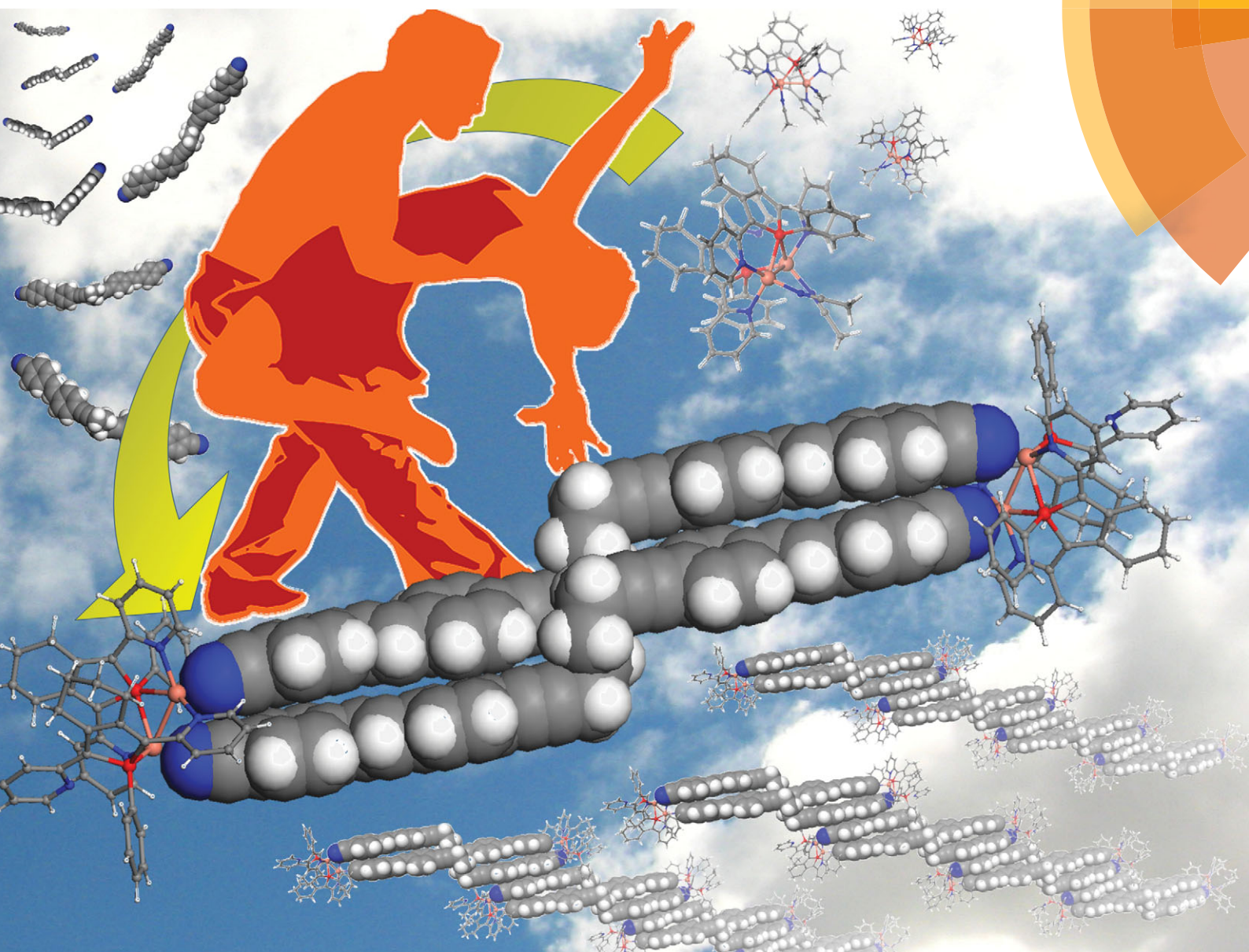


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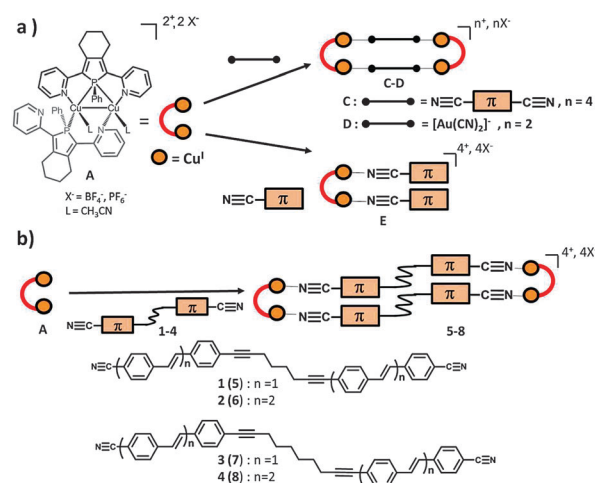
# Supramolecular metallacycles with a 'pseudo double-paracyclophane' structure based on flexible $\pi$ -conjugated linkers†‡

