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Communication

# Phenol-triggered supramolecular transformation of titanium–oxo cluster based coordination capsules

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ABSTRACT

Supramolecular transformations of coordination cage or capsule have received much attention recently, which help elucidate this natural self-assembly behavior in biological systems. The current study describes the first supramolecular transformation of titanium–organic coordination capsule triggered by phenol (and $H_3PO_3$). The structural alterations are accompanied by the reconstruction of 5-coordinated Ti centers to 6-coordinated ones. Meanwhile, different amounts of encapsulated phenol guest molecules can be identified, dependent on the sizes of the obtained cavities. In addition, they display much better visible light absorption and air stability than the isopropanol stabilized ones.


The design and synthesis of discrete metal-organic coordination capsules with specific geometries and cavities have been investigated extensively [1–5]. The interest in these materials stems not only from their remarkable structural characteristics but also from their promising applications in supramolecular chemistry and material science [6–9]. Most coordination capsules are one-pot synthesized through the self-assembly of metallic building blocks and organic ligands, generally accompanied by the annoyingly irrational and uncontrollable growth of polymetallic building vertices [10,11]. Recent investigations on supramolecular transformations of coordination cage open the new door for the controllable synthesis of cage or capsule compounds [12,13]. Various stimuli, including solvents, guests, light, post-modification reactions and so on, have been employed to trigger the transformation processes, which allow for the formation of new structures with specific properties and functions, as well as help elucidate stimuli-responsive structural reorganization processes in biological systems [14–18].

On the other hand, titanium-oxo coordination compounds have received significant attention in recent years due to their well-defined structure and numerous photocatalytic applications [19–26]. In contrast to extensively studied Ti-oxo clusters (TOC) and Ti-oxo MOFs, only two metal–organic coordination *quasi*-capsules with negligible small cavities have been constructed by polynuclear Ti–O building units [27,28], though few Ti–ligand cages using single Ti ion vertices were reported [29–32]. One key process to form such titanium supramolecular architectures is the formation of suitable titanium-oxo building blocks providing ligand-accessible coordination sites to be assembled into the desired molecules, which is unfortunately hampered by high charge density and the easy hydrolysis attributes of titanium ions. Recently, several Ti-carboxylate MOFs have been post-synthesized through supramolecular transformations [33,34]. Such transformation method rules out the disadvantage of easy hydrolysis of titanium ions, inspiring us to adapt similar strategies to synthesize titanium-oxo coordination capsules with new structures and specific properties. To the best of our knowledge, supramolecular transformation of titanium-oxo coordination capsule has not been reported to date.

Our previous work has demonstrated that phenol could be an effective solvent to synthesize highly stable TOCs through reprocessing the titanium-oxo clusters presynthesized in isopropanol [35]. During the process, the Ti—O cores containing 5-coordinated $Ti^{IV}$ centers would undergo reconstruction to give new cores fully comprising 6-coordinated $Ti^{IV}$ centers. Considering the easy reconstruction of titanium-oxo coordination compounds induced by phenol, we decided to utilize them to realize the supramolecular transformations of titanium–organic coordination capsules (Scheme 1). In this work, two titanium-oxo coordination compounds $[Ti_{12}O_4(OPr^i)_{32}(DBC)_4]$ (**PTC-74**, $HOPr^i$ = isopropanol, DBC = 1,4-dicarboxybenzene) and $[Ti_{18}O_6(HPO_3)_6(OPr^i)_{42}(BPDC)_3]$ (**PTC-261**, $H_3PO_3$ = phosphorous acid, BPDC = 4,4'-biphenyldicarboxylic acid)

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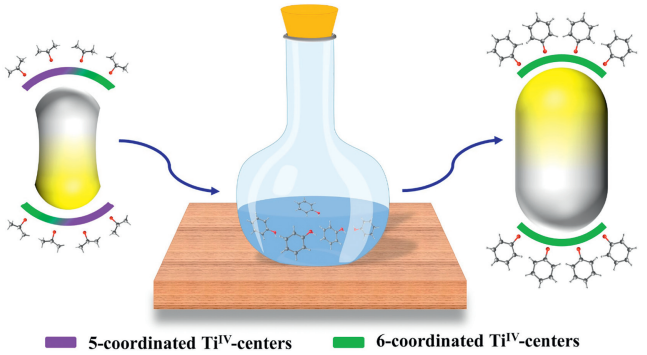


**Scheme 1.** Illustration of the phenol-triggered supramolecular transformation of titanium–organic coordination capsule.

