A Small Cationic Organo-Copper Cluster as Thermally Robust Highly Photo- and Electro Luminescent Material

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Abstract

Organic light emitting diodes (OLEDs) are revolutionizing display applications. In this aspect luminescent complexes of precious metals such as iridium, platinum, or ruthenium play a significant role. Emissive compounds of earth-abundant copper with equivalent performance are desired for practical, large-scale applications such as solid-state lighting and displays. Copper(I)-based emitters are well-known to suffer from weak spin-orbit coupling and a high reorganization energy upon photo-excitation. Here we report a cationic organo-copper cluster $[\text{Cu}_4(\text{PCP})_3]^+$ ($\text{PCP} = 2,6\text{-(PPh}_2)_2\text{C}_6\text{H}_3$) that features suppressed non-radiative decays, giving rise to a robust narrow-band green luminophore with a photoluminescent (PL) efficiency up to 93%. PL decay kinetics corroborated by DFT calculations reveal a complex emission mechanism involving contributions of both thermally activated delayed fluorescence (TADF) and phosphorescence. This robust compound was solution-processed into a thin-film in prototype OLEDs with external quantum efficiency up to 11% and a narrow emission bandwidth (65 nm FWHM).

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Introduction

The OLED technology, now present in a variety of consumer electronics, commercialized in an expanding multi-billion dollar market, has the potential to be a highly efficient, energy-economical solid-state lighting system with global economic impact.^{1–4} Coordination compounds with bright photoluminescence (PL) attract increased attention owing to their potential application in optoelectronic devices. In this regard, carbo-cyclometalated organometallic complexes of precious metals such as iridium or platinum, play a key role in the preparation of luminescent materials due to their high quantum efficiency and facile emission wavelength tuning.^{5–13} Currently, there are strong efforts to exchange cost-intensive and scarce precious metals in luminescent materials with economically viable alternatives in order to enable mass-market applications (e.g. large surface lighting and smart-labels). In this aspect, efficient emitters based on copper(I) complexes are intensively studied.^{14–19} The d^{10} configuration of Cu(I) avoids d–d transitions and hence, a ligand centered LUMO can participate in metal-to-ligand charge transfer (MLCT) processes. However, (pseudo)tetrahedral Cu(I) complexes are prone to significant distortion at their excited state, due to a formal transition in oxidation state from Cu(I) to Cu(II). The flattening distortion is regarded as a major cause for decreasing in PL quantum yields (PLQY).^{19–22} Additionally, Cu(I) compounds often suffer from dynamic processes in solution such as ligand dissociation via solvent coordination or ligand redistribution, which can increase the non-radiative transitions and is also reflected in a broad full width at half-maximum (FWHM) of the emission band.^{23–28} Thus, more rigid and coordinative inert structures may suppress non-radiative decays. This approach is predominantly addressed by utilization of sterically encumbered ligands^{20,21} or the design of poly-nuclear complexes with bridging ligands.^{18,22–24} Typical external quantum efficiencies (EQE_{max}) of OLEDs with Cu(I) complexes in the emission layer (EML) are reported to fall between 0.1–9%, with exceptional reports presenting values of 10–18.5%.^{29–31} Best OLED performances were attained with tri-coordinate Cu(I) complexes ($EQE_{max} = 18.5–22.5\%$)^{32,33} and using a halide-bridged dinuclear Cu(I) complex, reaching efficiencies comparable to Ir(III)-based devices ($EQE_{max} = 23\%$, 73 cdA^{-1} , $\lambda_{max} = 550\text{ nm}$, $L_{max} = 10000\text{ cdm}^{-2}$ at 10 V).³⁴ Very recently two-coordinate Cu(I) complexes with a carbene and amide ligand in co-planar arrangement were reported to suppress non-radiative decay reaching remarkable PLQY of up to 99% and EQE_{max} of 9.7%.^{25,26} The maximum luminance (L_{max}) for Cu-based devices range commonly between 180 cdm^{-2} and 17600 cdm^{-2} ,^{29,31} with peak performances reported between $34000–42000\text{ cdm}^{-2}$.³⁵ Current efficiencies (CE_{max}) remain typically below 60 cdA^{-1} ,^{29–31} with occasionally reported peaks between $65–73\text{ cdA}^{-1}$.^{32,34} Multi-core Cu(I) complexes with rigid geometries are reported to possess bright PL, for instance dinuclear Cu(I) species including halide bridged complexes,^{23,36–39} halide-free phosphine-bridged complexes,⁴⁰ as well as amide-bridged dinuclear complexes.^{18,22} Stollenz and co-workers presented luminescent multinuclear copper(I) arrays bridged by bisamidine ligands giving rise to coiled metal chains with close $d^{10}–d^{10}$ Cu(I) interactions.⁴¹ Rigid dinuclear amide-bridged Cu(I) structure with bulky ligand set were shown to afford narrow FWHM (2400 cm^{-1}) owing to a low reorganization energy and hampered solvent ligation in the excited

