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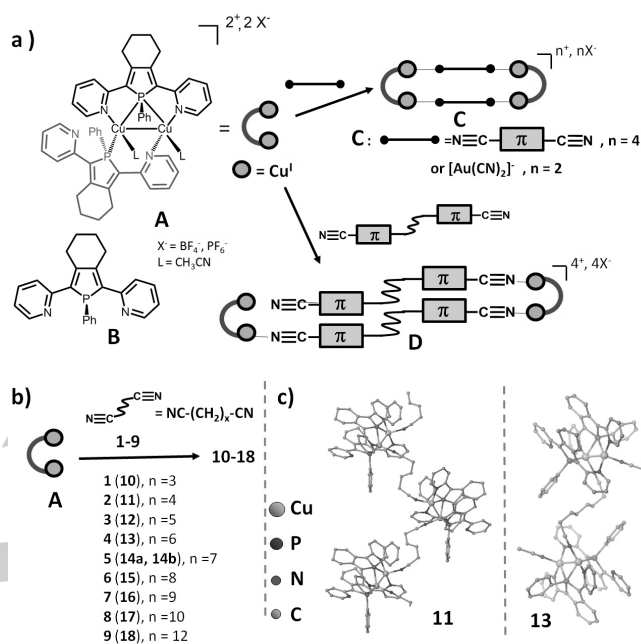
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# Can coordination-driven supramolecular self-assembly reactions be conducted from fully aliphatic linkers ?

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**Abstract:** A series of fully aliphatic cyano-capped ditopic linkers with increasing lengths were reacted with a pre-assembled Cu(I) bimetallic molecular clip bearing short intermetallic distances. It is shown that, depending on the length of the ditopic linkers, a rational design of unprecedented supramolecular compact metallacycles bearing fully aliphatic walls is possible. The specific pre-organized molecular arrangement of the molecular clip used favors stabilizing interlinker London dispersion interactions allowing, as the linkers' lengths increase, the selective formation of discrete compact metallacycles at the expense of 1D coordination polymers. The generalizability of this approach is demonstrated by reacting fully aliphatic cyano-capped linkers with two other types of pre-assembled Cu(I) bimetallic molecular clips also having short intermetallic distances.

One important concept associated with supramolecular chemistry<sup>[1]</sup> is self-assembly, which deals with the way discrete individual components interact via intermolecular interactions to afford high-order functional derivatives by their spontaneous assembly. Among the synthetic methods based on this concept, coordination-driven supramolecular (CDS) chemistry<sup>[2]</sup> has proved to be one of the most powerful contemporary synthetic approaches, providing an impressive number of increasingly complex supramolecular assemblies.<sup>[3]</sup> In the large majority of the syntheses conducted, the backbones of the multitopic linkers used are rigid aromatic  $\pi$ -conjugated moieties ensuring, upon their coordination on selected metal centers, a close control of the architectures of the resulting products. In contrast, fully aliphatic (FA) linkers<sup>[3]</sup> a priori challenge the key synthetic guiding rules of coordination-driven supramolecular chemistry,<sup>[4]</sup> since low predictability and selectivity in CDS processes are anticipated with such linkers. Indeed, these scaffolds present a high intrinsic conformational flexibility, which supposes an excessively high entropic cost to organize them within well-defined, ordered CDS assemblies. This has clearly restricted the introduction of FA linkers in CDS self-assembly reactions so far. However, such linkers present potentially very attractive features as compared to aromatic linkers.<sup>[5]</sup> They could afford



