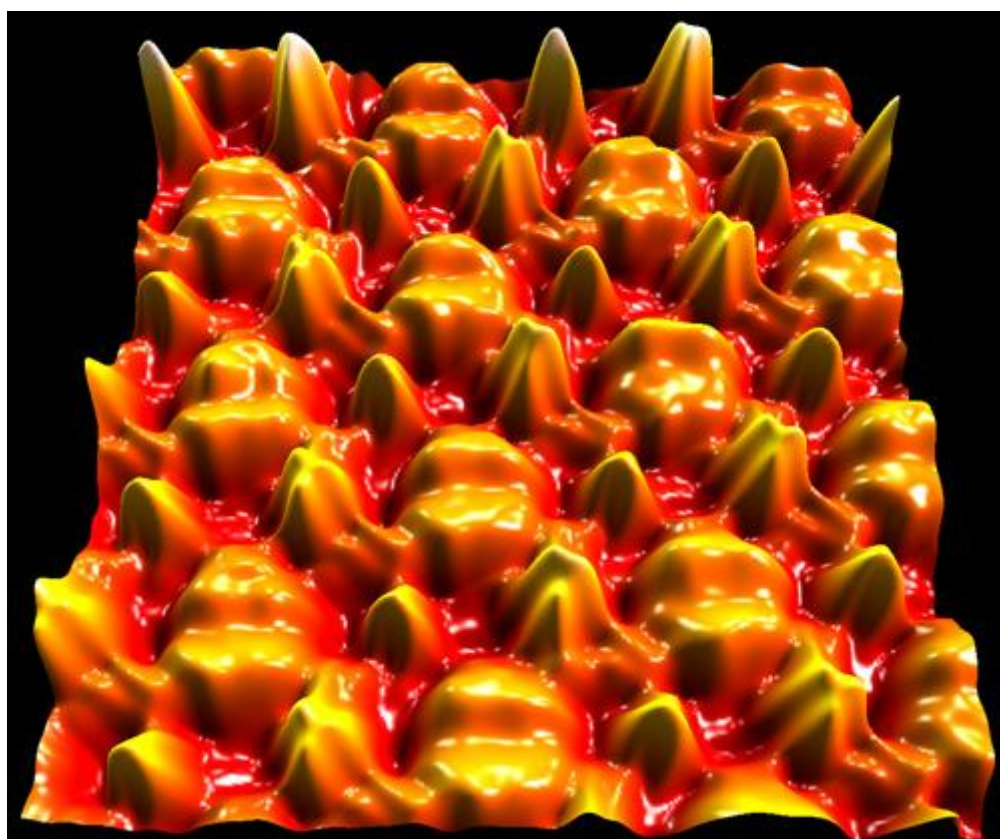# ChemComm

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**COMMUNICATION**

# Selective supramolecular assembly of multifunctional ligands on a Cu(111) surface: metallacycles, propeller trimers and linear chains†‡

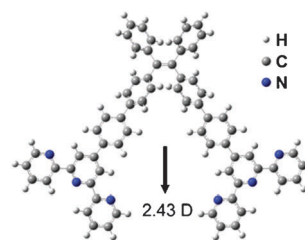**Weihua Wang,**[*a] **Shiyong Wang,**[a] **Yuning Hong,**[b] **Ben Zhong Tang**[b] **and Nian Lin**[a]

**We studied the supramolecular assembly of a multifunctional ligand, *cis*-bis-terpyridine tetraphenyl ethylene, on a Cu(111) surface by low-temperature scanning tunneling microscopy (STM). Three distinctive supramolecular structures, metallacycles, propeller-shaped clusters and extended linear chains, are formed under specific assembly conditions owing to different inter-molecular binding modes of Cu-coordination, van der Waals interaction and hydrogen bonding, respectively.**

There has been a rapid advancement in the fabrication of novel architectures making use of supramolecular self-assembly.[1–4] A large variety of specific binding modes has been explored offering the possibility to form supramolecular architectures of polygonal clusters, polyhedra, cages, grids, polymers and frameworks whose structure (size and shape) can be precisely controlled.[5–11] For molecules possessing multifunctions, *i.e.*, capable of invoking multiple inter-molecular interactions, the supramolecular organizations are determined by either a dominant binding mode or multiple interactions. In order to realize specific supramolecular structures, it is required to "select" an inter-molecular interaction which plays a dominant role in the self-assembly.

