Straightforward Preparation of a Solid-state Luminescent Cu-11 Polymetallic Assembly via Adaptive Coordination-driven Supramolecular Chemistry

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Straightforward preparation of a solid-state luminescent Cu_{11} polymetallic assembly via adaptive coordination-driven supramolecular chemistry

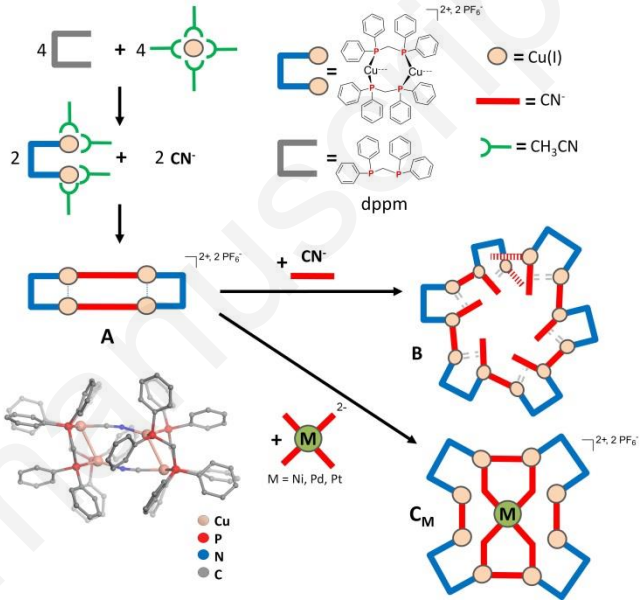
Sloane Evariste,[a] Mehdi El Sayed Moussa,[a] Hok-Lai Wong,[b] Guillaume Calvez,[a] Vivian Wing-Wah Yam,*[b] Christophe Lescop*[a]

Dedicated to the Pr. Dr. Manfred Scheer for his 65th birthday

Abstract : The tridentate dpmp ligand was reacted with Cu(I) salt and cyano ligand affording selectively and unexpectedly the polymetallic Cu_{11} complex **2**along one-step reaction. The formation of this derivative **2** can be explained by self-assembling processes controlled by adaptive coordination-driven supramolecular chemistry. The solid-state photophysical behaviour of **2** has been studied suggesting TADF properties.

Introduction

Coordination-driven supramolecular (CDS) chemistry synthetic strategy[1] is a powerful bottom-up synthetic approach that uses the robust, reversible and directional metal-to-ligand coordinative bonds to drive straightforward reactions toward the selective formation of discrete metallo-supramolecular architectures. In this approach, the choice of pre-defined individual building blocks (metal complexes and organic linkers) involved in predictable self-assembly processes is essential as it dictates the overall shape, size and symmetry of the resulting polymetallic assemblies. Currently, an intensive attention is focused on the preparation of advanced CDS architectures having increased structural complexity and new functionalities.[2] Interestingly, among the functionalities that were embedded within CDS assemblies, luminescence has been in proportion seldom reported[3,4] and the potential of light-emitting CDS derivatives is still mostly unexplored. Regarding the design of innovative luminescent materials, Cu(I) coordination complexes currently focus a great interest due to the enhanced room temperature solid state photophysical performances they can exhibit.[5] These emission behaviors are characterized by a large range of possible radiative relaxation processes with a rising attention being paid to derivatives exhibiting Thermally Activated Delayed Fluorescence (TADF).[5,6] In such derivatives, the thermal population of the lowest energy excited singlet state (S_1) from the lowest energy triplet excited state (T_1) can occur,



Scheme 1. Synthesis of the derivates **A**, **B** and $\mathbf{C_M}$ and X-ray structure of the dicationic metallacycle **A**.

inducing fast and efficient radiative relaxation to the ground state and remarkable room temperature (RT) solid-state luminescence properties.