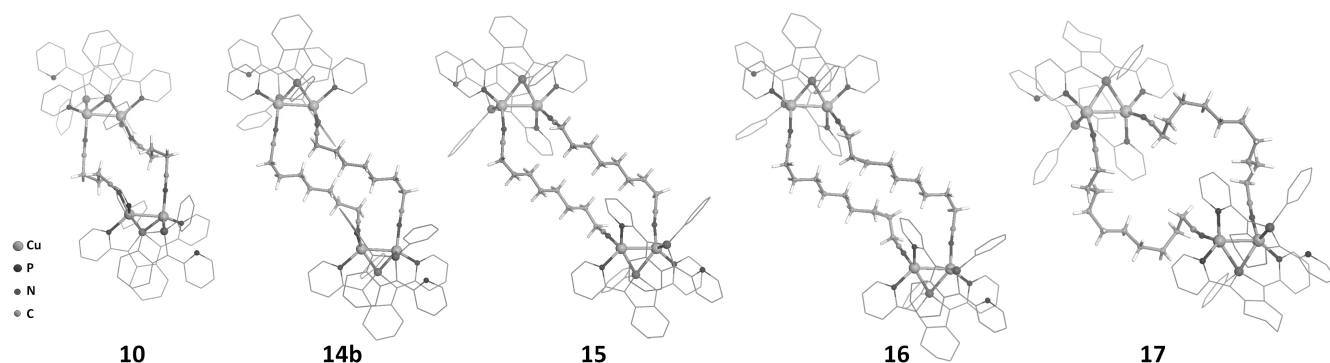
**Scheme 1.** (a) Molecular structures of the molecular clip **A** and of the ligand **B**; Synthesis of the assemblies **C-D**. (b) Synthesis of the derivatives **10-18**. (c) X-ray structures of the polycationic assemblies **11** and **13**.

supramolecular assemblies with unprecedented topologies and host-guest properties as well as induce original, multifunctional properties due to their significantly different electronic structures (HOMO-LUMO gap, electronic density distribution ...). To date, only a limited number of discrete supramolecular assemblies have been sporadically reported based on ditopic linkers bearing FA fragments,<sup>[6]</sup> and, to the best of our knowledge, no general study in this field has so far been conducted. These results prompted us to explore the reaction of a family of linear ditopic FA cyano-capped linkers **1-9** NC-(CH<sub>2</sub>)<sub>x</sub>-CN ( $x = 3-10, 12$ ) with the pre-assembled bimetallic Cu(I) U-shape molecular clip **A**<sup>[7]</sup> (Scheme 1b), stabilized by the hemilabile 2,5-bis(2-pyridyl)phosphole ligand **B** and bearing short intermetallic distances ( $d(\text{Cu}-\text{Cu}) = 2.55 \text{ \AA}$ ).<sup>[8]</sup>

Derivative **A** was previously identified as a versatile and strongly convergent 'U-shape' molecular clip for the CDS syntheses of a large series of compact metallacycles **C**<sup>[9]</sup> upon its reaction with various ditopic cyano-capped  $\pi$ -conjugated linkers<sup>[10]</sup> or with the metal-based linear linker  $[\text{Au}(\text{CN})_2]$  (Scheme 1a).<sup>[11]</sup> Within the resulting assemblies, specific inter-linkers interactions ( $\pi$ - $\pi$  or aurophilic intra- and intermolecular interactions) were observed, playing presumably a key role in the selective formation of these compact metallacycles, which was recently supported by the reaction of **A** with a series of cyano-capped ditopic linkers carrying both 'rigid'  $\pi$ -conjugated systems and 'flexible' linear

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**Figure 1.** Views of the X-ray crystal structures<sup>[13]</sup> of the tetracationic metallacycles **10**, **14b**, **15**, **16** and **17** (counteranions, H atoms of the ligands **B** and solvent molecules have been omitted for clarity).