In this report, we demonstrate how to control the two-dimensional (2D) supramolecular assembly of a multifunctional molecular ligand on a Cu(111) surface by providing conditions where one specific intermolecular interaction dominates the self-assembly.[12–18] The molecule is bis-terpyridine tetraphenyl ethylene§ (BTP-TPE, as shown in Scheme 1). It contains two terminal terpyridine (*tpy*) groups and a central tetraphenyl ethylene (*tpe*) group which is linked to the terminal *tpy* groups through two phenyl (*ph*) groups. The *tpy* groups take a conformation in which the two N atoms in the side pyridine rings point outside,[19] as shown in Scheme 1. The *tpy* group is known to coordinate with various metal ions.[20–26] This function also provides an acceptor (N of the pyridyl) for the hydrogen

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Scheme 1 *cis*-BTP-TPE molecule. The arrow indicates the DFT calculated dipole moment of 2.43 D.

bond. The *tpe* group gives rise to two molecular conformations: *trans*- and *cis*-isomers (*cf*. Scheme 1). The assembly of *trans*-isomers has been reported before.[25,26] In this study, we focus on the supramolecular self-organization of the *cis*-isomer. A density-functional theory (DFT) calculation shows that a *cis*-BTP-TPE molecule has a dipole moment of 2.43 D along the molecular symmetry axis (*cf*. Scheme 1), which may contribute to intermolecular van der Waals interaction. We found that under different self-assembly conditions the molecules assemble as three distinctive supramolecular structures: in the presence of Cu atoms, trimeric metallacycles that are stabilized by Cu-*tpy* coordination appear;[14,27–29] in the absence of Cu adatoms, propeller-shaped trimeric clusters that are stabilized by van der Waals interaction appear at low molecular coverage, while at high molecular coverage, an extended linear chain structure stabilized by inter-molecular hydrogen bonds appears.

On the Cu surface there exists two-dimensional gas of freely moving Cu adatoms whose density can be controlled by changing the surface temperature.[30] When the molecules were deposited with low molecular deposition rate (∼0.013 ML min⁻¹, 1 ML is defined as the surface fully covered by the flat-lying molecules) on the Cu(111) substrate which was held at room temperature, the Cu adatom density was sufficiently high so that the *tpy* endgroups of the molecules were coordinated by Cu effectively. In the presence of Cu adatoms, the molecules were connected through *tpy* groups by Cu-coordination. As a result, metallacycles were formed by the *cis*-isomers of the BTP-TPE molecules. In Fig. 1(a) several triangle-shaped metallacycles are highlighted by circles. Note that under the same sample preparation conditions, *trans*-BTP-TPE molecules form chain-like structures in which the neighboring *tpy* groups are connected by the same type of Cu-coordination.[25] Fig. 1(b) shows a high-resolution STM image of a metallacycle. The metallacycle structure has
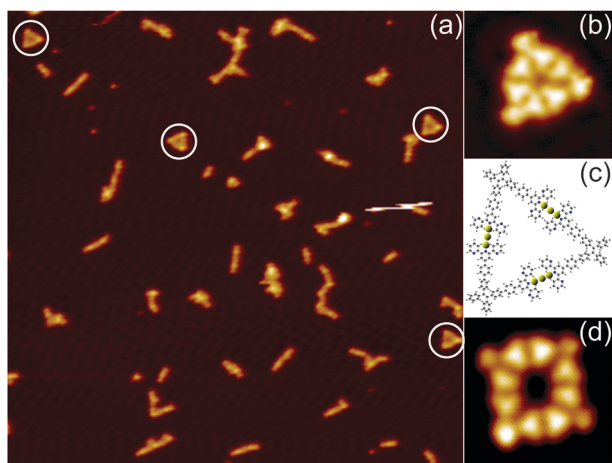
**Fig. 1** (a) (108 nm × 108 nm, −1.5 V, 0.5 nA) Large-scale STM image showing the triangular metallacycles (highlighted by circles) formed by *cis*-BTP-TPE molecules on the Cu(111) surface. (b) (8 nm × 8 nm, −0.2 V, 0.5 nA) High-resolution STM image of a triangular metallacycle formed by three *cis*-BTP-TPE molecules through coordination with Cu adatoms. (c) Structural model of the triangular metallacycle. (d) (8 nm × 8 nm, −0.2 V, 0.5 nA) High-resolution STM image of a square metallacycle formed by four *cis*-BTP-TPE molecules.

