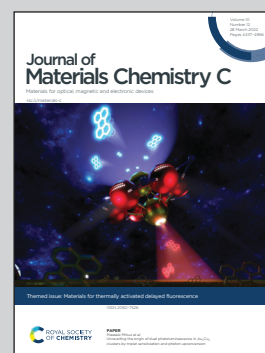


Showcasing research from the laboratory of Professors Catherine E. Housecroft and Edwin C. Constable, Department of Chemistry, University of Basel, Switzerland.

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The last decade has seen a surge of interest in the emissive behaviour of copper(I) coordination compounds. One of the most exciting features of copper(I) coordination compounds is their ability to exhibit thermally activated delayed fluorescence (TADF). In this review, we detail recent developments in the field of copper-based ionic transition metal complexes (Cu-iTMCs) for use in light-emitting electrochemical cells (LECs) and illustrate the significant contributions that our own research has made to the area.

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## TADF: Enabling luminescent copper(I) coordination compounds for light-emitting electrochemical cells

Catherine E. Housecroft \* and Edwin C. Constable 

The last decade has seen a surge of interest in the emissive behaviour of copper(I) coordination compounds, both neutral compounds that may have applications in organic light-emitting diodes (OLEDs) and copper-based ionic transition metal complexes (Cu-ITMCs) with potential use in light-emitting electrochemical cells (LECs). One of the most exciting features of copper(I) coordination compounds is their possibility to exhibit thermally activated delayed fluorescence (TADF) in which the energy separation of the excited singlet ( $S_1$ ) and excited triplet ( $T_1$ ) states is very small, permitting intersystem crossing (ISC) and reverse intersystem crossing (RISC) to occur at room temperature without the requirement for the large spin-orbit coupling inferred by the presence of a heavy metal such as iridium. In this review, we focus mainly in Cu-ITMCs, and illustrate how the field of luminescent compounds and those exhibiting TADF has developed. Copper(I) coordination compounds that class as Cu-ITMCs include those containing four-coordinate  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  ( $\text{P}^{\wedge}\text{P}$  = large-bite angle bisphosphane, and  $\text{N}^{\wedge}\text{N}$  is typically a diimine),  $[\text{Cu}(\text{P})_2(\text{N}^{\wedge}\text{N})]^+$  ( $\text{P}$  = monodentate phosphane ligand),  $[\text{Cu}(\text{P})(\text{tripodal-}\text{N}_3)]^+$ ,  $[\text{Cu}(\text{P})(\text{N}^{\wedge}\text{N})(\text{N})]^+$  ( $\text{N}$  = monodentate N-donor ligand),  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{S})]^+$  ( $\text{N}^{\wedge}\text{S}$  = chelating N,S-donor ligand),  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{P}^{\wedge}\text{S})]^+$  ( $\text{P}^{\wedge}\text{S}$  = chelating P,S-donor ligand),  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{NHC})]^+$  ( $\text{NHC}$  = N-heterocyclic carbene) coordination domains, dinuclear complexes with  $\text{P}^{\wedge}\text{P}$  and  $\text{N}^{\wedge}\text{N}$  ligands, three-coordinate  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  and two-coordinate  $[\text{Cu}(\text{N})(\text{NHC})]^+$  complexes. We pay particular attention to solid-state structural features, e.g.  $\pi$ -stacking interactions and other inter-ligand interactions, which may impact on photoluminescence quantum yields. Where emissive Cu-ITMCs have been tested in LECs, we detail the device architectures, and this emphasizes differences which make it difficult to compare LEC performances from different investigations.

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## Introduction

### Lighting: the 21st century CE landscape

In 2015, the United Nations Member States adopted the 2030 Agenda for Sustainable Development with 17 sustainable development goals (SDGs) identified.<sup>1</sup> The SDGs address all aspects of life on our planet and SDG 7 is concerned with the generation of clean and sustainable energy and the establishment of efficient technologies for energy consumption. A major user of the world's energy is lighting, which accounts for 15% of the energy consumption and 5% of the produced greenhouse gases.<sup>2</sup> Long-established lighting technologies such as the incandescent lamp are extremely inefficient and more efficient devices such as fluorescent tubes have unsustainable and ecologically harmful materials demands. Within Europe, efficient solid-state lighting devices such as light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs) have essentially replaced the earlier technologies.<sup>3</sup>

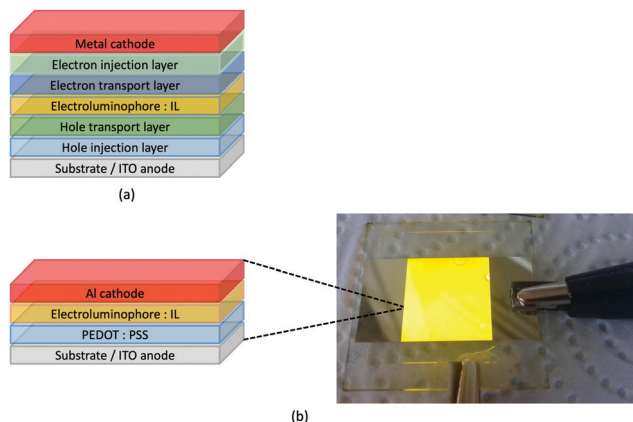
### The light-emitting electrochemical cell (LEC)

LEDs and OLEDs are relatively complex multicomponent or multilayer devices (Fig. 1a), usually fabricated in expensive facilities operating at high temperatures and low pressures, and using potentially explosive and toxic materials. An alternative technology is to be found in the light-emitting electrochemical cell (LEC) which is phenomenologically related to the OLED, and which began to be seriously considered as a viable technology in the mid-1990s. Although LECs bear some relationship to OLEDs, they also exhibit important differences including a simpler device architecture (Fig. 1b), the possibility of routinely using low temperature solution-based fabrication techniques, and less restricted cathode materials allowing manufacture under ambient conditions.<sup>4–8</sup>

One fundamental distinction between OLEDs and LECs is the nature of the active (emissive) material: in an OLED this is typically a neutral species, whereas in a LEC, it is charged. However, the use of ionic transition metal complexes (ITMCs) in OLEDs is not excluded.<sup>9,10</sup> Early LECs included luminescent polymers containing ionic salts.<sup>11</sup> The first LEC in which an

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**Fig. 1** (a) Schematic representation of the layers in a typical OLED; the cathode must consist of a metal with a low work function. (b) A working LEC (right) and a schematic illustration of a typical double-layer LEC. (ITO = indium tin oxide; PEDOT:PSS = poly(3,4-ethylenedioxythiophene): polystyrenesulfonate; IL = ionic liquid). Metals such as Ag or Au may replace Al as the cathode. In a single-layer LEC, the PEDOT:PSS hole injection layer is absent. In both devices, the substrate is usually glass. (Photo credit: Dr Collin Morris, University of Basel.)

*i*TMC was used as the emissive species was reported in 1996 and contained a  $[\text{Ru}(\text{bpy})_3]^{2+}$ -based material (bpy = 2,2'-bipyridine).<sup>12</sup> However, the low stability of Ru-*i*TMC-containing LECs under operating conditions and the fact that the emission colour is invariably orange-red, limit the potential applications of such devices. The next family of *i*TMCs to be developed contained iridium(III) coordination compounds, in particular  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$  complexes where  $\text{C}^{\wedge}\text{N}$  is a cyclometallated chelating ligand and  $\text{N}^{\wedge}\text{N}$  is a diimine or related chelating ligand. Advantages of iridium(III) over ruthenium(II) complexes lie in device stability and the ease of colour tuning the emission maxima.<sup>4,13–17</sup> A disadvantage of iridium, however, is its low earth-abundance (*ca.*  $3 \times 10^{-6}$  ppm).<sup>18</sup> With an earth's crustal abundance of *ca.* 50 ppm,<sup>18</sup> copper is an attractive alternative to iridium, and a wide variety of copper(I) coordination compounds has been designed for applications as electroluminescent materials in both OLEDs and LECs.

### Why choose copper(I)?

The seminal work of McMillin and coworkers in the late 1970s and early 1980s laid the foundation for the development of copper(I) coordination compounds in LECs. In 1978, Buckner and McMillin reported that excitation into the metal-to-ligand charge transfer (MLCT) bands of the heteroleptic complexes  $[\text{Cu}(\text{PPh}_3)_2(\text{bpy})]^+$  and  $[\text{Cu}(\text{dpe})(\text{bpy})]^+$  (dpe = (*E*)-bis(1,2-diphenylphosphano)ethane) led to photoluminescence (PL) originating from low-lying charge transfer excited states.<sup>19</sup> This was followed by a series of investigations which demonstrated the emission behaviours of heteroleptic  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  and  $[\text{Cu}(\text{PPh}_3)_2(\text{N}^{\wedge}\text{N})]^+$  and homoleptic  $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$  complexes in which  $\text{P}^{\wedge}\text{P}$  is a chelating bis(phosphane) and  $\text{N}^{\wedge}\text{N}$  is a bpy or phen-based ligand (phen = 1,10-phenanthroline).<sup>20–26</sup> Of particular importance is the fact that  $[\text{Cu}(2,9\text{-R}_2\text{phen})_2]^+$  (2,9-R<sub>2</sub>phen = 2,9-disubstituted-1,10-phenanthroline) were found to exhibit a long-lived emission

in solution at room temperature.<sup>23</sup> The photophysical properties of copper(I) complexes have been reviewed in detail,<sup>27–29</sup> and we highlight several salient points that are especially relevant to the design of emissive materials for applications in LECs.

Copper(I) has a  $d^{10}$  configuration and four-coordinate copper(I) complexes are tetrahedral or distorted tetrahedral. Upon excitation, the metal centre is formally oxidized with a concomitant flattening of the coordination geometry towards the square-planar environment favoured by copper(II). In the excited state, unless sufficiently protected by sterically demanding ligand-substituents, the Cu centre may be exposed to attack by nucleophiles including solvent molecules to give a five-coordinate exciplex. Steric hindrance resulting from the introduction of substituents into the 2,9-positions of phen in  $[\text{Cu}(\text{phen})_2]^+$  derivatives has a profound effect on the PL properties of the compounds.<sup>27,30</sup> Tuning of the emission behaviour can also be achieved through other substituent effects,<sup>31</sup> providing tremendous scope for ligand design. Upon going from homoleptic  $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$  to heteroleptic  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes, emission behaviour is enhanced. This is a consequence of the reduced flexibility of the  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  coordination sphere which leads to a decrease in the non-radiative deactivation suffered by  $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$  coordination compounds.<sup>32</sup> However, the solution PL of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  species is highly dependent upon solvent and the presence of O<sub>2</sub>. An increase in photoluminescence quantum yield (PLQY) upon removal of O<sub>2</sub> from a solution of a salt of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  is a consequence of the suppression of exciplex quenching. The design of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  and related emitters should, therefore, address appropriate steric shielding of the copper centre as we illustrate throughout this review.

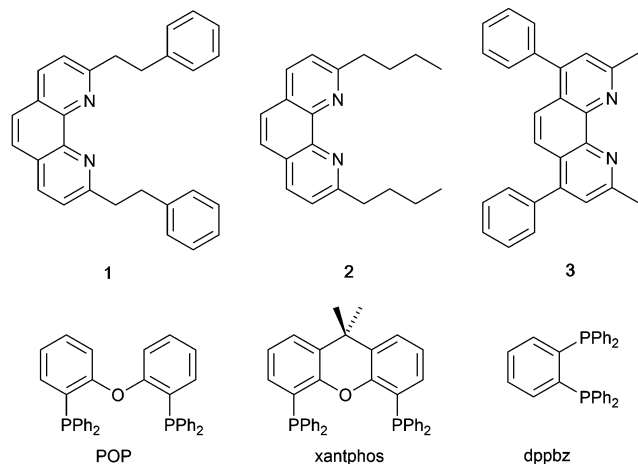
Efficient emitters are essential for applications in LECs. In *i*TMC-LECs containing iridium(III) complexes, the large spin-orbit coupling (SOC) of the third-row d-block metal leads to mixing of triplet and singlet states. After photoexcitation of an Ir-*i*TMC, fast intersystem crossing (ISC) from singlet to triplet excited states leads almost exclusively to spin-forbidden phosphorescence from the lowest triplet state (T<sub>1</sub>) to the ground-state S<sub>0</sub>.<sup>16</sup> Since copper is in the first row of the d-block, SOC is small, and the mechanism described for Ir-*i*TMCs does not pertain. However, one of the most exciting prospects for copper(I) coordination compounds is their potential to exhibit thermally activated delayed fluorescence (TADF) in which the S<sub>1</sub> and T<sub>1</sub> excited states lie close in energy, permitting ISC (and reverse intersystem crossing, RISC) to occur without the requirement for a heavy metal.<sup>33–36</sup>

We should also note that in four-coordinate  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes, the HOMO is typically largely located on the copper centre with some contribution from the phosphorus atoms, while the LUMO is localized on the  $\text{N}^{\wedge}\text{N}$  ligand.<sup>37</sup> As in octahedral cyclometallated  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$  (Hppy = 2-phenylpyridine) derivatives,<sup>16</sup> this spatial separation of the HOMO and LUMO character should allow for colour tuning of the emissions of heteroleptic copper(I) complexes. However, in practice, as we shall see later, this is less straightforward for copper(I) than for iridium(III).









**Scheme 1** Structures of 1,10-phenanthroline derivatives **1–3**, and the bis(phosphane)s POP, xantphos and dppbz.

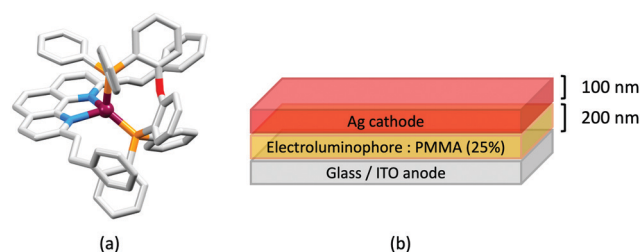
Slinker *et al.* for LECs based upon Ir-*i*TMCs.<sup>55</sup> Device C (Fig. 3b) showed a maximum current efficiency of  $0.16 \text{ cd A}^{-1}$  when the LEC was driven at 12 V.

In 2006, Armaroli reported the first application of mononuclear  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  emitters in LECs. The series of complexes incorporated the phen derivatives **1–3** with the bis(phosphane) POP (Scheme 1). The phen ligands contain 2,9-substituents to prevent flattening of the coordination sphere upon excitation (see earlier discussion) and we will see this feature repeatedly in  $\text{N}^{\wedge}\text{N}$  ligand design. POP and xantphos (Scheme 1) appear in many of the heteroleptic copper(i) complexes described in this review. Both are wide-bite angle chelating ligands,<sup>56</sup> and are commercially available. The POP backbone is conformationally flexible and for 284 crystal structures in the CSD (version 2020.3.1)<sup>50,51</sup> containing 326 independent chelating  $\{\text{Cu}(\text{POP})\}$  domains, the P–Cu–P angle ranges from  $103.08$  to  $121.78^\circ$  with a mean value of  $113.90^\circ$ . The single-crystal structure of  $[\text{Cu}(\text{POP})(\mathbf{1})][\text{BF}_4]$  (Fig. 4a) confirms a P–Cu–P angle of  $117.98(3)^\circ$ . The Cu(i) centre is in a distorted tetrahedral environment and the  $\text{Cu}\cdots\text{O}$  distance of  $3.226(2) \text{ \AA}$  is outside bonding range. Correlations of solid-state PLQY and  $\text{Cu}\cdots\text{O}$  distances demonstrate a general trend for increased PLQY values with longer  $\text{Cu}\cdots\text{O}$  separations,<sup>57</sup> and therefore the note by Armaroli *et al.* in 2006<sup>58</sup> that  $[\text{Cu}(\text{POP})(\mathbf{1})]^+$  exhibits

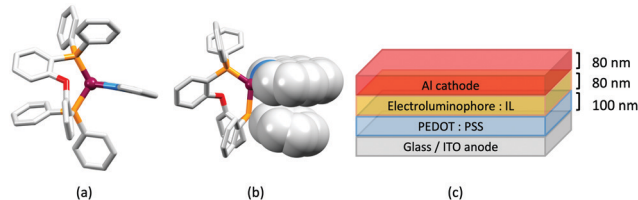
a long  $\text{Cu}\cdots\text{O}$  separation is significant. In deaerated  $\text{CH}_2\text{Cl}_2$  solutions,  $[\text{Cu}(\text{POP})(\mathbf{1})][\text{BF}_4]$ ,  $[\text{Cu}(\text{POP})(\mathbf{2})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{3})][\text{BF}_4]$  show emission maxima between 544 and 558 nm with PLQY values of 9, 26 and 27%, respectively. In 2006, these latter values were the highest reported for luminescent  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes incorporating phen-derivatives. Single-layer LECs with  $[\text{Cu}(\text{POP})(\mathbf{2})][\text{BF}_4]$  mixed with PMMA in the active layer (Fig. 4b) showed moderate efficiency, emitting green light after several minutes under 18 V bias. Notably, though, the performance was comparable to LECs based on  $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$  electrolumino-phores.<sup>58</sup>

No further progress was made with Cu-*i*TMCs until our own report in 2011 which demonstrated the potential for bpy-containing heteroleptic compounds in LECs.<sup>59</sup> We look at this study in some detail because of several general points which emerge that are relevant to later investigations. Comparisons of the single-crystal structures of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  with  $\text{N}^{\wedge}\text{N} = \text{bpy}$  or phen, and  $\text{P}^{\wedge}\text{P} = \text{POP}$  or dppbz (Scheme 1) revealed several notable features. The P–Cu–P angles of  $115.01(2)^\circ$  in  $[\text{Cu}(\text{POP})(\text{bpy})]^+$  (Fig. 5a) and  $119.18(2)^\circ$  in  $[\text{Cu}(\text{POP})(\text{phen})]^+$  (Fig. 5b) are significantly greater than in the corresponding dppbz complex cations ( $92.50(2)$  and  $87.14(8)^\circ$ ). In  $[\text{Cu}(\text{POP})(\text{phen})]^+$ , one phenyl ring of a  $\text{PPh}_2$  unit in POP engages in a  $\pi$ -stacking interaction with the phen ligand (Fig. 5b). Such interactions help to lock the molecular geometry, and contribute to increased PLQY.<sup>60</sup> Inspection of Fig. 5a reveals the potential for a face-to-face  $\pi$ -interaction between one phenyl ring of a  $\text{PPh}_2$  unit and one arene ring of the POP backbone. While the metrics of this interaction in  $[\text{Cu}(\text{POP})(\text{bpy})]^+$  are not consistent with an efficient interaction, similar contacts are a recurring feature in  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})]^+$  complexes, and indeed in other POP-containing compounds. We highlight the importance of intra-cation  $\pi$ -stacking interactions throughout this review.

Typical broad MLCT bands between 389 and 422 nm were observed in the absorption spectra of  $[\text{Cu}(\text{POP})(\text{bpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{POP})(\text{phen})][\text{PF}_6]$ ,  $[\text{Cu}(\text{dppbz})(\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{dppbz})(\text{phen})][\text{PF}_6]$ . Analysis of the emission behaviour was supplemented by density functional theory (DFT) calculations which confirmed the <sup>3</sup>MLCT character of the lowest triplet excited state (<sup>3</sup>T<sub>1</sub>). The calculated values of the vertical energy difference between the <sup>3</sup>T<sub>1</sub> and S<sub>0</sub> levels were in good agreement with the



**Fig. 4** (a) The structure of the  $[\text{Cu}(\text{POP})(\mathbf{1})]^+$  cation in  $[\text{Cu}(\text{POP})(\mathbf{1})][\text{BF}_4]$  (CSD refcode GIRJUN) showing the distorted tetrahedral Cu(i) environment and wide-bite angle ( $117.98(3)^\circ$ ) of POP (H atoms are omitted). The phen backbone is rigid ( $\text{N}-\text{Cu}-\text{N} = 80.86(10)^\circ$ ). (b) LEC architecture for a device containing  $[\text{Cu}(\text{POP})(\mathbf{2})][\text{BF}_4]$  as the electrolumino-phore.



