inorganic and organometallic chemistry, on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available. CCDC 2151291–2151294. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2tc02539f>







Table 1 Relevant  $^{31}\text{P}\{^1\text{H}\}^a$  and  $^{195}\text{Pt}\{^1\text{H}\}^b$  NMR data ( $\delta$  (ppm),  $J$  (Hz))

Compounds	$\delta$ Pt	$J_{\text{Pt,P}^{\text{trans-C6}}}$	$J_{\text{Pt,P}^{\text{trans-C1}}}$	$\delta$ P $^{\text{trans-C1}}$	$\delta$ P $^{\text{trans-C6}}$	$J_{\text{P,P}}$
5	-4271	2914.2		29.0		
6	-4208	2896.5		19.2		
7	-4384	2374.9	1559.7	-38.8 $\nu_{\text{A}}$	-39.4 $\nu_{\text{B}}$	42
8	-4983	2699.9	1964.2	50.4	43.4	6.3
9	-4917	2661.4	1956.2	47.0	39.8	4.4

<sup>a</sup> 162 MHz,  $\text{CD}_2\text{Cl}_2$ . <sup>b</sup> 86 MHz,  $\text{CD}_2\text{Cl}_2$ .

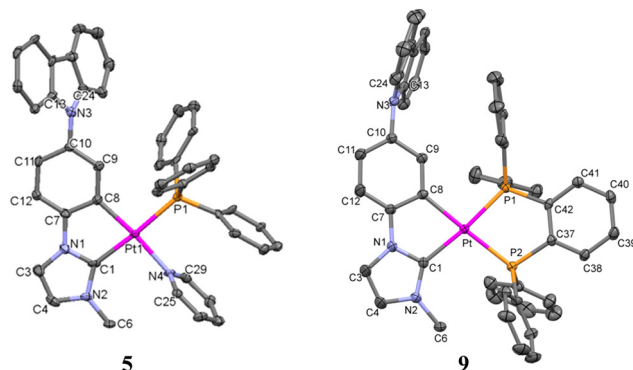


Fig. 1 Molecular structures of the cationic complexes **5** and **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules and  $\text{PF}_6^-$  have been omitted for clarity.

the P and X (N (**6**) and P (**7**, **9**)) atoms from the chelating phosphine ligands. Comparing the bite angle of these chelate ligands (P–Pt–X), it can be observed that it is lower for compound **7** ( $71.37(10)^\circ$ ), which forms a four-membered ring, than those observed for **6** and **9**, with six- and five-membered rings.

Bond distances and angles (Table S2, ESI $\ddagger$ ) are similar to those observed in other complexes with the same kinds of ligands.<sup>27,29,31,50</sup> The Cbz moiety (N3 and C13–C24) appears twisted with respect to the platinum coordination plane forming dihedral angles of  $59.21(3)^\circ$  for **5**,  $61.47(2)^\circ$  for **6**,  $54.39(17)^\circ$  for **7** and  $75.76(4)^\circ$  for **9**. In **5**, the interplanar angle between the platinum coordination plane and that of the pyridine is  $79.8(2)^\circ$ , while it is somewhat lower ( $53.7(1)^\circ$ ) for the complex with the chelate ligand, **6**. As commented before, this orientation of the pyridine ring has a great influence on the  $\text{H}_4$  signal in the  $^1\text{H}$  NMR spectra. Also, in their supramolecular structure, there are no close intermolecular Pt...Pt or  $\pi$ – $\pi$  interactions between the adjacent molecules, probably due to the great steric demand of the Cbz and phosphine groups.

