



Coordination-driven Supramolecular Synthesis based on Bimetallic Cu(I) Precursors: Adaptive Behavior and Luminescence

Christophe Lescop

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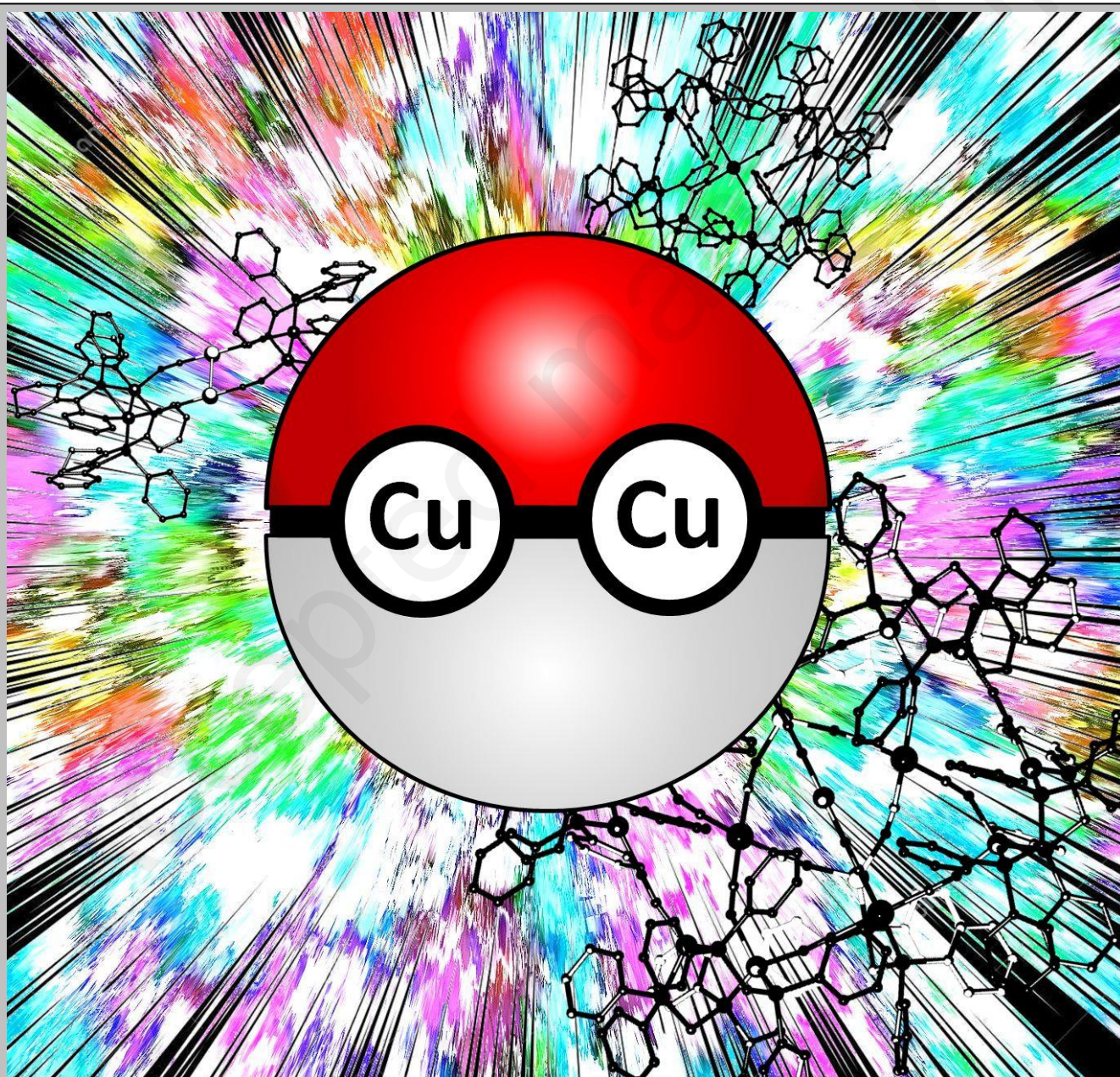
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**Coordination-driven
supramolecular synthesis
based on bimetallic Cu(I)
precursors : adaptive behavior
and luminescence properties.**

C. Lescop^{[a]*}



Abstract: Pre-organized adaptive Cu(I) bimetallic precursors can be successfully engaged in coordination-driven supramolecular reactions. Selective formation either of a large family of compact metallacycles or of polymetallic discrete assemblies and one-dimensional coordination polymers is rationalized taking into account the relative amplitudes of conformational flexibility allowed by the precursors used. It reveals the originality of the self-assembly processes conducted with such Cu(I)-based building blocks. In addition, exalted luminescence properties can be embedded in the resulting supramolecular assemblies due to the specific photophysical behaviors of Cu(I)-luminophores. General and straightforward access toward coordination-driven supramolecular assemblies featuring original architectures and multifunctional luminescence properties is therefore highlighted, taking advantage of both the specificities of the coordination chemistry and the electronic structure of derivatives based on the Cu(I) ion.

1. Introduction

Since more than three decades, an ever-growing scientific interest combined with major technological efforts have been devoted to the preparation of advanced molecular-based materials.¹ It has enabled impressive synthetic achievements allowing the development of new multifunctional systems and devices (such as light-emitting diodes, field-effect transistors, photovoltaic cells, smart sensors...).² In order to prepare such derivatives, sophisticated standard multistep syntheses combining in organic, organometallic and/or coordination chemistry procedures have been developed. However, these works have been frequently conducted on a case-by-case basis, targeting one (or a few structurally related) molecular scaffold and/or one specific property. As a result, the attractiveness of these new compounds or materials can be severely hampered by the constraints (high cost of production, long synthetic procedures eventually depending on the availability of diverse strategic raw resources, ...) and limitations (low overall yields, limited amount of material produced precluding large scale applications for the resulting devices, ...) associated with such synthetic procedures. Consequently, there is a considerable interest to devise general synthetic approaches to obtain attractive multifunctional molecular materials. With this in mind, a fruitful and appealing alternative to classic synthetic methodologies for constructing complex molecular scaffolds consists in the application of supramolecular self-assembly procedures.³ This powerful approach is based on the spontaneous assembly of rationally designed individual building blocks into well-defined supramolecular architectures. Such a process involves non-covalent kinetically labile bond formation (hydrogen bonding, π - π interaction, metal-ligand coordination, metallophilic interaction...)

allowing, under proper synthetic conditions, that the assembling processes undergo self-sorting and self-correction events until the individual building blocks can congregate into the final thermodynamically stable target product.

