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Research Paper

Straightforward coordination-driven supramolecular chemistry preparation of a discrete solid-state luminescent Cu₄ polymetallic compact assembly based on conformationally flexible building blocks.

Sloane Evariste, Chendong Xu, Guillaume Calvez, Christophe Lescop*

Dedicated to the Pr. Maurizio Peruzzini for his 65th birthday

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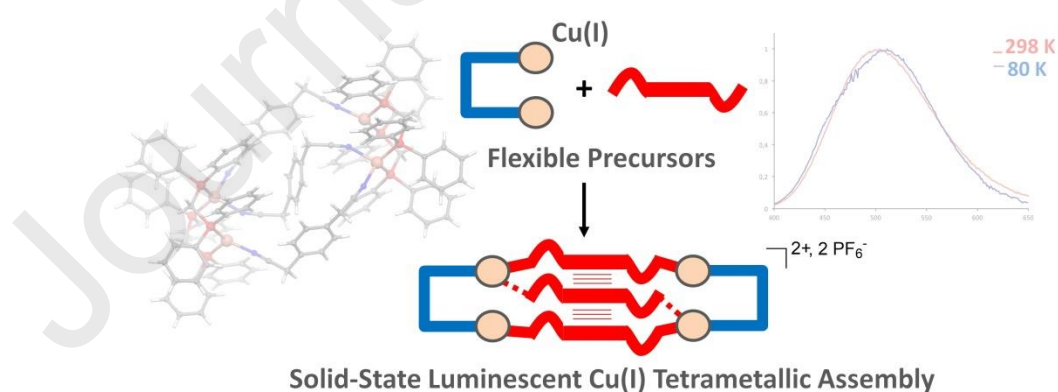
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Highlight

Luminescent discrete Cu(I) assembly is made from conformationally flexible precursors

Graphical Abstract



Keywords

Cu(I) complexes, Coordination-driven Supramolecular Chemistry, Luminescence, Solid-state structures and properties, Conformational flexibility.

Abstract

The ditopic nitrile-capped 1,4-phenylenediacetonitrile linker L_3 featuring partial conformational flexibility was reacted with a flexible pre-assembled Cu(I) dimer stabilized by the bis(diphenylphosphino)methane dppm ligand along adaptive coordination-driven supramolecular assembling processes. It resulted in the selective and unexpected formation of a compact tetrametallic assembly associating two bimetallic building blocks with three ditopic linkers. The solid-state photophysical studies of this original Cu(I)-based assembly were analysed and showed its attractive luminescence properties.

1. Introduction

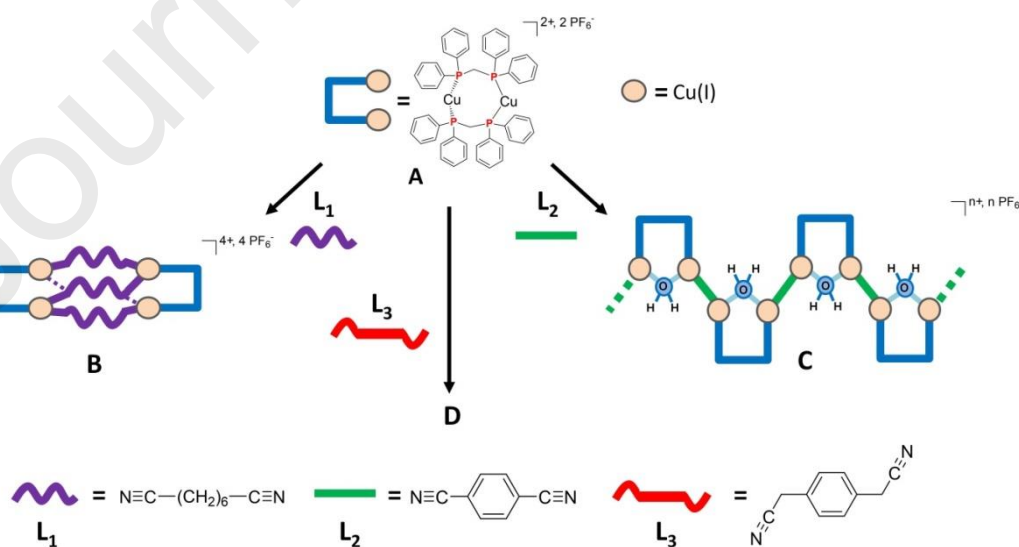
Coordination-driven supramolecular (CDS) synthesis¹ of advanced molecular assemblies currently attracts an extensive attention since it allows an easy and rational preparation of metallo-organic architectures bearing increased structural complexity.² In this approach, the choice of pre-designed individual building blocks (metal complexes and organic linkers) engaged in predictable and selective self-assembly events is crucial as it controls the overall shape, size and symmetry of the polymetallic assemblies prepared. So far, systems based on square-planar Pt(II) and Pd(II) metal centers constitute a predominant class of CDS self-assembled structures^{2,3} since these d^8 ions present usually high structural rigidity and adequate lability toward a large range of connecting ligands, which are key factors insuring the selectivity in such synthetic procedures. Nevertheless, the community has stepped up in the recent years efforts to develop several alternative and innovative synthetic approaches related to CDS chemistry,⁴ allowing the introduction of a great variety of metal ions in CDS self-assembled structures.

