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Self-assembled luminescent Cu(I) tetranuclear metallacycles based on 3,3'-bipyridine ligand

Florent Moutier, Jana Schiller, Guillaume Calvez* and Christophe Lescop*

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3,3'-bipyridine ligand **B** was reacted with pre-assembled $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ Cu(I) bimetallic flexible precursor **A** accordingly to coordination-driven supramolecular chemistry synthetic principles. Outcomes obtained revealed the necessity to formally introduce bridging halide X ions (X = Cl, Br or I) in order to conduct selectively and successfully coordination-driven supramolecular syntheses. Therefore, $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-X})]$ bimetallic connecting nodes presenting potential coordination angles of ca. 120° are generated, that lead upon reaction with the connecting ligand **B** to the selective formation of the new tetranuclear metallacycles **C_x**. These derivatives are luminescent in the solid-state at room temperature with high emission quantum yields and the study of the temperature dependence of their photophysical properties was conducted, suggesting a ligand **B** centered triplet origin for their luminescence.

Introduction

A fruitful and appealing alternative to classic synthetic methodologies for constructing complex discrete molecular scaffolds consists in the application of supramolecular self-assembly procedures.¹ In these approaches, the spontaneous recognition of rationally designed individual building blocks occurs, affording selectively well-defined discrete supramolecular architectures. These self-assembly processes are promoted by non-covalent kinetically labile bond formations, which take place along self-sorting and self-correction events until the individual building blocks gather into the final thermodynamically stable target product. Considering in this context the use of the metal-ligand coordination interaction, a plethora of multimetallic supramolecular assemblies have blossomed in the last decade,^{2,3} in particular accordingly to coordination driven supramolecular (CDS) chemistry synthetic principles.³ CDS processes rely on the use of pre-organized coordination complexes having predefined geometries (being in most cases hardly accessible from single metal center coordination sphere) and vacant coordination positions.³ These pre-organized precursors, obtained from the reaction of metal ions with specific assembling ligands, are associated with connecting polytopic ligands allowing the formation of targeted multimetallic derivatives whose sizes and geometries are controlled by the symmetry of the linking sites of the individual building blocks. Accordingly to this synthetic approach, a variety of attractive

multifunctional molecular devices or metallacycles bearing remarkable ability for selective encapsulation of certain guest species and/or original reactivity within their internal confined spaces could thus be prepared.³ Within the intricate CDS polymetallic assemblies reported, metallo-macrocycles are omnipresent. They constitute either the targeted scaffolds or serve as sub-units for the construction of more elaborated molecular architectures. So far, CDS systems based mostly on the Pt(II) and Pd(II) metal centers have been flourishing.^{2n-u,3a-d,4} Indeed, these ions combine strong preferences for a rigid square planar coordination sphere and highly directional thermodynamically stable but kinetically labile metal-ligand interactions with a large range of ligating coordination groups, which are key factors to ensure the success of CDS synthetic processes. Yet, in the recent years, alternatives to these leading trends have appeared allowing the introduction of a larger variety of metal centers and ligating groups.⁵

Thus, we have recently initiated the introduction of pre-assembled Cu(I) precursors such as the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ bimetallic fragment **A** (Scheme 1a, dppm = bis(diphenylphosphino)methane) in self-assembly procedures related to CDS syntheses.⁶ In these cases, the typical labile, flexible and low-directional coordination sphere of this ion, initially regarded a priori as strongly restrictive in conventional CDS chemistry, turned out to be very valuable to conduct the selective preparation of original CDS assemblies based on the Cu(I) ion. In addition, the obtained polymetallic derivatives present a variety of luminescence properties⁷ due to the versatile photophysical processes lying in Cu(I)-based derivatives (such as Thermally Activated Delayed Fluorescence (TADF)),^{7a,c} drawing new perspectives in the ready design of innovative and inexpensive luminescent supramolecular compounds. Very importantly, these previous studies highlighted a win-win situation, promoting the

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† Footnotes relating to the title and/or authors should appear here.

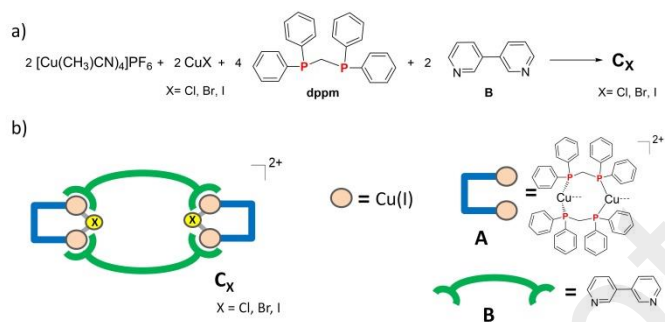
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