**Fig. 5** Structures of the complex cations (H atoms omitted) in (a)  $[\text{Cu}(\text{POP})(\text{bpy})][\text{PF}_6]$  and (b)  $[\text{Cu}(\text{POP})(\text{phen})][\text{PF}_6]$  (CSD refcodes OYUKID and OYUKUP). The face-to-face  $\pi$ -stacking interaction in  $[\text{Cu}(\text{POP})(\text{phen})]^+$  is shown in space-filling representation. (c) Architecture of the LEC devices containing  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  with  $\text{N}^{\wedge}\text{N} = \text{bpy}$  or phen, and  $\text{P}^{\wedge}\text{P} = \text{POP}$  or dppbz. The ionic liquid (IL) was  $[\text{BMIM}][\text{PF}_6]$  or  $[\text{EMIM}][\text{PF}_6]$ , and Cu-*i*TMC: IL molar ratios was 1 : 1 or 1 : 0.







In contrast, the lifetimes of LECs containing [Cu(xantphos)-(Mebpy)][PF<sub>6</sub>], [Cu(xantphos)(6-Etbpy)][PF<sub>6</sub>] and [Cu(POP)-(6-Etbpy)][PF<sub>6</sub>] were greater than 15, 40 and 80 hours, respectively, but at a cost of lower efficacy (1.9, 1.7 and 0.6 cd A<sup>-1</sup>).

## The TADF era in Cu-iTMCs begins

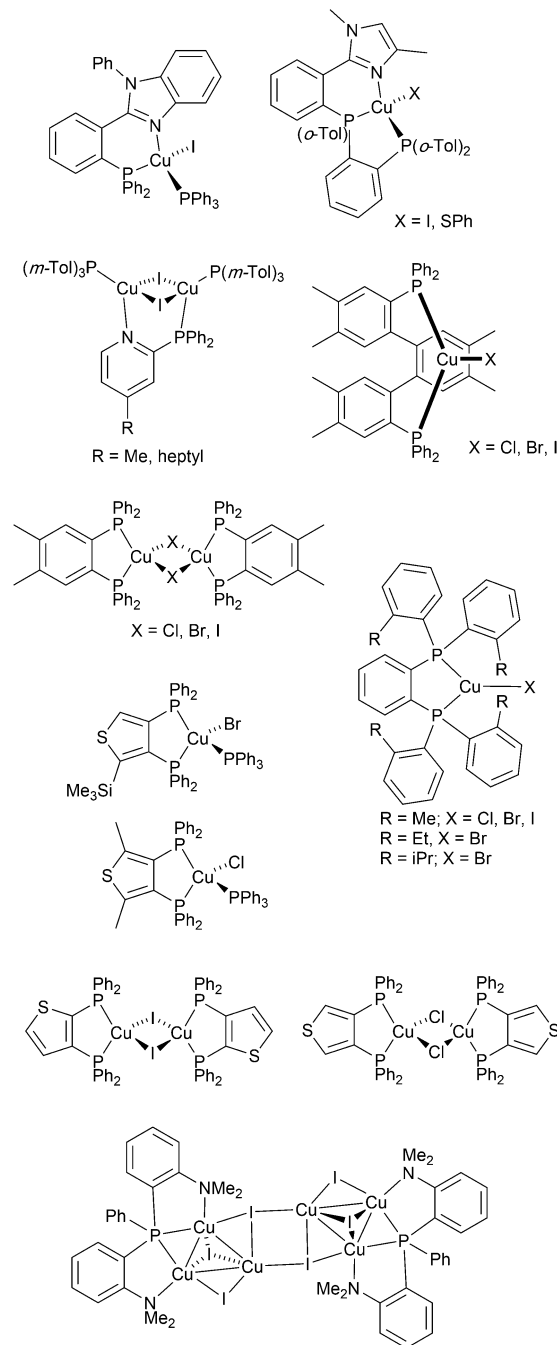
From 2012 onwards, reports of Cu-iTMCs exhibiting TADF grew considerably, although not all compounds have been tested in LECs. Heteroleptic copper(i) compounds for which TADF has been described include halide and pseudo-halide containing complexes including several {Cu<sub>x</sub>X<sub>y</sub>} clusters. Most of these are neutral and are of interest for OLEDs; selected examples which have been tested in OLED configurations are shown in Scheme 3.<sup>36,64–96</sup>

Copper(i) coordination compounds that class as Cu-iTMCs include those containing four-coordinate [Cu(P<sup>∧</sup>P)(N<sup>∧</sup>N)]<sup>+</sup>, [Cu(P)<sub>2</sub>(N<sup>∧</sup>N)]<sup>+</sup>, [Cu(P)(tripodal-N<sub>3</sub>)]<sup>+</sup>, [Cu(P)(N<sup>∧</sup>N)(N)]<sup>+</sup>, [Cu(P<sup>∧</sup>P)-(N<sup>∧</sup>S)]<sup>+</sup>, [Cu(P<sup>∧</sup>P)(P<sup>∧</sup>S)]<sup>+</sup>, [Cu(P<sup>∧</sup>P)(NHC)]<sup>+</sup> (NHC = N-heterocyclic carbene) coordination domains, dinuclear complexes with P<sup>∧</sup>P and N<sup>∧</sup>N ligands, three-coordinate [Cu(N<sup>∧</sup>N)(NHC)]<sup>+</sup> and two-coordinate [Cu(N)(NHC)]<sup>+</sup> complexes. We now consider emissive materials in each class, and provide insight into design of appropriate ligands and ligand combinations to enhance photoluminescence. In terms of applications in LECs, we note that efficient PL is not necessarily an indication that a Cu-iTMC will perform well as an electrolumiphore in a device. Selected neutral compounds with structures related to those in the classes of Cu-iTMCs but which have been designed for OLED applications are also included in our discussion.

## Mononuclear [Cu(P<sup>∧</sup>P)(N<sup>∧</sup>N)]<sup>+</sup> and [Cu(P)<sub>2</sub>(N<sup>∧</sup>N)]<sup>+</sup>

### 2,2'-Bipyridine derivatives with POP and xantphos

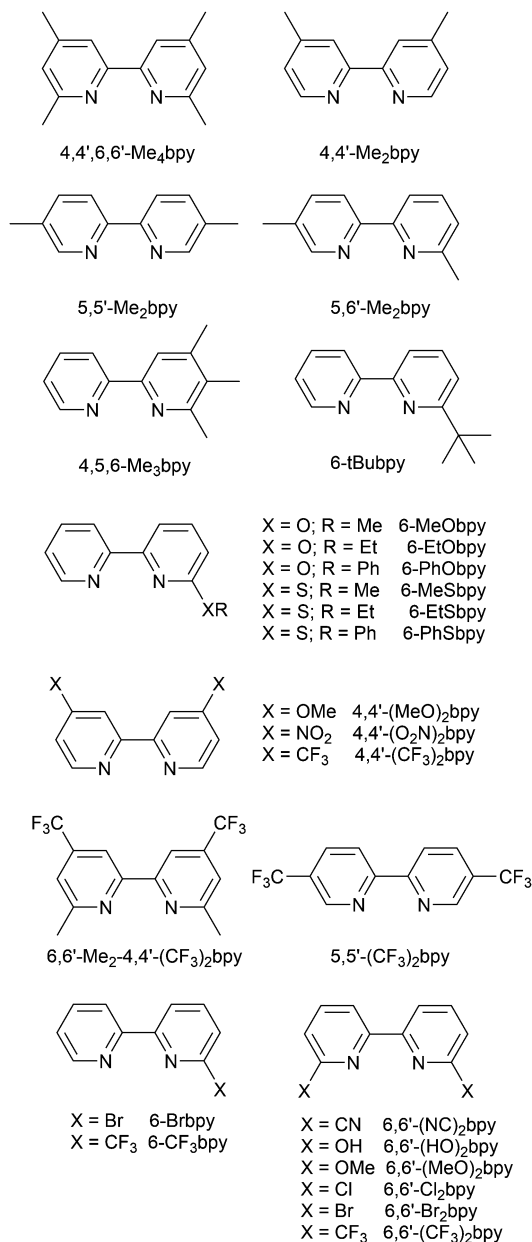
Scheme 4 illustrates the structures of the N<sup>∧</sup>N ligands discussed in this section. Around the same time that we were investigating the performances of LECs containing [Cu(POP)(6-Mebpy)][PF<sub>6</sub>] or [Cu(POP)(6,6'-Me<sub>2</sub>bpy)][PF<sub>6</sub>],<sup>63</sup> Yersin, Robertson and coworkers compared the photophysical properties of [Cu(POP)(4,4'-Me<sub>2</sub>bpy)][BF<sub>4</sub>] and [Cu(POP)(4,4',6,6'-Me<sub>4</sub>bpy)][BF<sub>4</sub>]. They demonstrated that the presence of the 6,6'-substituents led to a dramatic increase in room temperature solid-state PLQY from 9% for [Cu(POP)(4,4'-Me<sub>2</sub>bpy)][BF<sub>4</sub>] to 55% or 74% (enhanced when the sample was ground) for [Cu(POP)(4,4',6,6'-Me<sub>4</sub>bpy)][BF<sub>4</sub>].<sup>32</sup> These results are in accord with our findings that the solid-state PLQY of 43.2% for [Cu(POP)(6,6'-Me<sub>2</sub>bpy)][PF<sub>6</sub>] exceeds that of [Cu(POP)(6-Mebpy)][PF<sub>6</sub>] (9.5%)<sup>63</sup> and [Cu(POP)(bpy)][PF<sub>6</sub>] (3%).<sup>97</sup> The emission spectrum of a powdered sample of [Cu(POP)(4,4',6,6'-Me<sub>4</sub>bpy)][BF<sub>4</sub>] (λ<sub>exc</sub> = 350 nm) is broad at 300 K with λ<sub>max</sub><sup>em</sup>(PL) = 555 nm and a decay time of 11 μs. On cooling to 77 K, the emission undergoes a red-shift to 575 nm with PLQY = 47%, and the decay time increases to 87 μs. The ≈10-fold increase in the radiative rate on going from 77 to 300 K, coupled with the blue-shift from 575 to 555 nm, were rationalized in terms of TADF at 300 K (S<sub>1</sub> → S<sub>0</sub> emission), while



Scheme 3 Structures of selected neutral, TADF copper(i) complexes with Cu–X bonds which have been tested in OLEDs.

at 77 K, emission occurs from the T<sub>1</sub> state (T<sub>1</sub> → S<sub>0</sub>). In addition, Yersin and Robertson also confirmed that the restricted flexibility of the Cu coordination sphere caused by the presence of the 6,6'-dimethyl groups in the N<sup>∧</sup>N ligand (Fig. 8a) resulted in a decrease in non-radiative deactivation with a consequent increase of PLQY.<sup>32</sup> A comparison of PL behaviour of [Cu(POP)(Me<sub>n</sub>bpy)]<sup>+</sup> complexes in which Me<sub>n</sub>bpy carries different numbers of Me substituents in differing positions (Table 1) gives a clear conclusion: substitution at the 6-position or 6,6'-positions is essential for high PLQY values (Table 1). Similar trends are

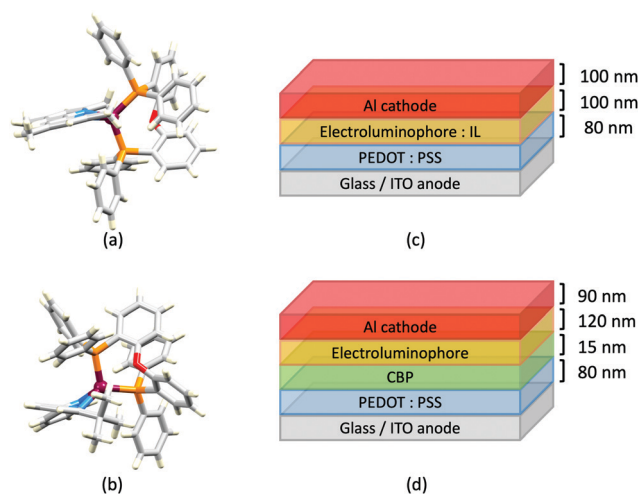




**Scheme 4** Structures of derivatives of bpy used in [Cu(P<sup>A</sup>P)(N<sup>A</sup>N)]<sup>+</sup> complexes. See also Scheme 2.

seen for analogous xantphos-containing compounds (Table 1), and the steric shielding of the Cu(I) centre in [Cu(xantphos)-(6,6'-Me<sub>2</sub>bpy)][PF<sub>6</sub>] was shown in Fig. 7b. However, the observation of Linfoot *et al.* that the PLQY of powdered [Cu(POP)(4,4',6,6'-Me<sub>4</sub>bpy)][BF<sub>4</sub>] depends upon the morphology of the sample<sup>32</sup> leads us to be cautious about further detailed interpretation of the PLQY data.

For some of the compounds in Table 1, emission data at 77 K have been reported and are presented in Table 2. In all cases, the longer decay time at 77 K *vs.* than at 300 K is consistent with TADF at ambient temperatures, even for complexes containing the parent bpy ligand. The second effect is a red-shift in the emission (compare  $\lambda_{\text{max}}^{\text{em}}$ (PL) at *ca.* 300 K in



**Fig. 8** Structures of the cations in (a) [Cu(POP)(4,4',6,6'-Me<sub>4</sub>bpy)][BF<sub>4</sub>] (CSD refcode COYHEF), and (b) [Cu(POP)(6-tBubpy)][PF<sub>6</sub>] (CSD refcode PUTSUV). (c) Architecture of the LECs containing the Cu-iTMCs shown in Table 3. IL = [EMIM][PF<sub>6</sub>], and Cu-iTMC: IL molar ratio = 4 : 1; LECs were driven using a pulsed current. The layer thicknesses shown apply to devices reported in ref. 98, and are typical. (d) Bilayer LEC architecture used for devices containing [Cu(POP)(6,6'-(MeO)<sub>2</sub>bpy)][PF<sub>6</sub>] in the active layer (CBP = 4,4'-bis(9-carbazolyl)-1,1'-biphenyl).

Table 1 with values at 77K in Table 2). For the compounds in Table 2, calculated values of  $\Delta E_{\text{ST}}$  are between 0.22 and 0.27 eV (*ca.*, 1800–2200 cm<sup>-1</sup>). The introduction of a *tert*-butyl substituent into the 6-position of bpy (Scheme 4) leads to a decrease in  $\Delta E_{\text{ST}}$  from 0.15 eV (1200 cm<sup>-1</sup>) for [Cu(POP)(6-tBubpy)]<sup>+</sup> to 0.17 eV (1370 cm<sup>-1</sup>) for [Cu(xantphos)(6-tBubpy)]<sup>+</sup>. However, the steric demands of the *tert*-butyl group cause significant elongation of the Cu–N bonds (*ca.* 0.26 Å longer than is typical), and the N–C–N torsion angle of the bpy unit (–28.8(8)°) is noticeably larger in [Cu(POP)(6-tBubpy)][PF<sub>6</sub>] (Fig. 8b) than in related compounds. These structural factors are likely to enhance radiationless decay from the T<sub>1</sub> state with concomitant reduced emission. The room temperature solid-state PLQYs of [Cu(POP)(6-tBubpy)][PF<sub>6</sub>] and

**Table 1** Room temperature PL emission maxima, PLQY values and decay lifetimes ( $\tau$ ) for solid-state [Cu(POP)(Me<sub>n</sub>bpy)]<sup>+</sup> and [Cu(xantphos)(Me<sub>n</sub>bpy)]<sup>+</sup> complexes

Complex cation	$\lambda_{\text{max}}^{\text{em}}$ ( $\lambda_{\text{exc}}$ )/nm	PLQY/%	$\tau/\mu\text{s}$	Ref.
[Cu(POP)(bpy)] <sup>+</sup> <sup>a</sup>	580 (390)	3.0	1.5	97
[Cu(POP)(6-Mebpy)] <sup>+</sup> <sup>a</sup>	567 (365)	9.5	2.6 <sup>c</sup>	63
[Cu(POP)(6,6'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	535 (365)	43.2	10.5 <sup>c</sup>	63
[Cu(POP)(5,5'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	585 (365)	2.7	2.3	98
[Cu(POP)(4,4'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>b</sup>	575 (350)	9	-	32
[Cu(POP)(5,6'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	553 (365)	12	6 <sup>c</sup>	99
[Cu(POP)(4,5,6-Me <sub>3</sub> bpy)] <sup>+</sup> <sup>a</sup>	518 (365)	42.7	9.3	98
[Cu(POP)(4,4',6,6'-bpy)] <sup>+</sup> <sup>b</sup>	555 (350)	55 (74) <sup>d</sup>	11 (13) <sup>d</sup>	32
[Cu(xantphos)(bpy)] <sup>+</sup> <sup>a</sup>	587 (390)	1.7	1.3	97
[Cu(xantphos)(6-Mebpy)] <sup>+</sup> <sup>a</sup>	547 (365)	33.8	9.7	37
[Cu(xantphos)(6,6'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	539 (365)	37.3	11.4	37
[Cu(xantphos)(5,5'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	571 (365)	6.3	5.1	98
[Cu(xantphos)(5,6'-Me <sub>2</sub> bpy)] <sup>+</sup> <sup>a</sup>	555 (365)	11	5 <sup>c</sup>	99
[Cu(xantphos)(4,5,6-Me <sub>3</sub> bpy)] <sup>+</sup> <sup>a</sup>	529 (365)	58.8	9.8	98

<sup>a</sup> [PF<sub>6</sub>]<sup>-</sup> salt. <sup>b</sup> [BF<sub>4</sub>]<sup>-</sup> salt. <sup>c</sup>  $\tau$  from a biexponential fit (see original work for details). <sup>d</sup> The higher value is for a ground sample.





**Table 2** Photoluminescence emission maxima and decay lifetimes ( $\tau$ ) for solid-state  $[\text{Cu}(\text{POP})(\text{Me}_n\text{bpy})]^+$  and  $[\text{Cu}(\text{xantphos})(\text{Me}_n\text{bpy})]^+$  complexes at 77 K

Complex cation	$\lambda_{\text{max}}^{\text{em}}(\lambda_{\text{exc}})/\text{nm}$	$\tau/\mu\text{s}$	Ref.
$[\text{Cu}(\text{POP})(\text{bpy})]^+{}^a$	610 (410)	16	97a
$[\text{Cu}(\text{POP})(5,5'\text{-Me}_2\text{bpy})]^+{}^a$	591 (410)	63	98
$[\text{Cu}(\text{POP})(4,5,6\text{-Me}_3\text{bpy})]^+{}^a$	566 (410)	81	98
$[\text{Cu}(\text{POP})(4,4',6,6'\text{-bpy})]^+{}^b$	575 (378)	87	32
$[\text{Cu}(\text{xantphos})(\text{bpy})]^+{}^a$	613 (410)	11	97a
$[\text{Cu}(\text{xantphos})(5,5'\text{-Me}_2\text{bpy})]^+{}^a$	594 (410)	44	98
$[\text{Cu}(\text{xantphos})(4,5,6\text{-Me}_3\text{bpy})]^+{}^a$	559 (410)	75	98

<sup>a</sup>  $[\text{PF}_6]^-$  salt. <sup>b</sup>  $[\text{BF}_4]^-$  salt.