A large scientific interest is devoted on the synthesis of CDS architectures having manifold new functionalities,^{2,3} but luminescence properties have been, in proportion, moderately reported.^{5,6} In most of the studies reported to date in this field, the emission behaviors observed in CDS scaffolds are either due to the intrinsic fluorescence properties of the π -conjugated multitopic linkers⁵ designed to build the targeted supramolecular architectures (and integrating also sometimes on purpose specific luminescence properties), or to those of the heavy metals (mostly Pt(II), Re(I), Ir(III), Au(I), Pd(II) or Ru(II) ions)⁶ based phosphorescent pre-assembled building blocks used.

Interestingly, there is now a great attention devoted to the preparation of luminescent Cu(I) coordination complexes because of the fascinating and various photophysical properties they can exhibit.⁷ These emission behaviors are characterized by a large range of possible radiative relaxation processes with a rising attention being paid to compounds bearing Thermally Activated Delayed Fluorescence (TADF).^{7,8} In such derivatives, remarkable room temperature (RT) solid-state luminescence properties are generated due to the possibility of thermal population of the lowest energy excited singlet state (S_1) from the lowest energy triplet excited state (T_1), inducing fast

efficient radiative relaxation to the ground state. Yet, the potential use of Cu(I) luminescent precursors acting as pre-organized building blocks to prepare CDS assemblies is still to date mostly unexplored. Indeed, unlike Pd(II) or Pt(II) metal centers, Cu(I) ions are assumed usually to exhibit labile and non-directional coordination spheres which is a priori highly detrimental to conduct selective CDS syntheses toward discrete well-defined metallo-supramolecular architectures.

We have recently shown that these typical and disadvantaging features of the coordination chemistry of Cu(I) ion can be overcome and even turn out to be very valuable to conduct successfully unprecedented CDS syntheses.^{9,10} Actually, innovative adaptive CDS processes could be realized by using a suitable molecular design of pre-assembled Cu(I) polymeric precursors, such as the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ bimetallic building block **A** (Scheme 1, dppm : bis(diphenyl-phosphino)methane). Thus it was demonstrated that this bimetallic fragment can act as conformationally flexible pre-organized precursor when reacted with a variety of metallacyano ligands acting as polytopic linkers, to allow the straightforward formation of innovative polymeric CDS assemblies bearing original solid-state luminescence properties.¹¹ Apart from cyano-based building blocks, the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ bimetallic fragment was also reacted with several nitrile-capped extended π -conjugated ditopic organic linear linkers of various length and π -conjugated internal cores.¹² These reactions gave access to a series of discrete or polymeric supramolecular assemblies bearing π -stacked compact metallacyclophanes whose backbone was closely related with the conformation and connectivity exhibited by the flexible bimetallic sub-units. In contrast, the fully aliphatic nitrile-capped flexible ditopic NC-(CH₂)₆-CN linker **L**₁ (Scheme 1) was also involved in self-assembly CDS processes with this dimeric Cu(I) unit, resulting in the unexpected formation of the discrete tetrametallic assembly **B**, gathering two $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ building blocks and three aliphatic linkers.¹³ The formation of such unusual compact metallacyclic assembly was assigned to the cumulating, within such confined and discrete scaffold, of weak but stabilizing inter-linker London intramolecular interactions between the aggregated fully aliphatic apolar -(CH₂)₆- fragments. Importantly, such an organization is also favoured by the conformational flexibility of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ sub-units (facile variation of the intermetallic distance and the coordination number of the metal ions without collapse of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ core).



Scheme 1: Synthesis of derivative **B**¹³, **C**¹⁴ and **D**.

Recently, this study was extended to the reaction of the 1,4-dicyanobenzene ditopic linker **L**₂ (Scheme 1) with the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment, affording the one-dimensional coordination polymer (1D-CP) **C** that presents in its repetition unit the first Cu(I) bimetallic unit in which a water molecule bridges two Cu(I) metal centers.¹⁴ This 1D-CP exhibits reversible solid-state luminescence vapochromism properties due to unique single-crystal to single-crystal transitions caused by the adsorption in the bulk crystals of volatile and mobile solvents vapors.

The differences observed in the derivatives **B** and **C** (dimensionality of the supramolecular architectures, composition and conformation of the bimetallic sub-units coordination spheres) have triggered us to study the reaction between the bimetallic pre-organized building block **A** with the 1,4-phenylenediacetonitrile linker **L**₃ (Scheme 1). This cyano-capped ditopic linker presents an interesting alternative and somehow intermediate molecular structure compared to those of **L**₁ and **L**₂. Indeed, this linker **L**₃ partially reproduces the aliphatic flexible scaffold of the linker **L**₁ with the presence of two methylene units, conferring a potential conformational flexibility to its backbone. On the other hand, **L**₃ bears also a rigid and potentially structuring central 1,4-substituted phenyl ring as in the linker **L**₂. Herein, we describe the reaction of the ligand **L**₃ with the bimetallic precursor **A** (Scheme 1), affording the new tetrametallic tetracationic discrete derivative **D**. Its synthesis, characterization, X-ray single crystal molecular structure and solid-state luminescence properties are reported.