To date, Cu(I) luminescent precursors acting as pre-organized building blocks to prepare CDS assemblies have almost never been reported. This is mostly assigned to the labile and non-directional coordination spheres that Cu(I) ions usually exhibit, which sets *a priori* a major drawback to conduct selective CDS syntheses toward discrete well-defined metallo-supramolecular architectures. Nevertheless, we have shown previously that this limitation may be overcome by applying a specific molecular design[1f] and we have thus highlighted that Cu(I) bimetallic precursors bearing short intermetallic distances and conformationally stable coordination directions can act as versatile pre-organized precursors for CDS syntheses toward compact metallacycles.[1f]

Recently, we have characterized (Scheme 1) a series of RT solid-state luminophores **A**, **B** and $\mathbf{C_M}$ based on the $[Cu_2(\mu_2\text{-dppm})_2]$ dicationic fragment (dppm = bis(diphenylphosphino)methane).[7] While their various photophysical properties were assigned to relaxation processes between ground and excited states located mostly at the $[Cu_2(\mu_2\text{-dppm})_2]$ fragments, these results revealed also that this dicationic fragment presents a remarkable conformational flexibility (variation of the intermetallic Cu(I)-Cu(I) distances and of the bite angle of the dppm ligands). This flexibility allows conducting unique adaptive CDS processes[7b] by using in particular the metallacycle**A**[7a] as pre-assembled flexible

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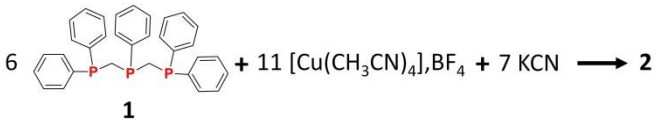
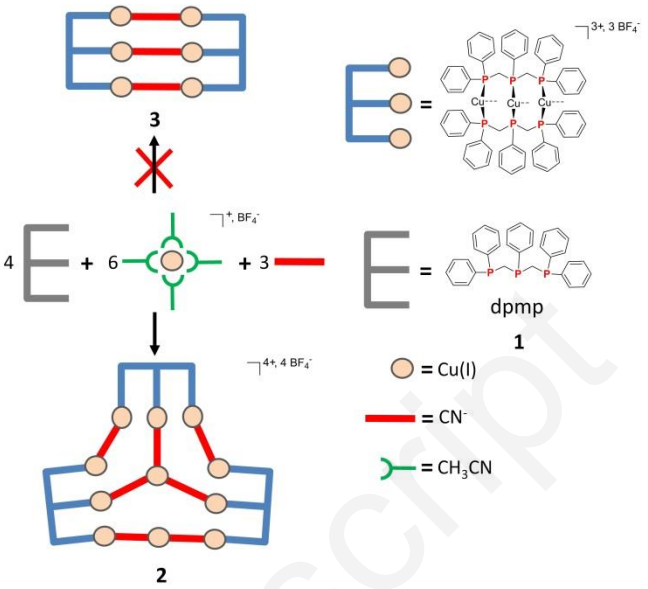
luminescent precursor bearing intrinsic efficient TADF properties.

These results have triggered us to extend our investigation to the use of other multidentate aromatic phosphane ligands in order to characterize alternative polymetallic Cu(I) assemblies along similar synthetic procedure than those applied to obtain **A**. Herein, we describe the reaction of the dpmp (dpmp = bis(diphenylphosphinomethyl)phenylphosphine) ligand **1** with Cu(I) ions and KCN, affording the Cu_{11}tetracationic derivative **2**. Its synthesis, characterization, X-ray single crystal molecular structure and solid-state luminescence properties are reported.



Scheme 2. Molecular structure of the dpmp ligand **1** and optimized synthesis of the Cu_{11} derivative **2**



Scheme 3. Schematic molecular structures of the targeted derivative **3** and of the derivative **2** obtained.

Results and Discussion

Dpmp ligand can be described as a tritopic ''longer'' analog of the ditopic dppm ligand. It has been reported previously that this ligand can stabilize Au(I),[8] Ag(I),[8c,9a] Pt(II)[9] or Cu(I)[10] ions in di- or trinuclear complexes bearing bridging or chelating coordination modes. More particularly, it has been shown that it is possible to form a series of discrete or one-dimensional coordination polymers bearing the linear trimeric cationic unit $[Cu_3(\mu\text{-}X)_2(\mu\text{-dpmp})_2]^+$ (X = Cl, Br, I).[10a] Therefore, considering the preparation of the tetrametallicmetallacycle **A** based on the ditopic ligand dppm (Scheme 1), we have initially anticipated that a similar reaction based on the tritopic dpmp ligand **1** could afford the discrete hexametallic assembly **3** bearing two peripheral $[Cu_3(\mu\text{-dpmp})_2]$ fragments.