$[\text{Cu}(\text{xantphos})(6\text{-tBubpy})][\text{PF}_6]$  are 1.1 and 9.6%, and  $\tau = 0.4$  and 3.3  $\mu\text{s}$ , respectively, values that are significantly lower than many of the methyl-substituted derivatives in Table 1.<sup>98</sup>

Some of the best performing copper-based LECs have been achieved using electrolumino-phores comprising  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  salts in which  $\text{N}^{\wedge}\text{N}$  is a simple derivative of bpy (Table 3). Most noteworthy is a LEC containing  $[\text{Cu}(\text{xantphos})(4,5,6\text{-Me}_3\text{bpy})][\text{PF}_6]$  with the device architecture shown in Fig. 8c. This reached a maximum luminance of 462  $\text{cd m}^{-2}$  and exhibited a device half-life of up to 98 hours. However, turn-on times are typically of the order of minutes or hours (Table 3). Faster turn-on times have been observed for LECs containing  $[\text{Cu}(\text{xantphos})(6\text{-Phbpy})][\text{PF}_6]$  (6-Phbpy = 6-phenyl-2,2'-bipyridine), but this is at the expense of luminance ( $\text{Lum}_{\text{max}} = 5 \text{ cd m}^{-2}$ ).<sup>37</sup> Included in Table 3 is a LEC containing  $[\text{Cu}(\text{POP})(6\text{-EtObpy})][\text{PF}_6]$ . This is one of a series of  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  Cu-iTMCs incorporating 6-RObpy or 6-RSbpy ligands (R = Me, Et, Ph, see Scheme 4) which are yellow emitters. Powdered samples have PLQYs up to 38%, with emission lifetimes  $\leq 10.2 \mu\text{s}$  at ca. 298 K. Lifetimes are extended to between 11 and 48  $\mu\text{s}$  at 77 K, consistent with TADF at ambient temperatures. A noteworthy feature of the LEC with  $[\text{Cu}(\text{POP})(6\text{-EtObpy})][\text{PF}_6]$  in the emitting layer was the relatively long device lifetime; the time for the EL to decay to half the maximum luminance was 200 hours.<sup>100</sup> The electron-donating properties of the MeO substituents have also been exploited by Barolo, Costa and coworkers in LECs containing  $[\text{Cu}(\text{POP})(6,6'\text{-(MeO)}_2\text{bpy})][\text{PF}_6]$  in the emitting layer. Powdered  $[\text{Cu}(\text{POP})(6,6'\text{-(MeO)}_2\text{bpy})][\text{PF}_6]$  has a PLQY of 14%, and in thin-film, this increases to 20% ( $\lambda_{\text{exc}} = 370 \text{ nm}$ ); TADF behaviour was not investigated. However, in terms of this review, this work is noteworthy for a change in LEC

design aimed at minimizing the irreversible formation of  $\text{Cu}(\text{II})$  species. By using the bilayer LEC architecture shown in Fig. 8d, the goal was to decouple hole/electron injection and transport.<sup>101</sup>

In 2017, Weber *et al.* published the results of an informative investigation correlating the effect of the  $\sigma$ -Hammett parameter,  $\sigma_p$ , of the substituents in the  $\text{N}^{\wedge}\text{N}$  ligands 4,4'- $\text{Me}_2\text{bpy}$ , 4,4'-( $\text{MeO}$ )<sub>2</sub>bpy, bpy and 4,4'-( $\text{O}_2\text{N}$ )<sub>2</sub>bpy (Scheme 4) on the PL and EL properties of  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{BF}_4]$ . The presence of MeO groups (with the most negative  $\sigma_p$ ) leads to the highest solid-state PLQY (18.9% compared to 9.7% for  $\text{N}^{\wedge}\text{N} = 4,4'\text{-Me}_2\text{bpy}$ , 0.51% for unsubstituted bpy, and no emission for  $\text{N}^{\wedge}\text{N} = 4,4'\text{-(O}_2\text{N)}_2\text{bpy}$ ). The latter is attributed to the different nature of the lowest excited state of  $[\text{Cu}(\text{xantphos})(4,4'\text{-(O}_2\text{N)}_2\text{bpy})]^+$  compared to that of the other members of this series of Cu-iTMCs. The absorption spectrum of  $[\text{Cu}(\text{xantphos})(4,4'\text{-(O}_2\text{N)}_2\text{bpy})][\text{BF}_4]$  exhibits a broad band centred at 503 nm with a shoulder at 423 nm (not present in compounds with 4,4'- $\text{Me}_2\text{bpy}$ , 4,4'-( $\text{MeO}$ )<sub>2</sub>bpy and bpy), and these are assigned to combinations of d-d, MLCT and intra-ligand transitions. There is a linear relationship between the  $\sigma_p$  values of the 4,4'-substituents in the bpy ligand and the values of  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  for solid  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{BF}_4]$  ( $\lambda_{\text{exc}} = 376 \text{ nm}$ ): 545 nm for  $\text{N}^{\wedge}\text{N} = 4,4'\text{-(MeO)}_2\text{bpy}$ , 570 nm for 4,4'- $\text{Me}_2\text{bpy}$ , and 600 nm for bpy.<sup>102</sup> This latter value compares with 587 nm reported for powdered  $[\text{Cu}(\text{xantphos})(\text{bpy})][\text{PF}_6]$  ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ).<sup>61</sup> Critically, Weber *et al.* note that the TADF effect in the Cu-iTMCs may depend upon the  $\sigma_p$  value of the 4,4'-substituents in the bpy ligand. The structure of the  $[\text{Cu}(\text{xantphos})(4,4'\text{-(MeO)}_2\text{bpy})]^+$  cation is depicted in Fig. 9a and b and it is worth noting that the  $\pi$ -stacking interaction between two phenyl rings of different  $\text{PPh}_2$  units is a common feature in  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})]^+$  complexes. Testing of LECs with the architecture shown in Fig. 9c and with  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{BF}_4]$  ( $\text{N}^{\wedge}\text{N} = 4,4'\text{-Me}_2\text{bpy}$ , 4,4'-( $\text{MeO}$ )<sub>2</sub>bpy, bpy and 4,4'-( $\text{O}_2\text{N}$ )<sub>2</sub>bpy) in the active layer (no IL was added) led to the conclusions that (i) nitro groups (positive  $\sigma_p$ ) gave no EL even though charge injection occurred, and (ii) methoxy groups (most negative  $\sigma_p$ ) resulted in the highest luminance (54  $\text{cd m}^{-2}$ ) and the most stable devices.<sup>102</sup> The correlations established in this work may provide a basis for further development of structure-property relationships in Cu-iTMCs.

The effects of electron-withdrawing (CN, Cl, Br,  $\text{CF}_3$ ) and electron-donating (OH) groups in the 6- and 6,6'-positions of bpy (Scheme 4) on the PL and EL properties of  $[\text{Cu}(\text{P})_2(\text{N}^{\wedge}\text{N})]^+$  and  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes have been explored in a series

**Table 3** Electroluminescence maxima and LEC performances (architectures as in Fig. 8c) measured using pulsed current driving. All complexes are  $[\text{PF}_6]^-$  salts

Complex cation	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	$J_{\text{avg}}/\text{A m}^{-2}$ <sup>a</sup>	$t_{\text{on}}/\text{min}$ <sup>b</sup>	$\text{Lum}_{\text{max}}/\text{cd m}^{-2}$	Ref.
$[\text{Cu}(\text{POP})(4,5,6\text{-Me}_3\text{bpy})]^+$	571	50	11	92	98
$[\text{Cu}(\text{xantphos})(4,5,6\text{-Me}_3\text{bpy})]^+$	570	100	13	462	98
$[\text{Cu}(\text{xantphos})(5,5'\text{-Me}_2\text{bpy})]^+$	589	100	19	130	98
$[\text{Cu}(\text{POP})(6\text{-EtObpy})]^+$	585	50	60	63	100
$[\text{Cu}(\text{xantphos})(6\text{-CF}_3\text{bpy})]^+$	589	100	137	109	61
$[\text{Cu}(\text{POP})(2\text{-Etphen})]^+$	582	100	25	451	98
$[\text{Cu}(\text{xantphos})(2\text{-Etphen})]^+$	580	100	122	153	98

<sup>a</sup>  $J_{\text{avg}}$  = average current density. <sup>b</sup> Time to reach maximum luminance ( $\text{Lum}_{\text{max}}$ ).



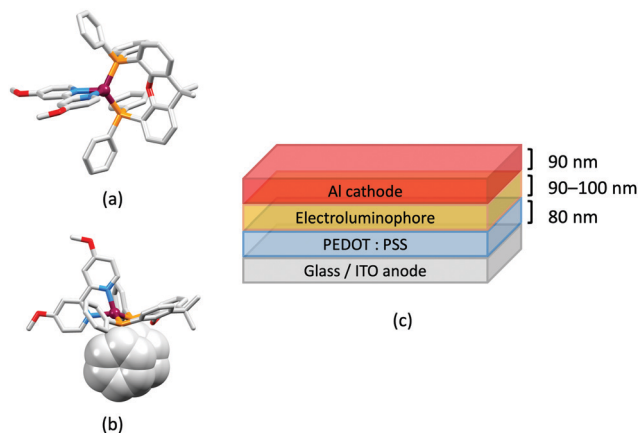


Fig. 9 (a) Structure of the cation in  $[\text{Cu}(\text{xantphos})(4,4'-(\text{MeO})_2\text{bpy})][\text{BF}_4]$  (CSD refcode VANYOB), and (b) illustration of the  $\pi$ -stacking interaction between adjacent  $\text{PPh}_2$  units. H atoms are omitted for clarity. (c) Architecture of the LECs containing the Cu-iTMCs  $[\text{Cu}(\text{xantphos})(4,4'-\text{R}_2\text{bpy})][\text{BF}_4]$  with  $\text{R} = \text{MeO}, \text{Me}, \text{H}$ . LECs were driven using a pulsed current.

of publications.<sup>97,103</sup> The Cu-iTMCs containing POP or xantphos and  $6,6'-\text{Cl}_2\text{bpy}$ ,  $6\text{-Brbpy}$  and  $6,6'-\text{Br}_2\text{bpy}$  are orange/red emitters in solution and yellow/orange emitters in the solid state. All the halogen-substituted Cu-iTMCs showed longer emission decay lifetimes at 77 K compared to ambient temperatures, consistent with TADF. However, the anticipated red-shift in the emission maximum on going from 298 to 77 K was not observed for  $[\text{Cu}(\text{POP})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  or  $[\text{Cu}(\text{POP})(6,6'-\text{Br}_2\text{bpy})][\text{PF}_6]$ , and this was attributed to the degree of relaxation attained by the emitting  $\text{T}_1$  state in the frozen Me-THF matrix. The emission behaviour of complexes in this series was strongly dependent upon the halogen substitution pattern, and DFT calculations revealed significant effects on the geometry of the emitting triplet state. For this series of Cu-iTMCs, the highest solid-state PLQY values were observed for  $[\text{Cu}(\text{xantphos})(6\text{-Brbpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{POP})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  (16.3, 14.8 and 17.1%, respectively). Fig. 10a illustrates that one chloro-substituent is accommodated in the 'bowl' of the xantphos ligand in  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})]^+$ , and this is a common structural feature in  $[\text{Cu}(\text{xantphos})(6,6'-\text{R}_2\text{bpy})]^+$  or  $[\text{Cu}(\text{xantphos})(6\text{-Rbpy})]^+$  cations.<sup>100</sup> Earlier, we noted that effective EL does not necessarily follow from efficient PL.

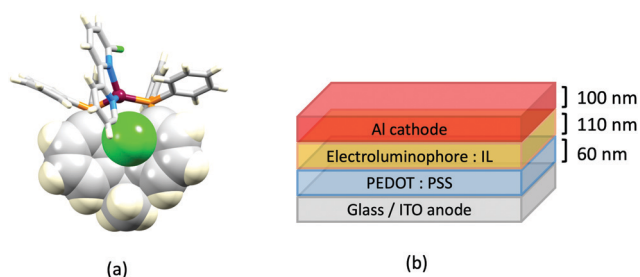


Fig. 10 (a) Structure of the cation in  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  (CSD refcode MEWXUK). (b) Architecture of LECs containing the Cu-iTMCs with halogen-substituted bpy ligands.  $\text{IL} = [\text{EMIM}][\text{PF}_6]$  and Cu-iTMC: IL molar ratio = 4 : 1. LECs were driven using a pulsed current.

Despite exhibiting solid-state PLQYs in the range 3.9–16.3%, none of the LECs incorporating Cu-iTMCs with  $6\text{-Brbpy}$  or  $6,6'-\text{Br}_2\text{bpy}$  showed any electroluminescence. In contrast, LECs with  $[\text{Cu}(\text{POP})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  in the active layers (Fig. 10b) exhibited very short turn-on times ( $< 5$  to 12 s) and orange EL ( $\lambda_{\text{max}}^{\text{em}}(\text{EL}) = 586$  and 587 nm). Values of  $\text{Lum}_{\text{max}}$  of 121 and 259  $\text{cd m}^{-2}$  were achieved for  $[\text{Cu}(\text{POP})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'-\text{Cl}_2\text{bpy})][\text{PF}_6]$ , respectively, with LECs driven using a pulsed current density of  $100 \text{ A m}^{-2}$ .<sup>97b</sup>

Several Cu-iTMCs containing the  $\text{CF}_3$ -functionalized bpy ligands shown in Scheme 4 proved to be very promising, both in terms of PL and EL. Fig. 11a shows the structure of the  $[\text{Cu}(\text{xantphos})(6\text{-CF}_3\text{bpy})]^+$  cation and again we see the hosting of the 6-substituent of the bpy ligand in the bowl-shaped cleft of xantphos, as well as the face-to-face  $\pi$ -stacking of two phenyl rings of different  $\text{Ph}_2$  units of xantphos. As is typical, solid-state PLQYs greatly surpassed solution emission behaviour. The highest PLQY (50.3%) was found for  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{-}6,6'-\text{Me}_2\text{bpy})][\text{PF}_6]$ . This compares with only 0.9% for  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{bpy})][\text{PF}_6]$ . However, it compares with 37.3% for  $[\text{Cu}(\text{xantphos})(6,6'-\text{Me}_2\text{bpy})][\text{PF}_6]$ , and once again emphasizes the importance of substituents in the  $6,6'$ -positions of bpy. Both  $[\text{Cu}(\text{POP})(4,4'-(\text{CF}_3)_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{bpy})][\text{PF}_6]$  showed weak emissions, and, in keeping with the trends observed by Weber *et al.*<sup>102</sup> discussed earlier, it is pertinent to note that the Hammett parameter,  $\sigma_p$ , for  $\text{CF}_3$  is +0.54.<sup>104</sup> Compounds containing  $5,5'-(\text{CF}_3)_2\text{bpy}$  were poorly emissive, even in the solid state. As well as providing insight into the effects of introducing  $\text{CF}_3$  substituents, our study in 2018<sup>61</sup> returned to the simple  $[\text{Cu}(\text{POP})(\text{bpy})]^+$  complex first reported in 2011,<sup>59</sup> and we demonstrated that  $[\text{Cu}(\text{POP})(\text{bpy})][\text{PF}_6]$  is a TADF emitter. We also looked again at the xantphos-containing compounds  $[\text{Cu}(\text{xantphos})(6\text{-Mebpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'-\text{Me}_2\text{bpy})][\text{PF}_6]$  (first reported in 2016),<sup>37</sup> and showed that, along with  $[\text{Cu}(\text{xantphos})(\text{bpy})][\text{PF}_6]$ , they also exhibited TADF. LECs (Fig. 11b) containing  $[\text{Cu}(\text{POP})(6\text{-CF}_3\text{bpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{xantphos})(6\text{-CF}_3\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{-}6,6'-\text{Me}_2\text{bpy})][\text{PF}_6]$  in their active layers exhibited orange EL ( $\lambda_{\text{max}}^{\text{em}}$  in the range 589 to 595 nm). The shortest turn-on time (8 min) was for the LEC with  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{-}6,6'-\text{Me}_2\text{bpy})][\text{PF}_6]$  and this also achieved the highest  $\text{Lum}_{\text{max}}$  ( $131 \text{ cd m}^{-2}$ ).<sup>61</sup>

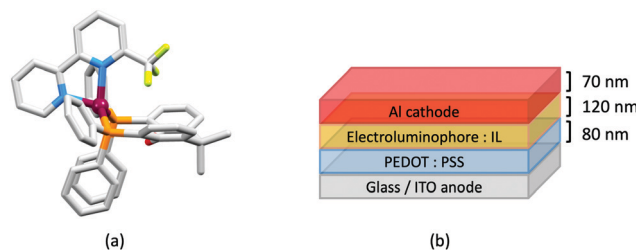


Fig. 11 (a) Structure of the  $[\text{Cu}(\text{xantphos})(6\text{-CF}_3\text{bpy})]^+$  cation in the  $[\text{PF}_6]^-$  salt (CSD refcode VICQUW); the  $6\text{-CF}_3$  bpy ligand is disordered over two sites and only the major occupancy site is shown. H atoms are omitted. (b) Architecture of LECs containing the Cu-iTMCs with  $\text{CF}_3$ -functionalized bpy ligands.  $\text{IL} = [\text{EMIM}][\text{PF}_6]$  and Cu-iTMC: IL molar ratio = 4 : 1. LECs were driven using a pulsed current.

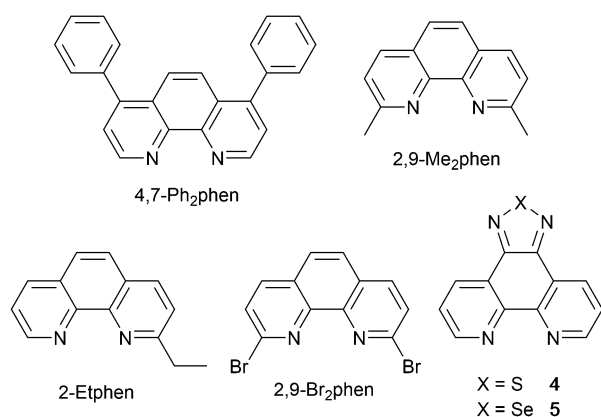


Jin *et al.* recently compared the PL behaviour of  $[\text{Cu}(\text{POP})(6,6'-(\text{HO})_2\text{bpy})][\text{ClO}_4]$  and  $[\text{Cu}(\text{POP})(6,6'-(\text{NC})_2\text{bpy})][\text{ClO}_4]$ , and also the effects of replacing the wide-bite angle POP by two monodentate phosphanes. Room temperature PLQYs are enhanced on going from two  $\text{PPh}_3$  to POP: for solid samples, PLQY = 10.4% for  $[\text{Cu}(\text{PPh}_3)_2(6,6'-(\text{HO})_2\text{bpy})][\text{ClO}_4]$  vs. 16.5% for  $[\text{Cu}(\text{POP})(6,6'-(\text{HO})_2\text{bpy})][\text{ClO}_4]$ , and 9.2% for  $[\text{Cu}(\text{PPh}_3)_2(6,6'-(\text{NC})_2\text{bpy})][\text{ClO}_4]$  vs. 13.5% for  $[\text{Cu}(\text{POP})(6,6'-(\text{NC})_2\text{bpy})][\text{ClO}_4]$ . A red-shift in the emission maximum on cooling to 77 K accompanied by extended values of  $\tau$  indicate TADF at room temperature for  $[\text{Cu}(\text{PPh}_3)_2(6,6'-(\text{HO})_2\text{bpy})][\text{ClO}_4]$  and  $[\text{Cu}(\text{PPh}_3)_2(6,6'-(\text{NC})_2\text{bpy})][\text{ClO}_4]$ . The analogous POP complexes also show longer  $\tau$  values at 77 K compared to 298 K. The focus of the study was the ability to tune emission maxima through altering the  $\pi$ -accepting ability of the phosphane ligand and electronic properties of the diimine ligand, and the EL characteristics were not explored.<sup>103</sup>

The bpy-containing derivatives overviewed in this section represent the largest group of N^N ligands in heteroleptic Cu-iTMCs that exhibit TADF and have been tested in LECs. Some of the best-performing LECs have been achieved with this family of electroluminophores, in particular  $[\text{Cu}(\text{xantphos})(4,5,6\text{-Me}_3\text{bpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(4,4'-(\text{CF}_3)_2\text{-}6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ . However, there is often a trade off between fast turn-on of the device and maximum luminance. Fig. 7–11 also reveal significant variability in the layer thicknesses and composition in the LECs; the extent to which these factors affect LEC figures of merit has not been extensively investigated.