state.²² Although PLQY can be high, mono-nuclear Cu(I) complexes with flexible large-bite-angle ligands²⁸ or dinuclear Cu(I) complexes with less sterically congested ligand spheres²⁷ can show significantly broadened FWHM (4700–5000 cm⁻¹) in their emission band.

In this context, we have prepared the clustered compound [Cu₄(PCP)₃][BF₄] (**[2]**[BF₄], PCP = 2,6-(PPh₂)₂C₆H₃, Figure 1) featuring a Cu₄-core and the bulky tridentate carbanionic bisphosphine ligand (PCP). In contrast to the rich variety of existing luminescent precious metal carbo-cyclometalated complexes (e.g. 2-phenylpyridine-type complexes), robust organometallic copper(I) compounds with (cyclo)-metallating ligands are very rarely used as luminophores.^{42,43} In an effort to avoid most problems associated with organo-copper compound synthesis (see ESI for more details) we have applied an alternative, novel, synthetic approach for the copper(I)-carbo-metallation, wherein C–Si bond cleavage is triggered by a tetrafluoro borate anion and the starting precursor was [Cu(NCCH₃)₄][BF₄]. Hence the direct CuX / MR_n (M=alkali-, alkaline earth metal, Zn, Al; X = halide) metathesis and the usage of strongly basic precursors such as [Cu(O^tBu)] can be avoided, as well as the aggregation of the organo-copper species with other metal salts is precluded (see ESI, Equation 4). The cluster **[2]**[BF₄] exhibits extraordinary photo- and electro-luminescent (EL) properties and is a rare example of a cationic organo-copper species giving rise to a new class of copper compounds for thermally robust and highly photo- and electro luminescent material. The vast majority of organo-copper compounds are of neutral or anionic nature (Gilman reagents). With respect to cationic copper clusters, structural precedence was given by Power and co-workers more than 20 years ago for [Cu₃Ph₂(PMDTA)₂][Ph₆Cu₅] (Figure 1, **A**; PMDTA = *N,N,N',N'',N''*-pentamethyldiethylenetriamine). However, dissolved in dimethylsulfide (DMS), the compound shows a dynamic equilibrium forming the neutral tetramer [CuPh]₄·(DMS)₂ and free PMDTA.⁴⁴ Very recently a family of discrete cationic dinuclear Cu(I) compounds chelated by 2,7-bis(fluoro-di(2-pyridyl)-methyl)-1,8-naphthyridine (DPFN) and various μ-bridging ligands (Figure 1, **B**) have been described by Tilley and co-workers.^{45–47}

Known cationic organo-copper species:

This work:

Figure 1. Cationic organo-copper compounds **A** and **B**, *PCP* ligand, and $[\text{Cu}_4(\text{PCP})_3]^+$.

Results and discussion

Synthetic aspects

The reaction of 2,6-F₂C₆H₃SiMe₃ (**1**) and LiPPh₂ afforded the ligand precursor 2,6-(PPh₂)C₆H₃SiMe₃ (**1**) as colorless solid. The reaction of **1** with [Cu(NCCH₃)₄][BF₄] in a 3:4 ratio gives rise to the formation of the tetranuclear organo-copper cluster compound $[\text{Cu}_4(\text{PCP})_3][\text{BF}_4]$ (**[2][BF₄]**, *PCP* = 2,6-(PPh₂)₂C₆H₃) as a bright green crystalline material in 60% yield (Figure 1). The [BF₄]⁻ counter anion serves as mild source for fluoride allowing for C–Si bond cleavage *via* release of Me₃SiF. Compound **[2][BF₄]** is poorly soluble in most common organic solvents except MeCN and CH₂Cl₂. Simple counter ion metathesis, *via* the reaction of **[2][BF₄]** and Na[BAr^F₄] (Ar^F = 3,5-(CF₃)₂C₆H₃) in a mixture of toluene and CH₂Cl₂, gives rise to the highly soluble compound $[\text{Cu}_4(\text{PCP})_3][\text{BAr}^{\text{F}}_4]$ (**[2][BAr^F₄]**).