4 eq. of ligand **1** were thus reacted at room temperature (RT) under air with 6 eq. of $[Cu(CH_3)CN)_4]BF_4$ in CH_2Cl_2. To the resulting colorless solution were added 3 eq. of KCN as a methanol suspension (Scheme 3). The resulting colorless reaction mixture was vigorously stirred overnight at room temperature, affording a colorless solution bearing a small amount of white precipitate which was then filtered. The $^{31}P\{^1H\}$ NMR spectrum of this clear and colorless crude solution showed a single broad signal centered at -15.4 ppm, very likely indicating an equilibrium between several species in solution. This solution was then left to crystallize by being submitted to pentane vapors diffusion allowing to obtain, after several days, an homogeneous batch of colorless crystals corresponding to the supramolecular assembly **2** (Scheme 2), with a yield of 80%. The derivative **2** is soluble in conventional polar solvents such as CH_2Cl_2, THF and $CHCl_3$ and is stable in the solid state under air at room temperature. Its $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 presents four broad signals centered at -19.7; -15.9; -13.7 and -12.2 ppm, which are chemical shifts typical of σ^3,λ^3-P aromatic phosphine ligands coordinated on Cu(I) metal centers. These $^{31}P\{^1H\}$ NMR data suggest coordination of the Cu(I) ions on all the phosphorus atoms of the ligand **1** within the structure of **2**, but also reveal that there is no free ligand **1** (the $^{31}P\{^1H\}$ NMR signals of **1** in CD_2Cl_2 are composed by a triplet at -33.5 ppm and a doublet at -22.8 ppm). Yet, the number of signals observed is intriguing considering the symmetry expected in the structure of the targeted supramolecular assembly **3** (Scheme 3).[note] The ^1H NMR spectrum of the derivative **2** in CD_2Cl_2 presents a large multiplet at 3.43 ppm assigned to the protons of the methylene moieties of the dpmp ligands and another broad multiplet centered at 7.05 ppm, which corresponds to the phenyl groups of dpmp ligands. In addition, the solid-state infrared spectrum of this compound reveals the presence of cyano groups with three groups of ν(C≡N) vibration bands centered at 2113, 2132 and 2161 cm^{-1}, suggesting at least three distinct types of coordination with respect to the cyano ligands. In agreement with the $^{31}P\{^1H\}$ NMR spectra, these IR spectrometry data suggest that the derivative **2**bear a gross molecular structure that is significantly different and less symmetrical than the structure of the targeted compound **3** (Scheme 3).

The molecular structure of the derivative **2** was established by X-ray diffraction studies on a single crystal obtained from pentane vapor diffusions within a CH_2Cl_2 solution of **2**. It reveals the unprecedented and unexpected formation of a Cu_{11} polymetallic discrete supramolecular assembly (Figure 1).X-ray diffraction studies were performed at 150 K on single crystals of the complex **2**. It crystallizes in the P2/c space group of the monoclinic system and gathers eleven Cu(I) ions, six ligands**1** and seven cyano ligands fragments (for the sake of simplicity of the description of the molecular structure of **2**, the assignment of the carbon and nitrogen atoms of the cyano ligands is arbitrary). Due to the symmetry elements associated with the P2/c space group, the asymmetric unit contains one half of the Cu_{11} assembly **2**, two BF_4^- anions and five disordered CH_2Cl_2 solvent molecules.

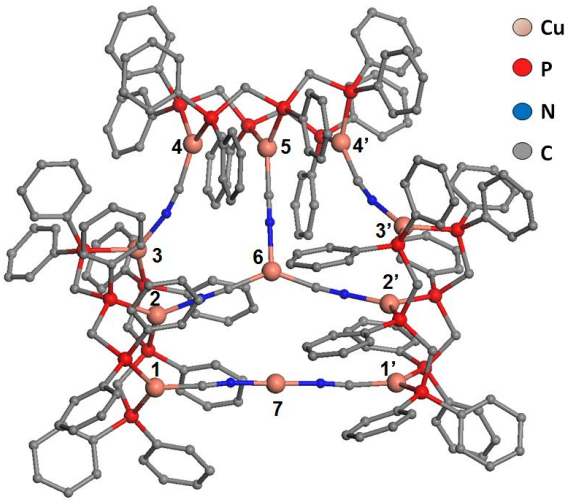


Figure 1. View of molecular X-ray structure of derivative **2**and labelling scheme of the Cu(I) atoms (counteranions, H atoms, solvent molecules have been omitted for clarity; location of the C and N atoms of the cyano ligands has been chosen arbitrarily).

