Supporting information

NMR experimental: Bruker Avance-300, Avance-400, Avance-500 and Avance-600 were used for solution NMR analysis. $^1$H NMR DOSY measurements were performed at 500.13 MHz with a 5 mm $^1$H/X z-gradient BBI probe and applying a PFGSTE pulse sequence using bipolar gradients. DOSY spectra were generated with the DOSY module of NMRNotebookTM software, via maximum entropy and inverse Laplace transform calculation. $^1$H NMR DOSY measurements were performed at 500.13 MHz with a 5 mm $^1$H/X z-gradient BBI probe and applying a PFGSTE pulse sequence using bipolar gradients. The thermogravimetric analyses (TGA) were performed on a Pyris 6 (PerkinElmer) apparatus. X-ray diffraction data were collected on a Bruker SMART CCD diffractometer with MoKα radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F$^2$ using SHELXS-97 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model). All of the reagents were purchased from commercial sources without further purification: Ti(OPr$i$)$_4$ (TCI), catechol (Fluka). Pyridine was distilled over KOH before used, the amount of water was determined by titration with a Karl Fischer apparatus (< 0.0015 %). The reaction leading to [Ti$_{10}$O$_{12}$(cat)$_8$(py)$_8$] was performed under air.

Procedure for the synthesis of Ti$_2$(cat)$_4$(DMA)$_2$

The reaction was conducted under a nitrogen atmosphere. To a stirred solution of catechol (1 g, 9.08 mmol) in dimethylacetamide (10 ml) was added Ti(OPr$i$)$_4$ (1.33 ml, 4.54 mmol). A dark red color appeared instantaneously in the medium. After one hour, a red precipitate was formed which was recovered by filtration on a fritted funnel, washed several times with diethyl ether (30 ml) and dried under reduced pressure to afford Ti$_2$(cat)$_4$(DMA)$_2$ as a dark red powder (2.8 g, 88 %). IR: 1610, 1483, 1478, 1465, 1407, 1245, 1205, 875, 811, 758, 741, 642, 629, 615 cm$^{-1}$. Anal. calcd for C$_{32}$H$_{34}$O$_{10}$Ti$_2$N$_2$ (MW 702.12): C 54.72; H 4.88; N 3.99. Found C 54.51; H 5.13; N 3.99.

Synthesis of [Ti$_{10}$O$_{12}$(cat)$_8$(Phpy)$_8$] complex

4-Phenylpyridine (1.4 eq) in CHCl$_3$ was mixed with a solution of Ti$_{10}$O$_{12}$(cat)$_8$(py)$_8$ (5 mg) in CHCl$_3$. The desired product was obtained by slow diffusion of diethyl ether into the mixture. The crystalline precipitate was filtered and dried under vacuum. $^{13}$C NMR (125 MHz,
CD₂Cl₂): 159.2 (C-O catecholato), 157.3 (C-O catecholato), 155.7 (C-O catecholato), 153.8 (C-O catecholato), 149.8 (C-H (2, 6) Phpy), 148.8 (C (4) Phpy), 137.2 (C (1) Phpy), 129.0 (C-H (3, 4, 5) Phpy), 126.9 (C-H (2, 6) Phpy), 121.3 (C-H (3, 5) Phpy), 120.9 (C-H catecholato), 120.5 (C-H catecholato), 120.0 (C-H catecholato), 119.7 (C-H catecholato), 119.5 (C-H catecholato), 117.7 (C-H catecholato), 115.2 (C-H catecholato), 112.1 (C-H catecholato) ppm.