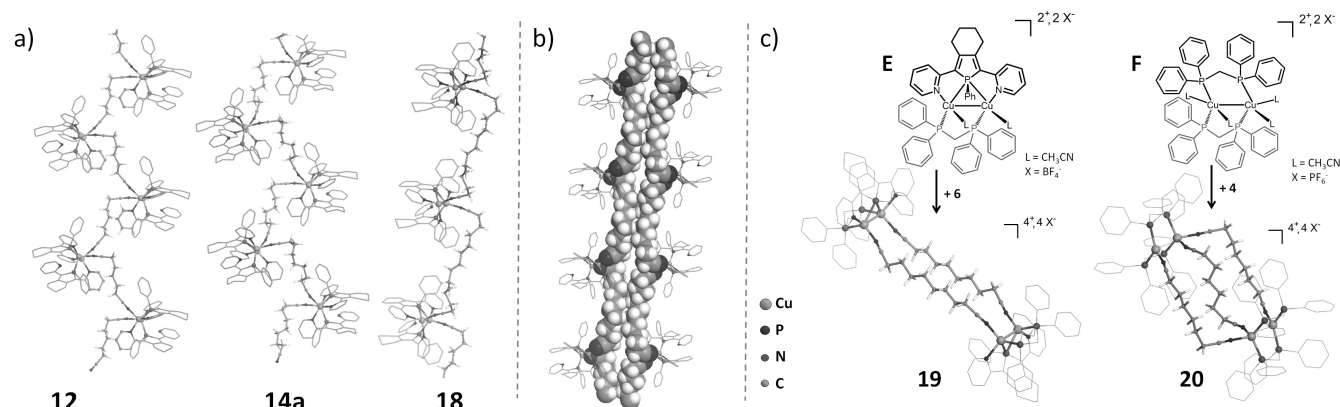
aliphatic moieties (Scheme 1a). Here, an unprecedented family of self-assembled compact 'pseudo double-paracyclophane' metallacycles **D** was obtained,<sup>[12]</sup> in which inter-linker intramolecular  $\pi$ - $\pi$  interactions were also observed. Notably, in the course of this study, the FA linkers **2** and **4** (Scheme 1b,c) were reacted with **A** affording both the one-dimensional coordination polymer (1-D CP) **11** and, quite surprisingly, the discrete 'open' tetrametallic supramolecular assembly **13**.<sup>[12]</sup>

The discrepancy observed in the molecular architectures of **11** and **13** motivated us to perform a systematic study varying the length of the linear aliphatic cyano-capped ditopic linkers reacted with **A**. The room temperature (RT) 1:1 reaction in  $\text{CH}_2\text{Cl}_2$  of the molecular clip **A** with the linkers **1-9** afforded, after crystallization, the derivatives **10-18** (Scheme 1b), respectively, as air-stable polycrystalline powders in good yields.<sup>[13]</sup> Among these compounds, all the discrete supramolecular assemblies are readily soluble in chlorinated solvents.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra recorded in  $\text{CD}_2\text{Cl}_2$ <sup>[11]</sup> indicate that the  $\text{Cu}_2(\text{B})_2$  moiety is maintained (Table S1), while  $^1\text{H}$  NMR spectra presented a single set of signals with a 1:1 integration ratio between the signals assigned for the ditopic ligands and the  $(\text{Cu})_2(\text{B})_2$  fragments. Infrared spectra show the presence of coordinated cyano groups ( $\nu(\text{C}=\text{N})$ , ca.  $2275\text{ cm}^{-1}$ , Table S1;  $\nu(\text{C}\equiv\text{N})$  for the free FA linkers, ca.  $2245\text{ cm}^{-1}$ ). The solid state molecular structures of all the derivatives **10-18** were established by X-ray diffraction studies<sup>[6,13]</sup> performed on single crystals obtained at RT from pentane diffusion into  $\text{CH}_2\text{Cl}_2$  crude solutions. In all the supramolecular structures **10-18**,  $\text{Cu}_2(\text{B})_2$  fragments present the coordination modes for the ligands **B** usually observed in the derivatives **A**, **C** and **D**.<sup>[7,10-12]</sup> All the P-phenyl substituents point towards the cyano-ligands, which correspond to a preferred configuration of the ligands **B** in which the sterical constraints in the  $(\text{Cu})_2(\text{B})_2$  fragments are minimized. In addition, all the metric parameters of the dicationic  $(\text{Cu})_2(\text{B})_2$  cores of the derivatives **10-18** are very similar to those of the molecular clip **A**<sup>[7]</sup> and the metallacycles **C-D** (Table S4).<sup>[10-12]</sup> Finally, no specific intra- or inter-molecular short contact interactions involving the ligands **B** are observed. All this allows to preclude sterical congestion effects at the  $(\text{Cu})_2(\text{B})_2$  fragments to justify the differences in the molecular architectures of the derivatives **10-18**.<sup>[6]</sup>