Notably, **[2]⁺** shows remarkable stability as dissociation, ligand exchange, or solvent coordination was not observed in various solvents. Furthermore, **[2][BAr^F₄]** shows high thermal stability; simultaneous thermo-gravimetric analysis and differential scanning calorimetry experiments indicate a decomposition onset above 377°C (see ESI, Figure S2).

X-ray diffraction analysis of **[2][BF₄]**

The molecular structure derived from the XRD study is shown in Figure 2. The structure reveals a small cationic cluster with four central copper atoms, which are chelated by three *PCP* ligands. The Cu₄-core resides in a slightly distorted rhombic arrangement (kite-type). The deviation from planarity reflected by an angle of 27.5° between the two planes defined by Cu1–Cu1a–Cu2 and Cu1–Cu1a–Cu2a. The copper metal centers have short interatomic distances of Cu1–Cu1a = 2.3157(12) Å, Cu1–Cu2 = Cu1a–Cu2a = 2.7248(8), and Cu1a–Cu2 = Cu1–Cu2a = 2.6538(8) Å, which are significantly shorter than the sum of their van der Waals radii (2.80 Å).⁴⁸ The atoms Cu1 and Cu1a, are only two-coordinated via the

bridging -and non-bridging phenylate ligand and show an extraordinary short Cu1–Cu1a distance. For comparison, a separation of 2.56 Å is observed in copper metal.⁴⁹ Similar cluster motifs show Cu–Cu distances in the range of 2.43–2.88 Å,^{50–53} and linear assemblies exhibit bond lengths between 2.46–2.75 Å.^{41,54} Complex **[2][BF₄]** clearly belongs to the group of compounds with the shortest Cu–Cu distances today, such as the linear Cu₃ complex (2.348(2) Å) reported by Strähle and co-workers.⁵⁵ Significantly, the two copper atoms, Cu2 and Cu2a, are solely coordinated by three P-donors (P1–P2–P3a and P1a–P2a–P3, respectively) in a trigonal planar fashion. Both [CuP₃] units are in mutual staggered position with respect to the Cu2–Cu2a trajectory (see ESI, Figure S4) and confining the purely organometallic core; that is, the core encompasses two copper atoms, Cu1 and Cu1a, coordinated by the carbon atoms C40 and C40a, respectively, which arise from two individual *PCP* ligands on opposite sides of the cluster. The observed Cu2–C40 distance (1.923(3) Å) compares well with Cu–C bonds found for [Cu(Mes)₂][–] (1.915(9) Å).⁵⁶ Additionally, both copper atoms share a bridging phenylate ligand (Cu1–C10 = Cu1a–C10 = 2.052(4) Å) originating from the third *PCP* unit. Such bridging motifs were observed for [Cu₂Ar] (Ar = aryl) fragments^{57,58} and the Cu–C_{bridge}–Cu distances are in range with previously reported structures.^{50,51}

Figure 2. Molecular structure of complex **[2][BF₄]** derived from single crystal X-ray diffraction analysis. Hydrogen atoms, CH₂Cl₂ solvent molecule and [BF₄][–] counter ion are omitted for clarity. Ligand scaffold drawn as wireframe, C of central phenylate units, Cu and P are depicted as thermal ellipsoids at 30% probability.