### Photophysical properties and theoretical calculations

The photophysical properties of the ionic compounds **5–9** have been investigated. Their absorption spectra in  $\text{CH}_2\text{Cl}_2$  solution are depicted in Fig. 2 and their data are listed in Table S3 (ESI $\ddagger$ ). They exhibit very similar absorption profiles with relatively intense bands around 290–350 nm that are normally attributed to intraligand transitions of the NHC ligand. Additionally, they show rather weak absorptions at  $\lambda > 370$  nm that appear slightly redshifted for the diphosphine derivatives (see the inset

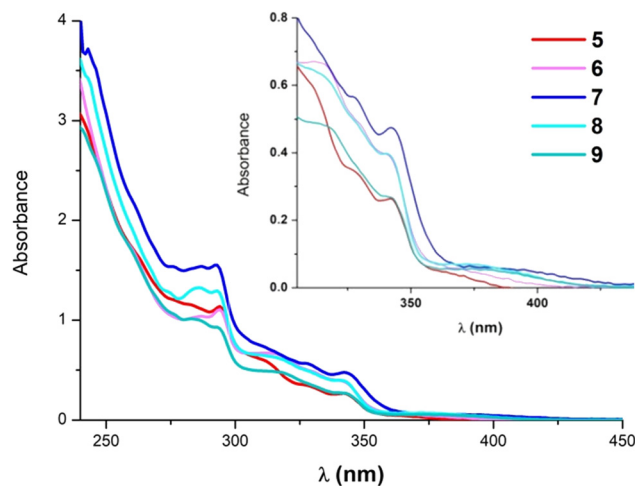


Fig. 2 UV-Vis spectra of **5–9** in  $\text{CH}_2\text{Cl}_2$  at  $5 \times 10^{-5}$  M. Inset: close-up for the 350–450 nm range.

of Fig. 2). These bands do not experience any significant wavelength shift with solvent polarity (Fig. S11, ESI $\ddagger$  for **9**).

A concentration dependence study of **5** and **7** in  $\text{CH}_2\text{Cl}_2$  showed that no significant ground state aggregation takes place in the concentration range from  $10^{-6}$  to  $10^{-3}$  M (see Fig. S12 and S13, ESI $\ddagger$ ). Therefore, the low energy absorptions at  $\lambda > 370$  nm are originated from electronic transitions within the mononuclear species. Besides, when comparing compounds with the same ancillary ligands but different  $\text{C}^*\text{C}^*$  groups  $[\text{Pt}(\text{R}-\text{C}^*\text{C}^*)(\text{PPh}_3)(\text{py})]\text{PF}_6$ , ( $\text{R} = -\text{CN}, -\text{CO}_2\text{Et}$ )<sup>31</sup> and  $[(\text{R}-\text{C}^*\text{C}^*)\text{Pt}(\text{P}^*\text{P})]\text{PF}_6$ , ( $\text{R} = -\text{H}, -\text{CN}, -\text{CO}_2\text{Et}$ ),<sup>27,29</sup> the absorption bands appear shifted to lower energies in these electron donating carbazolyl derivatives (**5** and **7–9**). Thus, these observations are indicating a great participation of the  $\text{C}^*\text{C}^*$  fragment in the electronic transitions.

To gain further knowledge on this matter, theoretical calculations (density functional theory (DFT) and time dependent density functional theory (TD-DFT)) were carried out for **5**, **7** and **9** in  $\text{CH}_2\text{Cl}_2$  (Tables S4 and S5, ESI $\ddagger$ ). Considering that the computational results of the diphosphine derivatives are very similar, those corresponding to **9** are available in the ESI $\ddagger$ . As shown in Fig. 3, the lowest energy calculated absorption ( $S_1$ ) fits well with the experimental one and its main contribution is the HOMO  $\rightarrow$  LUMO transition (69% **5** and 92% **7**, see Fig. 3). The assignment of these electronic transitions is based on the analysis of the frontier orbitals (Table S5, ESI $\ddagger$ ).

For both complexes, the HOMO is centered on the NHC ligand (99%), essentially on the Cbz fragment whereas the LUMO is distributed over the ancillary ligands (50% **5** and 28% **7**), the NHC (32% **5** and 43% **7**) and the Pt center (18% **5** and 29% **7**), with no participation of the Cbz fragment. Thus, the lowest energy absorption for both is attributed to a mixed transition  $\text{LL}'/\text{CT} [\pi(\text{NHC}) \rightarrow \pi^*(\text{L}')]/\text{ILCT} [[\text{NHC}]]$  and  $\text{LMCT} [\pi(\text{NHC}) \rightarrow \text{d}(\text{Pt})]$ , with the latter having a greater contribution in **7**.

