We describe the synthesis and characterisation of a robust $S_4$-symmetry titanium-based architecture bearing catecholato and pyridine ligands. This neutral complex formulated as $[\text{Ti}_{10}\text{O}_{12}-(\text{cat})_8(\text{py})_8]$ displays a tetrahedral inorganic core decorated by catecholato ligands with unusual coordination modes. In solution, the pyridine ligands are labile as attested by DOSY studies at variable temperature. The light absorption property in the visible domain ($\lambda_{\text{max}} = 411\text{ nm}$, $\epsilon = 10\ 800$) was also characterised for the complex.

In the field of materials science, crystalline coordination polymers (CPs) or metal–organic frameworks (MOFs) are of crucial importance owing to their high potentialities in separation,$^1$ gas storage,$^2$ drug delivery,$^3$ catalysis,$^4$ or magnetism.$^5$ Mainly, two synthetic routes have been explored to produce these crystalline materials. Usually, CPs are prepared under solvothermal conditions by reacting organic linkers with metal salts. In contrast to this direct approach, an alternative synthetic route has recently emerged involving a sequential self-assembly approach (SSA). The SSA concerns first the preparation of self-assembled systems that are, in a second step, self-assembled with organic connectors.$^6$ These self-assembled systems are coordination networks,$^7$ polymeric architectures$^8$ or metal–organic polyhedra (MOPs).$^9$ In order to realize a step-by-step synthesis of CPs from discrete inorganic complexes, several requirements must be met: first, the architectures should be characterized by well-defined geometries, high symmetries and excellent robustness. Second, the precursors should preferably be neutral entities in order to generate porous networks without the presence of counter-ions. Finally, labile ligands should decorate the edges of the structures to permit the formation of predictable structures through ligand substitution.

In our effort to generate titanium(IV)-MOFs that absorb light in the visible domain through a multistep approach, we report herein the straightforward synthesis, structural characterisation and behaviour in solution of a $S_4$-symmetry titanium(IV)-based architecture formulated as $[\text{Ti}_{10}\text{O}_{12}-(\text{cat})_8(\text{py})_8]$ (cat = catecholato, py = pyridine).

$[\text{Ti}_{10}\text{O}_{12}-(\text{cat})_8(\text{py})_8]$ was synthesized according to eqn (1) by reacting the readily available $[\text{Ti}_2(\text{cat})_4(\text{DMA})_2]^{\ddagger}$ (DMA = dimethylacetamide) complex in hot pyridine ($100\ ^\circ\text{C}$)$^{10}$ After 48 hours of reaction, dark red crystals began to appear in the medium. After one week, the crystals were collected in 53% yield. This yield is highly reproducible if the pyridine used as a solvent contains only traces of water. The reaction was repeated by introducing an increasing excess of water in the medium; in this case the $[\text{Ti}_{10}\text{O}_{12}-(\text{cat})_8(\text{py})_8]$ crystals were isolated in very poor yields (see ESI†).

$\begin{align*}
5[\text{Ti}_2(\text{cat})_4(\text{DMA})_2]^{\ddagger} + 12\text{H}_2\text{O} + 8\text{py} & \rightarrow [\text{Ti}_{10}\text{O}_{12}-(\text{cat})_8(\text{py})_8] + 12\text{catH}_2 + 10\text{DMA} \quad (1)
\end{align*}$

Crystal structure determination indicates the formation of a nano-sized $S_4$ symmetry architecture constructed around a tetrahedral inorganic core composed of ten titanium centres (see Fig. 1) that co-crystallised with six pyridine molecules.