NMR spectral analysis

The ³¹P{¹H} NMR spectrum of the ligand precursor **1** has a characteristic singlet at δ = –6.4 ppm for both PPh₂ units indicating both ³¹P nuclei in identical chemical environment. Correspondingly, the SiMe₃ moiety gives rise to a triplet resonance in the ²⁹Si{¹H} NMR spectrum at δ = –3.0 ppm with a ³J(²⁹Si³¹P) coupling constant of 7.9 Hz. The ³¹P{¹H} NMR spectrum of **[2]⁺** acquired at 223 K reveals

well-resolved triplets for three pairs of nonequivalent ^{31}P nuclei at $\delta = 12.9, 4.6$ and 1.7 ppm ($^2J(^{31}\text{P}-^{31}\text{P}) = 88, 78$ Hz), which is consistent with the molecular structure in the solid-state (see ESI, Figure S19). Upon warming, the three signals collapse into a broad signal, observed at $\delta = 6.5$ ppm at room temperature, which is consistent with fluxional behavior fast on the NMR time scale. Both Cu2 and Cu2a atoms are trigonal coordinated by three phosphine moieties, which reside in a mutual staggered conformation (see ESI, Figure S4). Marginal rotation around the Cu2–Cu2a trajectory gives rise to the interconversion of both staggered $[\text{CuP}_3]$ units. This process may be sufficiently fast at temperatures above 273 K to give rise to the coalescence of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances. Analysis of the DFT (B3LYP/DGDZVP) optimized structures with use of a simplified model of $[\mathbf{2}]^+$ (Figure S26) suggests the interconversion of both staggered conformations via an eclipsed structure with an energy barrier of $10.5 \text{ kJ}\cdot\text{mol}^{-1}$.

Photoluminescence analysis and microsecond kinetics study

The absorption spectra of $[\mathbf{2}][\text{BAR}^{\text{F}}_4]$ in THF has bands at 375 nm ($12870 \text{ M}^{-1}\text{cm}^{-1}$) and 454 nm ($1170 \text{ M}^{-1}\text{cm}^{-1}$), see Figure S22 in the Supporting Information. The cluster $[\mathbf{2}]^+$ shows bright green emission in solution as well as in the solid state. The room-temperature emission spectra of powder and THF solution show one featureless narrow band centered at 518 and 525 nm, respectively ($[\mathbf{2}][\text{BF}_4]$, Figure S23). Remarkable narrow emission bands are observed for $[\mathbf{2}][\text{BAR}^{\text{F}}_4]$ with a FWHM of 58 nm (solid) and 60 nm (solution). High photo luminescence quantum yields (PLQY) range between 0.50 for the solid and up to 0.79 for THF solutions at room temperature. At 77 K the PLQY increases to 0.71 for the solid and 0.93 for DCM frozen solutions of $[\mathbf{2}][\text{BAR}^{\text{F}}_4]$ (see ESI, Table S2). Investigation of the temperature resolved PL behavior of $[\mathbf{2}][\text{BAR}^{\text{F}}_4]$ revealed that heating the solid-state sample from 11 K to 440 K results the PL intensity to gradually decrease associated with a concomitant blue-shift of the peak maxima (Figure 3a,b). The plot of the continuous ramp of 220 spectra (2 Kmin^{-1}) reveals a shoulder at about 207 K indicating an inflection point for emission maxima change. In the temperature window from 11 K to 298 K the peak maximum shifts by 12 nm, from 530 nm to 518 nm. Noteworthy, upon heating the sample above ambient temperature (up to 440 K our experimental limitation) a slight red-shift can be observed with a local maximum of 520 nm at 397 K ($\Delta = 2 \text{ nm}$).

The microsecond PL kinetics (excitation at 454 nm) of $[\mathbf{2}][\text{BF}_4]$ in solution at room temperature reveal an intensity increase during few μs after the laser pulse followed by a decay with the lifetime of 11 μs (Figure 3c). A more detailed analysis of the emission in the initial period of time reveals a fast (shorter than a few ns) decrease of the prompt photoluminescence (PPL) signal and a slower (during $\sim 1.5 \mu\text{s}$) intensity increase corresponding to the subsequent population of the emitting state (Figure 3c). Then, $\sim 5 \mu\text{s}$ after the excitation, the signal starts to decrease again, corresponding to the delayed photoluminescence (DPL) decay with the lifetime of 11 μs . The delayed luminescence at room temperature appears to be stronger than the PPL. The emission of a solid-state sample at room temperature demonstrates very similar kinetic parameters (Figure 3e). The DPL lifetime of the powder