Considering the use of the metal-ligand coordination interaction to build discrete self-assembled multifunctional scaffolds, a plethora of multimetallic supramolecular assemblies have been blossoming, including some of the most spectacular artificial molecular systems synthesized by chemists.⁴ Consecutively to early works that established key design principles,⁵ an intense research activity is focused currently on the challenging preparation of advanced supramolecular architectures bearing increased structural complexity and new functionalities. Among the different general supramolecular synthetic approaches^{5,6} that have been conceptualized so far using metal to ligand coordination interaction, the coordination driven supramolecular (CDS) chemistry approach consists of the use of pre-organized coordination complexes having predefined geometries (being in most cases not accessible from single metal center coordination sphere) and vacant coordination positions.⁷ These pre-organized precursors are obtained from the reaction of the metal ions with specific assembling ligands and are subsequently associated with connecting polytopic ligands to allow the formation of targeted multimetallic supramolecular assemblies. In this powerful bottom-up approach, the desired sizes and geometries of the intricate scaffolds obtained can be defined and controlled thanks to a retrosynthetic analysis based on the symmetry of the linking sites of the individual building blocks. In complement of the molecular design of the polytopic connecting ligands, the choice of the metal ions is obviously crucial for the success and the selectivity of the syntheses conducted. The CDS chemistry approach presents a net preference for Pd(II) and Pt(II) metal centers.^{4a,5b,8} 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. In the recent years, alternatives to these leading trends have appeared allowing the introduction of a larger variety of metal centers and ligating groups.⁹ More importantly, while the success of the CDS chemistry strategy has initially relied on the use of conformationally stable building blocks, the initial synthesis 'rigidity' paradigms have been recently somehow questioned by innovative approaches which have allowed straightforward access, from relatively simple building blocks, to increasingly complex supramolecular assemblies having unique structures and reactivities.¹⁰ Thus, Nitschke^{10a} and Severin^{10b} have shown that subcomponent self-assembly allows preparing intricate supramolecular assemblies from simple building blocks with limited synthetic efforts. In these cases, the formation of the connecting ligand and its coordination to metal centers occurs along a single and selective process. These works revealed in addition that the structural diversity of CDS assemblies can be enlarged due to the introduction of selected degrees of flexibility in the building blocks and in the self-assembling events involved allowing the access to adaptive supramolecular architectures. These achievements support the efforts we have conducted in the previous years to introduce in CDS syntheses pre-

[a] Univ Rennes, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France.
E-mail: christophe.lescop@insa-rennes.fr

assembled Cu(I) ion polymetallic precursors presenting significant degrees of conformational flexibility. This personal account focusses on these investigations. In the first part, a general CDS approach based on 'U-shape' Cu(I) bimetallic pre-assembled precursors bearing restricted degree of conformational flexibility is outlined. The versatile formation of compact metallacycles is detailed, revealing specific synthetic rules and the crucial role played by lateral interlinker interactions in the selectivity of these syntheses. In the second part, recent results obtained from the use of alternative Cu(I) polymetallic precursors bearing larger degrees of conformational flexibility will be discussed, probing the impact of Cu(I) building blocks' flexibility in the outcome of the CDS processes. Moreover, the luminescence properties presented by the resulting metallo-organic supramolecular assemblies will be detailed.

Christophe Lescop was graduated in 1996 from the Ecole Nationale Supérieure de Chimie de Paris and obtained his PhD degree at the University of Grenoble I in 2000 under the supervision of the Professor D. Luneau at the Center de l'Energie Atomique of Grenoble. After a post-doctoral fellowship in the group of the Professor J. D. Wuest in the Université de Montréal, he joined as 'chargé de recherche CNRS' the Institut des Sciences Chimiques de Rennes (UMR 6226). In 2018, he was promoted 'directeur de recherche CNRS' in 2018. His main scientific interests are focussed on the preparation of new polymetallic species using supramolecular chemistry and the study of their solid-state structures and multifunctional properties.



2. The Cu(I) ion, an accurate metal center for the preparation of pre-assembled precursor for CDS assemblies bearing luminescence properties?

2.1. Structural considerations

Conversely to the "rigid" d^8 square planar Pd(II) and Pt(II) metal centers which are essential ions for CDS assembly processes, the d^{10} Cu(I) ion has been very sparsely introduced in such synthetic processes. Indeed, the Cu(I) metal ions can be seen as archetypes of metal centers bearing very labile and flexible coordination spheres. Linear, trigonal and tetrahedral coordination spheres tolerating large degrees of structural distortion have been described in the very numerous Cu(I) coordination complexes reported so far.^{1a,11} Moreover, the metal-ligand coordination interaction in the case of the Cu(I) ion is assumed to be highly non-directional, exhibiting a large bond length and angle variability for the same ligating fragment within

a family of related complexes. All these typical features of the coordination chemistry of the Cu(I) ions are a priori highly detrimental to conduct successfully CDS assembly synthetic processes since the geometry and the coordination number of the metal nodes within the targeted supramolecular assemblies appears to be hardly unpredictable and very difficult to control. Indeed, they might depend on manifold factors such as sterical effects, intra- and intermolecular interactions between the different building blocks in the self-assembled structures and in the solid-state packing, ... Indeed, very few studies have been conducted in CDS chemistry based on the Cu(I) ion. Yet, one can mention in this context the formation of the nano-sized fullerene-like molecules reported by Scheer from the reaction of polyelement-ligand complexes of group 15 elements (mostly pentaphosphaferrocene) with Cu(I) halide salt.^{6c,12} Therefore, in order to introduce the Cu(I) ion in CDS chemistry processes, a successful approach could be to apply a specific assembling ligand design that would force a pronounced limitation of the high flexibility of the Cu(I) coordination spheres and impose a high directionality at the level of the coordination links formed on the vacant sites of the metal ions on these precursors.

2.2. Luminescence properties of Cu(I) complexes

Among the overwhelming number of discrete metallo-organic supramolecular assemblies reported so far, study of luminescent CDS derivatives remains in proportion quite unexplored. In most of the studies conducted, the emission behaviors observed in CDS assemblies are either originated by the intrinsic fluorescence properties of the π -conjugated multitopic linkers¹³ or by the heavy metals (Pt(II), Re(I), Ir(III), Au(I), Pd(II) or Ru(II) ions) based phosphorescent building blocks¹⁴ used. Cu(I) coordination complexes currently witness a great attention because of the fascinating photophysical properties they can exhibit.^{1a,15} These emission behaviors are characterized by the large diversity of the radiative relaxation processes involved but a rising attention is paid to derivatives exhibiting Thermally Activated Delayed Fluorescence (TADF).^{15a,16} In such complexes, thermally activated population of the lowest energy excited singlet state (S_1) from the lowest energy triplet excited state (T_1) occurs.

While emissive Cu(I) complexes gain increasing attention in the OLED community because of their earth-abundancy and much cheaper prices as compared to late transition metal complexes such as Ir(III) and Pt(II) derivatives, the latter have attracted a deeper interest in the last two decades. The reasons for such preference for the study of phosphorescent heavy-metal emitters rather than Cu(I)-based materials rely in that, initially, the luminescence performances of Cu(I) metal-coordination complexes were largely underestimated. Indeed they were treated as if they were triplet-harvesting materials based on metal center bearing low spin-orbit coupling values. Long emission decay times were therefore assumed which favoured undesired non-radiative des-excitation pathways such as vibrational modes and/or easy structural alterations in the excited states, features that are directly associated with the

flexibility of the Cu(I) coordination spheres. Yet, Yersin established that TADF can govern the luminescence properties of some monometallic Cu(I) metal complexes,^{15a,16} in particular in the solid state, opening a large avenue to highly efficient luminescent metal-coordinated materials based on this cheap, abundant and non-strategic metal atom.

However, parameters to optimize in Cu(I) complexes to obtain efficient TADF emitters are numerous: stability of the Cu(I) metal centers toward spontaneous oxidation to Cu(II) under air, constitutional stability of the complexes in solution toward dissociations and ligand exchanges, favourable electronic configuration promoting TADF mechanism with in particular a $\Delta E(S_1 - T_1)$ energy difference allowing the thermal up-conversion transfer from the T_1 state to the S_1 state at ambient temperatures. In addition, a specific molecular design is mandatory to be conducted to stabilize Cu(I) ions in rigid, stable and controlled molecular environments. This would efficiently forbid major structural reorganisations in the excited states together with detrimental efficient vibration modes, precluding dominant non-radiative relaxation pathways to take place.

