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Coordination-Driven Hierarchical Organization of π-Conjugated Systems: From Molecular to Supramolecular π-Stacked Assemblies

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Abstract: The reaction of U-shaped, bimetallic, Cu^{I} complexes, assembled from a heteroditopic pincer, with cyano-capped π-conjugated linkers gives a straightforward access to π-stacked metallocyclophanes in good yields. In these assemblies, the π-walls have an almost face-to-face arrangement. The versatility of this rational supramolecular synthesis is demonstrated with the use of linkers that have nanoscale lengths (up to 27.7 Å), different chemical compositions (oligo(*para*-phenylenevinylene)s OPVs, oligo(phenylene)s, oligo(phenylethynylene)s), and alternative geometries (linear, angular). Linkers that incorporate an internal pyridyne moiety can also be employed. X-ray diffraction studies revealed that the metallocyclophanes based on linear linkers self-organize into infinite π-stacked columns in the solid state with intermolecular distances of about 3.6 Å. This approach, based on coordination-driven self-assembly, provides a novel and rational strategy for the stacking of extended π-systems in the solid state.

Keywords: coordination chemistry · conjugation · copper · phosphorus heterocycles · supramolecular chemistry

Introduction

In recent years, significant scientific interest combined with a major technological effort has been devoted to the use of π-conjugated systems as advanced materials for the development of new electronic devices (light-emitting diodes, field-effect transistors, photovoltaic cells, and so forth) with enhanced physical properties, low-energy consumption, and ease of manufacture in agreement with the development of a sustainable economy.[1] One of the most critical issues determining the performance of these types of device is the extent of long-range (micrometer regime) supramolecular organization of the π-conjugated components (oligomers and polymers)[1h,2] in the solid state, since intermolecular interactions alter physical properties of the bulk material.[3] For example, it is well established that long-range intermolecular π overlap between the conjugated systems increases the charge-carrier mobility,[4] a key property for the manufacture of efficient organic field effect transistors (OFETs). In order to tailor the supramolecular organization of π-conjugated systems, noncovalent, weak, secondary forces, such as π–π interactions,[5] hydrogen-bonding,[6] amphiphilic[7] or charge-transfer[8] interactions, and coordination bonds,[9] have been utilized. However, each of these different strategies necessitates sophisticated molecular engineering of the organic π systems and a case-by-case basis. Consequently, there is a considerable interest to devise fast, reliable, and general supramolecular approaches to obtain long-range π-stacking of conjugated systems. Within this area, the control of the hierarchical organization steps from an isolated molecule in solution to a π-stacked material remains a major challenge. Breaking this down, it is clear that the most basic element of this hierarchical process is the formation of π dimers. With this in mind, a fruitful molecular approach consists of investigating the local control of cofacial π–π interactions of two chromophores into well-defined covalent scaffolds such as [2,2]-paracyclophanes.[10] These derivatives have been the subject of unabated interest, since the synthesis of the parent molecule **A** (Figure 1) in 1949 and Cram's pioneering studies in the early 1950s.[11] Their structure consists of two π systems that are not directly connected, but are held parallel to one another in close proximity (ca. 3.1–3.4 Å). This structure is unique, since benzene, like other small conjugated π systems (naphthalene, thiophene, oligo-

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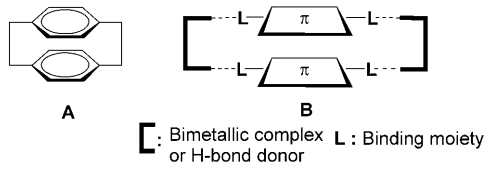


Figure 1. [2.2]Paracyclophane **A** and supramolecular analogues **B**.

(phenylenevinylene)s, etc.),[5a,12] prefers T-shaped edge-to-face or parallel-displaced interaction geometries in the solid state. Therefore, [2.2]-paracyclophanes are layered π-conjugated molecules par excellence.

After a long period of basic research devoted to the study of the intriguing interaction between the stacked π systems (three-dimensional aromaticity) and the resulting impact on their photophysical and chemical behavior,[13] [2.2]-paracyclophane-based derivatives have been gaining practical importance in numerous areas, such as materials science (precursors of insulating thin films[14] or semiconducting organic materials[15]), organometallic chemistry (ligand design),[16] supramolecular chemistry, and nano chemistry.[17] It is striking to note that methods of derivatization of the [2.2]-paracyclophane scaffold for these applications have almost exclusively involved the incorporation of lateral substituents on the benzene moieties of the parent compound **A** (Figure 1).[10,18] In this context, the development of a versatile and simple strategy to vary the π core of molecular [2.2]-paracyclophane derivatives and to readily generate a structural diversity by modifying the nature (length, constitution, topology, etc.) of their stacked π systems is of great interest.

It is hard to envisage the step-wise organic synthetic procedures that are readily accessible for the extensive diversification of the [2.2]-paracyclophane π core, since they are time- and yield-prohibitive and involve the need to overcome many synthetic challenges. An appealing alternative to classic synthetic methodologies for constructing complex molecules is the application of synthetic self-assembly.[9a,b,19] This powerful approach is based on the spontaneous assembly of rationally designed and preprogrammed individual building blocks into well-defined supramolecular architectures. Such a process involves noncovalent, kinetically labile, bond formation (hydrogen bonding, π–π interactions, metal–ligand coordination, etc.) such that, under proper synthetic conditions, the assemblages undergo self-sorting and self-correction processes until the individual building blocks congregate into the final target product. The retrosynthetic analysis for such a strategy is based on the overall shape of the desired assembly and the symmetry of the linking sites of the individual building blocks (directional-bonding approach).[20] In the last decades this powerful, rational approach has been used for the synthesis of a large variety of polygons by means of the assembly of organic multitopic π-conjugated linkers and metal centers.[21] It is important to note that, amongst the numerous supramolecular rectangles incorporating π-conjugated walls that have been reported, π-stacked [2.2]-paracyclophane analogues **B** (Figure 1, interplanar distance ca. 3.6 Å) are still rare (vide supra). Furthermore, no bimetallic molecular clip that allows a systematic variation of the length, structure, and geometry of the π linkers in order to create a structural diversity in π-stacked supramolecules **B** has been reported so far.

In this paper, we describe a general and versatile coordination-driven synthetic method for the preparation of π-stacked [2,2]-paracyclophane analogues **B** (Figure 1). This self-assembly strategy, based on unique, U-shaped, bimetallic Cu^{I}-complexes, allows an unprecedented structural variation of the π core with the incorporation of known conjugated π systems (oligo(*para*-phenylenevinylene)s OPVs[22] and oligo(phenylene)s,[23] oligo(phenylethynylene)s),[24] which are widely used for (opto)electronic applications. The versatility of this supramolecular synthetic method towards assemblies **B** relies not only on the ease of the π-core variation, but also on the modification of their length (varying from 2.7 to 22.6 Å)[25] and of their geometry (linear, angular). Moreover, it will be shown that the supramolecular assemblies **B** based on linear π connectors self-organize into infinite π-stacked columns in the solid state.[26] This coordination-driven long-range hierarchical organization of π-conjugated oligomers is unprecedented and its generality opens appealing perspectives for the design of advanced materials.

Results and Discussion

To build supramolecular analogues **B** of the [2.2]-paracyclophane **A**, two different synthetic approaches based on either the design of the π-conjugated walls (tailoring of L moieties, Figure 1) or of the metal/hydrogen-bond donor nodes have been reported. The first involves the modification of the π walls by heteroditopic chelating moieties (2-(phosphino)-ethoxy, 2-(phosphino)thioethoxy,[27] or oxamate)[28] in order to obtain linkers that will coordinate to metal centers to give assemblies of type **C** and **D** (Figure 2a). The second approach relies on the synthesis of bimetallic molecular clips programmed to assemble homoditopic π systems into supramolecules following the concepts of the "directional-bonding approach".[20a,b] According to this rational approach, the construction of metalloparacyclophanes **B** with π-stacked walls requires a molecular clip with a "U-shaped" geometry (two *cis* coordinatively labile sites) and a short intermetallic distance (ca. below 3.5 Å). Bimetallic complexes satisfying these criteria that have been used to construct π-stacked assemblies **B** and that have been characterized by X-ray diffraction study are scarce.

To the best of our knowledge, only the Re^{I} dimers **F** (assembled by hydroxo, alkoxo, or sulfide ligands),[29] the Zn^{II} dimer **G** (bridged by two μ-O atoms),[30] and the Ag^{I}- or Au^{I}-dimers **H** (based on diphosphine ligands),[31] afforded π-stacked supramolecular rectangles of type **B** (π–π distances, 3.6–3.7 Å) through the reaction with 4-pyridine-capped π systems (Figure 2b). Other peculiar examples affording "collapsed molecular rectangles" based on Re^{I} dimers

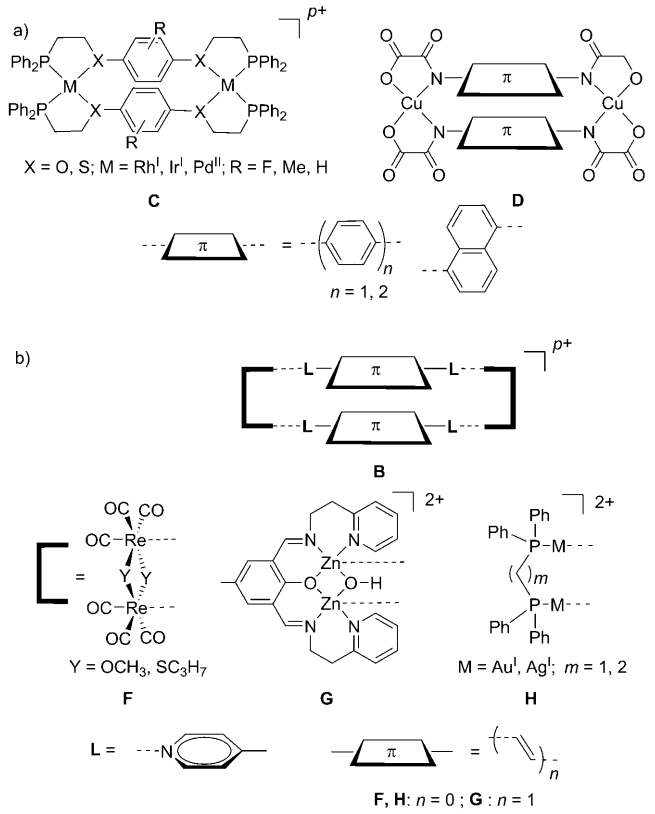


Figure 2. Synthesis of π-stacked supramolecular assemblies of type **B** using a) heteroditopic chelating moieties and b) U-shaped bimetallic molecular clips.

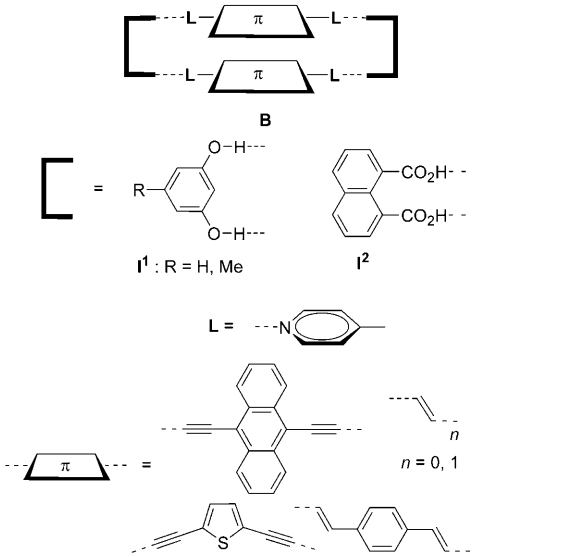


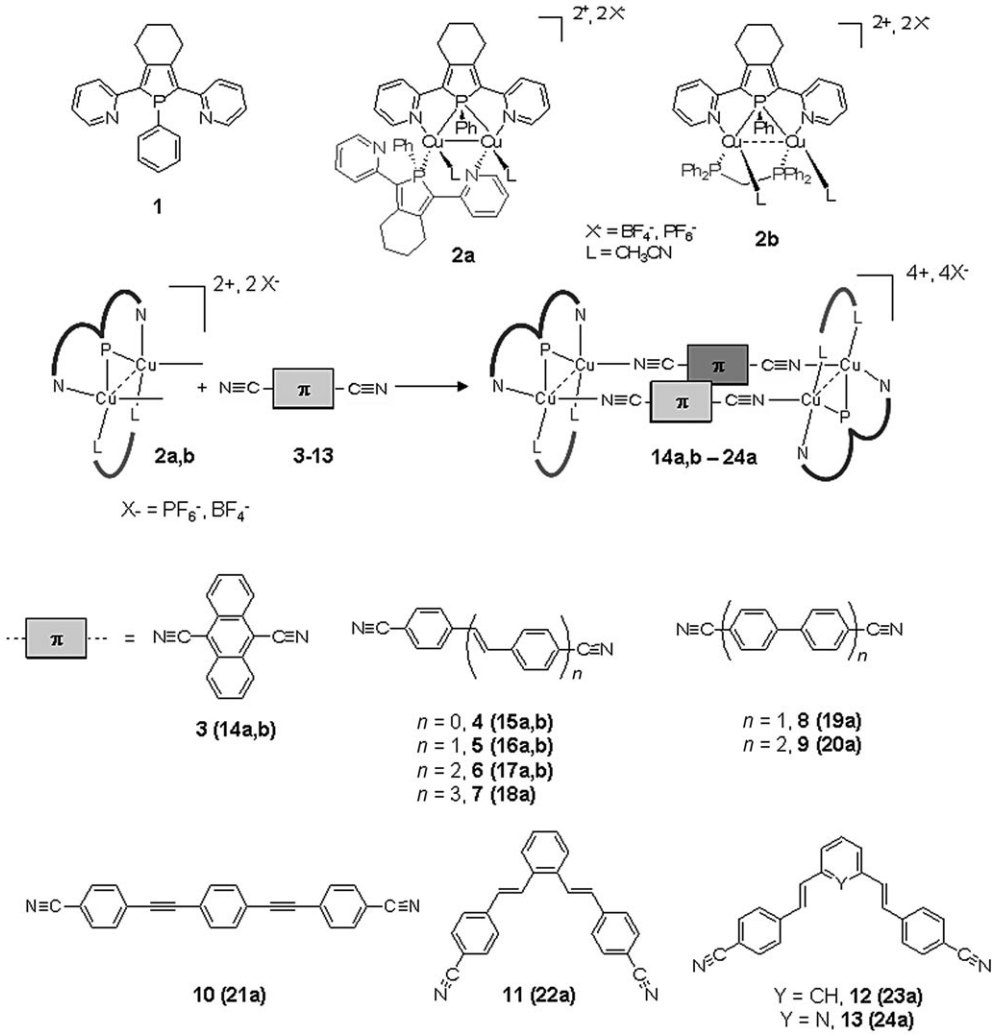
Figure 3. Synthesis of π-stacked supramolecular assemblies of type **B** by using hydrogen-bond donors.

bridged by bipyrimidine and bis-(benzimisazolate) ligands have also been structurally characterized.[32]

Only one approach towards architecture **B** based on hydrogen bonding has been investigated to date, with the co-crystallization of (4-pyridyl)-capped π-systems with resorcinol template $\mathbf{I^1}$ or 1,8-naphthalenedicarboxylic acid template $\mathbf{I^2}$ (Figure 3).[6g,33] The resulting assemblies are held together by four O−H···N hydrogen bonds and the π systems have a face-to-face arrangement (π–π distances, ca. 3.7–3.8 Å). It is worth noting that among all the supramolecular π-stacked assemblies **B** depicted in Figures 2 and 3, only the species based on hydrogen donor $\mathbf{I^1}$ and the anthracenyl or thienyl π linkers (Figure 3) aggregate into infinite π-stacked columns in the solid state.[33e]

These examples validate the use of the directional-bonding approach based on the design of programmed U-shaped clips for the synthesis of π-stacked [2.2]-paracyclophane analogues **B**. However, two important limitations have to be noted. Firstly, all the examples reported to date involve the use of 4-pyridyl moieties as coordination termini. The presence of this aromatic heterocycle influences the electronic properties (HOMO and LUMO levels) of the investigated π-conjugated systems, an effect that is even more pronounced upon coordination to metal centers in assemblies **B** (Figures 2 and 3).[20c] Secondly, the structural diversity in terms of chemical composition and geometry of the π systems that has been incorporated into assemblies **B** is rather limited (Figures 2 and 3).