is 9.8 μ s. The DPL decay shows clearly a lifetime elongation (Figure 3e,f) as the temperature decreases. The powder sample at 77 K is characterized by the luminescence lifetime $\tau = 100 \mu$ s (Figure 3f) which is an order of magnitude longer than that at room temperature. Shortly after the excitation, the low-temperature prompt luminescence decreases and then the intensity grows up again but the signal remains weaker than that at the maximum of PPL (Figure 5f). The DPL/PPL signal ratio becomes, therefore, much smaller on cooling the sample from 293 K to 77 K. Such a behavior is typical for emitters characterized by a PL mechanism involving temperature activated delayed fluorescence (TADF).⁵⁹ In contrast to many other Cu(I) complexes revealing TADF but no PPL,^{27,50,59} for [2][BF₄] the spontaneous luminescence signal is observed at both 77 K and 293 K. This can be indicative of a comparatively slow T₁ population process. On the basis of the PLQY Φ and lifetimes τ the radiative and non-radiative decay rate constants were estimated as $k_r = \Phi / \tau$ and $k_{nr} = (1 - \Phi) / \tau$, respectively. The solid-state k_r and k_{nr} values at room temperature are both equal to $5.1 \cdot 10^4 \text{ s}^{-1}$. On cooling down to 77K they decrease to $7.1 \cdot 10^3$ and $2.9 \cdot 10^3 \text{ s}^{-1}$, respectively, providing a faster radiative decay rate at low temperature as compared to the non-radiative processes. Interestingly, for THF solution, the radiative rate constant is higher even at room temperature ($k_r = 7.2 \cdot 10^4 \text{ s}^{-1}$, $k_{nr} = 1.9 \cdot 10^4 \text{ s}^{-1}$).

Using the assumptions suggested previously⁶⁰ and the experimental temperature dependence of the PL lifetime τ in the 200–330 K range we can estimate the energy gap between the S₁ and T₁ states $\Delta E_{(S_1-T_1)}$ as $580 \pm 30 \text{ cm}^{-1}$ ($0.072 \pm 0.004 \text{ eV}$) and the S₁ state lifetime $\tau_{(S_1)}$ as $140 \pm 30 \text{ ns}$ (see SI for the details). This S₁–T₁ energy gap (Figure 3d) agrees very well with the results of our DFT calculations (see below). The 12 nm temperature induced shift of the emission maximum corresponds to $\Delta E_{(S_1-T_1)} \sim 450 \text{ cm}^{-1}$ (0.056 eV) which also correlates with the estimated parameter. Knowing the $\Delta E_{(S_1-T_1)}$, $\tau_{(T_1)}$, and $\tau_{(S_1)}$ values, one can find the approximate ratio of the T₁ phosphorescence intensity to the total emission intensity at various temperatures. Then the fractional TADF emission intensity can be found as $I_{(S_1)}/I_{\text{total}} = 1 - I_{(T_1)}/I_{\text{total}}$, which gives the TADF contribution as 94%, 79% and 0.5% at 300 K, 200 K and 77 K, respectively (see SI for the details).

Figure 3. a) and b) Temperature dependent PL measurement of solid [Cu₄(PCP)₃][BARF₄]: 220 spectra recorded every minute applying a continuous ramp of 2 Kmin⁻¹ (11 K to 450 K with excitation at 390 nm (Xenon lamp)). c) Luminescence kinetics ($\lambda_{\text{ex}} = 454$ nm) of [2][BF₄] in THF solution at room temperature. Inset shows the initial part of the kinetic curve with the logarithmic time scale. The red line corresponds to the DPL exponential decay model. d) Quantitative B3LYP/DGDZVP diagram of the electronic states responsible for the photophysical properties of [2]⁺. The electronic energies were calculated with the optimized geometries of the S₀, S₁ and T₁ states. e) and f) Luminescence kinetics ($\lambda_{\text{ex}} = 454$ nm) of [2][BF₄] in the solid state at 293 K (e) and 77 K (f). Inset shows the initial part of the kinetic curve with the logarithmic time scale. The red line corresponds to the DPL exponential decay model.