introduction of Cu(I) metal centers in attractive luminescent CDS assemblies. Indeed, on the one hand, the integration of the Cu(I) ions within CDS intricate scaffolds bearing multiple chelates and metallacycle sub-units endows to this Cu(I)-based species a significant thermodynamic stability. Therefore, selective self-assembly processes toward a single product can be directed in solution. This is a marked contrast compared to the multiple equilibria typical of the fluxionality of the Cu(I) metal centres' coordination sphere that can govern the conventional solution coordination chemistry of the Cu(I) ion and frequently results in unpredictable mixtures of hetero- and homoleptic structures.⁸ Moreover, this has allowed establishing that, due to a suitable molecular design of pre-assembled Cu(I) polymeric building blocks, it is possible to proceed to a rationalization of the adaptative behaviors exhibited by the intrinsically conformationally flexible polymeric Cu(I) precursors used.^{6a,c} On the other hand, in these CDS assemblies, the Cu(I) metal centers are embedded within polycyclic supramolecular scaffolds having constrained geometries. These metal centers are thus subject to significantly reduced possibility of structural re-organization of their coordination sphere in the excited states. Therefore, the non-radiative deactivation pathways associated to such re-organization are greatly minimized within Cu(I)-based CDS assemblies which promotes emergence of enhanced photophysical properties in such self-assembled derivatives

Taking these observations into consideration, we have been motivated to explore further the use of CDS chemistry for the selective preparation of new luminescent Cu(I) metallacycles. Herein, we describe the one-step preparation of three new tetranuclear dicationic discrete metallacycles C_X ($X = \text{Cl}, \text{Br}, \text{I}$). Their synthesis, characterization, X-ray single crystal molecular structure and solid-state luminescence properties are reported.

Results and discussion

While previous preparation of Cu(I)-based CDS luminescent assemblies mostly focused on the use of cyano-based inorganic linkers⁶ and nitrile-terminated organic ditopic ligands,⁹ we have been interested to extend these investigations to the reaction of the pre-organized $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ bimetallic fragment **A** with pyridyl-terminated organic ligands. Indeed, such electron-rich nitrogen-donor polytopic linkers predominate in CDS syntheses due to the strong affinity of these moieties toward a large variety of metal ions and due to the high directionality of the coordination bonds formed. In this study, we have focussed more particularly on the use of the ditopic 3,3'-bipyridine ligand **B** since it was demonstrated that bis-monodentate ligands bearing the 3-pyridyl moiety as coordinating group present a strong tendency to form discrete polycyclic CDS-assemblies.^{2d,u,v, 3e,4b} Moreover, luminescent Cu(I) coordination polymers have been previously reported bearing **B** as connecting ligand between the metal centers,¹⁰ demonstrating the appealing photophysical properties



Scheme 1: a) Synthesis of derivatives C_X ; b) Schematic representation of the derivatives C_X .

that can arise from the association of Cu(I) metal centers with **B**. In the course of this study, we have observed that it is mandatory to introduce an additional μ_2 -bridging halide anion on the Cu(I) bimetallic unit of the pre-assembled $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ precursor, in order to prepare selectively new Cu(I) discrete polymeric derivatives. Indeed, as one equivalent of the in-situ formed $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ unit was reacted in CH_2Cl_2 under air at room temperature (RT) with one equivalent of ligand **B** a colourless clear solution was obtained. The slow diffusion of pentane vapors in this solution afforded after a few days a mixture of different colourless polycrystalline species having significantly distinct eye-perceived luminescence color under UV-Vis light excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$), ranging from blue-green to yellow. Unfortunately, the quality of these crystallites and their very low stability once removed from the mother solution did not allowed us to determine their X-ray crystal structures. It was also not possible to purify these species via a manual separation since the crystals collapsed in polycrystalline powder very quickly once removed from the mother solution. Yet, after a few weeks, we observed that a small amount of well-shaped new colorless crystals of the species C_{Cl} appeared in the crystallisation experiments. These crystals display at RT in the solid state an eye-perceived blue-cyan intense luminescence upon UV-Vis light excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$) and could be successfully collected in order to establish the solid-state molecular structure of C_{Cl} , thanks to a single crystal X-ray diffraction study experiment performed at low temperature. It revealed that this compound crystallizes in the triclinic space group P-1 (Table 1) with an asymmetric unit containing half of the discrete supramolecular assembly C_{Cl} , one hexafluorophosphate counter-anions and five disordered CH_2Cl_2 solvent molecules. The derivative C_{Cl} is a centrosymmetric dicationic tetrametallic metallacycle (Scheme 1b, Figure 1) resulting from the connection of two $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-Cl})]^{+}$ dimeric units by two ligands **B** acting as ditopic linkers. The metal centers present similar $\text{P}_2\text{Cl}_1\text{N}_1$ distorted tetrahedral coordination spheres (Table 2) and, compared to the other Cu(I) polymeric assemblies based on this bimetallic unit, the overall metric data at the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ sub-unit are classical.^{6,9} Yet, the intermetallic distance is quite large ($d(\text{Cu-Cu}) = 3.179(7) \text{ \AA}$, above the limit usually proposed for cuprophilic interactions)¹¹ as the result of the presence of a μ_2 -