Derivative **2** is based on a Cu_{10} metallacycle sub-unit(Figure 1) formed by the junction of three $[Cu_3(\mu\text{-dpmp})_2]$ fragments connected on the one hand, between the Cu(3) - Cu(4) and Cu(3') - Cu(4') atoms by a cyano ligand and on the other hand, between Cu(1) - Cu(1') atoms by a C≡N-Cu(7)-N≡C almost linear fragment (CN-Cu-NC angle, 179.4(2)°). In the central part of this Cu_{10} metallacycleis located a trigonal planar Cu(I) metal center (Cu(6), Figure 1) that is connected to the central metal centers of the three peripheral $[Cu_3(\mu\text{-dpmp})_2]$ fragments (namely, Cu(2), Cu(2') and Cu(5) atoms, Figure 1) via a bridging cyano ligand. As a result, a '$Cu_{11}(CN)_7$' inorganic core (Figure 2a) is formed that presents a slightly curved geometry (Figure 2b, maximum deviation from the mean plane defined by the '$Cu_{11}(CN)_7$' fragment = 1.050Å). Different types of Cu(I) ions coordination spheres are encountered in this structure: the copper ions of the $[Cu_3(\mu\text{-dpmp})_2]$ fragments and the Cu(6) ion located in the center of the metallacycle are distorted trigonal planar while the Cu(I) ion of the C≡N-Cu-N≡C fragment is linear with a CN-Cu-NC angle of 179.4(2)°.The metric parameters of this tetracationicmetallacycle **2**, including Cu-P (2,234 (2) - 2,275 (1) Å) and Cu- (CN) (1,854 - 1,983 Å) bond lengths, as well as Cu-(CN) angles (167.13 ° - 180.00 °), are in the orders of magnitude known in the literature for similar fragments.[7,10] The Cu-Cu intermetallic distances observed range between 3.010 and 3.212 (1) Å indicating that there is no metallophilic interaction between these metal centers. In addition, the distance observed between the Cu(7) metal center of the C≡N-Cu-N≡C fragment and the central Cu(6) ion is too large (4.609 Å) for an intramolecular cuprophilic interaction between these metal centers.Finally,derivatives**2** stack on the top of each other in the crystalline solid state along infinite columns (Figure 2c) that lie parallel to the *a*-axis of the unit cell, presumably due to the maximization of cumulative stabilizing CH-π interactions between most of the phenyl rings of the dpmp ligands **1**of neighboring assemblies. Interestingly, such intermolecular contacts affording infinite stacks of large cationic supramolecular are also observed within the single crystals of the derivatives $\mathbf{C_M}$ (Scheme 1) based on $[Cu_2(\mu\text{-dppm})_2]$ units.[7b] This suggests that such Cu(I) polymetallic units stabilized by aromatic

