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## Reducing Lifetime in Cu(I) Complexes with Thermally Activated. View Article Online Delayed Fluorescence and Phosphorescence promoted by Chalcogenolate-Diimine Ligand

Giliandro Farias<sup>+</sup>, Cristian A.M. Salla<sup>#</sup>, Renata S. Heying<sup>+</sup>, Adailton J. Bortoluzi<sup>+</sup>, Sergio F. Curcio<sup>\$</sup>, Thiago Cazati<sup>\$</sup>, Paloma L. dos Santos<sup>&</sup>, Andrew P. Monkman<sup>&</sup>, Bernardo de Souza<sup>+\*</sup>, Ivan H. Bechtold<sup>#\*</sup>

\*Corresponding authors: <u>bernardo.souza@ufsc.br</u>; tel: +55 48 37213608 <u>ivan.bechtold@ufsc.br</u>; tel: +55 48 37212304

<sup>+</sup>Department of Chemistry, Universidade Federal de Santa Catarina, 88040-900
<sup>+</sup>Department of Physics, Universidade Federal de Santa Catarina, 88040-900
<sup>+</sup>Florianópolis, SC, Brazil
<sup>+</sup>Department of Physics, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, MG, Brazil

<sup>&</sup>Department of Physics, Durham University, South Road, Durham, DH1 3LE, U.K.

#### ABSTRACT

Luminescent copper(I) complexes have drawn attention due to their promising performance as alternative optoelectronic materials to the well-known heavy transition metals complexes. Herein, we report the synthesis of six luminescent Cu(I) complexes with phosphines and 1,10-phenanthroline-derived ligands with thiadiazole and selenodiazole groups in order to evaluate the effect of heavy atom on their photophysical properties. Steady-state and time-resolved spectroscopy confirmed delayed fluorescence emission via a thermally activated delayed fluorescence mechanism in all cases. The experimental spectroscopic data was analyzed with detailed quantum-chemical calculations. Interestingly, these complexes did not show the expected "heavy atom effect", that enhances the spin-orbit coupling matrix elements, but nevertheless the addition of the heavier chalcogens contributed to reduce the photoluminescence lifetime to roughly 800 ns, which is the lowest reported so far for such TADF materials.

KEYWORDS: Copper(I) complexes, Heavy atom effect, TADF, phosphorescence View Article Online DOI: 10.1039/DOTC03660A

#### INTRODUCTION

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During the past three decades, many research groups have been studying alternative luminescent materials to replace the most successful, currently employed transition metal complexes, such as those of ruthenium, platinum, osmium, or iridium in organic light emitting diodes (OLEDS).<sup>1–4</sup> Cu(I) complexes gained attention due to their promising optoelectronic performance, because of their low cost and high photoluminescence quantum yields (PLQY), combined with easy color tuning by variation of ligands.<sup>5–8</sup> Indeed, copper appears to be particularly interesting due to its spin-orbit coupling (SOC) constant of  $\xi_{Cu}$ = 851 cm<sup>-1</sup>, which is known to facilitate ultrafast intersystem crossing (ISC) S<sub>n</sub> $\rightarrow$ T<sub>n</sub>.<sup>9</sup> Furthermore, mainly due to the pioneering work of McMillin, it is known that Cu(I) complexes can exhibit thermally activated delayed fluorescence (TADF).<sup>10–13</sup>

Heteroleptic complexes of the type [Cu(N^N)(P^P)]<sup>+</sup>, where N^N and P^P indicate chelating diamine and diphosphine ligands respectively, presented promising photophysical properties, *e.g.*, highly luminescent Cu(I) complexes, with long-lived excited-states. The low-lying Metal-to-Ligand Charge Transfer excited state (MLCT) of these copper complexes determines their photophysical properties, and allows emission in the visible region.<sup>6,14</sup> As the LUMO of these complexes is usually centered on the diamine, the HOMO-LUMO energy gap has been modulated employing different *N*-heterocyclics, such as phenanthroline,<sup>15,16</sup> bipyridyl-, pyrazolyl-,<sup>17</sup>triazolyl-,<sup>18</sup> as well as tetrazolyl-based ligands.<sup>19</sup> By using these ligands, a variety of emission colors, including blue and green, have already been reported.<sup>20–24</sup>

In contrast to the heavier metal elements, the SOC in copper is much weaker, and the ligands are not generally able to enhance the SOC in these complexes. Consequently, cuprous phosphorescent complexes usually possess long emission lifetimes of up to a hundred of microseconds. Unfortunately, the long decay times of triplet states facilitate triplet–triplet annihilation (TTA) and triplet-polaron quenching (TPA) in electroluminescence devices<sup>25</sup> limiting their efficiency. However, this detrimental effect can be avoided by the fact that many emissive cuprous complexes can also emit efficiently through TADF mechanism at room temperature, when there is a small energy gap between singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) states.<sup>26–29</sup> Designing these compounds with short

combined TADF and phosphorescence decay times and high PLQYs is still a challenge Article Online DOI: 10.1099/DOTC03660A For instance, radiative decay times of  $[Cu(N^N)(P^P)]^+$  complexes of less than 2–5 µs have not been reported so far.<sup>6,28,30</sup>

Recently, we reported two 1,10-phenanthroline-derived ligands with the thiadiazole and selenodiazole groups, where the heavy atom effect was observed in the photophysics of the ligands and ruthenium complexes. The ligand with a selenodiazole group showed an increase of 200 times in the spin-orbit coupling matrix elements and even phosphorescence emission,<sup>31</sup> and the ruthenium(II) complexes also had their properties altered.<sup>32</sup> These results pointed to a promising effect of the heavy atoms in luminescent complexes and a possibility to enhance the SOC in cuprous complexes.