2. Results and Discussion

2.1. Synthesis and characterization of the supramolecular assembly **D**

One equivalent of the in-situ formed $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment (obtained from the reaction of two equivalents of the dppm ligand with two equivalents of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in CH_2Cl_2) was reacted with 1.5 equivalent of the ligand **L**₃ (Scheme 1) in CH_2Cl_2 at room temperature (RT) and under air, affording a colorless limpid solution. Its RT $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad signal centred at ca. -9.4 ppm, suggesting an equilibrium between mixture of species in solution. Such chemical shift is typical of supramolecular assemblies bearing a $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ sub-unit. Upon pentane vapours diffusion into this crude solution, homogeneous batches of air stable colorless block-shaped crystals of derivatives **D** (Scheme 1) were isolated in good yields, revealing the selection upon crystallisation of a single species among those in dynamic equilibrium in solution. The infrared spectrum of the compound **D** shows typical bands of coordinated dppm ligands and, interestingly, two bands assigned to nitrile groups coordinated on Cu(I) metal centres ($\nu(\text{C}\equiv\text{N}) = 2251\text{ cm}^{-1}$ and 2273 cm^{-1} while $\nu(\text{C}\equiv\text{N}) = 2249\text{ cm}^{-1}$ for the free ligand **L**₃) together with the absence of coordinated acetonitrile ligands (as also suggested by the ^1H NMR spectrum of **D**). Altogether, these spectroscopic data are indicative of the substitution of the labile acetonitrile ligands initially carried by the Cu(I) metal centers via the coordination of the dppm ligands (affording a $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ moiety) and the ligand **L**₃, leading to the formation of a cationic assembly bearing two different kinds of nitrile groups.

2.2. Crystal structure of the supramolecular assembly D

The proposed structure was proven by a single-crystal X-ray diffraction study (Table 1) performed at low temperature on a single crystal of the derivative **D**, revealing that this compound crystallizes in the triclinic P-1 space group. The asymmetric unit contains half of a tetracationic discrete assembly **D**, two hexafluorophosphate counter-anions and five disordered CH₂Cl₂ solvent molecules.

Table 1. Crystal data and structure refinement for the derivative **D** after “squeeze” treatment²⁰ (values in *italic* are related to the relevant data before the squeeze treatment)

Molecular formula	$C_{130} H_{112} Cu_4 F_{24} N_6 P_{12}$ ($C_{140} H_{132} Cl_{20} Cu_4 F_{24} N_6 P_{12}$)
CCDC number	2027399
Molecular weight	2840.06 (3881.25)
<i>a</i> [Å]	12.6455(9)
<i>b</i> [Å]	15.2264(11)
<i>c</i> [Å]	21.8202(15)
α [°]	83.048(2)
β [°]	83.485(2)
γ [°]	71.767(2)
<i>V</i> [Å ³]	3948.3(5)
<i>Z</i>	1
ρ_{calcd} [Mg m ⁻³]	1.194 (1.548)
crystal system	Triclinic
space group	P-1
<i>T</i> [K]	150(2)
Wavelength Mo- <i>K</i> α (Å)	0.71073
Crystal size [mm]	0.58*0.17*0.12
μ (Mo- <i>K</i> α) [cm ⁻¹]	0.723 (1.139)
<i>F</i> (000)	1446 (1858)
θ limit (°)	2.44 - 27.46
Index ranges <i>hkl</i>	-16 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 19 -28 ≤ <i>l</i> ≤ 28
Reflections collected	77965
Independent reflections	18062
Reflections [<i>I</i> >2 σ (<i>I</i>)]	12550 (12666)
Data/restraints/ parameters	18062 / 0 / 795 (994)
Goodness-of-fit on <i>F</i> ²	1.070 (1.035)
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> 1= 0.0623 (0.0791) <i>wR</i> 2= 0.1700 (0.2063)
<i>R</i> indices (all data)	<i>R</i> 1= 0.0894 (0.1156) <i>wR</i> 2= 0.1837 (0.2327)

D is a discrete compact tetrametallic assembly gathering three linkers L_3 with two $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ fragments (Figure 1). The two external L_3 ligands have each of their nitrile groups coordinated to one of the two Cu(I) metal centers of a different $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ moiety ($d(\text{Cu-N}) = 1.989(3)$ and $2.037(4)$ Å). Therefore, a “[$\text{Cu}_4(\mu_2\text{-dppm})_4$](L_3) $_2$ ” metallacyclic sub-unit can be defined, in which the single internal ligand L_3 is included (Figure 1) with its terminal nitrile groups bearing a semi-bridging coordination mode ($d(\text{Cu-N}) = 2.075(3)$ and $2.498(4)$ Å) on the two Cu(I) metal centers of each of the two $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ fragments. Within the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ bimetallic sub-units, an intermetallic distance of 3.33 Å is observed, precluding therefore metallophilic interactions within **D** while, altogether, the other metric parameters of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ units are very similar to those observed in the polymetallic assemblies previously described bearing such bimetallic fragment.¹¹⁻¹⁴ This intermetallic distance in **D** is similar to the value found in **B** ($d(\text{Cu-Cu}) = 3.33$ Å)¹³ in which the metal centers coordination in the same than in **D** but is larger than in **C** ($d(\text{Cu-Cu}) = 3.13$ Å)¹⁴ where a bridging aqua ligand is observed between the metal centers of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ bimetallic sub-units. In the bulk crystal, derivatives **D** are isolated supramolecular assemblies that do not share specific short contact intermolecular interactions.