Derivative **10** is a tetracationic metallacycle (Figure 1) resulting from the coordination of two equivalents of the short FA linker **1**

on two molecular clips **A**. In this compact discrete cyclic assembly, neither free space nor guest molecules are observed inside the metallacycle. In contrast, by reacting the linkers **2** and **3** with **A**, the 1-D CPs **11**<sup>[12]</sup> (Scheme 1c) and **12** (Figure 2a) are selectively obtained. These two zig-zag 1-D CPs share very similar structural features with the coordination on each consecutive  $\text{Cu}_2(\text{B})_2$  fragments of two linkers having a relative divergent orientation. As previously reported,<sup>[12]</sup> when the reaction is conducted with the linker **4**, neither 1-D CP nor a discrete metallacycle formation can be achieved, but the discrete 'open' tetrametallic supramolecular derivative **13** is obtained (Scheme 1c). Even though attempts were made to force the full substitution of the acetonitrile ligands of the Cu(I) metal centers of **A**, reacting it with a large excess of the ligand **4**, the derivative **13** was always isolated exclusively upon crystallization.

Interestingly, the reaction of the molecular clip **A** with the FA linkers **5-9**, which have longer aliphatic backbones, afforded selectively distinctly different supramolecular architectures. The reaction of **A** with the linker **5** afforded two different types of crystals **14a** (needles) and **14b** (prisms) in nearly equal amounts and with an overall good yield.<sup>[13]</sup> **14a** is a 1D-CP (Figure 2a) in which, as observed in the derivatives **11** and **12**, the aliphatic fragments of two consecutive linkers **5** have a gross 'gauche' conformation and a divergent relative orientation. In strong contrast, the derivative **14b** is a compact metallacycle (Figure 1) bearing two aliphatic fragments mostly parallel with an 'eclipsed' configuration. The result of the reaction between **A** and the linkers **4** and **5** (derivatives **13** and **14a-b**, respectively) is therefore strikingly different in spite of the fact that these two linkers only differ in one methylene unit. Most particularly, it was by no means anticipated that a compact metallacycle structure could be obtained from the longer linker **5**, while the linkers **2-4** tended to form the 'open' supramolecular architectures **11**, **12** and **13**. Reinforcing this observation, the supramolecular assemblies **15** and **16** (Figure 1) obtained selectively from the linkers **6** and **7**, respectively, are also compact metallacycles. Their main solid state structural features are fully comparable with those observed in **14b**, including their two aliphatic fragments, in most parts parallel with a gross 'eclipsed' configuration. In addition, the reaction of the molecular clip **A**



**Figure 2.** Views of a) the X-ray crystal structures<sup>[13]</sup> of the polycationic 1D CPs **12**, **14a** and **18**; b) the solid state organization of two neighboring polymers in the derivative **18**; c) syntheses and the X-ray crystal structures of the tetracationic metallacycles **19** and **20** (counteranions, H atoms of the ligands **B** and dpmm ligands and solvent molecules have been omitted for clarity)..

with the ligand **8** afforded the supramolecular metallacycle **17** (Figure 1) in which the aliphatic backbones of the two aliphatic linkers **8** present a roughly 'gauche' configuration with a relative opposite orientation toward the center of the metallacycle. As a result, a narrow cavity is observed within the derivative **17** in which no guest molecule is included but two counter-anions are located closely above and below the mean plane of the metallacycle with a weak CH-F short contact interaction (ca. 2.45 Å, Figure S1).