Application of [2]⁺ as luminophore in OLED devices

We applied cluster [2]⁺ as a solution-processed dopant in the emissive layer of a prototype OLED device (Figure 4b). We used a simple device structure shown on Figure 4a, [ITO/PEDOT:PSS/TAPC/TAPC:[2][BARF₄]/B3PYMPM/LiF/Al] with PEDOT:PSS used as an hole injection layer, TAPC (di-[4-(N,N-di-p-tolyl-amino)-phenyl]cyclohexan) as hole transport layer, TAPC with [2][BARF₄] addition as emissive layer. LiF/Al electrode was thermally evaporated after the 50 nm of the electron transport layer B3PYMPM (4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine). Figure 4d–f shows the optoelectronic properties of the OLED device. The bright emission of 8900 cdm⁻²

is observed at 15 V. The device shows a EQE_{max} of 11.2% at 42 cdm^{-2} and good EQE values for the broad range of current densities (Figure 4d). Electroluminescence (EL) spectra for different driving voltage are shown in Figure 4f with FWHM changing from 75 nm to 65 nm as the driving voltage increases (Figure S25c). Associated *CIE 1931* chromaticity coordinates are (0.305,0.637) at 1000 Cd (Figure S25e) allowing to exceed the primary green sRGB (BT.709) color standard. The turn-on voltage that corresponds to 1 cdm^{-2} was remarkably low at only 2.4 V. Applying CBP as a bipolar host material, we achieved higher brightness of 19000 cdm^{-2} (Figure S25), however increasing the turn-on voltage of the device to 4.2 V, probably due to the deeper HOMO level of CBP (4,4'-Bis(*N*-carbazolyl)-1,1'-biphenyl) comparing to TAPC (6.0 eV vs. 5.5 eV) deteriorates the hole injection into the device. Subsequent voltage scans of the OLED devices show the severe degradation of the luminance and EQE, while almost no changes are visible for current density (Figure S25a–c), nevertheless the PL of the degraded pixel does not show difference from the fresh pixels indicating that the device performance degradation is not related to the change in $[\mathbf{2}]^+$. Application of more suitable bipolar hosting materials might further increase the performance of the $[\mathbf{2}]^+$ -based OLEDs.

Figure 4. a) Schematic architecture of the OLEDs structure. b) Emission from an OLED prototype with $[\mathbf{2}]^+$ as a luminophore. c) Green emission of crystalline $[\mathbf{2}][\text{BAr}^{\text{F}}_4]$ under UV (254 nm) light exposure. d) EQE and Current efficiency vs current density. e) Current density-luminance-voltage characteristics of the EL device. f) EL spectra for various driving voltages.

DFT calculations

To provide a detailed insight into the electronic structure of cation $[\mathbf{2}]^+$ and electronic density transformations in the processes of excitation, intersystem crossing and emission, DFT and time-dependent (TD) DFT calculations have been performed. The molecular geometries of $[\mathbf{2}]^+$ (Figure S27) in the S_0 , S_1 and T_1 states were optimized at the B3LYP/DGDZVP level of theory. Selected interatomic distances for the optimized structures are given in Table S3. The atom and arene ring notations are shown in Figure S27. Our calculations demonstrate that main changes in bond lengths on going from

the ground to the considered excited states are located within the tetranuclear copper fragment of the $C_{18}P_6Cu_4$ core bearing the Arene1–3 carbocycles. The $S_0 \rightarrow S_1$ adiabatic transition is accompanied by 0.05–0.12 Å shortening of the Cu1,Cu1a–Cu2,Cu2a bonds. The $S_0 \rightarrow T_1$ adiabatic transition leads to an elongation of the Cu1a–Cu2,Cu2a bonds but the Cu1–Cu2,Cu2a distances decrease so that the Cu2–Cu2a separation becomes 0.12 Å shorter (Table S3). The bonding angles are similar in the S_0 and S_1 states. However, noticeable angle changes take place on going from the S_0 to T_1 geometry, both the Cu_4 core and the Arene1–3 rings being involved (Table S3). The $[2]^+$ ground-state molecular structure undergoes, therefore, a larger conformational distortion in the T_1 triplet state as compared to the S_1 singlet.