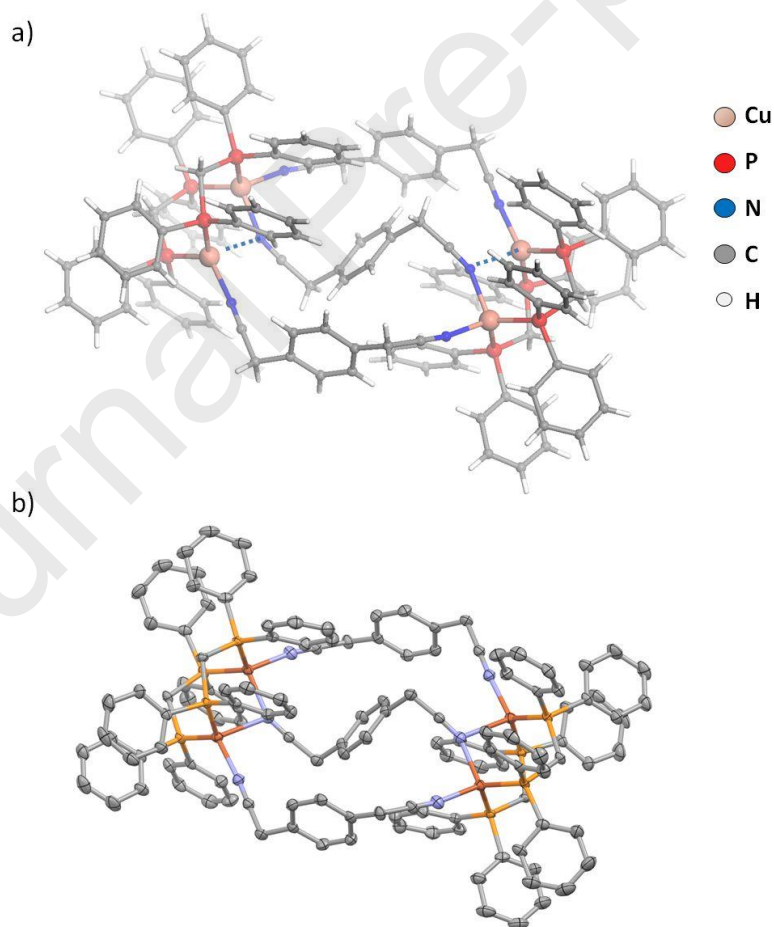


Figure 1. a) General view of the tetracationic derivative **D** molecular X-ray structure; the blue dotted lines represent the longer N-Cu bonds of the semi-bridging nitrile ligands (counter anions and solvent

molecules have been omitted for clarity). b) ORTEP view of the tetracationic derivative **D** molecular X-ray structure.

Interestingly, due to the intrinsic conformational flexibility of the ligand **L**₃, related to the presence of the two methylene units, the internal and external **L**₃ ligands in **D** present different conformations: the $-(\text{CH}_2)\text{-CN}$ fragments of the external **L**₃ ligands are *cis*-orientated regarding the central phenyl ring of the ligand **L**₃ while they are *trans*-orientated in the case of the internal ligands (Figure 2). Such a solid-state architecture is in agreement with the solid-state infrared spectrum of the compound **D** in which two different bands are observed for the nitrile groups stretching modes, suggesting the presence of two different kinds of nitrile groups (which in addition present also different coordination modes on the metal centers, terminal for the external linkers and semi-bridging for the internal linker) within the backbone of the derivative **D**.

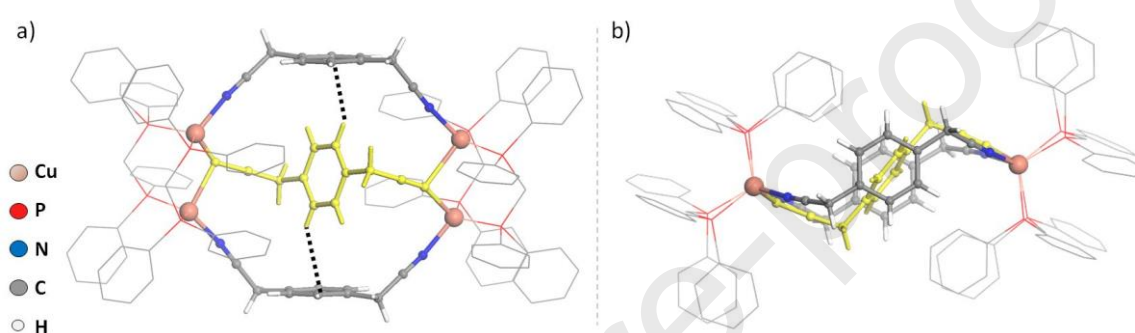


Figure 2. a) 'Top' and b) 'side' views of the molecular X-ray structure of the tetracationic derivative **D** highlighting the different conformations exhibited by the internal (shown in yellow) and external ligands **L**₃; the black dotted lines represent the shorter π -CH interaction contacts (counter anions and solvent molecules have been omitted for clarity, the dppm ligands' atoms are shown with the line representation while the other atoms are shown in the ball-and-stick representation)