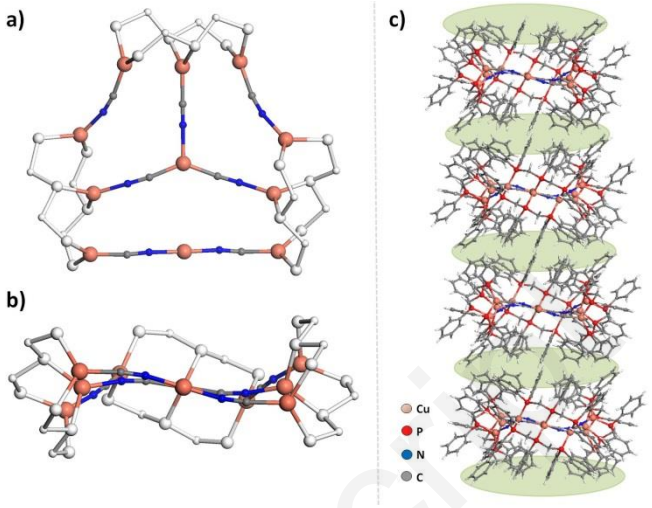


Figure 2.a) Top and b) lateral schematic views of the '$Cu_{11}(CN)_7$' inorganic core of the derivative **2**(counteranions, H atoms, solvent molecules and phenly rings of the ligands **1**have been omitted for clarity; location of the C and N atoms of the cyano ligands has been chosen arbitrarily); c) columnar solid state stacking of the derivative**2**, the green ellipses represent the intermolecular contact areas involving π-CH interactions (counteranions and solvent molecules have been omitted for clarity; location of the C and N atoms of the cyano ligands has been chosen arbitrarily)

polyphosphine can induce general structuration effects on the crystalline solid state of this family of supramolecular assemblies. Regarding that the first reaction we have performed was based on an incorrect stoichiometry considering the molecular formula of **2**, we reproduced the synthesis by using the right stoechiometry, as depicted in the scheme 2, allowing isolating **2** in a 86% yield as polycristalline powder. Interestingly, as the dpmp ligand **1** was reacted exclusively with CuCN, or as KCN is replaced by CuCN in the reaction of the scheme 2, the compound **2** is also selectively and reproducibly obtained in medium to good yields.

Regarding the large discrepancy observed between the targeted supramolecular structure**3** and the characterized molecular structure of **2** as well as the great structural complexity of **2** compared to the one expected in **3**, it is very likely that adaptative CDS processes[7b] are involved during these syntheses. As observed with the $[Cu_2(\mu\text{-dppm})_2]$ fragment along the syntheses of **A**, **B** and $\mathbf{C_M}$,[7] the $[Cu_3(\mu\text{-dpmp})_2]$ unit can display a large conformational flexibility that allows varying the intermetallic distances and the coordination bite angles without collapse of the structural integrity of this trinuclear building block. Indeed, considering the metric data observed in the solid state structure of **2** and those reported previously for the series of compounds based on the $[Cu_3(\mu\text{-X})_2(\mu\text{-dpmp})_2]^+$ (X = Cl, Br, I)units,[10] it can be seen for example that the intermetallic distance in the $[Cu_3(\mu\text{-dpmp})_2]$ units tolerates a remarkably large distribution, ranging from 2.7827(5) Å to 3.612(3) Å. Yet, conversely to the $[Cu_2(\mu\text{-dppm})_2]$ fragment in the scaffold of the metallacycle **A** in which the conformation of the peripheral bimetallic units allows the formation of a compact tetrametallic assembly bearing short intermetallic distances,[7a] a similar situation is not encountered for the $[Cu_3(\mu\text{-dpmp})_2]$ fragment in the structure of **2**. This forbids the formation of the targeted compact architecture **3** (Scheme 3). Instead, the higher nuclearity derivative **2** is selectively obtained in which larger

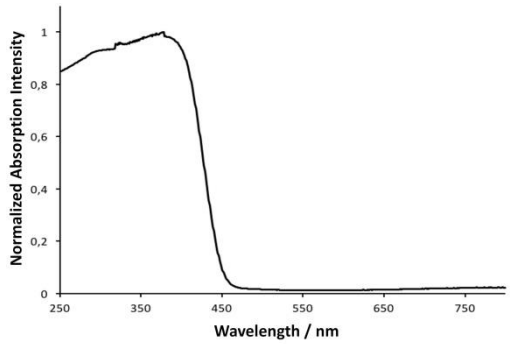


Figure 3. Solid-state room temperature absorption spectrum of the derivative **2**.