The $[2]^+$ frontier orbitals are spatially separated (Figure 5a), the HOMO being located mainly on the C40–Cu1–Cu1a–C40a fragment while the LUMO being contributed by the Arene3 ring bearing the C10 atom. Such a spatial separation usually leads to comparatively small exchange integrals and, accordingly, to close energies of the singlet S_1 and triplet T_1 lowest excited states.^{59,60} Indeed, the calculated $\Delta E(S_1-T_1)$ energy gap for the optimized geometries appears to be only 0.06 eV which can provide efficient TADF similar to other Cu(I) complexes.^{27,28,50} The theoretical $\Delta E(S_1-T_1)$ value coincide with that obtained from the mentioned above experimental blue shift of the emission band maximum from 530 to 518 nm on increasing temperature. The contribution of the copper wavefunctions to the $[2]^+$ orbitals estimated from the Mulliken population analysis decreases from 51% to 19% on going from HOMO to LUMO. The HOMO $\rightarrow$ LUMO electronic transition can be, therefore, considered as metal-to-ligand charge transfer (MLCT) accompanied by the ligand-to-ligand charge transfer (LLCT) corresponding to the electron density shift from the Cu1–C40 and Cu1a–C40a bonds to the Arene3 ring (Figure 5a). The HOMO is anti-bonding relative to all the Cu–Cu interactions which agrees with the DED increase on going from S_0 to S_1 (Figure S30). Two copper atom couples, Cu1, Cu1a and Cu2, Cu2a contribute unequally to the charge transfer. The electron density difference (EDD) map corresponding to the $S_0 \rightarrow S_1$ transition (Figure 5b) reveals higher contribution of the Cu1 and Cu1a electrons. This agrees well with the higher HOMO electron density located on Cu1 and Cu1a (Figure 5a).

The TD DFT model provides a shift between the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions $\Delta E_{\text{theor}} = 0.35$ eV which is very close to the experimental value $\Delta E_{\text{exptl}} = 0.37$ eV so the calculated relative positions of the excited levels are rather reliable. This makes it possible to construct a quantitative diagram of the electronic states responsible for the observed $[2]^+$ photophysical properties (Figure 3d). Our TD DFT calculations predict the S_2 and S_3 singlet states of $[2]^+$ to lie 0.22 and 0.26 eV, respectively, above the S_1 level at the optimized ground-state geometry. The computed oscillator strengths of the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions are close (0.0085, 0.0086 and 0.0068, respectively) so the corresponding absorption peaks can well overlap. It is possible, therefore, that the S_2 and S_3 states are populated together with the S_1 level by the 454 nm laser pulse used in the experiment.

To investigate the electronic density changes on going from one optimized structure to another we calculated the atomic charges of the $[2]^+$ core in the S_0 , S_1 and T_1 states using AIM^{61,62} and Hirshfeld⁶³

approaches. The two approaches, despite significant differences in the q values (Table S4) caused by the different methods of calculation, reveal similar trends in the charge changes. Interestingly, the Cu1 and Cu1a atoms bound to the negatively charged carbons appear to possess larger positive charges than Cu2 and Cu2a coordinated by the highly positive phosphorus atoms. The $q(\text{Cu1}, \text{Cu1a})$ values increase on going from S_0 to S_1 and T_1 which agrees with the MLCT transitions. Accordingly, the $q(\text{C10})$ value becomes more negative. The Cu2 and Cu2a charges change less compared to $q(\text{Cu1}, \text{Cu1a})$ which confirms the larger contribution of the latter to the light absorption and emission processes. The participation of the non-bridging C40 and C40a atoms in the CT processes is less significant as compared to Cu1, Cu1a and the bridging C10. However, our QTAIM computations also reveal the participation of the phosphorus wavefunctions in the electronic transitions, the contributions varying for the different P atoms. The strongest increase in the positive charge on electronic excitation is calculated for P1a, P2 and P3 (Table S4). The charge distribution changes in the $S_1 \rightarrow T_1$ intersystem crossing are much weaker than those in the transitions between the S_0 and S_1 singlet states. This is in accord with the EDD analysis (Figures 5b). Our calculations of the baricenters⁶⁴ of the charge transfer (see the Supporting Information) also agree well with such a conclusion.

Figure 5. a) Isosurfaces (isovalue 0.05) of the $[2]^+$ HOMO (left) and LUMO (right) frontier orbitals in the S_0 ground state. b) Isosurfaces of EDD corresponding to the $S_0 \rightarrow S_1$ vertical transition (left, isovalue is 0.003 a.u.) and $S_1 \rightarrow T_1$ intersystem crossing (right, isovalue is 0.0008 a.u.) in the $[2]^+$ ion. The negative and positive values are shown in blue and rose, respectively.