The photoluminescence properties were examined in poly(methyl methacrylate) (PMMA) films at a 5 wt% doping





Fig. 3 UV-Vis absorption spectra,  $S_1$  calculated transitions in  $\text{CH}_2\text{Cl}_2$  (bars) and molecular orbital plots (isovalue 0.03) of compounds **5** (left) and **7** (right).

Table 2 Photophysical data for **5–9** in 5 wt % PMMA films with  $\lambda_{\text{exc}} = 340$  nm

Comp.	$\lambda_{\text{em}}(\text{nm})$	$\tau(\mu\text{s})^a$	$\Phi_{\text{Ar}}/\Phi_{\text{Air}}$	$k_r^a$	$k_{\text{nr}}^a$
<b>5</b>	461, 481 <sub>max</sub>	22.6	0.47/0.39	$1.7 \times 10^4$	$2.7 \times 10^4$
<b>6</b>	467, 484 <sub>max</sub>	18.1	0.49/0.35	$1.9 \times 10^4$	$3.6 \times 10^4$
<b>7</b>	492 <sub>sh</sub> , 522 <sub>max</sub>	22.1	0.76/0.55	$2.5 \times 10^4$	$2.0 \times 10^4$
<b>8</b>	487 <sub>sh</sub> , 507 <sub>max</sub>	26.6	0.77/0.50	$1.8 \times 10^4$	$1.8 \times 10^4$
<b>9</b>	478 <sub>sh</sub> , 509 <sub>max</sub>	23.1	0.83/0.63	$2.7 \times 10^4$	$1.6 \times 10^4$

<sup>a</sup> In air;  $k_r = \Phi/\tau_{\text{exp}}$  and  $k_{\text{nr}} = (1 - \Phi)/\tau_{\text{exp}}$ .

concentration of the Pt compound (Table 2). As shown in Fig. 4, compounds **5** and **6** show blue emissions whereas the diphosphine derivatives (**7–9**) display green ones. Their emission lifetime decays fit to one rather long component ( $\sim 20$   $\mu\text{s}$ ) and their quantum yield (QY) measurements reach very high values under an Ar atmosphere, in particular those corresponding to the P<sup>^</sup>P derivatives (QY > 0.75). The excitation



Fig. 4 Normalized excitation (–) and emission (–) spectra of **5–9** in 5 wt% PMMA films (right;  $\lambda_{\text{exc}} = 340$  nm). Pictures of **5** and **7** were taken under 365 nm light.

spectra match the absorption ones, even though there is a remarkable increase in the intensity of the lowest energy band.

To assist in the photoluminescence discussion, the lowest energy triplet states for the optimized structures at the ground state have been calculated by TD-DFT in  $\text{CH}_2\text{Cl}_2$  (see Tables S4 and S5, the ESI<sup>†</sup> for the three lowest ones:  $T_1$ ,  $T_2$  and  $T_3$ ). In all cases,  $T_1$  energies are considerably lower than those for  $T_2$  (0.16 eV for **5**, 0.28 eV for **7** and 0.17 eV for **9**); thus, there are no close low-lying triplets. The calculated wavelengths of these  $T_1$  states follow the trend observed for the experimental phosphorescence data (calculated 429 **5**, 449 **7**, and 431 nm **9** vs. experimental 481 **5**, 522 **7**, and 509 nm **9**). Also, the geometry optimizations of the  $T_1$  states were carried out and their spin-density distributions calculated (Fig. S15, ESI<sup>†</sup>). They are mainly located on the C<sup>^</sup>C\* ligand (1.803 **5**, 1.712 **7**, and 1.753 **9**) and to a minor extent on the Pt center (0.150 **5**, 0.166 **7**, and 0.155 **9**) and the ancillary ligands (0.047 **5**, 0.122 **7**, and 0.092 **9**). This great contribution of C<sup>^</sup>C\* to the emissive state  $T_1$  agrees with the obtained  $K_r$  values ( $10^4$  order, Table 2).<sup>51</sup>