Anal. calcd for C₁₃₆H₁₀₄N₈O₂₈Ti₁₀, CHCl₃ (MW 2896.37): C 56.81; H 3.65; N 3.87. Found C 56.37; H 4.05; N 4.00.
Figure 1: $^1$H NMR spectra of [Ti$_{10}$O$_{12}$(cat)$_8$(py)$_8$] (CD$_2$Cl$_2$, 500 MHz)

Figure 2: $^{13}$C NMR spectra of [Ti$_{10}$O$_{12}$(cat)$_8$(py)$_8$] (CD$_2$Cl$_2$, 125 MHz)
Figure 3: $^{13}$C NMR spectra of $[[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_8\text{(py)}_8]]$ (CDCl$_3$, 125 MHz)

Figure 4: $^{13}$C NMR spectra of $[[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_8\text{(py)}_8]]$ (DMSO, 125 MHz)
Figure 5: $^{13}$C NMR spectrum of the compound which crystallized after dissolution of the $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_{8}(4,4'\text{-bipy})_{8}]_{\infty}$ precipitate in pyridine (CDCl$_3$, 125MHz). The $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_{8}(4,4'\text{-bipy})_{8}]_{\infty}$ precipitate was obtained by mixing $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_{8}(\text{py})_{8}]$ and 4,4'-bipyridine in CHCl$_3$. This spectrum is identical as the one recorded for $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_{8}(\text{py})_{8}]$.

Figure 6: $^{13}$C NMR spectrum of crystals obtained by reaction between Ti$_2$(cat)$_4$(DMA)$_2$ and pyridine without addition of water (CDCl$_3$, 125 MHz)
Figure 7: $^{13}$C NMR spectra of crystals obtained by reaction between Ti$_2$(cat)$_4$(DMA)$_2$ and pyridine with addition of water (10 µL) (CDCl$_3$, 125 MHz)

Figure 8: $^{13}$C NMR spectra of the [Ti$_{10}$O$_{12}$(cat)$_8$(Phpy)$_8$] microcrystalline powder obtained by mixing [Ti$_{10}$O$_{12}$(cat)$_8$(py)$_8$] with 4-Phenylpyridine in chloroform after diffusing diethylether (CD$_2$Cl$_2$, 125 MHz)
Figure 9: Powder X-Ray Diffraction patterns of [Ti_{10}O_{12}(cat)_{8}(py)_{8}] obtained after dissolving the [Ti_{10}O_{12}(cat)_{8}(4,4'-bipy)]_{\infty} precipitate and the one simulated from the single crystal diffraction data of [Ti_{10}O_{12}(cat)_{8}(py)_{8}] (red).

Figure 10: Powder X-Ray Diffraction patterns of [Ti_{10}O_{12}(cat)_{8}(py)_{8}] obtained by reacting Ti_{2}(cat)_{4}(DMA)_{2} and pyridine without water (blue), with 10 µL of water (green) and the one simulated from the single crystal diffraction data of [Ti_{10}O_{12}(cat)_{8}(py)_{8}] (red).
Figure 11: UV-visible spectra of $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_8\text{(py)}_8] \cdot \text{(py)}_6$ in CH$_2$Cl$_2$, c = 10$^{-5}$ mol.l$^{-1}$.

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<th>Volume of pyridine (mL)</th>
<th>Volume of water (µL)</th>
<th>Weight of [Ti$<em>{10}$O$</em>{12}$(cat)$_8$(py)$_8$] crystals (mg)</th>
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Table 1: Synthesis of $[\text{Ti}_{10}\text{O}_{12}\text{(cat)}_8\text{(py)}_8]$ performed with an increasing amount of water
Figure 12: Thermogravimetric analysis of [Ti₁₀O₁₂(cat)₈(py)₈]: The analysis was performed under air at a scan rate of 5 °C.min⁻¹. The 34 % weight obtained at 600 °C corresponds to the residual TiO₂ formed during the thermolysis process. The weight losses obtained are compatible with partially desolvated crystals displaying the [Ti₁₀O₁₂(cat)₈(py)₈]•(py)₄ formula. In this case the weight loss corresponding to the free pyridine molecules is evaluated as 12.7 % and the theoretical percentage of residual TiO₂ is 32.2 %.

Figure 13: Thermal ellipsoids plot of [Ti₁₀O₁₂(cat)₈(py)₈]