2.3. CDS processes based on Cu(I) ions luminescent precursors ?

Therefore there are close similarities in the structural requirements that need to be applied to design a Cu(I) derivative that could be an attractive pre-organised precursor to conduct CDS chemistry and an efficient luminophore. Thus, one can anticipate that a Cu(I)-based building-block that would present a good aptitude to conduct successfully selective CDS syntheses would also offer a potential and general entry to new supramolecular polymetallic assemblies bearing intrinsically luminescence properties.

3. CDS syntheses based on 'U-shape' Cu(I) bimetallic precursors for the formation of compact metallacycles

3.1. 'U-shape' Cu(I) bimetallic pre-assembled precursors for CDS syntheses

In 2005, in the course of the study the coordination chemistry of the 2,5-bis(2-pyridyl)phosphole ligand **3** (Figure 1), we have characterized by serendipity a new family of air stable Cu(I) dimers stabilized by N,P,N chelates bearing unique bridging phosphane coordination mode, which is a very unusual coordination mode in the family of phosphane ligands.¹⁷ Among these complexes, the derivatives **1** and **2** present two 'cisoid' labile acetonitrile ligands coordinated on the metal centers, conferring to these precursors a pre-assembled 'U-shape' geometry.

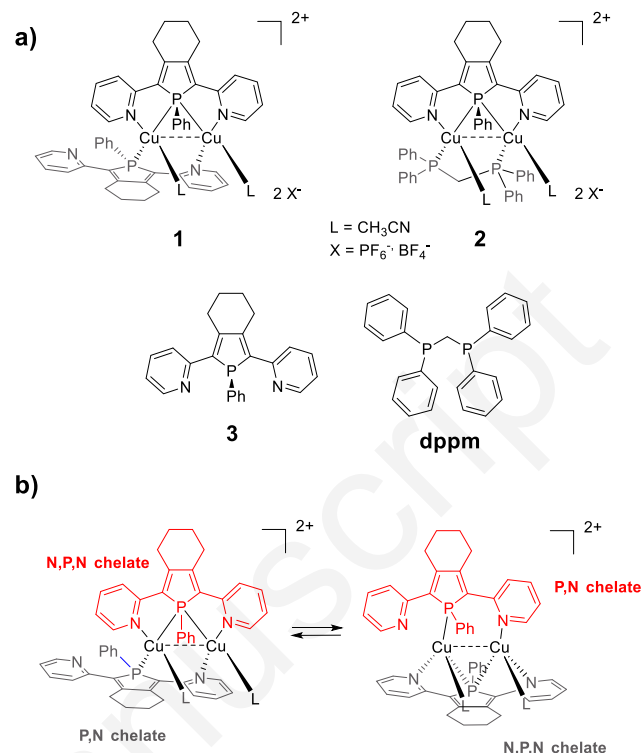


Figure 1. a) Molecular structures of the bimetallic complexes **1** and **2** and of the ligands **3** and dppm (bis(diphenyl-phosphino)methane), b) hemilabile fluxional coordination behavior of the ligands **3** in the coordination sphere of the complex **1**.

In addition, short metal-metal distances (**1**: 2.5552(8) Å ; **2**: 2.6696(7) Å) are generated as a consequence of the bridging phosphane coordination mode. Finally, in derivative **1**, it is also observed that the two ligands **3** exhibit in the coordination sphere of the metal ions an hemilabile fluxional coordination behavior in solution due to a fast intermolecular exchange between the N,P,N and the P,N ligands (Figure 1b) involving coordinated and pendant pyridine groups.^{17b} This feature confers to derivative **1** a remarkable conformational flexibility, clearly favoured by lability and fluxionality of the coordination sphere of the Cu(I) ions.

3.2. CDS syntheses toward Cu(I) compact supramolecular assemblies

The labile acetonitrile ligands coordinated to the Cu(I) ions of the derivatives **1** and **2** can be substituted by a variety of cyano-capped ditopic linkers, allowing the selective preparation, accordingly to the CDS chemistry principles, of a rich and original family of compact tetrametallic supramolecular assemblies **A** based on the Cu(I) ion (Figure 2).¹⁸ Varying the nature of the connecting ligands engaged in the reactions allowed to established guiding rules enlighting the specificities of such self-assembled syntheses using 'U-shape' pre-assembled

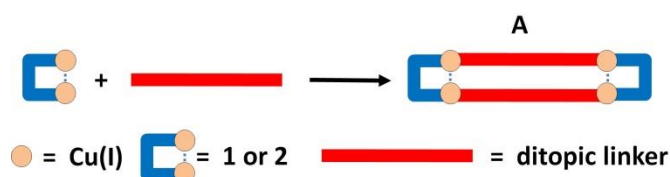


Figure 2. Synthesis of compact supramolecular metallacycles **A** using ditopic connecting ligands.

precursors based on Cu(I) ions and bearing short intermetallic distances. Firstly, when reacting short anionic ditopic linkers such as the cyano CN⁻ fragment, 'small' tetrametallic metallacycles such as **A**₁ (Figure 3a) were characterized.¹⁹ Their selective formation was assigned to a 'sterical protection effect'. This effect relies on the shape and the steric hindrance of the Cu(I) bimetallic units together with the rigidity of the parallel coordination positions at the two Cu(I) sites, that favor a regioselective 'face to face' orientation of the bimetallic fragments as unique self-assembling possibility (Figure 3a). As the length of the anionic ditopic linkers was formally increased by reacting building blocks such as the linear anionic gold(I) dicyanide [Au(CN)₂]⁻, formation of new compact metallacycles **A**₂ can also be achieved (Figure 3b).²⁰ In these assemblies, intramolecular Au(I)-Au(I) short distances (*d*(Au-Au); 3.3-3.5 Å) typical of stabilizing intramolecular lateral aurophilic interactions are observed and undeniably took part in the selection of the discrete metallacyclic scaffolds.

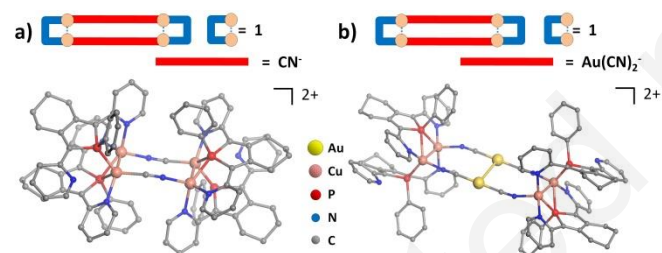
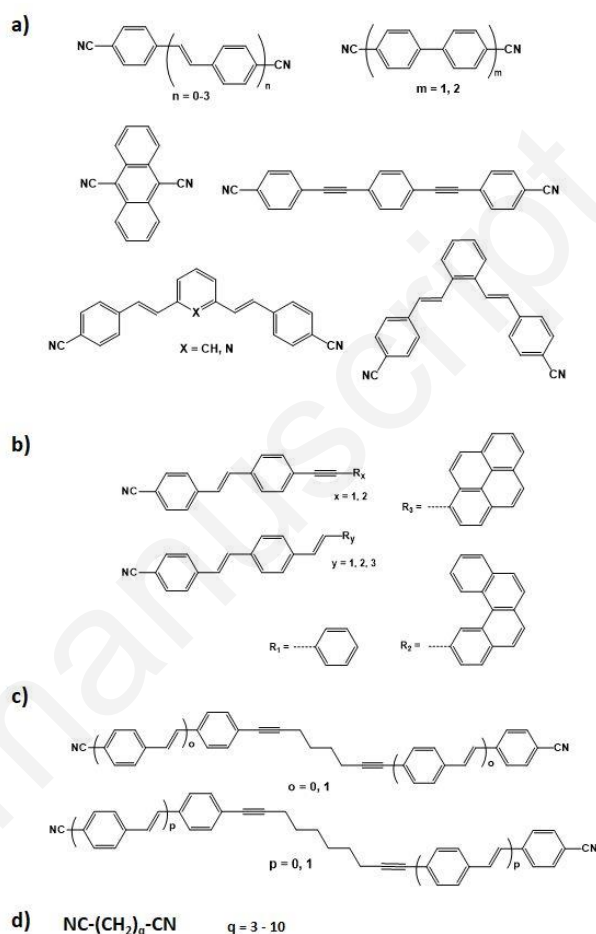


Figure 3. Schematic description and X-ray crystal structure of the metallacycles a): **A**₁ and b): **A**₂.