Structure of the molecular Cu^I-clips 2a,b and synthesis of the homoditopic connectors 3–13: Bis(2-pyridyl)phosphole derivative **1**[34] (Scheme 1) has recently emerged as a useful assembling N,P,N-pincer for the stabilization of bimetallic complexes, including metals with different coordination geometries (Pd^I, Pt^I, Cu^I, Ag^I).[35,36] In these dimers, the P atom of **1** adopts either a semi- or a symmetrical-bridging coordination mode, something that is very rare for σ^3,λ^3-R_3P phosphorus donors.[37] Among these bimetallic complexes, Cu^I derivatives **2a**,**b**[35] (Scheme 1) possess two available "*cisoid*" coordination sites (occupied by kinetically labile acetonitrile ligands) and, as a consequence of the bridging phosphane coordination mode, short metal–metal distances (*d*(Cu-Cu); **2a**: 2.551(1) Å; **2b**: 2.667(1) Å). Thus, bimetallic Cu^I complexes **2a**,**b** possess a constrained U-shaped geometry and are therefore potential molecular clips for the coordination-driven self-assembly of ditopic π-conjugated systems into π-stacked metallocyclophanes **B** (Figure 1). It is worth noting that the intermetallic distances in complexes **2a**,**b** are markedly shorter than those of dimers **F**[29] (ca. 3.8 Å), **G**[30] (ca. 3.6 Å), and **H**[31] (3.15 Å), which have already been used to prepare supramolecules **B** (Figure 2). In addition, the metal–metal distances in dimers **2a**,**b** are expected to be fixed, since the Cu^I_2 cores are assembled both by a tri- (derivative **1**) and a bidentate (derivative **1** or 1,2-bis(diphenylphosphino)methane, abbreviated as dppm) ligands. These properties make derivatives **2a**,**b** appealing clip structures to enforce stacking of the π walls within assemblies of type **B**. Another key feature of these Cu^I dimers is that they are readily accessible on gram scales and that they are easy to handle due to their air-stability and good solubility in conventional polar solvents (CH_2Cl_2, THF…).



Scheme 1.

To build π-stacked metallocyclophanes of type **B** (Figure 1) using Cu^{I} dimers **2a,b**, cyano-capped organic connectors were selected since 1) the Cu^{I}–(N≡CR) bond is thermodynamically stable, but kinetically labile, two important properties for coordination-driven self-assembly synthesis, and 2) the presence of the cyano-termini is expected to perturb the electronic properties of the π-conjugated systems only to a lesser extent. Derivatives **3**, **4**, and **8** (Scheme 1) are commercially available and compounds **9**[38a] and **10**[38b] were prepared according to literature procedures. The novel homoditopic oligo(*para*-phenylenevinylene)s (OPVs) **5**–**7** and **11**–**12** (Scheme 1), as well as the pyridine derivative **13**, were readily obtained using classic synthetic routes involving Wadsworth–Emmons reactions (affording only all-*trans* isomers) between 4-cyanobenzaldehyde and diethyl phosphonic esters. All new compounds were characterized by multinuclear NMR spectroscopy and mass spectrometry. Note that the absorption maxima of derivative **6** ($\lambda_{abs}=299$ nm, $\log\varepsilon=2.9$, Scheme 1) recorded in CH_2Cl_2 ($c=1\times10^{-4}$ mol L^{-1}) is similar to that of the corresponding parent OPV ($\lambda_{abs}=297$ nm, $\log\varepsilon=3.1$),[39] confirming that the cyano-termini have little influence on the electronic properties of these π-conjugated systems.

The X-ray structure of cyano-capped OPVs **5** and **6** (see Experimental Section) were investigated in order to gain insight into their solid-state organization before coordination. The shorter compound **5** participates in π-stacked arrays (π-/π distances, ca. 3.5 Å) with a lateral displacement of approximately 3.1 Å (Figure 4a). Two adjacent π-stacked arrays develop along parallel axes with a herringbone arrangement. In contrast, the arrangement of the longer OPV derivative **6** is much more complicated. Four molecules of **6** have a laterally displaced (offset, ca. 1.5 Å) π-stacked arrangement (π–π distances, ca. 3.4 Å), and are surrounded by four molecules of **6** involved in CH···π interactions (CH···π distances, ca. 2.8 Å; Figure 4b). These solid-state structures illustrate, once again,[5a] that face-to-face π-stacking is not a favored arrangement and that π-conjugated compounds with the same structural motif, but different lengths (**5**, 9.4 Å; **6**, 16.0 Å),[25] can exhibit very different organization

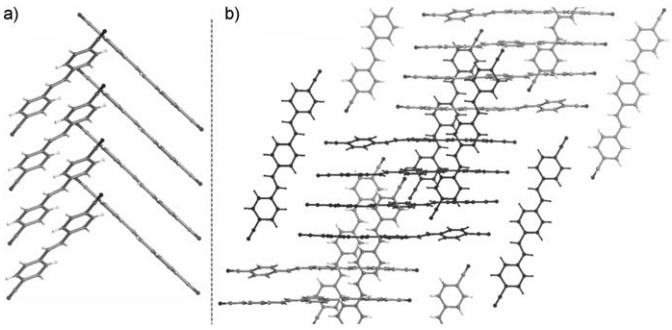


Figure 4. Solid-state organization of cyano-capped OPV **5** (a) and **6** (b).

in the solid state. This structure dependence, which is due to the maximization of dispersive and minimization of repulsive interactions, prevents a priori prediction the solid-state organization of these organic π systems from their molecular structures.

General synthetic strategy and solid-state structures of short (π-wall lengths <3 Å)[25] π-stacked metallocyclophanes: Complexes **2a**,**b** were first reacted in CH_2Cl_2 at 40 °C with anthracene-9,10-carbonitrile (**3**) and 1,4-dicyanobenzene (**4**, Scheme 1) in order to check their ability to act as molecular clips for the self-assembly of cyano-capped conjugated systems into π-stacked metallocyclophanes. The resulting assemblies **14a**,**b** and **15a**,**b** (Scheme 1) were isolated in good yields (ca. 60–70 %) upon crystallization from pentane diffusion into the reaction solutions. These supramolecular assemblies are isolated as air-stable powders that are soluble in common polar solvents (acetone, THF, CH_2Cl_2, etc.) except for derivative **14b**, which is poorly soluble in CH_2Cl_2. Elemental analyses support the proposed structures. The $^{31}P\{^1H\}$ NMR spectra of assemblies **14a**,**b** and **15a**,**b** (Table 1) display signals with chemical shifts and multiplicities that are similar to those of the corresponding free molecular clips **2a**,**b**.[35] These data indicate that the molecular structures of the Cu^I dimers featuring bridging P centers are maintained in the supramolecular assemblies. The room-temperature ^1H NMR spectra of derivatives **14a**,**b** and **15a**,**b** are fully consistent with their highly symmetrical structures and with the expected 1:1 (Cu_2)-clip/π-connector ratio. Interestingly, the ^1H NMR spectrum of derivative **14a** recorded at 213 K shows that the chemical shifts of the protons of the anthracene moieties are significantly shifted to lower frequency compared to those of the free linker **3** ($\Delta\delta =$ 1.8 ppm). In addition, the ^1H NMR signals the pyridine ligands of the Cu^I clips are displaced to higher frequency ($\Delta\delta = 0.3$–0.4 ppm). These coordination shifts, which are due to the cone effect arising from the presence of two anthracene moieties in derivative **14a**, are diagnostic of the presence of the metallacycle **14a** in solution and are fully consistent with π–π interaction between the two ditopic connectors within the targeted self-assembled metallocyclophanes.

The definite proof for the proposed structures was given by single X-ray diffraction studies. Single crystals of derivatives **14a**,**b** and **15a**,**b** were obtained at room temperature from pentane diffusion into solutions of the complexes in CH_2Cl_2 (see Experimental Section). All derivatives afforded homogeneous batches of crystals, which crystallize in the $P\bar{1}$ space group of the triclinic system. The asymmetric unit cells of **14a**,**b** and **15a**,**b** contain half a rectangle, two PF_6^- ions and various numbers of CH_2Cl_2 solvent molecules, the entire supramolecular assemblies being generated through an inversion center (Figure 5a). Derivatives **14a**,**b** and **15a**,**b** are metallacycles of type **B** (Figure 1) resulting from the coordination of the homoditopic connectors **3** and **4**, respectively, to the molecular clips **2a**,**b**, respectively All counterions and cocrystallized solvent molecules are located outside the self-assembled structures. Whatever the nature of the molecular clips, the four Cu^I centers of the supramolecular assemblies lie in the same plane defining a rectangle (Figure 5b). The metric parameters of the dicationic $Cu^I_2(\mathbf{1})_2$ and $Cu^I_2(\mathbf{1})$(dppm) cores of the metallacycles **14a**,**b** and **15a**,**b**,respectively, including the metal–metal and metal–μP distances or the directing (-C≡N)–Cu–Cu–(N≡C-) angles, are very similar to those of the corresponding molecular clips **2a**,**b** (Table 2). The Cu–cyano bond lengths are typical (1.98–2.09 Å), while the Cu–(N≡C-) angles vary from 165° to 180° (Figure 3b), revealing little steric stress within the metallacycles.

In all compounds, the benzene and anthracene moieties of the coordinated linkers are parallel as a result of hindered rotation (Figure 5). However, these two π walls exhibit different arrangements with respect to the plane defined by the Cu^I atoms. The angles between the benzene ring of linker **4** and the Cu_4 plane lie in the same range for both types of Cu^I clip (**15a**, 79.2°; **15b**, 79.6°, Figure 5c). In contrast, the corresponding angles associated with the anthracene moieties in assembly **14a** and **14b** based on $Cu^I_2(\mathbf{1})_2$ and $Cu^I_2(\mathbf{1})$(dppm) nodes, respectively, are markedly different (**14a**, 31.7°; **14b**, 81.4°; Figure 5c). In addition, the phosphole ligands have a different arrangement within the

Table 1. Selected $^{31}P\{^1H\}$ NMR data recorded in CH_2Cl_2 for molecular clips **2a**,**b**[35] and assemblies **14a**,**b**–**17a**,**b** and **18a**–**24a**.

Derivative	δ^{31}P [ppm] (^2J(P,P) [Hz])	Derivative	δ^{31}P [ppm] (^2J(P,P) [Hz])	Derivative	δ^{31}P [ppm] (^2J(P,P) [Hz])
2a	8.9 (brs)	**16a**	8.7 (brm)	**20a**	6.8 (brs)
2b	−1.6 (brs), 13.7 (brs, μ-P)	**16b**	−3.4 (d, 84), 12.8 (t, 84)	**21a**	7.9 (brs)
14a	3.2 (brs)	**17a**	8.7 (brs)	**22a**	7.8 (brs)
14b	−1.2 (brs), 14.5 (brs, μ-P)	**17b**	0.4 (d, 72.9), 16.5 (t, 72.9)	**23a**	7.7 (brs)
15a	7.2 (brm)	**18a**	7.5 (brs)	**24a**	7.5 (brs)
15b	3.2 (brs), 13.3 (t, 79.6, μ-P)	**19a**	8.9 (brs)		

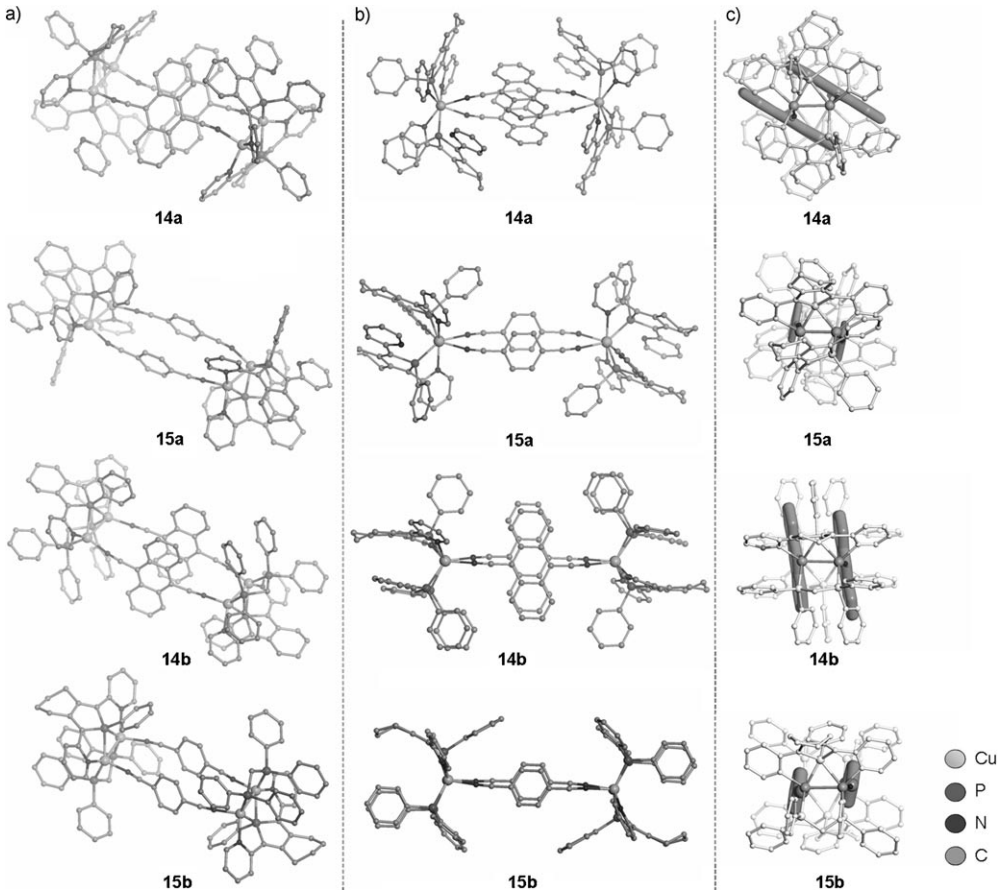


Figure 5. a) X-ray crystal structures of **14a**,**b** and **15a**,**b** (H atoms, counterions and solvents have been omitted for clarity). b) Views along the long sides of the Cu_4 rectangles. c) Views along the short sides of the Cu_4 rectangles.

two metallacycles **14a** and **15a** with anthracene- and benzene-based walls, respectively. As observed in the free molecular clip **2a**,[35] the P-phenyl substituents of the bridging P donors point towards the cyano ligands in assembly **15a**, whereas in assembly **14a** they point in the opposite direction (Figure 5a).

It is known that the bimetallic complex **2a** (Scheme 1) exhibits fluxional behavior in solution due to the hemilability of the N,P,N ligand **1** (intramolecular exchange between the pendant and coordinated pyridiyl groups resulting in interconversion of the P atoms),[35b,40] and it is very likely that this re-organization of the phosphole ligand within the $[Cu^{I}_2(\mathbf{1})_2]^{2+}$ cores during the supramolecular synthetic process is driven by steric strain minimization. It is therefore important to note that, compared to the other U-shaped bimetallic molecular clips **F**–**H** previously used (Figure 2), dimer **2a** exhibits different behavior since its $Cu^{I}_2(\mathbf{1})_2$ core can adapt its ligand conformation to satisfy the specific steric demand of the π-conjugated linkers, while keeping its rigid U-shaped topology (Figure 5). In spite of these different arrangements, all π walls of the connectors within the metallacycles **14a**,**b** and **15a**,**b** participate to π stacking (π–π distances: 3.4–3.5 Å). The lateral offset of the parallel π systems depends on the nature of the molecular clips. They are more pronounced for the $Cu^{I}_2(\mathbf{1})_2$ than for the $Cu^{I}_2(\mathbf{1})$(dppm) clips (Table 3), and in this latter case the π systems have a face-to-face arrangement (Figure 5b,c). Therefore, supramolecules **14a**,**b** and **15a**,**b** mimic the spatial organization that is encountered in the [2,2]-paracyclophane structure **A** (Figure 1). As anticipated from their U-shaped structure, molecular dimers **2a**,**b** are versatile molecular clips for the coordination-driven self-assembly of π-stacked metallocyclophanes upon reaction with linear ditopic chromophores. Thermodynamically disfavored face-to-face arrangements of symmetrical π-linkers can be obtained easily using these rigid bimetallic Cu^{I}_2 nodes.