In this structure, two types of the rarely observed coordination mode for the catecholato ligand are noticed.$^{11}$ The purple coloured catecholato ligand in Fig. 1 concerns the four ligands adopting a singly bridging chelate $\mu_2(\text{O},\text{O}',\text{O}'' \text{mode})$, whereas the singly bridging $\mu_2(\text{O},\text{O}'\text{mode})$ involves the formation of no bridging $\mu_2(\text{O},\text{O}')$ mode involving the formation of no bridging $\mu_2(\text{O},\text{O}')$ mode involving...
Ti–O(catecholato) bonds (average length = 1.8666 ± 0.0050 Å) as is usually observed in other titanium complexes. According to the continuous shape measures (CShM) concept, the titanium atoms are located in six-fold distorted octahedral environments. For the two Ti3 atoms that lie along the S4-symmetry axis, their coordination polyhedron is close to the perfect octahedral geometry in comparison with the coordination polyhedra of Ti1 and Ti2 (Ti1(CShM) = 2.016; Ti2(CShM) = 1.430; Ti3(CShM) = 1.321). The percentage of residual TiO2 determined by thermogravimetric analysis, the determination of N, C, H percentage and the X-ray powder diffraction analysis allow us to undoubtedly conclude that the selected single crystal used for the structure resolution was not a synthetic artefact (see ESI†).

The behaviour in solution of the [Ti10O12(cat)8(py)8] complex was evaluated by NMR techniques. The 1H NMR spectrum of [Ti10O12(cat)8(py)8]·(py)6 crystals dissolved in CD2Cl2 reveals the presence of two sets of signals. The three large signals at δ = 8.40, 7.53 and 7.10 ppm are attributed to pyridine highlighting an exchange process for these molecules. This dynamic behaviour is probably linked to the exchange between the pyridine ligands and free pyridine in solution. A second set of rather complex well-defined signals corresponding to the resonance of catecholato protons are observed (see ESI†). The analysis of the 13C NMR spectrum is much more straightforward since four signals with chemical shifts typical to Ti–OC(catecholato) are observed (δ = 159.10, 157.24, 155.53, 153.66 ppm) (see ESI†). This 13C NMR signature is in full accord with a S4-symmetry compound bearing two inequivalent catecholato ligands as determined in the solid-state for [Ti10O12(cat)8(py)8].

A clear and unambiguous explanation of the [Ti10O12·(cat)8(py)8] behaviour in solution was obtained from DOSY (Diffusion Ordered Spectroscopy) measurements at two temperatures. Fig. 2a and b show the DOSY maps of the [Ti10O12·(cat)8(py)8]·(py)6 crystals in CD2Cl2 at 298 K and 223 K. At room temperature, the DOSY experiment clearly suggests the decoordination of all the pyridine ligands as their diffusion (D = 1930 μm² s⁻¹) is very different from the one evaluated for the complex (D = 660 μm² s⁻¹). Furthermore, the hydrodynamic radius for the complex in solution calculated according to the Stokes–Einstein equation (Rh = 7.2 ± 0.7 Å) is in good accord with a theoretical one evaluated from a virtual [Ti10O12(cat)8] complex using a standard set of van der Waals radii of Rh =
8.1 ± 0.5 Å. At low temperature, the $^1$H NMR spectrum has changed drastically. At 223 K, sharp signals are predominant and resonances closely related to free pyridine in CD$_2$Cl$_2$ are found ($δ = 8.53, 7.69, 7.28$ ppm). Moreover, the presence of signals attributed to coordinated pyridine is noticed. Concerning the DOSY analysis at 223 K, a single complex diffuses in solution for which a hydrodynamic radius of $R_\text{h} = 10 ± 1$ Å is calculated. In this case, this experimental value is in the same range as the calculated one determined from the [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] structure ($R_\text{h} = 8.75 ± 0.5$ Å). Having proved no alteration for the [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] complex upon dissolution and the lability of the pyridine ligands, the question of the [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] stability in solution was tackled. In CD$_2$Cl$_2$ or CDCl$_3$ (not dried solvent), no modification of the spectrum of [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] was noticed after several days. Even upon addition of D$_2$O (10 µl) in the CDCl$_3$ solution of the complex, no structural alteration of [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] was noticed. Interestingly, this stability in solution contrasts strongly with the usual behaviour of titanium-based polynuclear aggregates.