Here we report the synthesis and characterization of six luminescent Cu(I) complexes with phosphines and 1,10-phenanthroline-derived ligands with the thiadiazole and selenodiazole groups, [1,2,5]thiadiazolo[3,4-*f*][1,10]phenanthroline (TDZP) and [1,2,5]selenadiazolo[3,4-*f*][1,10]phenanthroline (PhenSe) (Chart 1). The complexes have been fully characterized using steady-state and time-resolved spectroscopy, and for all them, crystals have been obtained allowing a full crystallographic analysis. The experimental spectroscopic data have been further rationalized by means of detailed quantum-chemical calculations.



Chart 1. Cu(I) complexes discussed in the introductory part.

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#### **RESULTS AND DISCUSSION**

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#### Synthesis and Characterization

The copper complexes were prepared in excellent yield by a quick reaction of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> with the phosphines and diimines ligands in CH<sub>2</sub>Cl<sub>2</sub>. All final complexes were obtained from crystallization in THF/dichloromethane and used without further purifications. A synthetic route for these is shown in Scheme S1. The obtained compounds are stable in air at least for several months without oxidizing.

The molecular structure of the complexes was determined by single crystal X-ray diffraction studies. The Cu(I) center in the four new complexes (**S1**, **Se1**, **S2** and **Se2**) has a distorted tetrahedral geometry, observed by the strong deviation from the tetrahedral angle around the Cu(I) center, where the dihedral angle between N-Cu-N and P-Cu-P planes are measured to be 76.6 ° for **S1**, 73.0 ° for **Se1**, 78.3 ° for **S2** and 70.5 ° for **Se2**. This situation reflects the specific steric requirements of the ligands, and the stabilization by intramolecular  $\pi$ -stacking interactions, found in many other transition complexes with phosphine ligands.<sup>15</sup> Also, for **S2** and **Se2**, most Cu-P and Cu-N distances are closer than those with PPh<sub>3</sub> ligand. The oxygen atom of the POP ligand in the complexes is at a distance of  $\approx 3$  Å away from the Cu(I) center, and opposite to the coordinated N atoms, indicating a weak interaction between the oxygen atom and Cu(I) center. This suggests that the POP ligand is in closer proximity to the copper atom due to the ether linkage, which is known to increase the probability of charger transfer from the metal to ligand (see below). Bond distances and angles are reported at Table 1 and are similar to those of **C1** and **C2** previously reported.<sup>15</sup>

	C1 <sup>a</sup>	<b>S1</b>	Se1	C2 <sup>a</sup>	<b>S2</b>	Se2
Cu-N1	2.080	2.0877(14)	2.087(2)	2.071	2.0716(13)	2.070(3)
Cu-N10	2.070	2.0827(14)	2.088(2)	2.063	2.0586(12)	2.040(2)
Cu-P1	2.271	2.2588(4)	2.2637(7)	2.261	2.2546(4)	2.2567(8)
Cu-P2	2.245	2.2662(5)	2.2731(8)	2.231	2.2238(4)	2.2197(8)
Cu⋯O	-	-	-	3.205	3.0391(10)	3.105(2)
N1-Cu-N10	80.90	80.01(5)	79.93(8)	80.83	80.75(5)	81.11(10)
P1-Cu-N1	115.44	117.88(4)	111.09(6)	110.81	105.87(4)	107.31(7)
P2-Cu-P1	118.69	116.151(17)	115.75(3)	108.12	112.573(15)	117.47(3)
N10-Cu-P2	103.60	112.67(4)	113.68(6)	109.08	119.99(4)	110.73(7)

 Table 1. Selected bond lengths [Å] for C1-Se2.

a 15

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Fig. 1. ORTEP plot (thermal ellipsoid with 50% probability) of the molecular structure of cation complexes S1, Se1, S2 and Se2. Hydrogens atoms and most of atoms labels are omitted for clarity.

Thermogravimetric analysis (TGA) of **C1–Se2** under nitrogen atmosphere revealed that the initial decomposition temperatures were close to 130 °C for **C1, S1, Se1** and **C2** and 350 °C for **S2** and **Se2** (See Fig. S7). Such thermal stability indicates that all the complexes can undergo thermal treatments until at least 100 °C in device fabrication.

Cyclic voltammetry in  $CH_2Cl_2$  solution was performed to estimate the HOMO and warticle Online DOI: 10.1039/DOTC03660A

LUMO levels from the oxidation and reduction potentials, respectively. Fig. 2 shows the cyclic voltammograms and Table 2 summarizes the electrochemical data. All complexes displayed one anodic process, which is attributed to the oxidation of the copper center. This process is usually quite positive and irreversible due to the dissociation of the complex in solution. The phosphine group had a small effect on the oxidation potential, with the complexes bound to triphenylphosphine having a higher potential when compared with the analogous with the POP ligand, in agreement with the obtained Cu-P distances. In addition, a cathodic process was observed for the complexes **S1**, **Se1**, **S2** e **Se2**. The reversible process of reduction was attributed to redox processes of the ligands TDZP e PhenSe, also observed for the free ligands.<sup>31</sup> The HOMO and LUMO energies obtained from voltammetry agree with the calculated trend from DFT, where the contribution from both the copper atom and the ligands on these frontier orbitals was predicted.