In addition, within the derivative **D**, the phenyl ring of the internal ligand is oriented almost perpendicularly to those of the external ligands (Figure 2, angle between the mean planes of the external and internal **L**₃ phenyl rings, 82.4°). Such relative orientation suggests that stabilizing intramolecular interlinker π -CH interactions occur (shorter distance between a phenyl proton of the internal **L**₃ ligand and the centroid of the external **L**₃ phenyl rings, 2.77 Å) within the backbone of the tetrametallic assembly **D**, which very likely contributes to its stability.

Therefore, the self-assembly CDS processes occurring during the association of the partially flexible ditopic linker **L**₃ with the pre-assembled precursor $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ lead to the formation of a discrete tetrametallic assembly **D** that resembles the architecture observed in **B** (Scheme 1),¹³ and do not afford a 1D-CP such as the **C** (Scheme 1).¹⁴ During these CDS processes, the ligand **L**₃ presents thus a behavior that is significantly similar to what is observed with the fully aliphatic flexible linker **L**₁ and is in a marked contrast with the results obtained with the rigid aromatic linker **L**₂. The introduction within the backbone of these nitrile-capped ditopic linkers of only a limited amount of methylene units can have therefore a critical impact on the fate of the self-assembly CDS processes conducted upon their coordination on the conformationally flexible $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ pre-assembled unit. Very likely, the possibility of associating reactive building blocks having both potential conformational

flexibilities is an important parameter to drive the CDS association process observed, which remains selective despite the lack of rigidity of both precursors used.

Comparing closely the self-assembled structures of the derivatives **B** and **D**, it is possible to highlight that these assemblies share common structural features (Figure 3). Both compounds present similar dimensions (distance between the Cu(I) metal centers of different bimetallic units connected by the external linkers: **B**,¹³ 11.6 Å ; **D**, 11.1 Å and intermetallic distances within the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ units: **B**,¹³ 3.33 Å ; **D**, 3.33 Å). In addition, the internal linkers almost fully fill (Figure 3) the internal cavities made in the metallacyclic sub-units resulting in the connection of the two $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ fragments by the two external linkers, affording in both cases compact supramolecular assemblies (Figure 3). Therefore, the possibility of creating cavities in the self-assembled structures in which additional linkers can get inserted and adapt their conformation to maximize stabilizing weak but cumulative interlinkers intramolecular interactions is also very likely a key parameter to drive the selective preparation of such discrete Cu(I) tetrametallic CDS assemblies.

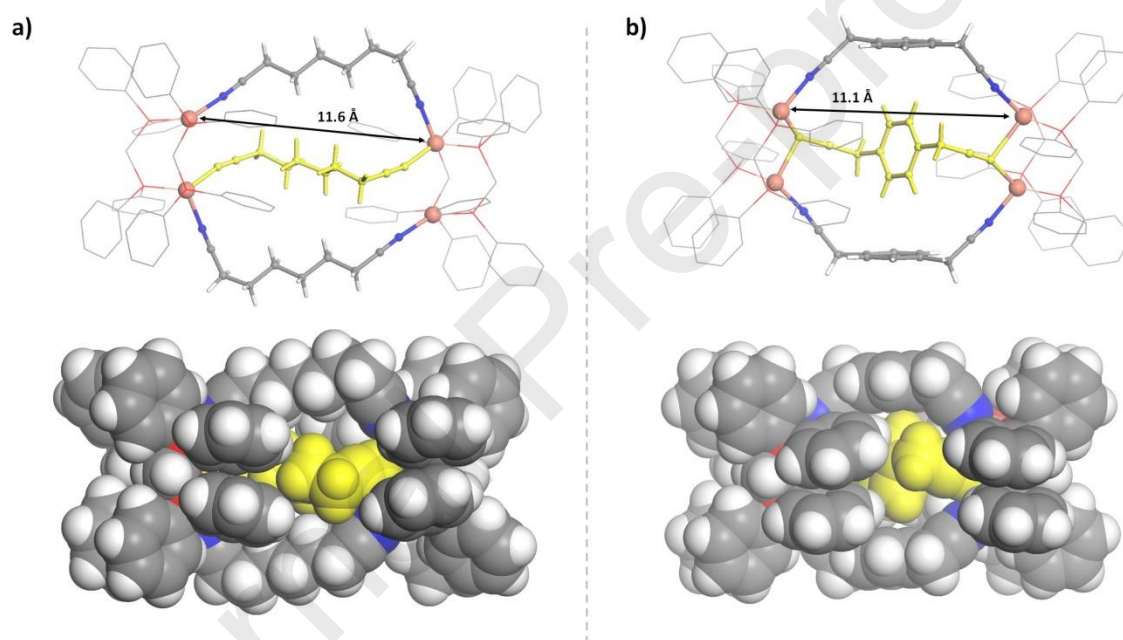


Figure 3. Comparative views of the stick and ball and CPK representations of the tetracationic compact assemblies a) **B**¹³ and b) **D**, the internal linkers are highlighted in yellow (counter anions and solvent molecules have been omitted for clarity).