It is noteworthy that in deuterated DMSO the stability of the complex is rather moderate. Although in this solvent the decomposition rate is rather slow and resonances closely related to free pyridine in CD$_2$Cl$_2$ are observed for the final product isolated by precipitation with diethylether. The $^1$H and $^{13}$C NMR analysis attests to the formation of [Ti$_{10}$O$_{12}$-(Phpy)$_8$]. When 4,4'-bipyridine reacts with [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$], a dark red precipitate insoluble in common organic medium is instantaneously obtained. In conclusion, we have reported the synthesis and characterisation of a new stable 5,5'-symmetry titanium-based architecture that incorporates both catecholato and labile pyridine ligands. Now, we envisaged reacting the [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] with polypyridyl ligands to generate Ti-O based CPs absorbing visible rather than ultra-violet light.

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Notes and references

† The reaction was conducted under air. In a 10 mm O.D. glass tube was suspended [Ti$_{10}$O$_{12}$-(bipy)$_8$] (100 mg, 0.14 mmol) in pyridine (7.5 ml). The tube was sealed under vacuum and heated at 100 °C for one week. Back to room temperature, small dark red crystals were isolated by filtration and dried under reduced pressure to afford [Ti$_{10}$O$_{12}$-(cat)$_8$(py)$_8$] ($53\%$). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): 8.42 (py-H, broad s), 7.54 (py-H, broad s), 7.18 (Cat-H, dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 4 H), 7.12 (py-H, broad s), 6.60 (Cat-H, complex, 8 H), 6.50 (Cat-H, complex, 12 H), 5.98 (Cat-H, dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 4 H), 6.39 (Cat-H, complex, 12 H), 119.9 (Cat-H, dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 4 H) ppm. $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): 159.1 (C-O catecholate), 157.2 (C-O catecholate), 155.5 (C-O catecholate), 153.7 (C-O catecholate), 149.8 (C-H (2.6 pyridine), 136.5 (C-H (pyridine), 123.7 (C-H (3,5) pyridine), 120.7 (C-H catecholate), 120.0 (C-H catecholate) ppm. IR: 1604, 1475, 1442, 1437, 1291, 1254, 1212, 1149, 112.1 (C=O catecholate), 155.5 (C=O catecholate), 153.7 (C-O catecholate), 149.8 (C-H (2.6 pyridine), 136.5 (C-H (pyridine), 123.7 (C-H (3,5) pyridine), 120.7 (C-H catecholate), 120.0 (C-H catecholate) ppm. IR: 1604, 1475, 1442, 1437, 1291, 1254, 1212, 1149, 112.1 (C=O catecholate) ppm.


10 For the synthesis of [Ti2(cat)4(DMA)2] see: C. Chaumont, E. Huen, C. Huguenard, P. Mobian and M. Henry, Polyhedron, 2013, 57, 70–76 or ESI.


12 For the synthesis of [Ti2(cat)4(DMA)2] see: C. Chaumont, E. Huen, C. Huguenard, P. Mobian and M. Henry, Polyhedron, 2013, 57, 70–76 or ESI.


14 Average between a maximum value corresponding to the longest distance from the barycentre of the molecule and a minimum value $R_{\text{min}} = (3V/4\pi)^{1/3}$ derived from the molecular volume (estimated according to A. Gavezotti, J. Am. Chem. Soc., 1983, 105, 5220–5225). Van der Waals radii used: H = 1.2 Å, C = 1.7 Å, O = 1.52 Å, N = 1.55 Å (see A. Bondi, J. Phys. Chem., 1964, 68, 441–451) and Ti = 1.45 Å (assumed). The theoretical $R_h$ value of the virtual [Ti10O12(cat)8] complex was calculated from the structure of [Ti10O12(cat)8(py)8] by removing the py ligands of the structure.