Therefore, the emission for all complexes would be attributed mainly to metal-perturbed  $^3\text{IL}$  [NHC] transitions with some contribution of LL/CT [ $\pi(\text{NHC}) \rightarrow \pi^*(\text{L}')$ ]. Similar to what occurs in the UV-vis absorptions, the emissions of **5** ( $\lambda_{\text{max}} = 481$  nm) and **7–9** ( $\lambda_{\text{max}} = 522$ – $507$  nm) appear shifted to lower energies in relation to those bearing different substituents in the C<sup>^</sup>C\* ligand [Pt(R-C<sup>^</sup>C\*)(py)(PPh<sub>3</sub>)]PF<sub>6</sub> (R = –CN, –CO<sub>2</sub>Et;  $\lambda_{\text{max}} \sim 470$  nm)<sup>31</sup> and [(R-C<sup>^</sup>C\*)Pt(P<sup>^</sup>P)]PF<sub>6</sub> (R = –H, –CN, –CO<sub>2</sub>Et;  $\lambda_{\text{max}} \sim 490$ – $476$  nm).<sup>27,29</sup> Thus, based on these spectroscopic observations and on the DFT calculations, the presence of an electron donating group (R = Cbz) in the C<sup>^</sup>C\* skeleton increases the energy of the HOMO and results in a red-shift in the emission bands.

#### Light-emitting electrochemical cells

Light-emitting electrochemical cells using complexes **5–9** as active materials were fabricated. Complexes were mixed with







Fig. 5 Time-dependence of the luminance [ $\text{cd m}^{-2}$ ] of LECs ITO/PEDOT:PSS/iTMC:IL(4 : 1)/Al, (iTMC: **7** (black), **8** (red) and **9** (blue)) with the active layer prepared from solutions in ACN (a) and DCM (b). All the devices shown were driven with a pulsed current with an average current density of  $50 \text{ A m}^{-2}$ .

could remain in the active films. The effect of retained solvents has been reported in the past as detrimental for the devices as it can lead to degradation pathways or quenching.<sup>57</sup> In view of this, and once the stability of the emitters was checked by NMR in  $\text{MeCN-}d_3$  at  $70^\circ\text{C}$  for at least 1 hour (Fig. S18, ESI<sup>†</sup> for **7**), we increased the annealing conditions of devices prepared from ACN in terms of time and temperature. To do this, we prepared a device using emitter **7** with a longer annealing time (4 h) at the same temperature ( $70^\circ\text{C}$ ) and a device using emitter **9** with a higher temperature annealing process ( $90^\circ\text{C}$ ) and a longer time (1 h). The performance of the device processed at  $70^\circ\text{C}$  for 4 h slightly improved with a maximum luminance of  $75 \text{ cd m}^{-2}$  (vs.  $61 \text{ cd m}^{-2}$ ), a CE of  $1.5 \text{ cd A}^{-1}$  (vs.  $1.2 \text{ cd A}^{-1}$ ) and a  $t_{50}$  of 11 min (vs. 13 min) (Fig. S19a, ESI<sup>†</sup>). On the other hand, the device processed at higher annealing temperature not only did not improve but it decreased, showing a maximum luminance of  $48 \text{ cd m}^{-2}$  (vs.  $57 \text{ cd m}^{-2}$ ), a CE of  $0.96 \text{ cd A}^{-1}$  (vs.  $1.1 \text{ cd A}^{-1}$ ) and a  $t_{50}$  of 7 min (vs. 43 min) (Fig. S19b, ESI<sup>†</sup>). These results, in particular the much lower  $t_{50}$ , could be an indication that the harsher annealing conditions are inducing a degradation of the emitter. The second aspect to be pointed out is the voltage during operation (Fig. S20, ESI<sup>†</sup>). When compared, the voltage of the devices prepared from ACN is significantly lower than the DCM, with values between 3 V and 3.5 V for ACN and values between 4 V and 5 V for DCM. The origin of this effect can also be related to the residual solvent present on the active layer, where it has been seen that the presence of a solvent decreases the resistance of the film, resulting in a lower turn-on voltage.<sup>57</sup> Lower voltages notoriously allow for longer lifetimes, and therefore higher  $t_{50}$ , but at the expense of lower luminance levels. All in all, these results point that the origin of the difference in the performance of devices processed from ACN and from DCM might reside in their different morphology. Indeed, in previous works, it has been seen that morphology can affect the performance of LEC devices.<sup>58–60</sup> However, atomic force microscopy (AFM) images show no significant differences between active films using emitter **7** processed from different solvents (Fig. S21, ESI<sup>†</sup>). Both layers are very flat and

homogeneous with no apparent phase separation or aggregation and with just small differences in the root mean square (RMS) roughness of the films (0.5 nm and 0.3 nm for ACN and DCM, respectively).