**Fig. 2.** Cyclic voltammograms of **C1-Se2** in  $1 \times 10^{-3}$  mol L<sup>-1</sup> CH<sub>2</sub>Cl<sub>2</sub> solutions under nitrogen atmosphere. The scanning rate is 100 mV s<sup>-1</sup>. Three electrodes electrochemical cell: Gold (working); Pt wire (auxiliary); and Ag/Ag+ (reference). Supporting electrolyte: 0.1 mol L<sup>-1</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub>.

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Complex	F.a/V	E <sub>ox</sub> <sup>a</sup> / V	E <sub>HOMO</sub> <sup>b</sup> / V	E <sub>LUMO</sub> <sup>b</sup> / V	Electrochemical	Optical
	L <sup>red</sup> / V				Bandgap / eV	Bandgap <sup>c</sup> / eV
C1	-	0.79	-5.59	-2.66 <sup>d</sup>	-	2.93
<b>S</b> 1	-1.83	0.88	-5.68	-2.97	2.71	2.75
Se1	-1.79	0.86	-5.66	-3.01	2.65	2.68
C2	-	0.75	-5.55	-2.81 <sup>d</sup>	-	2.74
S2	-1.81	0.83	-5.63	-2.99	2.64	2.69
Se2	-1.71	0.81	-5.61	-3.09	2.52	2.62

 Table 2. Electrochemical properties of C1-Se2.

<sup>a</sup> Determined from peak potentials. <sup>b</sup> Calculated from  $E_{HOMO} = -(4.8 + E_{ox})$  and  $E_{LUMO} = -(4.8 - E_{red})$ .<sup>c</sup> Calculated from the onset of the absorption spectra in solution. <sup>d</sup> Obtained from the sum of the LUMO energy and optical band gap.

#### **Photophysical Properties**

The UV-Vis absorption and emission of complexes **C1-Se2** were performed in CH<sub>2</sub>Cl<sub>2</sub> solution (see Fig. 2 and S9), and with the complexes dispersed 10 wt% in a PMMA matrix (Fig. 2 and S8). All photophysical data are summarized in Table 3. The complexes exhibited an intense absorption band around 250 nm, which is attributed to a  $\pi \rightarrow \pi^*$  transition of the phosphine ligand. The less intense absorption bands with maxima between 300 and 350 nm, are related to the diamine ligand,<sup>31</sup> and could be mainly attributed to intra-ligand charge transfer transitions. As the lower energy absorption band around 400 nm is not present in the ligands, it is safely assigned to spin allowed MLCT involving 3*d* orbitals of Cu(I) and  $\pi^*$  orbitals of diamine.<sup>6,15</sup> Moreover, the molar absorptivity for the MLCT follows the order PhenSe > TDZP > phen (in exception of **S1**) and POP > PPh<sub>3</sub>. However it is not related to the allowedness of the S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> transition, but to the existence of new MLCT states involving the thiadiazole and selenodiazole moieties with close energy, as verified by TD-DFT. The absorption in PMMA was found to be very similar to solution.

**Table 3.** Photophysical data for the Cu(I) complexes in CH<sub>2</sub>Cl<sub>2</sub> solution and 10 wt%PMMA films.

<b>Solution</b> <sup>a</sup>			PMMA films							
	λ <sub>abs</sub> (nm) / ε (L mol <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>em</sub> (nm)	$\lambda_{abs}(\mathbf{nm})$	λ <sub>em</sub> (nm)	Stokes shift (nm)	$\Phi^{\mathrm{b}}$	τ (μs) <sup>c</sup>	$k_r^{ m d}  imes$ $10^5  m s^{-1}$	$k_{nr}^{e} \times$ 10 <sup>5</sup> s <sup>-1</sup>	
C1	352 / 2772	606	350	550	10390	0.11	2.7	0.41	3.30	
<b>S1</b>	370 / 1808	610	370	577		0.04	1.1	0.36	8.73	
Se1	375 / 3232	615	380	592		0.08	1.1	0.73	8.36	
C2	391 / 2840	628	390	560	170	0.13	2.1	0.62	4.14	
S2	404 / 3881	624	395	594	199	0.06	1.2	0.50	7.83	
Se2	396 / 4252	637	400	605	205	0.08	0.8	1.00	11.50	

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 1.0×10<sup>-5</sup> mol L<sup>-1</sup>. <sup>b</sup> The uncertainty in  $\Phi$  was ±0.01. <sup>c</sup> The uncertainty of the lifetime was estimated in ± 0.1 µs. <sup>d</sup> $k_r = \Phi / \tau$ . <sup>e</sup> $k_{nr} = (1 - \Phi) / \tau$ .

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The emission from a degassed solution under excitation of the MLCT band is in the orange region, with maxima at 606, 610, 615, 628, 624 and 637 nm, for C1-Se2, respectively. The emission peaks observed using the PMMA matrix were located in the yellow-orange region, with maxima at 550, 577, 592, 560, 594 and 605 nm for C1-Se2, respectively. These spectra have broad and unstructured gaussian lineshapes, which is in accordance with the MLCT nature of the emitting state. Moreover, the luminescence properties strongly depend on the environment. For instance, as depicted in Fig. 3 and Fig. S9, C1 shows emission in  $\lambda_{max} = 604$  nm in solution and  $\lambda_{max} = 550$  nm in PMMA. Similar trends are observed for the other complexes. These observations can be explained considering the changes in the molecular geometry of the Cu(I) compounds, which take place after MLCT excitation. In the electronic ground state ( $d^{10}$  configuration), the complexes have a pseudo-tetrahedral coordination of the metal ion, whereas in the MLCT excited state, with a  $d^9$  configuration of the metal ion, a flattening distortion of the molecular structure occurs.<sup>7</sup> Therefore, in a rigid matrix these distortions are less favorable, and a higher energy emission is observed. Furthermore, as the emission results from a CT state, it is also influenced by the polarity of the solvent. Thus, as  $CH_2Cl_2$  has a larger polarity than PMMA, a lower energy emission in CH<sub>2</sub>Cl<sub>2</sub> was expected.