both with 5-coordinated $Ti^{IV}$ centers obtained in isopropanol were chosen as precursors to realize the supramolecular transformations induced by phenol. The reaction of coordination rectangle **PTC-74** with $H_3PO_3$ in phenol obtained a coordination capsule of $[Ti_{18}O_6(HPO_3)_6(DBC)_3(PhO)_{42}]\supset 2PhOH$ (**PTC-262**, PhOH = phenol). Meanwhile, the *quasi*-capsule like titanium-oxo coordination compound **PTC-261** could also be reprocessed in phenol to give another coordination capsule of $[Ti_{18}O_6(HPO_3)_6(BPDC)_3(PhO)_{42}]\supset 5PhOH$ (**PTC-263**) with much larger cavity, which owns the identical titanium oxo building blocks but different bridging ligands with that in **PTC-262**. Phenol guest molecules can be quantitative identified inside the post-synthesized capsules depending on the cavity dimension. In addition, they display much better visible light absorption and air stability than the isopropanol stabilized one.

The coordination rectangle **PTC-74** was firstly synthesized in isopropanol according to a modified literature method reported by us [36]. It consists of four $\{Ti_3\}^{\alpha}$ units and four DBC ligands, which are alternately connected in a rectangular style (Fig. 1a). Importantly, each $\{Ti_3\}^{\alpha}$ unit in **PTC-74** contains one 5-coordinated $Ti^{IV}$-center. According to our previous investigations, such 5-coordinated $Ti^{IV}$-centers might undergo reconstruction during phenol-thermal modification [35], and $H_3PO_3$ might facilitate the assembly of titanium coordination capsules [27]. Indeed, after treating **PTC-74** with phenol in the presence of $H_3PO_3$, yellow hexagonal crystals of **PTC-262** were discovered beside some previous reported red prism crystals of **PTC-184** (Fig. S1 in Supporting information) [35]. Full structural analysis by X-ray diffraction indicates that **PTC-262** is composed of six $\{Ti_3\}^{\beta}$ building units, six phosphite ligands and three terephthalic acid ligands. Every three building units are alternately linked with three phosphites to form a $Ti_9P_3$ entity, and then such two entities are further combined together with three terephthalic acid ligands to form the molecular capsule (Fig. 1b). The structure of the $\{Ti_3\}^{\beta}$ unit in **PTC-262** is different from its precursor unit in **PTC-74**, even though they share the same composition $\{Ti_3O_{13}\}$. The $\{Ti_3\}^{\alpha}$ unit in **PTC-74** comprises one $\mu_3$-O and two $\mu_2$-O atoms which are nearly coplanar with the three Ti atoms (Fig. 1c), while the $\{Ti_3\}^{\beta}$ unit in **PTC-262** contains one $\mu_3$-O and three $\mu_2$-O atoms which are located above and below the Ti-Ti-Ti plane, respectively (Fig. 1d). Such additional $\mu_2$-O atom in **PTC-262** makes its Ti atoms all 6-coordinated. Alternatively, **PTC-262** can be formed with pure phase and higher yield in the reaction of phenol with the dendritic crystalline precipitate produced by directly mixing of DBC, $H_3PO_3$ and $Ti(OPr^i)_4$ in isopropanol at 80 °C, though the precipitate is unsuitable for single crystal X-ray diffraction. It is worth noting that the one-pot synthesis of **PTC-262** *via* the reaction of $Ti(OPr^i)_4$ with DBC and $H_3PO_3$ in phenol failed, highlighting the advantages of post-synthesis in controllable synthesis of coordination capsules or cages.

