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Symmetry decrease between self-assembled circular TiO₄N₂-based helicates

Georges Khalil,^[a] Laurent Barloy,^[a] Nathalie Kyritsakas,^[b] Brice Kauffmann,^[c] Alain Chaumont,^{[a], [d]} Marc Henry,^[a] Pierre Mobian,^{*,[a]}

- [a] Dr G. Khalil, Dr L. Barloy, Prof. Dr. M. Henry, Dr. P. Mobian, Laboratoire de Chimie Moléculaire de l'Etat Solide, UMR 7140 UDS-CNRS, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France.
E-mail: mobian@unistra.fr; <http://complex-matter.unistra.fr/equipes-de-recherche/laboratoire-de-chimie-moleculaire-de-letat-solide/accueil/>
- [b] N Kyritsakas Laboratoire de Tectonique Moléculaire, UMR 7140 UDS-CNRS, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France.
- [c] Dr. B. Kauffmann, Univ. Bordeaux, IECB, UMS 3033/US 001, 2 rue Robert Escarpit, 33607 Pessac, France
- [d] Dr. A. Chaumont, Laboratoire de Modélisation et Simulations Moléculaires, UMR 7140 UDS-CNRS, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France.

Abstract: A multicomponent self-assembly reaction involving a bis-biphenolato ligand (LH₄), a 2,2'-bipyrimidine chelate substituted by two (anthryl)vinyl moieties (bAnt) and Ti(OⁱPr)₄ was investigated. An assembly ([Ti₃(L)₃(bAnt)₃]), composed of three homochiral TiO₄N₂ nodes, was characterized as being the thermodynamically-end product. The crystal structure of this circular helicate highlighted an absence of symmetry for this compact compound. DOSY ¹H NMR indicated that the nuclearity observed in the solid-state for [Ti₃(L)₃(bAnt)₃] was maintained in solution. An intermediate formulated as [Ti₄(L)₄(bAnt)₄] was isolated. The structural analysis revealed that [Ti₄(L)₄(bAnt)₄] was a symmetrical circular hollow helicate composed of four homochiral metallovertices. This study, supported by DFT calculation, brought some evidences on the sequences and the reasons leading to the symmetry decrease for this self-assembly process.

Self-assembly processes driven by transition metals are highly powerful methods to access complex architectures.^[1] These self-assembled architectures, which are impossible to obtain through conventional step-by-step synthetic strategies, result from the mutual programmed recognition between metal ions and organic ligands. An impressive number of rationally designed helicates,^[2] cages,^[3] squares,^[4] spheres,^[5] grids,^[6] topological non-trivial molecules^[7] and other architectures^[8] have been reported so far. Whereas the main interest in self-assembly is focused on the thermodynamically-end products, the characterization and the isolation of intermediate architectures generated during the self-assembly is rather scarce.^[9] This is mainly linked to the low energy barriers existing between each transient compounds. However, it is an important issue since the full identification of intermediates could provide fundamental information to apprehend some mechanistic aspects of a self-assembly reaction. Therefore, the isolation and characterization of one or several intermediates produced in the course of a self-assembly process is a challenging and major task.^[10]

Over the latest decade, our group has developed a titanium(IV)-based coordination chemistry involving a bis-biphenolato ligand named as LH₄ as shown in Chart 1, leading to neutral self-assembled helical structures.^[11,12] By following a multicomponent self-assembly approach with the 2,2'-bipyrimidine (bpym) chelate, a circular trinuclear bowl-shaped helicate constructed around octahedral TiO₄N₂ motifs, [Ti₃(L)₃(bpym)₃], was generated.^[13] This study also highlighted the formation of a tetranuclear intermediate ([Ti₄(L)₄(bpym)₄]) detected only by mass-spectrometry and ¹H NMR.

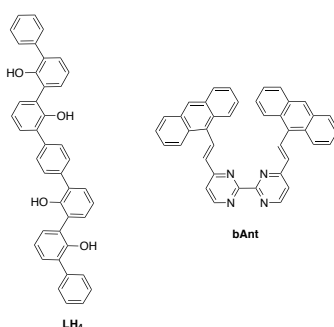


Figure 1

In an extension of this metallo-supramolecular chemistry based on a TiO₄N₂ motif, we report herein the synthesis of a trinuclear assembly through a multicomponent self-assembly approach involving LH₄ and a 2,2'-bipyrimidine chelate substituted by two (anthryl)vinyl moieties (bAnt) (Figure 1).^[14] The large substituents that decorate the 2,2'-bipyrimidine backbone are expected to influence the structure and / or the nuclearity of the final self-assembled product. Compounds LH₄, bAnt and Ti(OⁱPr)₄ reacted in an equimolar amount in dry toluene at 100 °C under solvothermal conditions as described in equation 1.