**Fig. 3.** Optical absorption spectra of the Cu(I) complexes in CH<sub>2</sub>Cl<sub>2</sub> solution  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> and emission spectra of the studied Cu(I) complexes 10 wt% in PMMA. Emission spectra were obtained with excitation at the lowest energy band absorption maximum.

The PLQY ( $\Phi$ ) and the excited-state lifetimes ( $\tau$ ) for the complexes embedded in the PMMA matrix are shown in Table 3. Interestingly, the presence of the heavy atom reduced both PLQY and lifetime of **S1**, **Se1**, **S2**, and **Se2**, compared to their reference compounds **C1** and **C2**. For complexes with TDZP and PhenSe, the lifetimes were measured in the range of 2.7 µs to 800 ns (Table S3 and Fig. S11). Based on these results, the radiative and nonradiative constants,  $k_r$  and  $k_{nr}$ , were calculated (Table 3). The  $k_r$ follow the order **Se1**> **C1**>**S1** and **Se2**> **C2**>**S2**, indicating that the presence of the PhenSe with a heavy atom enhances the radiative path, while TDZP do not. On the other hand, for all these new complexes the nonradiative path is enhanced too. Such an increase of the nonradiative rate is more pronounced in complexes with TDZP and PhenSe, and is attributed to the lower triplet energy (see below) and the intramolecular  $\pi$ -stacking interactions (comparing the dihedral angle). The presence of the thiadiazole and selenodiazole moieties, distort the complexes from their tetrahedral geometry, as mentioned before, increasing the know pseudo-Jahn-Teller effect in the excited state.<sup>33</sup>

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**Fig. 4.** Time resolved normalized emission spectra at room temperature for **C1-Se2** 10 wt% in PMMA, at 300K (a), 80K (b) and temperature dependence for compound **C1** from 80 K to 320 K, with a 50 K step (c).

Time-resolved spectroscopy was used to follow the excited state dynamics of complexes **C1-Se2**. At room temperature, the luminescence is characterized by a fast

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component followed by a slow bi-exponential decay. The decays obtained as a function Article Online of temperature for all complexes exhibit clear temperature dependence in the delayed fluorescence region (microsecond range), which is characteristic of a TADF mechanism. Fig. 4 shows the emission decays at room temperature (a) and at 80K (b) for all compounds. In Fig. 4c, a more detailed temperature dependence is shown for compound **C1** from 80 K to 320 K, with a 50 K step. In all compounds, the delayed fluorescence emission (microsecond range) shows higher intensity at higher temperatures, which is a characteristic of the TADF mechanism. On the other hand, the longer-lived emission (millisecond range) shows the opposite behavior, the intensity increases by cooling down the films, which is also consistent with a slower depopulation of the triplet state via rISC, thus increasing the phosphorescence intensity.

The time resolved emission spectra collected at room temperature and at 80K are shown in Fig. 5 for **C1** and S11-15 at the supporting information for **C2-Se2**. In the early-collected time resolved emission spectra (1-40 ns), a fast emission at high energy was observed, which is attributed to the prompt fluorescence component as suggested by Li and co-workers.<sup>36</sup> Afterwards, in the microsecond range a new emission is observed close to 550 nm, which is attributed to the triplet state of these compounds. Subsequently, a blue shift is observed in the microsecond range due to the thermal repopulation of the singlet state and consequent mixing of emitting species, i.e. delayed fluorescence and phosphorescence emission. The time resolved emission spectra collected at different temperatures shows a larger blue-shift at lower temperature. These observations are consistent with the presence of thermalized triplet states at higher temperatures.



**Fig. 5.** Time resolved normalized emission spectra at room temperature (up) and 80K (down) for **C1** 10 wt% in PMMA. Films were excited at 355 nm.

The S<sub>1</sub> and T<sub>1</sub> energies (Table 4) were obtained from the onset of the highest and the lowest energy emission from the time-resolved emission spectra at room temperature and 80 K ( $\mu$ s time frame), respectively. As can be observed, the S<sub>1</sub> energy decreases in the presence of the TDZP and PhenSe ligands and also for POP complexes, in agreement with the bathochromic shift observed in the absorption spectra and the steady state emission. The T<sub>1</sub> energy follows the same trend, being lower for **S1** and **Se2**. As the  $k_{nr}$ increases when the energy difference between T<sub>1</sub> and the ground state decreases,<sup>35</sup> the higher  $k_{nr}$  for complexes with TDZP and PhenSe ligands can be attributed to structural distortions, as mentioned before, and the lower triplet state energy for these complexes. In addition, the  $\Delta E(S_1-T_1)$  which is determinant to a faster TADF component into the emission, decreases for complexes with TDZP and PhenSe and POP ligands. Therefore, the lower lifetime obtained for **Se1** and **Se2** can be partially attributed to the fast reconversion from T<sub>1</sub> to S<sub>1</sub>, which corresponds to a faster TADF. However, such a low lifetime for Cu(I) complexes is only possible considering a component of phosphorescence into the emission. Thus, as the phosphorescence decay path depends on

both triplet energy and the SOC between the singlet and triplet states, one can expective Article Online Dol: 10.1039/DOTC03660A lower phosphorescence component for complexes with TDZP and PhenSe moieties.