W. Shen, M. El Sayed Moussa, Y. Yao and C. Lescop\*

**The straightforward synthesis of new supramolecular metallacycles having a 'pseudo double-paracyclophane' structure is presented. They are obtained from the reaction of a pre-assembled Cu(I) bimetallic precursor bearing short intermetallic distances with cyano-capped homoditopic  $\pi$ -conjugated linkers having flexible central cores.**

Coordination driven supramolecular synthetic chemistry is a powerful approach for the construction of discrete and stable complex molecular architectures such as macrocycles or cages, a topic which is currently of considerable interest.<sup>1,2</sup> Typically, the design of such coordination-based systems relies on reaction of multitopic metal centers and rigid organic linkers whose symmetry and connectivity are selected considering the overall shape of the target assembly (defining the "Directional-Bonding Approach"<sup>2g</sup>). The associations between these sub-units are directed by non-covalent interactions (metal–ligand bonds, metal–metal interaction...) that have to be strongly directional and kinetically labile to allow reasonably predictable, reproducible and selective syntheses. In so doing the topology of the ensuing products can be reasonably controlled and directed. In this field, we have previously described the general coordination-driven supramolecular synthesis of a series of stacked supramolecular assemblies **C**,<sup>3</sup> **D**<sup>4</sup> and **E**<sup>5</sup> (Scheme 1a). They were obtained from the reaction of the pre-assembled bimetallic Cu(I) U-shape molecular clip **A**<sup>6</sup> (Scheme 1a) bearing a hemilabile bridging phosphane coordination mode for the 2,5-bis(2-pyridyl)phosphole ligand **B**<sup>6</sup> and short intermetallic distances (2.551(1) Å, revealing cuprophillic interactions) with, respectively, a large variety of homoditopic rigid organic  $\pi$ -conjugated linkers, with the metal-based linear linker  $[\text{Au}(\text{CN})_2]^-$  and with a series of cyano-capped monotopic  $\pi$ -conjugated ligands. These results

suggested that the stabilizing non-covalent interlinker lateral interactions ( $\pi$ - $\pi$  interaction, aurophilic interaction) generated within these self-assembled structures could play a key role in the selective coordination driven synthetic processes conducted on pre-assembled polymetallic molecular clip **A** bearing short intermetallic distances, possibly complementing the "Directional-Bonding Approach" syntheses rule. This hypothesis has triggered us to explore whether such specificity of the molecular clip **A** could be exploited allowing a general access to original discrete supramolecular architectures. In this work, we have focused our attention on the reaction of ditopic linkers bearing central flexible fragments and terminal cyano capped  $\pi$ -conjugated moieties with the molecular clip **A** (Scheme 1b). Indeed, employing such flexible donor linkers challenges the coordination driven supramolecular chemistry principles as a loss of a noticeable amount of the pre-programmed assembling information that serves as a basis of product predictivity is generally anticipated.<sup>7</sup> This induces a lower selectivity in self-assembly supramolecular processes resulting in a mixture



**Scheme 1** (a) Molecular structure of the pre-assembled molecular clip **A**, synthesis of the supramolecular assemblies **C–E**; (b) synthesis of the supramolecular metallacycles **5–8** and structure of the linkers **1–4**.

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† Dedicated to the Prof. Dr Manfred Scheer on his 60th birthday.

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of unpredictable products whose yields and relative ratio may mostly depend upon minor experimental variations. This assumption *a priori* weakens the interest of polytopic flexible donor linkers in coordination driven supramolecular syntheses and still a limited number of examples exists that employ such linkers to generate discrete structures.<sup>7</sup>