Therefore, our DFT calculations provide a detailed description of the CT accompanying the excitation, ISC and emission processes in the $[2]^+$ ion. The close energies of the S_1 and T_1 states (Figure 3d) allows for the thermally activated population of the S_1 emissive state. The interplay between the processes involving excited states of the $[2]^+$ conformational isomers can contribute to the complicated kinetics of PL observed on the microsecond scale (Figures 3c,e,f).

Summary

While carbo-cyclometallated complexes of precious metals are ubiquitously used as luminophores in electro-luminescent devices, organometallic copper compounds remain almost absent for such applications due to synthetic difficulties, coordinative lability, and sensitivity of the Cu–C bond. Herein, we report the synthesis of a rare cationic organocopper cluster compound $[\text{Cu}_4(\text{PCP})_3][\text{A}]$, ($\text{A} = \text{BF}_4^-$ or $\text{BAr}^{\text{F}_4^-}$) by a mild carbometallation procedure involving the cleavage of a C–Si bond triggered by the F^- release from the $[\text{BF}_4]^-$ ion and subsequent formation of Me_3SiF and Cu–C bonds. The crystal structure of $[\mathbf{2}]^+$ reveals a Cu_4 -core in rhombic arrangement showing one of the shortest Cu–Cu interatomic distances (2.316 Å) reported today. The extraordinary oxidative and thermal stability of $[\mathbf{2}]^+$ is a direct result of the efficient Cu_4 -core steric shielding. Ligand dissociation, exchange and solvent coordination effects were not observed and the cluster does not show decomposition before 377°C. The photoluminescent properties remain intact even when the solid is exposed to moist air for extended periods of time. Despite the dynamic interconversion of two staggered conformation observed at ambient temperature by means of ^{31}P NMR spectroscopy, the Cu_4 -core itself is rather rigid, a feature that limits non-radiative decays caused by significant distortions in the excited state. As a result $[\mathbf{2}]^+$ shows very intensive green PL in both solid state and solution with high PLQY with narrow emission bands of 58 nm and 60 nm (FWHM), respectively.

Cluster $[\mathbf{2}]^+$ was utilized as a solution-processed dopant in the emissive layer for OLED devices. A representative device showed bright green emission of 8900 cdm^{-2} at 15 V with 65 nm FWHM with a remarkable low turn-on voltage of 2.4 V at 1 cdm^{-2} and EQE_{max} of 11.2% at 42 cdm^{-2} . Using rather simple structures we even obtained devices with a brightness of up to 19000 cdm^{-2} .

Our DFT calculations provide a detailed description of the CT process encompassing the excitation, ISC, and the emission processes in the $[\mathbf{2}]^+$ ion. The frontier orbitals are spatially well separated: The HOMO is mainly located at non-bridging Cu–C moieties, the LUMO on the bridging arene, resulting in a small ΔE (S_1 – T_1) energy gap allowing for the thermally activated population of the S_1 emissive state (RISC). MLCT mainly involves C-coordinated Cu atoms and the bridging arene. P-coordinated Cu atoms and the P atoms participate as well, but with smaller contribution. We observe a rather complex PL behavior with a dual-mode emission over a wide temperature range entailing contributions of TADF and phosphorescence. Estimation of the TADF fractional contribution to the overall PL suggest 94% emission from singlet-harvesting at high temperature (300K), while correspondingly at low temperature (77K) the fractional TADF contribution drops to 0.5%, that is, the emission stems almost entirely from phosphorescence.

We are currently aiming to further improve the structural rigidity of $[\mathbf{2}]^+$; In particular the tuning of the steric bulk could suppress the conformational interconversion and may allow for increased PL performance. We also seek to improve the OLED performance and therefore the study of the detailed mechanism behind device degradation is an important motif for future work.

Data availability

Crystallographic data reported in this Article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 1949031. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. All other data supporting the findings of this study are available within the Article and the Supplementary Information, or from the corresponding authors on reasonable request.

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Competing interests

J.B., M.V. and O.M. have filed two patent applications (Ger. Offen. (2018), DE 102017207804 A1 20181115; PCT Int. Appl. (2018), WO 2018206595 A1 20181115) based on some of the work described here.

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