symetrically bridging chloro ligand ($d(\text{Cu}-\text{Cl}) = 2.4034(12)$ and $2.4048(11)$ Å). Within the assembly C_{Cl} , the two μ_2 -chloro ligands (separated by ca. 4.55 Å) are located toward the center of the metallacycle and are orientated slightly outward of the mean plane defined by the four Cu(I) ions (deviation to the mean plane : 0.753 Å). The coordination of the ligands **B** on the two metal centers of the bimetallic units is also highly symmetrical with similar (Cu-Cu-N) angles (150.21 and 150.34°) and (Cu-N) bond lengths (both being of $2.121(3)$ Å). The torsion angle between the two 6-membered rings of the coordinated ligands **B** is 17.2° (Fig. 2c), which is significantly smaller than the torsion angle (43.6°) found in the previously reported Cu(I) 1D-CP based on the ligand **B**, in which in addition shorter (Cu-N) bond lengths have been observed ($d(\text{Cu}-\text{N}) = 2.034(3)$ Å).¹⁰ This highlights the sterical constraints applied on the backbone of the coordinated ligands **B** within the metallacyclic scaffold of C_{Cl} .

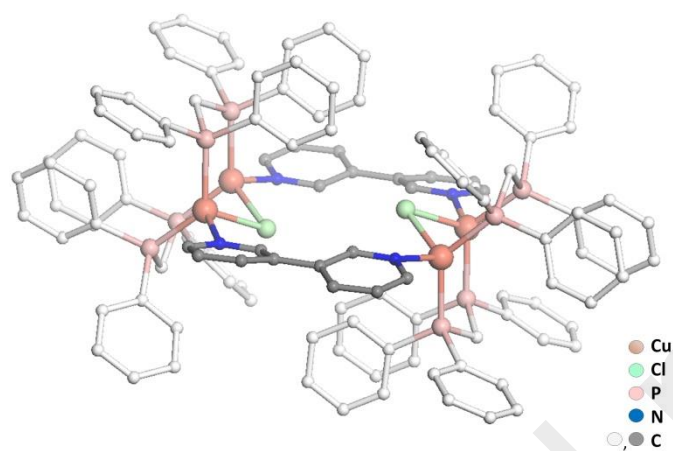


Fig. 1. a) Views of the molecular X-ray structures of the dicationic metallacycle C_{Cl} (counteranions, H atoms and solvent molecules have been omitted for clarity).

The origin of the bridging μ_2 -chloro ligand probably arises from slow chloride abstraction from CH_2Cl_2 solvent molecules under the crystallization condition applied. Similar examples that involve chloride abstraction have also been observed for the preparation of other multi-nuclear copper complexes.¹² Yet, considering the very slow crystallisation process of the metallacycle C_{Cl} , it is very likely that equilibria occur in the crystallisation tubes in which reactive secondary species are able to trap chloride atoms arising from CH_2Cl_2 solvent degradation. Indeed, after two additional months, the amount of crystals of C_{Cl} did not increase significantly, precluding further characterisations of this metallacycle at that stage.

Yet, this result suggests that the introduction of a μ_2 -bridging chloro ligand on the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ building unit could favour the preparation of stable metallacyclic species based on ligand **B**, by

Table 1. Crystal data and structure refinement for derivatives C_{Cl} , C_{Br} and C_{I} after squeeze treatment (values in italic are related to the relevant data before the squeeze treatment).