Characterization of nanoscopic (π-wall lengths >3 Å)[25] π-stacked metallocyclophanes based on OPV-based ditopic connectors: To evaluate the connector size limit in the coordination-driven self-assembly process towards π-stacked metallocyclophanes **B**, we have investigated the use of oligophenylvinylene (OPV) linkers **5**–**7** with increasing lengths (Scheme 1). OPVs were selected since they are among the most widely investigated organic materials for optoelectronic applications (organic light emitting diodes, photovoltaic cells, etc.).[22] The reaction of molecular clips **2a**,**b** with derivatives **5** and **6** in CH_2Cl_2 at 40°C for 15 h afforded the

Table 2. Selected bond lengths [Å], angles [°] and torsion angle of the Cu_2(Nμ-PN) moieties of molecular clips **2a**,**b**[35] and supramolecular assemblies **14a**,**b**–**16a**,**b**[1,2] and **17a**–**24a**.

	Cu−μP	Cu−N	Cu−Cu	N-Cu-μP	Cu-μP-Cu	μP-Cu-Cu	Cu-NC-	CN-Cu-Cu-NC
2a	2.293(1)	2.048(4)	2.5552(8)	86.14(1)	66.15(4)	55.17(3)	1.980(4)	34.1
	2.386(1)	2.043(4)		82.85(1)		58.68(3)	2.042(4)	
2b	2.2898(8)	2.057(2)	2.6696(7)	85.80(7)	67.19(2)	60.56(2)	2.018(2)	5.7
	2.5221(8)	2.061(2)		82.78(7)		52.248(19)	2.014(3)	
14a	2.3118(13)	2.096(4)	2.5622(10)	81.10(11)	66.16(3)	58.23(4)	2.035(4)	36.0
	2.3815(13)	2.037(4)		84.46(11)		55.62(3)	2.042(4)	
14b	2.4655(12)	2.058(3)	2.7446(11)	82.31(9)	68.34(4)	55.05(3)	1.976(3)	10.5
	2.4206(11)	2.074(3)		80.74(9)		56.60(3)	1.979(3)	
15a	2.2935(10)	2.052(3)	2.6117(9)	84.24(9)	67.82(3)	57.77(3)	2.089(3)	28.0
	2.3858(11)	2.049(3)		84.44(9)		54.41(2)	1.998(3)	
15b[1]	2.3196(18)	2.058(6)	2.6851(14)	85.97(17)	67.87(5)	58.97(5)	2.005(6)	7.2
	2.4838(19)	2.057(5)		83.97(16)		53.16(5)	2.003(6)	
16a	2.3994(11)	2.077(3)	2.6294(6)	83.87(9)	68.21(3)	53.87(3)	1.997(3)	27.0
	2.2871(11)	2.061(3)		85.94(10)		57.92(3)	2.058(4)	
16b[1][a]	2.3725(19)	2.040(5)	2.6826(12)	84.02(16)	67.38(6)	57.89(5)	1.982(6)	18.5
	2.4615(19)	2.065(5)		81.42(15)		54.73(5)	1.976(6)	
	2.368(2)	2.062(6)	2.7228(13)	83.64(17)	68.60(6)	57.34(5)	1.975(6)	19.2
	2.462(2)	2.067(6)		81.02(17)		54.07(5)	1.969(6)	
16b[2][a]	2.339(5)	2.102(7)	2.740(5)	85.2(3)	68.28(18)	59.25(16)	2.001(8)	14.3
	2.535(7)	2.048(7)		79.8(2)		52.46(9)	1.991(8)	
	2.444(6)	2.081(8)	2.780(5)	82.4(3)	70.02(15)	54.28(16)	1.957(9)	16.0
	2.402(6)	2.052(8)		84.3(2)		55.70(11)	1.968(8)	
17a	2.440(3)	2.086(6)	2.661(2)	85.90(18)	67.99(8)	53.79(6)	2.028(6)	30.0
	2.315(3)	2.117(7)		85.9(2)		58.22(8)	2.058(6)	
18a	2.2987(16)	2.040(4)	2.6019(12)	83.99(11)	67.33(5)	54.60(4)	2.002(4)	28.7
	2.3932(14)	2.070(4)		85.93(15)		58.07(4)	2.040(5)	
19a	2.347(2)	2.036(6)	2.5659(13)	85.3(2)	67.17(6)	55.39(5)	1.921(8)	33.3
	2.291(2)	2.034(7)		85.32(19)		57.44(6)	2.065(8)	
20a[b]	2.3659(19)	2.032(6)	2.5947(12)	85.06(15)	67.44(6)	55.21(5)	1.978(6)	30.6
	2.307(2)	2.029(6)		85.32(18)		57.36(5)	2.055(6)	
	2.4045(19)	2.069(6)	2.6100(12)	84.38(15)	67.64(6)	53.93(5)	1.961(6)	30.2
	2.281(2)	2.057(6)		84.13(17)		58.43(5)	2.024(6)	
21a	2.3128(13)	2.050(4)	2.5736(9)	84.95(11)	66.45(3)	58.09(4)	2.035(4)	28.7
	2.3831(13)	2.056(4)		83.53(11)		55.47(3)	2.004(4)	
22a[a]	2.328(2)	2.075(6)	2.6131(12)	85.37(19)	67.91(5)	56.45(5)	2.075(6)	35.6
	2.3502(19)	1.985(6)		85.86(17)		55.64(5)	2.041(6)	
	2.403(2)	2.031(6)	2.6121(14)	84.26(18)	67.74(6)	53.91(5)	1.983(5)	33.8
	2.2809(19)	2.071(7)		85.71(18)		58.35(6)	2.069(6)	
23a	2.3578(17)	2.042(4)	2.5820(9)	84.50(15)	67.27(4)	55.35(3)	1.984(5)	26.0
	2.3028(13)	2.023(5)		83.83(11)		57.38(4)	2.023(5)	
24a	2.2745(17)	2.064(6)	2.5539(11)	85.03(14)	67.08(6)	57.81(6)	1.967(7)	30.1
	2.347(2)	2.036(5)		83.40(19)		55.11(4)	1.947(8)	

[a] Non-centrosymmetric supramolecular assemblies. [b] Two independent supramolecular rectangles are present in the unit cell.

novel derivatives **16a**,**b** and **17a**,**b**, respectively (Scheme 1). These compounds were isolated as air-stable powders following filtration of the crude reaction mixture and crystallization by pentane diffusion into solutions of the complexes in CH_2Cl_2 (60–70% yields). Elemental analyses and multinuclear NMR spectroscopy are in accordance with the proposed structures and single crystals suitable for X-ray diffraction studies (see Experimental Section) were obtained for compounds **16a**,**b**[1,2] (crystallization of assembly **16b** afforded crystals of two isomers, namely **16b**[1] and **16b**[2]) and **17a**.

As observed for supramolecular assemblies **14a,b** and **15a,b**, these compounds have a general structure of type **B** that mimics the [2,2]-paracyclophane skeleton (Figure 6a), except **16b**[2] in which the four Cu^I atoms are not in the same plane (Cu-Cu-Cu-Cu dihedral angle, 73.4°; Figure 6b). It is interesting to note that the metallacyclophanes **16a** and **17a** featuring the $Cu^I_2(\mathbf{1})_2$ moieties are obtained as single diastereoisomers. Their μ-P atoms have a mutual *anti*-position with respect to the metallacycles with the P-phenyl substituents pointing towards the cyano-ligands (Figure 6b, derivatives **16a** and **17a**), an arrangement already observed in rectangle **15a** based on 1,4-dicyanobenzene linker (vide supra, Figure 5). In contrast, assembly **16b** based on the molecular clip **2b** is obtained as a mixture of diastereoisomers in the solid state: one centrosymmetric rectangle and one non-centrosymmetric twisted-ribbon in which the two μ-P centers adopt either an *anti*- (**16b**[1], Figure 6) or *syn*-arrangement (**16b**[2], Figure 6) with respect to the metallacycle.

These results clearly show that $[Cu^I_2(\mathbf{1})_2]^{2+}$ dimer **2a** is more attractive than $[Cu^I_2(\mathbf{1})(dppm)]^{2+}$ **2b** as a molecular clip for the synthesis of metallacyclophanes, since it affords

Table 3. Selected lengths [Å] and angles [°] of the supramolecular assemblies **14a**,**b**–**16a**,**b**[1,2] and **17a**–**24a**.

	Cu–Cu long distance [Å]	Overall length [Å]	Angle between the mean planes of the π walls and the Cu^{I}_{4} rectangle [°]	Lateral offsets of π walls [Å]	Intramolecular π–π distance [Å]	Intermolecular π–π distance [Å]
14a	11.7	24.4	31.7	1.8	3.4	–
14b	11.8	26.0	81.4	0.5	3.4	–
15a	11.8	25.3	79.2	1.4	3.4	–
15b	11.8	25.5	79.6	0.4	3.5	–
16a	18.3	32.3	49.3	1.3	3.3	3.5
16b[1][a]	18.1 18.2	31.0	87.2	1.1	3.4	3.8
16b[2][a]	18.2 18.3	32.7	–	1.4	3.3	3.4
17a	25.2	39.3	47.1	1.4–2.0[d]	3.4	3.2
18a	31.5	46.5	58.0	1.3–2.2[d]	3.4	3.1
19a[b]	15.5 15.7	29.7	–	0.9	3.7	–
20a[c]	24.4 24.4	39.6 39.5	69.6 57.3	0.5	3.4	3.5
21a	25.4	38.7	42.1	1.2	3.4	3.3
22a[a]	14.9 16.5	28.2	–	2.3	3.4	2.9
23a	20.0	33.8	–	2.5	3.7	–
24a	19.9	33.6	–	2.5	3.6	–

[a] These supramolecular assemblies are non-centrosymmetric. [b] Twisted-ribbon geometry. [c] Two independent supramolecular rectangles in the unit cell. [d] Several configurations of the π-systems are observed in the solid state for these assemblies.

these target supramolecules as single diastereoisomers. The fluxional coordination behavior (hemilability) of the heterotopic ligand **1**[35b,40] is very probably a key to this stereoselective supramolecular synthesis. It is very striking that the four metallacyclophanes **14a**–**17a** based on the $Cu^{I}_{2}(\mathbf{1})_2$ core are centrosymmetric diastereomers in spite of the fact that the $Cu^{I}_{2}(\mathbf{1})_2$ moieties themselves are non-symmetric, featuring one P,N-chelate (Figure 5 and Figure 6). This result shows that the centrosymmetric assemblies are very probably the most energetically favored arrangement amongst the numerous possible diastereomers. This high selectivity is a major advantage both for characterization purposes and for development of new materials for optoelectronic applications. Therefore, only the molecular clip **2a** was used in the following self-assembly experiments.

To determine whether there is a size limit for the OPV-based homoditopic connectors in this self-assembly synthesis, dimer **2a** was treated for 15 h in CH_2Cl_2 at 40° with the poorly soluble OPV-linker **7** (Scheme 1). The resulting clear red-orange solution shows a $^{31}P\{^{1}H\}$ NMR spectrum with a broad signal at a chemical shift that compares well with those of assemblies **14a**–**17a** (Table 1). Diffusion of pentane into the crude reaction solution gave a homogeneous batch of small red monocrystals (yield, 20%) that were submitted to X-ray diffraction analyses (see Experimental Section). Derivative **18a** is a supramolecular rectangle (Figure 6b) with a structure similar to that of the assemblies **16a** and **17a** (Figure 6). Note that the $Cu^{I}_{2}(\mathbf{1})_2$ moieties within supramolecule **18a** have the conformation found in **15a**–**17a** (vide infra), confirming that with clip **2a** the assembly process is highly stereoselective. To the best of our knowledge, **18a** is the longest supramolecular rectangle described to date, with an intermetallic long distance of 31.5 Å and a maximum overall dimension of 46.6 Å.

The solid-state characterization of derivatives **16a**–**18a** gives the unique opportunity to compare the organization within metallocyclophanes of OPV-based π walls with lengths varying from 9.4 to 22.6 Å.[25] In all cases, including the giant derivatives **17a** and **18a**, the π walls are parallel with short intramolecular distances (ca. 3.5 Å, Table 3) indicating that they are forced to participate in π–π interactions upon their integration into these supramolecular metallocyclophanes (Figure 6). Furthermore, in these nanosize assemblies, the π walls have an almost a face-to-face arrangement (Figure 6b, Table 3). These results highlight that Cu^{I} dimer **2a** is a versatile molecular clip for the construction of ditopic OPV oligomers within supramolecular π-stacked assemblies having a [2,2]-paracyclophane geometry. They also demonstrate the simplicity and power of coordination-driven supramolecular synthesis to prepare [2,2]-paracyclophane analogues with unprecedented nanosize lengths.

Variation of the chemical composition and geometry of the ditopic connectors: To check the scope of this synthetic approach for the generation of structurally diverse π-stacked paracyclophanes, π-conjugated linkers with chemical compositions or geometries other than linear OPVs were investigated. The π systems that have been selected, namely oligo(phenylene)s and oligo(phenylethynylene)s, are widely investigated and useful building blocks for the tailoring of semiconducting organic materials.[23,24] The molecular clip **2a** was reacted at 40 °C in CH_2Cl_2 with the cyano-capped oligophenyl linkers **8** and **9** and with the phenylethynyl-based connector **10** affording clear red-orange solution of assemblies **19a**, **20a**, and **21a**, respectively (Scheme 1). They exhibit solution-state $^{31}P\{^{1}H\}$ NMR signals similar to those recorded for derivatives **14a**–**18a** (Table 3). Red, single crystals suitable for X-ray diffraction studies (see Experimental Section) were grown upon pentane diffusion into CH_2Cl_2 solutions (yields: **19a**, 65%; **20a**, 69%; **21a**, 67%). X-ray structure resolutions revealed that these novel assemblies are π-stacked metallocyclophanes (Figure 7) with a general structure of type **B**. Compounds **20a** and **21a** are centrosymmetric rectangles with the four Cu atoms lying within the same plane (Table 3), whereas the non-centrosymmetric de-

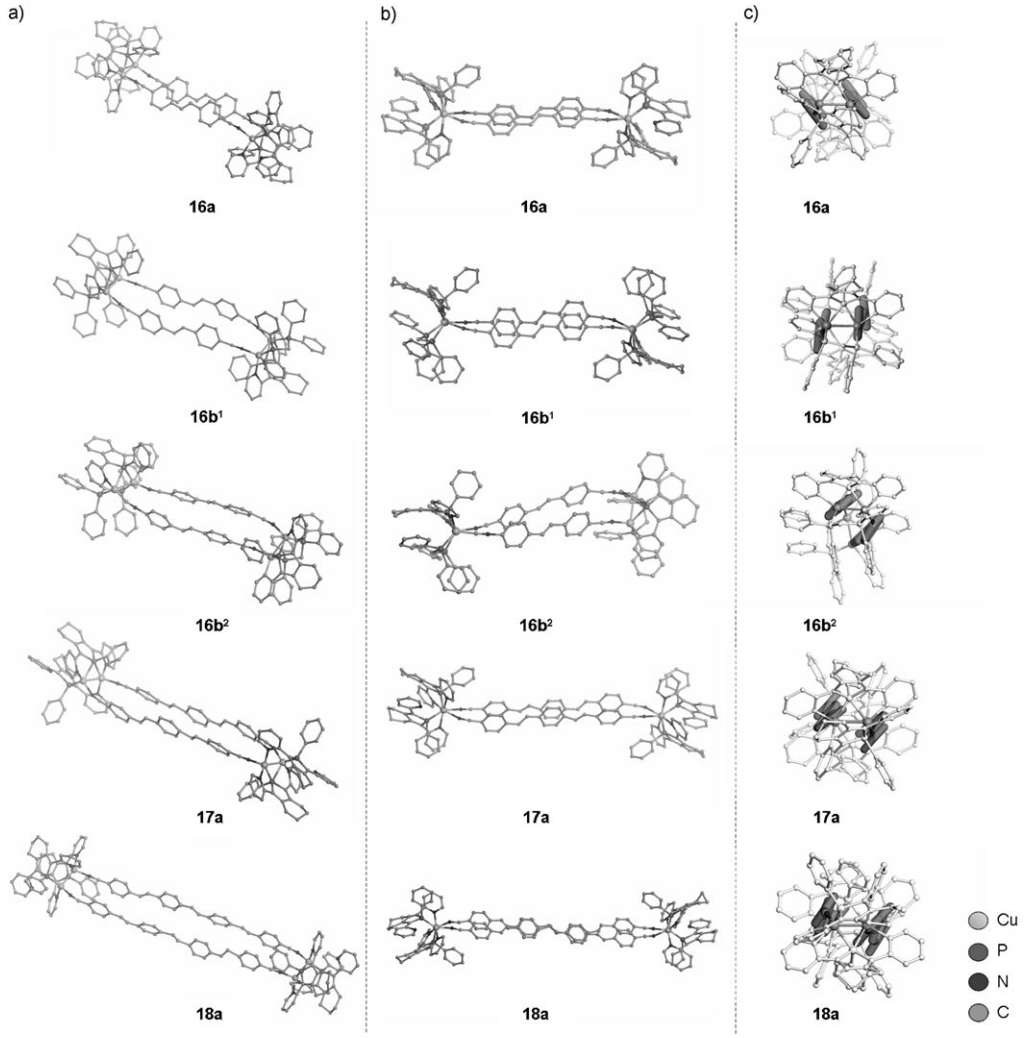


Figure 6. a) X-ray crystal structures of **16a**,**b**[1,2], **17a** and **18a** (H atoms, counterions and solvents have been omitted for clarity); for **16b**[2], **17a** and **18a** the conformational disorder of the connector is not shown, see Supporting Information. b) Views along the long sides of the Cu_4 quadrangle. c) Views along the short sides of the Cu_4 quadrangle.

rivative **19a** incorporating biphenyl-based linker **8** exhibits a "twisted ribbon" geometry as a result of the twist angles (32°–40°) around the central C–C bond of **8** (Figure 7b). Consequently, the axes of the two μ-P bridged Cu^I–Cu^I dimers are not parallel and exhibit a torsion angle of 53.9°. This twisted ribbon geometry is not observed in the longer supramolecular assembly **20a** (Figure 7b). Whatever the geometry of the assemblies **19a**–**21a**, their oligo(phenyl) and oligo(phenylethylene)-based π-conjugated walls have an almost face-to-face arrangement (Figure 7; lateral offset: **19a**, 0.9; **20a**, 0.5; **21a**, 1.2 Å) with short intramolecular contacts (<3.7 Å, Table 3) revealing π–π interactions. To the best of our knowledge, this is the first example of π-stacked derivatives of type **B** incorporating tetraphenyl (**20a**) and 1,4-(bisphenylethynyl)benzene (**21a**) walls. It is interesting to note that the stereochemistry of the $Cu^I_2(\mathbf{1})_2$ moieties in **19a**–**21a** is the same as that observed in the series **15a**–**18a**, showing that molecular clip **2a** the assembly process remains stereoselective whatever the chemical composition and the length of the ditopic π connectors.