This assumption was supported by the substitution reactions of the acetonitrile ligands of the precursors **1** and **2** by a large series of linear or angular neutral cyano-capped fully π -conjugated systems (Scheme 1a).²¹ In these cases, self-assembly reactions occurred in which the exchanges between coordinated acetonitrile ligands and ditopic linkers could not be promoted by strong electronic charge affinities such as those taking place between the positively charged Cu(I) centers and the anionic cyano fragments. Yet, as the extend of the π -conjugated systems was increased, selective and quantitative formation of compact π -stacked metallacycles occurs (Figure 4), providing additional clues about the factors ruling the CDS formation of these Cu(I)-based supramolecular assemblies. Indeed, similarly to the metallophilic lateral interactions observed in **A**₂ (Figure 3b), strong face-to-face π - π interlinker lateral intramolecular interactions are observed within the cores of the compact tetrametallic derivatives. This definitively pointed out

how crucial lateral interlinker interactions are in order to drive the selection of these compact metallacycle structures along CDS syntheses based on the Cu(I) dimers **1** and **2**.



Scheme 1. Molecular structure of the cyano-capped ligands used a) fully π -conjugated ditopic linkers, b) terminal ligands, c) mixed aliphatic-aromatic ditopic linkers, d) fully aliphatic linear ditopic linkers.

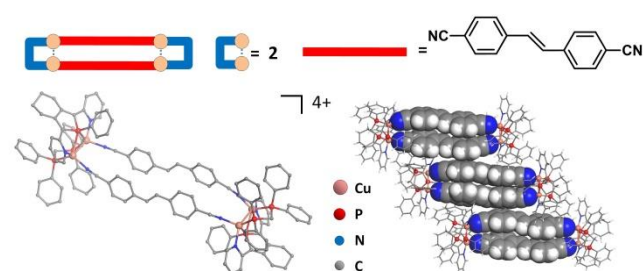


Figure 4. Schematic description, X-ray crystal structure and solid-state stacking of an example of a tetracationic compact π -stacked metallacycle.

In and of themselves, neither the short intermetallic distance in the U-shape molecular clip nor its steric congestion are therefore

the only decisive factors to be taken into account to drive the selective syntheses of such Cu(I) compact supramolecular metallacycles. As the length of the ditopic linker used is increased, secondary interactions arising between the linkers play a major role to direct supramolecular assembling processes toward discrete cyclic architectures at the expense of open oligomeric or polymeric species.

In all the new compact π -stacked metallacycles obtained, the intermetallic distances of the Cu(I) bimetallic units are mostly unchanged compared to those observed in the precursors **1** and **2**.^{21,22} In addition, within the tetrametallacyclic backbones, the π -stacked units present invariable features with the π -walls of the ditopic linkers being parallel and arranged in an almost face-to-face relative orientation. This suggests that quite strict rigidity constraints are imposed to the whole supramolecular backbones formed, which contrasts with the flexibility presented by the Cu(I) ion coordination spheres in the pre-assembled precursors used. Yet, careful examination of the conformation of the CDS assemblies obtained allows highlighting other features, that are related with the lability and the flexibility of the coordination sphere of the Cu(I) ion. Indeed, while in most of the solid-state structures characterized the P-phenyl fragments of the phosphole based ligand **3** are localized pointing in the direction of the coordinated nitrile units, a few show noticeable exceptions. The most significant case is observed when comparing the derivatives **A₃** and **A₄** resulting from the association of the bimetallic precursor **2** with, respectively, the 1,4-dicyanobenzene and the anthracene-9,10-carbonitrile ditopic linkers, bearing significantly similar lengths but different lateral sterical congestions (Figure 5). While all metric parameters in the coordination spheres of the Cu(I) ions in both assemblies are very similar,^{21b} the phosphole ligands have a different arrangement with the P-phenyl substituents pointing towards the cyano-ligands in the assembly **A₃** whereas pointing in the opposite direction in the metallacycle **A₄** (Figure 5).

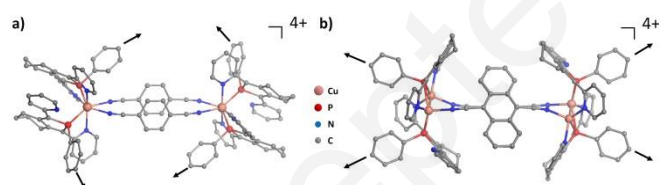


Figure 5. X-ray crystal structure of the tetracationic compact π -stacked metallacycle a) **A₃** and b) **A₄**. The black arrows represent the direction in which the P-Ph moieties of the phosphole ligands **3** are pointing.

It is very likely that this re-organization of the phosphole ligands within the Cu(I) bimetallic cores during the supramolecular synthetic process is driven by steric strain minimization and is permitted by the fluxional coordination behavior of the hemilabile N,P,N ligand in the coordination sphere of the Cu(I) ions. Therefore, these Cu(I)-based U-shape bimetallic molecular clips exhibit very valuable flexible behavior since they can adapt their assembling ligands conformation to optimize the specific steric demand related to the formation of these stacked supramolecular assemblies. In line with this, the (Cu- μ P-Cu)

coordination angles and the μ P-Cu distances about the bridging phosphorus atoms of the N,P,N chelates demonstrates also in these solid-state structures a large distribution.^{21,22} Therefore, the use of such Cu(I) bimetallic preorganized precursors bearing short intermetallic distances and an hemilabile flexible coordination sphere while keeping an overall stable structure is very valuable to conduct selective and very versatile CDS syntheses of original compact supramolecular metallacycles. These observations demonstrate that, accordingly to a rational design of Cu(I) precursors, it is possible to prepare innovative precursors based on this metal center for selective CDS syntheses.