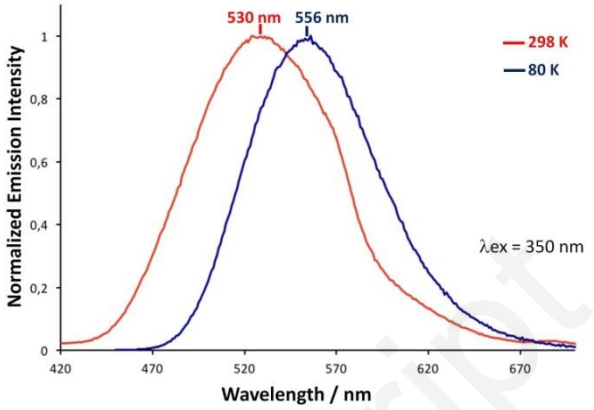


Figure 4. Solid state emission ~~absorption~~ spectrum of the derivative **2** at 80 K and at 298 K.

intermetallic distances and divergent coordination directions are observed at the $[Cu_3(\mu\text{-dpmp})_2]$ fragments. This is likely related to a higher level of flexibility of the tritopic ligand **1** compared to the ditopic dppm ligand. It results in the formation of the Cu_{11}metallacycle that is most probably endowed with a significant stabilization energy among all the possible scaffolds (including **3**) that can be obtained from reacting ligand **1**, Cu(I) ion and the cyano ligand.

These crystals are colorless under visible light but they display under UV irradiation (λ_{ex} = 365 nm) an eye-perceived green-yellow solid-state RT luminescence. The solid UV-visible absorption spectrum of the derivative **2** (Figure 3) presents a broad band centered at 377 nm, assigned to the π- π^* transitions of the aromatic moieties of the ligand **1**. No absorption is observed in the visible region of this spectrum which is in agreement with the white color of the polycrystalline powder recovered. At RT, under UV irradiation (λ_{ex} = 365 nm), the supramolecular derivative **2** in the solid state is emissive and display an eye-perceived greenish luminescence. As solid-state sample of **2** is cooled in liquid nitrogen, at the same excitation wavelength, an increase in the intensity of the emission is observed together with a change in the eye-perceived color of the emitted light is clearly observed, switching from greenish at RT to yellow at 80 K. When the sample is left to warm to room temperature, it gradually regains its initial eye-perceived greenish emission, which indicates that the compound **2** exhibits a reversible thermochromic luminescence behavior. The RT solid state emission spectrum recorded by excitation at 350 nm displays an intense broadband centered at 530 nm (Figure 4), associated with a moderate quantum yield of 9% and an average lifetime τ of 22 µs. At 80 K, its solid state emission spectrum exhibits a much more intense band (intensity is multiplied by 22) centered at 556 nm for an excitation wavelength of 350 nm (Figure 3b) characterizing the eye-perceived yellow emission observed when the compound **2**is cooled in liquid nitrogen under UV irradiation. The lifetime associated with this emission at 77 K is 268 µs and is therefore significantly longer (ca. 10-fold increase) that the lifetime measured at RT. Such a significant increase in the emission lifetime upon cooling in solid state luminescent Cu(I) systems has been previously reported for the thermally activated delayed fluorescence (TADF) Cu(I) complexes.[5,6] From these measurements, it is very tempting to affirm that the origin of the solid state emission properties of the Cu_{11} assembly **2** may be ascribed to TADF mechanism, although one cannot exclude the possibility that the increase in lifetime at low temperature is simply a result of the slowing down of nonradiative decay at low temperature. In addition, regarding the intricated molecular architecture of this derivative bearing symetrically different metal centers with different coordination spheres, coordination numbers and geometries, it is also questionable to firmly conclude about a single mechanism to explain the origin of this luminescence behaviour. Indeed, considering the complexity of the architecture and the diversity of the coordination sphere of the different Cu(I) ions embedded in the derivative **2**, temperature dependent competitive emissions arising from multiple species and site heterogeneity can indeed also occur, as it was suggested in the case of the study of the photophysical properties of the derivative **B** (scheme 1).[7b]

Yet, taking into account the large size of the derivative **2** and the large influence of the solid state packing on the geometry of this self-assembled structure in its ground state as well as in its potential re-organization in the excited states, it is unfortunately not possible to conduct full DFT geometry optimization of the excited states to get deep insights into the electronic origins of these different photophysical properties. Therefore, an extended investigation aimed to uncover the electronic processes occurring in the excited states upon UV-Vis excitation of the derivative **2**cannot be conducted in order to get deeper insights on itsphotophysical properties.