Finally, the EL spectra were characterized in both ACN and DCM (Fig. 6a, b and Table 3). In ACN, the EL peaks of **7**, **8** and **9** are centered at 523 nm, 528 nm and 519 nm while in DCM at 542 nm, 535 nm and 528 nm, respectively. The slight difference on the EL peaks between ACN- and DCM-processed devices is ascribed to optical effects arising from the differences in the thicknesses of the active layers (90 and 120 nm, respectively). The EL is very similar to the PL of the active layer films. In some cases, **8** from ACN and **7**, **8** and **9** from DCM, a slight red-shift of the EL can be observed. The red-shift of the EL of iTMCs can be common and was also previously observed in LECs based on Ir(III) and Cu(I) complexes.<sup>61,62</sup> The corresponding emission colours, expressed as CIE (Commission Internationale de l'Éclairage) coordinates, are shown in Fig. S22 (ESI<sup>†</sup>) and compiled in Table S8 (ESI<sup>†</sup>). The EL was also measured over time (for devices made from emitter **7**), down to their  $t_{50}$ , in order to observe the EL evolution during the degradation (Fig. S23, ESI<sup>†</sup>). The  $\lambda_{\text{max}}$  of the EL remains constant for devices processed from ACN and only slightly changes for devices processed from DCM (from 542 to 549 nm), an indication of the high stability of the EL over the lifetime of the device. Notably, as seen by the EL spectra and the CIE coordinates, the three devices emit in the green region. To our knowledge, these are the first reported green-emitting Pt(II)-based LECs.

In spite of their simplicity, iTMC-LECs fabricated from DCM solutions of the carbazole-appended compounds, **7–9**, showed an improved performance than PhOLEDs based on similar complexes bearing  $\text{R-C}^*\text{C}^*$  ( $\text{R} = \text{H}, \text{CN}$ ), since the optimal OLED, based on compound  $[\text{Pt}(\text{H-C}^*\text{C}^*)(\text{dppbz})]\text{PF}_6$  achieved a maximum luminance of  $200 \text{ cd m}^{-2}$  with a peak CE of 0.4, at 10 V.<sup>27</sup>

Similarly, devices made from compounds **5** and **6** were also fabricated. The active layers (iTMC:IL) showed very low PLQYs with values of 1% for both emitters. Devices made with **5** and **6**