This assumption has triggered us to investigate deeper the scale and limitation of the self-assembly processes based on the Cu(I) dimer **1** and alternative supramolecular self-assembled systems were characterised. Thus, dissymmetric π -conjugated systems (Scheme 1b) bearing only one terminal nitrile coordination group afforded a new series of infinite columnar π -stacks in the solid-state consecutively to their substitution reaction with the acetonitrile ligand carried by **1** (Figure 6a).²³ In addition, the reaction of the derivative **1** with a series of ditopic linkers bearing

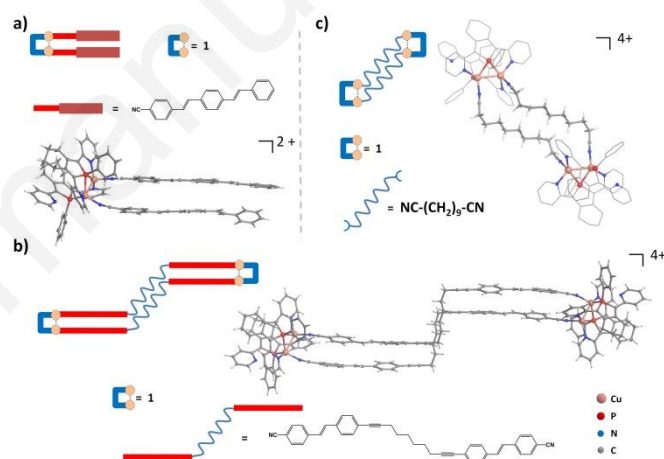


Figure 6. General structural scheme and X-ray crystal structure of selected compact supramolecular assemblies obtained from the precursor **1**.

central aliphatic flexible fragments and terminal cyano-capped rigid π -conjugated moieties (Scheme 1c) allowed the selective preparation of unprecedented “pseudo double-paracyclophane” scaffolds (Figure 6b),²⁴ revealing that, in spite of their intrinsic low rigidity and directionality, linkers bearing in their internal core linear aliphatic fragments can be successfully introduced in CDS processes. This observation was strongly supported by the characterisation of unprecedented series of compact tetrametallic Cu(I) metallacycles based on cyano-capped ditopic linkers bearing only linear aliphatic cores (Scheme 1d).²⁵ In these cases, it was indeed shown that the specific features of the Cu(I) precursor **1** induce a cumulation of weak but stabilizing lateral intramolecular London interactions within the cores of the self-assembled derivative that, similarly to the lateral intramolecular aurophilic or π - π interactions promote the

formation of tetrametallic supramolecular compact metallacycles (Figure 6c).

In addition, it is interesting to note that the compact supramolecular assemblies obtained revealed also a pronounced and original ability to subsequently self-assemble in the bulk solid state in oligomeric or polymeric one dimensional (1D) aggregates due to intermolecular aurophilic or π - π interactions (see an example in the figure 4).

4. Toward the CDS synthesis of luminescent polymetallic Cu(I) assemblies

4.1. Molecular design of an appropriate pre-organised Cu(I) precursor

The studies performed from the complexes based on the N,P,N ligand **3** reveal that a rich and original CDS chemistry can be developed based on bimetallic Cu(I) precursors, affording a large variety of self-assembled compact metallacycles. Regarding the current attention paid to solid-state luminescent Cu(I) complexes,^{15,16,26} the adaptation of this approach to the general preparation of new luminescent supramolecular precursors would open great perspectives of development and future studies. Yet, none of the supramolecular assemblies obtained from the derivatives **1** and **2** present luminescent properties in the solid-state and in solution under UV-vis light excitation. This is very likely due to the fact that the pre-assembled bimetallic complexes themselves are also non emissive. Very probably, relaxation processes in the excited states of these species converge to low-lying molecular orbitals localized on the extended π -conjugated systems of the phosphole-based ligand **3**, such orbitals being associated with very efficient non-radiative des-excitation pathways promoted by the bridging phosphane coordination mode.

Taking that into consideration, we have been triggered to apply the synthetic guiding rules established on the base of complexes **1** and **2** to other polymetallic Cu(I) precursors stabilized by assembling ligands bearing non extended π -conjugated system in their backbones. Due to its structural similarities with the Cu(I) dimers **1** and **2**, we have considered as potential candidate the complex **4** (Figure 7) in which two dppm ligands (Figure 1a) stabilize a Cu(I) dimer in a $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment. Yet, in this derivative, the coordination number of the metal centers are larger than in **1** and **2** since two labile acetonitrile ligands are coordinated on each tetrahedral Cu(I) ions.²⁷ In addition, larger intermetallic distances (ca. 3.7 Å) are observed in the solid states structures reported.²⁷ Finally, and importantly, solid-state luminescence properties have been mentioned²⁸ for this derivative making it an interesting precursor to probe how the CDS syntheses conducted from **1** and **2** could be adapted, affording potential access to new luminescent supramolecular derivatives.

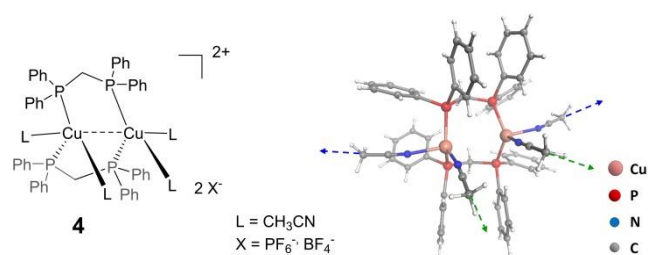


Figure 7. Chemical structure and X-ray crystal structure of the complex **4**, green and blue dotted arrows represent the potential coordination directions at the Cu(I) metal centers.

4.2. Preparation of one-dimensional polymers bearing π -stacked Cu(I) based compact metallacycles

In a first step, taking into consideration the important contribution taken by intramolecular lateral π - π interactions in the stabilization of the Cu(I) compact metallacycles **A** (Figure 4), the precursor **4** was reacted with a series of linear neutral cyano-capped π -conjugated systems. It resulted in one-dimensional coordination polymers (1D-CPs) **B** in which compact π -stacked metallocyclophanes are connected by ditopic π -conjugated organic linkers (Figure 8).²⁹ In these assemblies, the Cu(I) dimer units present an original 'F-shape' geometry with the two metal centers (intermetallic distance decrease to ca. 3.1 Å) having either a distorted trigonal planar or tetrahedral coordination sphere, in marked contrast with the exclusively trigonal planar coordination spheres observed in the U-shape fragments stemming from the precursors **1** and **2**. In the metallacycle sub-units in **B**, the two π -systems present π - π interactions and adopt a parallel-displaced arrangement, which is an energetically more favoured stacking than the face-to-face stacking observed in the π -stacked compact metallacycles obtained from **1** and **2**.²¹⁻²⁴ This difference highlights the remarkable flexibility presented by the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ units since the general 'U-shape' of the bimetallic units of the precursors **1** and **2** is preserved in their related compact supramolecular assemblies. Conversely, the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment adapts in a large extent its structure (coordination number, conformation, intermetallic distance...) in these 1D-CPs allowing optimization in the parallel-displaced arrangement of the weak but stabilizing π - π interactions. Moreover, this bimetallic unit can display metal centers with different coordination sphere numbers. This is due to the intrinsic flexibility of the Cu(I) ions coordination sphere but also of the dppm assembling ligand that exhibits an 'accordion-like' adaptable behavior, accepting large variation of its coordination bite angle without collapse of the gross $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment chemical structure. Such structural flexibility questions the pertinence of defining these self-assembly processes as owing to the CDS chemistry approach. Indeed, a net discrepancy is observed between the symmetry and the connectivity in the isolated pre-assembled bimetallic precursor and in the supramolecular assemblies characterized. Anyhow, there is also a clear analogy between the supramolecular