2.3. Solid state luminescence properties of the supramolecular assembly **D**

The crystals of **D** are colorless under visible light but they display under UV irradiation ($\lambda_{\text{ex}} = 365 \text{ nm}$) an eye-perceived light blue solid-state RT luminescence. The solid-state RT UV-visible absorption spectrum of the derivative **D** (Figure 4) presents a broad band centered at 290 nm and two shoulders at ca. 240 and 350 nm. These bands are assigned to the $\pi\text{-}\pi^*$ transitions centered on the aromatic moieties of the dppm ligands and on the ligand **L**₃ that also presents a strong absorption in the solid state between ca. 272 and 306 nm (Figure 4). No absorption is observed in the visible region of this spectrum which is in agreement with the white color of the polycrystalline powder obtained.

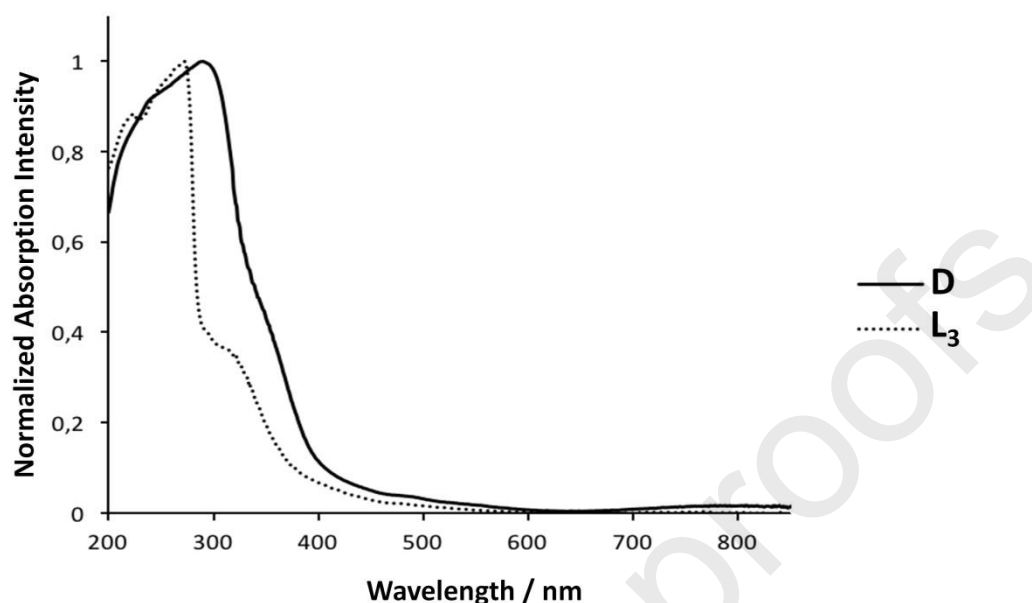


Figure 4. Solid-state room temperature absorption spectrum of the derivative **D** (plain line) and **L₃** (dotted line).

As solid-state sample of **D** is cooled in liquid nitrogen, with $\lambda_{\text{ex}} = 365$ nm, an increase in the intensity of the emission is observed together with a change in the eye-perceived color of the emitted light, switching from light blue at RT to greenish at 80 K. When the sample is left to warm to room temperature, it gradually regains its initial eye-perceived light blue emission, which indicates that the compound **D** exhibits a reversible thermochromic luminescence behavior. The solid-state emission spectrum recorded at 290 K by excitation at $\lambda_{\text{ex}} = 333$ nm displays an intense broad band centered at 508 nm (Figure 5), associated with a quantum yield of 33 % and a mono-exponential decay lifetime τ of 100 μs . At 80 K, its solid-state emission spectrum exhibits a much more intense band that is very moderately red-shifted compared to the band observed at high temperature, being centered at 510 nm ($\lambda_{\text{ex}} = 333$ nm), with a shoulder appearing at 440 nm (Figure 5). A bi-exponential decay time of $\tau_1 = 131$ μs and $\tau_2 = 450$ μs is measured at 80 K, being significantly longer than the lifetime measured at RT (the average decay time τ_{av} at 80 K is 424 μs , calculated accordingly to $\tau_{\text{av}} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$ with $A_1 = 703.33$ and $A_2 = 2351.11$ being the weights associated with τ_1 and τ_2 , respectively). Such a thermal dependence of the broad emission band measured explains the eye-perceived color change of the light emitted by the compound **D** upon cooling in the solid-state.