	C_{Cl}	C_{Br}	C_{I}
Molecular formula	$\text{C}_{120}\text{H}_{104}\text{Cl}_2\text{Cu}_4$ $\text{F}_{12}\text{N}_4\text{P}_{10}$ ($\text{C}_{130}\text{H}_{112}\text{Cl}_{22}\text{C}$ $u_4\text{F}_{12}\text{N}_4\text{P}_{10}$)	$\text{C}_{120}\text{H}_{104}\text{Br}_2\text{Cu}_4$ $\text{F}_{12}\text{N}_4\text{P}_{10}$ ($\text{C}_{130}\text{H}_{112}\text{Br}_2\text{Cl}_2$ $o\text{Cu}_4\text{F}_{12}\text{N}_4\text{P}_{10}$)	$\text{C}_{120}\text{H}_{104}\text{I}_2\text{Cu}_4$ N_4P_8 ($\text{C}_{132}\text{H}_{98}\text{I}_2\text{Cl}_{24}\text{C}$ $u_4\text{F}_{12}\text{N}_4\text{P}_{10}$)
CCDC number	2074606	2074608	2074607
Molecular weight	2464.83 (3302.00)	2553.75 (3390.92)	2357.79 (3636.60)
<i>a</i> (Å)	14.113(2)	14.182(3)	14.308(2)
<i>b</i> (Å)	14.181(2)	14.237(3)	14.297(2)
<i>c</i> (Å)	18.602(2)	18.585(3)	18.459(2)
α (°)	87.110(4)	87.431(6)	68.40156)
β (°)	69.039(4)	69.448(5)	87.648(5)
γ (°)	84.128(4)	84.493(6)	85.23156)
<i>V</i> (Å ³)	3458.0(8)	3497.2(12)	3498.7(3)
<i>Z</i>	1	1	1
<i>D_c</i> (g cm ⁻³)	1.184 (1.586)	1.213 (1.610)	1.119 (1.726)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
Temperature (K)	150(2)	150(2)	150(2)
Wavelength Mo-K α (Å)	0.71069	0.71069	0.71069
Crystal size (mm)	0.35 * 0.28 * 0.11	0.45 * 0.11 * 0.09	0.16 * 0.11 * 0.07
μ (mm ⁻¹)	0.819 (1.215)	1.343 (1.734)	1.171 (1.682)
<i>F</i> (000)	1260 (1668)	1296 (1704)	1194 (1806)
θ limit (°)	2.02 – 27.57	2.19 – 27.63	2.17 – 27.55
Index ranges <i>hkl</i>	-18 < <i>h</i> < 18 -17 < <i>k</i> < 18 -24 < <i>l</i> < 24	-18 < <i>h</i> < 18 -18 < <i>k</i> < 15 -24 < <i>l</i> < 24	-18 < <i>h</i> < 18 -17 < <i>k</i> < 18 -23 < <i>l</i> < 23
Reflections collected	70583	55169	56861
Independent reflections	15920	15866	15846
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	12697 (12710)	12432 (12827)	10729 (10872)
Data/restraints/parameters	15920 / 0 / 719 (15920/0/854)	15866 / 0 / 709 (15866/0/854)	15846 / 0 / 622 (15846/0/875)
Goodness-of-fit on <i>F</i> ²	1.088 (1.058)	1.088 (1.042)	1.105 (0.988)
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0680 (0.0891) <i>wR</i> ₂ = 0.1995 (0.2353)	<i>R</i> ₁ = 0.0852 (0.1127) <i>wR</i> ₂ = 0.2290 (0.2853)	<i>R</i> ₁ = 0.0857 (0.1143) <i>wR</i> ₂ = 0.2219 (0.2866)
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0802 (0.1082) <i>wR</i> ₂ = 0.2110 (0.2568)	<i>R</i> ₁ = 0.1009 (0.1329) <i>wR</i> ₂ = 0.2418 (0.3035)	<i>R</i> ₁ = 0.1188 (0.1607) <i>wR</i> ₂ = 0.2413 (0.3248)
Largest diff peak and hole (e Å ⁻³)	1.483 and -1.383 (2.209 and -1.730)	2.452 and -1.635 (4.816 and -1.559)	2.247 and -1.797 (3.434 and -1.857)

forcing this conformationally flexible $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment to adopt a suitable geometry promoting selective self-association processes.

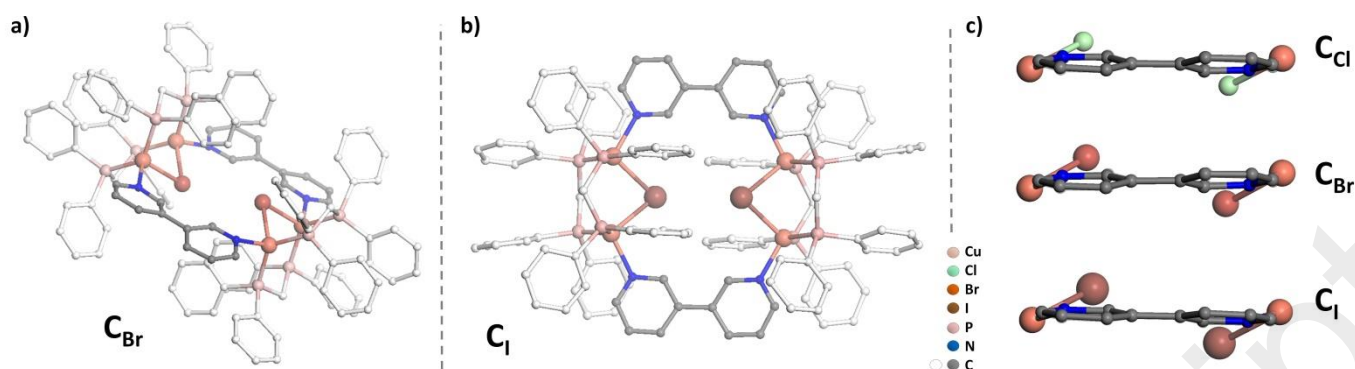


Fig. 2. Views of the molecular X-ray structures (counteranions, H atoms and solvent molecules have been omitted for clarity) of the dicationic derivatives a): \mathbf{C}_{Br} and b): \mathbf{C}_1 ; c) Simplified 'lateral' views of the X-ray structures of metallacycles \mathbf{C}_{Cl} , \mathbf{C}_{Br} and \mathbf{C}_1 .