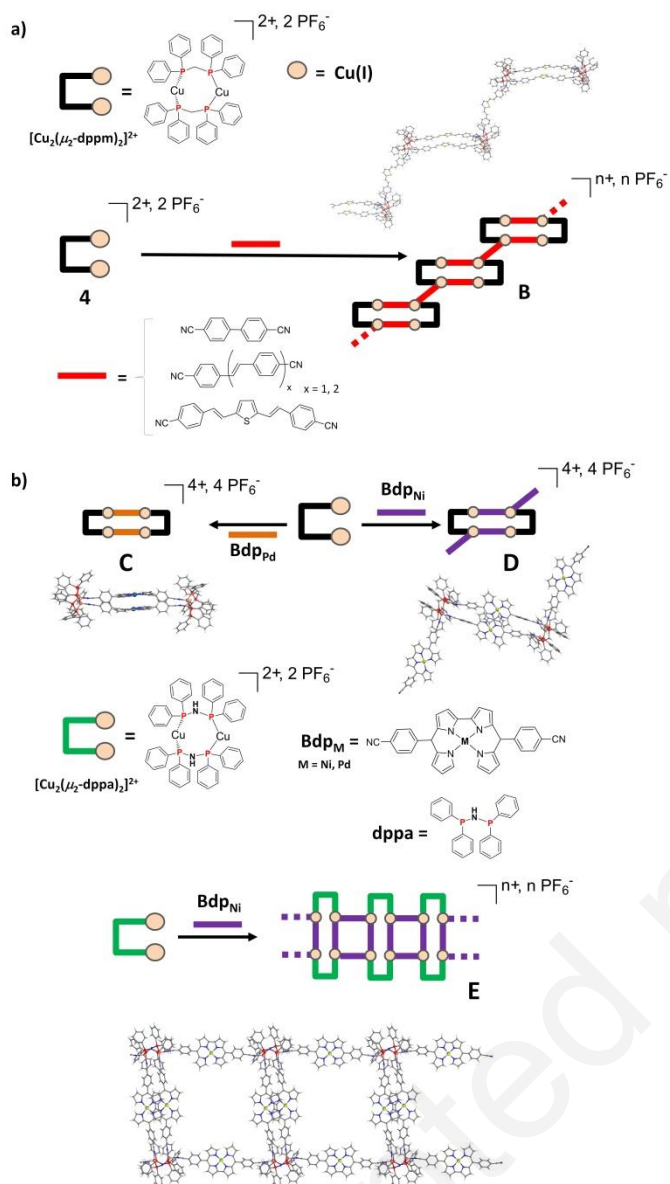


Figure 8. Preparation of the discrete and polymeric polymetallic assemblies **B**, **C**, **D** and **E** and selected examples of X-ray crystal structures.

scaffolds of the compact π -stacked metallacycles obtained from **1** and **2** according to conventional CDS concept and the 1D-CPs **B** prepared from **4** that incorporate compact π -stacked metallacycles sub-units in their backbones. Therefore, considering that this discrepancy is essentially the result of the large conformational flexibility of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ unit that "adapts" its geometry in the resulting self-assembled structure, and that, moreover, one cannot deny that the whole synthetic approach conducted is clearly inspired by the concept of CDS processes, we have recently suggested the term of 'adaptive CDS processes'³⁰ to qualify the self-assembly processes based

on the flexible $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment, and similar Cu(I) pre-assembled precursors.³¹

The versatility of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment was recently confirmed as this building-block was reacted with another series of ditopic cyano capped π -conjugated **Bdp_M** linkers based on central metallated 2,2'-bis-dipyrrin moiety (Figure 8b) bearing large non-planar π -walls. The structural variety of the pre-assembled Cu(I) precursor was also altered by changing the assembling dppm ligand by the dppa (bis(diphenylphosphino)amine) ligand. This affected the self-assembly processes, revealing that by applying small variations on the building blocks employed in CDS processes based on Cu(I) bimetallic precursors, it is possible to operate a rich harvest (derivatives **C**, **D** and **E**, figure 8b) among the various CDS structures that can be isolated.³² The structural adaptivity of the Cu(I) building blocks was strongly confirmed by the characterisation of diverse and original supramolecular discrete or polymeric Cu(I) derivatives always containing compact π -stacked metallacycles in which the coordination number of the two metal ions and the intermetallic distances (from 2.77 Å till 3.41 Å) was greatly altered without collapse of the general bimetallic gross scaffolds.

Regarding specifically luminescence properties, the study of the solid-state luminescence of the series of 1D-CPs **B** was not conducted so far, but deserves attention in the next future in particular in order to highlight the competitive effects that take place between relaxation processes lying on the Cu(I) building blocks and on the various extended π -conjugated linkers. In the case of the derivatives bearing metallated 2,2'-bis-dipyrrin fragments, the potential solid-state luminescence properties centered on the Cu(I) moieties are quenched due to the low absorption energies of the **Bdp_M** connecting ligands.

4.3. Luminescent Cu(I) discrete polymetallic assemblies via adaptive CDS synthetic process

4.3.1 Using the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ building block as pre-organized precursor

The $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ building block was also reacted with the 'short' anionic ditopic cyano linker affording quantitatively a 'small' tetrametallic Cu_4 assembly **F₁**,³³ similarly to the analogous reactions conducted from **1** and **2** in which a 'sterical protection effect' has been suggested.¹⁹ This derivative results in the selective self-association of two $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragments with two cyano ditopic linkers (Figure 9). Within **F₁**, the four Cu(I) metal centers are trigonal planar and the intermetallic distances within the peripheral bimetallic fragments are markedly shorter (2.8669(6) Å) than in the precursor **4** (ca. 3.7 Å). This result confirms the 'accordion-like' behavior of the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ fragment. Very importantly, in the solid state at RT, this tetrametallic Cu(I) compact metallacycle is a blue-luminophore (Figure 9c) that undergoes efficient TADF processes with a RT emissive quantum yield (EQY) of 72% and a TADF decay time at 298 K of ca. 40 μs .³³ The rather high $\Delta E(\text{S}_1\text{-T}_1)$ of 1560 cm^{-1} determined for such highly TADF luminescent derivative motivated to conduct TD-DFT studies. They revealed that

geometrical changes occur in the excited states (Figure 9b), in which the centro-symmetry of the metallacycle is broken. In the

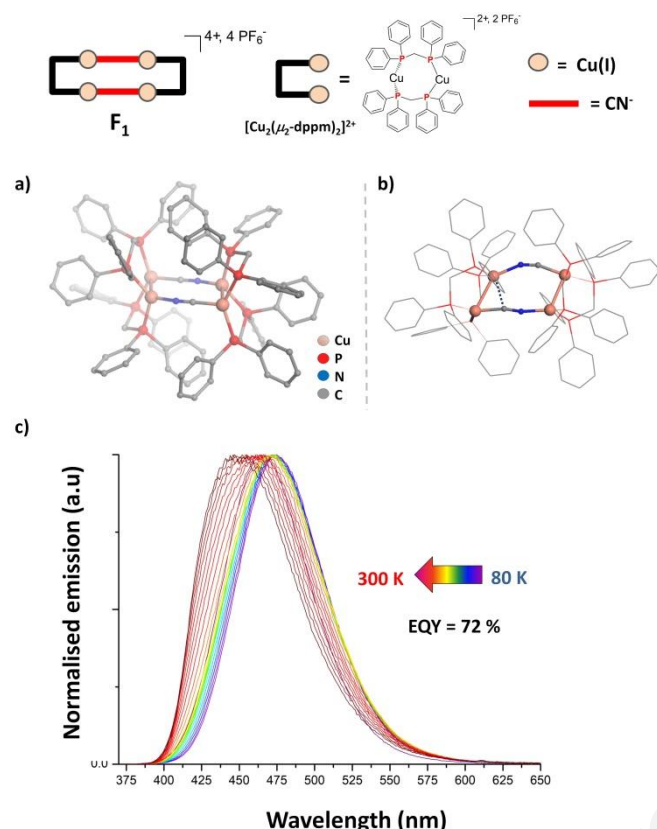


Figure 9. Schematic representation of the derivative F_1 and a) view of its X-ray crystal structure, b) calculated structure of its T_1 state and c) thermal variation of its solid-state emission spectrum ($\lambda_{ex} = 320$ nm).