Conclusions

The tridentate dpmp ligand reveals to be an attractive ligand to allow the straightforward preparation of high nuclearity Cu(I) supramolecular assemblies. Adaptive CDS chemistry processes likely guide the reactions conducted between this ligand, Cu(I) ions and cyano ligand acting as linkers between the $[Cu_3(\mu\text{-dpmp})_2]$ fragments formed to afford the Cu_{11} derivative **2**. Despite, so far, the guiding rules allowing to explain, rationalize and anticipate the adaptive CDS formation of derivative **2** are still mostly to be established, the preparation of the Cu_{11} derivative **2** highlights the structural diversity of the supramolecular assemblies embedded with luminescence properties that can be selectively obtained. Similarly to the dppm ligand and its association with the Cu(I) ion, the tridentate dpmp ligand therefore appears to be an appealing assembling ligand to design pre-organized precursors to conduct adaptive CDS. Efforts will be performed in the next future to explore deeper the versatility of such systems in order to allow preparation of

innovative luminescent supramolecular assemblies, as well as in the identification of alternative precursors for adaptive CDS based on some other assembling polytopic ligands.

Experimental Section

General remarks

All experiments were performed under ambient atmosphere. Commercially available reagents ($[Cu(CH_3CN)_4].BF_4$, KCN, and CuCN) were obtained from Sigma-Aldrich and were used as received without further purification. The dpmp ligand was prepared as previously reported.[12] ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a BrukerDPX200,AM300, AV400 or AV500 spectrometers.^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and were decoupled from the proton. Elemental analyses were performed by the CRMPO, University of Rennes 1.FT-IR measurements have been performed on a Perkin Elmer Frontier spectrometer using UATR (state absorption measurements have been recorded on a Perkin-Elmer Lambda 650 spectrometer using a 60 mm integrating sphere. Spectra have been recorded between 800 nm and 200 nm, on pellets. The UV/Vis absorption spectra were recorded on a Perkin-Elmer Lambda 650 spectrometer (double beam). Steady-state emission spectra and luminescence quantum yield measurements at room temperature were recorded on a Horiba Universal Attenuated Total Reflectance) accessory. Spectra have been recorded between 650 cm^{-1} and 4000 cm^{-1}, on pure samples. UV-vis solid- Jobin-Yvon (HJY) Fluorolog-3 (FL3-2iHR550) fluorescence spectrofluorometer equipped with a IR R928P PMT / HJY FL-1073 detector and with an integrating sphere. Low temperature measurements were allowed by using a Optistat CF (*Oxford Inst.*) in the range of 77 K to 300 K. Excited-state lifetimes at 77 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.

Synthesis details

To a dichloromethane solution (10 ml) of bis(diphenylphosphinomethyl)phenylphosphine (dpmp) (0.04 g, 0.08 mmol) was added $[Cu(CH_3CN)_4].BF_4$ (0.04 g, 0.12 mmol). Then, the resulting clear solution was left upon stearing for one hour and this reaction solution was added to a methanol suspension (4 ml) of potassium cyanide (0.004 g, 0.06 mmol). This mixture was stirred overnight at room temperature along the appearance of a few amount of white precipitate. This crude solution was filtered over cotton and was after left upon pentane vapour diffusion for one week, affording after crystallization the complex **2** (0.022 g, 0.011mmol, 86 %) as an air-stable colorless solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 3.43 (m, 24H, PCH_2P), 7.05 (m, 150H, H_{arom}).^{31}P NMR (162 MHz, CD_2Cl_2): δ = -19.7 (bs), -15.9 (bs), -13.7 (bs), -12.2 ppm (bs). IR (ν(C≡N)): 2113, 2132, 2161 cm^{-1}.Elemental analysis, calcd. (%) for $C_{201}H_{178}Cu_{11}N_7P_{18}B_4F_{12}Cl_2$: C 56.27 H 4.18, N 2.29; found: C 55.83, H 4.16, N 1.82.