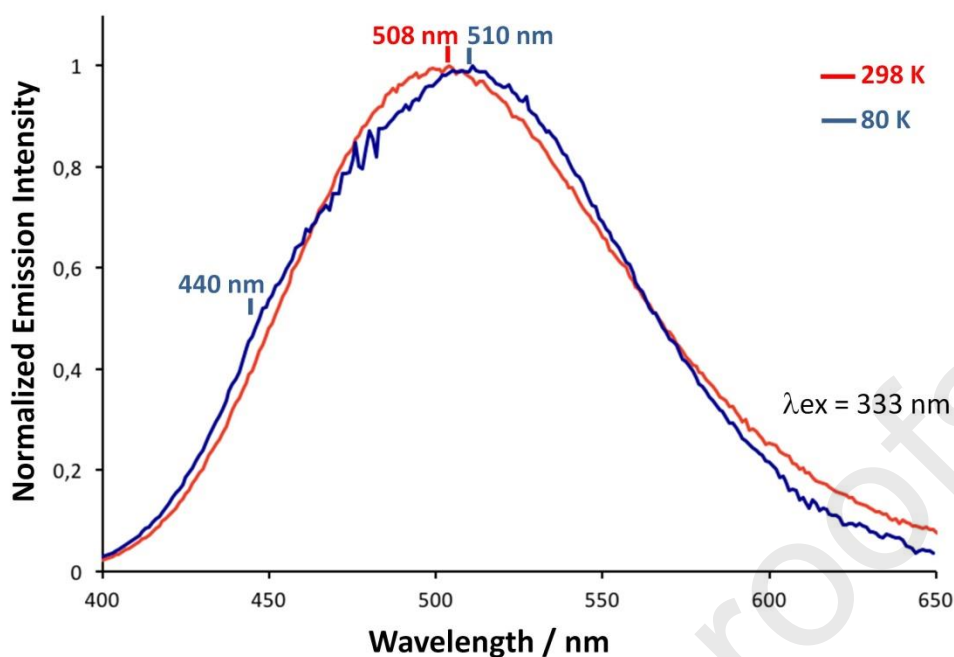


Figure 5. Solid state emission spectrum of the derivative **D** at 80 K and at 298 K ($\lambda_{\text{ex}} = 333$ nm).

This derivative **D** presents therefore photophysical properties that are markedly different of those observed for the assemblies **B** and **C**. Indeed, the derivative **B** is non-emissive in the solid-state at RT upon UV-visible light excitation, and only very weakly luminescent at 80 K (emitting an eye-perceived blueish light). Thus, in spite of their structural analogies (Figure 3), derivatives **B** and **D** exhibit significantly distinct luminescence behaviors. Otherwise, besides its specific luminescence vapochromic properties, the 1D-CP **C** (Scheme 1) present at RT an emission behavior that is typical of a $^3\text{MLCT}$ phosphorescence.¹⁴ At low temperature, the emission behavior of **C** was assigned to a metal-perturbed $^3\pi-\pi^*$ phosphorescence relaxation process mainly centered on the 1,4-dicyanobenzene L_2 connecting ligands,¹⁴ associated with the presence of a vibronic structuration of its emission spectrum at 80 K that is not observed for the assembly **D**.

Likely, the absence of a net vibronic structuration in the low temperature emission band precludes to suggest a $^3\pi-\pi^*$ phosphorescence centered on the nitrile-capped L_3 connecting ligands at low temperature, such as observed for **C**.¹⁴ Conversely, the relatively long decay time value as well as the RT k_r radiative rate constant value of $3.3 \times 10^3 \text{ s}^{-1}$ (ca. 10^3 s^{-1} for $^3\text{MLCT}$ phosphorescence of Cu(I) complexes)¹⁵ are in favor of a $^3\text{MLCT}$ phosphorescence process over the full range of temperature studied.

3. Conclusions

With these results, the interest of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]$ pre-organised building block **A** for the CDS preparation of new luminescent Cu(I) assemblies is confirmed. By reacting the partially flexible 1,4-phenylenediacetonitrile linker L_3 with the bimetallic unit **A**, it is possible to obtain selectively the compact tetrametallic assembly **D**. Along the synthesis of this derivative, the conformational flexibility of both precursors (variation of the coordination number of the metal ions and the

intermetallic distances in **A**, possibility of *trans*- or *cis*- orientation of the coordinating nitrile groups regarding the central phenyl moiety in **L**₃) very likely promotes the formation and the selection of this original discrete architecture. This study confirms the interest and the versatility of such synthetic approach adapting the CDS chemistry principles to conformationally flexible Cu(I) precursors and connecting ligands. In addition, due to the specificity of the photophysical radiative relaxation processes that can lie within such Cu(I) based derivatives, attractive and original solid-state luminescence properties can be embedded within the resulting multimetallic assemblies. Therefore, efforts will be continued in the next future in this area to explore deeper the versatility of such adaptive precursors to allow preparation of novel luminescent Cu(I)-based supramolecular assemblies, and understand the mechanisms ruling their photophysical properties.