In a first step, we have focused our attention on the reaction of the molecular clip **A** with the cyano-capped homoditopic linkers **1–4** (Scheme 1b) carrying both 'rigid'  $\pi$ -conjugated systems and 'flexible' linear  $-(CH_2)_n-$  aliphatic moieties of various lengths (shorter (**1,3**) or longer terminal  $\pi$ -systems (**2,4**); shorter,  $n = 4$  (**1,2**) or longer,  $n = 6$  (**3,4**) central aliphatic fragments). The new homoditopic linkers **1–4** were synthesized in medium to good yields according to a sequence of Sonogashira coupling and Wadsworth–Emmons reactions.<sup>8</sup> Their room temperature 1 : 1 reaction in  $CH_2Cl_2$  with the molecular clip **A** afforded after purification the supramolecular assemblies **5–8** (Scheme 1b), respectively, as orange polycrystalline air stable powders in medium to good yields.<sup>8</sup> The derivatives **5–8** are readily soluble in chlorinated solvents ( $CHCl_3, CH_2Cl_2$ ). Their multinuclear NMR characterization<sup>8</sup> indicates that the  $Cu^I_2(B)_2$  moiety is maintained along these reactions. Indeed, the  $^{31}P\{^1H\}$  NMR spectrum of the crude reactions, as well as those recorded for the crystalline samples dissolved in  $CD_2Cl_2$  show singlets at *ca.* +8 ppm that are similar to the signals registered for the precursor **A** as well as those recorded for the supramolecular assemblies **C–E** (Scheme 1a).

Moreover  $^1H$  NMR spectra presented a simple single set of signals, revealing highly symmetrical assemblies **5–8** in which the acetonitrile ligands carried by the molecular clip **A** have been substituted affording molecular species bearing a 1/1  $Cu^I_2(B)_2$ /linker ratio. The molecular structures of the assemblies **5–8** were established by X-ray diffraction studies<sup>8</sup> performed on single crystals<sup>9</sup> obtained at room temperature from pentane diffusion into  $CH_2Cl_2$  solutions. These four derivatives crystallize in the  $P\bar{1}$  space group of the triclinic system (Table S1, ESI†) with an inversion centre located in the centre of the tetracationic derivatives **5–8**. Unexpectedly, in spite of the various lengths of the linkers **1–4** and their flexible aliphatic central cores, assemblies **5–8** are metallocyclophanes formed from the coordination of two flexible linkers on two  $Cu^I_2(B)_2$  moieties (Fig. 1). In these solid state structures, the four  $BF_4^-$  counterions and the co-crystallization  $CH_2Cl_2$  solvent molecules are located outside the self-assembled molecules. In each metallocyclophane, the four Cu(I) atoms lie in the same plane and the metric parameters of the dicationic  $Cu^I_2(B)_2$  cores are very similar to those of the corresponding free molecular clip **A** and related tetracationic  $\pi$ -stacked rectangles **C** (Table S2, ESI†)<sup>3</sup> suggesting a strain-free coordination of the linkers **1–4** on the  $[Cu_2(B)_2]^{2+}$  units. In these assemblies, the  $-(CH_2)_n-$  central aliphatic strings have different configurations, reflecting their relative flexibility (Fig. 1): in the case of the derivative **5**, a *gauche* configuration is observed for each aliphatic chain of the two linkers **1** while in the metallocycles **6–8** the two aliphatic fragments are