In order to confirm this assumption, a CH_2Cl_2 solution of one equivalent of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$, one equivalent of CuCl and two equivalents of dppm ligand was prepared (Scheme 1a) and left upon stirring at room temperature (RT) under air for one hour, affording a colorless solution. To this solution one equivalent of the ligand **B** dissolved in CH_2Cl_2 was added, leading to a slightly yellowish colored clear solution that was left upon stirring at RT overnight. The crude solution was then left to crystallize under air at RT upon pentane vapor diffusions. After one week an homogeneous batch of well-shaped single crystals was obtained, that were identified by single crystal X-ray diffraction study as being crystals of the metallacycle \mathbf{C}_{Cl} . After filtration, the sample was dried affording an homogeneous sample of block-shaped colorless polycrystalline solid of \mathbf{C}_{Cl} with a yield of 66 %.

obtained in a good yield if CuCl is introduced in the reaction. Along this synthetic procedure, formally, a $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-Cl})]^+$ moiety can be considered as being formed as pre-assembled building unit. Such in-situ formed precursor presents very likely a significantly restricted degree of conformation freedom compared to the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment since the μ_2 -bridging chloro ligand locks the geometry of the bimetallic unit. This results in the formation of a bimetallic rigid $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-Cl})]^+$ connecting node bearing potentially two available coordination positions (one on each metal center) with a coordination angle of ca. 120° . In such situation, selective CDS assembling processes take place along which the ligand **B** is forced to adopt a N,N cisoid orientation of its two 3-pyridyl fragments resulting in the ready and selective formation of the metallacycle backbone of \mathbf{C}_{Cl} .

Importantly, this approach affording new $\text{Cu}(\text{I})$ CDS metallacycles is not only restricted to the introduction of a μ_2 -bridging chloro ligand on the $\text{Cu}(\text{I})$ bimetallic building blocks. Using CuBr or CuI instead of CuCl (Scheme 1a), the new metallacycles \mathbf{C}_{Br} and \mathbf{C}_1 could be also obtained selectively accordingly to a similar synthetic procedure. X-ray diffraction studies revealed that the crystals of these compounds are isostructural with those of \mathbf{C}_{Cl} (Table 1), gathering two $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-X})]$ ($\text{X} = \text{Br}$ or I) bimetallic building blocks in tetrametallic metallacycle via their coordination with two ligands **B** (Figure 2a,b). Within these dicationic assemblies, the intermetallic distance increases (\mathbf{C}_{Br} : 3.261(8) Å; \mathbf{C}_1 : 3.362(7) Å) with the atomic radius of the bridging halide atom but the μ_2 -symmetrically bridging coordination mode is preserved along the series (\mathbf{C}_{Br} : $d(\text{Cu-Br}) = 2.5211(10)$ and $2.5218(11)$ Å; \mathbf{C}_1 : $d(\text{Cu-I}) = 2.6636(12)$ and $2.6646(11)$ Å., Table 2). Inside these metallacycles, the deviations of the μ_2 -bridging halide ions from the mean plane defined by the four $\text{Cu}(\text{I})$ ions (\mathbf{C}_{Br} : 0.812 Å; \mathbf{C}_1 : 0.884 Å) are similar to the value found in derivative \mathbf{C}_{Cl} . Regarding the coordination displayed by the connecting ligands **B**, moderate differences are observed along the series of the three derivatives \mathbf{C}_{Cl} , \mathbf{C}_{Br} and \mathbf{C}_1 , in which the (Cu-Cu-N) angles are also symmetrical (150.27° and 150.76° in \mathbf{C}_{Br} ; 151.15° and 151.51° in \mathbf{C}_1). The (Cu-N) bond lengths are 2.109(4) Å and 2.121(5) Å in \mathbf{C}_{Br} and 2.119(6) Å and 2.124(5) Å

	\mathbf{C}_{Cl}	\mathbf{C}_{Br}	\mathbf{C}_1
Cu-Cu	3.180(4)	3.261(5)	3.362(5)
Cu - N	2.121(3) and 2.121(3)	2.109(4) and 2.121(5)	2.119(6) and 2.124(5)
Cu - X	2.4034(12) and 2.4048 (11)	2.5218(11) and 2.5211(10)	2.6646(11) and 2.6636(12)
Cu - P	2.2687(10), 2.2569(10), 2.2604(11) and 2.2527(11)	2.2682(15), 2.2567(14), 2.2595(16) and 2.2546(16)	2.2474(17), 2.2576(16), 2.2549(19) and 2.2539(19)
Cu-Cu-N	150.25(3), 150.37(4)	150.76(5), 150.27(6)	151.51(5), 151.15(5)
Cu-X-Cu	82.80(3)	80.58(2)	78.24(3)

Table 2. Selected intermetallic distances [Å] and angles [$^\circ$] in the derivatives \mathbf{C}_{Cl} , \mathbf{C}_{Br} and \mathbf{C}_1 .