calculated excited states structures, the coordination sphere of one of the Cu(I) metal center bears a limited pyramidalization while the other metal centers remain distorted trigonal. Concomitantly, a shortening of the intermetallic distances down to 2.6–2.7 Å occurs, associated with the generation of a small but significant spin-orbit coupling value that favours efficient radiative relaxation pathways.³³

While such an intramolecular reorganisation is very likely to be allowed by the ambidentate coordination ability of the cyano ligand, this also reveals a new appealing facet associated with the conformational flexibility of the Cu(I) bimetallic units. Indeed, it allows facile reorganisation processes in the excited states without vibrational high energetic cost and is highly beneficial for the exaltation of the solid-state luminescence properties. This reaction was extended to the longer linear gold(I) dicyanide $[Au(CN)_2]^-$ connecting ligand leading to the unexpected formation of the large Au_2Cu_{10} polymetallic assembly F_2 in place of the targeted Au_2Cu_4 compact metallacycle (Figure 10).^{31b} Similarly, as $[Pt(CN)_4]^{2-}$, aimed to act as square planar tetratopic connecting ligand, was also reacted with the pre-assembled $[Cu_2(\mu_2-dppm)_2]^{2+}$ building block, a Pt_4Cu_{11} derivative F_3 was

obtained selectively rather than the expected Pt_2Cu_8 assembly (Figure 10).^{31b} Along these syntheses, the $[Cu_2(\mu_2-dppm)_2]^{2+}$ unit

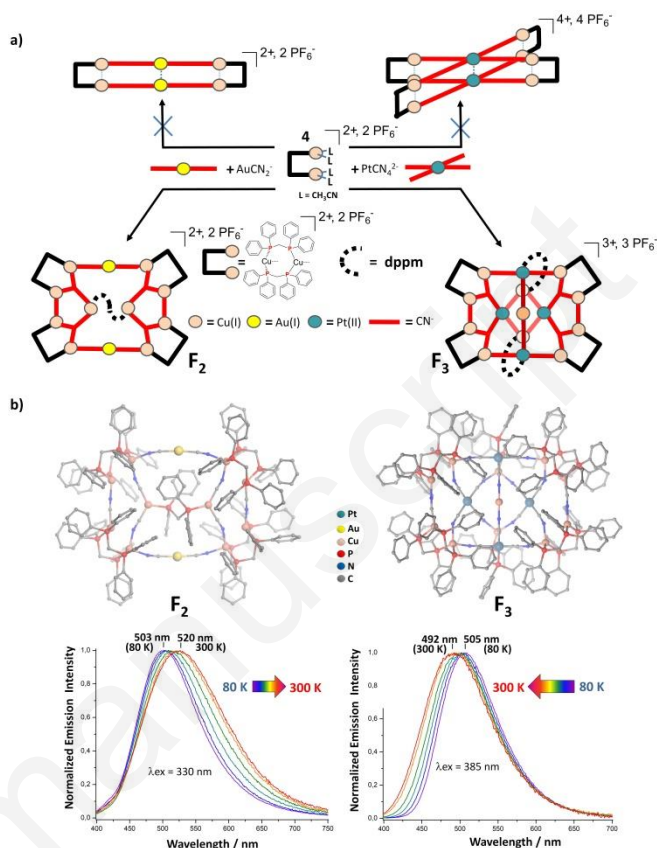


Figure 10. a) Syntheses and schematic representation of the derivatives F_2 and F_3 b) view of their X-ray crystal structures and of the thermal variation of their solid-state emission spectra.

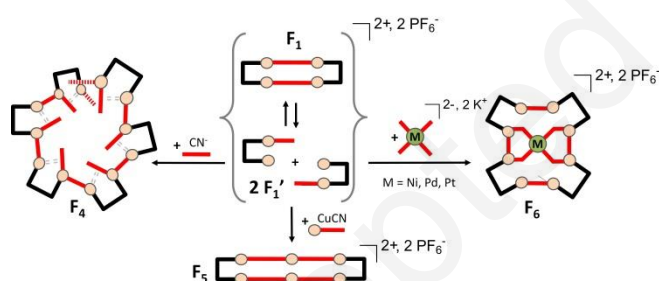
keeps its unique flexibility (modulation of the intermetallic distances and the coordination bite angle of the chelating dppm ligands) affording new examples of adaptive supramolecular syntheses. Nevertheless, the scope of the self-assembly processes goes further in these reactions. While in conventional CDS,^{5a,b} 'initial building blocks' cores are preserved within the self-assembled structures, concerted post-assembly intramolecular rearrangements of cyano-based and $[Cu_2(\mu_2-dppm)_2]^{2+}$ building blocks are presumed to occur along self-assembly steps leading to the unexpected high nuclearity supramolecular scaffolds finally characterized. While such outcomes clearly lack the criteria of prediction associated with conventional CDS synthesis, the pre-organisation of the Cu(I) ions in the precursor **4** revealed to be mandatory to ensure the success of such straightforward preparation of intricate polymetallic assemblies.

The Au_2Cu_{10} and Pt_4Cu_{11} derivatives F_2 and F_3 present exalted solid-state luminescence properties (Figure 10b, EQY for $F_2 = 70$ % and EQY for $F_3 = 63$ %) centered on the Cu(I) metal ions,^{31b} and taking benefit from valuable features: Cu(I) metal centers present in such polycyclic supramolecular scaffolds bear reduced possibility of large structural re-organisation of their

coordination sphere in the excited states due to the intrinsic geometrical constraints of being included in a cyclic backbone. In addition, associating in these backbones Cu(I) ions with heavy metal centers bearing high spin-orbit coupling constants promote efficient radiative deactivation pathways, revealing a 'heavy atom effect' to enhance the photoluminescence performances of these Cu(I) supramolecular assemblies.

4.3.2 Using the tetrametallic metallacycle F_1 as pre-organized precursor

In the tetrametallic metallacycle F_1 , the metal centers' trigonal planar coordination spheres can accept additional coordination of donor ligands, giving access to new polymetallic assemblies. As the metallacycle F_1 is reacted with, respectively KCN, CuCN or $K_2[M(CN)_4]$ metallo-ligands ($M = Ni, Pd, Pt$), a series of new solid-state luminescent supramolecular assemblies is selectively prepared.^{31a,b} Their formation can be explained by considering that the derivative F_1 is the result of the dimerization of $[Cu_2(\mu_2\text{-dppm})_2]CN$ fragments F_1' bearing coordinatively highly unsaturated and reactive Cu(I) metal centers (Scheme 2). Thanks to a putative reversible equilibrium in solution between F_1 and F_1' ,^{31a} a reaction of the latter with additional cyano-based building blocks take place affording the new polymetallic species (Scheme 2 and figure 11). Thus, the cyano ligand can be considered as formally inserted within the metal centers of F_1' affording $[Cu_2(\mu_2\text{-dppm})_2(CN)_2]$ fragments that self-assemble in the solid-state forming the remarkable helicoidal 1D-CP structure of F_4 .^{31a} In the case of the reaction with the CuCN building block, a formal inorganic ring extension is observed as a consequence of the coordination of the CuCN fragment to F_1' and the re-association of the resulting fragments.^{31b}



Scheme 2. Putative dissociation of F_1 in F_1' and preparation and schematic general structures of the assemblies F_4 , F_5 and F_6 .