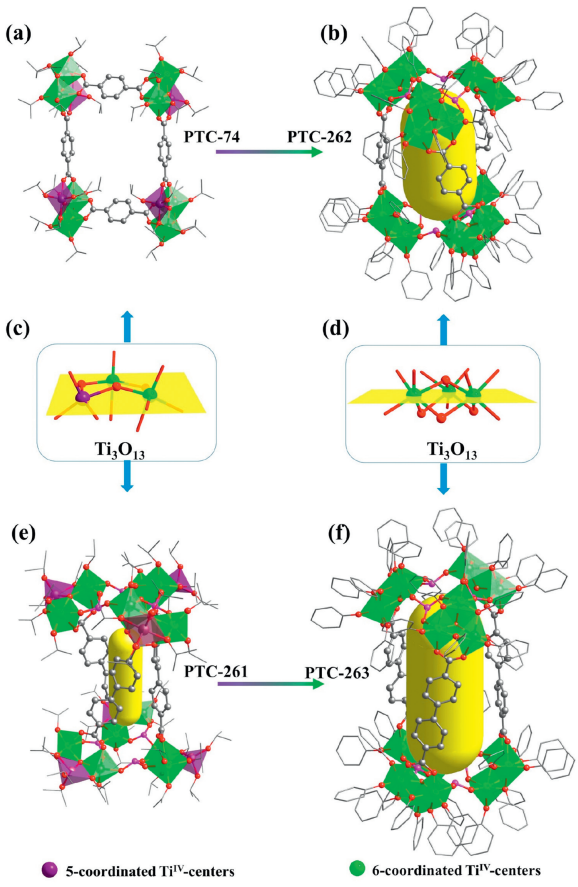


**Fig. 1.** Structures of (a) **PTC-74**, (b) **PTC-262**, (e) **PTC-261** and (f) **PTC-263**. Illustration of (c) the $\{Ti_3\}^{\alpha}$ units in **PTC-74** and **PTC-261**, (d) the $\{Ti_3\}^{\beta}$ units in **PTC-262** and **PTC-263**. Atom color codes: pink P; violet 5 coordinated Ti; green 6 coordinated Ti; red O; gray C. H atoms have been omitted for clarity.

Changing the length of the bridging ligand is an effective way to regulate the size of the cavity in capsule. We intended to synthesize the larger coordination rectangle by using BPDC instead of DBC, which might further transform into the larger capsule. Directly reaction of BPDC with $Ti(OPr^i)_4$ in isopropanol at 80 °C results no coordination rectangle but white amorphous precipitate. However, colorless hexagonal prismatic crystals of **PTC-261** could be obtained with high yield when $H_3PO_3$ was further added into the synthetic reaction system. Six $\{Ti_3\}^{\alpha}$ subunits, which are identical with the subunits in **PTC-74,** were assembled into the $\{Ti_{18}\}$ coordination capsule of **PTC-261** by $H_3PO_3$ and BPDC in isopropanol (Fig. 1e). The structure of quasi-capsule like **PTC-261** is similar to the previously reported sulfonates stabilized capsules (Fig. S3 in Supporting information) [27]. However, each $\{Ti_3\}^{\alpha}$ unit in **PTC-261** contains one 5-coordinated $Ti^{IV}$-center (Fig. 1c), since carboxylic acid has one less coordinated oxygen atom than sulfonic acid. Such 5-coordinated $Ti^{IV}$-centers in **PTC-261** terminated with isopropanol provide us with the fine opportunity to realize the supramolecular transformation triggered by phenol once again.

Consequently, **PTC-261** was also reprocessed in phenol, then a new capsule of **PTC-263** was discovered. Single-crystal X-ray diffraction analysis reveals that **PTC-263**, constructed from six $\{Ti_3\}^{\beta}$ units, six phosphorous acid ligands and three BPDC ligands, possesses analogous structure to **PTC-262** (Fig. 1f). The longer bridging BPDC ligands in **PTC-263** make it just like an "extended version" of **PTC-262.** The number of phenol ligands coordinated to **PTC-263** is identical to the number of isopropanol ligands in precursor **PTC-261**. As mentioned above, the $\{Ti_3\}^{\beta}$ unit in **PTC-263**

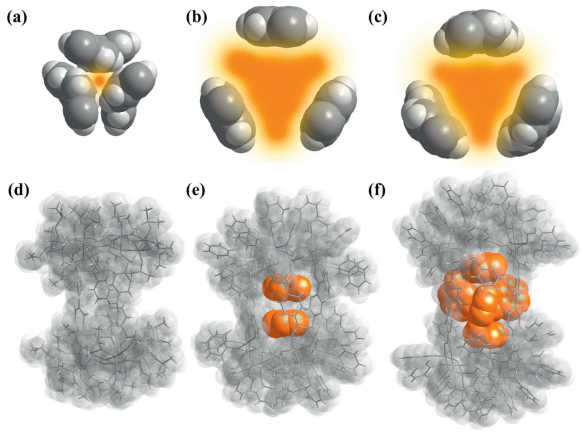


**Fig. 2.** The top view of the cavities in (a) **PTC-261**, (b) **PTC-262** and (c) **PTC-263**, highlighting in orange area. Illustration of the host–guest systems of in (d) **PTC-261**, (e) **PTC-262** and (f) **PTC-263**.

has the same composition $\{Ti_3O_{13}\}$ but different structure with the $\{Ti_3\}^{\alpha}$ unit in **PTC-261** (Fig. S4 in Supporting information). Additionally, carboxylate ligands in **PTC-263** are located further away from the central axis and two sides of this capsule are more curved (Fig. S5 in Supporting information). If propyl groups in isopropanol and benzene groups in terminal phenol are eliminated, **PTC-261** and **PTC-263** have the same components but different geometric configurations (Fig. S6 in Supporting information).