$C_{3v}$ symmetry. One can see that it is formed by 3 *cis*-BTP-TPE molecules with their *tpy* groups connected to each other in a head-to-head manner, and the *tpe* groups are located at the vertices of the triangle. Scanning tunneling spectroscopy experiments reveal that the *tpy* groups in the metallacycle have an electronic state in the range of 0.86 V to 1.06 V†, evidencing that the *tpy* groups are coordinated with Cu atoms.[25,26] DFT calculations suggest that there are three Cu adatoms between two neighboring *tpy* groups.[25] We propose a structural model of the triangular metallacycles as depicted in Fig. 1(c). Since the two *tpy* groups in a *cis*-molecule take an angle of about 60°, metallacycle consisting of three molecules in an equilateral triangle geometry is the most stable structure. Besides triangular metallacycles, square metallacycles composed by four molecules as shown in Fig. 1(d) were also observed. The square metallacycles are very rare, implying that they are energetically unfavored. Presumably for forming the square the two *tpy* groups of the *cis* molecules have to take a 90° angle which stresses the molecules.

When the molecules were deposited with high deposition rate (0.48 ML min$^{-1}$) on the Cu(111) substrate held at 200 K, the density of the Cu adatoms gas was significantly reduced (the density depends on the temperature exponentially), so the Cu-*tpy* coordination was suppressed and other types of inter-molecular interactions are expected to play dominant roles in supramolecular assembly. (The molecular deposition rate also plays a crucial role in the supramolecular assembly. The probability of Cu-coordination is suppressed at higher deposition rate and enhanced at lower deposition rate.) The molecular mobility on the Cu(111) surface is appreciable even at 200 K allowing the self-assembly process to take place.[25] At low molecular coverage (∼0.2 ML), propeller-shaped clusters were observed, as shown in Fig. 2(a). Each cluster consists of three molecules that are packed in a spiral arrangement. The three molecules are packed either into a clockwise or a counter-clockwise spiral. Fig. 2(b) shows two clusters of
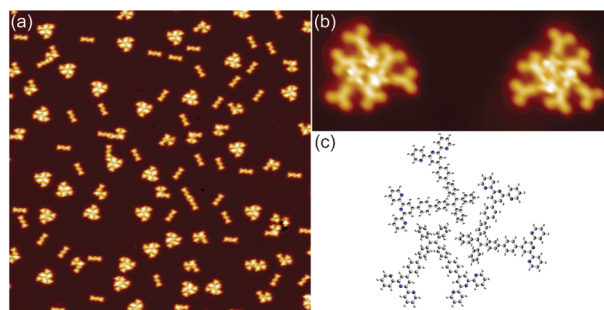


**Fig. 2** (a) (80 nm × 80 nm, −0.2 V, 0.5 nA) Large-scale STM image showing the assembly of low-coverage (0.2 ML) BTP-TPE molecules on the Cu(111) surface. (b) (6 nm × 15 nm, −0.2 V, 0.5 nA) High-resolution STM image of two propeller clusters of different chiralities. (c) Structural model of the propeller cluster in clockwise spiral.

different chiralities. In each cluster, the *tpe* group of a molecule points to the flank of the *tpy* arm, *i.e.*, the *ph* group, of the neighboring molecule. Based on the high-resolution STM data and the structural model (*cf.* Fig. 2(c)), we estimate that the distance between a N atom and the nearest H atom of the neighboring molecules is in the range of 3.3 Å to 3.6 Å, suggesting rather weak inter-molecular hydrogen bonding. Since the molecules in the propeller structure are spatially separated, π–π stacking between phenyl rings of neighboring molecules can be excluded. The 2.43 D molecular dipole moment (*cf.* Scheme 1) suggests that the molecules in the propeller clusters are further stabilized by a van der Waals interaction. It is worthwhile to note that the *trans*-BTP-TPE, which is non-polar, does not aggregate into such propeller clusters. The uniform size of three molecules per cluster can be understood as the following: in the propeller cluster, the three molecules are closely packed in a way that inter-molecular interaction is optimized. In contrast, a dimeric cluster is not stable due to the steric open sites. For a cluster consisting of four or more molecules, the inter-molecular interaction is weakened since the molecules cannot be packed as intimately as in the propeller structure.