4. Experimental section

3.1 Materials and instrumentation

All experiments were performed under ambient atmosphere. Commercially available reagents ([Cu(CH₃CN)₄].PF₆, dppm, and 1,4-phenylenediacetonitrile linker **L**₃) were obtained from Sigma-Aldrich and were used as received without further purification. ¹H and ³¹P NMR spectra were recorded on a Bruker AV400 spectrometers. ¹H NMR chemical shifts were reported in parts per million (ppm) relative to Me₄Si as external standard. ³¹P{¹H} NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to 85% H₃PO₄ respectively. FT-IR measurements have been performed on a Perkin Elmer Frontier spectrometer using UATR (Universal Attenuated Total Reflectance) accessory. Spectra have been recorded between 650 cm⁻¹ and 4000 cm⁻¹, on pure samples. UV-vis solid-state absorption measurements have been recorded on a Perkin-Elmer Lambda 650 spectrometer using a 60 mm integrating sphere. Spectra have been recorded between 850 nm and 200 nm. Steady-state emission spectra and luminescence quantum yield measurements were recorded on a Horiba Jobin Yvon (HJY) Fluorolog 3 (FL3-2iHR550) fluorescence spectrofluorometer equipped with an IR R928P PMT / HJY FL-1073 detector and with an integrating sphere. Low temperature measurements were allowed by using an OptistatCF (Oxford Inst.) in the range of 80 K to 300 K. Excited-state lifetimes in the range 80 K and 300 K were measured with a delta hub (TCSPC: Time Correlated-Single-Photon-Counting) + delta diode system allowing to measure excited-state lifetimes between 500 ps et 10 μs and with a pulsed xenon source (FL-1035) allowing to measure excited-state lifetimes longer than 10 μs. Solid sample was placed in a quartz sample holders inside the integrating sphere and the cryostat and maintained at the desired temperature until equilibrium was reached before recording the spectrum.

3.2 X-ray crystal structure determinations

Single crystal data collection for **D** was performed at 150 K with a D8 Venture Bruker AXS (Centre de Diffraction, Université de Rennes 1, France) with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflections were indexed, Lorentz-polarization corrected and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.¹⁷ Structure determinations were performed by direct methods with the solving program

SIR97,¹⁸ that revealed all the non-hydrogen atoms. SHELXL program¹⁹ was used to refine the structures by full-matrix least-squares based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Single crystal of all derivative **D** was coated in paratone oil, mounted at low temperature on the diffractometer goniometer as quickly as possible and X-ray data collection were performed at low temperature. Concerning the X-ray crystal structure resolution of **D**, 5 included dichloromethane solvent molecules were found being highly disordered. A correct modelling of the disorder of these solvent molecules was not possible. We have therefore proceeded to a 'squeeze' treatment²⁰ in order to remove the scattering contribution of these molecules which cannot be satisfactorily modelled. As a result, since these disordered molecules occupy a significant volume of the unit cell, an ALERT level A appears in the checkcif report since "VERY LARGE Solvent Accessible VOIDS" are present in the structure resolution. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.²¹ CCDC reference number 2027399 contains the supplementary crystallographic data for the reference measurements of the X-ray crystal structure of the derivative **D**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

3.3 Synthetic work

1,4-phenylenediacetonitrile (0.013 g, 0.081 mmol) was added dissolved in 2 ml of CH_2Cl_2 at room temperature to a clear solution of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (0.040 g, 0.108 mmol) and dppm ligand (0.042 g, 0.108 mmol) dissolved in 10 ml of CH_2Cl_2 (*stoichiometry was adapted regarding the X-ray molecular structure determined for D*). This reaction mixture was stirred overnight at room temperature. The resulting clear and colorless crude solution was then left upon pentane vapor diffusion for 2 weeks, affording after crystallization the derivative **D** (0.043 g, 0.015 mmol, 56% yield) as an air-stable polycrystalline colorless solid.

^1H NMR (400 MHz, CD_2Cl_2): δ = 3.42 (broad s, 8H, PCH_2P), 3.81 (broad s, 12H, $\text{N}\equiv\text{C}-\text{CH}_2-$), 7.10-7.50 (broad m, 92H, H_{arom}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.98 MHz): δ = -144.3 (sept, $^1J(\text{P},\text{F}) = 708$ Hz, PF_6^-), -9.4 (broad m, dppm)

IR (cm^{-1}): 681 (vs), 740 (vs), 779 (vs), 926 (s), 1053 (vs), 1181 (m), 1425 (vs), 1485 (m), 1513(s), 1570 (w), 1639 (w), 1926 (vw), 1481 (m), 2193 (vw), 2251 (U_{CN} , w), 2273 (U_{CN} , w), 2137 (U_{CN} , vw), 2929 (vw), 3069 (vw).

Elemental analysis, calcd. (%) for $\text{C}_{132}\text{H}_{116}\text{Cl}_4\text{Cu}_4\text{F}_{24}\text{N}_6\text{P}_{12}$: C 52.67, H 3.38, N 2.79; found: C 52.26, H 3.80, N 2.35.

CRedit authorship contribution statement

Sloane Evariste : Investigation, Formal analysis. **Chendong Xu** : Investigation. **Guillaume Calvez** : Project administration, Formal analysis. **Christophe Lescop** : Project administration, Formal analysis, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Luminescent discrete Cu(I) assembly is made from conformationally flexible precursors

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