### 1,10-Phenanthroline derivatives with POP and xantphos

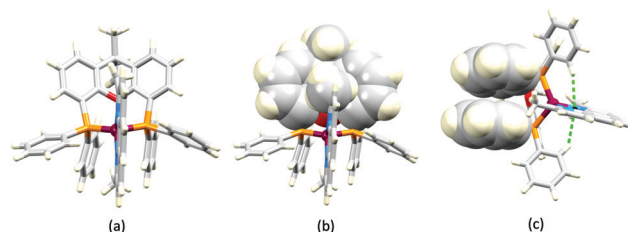
Although heteroleptic copper(i) complexes incorporating phen and its derivatives are well established (see earlier), investigations of TADF behaviour and investigations of LEC performances appear to be significantly fewer than for bpy-containing Cu-iTMCs. As part of a wider study which provides critical insight into trends in photophysical and electrochemical properties of heteroleptic copper(i) complexes containing phen and 4,7- $\text{Ph}_2\text{phen}$  (Scheme 5) including the role of intramolecular  $\pi$ -stacking



**Scheme 5** Structures of derivatives of phen used in  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes, and discussed here.

interactions in improving PLQY, Leoni *et al.* reported the emission spectra of powdered  $[\text{Cu}(\text{POP})(\text{phen})][\text{BF}_4]$  and of a thin-film between 338 and 78 K. The red-shift in  $\lambda_{\text{exc}}^{\text{em}}(\text{PL})$  coupled with an increase in the excited state lifetime demonstrate TADF at ambient temperatures. A general point of note is that  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes containing 4,7- $\text{Ph}_2\text{phen}$  tend to show red-shifted emission maxima compared to their phen analogues, *e.g.*  $\lambda_{\text{exc}}^{\text{em}}(\text{PL})$  for solid  $[\text{Cu}(\text{POP})(\text{phen})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(4,7\text{-Ph}_2\text{phen})][\text{BF}_4]$  are 566 and 581 nm, respectively. For this pair of compounds, the introduction of the Ph groups leads to slightly higher PLQY (11.3 vs. 15.0%) and longer  $\tau$  (14.08 vs. 17.72  $\mu\text{s}$ ) in a PMMA thin-film, but has little effect on the powdered material (36.6 vs. 35.3%, 12.75 vs. 11.72  $\mu\text{s}$ ).<sup>60</sup>

In order to restrict the flattening of the  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{phen})]^+$  coordination sphere upon excitation, substituents in the 2- or 2,9-positions of phen are required.<sup>60</sup> In view of the known relevance of intra-cation  $\pi$ -contacts (see above), it is pertinent to summarize typical structural features of  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{phen})]^+$  complexes. Fig. 12a displays the structure of the cation in  $[\text{Cu}(\text{xantphos})(2,9\text{-Me}_2\text{phen})][\text{BF}_4] \cdot \text{Et}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ .<sup>105</sup> Several features are of note because of their recurrence in other  $[\text{Cu}(\text{xantphos})(\text{phen})]^+$  derivatives. Fig. 12b shows that one substituent of 2,9- $\text{Me}_2\text{phen}$  is accommodated in the cavity of the xanthene unit (compare with Fig. 10). In addition, the P^P and N^N ligands associate through  $\text{CH} \cdots \pi$  contacts (Fig. 12c) between Ph units of xantphos and the  $\{\text{Cu}(\text{phen})\}$  unit. In keeping with  $[\text{Cu}(\text{xantphos})(\text{bpy})]^+$  cations (see earlier),  $[\text{Cu}(\text{xantphos})(2,9\text{-Me}_2\text{phen})]^+$  exhibits a  $\pi$ -stacking interaction between adjacent  $\text{PPh}_2$  units within the xantphos domain (Fig. 12c). These interactions should be compared with typical intramolecular interactions in POP-containing derivatives, exemplified by  $[\text{Cu}(\text{POP})(2,9\text{-Me}_2\text{phen})]^+$ . The CSD contains the structures of several salts of the latter, and two face-to-face  $\pi$ -stacking contacts recur, but appear to be mutually exclusive (see the later discussion of  $[\text{Cu}(\text{POP})(5)][\text{BF}_4]$ ). The first is between the phen unit and one phenyl ring of a  $\text{PPh}_2$  unit of POP. This interaction occurs in the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate salt of  $[\text{Cu}(\text{POP})(2,9\text{-Me}_2\text{phen})]^+$  (Fig. 13a).<sup>106</sup> The second involves one  $\text{PPh}_2$  phenyl ring and an arene ring of the POP backbone as seen in  $[\text{Cu}(\text{POP})(2,9\text{-Me}_2\text{phen})][\text{BF}_4]$  (Fig. 12b, compare with Fig. 6).<sup>107</sup> In  $[\text{Cu}(\text{POP})(2,9\text{-Me}_2\text{phen})][\text{BF}_4] \cdot \text{MeCN}$ ,<sup>108</sup>



**Fig. 12** (a) The structure of the  $[\text{Cu}(\text{xantphos})(2,9\text{-Me}_2\text{phen})]^+$  cation in the  $[\text{BF}_4]^-$  salt (CSD refcode GOZDEH). (b) The same view of the cation as in (a) showing the hosting of one Me substituent in the cavity of the xanthene unit (space-filling representation), and (c)  $\pi$ -stacking interaction between adjacent  $\text{PPh}_2$  units in xantphos (space-filling representation) and  $\text{CH} \cdots \pi$  contacts (hashed green lines) between Ph units of xantphos and the centroid of the Cu-phen chelate ring.





the cation (Fig. 12c) shows a  $\pi$ -stacking contact of the type shown in Fig. 12b, but the metrics of the interaction are not optimal. The same is true in [Cu(POP)(2,9-Me<sub>2</sub>phen)][PF<sub>6</sub>] $\cdot$ 0.5Et<sub>2</sub>O (CSD refcode CAPZID)<sup>109</sup> and in [Cu(POP)(2,9-Me<sub>2</sub>phen)][BF<sub>4</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub> (CSD refcode EDOCIJ).<sup>110</sup> These examples illustrate that in crystalline materials, crystallization conditions and the nature of the anion, play important roles in determining, not only lattice packing interactions, but also intra-cation  $\pi$ -contacts. They also indicate that structural data from a single-crystal structure may not necessarily translate to, for example, a thin-film or frozen matrix.

The promising PL and EL performances of [Cu(POP)(2)][BF<sub>4</sub>]<sup>+</sup> (2 = 2,9-Bu<sub>2</sub>phen, Scheme 1) were first reported by Armaroli *et al.* in 2006 (see earlier discussion).<sup>58</sup> Kato and coworkers have reported the emission behaviour of [Cu(xantphos)(2,9-Me<sub>2</sub>phen)][BF<sub>4</sub>]. In CH<sub>2</sub>Cl<sub>2</sub> solution, the complex has a PLQY of 24% at 298 K, and on going to a PMMA thin-film,  $\lambda_{\text{max}}^{\text{em}}$  undergoes a blue-shift (536 to 525 nm) and an increase in PLQY to 29%. At 77 K,  $\lambda_{\text{max}}^{\text{em}}$  red-shifts to 541 nm (PMMA film) and  $\tau$  increases from 18.5 to 182  $\mu$ s (values are from a bi-exponential fit to the decay), consistent with [Cu(xantphos)(2,9-Me<sub>2</sub>phen)]<sup>+</sup> being a TADF emitter at room temperature.<sup>105</sup> [Cu(POP)(2-Etphen)][PF<sub>6</sub>]<sup>+</sup> and [Cu(xantphos)(2-Etphen)][PF<sub>6</sub>]<sup>+</sup> (see Scheme 5 for 2-Etphen) also show TADF behaviour. The structure of the [Cu(POP)(2-Etphen)]<sup>+</sup> cation (Fig. 14a) shows the typical face-to-face  $\pi$ -stacking within the POP ligand, and the ethyl group engages in a C–H $\cdots$  $\pi$  interaction with an arene ring of the POP backbone (Fig. 14a). As in related structures, the bowl-shaped cavity of the xanthene unit in [Cu(xantphos)(2-Etphen)]<sup>+</sup> cation hosts the substituent on the N<sup>^</sup>N ligand, and two phenyl rings of xantphos are  $\pi$ -stacked (Fig. 14b). Powdered [Cu(POP)(2-Etphen)][PF<sub>6</sub>] and [Cu(xantphos)(2-Etphen)][PF<sub>6</sub>] emit with  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 558$  and 550 nm, respectively, and with PLQYs of 27.5 and 9.8%. Values of  $\tau$  of 8.7 and 10.2  $\mu$ s at 298 K increase to 27 and 14  $\mu$ s, respectively, on cooling to 77 K, but only the emission maximum for [Cu(xantphos)(2-Etphen)][PF<sub>6</sub>] undergoes a red-shift (to 557 nm). The blue-shift observed for [Cu(POP)(2-Etphen)][PF<sub>6</sub>] was attributed to intermolecular matrix effects in the frozen Me-THF glass. The 2-Etphen-containing compounds were incorporated into the active layers of LECs (Table 3) with the same architectures as shown in Fig. 8.

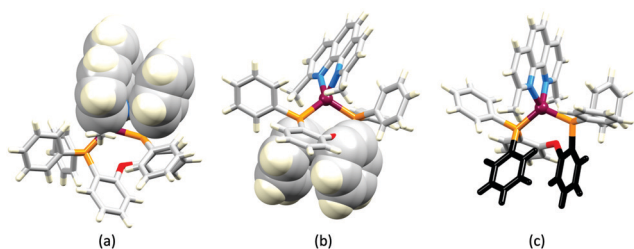


Fig. 13 The structures of the [Cu(POP)(2,9-Me<sub>2</sub>phen)]<sup>+</sup> cation in (a) the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate salt (CSD refcode ARURIP), and (b) [Cu(POP)(2,9-Me<sub>2</sub>phen)][BF<sub>4</sub>]<sup>+</sup> (refcode HOWQAO) with face-to-face  $\pi$ -stacking interaction shown in space-filling representation. (c) The structure of the cation in [Cu(POP)(2,9-Me<sub>2</sub>phen)][BF<sub>4</sub>] $\cdot$ MeCN (CSD refcode CAPLEN); the aromatic rings in black are poorly aligned for an efficient  $\pi$ -stacking contact but nonetheless, the evolution of this interaction is evident.

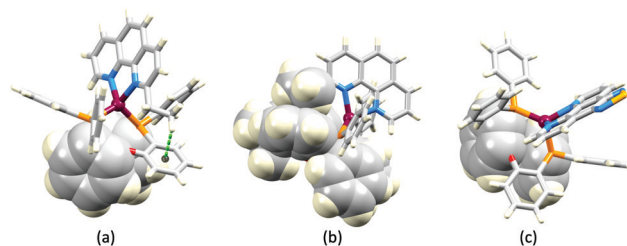


Fig. 14 (a) The structure of the [Cu(POP)(2-Etphen)]<sup>+</sup> cation in the [PF<sub>6</sub>]<sup>−</sup> salt (CSD refcode PUTSAB) highlighting  $\pi$ -stacking within the POP ligand (space-filling representation) and Et $\cdots$ POP CH $\cdots$  $\pi$  contact (hashed green line). (b) The structure of the [Cu(xantphos)(2-Etphen)]<sup>+</sup> cation in the [PF<sub>6</sub>]<sup>−</sup> salt (CSD refcode PUTTAC) showing  $\pi$ -stacking within the xantphos ligand (space-filling representation, bottom of diagram) and accommodation of the Et group in the xanthene-bowl (space-filling, left). (c) The structure of the [Cu(POP)(5)]<sup>+</sup> cation in the [BF<sub>4</sub>]<sup>−</sup> salt (CSD refcode PUYBET) with the  $\pi$ -stacking within the POP ligand shown in space-filling representation.

The LECs were driven by pulsed current and under an average current density of 100 A m<sup>−2</sup>. The LEC with [Cu(POP)(2-Etphen)][PF<sub>6</sub>] gave instantaneous EL, with an initial luminance of 273 cd m<sup>−2</sup> increasing over 25 minutes to a Lum<sub>max</sub> of 451 cd m<sup>−2</sup>. Although the LEC continued to emit light for 24 hours, the EL decay from Lum<sub>max</sub> to half this value was rapid (5.7 hours). Compared to the latter, LECs based on [Cu(xantphos)(2-Etphen)][PF<sub>6</sub>] were slower to turn on (122 minutes to reach Lum<sub>max</sub>) and had less intense EL (Lum<sub>max</sub> = 153 cd m<sup>−2</sup>), but a longer device lifetime (up to 98 hours).<sup>98</sup> These data should encourage further investigations with [Cu(POP/xantphos)(phen)]<sup>+</sup>-based electroluminophores in which the phen ligand bears a simple alkyl-substitution pattern. The introduction of bromo-substituents leads to weak emitters in solution, but powdered [Cu(POP)(2,9-Br<sub>2</sub>phen)][PF<sub>6</sub>] and [Cu(xantphos)(2,9-Br<sub>2</sub>phen)][PF<sub>6</sub>] ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 574$  and 554 nm) exhibit PLQYs of 24 and 45%, and excited-state lifetimes of 6.3 and 9.9  $\mu$ s, respectively. The photophysical properties of the complexes containing 2,9-phen are enhanced with respect to analogues containing 3,8- or 4,7-dibromo-1,10-phenanthrolines.<sup>111</sup> More detailed investigations of these compounds have not been carried out.

In [Cu(PPh<sub>3</sub>)<sub>2</sub>(4)][BF<sub>4</sub>], [Cu(POP)(4)][BF<sub>4</sub>], [Cu(PPh<sub>3</sub>)<sub>2</sub>(5)][BF<sub>4</sub>] and [Cu(POP)(5)][BF<sub>4</sub>], ligands 4 and 5 (Scheme 5) lack the steric hindrance imposed by 2,9-substituents in phen, and Farias *et al.* have assessed the effects of the chalcogen atoms in 4 and 5 on the photophysical properties of the complexes. The solid-state structure of [Cu(POP)(5)]<sup>+</sup> shows the expected  $\pi$ -stacking of phenyl and arene rings in POP, and Fig. 14c also reveals the close approach of one PPh<sub>2</sub> phenyl ring to the phen domain. However, no  $\pi$ -stacking interaction is established. In [Cu(POP)(4)][BF<sub>4</sub>] (CSD refcode PUXZUG), the dominant intracation packing is again within the POP framework. Compared to [Cu(PPh<sub>3</sub>)<sub>2</sub>(phen)][BF<sub>4</sub>] and [Cu(POP)(phen)][BF<sub>4</sub>], complexes containing 4 and 5 exhibit lower PLQYs (4 and 8% vs. 11% for the PPh<sub>3</sub> derivatives, and 6 and 8% vs. 13% for the POP derivatives, all in PMMA films), and excited-state lifetimes are shorter. Using steady-state and time-resolved spectroscopies, Farias *et al.* confirmed that the compounds with 4 and 5 are TADF emitters, and showed that the incorporation of the

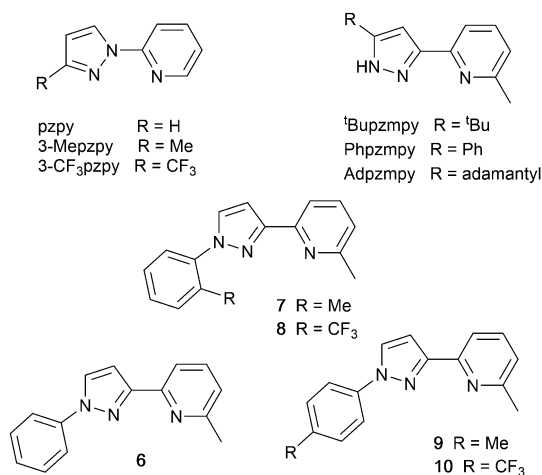


Se atom contributed to decreasing the PL lifetime to *ca.* 800 ns. This was claimed to be the lowest reported to date (2020) among similar TADF materials.<sup>112</sup>

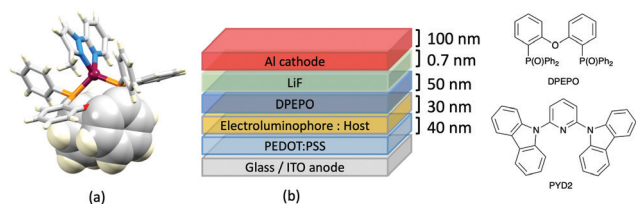
### Pyrazolyl pyridine derivatives with POP

Typically, the bpy and phen-containing compounds described in the previous sections are orange, yellow or green emitters. Moving from bpy or phen to an N<sup>∧</sup>N ligand comprising pyridine connected to a 5-membered N-heterocycle alters the bite angle of the chelating ligand and increases its ligand-field strength. This is a proven means of shifting emissions of [Cu(P<sup>∧</sup>P)(N<sup>∧</sup>N)]<sup>+</sup> complexes towards the blue.

Series of strongly green/blue- or blue-emitting [Cu(POP)(N<sup>∧</sup>N)][BF<sub>4</sub>] compounds have been reported in which N<sup>∧</sup>N is pzpy, 3-Meppzpy or 3-CF<sub>3</sub>-pzpy (Scheme 6 and Fig. 15a)<sup>113</sup> and <sup>t</sup>Bupzmpy, Phpzmpy or Adpzmpy (Scheme 6).<sup>114</sup> For the first series with pzpy, 3-Meppzpy or 3-CF<sub>3</sub>-pzpy, PLQYs of up to 45% were observed in deaerated CH<sub>2</sub>Cl<sub>2</sub> solution, and for solid-state [Cu(POP)(N<sup>∧</sup>N)][BF<sub>4</sub>] ( $\lambda_{\text{max}}^{\text{em}}$  = 490, 465 and 492 nm for N<sup>∧</sup>N = pzpy, 3-Meppzpy and 3-CF<sub>3</sub>-pzpy, respectively), the PLQYs were 56, 87 and 75%, respectively. The temperature dependence of the emission lifetimes and red-shifts in  $\lambda_{\text{max}}^{\text{em}}$ (PL) on going from 298 to 77 K, established TADF at ambient temperatures with  $\Delta E_{\text{ST}}$  lying in the range 0.17–0.18 eV.



**Scheme 6** Structures of pyrazolyl pyridine derivatives used in [Cu(P<sup>∧</sup>P)(N<sup>∧</sup>N)]<sup>+</sup> complexes.

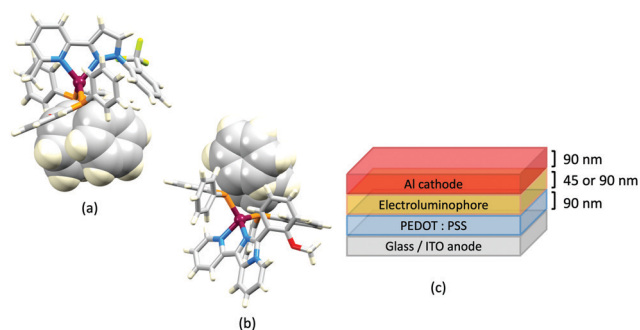


**Fig. 15** (a) Structure of the complex cation in [Cu(POP)(3-Meppzpy)][BF<sub>4</sub>]. 0.5CH<sub>2</sub>Cl<sub>2</sub> (CSD refcode VIZKEW) with Ph<sup>∧</sup>arene  $\pi$ -stacking within the POP ligand shown in space-filling representation. (b) Architecture of solution-processed OLEDs with [Cu(POP)(pzpy)][BF<sub>4</sub>] derivatives in the active layer. DPEPO = hole-blocking layer; active layer = 20 wt% Cu-iTMC in either DPEPO or PYD2 as host.