	C1	<b>S1</b>	Se1	C2	S2	Se2
$S_1 / eV$	2.77	2.67	2.68	2.73	2.57	2.54
<b>T</b> <sub>1</sub> / <b>eV</b>	2.53	2.46	2.51	2.52	2.43	2.42
$\Delta E_{S1-T1} / eV$	0.24	0.21	0.17	0.21	0.14	0.12

**Table 4.** Singlet and Triplet energies obtained from time-resolved spectroscopy.

Density Functional Theory/Time-Dependent DFT Approaches and Photophysical Interpretations

In order to achieve further insights into the nature of the excited states and the emission mechanism, the optimized geometries for the ground state of all complexes were obtained using DFT at the PBE0/def2-TVZP(-f) level. The  $S_0$  geometries are shown in Fig. S16 and the important lengths and angles are listed in Table S4. The vibrational frequencies confirm that the geometries correspond to a minimum of the surface energy potential, since no negative frequencies were found. Moreover, the predicted  $S_0$  geometry for all complexes are in good agreement with the experiment, where the maximum average error found for bond lengths was of 2.4%, and of 6.6% for bond angles, which supports further use of PBE0 in subsequent investigations.

The first insight into the electronic properties of these complexes can be obtained from the calculated HOMO and LUMO, see Fig. 6. For these complexes the HOMO (isosurface with transparency) is largely derived from a 3*d* atomic orbital of the copper (I) center with significant contributions from the coordinating phosphorous atoms, whereas the LUMO is mainly distributed over the diamine. However, the LUMO for C1 and C2 is mostly distributed over phenanthroline moiety, while for the complexes with TDZP and PhenSe the LUMO is centered at the thiazole and selenodiazole, respectively. Thus, the lower energy excited states are expected to be MLCT-like, but involving different  $\pi^*$  orbitals of diamine. Indeed, TD-DFT calculations showed that the low-lying S<sub>1</sub> and T<sub>1</sub> states are more than 88% HOMO→LUMO transitions in S<sub>1</sub> and mixed HOMO→LUMO and HOMO→LUMO-1 (both MLCT) for T<sub>1</sub> (Table S5-S7), being assigned as <sup>1</sup>MLCT and <sup>3</sup>MLCT, respectively.



**Fig. 6.** Frontier molecular orbitals of complexes **C1–Se2** calculated using PBE0/def2-TZVP(-f). The HOMO is shown as the isosurface with transparency.

The LUMO orbital centered at thiazole and selenodiazole moieties also minimize the HOMO and LUMO overlap (Fig. S17) by increasing the spatial separation of these orbitals. That results in a smaller  $\Delta E_{S1-T1}$ , as also obtained from the spectroscopic studies, and agrees well with the calculated  $\Delta E_{S1-T1}$  using the adiabatic energy for such states (Table 5). This larger spatial separation of HOMO and LUMO also reduce the oscillator strength *f* of the S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> transition (<sup>1</sup>MLCT) for complexes with TDZP and PhenSe ligands. Even so, the presence of these ligands resulted in new low energy MLCT states,  $d\rightarrow\pi^*$ (thiadiazole or selenodiazole), close to the  $d\rightarrow\pi^*$ (phen). The net result is a wider and more intense absorption band, as observed in the experimental spectra (compare Table S5-S7 and Fig. S18).

 Table 5. Data of SOC-TD-DFT and adiabatic energy difference for C1-Se2.

	C1	<b>S1</b>	Se1	C2	<b>S2</b>	Se2
$\langle T_1   \hat{H}_{SO}   S_0 \rangle^a$	22.50	24.55	6.09	37.79	26.07	4.44
$\langle T_1   \hat{H}_{SO}   S_1 \rangle^a$	17.11	8.12	2.01	27.65	2.76	0.96
$\langle T_1   \hat{H}_{SO}   S_2 \rangle^a$	6.37	24.42	9.07	6.32	2.59	9.70
$\langle T_1   \hat{H}_{SO}   S_3 \rangle^a$	157.98	156.94	112.72	119.62	152.47	99.99

$\langle T_1   \hat{H}_{SO}   S_4 \rangle^a$	166.35	17.36	130.82	128.53	211.05	116.72 <sup>View Article Online</sup> DOI: 10.1039/D0TC03660A
$\langle T_1   \hat{H}_{SO}   S_5 \rangle^a$	4.70	180.85	66.77	189.82	9.82	99.53
$\langle T_2   \hat{H}_{SO}   S_0 \rangle$	8.36	5.43	42.32	12.33	26.17	31.84
$\langle T_2   \hat{H}_{SO}   S_1 \rangle^a$	15.72	2.46	3.83	21.16	26.17	4.08
$\langle T_2   \hat{H}_{SO}   S_2 \rangle^a$	10.24	12.97	18.27	13.55	4.25	12.82
$(T_2 \hat{H}_{SO} S_3)^a$	22.37	2.51	71.51	34.32	14.77	118.22
$(T_2 \hat{H}_{SO} S_4)^a$	34.46	6.79	59.59	87.76	23.44	90.82
$\langle T_2   \hat{H}_{SO}   S_5 \rangle^a$	111.44	36.34	88.94	29.88	12.95	123.04
$\Sigma \langle T_j   \hat{H}_{SO}   S_i \rangle$	577.59	478.73	611.95	707.73	512.50	712.14
$S_1 {}^b\!/ eV$	2.79	2.35	2.16	2.79	2.46	2.29
$T_1 {}^b\!/ eV$	2.42	2.09	1.98	2.42	2.32	2.23
$\Delta E_{S1-T1}$ Theo / eV	0.37	0.26	0.18	0.37	0.14	0.06
$\Delta E_{S1\text{-}T1}Exp/eV$	0.24	0.21	0.17	0.21	0.14	0.12