The next step to estimate the versatility of our coordination-driven synthetic approach towards π-stacked metallocyclophanes **B** was to use angular π-ditopic linkers. To date, only the angular pyridyl-caped π-conjugated homoditopic connectors **J**[33e] and **K**[41] (coordination directional angles around 130°, Figure 8) have been reacted with the U-shaped molecular clips $\mathbf{I}^1$ (Figure 3) and the Pt^{II} dimer **L** (Figure 8), respectively, affording supramolecular metallacycles. Note that due to its long Pt–Pt distance (ca. 6.4 Å), dimer **L** cannot force the homoditopic connectors **K** to participate in π–π interactions and the π walls lie in the plane defined by the four Pt centers.[41] Following our investigation of linear OPV-based linkers, the angular connectors **11** and **12** with a 1,2- and a 1,3-distyrylbenzene core, respectively, were investigated (Scheme 1). It should be underlined that the use of connectors **11** and **12** to construct metallocyclophanes by

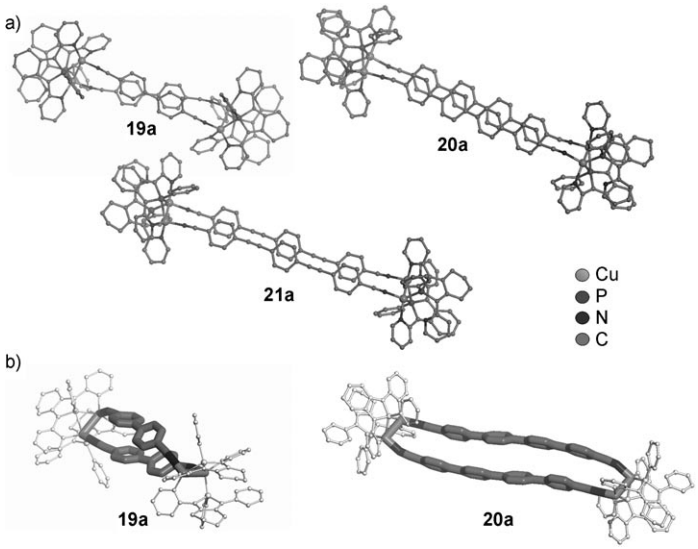


Figure 7. a) X-ray crystal structures of derivatives **19a**, **20a** (only one of the two crystallographically independent molecules of the asymmetric unit is shown) and **21a** (H atoms, counterions and solvents have been omitted for clarity). b) View showing the geometry of derivatives **19a** and **20a**.

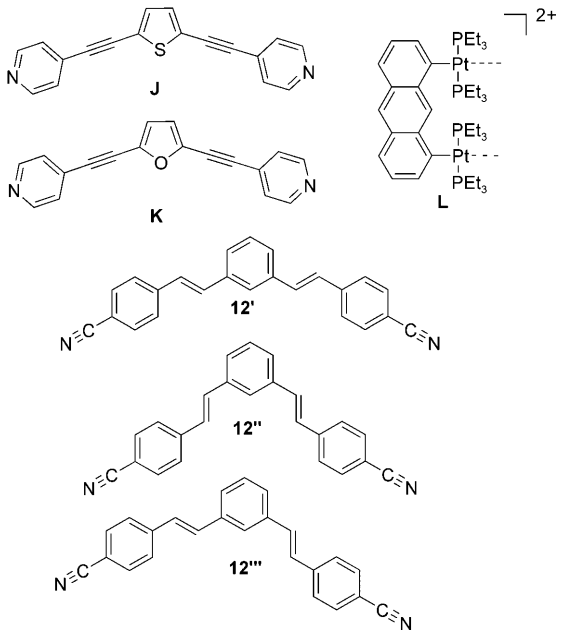


Figure 8. Chemical structure of the angular connectors **J** and **K** and of the Pt^{II} molecular clip **L**; view of three possible conformations of the angular linker **12**.

self-assembly is quite challenging since, compared to rigid linkers **J** and **K** (Figure 8), 1) their coordination directional angles are more acute (< 120°) and 2) their structure is flexible as a consequence of the possible *cisoid*/*transoid* conformation of their central core (see Figure 8 for the angular linker **12**). This structural flexibility is, a priori, a major drawback according to the principle of the directionnal bonding approach,[20] which request the use of rigid connectors.

According to the general procedure used with linear linkers, derivatives **11** and **12** were reacted with the molecular clip **2a** at 40 °C for 15 h in CH_2Cl_2 (Scheme 1), and pentane was allowed to diffuse into these solutions. This workup afforded homogenous batches of single-crystals of derivatives **22a** and **23a** (Scheme 1) suitable for X-ray diffraction studies (see Experimental Section) (yield: **22a**, 62%; **23a**, 56%). The crystals selected for the X-ray crystal structure determinations were typical of the bulk and there was no indication of polymorphism. Derivatives **22a** and **23a** are noncentrosymmetric, supramolecular metallacycles resulting from the coordination of two angular linkers to two molecular clips **2a** (Figure 9). In contrast to what is observed with

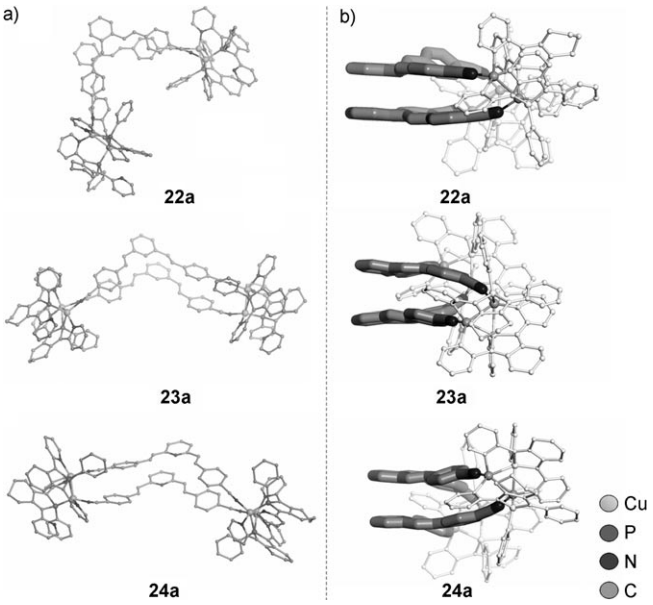


Figure 9. a) X-ray crystal structures of **22a**–**24a** (H atoms, counterions and solvents have been omitted for clarity. b) Views along the short sides of the Cu_4 quadrangles.

linear OPV-based ditopic linkers (Figure 6), the Cu atoms of derivatives **22a** and **23a** are not in the same plane (dihedral angles between the two Cu^{I}_2 axes: **22a**, 72.8°; **23a**, 65.0°; Figure 9). The two π linkers are located on the same side of the Cu_4 surface (Figure 9), and participate in π–π interactions as indicated by the short interplane distances (**22a**, ca. 3.3; **23a**, 3.6 Å, Table 3) with a "parallel displaced" arrangement (lateral offset, **22a**, 2.3; **23a**, 2.5 Å, Table 3, Figure 9b). The coordination directional angles of the ditopic linkers are very acute (**22a**, 75.7–79.4; **23a**, 104.0°; Figure 9) affording these π-stacked supramolecular [2.2]-paracyclophanes **22a** and **23a** with an unprecedented topology.

A general limitation of coordination-driven supramolecular synthesis is that the use of functional linkers is prohibited due to potential reactivity towards the metallic clips.[20] To check this point in our approach for the formation of π-

stacked [2,2]-paracyclophane analogues, the angular linker **13** with the geometry of connector **12** and bearing a central pyridine moiety (Scheme 1) was selected. The reaction of **13** with Cu^{I}-dimer **2a**, according to the general synthetic procedure used to prepare assembly **23a**, gave rise to derivative **24a** (75% yield, Scheme 1), which was characterized by an X-ray diffraction study (see Experimental Section). Assembly **24a** is a π-stacked metallocyclophane that is isostructural to derivative **23a** based on the non-functional linker **12** (Figure 9). The N atoms of the inner pyridine rings are uncoordinated and point in the same direction with an N···N distance of about 3.96 Å.

The coordination-driven synthesis of π-stacked assemblies **B** with very different structures in terms of chemical composition, length and geometry of the π walls clearly demonstrate that Cu^{I} dimer **2a** is a powerful and unique U-shaped molecular clip. These large architectures are spontaneously generated in good yields simply by mixing their component building blocks in solution at room temperature. This simple and rational supramolecular approach towards [2,2]-paracyclophane analogues **B** appears to be general as illustrated with the preparation of striking giant (Figure 6) and banana-shaped (Figure 9) derivatives that have no precedent in the literature.

[2,2]Metalloparacyclophane stacking pattern in the solid state: Assemblies **B** (Figure 1) can be regarded as the first hierarchical suprastructures towards the self-organization of π systems into long-range π-stacked columns, a solid-state packing that is of interest for molecular electronic. It is important to recall that such packing based on cyclophane subunits **B** has only one precedent in the literature (assemblies incorporating hydrogen donors **I**,[1] Figure 3)[33e] and has never been observed with metallocyclophanes **B**.

The supramolecular metallacycles built on "short" linear π-conjugated linkers **3**, **4**, and **8** (Scheme 1) do not exhibit intermolecular π interaction in the crystalline solid state. As illustrated with derivative **15a** (Figure 10), counterions (PF_6^-) and CH_2Cl_2 solvent molecules are located between the tetracationic supramolecular rectangle **15a** preventing any intermolecular interactions between the coordinated π walls to take place. Remarkably, on increasing the length of the linear OPV-based linkers (**4**→**5**–**7**, Scheme 1), the π-stacked metallocyclophanes self-organize in the solid state into infinite columns, with a parallel displaced arrangement (**16a**, **16b**[1,2], **17a**, **18a**; Figure 11). The lateral offset within the columns depends on the nature of the Cu^{I}-clip (**16a** (clip **2a**) versus **16b** (clip **2b**), Figure 11). However, in all cases, the short intermolecular distances (ca. 3.1–3.5 Å, Table 3) between the π walls of two neighboring supramolecules reveals intermolecular π–π interactions. Dispersion forces probably drive the unexpected formation of these metallocyclophane columnar π stacks, since they are observed for derivatives having extended π-conjugated walls only. Note that the presence of the Cu^{I} clips plays a major role in this supramolecular π-stacked organization, since the free cyano-capped linkers do not systematical exhibit this type of supramolecular arrangement in the solid state (Figure 4). The key role played by the Cu^{I} clips is further demonstrated by the fact that infinite π-stacked columns are also observed with the linear linkers **9** and **10** based on tetraphenyl and phenylethynylene moieties, respectively (**20a** and **21a**, Figure 9). It is particularly striking that despite using π-conjugated linkers with quite different chemical composition (OPV, oligo(phenyl), oligo(phenylethynylene)), the same general hierarchical organization is observed upon reaction with the Cu^{I}_2-clips **2a**,**b**: first a local face-to-face organization of two π systems within a metallocyclophane, then an infinite "parallel-displaced supramolecular arrangement" of these self-assembled structures in one direction. This supramolecular self-organization of π-conjugated oligomers in the solid state, although discovered by serendipity, seems to have a general and predictable character. Note that for all derivatives, the infinite π-stacked columns are parallel (see Figure 12a–c for derivatives **17a**, **18a**, and **20a**, and Supporting Information for the other derivatives). This arrangement generates channels that are filled by disordered CH_2Cl_2 solvent molecules, located in the vicinity of the π-conjugated linkers, and the PF_6^- or BF_4^-counterions that stand close to the dicationic Cu^{I}_2 clips (Figure 12d for derivative **17a** and Supporting Information for the other derivatives).

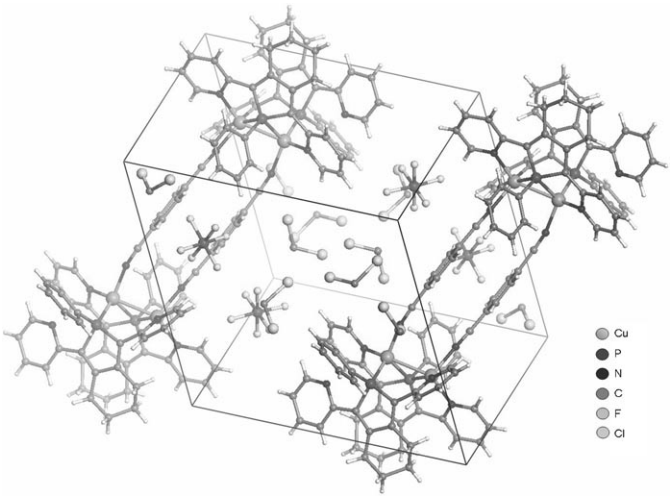


Figure 10. View of the unit cell for derivative **15a**; proton atoms of the CH_2Cl_2 solvent molecules have been removed for clarity.