The highest solid-state PLQY (87% for N<sup>∧</sup>N = 3-Meppzpy) corresponded to the shortest  $\tau$  value (12.2  $\mu$ s). Solution-processed OLEDs were fabricated using the three [Cu(POP)(N<sup>∧</sup>N)][BF<sub>4</sub>] salts with either DPEPO or PYD2 (also abbreviated in the literature to 26mCpY) as host materials (Fig. 15b). The best EL performance was found for [Cu(POP)(3-CF<sub>3</sub>-pzpy)][BF<sub>4</sub>]: PYD2 with the relative LUMO energies of [Cu(POP)(3-CF<sub>3</sub>-pzpy)][BF<sub>4</sub>] (−2.49 eV) and PYD2 (−2.2 eV) contributing to an efficient electron-hole recombination pathway. A Lum<sub>max</sub> of 2033 cd m<sup>−2</sup> was achieved for this device.<sup>113</sup> This work was extended to [Cu(POP)(N<sup>∧</sup>N)][BF<sub>4</sub>] with N<sup>∧</sup>N = 6–10 (Scheme 6) and these are highly-efficient TADF emitters. Structural characterization of all five compounds confirms that the steric requirements of the substituents in the pzpy ligands do not preclude intra-POP  $\pi$ -stacking (Fig. 16a). Solid materials were intense blue-green or blue emitters ( $\lambda_{\text{max}}^{\text{em}}$  in the range 464 to 481 nm at 298 K, PLQY = 82–99%) with a red-shift for spectra recorded at 77 K ( $\lambda_{\text{max}}^{\text{em}}$  in the range 487 to 513 nm). On doping in PMMA, all the Cu-iTMCs show sky-blue emissions, and for all but [Cu(POP)(8)][BF<sub>4</sub>],  $\tau$  values increase with decreasing rigidity of the matrix.<sup>115</sup>

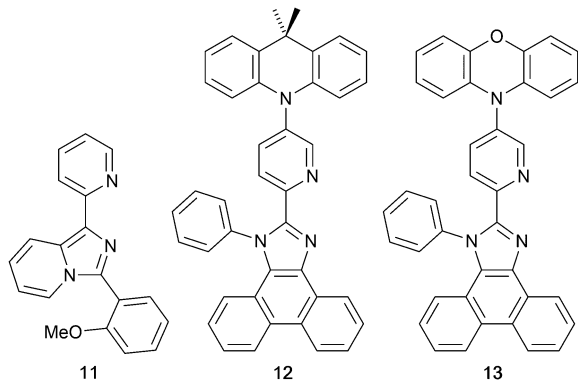
### Imidazolyl pyridine derivatives with POP and xantphos

The search for blue-emitting Cu-based LECs takes us from pyrazolyl- to imidazolyl-containing Cu-iTMCs. Ligand **11** (Scheme 7) was incorporated into [Cu(POP)(**11**)]PF<sub>6</sub> which gave a deep-blue emission at *ca.* 450 nm in solution, thin-film and the solid state. The structure of the [Cu(POP)(**11**)]<sup>+</sup> cation showed typical features (Fig. 16b). Unexpectedly, LECs fabricated with [Cu(POP)(**11**)]PF<sub>6</sub> in the active layer (Fig. 16c) were yellow emitters (EL = 550 nm), with luminances which depended both on the thickness of the active layer and on the pulsed current (1, 2.5, 5 or 7.5 mA). Detailed studies concluded that the origin of this large PL-to-EL shift lay in the fact that [Cu(POP)(**11**)]<sup>+</sup> did not exhibit TADF because of the exclusively ligand-centred character of the excited states. The lack of any charge-transfer character in the excited states resulted, respectively, in a blue-fluorescent and yellow phosphorescent PL and EL.<sup>116</sup> Ligands **12** and **13** were designed to possess intra-ligand charge-transfer character. Each of



**Fig. 16** Structures of the complex cations in (a) [Cu(POP)(**8**)]BF<sub>4</sub>·EtOH (CSD refcode JUFNOP) and (b) [Cu(POP)(**11**)]PF<sub>6</sub> showing Ph<sup>∧</sup>arene  $\pi$ -stacking in the POP ligand (space-filling representation). (c) LEC architecture for testing with [Cu(POP)(**11**)]PF<sub>6</sub> in the active layer; LECs were driven with a pulsed current.



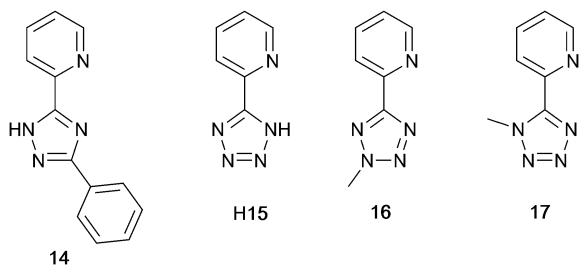


Scheme 7 Structures of imidazolyl pyridine derivatives used in  $[\text{Cu}(\text{P}^{\wedge}\text{P})-(\text{N}^{\wedge}\text{N})]^+$  complexes.

$[\text{Cu}(\text{POP})(\mathbf{12})][\text{BF}_4]$ ,  $[\text{Cu}(\text{POP})(\mathbf{13})][\text{BF}_4]$ ,  $[\text{Cu}(\text{xantphos})(\mathbf{12})][\text{BF}_4]$  and  $[\text{Cu}(\text{xantphos})(\mathbf{13})][\text{BF}_4]$  exhibits TADF. In solution at room temperature, values of  $\lambda_{\text{max}}^{\text{em}}$  lie between 514 to 537 nm ( $\lambda_{\text{exc}} = 365$  nm) with an  $\text{N}^{\wedge}\text{N}$  ligand-dominated excited state. Given the steric hindrance of the ligands which militate against significant flattening of the  $\text{Cu}(\text{i})$  coordination sphere, the low PLQYs (4.2–9.5%) were explained in terms of torsional dynamics of the  $\text{N}^{\wedge}\text{N}$  ligand framework in solution. PLQYs (42–71%) and decay lifetimes were significantly enhanced on going to thin films. Emission data for  $[\text{Cu}(\text{xantphos})(\mathbf{13})][\text{BF}_4]$  were recorded from 77 K to ambient temperature and confirmed TADF with longer  $\tau$  values at lower temperatures; the value of  $\Delta E_{\text{ST}} = 0.04$  eV (*ca.* 300  $\text{cm}^{-1}$ ) is also consistent with TADF. Solution-processed, multilayer OLEDs were fabricated with  $[\text{Cu}(\text{xantphos})(\mathbf{12})][\text{BF}_4]$  or  $[\text{Cu}(\text{POP})(\mathbf{13})][\text{BF}_4]$  hosted in bis(9*H*-carbazol-9-yl)pyridine in the active layer and using different doping levels. The maximum external quantum efficiency (EQE = 7.96%) was achieved with  $[\text{Cu}(\text{POP})(\mathbf{13})][\text{BF}_4]$ .<sup>9</sup>

### Tri- and tetrazolyl pyridine derivatives with POP, xantphos and $\text{PPh}_3$

The families of  $\text{N}^{\wedge}\text{N}$  ligands with pyridine connected to a 5-membered N-heterocycle include a number of triazole and tetrazole derivatives (Scheme 8), and, of course, the presence of an NH unit gives the potential for deprotonation accompanying coordination and the formation of a neutral rather than cationic  $\text{Cu}(\text{i})$  heteroleptic complexes. The  $\text{p}K_{\text{a}}$  values of triazole ( $\text{p}K_{\text{a}} = 9.4$ ) and tetrazole ( $\text{p}K_{\text{a}} = 4.9$ ) account for the fact that in



Scheme 8 Structures of tri- and tetrazolyl pyridine derivatives used in  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes.

the examples below, H15 binds to  $\text{Cu}(\text{i})$  as the conjugate base while  $\mathbf{14}$  remains protonated.

Xu *et al.* have reported the TADF emitters  $[\text{Cu}(\text{PPh}_3)_2(\mathbf{14})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{14})][\text{BF}_4]$ . The low intensity absorption maxima at 362 and 342 nm, respectively, were assigned to MLCT and ligand-to-ligand (LLCT) transitions. Solution emissions were weak, but in the solid state, emissions with  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 490$  and 512 nm with PLQYs of 89.97 and 27.82%, respectively, for  $[\text{Cu}(\text{PPh}_3)_2(\mathbf{14})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{14})][\text{BF}_4]$  were observed. Interestingly, it is the  $\text{PPh}_3$ , and not the wide bite-angle POP, derivative that performs the better of the two compounds. At 298 K, the excited-state decay times are 23.6 and 13.0  $\mu\text{s}$  and these increase to 269.0 and 210.1  $\mu\text{s}$  at 77 K. Values of  $\Delta E_{\text{ST}}$  are 0.09 and 0.04 eV (*ca.* 700 and 300  $\text{cm}^{-1}$ ), and these data, accompanied by the red-shift in  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  to 508 and 520 nm for  $[\text{Cu}(\text{PPh}_3)_2(\mathbf{14})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{14})][\text{BF}_4]$ , respectively, support TADF at ambient temperatures. Multilayer OLEDs were processed using these ionic complexes with 4,4',4''-tris(*N*-carbazolyl)triphenylamine as the host material. The OLEDs with  $[\text{Cu}(\text{PPh}_3)_2(\mathbf{14})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{14})][\text{BF}_4]$  showed green emissions ( $\lambda_{\text{max}}^{\text{em}}(\text{EL})$  to 520 and 539 nm), and the POP-containing electroluminophore yielded the higher  $\text{Lum}_{\text{max}}$  (1871 vs. 1437  $\text{cd m}^{-2}$ ), with the smaller  $\Delta E_{\text{ST}}$  being a contributing factor.<sup>10</sup> A small  $\Delta E_{\text{ST}}$  (*ca.* 0.18 eV, 1500  $\text{cm}^{-1}$ ) separation is also found for the neutral compound  $[\text{Cu}(\text{POP})(\mathbf{15})]$ , and a detailed theoretical investigation demonstrated that low-frequency vibrational modes associated with the torsional motion of the POP and  $\text{N}^{\wedge}\text{N}$  ligands lead to substantial Huang–Rhys factors<sup>117</sup> and, thereby, to rapid ISC and RISC (see Fig. 2).<sup>118</sup> Related studies which address the effects of both intramolecular and intermolecular interactions on photophysical properties, have been carried out on the cationic TADF emitters  $[\text{Cu}(\text{POP})(\mathbf{16})]^+$  and  $[\text{Cu}(\text{POP})(\mathbf{17})]^+$ .<sup>119</sup> These complexes exhibit both aggregation induced emission (AIE) and TADF. For the former phenomenon, enhanced emission in the solid state (as opposed to in solution) arises from molecular aggregation that restricts intramolecular rotation.  $[\text{Cu}(\text{POP})(\mathbf{16})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{17})][\text{BF}_4]$  are virtually non-emissive in  $\text{CH}_2\text{Cl}_2$  solutions, but thin-films spin-coated from  $\text{CH}_2\text{Cl}_2$  solution were bright emitters ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 533$  and 572 nm for  $\text{N}^{\wedge}\text{N} = \mathbf{16}$  and  $\mathbf{17}$ ) with very short decay times. In this form, the  $\text{Cu}$ -iTMCs were principally TADF emitters over a 320–170 K temperature range. Between 170 and 80 K, phosphorescence was the dominant decay path. A comparison of the PL of thin-films made with  $[\text{Cu}(\text{POP})(\mathbf{16})][\text{BF}_4]$  and  $[\text{Cu}(\text{POP})(\mathbf{17})][\text{BF}_4]$  in low- or high-molecular weight PMMA showed that the different PMMA hosts were able to suppress molecular vibrations to different extents. In low molecular weight PMMA, TADF contributed little to the emission, with vibrational quenching being most effective and ambient (rather than lower) temperatures. Moving to the high molecular weight PMMA leads to greater suppression of molecular vibrations within the  $\text{Cu}$ -iTMCs and opens up the TADF pathway. Ligands  $\mathbf{16}$  and  $\mathbf{17}$  differ only in the position of the methyl substituent in the tetrazole (Scheme 8). This leads to significant differences in crystal packing with the inter-cation interactions resulting in a 3D-supramolecular assembly in  $[\text{Cu}(\text{POP})(\mathbf{16})][\text{BF}_4]$ , but to 1D-chains in  $[\text{Cu}(\text{POP})(\mathbf{17})][\text{BF}_4]$ .

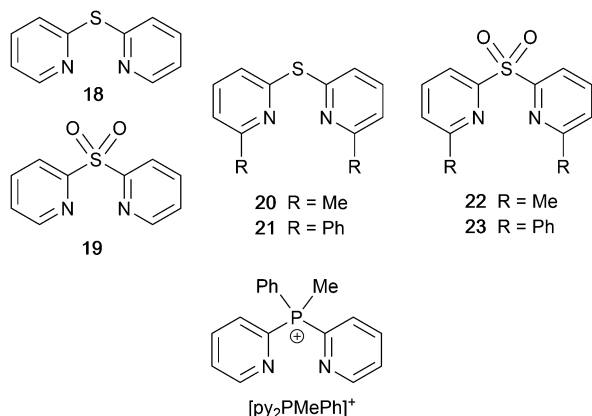




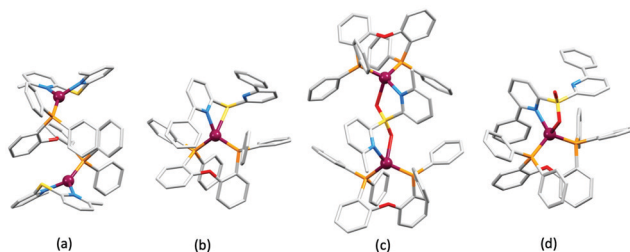
It follows that there is less distortion of the excited state of the complex with **16**, and consistent with this notion is the fact that the solid-state PLQY of  $[\text{Cu}(\text{POP})(\mathbf{16})][\text{BF}_4]$  (47.1%) is higher than that of  $[\text{Cu}(\text{POP})(\mathbf{17})][\text{BF}_4]$  (9.4%). Both complexes are put forward as potential candidates for lighting devices.<sup>120</sup>

### Derivatives of di(pyridin-2-yl)sulfane and related N^N ligands with POP

Scheme 9 shows a series of new N^N ligands incorporated into heteroleptic copper(i) coordination compounds, and designed with S in two different oxidation states. Unexpectedly, whereas **18** and **19** behave as N,N'-chelating ligands and form distorted tetrahedral  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})]^+$  complexes, ligand **20** gives a dinuclear complex with three-coordinate Cu(i) and bridging POP (Fig. 17a), while **21** behaves as an N,S-chelating ligand (Fig. 17b), and **22** and **23** bind through N- and O-donors in mono- and dinuclear complexes, respectively (Fig. 17c and d). All the compounds (as  $[\text{BF}_4]^-$  salts) are weakly emissive in  $\text{CH}_2\text{Cl}_2$  solution. Of the solution emissions, the most blue-shifted is for  $[\text{Cu}(\text{POP})(\mathbf{21})][\text{BF}_4]$  ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 456 \text{ nm}$ ) and this emission band is the only one to show structure; radiative decay from a ligand-centred excited state was proposed. Thin-films drop-cast from MeOH solutions of the complexes produced



**Scheme 9** Structures of di(pyridin-2-yl)sulfane (**18**) and di(pyridin-2-yl)sulfone (**19**) and some functionalized derivatives, and the structure of  $[\text{py}_2\text{PMePh}]^+$ . See also Scheme 16.



**Fig. 17** Structures of the complex cations (a)  $[\text{Cu}_2(\mathbf{20})_2(\mu\text{-POP})]^{2+}$  (CSD refcode SONBIJ), (b)  $[\text{Cu}(\text{POP})(\mathbf{21})]^+$  (refcode SONBOP), (c)  $[\text{Cu}_2(\text{POP})_2(\mu\text{-22})]^{2+}$  (refcode SONBAB), and (d)  $[\text{Cu}(\text{POP})(\mathbf{23})]^+$  (refcode SONBUV). Each was structurally characterized as the  $[\text{BF}_4]^-$  salt, and in the figures, H atoms are omitted for clarity.

more intense emissions than in solution, with values of  $\lambda_{\text{max}}^{\text{em}}$  in the range 518–572 nm. For each pair of complexes with sulfane and sulfone ligands, the emission undergoes a red-shift on going from S to  $\text{SO}_2$  unit. The highest solid-state PLQYs are for  $[\text{Cu}_2(\text{POP})_2(\mu\text{-22})][\text{BF}_4]_2$  (14%) and  $[\text{Cu}(\text{POP})(\mathbf{23})][\text{BF}_4]$  (20%). With the exception of  $[\text{Cu}(\text{POP})(\mathbf{21})][\text{BF}_4]$ , the emission maxima are red-shifted on going from 298 to 77 K, and PL lifetimes increase, consistent with TADF; in all cases,  $\Delta E_{\text{ST}} < 0.2 \text{ eV}$  ( $< 1600 \text{ cm}^{-1}$ ). For  $[\text{Cu}(\text{POP})(\mathbf{21})][\text{BF}_4]$ ,  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 526 \text{ nm}$  at 298 K and 528 nm at 77 K, while  $\tau$  decreases upon cooling. As with the solution emission (see above), the data point to a ligand-centred emission. While not tested in LECs, the TADF emitters are promising candidates for such application, and also open up the possibility of using sulfone-based N,O-coordinated diimine ligands.<sup>121</sup>

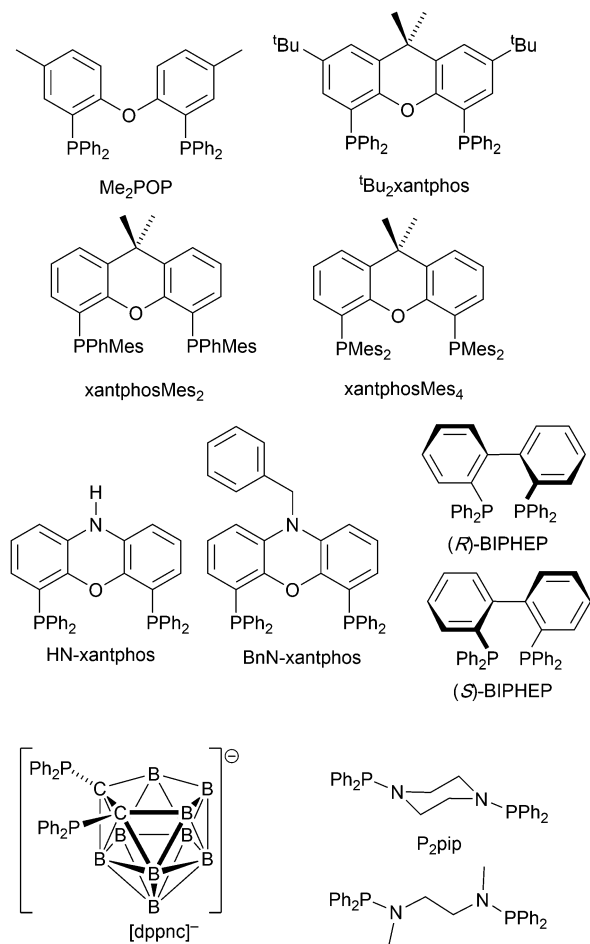
Use of the N^N ligands **18** and **19** has been extended by Gaillard, Costa and coworkers to include analogous ligands with bridging CMe<sub>2</sub>, NH, O and PPh units. This series of  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  complexes along with  $[\text{Cu}(\text{POP})(\text{py}_2\text{PMePh})][\text{PF}_6]_2$  (see Scheme 9) are weak emitters in solution, and for N^N = **18** or **19**, powdered samples also showed PLQY values  $< 1\%$ . However, for the remaining compounds, solid-state PLQYs were in the range 17–60%, with the maximum (also in thin film) being for the copper(i) complex with N^N =  $\text{py}_2\text{O}$ . With calculated values of  $\Delta E_{\text{ST}}$  in the range 0.05–0.22 eV (*ca.* 400–1700  $\text{cm}^{-1}$ ), the  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})]^+$  and  $[\text{Cu}(\text{POP})(\text{py}_2\text{PMePh})]^{2+}$  complexes were expected to exhibit TADF, and this was confirmed experimentally for representative examples.  $[\text{Cu}(\text{POP})(\text{py}_2\text{PMePh})][\text{PF}_6]_2$  is singled out from the series as exhibiting good electrochemical stability and high ionic conductivity, and a red-shifted emission ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 606 \text{ nm}$  in the solid state). LECs with  $[\text{Cu}(\text{POP})(\text{py}_2\text{PMePh})][\text{PF}_6]_2$  as the luminophore showed a yellow emission with a  $\text{Lum}_{\text{max}}$  of *ca.* 60  $\text{cd m}^{-2}$  and an efficacy of 0.2  $\text{cd A}^{-1}$ .<sup>122</sup>

### Complexes with wide-bite angle bis(phosphanes) other than POP and xantphos

The commercial accessibility of POP and xantphos contribute towards their being the most popular wide-bite angle bis-(phosphanes) in heteroleptic copper(i) compounds. However, the pool of ligands that fall in this category is large,<sup>56</sup> and in this section, we focus on other sterically demanding P^P ligands (Scheme 10) that have been used to stabilize  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes.