 $\overline{{}^{a}\sqrt{\Sigma}\langle T_{j\ (MS=0,\pm1)}|\hat{H}_{SO}|S_{i}\rangle^{2}} \ at \ the \ S_{0} \ optimized \ geometry; \ {}^{b} \ Adiabatic \ energy.$ 

For many Cu(I) complexes, SOC effects provide distinct phosphorescence decay paths in addition to the TADF via S<sub>1</sub>. Therefore, to evaluate both the phosphorescence and the TADF decay paths for C1-Se2 in terms of SOC, we calculate the SOC matrix elements between the first 10 singlet and triplet states,<sup>36</sup> on top of  $S_0$  geometries. The SOC matrix elements, between the first six singlets and the first two triplet states which should have the appreciable contribution to the phosphorescence and the TADF mechanism in these complexes, are shown in Table 5. As one can see, the SOC between  $S_1$  and  $T_1$ , both mainly involving the MLCT transition with same d orbital, decreases for complexes with TDZP and PhenSe and shows that the  $d \rightarrow \pi^*$  (thiadiazole or selenodiazole) transition does not result in a significant heavy atom effect in the SOC, even for **Se1** and **Se2**, where the selenium atom is present. As the SOC between these states is mostly associated with MLCT transitions, having components of both the copper and the phenanthroline ligand, the presence of the copper atom ultimately determines the magnitude of the SOC matrix element.<sup>37</sup> Also, as the SOC matrix elements have a distance dependence, it was observed that the ligands with thiadiazole and selenodiazole moleties have a LUMO that is too far from the copper atom, and their contribution to the SOC matrix elements decrease. On other hand, the SOC between states with  $d \rightarrow \pi^*$  (phen) configuration is close for all complexes and when high energy singlet states, i.e. S<sub>3</sub> or S<sub>4</sub>, are involved, as these states result from MLCT transitions involving different d orbitals

Journal of Materials Chemistry C Accepted Manuscrip

from that of  $T_1$  or  $T_2$  (see Fig. S19 and Table S5-S7) a high SOC matrix element View Article Online DOI: 10.1039/DOTC03660A observed.

By adding the SOC matrix elements, one can more accurately reflect about the phosphoresce and TADF decay paths, as both,  $k_{phosp}$  and  $k_{TADF}$  depend on that. In Table 5, the sum of SOC matrix elements of these complexes follows the order **Se1**> **C1**>**S1** and **Se2**>**C2**>**S2**, which is the same order of the radiative constant obtained experimentally. However, the  $k_{phosp}$  has a dependence on the triplet energy, while the  $k_{TADF}$  relies on an exponential of the  $\Delta E(S_1-T_1)$ . Thus, as the triplet energy decreases from **C1** to **Se1** and from **C2** to **Se2**, the phosphorescence rate should be higher for phenanthroline complexes, and the lower contribution of the phosphorescence into the emission should be found for TDZP complexes, due to the combined low triplet energy and SOC matrix elements. On the other hand, for the TADF path, as the  $\Delta E(S_1-T_1)$  also decreases from **C1** to **Se1** and from **C2** to **Se2**, this emission component should follow the same order.

We can conclude that, even structurally similar, the presence of TDZP and PhenSe ligands significantly change the photophysical properties, as shown in Scheme 1 for complexes **C2-Se2**. For these complexes, the introduction of thiadiazole and selenodiazole moieties resulted in a low-lying <sup>1,3</sup>MLCT state involving them. Thus, the lowest  $\Delta E_{S1-T1}$  values were found for those complexes with chalcogenide atoms, due to the minimization of the HOMO and LUMO overlap through increasing the spatial separation of the HOMO and LUMO, reducing the electron exchange by changing the ligand. Therefore, the  $k_{rISC}$ , which is determinant to the TADF mechanism and has an exponential dependence with the energy gap between these states, favors the reverse ISC for complexes **Se1** and **Se2**. In addition, the introduction of TDZP and PhenSe provides a slower phosphorescence decay path. Besides, the combined TADF and phosphorescence paths significantly decrease the overall lifetime, which can be explored further in more efficient materials.

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Scheme 1. Energy levels diagram for compounds C2-Se2. Vertical states and their major configuration obtained using the SOC-TD-DFT approach on top of  $S_0$  optimized geometry. The calculated  $\Delta E_{S1-T1}$  is the adiabatic energy difference for these states. The symbols ">" and ">>" compare the contribution of the same constant between the different compounds using C2 as reference.

#### CONCLUSION

The synthesis and characterization of a new series of copper(I) complexes with phenanthroline ligands was presented. The complexes showed thermally activated delayed fluorescence emission determined by steady-state and time-resolved spectroscopy. The experimental spectroscopic data were further rationalized by means of detailed quantum-chemical calculations. The molecules studied here did not show the classical heavy-atom effect in terms of the spin-orbit coupling matrix elements, where reduction in the  $\Delta E_{S1-T1}$  energy gap, which is determinant for the TADF mechanism by favoring the reverse ISC, combined to the phosphorescence decay, decreased the lifetime of the complexes. This is achieved through increasing the spatial separation of HOMO and LUMO. For **Se2**, the lifetime was as low as 800 ns, the lowest reported so far for [Cu(N^N)(P^P)]<sup>+</sup> complexes. These results point to new a way of reducing the lifetime in copper(I) complexes, minimizing the HOMO and LUMO overlap by increasing their spatial distance.

#### **EXPERIMENTAL SECTION**

#### General Procedures

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All starting materials were purchased from Aldrich, Acros, Merck or Vetec and were used without further purification.