In contrast, none of the derivatives **22a**–**24a** based on the angular connectors **11**–**13**, respectively (Scheme 1), form infinite networks of intermolecular π–π interacting molecules. In the solid state, the supramolecular assembly **22a** aggregates into dimers that exhibit parallel displaced π–π interactions (intermolecular distances, ca. 3.0 Å) providing an example of a solid-state discrete stack of four aromatic molecules (Figure 13a).[42] In this case, a PF_6^- counterion is located in the concave cavity formed by the assembled angular connectors **11** (Figure 13b). The isostructural derivatives **23a** and **24a** are isolated supramolecules in the solid-state with no intermolecular π contacts (shortest intermolecular distances between π walls, ca. 10 Å, Figure 14). Therefore,

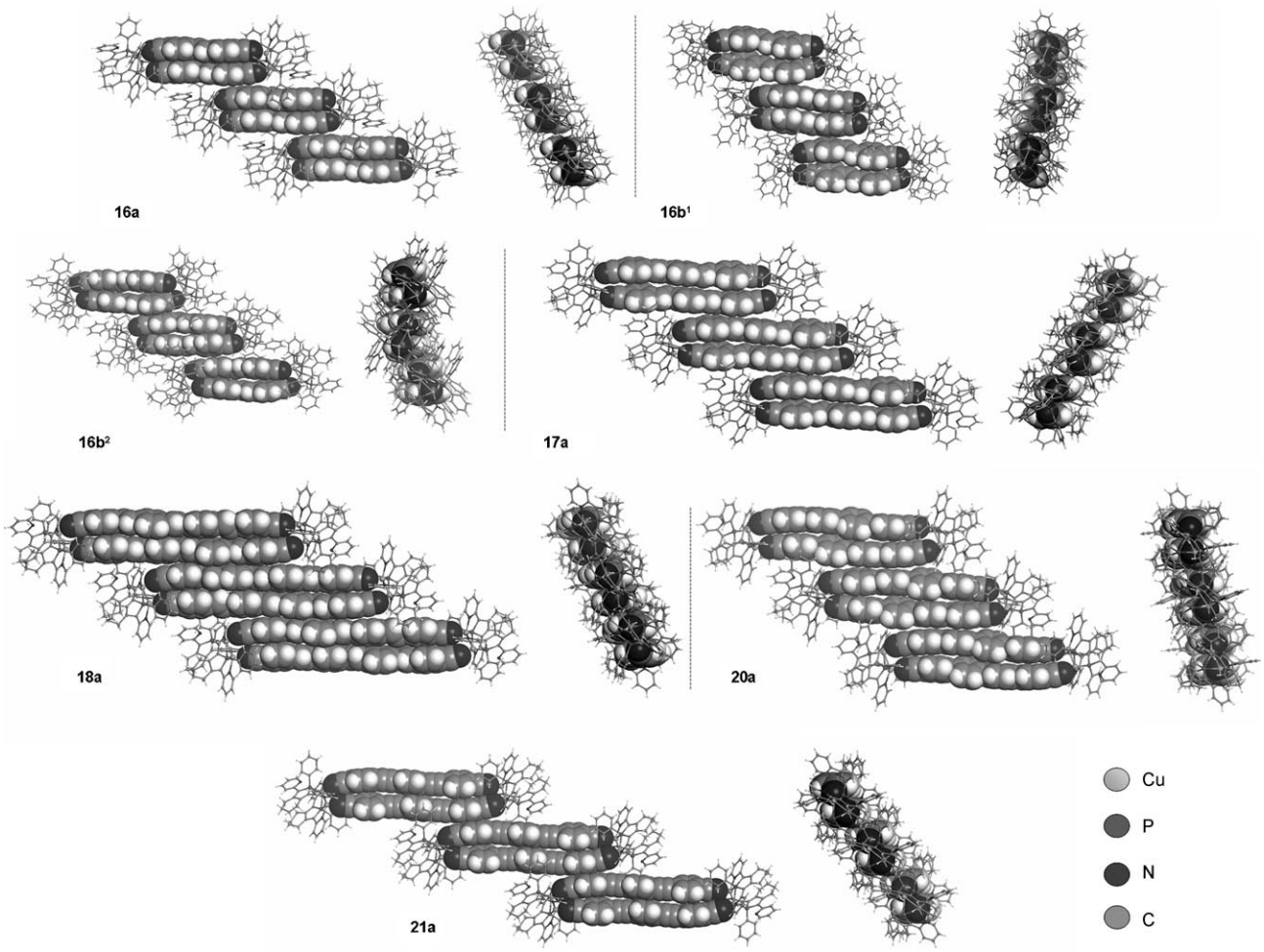


Figure 11. "Side" and "lateral" views of the stacking patterns of π-stacked metallocyclophanes **16a**, **16b**[1,2], **17a**, **18a**, **20a**, and **21a** observed in single crystals.

the geometry of the π connectors has a dramatic influence on the dimensionality of the supramolecular π-stacked arrays with the formation of infinite stack with linear linkers (Figure 11) and tow- or fourfold stacks with angular linkers (Figures 13 and 14). These structure–supramolecular-organization relationships open interesting perspectives for the development of a rational approach towards well-defined discrete or infinite π-stacked organic materials.

Conclusion

In summary, we have developed a straightforward and versatile supramolecular synthesis of π-stacked [2,2]-paracyclophane analogues **B** (Figure 1) based on the use of U-shaped Cu^{I}_{2} molecular clips and homoditopic cyano-capped conjugated linkers. The versatility of Cu^{I}-clip **2a** for generating structural diversity has been demonstrated with the use of linkers that have nanoscale lengths (up to 27.7 Å), different chemical compositions (oligo(*para*-phenylenevinylene)s OPVs, oligo(phenylene)s, oligo(phenylethynylene)s), and alternative geometries (linear, angular). The key properties of clip **2a** that result in this versatility are 1) its short intermetallic distance, due to the presence of bridging P centers, 2) its structural rigidity, and 3) the hemilability of its assembling heterotopic N,P,N-ligands. This rational synthetic approach, based on the concepts of the directional-bonding approach,[20] gives rise to an easy to perform and unique chemical engineering methodology for the generation of π-stacked paracyclophane derivatives. The organization of the linear linkers within π-stacked supramolecules results in the formation of infinite columns in which all the π-systems overlap (π–π distances, ca 3.5 Å). Notably, this hierarchical long-range supramolecular organization of linear π-conjugated systems is quite general. Therefore, the use of molecular clips **2a** provides a rational strategy for the stacking of extended π systems in the solid state, providing a minimal alteration of their structure (introduction of terminal cyano moiety), a problem which is a major issue in plastic electronics.

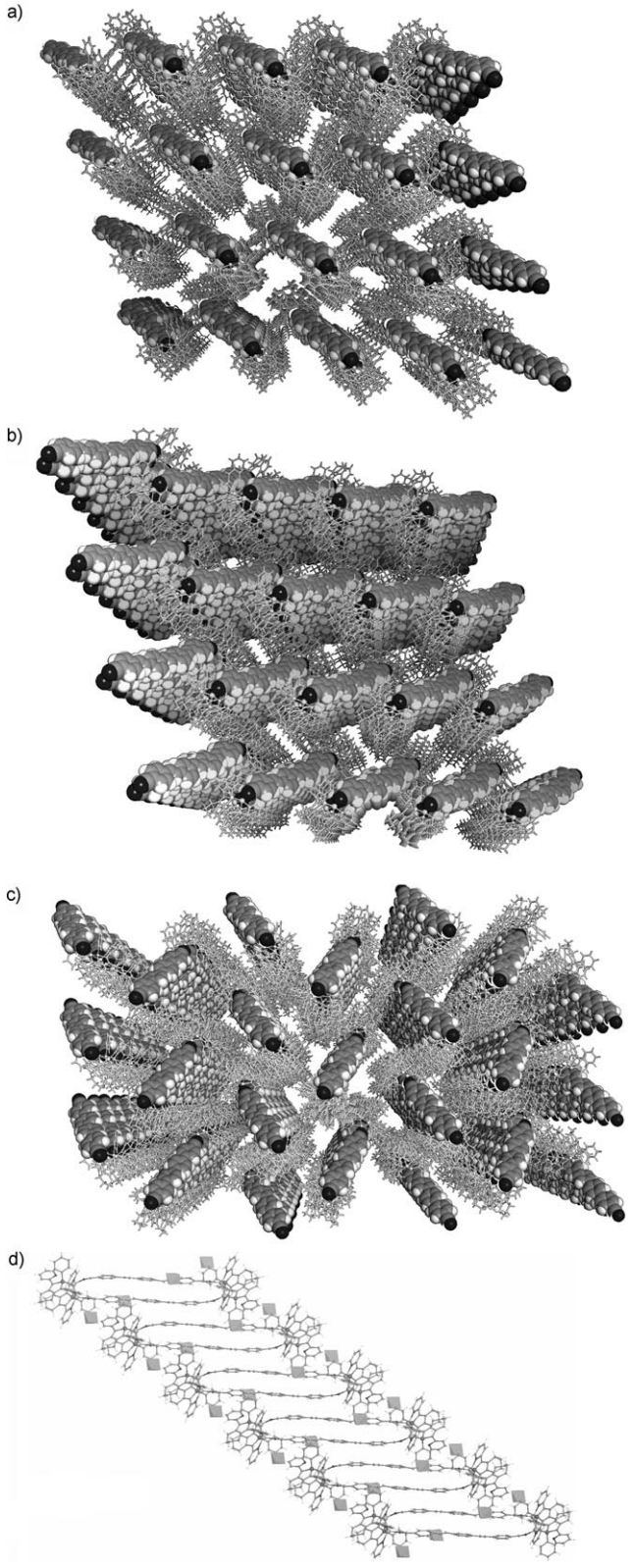


Figure 12. View of the columnar stacks of derivatives a) **17a**, b) **18a**, and c) **20a**, PF_6^- counterions and disordered CH_2Cl_2 molecules have been omitted. d) Location of the PF_6^- counterions for derivative **17a**, PF_6^- counterions are represented as polygons, while the supramolecular rectangles are shown in stick and ball style; disordered CH_2Cl_2 molecules have been omitted.

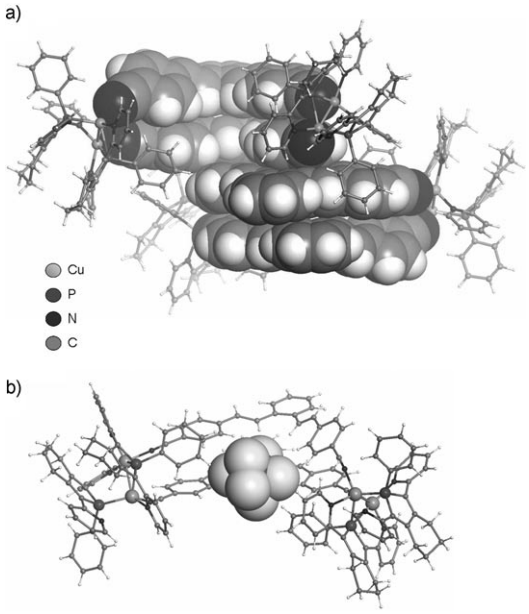


Figure 13. a) Supramolecular dimer observed in single crystals of metallacycle **22a**. b) Location of a PF_6^- ion in the pocket defined by the curved structure of derivative **22a**.

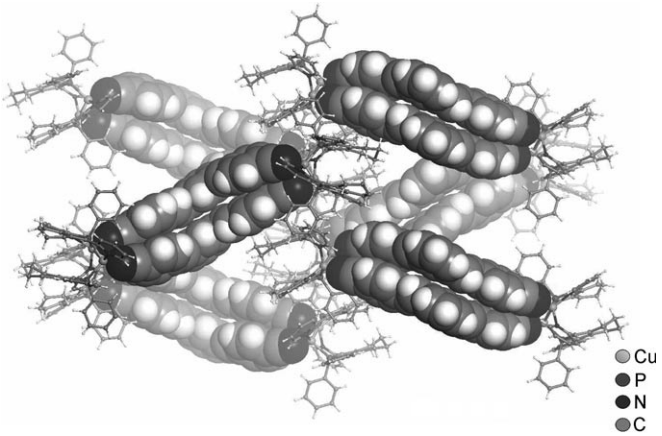


Figure 14. Organization of the neighboring metallacycles in the single crystals of supramolecular assembly **23a**.

Experimental Section

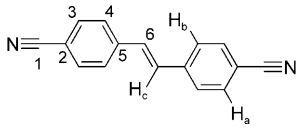
All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (diethyl ether) or from phosphorus pentoxide (dichloromethane, acetonitrile). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AV300, DPX200, 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. Elemental analyses were performed by the CRMPO, University of Rennes at Rennes France.

Intermediates 4,4′-bis[(diethoxyphosphoryl)methyl]stilbene **P5,**[43] 1,2-bis[(diethoxyphosphoryl)methyl]benzene **P6,**[44,46] 1,3-bis[(diethoxyphosphoryl)methyl]benzene **P7**[45,46] and 2,6-bis[(diethoxyphosphoryl)methyl]-pyridine **P8,**[47] the π-conjugated connectors **9**[48] and **10,**[49] the ligand **1**[34]

and the PF_6^- salts of the molecular clips **2a** and **2b**[35] were synthesized according to procedures previously published. The BF_4^- salt of the molecular clip **2a** was prepared according to the same route than the PF_6^- salts using $[Cu(CH_3CN)_4]BF_4$ as Cu^I source instead of $[Cu(CH_3CN)_4]PF_6$.

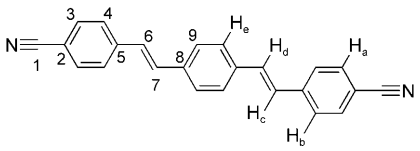
Synthesis of diethyl 4-cyanobenzylphosphonate (P2): Triethyl phosphite (2.5 equiv, 2.2 mL, 12.7 mmol) was added to a solution of the 4-(bromomethyl)benzonitrile (1 g, 5.1 mmol) in $CHCl_3$ (20 mL). The mixture was stirred at 60 °C for 12 h and the solvent was removed under vacuum. The oily product was washed with pentane and a solid was obtained as a white hydroscopic powder (1.13 g, 88 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.31$ (t, $^3J(H,H) = 7.1$ Hz, 6H; O-CH_2-CH_3), 3.23 (d, $^2J(P,H) = 22.3$ Hz, 2H; Ph-CH_2-PO(OEt)$_2$,), 4.16 (q, $^3J(P,H) = 7.1$ Hz, $^3J(H,H) = 7.1$ Hz, 4H; O-CH_2-CH_3) 7.51 ppm (AB system, $\nu_{AB} = 38.1$ Hz, $^3J(H,H) = 8.0$ Hz, 4H; H_3 and H_4); $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$): $\delta = 16.1$ (s, O-CH_2-CH_3), 33.2 (d, $^1J(P,C) = 137.7$ Hz, C_6), 62.8 (d, $^2J(P,C) = 6.74$ Hz, P-O-CH_2-CH_3), 111.3 (s, C_2), 118.4 (s, C_1), 131 (s, C_3), 132.6 (s, C_4), 138.1 ppm (d, $^2J(P,C) = 9.0$ Hz, C_5); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 25.6$ ppm; HR-MS (EI): *m/z* calcd for $C_{12}H_{16}NO_3P$: 253.0867; found: 253.0861 $[M]^+$.

Synthesis of the linker (5): NaH (5 equiv, 0.117 g, 5 mmol) was added to a solution of the phosphonate derivative **P2** (0.250 g, 0.980 mmol) in THF (20 mL). This mixture was stirred for 30 min at room temperature



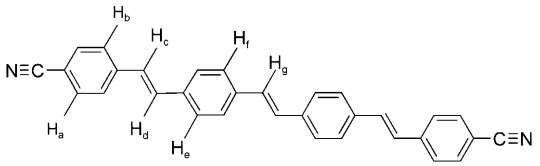
and then 4-cyanobenzaldehyde (1 equiv, 0.170 g, 0.980 mmol) was added. This mixture was stirred for one night at 65 °C. After addition of water (20 mL) and extraction with dichloromethane (3×20 mL), the derivative **5** was obtained as air-stable white needles (0.180 g, 0.781 mmol, 70 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.22$ (s, 2H; H_c), 7.66 ppm (AB system, $\nu_{AB} = 11.3$ Hz, $^3J(H,H) = 8.6$ Hz, 4H; H_a and H_b); $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2): $\delta = 112.3$ (s, C_2), 119.5 (s, C_1), 127.7 (s, C_3), 130.7 (s, C_6), 133.1 (s, C_4), 141.1 ppm (s, C_5); HR-MS (EI): *m/z* calcd for $C_{16}H_{10}N_2$: 230.0844; found: 230.0848 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{10}N_2$ (230.264 g mol^{-1}): C 83.46, H 4.38, N 12.17; found C 83.61, H 4.31, N 11.98.

Synthesis of the linker (6): NaH (5 equiv, 0.12 g, 5 mmol) was added to a solution of the phosphonate derivative **P2** (2 equiv, 0.5 g, 2 mmol) in THF (20 mL). This mixture was stirred for 30 min at room temperature and then terphtaldehyde (1 equiv, 0.131 g, 1 mmol) was added. This mix-



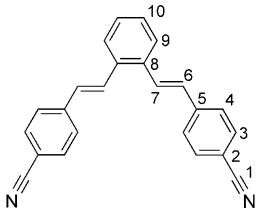
ture was stirred for one night at 65 °C. After addition of water (20 mL) and extraction with dichloromethane (5×20 mL), the derivative **6** was obtained as air-stable yellow needles (0.262 g, 0.788 mmol, 80 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.21$ (AB system, $\nu_{AB} = 15.6$ Hz, $^3J(H,H) = 13.8$ Hz, 4H; H_d and H_c), 7.62 (s, 4H; H_e), 7.67 ppm (AB system, $\nu_{AB} = 13.3$ Hz, $^3J(H,H) = 8.1$ Hz, 8H; H_a and H_b); $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2): $\delta = 112.3$ (s, C_2), 115.7 (s, C_1), 126.3 (s, C_9), 127.7 (s, C_3), 128.3 (s, C_7), 130.7 (s, C_6), 133.1 (s, C_4), 134.4 (s, C_8), 141.1 ppm (s, C_5); HR-MS (EI): *m/z* calcd for $C_{24}H_{16}N_2$: 332.1314; found: 332.1313 $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.40 g mol^{-1}): C 86.72, H 4.85, N 8.43; found C 86.63, H 4.71, N 8.68.