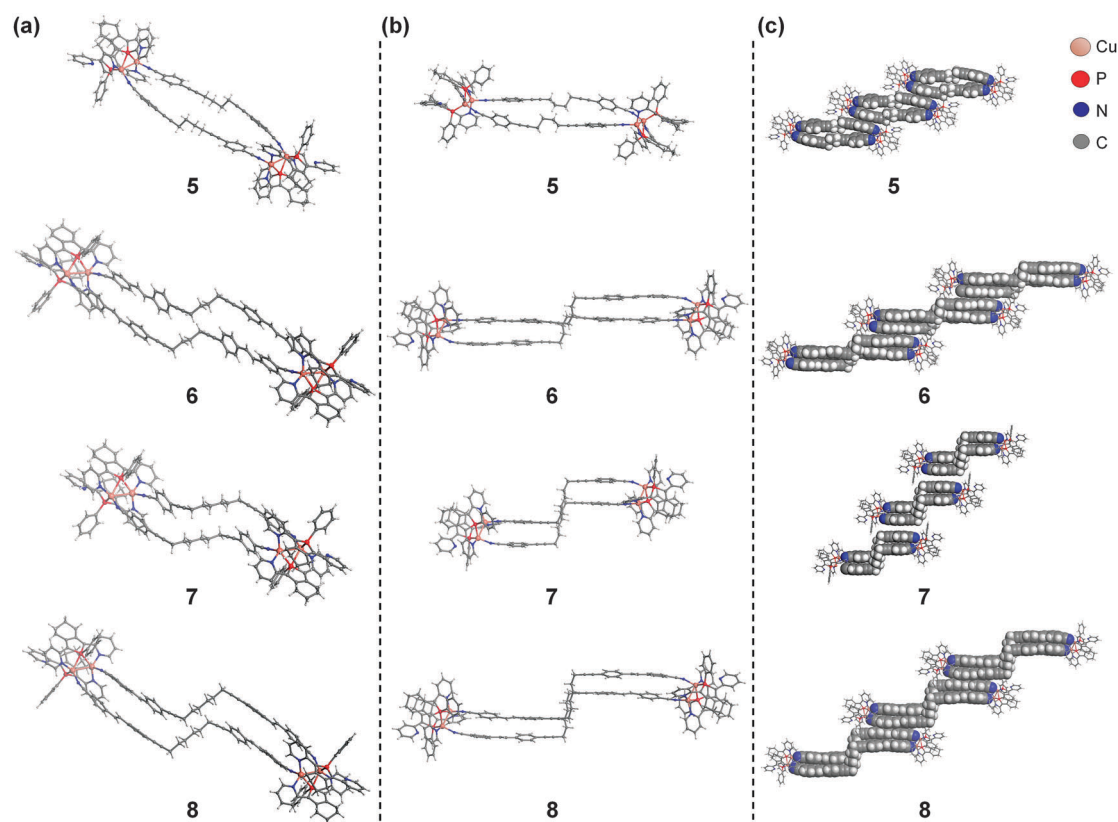


Fig. 1 (a) General and (b) lateral views of the X-ray crystal structures of the tetracationic supramolecular metallocycles **5–8**; (c) view of the stacking patterns of **5–8** observed in single crystals. (counteranions and solvent molecules have been omitted for clarity).



mostly parallel with an 'eclipsed' configuration. No short contacts are observed between the central aliphatic strings. Probably as a result of a steric congestion of the imbricated  $-(CH_2)_n-$  fragments located in the central part of the metallocyclophanes, the lateral offset of the neighbouring  $\pi$ -systems is larger within derivatives **5–8** than in the supramolecular rectangles **C**, but it does not forbid intramolecular  $\pi$ - $\pi$  interaction to occur. The  $\pi$ - $\pi$  interaction is weak in the case of assembly **5** (quite large inter  $\pi$ -planes distances, *ca.* 3.7 Å, and limited area of  $\pi$ -surface involved are observed; see Fig. S7, ESI†) but it is more significant for derivative **7** based on the same short  $\pi$ -systems but having a longer and 'eclipsed' aliphatic central fragments. Assemblies **6,8** based on linkers having longer  $\pi$ -systems exhibit very similar features: the  $\pi$ -conjugated fragments are almost planar (maximum deviation to the mean plane: **6**, 0.252 Å; **8**, 0.209 Å), parallel (angle between the mean plane of two interacting  $\pi$ -moiety: **6**, 5.22°; **8**, 1.71°) and participate in similar  $\pi$ - $\pi$  interactions (inter  $\pi$ -plane distances: *ca.* 3.4–3.5 Å) with a large area of their surface involved (see Fig. S7, ESI†). Therefore in these assemblies, despite the different configurations exhibited by the aliphatic moieties of the linkers, the  $\pi$ -fragments of the homoditopic linkers participate to intramolecular  $\pi$ - $\pi$  interaction, similarly to what is observed in the metallocyclophanes **C**<sup>3</sup> (Scheme 1a). As a result, solid state arrangement of the aliphatic and aromatic fragments of the ligands **2–4** in self-assembled derivatives **6–8** induces the formation of an unprecedented 'pseudo double-paracyclophane' structure (see Fig. 1b) having large lengths (**6**, 52.4 Å; **8**, 52.3 Å). In addition, a remarkable feature observed in the solid state structure of most of the  $\pi$ -stacked supramolecular assemblies of type **C** and **E** (Scheme 1a) is their self-organization within infinite  $\pi$ -stacked columns due to intermolecular  $\pi$ - $\pi$  interactions,<sup>3</sup> affording a very general approach to arrange symmetrical linear  $\pi$ -conjugated organic systems in infinite molecular networks in which all the  $\pi$ -systems overlap. Interestingly, intermolecular  $\pi$ - $\pi$  interactions (inter  $\pi$ -plane distances: *ca.* 3.3–3.5 Å) are also observed in the solid state structure of the derivatives **5**, **6** and **8** leading to the supramolecular organization of these self-assembled metallacycles in infinite columns bearing discrete stacks of four aromatic moieties separated by imbricated  $-(CH_2)_n-$  fragments (Fig. 1c).<sup>10</sup>