Thus, the presence of chloride anions in the synthesis conducted induces a complete alteration of the self-assembly processes occurring as the pre-assembled $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ precursor is reacted with the ligand **B**. Indeed, instead of a mixture of unidentified species obtained in a first step, followed by a very slow and low-efficient conversion to the derivative \mathbf{C}_{Cl} , this metallacycle can be directly and selectively

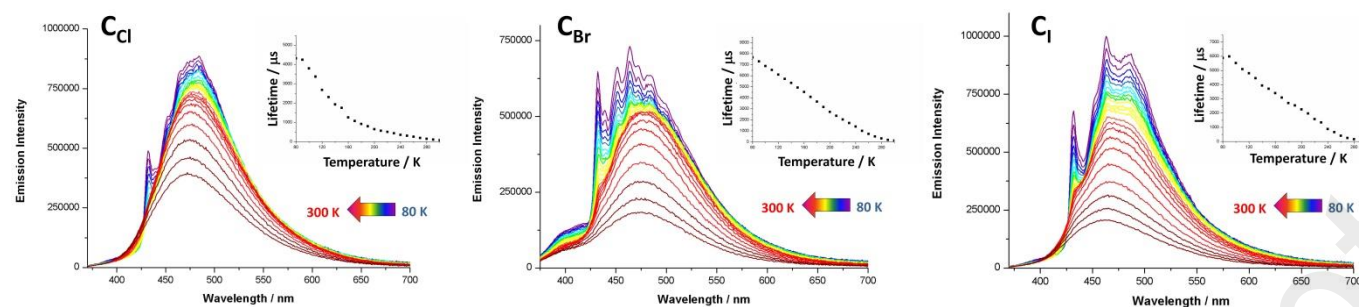


Fig. 3. Temperature dependence (80 K to 300 K) of the solid-state emission spectra of metallacycles C_{Cl} , C_{Br} and C_I upon excitation at 325 nm,[‡] insert: plot of their emission decay lifetime against temperature (80 K to 300 K).

in C_I and therefore do not significantly differ from the values observed in C_{Cl} (Table 2). Finally, the torsion angle between the two rings of the coordinated ligands **B** is 15.9° in C_{Br} and 9.8° in C_I (Figure 2c), confirming thus that the ligands **B** within these assemblies are forced upon coordination to present a remarkable planarity whose extent is enhanced as the μ_2 -symmetrically bridging ligand changes from chloride to bromide and to iodide. Therefore, in the molecular structure of the series of tetrametallic metallacycles C_x ($X = Cl, Br, I$), the variation of the nature of the μ_2 -bridging halide mostly affects the metric data at the Cu(I) dimer and the conformation presented by the ligands **B**, but the gross molecular structures are similar. Interestingly, a related Cu(I) complex of tetramesityl substituted ferrocene bisphosphine [Fe(CpPMe₂)₂*(CuBr)₂]₂, that presents a comparable metallacyclic structure in which Cu(I) dimers are bridged by μ_2 -bromide atoms was recently described by Pietschnig et al.¹³ In this derivative, the intermetallic distance in the Cu(I) dimer ($d(Cu-Cu) = 2.93 \text{ \AA}$) is shorter than in C_{Br} and the deviations from the mean plane defined by the four Cu(I) ions of 1.135 Å are significantly larger than those observed in C_{Br} suggesting overall larger steric constraints within this metallacycle core.

The crystals of C_{Cl} , C_{Br} and C_I are colorless under visible light and display under UV irradiation ($\lambda_{ex} = 365 \text{ nm}$) an eye-perceived light blue-cyan solid-state RT luminescence. The solid-state RT UV-visible absorption spectra of the derivatives C_{Cl} , C_{Br} and C_I (Fig. S10-12) exhibits a strong and broad absorption band in the near UV region centered at ca. 300 nm, typical of $\pi-\pi^*$ transition centered on the aromatic rings of dppm and ligands **B**. The excitation spectra (Fig. S4-S6) for these compounds reveals two maxima at ca. 325 nm and ca. 370 nm. In their emission spectra, derivatives C_{Cl} , C_{Br} and C_I displays at 300 K a broad featureless band centered at $\lambda_{max} = 475, 476$ and 464 nm respectively (Fig. 4, Table 3).[‡] In the solid state, these compounds present RT lifetimes of the excited state of 74 μs , 119 μs and 70 μs and their RT emission quantum yields (EQY) reach 80%, 60% and 54% for C_{Cl} , C_{Br} and C_I respectively.[§] Such solid-state RT EQY values are remarkably high for derivatives bearing RT lifetimes whose values of several tenths of microseconds indicate a triplet origin for the luminescence observed. Moreover, the RT EQY value progression is reversed compared to the increase of the

atomic number of μ_2 -bridging halide ligand. This is quite unusual in luminescent Cu(I)-halide derivatives in which the increment of the spin-orbit coupling associated with heavier halides usually promotes efficient radiative relaxation processes via external heavy-atom effects. To get more insights about the emission properties of derivatives C_{Cl} , C_{Br} and C_I , temperature dependent photophysical characterizations were conducted upon temperature cooling from 300 K to 80 K. In the emission spectra of C_{Cl} under excitation at 325 nm,[‡] a gradual and very moderate red-shift (Fig. 4) of the large band observed upon cooling at 300 K ($\lambda_{max} = 475 \text{ nm}$) is observed with a net increase of the signal intensity. This intensity enhancement is accompanied in the lowest temperature by a progressive structuration of the emission band yielding at 80 K a large signal bearing an apparent vibronic sub-structure with two maxima centered at 432 and 484 nm (for which is observed the highest intensity signal) and three shoulders at 452, 465 and 502 nm (Table 3). Regarding the thermal variation of the lifetimes of the excited state of C_{Cl} , a continual and significant increase of the decay time is observed upon cooling, reaching 4.3 ms at 80 K (Fig. 4, Table 3).[§] Comparable temperature dependant profiles are observed for the emission spectra and the lifetimes of the excited state of C_{Br} and C_I (Fig. 4, Table 3). In comparison, the low temperature emission spectrum of the free ligand **B** (Fig. S16) is characterized by a large unstructured band centered at 455 nm ($\lambda_{ex} = 320 \text{ nm}$) associated with a considerably shorter decay time of the excited state (4.5 ns) at 80 K, typical of purely organic fluorescence. Note that in the temperature dependent emission spectra of the derivative C_{Br} (Fig. 3) a weak and large additional band appears between 375-425 nm associated with a decay time of the excited state of 3.5 ns that can likely be assigned to a residual ligand centred luminescence.