An orange solid was formed during the reaction. The composition of this solid was analysed at regular intervals. After two days of reaction, the solid was isolated and dissolved in CD_2Cl_2 . The resulting ^1H NMR spectrum was highly complex in the aromatic region and did not permit to extract useful information about the composition of the solution. However, by DOSY NMR analysis, only a single diffusion was measured at $D = 400 \pm 40 \mu\text{m}^2 \text{s}^{-1}$ for the medium reflecting the high selectivity of the reaction (see SI). According to the Stokes-Einstein equation, a hydrodynamic radius of $R_h = 11.8 \pm 1.1 \text{ \AA}$ was found for this species. A molecular volume of $6900 \pm 700 \text{ \AA}^3$ was determined for this assembly in solution when a spherical model was applied for calculation. Comparatively, a volume of $1900 \pm 200 \text{ \AA}^3$ of a previously reported monomeric titanium (see SI)^[15] complex was calculated from its crystal structure with the PACHA software.^[16] This monomeric complex incorporated the bAnt ligand and two 6,6'-diphenyl-2,2'-biphenolato ligands. This volume corresponded to a volume three times inferior to the one determined for the molecule resulting from eq. 1. Therefore, the formation of a compound formed with three TiO_4N_2 motifs was anticipated. The solid was also submitted to ESI-MS analysis. The spectrum is given in figure 2. At high m/z , only one species was detected. Two peaks were observed at $m/z = 2490.64$ and $m/z = 1808.54$ that corresponded according the simulated isotopic profile to the formulas $[\text{Ti}_3(\text{L})_3(\text{bAnt})\text{H}]^+$ (calcd $m/z = 2490.62$) and $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3\text{H}_2]^{2+}$ (calcd $m/z = 1808.53$) respectively.

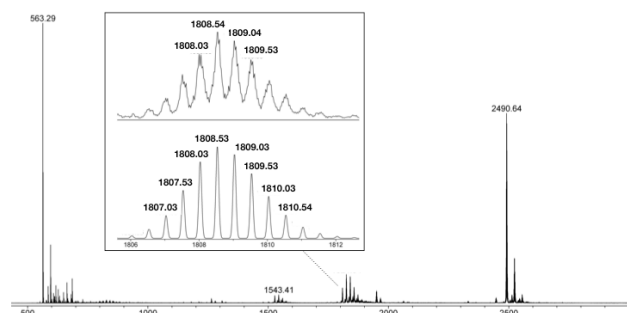
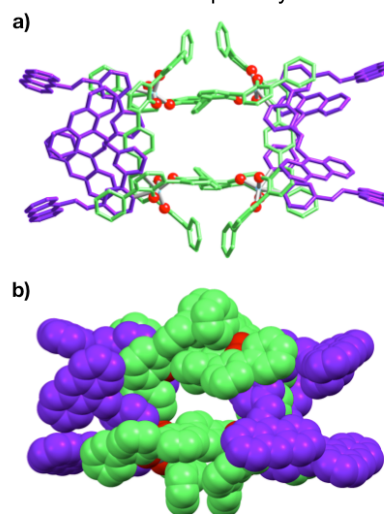


Figure 2. ESI-MS spectrum of the self-assembly reaction solution obtained after two days at 100°C . The enlargement shows the experimental and the simulated isotopic profile for the peak at $m/z = 1808.54$.

Through a careful inspection of the crystalline solids, single crystals suitable for X-ray analysis were found. Figure 3 shows two views of the crystal structure resolved for the complex. This structure confirmed the conclusion drawn from the solution studies since the structure of a complex formulated as $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ was determined. The complex crystallizes