The measurements of carbon, hydrogen and nitrogen percentages of the ligands and the synthesized complexes were performed on a C, H, N - Perkin-Elmer 2400 elemental analyzer. The spectra in the infrared region were obtained in a Perkin Elmer Spectrum 100 spectrophotometer, in the region of 4000 to 450 cm<sup>-1</sup>. The method of attenuated total reflectance (ATR) was used to analyze all samples.

The X-ray diffraction analysis was performed on a Bruker APEX II DUO diffractometer using radiation generated by a molybdenum tube (MoK $\alpha\lambda$  = 0.71073 Å) and graphite monochromator. During analyses the sample were sustained at 200K. The crystal structures was solved by direct methods and refined by the least squares method with complete matrix, using the programs Bruker APEX II software package<sup>38</sup> and SHELXL-2018 respectively.<sup>39</sup> The graphical representations of the molecular structures were generated using the program PLATON.<sup>40</sup> Squeeze procedure was applied to **S1** and **Se1** complexes using PLATON Crystallographic Tools.<sup>40</sup> Disordered counterion and solvate were modeled for **Se2** complex. Full crystallographic tables (including structure factors) for both complexes have been deposited with the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk.

Emission decay were obtained through the time-correlated single photon counting technique, using aFluoTime200 (PicoQuant) spectrometer. The excitation was performed by a 401 nm pulsed diode laser with repetition rate ranging from 0.25 to 20.0 MHz. Emission was collected perpendicular to excitation and passed through a polarizer set at the magic angle. The detection system consisted of a monochromator and a microchannel plate photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the emission decays to a convolution of the instrument response function and the sum of exponentials using the FluoFit® software. The plots of weighted residuals and reduced

chi-squared ( $\chi^2$ ) were used to accurately determine the quality of the fittings during the variable online analysis procedure.

Synthesis and Characterization

[Cu(Phen)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (C1). Under argon, PPh<sub>3</sub> (105 mg, 0.4 mmol) was dissolved in dry dichloremethane (20 mL). Tetrakis(acetonitrile)copper(I) tetrafluoroborate (63 mg, 0.2 mmol) was added to this solution, and the reaction mixture was refluxed for 30 min, then Phen (40 mg, 0.2 mmol) was added. The mixture was refluxed for another half hour. The solvent was removed by evaporation. The crude product was further purified by recrystallization from the mixed solvent of tetrahydrofuran/dichloromethane (80:20). Yield: 61 %; IR (KBr), in cm<sup>-1</sup>: v (C-Har) 3057 – 2862, v (C=N e C=C) 1670 – 1432, v (B-F) 1055,  $\delta$  (C-Har) 843 – 510; C<sub>48</sub>H<sub>38</sub>BCuF<sub>4</sub>N<sub>2</sub>P<sub>2</sub> (855.13): calcd. C 67.13, H 4.80, N 3.28; found C 67.42, H 4.48, N 3.28.

[Cu(TDZP)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (**S1**). **S1** was synthesized by the same method that of **C1**, except that Phen was replaced by TDZP (48 mg, 0.2 mmol). Yield: 90 %; IR (KBr), in cm<sup>-1</sup>:  $\nu$  (C-Har) 3057,  $\nu$  (C=N e C=C) 1585 – 1399,  $\nu$  (B-F) 1053,  $\delta$  (C-Har) 817 – 515; C<sub>46</sub>H<sub>42</sub>BCuF<sub>4</sub>N<sub>4</sub>P<sub>2</sub>S+1.5 THF (1021.35): calcd. C 63.35, H 4.51, N 5.12; found C 63.50, H 4.74, N 5.49.

[Cu(PhenSe)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (**Se1**). **Se1** was synthesized by the same method that of **C1**, except that Phen was replaced by PhenSe (57 mg, 0.2 mmol). Yield: 87 %; IR (KBr), in cm<sup>-1</sup>: v (C-Har) 3050 – 2849, v(C=N e C=C) 1599 – 1399, v (B-F) 1059,  $\delta$  (C-Har) 816 – 512; C<sub>48</sub>H<sub>44</sub>BCuF<sub>4</sub>N<sub>4</sub>P<sub>2</sub>Se+2 THF: calcd. C 60.51, H 4.66, N 4.75; found C 60.91, H 4.75, N 5.07.

[Cu(Phen)(POP)]BF<sub>4</sub> (C2). C2 was synthesized by the same method that of C1, except that PPh3 was replaced by POP (107 mg, 0.2 mmol). Yield: 90 %; IR (KBr), in cm<sup>-1</sup>: v (C-Har) 3058 – 2954, v (C=N e C=C) 1768 – 1435, v (C-O) 1207, v (B-F) 1054,  $\delta$  (C-Har) 846 - 513. C<sub>48</sub>H<sub>40</sub>BCuF<sub>4</sub>N<sub>2</sub>OP<sub>2</sub>+1 THF: calcd. C 64.52, H 4.77, N 2.95; found C 64.76, H 4.64, N 2,89.

 $[Cu(TDZP)(POP)]BF_4$  (S2). S2 was synthesized by the same method that of C2, except that Phen was replaced by TDZP (48 mg, 0.2 mmol). Yield: 93 %; IR (KBr), in cm<sup>-1</sup>: v

(C-Har) 3050, v (C=N e C=C) 1566 – 1405; v (C-O) 1212; v (B-F) 1053;  $\delta$  (C-Har) 81/6<sup>w</sup> Article Online - 497. C<sub>56</sub>H<sub>50</sub>BCuF<sub>4</sub>N<sub>4</sub>O<sub>3</sub>P<sub>2</sub>S: calcd. C 62.84; H 4.58; N 5.18; found C 62.78; H 4.70; N 5.23.