The values of the recorded emission lifetimes clearly indicate a triplet origin of the luminescence arising from these Cu(I) metallacycles and, together with the general thermal variation of the profiles of the emission spectra, preclude to suggest a TADF process to explain the overall temperature-dependent data collected for the photophysical properties of these three metallacycles, in spite of the high RT EQY measured.

Table 3. Photophysical data ($\lambda_{\text{ex}} = 325$ nm) for derivatives **C_{Cl}**, **C_{Br}**, and **C_I** at 298 K and 80 K in the solid state.

	λ_{em} (nm) ^a	Φ_{em}	τ_{obs} (μs) ^a	k_r (s^{-1}) ^b	k_{nr} (s^{-1}) ^c
C_{Cl}	475 (432, 452, [§] 465, [§] 484, 502 [§])	80	74 (4315)	1.1×10^4	2.7×10^3
C_{Br}	476 (432, 452, 464, 484, [§] 500 [§])	60	119 (7660)	5.0×10^3	3.4×10^3
C_I	464 (432, 452, [§] 462, 486, 50 [§])	54	70 (5881)	7.7×10^3	6.6×10^5

^a Data recorded at 80 K are given in parentheses; ^b $k_r = \Phi_{\text{em}}/\tau_{\text{obs}}$; ^c $k_{\text{nr}} = (1 - \Phi_{\text{em}})/\tau_{\text{obs}}$; [§]: shoulder

Regarding specifically the RT photophysical behaviors for this series of metallacycles, the k_r radiative rate constant values are in agreement with a ³MLCT phosphorescence in which the high temperature large emission bands can be assigned to radiative processes involving likely electronic densities located on the 3,3'-bipyridine ligands **B**. Yet, the large enhancement of the decay times of the excited states as the temperature decrease, together with the vibronic structuration that appears in the low temperature emission band, suggest at low temperature a ³ π - π^* ³ILCT phosphorescence centered on the connecting ligands **B**. Such vibronic structuration is indeed not observed in the thermal variation of related TADF luminescent polymetallic supramolecular assemblies based on the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ moiety and cyano-based connecting inorganic ligands,^{6b-d} in which radiative processes mostly rely on transitions from the highest occupied molecular orbitals (HOMOs), being metal-cyano antibonding, to the lowest unoccupied molecular orbital (LUMO) having MLCT character involving the four metal centres of the metallacycle and the dppm ligands. Conversely, in a 1D-coordination polymer based on related $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-OH}_2)]^{2+}$ dicationic fragments connected by 1,4-dicyanobenzene connecting ditopic ligands,^{9d} a similar progressive structuration of the emission band is observed upon temperature cooling. In the case of this 1D-coordination polymer, the low temperature photophysical properties were assigned to 1,4-dicyanobenzene ligand-centered ³ π - π^* phosphorescence which supports the activation of such radiative processes in the low temperature luminescence properties of derivatives **C_{Cl}**, **C_{Br}** and **C_I**. Considering these observations, it is likely that purely ligand-centered ³ π - π^* phosphorescence occurs at low temperature and tends to vanish at higher temperatures due to a thermally activated interconversion between ³ILCT and ³MLCT states.^{8,14}

Interestingly, it is worth noting that only a minor contribution of the orbital lying on the semi-bridging aqua ligand $\mu_2\text{-OH}_2$ was observed in the electronic excitation process in the previously reported 1D-coordination polymer based on the $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-OH}_2)]^{2+}$ dicationic unit and the 1,4-dicyanobenzene connecting ditopic ligand.^{9d} Regarding the