in the centrosymmetric $P-1$ space group with two molecules per unit cell. This compact compound (Fig 3b) is characterized by homochiral octahedral metal vertices. Also, the bis-biphenolato strand arrangement within this structure induces a helical chirality for the complex. Thus, in the unit cell the $M-\Delta, \Delta, \Delta$ and $P-\Lambda, \Lambda, \Lambda$ enantiomers are found. In this compact architecture (Fig 2b), all the anthryl groups point outside the cyclic framework defined by the $\text{Ti}_3(\text{L})_3$ motif and the absence of symmetry for the whole structure is characterized (C_1). Overall, this means that substituents decorating the bpym chelate deeply influence the symmetry of the trinuclear architecture, since the bowl-shaped trinuclear species formed with the unsubstituted bpym ligand, e.g. $[\text{Ti}_3(\text{L})_3(\text{bpym})_3]$, displays a C_3 symmetry in solution and in the solid-state.^[13] The reaction performed in toluene was repeated but this time the media were heated for less prolonged periods (3 hours, 6 hours and 24 hours). In both cases, a solid was formed in a very low amount. The solids and the solutions were analysed by ESI-MS. Both spectra displayed peaks assigned to the free ligands. Nevertheless, for the spectrum of the solution (3 hours), two peaks corresponded to the $[\text{Ti}(\text{LH}_2)_2(\text{bAnt})]$ species were found (calcd. for $[\text{Ti}(\text{LH}_2)_2(\text{bAnt})\text{H}]^+$: $m/z = 1804.57$) (see SI), hinting that $[\text{Ti}(\text{LH}_2)_2(\text{bAnt})]$ was an early intermediate of the self-assembly process. Remarkably, in the solid obtained after 24 hours, a crystal suitable for X-Ray analysis was extracted. Figure 3 displays the crystal structure of the complex. The resolved structure reveals a compound incorporating four TiO_4N_2 units formulated as $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ (CCDC number 1998489). This circular tetranuclear helicate, which counts 572 atoms, adopts in the solid state a D_2 -symmetry with the four metallo-corners showing the same chirality. The two stereoisomers, $M-\Delta, \Delta, \Delta, \Delta$ and $P-\Lambda, \Lambda, \Lambda, \Lambda$, are found in the unit

cell. The spacefill model of $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ (Fig 4b) attests to a large assembly characterized by a voluminous central cavity.

The crystals of $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ and $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ had a very low diffracting power, consequently the high R_1 parameters of the resolved crystal structures were too high to afford accurate metrical parameters. Therefore, the crystal structures were used as a starting point to generate computed molecular models. The $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ and $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ architectures were modelled in the gas phase using density functional theory (DFT) (see SI).

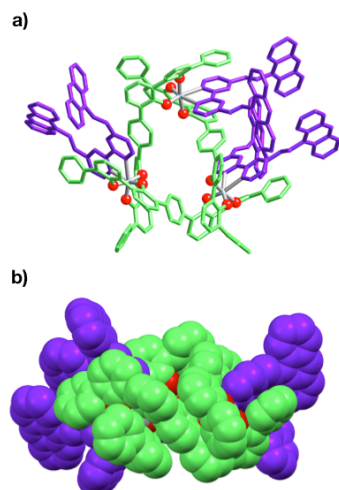
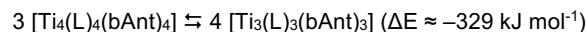


Figure 3. Two views of the solid-state structure of $M\text{-}\Delta,\Delta,\Delta\text{-}[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ obtained from single-crystal X-ray crystallography (ball and stick model in a), spacefill model revealing the compactness of the structure in b)). H atoms are omitted for clarity. Ti atoms are in blue, O atoms are in red, the L strands are in green and the bAnt ligands are in purple.

Figure 4. Two views of the solid-state structure of $M\text{-}\Delta,\Delta,\Delta\text{-}[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ obtained from single-crystal X-ray crystallography (ball and stick model in a), spacefill model in b)). H atoms are omitted for clarity. Ti atoms are in blue, O atoms are in red, the L strands are in green and the bAnt ligands are in purple.

These models are very close to the experimental structures. Like the crystal structures shown, the $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ and the $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ models are tetranuclear and trinuclear helicates respectively. Interestingly, the molecular models computed in a gas phase show also a loss of symmetry going from the tetrameric to the trimeric aggregate. The computed model of $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ displays a C_2 -symmetry that represents a decrease of symmetry related to its solid-state structure. Nevertheless, the $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$ model is still characterized by the absence of symmetry. In $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$, the intermetallic distances are consistent with a C_2 symmetry as the quadrilateral formed by the four titanium atoms within $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ display two opposite identical sides ($d(\text{Ti-Ti}) = 9.414 \text{ \AA}$), whereas the two other sides are measured at $d(\text{Ti-Ti}) = 9.173 \text{ \AA}$ and 9.016 \AA . A volume of $\approx 400 \pm 50 \text{ \AA}^3$ for the internal cavity within $[\text{Ti}_4(\text{L})_4(\text{bAnt})_4]$ is estimated from its computed model. For $[\text{Ti}_3(\text{L})_3(\text{bAnt})_3]$, the three metals are disposed forming a triangle having all different sides ($d(\text{Ti-Ti}) = 8.156 \text{ \AA}$, 8.771 \AA and 9.577 \AA). The metrical analysis of the coordination spheres of these models reveals that the Ti-O and Ti-N distances are similar for both complexes and these distances are in line with those found in related architectures (Table 1 in SI). Also, this analysis points out that the Ti-O bonds are much shorter than the Ti-N bonds, which is an expected feature for TiO_4N_2 -based species.