Earlier, we described the small  $\Delta E_{\text{ST}}$  (*ca.* 0.18 eV, 1500  $\text{cm}^{-1}$ ) separation in the tetrazole-containing  $[\text{Cu}(\text{POP})(\mathbf{15})]$ , and theoretical studies indicate that introducing methyl substituents into the backbone of POP to give Me<sub>2</sub>POP (Scheme 15) has little effect on the T<sub>1</sub>–S<sub>1</sub> energy gap.<sup>118</sup> There appear to be no experimental investigations of the effects on the properties of  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})]^+$ -type complexes of modifying the POP ligand, and there are only limited studies on complexes incorporating modified xantphos ligands. In 2019, we reported the use of the 'Bu<sub>2</sub>xantphos ligand (Scheme 15). The strategy behind introducing *tert*-butyl groups was to produce greater spatial separation of Cu-ITMC cations in the active layer in a LEC. Across the series  $[\text{Cu}(\text{Bu}_2\text{xantphos})(\text{bpy})][\text{PF}_6]$ ,  $[\text{Cu}(\text{Bu}_2\text{xantphos})(6\text{-Me bpy})][\text{PF}_6]$





Scheme 10 Structures of wide-bite angle bis(phosphanes) used in  $[\text{Cu}(\text{P}^{\text{A}}\text{P})(\text{N}^{\text{A}}\text{N})]^+$  complexes. See Scheme 1 for POP and xantphos.

(Fig. 18a) and  $[\text{Cu}(\text{tBu}_2\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ , the  $\text{Cu}^+$  oxidation moves to higher potential (+0.76, +0.83, +0.85 V vs.  $\text{Fc}/\text{Fc}^+$ ) in keeping with the increased steric demands of the bpy ligand. Both the solution and solid-state emission maxima for  $[\text{Cu}(\text{tBu}_2\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  are blue-shifted on going from bpy to 6-Mebpy to 6,6'-Me<sub>2</sub>bpy: in solution,  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 652, 605, 566 \text{ nm}$ , and for powder,  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 584, 552, 522 \text{ nm}$ . Emission spectra at 77 K exhibit maxima at 597, 578 and 555 nm, all red-shifted with respect to the solids at 298 K. This, and the extended  $\tau$  values on going from 298 to 77 K (1.95 to 27.6  $\mu\text{s}$  for  $\text{N}^{\wedge}\text{N} = \text{bpy}$ , 6.32 to 56.3  $\mu\text{s}$  for 6-Mebpy, 13.8 to 92.1  $\mu\text{s}$  for 6,6'-Me<sub>2</sub>bpy) are consistent with TADF behaviour. Both solid-state and frozen matrix emission decays were fitted biexponentially. The room temperature solid-state PLQYs for these  $[\text{Cu}(\text{tBu}_2\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  compounds range from 3 to 59%, although in thin-films, values are lower. The trend of increasing PLQY with increasing steric demands of the  $\text{N}^{\wedge}\text{N}$  ligand are replicated in the luminances of LECs fabricated as shown in Fig. 18b. The LECs had a fast turn-on times (1–4.5 minutes) to reach  $\text{Lum}_{\text{max}}$  of 20, 230 and 370  $\text{cd m}^{-2}$  for  $\text{N}^{\wedge}\text{N} = \text{bpy}$ , 6-Mebpy and 6,6'-Me<sub>2</sub>bpy, respectively. However, the low EQE of 1.0% for the brightest LECs indicates that non-radiative losses dominate

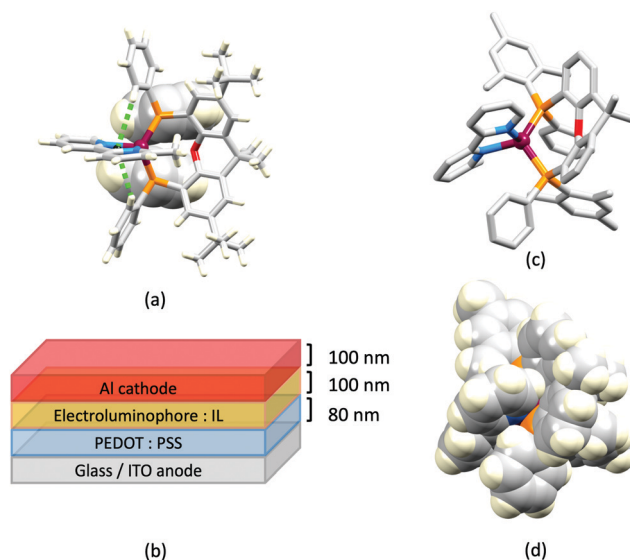


Fig. 18 (a) Structure of the cation in  $[\text{Cu}(\text{tBu}_2\text{xantphos})(6\text{-Mebpy})][\text{PF}_6]$  (CSD refcode HIJRAW).  $\pi$ -Stacking between phenyl rings of different  $\text{PPh}_2$  groups (space-filling representation) and  $\text{C-H}_{\text{phenyl}} \cdots \text{bpy}$  interactions (green hashed lines) are highlighted. (b) Architecture of the LECs containing  $[\text{Cu}(\text{tBu}_2\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphosMes}_2)(\text{N}^{\wedge}\text{N})][\text{PF}_6]$ ; IL =  $[\text{EMIM}][\text{PF}_6]$ , and Cu-iTMC: IL molar ratio = 4:1; LECs were driven using a pulsed current. (c) Structure of the cation in  $[\text{Cu}(\text{xantphosMes}_2)(6\text{-Mebpy})][\text{PF}_6]$  (refcode YITSOM); H atoms omitted, and (d) a space-filling representation of the  $[\text{Cu}(\text{xantphosMes}_2)(6\text{-Mebpy})]^+$  cation in the same orientation as in (c).

in the recombination of injected electrons and holes, and a comparison of the performances of LECs containing  $[\text{Cu}(\text{tBu}_2\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  reveals with the  $\text{tBu}$  groups have a negligible influence.<sup>123</sup>

Modification of the xantphos ligand has also involved replacing the  $\text{PPh}_2$  units by  $\text{PMesPh}$  and  $\text{PMes}_2$  ( $\text{Mes} = \text{mesityl}$ ). The wide-bite angle ligand  $\text{xantphosMes}_4$  (Scheme 10) proved to be too sterically demanding to form  $[\text{Cu}(\text{xantphosMes}_4)(\text{N}^{\wedge}\text{N})]^+$  even for unsubstituted bpy. For  $\text{xantphosMes}_2$  (Scheme 10), it was possible to isolate  $[\text{Cu}(\text{xantphosMes}_2)(\text{N}^{\wedge}\text{N})][\text{PF}_6]$  with  $\text{N}^{\wedge}\text{N} = \text{bpy}$  and 6-Mebpy (Fig. 18c), but not 6,6'-Me<sub>2</sub>bpy. The combined steric demands of the  $\text{xantphosMes}_2$  and 6-Mebpy ligands can be appreciated by looking at Fig. 18d. Comparisons of PL data for  $[\text{Cu}(\text{xantphosMes}_2)(\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphosMes}_2)(6\text{-Mebpy})][\text{PF}_6]$  at 298 K (powder) and 77 K (frozen matrix) confirmed red-shifting of emission maxima (589 to 594 nm for bpy, 547 to 587 nm for 6-mebpy) and increased decay times (1.19 to 20.0  $\mu\text{s}$  for bpy, 6.62 to 19.7  $\mu\text{s}$  for 6-Mebpy), indicative of TADF behaviour at ambient temperatures. LECs with the architecture shown in Fig. 18b were tested with  $[\text{Cu}(\text{xantphosMes}_2)(\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphosMes}_2)(6\text{-Mebpy})][\text{PF}_6]$  in the active layer, but no EL was observed for the former device. This correlates with the low PLQY (1.9%) of solid  $[\text{Cu}(\text{xantphosMes}_2)(\text{bpy})][\text{PF}_6]$  at room temperature. The LEC with  $[\text{Cu}(\text{xantphosMes}_2)(6\text{-Mebpy})][\text{PF}_6]$  exhibited a fast turn-on time (it reached  $\text{Lum}_{\text{max}}$  in <1 minute) but only a moderate  $\text{Lum}_{\text{max}}$  (50  $\text{cd m}^{-2}$ ).<sup>123</sup> Thus, the modifications of xantphos, either with bulky peripheral groups, or with P-substituents more sterically demanding than phenyl, do not

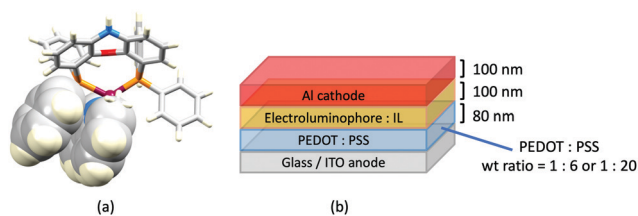


appear to enhance PL or EL properties, and these latter investigations tend to suggest that, with xantphos at least, the choice of  $N^{\wedge}N$  ligand is the dominant factor.

Despite being commercially available, HN-xantphos (Scheme 10) has received far less attention than xantphos, especially with respect to heteroleptic copper(i) coordination compounds.<sup>124–129</sup> We focus on those studies directed towards applications in LECs. We have already seen that among some of the best performing LEC-emitters are  $[\text{Cu}(\text{xantphos})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ , and we reported a comparison of the PL and EL behaviours of their HN-xantphos analogues in 2020, along with the effects of replacing the NH by an *N*-benzyl group (BnN-xantphos, Scheme 10). The crystal structure of  $[\text{Cu}(\text{HN-xantphos})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$  reveals an inter-ligand face-to-face  $\pi$ -stacking interaction between a phenyl ring of a  $\text{PPh}_2$  unit and the bpy domain (Fig. 19a). A similar intramolecular interaction occurs in  $[\text{Cu}(\text{BnN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ . In solution,  $[\text{Cu}(\text{BnN-xantphos})(N^{\wedge}N)][\text{PF}_6]$  with  $N^{\wedge}N = \text{bpy}$ , 6-Me<sub>2</sub>bpy and 6,6'-Me<sub>2</sub>bpy are weakly emissive; the analogous compounds containing HN-xantphos are unstable in  $\text{CH}_2\text{Cl}_2$  with respect to ligand redistribution. The emission data for powdered samples are given in Table 4 and show similar trends to those for  $[\text{Cu}(\text{xantphos})(N^{\wedge}N)][\text{PF}_6]$  with  $N^{\wedge}N = \text{bpy}$ , 6-Me<sub>2</sub>bpy and 6,6'-Me<sub>2</sub>bpy in Table 1 with  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  undergoing a blue shift, and PLQY and  $\tau$  increasing on going from bpy to 6-Me<sub>2</sub>bpy to 6,6'-Me<sub>2</sub>bpy. Although the calculated values of  $\Delta E_{\text{ST}}$  (0.14–0.20 eV, *ca.* 1100–1600  $\text{cm}^{-1}$ ) are small enough to allow RISC to occur (Fig. 2), an analysis of the oscillator strengths for electronic transitions suggests that the RISC process leads to non-radiative decay rather than TADF. Because of the high

solid-state PLQY of  $[\text{Cu}(\text{BnN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ , this compound was selected for inclusion in the active layer of LECs, the latter being fabricated as shown in Fig. 19b. An interesting aspect of this investigation was the effect of using commercial PEDOT: PSS with different weight ratios in the hole-injection layer. The time to reach a luminance of 100  $\text{cd m}^{-2}$  was only 7 s with 1:20 PEDOT: PSS for LECs driven using current densities of 50 or 100  $\text{A m}^{-2}$ . In contrast, this turn-on time was 185 s (at 50  $\text{A m}^{-2}$ ) or 12 s (at 100  $\text{A m}^{-2}$ ) for the 1:6 PEDOT: PSS. It is the latter composition that is most commonly employed in LECs. Values of  $\text{Lum}_{\text{max}}$  also depended on the PEDOT: PSS composition, reaching 203 or 355  $\text{cd m}^{-2}$ . Overall, the LECs with  $[\text{Cu}(\text{BnN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  showed good lifetimes, intense EL and EQE >1%, making them some of the best performing devices with  $[\text{Cu}(\text{P}^{\wedge}\text{P})(N^{\wedge}N)]^+$  emitters.<sup>127</sup>

The chiral BIPHEP ligand (Scheme 10) is also commercially available and the racemic form was used to prepare  $[\text{Cu}(\text{BIPHEP})(N^{\wedge}N)][\text{PF}_6]$  in which  $N^{\wedge}N = \text{bpy}$ , 6-Me<sub>2</sub>bpy, 6-Etbpy and 5,5'-Me<sub>2</sub>bpy. As we have seen,  $[\text{Cu}(\text{P}^{\wedge}\text{P})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  compounds are some of the most emissive of this family, but attempts to synthesize  $[\text{Cu}(\text{BIPHEP})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$  gave only inseparable mixtures of homo- and heteroleptic complexes, presumably due to excessive steric demands of the two ligands within the four-coordinate environment of copper(i). Although in the solid state, the steric demands of the ligands in the  $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})]^+$  cation protect the Cu(i) centre, there are no face-to-face  $\pi$ -stacking interactions (Fig. 20a). In contrast, in  $[\text{Cu}(\text{BIPHEP})(\text{bpy})]^+$ ,  $[\text{Cu}(\text{BIPHEP})(6\text{-Me}_2\text{bpy})]^+$  and  $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})]^+$ , one  $\text{PPh}_2$  phenyl ring engages in a stacking contact with one ring of the BIPHEP backbone. As is typical of most  $[\text{Cu}(\text{P}^{\wedge}\text{P})(N^{\wedge}N)][\text{X}]$  salts, solution emissions of the BIPHEP derivatives were very weak, but in the solid state, PLQYs are 3–14%, the highest being for  $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]$ . The yellow emitters have emission maxima at 566 nm for  $N^{\wedge}N = \text{bpy}$ , 568 nm for 6-Me<sub>2</sub>bpy, 582 for 6-Etbpy, and 558 nm for 5,5'-Me<sub>2</sub>bpy. On going from 298 to 77 K, these shift to 615, 595, 590 and 600 nm, respectively, and the decay lifetimes increase from 3 to 45  $\mu\text{s}$  for  $[\text{Cu}(\text{BIPHEP})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$ , 1 to 53  $\mu\text{s}$  for  $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})][\text{PF}_6]$ , and 8 to 49  $\mu\text{s}$  for  $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]$ , consistent with TADF at ambient temperatures. Despite the large increase in  $\tau$  for  $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})][\text{PF}_6]$ , this complex showed only a small

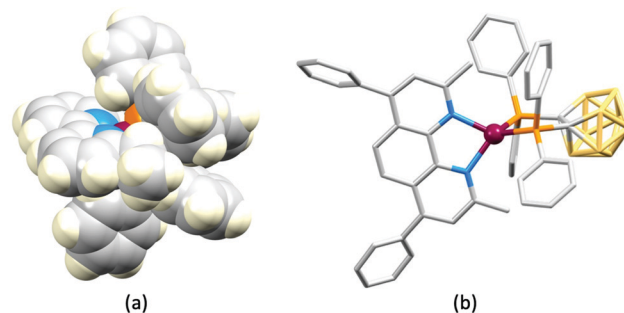


**Fig. 19** (a) Structure of the cation in  $[\text{Cu}(\text{HN-xantphos})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$  with the  $\text{Ph} \cdots \text{bpy}$   $\pi$ -stacking interaction shown in space-filling representation (CSD refcode TUHXEC). (b) Architecture of the LECs containing  $[\text{Cu}(\text{BnN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ ; IL = [EMIM][PF<sub>6</sub>], and Cu-iTMC: IL molar ratio = 4:1; two compositions of the hole-injection layer were used; LECs were driven using a pulsed current.

**Table 4** Room temperature PL emission maxima, PLQY values and decay lifetimes ( $\tau$ ) for solid-state  $[\text{Cu}(\text{RN-xantphos})(\text{Me}_n\text{bpy})]^+$  complexes (R = H, Bn;  $n = 0, 1, 2$ ). Data from Arnosti *et al.*<sup>127</sup>

Compound	$\lambda_{\text{max}}^{\text{em}}/\text{nm}^a$	PLQY/%	$\tau/\mu\text{s}$
$[\text{Cu}(\text{HN-xantphos})(\text{bpy})][\text{PF}_6]$	555	5	1.77
$[\text{Cu}(\text{HN-xantphos})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$	535	17	10.8
$[\text{Cu}(\text{HN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$	518	14	14.2
$[\text{Cu}(\text{BnN-xantphos})(\text{bpy})][\text{PF}_6]$	575	2	1.8
$[\text{Cu}(\text{BnN-xantphos})(6\text{-Me}_2\text{bpy})][\text{PF}_6]$	550	8	7.5
$[\text{Cu}(\text{BnN-xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$	520	55	17.4

<sup>a</sup>  $\lambda_{\text{exc}} = 365 \text{ nm}$ .

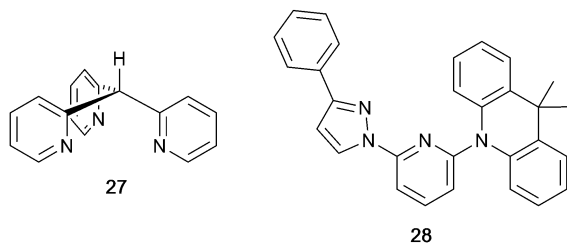


**Fig. 20** (a) Structure of the cation in  $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})][\text{PF}_6]$  in space-filling representation (CSD refcode WOXHEZ). (b) Structure of  $[\text{Cu}(\text{dppnc})(2,9\text{-Me}_2\text{-4,7-Ph}_2\text{phen})]$  (CSD refcode MUJXOG) with H atoms omitted.