The assemblies **14b**, **15**, **16** and **17** are, together with the derivative **10**, the first examples of compact metallacycle architectures obtained from FA linkers according to a synthesis derived from the CDS synthetic approach. Notably, the formation of **10** can be assigned to a 'sterical protection effect' previously observed with short pseudo-halogenide linkers,<sup>[9,14]</sup> relying on specific stereo-geometric restriction effects related to the shape and the steric hindrance of the Cu<sub>2</sub>(**1**)<sub>2</sub> units and on the short length of the linker **1**.<sup>[14]</sup> In contrast, the selection of the discrete metallacycle architectures **14b**, **15**, **16** and **17** must be related to a stabilization of the ring structure depending on the length of the linkers. Notably, the close pairing of two linear aliphatic fragments within such metallacycle scaffolds affords confined areas in which these FA apolar fragments are aggregated inducing a significant overall enthalpic gain in London dispersion interactions. In the case of the shorter FA ditopic linkers **3-5**, due to a smaller amount of methylene fragments involved, the stabilization associated with such interactions can be negligible and cannot compensate the entropic loss related to their organization within discrete supramolecular assemblies. On the contrary, as the length of the aliphatic fragment is increased, a substantial stabilization favoring the metallacycle architecture may result from the cumulation of London dispersion interactions. Therefore, a delicate balance between competitive enthalpic and entropic parameters can explain the structural variation observed along the series of the supramolecular assemblies **10-16**. This can be illustrated in the 'hollow' metallacycle molecular architecture of the derivative **17** in which only a portion of the aliphatic linkers shares interlinker London dispersion interactions, while a significant amount of intralinker London dispersion

interactions is also observed due to the specific gross 'gauche' conformation adopted by these linkers' backbones.

Increasing the length of the aliphatic chains of the FA linkers architectures could therefore afford another kind of supramolecular architecture. The NC-(CH<sub>2</sub>)<sub>12</sub>-CN ditopic linker **9** was prepared and reacted with **A**, affording selectively the 1D CP **18** (Figure 2a).<sup>[13]</sup> This derivative has a gross organization that compares to those observed in the assemblies **11**, **12** and **14a**, but its extended solid-state organization (Figure 2b) is markedly different. Indeed, while the zig-zag polymeric chains of the derivatives **11**, **12** and **14a** are well isolated from each other in the crystal packing (Figure S2), the linear 1D CP **18** are arranged in dimers in the solid state (Figure 2b). An aggregation of neighboring -(CH<sub>2</sub>)<sub>12</sub>- units belonging to two different chains occurs, leading to the formation of patterns mimicking locally the organization of the FA linkers found in the metallacycles **14b**, **15** and **16** (Figure 1). Therefore, even though a discrete metallacycle structure is not formed using the longer FA linker **9**, dispersion forces between the -(CH<sub>2</sub>)<sub>12</sub>- long chains can control the solid state extended organization.

Importantly, the self-assembly processes observed herein do not fit strictly the guiding rules of the CDS chemistry, since the geometric constraints of the organic linkers do not impose the geometry of the supramolecular assemblies obtained. However, the Cu(I) molecular clip **A** presents a very specific molecular pre-organization (short intermetallic distances, strongly directional and convergent U-shape geometry) allowing to implement significantly these guiding rules via the formation of stabilizing interlinkers' interactions.<sup>[9-11]</sup> In the case of the syntheses of the compact metallacycles **C** and **D** (Scheme 1), the directionality of the rigid linkers used and the strength of the interlinkers' interactions induced ( $\pi$ - $\pi$  or metallophilic interactions) imply a strong enthalpic stabilization and a negligible entropic cost, promoting the general and selective formation of these metallacycles. Therefore the series of results described herein highlights a novel aspect of such self-assembling processes, demonstrating most particularly the access to an unprecedented family of coordination-driven supramolecular metallacycles bearing FA walls. Very importantly, the crucial role of the CDS processes to force compact



metallacycle formation is confirmed by the fact that, as **A** was reacted in the same condition with a family of cyano-capped FA monotopic ligands NC-(CH<sub>2</sub>)<sub>o</sub>-CH<sub>3</sub> (o = 6, 8, 10), no substitution of the acetonitrile ligands occurred and the starting materials were recovered unreacted.