[Cu(PhenSe)(POP)]BF<sub>4</sub> (Se2). Se2 was synthesized by the same method that of C2, except that Phen was replaced by PhenSe (57 mg, 0.2 mmol). Yield: 94 %; IR (KBr), in cm<sup>-1</sup>: v (C-Har) 3064 – 2856, v (C=N e C=C) 1566 – 1434; v (C-O) 1212; v (B-F) 1059;  $\delta$  (C-Har) 872 - 512. C<sub>56</sub>H<sub>50</sub>BCuF<sub>4</sub>N<sub>4</sub>O<sub>3</sub>P<sub>2</sub>Se: calcd. C 60.34, H 4.23, N 4.87; found: C 60.15, H 4.51, N 5.01.

#### Thermogravimetric Analyses and Cyclic Voltammetry Studies

The thermogravimetric analysis was performed with approximately 2 mg of sample in a platinum crucible, with a nitrogen flow of 100 mL min<sup>-1</sup> and a heating ramp of 10 °C min<sup>-1</sup> in a temperature range of 30-900 °C. The equipment used is of the brand Shimadzu, model TGA-50.

The redox behavior of the complexes was investigated by square wave voltammetry in a potentiostat-galvanostat BAS (Bioanalytical Systems, Inc.) model Epsilon. A concentration of  $2.5 \times 10^{-4}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution was used under nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate (0.1 mol L<sup>-1</sup>) was used as support electrolyte and the electrochemical cell was composed of three electrodes: work - vitreous carbon; auxiliary - platinum wire; reference - Ag/Ag<sup>+</sup>. For correction of the reference electrode the ferrocene (E<sub>1/2</sub> *vs* NHE = 398 mV) was used.

#### Spectroscopic Measurements

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The electronic spectra in the ultraviolet, visible and near infrared regions were obtained for all the complexes in the range of 200–800 nm in a Perkin-Elmer spectrophotometer model Lambda-750. The values of  $\varepsilon$  are given in L mol<sup>-1</sup> cm<sup>-1</sup>. The emission spectra were obtained on a Varian Cary Eclipse Fluorescence spectrophotometer. The spectroscopy measurements were performed in CH<sub>2</sub>Cl<sub>2</sub> solution and solid state using PMMA matrix containing 10 wt% of **C1-Se2**. The analyzes were performed using spectroscopic grade solvents, substrates and quartz cuvettes with a capacity of 1 mL and 1.00 cm of optical path at 25 °C. Absolute quantum yields ( $\Phi$ ) were

made using a Hamamatsu Photonics Absolute Quantum Yield Measurement Systemw Article Online DOI: 20:1039/DOTC03660A model c9920-02G which is based on the integrating sphere method.

Singlet-excited state photoluminescence decay curves were recorded using the time-correlated individual photon counting method on a FluoTime200 (PicoQuant). The excitation was provided using a 401 nm pulsed diode laser with repeating rates ranging from 5.0 to 20 MHz. Photoluminescence was collected perpendicular to the excitation and passed through a polarizer adjusted at the magic angle. The detection system consists of a monochromator and a multi-channel base photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the fluorescence for a convolution of the instrument's response function and a sum of exponentials using the FluoFit® software. The considered residual plots and the chi-square ( $\chi^2$ ) were used to accurately determine the quality of the accessories during the analysis procedure.

Time resolved spectra were obtained by exciting the sample with a Nd:YAG laser (EKSPLA), 10 Hz, 355 nm. Sample emission was directed onto a spectrograph and gated iCCD camera (Stanford Computer Optics). The films were produced by spin coating on quartz subtrates.

#### Theoretical methods

Geometry optimizations of complexes **C1-Se2** were carried out in vacuum, using the Orca 4.0.1 software package<sup>41</sup> at the DFT level using the PBE0<sup>42,43</sup> and the basis set Def2-TZVP(-F) for all atoms.<sup>44–46</sup> The calculations also included Grimme's dispersion correction with damping D3BJ<sup>47,48</sup> and the RIJCOSX algorithm was employed to accelerate the evaluation of the integrals, using the resolution of identity approximation for the Coulomb part (RIJ), and the chain of spheres approach for the exchange (COSX).<sup>49,50</sup> RIJCOSX requires the specification of an auxiliary basis set for the Coulomb part and a numerical integration grid for the exchange part, discussed elsewhere. The vibrational frequencies for both complexes showed no imaginary frequencies. Timedependent density functional theory (TD-DFT) under Tamn-Dancoff approximation<sup>49</sup> (TDA) was employed to obtain the first 50 singlet excited states, differing only on the basis set chosen: ZORA-Def2-TZVP(-F) for all atoms, including ZORA relativistic corrections.<sup>51,52</sup>To include solvent effects in the excited state energies, the conductor-like polarizable continuum model<sup>53</sup> (CPCM) was used, using acetonitrile as solvent.TD-DFT/TDA was also employed to optimize the geometry of the first singlet excited state. The first triplet was optimized from the ground state of UKS calculation. The SOC on toev Article Online of the TD-DFT results were done by using quasi-degenerate perturbation theory.<sup>35,54</sup> The SOC integrals used here were calculated using a mean-field method named as RI-SOMF(1X) and described elsewhere.<sup>55</sup> The geometric representations of the complexes were obtained using the Chemcraft program.<sup>56</sup>

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Cu(I) complexes without the expected heavy atom effect to enhance the spin-orbit coupling matrix elements, but with reduced photoluminescence lifetime.

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