In order to confirm the critical importance of the  $\pi$ -conjugated fragments in the core of the linkers **1–4** to drive the formation of supramolecular metallacycles **5–8**, we carried out a reaction of the molecular clip **A** with the cyano-capped homoditopic linkers **9**, **10** bearing only  $-(CH_2)_n-$  cores. Reaction of adiponitrile ( $n = 4$ ) **9** (Fig. 2a) with the molecular clip **A** in  $CH_2Cl_2$  in a 1 : 1 ratio afforded derivative **11** (71% yield),<sup>8</sup> which was characterized by an X-ray diffraction study.<sup>9</sup> This compound is a one dimensional coordination polymer (Fig. 2b) in which two consecutive  $Cu^I_2(B)_2$  fragments are connected by one linker **9**. The 1 : 1 reaction of the precursor **A** with the longer linker suberonitrile ( $n = 6$ ) **10** afforded good yields after treatment of clear orange powders with the derivative **12**. Conversely to **11**, the compound **12** is readily soluble in chlorinated solvents and NMR spectroscopies<sup>8</sup> suggest that during this reaction only a partial substitution of the acetonitrile ligands carried by the  $Cu^I_2(B)_2$  fragment in **A** occurred. This is confirmed by the crystal structure of **12**, determined from single crystals grown by pentane vapour diffusion in  $CH_2Cl_2$  solutions of **12**.<sup>8</sup> In contrast to the

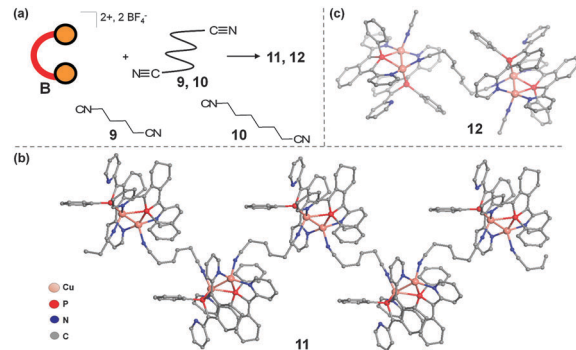


Fig. 2 (a) Synthesis of the derivatives **11** and **12**. (b) X-ray crystal structures of (b) the cationic coordination polymer **11** and (c) the tetracationic derivative **12** (H atoms, counteranions and solvent molecules have been omitted for clarity).

polymeric assembly **11**, the derivative **12** is a molecular species in which two  $Cu^I_2(B)_2$  fragments are connected due to the coordination of one equivalent of the linker **10** on one metal center of each  $Cu^I_2(B)_2$  fragment while the second  $Cu^I$  metal center is still coordinated to an acetonitrile ligand (Fig. 2c). Note that up to 10 equivalents of **10** were reacted with the molecular clip **B** but the derivative **12** was the only species that was obtained in the solid state. Finally, derivatives **11** and **12** are isolated in the solid state as no specific intermolecular contacts between isolated molecular entities are observed. Although the  $(Cu^I)_2$  nodes retain a U-shape topology in the assemblies **11** and **12** no metallacycle is formed showing that the geometry of the bimetallic molecular clip **A** is not directing exclusively the formation of metallacycle structures. These solid state structures confirm that the molecular clip **A** does not present any specific proneness to afford systematically supramolecular metallacycles due to its reaction on homoditopic linkers and highlight the key role played by the intramolecular  $\pi$ - $\pi$  interactions between the  $\pi$ -walls of the linkers to allow the selective formation of supramolecular metallacycles based on the flexible linkers **1–4**.

These results demonstrate that according to a rational design of the individual molecular building blocks, the synthesis rules requested to apply a coordination-driven supramolecular synthesis can be supplemented by the intentional occurrence of non-covalent lateral  $\pi$ - $\pi$  interactions between the assembled subunits to give a general access to original supramolecular assemblies. This is allowed due to the use of pre-assembled polymetallic molecular clip bearing specific molecular organizations such as those encountered in the U-shape molecular clip **A** (short intermetallic distances, structural rigidity and hemilability of the N,P,N ligand **B**).<sup>3</sup> In the near future, the versatility of this approach will be studied, extending the scope of the polytopic linkers used with the variation of the "ratio" rigid/flexible fragment, of the nature of the flexible moiety and of the connectivity of the linkers. The characterisation of a large series of new discrete supramolecular assemblies bearing original structural features and functionalities is expected.

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- For experimental details, spectroscopic and X-ray diffraction data, see ESI†.
- Careful examination of the several crystallization batches and unit cell determination of single crystals randomly selected did not evidence the formation of other polymorphs.
- Concerning the assembly 7, solid state intermolecular distances between the  $\pi$ -moieties of the linkers 3 (ca. 4.8 Å) are too large for intermolecular  $\pi$ - $\pi$  interactions.