Since the molecular pre-organization encountered in the bimetallic molecular clip **A** appears to be a key parameter to drive CDS reaction from FA linkers, we have probed the generalizability and versatility of this synthetic approach using the bimetallic pre-assembled Cu(I) precursors **E** and **F** (Figure 2c) having larger intermetallic distances (d(Cu-Cu) = 2.67 Å (**E**);<sup>[7b,10b]</sup> 3.76 Å (**F**)<sup>[15]</sup>) and an alternative potential connectivity. Preliminary experiments were conducted, reacting **E** with **6** and **F** with **4** affording the new discrete compact supramolecular assemblies **19** and **20**, respectively (Figure 2c). In the metallacycle **19** (d(Cu-Cu) = 2.70 Å), the ligands' organization of the Cu<sub>2</sub>(**A**)(dppm) fragments (dppm, bis(diphenylphosphino)methane) is similar to those observed in the free precursor **E**,<sup>[7b]</sup> while the gross metric parameters compare to those of the assembly **15**, including close contacts between the linear cores of the two parallel FA linkers. This suggests that the self-assembling reaction processes observed in the reactions of the derivative **A** with FA linkers can be adapted to other bimetallic precursors having short intermetallic distances. Finally, very interestingly, while the reaction of **A** with **4** afforded the discrete open assembly **13** (Scheme 1),<sup>[12]</sup> the derivative **20**, obtained in a moderate yield, is a discrete compact assembly gathering three FA linkers **4** with two Cu<sub>2</sub>(dppm)<sub>2</sub> fragments having intermetallic distances notably shorter (d(Cu-Cu) = 3.33 Å) than in the precursor **F**. Each of the three FA linkers **4** is coordinated on one metal center of each of the Cu<sub>2</sub>(dppm)<sub>2</sub> fragments (one Cu(I) ion being distorted tetragonally, while the other one is distorted trigonal, defining a 'F-shape'<sup>[16]</sup> molecular clip). They have a gross 'eclipsed' conformation and are mostly parallel with short intramolecular interlinker-close contacts. Therefore, the three independent FA linkers **4** are aggregated within the derivative **20**, which induces significant London dispersion forces stabilization allowing the selective synthesis of such discrete compact supramolecular assembly.

The presented results reveal that, if implemented by cumulative inter-linker London interactions, CDS synthetic processes can be adapted to the use of FA ditopic linkers. This can be achieved by using specific polymetallic molecular clips bearing short intermetallic contacts and strong conformational stability, allowing interlinkers London dispersion interactions to be generated. Importantly, rational syntheses of very unusual compact supramolecular metallacycle gathering a pre-determined number of FA units can be conducted and modulated depending on the length of the -(CH<sub>2</sub>)<sub>x</sub>- chains. Therefore, this approach provides a unique and general synthetic tool to organize rationally FA moieties within unprecedented discrete or infinite supramolecular architectures. Regarding the current attention paid to solid-state luminescent Cu<sup>I</sup> complexes,<sup>[17]</sup> this approach may be attractive for the preparation of innovative new luminescent multifunctional supramolecular materials.<sup>[18]</sup>

## Acknowledgements

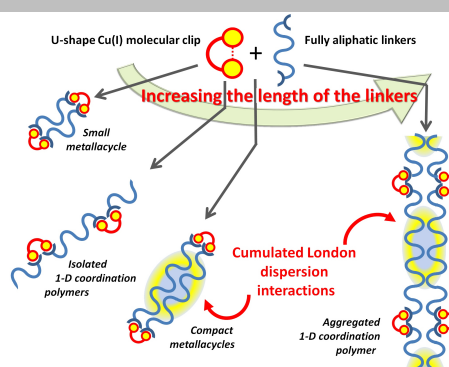
This work was supported by the ANR (P-OPTOELECTR-MOLMAT), the French Research Ministry and the CNRS. C.L. thanks the Alexander von Humboldt Foundation for a fellowship for experienced researcher. B.S acknowledge the SDLM doctoral school for an incoming mobility grant. The German team is grateful to the European Research Council (ERC) for the support in the SELFPHOS project AdG-339072. Dr. E. Caytan is thanked for insightful discussions about DOSY NMR measurements.

**Keywords:** metallacycle • coordination-driven supramolecular chemistry • aliphatic linkers • London dispersion interactions • Cu(I)

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The coordination-driven supramolecular chemistry of a series of cyano-capped fully aliphatic linkers of various lengths with pre-organized Cu(I) dimers having short intermetallic distances is studied. It is revealed that, thanks to the cumulation of London dispersion interactions between the methylene units, specific selective self-assembly reactions from such linkers having non-directional backbones can be conducted.



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