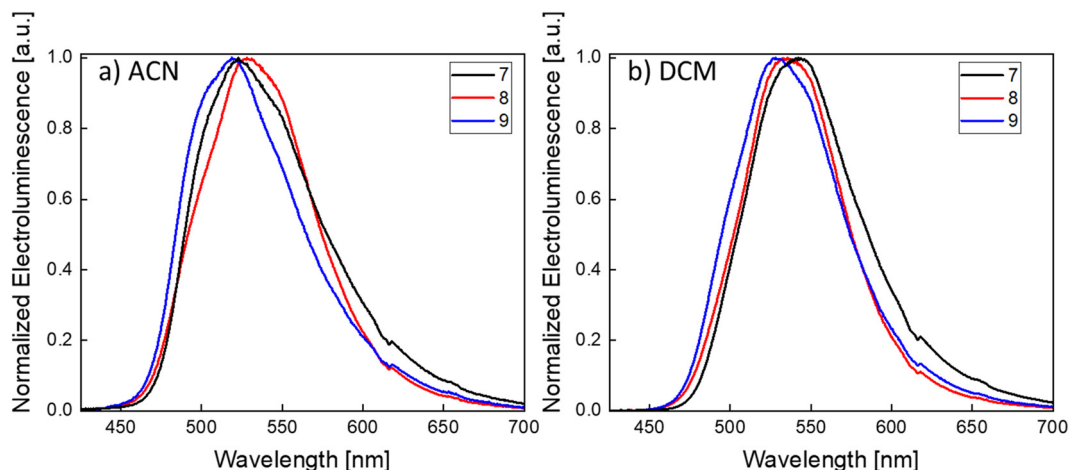


Fig. 6 Normalized electroluminescence spectra of LEC devices ITO/PEDOT:PSS/iTMC:IL(4 : 1)/Al, (iTMC: **7** (black), **8** (red) and **9** (blue)) with the active layer prepared from solutions in ACN (a) and DCM (b).

turned-on, showing the classic voltage evolution over time of a LEC (Fig. S24, ESI<sup>†</sup>); however their performance was extremely poor. For emitter **6**, the maximum observed luminance was  $4 \text{ cd m}^{-2}$  (Fig. S24b, ESI<sup>†</sup>) while for emitter **5** the luminance was lower than the sensitivity of our LEC lifetime characterization setup (less than *ca.*  $1 \text{ cd m}^{-2}$ ). For emitter **6**, it was also possible to measure the EL spectra, which showed a blue emission centered at 491 nm (CIE 0.2343, 0.4776). The very low QY of emitters **5** and **6** somewhat predicts the very low EL observed on these devices.

## Conclusions

Platinum(II) complexes bearing new carbazole-appended cyclometallated N-heterocyclic carbenes such as [Pt(Cbz-C<sup>∧</sup>C\*)Cl(NCCH<sub>3</sub>)](**3**), [Pt(Cbz-C<sup>∧</sup>C\*)Cl(PPh<sub>3</sub>)](**4**), [Pt(Cbz-C<sup>∧</sup>C\*)(PPh<sub>3</sub>)(py)]PF<sub>6</sub> (**5**), [Pt(Cbz-C<sup>∧</sup>C\*)(P<sup>∧</sup>N)]PF<sub>6</sub> (**6**), and [Pt(Cbz-C<sup>∧</sup>C\*)(P<sup>∧</sup>P)]PF<sub>6</sub> (P<sup>∧</sup>P: dpmm **7**; dppe, **8**; dpbbz, **9**) have been prepared by a stepwise procedure from 9-(4-bromo-phenyl)-9H-carbazole, imidazole, [Pt(μ-Cl)(η<sup>3</sup>-2-Me-C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>] and the corresponding ancillary ligands and then exhaustively characterized. The presence of an electron donating group (R = Cbz) in the R-C<sup>∧</sup>C\* skeleton of these complexes increases the energy of the HOMO compared with those of similar complexes bearing R-C<sup>∧</sup>C\* (R = H, CN, and CO<sub>2</sub>Et), shifting their emissions from blue to green. In spite of the simplicity, iTMC-LECs fabricated from the DCM solutions of the carbazole-appended compounds, **7–9**, operate at a 4–5 V voltage, and achieve luminance values of 265, 187 and  $180 \text{ cd m}^{-2}$  with peak CEs of 5.7, 3.7 and  $3.6 \text{ cd A}^{-1}$ , respectively. Thus, we have tactically brought together the strong electron-donating abilities and good hole transporting properties from Pt(C<sup>∧</sup>C\*) and Cbz groups to prepare the first green-emitting iTMC-LECs based on mononuclear Pt(II) complexes.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

This work was supported by the “Ministerio de Ciencia Innovación y Universidades”/FEDER (Project PGC2018-094749-B-I00) and the Gobierno de Aragón (Grupo E17\_20R: Química Inorgánica y de los Compuestos Organometálicos). The authors thank the Centro de Supercomputación de Galicia (CESGA) for generous allocation of computational resources. The authors acknowledge support from Comunitat Valenciana (IDIFEDER/2020/063, PROMETEU/2020/077 and CIGE/2021/027), the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program Grant agreement No. 834431 and the Spanish Ministry of Science, Innovation and Universities (MICIU) (RTI2018-095362-A-I00 and EQC2018-004888-P).

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