Next, the total energies associated of two modeled structures were determined to be $E([\text{Ti}_3(\text{L})_3(\text{bAnt})_3]) = -11202.1722086 \text{ Ha}$ and $E([\text{Ti}_4(\text{L})_4(\text{bAnt})_4]) = -14936.1877512 \text{ Ha}$. This permitted to evaluate the total energy change ΔE occurring upon transformation of tetramers into trimers:



This means that the low-symmetry trinuclear assembly was significantly more stable than the high-symmetry tetranuclear architecture. This rises the interesting question of the driving factors favoring such symmetry lowering. From a thermodynamical standpoint, such a structural rearrangement could be favored for energetic and/or entropic reasons. First, existence of a rather larger central cavity in the tetramer relative to the trimer means that more solvent molecules are doomed to be immobilized in the tetramer. Upon transformation into a trimer, such immobilized molecules are freed, conferring a large positive entropy change for the tetramer to trimer transformation. A large positive change in entropy is thus expected in favor of the trimer. Second, from DFT calculations, we know that the trimer is also the more stable configuration. In order to get a clue about the reasons for destabilization of the tetramer, we have considered three different kind of interactions: total nuclei-nuclei repulsions (N-N), total nuclei-electrons attractions (N-E) and total electron-electron repulsions (E-E). Now, considering that the trimer contributes to 66 Ti-valence electrons against 88 for the tetramer, we may compare the average interaction energy per Ti-atom in the trimer ($-169.729882 \text{ Ha Ti}^{-1}$) versus the same interaction in the tetramer ($-169.72940625 \text{ Ha Ti}^{-1}$). The difference of $-1.25 \text{ kJ mol}^{-1} \text{ Ti}^{-1}$ in favor of the trimer shows that the energetic stabilization is scarcely governed by Ti-atoms. But, if we include the electronic contributions due to the ligands, we have 1877 electrons interacting in the trimer against 2724 electrons in the tetramer. Comparing the average interaction energy per electron in the trimer (-5.968 Ha e^{-1}) versus the same interaction in the tetramer (-5.424 Ha e^{-1}), we obtain a very significant difference of $-1428 \text{ kJ mol}^{-1} \text{ e}^{-1}$ in favor of the trimer. As $E(\text{N-N} + \text{N-E}) = -69.815 \text{ Ha e}^{-1}$ in the trimer versus $-70.601 \text{ Ha e}^{-1}$ in the tetramer, it follows that ignoring electron-electron repulsions, the tetramer is more stable by -2063 kJ

mol⁻¹ e⁻¹. Yet, taking into account the E-E term (63.845 Ha e⁻¹ in the trimer versus 65.177 Ha e⁻¹ in the tetramer), it transpires that the tetramer is destabilized by +3497 kJ mol⁻¹ e⁻¹ through electronic repulsions. It is thus quite clear that the origin of the energetic stabilization of the trimer lies in the fact that despite its lower stability from a static (N-N + N-E) viewpoint, it is the atomic spatial disposition that strongly minimizes electronic repulsions from a dynamic (E-E) viewpoint. Overall, the self-assembly reaction involving LH₄, Ti(OⁱPr)₄ and bAnt shed light on the self-assembly process relying on the TiO₄N₂ motif. This self-assembly process ended to the quantitative formation of the thermodynamically stable dissymmetric circular helicate [Ti₃(L)₃(bAnt)₃], where the absence of symmetry within this architecture is correlated to the presence of bulky (anthryl)vinyl substituents decorating the diimine chelate. Retrospectively, the use of toluene to conduct the self-assembly reaction was of crucial importance because it permitted to engender the precipitation of the symmetric synthetic intermediate [Ti₄(L)₄(bAnt)₄]. Also, we have shown that this intermediate is originated from the initial [Ti(LH₂)₂(bAnt)] complex. Importantly, this investigation pointed out when the symmetry loss happened in the course of the self-assembly process conducted with the TiO₄N₂ motif. As evidenced by the passage from the symmetric [Ti₄(L)₄(bAnt)₄] architecture to the C₁ circular helicate [Ti₃(L)₃(bAnt)₃], the symmetry decrease^[17] appended at the latest stages of the self-assembly process. Finally, it is the atomic spatial disposition in the trimer that strongly minimizes electronic repulsions, which explains why a loss of symmetry occurred for this self-assembly reaction.

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Keywords: circular helicate • self-assembly • TiO₄N₂ motif • symmetry breaking

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