Finally, the square planar $[M(CN)_4]^{2-}$ building block behaves as a template to connect four F_1' units in discrete Cu_8M polymetallic assemblies F_6 .^{31a} In this family of new derivatives the metric data of the $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ fragments undergo significant alterations while the structural integrity of the bimetallic unit is preserved, as previously observed in the other self-association processes based on this flexible pre-assembled fragment. Therefore, the tetrametallic metallacycle F_1 can be defined as an original source of highly reactive and adaptive bimetallic precursors for the CDS preparation of new polymetallic species.

As previously stated, such self-assembly processes do not meet the basic requirements of strict rigidity of the building blocks and

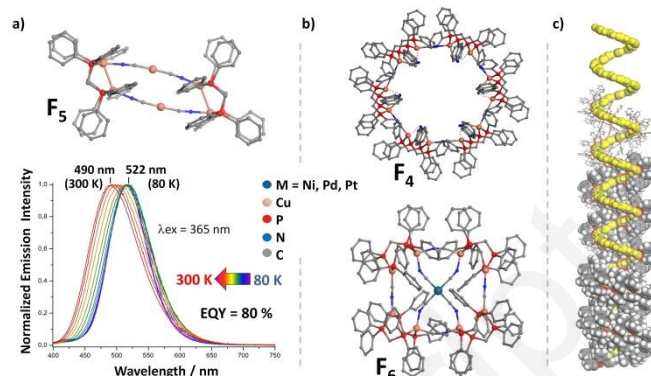


Figure 11. a) X-ray crystal structure and thermal variation of the solid-state emission spectrum of F_5 ; b) X-ray crystal structure of F_4 (view along the c axis) and F_6 ; c) view of the 1D helicoidal polymer formed in F_4 with a gradual CPK style to stick-and-ball style to a removal of the dppm ligands, the $(CuCN)_n$ helicoidal chain located in the wall of the 1D channels formed being shown in CPK style in yellow.

prediction of the molecular structure of the synthesized assembly that are inherent to conventional CDS chemistry. Yet, taking into account the conformational flexibility allowed by the Cu(I) precursors used, the synthetic process can be rationalized, and is believed to be extended to the preparation of other families of multimetallic species.

Last but not least, these new polymetallic derivatives present a large variety of solid-state luminescence properties. The derivative F_4 is a yellow solid-state luminophore at RT as a result of metal-perturbed dppm ligand-centered phosphorescence without occurrence of a TADF process.^{31a} Conversely, the metallacycle F_5 is a green-luminophore bearing efficient TADF processes with a RT emissive quantum yield of 80% (Figure 11a).^{31b} Finally, the series of polymetallic species F_6 presented different photophysical properties with an enhancement of the RT luminescence magnitude depending on the nature of the central M ion ($Ni < Pd << Pt$).^{31a} TD-DFT calculations^{31a} suggested implication of the electronic density of the central metal atom in the overall electronic transition upon the excitation process, associated with an increase of the spin-orbit coupling components both in the non-radiative and radiative processes.^{31a} As a result, a competition between spontaneous phosphorescence and TADF along this series was suggested, in agreement with the measured photophysical properties.

5. Conclusion

The typical features of the coordination chemistry of Cu(I) ion (labile, flexible and low-directional coordination spheres) that were initially regarded as being strongly restrictive for the use of this ion in conventional CDS chemistry can turn out to be very valuable to conduct successfully and selectively the preparation

of new polymetallic supramolecular assemblies. Due to a suitable molecular design of pre-assembled Cu(I) polymetallic building blocks, these anticipated limitations can not only be circumvented but also be exploited to pave the way for adaptive behaviors giving access to polymetallic supramolecular assemblies bearing original architectures and attractive luminescence properties. Yet, this intrinsic flexibility of the Cu(I) building blocks makes it certainly illusory to envisage a strict prediction of all the supramolecular architectures obtained. Nevertheless, the rationalisation of the adaptive behaviors^{30,31} displayed by the studied Cu(I) pre-assembled precursors allows to establish guiding rules that explain and subsequently control the formation of the characterized polymetallic derivatives and very likely will be extended to the reasoned preparation of other original polymetallic assemblies. By varying the nature of the flexible pre-assembled building blocks studied, new avenues toward innovative classes of supramolecular materials exhibiting manifold functionalities can be anticipated. With this in mind, extended investigations will be devoted to new Cu(I) precursors stabilized by different classes of assembling ligands such as phosphine or carbenes ligands. In addition, high attention will be paid to the extension of these studies to other metal ions with a particular focus for the Ag(I) ion³⁵ which is known to presents also very flexible and labile coordination spheres.

Finally, it is important to state that there are definitively several steps that still have to be addressed in this work in order to progress toward concrete technological applications based on Cu(I) CDS assemblies. Among them, the question of the persistence of these species in solution, or within specific matrix, is clearly an issue that still needs to be answered. Indeed, the intrinsic conformational flexibility of these assemblies makes solution NMR studies not trivial, and they have been mostly inconclusive for the derivatives presented in the section 3 when the motivation was to show clearly the persistence in solution of the X-ray structure determined in the solid state. Intensive and encouraging studies are currently undergone for the family of derivatives described in the section 4 in order to highlight their stability in solution. These investigations are of major interest from the perspective of studying the luminescent properties and hierarchical self-assembly processes in solution. They are also mandatory in order to achieve the transfer of these new synthetic outcomes toward concrete technological applications, since they will contribute for the set-up of controlled and reproducible procedures to prepare devices in which the specifics of the Cu(I)-based supramolecular assemblies will be taken advantage of. So far, the characterized supramolecular Cu(I) assemblies present various luminescence properties supplying new source for emissive derivatives that may deserve general interest not only as innovative emitters for lighting applications such as in OLEDs but also as new sources of stimuli responsive multifunctional luminescent materials.^{15c,34} Indeed, the large flexibility and lability of the Cu(I) ion coordination sphere render the gross conformation of such Cu(I) species potentially very sensitive to external stimuli, which concomitantly may induce alteration of their photophysical properties. Therefore, these new Cu(I)-based CDS luminophors do present multiple and original facets (such as thermochromic,

vapochromic or mechanochromic luminescence) that open great perspectives of potential development in various fields of applications such as sensing and detection of volatile harmful chemical substances or non-destructive testing of materials. However, synthetic investigation in the field of Cu(I)-based CDS assemblies remains still mostly in its infancy. Therefore, regarding outcomes that might be achieved in the next future, fields of technological applications associated with these compounds could be likely greatly enlarged to other areas of molecular electronics (e.g. spintronics, light harvesting, energy conversion,...) or unprecedented scopes of applications that the unique specificities of Cu(I)-derivatives could open access.

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Keywords: Coordination driven supramolecular chemistry • polymetallic complexes • Cu(I) ion • luminescent molecular materials • Conformational flexibility

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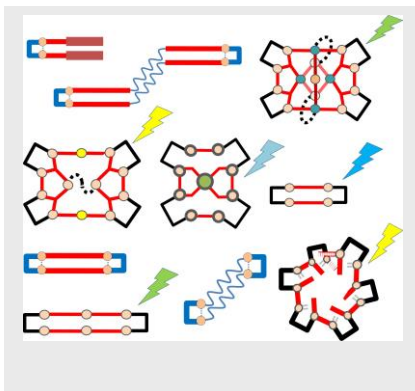
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PERSONAL ACCOUNT

Pre-organized adaptive Cu(I) bimetallic building blocks allow conducting selective coordination-driven supramolecular syntheses. Rational preparations of original multimetallic species are achieved, including highly luminescent solid-state derivatives.



*Christophe Lescop**

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Coordination-driven supramolecular synthesis based on bimetallic Cu(I) precursors : adaptive behavior and luminescence properties.