The cavities in molecular capsules can provide unique chemical environments, serving as supramolecular containers, depending on their dimension and composition. Therefore, the host–guest systems of the three synthesized coordination capsules are different. The cavity of **PTC-261** is too small to hold any guest molecules for the reason that the three bridge BPDC ligands in the capsule are entangled with each other (Figs. 2a and d). However, carboxylate ligands in **PTC-262** and **PTC-263** are located further away from the central axis than that in **PTC-261**, offering the two capsules much larger cavity than that in **PTC-261** ( Figs. 2b and c). As a result, two phenolic molecules are located horizontally at both sides of the cavity in **PTC-262** (Fig. 2e). Meanwhile, apart from two side located molecules, three other phenolic molecules are vertically situated on the waistline of the largest capsule **PTC-263** (Fig. 2f). Consequently, five phenolic guest molecules are fixed in the cavity in **PTC-263,** presenting a triangular bipyramid configuration (Fig. 2f). These three capsules successfully show us the case of accurately controlling the quantity of guest molecules at molecular level depending on the size of the cavities.

Since titanium-oxo coordination capsules **PTC-261** and **PTC-263** have the same components but different geometric configurations if propyl groups in isopropanol and benzene groups in terminal phenol are eliminated, the differences in their light absorption and stability properties were also studied. The phenol-triggered capsule **PTC-263** represents orange color while its precursor **PTC-261** terminated with isopropanol is colorless. The solid-state UV–vis absorption studies were further applied to evaluate their optical properties. Both isopropanol stabilized **PTC-261** and phenol (solid state at room temperature) present no obvious absorption in the visible light range (Fig. 3a). However, **PTC-263** which was transformed from **PTC-261** triggered by phenol can significantly red-shift the absorption edge to ~650 nm (Fig. 3a). Therefore, the incorporation of phenol with Ti—O core could significant narrow its bandgap, which should attribute to the penetration of highest occupied phenol levels into the bandgap of

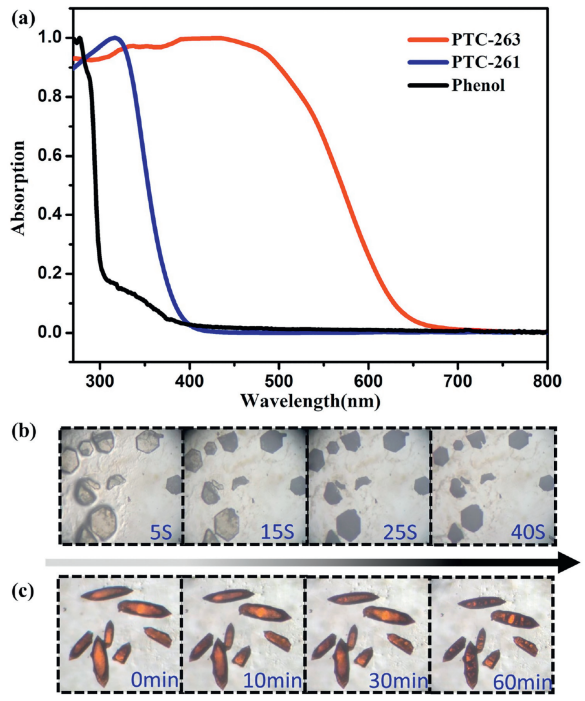


**Fig. 3.** (a) The solid-state absorption spectra of phenol, **PTC-263** and its precursor **PTC-261**. The time dependent crystal photos of (b) **PTC-261** and (c) **PTC-263** in the air.

the Ti—O core [37]. In addition, the crystals of **PTC-263** could survive in the air for half an hour, while its precursor crystals were weathered and losing crystallinity as soon as they were taken out from isopropanol (Figs. 3b and c and Fig. S11 in Supporting information). As we know, isopropanol is much more volatile than phenol, indicating that the volatility of solvent has a great influence on the crystalline stability of discrete coordination capsules. Therefore, phenolic titanium-oxo coordination capsules display much better visible light absorption and air stability than the isopropanol stabilized ones with similar cores.

In summary, we have successfully realized the supramolecular transformation of titanium–organic coordination capsules in the presence of phenol (and $H_3PO_3$), which is accompanied by the reconstruction of 5-coordinated Ti centers to 6-coordinated ones. Meanwhile, different amounts of encapsulated phenol guest molecules can be identified, dependent on the sizes of the obtained cavities. In addition, they display much better visible light absorption and air stability than the isopropanol stabilized ones. Therefore, the developed strategy provides an innovative approach for structural modulation of titanium–organic coordination capsules, which might also be applied to other supramolecular systems.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2021.01.010.

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