similarities in the local molecular structures of the Cu(I) dimer in this coordination polymer and the metallacycles reported herein ($[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-OH}_2)]^{2+}$ fragments versus $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-X}_2)]^+$ moieties, X = Cl, Br, I), a similar electronic structure could explain the relatively low and unusual impact of the variation of the μ_2 -bridging halide atom on the photophysical properties of the metallacycles **C_{Cl}**, **C_{Br}** and **C_I**. Unfortunately, the computational cost of the full TD-DFT geometry optimizations of the excited states of the large assemblies **C_{Cl}**, **C_{Br}** and **C_I** studied here, that would allow getting deep insights of the photophysical mechanisms, revealed to be too prohibitive to be conducted along this study. In this context, it is not straightforward to account the origin of the high solid-state RT EQY exhibited by these metallacyclic triplet luminophores. It was previously observed that the overall multicyclic networks built in such Cu(I)-based CDS assemblies clearly induce structural constraints that significantly hamper highly detrimental non-radiative relaxation pathways and structural re-organisation in the excited states. The RT values of the k_{nr} non-radiative rate constants in this series of metallacycles reveals that non-radiative decays are quite small and more effectively suppressed in the case of the lighter bridging halides. This may be related to backbones bearing shorter intermetallic distances. Indeed, in the one hand, this might be responsible of overall lower degrees of conformational flexibilities allowed in the solid state in more compact and rigid assemblies. In the other hand, shorter intermetallic distances associated with lighter bridging halides also induce higher spin-orbit coupling constants^{6b} which impacts the electronic processes, facilitating radiative desexcitation pathways. This is supported by the higher k_r radiative rate constant values obtained for the μ_2 -Cl bridged derivative **C_{Cl}** (Table 3). Therefore, varying the nature of the bridging halides in this family of metallacycles leads to a dual effect, favouring the lighter halide regarding both radiative and non-radiative processes for the exaltation of the solid-state luminescence properties.

Finally, the pronounced planarity observed in the solid-state for the 3,3'-bipyridine ligands **B** in **C_{Cl}**, **C_{Br}** and **C_I** reveals that the coordination of these ditopic ligands on the $[\text{Cu}_2(\mu_2\text{-dppm})_2(\mu_2\text{-X})]^+$ units locks their conformation within these self-assembled metallacycles in an arrangement that promotes an efficient overlap of the π -orbitals along the ligands **B** quasi-planar backbones. This induces a stabilization of the molecular orbitals located on these 3,3'-bipyridine ligands in **C_{Cl}**, **C_{Br}** and **C_I** and supports the assumptions that ³MLCT and ³ILCT phosphorescence radiative relaxation processes occur in these metallacycles being based on molecular orbitals lying at least partially on these connecting ligands **B**. Very likely, such conformational constraints applied on the coordinated ligands **B** in derivatives **C_{Cl}**, **C_{Br}**, and **C_I** contribute to the differences observed between the photophysics of these metallacycles and those of the previously reported luminescent Cu(I) coordination polymer bearing the 3,3'-bipyridine ligands in a twisted conformation.¹⁰ Indeed, in this latter case, it was concluded that the recorded emission could be attributed to the delayed fluorescence from the ¹(M+X)LCT excited state at

RT and changed to simple phosphorescence from the same triplet excited state at 77 K, suggesting radiative relaxation processes involving a larger contribution of molecular orbitals centred on the inorganic part of this derivative.¹⁰

Therefore, by forcing upon self-assembly processes the 3,3'-bipyridine scaffolds to be almost planar (Fig. 2c), the radiative relaxations pathways in derivatives **C_{Cl}**, **C_{Br}** and **C_I** are significantly altered compared to the luminescent Cu(I) coordination polymer bearing the 3,3'-bipyridine ligands reported previously. This clearly demonstrate in such Cu(I)-based supramolecular assemblies the great dependence of the photophysical properties to the molecular engineering applied.

Conclusions

All in all, this study confirms the interest of synthetic approach adapting the CDS chemistry principles to conformationally flexible Cu(I) precursors. In particular, the versatility of [Cu₂(μ₂-dppm)₂] bimetallic units is highlighted, revealing in the case of the use of 3-pyridyl terminated connecting ligands that it is necessary to introduce μ₂-X bridging halide ligands to lock the Cu(I) dimer fragment in a conformation that allows conducting selective CDS self-assembly processes. As a result, bimetallic node presenting potential coordination directions of ca. 120° are obtained. Moreover, the variety and peculiarities of the photophysical processes reported for Cu(I) CDS supramolecular assemblies are enriched with this new series of tetrametallacycles that behave as ligand centred triplet luminophores bearing high RT EQY. These behaviours are assigned to the specific molecular organisation forced within these self-assembled structures and draw appealing perspectives for future investigations varying in particular the internal cores of the 3-pyridyl terminated connecting ligands involved in these reactions. Finally, it is worth to stress that both the gross structural parameters of these metallacycles and their photophysics in the solid-state are comparable, regardless the nature of the bridging halide atoms. This is rather unusual and highlights in the one hand the specificities that can be associated with the use of conformationally flexible Cu(I) bimetallic precursors. In the other hand, this reveals the originality of the radiative relaxation processes that can lay in such self-assembled CDS assemblies based on the Cu(I) ion.

Author Contributions

Florent Moutier: Investigation, Formal analysis. **Janna Schiller**: Investigation, Formal analysis. **Guillaume Calvez**: Formal analysis. **Christophe Lescop**: Project administration, Formal analysis, Writing

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ These temperature dependant behaviour do not depend on the excitation energy and similar results were obtained with λ_{ex} = 375 nm.

§ These emission decay times are mono-exponential.

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