Synthesis of the linker (7): NaH (10 equiv, 0.19 g, 8 mmol) was added to a solution of the derivative **P5** (1 equiv, 0.4 g, 0.8 mmol) THF (20 mL).

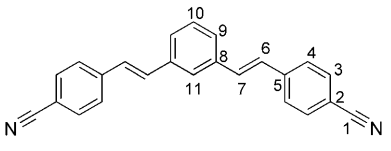


This mixture was stirred for 1 h at room temperature and then 4-cyanobenzaldehyde (2 equiv, 0.210 g, 1.6 mmol) was added. This mixture was stirred for one night at 65 °C. After addition of water (20 mL) and extraction with dichloromethane (5×60 mL), the derivative **7** was obtained as an air-stable yellow powder (0.156 g, 0.4 mmol, 45 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.50$ (s, 2H; H_g), 6.86–7.01 (m, 4H; H_c and H_d), 7.13–7.22 (m, 8H; H_e and H_f), 7.34–7.44 ppm (m, 8H; H_a and H_b); HR-MS (EI): *m/z* calcd for $C_{32}H_{22}N_2$: 434.1783; found: 434.1758 $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{22}N_2$ (434.53 g mol^{-1}): C 88.45, H 5.10, N 6.45; found C 88.17, H 4.91, N 6.63.

Synthesis of the linker (11): Derivative **P6** (1.0 g, 2.6 mmol) in THF (20 mL) was added dropwise to a suspended solution of sodium hydride (0.26 g, 11 mmol) in THF (100 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. 4-Formylbenzonitrile **P3** (0.75 g, 5.7 mmol) in THF (20 mL) was added to this solution. The reaction mixture was stirred for 6 h, and then was filtered on short silica column. The product was the first to be eluted and inorganic salt was retained. The volatile materials were removed under vacuum. Compound **11** was recrystallized from THF (10 mL) and was obtained as a light orange solid (0.43 mg, yield 50 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.04$ (d, $^3J(H,H) = 16.2$ Hz, 2H; H_6), 7.40–7.43 (m, 2H; H_{10}), 7.65 (d, $^3J(H,H) = 16.2$ Hz, 2H; H_7) 7.68–7.71 ppm (brs, 10H; H_3, H_4, H_9); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 111.0$ (s, C_2), 118.9 (s, C_1), 126.9 (s, C_9), 127.1 (s, C_4), 128.7 (s, C_{10}), 129.6 (s, C_7), 129.9 (s, C_6), 132.6 (s, C_3), 135.5 (s, C_8), 141.7 ppm (C_5); HR-MS (EI): *m/z* calcd for $C_{24}H_{16}N_2$: 332.1314; found: 332.1318; elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.40 g mol^{-1}): C 86.72, H 4.85, N 8.43; found C 86.55, H 4.91, N 8.59.

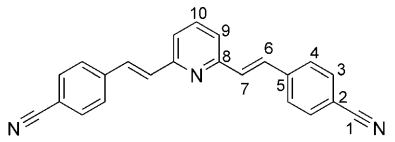


Synthesis of the linker (12): Derivative **P7** (1.0 g, 2.6 mmol) in THF (20 mL) was added dropwise to a suspended solution of sodium hydride (0.26 g, 11 mmol) in THF (100 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. 4-Formylbenzonitrile **P3** (0.75 g, 5.7 mmol) in THF (20 mL) was added to this solution. The reaction mixture was stirred for 6 h, and then was filtered on short silica column. The product was the first to be eluted in the front and inorganic salt was retained. The volatile materials were removed under vacuum. The derivative **12** was recrystallized from THF (10 mL) and was obtained as a white solid (0.57 g, yield 66 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta =$ 7.23 (d, $^3J(H,H) = 16.4$ Hz, H_6), 7.32 (d, 2H; $^3J(H,H) = 16.4$ Hz, 2H; H_7), 7.44–7.49 (m, 1H; H_{10}), 7.55–7.58 (m, 2H; H_9), 7.68 (d, $^3J(H,H) = 8.7$ Hz, 2H; H_3), 7.72 (d, $^3J(H,H) = 8.7$ Hz, 4H; H_4), 7.76 ppm (s, 1H; H_{11}); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 110.8$ (s, C_2), 119.0 (s, C_1), 125.4 (s, C_{11}), 126.9 (s, C_9, C_4), 127.4 (s, C_6), 129.3 (s, C_{10}), 131.7 (s, C_7), 132.6 (s, C_3), 137.2 (s, C_8), 141.6 ppm (s, C_5); HR-MS (EI): *m/z* calcd for $C_{24}H_{16}N_2$:



332.1314; found: 332.1318 $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.40 g mol^{-1}): C 86.72, H 4.85, N 8.43; found C 86.71, H 4.69, N 8.43.

Synthesis of the linker (13): Derivative **P8** (0.200 g, 0.53 mmol) in THF (10 mL) was added dropwise to a suspended solution of sodium hydride (0.52 g, 22 mmol) in THF (10 mL) at 0 °C. The reaction mixture was



warmed to room temperature and stirred for 6 h. 4-Formylbenzonitrile (0.121 g, 0.94 mmol) in THF (10 mL) was added to this solution. The reaction mixture was stirred for 2 h, and then was filtered on short silica column. The product was the first to be eluted and inorganic salt was retained. The volatile materials were removed in vacuum. The derivative **13** was recrystallized from EtOH (5 mL) and was obtained as a white solid (0.070 g, yield 40 %). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 7.34$ (s, 2H; H_9 Py), 7.35 (AB system, $\nu_{AB} = 17.2$ Hz, $^3J(H,H) = 10.8$ Hz, 4H; $H_{6,7}$), 7.65–7.69 (m, 8H; $H_{3,4}$), 7.72 ppm (t, $J = 6.5$ Hz, 1H; H_{10} Py); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): $\delta = 111.8$ (s, C_2), 119.5 (s, C_1), 122.4 (s, C_9), 127.9 (s, C_4), 131.5 (s, C_7), 131.7 (s, C_6), 132.8 (s, C_3), 137.8 (s, C_{10}), 141.5 (C_5), 154.9 ppm (s, C_8); HR-MS (EI): m/z calcd for $C_{23}H_{15}N_3$: 333.1266; found: 333.1254 $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{15}N_3$ (333.39 g mol^{-1}): C 82.86, H 4.54, N 12.60; found C 86.65, H 4.63, N 12.41.

General procedure for the synthesis of the supramolecular rectangles: A solution of the ditopic cyano-based connector in CH_2Cl_2 (10 mL) was added to a solution of **2a** or **2b** in CH_2Cl_2 (15 mL). This mixture was stirred for 15 h at 40 °C and then it was filtered and the volatile materials were removed under vacuum. The solid residues were washed with Et_2O (3 × 10 mL) and the supramolecular complexes were isolated as air-stable powders. Crystals suitable for X-ray diffraction study were obtained at room temperature from slow diffusion of pentane into a solution of these derivatives in CH_2Cl_2. These batches of crystals were dried under vacuum at room temperature overnight. Yields indicated correspond to the materials recovered after such crystallizations and after these materials have been left under vacuum for one night at room temperature.

Synthesis of supramolecular assembly (14a): Following the general procedure, the reaction of **2a** (0.200 g, 0.16 mmol) with **3** (1 equiv, 0.037 g, 0.16 mmol) afforded **14a** as an air-stable red solid (0.138 g, 0.05 mmol, 62 % yield). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.07$–1.23 (m, 4H; C=CH_2CH_2), 1.28–1.45 (m, 4H; C=CH_2CH_2), 1.52–1.69 (m, 4H; C=CH_2CH_2), 1.71–1.86 (m, 4H; C=CH_2CH_2), 2.41–2.61 (m, 4H; C=CH_2), 2.85–3.00 (m, 4H; C=CH_2), 3.04–3.20 (m, 4H; C=CH_2), 3.32–3.50 (m, 4H; C=CH_2), 6.30–6.46 (m, 4H; $H_{anthracene}$), 6.47–6.56 (m, 4H; $H_{anthracene}$), 6.77–6.96 (m, 4H; $H_{anthracene}$), 7.23 (t, $^3J(H,H) = 7.2$, 7.2 Hz, 8H; *m*-Ph), 7.28–7.45 (m, 20H; $H_{5'}$ Py, $H_{anthracene}$, *o*-Ph and *p*-Ph), 7.60 (d, $J(H_{3'},H_{4'}) = 7.5$ Hz, 4H; $H_{3'}$ Py), 7.68 (dd, $^3J(H_5,H_6) = 5.2$ Hz, $^3J(H_5,H_4) = 7.1$ Hz, 4H; H_5 Py), 7.95 (dd, $^3J(H_{4'},H_{5'}) = 7.4$ Hz, $^3J(H_{4'},H_{3'}) = 7.5$ Hz, 4H; $H_{4'}$ Py), 8.32 (d, $^3J(H_3,H_4) = 8.0$ Hz, 4H; H_3 Py), 8.39 (d, 4H; $^3J(H_{6'},H_{5'}) = 4.9$ Hz, $H_{6'}$ Py), 8.46 (dd, $^3J(H_4,H_5) = 7.1$ Hz, $^3J(H_4,H_3) = 8.0$ Hz, 4H; H_4 Py), 8.70 ppm (d, $^3J(H_6,H_5) = 5.2$ Hz, 4H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): $\delta = -144.3$ (sept,$^1J(P,F) = 710$ Hz, PF_6), 3.2 ppm (brs, $P_{phosphole}$); elemental analysis calcd (%) for $C_{129}H_{103}Cu_4F_{24}N_{12}P_8$ (2779.21 g mol^{-1}): C 55.75, H 3.74, N, 6.05; found: C 55.81, H 3.69, N 6.00.

Synthesis of supramolecular assembly (14b): Following the general procedure, the reaction of **2b** (0.200 g, 0.16 mmol) with **3** (1 equiv, 0.037 g, 0.16 mmol) afforded **14b** as an air-stable red solid (0.161 g, 0.056 mmol, 70 % yield). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): $\delta = -144.1$ (sept, $^1J(P,F) = 711$ Hz, PF_6), −1.2 (brs, P_{dppm}), 14.5 ppm (brs, $P_{phosphole}$); elemental analysis calcd (%) for $C_{131}H_{104}Cl_2Cu_4F_{24}N_8P_{10}$ (**14b** × CH_2Cl_2; 2876.19 g mol^{-1}): C 54.61, H 3.64, N 3.89; found: C 54.83; H 3.59; N 4.02.

Synthesis of supramolecular assembly (15a): Following the general procedure, the reaction of **2a** (0.200 g, 0.16 mmol) with **4** (10 equiv, 0.207 g, 1.62 mmol) afforded **15a** as an air-stable red solid (0.133 g, 0.06 mmol, 75 % yield). ^{1}H NMR(500 MHz, CD_2Cl_2): $\delta = 2.01$ (brs, 8H; C=CCH_2CH_2), 2.91 (brs, 6H; C=CCH_2), 3.13 (brs, 2H; C=CCH_2), 7.18–7.40 (brm, 28H; H_5 Py, *o*,*m*,*p*-Ph), 7.56 (s, 8H; H_4 Py), 7.60 (s, 8H; N≡$CCCH$), 7.87 (s, 8H; H_3 Py), 8.35 ppm (brs, 8H; H_6 Py); ^{13}C{^{1}H} NMR (300 MHz, CD_2Cl_2): $\delta = 21.0$ (s, C=CCH_2CH_2), 26.5 (s, C=CCH_2), 115.9 (CuN≡$CCCH$), 116.9 (brs, CuN≡$CCCH$), 122.6 (brs, C_5 Py), 123.8 (brs, C_3 Py), 129.1 (brs, *m*-Ph), 130.7 (brs, *p*-Ph), 131.2 (brs, N≡$CCCH$), 132.3 (brs, *o*-Ph), 138.7 (brs, C_4 Py), 149.1 ppm (brs, C_6 Py); C_2 Py, C_α, C_β, and *ipso*-Ph were not observed. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = -142.8$ (sept, $^1J(P,F) = 710$ Hz, PF_6), 7.2 ppm (brm, 2P, $\nu_{1/2} = 115$ Hz, P); elemental analysis calcd (%) for $C_{113}H_{94}Cl_2Cu_4F_{24}N_{12}P_8$ (**15a** × CH_2Cl_2; 2648.88 g mol^{-1}): C 51.24, H 3.58, N 6.35; found: C 51.41, H 3.79, N 5.95.

Synthesis of supramolecular assembly (15b): Following the general procedure, the reaction of **2b** (0.200 g, 0.16 mmol) with 1,4-dicyanobenzene **4** (4 equiv, 0.081 g, 0.631 mmol) afforded **15b** as an air-stable yellow and orange solid (0.125 g, 0.054 mmol, 67 % yield). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.87$–1.96 (m, 4H; C=CH_2CH_2), 2.05–2.20 (m, 4H; C=CH_2CH_2), 2.86–3.00 (m, 4H; C=CCH_2), 3.12–3.26 (m, 2H; H_δ), 3.28–3.40 (m, 4H; C=CCH_2), 3.55–3.68 (m, 2H; H_δ), 7.05–7.09 (m, 8H; *m*-Ph_{dppm}), 7.14–7.21 (m, 8H; *m*-Ph_{dppm}), 7.30 (t, $^3J(H,H) = 7.03$ Hz, 4H; *m*-Ph), 7.34 (d, $^3J(H,H) = 6.61$ Hz, 4H; H_5 Py), 7.40–7.60 (brm, 30H; o,p-Ph_{dppm}, o,p-Ph), 7.79 (s, 8H; H_a), 7.79 (d, $^3J(H,H) = 7.60$ Hz, 4H; H_3 Py), 8.05 (t, $^3J(H,H) = 6.61$, 7.60 Hz, 4H; H_4 Py), 8.32 ppm (brs, 4H; H_6 Py); ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): $\delta = 18.80$ (s, C=CCH_2CH_2), 22.32 (s, C=CCH_2), 34.11 (brs, C_δ), 122.63 (s, C_5 Py), 124.12 (s, C_3 Py), 129.11 (brs, C_{Ph}), 129.60 (brs, C_{Ph}), 131.24 (brs, C_{Ph}), 132.02 (brs, C_{Ph}), 133.56 (brs, C_{Ph}), 139.03 (s, C_4 Py), 151.17 ppm (s, C_6 Py); C_2 Py, C_α, C_β, and *ipso*-Ph were not observed; ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = -145.0$ (sept, $^1J(P,F) = 706$ Hz, PF_6), 3.2 (brm, 2P, $\nu_{1/2} = 56.7$ Hz, P_{dppm}), 13.3 ppm (t, $^2J(P,P) = 79.6$ Hz, $P_{phosphole}$); elemental analysis calcd (%) for $C_{114}H_{94}Cu_4F_{24}N_8P_{10}$ (2592.18 g mol^{-1}): C 52.75, H 3.65, N 4.32; found: C 52.59; H 3.49; N 4.12.

Synthesis of supramolecular assembly (16a): Following the general procedure, the reaction of **2a** (0.200 g, 0.16 mmol) with **5** (1 equiv, 0.037 g, 0.16 mmol) afforded **16a** as an air-stable red solid (0.150 g, 0.54 mmol, 67 % yield).^{1}H NMR (300 MHz,CD_2Cl_2): $\delta = 1.45$–2.01 (brm, 16H; C=CH_2CH_2), 2.45–2.78 (brm, 8H; C=CH_2), 2.98–3.17 (m, 8H; C=CH_2), 7.20 (s, 4H; H_c), 7.27 (brs, 8H; H_5 Py), 7.33–7.54 (m, 28H; H_{ph} and H_a), 7.59 (d, $^3J(H,H) = 8.2$ Hz, 8H; H_b), 7.68 (d, $^3J(H,H) = 7.2$ Hz, 8H; H_3 Py), 7.96 (dd, $^3J(H,H) = 7.2$, 7.5 Hz, 8H; 8H; H_4 Py), 8.45 ppm (brs, 8H; H_6 Py); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): $\delta = -144.9$ (sept, $^1J(P,F) = 711$ Hz, PF_6), 8.7 ppm (brm, $\nu_{1/2} = 128.0$ Hz, $P_{phosphole}$); elemental analysis calcd (%) for $C_{129}H_{106}Cl_2Cu_4F_{24}N_{12}P_8$ (**16a** × CH_2Cl_2, 2848.27 g mol^{-1}): C 54.30, H 3.74, N 5.89;. found: C 54.63, H 3.55, N 5.65.