When the molecular coverage was increased to ∼0.5 ML under the same preparation conditions, *i.e.*, the deficiency of Cu adatoms, the molecules assembled as extended linear chains along with the propeller clusters, as shown in Fig. 3(a). The chains follow the [11$\bar{2}$] directions of the Cu(111) surface. Fig. 3(b) shows a high-resolution STM image of the chain structure, revealing that the chain consists of double-row molecules organized in a staggered manner. Based on the sub-molecular resolution STM images, we propose a structural model of the chain as shown in Fig. 3(c). The molecules in the same row point to the same direction and they are at an angle of 60° with respect to the molecules in the neighboring row. In the staggered arrangement, the *tpy* group of a molecule approaches the *tpe* group of a neighboring row molecule with a N–H distance of ∼1.8 Å. (Note this value is estimated by superposing the free molecular model to the STM image.) This distance allows forming an appreciable N···H–C hydrogen bond. Thus we propose that the molecules in the neighboring rows within a chain are linked by N···H–C hydrogen bonds.[31,32]

In the propeller clusters, all *tpy* groups point outwards. These groups are positively charged due to the molecular dipole, so the
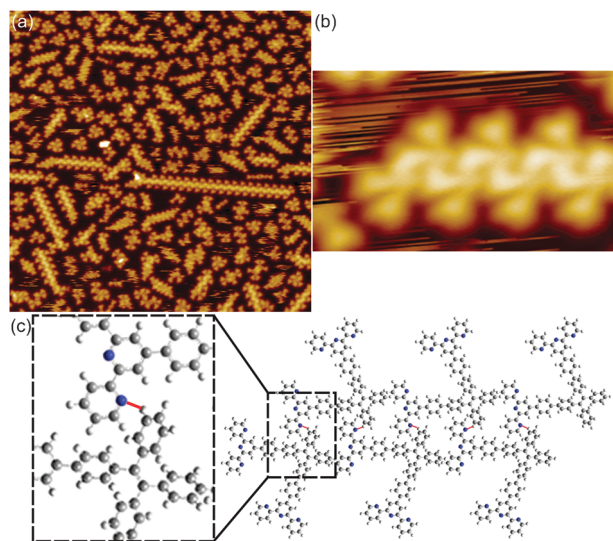
**Fig. 3** (a) (80 nm × 80 nm, −1.6 V, 0.5 nA) Large-scale STM image showing the assembly of high-coverage (0.5 ML) BTP-TPE molecules on the Cu(111) surface. (b) (6 nm × 12 nm, 1.4 V, 0.5 nA) High-resolution STM image of a section of a chain. (c) Structural model of the chain. The hydrogen bonds between neighbouring molecules are indicated by red lines. The dashed rectangle highlights the N···H–C hydrogen bonding.

periphery of the propeller cluster is positively charged. This charge distribution results in a long-range Coulomb repulsion between the propeller clusters. This repulsive interaction is evidenced by the fact that the clusters shown in Fig. 2(a) are distributed sparsely. At higher molecular coverage, the separation between the clusters is reduced, which will lead to enhanced repulsion. An effective way to reduce this repulsion is the formation of the extended chain-like structure since the molecules incorporated in the chains do not repel each other. So, the 1D chain structure emerges at high molecular coverage.

In summary, the supramolecular self-organization of *cis*-BTP-TPE is investigated by low-temperature STM. Supramolecular assemblies of distinctive topologies including triangular metallacycles, propeller trimeric clusters and extended linear chains are selectively formed under specific conditions. Each structure is stabilized by a dominant inter-molecular interaction such as metal–ligand coordination, van der Waals interaction or hydrogen bonding.

## Notes and references

§ The molecule was synthesized as reported.[25] The molecules (in powder form) were evaporated under ultra-high vacuum from a molecular beam evaporator at 405–425 K. The Cu(111) substrate was held at 300 K or 200 K during deposition. After deposition the sample was immediately transferred into the low-temperature STM. The sample was studied by STM at 77 K or 4.9 K.

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