Scheme 12 Structures of the tripodal ligand **27** and bidentate ligand **28**.

motifs are represented in  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})][\text{X}]$  ( $\text{X}^- = \text{PF}_6^-$ ,  $\text{BF}_4^-$  and  $\text{BPh}_4^-$ )<sup>135</sup> and  $[\text{Cu}(\text{PAr}_3)(\mathbf{27})][\text{PF}_6]$  (Ar = Ph, 2-MeC<sub>6</sub>H<sub>4</sub>, 2-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>) (see Scheme 12 for **27**).<sup>136</sup> These are deep-blue emitters, and in the first series, the counter-ion has a significant impact on the solid-state emission properties of  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})][\text{X}]$ . TD-DFT calculations show that  $\Delta E_{\text{ST}}$  is 810 cm<sup>-1</sup> (0.10 eV) for  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})]^+$ , consistent with TADF behaviour. Indeed, red-shifted emission maxima are observed for powder samples on going from 300 to 77 K (466 to 478 nm for  $\text{X}^- = \text{PF}_6^-$ , 449 to 462 nm for  $\text{X}^- = \text{BF}_4^-$ , 452 to 462 nm for  $\text{X}^- = \text{BPh}_4^-$ ) and decay lifetimes increase (14 to 26  $\mu\text{s}$ , 7.5 to 19  $\mu\text{s}$ , and 5.4 to 25  $\mu\text{s}$  for  $\text{PF}_6^-$ ,  $\text{BF}_4^-$  and  $\text{BPh}_4^-$  salts, respectively). The counter-ion also affects the solid-state PLQYs with 43% for  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})][\text{PF}_6]$  and 7% for  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})][\text{BPh}_4]$ .<sup>135</sup> Changing the aryl groups in  $[\text{Cu}(\text{PAr}_3)(\mathbf{27})][\text{PF}_6]$  from Ph to 2-MeC<sub>6</sub>H<sub>4</sub> or 2-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub> has a dramatic effect on the PLQY, even in solution. Upon excitation,  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})]^+$  undergoes significant distortion leading to non-radiative deactivation and emission quenching; the solution PLQY for  $[\text{Cu}(\text{PPh}_3)(\mathbf{27})][\text{PF}_6]$  is <1%. When the steric demands of PAr<sub>3</sub> increase, the non-radiative pathways decrease, and the solution PLQY values increase dramatically to 58% for  $[\text{Cu}\{\text{P}(2\text{-MeC}_6\text{H}_4)_3\}(\mathbf{27})][\text{PF}_6]$ , and 76% for  $[\text{Cu}\{\text{P}(2\text{-}^t\text{BuC}_6\text{H}_4)_3\}(\mathbf{27})][\text{PF}_6]$ . Fig. 21a shows the structure of the  $[\text{Cu}\{\text{P}(2\text{-MeC}_6\text{H}_4)_3\}(\mathbf{27})]^+$  cation, and illustrates that the Me substituents of the tolyl groups provide additional steric protection for the Cu(i) centre. On going from CH<sub>2</sub>Cl<sub>2</sub> solutions of  $[\text{Cu}(\text{PAr}_3)(\mathbf{27})][\text{PF}_6]$  to powders,  $\lambda_{\text{max}}^{\text{em}}$  (PL) blue-shifts, and a blue-shift is also seen along the series PPh<sub>3</sub> to P(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> or P(2-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. Both trends are consistent with greater rigidity of the system. The solid-state PLQY is highest for

$[\text{Cu}\{\text{P}(2\text{-MeC}_6\text{H}_4)_3\}(\mathbf{27})][\text{PF}_6]$  (86%). A thorough investigation of this complex reveals a notably fast phosphorescence decay rate ( $5 \times 10^4 \text{ s}^{-1}$ ) and although TADF takes effect above 160 K, phosphorescence of  $[\text{Cu}\{\text{P}(2\text{-MeC}_6\text{H}_4)_3\}(\mathbf{27})][\text{PF}_6]$  prevails over TADF (60% vs. 40%) at 298 K.<sup>136</sup> This is a very promising family of Cu-iTMCs and one that deserves further investigations in emitting devices.

In  $[\text{Cu}(\text{PPh}_3)(\mathbf{28})(\text{NCMe})][\text{BF}_4]$ , the crystal structure reveals inter-ligand  $\pi$ -stacking (Fig. 21b) and significant steric protection of the Cu(i) centre. The powdered compound exhibits a blue-green emission ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 492 \text{ nm}$ ) with PLQY = 27.9% and  $\tau = 235 \mu\text{s}$ , and it is proposed that this originates from ILCT excited states. The variable temperature emission behaviour supports a TADF mechanism at ambient temperatures.<sup>137</sup>

## Mononuclear $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{S})]^+$ and $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{P}^{\wedge}\text{S})]^+$

We recently investigated the effects of replacing the N<sup>^</sup>N donor set by the N<sup>^</sup>S ligands **29–34** (Scheme 13).  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\mathbf{29})][\text{PF}_6]$  and  $[\text{Cu}(\text{P}^{\wedge}\text{P})(\mathbf{30})][\text{PF}_6]$  with P<sup>^</sup>P = POP and xantphos<sup>138</sup> and  $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{S})][\text{PF}_6]$  with N<sup>^</sup>S = **31**, **32**, **33** and **34**<sup>139</sup> are very weakly emissive in the solid state. Powdered samples of  $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{S})][\text{PF}_6]$  with N<sup>^</sup>S = **31**, **32**, **33** and **34** are yellow emitters with PLQYs in the range 4.7–10.8%, the highest value being for  $[\text{Cu}(\text{xantphos})(\mathbf{31})][\text{PF}_6]$ . This compound was incorporated as the electrolumiphore in a LEC, but exhibited poor EL and poor charge transporting properties.<sup>139</sup>

The neutral complex  $[\text{Cu}(\text{dppb})(\mathbf{35})]$  (dppb = 1,2-bis(diphenylphosphano)benzene, H<sub>35</sub> is shown in Scheme 13) is a green emitter. In the solid state,  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 521 \text{ nm}$  and PLQY = 52% at 293 K, and the corresponding values at 77 K are 534 nm and 73%, with an increased decay lifetime on cooling. With a value of  $\Delta E_{\text{ST}}$  of 309 cm<sup>-1</sup> (0.038 eV),  $[\text{Cu}(\text{dppb})(\mathbf{35})]$  shows efficient TADF behaviour at room temperature. The strong electron-donating character of the  $[\mathbf{35}]^-$  ligand reduces the Cu contribution to the highest occupied MOs of  $[\text{Cu}(\text{dppb})(\mathbf{35})]$ , and as a result, LLCT rather than MLCT character in the excited states becomes important. Solution-processed OLEDs with an active layer comprising 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl doped with 10%  $[\text{Cu}(\text{dppb})(\mathbf{35})]$  were fabricated. Additional doping with di-[4-(N,N-ditolylamino)phenyl]cyclohexane contributed to the best OLED current efficiency of 21.3 cd A<sup>-1</sup> and EQE<sub>max</sub> of 7.8%.<sup>140</sup>

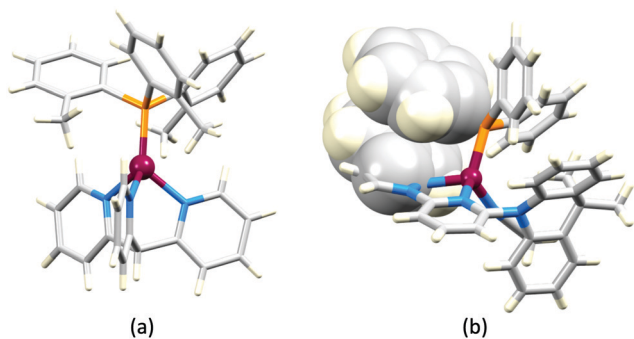
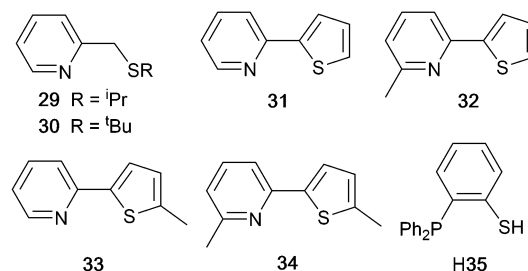


Fig. 21 (a) Structure of the cation in  $[\text{Cu}\{\text{P}(2\text{-MeC}_6\text{H}_4)_3\}(\mathbf{27})][\text{PF}_6]$  (CSD refcode HIRJEA). (b) The structure of  $[\text{Cu}(\text{PPh}_3)(\mathbf{28})(\text{NCMe})]^+$  in the  $[\text{BF}_4]^-$  salt (refcode NAVFUO) showing  $\pi$ -stacking between one phenyl ring of PPh<sub>3</sub> and the phenyl ring of **28**.

Scheme 13 Structures of chelating N<sup>^</sup>S and P<sup>^</sup>S ligands.





$\lambda_{\text{max}}^{\text{em}}(\text{PL})$  of a pristine thin-film (*ca.* 554 nm). Under a driving voltage of 5 V, the LEC had a fast a turn-on to reach a  $\text{Lum}_{\text{max}}$  of  $108 \text{ cd m}^{-2}$ . However, the decay of the EL was rapid. A longer EL lifetime was achieved at the expense of brightness with a 4 V driving voltage. This contribution from Brüggeler and De Cola in 2014 is noteworthy for being a relatively early report of TADF heteroleptic copper(i) emitters proven to function in LECs.<sup>143</sup>

We now move to polynuclear copper(i) complexes featuring bridging N-donor ligands. The majority are neutral compounds and are included because of some notable PL and device performances.  $[\text{Cu}_2(\text{POP})_2(\mu\text{-37})_2]$  (Fig. 22d),  $[\text{Cu}_2(\text{POP})_2(\mu\text{-38})_2]$  and  $[\text{Cu}_2(\text{POP})_2(\mu\text{-39})_2]$  differ in the functionalization of a phenyl ring in the bis(N^N) ligand (Scheme 14). As is typical, relatively low solution PLQYs are enhanced on going to a more rigid matrix. In PMMA films (20% weight concentration), PLQYs of 20, 16 and 26% ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 514, 506$  and  $512 \text{ nm}$ ) for  $[\text{Cu}_2(\text{POP})_2(\mu\text{-37})_2]$ ,  $[\text{Cu}_2(\text{POP})_2(\mu\text{-38})_2]$  and  $[\text{Cu}_2(\text{POP})_2(\mu\text{-39})_2]$ , respectively, are observed, and further improvement in PLQY is seen when moving from PMMA to PYD2 (see Fig. 15 for PYD2). The compounds are TADF emitters at ambient temperatures. On going from 298 to 77 K, values of  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  for solid  $[\text{Cu}_2(\text{POP})_2(\mu\text{-37})_2]$ ,  $[\text{Cu}_2(\text{POP})_2(\mu\text{-38})_2]$  and  $[\text{Cu}_2(\text{POP})_2(\mu\text{-39})_2]$  red-shift from 509, 519 and 503 nm, respectively, to 523, 546 and 516 nm, and decay lifetimes increase (5.5, 16 and 5.5  $\mu\text{s}$  to 158, 356 and 209  $\mu\text{s}$ , respectively). The experimentally determined  $S_1\text{-}T_1$  separations,  $\Delta E_{\text{ST}}$ , are 0.089, 0.132 and 0.094 eV (*ca.* 700, 1060, 800  $\text{cm}^{-1}$ ) for  $[\text{Cu}_2(\text{POP})_2(\mu\text{-37})_2]$ ,  $[\text{Cu}_2(\text{POP})_2(\mu\text{-38})_2]$  and  $[\text{Cu}_2(\text{POP})_2(\mu\text{-39})_2]$ , respectively. The promising PL properties of these compounds led to them being used as electroluminophores in solution-processed, multilayer OLEDs with PYD2 (see Fig. 15) as the host material. The OLED with  $[\text{Cu}_2(\text{POP})_2(\mu\text{-39})_2]$  exhibited the highest values of EQE (8.3%) and  $\text{Lum}_{\text{max}}$  ( $2525 \text{ cd m}^{-2}$ ), with the hole-transporting properties of the carbazole group in 39 contributing to the performance.<sup>144</sup>

In 2019, Titov *et al.* reported the first example of a cyclic tricopper(i) pyrazolate displaying TADF behaviour.<sup>145</sup>  $[\text{Cu}_3(\text{dppm})(\mathbf{40})_3]$  (Scheme 14 shows H40, and dppm = bis(diphenylphosphano)methane) contains two Cu(i) centres bridged by both N^N and P^P domains and one two-coordinate Cu(i) bound only by N-donors (Fig. 23a). The authors comment that the photophysical properties are influenced by intramolecular structural features rather than by intermolecular interactions. It is worth noting, therefore, that the crystal structure of  $[\text{Cu}_3(\text{dppm})(\mathbf{40})_3]$  exhibits  $\pi$ -stacking between two Ph rings of dppm (Fig. 23b), reminiscent of the intra-POP interactions described earlier. On going from 298 to 77 K, the solid-state emission of  $[\text{Cu}_3(\text{dppm})(\mathbf{40})_3]$  shifts from 514 to 554 nm, and  $\tau$  increases from 32.7 to 148.6  $\mu\text{s}$ , consistent with TADF behaviour. The value of  $\Delta E_{\text{ST}}$  derived from experimental data is estimated to be  $1080 \pm 60 \text{ cm}^{-1}$  ( $0.13 \pm 0.01 \text{ eV}$ ). The PL properties suggest that this and related trinuclear species may find applications in lighting devices, but no relevant OLED data are yet available.

The metallopolymer  $[\mathbf{41}][\text{BF}_4]_{2n}$  was prepared by condensation of [3,3'-bipyridine]-6,6'-dicarbaldehyde and 1,1'-biphenyl-4,4'-diamine in the presence of  $\text{Cu}(\text{BF}_4)_2$  and POP. A DMF solution of the polymer gave an emission with  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 780 \text{ nm}$ , but after

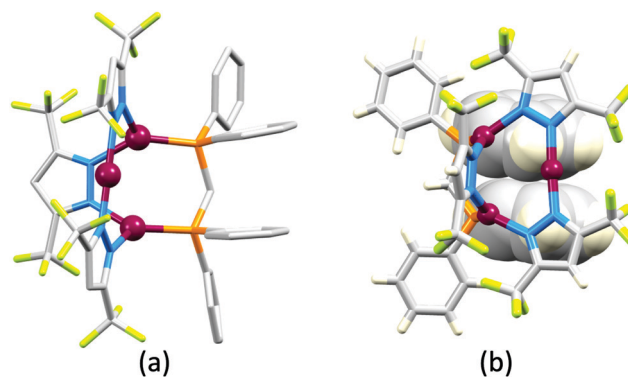


Fig. 23 (a) Structure of  $[\text{Cu}_3(\text{dppm})(\mathbf{40})_3]$  (CSD refcode NOGZOB) with H atoms omitted, and (b) view of the same molecule showing the  $\pi$ -stacking within the dppm ligand.

heating at  $160 \text{ }^\circ\text{C}$ , a yellow gel formed for which  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 580 \text{ nm}$ ; cooling reversed the sol-gel transition. The changes were attributed to reversible dissociation of the complex. LECs were fabricated using an architecture similar to that shown in Fig. 22c, with a  $100 \pm 20 \text{ nm}$  active layer and  $100 \text{ nm}$  Al cathode layer. With an onset voltage of *ca.* 4 V, a value of  $\text{Lum}_{\text{max}} = 3 \text{ cd m}^{-2}$  was reached. At low bias, the EL was in the IR region, but an increase in voltage produced a blue-shift eventually giving yellow EL. The process was reversible and, by analogy with the solgel transition, was explained in terms of reversible dissociation of  $[\text{Cu}(\text{POP})]^+$  domains from the organic polymer backbone. Although TADF was not demonstrated in this system, the investigation is of relevance for this review in terms of establishing the effects of heat on PL and of higher bias in LECs containing heteroleptic copper(i) emitters.<sup>146</sup>

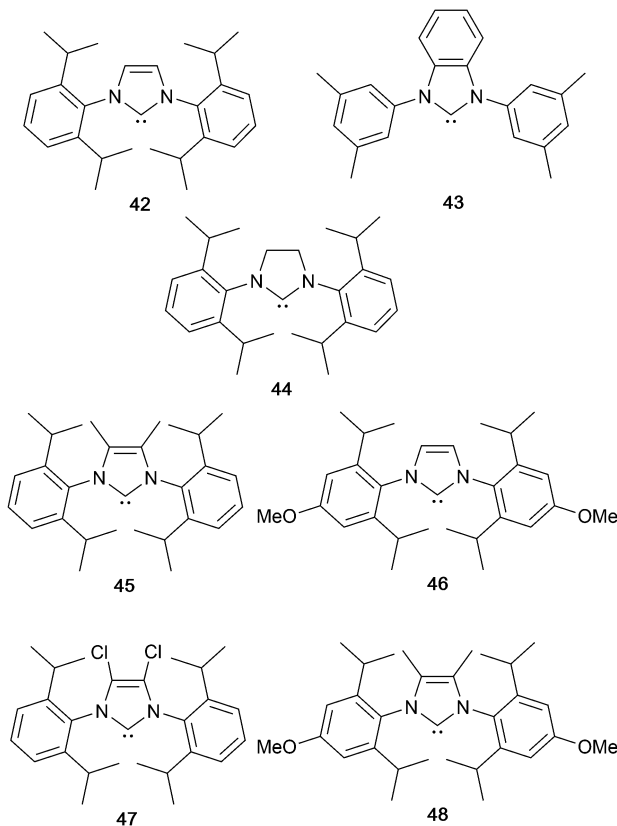
## Copper(i) complexes with N-heterocyclic carbenes

N-Heterocyclic carbenes (NHCs) are characterized by exhibiting strong  $\sigma$ -donating and weak  $\pi$ -accepting properties. The potential for employing NHC ligands in emissive three-coordinate copper(i) compounds was described by Thompson and coworkers between 2010 and 2014.<sup>147-149</sup> In 2019, Danopoulos *et al.* provided a thorough overview of the field of NHC copper complexes including cyclic alkyl-amino carbenes (cAACs),<sup>150</sup> and we have therefore chosen to focus on early pivotal investigations, and then on Cu-iTMCs (*i.e.* ionic complexes) which incorporate NHC ligands.