Synthesis of supramolecular assembly (16b): Following the general procedure, the reaction of **2b** (0.200 g, 0.16 mmol) with connector **5** (1 equiv, 0.037 g, 0.16 mmol) afforded **16b** as an air-stable orange-yellow solid (0.141 g, 0.05 mmol, 63 % yield). ^{1}H NMR (500 MHz, CD_2Cl_2/CD_3CN): $\delta = 1.61$–1.68 (m, 4H; C=CH_2CH_2), 1.83–1.90 (m, 4H; C=CH_2CH_2), 2.17–2.36 (m, 4H; C=CCH_2), 2.88 (dt, $^3J(H,H) = 11.09$ Hz, $^2J(H,P) = 12.60$ Hz, 2H; H_δ), 3.07–3.21 (m, 4H; C=CCH_2), 3.72 (dt, $^3J(H,H) = 11.09$, 12.60 Hz, 2H; H_δ), 6.97 (d, $^3J(H,H) = 7.61$ Hz, 8H; H_{ph}), 7.15 (t, $^3J(H,H) = 7.30$, 7.61 Hz, 8H; H_{ph}), 7.20 (t, $^3J(H,H) = 7.46$, 7.46 Hz, 8H; H_{ph}), 7.26 (t, $^3J(H,H) = 7.30$, 7.30 Hz, 4H; H_{ph}), 7.3–7.41 (brm, 12H; 4H$_5$ Py, 8H_{ph}), 7.47 (dt, $^3J(H,H) = 6.05$, 5.79 Hz, 8H; H_{Ph}), 7.54 (s, 4H; H_a), 7.62 (t, $^3J(H,H) = 7.26$, 7.26 Hz, 4H; H_{Ph}), 7.83–7.88 (m, 20H; H_3 Py, H_{Ph}), 7.96 (t, $^3J(H,H) = 7.45$, 7.45 Hz, 4H; H_4 Py), 8.64 ppm (d, $^3J(H,H) = 4.80$ Hz, 4H; H_6 Py); ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2/CD_3CN,): $\delta = 21.6$ (s, C=CCH_2CH_2), 24.3 (brs, C_δ), 27.5 (s, C=CCH_2), 123.6 (s, C_5 Py), 124.4 (s, C_3 Py), 127.6 (brs, C_{Ph}), 128.8 (brs, C_{Ph}), 129.6 (brs, C_{Ph}), 130.4 (s, C_6), 132.7 (brs, C_{Ph}), 133.5 (brs, C_{Ph}), 139.0 (s, C_4 Py), 150.2 ppm (s, C_6 Py); C_2 P_y, C_α, C_β, and *ipso*-Ph were not observed; ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2/CD_3CN): $\delta = -144.4$ (sept, $^1J(P,F) = 711$ Hz, PF_6), −3.4 (d, $^2J(P,P) = 84$ Hz, 2P, P_{dppm}), 12.8 (t, $^2J(P,P) = 84$, 84 Hz, $P_{phosphole}$);

elemental analysis calcd (%) for $C_{130}H_{106}Cu_4F_{24}N_8P_{10}$ (2796.28 g mol^{-1}): C 55.76, H 3.82, N 4.00; found: C 55.45, H 3.65, N 5.85.

Synthesis of supramolecular assembly (17a): Following the general procedure, the reaction of **2a** (0.400 g, 0.32 mmol) with **6** (1 equiv, 0.106 g, 0.32 mmol) afforded after crystallization **17a** as an air-stable red solid (0.313 g, 0.10 mmol, 63% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.57–1.76 (m, 8H; C=CH_2CH_2), 1.90–2.05 (m, 8H; C=CH_2CH_2), 2.38–2.55 (m, 8H; C=CH_2), 3.10–3.25 (m, 8H; C=CH_2), 6.70–6.81 (m, 8H; H_{Ph}),7.03–7.08 (m, 8H; H_{Ph}), 6.90 (d, ^3J(H,H) = 16.3 Hz, 4H; H_d), 7.14 (d, ^3J(H,H) = 16.3 Hz, 4H; H_c), 7.32 (t, ^3J(H,H) = 7.8, 7.8 Hz, 4H; H_{Ph}), 7.37 (d,^3J(H,H) = 6.5 Hz, 8H; H_5 Py), 7.53 (d, ^3J(H,H) = 8.1 Hz, 8H; H_3 Py), 7.62 (s, 8H; H_e), 7.66 (d, ^3J(H,H) = 8.3 Hz, 8H; H_b), 7.71 (d, ^3J(H,H) = 8.3 Hz, 8H; H_a) 7.80 (t, ^3J(H,H) = 6.5, 8.1 Hz, 8H; H_4 Py), 8.35 ppm (brs, 8H; H_6 Py). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = −141.0 (sept, ^1J(P,F) = 709 Hz, PF_6), 8.7 ppm (brs, $P_{phosphole}$); elemental analysis calcd (%) for $C_{145}H_{118}Cl_2Cu_4F_{24}N_{12}P_8$ (**17a** × CH_2Cl_2 3052.37 g mol^{-1}): C 56.96, H 3.89, N 5.50;. found: C 57.23, H 3.67, N 5.83.

Synthesis of supramolecular assembly (17b): Following the general procedure, the reaction of **2b** (0.400 g, 0.42 mmol) with **6** (1 equiv, 0.16 g, 0.42 mmol) afforded **17b** as an air-stable yellow solid (0.798 g, 65% yield). ^{1}H NMR(300 MHz, CD_2Cl_2): δ = 1.57–1.76 (m, 4H; C=CH_2CH_2), 1.90–2.05 (m, 4H; C=CH_2CH_2), 2.38–2.55 (m, 4H; C=CH_2), 2.87–3.00 (m, 2H; H_δ), 3.10–3.25 (m, 4H; C=CH_2), 3.35–3.55 (m, 2H; H_δ), 6.70 (m, 8H; *m*-Ph_{dppm}), 7.03 (m, 8H; *m*-Ph_{dppm}), 6.90 (d, ^3J(H,H) = 16.3 Hz, 4H; H_d), 7.14 (d, ^3J(H,H) = 16.3 Hz, 4H; H_c), 7.32 (t, ^3J(H,H) = 7.8, 7.8 Hz, 4H; *m*-Ph), 7.37 (d, ^3J(H,H) = 6.5 Hz, 4H; H_5 Py),7.39–7.51 (m, 30H; *o*- and *p*-Ph_{dppm}, *o*- and *p*-Ph), 7.53 (d, ^3J(H,H) = 8.1 Hz, 4H; H_3 Py), 7.62 (s, 8H; H_e), 7.66 (d, ^3J(H,H) = 8.3 Hz, 8H; H_b), 7.71 (d, ^3J(H,H) = 8.3 Hz, 8H; H_a), 7.80 (dd, ^3J(H,H) = 6.5, 8.1 Hz, 4H; H_4 Py), 8.35 ppm (brs, 4H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = −144.3 (sept, ^1J(P,F) = 709.5 Hz, PF_6), 0.40 (d, ^2J(P,P) = 72.9 Hz, P_{dppm}), 16.50 ppm (t, ^2J(P,P) = 72.9 Hz, $P_{phosphole}$); elemental analysis calcd (%) for $C_{146}H_{118}Cu_4F_{24}N_8P_{10}$ (3004.44): C 58.37, H 3.96, N, 3.73; found: C 58.61, H, 3.79, N 3.80.

Synthesis of supramolecular assembly (18a): Following the general procedure, the reaction of **2a** (51.2 g, 0.046 mmol) with **7** (1 equiv, 20 mg, 0.046 mmol) dissolved in CH_2Cl_2 (100 mL) afforded after crystallization **18a** as an air-stable red solid (13 g, 0.010 mmol, 20% yield). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = 7.5 ppm (brs); elemental analysis calcd (%) for $C_{162}H_{132}B_4Cl_4Cu_4F_{16}N_{12}P_4$ (**18a** × 2 CH_2Cl_2; 3108.57 g mol^{-1}): C 62.48, H 4.27, N 5.40; found: C 62.64, H 4.56, N 5.17.

Synthesis of supramolecular assembly (19a): Following the general procedure, the reaction of **2a** (0.168 g, 0.136 mmol) with **8** (1 equiv, 0.028 g, 0.137 mmol) afforded after crystallization **19a** as an air-stable orange solid (0.12 g, 0.044 mmol, 65% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.83–1.95 (brs, 16H; C=CH_2CH_2), 3.03–3.17 (brs, 16H; C=CH_2), 7.35–7.42 (brm, 28H; H_5 Py, o,m,p-Ph), 7.47 (s, 8H; H_b), 7.64 (s, 8H; H_a), 7.60–7.68 (brs, 8H; H_4 Py), 7.95–8.06 (brs, 8H; H_3 Py), 8.38–8.55 ppm (brs, 8H; H_6 Py). ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ = −139.4 (sept, ^1J(P,F) = 700 Hz, PF_6), 8.9 (brs, $\nu_{1/2}$ = 150 Hz, $H_{phosphole}$); elemental analysis calcd (%) for $C_{124}H_{100}Cu_4F_{24}N_{12}P_8$ (2712.29 g mol^{-1}): C 54.83, H 3.71, N 6.19; found: C 54.98, H 3.66, N 6.11.

Synthesis of supramolecular assembly (20a): Following the general procedure, the reaction of **2a** (0.400 g, 0.32 mmol) with **9** (1 equiv, 0.114 g, 0.32 mmol) afforded after crystallization **20a** as an air-stable red solid (0.328 g, 0.11 mmol, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (brs, 8H; C=CH_2CH_2), 1.97–1.80 (m, 8H; C=CH_2CH_2), 2.71–2.4 (m, 8H; C=CH_2), 3.02–2.98 (m, 8H; C=CH_2), 7.3 (d, J(H,H) = 7.3 Hz, 8H; H_5 Py), 7.42 (t, ^3J(H,H) = 7.4 Hz, 20H; H_{Ph}), 7.62 (d, J(H,H) = 7.6 Hz, 8H; H_3 Py), 7.66 (dd, ^3J(H,H) = 18.3, 8.4 Hz, 32H; H_{Ar}), 7.95 (t, ^3J(H,H) = 7.9 Hz, 8H; H_4 Py), 8.51 ppm (brs, 8H; H_6 Py). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = −142.4 (sept, ^1J(P, F) = 702 Hz, PF_6), 6.8 ppm (br, $P_{phosphole}$); elemental analysis calcd (%) for $C_{148}H_{116}Cu_4F_{24}N_{12}P_8$ (3016.41 g mol^{-1}): C 58.85, H 3.87, N 5.56; found: C 58.65, H 3.74, N 5.21.

Synthesis of supramolecular assembly (21a): Following the general procedure, the reaction of **2a** (0.203 g, 0.18 mmol) with **10** (1 equiv, 0.060 g, 0.18 mmol) afforded after crystallization **21a** as an air-stable red solid (0.164 g, 0.06 mmol, 67% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.41–2.01 (brm, 16H; C=CH_2CH_2), 2.45–2.73 (brm, 8H; C=CH_2), 2.92–3.18 (m, 8H; C=CH_2), 7.25 (d, ^3J(H,H) = 6.8 Hz, 8H; H_5 Py), 7.32–7.53 (brm, 20H; H_{Ph}), 7.58 (s, 8H; H_c), 7.67–7.88 (brm, 24H; H_a, H_b and H_3 Py), 7.93 (dd, ^3J(H,H) = 7.2, 7.4 Hz, 8H; H_4 Py), 8.44 ppm (brs, 8H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): 7.9 (brs, $P_{phosphole}$); elemental analysis calcd (%) for $C_{146}H_{112}B_4Cl_4Cu_4F_{16}N_{12}P_8$ (**21a** × 2 CH_2Cl_2; 2896.41 g mol^{-1}): C 60.43, H 3.89, N 5.79; found: C 60.11, H 3.62, N 5.47.

Synthesis of supramolecular assembly (22a): Following the general procedure, the reaction of **2a** (0.400 g, 0.32 mmol) with **11** (1 equiv, 0.106 g, 0.32 mmol) afforded after crystallization **22a** as an air-stable red solid (0.298 g, 0.10 mmol, 62% yield). ^{1}H NMR (300 MHz,CD_2Cl_2): δ = 1.22–1.95 (brm, 16H; C=CH_2CH_2), 2.08–2.43 (brm, 8H; C=CH_2), 2.58–3.22 (m, 8H; C=CH_2CH_2), 6.73 (d, ^3J(H,H) = 16 Hz, 4H; H_c), 7.06–7.14 (m, 4H; H_f), 7.22–7.48 (m, 36H; H_{Ph}, H_5 Py and $H_{e,d}$), 7.48–7.62 (m, 24H; H_3 and $H_{a,b}$), 7.83 (brs, 8H; H_4 Py), 8.36 ppm (brs, 8H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = −143.4 (sept, ^1J(P, F) = 703 Hz, PF_6), 7.80 ppm (brs); elemental analysis calcd (%) for $C_{145}H_{118}Cl_2Cu_4F_{24}N_{12}P_8$ (**22a** × CH_2Cl_2; 3052.37 g mol^{-1}): C 56.96, H 3.89, N 5.50; found: C 57.15, H 3.74, N 5.73.

Synthesis of supramolecular assembly (23a): Following the general procedure, the reaction of **2a** (0.400 g, 0.36 mmol) with **12** (1 equiv, 0.106 g, 0.32 mmol) afforded after crystallization **23a** as an air-stable red solid (0.284 g, 0.10 mmol, 56% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.57–1.76 (m, 8H; C=CH_2CH_2), 1.90–2.05 (m, 8H; C=CH_2CH_2), 2.38–2.55 (m, 8H; C=CH_2), 3.10–3.25 (m, 8H; C=CH_2), 7.14 (d, ^3J(H,H) = 16.5 Hz, 4H; H_c), 7.20 (d, ^3J(H,H) = 16.5 Hz, 4H; H_7), 7.32–7.49 (m, 34H; H_{ph}, H_a, H_e, H_f), 7.27 (d, ^3J(H,H) = 6.9 Hz, 8H; H_5 Py), 7.56 (d, ^3J(H,H) = 8.1 Hz, 8H; H_3 Py),7.65 (d, ^3J(H,H) = 8.7 Hz, 8H; H_b), 7.66 (s, 2H; H_g), 7.96 (t, ^3J(H,H) = 6.9, 8.1 Hz, 8H; H_4 Py), 8.48 ppm (brs, 8H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = 7.70 (brs, $P_{phosphole}$); elemental analysis calcd (%) for $C_{144}H_{116}B_4Cu_4F_{16}N_{12}P_4$ (2739.84 g mol^{-1}): C 63.13, H 4.27, N 6.13; found: C 63.01, H 4.22, N 5.91.

Synthesis of supramolecular assembly (24a): Following the general procedure, the reaction of **2a** (0.400 g, 0.32 mmol) with **13** (1 equiv, 0.107 g, 0.32 mmol) afforded after crystallization **24a** as an air-stable red solid (0.304 g, 0.12 mmol, 75% yield). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.75–1.90 (m, 8H; C=CH_2CH_2), 2.32–2.62 (m, 4H; C=CH_2), 2.89–3.00 (m, 8H; C=CH_2), 7.00–7.30 (m, 32H; H_5 Py, m, *p*-Ph, H_c, H_d, H_e), 7.31–7.40 (m, 8H; H_3 Py), 7.45–7.59 (m, 16H; H_a and H_b), 7.55–7.69 (m, 8H; *o*-Ph), 7.82–7.98 (m, 10H; H_4 Py and H_f), 8.43 ppm (brs, 8H; H_6 Py); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = −143.4 (sept, ^1J(P, F) = 703 Hz, PF_6), 7.49 ppm (brs); elemental analysis calcd (%) for $C_{143}H_{116}Cl_2Cu_4F_{24}N_{14}P_8$ (**24a** × CH_2Cl_2; 3054.36 g mol^{-1}): C 56.14, H 3.82, N 6.41; found: C 56.31, H 3.77, N 6.47.