Crystallography data details

Single crystals of **2** suitable for X-ray crystal analyses were obtained by slow diffusion of vapors of pentane into crude mother solutions. Data collection was performed at 150 K with a D8 Venture Bruker AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-Kα radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the DENZO program of the Kappa CCD software package. The data merging process was performed using the SCALEPACK program.[13] Structure determinations were performed by direct methods with the solving program SIR97,[14] that revealed all the non-hydrogen atoms. SHELXL programs[15] 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 idealised positions and refined with isotropic displacement parameters. In the crystal lattice of derivative **2**, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and their counter-anions. These solvent molecules in most cases have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induce a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mounted at low temperature as quickly as possible on the diffractometer goniometer and X-ray data collection was performed at low temperature. The included dichloromethane solvent molecules and the BF_4^- counter anions were found to be highly disordered and a correct modelling of their disorder was not possible, leading to rather high anisotropic displacement parameters for some of their atoms. We have therefore proceeded to a 'squeeze' treatment[16] 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 A appears in the checkcif reports since " VERY LARGE Solvent Accessible VOIDs" are present in the structure resolution. Finally, due to the large size of the molecule and the number of different coordinated cyano ligands, the relative C/N occupancies of the atom sites of each cyano ligand were not ponderated in order to avoid over-parametrization and excessive refinement times. Therefore, the location of the C and N atoms is arbitrary. Table 1 gives the crystallographic data for the derivatives **2.** Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[17] CCDC reference number 1961054 contains the supplementary crystallographic data for the reference measurements of the X-ray crystal structures of the derivative**2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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

Molecular formula	$C_{199}H_{174}Cu_{11}N_7P_{18}$ *($C_{209}H_{186}B_4Cl_{20}Cu_{11}F_{16}N_7P_{18}$)*
CCDC number	1961054
Molecular weight	3919.85 (*5108.29)*
a[Å]	22.209(2)
b[Å]	18.738(1)
c[Å]	26.375(2)
α[°]	90
β[°]	99.947(2)

γ[°]	90
V[Å^3]	10811.0(14)
Z	2
ρ_{calcd} [Mg m^{-3}]	1.204*(1.569)*
crystal system	Monoclinic
space group	P2/c
T[K]	150(2)
Wavelength Mo-$K\alpha$ (Å)	0.71069
Crystal size [mm]	0.35 * 0.08 * 0.06
μ ($Mo_{K\alpha}$) [cm^{-1}]	1.238*(1.506)*
F(000)	4012*(5164)*
θ limit (°)	0.93 – 26.46
Index ranges *hkl*	-7 ≤ h ≤ 7, -9 ≤ k ≤ 8, -63 ≤ l ≤ 31
Reflections collected	54068
Independent reflections	22124
Reflections [I>2σ(I)]	11841
Data/restraints/ parameters	22124/ 0 / 1061 *(22124/ 0 / 1310)*
Goodness-of-fit on F^2	0.916*(1.006)*
Final R indices [I>2σ(I)]	R1= 0.0542*(0.0667)* ωR2= 0.1495*(0.1780)*
R indices (all data)	R1= 0.1041 *(0.1457)* ωR2= 0.1643*(0.2343)*
Largest diff peak and hole (e Å^{-3})	0.590*(1.724)* and -0.806*(-1.197)*

Acknowledgements

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Keywords: supramolecular assemblies • polymetallic complexes • Cu(I) • luminescent molecular materials • coordination chemistry

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[11] Note that the number of signals observed in the $^{31}P\{^{1}H\}$ NMR spectrum is also not in agreement with the multiplicity expected considering the X-ray solid state structure of the derivative **2**. Such discrepancy is assigned to the high conformational flexibility of these Cu(I) polymetallic supramolecular assemblies combined with their low-symmetry due to the non-planarity of the '$Cu_{11}(CN)_7$' metallacyclic unit. It results from this several diastereoisomers engaged in solution in dynamic exchange processes and having different NMR signatures. As a consequence of these intensive intramolecular exchanges, occurs in solution a large collection of conformers having different NMR signals that possibly overlap.

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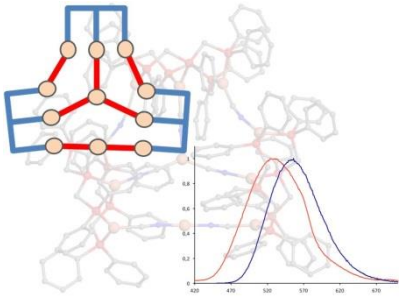
FULL PAPER

A solid-state luminescent Cu_{11} polymetallic assembly is obtained selectively accordingly to adaptive coordination-driven supramolecular association processes.



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Straightforward preparation of a solid-state luminescent Cu_{11} polymetallic assembly via adaptive coordination-driven supramolecular chemistry

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