### Three-coordinate copper

With respect to TADF, a comparison of the properties of  $[\text{Cu}(\mathbf{42})(\text{py}_2\text{BME}_2)]$  and  $[\text{Cu}(\mathbf{43})(\text{py}_2\text{BME}_2)]$  is highly instructive; NHCs **42** and **43** are shown in Scheme 15, and  $[\text{py}_2\text{BME}_2]^-$  (dimethyldi(pyridin-2-yl)borate) acts as an N^N ligand in an analogous fashion to  $[\text{pz}_2\text{BH}_2]^-$  (see Fig. 6). At 300 K, solid  $[\text{Cu}(\mathbf{42})(\text{py}_2\text{BME}_2)]$  and  $[\text{Cu}(\mathbf{43})(\text{py}_2\text{BME}_2)]$  are blue and yellow emitters, respectively, with  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 475$  and  $575 \text{ nm}$  and PLQYs of 76 and 73%. At 77 K,  $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 490$  and  $585 \text{ nm}$ , respectively, and values of  $\tau$  are 34 and 21  $\mu\text{s}$ , compared to 11

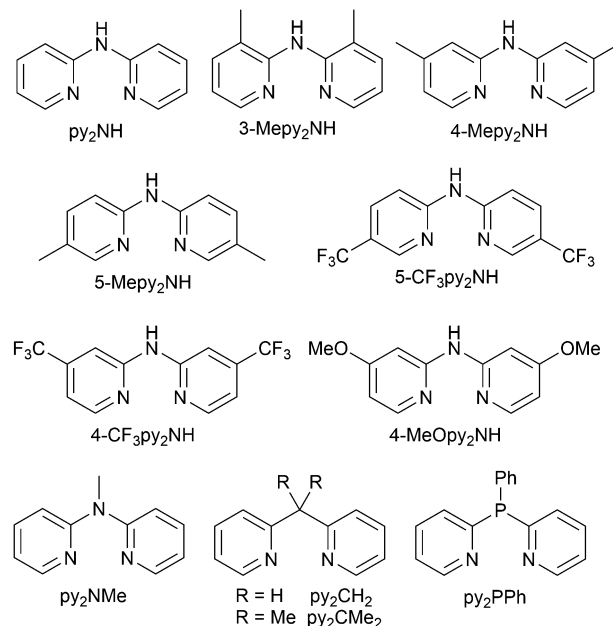




Scheme 15 Structures of NHC ligands 42–48.

and 18  $\mu\text{s}$  at 300 K. For  $[\text{Cu}(\mathbf{42})(\text{py}_2\text{BMe}_2)]$ ,  $\Delta E_{\text{ST}}$  is  $740\text{ cm}^{-1}$  (0.092 eV) allowing this complex to exhibit TADF behaviour at ambient temperatures.  $[\text{Cu}(\mathbf{42})(\text{py}_2\text{BMe}_2)]$  shows two radiative decay paths: 62% TADF vs. 38% phosphorescence. In contrast, on going from  $\mathbf{42}$  to  $\mathbf{43}$ , expanding the conjugation and replacing the 2,6-isopropyl by 3,5-dimethyl groups lead to a significantly increased value of  $\Delta E_{\text{ST}}$  in  $[\text{Cu}(\mathbf{43})(\text{py}_2\text{BMe}_2)]$  ( $3000\text{ cm}^{-1}$ , 0.37 eV) which militates against RISC and, therefore, TADF. The different  $\text{N}_{\text{NHC}}\text{-C}_{\text{NHC}}\text{-Cu-N}_{\text{py}}$  torsion angles of  $5^\circ$  in  $[\text{Cu}(\mathbf{42})(\text{py}_2\text{BMe}_2)]$  vs.  $70^\circ$  in  $[\text{Cu}(\mathbf{43})(\text{py}_2\text{BMe}_2)]$  are key to the different photophysical behaviours, and lay the foundations for rational structural design within this family of copper(I) emitters.<sup>39</sup> Thus, NHCs containing 2,6-isopropylphenyl substituents (e.g.  $\mathbf{42}$ ,  $\mathbf{44}$ – $\mathbf{48}$  in Scheme 15) are popular choices for NHC copper(I) complexes.

Replacement of the  $[\text{BMe}_2]^-$  unit in  $[\text{py}_2\text{BMe}_2]^-$  by  $\text{CR}_2$ , NR or PR leads to neutral  $\text{N}^{\wedge}\text{N}$  ligands and an entry into NHC-containing Cu-iTMCs for LECs. This strategy complements the investigations of the luminescent three-coordinate complexes  $[\text{Cu}(\text{phen})(\mathbf{42})]^+$ ,<sup>147,151,152</sup>  $[\text{Cu}(\text{bpy})(\mathbf{42})]^+$  and  $[\text{Cu}(4,4'\text{-Me}_2\text{bpy})(\mathbf{42})]^+$ .<sup>151,152</sup> Attempts to isolate  $[\text{Cu}(2,9\text{-Me}_2\text{phen})(\mathbf{42})][\text{PF}_6]$  led only to the homoleptic complexes  $[\text{Cu}(2,9\text{-Me}_2\text{phen})_2][\text{PF}_6]$  (four-coordinate Cu) and  $[\text{Cu}(\mathbf{42})_2][\text{PF}_6]$  (two-coordinate Cu), indicating that the combined steric demands of the Me groups in 2,9-Me<sub>2</sub>phen and the <sup>i</sup>Pr substituents in  $\mathbf{42}$  are too great for a three-coordinate Cu(I) centre.<sup>151</sup>  $[\text{Cu}(\text{phen})(\mathbf{42})][\text{OTf}]$ ,<sup>147</sup>  $[\text{Cu}(\text{phen})(\mathbf{42})][\text{PF}_6]$ ,  $[\text{Cu}(\text{bpy})(\mathbf{42})][\text{PF}_6]$  and  $[\text{Cu}(4,4'\text{-Me}_2\text{bpy})(\mathbf{42})][\text{PF}_6]$ <sup>151</sup> are weakly emissive in solution, with some enhancement seen for  $[\text{Cu}(\text{phen})(\mathbf{42})][\text{OTf}]$  in

Scheme 16 Structures of di(pyridin-2-yl)amine  $\text{N}^{\wedge}\text{N}$  ligands.

frozen 2-MeTHF at 77 K.<sup>147</sup> In contrast, use of di(pyridin-2-yl)amines  $\text{py}_2\text{NH}$ , 3-Mepy<sub>2</sub>NH, 4-Mepy<sub>2</sub>NH and 5-py<sub>2</sub>NH (Scheme 16) lead to the respective  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\mathbf{42})][\text{PF}_6]$  complexes which are blue-emitters in the solid state ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 436\text{--}488\text{ nm}$ ) with PLQYs in the range 5–86%, the highest being for  $[\text{Cu}(3\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$ . Decay lifetimes are between 17 and 44  $\mu\text{s}$ .<sup>151,152</sup> The emission properties of  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{44})][\text{PF}_6]$  ( $\lambda_{\text{max}}^{\text{em}}(\text{PL}) = 484\text{ nm}$ , PLQY = 88%,  $\tau = 51\text{ }\mu\text{s}$ ) are similar to those of  $[\text{Cu}(3\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$ . This series of compounds represented the first  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  species with high PLQYs and blue emissions. Critically, use of a di(pyridin-2-yl)amine rather than a planar (e.g. bpy or phen)  $\text{N}^{\wedge}\text{N}$  domain modifies the structure (Fig. 24) such that there is an increase in the HOMO–LUMO separation. An important structural feature of this series of heteroleptic complexes is intramolecular, inter-ligand  $\text{CH}\cdots\pi$  interactions between pyridine CH and *N*-phenyl substituents (Fig. 24c).<sup>151</sup> This interaction appears to be especially important in improving the air and moisture stability of the compounds in the solid state.<sup>153</sup> The investigations of  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  Cu-iTMCs were extended to a wider range of NHC (Scheme 15) and  $\text{py}_2\text{NH}$ -type  $\text{N}^{\wedge}\text{N}$  (Scheme 16) ligands in order to establish structure–property relationships and to demonstrate TADF in three-coordinate  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  complexes.<sup>154</sup> In respect of the  $\text{N}^{\wedge}\text{N}$  ligands, the presence of electron-donating groups (Me, OMe) leads to a blue-shifted emission, whereas electron-withdrawing groups ( $\text{CF}_3$ ) cause a red-shift; going from  $\text{py}_2\text{NH}$  to  $\text{py}_2\text{NMe}$  leads to a small blue-shift in  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  of  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$ . A correlation between the presence of  $\text{H}_{\text{N}^{\wedge}\text{N}}\cdots\text{F}_{\text{anion}}$  contacts and enhanced PLQY was also proposed. It was also noted that along the series  $[\text{Cu}(\text{py}_2\text{NH})(\text{NHC})][\text{PF}_6]$  in which NHC =  $\mathbf{42}$ ,  $\mathbf{45}$ ,  $\mathbf{46}$ ,  $\mathbf{47}$  and  $\mathbf{48}$  (Scheme 15), an increase of the  $\sigma$ -donation of the NHC corresponds to an increase in the solid-state PLQY (e.g. 17% for  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{47})][\text{PF}_6]$ ), 22% for  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  and 64% for  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{48})][\text{PF}_6]$ .



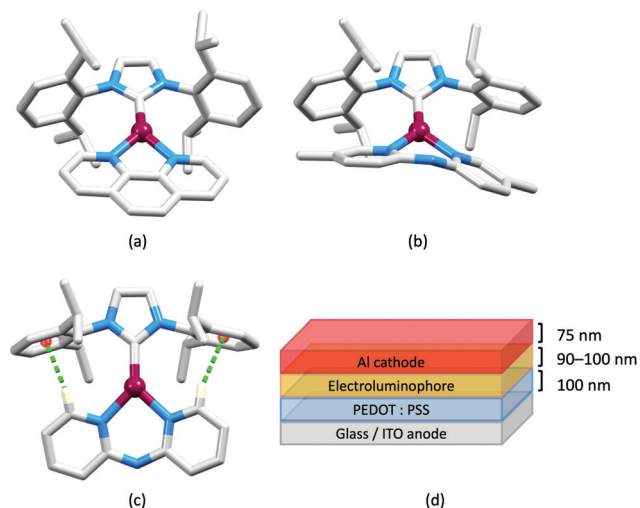


Fig. 24 Comparison of the structures of the  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  cations in (a)  $[\text{Cu}(\text{phen})(\mathbf{42})][\text{BF}_4]$  (CSD refcode SORNOE) and (b)  $[\text{Cu}(5\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  (refcode SORPIA). (c) Intramolecular  $\text{CH}\cdots\pi$  interactions in  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  (refcode SORPOG). (d) Architecture of the LECs containing Cu-iTMCs with NHC and  $\text{py}_2\text{NH}$ -type  $\text{N}^{\wedge}\text{N}$  ligands; LECs were driven using a pulsed current.

This correlates to a trend in the  $\text{Cu}-\text{C}_{\text{NHC}}$  bond length: the shorter the  $\text{Cu}-\text{C}_{\text{NHC}}$ , the higher the PLQY. LECs have been fabricated with the configuration shown in Fig. 24d with  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$ ,  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{48})][\text{PF}_6]$ ,  $[\text{Cu}(4\text{-CF}_3\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  or  $[\text{Cu}(3\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  in the active layer. LECs with  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  and  $[\text{Cu}(3\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  exhibited  $\text{Lum}_{\text{max}} = 56$  and  $310 \text{ cd m}^{-2}$ , respectively, and use of  $[\text{Cu}(3\text{-Mepy}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  provided the first blue-emitting copper-based LEC ( $\lambda_{\text{max}}^{\text{em}}(\text{EL}) = 490\text{--}500 \text{ nm}$ ). Gaillard, Costa and coworkers note that one difficulty is that the  $[\text{Cu}(\text{py}_2\text{NH})(\text{NHC})][\text{PF}_6]$  complexes slowly degrade in solution (see later).<sup>154</sup>

Gaillard, Costa and coworkers have extended the use of  $\text{py}_2\text{NH}$ -type ligands to  $\text{py}_2\text{CH}_2$ ,  $\text{py}_2\text{CMe}_2$  and  $\text{py}_2\text{PPh}$  (Scheme 16), each combined with NHC **42** in  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})][\text{PF}_6]$  salts. Along the series  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\mathbf{42})][\text{PF}_6]$ , the solid-state emission  $\lambda_{\text{max}}^{\text{em}}(\text{PL})$  at 298 K is red-shifted for  $\text{N}^{\wedge}\text{N} = \text{py}_2\text{CH}_2$ ,  $\text{py}_2\text{CMe}_2$  and  $\text{py}_2\text{PPh}$  (473, 474 and 503 nm, respectively) compared to 463 nm for  $\text{py}_2\text{NH}$ . PLQYs are lowest for  $[\text{Cu}(\text{py}_2\text{CH}_2)(\mathbf{42})][\text{PF}_6]$  (15%) and highest for  $[\text{Cu}(\text{py}_2\text{PPh})(\mathbf{42})][\text{PF}_6]$  (86%). On going from 298 to 77 K, all compounds show a red-shifted emission and extended  $\tau$  values, e.g. 503 to 519 nm, and 13 to 87  $\mu\text{s}$  for  $[\text{Cu}(\text{py}_2\text{PPh})(\mathbf{42})][\text{PF}_6]$ , consistent with TADF. The nature of the bridging group in the  $\text{py}_2\text{X}$  ligand does not have a significant effect on  $\Delta E_{\text{ST}}$ , values of which were determined as 0.095 eV (ca.  $760 \text{ cm}^{-1}$ ) for  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$ , 0.12 eV (ca.  $1000 \text{ cm}^{-1}$ ) for  $[\text{Cu}(\text{py}_2\text{CH}_2)(\mathbf{42})][\text{PF}_6]$ , 0.10 eV (ca.  $800 \text{ cm}^{-1}$ ) for  $[\text{Cu}(\text{py}_2\text{CMe}_2)(\mathbf{42})][\text{PF}_6]$ , and 0.10 eV (ca.  $800 \text{ cm}^{-1}$ ) for  $[\text{Cu}(\text{py}_2\text{PPh})(\mathbf{42})][\text{PF}_6]$ . This series of TADF-emitters was incorporated into LECs with an architecture similar to that shown in Fig. 25d, but with layer thicknesses of 70 nm PEDOT:PSS, 90 nm electrolumiphore, and 90 nm Al. Compared to the complexes containing  $\text{py}_2\text{NH}$  and  $\text{py}_2\text{CH}_2$ ,  $[\text{Cu}(\text{py}_2\text{CMe}_2)(\mathbf{42})][\text{PF}_6]$  and  $[\text{Cu}(\text{py}_2\text{PPh})(\mathbf{42})][\text{PF}_6]$  showed enhanced ionic mobilities which allowed the LECs to be driven under lower pulsed currents.

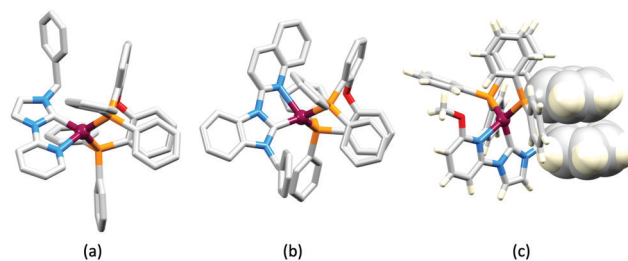


Fig. 25 Structures of (a) the  $[\text{Cu}(\text{POP})(\mathbf{49})]^+$  cation, and (b) the  $[\text{Cu}(\text{POP})(\mathbf{50})]^+$  cation in their  $[\text{PF}_6]^-$  salts (CSD refcodes QAKPIE and QAKPUQ). H atoms are omitted for clarity. (c) Structure of the  $[\text{Cu}(\text{POP})(\mathbf{52})]^+$  cation in the  $[\text{PF}_6]^-$  salt (refcode ZIKTEV) showing (space-filling representation) the  $\pi$ -stacking between the Ph ring in **52** and one arene ring of the POP backbone; there is a second  $\pi$ -stacking contact within the POP ligand (top of figure).

Fast turn-on with values of  $\text{Lum}_{\text{max}} = 6.2$  and  $13 \text{ cd m}^{-2}$  and efficacy = 0.19 and  $0.39 \text{ cd A}^{-1}$ , respectively, were achieved at the lowest applied current (0.5 mA).<sup>155</sup> The development of NHC Cu-iTMCs for blue- and green-emitting LECs has gained momentum, but as previously mentioned, degradation of  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{NHC})]^+$  species during solution processing is problematic. An important contribution which addresses device optimization demonstrates the use of ionic additives, as well as a hole transporter. With such modifications, the  $\text{Lum}_{\text{max}}$  of LECs containing  $[\text{Cu}(\text{py}_2\text{NH})(\mathbf{42})][\text{PF}_6]$  could be boosted from 20 to  $160 \text{ cd m}^{-2}$ , and the efficiency from 0.17 to  $1.2 \text{ cd A}^{-1}$ .<sup>153</sup>

## Two-coordinate copper

In 2019, Marian and coworkers reported the TADF behaviour of a series of two-coordinate Cu-iTMCs. Initial findings were that  $[\text{Cu}(\text{py})(\mathbf{42})][\text{BF}_4]$ ,  $[\text{Cu}(2\text{-Mepy})(\mathbf{42})][\text{BF}_4]$  and  $[\text{Cu}(2\text{-Phpy})(\mathbf{42})][\text{BF}_4]$  ( $\text{py} = \text{pyridine}$ , 2-Mepy = 2-methylpyridine, 2-Phpy = 2-phenylpyridine) were poorly or non-emissive in single crystal form or in solution, although in powder form or thin films, the cation-anion pairing through the formation of Cu-F-B interactions turned on a blue or blue-green PL.<sup>156</sup> This was followed up with a theoretical investigation of  $[\text{Cu}(\text{py})(\mathbf{42})][\text{BF}_4]$ ,  $[\text{Cu}(2\text{-Mepy})(\mathbf{42})][\text{BF}_4]$  and  $[\text{Cu}(2\text{-Phpy})(\mathbf{42})][\text{BF}_4]$  which showed that the PL is quenched by locally excited triplet states if, as in **42**, the NHC ligand carries two diisopropylphenyl substituents. Replacement of 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$  in the NHC ligand **42** in  $[\text{Cu}(\text{py})(\mathbf{42})]^+$  by adamantyl groups suppresses emission quenching and the theoretical study predicts that TADF will then be efficient. Further, introducing electron-withdrawing or -donating substituents into the 4-position in the py ligand should lead to emission tuning over the UV, blue and green regions.<sup>157</sup> Although these results should motivate synthetic investigations, the predictions do not yet appear to have been experimentally established. Extensive calculational studies from Marian and coworkers in 2020, should provide ground rules for structure design in NHC copper(i) coordination compounds. One pertinent conclusion relevant to two-coordinate (linear) complexes is that only species with  $\text{S}_1$  and  $\text{T}_1$  states with LLCT character have sufficiently small values of  $\Delta E_{\text{ST}}$  to facilitate TADF. Complexes in which MLCT character predominates in the  $\text{S}_1$  and  $\text{T}_1$  excited states tend to decay by phosphorescence.<sup>41</sup>







There have been a number of endeavours to develop structure–property relationships to assist the synthetic chemist in ligand design,<sup>57,60,102,154</sup> but often, simple ligands such as 6,6'-Me<sub>2</sub>bpy or 2,9-Me<sub>2</sub>phen have proved to be the best performing. It is critical that the N<sup>∧</sup>N ligand possesses appropriate substituents to prevent flattening of the coordination sphere excited state. As far as wide-bite angle bis(phosphanes) are concerned, POP and xantphos remain the most popular, but RN-xantphos ligands (derived from the commercially available HN-xantphos) deserve further exploitation in [Cu(RN-xantphos)(N<sup>∧</sup>N)]<sup>+</sup> coordination compounds.

Most of the heteroleptic copper(i) complexes incorporating N- and P-donor ligands are red, orange or yellow emitters. Colour tuning into the blue region of the spectrum has been most notably achieved by moving to NHC-containing compounds. This area remains a valuable playground for the synthetic chemist.

Our longstanding interest in structural chemistry has led us to put an emphasis in this review on solid-state structural features such as  $\pi$ -stacking interactions and other inter-ligand interactions which may impact on PLQYs. Since it has been established that, for [Cu(P<sup>∧</sup>P)(phen)]<sup>+</sup> derivatives, there is a direct relationship between the number of intramolecular  $\pi$ -interactions in the ground state and the PLQY value,<sup>60</sup> it is invaluable to correlate crystal-structural features with solid-state photophysical behaviour.

Finally, although we have, where possible, reported LEC performances, it is difficult to compare device figures-of-merit because of the differing LEC configurations and operating conditions. There are only a few investigations that focus on device optimization for a given Cu-iTMC electroluminophore, and we conclude that this is one area that is ripe for future development.

## Author contributions

C. E. H. and E. C. C. contributed equally to the writing of this review.

## Conflicts of interest

There are no conflicts to declare.

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