X-ray crystallographic study: Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of π-conjugated connectors **5** and **6** and of supramolecular assemblies **14a,b**, **15a,b**, **16a,b**[1],**b**[2], **17a**, **18a**, **19a**, **20a**, **21a**, **22a**, **23a** and **24a** at room temperature. Single-crystal data collection was performed at 120 K with a Nonius KappaCCD diffractometer or at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[50] Structure determinations were performed by direct methods with the solving program SIR97,[51] that revealed all the non-hydrogen atoms. The SHELXL program[52] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. In the crystal lattices of the coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and to their counterions (hexafluorophosphate for **14a,b**, **15a,b**, **16a,b**[1], **17a**, **19a**, **20a**, **22a**, **24a** and tetrafluoroborate for **21a** and **23a**). These solvent molecules in most cases have a strong tendency to leave the bulk crystal through evaporation once the crystals are removed from their mother solution, a process that induces 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 (100 K) as quickly as possible on the diffractometer gionometer and X-ray data collection were performed at low temperature (100 K). In most cases, X-ray crystal structure resolution revealed these solvent molecules to be highly disordered. In the case of the supramolecular assemblies **14a,b**, **15a,b**, **16a,b[1]**, **17a** and **21a**, modeling of the disorder of these solvent molecules was possible leading to rather high anisotropic displacement parameters for some of their atoms. As a consequence, final agreement (R) factors were determined with modest values in some cases. Nevertheless, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes were always satisfactory. This allowed a primarily assignment of these modest R factors to an inadequate modeling of the disordered species exterior to these supramolecular assemblies and gave confidence to the treatment of the structural resolution of these derivatives. In addition, in the case of derivative **17a**, one part of the styryl moiety of the ditopic connector **17a** was disordered into two statistically nearly equal positions. The modeling of this disorder was not possible for the atoms of the neighboring phenyl rings. As a consequence, some of these atoms have rather high anisotropic displacement parameters. The crystallographic data for the derivatives **14a,b**, **15a,b**, **16a,b[1]**, **17a** and **21a** are given in Tables 4–6 In the case of the supramolecular assemblies **19a**, **20a**, **22a**, **23a** and **24a**, disordered CH_2Cl_2 molecules occupy an important volume of the crystal cell and were found highly disorder. A modeling of these disorders was not possible and we used a "squeeze" treatment in order to remove the scattering contribution of these molecules, which could not be satisfactory modeled. In these cases, anisotropic displacement parameters associated with the atoms of the cationic coordination complexes were always satisfactory except in the case of the derivative **24a**, for which two carbon atoms were refined with isotropic displacement parameters (derivatives **23a**, for which all atoms were refined with satisfactory anisotropic displacement parameters, and derivative **24a** are isostructural). The crystallographic data for the derivatives **19a**, **20a**, **22a**, **23a** and **24a** after this squeeze treatment are given in Tables 5 and 6. Table S1 (see Supporting Information) gives the crystallographic data for the derivatives **19a**, **20a**, **22a**, **23a** and **24a** before squeeze treatment. Finally, in the case of the supramolecular assemblies **16b[2]** and **18a**, disordered CH_2Cl_2 molecules and disordered counterions were highly delocalized and it was not possible to localize them. We used a squeeze treatment in order to remove the scattering contribution of these molecules (CH_2Cl_2 molecules and counterions) which could not be satisfactory modeled. Table 5 gives the crystallographic data for the derivatives **16b[2]** and **18a** after this squeeze treatment. Table S1 (see Supporting Information) gives the crystallographic data for the derivatives **16b[2]** and **18a** before such squeeze treatment. In addition, in the case of the derivative **16b[2]** one part of the styryl moiety of one of the ditopic connector **5** is disordered into two positions that were refined with relative occupancy. As a consequence and due to the poor quality of the X-ray data collection for the crystals of **16b[2]** due to rapid desolvatation of the included solvent molecules, some of the atoms involved in this disorder modeling had to be refined with isotropic displacement parameters. Finally, in the case of derivative **18a**, the central double bond of the ditopic connector **18a** was disordered into two statistically equal positions. The modeling of the resulting disorder was not possible for the atoms of the neighboring phenyl rings. As a consequence, some of these atoms have rather high anisotropic displacement parameters. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[53] CCDC-293234 (**15a**), 293235 (**15b**), 293236 (**14a**,), 293237 (**14b**), 293238 (**16a**), 293239 (**16b[1]**), 293240 (**17a**), 293241 (**5**), 293242 (**6**), 755226 (**16b[2]**), 755227 (**18a**), 755228 (**19a**), 755229 (**20a**), 755230 (**21a**), 755231 (**22a**), 755232 (**23a**), and 755234 (**24a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for π-conjugated connectors **5** and **6** and of supramolecular assemblies **14a**,**b**, **15a**,**b**.

	5	2.5**6**	**14a**$[PF_6]_4$·12 CH_2Cl_2	**14b**$[PF_6]_4$·6 CH_2Cl_2	**15a**$[PF_6]_4$·11 CH_2Cl_2	**15b**$[PF_6]_4$·8 CH_2Cl_2
formula	C_8H_5N	$C_{60}H_{40}N_5$	$C_{128}H_{33}Cu_4F_{24}N_{12}P_8$· 12 CH_2Cl_2	$C_{130}H_{94}Cu_4F_{24}N_8P_{10}$· 6 CH_2Cl_2	$C_{113}H_{74}Cu_4F_{24}N_{12}P_8$· 11 CH_2Cl_2	$C_{114}H_{82}Cu_4F_{24}N_8P_{10}$· 8 CH_2Cl_2
M_r	115.13	830.97	3771.14	3127.70	3491.95	3263.14
a [Å]	4.7529(3)	9.925(5)	15.496(1)	11.563(5)	14.570(5)	11.877(1)
b [Å]	10.5673(6)	12.407(5)	15.617(2)	13.188(5)	15.755(5)	16.286(1)
c [Å]	11.9098(6)	17.888(5)	16.510(1)	22.355(5)	16.378(5)	18.499(1)
α [°]	90	98.691(5)	97.191(2)	84.912(5)	81.781(5)	99.877(2)
β [°]	97.9080(10)	100.221(5)	99.695(1)	80.661(5)	72.909(5)	103.361(2)
γ [°]	90	91.726(5)	98.600(2)	76.286(5)	86.587(5)	93.677(2)
V [Å^3]	592.48(6)	2139.2(15)	3847.5(6)	3263(2)	3556(2)	3410(1)
Z	4	2	1	1	1	1
ρ_{calcd} [Mg m^{-3}]	0.077	1.290	1.628	1.591	1.631	1.589
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T [K]	120(2)	120(2)	100(2)	100(2)	120(2)	100(2)
crystal size [mm]	0.4×0.15×0.15	0.3×0.3×0.1	0.2×0.2×0.1	0.4×0.4×0.3	0.3×0.2×0.1	0.1×0.1×0.1
μ ($Mo_{K\alpha}$) [cm^{-1}]	0.077	0.076	1.129	1.019	1.178	1.130
F(000)	240	870	1896	1580	1750	1640
θ range [°]	3.45–27.46	1.66–27.56	1.27–27.55	2.77–27.49	3.32–27.51	5.23–27.57
index ranges	$-6\le h\le 6$	$-12\le h\le 12$	$-20\le h\le 20$	$-15\le h\le 15$	$-18\le h\le 18$	$-15\le h\le 15$
	$-11\le k\le 13$	$-16\le k\le 16$	$-20\le k\le 20$	$-17\le k\le 17$	$-20\le k\le 20$	$-21\le k\le 19$
	$-10\le l\le 15$	$-23\le l\le 23$	$-21\le l\le 21$	$-29\le l\le 29$	$-21\le l\le 21$	$-23\le l\le 24$
reflns collected	4517	31829	69250	28203	29496	28183
independent reflns	1347	31829	17704	14878	16116	15415
reflections [$I>2\sigma(I)$]	1206	7681	14080	12262	13381	9119
data/restraints/parameters	1347/0/82	9791/0/587	17704/0/958	14878/0/875	16116/0/851	15415/0/856
goodness-of-fit on F^2	1.077	1.034	1.054	1.020	1.031	1.040
final R indices [$I>2\sigma(I)$]	$R1=0.0366$	$R1=0.0452$	$R1=0.0781$	$R1=0.0617$	$R1=0.0657$	$R1=0.0809$
	$wR2=0.1055$	$wR2=0.1209$	$wR2=0.2138$	$wR2=0.1588$	$wR2=0.1858$	$wR2=0.2101$
R indices (all data)	$R1=0.0404$	$R1=0.0611$	$R1=0.0990$	$R1=0.0752$	$R1=0.0792$	$R1=0.1435$
	$wR2=0.1086$	$wR2=0.1330$	$wR2=0.2385$	$wR2=0.1706$	$wR2=0.2024$	$wR2=0.2471$
largest diff peak/hole [e Å^{-3}]	0.319/−0.196	0.720/−0.363	3.180/−2.225	2.874/−2.005	1.551/−1.105	0.889/−0.765

Table 5. Crystal data and structure refinement for supramolecular assemblies **16a**,**b**[1],**b**[2], **17a**, **18a**, **19a**.

	16a$[PF_6]_4$·6 CH_2Cl_2	**16b**[1]$[PF_6]_4$·5 CH_2Cl_2	**16b**[2]	**17a**$[PF_6]_4$·14 CH_2Cl_2	**18a**	**19a**$[PF_6]_4$
formula	$C_{128}H_{104}Cu_4F_{24}N_{12}P_8$· 6 CH_2Cl_2	$C_{130}H_{102}Cu_4F_{24}N_8P_{10}$· 5 CH_2Cl_2	$C_{130}H_{106}Cu_4N_8P_6$	$C_{141}H_{100}Cu_4F_{24}N_{12}P_8$· 14 CH_2Cl_2	$C_{106}H_{128}Cu_4N_{12}P_4$	$C_{124}H_{100}Cu_4F_{24}N_{12}P_8$
M_r	3277.71	3220.69	2220.21	4056.47	2596.78	2716.08
a [Å]	12.9509(5)	21.005(5)	11.80(3)	13.525(11)	13.325(1)	29.377(1)
b [Å]	16.0253(8)	24.342(5)	23.32(6)	19.33(2)	16.907(1)	14.884(1)
c [Å]	17.0867(9)	28.028(5)	27.10(8)	20.169(16)	19.953(2)	32.264(1)
α [°]	84.578(2)	90.000(5)	105.88(12)	104.45(3)	70.267(4)	90
β [°]	86.377(2)	106.742(5)	99.86(8)	107.66(2)	87.088(4)	96.641(1)
γ [°]	77.343(2)	90.000(5)	97.90(8)	103.88(3)	79.459(5)	90
V [Å^3]	3441.3(3)	13723(5)	6932(32)	4571(7)	4131.4(7)	14013(1)
Z	1	4	2	1	1	4
ρ_{calcd} [Mg m^{-3}]	1.582	1.559	1.064	1.474	1.044	1.287
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P21/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
T [K]	100(2)	100(2)	95(2)	120(2)	100(2)	100(2)
crystal size [mm]	0.2×0.1×0.05	0.15×0.10×0.05	0.1×0.06×0.04	0.3×0.15×0.1	0.4×0.15×0.05	0.1×0.07×0.02
μ ($Mo_{K\alpha}$) [cm^{-1}]	1.023	1.009	0.718	0.991	0.593	0.770
F(000)	1660	6520	2296	2045	1348	5520
θ range [°]	2.40–27.53	0.76–27.64	2.08–27.64	2.24–27.6	1.30–26.33	2.74–26.00
index ranges	$-16\le h\le 16$	$-27\le h\le 27$	$-15\le h\le 15$	$-17\le h\le 17$	$-16\le h\le 15$	$-36\le h\le 35$
	$-20\le k\le 20$	$-28\le k\le 31$	$-30\le k\le 30$	$-24\le k\le 24$	$-21\le k\le 15$	$-18\le k\le 18$
	$-22\le l\le 22$	$-36\le l\le 35$	$-34\le l\le 34$	$-26\le l\le 25$	$-24\le l\le 21$	$-39\le l\le 39$
reflns collected	67250	174440	55915	73592	19797	25131
independent reflns	15751	31738	31185	19939	15374	13544
reflections [$I>2\sigma(I)$]	10128	13094	9284	9172	7000	5732
data/restraints/parameters	15751/0/874	31738/0/1765	31185/0/1295	19939/0/1148	15374/0/820	13554/0/775
goodness-of-fit on F^2	1.017	1.028	0.767	1.053	0.851	0.985
final R indices [$I>2\sigma(I)$]	$R1=0.0578$	$R1=0.0745$	$R1=0.0932$	$R1=0.0927$	$R1=0.0750$	$R1=0.1049$
	$wR2=0.1432$	$wR2=0.1806$	$wR2=0.1909$	$wR2=0.2487$	$wR2=0.1781$	$wR2=0.2642$
R indices (all data)	$R1=0.1067$	$R1=0.2162$	$R1=0.2251$	$R1=0.2050$	$R1=0.1397$	$R1=0.2040$
	$wR2=0.16666$	$wR2=0.2446$	$wR2=0.2286$	$wR2=0.3059$	$wR2=0.2011$	$wR2=0.3075$
largest diff peak/hole [e Å^{-3}]	1.189/−1.061	1.011/−0.855	1.526/−0.701	1.016/−1.558	0.985/−0.639	1.250/−0.662

Table 6. Crystal data and structure refinement for supramolecular assemblies **20a**, **21a**, **22a**, **23a** and **24a**.

	20a$[PF_6]_4$	**21a**$[BF_4]_4$·6 CH_2Cl_2	2**22a**$[PF_6]_4$	**23a**$[BF_4]_4$	**24a**$[PF_6]_4$
formula	$C_{148}H_{116}Cu_4F_{24}N_{12}P_8$	$C_{144}H_{108}Cu_4F_{16}N_{12}P_4B_4$· 6 CH_2Cl_2	$C_{288}H_{232}Cu_8F_{48}N_{24}P_{16}$	$C_{144}H_{116}B_4Cu_4F_{16}N_{12}P_4$	$C_{142}H_{114}Cu_4F_{24}N_{14}P_8$
M_r	3020.45	3241.266	6005.05	2739.77	2974.39
a [Å]	20.456(2)	13.893(2)	16.886(2)	14.990(3)	14.825(2)
b [Å]	35.311(3)	15.642(3)	21.426(2)	31.892(5)	31.840(4)
c [Å]	24.437(2)	20.412(3)	22.094(2)	40.379(6)	39.873(6)
α [°]	90	111.880(8)	90.696(5)	90	90
β [°]	99.287(5)	107.299(9)	98.891(5)	90	90
γ [°]	90	102.844(9)	102.940(5)	90	90
V [Å^3]	17420(1)	3641.7(11)	7688(2)	19304(5)	18821(4)
Z	4	1	1	4	4
ρ_{calcd} [Mg m^{-3}]	1.152	1.478	1.297	0.943	1.050
crystal system	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pbcn$	$Pbcn$
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
crystal size [mm]	0.3×0.1×0.03	0.18×0.12×0.05	0.2×0.2×0.1	0.2×0.1×0.03	0.12×0.10×0.03
μ ($Mo_{K\alpha}$) [cm^{-1}]	0.626	0.917	0.710	0.522	0.578
F(000)	6160	1648	3061	5616	6064
θ range [°]	1.02–27.73	1.18–26.42	1.25–26.72	2.77–27.49	1.02–26.17
index ranges	$-26\le h\le 23$	$-17\le h\le 17$	$-21\le h\le 21$	$-18\le h\le 17$	$-18\le h\le 12$
	$-46\le k\le 46$	$-19\le k\le 19$	$-26\le k\le 26$	$-19\le k\le 39$	$-39\le k\le 22$
	$-19\le l\le 31$	$-25\le l\le 25$	$-27\le l\le 27$	$-49\le l\le 49$	$-34\le l\le 49$
reflns collected	158872	35083	99148	81149	93107
independent reflns	40558	14849	31674	19439	18786
reflections [$I>2\sigma(I)$]	12108	11387	16748	7301	5264
data/restraints/parameters	40558/0/1765	14849/0/911	31674/0/1799	19439/0/829	18786/6/807
goodness-of-fit on F^2	0.919	1.076	1.044	0.828	0.792
final R indices [$I>2\sigma(I)$]	$R1=0.0851$	$R1=0.0638$	$R1=0.0972$	$R1=0.0785$	$R1=0.0838$
	$wR2=0.2014$	$wR2=0.1776$	$wR2=0.2751$	$wR2=0.1669$	$wR2=0.2054$
R indices (all data)	$R1=0.2215$	$R1=0.0879$	$R1=0.1495$	$R1=0.1831$	$R1=0.2456$
	$wR2=0.2324$	$wR2=0.2058$	$wR2=0.3002$	$wR2=0.1923$	$wR2=0.2455$
largest diff peak/hole [e Å^{-3}]	0.792/−0.665	1.425/−1.070	1.916/−0.908	1.042/−0.547	0.997/−0.605

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